

Supporting Information

Silver-Catalyzed Intramolecular Oxycyclization of Alkynes to Bridged Bicyclic Ketals

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Characterization of compounds **2a-d**, **2f-i**, **3a**, **4b** and **5b** are therein.

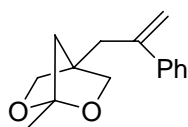
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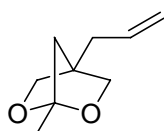
1. General experimental procedure:

To a mixture of silver triflate (5 mol%) in toluene was added a solution of bis-homopropargylic diol **1a-i** in toluene at 0 °C under argon atmosphere. The resulting mixture was stirred for 10min at room temperature. Upon completion of the reaction, the solvent was removed under vacuum and the crude product was subjected for flash column chromatography (EtOAc : *n*-hexane = 1 : 10) to afford the pure product as a colorless liquid.

2. Spectroscopic data of compounds

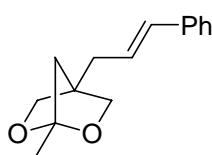


Spectroscopic data of compound 2a: ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.29 (m, 5H), 5.28 (d, *J* = 1.2 Hz, 1H), 5.07 (d, *J* = 1.2 Hz, 1H), 3.65-3.58 (m, 4H), 2.84 (s, 1H), 1.51 (s, 2H), 1.45 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 145.29, 141.31, 128.48, 127.86, 126.15, 115.74, 108.32, 76.41, 48.73, 45.03, 34.80, 17.87; IR (NaCl, cm⁻¹) 1621, 1482, 1396; HRMS calculated for C₁₅H₁₈NaO₂ 253.1204; found, 253.1207.

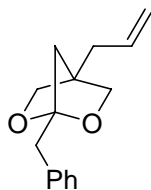


Spectroscopic data of compound 2b: ¹H NMR (400 MHz, CDCl₃) δ 5.80-5.70 (m, 1H), 5.11-5.06 (m, 2H), 3.79-.74 (m, 4H), 2.4 (d, *J* = 7.6 Hz, 2H), 1.70

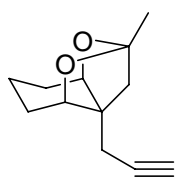
(s, 2H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.27, 117.83, 108.38, 76.20, 48.69, 44.09, 32.76, 17.89.¹



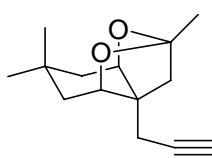
Spectroscopic data of compound 2c: ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.29 (m, 4H), 7.26-7.21 (m, 1H), 6.44 (d, $J = 16.0$ Hz, 1H), 6.14 (dt, $J = 16.0, 7.2$ Hz, 1H), 3.84-3.80 (m, 4H), 2.50 (dd, $J = 7.4, 1.2$ Hz, 2H), 1.76 (s, 2H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.57, 133.64, 129.28, 128.17, 126.80, 125.49, 109.17, 77.02, 49.97, 44.88, 32.64, 18.64.¹



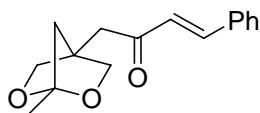
Spectroscopic data of compound 2d: ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.27 (m, 4H), 7.26-7.22 (m, 1H), 5.75-5.65 (m, 1H), 5.07-5.03 (m, 2H), 3.81 (d, $J = 5.6$ Hz, 2H), 3.71 (d, $J = 6.0$ Hz, 2H), 3.13 (s, 2H), 2.29 (d, $J = 7.2$ Hz, 2H), 1.58 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 136.90, 133.51, 130.23, 128.40, 126.77, 118.14, 110.94, 76.54, 48.19, 42.54, 38.80, 33.02.¹



Spectroscopic data of compound 2f: ^1H NMR (400 MHz, CDCl_3) δ 4.13 (d, $J = 3.2$ Hz, 2H), 2.38 (d, $J = 2.8$ Hz, 2H), 2.04 (t, $J = 2.8$ Hz, 1H), 2.03-1.96 (m, 1H), 1.94 (s, 2H), 1.88 (s, 1H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 106.56, 79.57, 78.20, 70.71, 47.08, 24.48, 17.98, 17.81, 13.12; IR (NaCl, cm^{-1}) 2119, 1454, 1398; HRMS calculated for $\text{C}_{12}\text{H}_{16}\text{NaO}_2$ 215.1048; found, 215.1052.

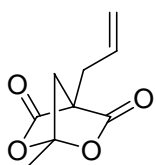


Spectroscopic data of compound 2g: ^1H NMR (400 MHz, CDCl_3) δ 4.18 (s, 2H), 2.34 (d, $J = 2.4$ Hz, 2H), 2.04 (t, $J = 2.8$ Hz, 1H), 1.96 (s, 2H), 1.90 (d, $J = 3.2$ Hz, 1H), 1.86 (d, $J = 2.8$ Hz, 1H), 1.52 (s, 3H), 1.34 (d, $J = 15.2$ Hz, 2H), 1.31 (s, 3H), 0.94 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 107.84, 80.27, 79.91, 71.42, 47.67, 47.48, 37.62, 36.08, 31.52, 28.90, 18.97, 18.83; IR (NaCl, cm^{-1}) 2121, 1621, 1473; HRMS calculated for $\text{C}_{14}\text{H}_{20}\text{NaO}_2$ 243.1361; found, 243.1362.

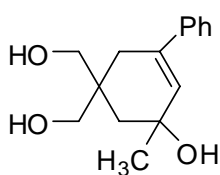


Spectroscopic data of compound 2h: ^1H NMR (400 MHz, CDCl_3) δ 7.57-7.53 (m, 3H), 7.43-7.40 (m, 3H), 6.72 (d, $J = 16.0$ Hz, 1H), 4.06 (d, $J = 6.0$ Hz, 2H), 3.83 (d, $J = 6.4$ Hz, 2H), 3.01 (s, 2H), 1.87 (s, 2H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.34, 143.83, 134.30, 131.14, 129.31, 128.65, 126.09, 108.22, 76.30, 46.91, 45.36, 40.08, 18.08; IR (NaCl, cm^{-1}) 1733, 1684; HRMS calculated for $\text{C}_{16}\text{H}_{18}\text{NaO}_3$ 281.1154; found, 281.1150.

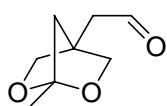
¹ S. Antoniotti, E. Genin, V. Michelet, J.-P. Genêt *J. Am. Chem. Soc.* 2005, **127**, 9976.



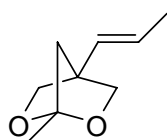
Spectroscopic data of compound 2i: ^1H NMR (400 MHz, CDCl_3) δ 5.84-5.73 (m, 1H), 5.26-5.17 (m, 2H), 2.73 (d, $J = 7.6$ Hz, 2H), 2.64 (s, 2H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.41, 130.73, 120.28, 110.25, 60.50, 50.77, 27.84, 17.56; IR (NaCl, cm^{-1}) 1717, 11653; HRMS calculated for $\text{C}_9\text{H}_{10}\text{NaO}_4$ 205.0477; found, 205.0180.



Spectroscopic data of compound 3a: ^1H NMR (400 MHz, CDCl_3) δ 7.44-7.41 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.22 (m, 1H), 6.44 (s, 1H), 3.92 (d, $J = 7.2$ Hz, 1H), 3.86-3.80 (m, 3H), 2.65 (s, 2H), 1.81 (s, 2H), 1.66 bs, 3H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.85, 136.44, 128.78, 128.27, 127.28, 124.96, 80.98, 78.77, 65.72, 48.81, 43.95, 42.99, 25.93; IR (NaCl, cm^{-1}) 3413, 1653, 1559; HRMS calculated for $\text{C}_{15}\text{H}_{20}\text{NaO}_3$ 271.1310; found, 271.1312.

