Stereoselective Synthesis and Antitumoral Activity of *Z*-Enyne Pseudoglycosides

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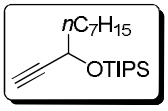
Contents

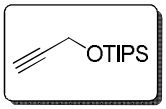
1 ADDITIONAL EXPERIMENTAL PROCEDURES

1.1 General Procedure for the Synthesis of TIPS protected alcohols

To a 50 mL flask under argon atmosphere containing a solution of the imidazol (1.7 g; 25 mmol) and the appropriate alkyne (10 mmol) in CH_2Cl_2 (20 mL) at 0°C was slowly added TIPSCl (2.30 g; 2.52 mL; 12 mmol). The resulting solution was allowed to reach the room temperature and stirred for 24 h. After this period, the reaction was cooled back to 0°C and a 3% HCl solution (20 mL) was slowly added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (10 mL). The combined organic phases were then washed with a saturated solution of $NaHCO_3$ (2 x 50 mL) and brine (1 x 50 mL) and dried over $MgSO_4$. The solvent was removed *in vacuo* and the residue was purified by silica gel chromatography [hexanes/EtOAc (9.5:0.5)].



(Dec-1-yn-3-yloxy)triisopropylsilane (**1c**):[1]: Colorless oil; 91% (2.82 g); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.48-4.46 (m, 1H), 2.38 (d, *J* = 1.6 Hz, 1H), 1.72-1.67 (m, 2H), 1.49-1.20 (m, 10H), 1.07-1.06 (m, 21H), 0.89 (t, *J* = 8.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 85.5, 71.6, 62.6, 38.5, 31.5, 29.0, 28.9, 24.5, 22.4, 17.7, 13.8, 11.9.

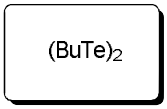


Triisopropyl(prop-2-ynyloxy)silane (**1d**)[1]: Colorless oil; 93% (1.97 g); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (d, *J* = 2.4 Hz, 2H), 2.38 (t, *J* = 2.4 Hz, 1H), 1.11-1.04 (m, 21H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 82.4, 72.6, 51.7, 17.8, 11.9.

1.2 Synthesis of Dibutyl Ditelluride

To a 500 mL flask under argon containing elemental tellurium (5.16 g; 40 mmol) [dried at 85° C prior to use in an oven] was added anhydrous THF (200 mL). The suspension was cooled to 0°C and *n*-BuLi (50 mmol, 31 mL of a 1.6 M solution in hexanes) was slowly added. The reaction was stirred at room temperature for 1 h while open to the atmosphere (O_2). After this period, a saturated solution of NH_4Cl (20 mL) was slowly added and the reaction was stirred for 2h. The organic layer was isolated and the aqueous layer was extracted with ethyl acetate (1 × 30 mL). The combined organic phases were dried over $MgSO_4$ and filtered. Concentration *in vacuo* provided the tittle compound as a red oil which was used directly without further purification.

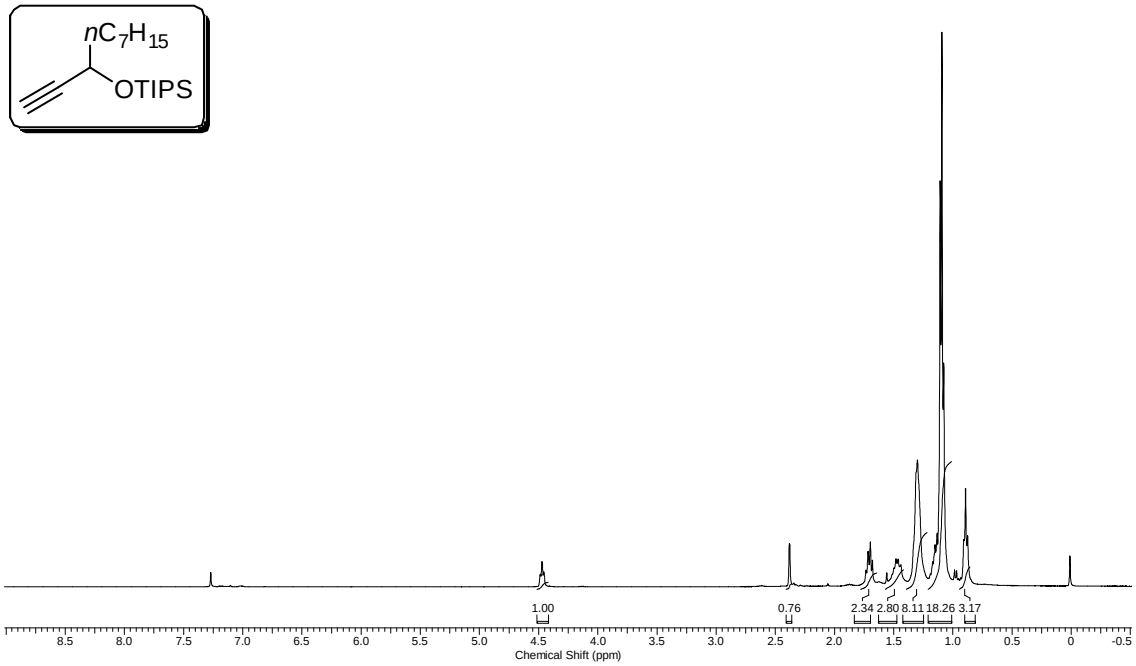
[1] J. M. Oliveira, D. J. Palmeira, J. V. Comasseto; P. H. Menezes, *J. Braz. Chem. Soc.*, 2010, **21**, 362-366.



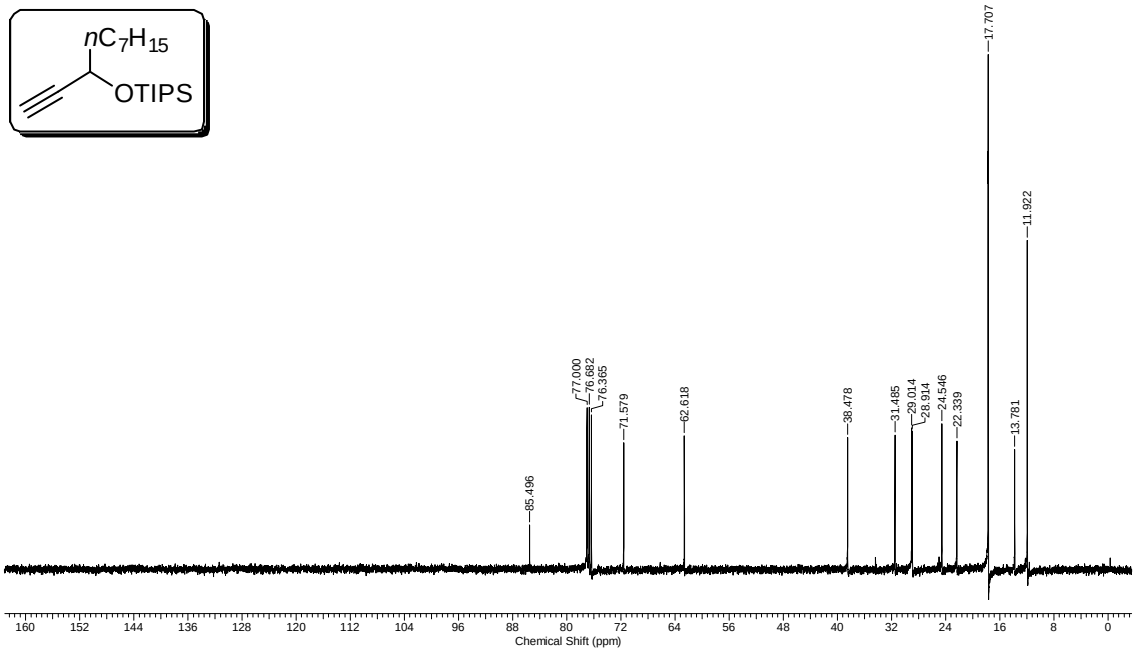
Dibutylditelluride:[2] Reddish oil; 90% (6.73 g); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10 (t, *J* = 7.8 Hz, 4H), 1.80-1.60 (m, 4H), 1.46-1.30 (m, 4H), 0.92 (t, *J* = 7.5 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 35.6, 24.5, 13.3, 4.2; ^{125}Te NMR (94.6 MHz, $CDCl_3$) δ 127.8.

[2] J. C. R. Freitas, D. J. Palmeira, R. A. Oliveira, P. H. Menezes, R. O. Silva, *Magn. Res. Chem.*, 2012, **50**, 481–487.

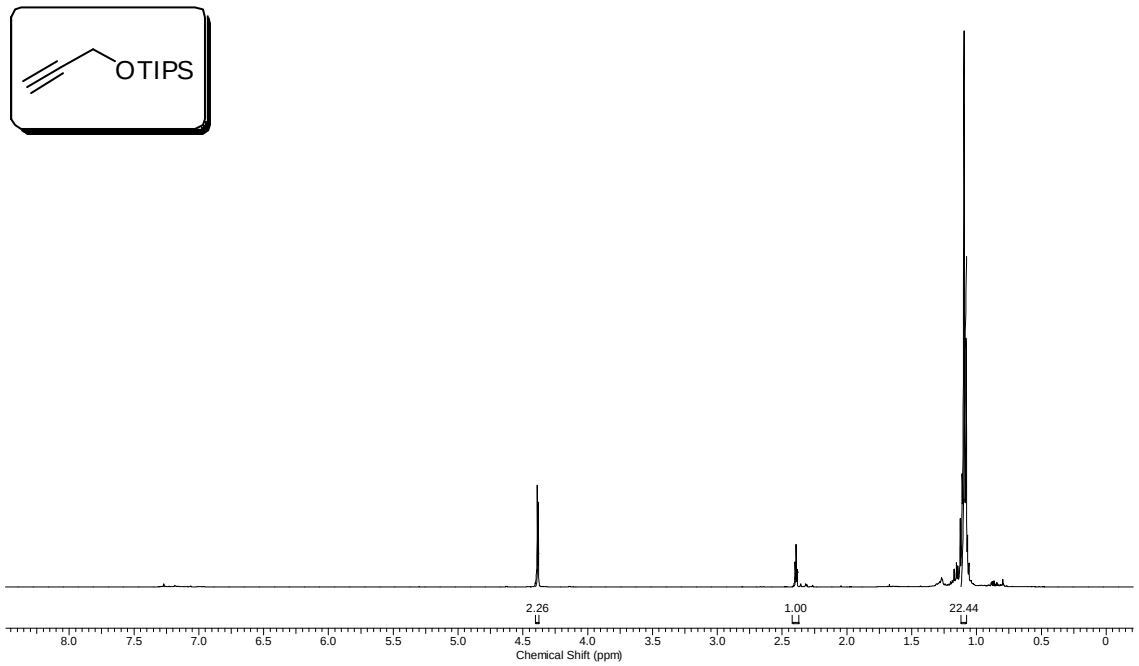
3. SPECTRA



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **1c**.



^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **1c**.



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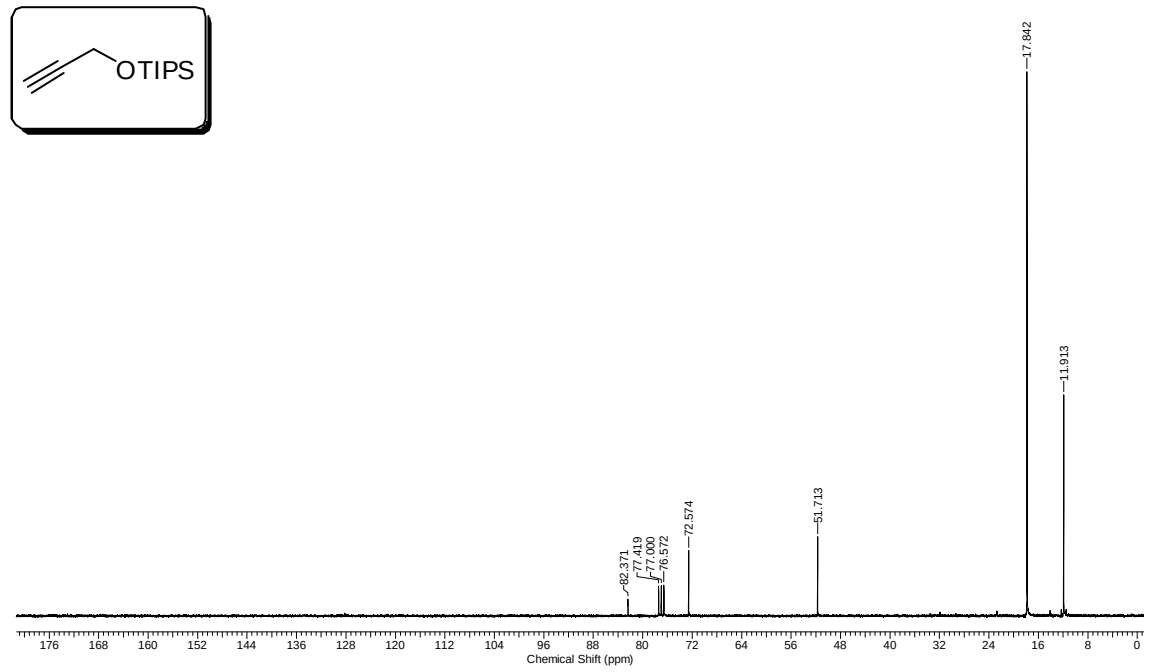
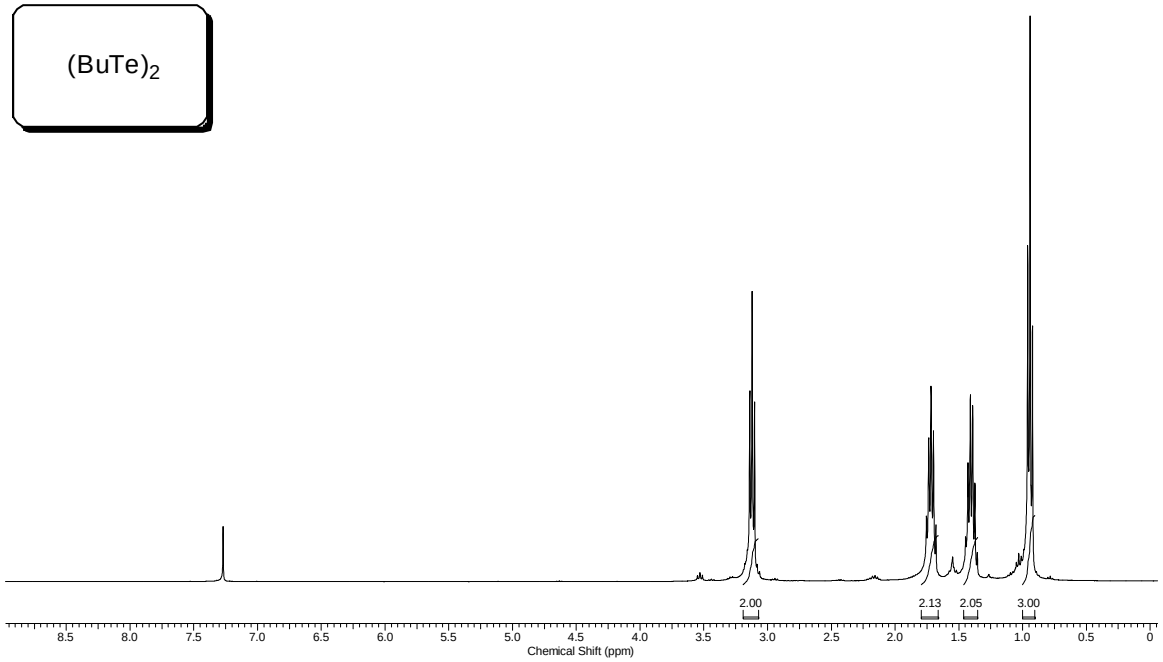
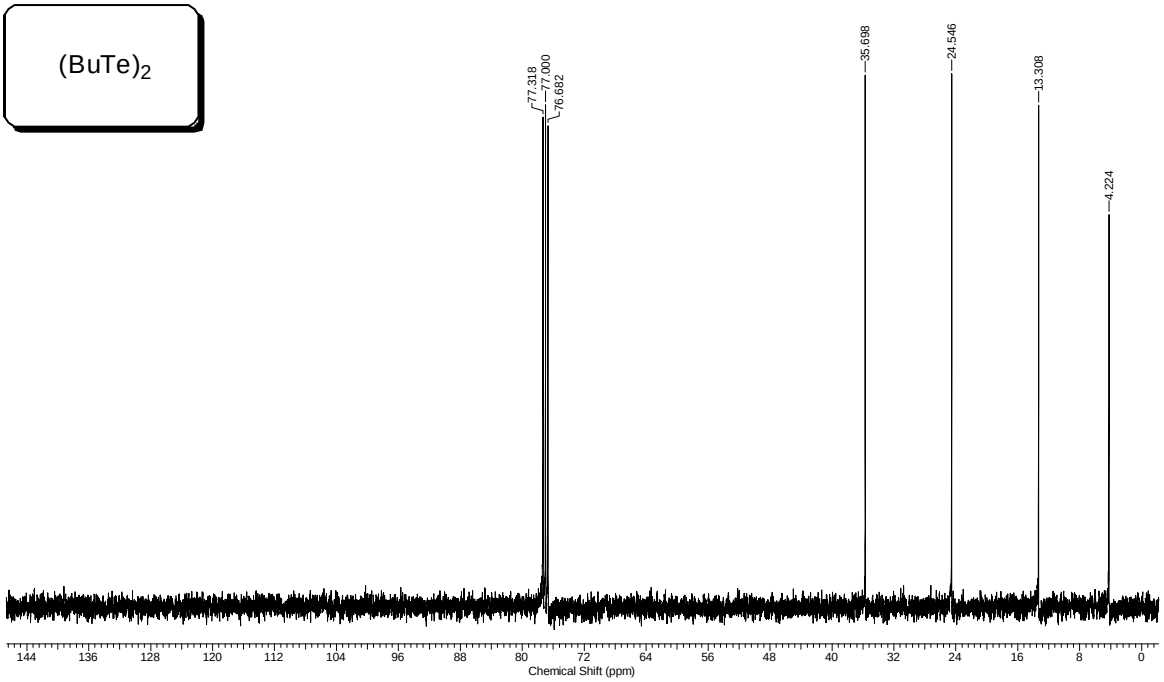


