

## Supporting Information

### Diastereoselective allylation-based asymmetric total synthesis of 1,10-*seco*-guaianolides

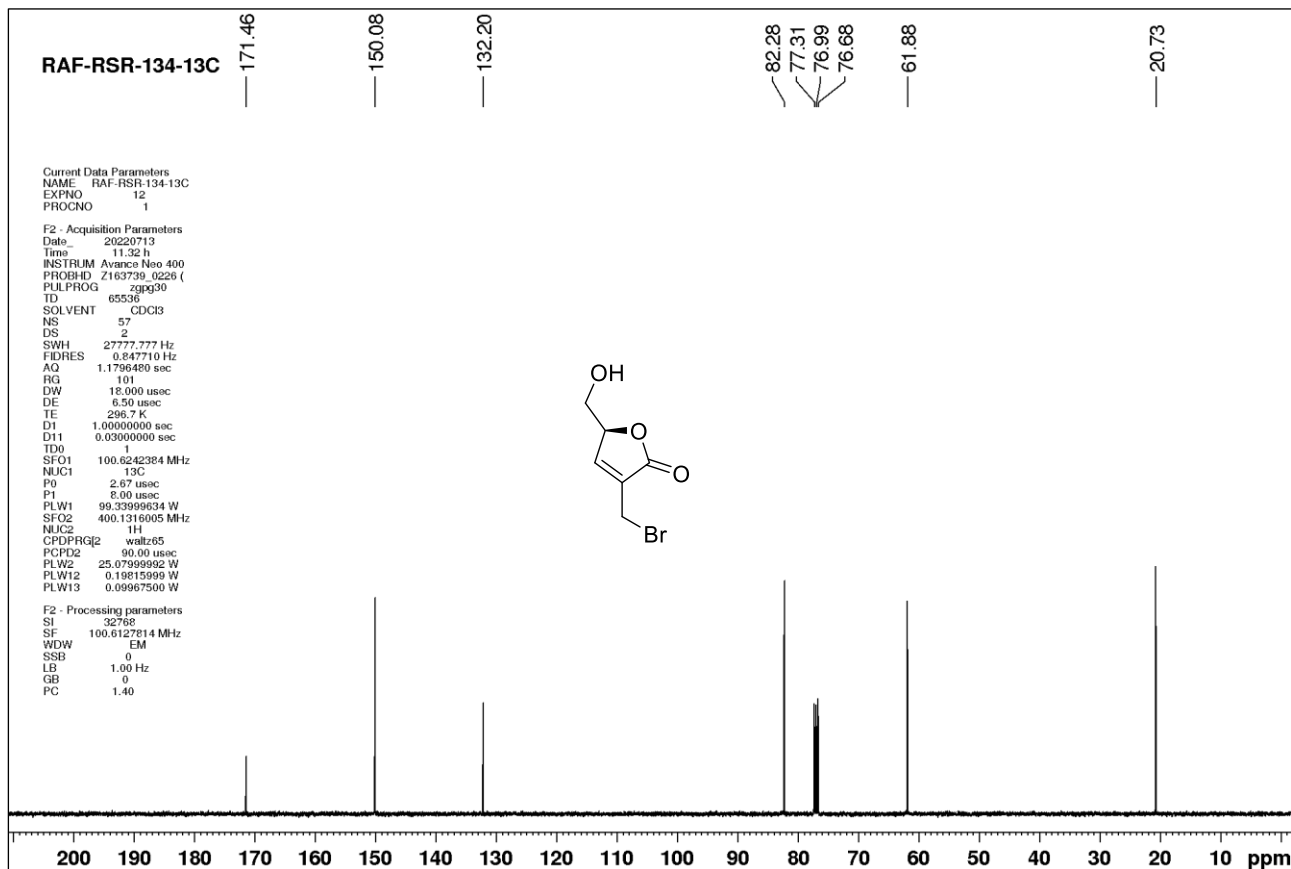
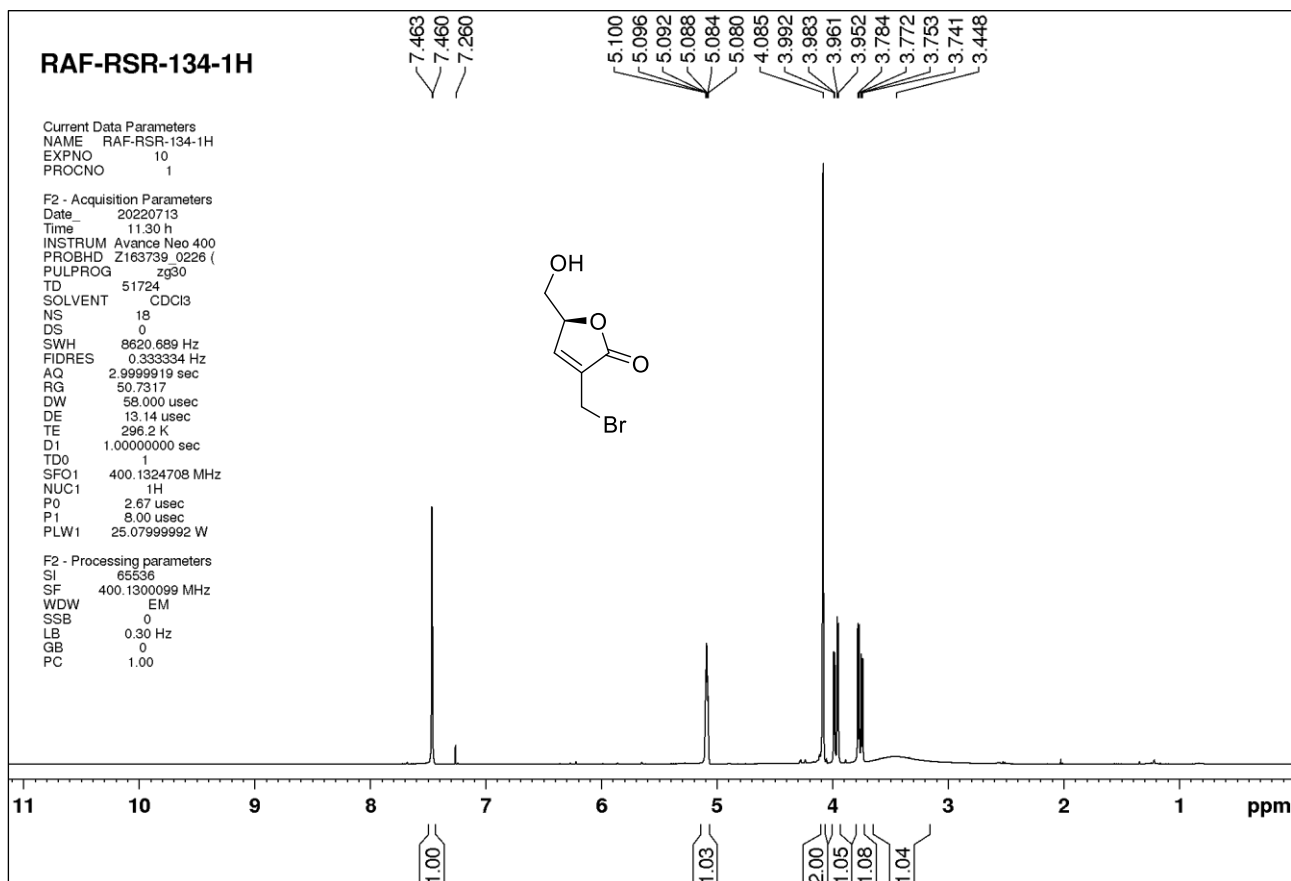
Rodney A. Fernandes,\* and Ravikant S. Ranjan

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076,  
Maharashtra, India

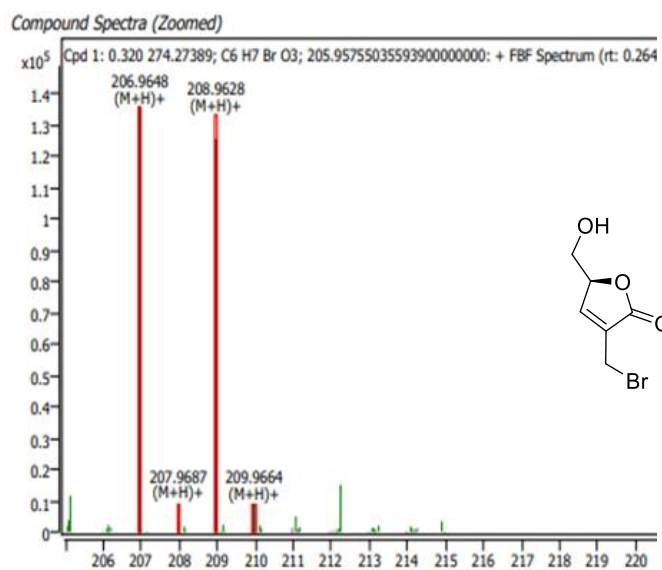
Email: [rfernand@chem.iitb.ac.in](mailto:rfernand@chem.iitb.ac.in)

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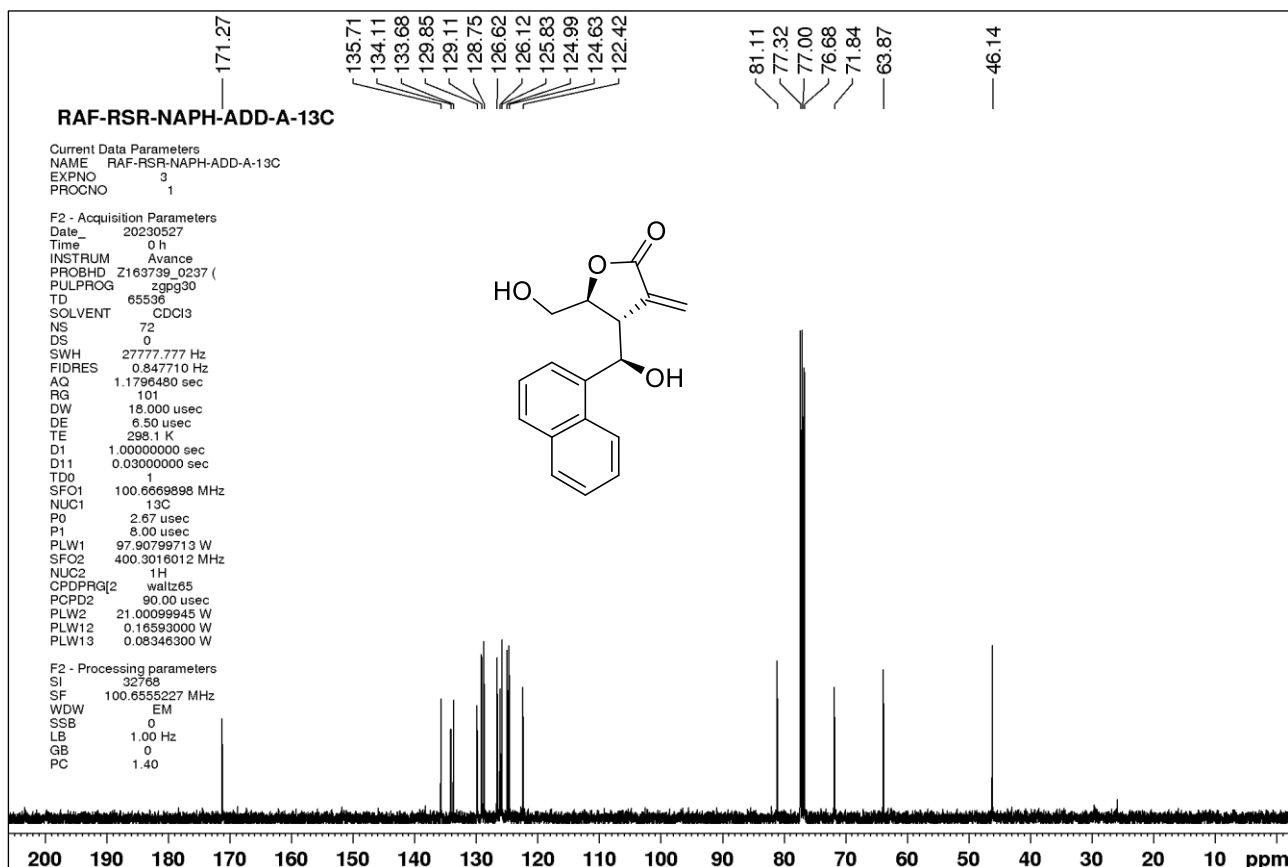
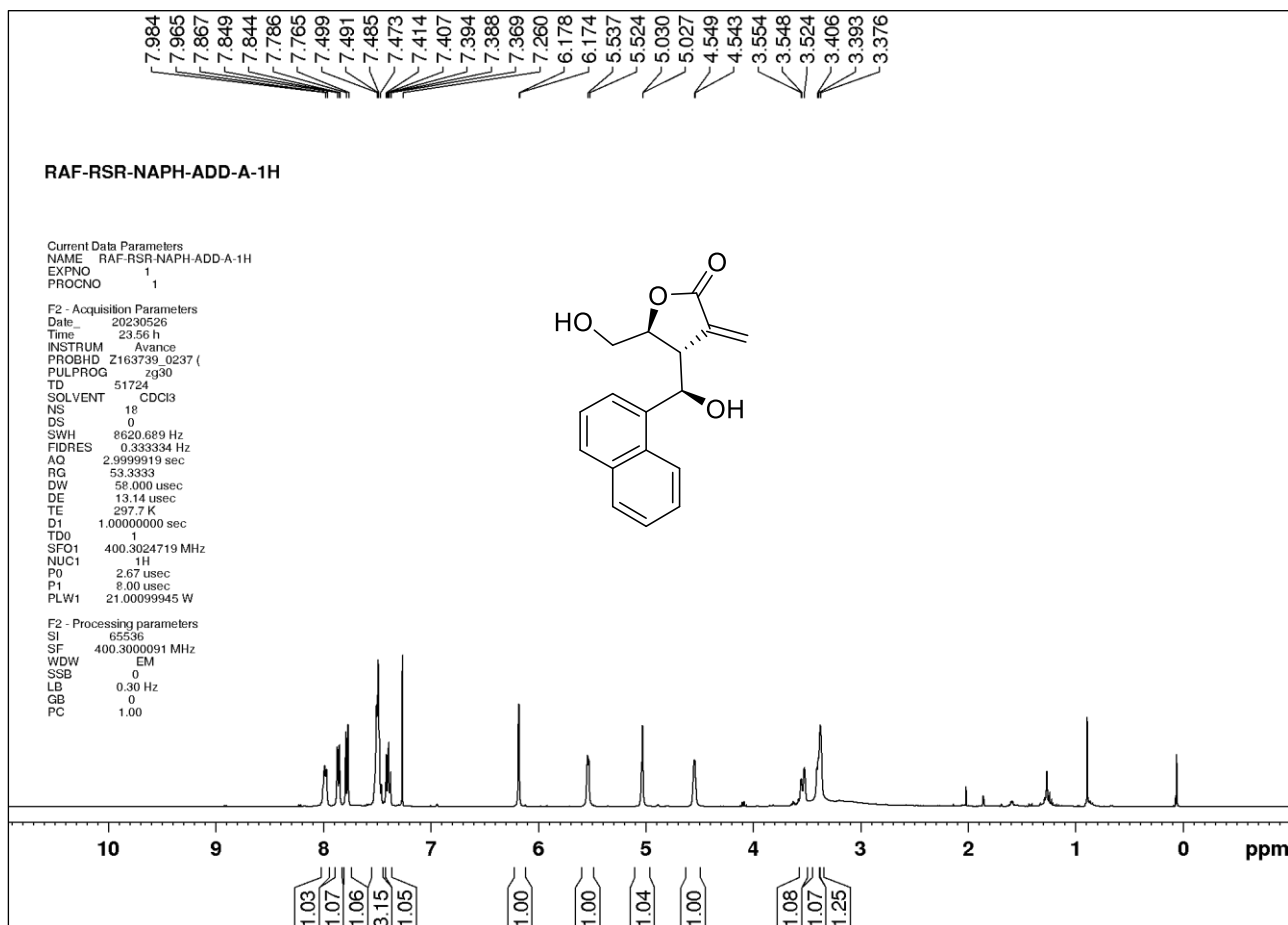
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3b**



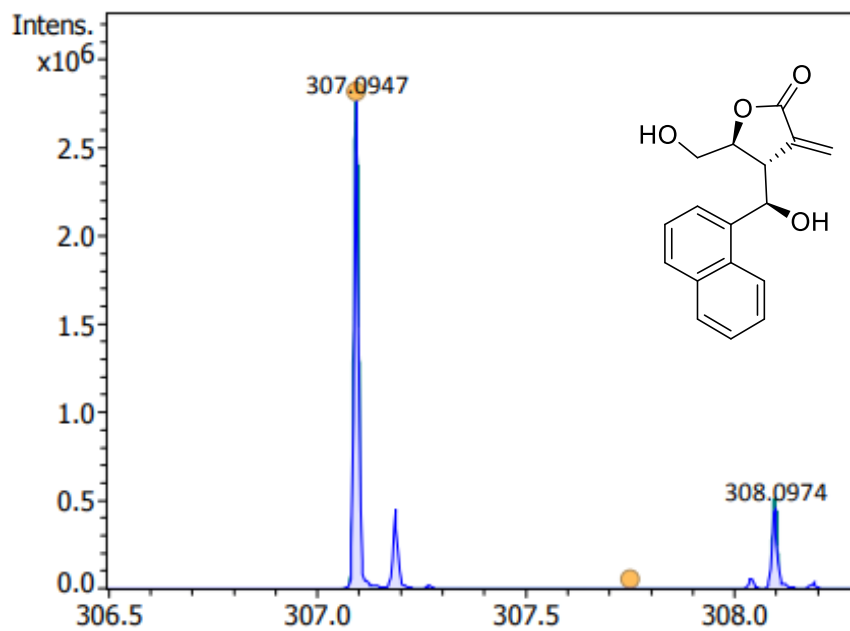
**3b**: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_6H_8O_3Br$  206.9648; Found: 206.9648.



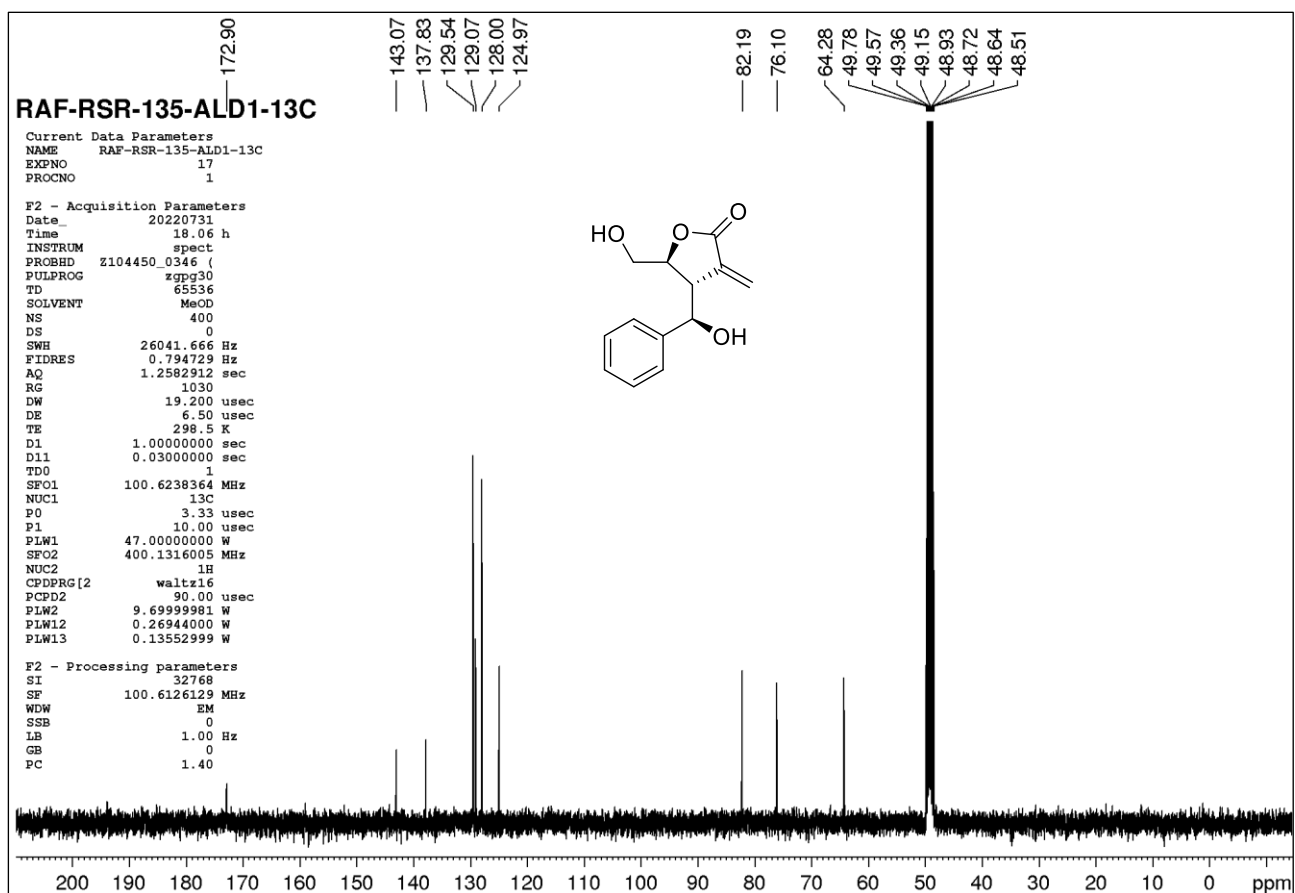
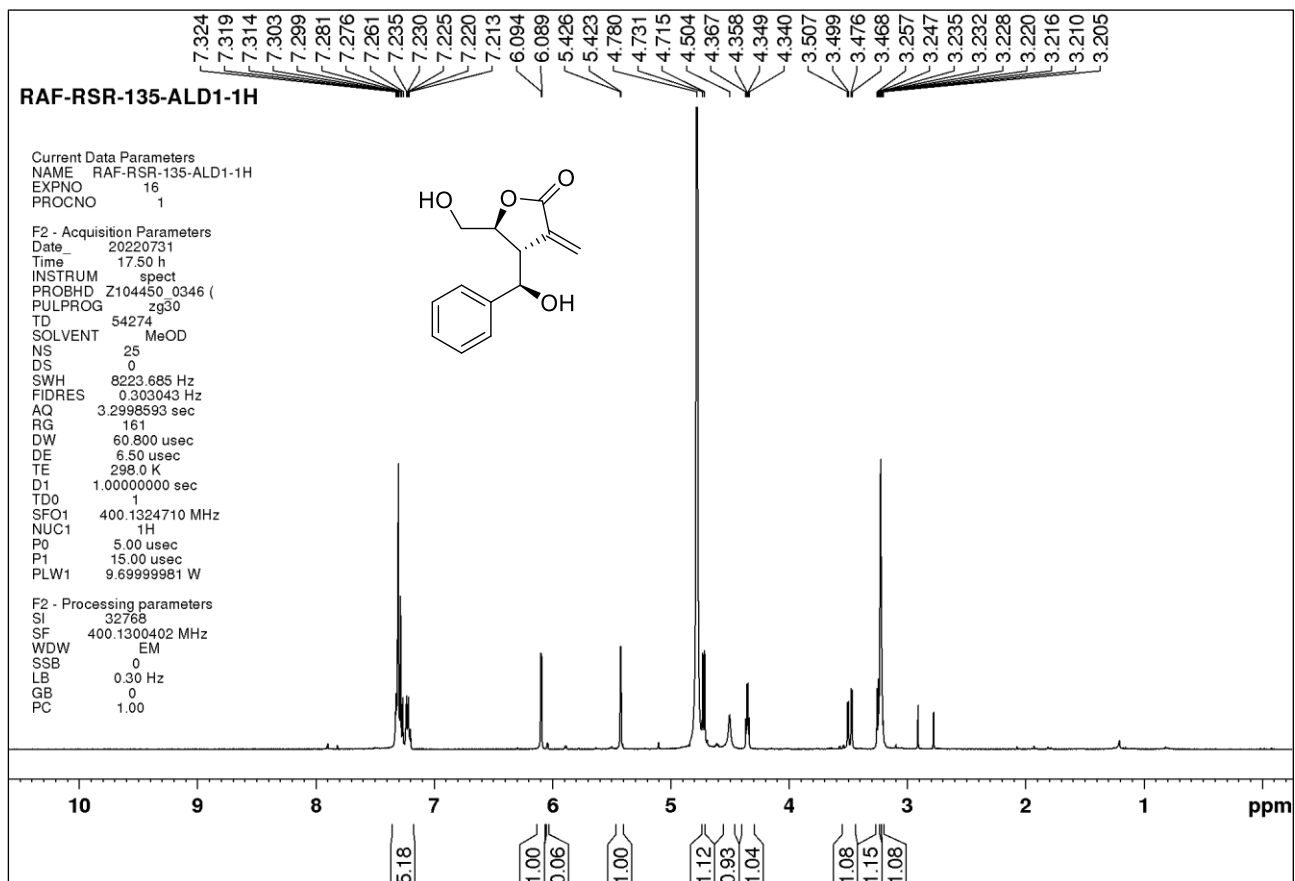
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **7a**



