SUPPORTING INFORMATION:

Synthesis of benzocycloheptanones through coupling of δ,ε-unsaturated chromium carbene complexes and 2-alkynylbenzoyl derivatives

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General Experimental:
Nuclear Magnetic Resonance (^{1}H and ^{13}C) spectra were recorded on a Varian 300 MHz or a 400 MHz spectrometer. Chemical shifts are reported in parts per million (δ) downfield from the reference tetramethylsilane. Coupling constants (J) are reported in hertz (Hz). The following symbols have been used to indicate multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). A Perkin-Elmer 1720X spectrometer was used to record the infrared spectra and band positions are reported in reciprocal centimeters (cm^{-1}). Only key diagnostic bands are reported, C-H stretching frequencies in the region 2800-3100 cm^{-1} are not reported. Mass spectra (MS) were obtained at the University of California at Riverside or at the University of Nebraska. Flash column chromatography was performed using thick walled glass columns and "flash grade" silica. Thin layer chromatography was done using precoated 0.25mm silica gel plates purchased from Sorbtech. The relative proportion of solvents in mixed chromatography solvents refers to the volume: volume ratio. All commercially available reagents were purchased in reagent grade and used without purification. THF and dioxane were distilled from sodium benzophenone ketyl. All reactions were performed in an inert atmosphere created by a slight positive pressure (ca. 0.1 psi) of nitrogen.

Alkyne-carbonyl Compounds. These compounds were prepared according to literature methods: 2-(2-trimethylsilylethynyl)benzophenone (**5a**),[1] 2-(2-trimethylsilylethynyl)benzaldehyde **(5b)**,[1] 2-enthynylbenzaldehyde (**5c**),[2] 2-(1-hexyn-1yl)benzaldehyde (**5d**),[1] 2-(3-acetoxy-1-propyn-1-yl)benzaldehyde (**5e**),[3] and 2-(2-trimethylsilylethynyl)acetophenone.[4]

Carbene complex **1a**. Lithium metal (187 mg, 26.8 mmol) was added to ether (5 mL) under nitrogen at room temperature portion-wise. To this mixture was added 5-bromo-1-pentene (0.500 g, 3.35 mmol, half of the total quantity) dropwise. Once turbidity began and the reaction had initiated, the mixture was cooled to 0 ^{o}C and the additional 5-bromo-1-pentene (0.500 g, 3.35 mmol) was added dropwise over a 20min period. Once reaction was complete (2 h) the solution was transferred via cannula to a rapidly-stirred suspension of chromium hexacarbonyl (1.476g, 6.71 mmol) in ether (20 mL) at 0 ^{o}C. This mixture was stirred at 0 ^{o}C for 30 min and then at room temperature for 1 h. The solvent was removed on a rotary evaporator then saturated aqueous tetramethylammonium bromide was added to the solution. The precipitate was extracted into dichloromethane and cooled to 0 ^{o}C. Methyl triflate (1.44 mL, 10.1 mmol) was added and the mixture was stirred at 0 ^{o}C for 30 min and room temperature for 2 h. Then the solvent was evaporated and the compound was purified via flash chromatography on silica gel using pure hexane as the eluent. A yellow solid identified a carbene complex **1a** (1.22 g, 60% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 5.76 (ddt, 1H, J = 17.1, 10.1, 6.6 Hz), 5.04 (br d, 1H, J = 17.1 Hz), 5.01 (br d, 1H, J = 10.1 Hz), 4.78 (s, 3H), 3.33 (t, 2H, J = 7.7 Hz), 2.07 (br q, 2H, J = 7.1 Hz), 1.59 (quintet, 2H, J = 7.5 Hz). The spectral data are in agreement with those previously reported for this compound.[5]

Carbene complex **1b**. To a solution of 3,3-dimethyl-5-iodo-1-pentene[6] (500 mg, 2.20 mmol) in diethyl ether (10 mL) at -78 ^{o}C was added and *t*-Butyl lithium (2.58 mL of a 1.7M pentane solution, 4.40 mmol) dropwise via syringe. The solution was stirred for 30 min and then warmed to 0 ^{o}C. After 1 h this solution was added to a

[1] Jiang, D.; Herndon, J.W. *Organic Letters* **2000**, *2*, 1267-1269.
[2] Dell'Aqua, M.; Facoetti, D.; Abbiati, G.; Rossi, E. *Synthesis* **2010**, 2367-2378.
[3] Shu, X. Z.; Zhao, S. C.; Ji, K. G.; Zheng, Z. J.; Liu, X. Y.; Liang, Y. M. *Eur. J. Org. Chem.* **2009**, 117-122.
[4] Duan, S.; Cress, K.; Waynant, K.; Ramos-Miranda, E.; Herndon, J. W. *Tetrahedron* **2007**, *63*, 2959-2965.
[5] Xu, Y. C.; Wulff, W. D. *J. Org. Chem.* **1987**, *52*, 3263-3275.
[6] Prepared from commercially-available methyl 3,3-dimethyl-4-pentenoate via reduction to the alcohol with $LiAlH_4$, conversion to the tosylate, followed by conversion to the iodide. Use of this compound has been reported. a. Zhao, Z.; Ding, Y.; Zhao, G. *J. Org. Chem.* **1998**, *63*, 9285-9291. b. Grieco, P. A.; Walker, J. K. *Tetrahedron* **1997**, *53*, 8975-8996.

suspension of chromium hexacarbonyl (484 mg, 2.20 mmol) at 0 ^{o}C, and then stirred at 0 ^{o}C for 30 min and followed by room temperature for 1 h. This solution was then added to a saturated aqueous solution of tetramethylammonium bromide. The precipitate was extracted into dichloromethane and cooled to 0 ^{o}C. Methyl triflate (0.47 mL, 3.3 mmol) was added dropwise at 0 ^{o}C. The mixture was then stirred for 30 min at 0 ^{o}C and then at room temperature for 1 h. The mixture was poured into saturated aqueous sodium bicarbonate solution in a separatory funnel and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the compound was purified through flash chromatography on silica gel using pure hexane as the eluent. An orange colored oil (418 mg, 57%) identified as carbene complex **1b** was obtained. ^{1}H NMR ($CDCl_3$): δ 5.73 (dd, 1H, J = 17.5, 10.9 Hz), 5.00 (dd, 1H, J = 10.9, 1.2 Hz), 4.95 (dd, 1H, J = 17.5, 1.2 Hz), 4.75 (s, 3H), 3.22 (m, 2H), 1.43 (m, 2H), 1.01 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 364.1, 223.2, 216.4, 147.0, 111.5, 67.5 (broad), 58.8 (broad), 38.3, 36.4, 26.4.

Carbene complex **1c**. To a solution of 6-iodo-1-hexene (500 mg, 2.38 mmol) in diethyl ether (10 mL) at -78 ^{o}C was added and *t*-Butyl lithium (2.8 mL of a 1.7M pentane solution, 4.76 mmol) dropwise via syringe. The solution was stirred for 30 min at -78 ^{o}C. After 1 h this solution was added to a suspension of chromium hexacarbonyl (471 mg, 2.38 mmol) at 0 ^{o}C, and then stirred at 0 ^{o}C for 30 min and followed by room temperature for 1 h. This solution was then added to a saturated aqueous solution of tetramethylammonium bromide. The precipitate was extracted into dichloromethane and cooled to 0 ^{o}C. Methyl triflate (0.510 mL, 3.21 mmol) was added dropwise at 0 ^{o}C. The mixture was then stirred for 30 min at 0 ^{o}C and then at room temperature for 1 h. The mixture was poured into saturated aqueous sodium bicarbonate solution in a separatory funnel and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the compound was purified through flash chromatography on silica gel using pure hexane as the eluent. An orange colored oil (496 mg, 57%) identified as carbene complex **1c** was obtained. ^{1}H NMR ($CDCl_3$): δ 5.79 (ddt, 1H, J = 17.0, 10.3, 6.6 Hz), 5.02 (br d, 1H, J = 17.0 Hz), 4.97 (br d, 1H, J = 10.3 Hz), 4.78 (s, 3H), 3.32 (t, 2H, J = 7.5 Hz), 2.06 (br q, 2H, J = 6.9 Hz), 1.58-1.34 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 363.4, 223.1, 216.4, 138.2, 114.8, 67.6 (broad), 62.8 (broad), 33.38, 33.36, 23.4, 25.7. On one experimental run, a carbene complex devoid of alkene functionality was obtained, which is likely the cyclopentylmethylcarbene complex obtained through Bailey cyclization[7] of 5-hexenyllithium. In this case the 5-hexenyllithium intermediate was not properly kept at -78 ^{o}C prior to reaction with chromium hexacarbonyl.

Carbene complex **2a**. To a solution of 1-allyl-2-bromobenzene[8] (300 mg, 1.53 mmol) in diethyl ether (10 mL) was added *n*-butyllithium (0.96 mL of a 1.6M hexane solution, 1.53 mmol) dropwise at -78 ^{o}C. The solution was stirred for 30 min, and then warmed to 0 ^{o}C. The solution was stirred for an additional 1 h and then added to a suspension of chromium hexacarbonyl (337 mg, 1.53 mmol) at 0 ^{o}C then stirred at 0 ^{o}C for 30 min and at room temperature for 1 h. The mixture was added to a saturated aqueous solution of tetramethylammonium bromide. The precipitate was extracted into dichloromethane and cooled to 0 ^{o}C. Methyl triflate (0.33 mL, 2.3 mmol) was added dropwise at 0 ^{o}C and the solution was then stirred for 1 h at 0 ^{o}C and then at room temperature for 1 h. The mixture was poured it into a saturated aqueous sodium bicarbonate solution in a separatory funnel and the organic layer was dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was purified via flash chromatography on silica gel using pure hexane as the eluent. An orange red colored oil (261 mg, 53%) identified as carbene complex **2a** was obtained, however this oil rapidly acquired a brown color. ^{1}H NMR ($CDCl_3$) (very poorly resolved – precipitate in NMR tube within

[7] Bailey, W. F.; Nurmi, T. T.; Patricia, J. J.; Wang, W. *J. Am. Chem. Soc.* **1987**, *109*, 2442-2448.
[8] Hazimeh, H.; Mattalia, J. M.; Marchi-Delapierre, C.; Kanoufi, F.; Combellas, C.; Chanon, M. *Eur. J. Org. Chem.* **2009**, 2775-2787.

seconds of sample preparation): δ 7.40-7.17 (m, 3H), 6.88 (m, 1H), 5.90 (m, 1H), 5.20-5.27 (m, 2H), 4.32 (br s, 3H), 3.21 (m, 2H).

Carbene complex **2b**. To a solution of 1-bromo-2-(1-buten-4-yl)benzene[9] (602 mg, 2.86 mmol) in diethyl ether (10 mL) was added *n*-butyllithium (1.8 mL of a 1.6M hexane solution, 2.86 mmol) dropwise at -78 °C. The solution was stirred for 30 min, and then warmed to 0 °C and stirred an additional 1 h. This solution was transferred to a suspension of chromium hexacarbonyl (629 mg, 1.1 mmol) in diethyl ether (10 mL) at 0 °C and then stirred at 0 °C for 30 min and then at room temperature for 1 h. This solution was added to saturated aqueous solution of tetramethylammonium bromide. The precipitate was extracted into dichloromethane and cooled it to 0 °C. Methyl triflate (0.61 mL, 4.28 mmol) was added dropwise via syringe and the mixture was stirred for 1 h at 0 °C and then at room temperature for 1 h. The mixture was poured into saturated aqueous sodium bicarbonate solution in a separatory funnel and the organic layer was dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue was purified through flash chromatography on silica gel using pure hexane as the eluent. An orange colored oil (550 mg, 52%) identified as carbene complex **2b** was obtained. ^{1}H NMR ($CDCl_3$) (poorly resolved): δ 7.40-7.15 (m, 3H), 6.87 (m, 1H), 5.85 (ddt, 1H, J = 17.2, 10.5, 6.1 Hz), 5.08 (br d, 1H, J = 17.2 Hz), 5.02 (br d, 1H, J = 10.5 Hz), 4.36 (s, 3H), 2.59-2.29 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 359.4, 224.2, 215.9, 137.2, 132.7, 130.2, 129.0, 128.3, 127.5, 127.3, 126.0, 115.4, 66.0, 35.6, 33.8.

General procedure for the coupling of alkyne-carbonyl compounds and carbene complexes. To an 0.05M solution of alkyne-ketone in dry dioxane at reflux under a nitrogen atmosphere was added via syringe an 0.2M solution of carbene complex in dry dioxane dropwise over a 10min period. The system was refluxed for 16 h, after which time a green suspension was present. Then the reaction was cooled to room temperature, filtered through Celite, and the solvent was removed on a rotary evaporator. To the residue after evaporation was added a 9:1 methanol:water solution (10 mL) and 1M aqueous HCl. The mixture was stirred at room temperature for 6 h, then extracted with diethyl ether, washed with brine, and dried over sodium sulfate. The solvent was removed on a rotary evaporator and the residue after evaporation was purified by flash chromatography in silica gel.

Reaction in entry A – naphthocycloheptanone **7a**. The general procedure was followed using alkyne-ketone **5a** (250 mg, 0.899 mmol) and carbene complex **1a** (300 mg, 0.989 mmol). Final purification was achieved by flash chromatography on silica gel using of 9:1 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **7a** (200 mg 77% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 8.17 (d, 1H, J= 8.5 Hz), 7.92 (dd, 1H, J = 8.5. 1.0 Hz), 7.56 (ddd, 1H, J = 8.3, 7.7, 1.1 Hz), 7.52-7.42 (m, 5H), 7.41 (ddd, 1H, J = 8.4, 7.7, 1.0 Hz), 7.30 (s, 1H), 4.26 (s, 2H), 3.15 (t, 2H, J = 6.3 Hz), 2.66 (t, 2H, J = 7.0 Hz), 2.14 (quintet, 2H, J = 6.7 Hz); ^{13}C NMR ($CDCl_3$): δ 208.8, 140.5, 139.9, 137.7, 131.9, 131.1, 130.0, 129.0, 128.31, 128.26, 127.3, 126.8, 126.4, 125.2, 123.4, 43.9, 43.0, 33.3, 26.7; HRMS (ESI): calcd for $C_{21}H_{19}O$ 287.1436, found 287.1437.