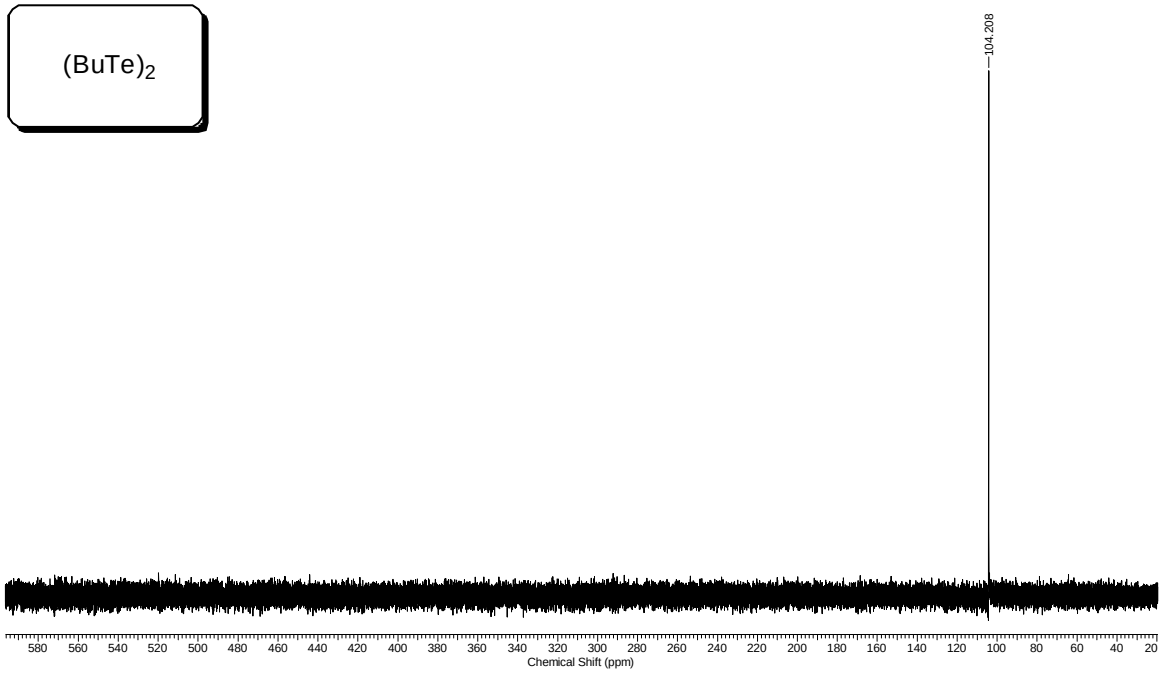
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **1d**.



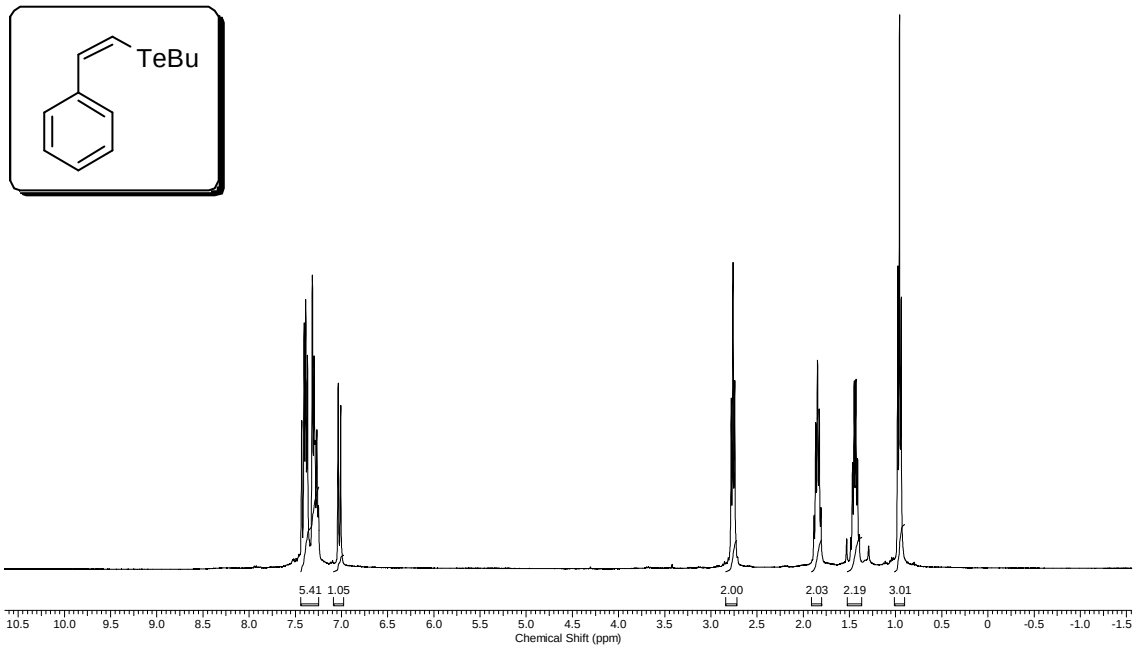
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of dibutylditelluride.



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of dibutylditelluride.



^{125}Te NMR spectrum (126 MHz, $CDCl_3$) of dibutylditelluride.



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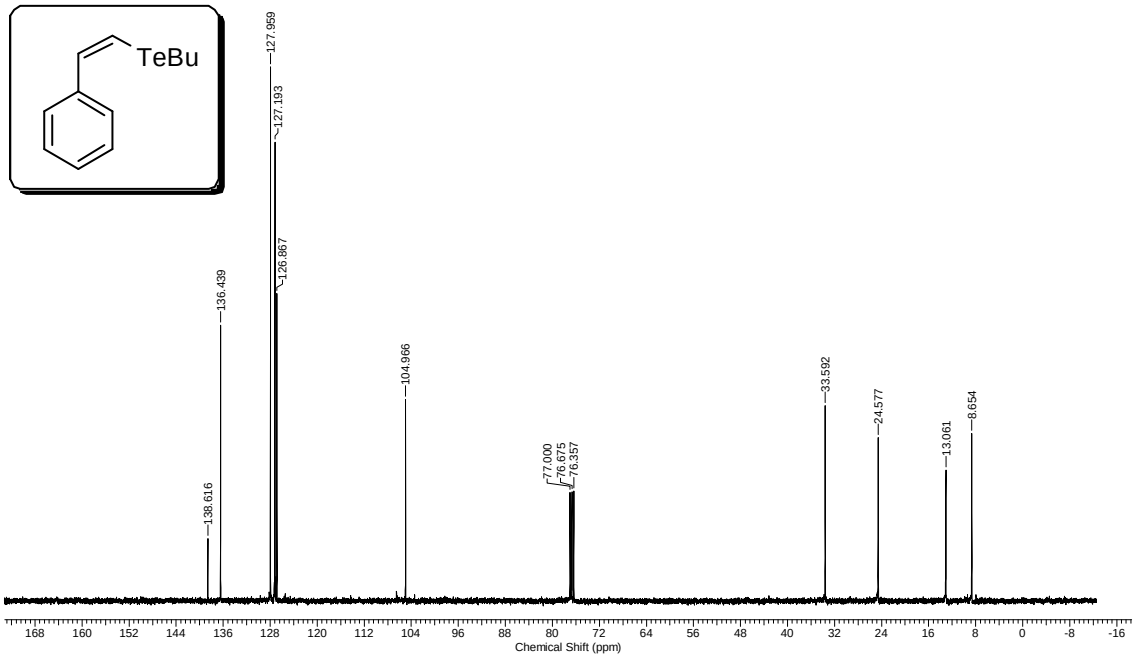
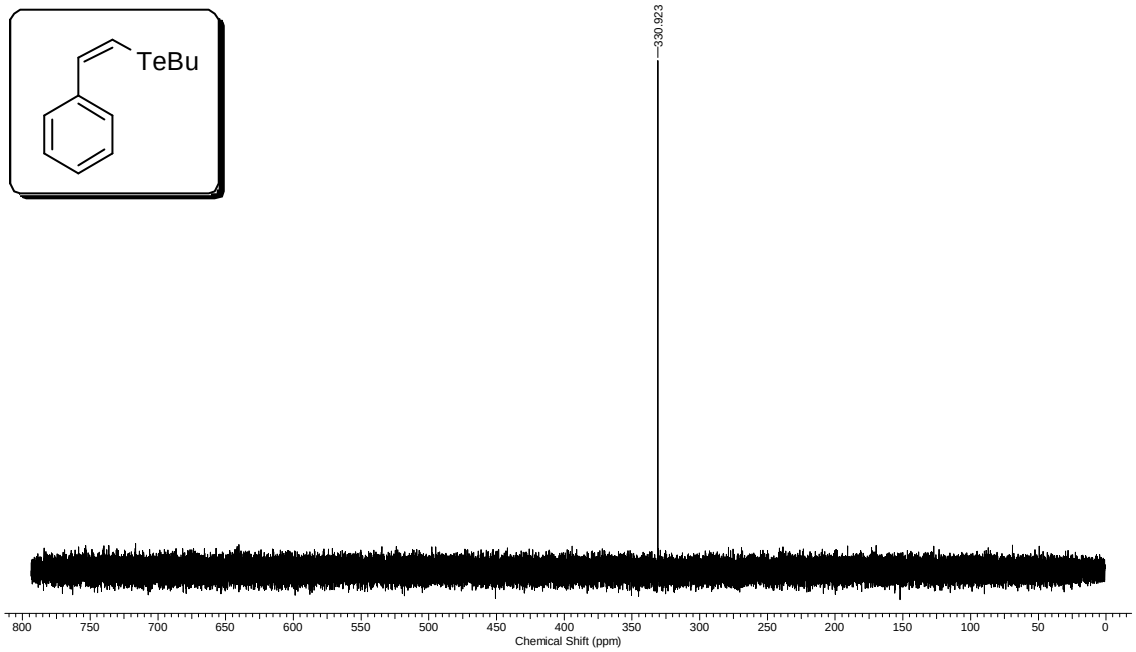
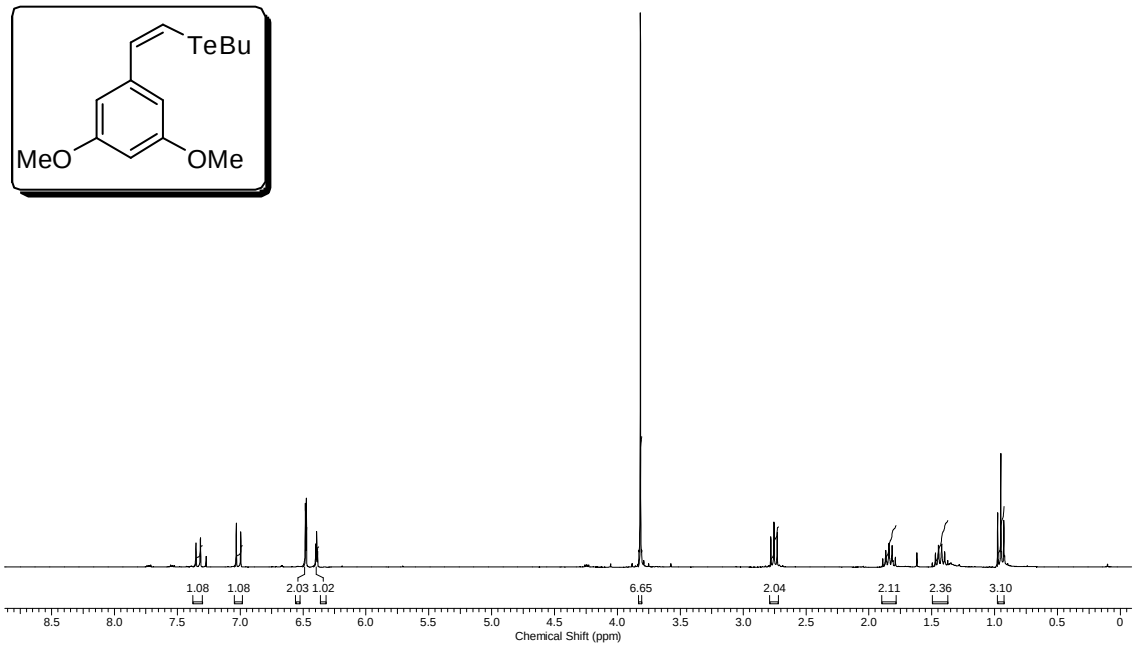


^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **2a**.



^{125}Te NMR spectrum (94.6 MHz, $CDCl_3$) of composto **2a.**



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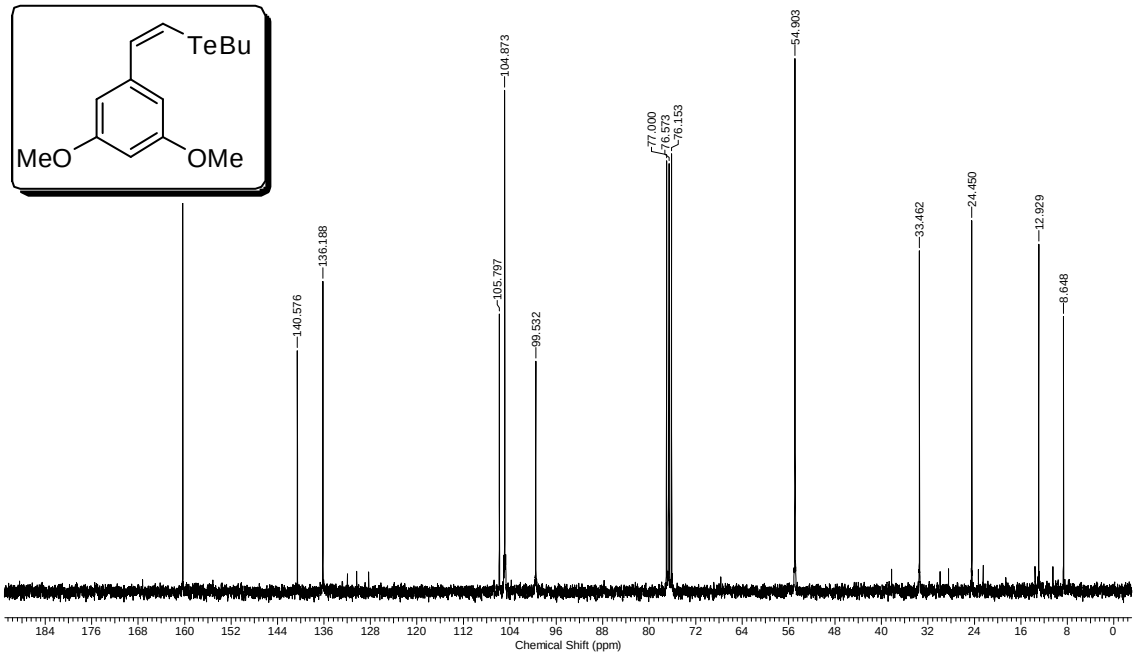
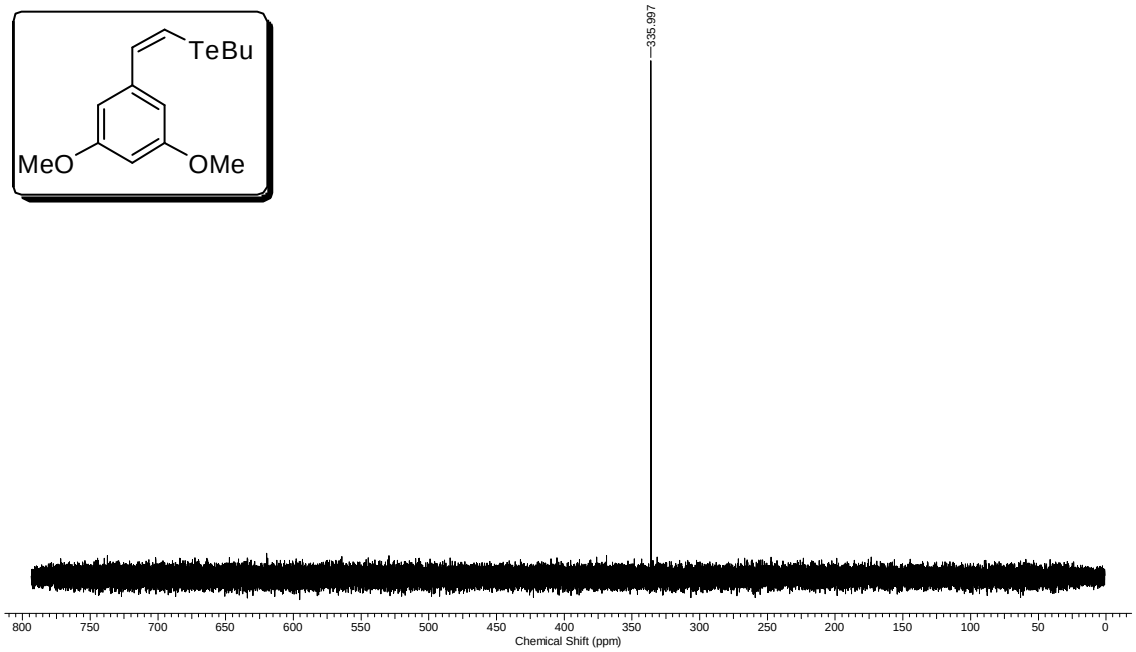
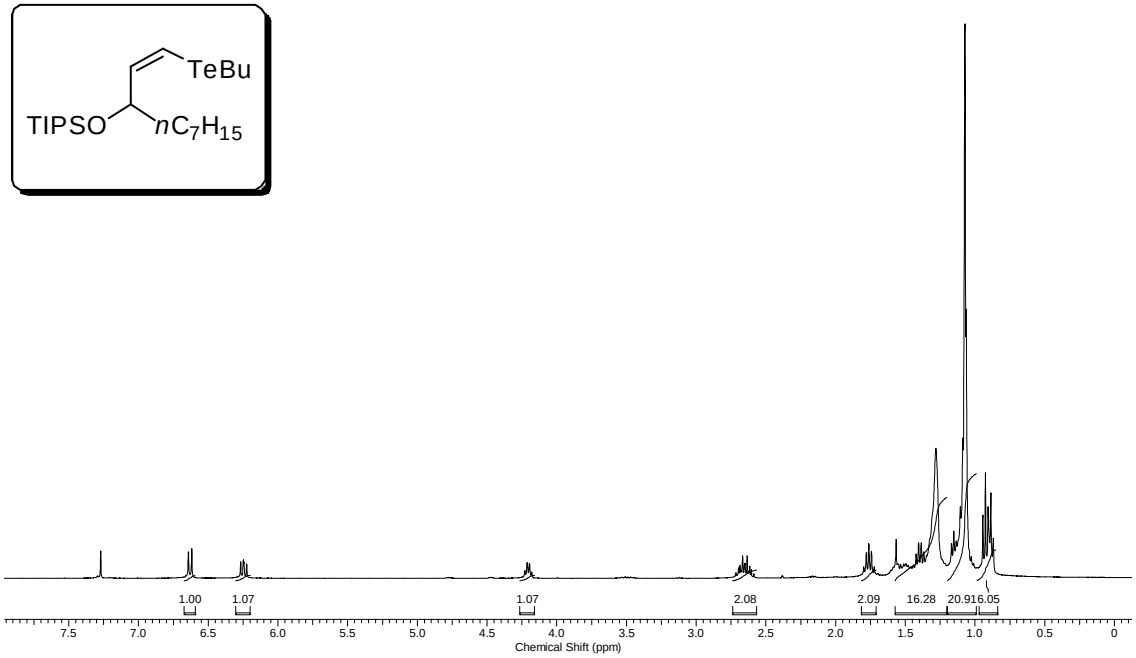


