Cu-Catalyzed C-C Bond Formation of Vinylidene Cyclopropanes with Carbon Nucleophiles

*Jichao Chen, Shang Gao and Ming Chen**

Department of Chemistry and Biochemistry

Auburn University

E-mail: mzc0102@auburn.edu

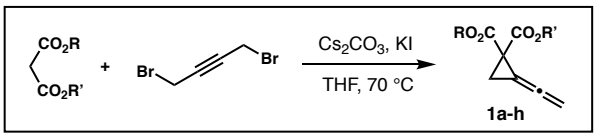
Supporting Information: Experimental Procedures, Tabulated Spectroscopic Data, ^{1}H and ^{13}C Spectra of New Compounds

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).

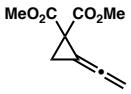
Proton nuclear magnetic resonance (^{1}H NMR) spectra were acquired on commercial instruments (400 and 600 MHz) at Auburn University NMR facility. Carbon-13 nuclear magnetic resonance (^{13}C NMR) spectra were acquired at 101 and 151 MHz. The proton signal for the residual non-deuterated solvent (δ 7.26 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.

1-Pentynylboronic acid pinacol ester, 3-methoxy-1-propyn-1-ylboronic acid pinacol ester and diethyl malonate were purchased from Sigma Aldrich. Benzyl *tert*-butyl malonate, *tert*-butyl ethyl malonate, 2-((*tert*-butyldimethylsilanyl)-ethynyl) boronic acid pinacol ester, 2-phenyl-1-ethynylboronic acid pinacol ester, 5-chloropent-1-ynylboronic acid pinacol ester, dibenzyl malonate were purchased from Combi-Blocks. Dipropyl malonate was purchased from TCI America. Dimethyl malonate was purchased from Oakwood. Diisopropyl malonate was purchased from Arctom. Di-*tert*-Butyl malonate was purchased from Ark Pharm. KOMe was purchased from Alfa Aesar. CuCl, LiO^tBu, NaO^tBu, KO^tBu, LiOMe, NaOMe were purchased from Strem.

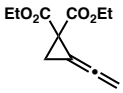


General procedure I for the synthesis of vinylidene cyclopropanes 1a-h: To a 10 mL reaction vial was added malonate (1 mmol, 1.0 equiv), 1,4-dibromo-2-butyne[1] (1 mmol, 1.0 equiv) and THF (5 mL). Cs_2CO_3 (2.5 mmol, 2.5 equiv) and KI (0.1 mmol, 10 mol %) were added to the vial and the mixture was stirred at 70 °C for 12 h. The reaction mixture was filtered through a pad of Celite 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 **1a-h**.



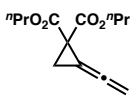
Dimethyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1a)

Prepared according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.22 (t, *J* = 4.9 Hz, 2H), 3.77 (s, 6H), 2.46 (t, *J* = 4.9 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 167.9, 83.7, 83.5, 53.4, 35.5, 20.3. The spectroscopic data for this compound were in agreement with previously reported data.[2]



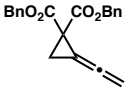
Diethyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1b)

Prepared according to general procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (t, *J* = 5.0 Hz, 2H), 4.22 (q, *J* = 7.1 Hz, 4H), 2.41 (t, *J* = 5.0 Hz, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 167.5, 83.32, 83.30, 62.2, 35.9, 20.1, 14.3. HRMS (ESI^+): m/z for $C_{11}H_{15}O_4$ $[M+H]^+$ calcd. 211.0970, found 211.0974.



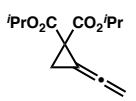
Dipropyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1c)

Prepared according to the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (t, *J* = 5.0 Hz, 2H), 4.13 (t, *J* = 6.6 Hz, 4H), 2.43 (t, *J* = 5.0 Hz, 2H), 1.67 (tq, *J* = 6.7, 7.3 Hz, 4H), 0.94 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 167.6, 83.5, 83.3, 67.8, 36.0, 22.2, 20.2, 10.6. HRMS (ESI^+): m/z for $C_{13}H_{18}O_4Na$ $[M+Na]^+$ calcd. 261.1103, found 261.1114.



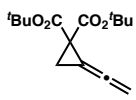
Dibenzyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1d)

Prepared according to the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$ δ 7.28 – 7.36 (m, 10H), 5.19 – 5.21 (m, 6H), 2.49 (t, *J* = 5.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 167.2, 135.7, 128.9, 128.6, 128.3, 83.7, 83.6, 67.8, 35.8, 20.5. HRMS (ESI^+): m/z for $C_{21}H_{18}O_4Na$ $[M+Na]^+$ calcd. 357.1103, found 357.1103.



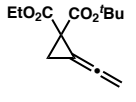
Diisopropyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1e)

Prepared according to the general procedure. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (t, *J* = 5.0 Hz, 2H), 5.06 (hept, *J* = 6.3 Hz, 2H), 2.36 (t, *J* = 5.0 Hz, 2H), 1.252 (d, *J* = 6.3 Hz, 6H), 1.248 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.9, 167.1, 83.1, 82.9, 69.8, 36.4, 22.0, 21.9, 19.9. HRMS (ESI^+): m/z for $C_{13}H_{19}O_4$ $[M+H]^+$ calcd. 239.1283, found 239.1295.



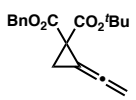
Di-tert-butyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1f)

Prepared according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.17 (t, *J* = 4.8 Hz, 2H), 2.28 (t, *J* = 4.8 Hz, 2H), 1.47 (s, 18H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.8, 166.8, 82.8, 82.6, 82.5, 38.0, 28.2, 19.6. HRMS (ESI^+): m/z for $C_{15}H_{22}O_4Na$ $[M+Na]^+$ calcd. 289.1416, found 289.1418.



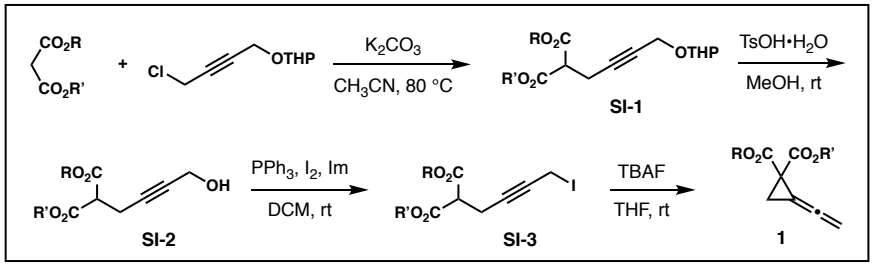
1-(*Tert*-butyl) 1-ethyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1g)

Prepared according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.19 (t, *J* = 4.6 Hz, 2H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.33 – 2.37 (m, 2H), 1.46 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 167.9, 166.5, 83.1, 83.0, 82.8, 62.2, 36.9, 28.2, 19.9, 14.4. HRMS (ESI^+): m/z for $C_{13}H_{18}O_4Na$ $[M+Na]^+$ calcd. 261.1103, found 261.1110.



1-Benzyl 1-(*tert*-butyl) 2-vinylidenecyclopropane-1,1-dicarboxylate (1h)

Prepared according to the general procedure. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.36 (m, 5H), 5.18 – 5.22 (m, 4H), 2.36 – 2.41 (m, 2H), 1.39 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.8, 167.7, 166.3, 135.7, 128.8, 128.6, 128.5, 83.20, 83.17, 82.9, 67.7, 36.9, 28.1, 20.1. HRMS (ESI^+): m/z for $C_{18}H_{20}O_4Na$ $[M+Na]^+$ calcd. 323.1259, found 323.1270.



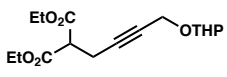
General procedure II for the synthesis of vinylidene cyclopropanes 1: To a solution of malonate (12 mmol, 1.2 equiv) and 2-(4-chloro-2-butynyloxy)-tetrahydropyran[3] (1.9 g,

10 mmol, 1.0 equiv) in CH_3CN (50 mL) was added K_2CO_3 (2.8 g, 20 mmol, 2.0 equiv). The mixture was stirred at 80 °C for 12 h. The reaction mixture was filtered through a pad of Celite 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 **SI-1**.

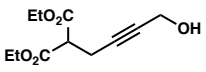
To a solution of **SI-1** (7 mmol, 1.0 equiv) in MeOH (40 mL) was added $TsOH{\cdot}H_2O$ (120 mg, 0.7 mmol, 10 mol %). The mixture was stirred at ambient temperature for 12 h. The reaction mixture was concentrated under reduced pressure and purification of the resulting crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **SI-2**.

To a solution of triphenylphosphine (2.2 g, 8.4 mmol, 1.4 equiv) and imidazole (0.57 g, 8.4 mmol, 1.4 equiv) in anhydrous CH_2Cl_2 (60 mL) was added iodine (2.13 g, 8.4 mmol, 1.4 equiv). The mixture was stirred at ambient temperature for 15 min. A solution of **SI-2** (6 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL) was added and the mixture was stirred at ambient temperature for 30 min. Then the reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed sequentially with saturated Na_2SO_3 (3 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **SI-3**.

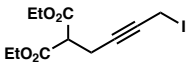
To a solution of **SI-3** (1 mmol, 1.0 equiv) in THF (10 mL) was added a solution of $TBAF{\cdot}H_2O$ (2 mmol, 2.0 equiv) in THF (2 mL). The mixture was kept stirring at ambient temperature for 10 min. The solution was concentrated under reduced pressure till ~2 mL solution left in the flask and Et_2O (30 mL) was added. The solution was filtered through a pad of silica gel (to remove most of TBAF) and the filtrate 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 **1**. Compounds **1a** and **1b** were also synthesized using this route.



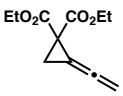
Diethyl 2-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)but-2-yn-1-yl)malonate (SI-1b) Prepared according to the general procedure to give compound **SI-1b** as colorless oil in 73% yield (2.28 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (t, *J* = 3.3 Hz, 1H), 4.11 – 4.24 (m, 6H), 3.75 – 3.81 (m, 1H), 3.52 (t, *J* = 7.8 Hz, 1H), 3.45 – 3.51 (m, 1H), 2.78 (dt, *J* = 7.7, 2.1 Hz, 2H), 1.65 – 1.81 (m, 2H), 1.45 – 1.60 (m, 4H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 96.8, 82.2, 78.3, 62.2, 62.0, 54.6, 51.6, 30.5, 25.6, 19.3, 19.1, 14.3.



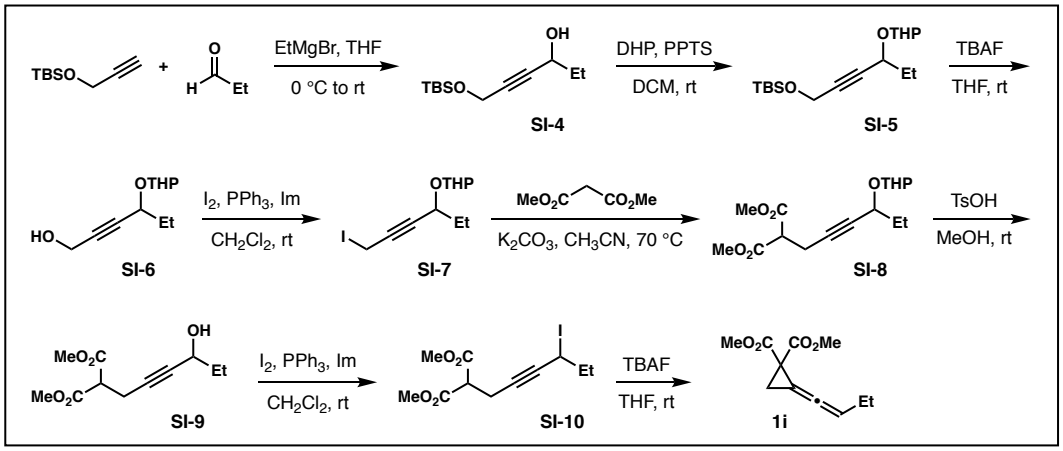
Diethyl 2-(4-hydroxybut-2-yn-1-yl)malonate (SI-2b) Prepared according to the general procedure to give compound **SI-2b** as colorless oil in 90% yield (1.44 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.16 – 4.22 (m, 6H), 3.51 (t, J = 7.7 Hz, 1H), 2.77 (dt, J = 7.7, 2.1 Hz, 2H), 2.41 (t, J = 5.5 Hz, 1H), 1.24 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 81.7, 80.9, 62.1, 51.5, 51.2, 19.0, 14.3.



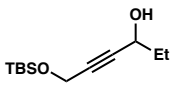
Diethyl 2-(4-iodobut-2-yn-1-yl)malonate (SI-3b) Prepared according to the general procedure to give compound **SI-3b** as light yellow oil in 87% yield (1.76 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 – 4.24 (m, 4H), 3.63 (t, J = 2.4 Hz, 2H), 3.51 (t, J = 7.7 Hz, 1H), 2.78 (dt, J = 7.7, 2.4 Hz, 2H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 82.0, 79.3, 62.1, 51.3, 19.4, 14.4, -17.9.



Diethyl 2-vinylidenecyclopropane-1,1-dicarboxylate (1b) Prepared according to the general procedure II to give compound **1b** as colorless oil in 66% yield (139 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 (t, J = 5.0 Hz, 2H), 4.22 (q, J = 7.1 Hz, 4H), 2.41 (t, J = 5.0 Hz, 2H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 167.5, 83.3, 83.3, 62.2, 35.9, 20.1, 14.3. HRMS (ESI$^+$): m/z for $C_{11}H_{15}O_4$ $[M+H]^+$ calcd. 211.0970, found 211.0974.

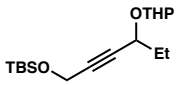


Procedure for the synthesis of vinylidene cyclopropane 1i:

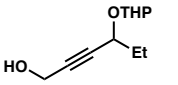


6-((*tert*-Butyldimethylsilyl)oxy)hex-4-yn-3-ol (SI-4) To a solution of propargyl alcohol TBS ether (1.7 g, 10 mmol, 1.0 equiv) in anhydrous THF (25 mL) was added a solution of ethyl magnesium bromide (3 M in Et_2O, 3.4 mL, 10 mmol, 1.0 equiv) at ambient temperature. The resulting mixture was stirred for 2 h and

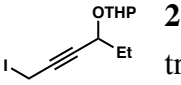
cooled to 0 °C in an ice/water bath, and a solution of propionaldehyde (0.87 g, 15 mmol, 1.5 equiv) in THF (5 mL) was added via cannula. The reaction mixture was warmed to ambient temperature and stirred for 6 h. Water (0.5 mL) was added and the resulting mixture was filtered through a pad of silica gel. 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 **SI-4** as colorless oil in 72% yield (1.65 g). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.35 (*app.* s, 3H), 1.84 (d, J = 5.1 Hz, 1H), 1.68 – 1.75 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H), 0.90 (s, 9H), 0.11 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 85.8, 83.8, 64.1, 52.1, 31.0, 26.1, 18.7, 9.8, -4.8. The spectroscopic data for this compound were in agreement with previously reported data.[4]



***tert*-Butyldimethyl((4-((tetrahydro-2*H*-pyran-2-yl)oxy)hex-2-yn-1-yl)oxy)silane (SI-5)** To a solution of **SI-4** (1.65 g, 7.2 mmol, 1.0 equiv) and dihydropyran (8.5 mL, 9.4 mmol, 1.3 equiv) in anhydrous CH_2Cl_2 (20 mL) was added pyridinium *p*-toluenesulfonate (181 mg, 0.72 mmol, 10 mol %). The mixture was stirred at ambient temperature for 12 h. After the reaction is complete, the reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed sequentially with saturated $NaHCO_3$ (2 x 30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to obtain crude product **SI-5** for next step without further purification.

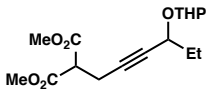


4-((Tetrahydro-2*H*-pyran-2-yl)oxy)hex-2-yn-1-ol (SI-6) To a solution of crude **SI-5** in THF (15 mL) and H_2O (0.5 mL) was added a solution of TBAF·H_2O (4.5 g, 14.4 mmol) in THF (5 mL). The mixture was stirred at ambient temperature for 3 h. The reaction mixture was concentrated till ~ 5 mL left. Et_2O (50 mL) was added and the mixture was filtered through a pad of silica gel. The filtrate 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 **SI-6** as colorless oil.

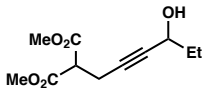


2-((6-Iodohex-4-yn-3-yl)oxy)tetrahydro-2*H*-pyran (SI-7) To a solution of triphenylphosphine (2.2 g, 8.4 mmol, 1.4 equiv) and imidazole (571 mg, 8.4 mmol, 1.4 equiv) in anhydrous CH_2Cl_2 (50 mL) was added iodine (2.13 g, 8.4 mmol, 1.4 equiv). The mixture was stirred at ambient temperature for 15 min. A solution of **SI-6** (6 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added and the mixture was stirred at ambient temperature for 30 min. Then the reaction mixture was diluted with CH_2Cl_2 (100 mL) and washed sequentially with saturated Na_2SO_3 (3 x 50 mL) and brine (50 mL). The organic

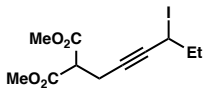
layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **SI-7** as light yellow oil.



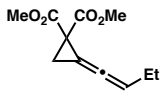
Dimethyl 2-(4-((tetrahydro-2*H*-pyran-2-yl)oxy)hex-2-yn-1-yl)malonate (SI-8) To a solution of **SI-7** (5 mmol, 1.0 equiv) and dimethyl malonate (792 mg, 6 mmol, 1.2 equiv) in CH_3CN (30 mL) was added K_2CO_3 (1.38 g, 10 mmol, 2.0 equiv) and the mixture was stirred at 70 °C for 12 h. Then the reaction mixture was filtered through a pad of silica gel and the solution was concentrated under reduced pressure to obtain crude product **SI-8** without further purification for next step.



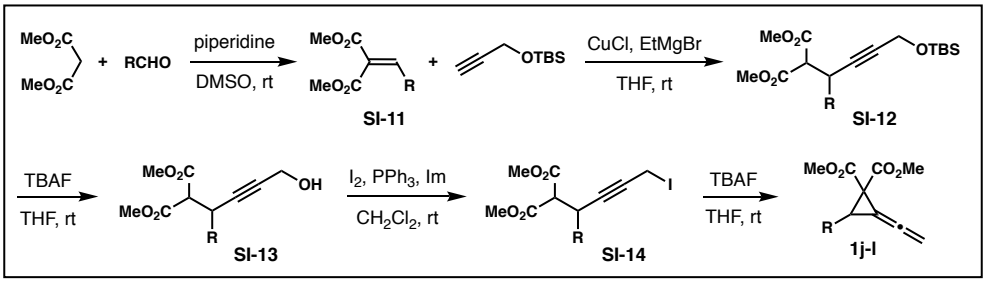
Dimethyl 2-(4-hydroxyhex-2-yn-1-yl)malonate (SI-9) To a solution of crude **SI-8** in MeOH (40 mL) was added $TsOH{\cdot}H_2O$ (120 mg, 0.7 mmol) and the mixture was stirred at ambient temperature for 12 h. The reaction mixture was concentrated under reduced pressure and purification of the resulting crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **SI-9** as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.23 – 4.26 (m, 1H), 3.75 (s, 6H), 3.58 (t, J = 7.7 Hz, 1H), 2.80 (dd, J = 7.7, 1.2 Hz, 2H), 2.23 (s, 1H), 1.58 – 1.70 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.75, 168.74, 83.6, 80.8, 63.9, 53.2, 51.3, 31.1, 19.0, 9.6.



Dimethyl 2-(4-iodohex-2-yn-1-yl)malonate (SI-10) To a solution of triphenylphosphine (1.13 g, 4.3 mmol, 1.4 equiv) and imidazole (292 mg, 4.3 mmol, 1.4 equiv) in anhydrous CH_2Cl_2 (30 mL) was added iodine (1.09 g, 4.3 mmol, 1.4 equiv). The mixture was stirred at ambient temperature for 15 min. A solution of **SI-9** (700 mg, 3.1 mmol, 1.0 equiv) in CH_2Cl_2 (6 mL) was added and the mixture was stirred at ambient temperature for 30 min. Then the reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed sequentially with saturated Na_2SO_3 (3 x 30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and 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 **SI-10** as light yellow oil in 87% yield (911 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.48 (*app.* t, J = 6.2 Hz, 1H), 3.77 (s, 6H), 3.59 (t, J = 7.8 Hz, 1H), 2.82 (dd, J = 7.7, 1.9 Hz, 2H), 1.87 (dq, J = 7.2, 7.2 Hz, 2H), 1.00 (t, J = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.65, 168.63, 83.9, 82.8, 53.3, 51.0, 34.8, 19.5, 14.0, 13.5.



Dimethyl 2-(but-1-en-1-ylidene)cyclopropane-1,1-dicarboxylate (1i) To a solution of **SI-10** (500 mg, 1.48 mmol, 1.0 equiv) in THF (15 mL) was slowly added a solution of TBAF·H_2O (932 mg, 2.96 mmol, 2.0 equiv) in THF (3 mL). Upon completion of the addition, the mixture was kept stirring at ambient temperature for 30 min. Then the solution was concentrated under reduced pressure till ~3 mL left. Et_2O (30 mL) was added and the resulting mixture was filtered through a pad of silica gel. The filtrate was concentrated under reduced pressure and purification of the crude product was performed by flash column chromatography (gradient elution with hexane and ethyl acetate) to give product **1i** as colorless oil in 81% yield (252 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.74 (tt, J = 5.2, 5.2 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.44 (d, J = 4.5 Hz, 2H), 2.14 (dq, J = 6.8, 6.8 Hz, 2H), 1.01 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 188.2, 168.3, 102.9, 85.8, 53.3, 53.2, 34.9, 22.7, 20.0, 13.0. HRMS (ESI^+): m/z for $C_{11}H_{15}O_4$ $[M+H]^+$ calcd. 211.0970, found 211.0978.



General procedure for the synthesis of vinylidene cyclopropanes 1j-l:

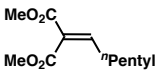
To a solution of freshly distilled aldehyde (20 mmol, 1.0 equiv) in anhydrous DMSO (20 mL) containing 3Å molecular sieves was added piperidine (0.4 mL, 4 mmol, 20 mol %), and the solution was kept stirring at ambient temperature for 15 min. Dimethyl malonate (2.64 g, 20 mmol, 1.0 equiv) was added and the resulting mixture was stirred at ambient temperature for 12 h. The precipitate and molecular sieves were removed by filtration. Water (50 mL) was added and the resulting mixture was extracted with Et_2O (3 x 50 mL). The combined organic extracts were washed with water (2 x 30 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered and 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 **SI-11**.

To a solution of propargyl alcohol TBS ether (10 mmol, 1.0 equiv) in anhydrous THF (30 mL) at ambient temperature was added a solution of ethylmagnesium bromide (3 M in Et_2O, 3.4 mL, 10 mmol, 1.0 equiv). The resulting mixture was stirred for 2 h and then cooled to 0 °C in an ice/water bath. CuCl (50 mg, 0.5 mmol, 5 mol %) was added followed by addition of a solution of **SI-11** (10 mmol, 1.0 equiv) in THF (10 mL). The mixture was warmed to ambient temperature and stirred for 30 min. The reaction mixture was diluted with Et_2O (100 mL) and filtered through a pad of silica gel. The filtrate 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 **SI-12**.

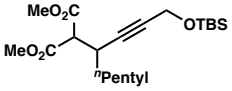
To a solution of **SI-12** (7 mmol, 1.0 equiv) in THF (20 mL) and H_2O (0.5 mL) was added a solution of TBAF·H_2O (4.4 g, 14 mmol, 2.0 equiv) in THF (5 mL), and the mixture was kept stirring at ambient temperature for 1 h. The reaction mixture was concentrated under reduced pressure till ~ 5 mL left in the flask. Et_2O (50 mL) was added and the mixture was filtered through a pad of silica gel. The filtrate 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 **SI-13**.

To a solution of triphenylphosphine (1.83 g, 7 mmol, 1.4 equiv) and imidazole (476 mg, 7 mmol, 1.4 equiv) in anhydrous CH_2Cl_2 (50 mL) was added iodine (1.77 g, 7 mmol, 1.4 equiv). The mixture was stirred at ambient temperature for 15 min. A solution of **SI-13** (5 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added and the mixture was stirred at ambient temperature for 30 min. The reaction mixture was diluted with CH_2Cl_2 (50 mL) and washed sequentially with saturated Na_2SO_3 (3 x 50 mL) and brine (50 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and 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 **SI-14**.

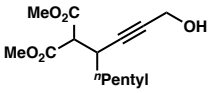
To a solution of **SI-14** (1 mmol, 1.0 equiv) in THF (10 mL) was slowly added a solution of TBAF·H_2O (2 mmol, 2.0 equiv) in THF (2 mL). Upon completion of the addition, the mixture was kept stirring at ambient temperature for 10 min. Then the solution was concentrated under reduced pressure till ~3 mL left in the flask. Et_2O (30 mL) was added. The resulting mixture was filtered through a pad of silica gel and the filtrate 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 **1j-l**.



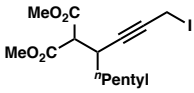
Dimethyl 2-hexylidenemalonate (SI-11k) Prepared according to general procedure. The crude mixture was purified with column chromatography to give compound **SI-11k** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (t, J = 7.9 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.28 (dt, J = 7.7, 7.4 Hz, 2H), 1.48 (*apps.* p, J = 7.2 Hz, 2H), 1.26 – 1.31 (m, 4H), 0.88 (t, J = 6.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 164.8, 151.0, 128.2, 52.6, 52.5, 31.7, 30.1, 28.3, 22.7, 14.2.



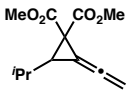
Dimethyl 2-(1-((*tert*-butyldimethylsilyl)oxy)non-2-yn-4-yl)malonate (SI-12k) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **SI-12k** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.28 (d, J = 1.6 Hz, 2H), 3.743 (s, 3H), 3.737 (s, 3H), 3.47 (d, J = 9.5 Hz, 1H), 3.16 (br, 1H), 1.53 – 1.57 (m, 1H), 1.40 – 1.50 (m, 3H), 1.23 – 1.29 (m, 4H), 0.86 – 0.89 (m, 12H), 0.09 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 84.3, 82.1, 56.7, 53.0, 52.9, 52.1, 32.8, 32.3, 31.7, 27.1, 26.1, 22.8, 18.6, 14.4, -4.8.



Dimethyl 2-(1-hydroxynon-2-yn-4-yl)malonate (SI-13k) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **SI-13k** as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.22 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 3.47 (d, J = 9.1 Hz, 1H), 3.16 (*br*, 1H), 1.73 (s, 1H), 1.37 – 1.54 (m, 4H), 1.28 – 1.30 (m, 4H), 0.88 (t, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.4, 168.3, 85.5, 81.9, 56.6, 53.03, 53.01, 51.5, 32.8, 32.3, 31.7, 27.1, 22.8, 14.3.

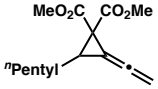


Dimethyl 2-(1-iodonon-2-yn-4-yl)malonate (SI-14k) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **SI-14k** as light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.75 (s, 3H), 3.67 (d, J = 2.3 Hz, 2H), 3.45 (d, J = 9.3 Hz, 1H), 3.15 – 3.18 (m, 1H), 1.47 – 1.52 (m, 2H), 1.38 – 1.45 (m, 2H), 1.23 – 1.32 (m, 4H), 0.89 (t, J = 6.9 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.24, 168.17, 85.6, 80.5, 56.3, 53.2, 53.1, 32.7, 32.5, 31.6, 27.0, 22.8, 14.4, -17.6.

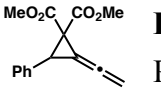


Dimethyl 2-isopropyl-3-vinylidenecyclopropane-1,1-dicarboxylate (1j) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **1j** as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.20 (dd, J = 10.8, 4.5 Hz, 1H), 5.14 (dd, J = 10.5, 4.7 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 2.60 (ddd, J = 10.0, 5.0, 4.8 Hz, 1H), 1.43 – 1.51 (m, 1H), 1.06 (d, J = 10.6

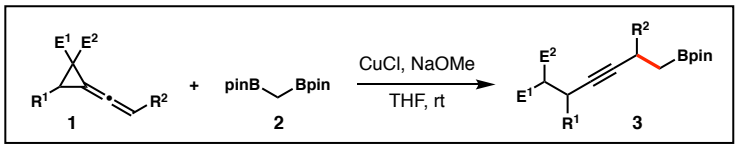
Hz, 3H), 1.05 (d, J = 10.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.5, 168.4, 167.0, 86.0, 82.5, 53.4, 53.1, 41.2, 39.6, 29.5, 22.3, 21.7. The spectroscopic data for this compound were in agreement with previously reported data.[2]



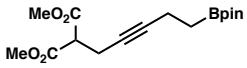
Dimethyl 2-pentyl-3-vinylidenecyclopropane-1,1-dicarboxylate (1k) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **1k** as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.21 (dd, J = 10.8, 4.9 Hz, 1H), 5.15 (dd, J = 10.8, 4.8 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.78 – 2.82 (m, 1H), 1.69 (ddt, J = 13.6, 6.8, 6.6 Hz, 1H), 1.44 – 1.47 (m, 2H), 1.35 – 1.41 (m, 1H), 1.28 – 1.29 (m, 4H), 0.87 (*app.* s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 168.5, 167.0, 86.6, 82.7, 53.4, 53.2, 40.7, 32.7, 31.5, 28.7, 28.5, 22.8, 14.4. HRMS (ESI^+): m/z for $C_{14}H_{21}O_4$ $[M+H]^+$ calcd. 253.1440, found 253.1448. ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.21 (dd, J = 10.8, 4.9 Hz, 1H), 5.15 (dd, J = 10.8, 4.8 Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 2.78 – 2.82 (m, 1H), 1.65 – 1.72 (m, 1H), 1.42 – 1.50 (m, 2H), 1.35 – 1.42 (m, 1H), 1.22 – 1.35 (m, 4H), 0.87 (*app.* s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 193.7, 168.5, 167.0, 86.6, 82.7, 53.4, 53.2, 40.7, 32.7, 31.5, 28.7, 28.5, 22.8, 14.4. HRMS (ESI^+): m/z for $C_{14}H_{21}O_4$ $[M+H]^+$ calcd. 253.1440, found 253.1448.



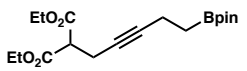
Dimethyl 2-phenyl-3-vinylidenecyclopropane-1,1-dicarboxylate (1l) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **1l** as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 –7.31 (m, 5H), 5.43 (dd, J = 11.3, 4.9 Hz, 1H), 5.32 (dd, J = 11.3, 4.8 Hz, 1H), 4.08 (dd, J = 4.8, 4.7 Hz, 1H), 3.82 (s, 3H), 3.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 195.6, 167.8, 165.5, 133.3, 128.8, 128.6, 128.3, 84.8, 83.5, 53.6, 52.8, 43.7, 36.1. The spectroscopic data for this compound were in agreement with previously reported data.[2]



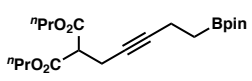
General procedure for the synthesis of homopropargylic boronate 3: In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 10 mol %), NaOMe (0.1 mmol, 1.0 equiv, NaO^{t}Bu was used in the case of **3d**), and THF (0.5 mL). The resulting mixture was stirred for 15 min at ambient temperature. Bisboryl methane **2** (0.11 mmol, 1.1 equiv) was added to the vial, and the mixture was stirred for 5 min. Then vinylidene cyclopropane **1** (0.1 mmol, 1.0 equiv) was added, and the reaction mixture was stirred for 6 – 12 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 **3**. (An Ar glove box is not required. The reaction conducted using air-free Schlenk technic provided the product in a similar yield. However, the reaction needs to be protected from exposure to air.)



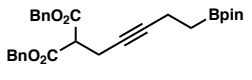
Dimethyl 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3a) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3a** as colorless oil in 87% yield (28 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.54 (t, J = 7.8 Hz, 1H), 2.72 – 2.73 (m, 2H), 2.21 (t, J = 7.6 Hz, 2H), 1.24 (s, 12H), 0.98 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 84.6, 83.6, 74.9, 53.1, 51.8, 25.1, 19.2, 13.7, 11.6. HRMS (ESI$^+$): m/z for $C_{16}H_{25}BO_6Na$ $[M+Na]^+$ calcd. 347.1642, found 347.1667. 1 mmol scale reaction gave compound **3a** in 75% yield (243 mg).



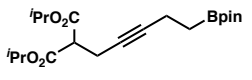
Diethyl 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3b) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3b** as colorless oil in 77% yield (27 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.19 – 4.23 (m, 4H), 3.49 (t, J = 7.8 Hz, 1H), 2.71 – 2.72 (m, 2H), 2.21 (t, J = 7.6 Hz, 2H), 1.23 – 1.28 (m, 18H), 0.98 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 84.4, 83.6, 75.1, 62.0, 52.1, 25.1, 19.1, 14.4, 13.7, 11.5. HRMS (ESI$^+$): m/z for $C_{18}H_{29}BO_6Na$ $[M+Na]^+$ calcd. 375.1955, found 375.1974.



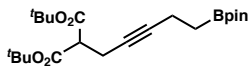
Dipropyl 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3c) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3c** as colorless oil in 68% yield (26 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.07 – 4.14 (m, 4H), 3.52 (t, *J* = 7.8 Hz, 1H), 2.71 – 2.73 (m, 2H), 2.20 (t, *J* = 7.6 Hz, 2H), 1.66 (tq, *J* = 6.9, 7.2 Hz, 4H), 1.24 (s, 12H), 0.98 (t, *J* = 7.7 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 84.3, 83.6, 75.1, 67.5, 52.1, 25.1, 22.2, 19.2, 13.7, 10.7. HRMS (ESI$^+$): m/z for $C_{20}H_{33}BO_6Na$ $[M+Na]^+$ calcd. 403.2268, found 403.2298.



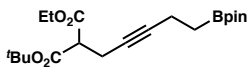
Dibenzyl 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3d) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3d** as colorless oil in 55% yield (26 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 – 7.32 (m, 10H), 5.16 (s, 4H), 3.63 (t, *J* = 7.8 Hz, 1H), 2.76 – 2.77 (m, 2H), 2.17 (t, *J* = 7.6 Hz, 2H), 1.23 (s, 12H), 0.95 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.3, 135.5, 128.9, 128.7, 128.5, 84.7, 83.6, 74.9, 67.6, 52.1, 25.1, 19.2, 13.7. HRMS (ESI$^+$): m/z for $C_{28}H_{33}BO_6Na$ $[M+Na]^+$ calcd. 499.2268, found 499.2314.



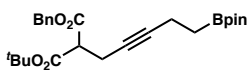
Diisopropyl 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3e) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3e** as colorless oil in 76% yield (29 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.05 (hept, *J* = 6.0 Hz, 2H), 3.41 (t, *J* = 7.8 Hz, 1H), 2.69 (*app.* d, *J* = 7.8 Hz, 2H), 2.20 (t, *J* = 7.7 Hz, 2H), 1.24 (*app.* s, 24H), 0.98 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.2, 84.2, 83.6, 75.2, 69.4, 52.4, 25.1, 22.0, 21.9, 19.0, 13.7, 11.7. HRMS (ESI$^+$): m/z for $C_{20}H_{33}BO_6Na$ $[M+Na]^+$ calcd. 403.2268, found 403.2258.



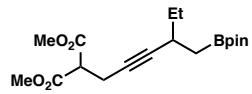
Di-*tert*-butyl 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3f) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3f** as colorless oil in 78% yield (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.28 (t, *J* = 7.9 Hz, 1H), 2.61 (*app.* d, *J* = 7.8 Hz, 2H), 2.21 (t, *J* = 7.7 Hz, 2H), 1.45 (s, 18H), 1.24 (s, 12H), 0.99 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 84.0, 83.6, 82.0, 75.5, 53.8, 28.2, 25.1, 19.0, 13.7. HRMS (ESI$^+$): m/z for $C_{22}H_{37}BO_6Na$ $[M+Na]^+$ calcd. 431.2581, found 431.2604.



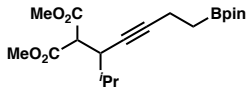
1-(*Tert*-butyl) 3-ethyl 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3g) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3g** as colorless oil in 74% yield (28 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.15 – 4.25 (m, 2H), 3.39 (t, J = 7.9 Hz, 1H), 2.66 – 2.67 (m, 2H), 2.21 (t, J = 7.6 Hz, 2H), 1.45 (s, 9H), 1.24 – 1.28 (m, 15H), 0.99 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 167.7, 84.1, 83.6, 82.4, 75.3, 61.7, 52.9, 28.2, 25.1, 19.1, 14.5, 13.7, 11.7. HRMS (ESI$^+$): m/z for $C_{20}H_{33}BO_6Na$ $[M+Na]^+$ calcd. 403.2268, found 403.2271.



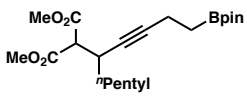
1-Benzyl 3-(*tert*-butyl) 2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3h) Prepared according to the general procedure to give compound **3h** as colorless oil in 68% yield (30 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.36 (m, 5H), 5.22 (d, $J_{A,B}$ = 12.3 Hz, 1H), 5.15 (d, $J_{A,B}$ = 12.3 Hz, 1H), 3.46 (t, J = 7.8 Hz, 1H), 2.68 – 2.70 (m, 2H), 2.19 (t, J = 7.7 Hz, 2H), 1.38 (s, 9H), 1.24 (s, 12H), 0.98 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 167.4, 135.8, 128.8, 128.62, 128.57, 84.3, 83.6, 82.5, 75.2, 67.3, 52.9, 28.1, 25.1, 19.1, 13.7, 11.6. HRMS (ESI$^+$): m/z for $C_{25}H_{35}BO_6Na$ $[M+Na]^+$ calcd. 465.2424, found 465.2404.



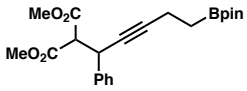
Dimethyl-2-(4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-hex-2-yn-1-yl)malonate (3i) Prepared according to the general procedure to give compound **3i** as colorless oil in 85% yield (30 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.55 (t, J = 7.8 Hz, 1H), 2.74 (dd, J = 7.9, 1.4 Hz, 2H), 2.38 – 2.46 (m, 1H), 1.41 – 1.48 (m, 1H), 1.31– 1.39 (m, 1H), 1.24 (s, 12H), 0.91 – 1.00 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.0, 87.4, 83.5, 76.0, 53.1, 51.9, 30.8, 29.2, 25.2, 25.0, 19.3, 18.6, 12.1. HRMS (ESI$^+$): *m/z* for $C_{18}H_{29}BO_6Na$ $[M+Na]^+$ calcd. 375.1955, found 375.1960.



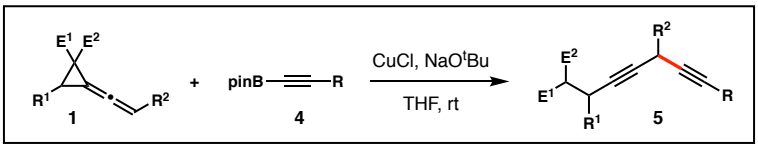
Dimethyl-2-(2-methyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-4-yn-3-yl)malonate (3j) Prepared according to the general procedure to give compound **3j** as colorless oil in 82% yield (30 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.72 (s, 3H), 3.50 (d, J = 11.1 Hz, 1H), 3.08 – 3.15 (m, 1H), 2.20 – 2.27 (m, 2H), 1.65 – 1.70 (m, 1H), 1.24 (s, 12H), 0.98 – 1.01 (m, 5H), 0.90 (d, J = 6.6 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.7, 168.5, 86.8, 83.6, 75.8, 55.5, 53.1, 39.1, 29.2, 25.14, 25.13, 22.1, 17.0, 13.7, 11.9. HRMS (ESI$^+$): *m/z* for $C_{19}H_{32}BO_6$ $[M+H]^+$ calcd. 367.2292, found 367.2284.



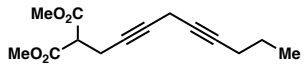
Dimethyl-2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-3-yn-5-yl)malonate (3k) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3k** as colorless oil in 86% yield (34 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.75 (s, 3H), 3.73 (s, 3H), 3.41 (d, *J* = 9.8 Hz, 1H), 3.05 – 3.11 (m, 1H), 2.22 (*app.* t, *J* = 7.0 Hz, 2H), 1.51 – 1.56 (m, 1H), 1.40 – 1.47 (m, 1H), 1.32 – 1.40 (m, 2H), 1.26 – 1.30 (m, 4H), 1.24 (s, 12H), 0.98 (t, *J* = 7.7 Hz, 2H), 0.87 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 168.5, 85.5, 83.5, 78.4, 57.2, 53.00, 52.98, 33.1, 32.4, 31.7, 27.1, 25.12, 25.11, 22.9, 14.4, 13.7, 11.9. HRMS (ESI^+): *m/z* for $C_{21}H_{35}BO_6Na$ $[M+Na]^+$ calcd. 417.2424, found 417.2422.



Dimethyl-2-(1-phenyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (3l) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **3l** as colorless oil in 72% yield (29 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.28 (dd, *J* = 7.7, 7.4 Hz, 2H), 7.23 (dd, *J* = 7.0, 6.9 Hz, 1H), 4.34 (*app.* d, *J* = 10.6 Hz, 1H), 3.79 (s, 3H), 3.72 (d, *J* = 10.6 Hz, 1H), 3.50 (s, 3H), 2.26 (td, *J* = 7.7, 1.5 Hz, 2H), 1.20 (s, 12H), 1.01 (t, *J* = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 167.5, 138.9, 128.8, 128.5, 127.8, 86.7, 83.6, 77.9, 60.0, 53.2, 52.9, 38.3, 25.08, 25.07, 13.8, 11.7. HRMS (ESI^+): *m/z* for $C_{22}H_{29}BO_6Na$ $[M+Na]^+$ calcd. 423.1955, found 423.1973.

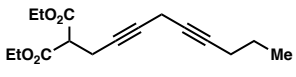


General procedure for the synthesis of skipped diynes 5: In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 10 mol %), NaO^{t}Bu (0.11 mmol, 1.1 equiv) and THF (0.5 mL). The mixture was stirred for 15 min at ambient temperature. Alkynyl boronate **6** (0.11 mmol, 1.1 equiv) was added, and the mixture was stirred for 5 min. Then vinylidene cyclopropane **1** (0.1 mmol, 1.0 equiv) was added, and the mixture was stirred for 1 – 24 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 (hexane/ethyl acetate) to give product **7**.



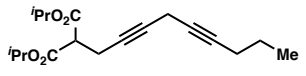
Dimethyl 2-(nona-2,5-diyn-1-yl)malonate (5a)

Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5a** as colorless oil in 76% yield (19 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.77 (s, 6H), 3.59 (t, J = 7.8 Hz, 1H), 3.09 – 3.10 (m, 2H), 2.77 (dt, J = 7.7, 2.2 Hz, 2H), 2.11 – 2.13 (m, 2H), 1.50 (tq, J = 7.3, 7.3 Hz, 2H), 0.96 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 169.0, 80.6, 77.6, 76.4, 75.0, 52.8, 51.6, 22.8, 20.9, 19.1, 13.7, 9.6. HRMS (EI$^+$): m/z for $C_{14}H_{18}O_4$ $[M]^+$ calcd. 250.1205, found 250.1192.



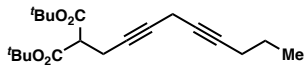
Diethyl 2-(nona-2,5-diyn-1-yl)malonate (5b)

Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5b** as colorless oil in 65% yield (18 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.22 (q, J = 6.6 Hz, 4H), 3.53 (t, J = 7.8 Hz, 1H), 3.09 – 3.10 (m, 2H), 2.75 – 2.77 (m, 2H), 2.10 – 2.12 (m, 2H), 1.50 (tq, J = 7.2, 7.2 Hz, 2H), 1.28 (t, J = 7.1 Hz, 6H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 168.6, 80.6, 77.5, 76.5, 75.0, 62.0, 51.8, 22.8, 20.9, 19.0, 14.3, 13.7, 9.6. HRMS (EI$^+$): m/z for $C_{16}H_{22}O_4$ $[M]^+$ calcd. 278.1518, found 278.1514.



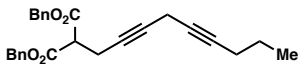
Diisopropyl 2-(nona-2,5-diyn-1-yl)malonate (5c)

Prepared according to the general procedure give compound **5c** as colorless oil in 81% yield (25 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.07 (hept, J = 6.3 Hz, 2H), 3.46 (t, J = 7.8 Hz, 1H), 3.09 (*app.* s, 2H), 2.73 (*app.* d, J = 7.7 Hz, 2H), 2.10 – 2.12 (m, 2H), 1.49 (tq, J = 7.2, 7.2 Hz, 2H), 1.25 (d, J = 6.0 Hz, 6H), 1.24 (d, J = 5.9 Hz, 6H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 80.9, 77.0, 76.3, 74.2, 69.5, 52.0, 22.4, 22.0, 21.9, 21.0, 18.9, 13.9, 10.1. HRMS (EI$^+$): m/z for $C_{18}H_{26}O_4$ $[M]^+$ calcd. 306.1831, found 306.1824.



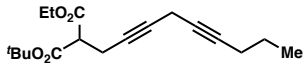
Di-*tert*-butyl 2-(nona-2,5-diyn-1-yl)malonate (5d)

Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5d** as colorless oil in 69% yield (23 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.33 (t, J = 7.8 Hz, 1H), 3.10 (*app.* s, 2H), 2.65 (*app.* d, J = 7.8 Hz, 2H), 2.10 – 2.12 (m, 2H), 1.46 – 1.52 (m, 20H), 0.95 (t, J = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.9, 82.2, 80.8, 76.7, 76.6, 74.3, 53.4, 28.2, 22.4, 21.0, 18.9, 13.9, 10.0. HRMS (ESI$^+$): m/z for $C_{20}H_{30}O_4Na$ $[M+Na]^+$ calcd. 357.2042, found 357.2049.



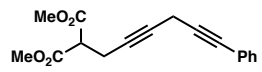
Dibenzyl 2-(nona-2,5-diyn-1-yl)malonate (5e)

Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5e** as colorless oil in 82% yield (33 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 – 7.33 (m, 10H), 5.17 (s, 4H), 3.66 (t, *J* = 7.7 Hz, 1H), 3.01 – 3.02 (m, 2H), 2.80 – 2.81 (m, 2H), 2.10 – 2.12 (m, 2H), 1.49 (tq, *J* = 7.3, 7.3 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 168.4, 136.7, 129.3, 129.0, 128.8, 80.7, 77.8, 76.5, 75.0, 67.6, 52.0, 22.8, 21.0, 19.2, 13.7, 9.7. HRMS (ESI^+): m/z for $C_{26}H_{26}O_4Na$ $[M+Na]^+$ calcd. 425.1729, found 425.1723.



1-(*Tert*-butyl) 3-ethyl 2-(nona-2,5-diyn-1-yl)malonate (5f)

Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5f** as colorless oil in 72% yield (22 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.16 – 4.25 (m, 2H), 3.43 (t, *J* = 7.8 Hz, 1H), 3.09 (*app.* s, 2H), 2.70 (*app.* d, *J* = 7.4 Hz, 2H), 2.10 – 2.12 (m, 2H), 1.47 – 1.52 (m, 2H), 1.46 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H), 0.95 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 167.6, 82.6, 80.9, 76.9, 76.4, 74.3, 61.8, 52.5, 28.2, 22.4, 21.0, 19.0, 14.4, 13.9, 10.1. HRMS (ESI^+): m/z for $C_{18}H_{26}O_4Na$ $[M+Na]^+$ calcd. 329.1729, found 329.1724.

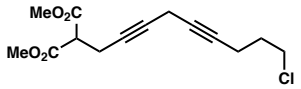


Dimethyl 2-(6-phenylhexa-2,5-diyn-1-yl)malonate (5g)

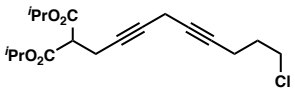
Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5g** as colorless oil in 53% yield (15 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 – 7.42 (m, 2H), 7.29 – 7.30 (m, 3H), 3.77 (s, 6H), 3.62 (t, *J* = 7.7 Hz, 1H), 3.35 (*app.* s, 2H), 2.79 – 2.81 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 132.0, 128.6, 128.4, 123.3, 83.9, 80.8, 76.6, 76.4, 53.3, 51.3, 19.1, 10.8. HRMS (EI^+): m/z for $C_{17}H_{16}O_4$ $[M]^+$ calcd. 284.1049, found 284.1070.

Diisopropyl 2-(6-phenylhexa-2,5-diyn-1-yl)malonate (5h)

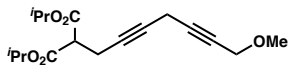
Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5h** as colorless oil in 56% yield (19 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.41 (m, 2H), 7.28 – 7.29 (m, 3H), 5.07 (hept, *J* = 6.1 Hz, 2H), 3.49 (t, *J* = 7.8 Hz, 1H), 3.35 (*app.* s, 2H), 2.75 – 2.77 (m, 2H), 1.24 – 1.25 (m, 12H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 132.0, 128.5, 128.4, 123.3, 84.0, 80.8, 76.9, 76.0, 69.6, 51.9, 22.0, 21.9, 18.9, 10.8. HRMS (EI^+): m/z for $C_{21}H_{24}O_4$ $[M]^+$ calcd. 340.1675, found 340.1660.



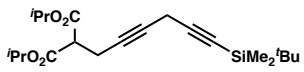
Dimethyl 2-(9-chlorononа-2,5-diyn-1-yl)malonate (5i) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5i** as colorless oil in 74% yield (21 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.77 (s, 6H), 3.64 (t, *J* = 6.3 Hz, 2H), 3.58 (t, *J* = 7.7 Hz, 1H), 3.08 – 3.09 (m, 2H), 2.77 – 2.78 (m, 2H), 2.34 – 2.36 (m, 2H), 1.93 (tt, *J* = 6.5 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 79.0, 77.0, 76.2, 75.3, 53.2, 51.3, 44.1, 31.6, 19.1, 16.4, 10.1. HRMS (EI^+): m/z for $C_{14}H_{17}ClO_4$ $[M]^+$ calcd. 284.0815, found 284.0828.



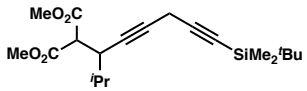
Diisopropyl 2-(9-chlorononа-2,5-diyn-1-yl)malonate (5j) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5j** as colorless oil in 82% yield (28 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.07 (hept, *J* = 6.0 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H), 3.46 (t, *J* = 7.8 Hz, 1H), 3.08 (*app.* s, 2H), 2.73 (*app.* d, *J* = 7.7 Hz, 2H), 2.33 – 2.35 (m, 2H), 1.93 (tt, *J* = 6.5 Hz, 2H), 1.25 (d, *J* = 6.0 Hz, 6H), 1.24 (d, *J* = 5.8 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 78.9, 76.6, 76.5, 75.3, 69.6, 51.9, 44.1, 31.6, 22.0, 21.9, 18.9, 16.4, 10.1. HRMS (EI^+): m/z for $C_{18}H_{25}ClO_4$ $[M]^+$ calcd. 340.1441, found 340.1454.



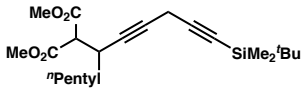
Diisopropyl 2-(7-methoxyhepta-2,5-diyn-1-yl)malonate (5k) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5k** as colorless oil in 78% yield (24 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.07 (hept, *J* = 6.1 Hz, 2H), 4.07 (*app.* s, 2H), 3.46 (t, *J* = 7.7 Hz, 1H), 3.36 (s, 3H), 3.16 (*app.* s, 2H), 2.73 (*app.* d, *J* = 7.7 Hz, 2H), 1.25 (d, *J* = 6.2 Hz, 6H), 1.24 (d, *J* = 6.1 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 81.1, 76.9, 76.4, 75.8, 69.6, 60.3, 58.0, 51.9, 22.0, 21.9, 18.9, 10.2. HRMS (ESI^+): *m*/*z* for $C_{17}H_{25}O_5$ $[M+H]^+$ calcd. 309.1702, found 309.1717.



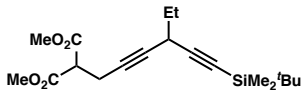
Diisopropyl-2-(6-(*tert*-butyldimethylsilyl)hexa-2,5-diyn-1-yl) malonate (5l) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5l** as colorless oil in 87% yield (33 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.07 (hept, *J* = 6.1 Hz, 2H), 3.45 (t, *J* = 7.8 Hz, 1H), 3.16 (*app.* s, 2H), 2.72 – 2.74 (m, 2H), 1.25 (d, *J* = 6.0 Hz, 6H), 1.24 (d, *J* = 5.8 Hz, 6H), 0.91 (s, 9H), 0.07 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.0, 100.8, 83.3, 76.7, 75.9, 69.6, 51.9, 26.4, 22.0, 21.9, 18.9, 16.9, 11.2, -4.3. HRMS (ESI^+): *m*/*z* for $C_{21}H_{34}O_4SiNa$ $[M+Na]^+$ calcd. 401.2124, found 401.2135.



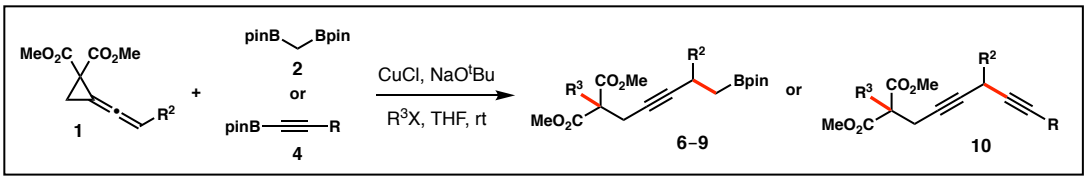
Dimethyl-2-(8-(*tert*-butyldimethylsilyl)-2-methylocta-4,7-diyn-3-yl)malonate (5m) Prepared according to the general procedure to give compound **5m** as colorless oil in 68% yield (25 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.74 (s, 3H), 3.54 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.17 (m, 3H), 1.69 – 1.73 (m, 1H), 1.02 (d, *J* = 6.6 Hz, 3H), 0.92 – 0.93 (m, 12H), 0.07 (s, 6H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 168.4, 168.3, 102.4, 82.9, 79.0, 78.0, 55.3, 52.9, 52.8, 39.3, 29.6, 26.3, 22.0, 17.0, 16.9, 10.7, -4.5. HRMS (ESI$^+$): *m*/*z* for $C_{20}H_{33}O_4Si$ $[M+H]^+$ calcd. 365.2148, found 365.2148.



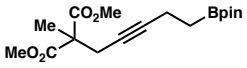
Dimethyl-2-(1-(*tert*-butyldimethylsilyl)undeca-1,4-diyn-6-yl) malonate (5n) Prepared according to the general procedure. The crude mixture was purified by column chromatography to give compound **5n** as colorless oil in 82% yield (32 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.76 (s, 3H), 3.74 (s, 3H), 3.45 (d, *J* = 9.6 Hz, 1H), 3.17 (d, *J* = 2.0 Hz, 2H), 3.10 – 3.14 (m, 1H), 1.53 – 1.55 (m, 1H), 1.37 – 1.48 (m, 3H), 1.24 – 1.30 (m, 4H), 0.92 (s, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.07 (s, 6H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 168.5, 168.4, 102.3, 82.9, 80.4, 77.7, 56.9, 52.8, 52.7, 33.2, 32.5, 32.0, 27.5, 26.3, 23.2, 17.0, 14.3, 10.7, -4.5. HRMS (ESI$^+$): *m*/*z* for $C_{22}H_{37}O_4Si$ $[M+H]^+$ calcd. 393.2461, found 393.2453.



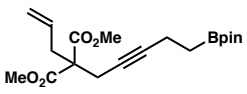
Dimethyl-2-(6-(butyldimethylsilyl)-4-ethylhexa-2,5-diyn-1-yl)malonate (5o) Prepared according to the general procedure to give compound **5o** as colorless oil in 83% yield (29 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.76 (s, 6H), 3.59 (t, *J* = 7.8 Hz, 1H), 3.28 (*app.* t, *J* = 6.2 Hz, 1H), 2.78 (dd, *J* = 7.7, 1.3 Hz, 2H), 1.67 (dq, *J* = 7.0, 7.0 Hz, 2H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.91 (s, 9H), 0.079 (s, 3H), 0.076 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 168.8, 105.2, 83.5, 80.8, 76.8, 53.2, 51.5, 29.6, 26.4, 25.9, 19.2, 16.9, 11.5, -4.3. HRMS (ESI$^+$): *m*/*z* for $C_{19}H_{31}O_4Si$ $[M+H]^+$ calcd. 351.1992, found 351.1980



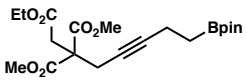
General procedure for the three-component reactions: In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 10 mol %), NaO^{t}Bu (0.11 mmol, 1.1 equiv) and THF (0.5 mL). The resulting mixture was stirred for 15 min at ambient temperature. Bis[(pinacolato)boryl]methane **2** or alkynyl boronate **4** (0.11 mmol, 1.1 equiv) was added, and the mixture was stirred for 5 min. Then vinylidene cyclopropane **1** (0.1 mmol, 1.0 equiv) and R^3X (0.2 mmol, 2.0 equiv) were added sequentially and the mixture was stirred at ambient temperature. Upon complete consumption of vinylidene cyclopropane **1**, the reaction mixture was filtered through a short 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.



