Enantioselective Syntheses of Homopropargylic Alcohols via Asymmetric Allenylboration

*Mengzhou Wang, Shahriar Khan, Evangelos Miliordos and Ming Chen**

Department of Chemistry and Biochemistry

Auburn University

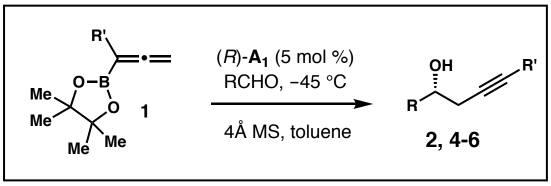
E-mail: mzc0102@auburn.edu

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

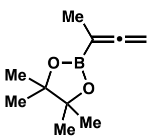
General Experimental Details. All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, diethyl ether and toluene were purified by passing through a solvent column composed of activated A-1 alumina. Unless indicated otherwise, all reactions were conducted under an atmosphere of 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 100 and 151 MHz. The proton signal for the residual non-deuterated solvent (δ 7.26 for $CHCl_3$) was used as an internal reference for ^{1}H NMR spectra. For ^{13}C NMR spectra, chemical shifts are reported relative to the δ 77.36 resonance of $CHCl_3$. Coupling constants are reported in Hz. Optical rotations were measured on a Perkin Elmer 241 Automatic Polarimeter. High-resolution mass spectra were recorded on a commercial high-resolution mass spectrometer via the Micro Mass/Analytical Facility operated by the College of Chemistry and Biochemistry, Auburn University.

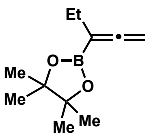
Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (ceric sulfate and ammonium molybdate in aqueous sulfuric acid) or $KMnO_4$.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



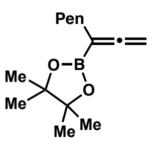
General procedure for syntheses of homopropargyl alcohols: To a reaction flask containing a stirring bar and freshly activated 4 Å MS (50 mg) was added phosphoric acid (*R*)-$\mathbf{A_1}$ (3.8 mg, 0.005 mmol). Toluene (0.3 mL) was added to the flask followed by drop wise addition of freshly distilled aldehydes (0.1 mmol, if it is a liquid). The mixture was placed in a −45 ˚C cold bath and stirred for 15 min. Allenylboronate **1**[1] (0.12 mmol) was added slowly to the reaction mixture via a microliter syringe. The mixture was kept at −45 ˚C and stirred for 48 h. After complete consumption of the aldehydes, saturated $NaHCO_3$ (1.0 mL) was added to the reaction mixture followed by slow addition of 30% H_2O_2 (0.5 mL) at 0 ˚C. The reaction was stirred vigorously for 2 h. Brine (1 mL) and Et_2O (0.5 mL) were added, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 1 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography (gradient elution with hexane and Et_2O) provided the product.



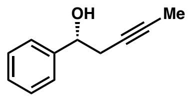
2-(Buta-2,3-dien-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1a). Prepared according to the known procedure,[1] colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.58 (q, *J* = 3.1 Hz, 2H), 1.71 (t, *J* = 3.1 Hz, 3H), 1.27 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 215.8, 84.1, 70.5, 25.1, 15.6.



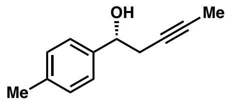
4,4,5,5-Tetramethyl-2-(penta-1,2-dien-3-yl)-1,3,2-dioxaborolane (1b). Prepared according to the known procedure,[1] colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.65 (app. t, *J* = 3.2 Hz, 2H), 2.03-2.07 (m, 2H), 1.27 (s, 12H), 1.03 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 214.9, 84.0, 72.0, 25.1, 22.7, 13.9.



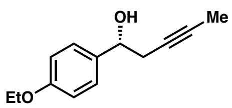
4,4,5,5-Tetramethyl-2-(octa-1,2-dien-3-yl)-1,3,2-dioxaborolane (1c). Prepared according to the known procedure,[1] colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.62 (app. t, *J* = 2.9 Hz, 2H), 2.01-2.04 (m, 2H), 1.41-1.46 (m, 2H), 1.28-1.32 (m, 4H), 1.27 (s, 12H), 0.88 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 215.2, 83.9, 71.4, 31.7, 29.4, 29.1, 25.0, 22.8, 14.4.



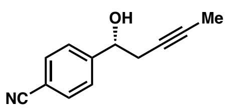
(*R*)-1-Phenylpent-3-yn-1-ol (2a). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 15 mg product **2a** as colorless oil in 94% yield. The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 °C); t_1 = 7.31 min, t_2 = 7.82 min [(Chiralpak IC) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 73.8° (c 0.67, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34-7.38 (m, 4H), 7.28-7.30 (m, 1H), 4.81 (dd, *J* = 7.9, 4.7 Hz, 1H), 2.52-2.62 (m, 2H), 2.08 (br, 1H), 1.81 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 128.7, 128.1, 126.1, 79.1, 75.6, 73.0, 30.4, 3.9; HRMS (EI): *m/z* for $C_{11}H_{12}O$ $[M]^+$ calcd. 160.0888, found: 160.0900.



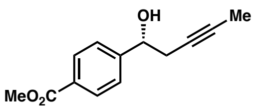
(*R*)-1-(P-tolyl)pent-3-yn-1-ol (2b). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 15 mg compound **2b** as colorless oil in 86% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 °C); t_1 = 10.5 min, t_2 = 11.1 min [(Chiralpak IG) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 10.9° (c 1.53, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.76 (dd, *J* = 7.8, 4.8 Hz, 1H), 2.50-2.57 (m, 2H), 2.33 (s, 3H), 1.80 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.1, 137.8, 129.4, 126.0, 78.9, 75.7, 72.8, 30.3, 21.5, 4.0; HRMS (EI): *m/z* for $C_{12}H_{12}$ $[M-H_2O]^+$ calcd. 156.0939, found: 156.0947.



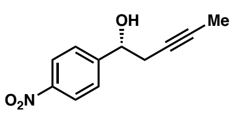
(*R*)-1-(4-Ethoxyphenyl)pent-3-yn-1-ol (2c). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 19 mg compound **2c** as colorless oil in 93% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 °C); t_1 = 12.0 min, t_2 = 11.4 min [(Chiralpak IA) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 13.9° (c 1.33, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 4.75 (app. t, *J* = 6.6 Hz, 1H), 4.02 (q, *J* = 7.0 Hz, 2H), 2.53-2.56 (m, 2H), 2.40 (br, 1H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.41 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.8, 135.1, 127.3, 114.6, 78.9, 75.7, 72.6, 63.7, 30.3, 15.2, 3.9; HRMS (EI): *m/z* for $C_{13}H_{14}O$ $[M-H_2O]^+$ calcd. 186.1045, found: 186.1046.



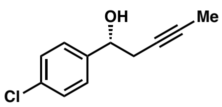
(*R*)-4-(1-Hydroxypent-3-yn-1-yl)benzonitrile (2d). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 17 mg compound **2d** as colorless oil in 92% yield. The enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 9.47 min, t_2 = 9.98 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 26.9° (c 1.53, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 4.80-4.92 (m, 1H), 2.60-2.65 (m, 1H), 2.46-2.56 (m, 2H), 1.81 (t, *J* = 2.4 Hz, 3H), 1.55 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.3, 132.6, 126.8, 119.1, 111.8, 80.0, 74.4, 72.1, 30.3, 3.9; HRMS (EI): *m/z* for $C_{12}H_{11}NO$ $[M]^+$ calcd. 185.0841, found: 185.0854.



(*R*)-4-(1-Hydroxypent-3-yn-1-yl)-methyl-benzoate (2e). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 20 mg product **2e** as colorless oil in 92% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 ˚C); t_1 = 10.9 min, t_2 = 12.0 min [(Chiralpak IE) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 16.5° (c 1.60, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 4.87 (dd, *J* = 7.8, 4.7 Hz, 1H), 3.91 (s, 3H), 2.60-2.65 (m, 1H), 2.51-2.56 (m, 2H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.56 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.3, 148.2, 130.0, 129.8, 126.0, 79.5, 74.9, 72.4. 52.4, 30.3, 3.9; HRMS (EI): *m/z* for $C_{13}H_{14}O_3$ $[M]^+$ calcd. 218.0943, found: 218.0940.

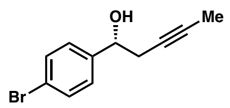


(*R*)-1-(4-Nitrophenyl)pent-3-yn-1-ol (2f). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 20 mg compound **2f** as colorless oil in 98% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 ˚C); t_1 = 16.3 min, t_2 = 17.7 min [(Chiralpak IA) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 19.2° (c 1.53, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 4.92 (app. s, 1H), 2.63-2.67 (m, 1H), 2.52-2.57 (m, 2H), 1.81 (t, *J* = 2.4 Hz, 3H), 1.55 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 147.8, 126.9, 123.9, 80.1, 74.3, 71.9, 30.4, 3.8; HRMS (EI): *m/z* for $C_{11}H_{10}NO_2$ $[M\text{-}OH]^+$ calcd. 188.0712, found: 188.0714.

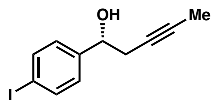


(*R*)-1-(4-Chlorophenyl)pent-3-yn-1-ol (2g). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 16 mg compound **2g** as colorless oil in 82% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 ˚C); t_1 = 9.10 min, t_2 = 9.79 min [(Chiralpak IA) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 26.0° (c 1.07, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (app. s, 4H), 4.79 (dd, *J* = 7.5, 5.0 Hz, 1H), 2.47-2.64 (m, 2H), 2.43 (br, 1H), 1.81 (t, *J* = 2.5

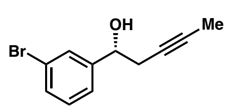
Hz, 3H), 1.56 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 141.6, 133.8, 128.9, 127.5, 79.4, 75.1, 72.2, 30.4, 3.9; HRMS (EI): *m/z* for $C_{11}H_{11}ClO$ $[M]^+$ calcd. 194.0498, found: 194.0493.



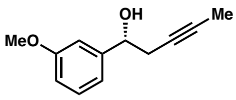
(*R*)-1-(4-Bromophenyl)pent-3-yn-1-ol (2h). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 20 mg compound **2h** as colorless oil in 84% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 ˚C); t_1 = 9.68 min, t_2 = 10.6 min [(Chiralpak IA) hexane/i-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 18.3° (c 1.33, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 4.76-4.78 (m, 1H), 2.56-2.60 (m,1H), 2.48-2.54 (m, 1H), 2.42 (br, 1H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.55 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.1, 131.8, 127.8, 121.9, 79.5, 75.0, 72.3, 30.3, 3.9; HRMS (EI): *m/z* for $C_{11}H_{11}BrO$ $[M]^+$ calcd. 237.9993, found: 237.9999.



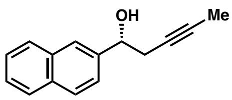
(*R*)-1-(4-Iodophenyl)pent-3-yn-1-ol (2i). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 20 mg compound **2i** as colorless oil in 70% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 ˚C); t_1 = 10.4 min, t_2 = 11.9 min [(Chiralpak IA) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 21.4° (c 1.33, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.3 Hz, 2H), 4.75-4.77 (m, 1H), 2.55-2.60 (m, 1H), 2.48-2.54 (m, 1H), 2.42 (d, *J* = 3.1 Hz, 1H), 1.80 (t, *J* = 2.4 Hz, 3H), 1.56 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.8, 137.7, 128.1, 93.5, 79.5, 75.0, 72.3, 30.3, 3.9; HRMS (EI): *m/z* for $C_{11}H_{11}IO$ $[M]^+$ calcd. 285.9855, found: 285.9853.



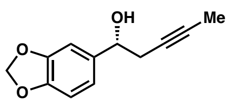
(*R*)-1-(3-Bromophenyl)pent-3-yn-1-ol (2j). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 22 mg compound **2j** as colorless oil in 92% yield. The enantiomeric excess was determined by HPLC analysis to be 92% ee (254 nm, 25 ˚C); t_1 = 6.34 min, t_2 = 6.95 min [(Chiralpak IG) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]D^{25}$ = 14.4° (c 1.73, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.42 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.7 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 4.76-4.79 (m, 1H), 2.57-2.62 (m, 1H), 2.49-2.54 (m, 1H), 2.45 (d, *J* = 2.3 Hz, 1H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.56 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.4, 131.1, 130.3, 129.3, 124.7, 122.9, 79.6, 75.0, 72.2, 30.4, 3.9; HRMS (EI): *m/z* for $C_{11}H_{11}BrO$ $[M]^+$ calcd. 237.9993, found: 238.0002.



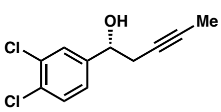
(*R*)-1-(3-Methoxyphenyl)pent-3-yn-1-ol (2k). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 17 mg compound **2k** as colorless oil in 89% yield. The enantiomeric excess was determined by HPLC analysis to be 97% ee (254 nm, 25 ˚C); t_1 = 9.78 min, t_2 = 10.8 min [(Chiralpak IB) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 19.4° (c 1.47, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.25-7.28 (m, 1H), 6.95 (d, *J* = 7.9 Hz, 2H), 6.83 (dd, *J* = 8.2, 1.8 Hz, 1H), 4.79 (dd, *J* = 8.0, 4.6 Hz, 1H), 3.82 (s, 3H), 2.51-2.63 (m, 2H), 2.41 (br, 1H), 1.82 (t, *J* = 2.5 Hz, 3H), 1.56 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 144.8, 129.8, 118.3, 113.6, 111.5, 79.1, 75.5, 72.9, 55.6, 30.4, 3.9; HRMS (EI): *m/z* for $C_{12}H_{14}O_2$ $[M]^+$ calcd. 190.0994, found: 190.1006.



(*R*)-1-(Naphthalen-2-yl)pent-3-yn-1-ol (2l). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 20 mg compound **2l** as colorless oil in 95% yield. The enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 11.0 min, t_2 = 12.2 min [(Chiralpak IG) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 20.1° (c 1.53, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.83-7.85 (m, 4H), 7.45-7.50 (m, 3H), 4.99 (dd, *J* = 7.9, 4.8 Hz, 1H), 2.61-2.75 (m, 2H), 2.52 (br, 1H), 1.82 (t, *J* = 2.4 Hz, 3H), 1.55 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.5, 133.5, 133.4, 128.5, 128.3, 128.0, 126.5, 126.2, 124.9, 124.1, 79.2, 75.5, 73.0, 30.3, 3.9; HRMS (EI): *m/z* for $C_{15}H_{14}O$ $[M]^+$ calcd. 210.1045, found: 210.1069.

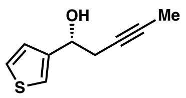


(*R*)-1-(Benzo[*d*][1,3]dioxol-5-yl)pent-3-yn-1-ol (2m). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 19 mg compound **2m** as colorless oil in 93% yield. The enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 9.21 min, t_2 = 10.4 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 10.9° (c 1.67, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.90 (d, *J* = 1.2 Hz, 1H), 6.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.95 (s, 2H), 4.71-4.74 (m, 1H), 2.49-2.58 (m, 2H), 2.36 (d, *J* = 3.1 Hz, 1H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.56 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.0, 147.4, 137.2, 119.5, 108.4, 106.6, 101.4, 79.1, 75.5, 72.8, 30.4, 3.9; HRMS (EI): *m/z* for $C_{12}H_{10}O_2$ $[M-H_2O]^+$ calcd. 186.0681, found: 186.0677.

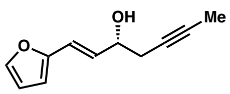


(*R*)-1-(3,4-Dichlorophenyl)pent-3-yn-1-ol (2n). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 16 mg compound

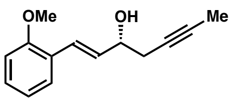
2n as colorless oil in 70% yield. The enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 6.32 min, t_2 = 6.81 min [(Chiralpak ID) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 14.1˚ (c 0.73, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.49 (s, 1H), 7.41 (d, *J* = 8.3 Hz, 1H), 7.20 (d, *J* = 8.3 Hz, 1H), 4.76 (dd, *J* = 7.5, 4.9 Hz, 1H), 2.47-2.61 (m, 3H), 1.81 (t, *J* = 2.1 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.2, 132.8, 131.9, 130.7, 128.2, 125.4, 79.9, 74.6, 71.6, 30.3, 3.9; HRMS (EI): *m/z* for $C_{11}H_9Cl_2$ $[M\text{-}OH]^+$ calcd. 211.0081, found: 211.0088.



(*R*)-1-(Thiophen-3-yl)pent-3-yn-1-ol (2o). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 15 mg compound **2o** as colorless oil in 90% yield. The enantiomeric excess was determined by HPLC analysis to be 90% ee (254 nm, 25 ˚C); t_1 = 6.92 min, t_2 = 7.43 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 18.8˚ (c 1.13, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.30 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.27 (d, *J* = 0.9 Hz, 1H), 7.10 (dd, *J* = 5.0, 1.0 Hz, 1H), 4.88-4.91(m, 1H), 2.57-2.62 (m, 1H), 2.63-2.68 (m, 1H), 2.39 (d, *J* = 4.0 Hz, 1H), 1.82 (t, *J* = 2.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.5, 126.4, 125.9, 121.4, 79.3, 75.3, 69.3, 29.5, 4.0; HRMS (EI): *m/z* for C_9H_8S $[M\text{-}H_2O]^+$ calcd. 148.0347, found: 148.0350.

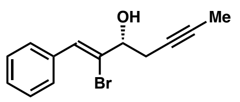


(*R*,*E*)-1-(Furan-2-yl)hept-1-en-5-yn-3-ol (2p). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 14 mg compound **2p** as colorless oil in 81% yield. The enantiomeric excess was determined by HPLC analysis to be 81% ee (254 nm, 25 ˚C); t_1 = 7.06 min, t_2 = 7.76 min [(Chiralpak IA) [(Chiralpak) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 9.87˚ (c 1.73, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.35 (app. s, 1H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.37 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.26 (d, *J* = 3.1 Hz, 1H), 6.20 (dd, *J* = 15.8, 5.9 Hz, 1H), 4.35-4.40 (m, 1H), 2.49-2.55 (m, 1H), 2.40-2.45 (m, 1H), 2.11 (d, *J* = 4.7 Hz, 1H), 1.82 (t, *J* = 2.5 Hz, 3H), 1.55 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 152.6, 142.4, 129.3, 119.4, 111.6, 108.7, 79.2, 74.9, 70.9, 28.5, 3.9; HRMS (EI): *m/z* for $C_{11}H_{10}O$ $[M\text{-}H_2O]^+$ calcd. 158.0732, found: 158.0738.

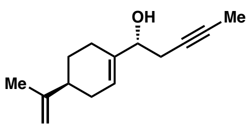


(*R*,*E*)-1-(2-Methoxyphenyl)hept-1-en-5-yn-3-ol (2q). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 17 mg compound **2q** as colorless oil in 79% yield. The enantiomeric excess was determined by HPLC analysis to be 88% ee (254 nm, 25 ˚C); t_1 = 8.98 min, t_2 = 9.56 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 6.00˚ (c 1.13, $CHCl_3$);

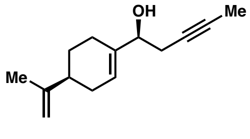
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.21-7.25 (m, 1H), 6.96 (d, *J* = 16.1 Hz, 1H), 6.93 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 8.2 Hz, 1H), 6.29 (dd, *J* = 16.1, 6.5 Hz, 1H), 4.39-4.44 (m, 1H), 3.85 (s, 3H), 2.51-2.56 (m, 1H), 2.44-2.49 (m, 1H), 2.11 (d, *J* = 4.4 Hz, 1H), 1.82 (t, *J* = 2.5 Hz, 3H), 1.55 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.1, 131.4, 129.2, 127.3, 126.2, 125.8, 120.9, 111.2, 78.9, 75.2, 71.9, 55.8, 28.5, 4.0; HRMS (EI): *m/z* for $C_{14}H_{14}O$ $[M-H_2O]^+$ calcd. 198.1045, found: 198.1056.



(*R*,*Z*)-2-Bromo-1-phenylhept-1-en-5-yn-3-ol (2r). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 24 mg compound **2r** as colorless oil in 91% yield. The enantiomeric excess was determined by HPLC analysis to be 98% ee (254 nm, 25 ˚C); t_1 = 6.83 min, t_2 = 7.30 min [(Chiralpak IB) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 0.324° (c 1.87, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.5 Hz, 2H), 7.36-7.38 (m, 2H), 7.32 (app. t, *J* = 7.3 Hz, 1H), 7.16 (s, 1H), 4.42 (app. q, *J* = 6.0 Hz, 1H), 2.62-2.74 (m, 2H), 2.45 (d, *J* = 5.7 Hz, 1H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.55 (H_2O); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.4, 129.5, 129.0, 128.51, 128.50, 127.8, 79.7, 76.1, 74.2, 27.3, 3.9. HRMS (EI): *m/z* for $C_{13}H_{11}Br$ $[M-H_2O]^+$ calcd. 246.0044, found: 246.0051.

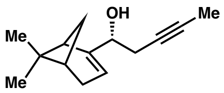


(*R*)-1-((*S*)-4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-3-yn-1-ol (4a). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 17 mg compound **4a** as colorless oil in 83% yield, d.r. > 20:1. $[\alpha]_D^{25}$ = −9.15° (c 0.33, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.73-5.76 (m, 1H), 4.69-4.73 (m, 2H), 4.10-4.13 (m, 1H), 2.38-2.41 (m, 2H), 2.10-2,20 (m, 3H), 1.91-2.01 (m, 3H), 1.82-1.87 (m, 1H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.73 (s, 3H), 1.55 (H_2O), 1.44-1.49 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 138.4, 123.8, 109.0, 78.7, 75.9, 74.5, 41.4, 30.7, 27.7, 26.6, 24.3, 21.1, 4.0; HRMS (EI): *m/z* for $C_{14}H_{18}$ $[M-H_2O]^+$ calcd. 186.1409, found: 186.1418.

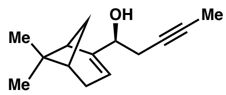


(*S*)-1-((*S*)-4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl)pent-3-yn-1-ol (5a). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 16 mg compound **5a** as colorless oil in 78% yield, d.r. > 20:1. $[\alpha]_D^{25}$ = −33.8° (c 0.53, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.74-5.77 (m, 1H), 4.69-4.73 (m, 2H), 4.07-4.13 (m, 1H), 2.33-2.45 (m, 2H), 2.14-2.20 (m, 2H), 1.91-2.12 (m, 4H), 1.82-1.86 (m, 1H), 1.81 (t, *J* = 2.5 Hz, 3H), 1.73 (s, 3H), 1.43-1.50 (m, 1H); ^{13}C NMR

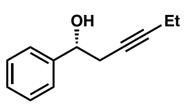
(151 MHz, $CDCl_3$) δ 150.1, 138.2, 122.6, 109.0, 78.8, 75.7, 74.2, 41.3, 30.6, 27.6, 26.9, 25.0, 21.2, 4.0; HRMS (EI): *m/z* for $C_{14}H_{18}$ $[M\text{-}H_2O]^+$ calcd. 186.1409, found: 186.1426.



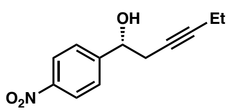
(*R*)-1-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)pent-3-yn-1-ol (4b). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 15 mg compound **4b** as colorless oil in 74% yield, d.r. = 12:1. $[\alpha]_D^{25}$ = −9.25° (c 0.40, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.49-5.53 (m, 1H), 4.08-4.14 (m, 1H), 2.38-2.43 (m, 1H), 2.28-2.37 (m, 3H), 2.19-2.27 (m, 2H), 2.07-2.12 (m, 1H), 1.96 (d, *J* = 3.0 Hz, 1H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.55 (H_2O), 1.28 (s, 3H), 1.17 (d, *J* = 8.6 Hz, 1H), 0.81 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.1, 119.1, 78.7, 75.7, 73.3, 42.1, 41.2, 38.2, 32.1, 31.4, 26.5, 26.3, 21.7, 3.9; HRMS (EI): *m/z* for $C_{14}H_{18}$ $[M\text{-}H_2O]^+$ calcd. 186.1409, found: 186.1421.



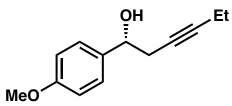
(*S*)-1-((1*R*,5*S*)-6,6-Dimethylbicyclo[3.1.1]hept-2-en-2-yl)pent-3-yn-1-ol (5b). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 17 mg compound **5b** as colorless oil in 83% yield, d.r. = 15:1. $[\alpha]_D^{25}$ = −29.6° (c 0.53, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 5.51-5.54 (m, 1H), 4.10 (app. t, *J* = 5.7 Hz, 1H), 2.35-2.41 (m, 2H), 2.21-2.31 (m, 3H), 2.16 (t, *J* = 5.2 Hz, 1H), 2.07-2.12 (m, 1H), 1.92 (s, 1H), 1.79 (t, *J* = 2.5 Hz, 3H), 1.28 (s, 3H), 1.16 (d, *J* = 8.6 Hz, 1H), 0.83 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.9, 118.3, 78.5, 75.8, 73.0, 42.7, 41.3, 38.2, 32.1, 31.4, 26.5, 26.1, 21.7, 3.9; HRMS (EI): *m/z* for $C_{14}H_{18}$ $[M\text{-}H_2O]^+$ calcd. 186.1409, found: 186.1417.



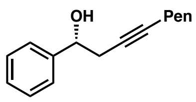
(*R*)-1-Phenylhex-3-yn-1-ol (6a). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 14 mg compound **6a** as colorless oil in 80% yield. The enantiomeric excess was determined by HPLC analysis to be 94% ee (254 nm, 25 °C); t_1 = 6.45 min, t_2 = 7.10 min [(Chiralpak IC) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 10.9° (c 0.53, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.34-7.39 (m, 4H), 7.27-7.31 (m, 1H), 4.82 (dd, *J* = 7.9, 4.7 Hz, 1H), 2.54-2.64 (m, 2H), 2.48 (br, 1H), 2.14-2.33 (m, 2H), 1.55 (H_2O), 1.15 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 128.7, 128.1, 126.1, 85.3, 75.7, 73.0, 30.5, 14.5, 12.8; HRMS (EI): *m/z* for $C_{12}H_{14}O$ $[M]^+$ calcd. 174.1045, found: 174.1049.



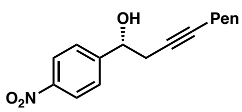
(*R*)-1-(4-Nitrophenyl)hex-3-yn-1-ol (6b). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 20 mg compound **6b** as colorless oil in 91% yield. The enantiomeric excess was determined by HPLC analysis to be 96% ee (254 nm, 25 ˚C); t_1 = 8.11 min, t_2 = 8.91 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 8.57° (c 1.67, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.6 Hz, 2H), 4.92 (dd, *J* = 7.2, 5.1 Hz, 1H), 2.64-2.69 (m, 1H), 2.54-2.62 (m, 2H), 2.18 (qt, *J* = 7.5, 2.2 Hz, 2H), 1.57 (H_2O), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 147.7, 127.0, 123.9, 86.2, 74.4, 71.9, 30.4, 14.4, 12.7; HRMS (EI): *m/z* for $C_{12}H_{12}NO_2$ $[M-OH]^+$ calcd. 202.0868, found: 202.0860.



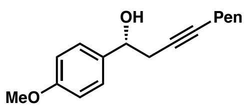
(*R*)-1-(4-Methoxyphenyl)hex-3-yn-1-ol (6c). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 13 mg compound **6c** as colorless oil in 64% yield. The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 ˚C); t_1 = 7.56 min, t_2 = 8.17 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 8.10° (c 0.73, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.77 (dd, *J* = 7.2, 5.5 Hz, 1H), 3.81 (s, 3H), 2.55-2.58 (m, 2H), 2.16-2.21 (m, 2H), 1.85 (br, 1H), 1.12 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 135.4, 127.3, 114.1, 85.2, 75.8, 72.6, 55.6, 30.4, 14.5, 12.8; HRMS (EI): *m/z* for $C_{13}H_{16}O_2$ $[M]^+$ calcd. 204.1150, found: 204.1130.



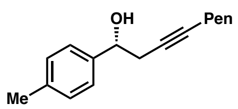
(*R*)-1-Phenylnon-3-yn-1-ol (6d). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 16 mg compound **6d** as colorless oil in 74% yield. The enantiomeric excess was determined by HPLC analysis to be 96% ee (254 nm, 25 ˚C); t_1 = 5.58 min, t_2 = 5.98 min [(Chiralpak IC) hexane/*i*-PrOH, 95:5, 1.0 mL/min]; $[\alpha]_D^{25}$ = 9.70° (c 1.00, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.33-7.40 (m, 4H), 7.27-7.30 (m, 1H), 4.81 (dd, *J* = 7.8, 4.9 Hz, 1H), 2.55-2.66 (m, 2H), 2.16 (tt, *J* = 7.1, 2.2 Hz, 2H), 1.94 (br, 1H), 1.55 (H_2O), 1.45-1.52 (m, 2H), 1.23-1.39 (m, 4H), 0.90 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 128.7, 128.1, 126.1, 84.0, 76.2, 72.9, 31.4, 30.5, 28.9, 22.6, 19.0, 14.4; HRMS (EI): *m/z* for $C_{15}H_{20}O$ $[M]^+$ calcd. 216.1514, found: 216.1527.



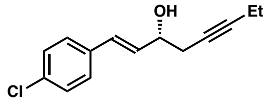
(*R*)-1-(4-Nitrophenyl)non-3-yn-1-ol (6e). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 24 mg compound **6e** as colorless oil in 92% yield. The enantiomeric excess was determined by HPLC analysis to be 95% ee (254 nm, 25 ˚C); t_1 = 7.05 min, t_2 = 7.73 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 8.10° (c 0.93, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 4.92 (dd, *J* = 7.2, 5.1 Hz, 1H), 2.65-2.70 (m, 1H), 2.54-2.61 (m, 1H), 2.15 (tt, *J* = 7.0, 2.1 Hz, 2H), 1.43-1.50 (m, 2H), 1.28-1.33 (m, 4H), 0.89 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 147.8, 127.0, 123.9, 85.1, 75.0, 71.9, 31.4, 30.4, 28.8, 22.5, 19.0, 14.3; HRMS (EI): *m/z* for $C_{15}H_{19}NO_3$ $[M]^+$ calcd. 261.1365, found: 261.1364.



(*R*)-1-(4-Methoxyphenyl)non-3-yn-1-ol (6f). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 15 mg compound **6f** as colorless oil in 61% yield. The enantiomeric excess was determined by Mosher ester analysis[2] to be 90% ee; $[\alpha]_D^{25}$ = 4.64° (c 0.73, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 8.6 Hz, 2H), 4.77 (dd, *J* = 7.2, 5.6 Hz, 1H), 3.80 (s, 3H), 2.54-2.62 (m, 2H), 2.14-2.19 (m, 2H), 1.45-1.51 (m, 2H), 1.25–1.36 (m, 4H), 0.89 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 135.3, 127.4, 114.1, 83.9, 76.4, 72.6, 55.6, 31.4, 30.4, 29.0, 22.6, 19.1, 14.3; HRMS (EI): *m/z* for $C_{16}H_{20}O$ $[M-H_2O]^+$ calcd. 228.1514, found: 228.1532.



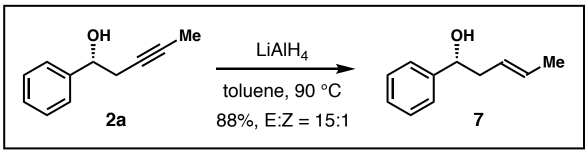
(*R*)-1-(*p*-Tolyl)non-3-yn-1-ol (6g). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 16 mg compound **6g** as colorless oil in 70% yield. The enantiomeric excess was determined by Mosher ester analysis[2] to be 93% ee; $[\alpha]_D^{25}$ = 4.62° (c 0.87, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 4.78 (dd, *J* = 7.6, 5.1 Hz, 1H), 2.54-2.64 (m, 2H), 2.34 (s, 3H), 2.16 (tt, *J* = 7.1, 2.2 Hz, 2H), 1.77 (br, 1H), 1.44-1.51 (m, 2H), 1.24–1.36 (m, 4H), 0.89 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 140.2, 137.8, 129.4, 126.0, 83.9, 76.4, 72.8, 31.4, 30.4, 29.0, 22.6, 21.5, 19.1, 14.3; HRMS (EI): *m/z* for $C_{16}H_{20}$ $[M-H_2O]^+$ calcd. 212.1565, found: 212.1578.