Reaction in entry B – naphthocycloheptanone **7b**. The general procedure was followed using alkyne-aldehyde **5b** (250 mg, 1.23 mmol) and carbene complex **1a** (376 mg, 1.23 mmol). Final purification was achieved by flash chromatography on silica gel using 85:15 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **7b** (189.4 mg 73% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 8.11 (d, 1H, J = 8.4 Hz), 7.85 (d, 1H, J

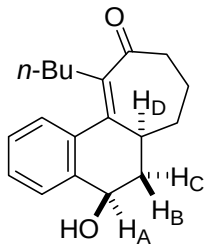
[9] Watson, I. D. G.; Ritter, S.; Toste, F. D. *J. Am. Chem. Soc.* **2009**, *131*, 2056-2057.

= 8.2 Hz), 7.76 (d, 1H, J = 8.2 Hz), 7.55 (ddd, 1H, J = 8.4, 6.9, 1.6 Hz), 7.47 (ddd, 1H, J = 8.2, 6.9, 1.1 Hz), 7.34 (d, 1H, J = 8.4 Hz), 4.21 (s, 2H), 3.12 (t, 2H, J = 6.8 Hz), 2.61 (t, 2H, J = 6.8 Hz), 2.11 (quintet, 2H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 208.8, 138.2, 132.8, 131.6, 128.8, 128.7, 127.8, 127.7, 126.5, 125.1, 123.3, 43.8, 43.0, 33.2, 26.6; HRMS (ESI): calcd for $C_{15}H_{15}O$ (M+H) 211.1117, found 211.1114.

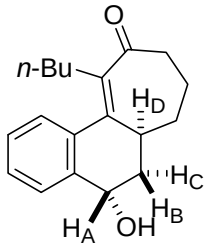
Reaction in entry C – naphthocycloheptanone **7c**. The general procedure was followed using silylated alkyne-aldehyde **5b** (205 mg, 1.01 mmol) and carbene complex **1b** (335 mg, 1.01 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **7c** (181 mg 75% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 8.17 (d, 1H, J = 8.0 Hz), 7.79 (dd, 1H, J = 8.0, 1.2 Hz), 7.73 (d, 1H, J = 8.8 Hz), 7.58 (d, 1H, J = 8.8 Hz), 7.54 (ddd, 1H, J = 8.8, 7.0, 1.8 Hz), 7.46 (ddd, 1H, J = 8.0, 7.0, 1.2 Hz), 4.43 (s, 2H); 2.68 (t, 2H, J = 5.6 Hz), 2.29 (t, 2H, J = 5.6 Hz), 1.50 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 209.5, 143.4, 132.5, 132.4, 128.2, 127.5, 126.64, 126.58, 125.6, 125.4, 123.8, 42.0, 40.2, 38.9. 38.0, 32.3; HRMS (ESI): calcd for $C_{17}H_{19}O$ (M+1) 239.1430, found 239.1428.

Reaction in entry D – naphthocycloheptanone **7c**. The general procedure was followed using 2-ethynylbenzaldehyde (**5c**) (200 mg, 1.53 mmol) and carbene complex **1b** (508.4 mg, 1.53 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **7c** (255 mg, 62% yield) was obtained. The spectral data were identical to the same compound prepared via the silylated alkyne in the entry C.

Reaction in entry E – alcohol **11**. The general procedure was followed using alkyne-aldehyde **5d** (150 mg, 0.805 mmol) and carbene complex **1a** (245 mg, 0.805 mmol). Final purification was achieved by flash chromatography on silica gel using 4:1 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **11** (178 mg 78% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.60 (d, 1H, J = 7.8 Hz), 7.40 (td, 1H, J = 7.4, 1.5 Hz), 7.39 (d, 1H, J = 7.4 Hz), 7.31 (t, 1H, J = 7.8 Hz), 4.56 (br d, 1H, J = 11.7 Hz), 2.88 (tt, 1H, J = 11.3, 6.6 Hz), 2.70-2.50 (m. 2H), 2.47-2.21 (m, 3H), 2.05 (br s, 1H), 2.00-1.74 (m, 3H), 1.51-1.23 (m, 5H), 1.16 (q, 1H, J = 11.3 Hz), 0.92 (t, 3H, J = 7.1 Hz), ^{1}H NMR ($CDCl_3/D_2O$): the peak at δ 4.56 becomes dd, J = 12.0, 3.7 Hz; ^{13}C NMR ($CDCl_3$): δ 211.9, 144.2, 139.7, 139.1, 131.8, 128.5, 126.2, 121.7, 68.2, 41.5, 39.0, 34.3, 32.2, 31.0, 30.5, 22.9, 19.8, 13.9; HRMS (ESI): calcd for $C_{19}H_{25}O_2$ (M+1) 285.1849, found 285.1844; calcd for $C_{19}H_{23}O$ (M-OH) 267.1743, found 267.1743.



11



iso-11

The observed coupling pattern for the proton at δ 4.56 (J = 12.0, 3.7 Hz) is consistent only with the indicated stereochemistry. In the energy-minimized structure for **11** (*n*-butyl replaced by methyl), the dihedral angles involving this proton are H_ACCH_B = 179° ($10\cos^2\Theta$ = 10) and H_ACCH_C = 65° ($10\cos^2\Theta$ = 1.7). In the energy-minimized structure for the stereoisomeric compound (iso-**11**) the dihedral angles involving this proton are H_ACCH_B = 57° ($10\cos^2\Theta$ = 3.0) and H_ACCH_C = 59° ($10\cos^2\Theta$ = 2.7). Furthermore, the peak at δ 1.16 (q, J = 11.3 Hz) could only reasonably represent H_B, which would have a large geminal coupling with H_C and large diaxial couplings to H_A and H_D (H_BCCH_D dihedral angle = 170°). The only other protons coupled to three other protons are either allylic or α to the ketone group and anticipated to have much higher chemical shifts.

Reaction in entry F – methylenecycloheptanone **10**. The general procedure was followed using alkyne-aldehyde **5e** (205 mg, 1.01 mmol) and carbene complex **1a** (308 mg, 1.01 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **10** (166 mg, 74%) obtained. ^{1}H NMR ($CDCl_3$): δ 8.09 (m, 1H), 7.88 (m, 1H), 7.84 (d, 1H), J = 8.4 Hz), 7.53-7.44 (m, 2H), 7.37 (d, 1H, J = 8.4 Hz), 6.97 (d, 1H, J = 2.0 Hz), 5.67 (d, 1H, J = 2.0 Hz), 2.97 (t, 2H, J = 7.1 Hz), 2.49 (t, 2H, J = 7.1 Hz), 2.13 (quintet, 2H, J = 7.1 Hz); ^{13}C NMR: δ 200.2, 143.8, 135.5, 133.8, 133.0, 131.0, 128.5, 128.3, 127.5, 126.9, 126.3, 125.1, 124.8, 38.5, 31.4, 125.8; HRMS (DART): calcd for $C_{17}H_{19}O_3$ (M+1) 223.1123, found 223.1127.

Reaction in entry G – naphthocycloheptanone **7g**. The general procedure was followed using alkyne-aldehyde **5f** (150 mg, 0.572 mmol) and carbene complex **1a** (174 mg, 0.572 mmol). Final purification was achieved by flash chromatography on silica gel using of 7:3 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **7g** (117.4 mg 76% yield) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.58 (d, 1H, J = 8.1 Hz), 7.30 (s, 1H), 7.18 (d, 1H, J = 8.1 Hz), 7.12 (s, 1H), 4.11 (s, 2H), 4.04 (s, 3H), 4.00 (s, 3H), 3.06 (t, 2H, J = 6.8 Hz), 2.58 (t, 2H, J = 6.8 Hz), 2.08 (quintet, 2H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$): δ 209.2, 150.0, 148.8, 136.4, 128.7, 127.4, 127.3, 126.1, 126.0, 107.0, 102.2, 55.83, 55.80, 44.3, 42.8, 26.6, HRMS (ESI): calcd for $C_{17}H_{19}O_3$ (M+1) 271.1321, found 271.1329.

Reaction in entry H – naphthocycloheptanone **7h**. The general procedure was followed using alkyne-ketone **5g** (185 mg, 0.85 mmol) and carbene complex **1b** (284 mg, 0.85 mmol). Final purification was achieved by flash chromatography on silica gel using 9:1 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **7h** (172 mg, 80%) obtained. ^{1}H NMR ($CDCl_3$): δ 8.20 (dd, 1H, J = 8.4, 1.5 Hz), 7.87 (dd, 1H, J = 7.5, 2.2 Hz), 7.60-7.47 (m, 2H), 7.43 (s, 1H), 4.41 (s, 2H), 2.69 (s, 3H) overlapping with 2.72-2.63 (m, 2H), 2.28 (m, 2H), 1.50 (s, 6H); ^{13}C NMR ($CDCl_3$): δ 209.6, 142.9, 133.1, 132.5, 131.8, 127.4, 126.2, 125.2, 124.3, 124.2, 123.7, 42.0, 40.0, 38.8, 38.0, 32.2, 19.8; HRMS (ESI): calcd for $C_{18}H_{21}O$ (M+1) 253.1593, found 253.1603.

Thermolysis of carbene complex **2a** to afford tetralone (**13a**). The general procedure was followed using alkyne-benzophenone **5a** (200 mg, 0.72 mmol) and carbene complex **2a** (279 mg, 0.79 mmol). Final purification was achieved by flash chromatography on silica gel using of 85:15 hexane:ethyl acetate as the eluent. A light yellow colored oil identified as tetralone (105 mg, 91%) obtained. A similar yield was obtained if alkyne-benzophenone **5a** was omitted. ^{1}H NMR ($CDCl_3$): δ 8.02 (dd, 1H, J = 7.7, 1.1 Hz), 7.44 (td, 1H, J = 7.7, 1.1 Hz), 7.28 (br t, 1H, J = 7.7 Hz), 7.23 (br d, 1H, J = 7.7 Hz), 2.95 (t, 2H, J = 6.3 Hz), 2.64 (t, 2H, J = 7.0 Hz), 2,12 (quintet, 2H, J = 6.7 Hz). The data were in agreement with those previously reported for this compound.[10]

Formation of cyclopropane **12b**. The general procedure was followed using only carbene complex **2b** (725 mg, 1.98 mmol) and no alkyne and omission of the HCl treatment step. Final purification was achieved by flash chromatography on silica gel using 85:15 hexane:ethyl acetate as the eluent. A colorless oil identified as compound **12b** (292 mg, 85%) was obtained. ^{1}H NMR ($CDCl_3$): δ 7.63 (d, 1H, J = 7.7 Hz), 7.27 (br t, 1H, J = 7.5 Hz), 7.14 (td, 1H, J = 7.5, 1.3 Hz), 7.09 (br d, 1H, J = 7.5 Hz), 3.33 (s, 3H), 2.65 (dd, 1H, J = 7.0, 5.0 Hz), 2.38 (td, 1H, J = 15.2, 15.2, 6.6 Hz), 2.11-1.99 (m, 1H), 1.86-1.69 (m, 2H), 1.25 (dd, 1H, J = 10.0, 5.7 Hz), 1.05

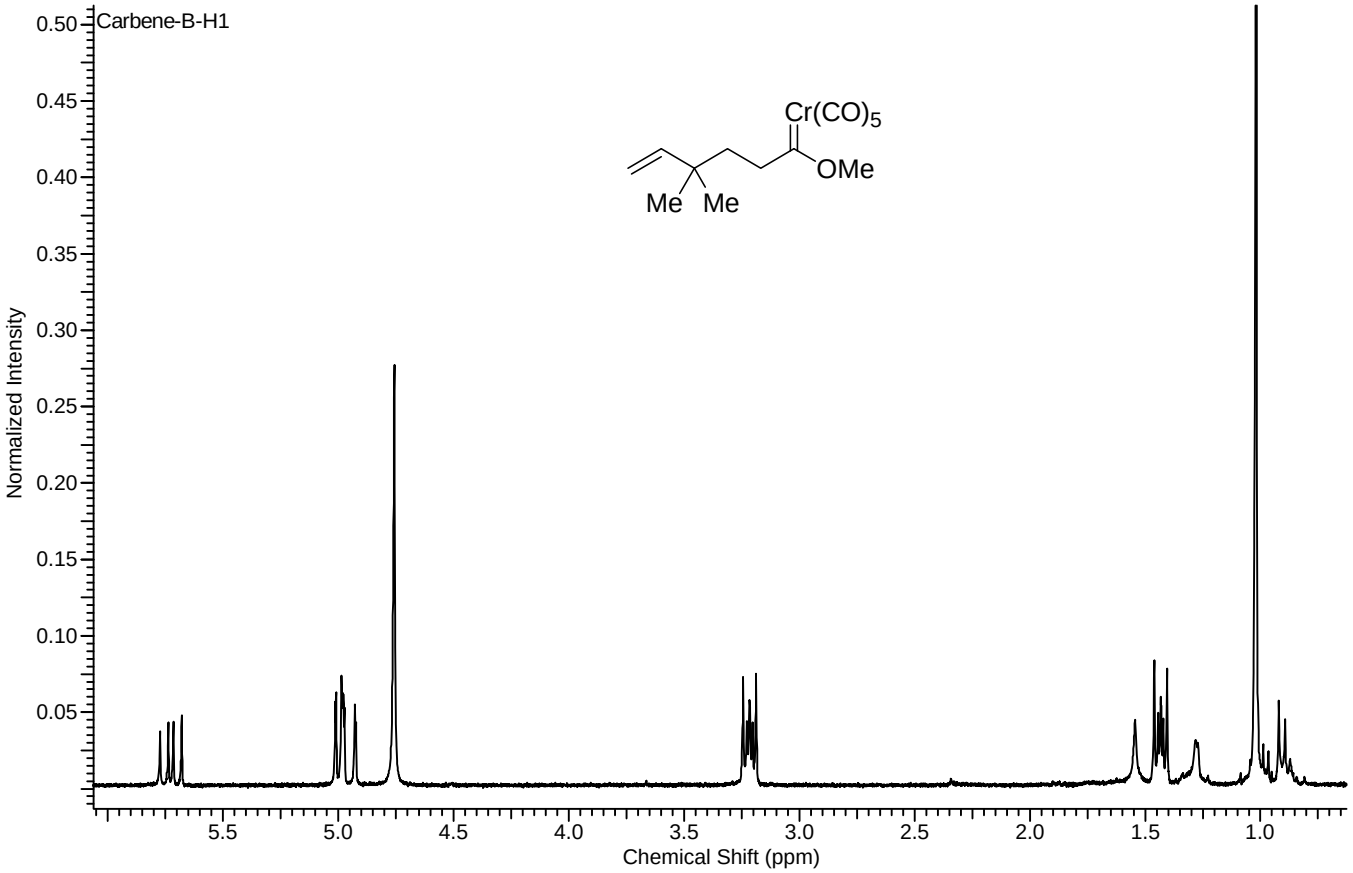
[10] This is a commercially available compound present in numerous NMR databases, including Aldrich and SDBS.