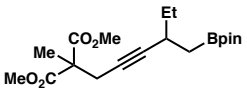
Dimethyl-2-methyl-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (6) Prepared according to the general procedure from **1a** with iodomethane as the trapping agent. The crude mixture was purified by column chromatography to give compound **6** as colorless oil in 83% yield (28 mg).. ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.72 (s, 6H), 2.72 (*app.* s, 2H), 2.20 – 2.23 (m, 2H), 1.52 (s, 3H), 1.24 (s, 12H), 0.99 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 85.5, 83.6, 74.1, 53.8, 53.1, 26.5, 25.1, 20.3, 13.7. HRMS (ESI$^+$): *m/z* for $C_{17}H_{28}BO_6$ $[M+H]^+$ calcd. 339.1979, found 339.1978.



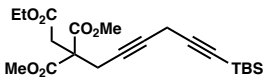
Dimethyl-2-allyl-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-yn-1-yl)malonate (7) Prepared according to the general procedure from **1a** with allylic iodide as the trapping agent. The crude mixture was purified by column chromatography to give compound **7** as colorless oil in 66% yield (24 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.58 – 5.65 (m, 1H), 5.16 (d, J = 17.0 Hz, 1H), 5.10 (d, J = 10.0 Hz, 1H), 3.72 (s, 6H), 2.78 (d, J = 7.4 Hz, 2H), 2.73 (*app.* s, 2H), 2.22 (*app.* t, J = 7.6 Hz, 2H), 1.24 (s, 12H), 1.00 (t, J = 7.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 132.3, 120.0, 85.7, 83.6, 73.7, 57.6, 53.1, 36.8, 25.1, 23.3, 13.7. HRMS (ESI$^+$): *m/z* for $C_{19}H_{30}BO_6$ $[M+H]^+$ calcd. 365.2135, found 365.2125.



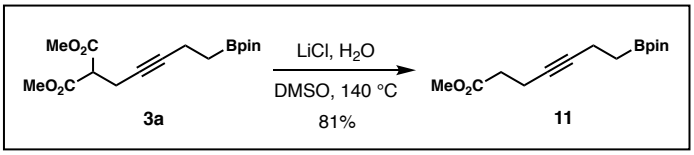
1-Ethyl-2,2-dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-4-yne-1,2,2-tricarboxylate (8) Prepared according to the general procedure from **1a** with ethyl bromoacetate as the trapping agent. The crude mixture was purified by column chromatography to give compound **8** as colorless oil in 80% yield (33 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.12 (q, J = 7.0 Hz, 2H), 3.74 (s, 6H), 3.15 (s, 2H), 2.92 (*app.* s, 2H), 2.21 (*app.* t, J = 7.4 Hz, 2H), 1.24 – 1.25 (m, 15H), 0.98 (t, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.9, 170.1, 86.1, 83.6, 73.6, 61.2, 55.5, 53.4, 37.3, 25.1, 24.4, 14.4, 13.7, 11.7. HRMS (ESI$^+$): *m*/*z* for $C_{20}H_{31}BO_8Na$ $[M+Na]^+$ calcd. 433.2010, found 433.2034.



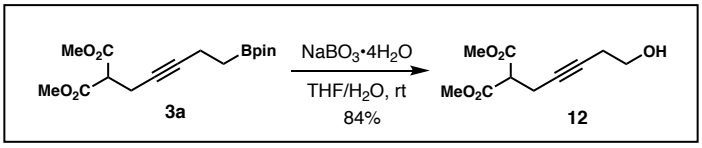
Dimethyl-2-methyl-2-(4-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hex-2-yn-1-yl)malonate (9) Prepared according to the general procedure from **1i** with iodomethane as the trapping agent. The crude mixture was purified by column chromatography to give compound **9** as colorless oil in 79% yield (29 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.72 (s, 6H), 2.73 (d, J = 1.4 Hz, 2H), 2.39 – 2.46 (m, 1H), 1.52 (s, 3H), 1.41 – 1.48 (m, 1H), 1.31 – 1.39 (m, 1H), 1.24 (s, 12H), 0.92 – 1.01 (m, 5H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 172.0, 88.2, 83.5, 75.2, 53.9, 53.1, 30.8, 29.2, 26.6, 25.1, 25.0, 20.3, 18.8, 12.1. HRMS (ESI$^+$): *m*/*z* for $C_{19}H_{31}BO_6Na$ $[M+Na]^+$ calcd. 389.2111, found 389.2101.



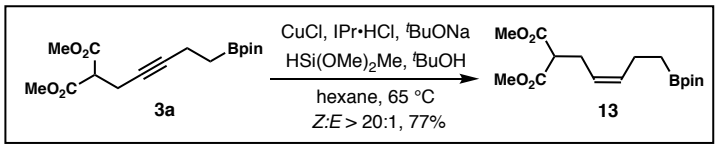
1-Ethyl-2,2-dimethyl-8-(*tert*-butyldimethylsilyl)octa-4,7-diyne-1,2,2-tricarboxylate (10) Prepared according to the general procedure from **1a** and alkynyl boronate **4e** with ethyl bromoacetate as the trapping agent. The crude mixture was purified by column chromatography to give compound **10** as colorless oil in 73% yield (30 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.13 (q, J = 7.1 Hz, 2H), 3.75 (s, 6H), 3.15 (*app.* s, 4H), 2.97 (*app.* s, 2H), 1.25 (t, J = 7.1 Hz, 3H), 0.92 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 169.9, 100.7, 83.5, 77.8, 75.2, 61.2, 55.3, 53.5, 37.3, 26.3, 24.3, 16.9, 14.4, 11.3, -4.4. HRMS (ESI$^+$): *m*/*z* for $C_{21}H_{32}O_6SiNa$ $[M+Na]^+$ calcd. 431.1866, found 431.1880.



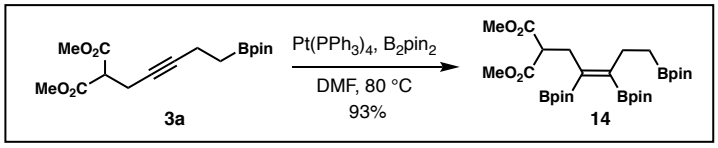
Methyl 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-4-ynoate (11) To a reaction vial containing a Teflon-coated magnetic stirring bar were sequentially added compound **3a** (0.06 mmol, 1.0 equiv), LiCl (0.12 mmol, 2.0 equiv), H_2O (0.12 mmol, 2.0 equiv) and DMSO (0.2 mL). The resulting mixture was stirred at 140 °C for 4 h, and then cooled to ambient temperature. Water (0.5 mL) was added, and the mixture was extracted with Et_2O (3 x 1 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (hexane/ethyl acetate) to give product **11** as colorless oil in 81% yield (13 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.68 (s, 3H), 2.48 – 2.51 (m, 2H), 2.43 – 2.45 (m, 2H), 2.23 (*app.* t, J = 7.4 Hz, 2H), 1.24 (s, 12H), 1.00 (t, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 172.7, 83.7, 82.9, 78.3, 51.7, 34.2, 25.0, 15.0, 13.9, 12.0. HRMS (ESI$^+$): *m/z* for $C_{14}H_{24}BO_4$ $[M+H]^+$ calcd. 267.1768, found 267.1767.



Dimethyl 2-(5-hydroxypent-2-yn-1-yl)malonate (12) To a reaction vial containing a Teflon-coated magnetic stirring bar were added compound **3a** (0.1 mmol, 1.0 equiv) and THF (0.5 mL). An aqueous solution of $NaBO_3$•$4H_2O$ (0.2 mmol, 2.0 equiv in 0.5 mL water) was added to the vial. The reaction mixture was stirred at ambient temperature for 16 h. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 1 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (hexane/ethyl acetate) to give product **12** as colorless oil in 84% yield (18 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.77 (s, 6H), 3.66 (t, J = 5.8 Hz, 2H), 3.58 (t, J = 7.5 Hz, 1H), 2.75 – 2.77 (m, 2H), 2.38 – 2.40 (m, 2H), 1.94 (br, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 79.9, 78.2, 61.4, 53.3, 51.5, 23.4, 19.2. HRMS (ESI$^+$): m/z for $C_{10}H_{14}O_5Na$ $[M+Na]^+$ calcd. 237.0739, found 237.0750.

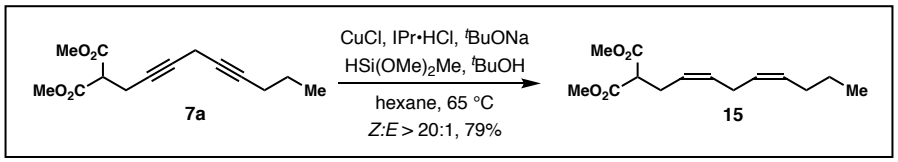


Dimethyl-(*Z*)-2-(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-1-yl)malonate (13) In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 10 mol %), IPr•HCl (0.01 mmol, 10 mol %), NaO^{t}Bu (0.03 mmol, 30 mol %) and hexane (0.5 mL). The mixture was stirred for 15 min at ambient temperature. Compound **3a** (0.1 mmol, 1.0 equiv), $HSi(OMe)_2Me$ (0.4 mmol, 4.0 equiv) and ^{t}BuOH (0.2 mmol, 2.0 equiv) were added to the mixture sequentially. The vial was sealed with a cap containing a PTFE-lined silicone septum and removed from the glove box stirring at 65 °C for 2 h. The reaction mixture was cooled to ambient temperature and filtered through a pad of silica gel. The solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (hexane/ethyl acetate) to give product **13** as colorless oil in 77% yield (25 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.49 (dt, *J* = 9.2, 7.6 Hz, 1H), 5.23 (dt, *J* = 9.2, 7.7 Hz, 1H), 3.73 (s, 6H), 3.40 (t, *J* = 7.6 Hz, 1H), 2.66 (dd, *J* = 7.3, 7.3 Hz, 2H), 2.15 (dt, *J* = 7.4, 7.3 Hz, 2H), 1.24 (s, 12H), 0.83 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 135.5, 123.8, 83.4, 52.9, 52.1, 27.0, 25.2, 22.0. HRMS (ESI^+): m/z for $C_{16}H_{27}BO_6Na$ $[M+Na]^+$ calcd. 349.1798, found 349.1801.

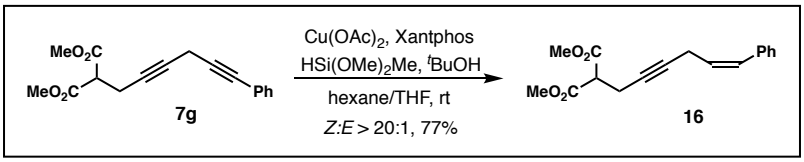


Dimethyl-(*Z*)-2-(2,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-1-yl)malonate (14) In an Ar-filled glove box, $Pt(PPh)_4$ (0.0025 mmol, 5 mol %), B_2Pin_2 (0.15 mmol, 3 equiv), compound **3a** (0.05 mmol, 1.0 equiv), DMF (0.5 mL) and a Teflon-coated magnetic stirring bar were sequentially added into a 1-dram vial. The vial was sealed with a cap containing a PTFE-lined silicone septum and removed from the glove box stirring at 80 °C for 3 h. The mixture was cooled to ambient temperature and water (1 mL) was added. The reaction mixture was extracted with Et_2O (3 x 1 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and

concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (hexane/ethyl acetate) to give product **14** as colorless oil in 93% yield (27 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 3.73 (t, *J* = 7.4 Hz, 1H), 3.69 (s, 6H), 2.82 (d, *J* = 7.4 Hz, 2H), 2.31 (t, *J* = 8.5 Hz, 2H), 1.28 (s, 12H), 1.25 (s, 12H), 1.23 (s, 12H), 0.83 (t, *J* = 8.4 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.3, 83.8, 83.7, 83.2, 52.6, 51.8, 29.4, 25.6, 25.4, 25.2. HRMS (ESI^+): m/z for $C_{28}H_{49}B_3O_{10}Na$ $[M+Na]^+$ calcd. 601.3503, found 601.3485.



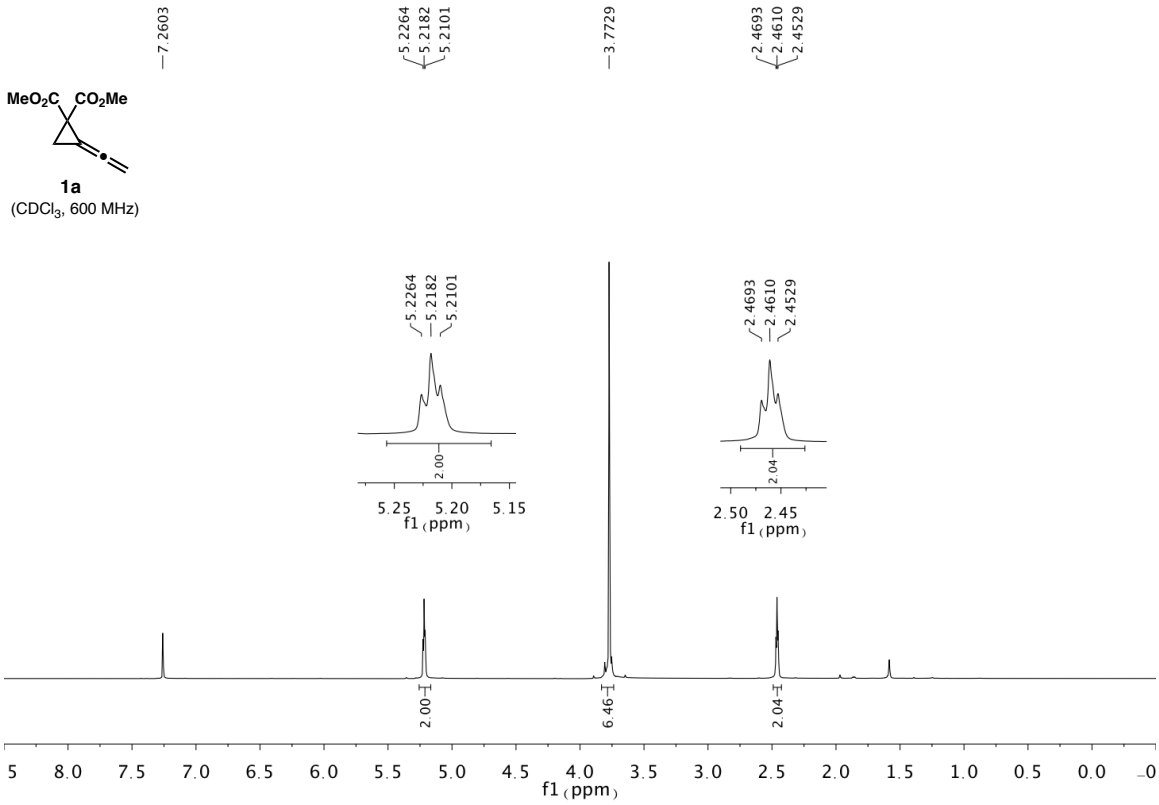
Dimethyl 2-((2*Z*,5*Z*)-nona-2,5-dien-1-yl)malonate (15) In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added CuCl (0.01 mmol, 20 mol %), IPr•HCl (0.01 mmol, 20 mol %), NaO^{t}Bu (0.03 mmol, 60 mol %) and hexane (0.5 mL). The mixture was stirred for 15 min at ambient temperature. Compound **7a** (0.05 mmol, 1.0 equiv), $HSi(OMe)_2Me$ (0.4 mmol, 8.0 equiv) and ^{t}BuOH (0.2 mmol, 4.0 equiv) were added to the mixture sequentially. The vial was sealed with a cap containing a PTFE-lined silicone septum and removed from the glove box stirring at 65 °C for 2 h. The reaction mixture was cooled to ambient temperature and filtered through a pad of silica gel. The solution was concentrated under reduced pressure. Purification of the crude product was performed by flash column chromatography (hexane/ethyl acetate) to give product **15** as colorless oil in 79% yield (10 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.44 – 5.48 (m, 1H), 5.38 – 5.42 (m, 1H), 5.28 – 5.33 (m, 2H), 3.74 (s, 6H), 3.41 (t, *J* = 7.6 Hz, 1H), 2.81 (dd, *J* = 6.2, 5.9 Hz, 2H), 2.68 (dd, *J* = 7.3, 7.0 Hz, 2H), 2.03 (dt, *J* = 7.1, 6.3 Hz, 2H), 1.37 (tq, *J* = 7.3, 7.3 Hz, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 131.9, 130.8, 127.6, 124.9, 53.0, 51.9, 29.6, 27.0, 25.9, 23.1, 14.2. HRMS (ESI^+): m/z for $C_{14}H_{22}O_4Na$ $[M+Na]^+$ calcd. 277.1416, found 277.1414.

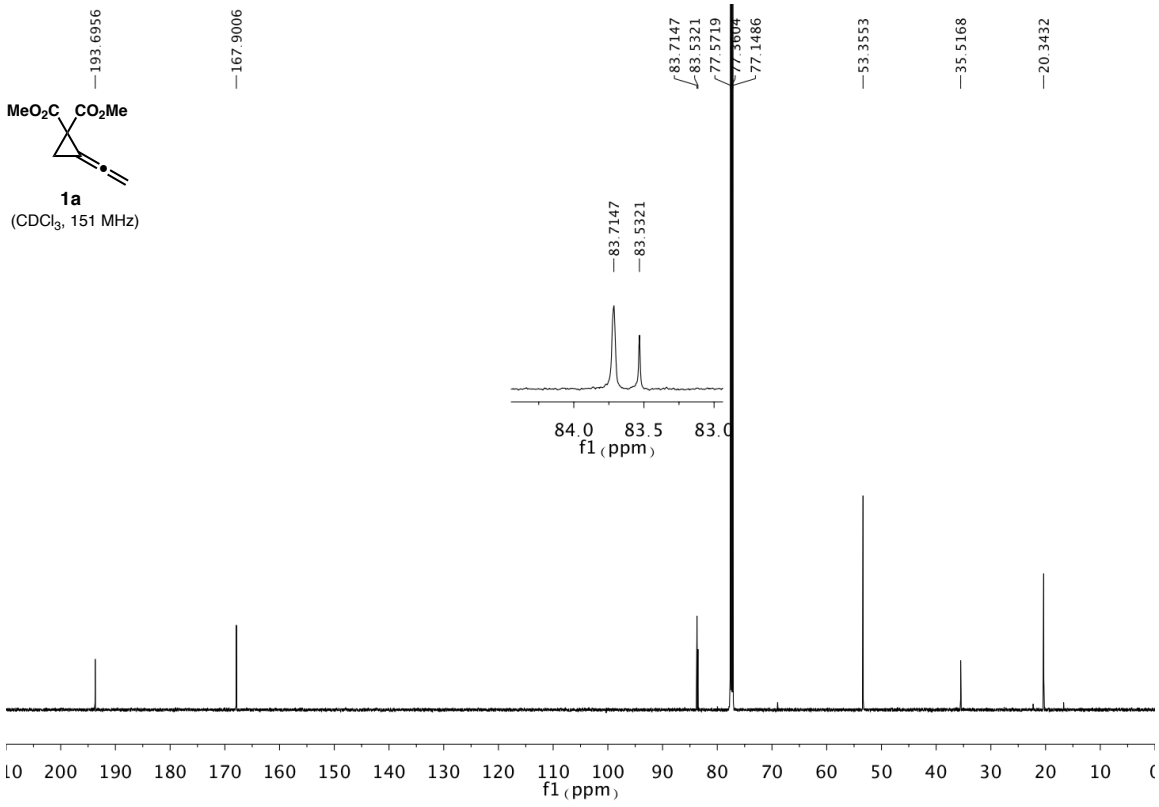


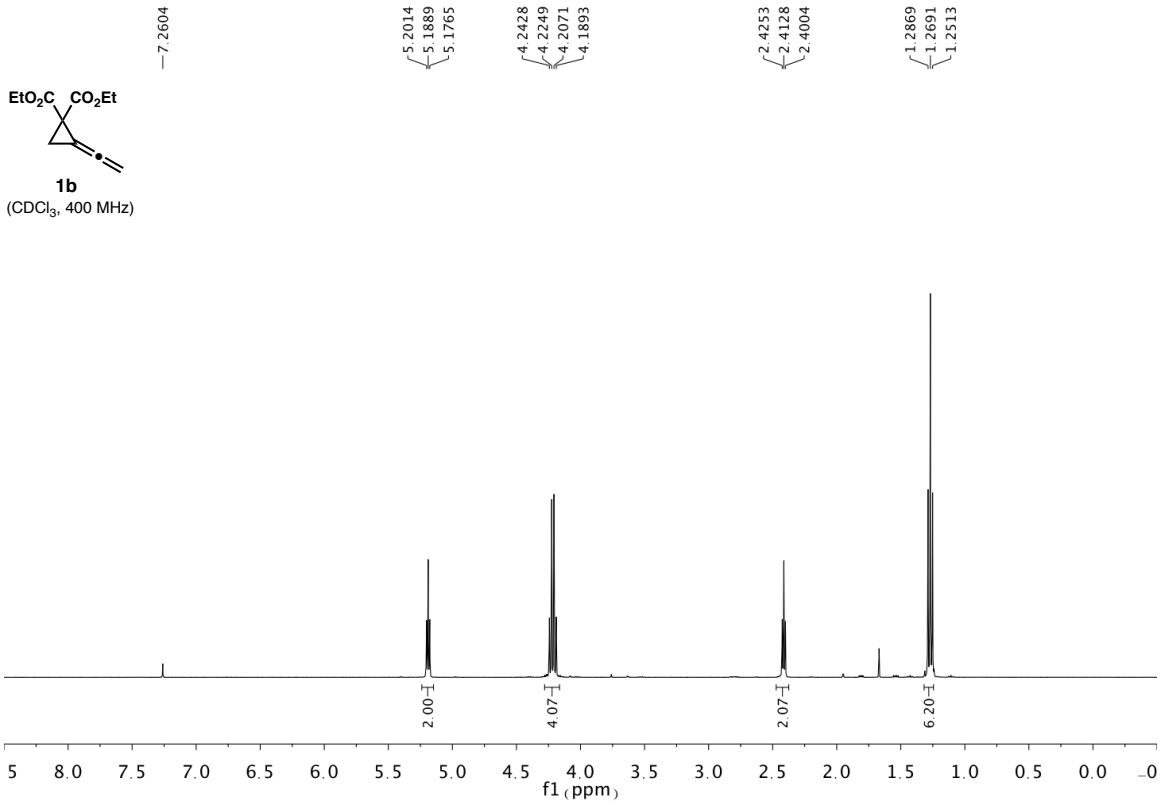
Dimethyl (*Z*)-2-(6-phenylhex-5-en-2-yn-1-yl)malonate (16) In an Ar-filled glove box, to a reaction vial containing a Teflon-coated magnetic stirring bar were added $Cu(OAc)_2$ (0.01 mmol, 20 mol %) and Xantphos (0.01 mmol, 20 mol %), THF (0.3 mL) and hexane (0.3 mL). The mixture was stirred for 15 min at ambient temperature. Compound **7g** (0.05 mmol, 1.0 equiv), $HSi(OMe)_2Me$ (0.1 mmol, 2.0 equiv) and ^{t}BuOH (0.1 mmol, 2.0 equiv) were added sequentially to the vial, and the mixture was stirred for 6 h. The reaction mixture was then 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 (hexane/ethyl acetate) to give product **16** as colorless oil in 77% yield (11 mg). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.36 (m, 2H), 7.23 – 7.28 (m, 3H), 6.49 (d, J = 11.3 Hz, 1H), 5.69 (dt, J = 11.1, 7.4 Hz, 1H), 3.76 (s, 6H), 3.59 (t, J = 7.7 Hz, 1H), 3.11 (d, J = 5.8 Hz, 2H), 2.78 (d, J = 7.6 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.9, 136.7, 130.7, 129.0, 128.6, 127.4, 127.0, 80.9, 76.2, 53.2, 51.6, 19.3, 18.9. HRMS (ESI^+): m/z for $C_{17}H_{18}O_4Na$ $[M+Na]^+$ calcd. 309.1103, found 309.1096.

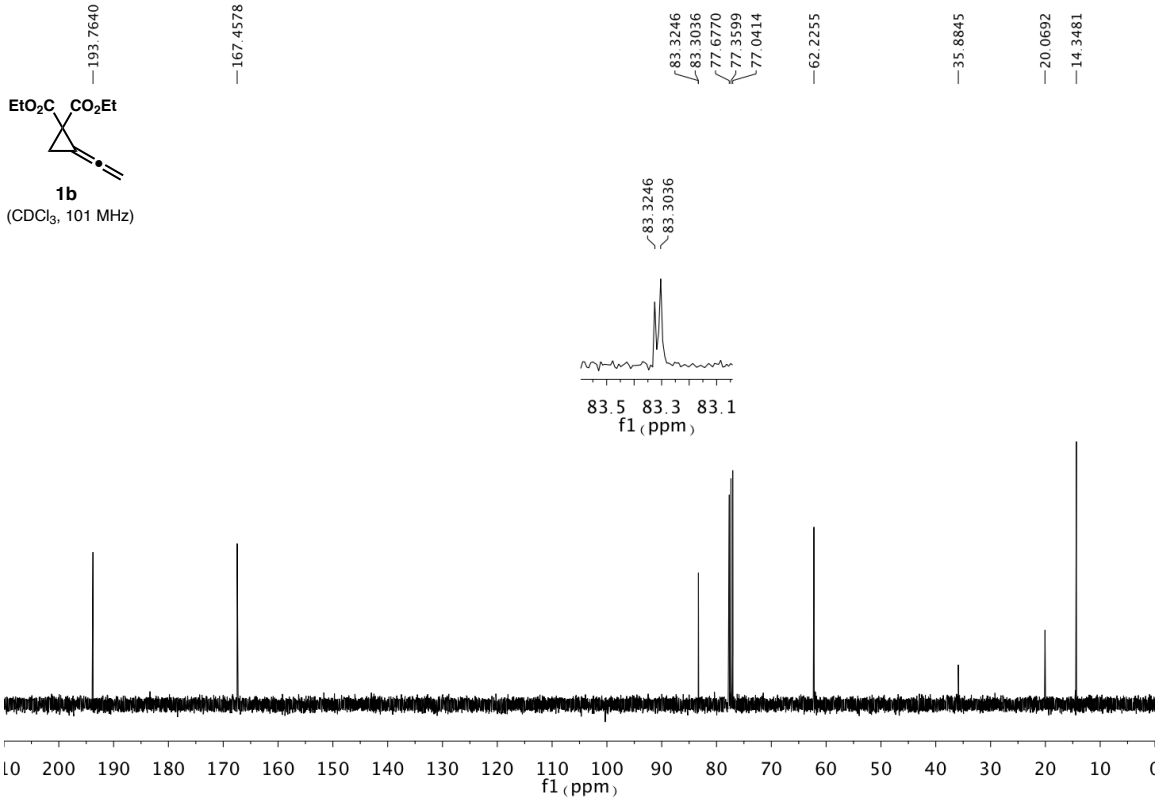
Reference:

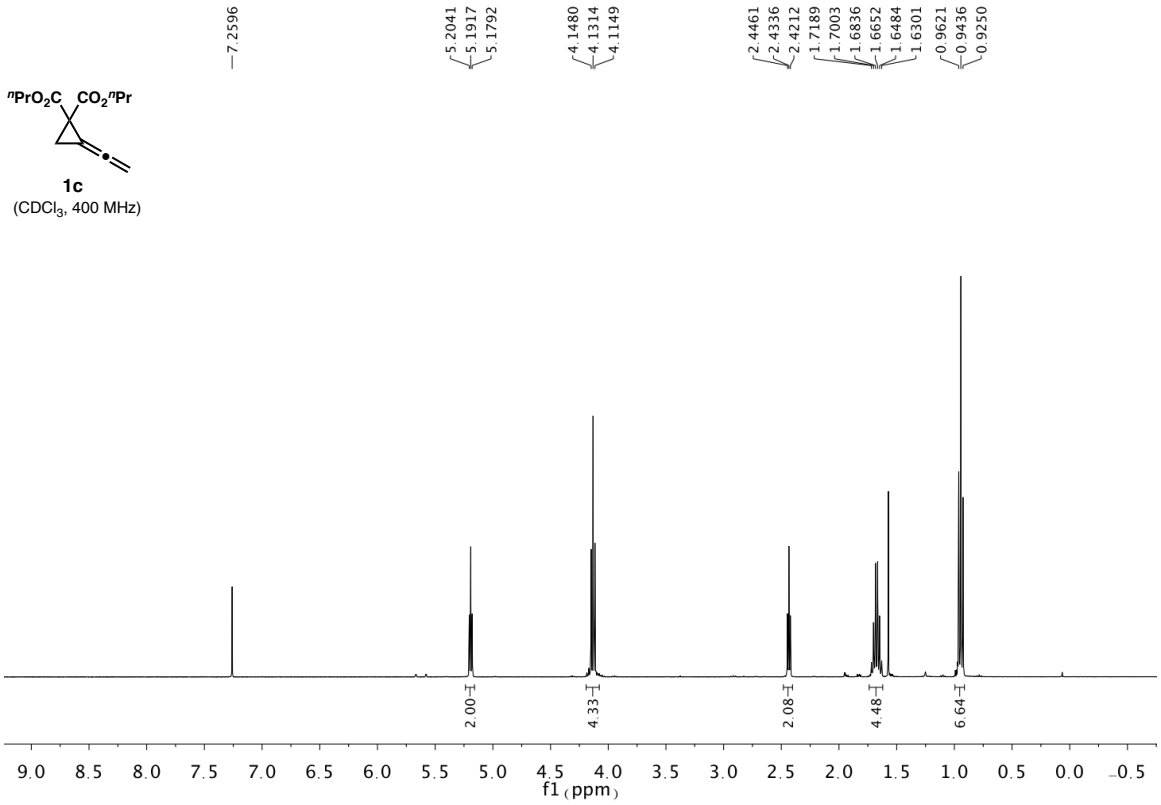
1. Iafe, R. G.; Kuo, J. L.; Hochstatter, D. G.; Saga, T.; Turner, J. W.; Merlic, C. A. *Org. Lett.* **2013**, *15*, 582.
2. Campbell, M. J.; Pohlhaus, P. D.; Min, G.; Ohmatsu, K.; Johnson, J. S. *J. Am. Chem. Soc.* **2008**, *130*, 9180.
3. Trost, B. M.; Rudd. M. T. *J. Am. Chem. Soc.*, 2005, **127**, 4763
4. Shinohara, R.; Ogawa, N.; Kawashima, H.; Wada, K.; Saito, S.; Yamazaki, T.; Kobayashi, Y. *Eur. J. Org. Chem.* **2019**, 1461.

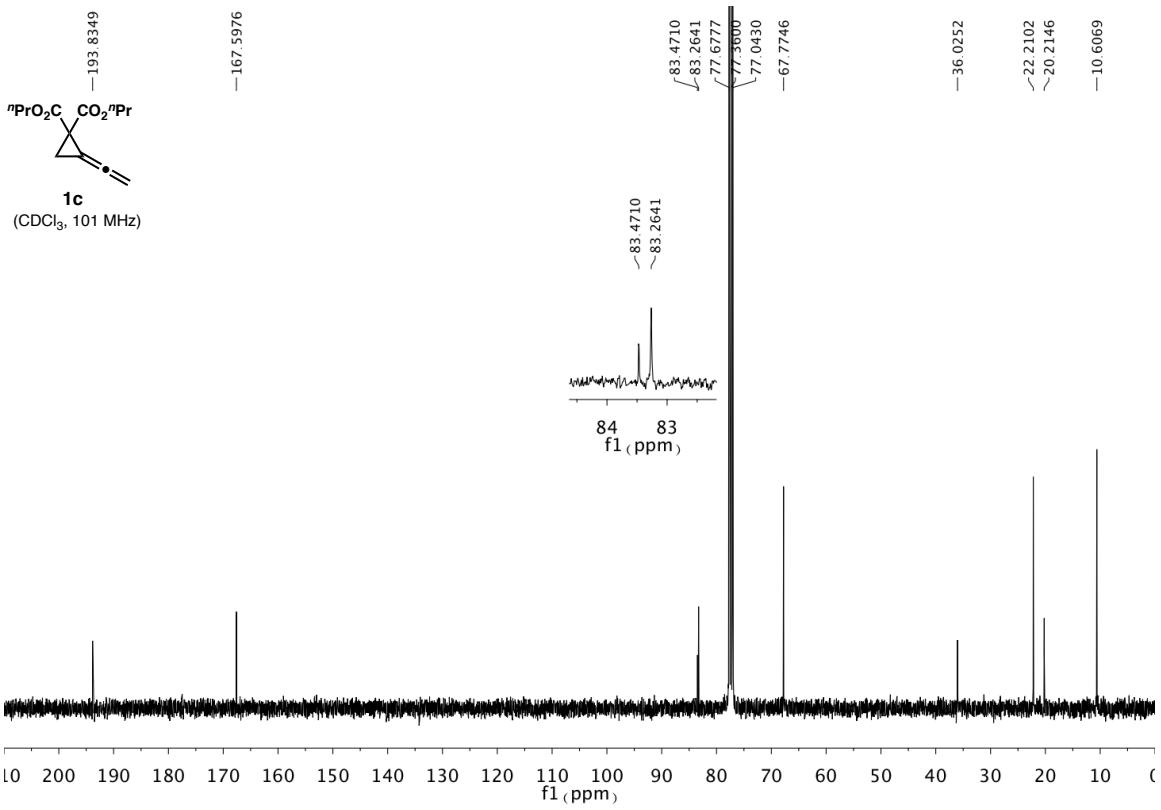

7.2603
5.2264
5.2182
5.2101
3.7729
2.4693
2.4610
2.4529
MeO2C CO2Me
1a
(CDCl3, 600 MHz)
2.00
2.04
2.00
6.46
2.04
f1 (ppm)

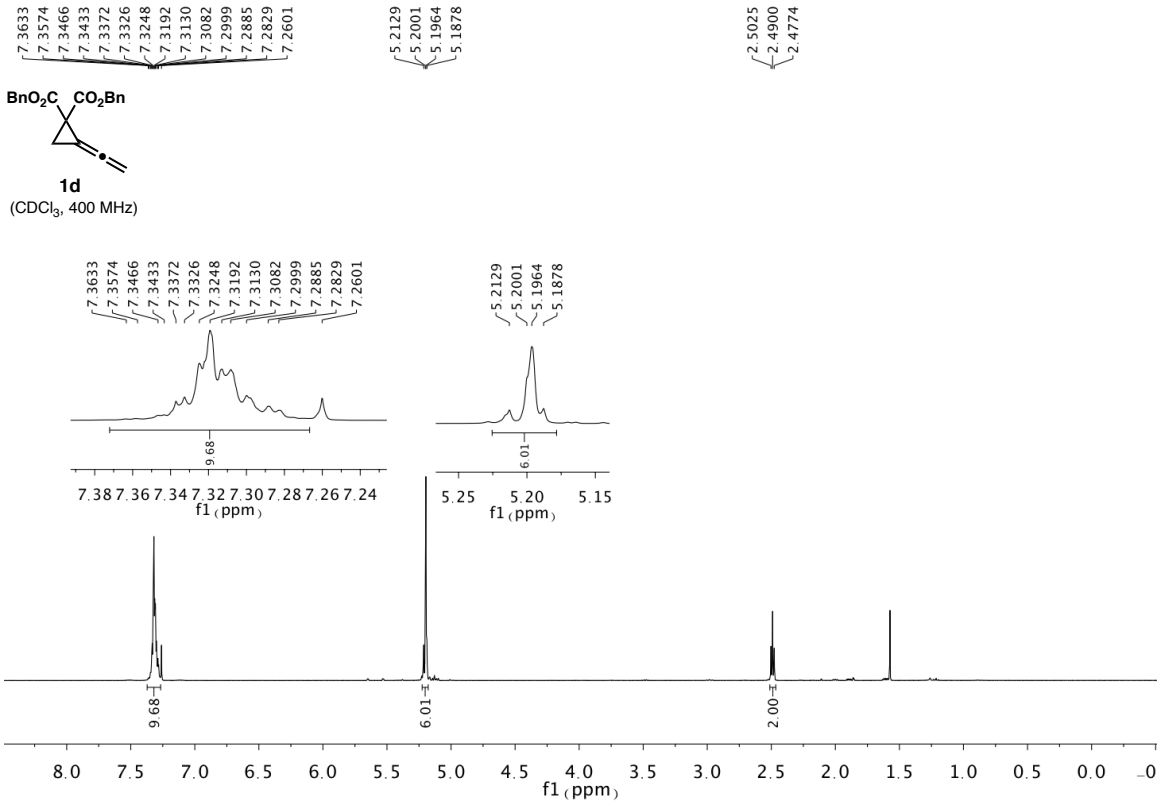

193.6956
167.9006
83.7147
83.5321
77.5719
77.3604
77.1486
53.3553
35.5168
20.3432
MeO2C CO2Me
1a
(CDCl3, 151 MHz)
f1 (ppm)

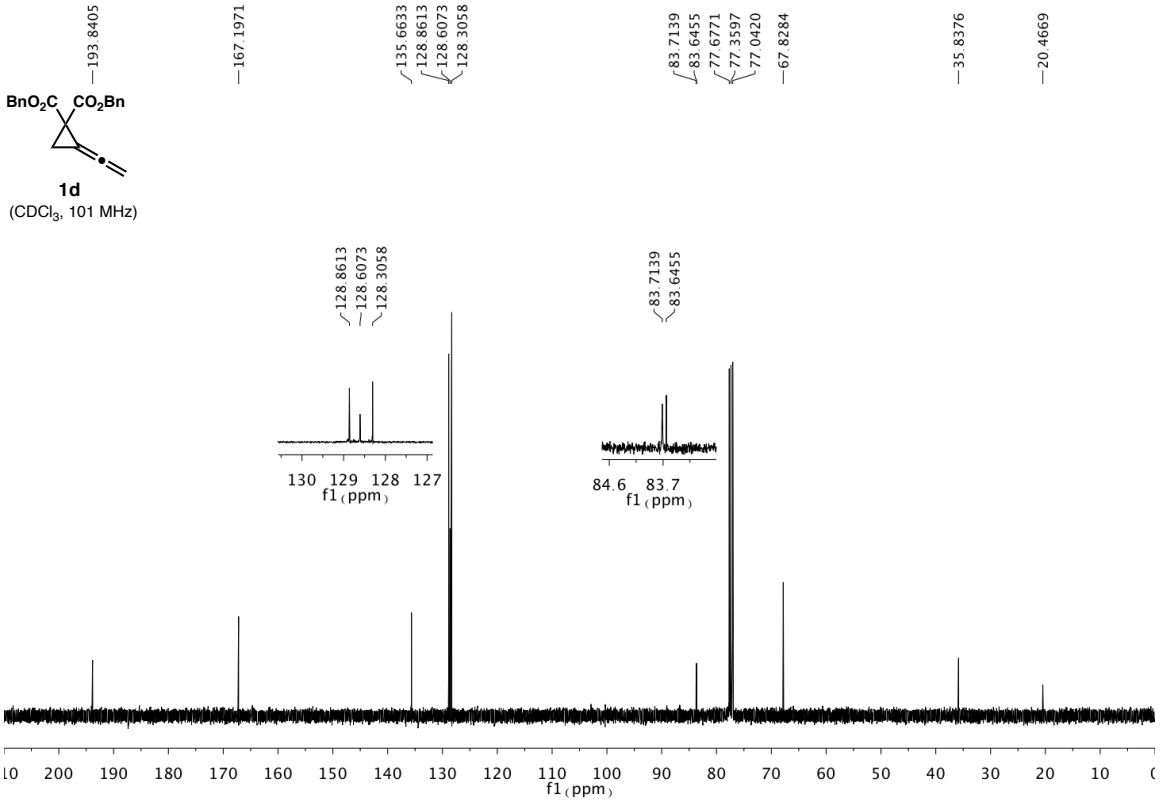

7.2604
5.2014
5.1889
5.1765
4.2428
4.2249
4.2071
4.1893
2.4253
2.4128
2.4004
1.2869
1.2691
1.2513
EtO2C CO2Et
1b
(CDCl3, 400 MHz)
2.00
4.07
2.07
6.20
f1 (ppm)

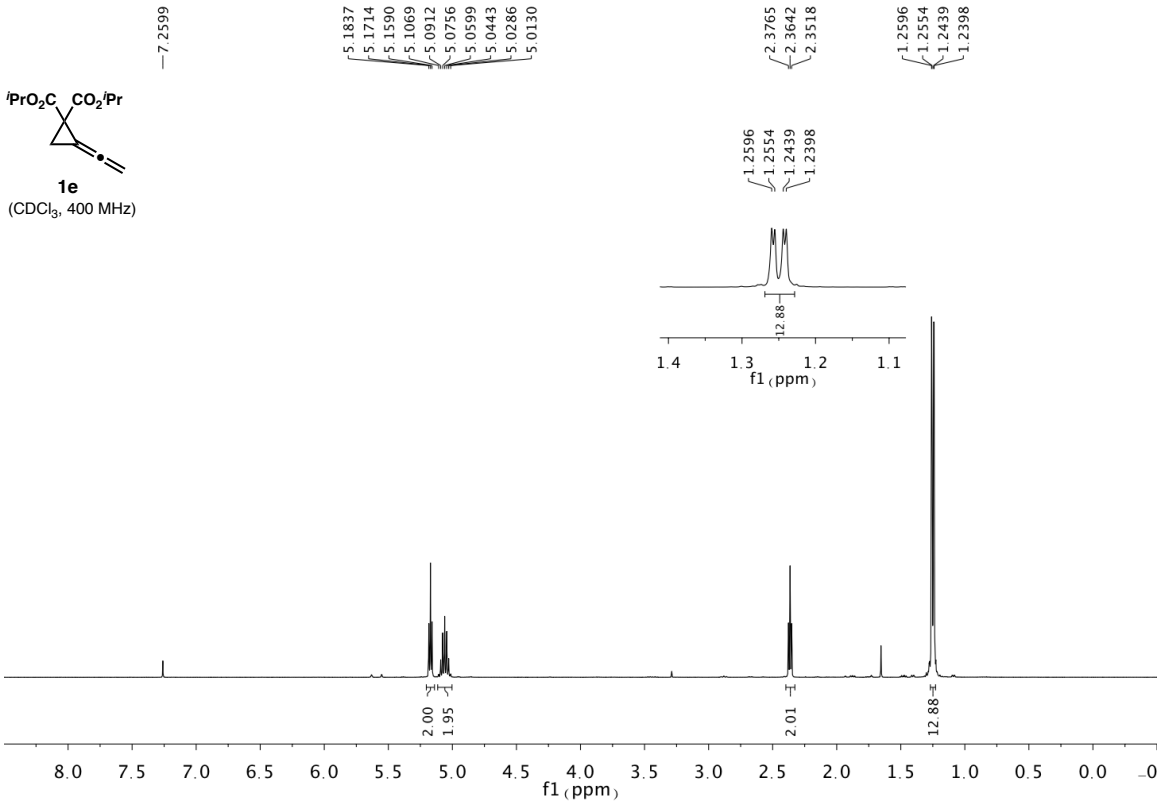

193.7640
167.4578
83.3246
83.3036
77.6770
77.3599
77.0414
62.2255
35.8845
20.0692
14.3481
EtO2C CO2Et
1b
(CDCl3, 101 MHz)
83.3246
83.3036
83.5 83.3 83.1
f1 (ppm)
f1 (ppm)

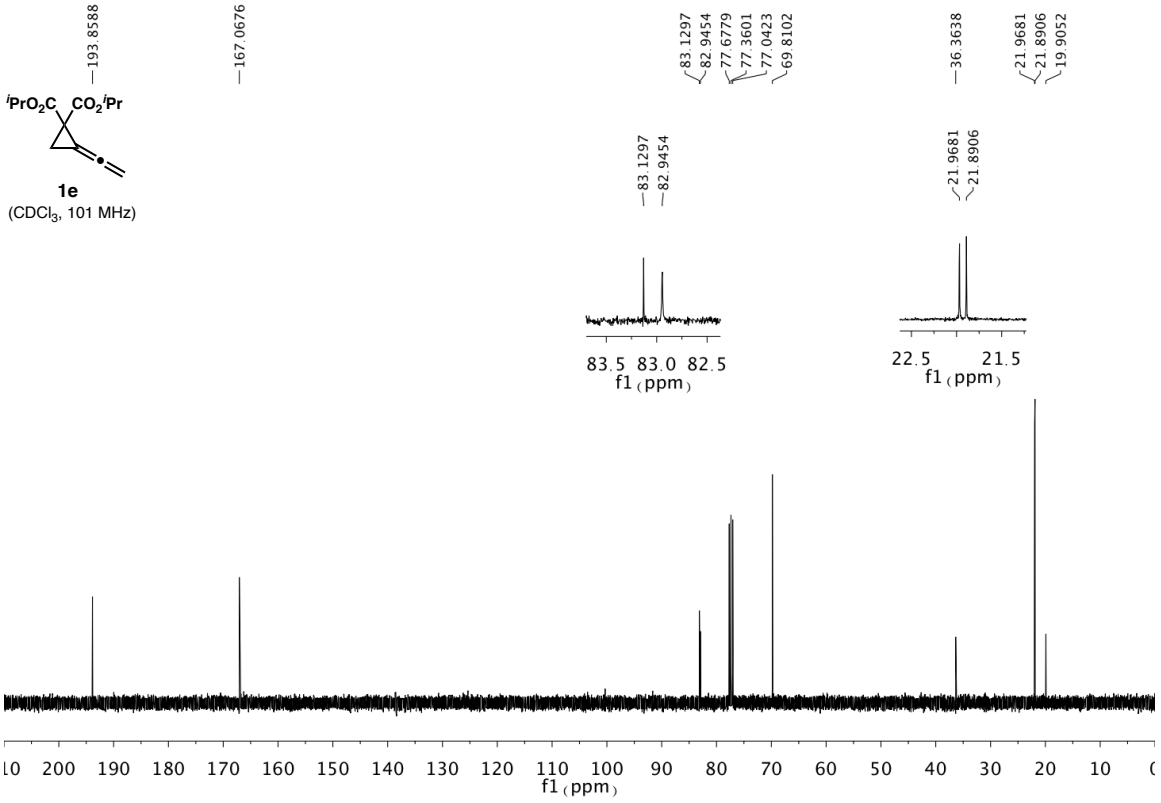

7.2596
5.2041
5.1917
5.1792
4.1480
4.1314
4.1149
2.4461
2.4336
2.4212
1.7189
1.7003
1.6836
1.6652
1.6484
1.6301
0.9621
0.9436
0.9250
2.00
4.33
2.08
4.48
6.64
f1 (ppm)

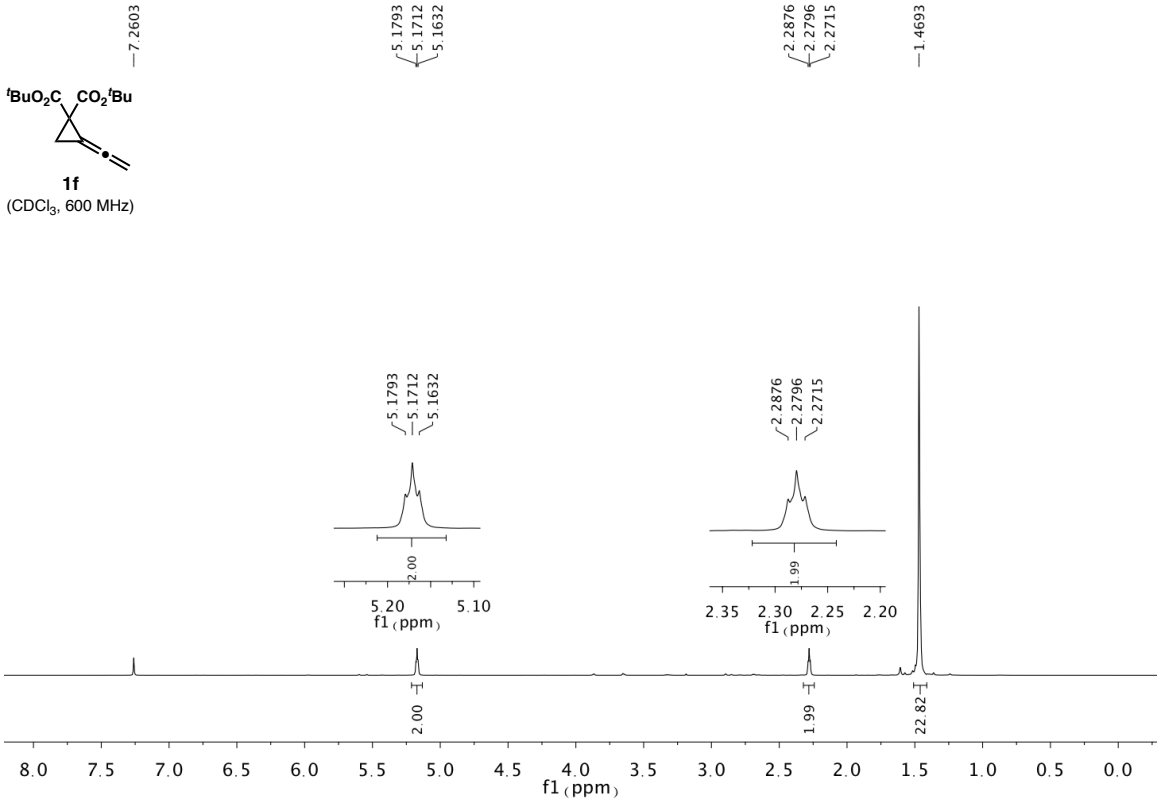

193.8349
167.5976
83.4710
83.2641
77.6777
77.3600
77.0430
67.7746
36.0252
22.2102
20.2146
10.6069
f1 (ppm)

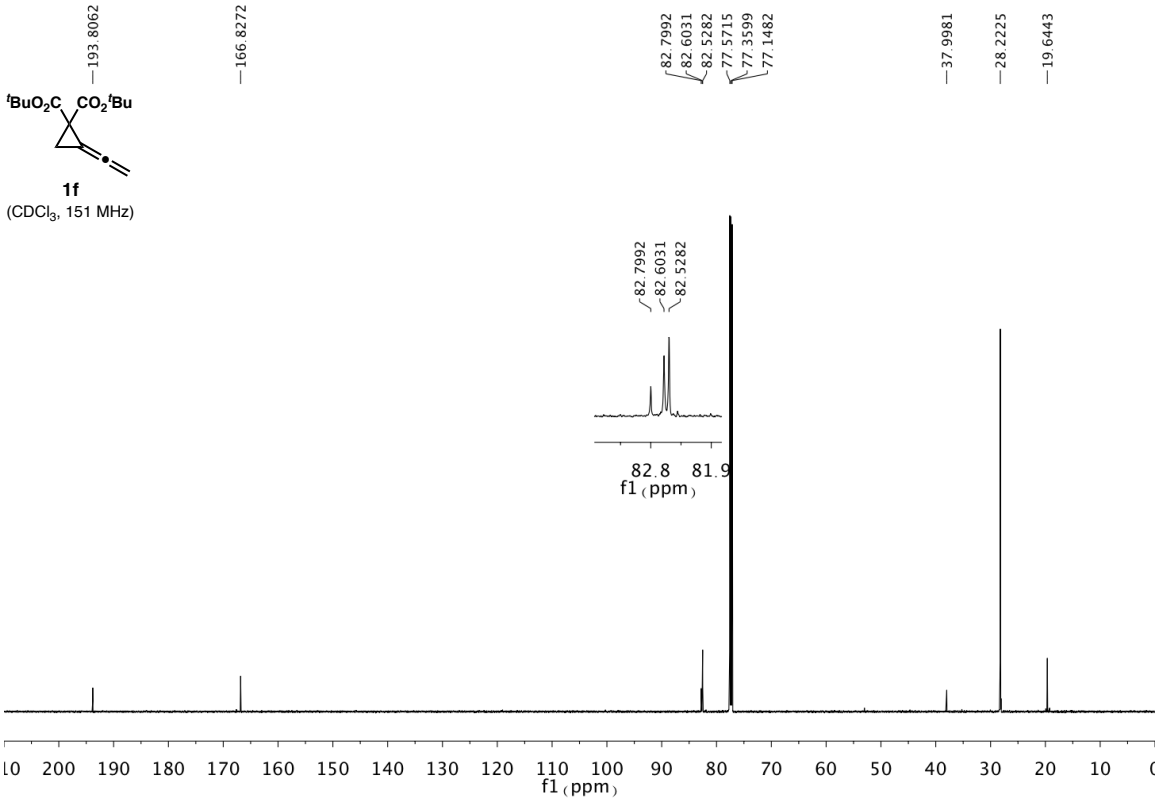

7.3633
7.3574
7.3466
7.3433
7.3372
7.3326
7.3248
7.3192
7.3130
7.3082
7.2999
7.2885
7.2829
7.2601
5.2129
5.2001
5.1964
5.1878
2.5025
2.4900
2.4774
BnO2C CO2Bn
1d
(CDCl3, 400 MHz)
9.68
6.01
2.00
f1 (ppm)

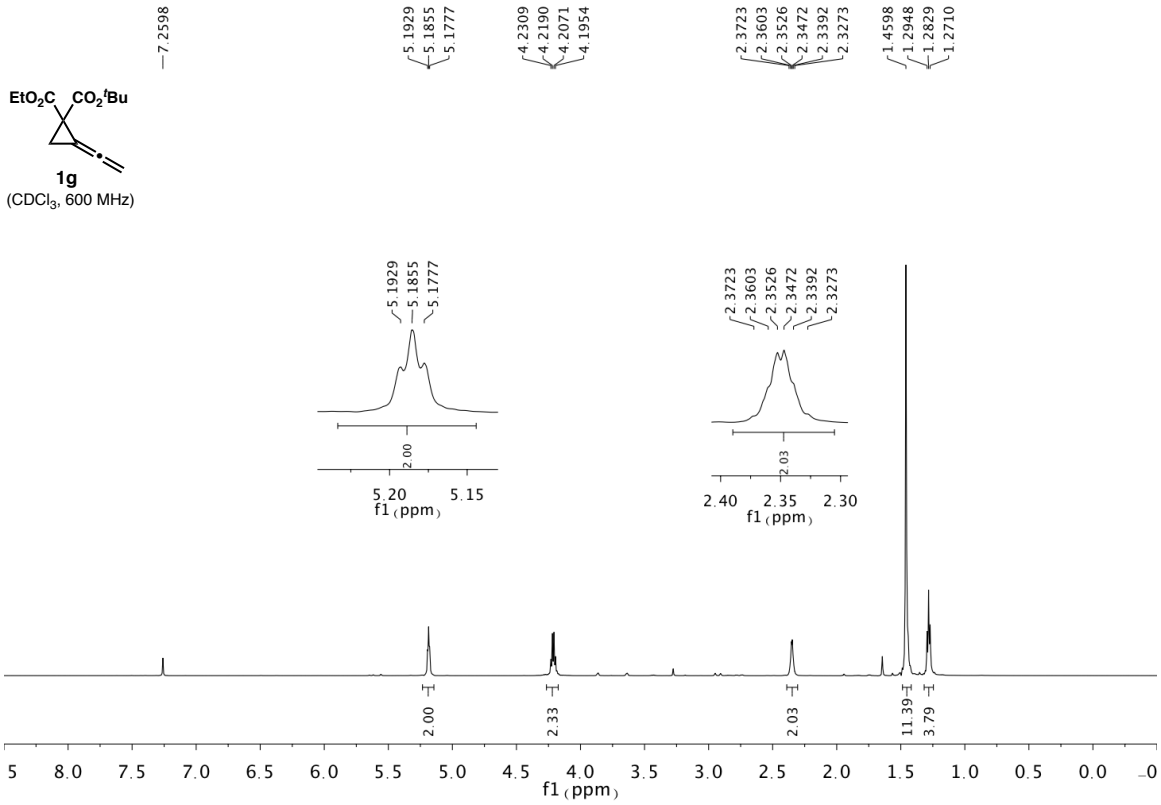

193.8405
167.1971
135.6633
128.8613
128.6073
128.3058
83.7139
83.6455
77.6771
77.3597
77.0420
67.8284
35.8376
20.4669
BnO2C CO2Bn
1d
(CDCl3, 101 MHz)
f1 (ppm)

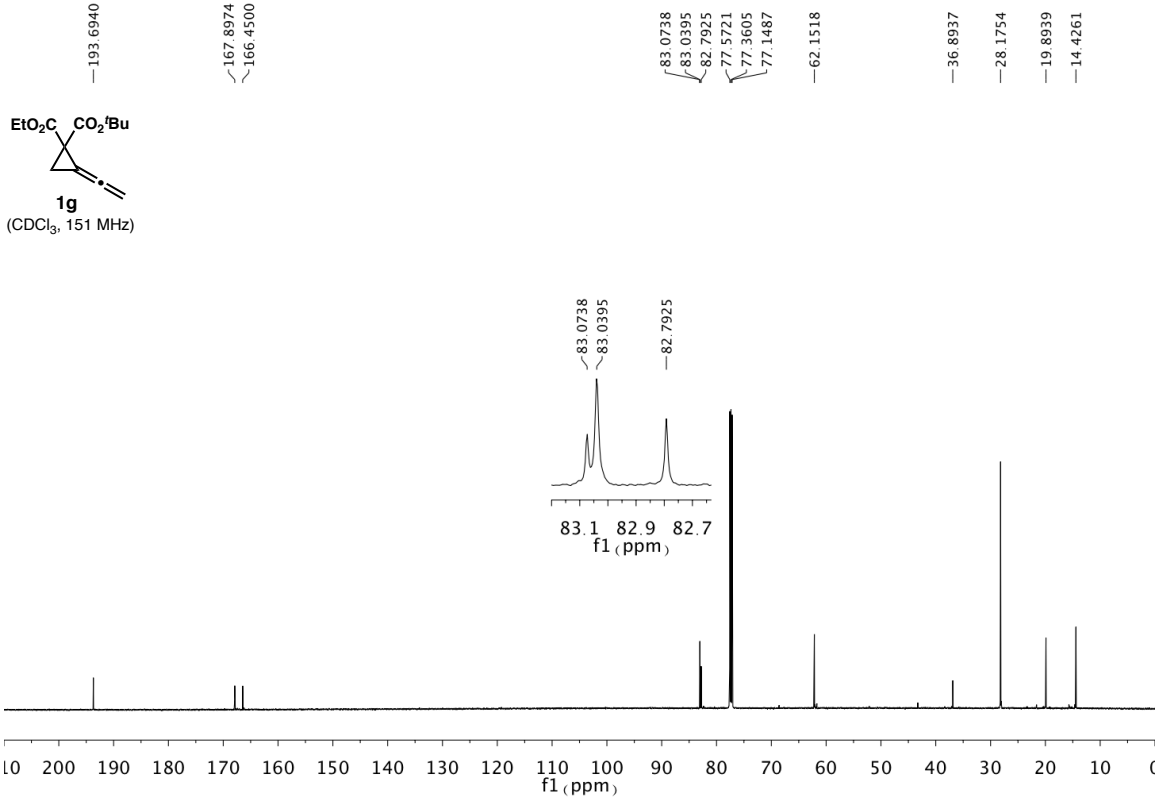

7.2599
5.1837
5.1714
5.1590
5.1069
5.0912
5.0756
5.0599
5.0443
5.0286
5.0130
2.3765
2.3642
2.3518
1.2596
1.2554
1.2439
1.2398
iPrO2C CO2iPr
1e
(CDCl3, 400 MHz)
12.88
f1 (ppm)
2.00
1.95
2.01
12.88