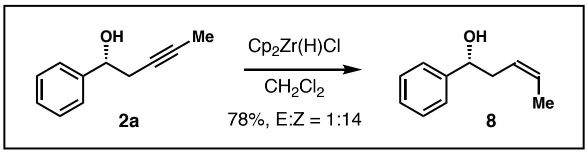
(*R*,*E*)-1-(4-Chlorophenyl)oct-1-en-5-yn-3-ol (6h). Prepared according to the general procedure. The crude mixture was purified by flash column chromatography to give 16 mg compound **6h** as colorless oil in 68% yield. The enantiomeric excess was determined by HPLC analysis to be 90% ee (254 nm, 25 ˚C); t_1 = 7.19 min, t_2 = 7.72 min [(Chiralpak IA) hexane/*i*-PrOH, 90:10, 1.0 mL/min]; $[\alpha]_D^{25}$ = 4.65° (c 0.73, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.6 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 6.60

(d, J = 15.9 Hz, 1H), 6.24 (dd, J = 15.9, 6.1 Hz, 1H), 4.40 (dt, J = 10.6, 5.2 Hz, 1H), 2.55 (ddt, J = 16.4, 5.0, 2.3 Hz, 1H), 2.47 (ddt, J = 16.4, 6.8, 2.3 Hz, 1H), 2.15-2.22 (m, 2H), 1.58 (H_2O), 1.13 (t, J = 7.5 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 135.4, 133.7, 131.4, 130.0, 129.1, 128.1, 85.6, 75.0, 71.1, 28.5, 14.5, 12.8; HRMS (EI): *m/z* for $C_{14}H_{15}ClO$ $[M]^+$ calcd. 234.0811, found: 234.0811.

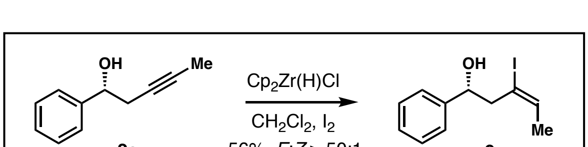
1 mmol-scale reaction: To a reaction flask containing a stirring bar and freshly activated 4 Å MS (500 mg) was added phosphoric acid (*R*)-$\mathbf{A_1}$ (38 mg, 0.05 mmol). Toluene (5 mL) was added to the flask followed by drop wise addition of freshly distilled benzaldehyde (106 mg, 1 mmol). The mixture was placed in a −45 ˚C cold bath and stirred for 15 min. Allenylboronate **1a** (216 mg, 1.2 mmol) was added slowly to the reaction mixture via a microliter syringe. The mixture was kept at −45 ˚C and stirred for 48 h. After complete consumption of benzaldehyde, saturated $NaHCO_3$ (10 mL) was added to the reaction mixture followed by slow addition of 30% H_2O_2 (2.5 mL) at 0 ˚C. The reaction was stirred vigorously for 3 h. Brine (10 mL) and Et_2O (10 mL) were added, the organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by flash chromatography (gradient elution with hexane and Et_2O, 50:1 to 2:1) provided 141 mg product **2a** in 88% yield with 95% ee.



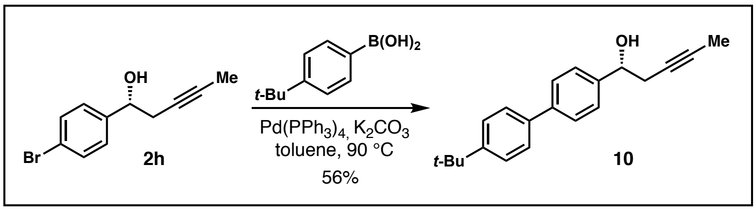
(*R,E*)-1-Phenylpent-3-en-1-ol (7): To an oven-dried 25 mL round-bottom flask equipped with a stirring bar was added lithium aluminum hydride powder (38 mg, 1.0 mmol, 3.3 equiv) and toluene (5 mL). The mixture was stirred for 5 minutes and a solution of alcohol **2a** (48 mg, 0.30 mmol) in toluene (5 mL) was added slowly to the flask. Then the flask was equipped with a condenser, the apparatus was placed under an argon atmosphere and the reaction mixture was stirred at 90 ˚C for 24 h. The reaction progress was monitored by TLC. After the complete consumption of alcohol **2a**, the mixture was cooled to ambient temperature and then placed in an ice bath. To the reaction mixture was added diethyl ether (10 mL), water (230 μL) dropwise via syringe, then 20 wt % KOH (230 μL), and then water (690 μL). The reaction mixture was stirred at room temperature for 1 h. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3 x 5 mL), and the combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The *E/Z* ratio (*E/Z* = 15:1) was determined by ^{1}H NMR of the crude reaction mixture. Purification of the crude product was performed by flash column chromatography to give allylic alcohol **7** in 88% yield (42 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33-7.42 (m, 4H), 7.26-7.31 (m, 1H), 5.58-5.65 (dqt, J = 15.2, 6.4, 1.3 Hz, 1H), 5.40-5.47 (m, 1H), 4.68 (dd, *J* = 8.4, 4.5 Hz, 1H), 2.43-2.50 (m, 1H), 2.35-2.42 (m, 1H), 1.78 (br, 1H), 1.70 (ddt, *J* = 6.4, 1.2, 1.2 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 129.9, 128.7, 127.7, 127.1, 126.1, 73.7, 43.2, 18.5; HRMS (EI): *m/z* for $C_{11}H_{12}$ $[M-H_2O]^+$ calcd. 144.0939, found: 144.0938.



(*Z*)-1-Phenylpent-3-en-1-ol (8): In an Ar-filled glove box, to a 20 mL oven-dried reaction flask equipped with a Teflon-coated magnetic stirring bar was added $Cp_2Zr(H)Cl$ (231 mg, 0.9 mmol). The flask was sealed with a rubber septum, removed from the glove box. CH_2Cl_2 (2.0 mL) was added to the reaction flask and the resulting suspension was stirred at ambient temperature for 5 minutes. To the suspension was added a solution of compound **2a** (48 mg, 0.3 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred at room temperature for 3 h to form a clear yellow solution. H_2O (1 mL) was added to the reaction mixture and the reaction was stirred for 30 minutes. Then brine (5 mL) and CH_2Cl_2 (5 mL) were added. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The *E/Z* ratio (*E/Z* = 1:14) was determined by ^{1}H NMR of the crude reaction mixture. Purification of the crude product was performed by flash column chromatography to give allylic alcohol **8** in 78% yield (38 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32-7.45 (m, 4H), 7.26-7.30 (m, 1H), 5.62-5.69 (dqt, *J* = 10.9, 6.8, 1.5 Hz, 1H), 5.39-5.46 (m, 1H), 4.72 (dd, *J* = 8.0, 5.2 Hz, 1H), 2.53-2.62 (m, 1H), 2.43-2.50 (m, 1H), 1.77 (br, 1H), 1.61 (app. dt, *J* = 6.8, 0.9 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.3, 128.7, 128.1, 127.8, 126.1, 125.9, 74.1, 37.2, 13.3; HRMS (EI): *m/z* for $C_{11}H_{12}$ $[M-H_2O]^+$ calcd. 144.0939, found: 144.0951.



(*E*)-3-Iodo-1-phenylpent-3-en-1-ol (9): In an Ar-filled glove box, to a 20 mL oven-dried reaction flask equipped with a Teflon-coated magnetic stirring bar was added $Cp_2Zr(H)Cl$ (154 mg, 0.6 mmol). The flask was sealed with a rubber septum, removed from the glove box. CH_2Cl_2 (2.0 mL) was added to the reaction flask and the resulting suspension was stirred at ambient temperature for 5 minutes. To the suspension was added a solution of compound **2a** (32 mg, 0.2 mmol) in CH_2Cl_2 (2 mL). The resulting mixture was stirred at room temperature for 3 h to form a clear yellow solution. A solution of I_2 (101 mg, 0.4 mmol) in CH_2Cl_2 (2.0 mL) was added and the reaction mixture was stirred for 30 minutes. Then CH_2Cl_2 (5 mL), a solution of saturated $Na_2S_2O_3$ (5 mL) and a solution of saturated $NaHCO_3$ (5 mL) were added sequentially. After stirring at ambient temperature for 1 h, the organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The *E/Z* ratio (*E/Z* > 50:1) was determined by ^{1}H NMR of the crude reaction mixture. Purification of the crude product was performed by chromatography to give compound **9** in 56% yield (32 mg) as colorless oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39-7.43 (m, 2H), 7.33-7.38 (m, 2H), 7.27-7.31 (m, 1H), 6.37 (q, J = 7.1 Hz, 1H), 4.99 (dd, J = 8.2, 4.9 Hz, 1H), 2.94 (dd, J = 14.3, 8.3 Hz, 1H), 2.67 (ddt, J = 14.3, 4.9, 0.9 Hz, 1H), 1.63 (br, 1H), 1.53 (d, J = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.3, 139.6, 128.8, 128.1, 126.2, 97.6, 73.2, 48.4, 16.9; HRMS (EI): *m/z* for $C_{11}H_{11}I$ $[M-H_2O]^+$ calcd. 269.9892, found: 269.9886.



(*R*)-1-(4'-(Tert-butyl)-[1,1'-biphenyl]-4-yl)pent-3-yn-1-ol (10): In an Ar-filled glove box, $Pd(PPh_3)_4$ (6 mg, 0.005 mmol, 3 mol %), (4-(*tert*-butyl)phenyl)boronic acid (77 mg, 0.43 mmol, 2.5 equiv), K_2CO_3 (47 mg, 0.34 mmol, 2.0 equiv), toluene (1.0 mL) and a Teflon-coated magnetic stirring bar were sequentially added into a 1-dram vial. The mixture was stirred for 15 min and alcohol **2h** (40 mg, 0.17 mmol) was added. The vial was sealed with a cap containing a PTFE-lined silicone septum, removed from the glove box and stirred at 90 ˚C for 36 h. The reaction progress was monitored by TLC. After the complete consumption of alcohol **2h**, the reaction mixture was cooled to room temperature and EtOAc (1 mL) was added. The resulting mixture was filtered through a short pad of Celite. Brine (5 mL) and EtOAc (5 mL) were added; the organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic extracts were dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. Purification of the crude product was performed by chromatography to give compound **10** in 56% yield (28 mg) as colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.1 Hz, 2H), 4.86 (dd, J = 7.9, 4.8 Hz, 1H), 2.55-2.69 (m, 2H), 1.83 (t, J = 2.3 Hz, 3H), 1.37 (s, 9H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7, 141.9, 140.9, 138.3, 127.3, 127.1, 126.5, 126.1, 79.1, 75.6, 72.8, 34.9, 31.7, 30.3, 3.9; HRMS (EI): *m/z* for $C_{21}H_{24}O$ $[M]^+$ calcd. 292.1827, found: 292.1798.

Computational studies: The density functional theory was employed combined with the cc-pVDZ basis set.[3] Implicit solvent effects were considered via the SMD solvation model with a dielectric constant of 2.3741 (toluene). Dispersion effects were incorporated in using the B97D functional which includes dispersion by construction.[4] Harmonic vibrational frequencies were calculated to ensure that the existence of only one imaginary frequency for every transition state. The harmonic approximation was subsequently used to calculate free energies at −40 ˚C. The Gaussian16 electronic structure package was invoked.[5]

Table S1. Cartesian coordinates and absolute electronic energies of the transition states **TS-1**, **TS-2**, **TS-3**, and **TS-4** at the B97D/cc-pVDZ level of theory with temperature and solvent corrections.

TS-1 (Energy = -3492.38302909 a.u.)

C	-4.016666	-0.226088	0.350272
C	-3.984605	-1.254217	1.329805
C	-4.506155	-2.519696	0.995354
C	-5.034221	-2.800398	-0.274824
C	-5.011155	-1.778936	-1.239712
C	-4.512662	-0.495392	-0.954058
O	-1.522075	0.805420	-0.540394
P	-0.164511	0.199150	0.228839
C	-2.313365	1.667068	0.226606
O	0.694761	-0.304354	-1.012327
O	0.568846	1.589138	0.783217
C	-1.872462	2.976587	0.443558
C	-3.561994	1.161230	0.695979
C	0.577995	2.728952	-0.020421
C	-0.607352	3.450160	-0.193558
C	-4.362919	2.018507	1.439121
C	1.836919	3.126905	-0.561975
C	1.875009	4.308312	-1.291801

TS-2 (Energy = -3492.37743396 a.u.)

B	-0.129222	-3.857225	0.389115
C	0.995754	-4.262539	-0.898773
C	0.291289	-4.698699	-1.880590
C	-0.858288	-4.827730	-2.614613
C	2.462637	-4.091545	-0.634789
O	-0.359428	-5.025493	1.197916
C	-0.468188	-4.566624	2.571782
O	0.399649	-2.799605	1.263230
C	0.549358	-3.364854	2.611914
C	-1.918894	-4.113874	2.828365
H	-2.185321	-3.252371	2.192774
H	-2.598995	-4.951240	2.585009
H	-2.073118	-3.831335	3.886586
C	-0.107462	-5.724332	3.503999
H	-0.873530	-6.518408	3.424120
H	0.871913	-6.160046	3.241938
H	-0.076465	-5.378574	4.554997
C	0.228076	-2.279551	3.639349

C	3.071205	2.296665	-0.374178
C	3.626739	1.609838	-1.488609
C	4.832386	0.902250	-1.321008
C	5.491944	0.832849	-0.083612
C	4.901617	1.485746	1.011286
C	3.704017	2.215166	0.895624
O	-0.408906	-0.721304	1.397203
H	-4.498415	-3.317320	1.747889
H	-5.401271	-1.982491	-2.243911
H	-5.343595	1.672167	1.784583
H	2.831666	4.655981	-1.696905
H	5.254328	0.378742	-2.184104
H	5.392410	1.424424	1.991078
H	0.714286	-1.374762	-1.071501
C	3.308276	-2.918764	-1.348772
C	3.592507	-2.141784	-0.363750
C	3.480048	-1.697121	0.926440
O	1.550296	-4.863786	-1.716156
B	1.800495	-3.715664	-0.909842
O	1.943572	-4.024046	0.556394
O	0.674099	-2.771116	-1.145682
C	1.906247	-2.996816	1.387974
C	-0.231525	-3.351130	-2.141560
C	2.171641	-3.258508	2.819399
C	2.898233	-4.388166	3.254740
C	1.674585	-2.332053	3.763607
C	1.905613	-2.534764	5.132202
C	3.127147	-4.583853	4.623812
C	2.634992	-3.657724	5.564428
C	0.127030	-4.880859	-2.019106
C	-0.614401	-5.559971	-0.852502
C	-0.082764	-5.676965	-3.307728
C	-1.661703	-2.973599	-1.755772
C	0.124470	-2.753574	-3.510177
C	3.868279	-3.173398	-2.716068
H	1.154291	-2.221009	1.181310
H	3.271348	-5.102613	2.512669
H	1.091628	-1.473390	3.409828
H	1.511899	-1.818517	5.863622
H	3.689445	-5.462589	4.963170
H	2.816884	-3.815451	6.634775
H	-0.515452	-4.971758	0.076309
H	-0.171076	-6.558377	-0.683433
H	-1.689431	-5.683337	-1.081699
H	-0.756798	-1.822953	3.458362
H	0.996422	-1.486292	3.602676
H	0.234716	-2.717533	4.655472
C	2.006625	-3.820707	2.770085
H	2.227202	-4.670959	2.104553
H	2.676164	-2.980934	2.514234
H	2.207625	-4.128265	3.813197
O	-1.336277	-3.292287	-0.315140
C	-2.059757	-4.084397	-1.074988
H	-2.260378	-5.096777	-0.680556
C	-3.121382	-3.447226	-1.887406
C	-4.202792	-4.230362	-2.345603
C	-3.038335	-2.082061	-2.241455
C	-5.194824	-3.654763	-3.153041
C	-4.030179	-1.515005	-3.051379
C	-5.107011	-2.297204	-3.510473
H	-4.260668	-5.289651	-2.064046
H	-2.184668	-1.490389	-1.895361
H	-6.038548	-4.262933	-3.500994
H	-3.960099	-0.457217	-3.322621
H	-5.880395	-1.847238	-4.145107
O	-0.814190	1.532007	-0.687652
P	0.105145	0.193095	-0.305612
O	1.438530	0.885276	0.446361
O	0.375855	-0.608421	-1.547059
O	-0.618409	-0.482508	0.953565
H	-0.238237	-1.442475	1.092794
C	-0.906459	2.594835	0.212003
C	0.205011	3.414809	0.429346
C	-2.189091	2.836293	0.793610
C	-2.312032	3.912601	1.662099
H	-3.289471	4.133683	2.105171
C	2.085233	1.908221	-0.244902
C	1.482183	3.167846	-0.303293
C	3.371028	1.621719	-0.794783
C	4.018020	2.640997	-1.481807
H	5.012472	2.454263	-1.903026
C	4.018970	0.284357	-0.603562
C	4.202562	-0.582911	-1.714488
C	4.486767	-0.099034	0.682527
C	4.895597	-1.791934	-1.520244
C	5.153436	-1.330147	0.827024
C	5.377766	-2.187967	-0.262261
H	5.045378	-2.462382	-2.375365

H	0.177651	-6.737809	-3.134000
H	0.551290	-5.293368	-4.125504
H	-1.142468	-5.628542	-3.623308
H	-1.804467	-1.883466	-1.853208
H	-1.893848	-3.255781	-0.716729
H	-2.380398	-3.469186	-2.431937
H	1.135138	-3.062587	-3.827750
H	0.091165	-1.651065	-3.445284
H	-0.601002	-3.077891	-4.278992
C	3.142116	2.897410	2.143385
C	4.132721	3.939856	2.702941
C	2.765759	1.860251	3.222677
H	2.220495	3.436732	1.865163
H	4.387847	4.698408	1.937536
H	3.691769	4.459790	3.576457
H	5.074061	3.457892	3.033547
H	2.003299	1.158429	2.841327
H	3.653216	1.279133	3.543295
H	2.352140	2.369174	4.116081
C	2.953818	1.601109	-2.862856
C	2.893919	0.185267	-3.473821
C	3.668734	2.565814	-3.832579
H	1.914190	1.948894	-2.735729
H	2.470088	-0.533979	-2.754752
H	2.262873	0.195539	-4.384050
H	3.899607	-0.168906	-3.772759
H	3.673008	3.603136	-3.448923
H	4.722384	2.254152	-3.981330
H	3.167639	2.564718	-4.821389
C	6.827941	0.117919	0.092112
C	7.985261	1.122021	-0.112590
C	7.011880	-1.103142	-0.827043
H	6.872397	-0.234223	1.143023
H	7.892173	1.983632	0.576278
H	8.965166	0.634756	0.064371
H	7.974451	1.512625	-1.150138
H	6.178562	-1.823081	-0.718002
H	7.068240	-0.800109	-1.891149
H	7.957273	-1.624921	-0.582124
C	-3.416294	-1.018299	2.730092
C	-2.581104	-2.208128	3.244354
C	-4.547984	-0.696723	3.729882
H	-2.740566	-0.147341	2.674616
H	-1.815535	-2.499887	2.505580
H	5.508426	-1.619222	1.822521
C	-3.362527	1.971410	0.450055
C	-3.901339	1.082234	1.419586
C	-3.940581	2.048254	-0.844916
C	-5.011144	0.292239	1.071239
C	-5.046859	1.231012	-1.144379
C	-5.591293	0.339379	-0.207248
H	-5.422669	-0.398555	1.814762
H	-5.493085	1.284845	-2.145334
C	3.657403	-0.257225	-3.105601
C	2.836632	-1.424594	-3.692486
C	4.800343	0.141340	-4.062472
H	2.973261	0.603587	-3.012427
H	2.017711	-1.704221	-3.007811
H	2.393370	-1.118794	-4.661070
H	3.472143	-2.312256	-3.883144
H	5.368399	1.009607	-3.676259
H	5.512084	-0.698823	-4.193059
H	4.396902	0.406432	-5.060291
C	4.302814	0.772877	1.925770
C	5.660621	1.167651	2.543165
C	3.407930	0.064246	2.964368
H	3.794932	1.707596	1.634232
H	6.293159	1.702009	1.807757
H	5.506808	1.830502	3.417833
H	6.217781	0.274166	2.887730
H	2.431933	-0.194111	2.518443
H	3.887365	-0.865458	3.329852
H	3.232517	0.723164	3.837992
C	6.147036	-3.496120	-0.112973
C	5.805297	-4.261654	1.179439
C	7.666621	-3.229294	-0.194731
H	5.869859	-4.136914	-0.974206
H	4.716220	-4.425173	1.277548
H	6.310917	-5.247016	1.183839
H	6.149670	-3.709380	2.075740
H	7.932910	-2.724254	-1.143348
H	7.987597	-2.575599	0.641207
H	8.236740	-4.177991	-0.130253
C	-3.424281	3.003650	-1.921185
C	-4.484806	4.074643	-2.253663
C	-2.986714	2.249022	-3.192638
H	-2.537922	3.531490	-1.530551
H	-4.766922	4.650375	-1.350654

H	-2.065537	-1.923752	4.182302
H	-3.217948	-3.086369	3.470765
H	-5.116959	0.201987	3.427943
H	-5.258313	-1.545721	3.794859
H	-4.131968	-0.518062	4.741844
C	-4.523947	0.558949	-2.062492
C	-5.946250	0.787194	-2.615114
C	-3.548469	0.179005	-3.197324
H	-4.180681	1.518798	-1.639138
H	-6.647171	1.076183	-1.807889
H	-5.937710	1.593152	-3.375495
H	-6.340261	-0.129064	-3.097729
H	-2.514815	0.099903	-2.815930
H	-3.830633	-0.791184	-3.652455
H	-3.568236	0.949521	-3.993792
C	-5.635405	-4.166078	-0.591376
C	-4.914919	-4.860910	-1.764743
C	-7.146551	-4.043993	-0.882551
H	-5.509776	-4.799862	0.308951
H	-3.840744	-5.003633	-1.544405
H	-5.366851	-5.852927	-1.963724
H	-4.998953	-4.258286	-2.690849
H	-7.680599	-3.575131	-0.033443
H	-7.320213	-3.418656	-1.780888
H	-7.591319	-5.041866	-1.069057
H	-4.925893	6.072899	3.625084
C	-4.303475	5.439096	2.981761
C	-4.739788	4.174851	2.613816
H	-5.705530	3.790792	2.965949
C	-3.937334	3.334257	1.783350
C	-2.667528	3.824402	1.297473
C	-2.240206	5.122551	1.713300
H	-1.266683	5.493816	1.380385
C	-3.036726	5.908556	2.535234
H	-2.682890	6.899209	2.845929
H	-2.579466	7.014533	-2.484719
C	-1.663316	6.476329	-2.212448
C	-0.405444	6.935724	-2.693149
H	-0.354687	7.831914	-3.323418
C	0.749960	6.236627	-2.377030
H	1.725436	6.563945	-2.758574
C	0.698595	5.063527	-1.563565
C	-0.572516	4.620351	-1.037124
C	-1.745067	5.349365	-1.405616
H	-4.096232	4.783558	-3.011942
H	-5.403933	3.607828	-2.660717
H	-2.221457	1.488618	-2.955212
H	-3.851081	1.747588	-3.672087
H	-2.559319	2.956682	-3.930166
C	-3.311612	0.950430	2.823991
C	-3.143454	-0.521887	3.248842
C	-4.178026	1.708041	3.852499
H	-2.306945	1.407431	2.817875
H	-2.590192	-1.082657	2.477229
H	-2.582869	-0.578512	4.201873
H	-4.120929	-1.016855	3.409423
H	-4.266033	2.781602	3.599632
H	-5.201405	1.282701	3.883672
H	-3.739934	1.625079	4.867496
C	-6.777008	-0.548784	-0.563300
C	-8.069861	-0.030385	0.102369
C	-6.524008	-2.023174	-0.189487
H	-6.911252	-0.492670	-1.661852
H	-8.284954	1.013721	-0.197789
H	-8.936980	-0.661312	-0.179173
H	-7.973361	-0.054012	1.206479
H	-5.576030	-2.387500	-0.623850
H	-6.471324	-2.147823	0.910345
H	-7.349738	-2.662570	-0.559373
C	3.417828	3.919004	-1.671735
C	2.126348	4.194930	-1.084142
C	1.530607	5.469878	-1.331339
H	0.540830	5.684459	-0.918275
C	2.185307	6.430275	-2.090890
H	1.703452	7.399002	-2.271292
C	3.470469	6.167594	-2.642095
H	3.978702	6.937242	-3.235771
C	4.069629	4.933328	-2.437543
H	5.053218	4.709160	-2.869571
H	1.915177	6.873590	3.064275
C	1.044254	6.281366	2.757836
C	-0.230141	6.551511	3.329705
H	-0.339911	7.357305	4.065758
C	-1.326119	5.783685	2.964458
H	-2.312431	5.966467	3.409570
C	-1.197310	4.727181	2.011932
C	0.088085	4.474196	1.402388
C	1.199431	5.270257	1.818855

H	-2.719958	5.006125	-1.048809
H	3.221485	-2.707264	-3.483096
H	3.883885	-4.259400	-2.918886
H	4.886531	-2.756916	-2.817130
H	4.243933	-2.015811	1.651357
H	3.038212	-0.709683	1.118892

TS-3 (Energy = -3492.36857219 a.u.)

B	-3.233149	2.676302	-1.095800
C	-2.320356	4.088039	-0.595173
C	-1.960063	3.923086	0.629321
C	-1.993117	3.332679	1.863683
C	-2.099101	5.158890	-1.624980
O	-2.290174	1.714111	-1.734171
C	-3.038610	1.103859	-2.852787
O	-4.228298	3.000645	-2.068048
C	-3.945811	2.305506	-3.305685
C	-3.842722	-0.079502	-2.290525
H	-4.604109	0.268930	-1.571536
H	-3.160446	-0.772575	-1.770722
H	-4.350368	-0.629028	-3.104427
C	-2.033101	0.624569	-3.898112
H	-1.444348	-0.216244	-3.498493
H	-1.338210	1.430559	-4.188377
H	-2.569854	0.273805	-4.800058
C	-5.278013	1.875314	-3.929333
H	-5.891443	1.305037	-3.211332
H	-5.847717	2.772829	-4.235298
H	-5.104310	1.253104	-4.828369
C	-3.215870	3.263731	-4.264084
H	-2.214791	3.521590	-3.880340
H	-3.808672	4.191520	-4.362257
H	-3.102659	2.813379	-5.267988
O	-3.888676	2.143127	0.155153
C	-3.112286	1.724956	1.134584
H	-2.190662	1.197139	0.856280
C	-3.761851	1.252103	2.375654
C	-3.024733	0.398150	3.225231
C	-5.092999	1.592773	2.699159
C	-3.619964	-0.118792	4.384860
C	-5.680591	1.075792	3.861553
C	-4.947911	0.218624	4.705358
H	-1.993762	0.139367	2.958261
H	-5.657736	2.244348	2.023863

H	2.186510	5.071009	1.392454
H	3.044549	-4.157387	-1.569294
H	2.819113	-4.872570	0.062822
H	2.644251	-3.113867	-0.160087
H	-1.301417	-5.821558	-2.782400
H	-1.041444	-4.090177	-3.411016

TS-4 (Energy = -3492.38115447 a.u.)

B	1.275224	-3.805388	-1.087581
C	2.601399	-4.112753	-2.213274
C	3.674742	-4.235604	-1.517321
C	4.435527	-4.080477	-0.387467
C	2.249967	-4.222561	-3.667649
O	0.645847	-5.052099	-0.767438
C	-0.775180	-4.771342	-0.619251
O	0.267354	-2.924632	-1.686422
C	-1.024297	-3.636234	-1.690127
O	1.892267	-3.056004	0.062957
C	2.778758	-3.682015	0.804094
H	2.596435	-4.757636	0.979829
C	3.389987	-2.917884	1.917020
C	4.237725	-3.588790	2.827039
C	3.124463	-1.542584	2.090458
C	4.823060	-2.890819	3.891494
C	3.706129	-0.851011	3.161903
C	4.559444	-1.517721	4.059024
H	4.435671	-4.659798	2.692146
H	2.443230	-1.034175	1.404830
H	5.481930	-3.415767	4.593822
H	3.487738	0.213217	3.292079
H	5.015039	-0.970313	4.893468
H	-5.162465	2.174286	1.990080
C	-4.202562	2.387841	1.506070
C	-3.535595	1.367780	0.841197
C	-3.667871	3.705924	1.590094
C	-2.312869	1.694836	0.181946
C	-2.424181	4.014578	0.921530
C	-1.773194	2.983694	0.151052
O	-1.679186	0.684318	-0.538068
C	-0.535440	3.258086	-0.636251
P	-0.238585	0.062173	0.059018
C	0.621331	2.509828	-0.402390
C	-0.484206	4.285615	-1.647350
O	0.581907	1.448733	0.505510

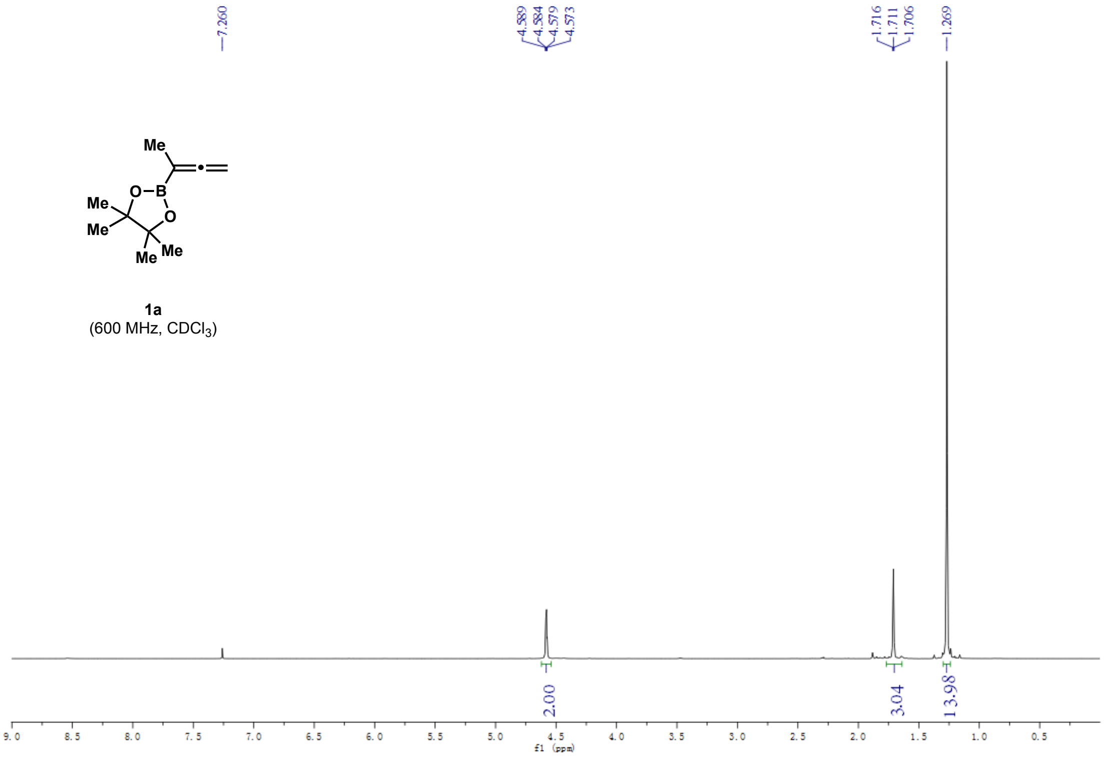
H	-3.047343	-0.788527	5.037363	O	-0.349264	-0.859093	1.240504
H	-6.718056	1.332120	4.108694	O	0.433215	-0.438289	-1.299999
H	-5.414267	-0.188157	5.611162	C	1.892001	2.825008	-0.972677
H	5.728911	1.589314	0.930675	C	0.780544	4.585064	-2.279030
C	5.057627	0.761714	0.679849	C	-1.641763	5.004718	-2.076136
C	3.750714	1.041729	0.307387	H	0.351048	-1.477695	-1.423337
C	5.520265	-0.574353	0.840359	C	1.947685	3.865345	-1.889794
C	2.929587	-0.054418	-0.098406	C	0.840131	5.606859	-3.275003
C	4.627673	-1.674015	0.557764	H	2.913599	4.145783	-2.325369
C	3.331430	-1.392832	-0.022509	C	-1.552354	5.984221	-3.056322
O	1.691304	0.259100	-0.668534	C	-0.300993	6.297601	-3.656473
C	2.437795	-2.491596	-0.490744	H	-2.456832	6.517553	-3.373531
P	0.306870	-0.022407	0.215846	H	-2.610389	4.769276	-1.625520
C	1.100876	-2.551016	-0.085594	H	1.810148	5.827302	-3.738494
C	2.918881	-3.542187	-1.362084	H	-0.243577	7.077311	-4.425823
O	0.584402	-1.566203	0.760760	H	5.449879	-0.200299	-1.471167
O	0.037614	0.887068	1.386953	C	4.958123	0.554517	-0.848103
O	-0.794236	-0.134769	-0.932328	C	5.523844	0.888775	0.395221
C	0.225596	-3.638759	-0.397462	C	6.821098	0.245454	0.871498
C	2.086348	-4.699401	-1.592667	C	4.866453	1.846606	1.182509
H	-1.380244	0.718878	-1.157620	H	5.291255	2.110925	2.159221
C	0.762062	-4.726335	-1.069123	C	3.679725	2.475351	0.760408
H	0.129844	-5.597913	-1.270967	C	3.026424	3.506277	1.682436
C	2.578416	-5.768436	-2.401736	C	3.133679	2.126843	-0.503092
C	3.826284	-5.690304	-3.003019	C	3.767783	1.145700	-1.310764
C	4.624493	-4.526959	-2.824293	C	3.190035	0.731361	-2.663308
C	4.183383	-3.481902	-2.022987	C	3.911097	1.467551	-3.812266
H	1.934919	-6.643853	-2.556287	C	3.240885	-0.792660	-2.885033
H	4.190148	-6.512969	-3.630624	H	3.817450	2.565456	-3.712819
H	5.595741	-4.450024	-3.327989	H	3.483720	1.171671	-4.791520
H	4.806396	-2.591984	-1.898331	H	4.991125	1.216223	-3.817816
C	6.826408	-0.839863	1.354313	H	4.279756	-1.153150	-3.022153
C	7.232383	-2.136768	1.630654	H	2.676506	-1.056845	-3.799746
H	8.233649	-2.329371	2.034848	H	2.797043	-1.332614	-2.032847
C	6.333026	-3.217130	1.414540	C	6.757848	-1.293980	0.822946
H	6.638622	-4.239486	1.668309	C	8.021398	0.764842	0.051201
C	5.066223	-2.992231	0.891914	H	5.888593	-1.675413	1.388066
H	4.388595	-3.836055	0.738844	H	7.679394	-1.733500	1.253351
H	7.491465	0.010794	1.549949	H	6.679097	-1.646712	-0.224540
C	-5.434507	-3.093655	1.026045	C	2.530968	2.850998	2.988458
C	-3.966806	-3.319752	0.679952	C	3.981827	4.679458	1.983711
C	-2.976576	-3.484387	1.661765	H	4.882691	4.331743	2.526808
H	-3.264534	-3.519554	2.717719	H	3.475264	5.435623	2.615927
C	-1.615930	-3.607267	1.329149	H	4.315461	5.172740	1.050026