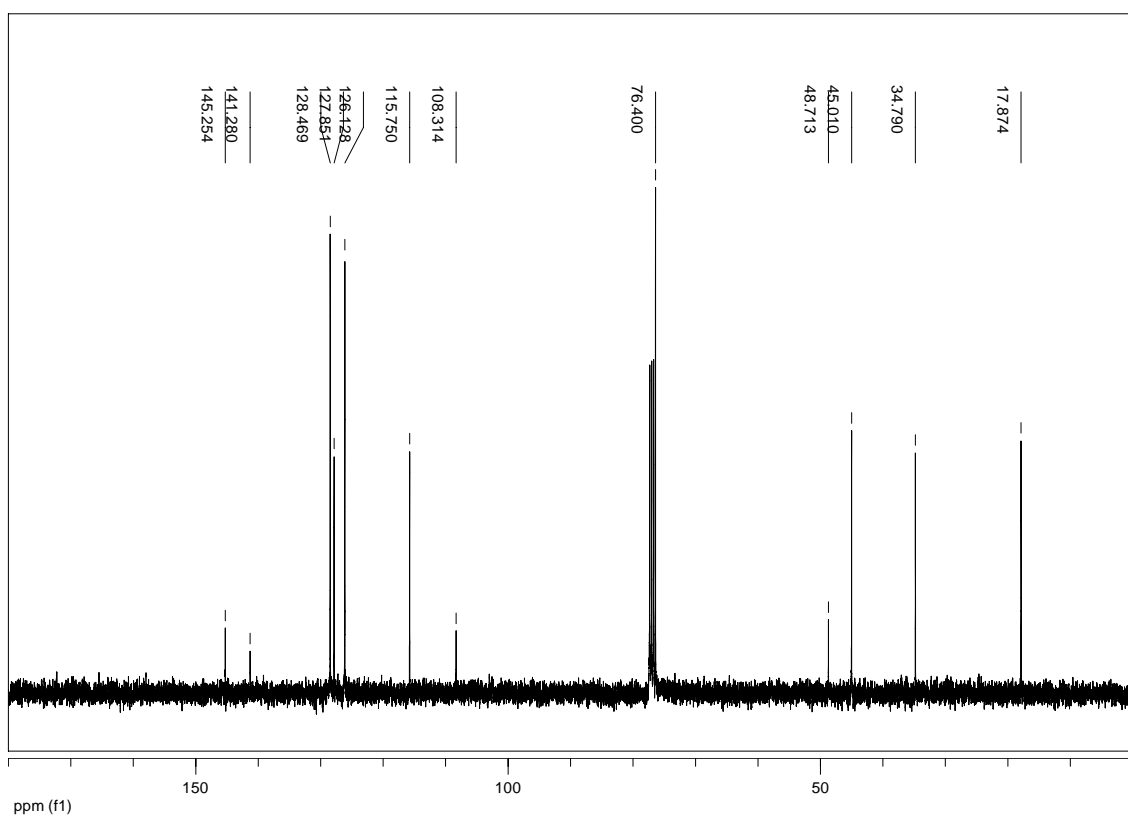
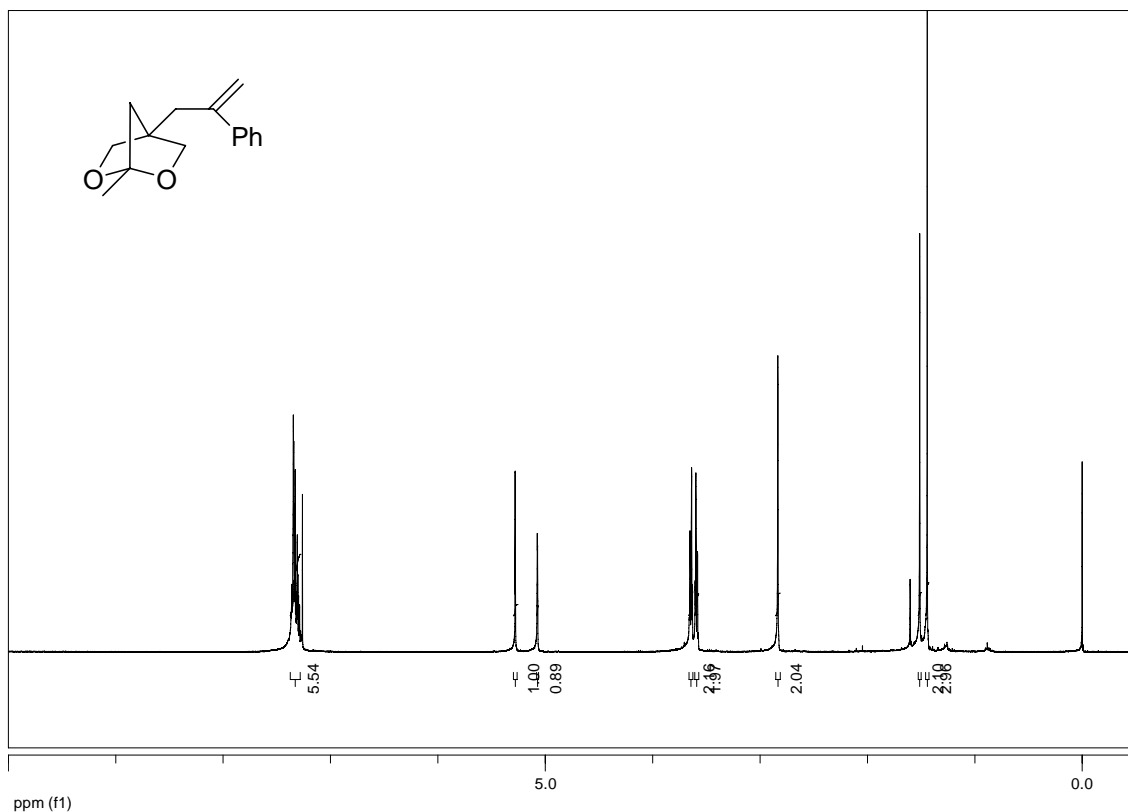


Spectroscopic data of compound 4b: ^1H NMR (400 MHz, CDCl_3) δ 9.79 (t, $J = 1.6$ Hz, 1H), 4.01-3.98 (m, 2H), 3.81-3.77 (m, 2H), 2.79 (d, $J = 1.2$ Hz, 2H), 1.87 (s, 2H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.77, 108.08, 75.69, 45.66, 44.37, 42.55, 17.71; IR (NaCl, cm^{-1}) 1749; HRMS calculated for $\text{C}_8\text{H}_{12}\text{NaO}_3$ 179.0684; found, 179.0685.