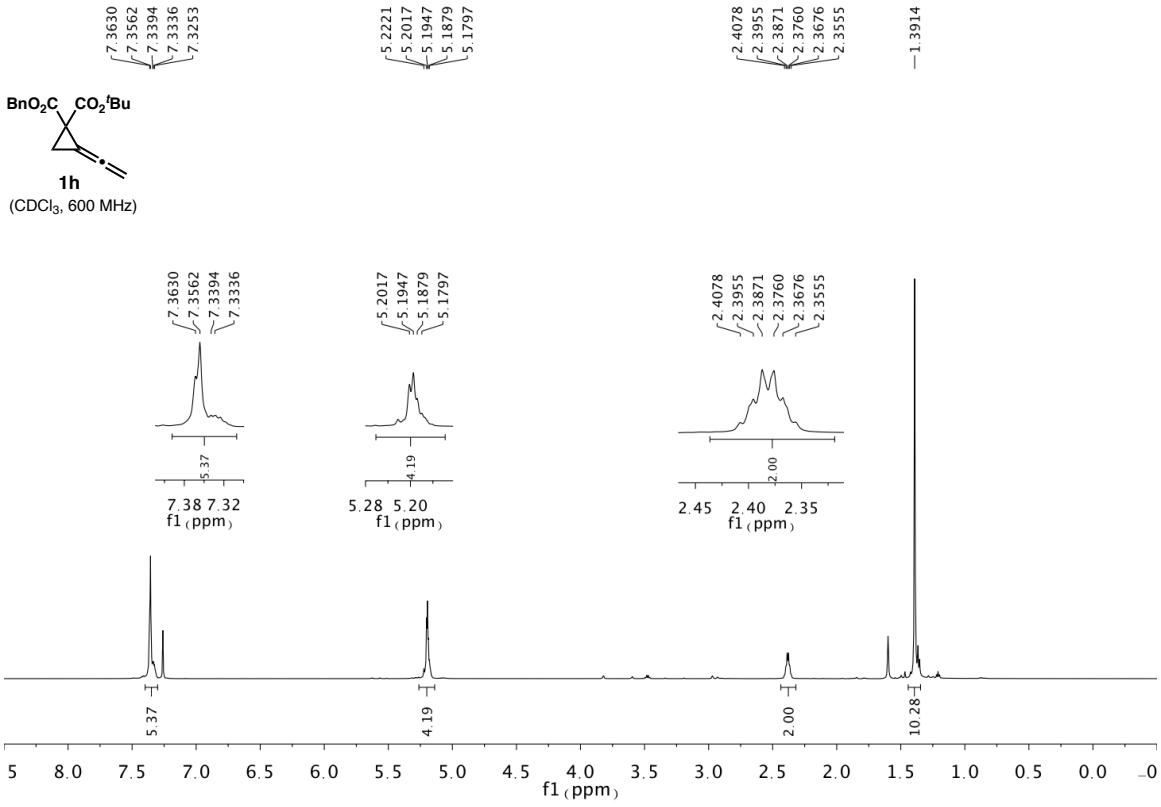

193.8588
167.0676
83.1297
82.9454
77.6779
77.3601
77.0423
69.8102
36.3638
21.9681
21.8906
19.9052
iPrO2C CO2iPr
1e
(CDCl3, 101 MHz)
f1 (ppm)

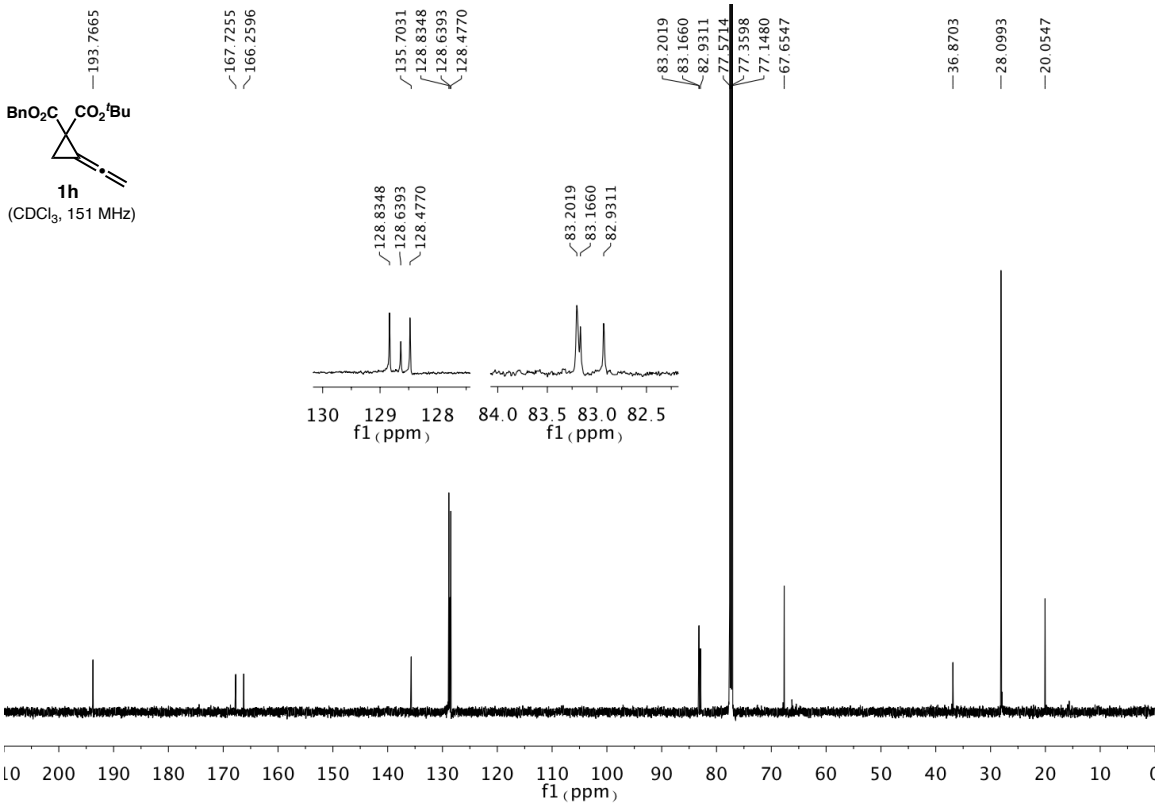

7.2603
5.1793
5.1712
5.1632
2.2876
2.2796
2.2715
1.4693
^{t}BuO$_2$C CO$_2$^{t}Bu
1f
(CDCl$_3$, 600 MHz)
2.00
1.99
22.82
f1 (ppm)

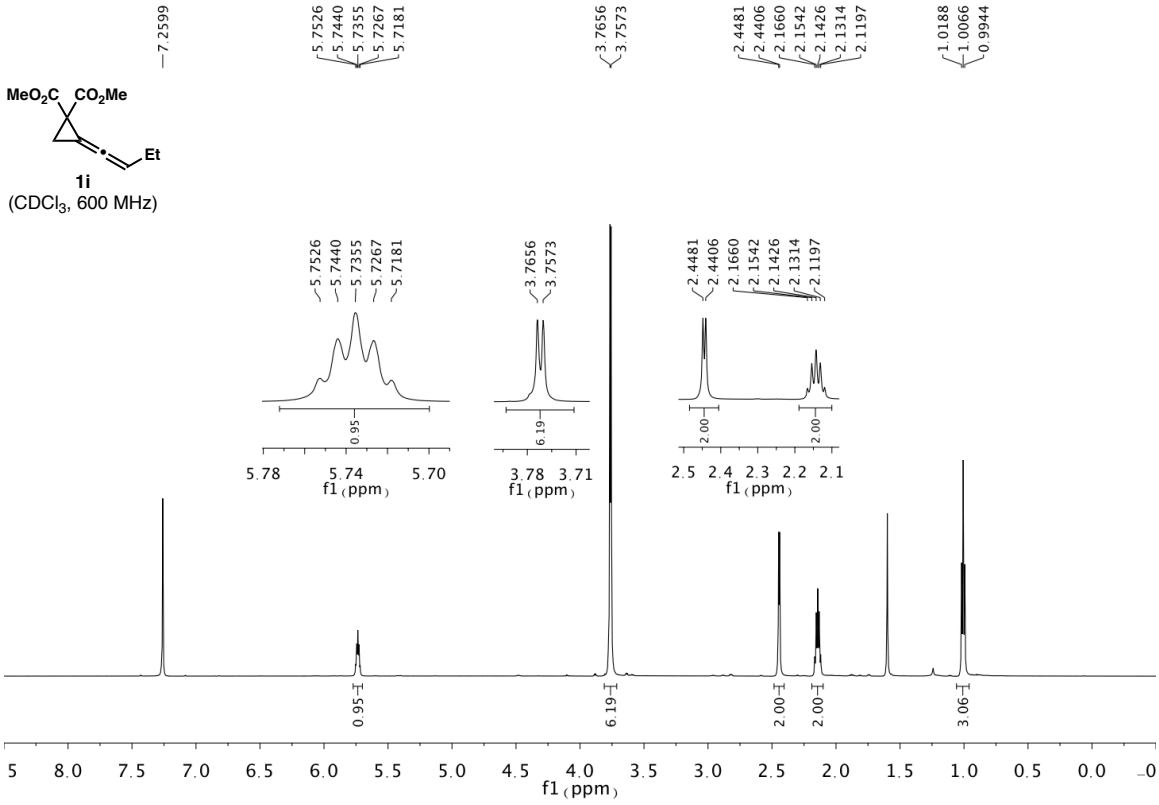

193.8062
166.8272
82.7992
82.6031
82.5282
77.5715
77.3599
77.1482
37.9981
28.2225
19.6443
^{t}BuO$_2$C CO$_2$^{t}Bu
1f
(CDCl$_3$, 151 MHz)
f1 (ppm)

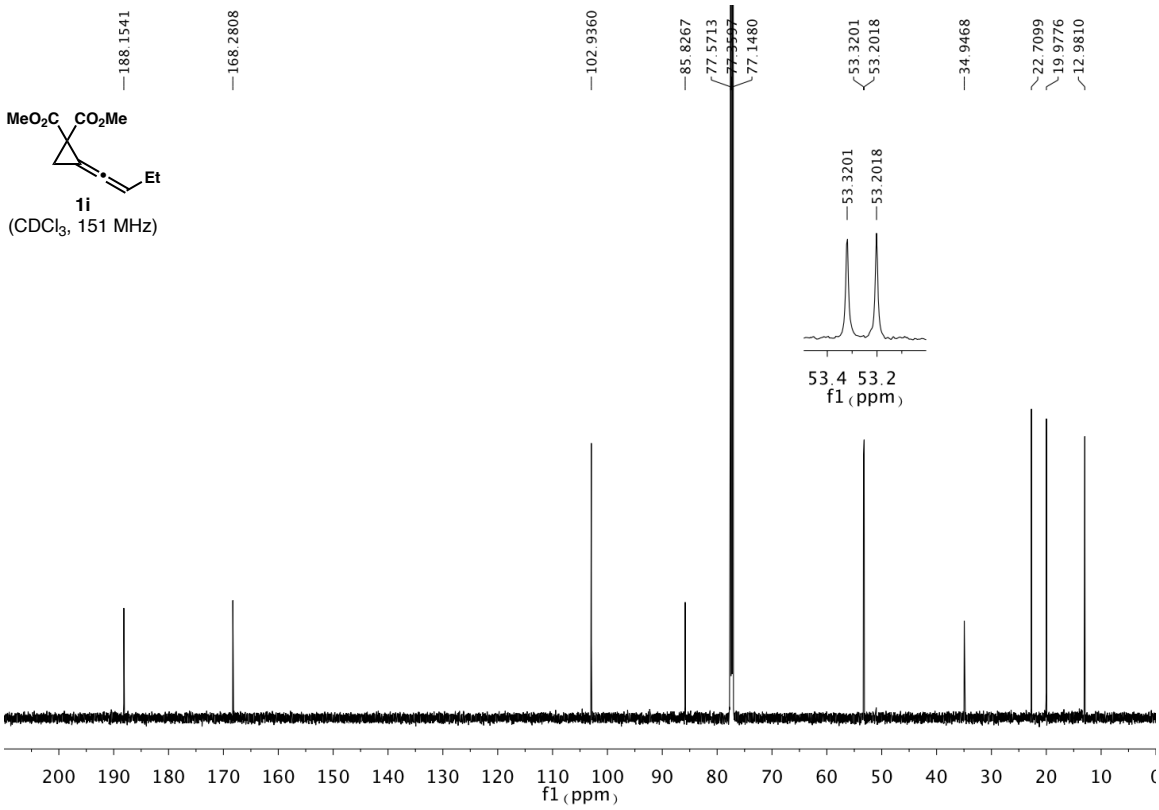

7.2598
5.1929
5.1855
5.1777
4.2309
4.2190
4.2071
4.1954
2.3723
2.3603
2.3526
2.3472
2.3392
2.3273
1.4598
1.2948
1.2829
1.2710
EtO2C CO2tBu
1g
(CDCl3, 600 MHz)
2.00
2.03
f1 (ppm)
2.00
2.33
2.03
11.39
3.79

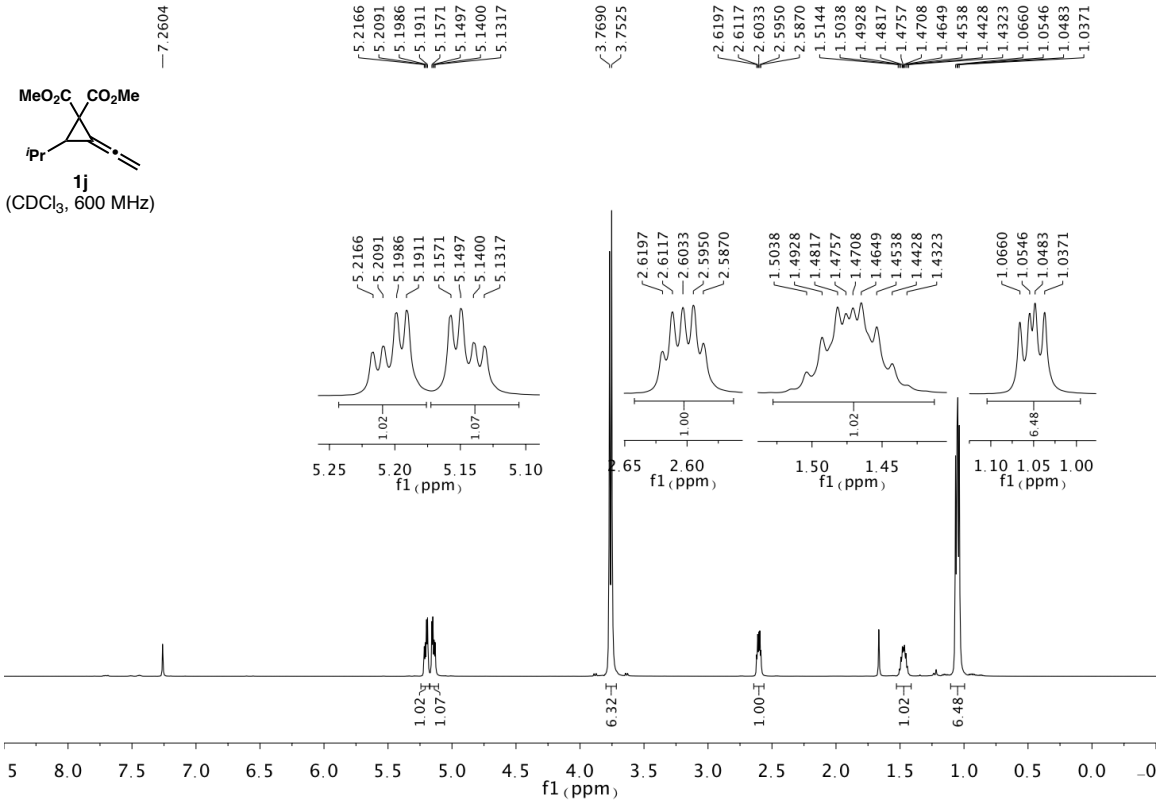

193.6940
167.8974
166.4500
83.0738
83.0395
82.7925
77.5721
77.3605
77.1487
62.1518
36.8937
28.1754
19.8939
14.4261
EtO2C CO2tBu
1g
(CDCl3, 151 MHz)
f1 (ppm)

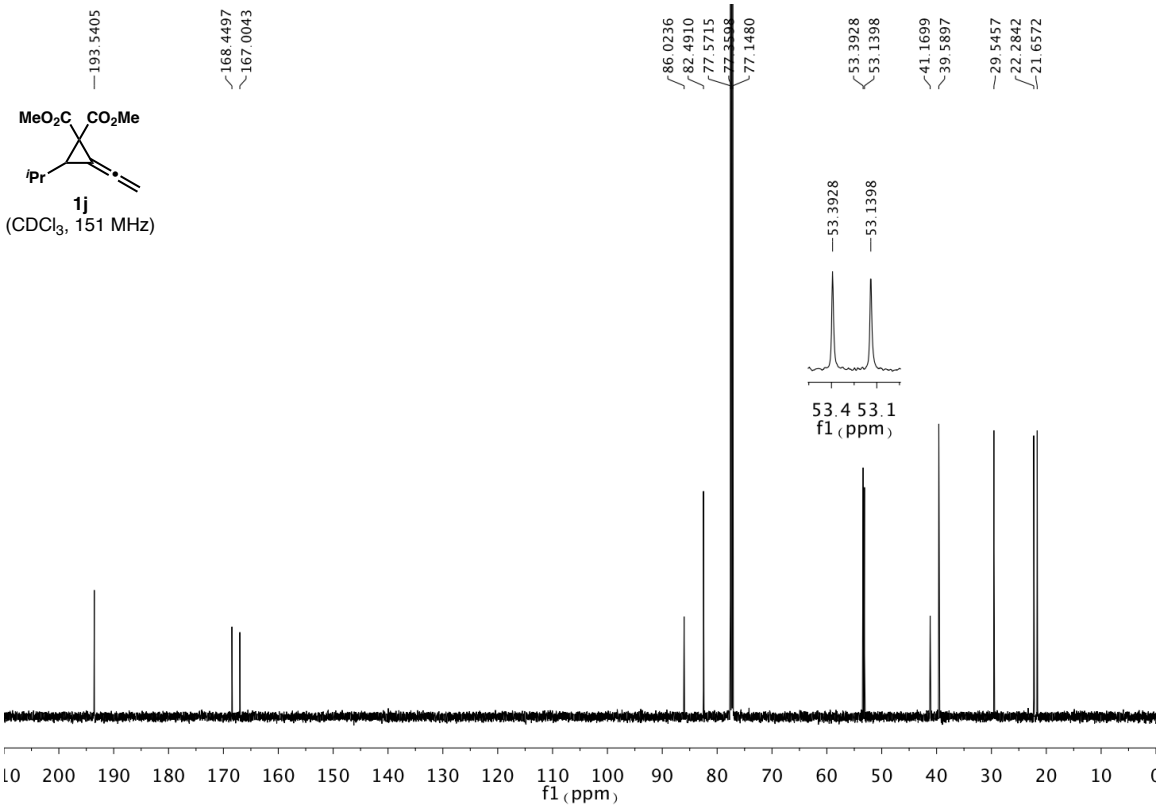

7.3630
7.3562
7.3394
7.3336
7.3253
5.2221
5.2017
5.1947
5.1879
5.1797
2.4078
2.3955
2.3871
2.3760
2.3676
2.3555
1.3914
BnO2C CO2tBu
1h
(CDCl3, 600 MHz)
5.37
4.19
2.00
10.28
f1 (ppm)

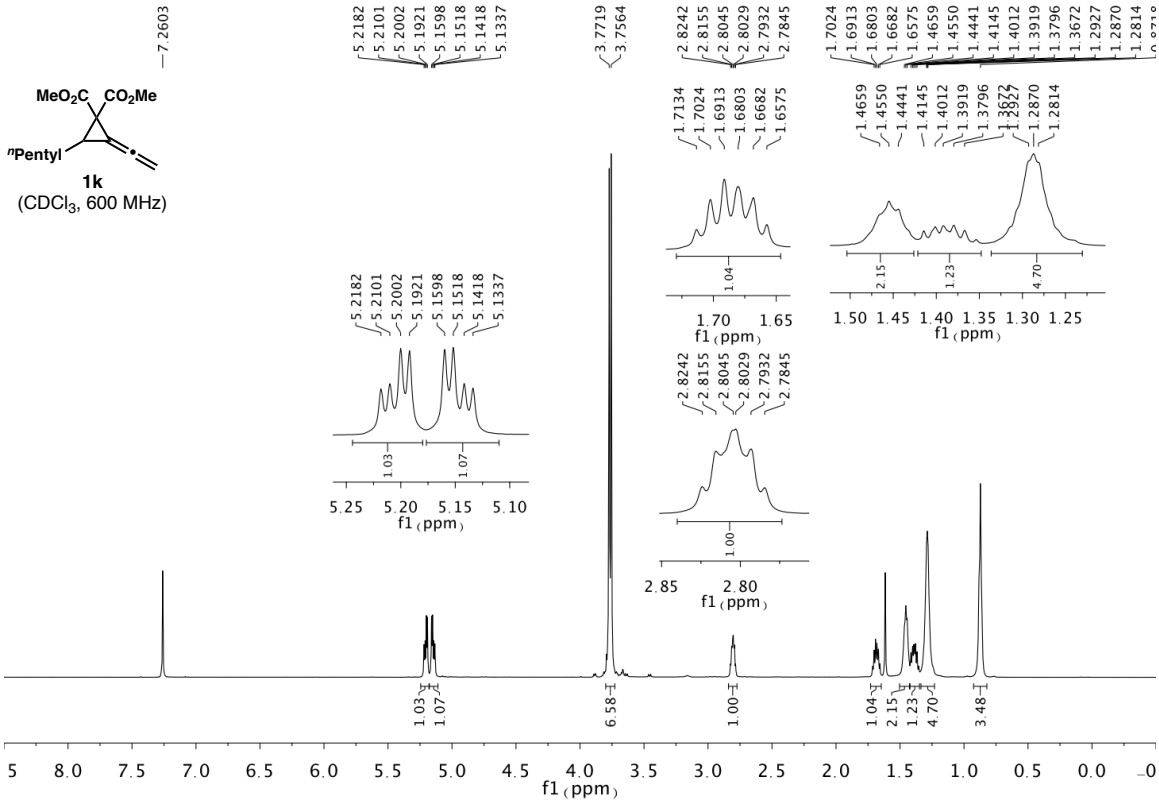

193.7665
167.7255
166.2596
135.7031
128.8348
128.6393
128.4770
83.2019
83.1660
82.9311
77.5714
77.3598
77.1480
67.6547
36.8703
28.0993
20.0547
BnO2C CO2tBu
1h
(CDCl3, 151 MHz)
f1 (ppm)

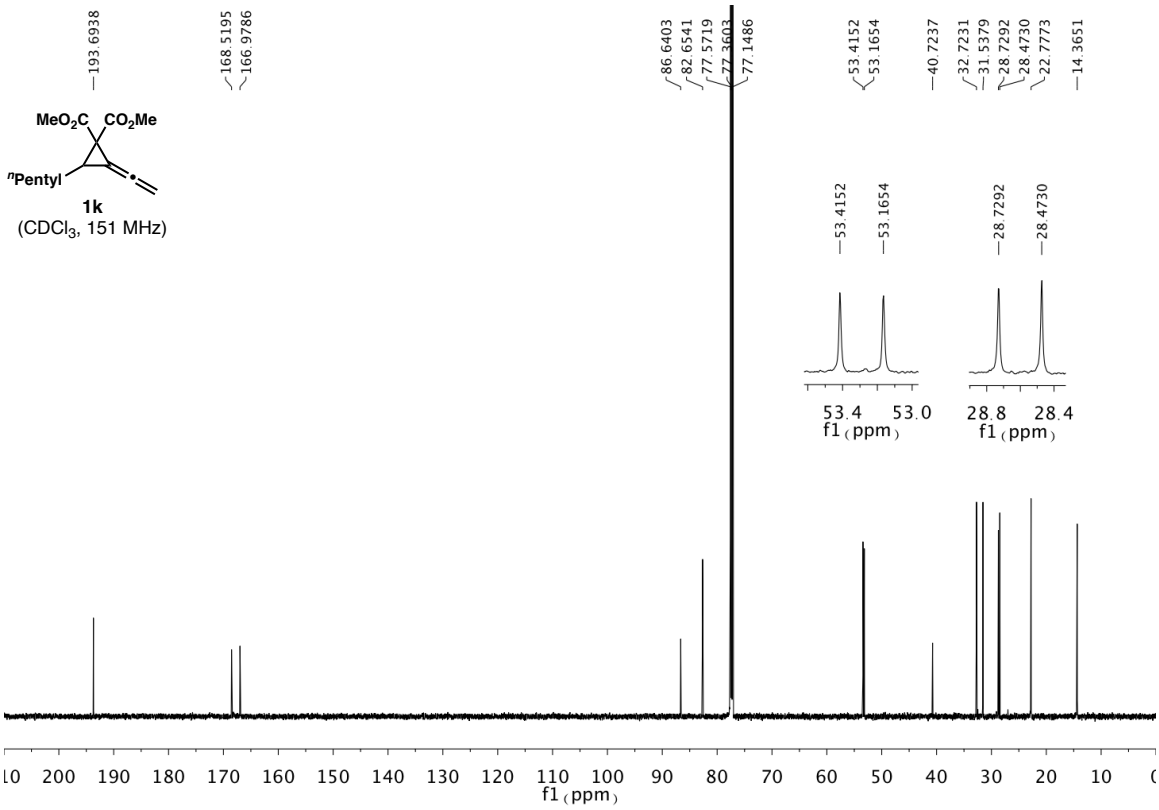

MeO2C CO2Me
Et
1i
(CDCl3, 600 MHz)
f1 (ppm)

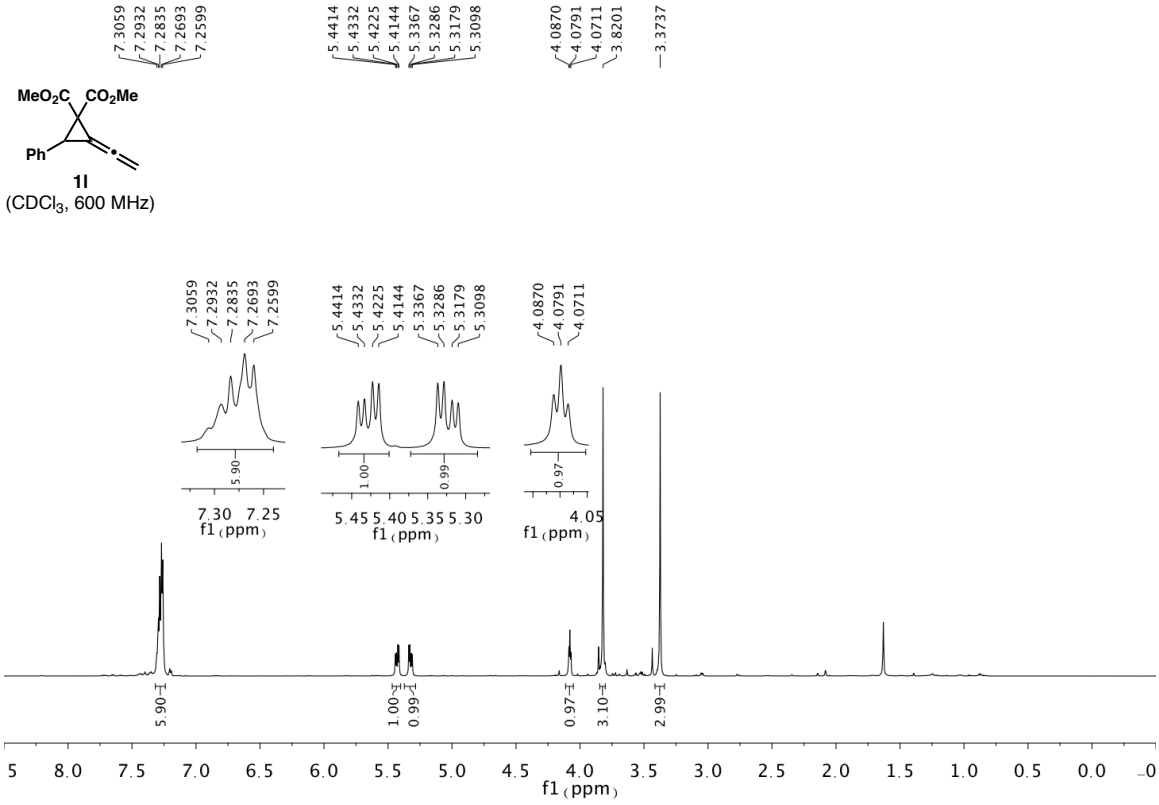

MeO2C CO2Me
Et
1i
(CDCl3, 151 MHz)
f1 (ppm)

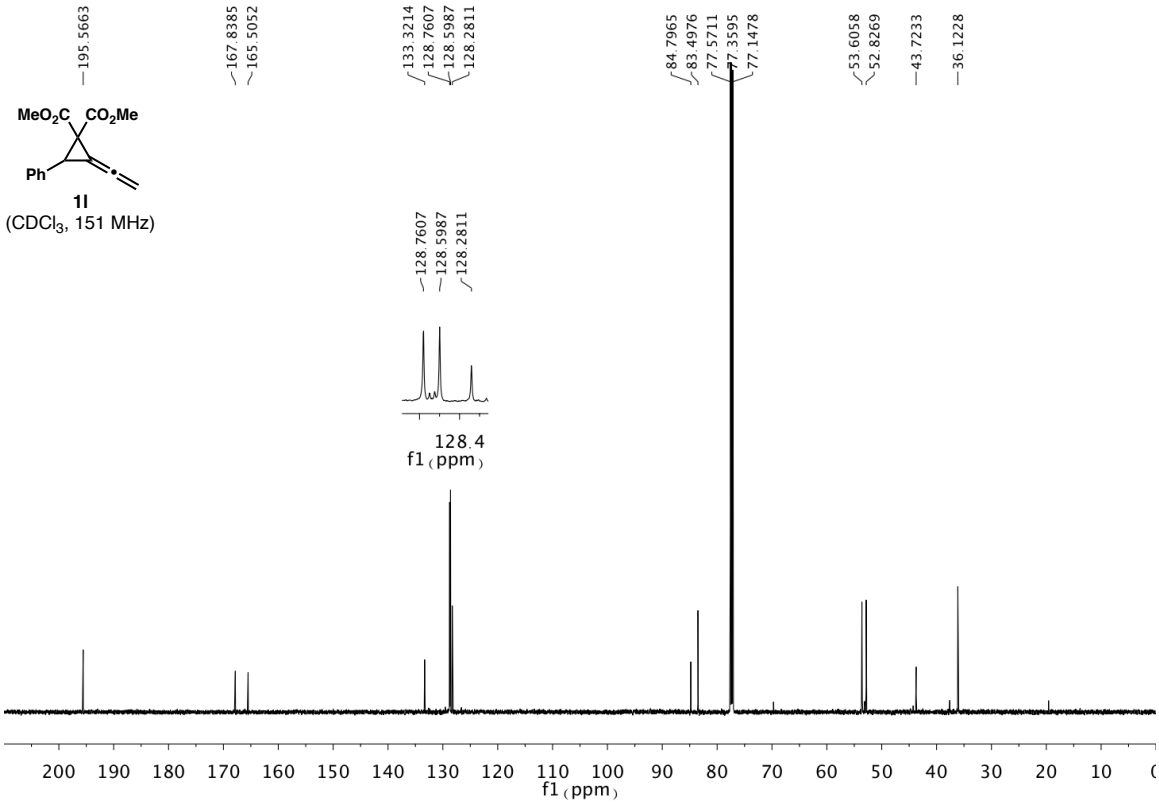

MeO2C CO2Me
iPr
1j
(CDCl3, 600 MHz)
f1 (ppm)

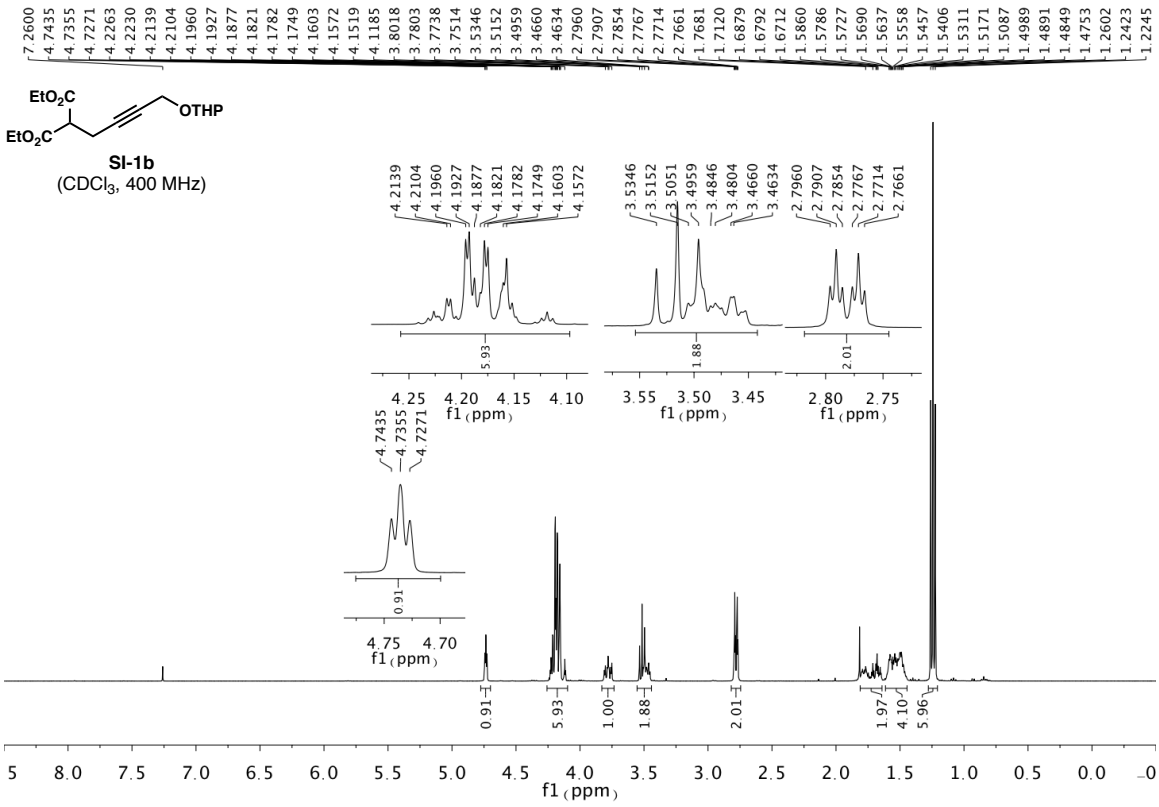

MeO2C CO2Me
iPr
1j
(CDCl3, 151 MHz)
f1 (ppm)

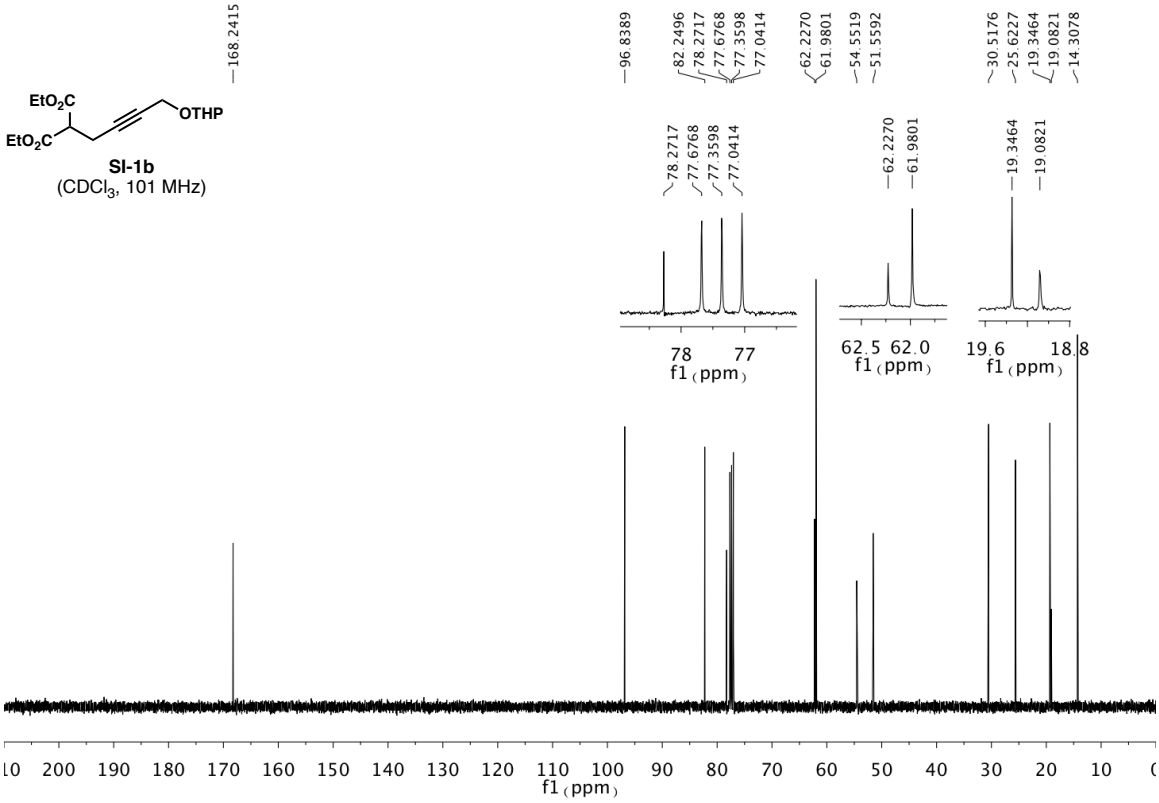

MeO2C CO2Me
nPentyl
1k
(CDCl3, 600 MHz)
f1 (ppm)

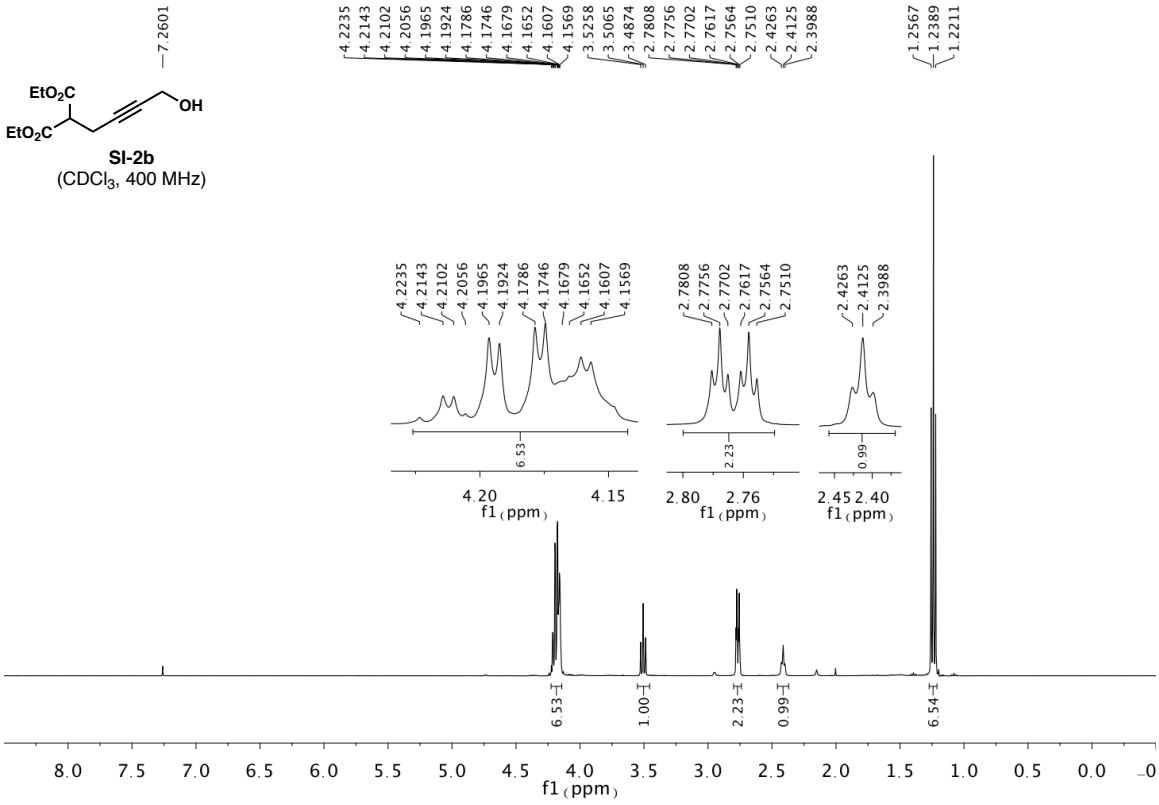

MeO2C CO2Me
nPentyl
1k
(CDCl3, 151 MHz)
f1 (ppm)

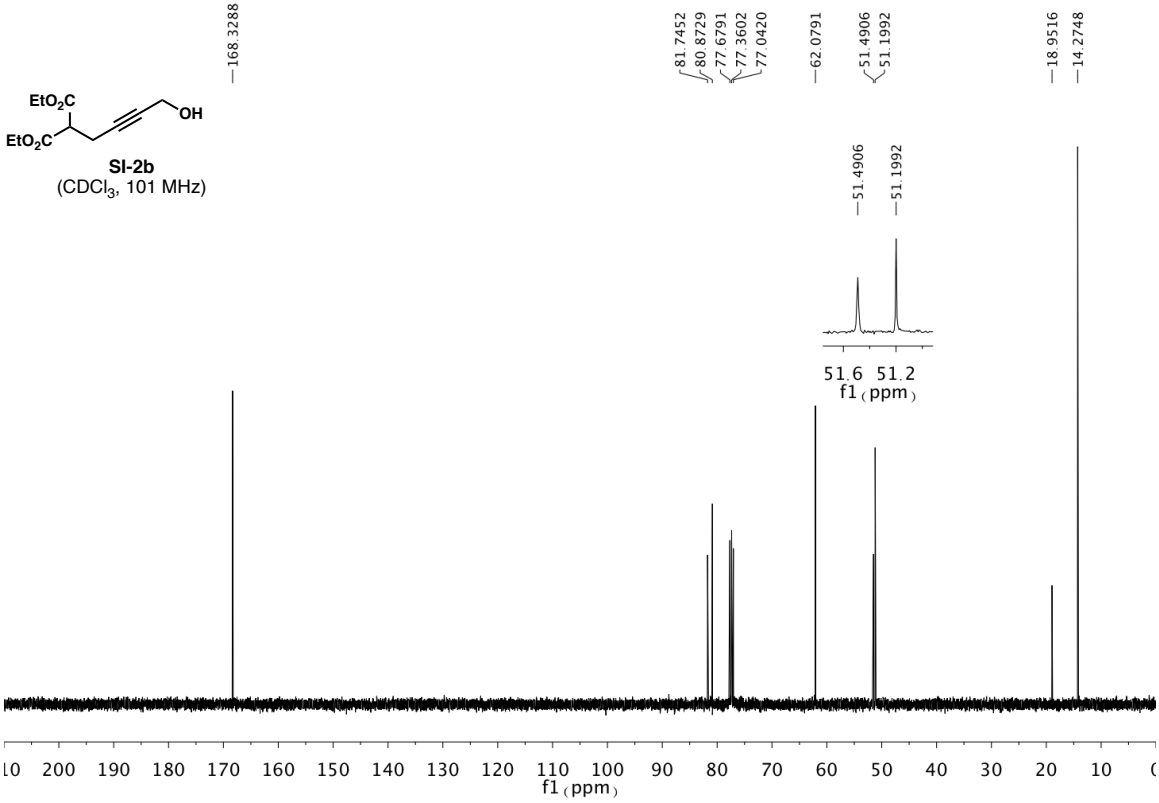

7.3059
7.2932
7.2835
7.2693
7.2599
5.4414
5.4332
5.4225
5.4144
5.3367
5.3286
5.3179
5.3098
4.0870
4.0791
4.0711
3.8201
3.3737
MeO2C CO2Me
Ph
1l
(CDCl3, 600 MHz)
5.90
1.00
0.99
0.97
7.30 7.25
5.45 5.40 5.35 5.30
4.05
f1 (ppm)
5.90
1.00
0.99
0.97
3.10
2.99
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

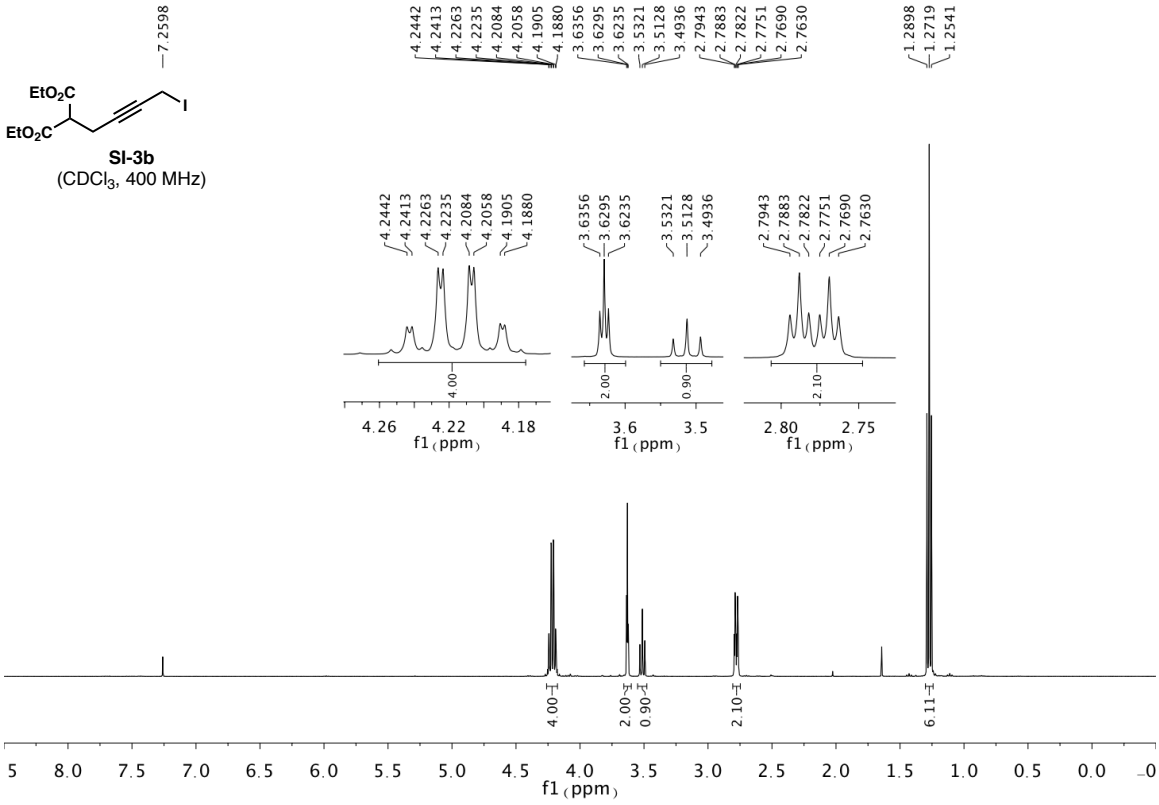

195.5663
167.8385
165.5052
133.3214
128.7607
128.5987
128.2811
84.7965
83.4976
77.5711
77.3595
77.1478
53.6058
52.8269
43.7233
36.1228
MeO2C CO2Me
Ph
1l
(CDCl3, 151 MHz)
128.7607
128.5987
128.2811
128.4
f1 (ppm)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

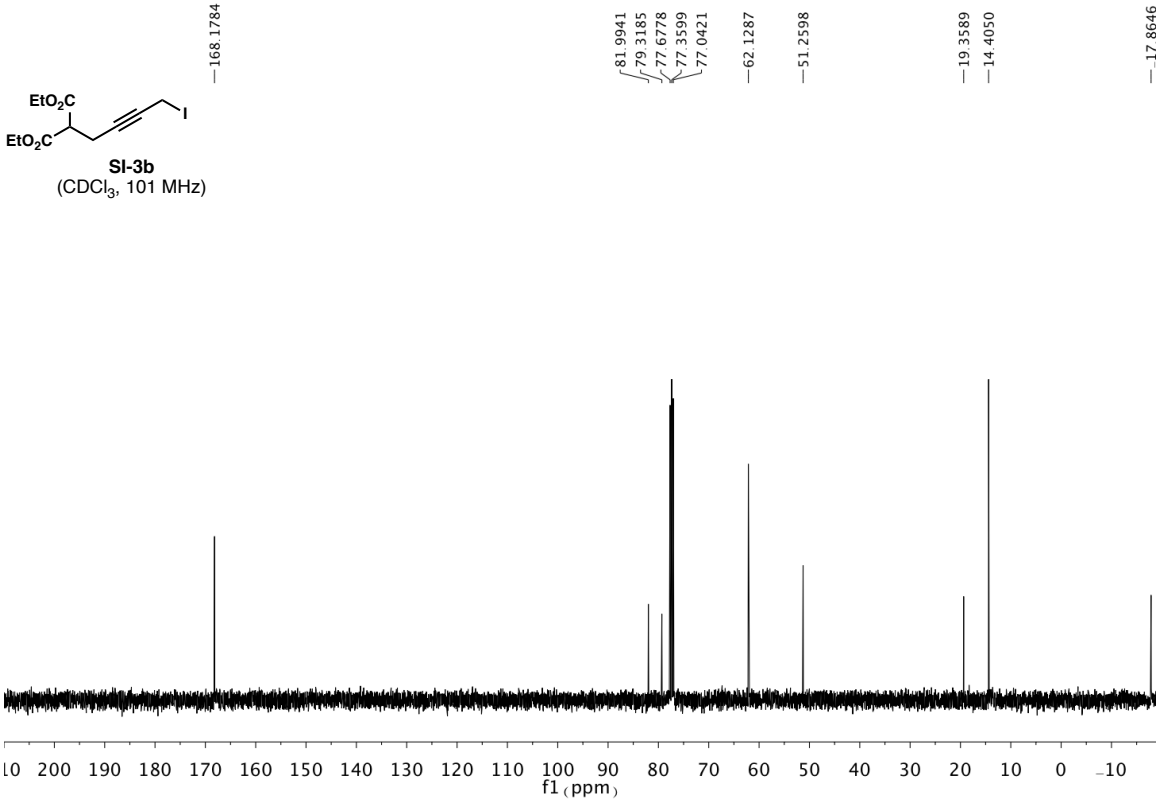

EtO2C
EtO2C
OTHP
SI-1b
(CDCl3, 400 MHz)
f1 (ppm)

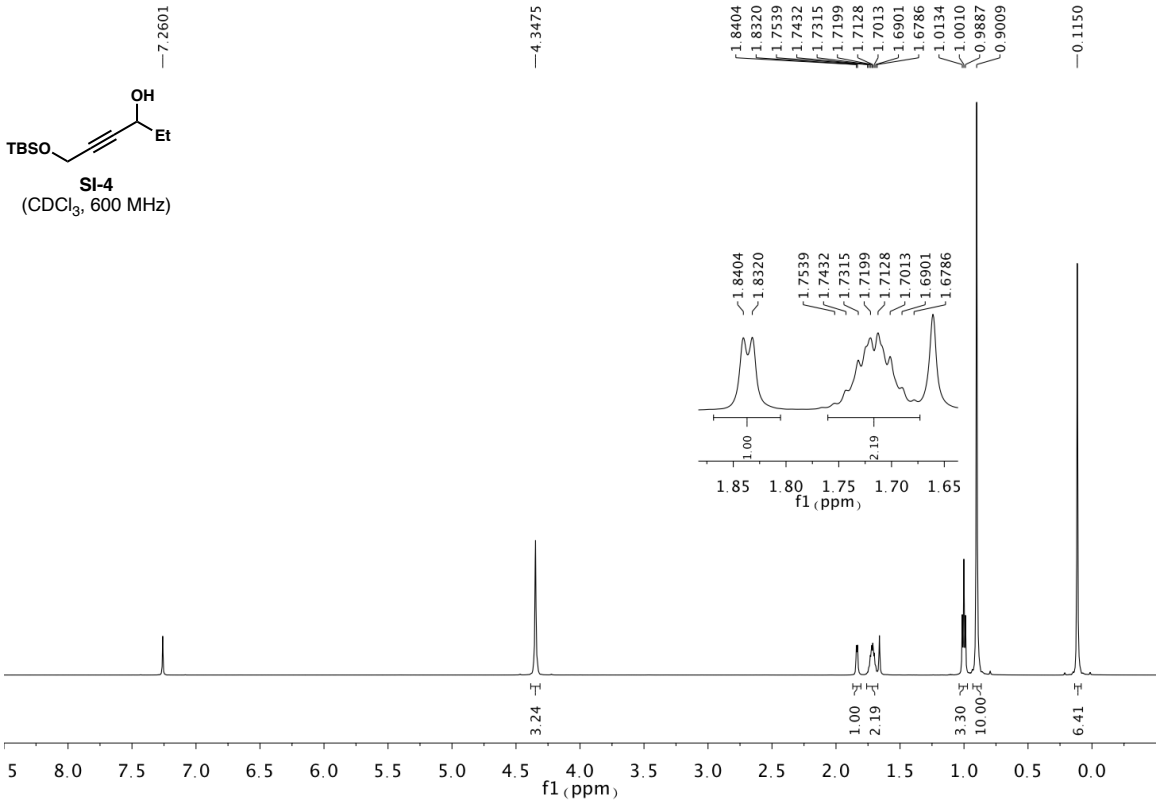

EtO2C
EtO2C
OTHP
SI-1b
(CDCl3, 101 MHz)
f1 (ppm)

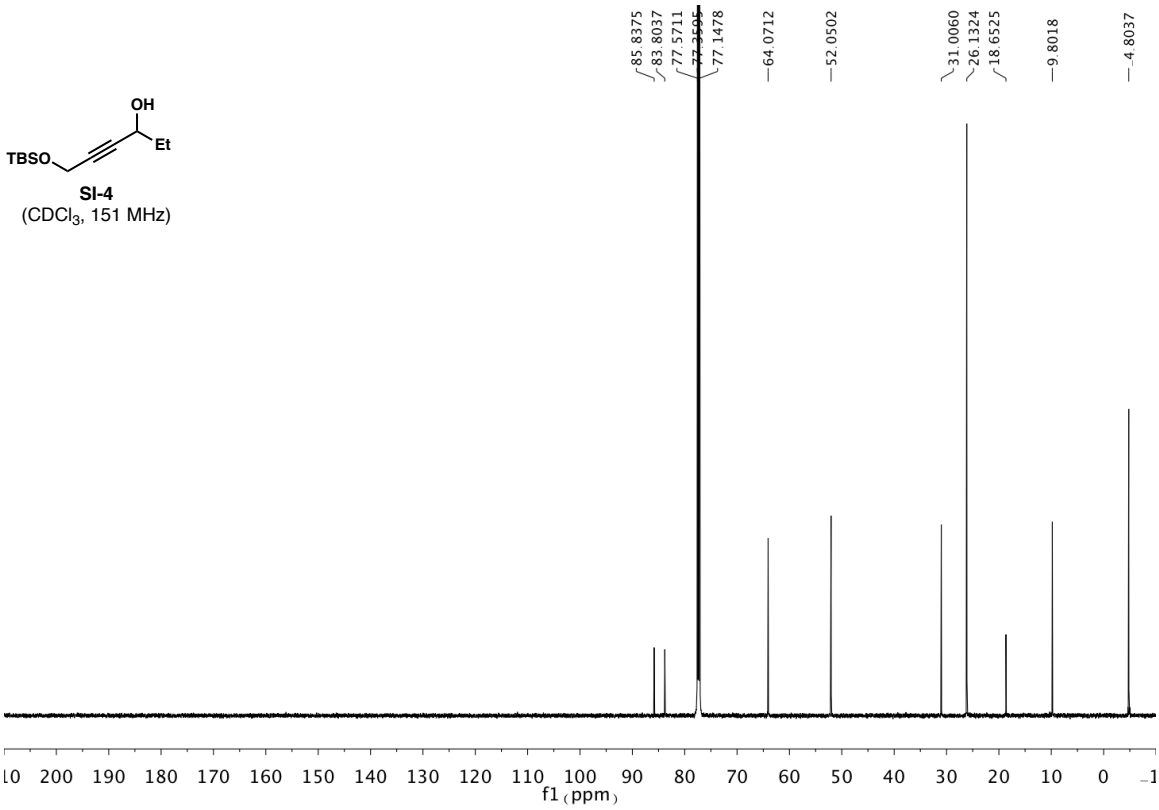

EtO2C
EtO2C
OH
SI-2b
(CDCl3, 400 MHz)
7.2601
4.2235
4.2143
4.2102
4.2056
4.1965
4.1924
4.1786
4.1746
4.1679
4.1652
4.1607
4.1569
3.5258
3.5065
3.4874
2.7808
2.7756
2.7702
2.7617
2.7564
2.7510
2.4263
2.4125
2.3988
1.2567
1.2389
1.2211
6.53
2.23
0.99
6.54
f1 (ppm)