(t, 1H, J = 5.8 Hz), ^{13}C NMR ($CDCl_3$): δ 137.4, 133.7, 128.4, 126.1, 125.3, 124.6, 60.8, 54.8, 25.9, 21.1, 19.0, 17.2, HRMS (TOF-EI): calcd for $C_{12}H_{14}O$ (M+) 174.1045, found 174.1042.

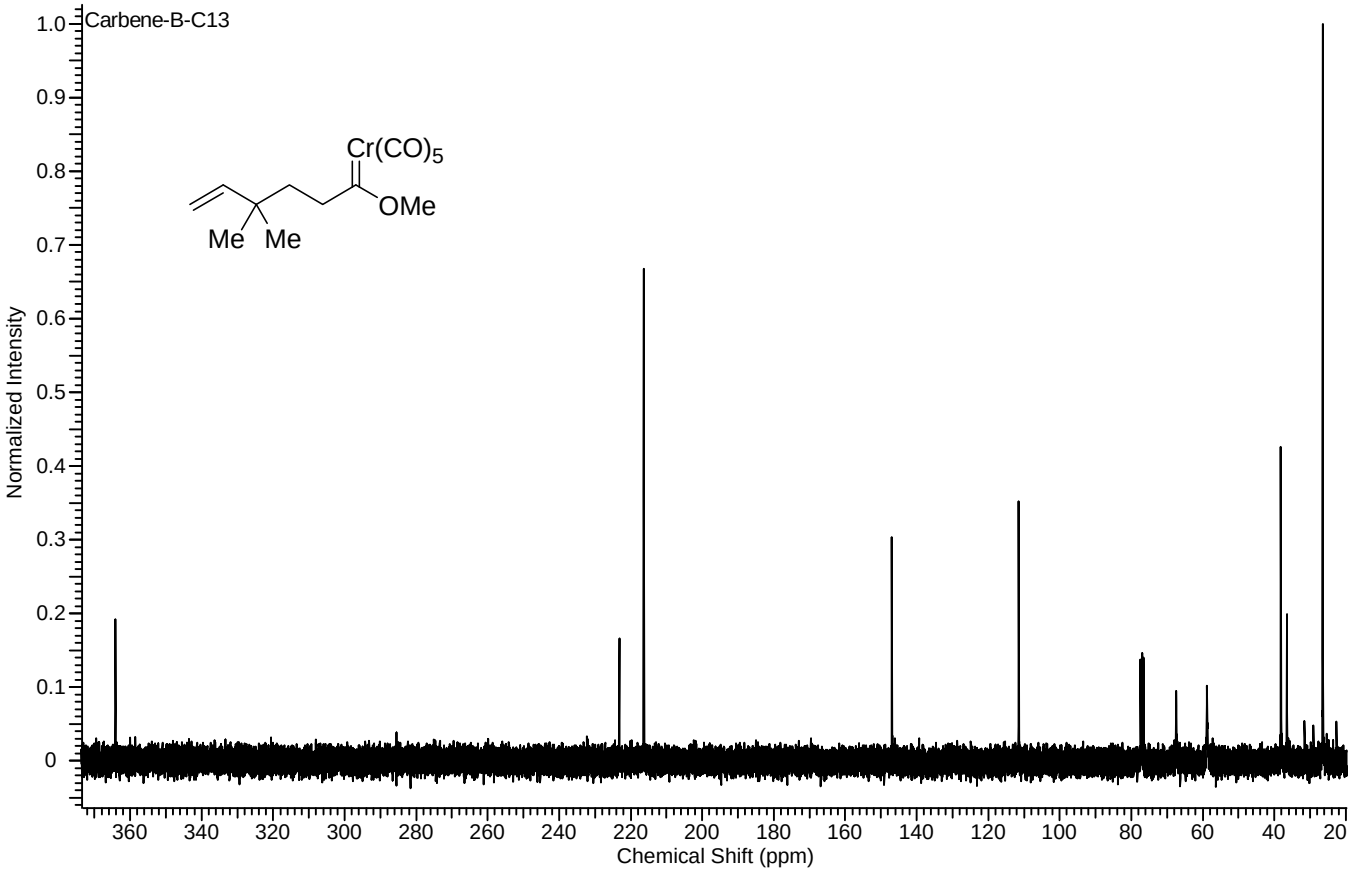
Thermolysis of carbene complex **2b** to afford methyltetralone **13b**. The general procedure was followed using alkyne-benzophenone **5a** (200 mg, 0.72 mmol) and carbene complex **2a** (270 mg, 0.79 mmol). Final purification was achieved by flash chromatography on silica gel using of 85:15 hexane:ethyl acetate as the eluent. A light yellow colored oil identified as α-methyltetralone **13b** (244 mg, 93%) obtained. A similar yield was obtained if alkyne-benzophenone **5a** was omitted. ^{1}H NMR ($CDCl_3$): δ 8.05 (dd, 1H, J = 7.8, 1.3 Hz), 7.46 (td, 1H, J = 7.5, 1.5 Hz), 7.31 (br t, 1H, J = 7.6 Hz), 7.24 (br d, 1H, J = 7.6 Hz), 3.14-2.91 (m, 2H), 2.60 (dddd, 1H, J = 13.6, 12.0, 6.8, 4.4 Hz), 2.21 (dq, 1H, J = 13.3, 4.4 Hz), 1.90 (dddd, 1H, J = 13.2, 12.0, 10.7, 5.2 Hz), 1.28 (d, 3H, J = 6.4 Hz). The spectral data are in agreement with those previously assigned for this compound.[11]

[11] Buksha, S.; Coumbarides, G. S.; Dingjan, N.; Eames, J.; Suggate, M. J.; Weerasooriya, N. *J. Label. Compd. Radiopharm.* **2006**, *49*, 757-771.

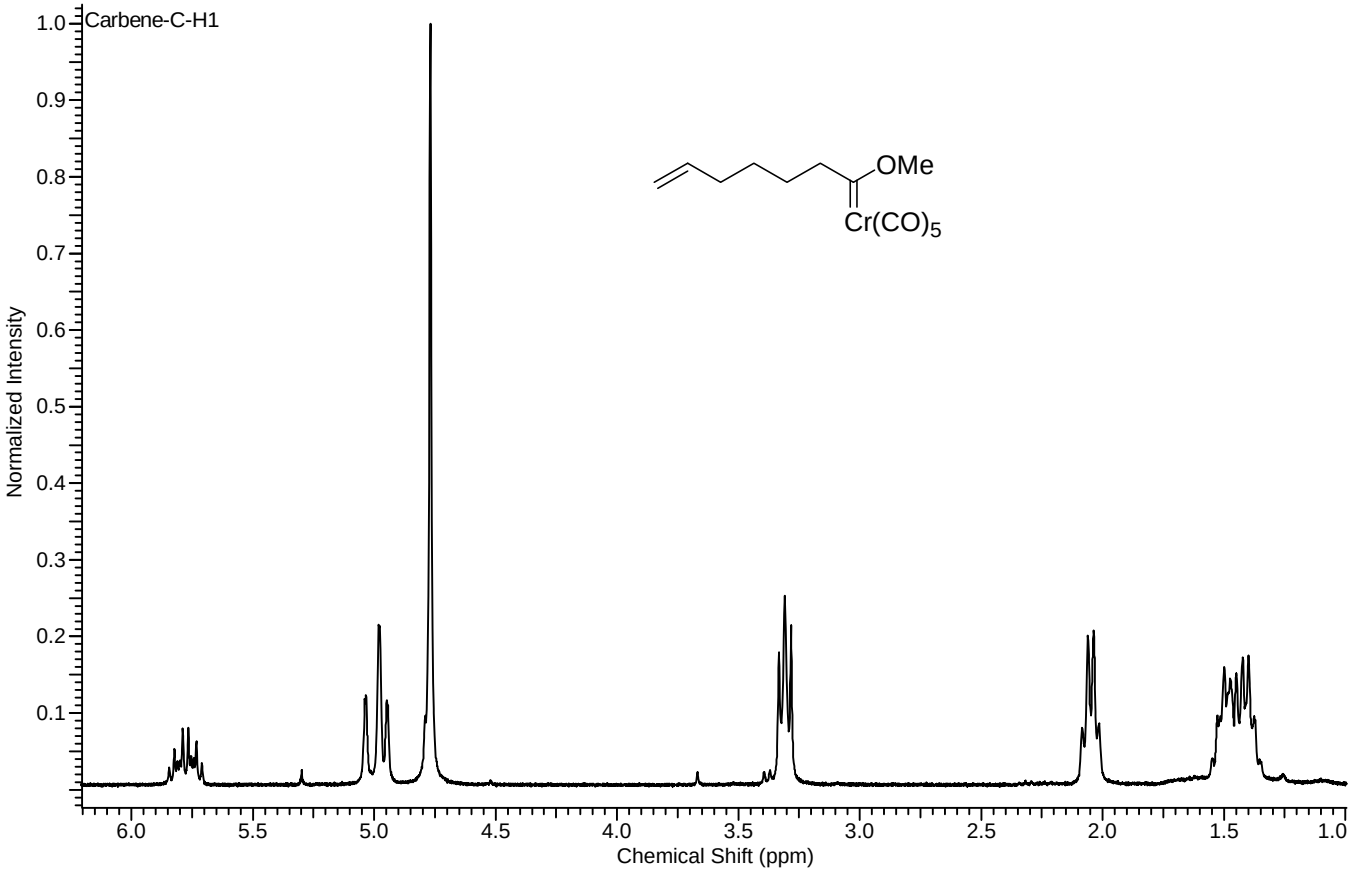
Proton NMR Spectrum of Carbene Complex **1b**



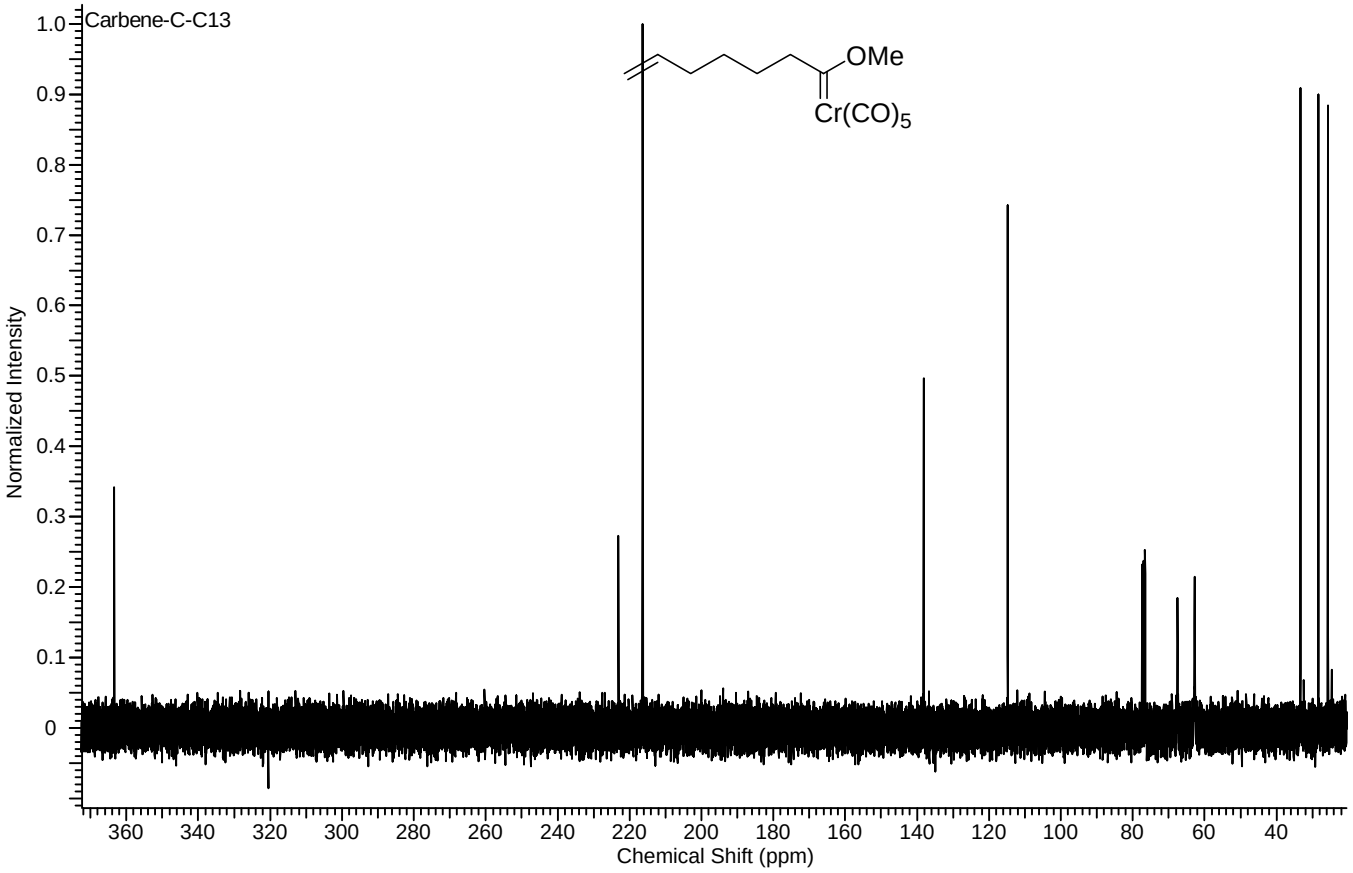
Carbon-13 NMR Spectrum of Compound **1b**