^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **2b**.



^{125}Te NMR spectrum (94.6 MHz, $CDCl_3$) of composto **2b.**



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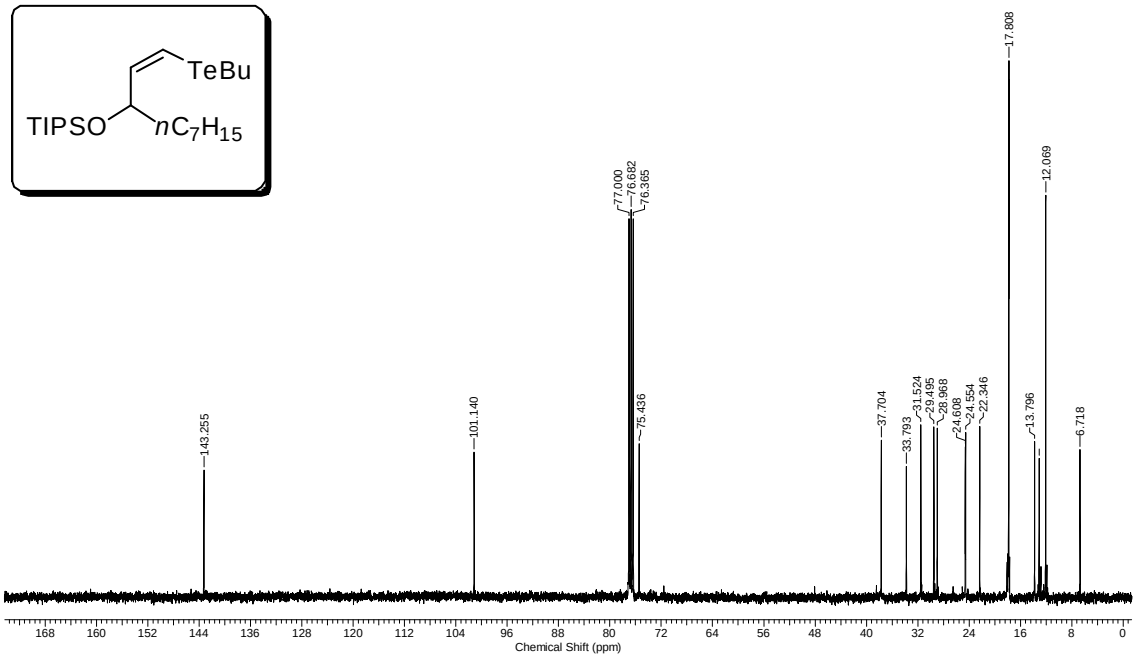

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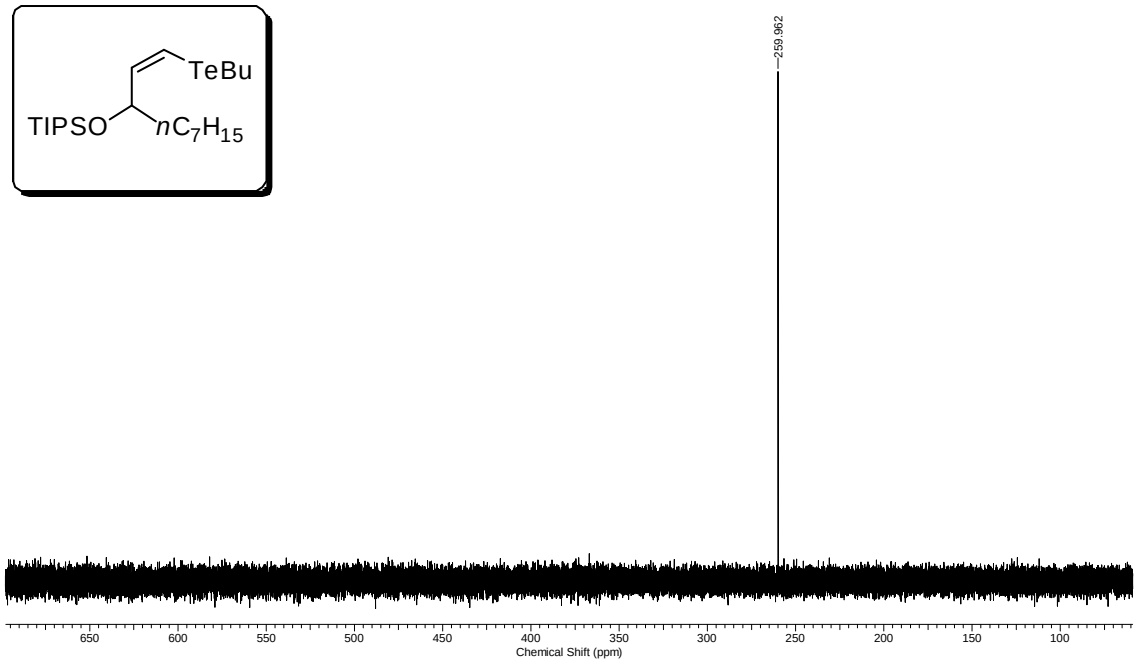
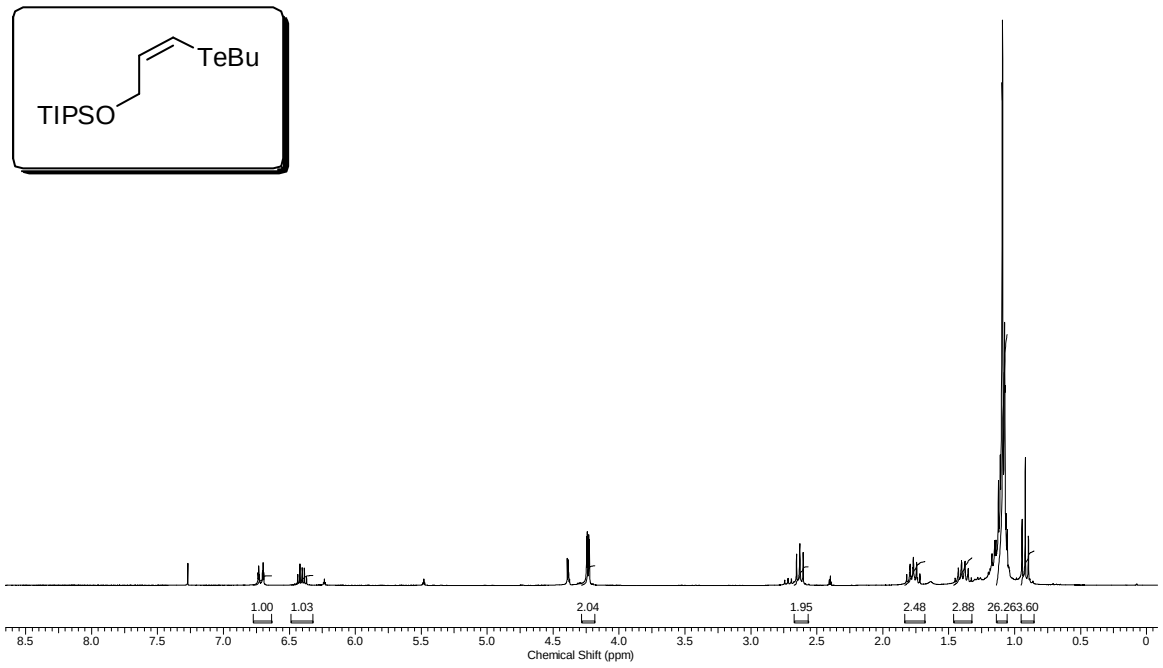


^{125}Te NMR spectrum (94.6 MHz, $CDCl_3$) of composto **2c.**



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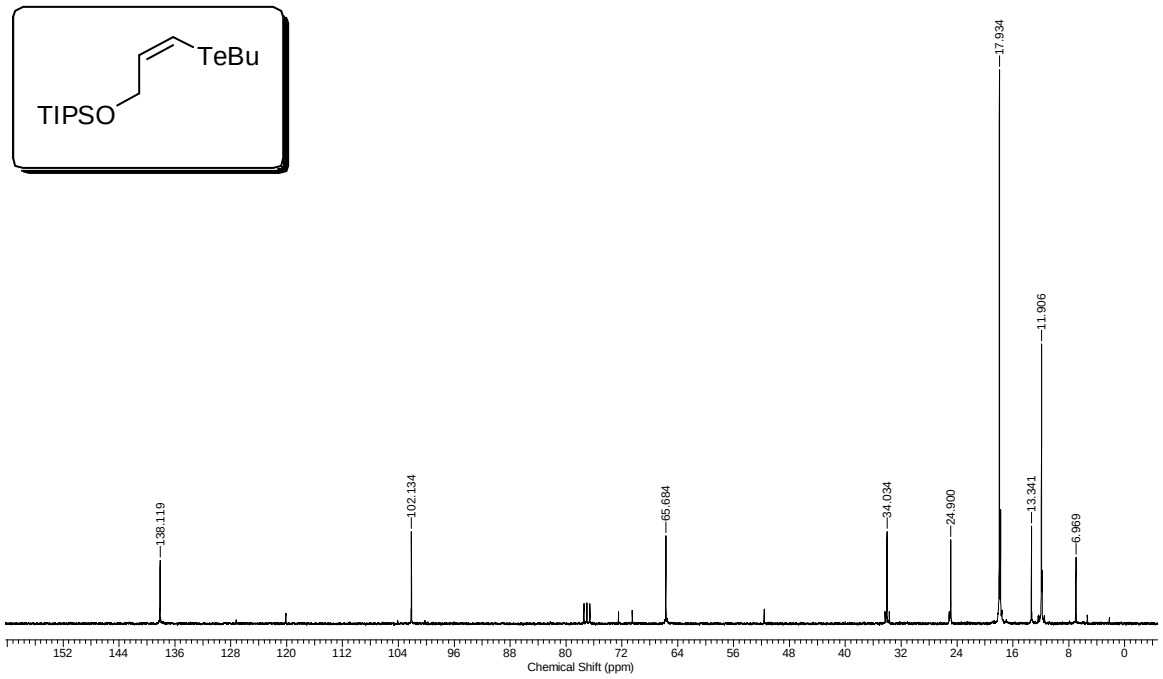

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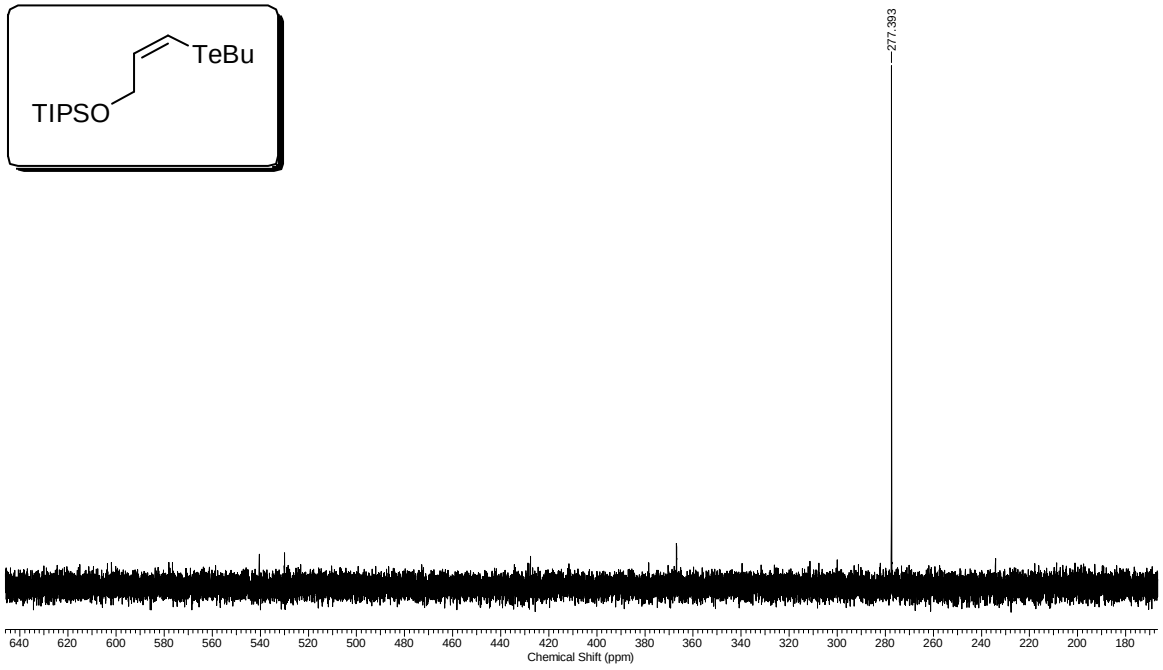
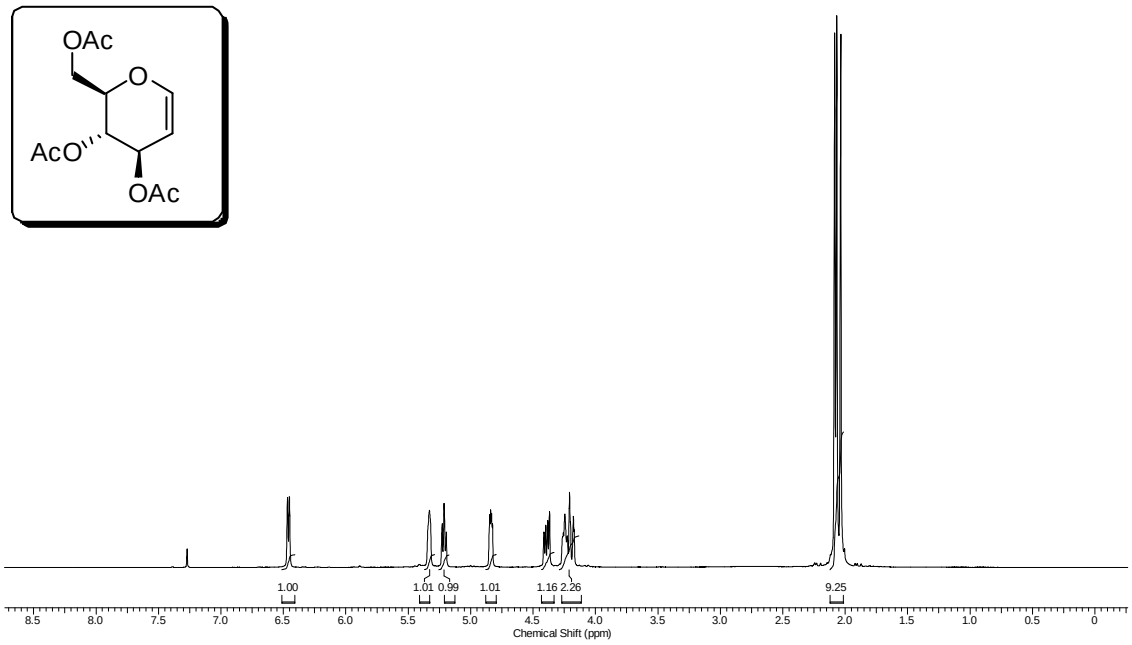
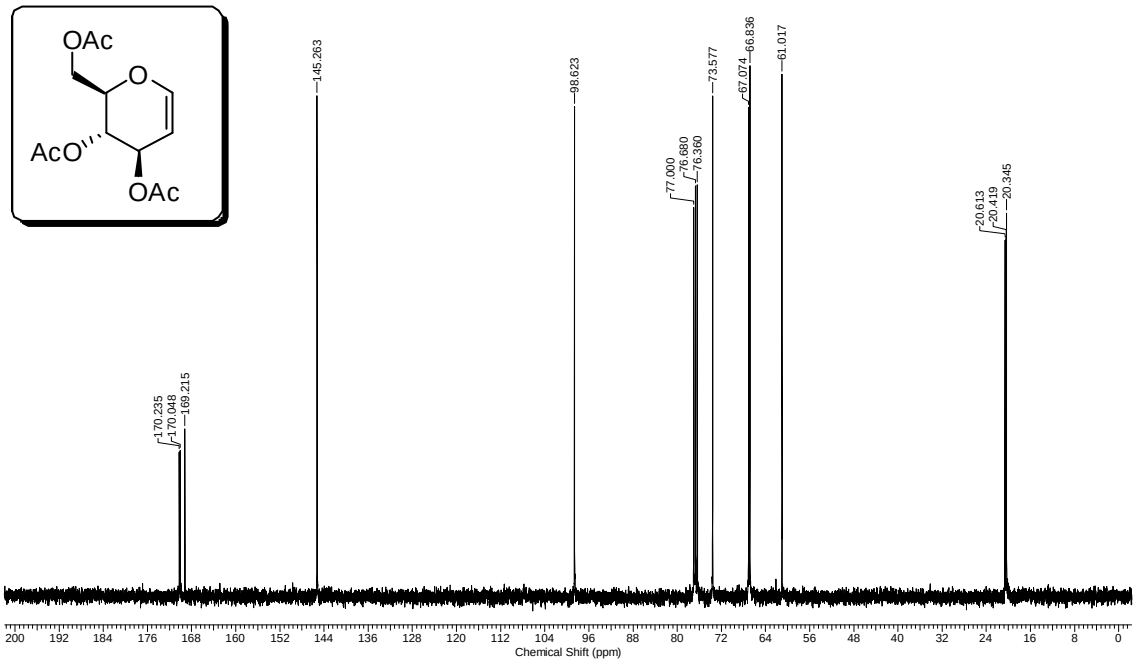