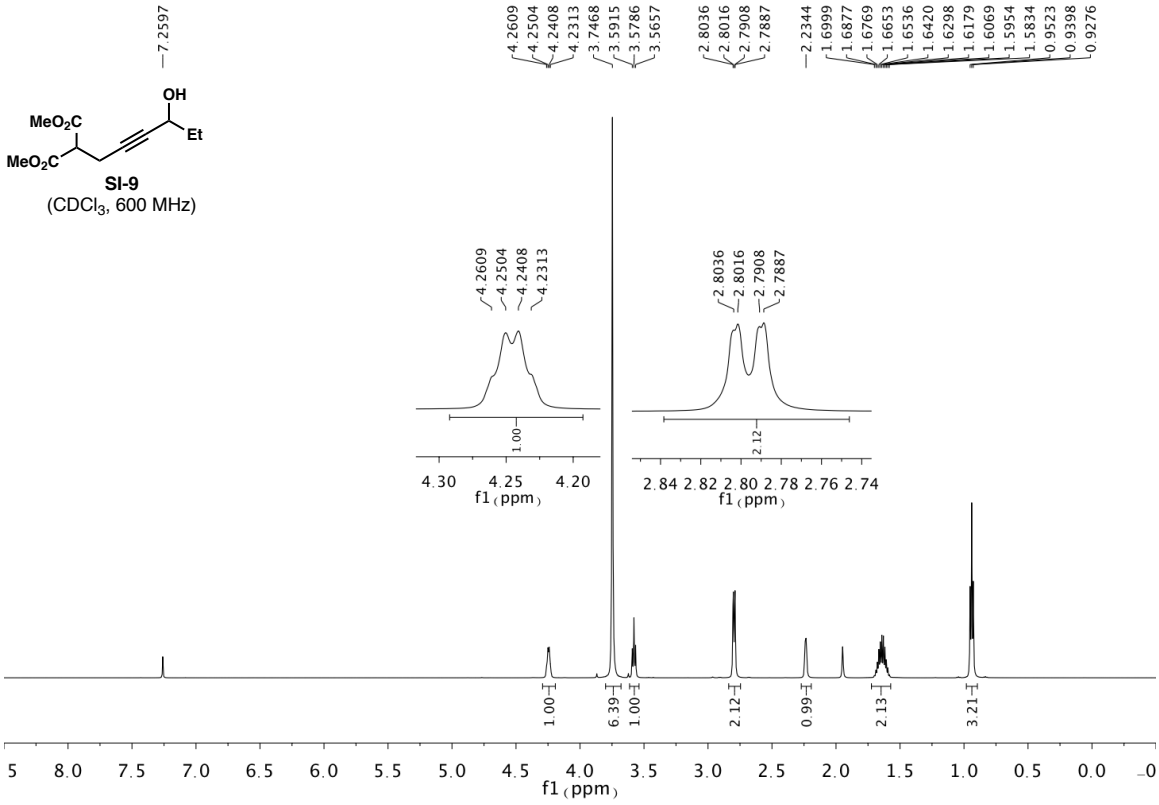

EtO2C
EtO2C
OH
SI-2b
(CDCl3, 101 MHz)
168.3288
81.7452
80.8729
77.6791
77.3602
77.0420
62.0791
51.4906
51.1992
18.9516
14.2748
f1 (ppm)

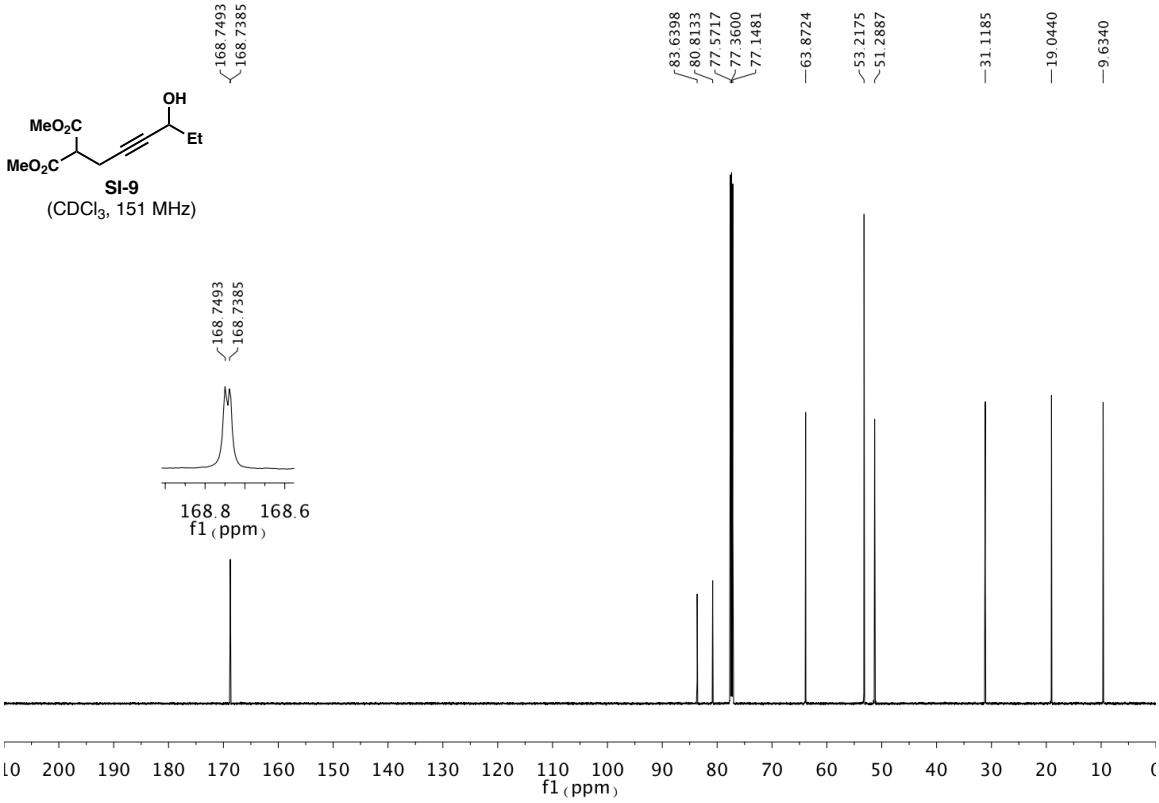

EtO2C
EtO2C
I
SI-3b
(CDCl3, 400 MHz)
7.2598
4.2442
4.2413
4.2263
4.2235
4.2084
4.2058
4.1905
4.1880
3.6356
3.6295
3.6235
3.5321
3.5128
3.4936
2.7943
2.7883
2.7822
2.7751
2.7690
2.7630
1.2898
1.2719
1.2541
4.00
2.00
0.90
2.10
6.11
f1 (ppm)

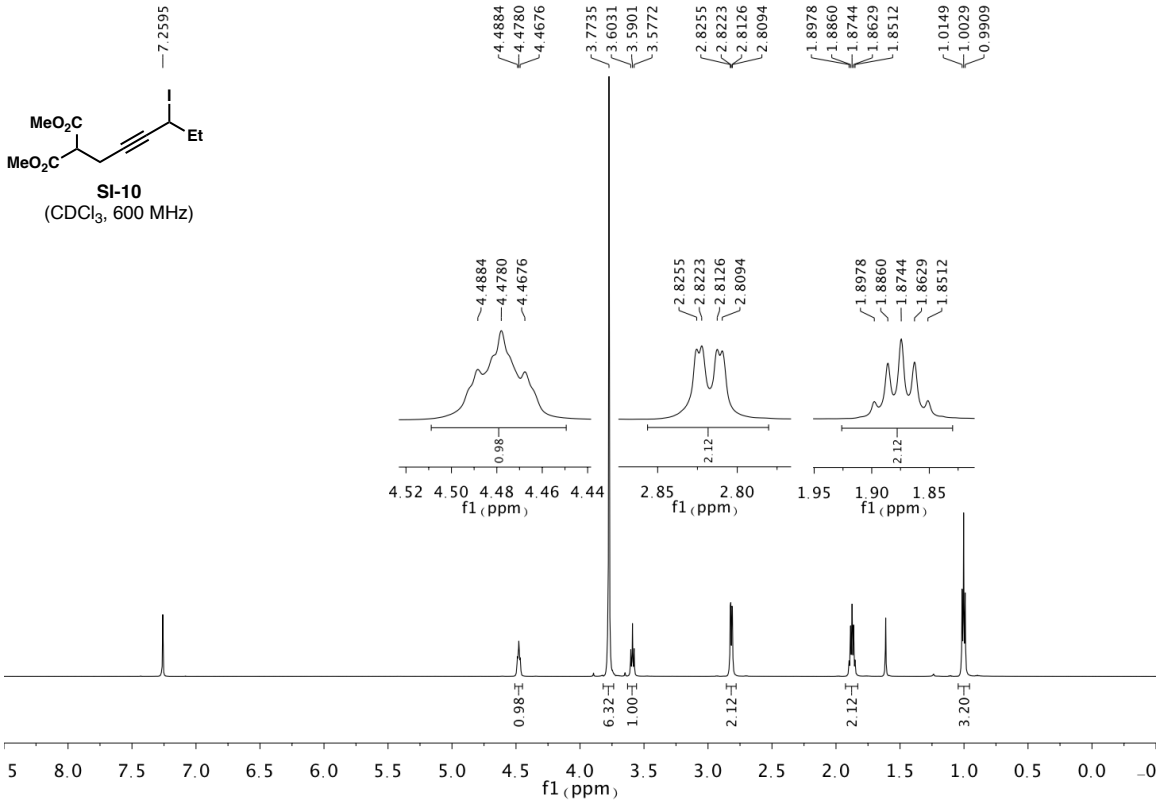

EtO2C
EtO2C
I
SI-3b
(CDCl3, 101 MHz)
168.1784
81.9941
79.3185
77.6778
77.3599
77.0421
62.1287
51.2598
19.3589
14.4050
17.8646
f1 (ppm)

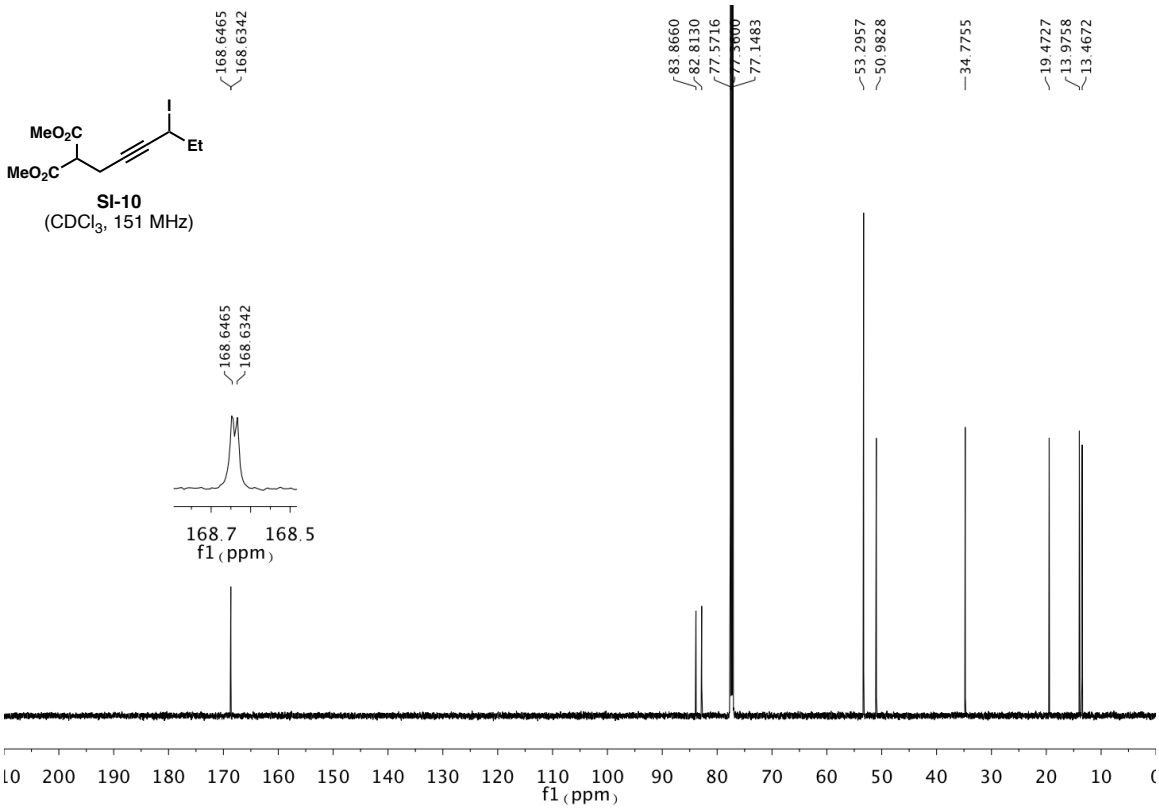

7.2601
4.3475
1.8404
1.8320
1.7539
1.7432
1.7315
1.7199
1.7128
1.7013
1.6901
1.6786
1.0134
1.0010
0.9887
0.9009
0.1150
OH
Et
TBSO
SI-4
(CDCl3, 600 MHz)
3.24
1.00
2.19
3.30
10.00
6.41
f1 (ppm)

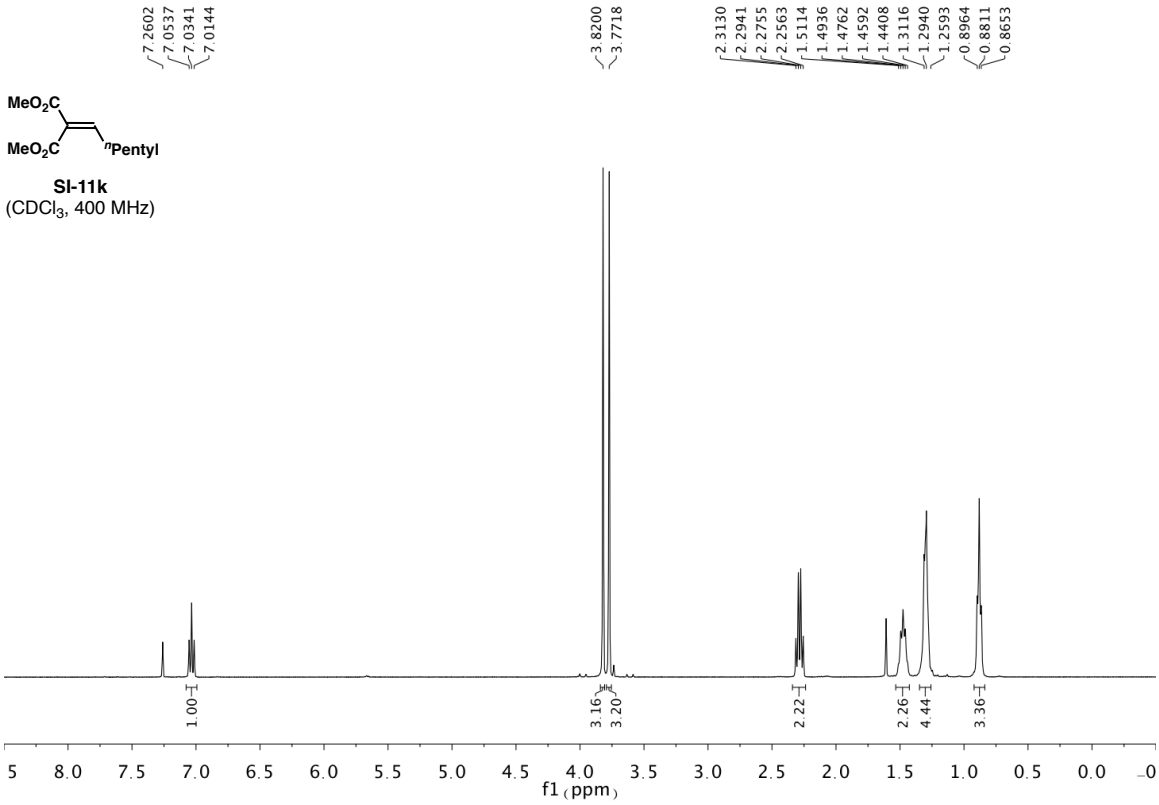

85.8375
83.8037
77.5711
77.3505
77.1478
64.0712
52.0502
31.0060
26.1324
18.6525
9.8018
4.8037
OH
Et
TBSO
SI-4
(CDCl3, 151 MHz)
f1 (ppm)

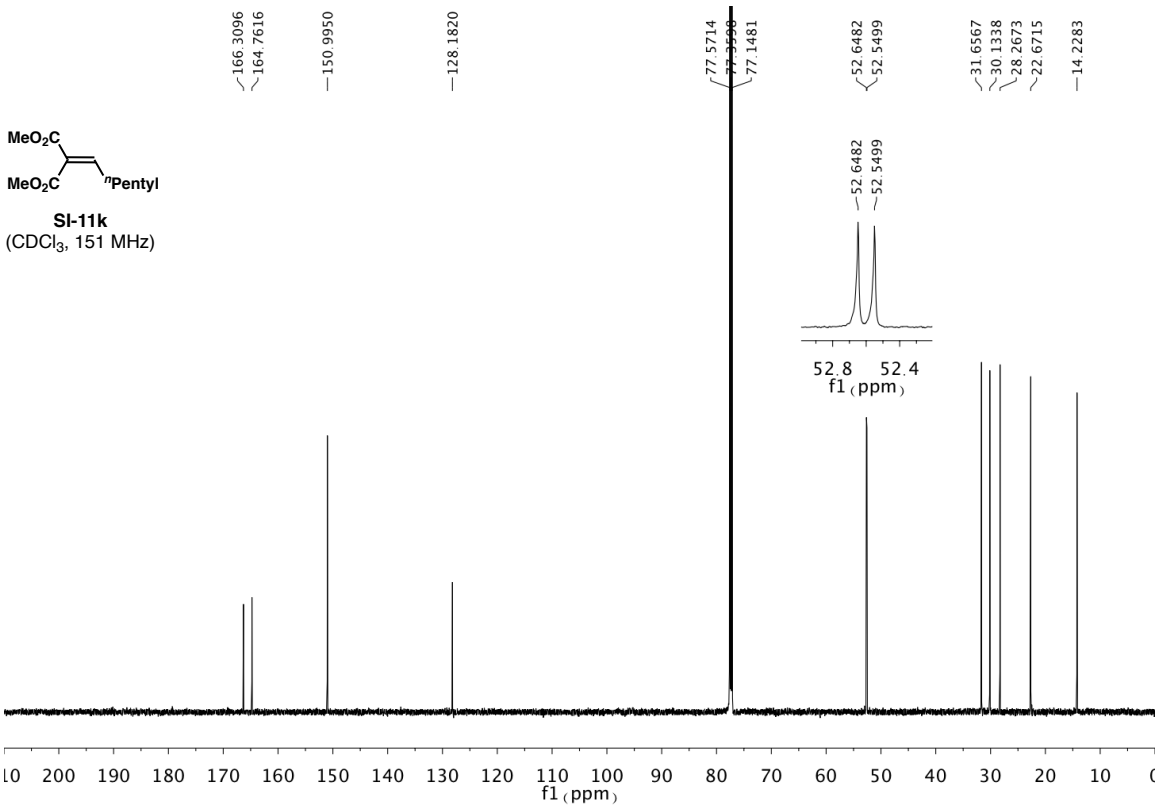

7.2597
4.2609
4.2504
4.2408
4.2313
3.7468
3.5915
3.5786
3.5657
2.8036
2.8016
2.7908
2.7887
2.2344
1.6999
1.6877
1.6769
1.6653
1.6536
1.6420
1.6298
1.6179
1.6069
1.5954
1.5834
0.9523
0.9398
0.9276
OH
MeO2C
Et
MeO2C
SI-9
(CDCl3, 600 MHz)
1.00
2.12
f1 (ppm)
1.00
6.39
1.00
2.12
0.99
2.13
3.21
f1 (ppm)

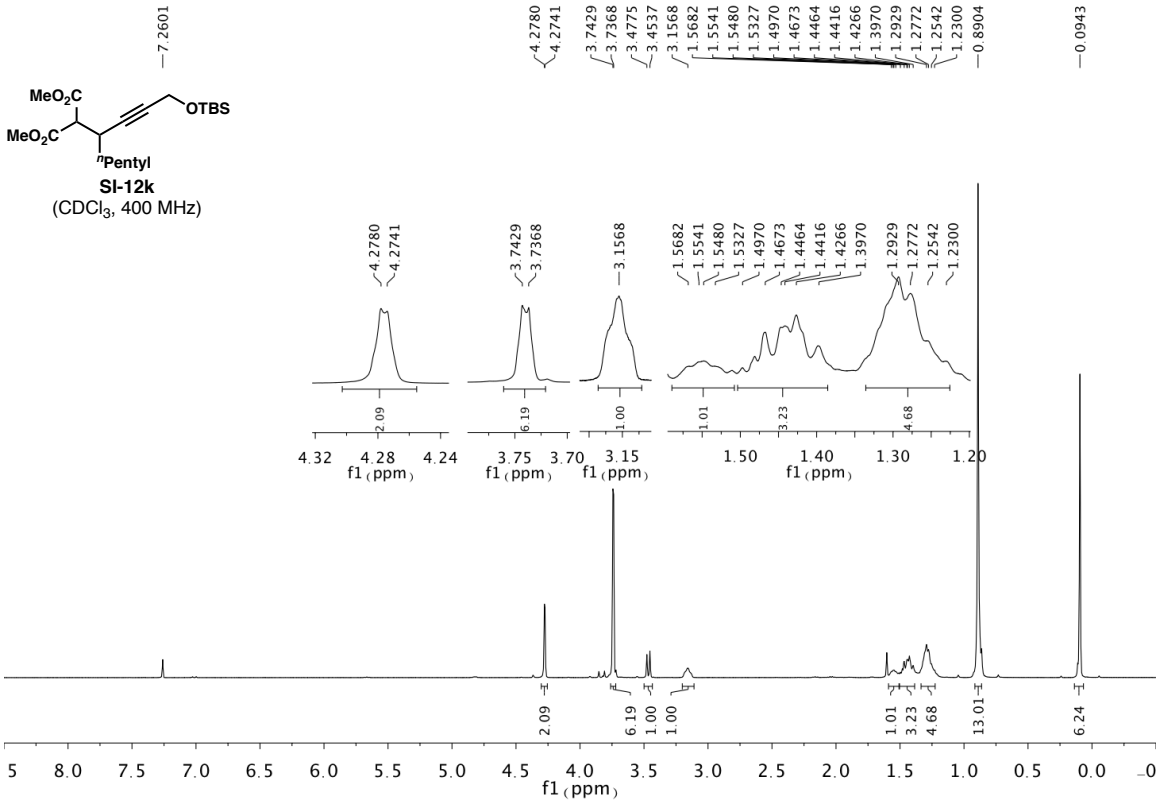

168.7493
168.7385
83.6398
80.8133
77.5717
77.3600
77.1481
63.8724
53.2175
51.2887
31.1185
19.0440
9.6340
OH
MeO2C
Et
MeO2C
SI-9
(CDCl3, 151 MHz)
168.7493
168.7385
168.8
168.6
f1 (ppm)
f1 (ppm)

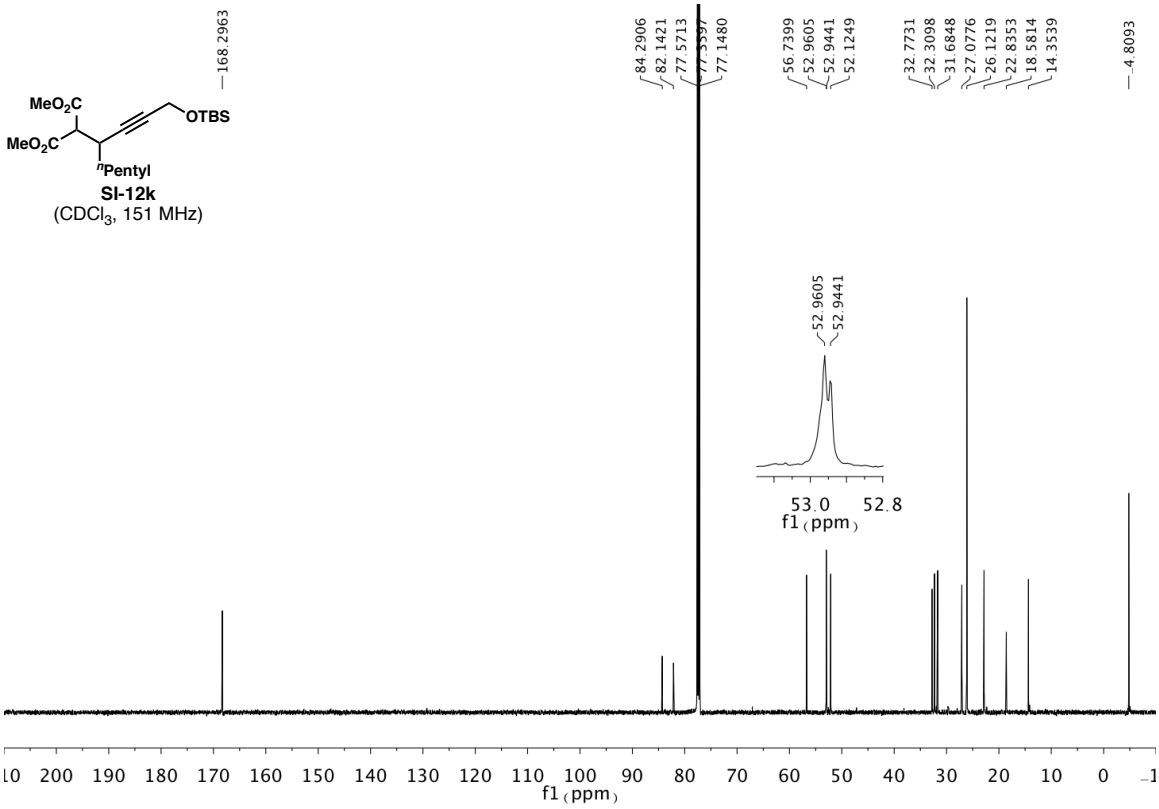

MeO2C
MeO2C
I
Et
SI-10
(CDCl3, 600 MHz)
7.2595
4.4884
4.4780
4.4676
3.7735
3.6031
3.5901
3.5772
2.8255
2.8223
2.8126
2.8094
1.8978
1.8860
1.8744
1.8629
1.8512
1.0149
1.0029
0.9909
0.98
2.12
2.12
0.98
6.32
1.00
2.12
2.12
3.20
f1 (ppm)

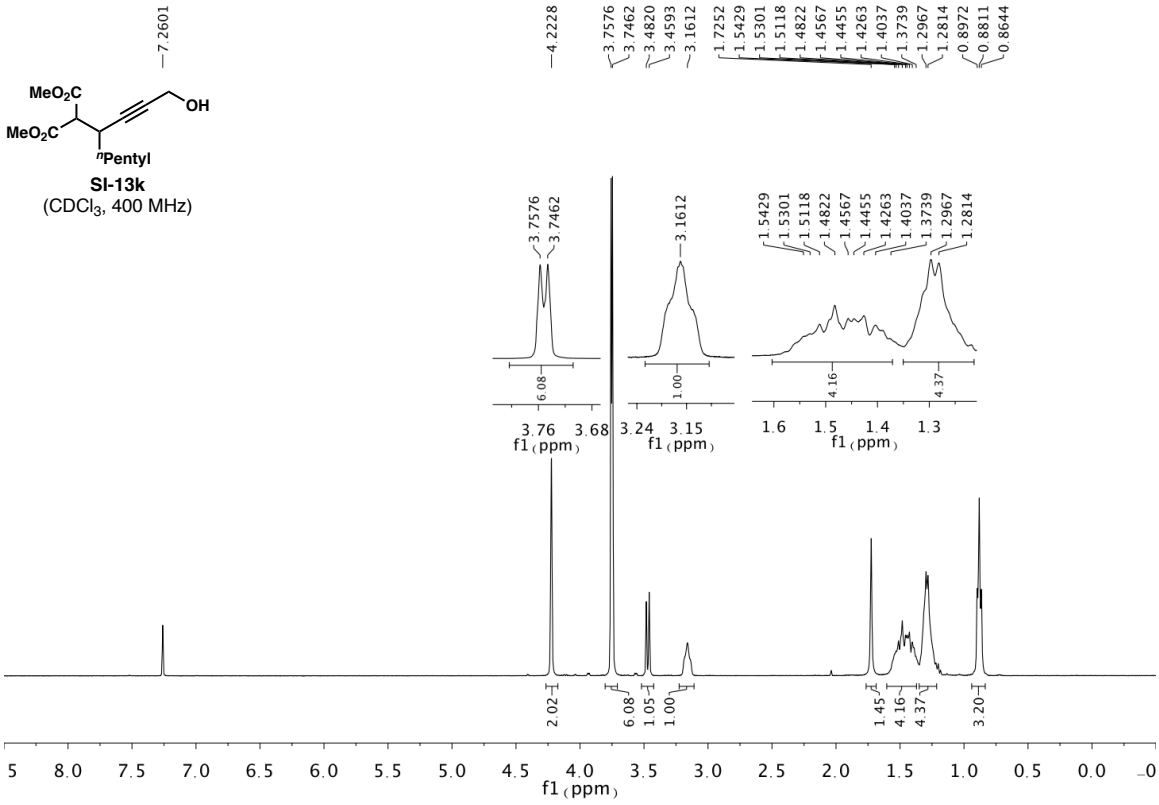

MeO2C
MeO2C
I
Et
SI-10
(CDCl3, 151 MHz)
168.6465
168.6342
83.8660
82.8130
77.5716
77.3000
77.1483
53.2957
50.9828
34.7755
19.4727
13.9758
13.4672
f1 (ppm)

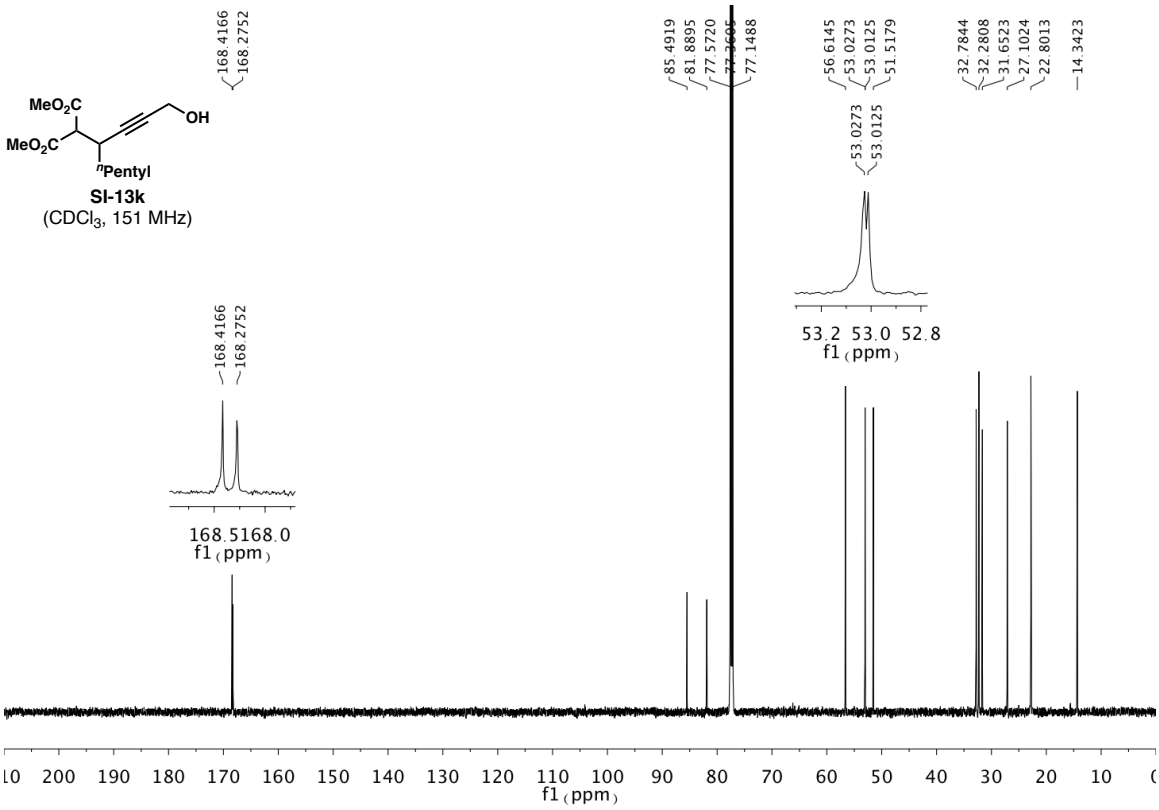

7.2602
7.0537
7.0341
7.0144
3.8200
3.7718
2.3130
2.2941
2.2755
2.2563
1.5114
1.4936
1.4762
1.4592
1.4408
1.3116
1.2940
1.2593
0.8964
0.8811
0.8653
MeO2C
MeO2C
nPentyl
SI-11k
(CDCl3, 400 MHz)
1.00
3.16
3.20
2.22
2.26
4.44
3.36
f1 (ppm)

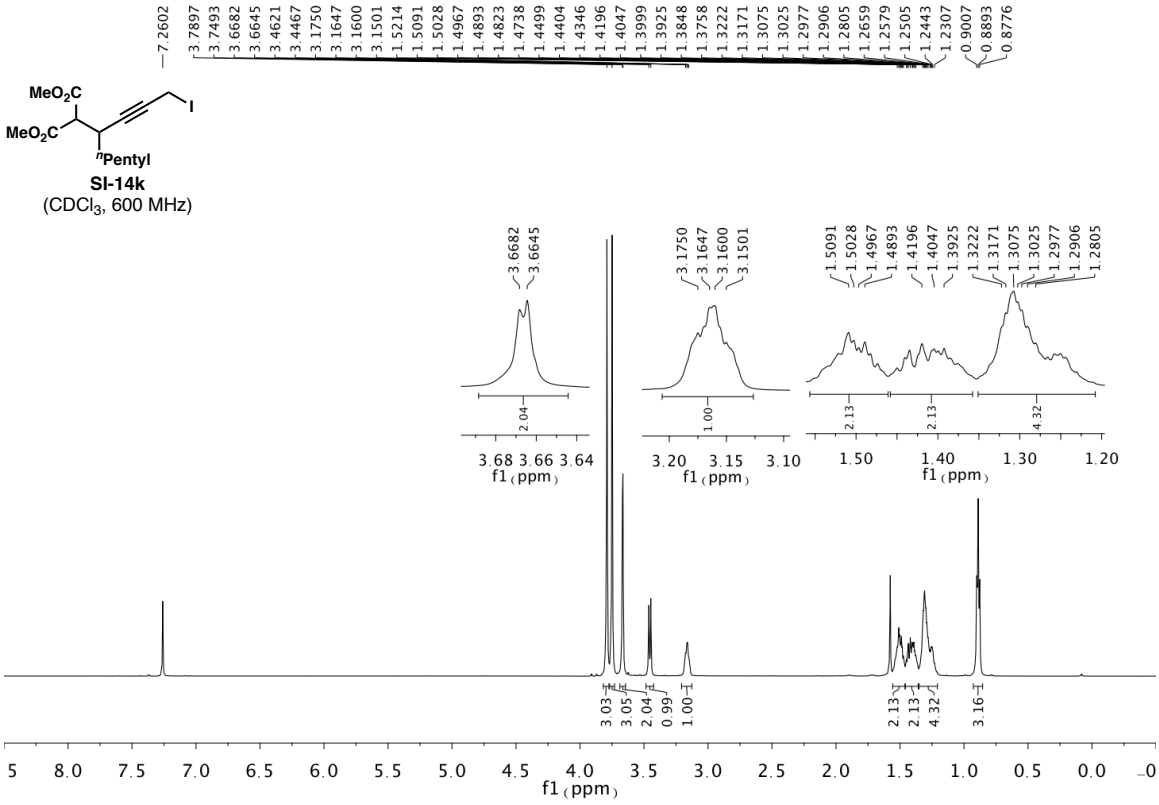

166.3096
164.7616
150.9950
128.1820
77.5714
77.3590
77.1481
52.6482
52.5499
31.6567
30.1338
28.2673
22.6715
14.2283
MeO2C
MeO2C
nPentyl
SI-11k
(CDCl3, 151 MHz)
52.8
52.4
f1 (ppm)

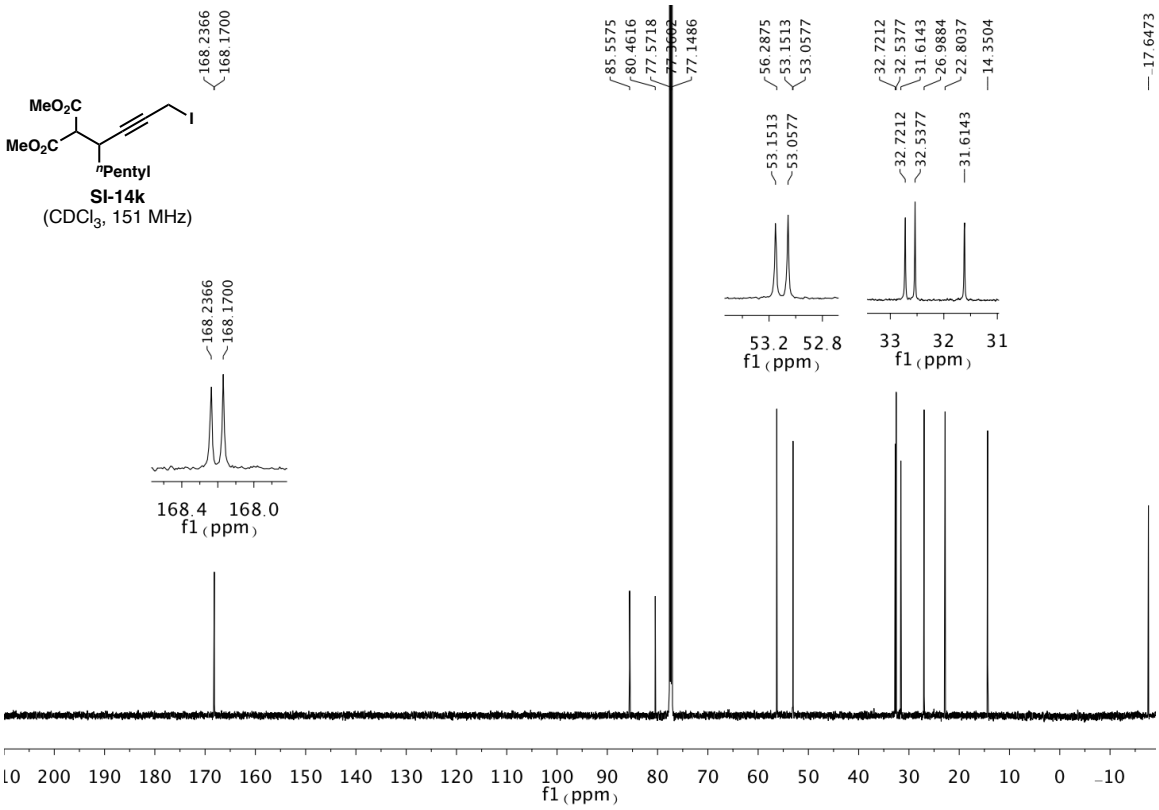

MeO2C
MeO2C
OTBS
nPentyl
SI-12k
(CDCl3, 400 MHz)
f1 (ppm)

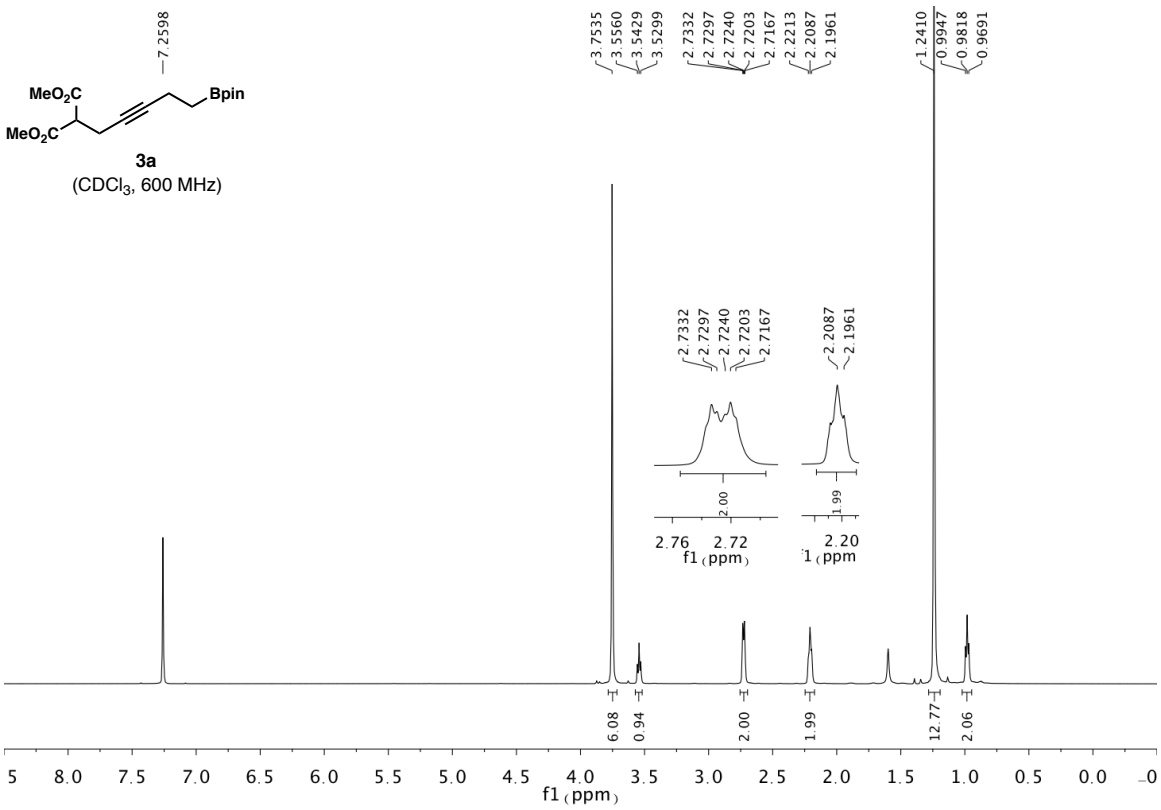

MeO2C
MeO2C
OTBS
nPentyl
SI-12k
(CDCl3, 151 MHz)
f1 (ppm)

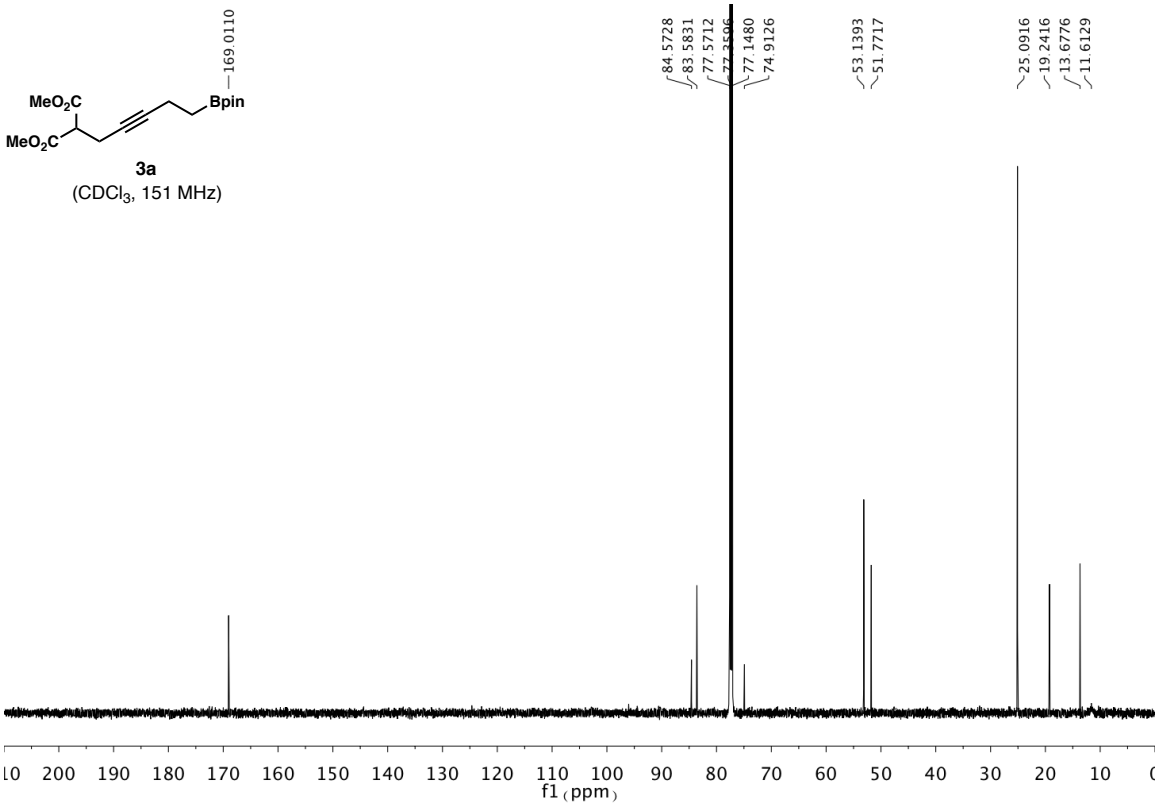

MeO2C
MeO2C
OH
nPentyl
SI-13k
(CDCl3, 400 MHz)
7.2601
4.2228
3.7576
3.7462
3.4820
3.4593
3.1612
1.7252
1.5429
1.5301
1.5118
1.4822
1.4567
1.4455
1.4263
1.4037
1.3739
1.2967
1.2814
0.8972
0.8811
0.8644
2.02
6.08
1.05
1.00
1.45
4.16
4.37
3.20
f1 (ppm)

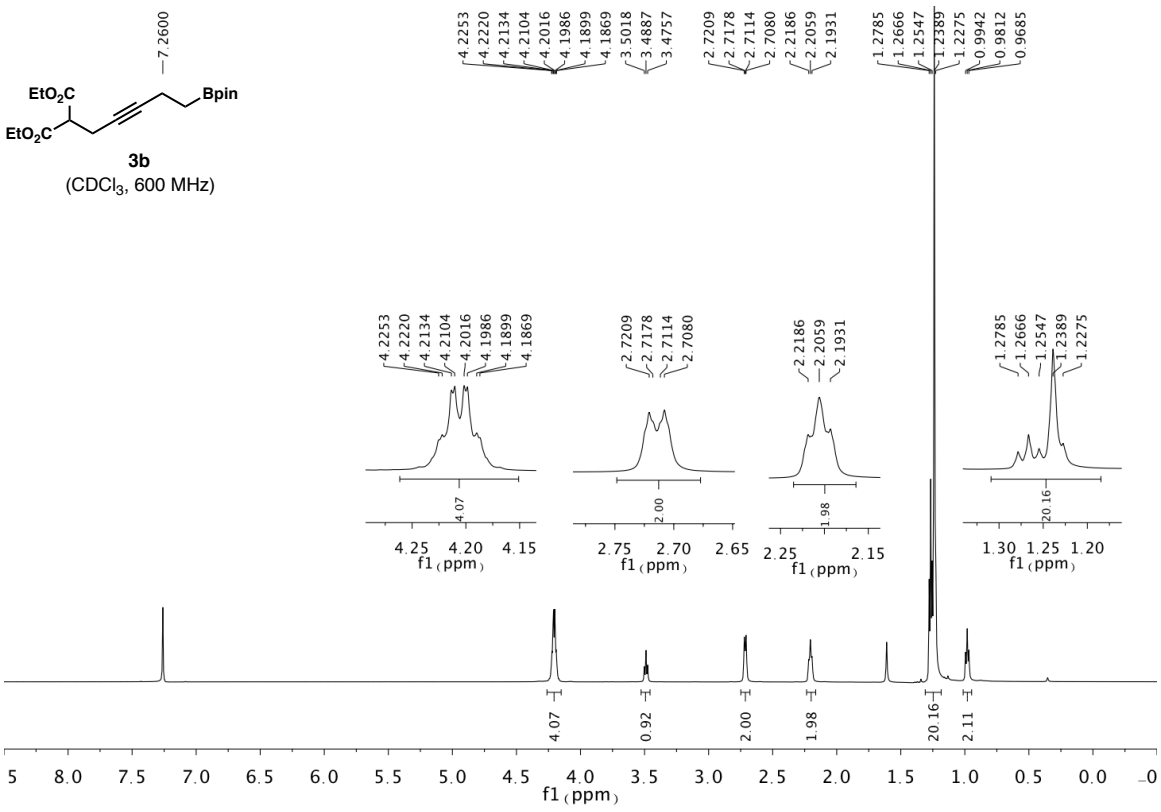

MeO2C
MeO2C
OH
nPentyl
SI-13k
(CDCl3, 151 MHz)
168.4166
168.2752
85.4919
81.8895
77.5720
77.3605
77.1488
56.6145
53.0273
53.0125
51.5179
32.7844
32.2808
31.6523
27.1024
22.8013
14.3423
168.5168.0
f1 (ppm)
53.2 53.0 52.8
f1 (ppm)

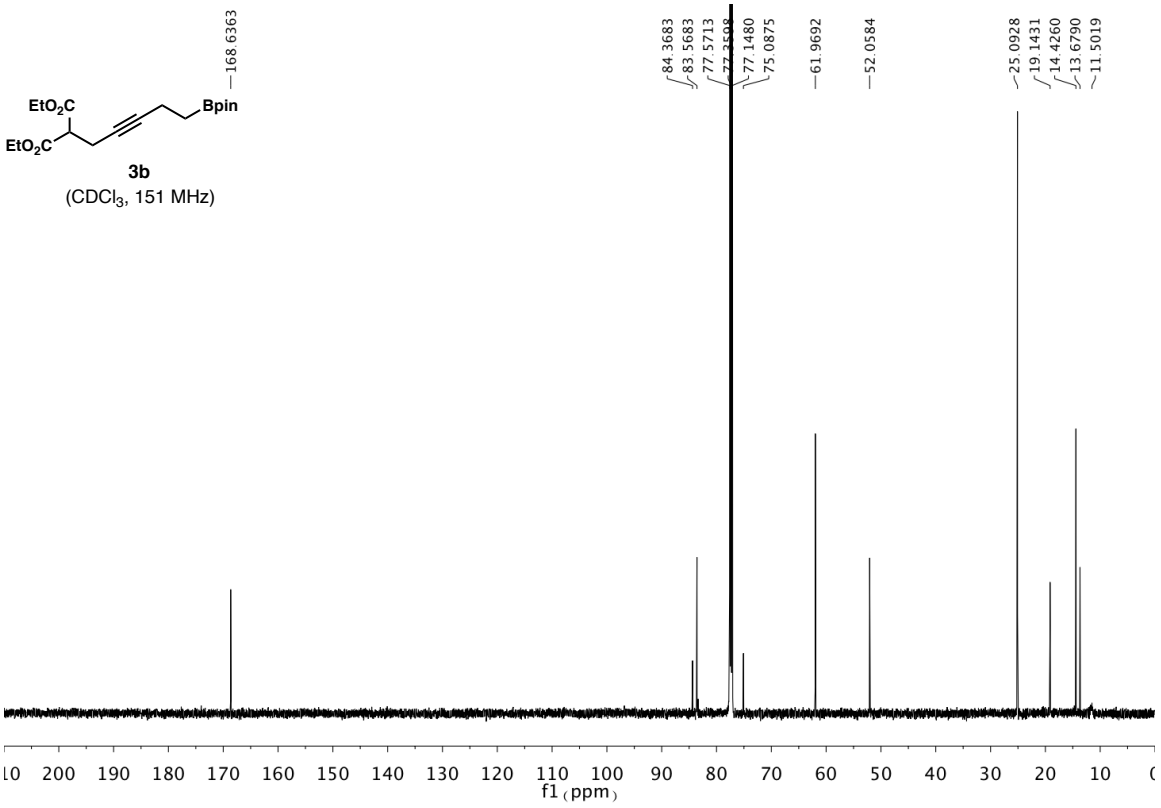

MeO2C
MeO2C
nPentyl
I
SI-14k
(CDCl3, 600 MHz)
f1 (ppm)

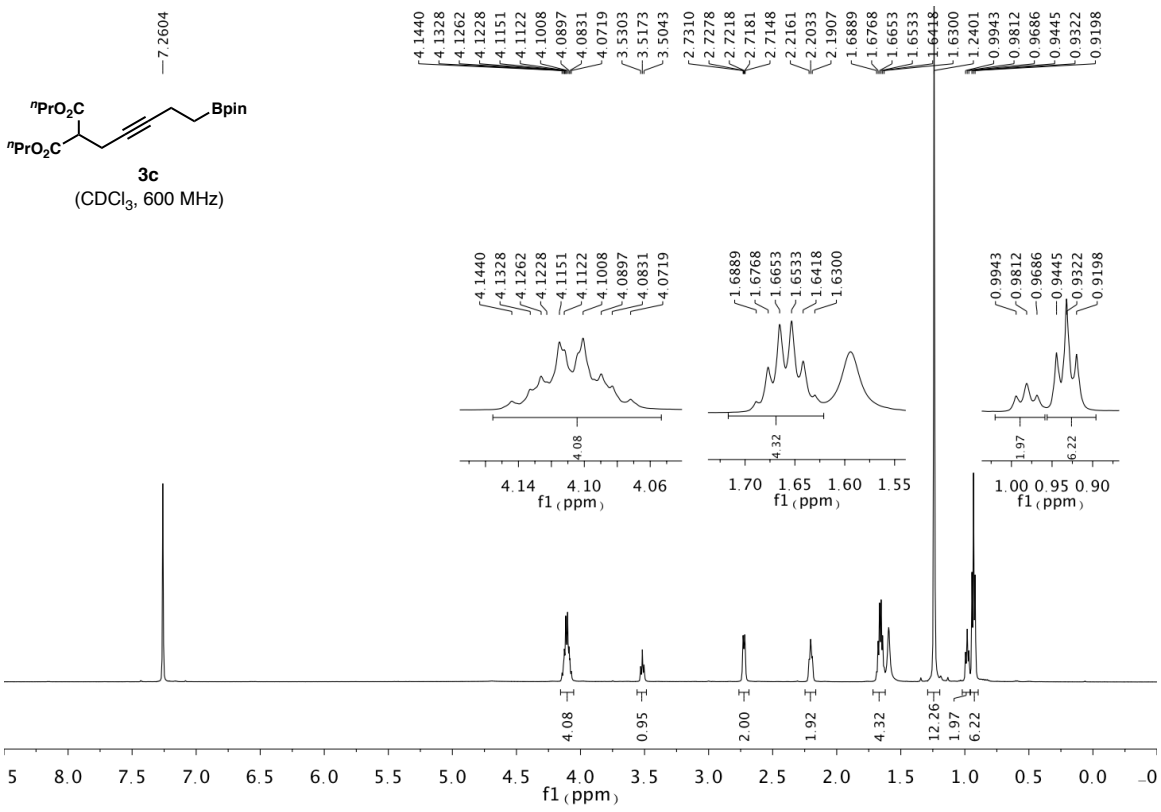

MeO2C
MeO2C
nPentyl
I
SI-14k
(CDCl3, 151 MHz)
f1 (ppm)

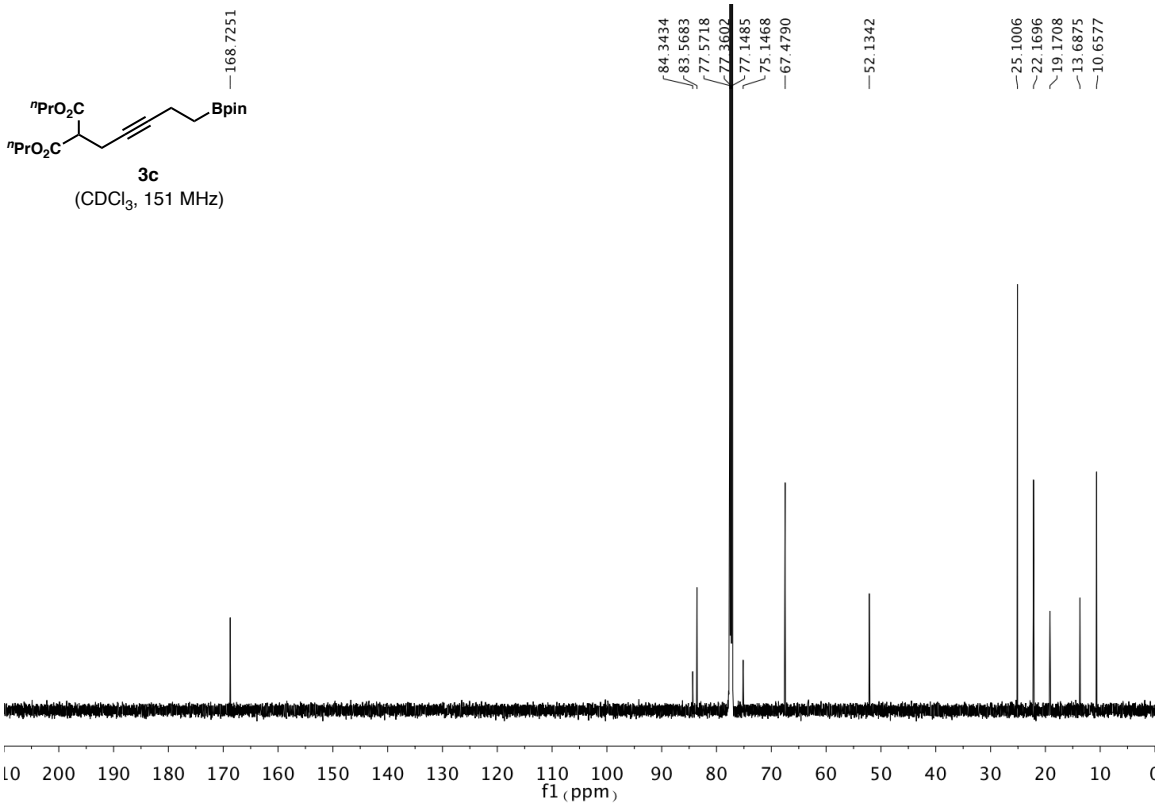

7.2598
MeO2C
MeO2C
Bpin
3a
(CDCl3, 600 MHz)
3.7535
3.5560
3.5429
3.5299
2.7332
2.7297
2.7240
2.7203
2.7167
2.2213
2.2087
2.1961
1.2410
0.9947
0.9818
0.9691
6.08
0.94
2.00
1.99
12.77
2.06
f1 (ppm)

