Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

C–C Bond Migration in the Cycloisomerization of 1,6-Enynes

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Materials and Methods

Reactions were performed under an argon atmosphere unless otherwise noted. Tetrahydrofuran, toluene, and benzene were purified by passing through activated alumina columns. All other reagents were used as received unless otherwise noted. Commercially available chemicals were purchased from Alfa Aesar (Ward Hill, MA), Sigma-Aldrich (St. Louis, MO), Oakwood Products, (West Columbia, SC), Strem (Newburyport, MA) and TCI America (Portland, OR). Qualitative TLC analysis was performed on 250 mm thick, 60 Å, glass backed, F254 silica (Silicycle, Quebec City, Canada). Visualization was accomplished with UV light and exposure to *p*-anisaldehyde or ceric ammonium molybdate (CAM) solutions followed by heating. Flash chromatography was performed using Silicycle silica gel (230-400 mesh). NMR spectra were acquired at both the Colorado State University Central Instrument Facility on an Agilent (Varian) 400-MR and at the University of Georgia Chemical Sciences Magnetic Resonance Facility on a Varian Mercury Plus 400 MHz NMR. ^{1}H NMR spectra were acquired at 400 MHz and are reported relative to $SiMe_4$ (δ 0.00). ^{13}C NMR spectra were at 100 MHz and are reported relative to $SiMe_4$ (δ 0.0). All IR spectra were obtained on NaCl plates (film) with a Bruker Tensor 27. Gas chromatography was performed on a Varian CP-3800 gas chromatograph. High resolution mass spectrometry data were acquired by the Colorado State University Central Instrument Facility on an Agilent 6210 TOF LC/MS and by the Proteomics and Mass Spectrometry Facility at the University of Georgia on a Thermo Orbitrap Elite.

Enyne Cycloisomerizations

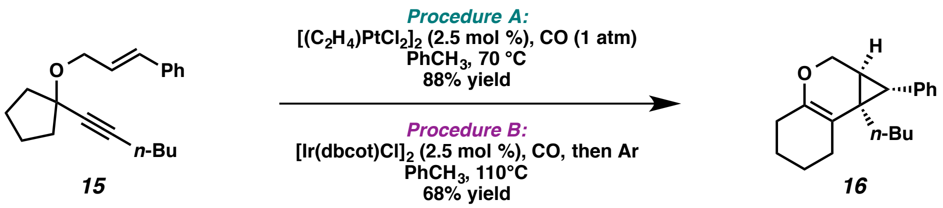
General Notes: All solvents used were anhydrous and all reactions were performed in flame-dried glassware. Without the addition of triethylamine to the flash chromatography eluent, decreased yields were observed. In the cycloisomerizations run with [Ir(dbcot)Cl]$_2$, 1,3-bis(diphenylphosphino)propane (dppp) was added in the work up to chelate the iridium. NMR spectra for the cycloisomerization products were taken in d_6-benzene, since the products decomposed in $CDCl_3$.

A. General procedure for the cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by Zeise's dimer ([(C_2H_4)$PtCl_2$]$_2$). To a solution of the 1,6-enyne (1 equiv) in toluene (0.06 M) in a 2-dram vial under argon at 23 °C was quickly added Zeise's dimer (2.5 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at the described temperature until all of the starting material was consumed, as determined by TLC. The reaction mixture was allowed to cool to ambient temperature and diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography to afford the product enol ether.

General procedure for the *scaled-up* cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by Zeise's dimer ([(C_2H_4)$PtCl_2$]$_2$). To a solution of the 1,6-enyne (1 equiv) in toluene (0.15 M) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added Zeise's dimer (2.5 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at the described temperature until all of the starting material was consumed, as determined by TLC. The reaction mixture was allowed to cool to ambient temperature, and the volatile materials were removed by rotary evaporation. The resulting residue was purified by flash chromatography to afford the product enol ether.

B. General procedure for the cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by [Ir(dbcot)Cl]$_2$. To a solution of the 1,6-enyne (1 equiv) in toluene (0.06 M) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added [Ir(dbcot)Cl]$_2$ (2.5 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C until all of the starting material was consumed, as determined by TLC. The reaction was allowed to cool to ambient temperature and diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (0.25 equiv) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography to afford the product enol ether.

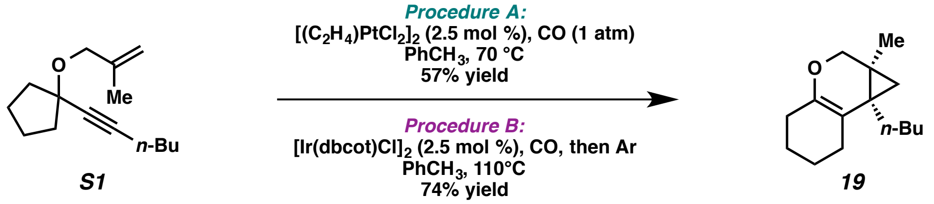
C. General procedure for the cycloisomerization of oxygen-tethered 1,6-enynes catalyzed by $PtCl_2$. To a solution of the 1,6-enyne (1 equiv) in toluene (0.06 M) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (7 mol %). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at the described temperature until all of the starting material was consumed, as determined by TLC. The reaction mixture was allowed to cool to ambient temperature and diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography to afford the product enol ether.



Tricycle 16. ***Procedure A*****:** To a solution of enyne **15** (16.0 mg, 56.7 μmol) in toluene (0.92 mL) in a 2-dram vial under argon at 23 °C was quickly added [(C_2H_4)$PtCl_2$]$_2$ (0.9 mg, 1.53 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 43 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **16** (14.1 mg, 88% yield, R_f = 0.70 in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a yellow oil.

Procedure B**:** To a solution of enyne **15** (16.9 mg, 59.8 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added [Ir(dbcot)Cl]$_2$ (1.3 mg, 1.53 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 15.5 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2w/ 0.5% Et_3N eluent), affording tricycle **16** (11.5 mg, 68% yield) as a yellow oil.

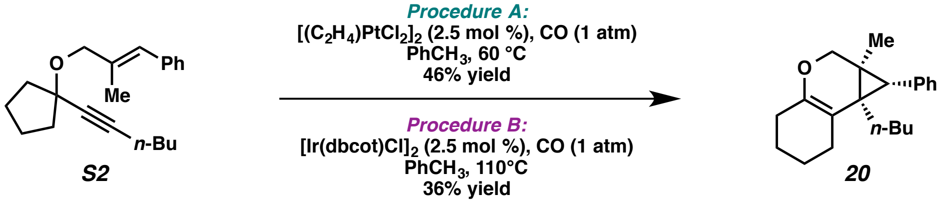
Tricycle 16: ^{1}H NMR (400 MHz; C_6D_6): δ 7.21-7.18 (m, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 7.09-7.04 (m, 3H), 4.08 (dd, *J* = 10.8, 4.5 Hz, 1H), 3.92 (dd, *J* = 10.9, 2.4 Hz, 1H), 2.29 (d, *J* = 5.5 Hz, 1H), 2.26-2.02 (m, 4H), 1.65-1.09 (m, 10H), 0.82 (d, *J* = 14.6 Hz, 3H), 0.62 (ddd, *J* = 14.0, 11.1, 5.7 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 147.8, 139.1, 129.4, 128.4, 126.2, 110.8, 64.5, 38.4, 30.2, 29.3, 28.1, 26.4, 25.6, 25.3, 23.8, 23.4, 23.3, 14.5; IR (film) 2929, 2858, 1673, 1447, 1145 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2045.



Tricycle 19. ***Procedure A***: To a solution of enyne **S1** (31.5 mg, 143 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.74 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 19 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **19** (17.9 mg, 57% yield, R_f = 0.81 in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a colorless oil.

Procedure B: To a solution of enyne **S1** (13.3 mg, 60.4 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 15.5 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation ,and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **19** (9.9 mg, 74% yield) as a colorless oil.

Tricycle 19: ^{1}H NMR (400 MHz; C_6D_6): δ 3.74 (q, *J* = 12.4 Hz, 2H), 2.27-2.06 (m, 4H), 1.95-1.87 (m, 2H), 1.60-1.40 (m, 4H), 1.33-1.23 (m, 4H), 0.97 (d, *J* = 4.6 Hz, 3H), 0.93-0.91 (m, 3H), 0.41 (s, 1H), 0.35 (d, *J* = 3.6 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 147.5, 110.9, 70.5, 31.2, 30.6, 30.2, 28.1, 26.8, 25.5, 23.9, 23.8, 23.6, 23.3, 17.2, 14.4; IR (film) 2930, 2860, 1674, 1457, 1158 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{24}O + H]^+$: 221.1900, found 221.1894.

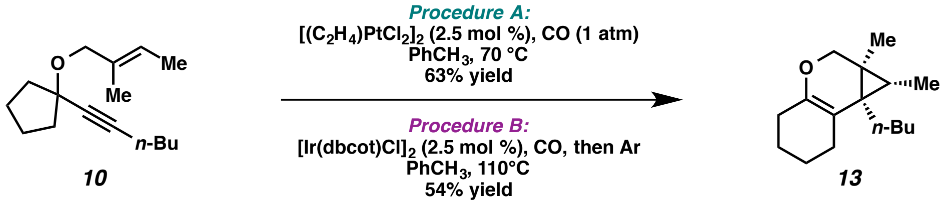


Tricycle 20. ***Procedure A*****:** To a solution of enyne **S2** (29.3 mg, 98.8 μmol) in toluene (1.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (1.5 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 60 °C for 24 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was

stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 6:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **20** (13.4 mg, 46% yield, R_f = 0.75 in 1:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a colorless oil.

Procedure B (under CO)**:** To a solution of enyne **S2** (23.6 mg, 79.6 μmol) in toluene (1.2 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.7 mg, 1.97 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The reaction vessel was then sealed and the reaction mixture was stirred at 110 °C for 27 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **20** (8.4 mg, 36% yield) as a colorless oil.

Tricycle 20: ^{1}H NMR (400 MHz; C_6D_6): δ 7.27-7.07 (m, 5H), 3.86 (ABq, J_{AB} = 10.6 Hz, $\Delta\upsilon_{AB}$ = 49.6 Hz, 2H), 2.31-2.24 (m, 1H), 2.22-2.12 (m, 2H), 1.90-1.80 (m, 1H), 1.65-1.42 (m, 6H), 1.39-1.27 (m, 1H), 1.22-1.12 (m, 2H), 0.99 (s, 3H), 0.98-0.91 (m, 1H), 0.83-0.79 (m, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 147.8, 138.0, 131.2, 130.2, 128.5, 126.4, 111.6, 71.2, 38.5, 29.9, 28.8, 28.1, 27.8, 27.4, 25.6, 23.9, 23.6, 23.3, 14.5, 14.4; IR (film) 2930, 2859, 1497, 1156, 1156 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{21}H_{28}O + H]^+$: 297.2213, found 297.2212.

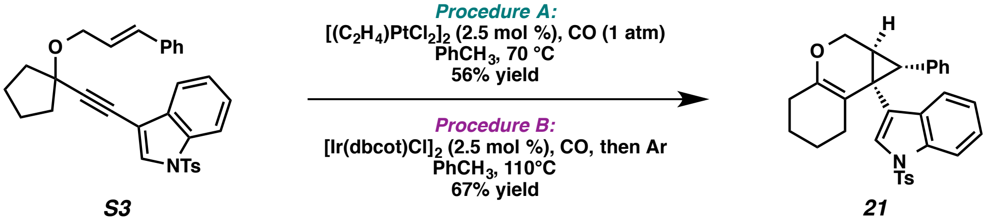


Tricycle 13. ***Procedure A*****:** To a solution of enyne **10** (15.5 mg, 66.1 μmol) in toluene (1.1 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (1.0 mg, 1.65 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 17 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **13** (9.8 mg, 63% yield, R_f = 0.84 in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a colorless oil.

Procedure B: To a solution of enyne **10** (14.4 mg, 61.4 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 15.5 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 50:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **13** (7.8 mg, 54% yield) as a colorless oil.

Tricycle 13: ^1H NMR (400 MHz; C_6D_6): δ 3.74 (q, *J* = 10.8 Hz, 2H), 2.24-2.04 (m, 4H), 1.98-1.91 (m, 1H), 1.56-1.44 (m, 4H), 1.34-1.28 (m, 4H), 1.02 (t, *J* = 3.1 Hz, 2H), 0.92 (t, *J* = 7.0 Hz, 6H), 0.88 (s, 3H);

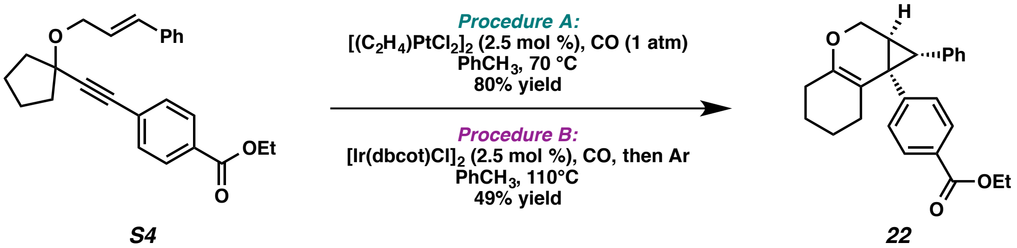
^{13}C NMR (100 MHz; C_6D_6): δ 147.2, 112.4, 71.2, 30.0, 28.2, 27.7, 26.9, 25.6, 24.9, 23.9, 23.8, 23.3, 20.6, 14.4, 12.0, 9.0; IR (film) 2926, 2956, 1457, 1157 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{26}O + H]^+$: 235.2056, found 235.2050.



Tricycle 21. ***Procedure A*:** To a solution of enyne **S3** (78.0 mg, 157 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 20.5 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **21** (43.6 mg, 56% yield, R_f = 0.67 in 2:1 CH_2Cl_2/hexanes, stained purple with *p*-anisaldehyde) as a colorless oil.

***Procedure B*:** To a solution of enyne **S3** (49.7 mg, 99.9 μmol) in toluene (1.7 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (2.2 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 15 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 9:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **21** (33.1 mg, 67% yield) as a colorless oil.

Tricycle 21: ^1H NMR (400 MHz; C_6D_6): δ 8.15 (d, *J* = 8.2 Hz, 1H), 7.54-7.52 (m, 1H), 7.42 (d, *J* = 8.3 Hz, 2H), 7.07-6.96 (m, 2H), 6.92-6.85 (m, 4H), 6.68 (d, *J* = 7.0 Hz, 2H), 6.51 (d, *J* = 8.1 Hz, 2H), 3.98-3.91 (m, 2H), 2.71 (d, *J* = 6.0 Hz, 1H), 2.19-2.00 (m, 3H), 1.84 (dt, *J* = 5.8, 2.8 Hz, 1H), 1.68 (s, 3H), 1.53-1.44 (m, 2H), 1.41-1.11 (m, 5H), 0.38-0.34 (m, 2H); ^{13}C NMR (100 MHz; C_6D_6): δ 179.4, 144.2, 138.8, 132.6, 129.7, 128.5, 128.2, 127.9, 127.2, 126.1, 124.9, 123.4, 114.2, 62.9, 28.2, 26.5, 23.6, 23.2, 21.1; IR (film) 2929, 2858, 1447, 1188 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{31}H_{29}NO_3S + H]^+$: 496.1941, found 496.1926.

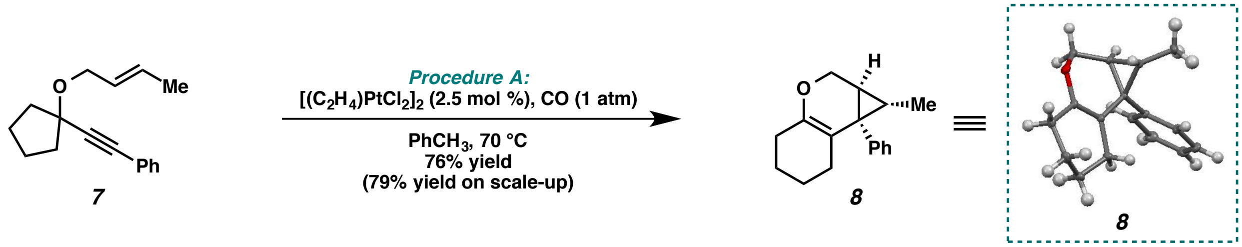


Tricycle 22. ***Procedure A*****:** To a solution of enyne **S4** (55.7 mg, 149 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 20.5 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash

chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **22** (44.6 mg, 80% yield, R_f = 0.55 in 2:1 CH_2Cl_2/hexanes, stained purple with *p*-anisaldehyde) as a yellow oil.

***Procedure B*:** To a solution of enyne **S4** (34.6 mg, 99.6 μmol) in toluene (1.7 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (2.2 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 15 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **22** (16.8 mg, 49% yield) as a yellow oil.

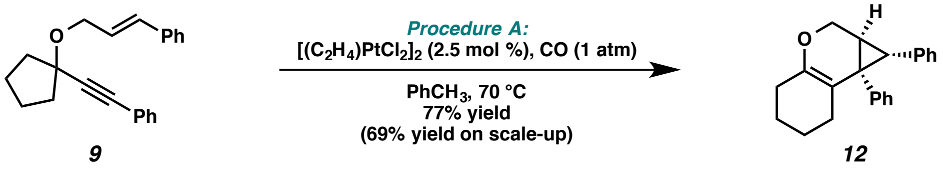
Tricycle 22: ^{1}H NMR (400 MHz; C_6D_6): δ 8.02 (d, *J* = 8.3 Hz, 2H), 6.97-6.91 (m, 5H), 6.59 (dd, *J* = 7.6, 1.9 Hz, 2H), 4.12-4.05 (m, 2H), 4.04-3.92 (m, 2H), 2.74 (d, *J* = 5.8 Hz, 1H), 2.27-2.05 (m, 2H), 1.93-1.91 (m, 1H), 1.90-1.86 (m, 1H), 1.61-1.58 (m, 1H), 1.46-1.39 (m, 3H), 1.31-1.23 (m, 1H), 0.98 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 166.2, 146.5, 144.4, 138.6, 132.5, 129.4, 126.0, 111.4, 62.5, 60.7, 36.7, 34.7, 30.8, 28.2, 27.0, 23.5, 23.1, 14.3; IR (film) 2931, 2859, 1716, 1274, 1101 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{26}O_3 + H]^+$: 375.1955, found 375.1943.



Tricycle 8. ***Procedure A*:** To a solution of enyne **7** (36.7 mg, 153 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.74 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 19 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **8** (27.9 mg, 76% yield, $R_f = 0.81$ in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a colorless oil.

Procedure A (Scale-up): To a solution of enyne **7** (0.272 g, 1.13 mmol) in toluene (7.5 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (16.6 mg, 0.0283 mmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 20 h. The reaction mixture was allowed to cool to ambient temperature, and the volatile materials were removed by rotary evaporation. The resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **8** (0.215 g, 79% yield) as a colorless oil.

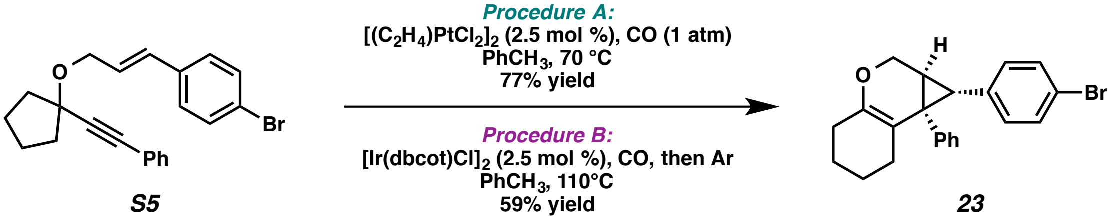
Tricycle 8: ^{1}H NMR (400 MHz; C_6D_6): δ 7.22-7.17 (m, 4H), 7.10 (tt, *J* = 6.8, 2.2 Hz, 1H), 4.05-3.94 (m, 2H), 2.22-1.95 (m, 4H), 1.73 (dq, *J* = 15.4, 4.0 Hz, 1H), 1.45-1.35 (m, 4H), 1.13 (td, *J* = 4.9, 2.3 Hz, 1H), 0.86 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 145.5, 141.0, 132.0, 128.3, 126.6, 112.3, 63.2, 31.8, 29.9, 28.2, 27.4, 25.8, 23.7, 23.3, 16.1; IR (film) 2928, 2858, 1670, 1445, 1150 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{17}H_{20}O + H]^+$: 241.1587, found 241.1583.



Tricycle 12. ***Procedure A*****:** To a solution of enyne **9** (45.1 mg, 149 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 18 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **12** (34.7 mg, 77% yield, $R_f = 0.80$ in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a yellow oil.

Procedure A (Scale-up): To a solution of enyne **9** (0.127 g, 420 μmol) in toluene (2.8 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (6.2 mg, 10.5 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 41 h. The reaction mixture was allowed to cool to ambient temperature, and the volatile materials were removed by rotary evaporation. The resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **12** (87.5 mg, 69% yield) as a yellow oil.

Tricycle 12: ^{1}H NMR (400 MHz; C_6D_6): δ 6.99-6.91 (m, 8H), 6.65 (dd, *J* = 7.7, 1.6 Hz, 2H), 4.09-3.99 (m, 2H), 2.75 (d, *J* = 5.8 Hz, 1H), 2.28-2.07 (m, 2H), 2.02-1.95 (m, 2H), 1.72-1.66 (m, 1H), 1.46-1.38 (m, 3H), 1.31-1.25 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.1, 139.2, 132.4, 128.1, 127.9, 126.7, 125.7, 112.3, 62.7, 36.7, 34.9, 31.3, 28.3, 27.2, 23.6, 23.2; IR (film) 2928, 1666, 1496, 1191 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{22}O + H]^+$: 303.1743, found 303.1740.

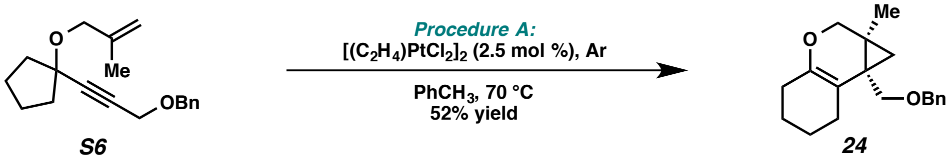


Tricycle 23. ***Procedure A*****:** To a solution of enyne **S5** (16.4 mg, 43.0 μmol) in toluene (0.70 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (0.6 mg, 1.02 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 18 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **23** (12.7 mg, 77% yield, R_f = 0.79 in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a colorless oil.

Procedure B**:** To a solution of enyne **S5** (20.5 mg, 53.8 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 6 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-

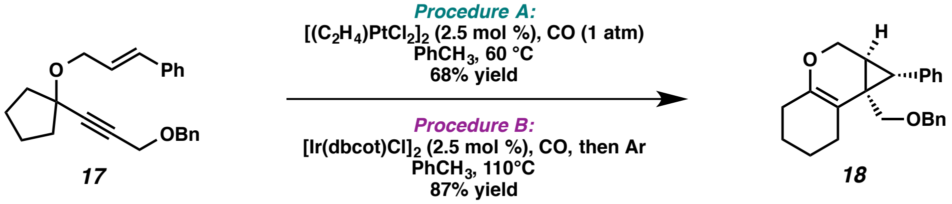
Bis(diphenylphosphino)propane (dppp) (7.4 mg, 17.9 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **23** (12.0 mg, 59% yield) as a colorless oil.

Tricycle 23: ^{1}H NMR (400 MHz; C_6D_6): δ 7.04-7.02 (m, 2H), 6.97-6.95 (m, 3H), 6.89-6.87 (m, 2H), 6.27-6.25 (m, 2H), 4.03-3.92 (m, 2H), 2.57 (d, *J* = 5.8 Hz, 1H), 2.26-2.05 (m, 2H), 1.98-1.89 (m, 1H), 1.83-1.79 (m, 1H), 1.70-1.60 (m, 1H), 1.46-1.37 (m, 3H), 1.30-1.21 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.2, 138.6, 138.3, 132.3, 130.9, 129.7, 126.9, 119.5, 112.0, 62.5, 35.9, 35.0, 31.5, 28.2, 27.1, 23.5, 23.2; IR (film) 2928, 2858, 1668, 1491, 1145 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{21}BrO + H]^+$: 381.0849, found 381.0842.



Tricycle 24. ***Procedure A:*** To a solution of enyne **S6** (24.8 mg, 87.2 μmol) in toluene (1.3 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (1.3 mg, 2.21 μmol). The solution was stirred at 70 °C for 23 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **24** (12.8 mg, 52% yield, R_f = 0.30 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a colorless oil.

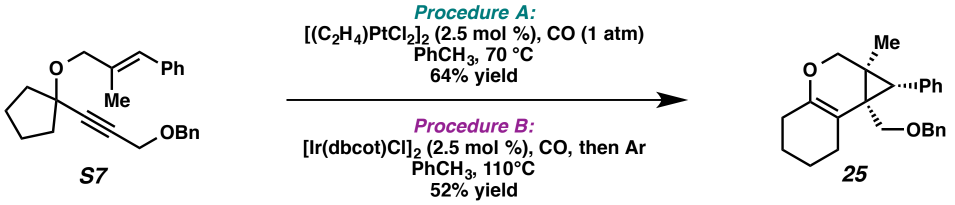
Tricycle 24: ^{1}H NMR (400 MHz; C_6D_6): δ 7.30-7.28 (m, 2H), 7.18-7.15 (m, 2H), 7.11-7.07 (m, 1H), 4.28 (ABq, J_{AB} = 12.0 Hz, $\Delta\upsilon_{AB}$ = 42.0 Hz, 2H), 3.77 (d, J = 10.4 Hz, 1H), 3.72 (ABq, J_{AB} = 10.2 Hz, $\Delta\upsilon_{AB}$ = 65.7 Hz, 2H), 2.91 (d, J = 10.4 Hz, 1H), 2.57-2.50 (m, 1H), 2.22-2.05 (m, 3H), 1.63-1.38 (m, 4H), 1.23-1.20 (m, 1H), 0.99 (s, 3H), 0.41-0.40 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.2, 139.2, 128.5, 128.2, 127.7, 110.7, 73.1, 71.3, 68.0, 28.1, 28.0, 25.0, 24.5, 23.6, 23.2, 22.9, 16.0; IR (film) 2929, 2856, 1678, 1454, 1075 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O_2 + H]^+$: 285.1849, found 285.1848.



Tricycle 18. ***Procedure A*****:** To a solution of enyne **17** (34.5 mg, 99.6 μmol) in toluene (1.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (1.5 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 60 °C for 20 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **18** (23.4 mg, 68% yield, R_f = 0.46 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a colorless oil.

Procedure B**:** To a solution of enyne **17** (17.5 mg, 50.5 μmol) in toluene (0.77 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.1 mg, 1.25 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 1.50 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **18** (15.2 mg, 87% yield) as a colorless oil.

Tricycle 18: ^{1}H NMR (400 MHz; C_6D_6): δ 7.14-7.02 (m, 10H), 4.10 (ABq, J_{AB} = 12.0 Hz, $\Delta\upsilon_{AB}$ = 30.2 Hz, 2H), 4.01-3.91 (m, 2H), 3.50 (d, J = 10.5 Hz, 1H), 2.94 (d, J = 10.5 Hz, 1H), 2.60 (d, J = 5.9 Hz, 1H), 2.57-2.50 (m, 1H), 2.31-2.07 (m, 3H), 1.80-1.77 (m, 1H), 1.61-1.49 (m, 4H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.7, 139.3, 138.3, 129.3, 128.5, 128.2, 127.9, 127.5, 126.4, 111.2, 72.8, 71.1, 62.5, 35.2, 28.2, 27.3, 26.5, 25.4, 23.7, 23.3; IR (film) 3028, 2929, 2858, 1672, 1453, 1096 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{24}H_{26}O_2 + H]^+$: 347.2006, found 347.2009.

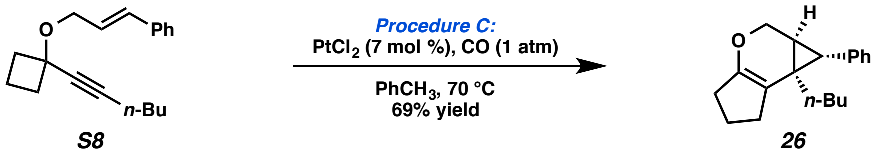


Tricycle 25. ***Procedure A*:** To a solution of enyne **S7** (52.9 mg, 148 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.75 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 18 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The

volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **25** (34.1 mg, 64% yield, R_f = 0.42 in 2:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a yellow oil.

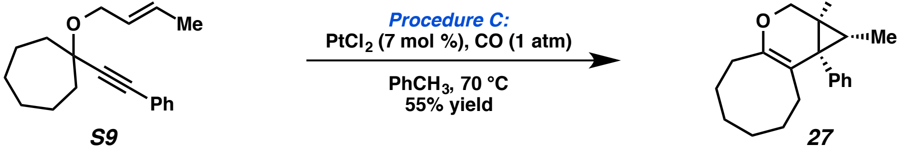
***Procedure B*:** To a solution of enyne **S7** (28.1 mg, 77.9 μmol) in toluene (1.2 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.7 mg, 1.97 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **25** (14.5 mg, 52% yield) as a yellow oil.

Tricycle 25: ^{1}H NMR (400 MHz; C_6D_6): δ 7.22 (d, J = 7.2 Hz, 2H), 7.13 (dt, J = 5.9, 2.1 Hz, 4H), 7.10-7.02 (m, 4H), 4.09 (ABq, J_{AB} = 12.0 Hz, $\Delta\upsilon_{AB}$ = 26.4 Hz, 2H), 3.85 (d, J = 10.0 Hz, 1H), 3.79 (ABq, J_{AB} = 10.0 Hz, $\Delta\upsilon_{AB}$ = 120.1 Hz, 2H), 3.00 (d, J = 10.0 Hz, 1H), 2.84 (s, 1H), 2.64-2.57 (m, 1H), 2.32-2.25 (m, 1H), 2.19-2.13 (m, 2H), 1.65-1.45 (m, 4H), 1.09 (s, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.5, 139.2, 137.6, 130.8, 128.6, 128.5, 127.9, 127.6, 126.5, 111.5, 73.3, 69.2, 68.4, 36.5, 31.9, 28.1, 27.7, 25.1, 23.7, 23.6, 23.1, 13.1; IR (film) 2930, 2856, 1678, 1445, 1155 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{28}O_2 + H]^+$: 361.2162, found 361.2169.



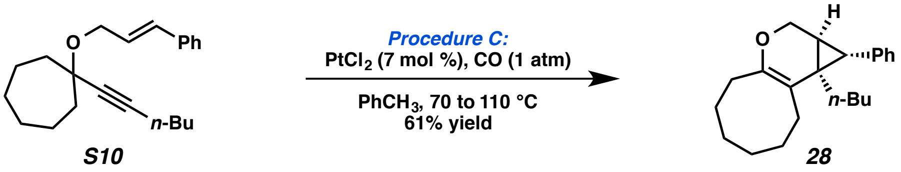
Tricycle 26. ***Procedure C*:** To a solution of enyne **S8** (40.6 mg, 151 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (2.8 mg, 1.05 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **26** (27.9 mg, 69% yield, R_f = 0.86 in 2:1 CH_2Cl_2/hexanes, stained brown with *p*-anisaldehyde) as a colorless oil.

Tricycle 26: ^1H NMR (400 MHz; C_6D_6): δ 7.20-7.13 (m, 2H), 7.06 (dd, *J* = 7.3, 5.0 Hz, 3H), 4.19-4.16 (m, 1H), 4.01 (dd, *J* = 10.7, 2.9 Hz, 1H), 2.54-2.32 (m, 4H), 1.94-1.84 (m, 1H), 1.75-1.66 (m, 2H), 1.59-1.52 (m, 1H), 1.41-1.07 (m, 8H), 0.81 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 150.3, 138.9, 129.2, 128.4, 126.2, 113.1, 64.2, 37.4, 31.8, 30.6, 29.9, 29.8, 26.5, 26.0, 23.2, 19.5, 14.4; IR (film) 3026, 2960, 1682, 1464, 1152, 698 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1910.



Tricycle 27. ***Procedure C*:** To a solution of enyne **S9** (40.9 mg, 152 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (2.8 mg, 1.05 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 1:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **27** (22.5 mg, 55% yield, R_f = 0.85 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a colorless oil.

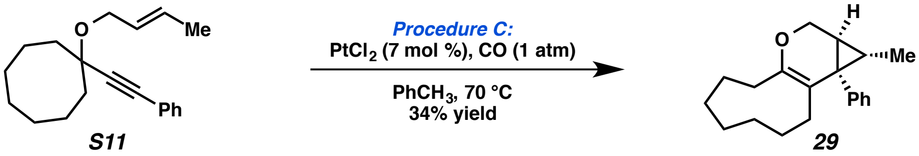
Tricycle 27: ^{1}H NMR (400 MHz; C_6D_6): δ 7.26-7.24 (m, 2H), 7.16 (d, *J* = 14.8 Hz, 2H), 7.08 (dd, *J* = 8.5, 6.1 Hz, 1H), 4.05-3.93 (m, 2H), 2.33-2.16 (m, 2H), 2.08 (d, *J* = 6.3 Hz, 1H), 1.67-1.33 (m, 8H), 1.20-1.13 (m, 2H), 1.05 (dt, *J* = 5.3, 2.6 Hz, 1H), 0.90 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 148.0, 141.6, 132.0, 127.9, 126.6, 112.9, 63.4, 31.7, 31.3, 30.3, 29.6, 29.3, 27.53, 27.51, 26.8, 25.8, 16.3; IR (film) 2923, 2851, 1658, 1493, 1164, 703 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1897.



Tricycle 28. ***Procedure C*:** To a solution of enyne **S10** (12.7 mg, 40.9 μmol) in toluene (0.67 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (0.7 mg, 2.63 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 21 h, then at 110 °C for 24 h. The reaction mixture was allowed to

cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **28** (7.7 mg, 61% yield, R_f = 0.84 in 2:1 CH_2Cl_2/hexanes, stained purple with *p*-anisaldehyde) as a yellow oil.

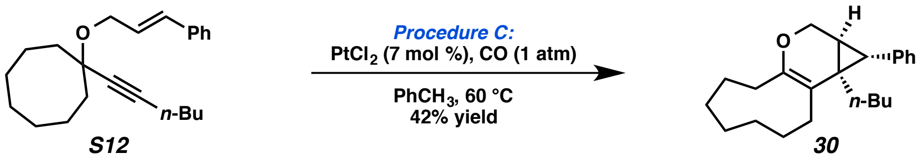
Tricycle 28: ^{1}H NMR (400 MHz; C_6D_6): δ 7.19-7.17 (m, 2H), 7.13-7.11 (m, 2H), 7.09-7.05 (m, 1H), 4.04-3.97 (m, 2H), 2.42 (d, J = 5.7 Hz, 1H), 2.39-2.14 (m, 4H), 1.79-1.10 (m, 14H), 0.82 (t, J = 7.3 Hz, 3H), 0.58 (ddd, J = 14.1, 11.1, 5.8 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 139.1, 129.3, 128.4, 126.2, 110.4, 63.5, 36.3, 31.6, 30.4, 30.3, 30.1, 29.5, 27.6, 26.9, 25.7, 25.6, 25.4, 23.2, 14.5; IR (film) 2924, 2854, 1660, 1447, 1128, 698 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{30}O + H]^+$: 311.2369, found 311.2355.



Tricycle 29. ***Procedure C*:** To a solution of enyne **S11** (42.8 mg, 152 µmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (2.8 mg, 1.05 µmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 70 °C for 20.5 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle

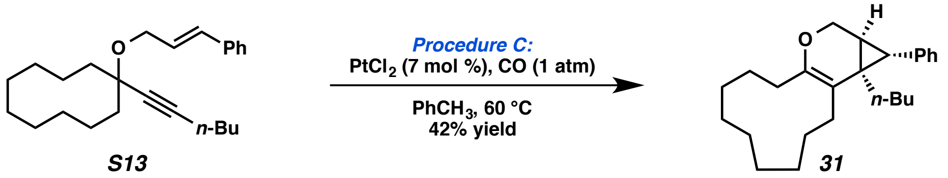
29 (13.6 mg, 34% yield, R_f = 0.85 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Tricycle 29: ^{1}H NMR (400 MHz; C_6D_6): δ 7.28-7.26 (m, 2H), 7.18-7.15 (m, 2H), 7.11-7.06 (m, 1H), 3.99 (qd, *J* = 11.3, 3.2 Hz, 2H), 2.33-2.17 (m, 2H), 2.11 (dd, *J* = 4.2, 3.1 Hz, 1H), 1.69-1.59 (m, 2H), 1.51-1.30 (m, 10H), 1.08 (dd, *J* = 3.1, 2.1 Hz, 1H), 0.91 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 148.6, 141.8, 132.1, 128.2, 126.6, 114.6, 64.2, 31.0, 30.4, 29.7, 28.2, 26.8, 26.5, 26.2, 25.7, 25.5, 25.4, 16.3; IR (film) 2926, 2853, 1653, 1493, 1146, 704 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2056.



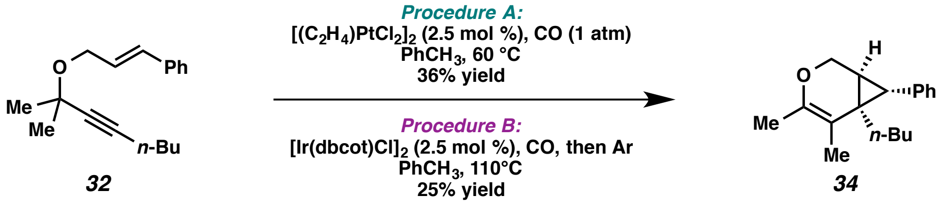
Tricycle 30. ***Procedure C*****:** To a solution of enyne **S12** (19.6 mg, 60.4 μmol) in toluene (1.0 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (1.2 mg, 4.51 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 60 °C for 21 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **30** (8.3 mg, 42% yield, R_f = 0.87 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Tricycle 30: ^{1}H NMR (400 MHz; C_6D_6): δ 7.20-7.17 (m, 1H), 7.15-7.13 (m, 2H), 7.10-7.06 (m, 1H), 4.04 (dd, *J* = 10.7, 4.0 Hz, 1H), 3.98-3.94 (m, 1H), 2.42 (d, *J* = 5.7 Hz, 1H), 2.39-2.30 (m, 3H), 2.21-2.15 (m, 1H), 1.81-1.08 (m, 19H), 0.82 (t, *J* = 7.3 Hz, 3H), 0.60 (ddd, *J* = 14.1, 11.2, 5.7 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 150.8, 139.1, 129.3, 128.4, 126.3, 111.3, 64.1, 37.0, 30.6, 30.4, 29.7, 27.1, 26.9, 26.5, 26.2, 25.6, 25.5, 24.9, 24.3, 23.3, 14.5; IR (film) 2926, 2856, 1654, 1497, 1183 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{23}H_{32}O + H]^+$: 325.2526, found 325.2517.



Tricycle 31. ***Procedure C*****:** To a solution of enyne **S13** (21.1 mg, 59.8 µmol) in toluene (1.0 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (1.2 mg, 4.51 µmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 60 °C for 21 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 10:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **31** (8.9 mg, 42% yield, R_f = 0.86 in 2:1 CH_2Cl_2/hexanes, stained brown/blue in *p*-anisaldehyde) as a colorless oil.

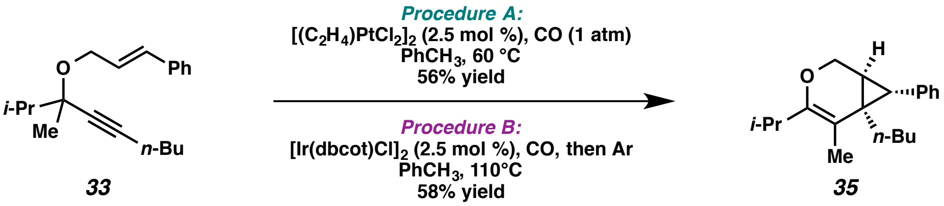
Tricycle 31: ^{1}H NMR (400 MHz; C_6D_6): δ 7.22-7.19 (m, 4H), 7.11-7.07 (m, 1H), 4.26 (dd, *J* = 11.3, 6.3 Hz, 1H), 3.62 (dd, *J* = 11.4, 4.6 Hz, 1H), 2.54-2.39 (m, 2H), 2.30-2.21 (m, 2H), 2.18 (d, *J* = 5.2 Hz, 1H), 2.00-1.89 (m, 2H), 1.74-1.08 (m, 18H), 0.80 (t, *J* = 7.3 Hz, 3H), 0.69 (ddd, *J* = 14.0, 11.1, 5.7 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 151.3, 139.1, 129.1, 128.4, 126.3, 112.4, 66.9, 39.5, 29.9, 29.7, 29.3, 27.8, 26.8, 26.44, 26.40, 26.3, 25.8, 25.53, 25.48, 25.2, 23.2, 22.4, 14.4; IR (film) 2927, 2857, 1498, 1154, 721 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{36}O + H]^+$: 353.2839, found 353.2831.



Bicycle 34. ***Procedure A*****:** To a solution of enyne **32** (20.6 mg, 80.3 μmol) in toluene (1.2 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (1.2 mg, 2.04 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 60 °C for 19.5 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (50:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 2:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording bicycle **34** (7.5 mg, 36% yield, R_f = 0.78 in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a yellow oil.

Procedure B**:** To a solution of enyne **32** (15.6 mg, 60.8 μmol) in toluene (0.92 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 18 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (6.2 mg, 15.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 50:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording bicycle **34** (3.9 mg, 25% yield) as a yellow oil.

Bicycle 34: ^{1}H NMR (400 MHz; C_6D_6): δ 7.16 (d, *J* = 14.7 Hz, 3H), 7.08-7.06 (m, 2H), 4.10 (dd, *J* = 11.0, 5.1 Hz, 1H), 3.80 (dd, *J* = 11.0, 3.4 Hz, 1H), 2.17 (d, *J* = 5.4 Hz, 1H), 1.79 (d, *J* = 0.9 Hz, 3H), 1.70 (d, *J* = 0.9 Hz, 3H), 1.65-1.58 (m, 1H), 1.47 (td, *J* = 5.3, 3.4 Hz, 1H), 1.36-1.09 (m, 4H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.61 (ddd, *J* = 14.0, 10.9, 5.9 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 146.2, 139.1, 129.4, 126.2, 108.5, 65.4, 38.7, 30.0, 27.2, 25.4, 23.2, 16.8, 14.4, 14.0; IR (film) 2956, 2859, 2017, 1948, 1384, 1150 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{24}O + H]^+$: 257.1900, found 257.1888.



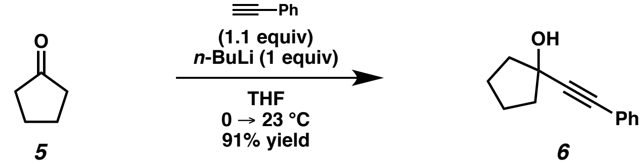
Bicycle 35. ***Procedure A*****:** To a solution of enyne **33** (42.2 mg, 148 μmol) in toluene (2.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (2.2 mg, 3.74 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 60 °C for 20 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes w/ 0.5% Et_3N → 9:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording bicycle **35** (23.8 mg, 56% yield, R_f = 0.78 in 2:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a yellow oil.

Procedure B: To a solution of enyne **33** (28.9 mg, 102 μmol) in toluene (1.5 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (2.2 mg, 2.55 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the reaction mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the reaction mixture in the same manner. The septum was quickly replaced with a Teflon cap, and the reaction mixture was stirred at 110 °C for 23 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (10.3 mg, 25.0 μmol) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 20:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording bicycle **35** (16.9 mg, 58% yield) as a yellow oil.

Bicycle 35: ^{1}H NMR (400 MHz; C_6D_6): δ 7.18-7.14 (m, 2H), 7.08-7.06 (m, 3H), 4.19 (ddd, *J* = 11.1, 5.9, 0.9 Hz, 1H), 3.65 (dd, *J* = 11.1, 4.1 Hz, 1H), 2.80-2.69 (m, 1H), 2.05 (d, *J* = 5.1 Hz, 1H), 1.73 (d, *J* = 1.0 Hz, 3H), 1.65-1.58 (m, 1H), 1.52-1.48 (m, 1H), 1.40-1.21 (m, 4H), 1.18 (dd, *J* = 6.8, 1.1 Hz, 3H), 1.13 (dd, *J* = 6.8, 1.0 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H), 0.64-0.57 (m, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 154.6, 139.1, 133.7, 129.4, 127.1, 126.2, 107.4, 67.3, 39.2, 30.2, 30.0, 29.8, 29.0, 27.4, 25.0, 23.1, 20.3, 20.2, 14.4, 13.3; IR (film) 2929, 2859, 1454, 1094, 698 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{28}O + H]^+$: 285.2213, found 285.2201.

Substrate Synthesis

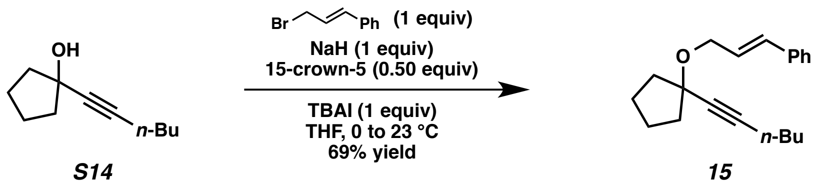
General procedure for the synthesis of tertiary propargyl alcohols. To a solution of the terminal alkyne (1.1 equiv) in THF (0.30 M) at 0 °C was slowly added *n*-BuLi (2.5 M in hexane, 1 equiv). The reaction mixture was stirred at 0 °C for 30 min, then the ketone (1 equiv) was added. The reaction mixture was allowed to warm to ambient temperature and was stirred until the ketone was consumed, as determined by TLC. The reaction mixture was then diluted with aq. 1 M HCl and the mixture was transferred to a separatory funnel. The layers were separated, and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the crude residue was purified by flash chromatography to afford the alcohol.



Alcohol 6. To a solution of phenylacetylene (4.23 mL, 38.5 mmol) in THF (116 mL) at 0 °C was slowly added *n*-BuLi (2.5 M in hexane, 14.0 mL, 35.0 mmol) via an addition funnel. The reaction mixture was stirred at 0 °C for 30 min, then ketone **5** (3.10 mL, 35.0 mmol) was added dropwise. The reaction mixture was allowed to warm to ambient temperature and was stirred for 19 h. The reaction mixture was then diluted with sat. aq. NH_4Cl (50 mL) and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (100 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation and the resulting residue was purified by flash chromatography (100% hexanes → 4:1 hexanes/EtOAc eluent), affording alcohol **6** (5.95 g, 91% yield, $R_f = 0.33$ in 4:1 hexanes/EtOAc, stained blue with *p*-anisidine) as a white solid.

All spectroscopic data were consistent with previously reported values.[1]

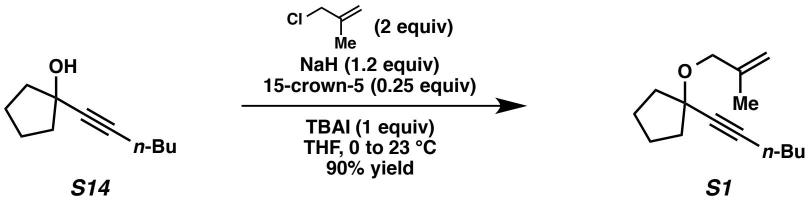
General procedure for the alkylation of tertiary propargylic alcohols to give oxygen-tethered 1,6-enynes. To a solution of the tertiary propargylic alcohol (1 equiv) in THF (0.20 M) in a flame-dried flask under argon at 0 °C was added NaH (1.2 equiv, 60% dispersion in mineral oil). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.25 equiv), tetrabutylammonium iodide (TBAI) (1 equiv), and the allylic halide (1 equiv). The resulting mixture was stirred at ambient temperature until completion, as determined by TLC. The reaction mixture was quenched with sat. aq. NH_4Cl. The layers were separated, and the aqueous layer was extracted with Et_2O (3x). The combined organic layers were washed with brine, then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography to afford the ether.



Enyne 15. To a solution of tertiary propargyl alcohol **S14**[2] (0.166 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (40.0 mg, 60% dispersion in mineral oil, 1.00 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (99.0 µL, 0.500 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 16 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$. The volatile materials were removed by

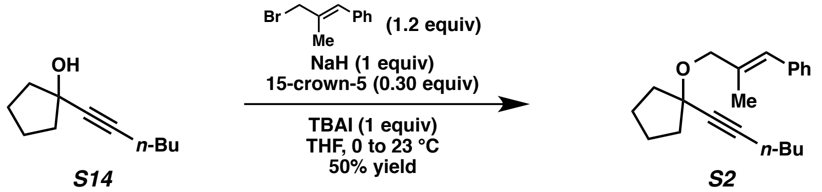
rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 → 2:1 hexanes/CH_2Cl_2 eluent), affording enyne **15** (0.195 g, 69% yield, R_f = 0.67 in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisidine) as a yellow oil.

Enyne 15: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.37 (m, 2H), 7.32-7.28 (m, 2H), 7.24-7.19 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.23 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.24 (t, *J* = 7.0 Hz, 2H), 2.06-1.99 (m, 2H), 1.92-1.85 (m, 2H), 1.80-1.69 (m, 4H), 1.55-1.40 (m, 4H), 0.92 (d, *J* = 14.5 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.2, 131.6, 128.6, 127.5, 127.3, 126.6, 85.6, 81.7, 80.8, 65.7, 39.9, 31.1, 23.5, 22.1, 18.6, 13.8; IR (film) 2959, 2872, 1496, 1053, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2056.



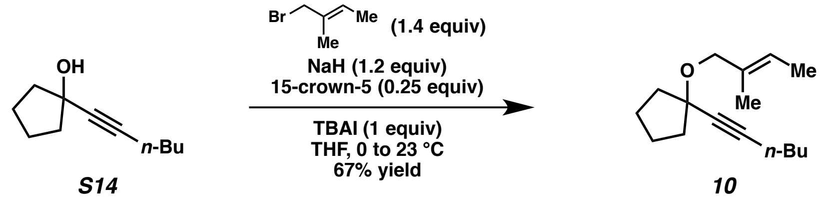
Enyne S1. To a solution of tertiary propargyl alcohol **S14** (0.415 g, 2.49 mmol) in THF (13 mL) at 0 °C was added NaH (0.125 g, 60% dispersion in mineral oil, 3.14 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.120 mL, 0.625 mmol), tetrabutylammonium iodide (0.924 g, 2.50 mmol), and methallyl chloride (0.550 mL, 5.57 mmol). The resulting mixture was stirred at ambient temperature for 19.5 h. The reaction mixture was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine (40 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 5:1 hexanes/EtOAc eluent), affording enyne **S1** (0.470 g, 90% yield, R_f = 0.85 in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S1: ^{1}H NMR (400 MHz; CDCl$_3$): δ 4.98 (dd, *J* = 2.2, 0.9 Hz, 1H), 4.84 (t, *J* = 1.1 Hz, 1H), 3.94 (s, 2H), 2.21 (t, *J* = 6.9 Hz, 2H), 2.03-1.96 (m, 2H), 1.88-1.78 (m, 2H), 1.75 (s, 3H), 1.74-1.65 (m, 4H), 1.53-1.38 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 143.3, 111.4, 85.2, 81.8, 80.6, 77.2, 68.7, 39.8, 31.1, 23.5, 22.1, 20.0, 18.6, 13.8; IR (film) 2960, 2873, 1452, 1094 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{15}H_{24}O + H]^+$: 221.1900, found 221.1902.



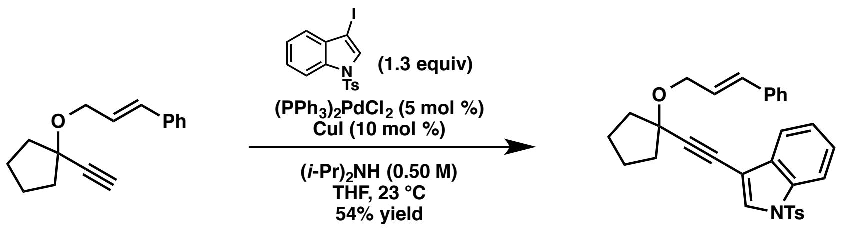
Enyne S2. To a solution of tertiary propargyl alcohol **S14** (0.167 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (40.0 mg, 60% dispersion in mineral oil, 1.00 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (60.0 µL, 0.303 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and 3-bromo-2-methyl-1-phenyl-1-propene[3] (0.258 g, 1.22 mmol). The resulting mixture was stirred at ambient temperature for 20 h. The reaction mixture was quenched with sat. aq. NH$_4$Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et$_2$O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over MgSO$_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (20:1 hexanes/CH$_2$Cl$_2$ → 1:1 hexanes/CH$_2$Cl$_2$ eluent), affording enyne **S2** (0.148 g, 50% yield, R_f = 0.63 in 1:1 hexanes/CH$_2$Cl$_2$, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S2: ^{1}H NMR (400 MHz; CDCl$_3$): δ 7.34-7.27 (m, 4H), 7.21-7.17 (m, 1H), 6.53 (s, 1H), 4.09 (s, 2H), 2.24 (t, *J* = 6.9 Hz, 2H), 2.08-2.01 (m, 2H), 1.90 (s, 3H), 1.88-1.84 (m, 2H), 1.82-1.69 (m, 4H), 1.53-1.40 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 138.1, 136.2, 129.1, 128.1, 126.3, 126.1, 98.8, 85.4, 81.8, 80.8, 70.9, 39.9, 31.1, 23.5, 22.1, 18.6, 15.9, 13.8; IR (film) 2959, 2872, 1446, 1047 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{21}H_{28}O + H]^+$: 297.2213, found 297.2208.



Enyne 10. To a solution of tertiary propargyl alcohol **S14** (0.166 g, 0.996 mmol) in THF (5.0 mL) at 0 °C was added NaH (40.0 mg, 60% dispersion in mineral oil, 1.00 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (60.0 μL, 0.303 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and 3-bromo-2-methyl-1-methyl-1-propene[4] (0.208 g, 1.40 mmol). The resulting mixture was stirred at ambient temperature for 16 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (40 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **10** (0.158 g, 67% yield, R_f = 0.71 in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

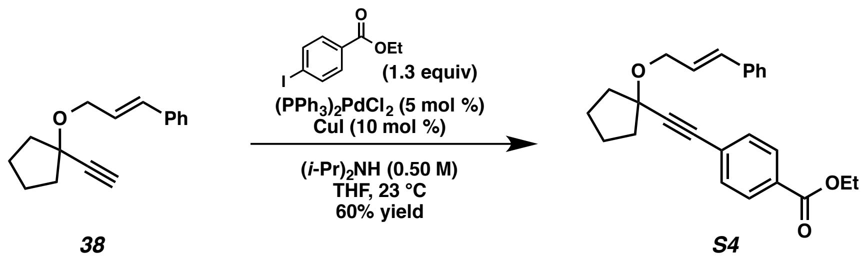
Enyne 10: ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.51 (q, *J* = 6.28 Hz, 1H), 3.90 (s, 2H), 2.22 (t, *J* = 6.9 Hz, 2H), 2.02-1.96 (m, 2H), 1.86-1.78 (m, 2H), 1.76-1.67 (m, 4H), 1.65 (d, *J* = 1.0 Hz, 3H), 1.61 (dt, *J* = 6.7, 0.9 Hz, 3H), 1.51-1.39 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 133.8, 121.9, 85.1, 82.0, 80.5, 70.9, 39.8, 31.1, 23.4, 22.1, 18.6, 14.0, 13.8, 13.4; IR (film) 2960, 2934, 2861, 1449, 1046 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{26}O + H]^+$: 235.2056, found 235.2050.



38 ***S3***

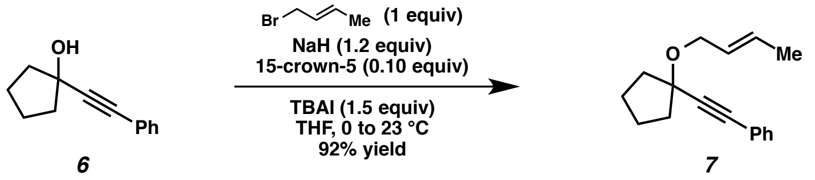
Enyne S3. To $(PPh_3)_2PdCl_2$ (52.7 mg, 75.1 μmol) and CuI (28.6 mg, 0.150 mmol) under argon was added $(i\text{-}Pr)_2NH$ (3.0 mL). The reaction mixture was stirred for 5 min, then 3-iodo-1-tosylindole[5] (0.775 g, 1.95 mmol) was added, and the mixture was stirred for an additional 5 min. Terminal alkyne **38** (0.339 g, 1.50 mmol) was then added as a 0.50 M solution in THF. Additional THF (ca. 3.0 mL) was added to maintain dissolution. The mixture was stirred for 14 h, after which the reaction mixture was partitioned between 1 M aq. HCl (10 mL) and Et_2O (5.0 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 5.0 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **S3** (0.406 g, 54% yield, $R_f = 0.33$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a brown amorphous solid.

Enyne S3: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.97 (d, $J = 8.3$ Hz, 1H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.72 (s, 1H), 7.61 (d, $J = 7.7$ Hz, 1H), 7.38 (t, $J = 8.2$ Hz, 3H), 7.34-7.28 (m, 3H), 7.23 (t, $J = 8.3$ Hz, 3H), 6.65 (d, $J = 16.1$ Hz, 1H), 6.40-6.33 (m, 1H), 4.36-4.34 (m, 2H), 2.35 (s, 3H), 2.22-2.04 (m, 4H), 1.90-1.78 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 145.4, 135.1, 134.3, 131.9, 130.2, 128.8, 128.6, 127.7, 127.1, 127.0, 126.6, 125.6, 123.8, 120.6, 113.7, 95.5, 81.2, 77.4, 66.1, 40.1, 23.6, 21.7; IR (film) 2966, 1376, 1175, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{31}H_{29}NO_3S + H]^+$: 496.1941, found 496.1960.



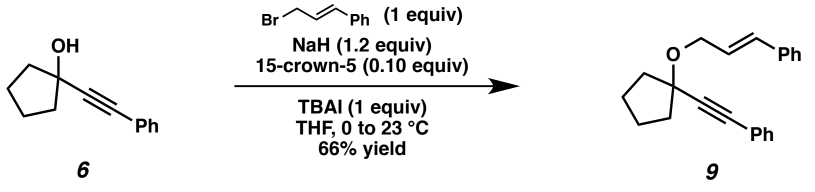
Enyne S4. To $(PPh_3)_2PdCl_2$ (52.7 mg, 75.1 μmol) and CuI (28.6 mg, 0.150 mmol) under argon was added $(i\text{-}Pr)_2NH$ (3.0 mL). The reaction mixture was stirred for 5 min, then ethyl 4-iodobenzoate (0.330 mL, 1.95 mmol) was added, and the mixture was stirred for an additional 5 min. Terminal alkyne **38** (0.339 g, 1.50 mmol) was then added as a 0.50 M solution in THF. Additional THF (ca. 3.0 mL) was added to maintain dissolution. The mixture was stirred for 14 h, after which the reaction mixture was partitioned between 1 M aq. HCl (10 mL) and Et_2O (5.0 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 5.0 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **S4** (0.338 g, 60% yield, $R_f = 0.42$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S4: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.99-7.97 (m, 2H), 7.50-7.48 (m, 2H), 7.40-7.38 (m, 2H), 7.30 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.24-7.20 (m, 1H), 6.63 (t, *J* = 14.3 Hz, 1H), 6.39-6.27 (m, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 4.32 (dd, *J* = 5.9, 1.4 Hz, 1H), 2.20-2.01 (m, 4H), 1.88-1.75 (m, 4H), 1.40 (d, *J* = 14.3 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.9, 131.7, 129.5, 128.6, 127.7, 126.6, 94.2, 84.6, 81.0, 66.1, 61.3, 39.9, 23.6, 14.5; IR (film) 2965, 1719, 1272, 1106 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{26}O_3 + H]^+$: 375.1955, found 375.1935.



Enyne 7. To a solution of tertiary propargyl alcohol **6** (0.150 g, 0.805 mmol) in THF (4.0 mL) at 0 °C was added NaH (38.9 mg, 60% dispersion in mineral oil, 0.973 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (16.0 μL, 81.0 μmol), tetrabutylammonium iodide (0.451 g, 1.22 mmol), and crotyl bromide (83.3 μL, 0.810 mmol). The resulting mixture was stirred at ambient temperature for 24 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/Et_2O eluent), affording enyne **7** (0.179 g, 92% yield, $R_f = 0.71$ in 4:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

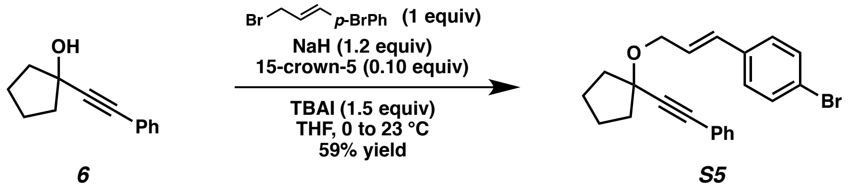
Enyne 7: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.43 (td, *J* = 3.8, 1.7 Hz, 2H), 7.30 (t, *J* = 3.2 Hz, 3H), 5.79-5.60 (m, 2H), 4.08 (d, *J* = 6.1 Hz, 2H), 2.13-1.96 (m, 4H), 1.86-1.74 (m, 4H), 1.71 (dd, *J* = 6.2, 0.9 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.8, 129.1, 128.36, 128.35, 128.2, 126.6, 91.2, 84.9, 80.8, 66.1, 39.9, 23.6, 18.0; IR (film) 2965, 2857, 1443, 1088 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{17}H_{20}O + H]^+$: 241.1587, found 241.1587.



Enyne 9. To a solution of tertiary propargyl alcohol **6** (0.187 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension

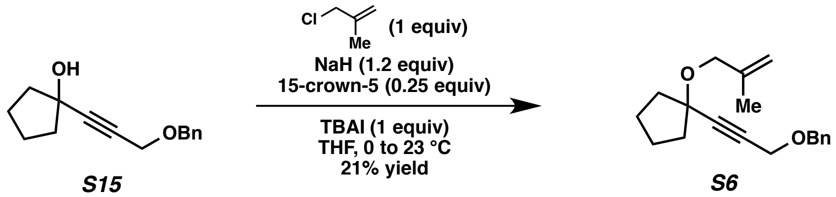
was added sequentially 15-crown-5 (20.0 μL, 0.101 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.198 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 20 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **9** (0.201 g, 66% yield, R_f = 0.62 in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 9: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.45-7.43 (m, 2H), 7.40-7.38 (m, 2H), 7.30 (dd, *J* = 8.5, 5.3 Hz, 5H), 7.24-7.20 (m, 1H), 6.64 (d, *J* = 15.9 Hz, 1H), 6.36 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.33 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.19-2.01 (m, 4H), 1.89-1.76 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.2, 131.9, 131.8, 128.6, 128.4, 128.3, 127.6, 127.1, 126.6, 123.2, 91.0, 85.2, 81.1, 66.0, 39.9, 23.6; IR (film) 2965, 1598, 1445, 1048 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{22}O + H]^+$: 303.1743, found 303.1743.