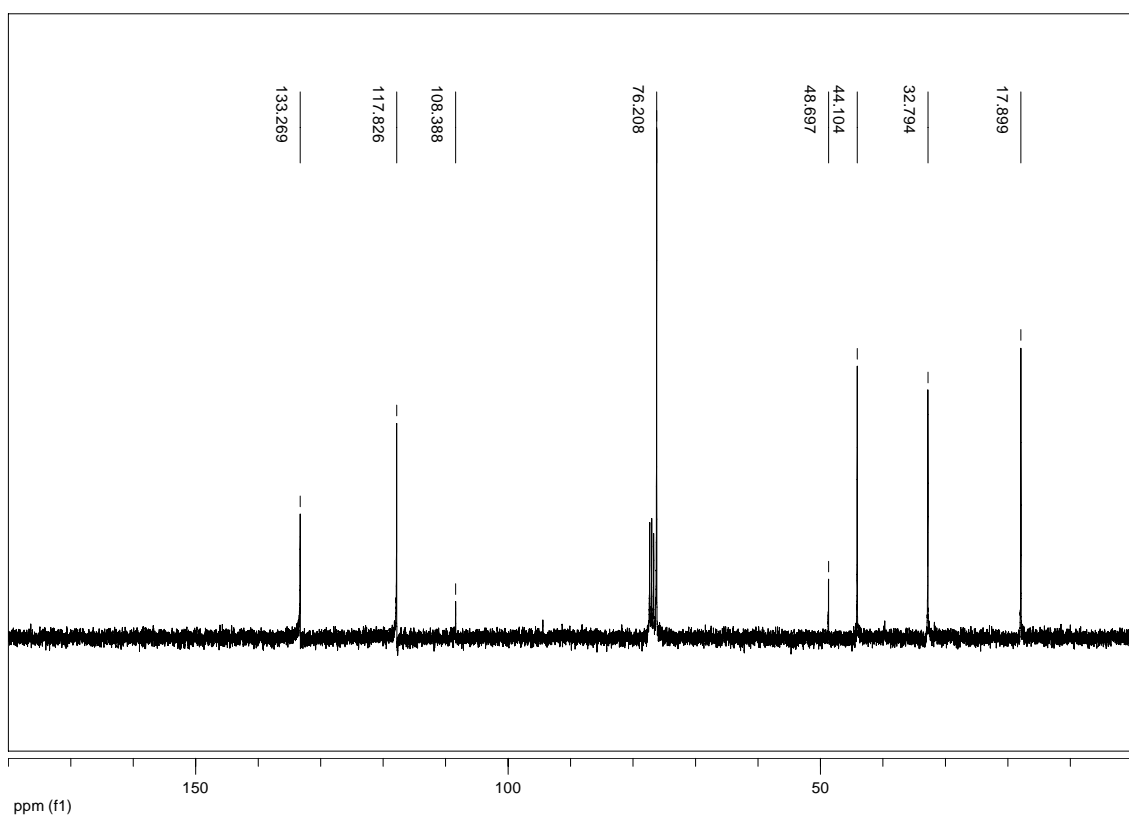
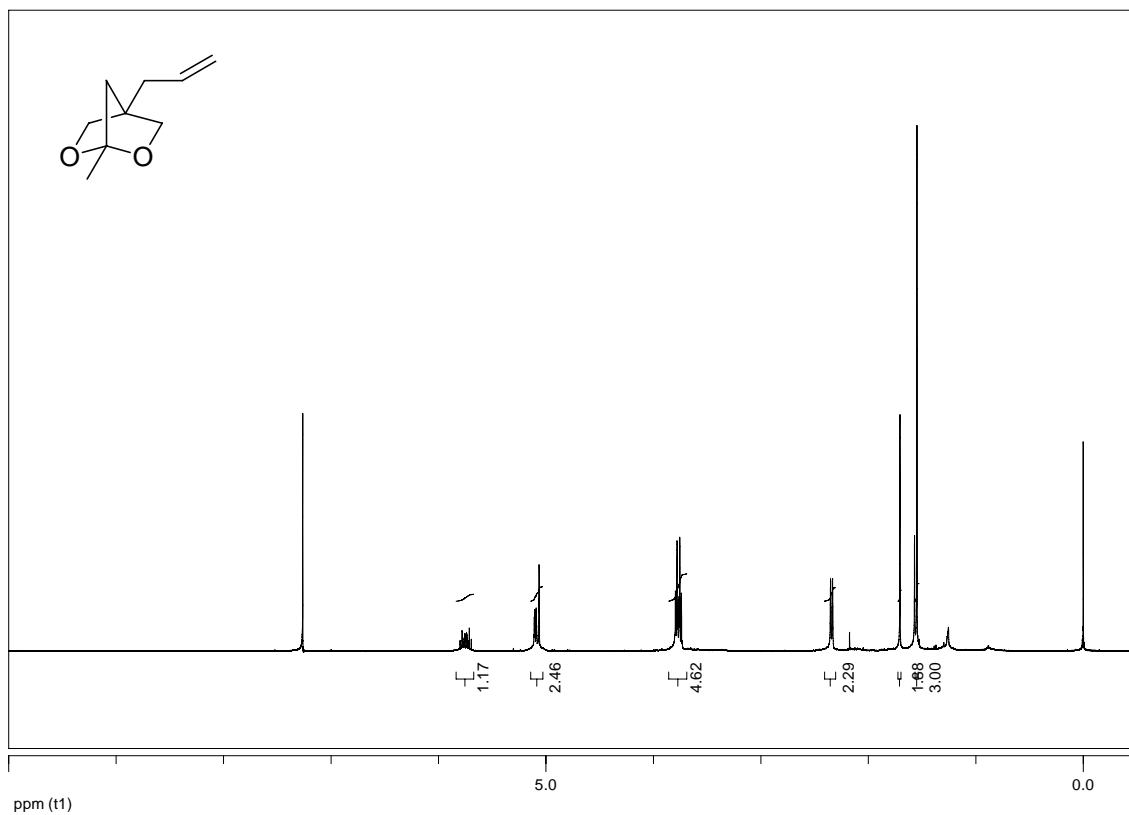


Spectroscopic data of compound 5b: ^1H NMR (400 MHz, CDCl_3) δ 5.55 d, $J = 16.0$ Hz, 1H), 5.51 (dq, $J = 16.0, 6.0$ Hz, 1H), 3.82 (s, 4H), 1.80 (s, 2H), 1.71 (d, $J = 4.8$ Hz, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 127.95, 125.85, 109.14, 77.63, 51.06, 45.85, 18.59, 18.19; HRMS calculated for $\text{C}_9\text{H}_{14}\text{NaO}_2$ 177.0891; found, 177.0894.

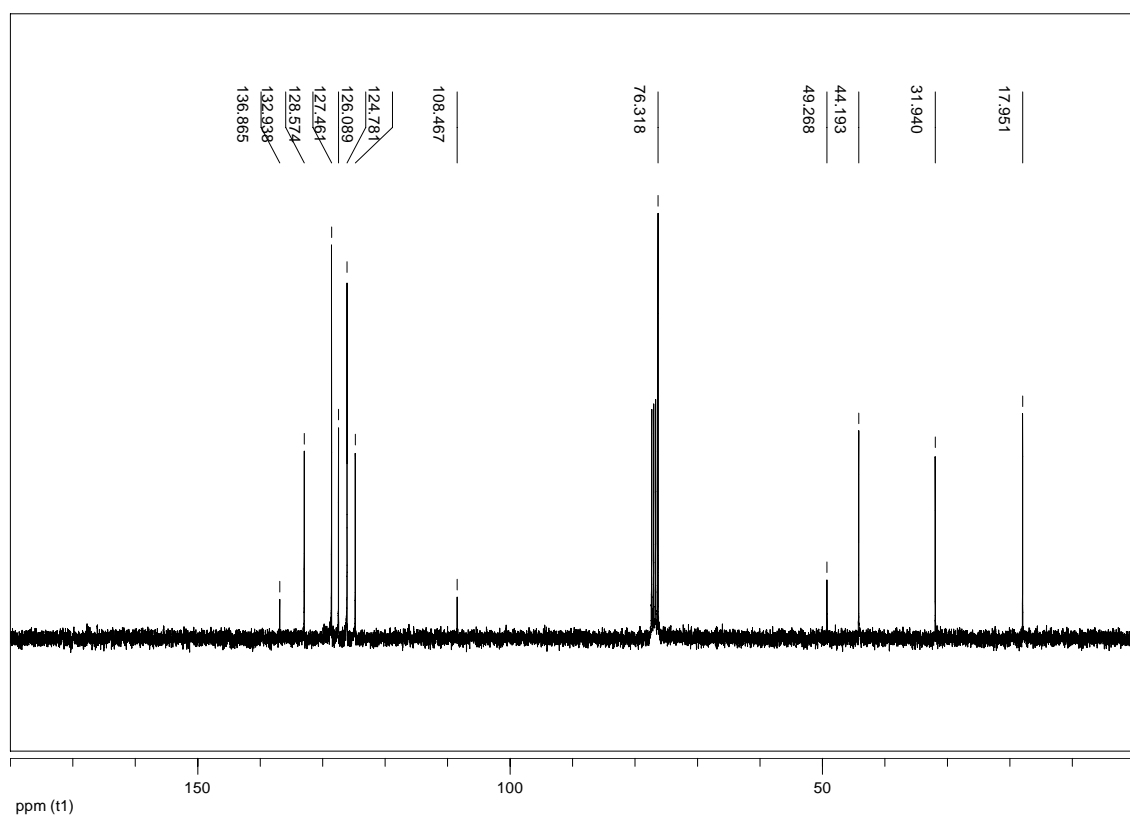
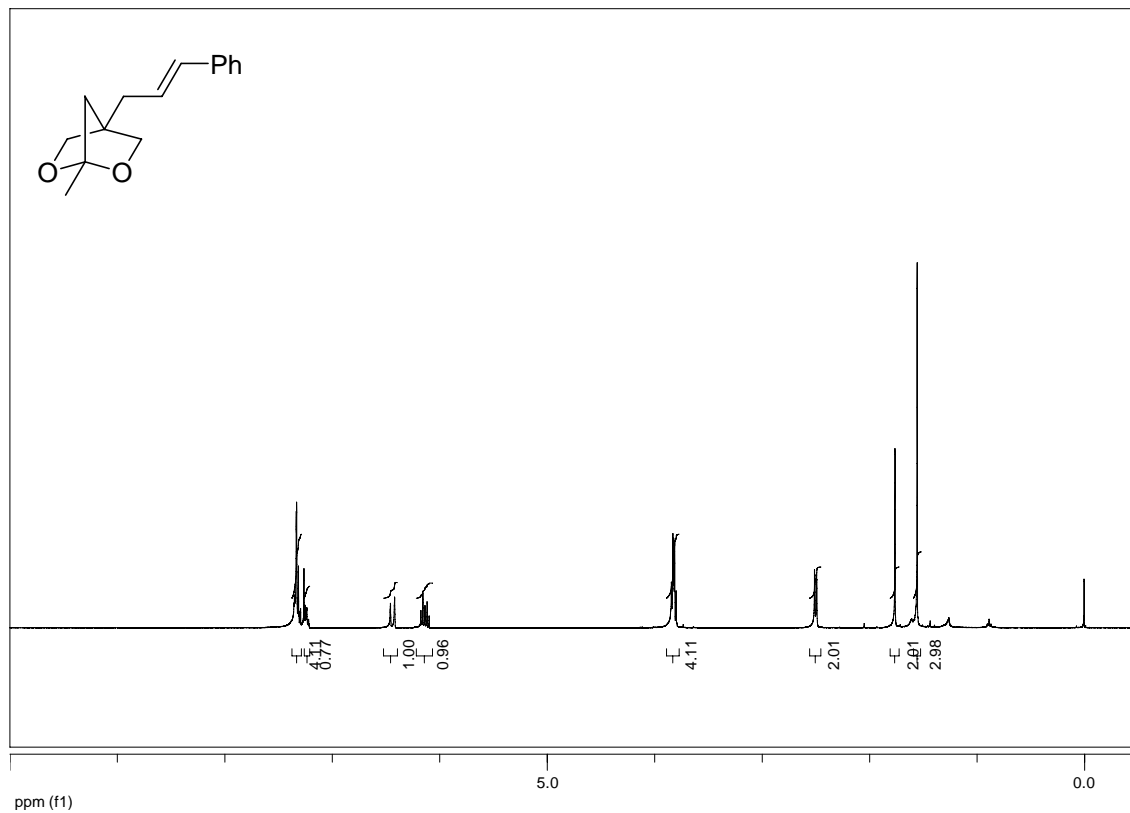
^1H and ^{13}C NMR of Compound **2a**