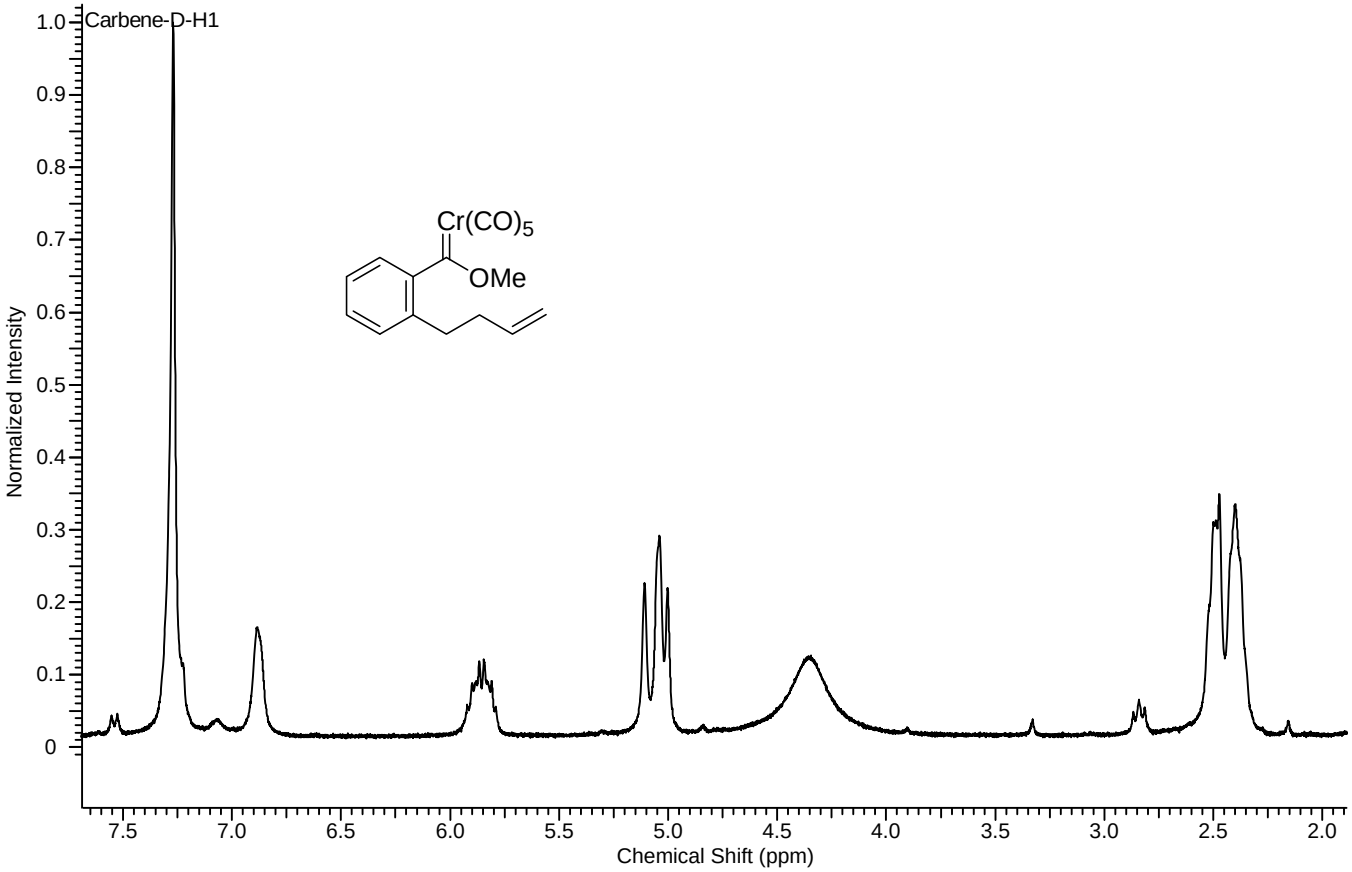
Proton NMR spectrum of Carbene Complex **1c**



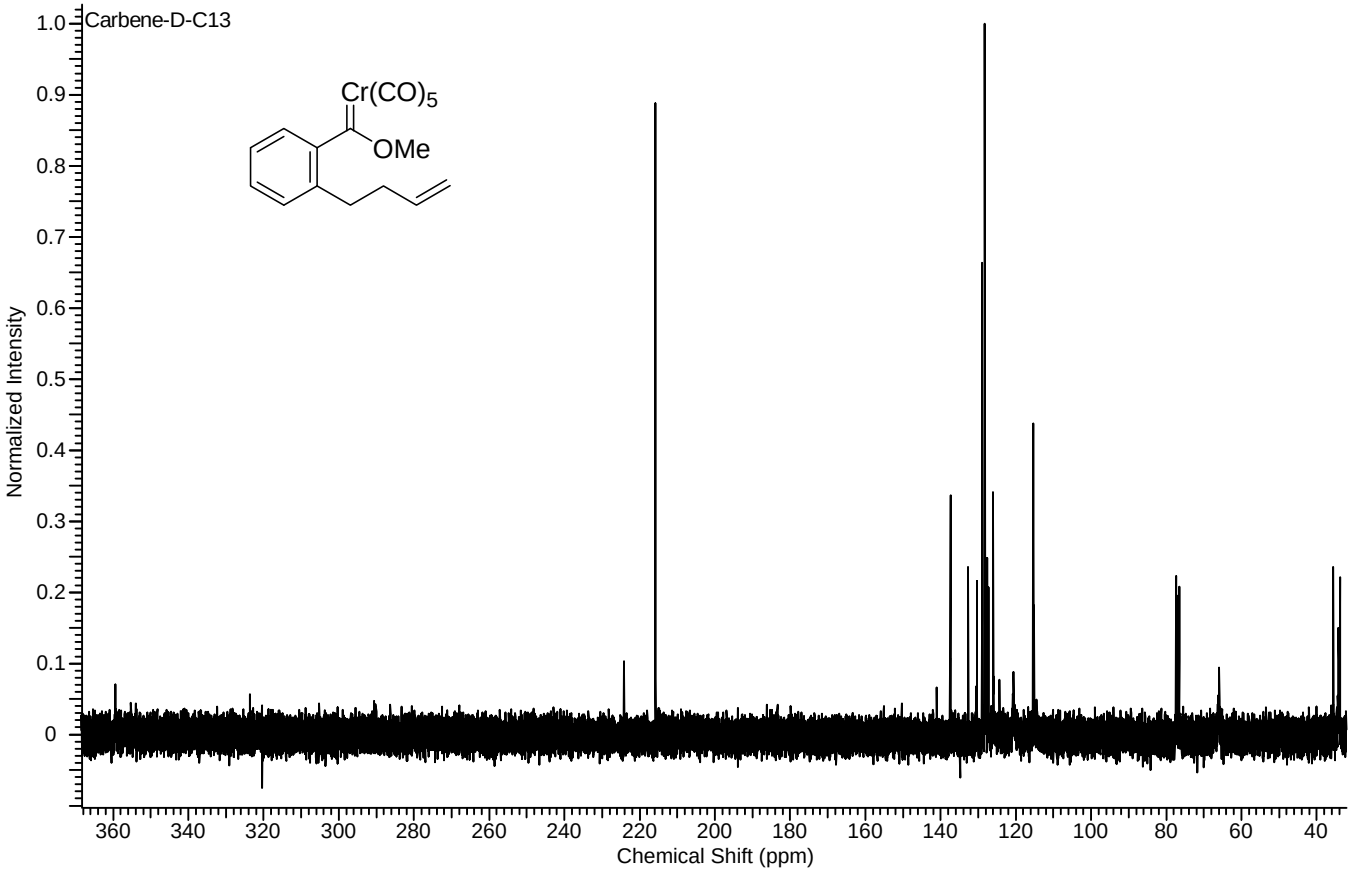
Carbon-13 NMR Spectrum of Carbene Complex **1c**



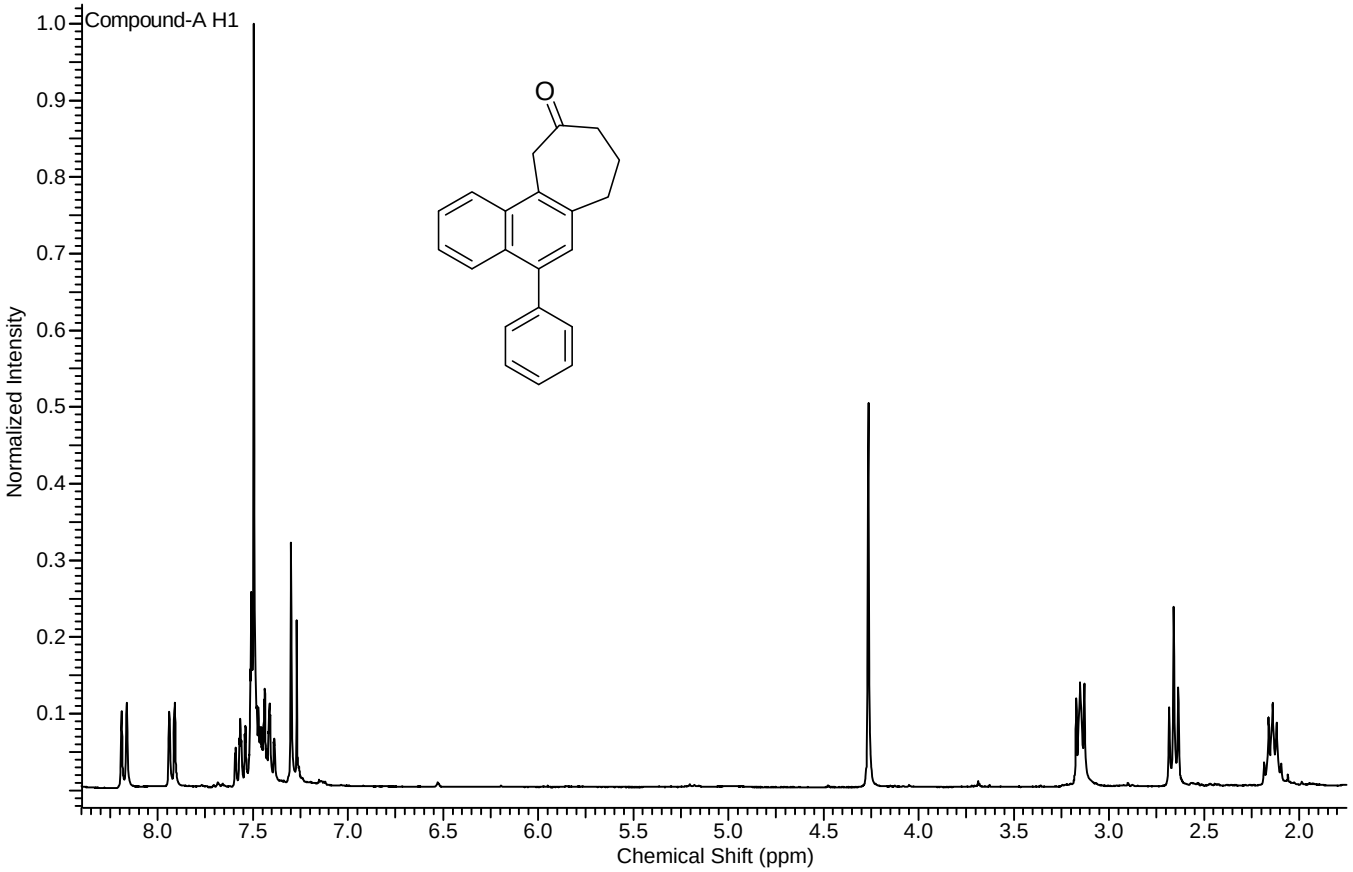
Proton NMR Spectrum of Carbene Complex **2b**



