

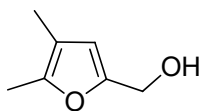
# **Selective Functionalization of Achmatowicz Rearrangement Products by Reactions with Potassium Organotrifluoroborates under Transition-Metal-Free Conditions**

Silvia Roscales, Víctor Ortega, and Aurelio G. Csáky\*

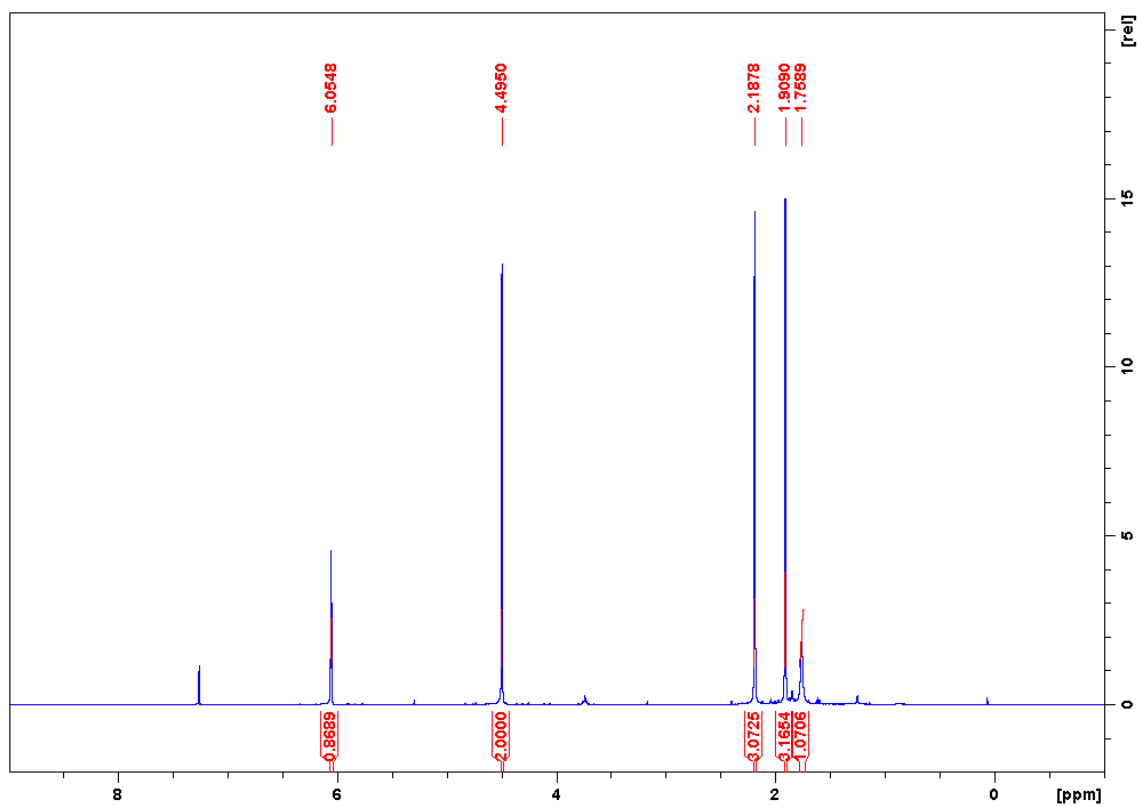
Instituto Pluridisciplinar, Universidad Complutense, Campus de Excelencia Internacional Moncloa, Paseo  
de Juan XXIII, 1, 28040 Madrid, Spain

## **Supporting Information**

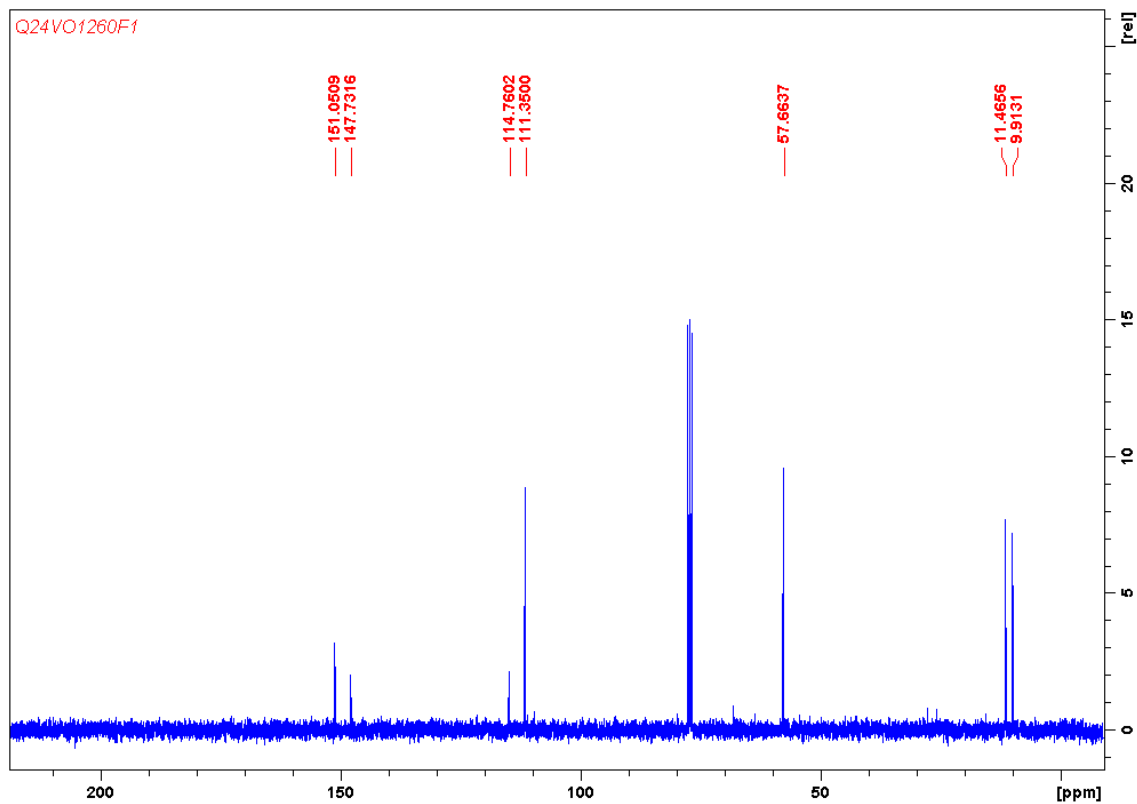
Copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, and NOE determinations.....S2 – S65

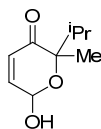


1h,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

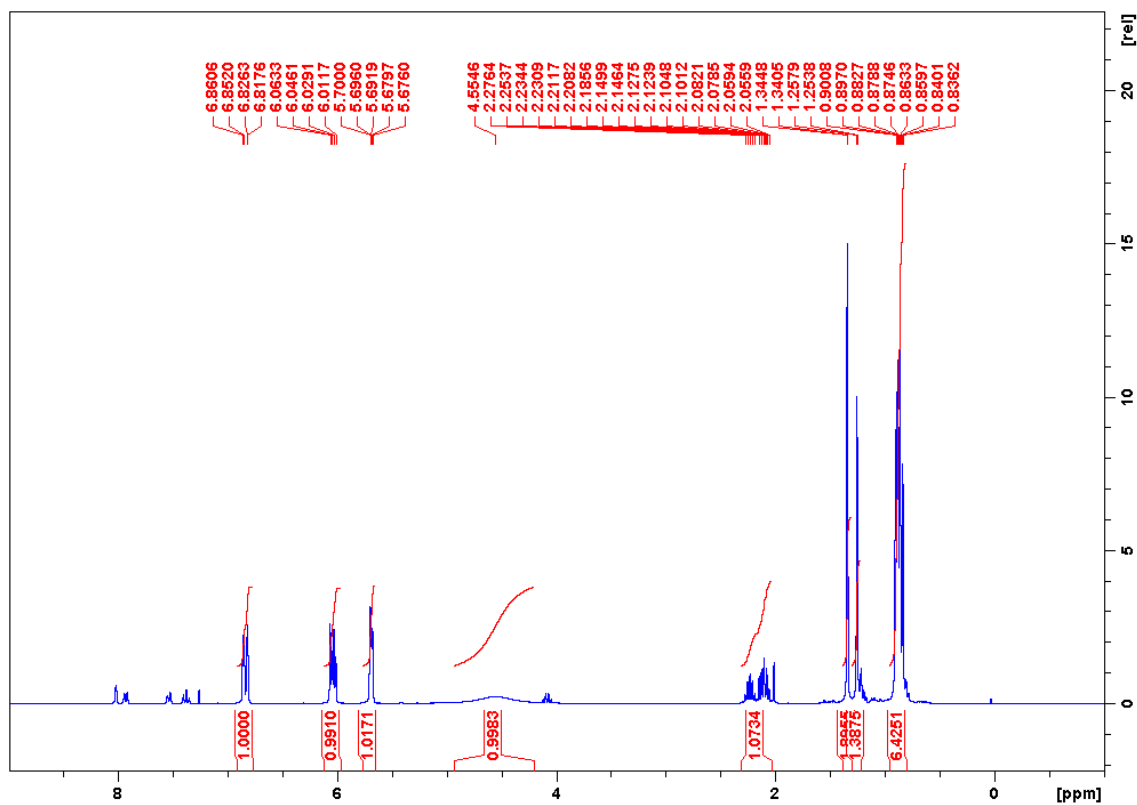


1h,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

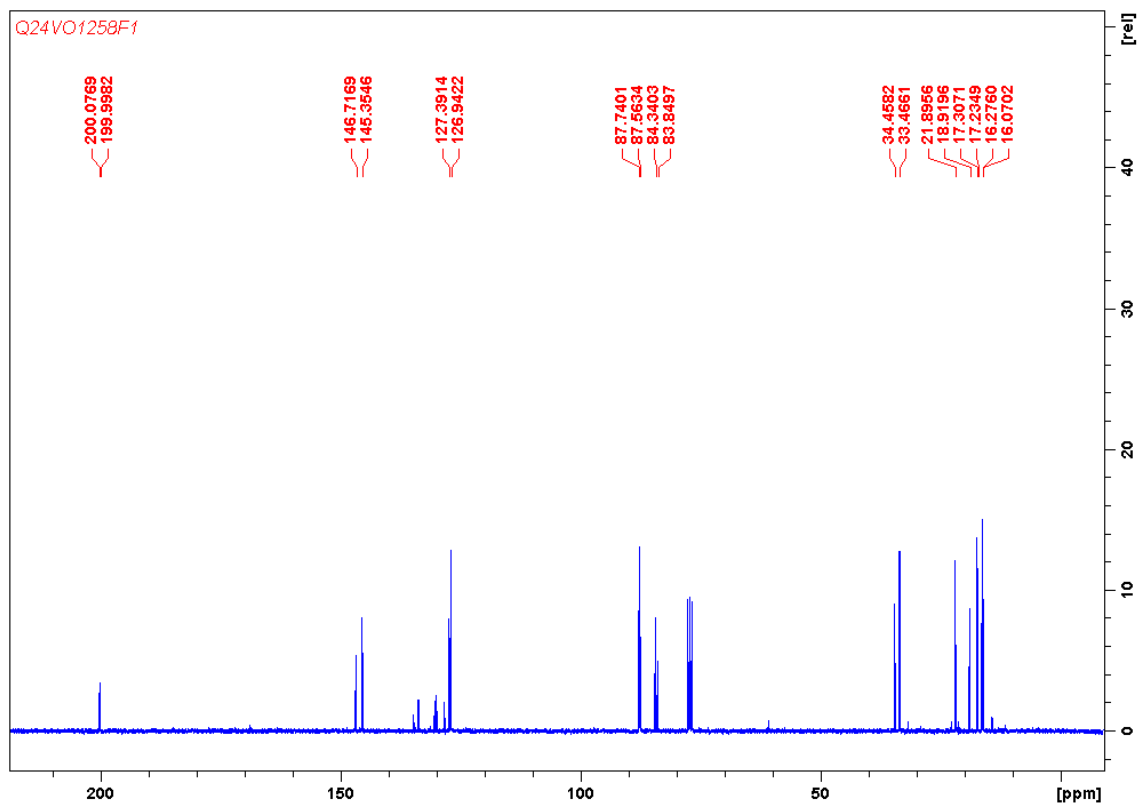


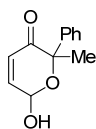


2d,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

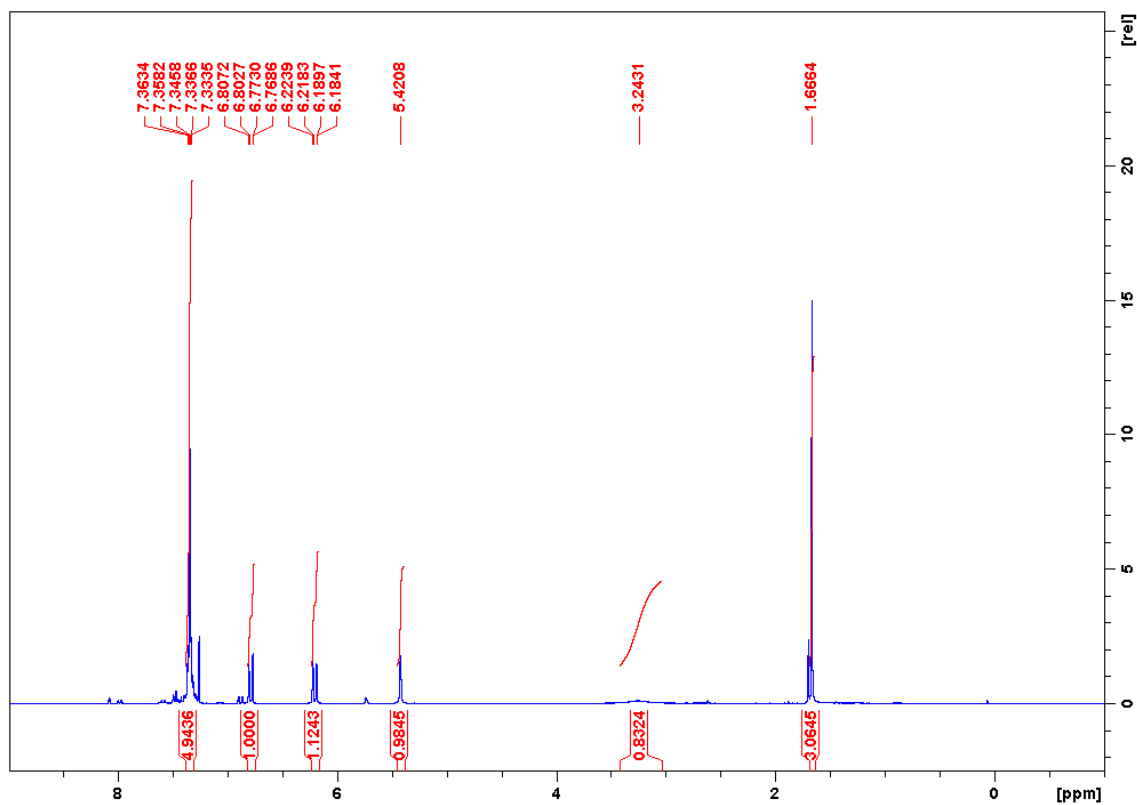


2d,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

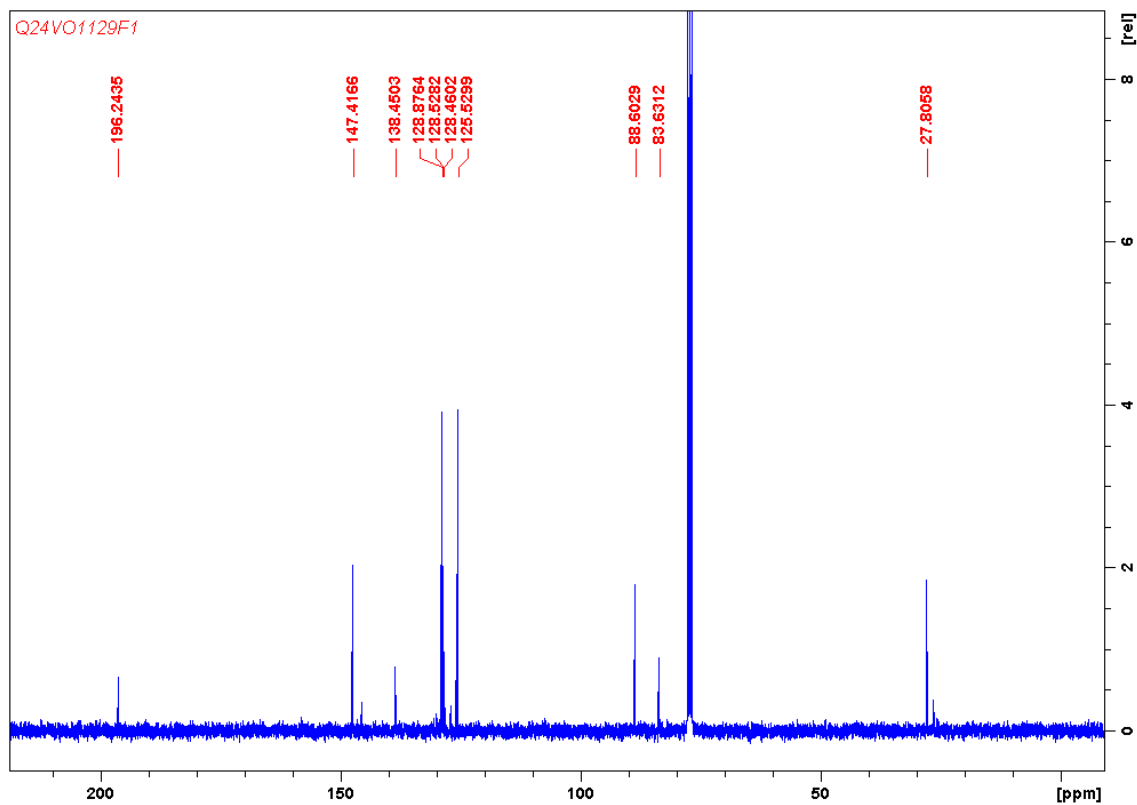


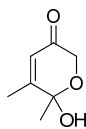


2e,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

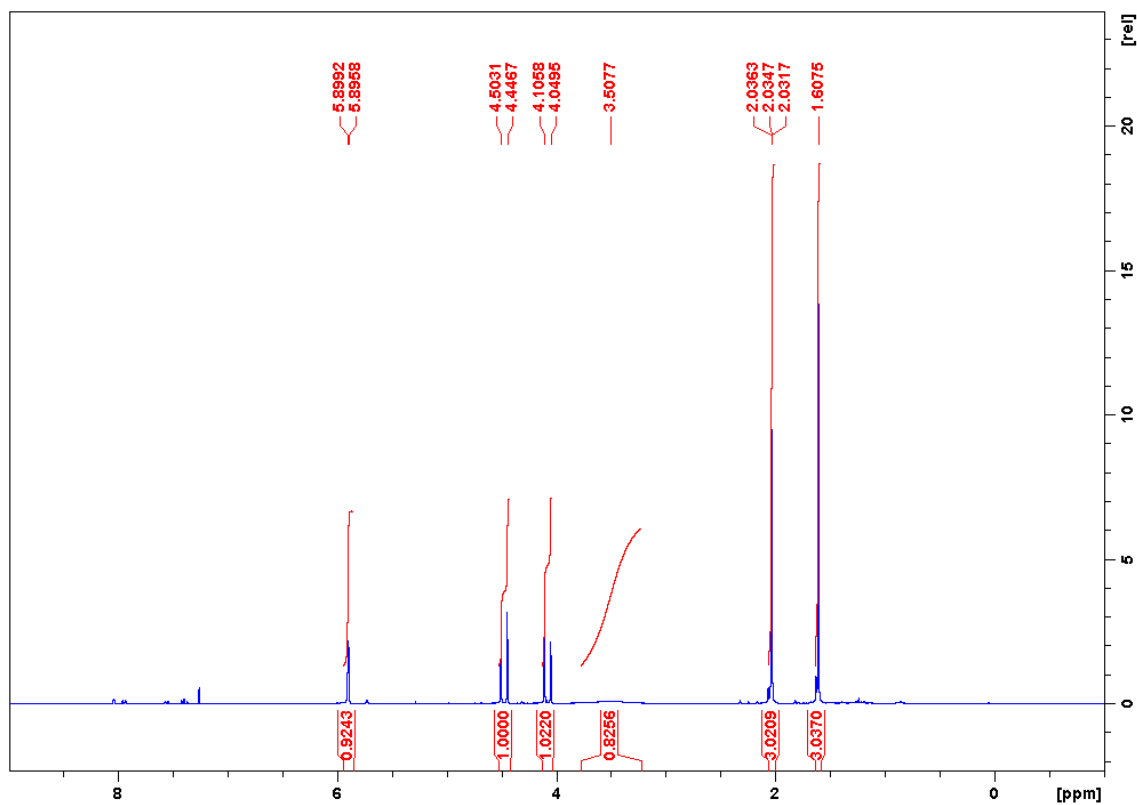


2e,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

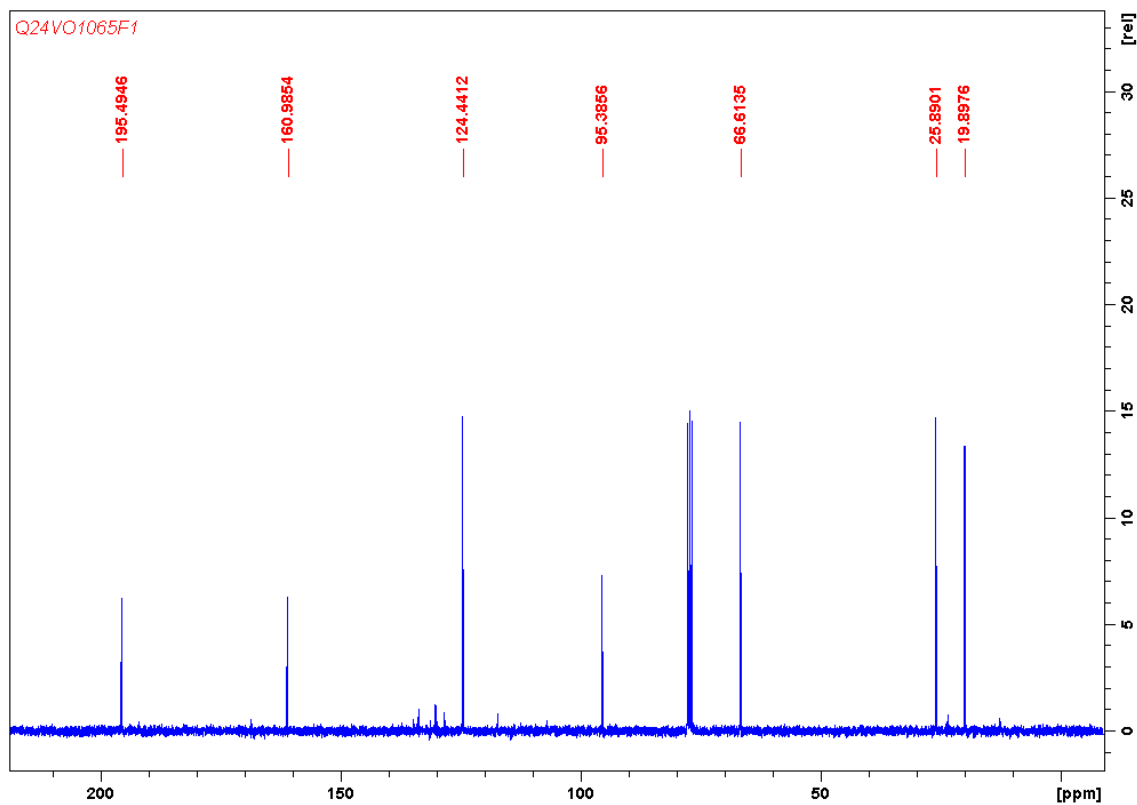


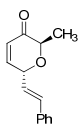


2h,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

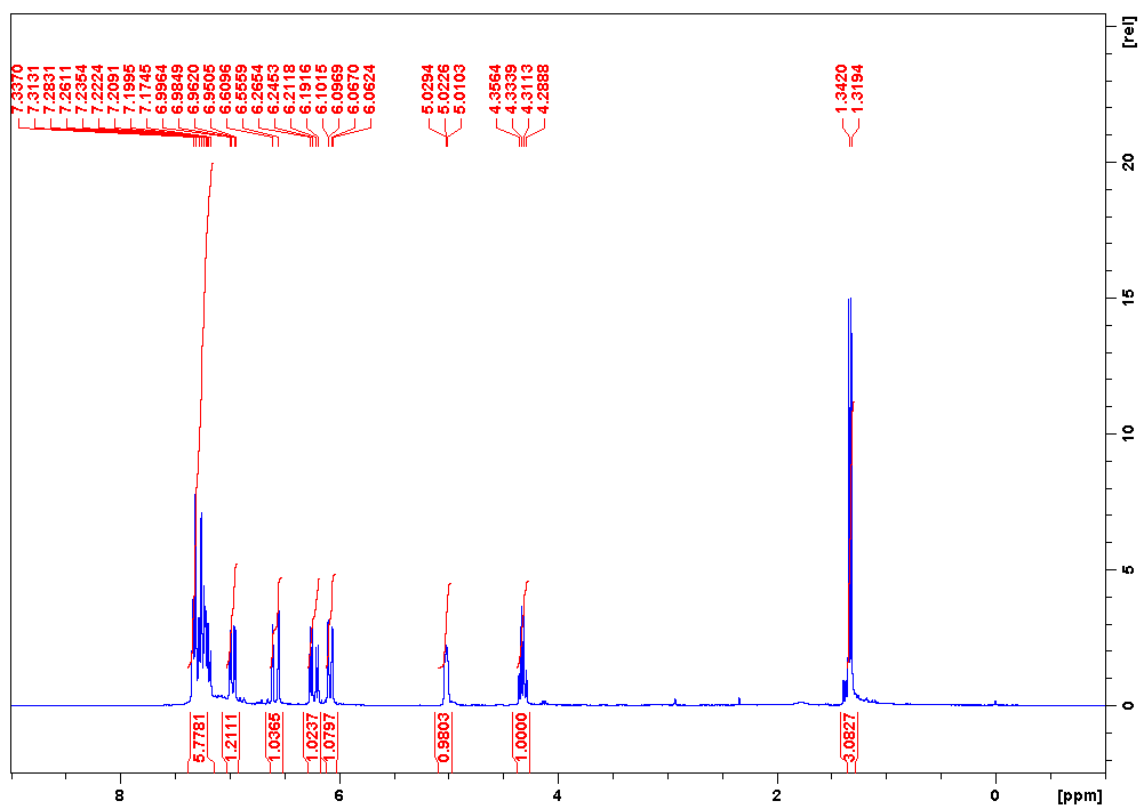


2h,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

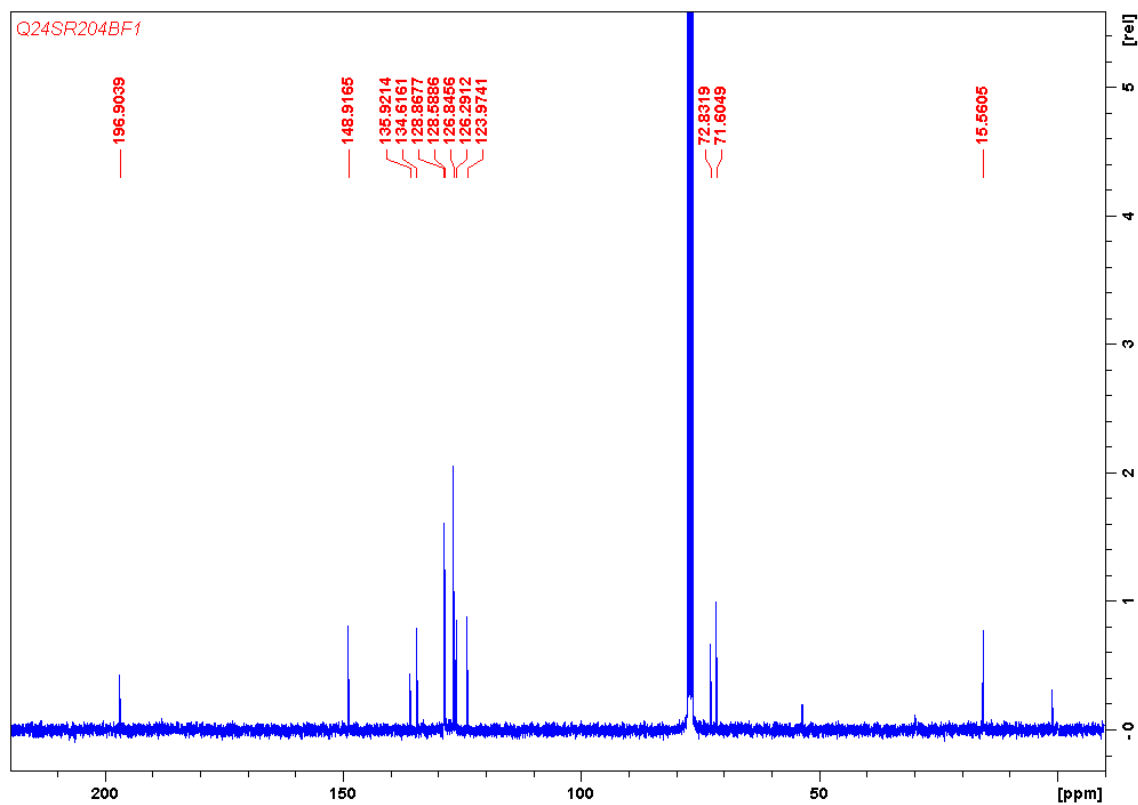




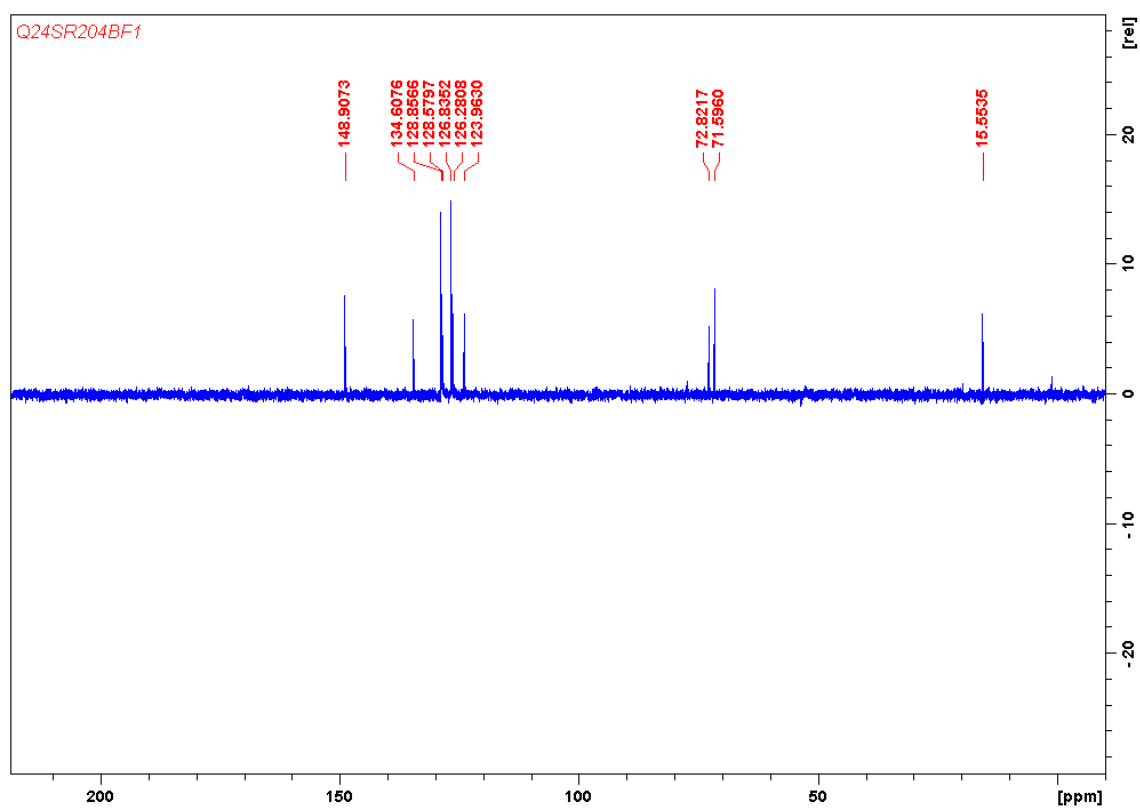
10a,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



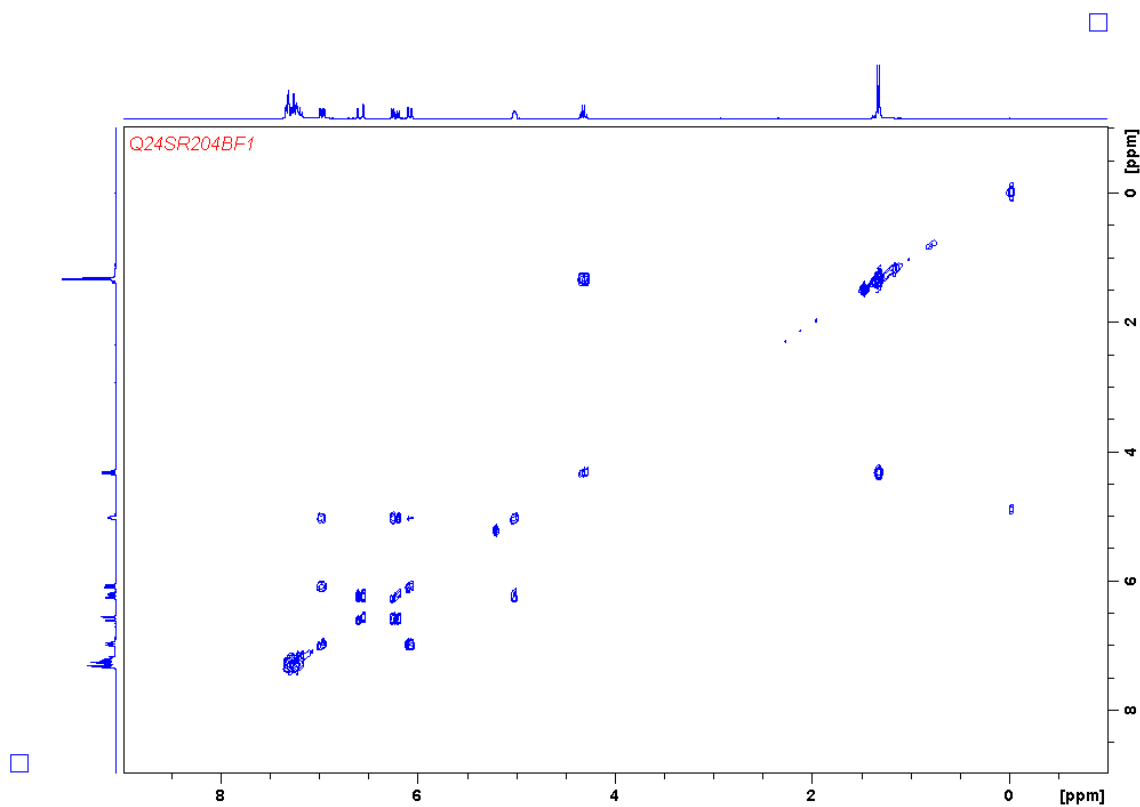
10a,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



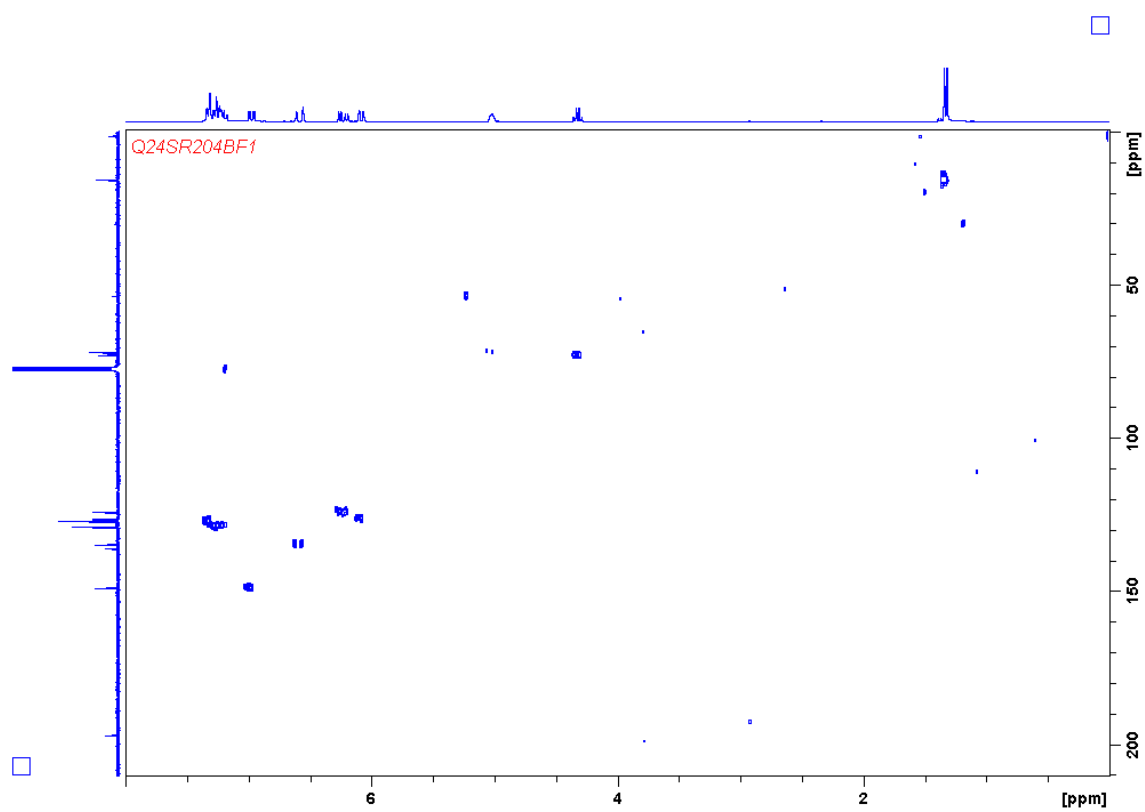
# 10a, DEPT 135 (75 MHz, CDCl<sub>3</sub>)



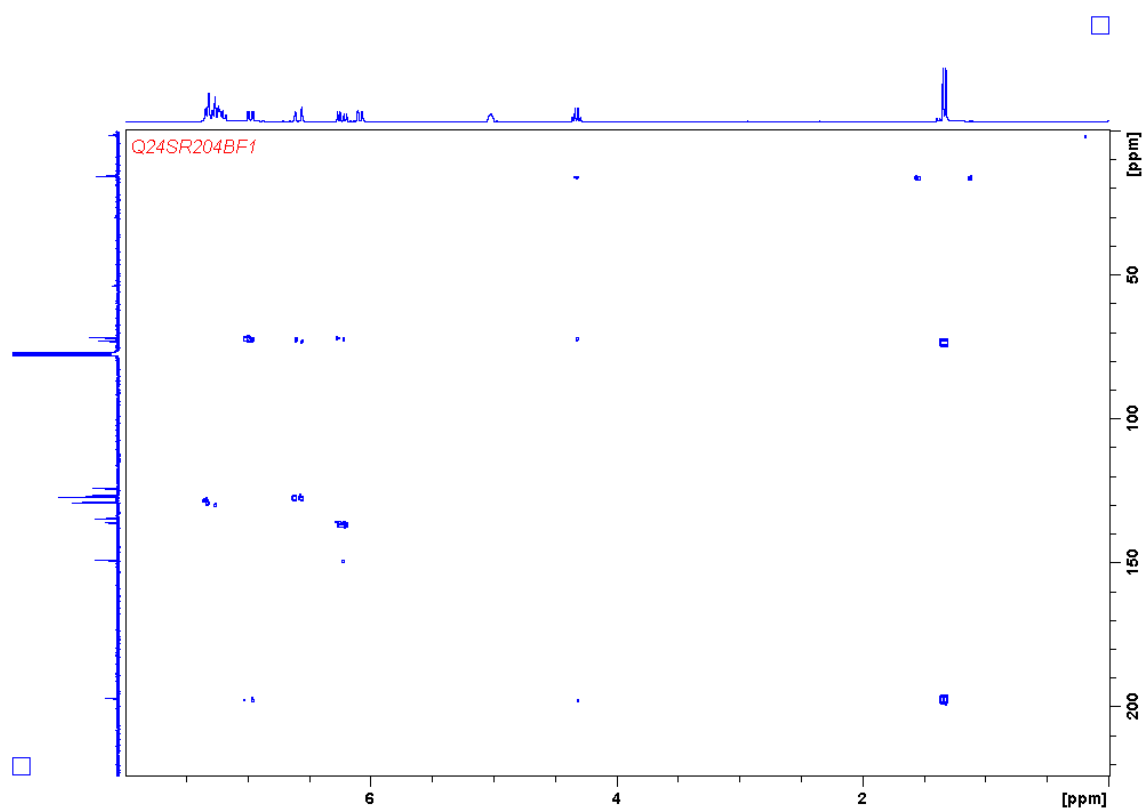
# 10a, COSY (CDCl<sub>3</sub>)



**10a, HMQC (CDCl<sub>3</sub>)**

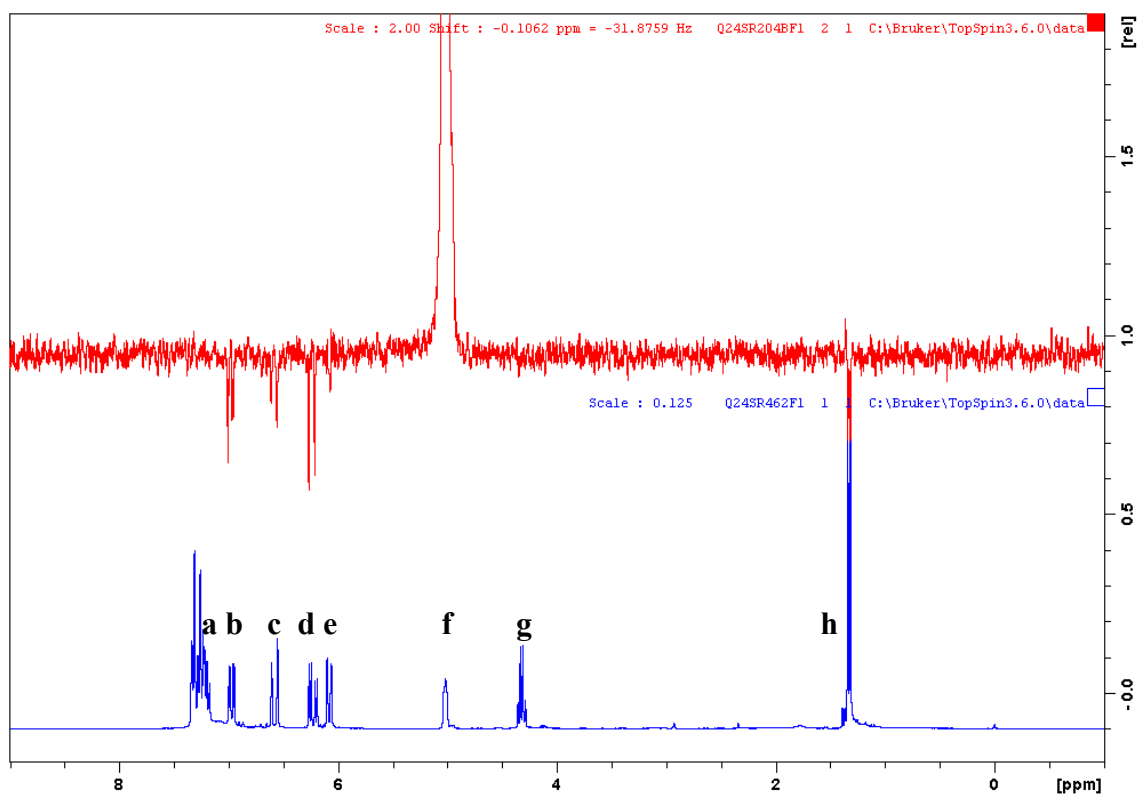
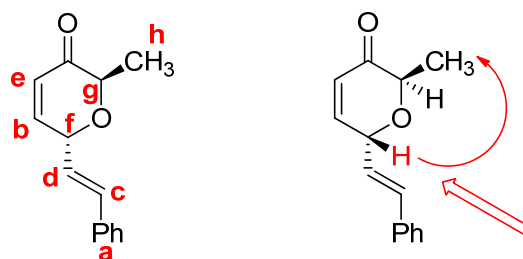