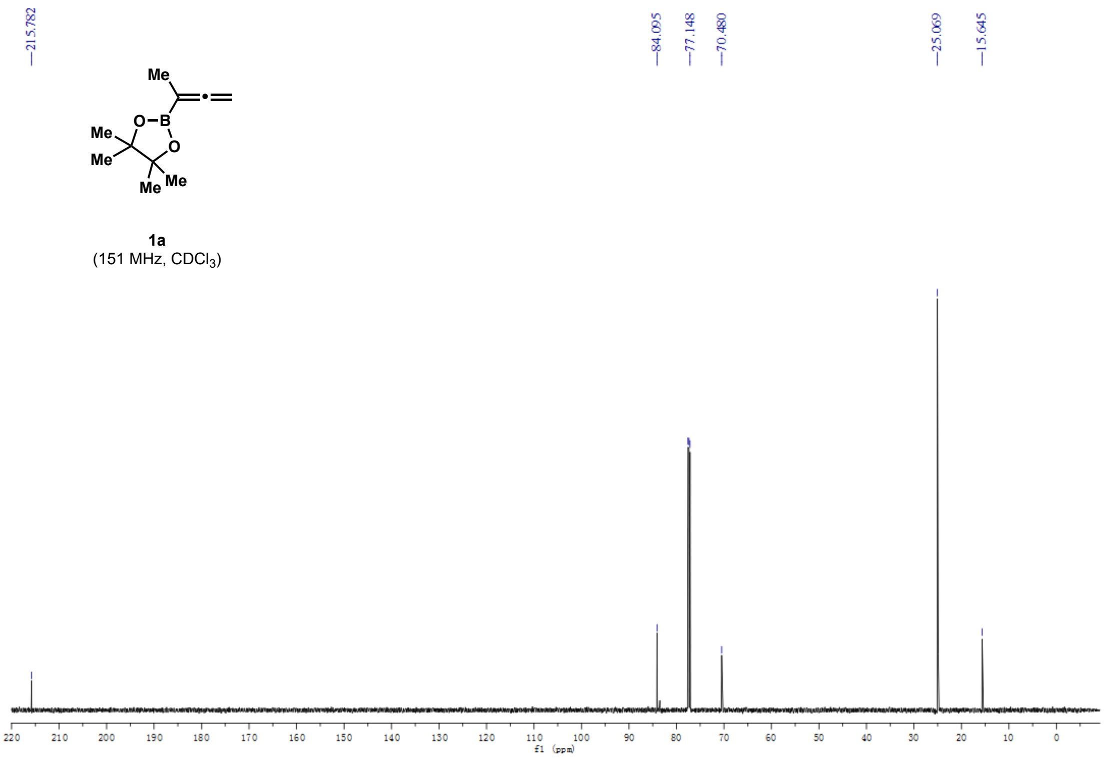
C	-0.615259	-3.847413	2.461621	H	1.832318	2.022061	2.774476
C	-1.223573	-3.562592	-0.037613	H	2.006912	3.597246	3.617973
C	-2.205694	-3.404210	-1.056077	H	3.383108	2.453597	3.575551
C	-1.970700	-3.371063	-2.578165	H	7.910356	0.486956	-1.016242
C	-3.555339	-3.291929	-0.661439	H	8.969473	0.326018	0.422215
H	-4.318153	-3.159446	-1.440939	H	8.099505	1.867881	0.109303
C	-5.897538	-3.847036	2.286011	C	-1.541863	-6.068538	-0.882254
H	-6.032528	-3.458947	0.166345	C	-1.040542	-4.279823	0.816263
C	-5.698964	-1.579343	1.181225	C	-2.134474	-2.647982	-1.336919
H	-5.106912	-1.173007	2.021694	C	-1.239662	-4.183282	-3.107154
H	-6.771056	-1.386386	1.387135	C	-4.333763	4.725292	2.336598
H	-5.412798	-1.026491	0.266576	C	-1.880938	5.326847	1.079897
H	-5.666620	-4.928138	2.222562	C	-2.546133	6.291413	1.824844
H	-6.990490	-3.729486	2.419078	C	-3.789631	5.996170	2.450164
H	-5.409610	-3.442513	3.194545	H	-5.281477	4.474915	2.829996
C	-0.848241	-5.237134	3.092975	H	-0.923260	5.567453	0.609586
C	-0.673795	-2.741371	3.534407	H	-2.104720	7.289417	1.935719
H	0.404588	-3.848319	2.041463	H	-4.307332	6.769611	3.030535
H	-1.857326	-5.299409	3.546783	C	-4.112449	-0.014308	0.748951
H	-0.101053	-5.431948	3.888099	C	-3.889093	-0.956741	1.787621
H	-0.766495	-6.038943	2.333373	C	-3.078855	-0.588370	3.031041
H	-1.661045	-2.725626	4.036386	C	-4.475547	-2.232171	1.674218
H	-0.488940	-1.749473	3.085713	H	-4.315560	-2.968846	2.470120
H	0.096104	-2.921908	4.310561	C	-5.264446	-2.597752	0.570540
C	-0.670825	-2.741909	-3.124465	C	-5.921281	-3.972843	0.504543
H	-2.795209	-2.741369	-2.964898	C	-5.459422	-1.649641	-0.447840
C	-2.177405	-4.778400	-3.183146	H	-6.064946	-1.918360	-1.320765
H	-1.381221	-5.470095	-2.847781	C	-4.897098	-0.361852	-0.382233
H	-2.140973	-4.729142	-4.290230	C	-5.123197	0.610160	-1.541943
H	-3.153548	-5.206309	-2.883814	C	-5.645200	-4.699506	-0.826515
H	-0.365867	-1.854872	-2.546785	C	-7.441353	-3.854488	0.749259
H	-0.846405	-2.430713	-4.172833	H	-4.559022	-4.811795	-1.003965
H	0.171539	-3.452483	-3.132506	H	-6.074953	-4.142845	-1.682327
H	2.272624	5.076695	-1.572842	H	-6.101631	-5.708850	-0.818292
C	2.490840	4.510178	-0.659773	H	-7.651837	-3.366262	1.720492
C	2.913605	3.174955	-0.775567	H	-7.919431	-4.854711	0.748553
C	3.069741	2.585652	-2.178080	H	-7.915435	-3.246498	-0.047088
C	3.216962	2.435970	0.402392	C	-2.280596	-1.764283	3.624165
C	3.044307	3.032802	1.684395	C	-4.007960	0.011415	4.109600
C	3.284639	2.372607	3.056851	H	-4.540050	0.906168	3.738426
C	2.620935	4.378256	1.736029	H	-3.422875	0.303944	5.004611
H	2.487286	4.848279	2.720418	H	-4.766760	-0.734610	4.421831
C	2.353175	5.138464	0.589324	H	-1.657329	-2.250765	2.855883
C	1.926380	6.597199	0.698626	H	-2.948320	-2.520344	4.083960

C	4.173828	3.322684	-2.965636
C	1.734880	2.611255	-2.952846
H	3.382371	1.532136	-2.088398
H	3.913665	4.390354	-3.107947
H	4.304784	2.866530	-3.967227
H	5.143399	3.276303	-2.432380
H	1.408627	3.653027	-3.144432
H	0.937919	2.093928	-2.390368
H	1.852094	2.109195	-3.933885
C	0.520697	6.814532	0.105418
C	2.951341	7.531479	0.022047
H	1.888840	6.851797	1.776465
H	0.515690	6.577925	-0.975872
H	0.201403	7.869108	0.225709
H	-0.223769	6.161822	0.599614
H	3.019216	7.317000	-1.063045
H	3.960666	7.402339	0.458678
H	2.651125	8.591690	0.141234
C	2.909010	0.886205	3.226286
H	2.612299	2.927434	3.741503
C	4.718996	2.637106	3.569979
H	5.465299	2.057406	2.996181
H	4.802425	2.331555	4.632546
H	4.981695	3.710417	3.495835
H	1.918714	0.672675	2.791001
H	2.867481	0.658356	4.310491
H	3.650152	0.203319	2.778070
H	-1.817686	6.116813	-1.156814
H	-3.017340	5.287034	-2.223073
H	-1.290695	4.854592	-2.317926
H	-1.112933	2.782835	2.223444
H	-2.652224	3.767845	2.631159
H	-1.611343	-1.388215	4.422055
C	-6.614049	0.741964	-1.913375
C	-4.284896	0.195224	-2.770003
H	-7.222137	1.030355	-1.033940
H	-7.019088	-0.208865	-2.312207
H	-6.744350	1.514537	-2.696598
H	-3.209520	0.169006	-2.519812
H	-4.435309	0.914025	-3.600442
H	-4.585827	-0.810061	-3.126958
H	-4.776372	1.610397	-1.227328
H	-5.490850	-4.583813	1.323023
H	-2.347784	0.184296	2.734500
H	6.971401	0.548191	1.926936
H	2.144547	3.927693	1.170604
H	2.126631	1.025770	-2.676556
H	-2.632902	-5.887175	-0.859840
H	-1.299641	-6.803432	-0.091571
H	-1.270700	-6.506723	-1.858235
H	-2.232631	-4.662099	-3.193009
H	-0.466581	-4.925389	-3.368051
H	-1.192275	-3.348479	-3.830664
H	-3.107343	-3.169099	-1.326881
H	-2.186123	-1.852138	-2.099940
H	-1.988993	-2.185195	-0.349320
H	-2.124474	-4.154210	0.993954
H	-0.548118	-3.311379	1.006524
H	-0.649424	-5.031443	1.527264
H	1.569076	-3.399869	-3.945959
H	1.709112	-5.171298	-3.851584
H	3.150490	-4.195438	-4.306739
H	5.028339	-3.159162	-0.283934
H	4.845423	-4.963696	0.125258

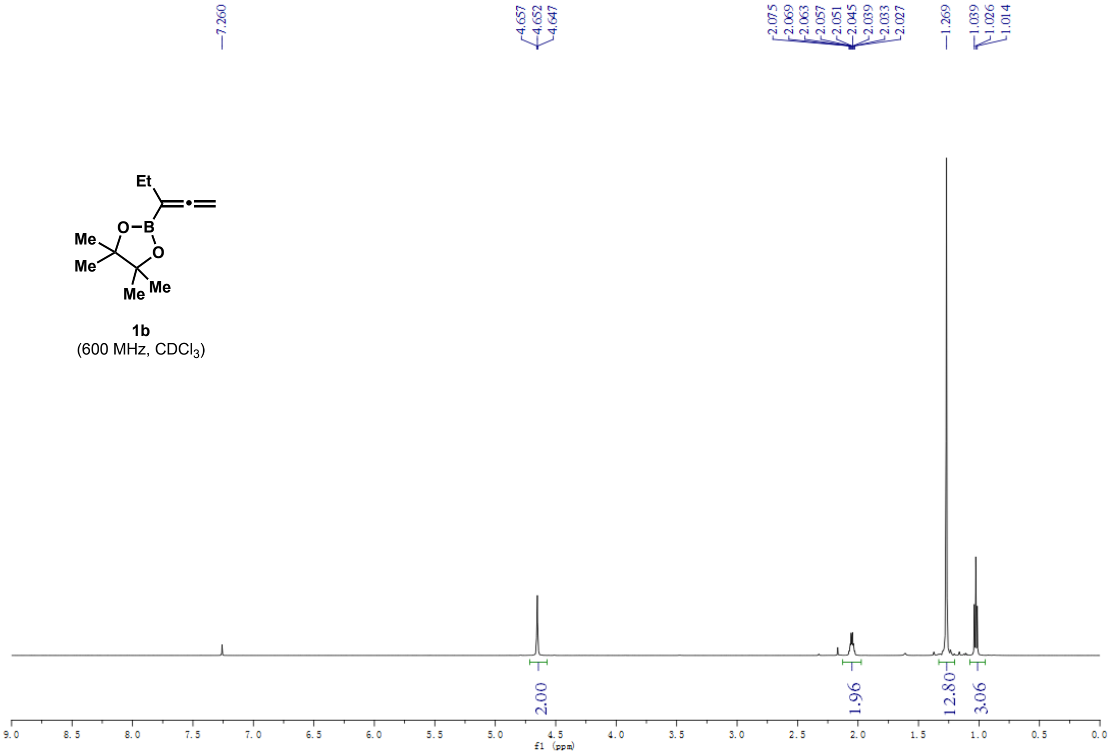
References Cited in Supporting Information:

1. Allenylboronates **1a**-**c** were prepared according to the reported procedures:
   (a) Ito, H.; Sasaki, Y.; Sawamura, M. *J. Am. Chem. Soc*. **2008**, *130*, 15774.
   (b) Zhao, T. S. N.; Yang, Y.; Lessing, T.; Szabó, K. J. *J. Am. Chem. Soc.* **2014**, *136*, 7563.
2. (a) Dale, J. A.; Mosher, H. S. *J. Am. Chem. Soc.* **1973**, *95*, 512. (b) Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc*. **1991**, *113*, 4092.
3. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B*, **2009**, *113*, 6378.
4. Grimme, S. *J. Comp. Chem.* **2006**, *27*, 1787.
5. Gaussian 16, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

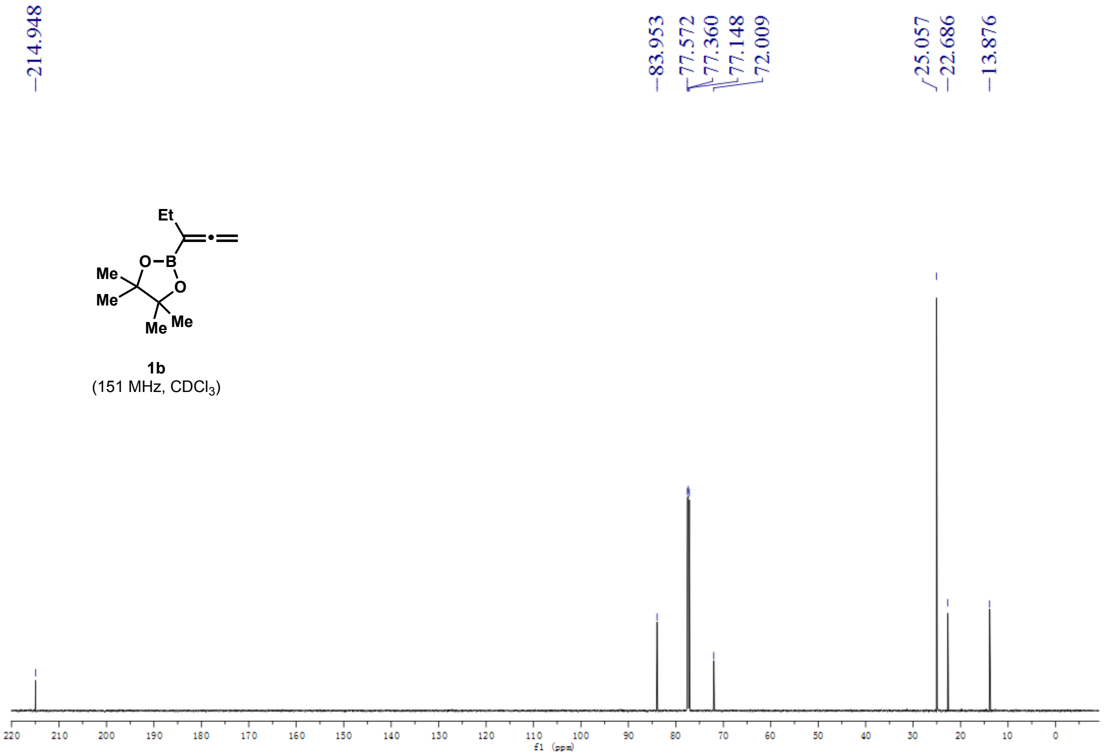

7.260
4.589
4.584
4.579
4.573
1.716
1.711
1.706
1.269
Me
O
B
O
Me
Me
Me
Me
1a
(600 MHz, CDCl$_3$)
2.00
3.04
13.98
f1 (ppm)

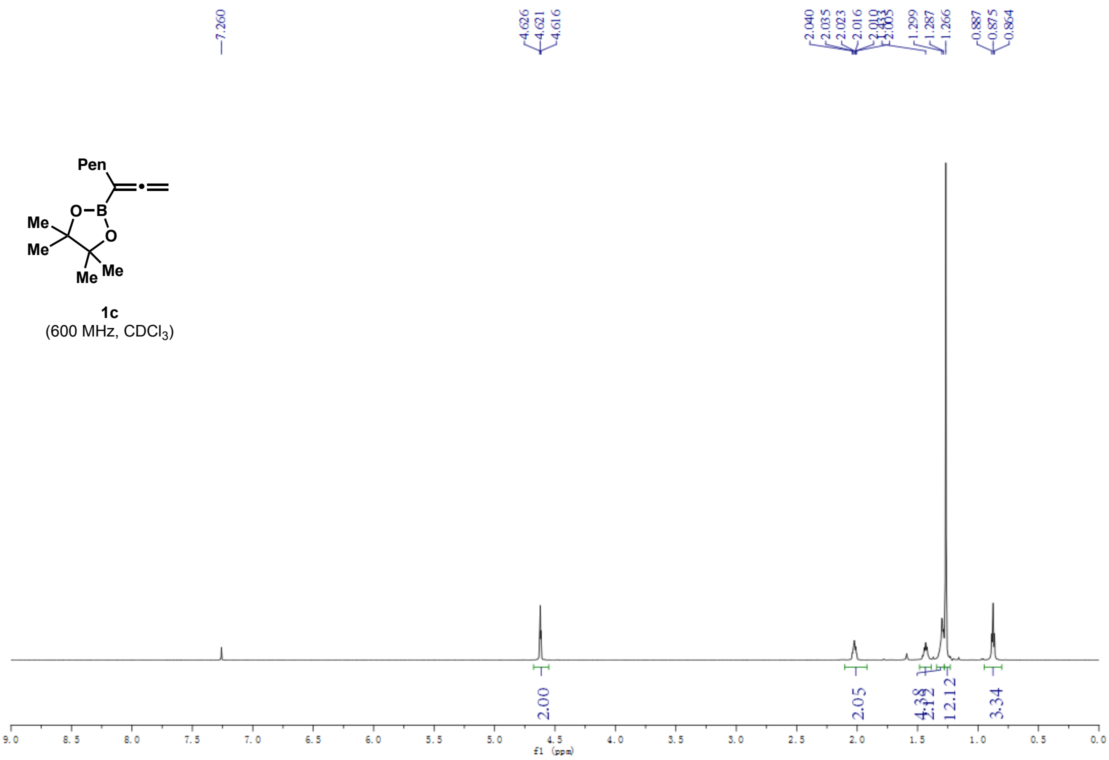

215.782
84.095
77.148
70.480
25.069
15.645
Me
O
B
O
Me
Me
Me
Me
1a
(151 MHz, CDCl$_3$)
f1 (ppm)

1b
(600 MHz, $CDCl_3$)

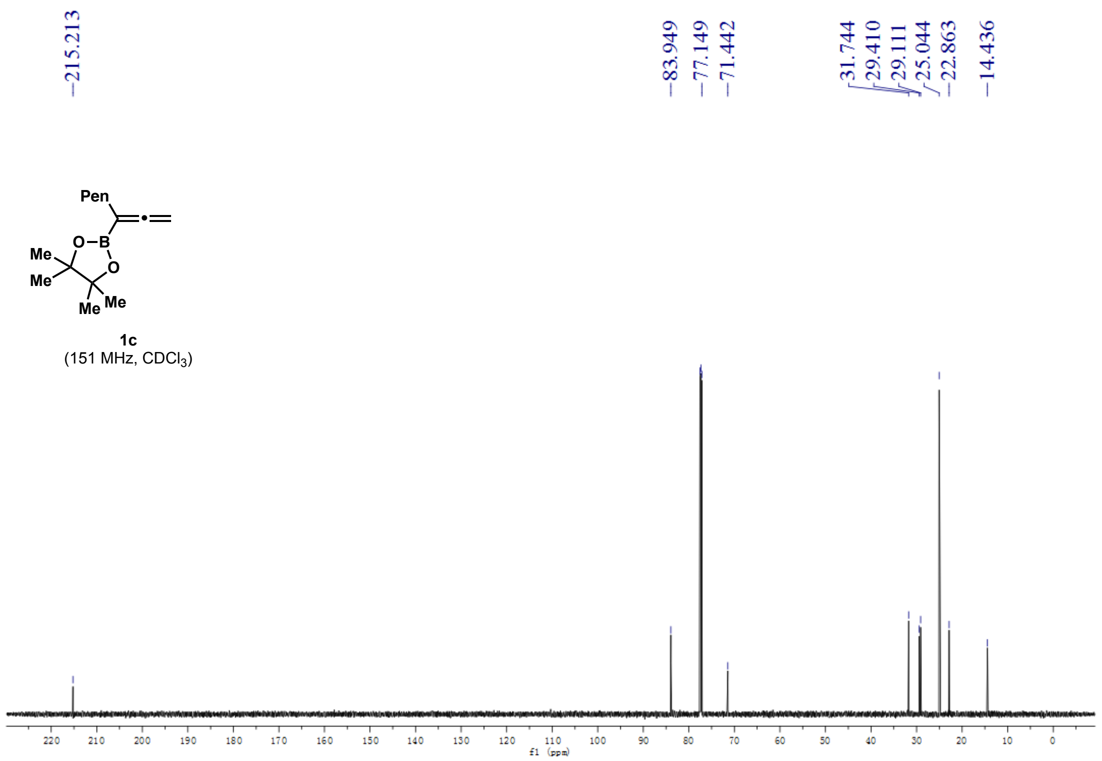


1b
(151 MHz, $CDCl_3$)

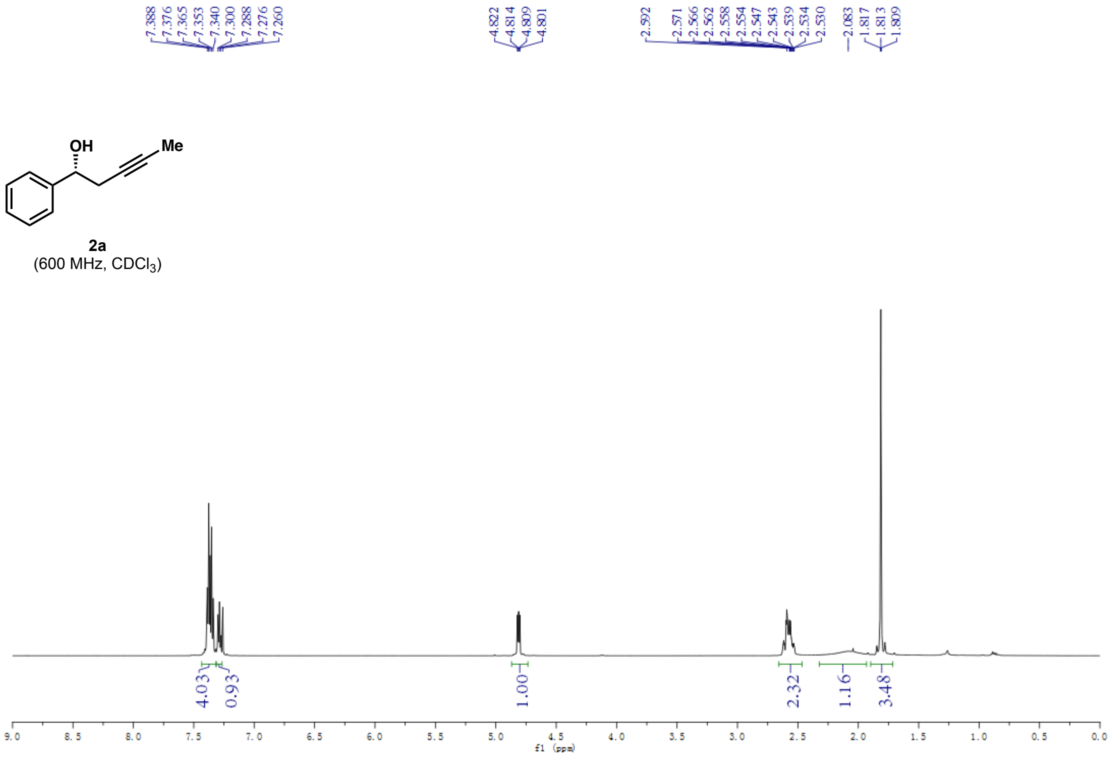




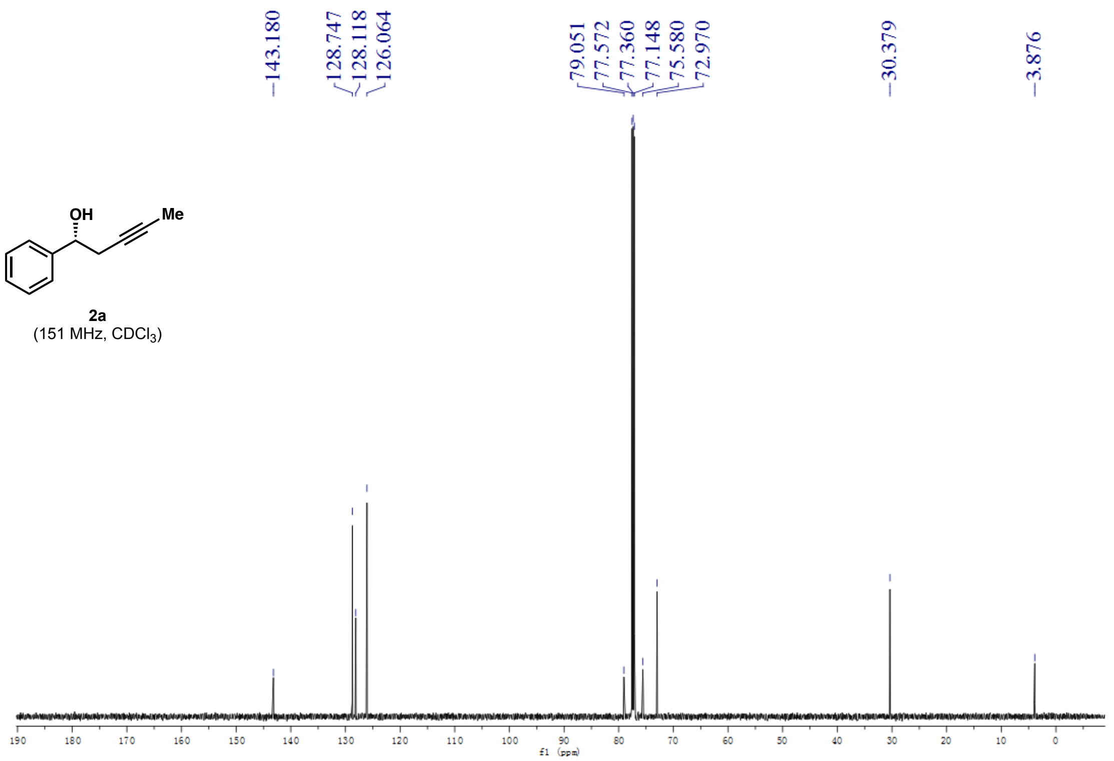
1c
(600 MHz, $CDCl_3$)



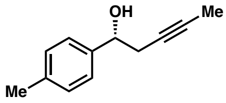
1c
(151 MHz, $CDCl_3$)



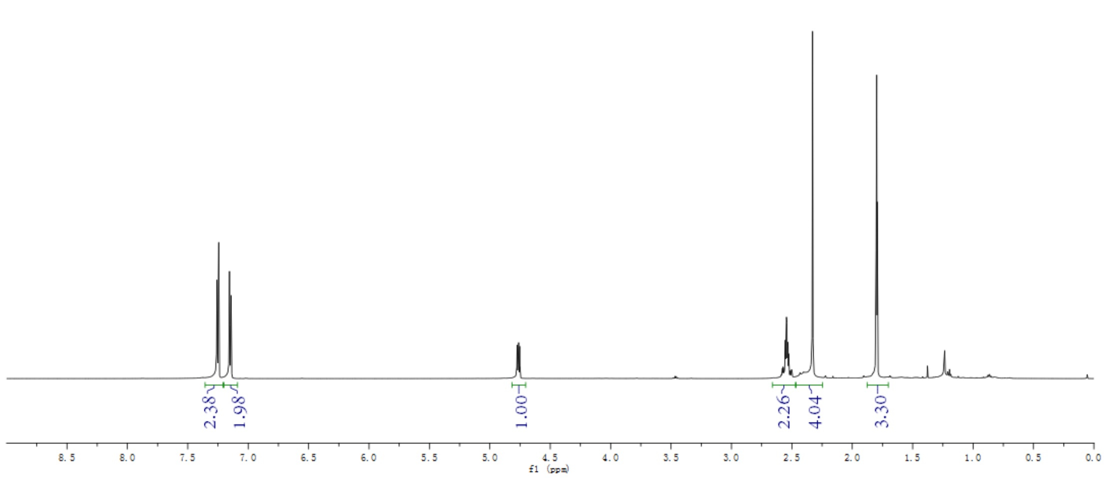
2a
(600 MHz, $CDCl_3$)

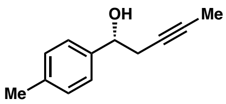


2a
(151 MHz, $CDCl_3$)

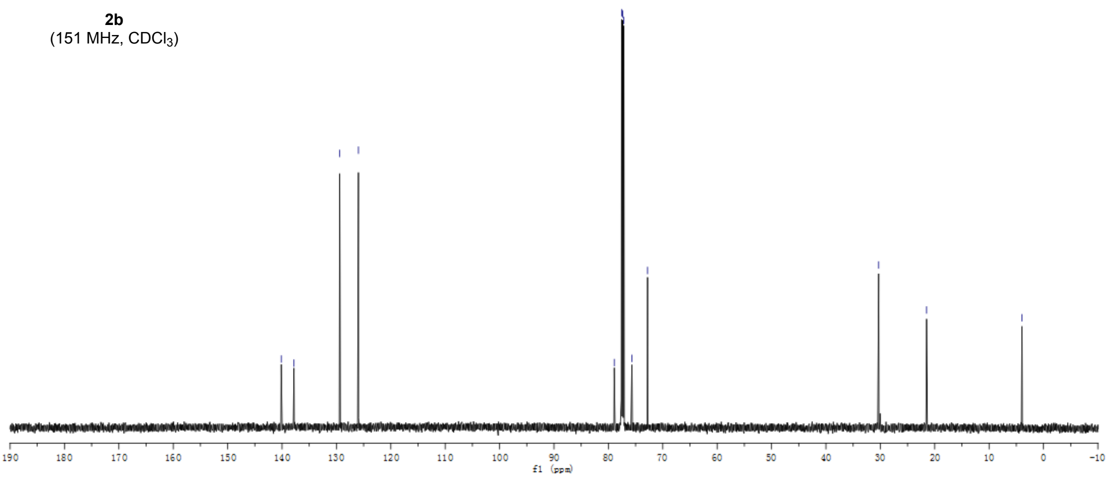


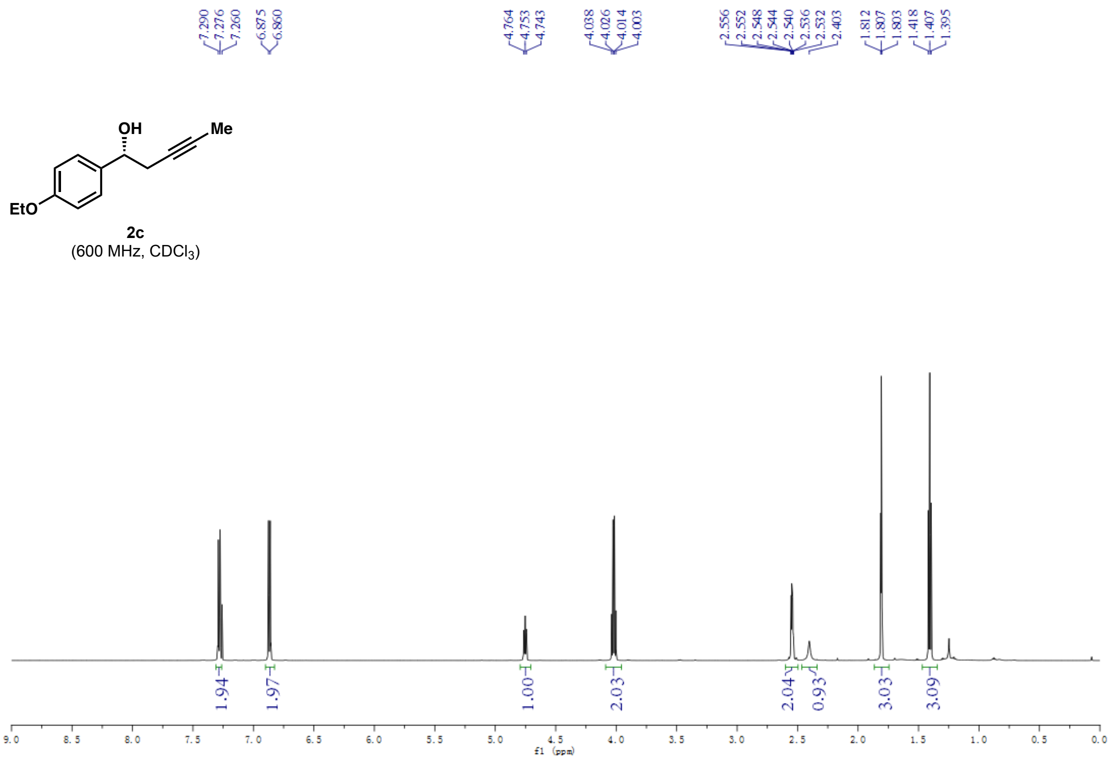
2b
(600 MHz, $CDCl_3$)