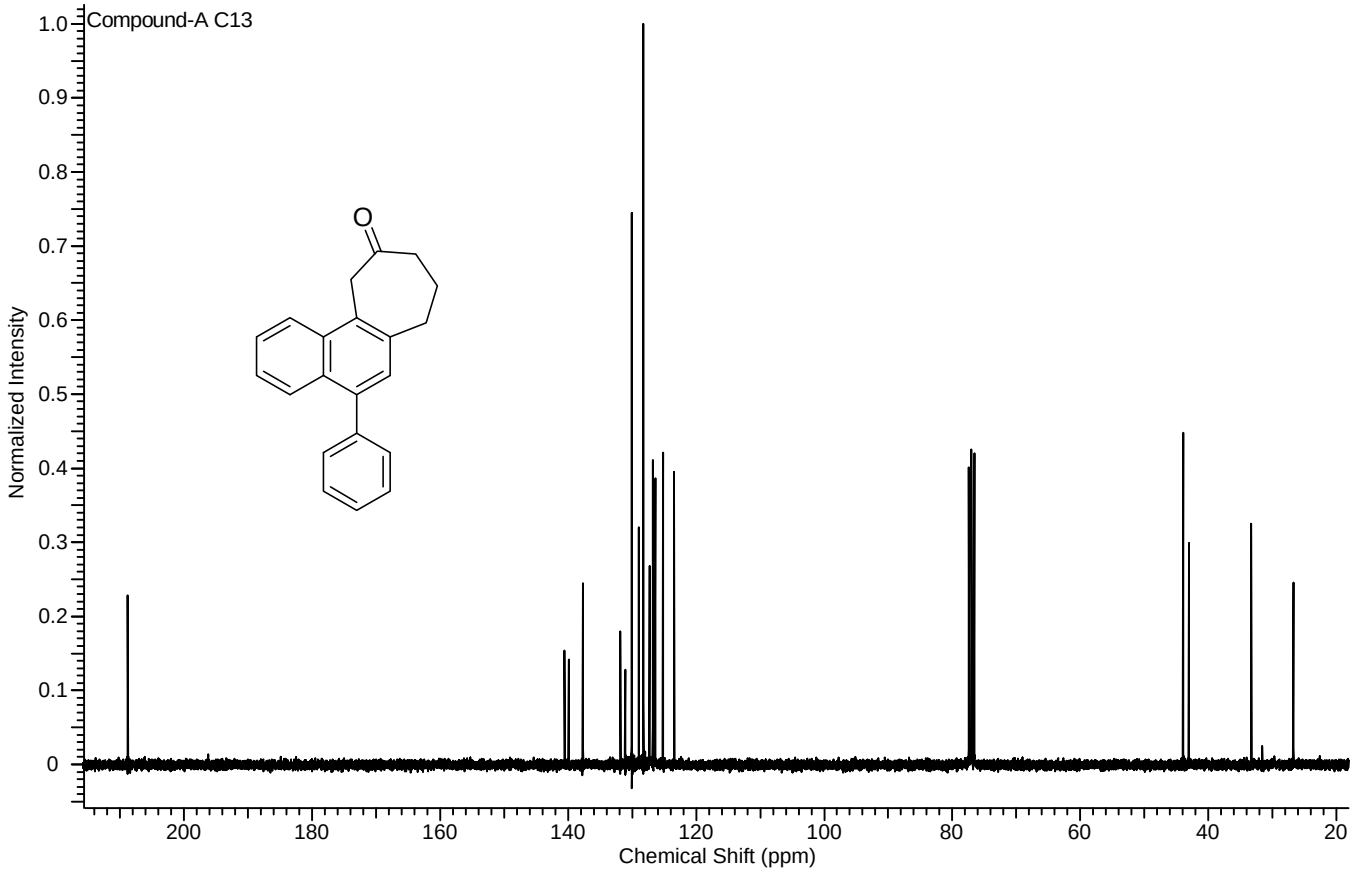
Carbon-13 NMR Spectrum of Carbene Complex **2b**



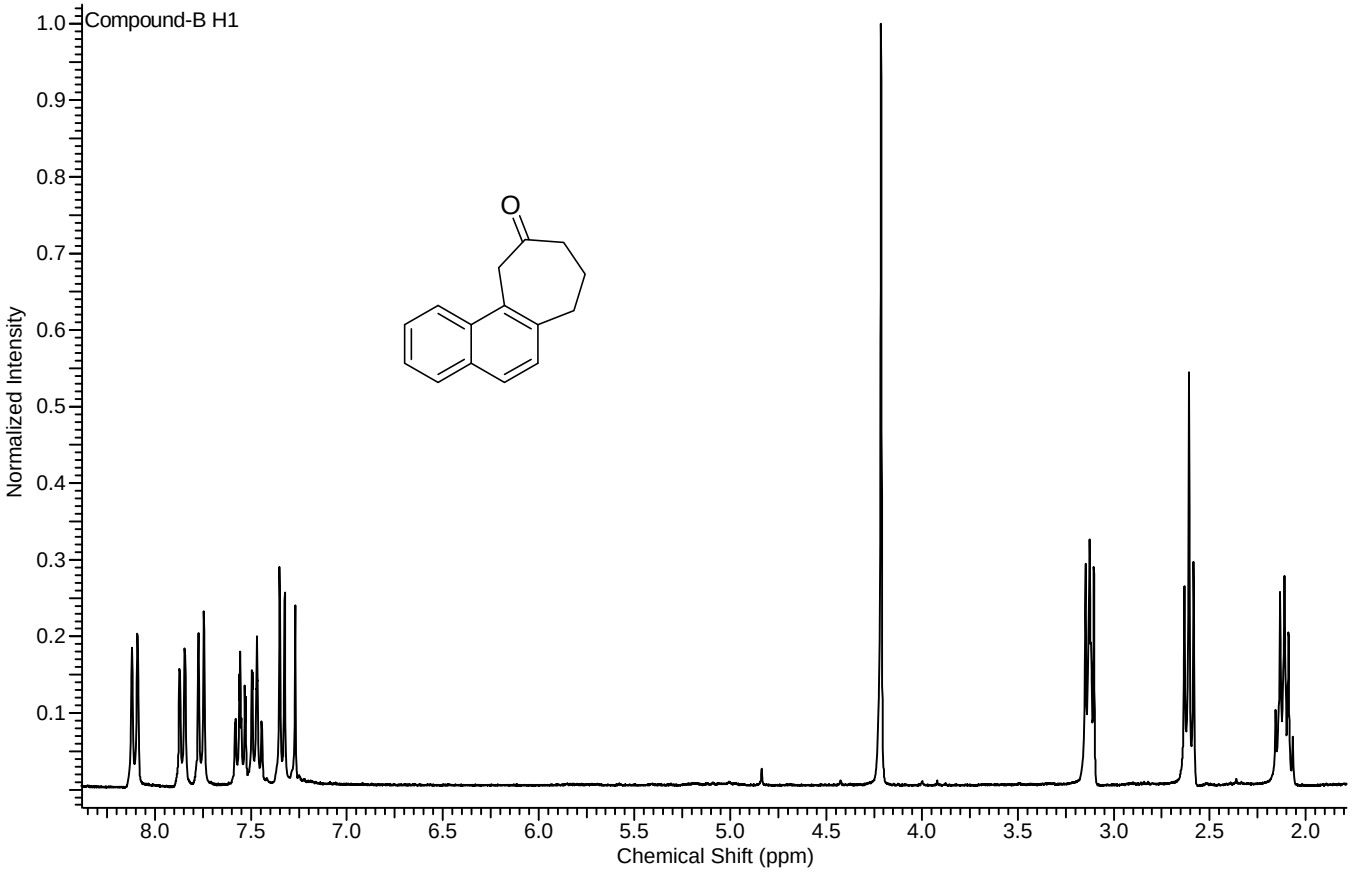
Proton NMR Spectrum of Compound **7a**



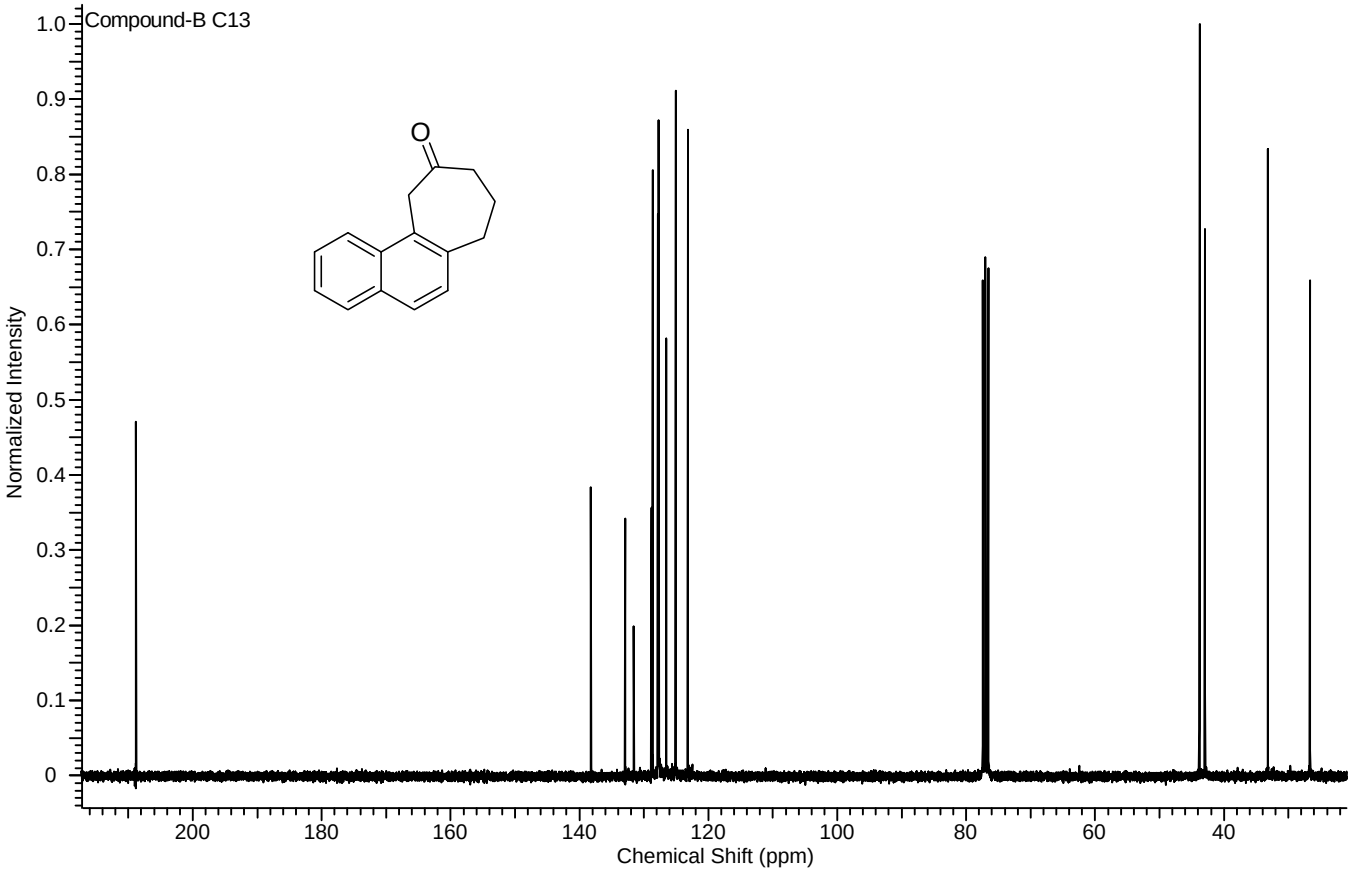
Carbon-13 NMR Spectrum of Compound **7a**