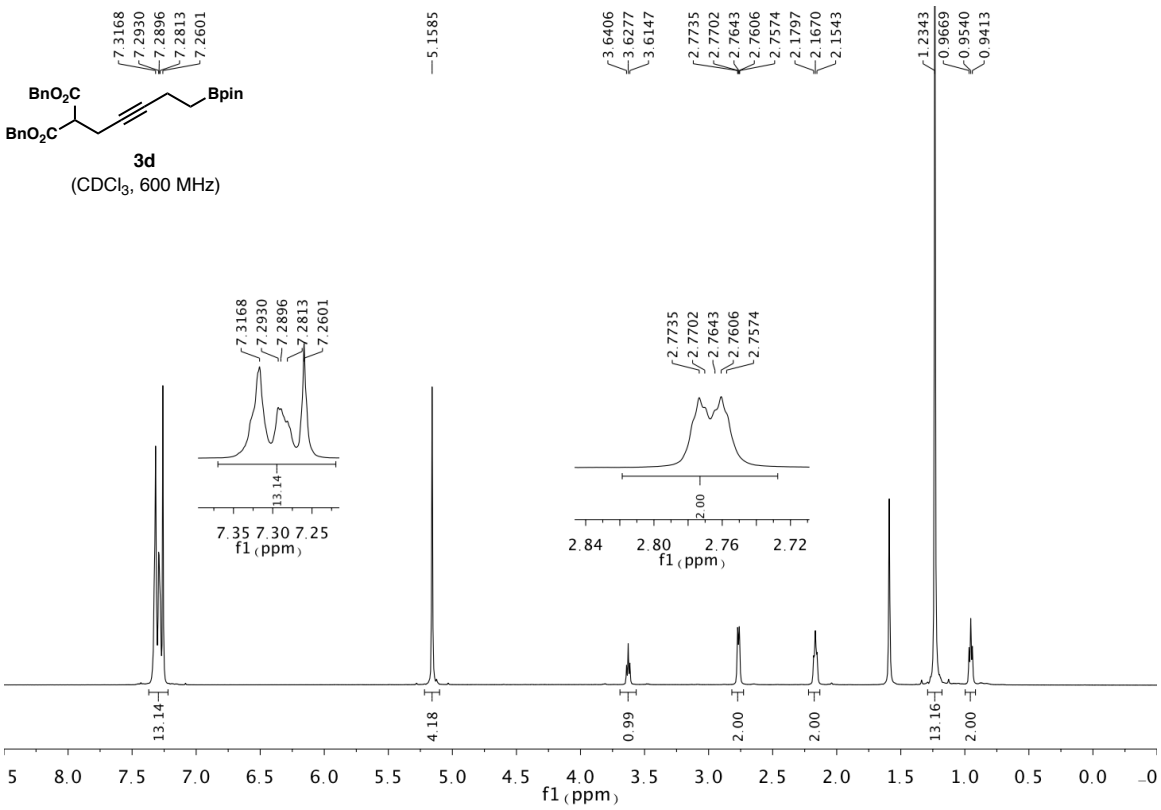

169.0110
MeO2C
MeO2C
Bpin
3a
(CDCl3, 151 MHz)
84.5728
83.5831
77.5712
77.1480
74.9126
53.1393
51.7717
25.0916
19.2416
13.6776
11.6129
f1 (ppm)

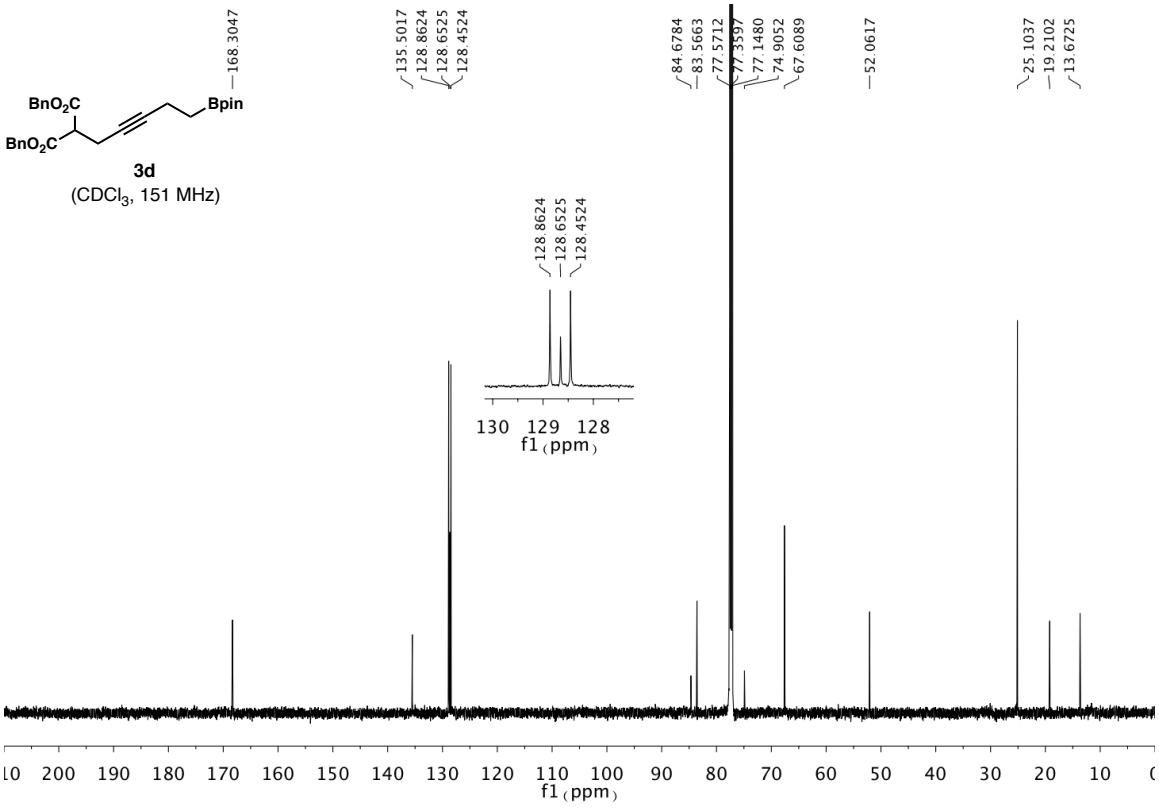

EtO2C
EtO2C
Bpin
3b
(CDCl3, 600 MHz)
7.2600
4.2253
4.2220
4.2134
4.2104
4.2016
4.1986
4.1899
4.1869
3.5018
3.4887
3.4757
2.7209
2.7178
2.7114
2.7080
2.2186
2.2059
2.1931
1.2785
1.2666
1.2547
1.2389
1.2275
0.9942
0.9812
0.9685
4.07
2.00
1.98
20.16
4.07
0.92
2.00
1.98
20.16
2.11
f1 (ppm)

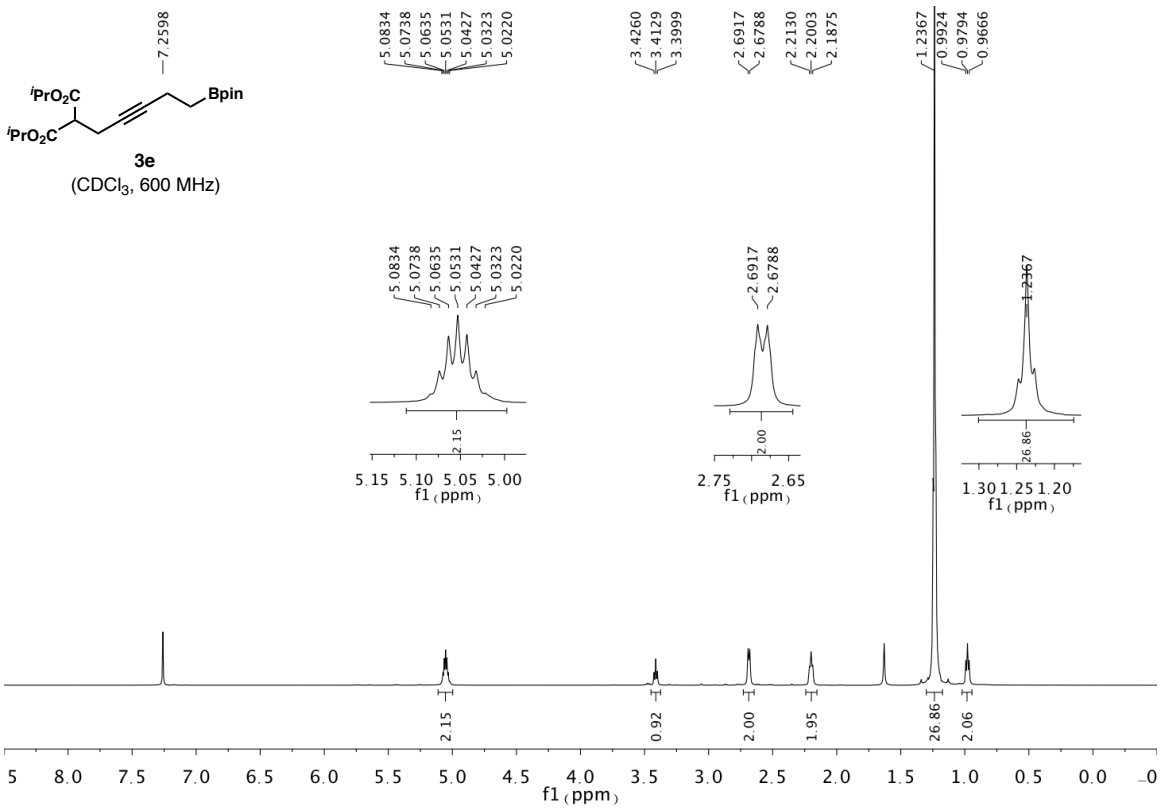

EtO2C
EtO2C
Bpin
3b
(CDCl3, 151 MHz)
168.6363
84.3683
83.5683
77.5713
77.3508
77.1480
75.0875
61.9692
52.0584
25.0928
19.1431
14.4260
13.6790
11.5019
f1 (ppm)

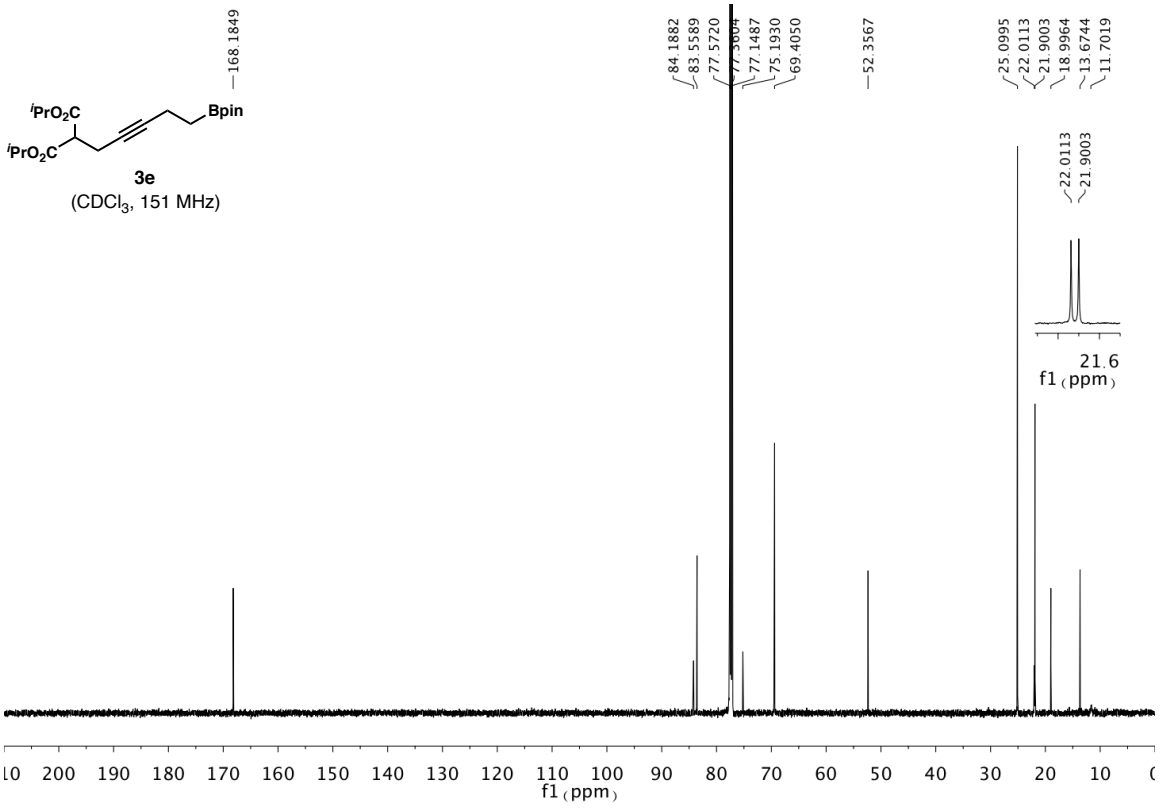

7.2604
nPrO2C
nPrO2C
Bpin
3c
(CDCl3, 600 MHz)
4.1440
4.1328
4.1262
4.1228
4.1151
4.1122
4.1008
4.0897
4.0831
4.0719
3.5303
3.5173
3.5043
2.7310
2.7278
2.7218
2.7181
2.7148
2.2161
2.2033
2.1907
1.6889
1.6768
1.6653
1.6533
1.6418
1.6300
1.2401
0.9943
0.9812
0.9686
0.9445
0.9322
0.9198
4.08
0.95
2.00
1.92
4.32
12.26
1.97
6.22
f1 (ppm)

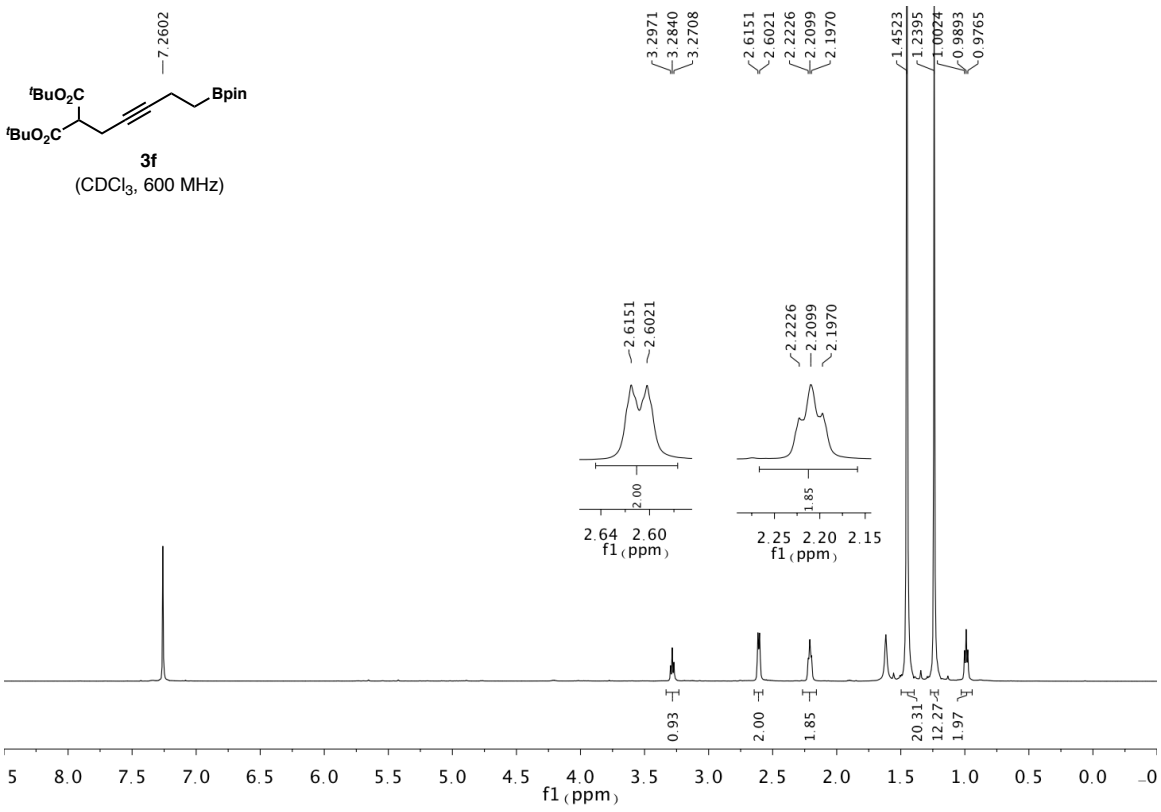

168.7251
nPrO2C
nPrO2C
Bpin
3c
(CDCl3, 151 MHz)
84.3434
83.5683
77.5718
77.3602
77.1485
75.1468
67.4790
52.1342
25.1006
22.1696
19.1708
13.6875
10.6577
f1 (ppm)

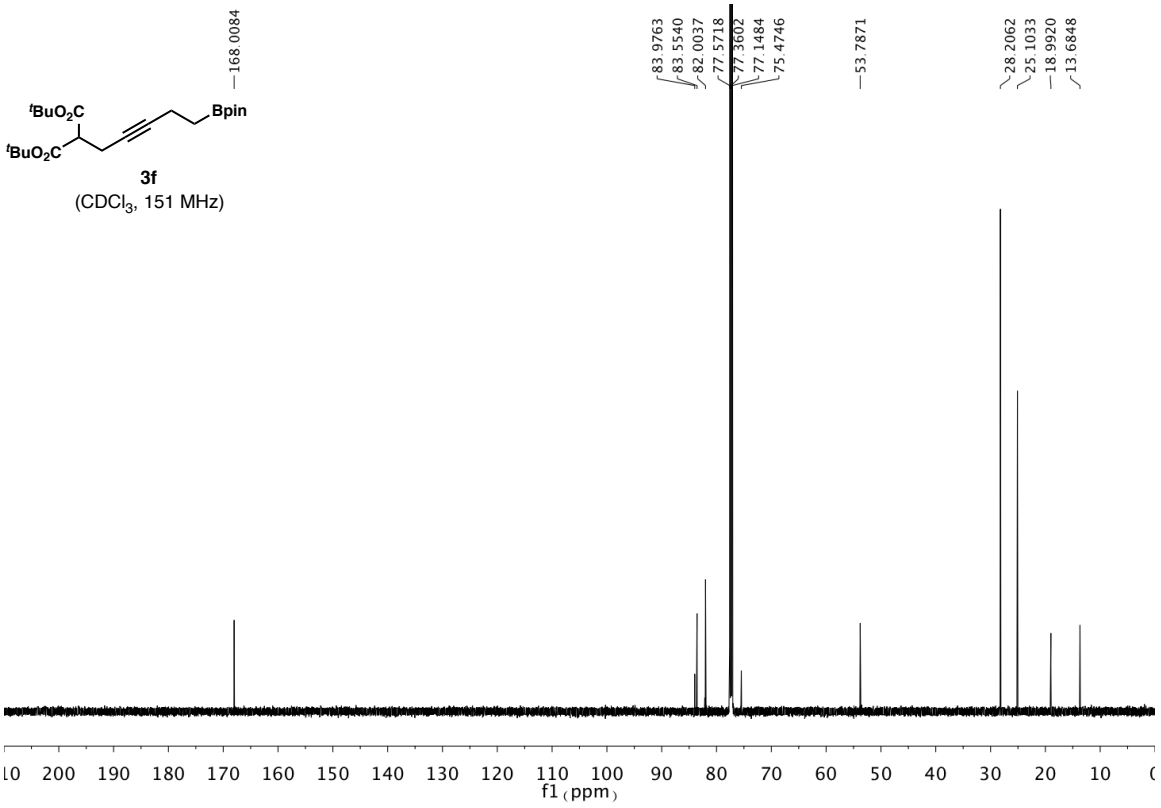

7.3168
7.2930
7.2896
7.2813
7.2601
5.1585
3.6406
3.6277
3.6147
2.7735
2.7702
2.7643
2.7606
2.7574
2.1797
2.1670
2.1543
1.2343
0.9669
0.9540
0.9413
BnO2C
BnO2C
Bpin
3d
(CDCl3, 600 MHz)
13.14
4.18
0.99
2.00
2.00
13.16
2.00
7.35 7.30 7.25
f1 (ppm)
2.84 2.80 2.76 2.72
f1 (ppm)

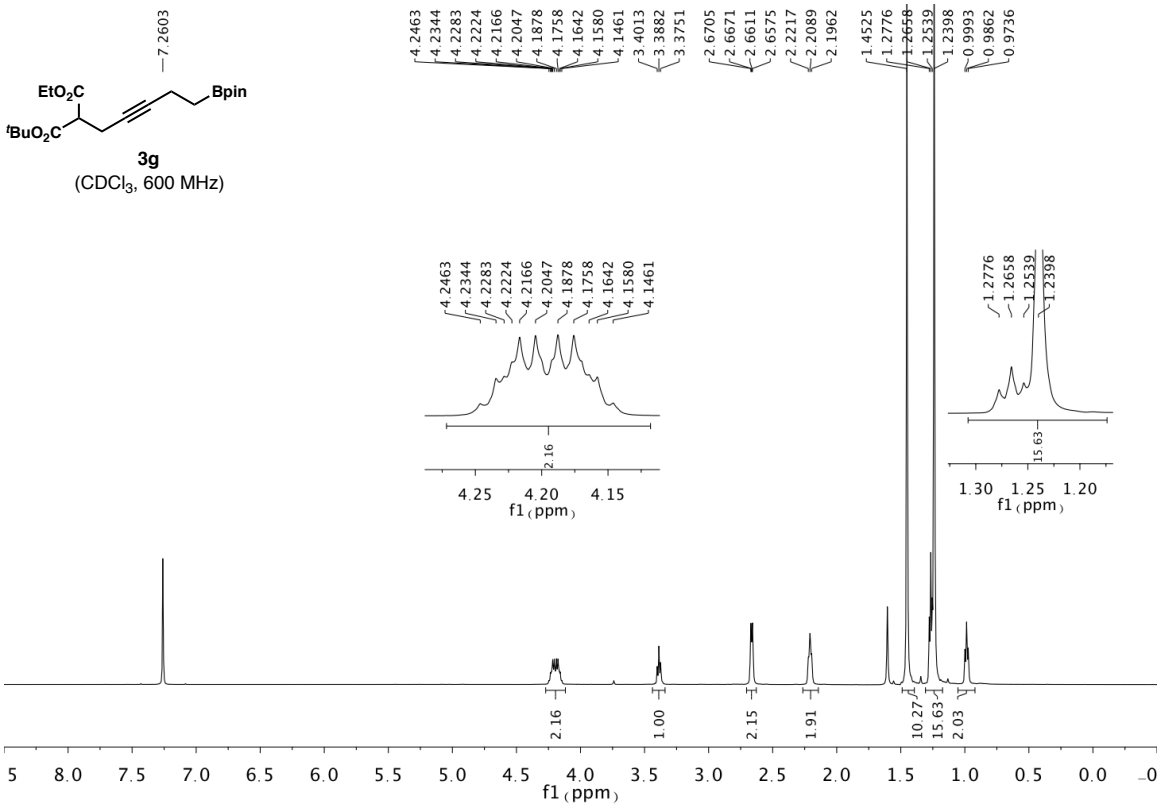

168.3047
135.5017
128.8624
128.6525
128.4524
84.6784
83.5663
77.5712
77.3597
77.1480
74.9052
67.6089
52.0617
25.1037
19.2102
13.6725
BnO2C
BnO2C
Bpin
3d
(CDCl3, 151 MHz)
130 129 128
f1 (ppm)
f1 (ppm)

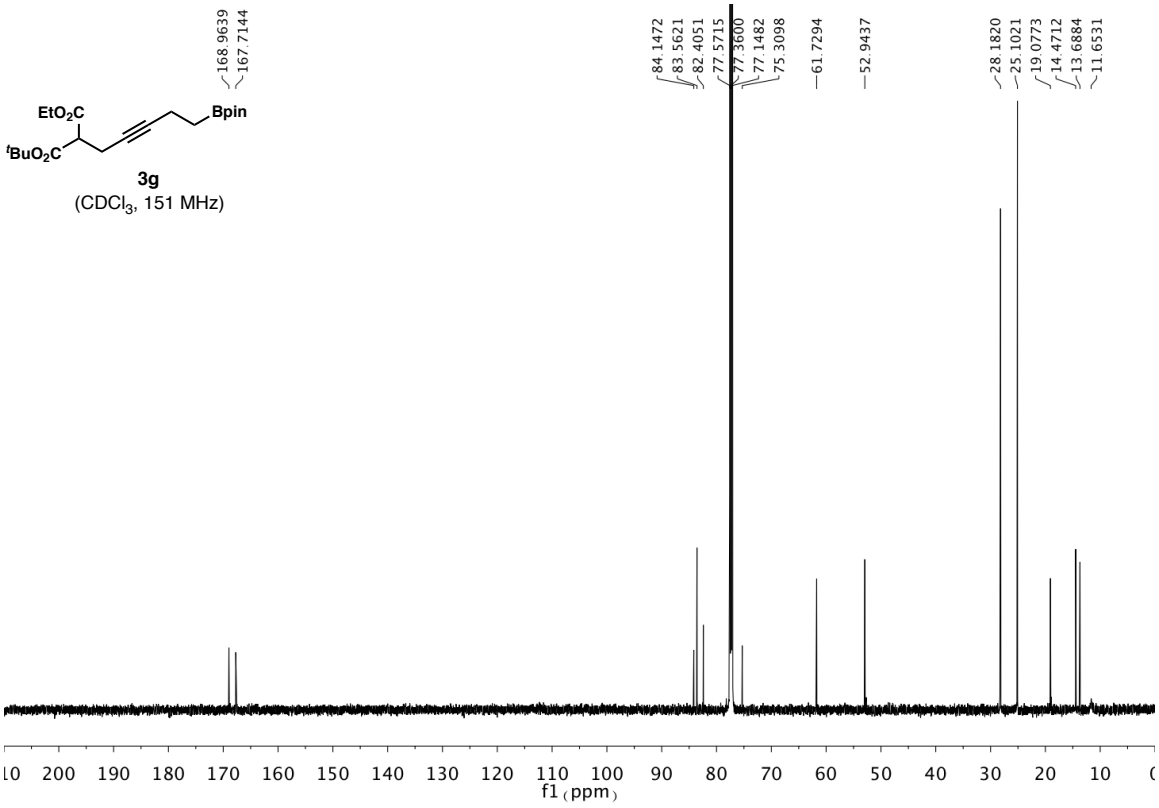

7.2598
5.0834
5.0738
5.0635
5.0531
5.0427
5.0323
5.0220
3.4260
3.4129
3.3999
2.6917
2.6788
2.2130
2.2003
2.1875
1.2367
0.9924
0.9794
0.9666
iPrO2C
iPrO2C
Bpin
3e
(CDCl3, 600 MHz)
2.15
2.00
26.86
f1 (ppm)
2.15
0.92
2.00
1.95
26.86
2.06

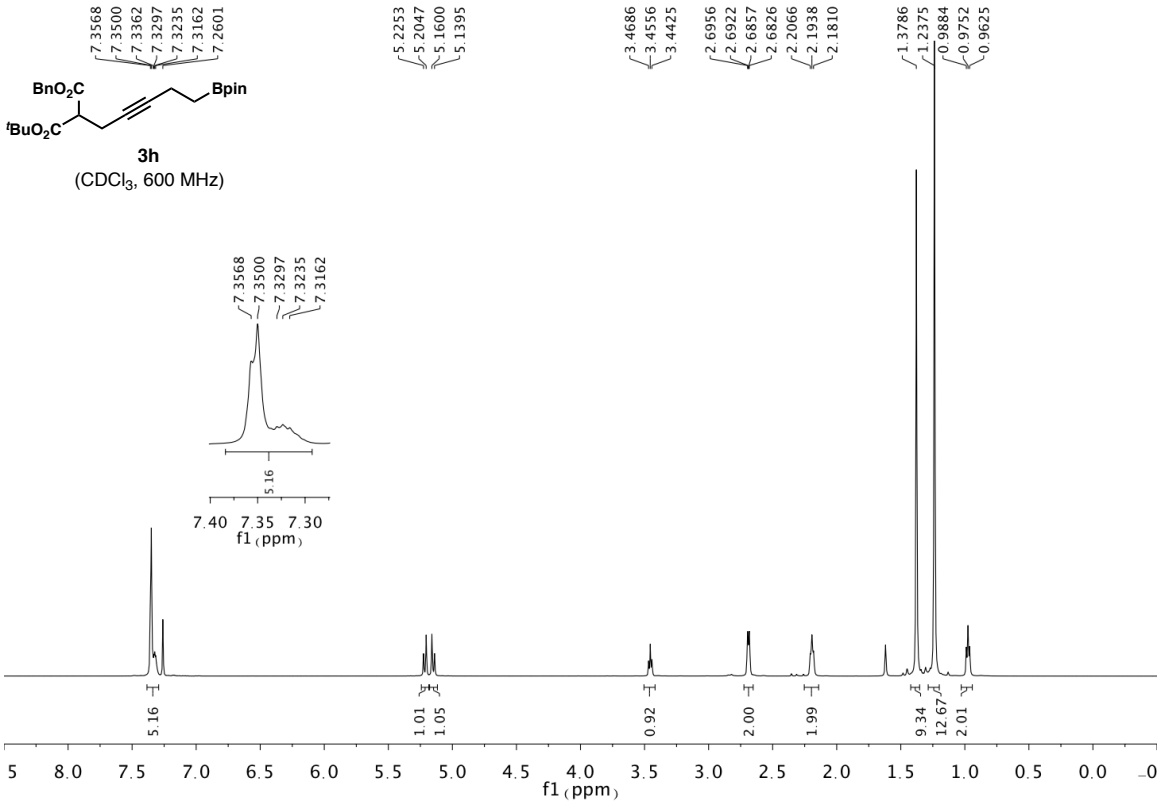

168.1849
84.1882
83.5589
77.5720
77.3604
77.1487
75.1930
69.4050
52.3567
25.0995
22.0113
21.9003
18.9964
13.6744
11.7019
iPrO2C
iPrO2C
Bpin
3e
(CDCl3, 151 MHz)
f1 (ppm)

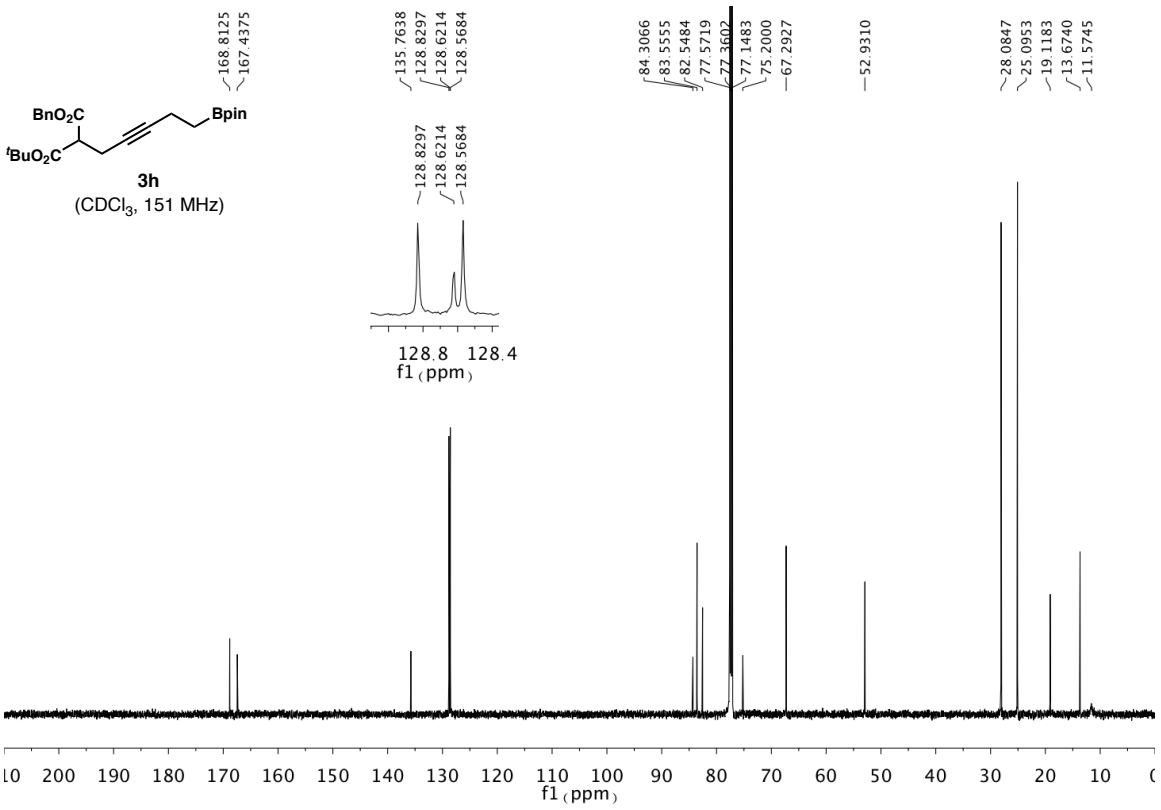

7.2602
tBuO2C
tBuO2C
Bpin
3f
(CDCl3, 600 MHz)
3.2971
3.2840
3.2708
2.6151
2.6021
2.2226
2.2099
2.1970
1.4523
1.2395
1.0024
0.9893
0.9765
2.00
1.85
2.64 2.60
2.25 2.20 2.15
f1 (ppm)
0.93
2.00
1.85
20.31
12.27
1.97

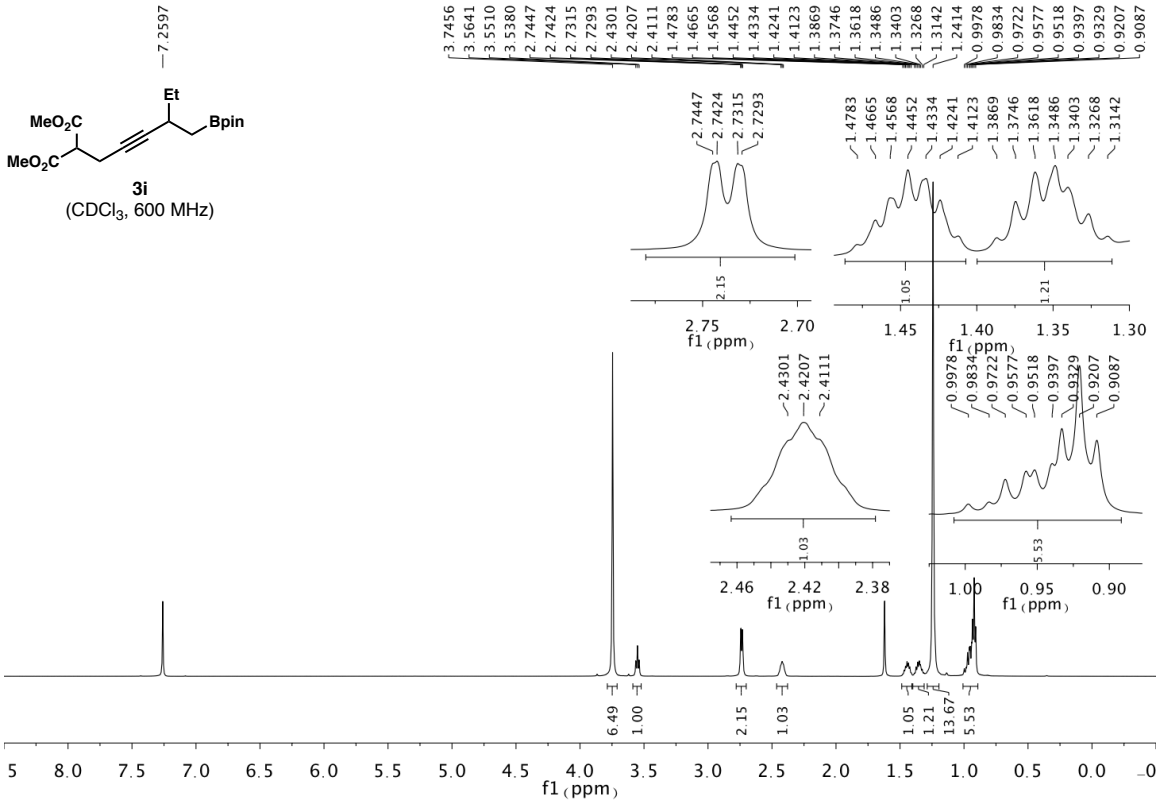

168.0084
tBuO2C
tBuO2C
Bpin
3f
(CDCl3, 151 MHz)
83.9763
83.5540
82.0037
77.5718
77.3602
77.1484
75.4746
53.7871
28.2062
25.1033
18.9920
13.6848
f1 (ppm)

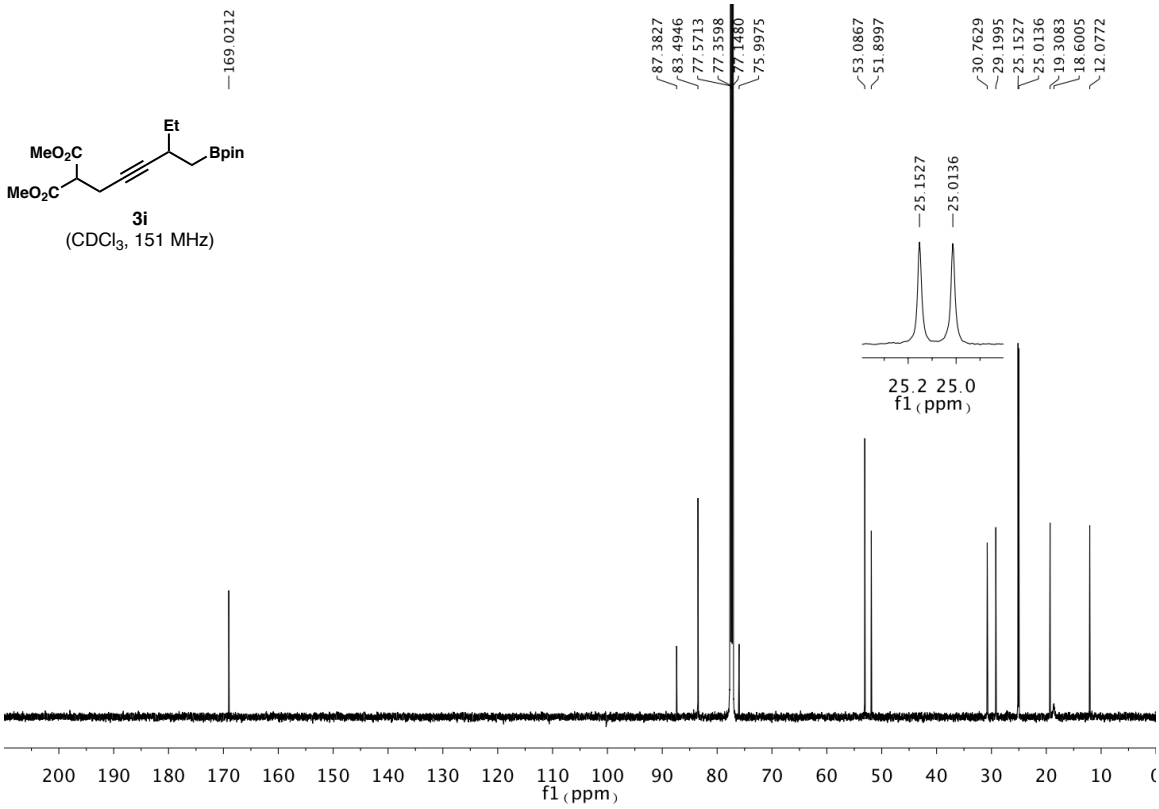

7.2603
EtO2C
tBuO2C
Bpin
3g
(CDCl3, 600 MHz)
4.2463
4.2344
4.2283
4.2224
4.2166
4.2047
4.1878
4.1758
4.1642
4.1580
4.1461
3.4013
3.3882
3.3751
2.6705
2.6671
2.6611
2.6575
2.2217
2.2089
2.1962
1.4525
1.2776
1.2658
1.2539
1.2398
0.9993
0.9862
0.9736
2.16
4.25
4.20
4.15
f1 (ppm)
15.63
1.30
1.25
1.20
f1 (ppm)
2.16
1.00
2.15
1.91
10.27
15.63
2.03
f1 (ppm)

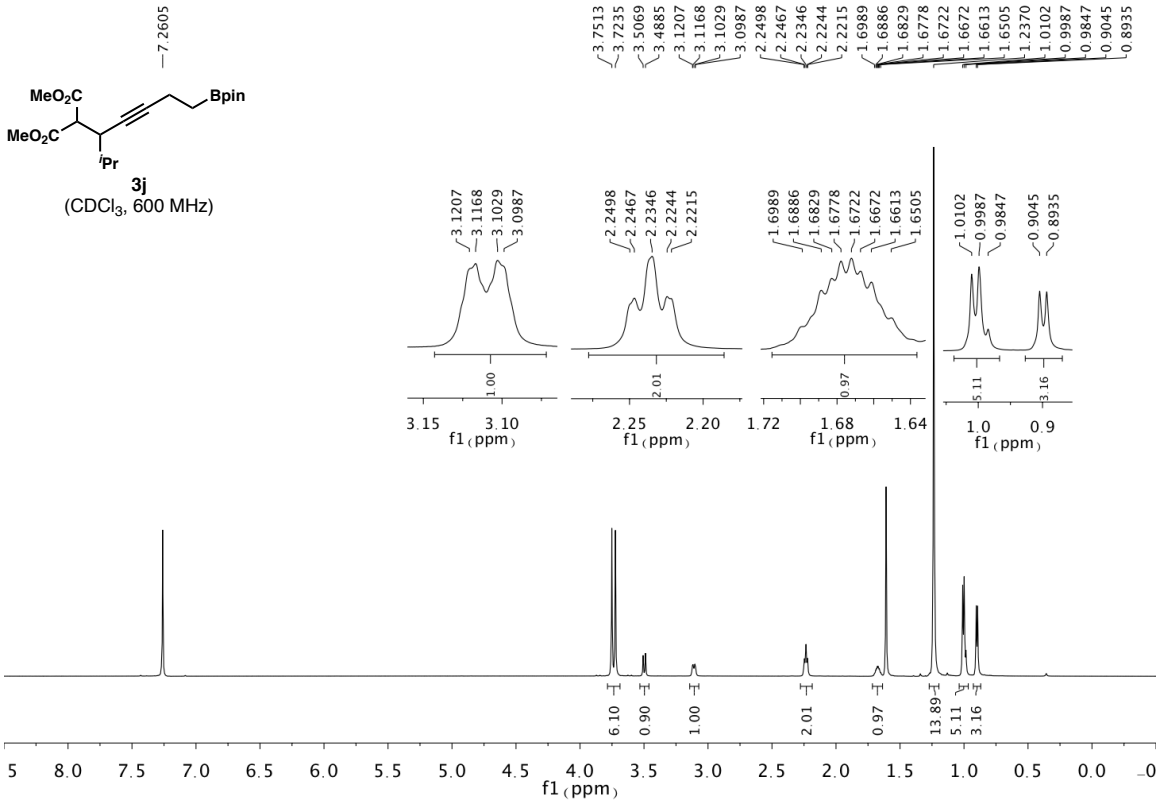

168.9639
167.7144
EtO2C
tBuO2C
Bpin
3g
(CDCl3, 151 MHz)
84.1472
83.5621
82.4051
77.5715
77.3600
77.1482
75.3098
61.7294
52.9437
28.1820
25.1021
19.0773
14.4712
13.6884
11.6531
f1 (ppm)

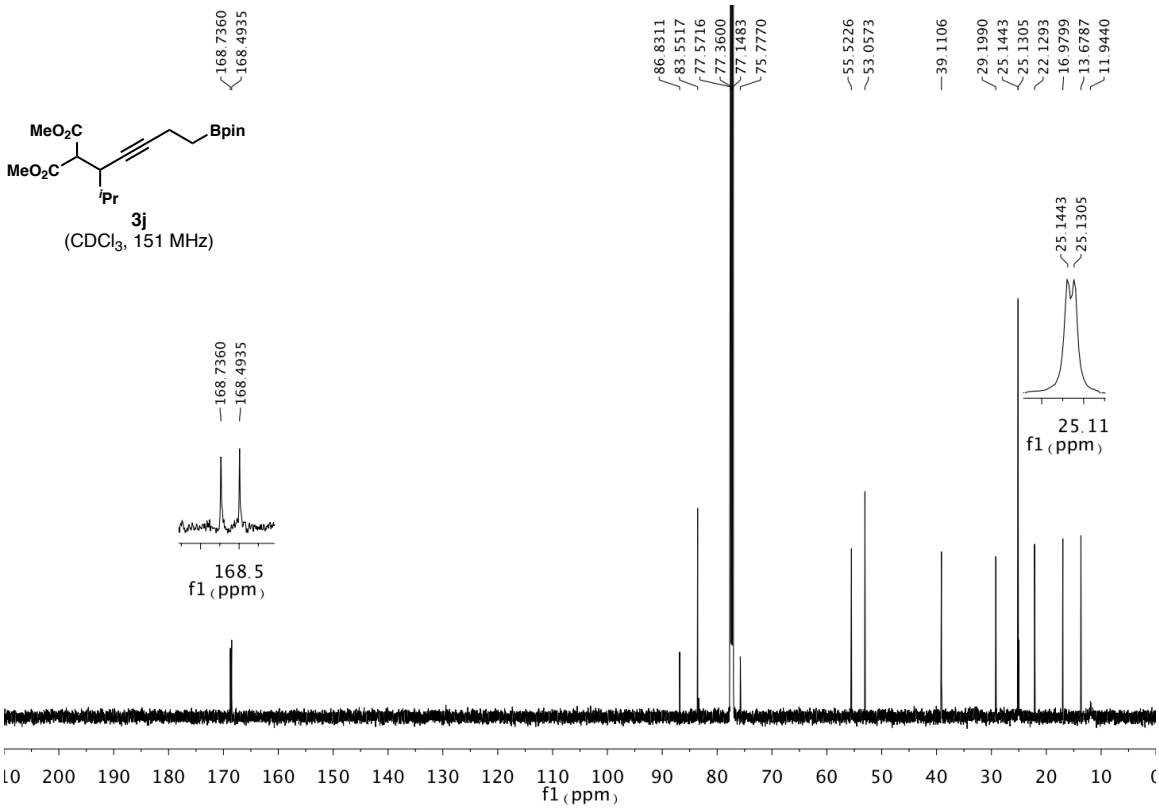

7.3568
7.3500
7.3362
7.3297
7.3235
7.3162
7.2601
5.2253
5.2047
5.1600
5.1395
3.4686
3.4556
3.4425
2.6956
2.6922
2.6857
2.6826
2.2066
2.1938
2.1810
1.3786
1.2375
0.9884
0.9752
0.9625
BnO2C
tBuO2C
Bpin
3h
(CDCl3, 600 MHz)
5.16
1.01
1.05
0.92
2.00
1.99
9.34
12.67
2.01
f1 (ppm)

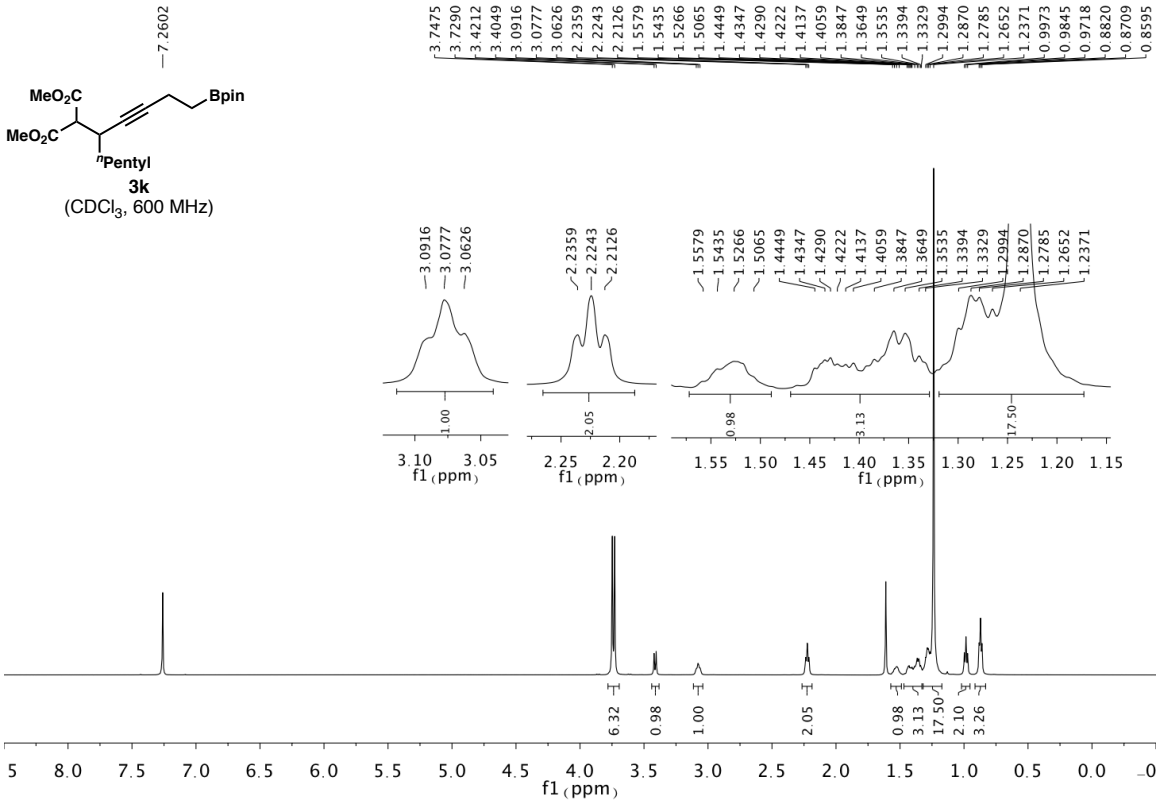

168.8125
167.4375
135.7638
128.8297
128.6214
128.5684
84.3066
83.5555
82.5484
77.5719
77.3602
77.1483
75.2000
67.2927
52.9310
28.0847
25.0953
19.1183
13.6740
11.5745
BnO2C
tBuO2C
Bpin
3h
(CDCl3, 151 MHz)
f1 (ppm)

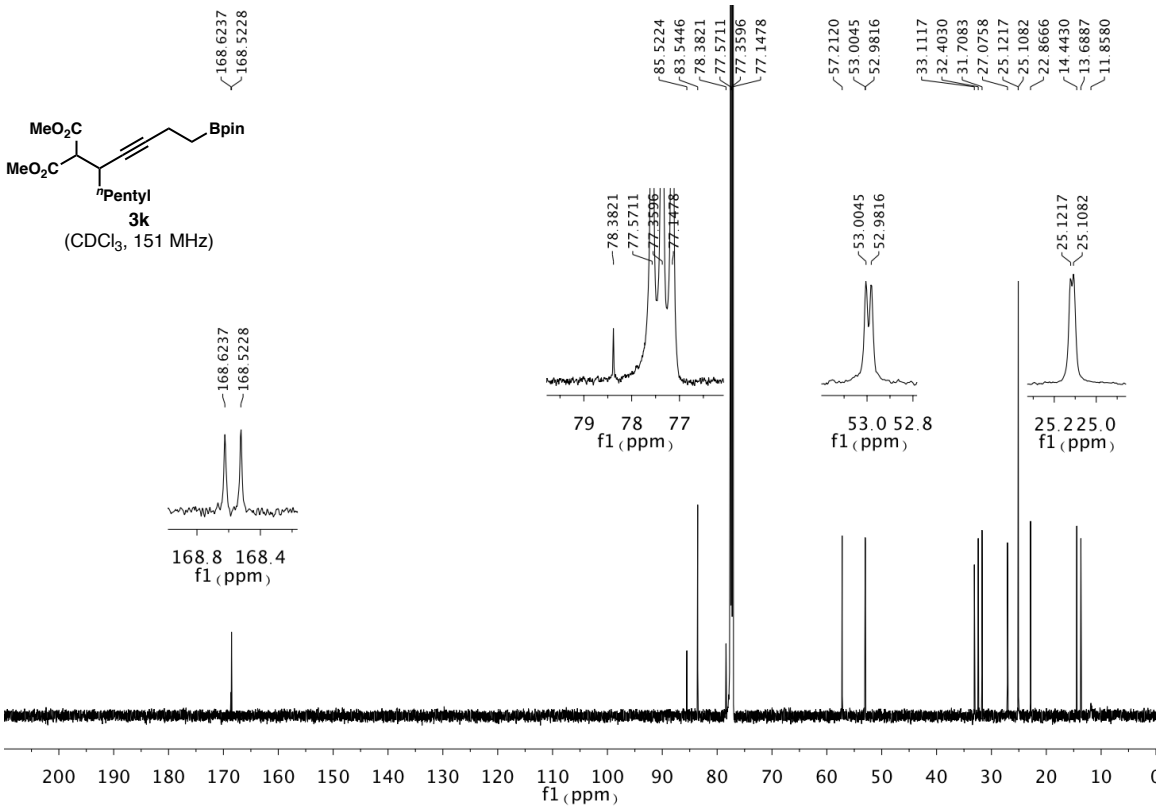

MeO2C
MeO2C
Et
Bpin
3i
(CDCl3, 600 MHz)
7.2597
3.7456
3.5641
3.5510
3.5380
2.7447
2.7424
2.7315
2.7293
2.4301
2.4207
2.4111
1.4783
1.4665
1.4568
1.4452
1.4334
1.4241
1.4123
1.3869
1.3746
1.3618
1.3486
1.3403
1.3268
1.3142
1.2414
0.9978
0.9834
0.9722
0.9577
0.9518
0.9397
0.9329
0.9207
0.9087
6.49
1.00
2.15
1.03
1.05
1.21
13.67
5.53
f1 (ppm)

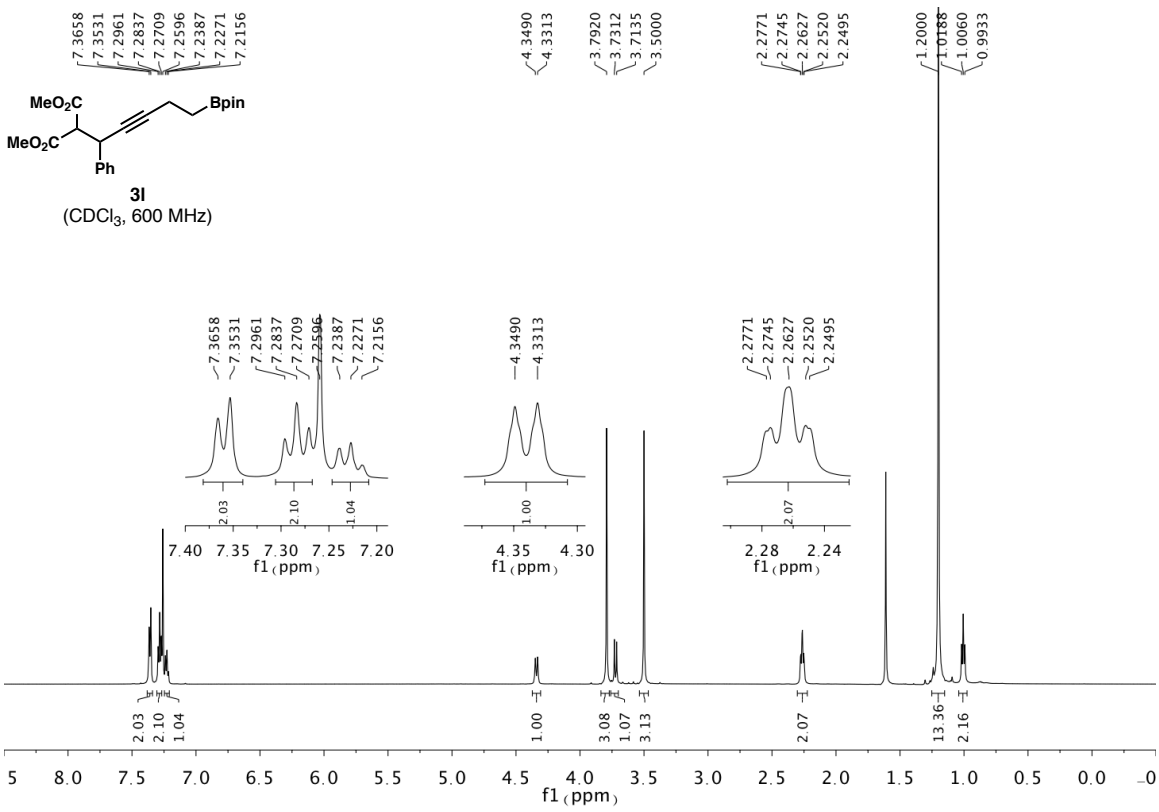

MeO2C
MeO2C
Et
Bpin
3i
(CDCl3, 151 MHz)
169.0212
87.3827
83.4946
77.5713
77.3598
77.1480
75.9975
53.0867
51.8997
30.7629
29.1995
25.1527
25.0136
19.3083
18.6005
12.0772
f1 (ppm)