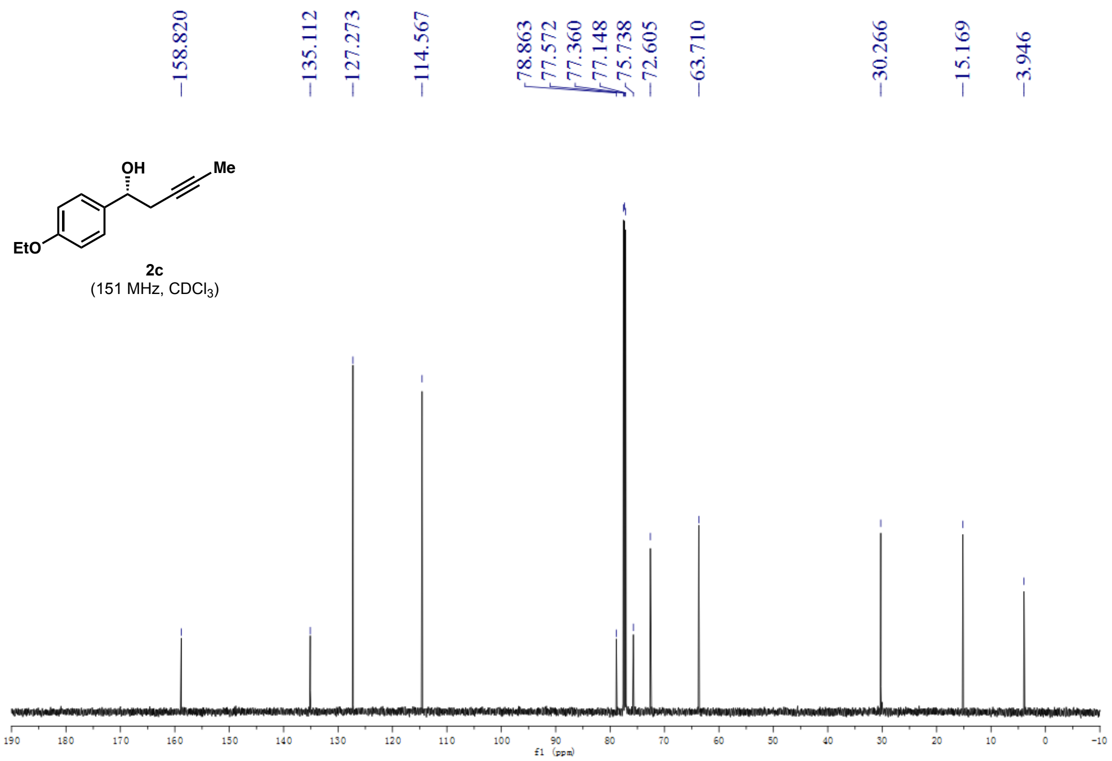


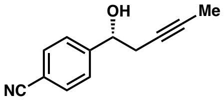


2b
(151 MHz, $CDCl_3$)

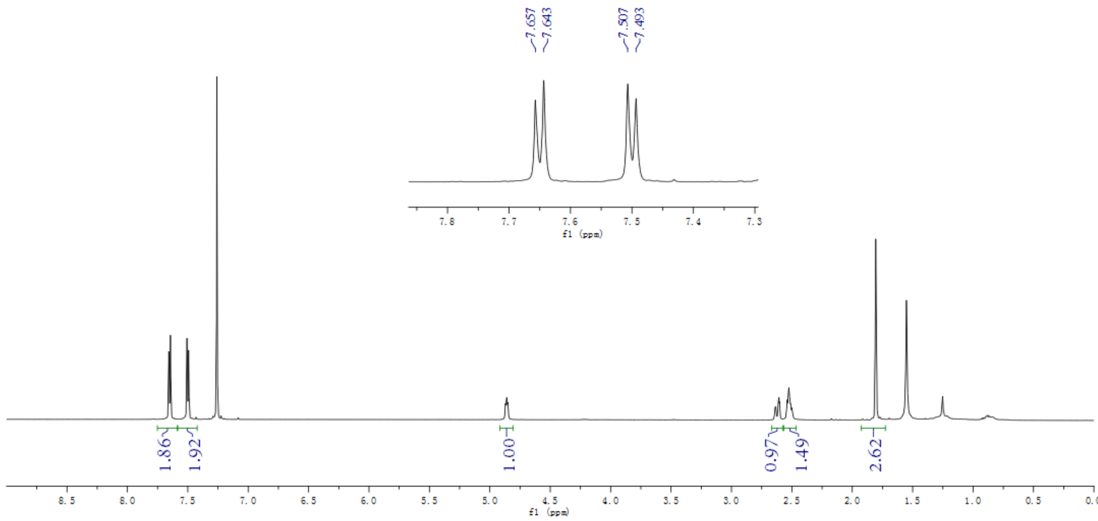


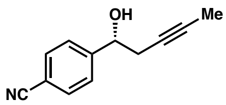

7.290
7.276
7.260
6.875
6.860
4.764
4.753
4.743
4.038
4.026
4.014
4.003
2.556
2.552
2.548
2.544
2.540
2.536
2.532
2.403
1.812
1.807
1.803
1.418
1.407
1.395
OH
Me
EtO
2c
(600 MHz, CDCl3)
1.94
1.97
1.00
2.03
2.04
0.93
3.03
3.09
f1 (ppm)


158.820
135.112
127.273
114.567
78.863
77.572
77.360
77.148
75.738
72.605
63.710
30.266
15.169
3.946
OH
Me
EtO
2c
(151 MHz, CDCl3)
f1 (ppm)

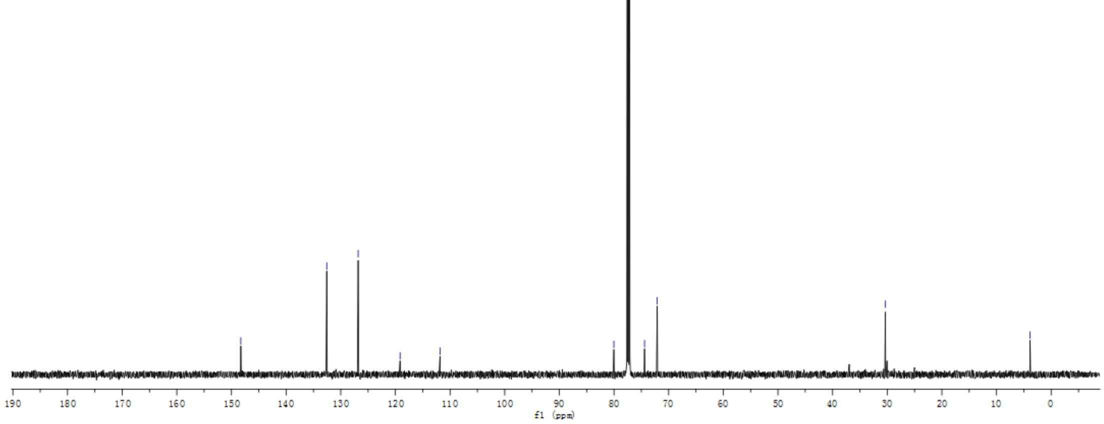


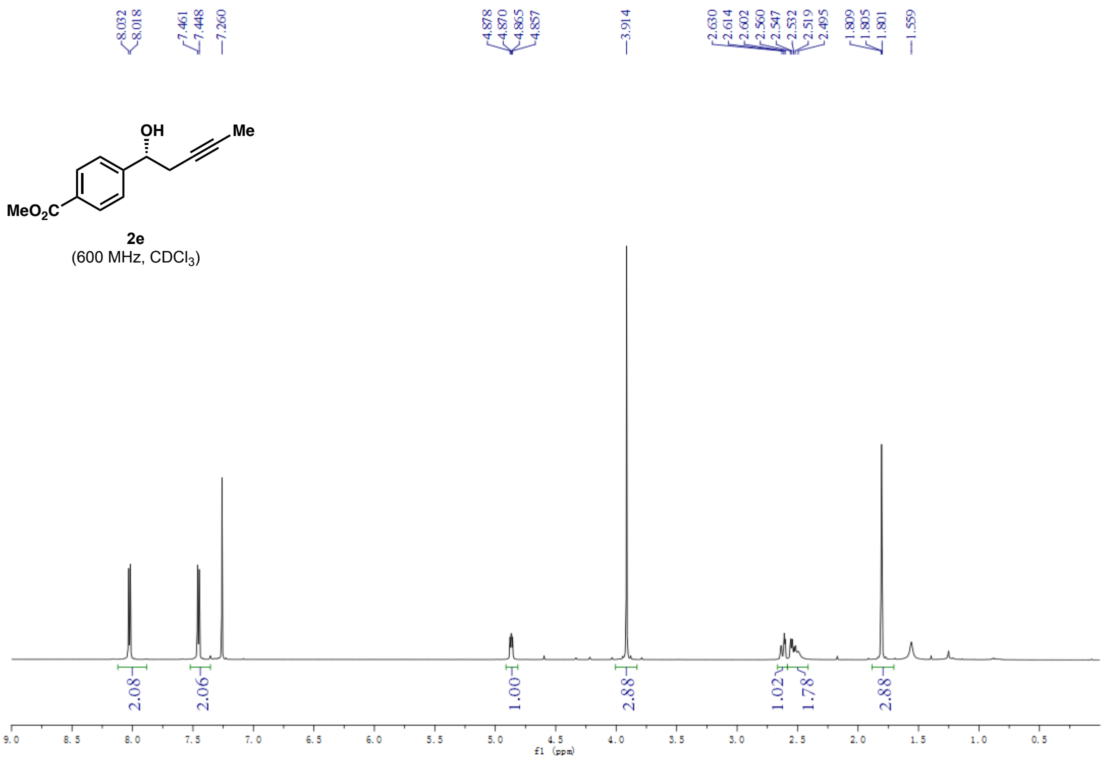
2d
(600 MHz, $CDCl_3$)



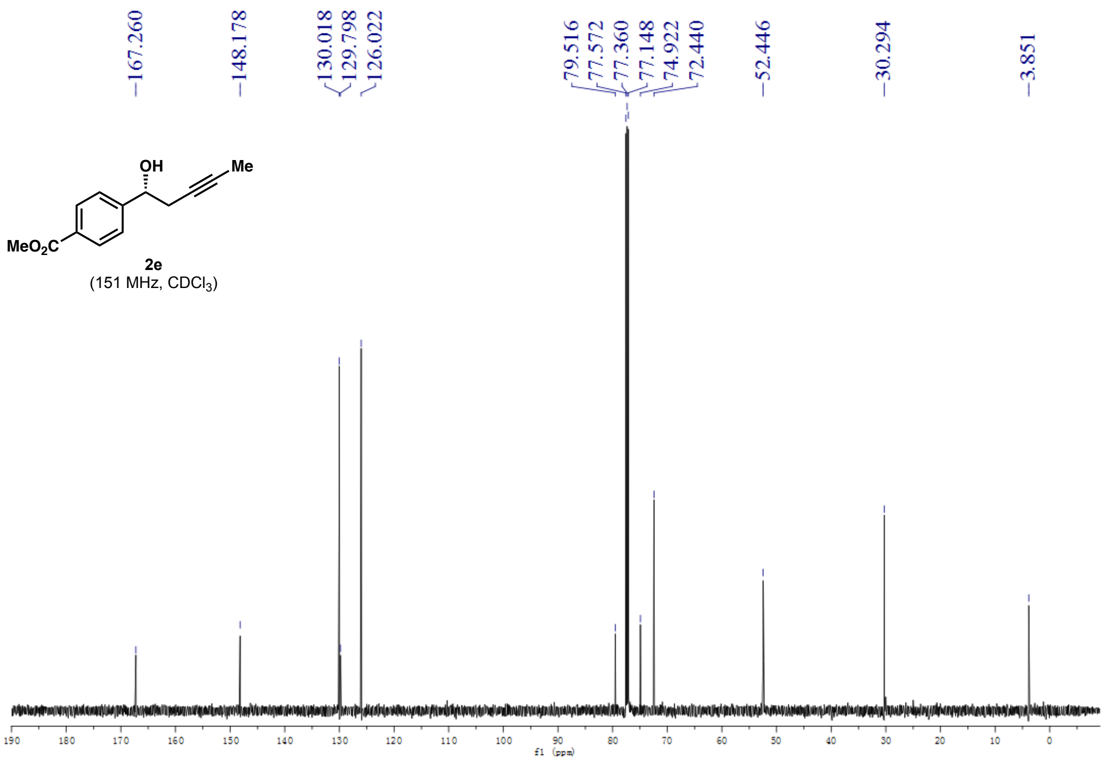


2d
(151 MHz, $CDCl_3$)

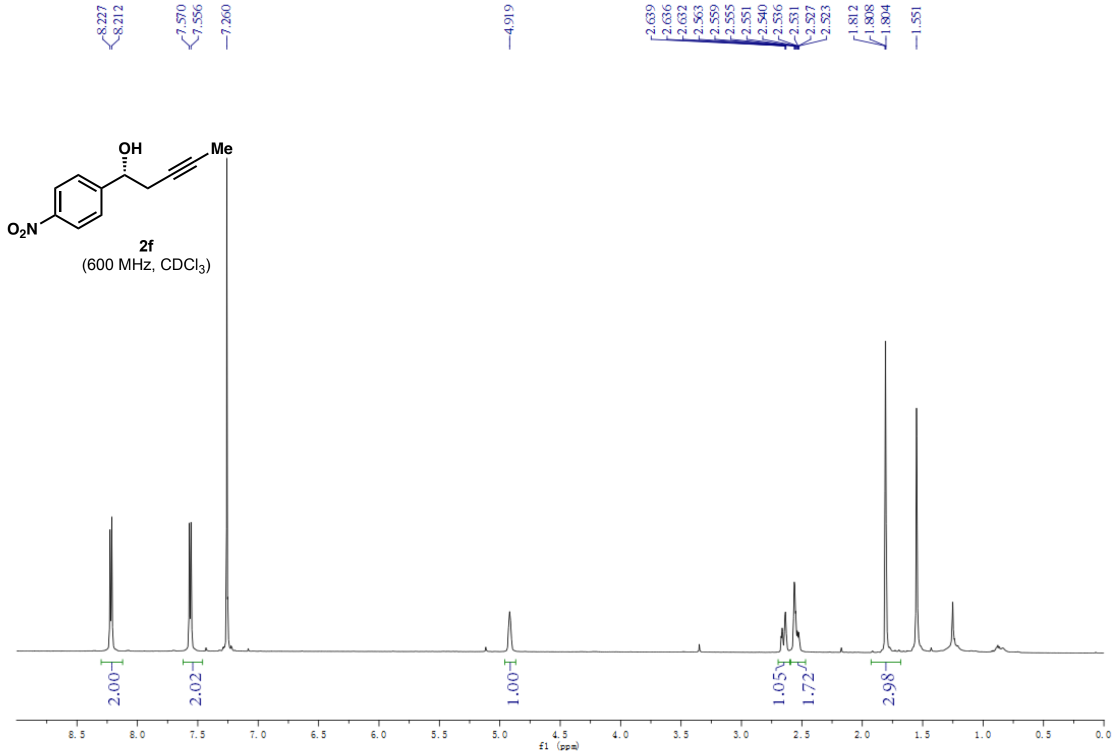


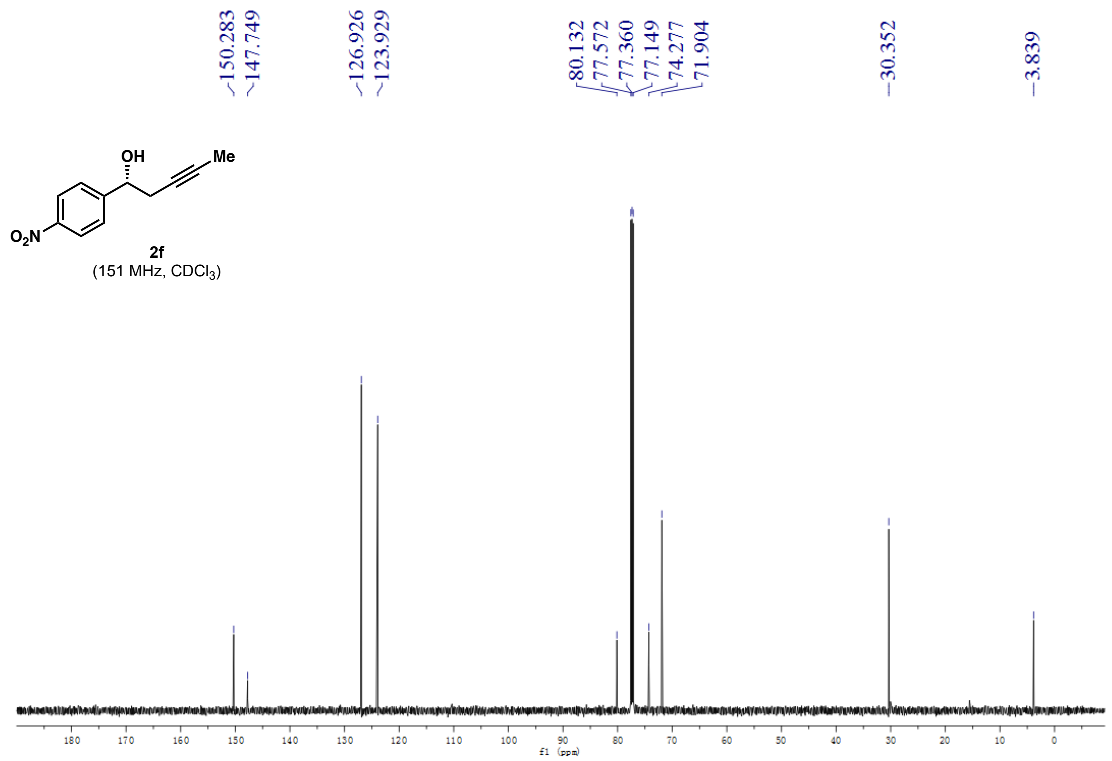


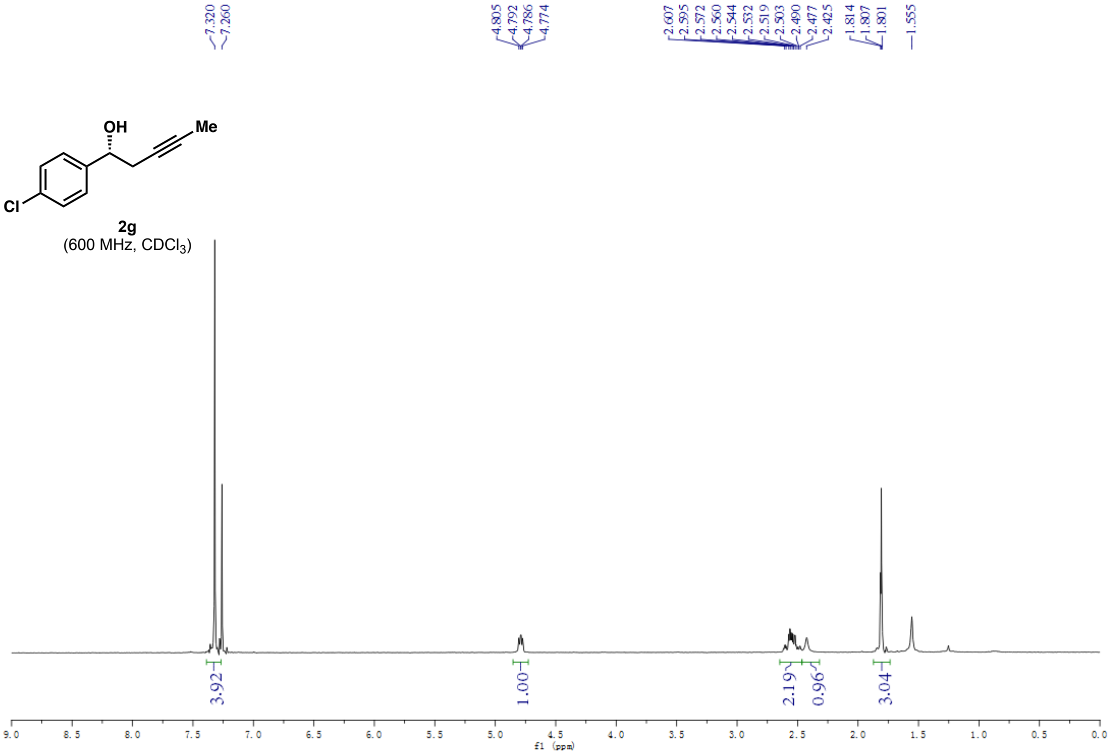
2e
(600 MHz, CDCl3)
8.032
8.018
7.461
7.448
7.260
4.878
4.870
4.865
4.857
3.914
2.630
2.614
2.602
2.560
2.547
2.532
2.519
2.495
1.809
1.805
1.801
1.559
2.08
2.06
1.00
2.88
1.02
1.78
2.88
f1 (ppm)



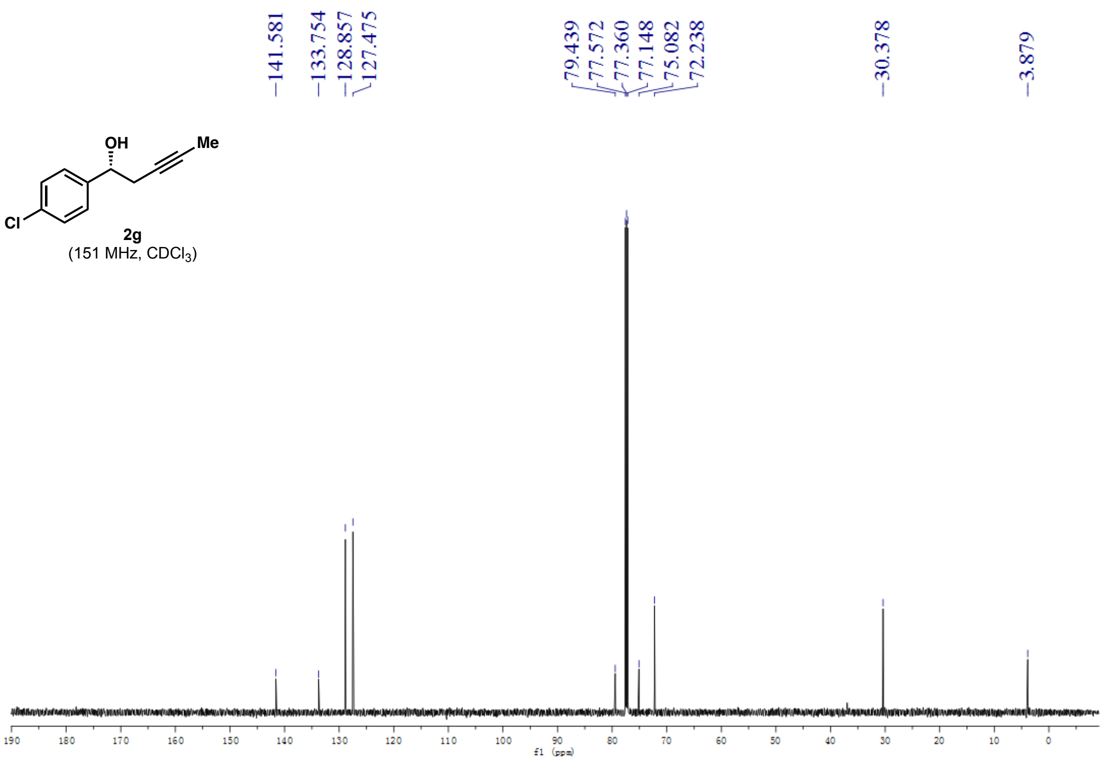
2e
(151 MHz, CDCl3)
167.260
148.178
130.018
129.798
126.022
79.516
77.572
77.360
77.148
74.922
72.440
52.446
30.294
3.851
f1 (ppm)


2f
(600 MHz, $CDCl_3$)

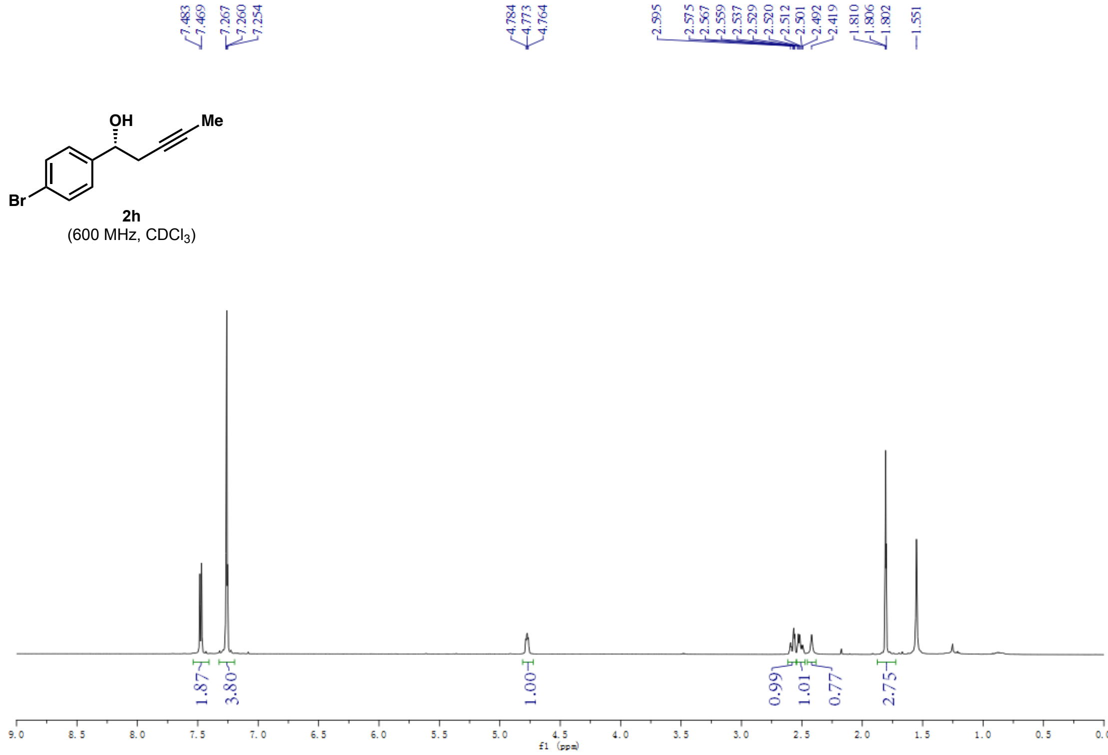

2f
(151 MHz, $CDCl_3$)



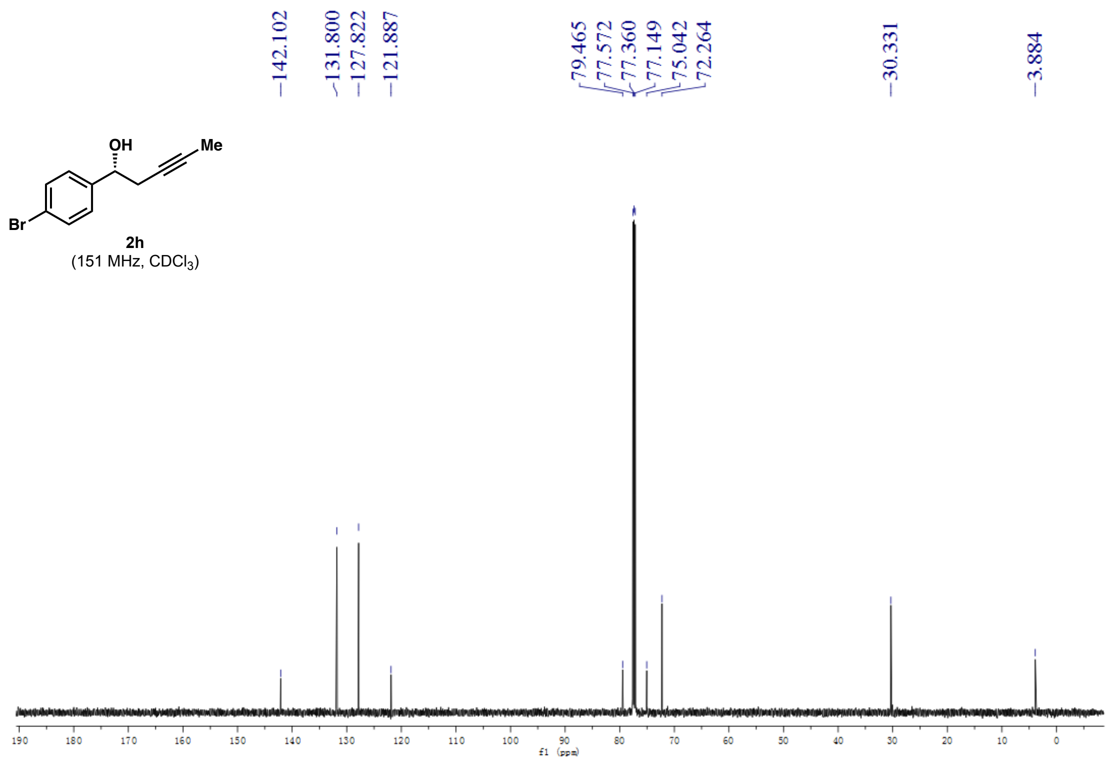
2g
(600 MHz, $CDCl_3$)



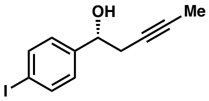
2g
(151 MHz, $CDCl_3$)



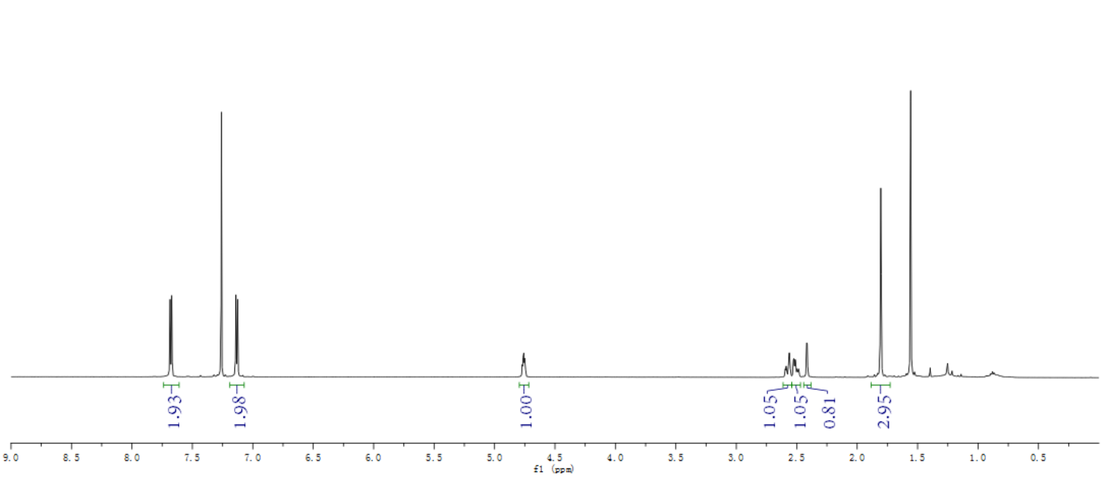
2h
(600 MHz, $CDCl_3$)

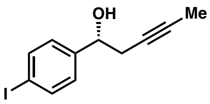


2h
(151 MHz, $CDCl_3$)