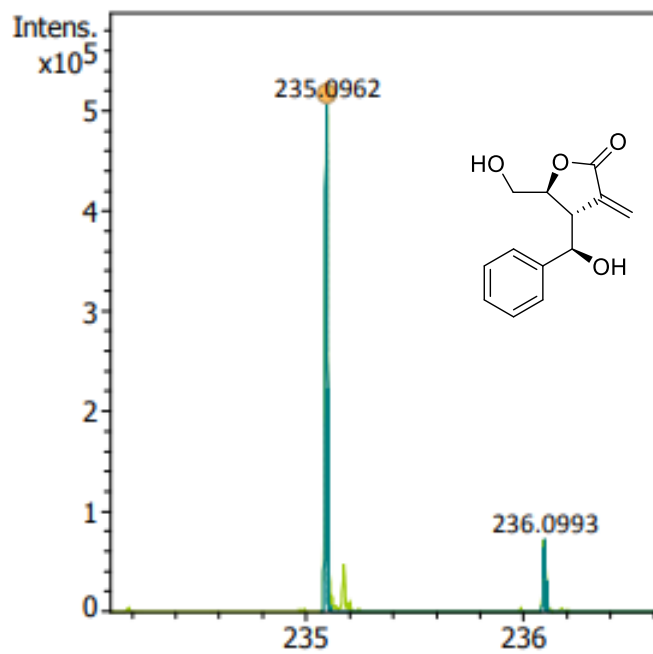
**7a:** HRMS (ESI-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{17}H_{16}O_4Na$  307.0941; Found: 307.0947.



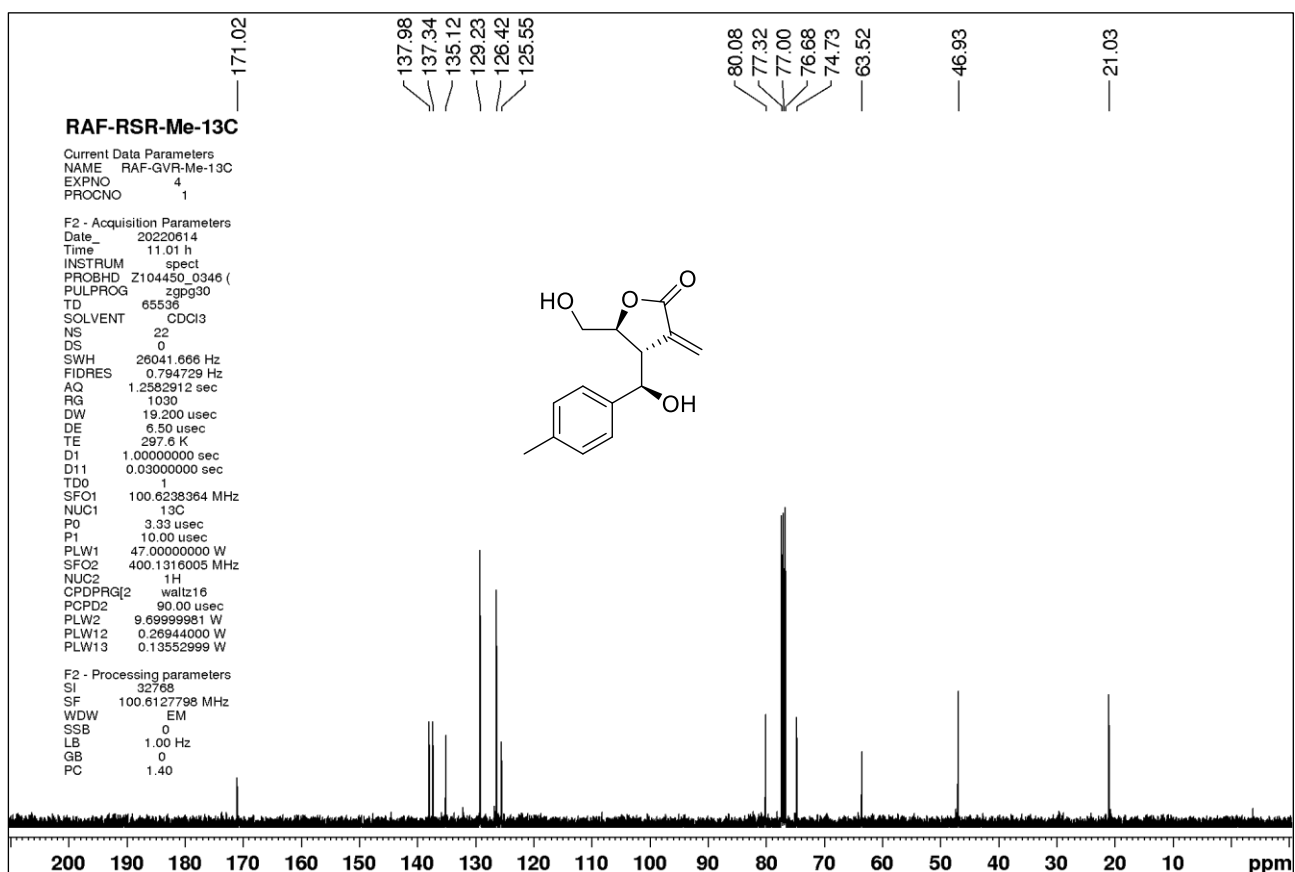
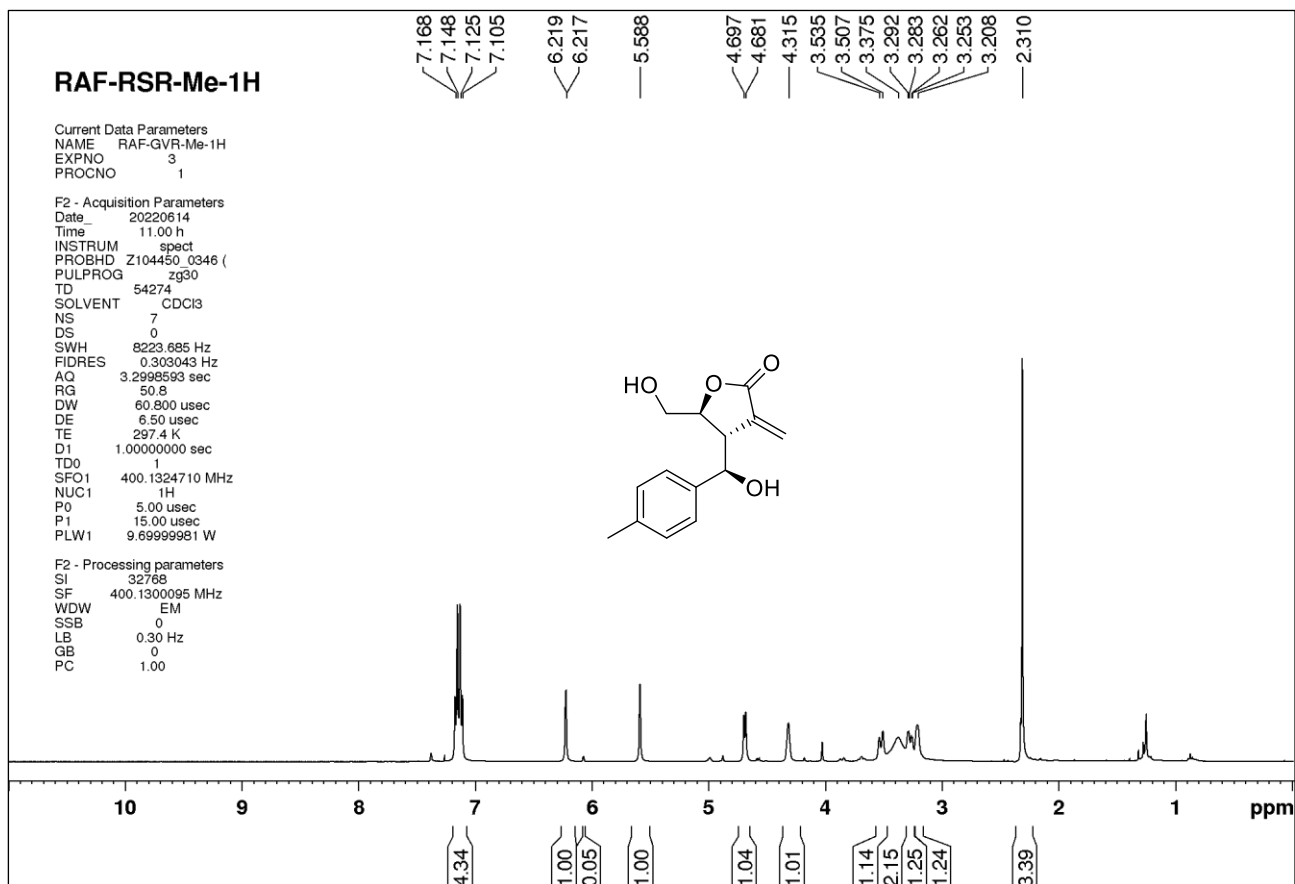
$^1\text{H}$  NMR (400 MHz, MeOH- $d_4$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, MeOH- $d_4$ ) of compound **7b**



**7b:** HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{15}O_4$  235.0966; Found: 235.0962.

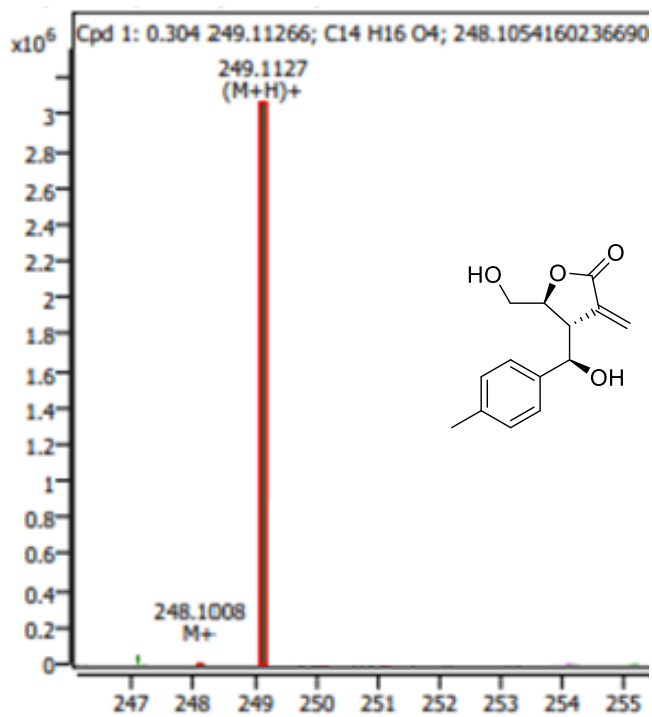


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **7c**

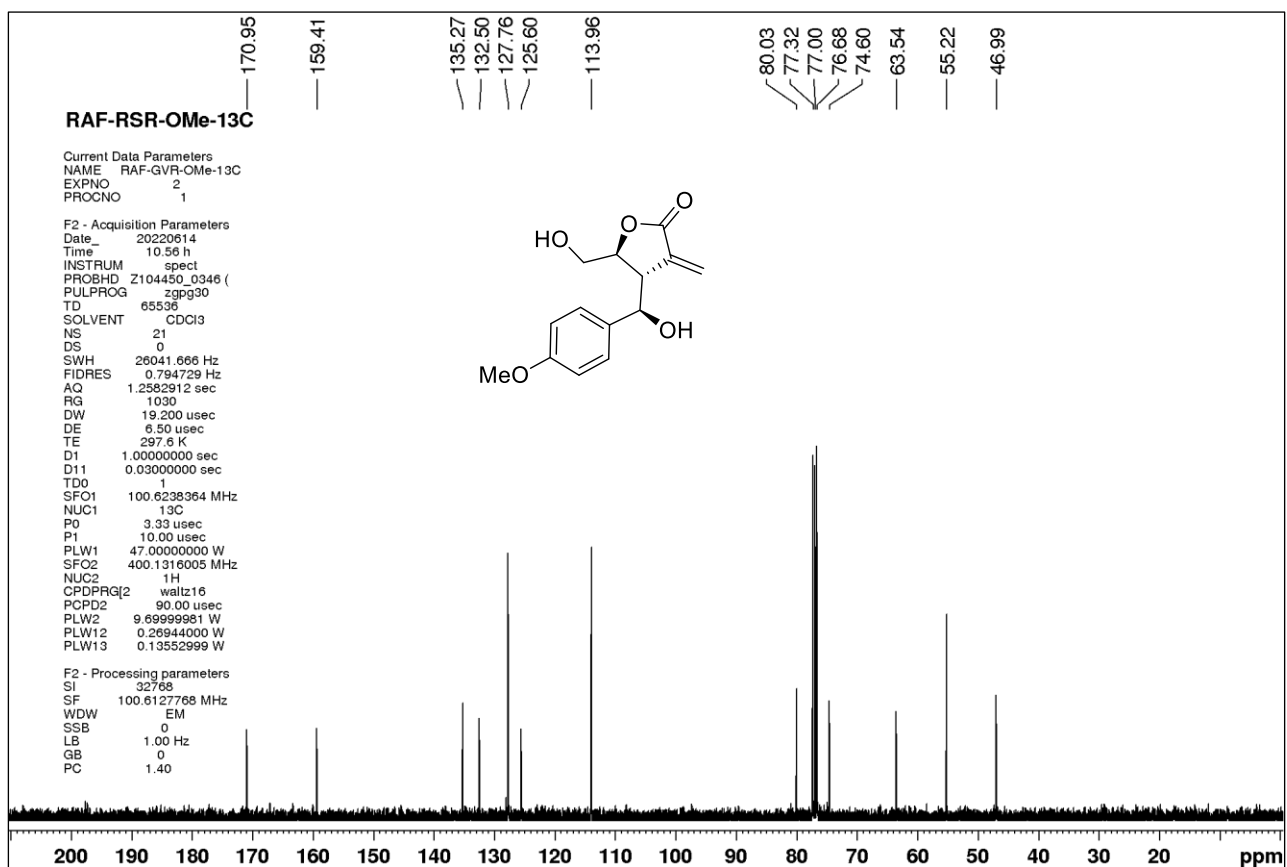
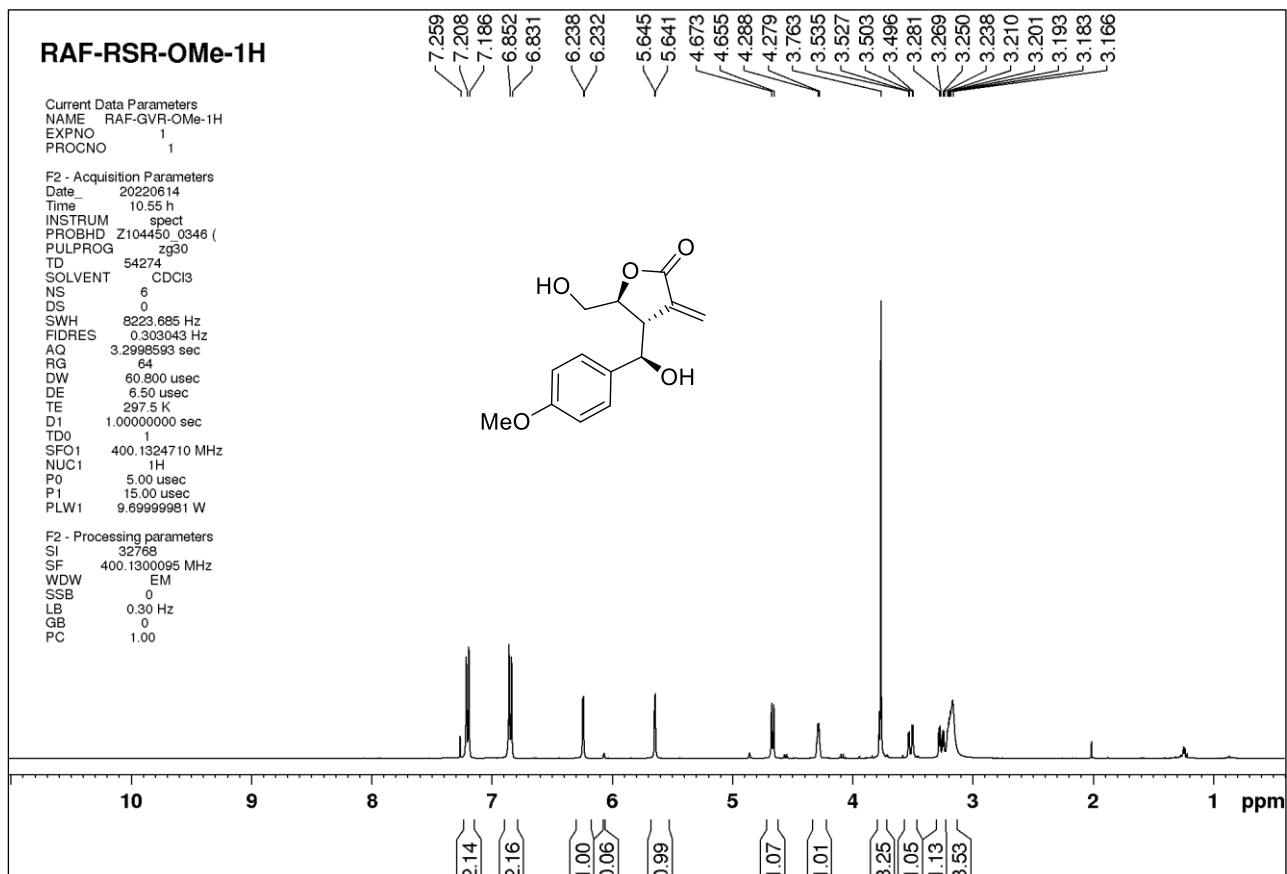




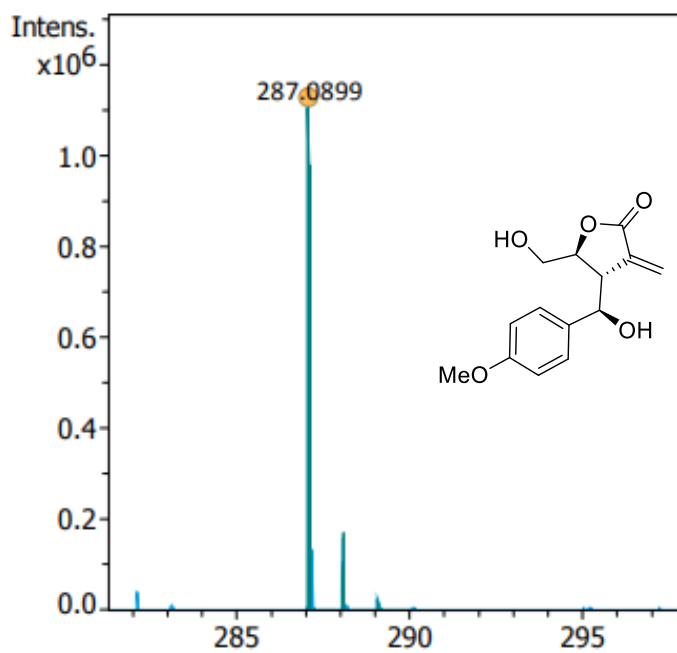
7c: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{14}H_{17}O_4$  249.1127; Found: 249.1127.