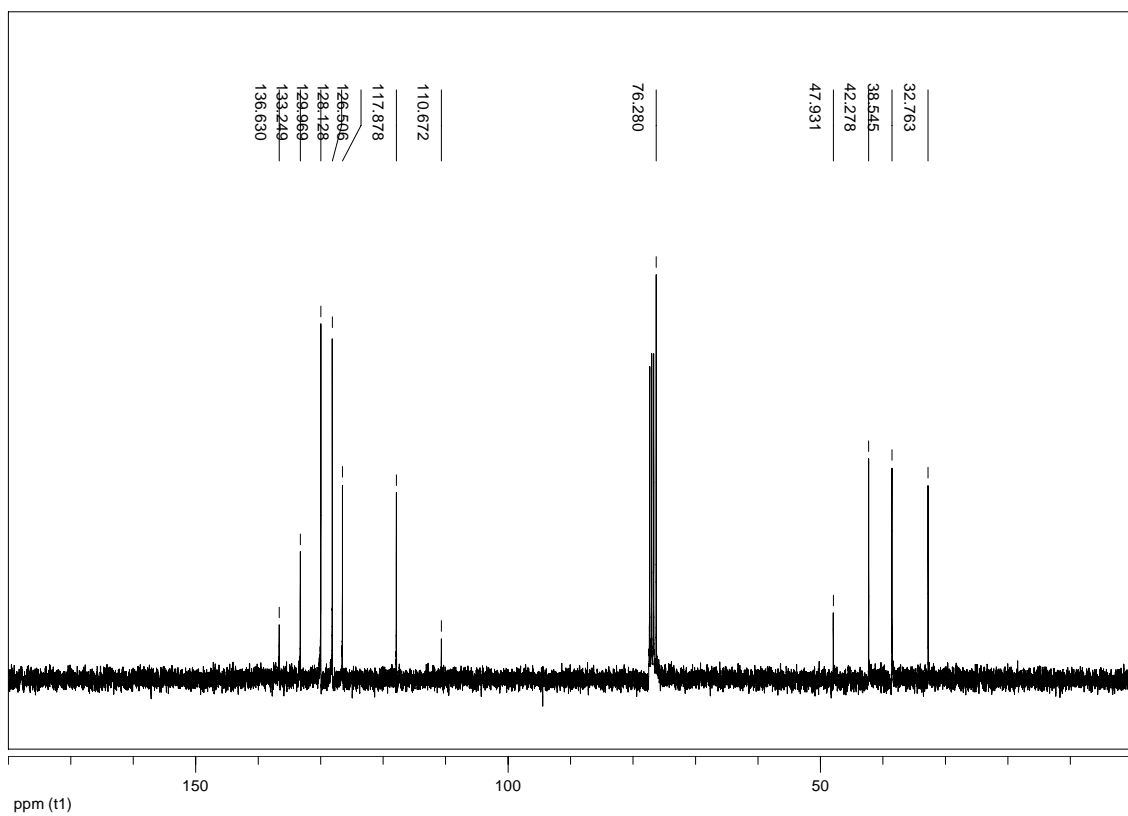
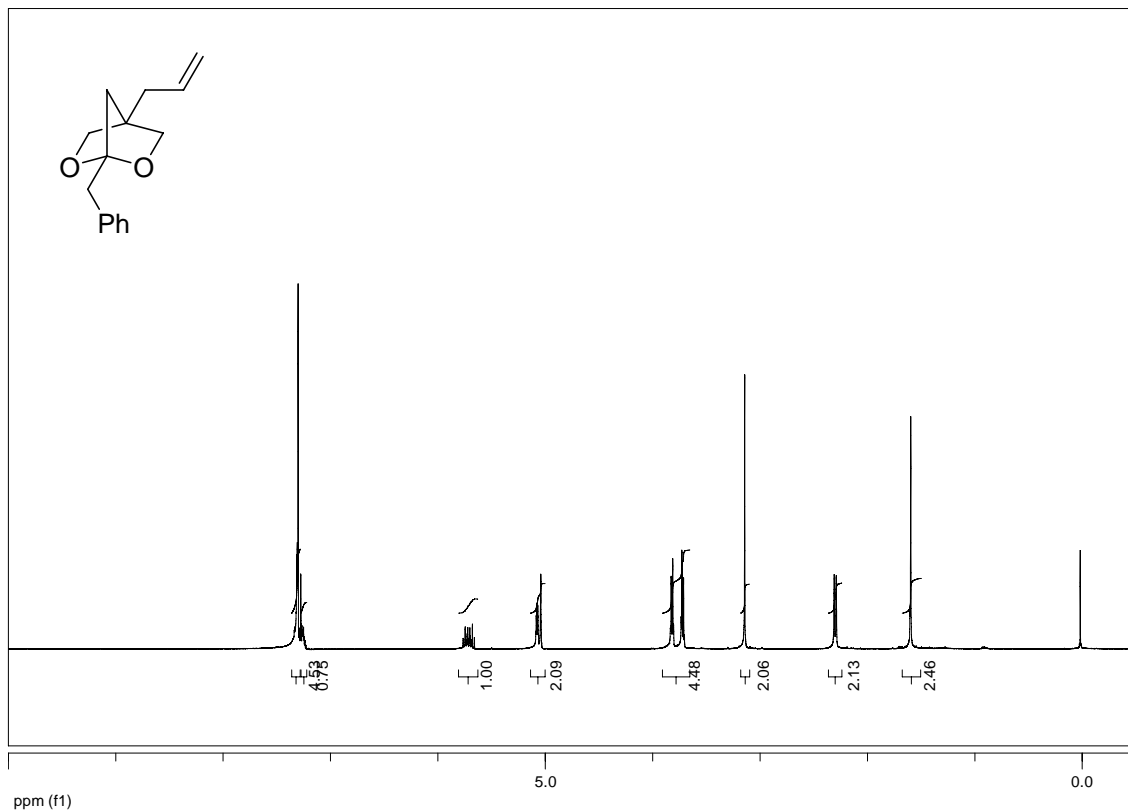
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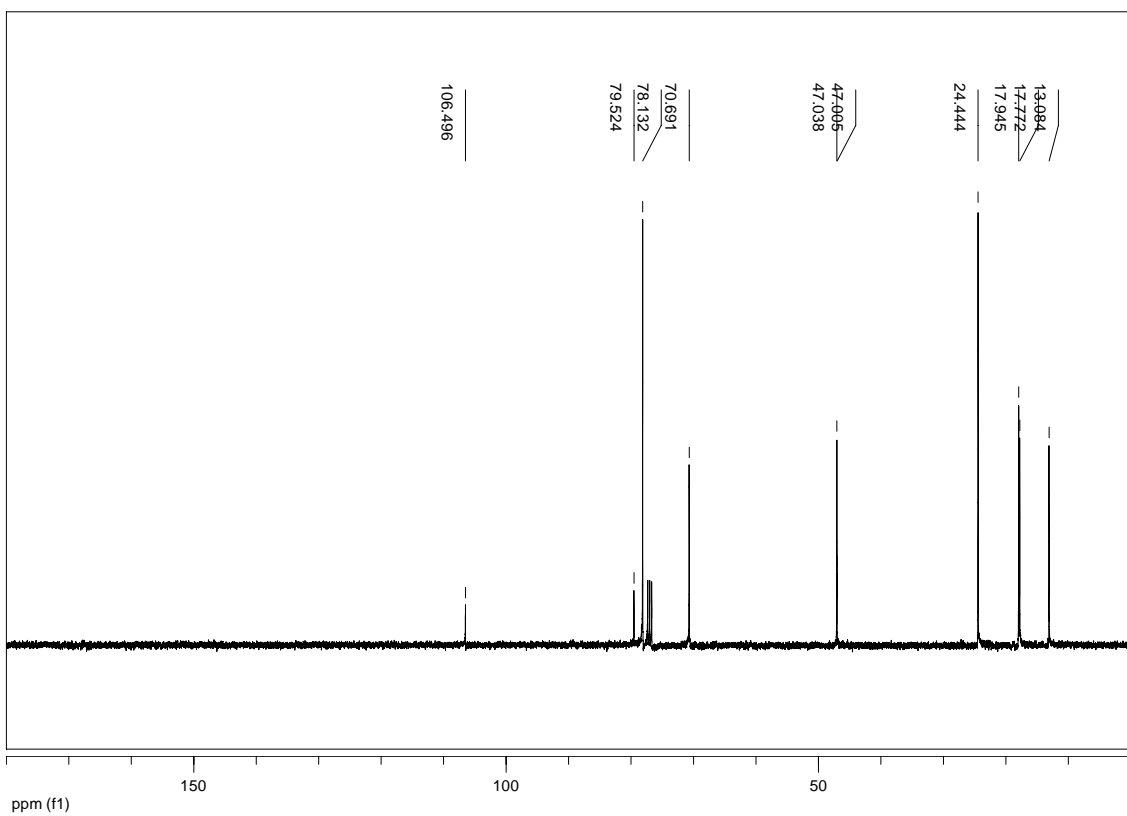
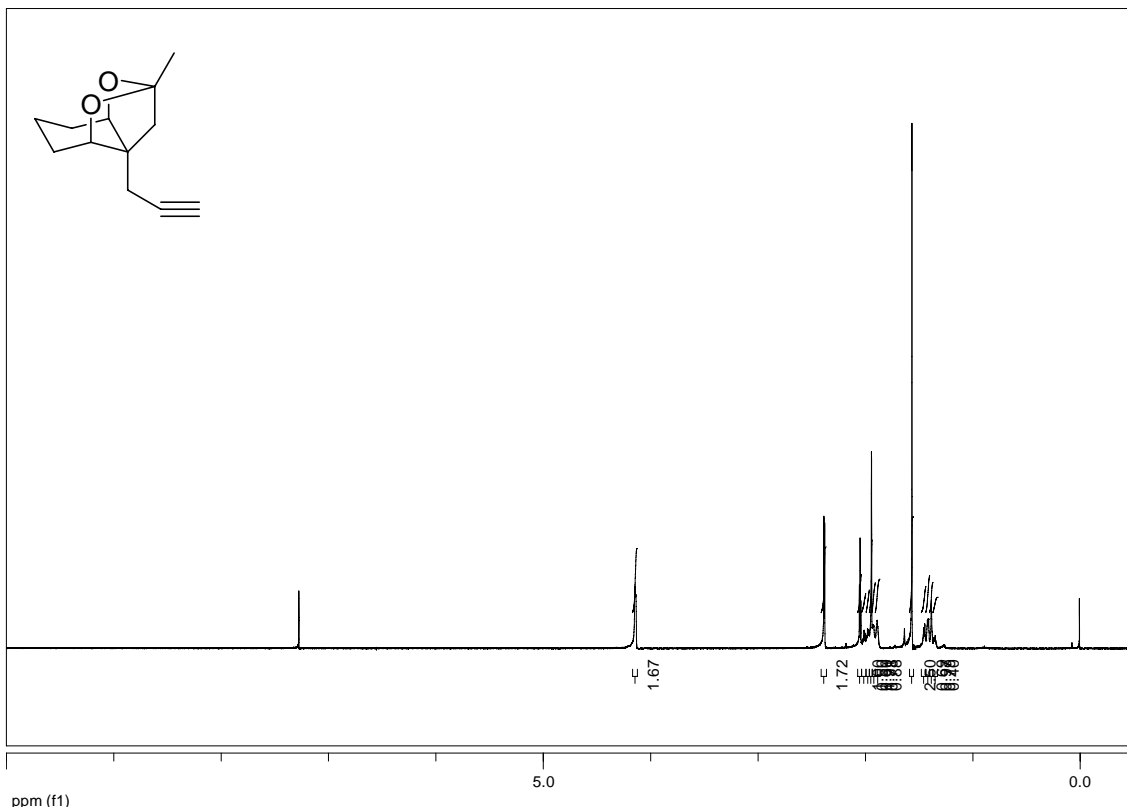
^1H and ^{13}C NMR of Compound **2c**