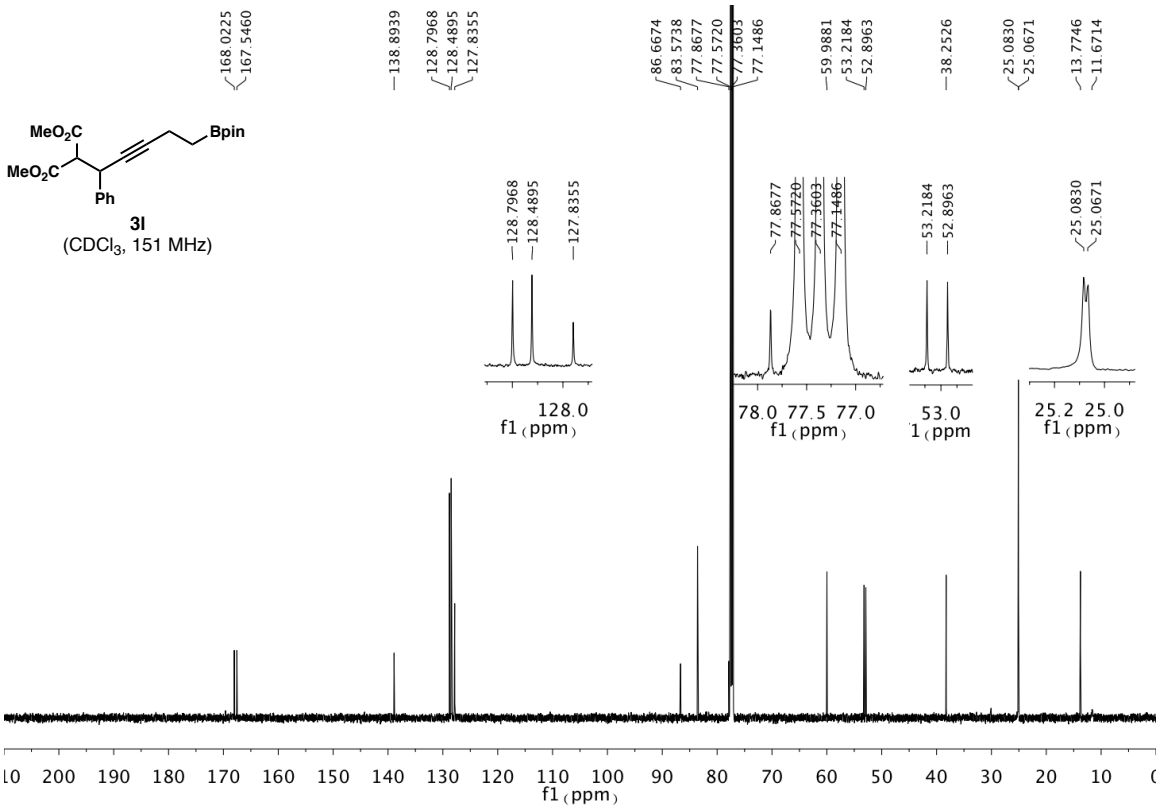

MeO2C
MeO2C
iPr
Bpin
3j
(CDCl3, 600 MHz)
f1 (ppm)

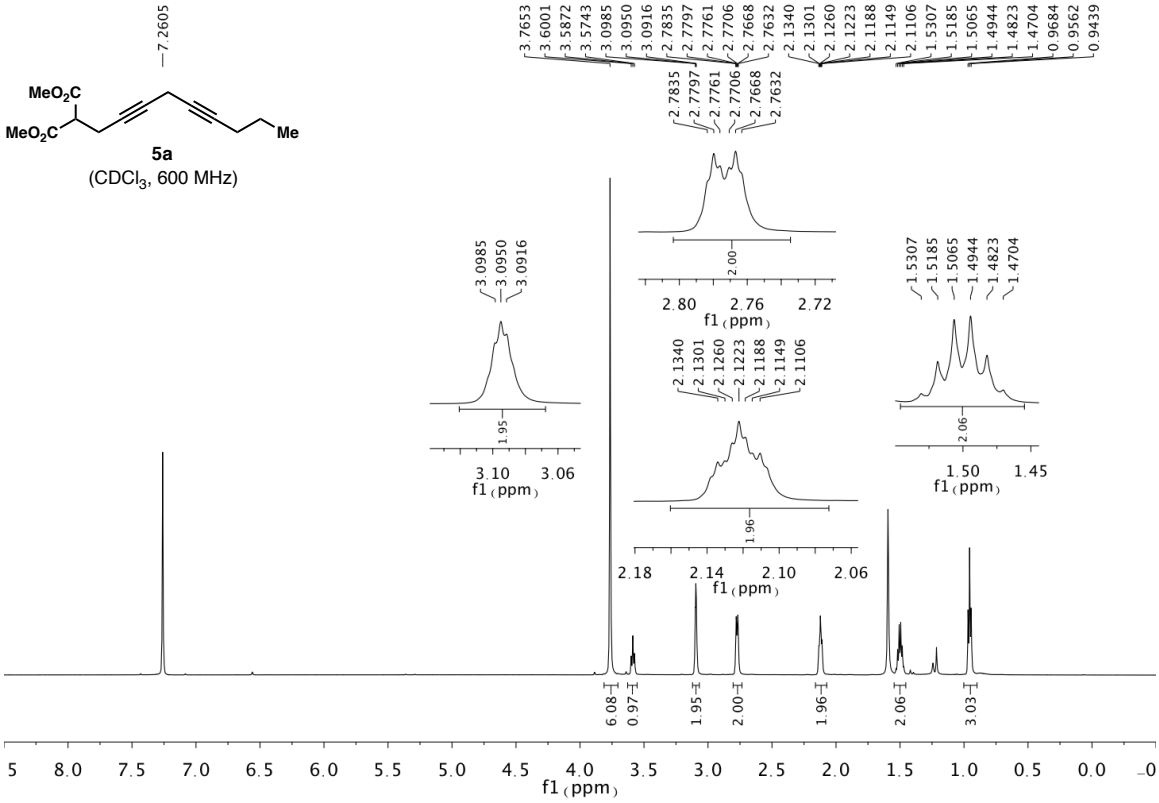

MeO2C
MeO2C
iPr
Bpin
3j
(CDCl3, 151 MHz)
168.5
25.11
f1 (ppm)

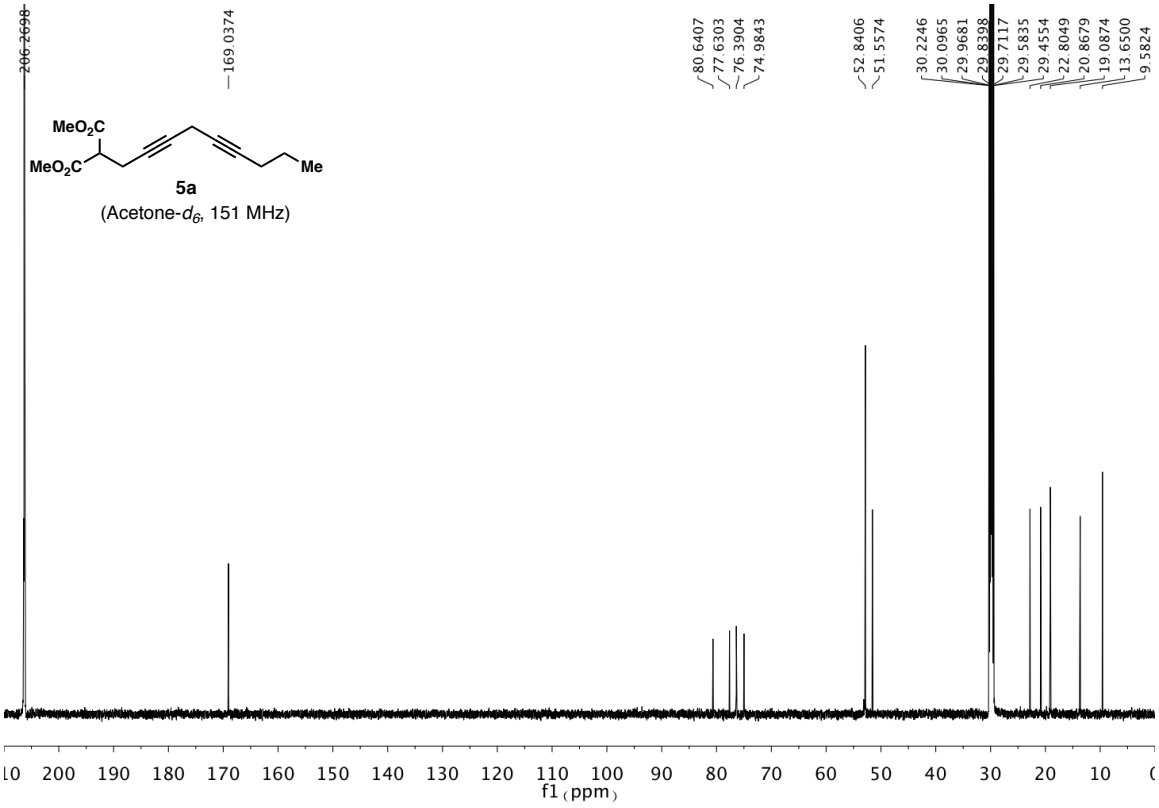

MeO2C
MeO2C
Bpin
nPentyl
3k
(CDCl3, 600 MHz)
7.2602
3.7475
3.7290
3.4212
3.4049
3.0916
3.0777
3.0626
2.2359
2.2243
2.2126
1.5579
1.5435
1.5266
1.5065
1.4449
1.4347
1.4290
1.4222
1.4137
1.4059
1.3847
1.3649
1.3535
1.3394
1.3329
1.2994
1.2870
1.2785
1.2652
1.2371
0.9973
0.9845
0.9718
0.8820
0.8709
0.8595
6.32
0.98
1.00
2.05
0.98
3.13
17.50
2.10
3.26
f1 (ppm)

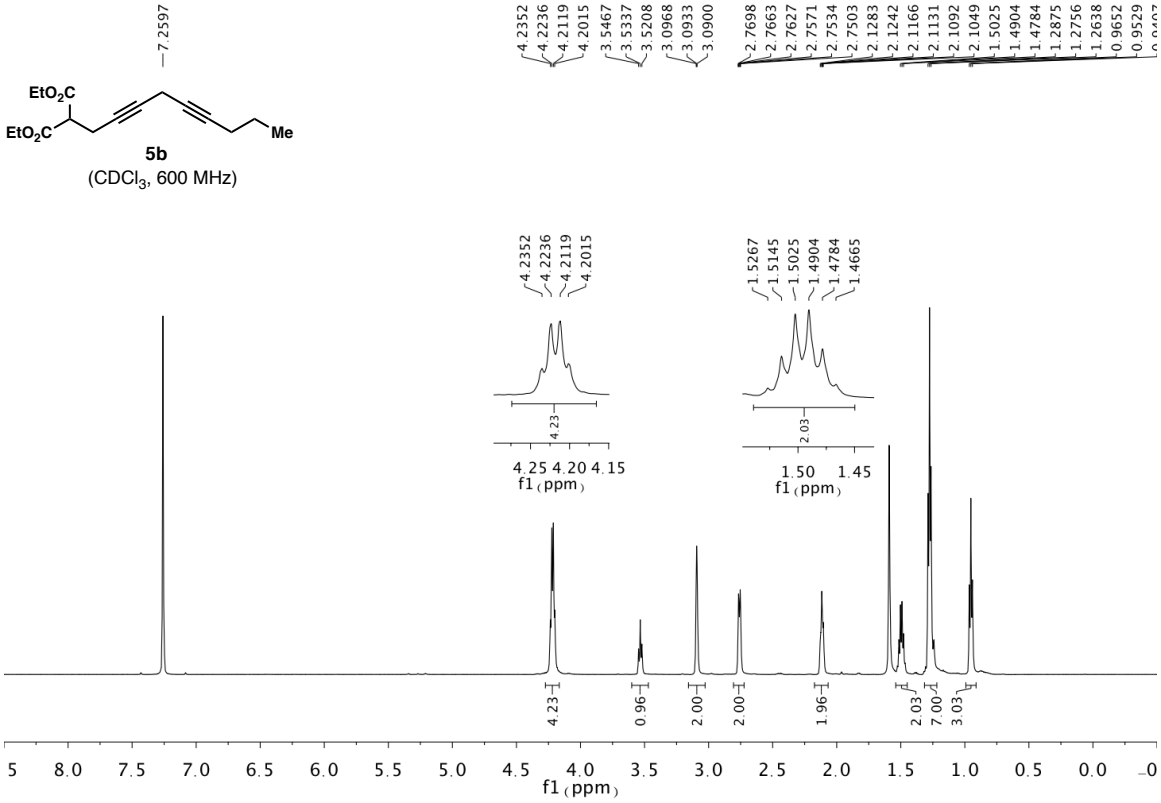

MeO2C
MeO2C
Bpin
nPentyl
3k
(CDCl3, 151 MHz)
168.6237
168.5228
85.5224
83.5446
78.3821
77.5711
77.3596
77.1478
57.2120
53.0045
52.9816
33.1117
32.4030
31.7083
27.0758
25.1217
25.1082
22.8666
14.4430
13.6887
11.8580
f1 (ppm)

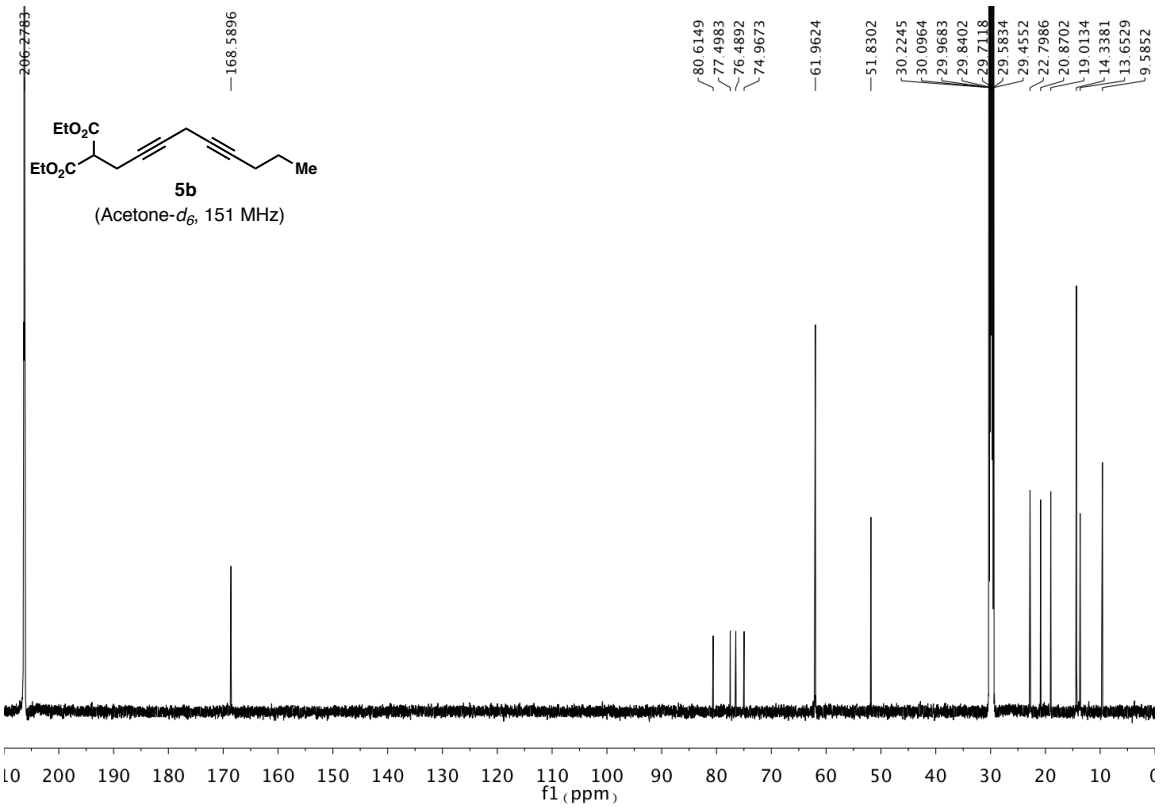

MeO2C
MeO2C
Bpin
Ph
3l
(CDCl3, 600 MHz)
7.3658
7.3531
7.2961
7.2837
7.2709
7.2596
7.2387
7.2271
7.2156
4.3490
4.3313
3.7920
3.7312
3.7135
3.5000
2.2771
2.2745
2.2627
2.2520
2.2495
1.2000
1.0188
1.0060
0.9933
2.03
2.10
1.04
1.00
3.08
1.07
3.13
2.07
13.36
2.16
f1 (ppm)

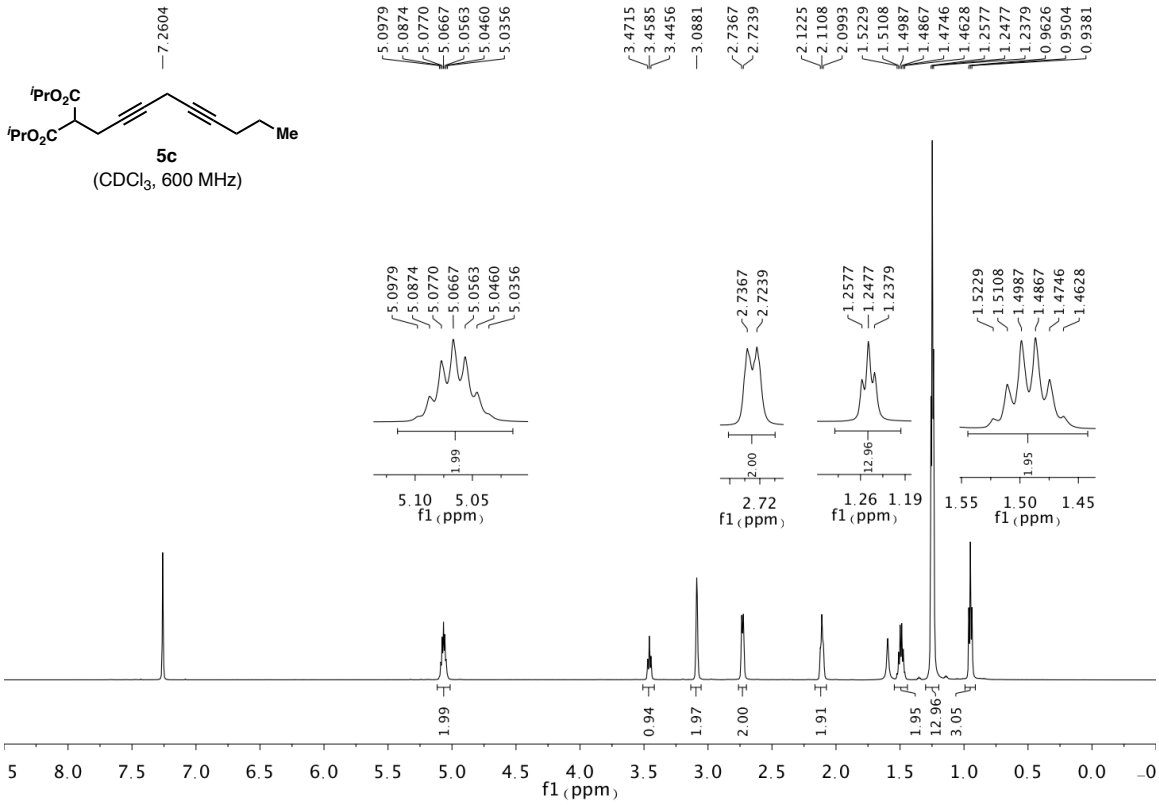

MeO2C
MeO2C
Bpin
Ph
3l
(CDCl3, 151 MHz)
168.0225
167.5460
138.8939
128.7968
128.4895
127.8355
86.6674
83.5738
77.8677
77.5720
77.3603
77.1486
59.9881
53.2184
52.8963
38.2526
25.0830
25.0671
13.7746
11.6714
f1 (ppm)

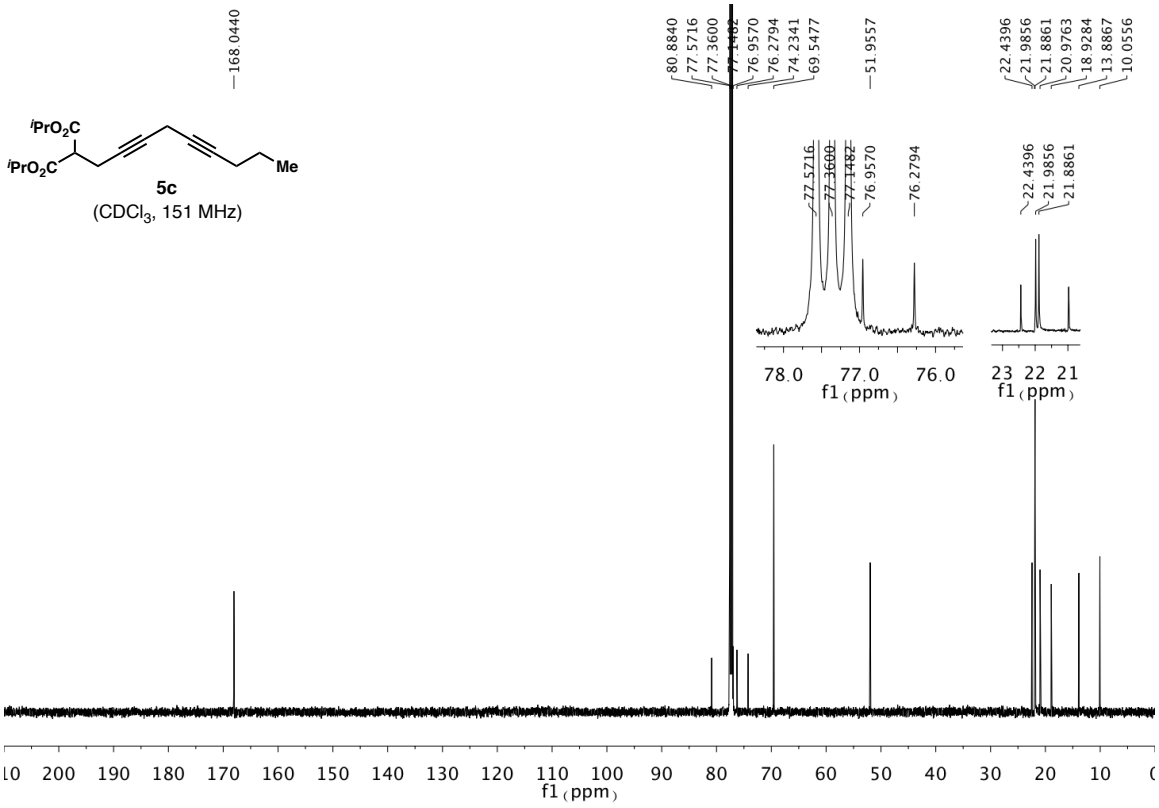

MeO2C
MeO2C
Me
5a
(CDCl3, 600 MHz)
f1 (ppm)

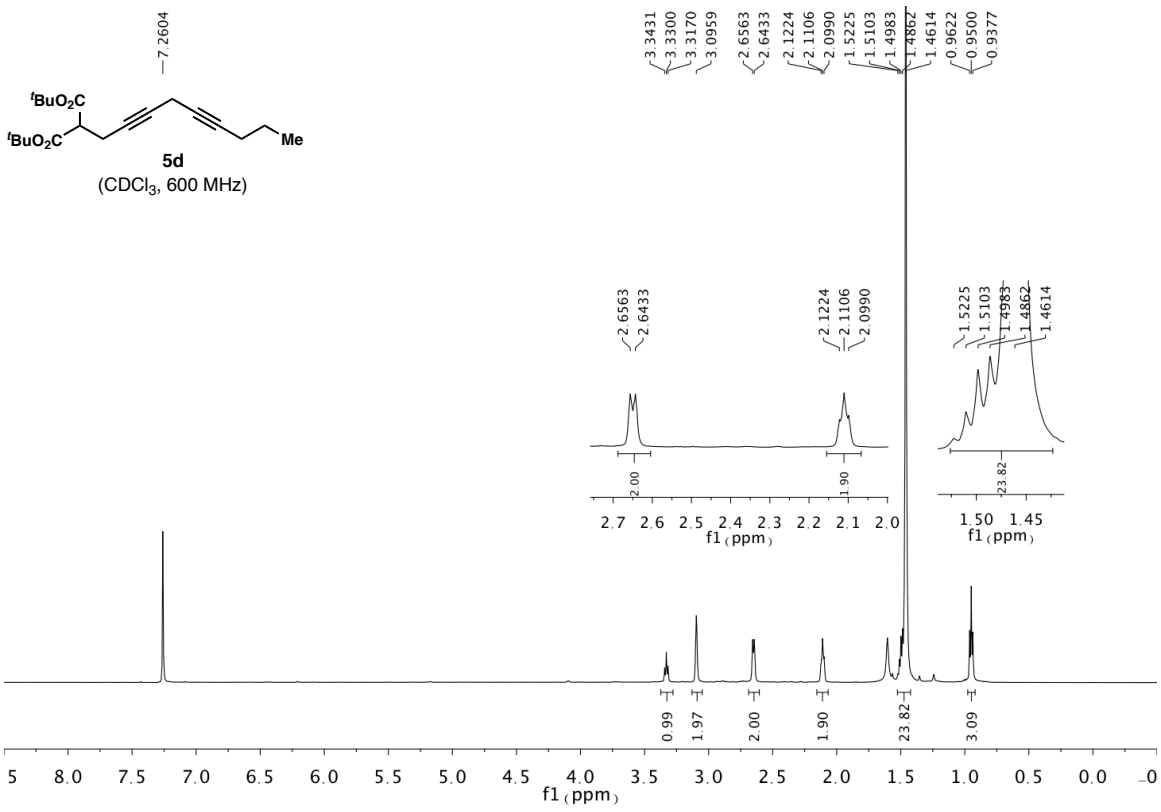

MeO2C
MeO2C
Me
5a
(Acetone-d6, 151 MHz)
f1 (ppm)

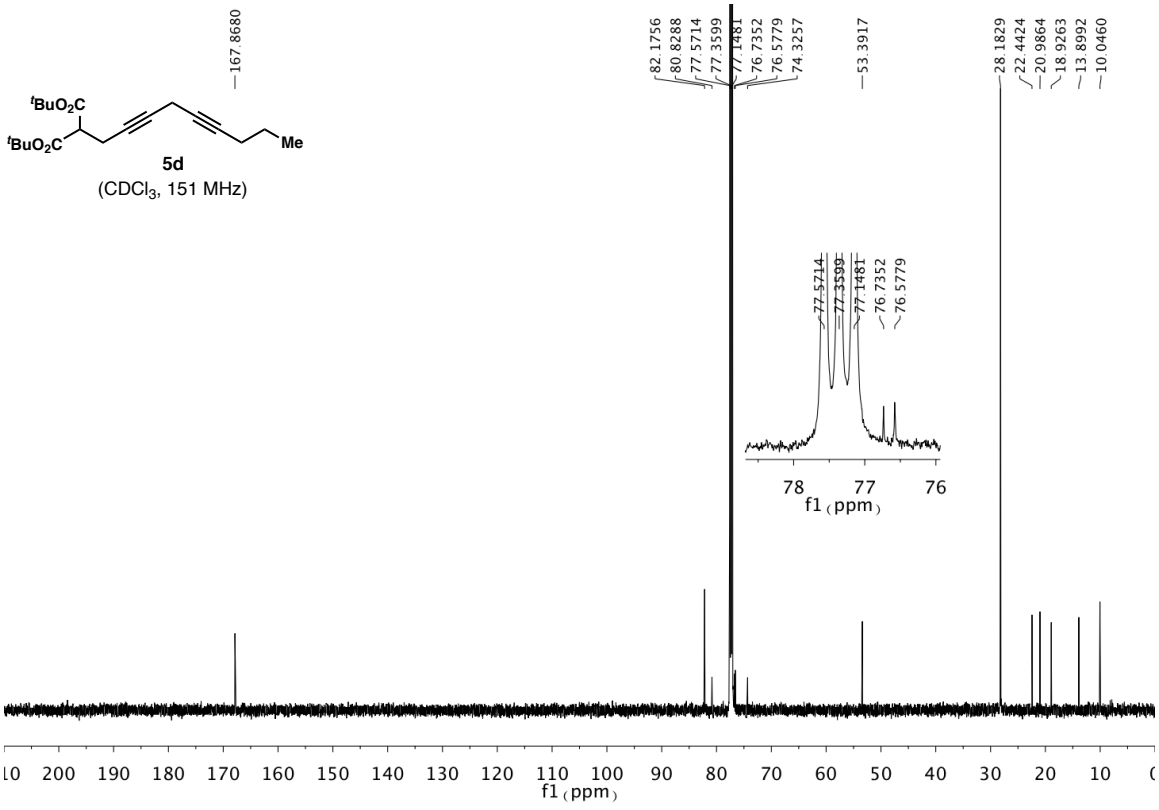

EtO2C
EtO2C
Me
5b
(CDCl3, 600 MHz)
7.2597
4.2352
4.2236
4.2119
4.2015
3.5467
3.5337
3.5208
3.0968
3.0933
3.0900
2.7698
2.7663
2.7627
2.7571
2.7534
2.7503
2.1283
2.1242
2.1166
2.1131
2.1092
2.1049
1.5025
1.4904
1.4784
1.2875
1.2756
1.2638
0.9652
0.9529
1.5267
1.5145
1.5025
1.4904
1.4784
1.4665
4.23
2.03
4.25 4.20 4.15
f1 (ppm)
1.50 1.45
f1 (ppm)
4.23
0.96
2.00
2.00
1.96
2.03
7.00
3.03
f1 (ppm)

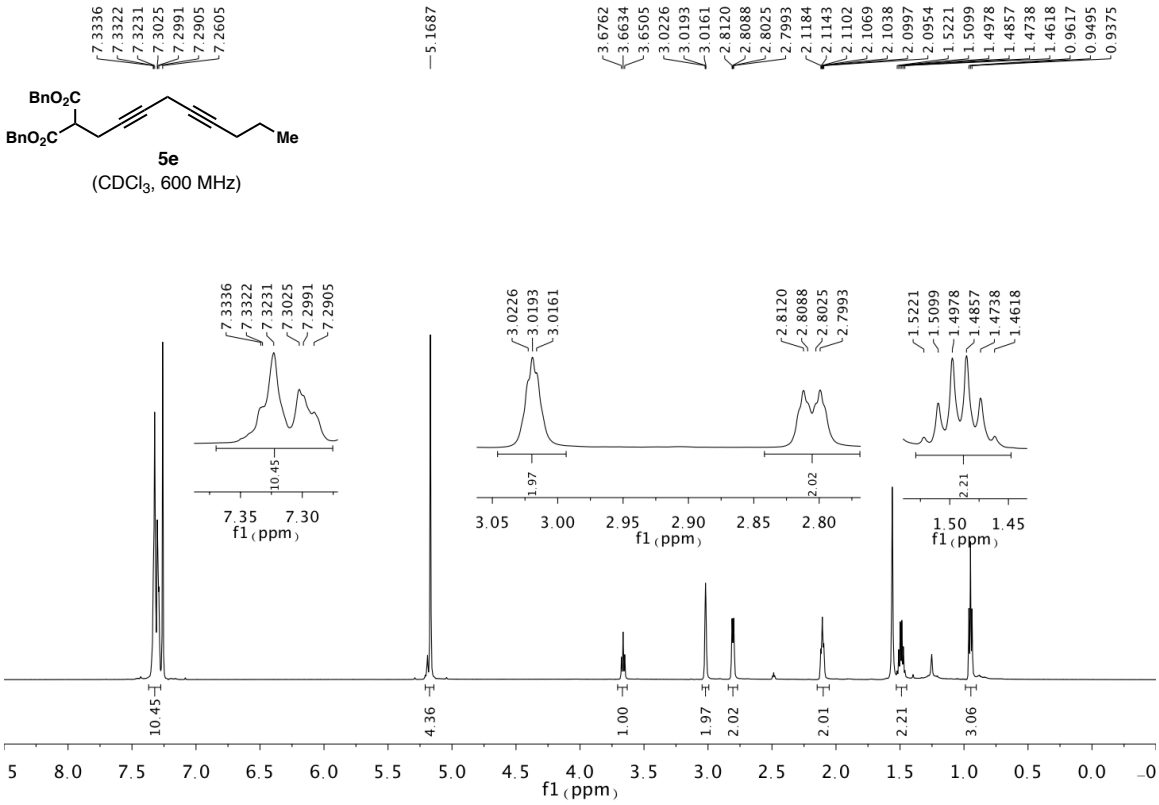

206.2783
168.5896
EtO2C
EtO2C
Me
5b
(Acetone-d6, 151 MHz)
80.6149
77.4983
76.4892
74.9673
61.9624
51.8302
30.2245
30.0964
29.9683
29.8402
29.7118
29.5834
29.4552
22.7986
20.8702
19.0134
14.3381
13.6529
9.5852
f1 (ppm)

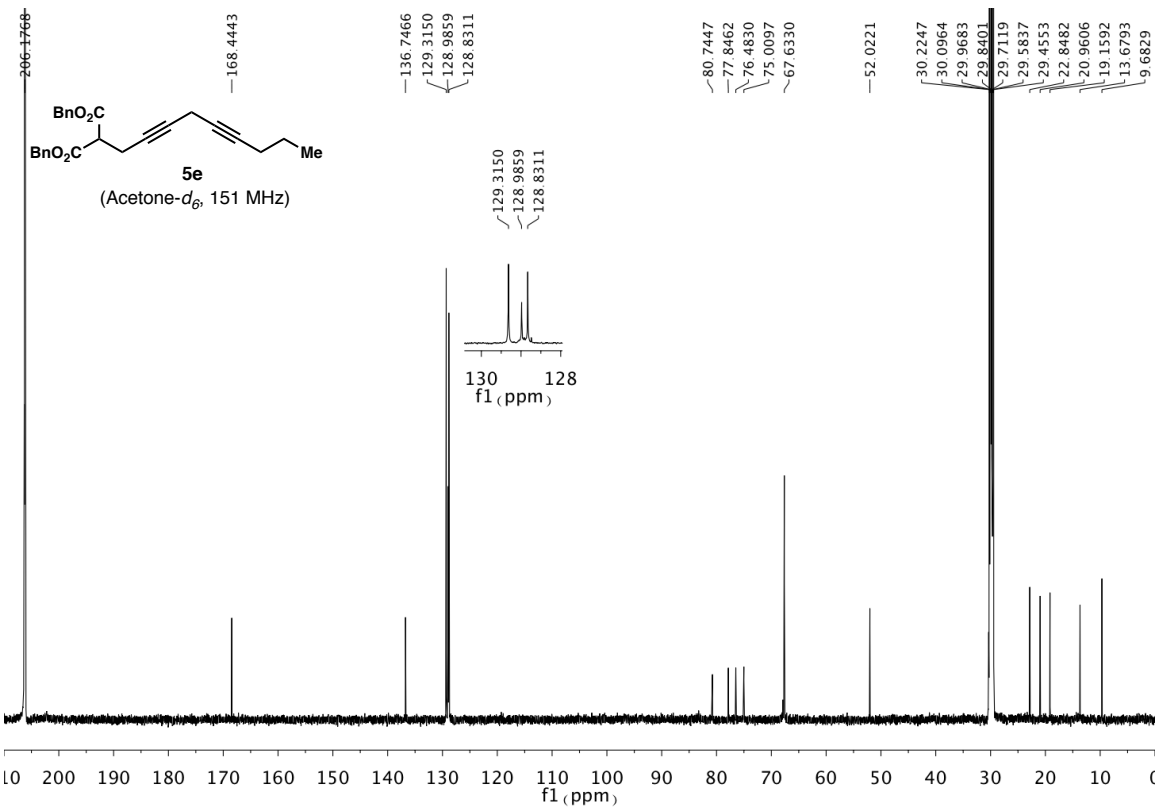

7.2604
5.0979
5.0874
5.0770
5.0667
5.0563
5.0460
5.0356
3.4715
3.4585
3.4456
3.0881
2.7367
2.7239
2.1225
2.1108
2.0993
1.5229
1.5108
1.4987
1.4867
1.4746
1.4628
1.2577
1.2477
1.2379
0.9626
0.9504
0.9381
iPrO2C
iPrO2C
Me
5c
(CDCl3, 600 MHz)
1.99
2.00
12.96
1.95
1.99
0.94
1.97
2.00
1.91
1.95
12.96
3.05
f1 (ppm)

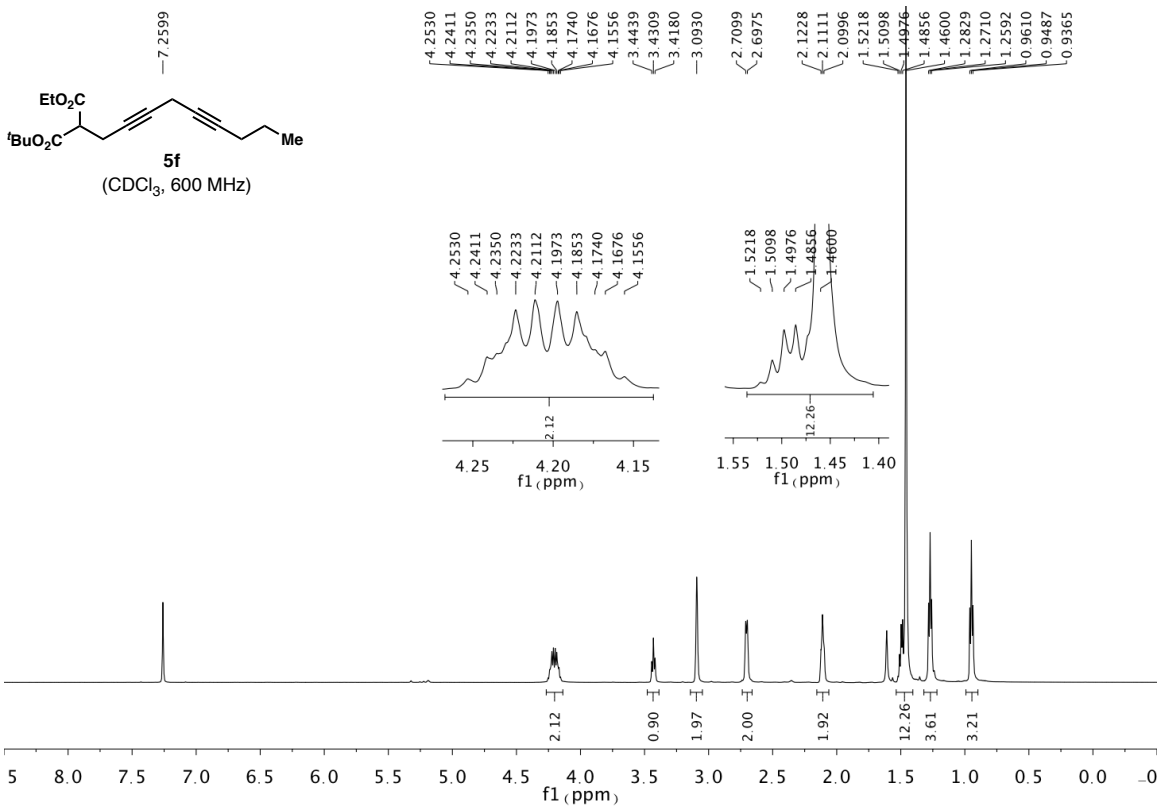

168.0440
80.8840
77.5716
77.3600
77.1482
76.9570
76.2794
74.2341
69.5477
51.9557
22.4396
21.9856
21.8861
20.9763
18.9284
13.8867
10.0556
iPrO2C
iPrO2C
Me
5c
(CDCl3, 151 MHz)
f1 (ppm)

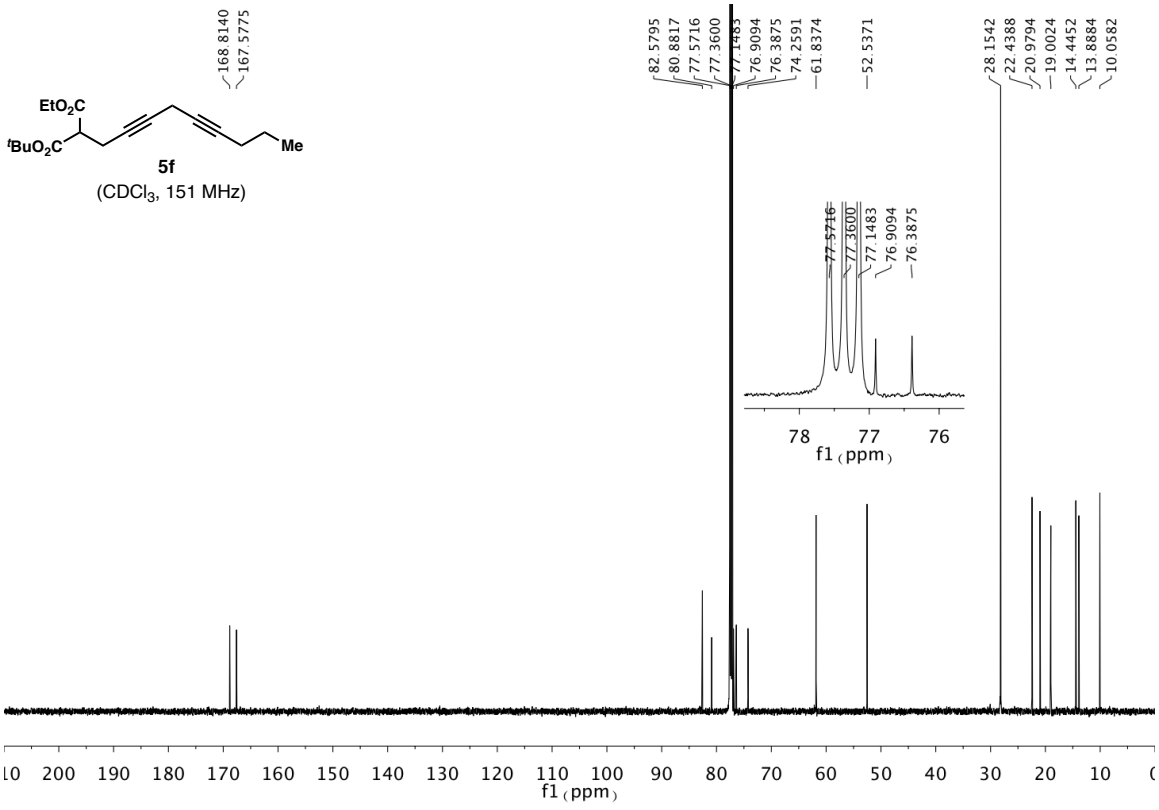

7.2604
3.3431
3.3300
3.3170
3.0959
2.6563
2.6433
2.1224
2.1106
2.0990
1.5225
1.5103
1.4983
1.4862
1.4614
0.9622
0.9500
0.9377
tBuO2C
tBuO2C
Me
5d
(CDCl3, 600 MHz)
0.99
1.97
2.00
1.90
23.82
3.09
f1 (ppm)

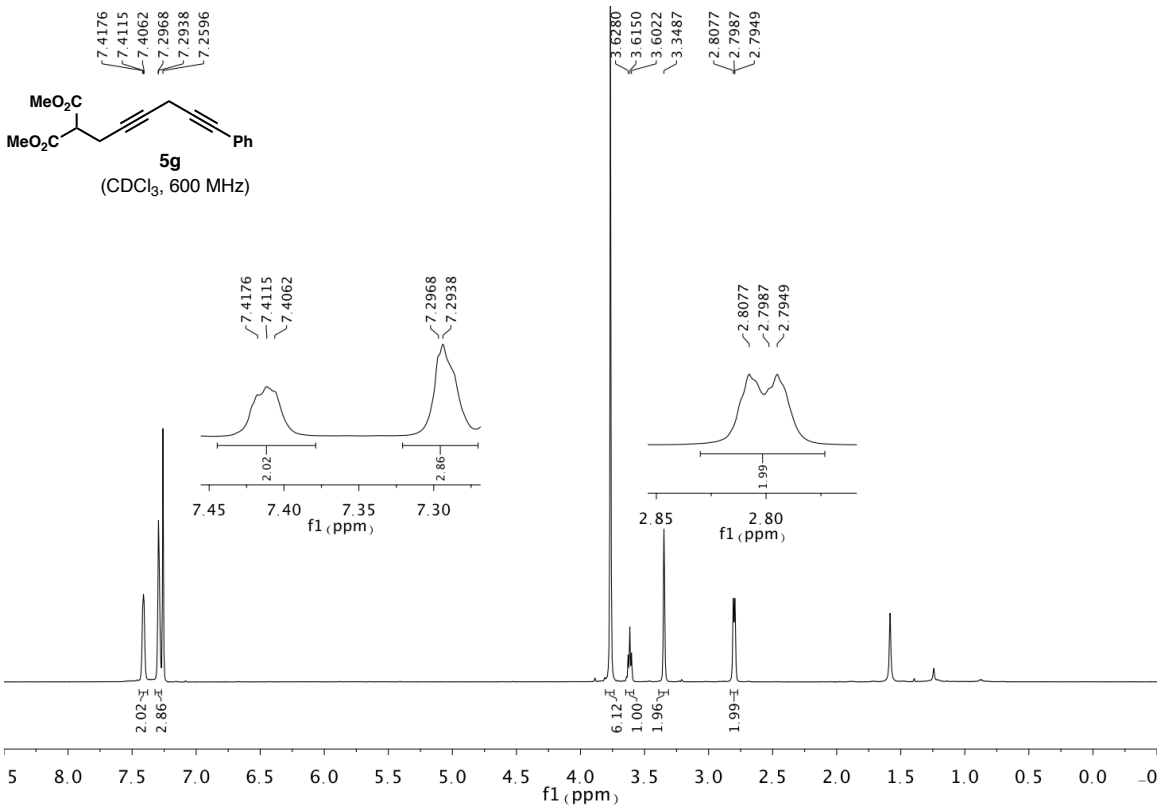

167.8680
82.1756
80.8288
77.5714
77.3599
77.1481
76.7352
76.5779
74.3257
53.3917
28.1829
22.4424
20.9864
18.9263
13.8992
10.0460
tBuO2C
tBuO2C
Me
5d
(CDCl3, 151 MHz)
f1 (ppm)

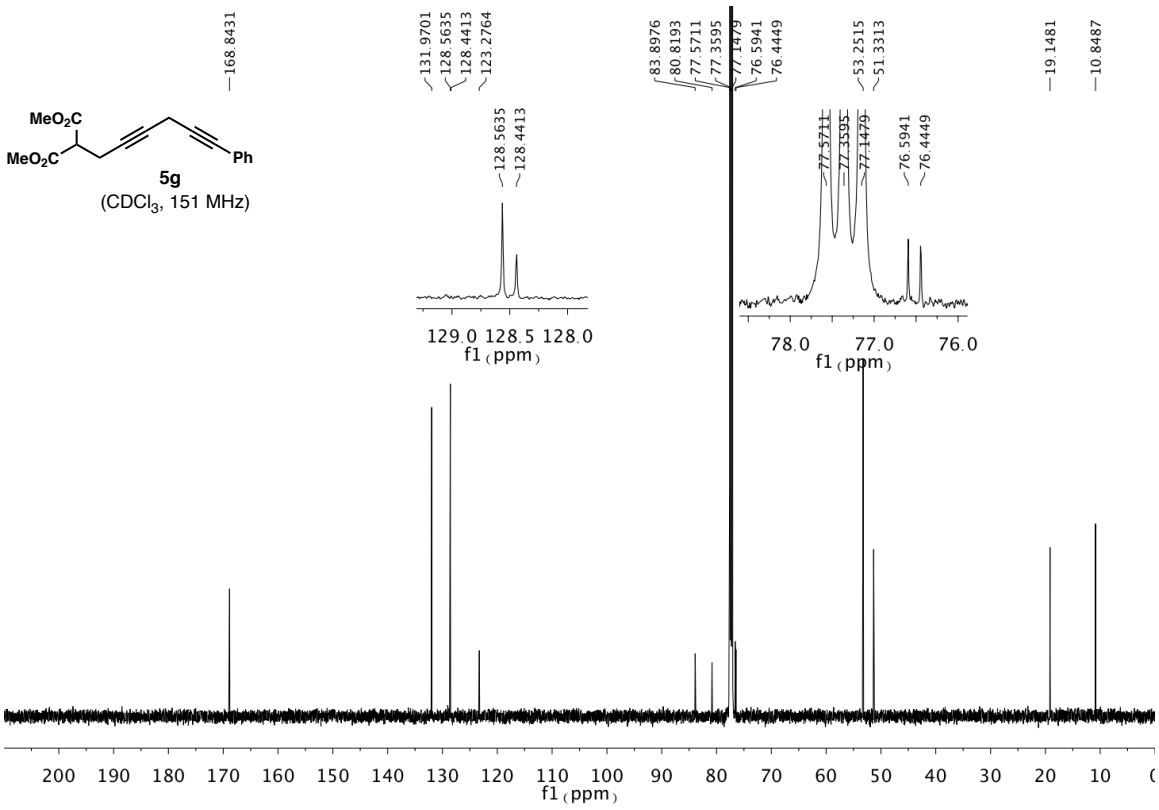

BnO2C
BnO2C
Me
5e
(CDCl3, 600 MHz)
f1 (ppm)

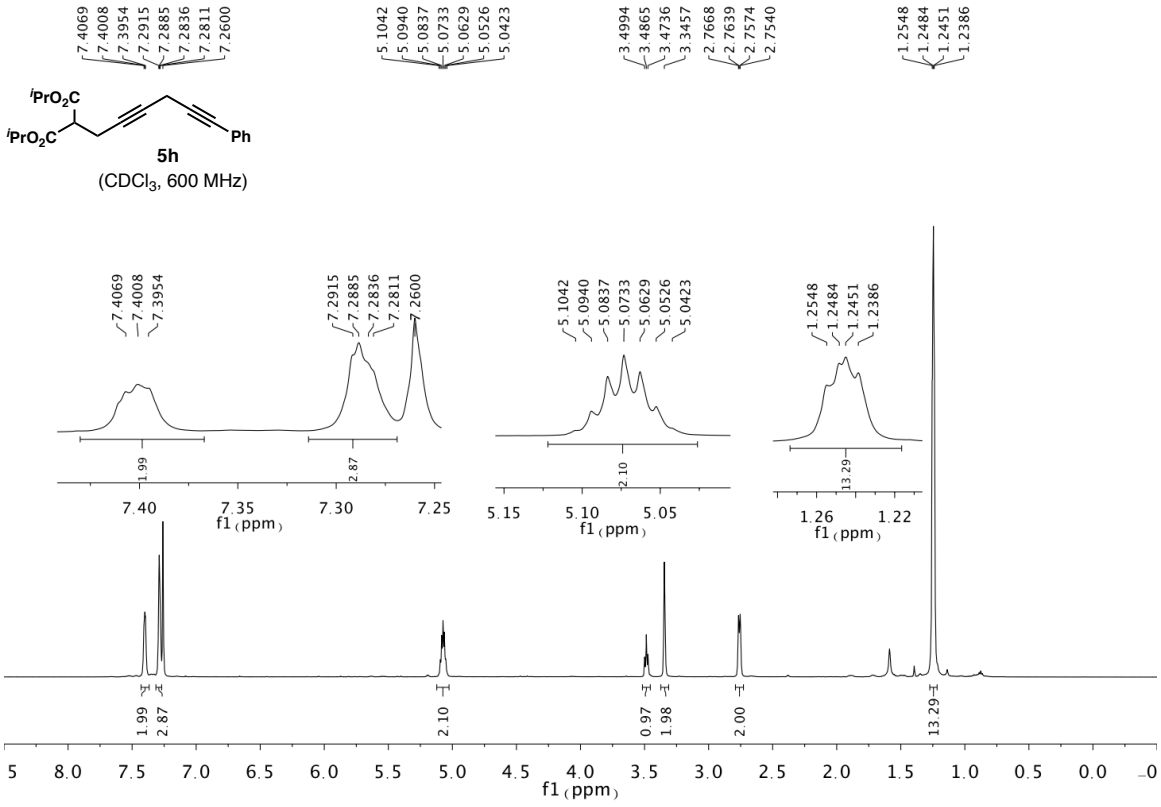

BnO2C
BnO2C
Me
5e
(Acetone-d6, 151 MHz)
f1 (ppm)

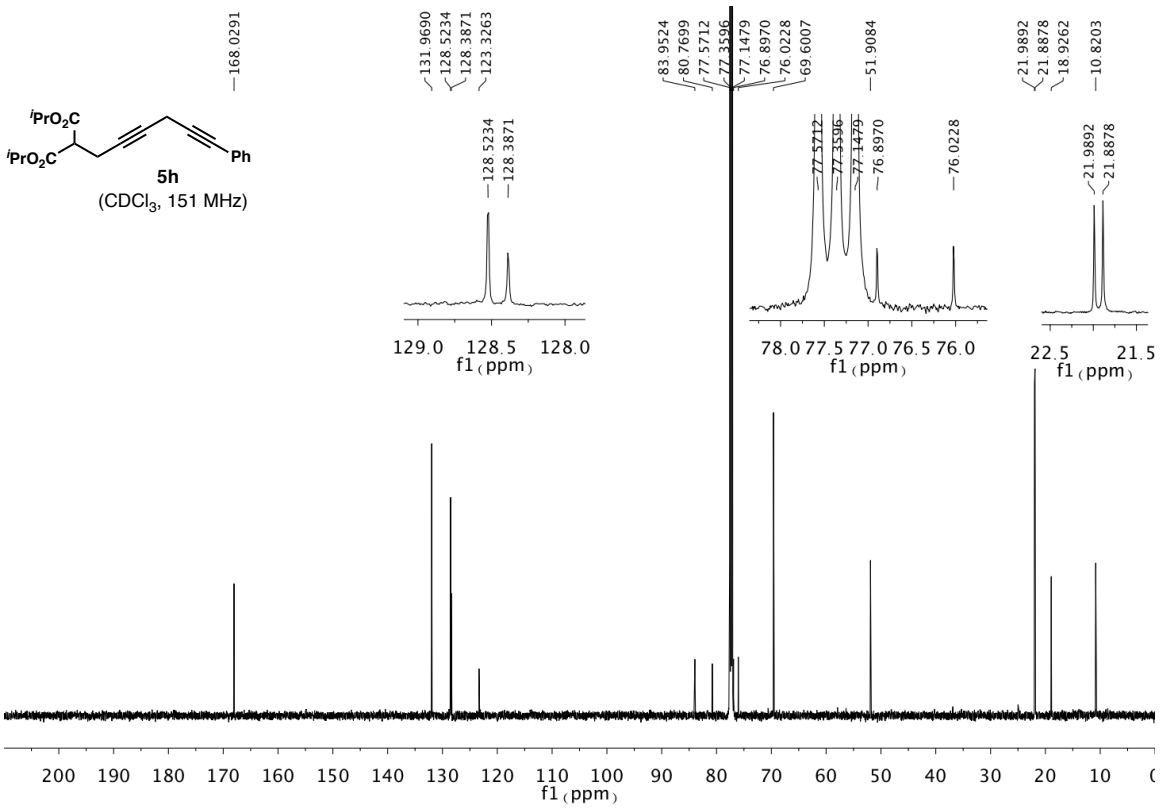

EtO2C
tBuO2C
Me
5f
(CDCl3, 600 MHz)
f1 (ppm)

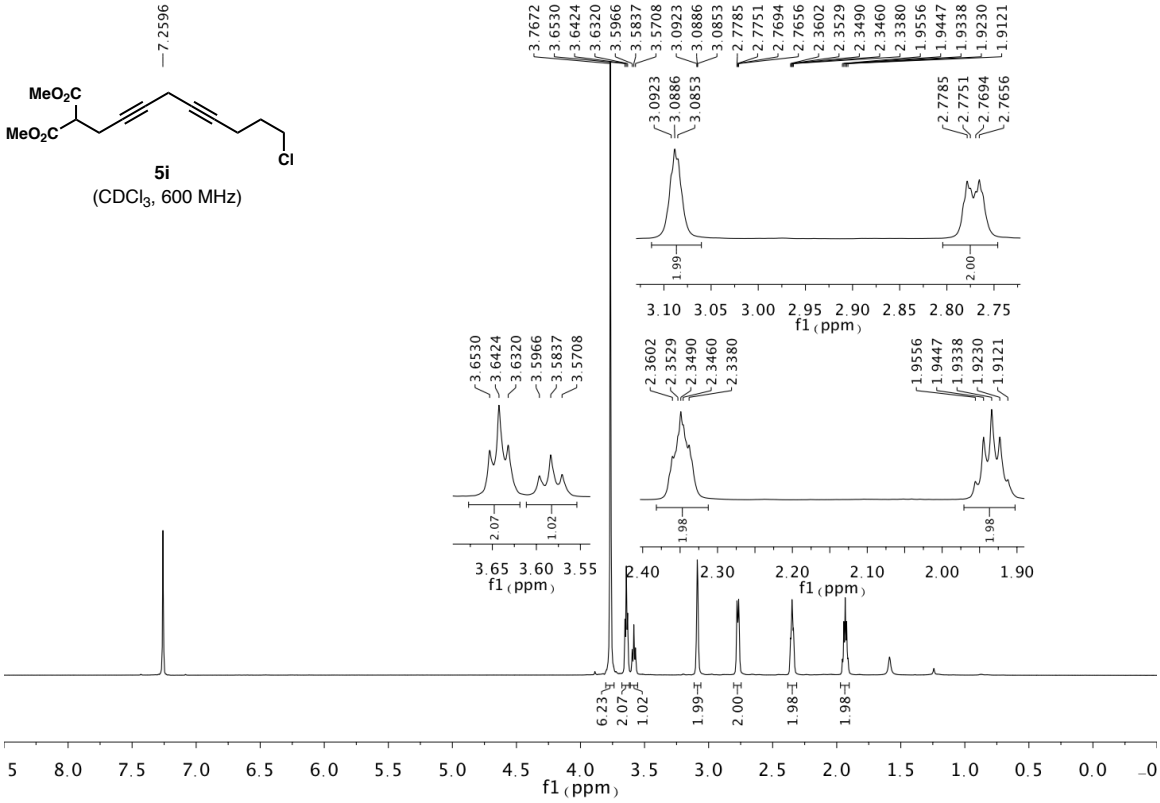

EtO2C
tBuO2C
Me
5f
(CDCl3, 151 MHz)
f1 (ppm)