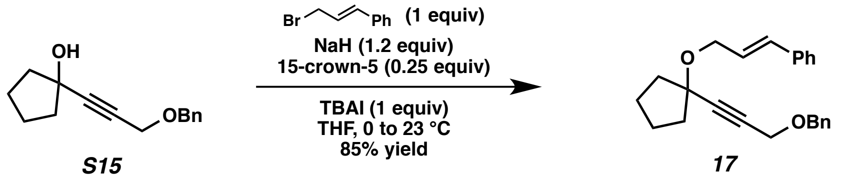
Enyne S5. To a solution of tertiary propargyl alcohol **6** (0.140 g, 0.750 mmol) in THF (3.8 mL) at 0 °C was added NaH (36.0 mg, 60% dispersion in mineral oil, 0.900 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (15.0 μL, 75.8 μmol), tetrabutylammonium iodide (0.420 g, 1.14 mmol), and *p*-bromocinnamyl bromide[6] (0.207 g, 0.750 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **S5** (0.169 g, 59% yield, $R_f = 0.71$ in 4:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S5: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.44-7.41 (m, 4H), 7.31 (t, *J* = 3.2 Hz, 3H), 7.24 (d, *J* = 8.5 Hz, 2H), 6.58 (d, *J* = 15.8 Hz, 1H), 6.35 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.31 (dd, *J* = 5.8, 1.2 Hz, 2H), 2.17-1.99 (m, 4H), 1.85-1.76 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 136.1, 131.8, 131.7, 128.4, 128.3, 128.1, 128.0, 98.8, 77.4, 77.0, 69.9, 39.9, 23.6; IR (film) 2965, 1488, 1071 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{21}BrO + H]^+$: 381.0849, found 381.0844.



Enyne S6. To a solution of tertiary propargyl alcohol **S15** (0.150 g, 0.652 mmol) in THF (3.3 mL) at 0 °C was added NaH (31.2 mg, 60% dispersion in mineral oil, 0.780 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (32.0 μL, 0.163 mmol), tetrabutylammonium iodide (0.240 g, 0.650 mmol), and methallyl chloride (64.2 μL, 0.650 mmol). The resulting mixture was stirred at ambient temperature for 22 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 10:1 hexanes/EtOAc eluent), affording enyne **S6** (38.3 mg, 21% yield, $R_f = 0.81$ in 3:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

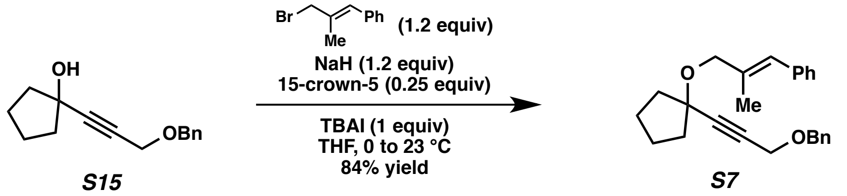
Enyne S6: ^{1}H NMR (400 MHz; CDCl$_3$): δ 7.36 (d, *J* = 4.4 Hz, 4H), 7.31 (td, *J* = 6.6, 3.7 Hz, 1H), 5.00 (s, 1H), 4.86 (s, 1H), 4.61 (s, 2H), 4.23 (s, 2H), 3.97 (s, 2H), 2.06 (td, *J* = 10.8, 4.4 Hz, 2H), 1.95-1.88 (m, 2H), 1.81-1.70 (m, 7H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 143.0, 137.6, 128.6, 128.2, 128.0, 111.5, 88.5, 80.6, 80.5, 71.5, 68.9, 57.6, 39.7, 23.5, 20.0; IR (film) 2969, 2856, 1496, 1091 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O_2 + H]^+$: 285.1849, found 285.1851.



Enyne 17. To a solution of tertiary propargyl alcohol **S15** (0.172 g, 0.749 mmol) in THF (3.8 mL) at 0 °C was added NaH (36.0 mg, 60% dispersion in mineral oil, 0.900 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (37.6 μL, 0.190 mmol), tetrabutylammonium iodide (0.280 g, 0.758 mmol), and cinnamyl bromide (0.147 g, 0.746 mmol). The resulting mixture was stirred at ambient temperature for 22 h. The reaction mixture was quenched with sat. aq. NH$_4$Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et$_2$O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over MgSO$_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **17** (0.221 g, 85% yield, R_f = 0.77 in 3:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

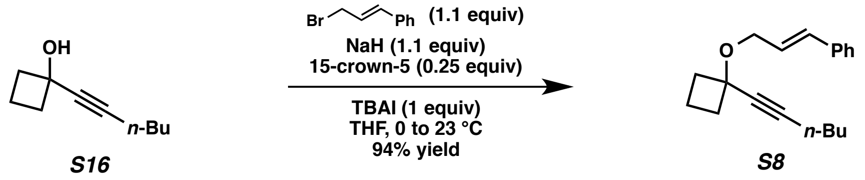
Enyne 17: ^{1}H-NMR (400 MHz; CDCl$_3$): δ 7.39-7.34 (m, 5H), 7.31 (t, *J* = 7.5 Hz, 3H), 7.23 (dd, *J* = 8.3, 6.1 Hz, 2H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.62 (s, 2H), 4.27-4.26 (m, 4H), 2.12-2.05 (m, 2H), 2.00-1.92 (m, 2H), 1.84-1.72 (m, 4H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 137.6, 137.1, 131.8, 128.6, 128.2, 128.0, 127.6, 126.9, 126.6, 88.4, 80.9, 80.6, 71.6, 65.9, 57.7, 39.8, 23.5; IR (film)

2963, 2856, 1496, 1073 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{24}H_{26}O_2 + H]^+$: 347.2006, found 347.2011.



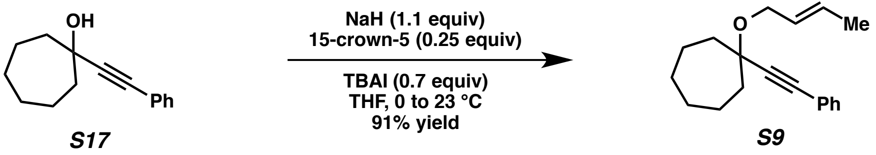
Enyne S7. To a solution of tertiary propargyl alcohol **S15** (0.110 g, 0.475 mmol) in THF (2.4 mL) at 0 °C was added NaH (23.0 g, 60% dispersion in mineral oil, 0.571 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (23.8 µL, 0.120 mmol), tetrabutylammonium iodide (0.175 g, 0.475 mmol), and 3-bromo-2-methyl-1-phenyl-1-propene (0.101 g, 0.475 mmol). The resulting mixture was stirred at ambient temperature for 15 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **S7** (0.144 g, 84% yield, $R_f = 0.55$ in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S7: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.35 (dd, *J* = 6.0, 4.0 Hz, 3H), 7.30 (dt, *J* = 12.7, 6.1 Hz, 5H), 7.22-7.18 (m, 1H), 6.54 (s, 1H), 4.62 (s, 2H), 4.25 (s, 2H), 4.12 (s, 2H), 2.14-1.92 (m, 4H), 1.92 (s, 3H), 1.84-1.72 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 138.0, 137.6, 135.9, 129.1, 128.6, 128.3, 128.2, 128.0, 126.4, 126.3, 88.5, 80.8, 80.6, 71.6, 71.2, 57.6, 39.8, 23.5, 15.9; IR (film) 2964, 2855, 1683, 1493, 1089 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{25}H_{28}O_2 + H]^+$: 361.2162, found 361.2162.



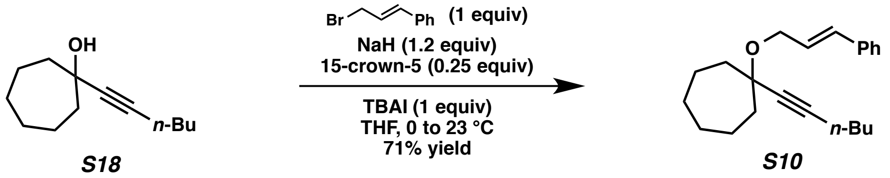
Enyne S8. To a solution of tertiary propargyl alcohol **S16**[7] (0.378 g, 2.48 mmol) in THF (10 mL) at 0 °C was added NaH (0.111 g, 60% dispersion in mineral oil, 2.75 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.120 mL, 0.625 mmol), tetrabutylammonium iodide (0.646 g, 1.75 mmol), and cinnamyl bromide (0.542 g, 2.75 mmol). The resulting mixture was stirred at ambient temperature for 19 h. The reaction mixture was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **S8** (0.629 g, 94% yield, $R_f = 0.58$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S8: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.40-7.38 (m, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.24-7.20 (m, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.1 Hz, 1H), 4.17 (dd, *J* = 6.1, 1.2 Hz, 2H), 2.35-2.24 (m, 6H), 1.93-1.78 (m, 2H), 1.57-1.40 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.1, 132.2, 128.6, 127.6, 126.7, 126.6, 85.8, 81.6, 73.1, 65.3, 36.5, 31.1, 22.1, 18.7, 13.8, 13.5; IR (film) 2935, 2861, 1450, 1128, 735 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1901.



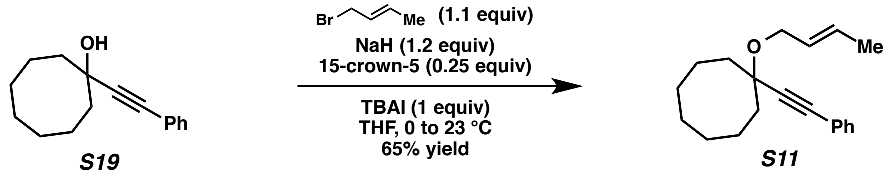
Enyne S9. To a solution of tertiary propargyl alcohol **S17** (2.14 g, 10.0 mmol) in THF (40 mL) at 0 °C was added NaH (0.442 g, 60% dispersion in mineral oil, 11.1 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.495 mL, 2.50 mmol), tetrabutylammonium iodide (2.58 g, 6.98 mmol), and crotyl bromide (1.13 mL, 11.0 mmol). The resulting mixture was stirred at ambient temperature for 19 h. The reaction mixture was quenched with sat. aq. NH_4Cl (50 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 40 mL). The combined organic layers were washed with brine (100 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/EtOAc eluent), affording enyne **S9** (2.44 g, 91% yield, $R_f = 0.75$ in 9:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S9: ^1H NMR (400 MHz; $CDCl_3$): δ 7.44-7.42 (m, 2H), 7.30 (t, *J* = 3.3 Hz, 3H), 5.79-5.60 (m, 2H), 4.10 (d, *J* = 6.0 Hz, 2H), 2.09 (dd, *J* = 13.9, 8.0 Hz, 2H), 1.98-1.92 (m, 2H), 1.71 (d, *J* = 6.2 Hz, 3H), 1.69-1.56 (m, 8H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.8, 128.8, 128.6, 128.4, 128.2, 123.3, 98.9, 92.0, 77.5, 65.0, 40.3, 28.5, 22.3, 18.0; IR (film) 2929, 2856, 1444, 1041, 755 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{19}H_{24}O + H]^+$: 269.1900, found 269.1900.



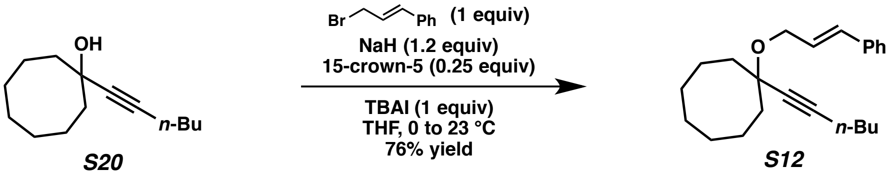
Enyne S10. To a solution of tertiary propargyl alcohol **S18** (0.505 g, 2.21 mmol) in THF (11 mL) at 0 °C was added NaH (0.104 g, 60% dispersion in mineral oil, 2.60 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (43.5 µL, 0.220 mmol), tetrabutylammonium iodide (0.815 g, 2.21 mmol), and crotyl bromide (0.235 mL, 2.28 mmol). The resulting mixture was stirred at ambient temperature for 18 h. The reaction mixture was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 4:1 hexanes/Et_2O eluent), affording enyne **S10** (0.406 g, 65% yield, R_f = 0.79 in 4:1 hexanes/EtOAc, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne S10: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.44-7.41 (m, 2H), 7.30 (t, *J* = 3.2 Hz, 3H), 5.78-5.60 (m, 2H), 4.08 (d, *J* = 6.0 Hz, 2H), 2.10-1.95 (m, 4H), 1.71 (dd, *J* = 6.2, 0.9 Hz, 3H), 1.68-1.56 (m, 10H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.8, 128.7, 128.6, 128.4, 128.2, 123.3, 91.9, 85.2, 77.3, 64.8, 35.1, 28.2, 24.7, 21.9, 18.0; IR (film) 2923, 2855, 1444, 1038, 755 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O + H]^+$: 283.2056, found 283.2053.



Enyne S11. To a solution of tertiary propargyl alcohol **S19** (0.194 g, 0.999 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (49.5 µL, 0.250 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **S11** (0.220 g, 71% yield, R_f = 0.82 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

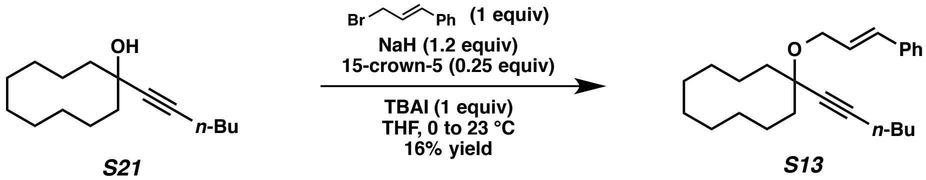
Enyne S11: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.21 (dd, *J* = 8.2, 6.3 Hz, 1H), 6.61 (d, *J* = 16.0 Hz, 1H), 6.33 (dt, *J* = 15.8, 5.9 Hz, 1H), 4.25 (dd, *J* = 5.9, 1.1 Hz, 2H), 2.24 (t, *J* = 6.9 Hz, 2H), 2.01-1.85 (m, 4H), 1.70-1.39 (m, 12H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.3, 131.3, 128.6, 127.7, 127.5, 126.6, 86.0, 82.6, 77.6, 64.6, 40.6, 31.1, 28.5, 22.2, 22.1, 18.6, 13.8; IR (film) 2932, 2859, 1496, 1058, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{22}H_{30}O + H]^+$: 311.2369, found 311.2362.



Enyne S12. To a solution of tertiary propargyl alcohol **S20** (0.209 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 g, 60% dispersion in mineral oil, 1.20 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (49.5 µL, 0.250 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (20 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1

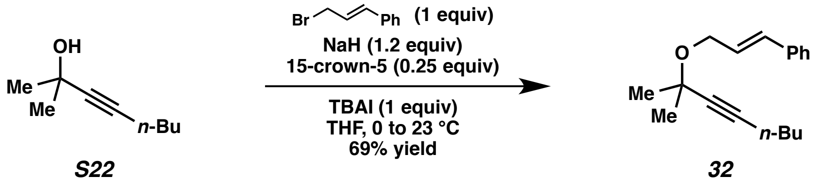
hexanes/CH_2Cl_2 eluent), affording enyne **S12** (0.247 g, 76% yield, $R_f = 0.86$ in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

Enyne S12: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.37 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.23 (dd, *J* = 5.9, 1.5 Hz, 2H), 2.23 (t, *J* = 6.9 Hz, 2H), 2.03-1.84 (m, 4H), 1.69-1.40 (m, 14H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.3, 131.3, 128.6, 127.4, 126.6, 98.9, 85.7, 82.4, 64.4, 35.3, 31.1, 28.3, 24.7, 22.1, 21.9, 18.5, 13.8; IR (film) 2927, 2857, 1496, 1111, 963 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{23}H_{32}O + H]^+$: 325.2526, found 325.2517.



Enyne S13. To a solution of tertiary propargyl alcohol **S21** (0.298 g, 1.26 mmol) in THF (6.3 mL) at 0 °C was added NaH (60.4 mg, 60% dispersion in mineral oil, 1.51 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (63.3 μL, 0.320 mmol), tetrabutylammonium iodide (0.465 g, 1.26 mmol), and cinnamyl bromide (0.249 g, 1.26 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction mixture was quenched with sat. aq. NH_4Cl (15 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 15 mL). The combined organic layers were washed with brine (30 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (10:1 hexanes/CH_2Cl_2 → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **S13** (72.7 mg, 16% yield, $R_f = 0.89$ in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a yellow oil.

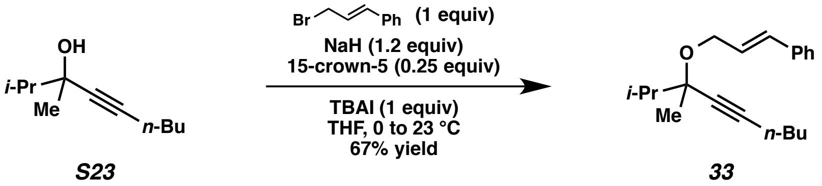
Enyne S13: ^{1}H NMR (400 MHz; CDCl$_3$): δ 7.39-7.37 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.9 Hz, 1H), 4.23 (dd, *J* = 5.9, 1.4 Hz, 2H), 2.23 (t, *J* = 6.9 Hz, 2H), 2.04-1.97 (m, 2H), 1.82 (dt, *J* = 14.2, 6.9 Hz, 2H), 1.71-1.38 (m, 18H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 137.3, 131.5, 128.6, 127.5, 126.6, 86.1, 82.0, 77.7, 64.3, 33.3, 31.2, 26.5, 26.0, 23.9, 22.1, 21.4, 18.5, 13.8; IR (film) 2924, 1446, 1054, 962 cm^{-1}; HRMS (ESI+) *m/z* calc'd for (M + H)$^+$ [$C_{25}H_{36}O$ + H]$^+$: 353.2839, found 353.2828.



Enyne 32. To a solution of tertiary propargyl alcohol **S22**^{8} (0.140 g, 0.998 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (49.5 µL, 0.250 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 19 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 → 1:1:1 hexanes/CH_2Cl_2/EtOAc eluent), affording enyne **32** (0.183 g, 69% yield, R_f = 0.71 in 2:1 CH_2Cl_2/hexanes, stained blue with *p*-anisaldehyde) as a colorless oil.

Enyne 32: ^{1}H NMR (400 MHz; CDCl$_3$): δ 7.40-7.38 (m, 2H), 7.30 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.24-7.22 (m, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.26 (dd, *J* = 6.0, 1.5 Hz, 2H), 2.22 (t, *J* = 7.0 Hz, 2H), 1.49 (s, 6H), 1.54-1.39 (m, 10H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; CDCl$_3$):

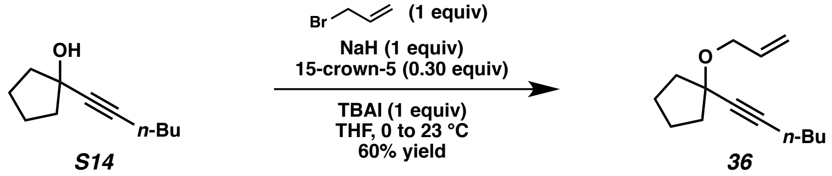
δ 137.2, 131.7, 128.6, 127.5, 127.3, 126.6, 84.9, 82.4, 70.7, 65.1, 31.0, 29.4, 22.1, 18.5, 13.8; IR (film) 2932, 2862, 1449, 1185 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{18}H_{24}O + H]^+$: 257.1900, found 257.1888.



Enyne 33. To a solution of tertiary propargyl alcohol **S23**[9] (0.706 g, 4.20 mmol) in THF (21 mL) at 0 °C was added NaH (0.201 g, 60% dispersion in mineral oil, 5.04 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.208 mL, 1.05 mmol), tetrabutylammonium iodide (1.55 g, 4.20 mmol), and cinnamyl bromide (0.827 g, 4.20 mmol). The resulting mixture was stirred at ambient temperature for 16.5 h. The reaction mixture was quenched with sat. aq. NH_4Cl (25 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (50 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **33** (0.800 g, 67% yield, $R_f = 0.86$ in 2:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a yellow oil.

Enyne 33: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.38 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.30 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.23-7.19 (m, 1H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.33 (dt, *J* = 15.9, 5.8 Hz, 1H), 4.32-4.19 (m, 2H), 2.24 (t, *J* = 6.9 Hz, 2H), 1.93 (dt, *J* = 13.5, 6.8 Hz, 1H), 1.55-1.40 (m, 4H), 1.36 (s, 3H), 1.04 (d, *J* = 6.8 Hz, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 137.3, 131.1, 128.6, 127.7, 127.4, 126.6, 86.5, 80.8, 77.4, 64.6, 37.5, 31.1, 23.2, 22.1, 18.5, 18.3, 17.4, 13.8; IR (film) 2961, 2933, 1496, 1205, 964 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{28}O + H]^+$: 285.2213, found 285.2205.

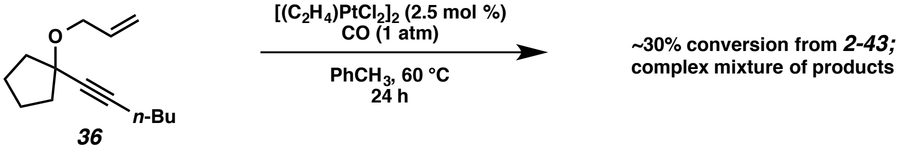
Unsuccessful Substrates



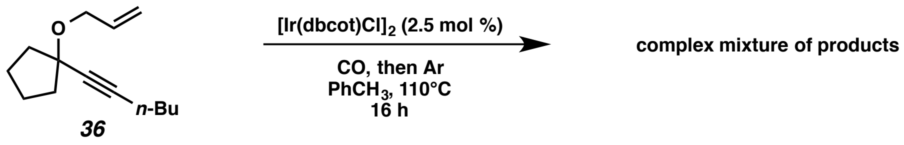
Enyne 36. To a solution of tertiary propargyl alcohol **S14** (0.168 g, 1.00 mmol) in THF (5.0 mL) at 0 °C was added NaH (40.0 mg, 60% dispersion in mineral oil, 1.00 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (60.0 μL, 0.300 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and allyl bromide (86.0 μL, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 20 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (20:1 hexanes/CH_2Cl_2 → 4:1 hexanes/CH_2Cl_2 eluent), affording enyne **36** (0.124, 60% yield, R_f = 0.55 in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisaldehyde) as a colorless oil.

All spectroscopic data were consistent with previously reported values.[10]

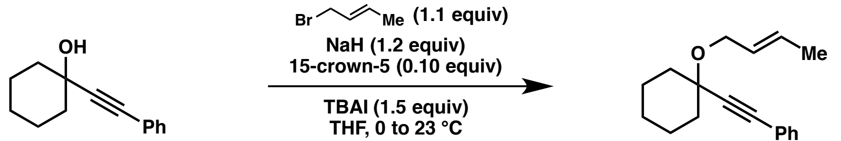
Attempted Cycloisomerization of Enyne 36:



***Procedure A*:** To a solution of enyne **36** (20.7 mg, 0.100 mmol) in toluene (1.54 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (1.5 mg, 0.00250 mmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s). The balloon and outlet were then removed, and the solution was stirred at 60 °C for 24 h. The reaction was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was analyzed by ^1H NMR. Enyne **36** was partly consumed, but the desired product was not detected.



***Procedure B*:** To a solution of enyne **36** (12.0 mg, 60.0 μmol) in toluene (0.920 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.3 mg, 1.50 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap, and the solution was stirred at 110 °C for 16 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was analyzed by ^1H NMR. Enyne **36** was completely consumed, but the desired product was not detected.

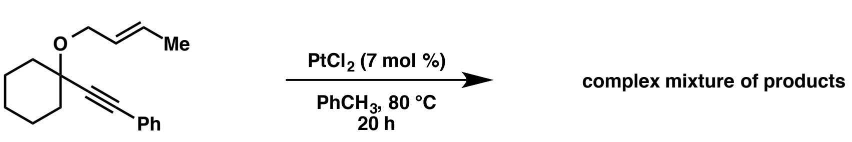


S24 ***37***

Enyne 37. To a solution of tertiary propargyl alcohol **S24** (0.200 g, 0.998 mmol) in THF (5.0 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.020 mL, 0.0998 mmol), tetrabutylammonium iodide (0.369 g, 0.998 mmol), and cinnamyl bromide (0.11 mL, 1.10 mmol). The resulting mixture was stirred at ambient temperature for 20 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/EtOAc → 20:1 hexanes/EtOAc eluent), affording enyne **37** (0.176, 70% yield, R_f = 0.90 in 3:1 hexanes/EtOAc, visualized by UV) as a pale yellow oil.

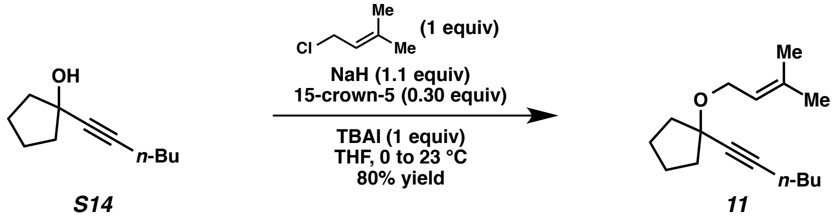
Enyne 37: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.45-7.43 (m, 2H), 7.31-7.30 (m, 3H), 5.80-5.72 (m, 1H), 5.69-5.62 (m, 1H), 4.13 (dt, *J* = 6.2, 1.0 Hz, 2H), 2.05-2.00 (m, 2H), 1.71 (dd, *J* = 6.2, 1.2 Hz, 3H), 1.66-1.54 (comp. m, 7H), 1.35-1.25 (m, 1H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.7, 128.4, 128.2, 128.1, 123.3, 123.1, 90.7, 86.1, 75.8, 64.3, 37.4, 25.5, 23.0, 17.9; HRMS (ESI+) *m/z* calc'd for $(M + Na)^+$ $[C_{18}H_{22}O + Na]^+$: 277.1563, found 277.1549.

Attempted Cycloisomerization of Enyne 37:



37

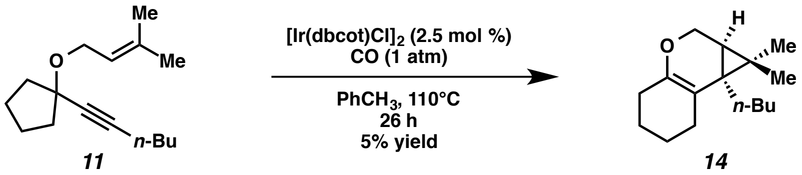
To a solution of enyne **37** (0.2552 mg, 1.00 mmol) in toluene (17.5 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (18.6 mg, 0.0700 mmol). The reaction mixture was stirred at 80 °C for 20 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was analyzed by ^1H NMR. Enyne **37** was completely consumed, but the majority of the crude product was a complex mixture from which the desired product could not be detected. The reaction was also performed at 60 °C. The same results were obtained.



Enyne 11. To a solution of tertiary propargyl alcohol **S14** (1.67 g, 10.0 mmol) in THF (50 mL) at 0 °C was added NaH (0.450 g, 60% dispersion in mineral oil, 11.0 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.60 mL, 3.00 mmol), tetrabutylammonium iodide (3.69 g, 10.0 mmol), and prenyl chloride (1.13 mL, 10.0 mmol). The resulting mixture was stirred at ambient temperature for 20 h. The reaction mixture was quenched with sat. aq. NH_4Cl (50 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (100 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 → 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **11** (1.874 g, 80% yield, $R_f = 0.67$ in 1:1 hexanes/CH_2Cl_2, stained blue with *p*-anisidine) as a yellow oil.

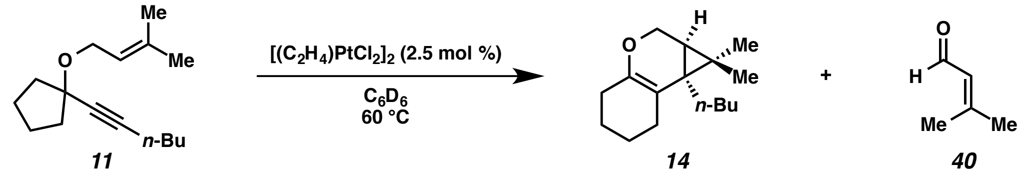
Enyne 11: ^{1}H NMR (400 MHz; CDCl$_3$): δ 5.37-5.33 (m, 1H), 4.03 (d, *J* = 7.0 Hz, 2H), 2.22 (t, *J* = 6.9 Hz, 2H), 2.00-1.78 (comp. m, 4H), 1.73 (s, 3H), 1.68 (s, 3H), 1.51-1.31 (comp. m, 8H), 0.91 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; CDCl$_3$): δ 123.3, 121.7, 85.1, 80.2, 75.8, 61.2, 42.6, 39.7, 30.9, 25.9, 23.2, 21.9, 18.4, 13.6; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{16}H_{26}O + H]^+$: 235.2056, found 235.2044.

Attempted Cycloisomerization of Enyne 11:



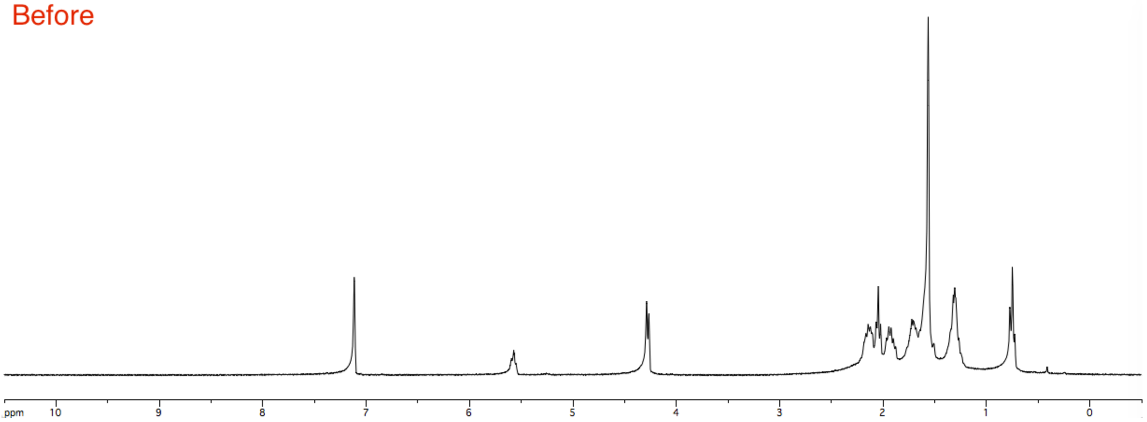
To a solution of enyne **11** (28.5 mg, 0.120 mmol) in toluene (2.60 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added [Ir(dbcot)Cl]$_2$ (2.6 mg, 0.00300 mmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), and the vessel was sealed. The reaction mixture was stirred at 110 °C for 26 h, and then it was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al$_2$O$_3$ (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH$_2$Cl$_2$ → 6:1 hexanes/CH$_2$Cl$_2$ eluent), affording tricycle **14** (1.4 mg, 5% yield, R$_f$ = 0.66 in 1:1 hexanes/CH$_2$Cl$_2$, stained orange with *p*-anisidine) as a yellow oil.

Also see: **Preliminary Results with Zeise's Dimer (Table 3)**

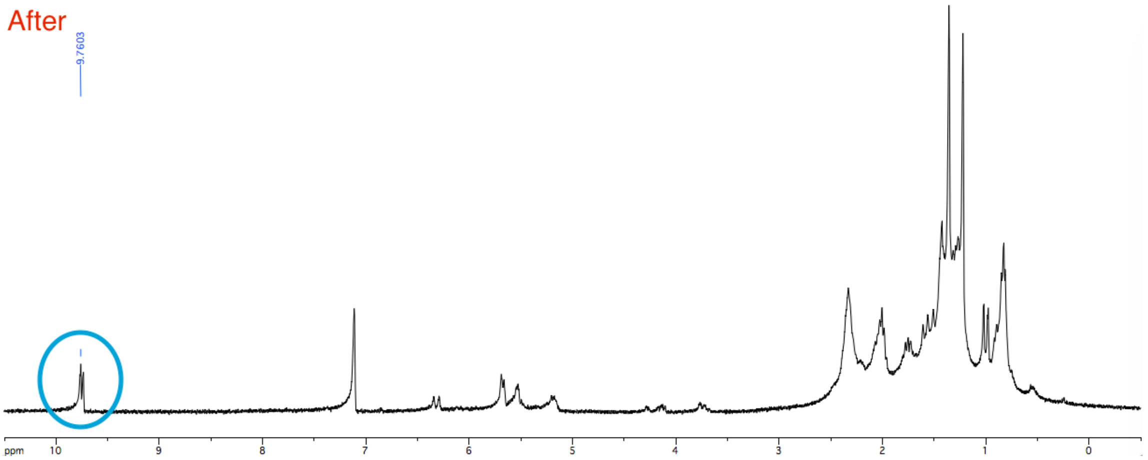


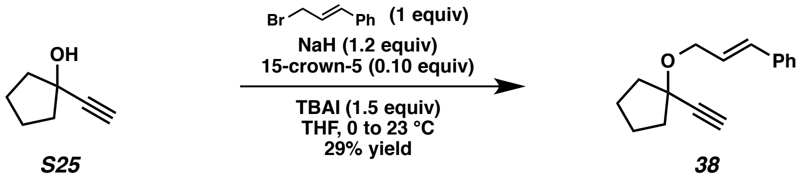
NMR Experiment: To enyne **11** (8.6 mg, 0.0300 mmol) in C_6D_6 (0.460 mL) was added $[(C_2H_4)PtCl_2]_2$ (0.5 mg, 0.000750 mmol). The reaction mixture was transferred to an NMR tube. A ^{1}H NMR was taken of the starting reaction mixture. The NMR tube was then heated at 60 °C for 21 h, and a second ^{1}H NMR was taken that revealed the formation of an aldehyde peak at 9.76 ppm. This peak, the broadened multiplet at 5.72, and the singlets at 1.38 and 1.25 are indicative of aldehyde **40**.

Before



After

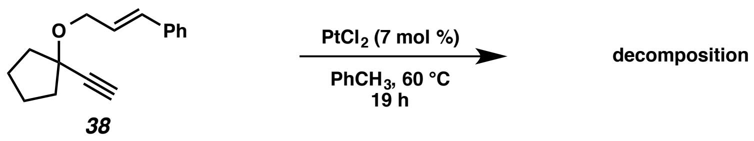




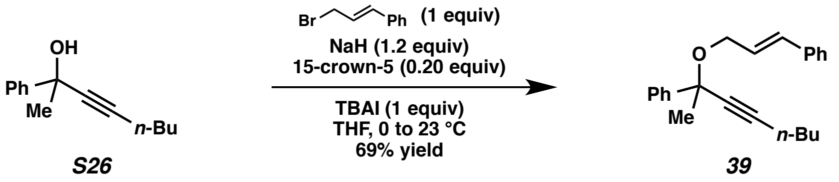
Enyne 38. To a solution of tertiary propargyl alcohol **S25**[11] (0.992 g, 9.00 mmol) in THF (45 mL) at 0 °C was added NaH (0.432 g, 60% dispersion in mineral oil, 10.8 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.18 mL, 0.900 mmol), tetrabutylammonium iodide (4.99 g, 13.5 mmol), and cinnamyl bromide (1.77 g, 9.00 mmol). The resulting mixture was stirred at ambient temperature for 14 h. The reaction mixture was quenched with sat. aq. NH_4Cl (40 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 40 mL). The combined organic layers were washed with brine (80 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/Et_2O → 4:1 hexanes/Et_2O eluent), affording enyne **38** (0.598 g, 29% yield, R_f = 0.85 in 3:1 hexanes/EtOAc, visualized by UV) as a colorless oil.

Enyne 38: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 6.62 (d, *J* = 15.9 Hz, 1H), 6.32 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.25 (dd, *J* = 6.0, 1.4 Hz, 2H), 2.51 (s, 1H), 2.11-2.05 (m, 2H), 1.99-1.93 (m, 2H), 1.84-1.71 (m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 136.9, 131.7, 128.4, 127.5, 126.6, 126.5, 85.5, 80.2, 72.9, 65.7, 39.6, 23.3; HRMS (ESI+) *m/z* calc'd for $(M + Na)^+$ $[C_{16}H_{18}O + Na]^+$: 249.1250, found 249.1237.

Attempted Cycloisomerization of Enyne 38:



To a solution of enyne **38** (90.5 mg, 0.400 mmol) in toluene (4.0 mL) in a 2-dram vial under argon at 23 °C was quickly added $PtCl_2$ (7.5 mg, 0.0280 mmol). The reaction mixture was stirred at 60 °C for 19 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was analyzed by ^{1}H NMR. Enyne **38** was not completely consumed, but the majority of the crude product mixture was decomposition products.

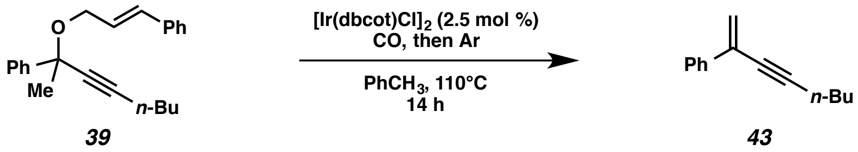


Enyne 39. To a solution of tertiary propargyl alcohol **S26** (0.202 g, 1.00 mmol) in THF (5.00 mL) at 0 °C was added NaH (48.0 mg, 60% dispersion in mineral oil, 1.20 mmol). The reaction mixture was allowed to warm to ambient temperature and was stirred until gas evolution was visibly complete. To this suspension was added sequentially 15-crown-5 (0.050 mL, 0.250 mmol), tetrabutylammonium iodide (0.369 g, 1.00 mmol), and cinnamyl bromide (0.197 g, 1.00 mmol). The resulting mixture was stirred at ambient temperature for 19 h. The reaction mixture was quenched with sat. aq. NH_4Cl (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were washed with brine (25 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2

→ 1:1 hexanes/CH_2Cl_2 eluent), affording enyne **39** (0.192 g, 60% yield, R_f = 0.85 in 1:2 hexanes/CH_2Cl_2, stained purple with *p*-anisidine) as a yellow oil.

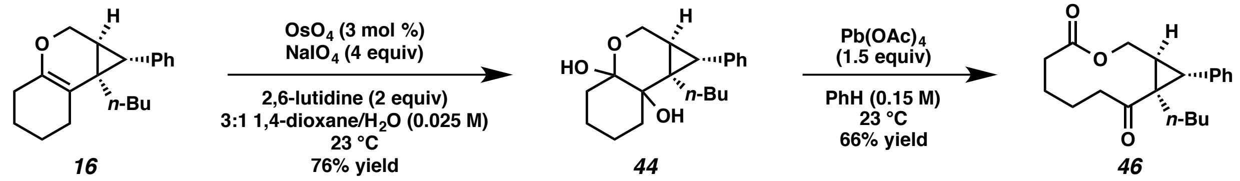
Enyne 39: ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.65 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.39-7.36 (comp. m, 4H), 7.32-7.28 (comp. m, 3H), 7.24-7.20 (m, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.31 (dt, *J* = 15.9, 6.0 Hz, 1H), 4.27 (ddd, *J* = 12.2, 6.0, 1.4 Hz, 1H), 3.79 (ddd, *J* = 12.2, 6.0, 1.4 Hz, 1H), 2.37 (t, *J* = 7.0 Hz, 2H), 1.75 (s, 3H), 1.62-1.56 (m, 2H), 1.49 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 131.6, 128.4, 128.2, 127.6, 127.4, 126.6, 126.4, 126.0, 88.3, 83.7, 80.2, 76.2, 75.8, 65.7, 33.3, 30.9, 22.0, 18.5, 13.6; HRMS (ESI+) *m/z* calc'd for $(M + Na)^+$ $[C_{23}H_{26}O + Na]^+$: 341.1876, found 341.1859.

Attempted Cycloisomerization of Enyne 39:



Procedure B: To a solution of enyne **39** (15.4 mg, 50.0 μmol) in toluene (0.770 mL) in a 16 x 125 mm glass culture tube under argon at 23 °C was quickly added $[Ir(dbcot)Cl]_2$ (1.1 mg, 1.25 μmol). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the solution turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the solution in the same manner. The septum was quickly replaced with a Teflon cap, and the solution was stirred at 110 °C for 14 h. The reaction mixture was allowed to cool to ambient temperature and was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was analyzed by ^{1}H NMR. Enyne **39** was completely consumed, and alkene **43** was the major product. All spectroscopic data were consistent with previously reported values.[12]

Oxidative Cleavage to Macrolactones

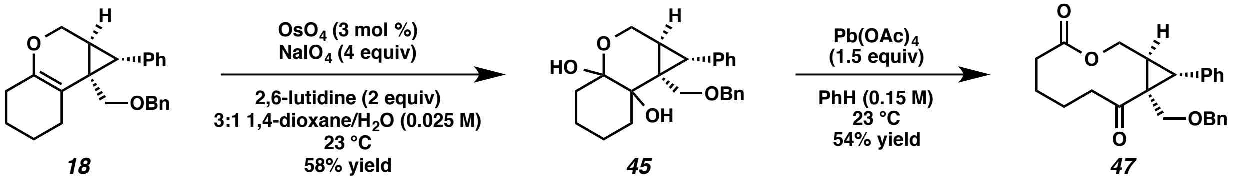


Diol 44. To a solution of tricycle **16** (67.6 mg, 0.239 mmol) in 1,4-dioxane (7.5 mL) at 23 °C was added OsO_4 (50.0 µL, 4% solution in H_2O, 0.00750 mmol), followed by 2,6-lutidine (57.6 µL, 0.500 mmol). The reaction mixture was stirred for 5 min, then $NaIO_4$ (0.214 g, 1.00 mmol) was added as a solution in H_2O (2.5 mL). The resulting mixture was stirred at ambient temperature for 1.5 d, after which the mixture was quenched with 1 M aq. HCl (5 mL) and diluted with EtOAc (5 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (1 x 5 mL). The combined organic layers were washed sequentially with sat. aq. $Na_2S_2O_3$ (10 mL) and brine (10 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/CH_2Cl_2 → EtOAc eluent), affording diol **44** (57.4 mg, 76% yield, R_f = 0.77 in 1:1 hexanes/EtOAc, stained with CAM) as a green oil.

Diol 44: ^1H NMR (400 MHz; C_6D_6): δ 7.15-7.06 (m, 5H), 4.23 (dd, *J* = 10.6, 4.0 Hz, 1H), 3.69 (d, *J* = 10.6 Hz, 1H), 2.39 (d, *J* = 1.5 Hz, 1H), 2.20 (d, *J* = 6.1 Hz, 1H), 1.96-1.92 (m, 2H), 1.68-1.61 (m, 2H), 1.54-1.47 (m, 4H), 1.45-1.40 (m, 2H), 1.20 (dd, *J* = 6.0, 3.9 Hz, 1H), 1.16-0.90 (m, 3H), 0.69 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 139.2, 129.3, 126.1, 94.4, 70.7, 59.8, 36.5, 35.7, 35.6, 31.9, 31.5, 30.3, 23.7, 23.1, 21.6, 21.2, 14.0; IR (film) 3400, 2935, 2869, 1712, 1064 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M - H)^-$ $[C_{20}H_{28}O_3 - H]^-$: 315.1960, found 315.1959.

Macrolactone 46. To a solution of diol **44** (25.3 mg, 0.0780 mmol) in benzene (0.70 mL) at 23 °C was added $Pb(OAc)_4$ (53.2 mg, 0.120 mmol). The reaction mixture was stirred at ambient temperature for 3.5 h, after which ethylene glycol (1.0 mL) was added, and the mixture was allowed to stir for 1 h. The reaction mixture was diluted with Et_2O (1.5 mL), and the layers were separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 4:1 hexanes/EtOAc eluent), affording macrolactone **46** (16.3 mg, 66% yield, $R_f = 0.83$ in 1:1 hexanes/EtOAc, stained with CAM) as a colorless oil.

Macrolactone 46: ^{1}H NMR (400 MHz; C_6D_6): δ 7.09-7.01 (m, 3H), 6.96 (dd, *J* = 5.2, 3.2 Hz, 2H), 4.54 (dd, *J* = 11.6, 6.6 Hz, 1H), 3.80 (dd, *J* = 11.6, 6.6 Hz, 1H), 3.34 (d, *J* = 6.9 Hz, 1H), 2.63 (ddd, *J* = 16.8, 10.8, 2.4 Hz, 1H), 2.15 (m, 2H), 2.05-1.90 (m, 2H), 1.85-1.72 (m, 2H), 1.44-1.31 (m, 4H), 0.96-0.74 (m, 4H), 0.51 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz; C_6D_6): δ 206.5, 172.0, 137.2, 128.9, 128.2, 126.5, 62.4, 44.3, 39.5, 34.6, 34.0, 31.1, 30.5, 28.7, 23.0, 22.8, 13.5; IR (film) 2933, 2872, 1737, 1698, 1233 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + H)^+$ $[C_{20}H_{26}O_3 + H]^+$: 315.1960, found 315.1962.



Diol 45. To a solution of tricycle **18** (34.5 mg, 0.0907 mmol) in 1,4-dioxane (3.0 mL) at 23 °C was added OsO_4 (19.0 μL, 4% solution in H_2O, 2.72 μmol), followed by 2,6-lutidine (20.9 μL, 0.0194 mmol). The reaction mixture was stirred for 5 min, then $NaIO_4$ (85.6 mg, 0.400 mmol) was added as a solution in H_2O (1.0 mL). The resulting mixture was stirred at ambient temperature for 3 d, after which the mixture was quenched with 1 M aq. HCl (3 mL) and diluted with EtOAc (3 mL). The layers were separated, and the aqueous layer was extracted with EtOAc (1 x 3 mL). The combined organic layers were washed

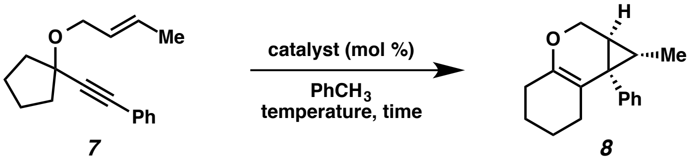
sequentially with sat. aq. $Na_2S_2O_3$ (5 mL) and brine (5 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 1:1 hexanes/EtOAc eluent), affording diol **45** (20.0 mg, 58% yield, R_f = 0.66 in 1:1 hexanes/EtOAc, stained with CAM) as a green oil.

Diol 45: ^1H NMR (400 MHz; C_6D_6): δ 7.14-6.95 (m, 10H), 4.42 (dd, *J* = 11.1, 4.5 Hz, 1H), 3.87-3.80 (m, 2H), 3.75 (d, *J* = 11.2 Hz, 2H), 3.36 (d, *J* = 9.5 Hz, 1H), 2.80 (d, *J* = 9.5 Hz, 1H), 2.32 (d, *J* = 6.3 Hz, 1H), 2.15-2.02 (m, 2H), 1.91-1.84 (m, 2H), 1.65-1.52 (m, 2H), 1.47-1.41 (m, 1H), 1.12 (dd, *J* = 6.2, 4.6 Hz, 1H); ^{13}C NMR (100 MHz; C_6D_6): δ 138.2, 137.9, 129.4, 128.7, 128.4, 128.0, 127.9, 126.6, 94.1, 73.1, 72.3, 71.0, 58.9, 36.2, 35.3, 33.5, 30.8, 22.9, 21.2, 19.9; IR (film) 3449, 2933, 2865, 1498, 1071 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{28}O_4 + Na]^+$: 403.1885, found 403.1889.

Macrolactone 47. To a solution of diol **45** (25.3 mg, 0.0780 mmol) in benzene (0.70 mL) at 23 °C was added $Pb(OAc)_4$ (53.2 mg, 0.120 mmol). The reaction mixture was stirred at ambient temperature for 3.5 h, after which ethylene glycol (1.0 mL) was added, and the mixture was allowed to stir for 1 h. The reaction mixture was diluted with Et_2O (1.5 mL), and the layers were separated. The organic layer was washed with sat. aq. $NaHCO_3$ (2 mL), then dried over $MgSO_4$. The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 4:1 hexanes/EtOAc eluent), affording macrolactone **47** (16.3 mg, 66% yield, R_f = 0.83 in 1:1 hexanes/EtOAc, stained with CAM) as a colorless oil.

Macrolactone 47: ^1H NMR (400 MHz; C_6D_6): δ 7.11-7.00 (m, 8H), 6.93-6.91 (m, 2H), 4.43 (dd, *J* = 11.7, 6.8 Hz, 1H), 3.93-3.81 (m, 3H), 3.57 (d, *J* = 6.9 Hz, 1H), 2.89 (ddd, *J* = 16.6, 9.2, 2.4 Hz, 1H), 2.61 (d, *J* = 10.5 Hz, 1H), 2.44 (ddd, *J* = 16.6, 9.2, 2.4 Hz, 1H), 2.13-2.06 (m, 1H), 2.01-1.88 (m, 1H), 1.84-1.74 (m, 1H), 1.71 (q, *J* = 6.8 Hz, 1H), 1.44-1.30 (m, 4H); ^{13}C NMR (100 MHz; C_6D_6): δ 205.5, 172.0, 136.9, 129.6, 128.5, 128.2, 127.9, 127.6, 126.9, 99.3, 73.1, 69.6, 62.1, 42.8, 39.8, 34.90, 34.87, 29.2, 22.93, 22.91, 13.4 IR (film) 2926, 2856, 1735, 1698, 1231, 1154 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $(M + Na)^+$ $[C_{24}H_{26}O_4 + Na]^+$: 401.1729, found 401.1733.

Catalyst Optimization (Table 1)



General procedure: To a 2-dram vial under argon containing enyne **7** (14.0 mg, 0.0583 mmol) and 4,4'-di-*tert*-butylbiphenyl (internal standard, 5.3 mg, 0.0199 mmol) in toluene (0.900 mL, 0.065 M) at 23 °C was added the catalyst. The reaction mixture was stirred at the indicated temperature for the indicated time, and then was passed through a short plug of Al_2O_3 (hexanes → 9:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation. The crude residue was then diluted with CH_2Cl_2 (3 mL), and the sample was analyzed by GC. The catalyst screen results are reported in Table 1.

GC Method

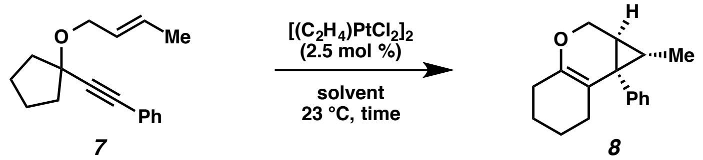
150 °C for 60 min

Retention times: **7** = 16.60 min; **8** = 15.98 min, internal standard = 47.40 min

GC Column

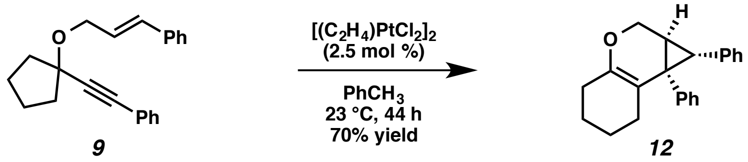
Agilent Technologies CP-Sil 8 CB (15 x 0.25)

Solvent Optimization (Table 2)

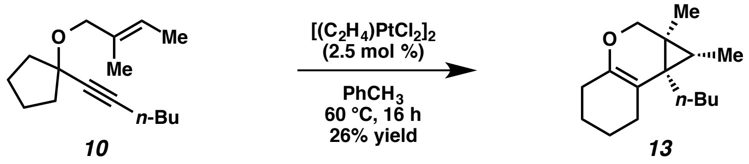


General procedure: To a 2-dram vial under argon containing enyne **7** (14.0 mg, 0.0583 mmol) and 4,4'-di-*tert*-butylbiphenyl (internal standard, 5.3 mg, 0.0199 mmol) in the indicated solvent (0.900 mL, 0.065 M) at 23 °C was added $[(C_2H_4)PtCl_2]_2$ (0.9 mg, 0.00146 mmol). The reaction mixture was stirred at ambient temperature for the indicated time, and then was passed through a short plug of Al_2O_3 (hexanes → 9:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation. The crude residue was then diluted with CH_2Cl_2 (3 mL), and the sample was analyzed by GC. The solvent screen results are reported in Table 2. The same GC method and column were used as above in catalyst optimization.

Preliminary Results with Zeise's Dimer (Table 3)

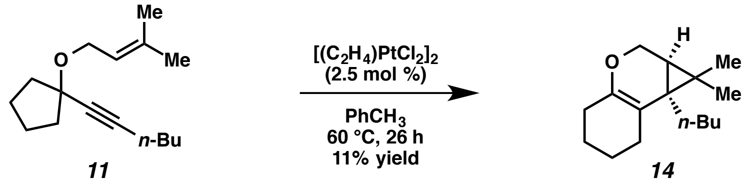


Tricycle 12. To a solution of enyne **9** (15.5 mg, 50.0 μmol) in toluene (0.77 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (0.8 mg, 1.25 μmol). The reaction mixture was stirred at ambient temperature for 44 h, then was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N eluent), affording tricycle **12** (10.9 mg, 70% yield, R_f = 0.61 in 1:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a colorless oil.



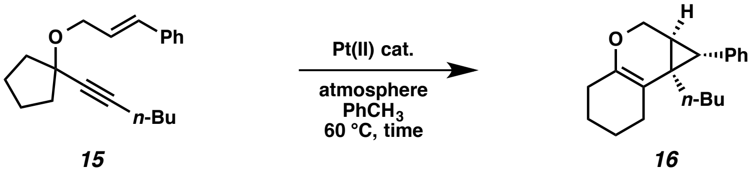
Tricycle 13. To a solution of enyne **10** (23.7 mg, 0.100 mmol) in toluene (1.50 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (1.5 mg, 0.00250 mmol). The reaction mixture was stirred at 60 °C for 16 h, then was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (9:1 hexanes/CH_2Cl_2 w/ 0.5% Et_3N → 5:1 hexanes/CH_2Cl_2

w/ 0.5% Et_3N eluent), affording tricycle **13** (6.1 mg, 26% yield, $R_f = 0.81$ in 1:1 CH_2Cl_2/hexanes, stained orange with *p*-anisaldehyde) as a colorless oil. When the same reaction was performed at ambient temperature, low conversion from enyne **10** was observed.



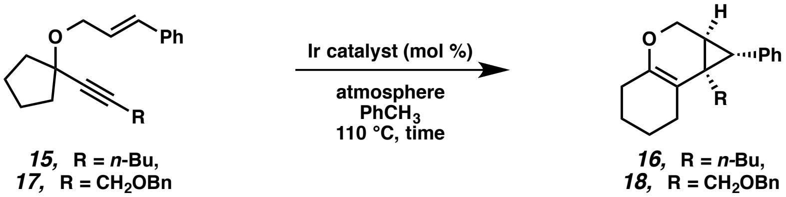
Tricycle 14. To a solution of enyne **11** (75.1 mg, 0.320 mmol) in toluene (4.90 mL) in a 2-dram vial under argon at 23 °C was quickly added $[(C_2H_4)PtCl_2]_2$ (4.7 mg, 0.00800 mmol). The reaction mixture was stirred at 60 °C for 26 h, then was diluted with an approximately equal amount of hexanes. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (100% hexanes → 9:1 hexanes/CH_2Cl_2 eluent), affording tricycle **14** (8.1 mg, 11% yield, $R_f = 0.63$ in 1:1 CH_2Cl_2/hexanes, stained red with *p*-anisaldehyde) as a colorless oil. When the same reaction was performed at ambient temperature, almost no reaction occurred.

Effect of CO Atmosphere (Table 4)



General Procedure: The reaction were performed as described in *Procedure A* (for [(C_2H_4)$PtCl_2$]$_2$) and *Procedure C* (for $PtCl_2$), except the atmospheres were varied. The reactions run under argon were assembled under argon in 2 dram vials equipped with rubber septa. After the catalyst was added, the rubber septum was quickly replaced with a Teflon cap. The reactions run under CO were assembled under air in 2 dram vials equipped with screw caps with septa. After the catalyst was added, CO was bubbled through the reaction mixture using a balloon and needle outlet. The reaction mixtures were heated at 60 °C for the indicated time and then were worked up and purified according to the *General Procedures.*

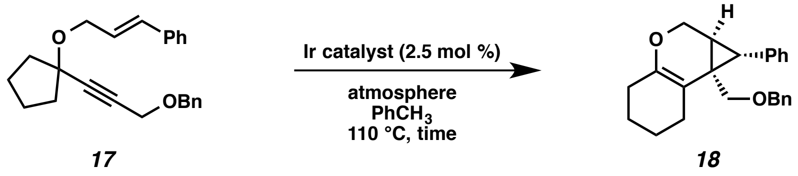
Ir Catalyst Screen (Table 5)



General procedure: To a 2-dram vial containing either enyne **15** or **17** (0.0500 mmol) in toluene (0.065 M) at 23 °C was added the catalyst. The reactions performed under argon were purged by bubbling argon through the reaction mixture for 1 min. The reactions performed under CO were purged by bubbling CO through the reaction mixture for 1 min. For the “CO, then Ar” reactions, CO was bubbled through the reaction mixture for 1 min, then argon was bubbled through for 1 min. The reaction mixture was stirred at 110 °C for the indicated time, and then was passed through a short plug of Al_2O_3 (hexanes → 9:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation. The crude residue was then analyzed by ^{1}H NMR to determine conversion. Isolated yields were obtained after purification by flash chromatography. The Ir catalyst screen results are reported in Table 5.

Vaska’s complex, $[Ir(cod)Cl]_2$, and $[Ir(coe)_2Cl]_2$ are commercially available. $Ir_4(CO)_{12}$,[13] $Ir(CO)_2(acac)$,[14] and $[Ir(dbcot)Cl]_2$[15] were synthesized as previously reported.

CO vs. CO, then Ar (Table 6)



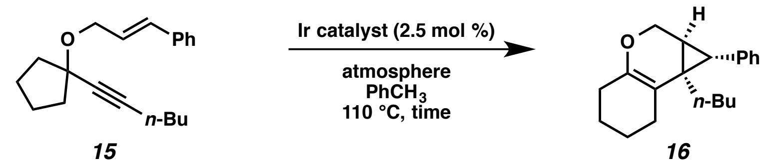
General procedure: Each reaction was performed on a 0.0500 mmol to 0.0750 mmol scale in toluene (0.065 M). The reactions performed under CO were purged by bubbling CO through the reaction mixture for 1 min. For the "CO, then Ar" reactions, CO was bubbled through the reaction mixture for 1 min, then argon was bubbled through for 1 min. The reaction mixture was stirred at 110 °C for the time indicated below, and then was passed through a short plug of Al_2O_3 (hexanes → 9:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography to obtain isolated yields.

$[Ir(dbcot)Cl]_2$: CO, 15 h; CO, then Ar; 16 h

$[Ir(cod)Cl]_2$: CO, 22 h; CO, then Ar; 17 h

$[Ir(coe)_2Cl]_2$: CO, 15 h; CO, then Ar; 15 h

Ir(I) Experiments where Displaced Ligand was Removed (Table 7)



In a representative procedure, a 16 x 125 mm glass culture tube was charged with [Ir(dbcot)Cl]$_2$ (1.3 mg, 0.00150 mmol) and toluene (0.92 mL). CO was bubbled through the solution using a balloon and needle outlet (ca. 30 s), during which time the mixture turned a dark-blue/black color. The balloon was removed, and argon was bubbled through the solution in the same manner. The tube containing the catalyst mixture was then centrifuged for ~30 s to concentrate the black solid at the bottom of the tube. The toluene was carefully removed using a needle and syringe. The remaining black solid was dried under vacuum, then the tube was backfilled with argon. Fresh toluene (0.92 mL) and enyne **15** (17.6 mg, 0.0600 mmol) were added. The septum was quickly replaced with a Teflon cap, and the solution was stirred at 110 °C for 22 h. The reaction was allowed to cool to ambient temperature and diluted with an approximately equal amount of hexanes. 1,3-Bis(diphenylphosphino)propane (dppp) (0.25 equiv) was also added to the mixture. The mixture was stirred for 15 min, then passed through a small plug of Al_2O_3 (hexanes → 1:1 hexanes/EtOAc eluent). The volatile materials were removed by rotary evaporation, and the resulting residue was purified by flash chromatography (99:1 hexanes/CH_2Cl_2 → 9:1 hexanes/CH_2Cl_2 eluent), affording tricycle **16** (11.2 mg, 64% yield) as a colorless oil.

Crystallographic Data for Product 8

Table 1 Crystal data and structure refinement for 8

Identification code	**8**
Empirical formula	$C_{17}H_{20}O$
Formula weight	240.33
Temperature/K	100(2)
Crystal system	monoclinic
Space group	Cc
a/Å	16.9694(6)
b/Å	10.1758(6)
c/Å	7.7382(3)
α/°	90.00
β/°	92.801(3)
γ/°	90.00
Volume/Å^3	1334.61(11)
Z	4
ρ_{calc}mg/mm^3	1.196
m/mm^{-1}	0.072
F(000)	520.0
Crystal size/mm^3	0.57 × 0.47 × 0.37
2Θ range for data collection	4.66 to 78.76°
Index ranges	$-30 \leq h \leq 30$, $-18 \leq k \leq 17$, $-13 \leq l \leq 13$
Reflections collected	28192
Independent reflections	7745[R(int) = 0.0359]
Data/restraints/parameters	7745/2/164
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0323, wR_2 = 0.0884
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0898
Largest diff. peak/hole / e Å^{-3}	0.44/-0.21
Flack parameter	0.3(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 8. U$_{eq}$ is defined as 1/3 of of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	2433.8(3)	3952.5(5)	7948.6(6)	17.52(8)
C1	2547.6(3)	2872.7(5)	6904.3(7)	14.09(8)
C2	1791.7(3)	2460.5(6)	5986.7(8)	19.35(9)
C3	1850.2(4)	1084.4(7)	5229.4(9)	22.48(11)
C4	2626.8(4)	936.6(7)	4327.2(9)	23.85(11)
C5	3338.8(3)	1121.1(6)	5597.0(7)	16.95(9)
C6	3249.0(3)	2268.5(5)	6809.1(6)	12.15(7)
C7	3942.0(3)	2700.0(5)	7954.2(6)	11.92(7)
C8	3837.1(3)	4030.3(5)	8789.1(7)	14.49(8)
C9	3109.2(4)	4787.4(5)	8212.4(7)	16.49(9)
C10	3797.7(3)	2817.6(5)	9894.9(7)	14.76(8)
C11	4442.3(4)	2563.0(7)	11270.5(8)	20.96(10)
C12	4740.9(3)	2293.9(5)	7406.4(6)	12.97(8)
C13	5046.6(3)	1060.0(5)	7863.3(7)	15.81(8)
C14	5767.5(3)	641.1(6)	7284.9(8)	19.55(10)
C15	6195.8(3)	1450.8(7)	6225.0(8)	21.97(11)
C16	5901.4(4)	2685.1(7)	5771.5(9)	22.63(11)
C17	5180.1(3)	3107.7(6)	6366.3(7)	18.19(9)

Table 3 Anisotropic Displacement Parameters (Å^2×10^3) for 8. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+...+2hka×b×U$_{12}$]

Atom	U$_{11}$	U$_{22}$	U$_{33}$	U$_{23}$	U$_{13}$	U$_{12}$
O1	14.84(16)	18.22(18)	19.61(17)	-2.34(13)	1.96(13)	5.73(13)
C1	12.34(17)	16.17(19)	13.70(18)	0.70(15)	0.04(14)	2.79(15)
C2	12.57(18)	24.7(2)	20.3(2)	1.57(19)	-3.27(16)	2.21(18)
C3	17.8(2)	25.2(3)	23.7(2)	-1.1(2)	-7.12(19)	-1.9(2)
C4	23.1(2)	29.3(3)	18.6(2)	-7.7(2)	-5.11(19)	1.3(2)
C5	16.23(19)	18.1(2)	16.3(2)	-5.30(16)	-0.91(16)	1.76(16)
C6	11.37(16)	13.34(17)	11.73(17)	-0.35(14)	0.27(13)	1.77(13)
C7	11.48(16)	12.08(17)	12.16(16)	-0.98(13)	0.32(13)	2.06(13)
C8	16.38(19)	12.38(18)	14.58(18)	-2.00(14)	-0.54(15)	2.79(15)
C9	20.1(2)	13.96(18)	15.4(2)	-0.88(15)	0.22(16)	5.40(16)
C10	15.80(18)	16.97(19)	11.42(17)	-0.03(15)	-0.25(14)	3.90(15)
C11	23.2(2)	23.6(2)	15.4(2)	-0.89(18)	-5.02(18)	6.3(2)
C12	11.34(16)	13.65(18)	13.90(18)	-1.38(14)	0.53(13)	0.99(14)
C13	13.53(18)	14.78(19)	19.1(2)	-0.92(16)	1.10(15)	2.91(15)
C14	15.02(19)	21.1(2)	22.5(2)	-5.00(19)	0.28(17)	5.70(17)
C15	13.24(19)	31.1(3)	21.9(2)	-7.8(2)	3.17(17)	1.79(19)
C16	19.0(2)	28.2(3)	21.3(3)	-2.0(2)	7.13(19)	-3.2(2)
C17	18.1(2)	18.3(2)	18.5(2)	1.32(17)	3.85(17)	0.02(17)

Table 4 Bond Lengths for 8.