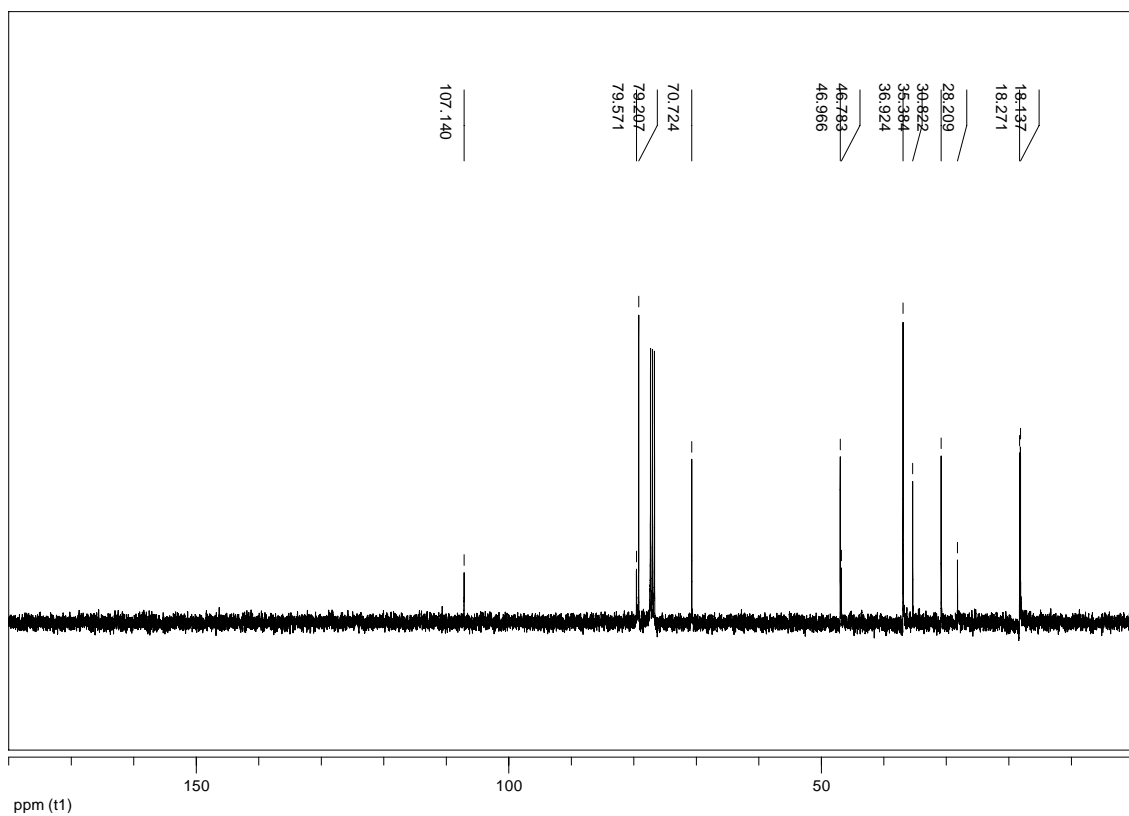
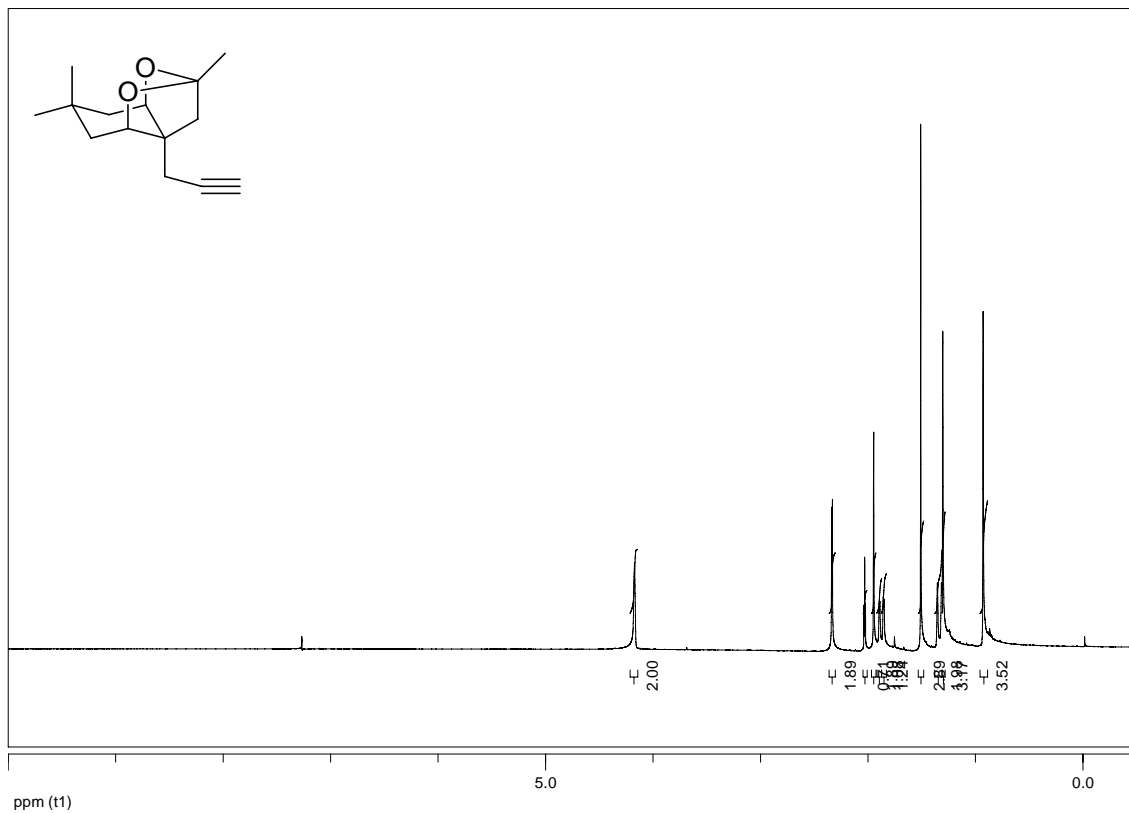
^1H and ^{13}C NMR of Compound **2d**