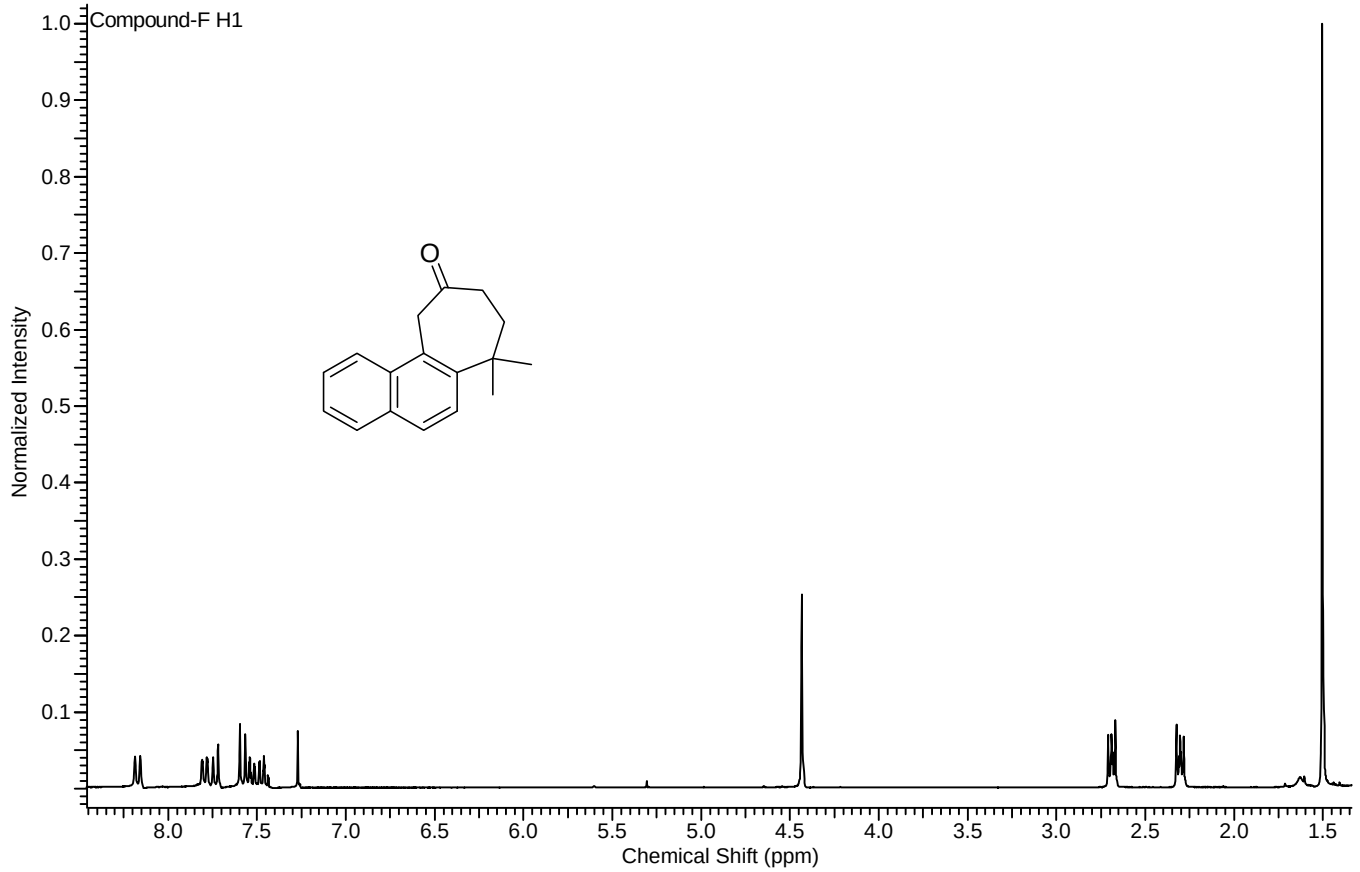
Proton NMR Spectrum of Compound **7b**



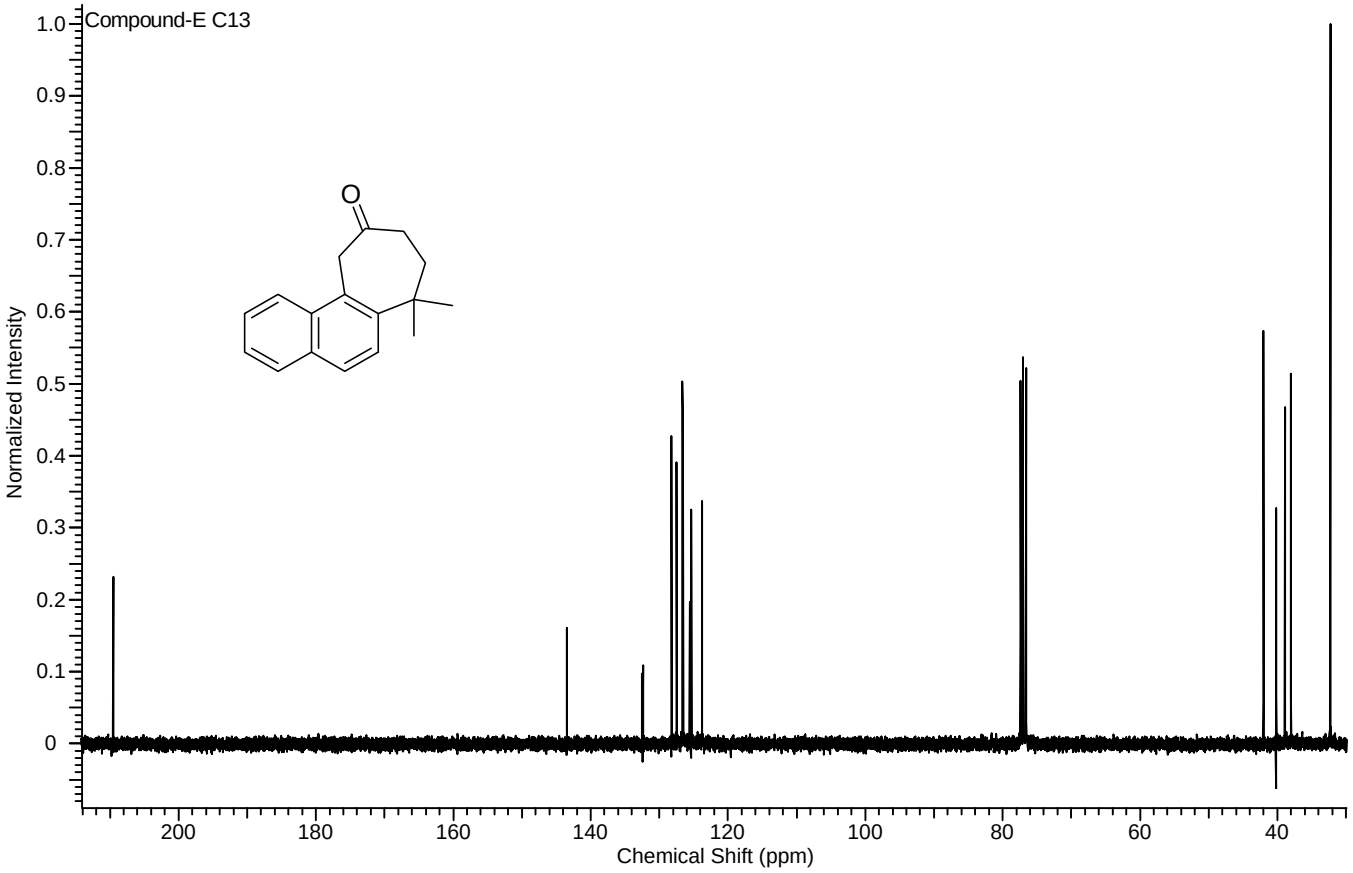
Carbon-13 NMR Spectrum of Compound **7b**



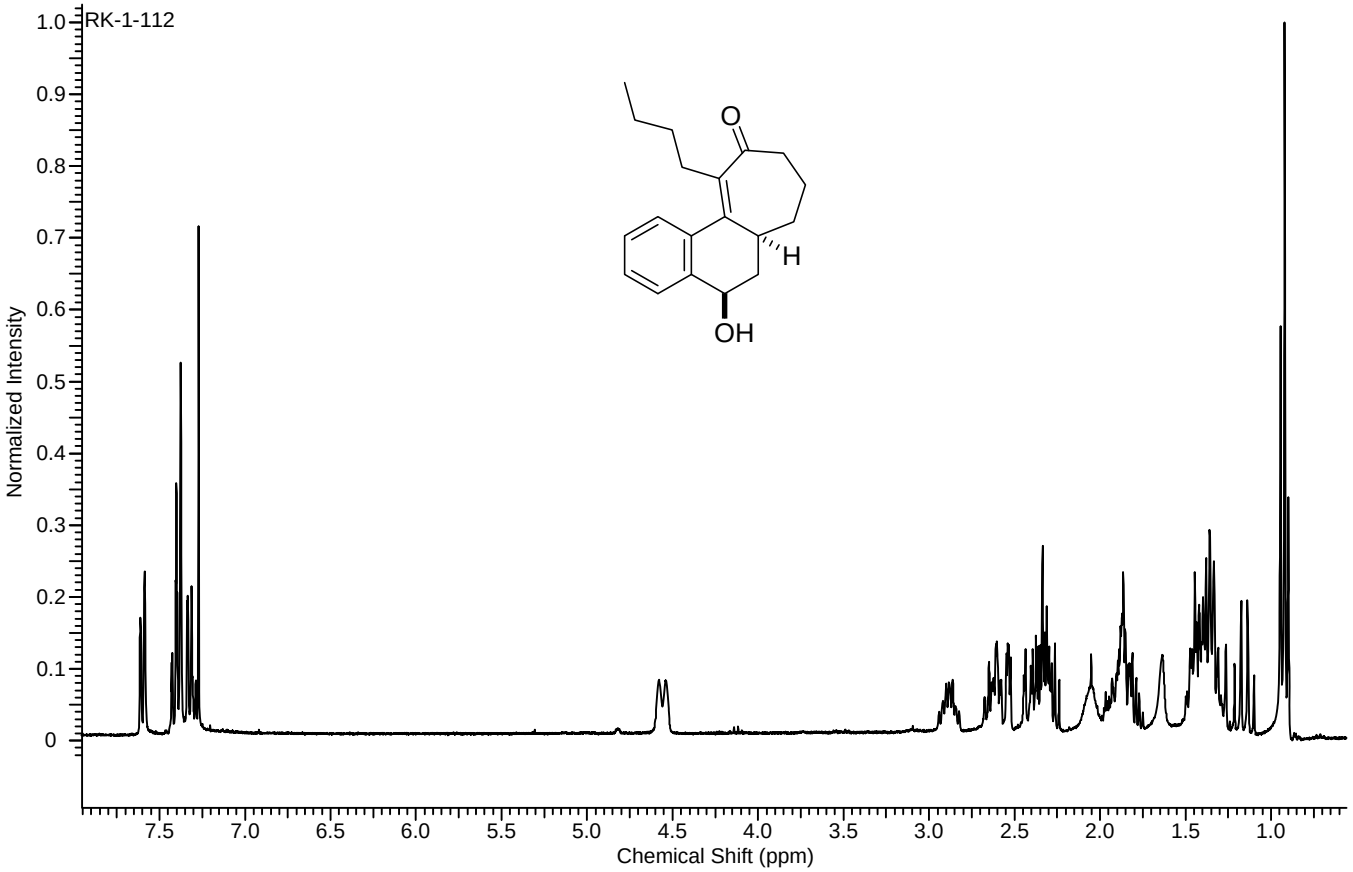
Proton NMR Spectrum of Compound **7c**



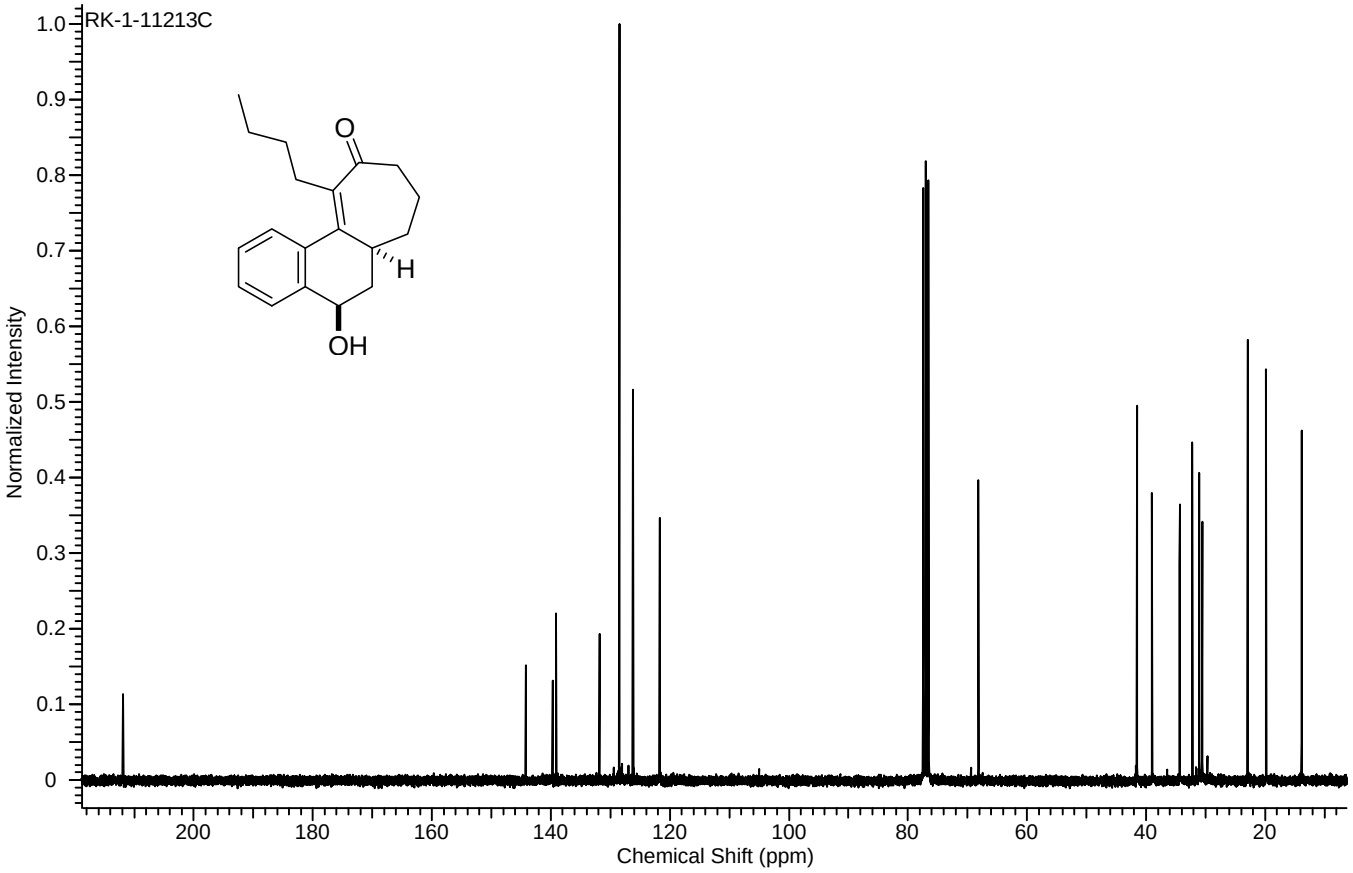
Carbon-13 NMR Spectrum of Compound **7c**