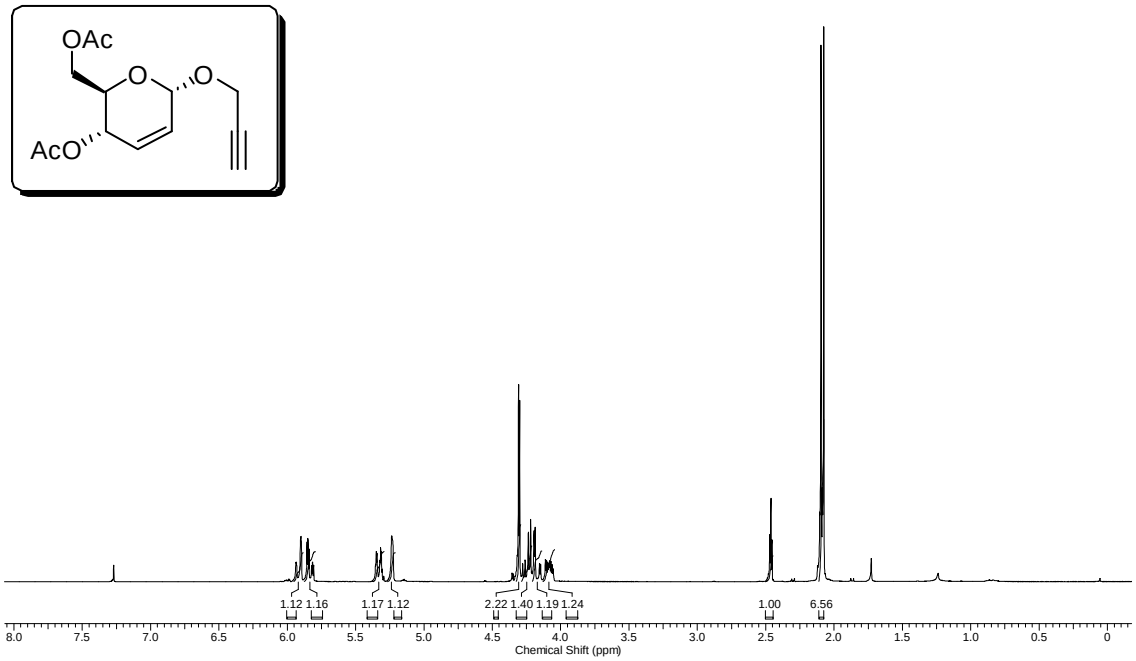
^{125}Te NMR spectrum (94.6 MHz, $CDCl_3$) of composto **2d.**



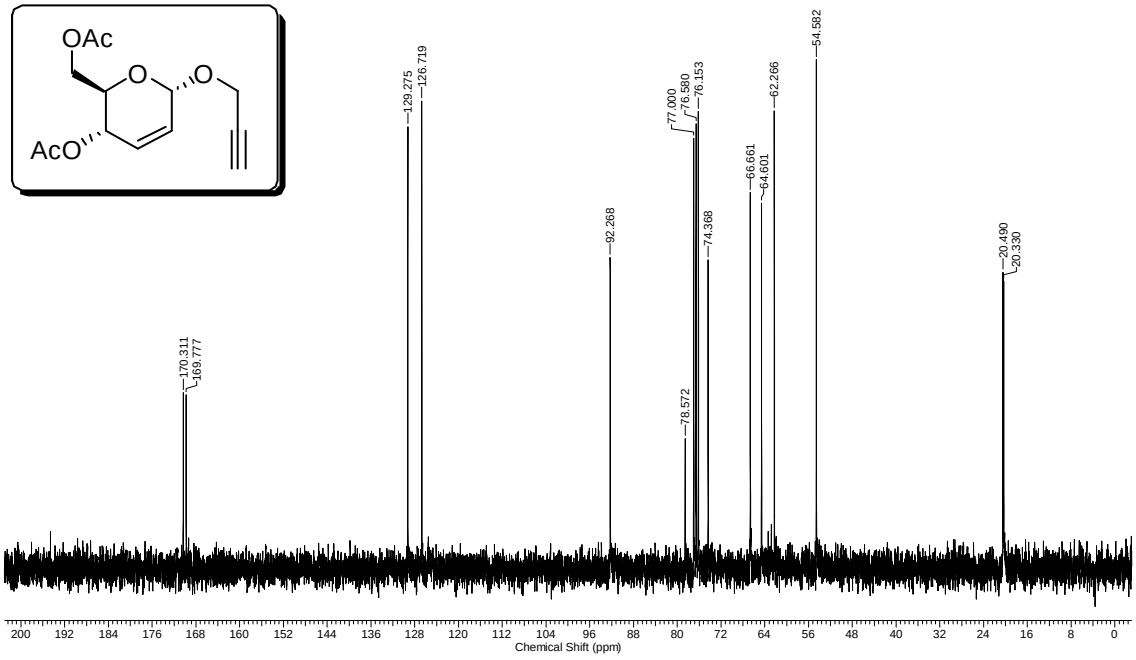
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **4**.



^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **4**.



^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **5a**.



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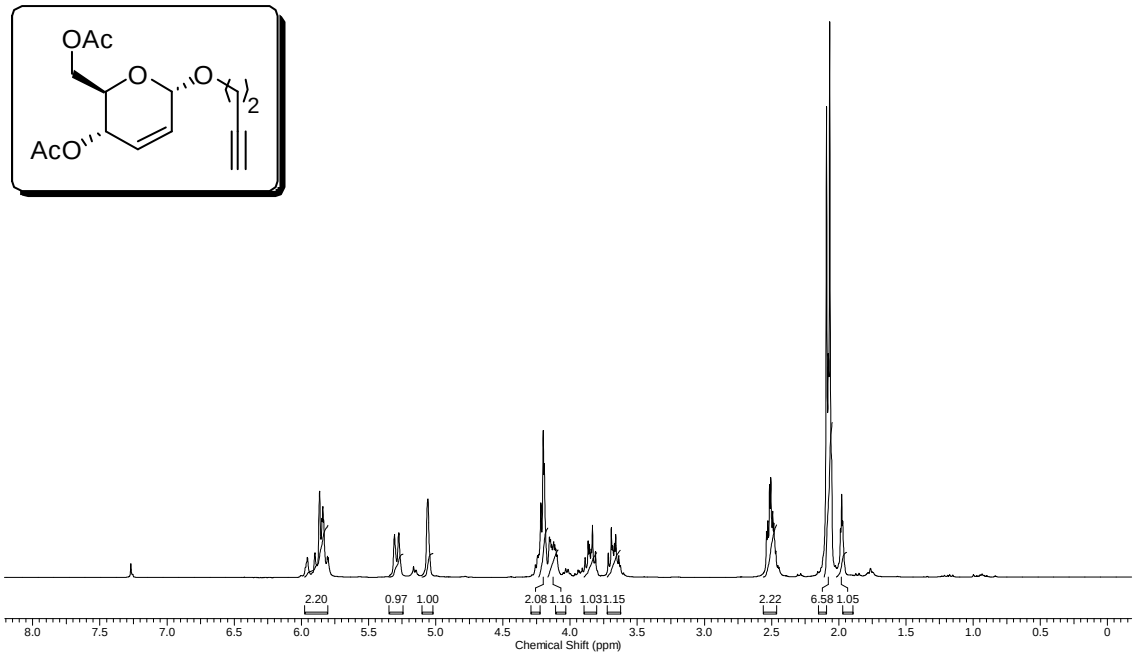

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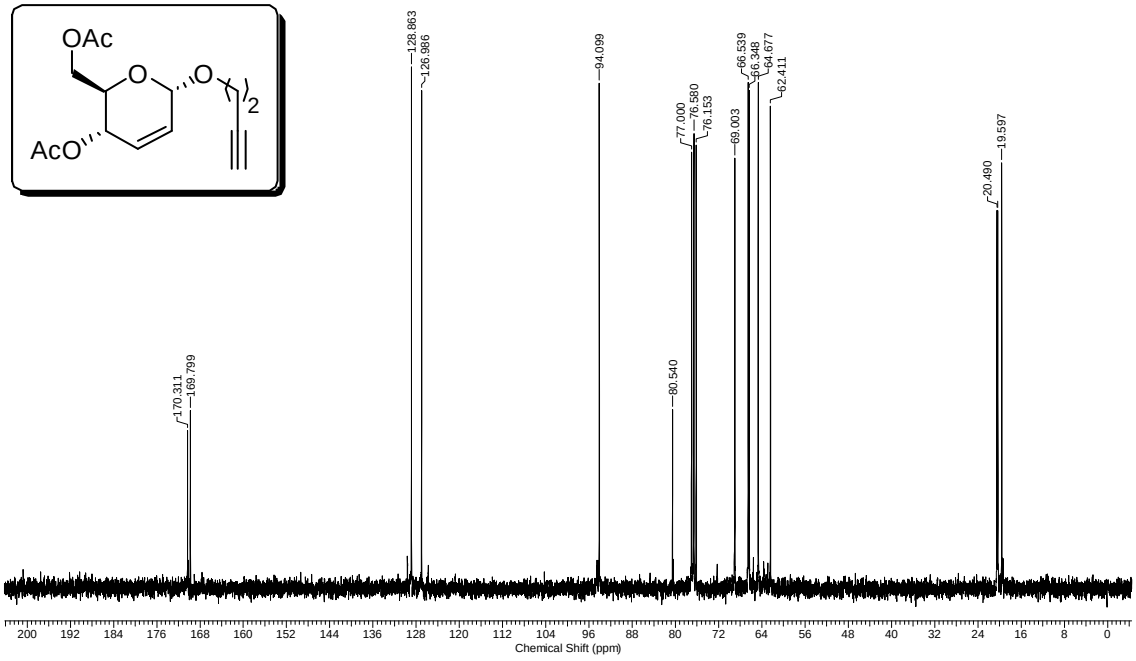

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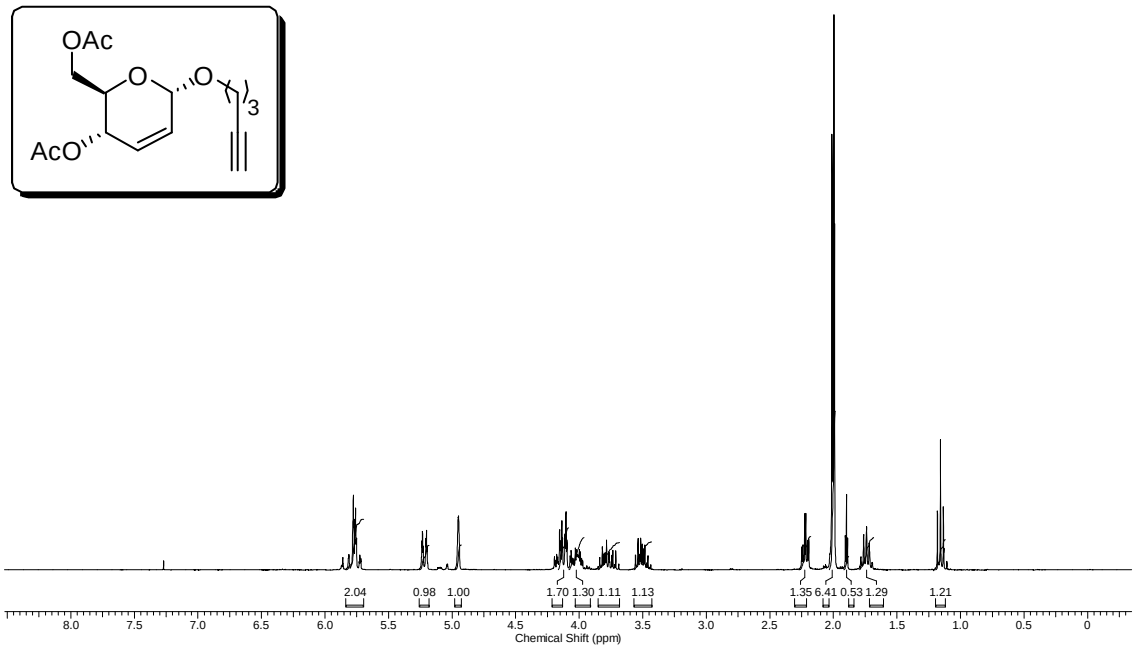