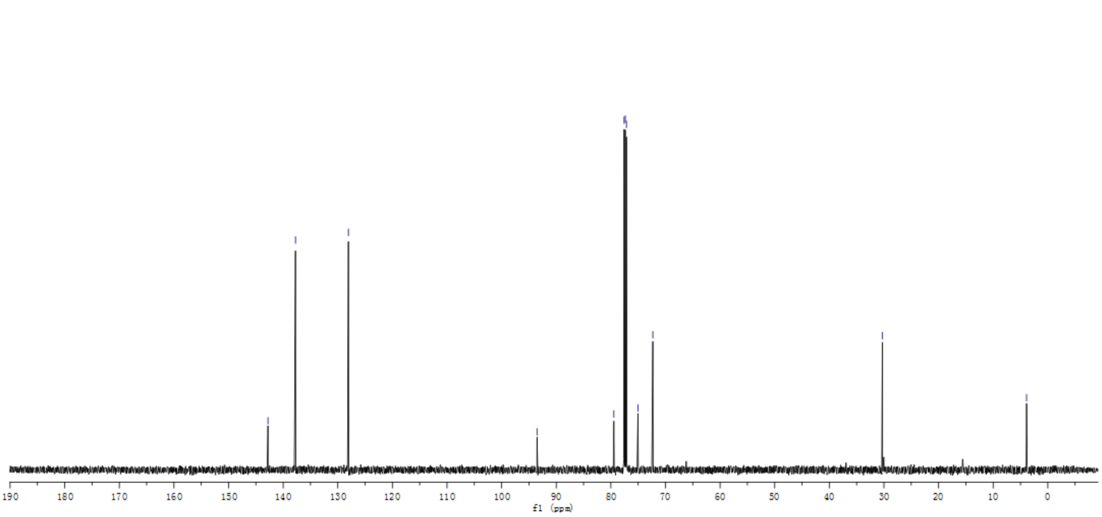


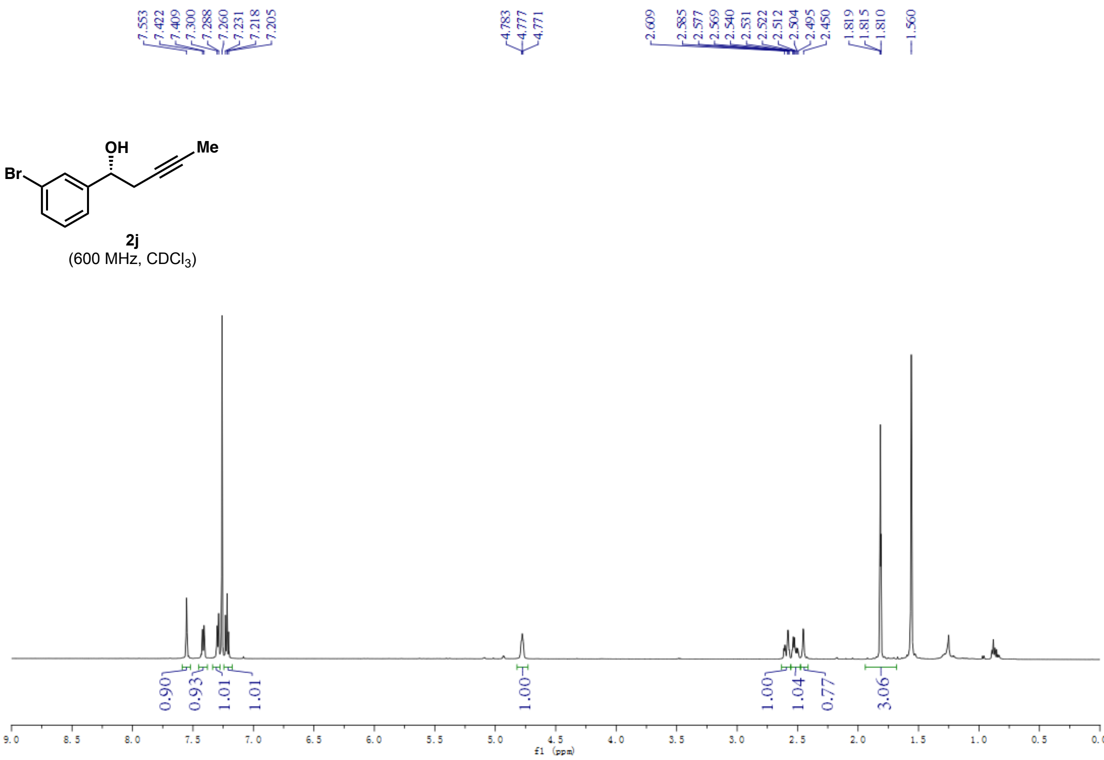
2i
(600 MHz, $CDCl_3$)



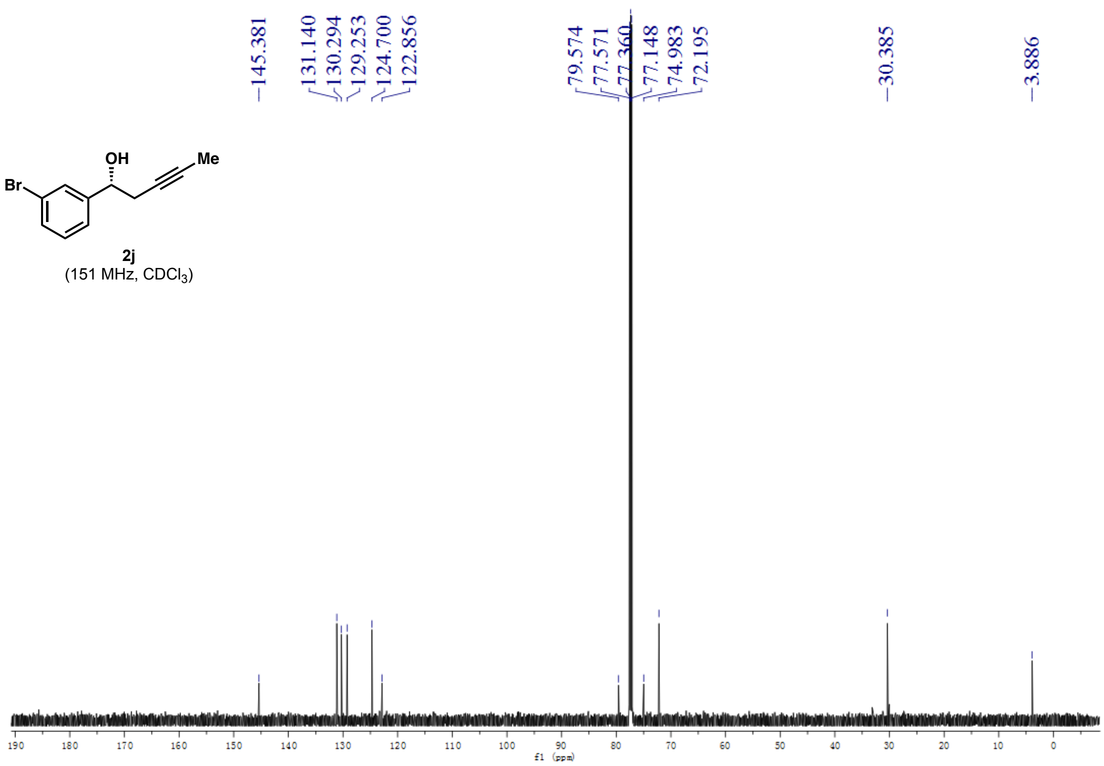


2i
(151 MHz, $CDCl_3$)

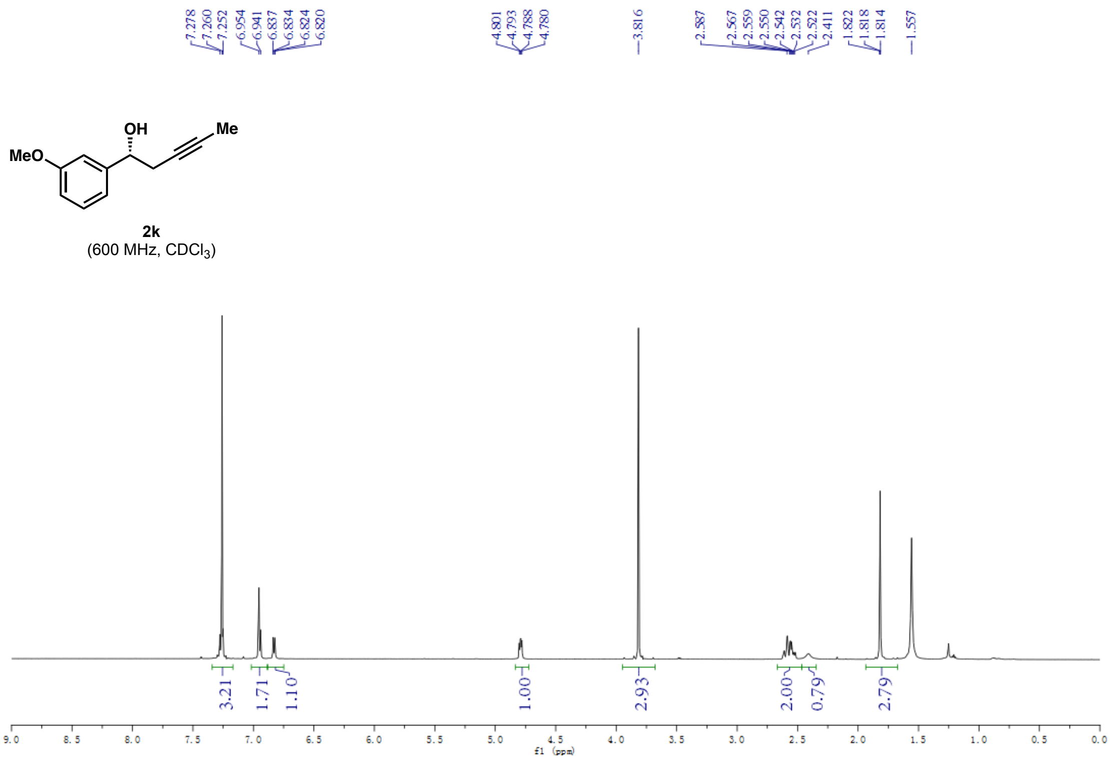


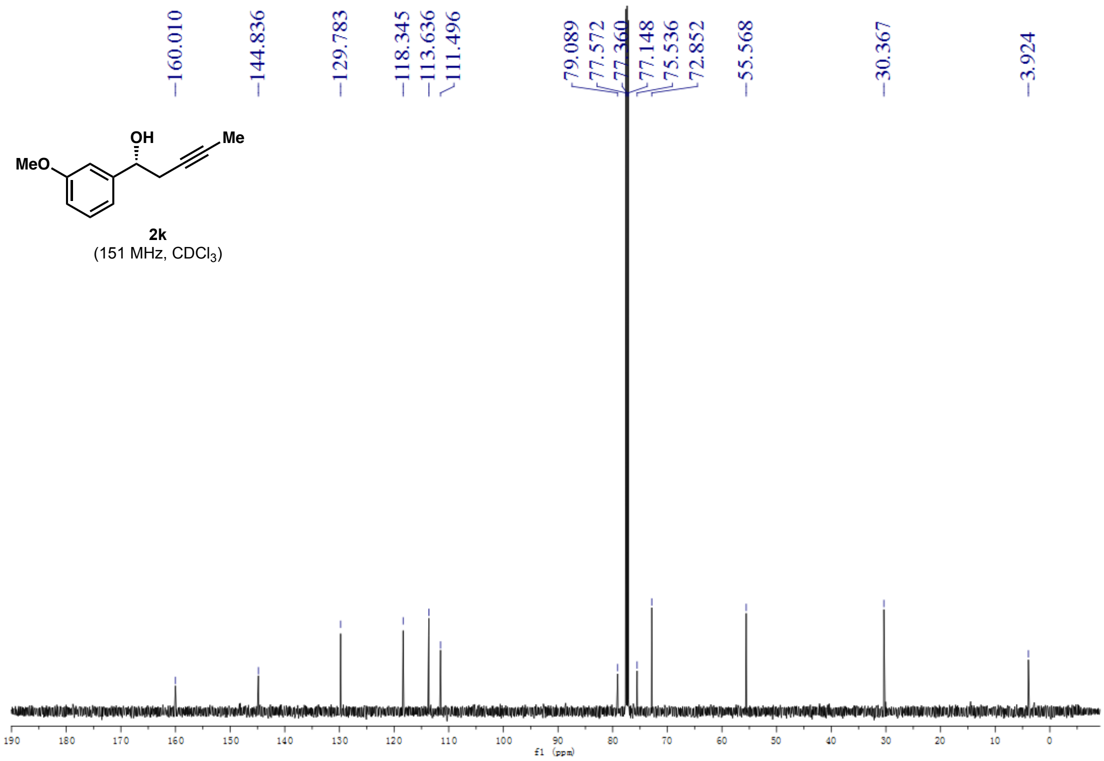


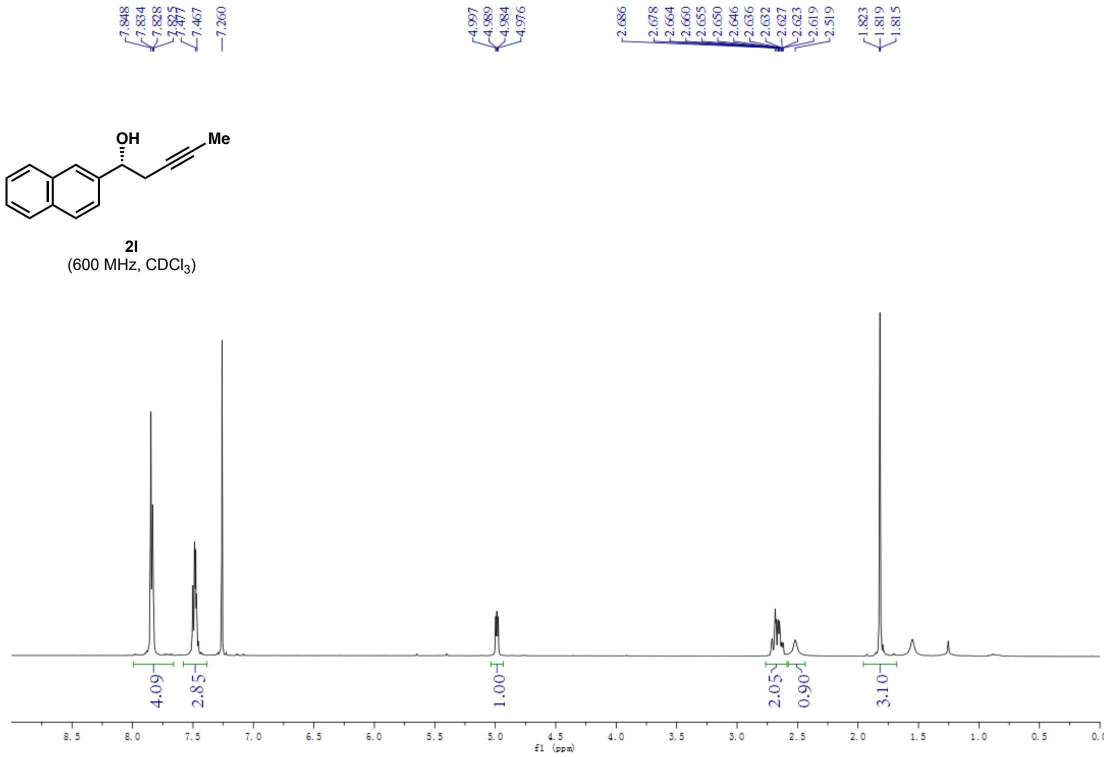
OH
Me
Br
2j
(600 MHz, $CDCl_3$)
f1 (ppm)



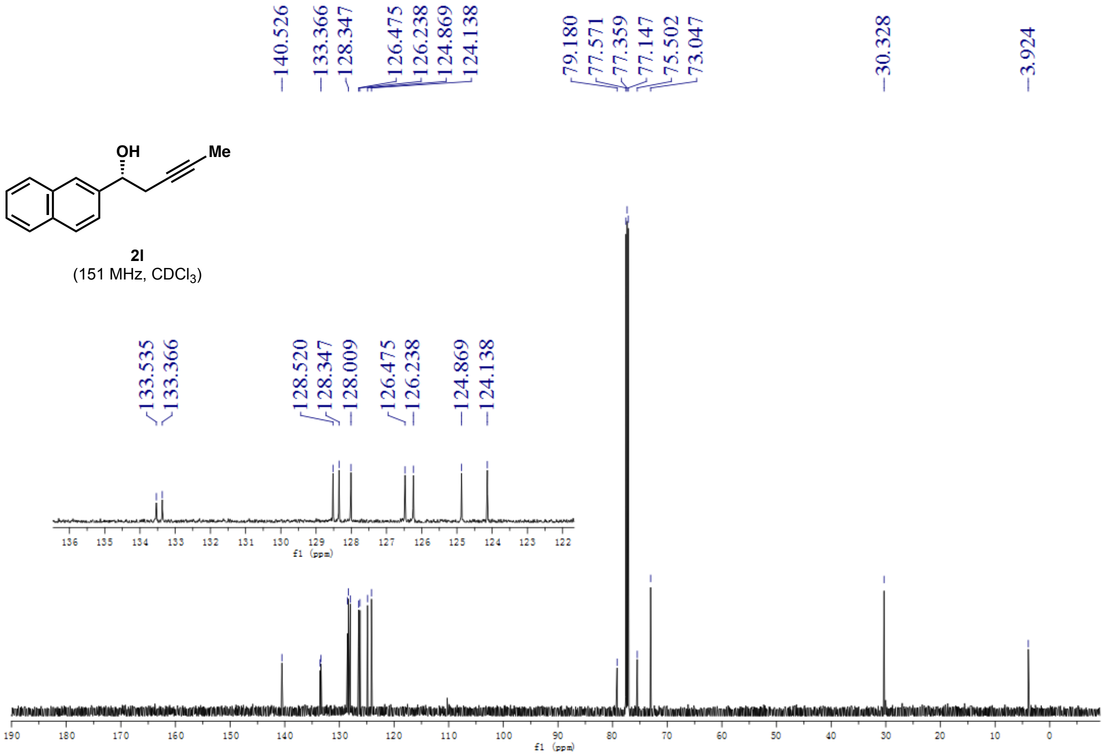
145.381
131.140
130.294
129.253
124.700
122.856
79.574
77.571
77.360
77.148
74.983
72.195
30.385
3.886
OH
Me
Br
2j
(151 MHz, $CDCl_3$)
f1 (ppm)


7.278
7.260
7.252
6.954
6.941
6.837
6.834
6.824
6.820
4.801
4.793
4.788
4.780
3.816
2.587
2.567
2.559
2.550
2.542
2.532
2.522
2.411
1.822
1.818
1.814
1.557
OH
MeO
Me
2k
(600 MHz, CDCl3)
3.21
1.71
1.10
1.00
2.93
2.00
0.79
2.79
f1 (ppm)

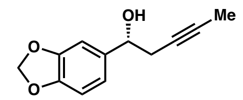

160.010
144.836
129.783
118.345
113.636
111.496
79.089
77.572
77.360
77.148
75.536
72.852
55.568
30.367
3.924
OH
MeO
Me
2k
(151 MHz, CDCl3)
f1 (ppm)



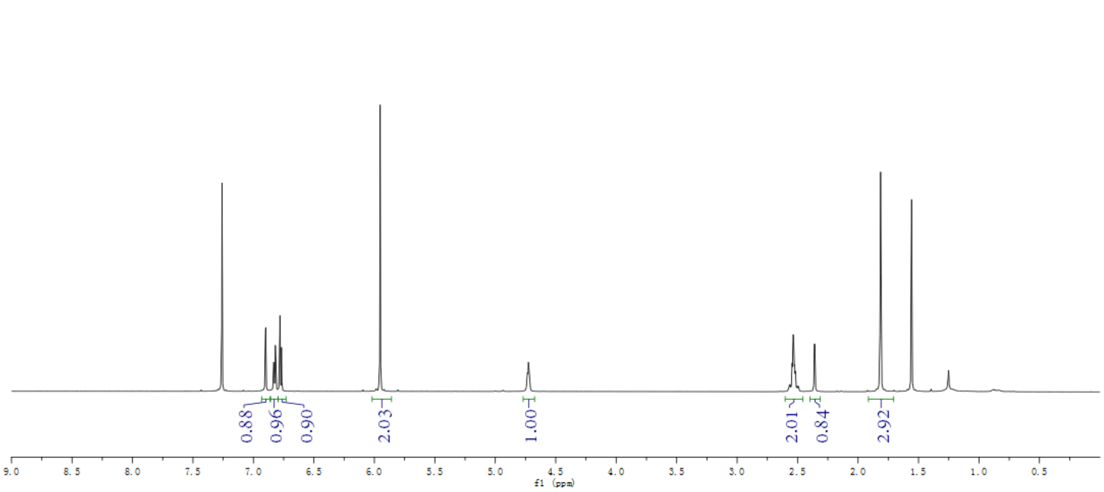
2l
(600 MHz, $CDCl_3$)

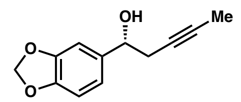


2l
(151 MHz, $CDCl_3$)

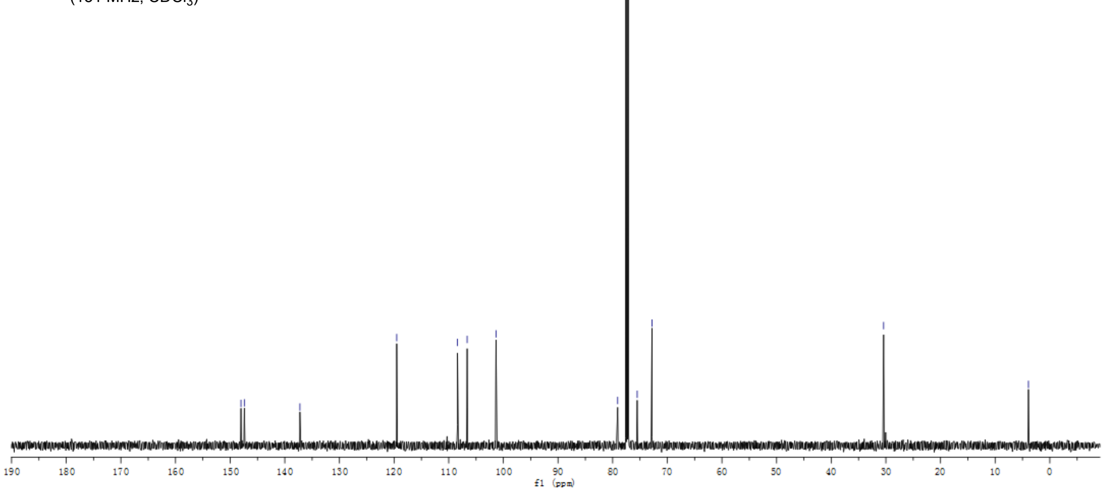


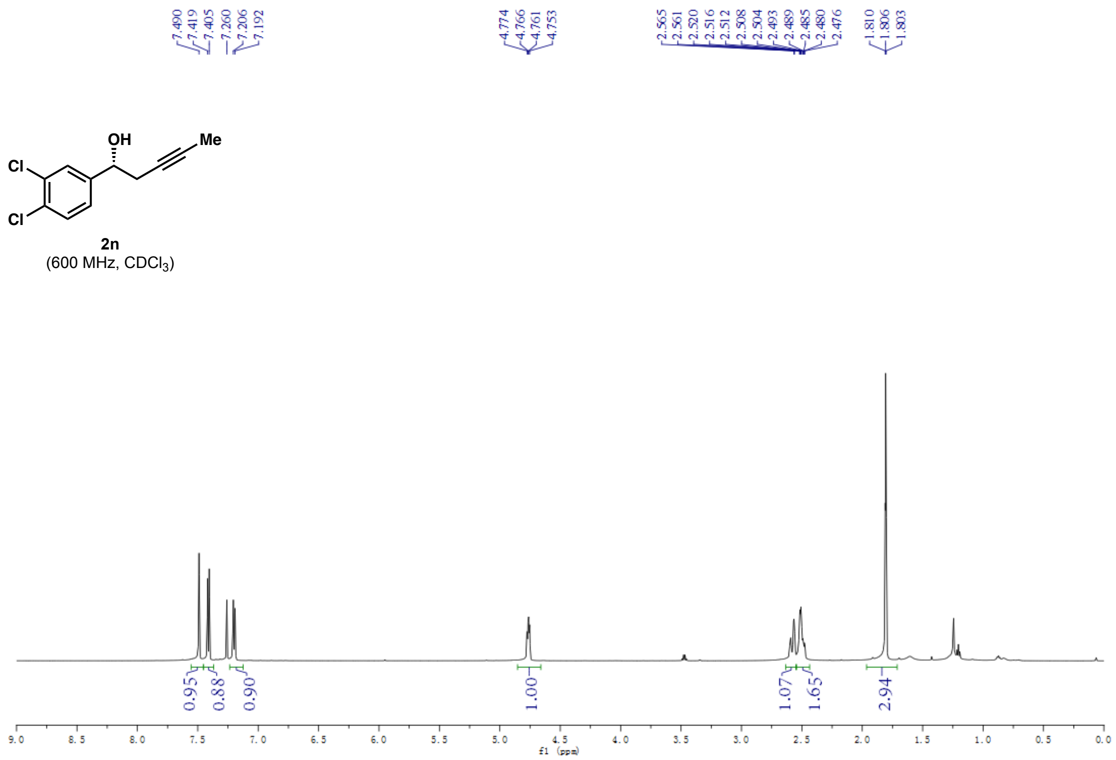
2m
(600 MHz, $CDCl_3$)

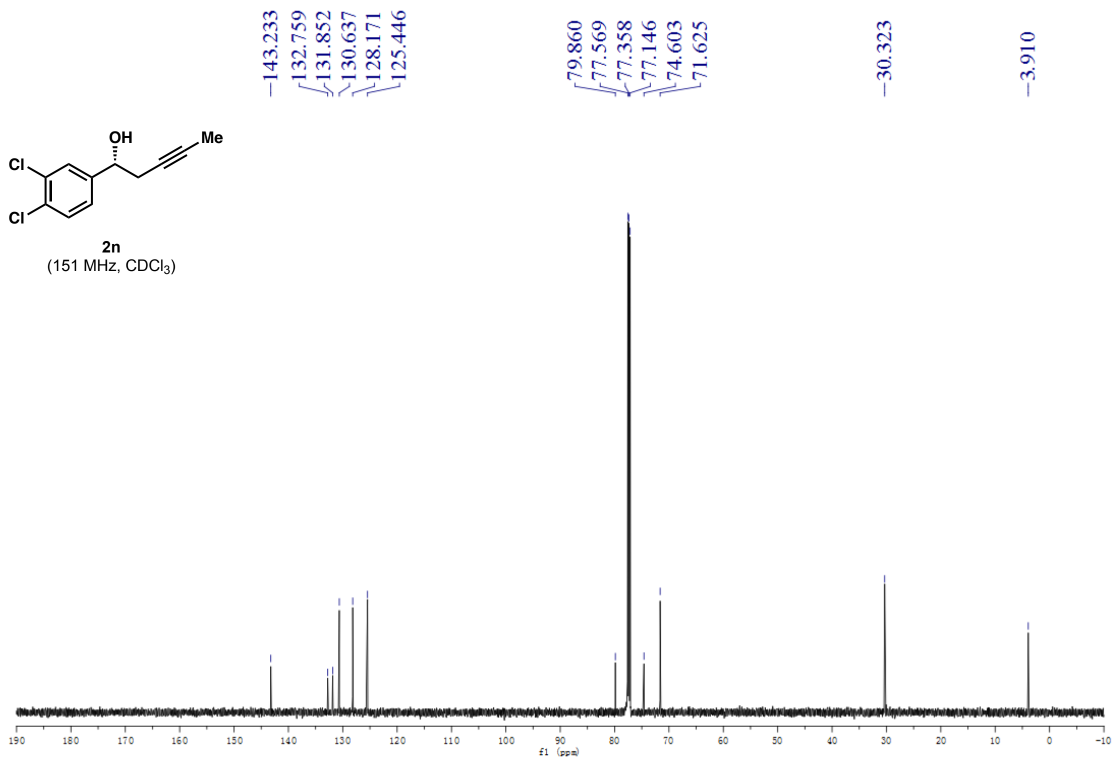


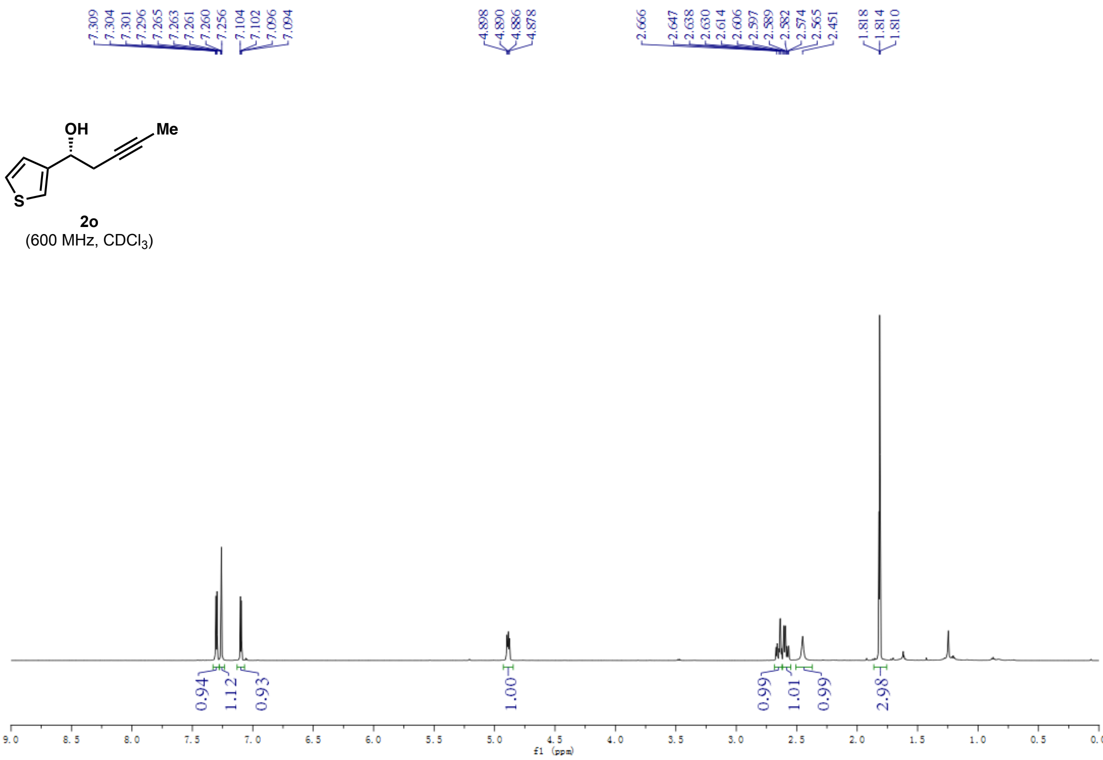


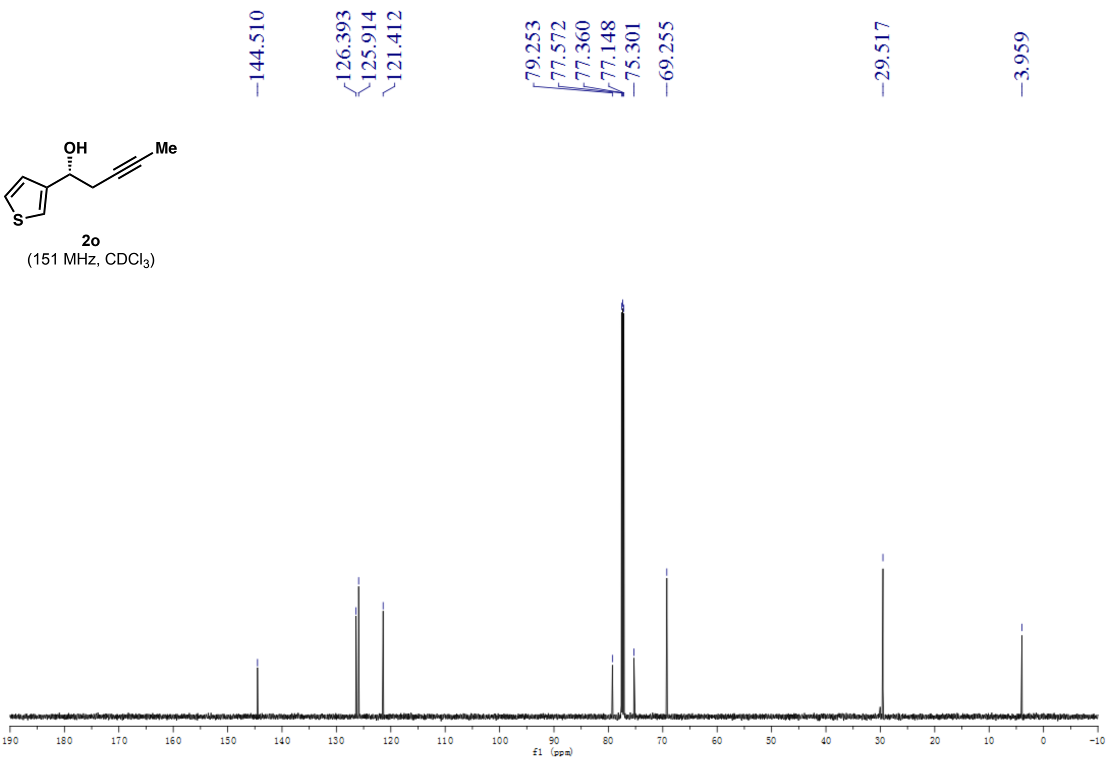
2m
(151 MHz, $CDCl_3$)