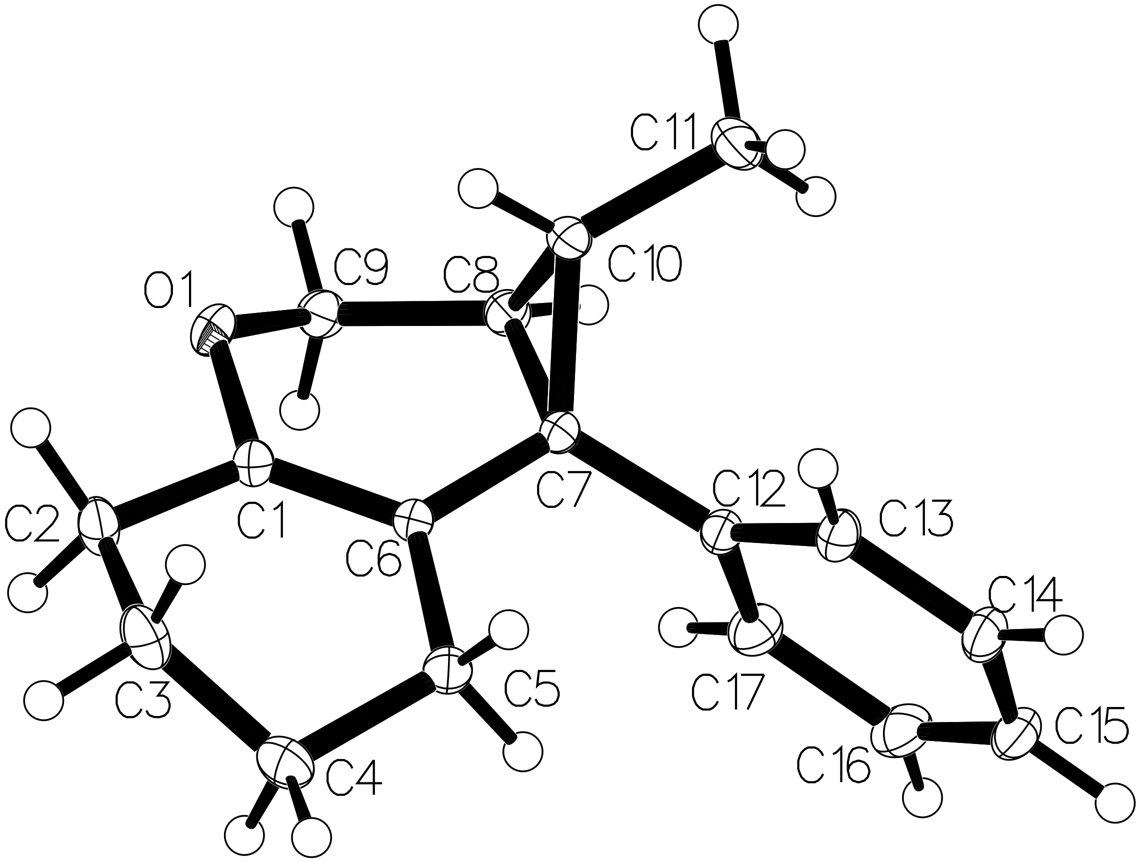
Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C1	1.3830(7)	C7	C12	1.4982(7)
O1	C9	1.4332(8)	C8	C9	1.5048(8)
C1	C2	1.4955(8)	C8	C10	1.5051(8)
C1	C6	1.3449(7)	C10	C11	1.5109(8)
C2	C3	1.5230(10)	C12	C13	1.3974(7)
C3	C4	1.5285(10)	C12	C17	1.3956(8)
C4	C5	1.5313(8)	C13	C14	1.3899(7)
C5	C6	1.5100(7)	C14	C15	1.3922(10)
C6	C7	1.5030(7)	C15	C16	1.3903(10)
C7	C8	1.5142(7)	C16	C17	1.3965(8)
C7	C10	1.5380(7)			

Table 5 Bond Angles for 8.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	O1	C9	114.88(4)	C12	C7	C10	119.15(4)
O1	C1	C2	111.06(4)	C9	C8	C7	116.30(4)
C6	C1	O1	122.98(5)	C9	C8	C10	121.98(5)
C6	C1	C2	125.92(5)	C10	C8	C7	61.25(3)
C1	C2	C3	111.72(5)	O1	C9	C8	112.20(4)
C2	C3	C4	109.88(5)	C8	C10	C7	59.67(3)
C3	C4	C5	111.45(5)	C8	C10	C11	119.36(5)
C6	C5	C4	113.14(5)	C11	C10	C7	122.02(5)
C1	C6	C5	120.26(5)	C13	C12	C7	120.41(5)
C1	C6	C7	120.21(4)	C17	C12	C7	121.04(5)
C7	C6	C5	119.49(4)	C17	C12	C13	118.49(5)
C6	C7	C8	114.07(4)	C14	C13	C12	121.05(5)
C6	C7	C10	116.18(4)	C13	C14	C15	120.08(6)
C8	C7	C10	59.08(3)	C16	C15	C14	119.46(5)
C12	C7	C6	116.44(4)	C15	C16	C17	120.32(6)
C12	C7	C8	119.61(4)	C12	C17	C16	120.58(6)

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 8.

Atom	***x***	***y***	***z***	**U(eq)**
H2A	1657	3092	5045	23
H2B	1362	2481	6808	23
H3A	1401	929	4388	27
H3B	1824	424	6164	27
H4A	2648	1596	3390	29
H4B	2650	53	3797	29
H5A	3417	309	6288	20
H5B	3817	1256	4934	20
H8	4329	4565	8964	17
H9A	2998	5456	9097	20
H9B	3207	5253	7120	20
H10	3255	2567	10223	18
H11A	4946	2888	10872	31
H11B	4482	1617	11493	31
H11C	4317	3020	12338	31
H13	4757	499	8581	19
H14	5968	-199	7613	23
H15	6685	1162	5815	26
H16	6192	3244	5054	27
H17	4987	3957	6060	22


C11
O1
C9
C8
C10
C2
C1
C7
C12
C13
C6
C14
C3
C5
C17
C15
C16
C4

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Spectra Compilation

C–C Bond Migration in the Cycloisomerization of 1,6-Enynes

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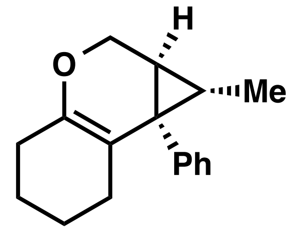
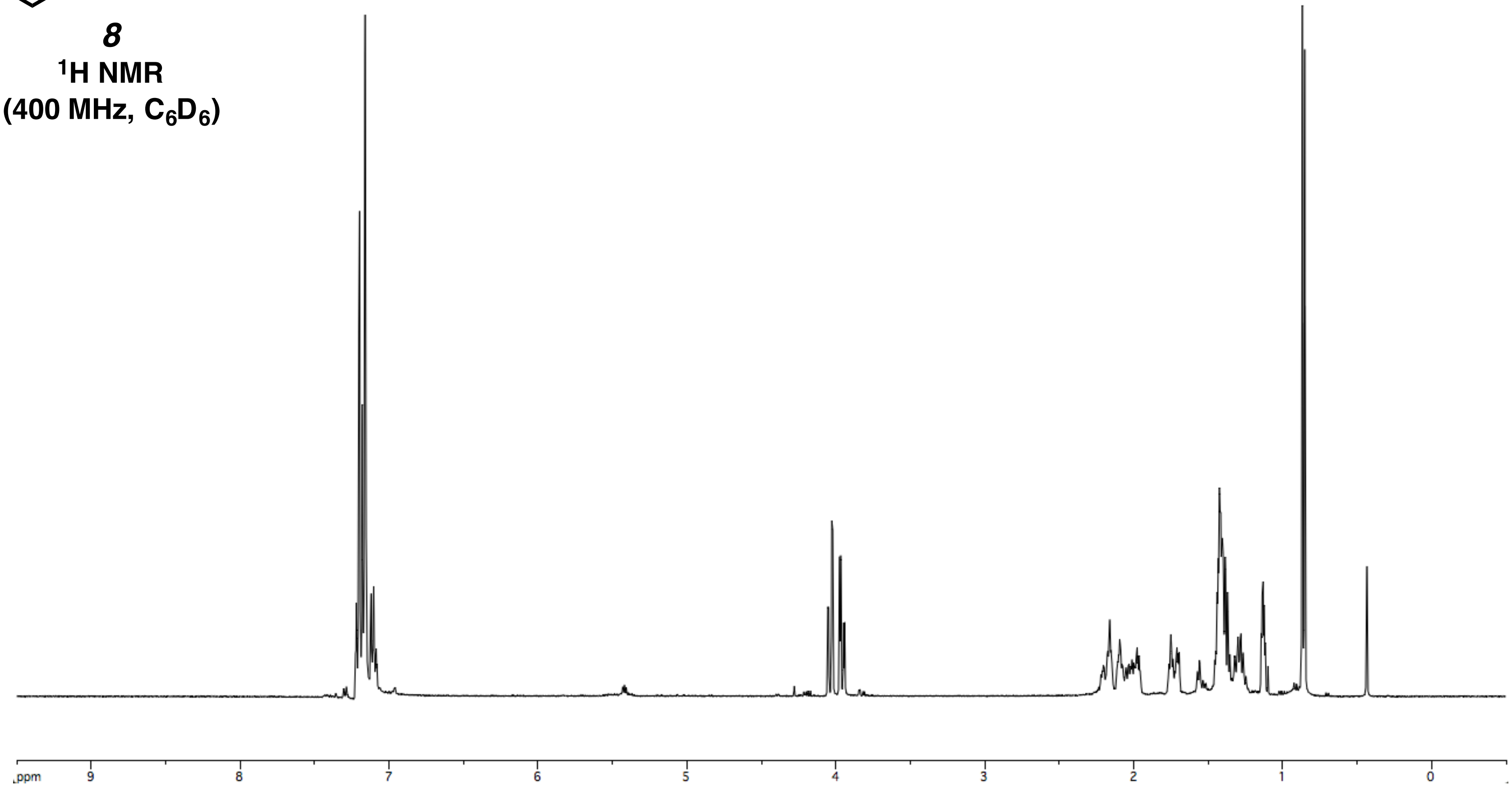
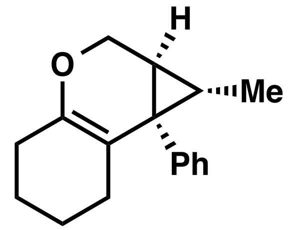


8

^{1}H NMR

(400 MHz, C_6D_6)

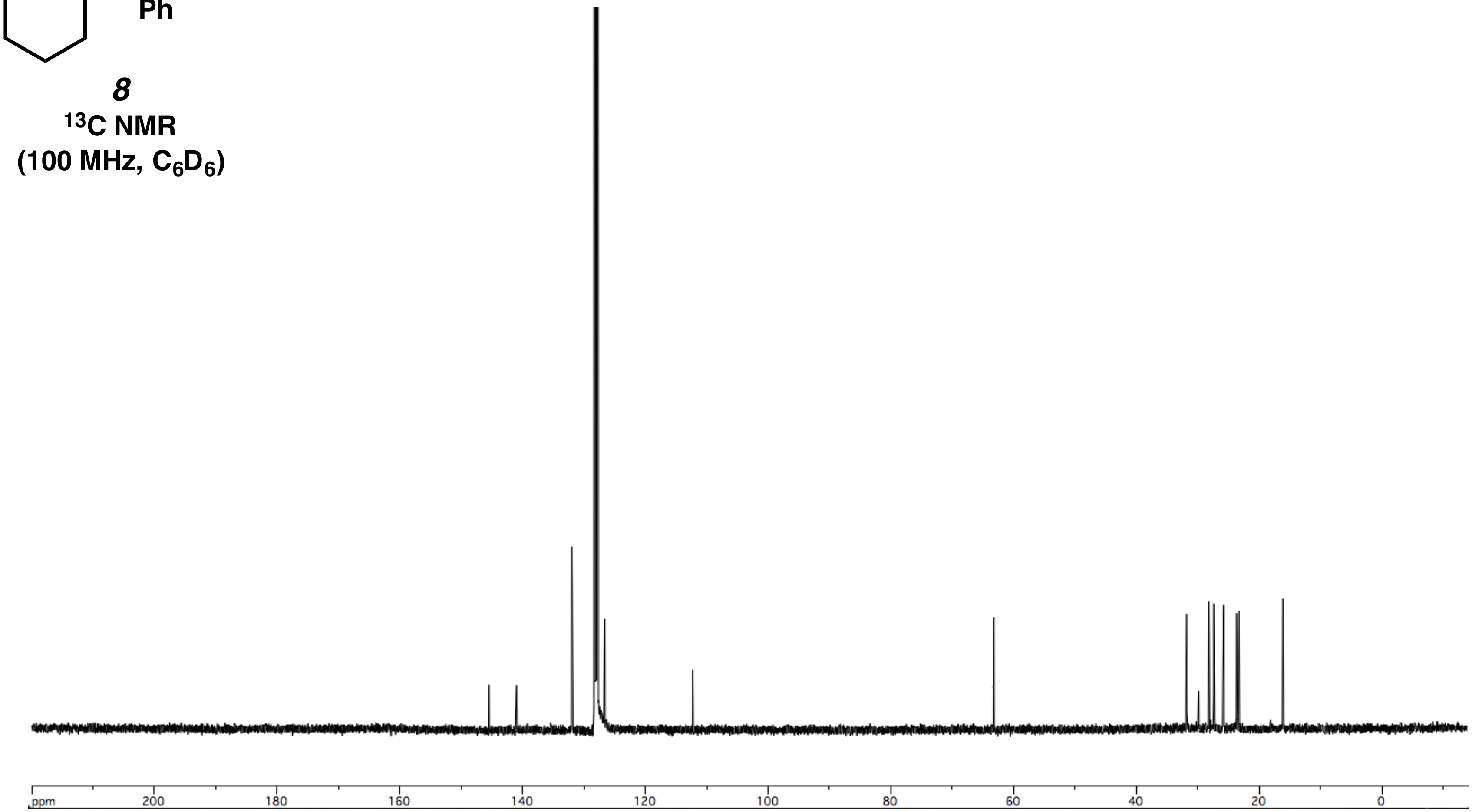


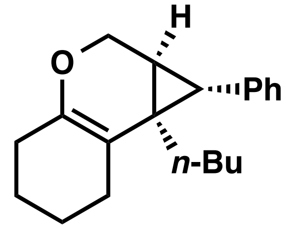


8

^{13}C NMR

(100 MHz, C_6D_6)

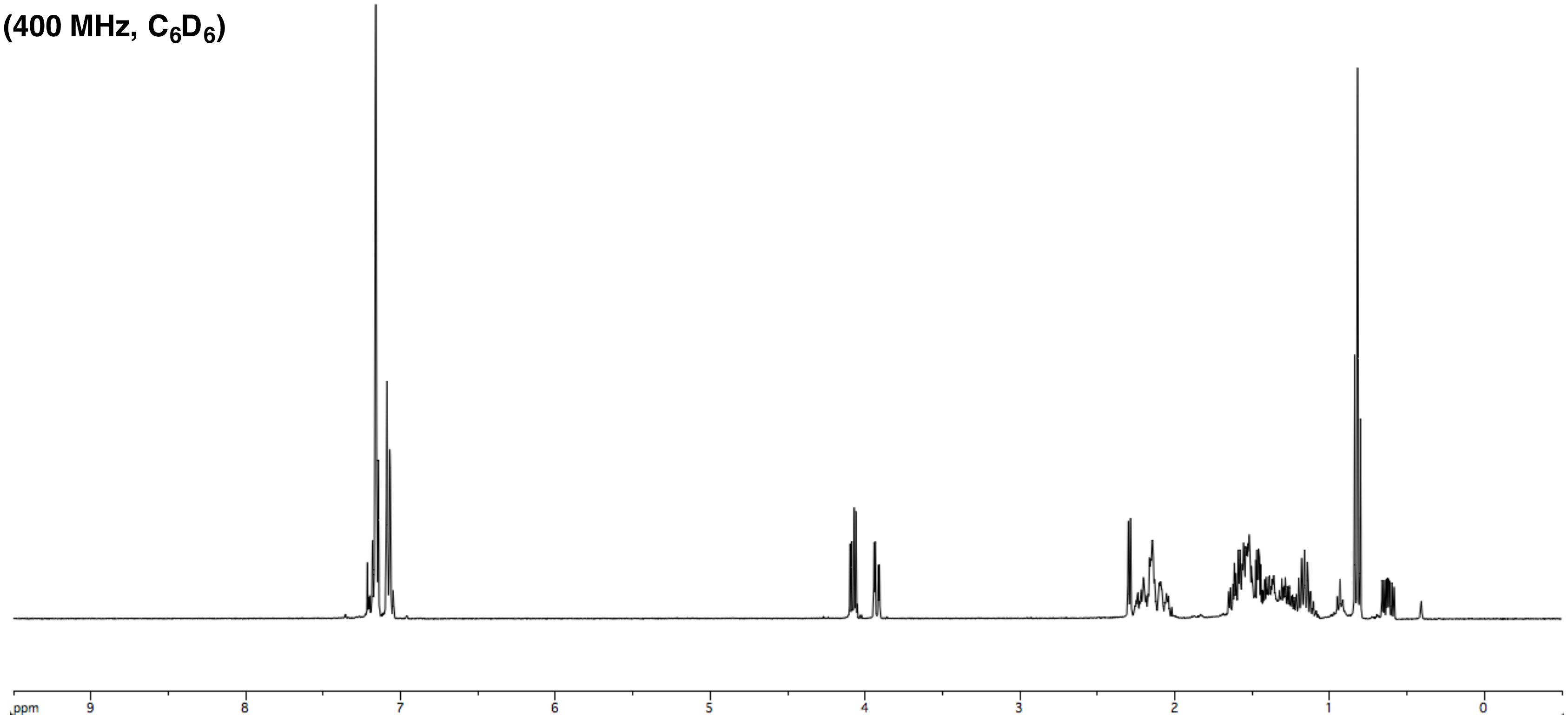


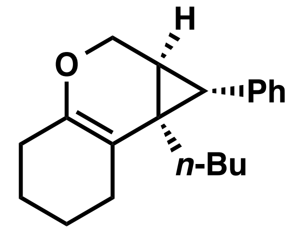


16

^{1}H NMR

(400 MHz, C_6D_6)

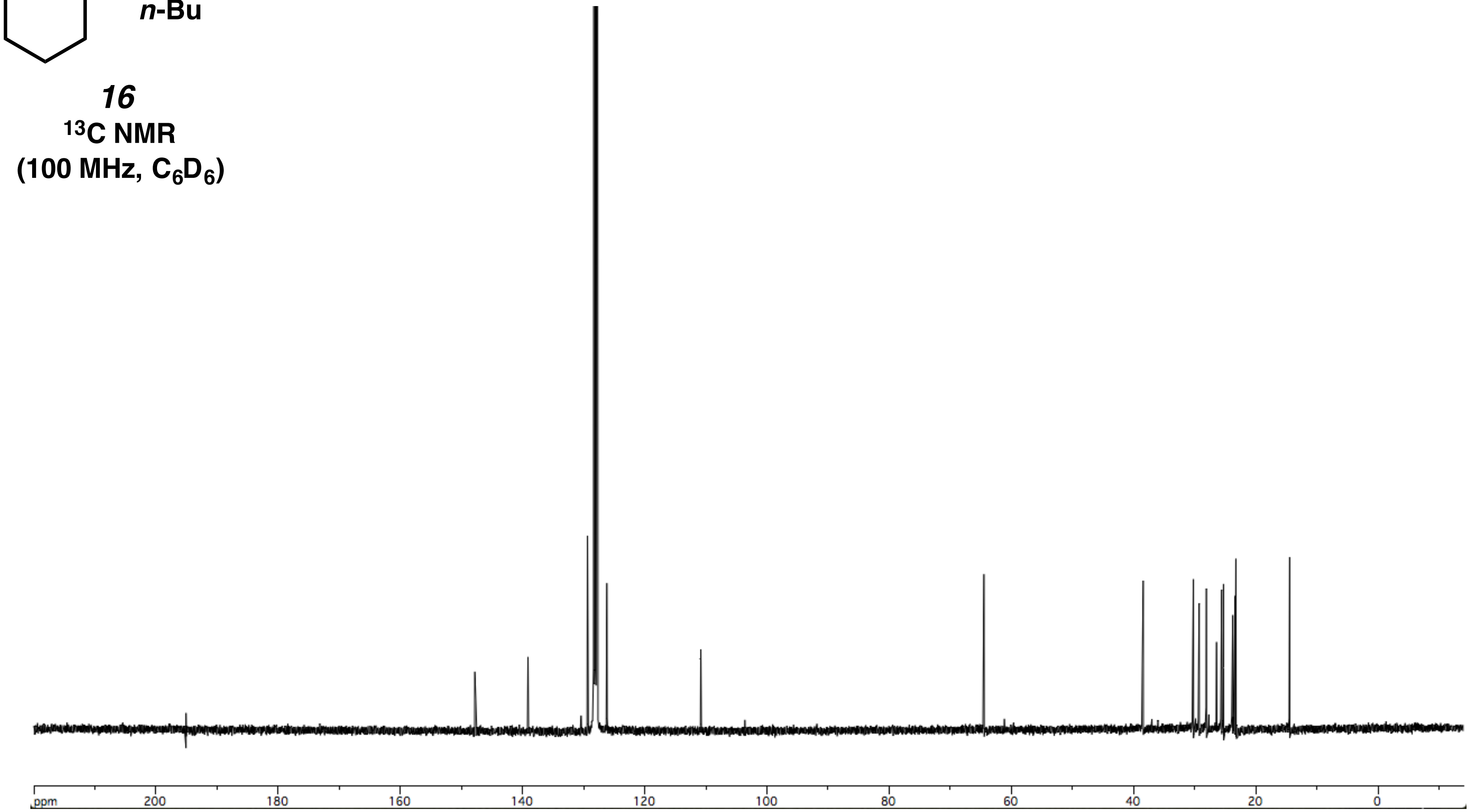


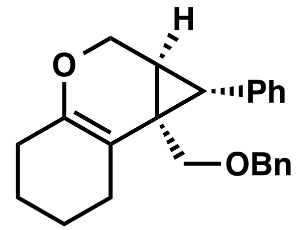


16

^{13}C NMR

(100 MHz, C_6D_6)

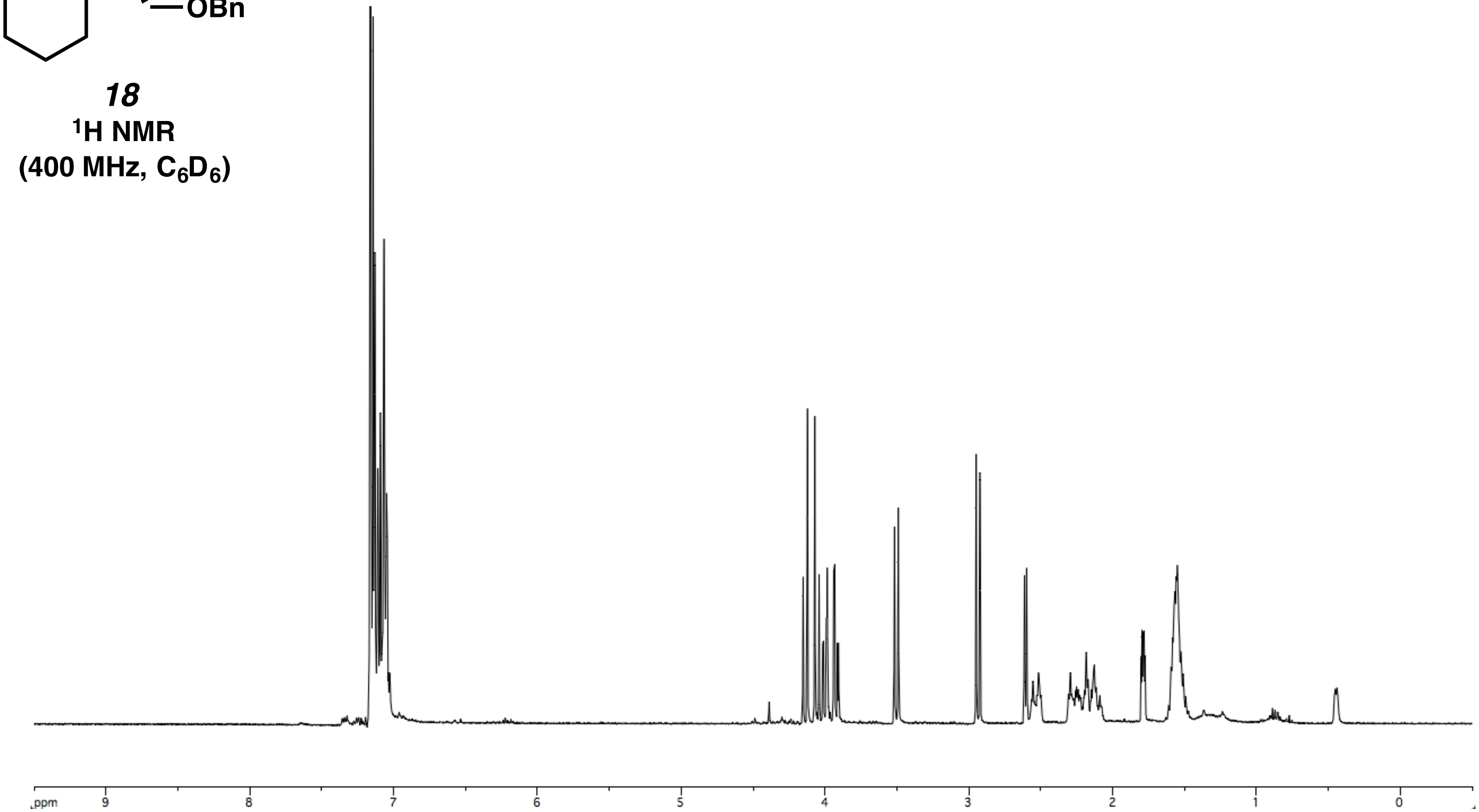


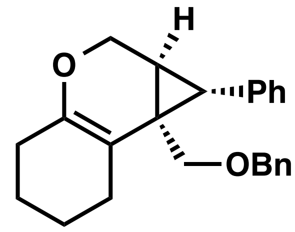


18

^{1}H NMR

(400 MHz, C_6D_6)

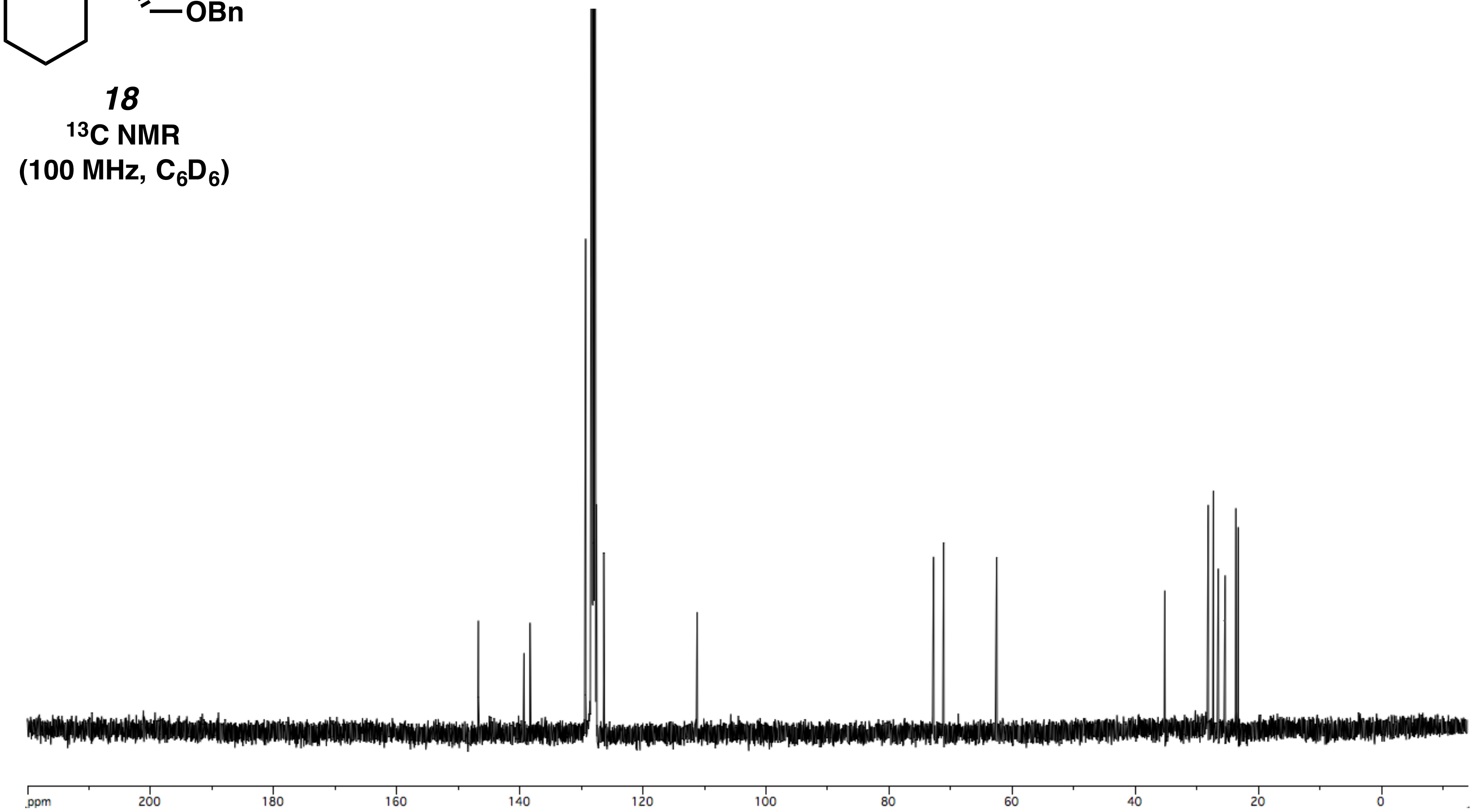


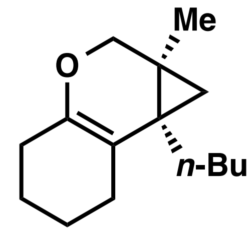


18

^{13}C NMR

(100 MHz, C_6D_6)

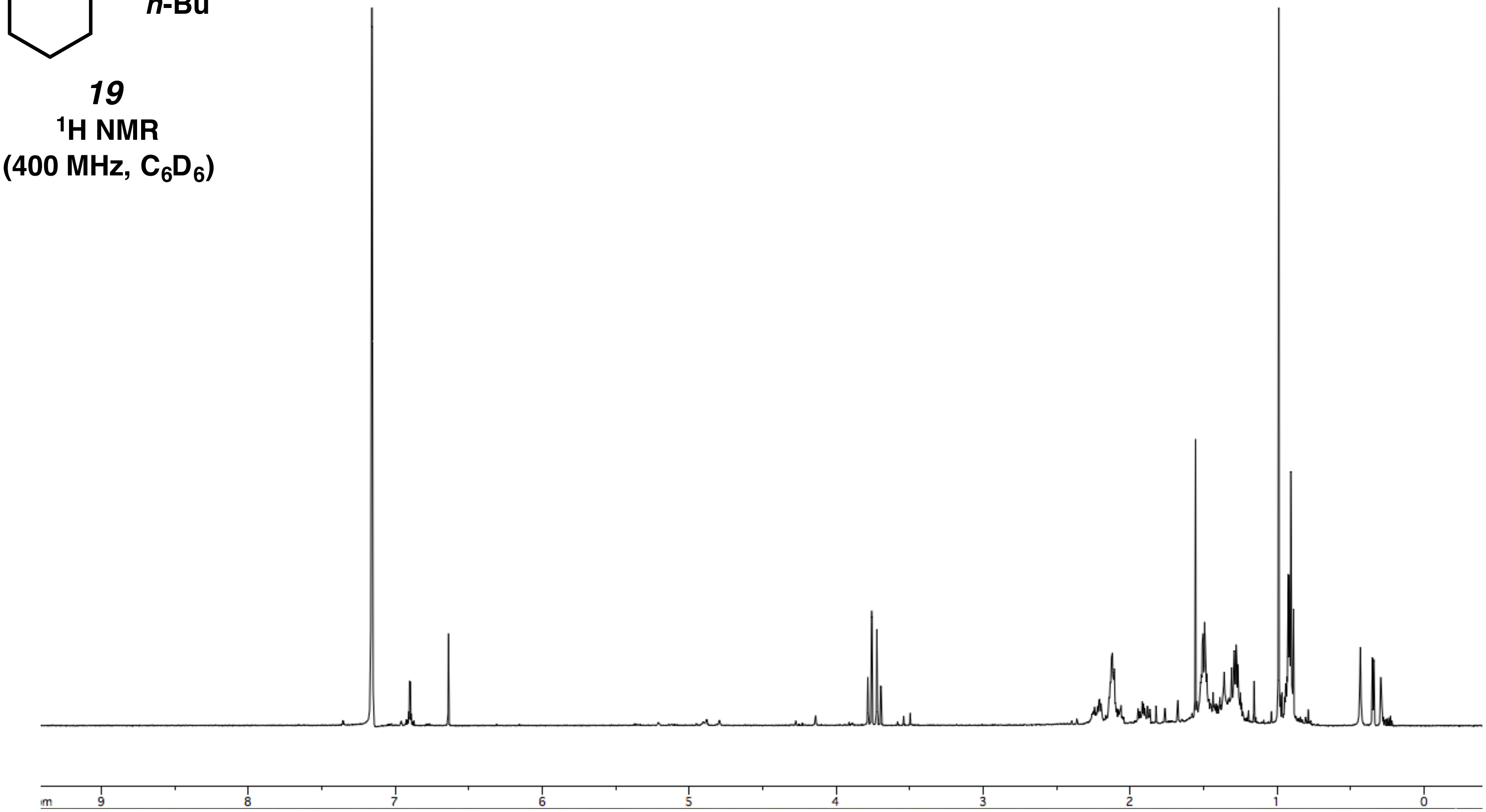


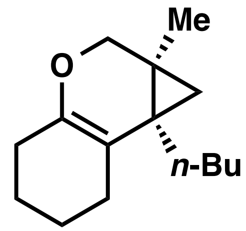


19

^{1}H NMR

(400 MHz, C_6D_6)

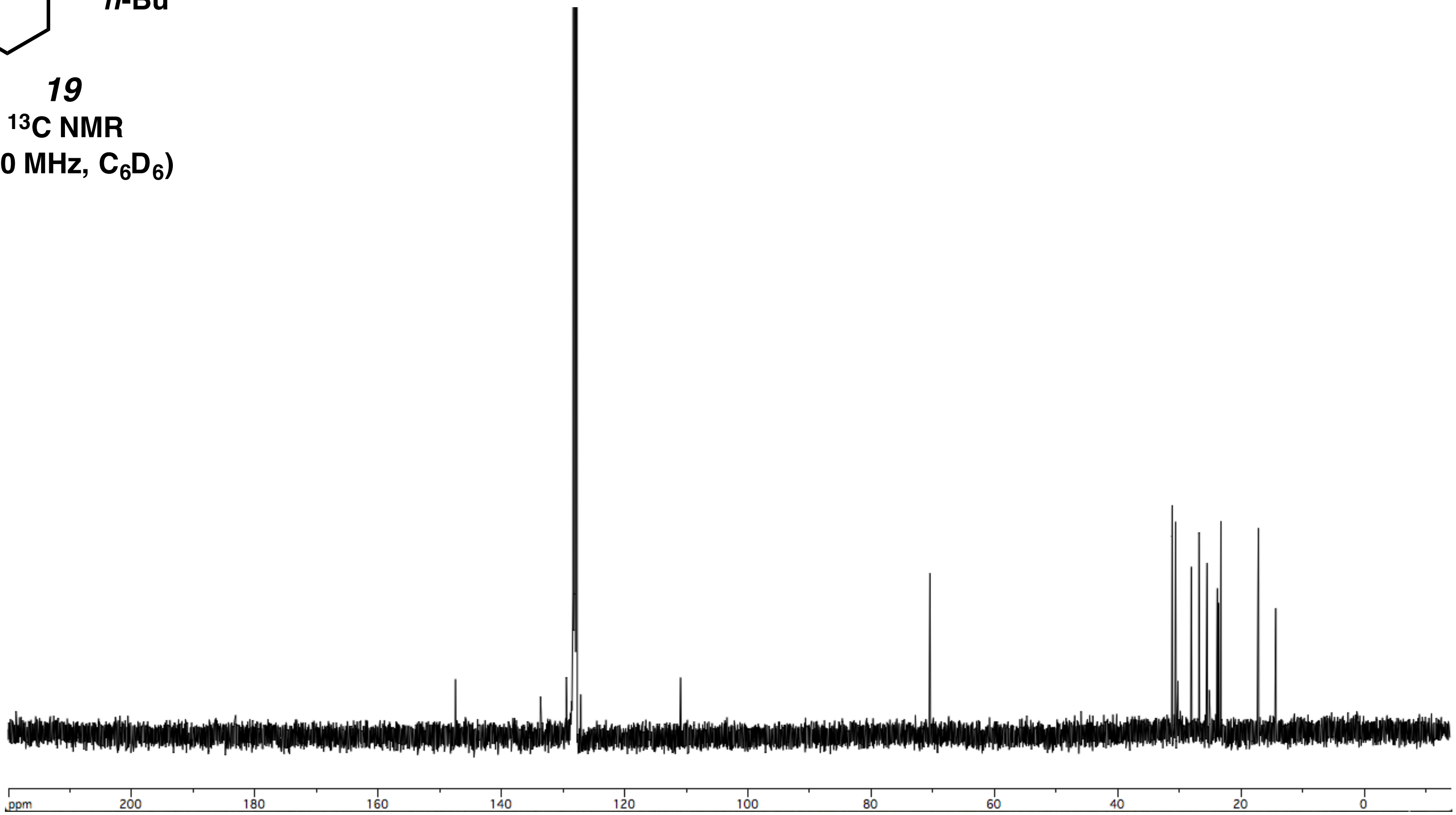


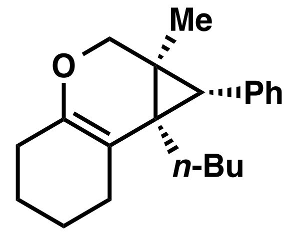


19

^{13}C NMR

(100 MHz, C_6D_6)

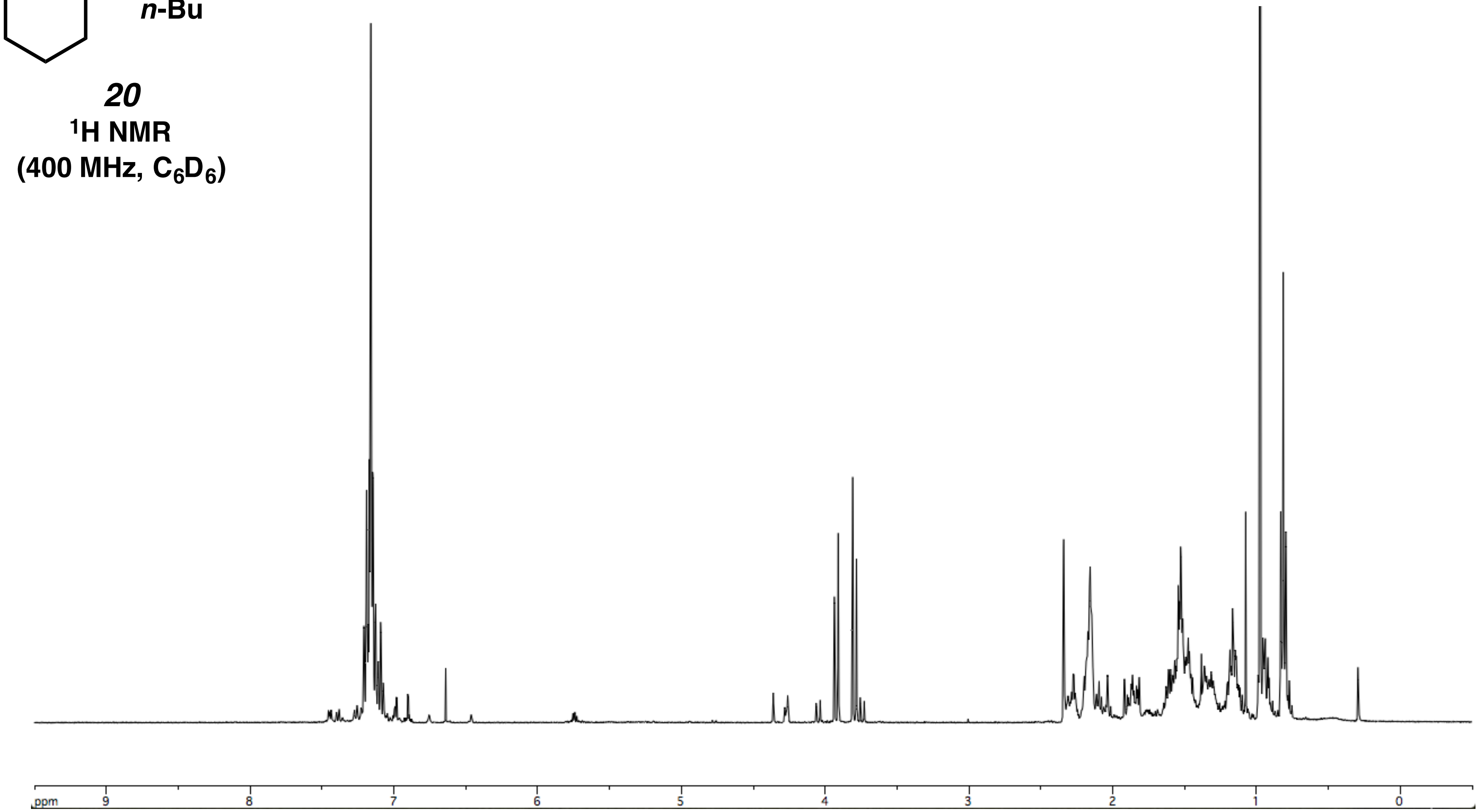


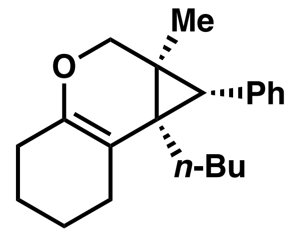


20

^{1}H NMR

(400 MHz, C_6D_6)





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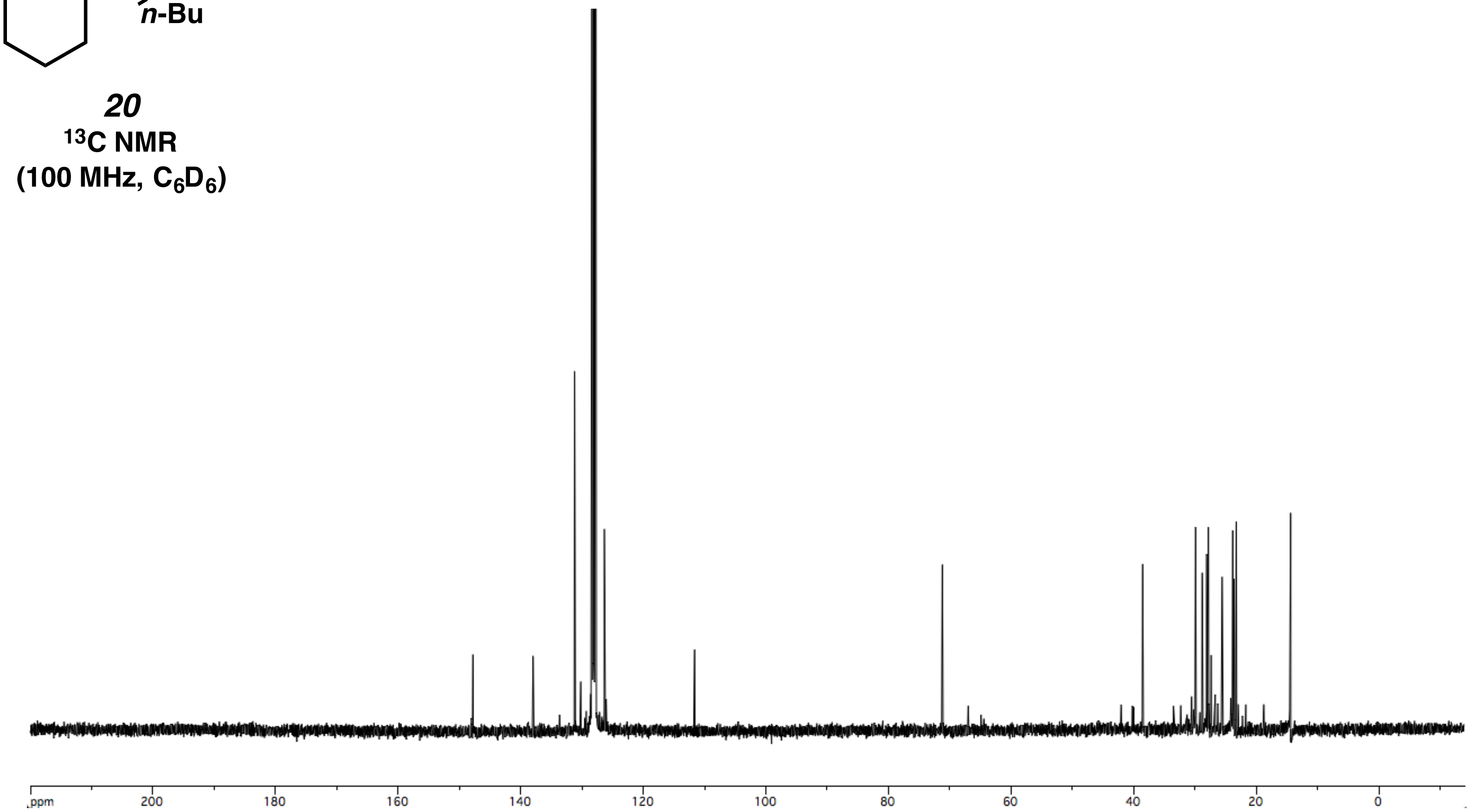
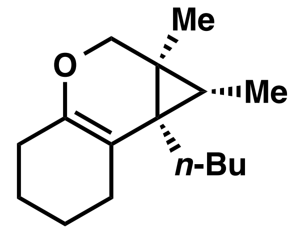
(100 MHz, C_6D_6)





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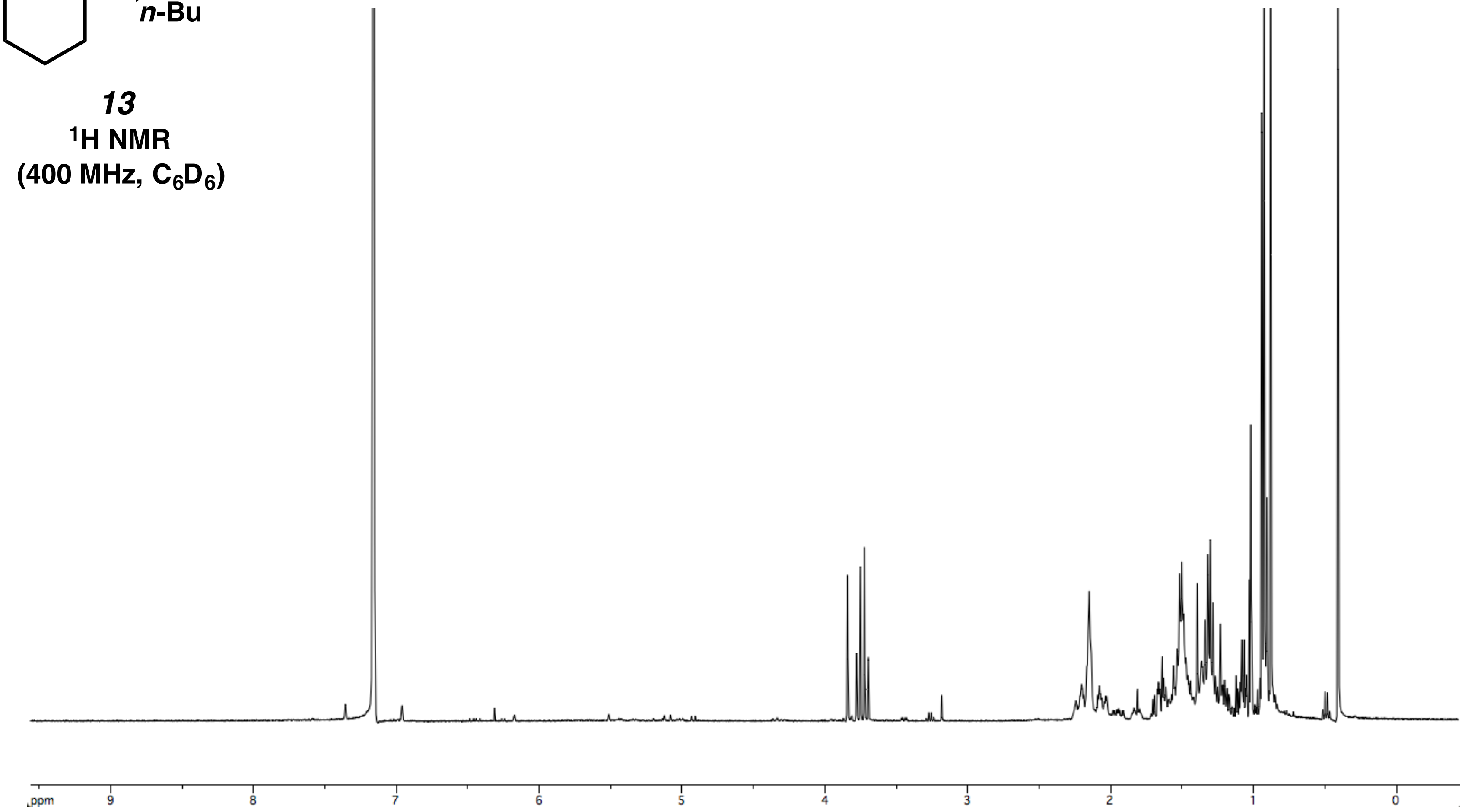
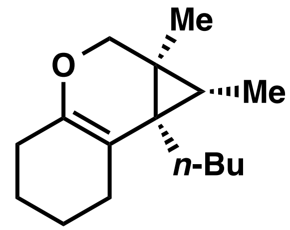
^{1}H NMR

(400 MHz, C_6D_6)





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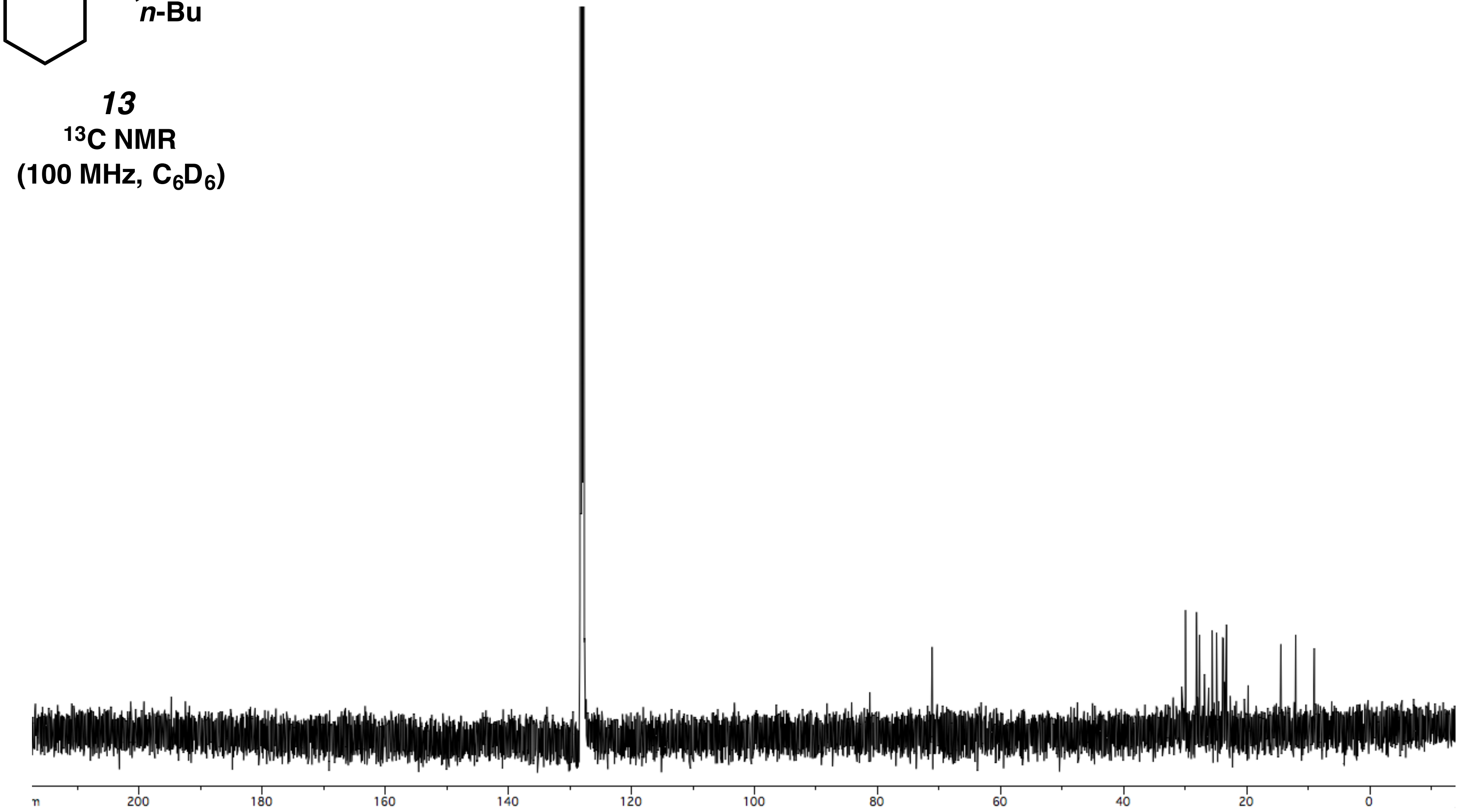
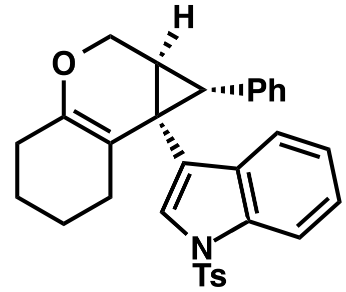
^{13}C NMR

(100 MHz, C_6D_6)

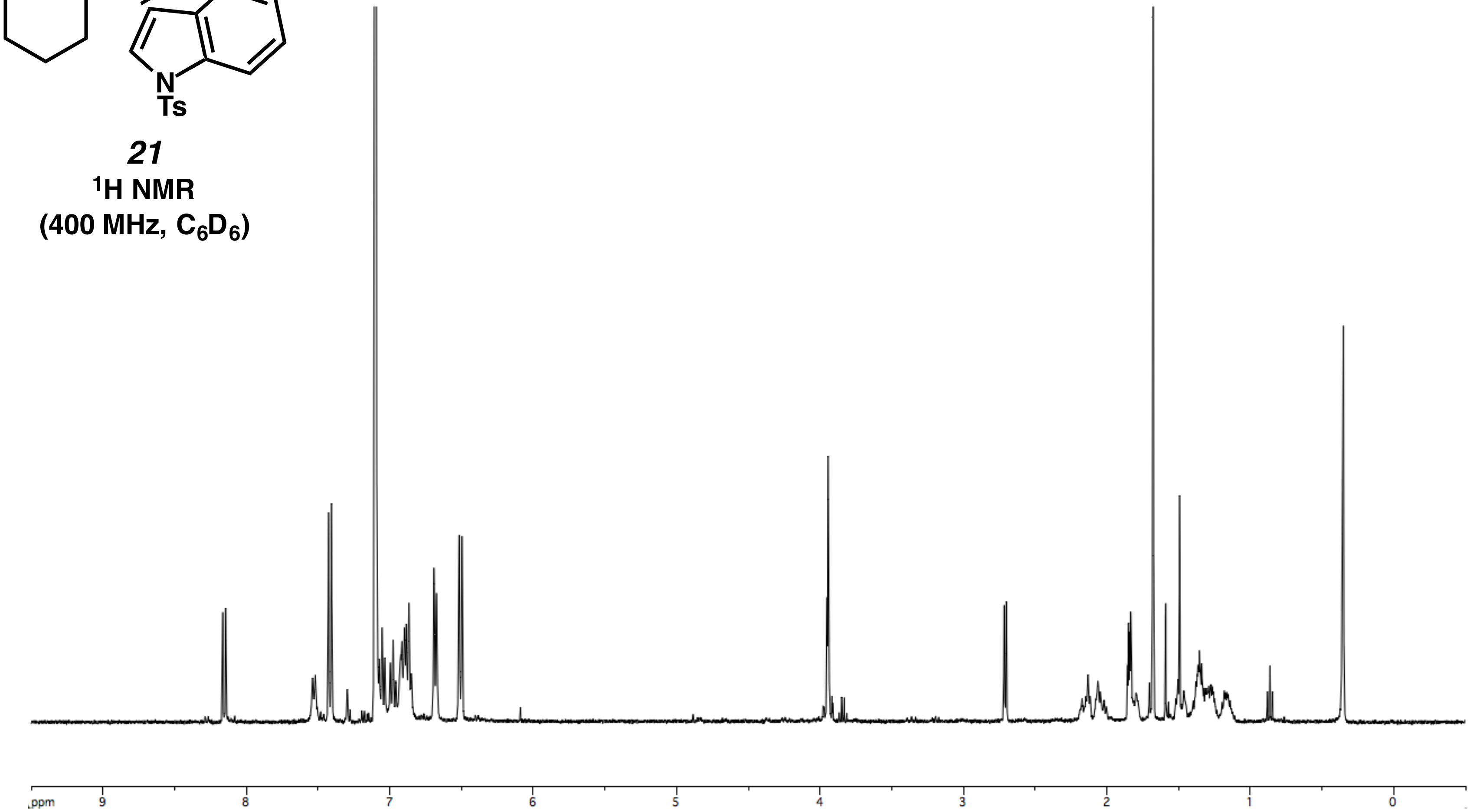


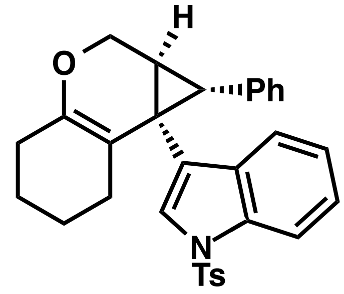


21

^{1}H NMR

(400 MHz, C_6D_6)





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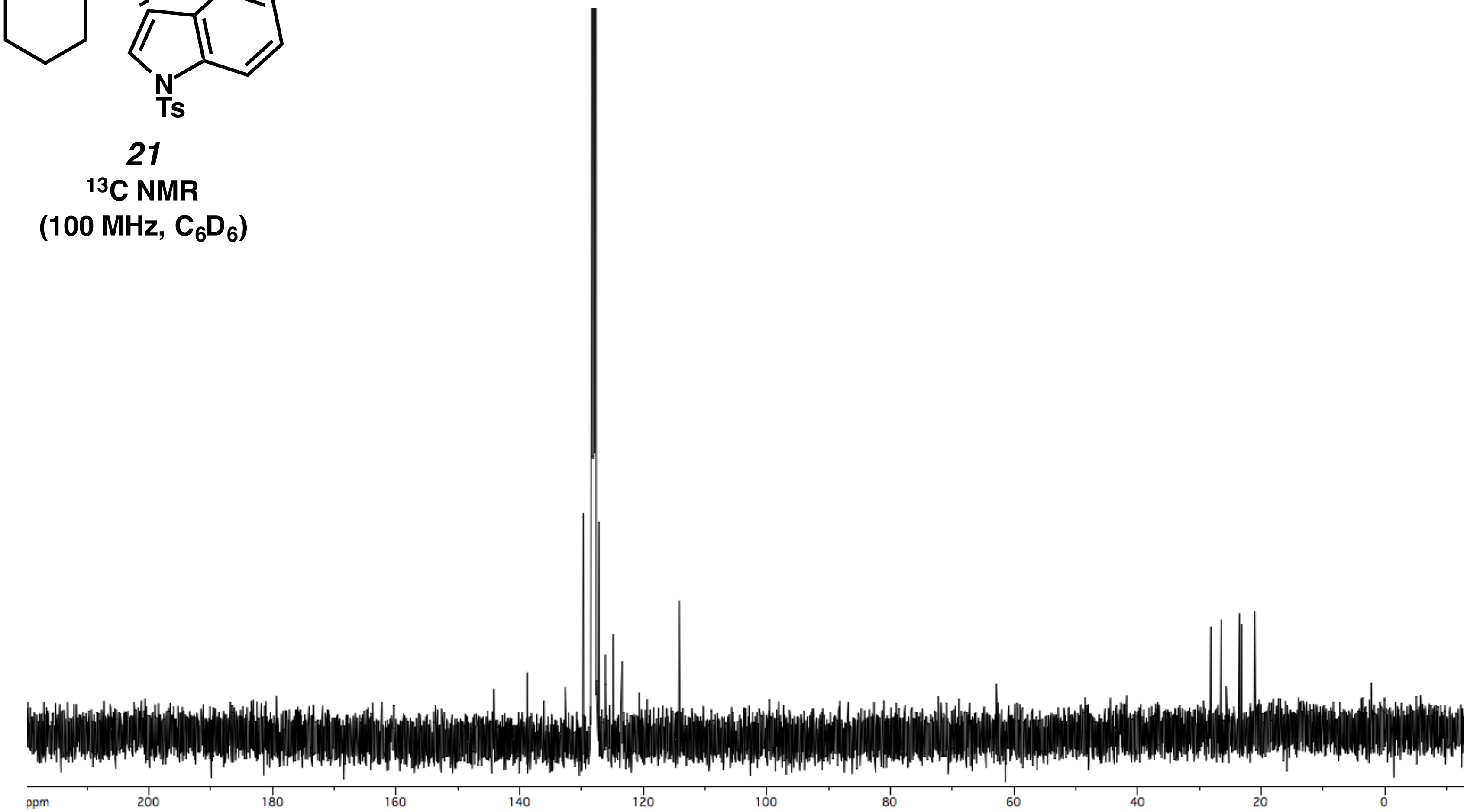
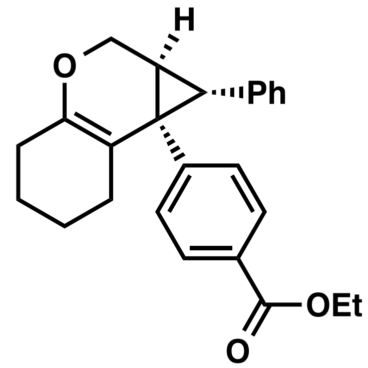
^{13}C NMR

(100 MHz, C_6D_6)