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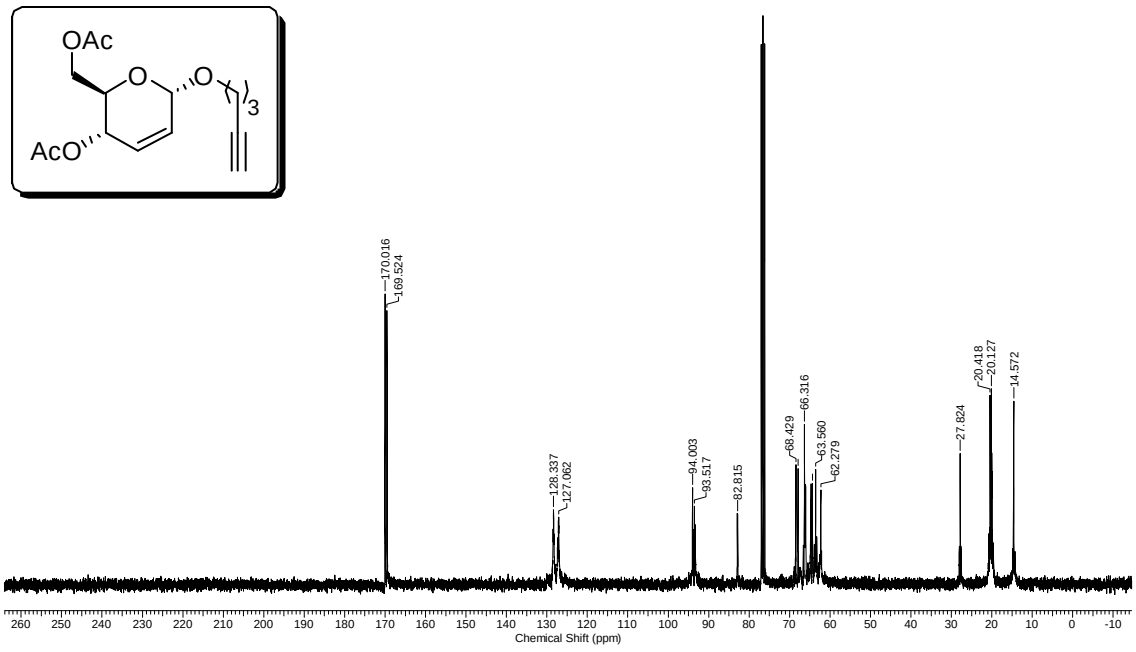
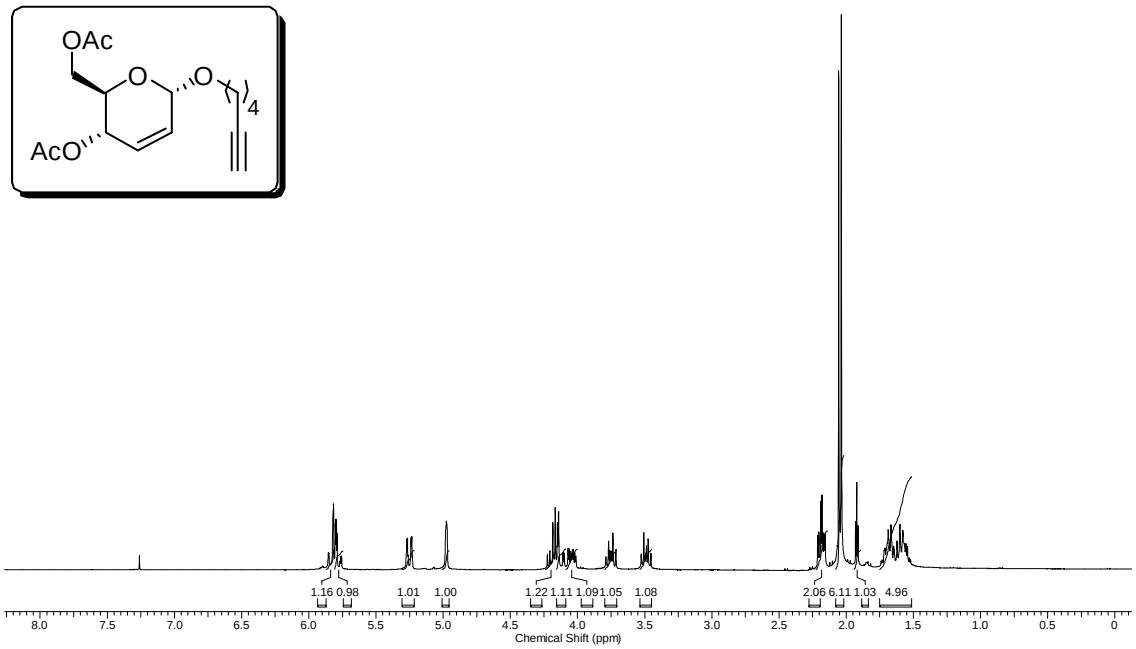


^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **5c**.



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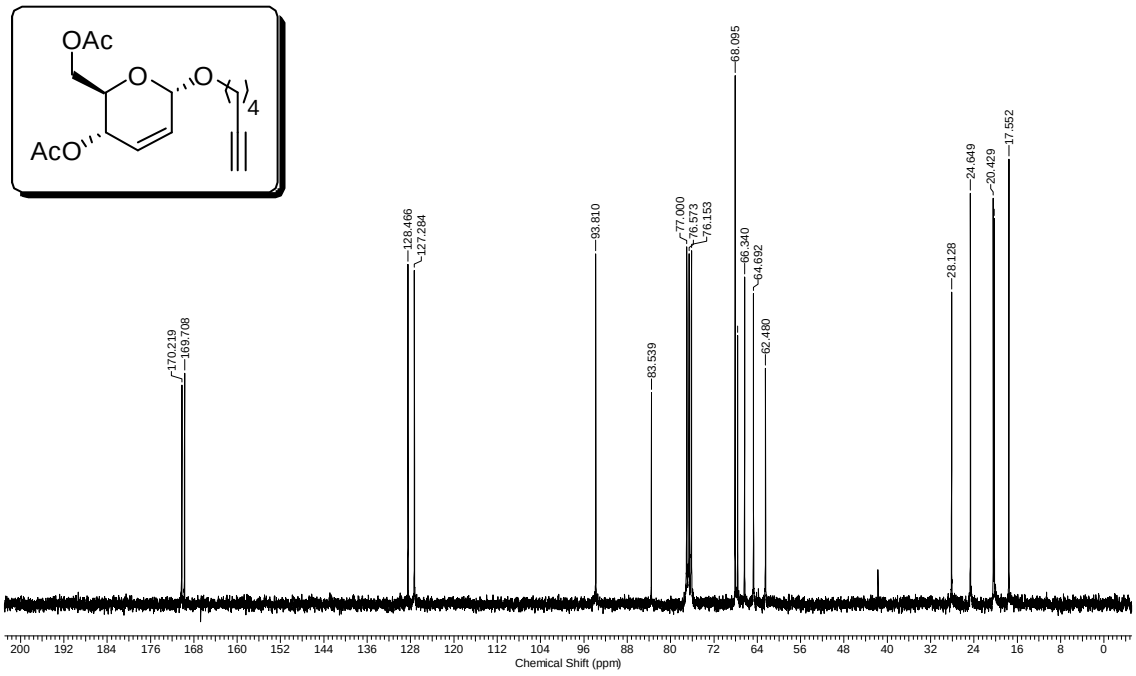

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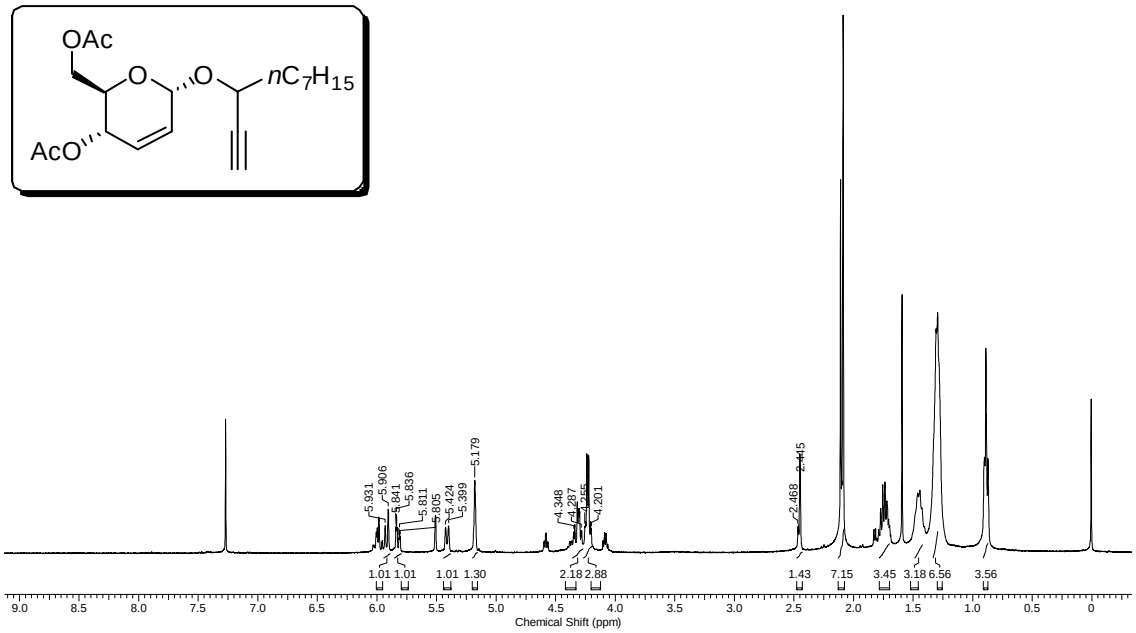

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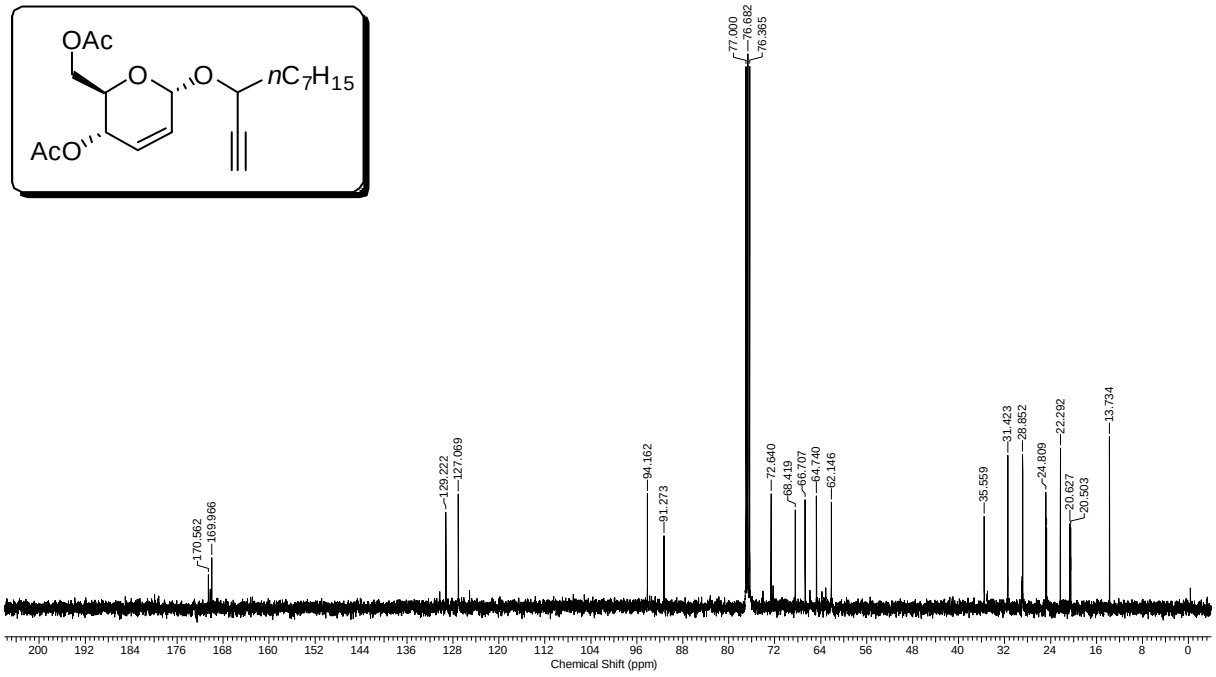

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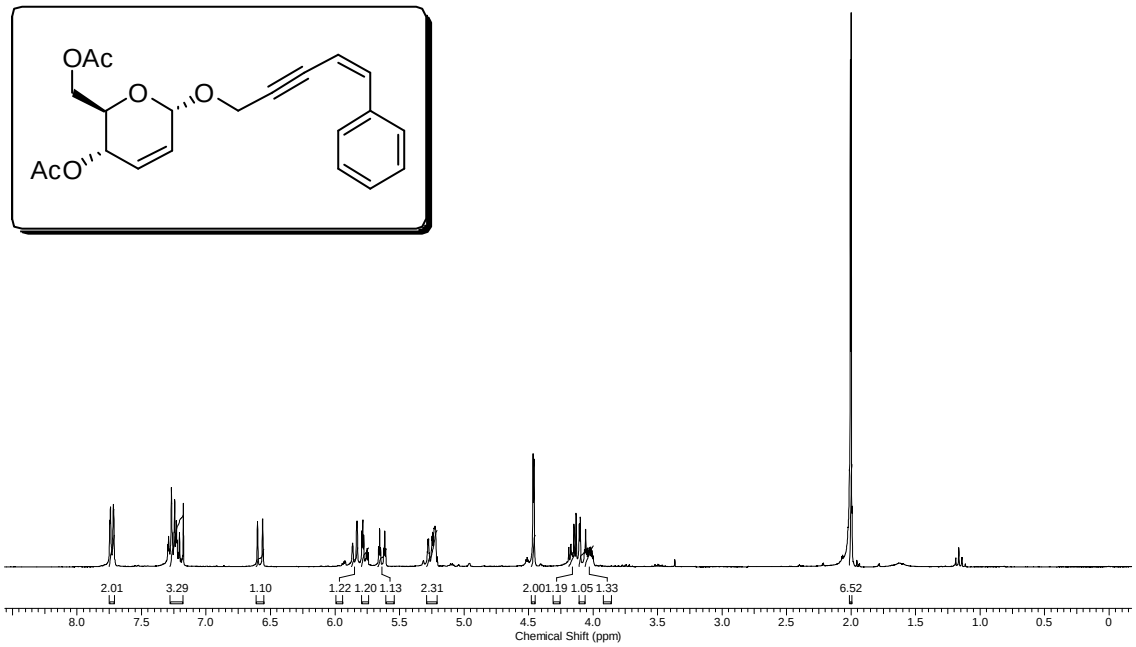

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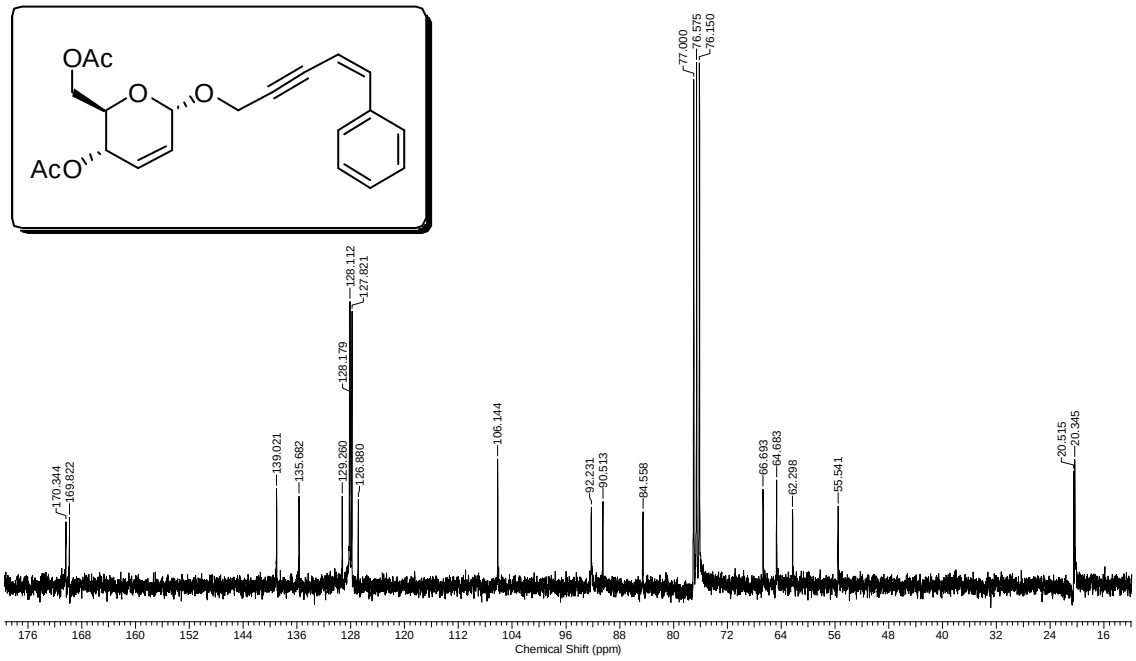

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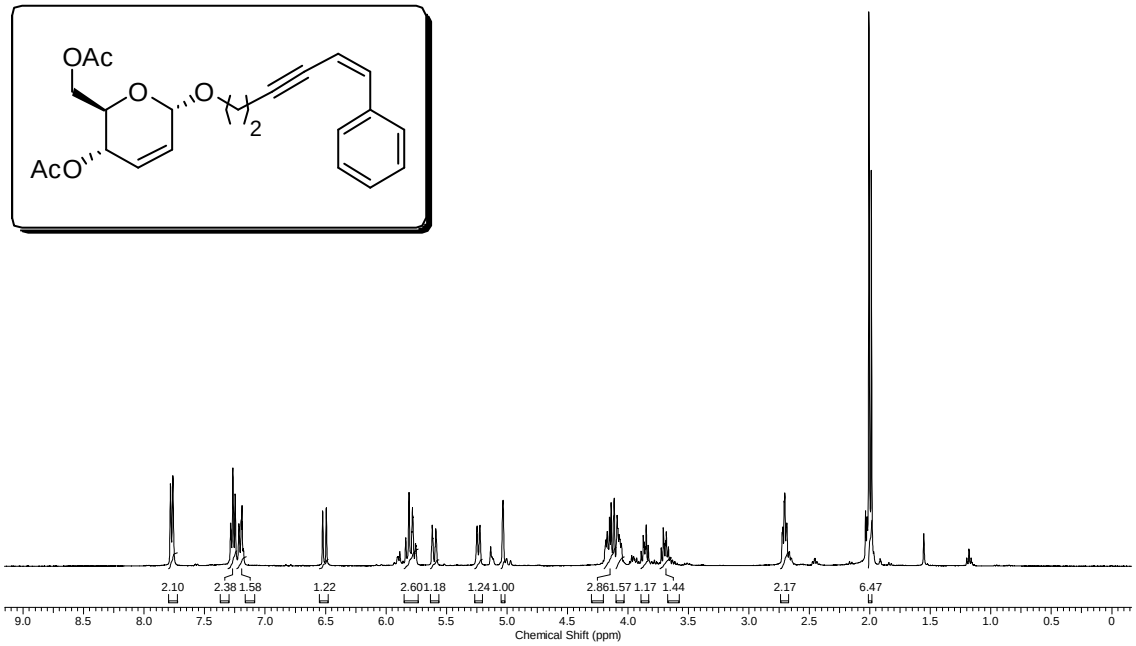