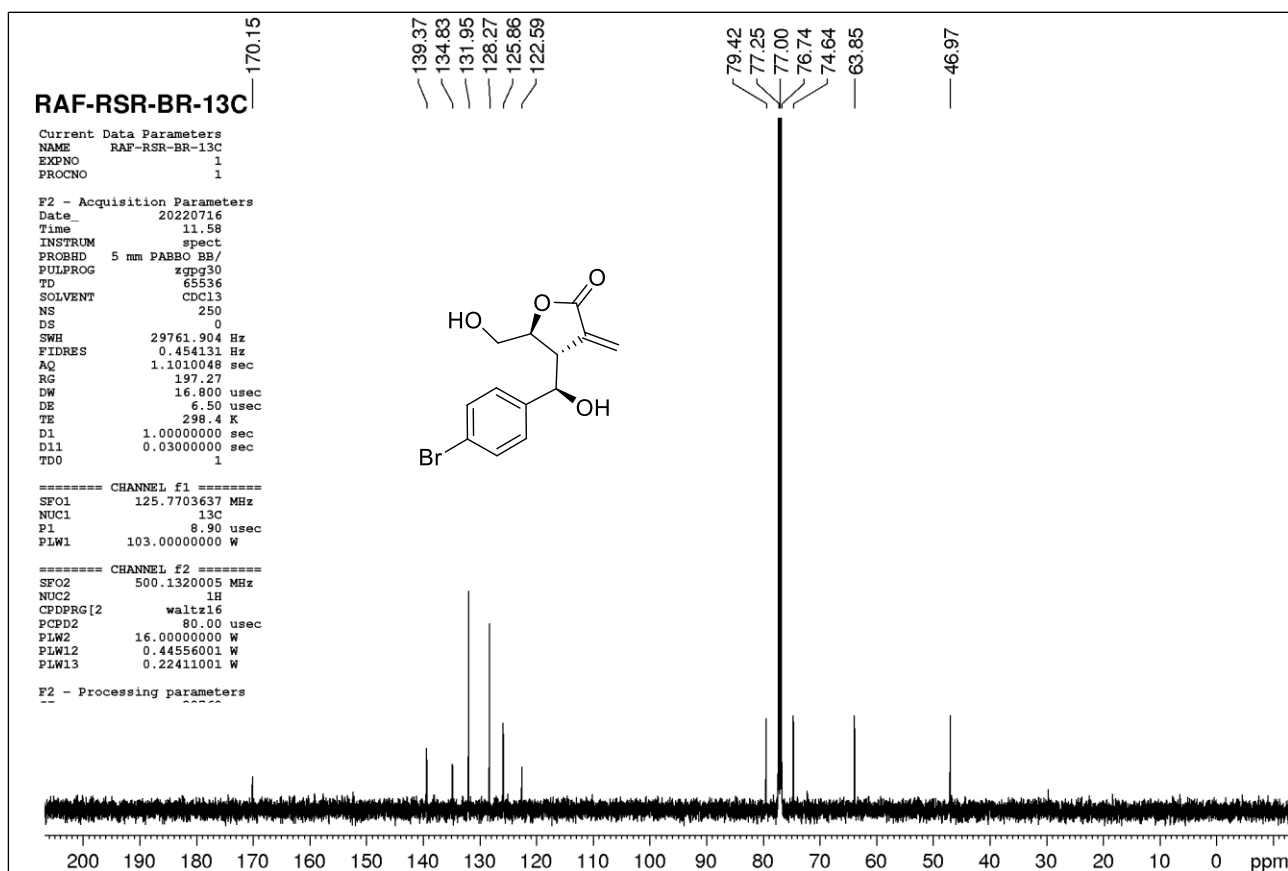
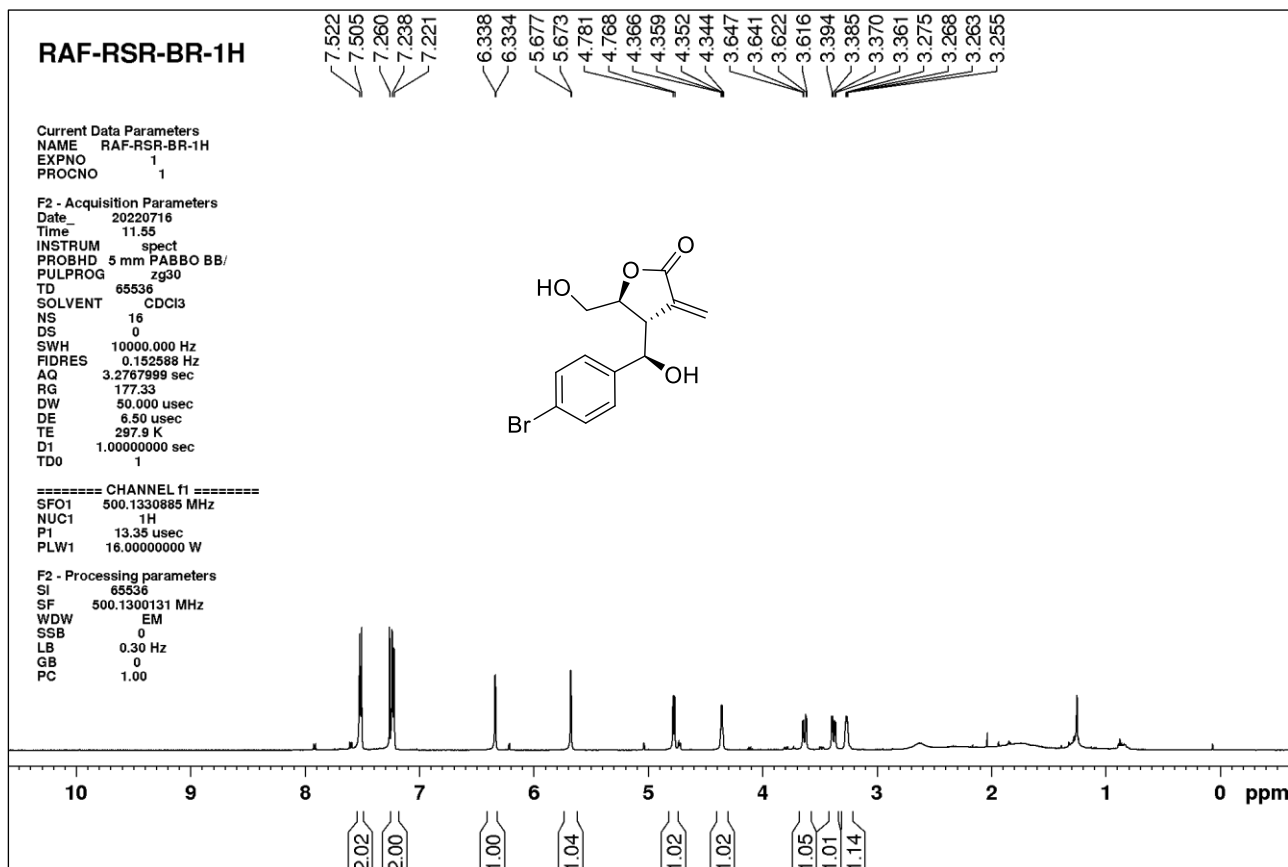
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$ { $^1\text{H}$ } NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **7d**



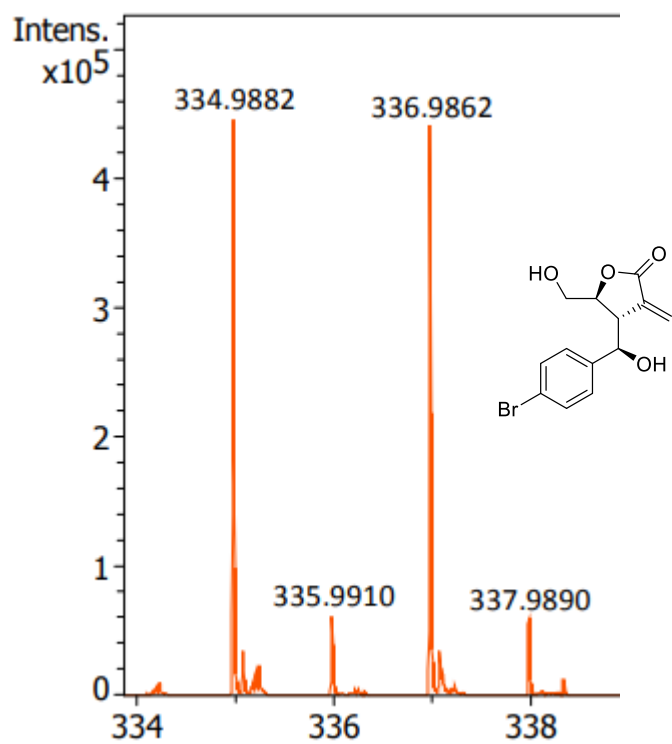
**7d:** HRMS (ESI-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{14}H_{16}O_5Na$  287.0890; Found 287.0899.



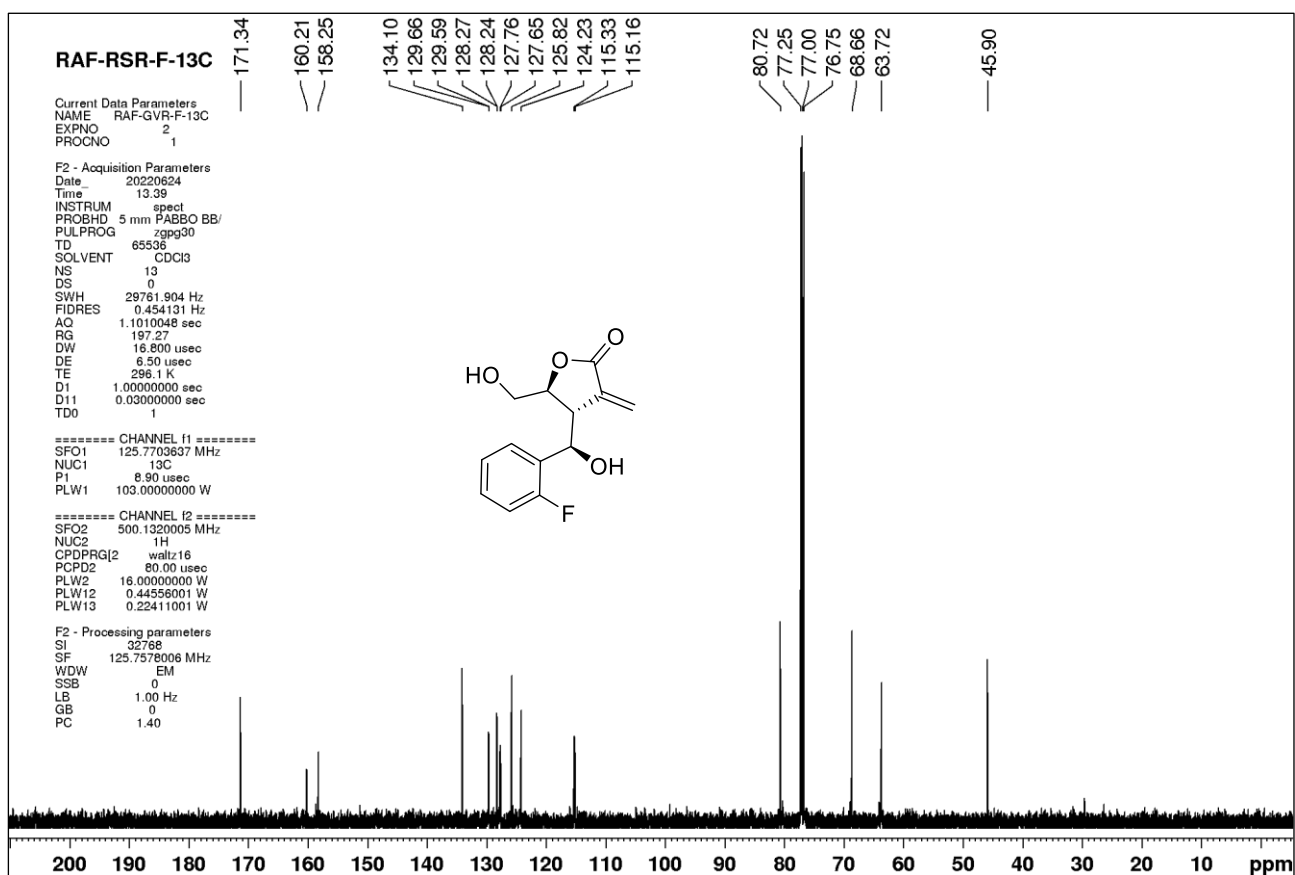
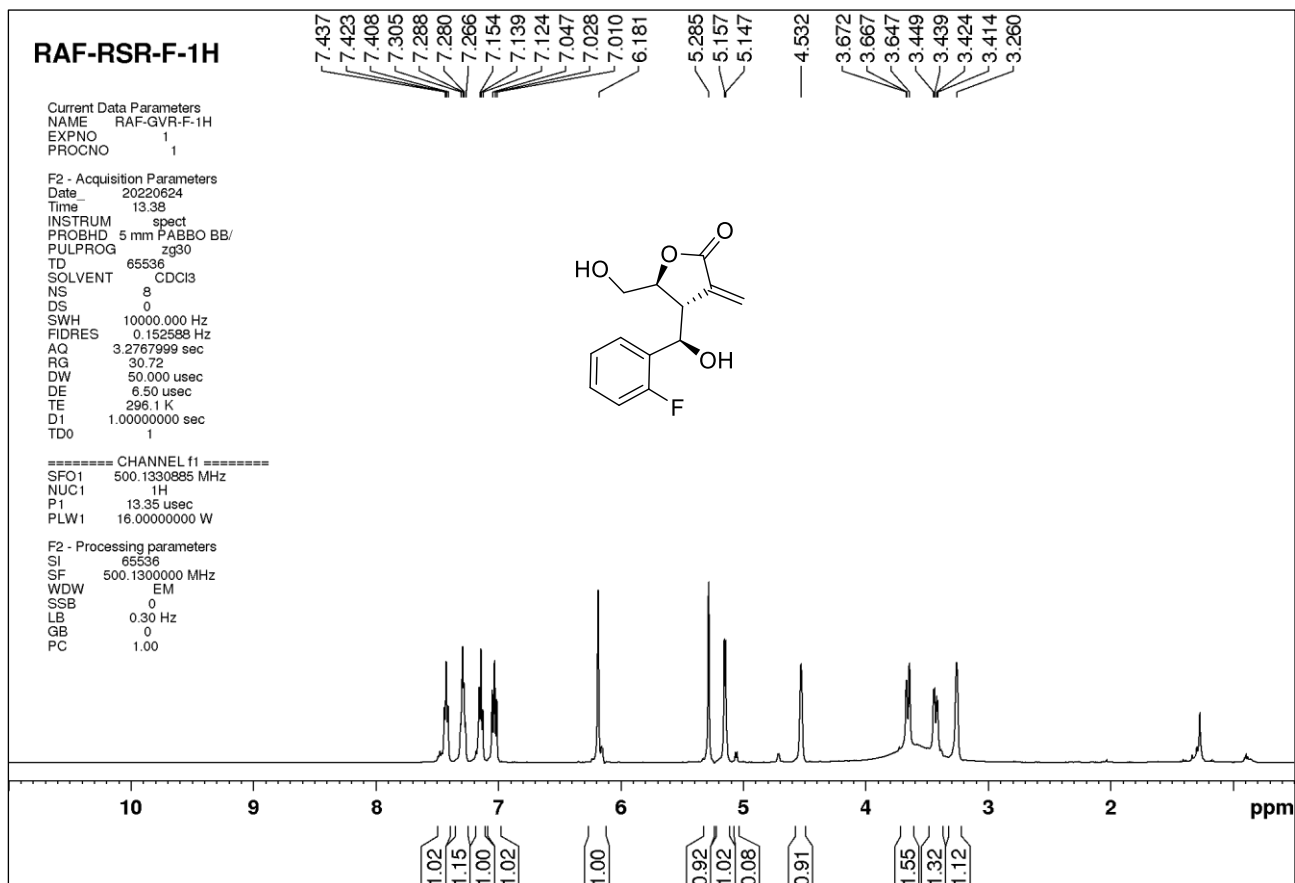
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound **7e**



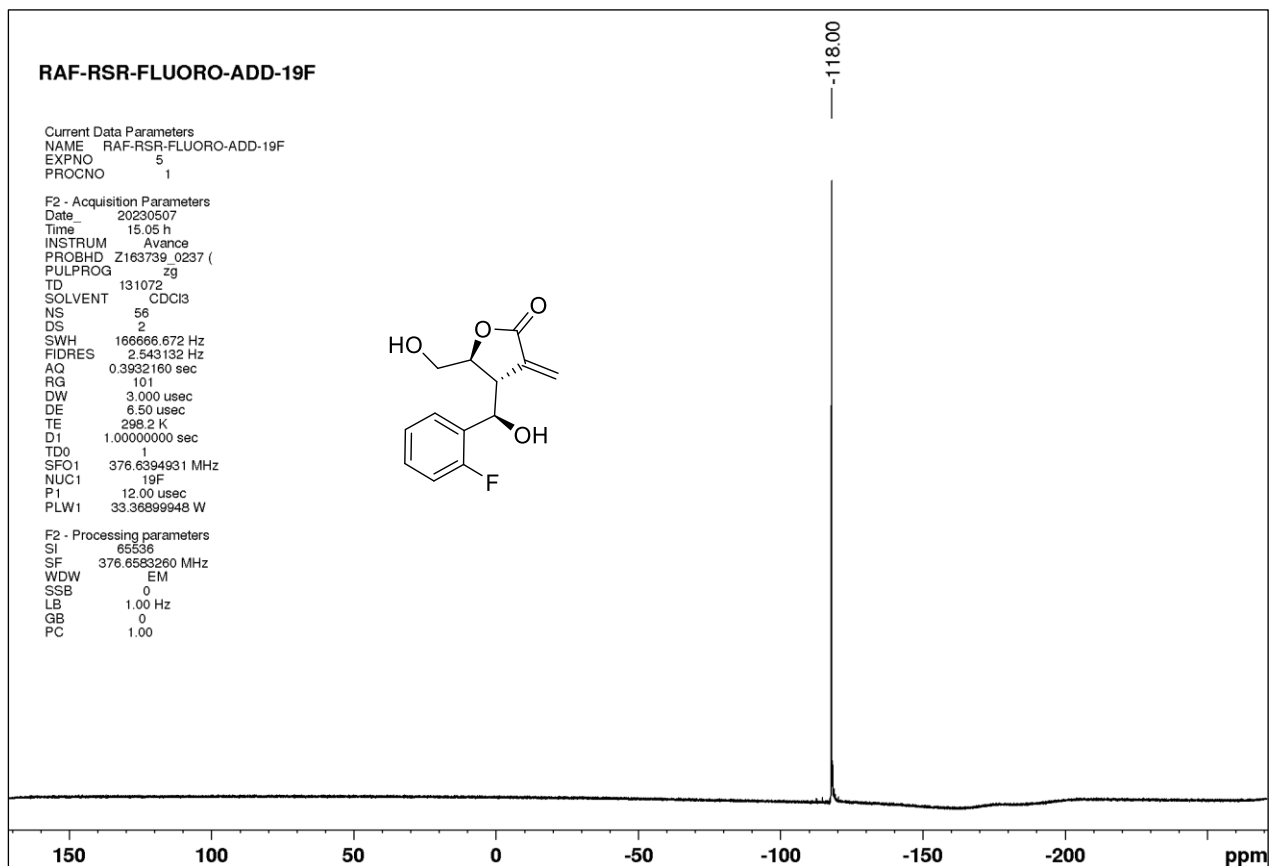
7e: HRMS (ESI-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{13}H_{13}O_4BrNa$  334.9889; Found 334.9882.