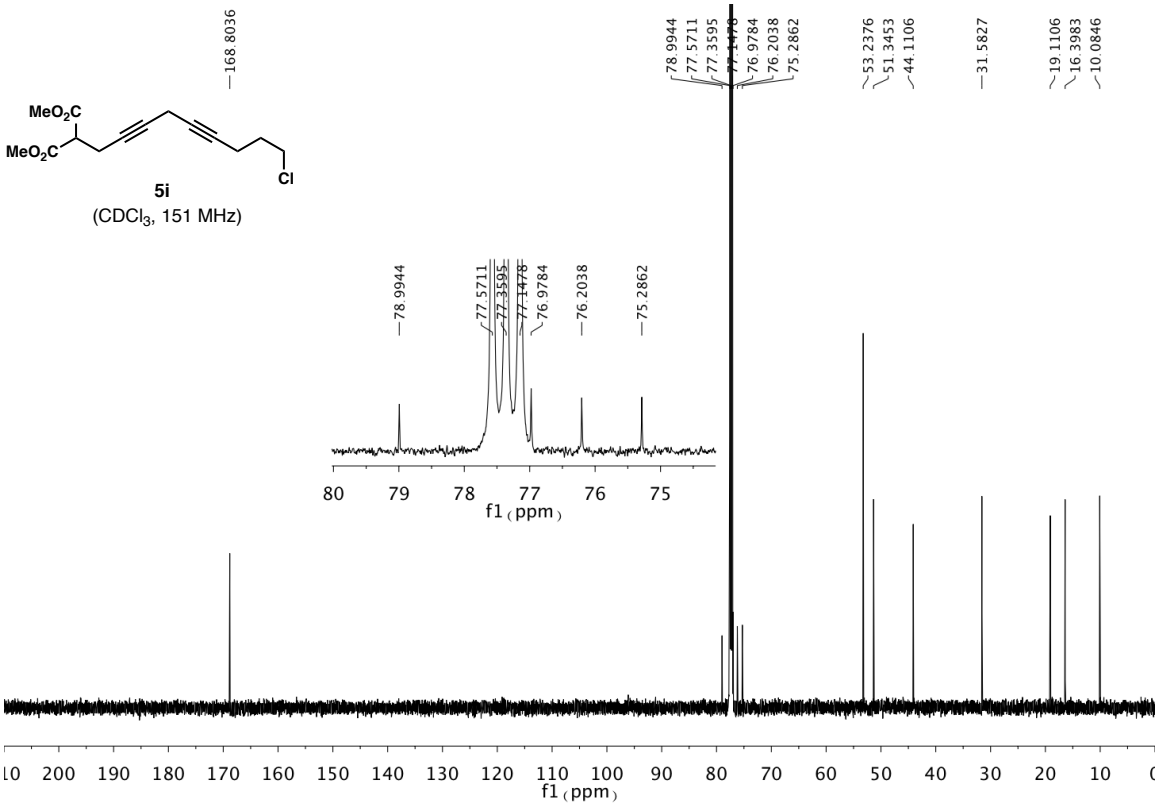

7.4176
7.4115
7.4062
7.2968
7.2938
7.2596
3.6280
3.6150
3.6022
3.3487
2.8077
2.7987
2.7949
MeO2C
MeO2C
Ph
5g
(CDCl3, 600 MHz)
2.02
2.86
6.12
1.00
1.96
1.99
f1 (ppm)

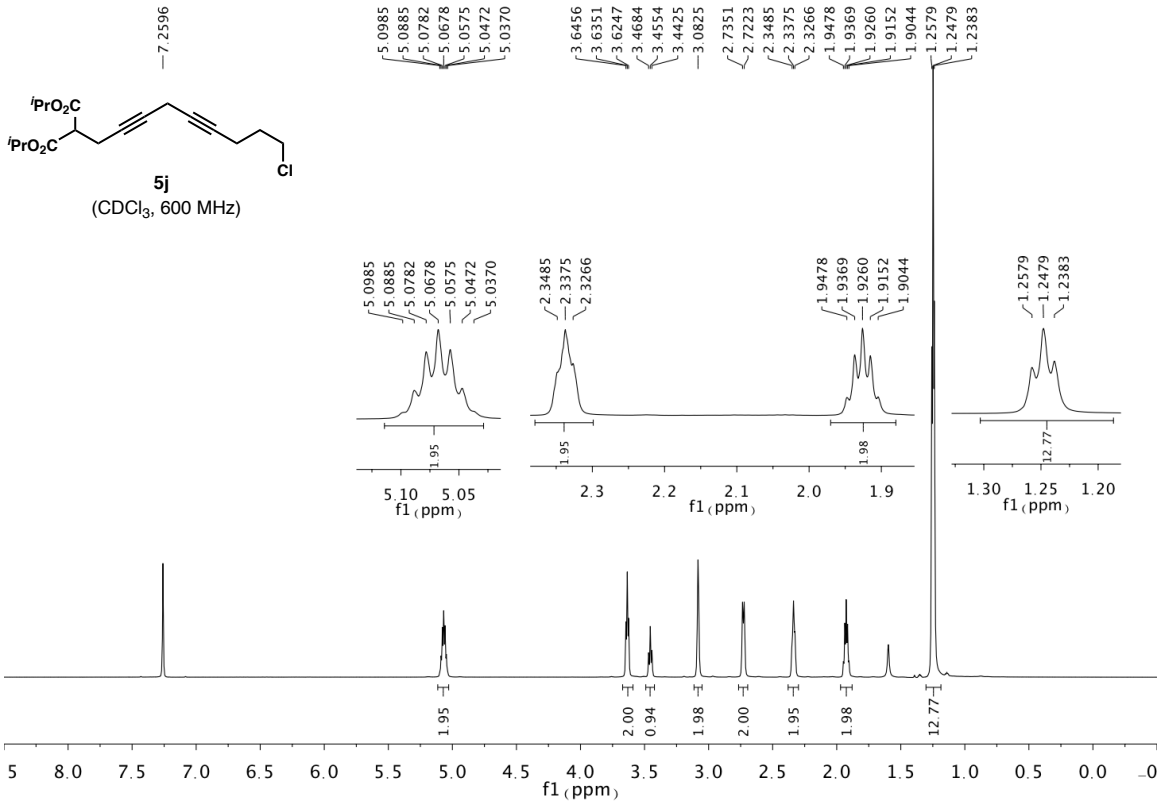

168.8431
131.9701
128.5635
128.4413
123.2764
83.8976
80.8193
77.5711
77.3595
77.1479
76.5941
76.4449
53.2515
51.3313
19.1481
10.8487
MeO2C
MeO2C
Ph
5g
(CDCl3, 151 MHz)
f1 (ppm)

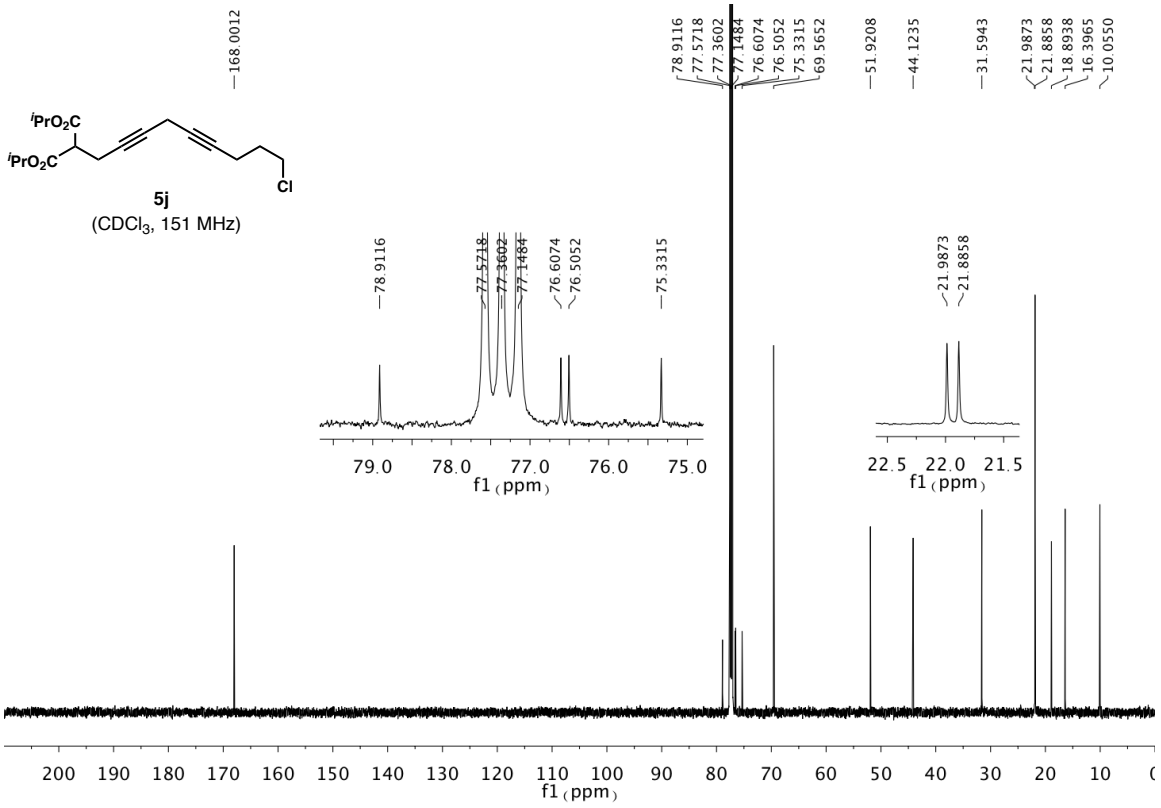

7.4069
7.4008
7.3954
7.2915
7.2885
7.2836
7.2811
7.2600
5.1042
5.0940
5.0837
5.0733
5.0629
5.0526
5.0423
3.4994
3.4865
3.4736
3.3457
2.7668
2.7639
2.7574
2.7540
1.2548
1.2484
1.2451
1.2386
iPrO2C
iPrO2C
Ph
5h
(CDCl3, 600 MHz)
1.99
2.87
2.10
0.97
1.98
2.00
13.29
f1 (ppm)

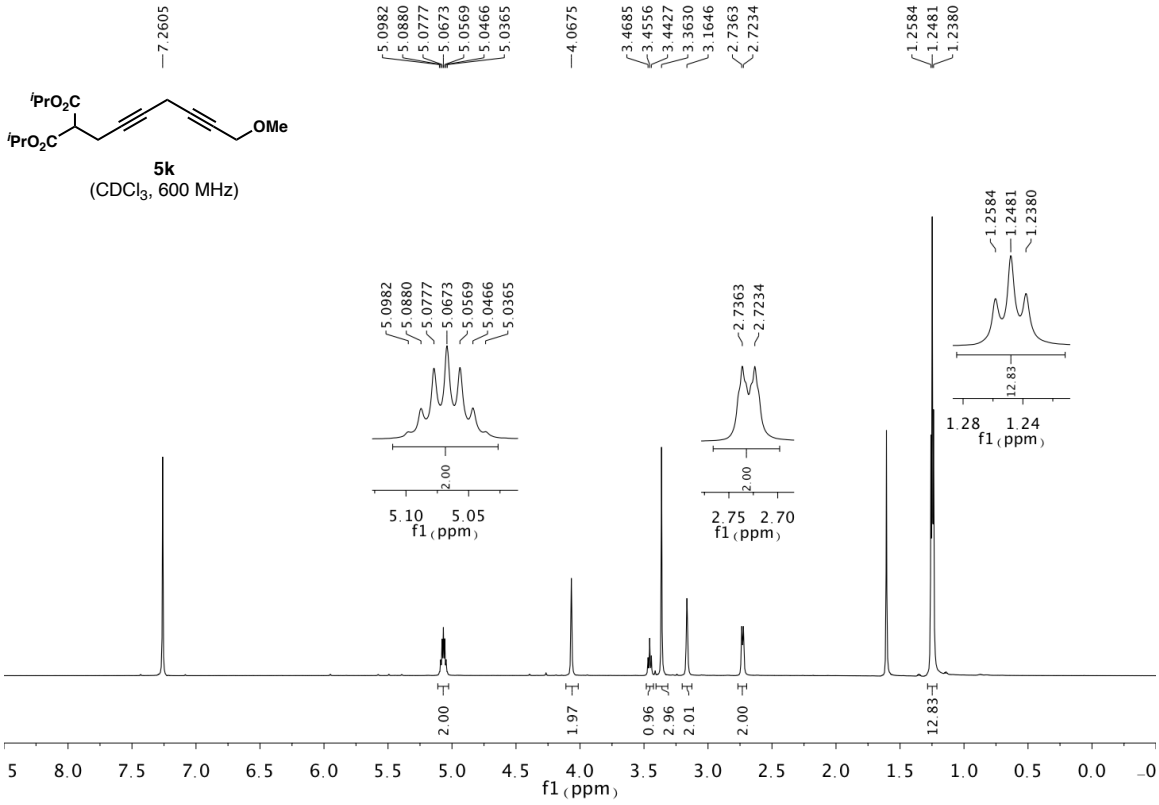

168.0291
131.9690
128.5234
128.3871
123.3263
83.9524
80.7699
77.5712
77.3596
77.1479
76.8970
76.0228
69.6007
51.9084
21.9892
21.8878
18.9262
10.8203
iPrO2C
iPrO2C
Ph
5h
(CDCl3, 151 MHz)
f1 (ppm)

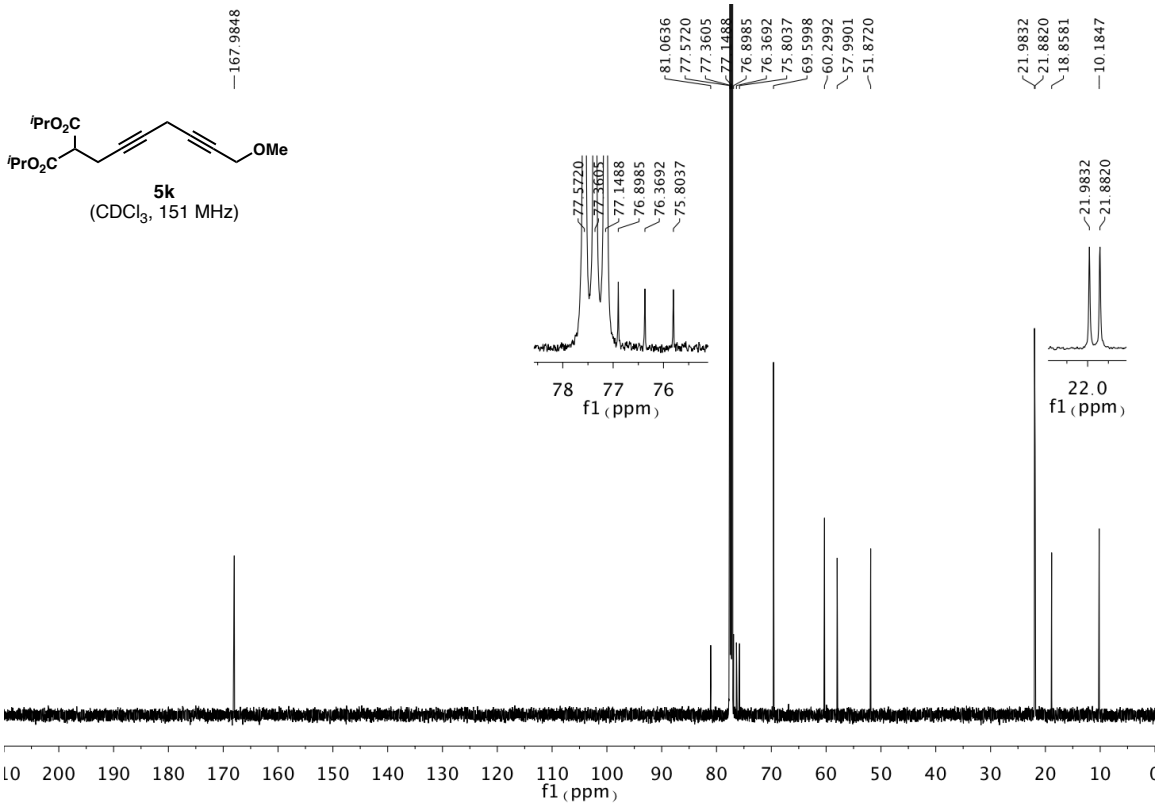

MeO2C
MeO2C
Cl
5i
(CDCl3, 600 MHz)
f1 (ppm)

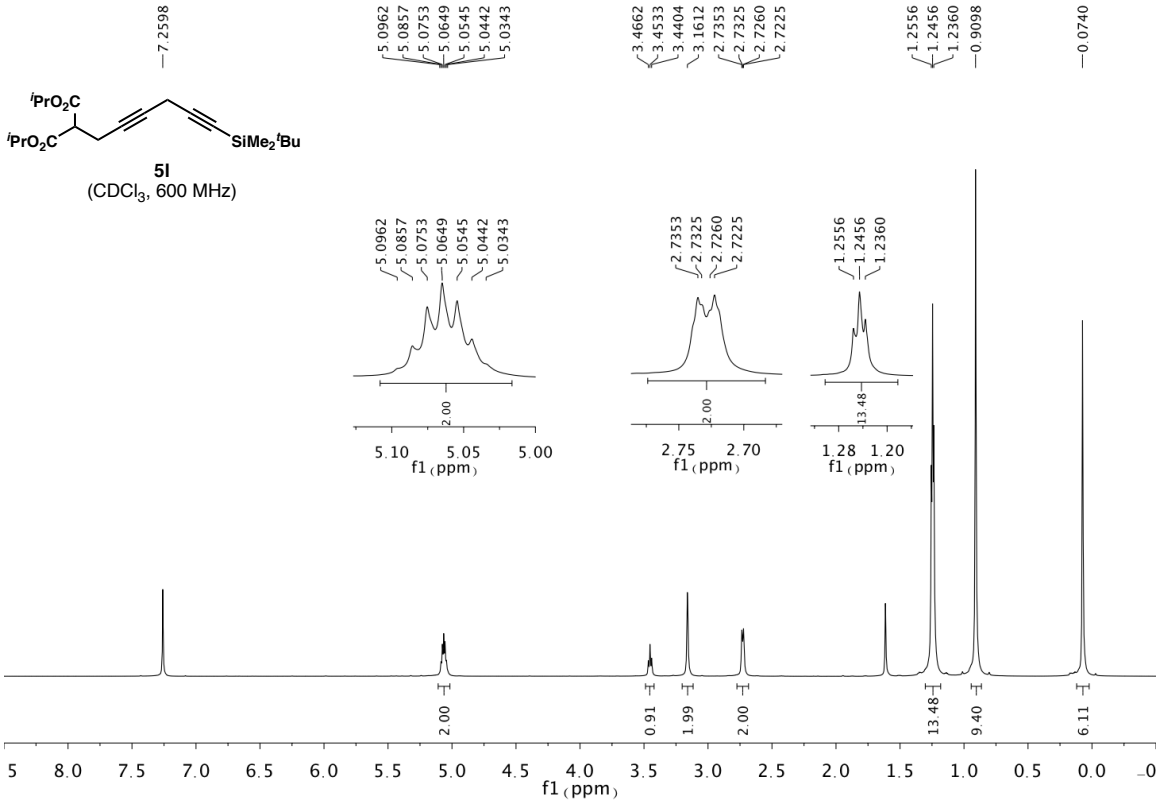

MeO2C
MeO2C
Cl
5i
(CDCl3, 151 MHz)
f1 (ppm)

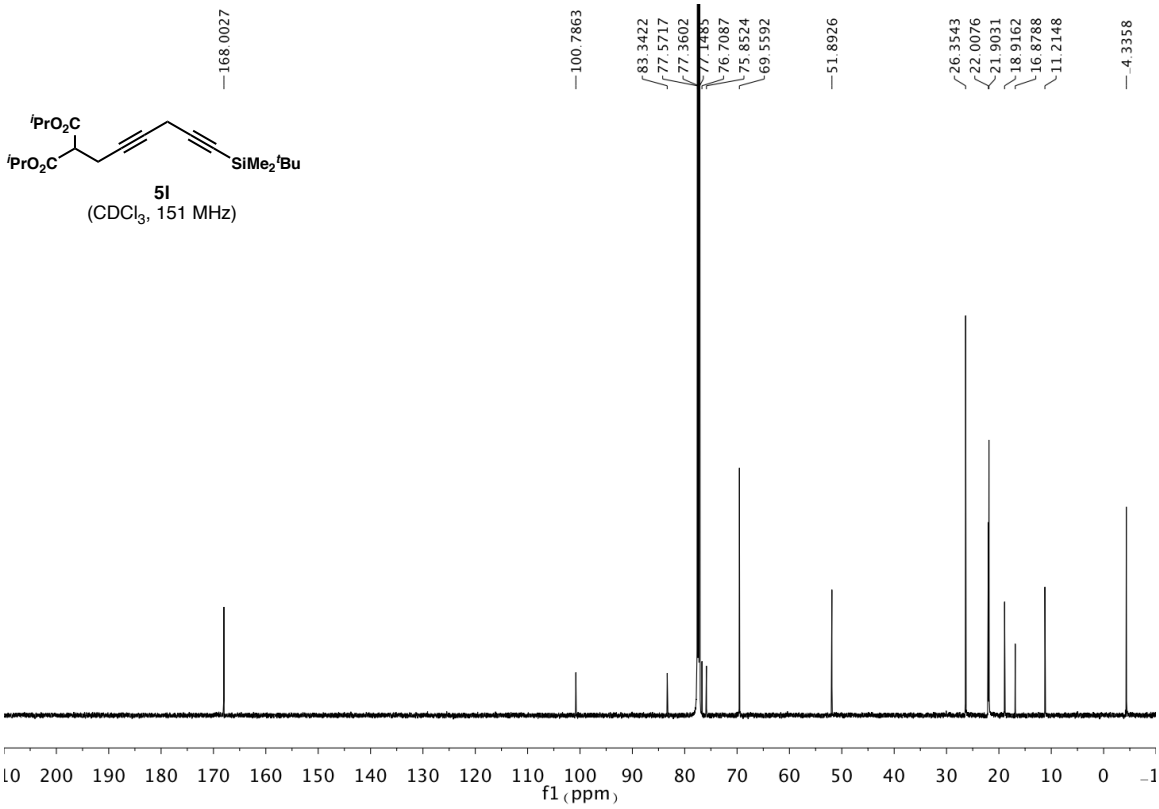

5j
(CDCl3, 600 MHz)
Cl

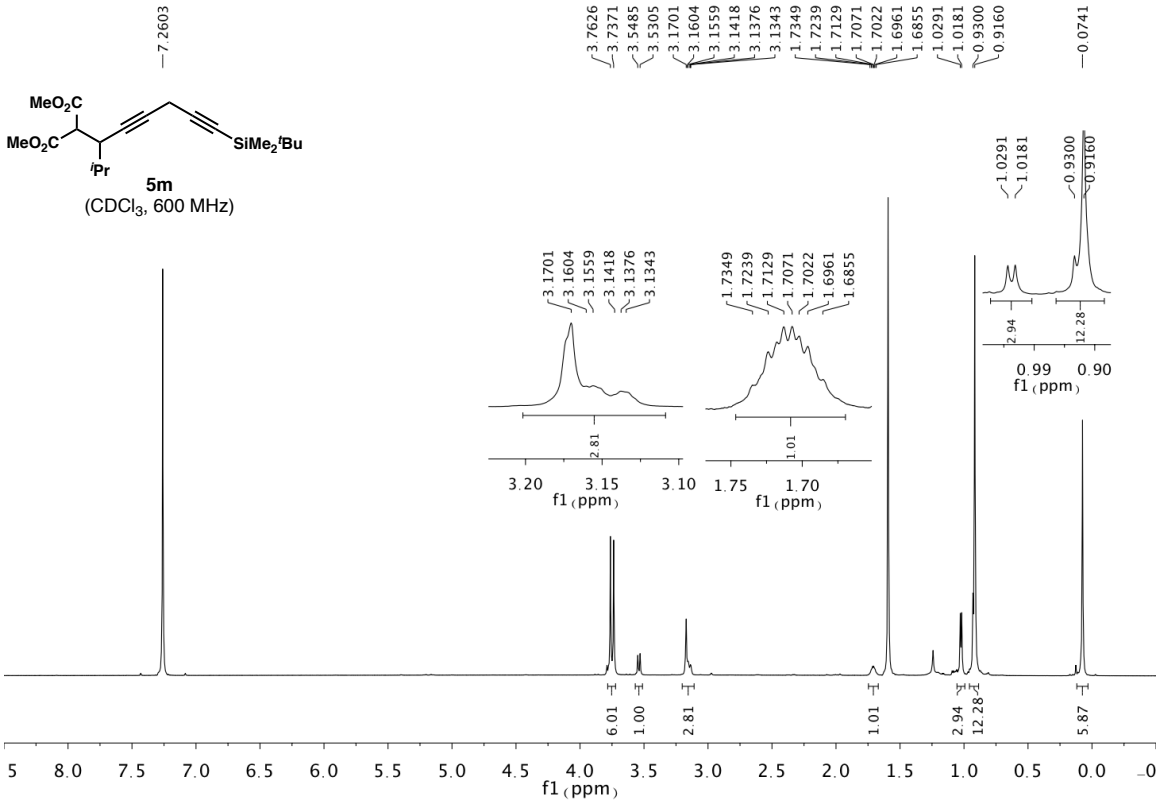

5j
(CDCl3, 151 MHz)
Cl

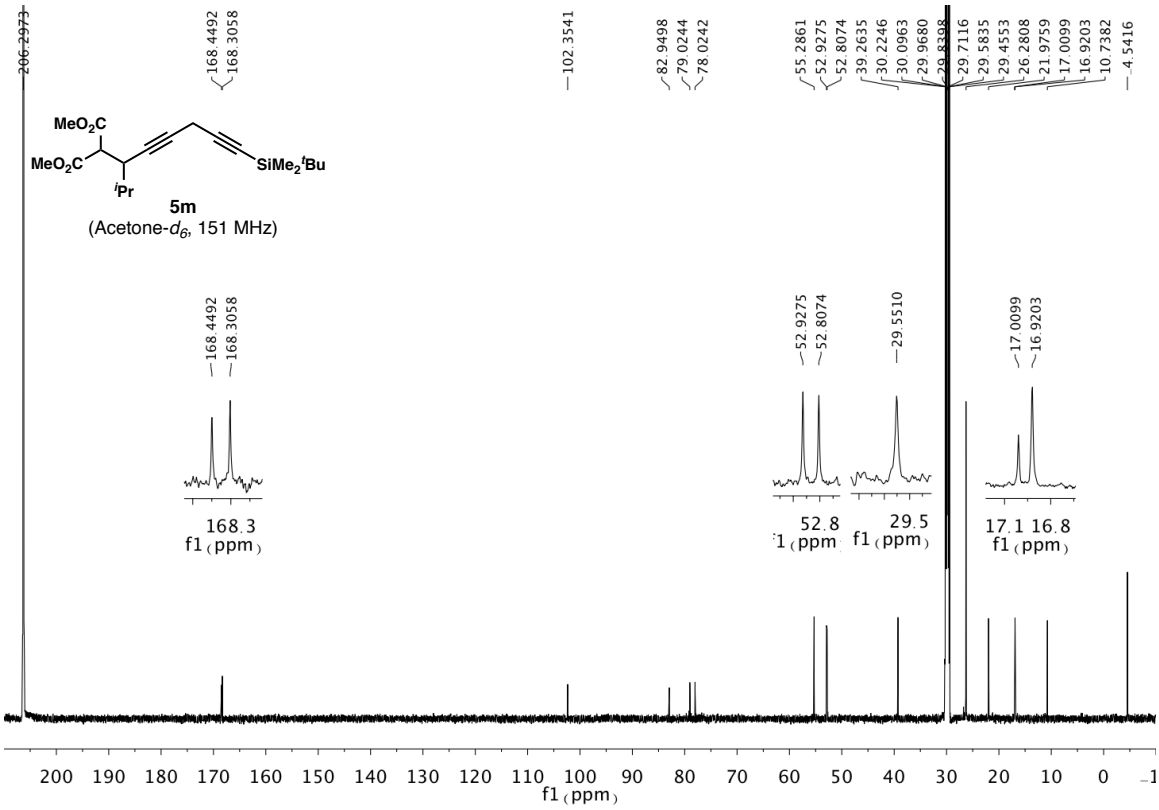

7.2605
5.0982
5.0880
5.0777
5.0673
5.0569
5.0466
5.0365
4.0675
3.4685
3.4556
3.4427
3.3630
3.1646
2.7363
2.7234
1.2584
1.2481
1.2380
iPrO2C
iPrO2C
OMe
5k
(CDCl3, 600 MHz)
2.00
1.97
0.96
2.96
2.01
2.00
12.83
f1 (ppm)

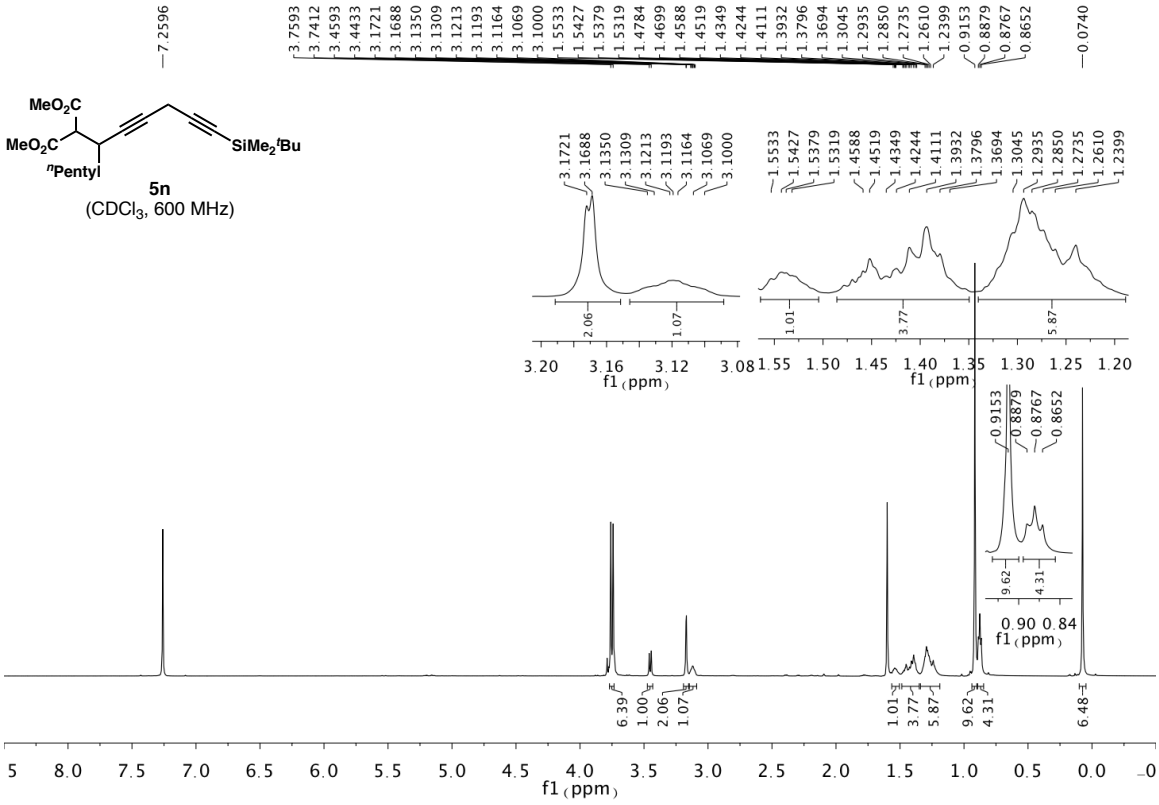

167.9848
81.0636
77.5720
77.3605
77.1488
76.8985
76.3692
75.8037
69.5998
60.2992
57.9901
51.8720
21.9832
21.8820
18.8581
10.1847
iPrO2C
iPrO2C
OMe
5k
(CDCl3, 151 MHz)
f1 (ppm)

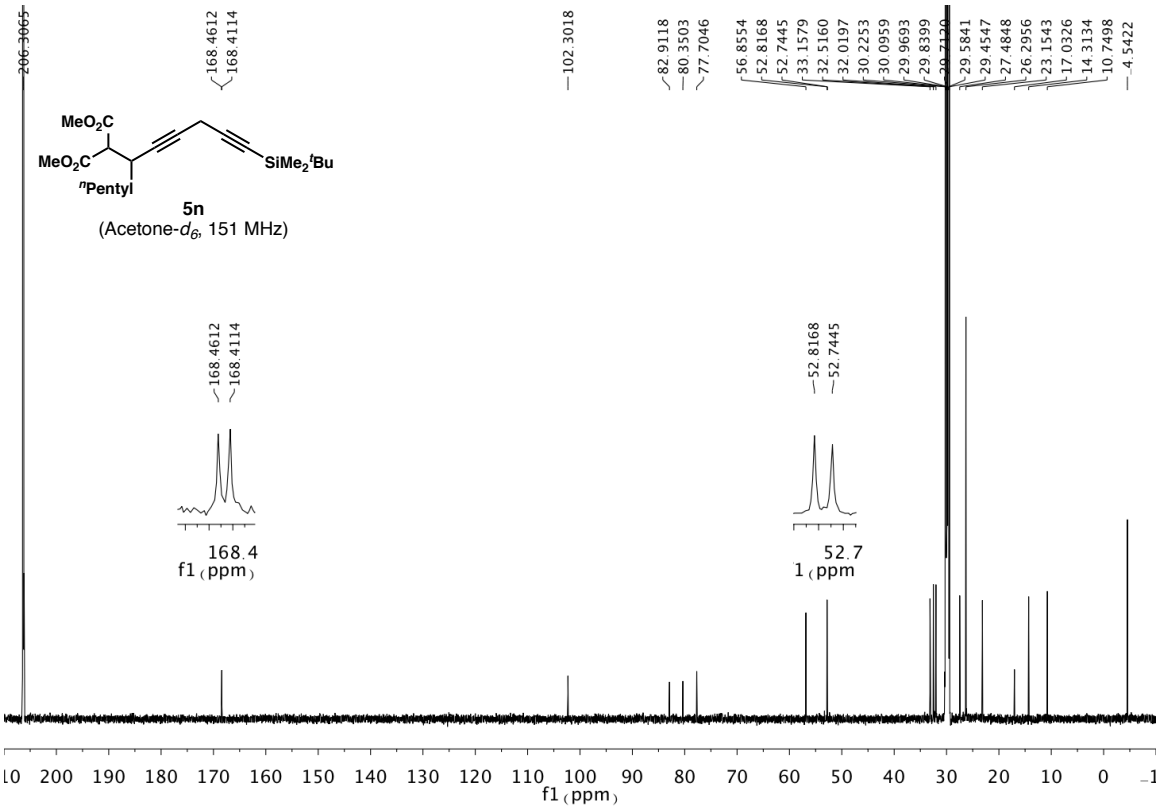

7.2598
5.0962
5.0857
5.0753
5.0649
5.0545
5.0442
5.0343
3.4662
3.4533
3.4404
3.1612
2.7353
2.7325
2.7260
2.7225
1.2556
1.2456
1.2360
0.9098
0.0740
iPrO2C
iPrO2C
SiMe2tBu
5l
(CDCl3, 600 MHz)
2.00
0.91
1.99
2.00
13.48
9.40
6.11
f1 (ppm)

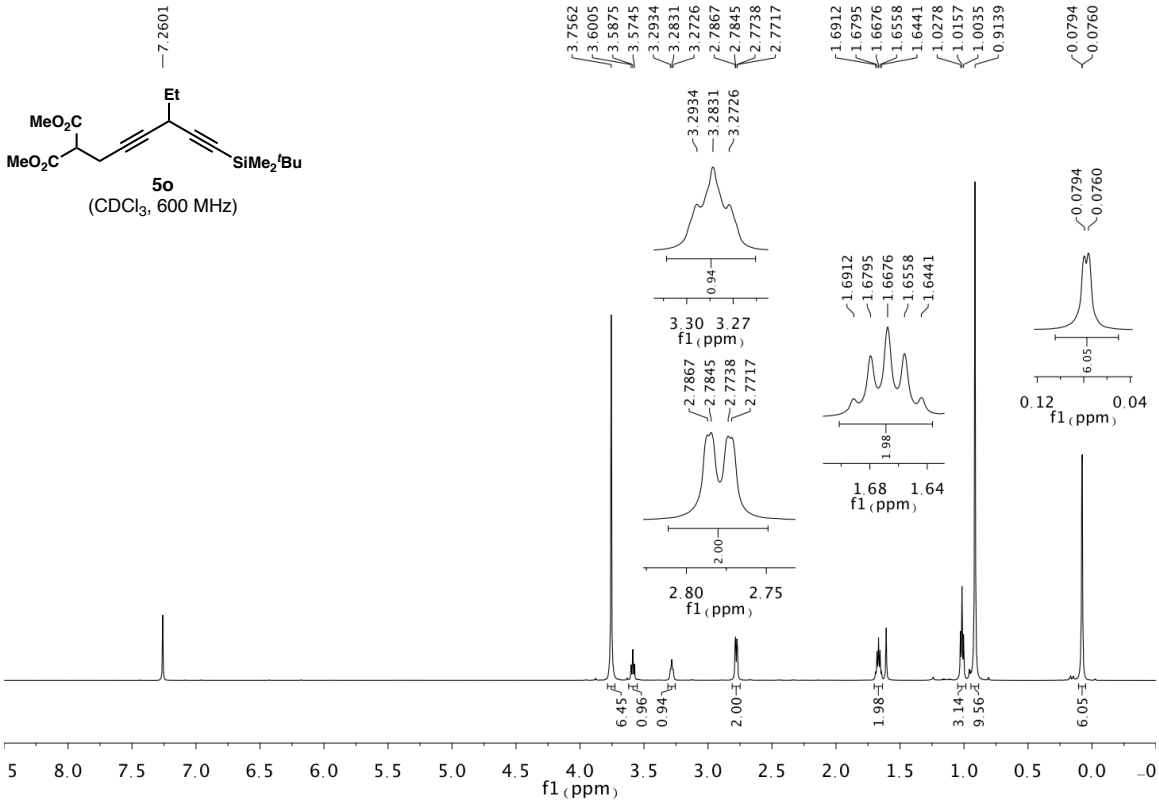

168.0027
100.7863
83.3422
77.5717
77.3602
77.1485
76.7087
75.8524
69.5592
51.8926
26.3543
22.0076
21.9031
18.9162
16.8788
11.2148
4.3358
iPrO2C
iPrO2C
SiMe2tBu
5l
(CDCl3, 151 MHz)
f1 (ppm)

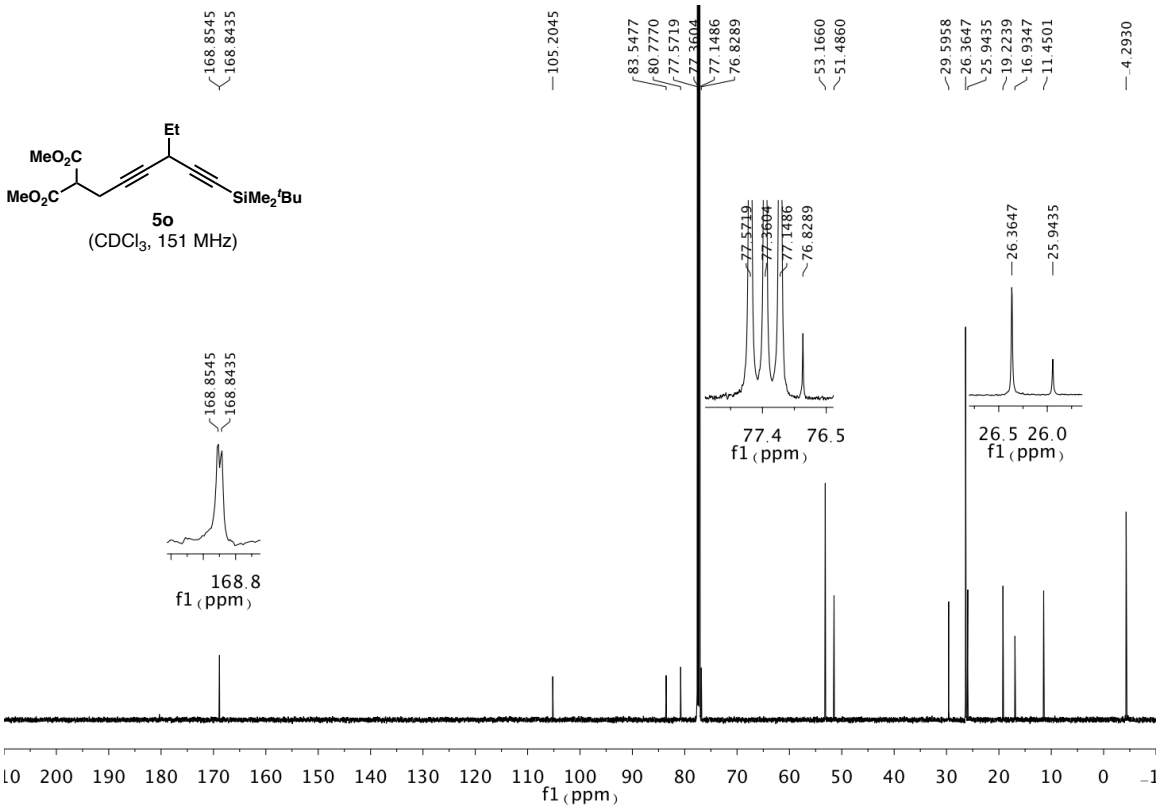

MeO2C
MeO2C
iPr
SiMe2tBu
5m
(CDCl3, 600 MHz)
f1 (ppm)

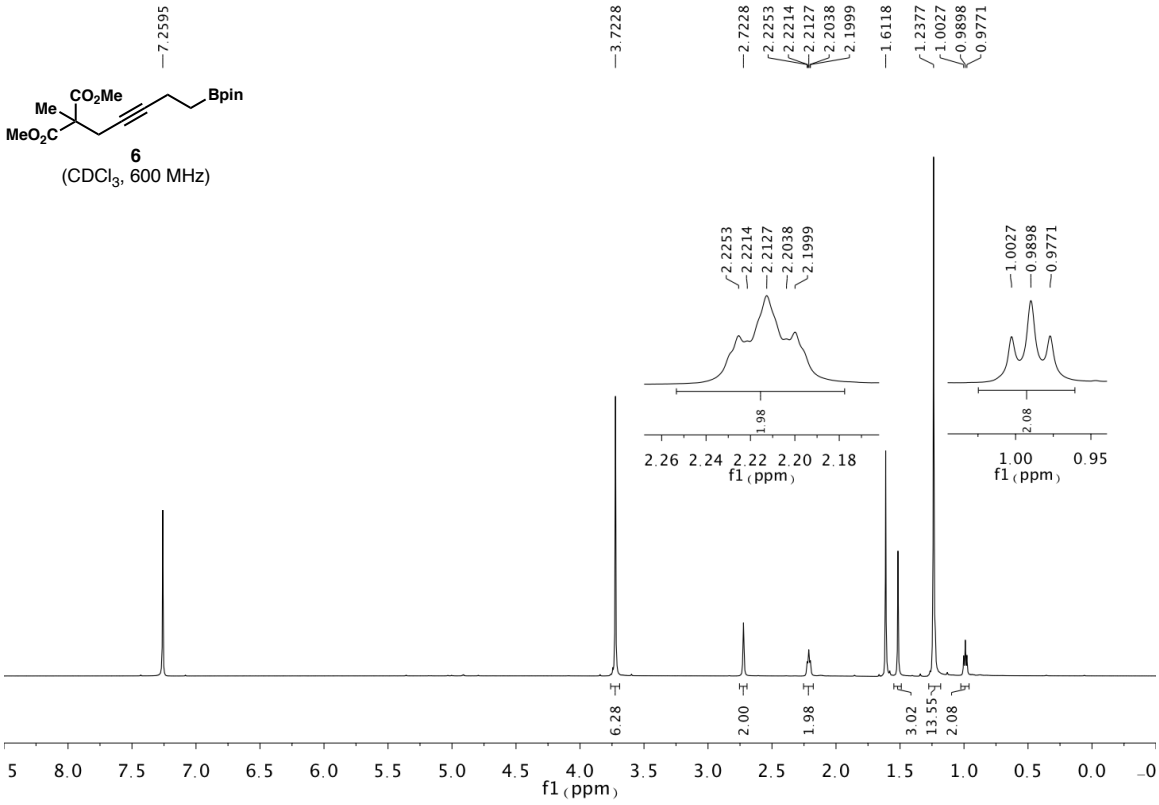

MeO2C
MeO2C
iPr
SiMe2tBu
5m
(Acetone-d6, 151 MHz)
f1 (ppm)

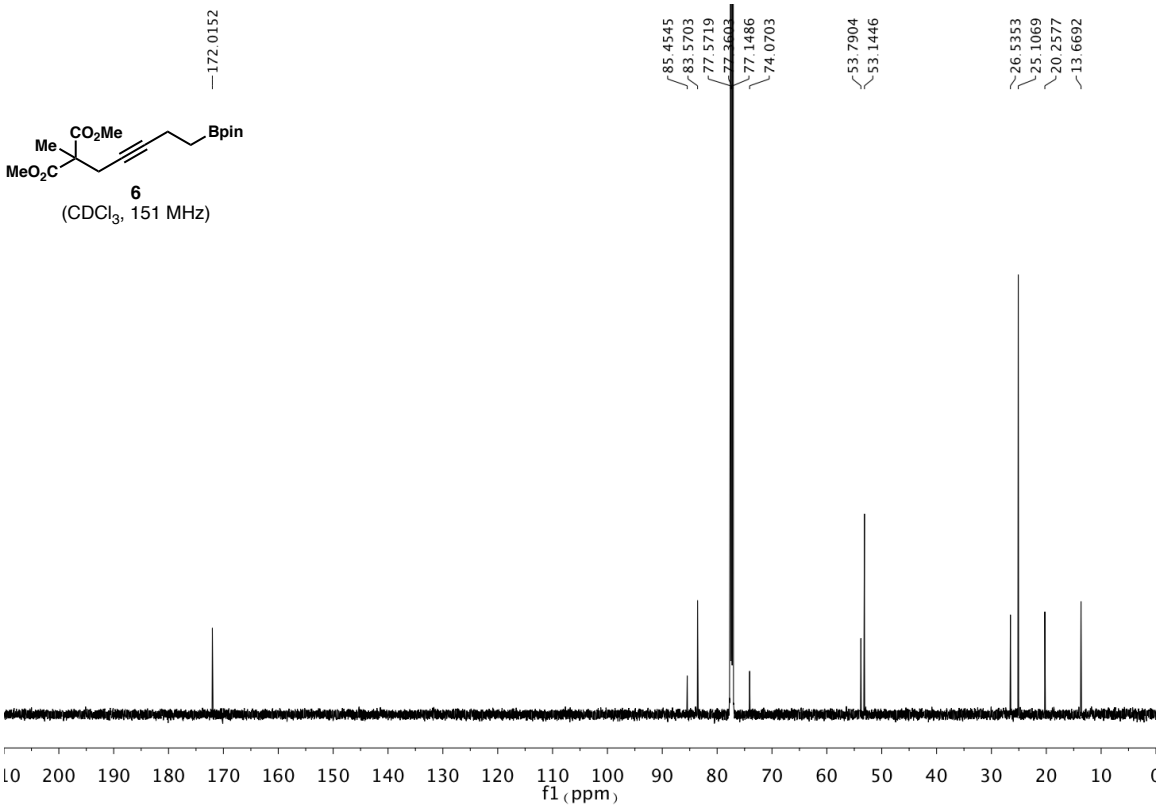

MeO2C
MeO2C
nPentyl
SiMe2tBu
5n
(CDCl3, 600 MHz)
f1 (ppm)

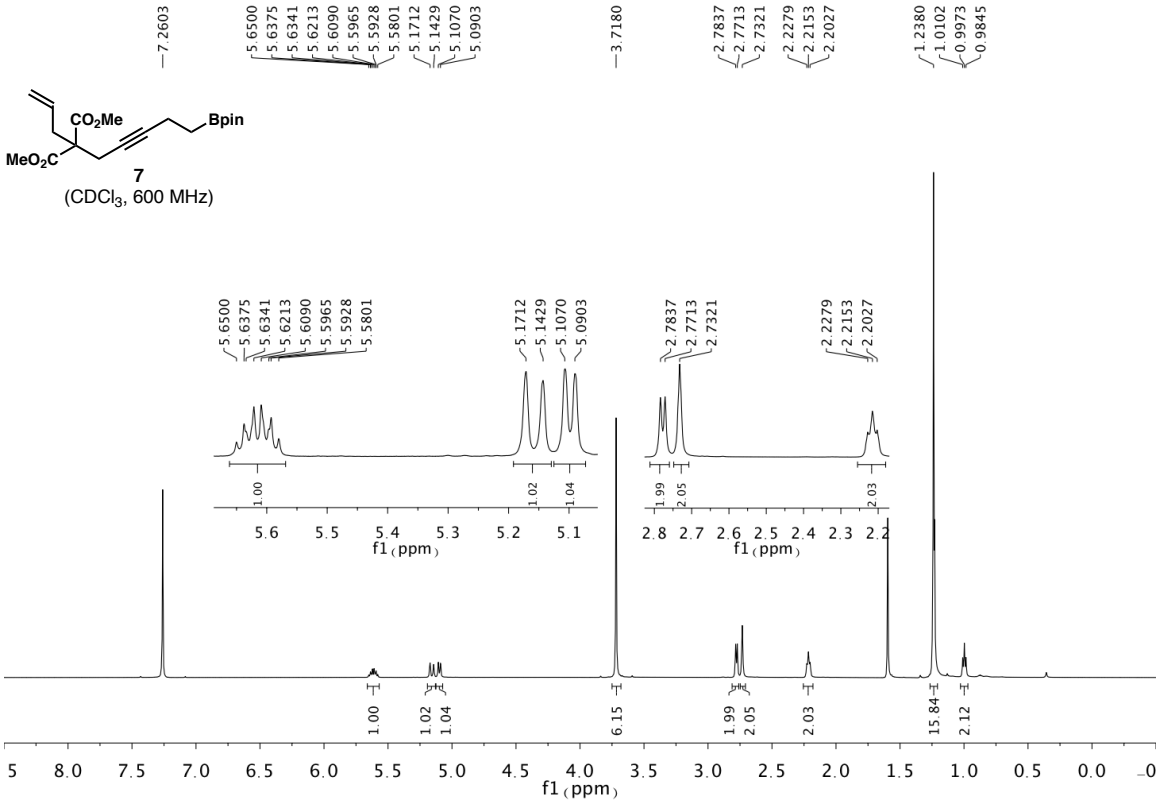

MeO2C
MeO2C
nPentyl
SiMe2tBu
5n
(Acetone-d6, 151 MHz)
168.4
52.7
f1 (ppm)

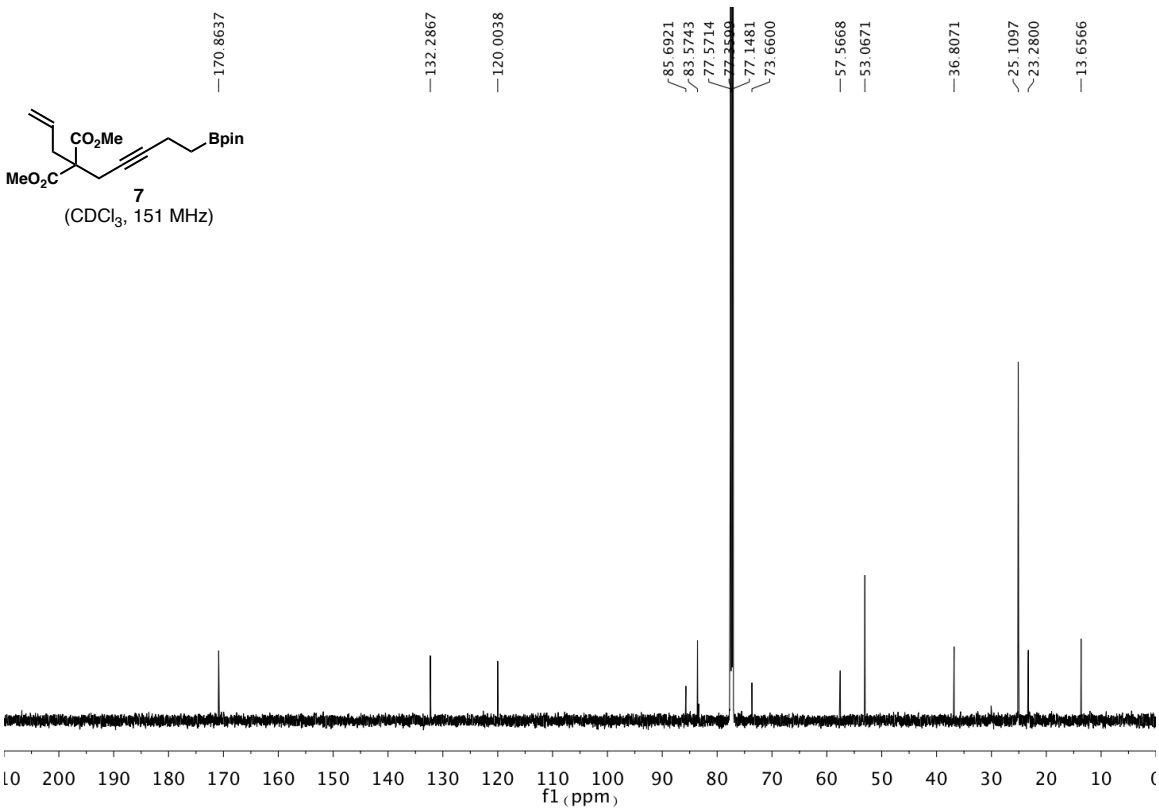

7.2601
Et
MeO2C
MeO2C
SiMe2tBu
5o
(CDCl3, 600 MHz)
3.7562
3.6005
3.5875
3.5745
3.2934
3.2831
3.2726
2.7867
2.7845
2.7738
2.7717
1.6912
1.6795
1.6676
1.6558
1.6441
1.0278
1.0157
1.0035
0.9139
0.0794
0.0760
6.45
0.96
0.94
2.00
1.98
3.14
9.56
6.05
f1 (ppm)

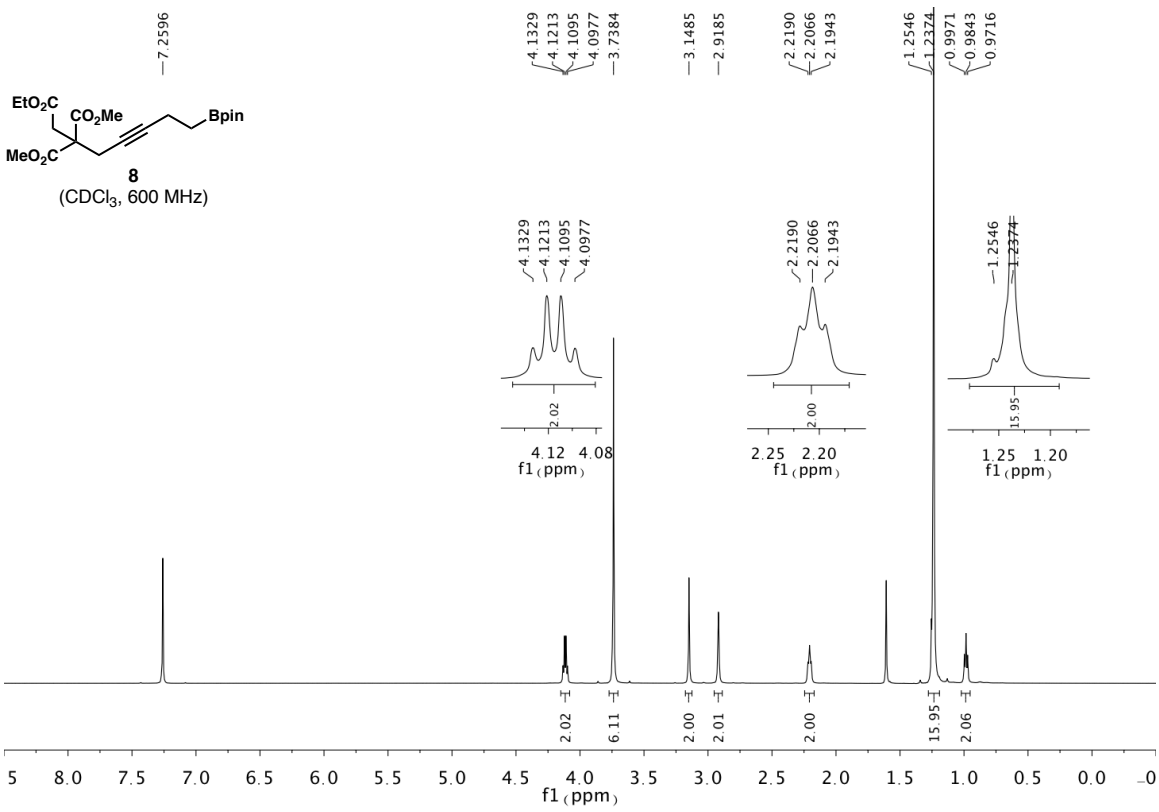

168.8545
168.8435
105.2045
83.5477
80.7770
77.5719
77.3604
77.1486
76.8289
53.1660
51.4860
29.5958
26.3647
25.9435
19.2239
16.9347
11.4501
4.2930
Et
MeO2C
MeO2C
SiMe2tBu
5o
(CDCl3, 151 MHz)
f1 (ppm)