**10a, HMBC (CDCl<sub>3</sub>)**

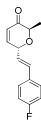




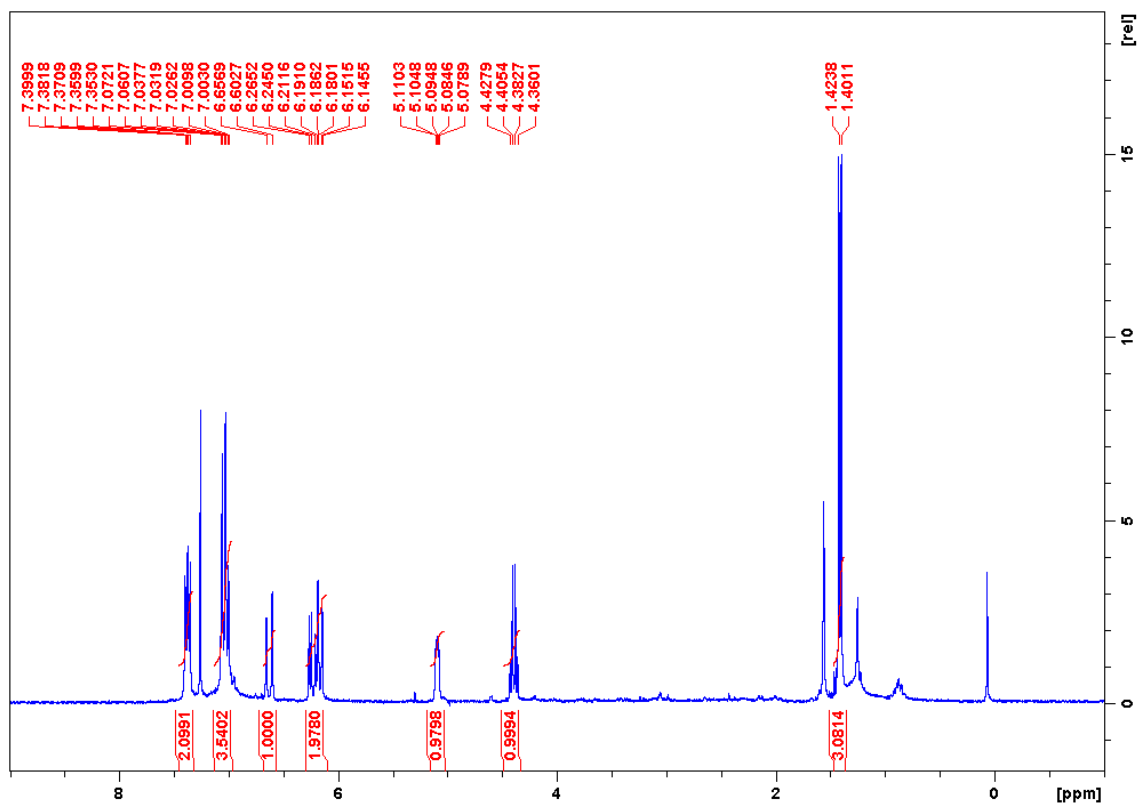
**10a, NOE (CDCl<sub>3</sub>)**



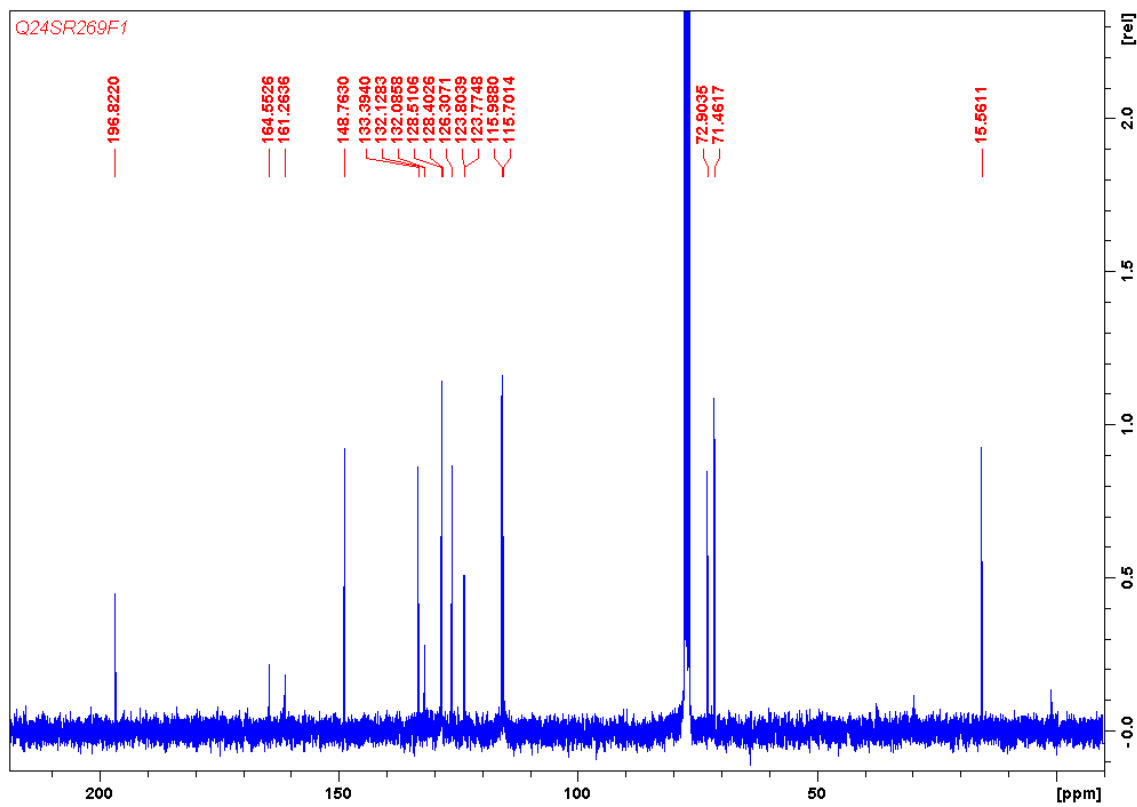
- a:** 7.17-7.39 (m, 5H).
- b:** 7.00 (dd,  $J = 10.4$  Hz,  $J = 3.5$  Hz, 1H).
- c:** 7.60 (d,  $J = 16.1$  Hz, 1H).
- d:** 6.24 (dd,  $J = 16.1$  Hz,  $J = 6.2$  Hz, 1H).
- e:** 6.10 (dd,  $J = 10.4$  Hz,  $J = 1.7$  Hz, 1H).
- f:** 5.01-5.08 (m, 1H).
- g:** 4.34 (c.  $J = 6.8$  Hz, 1H).
- h:** 1.34 (d,  $J = 6.8$  Hz, 3H).

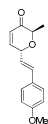


10b,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

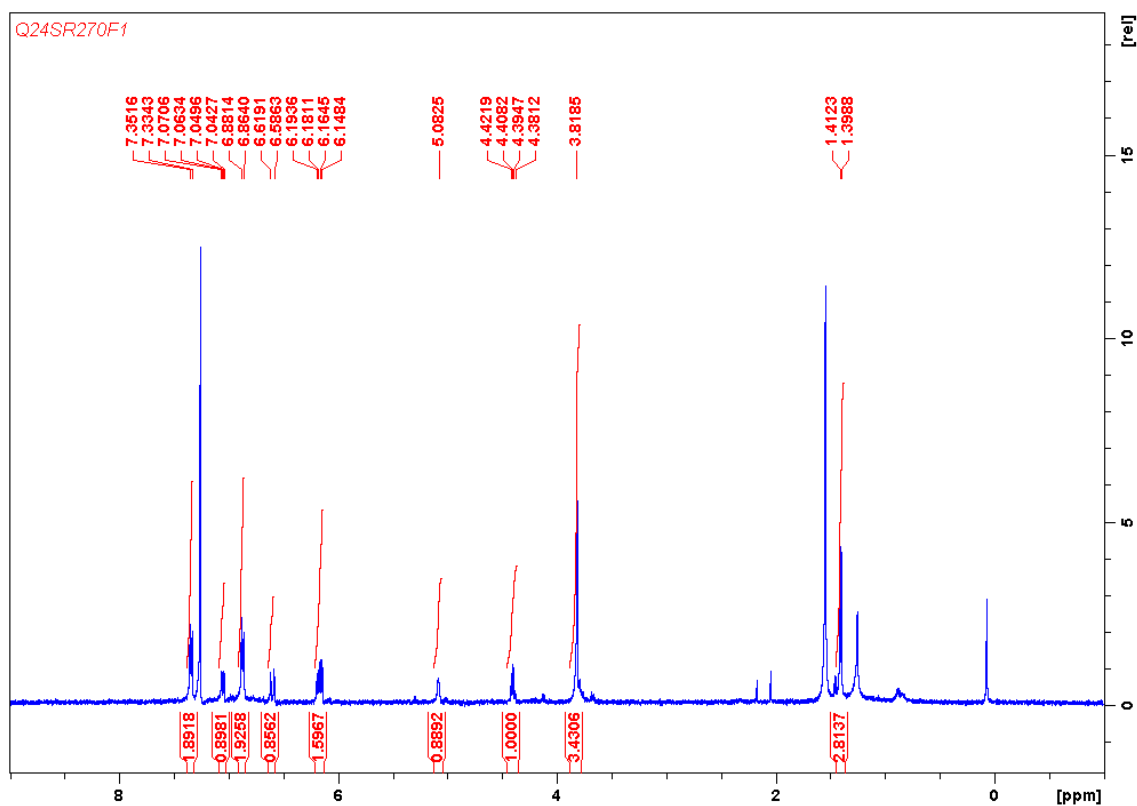


10b,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

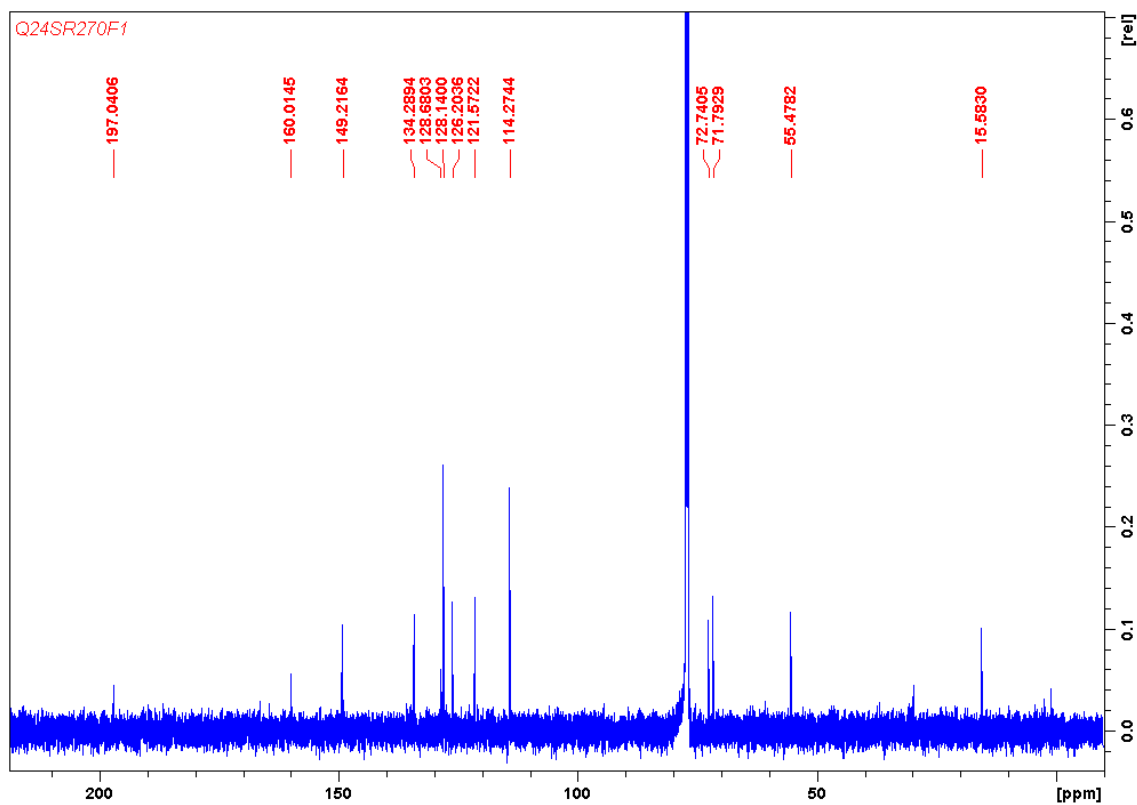


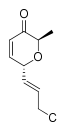


10c,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

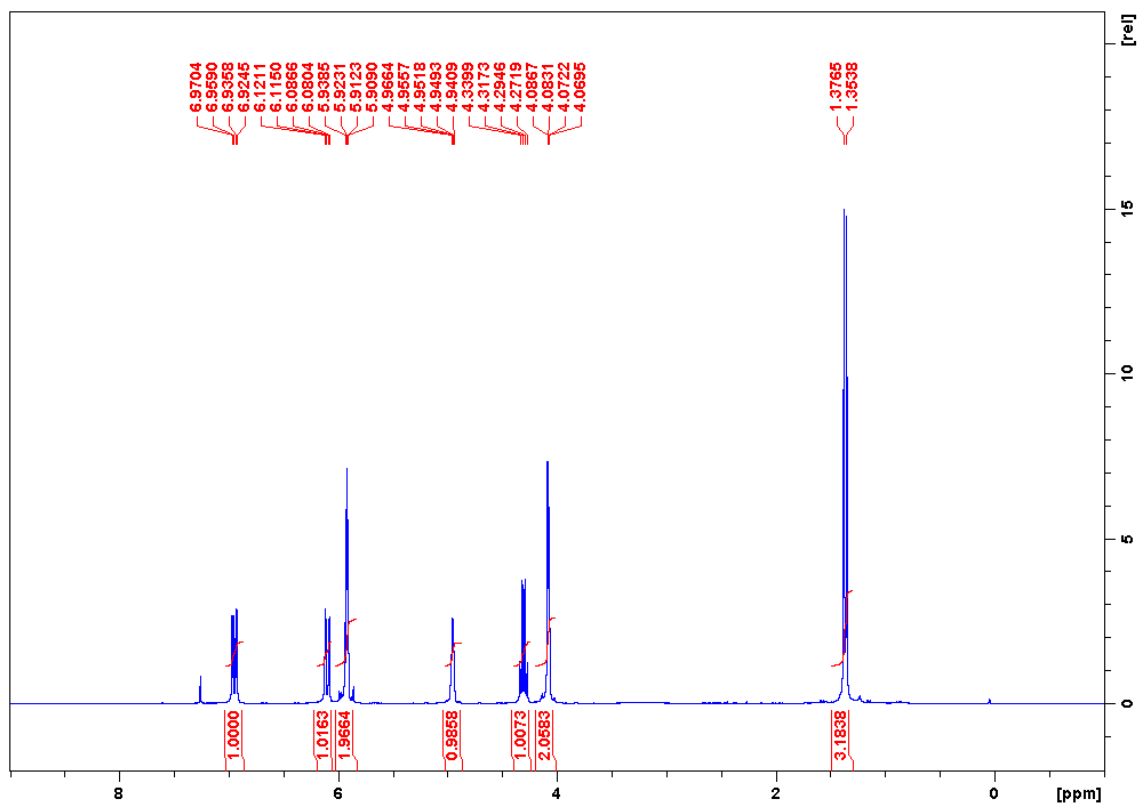


10c,  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

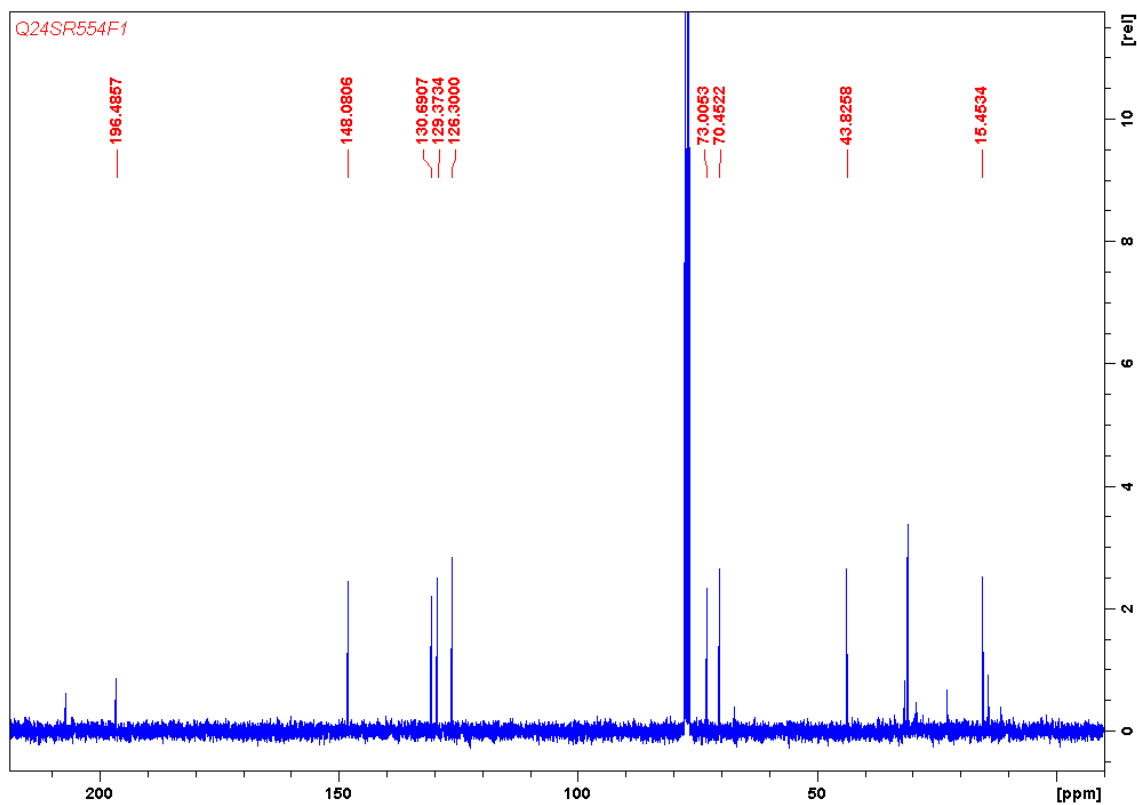


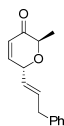


10d,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

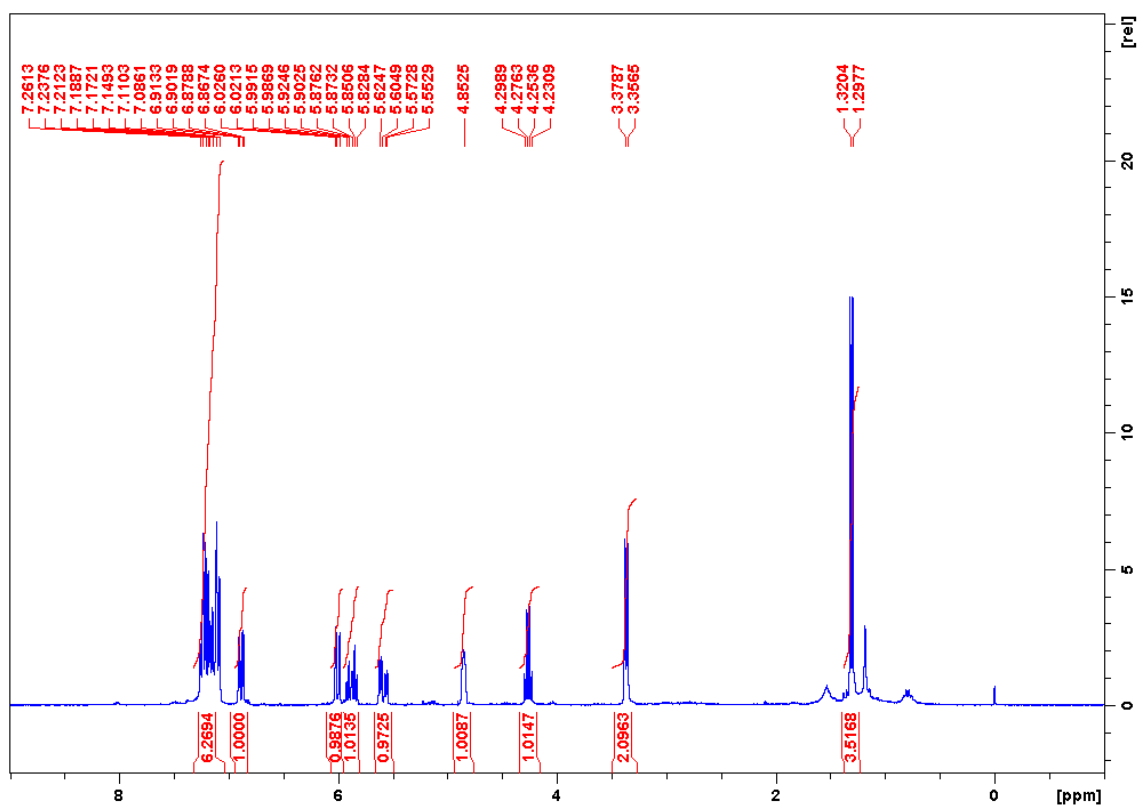


10d,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

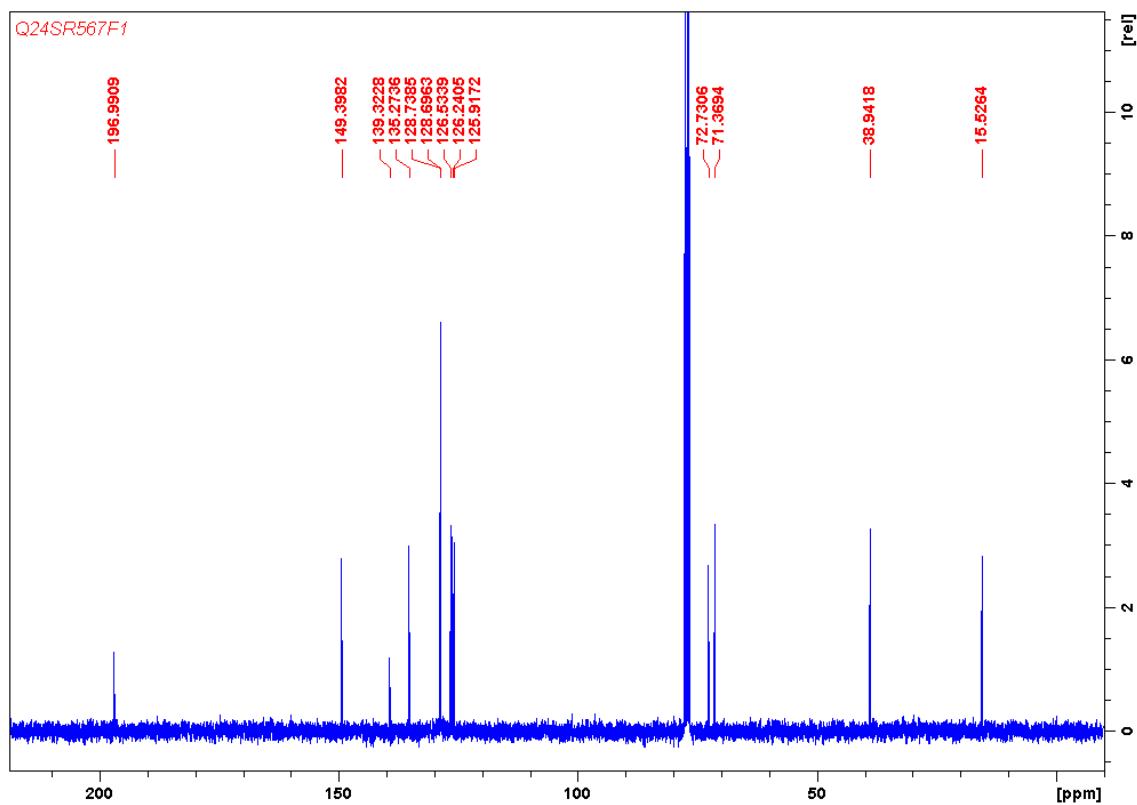


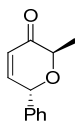


10e,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

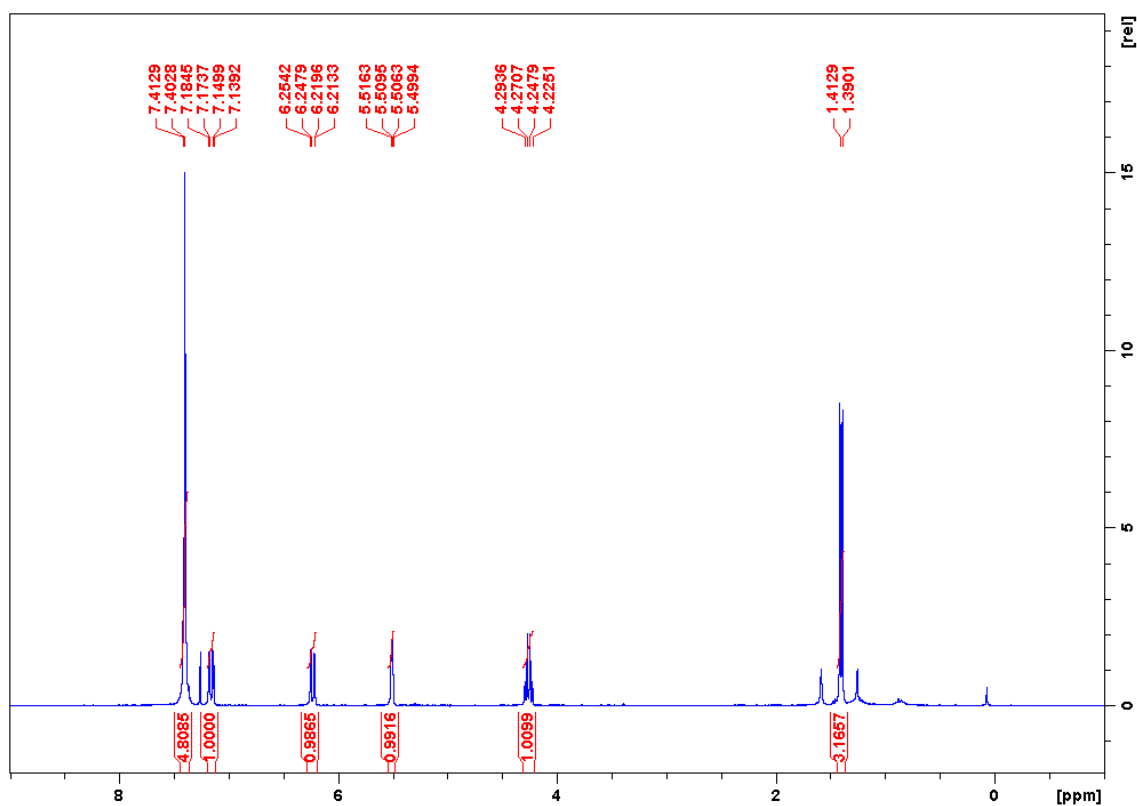


10e,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

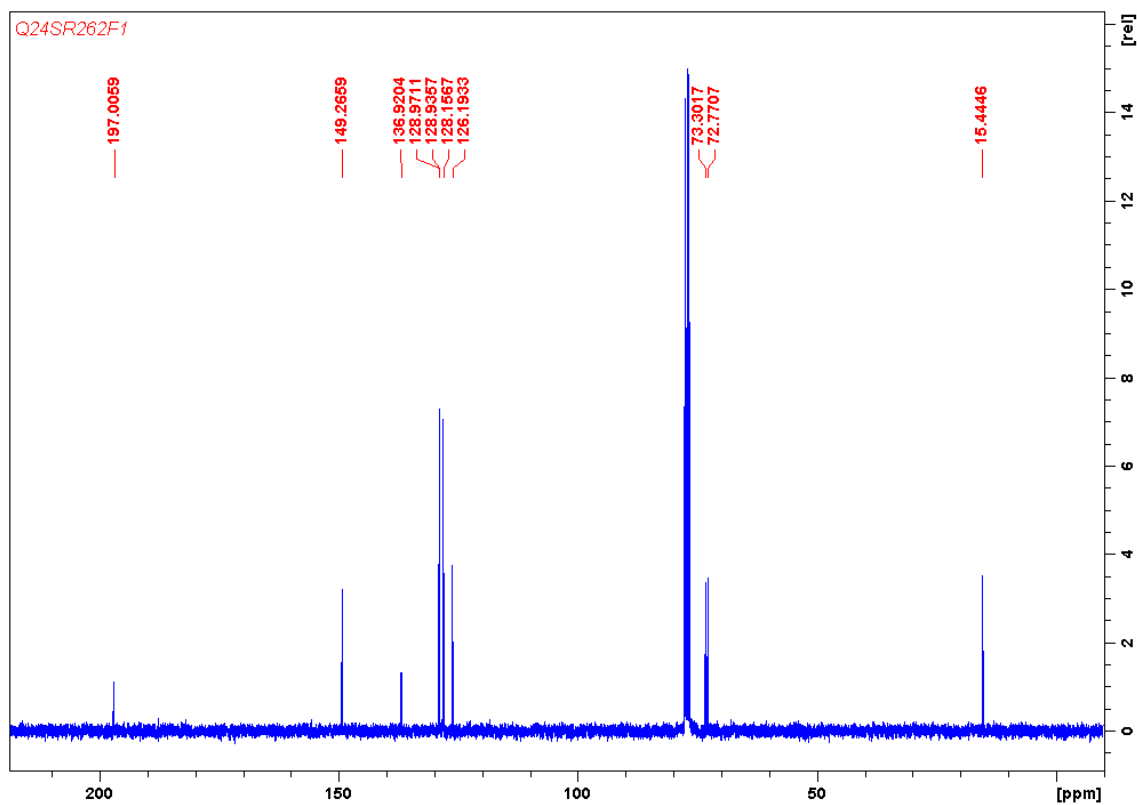




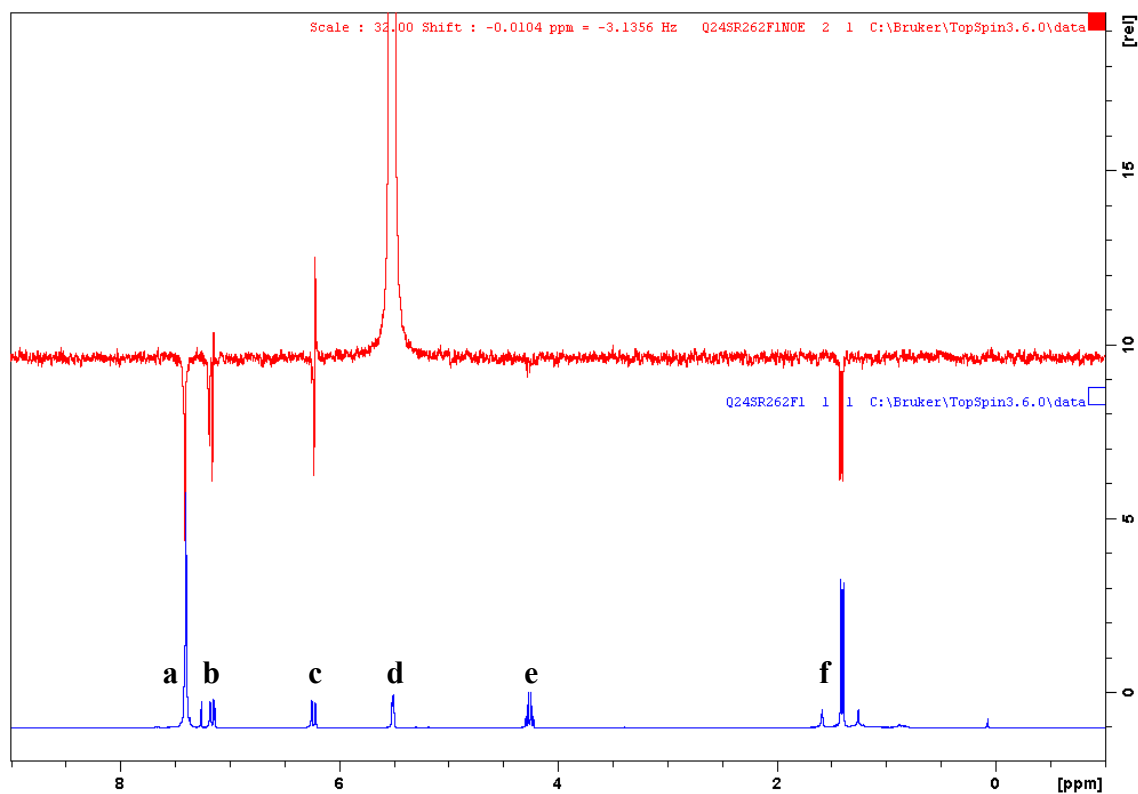
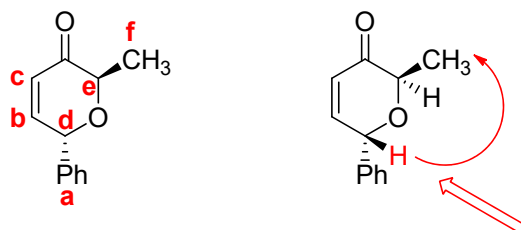
10f,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



10f,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



**10f, NOE (CDCl<sub>3</sub>)**



**a:** 7.37-7.43 (m, 5H).

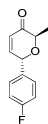
**b:** 7.16 (dd,  $J = 10.4$  Hz,  $J = 3.1$  Hz, 1H).

**c:** 6.23 (dd,  $J = 10.4$  Hz,  $J = 1.9$  Hz, 1H).

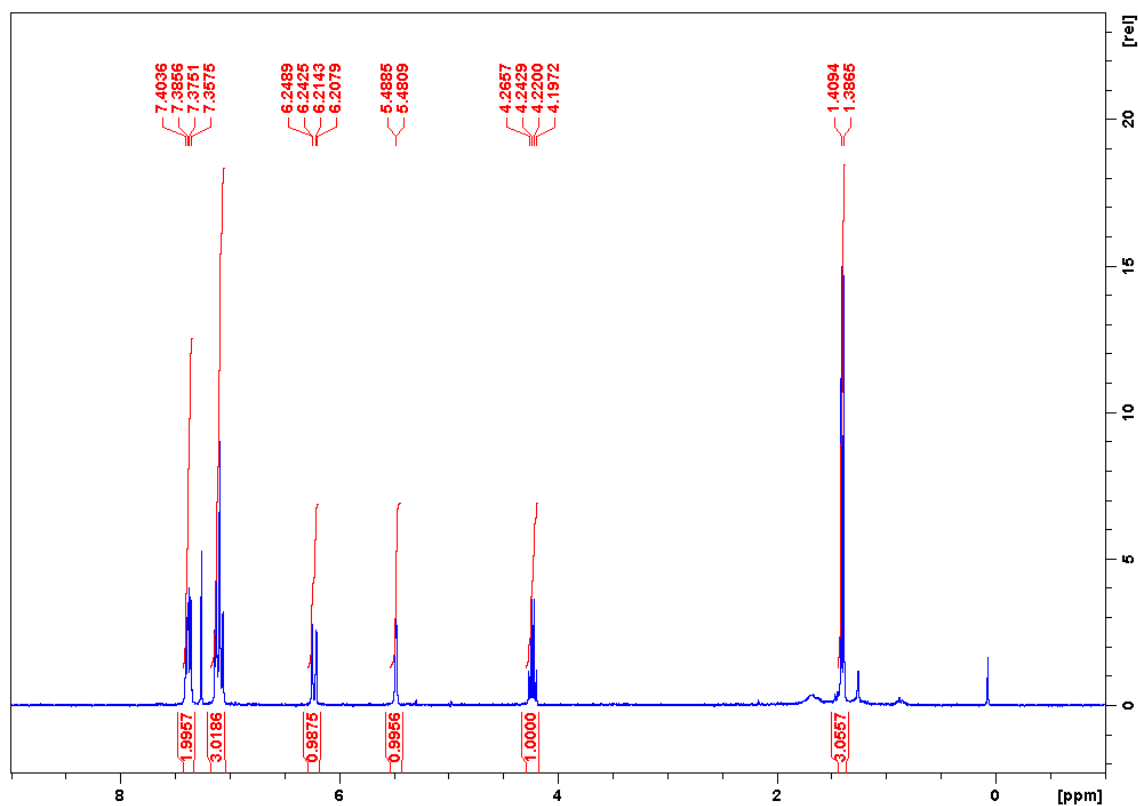
**d:** 5.48-5.54 (m, 1H).

**e:** 4.26 (c,  $J = 6.9$  Hz, 1H).

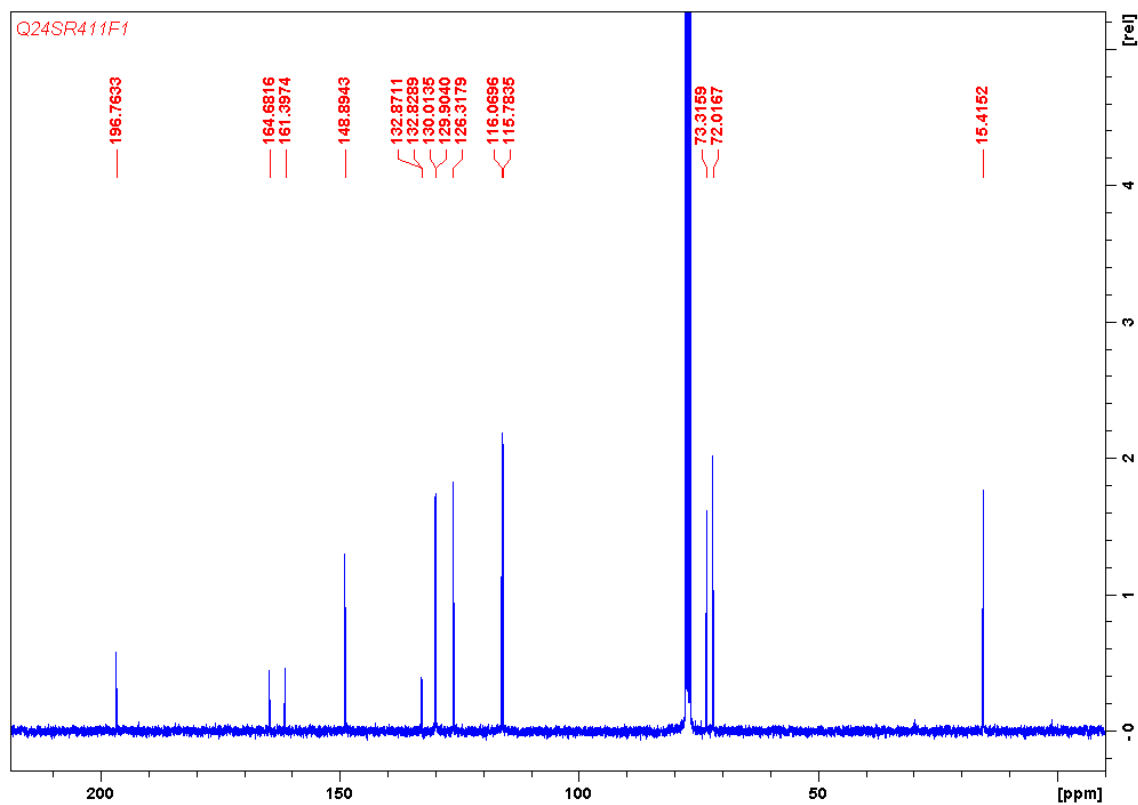
**f:** 1.40 (d,  $J = 6.9$  Hz, 3H).