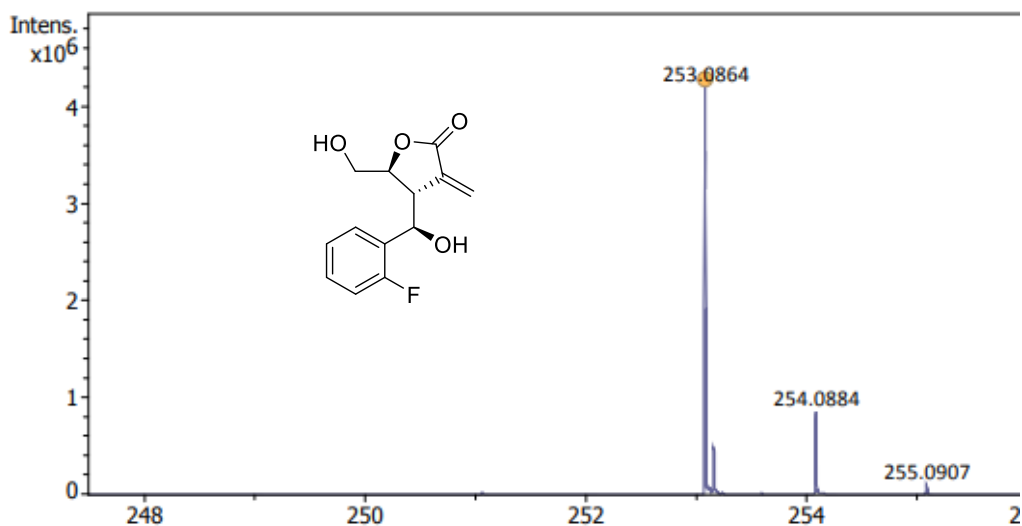
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound **7f**



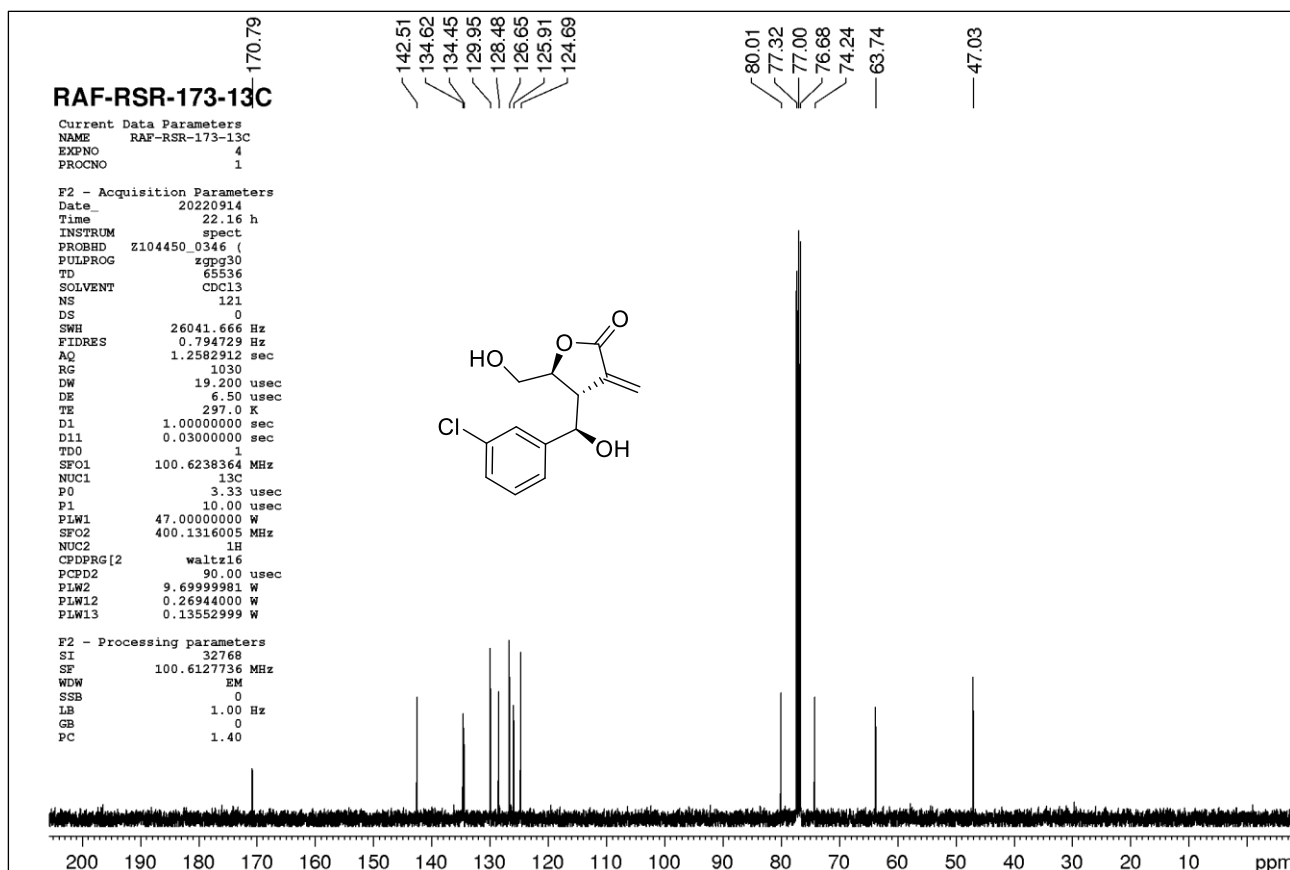
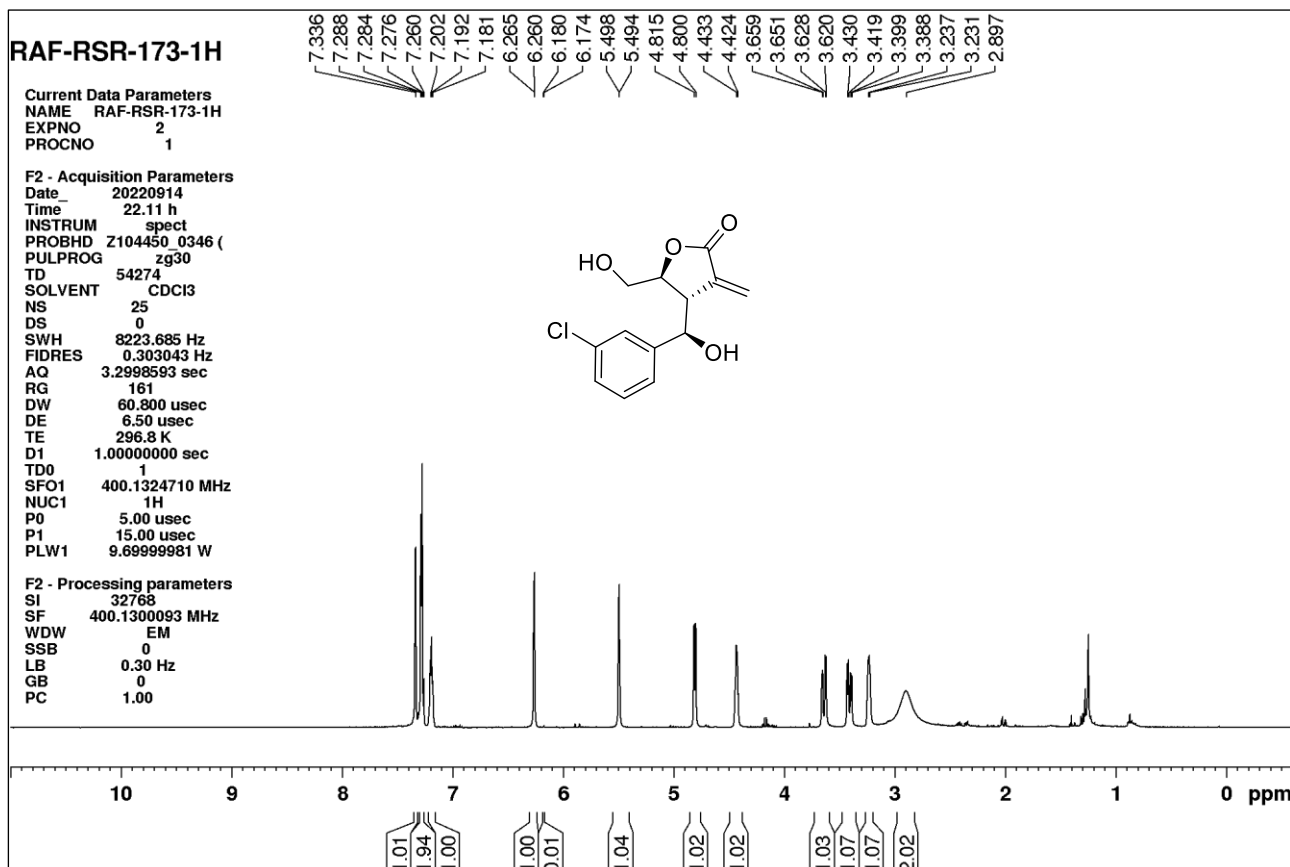
$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of compound **7f**



**7f**: HRMS (ESI-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_4\text{F}$  253.0871; Found 253.0864.

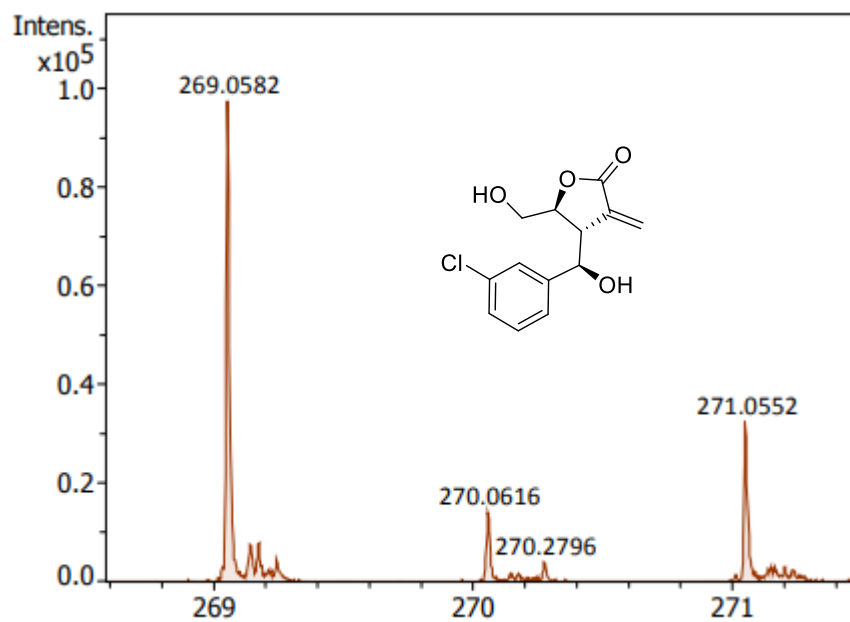


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **7g**

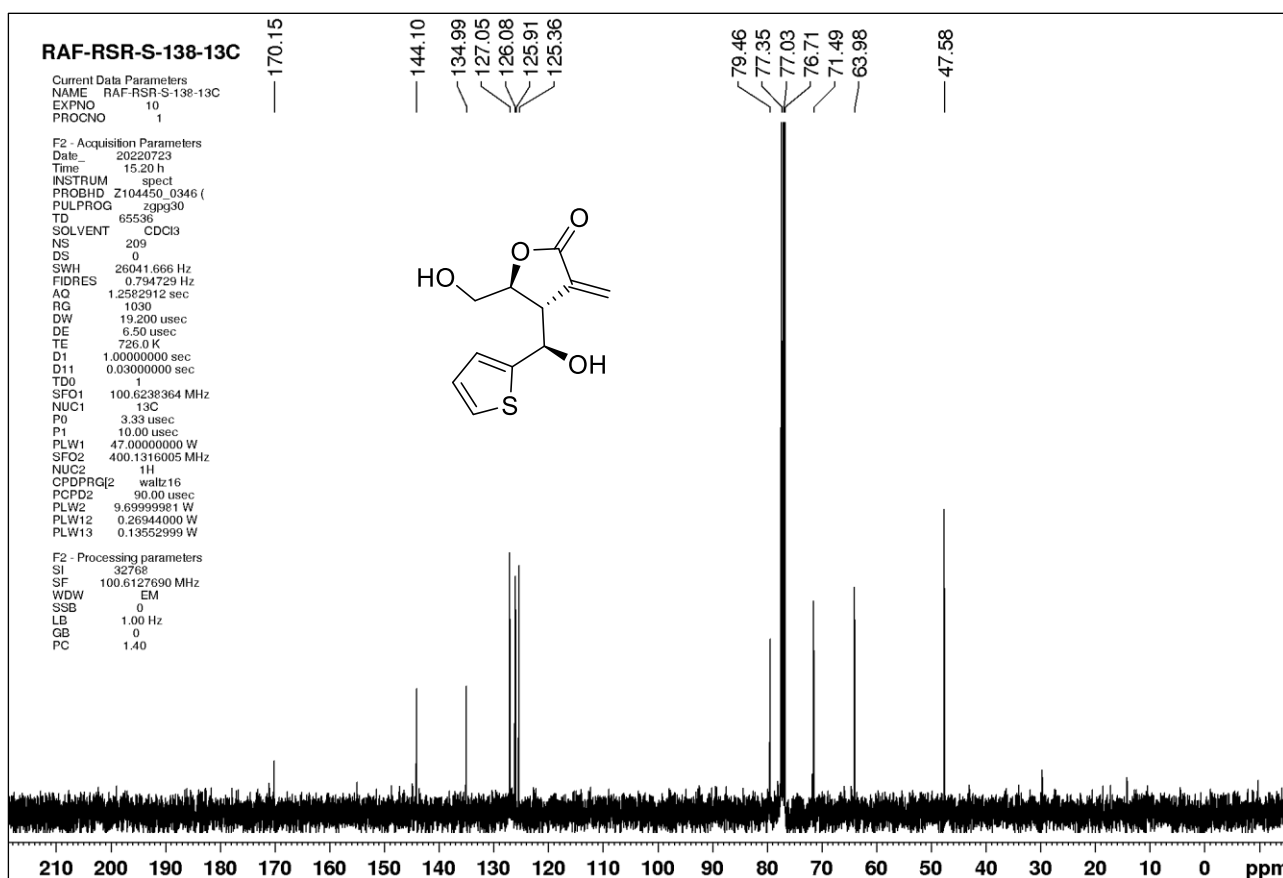
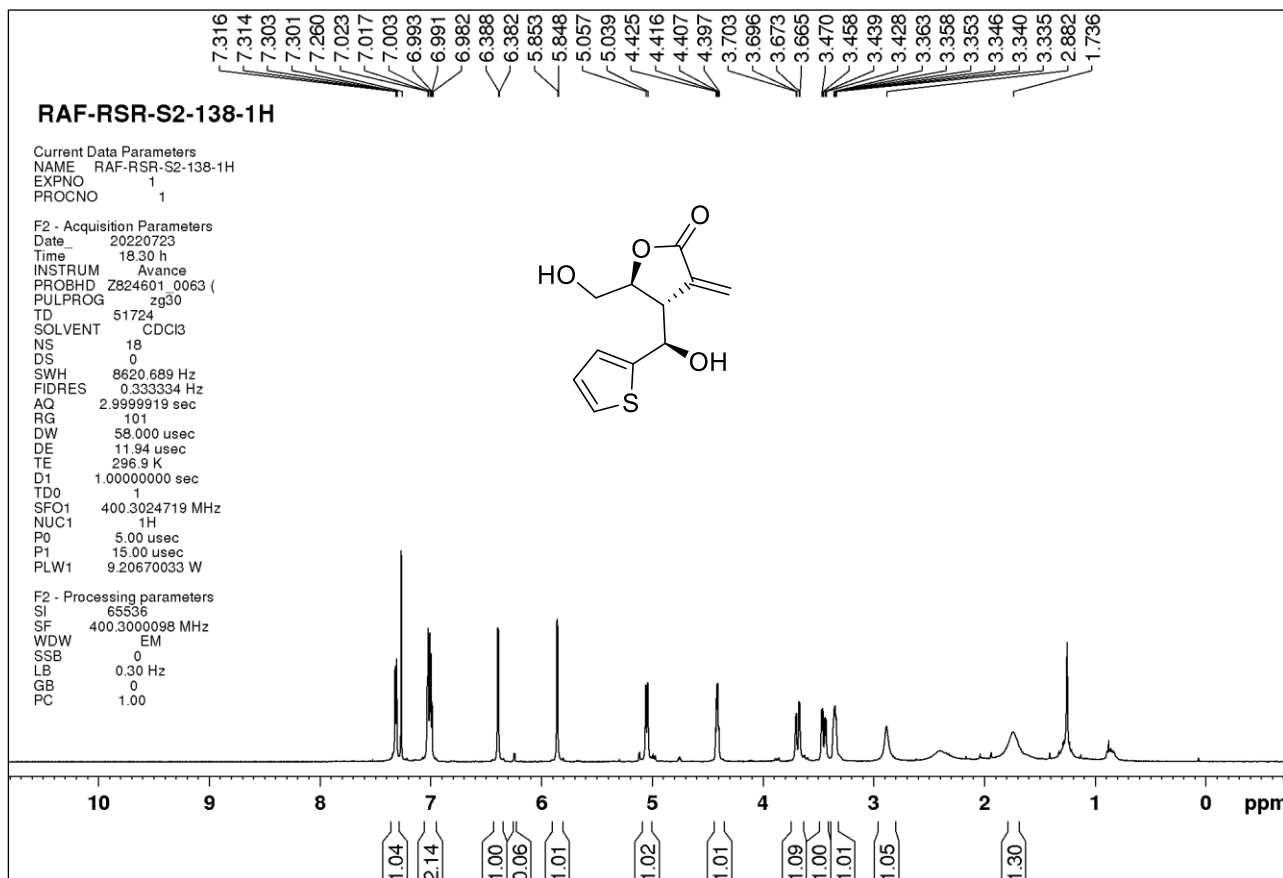




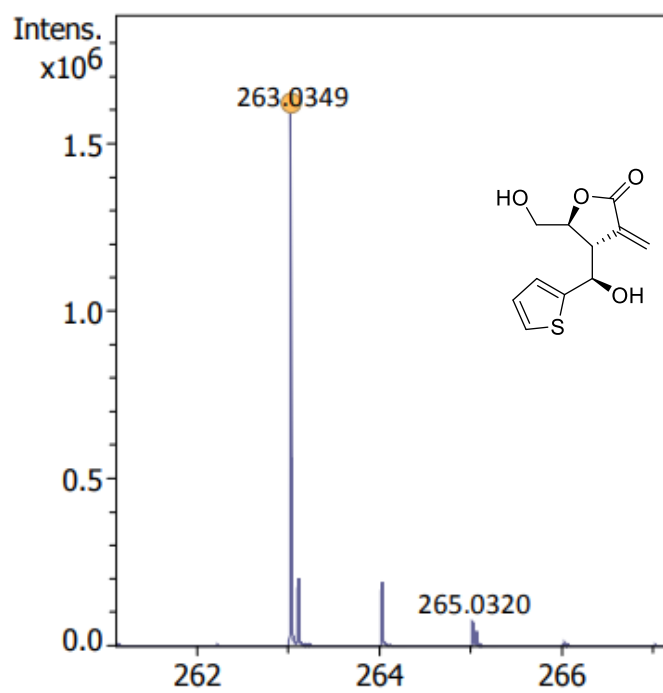
**7g:** HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{14}ClO_4$  269.0580; Found 269.0582.



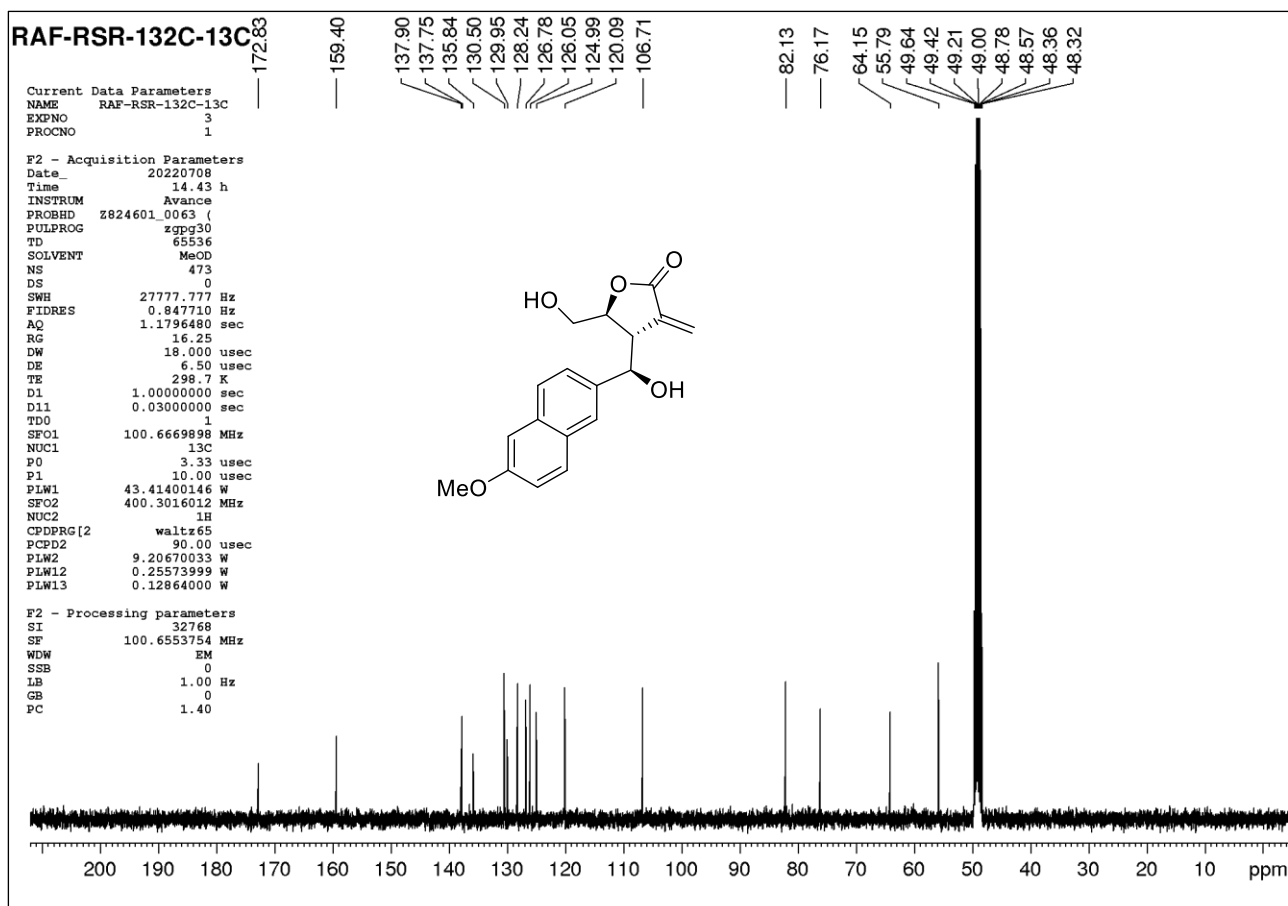
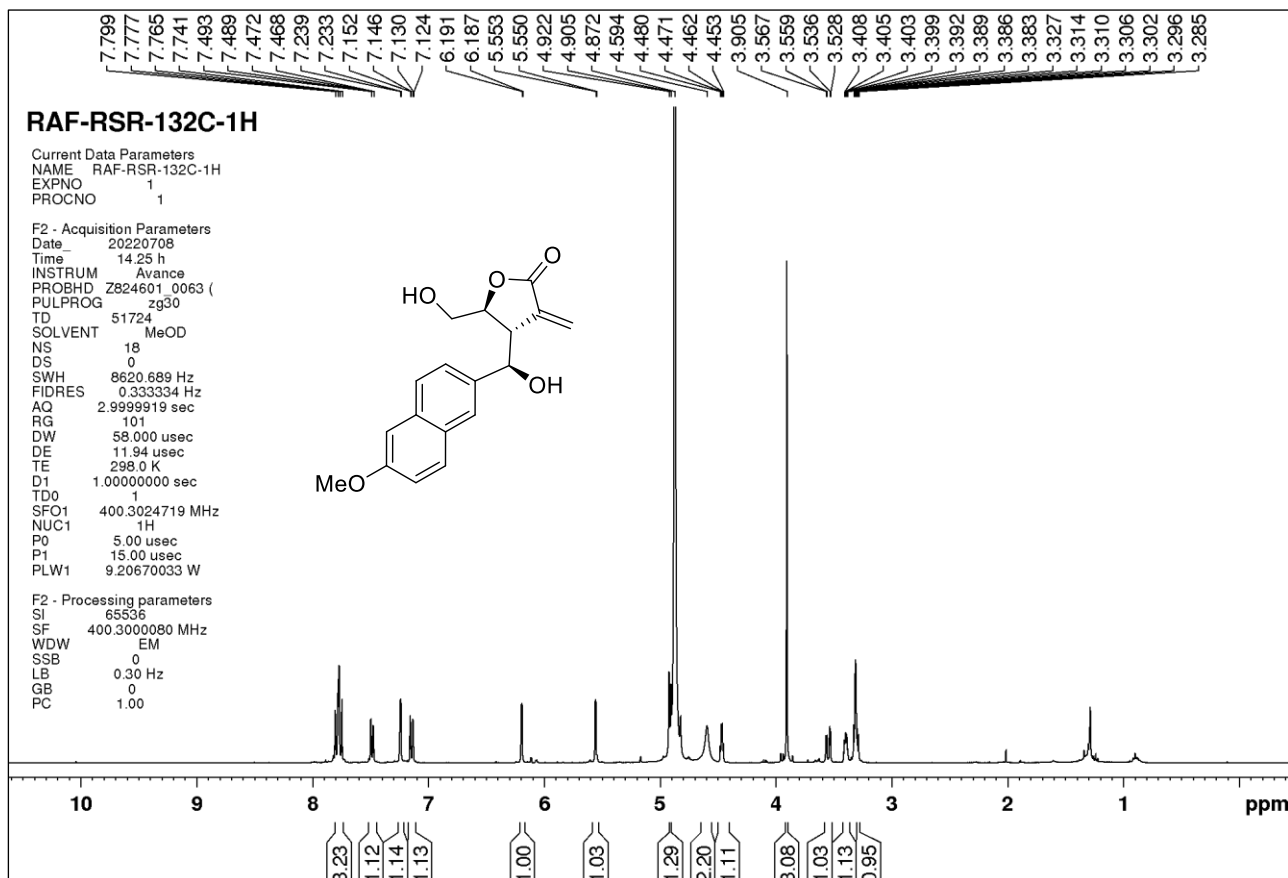
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **7h**