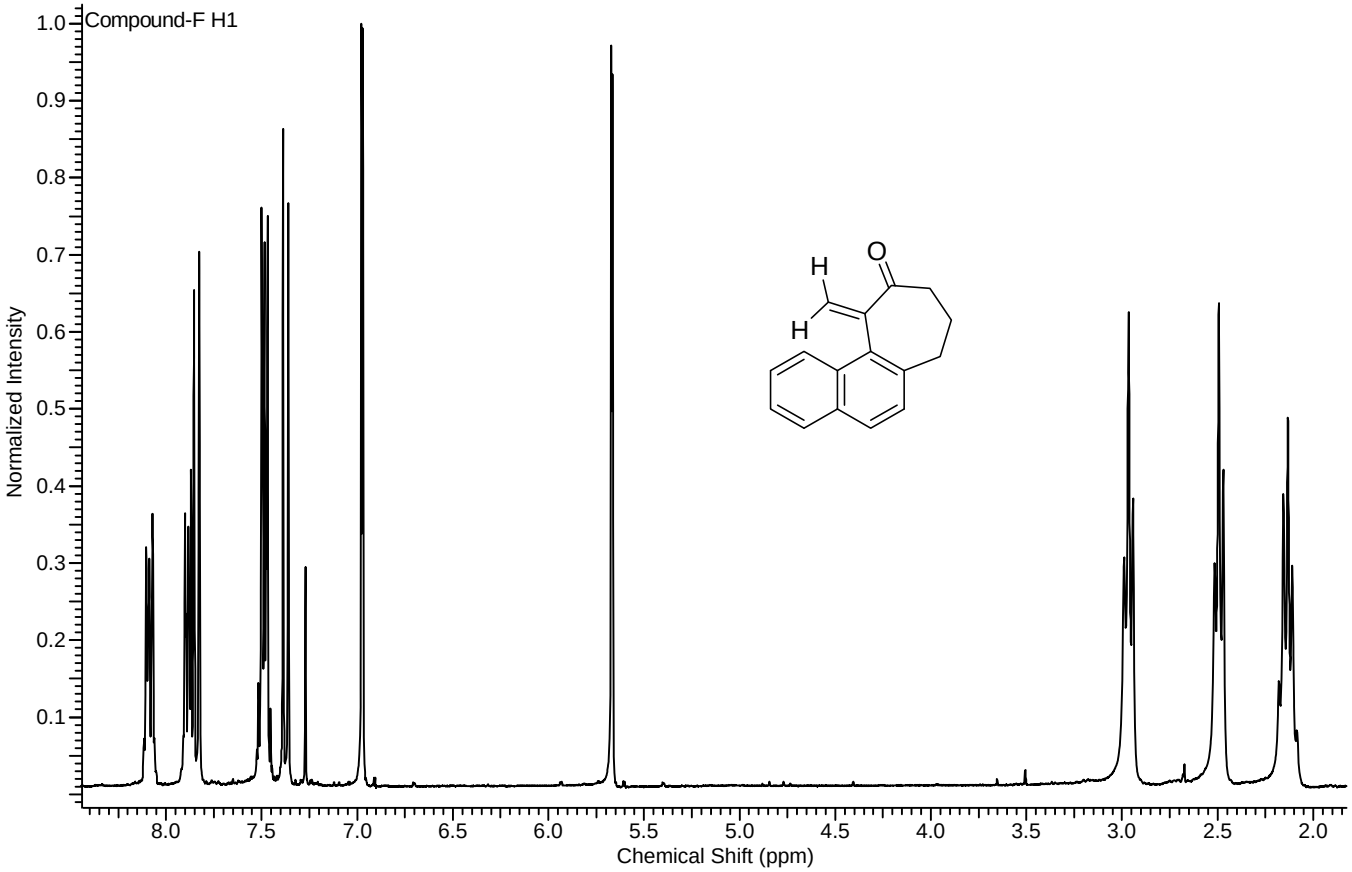
Proton NMR Spectrum of Compound **11**



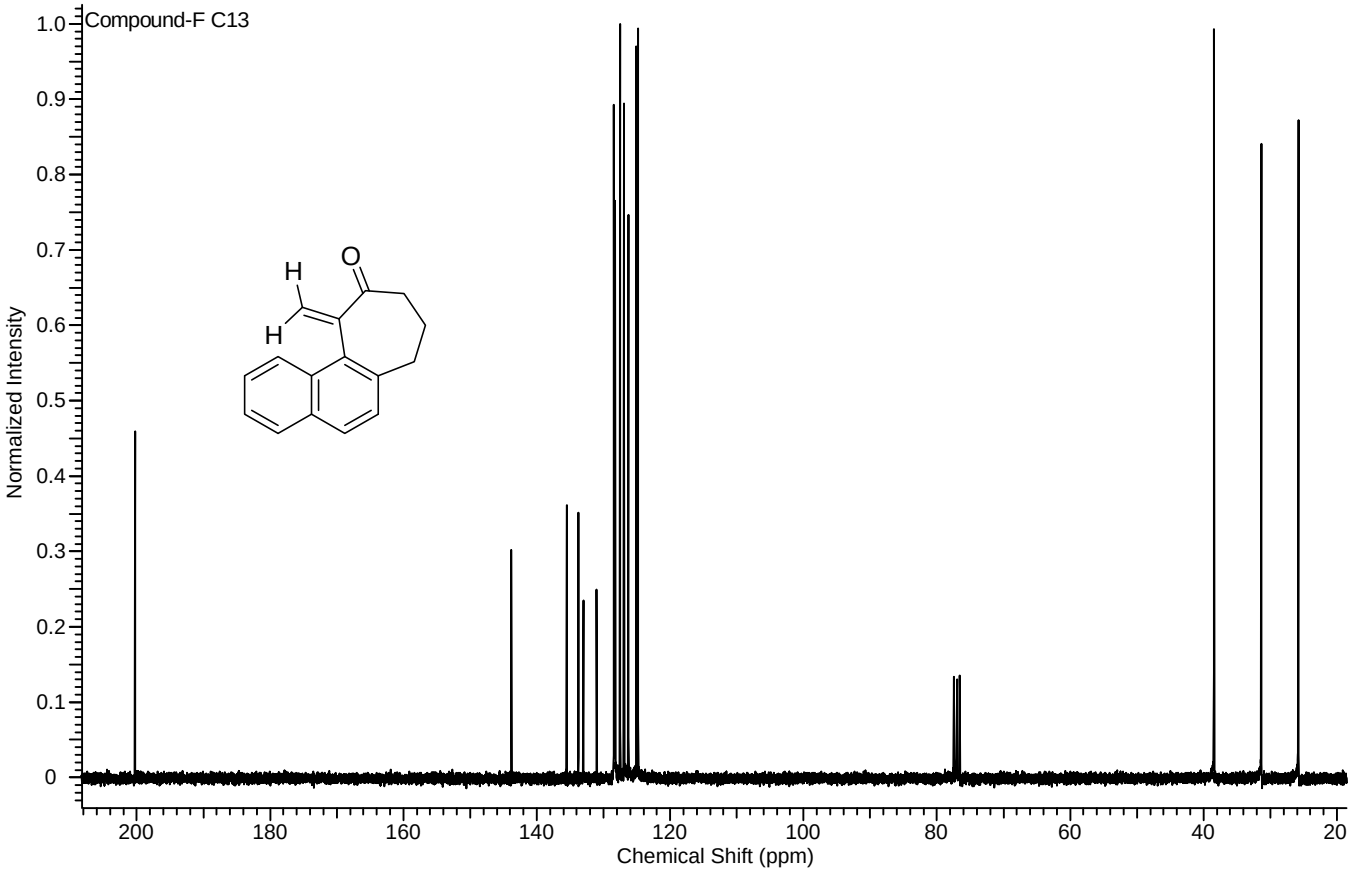
Carbon-13 NMR Spectrum of compound **11**



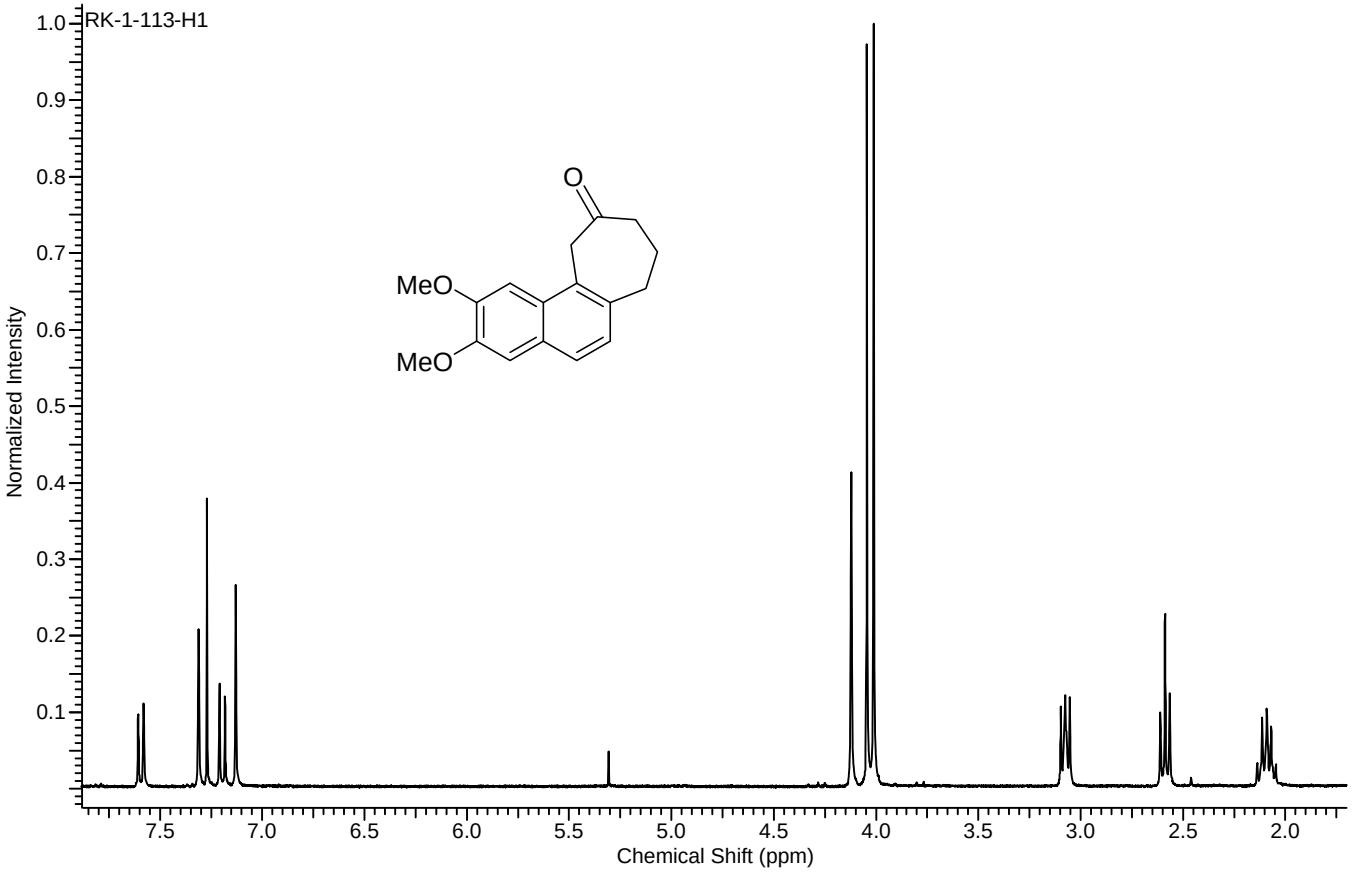
Proton NMR Spectrum of Compound **10**



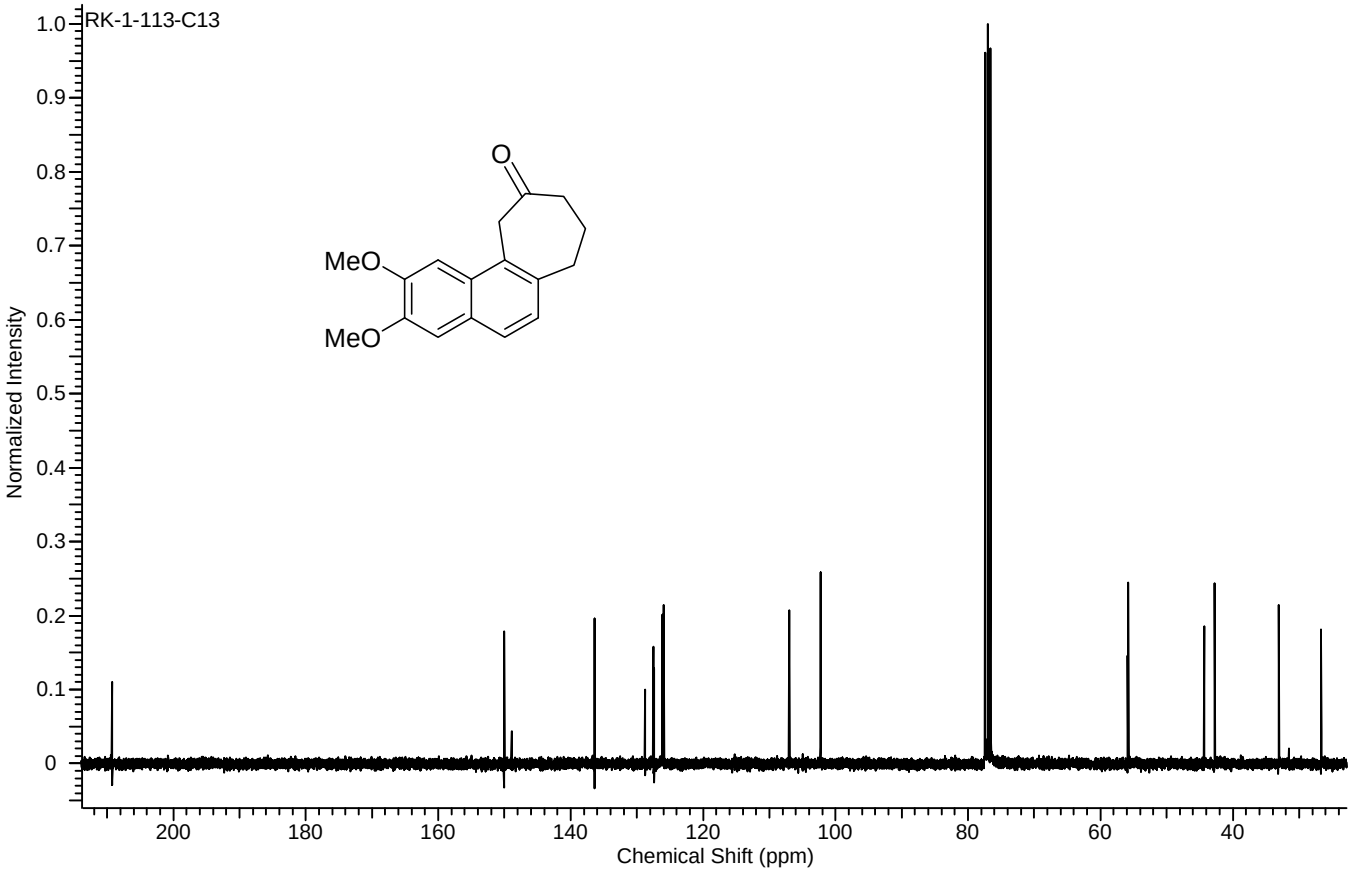
Carbon-13 NMR Spectrum of Compound **10**