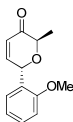
10g,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



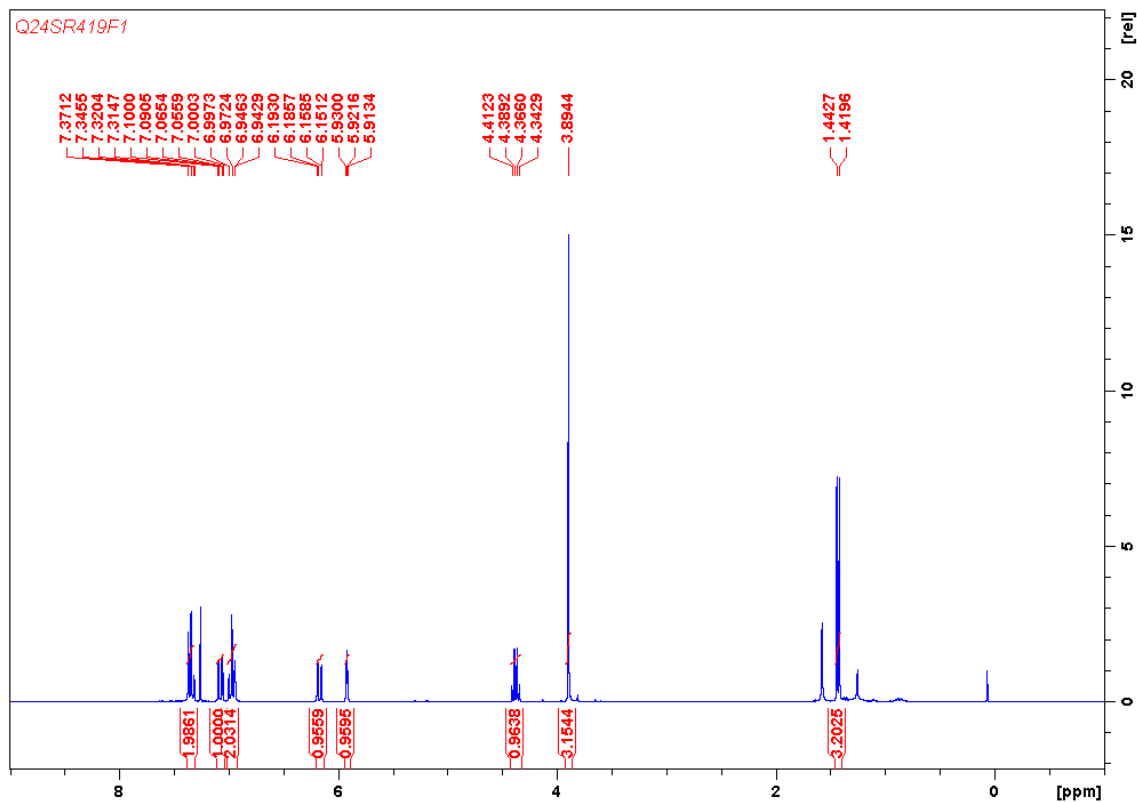
10g,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



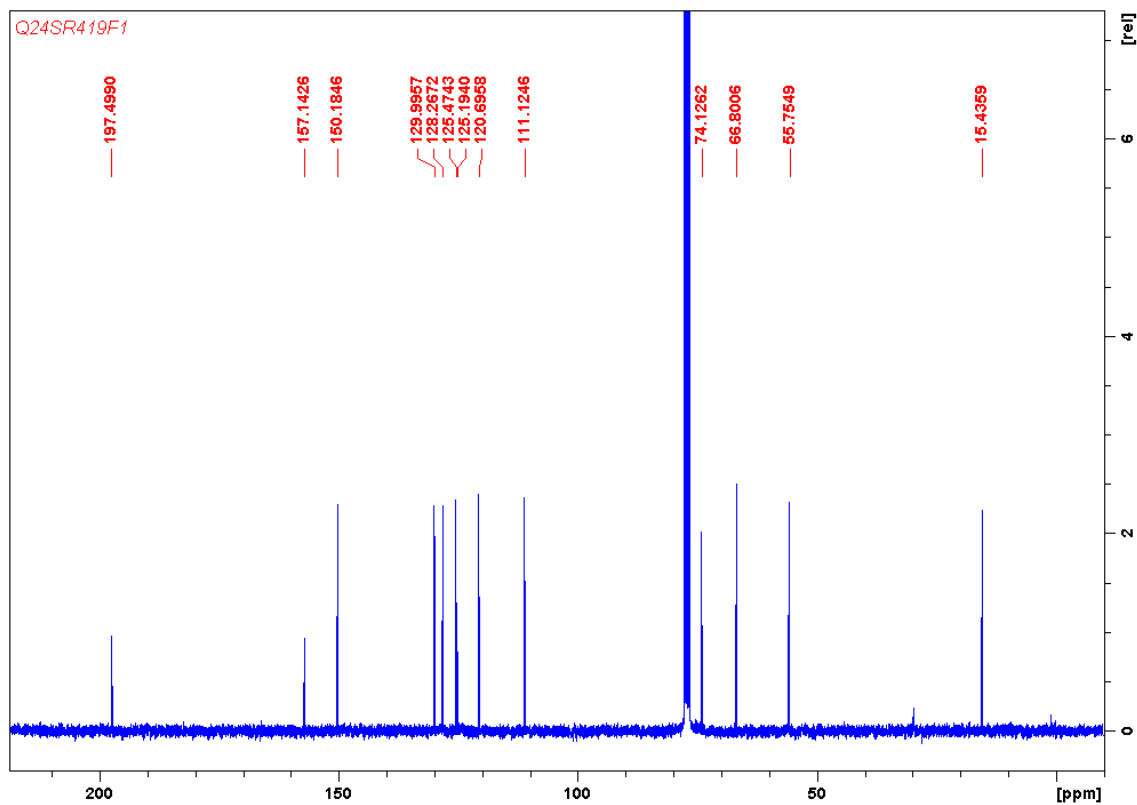


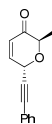


10h,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

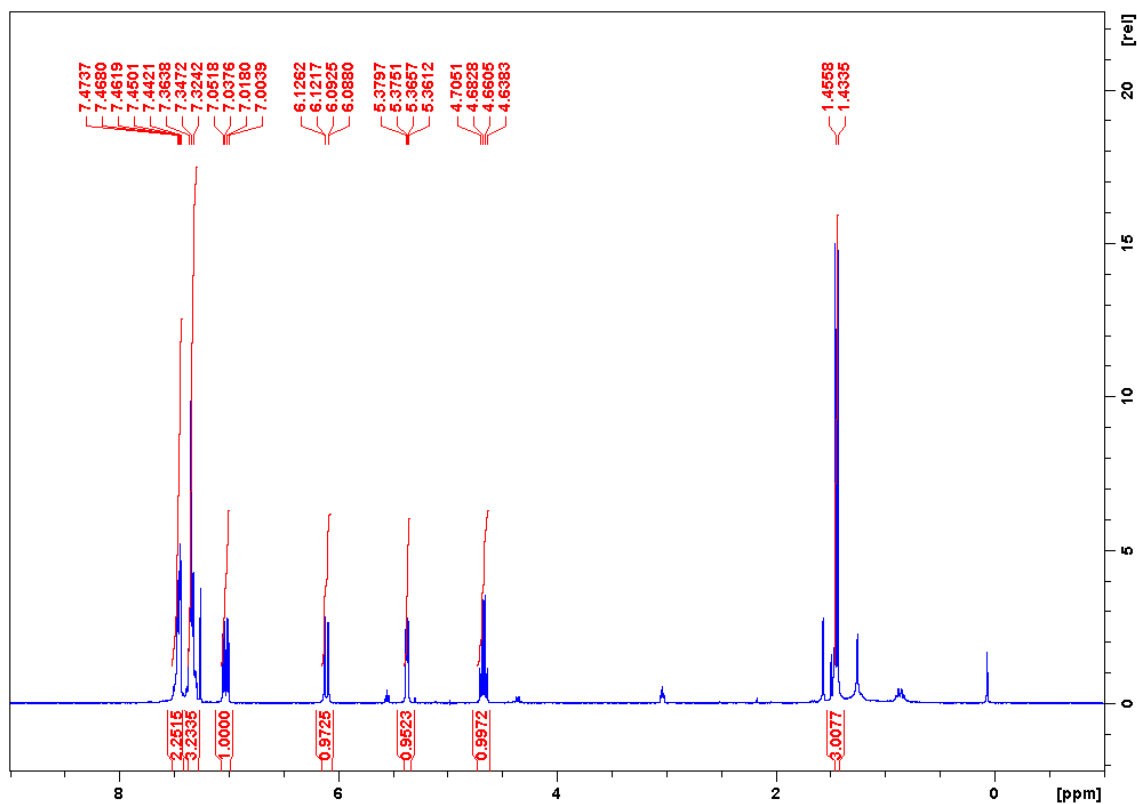


10h,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

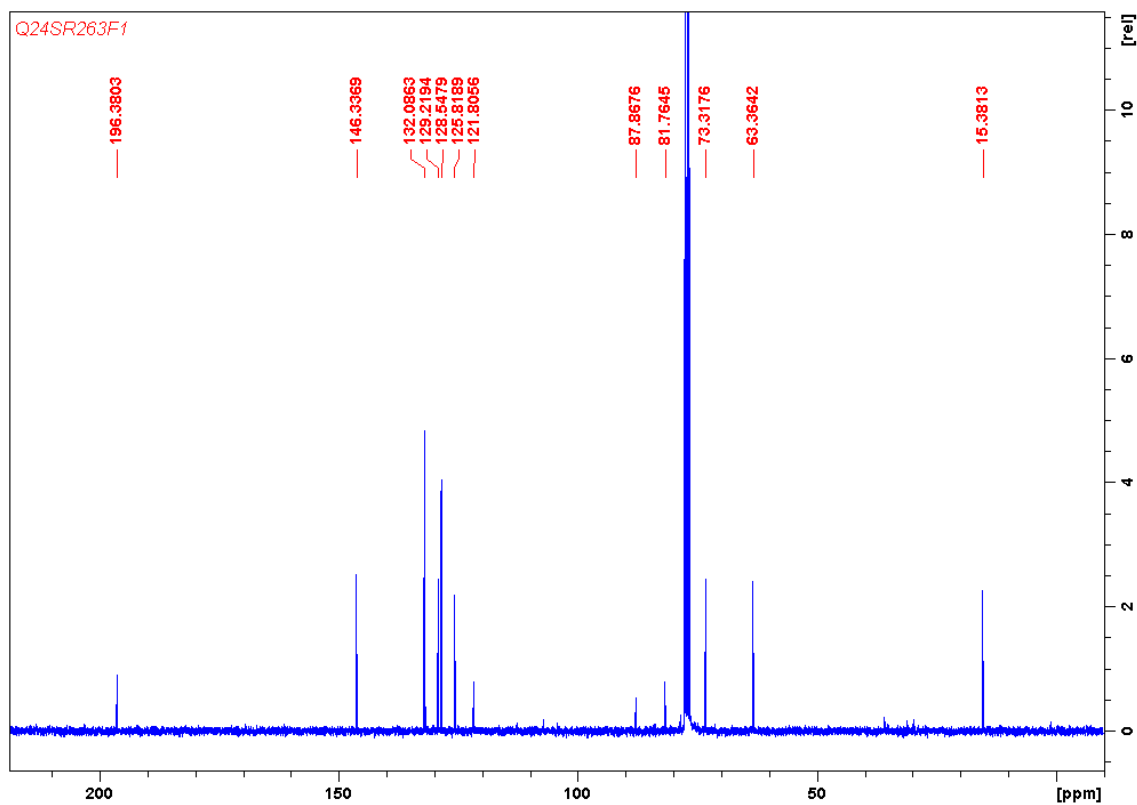




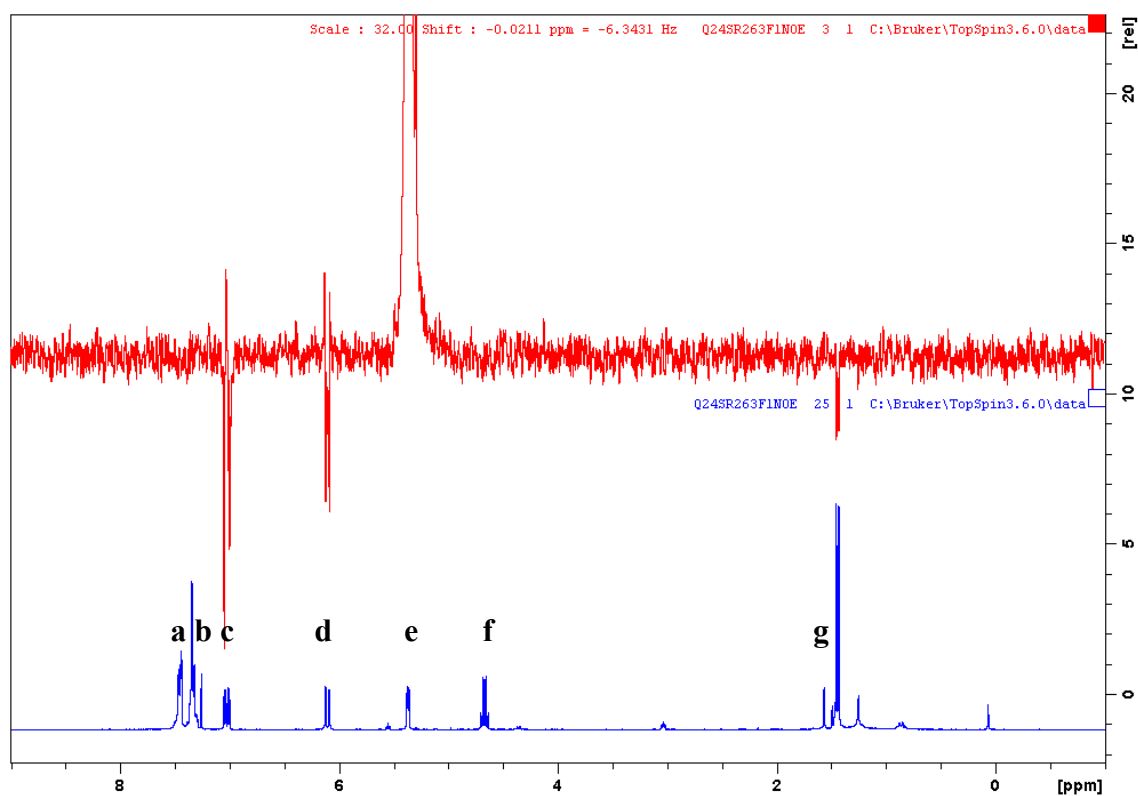
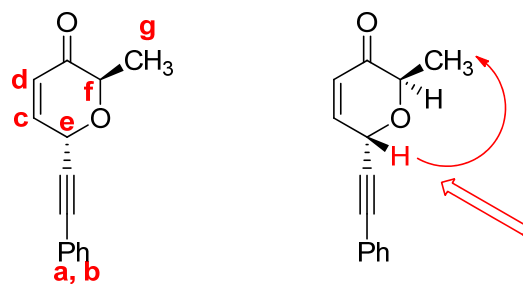
10i,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



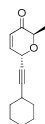
10i,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



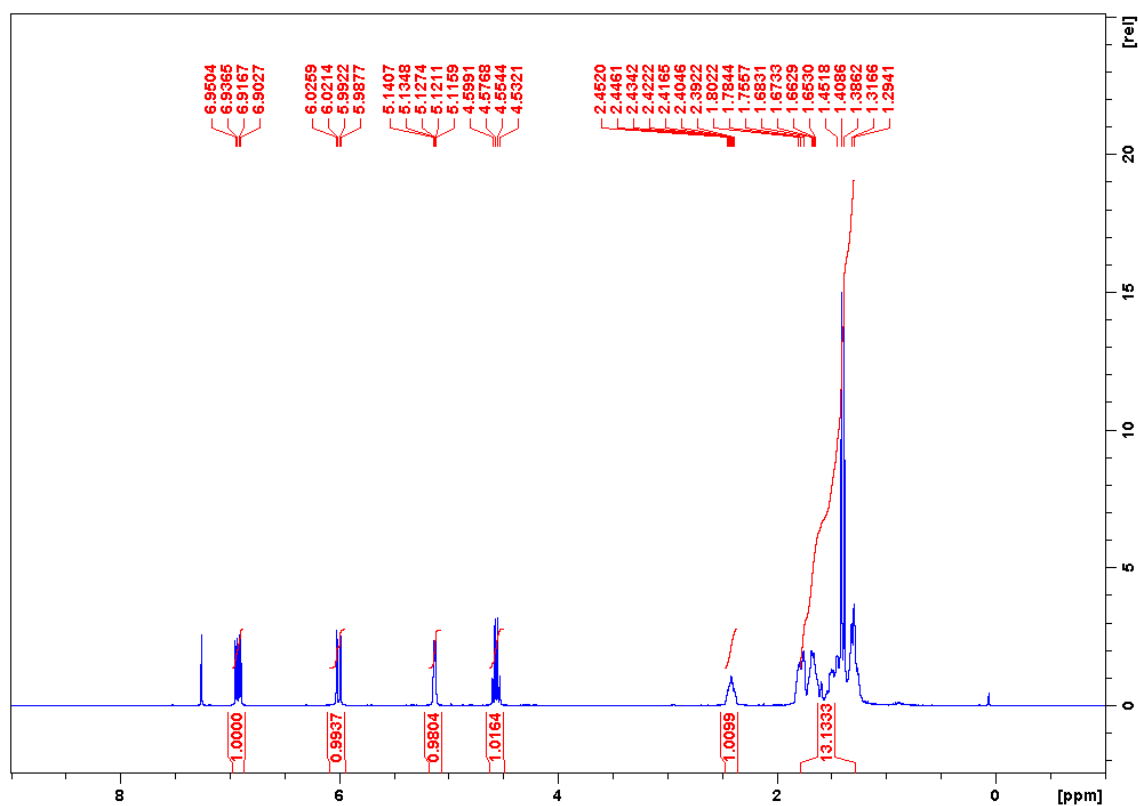
**10i, NOE (CDCl<sub>3</sub>)**



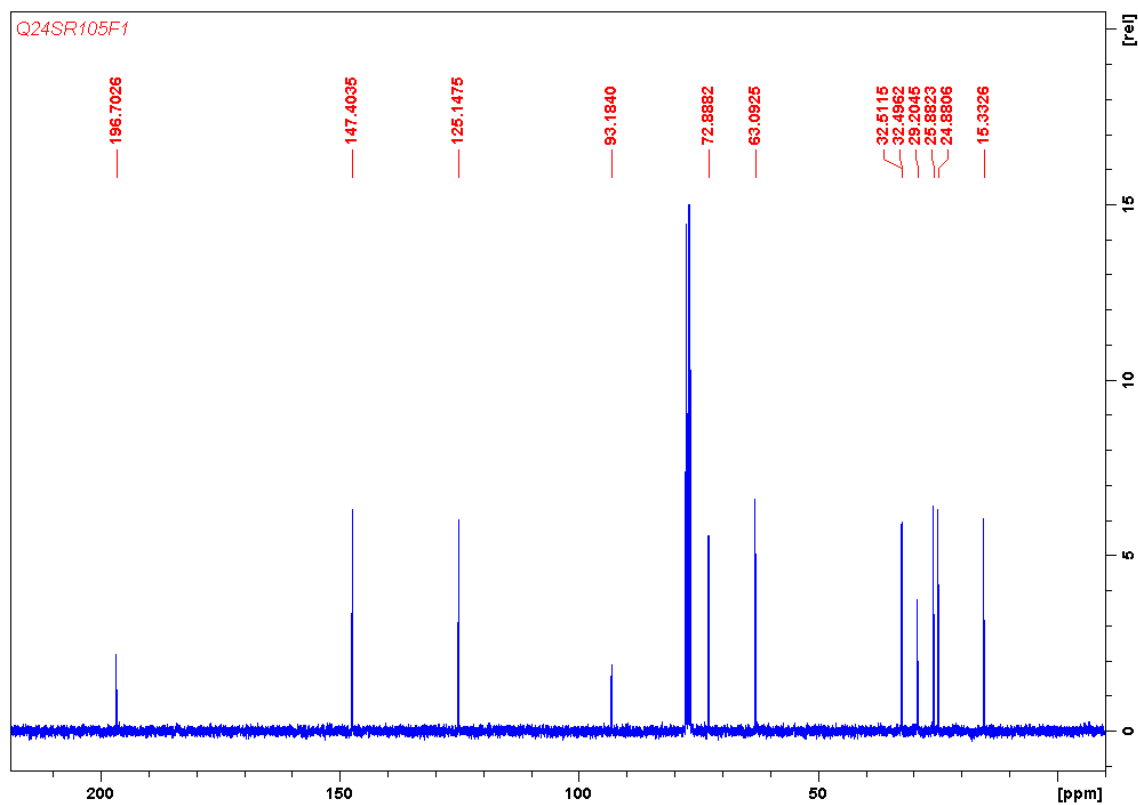
- a:** 7.43-7.50 (m, 2H).
- b:** 7.32-7.38 (m, 3H).
- c:** 7.03 (dd,  $J = 10.2$  Hz,  $J = 4.2$  Hz, 1H).
- d:** 6.11 (dd,  $J = 10.2$  Hz,  $J = 1.5$  Hz, 1H).
- e:** 5.37 (dd,  $J = 4.2$  Hz,  $J = 1.5$  Hz, 1H).
- f:** 4.67 (c.  $J = 6.7$  Hz, 1H).
- g:** 1.44 (d,  $J = 6.7$  Hz, 3H)

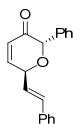


10j,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

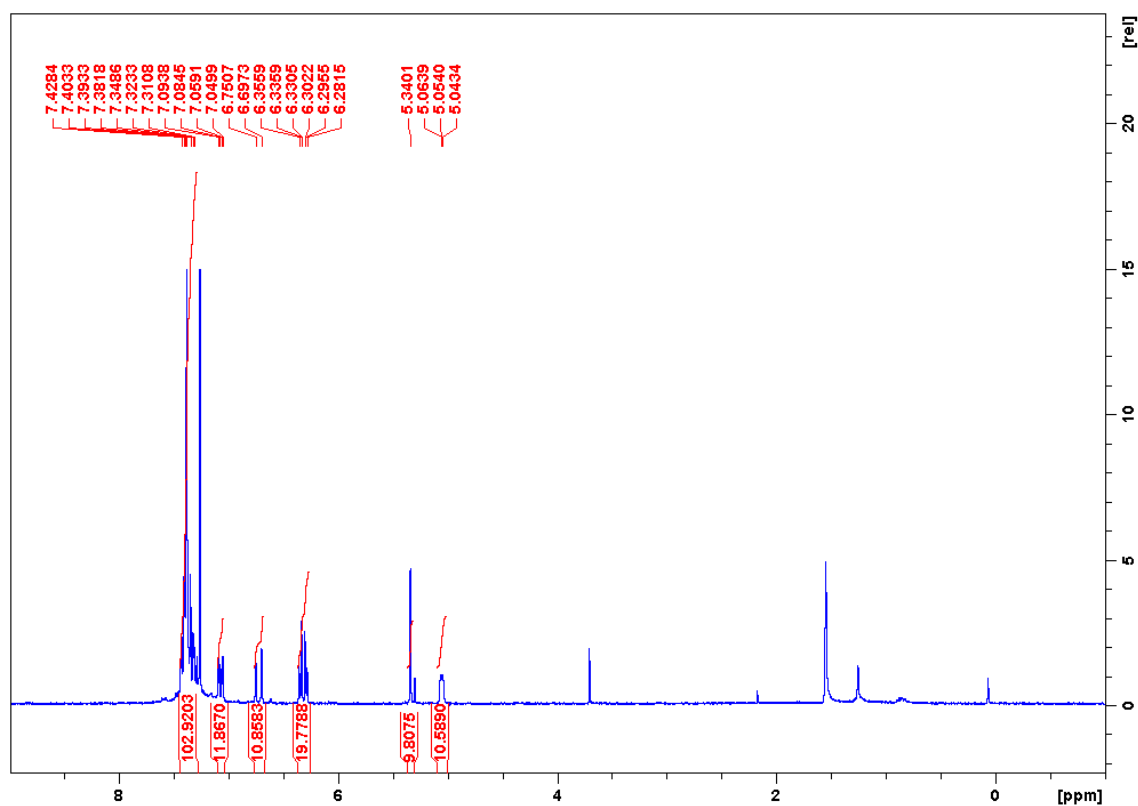


10j,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

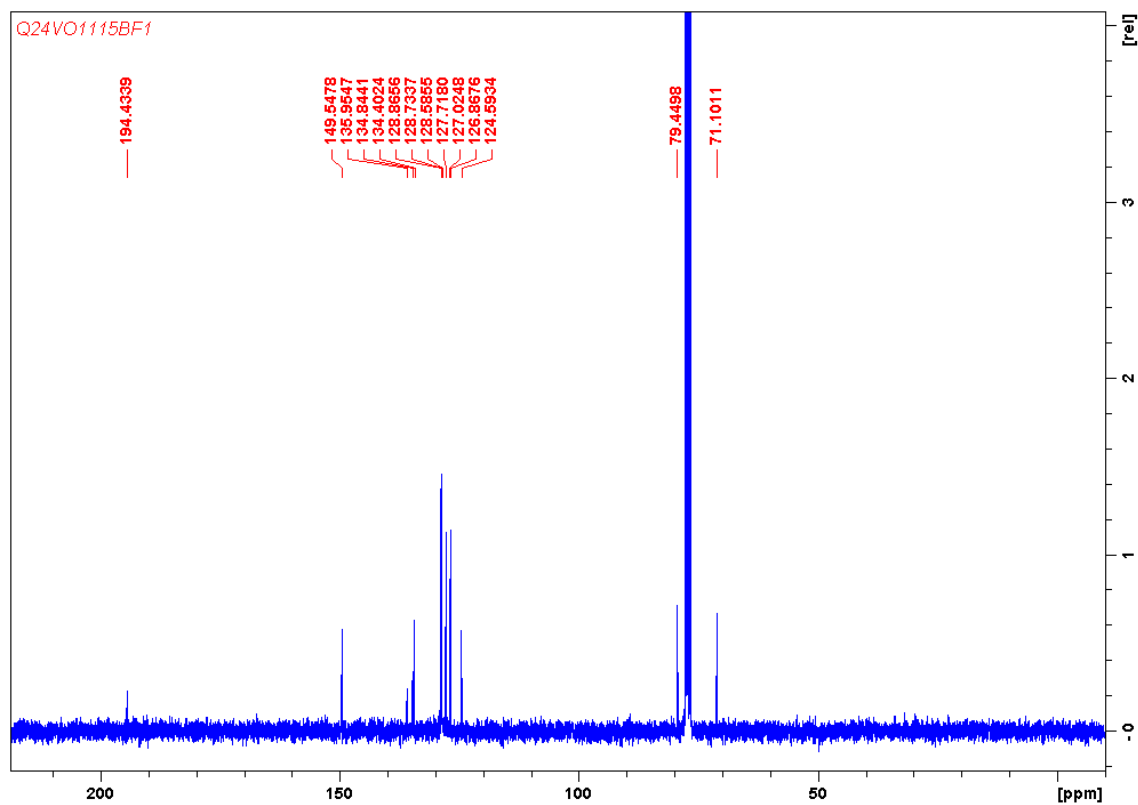


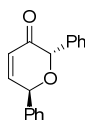


10k,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

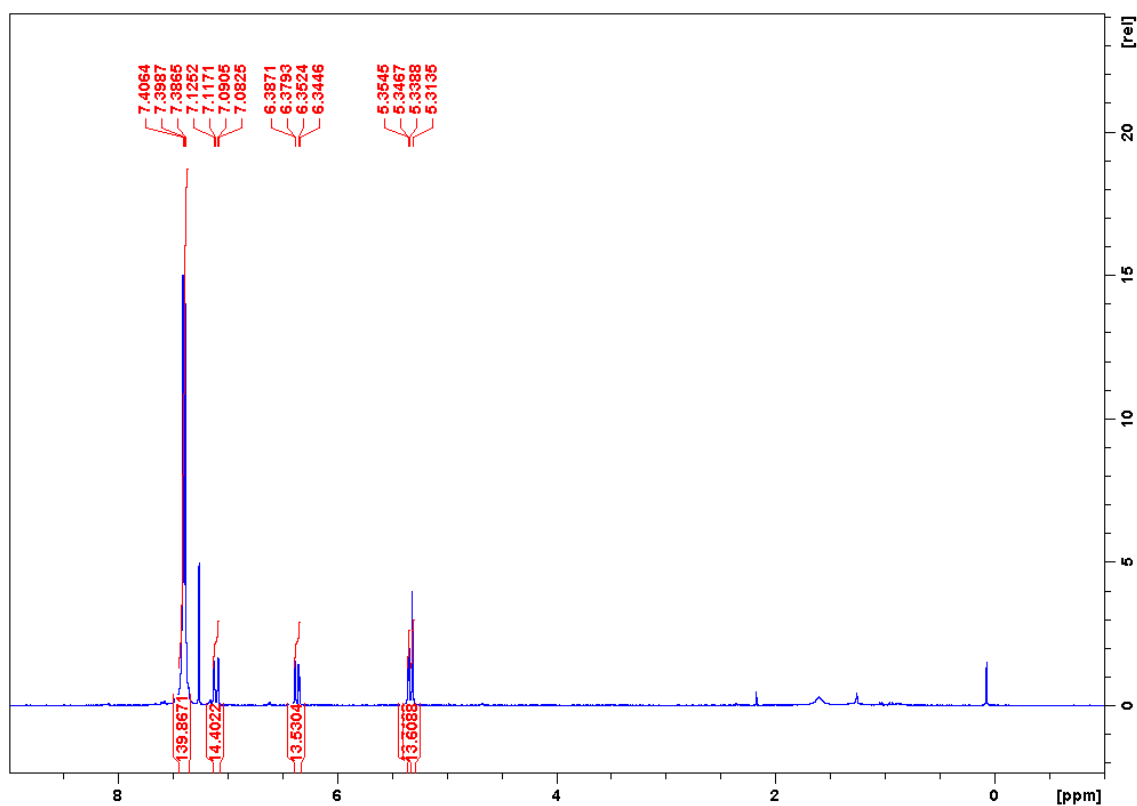


10k,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

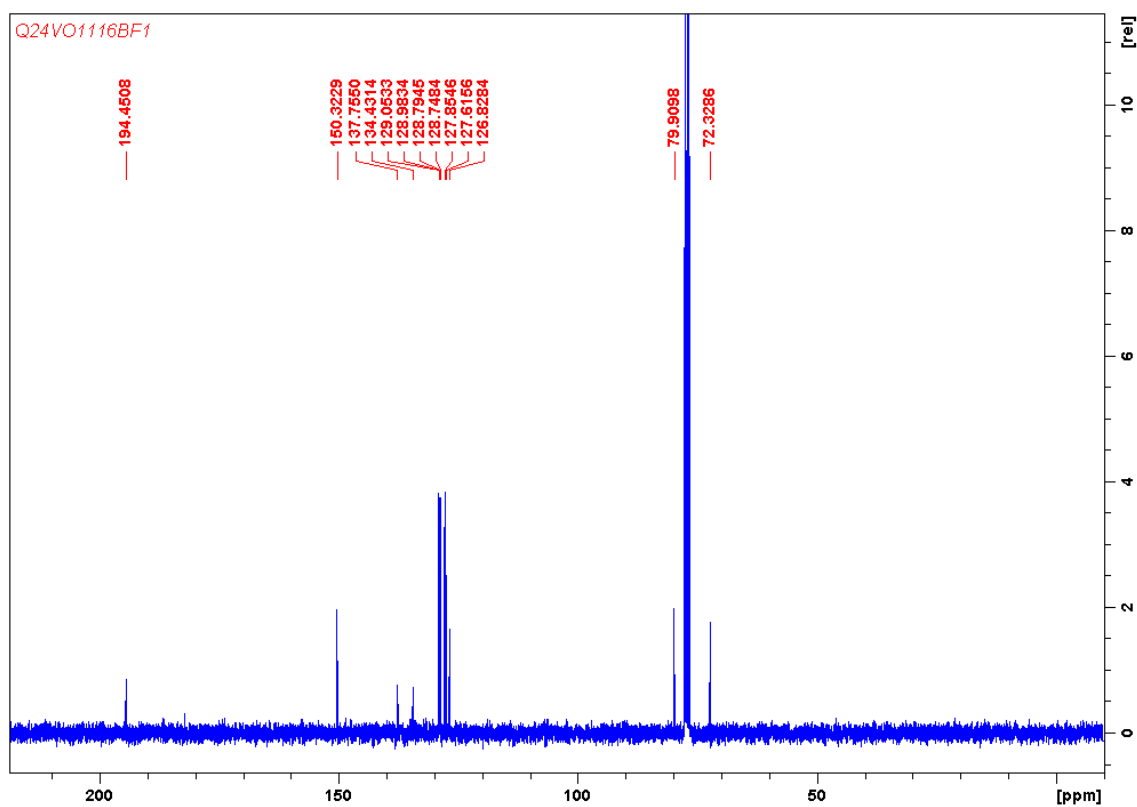


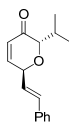


10l,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

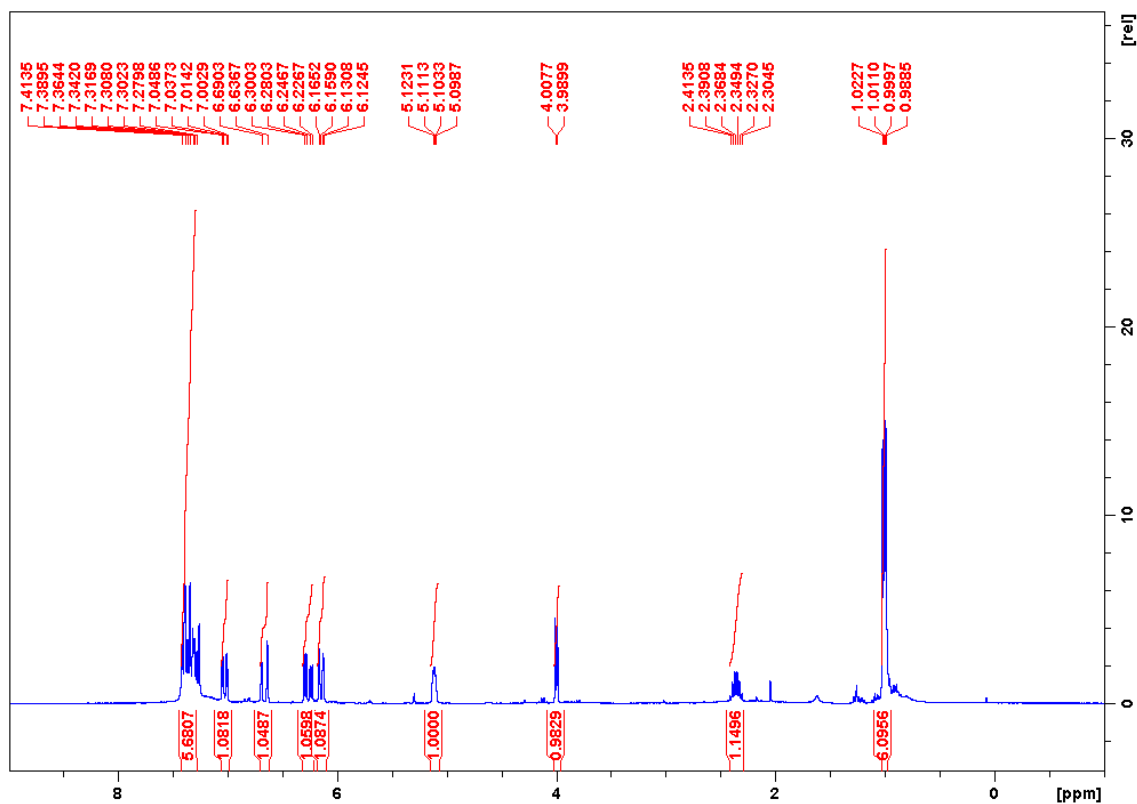


10l,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

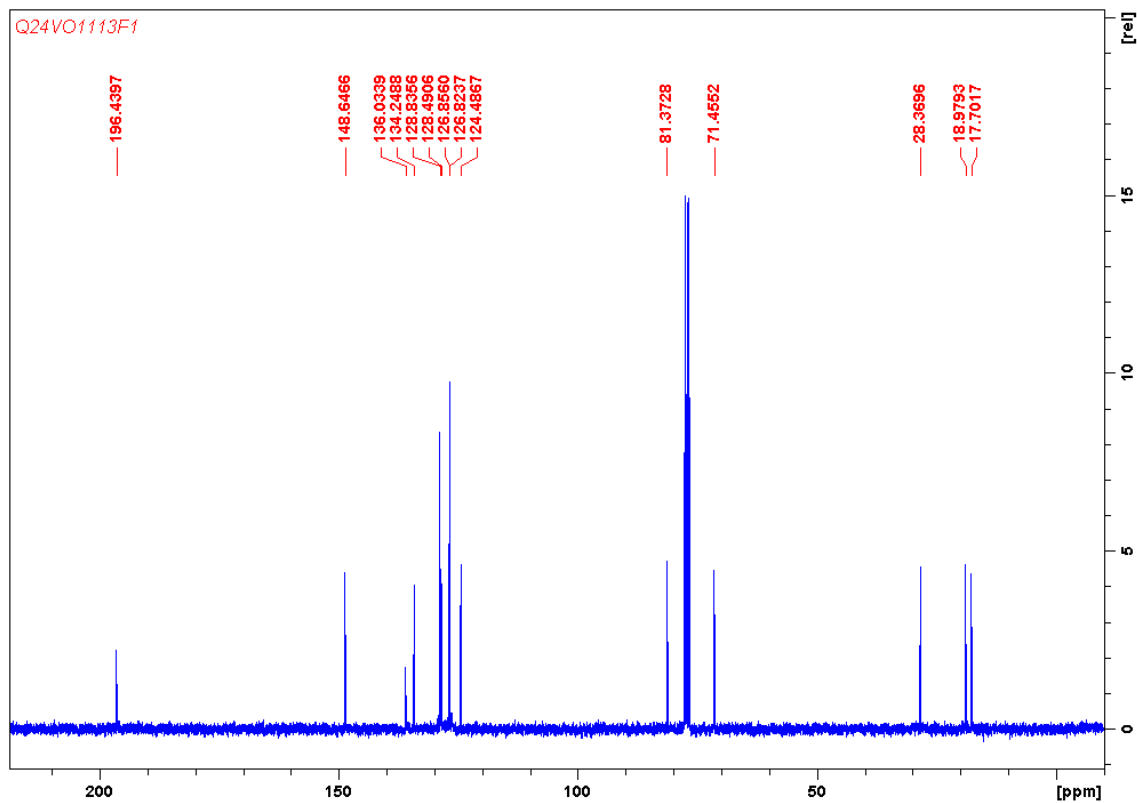


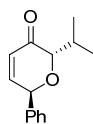


10m,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

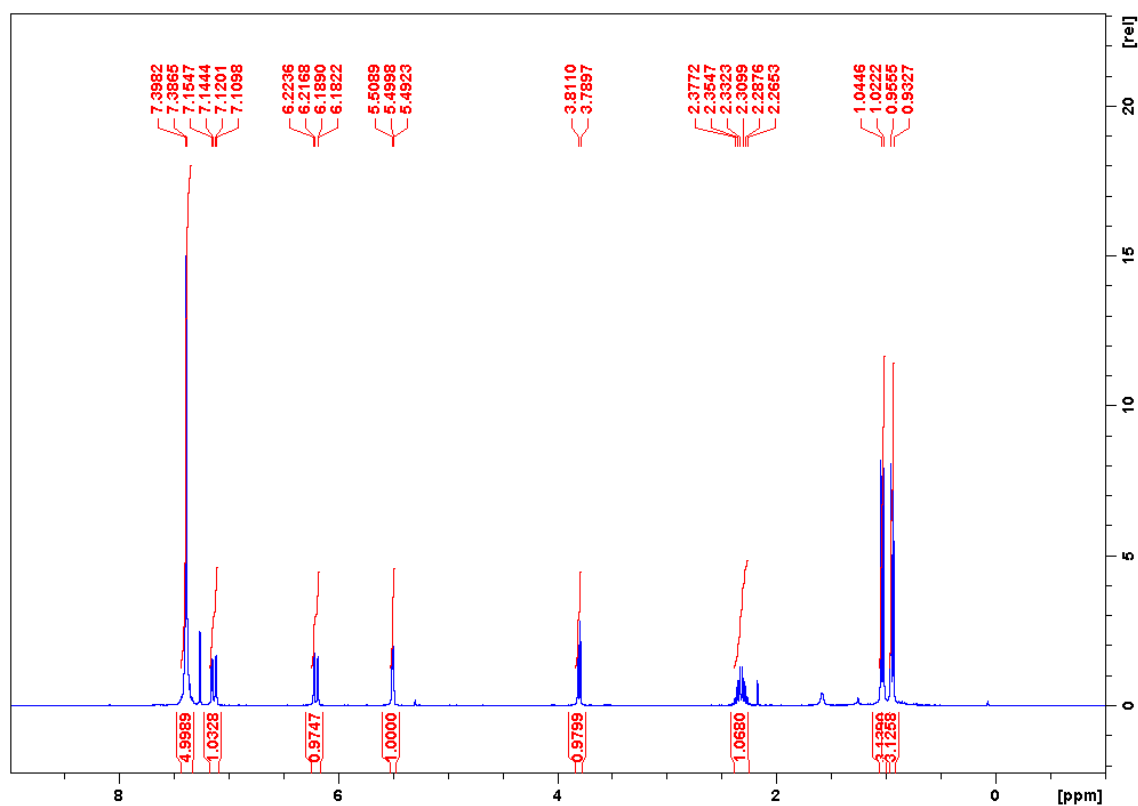


10m,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

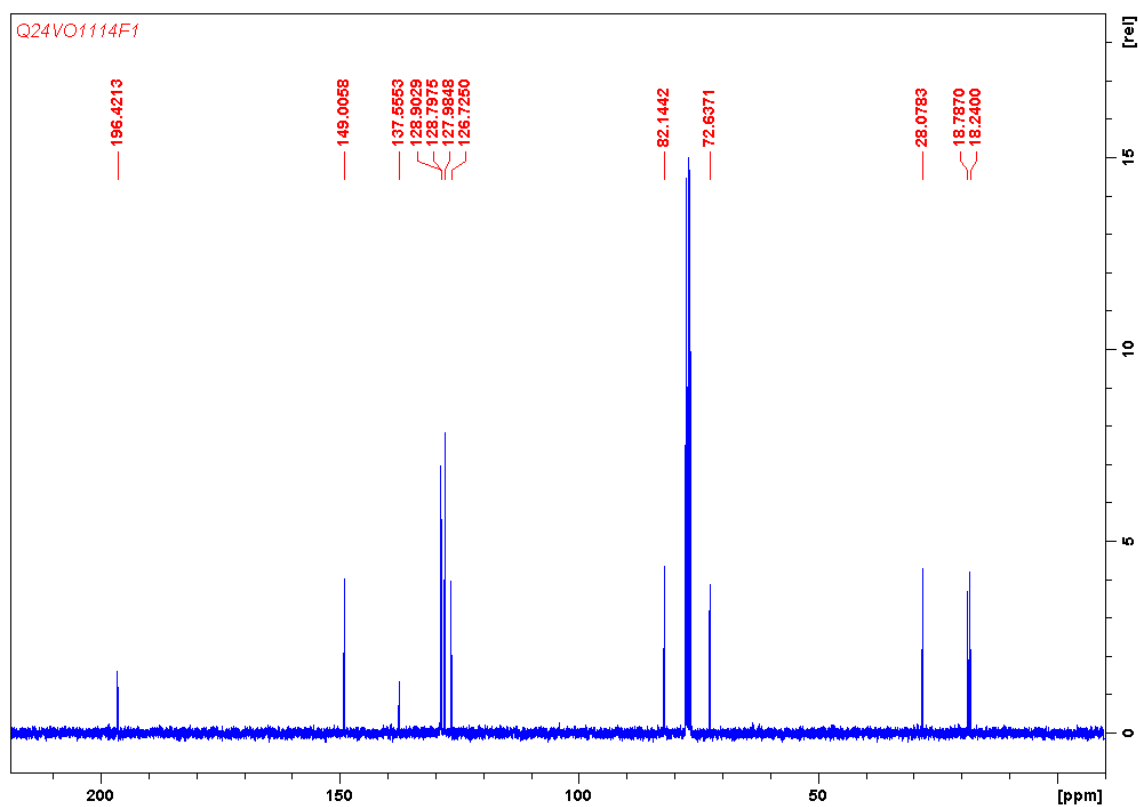




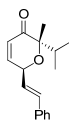
10n,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



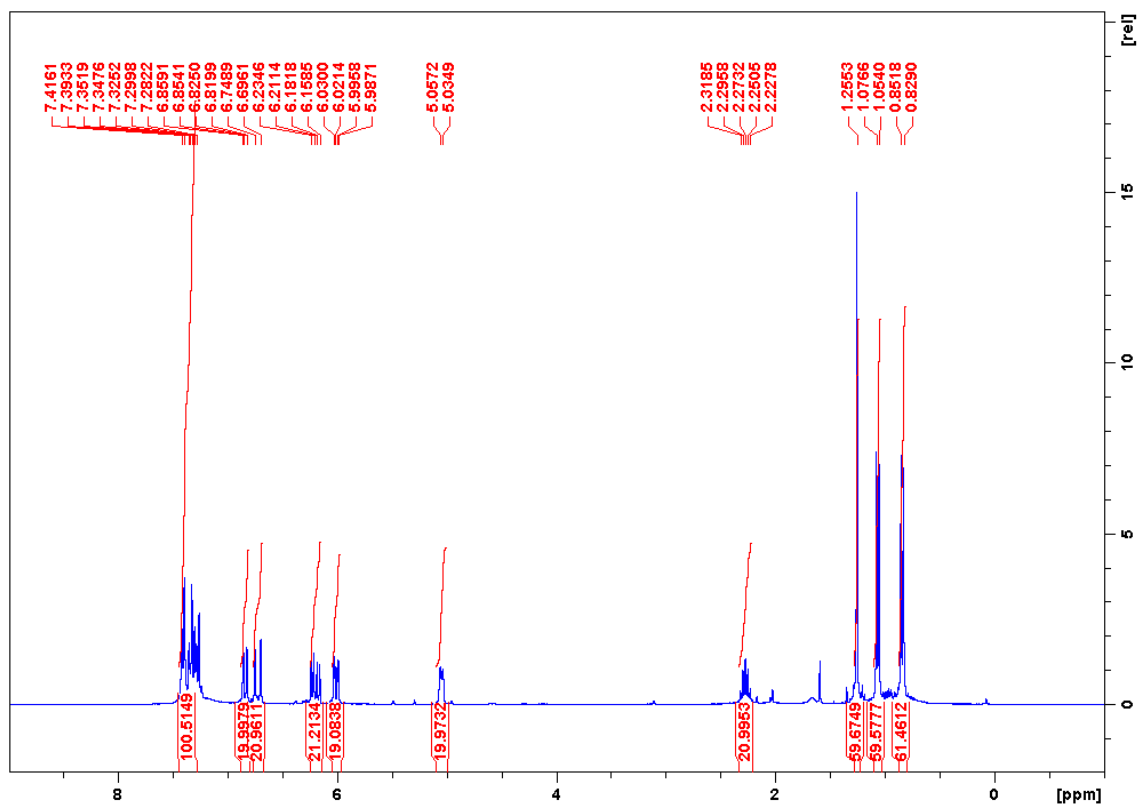
10n,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