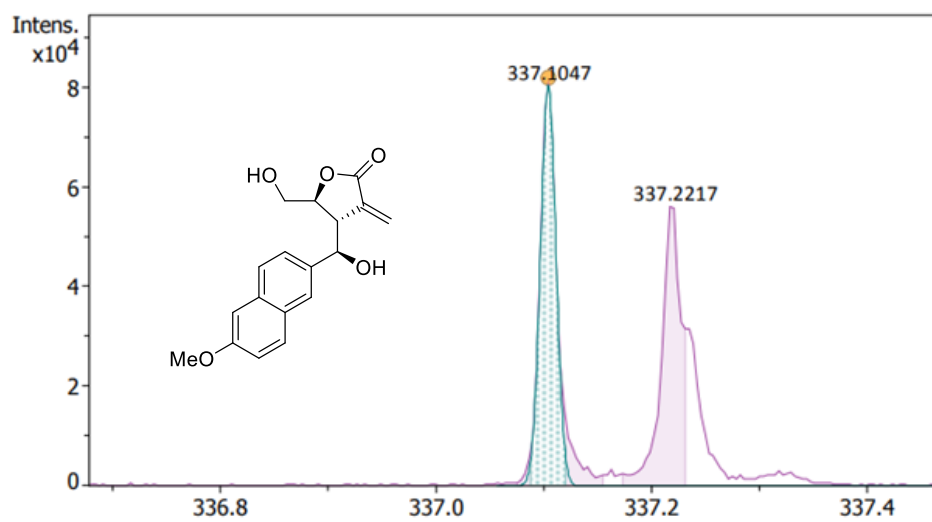
**7h:** HRMS (ESI-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{11}H_{12}O_4SNa$  263.0349; Found 263.0349.



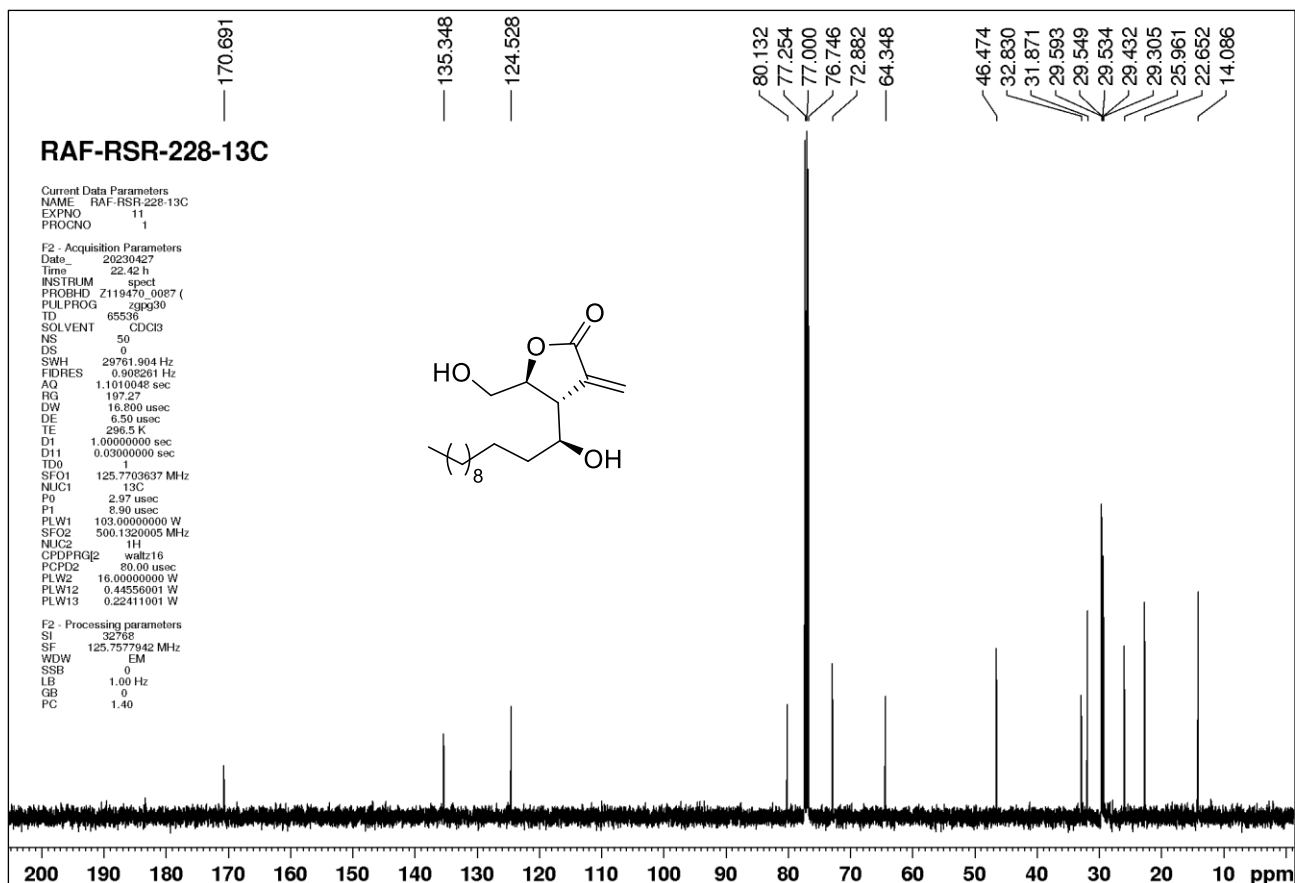
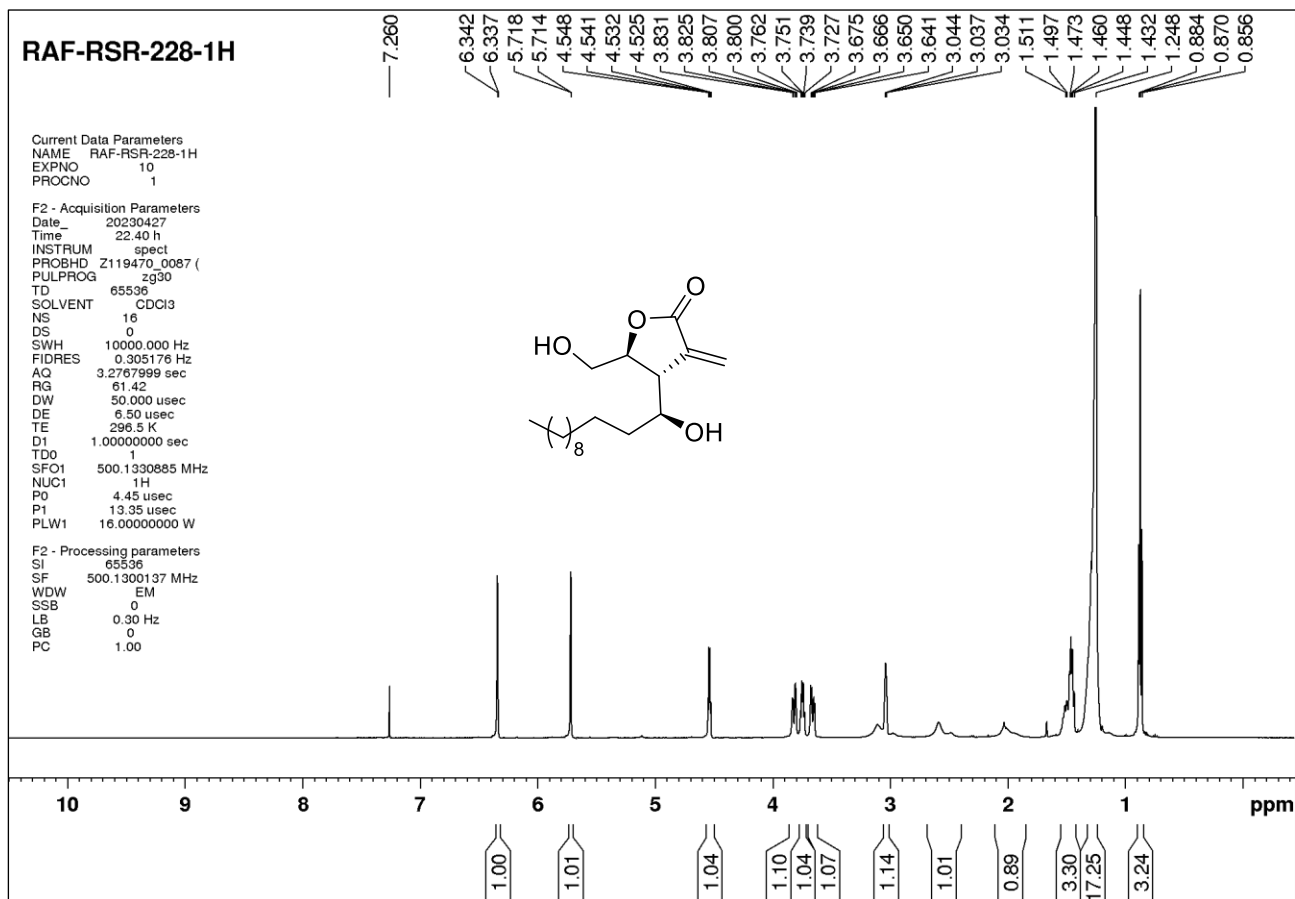
<sup>1</sup>H NMR (400 MHz, MeOH-d<sub>4</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, MeOH-d<sub>4</sub>) of compound **7i**



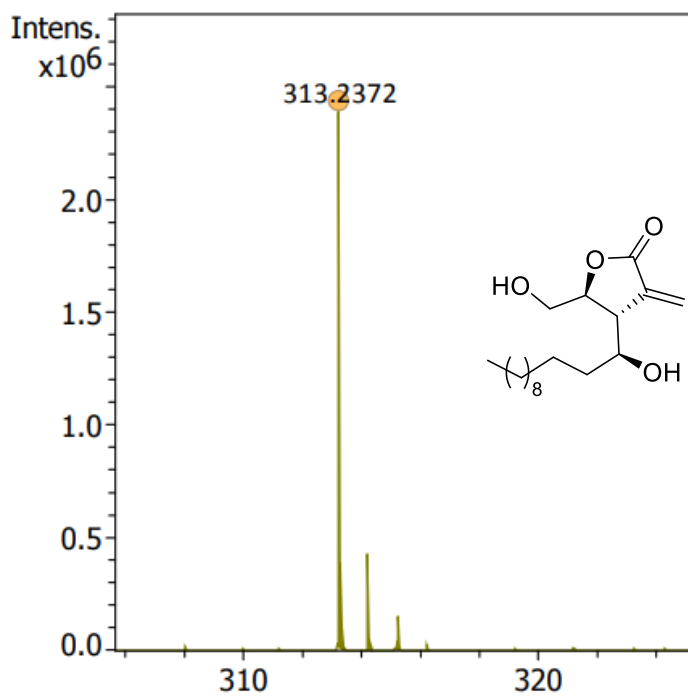
**7i:** HRMS (ESI-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{18}H_{18}O_5Na$  337.1046; Found 337.1047.



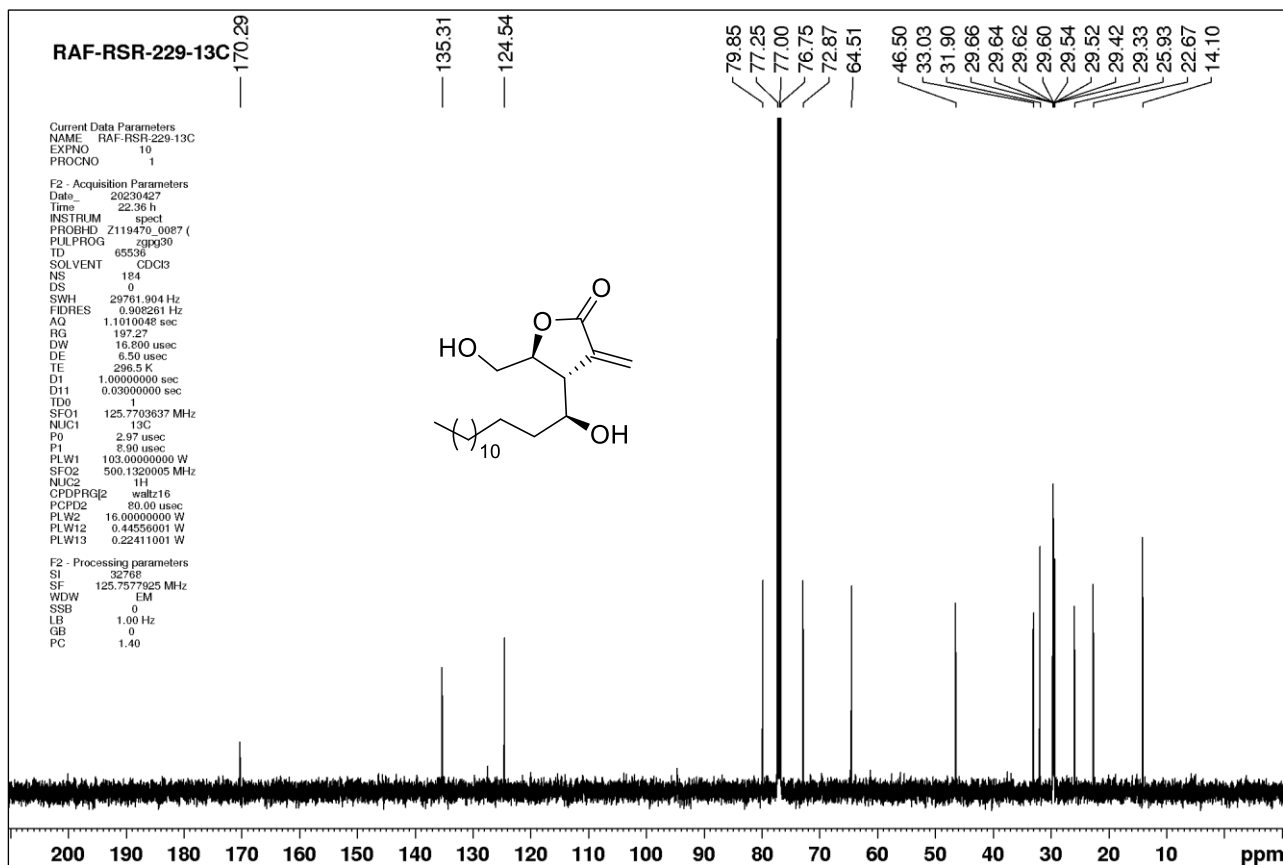
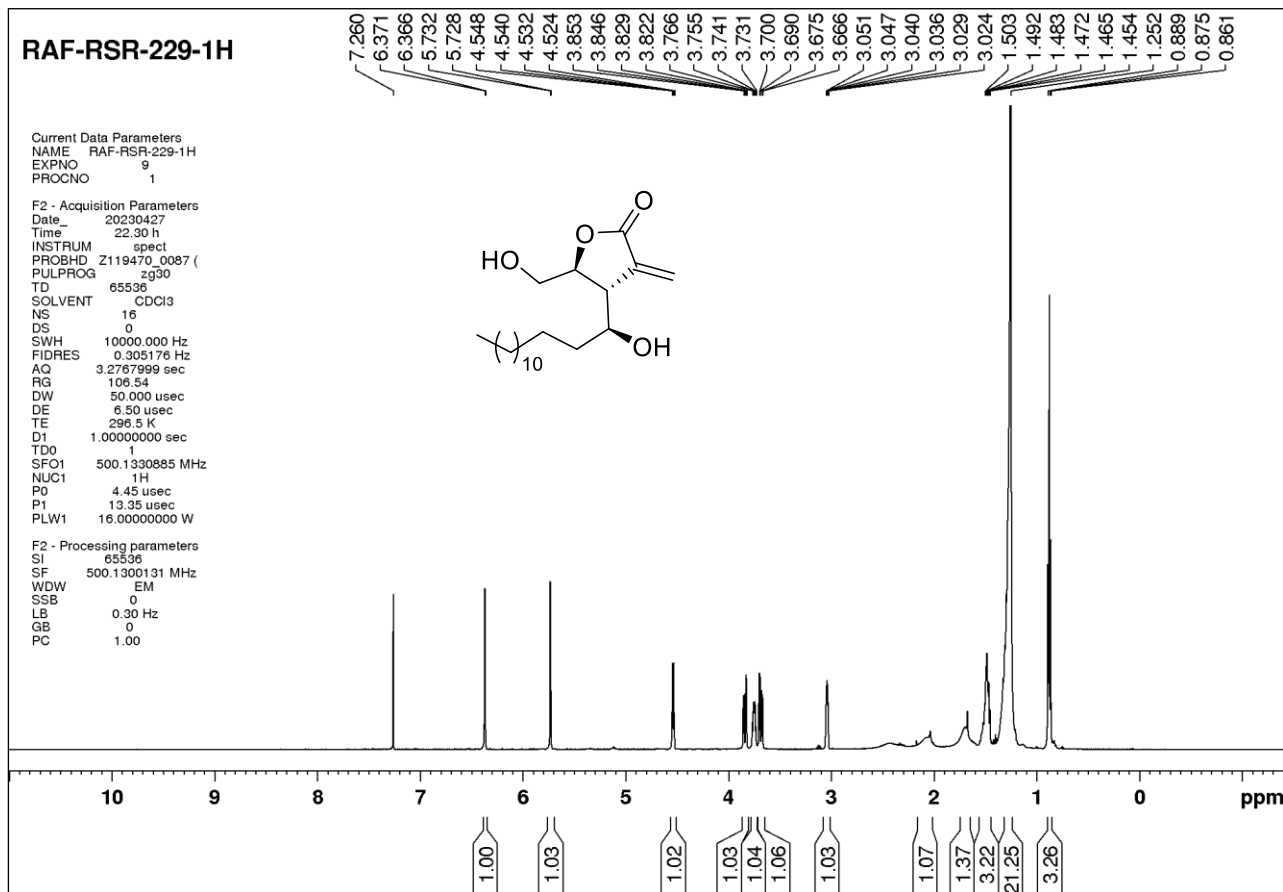
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) of compound **7j**



7j: HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{18}H_{33}O_4$  313.2374; Found 313.2372.