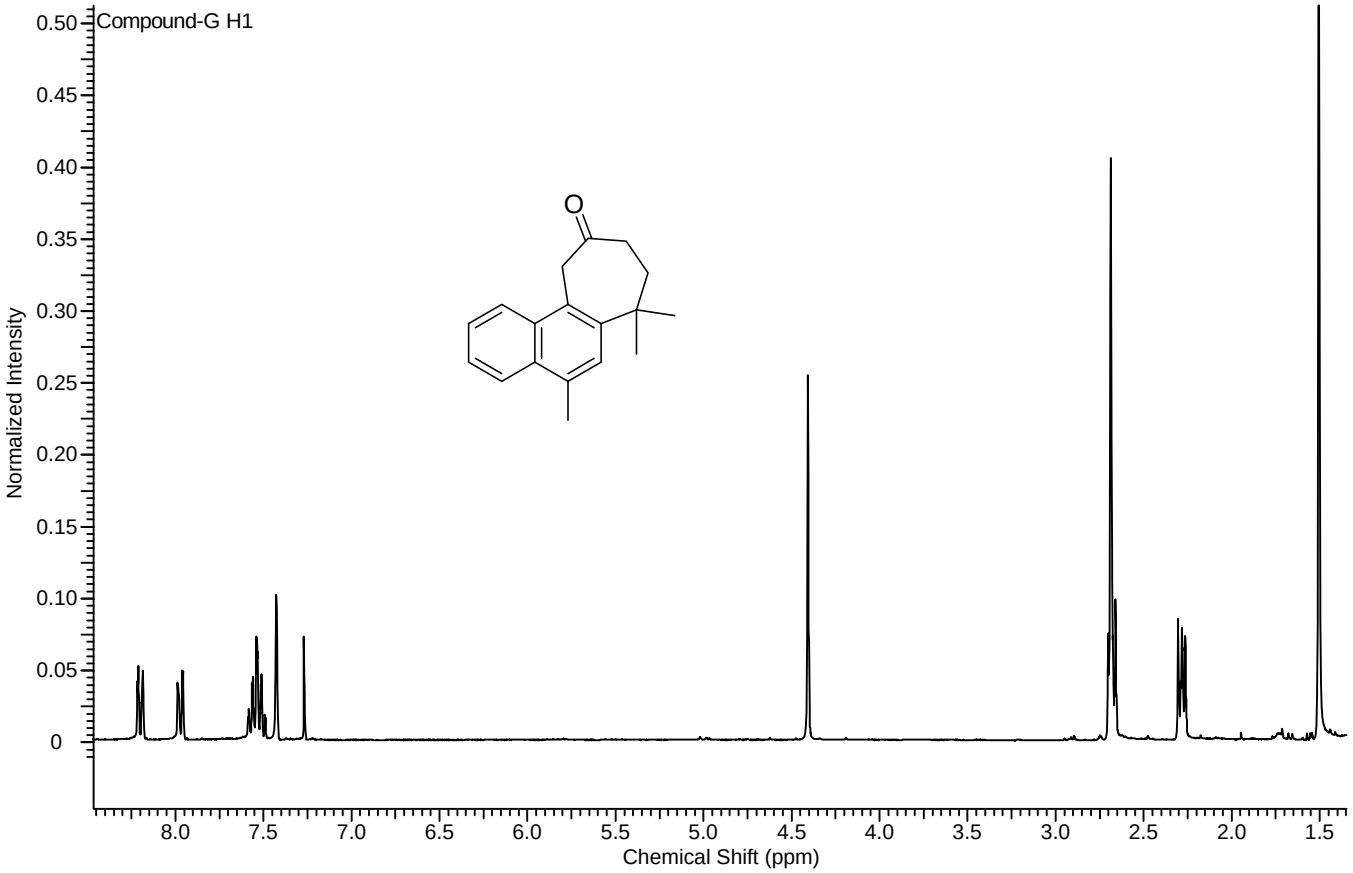
Proton NMR Spectrum of Compound **7g**



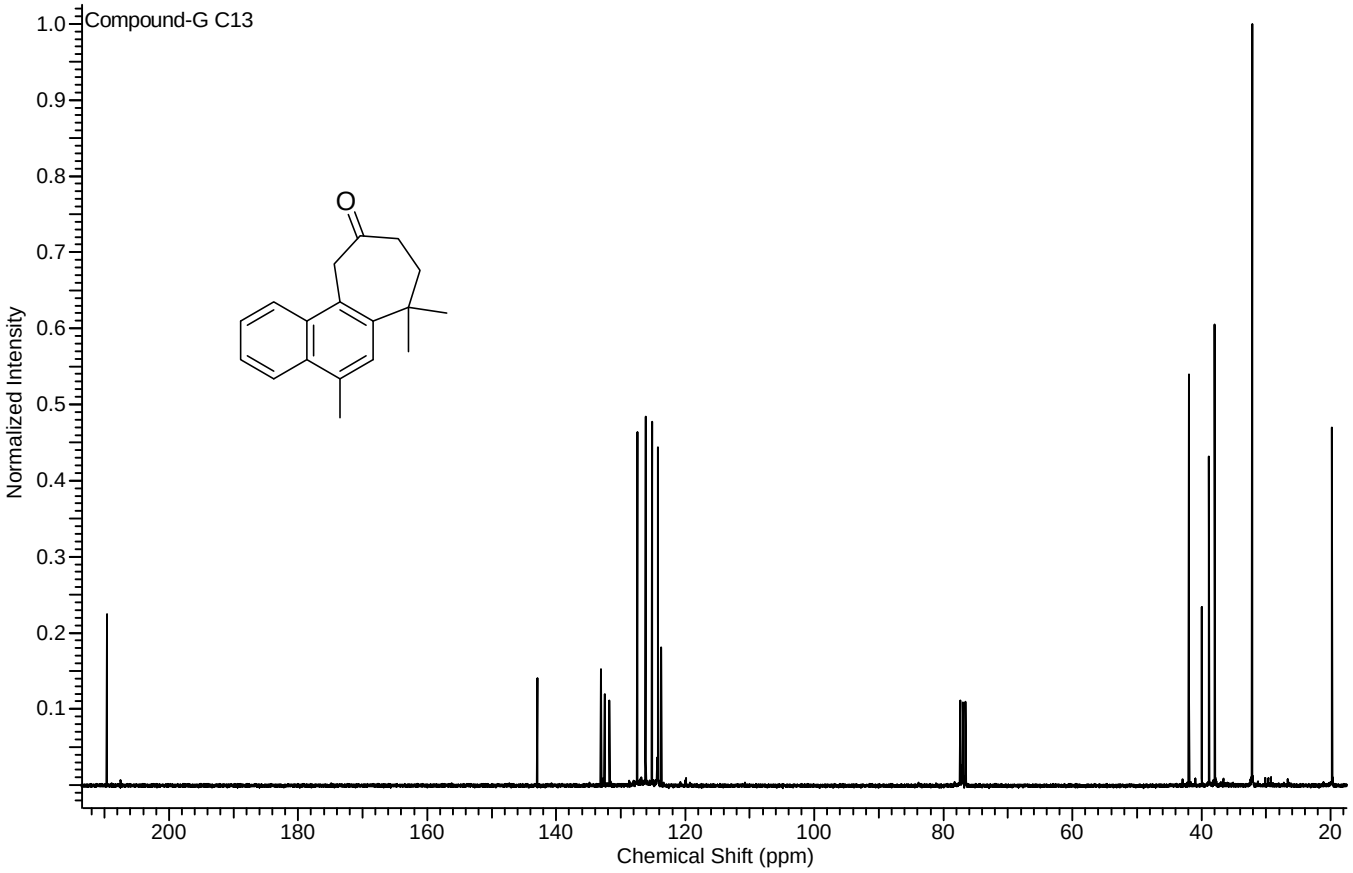
Carbon-13 NMR Spectrum of Compound **7g**



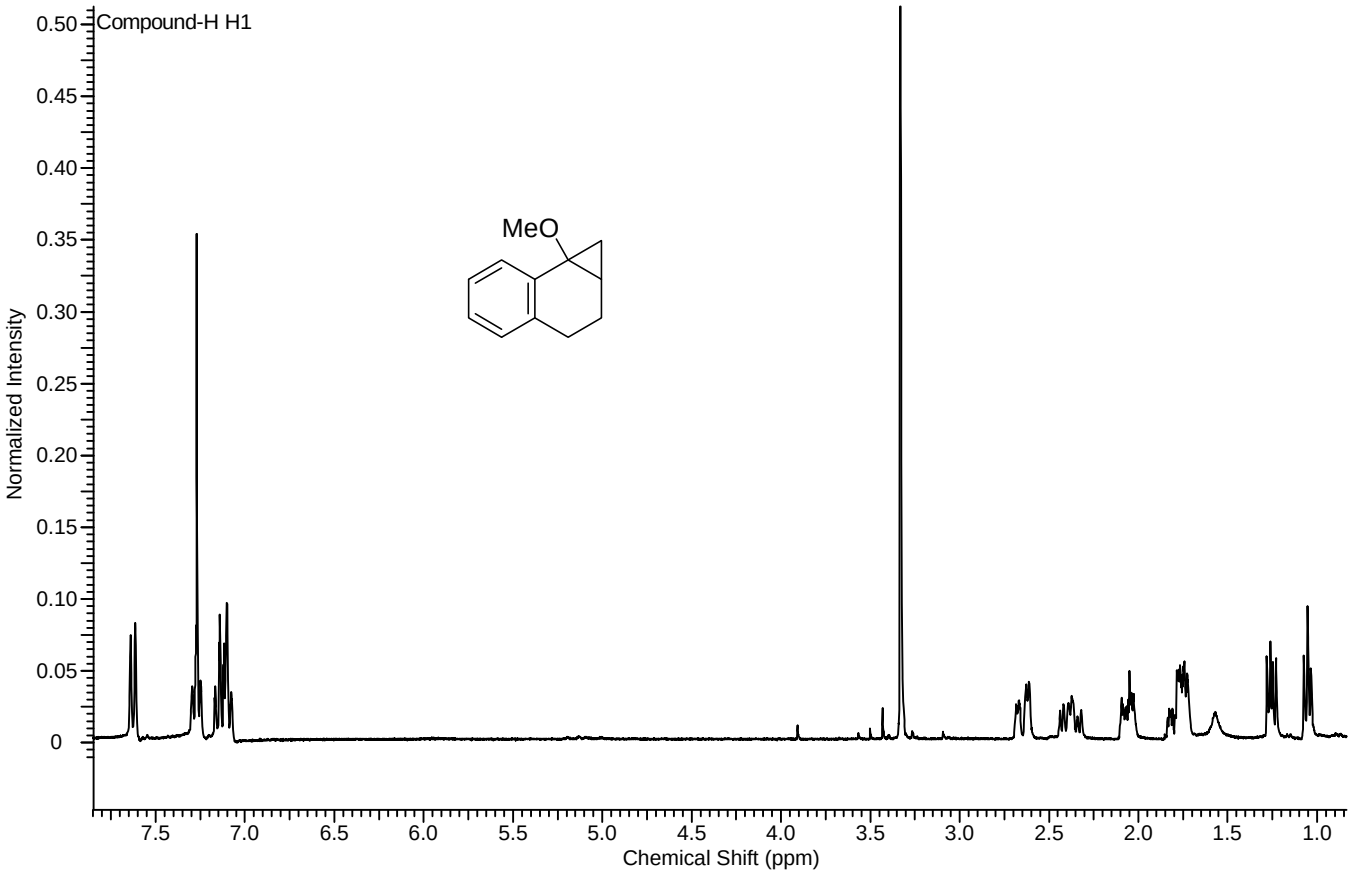
Proton NMR Spectrum of Compound **7h**



Carbon-13 NMR Spectrum of Compound **7h**



Proton NMR Spectrum for Compound **12b**



Carbon-13 NMR Spectrum of Compound **12b**