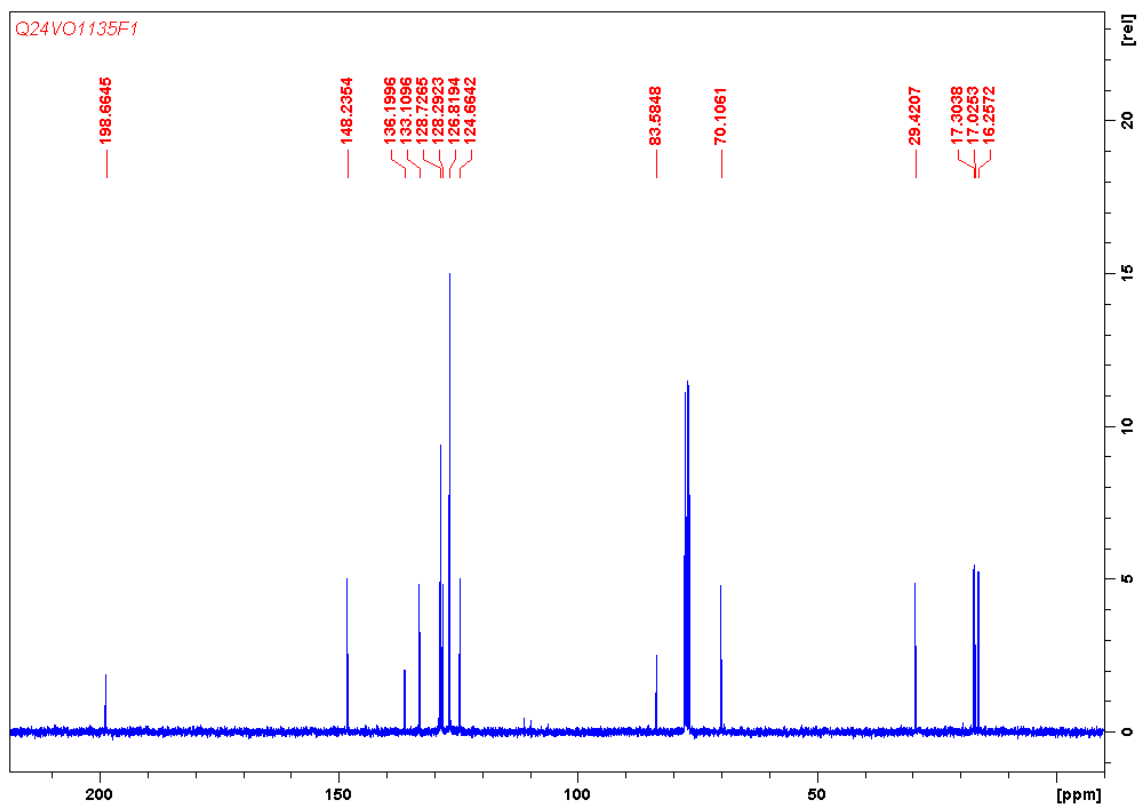


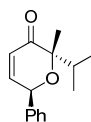


10o,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

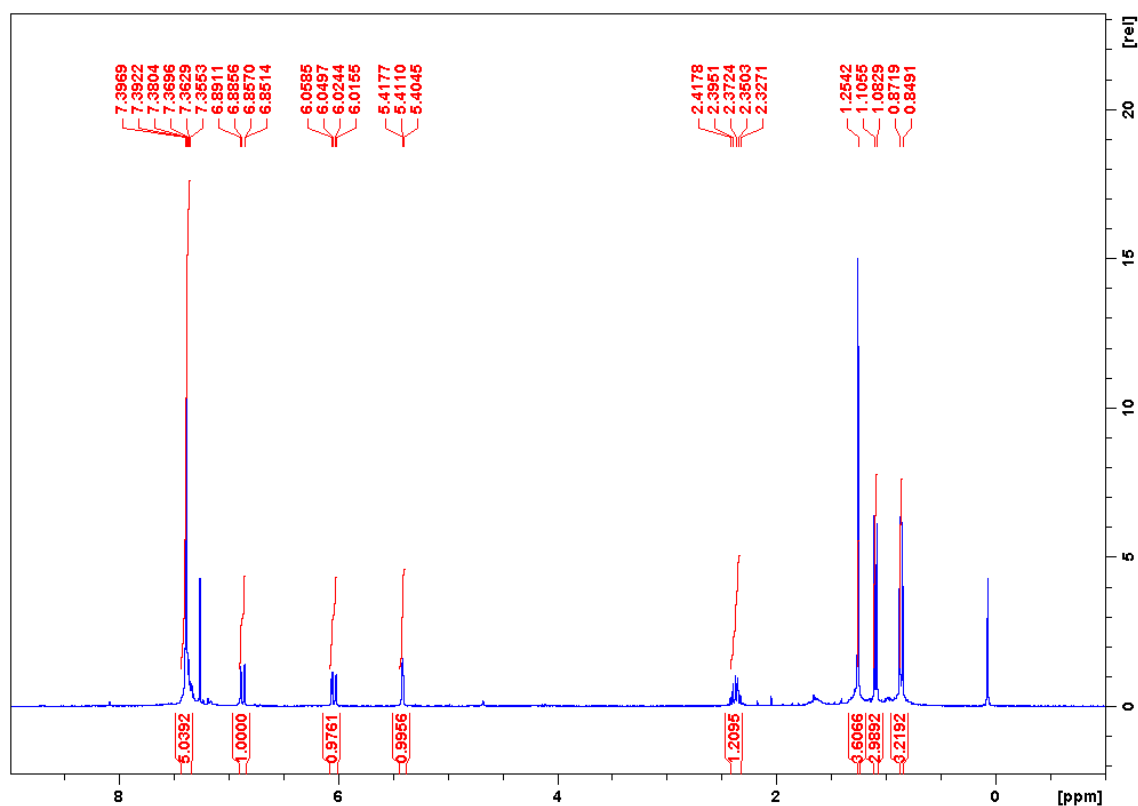


10o,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

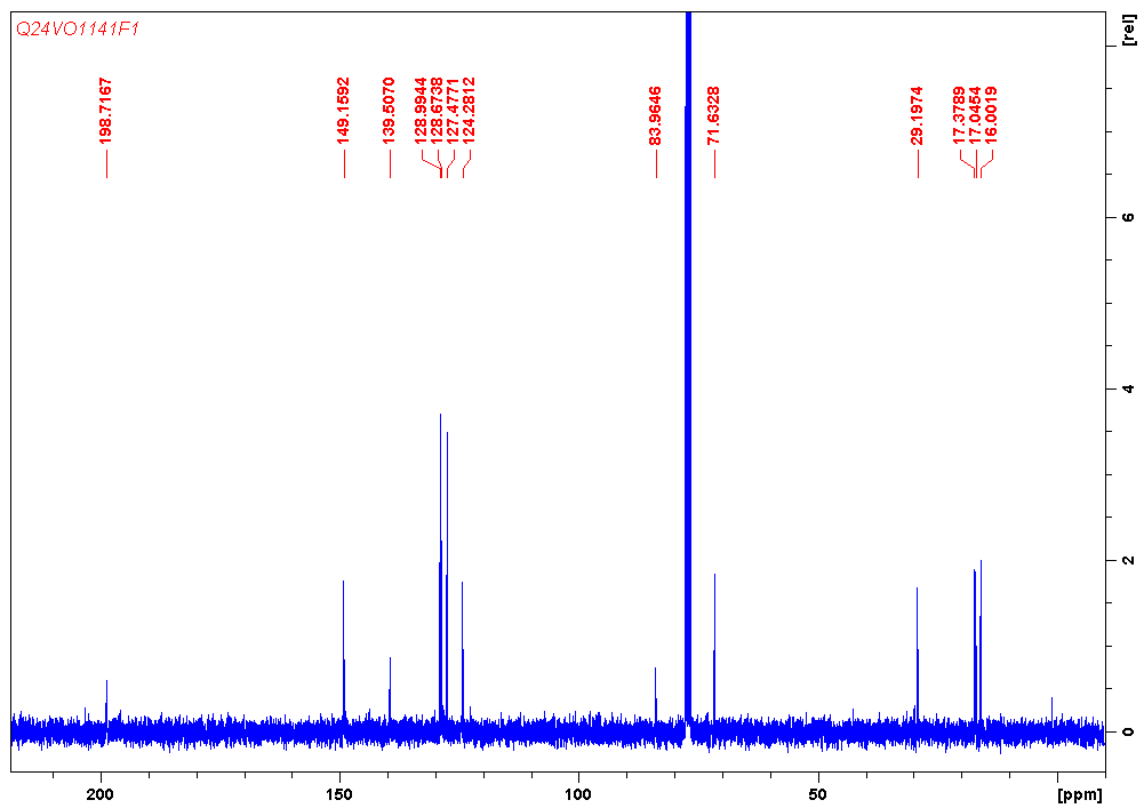




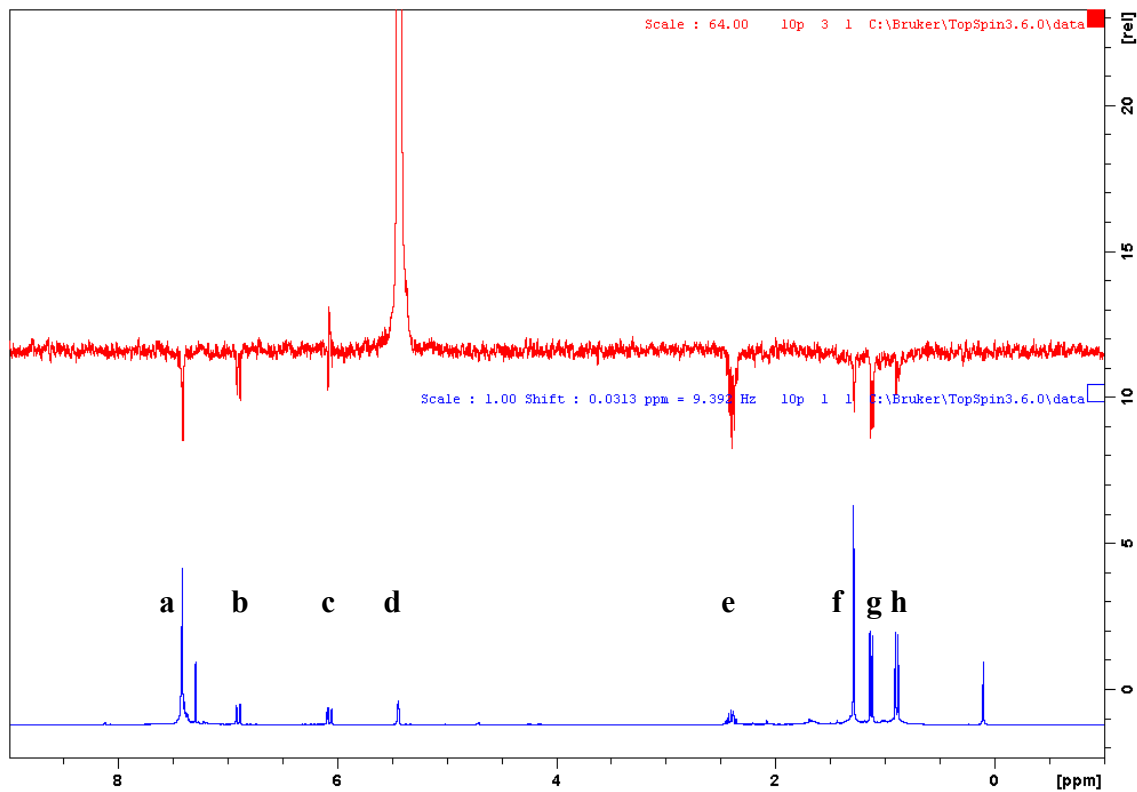
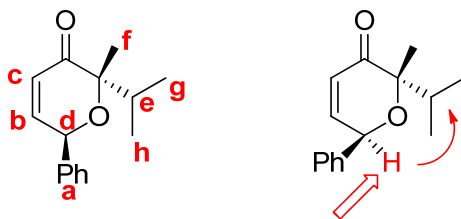
10p,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



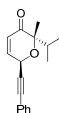
10p,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



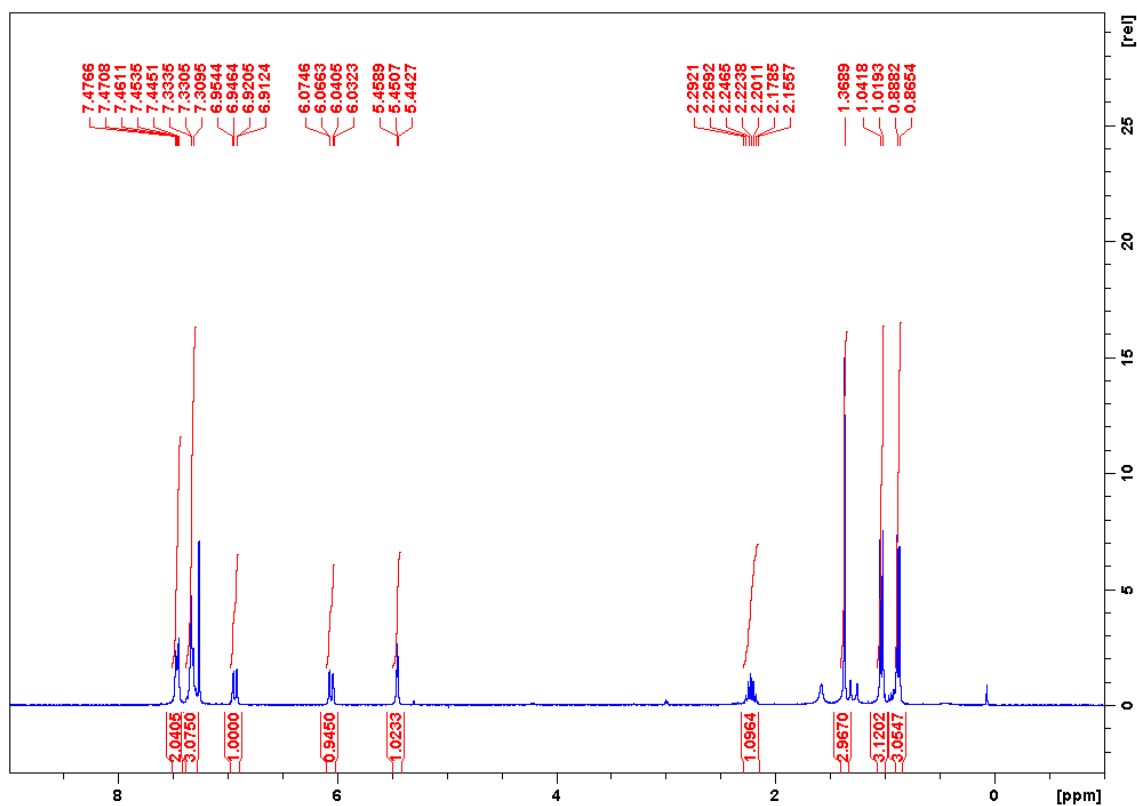
**Compound 10p, NOE (300 MHz, CDCl<sub>3</sub>)**



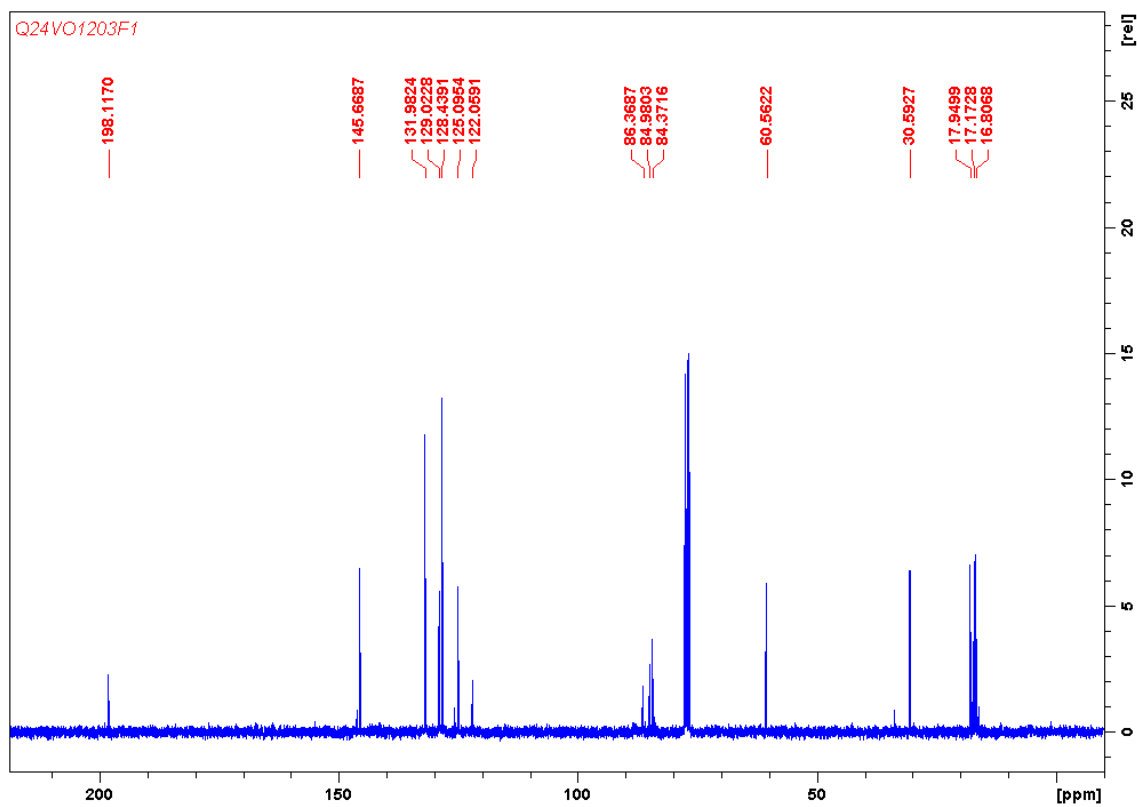
- a:** 7.40-7.36 (m, 5H).  
**b:** 6.87 (dd,  $J = 10.3$  Hz,  $J = 1.7$  Hz, 1H).  
**c:** 6.04 (dd,  $J = 10.3$  Hz,  $J = 2.6$  Hz, 1H).  
**d:** 5.40-5.42 (m, 1H).  
**e:** 2.42-2.32 (m, 1H).  
**f:** 1.25 (s, 3H).  
**g:** 1.09 (d,  $J = 6.8$  Hz, 3H).  
**h:** 0.86 (d,  $J = 6.8$  Hz, 3H).

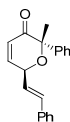


10q,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

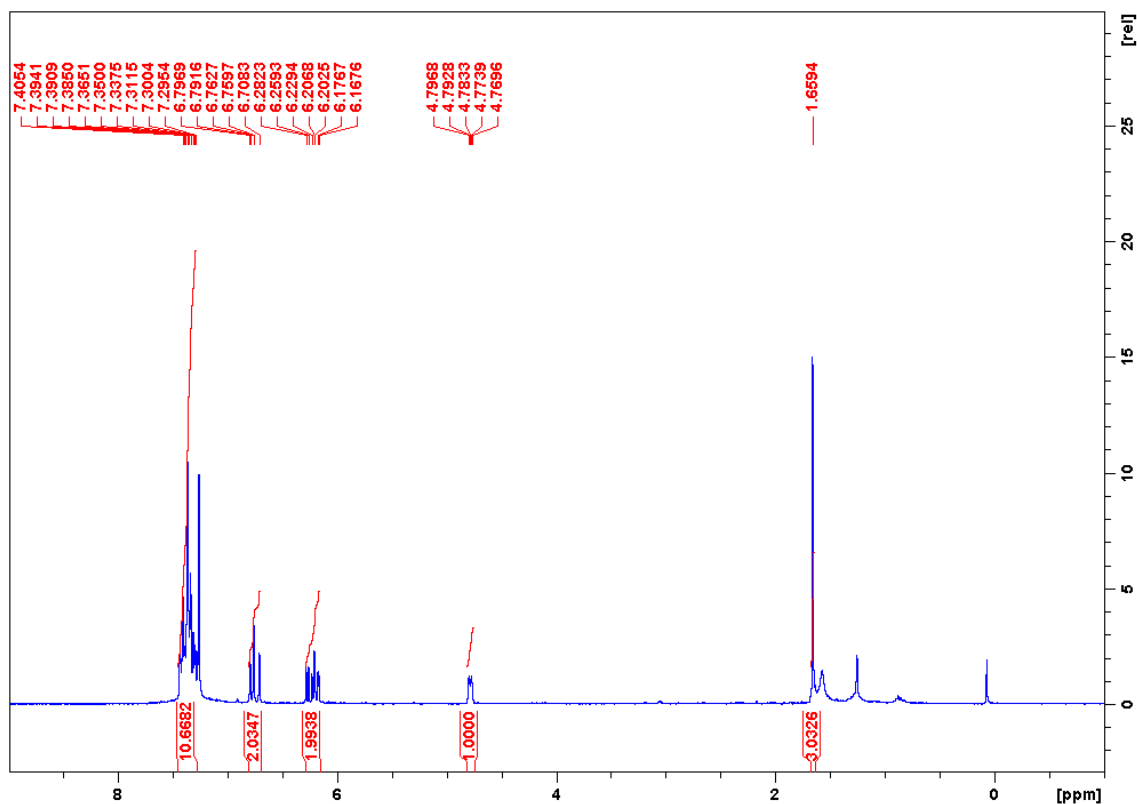


10q,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

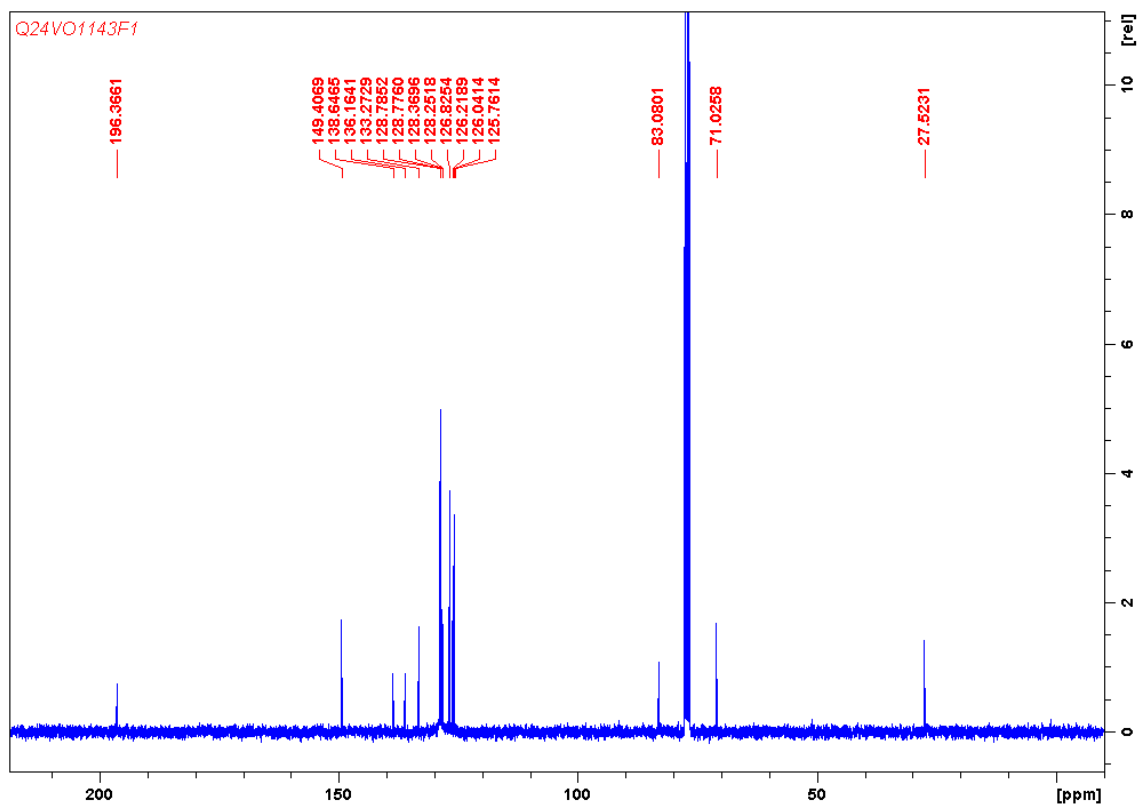


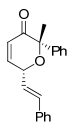


10r (major diastereomer),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

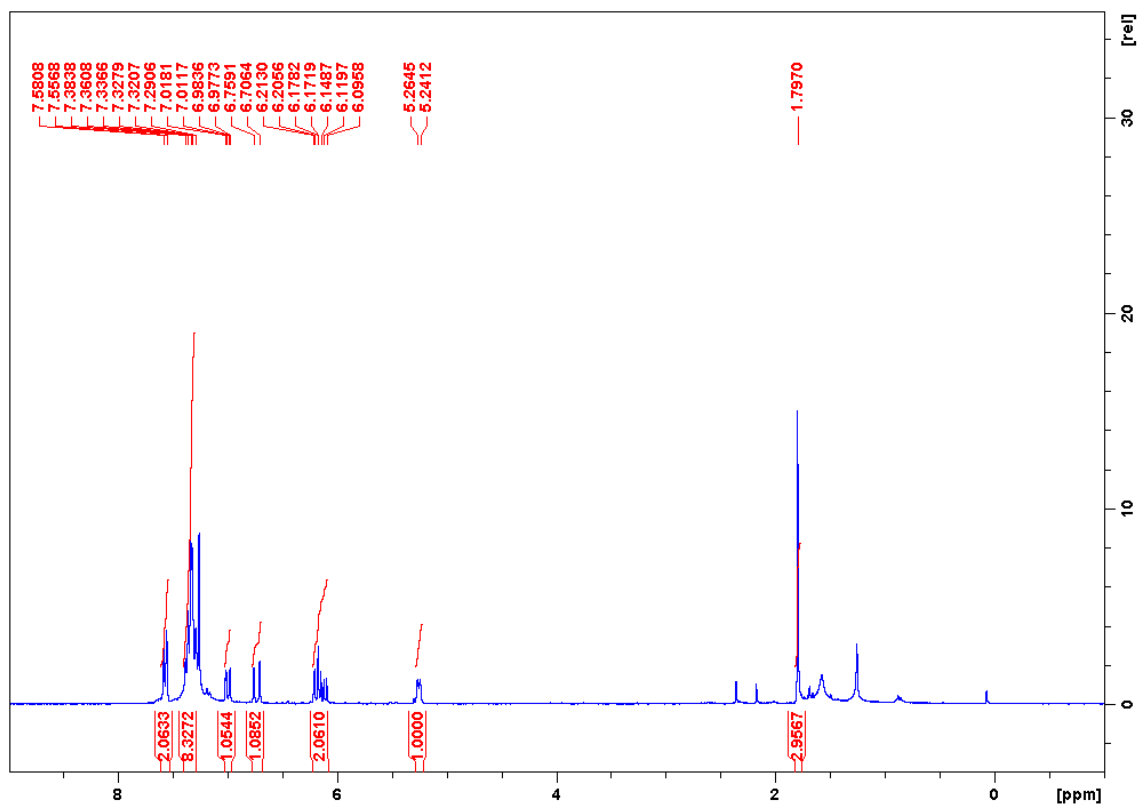


10r (major diastereomer),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

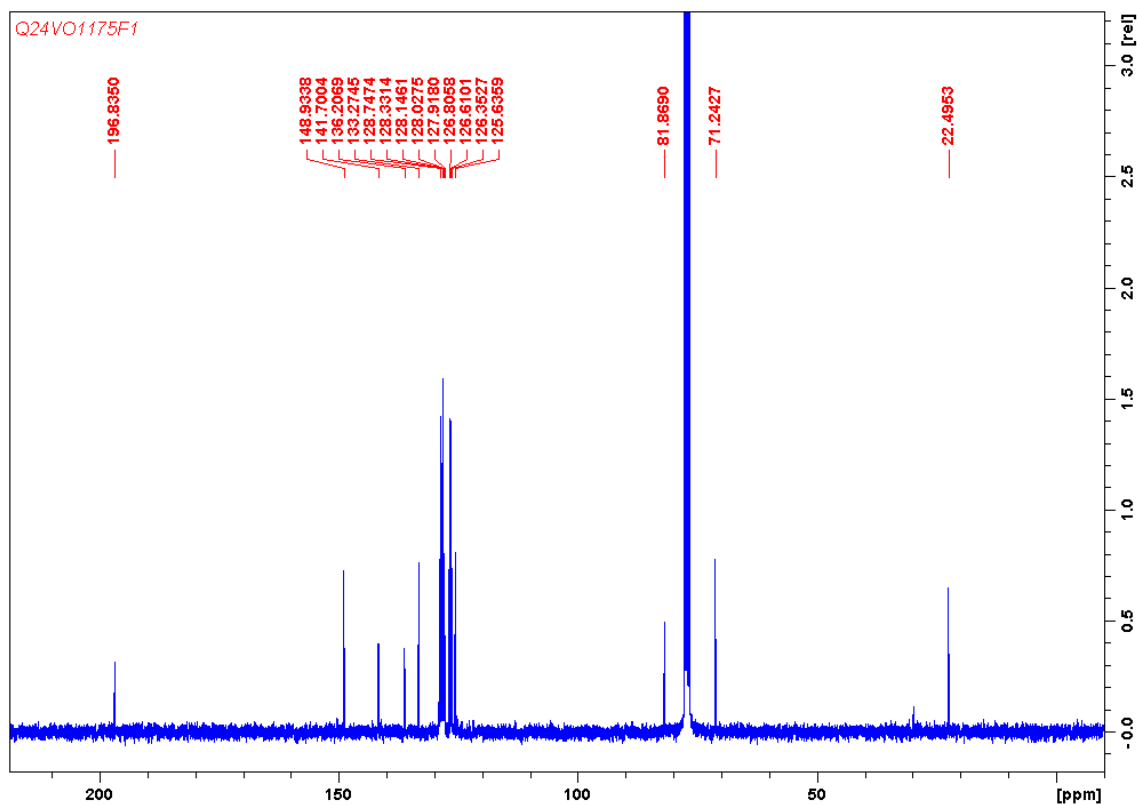


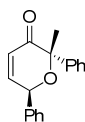


10r (minor diastereomer),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

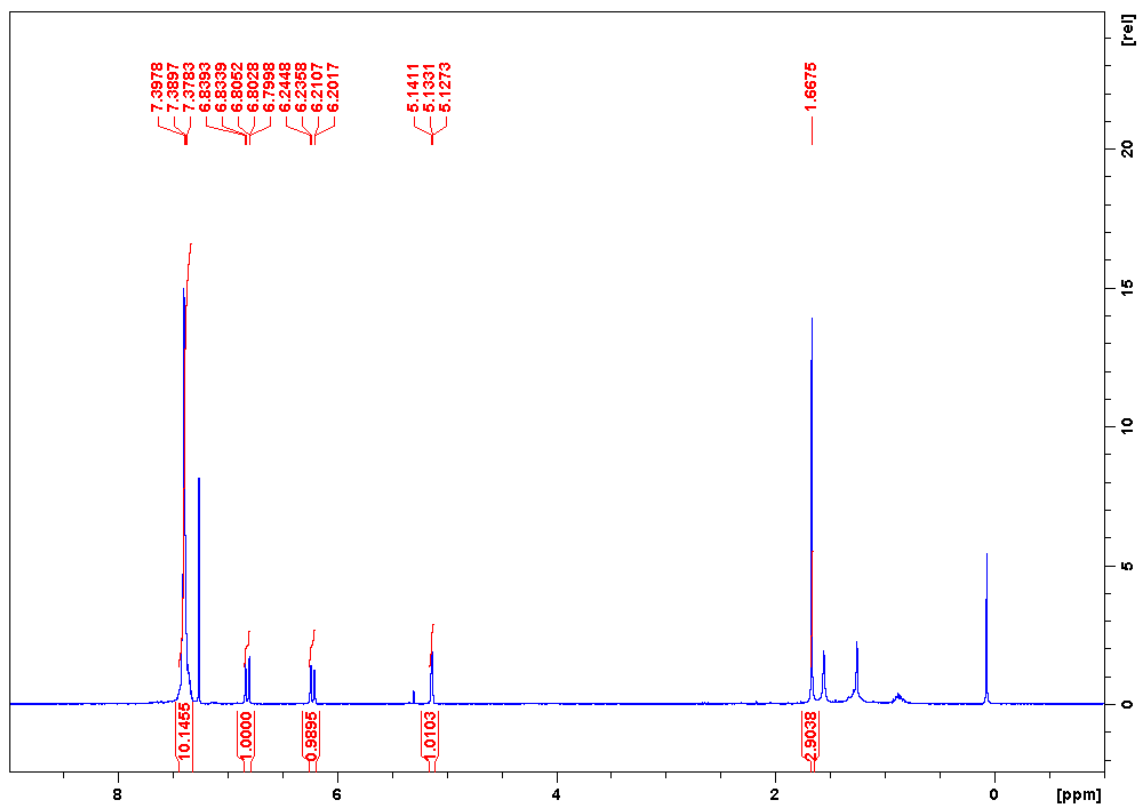


10r (minor diastereomer),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

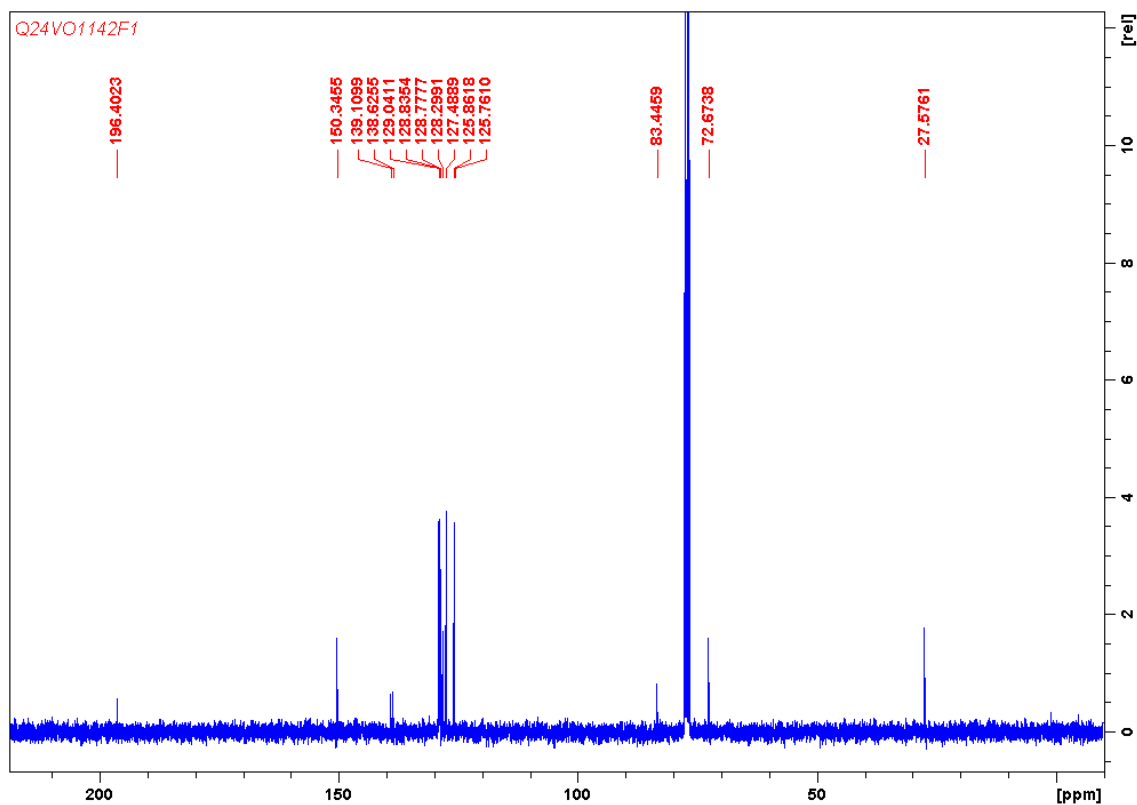


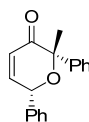


10s (major diastereomer),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

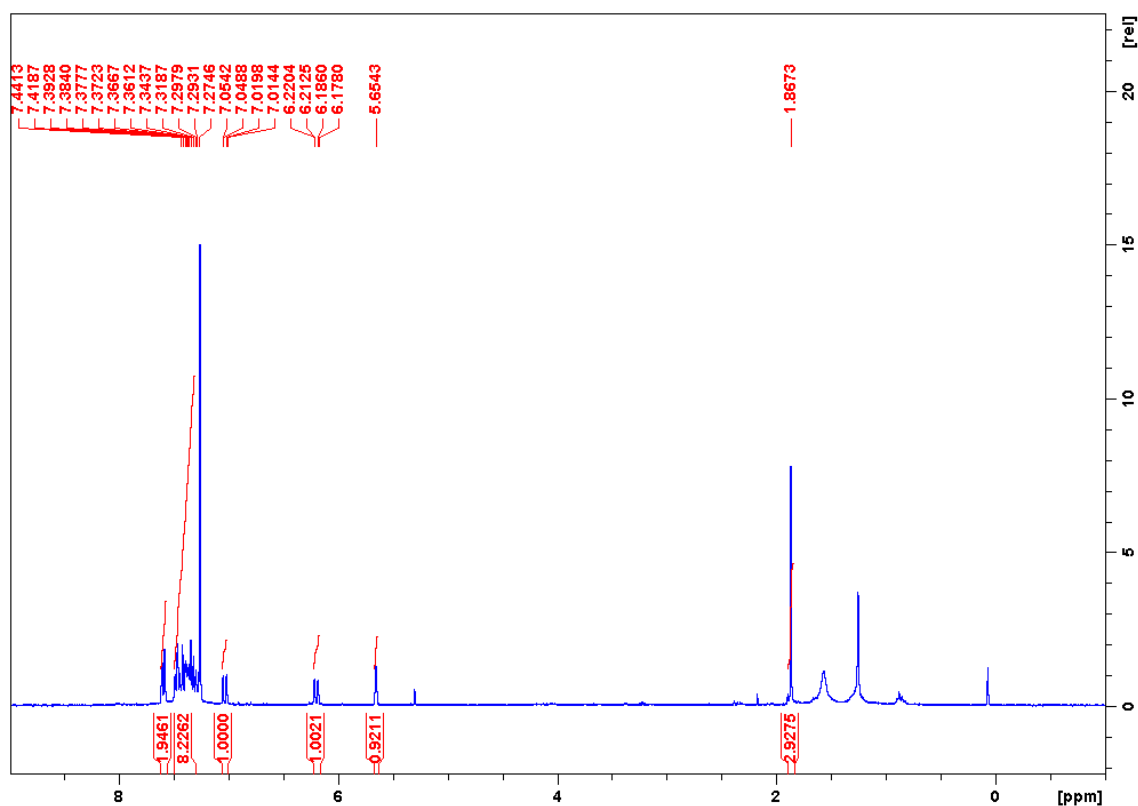


10s (major diastereomer),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

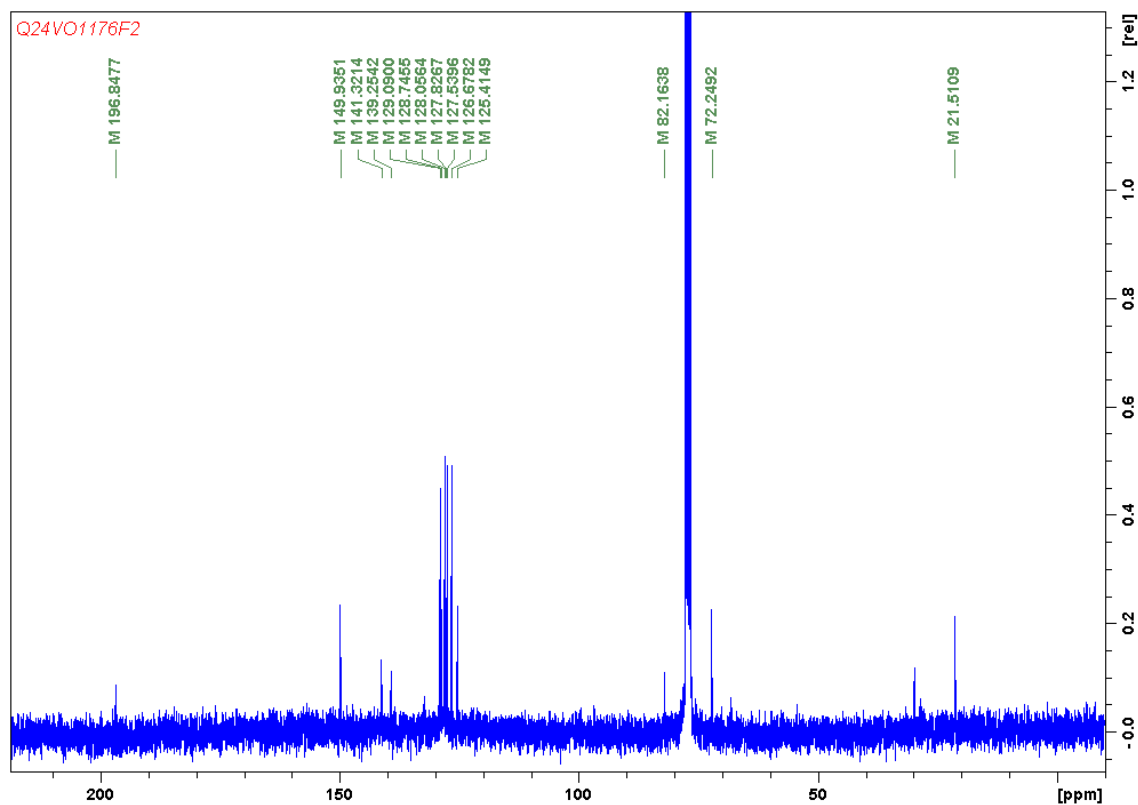




10s (minor diastereomer),  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

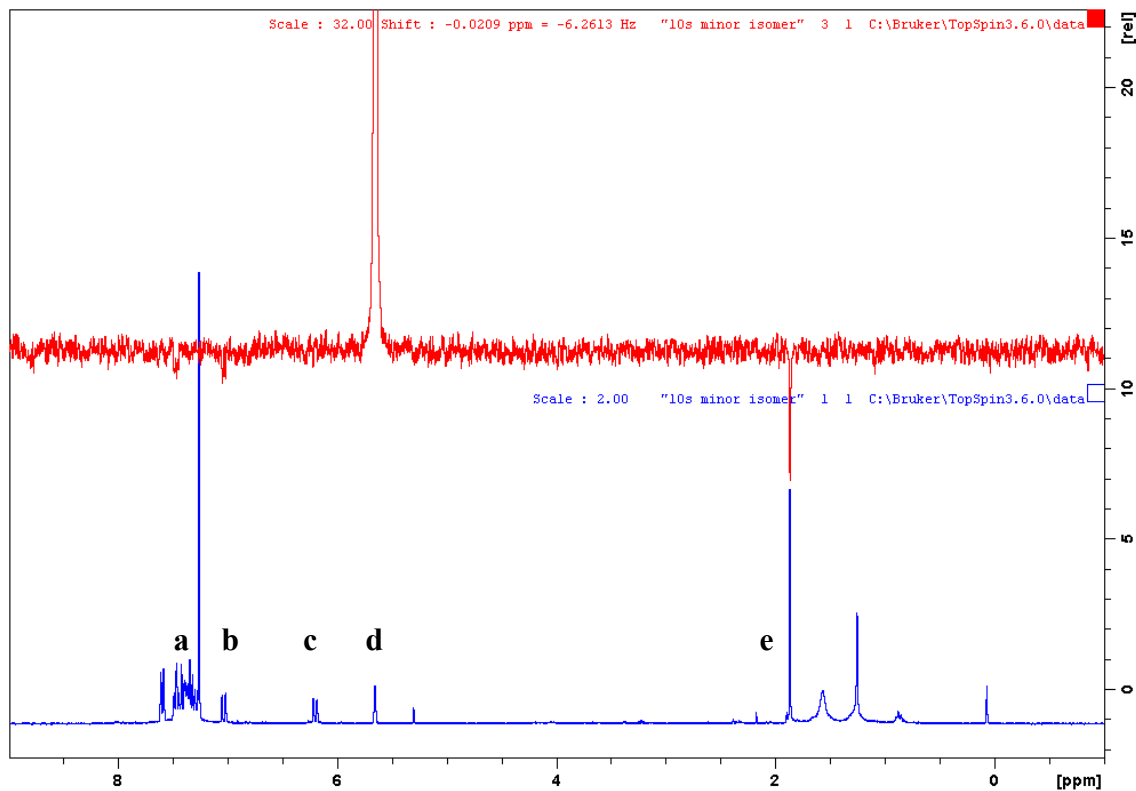
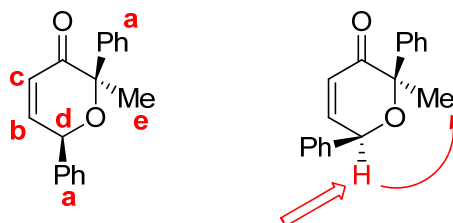


10s (minor diastereomer),  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )





**Compound 10s (minor diastereomer), NOE (300 MHz, CDCl<sub>3</sub>)**



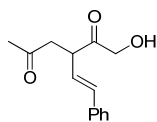
**a:** 7.60-7.29 (m, 10H).