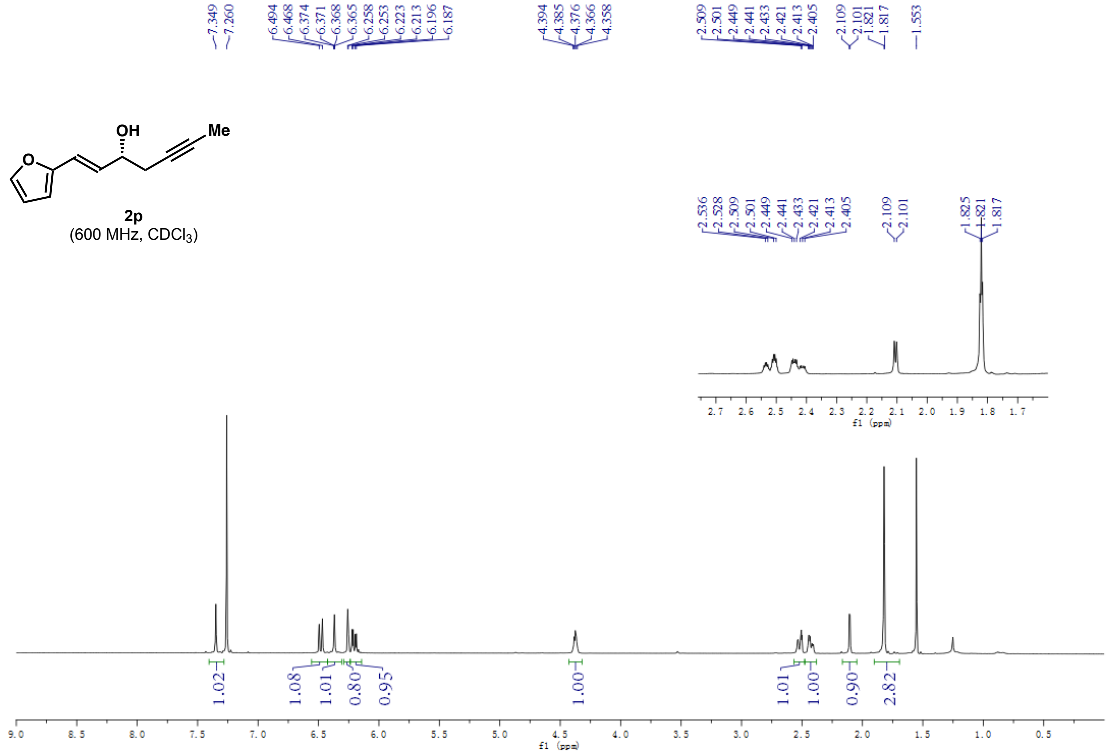



7.490
7.419
7.405
7.260
7.206
7.192
4.774
4.766
4.761
4.753
2.565
2.561
2.520
2.516
2.512
2.508
2.504
2.493
2.489
2.485
2.480
2.476
1.810
1.806
1.803
OH
Me
Cl
Cl
2n
(600 MHz, CDCl3)
0.95
0.88
0.90
1.00
1.07
1.65
2.94
f1 (ppm)

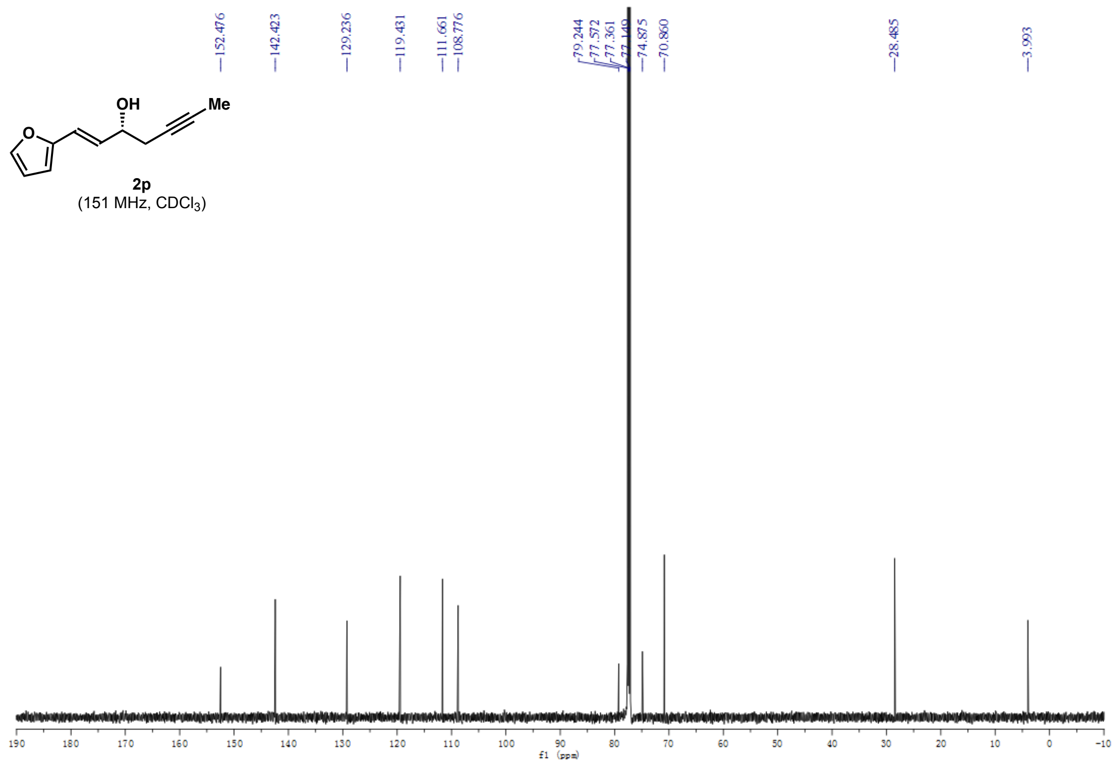

143.233
132.759
131.852
130.637
128.171
125.446
79.860
77.569
77.358
77.146
74.603
71.625
30.323
3.910
OH
Me
Cl
Cl
2n
(151 MHz, CDCl3)
f1 (ppm)


7.309
7.304
7.301
7.296
7.265
7.263
7.261
7.260
7.256
7.104
7.102
7.096
7.094
4.898
4.890
4.886
4.878
2.666
2.647
2.638
2.630
2.614
2.606
2.597
2.589
2.582
2.574
2.565
2.451
1.818
1.814
1.810
OH
Me
S
2o
(600 MHz, CDCl3)
0.94
1.12
0.93
1.00
0.99
1.01
0.99
2.98
f1 (ppm)

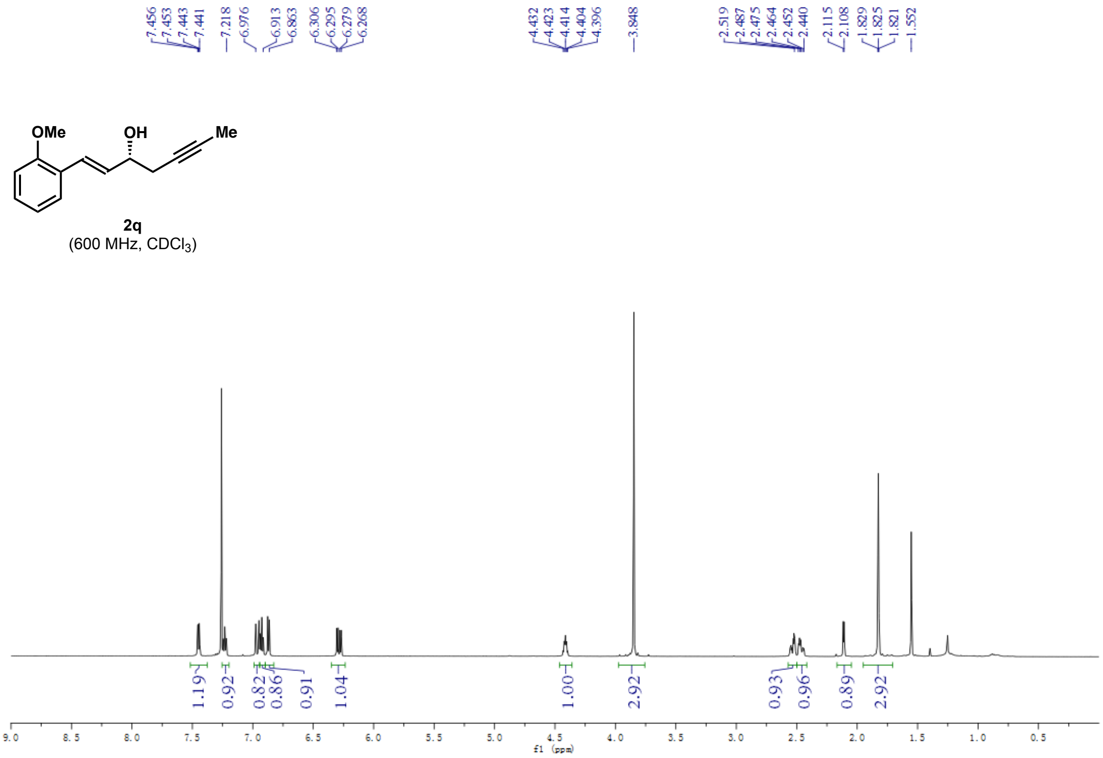

144.510
126.393
125.914
121.412
79.253
77.572
77.360
77.148
75.301
69.255
29.517
3.959
OH
Me
S
2o
(151 MHz, CDCl3)
f1 (ppm)

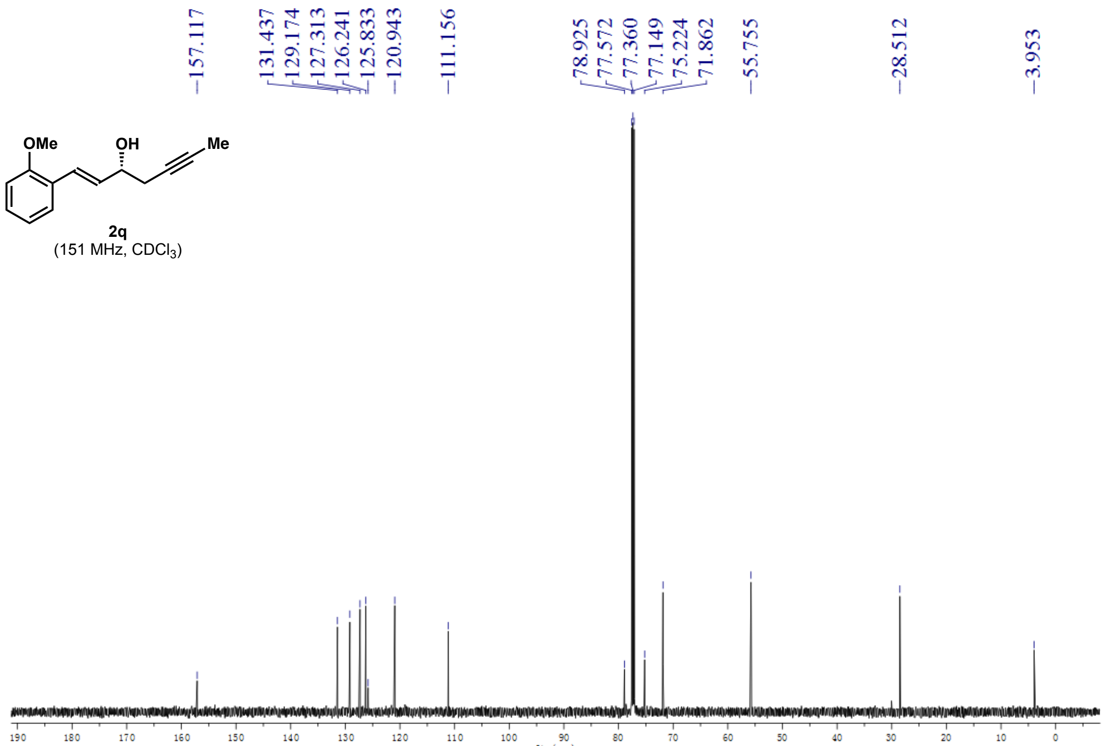


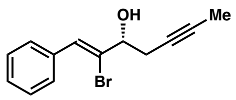
2p
(600 MHz, $CDCl_3$)



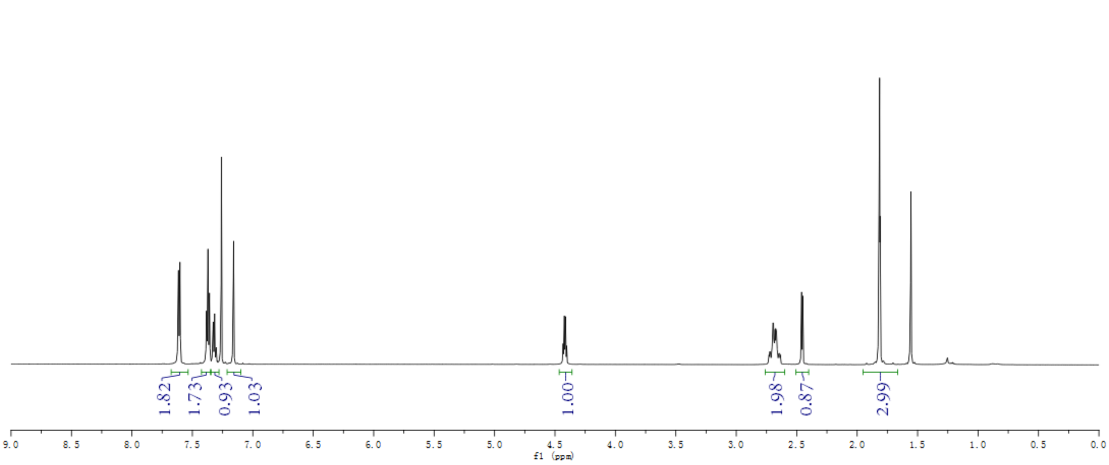
2p
(151 MHz, $CDCl_3$)

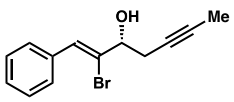

OMe
OH
Me
2q
(600 MHz, CDCl3)


OMe
OH
Me
2q
(151 MHz, CDCl3)

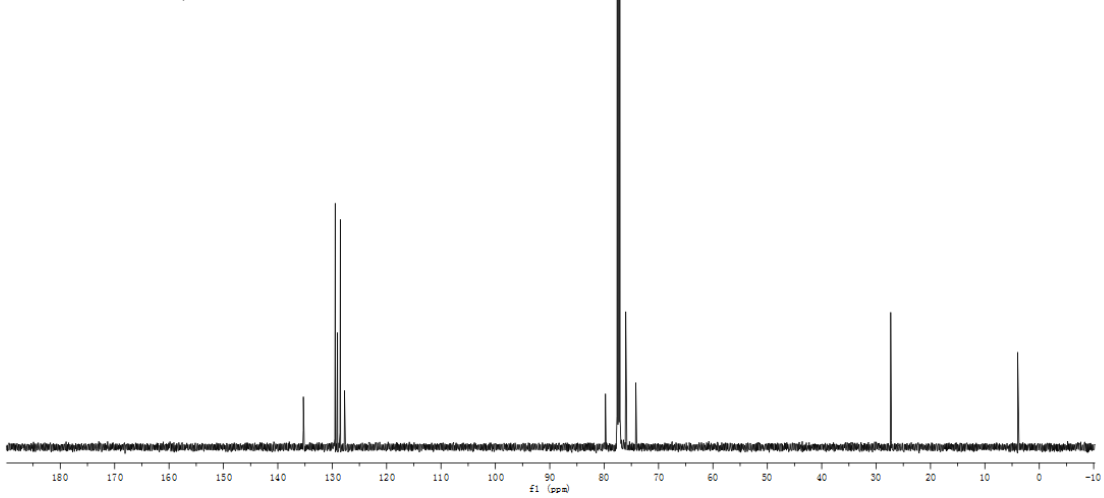


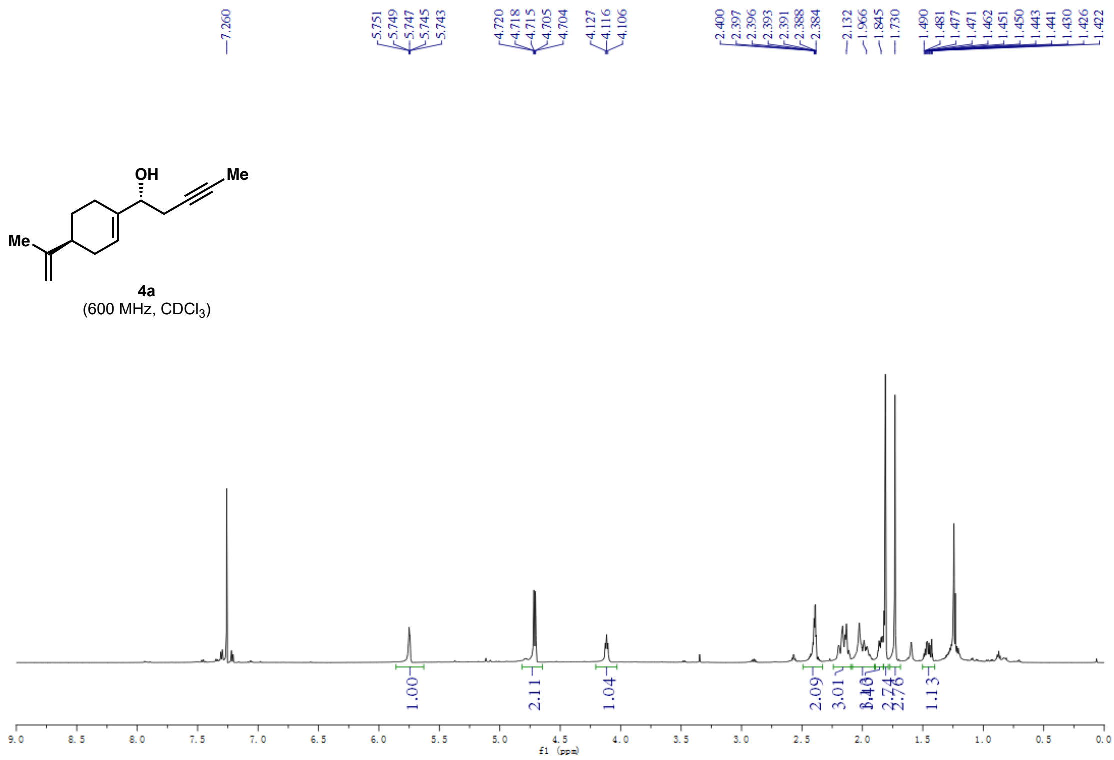
2r
(600 MHz, $CDCl_3$)



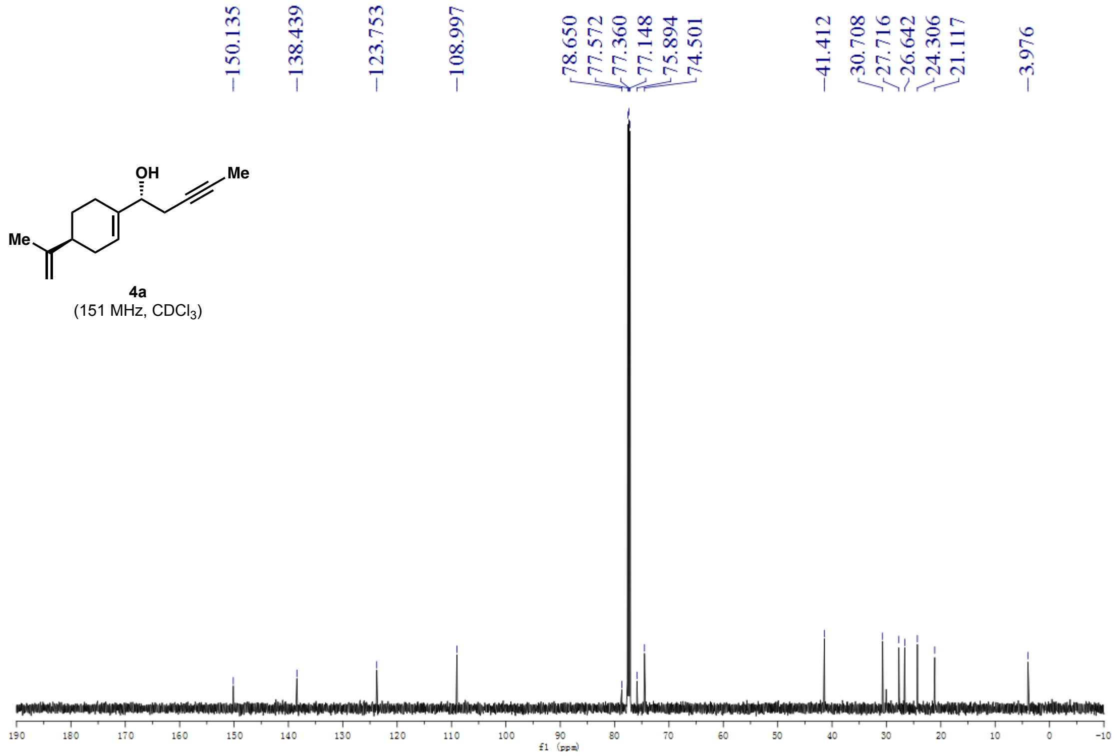


2r
(151 MHz, $CDCl_3$)

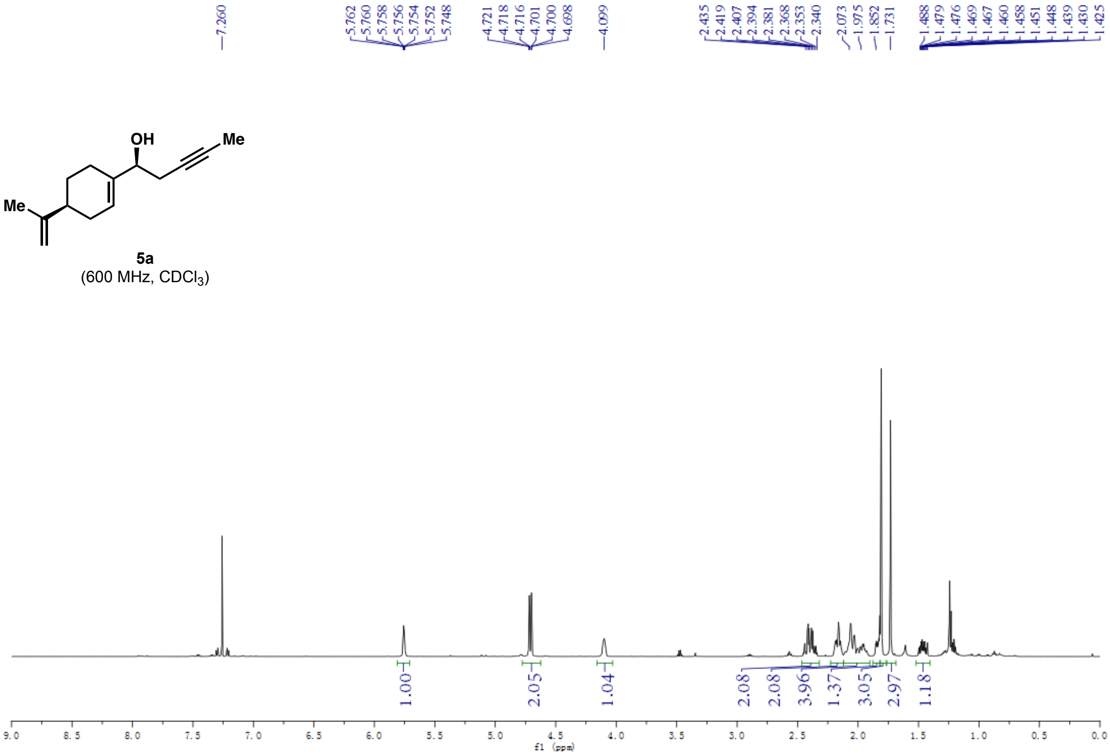


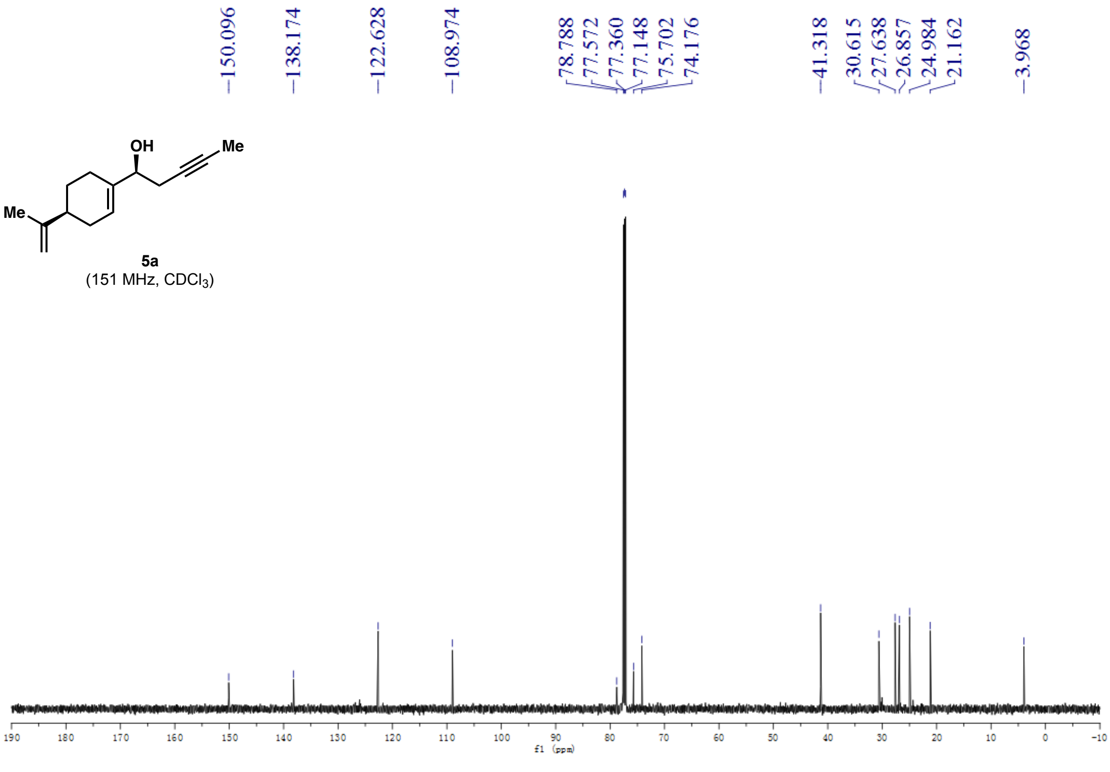


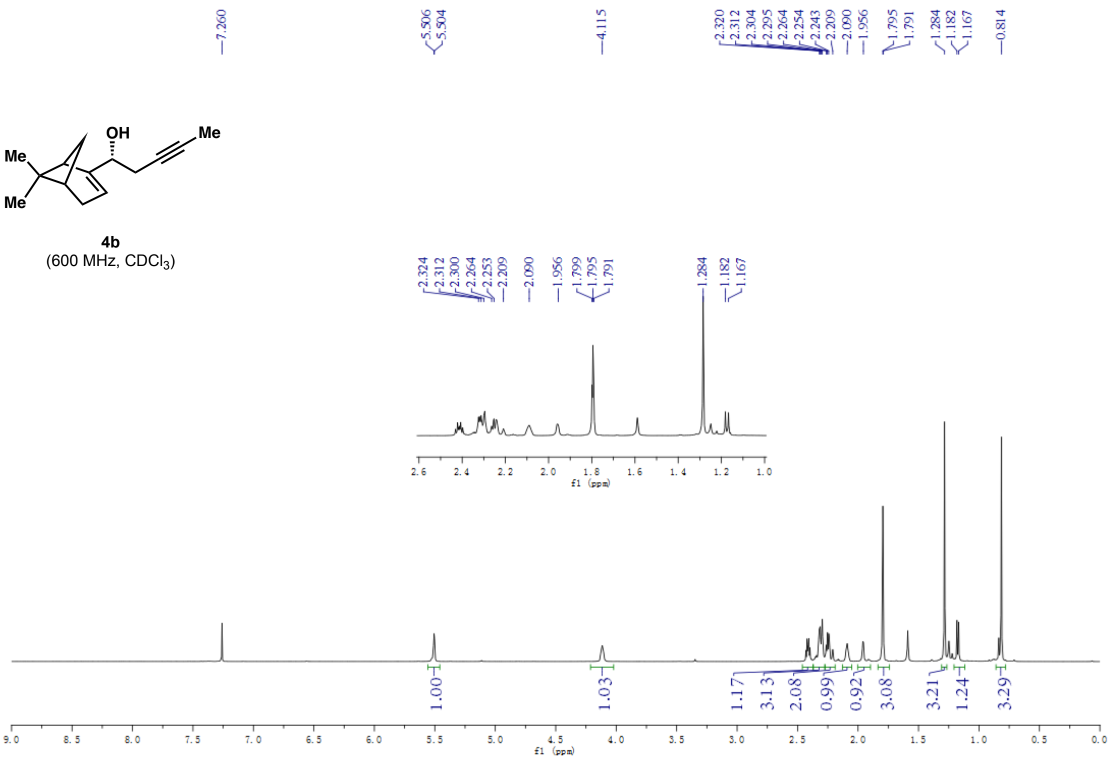
4a
(600 MHz, $CDCl_3$)



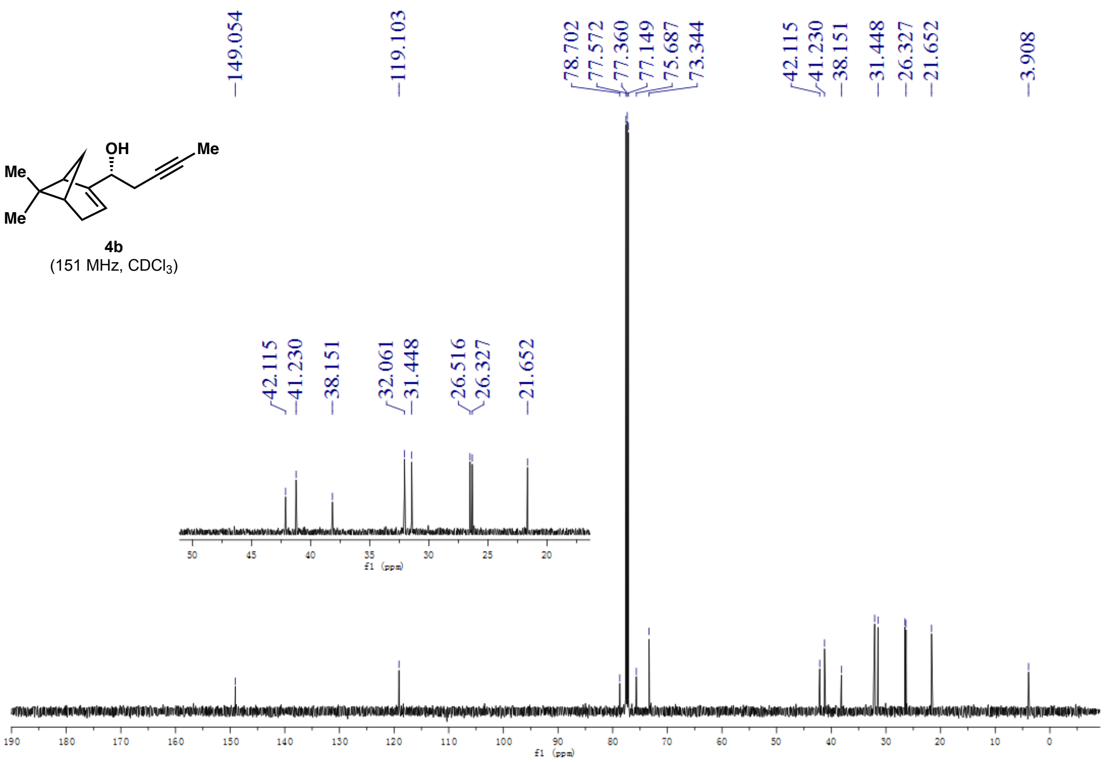
4a
(151 MHz, $CDCl_3$)


7.260
5.762 5.760 5.758 5.756 5.754 5.752 5.748
4.721 4.718 4.716 4.701 4.700 4.698
4.099
2.435 2.419 2.407 2.394 2.381 2.368 2.353 2.340
2.073 1.975 1.852 1.731
1.488 1.479 1.476 1.469 1.467 1.460 1.458 1.451 1.448 1.439 1.430 1.425
OH
Me
Me
5a
(600 MHz, $CDCl_3$)
1.00 2.05 1.04 2.08 2.08 3.96 1.37 3.05 2.97 1.18
f1 (ppm)