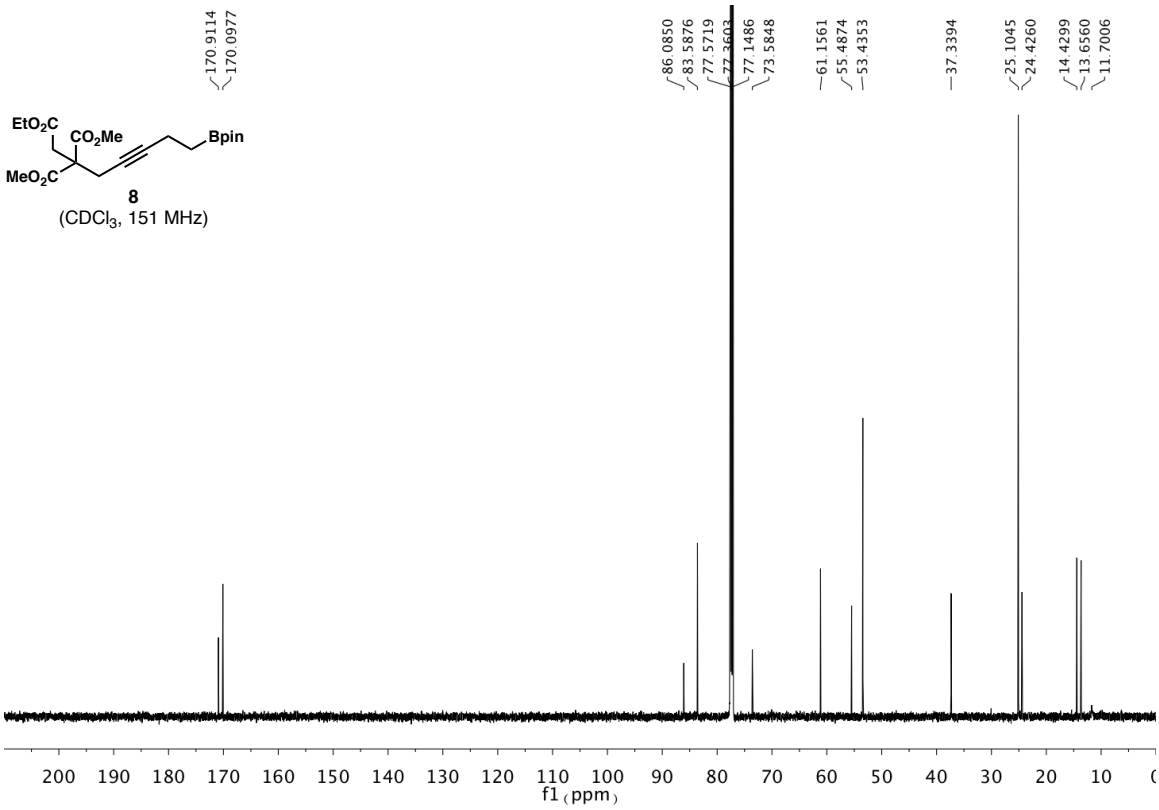

7.2595
3.7228
2.7228
2.2253
2.2214
2.2127
2.2038
2.1999
1.6118
1.2377
1.0027
0.9898
0.9771
CO2Me
Me
MeO2C
Bpin
6
(CDCl3, 600 MHz)
1.98
2.08
f1 (ppm)
6.28
2.00
1.98
3.02
13.55
2.08

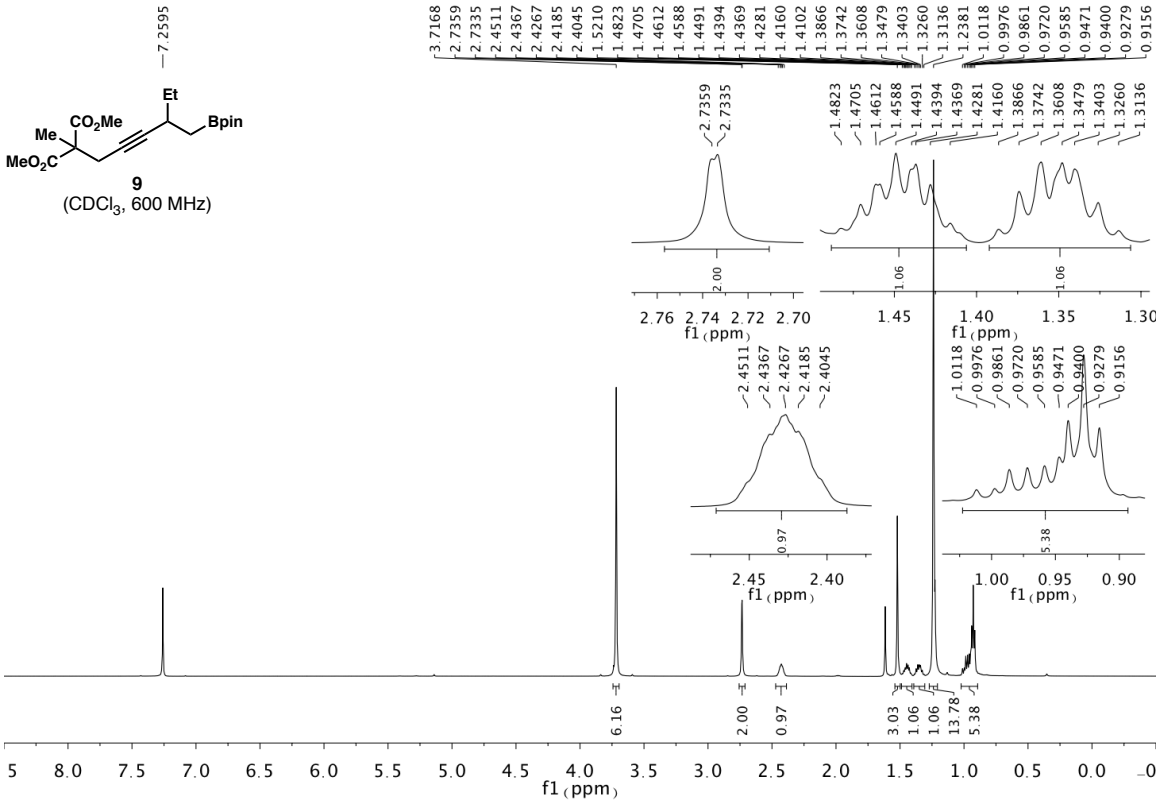

172.0152
85.4545
83.5703
77.5719
77.3603
77.1486
74.0703
53.7904
53.1446
26.5353
25.1069
20.2577
13.6692
CO2Me
Me
MeO2C
Bpin
6
(CDCl3, 151 MHz)
f1 (ppm)

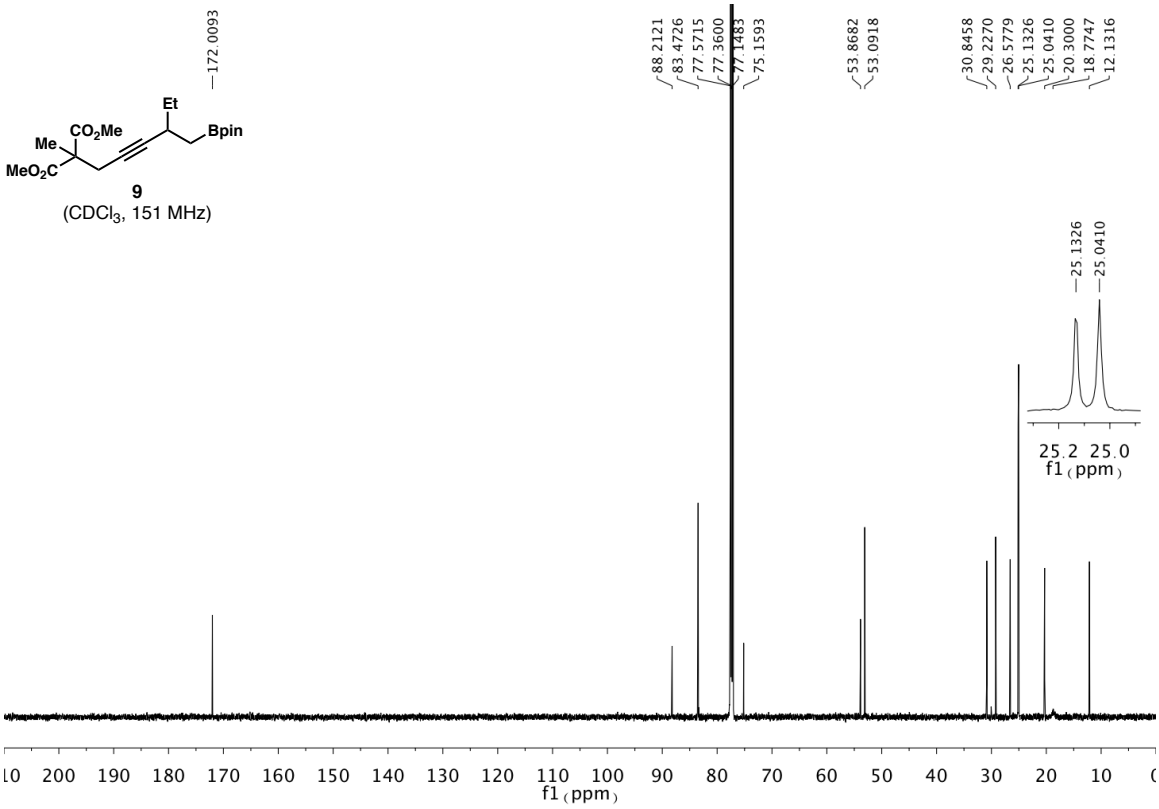

7.2603
5.6500
5.6375
5.6341
5.6213
5.6090
5.5965
5.5928
5.5801
5.1712
5.1429
5.1070
5.0903
3.7180
2.7837
2.7713
2.7321
2.2279
2.2153
2.2027
1.2380
1.0102
0.9973
0.9845
CO2Me
MeO2C
Bpin
7
(CDCl3, 600 MHz)
1.00
1.02
1.04
6.15
1.99
2.05
2.03
15.84
2.12
f1 (ppm)

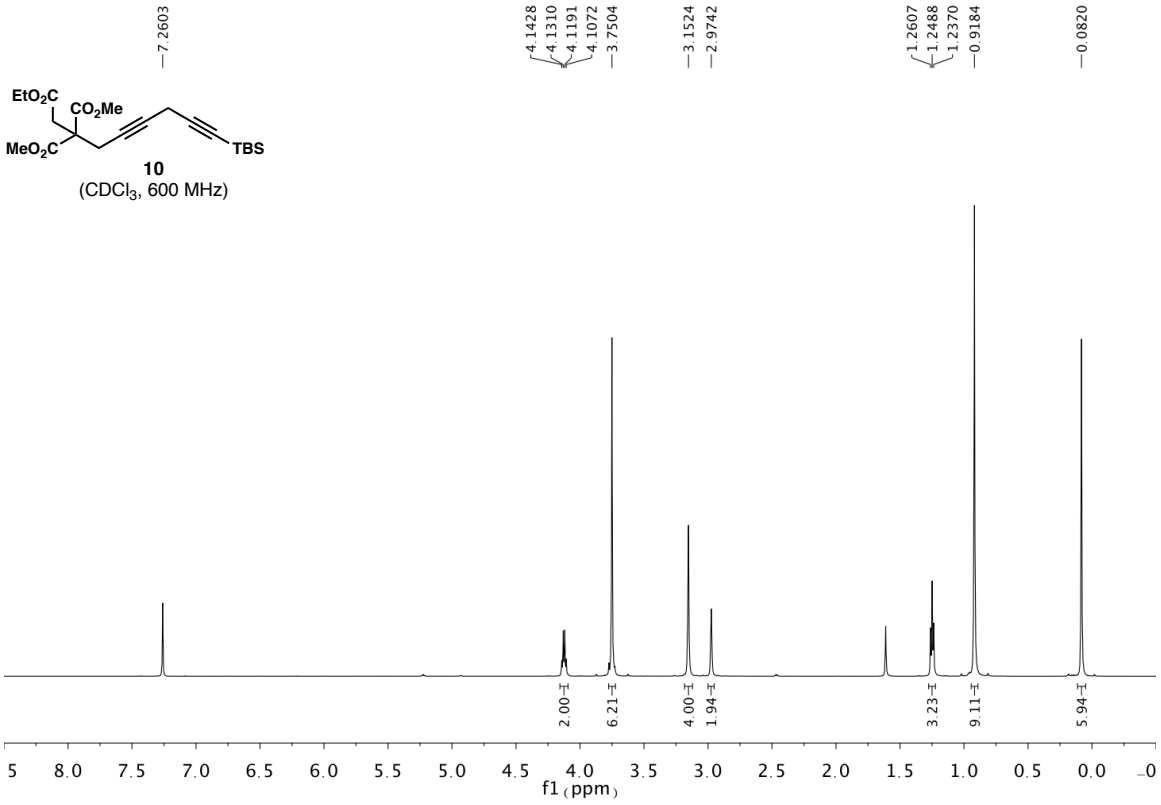

170.8637
132.2867
120.0038
85.6921
83.5743
77.5714
77.3590
77.1481
73.6600
57.5668
53.0671
36.8071
25.1097
23.2800
13.6566
CO2Me
MeO2C
Bpin
7
(CDCl3, 151 MHz)
f1 (ppm)

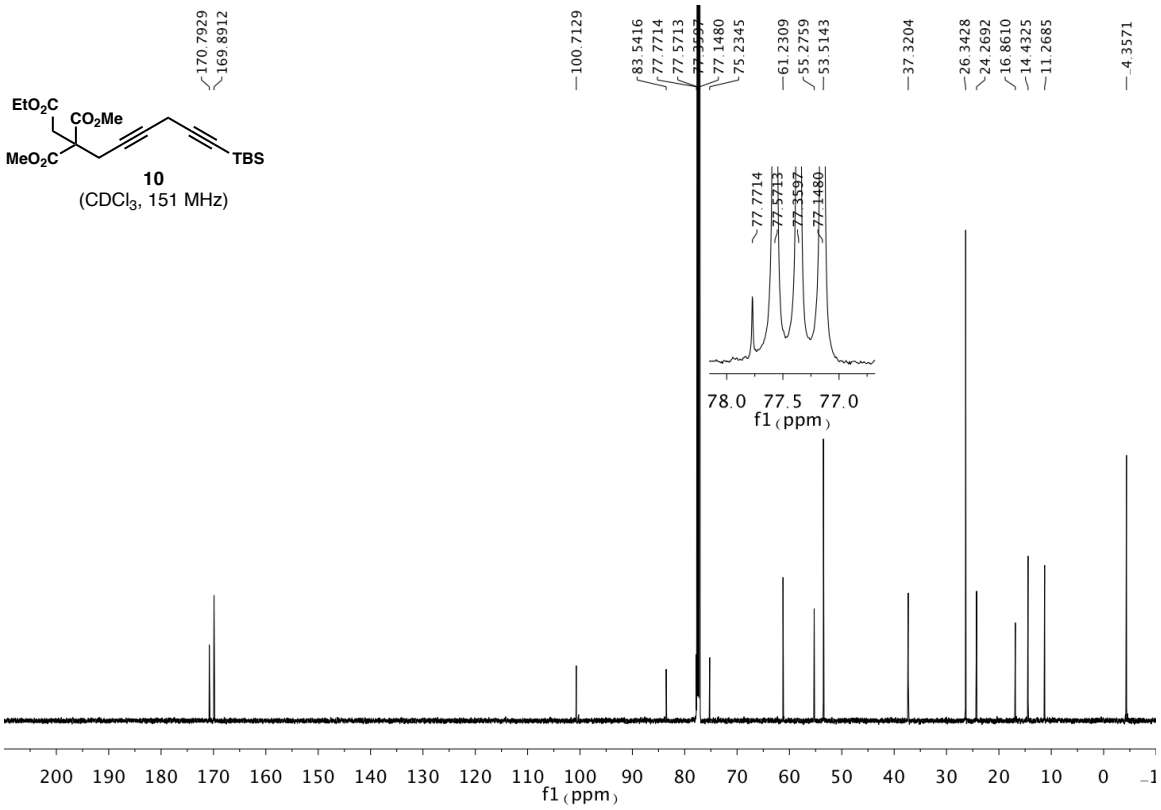

EtO2C
CO2Me
MeO2C
Bpin
8
(CDCl3, 600 MHz)
7.2596
4.1329
4.1213
4.1095
4.0977
3.7384
3.1485
2.9185
2.2190
2.2066
2.1943
1.2546
1.2374
0.9971
0.9843
0.9716
2.02
6.11
2.00
2.01
2.00
15.95
2.06
f1 (ppm)

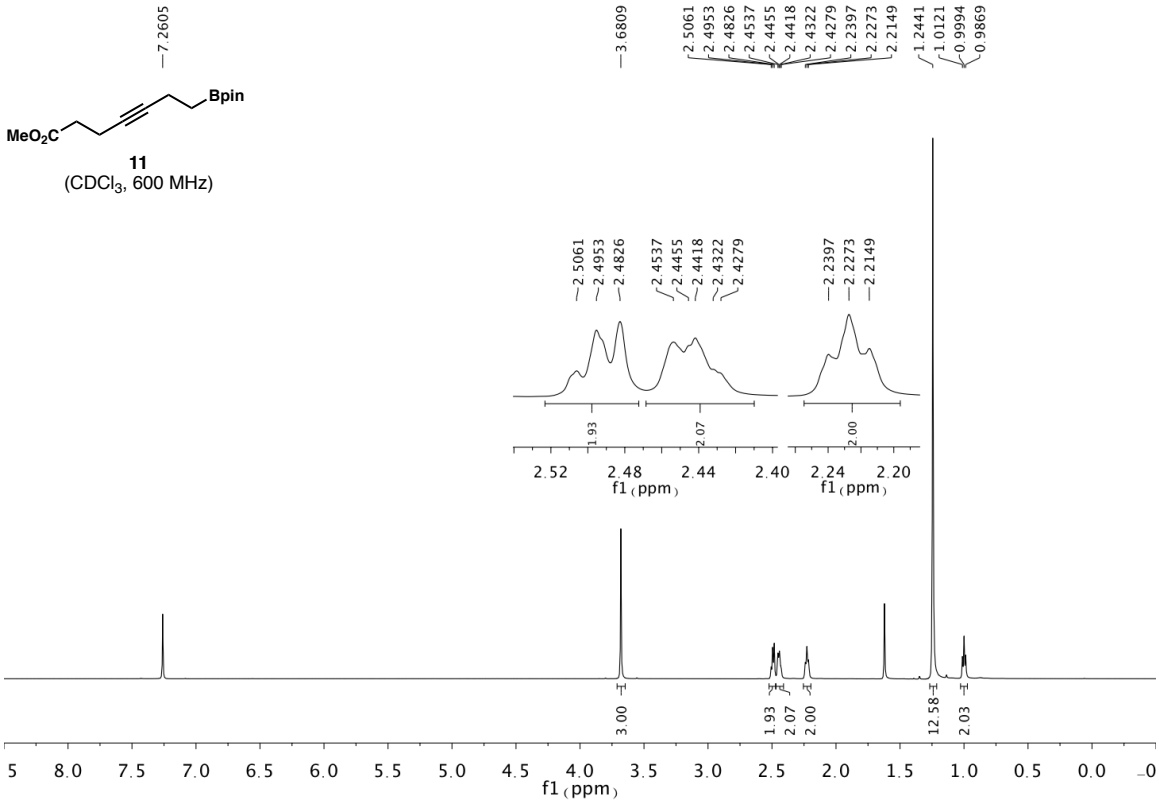

EtO2C
CO2Me
MeO2C
Bpin
8
(CDCl3, 151 MHz)
170.9114
170.0977
86.0850
83.5876
77.5719
77.3603
77.1486
73.5848
61.1561
55.4874
53.4353
37.3394
25.1045
24.4260
14.4299
13.6560
11.7006
f1 (ppm)

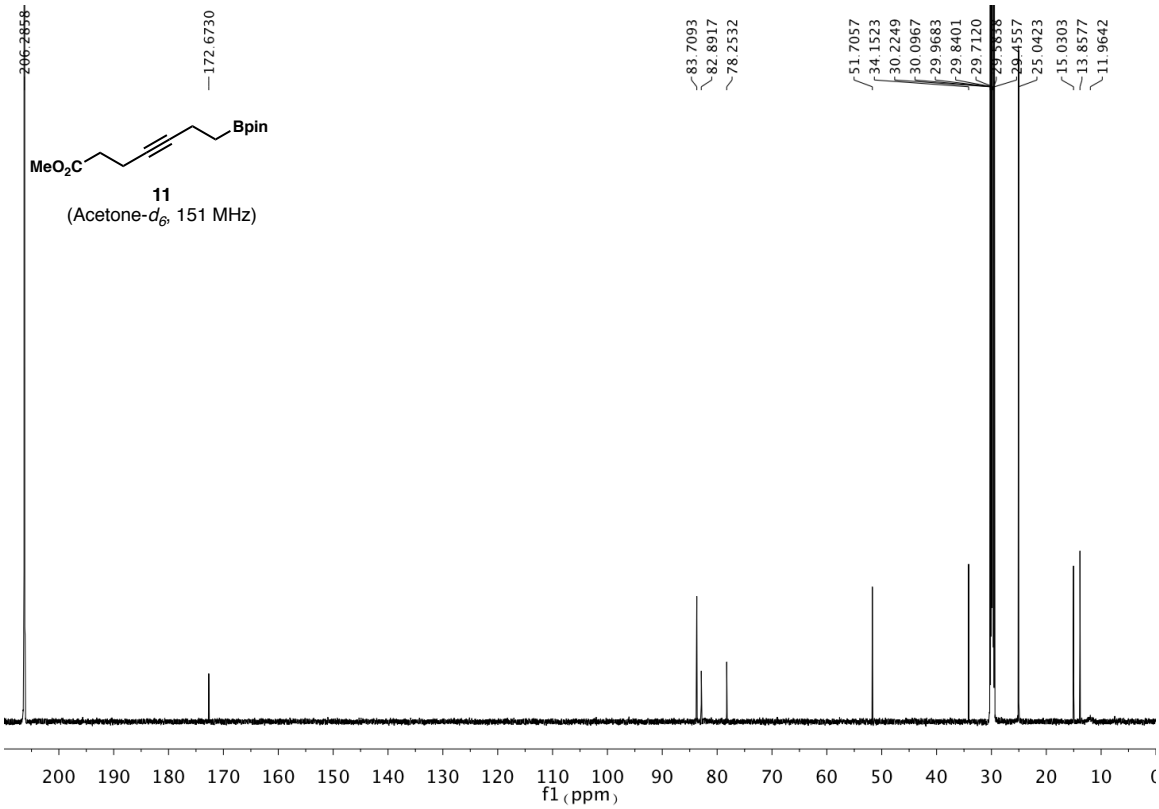

9
(CDCl3, 600 MHz)
Et
CO2Me
Me
MeO2C
Bpin

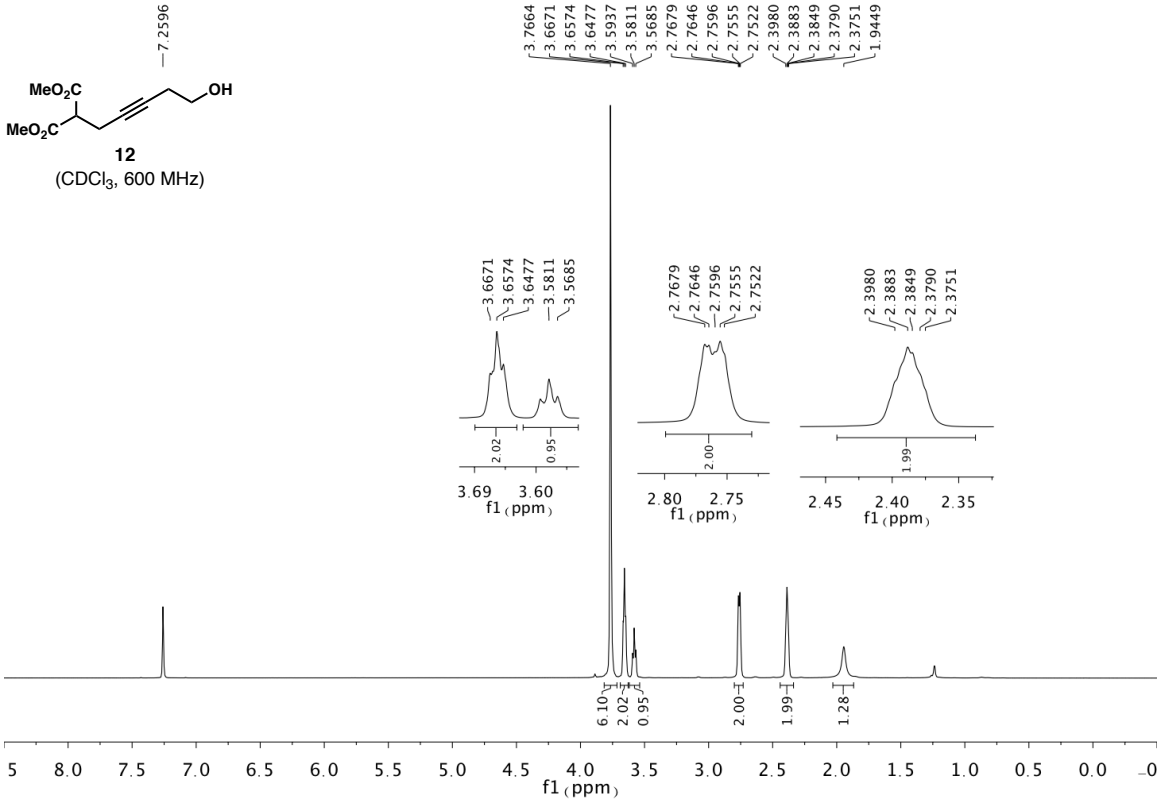

9
(CDCl3, 151 MHz)
Et
CO2Me
Me
MeO2C
Bpin

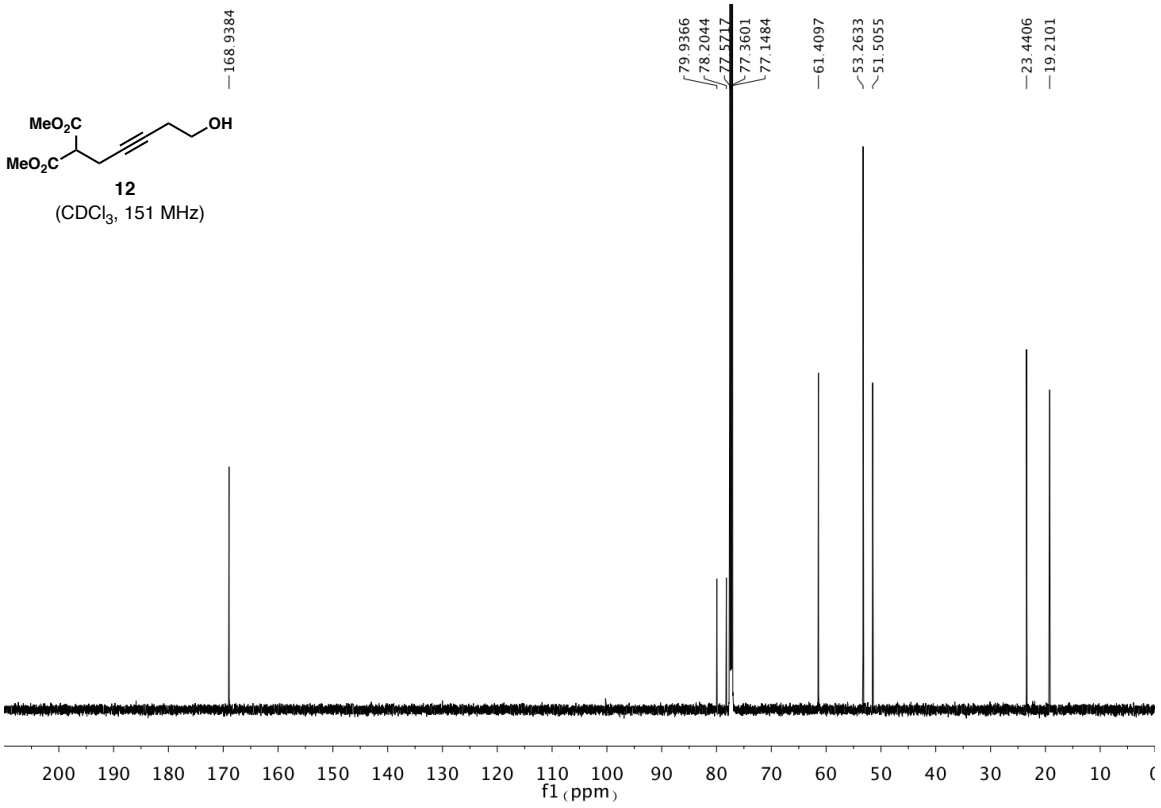

7.2603
4.1428
4.1310
4.1191
4.1072
3.7504
3.1524
2.9742
1.2607
1.2488
1.2370
0.9184
0.0820
EtO2C
CO2Me
MeO2C
TBS
10
(CDCl3, 600 MHz)
2.00
6.21
4.00
1.94
3.23
9.11
5.94
f1 (ppm)

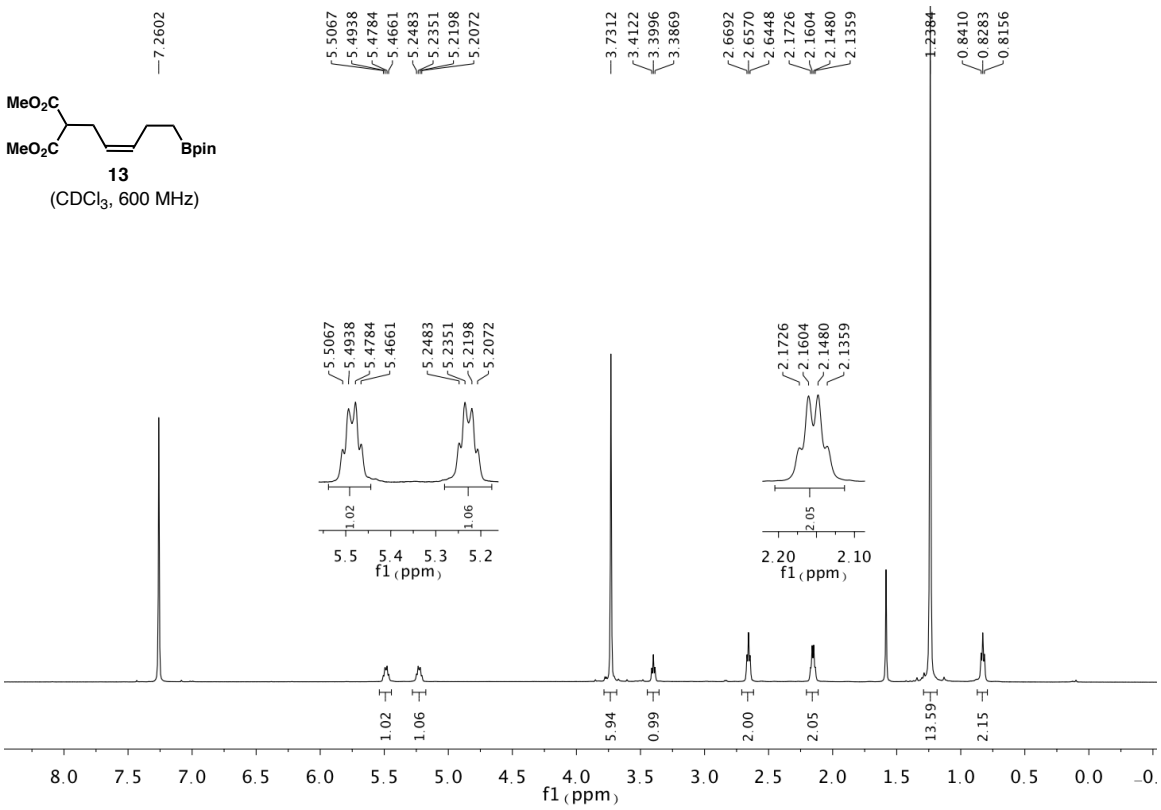

170.7929
169.8912
100.7129
83.5416
77.7714
77.5713
77.3597
77.1480
75.2345
61.2309
55.2759
53.5143
37.3204
26.3428
24.2692
16.8610
14.4325
11.2685
4.3571
EtO2C
CO2Me
MeO2C
TBS
10
(CDCl3, 151 MHz)
78.0
77.5
77.0
f1 (ppm)

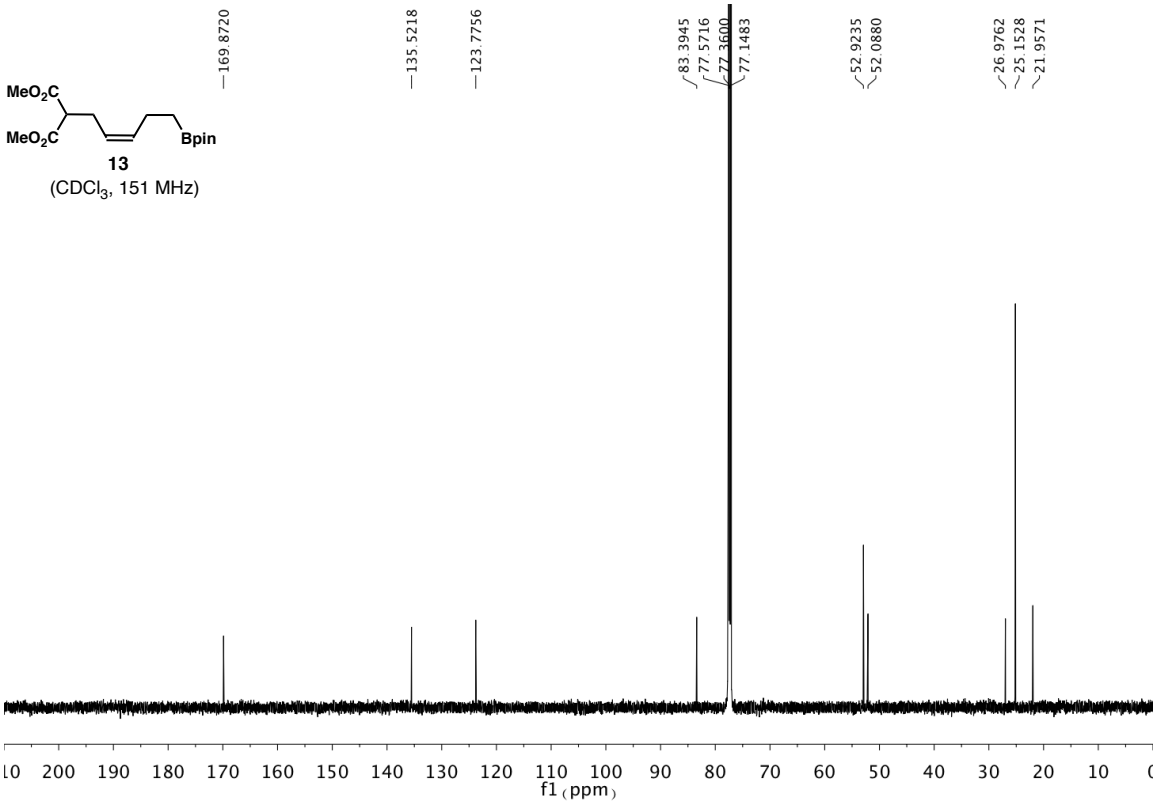

7.2605
3.6809
2.5061
2.4953
2.4826
2.4537
2.4455
2.4418
2.4322
2.4279
2.2397
2.2273
2.2149
1.2441
1.0121
0.9994
0.9869
Bpin
MeO2C
11
(CDCl3, 600 MHz)
1.93
2.07
2.00
2.52
2.48
2.44
2.40
2.24
2.20
f1 (ppm)
3.00
12.58
2.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

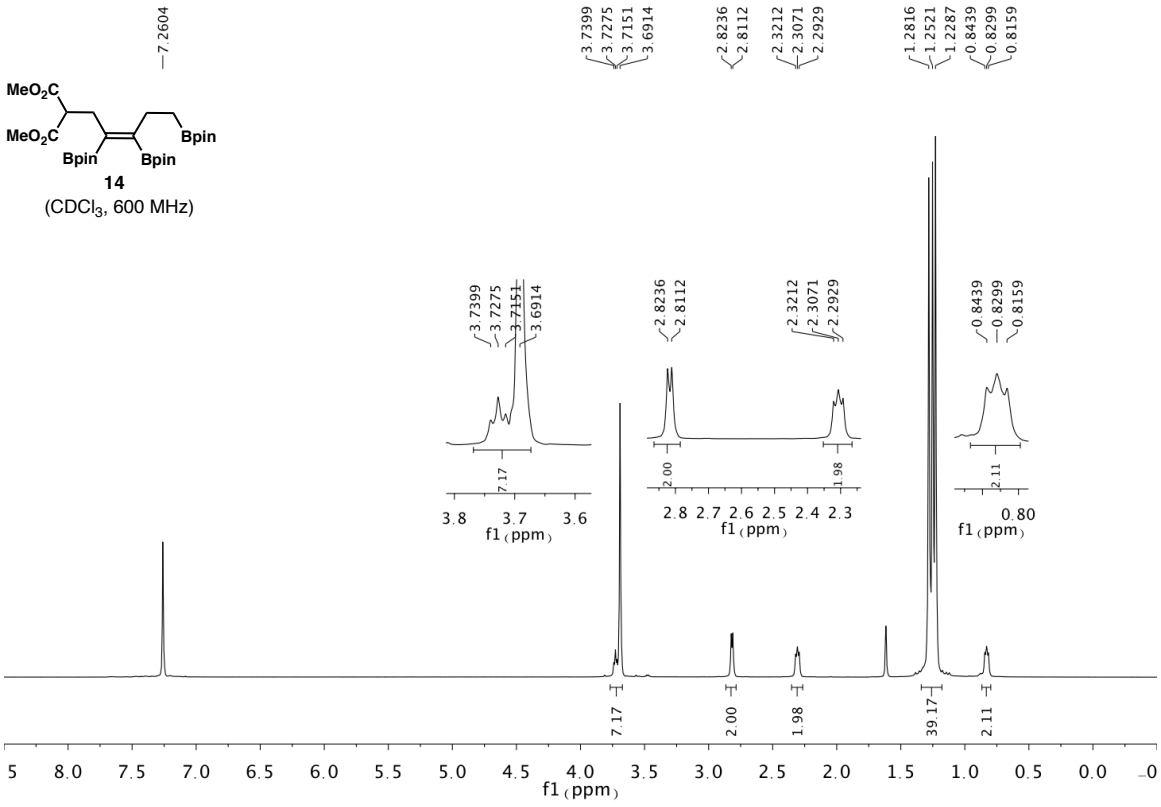

206.2858
172.6730
83.7093
82.8917
78.2532
51.7057
34.1523
30.2249
30.0967
29.9683
29.8401
29.7120
29.4557
25.0423
15.0303
13.8577
11.9642
Bpin
MeO2C
11
(Acetone-d6, 151 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

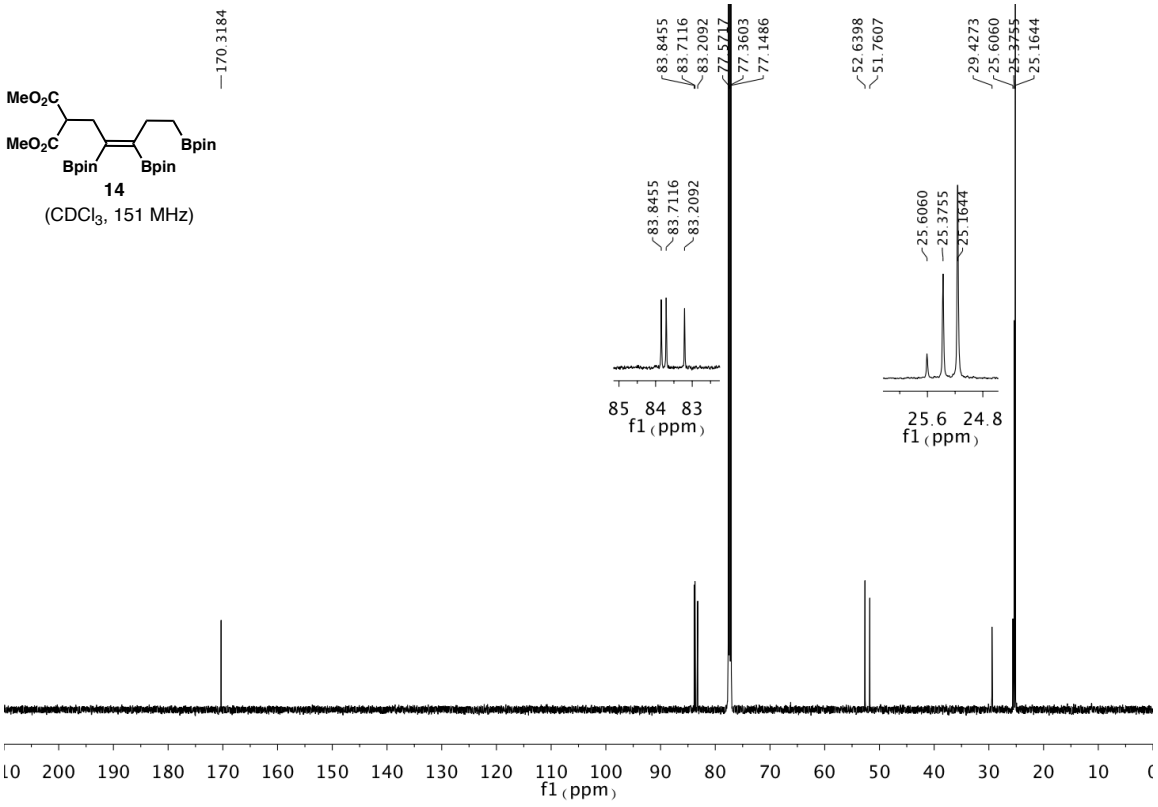

7.2596
MeO2C
MeO2C
OH
12
(CDCl3, 600 MHz)
3.7664
3.6671
3.6574
3.6477
3.5937
3.5811
3.5685
2.7679
2.7646
2.7596
2.7555
2.7522
2.3980
2.3883
2.3849
2.3790
2.3751
1.9449
6.10
2.02
0.95
2.00
1.99
1.28
f1 (ppm)

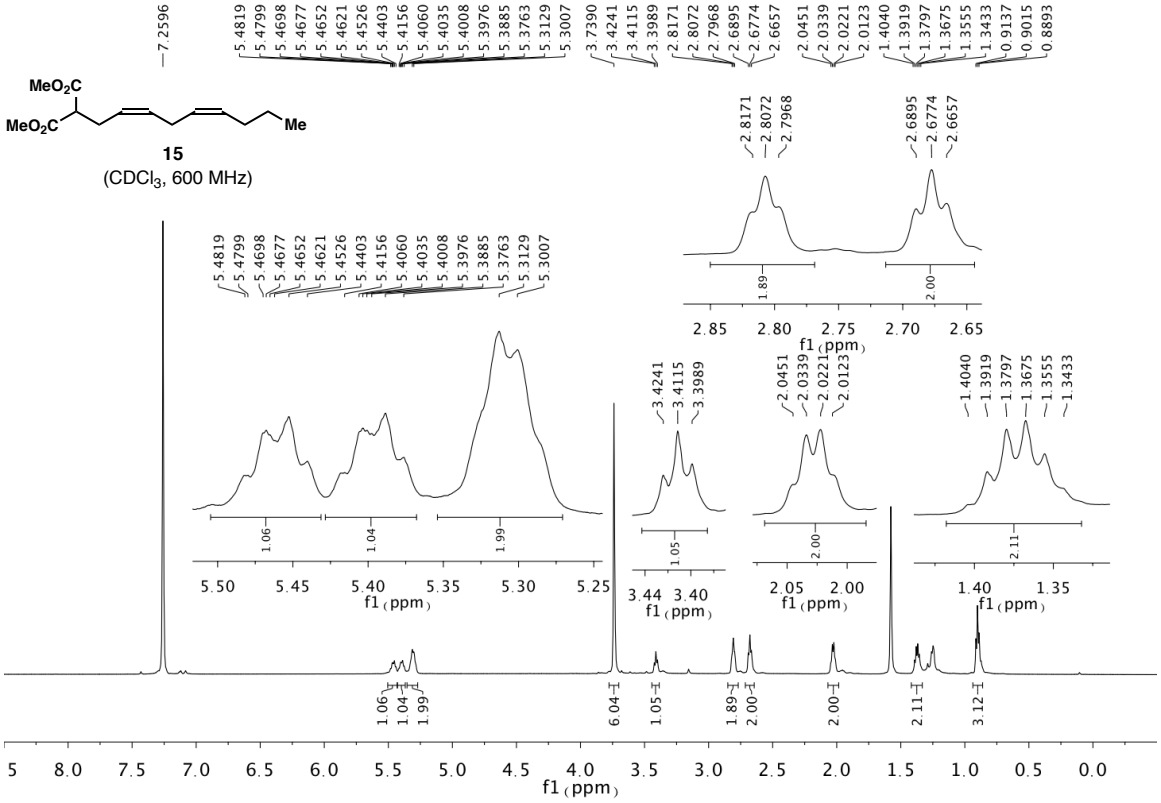

168.9384
MeO2C
MeO2C
OH
12
(CDCl3, 151 MHz)
79.9366
78.2044
77.5717
77.3601
77.1484
61.4097
53.2633
51.5055
23.4406
19.2101
f1 (ppm)

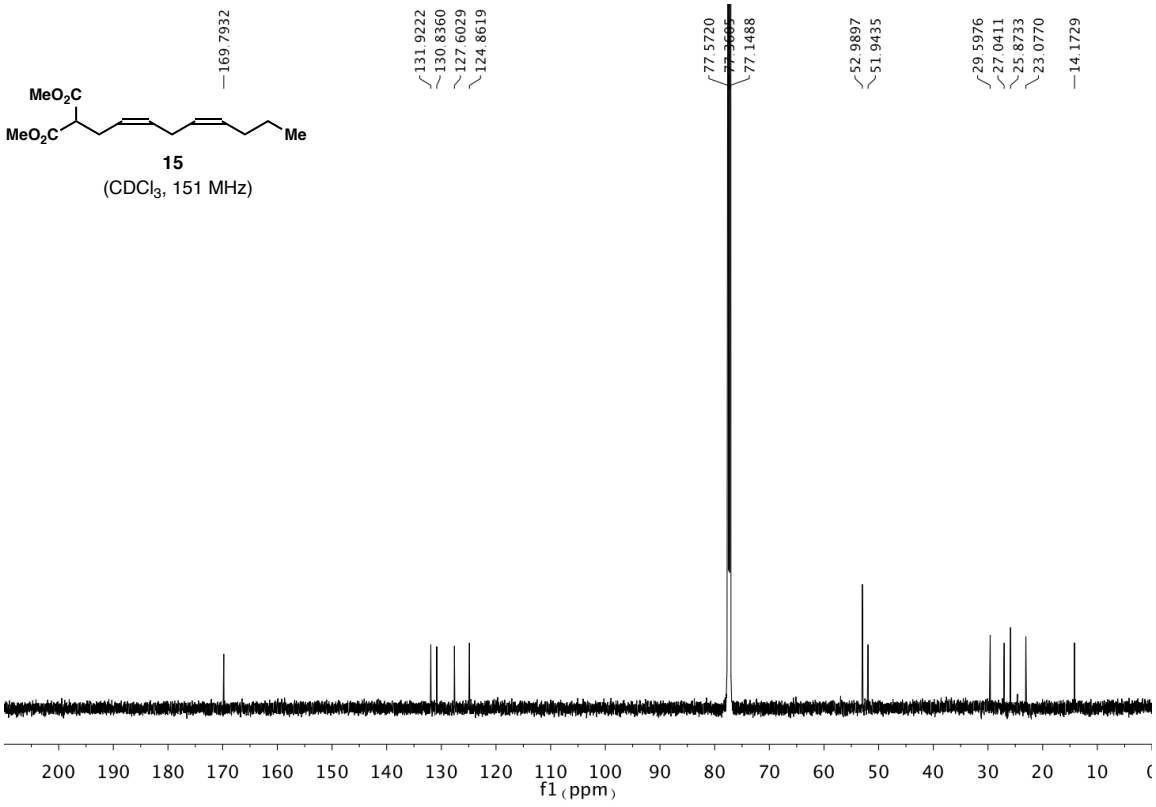

MeO2C
MeO2C
Bpin
13
(CDCl3, 600 MHz)
7.2602
5.5067
5.4938
5.4784
5.4661
5.2483
5.2351
5.2198
5.2072
3.7312
3.4122
3.3996
3.3869
2.6692
2.6570
2.6448
2.1726
2.1604
2.1480
2.1359
1.2384
0.8410
0.8283
0.8156
1.02
1.06
5.94
0.99
2.00
2.05
13.59
2.15
f1 (ppm)

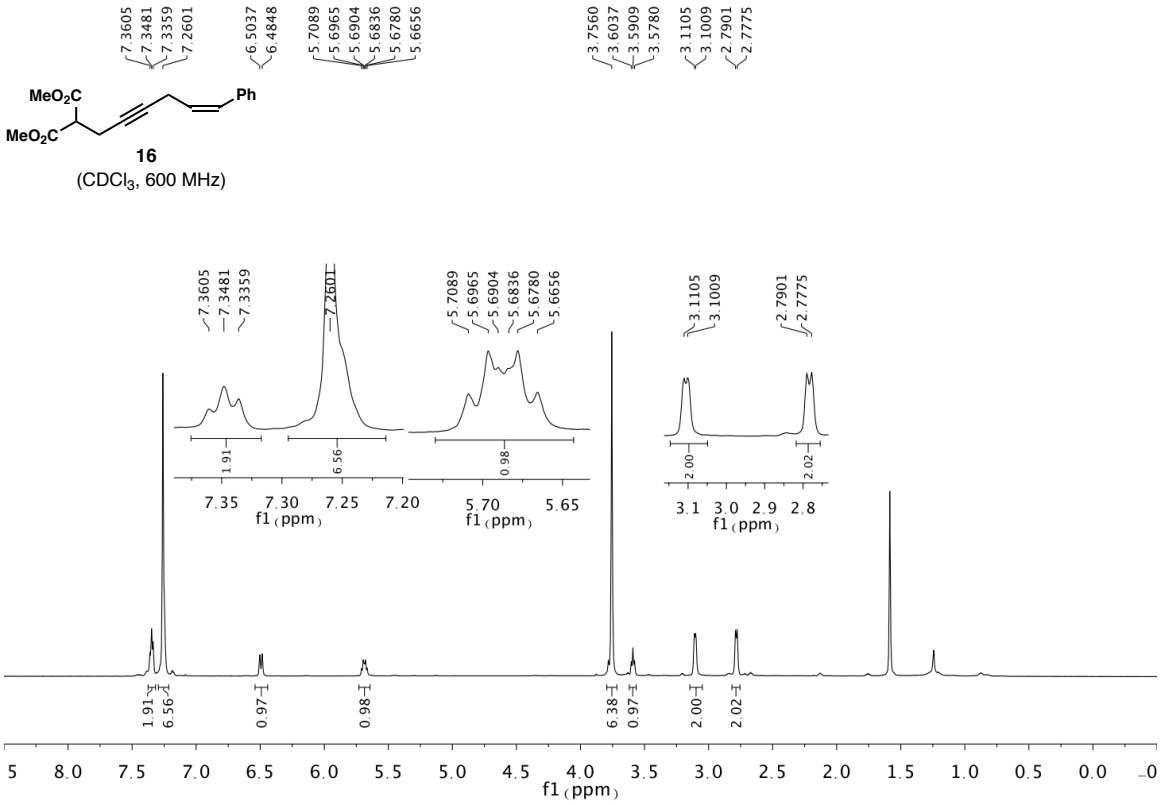

MeO2C
MeO2C
Bpin
13
(CDCl3, 151 MHz)
169.8720
135.5218
123.7756
83.3945
77.5716
77.3600
77.1483
52.9235
52.0880
26.9762
25.1528
21.9571
f1 (ppm)

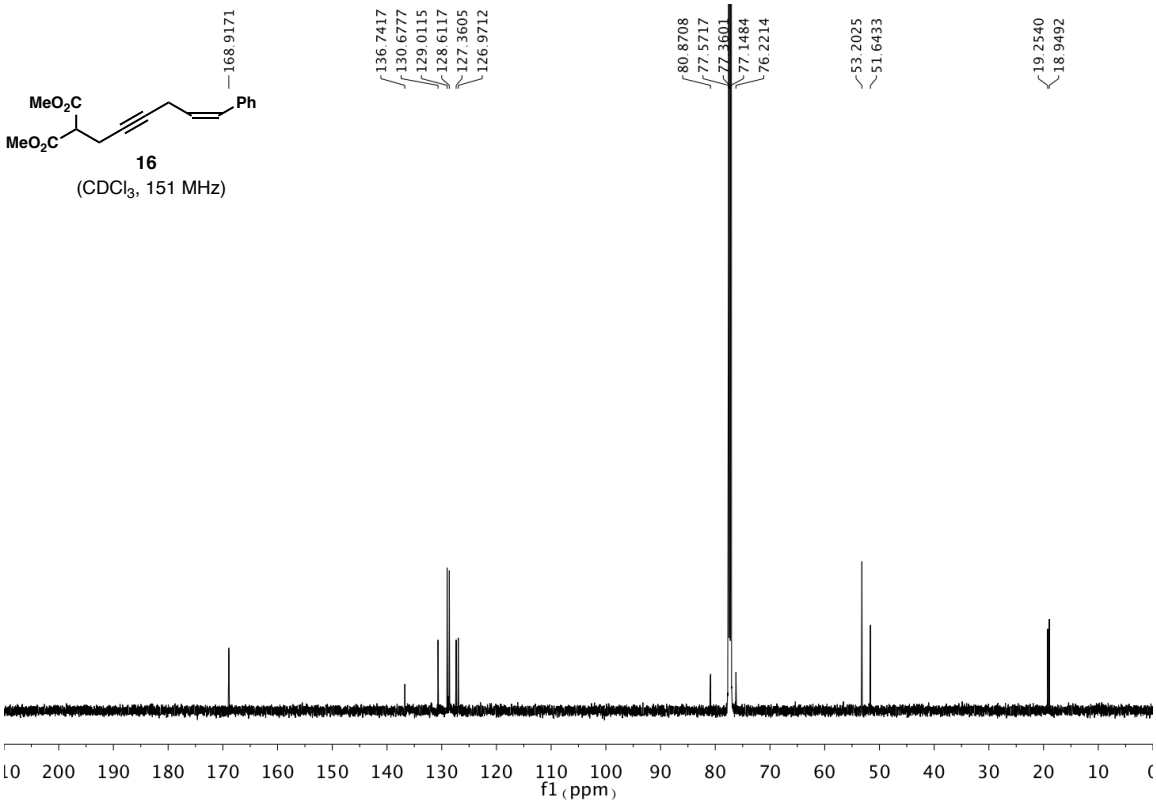

MeO2C
MeO2C
Bpin
Bpin
Bpin
14
(CDCl3, 600 MHz)
7.2604
3.7399
3.7275
3.7151
3.6914
2.8236
2.8112
2.3212
2.3071
2.2929
1.2816
1.2521
1.2287
0.8439
0.8299
0.8159
7.17
2.00
1.98
39.17
2.11
f1 (ppm)


MeO2C
MeO2C
Bpin
Bpin
Bpin
14
(CDCl3, 151 MHz)
170.3184
83.8455
83.7116
83.2092
77.5717
77.3603
77.1486
52.6398
51.7607
29.4273
25.6060
25.3755
25.1644
f1 (ppm)


MeO2C
MeO2C
Me
15
(CDCl3, 600 MHz)
f1 (ppm)


MeO2C
MeO2C
Me
15
(CDCl3, 151 MHz)
f1 (ppm)


7.3605
7.3481
7.3359
7.2601
6.5037
6.4848
5.7089
5.6965
5.6904
5.6836
5.6780
5.6656
3.7560
3.6037
3.5909
3.5780
3.1105
3.1009
2.7901
2.7775
MeO2C
MeO2C
Ph
16
(CDCl3, 600 MHz)
1.91
6.56
0.97
0.98
6.38
0.97
2.00
2.02
f1 (ppm)


168.9171
136.7417
130.6777
129.0115
128.6117
127.3605
126.9712
80.8708
77.5717
77.3601
77.1484
76.2214
53.2025
51.6433
19.2540
18.9492
MeO2C
MeO2C
Ph
16
(CDCl3, 151 MHz)
f1 (ppm)