**b:** 7.03 (dd,  $J = 10.3$  Hz,  $J = 1.6$  Hz, 1H).

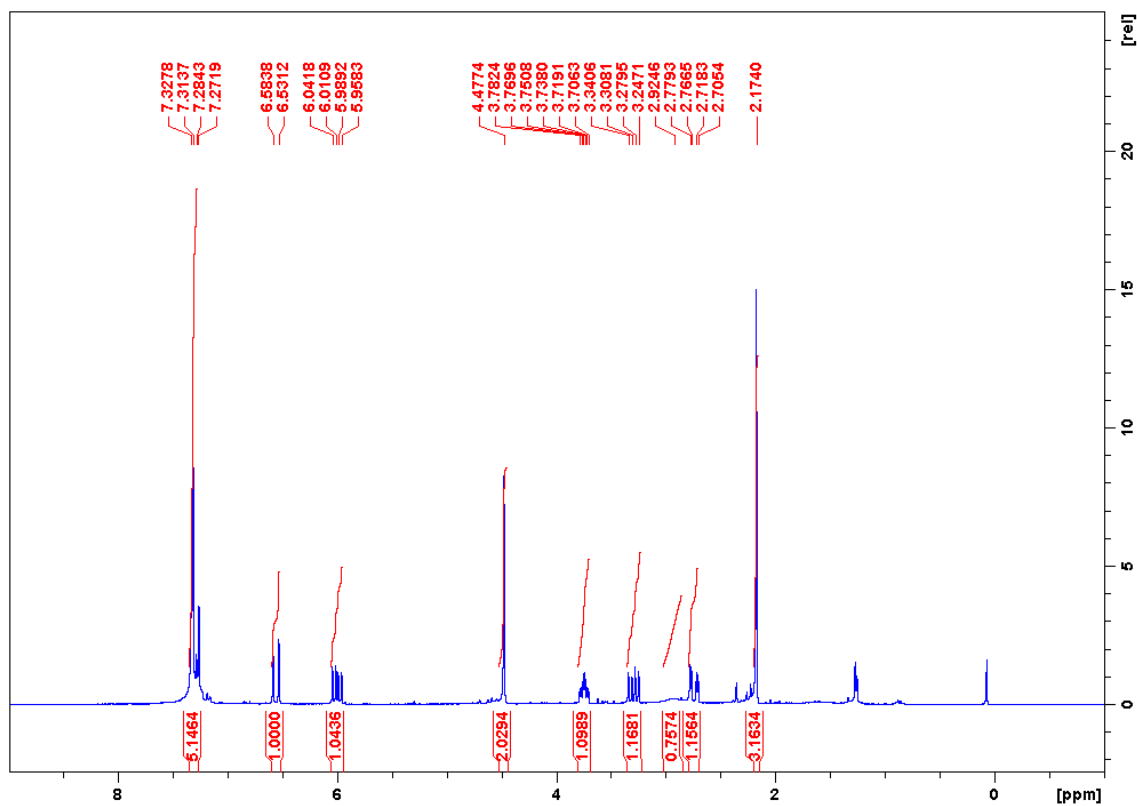
**c:** 6.20 (dd,  $J = 10.3$  Hz,  $J = 2.4$  Hz, 1H).

**d:** 5.65 (s, 1H).

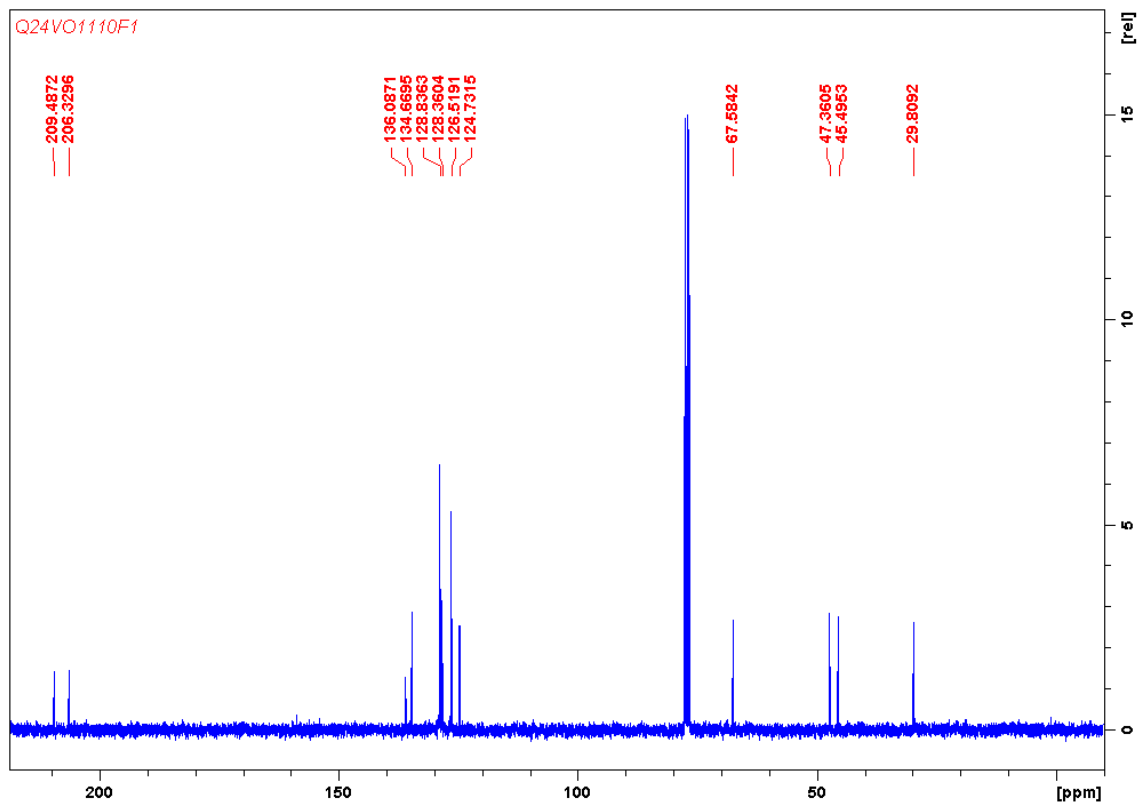
**e:** 1.87 (s, 3H).

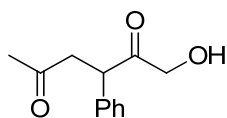


13a,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

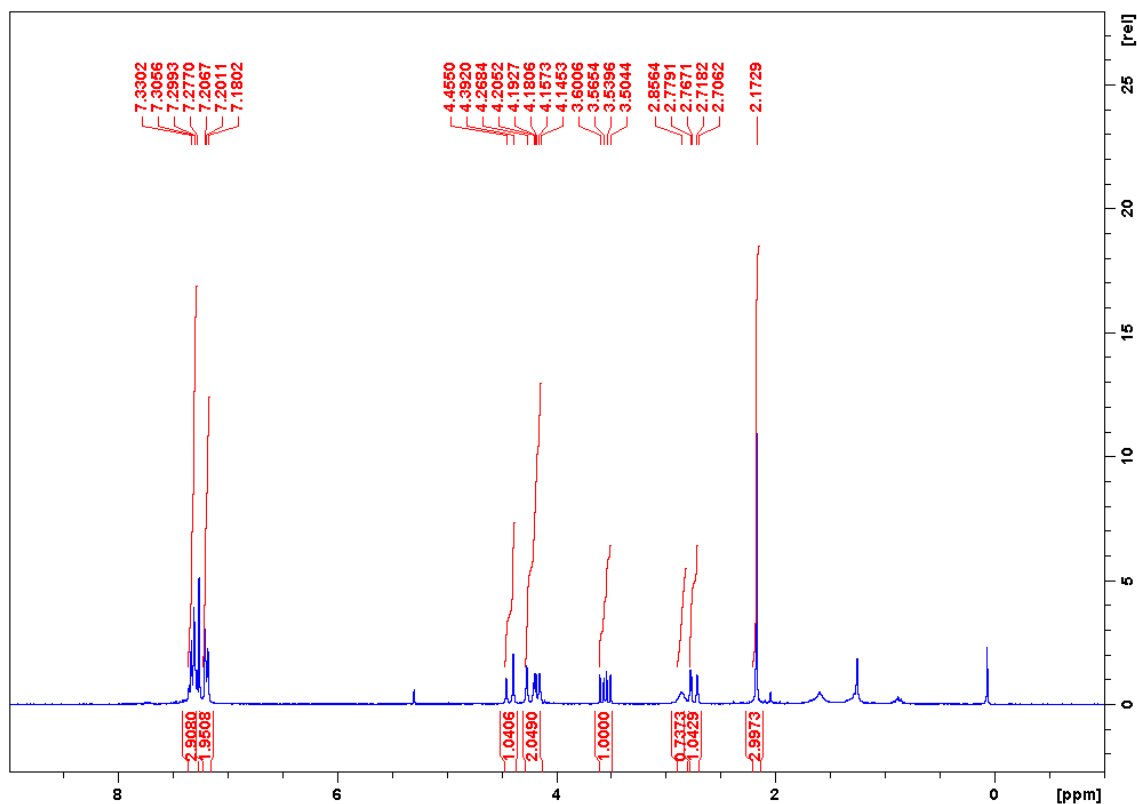


13a,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

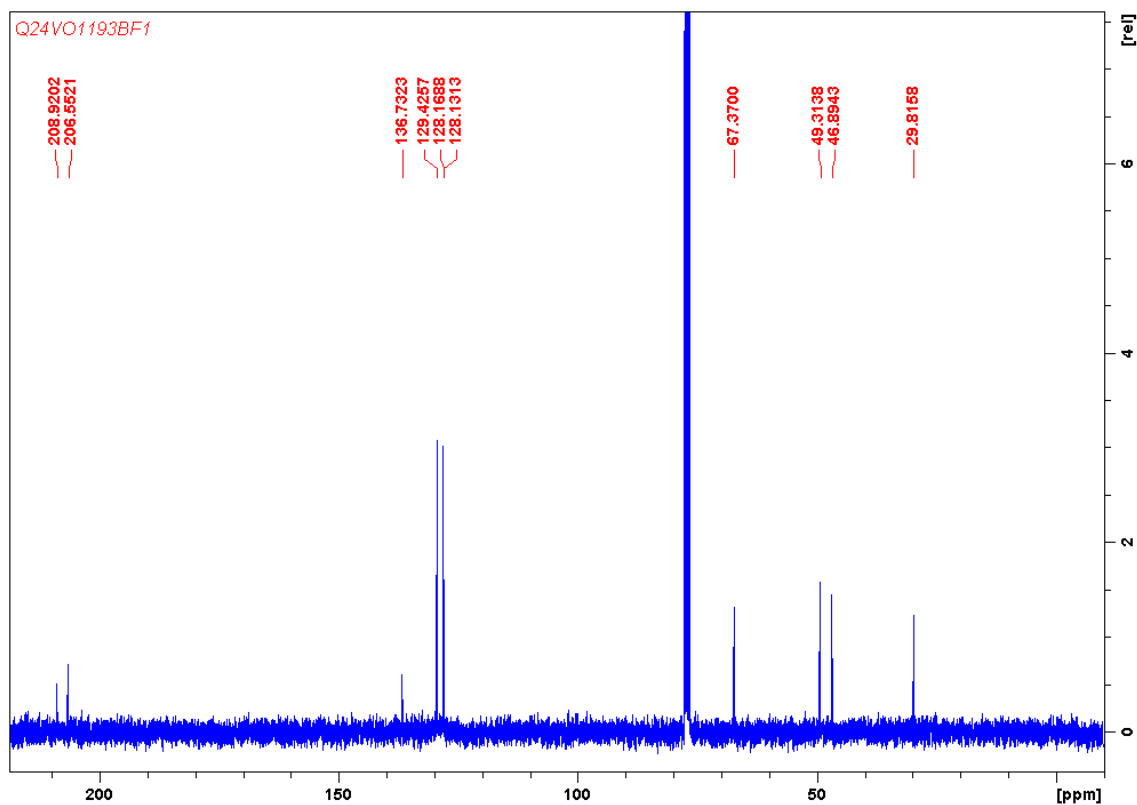


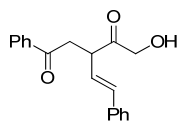


13b,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

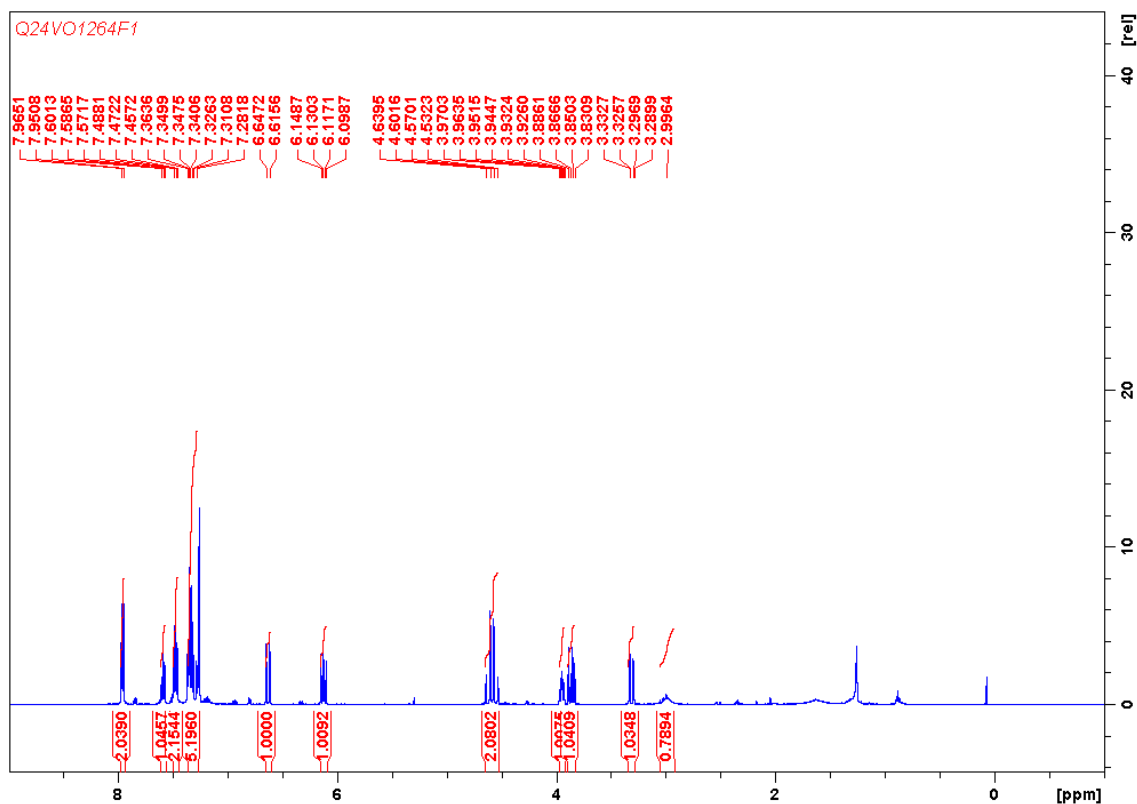


13b,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

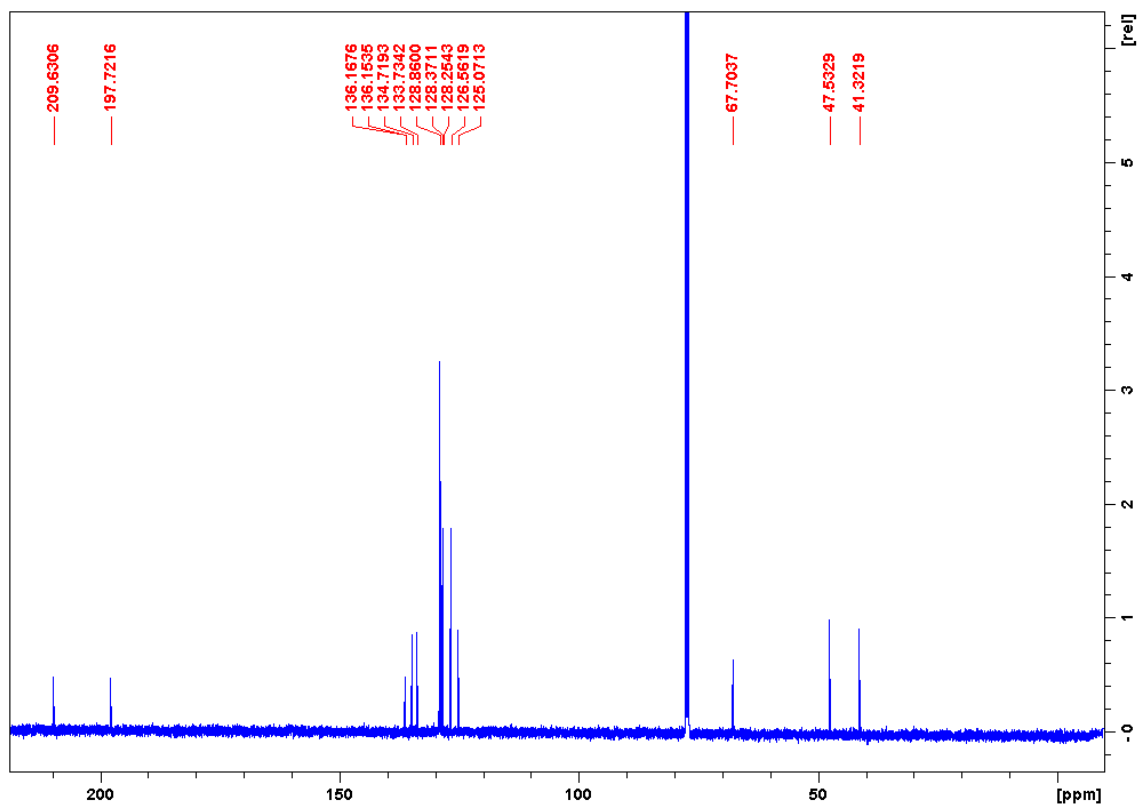


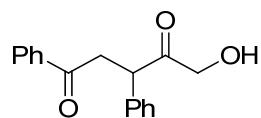


13c,  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )

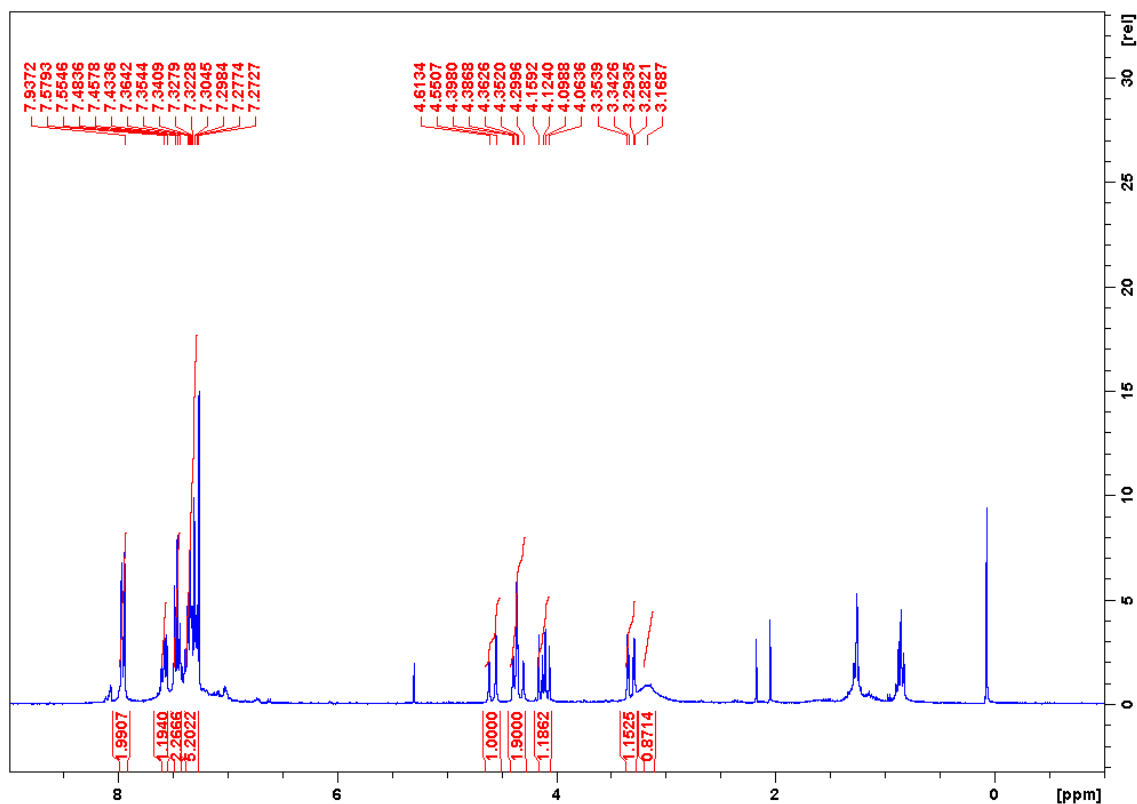


13c,  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )

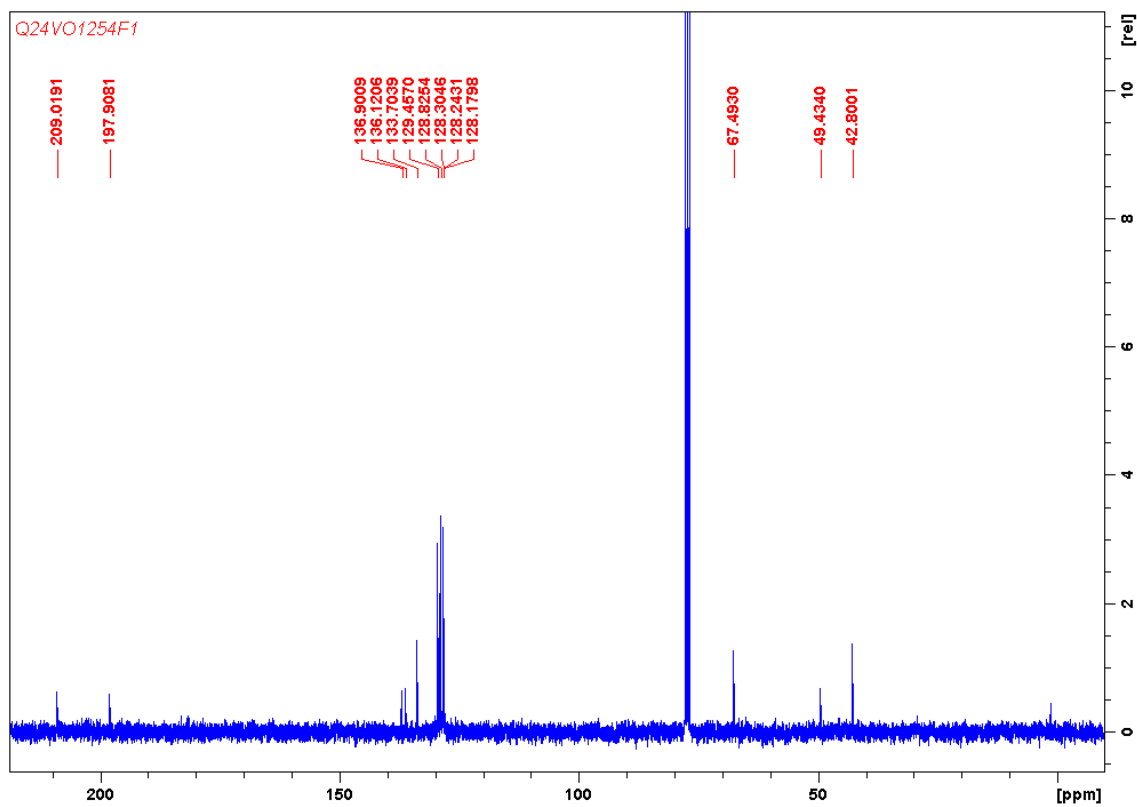


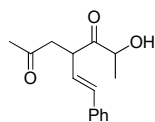


13d,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

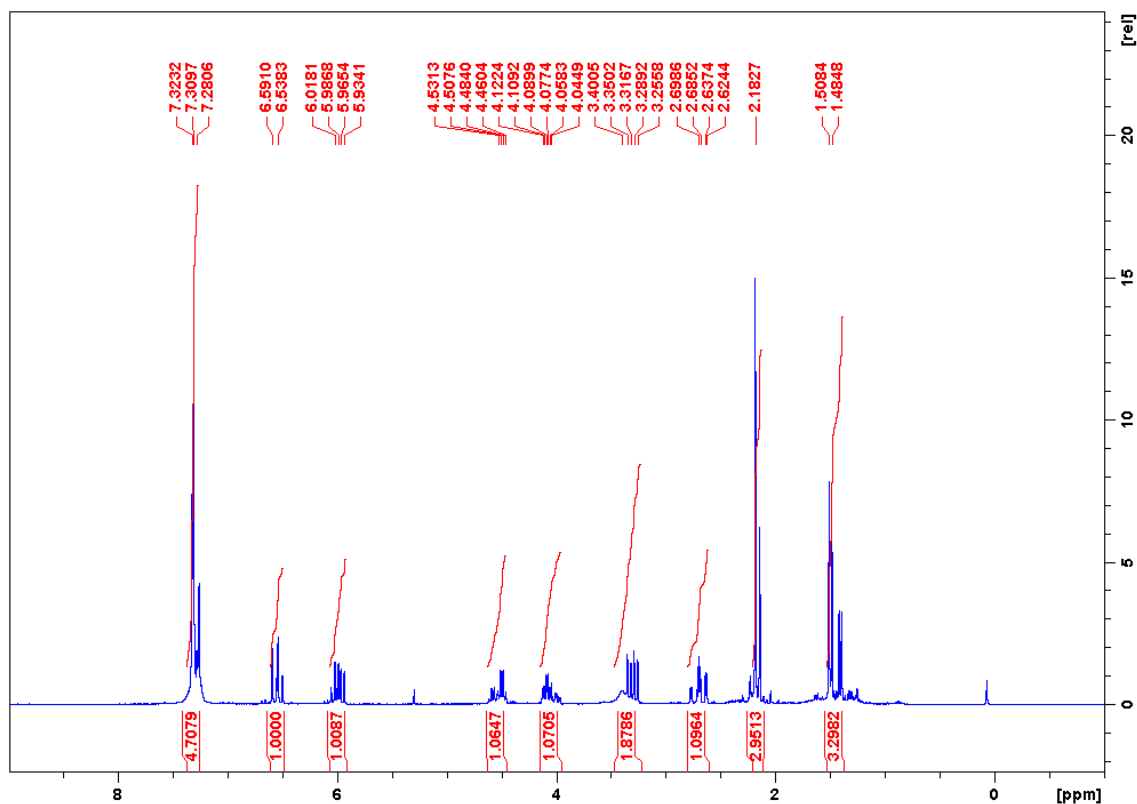


13d,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

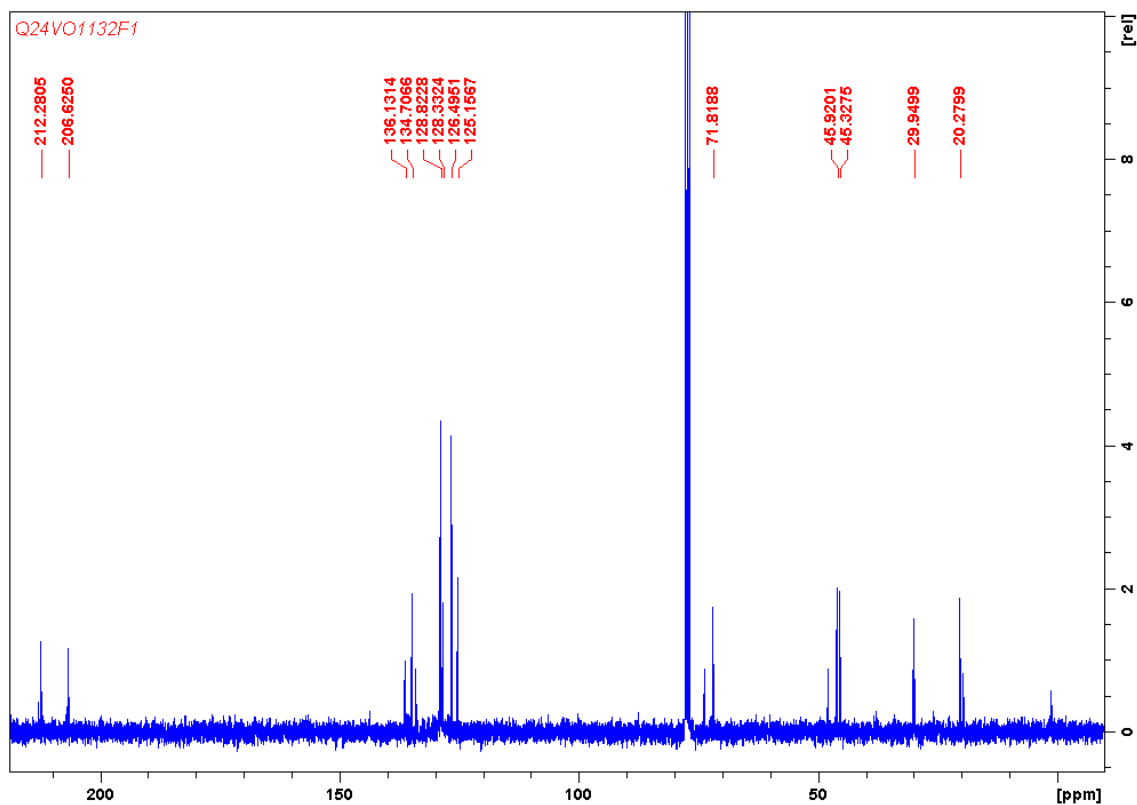


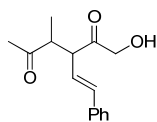


13e,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

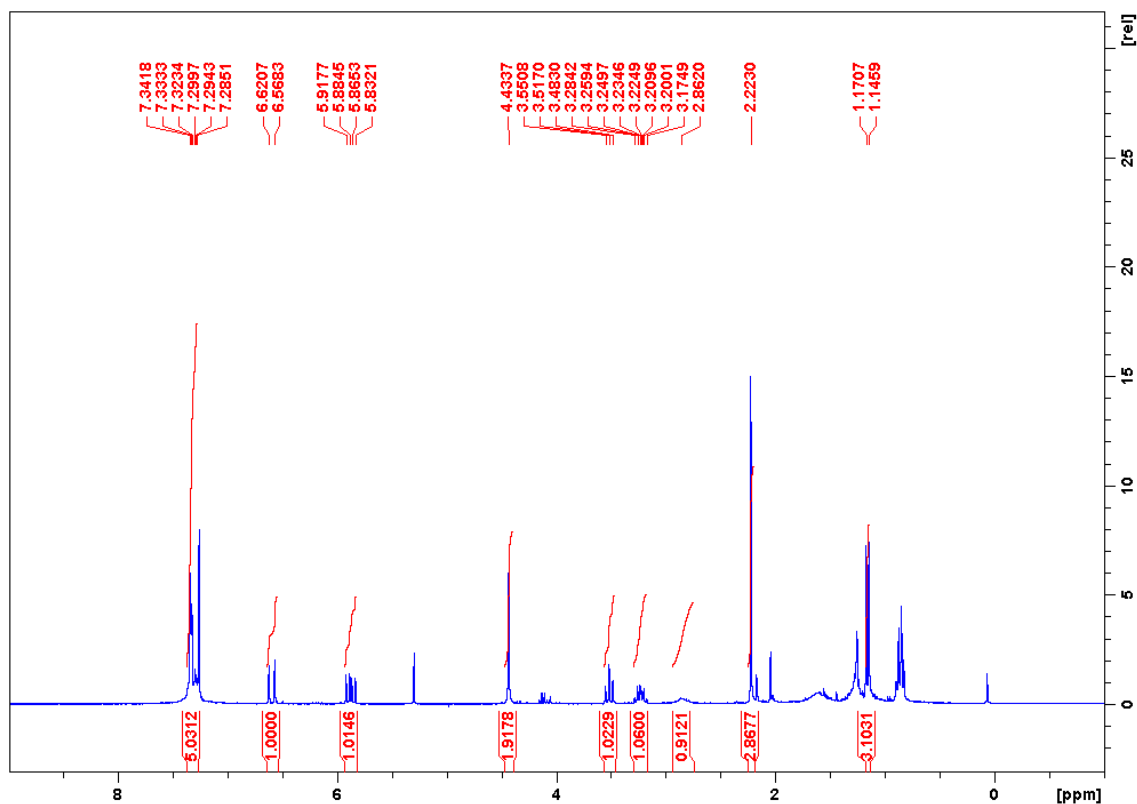


13e,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

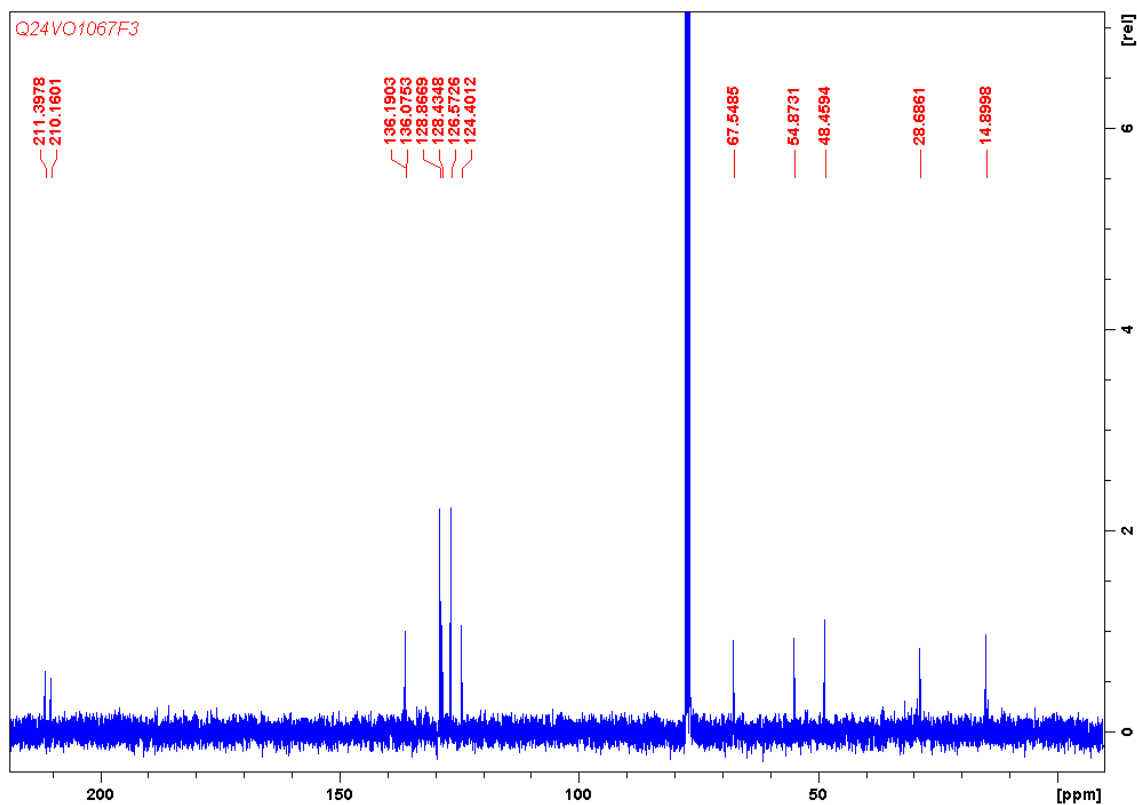


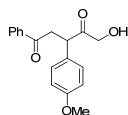


13f,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

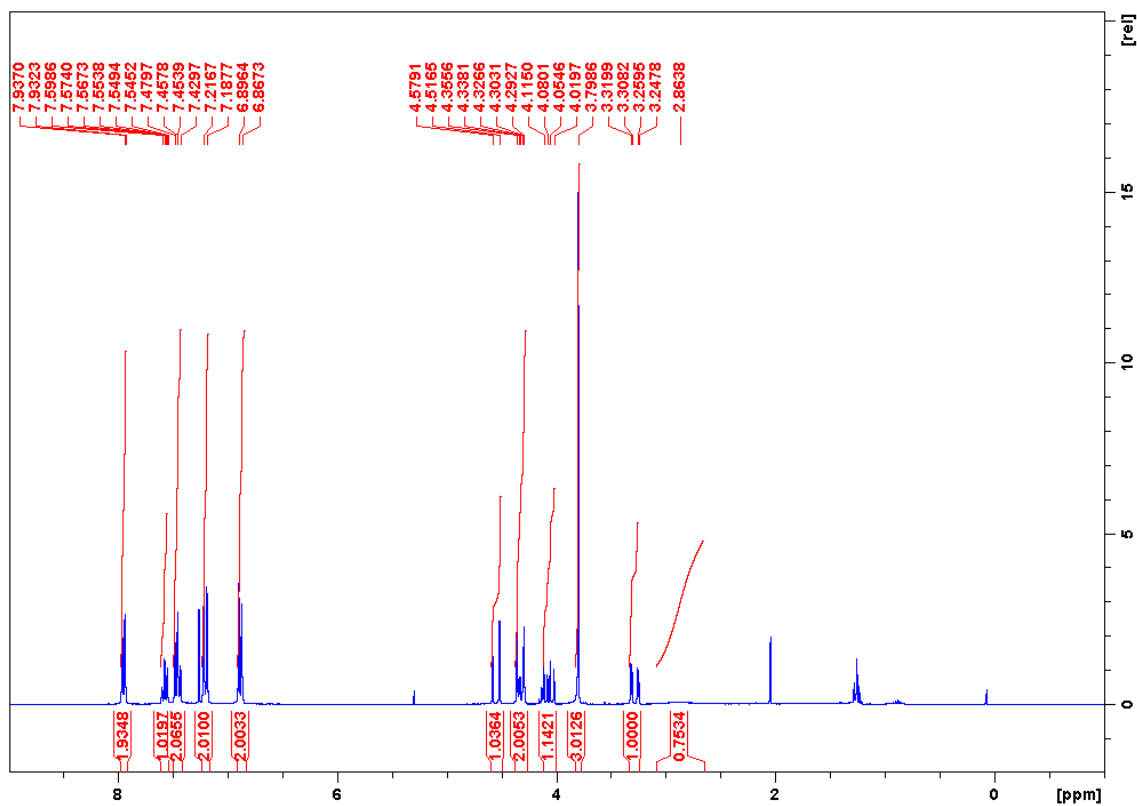


13f,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

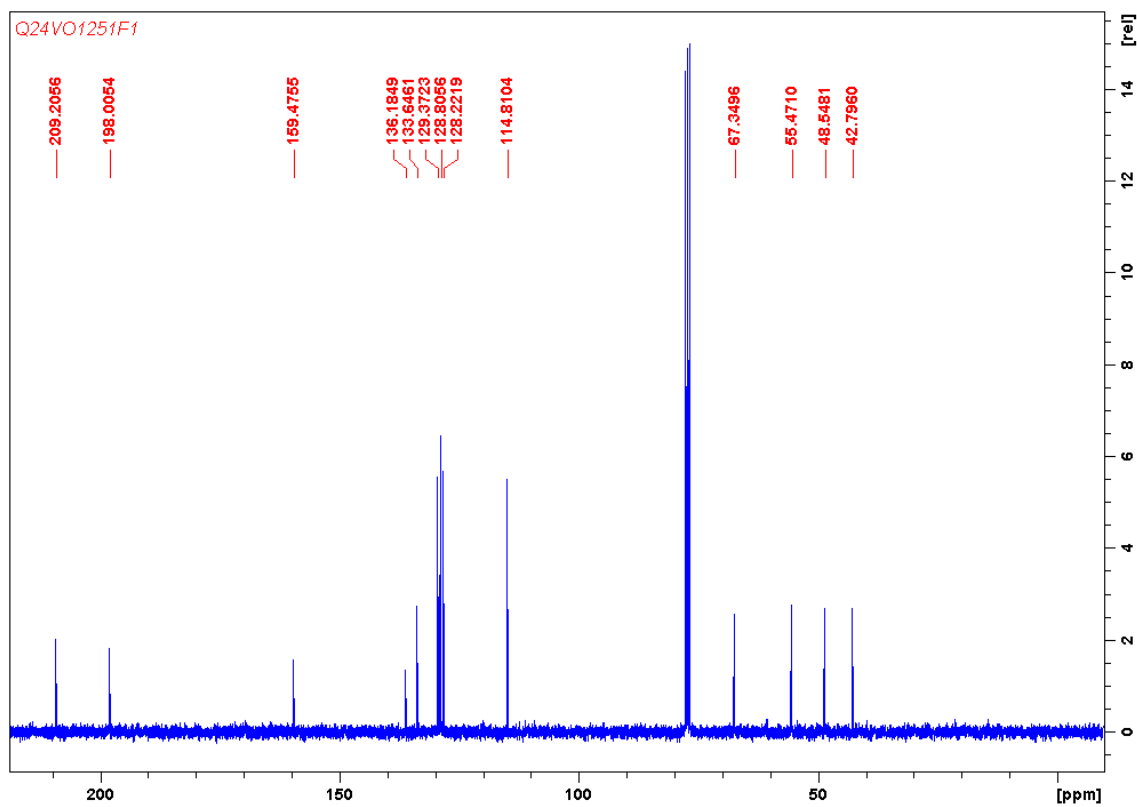




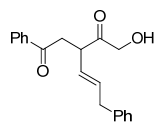
13g,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