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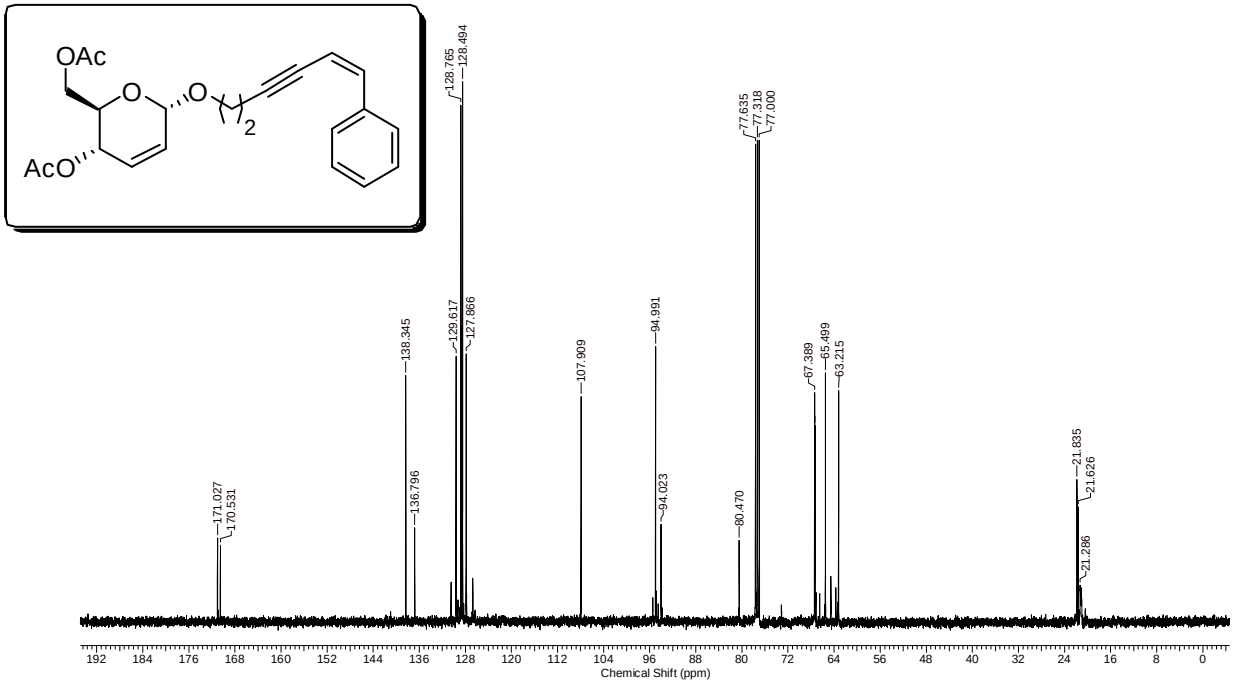

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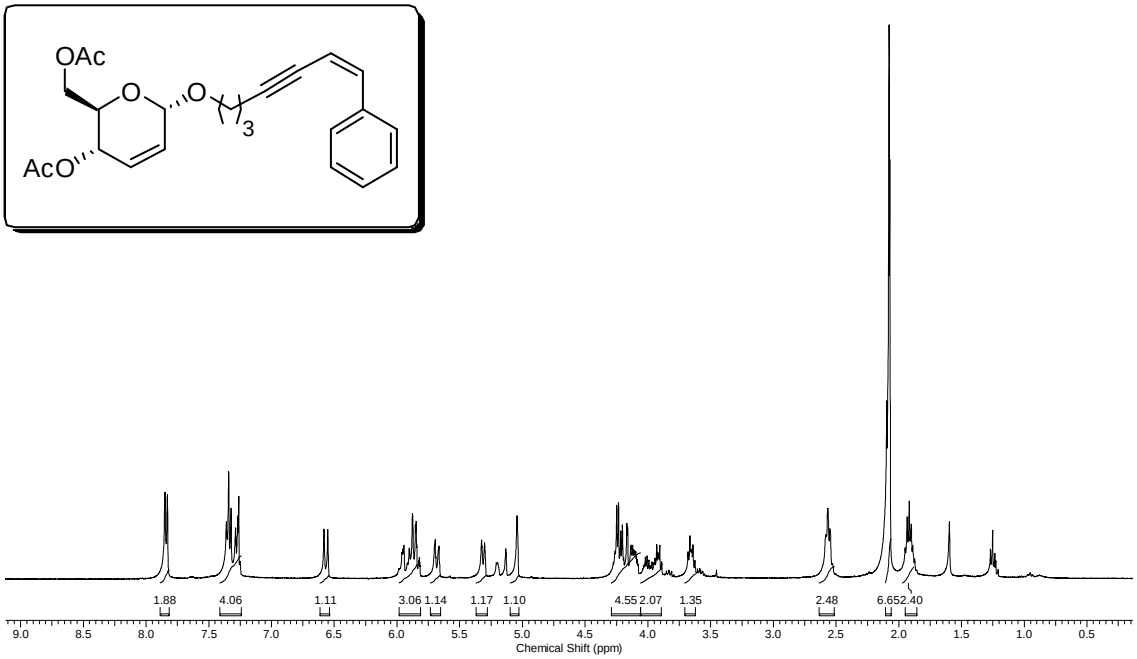

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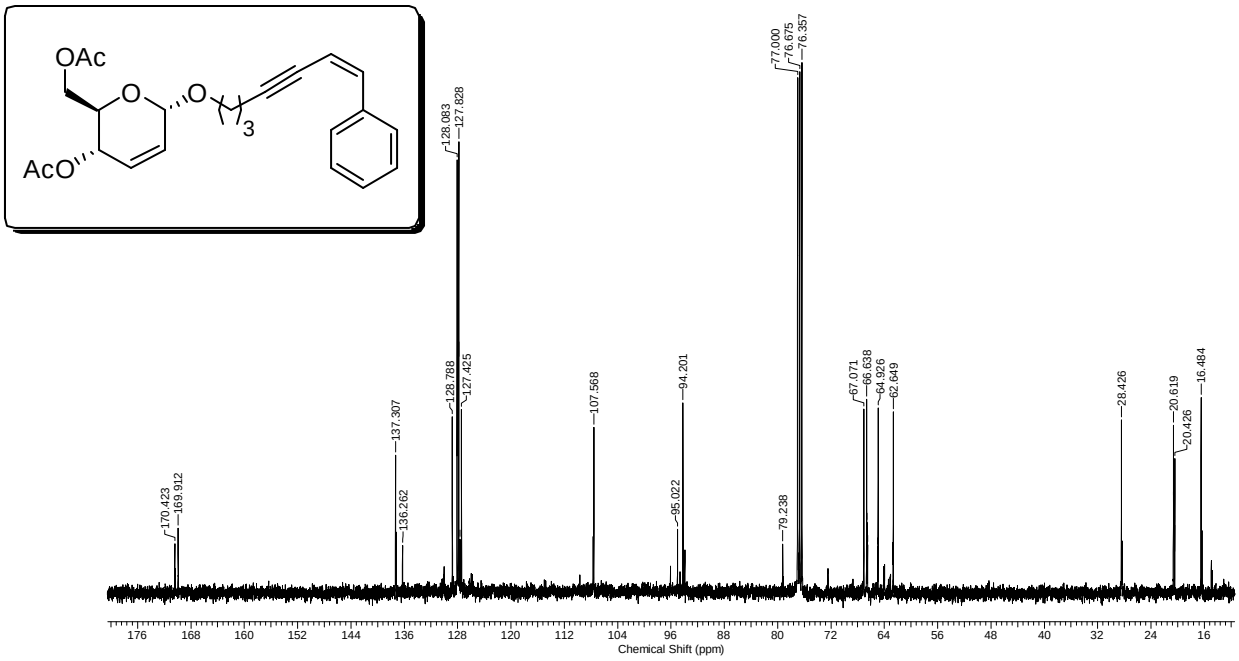

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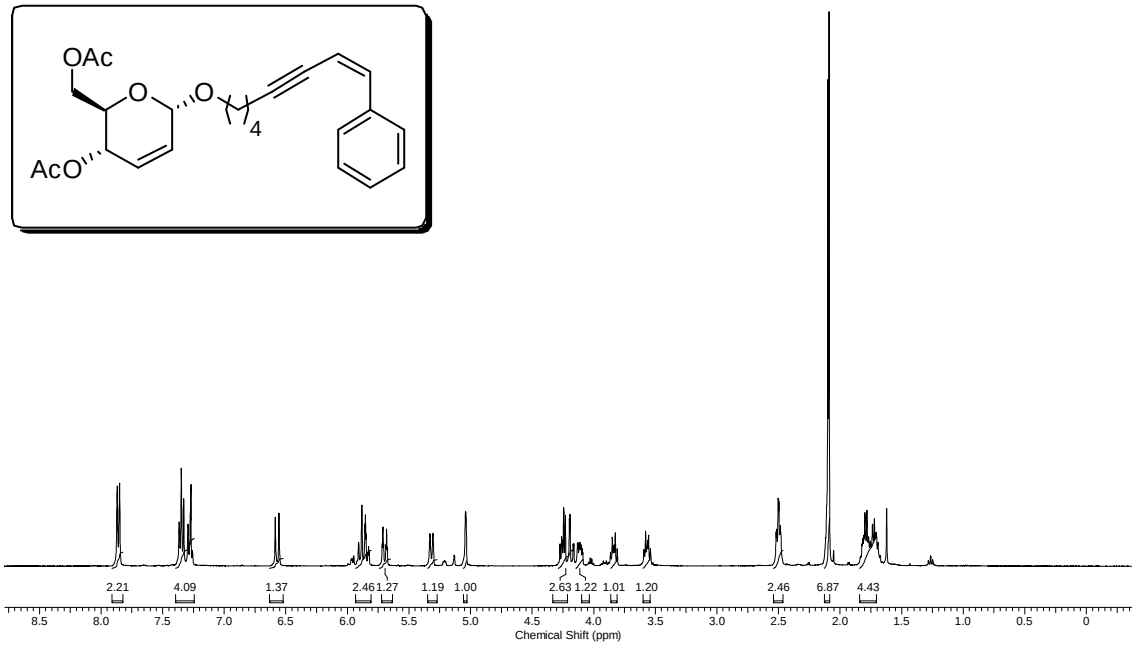

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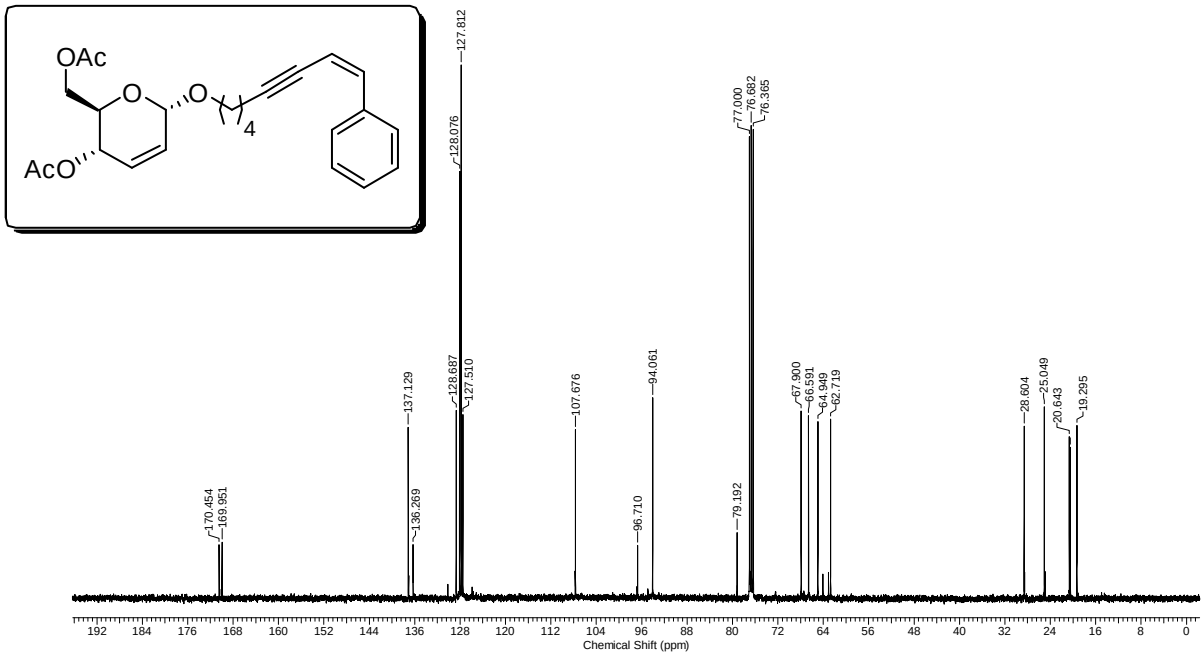
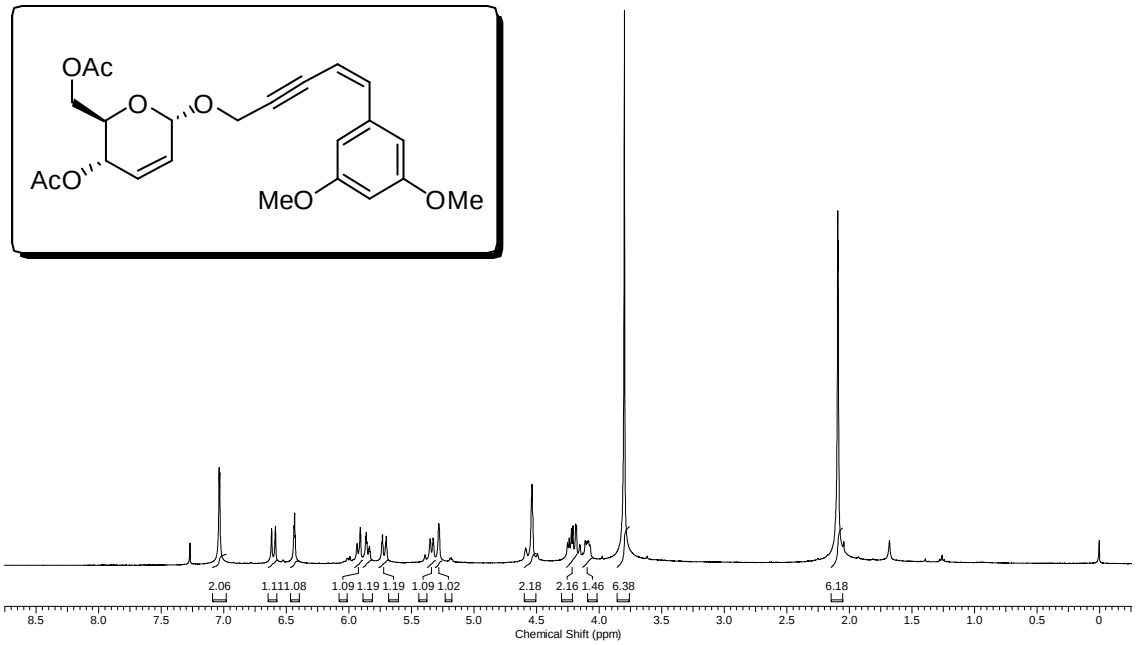
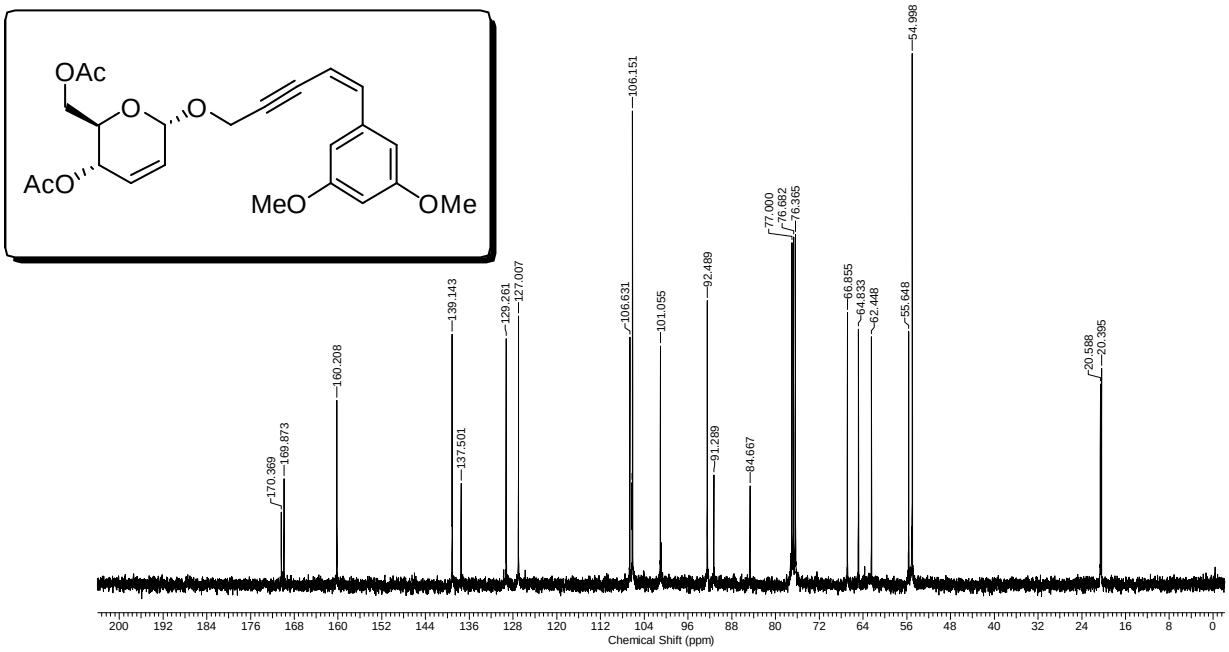