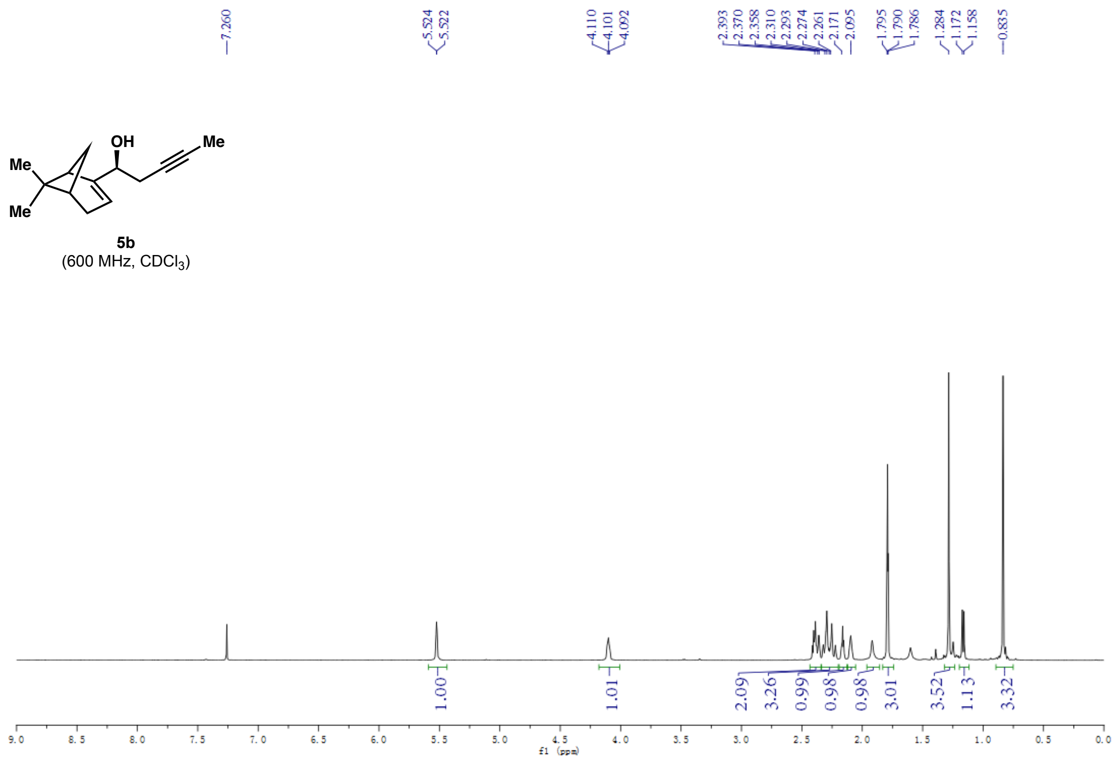

150.096
138.174
122.628
108.974
78.788 77.572 77.360 77.148 75.702 74.176
41.318
30.615 27.638 26.857 24.984 21.162
3.968
OH
Me
Me
5a
(151 MHz, $CDCl_3$)
f1 (ppm)

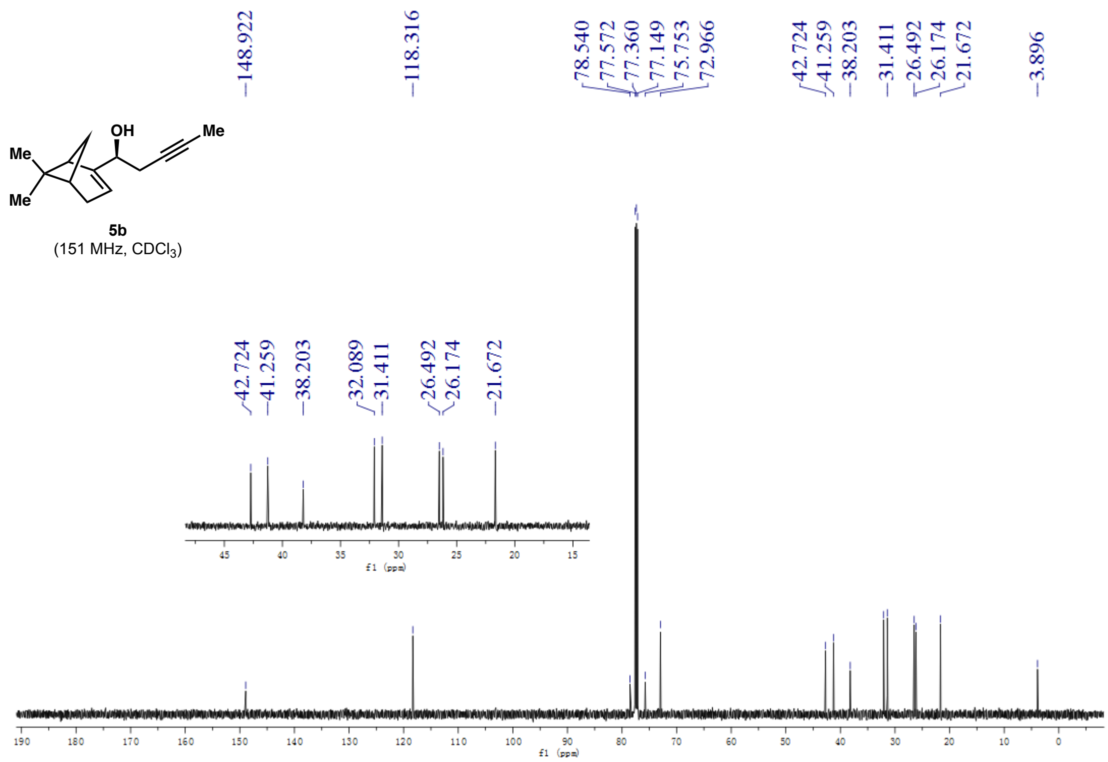


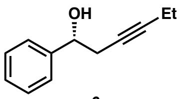
7.260
5.506
5.504
4.115
2.320
2.312
2.304
2.295
2.264
2.254
2.243
2.209
2.090
1.956
1.795
1.791
1.284
1.182
1.167
0.814
OH
Me
Me
Me
4b
(600 MHz, CDCl3)
1.00
1.03
1.17
3.13
2.08
0.99
0.92
3.08
3.21
1.24
3.29
f1 (ppm)



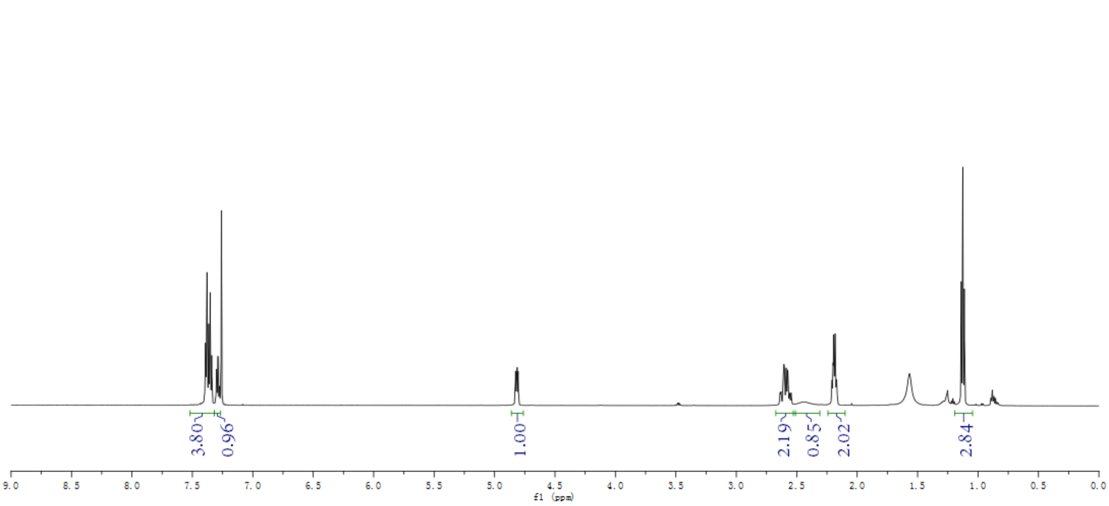
149.054
119.103
78.702
77.572
77.360
77.149
75.687
73.344
42.115
41.230
38.151
31.448
26.327
21.652
3.908
OH
Me
Me
Me
4b
(151 MHz, CDCl3)
42.115
41.230
38.151
32.061
31.448
26.516
26.327
21.652
f1 (ppm)

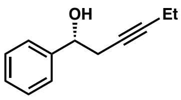

OH
Me
Me
Me
5b
(600 MHz, CDCl3)
7.260
5.524
5.522
4.110
4.101
4.092
2.393
2.370
2.358
2.310
2.293
2.274
2.261
2.171
2.095
1.795
1.790
1.786
1.284
1.172
1.158
0.835
1.00
1.01
2.09
3.26
0.99
0.98
0.98
3.01
3.52
1.13
3.32
f1 (ppm)


OH
Me
Me
Me
5b
(151 MHz, CDCl3)
148.922
118.316
78.540
77.572
77.360
77.149
75.753
72.966
42.724
41.259
38.203
31.411
26.492
26.174
21.672
3.896
42.724
41.259
38.203
32.089
31.411
26.492
26.174
21.672
f1 (ppm)

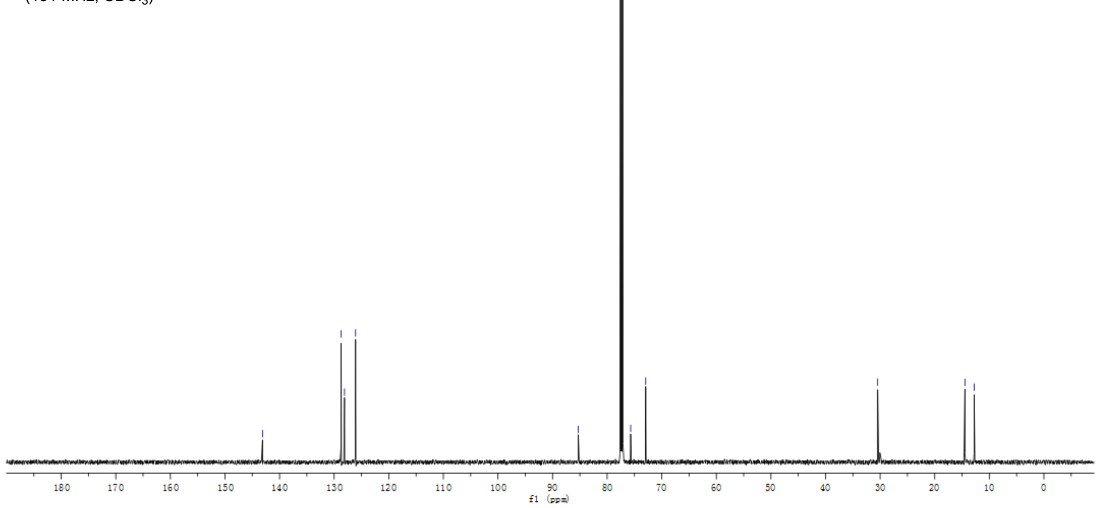


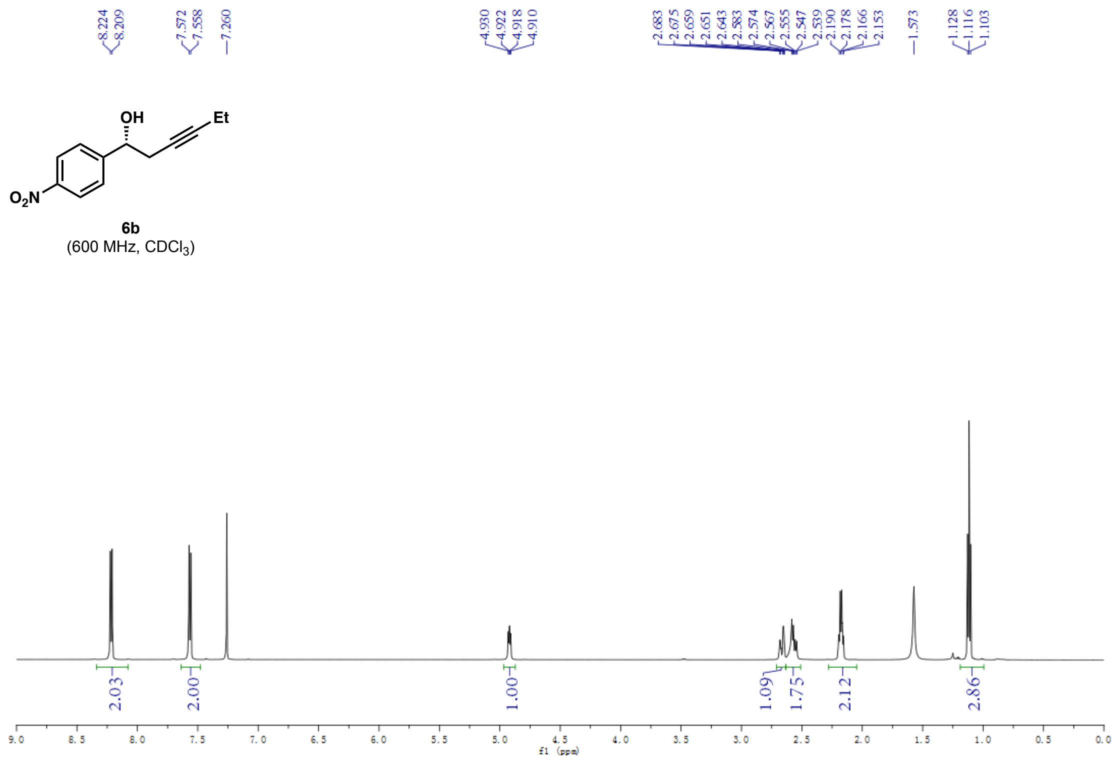
6a
(600 MHz, $CDCl_3$)



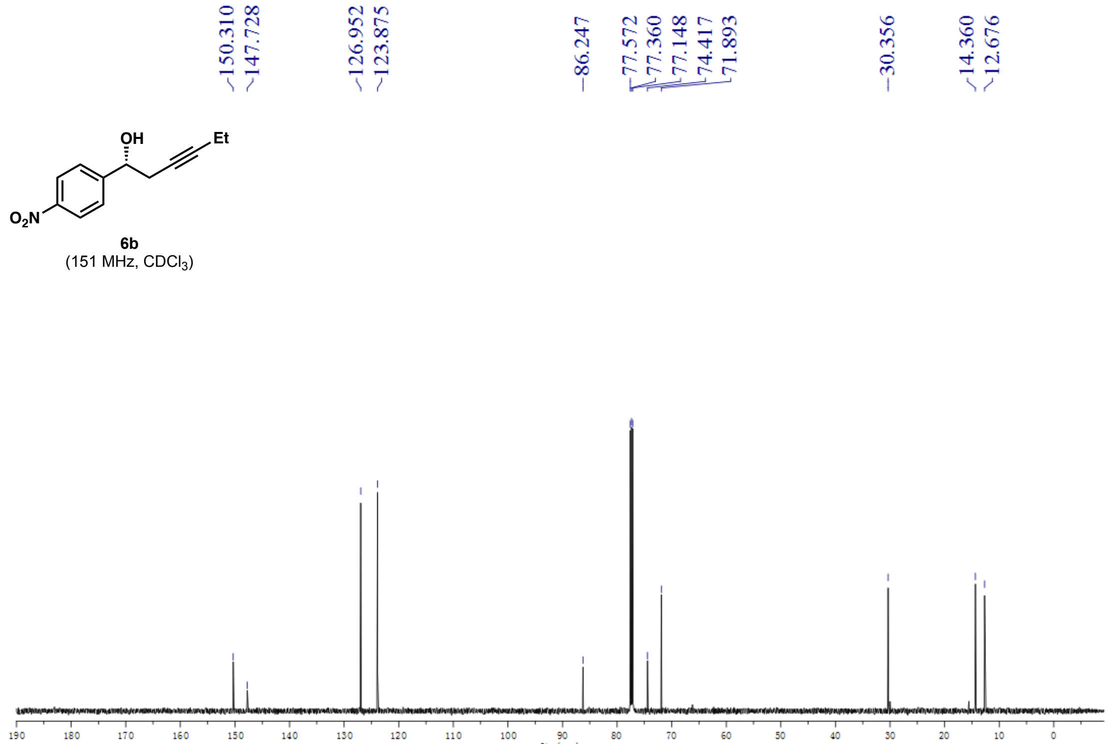


6a
(151 MHz, $CDCl_3$)

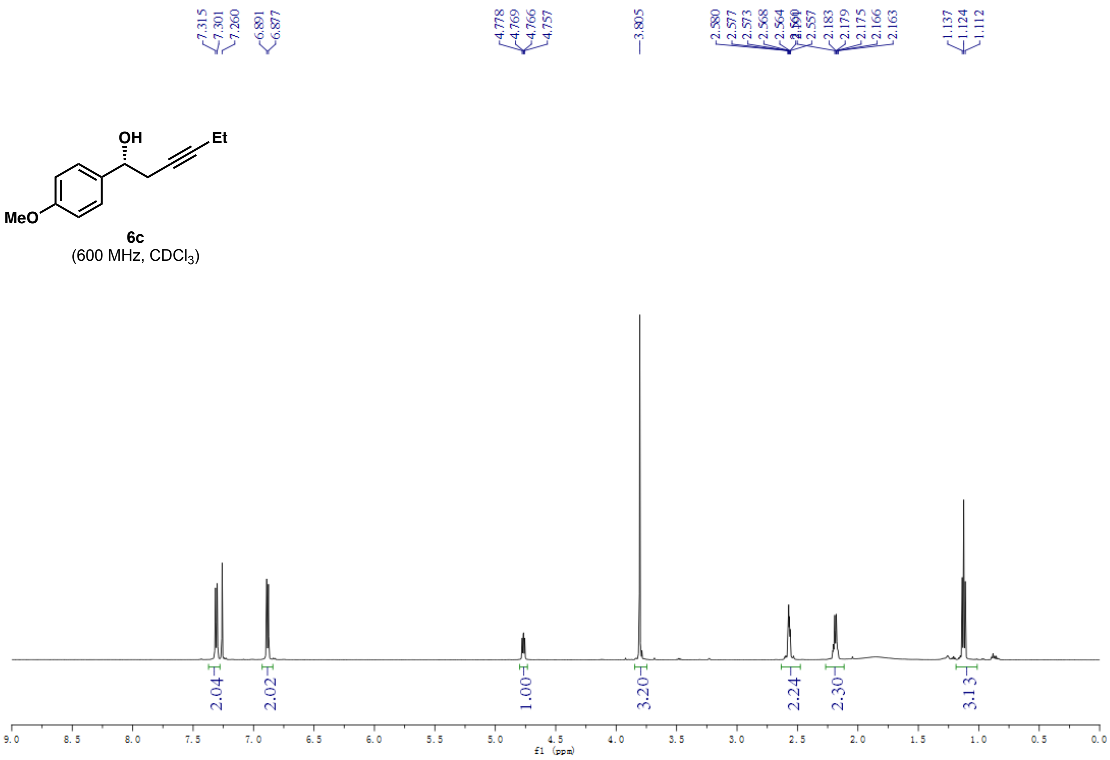


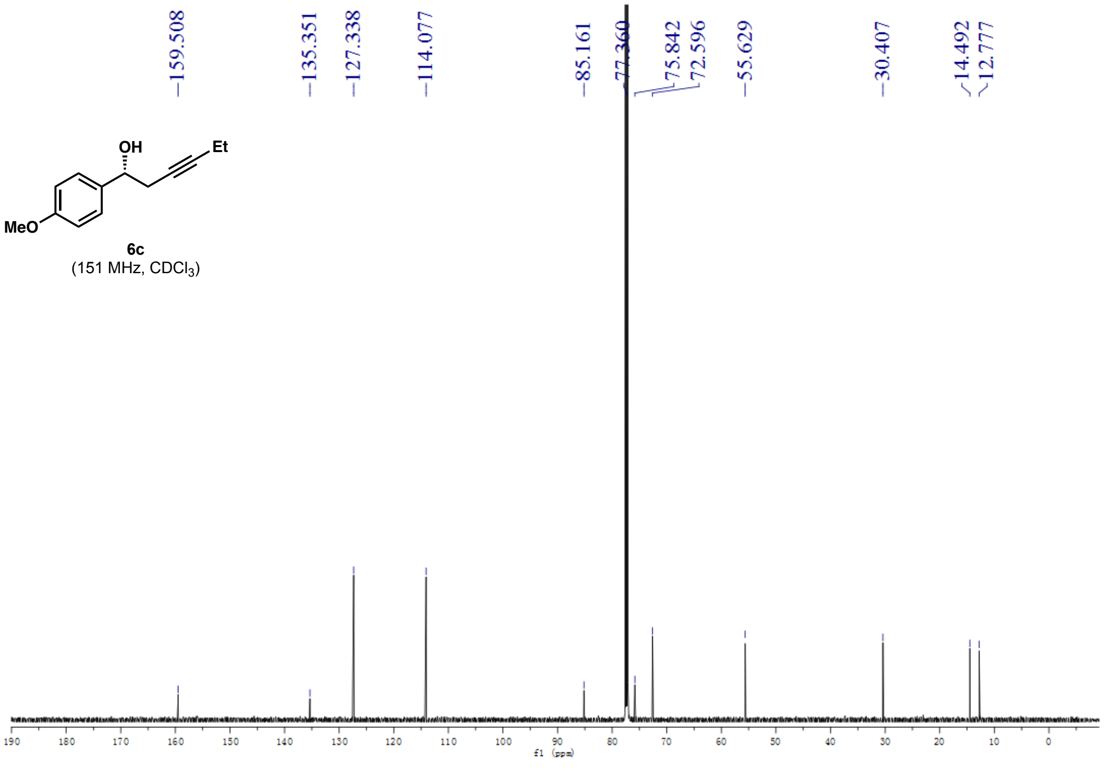


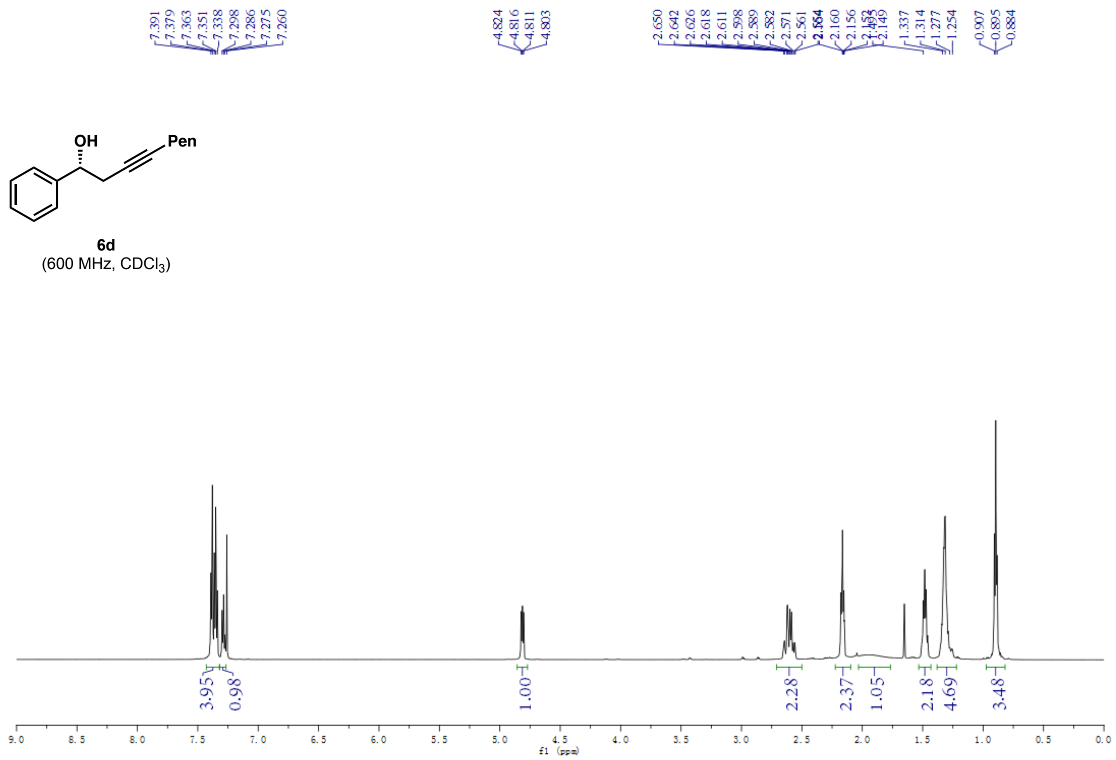
6b
(600 MHz, $CDCl_3$)

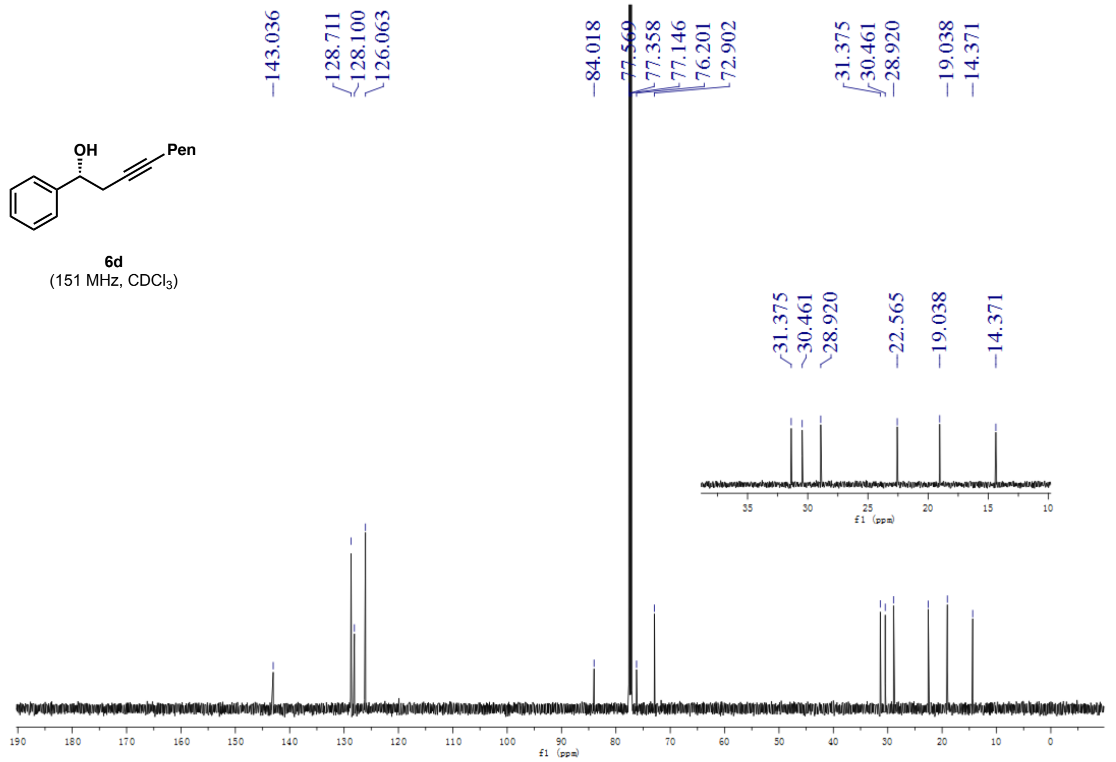


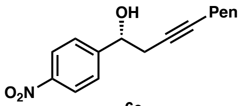
6b
(151 MHz, $CDCl_3$)


7.315
7.301
7.260
6.891
6.877
4.778
4.769
4.766
4.757
3.805
2.580
2.577
2.573
2.568
2.564
2.557
2.183
2.179
2.175
2.166
2.163
1.137
1.124
1.112
OH
Et
MeO
6c
(600 MHz, CDCl3)
2.04
2.02
1.00
3.20
2.24
2.30
3.13
f1 (ppm)

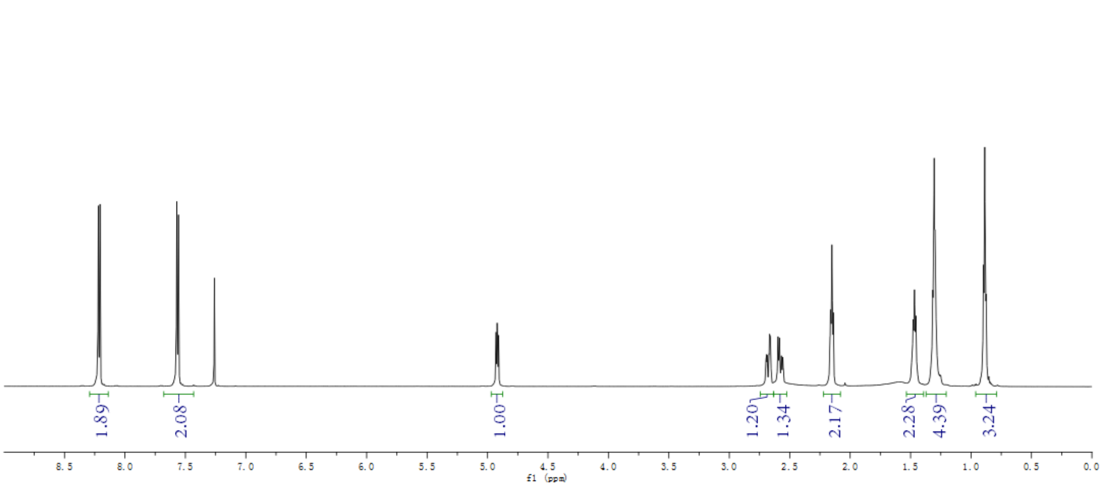

159.508
135.351
127.338
114.077
85.161
77.360
75.842
72.596
55.629
30.407
14.492
12.777
OH
Et
MeO
6c
(151 MHz, CDCl3)
f1 (ppm)

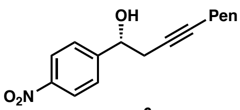




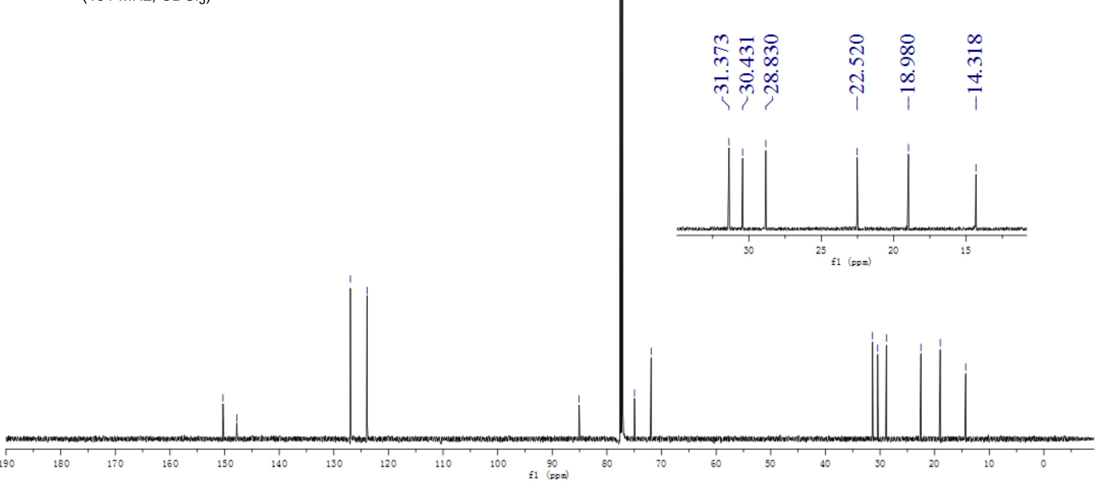


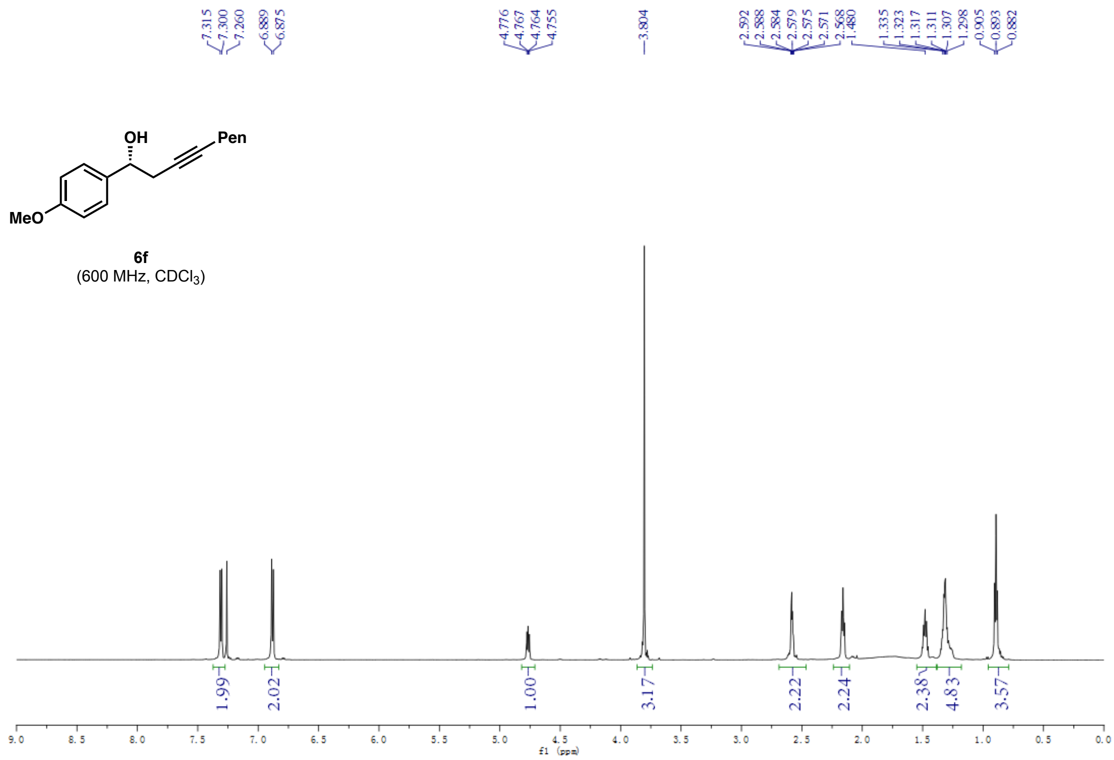
6e
(600 MHz, $CDCl_3$)