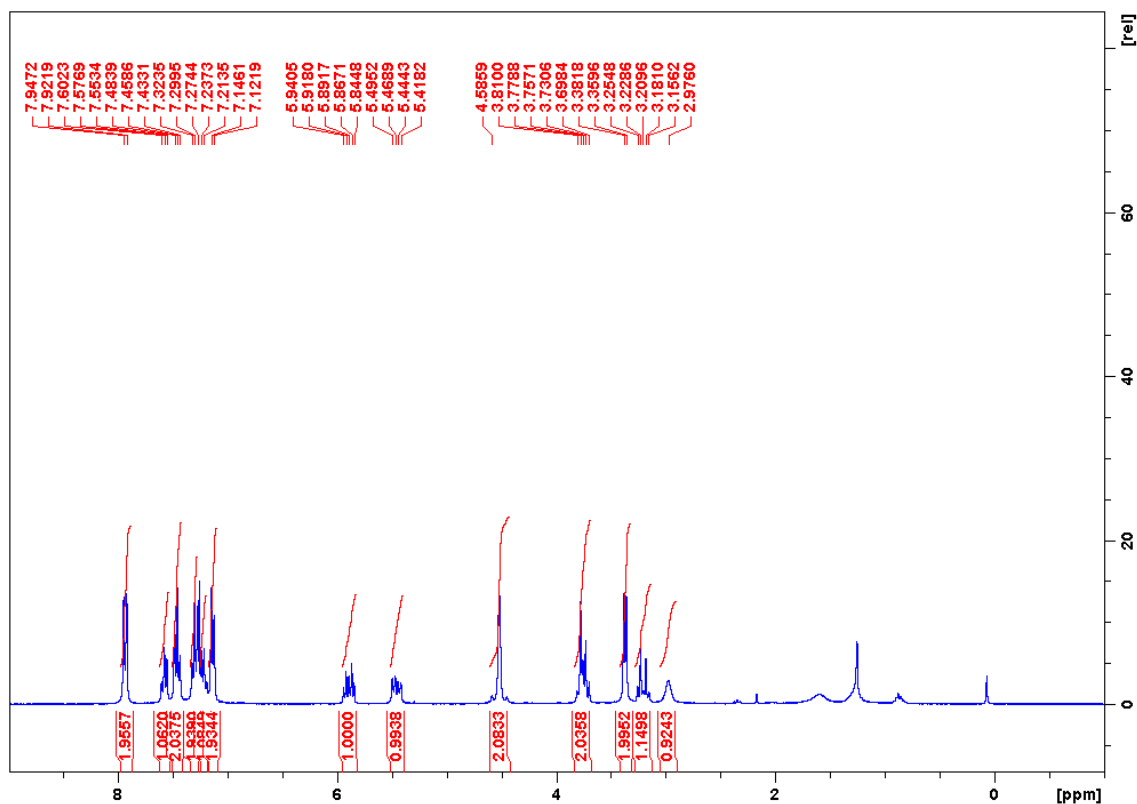
13g,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



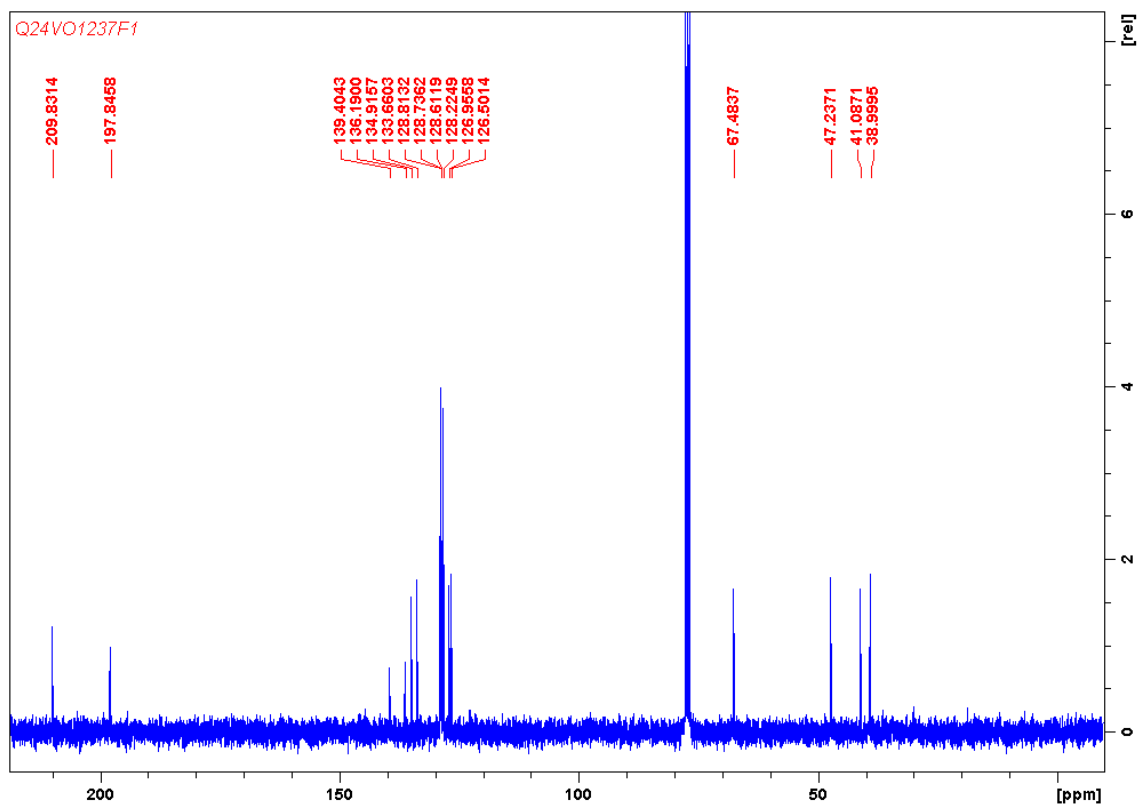


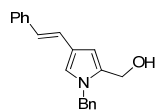


13h,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

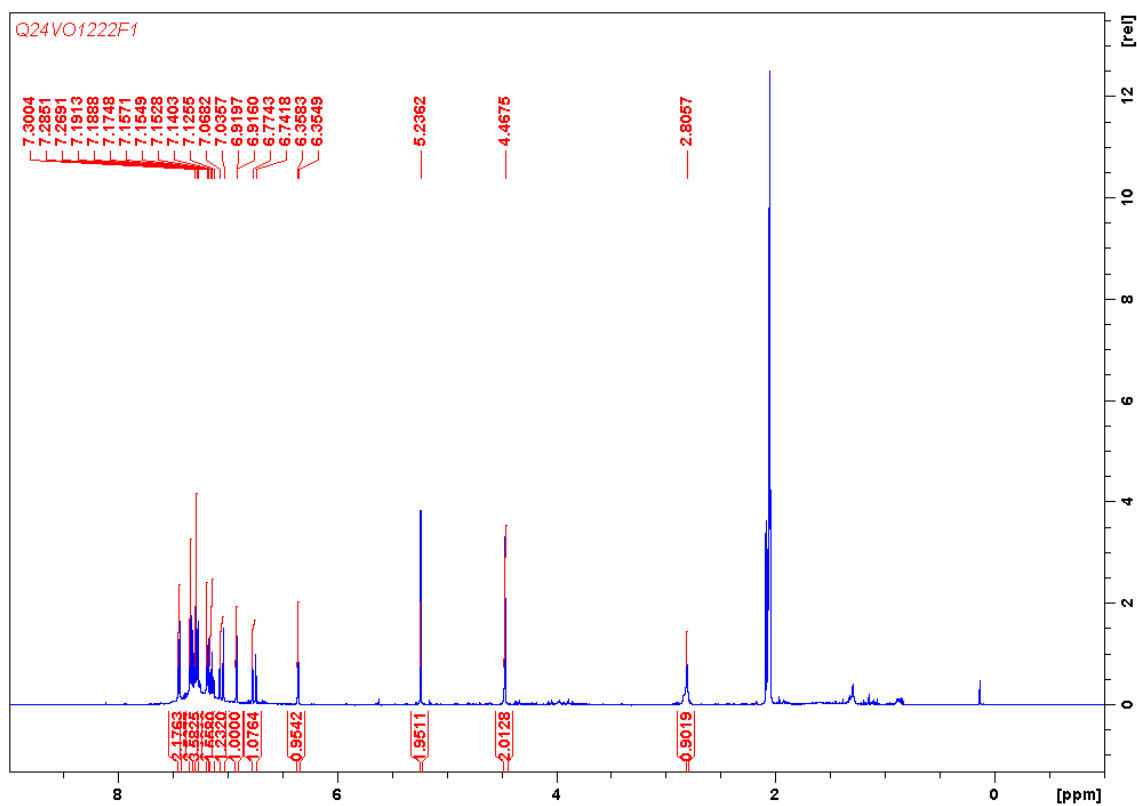


13h,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

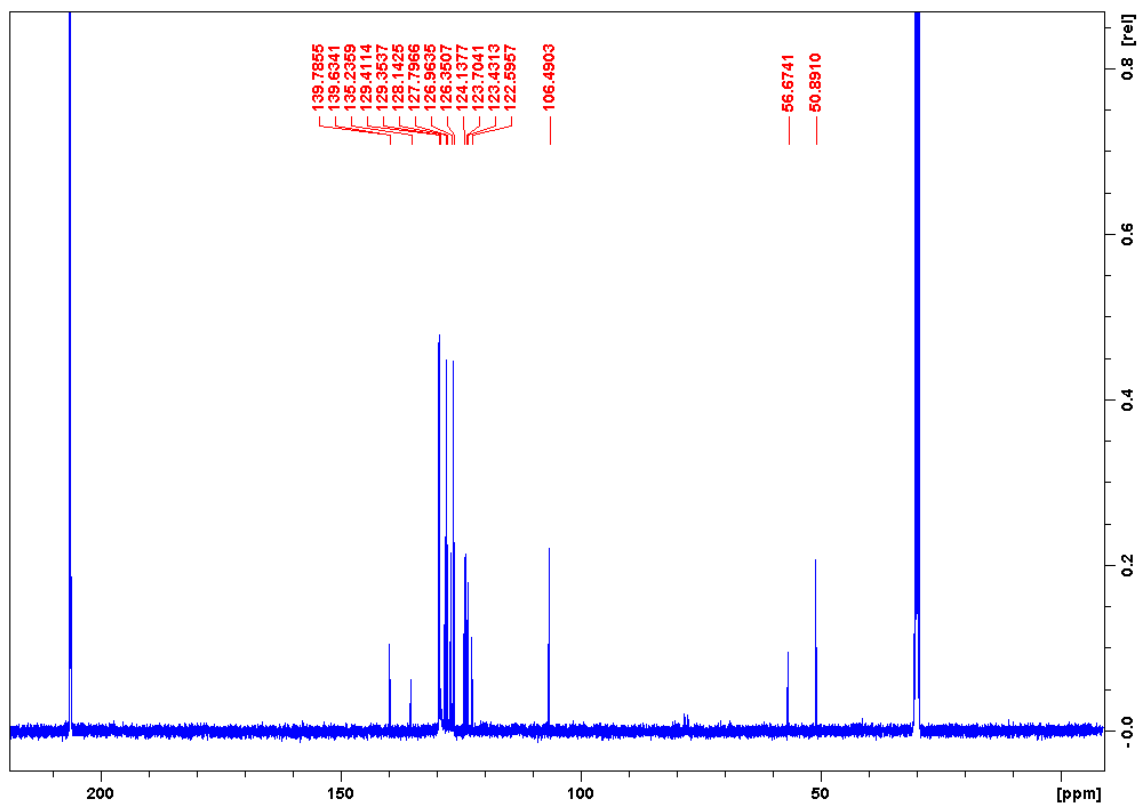


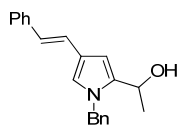


14a,  $^1\text{H}$  NMR (500 MHz, acetone- $d_6$ )

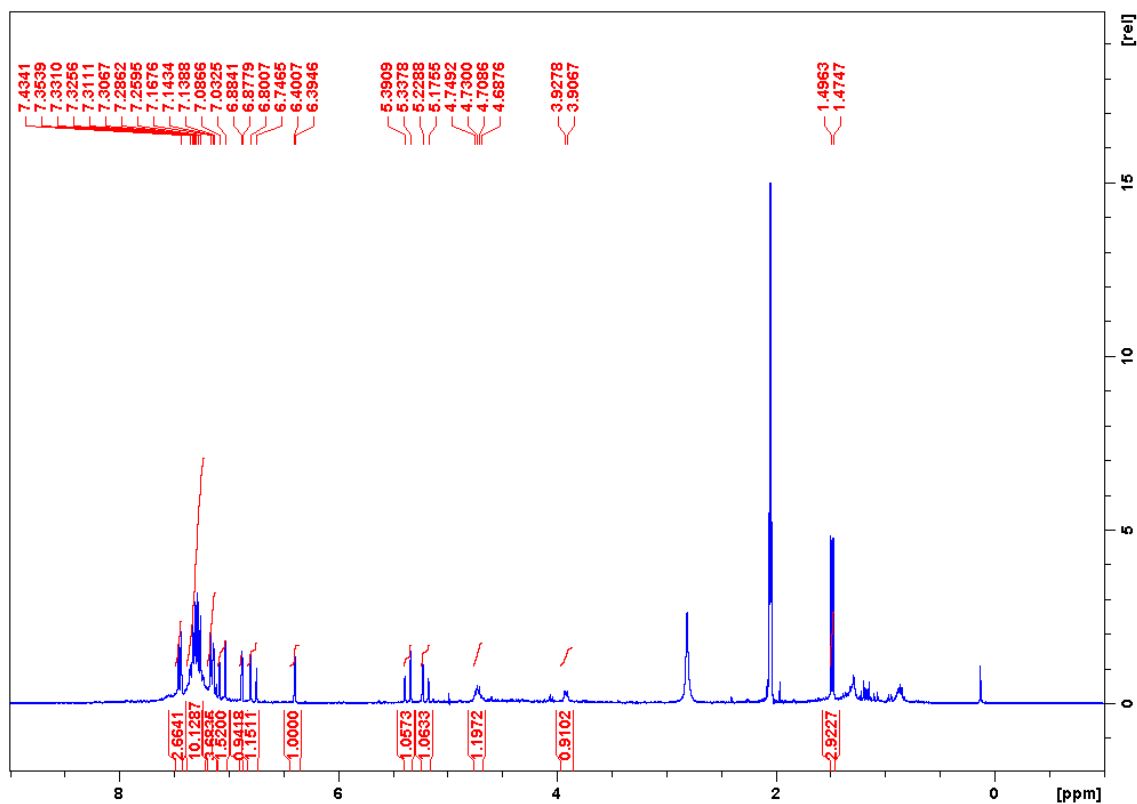


14a,  $^{13}\text{C}$  NMR (125 MHz, acetone- $d_6$ )

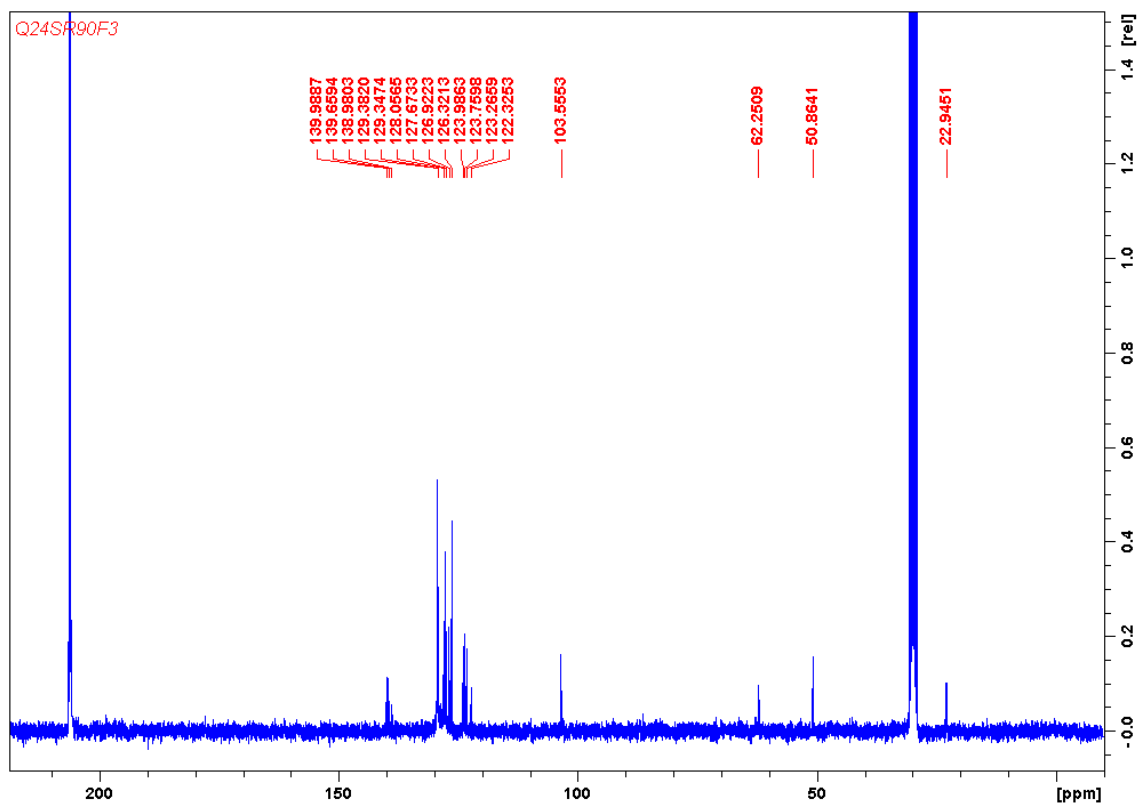




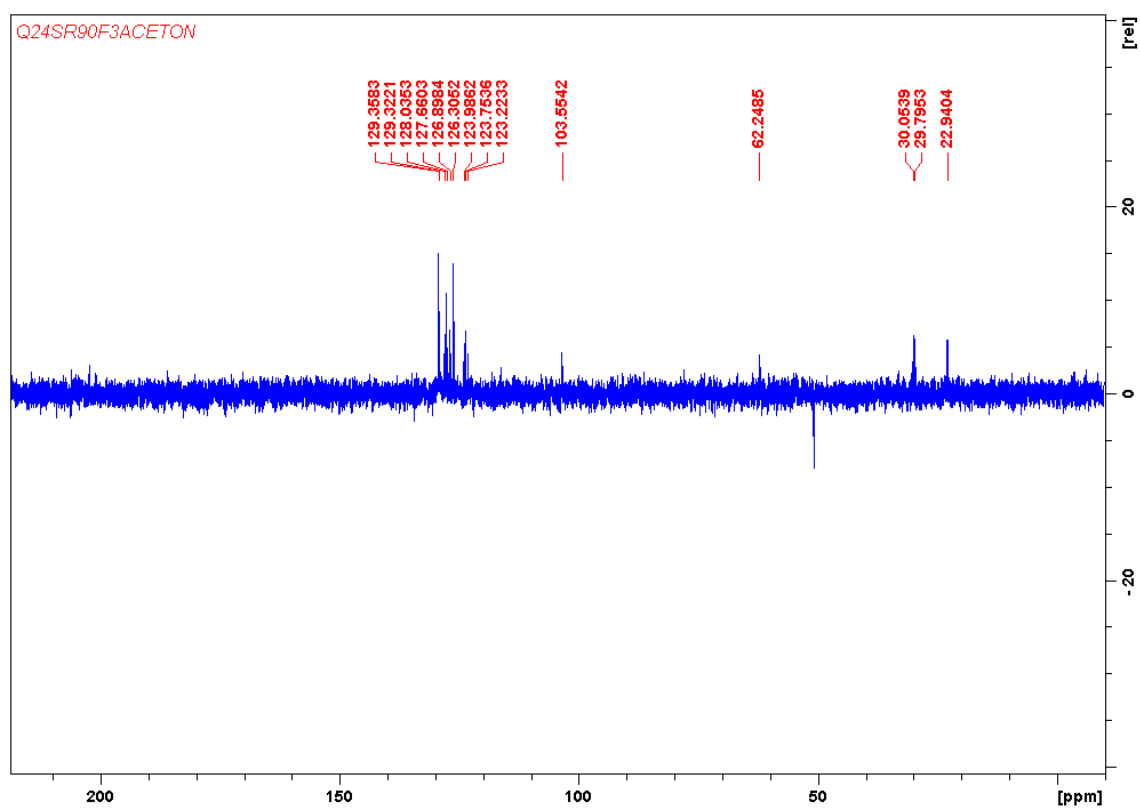
14b,  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )



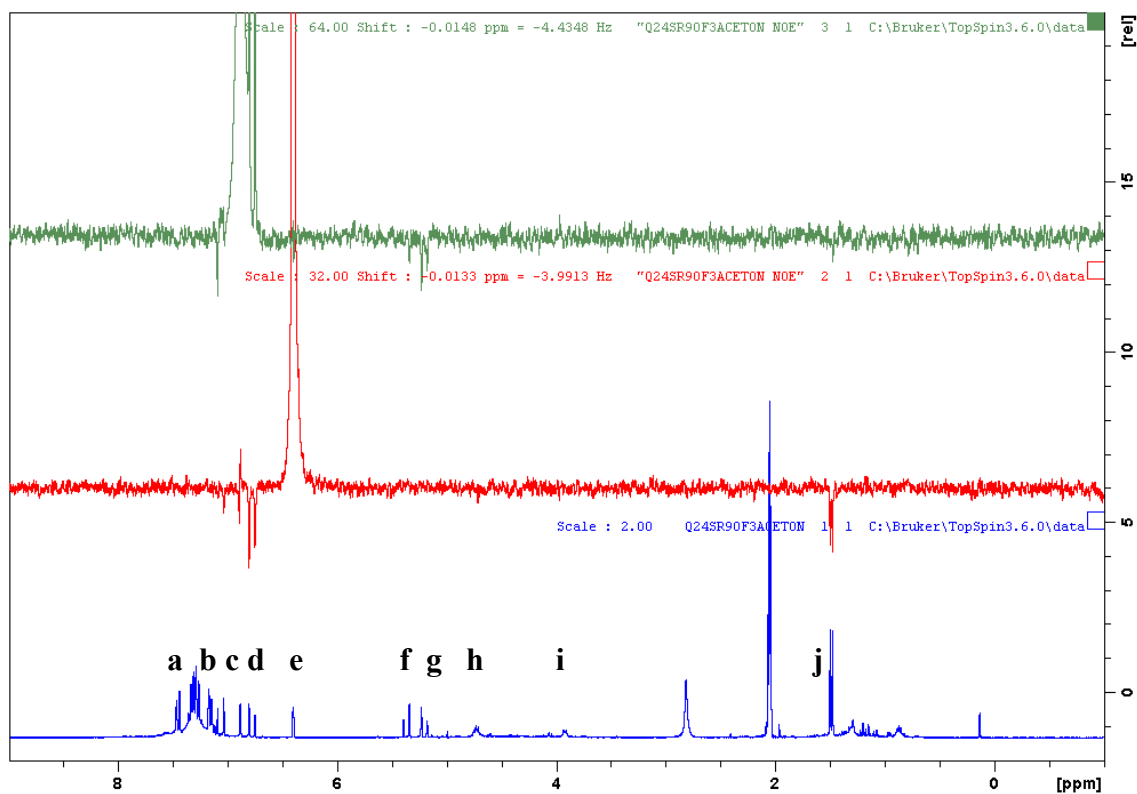
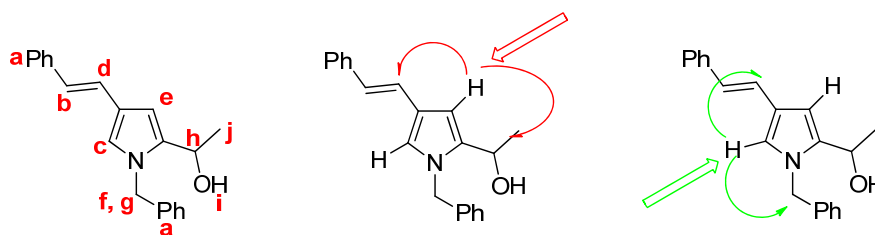
14b,  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )



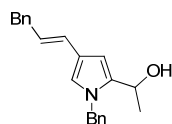
14b, DEPT (75 MHz, acetone-d6)



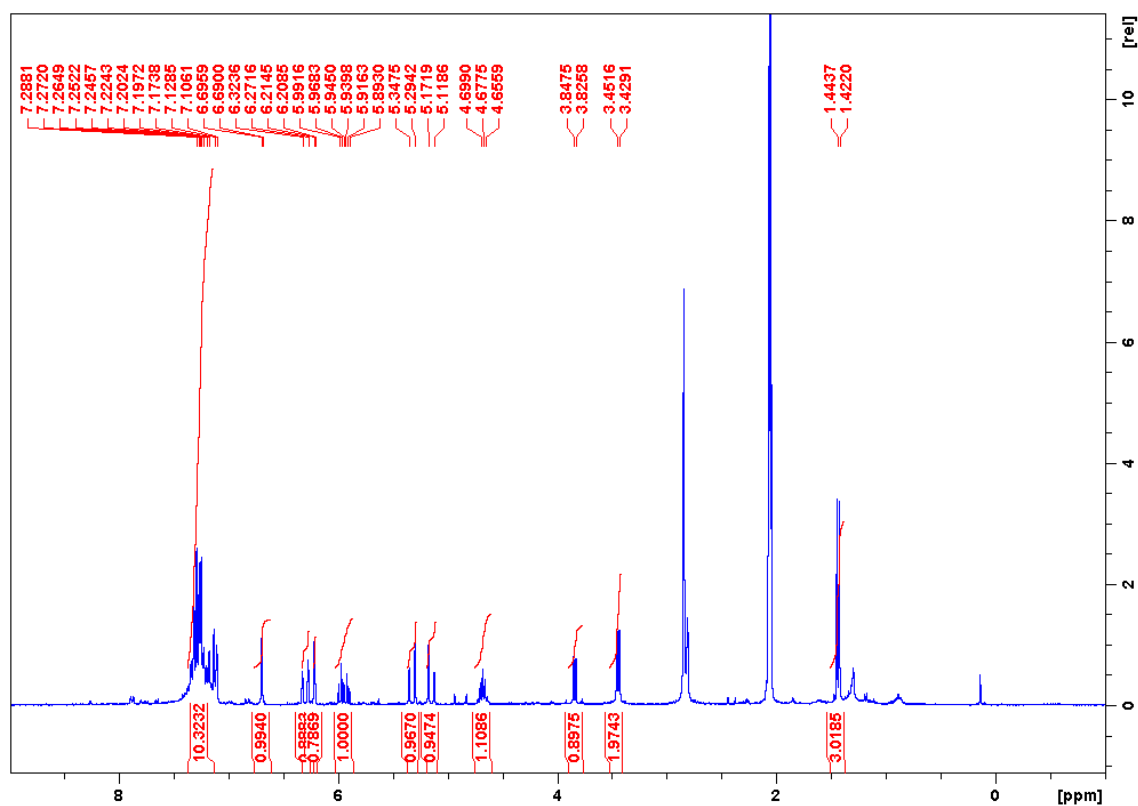
# 14b, NOE (acetone-d6)



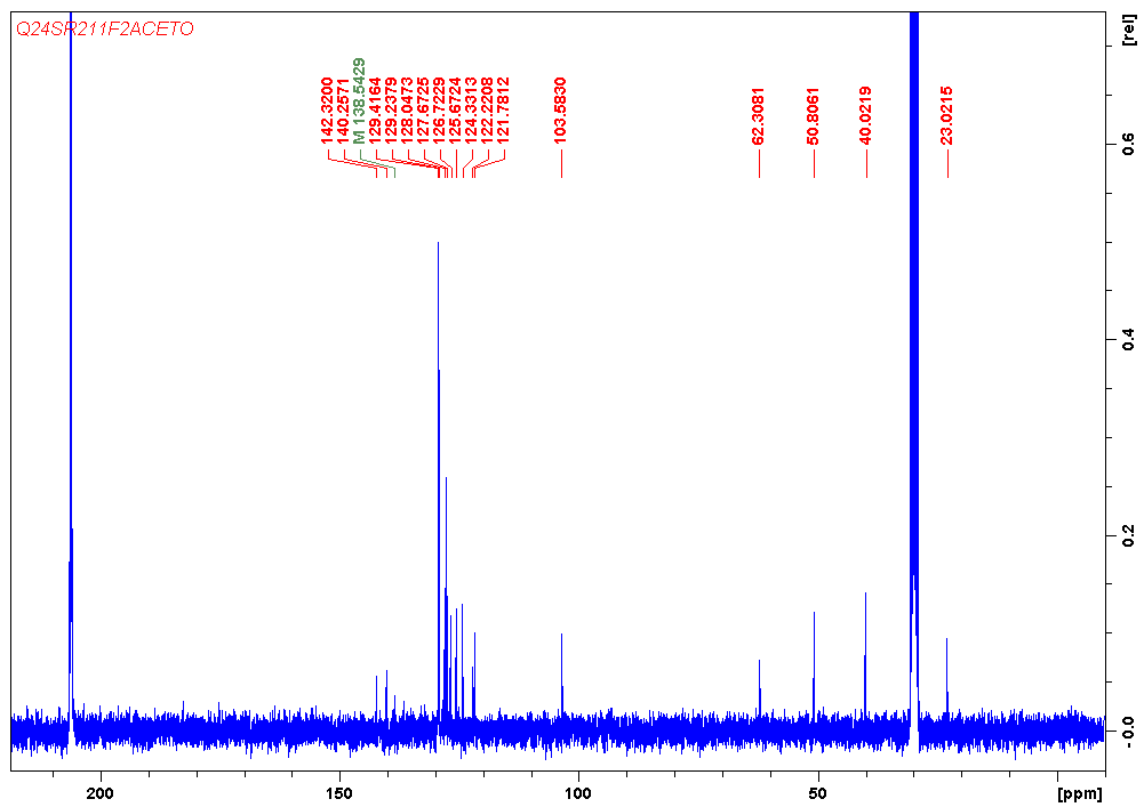
- a: 7.42-7.18 (m, 10H).
- b: 7.06 (d,  $J = 16.2$  Hz, 1H).
- c: 6.88 (d,  $J = 1.7$  Hz, 1H).
- d: 6.77 (d,  $J = 16.2$  Hz, 1H).
- e: 6.40 (d,  $J = 1.7$  Hz, 1H).
- f: 5.36 (d,  $J = 16.0$  Hz, 1H).
- g: 5.20 (d,  $J = 16.0$  Hz, 1H).
- h: 4.70 (q,  $J = 6.3$  Hz, 1H).
- i: 3.91 (d,  $J = 6.3$  Hz, 1H).
- j: 1.48 (d,  $J = 6.3$  Hz, 3H).

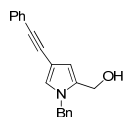


14c,  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )

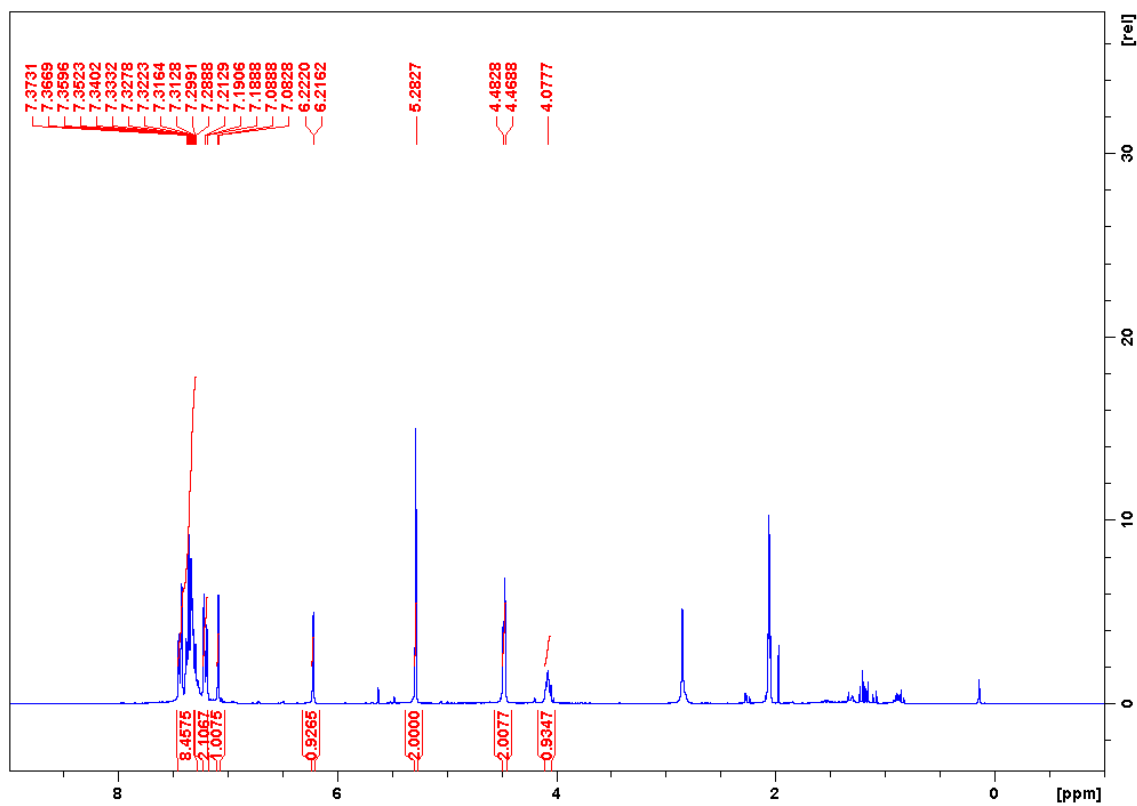


14c,  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )

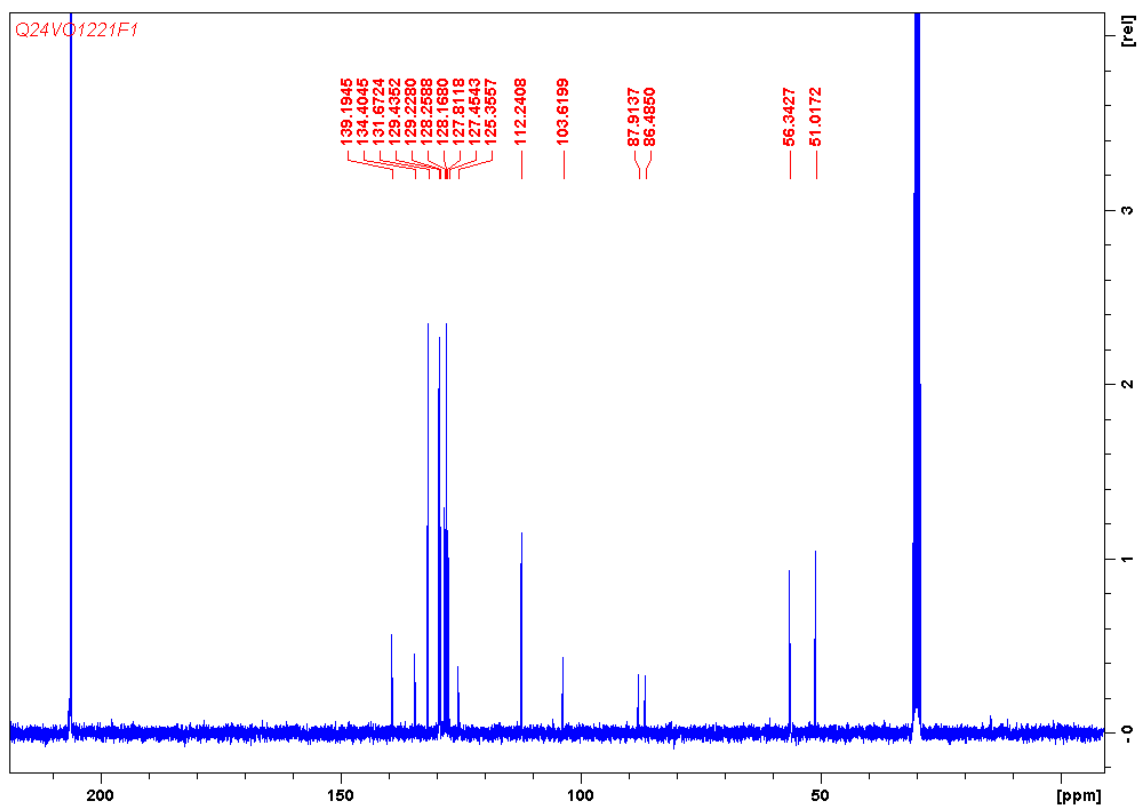


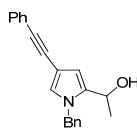


14d,  $^1\text{H}$  NMR (300 MHz, acetone- $\text{d}_6$ )

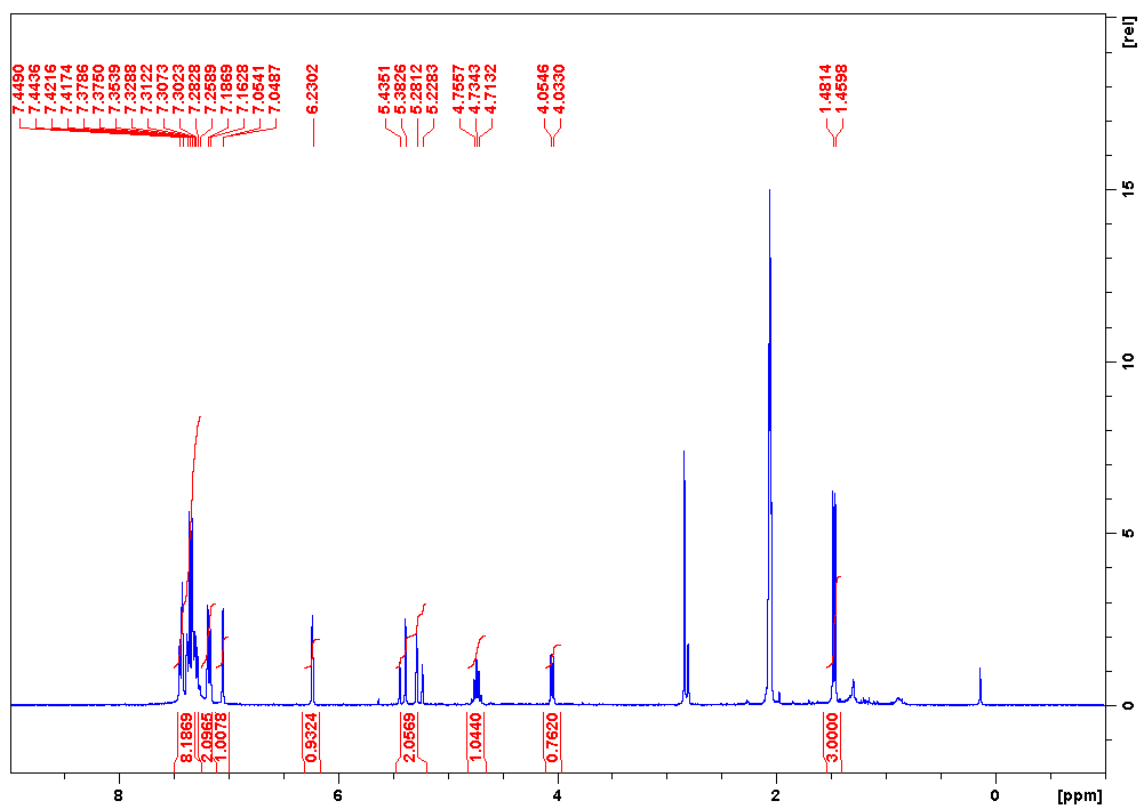


14d,  $^{13}\text{C}$  NMR (75 MHz, acetone- $\text{d}_6$ )

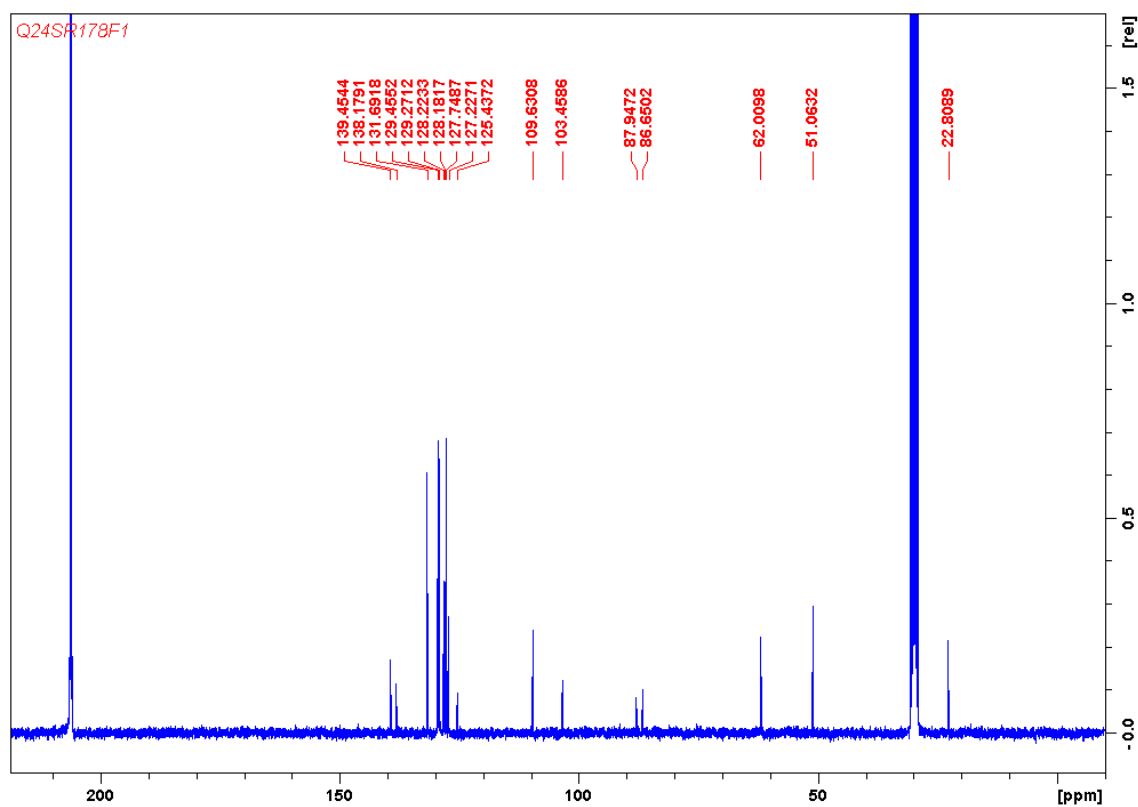




14e,  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )