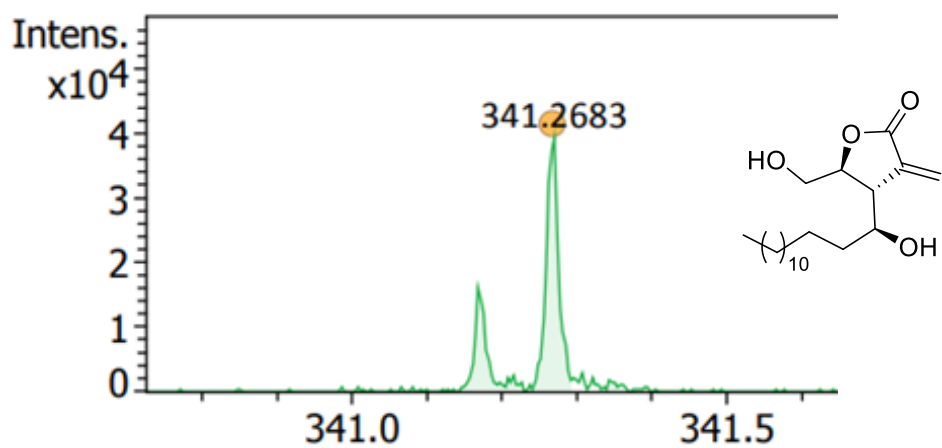


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) of compound **7k**

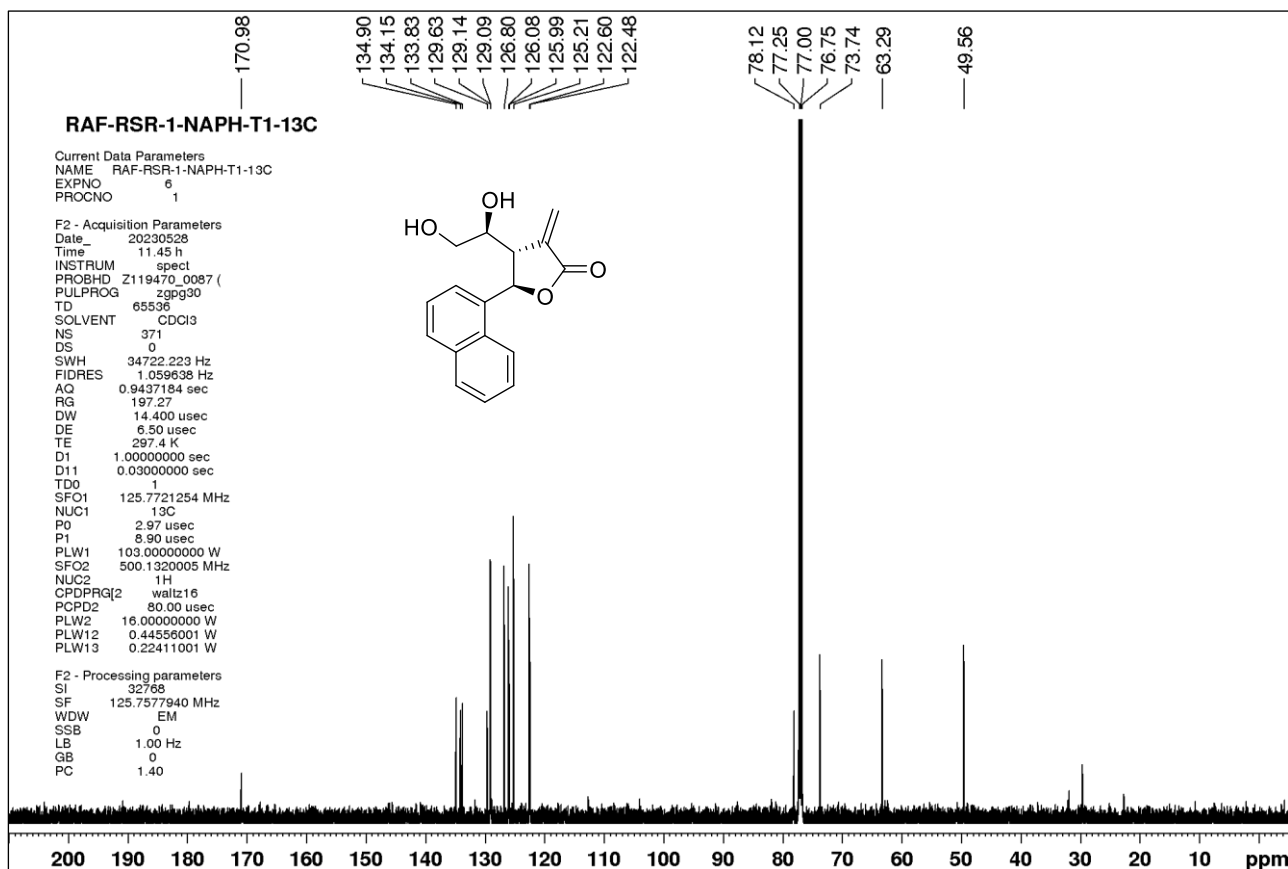
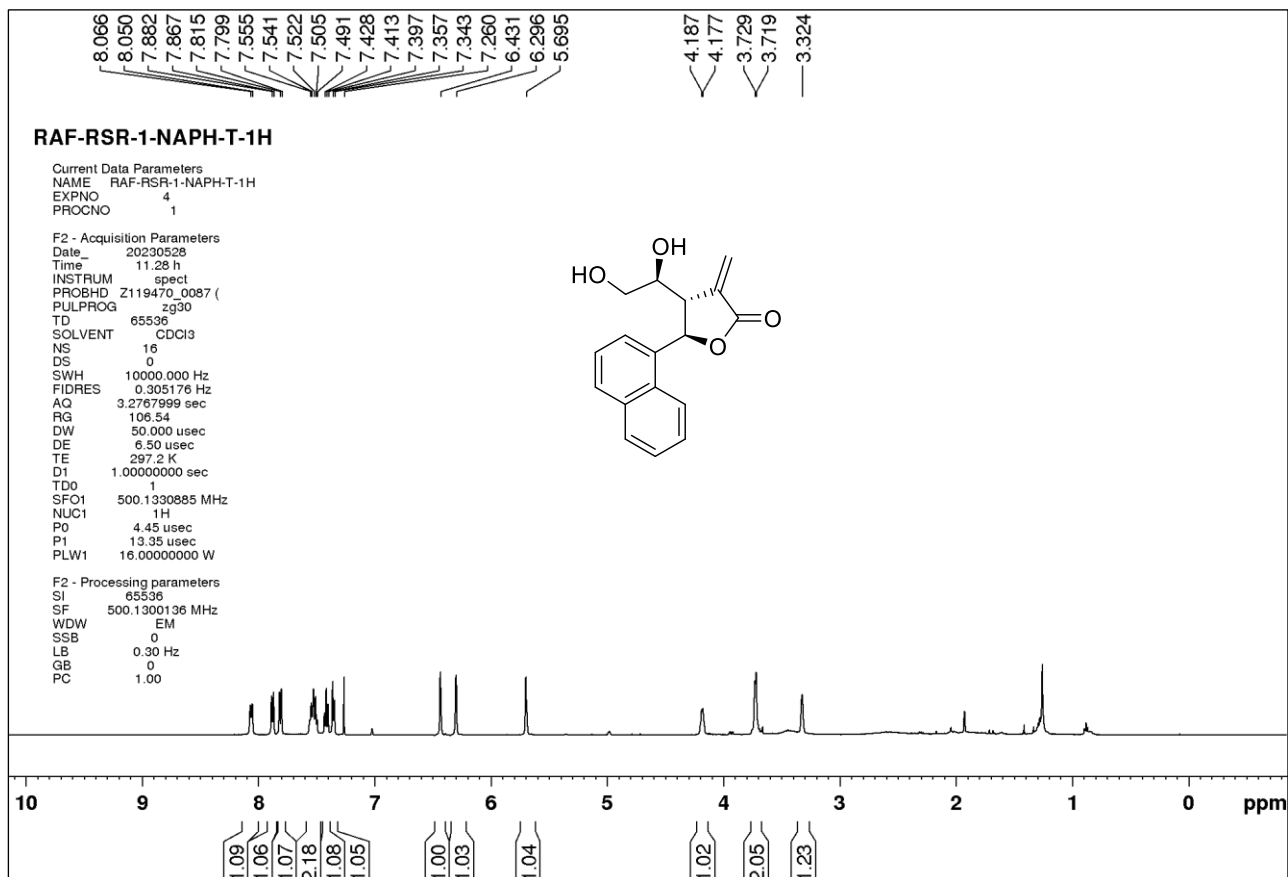




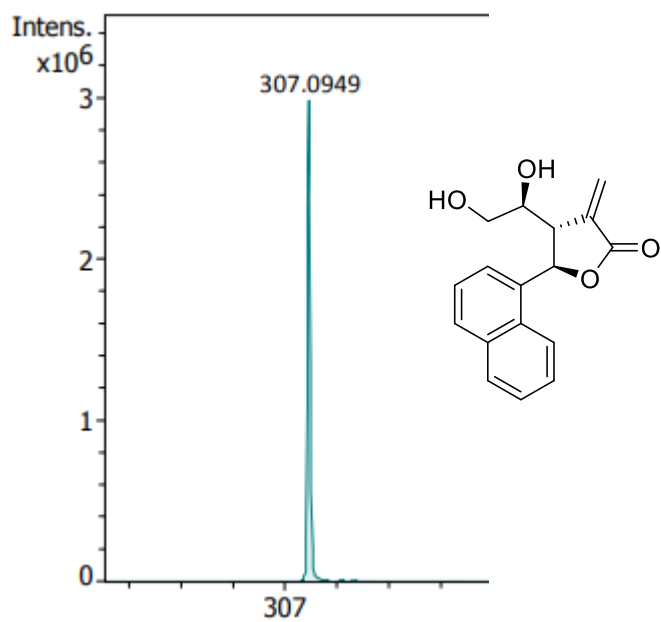
**7k:** HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{37}O_4$  341.2687; Found 341.2683.



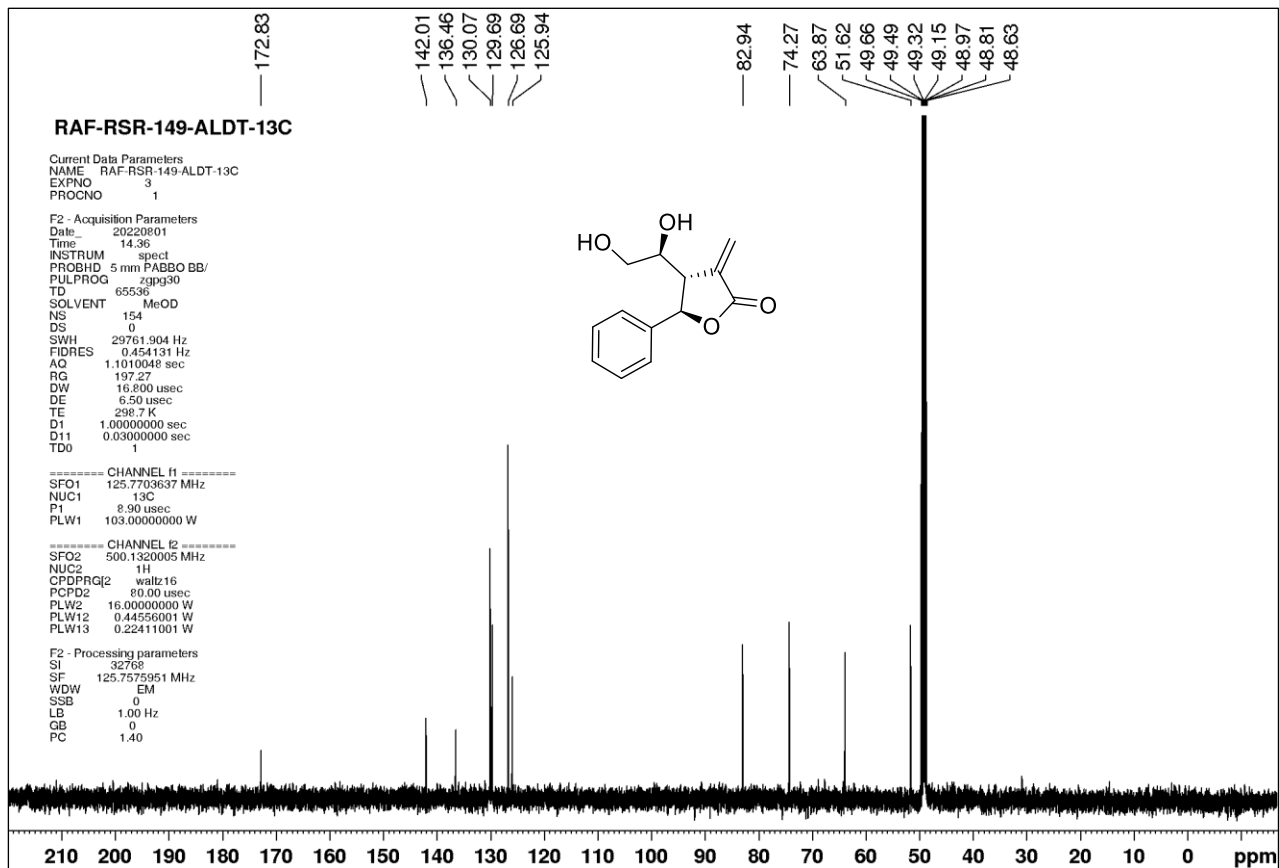
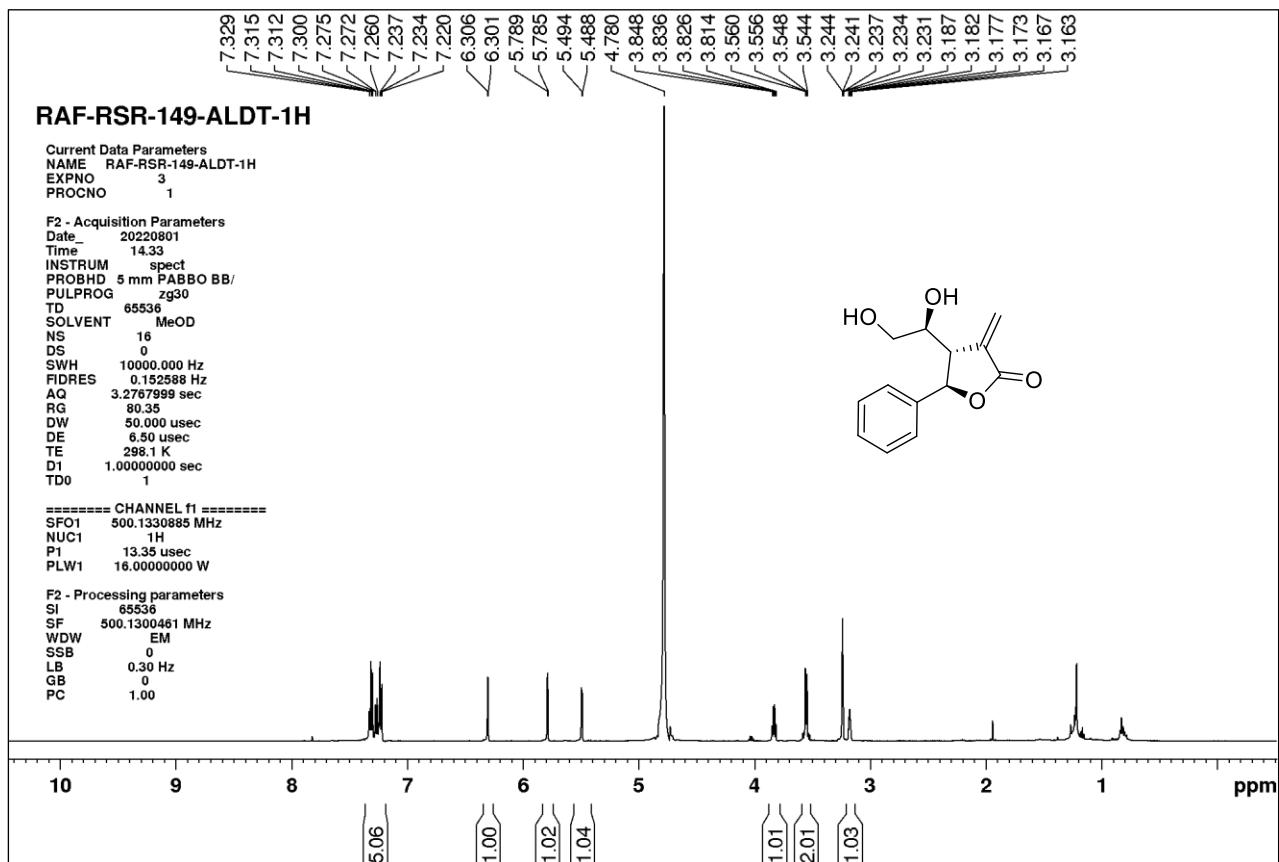
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound **8a**



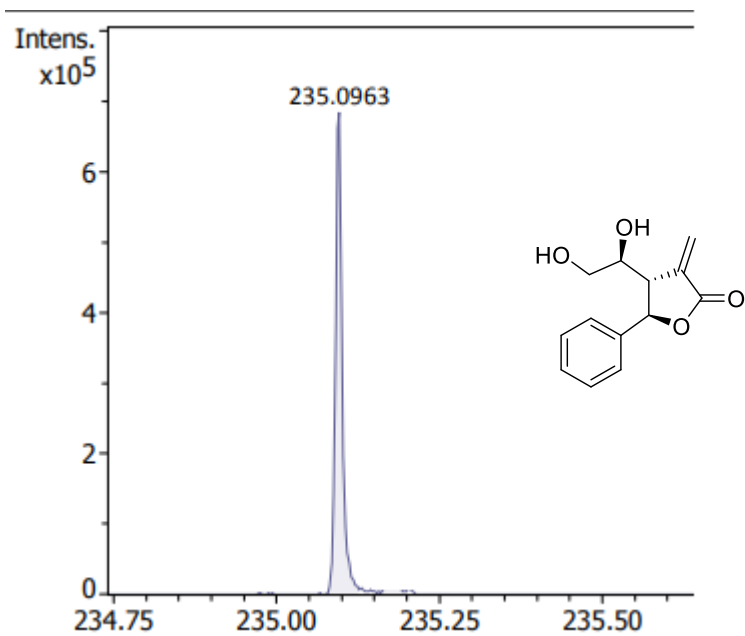
**8a:** HRMS (ESI-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{17}H_{16}O_4Na$  307.0941; Found: 307.0949.



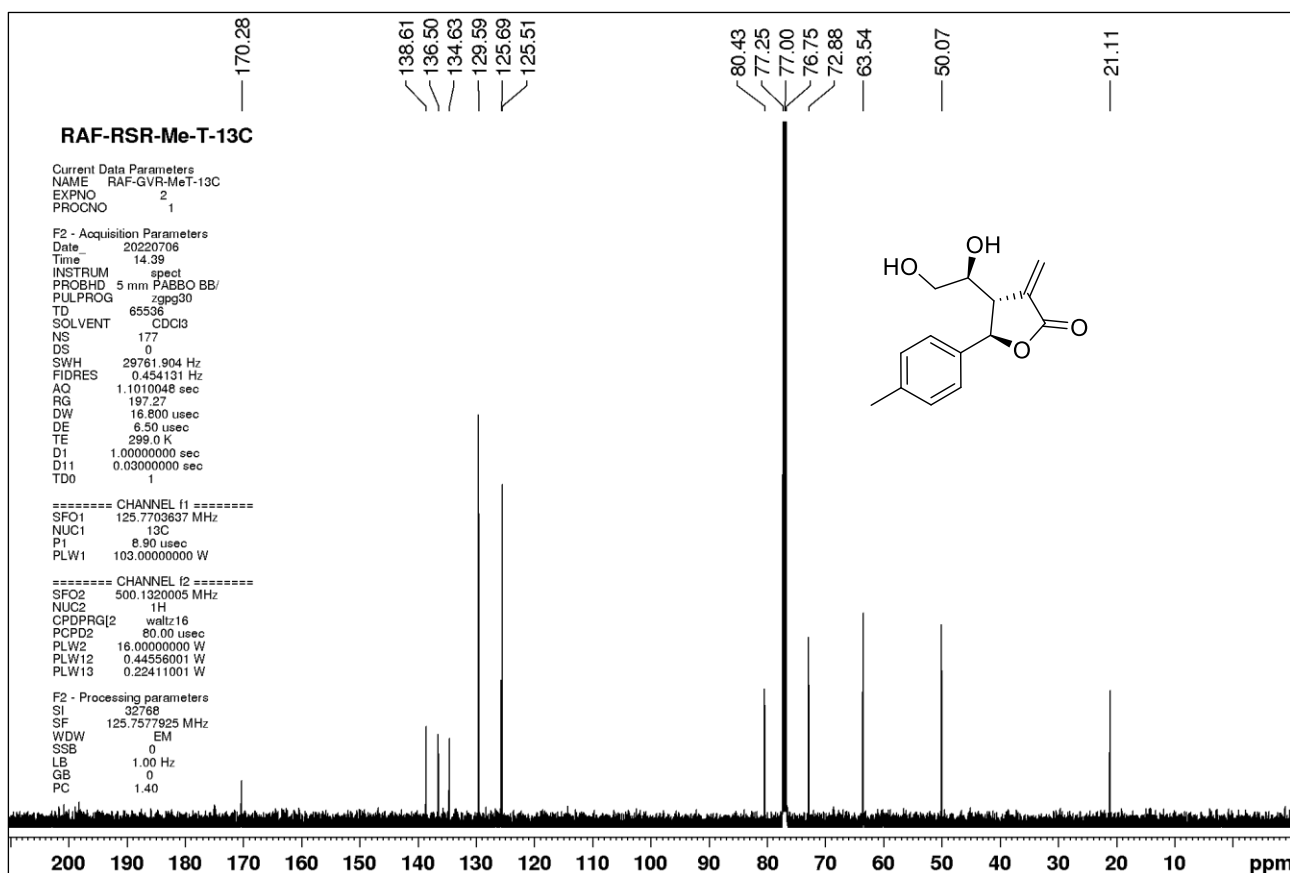
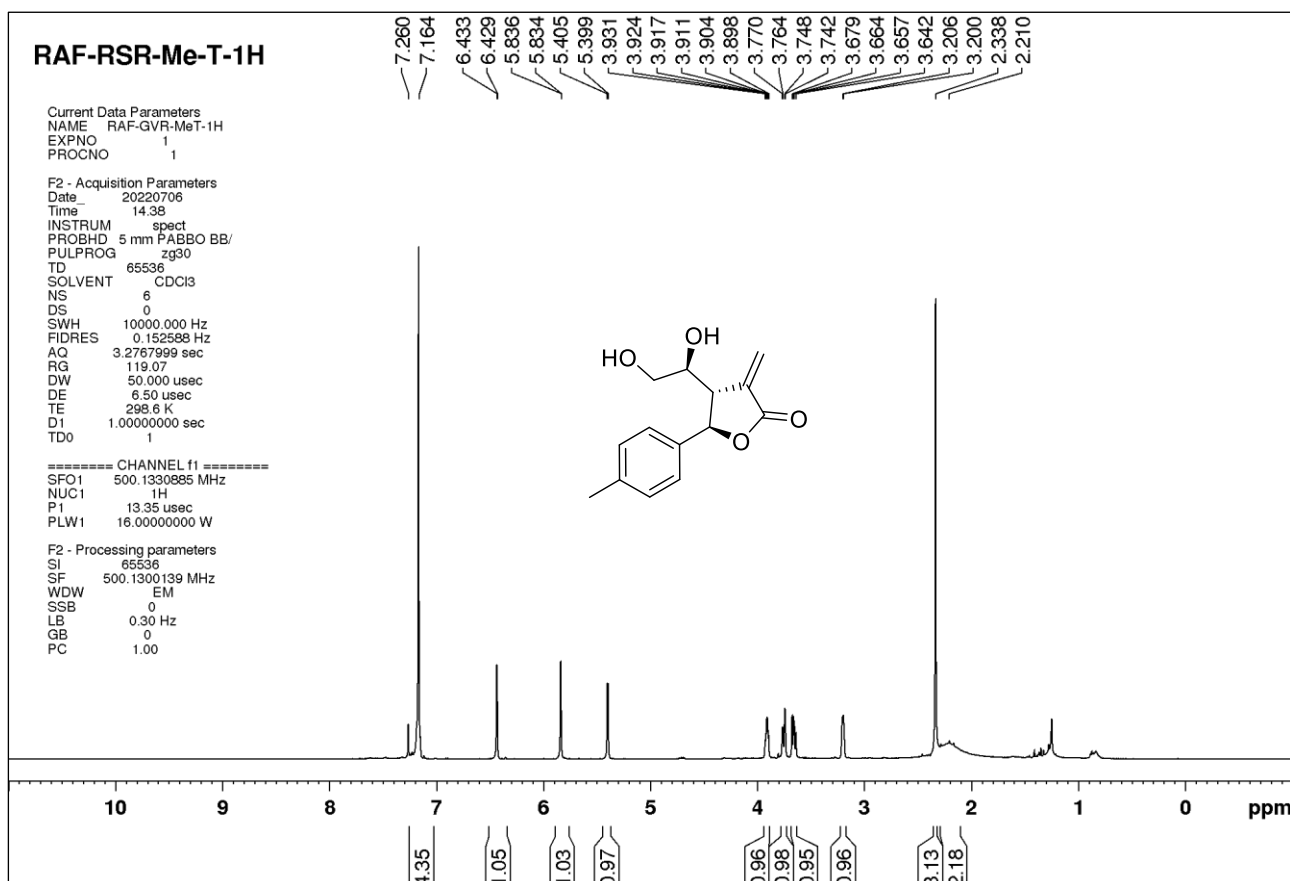
$^1\text{H}$  NMR (500 MHz, MeOH- $d_4$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz, MeOH- $d_4$ ) of compound **8b**