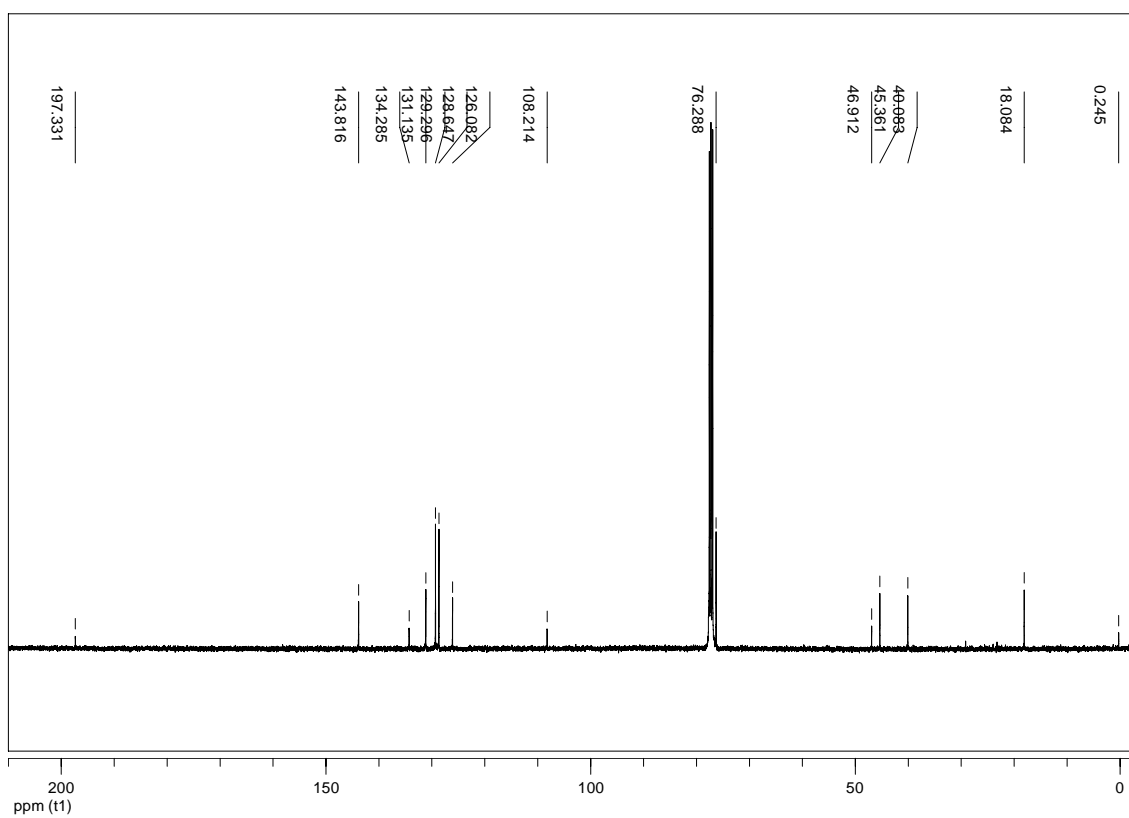
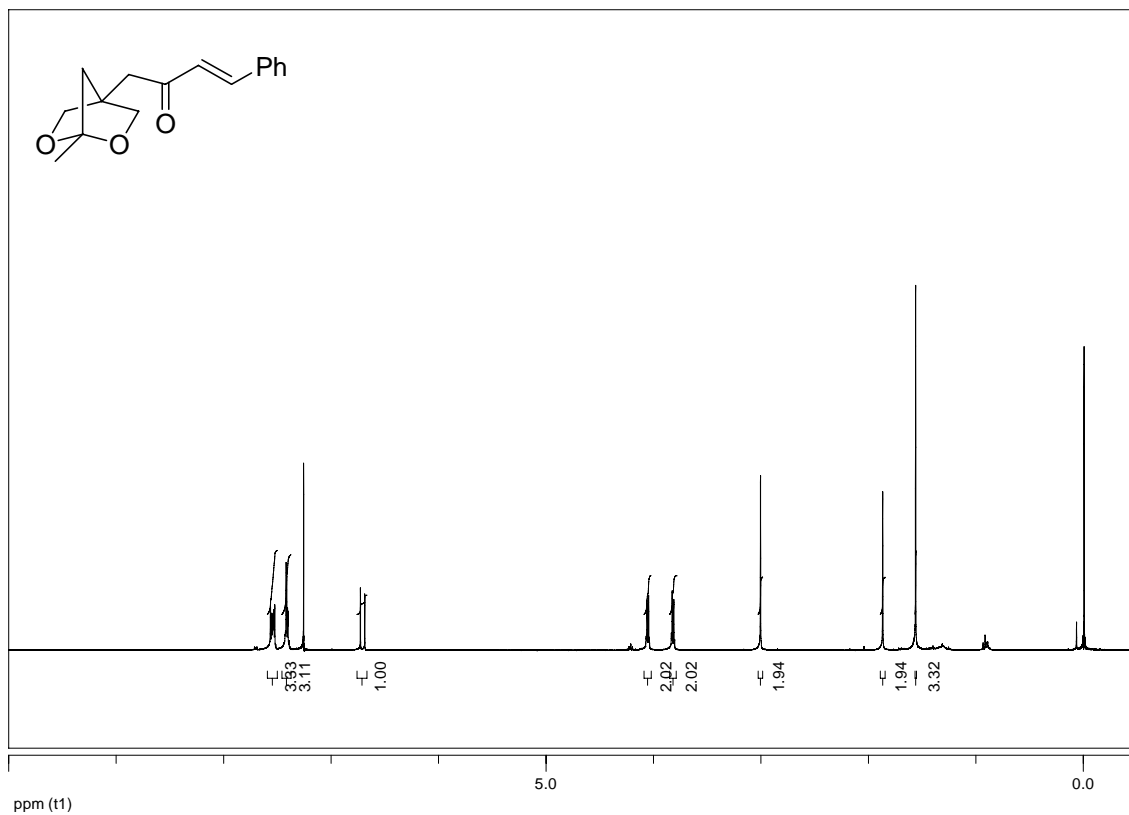
^1H and ^{13}C NMR of Compound **2f**