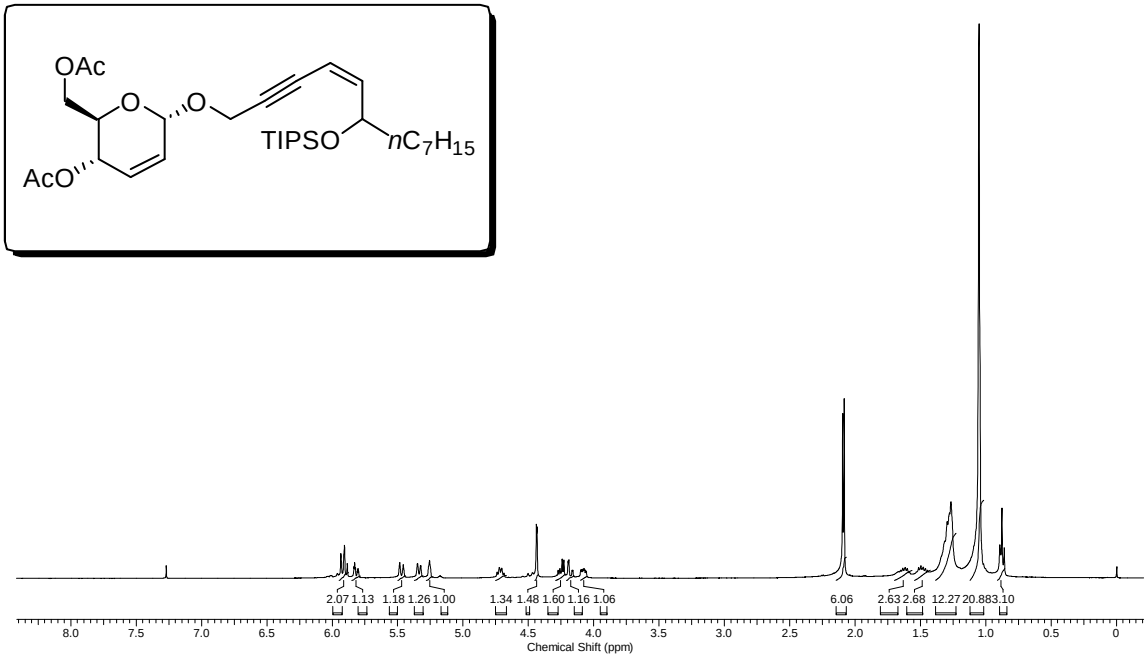
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **6d**.



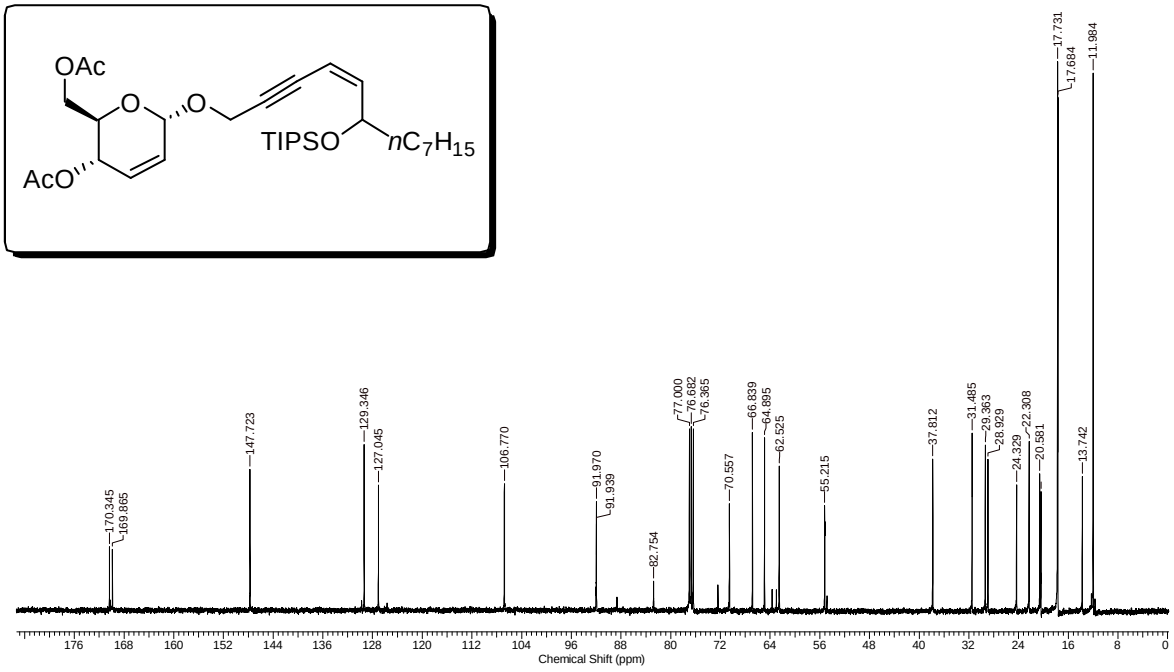
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6e**.



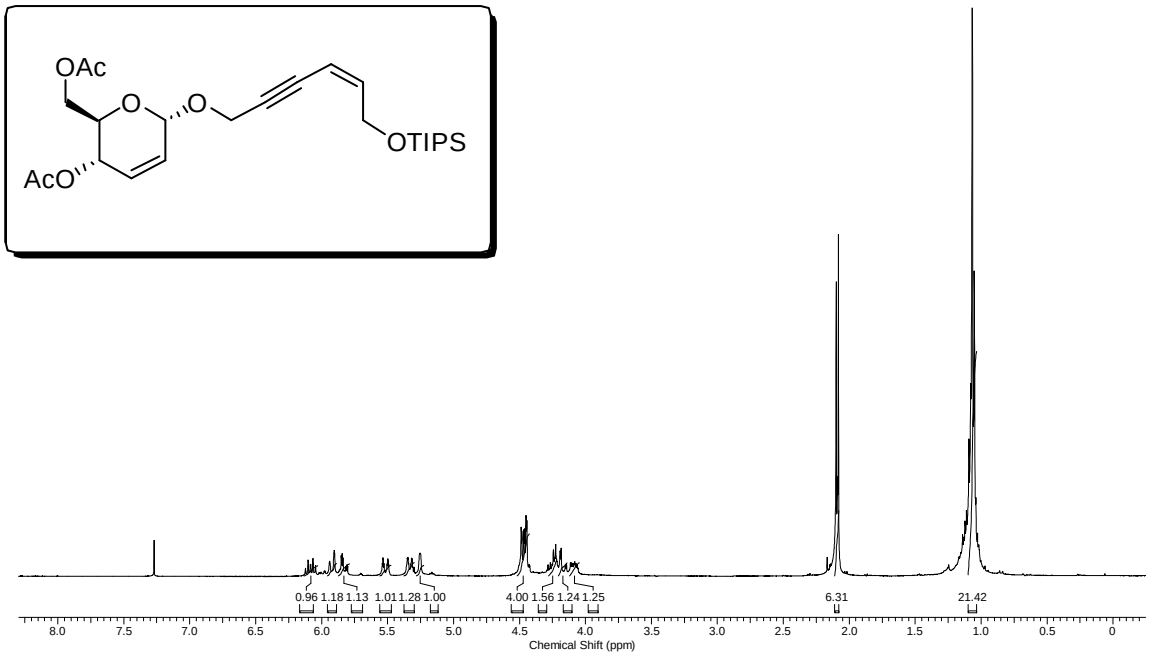
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **6e**.



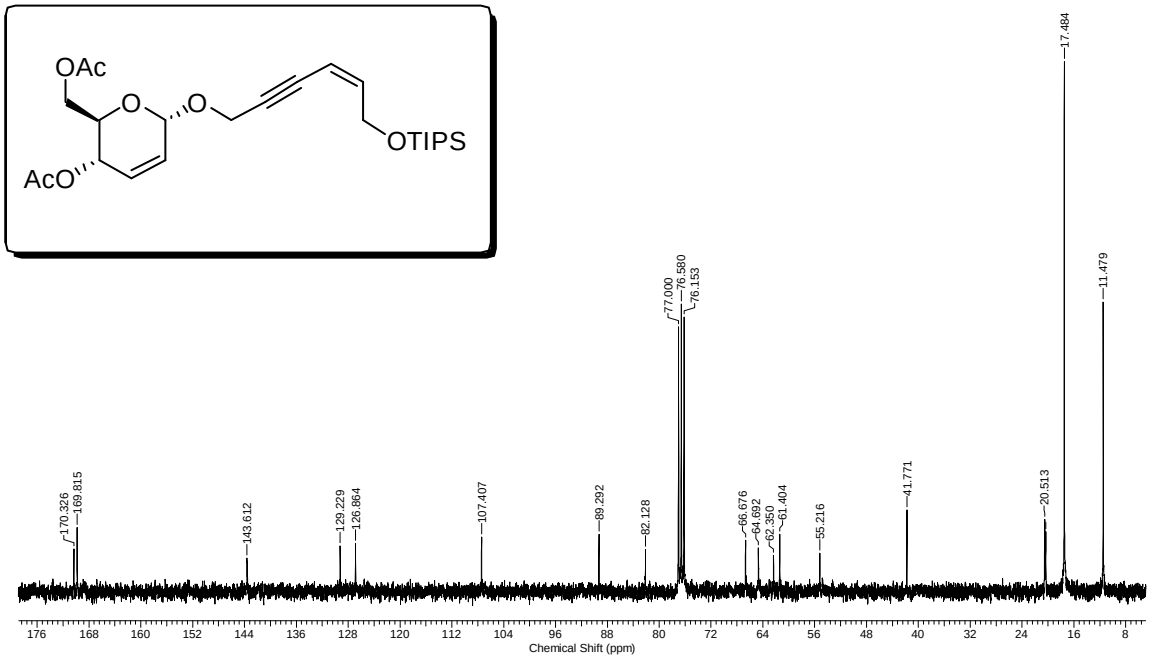
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **6f**.



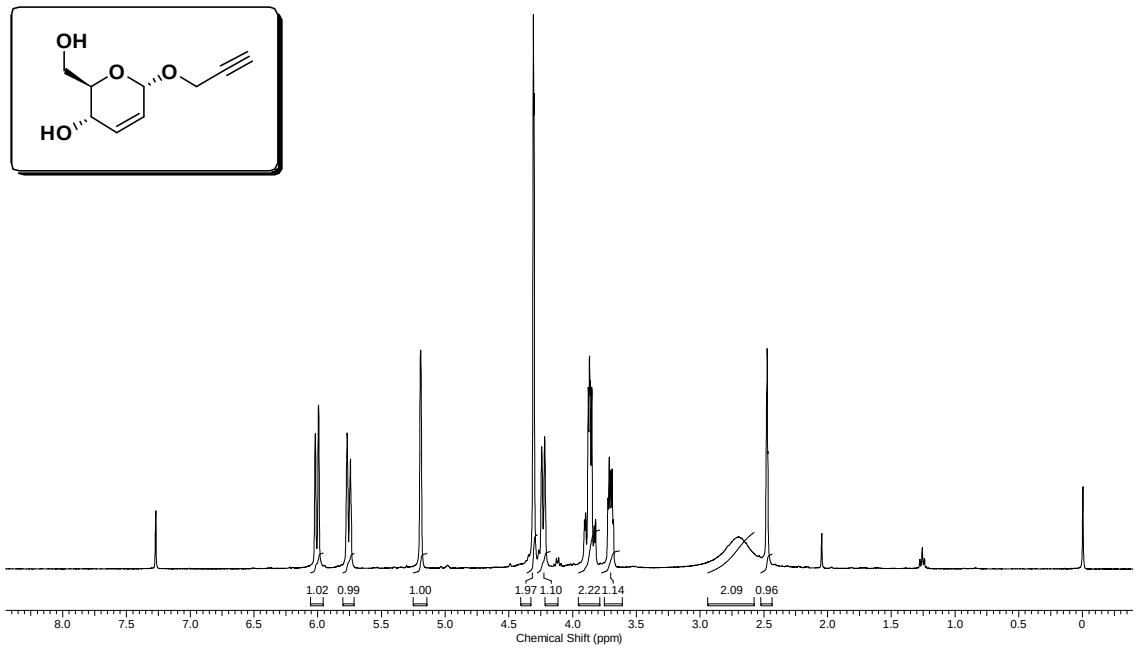
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **6f**.



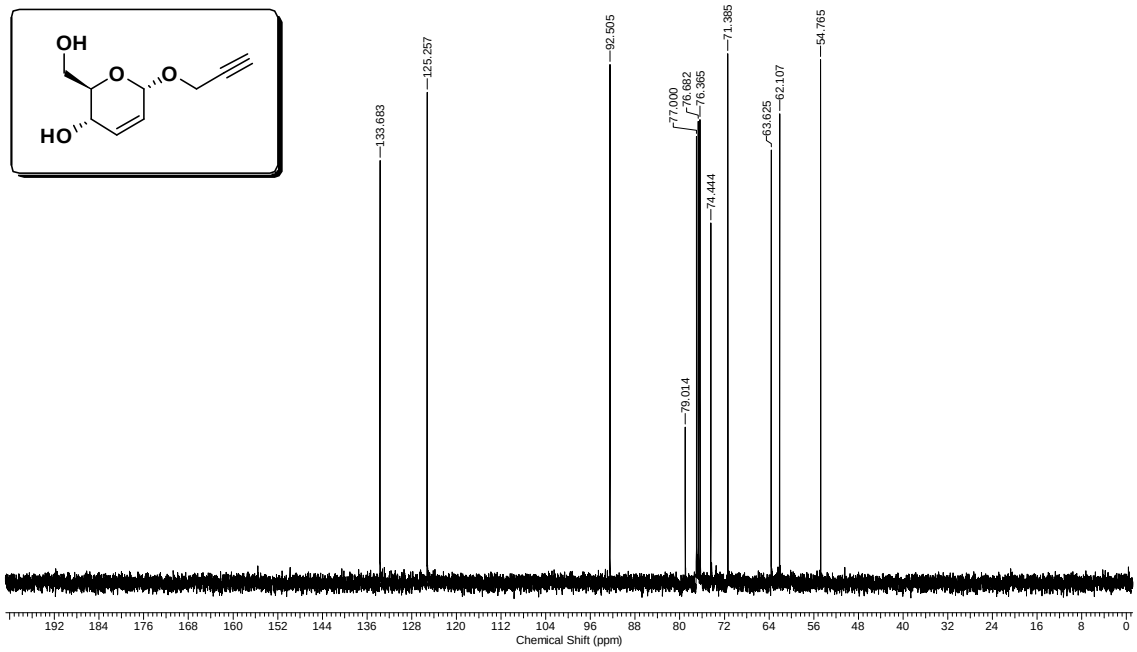
^{1}H NMR spectrum (300 MHz, $CDCl_3$) of compound **6g**.