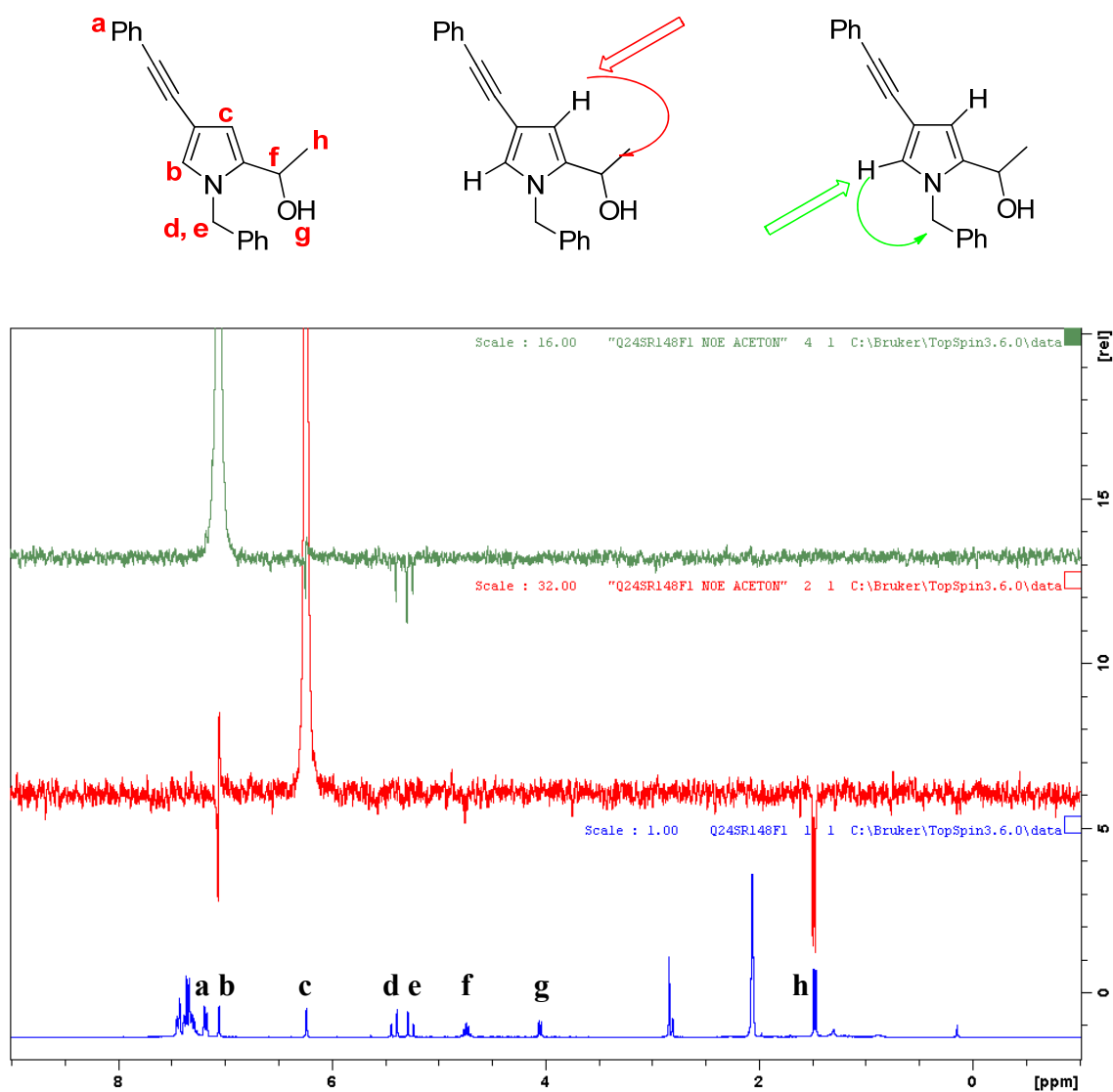


14e,  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )

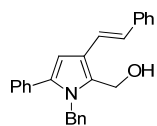




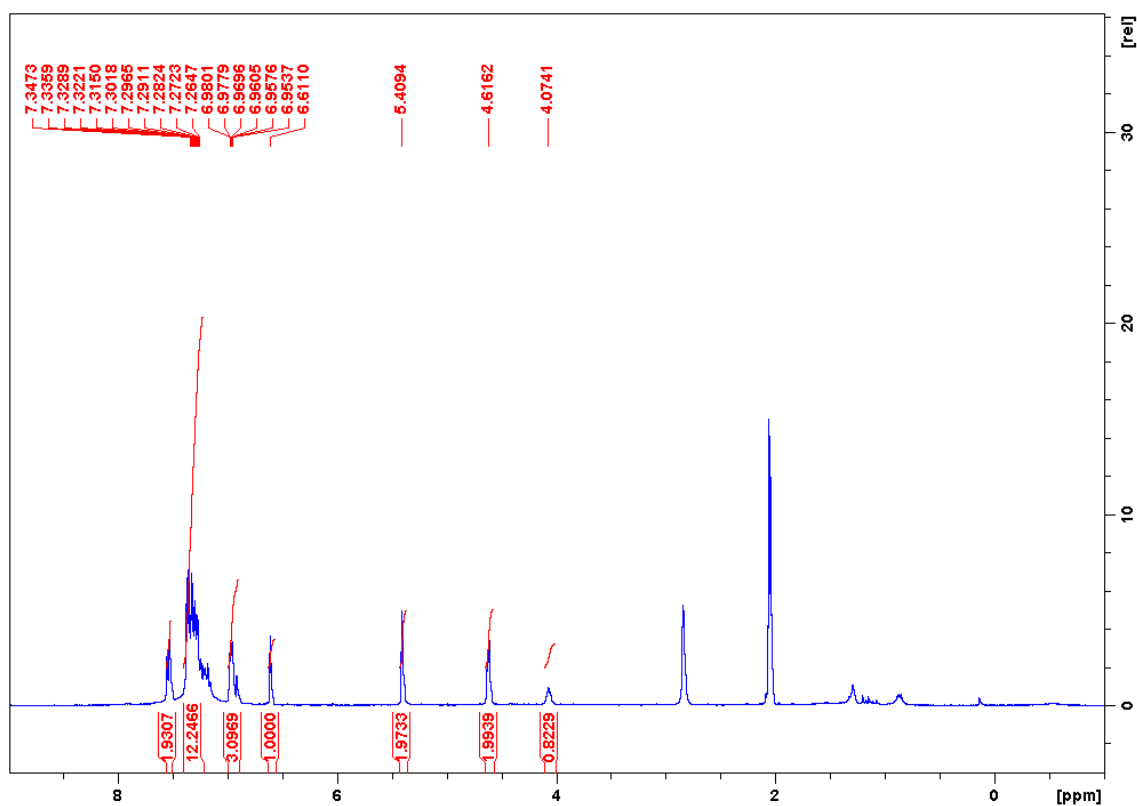
**14e, NOE (acetone-d<sub>6</sub>)**



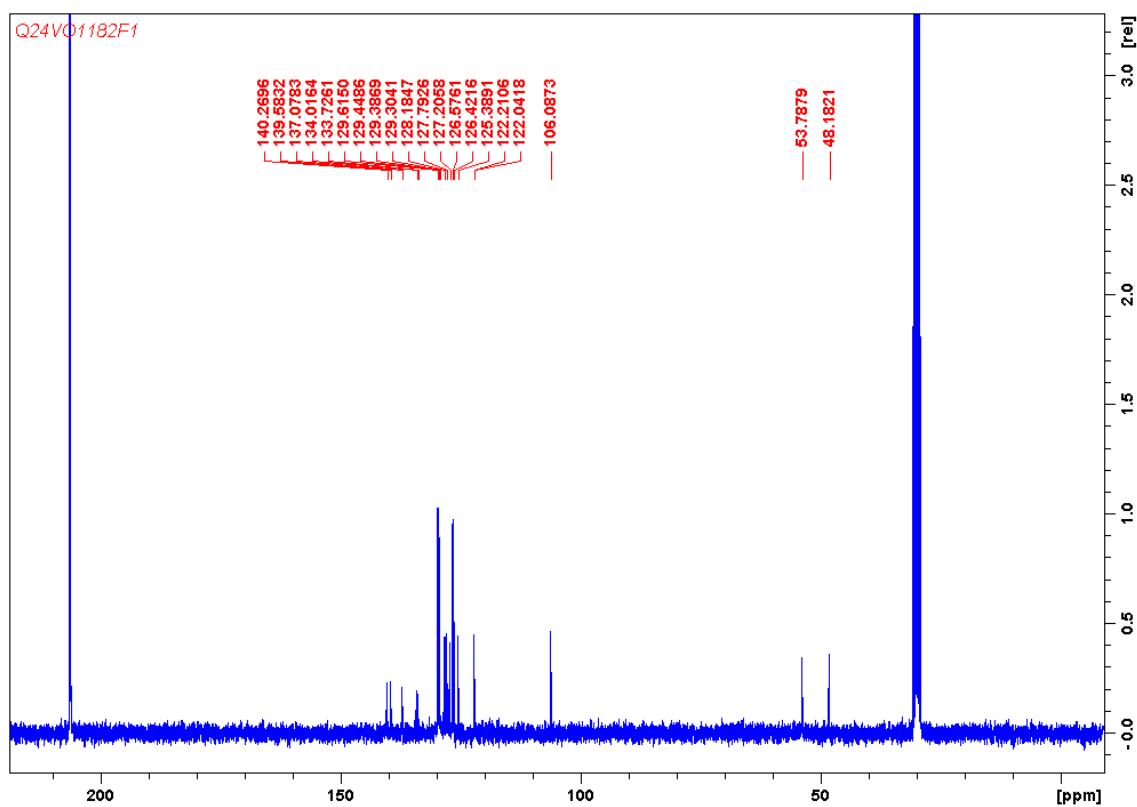
- a:** 7.25-7.17 (m, 10H).  
**b:** 7.05 (d,  $J = 1.7$  Hz, 1H).  
**c:** 6.23 (d,  $J = 1.0$  Hz, 1H).  
**d:** 5.41 (d,  $J = 15.8$  Hz, 1H).  
**e:** 5.25 (d,  $J = 15.8$  Hz, 1H).  
**f:** 4.73 (q,  $J = 6.5$  Hz, 1H).  
**g:** 4.04 (d,  $J = 6.5$  Hz, 1H).  
**h:** 1.43 (d,  $J = 6.5$  Hz, 3H).



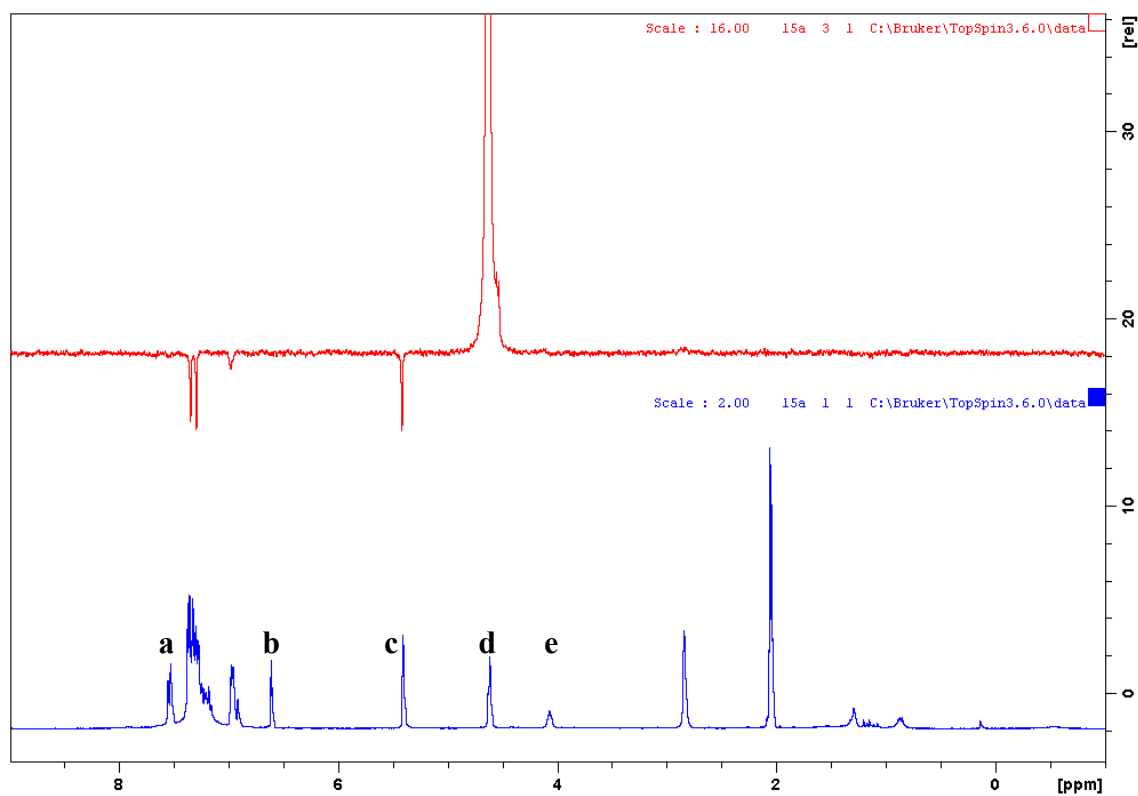
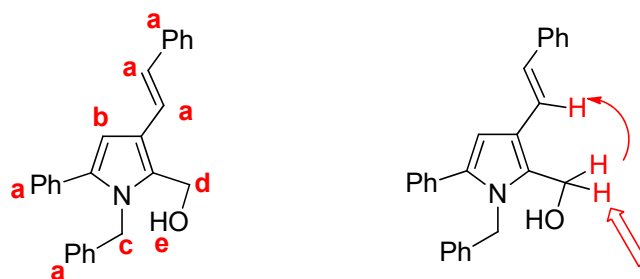
15a,  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )



15a,  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )



**15a, NOE (300 MHz, acetone-d<sub>6</sub>)**



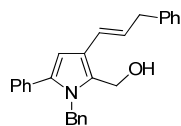
**a:** 7.55-6.96 (m, 17H).

**b:** 6.61 (s, 1H).

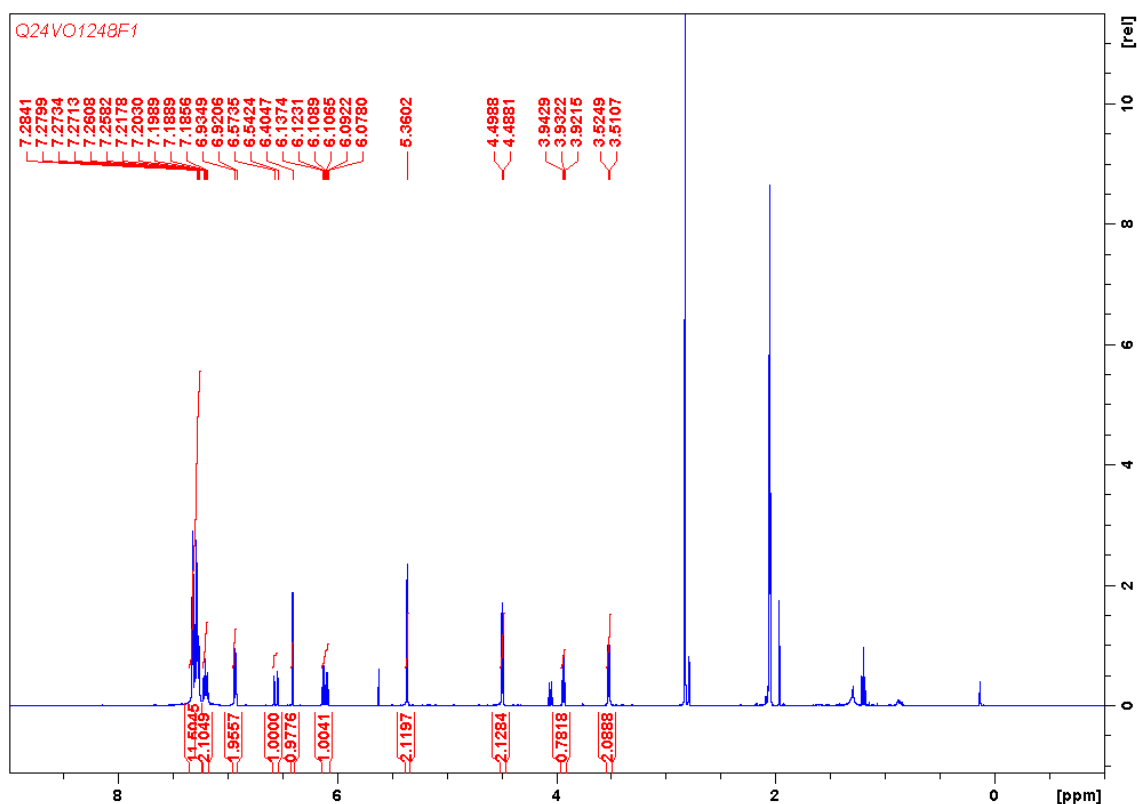
**c:** 5.41 (s, 2H).

**d:** 4.62 (s, 2H).

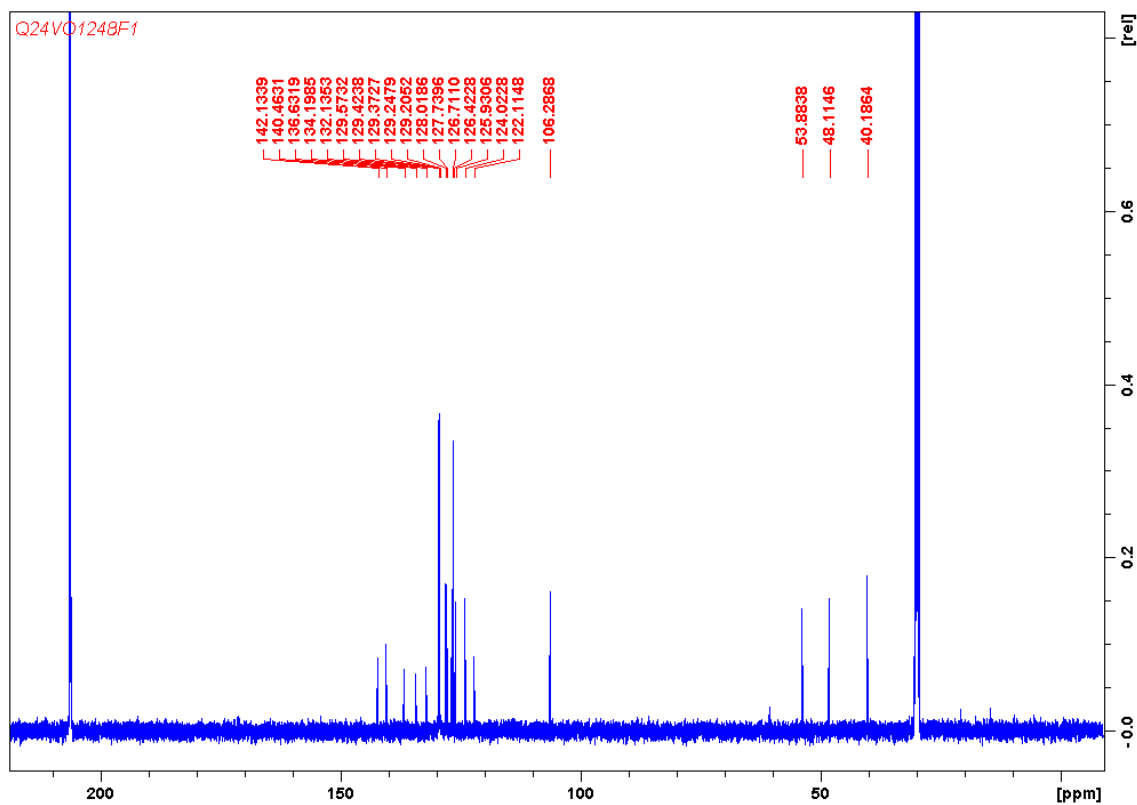
**e:** 4.07 (bs, 1H).

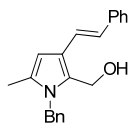


15b,  $^1\text{H}$  NMR (500 MHz, acetone- $\text{d}_6$ )

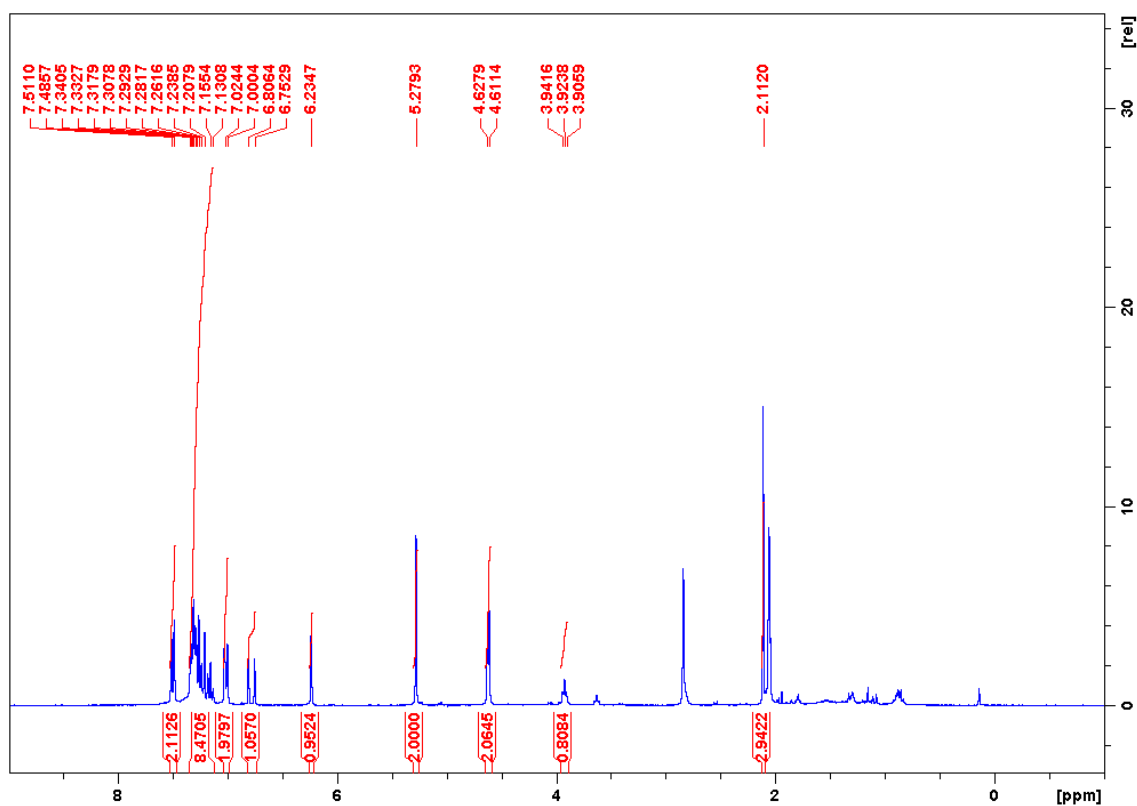


15b,  $^{13}\text{C}$  NMR (125 MHz, acetone- $\text{d}_6$ )

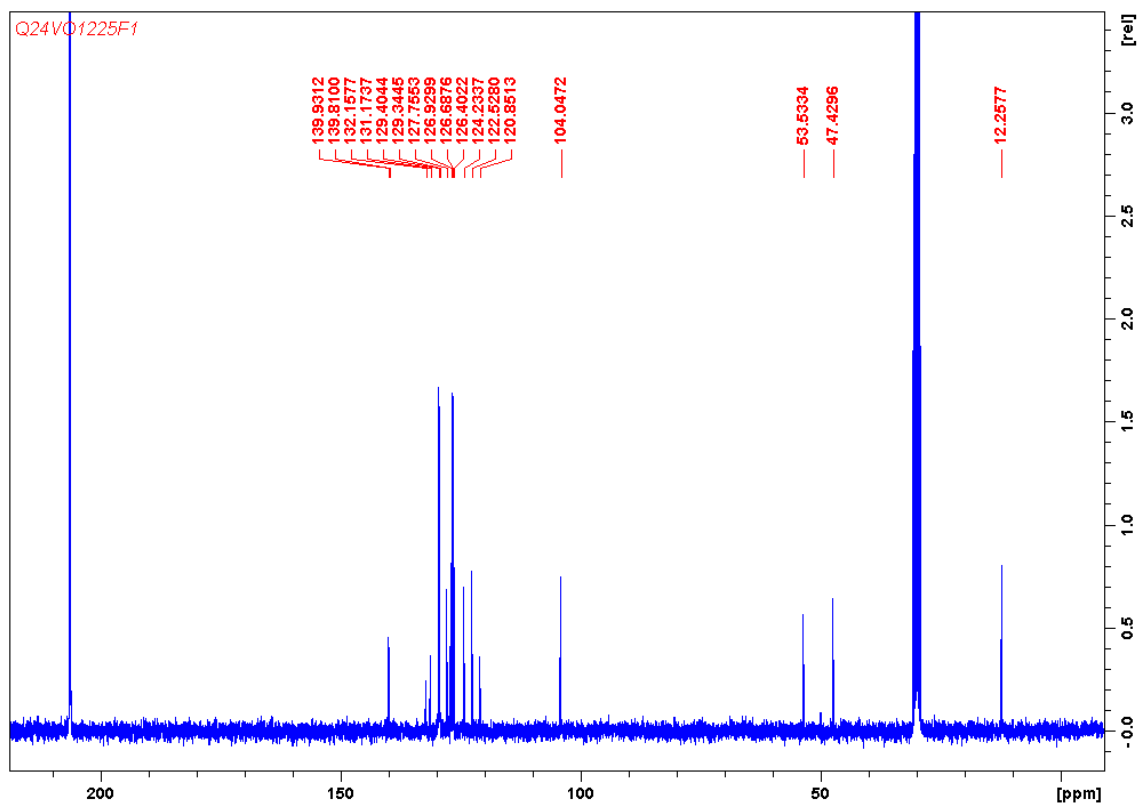




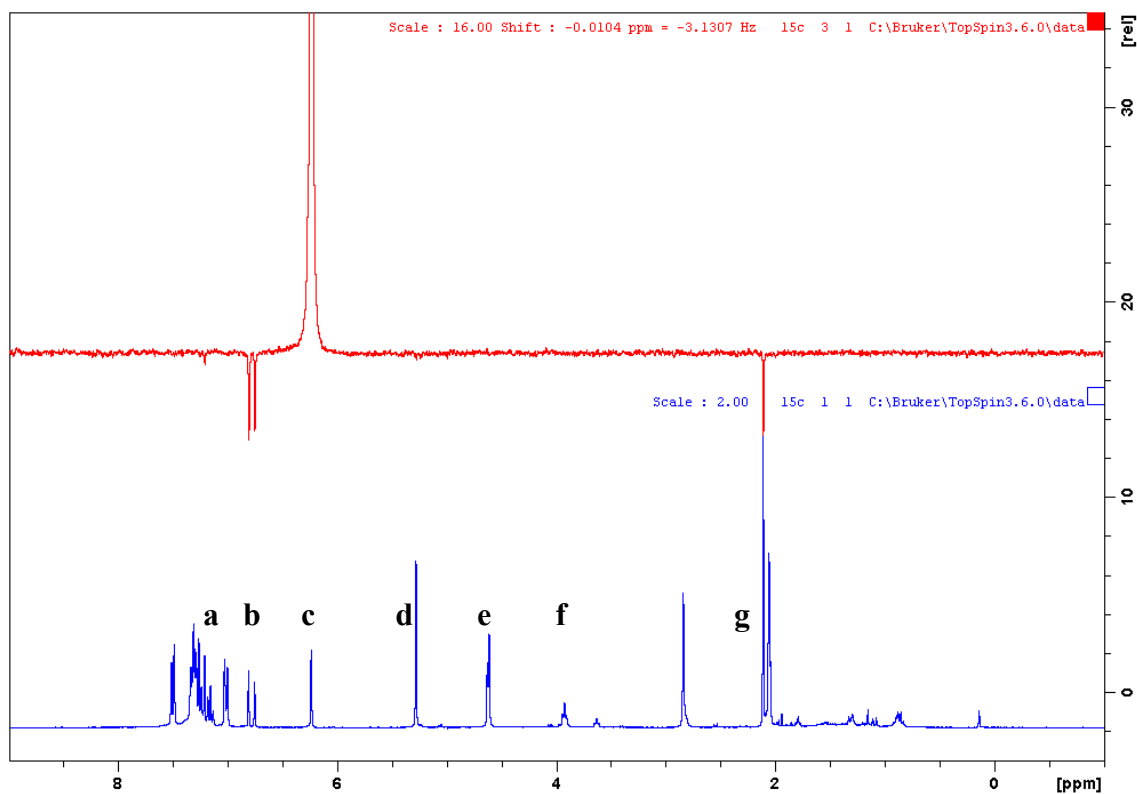
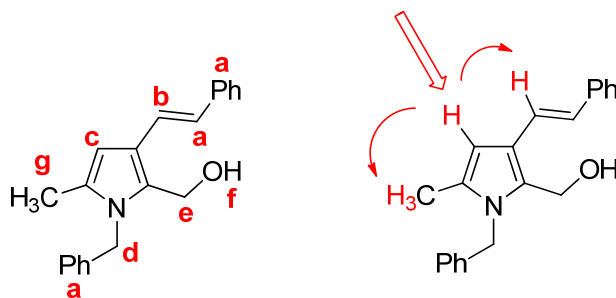
**15c,  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )**



**15c,  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )**



**15c, NOE (300 MHz, acetone-d<sub>6</sub>)**



**a:** 7.50-7.01 (m, 11H).

**b:** 6.78 (d,  $J = 16.1$  Hz, 1H).

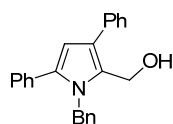
**c:** 6.23 (s, 1H).

**d:** 5.28 (s, 2H).

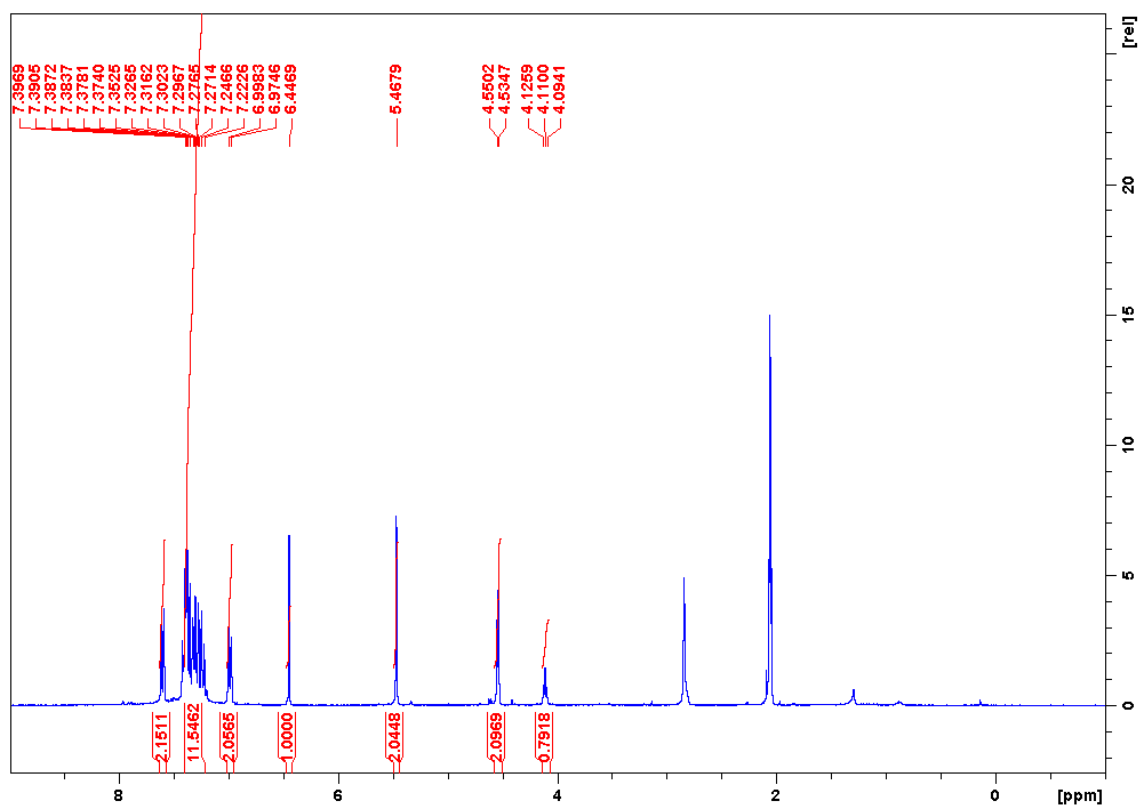
**e:** 4.62-4.61 (m, 2H).

**f:** 3.92 (t,  $J = 5.4$  Hz, 1H).

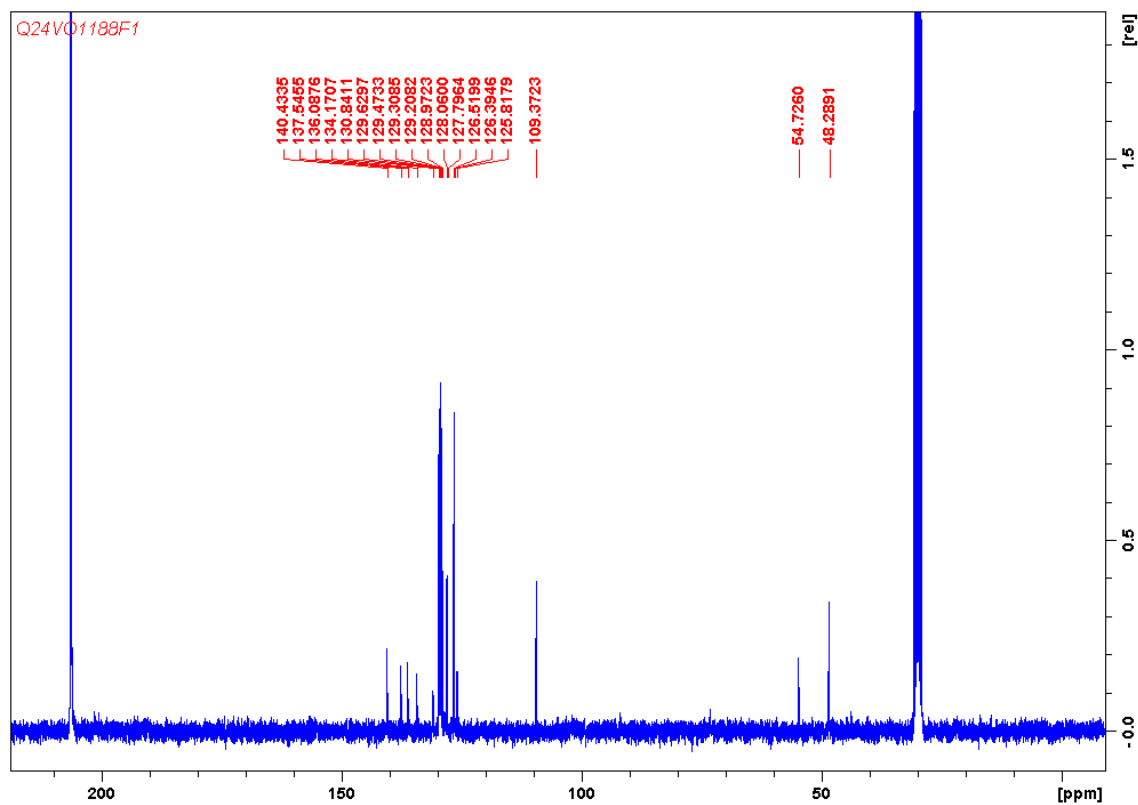
**g:** 2.11 (s, 3H).

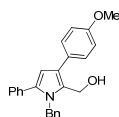


15d,  $^1\text{H}$  NMR (300 MHz, acetone- $\text{d}_6$ )

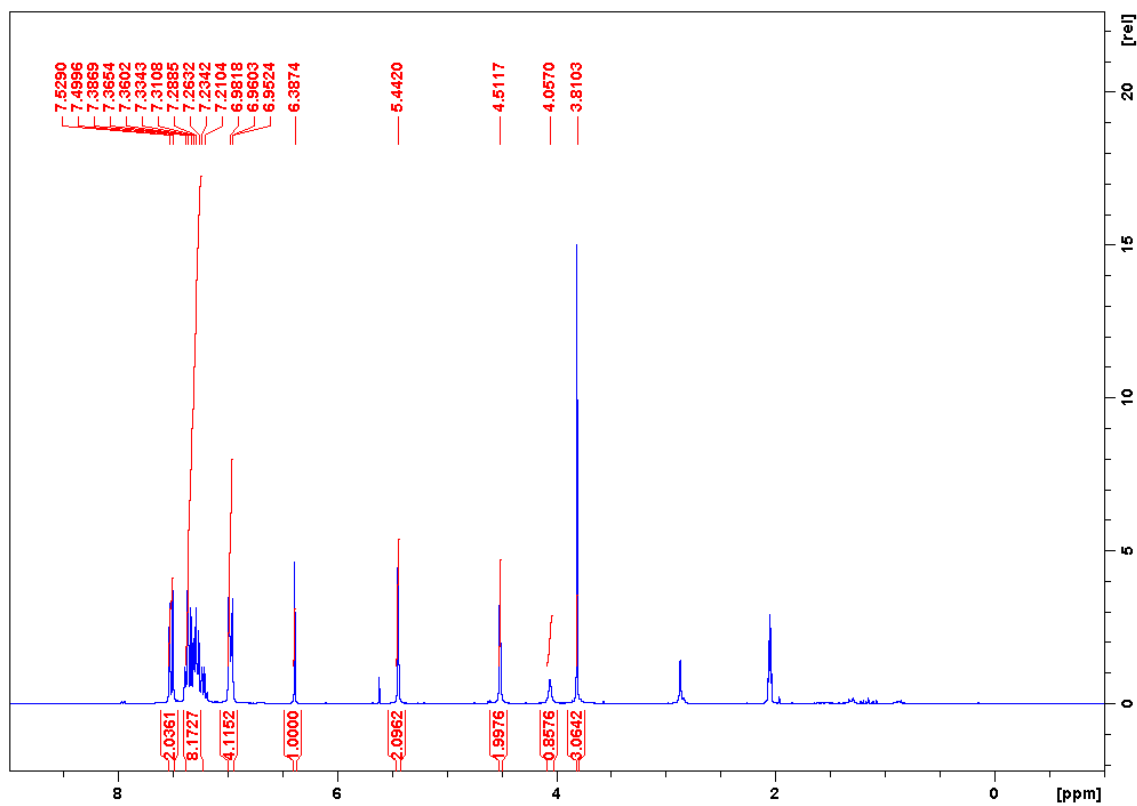


15d,  $^{13}\text{C}$  NMR (75 MHz, acetone- $\text{d}_6$ )

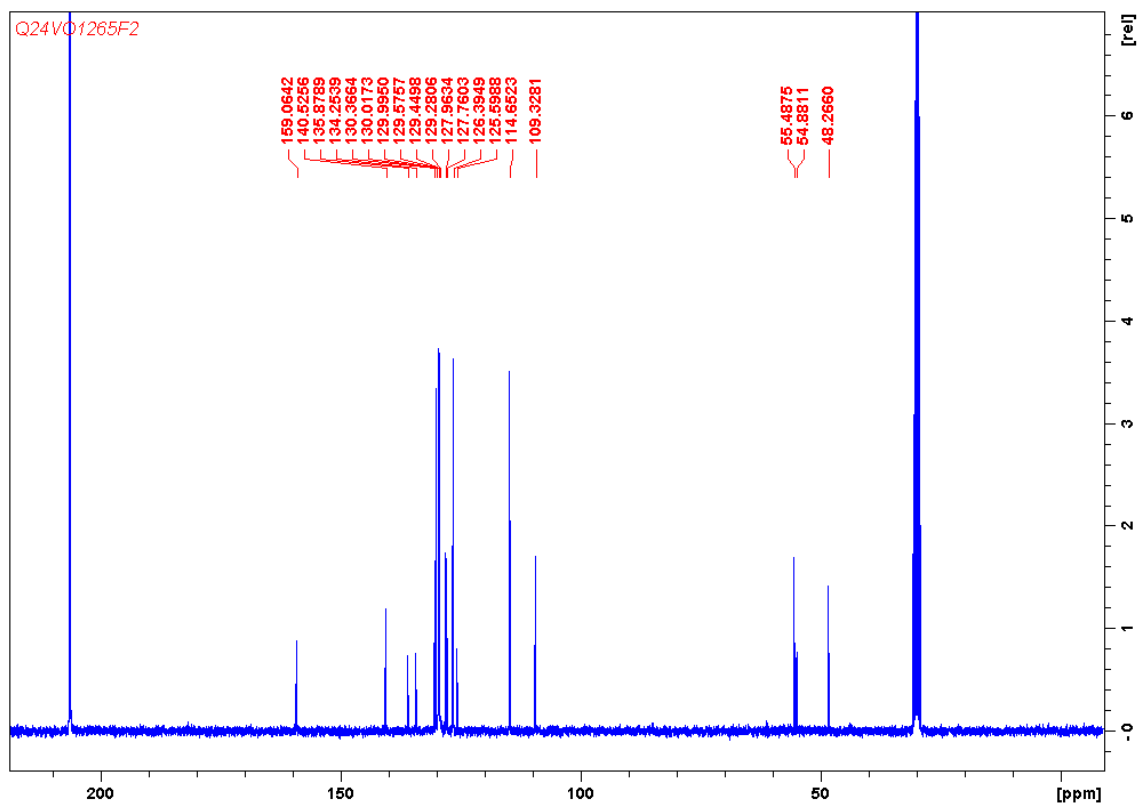




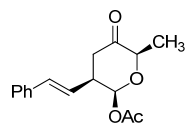
**15e,  $^1\text{H}$  NMR (300 MHz, acetone- $d_6$ )**



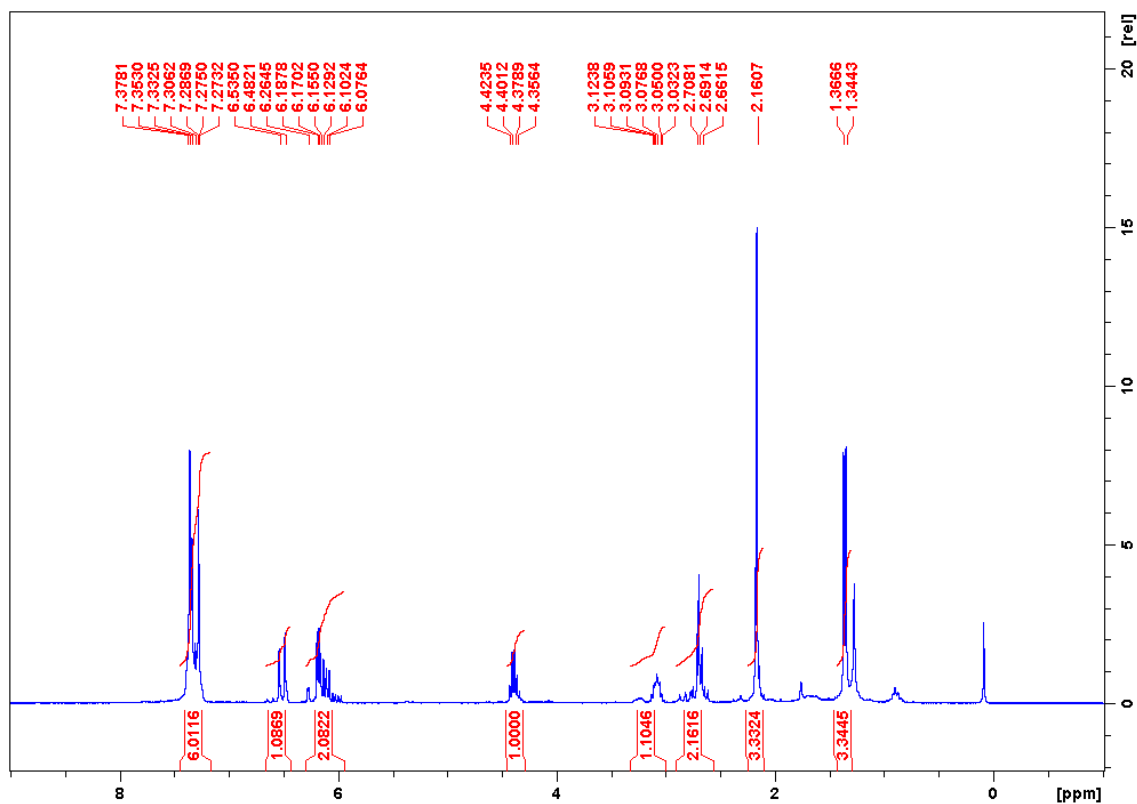
**15e,  $^{13}\text{C}$  NMR (75 MHz, acetone- $d_6$ )**