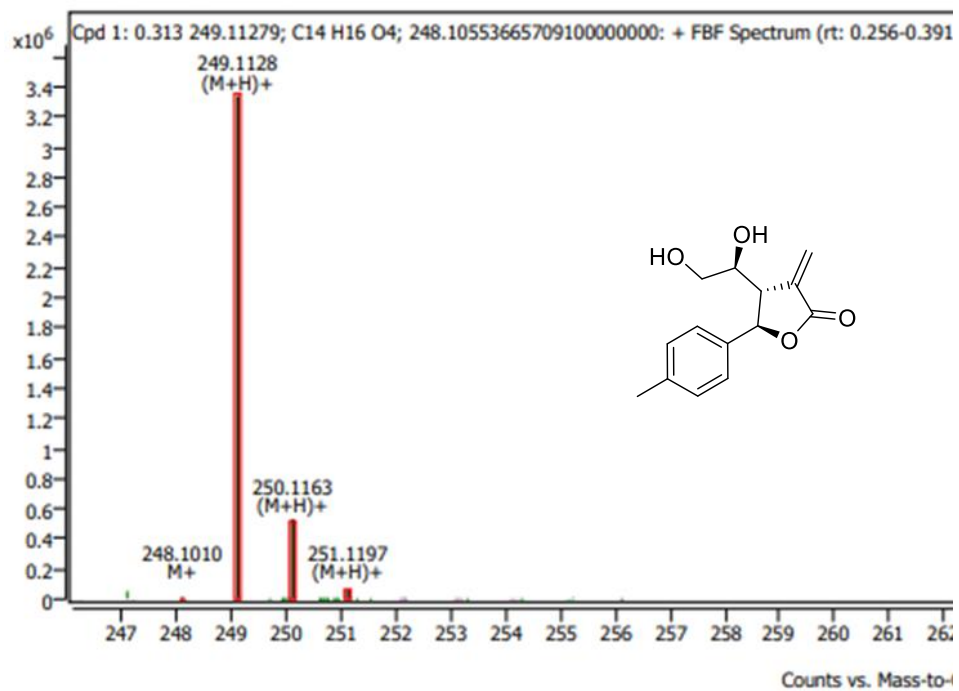
**8b:** HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{15}O_4$  235.0966; Found 235.0963.



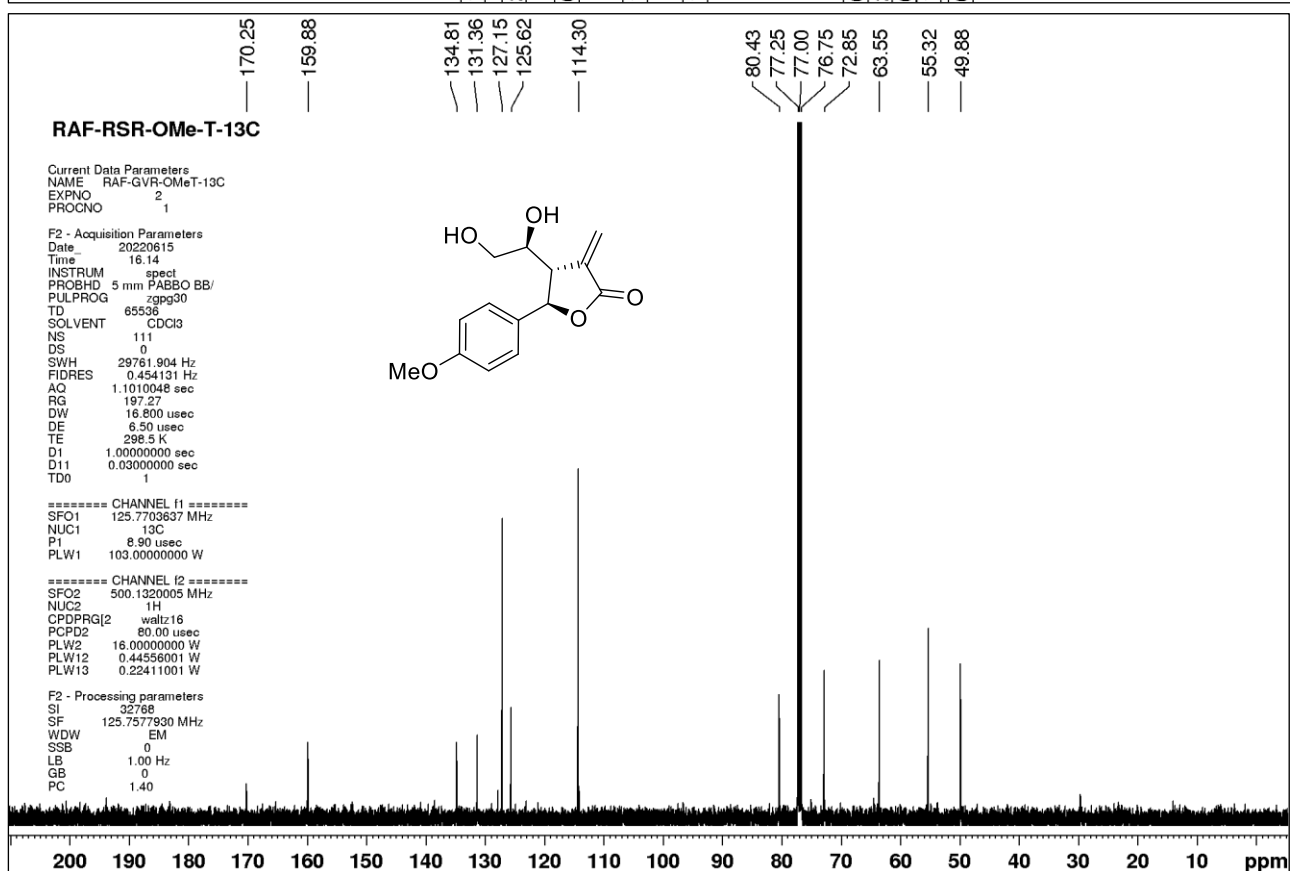
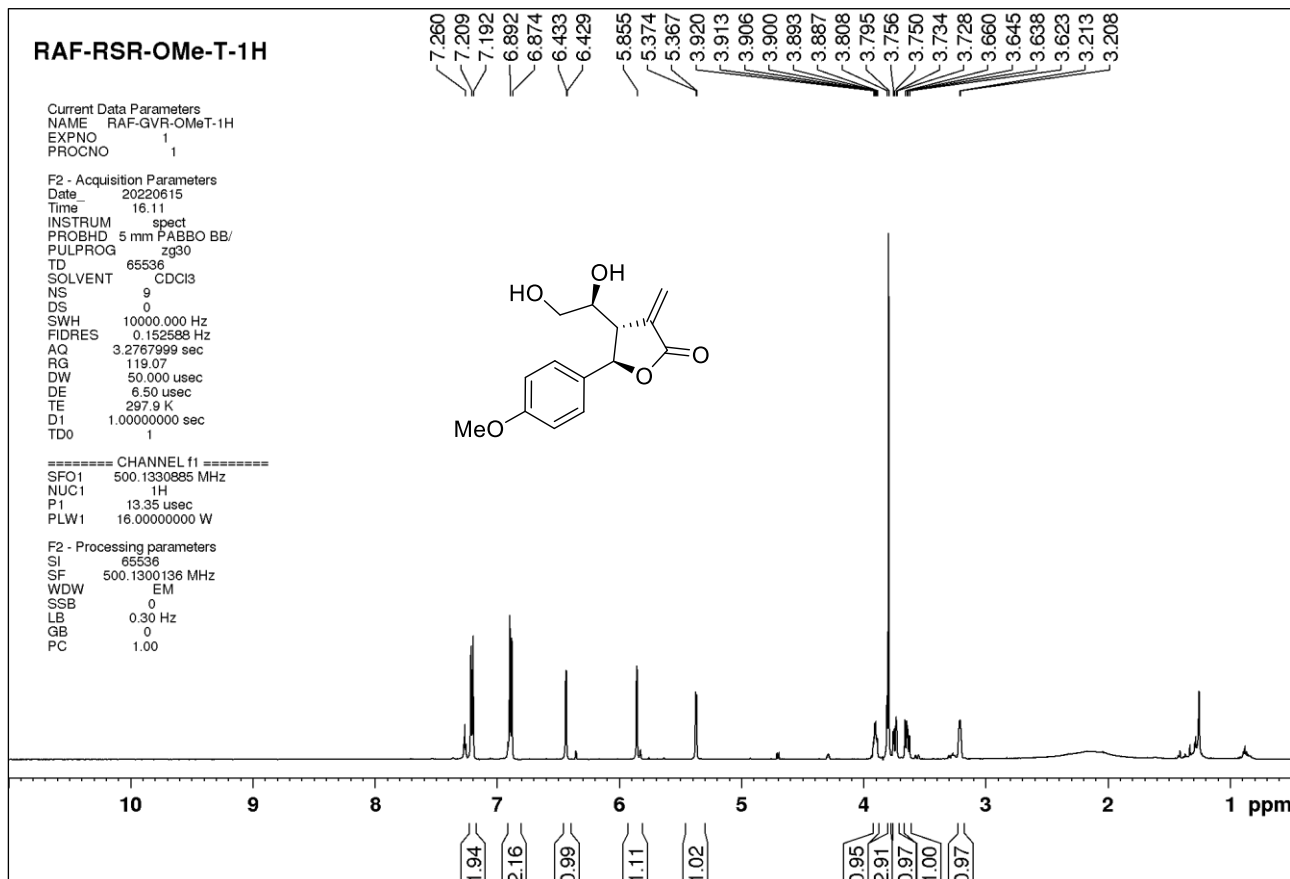
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound **8c**



**8c:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{14}H_{17}O_4$  249.1127; Found 249.1128.



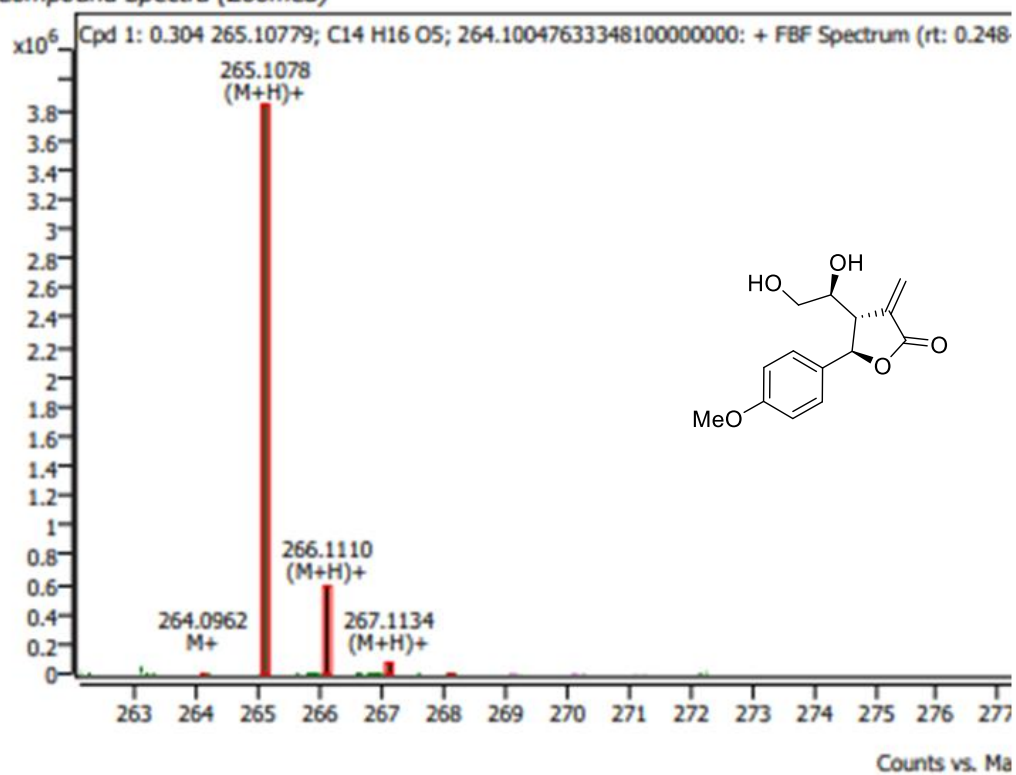
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound **8d**



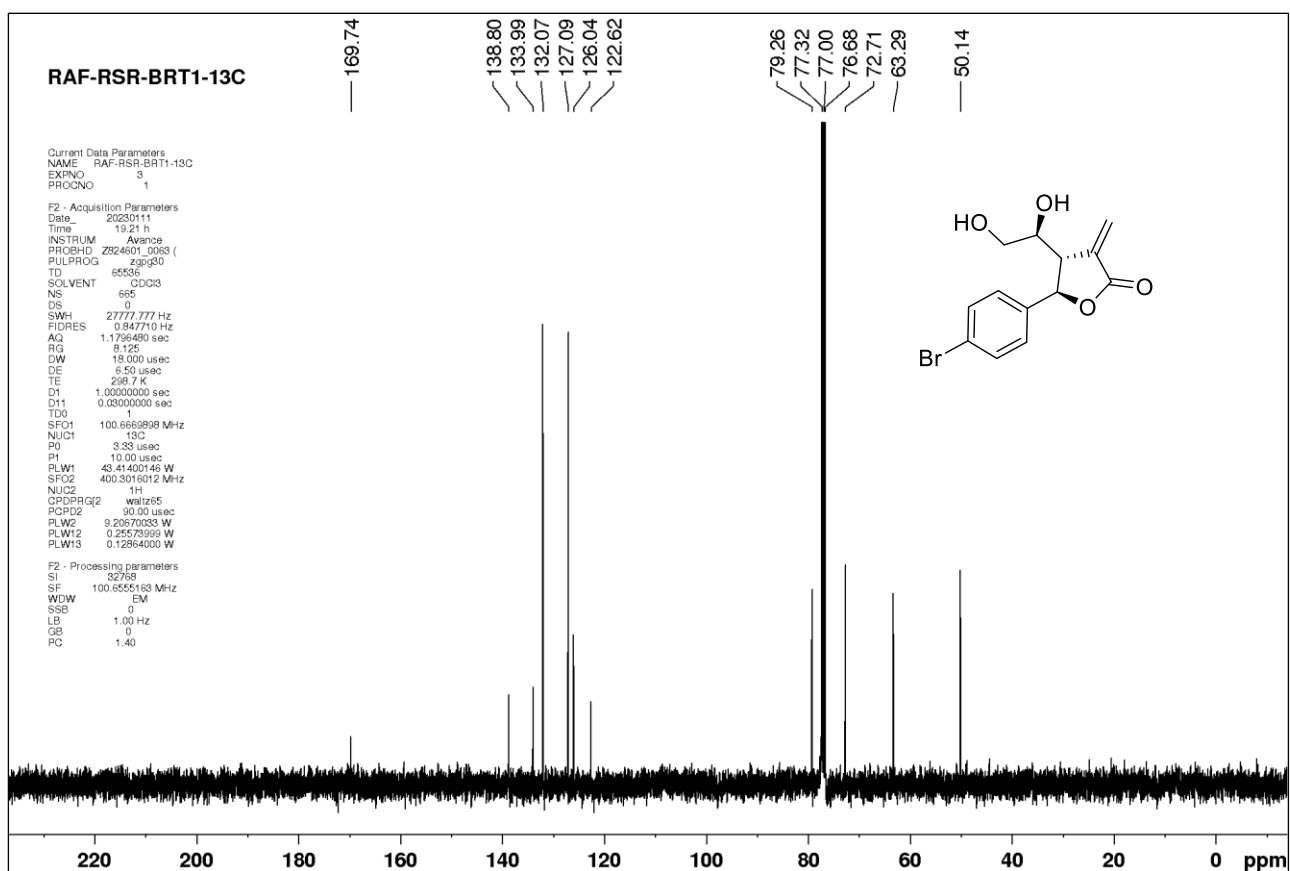
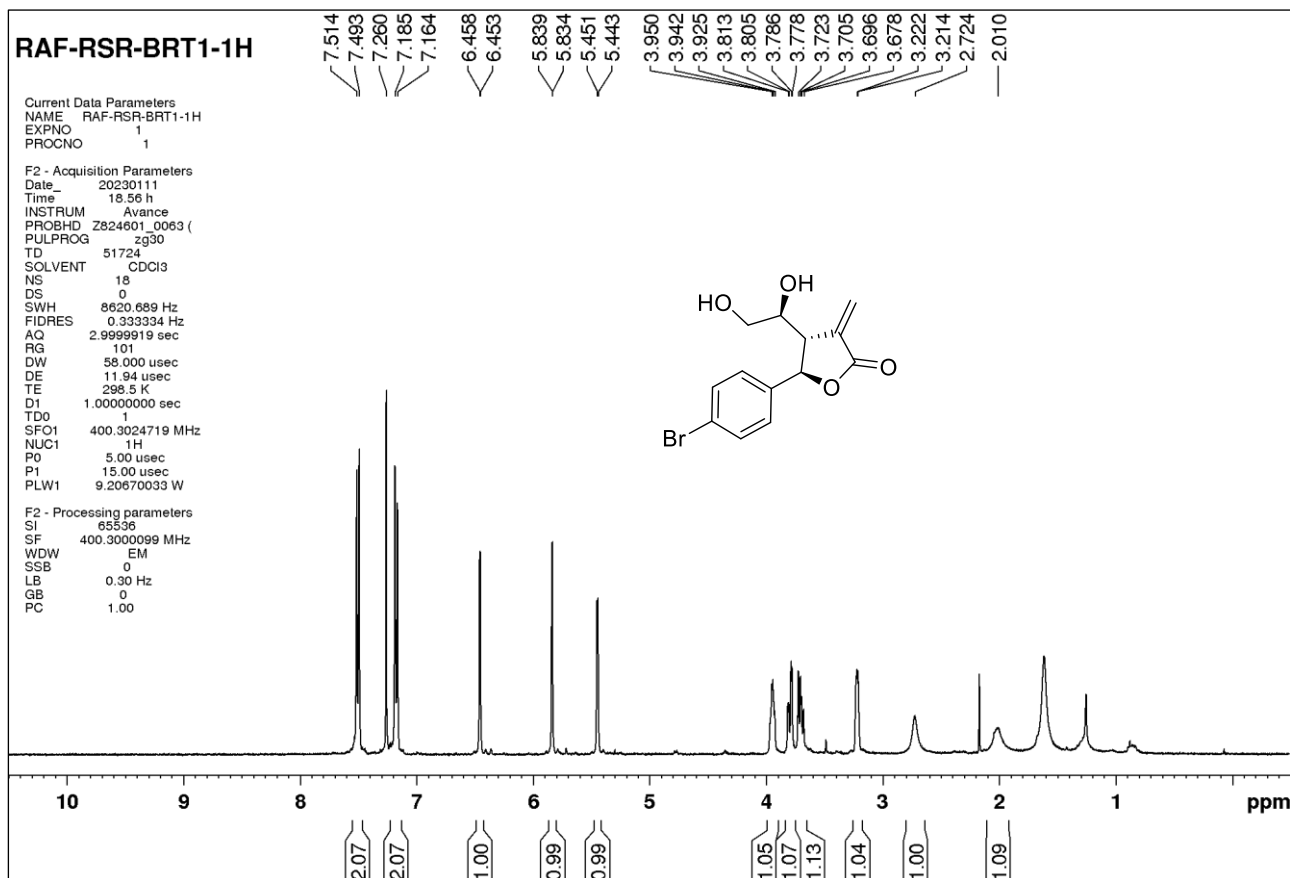