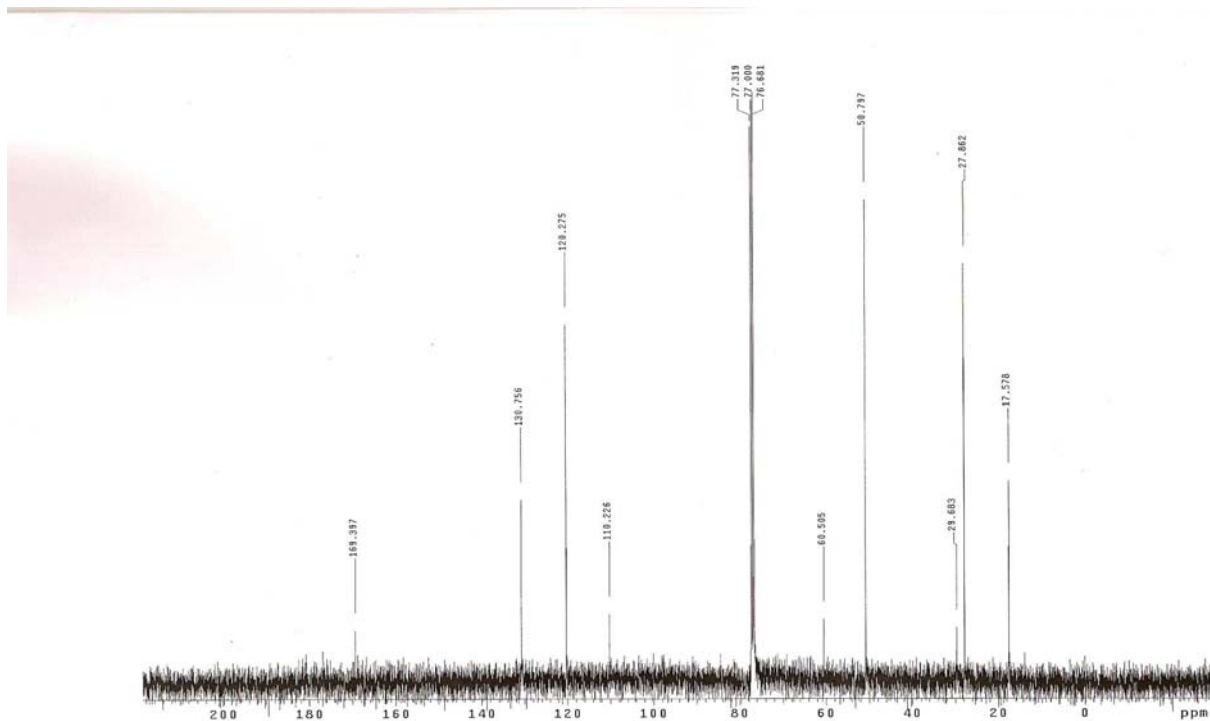
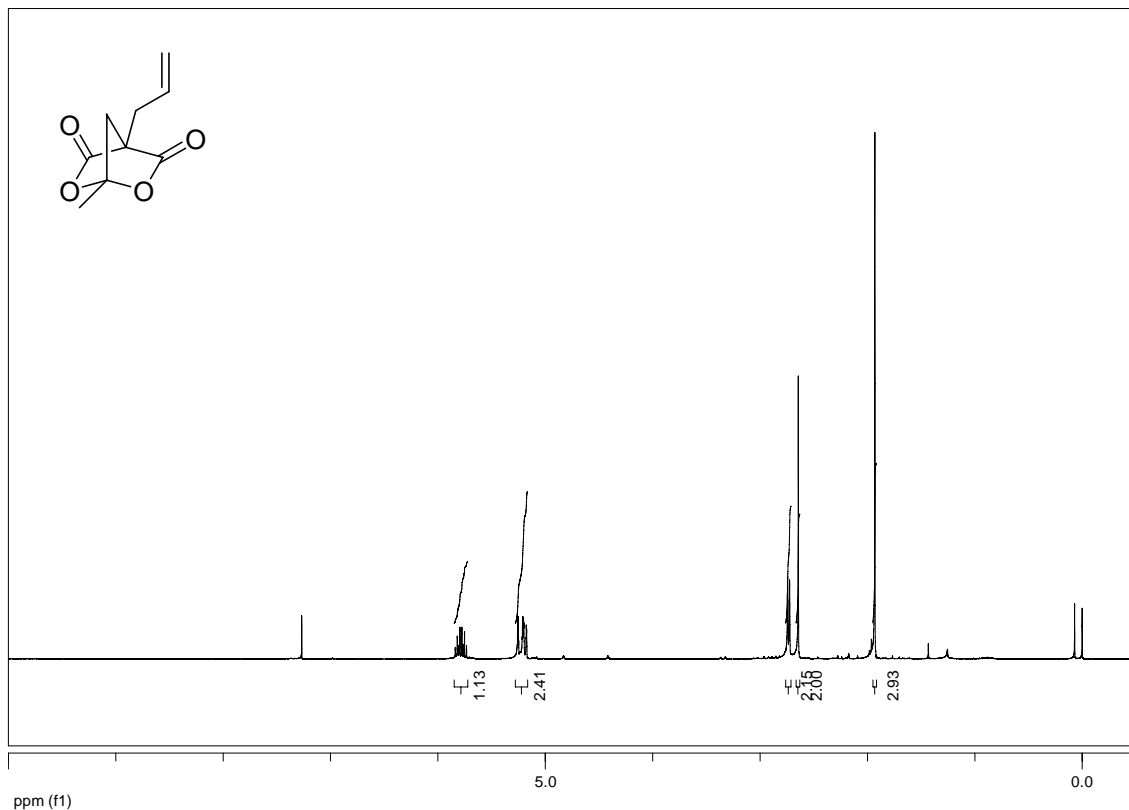
^1H and ^{13}C NMR of Compound **2g**



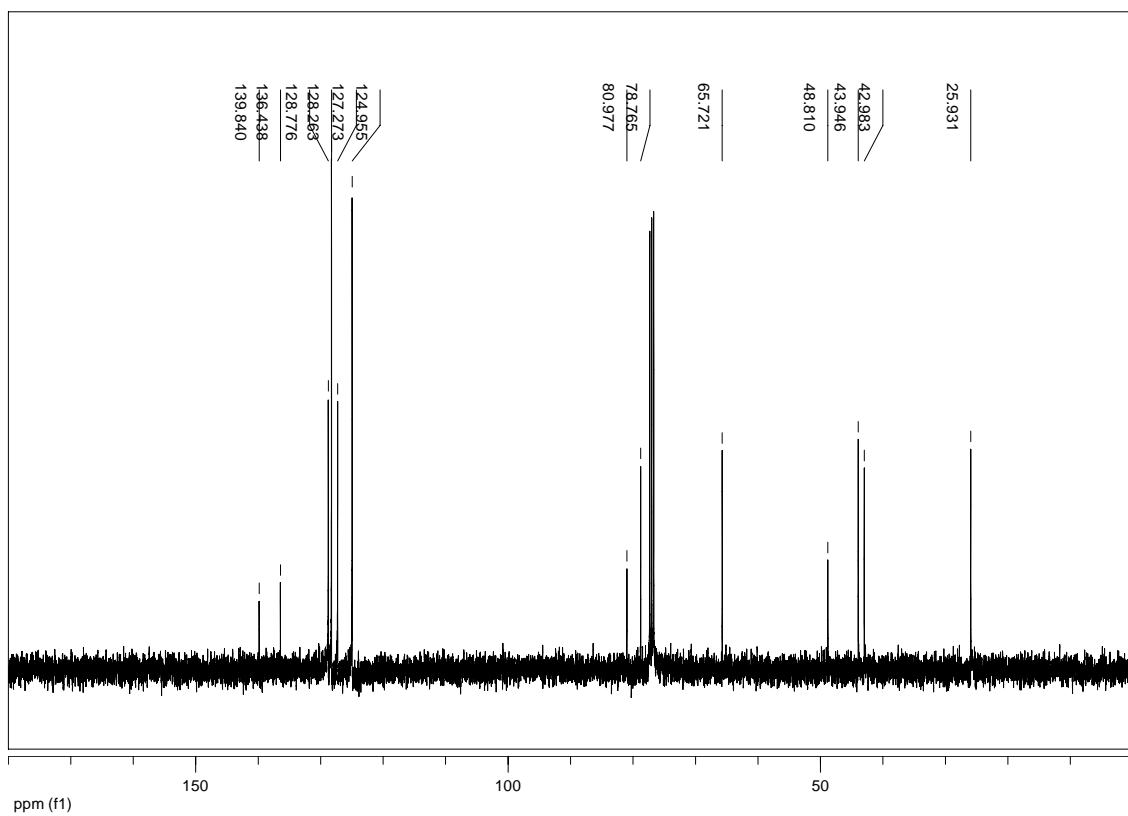
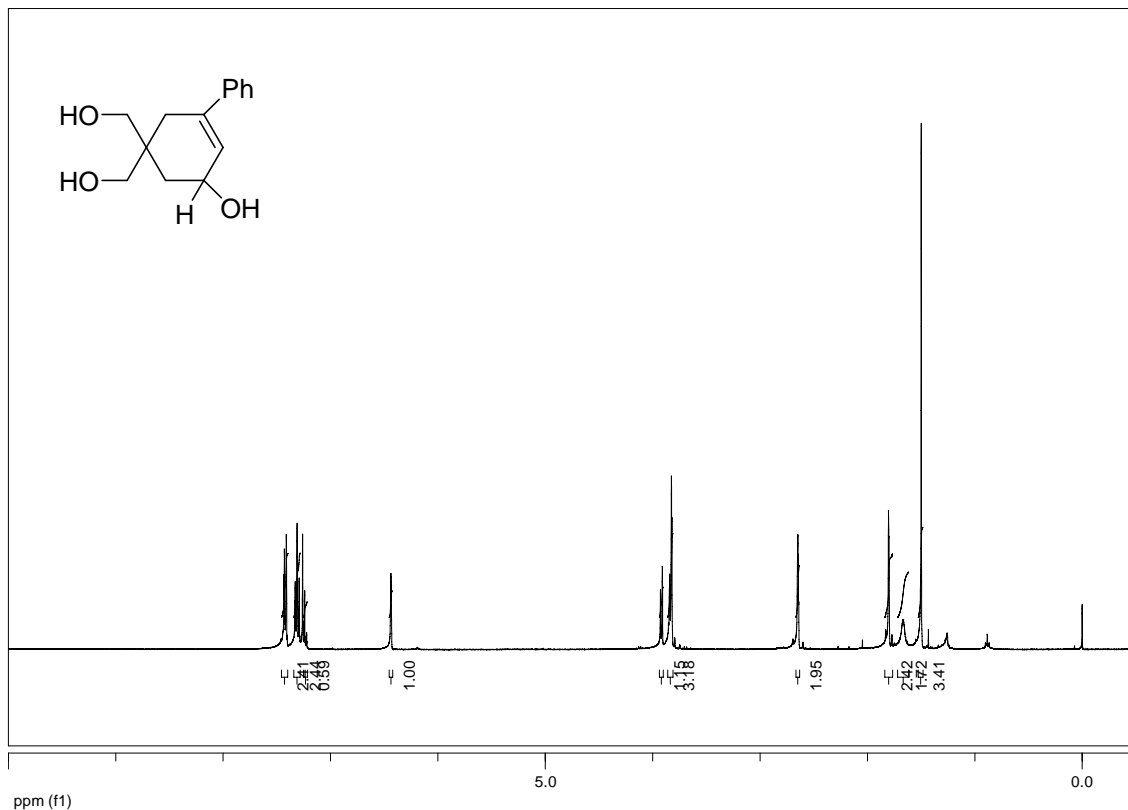
^1H and ^{13}C NMR of Compound **2h**