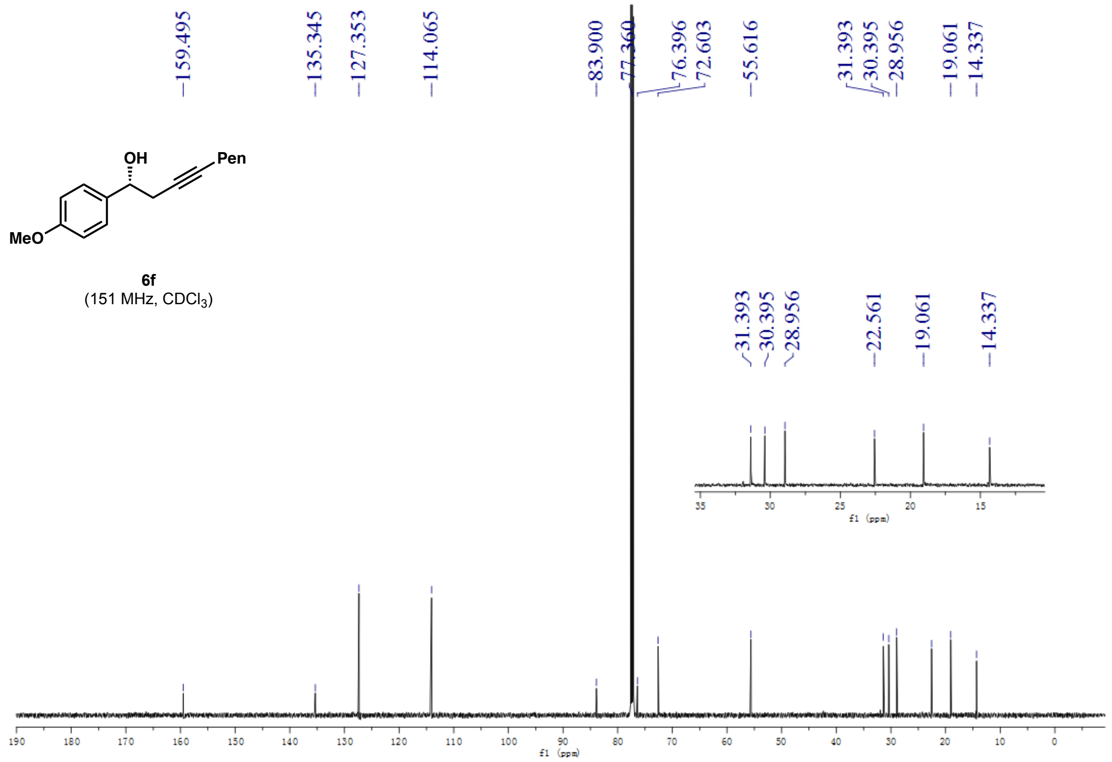


6e
(151 MHz, $CDCl_3$)

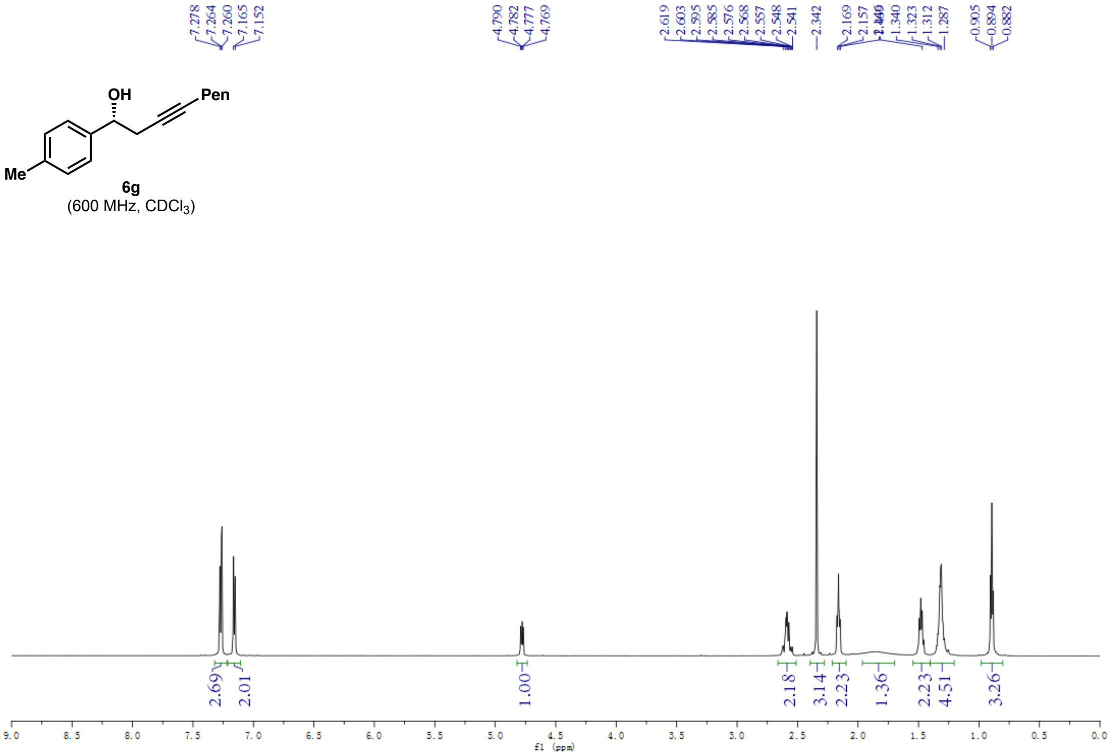


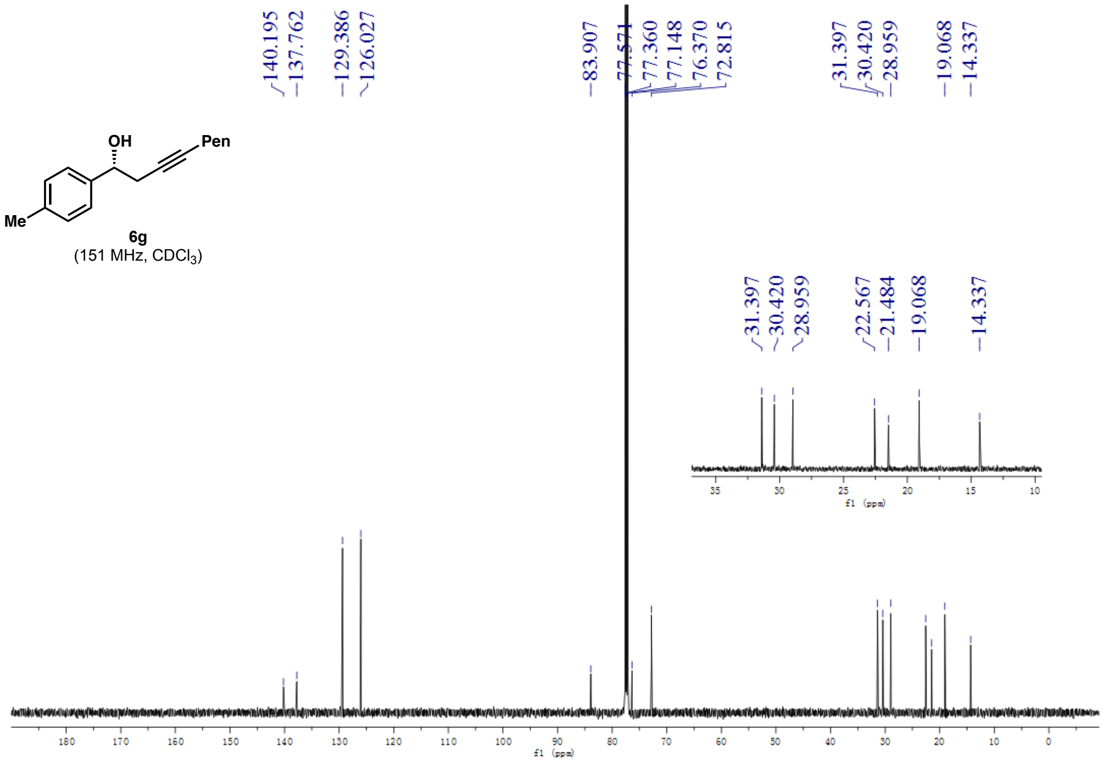


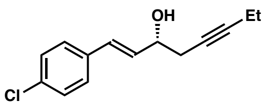
6f
(600 MHz, $CDCl_3$)



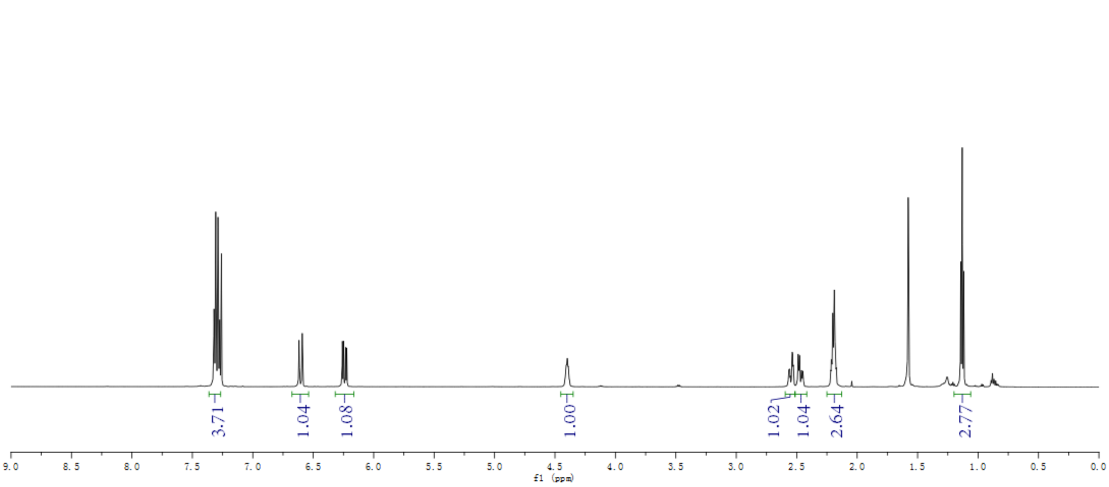
6f
(151 MHz, $CDCl_3$)

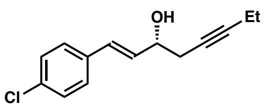

OH
Pen
Me
6g
(600 MHz, CDCl3)
7.278
7.264
7.260
7.165
7.152
4.790
4.782
4.777
4.769
2.619
2.603
2.595
2.585
2.576
2.568
2.557
2.548
2.541
2.342
2.169
2.157
1.340
1.323
1.312
1.287
0.905
0.894
0.882
2.69
2.01
1.00
2.18
3.14
2.23
1.36
2.23
4.51
3.26
f1 (ppm)


140.195
137.762
129.386
126.027
83.907
77.571
77.360
77.148
76.370
72.815
31.397
30.420
28.959
19.068
14.337
OH
Pen
Me
6g
(151 MHz, CDCl3)
31.397
30.420
28.959
22.567
21.484
19.068
14.337
f1 (ppm)

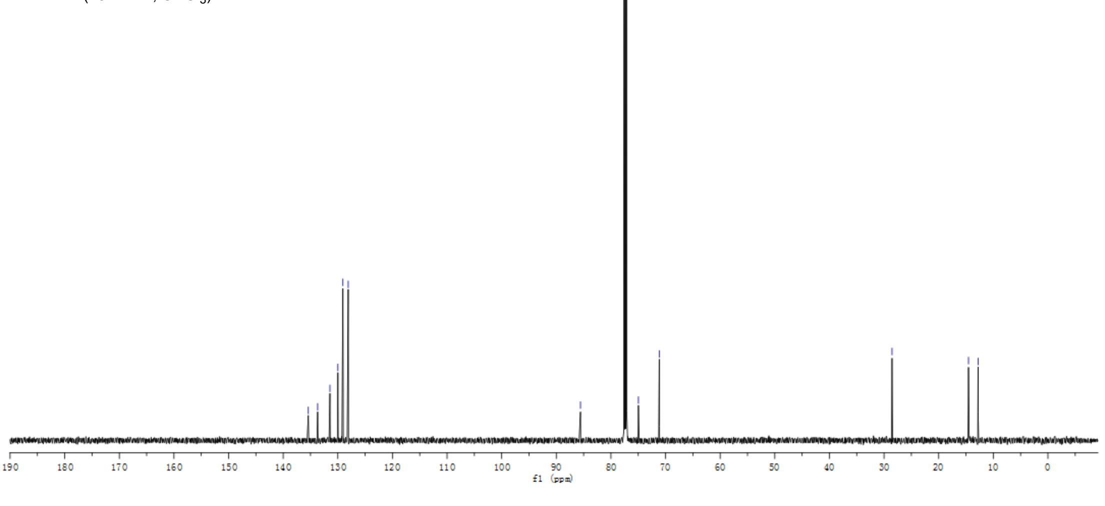


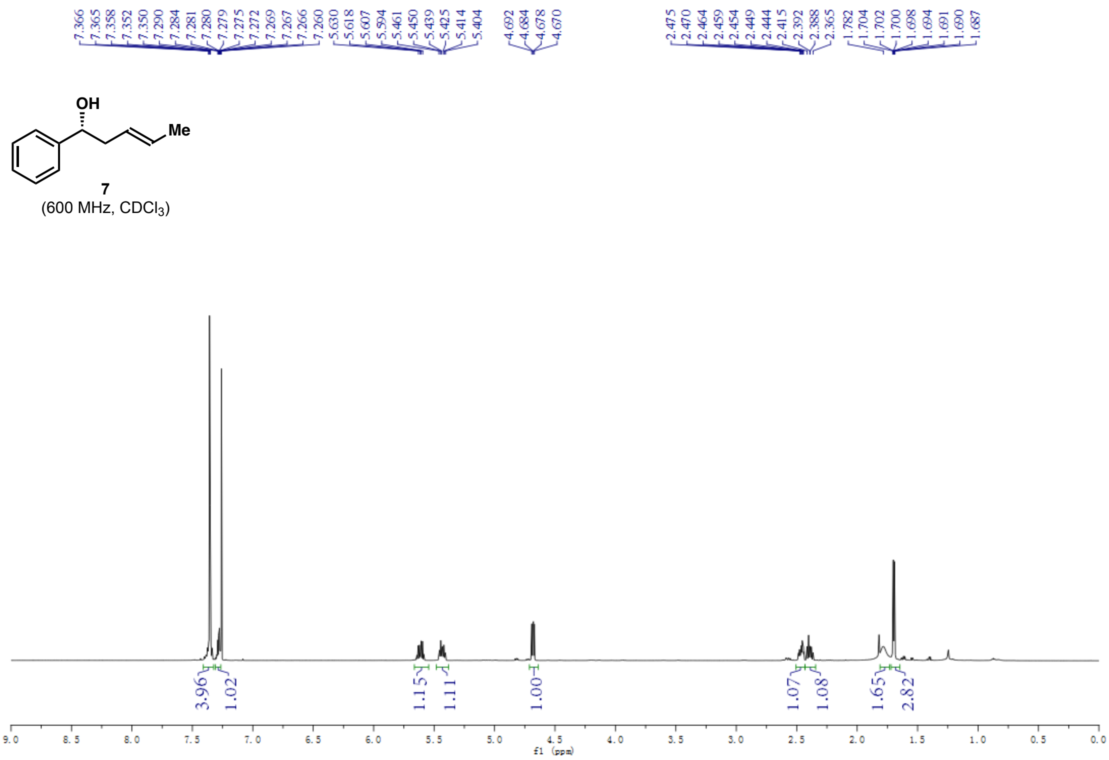
6h
(600 MHz, $CDCl_3$)

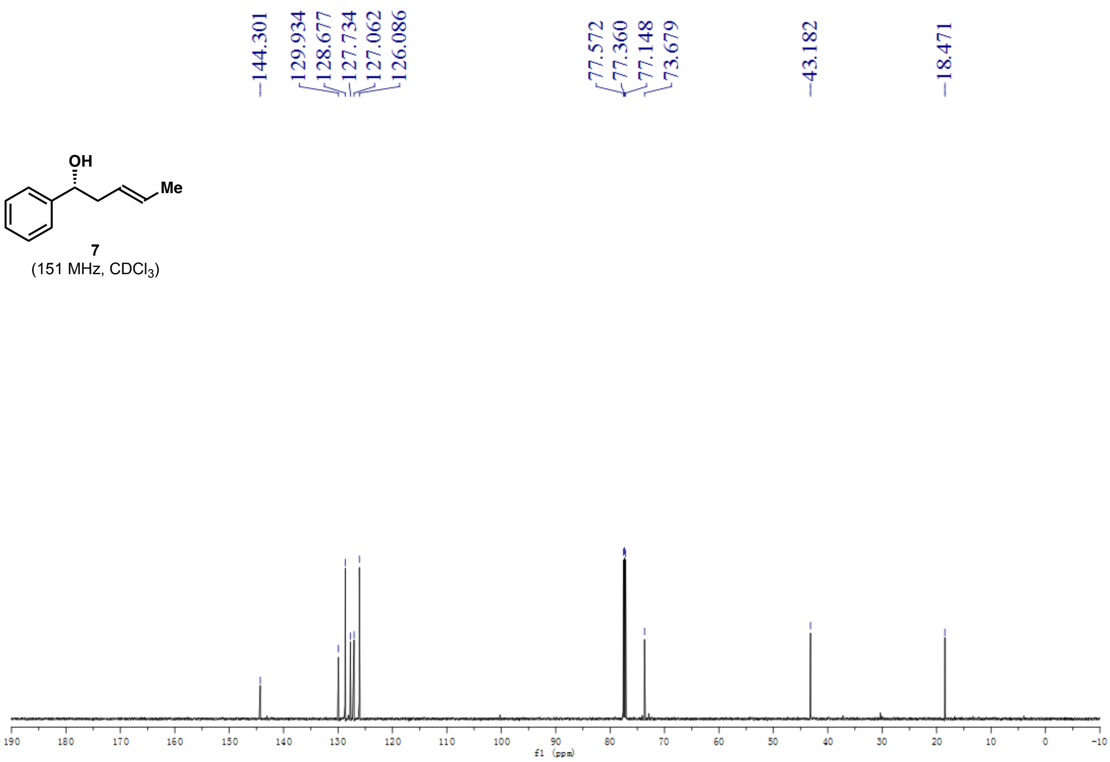


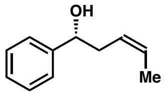


6h
(151 MHz, $CDCl_3$)

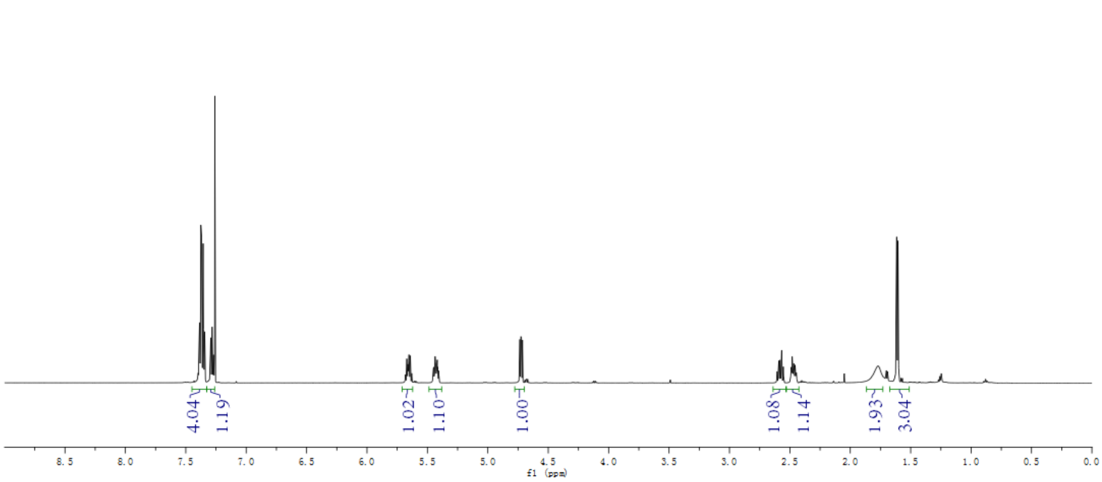


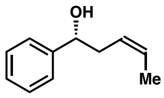

7.366 7.365 7.358 7.352 7.350 7.290 7.284 7.281 7.280 7.279 7.275 7.272 7.269 7.267 7.266 7.260 5.630 5.618 5.607 5.594 5.461 5.450 5.439 5.425 5.414 5.404 4.692 4.684 4.678 4.670 2.475 2.470 2.464 2.459 2.454 2.449 2.444 2.415 2.392 2.388 2.365 1.782 1.704 1.702 1.700 1.698 1.694 1.691 1.690 1.687
OH
Me
7
(600 MHz, $CDCl_3$)
3.96 1.02 1.15 1.11 1.00 1.07 1.08 1.65 2.82
f1 (ppm)


144.301 129.934 128.677 127.734 127.062 126.086 77.572 77.360 77.148 73.679 43.182 18.471
OH
Me
7
(151 MHz, $CDCl_3$)
f1 (ppm)

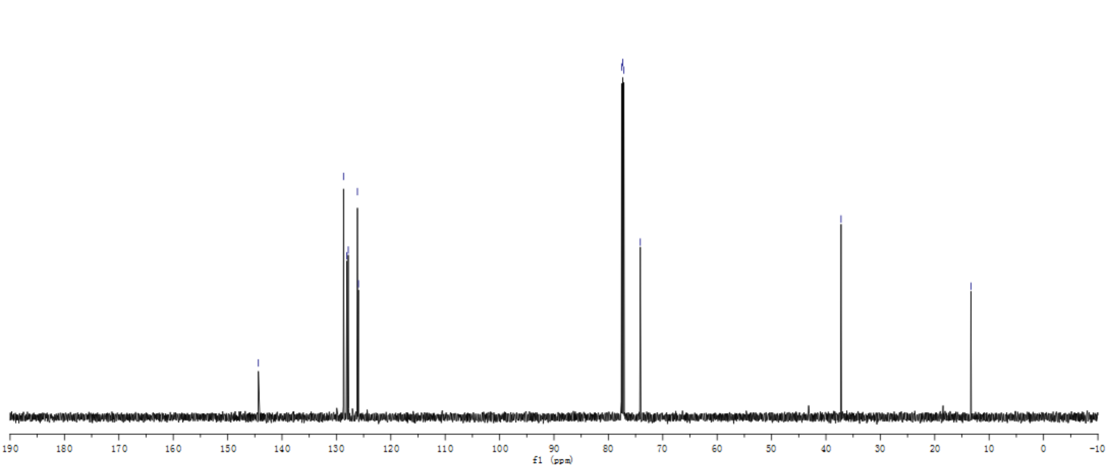


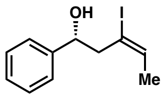
8
(600 MHz, $CDCl_3$)



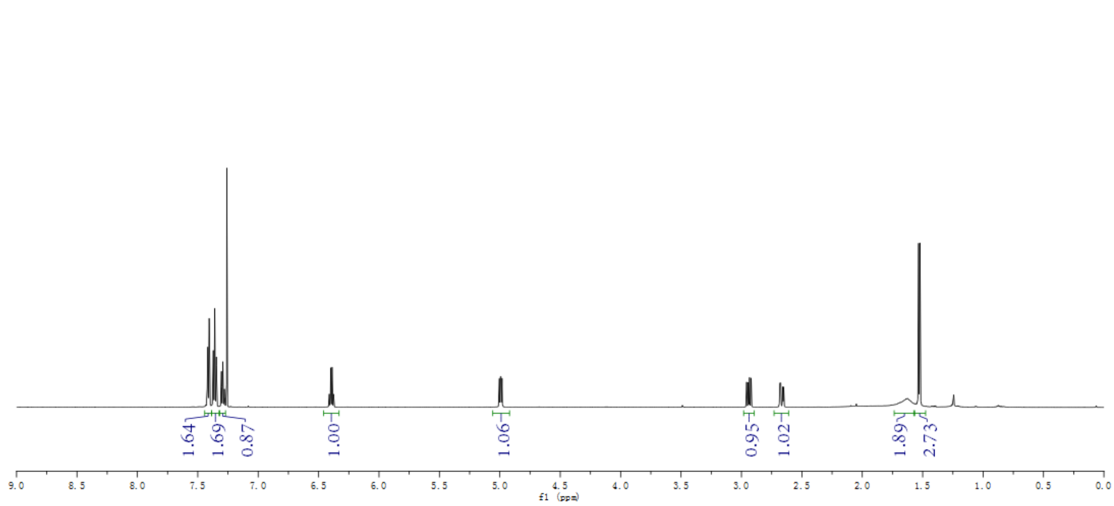


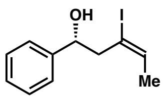
8
(151 MHz, $CDCl_3$)



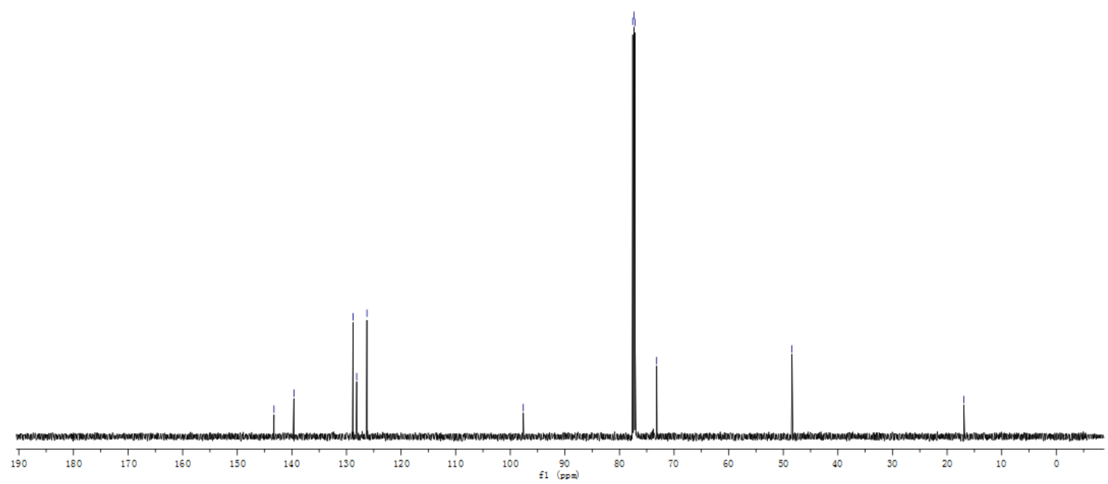


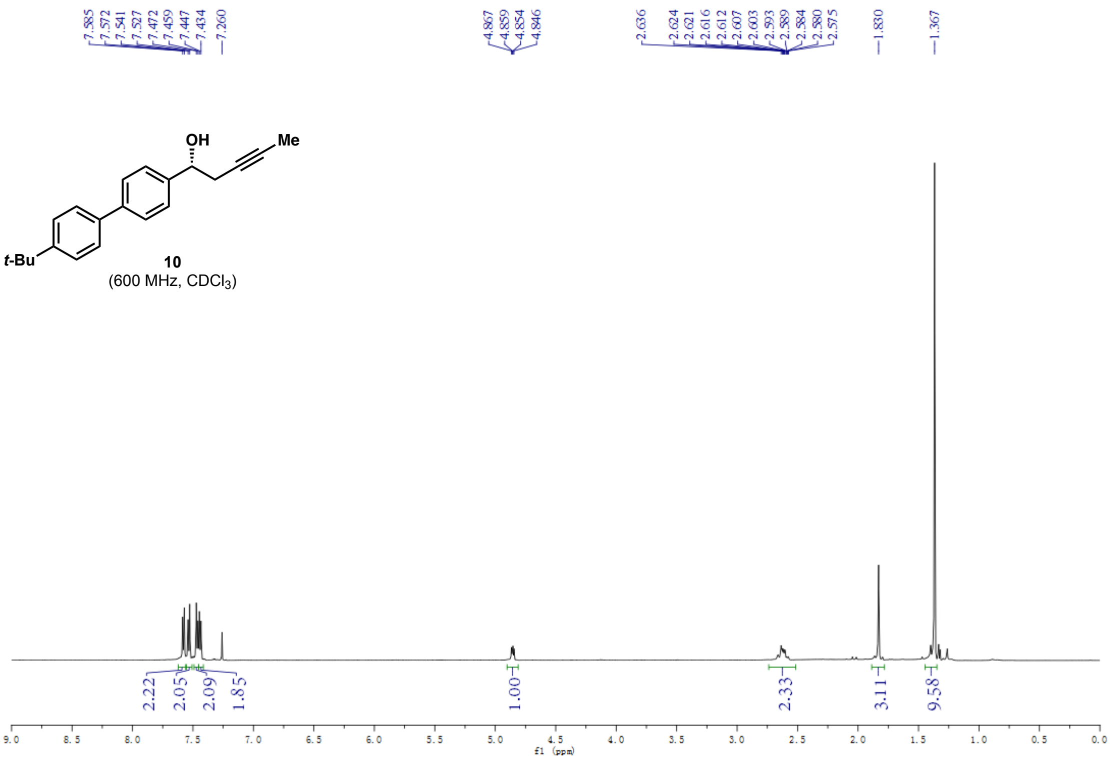
9
(600 MHz, $CDCl_3$)



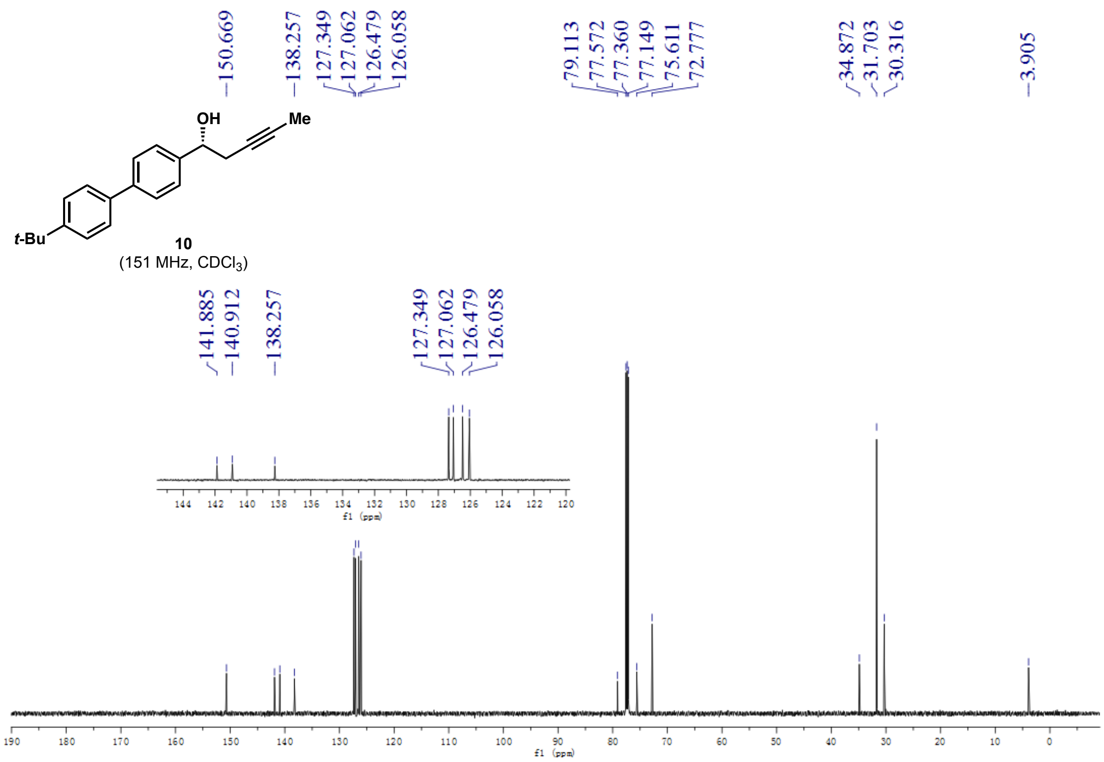


9
(151 MHz, $CDCl_3$)





10
(600 MHz, $CDCl_3$)



10
(151 MHz, $CDCl_3$)