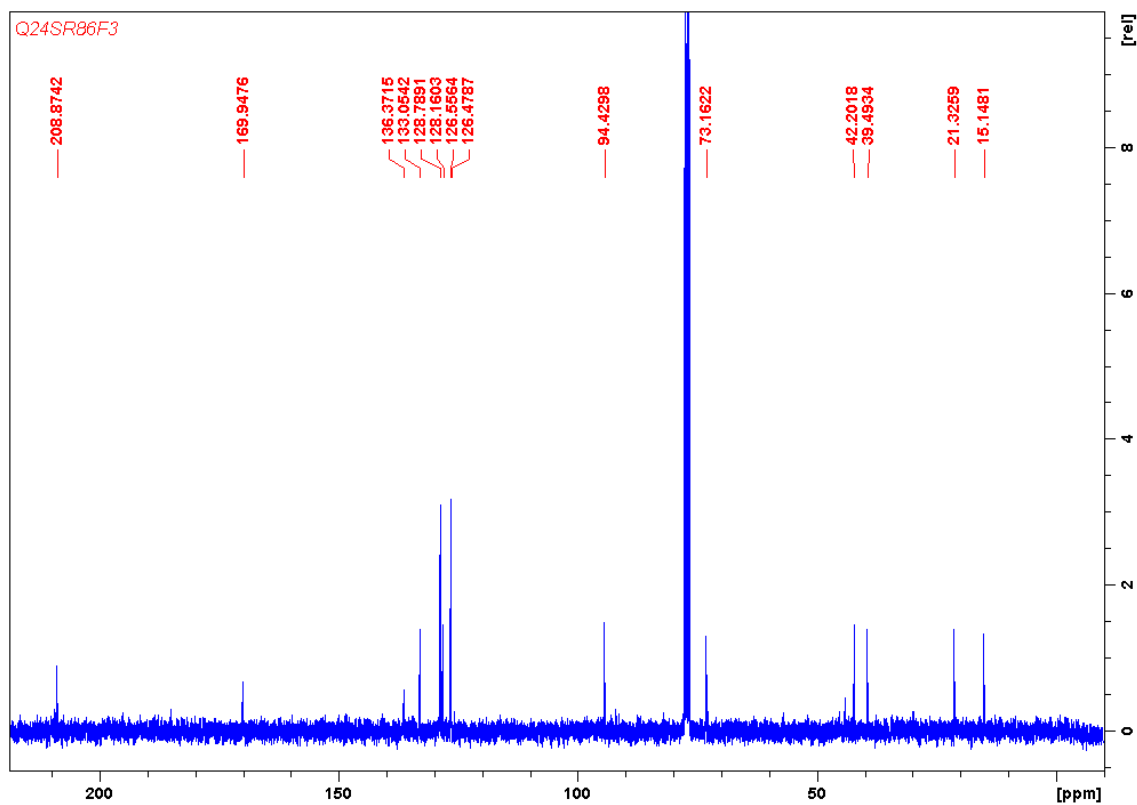




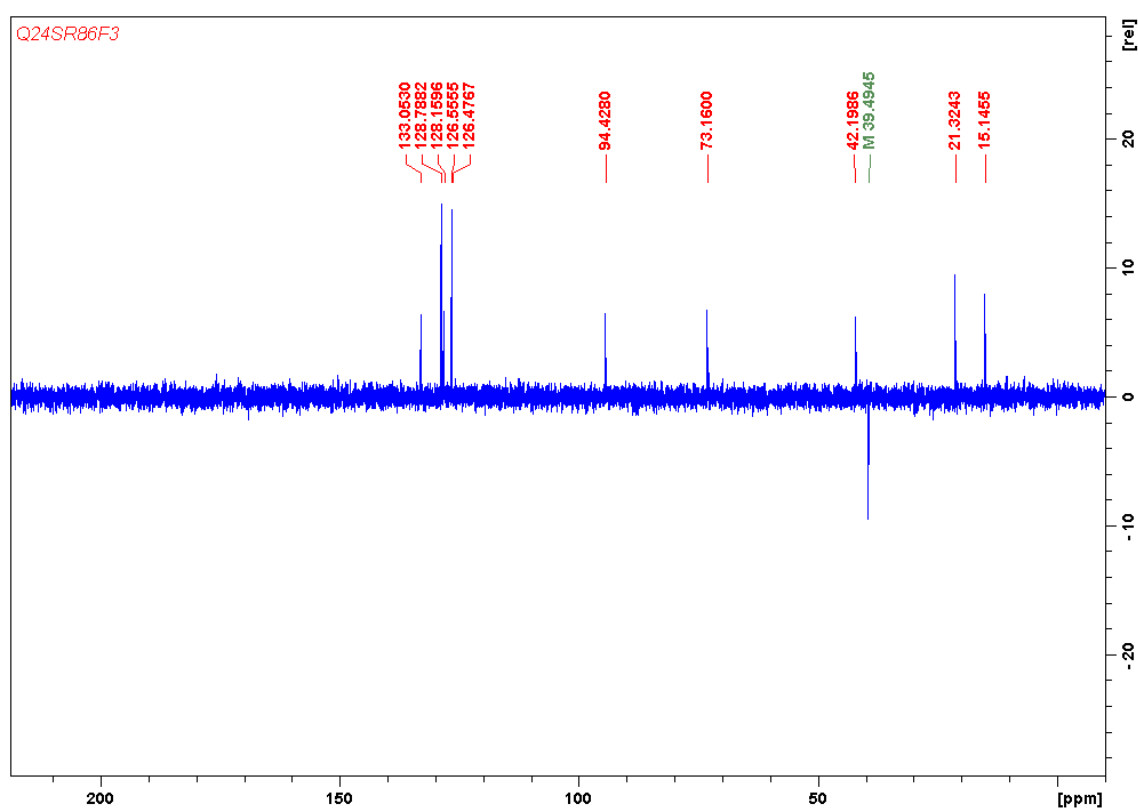
16a,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



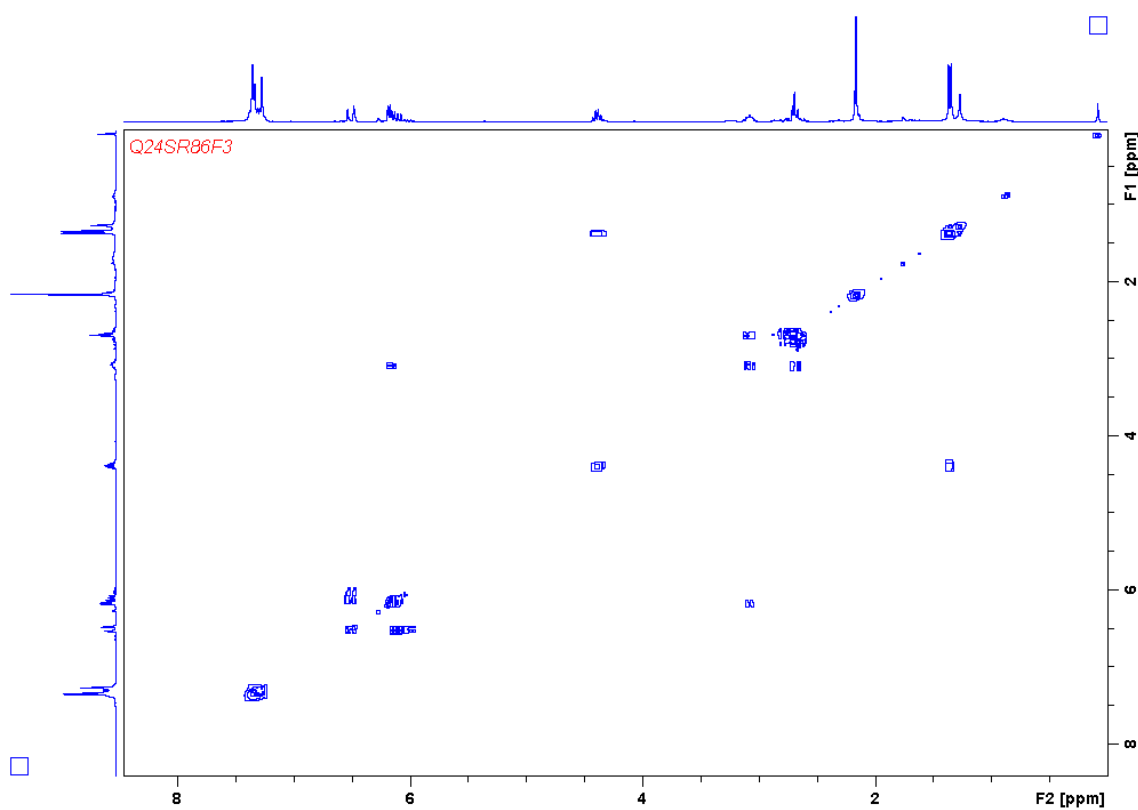
16a,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )



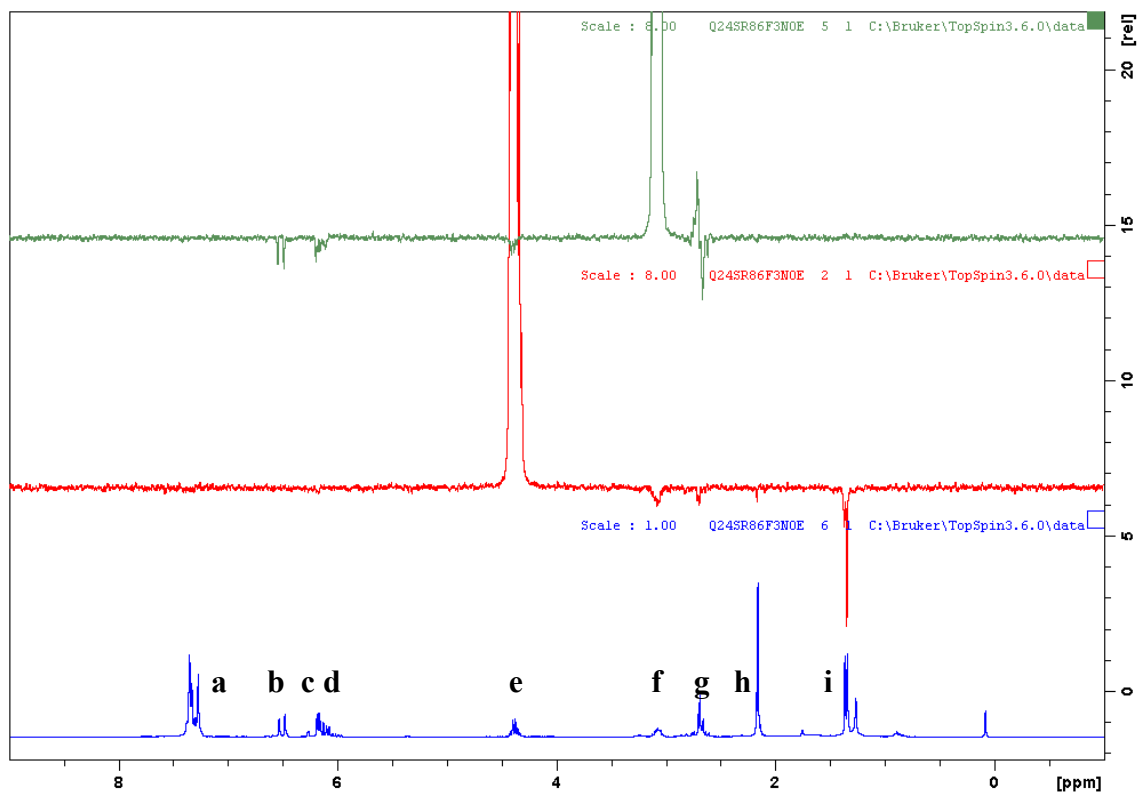
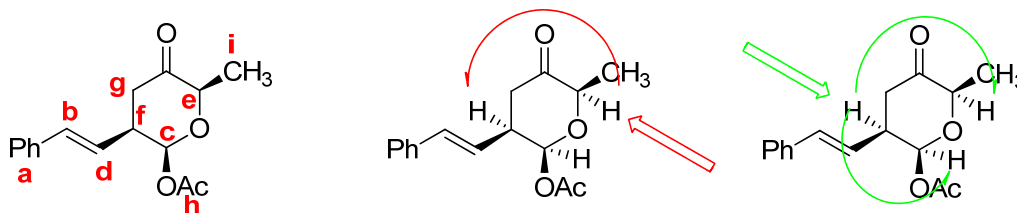
# 16a, DEPT (75 MHz, CDCl<sub>3</sub>)



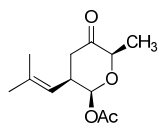
# 16a, COSY (CDCl<sub>3</sub>)



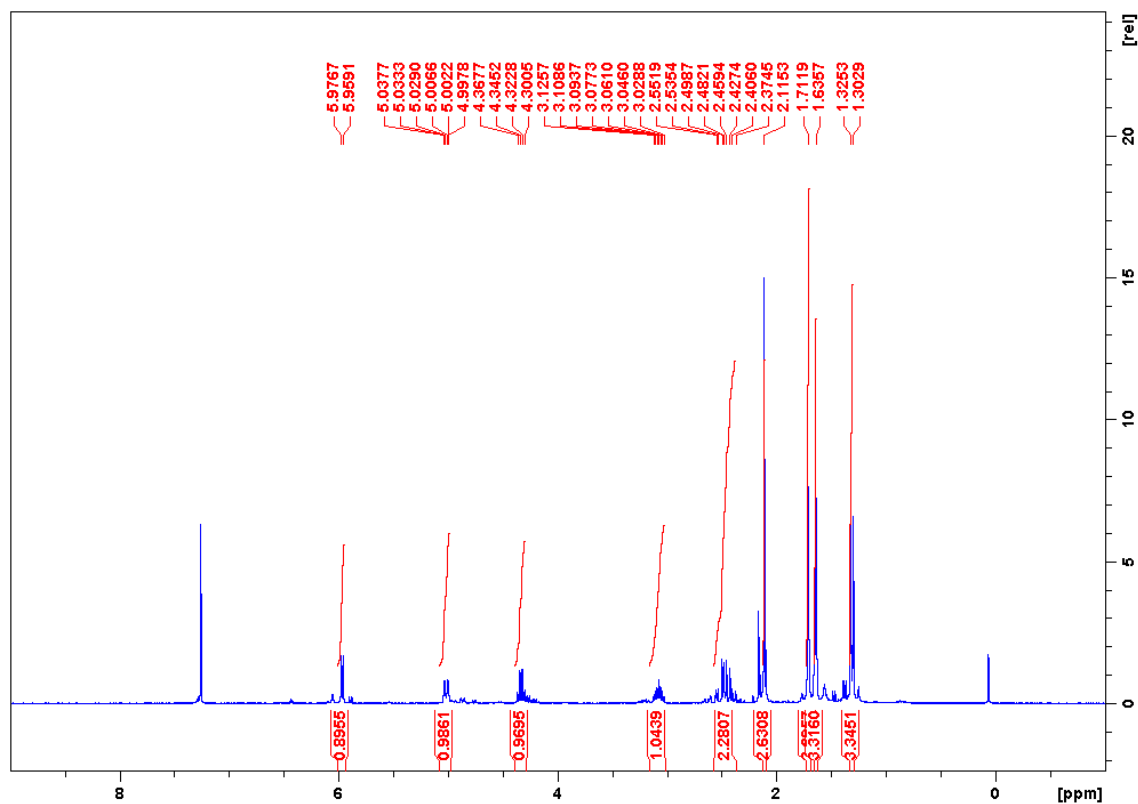
**16a, NOE (CDCl<sub>3</sub>)**



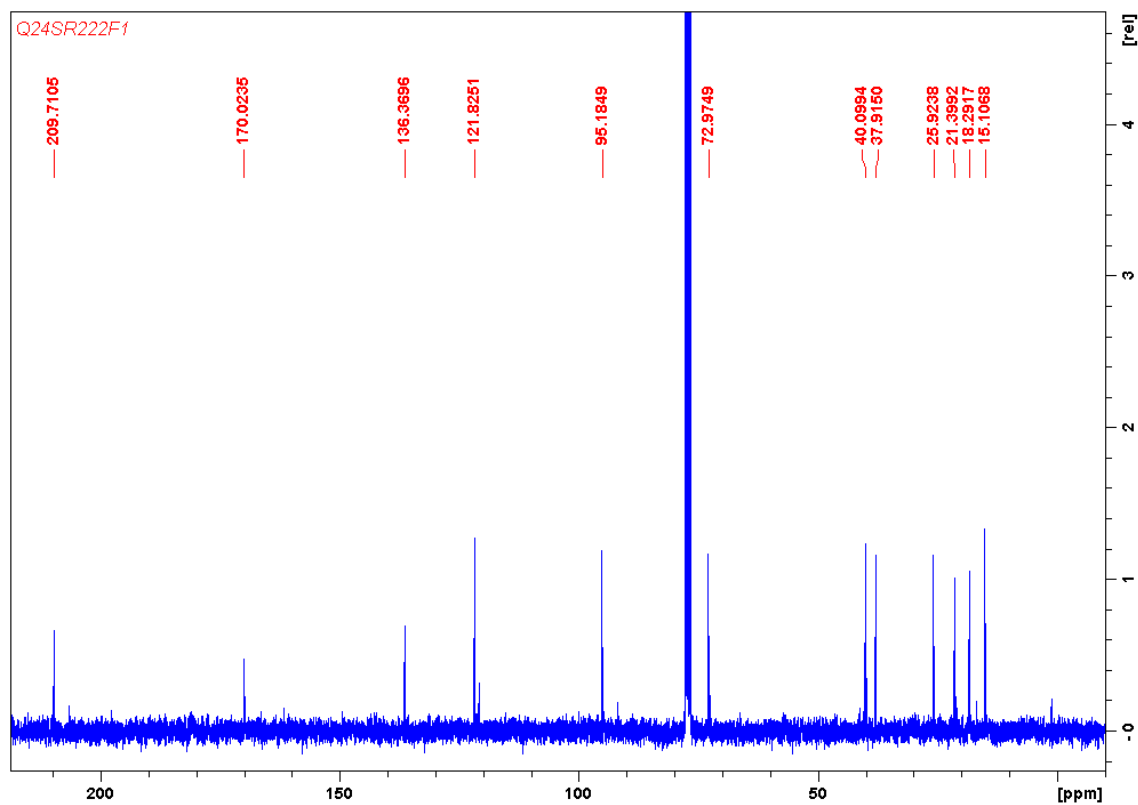
- a:** 7.14-7.34 (m, 5H).
- b:** 6.42 (d,  $J = 15.8$  Hz, 1H).
- c:** 6.09 (d,  $J = 5.4$  Hz, 1H).
- d:** 6.03 (dd,  $J = 15.8$  Hz,  $J = 7.7$  Hz, 1H).
- e:** 4.31 (q,  $J = 6.8$  Hz, 1H).
- f:** 2.93-3.06 (m, 1H).
- g:** 2.51-2.69 (m, 2H).
- h:** 2.08 (s, 3H).
- i:** 1.27 (d,  $J = 6.8$  Hz, 3H).

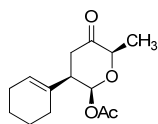


16b,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

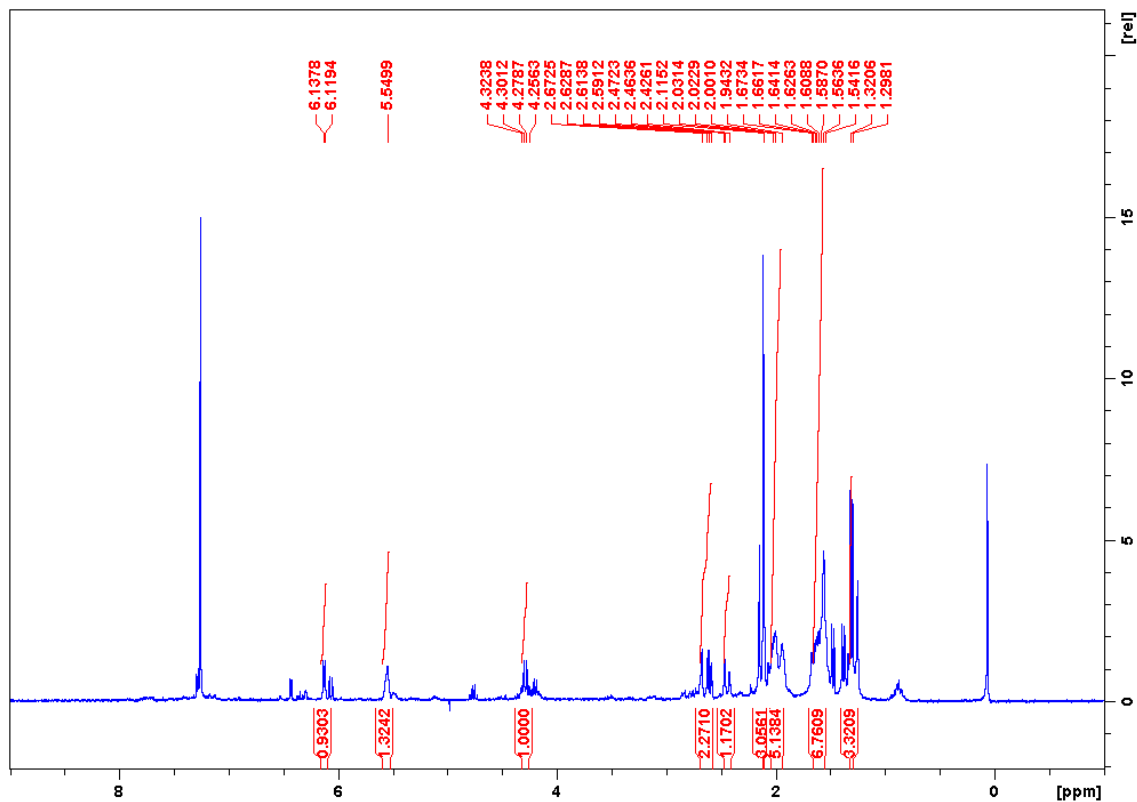


16b,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

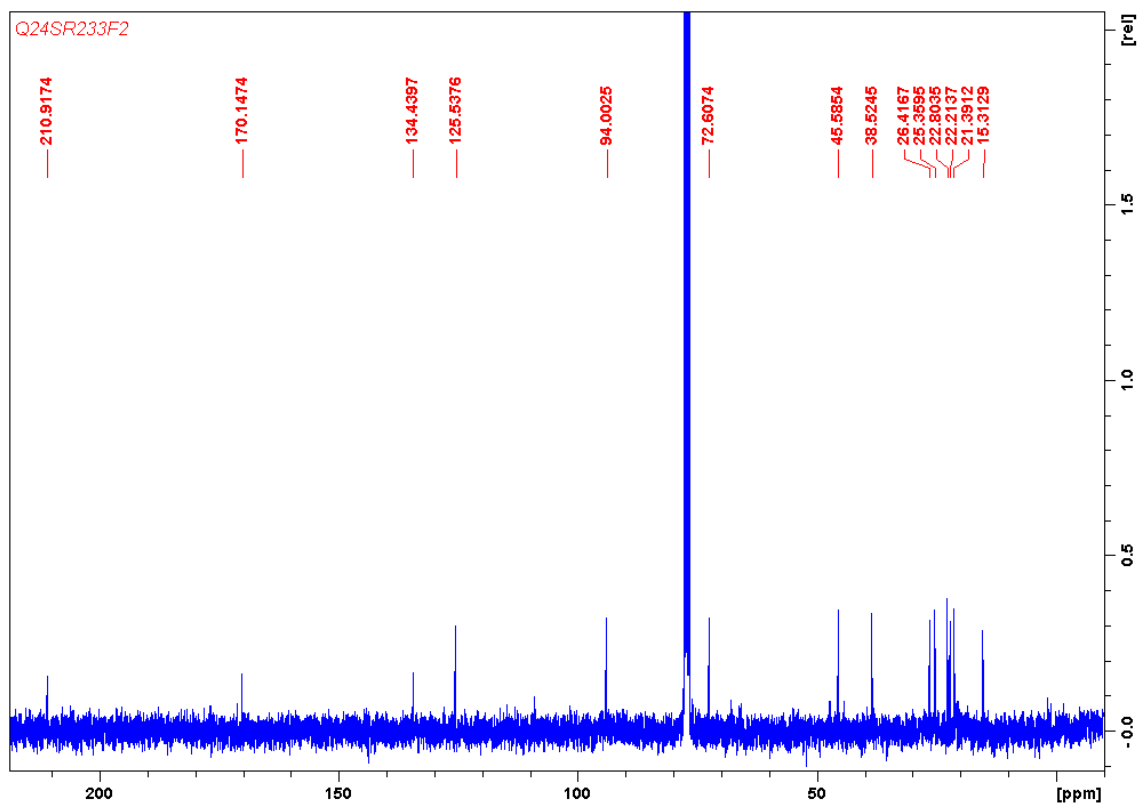


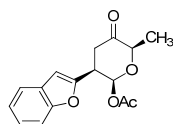


16c,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

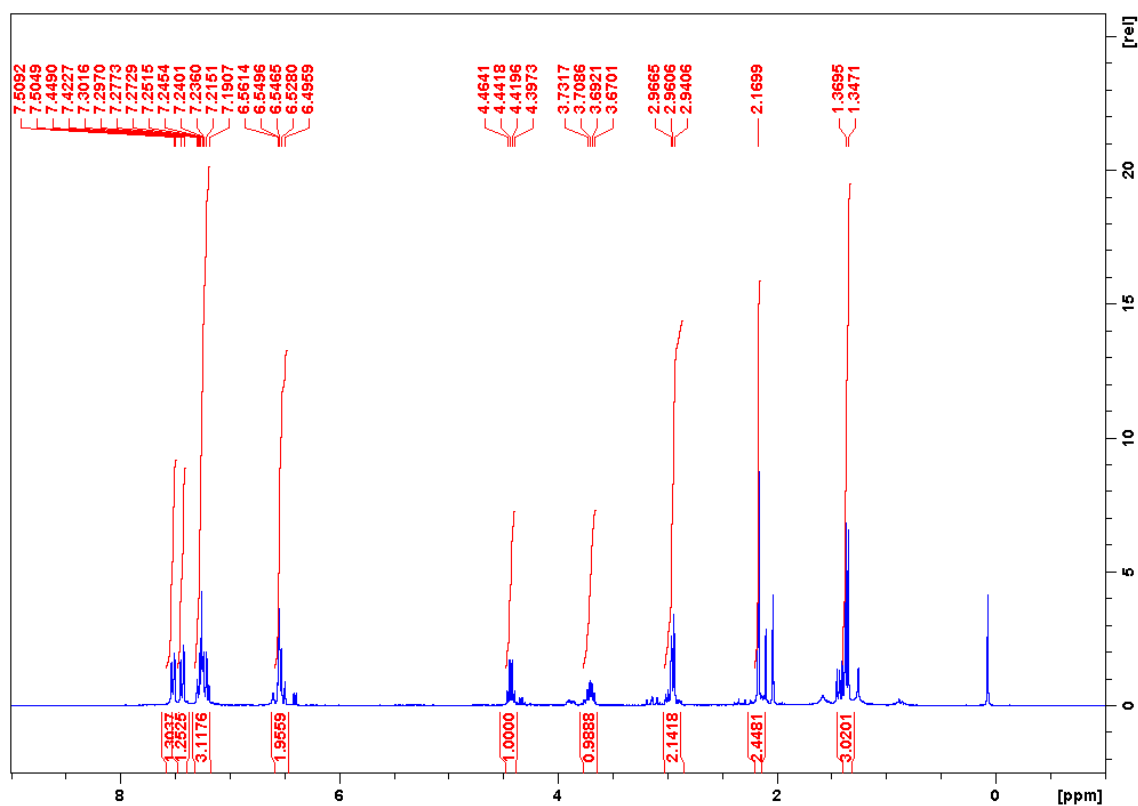


16c,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

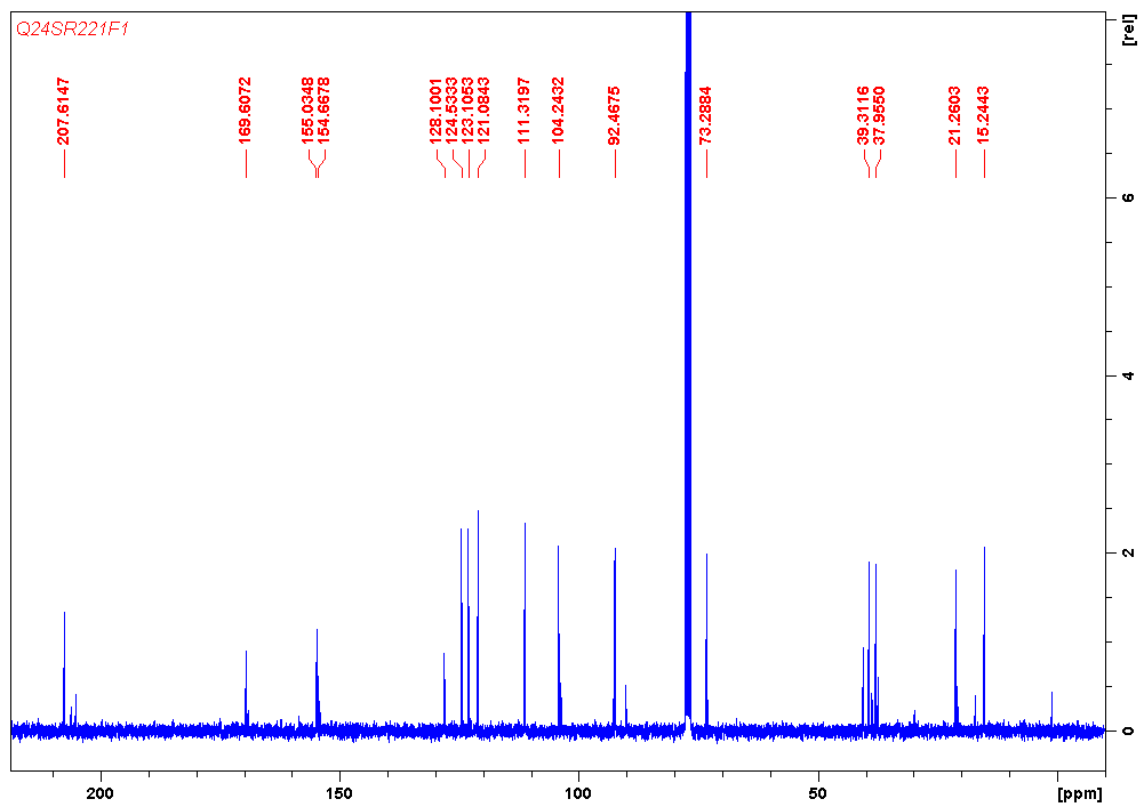


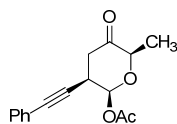


16d,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )

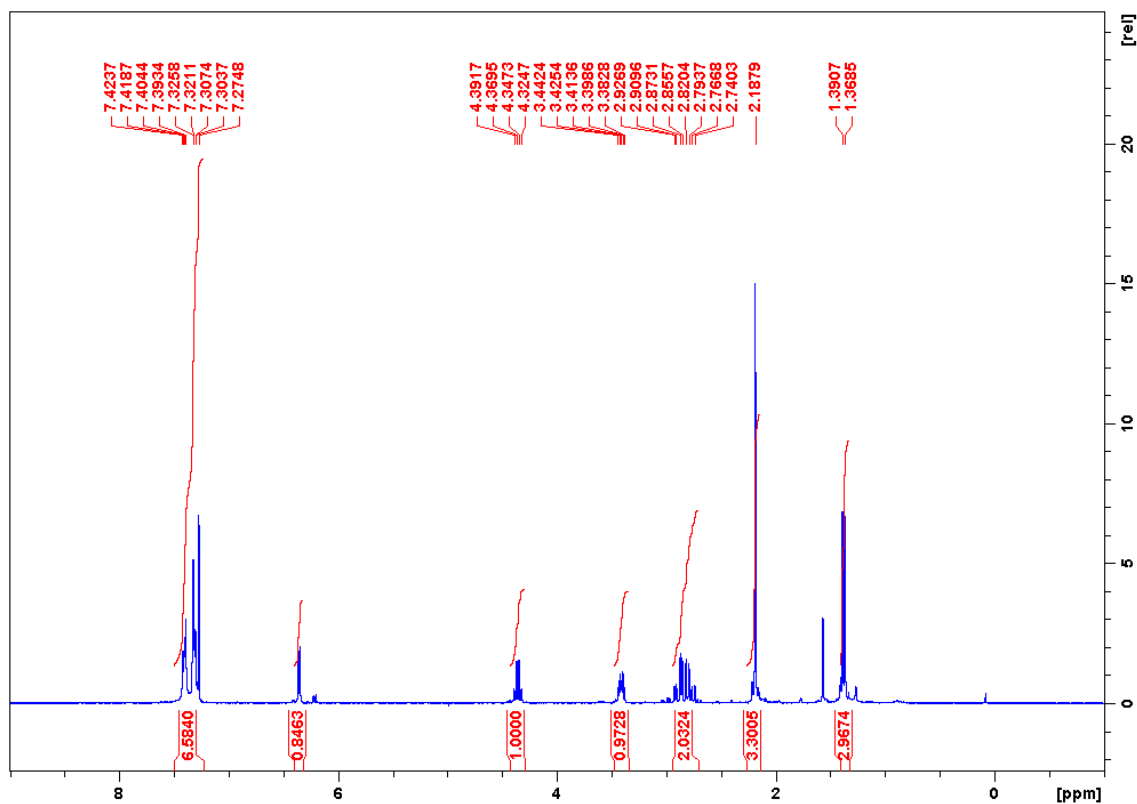


16d,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

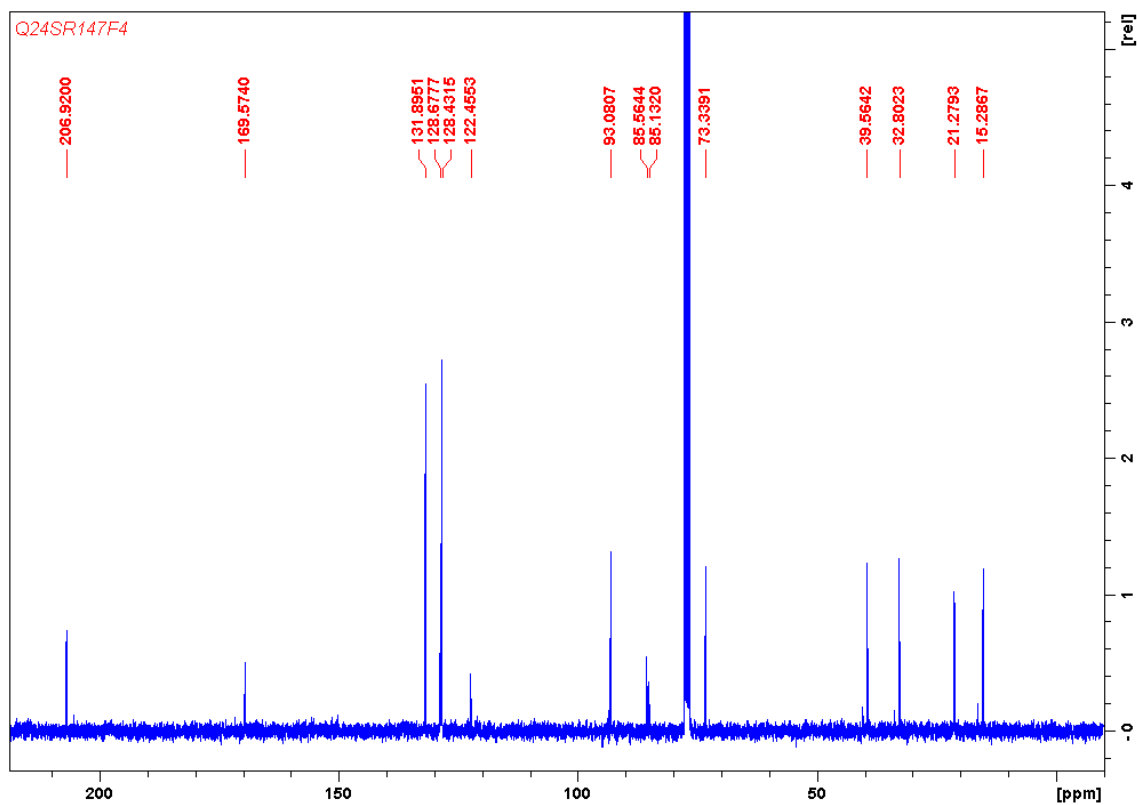




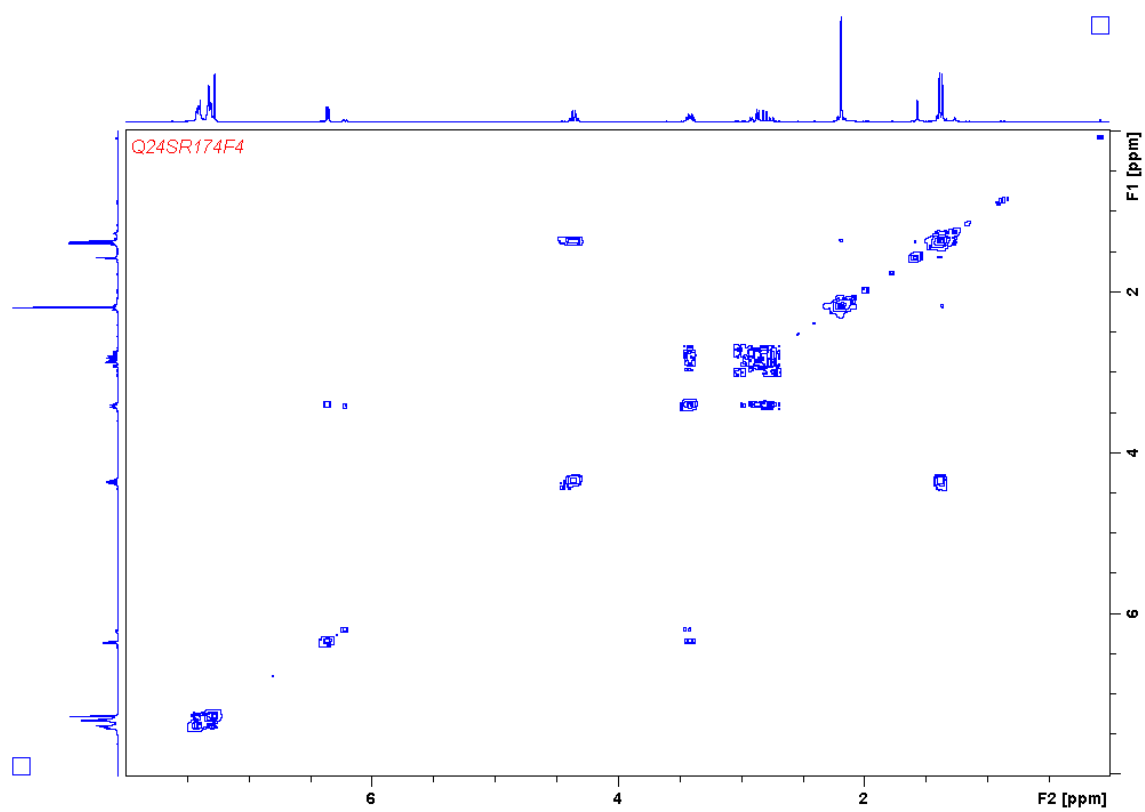
16e,  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )



16e,  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )

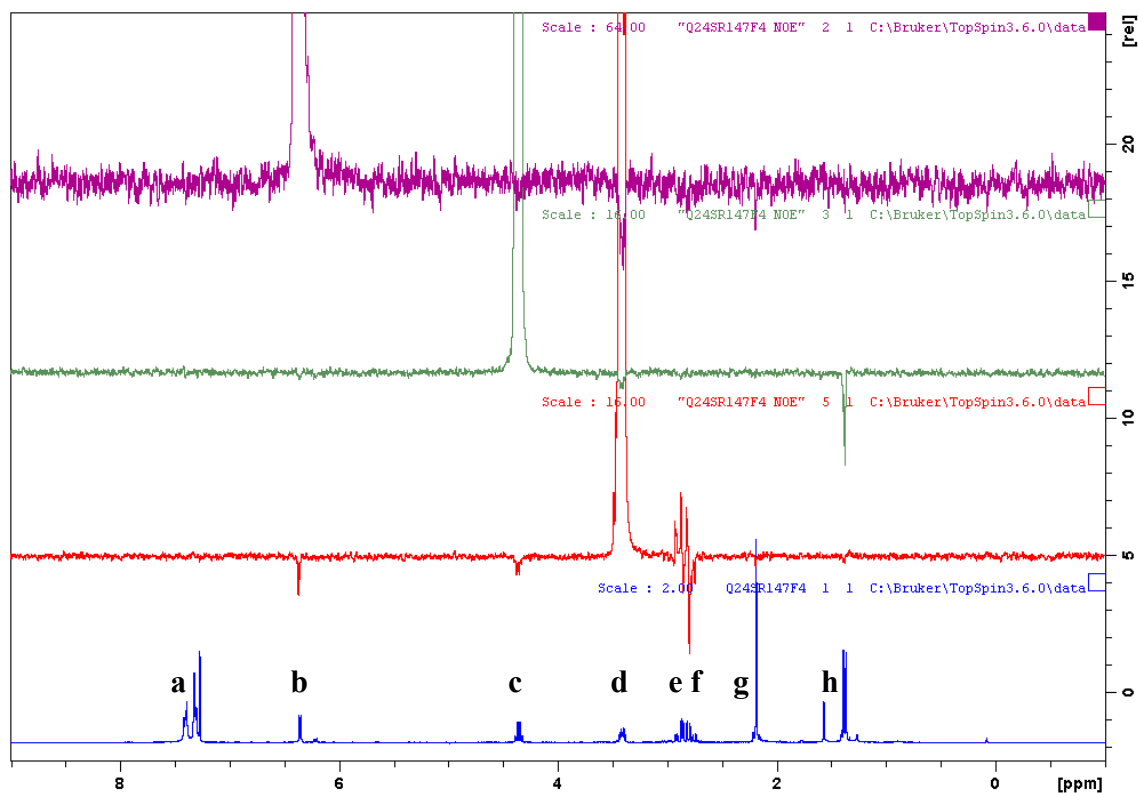
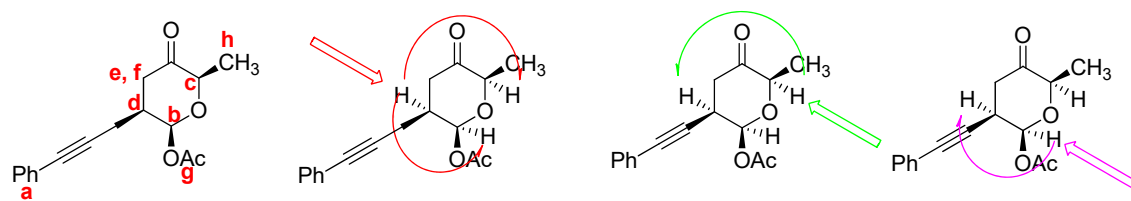


16e, COSY (CDCl<sub>3</sub>)





**16e, NOE (CDCl<sub>3</sub>)**



- a:** 7.23-7.46 (m, 5H).  
**b:** 6.36 (d,  $J = 4.6$  Hz, 1H).  
**c:** 4.36 (q,  $J = 6.9$  Hz, 1H).  
**d:** 3.37-3.45 (m, 1H).  
**e:** 2.89 (dd,  $J = 16.0$  Hz,  $J = 5.4$  Hz, 1H).  
**f:** 2.78 (dd,  $J = 16.0$  Hz,  $J = 8.0$  Hz, 1H).  
**g:** 2.18 (s, 3H).  
**h:** 1.38 (d,  $J = 6.5$  Hz, 3H).