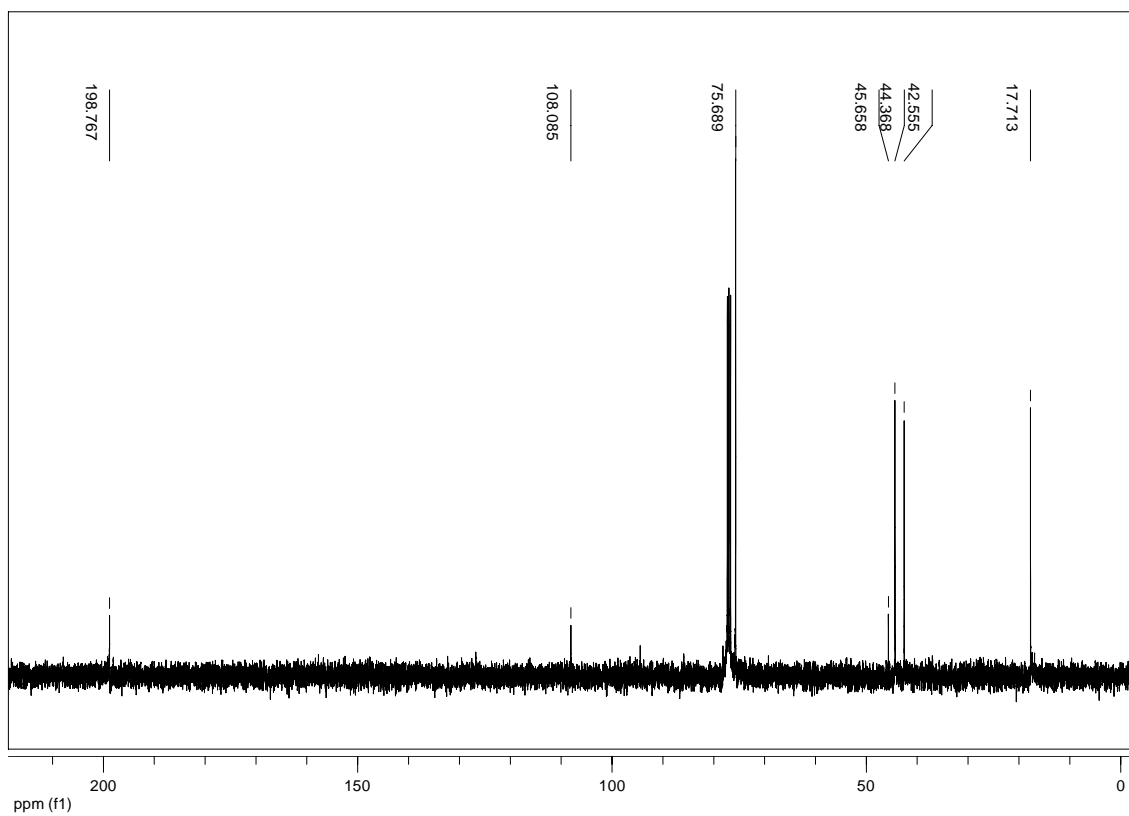
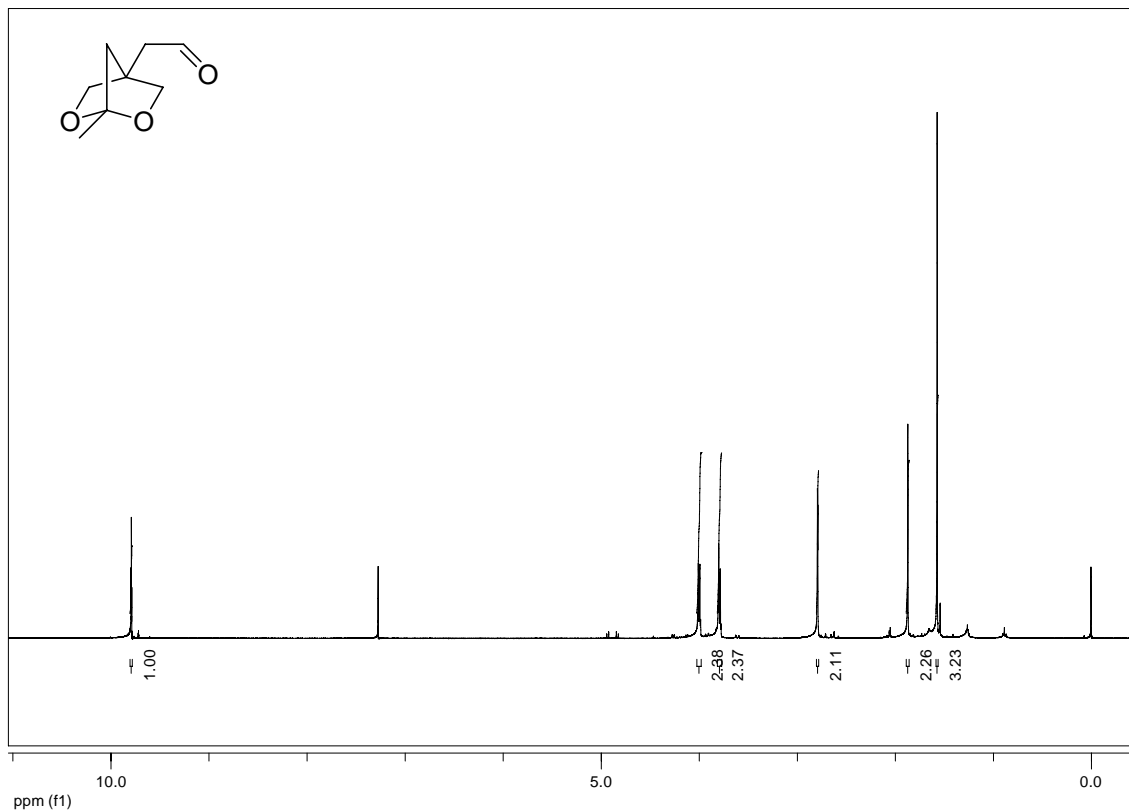
^1H NMR of Compound **2i**



^1H and ^{13}C NMR of Compound **3a**



^1H and ^{13}C NMR of Compound **4b**



^1H and ^{13}C NMR of Compound **5b**