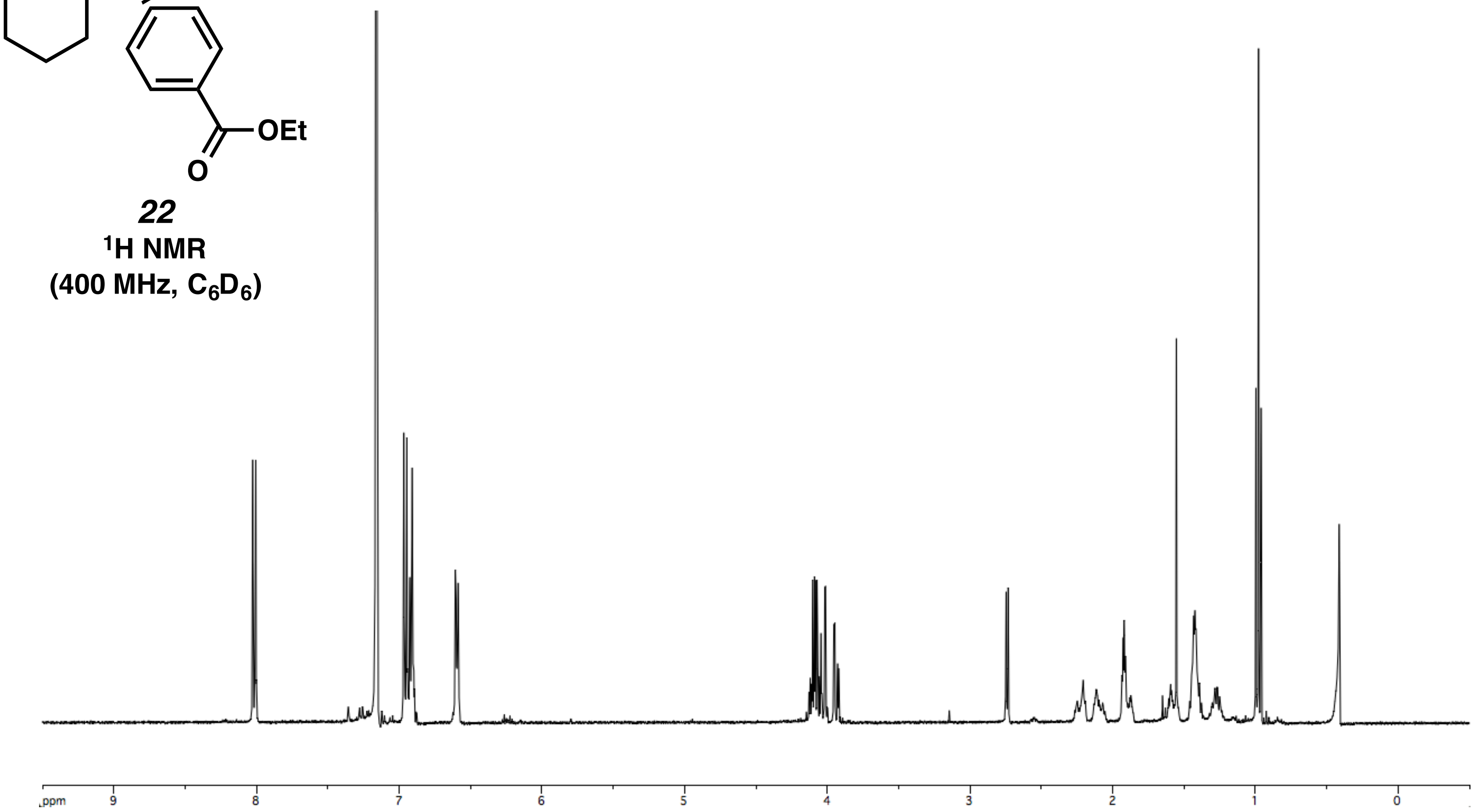


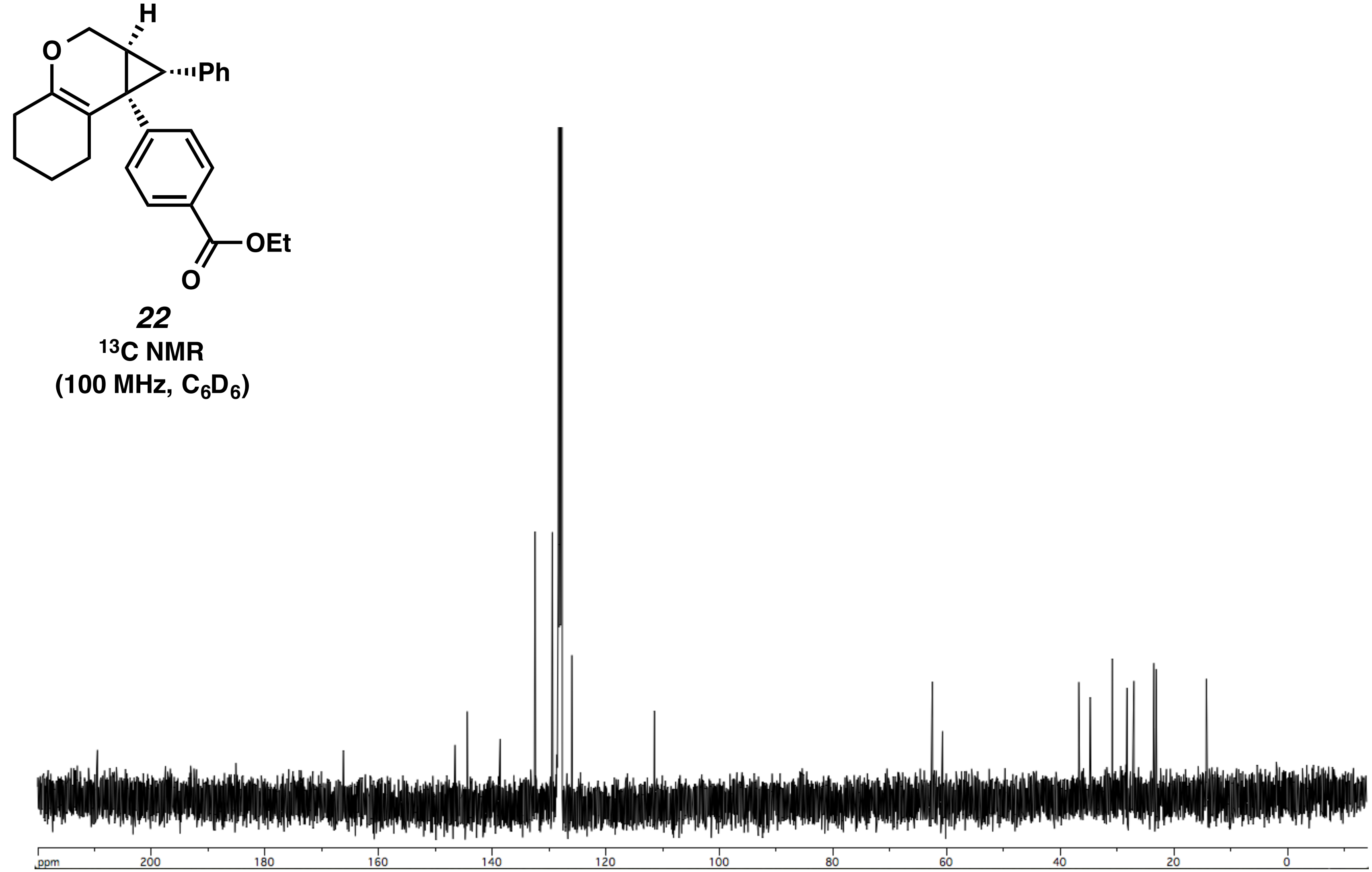


22

^{1}H NMR

(400 MHz, C_6D_6)





22

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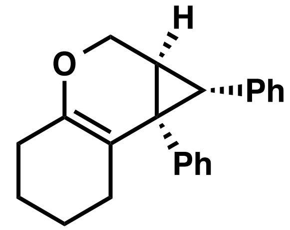
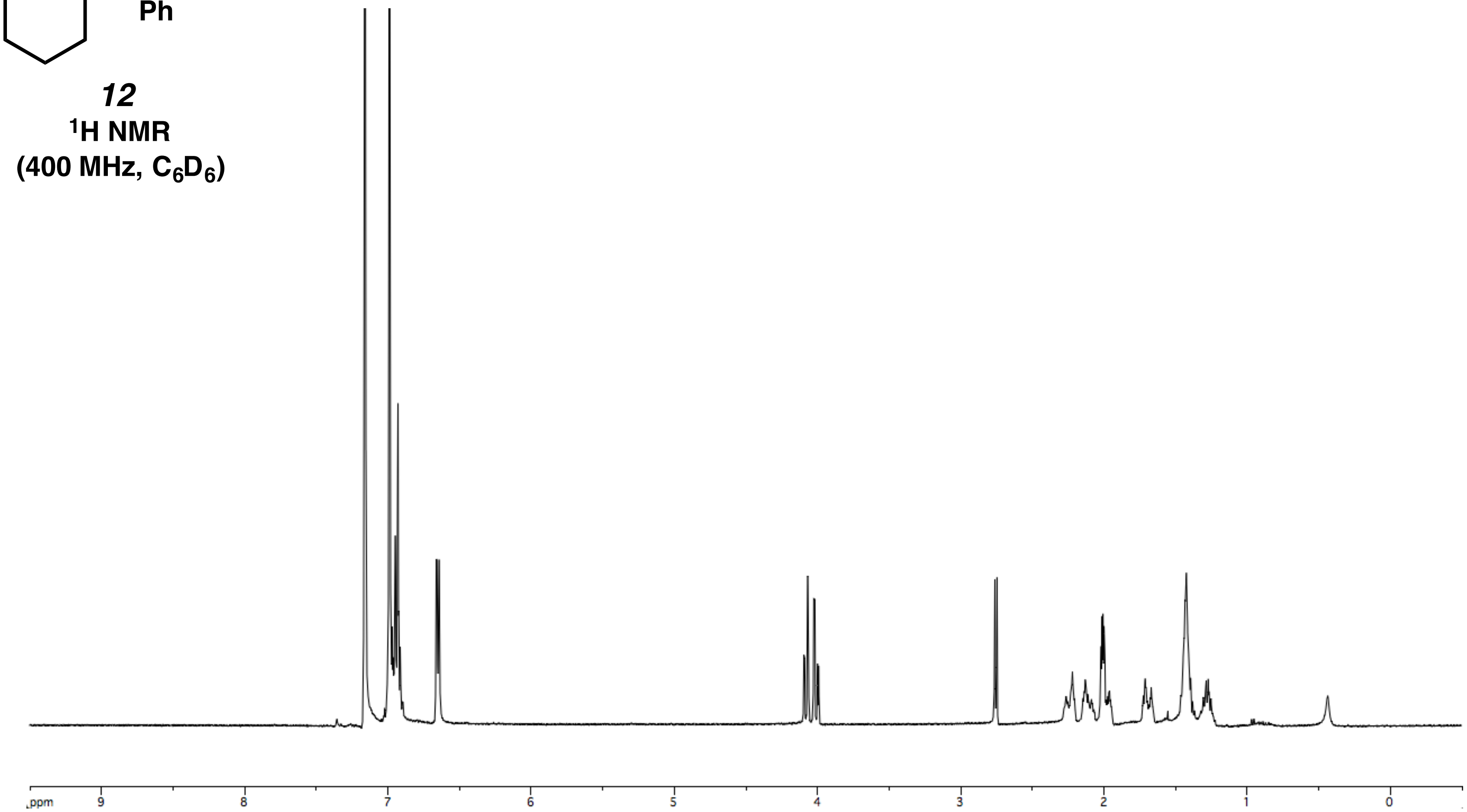
(100 MHz, C_6D_6)

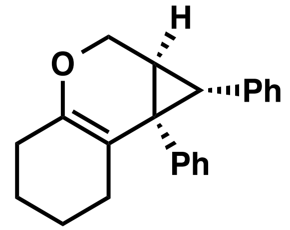


12

^{1}H NMR

(400 MHz, C_6D_6)

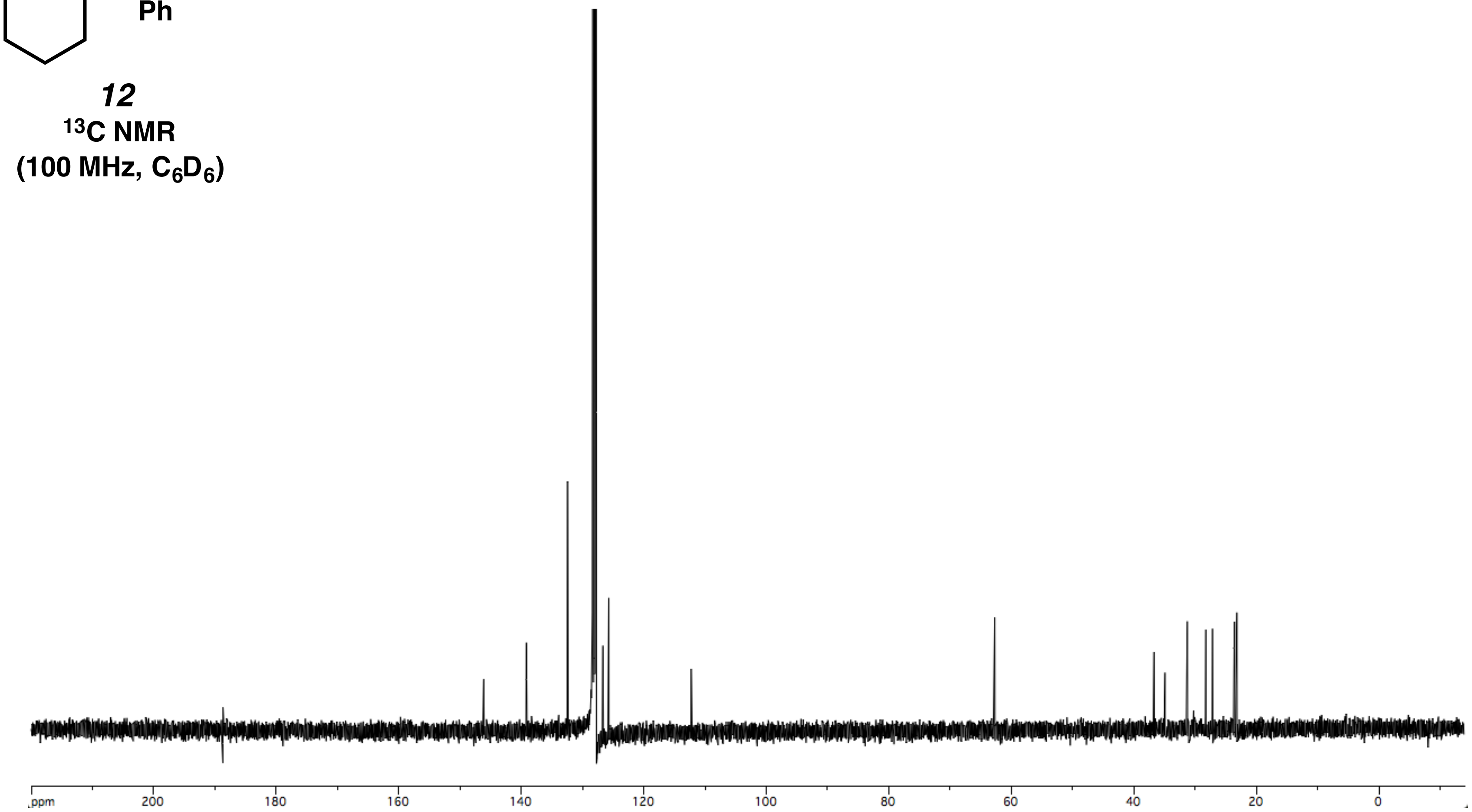


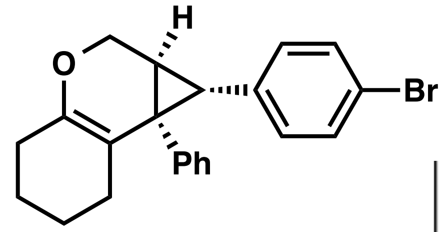


12

^{13}C NMR

(100 MHz, C_6D_6)

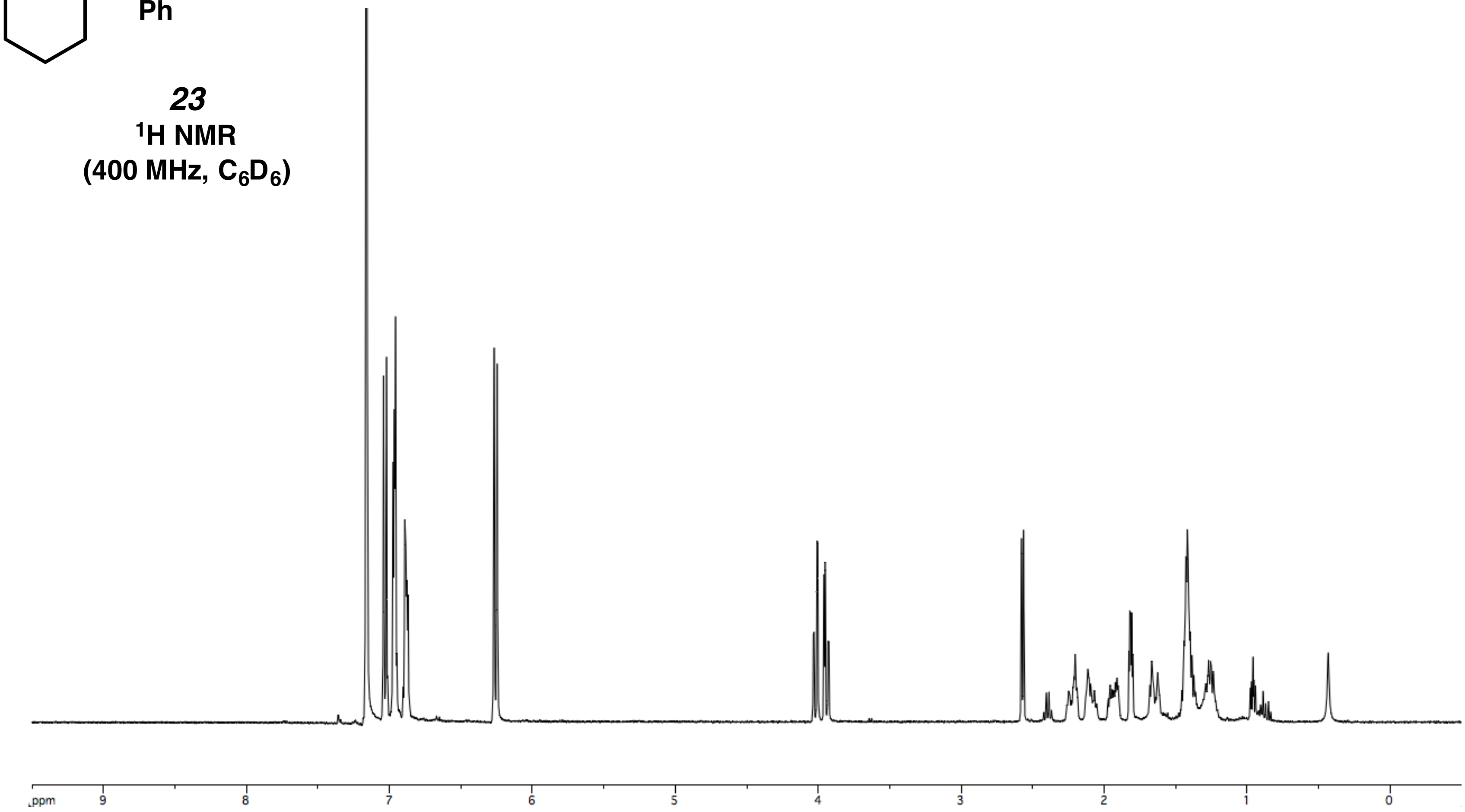


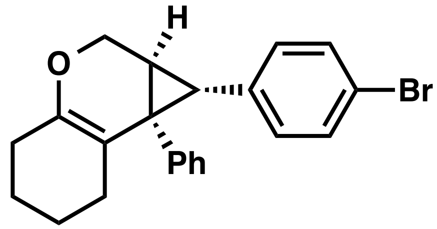


23

^{1}H NMR

(400 MHz, C_6D_6)





23

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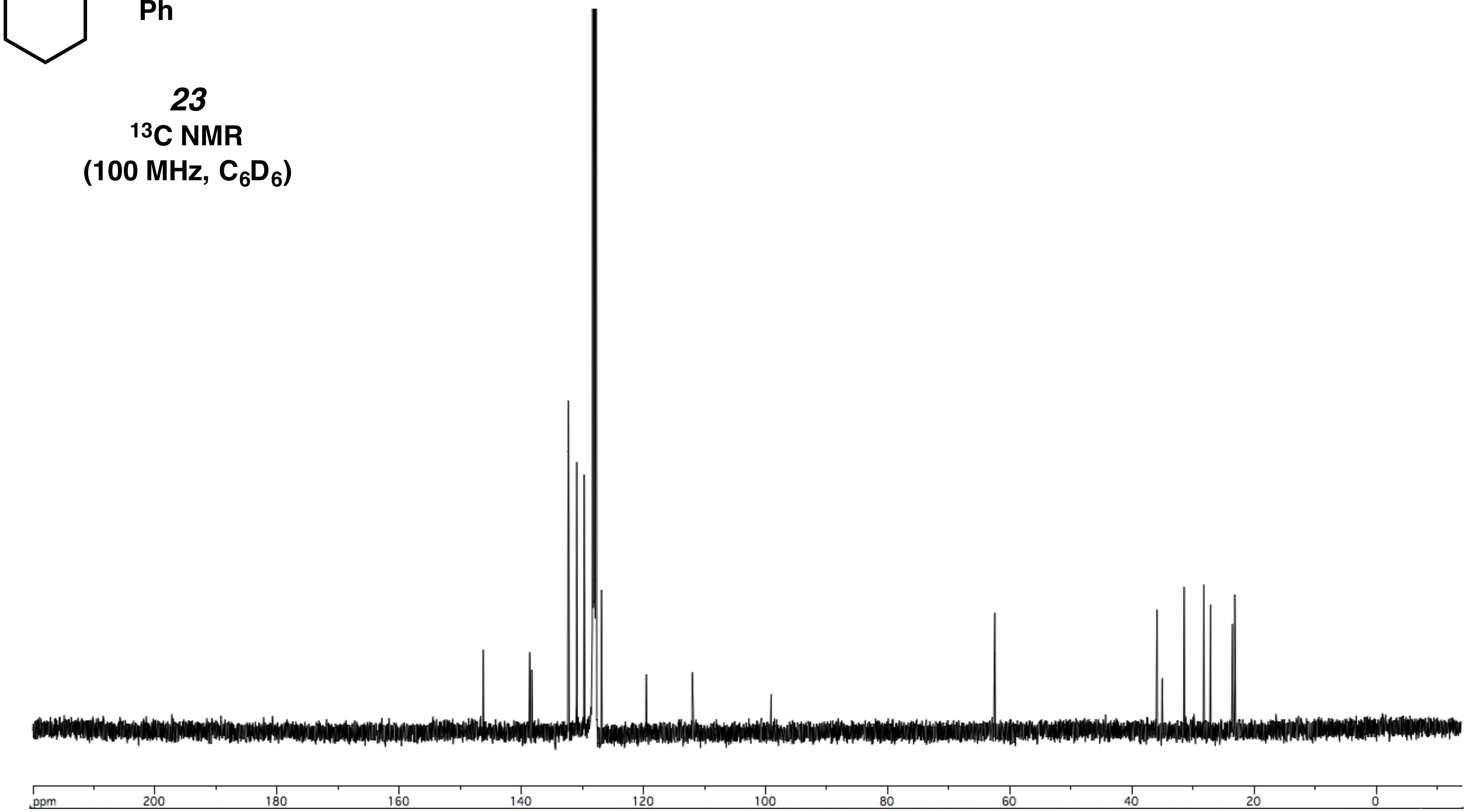
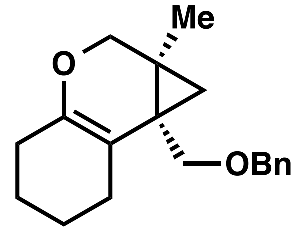
(100 MHz, C_6D_6)

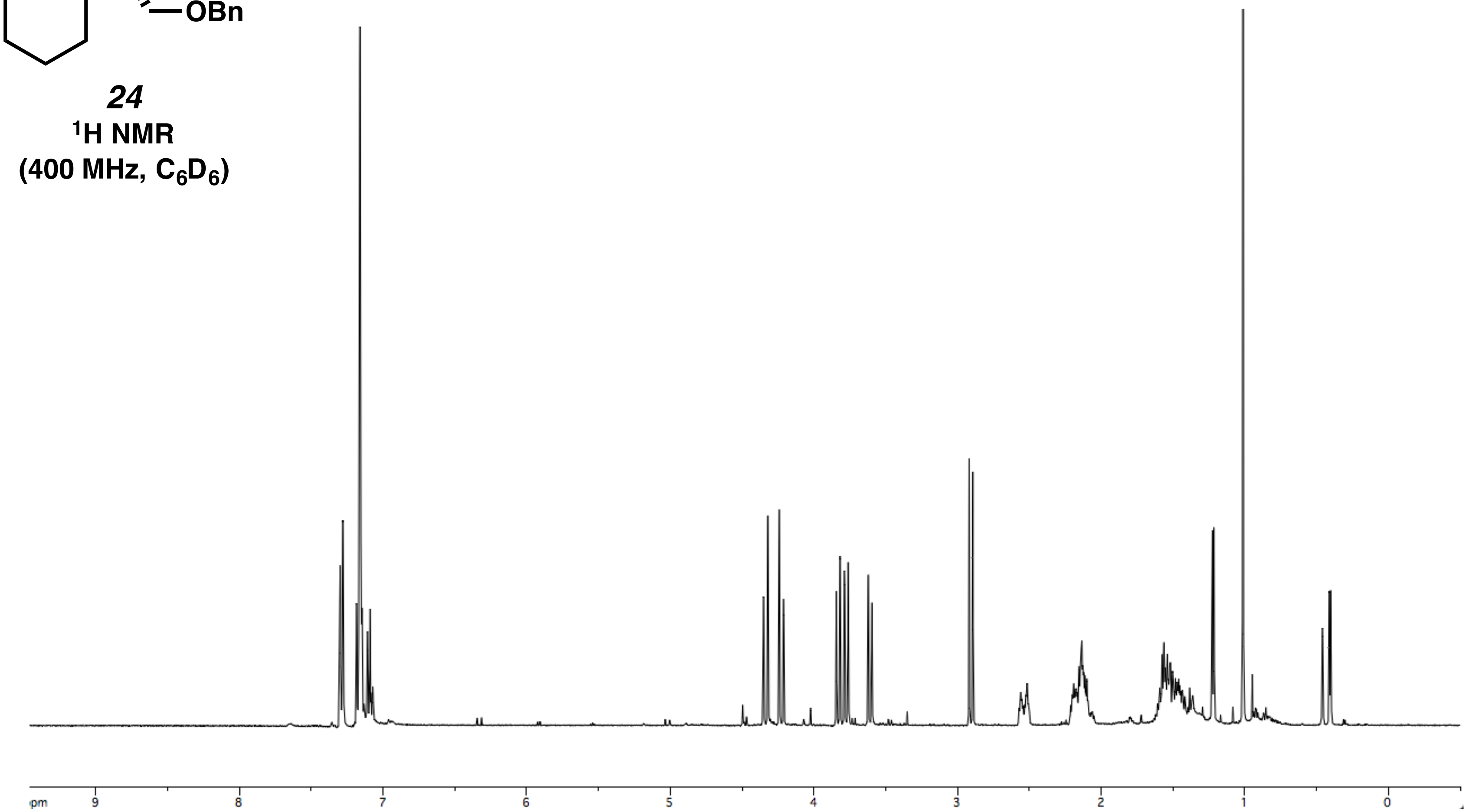


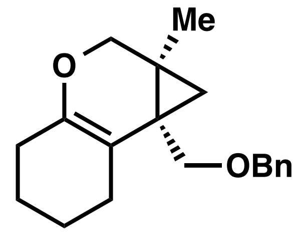


24

^{1}H NMR

(400 MHz, C_6D_6)





24

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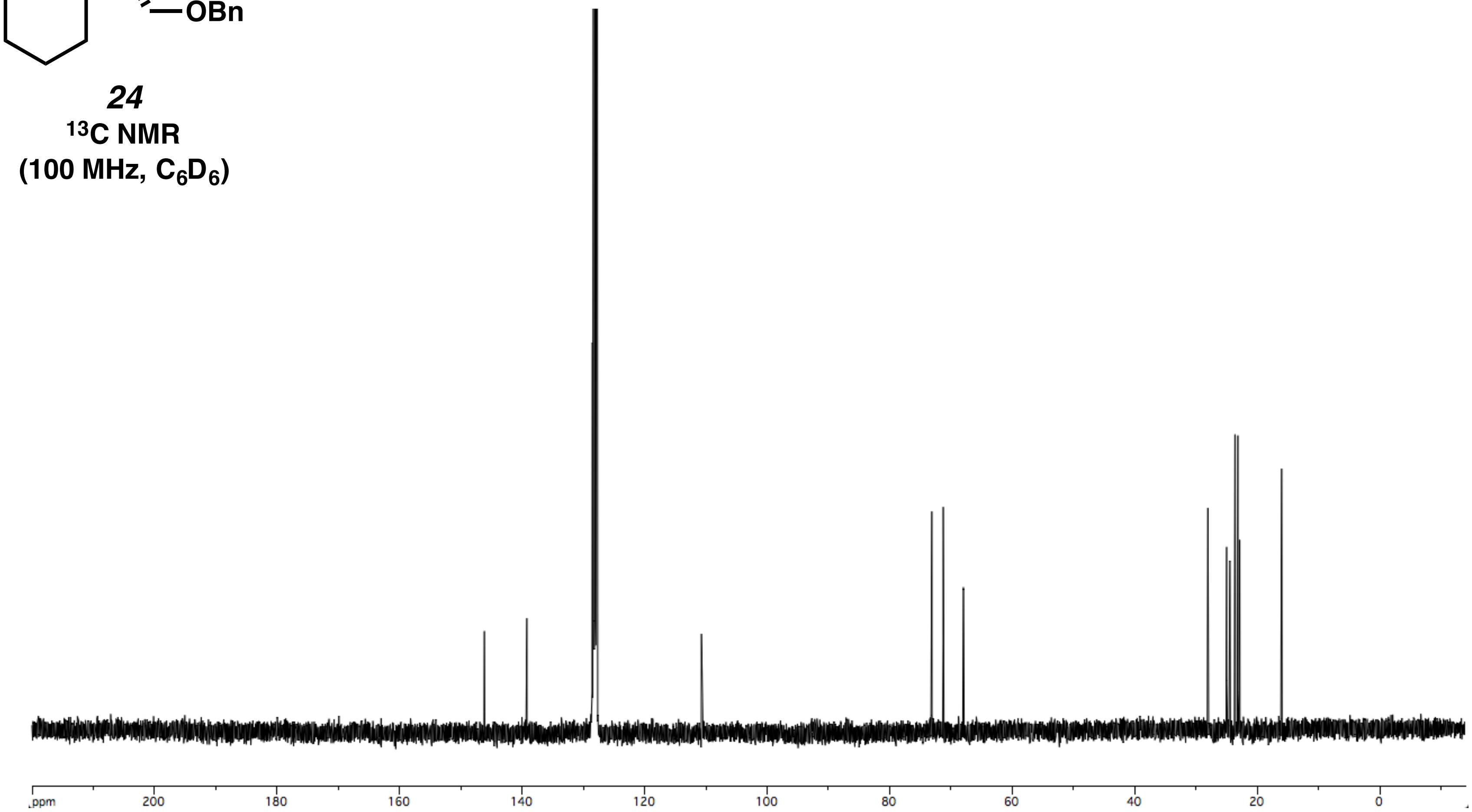
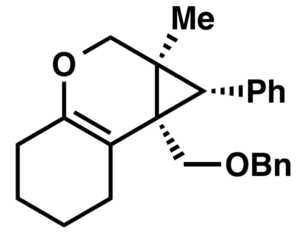
(100 MHz, C_6D_6)

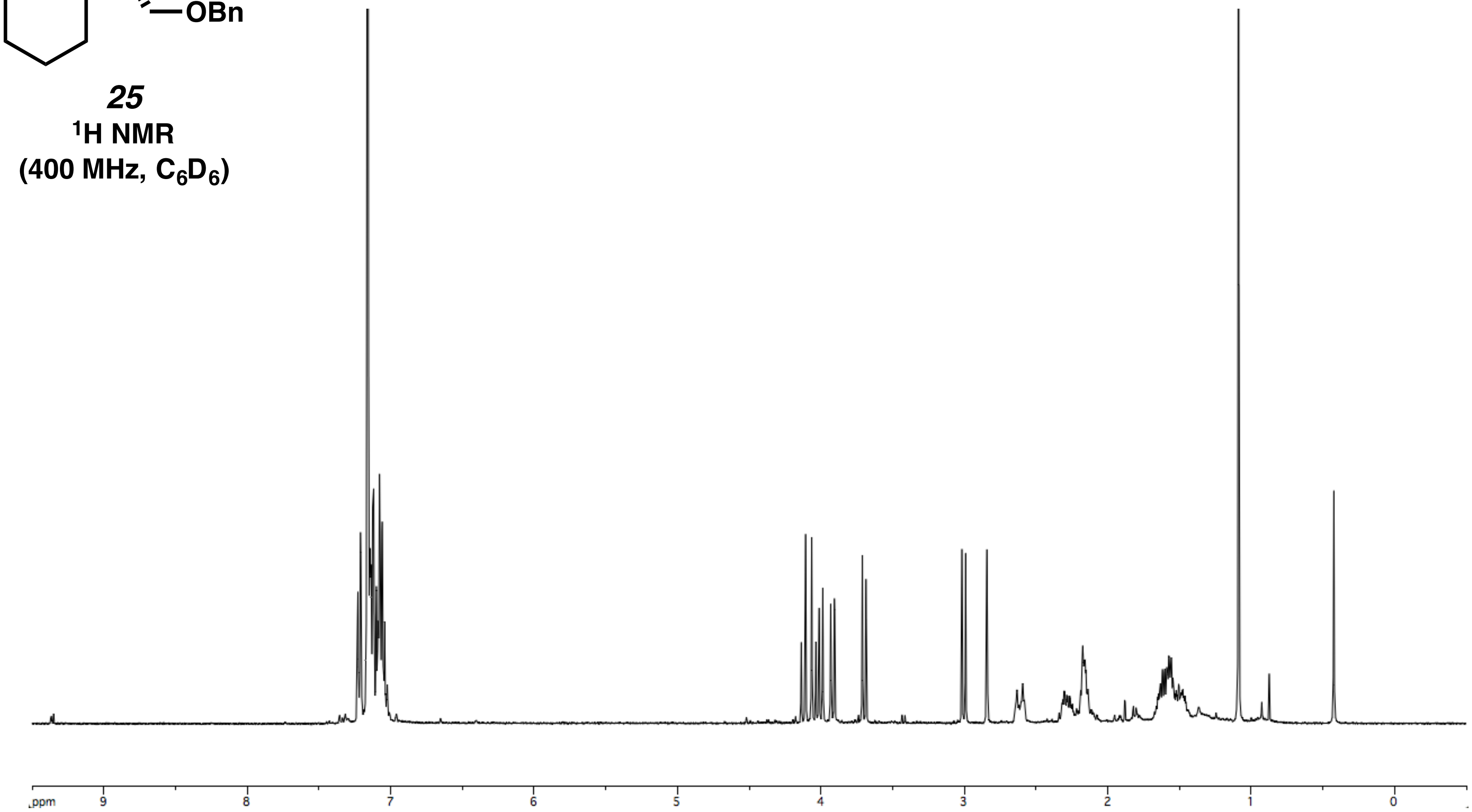


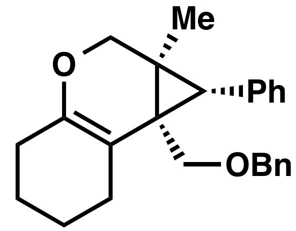


25

^{1}H NMR

(400 MHz, C_6D_6)





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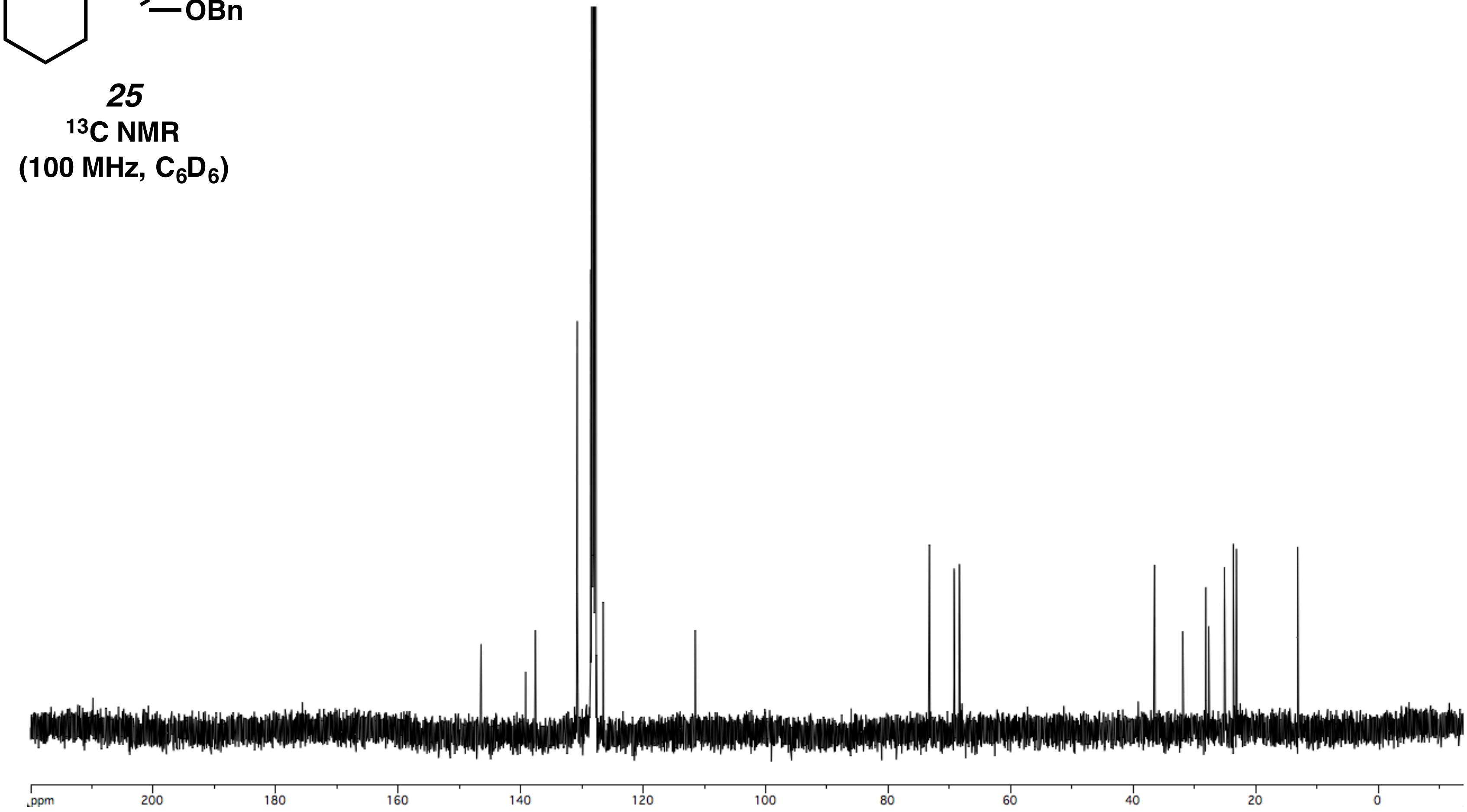
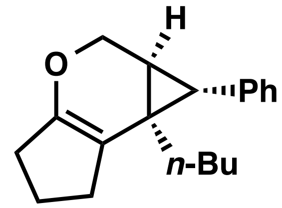
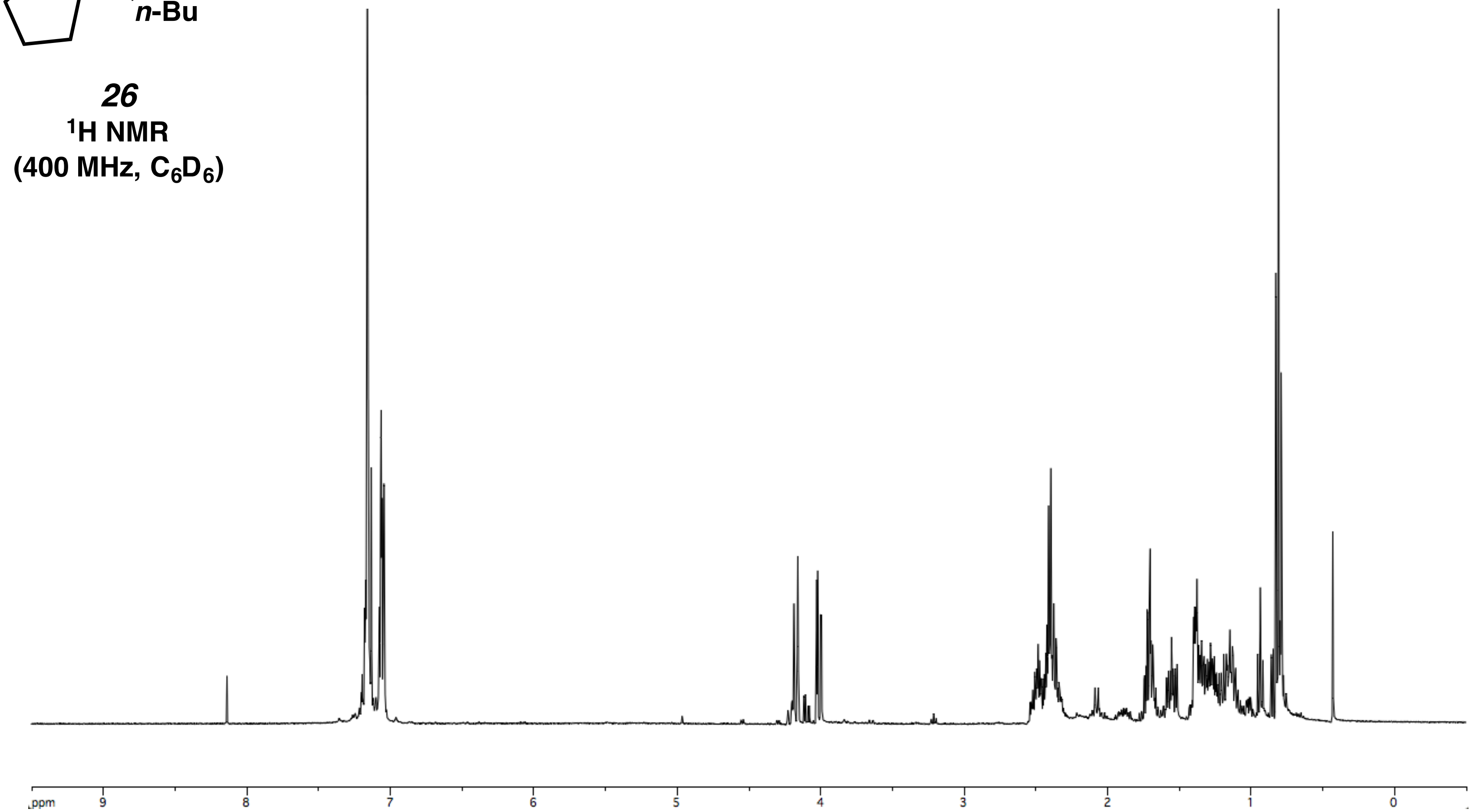
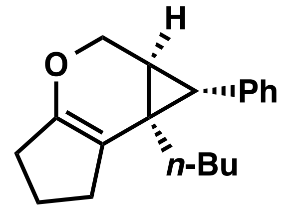
(100 MHz, C_6D_6)





26
^{1}H NMR
(400 MHz, C_6D_6)

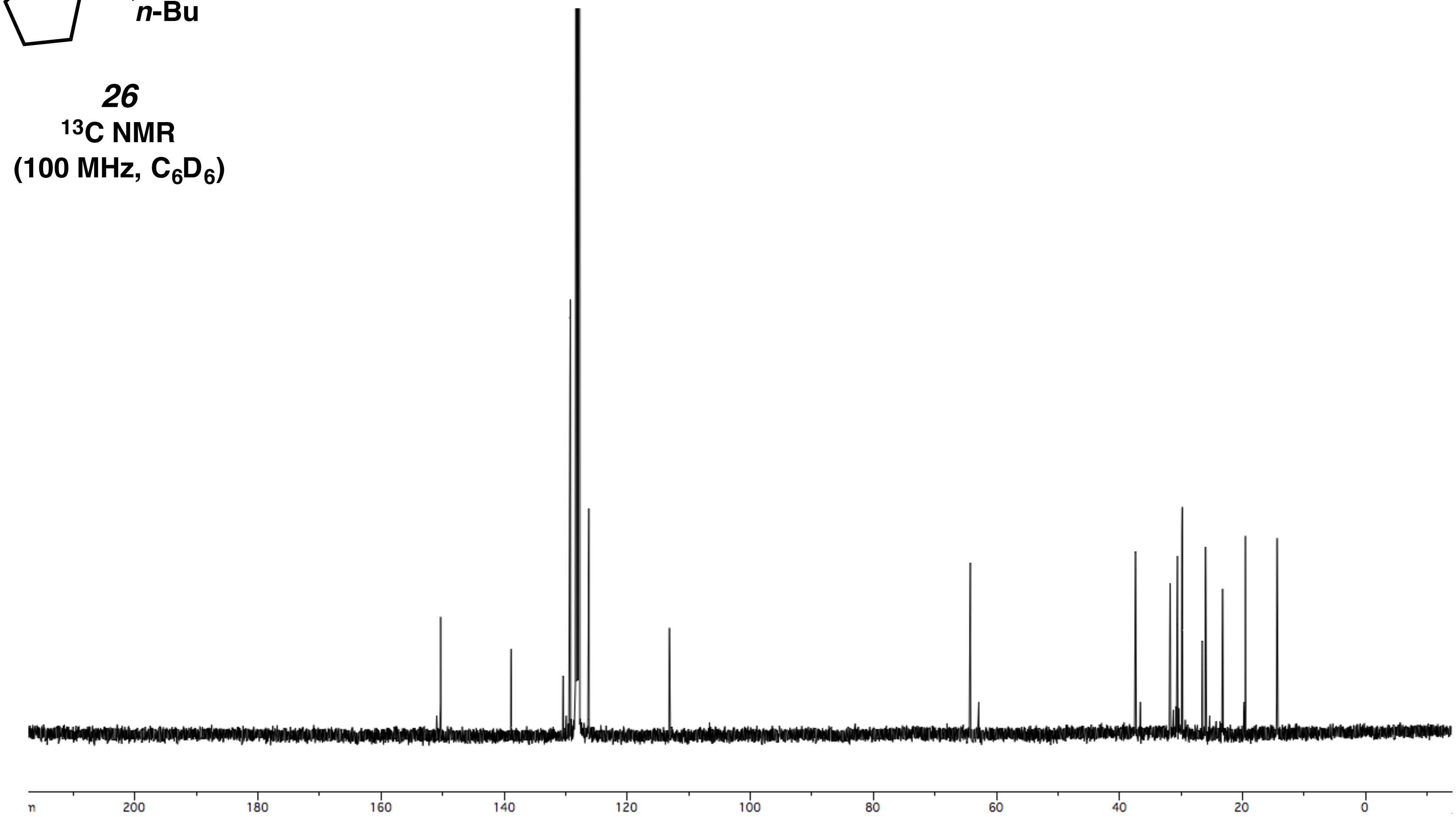


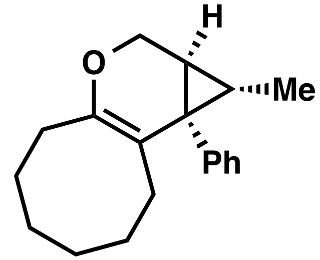


26

^{13}C NMR

(100 MHz, C_6D_6)

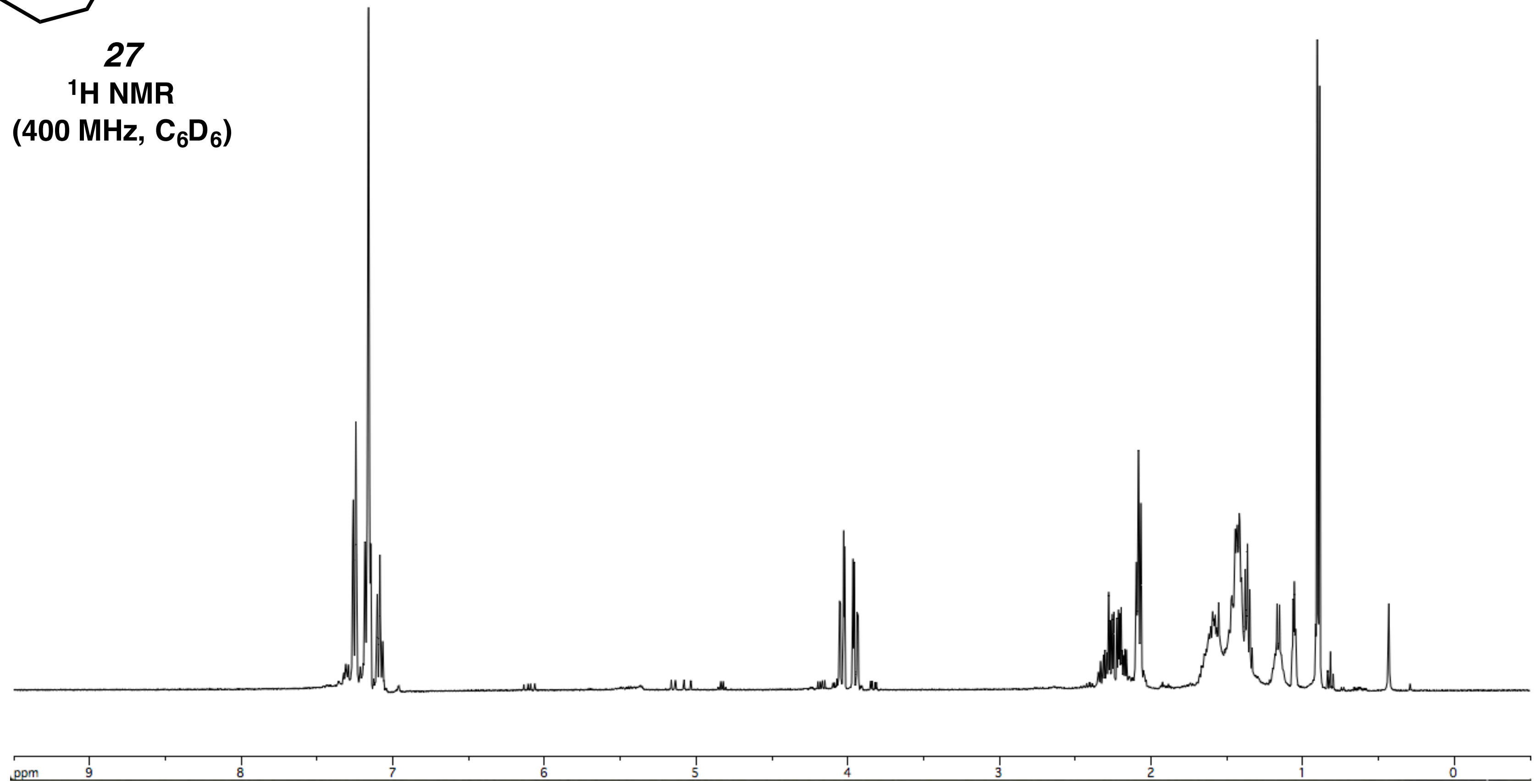


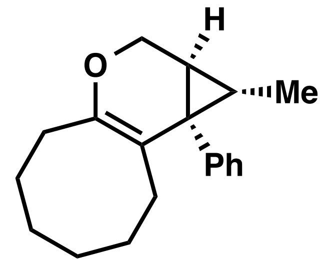


27

^{1}H NMR

(400 MHz, C_6D_6)





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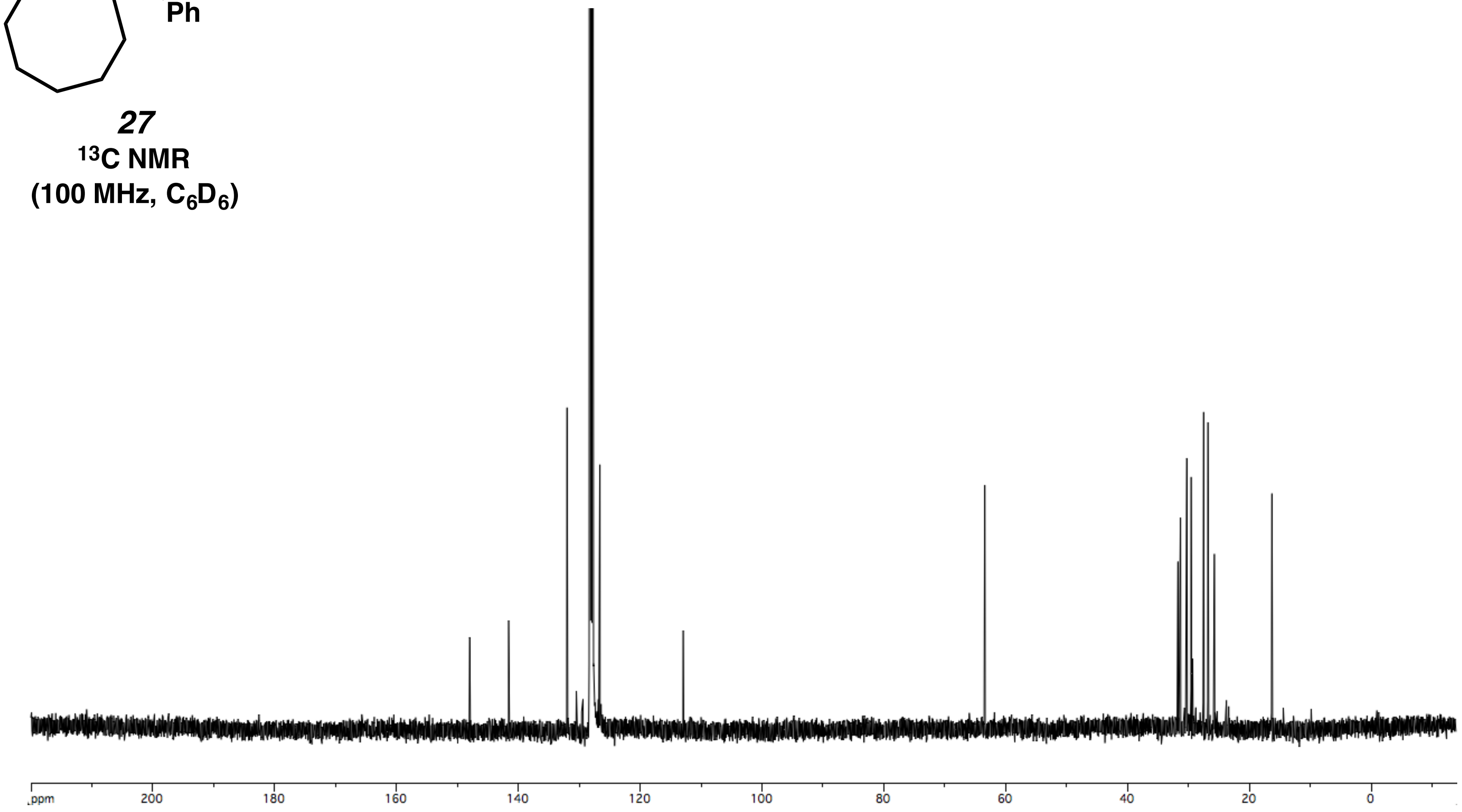
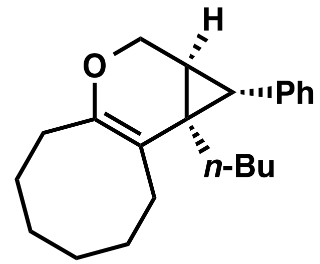
(100 MHz, C_6D_6)





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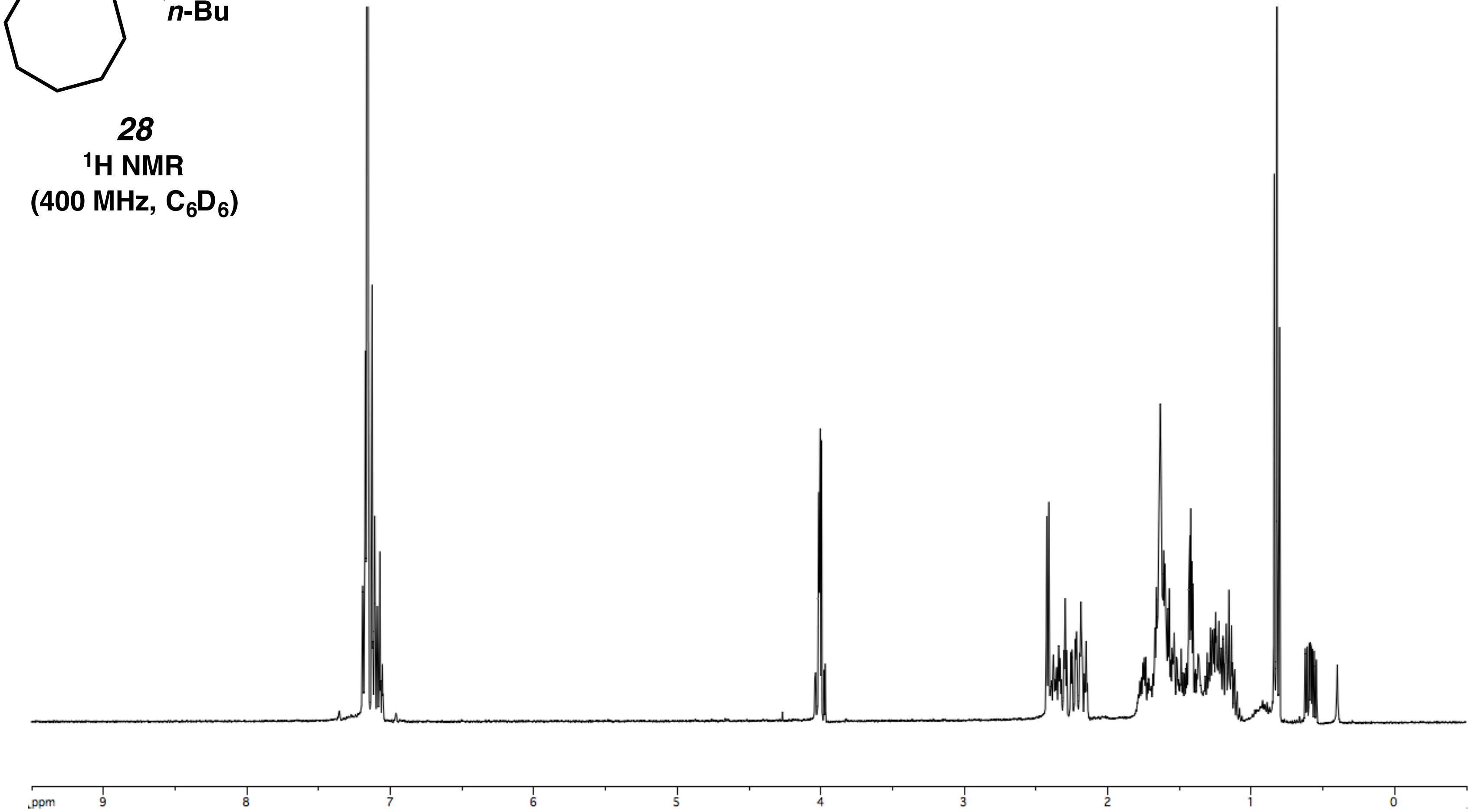
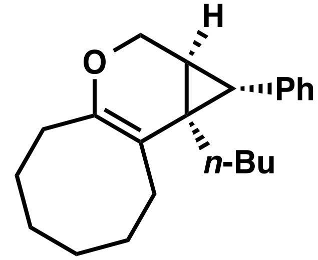
(400 MHz, C_6D_6)





28

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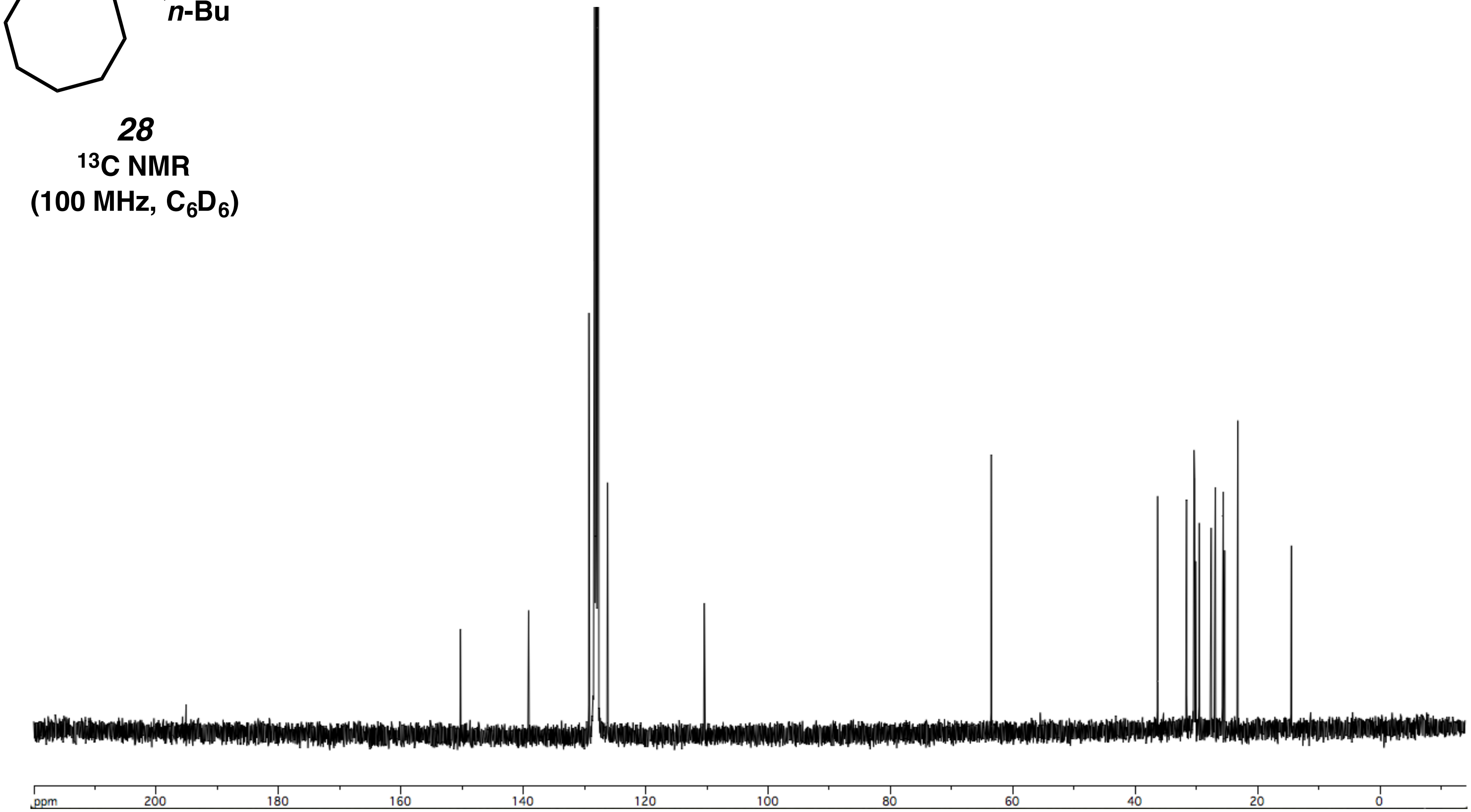
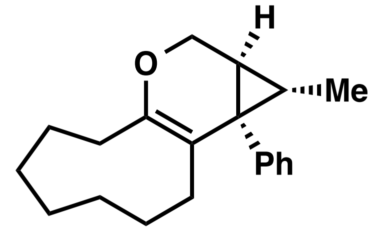
(100 MHz, C_6D_6)