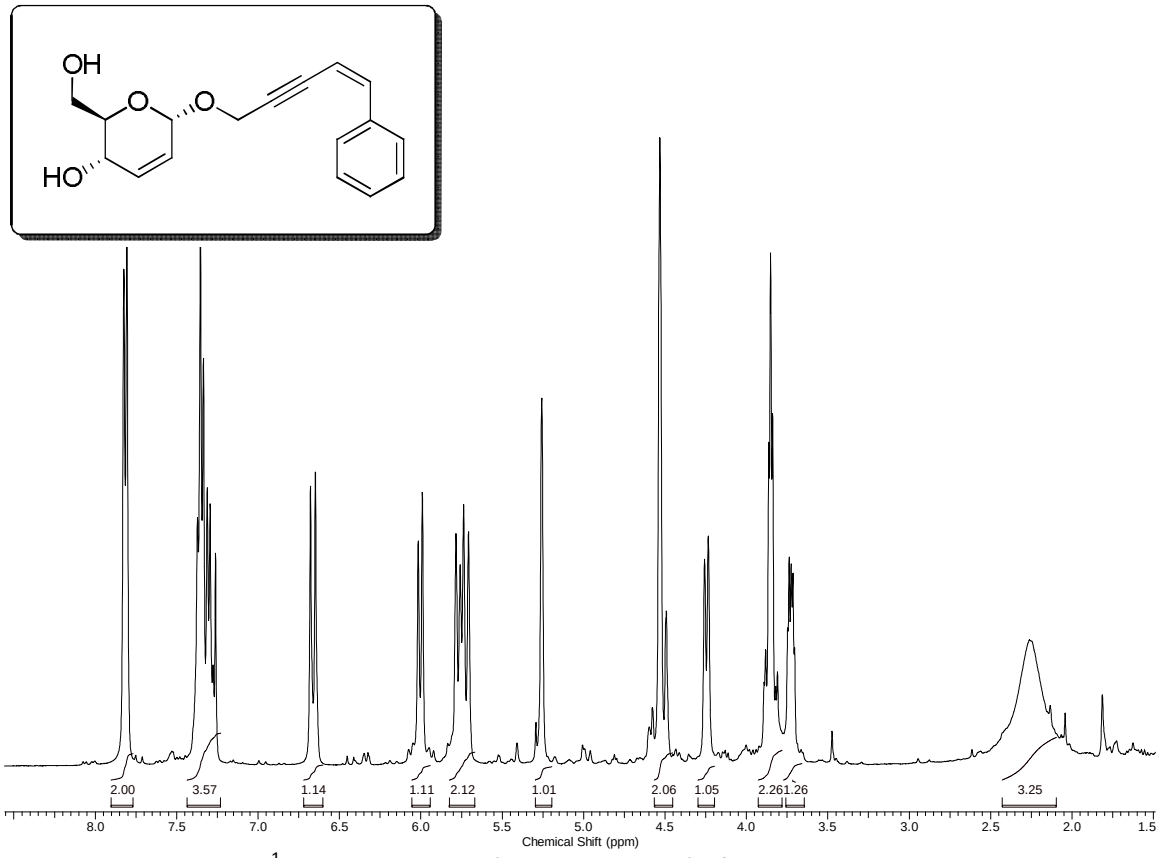
^{13}C NMR spectrum (75 MHz, $CDCl_3$) of compound **6g**.



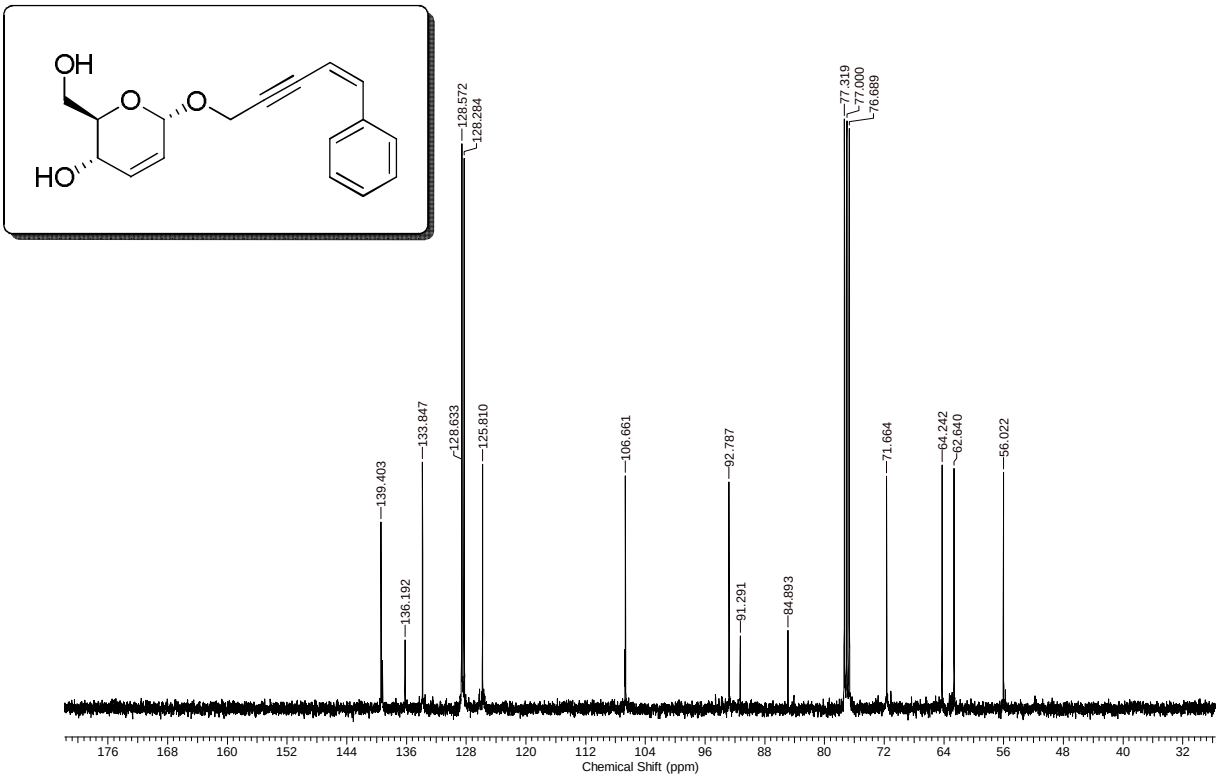
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **7**.



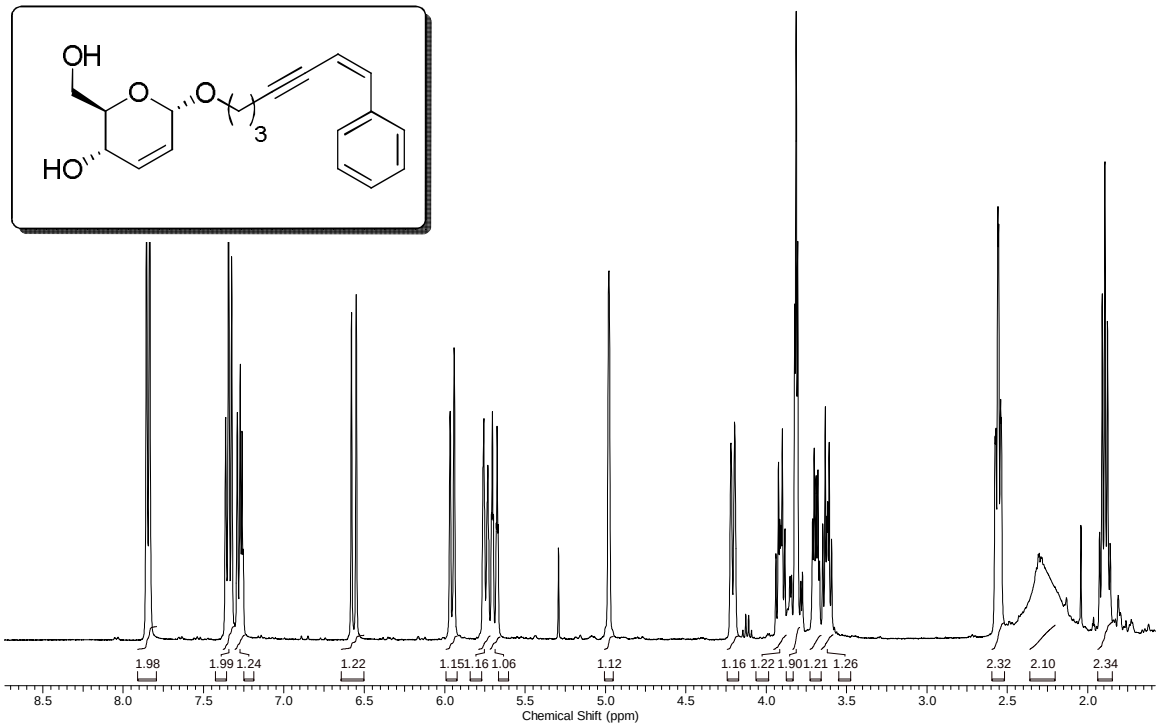
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **7**.



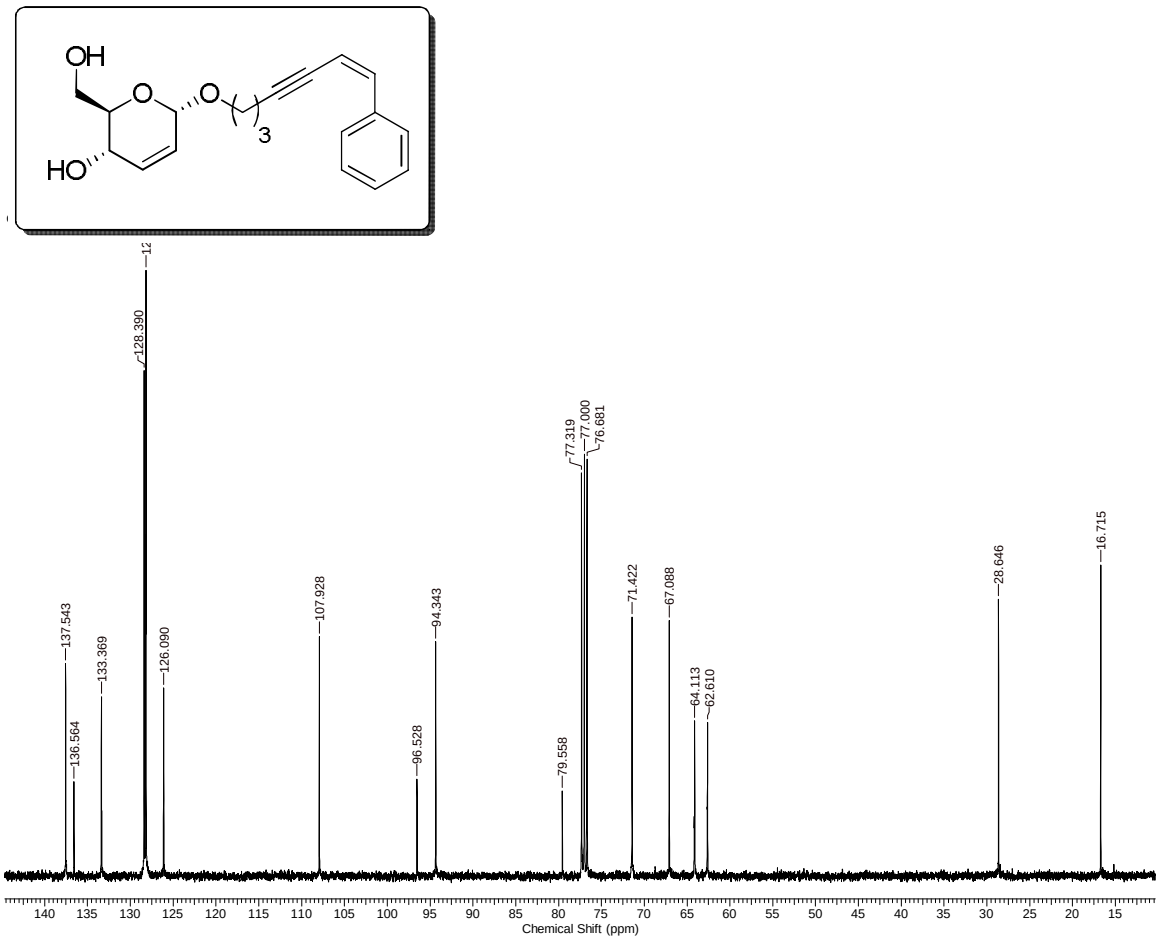
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8**.



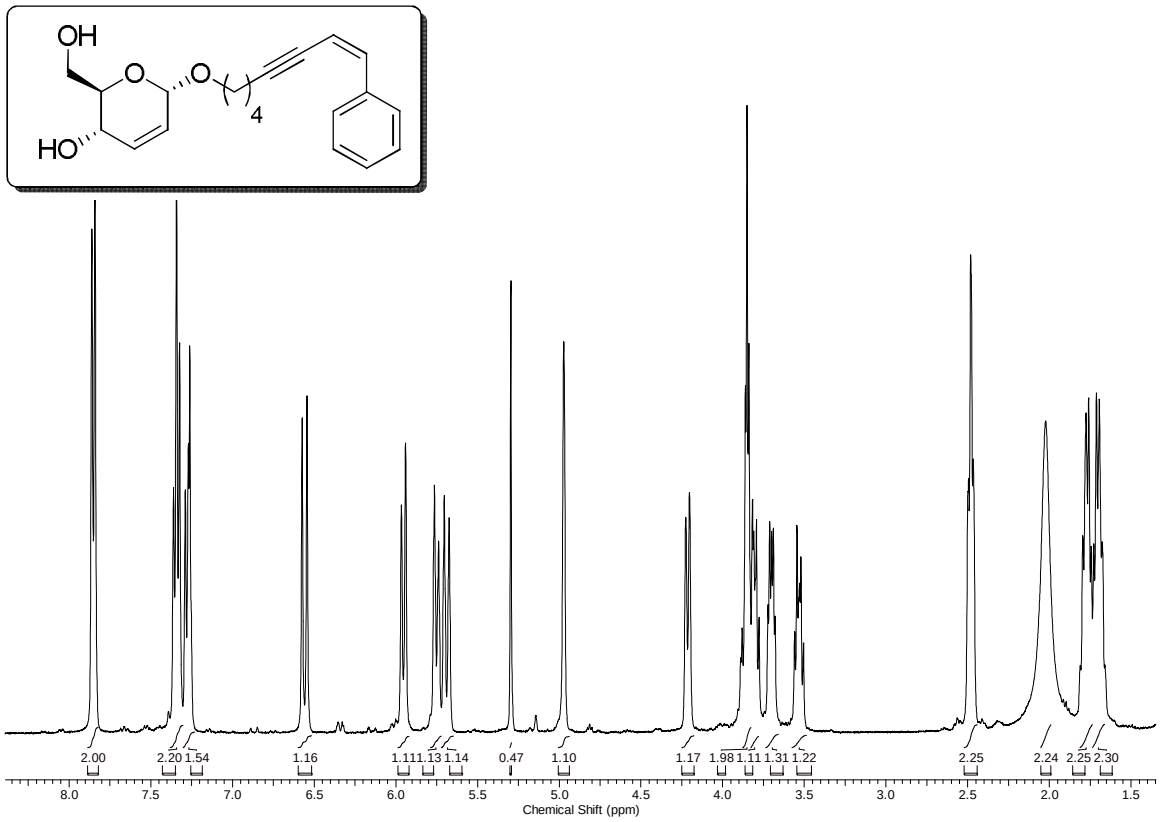
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8**.



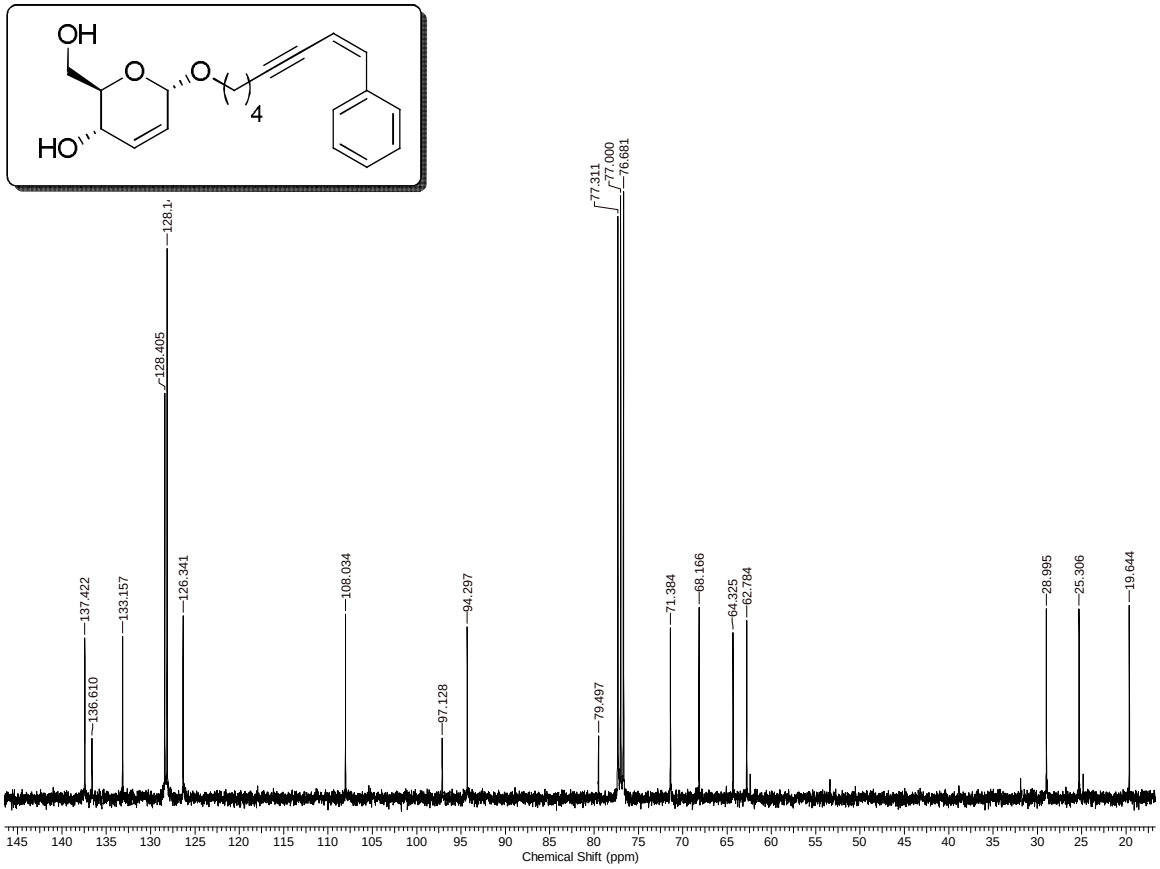
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **9**.



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **9**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **10**.



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **10**.