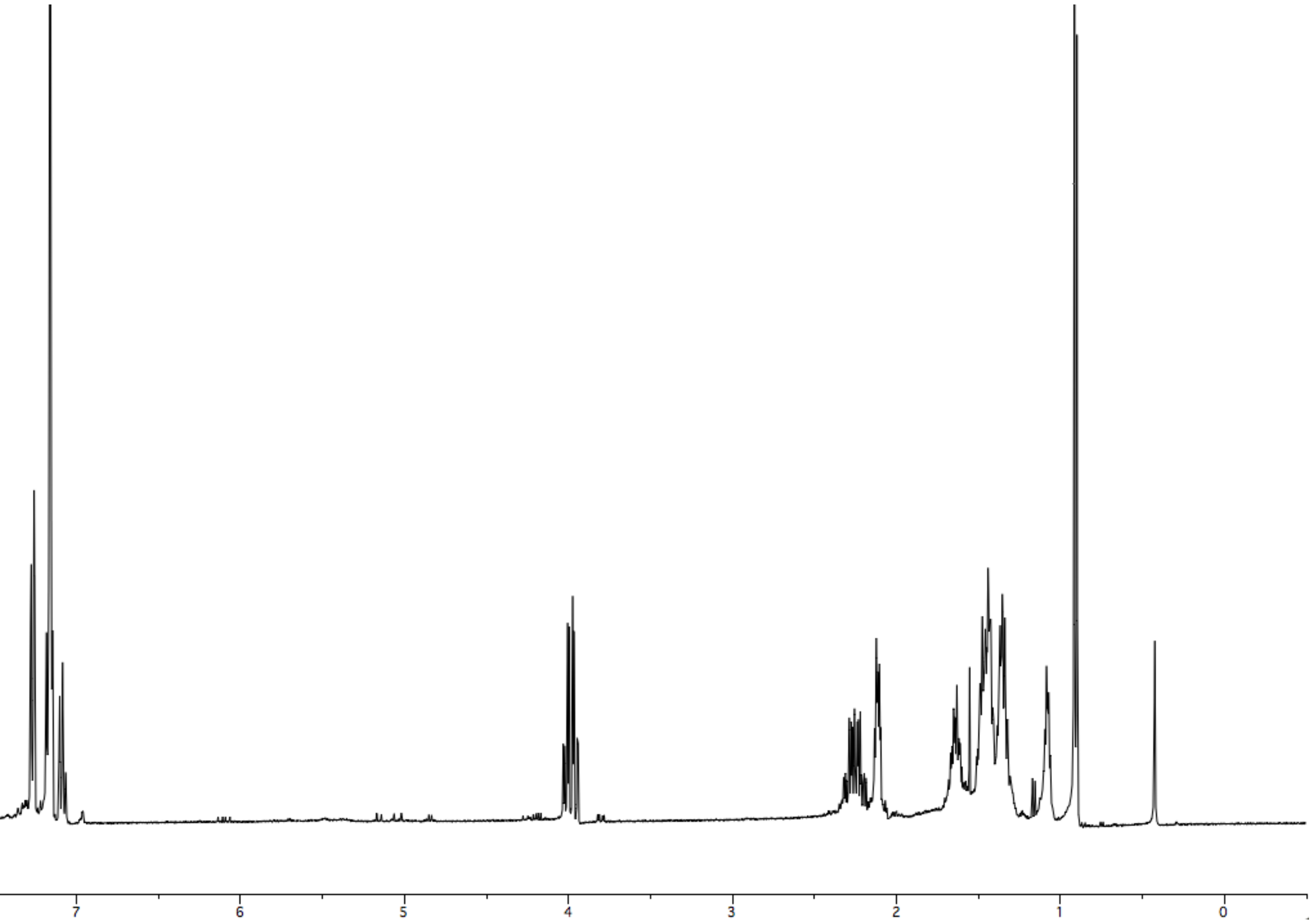


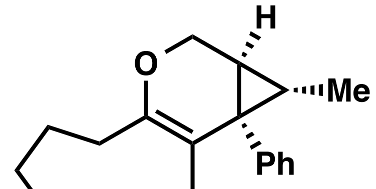


29

^{1}H NMR

(400 MHz, C_6D_6)





29

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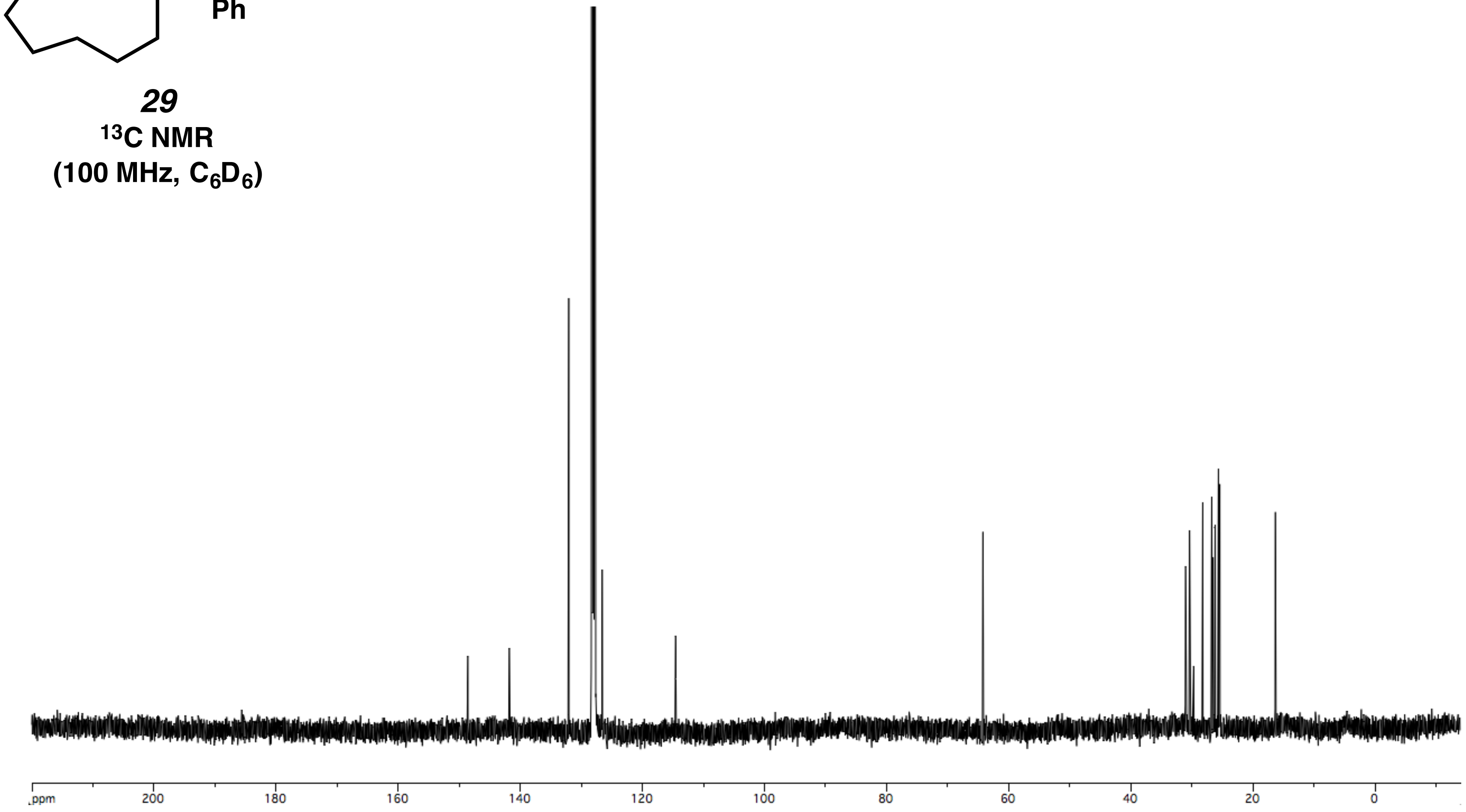
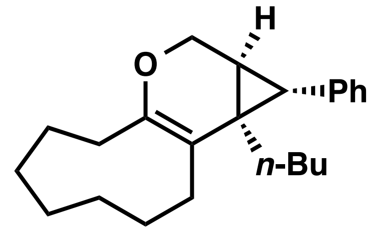
(100 MHz, C_6D_6)

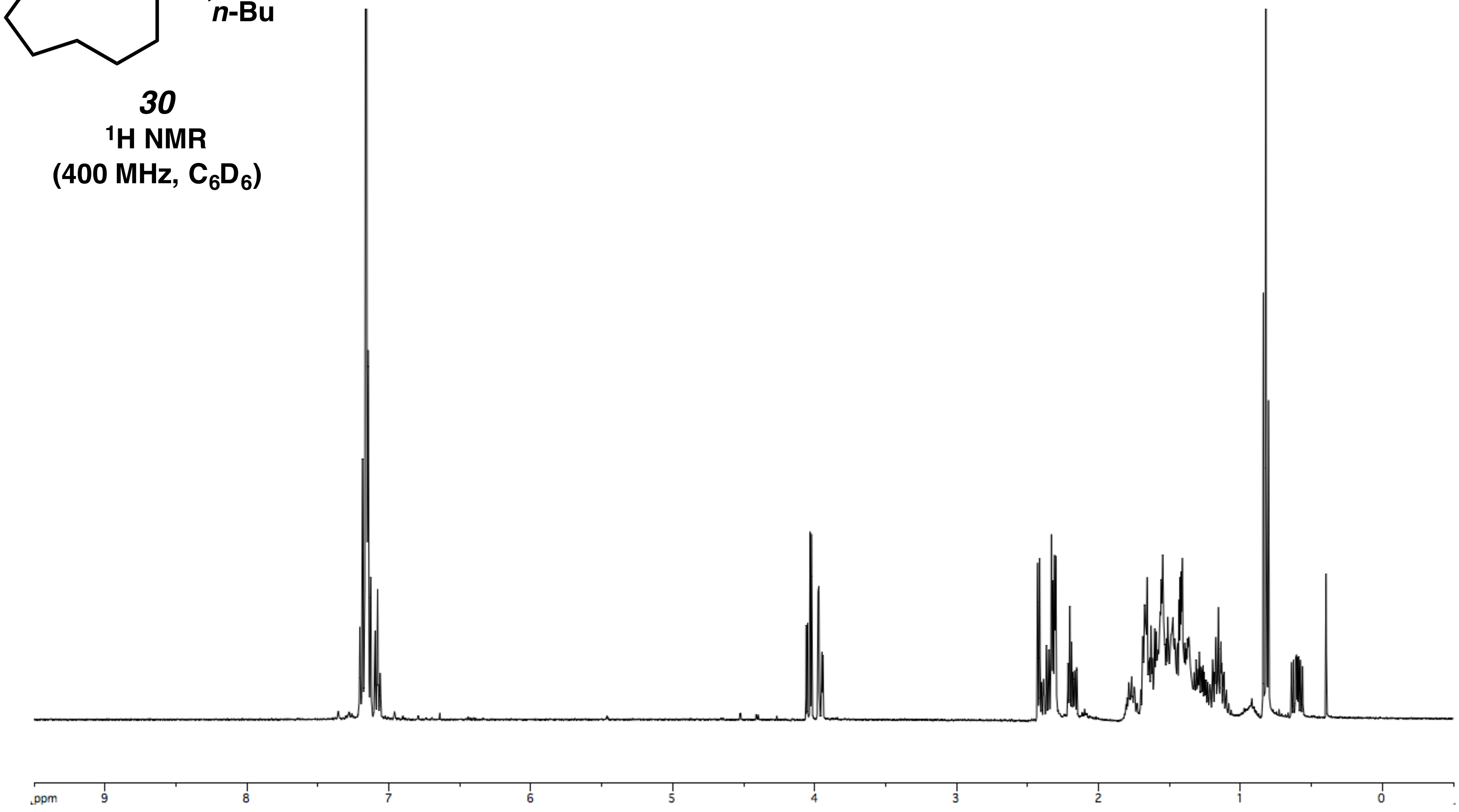


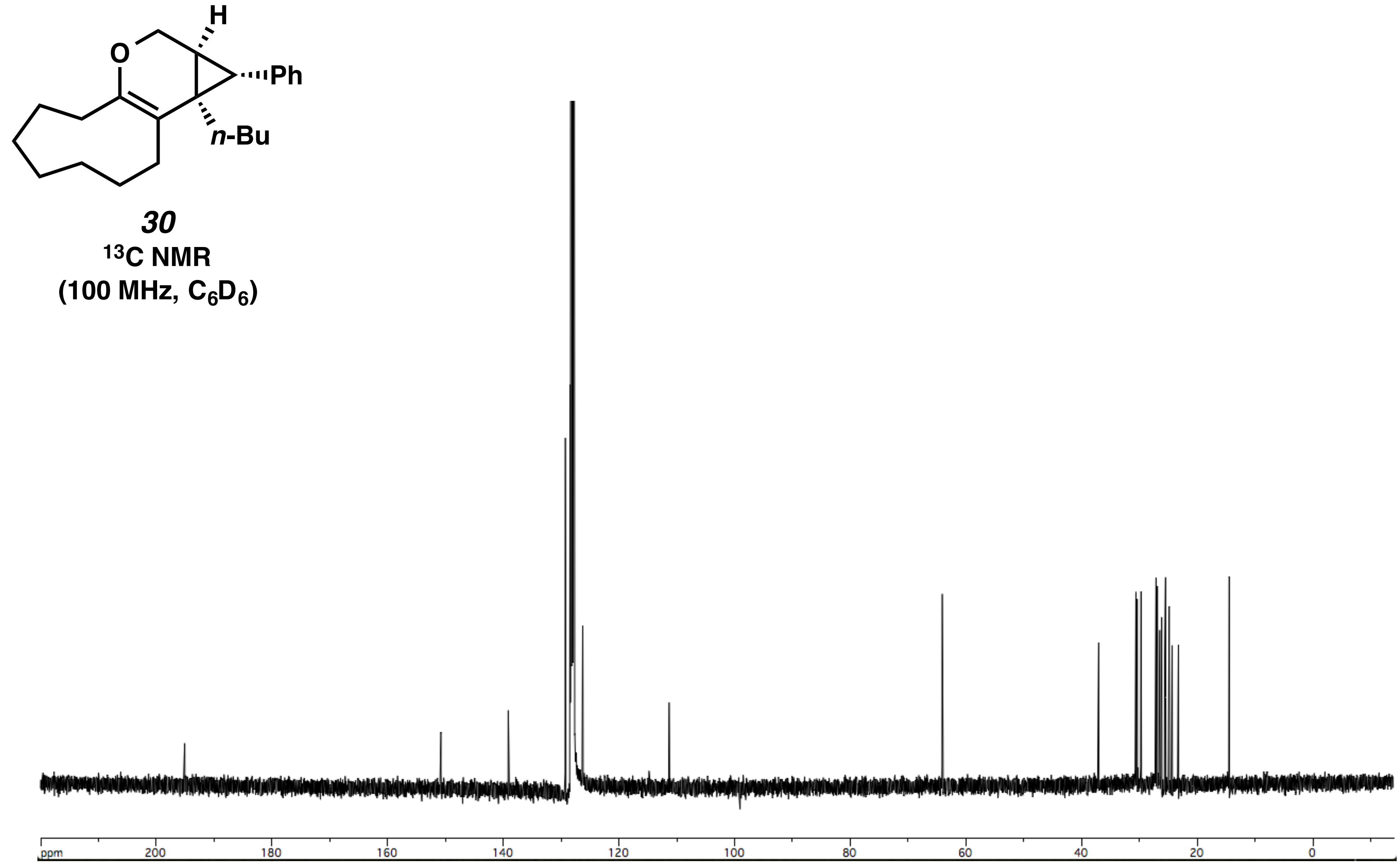


30

^{1}H NMR

(400 MHz, C_6D_6)

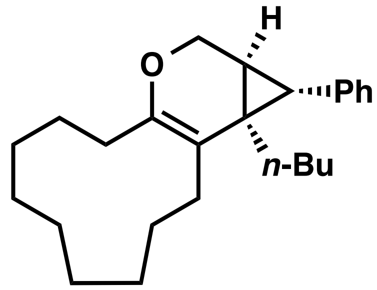




30

^{13}C NMR

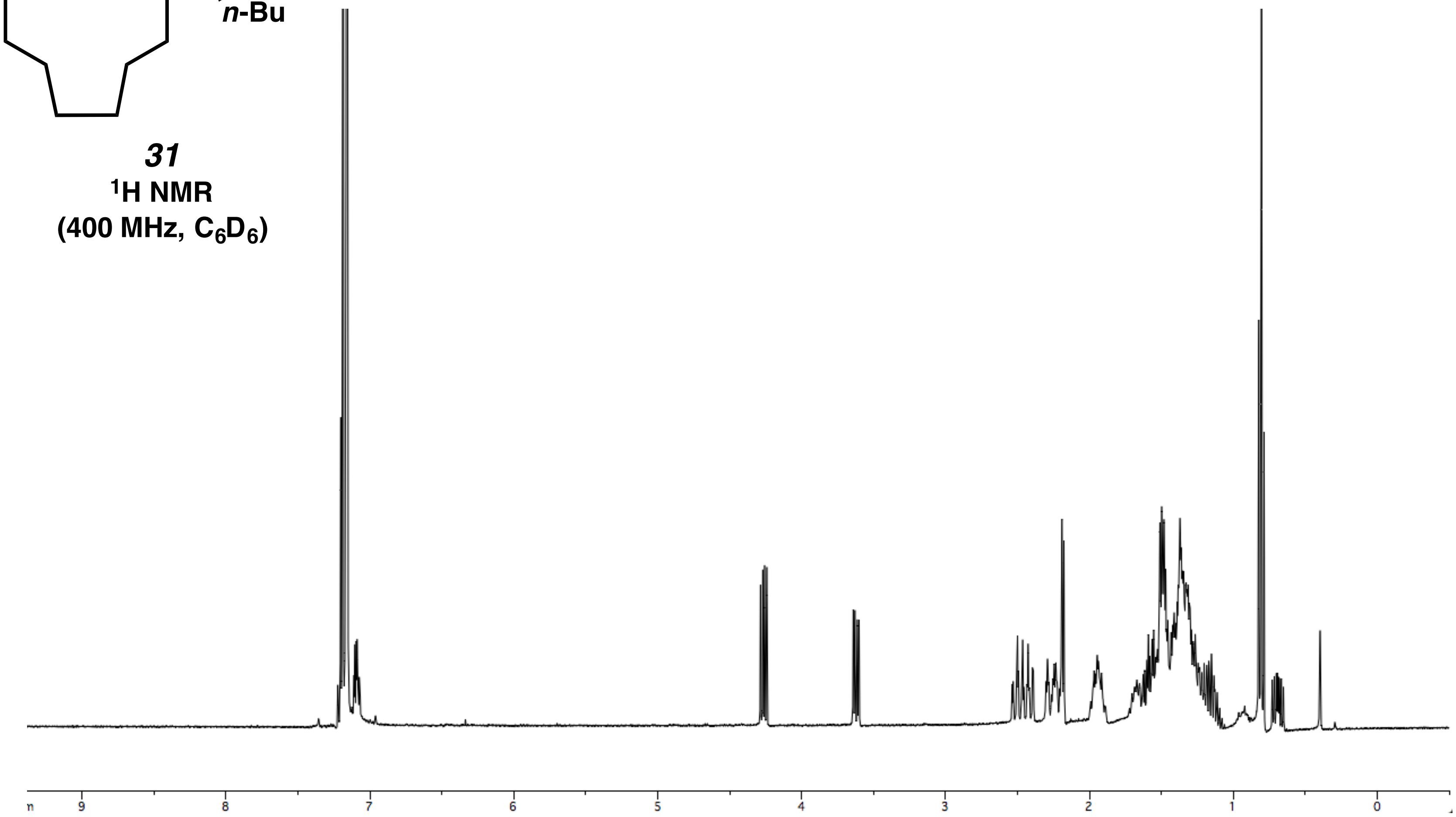
(100 MHz, C_6D_6)

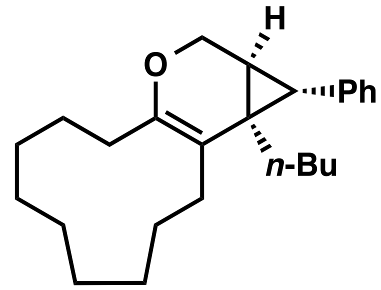


31

^{1}H NMR

(400 MHz, C_6D_6)

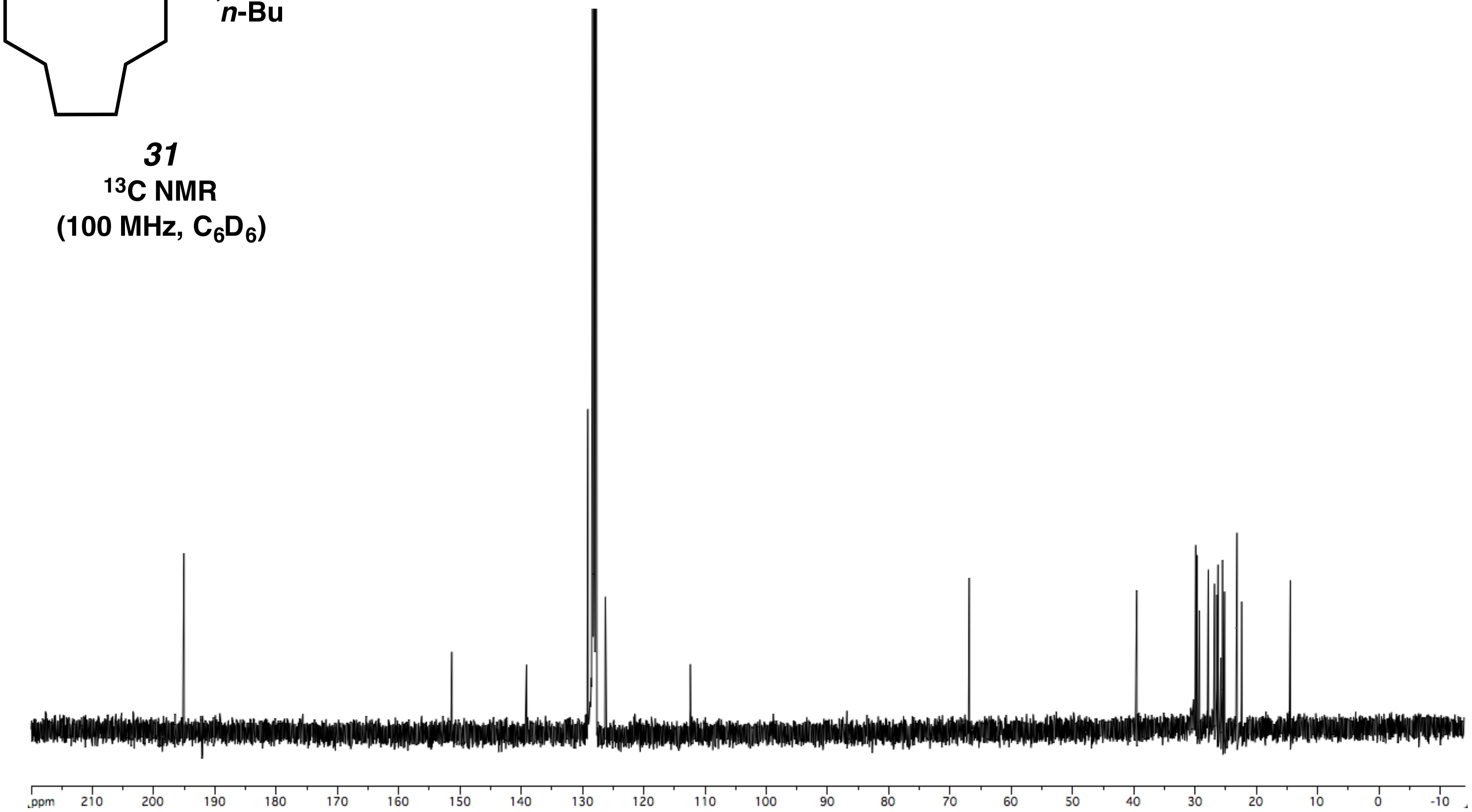


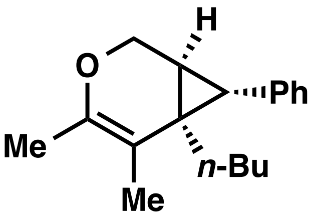


31

^{13}C NMR

(100 MHz, C_6D_6)

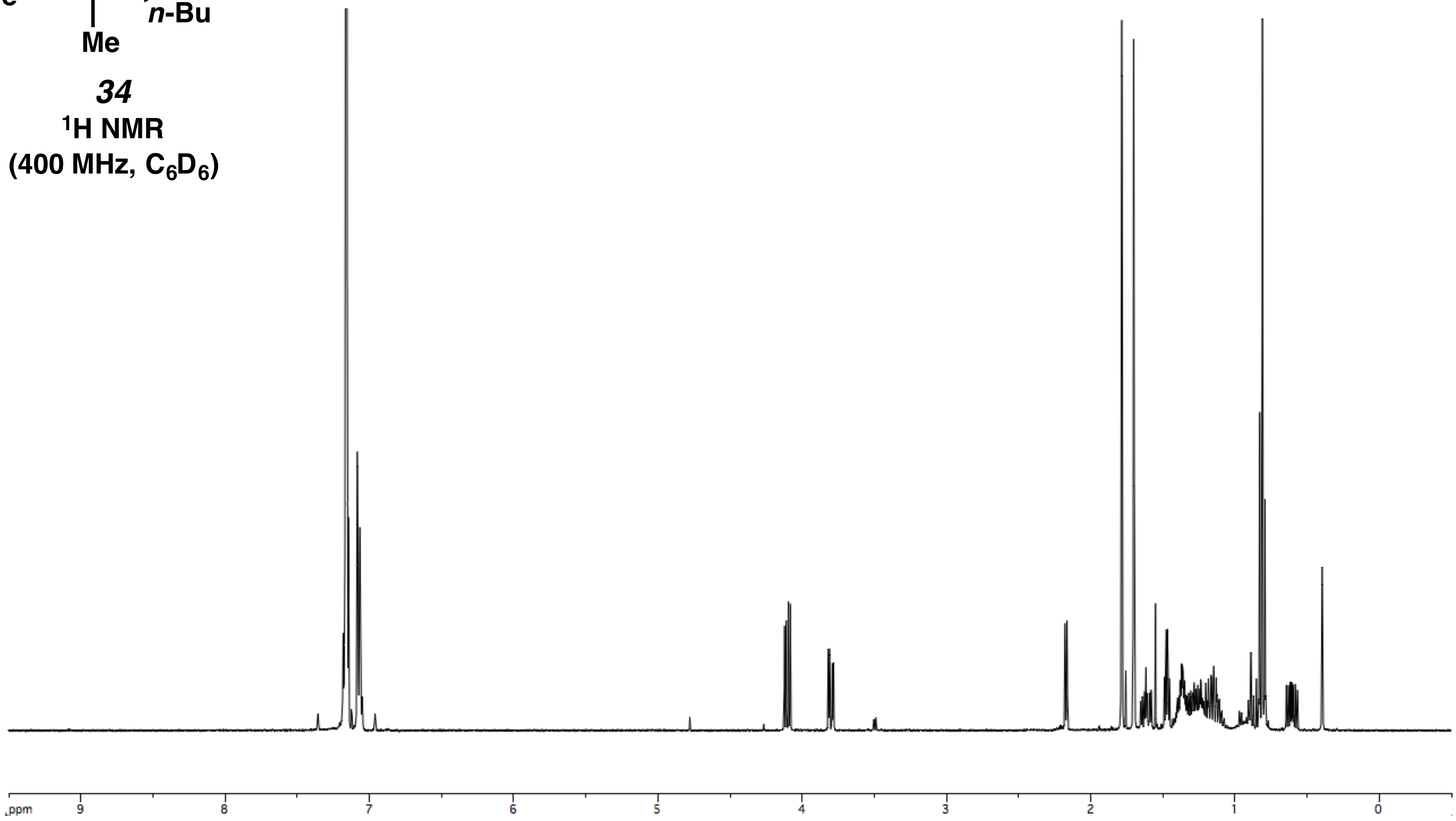


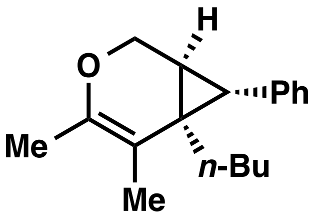


34

^{1}H NMR

(400 MHz, C_6D_6)





34

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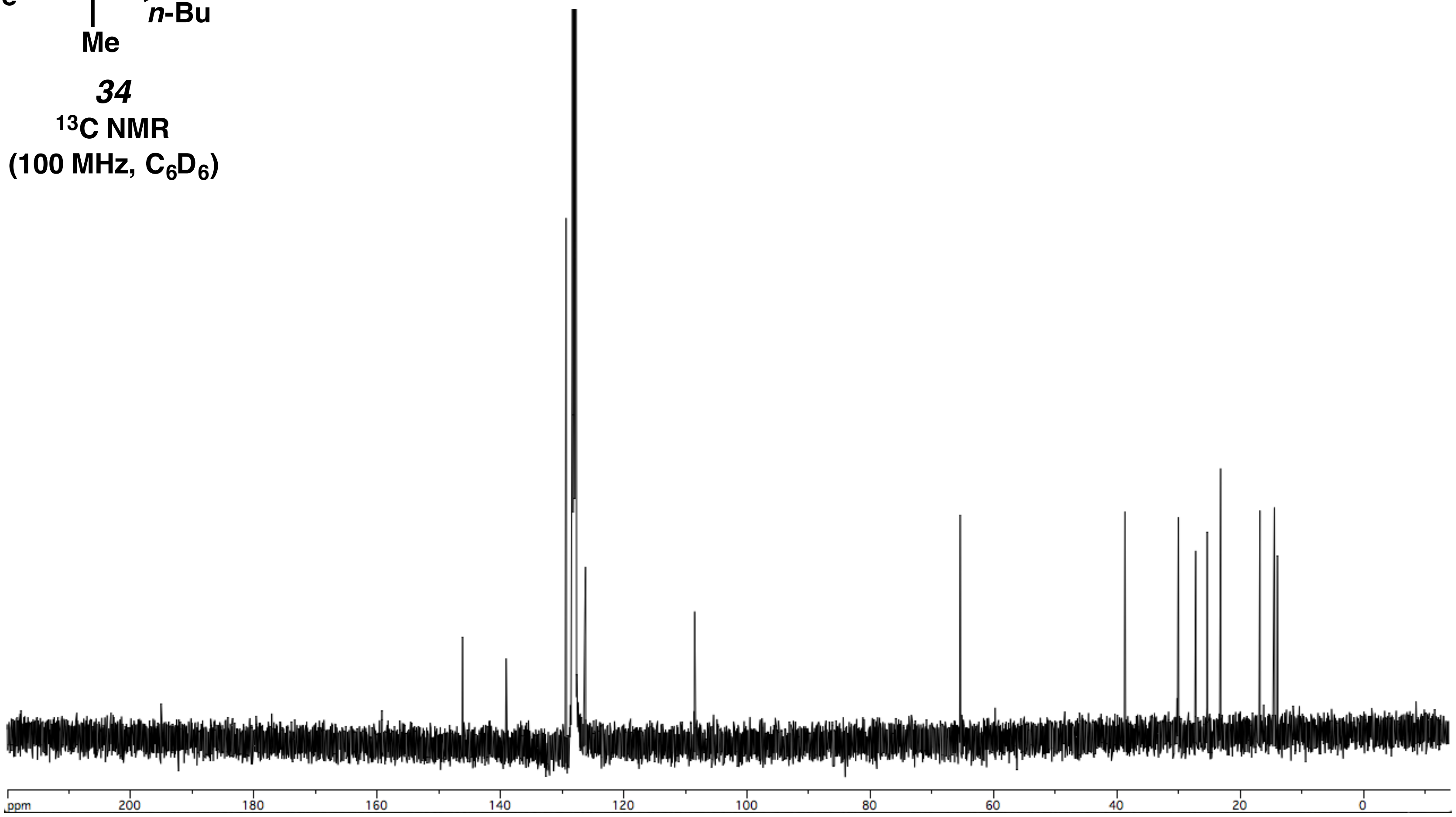
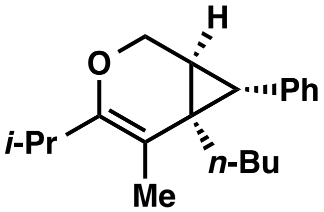
(100 MHz, C_6D_6)

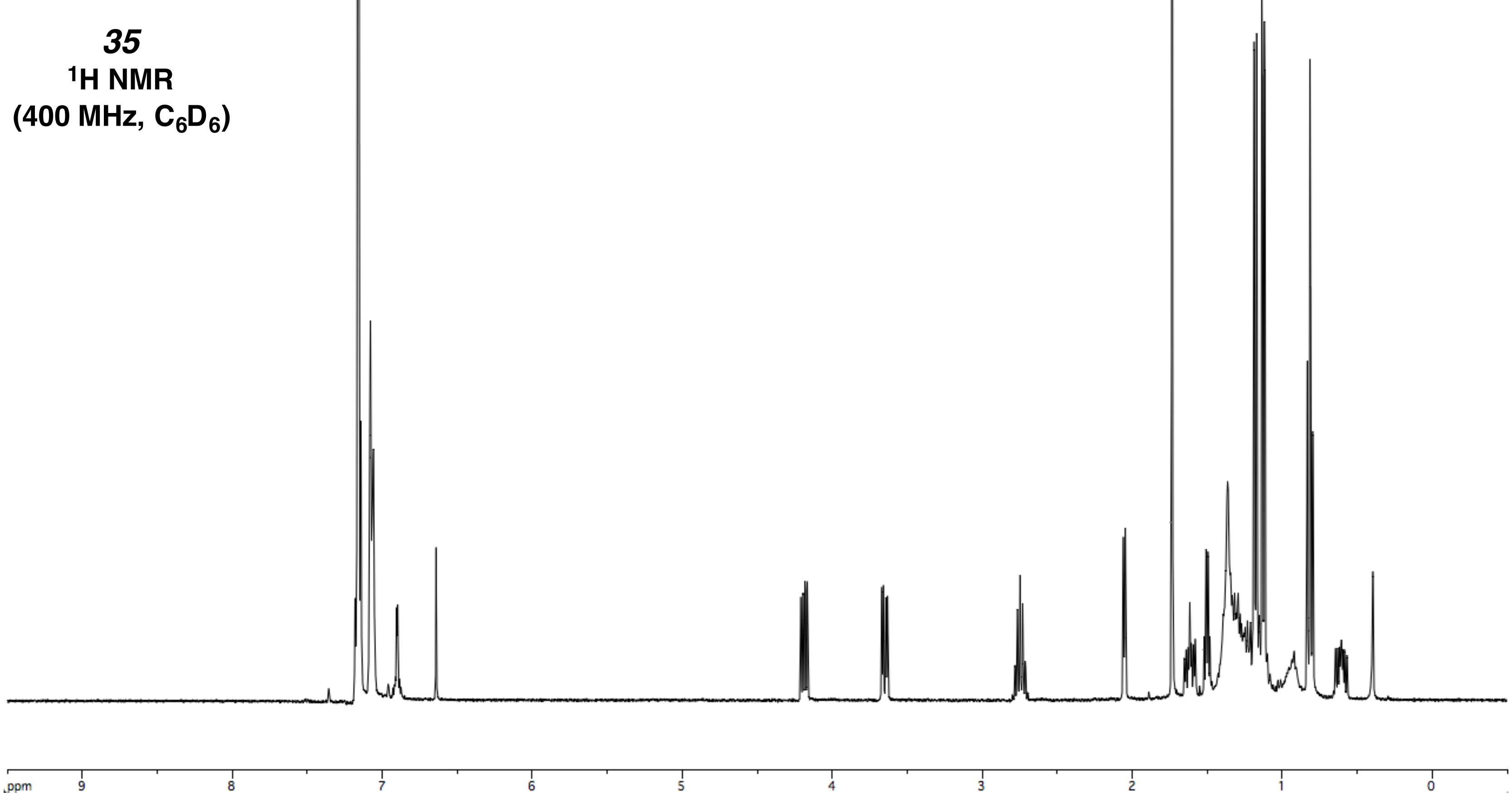


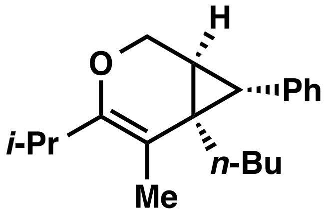


35

^{1}H NMR

(400 MHz, C_6D_6)

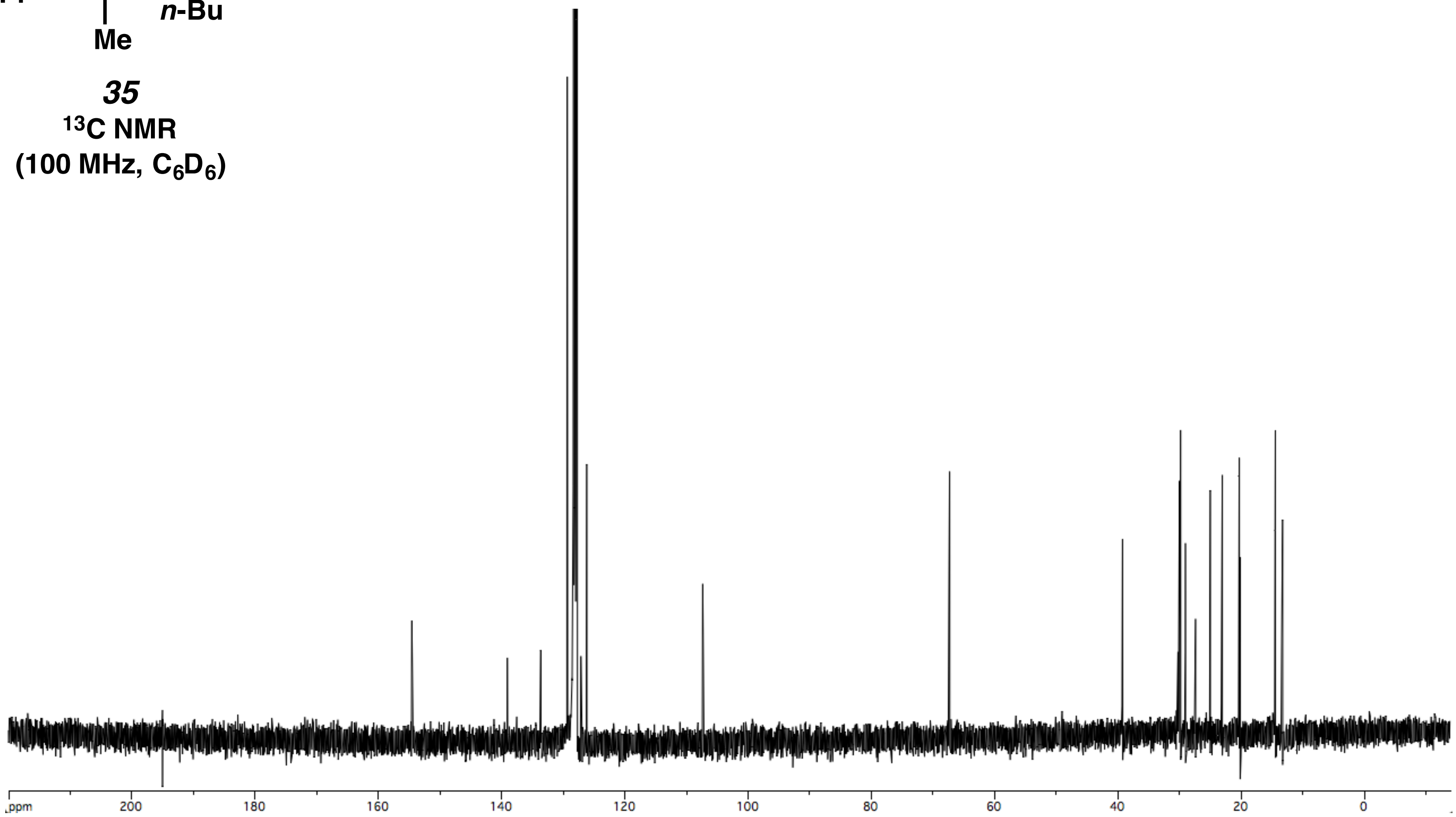


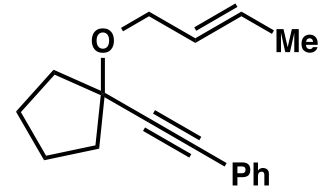


35

^{13}C NMR

(100 MHz, C_6D_6)

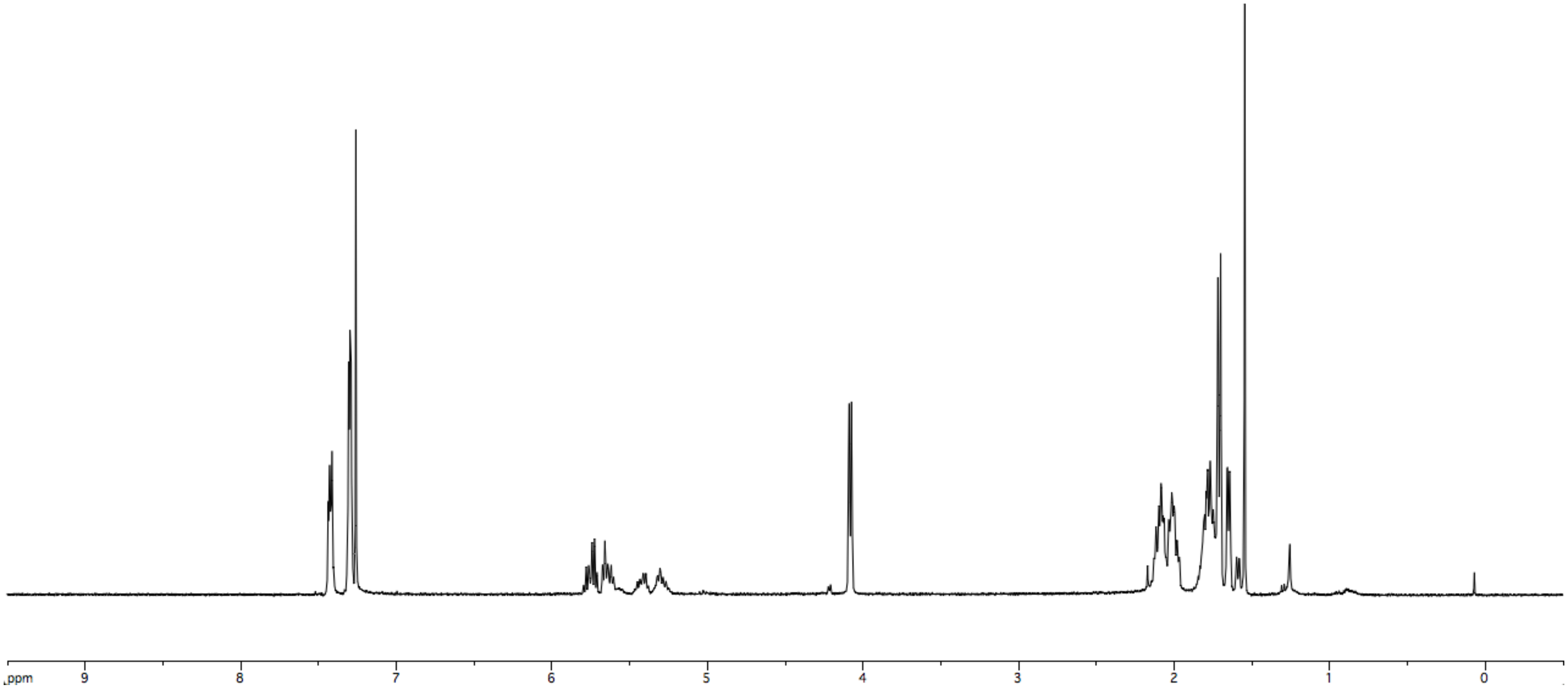


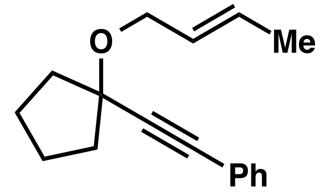


7

^{1}H NMR

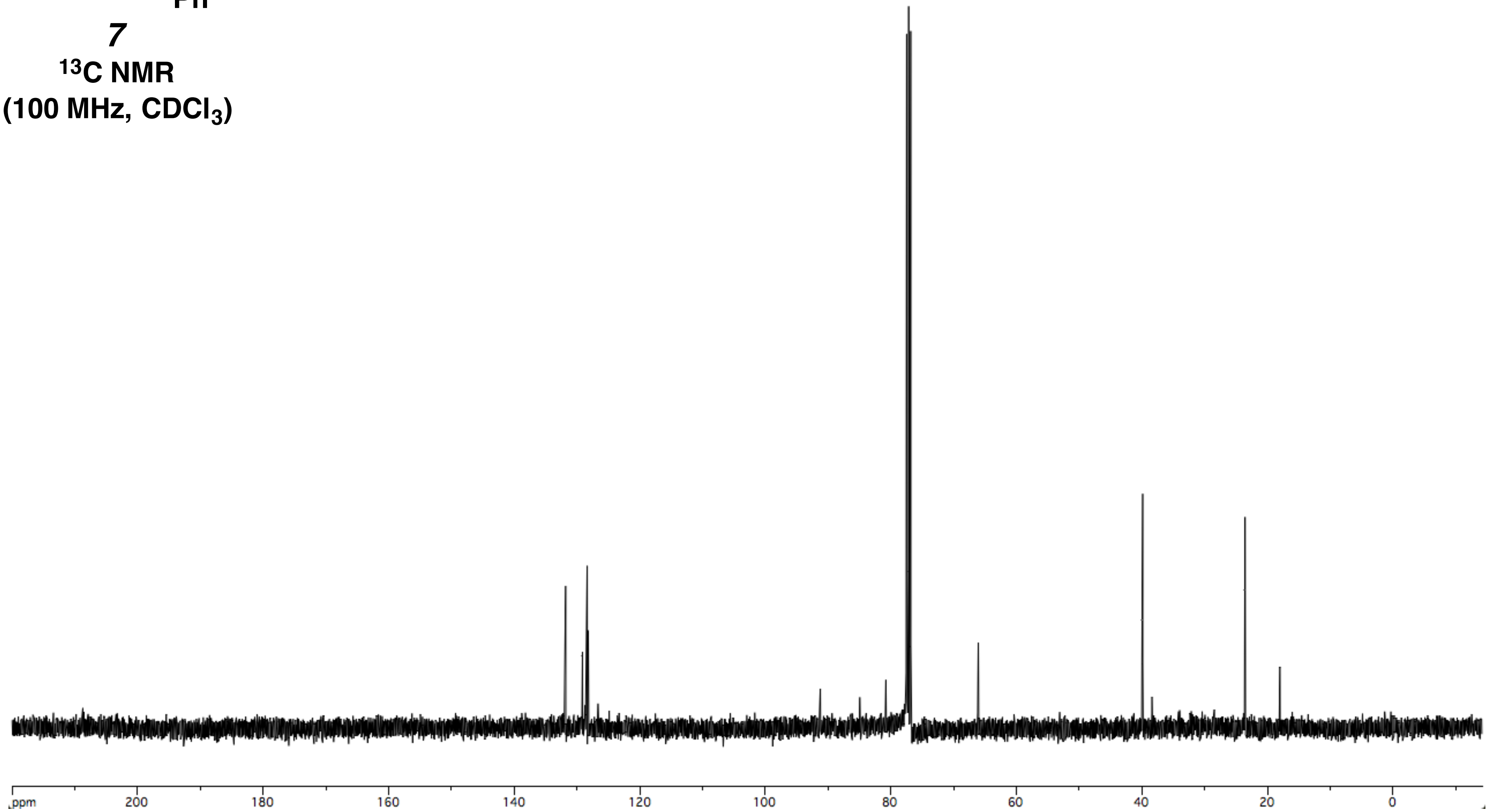
(400 MHz, $CDCl_3$)

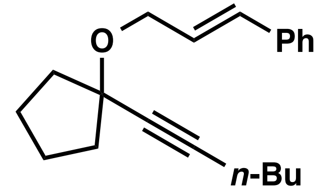




7

^{13}C NMR
(100 MHz, $CDCl_3$)

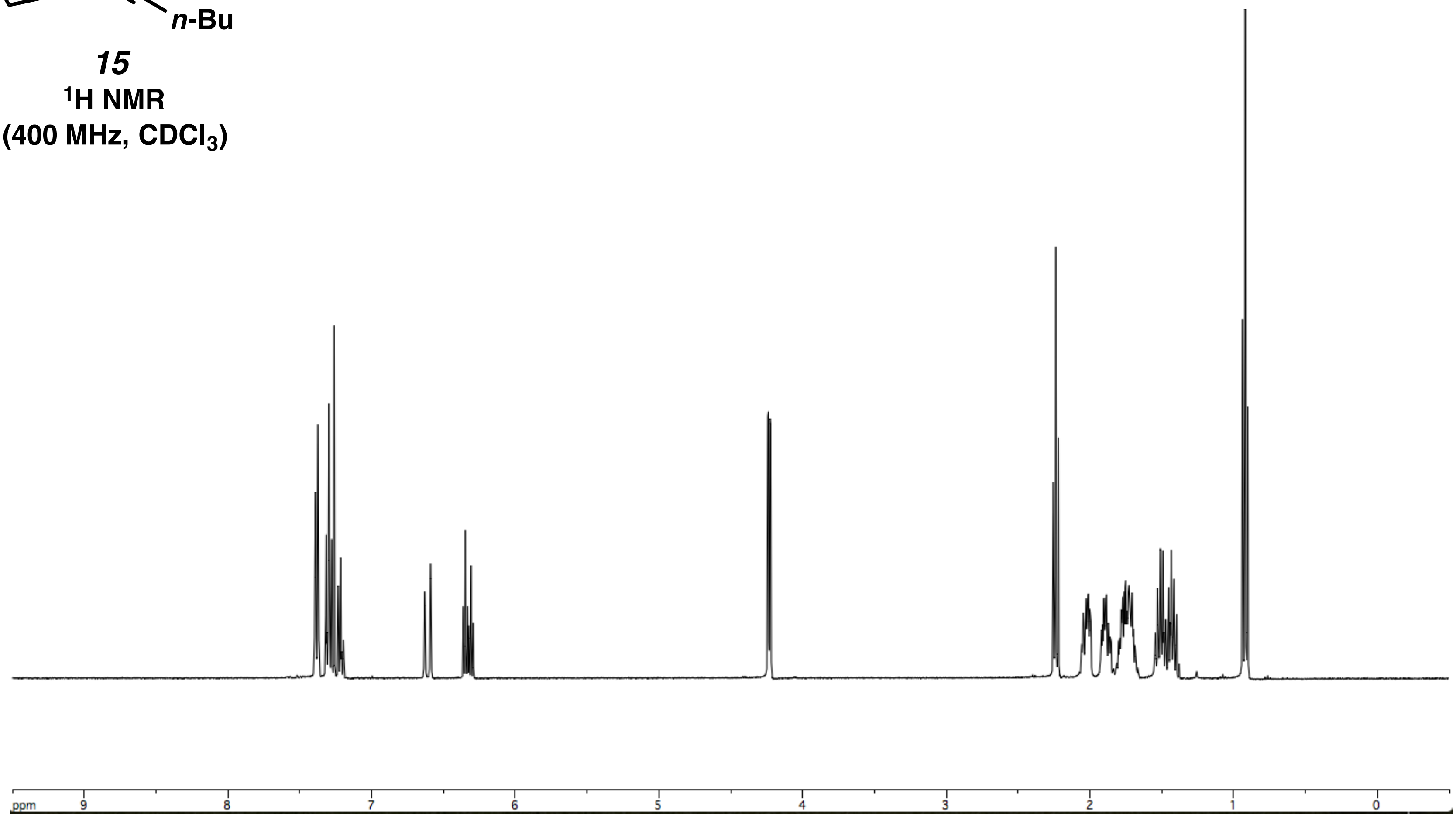


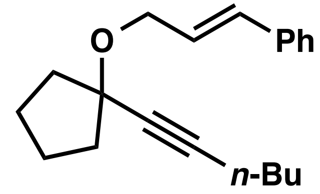


15

^{1}H NMR

(400 MHz, $CDCl_3$)

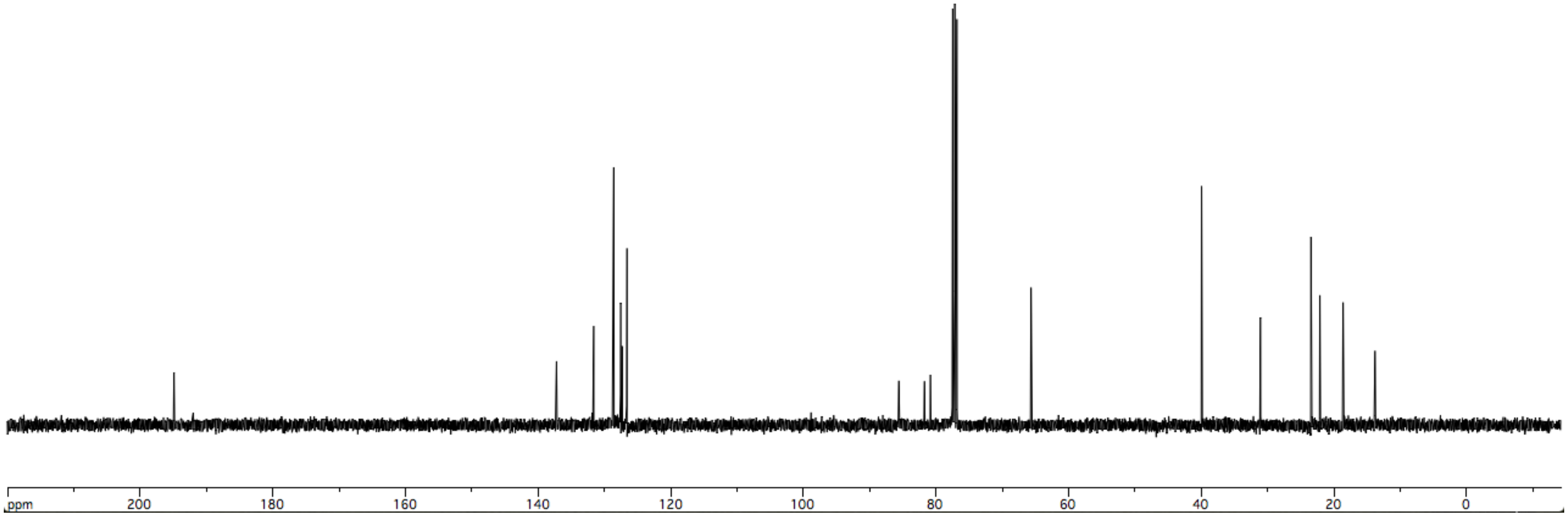


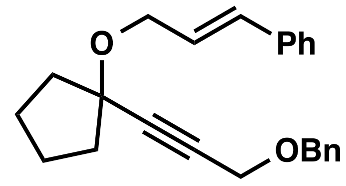


15

^{13}C NMR

(100 MHz, $CDCl_3$)

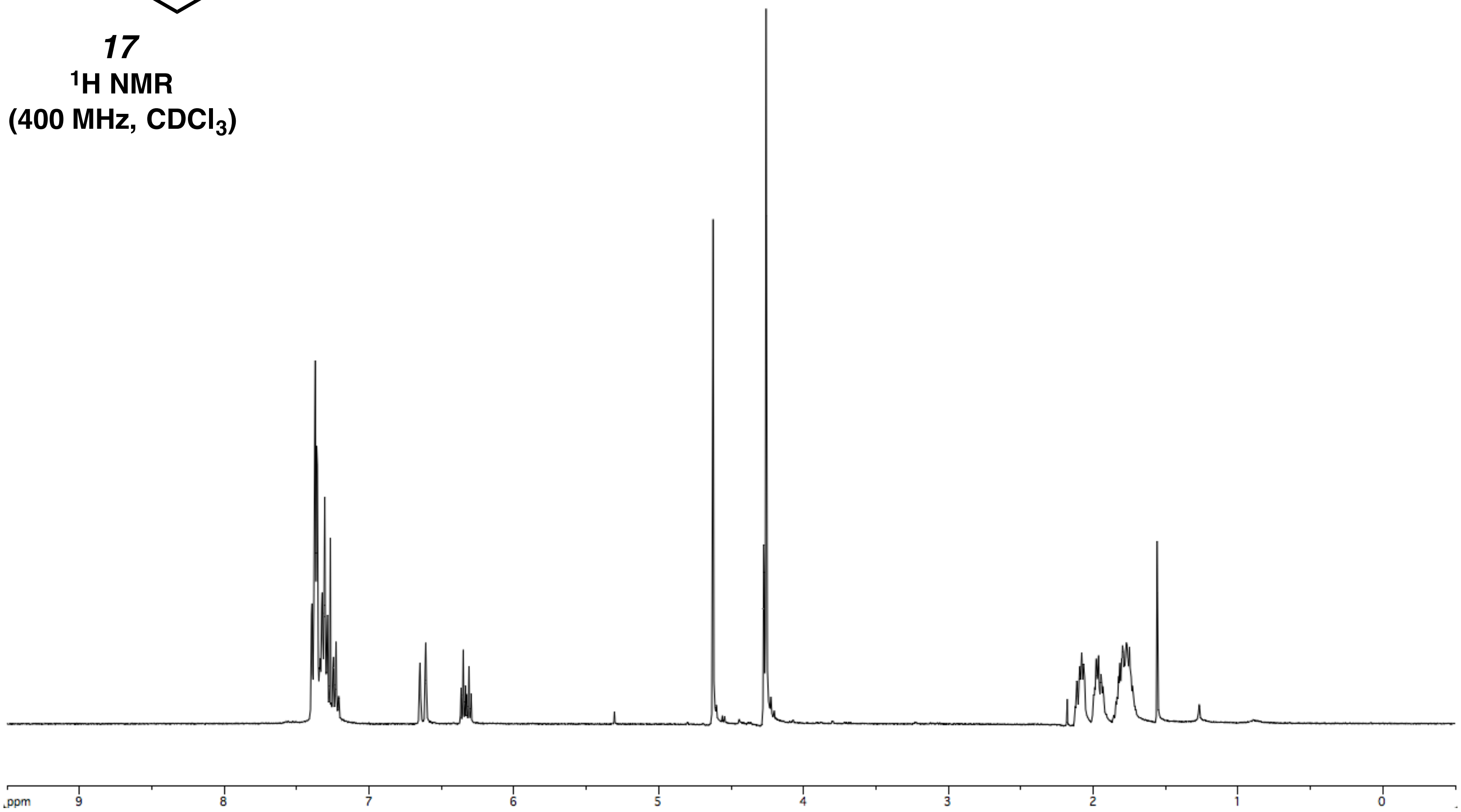


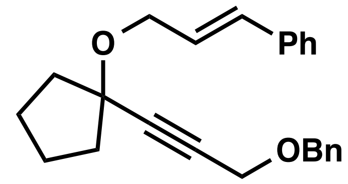


17

^{1}H NMR

(400 MHz, $CDCl_3$)

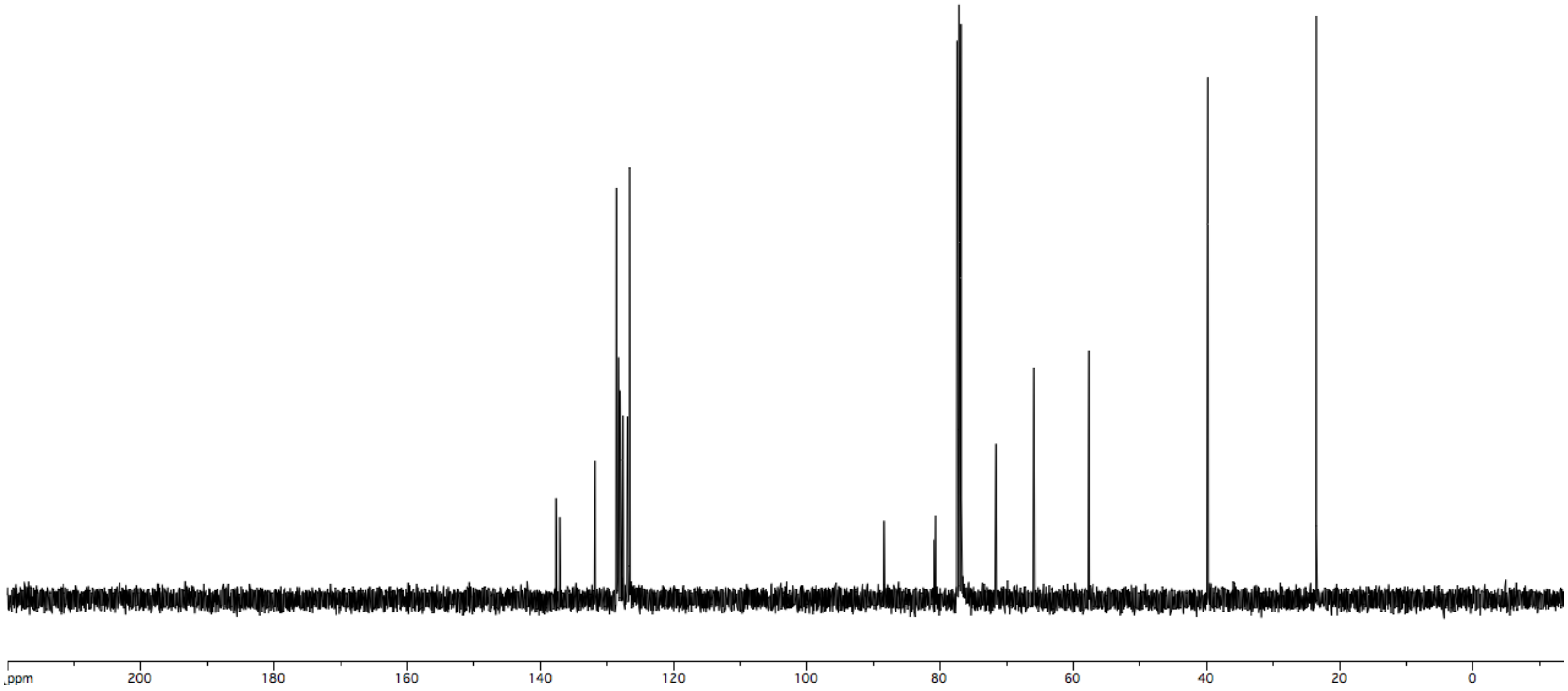


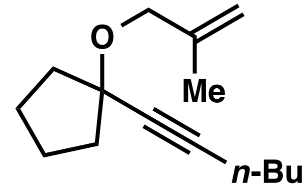


17

^{13}C NMR

(100 MHz, $CDCl_3$)

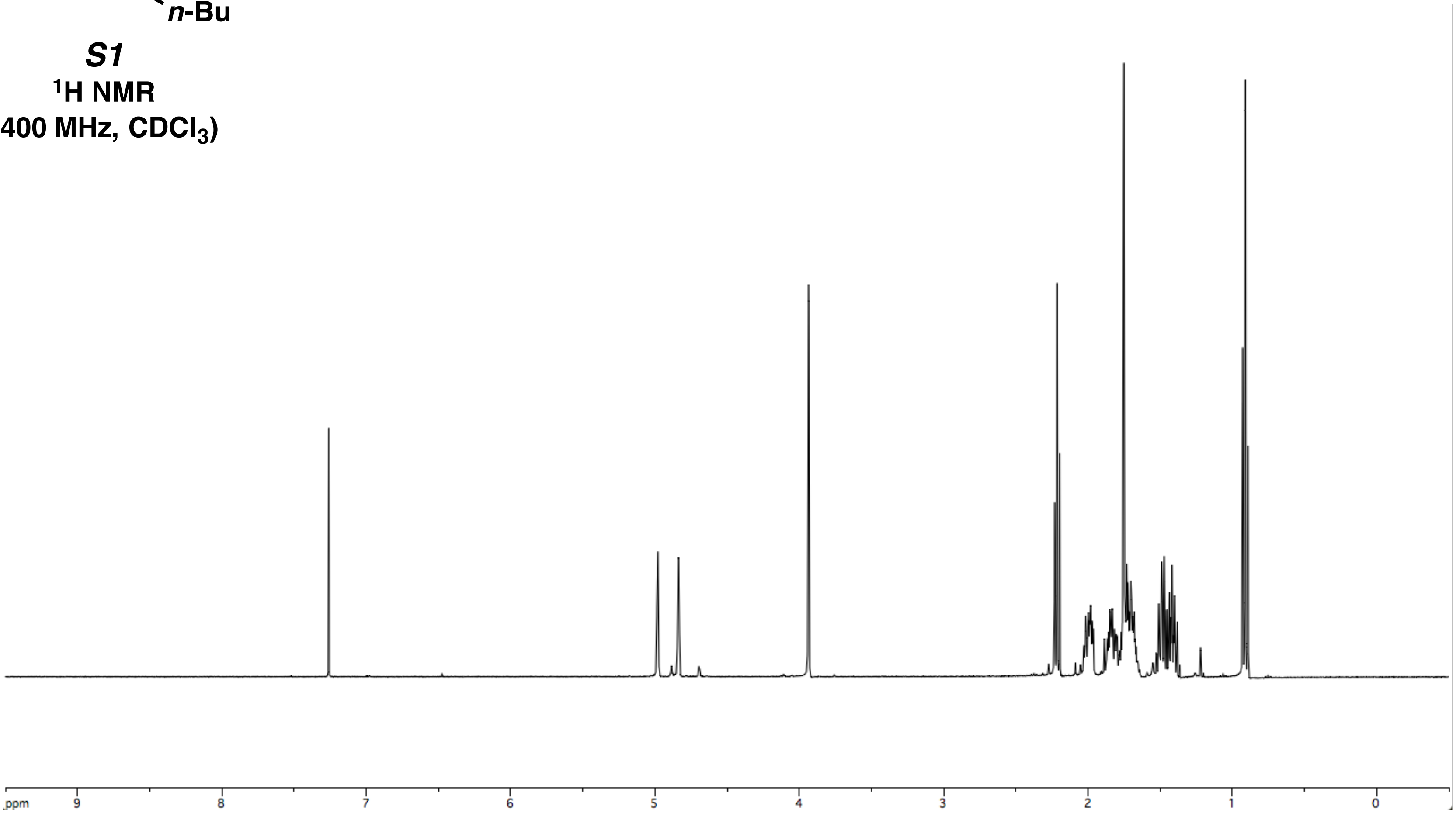


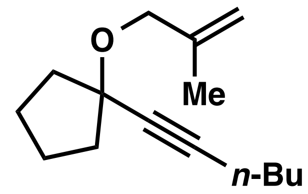


S1

^{1}H NMR

(400 MHz, $CDCl_3$)

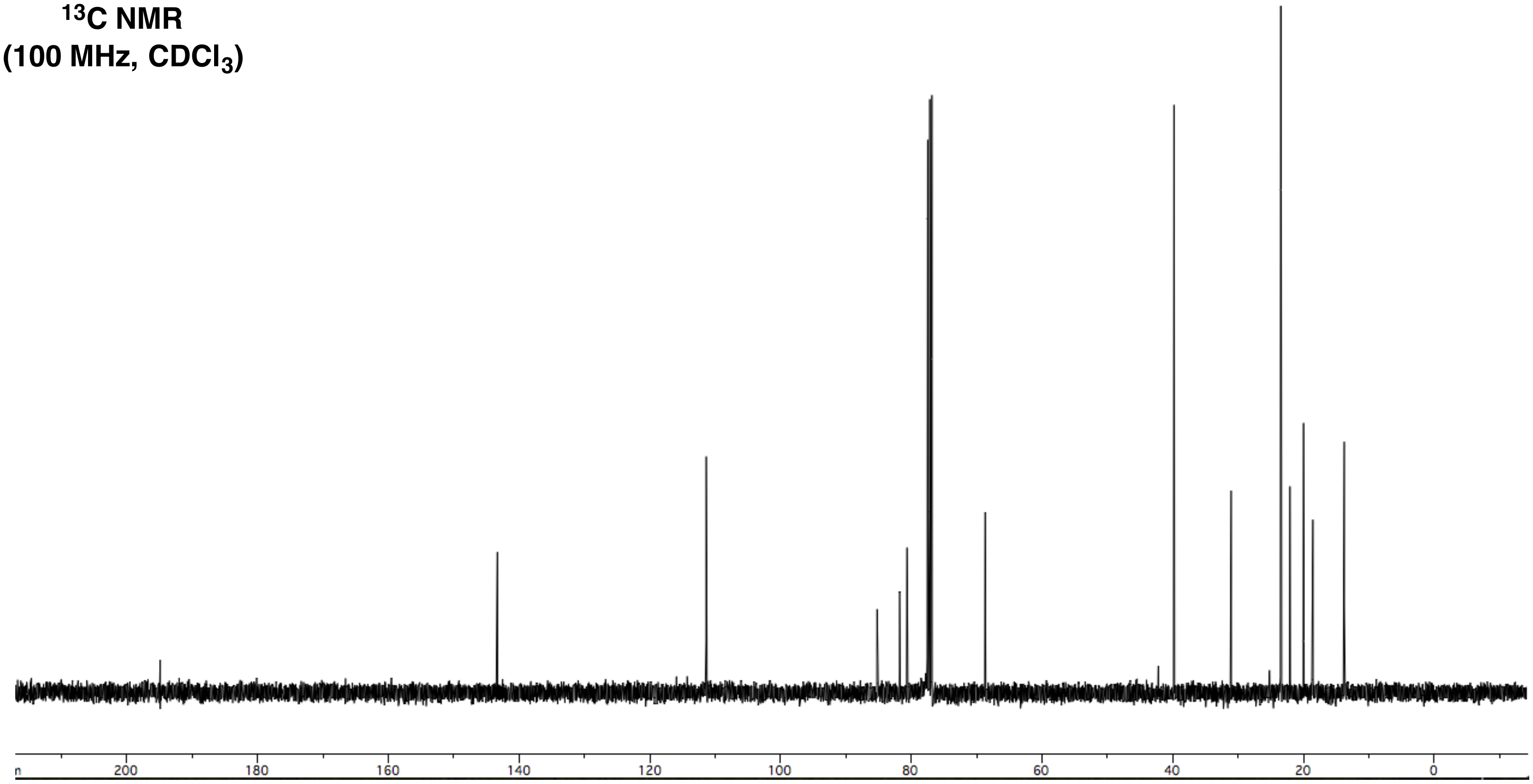


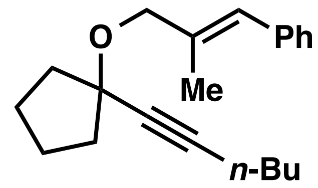


S1

^{13}C NMR

(100 MHz, $CDCl_3$)

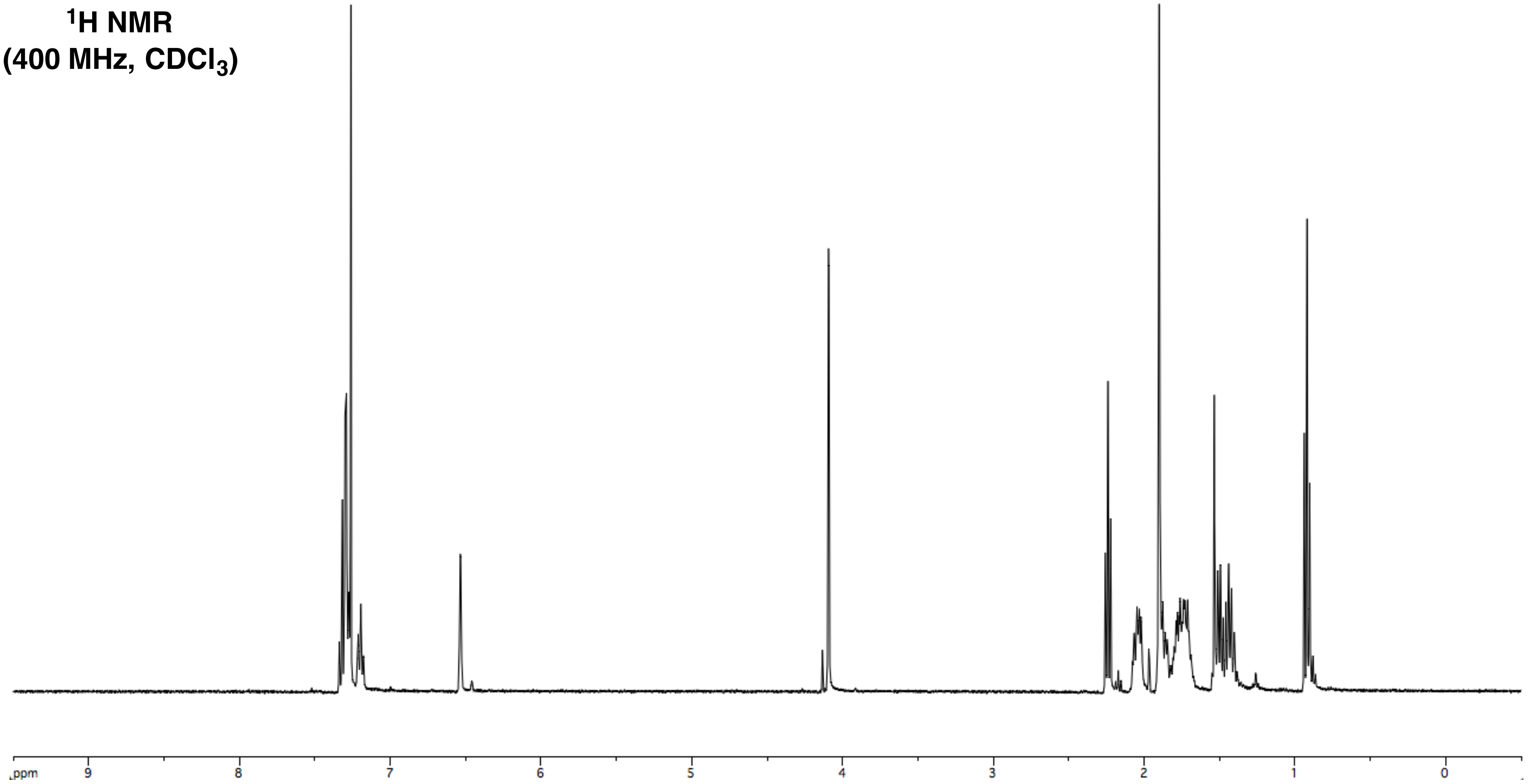


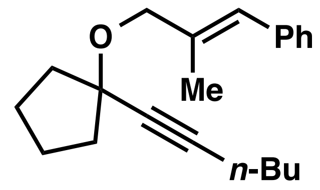


S2

^{1}H NMR

(400 MHz, $CDCl_3$)

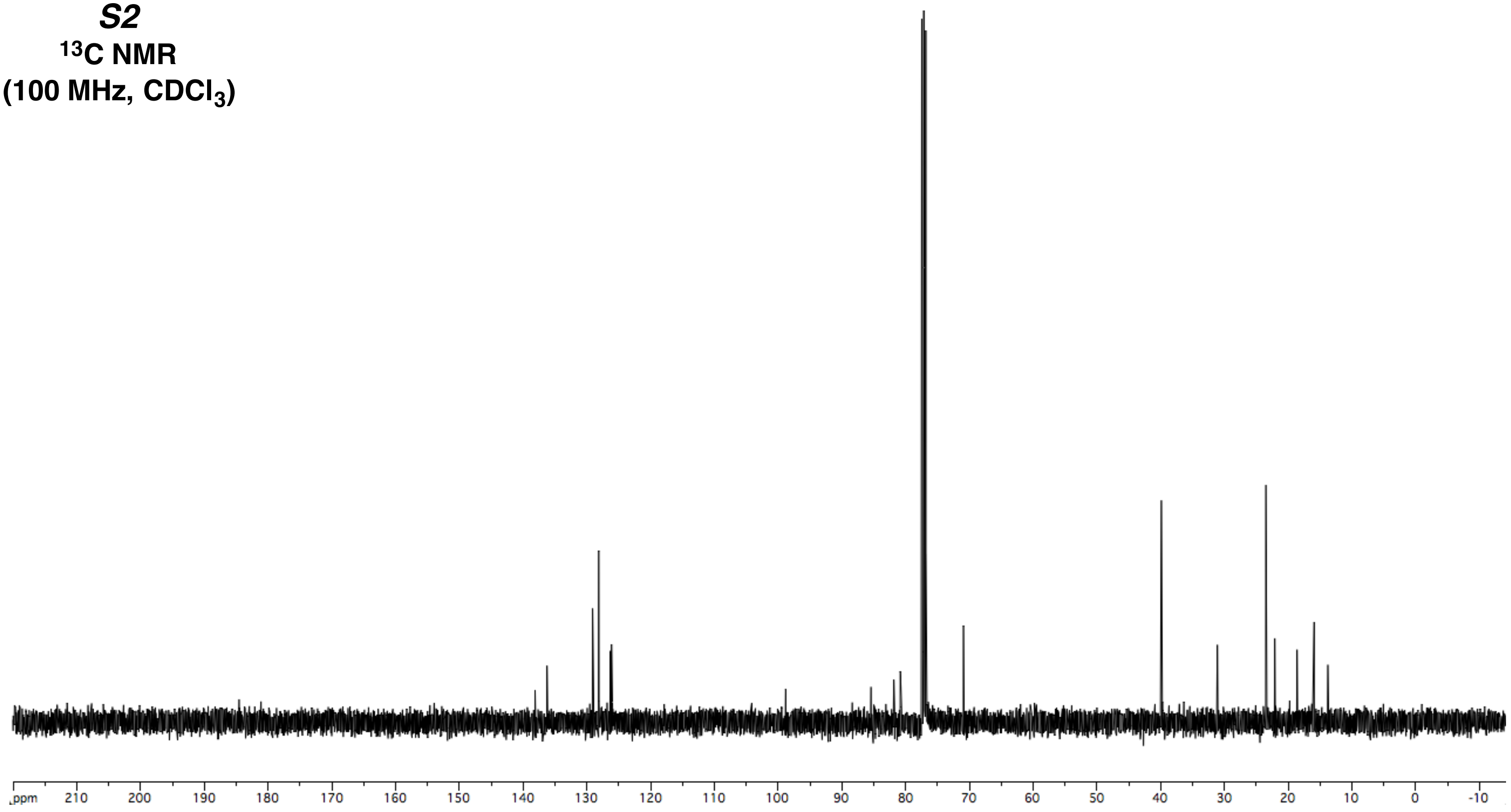


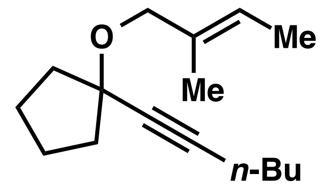


S2

^{13}C NMR

(100 MHz, $CDCl_3$)

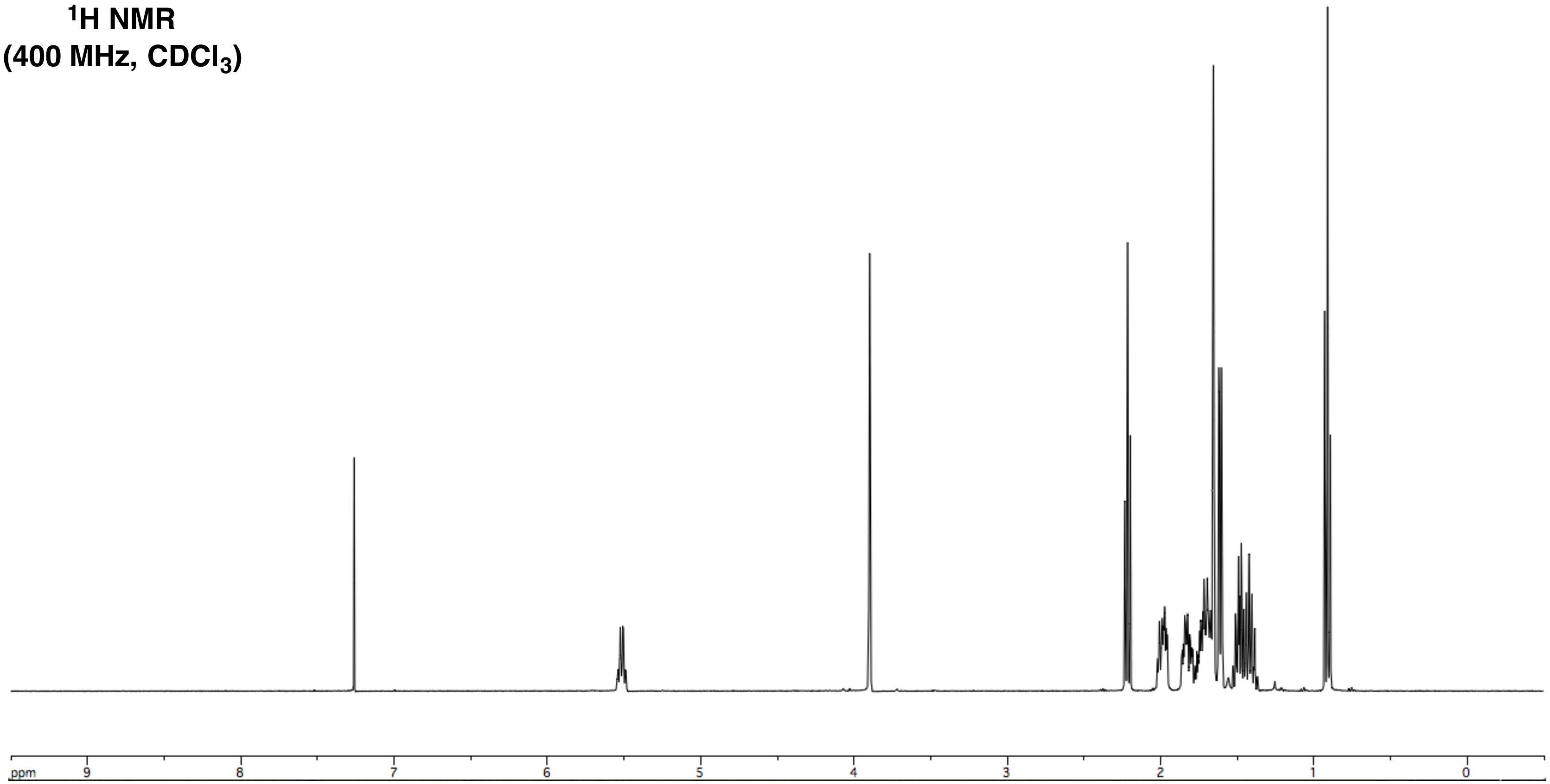


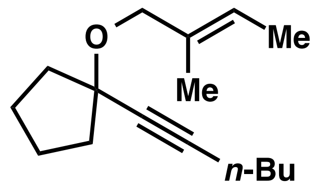


10

^{1}H NMR

(400 MHz, $CDCl_3$)

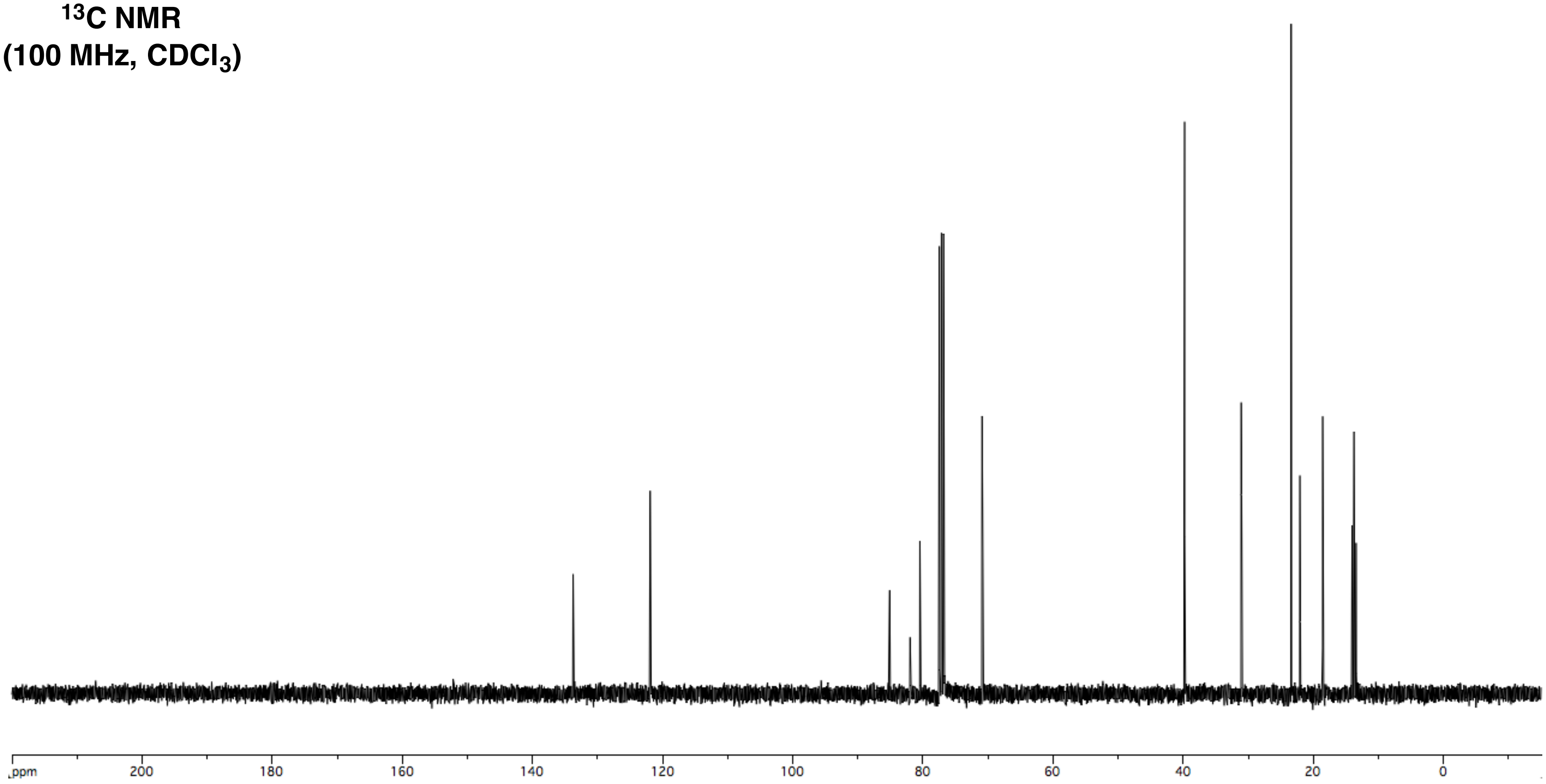


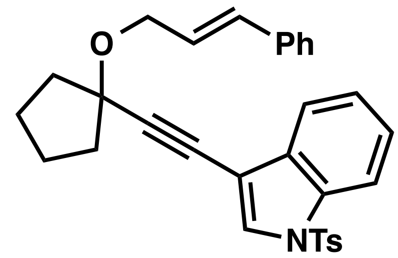


10

^{13}C NMR

(100 MHz, $CDCl_3$)

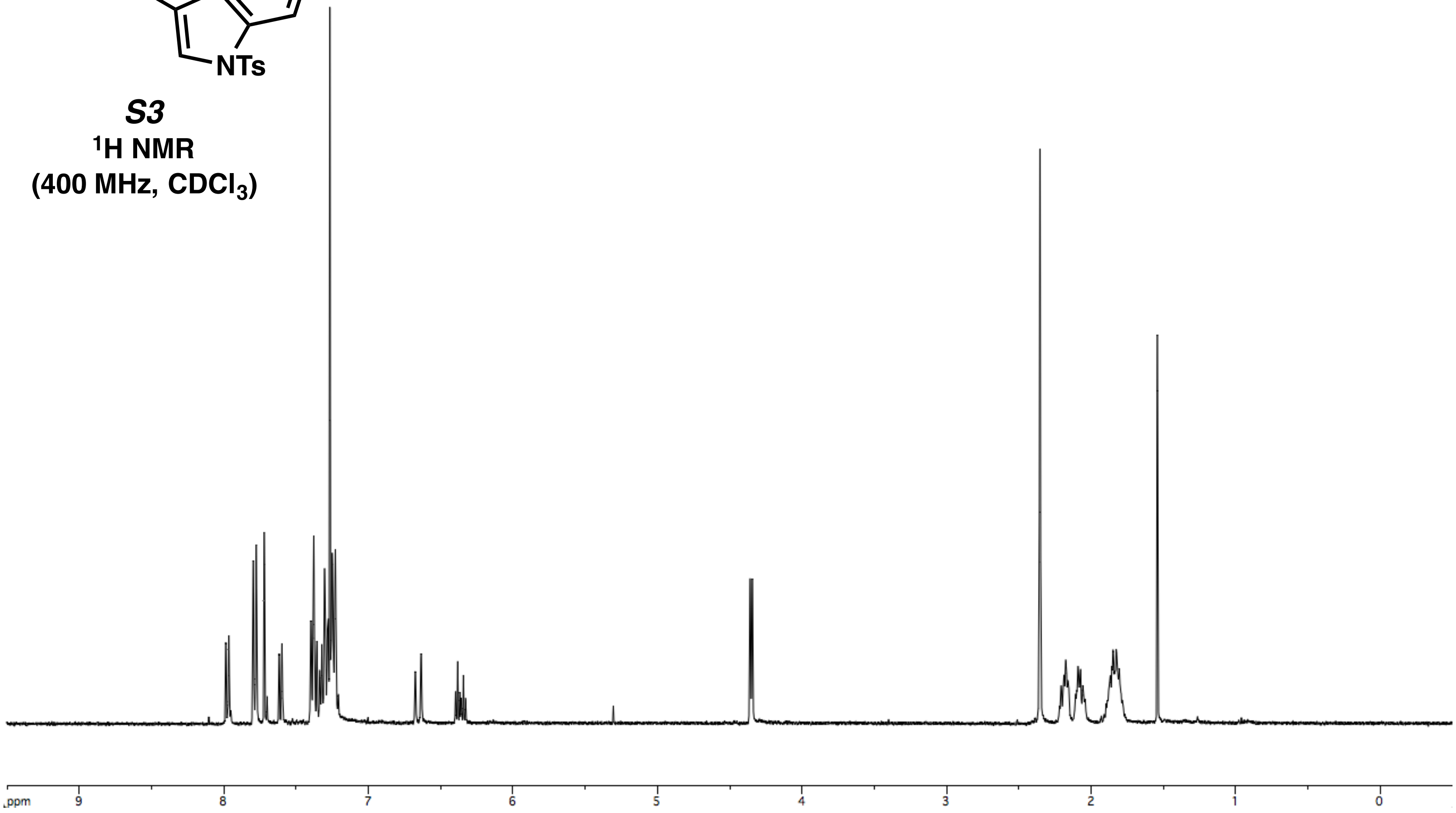


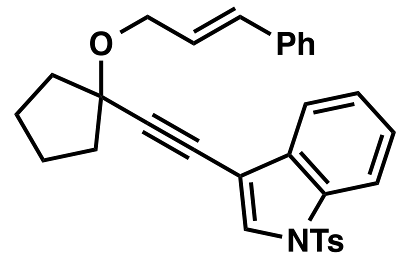


S3

^{1}H NMR

(400 MHz, $CDCl_3$)

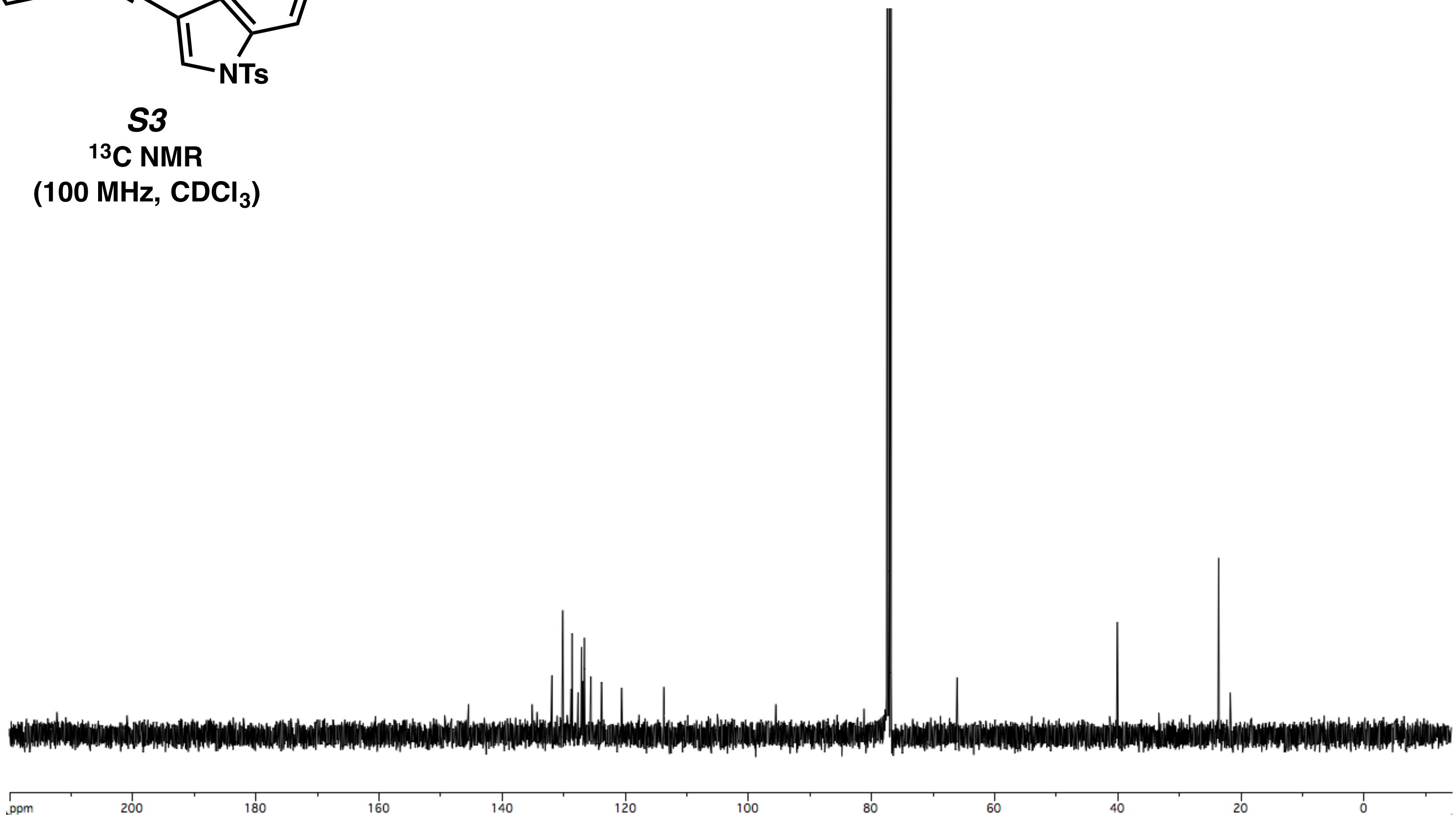


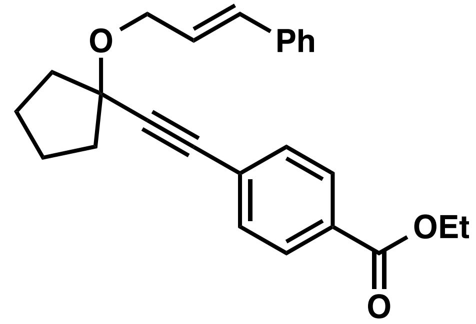


S3

^{13}C NMR

(100 MHz, CDCl$_3$)

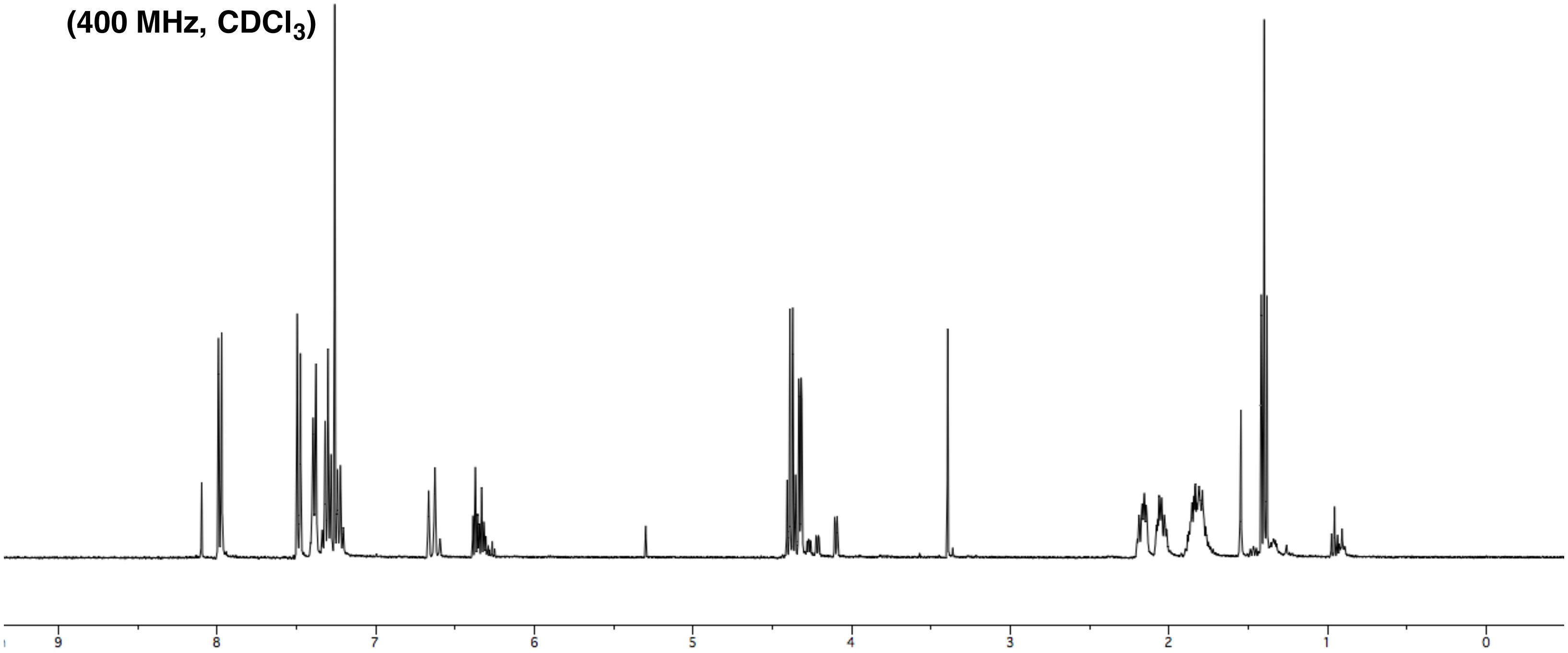


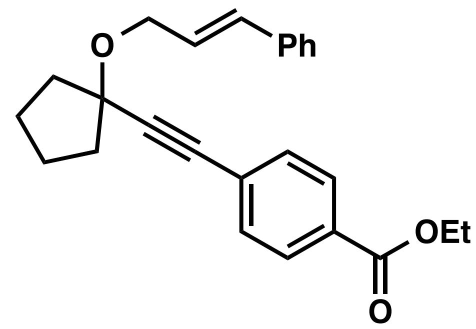


S4

^{1}H NMR

(400 MHz, $CDCl_3$)

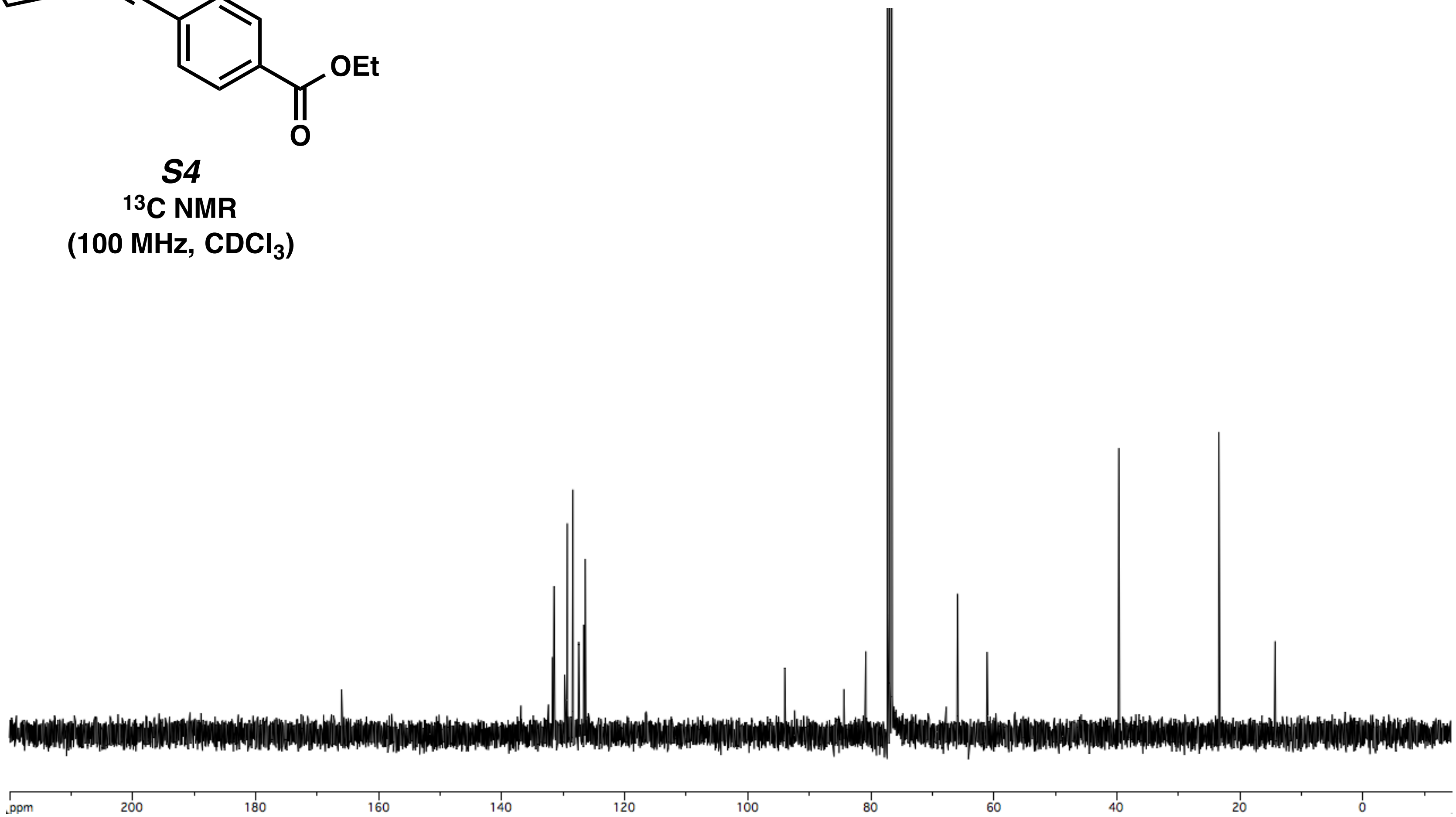


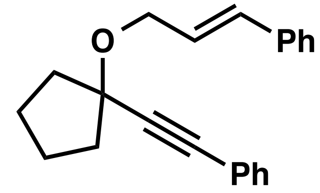


S4

^{13}C NMR

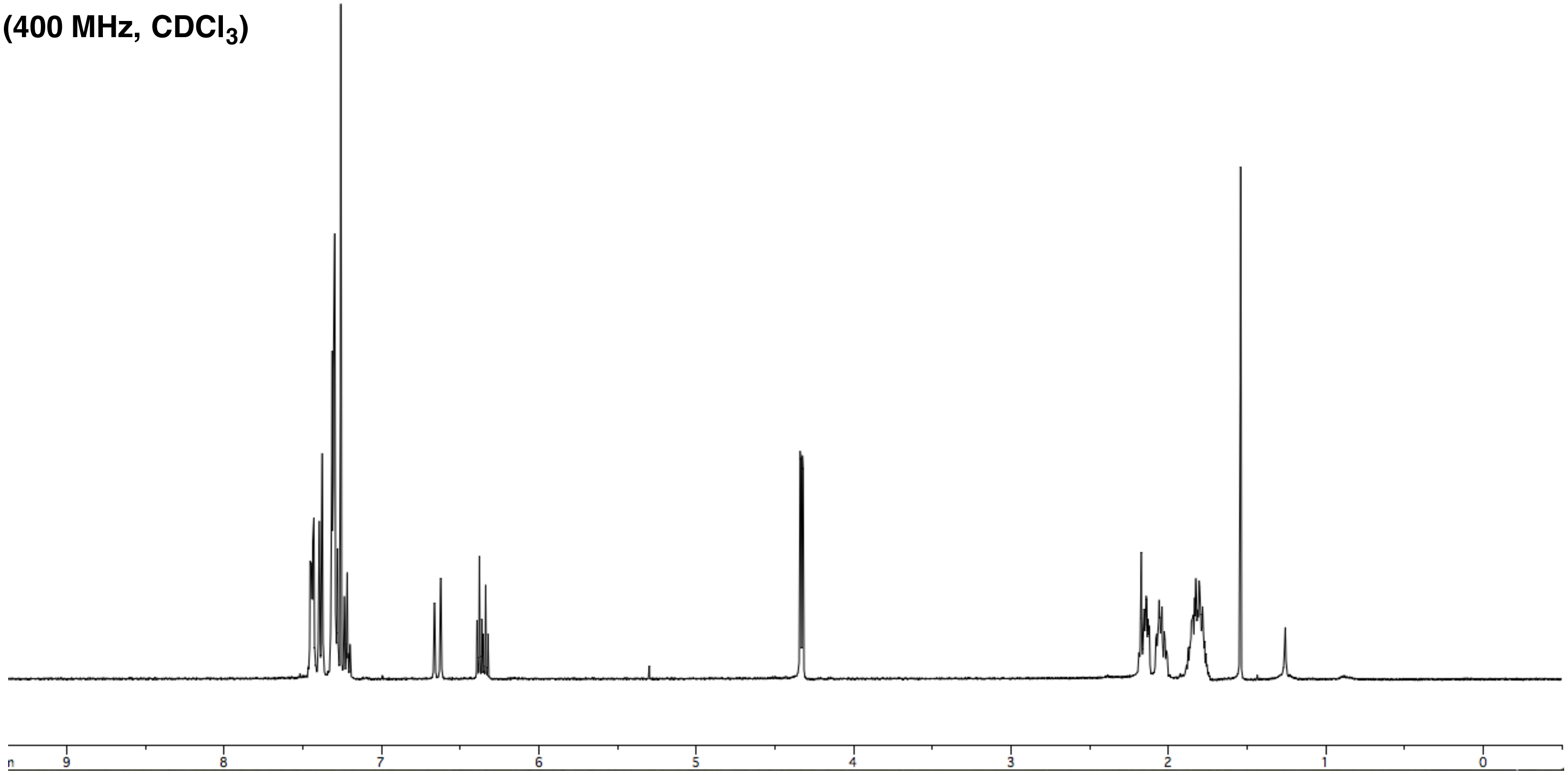
(100 MHz, $CDCl_3$)

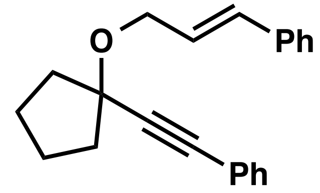




9

^{1}H NMR
(400 MHz, CDCl$_3$)

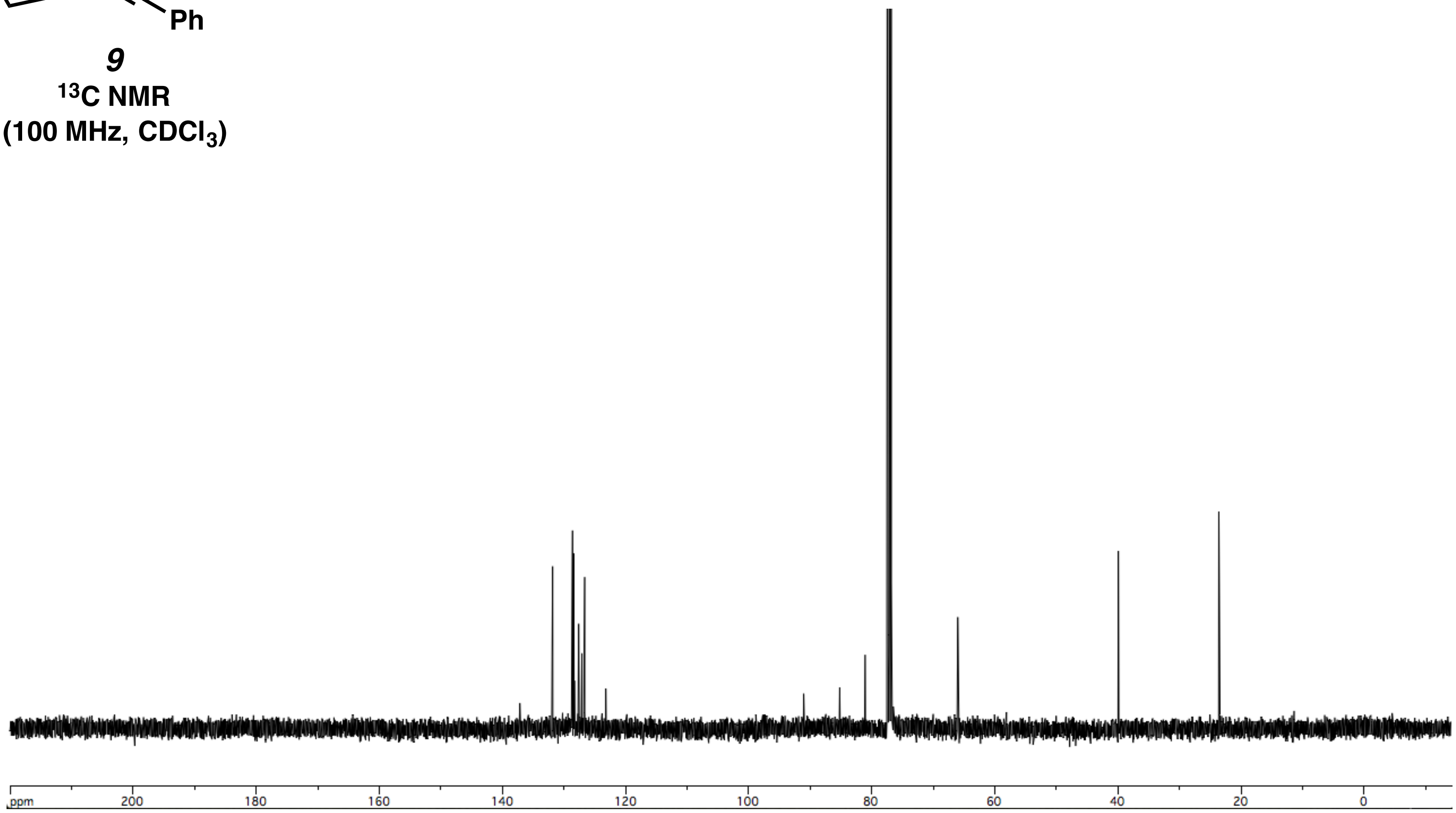


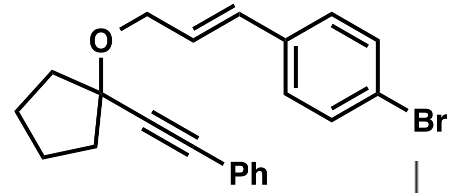


9

^{13}C NMR

(100 MHz, $CDCl_3$)

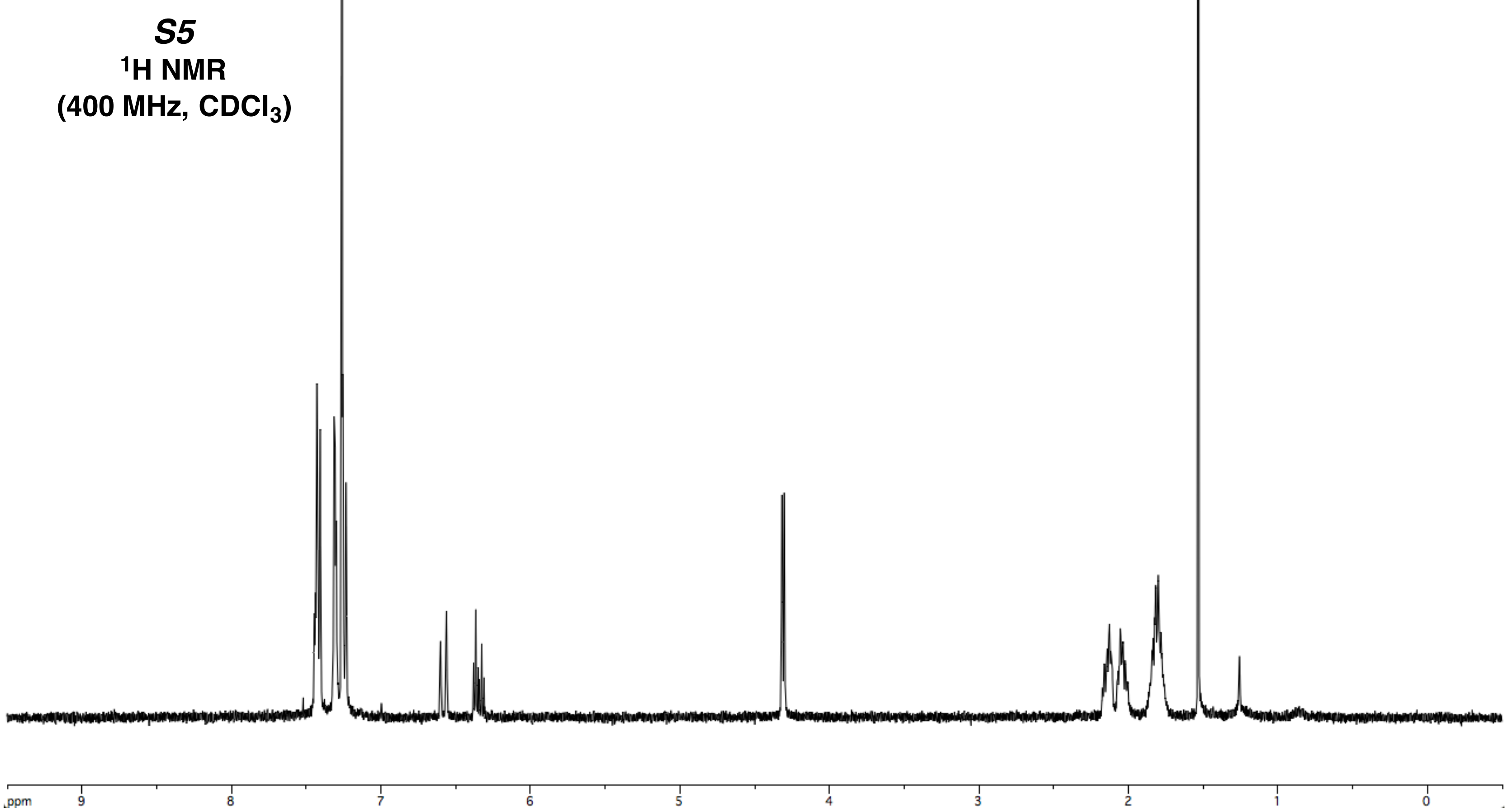


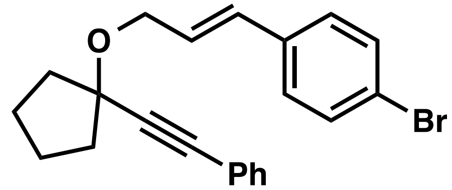


S5

^{1}H NMR

(400 MHz, $CDCl_3$)

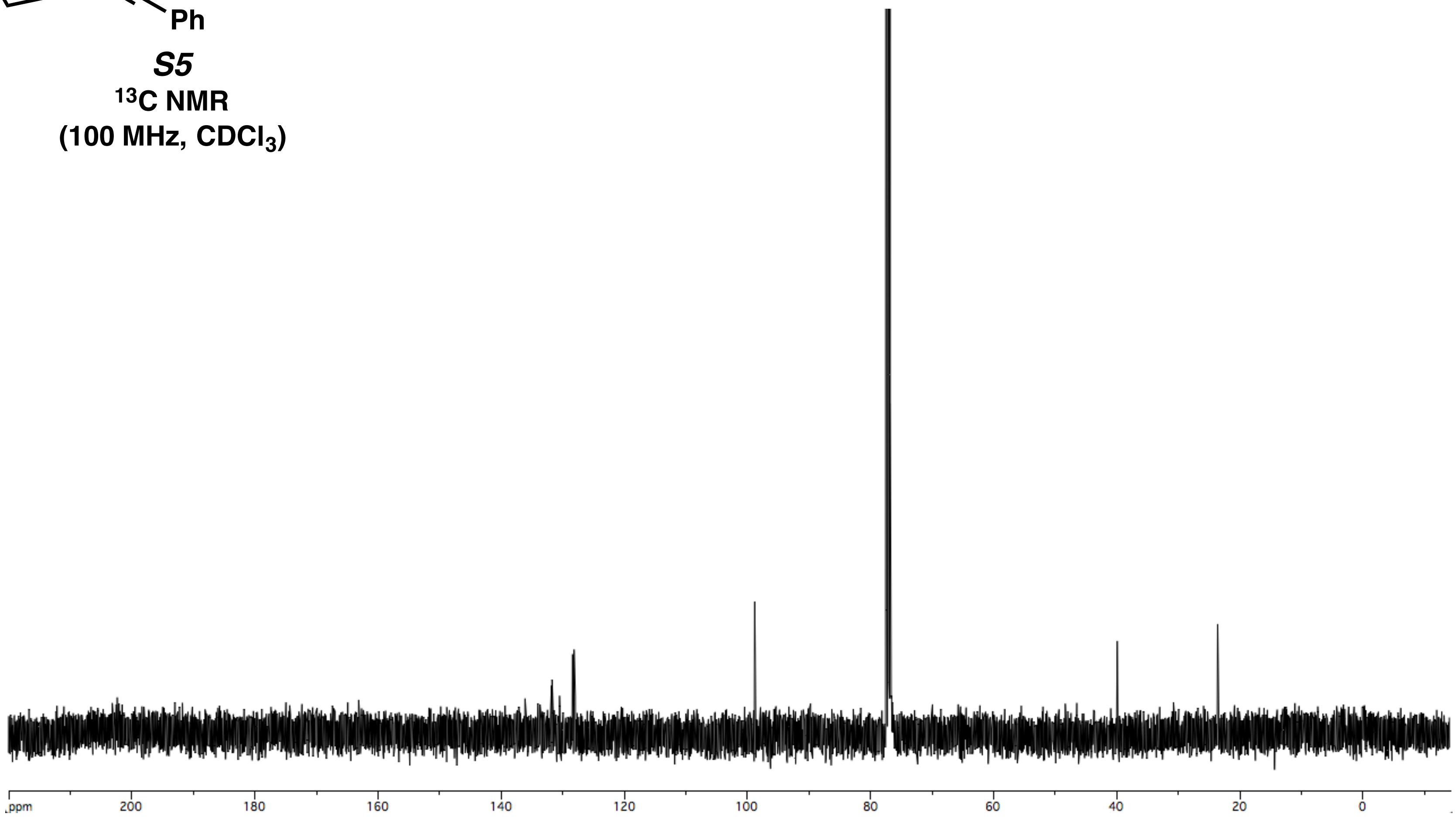


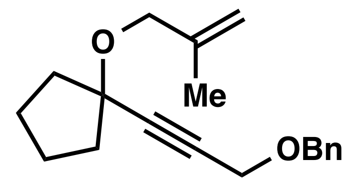


S5

^{13}C NMR

(100 MHz, CDCl$_3$)

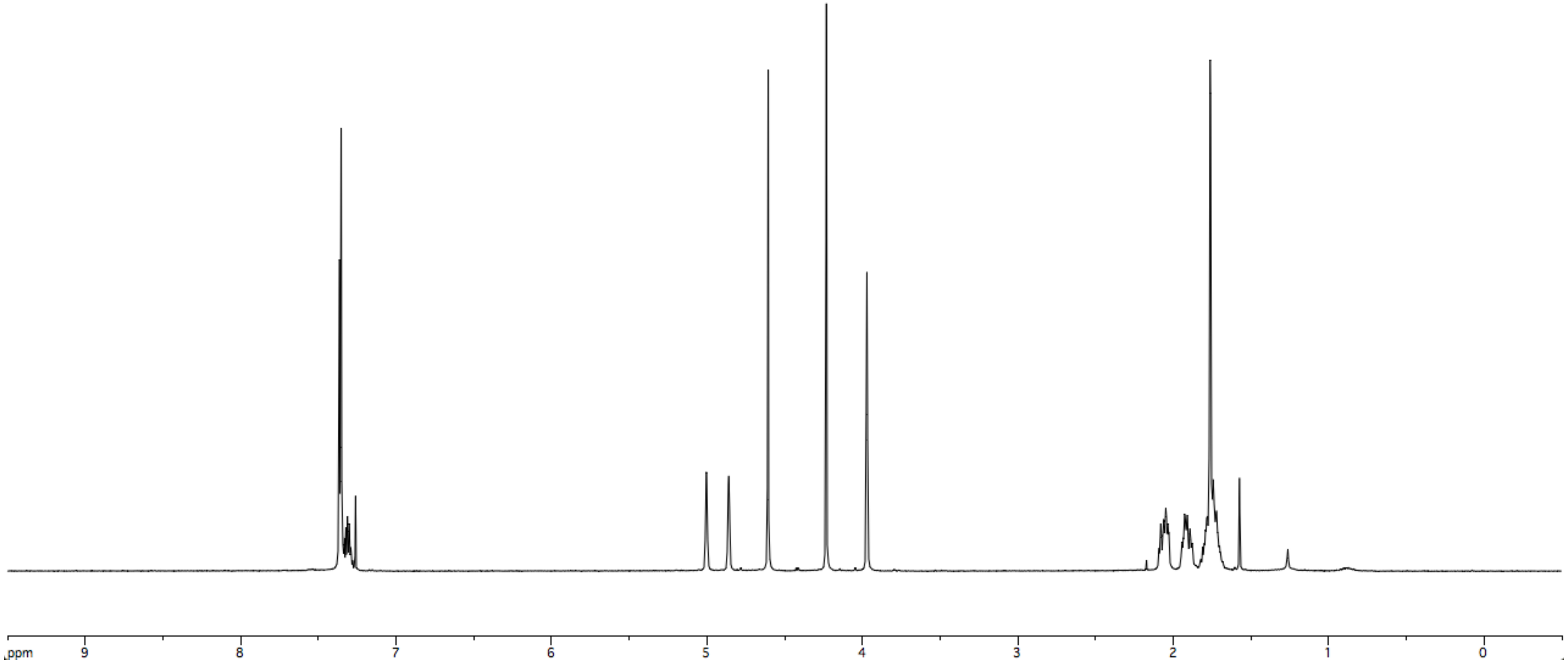


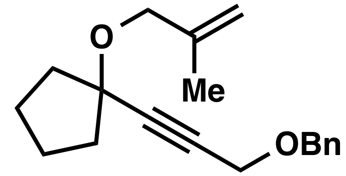


S6

^{1}H NMR

(400 MHz, $CDCl_3$)

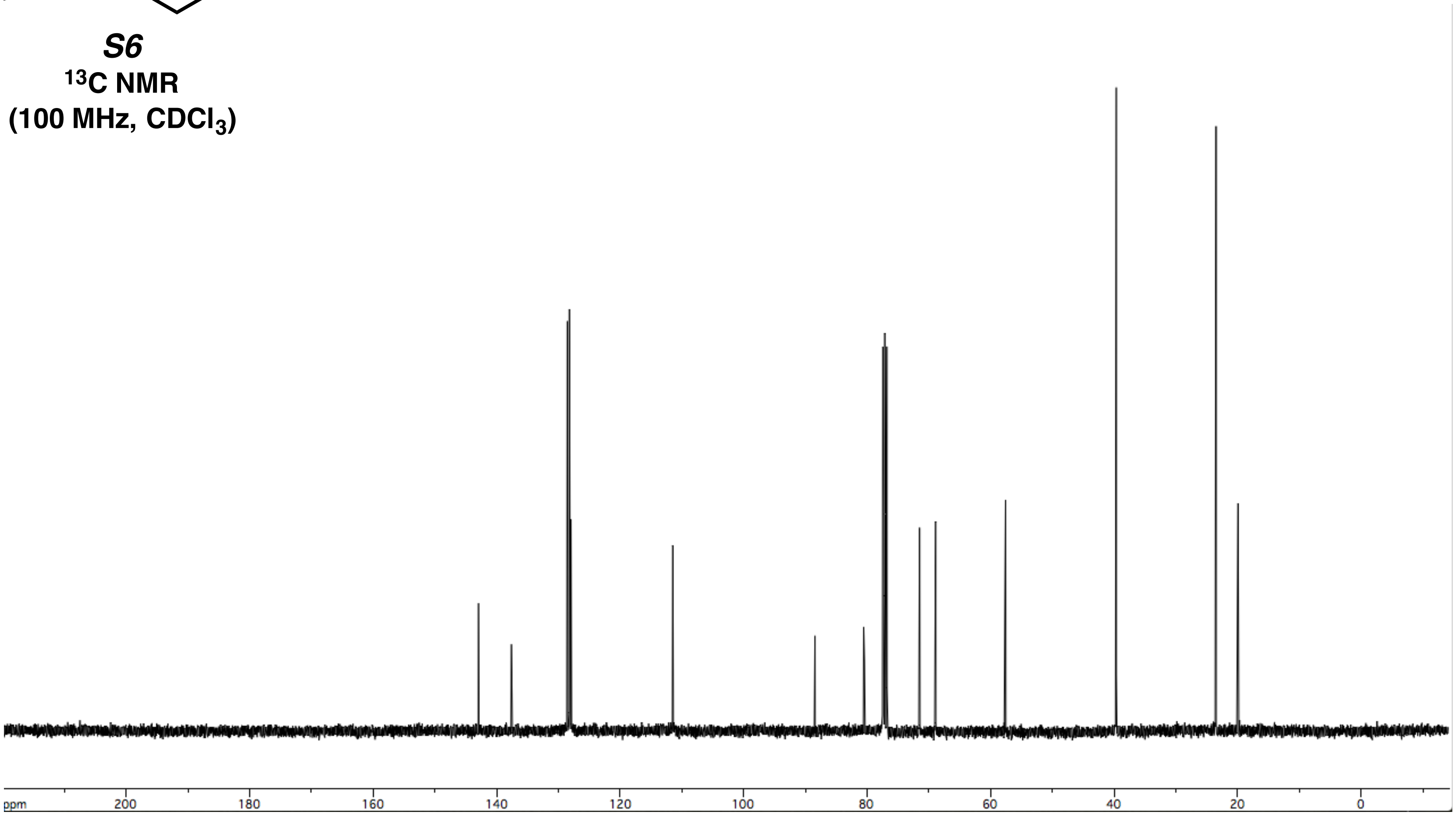


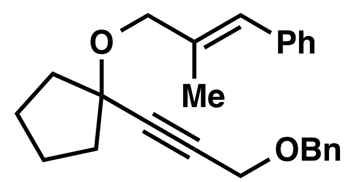


S6

^{13}C NMR

(100 MHz, $CDCl_3$)

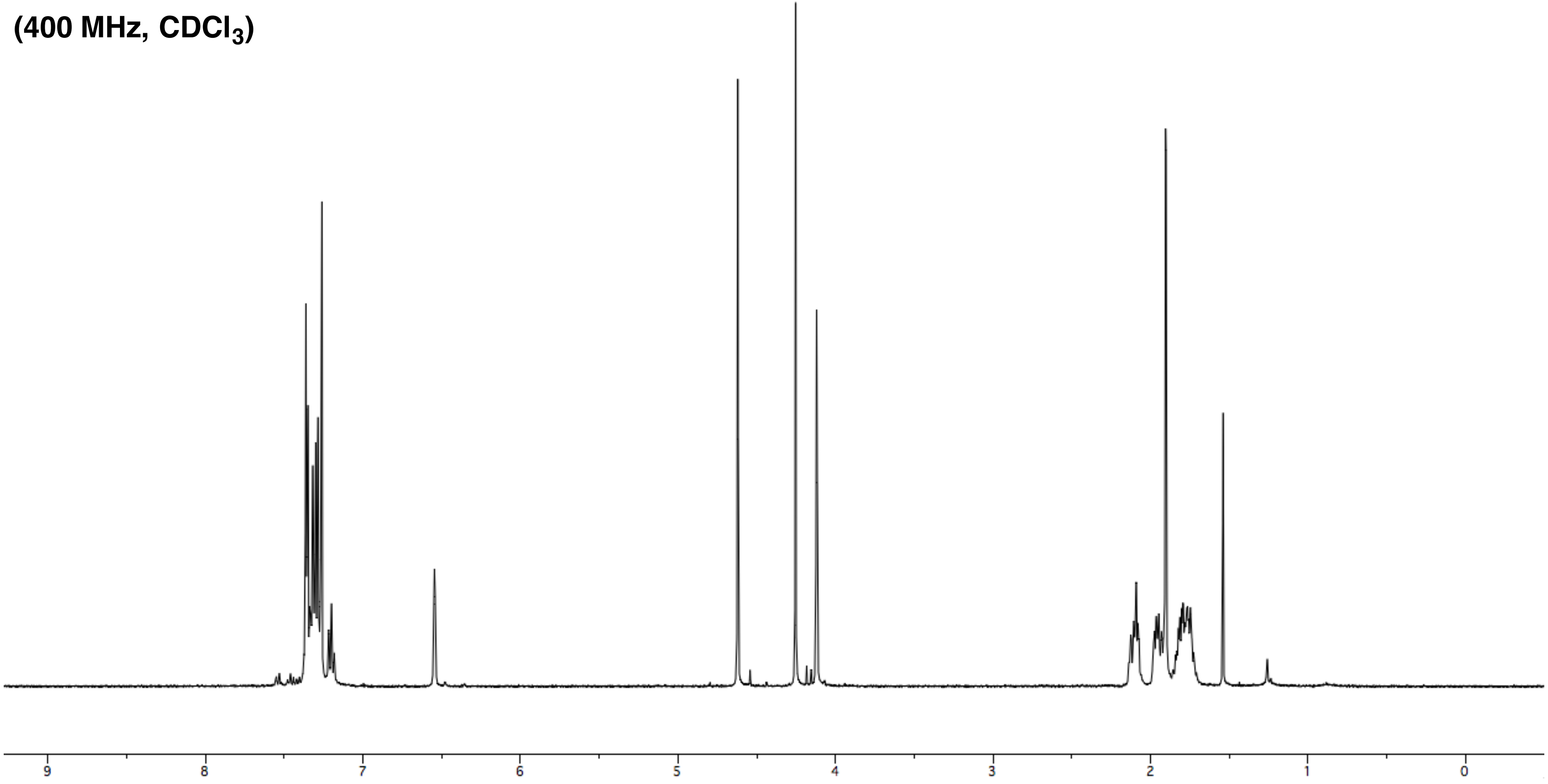


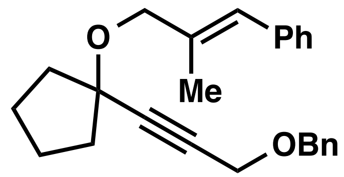


S7

^{1}H NMR

(400 MHz, $CDCl_3$)

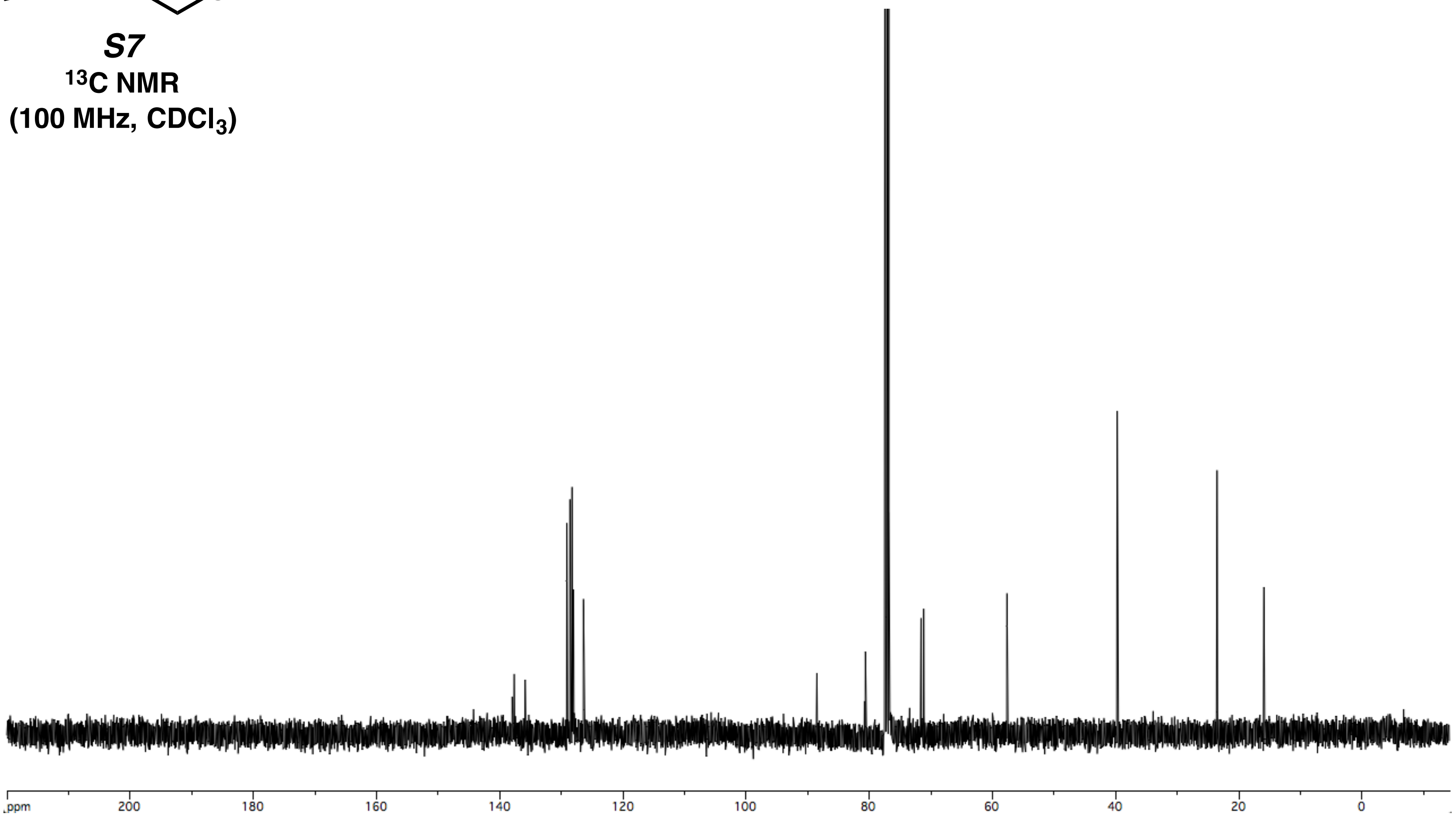


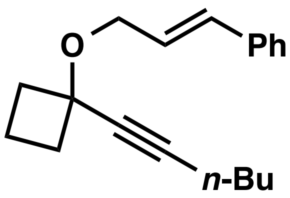


S7

^{13}C NMR

(100 MHz, $CDCl_3$)

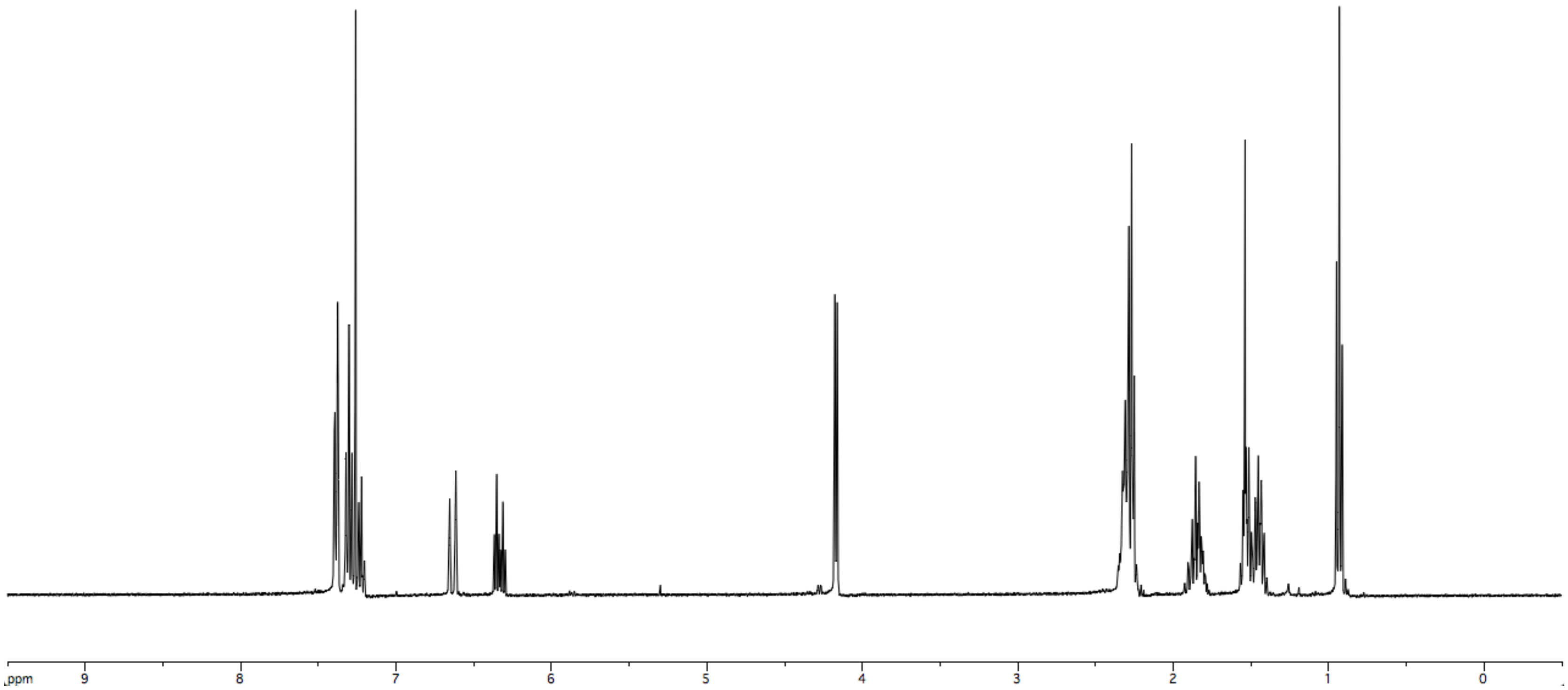


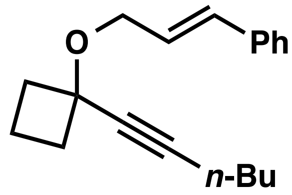


S8

^{1}H NMR

(400 MHz, $CDCl_3$)

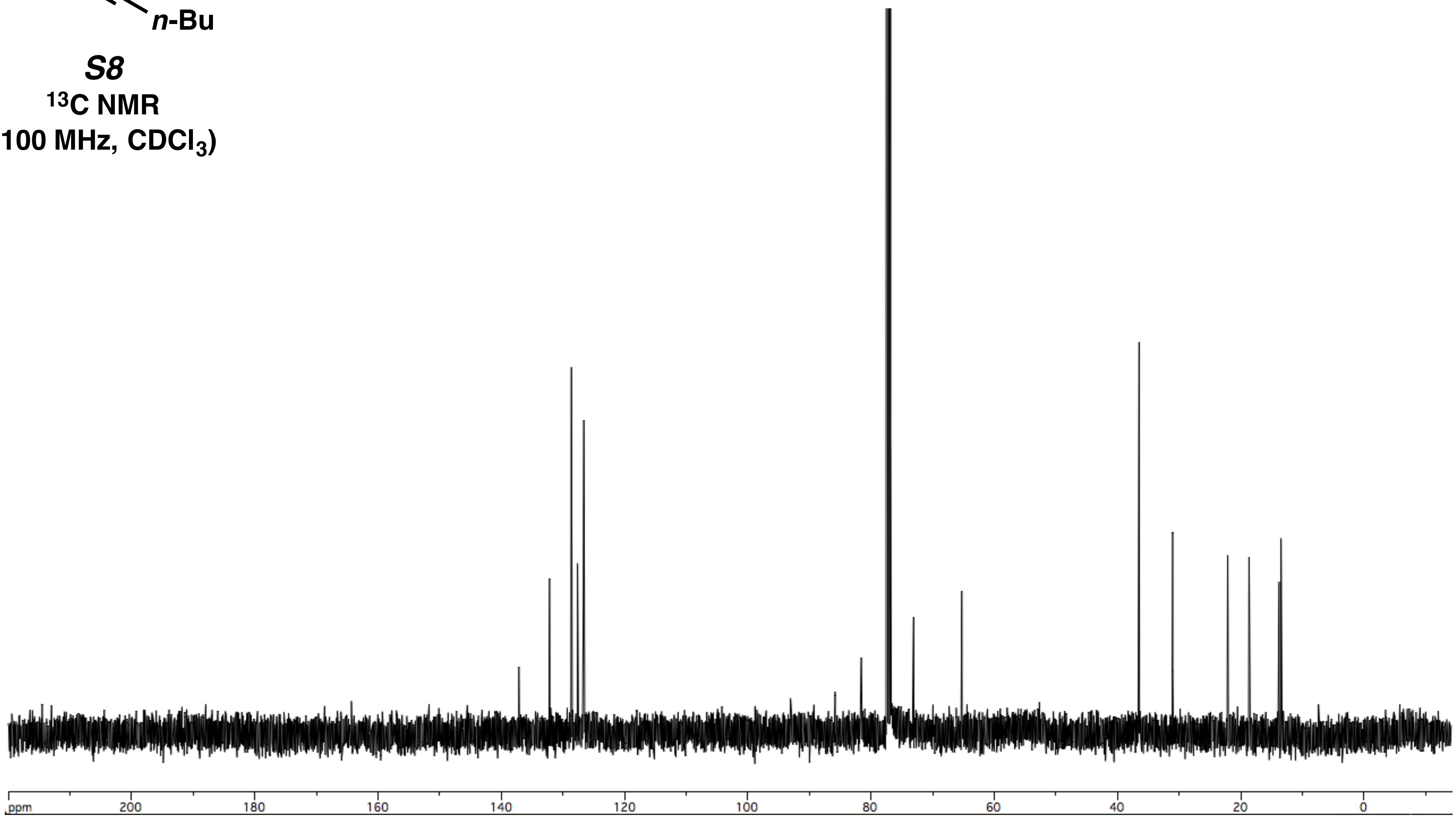


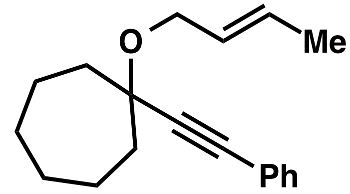


S8

^{13}C NMR

(100 MHz, $CDCl_3$)

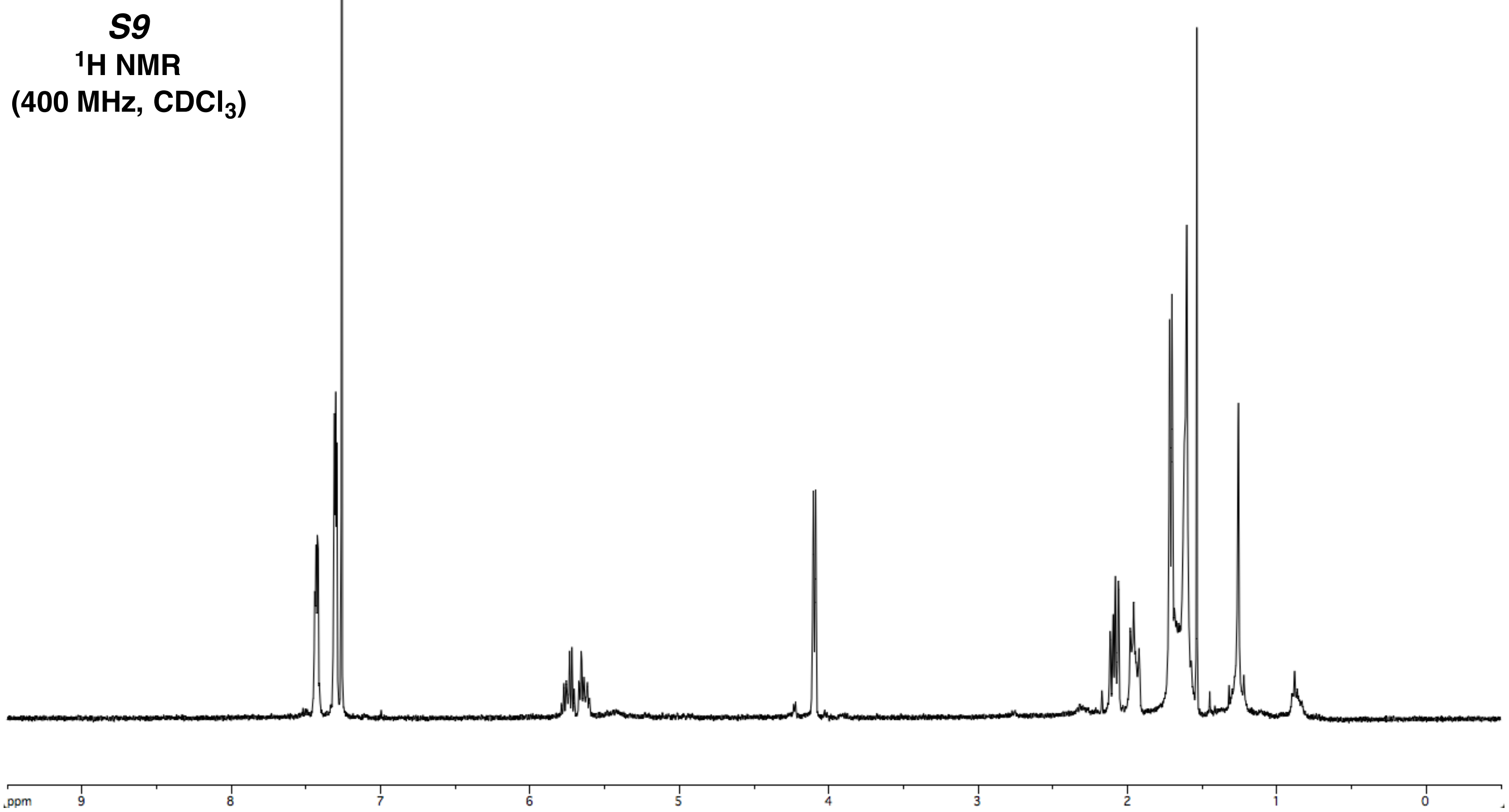


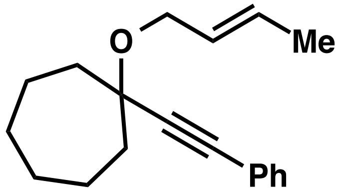


S9

^{1}H NMR

(400 MHz, $CDCl_3$)

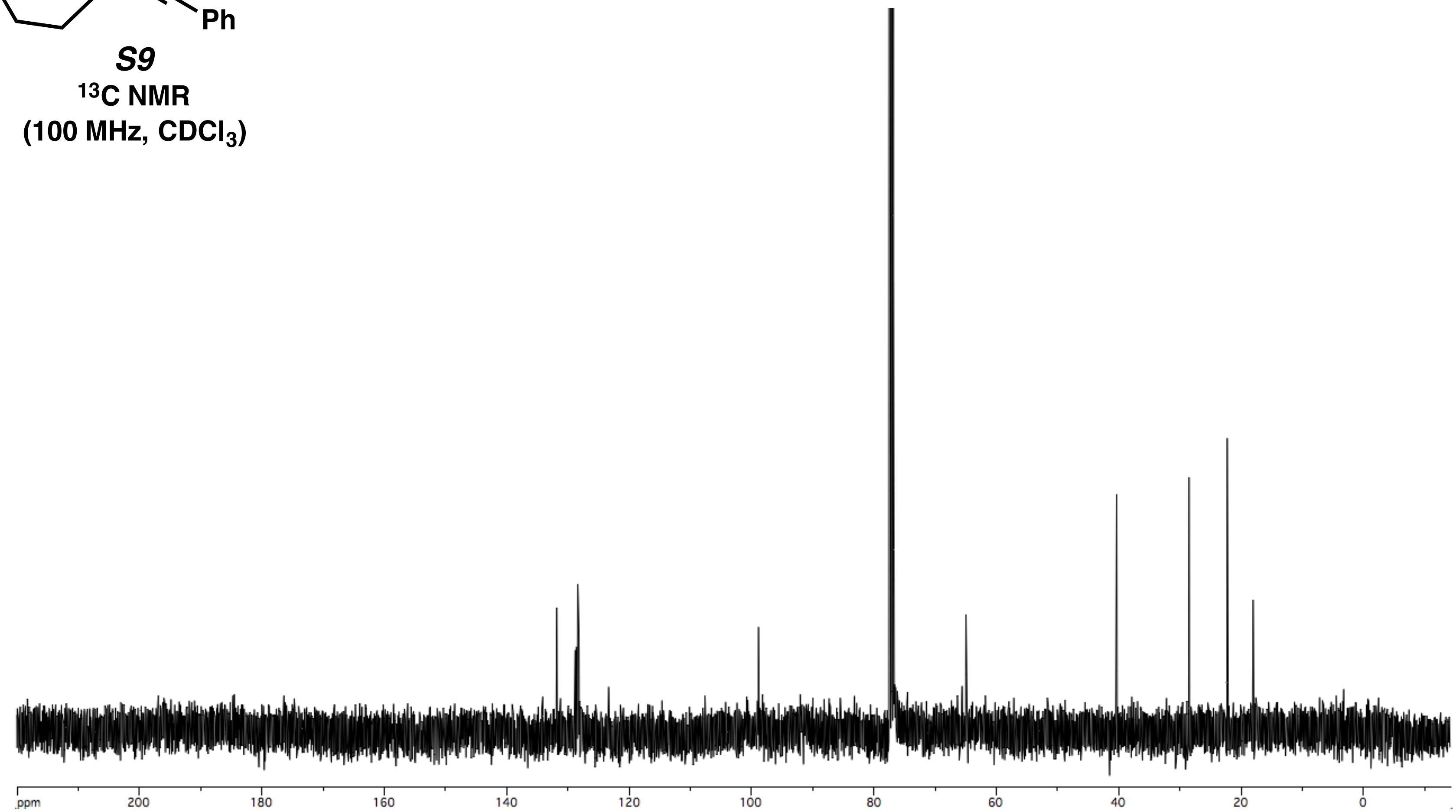


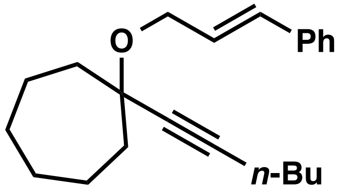


S9

^{13}C NMR

(100 MHz, $CDCl_3$)

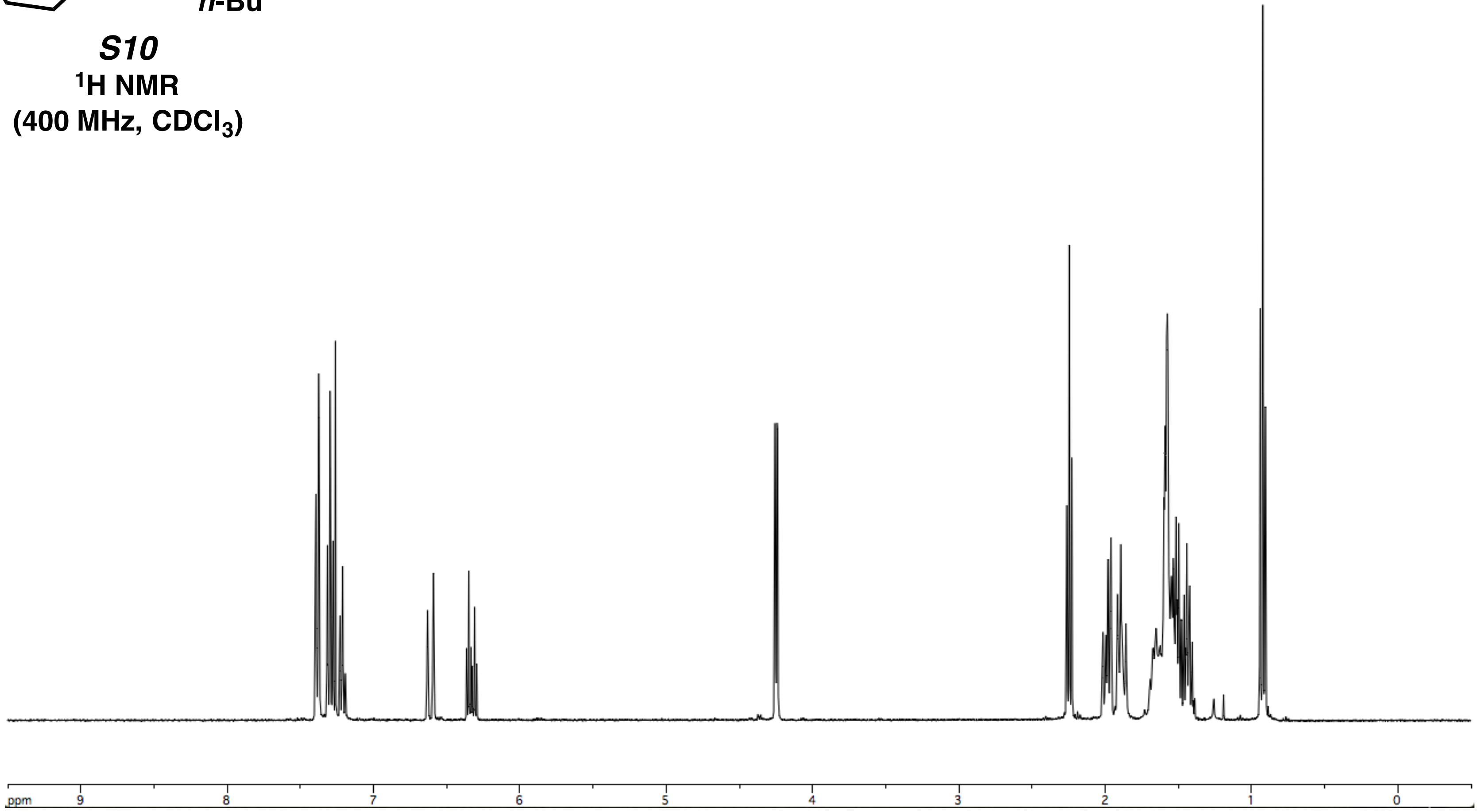


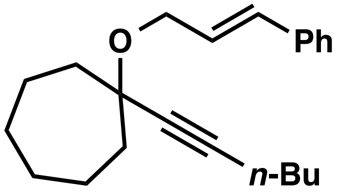


S10

^{1}H NMR

(400 MHz, $CDCl_3$)

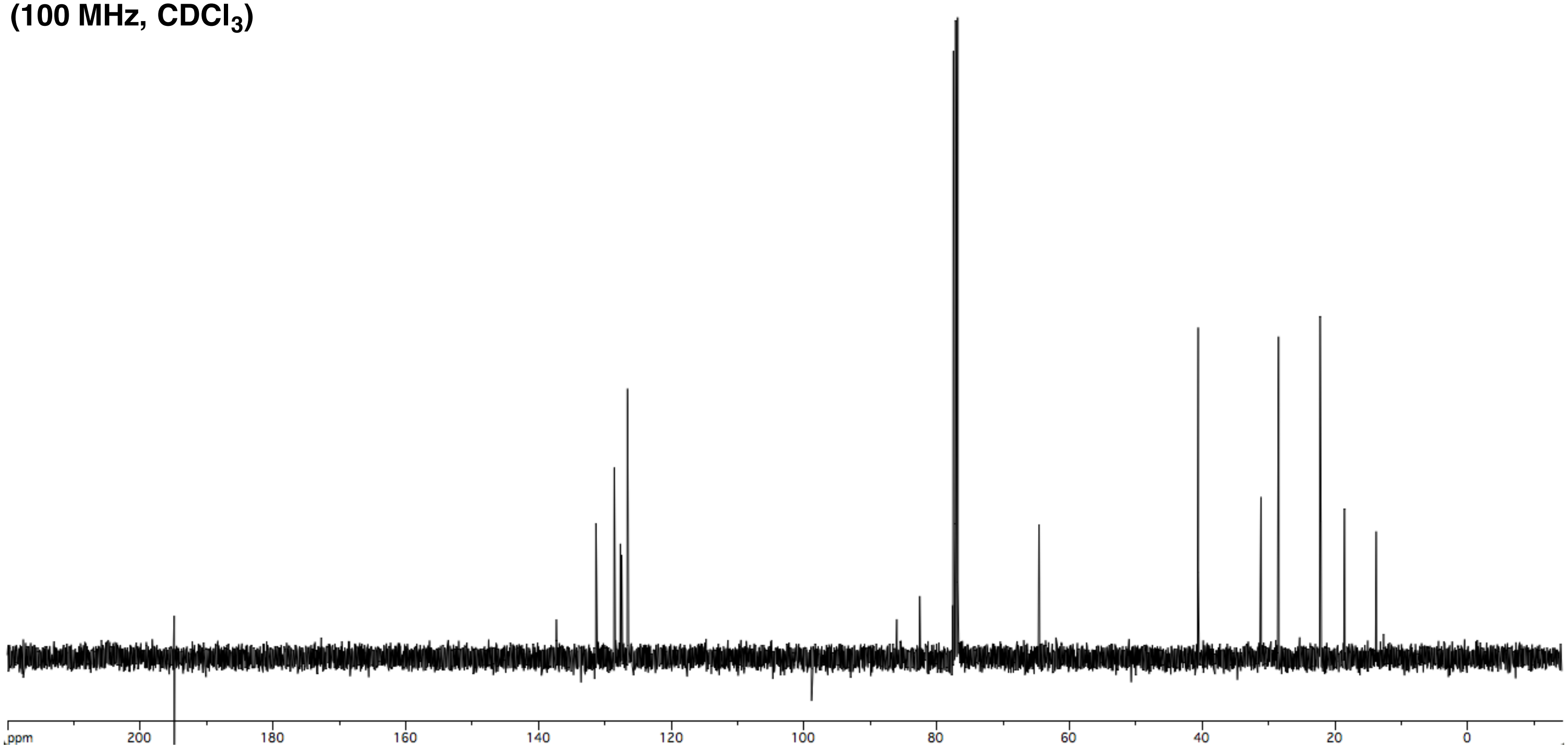


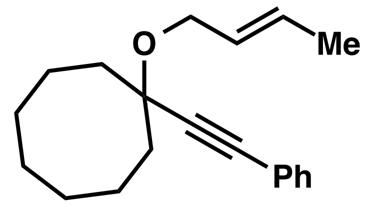


S10

^{13}C NMR

(100 MHz, $CDCl_3$)

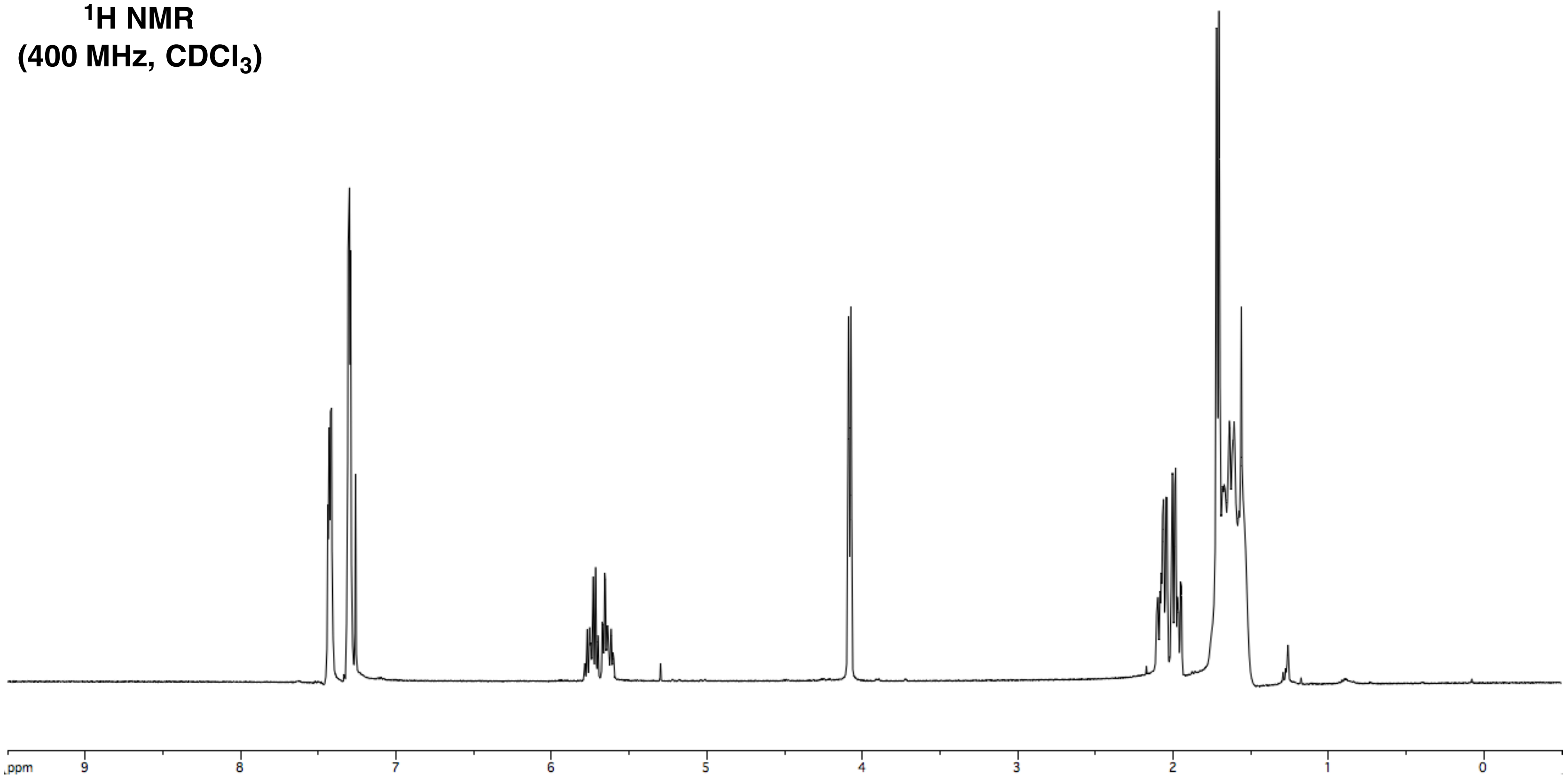


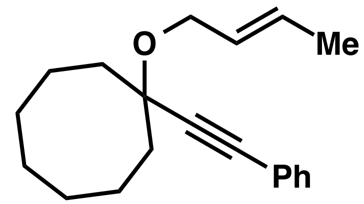


S11

^{1}H NMR

(400 MHz, $CDCl_3$)

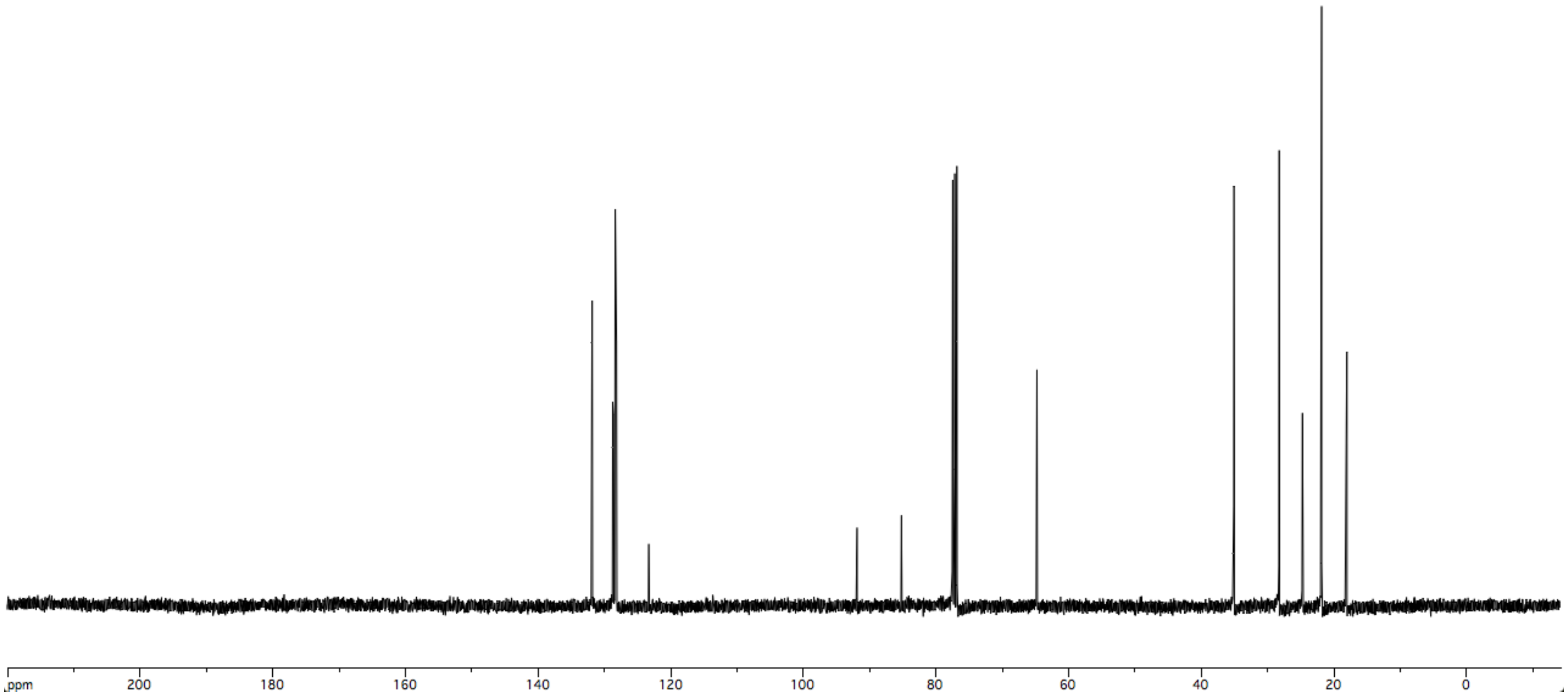


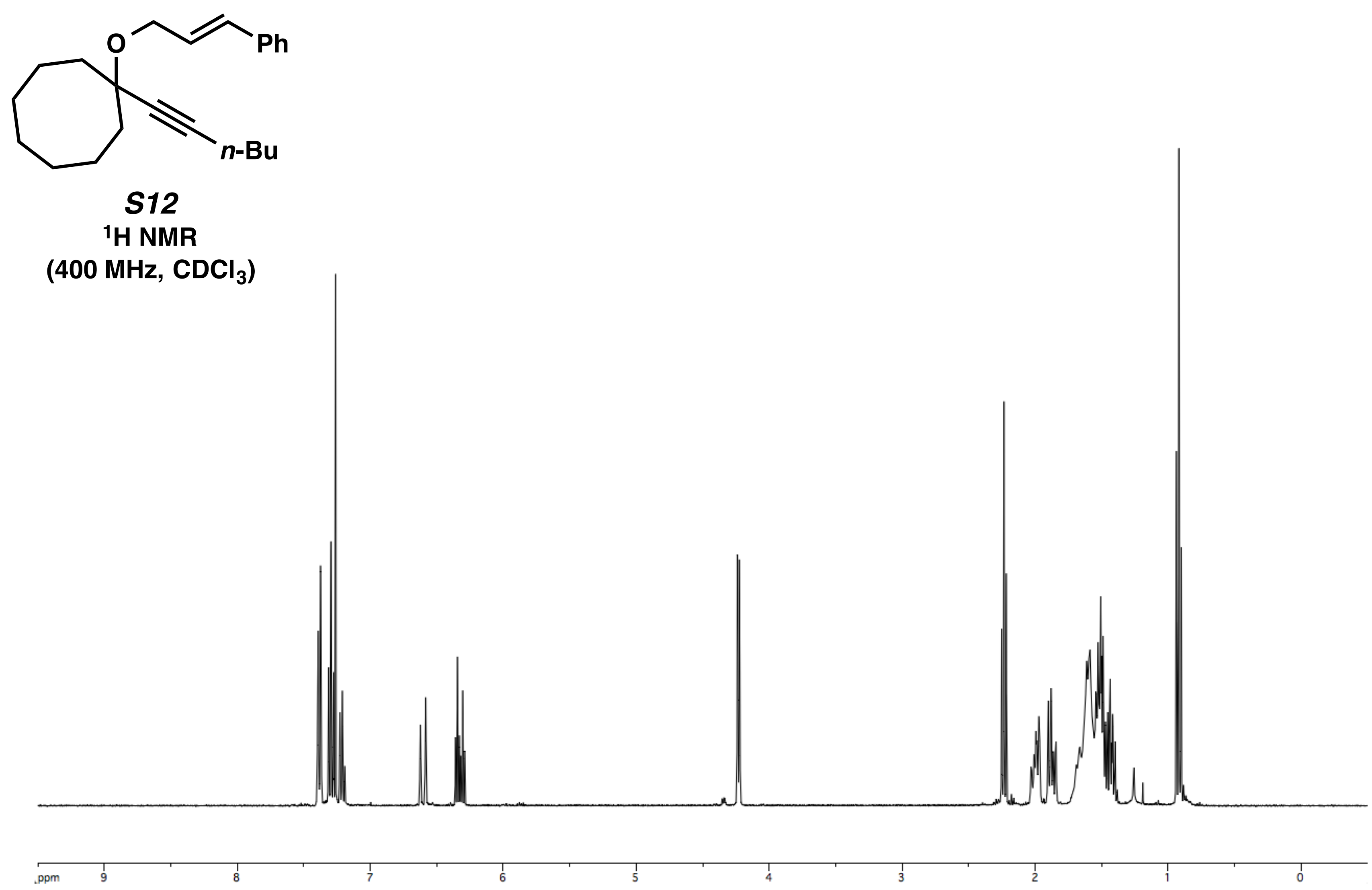


S11

^{13}C NMR

(100 MHz, $CDCl_3$)

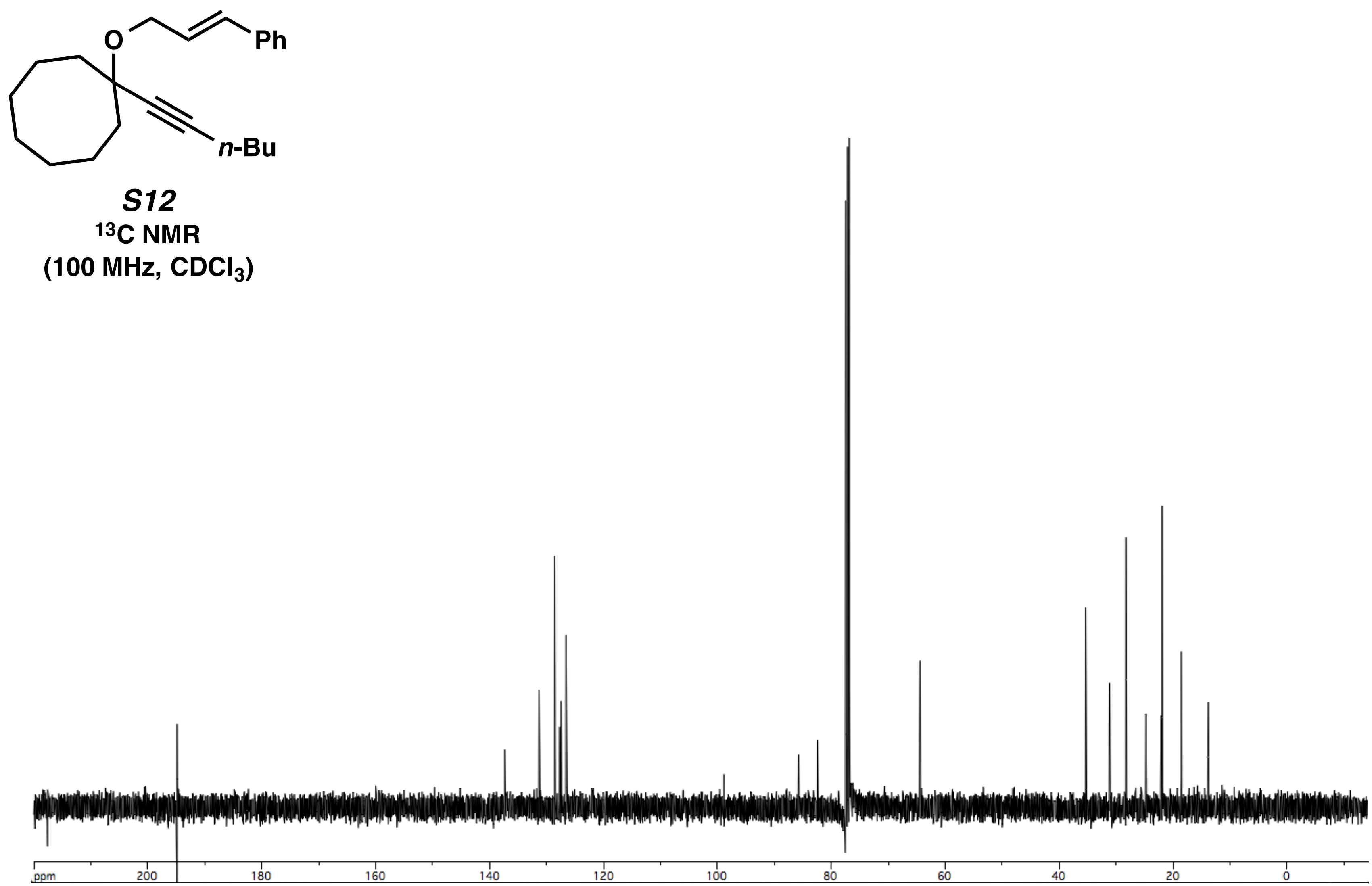




S12

^{1}H NMR

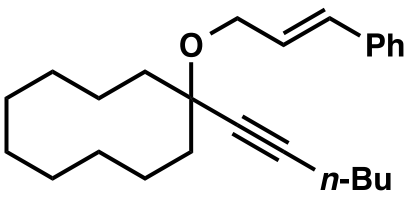
(400 MHz, $CDCl_3$)



S12

^{13}C NMR

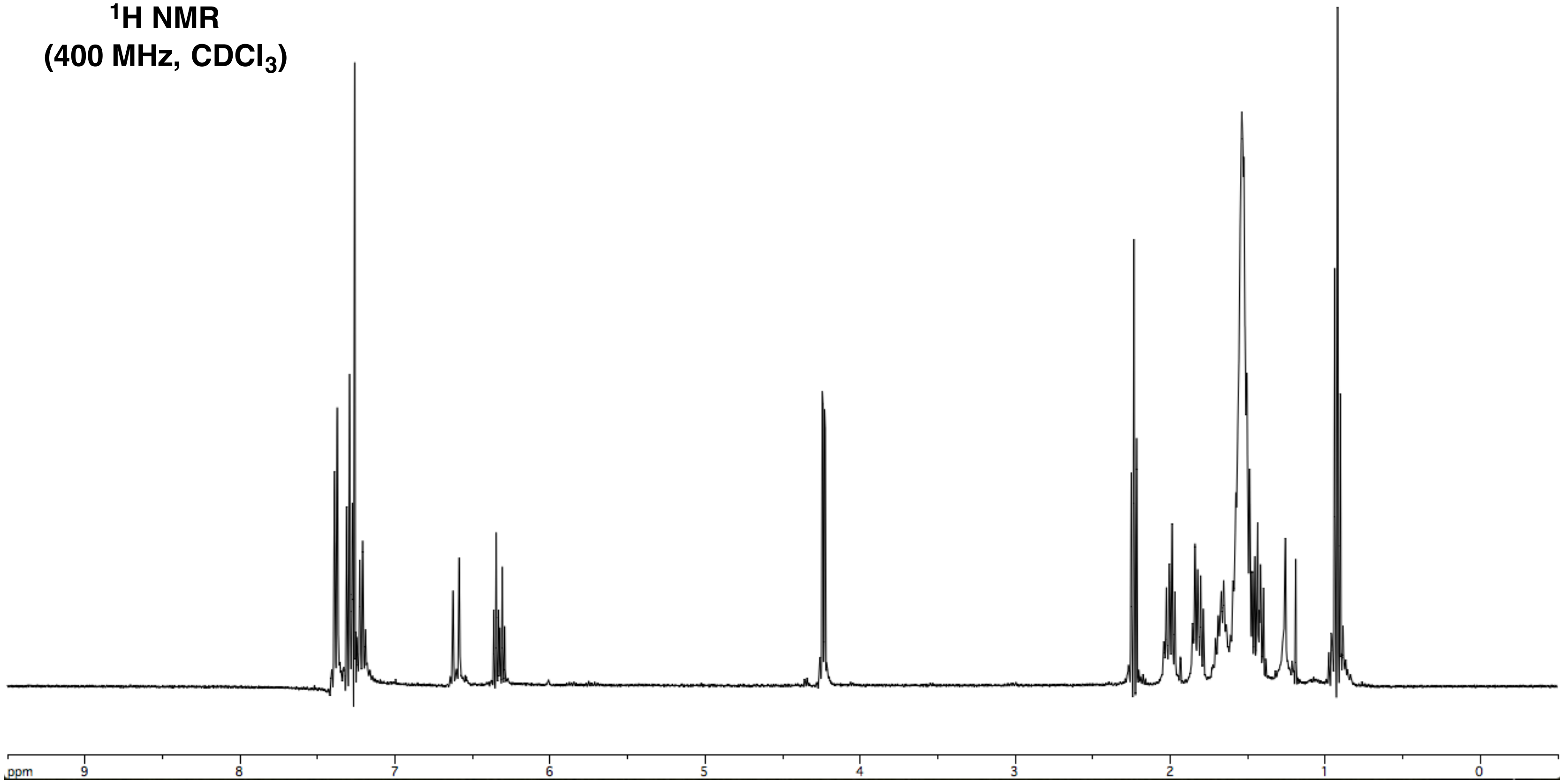
(100 MHz, $CDCl_3$)

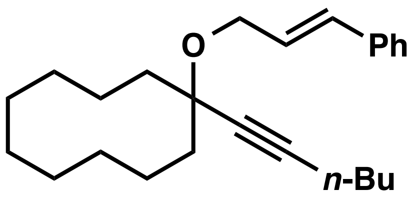


S13

^{1}H NMR

(400 MHz, $CDCl_3$)

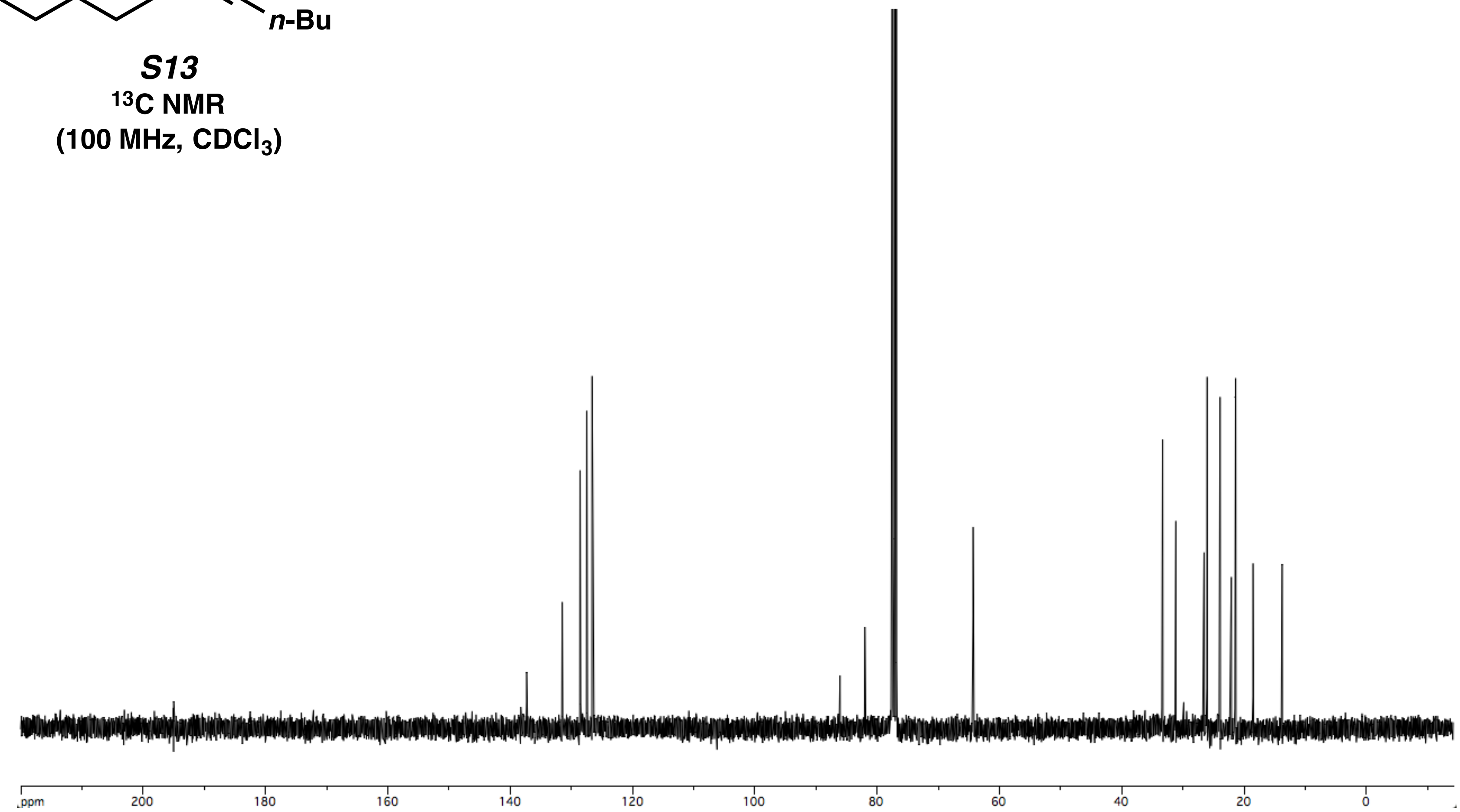


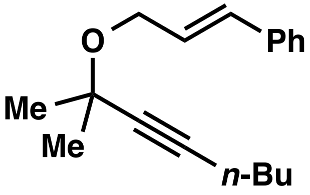


S13

^{13}C NMR

(100 MHz, $CDCl_3$)

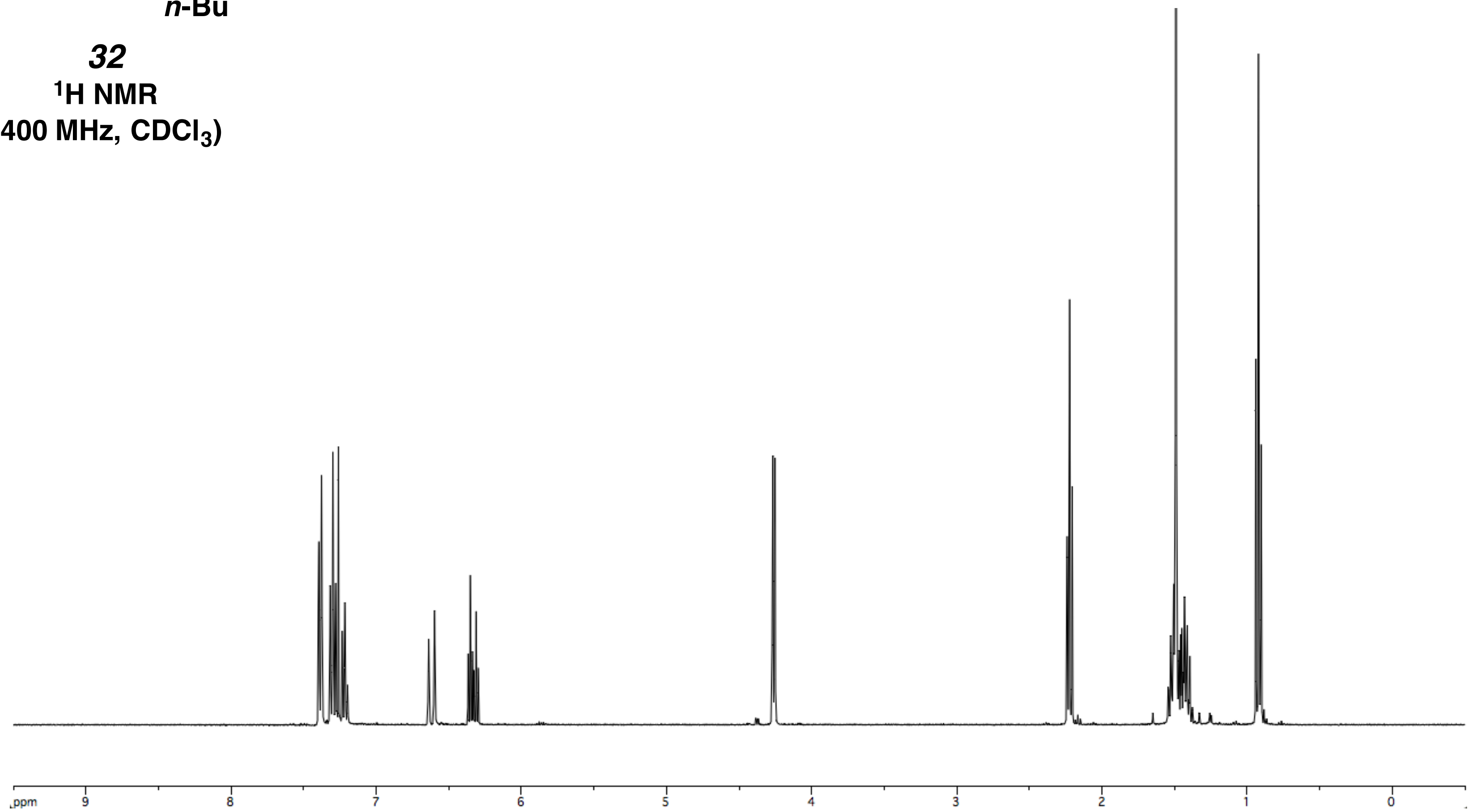


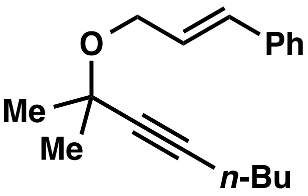


32

^{1}H NMR

(400 MHz, $CDCl_3$)

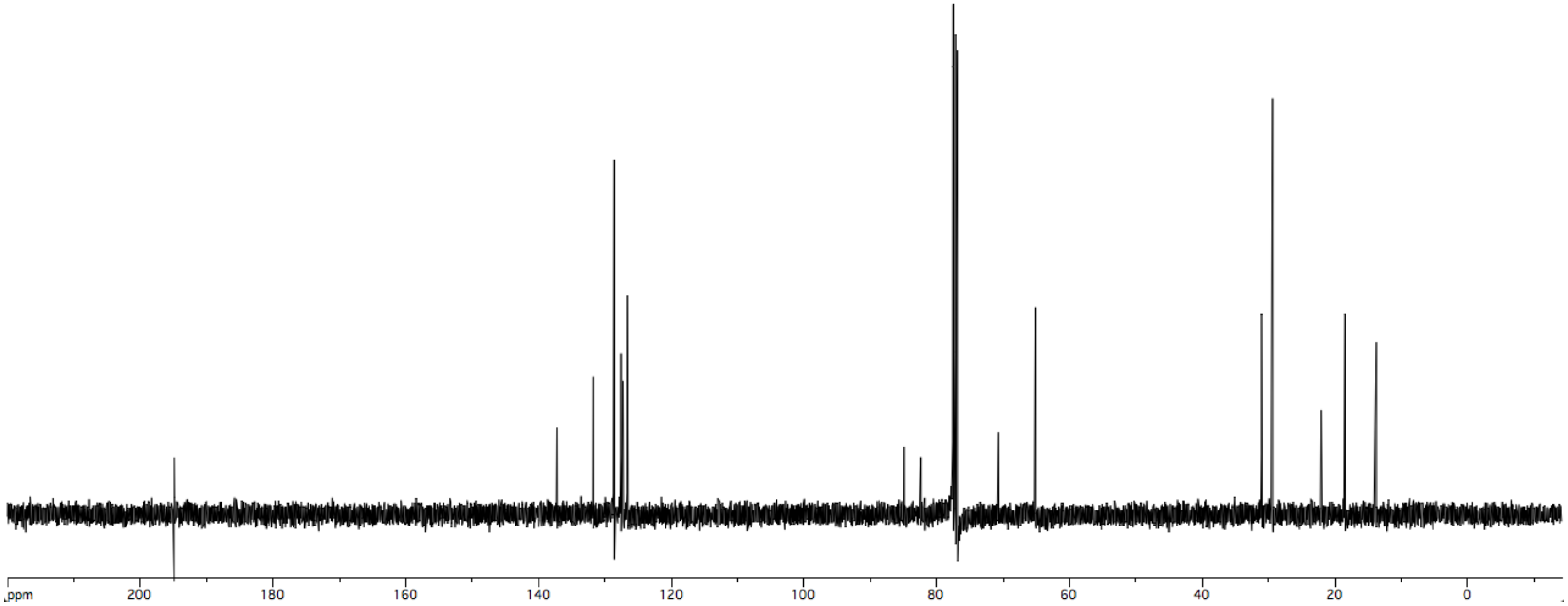


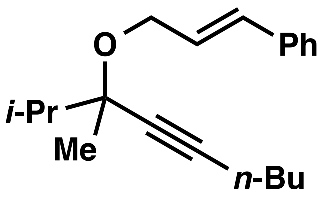


32

^{13}C NMR

(100 MHz, $CDCl_3$)

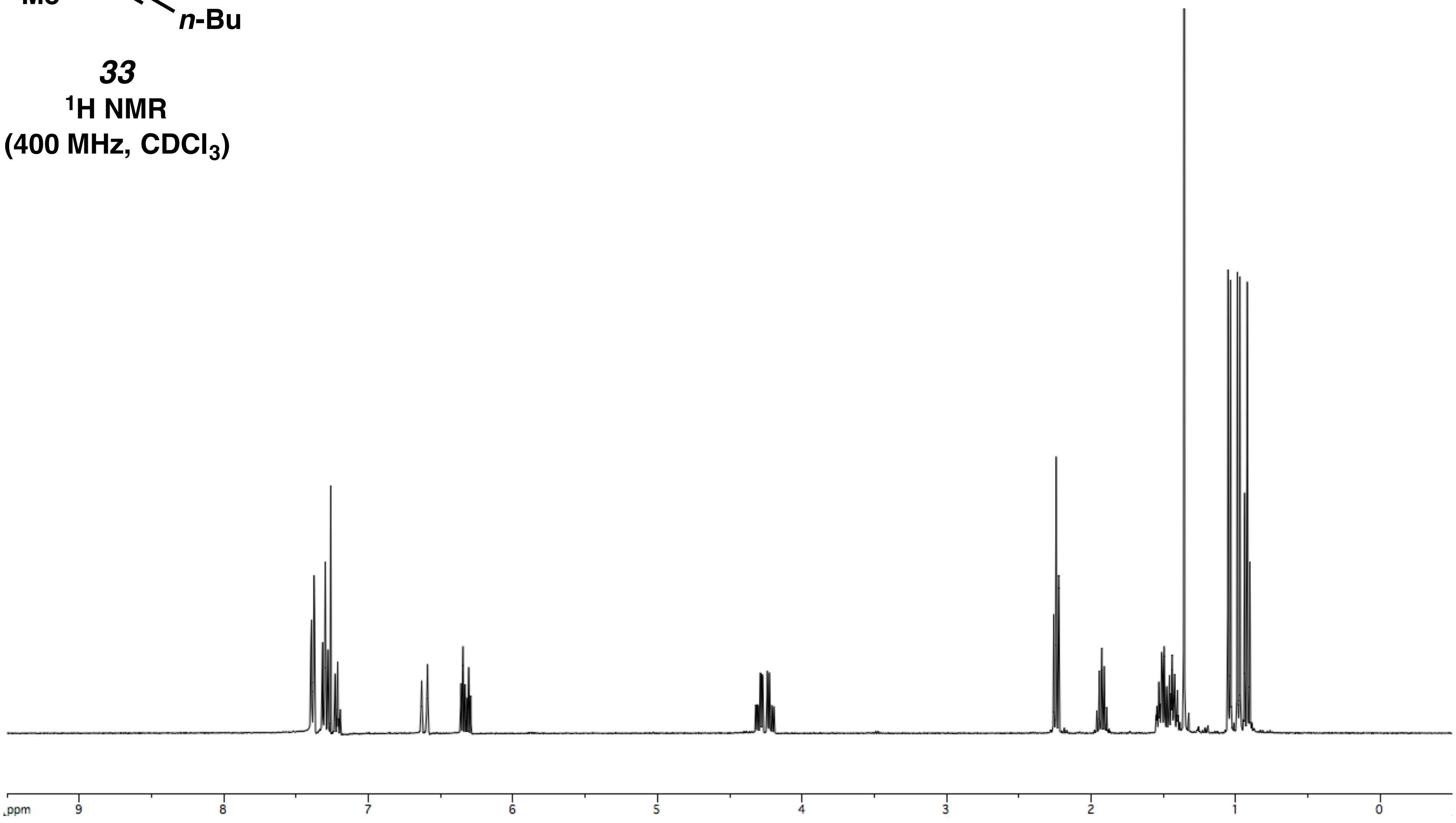


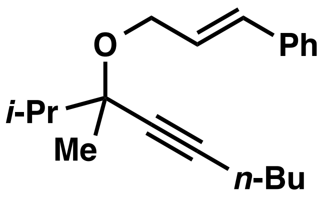


33

^{1}H NMR

(400 MHz, $CDCl_3$)

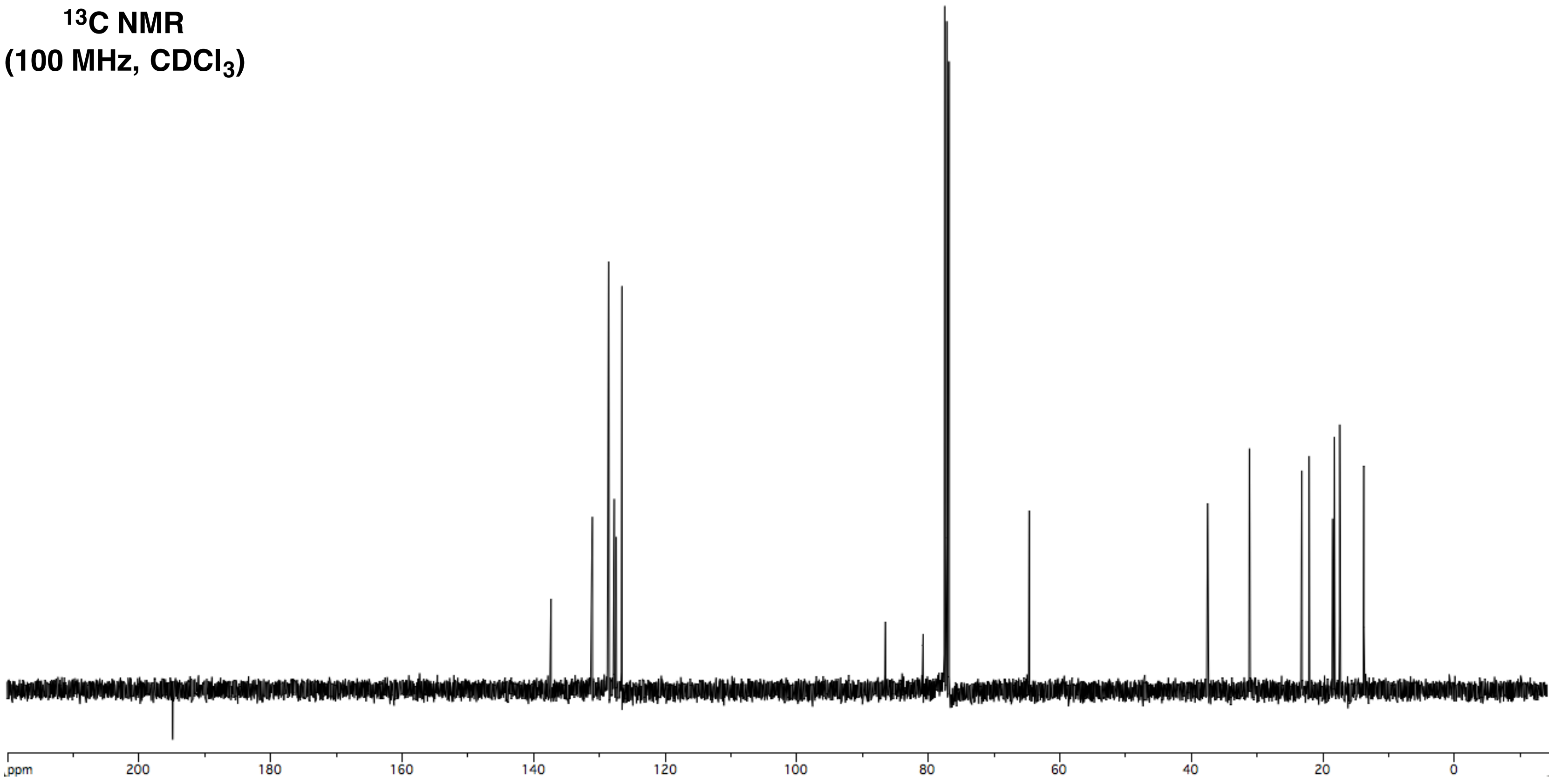


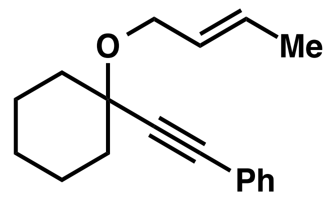


33

^{13}C NMR

(100 MHz, $CDCl_3$)

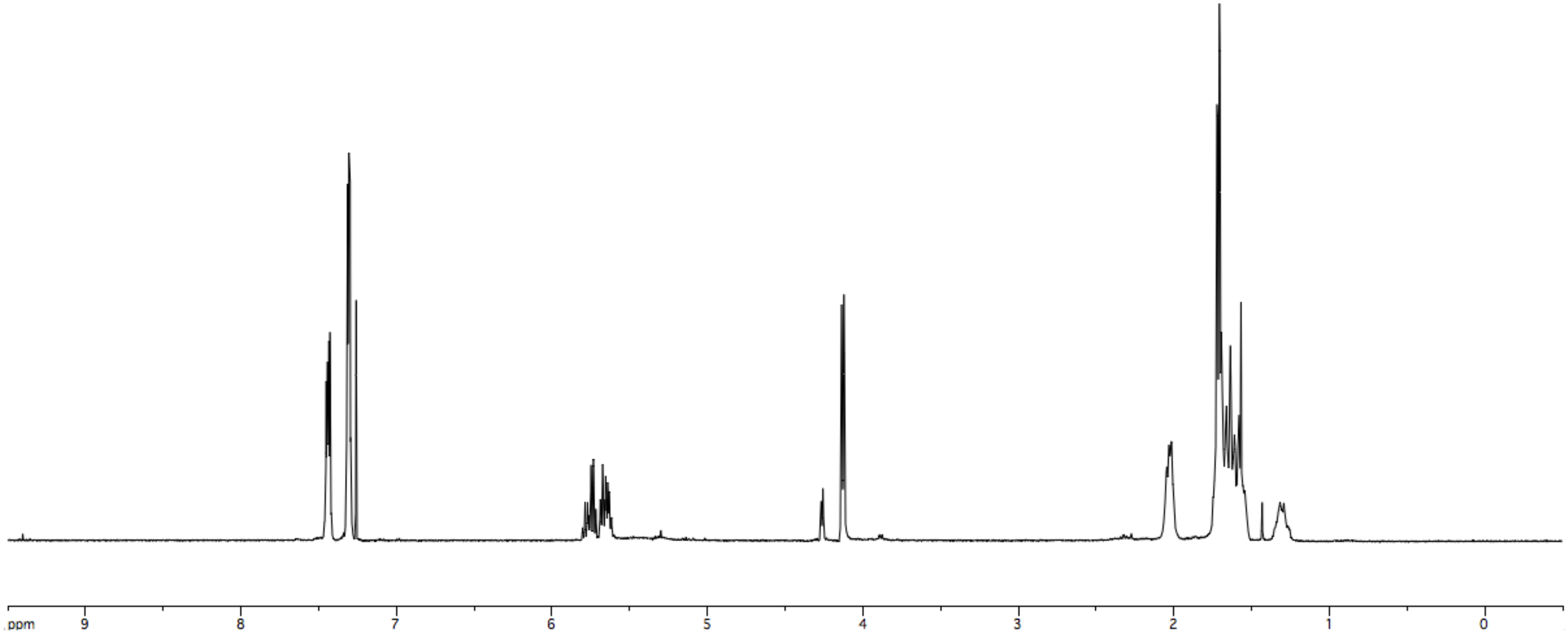


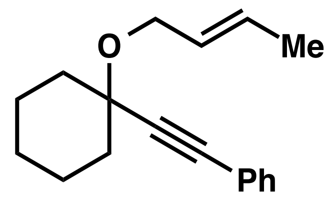


37

^{1}H NMR

(400 MHz, $CDCl_3$)

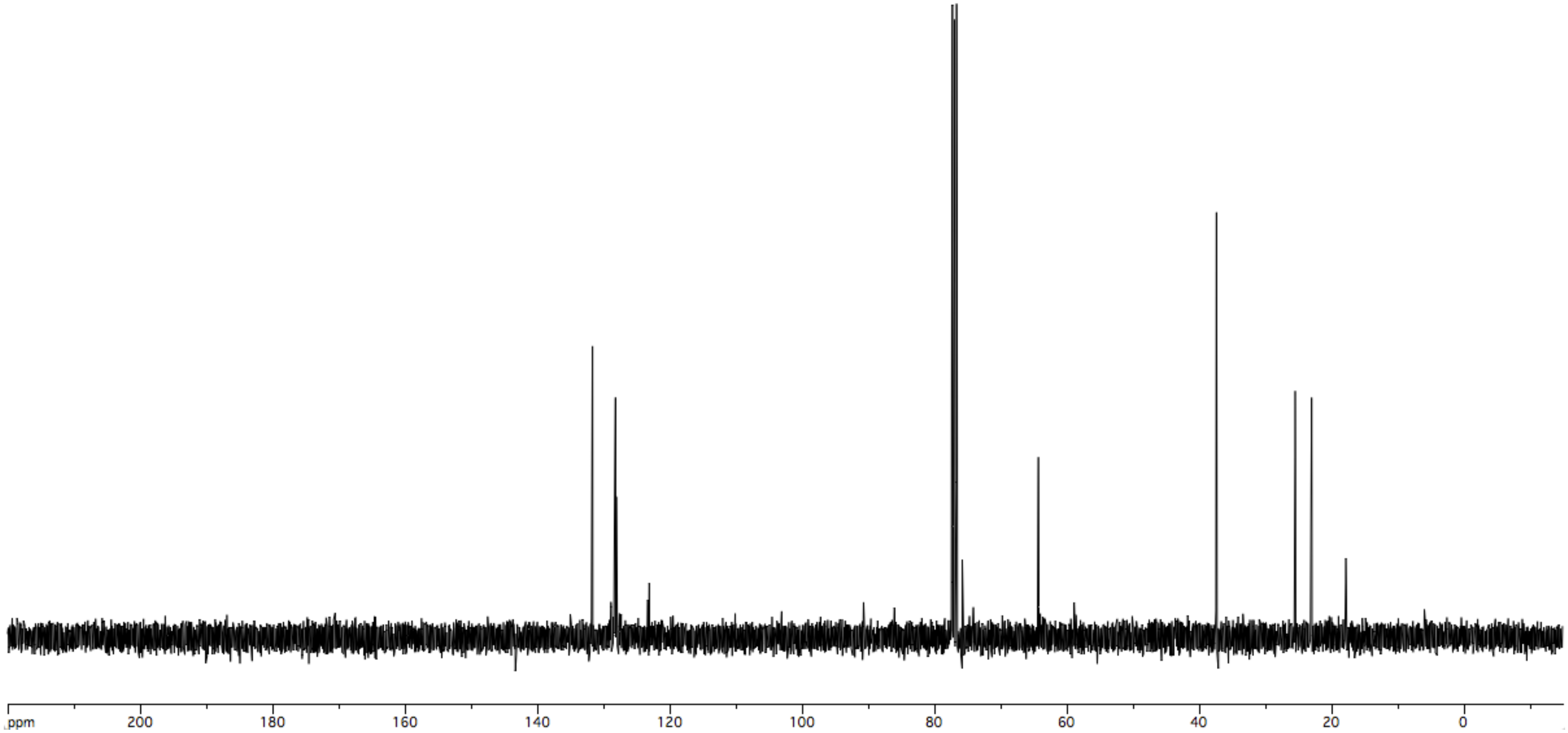


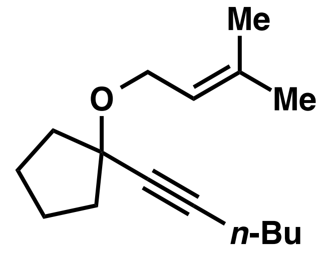


37

^{13}C NMR

(100 MHz, $CDCl_3$)

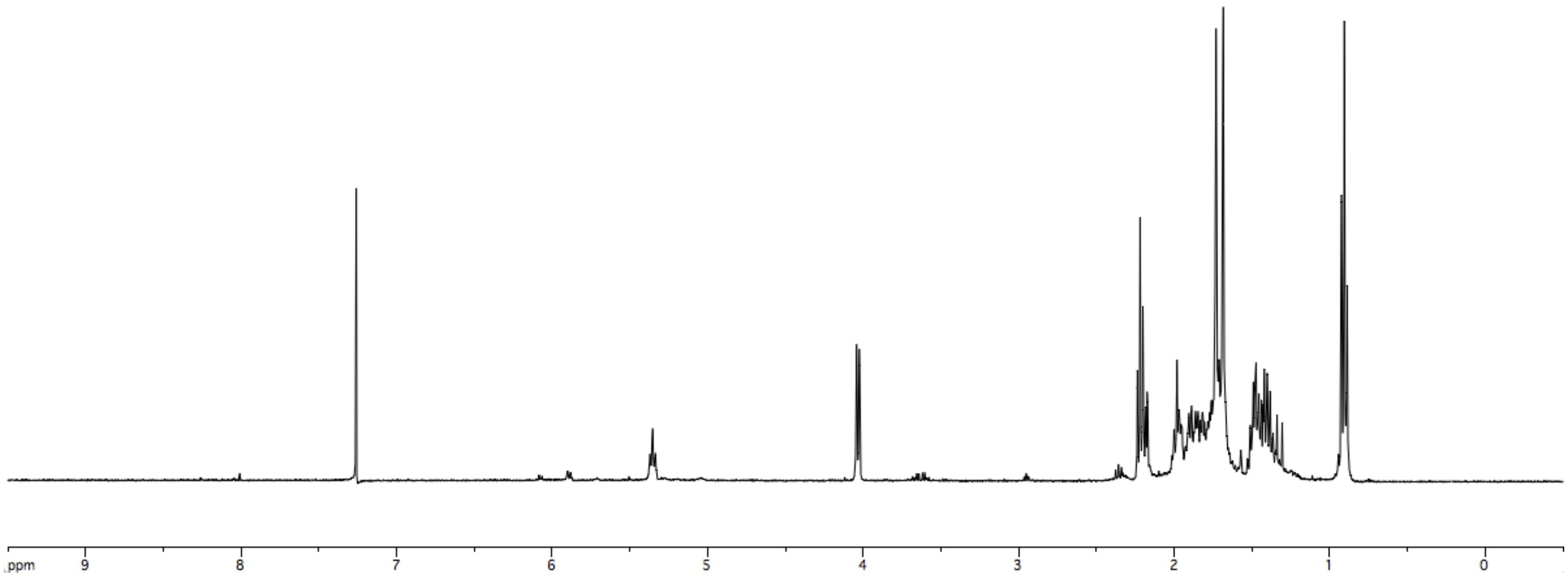


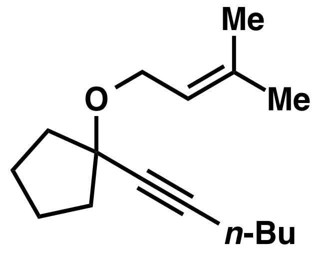


11

^{1}H NMR

(400 MHz, $CDCl_3$)

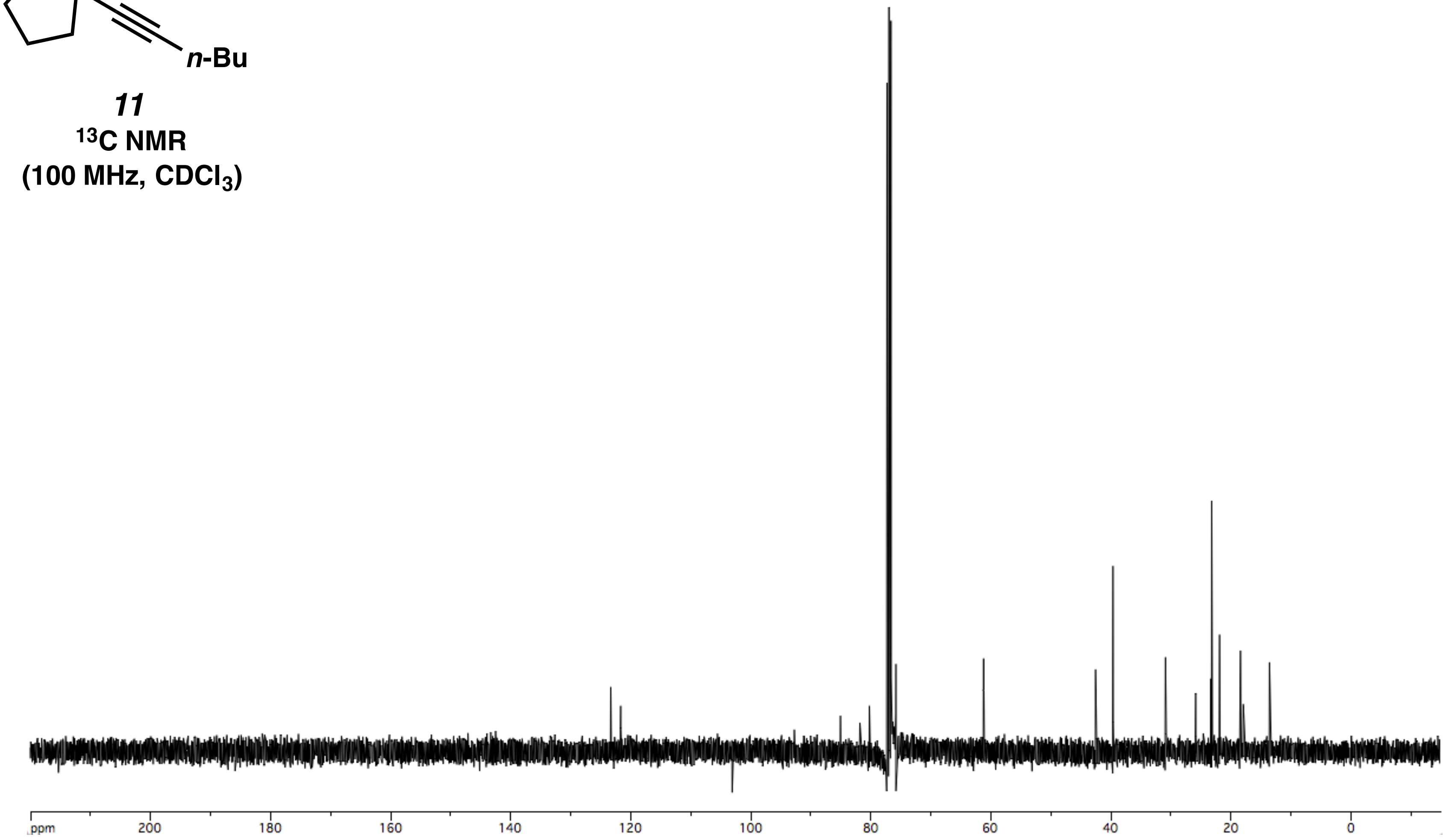


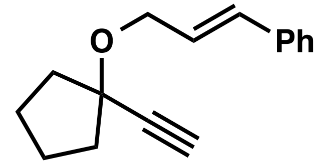


11

^{13}C NMR

(100 MHz, $CDCl_3$)

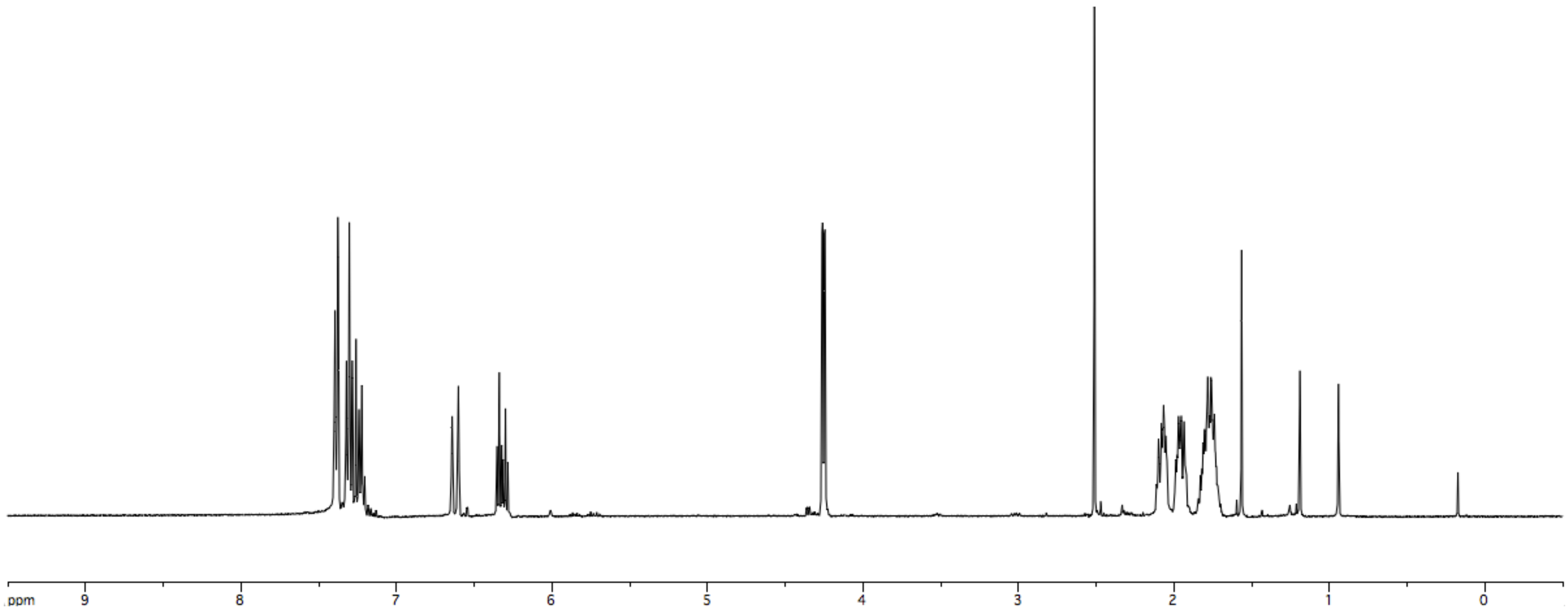


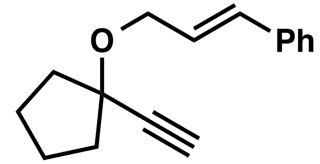


38

^{1}H NMR

(400 MHz, $CDCl_3$)

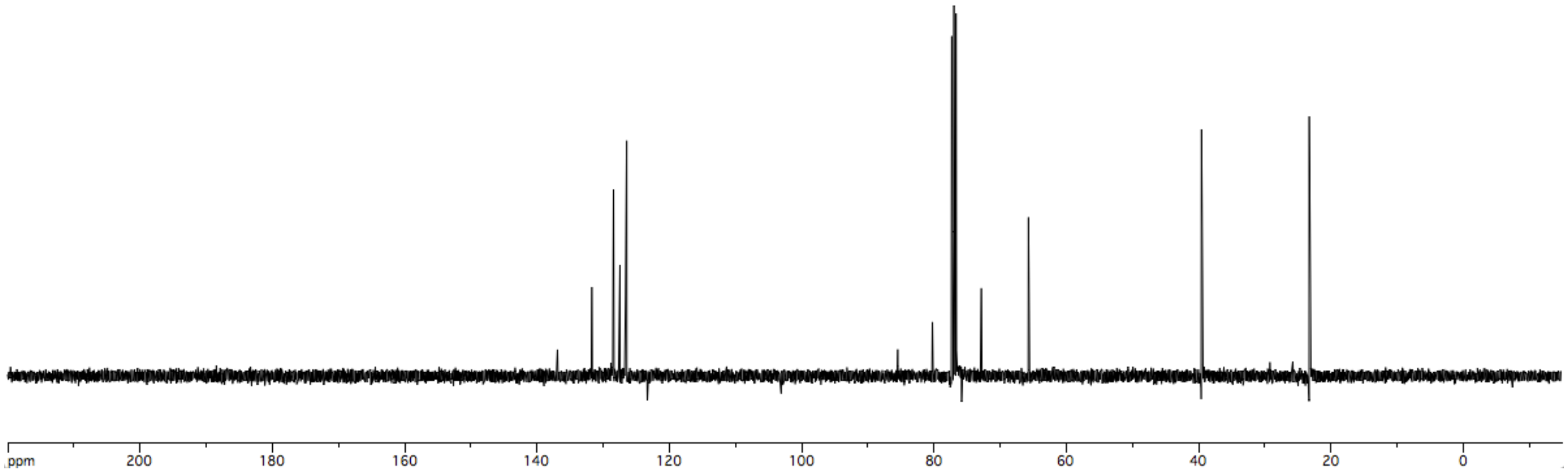


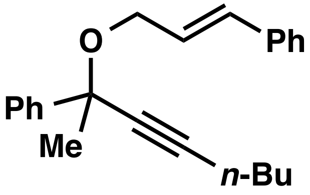


38

^{13}C NMR

(100 MHz, $CDCl_3$)

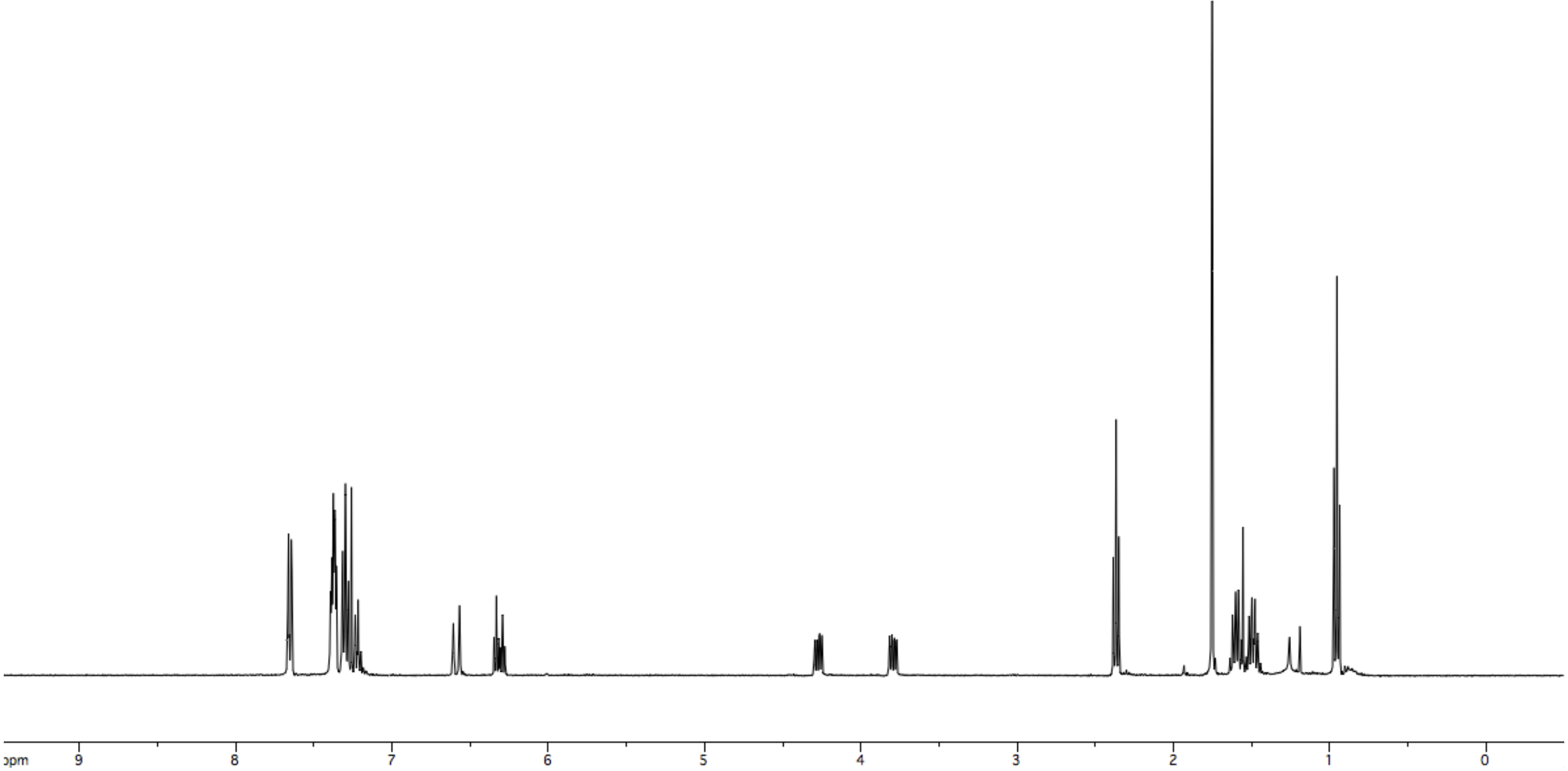


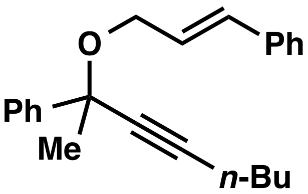


39

^{1}H NMR

(400 MHz, $CDCl_3$)

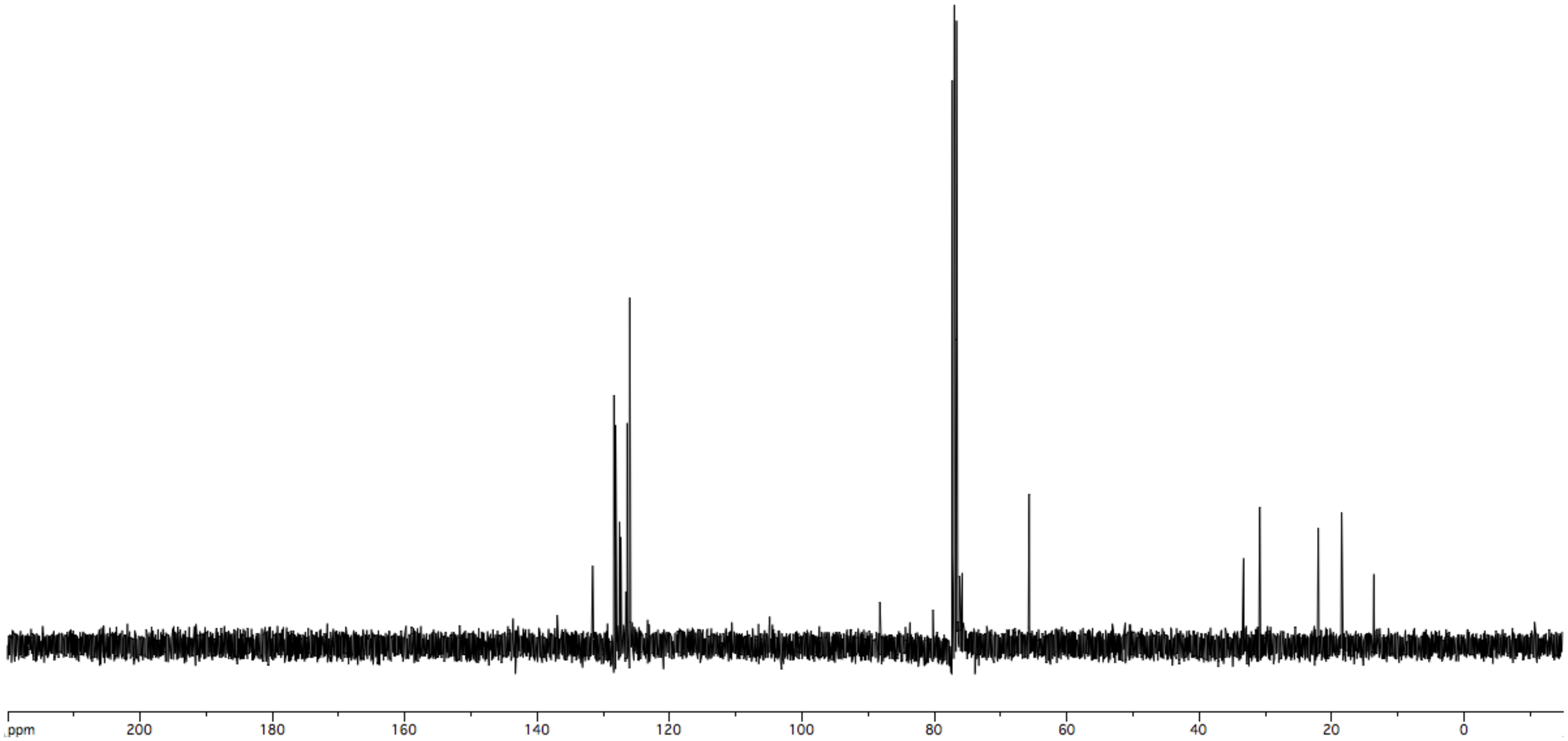


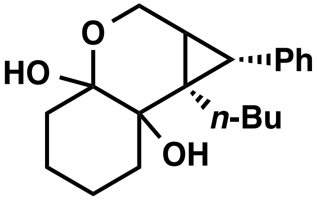


39

^{13}C NMR

(100 MHz, $CDCl_3$)

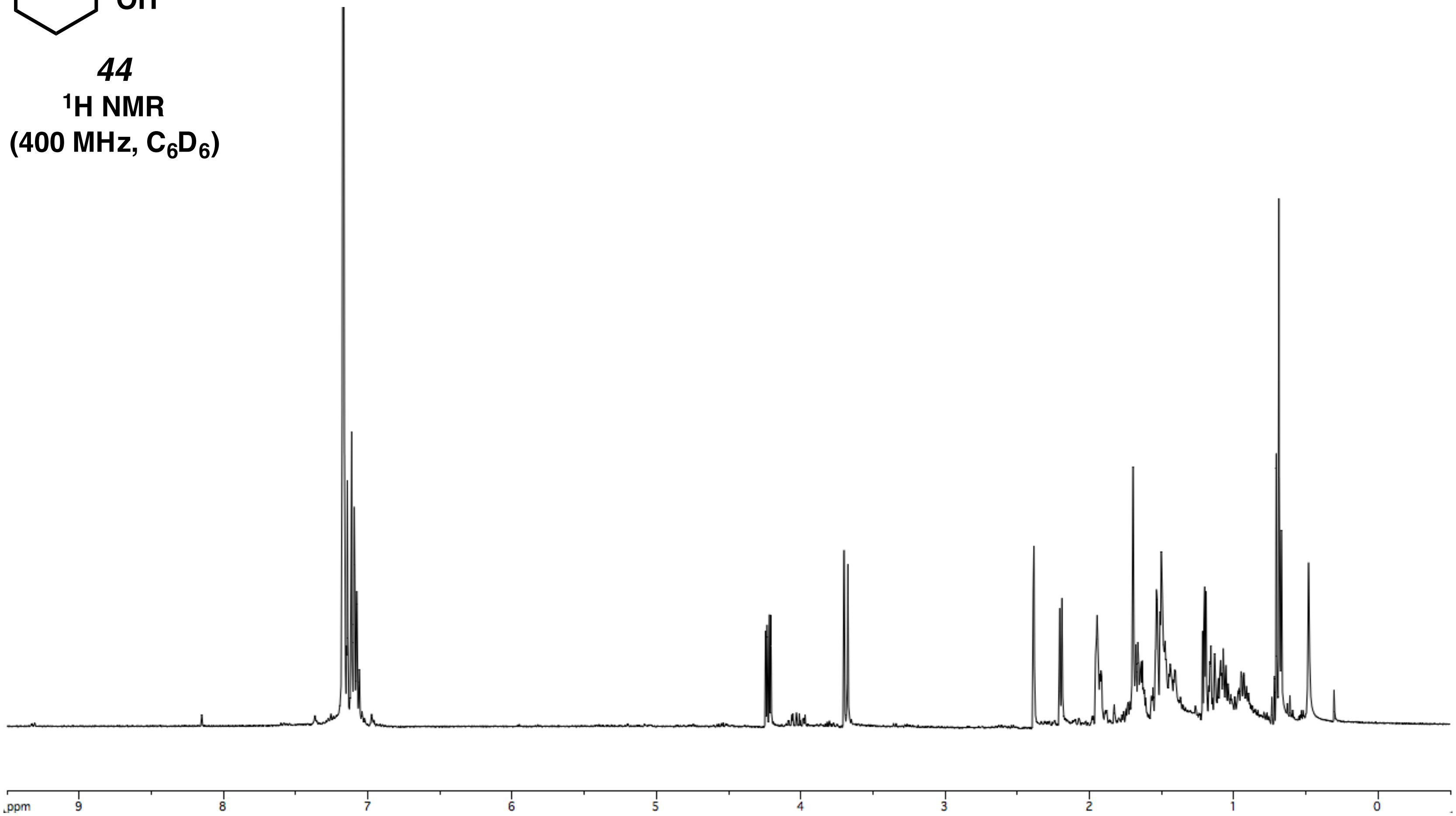


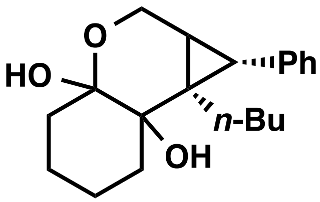


44

^{1}H NMR

(400 MHz, C_6D_6)

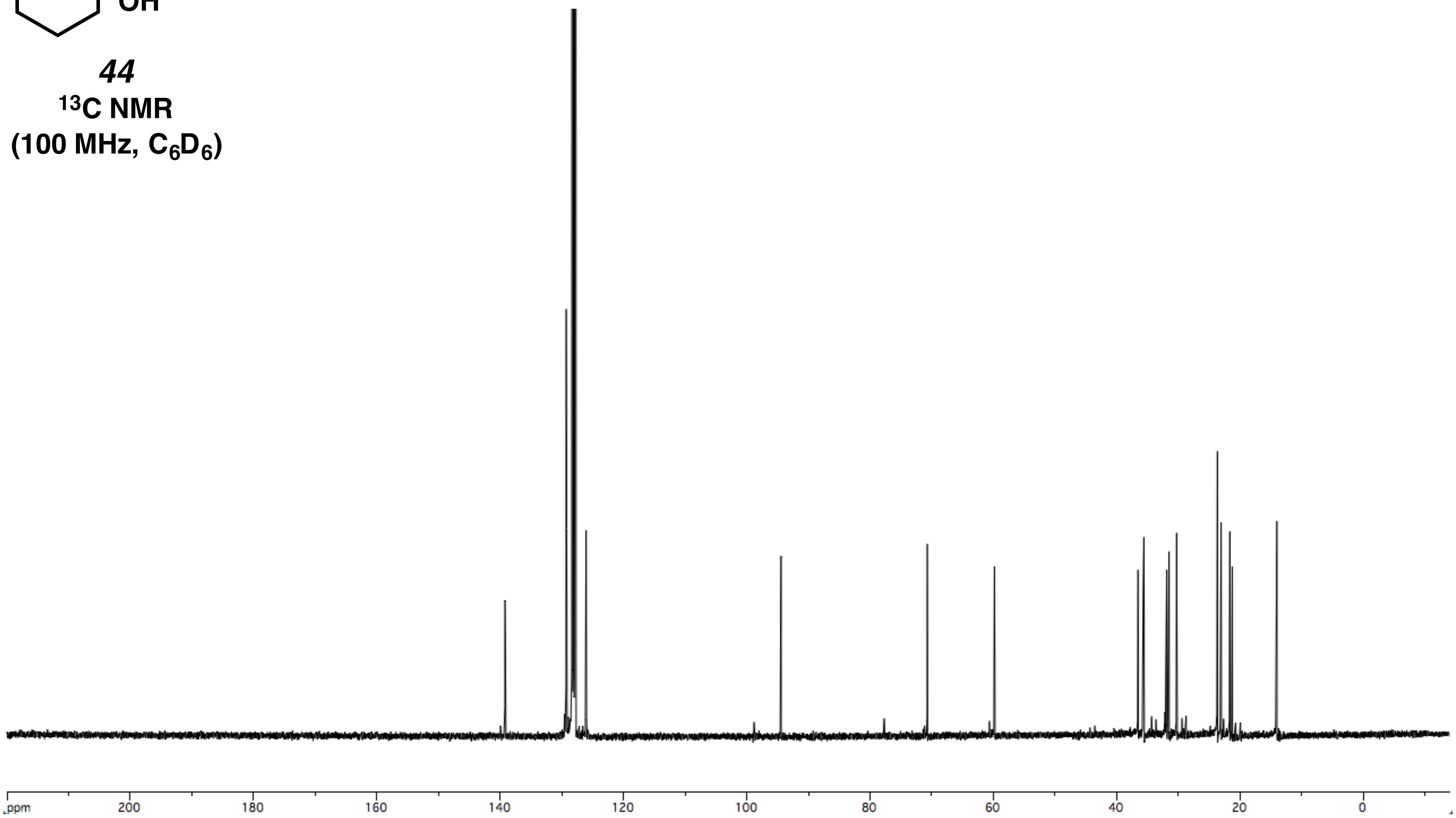


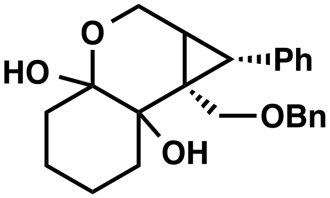


44

^{13}C NMR

(100 MHz, C_6D_6)

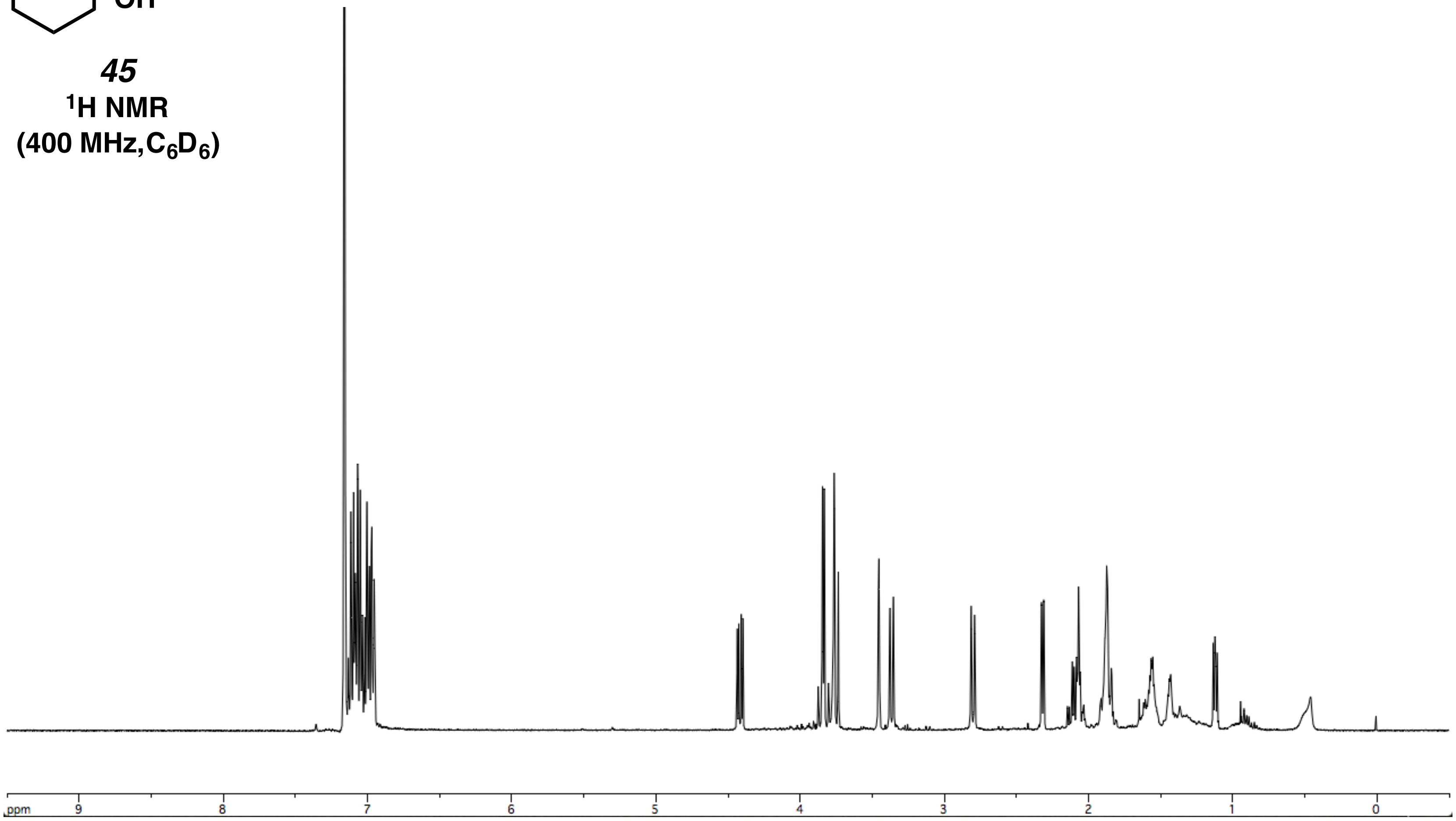


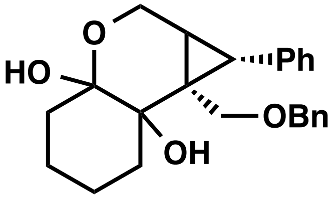


45

^{1}H NMR

(400 MHz,C_6D_6)

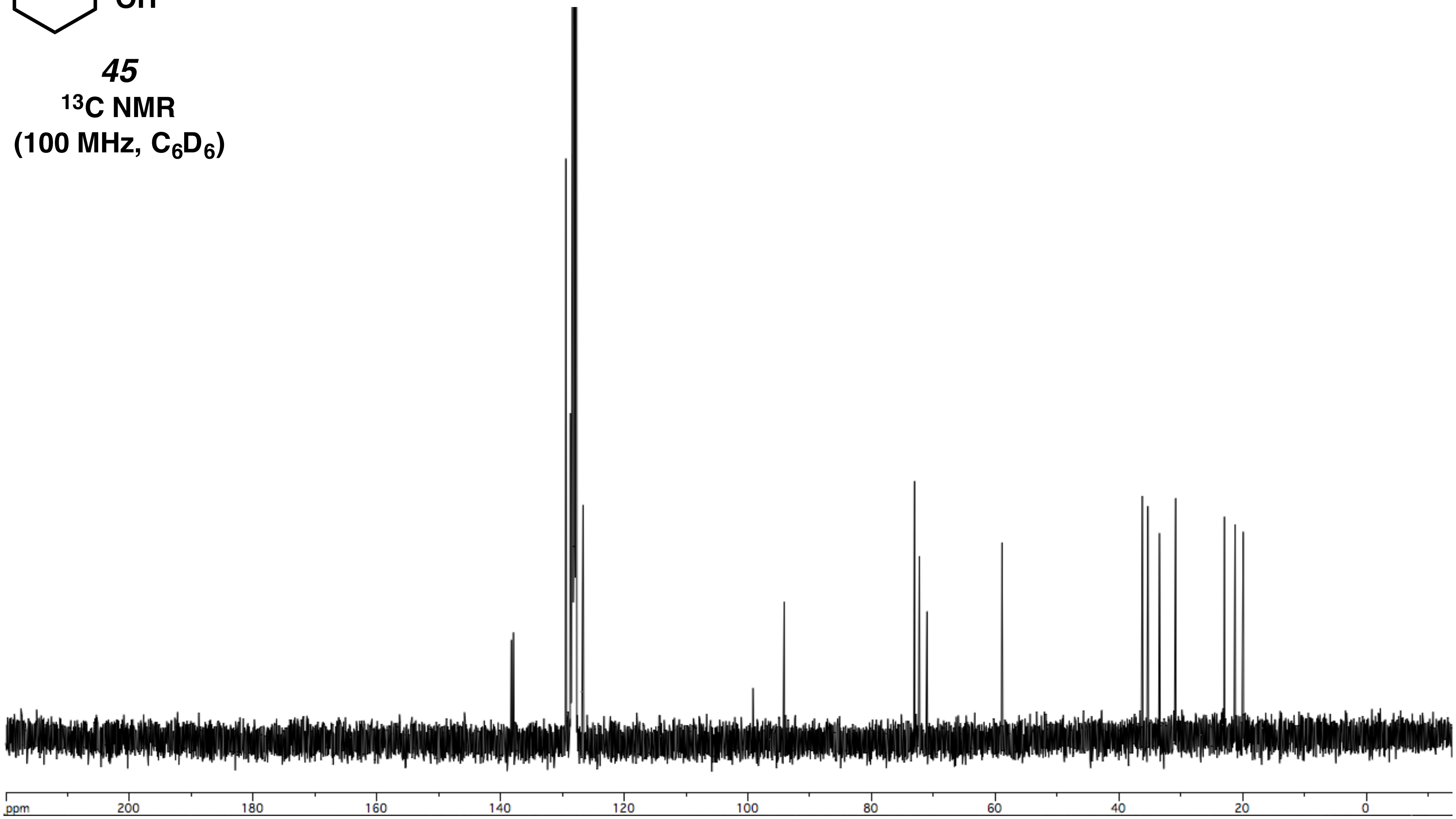


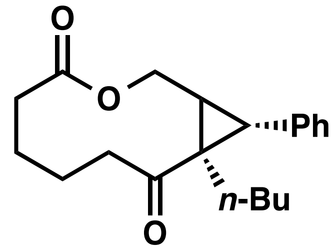


45

^{13}C NMR

(100 MHz, C_6D_6)

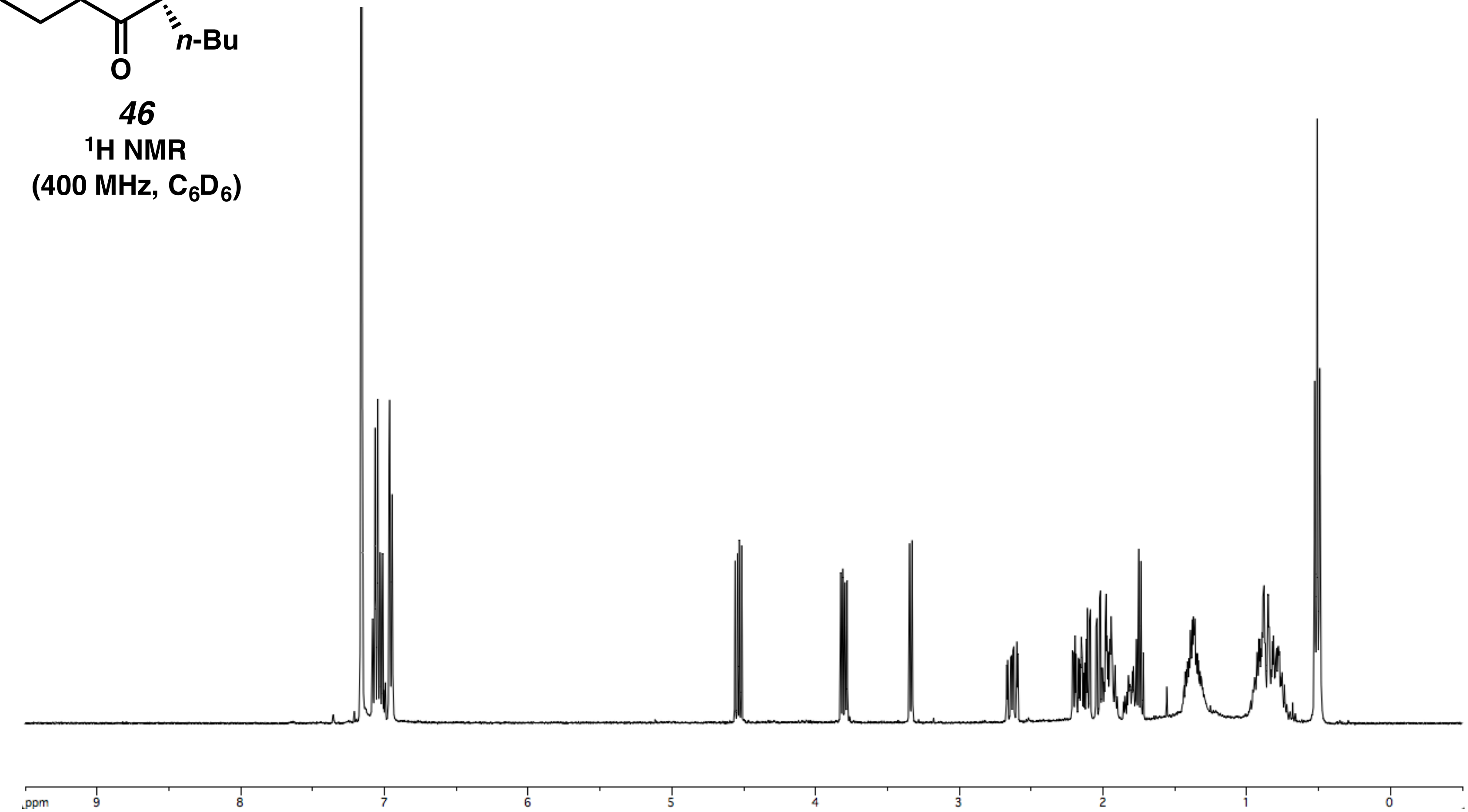


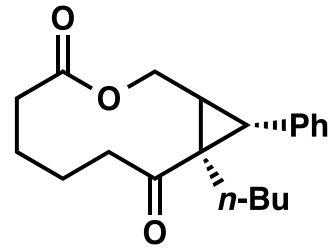


46

^{1}H NMR

(400 MHz, C_6D_6)

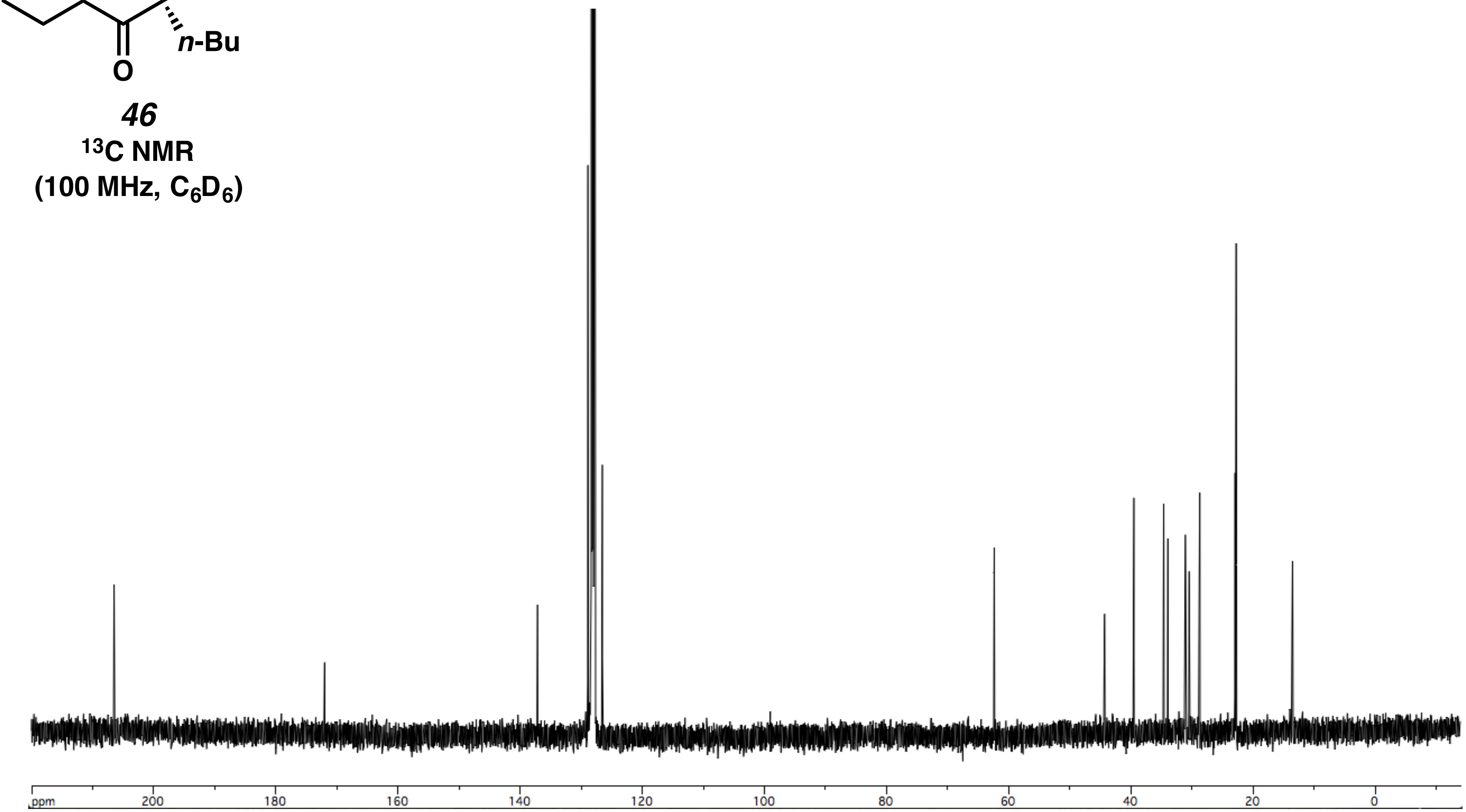


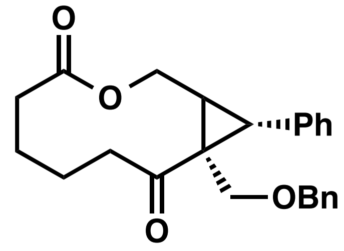


46

^{13}C NMR

(100 MHz, C_6D_6)

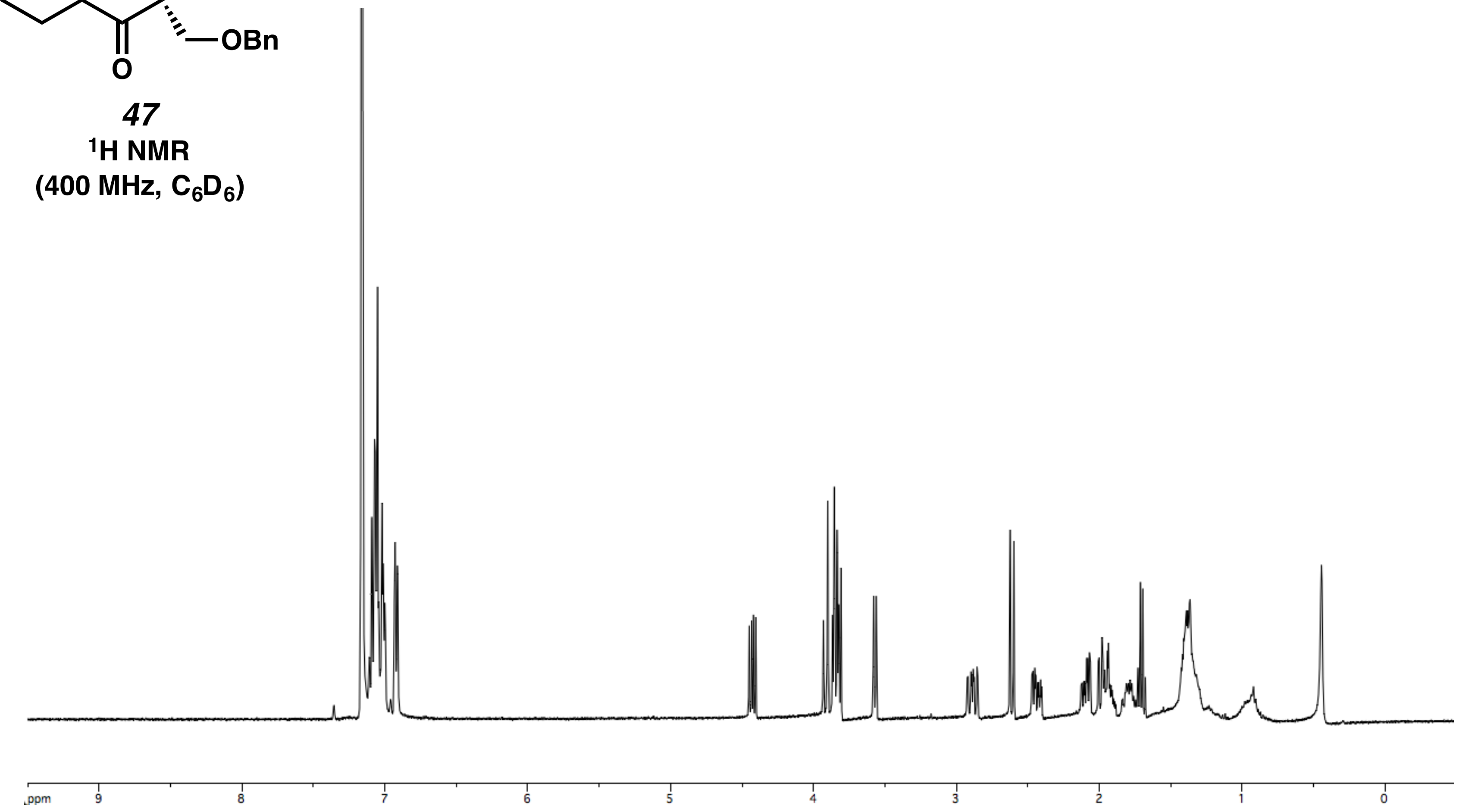


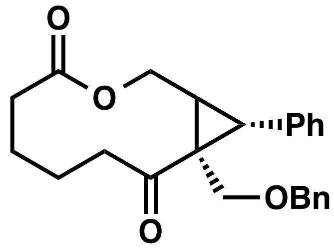


47

^{1}H NMR

(400 MHz, C_6D_6)





47

^{13}C NMR

(100 MHz, C_6D_6)