**8d:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{14}H_{17}O_5$  265.1078; Found 265.1078.

Compound Spectra (Zoomed)

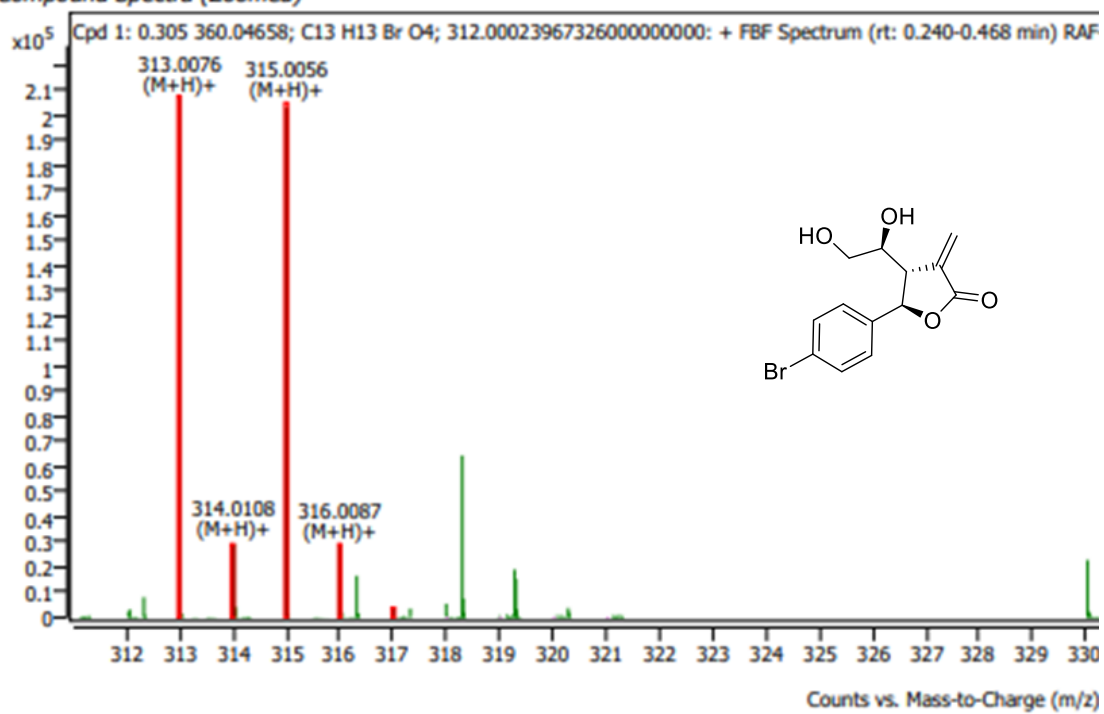


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **8e**

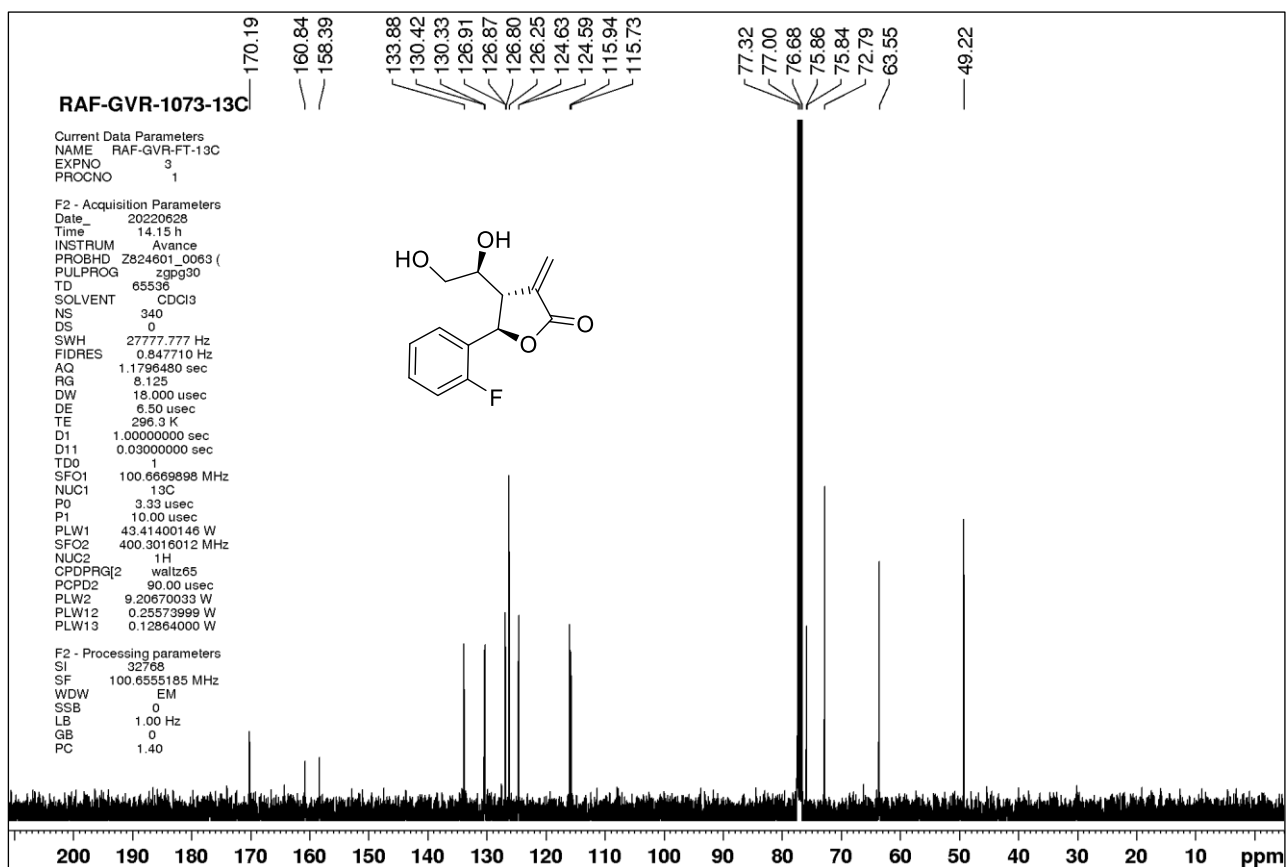
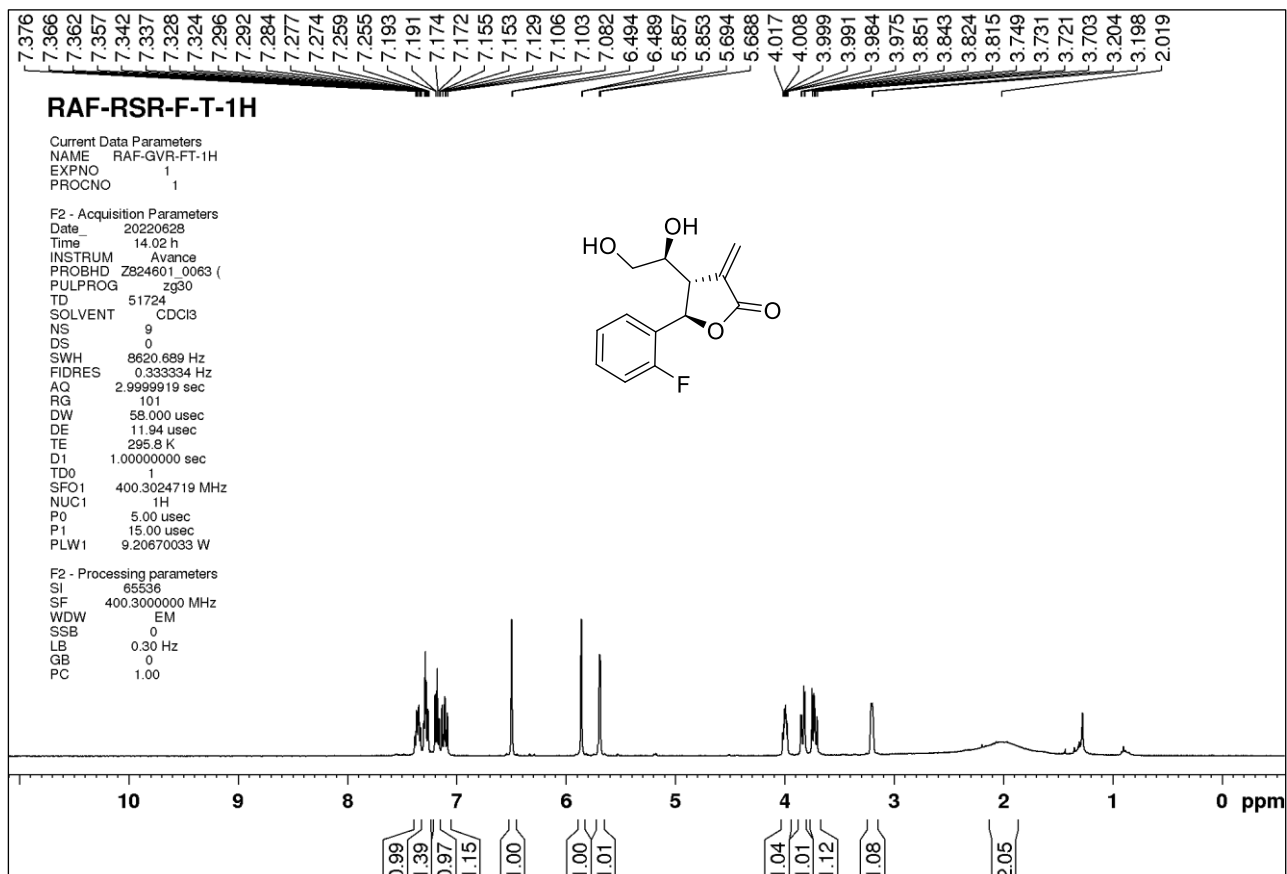


**8e:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{14}BrO_4$  313.0075; Found 313.0076.

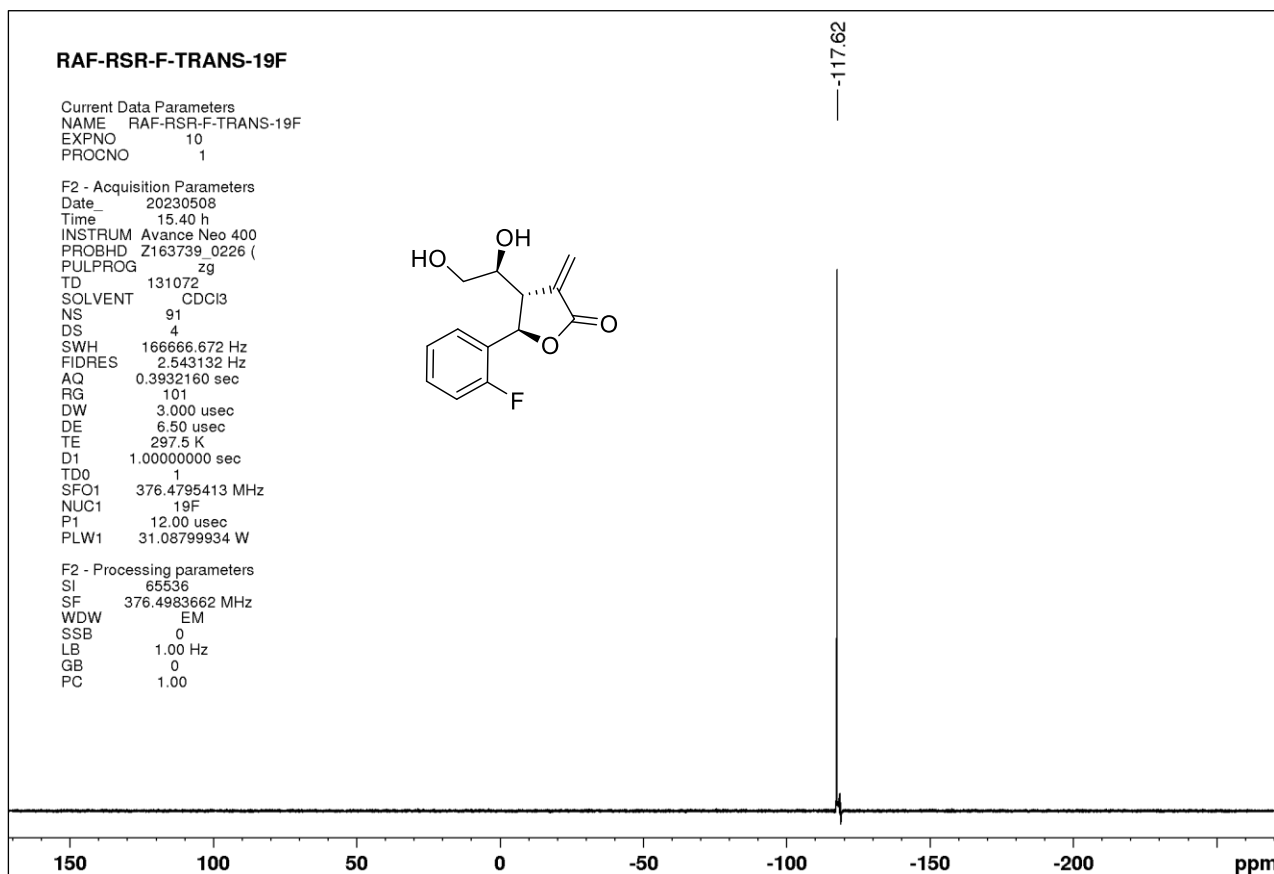
Compound Spectra (Zoomed)



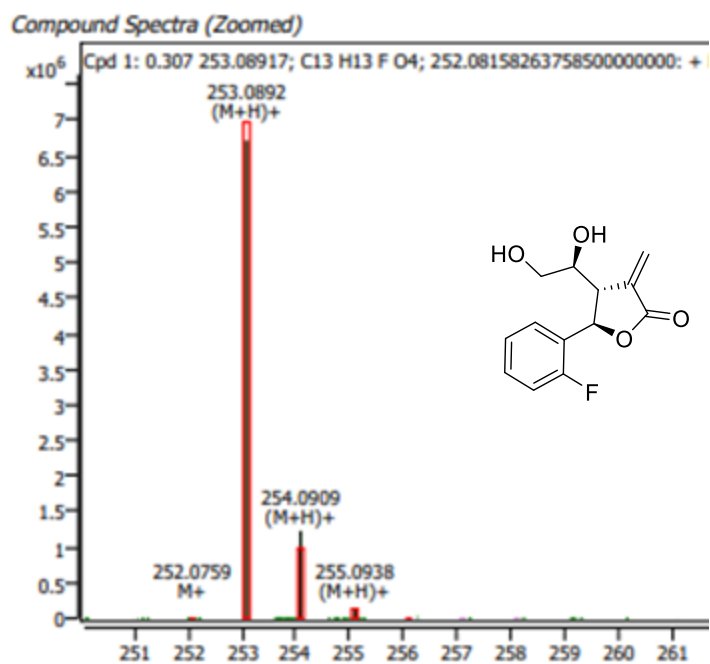
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) of compound **8f**



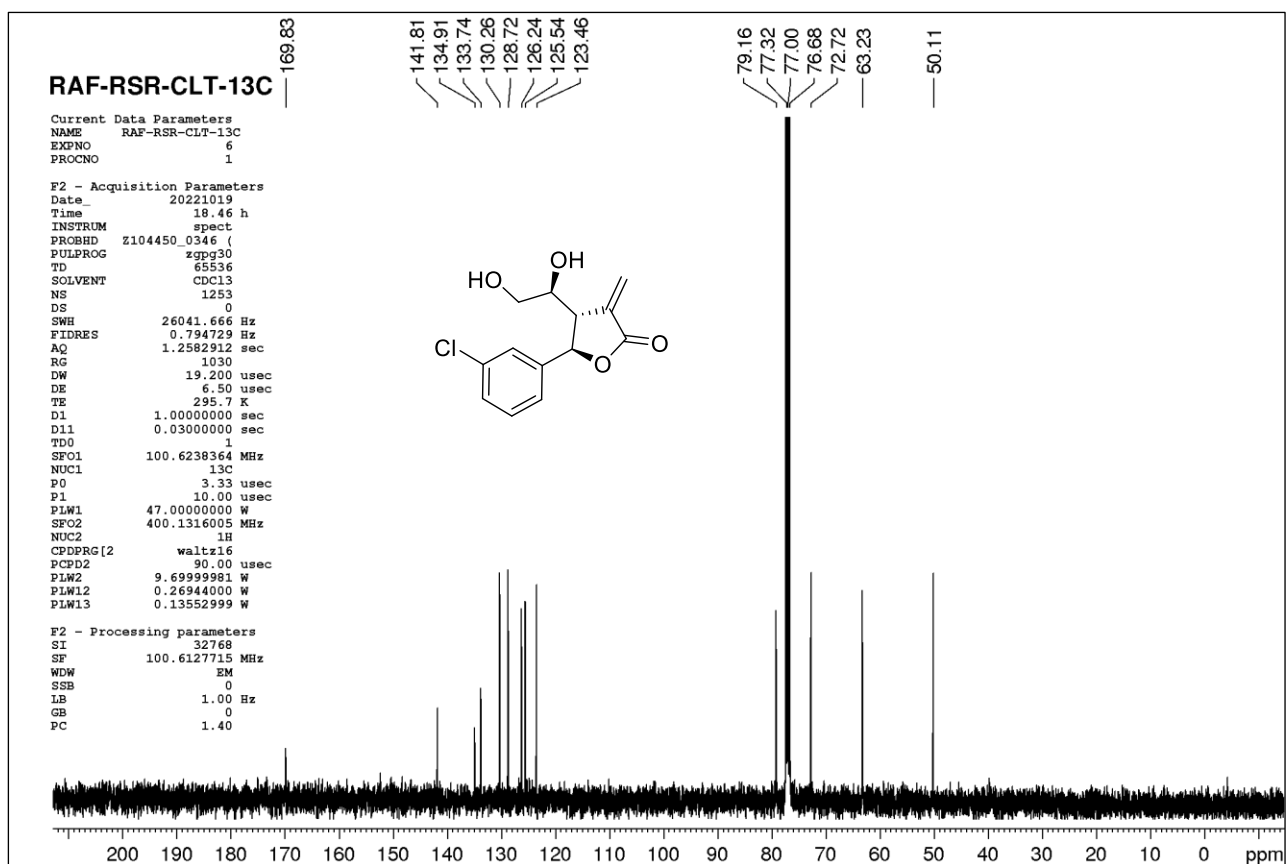
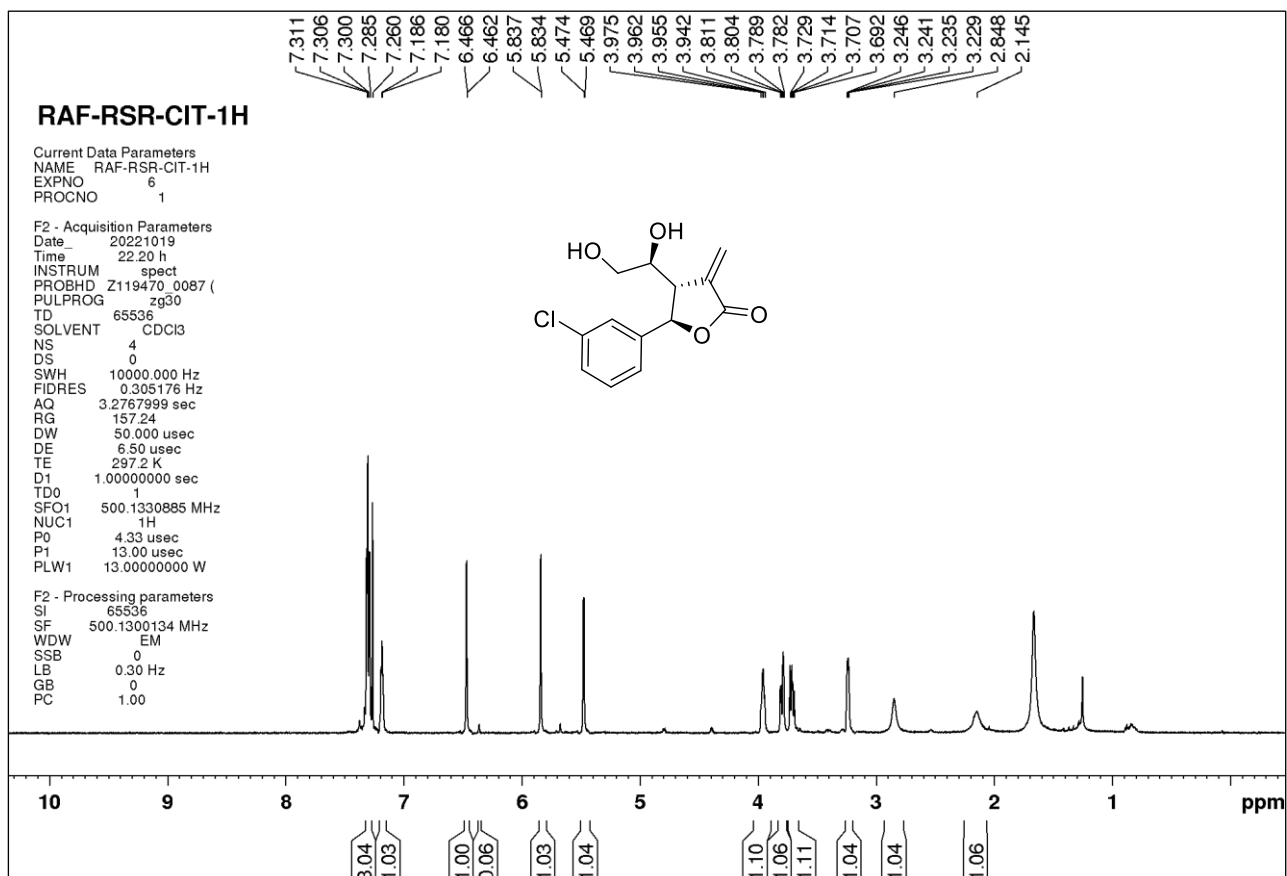
$^{19}\text{F}\{^1\text{H}\}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of compound **8f**



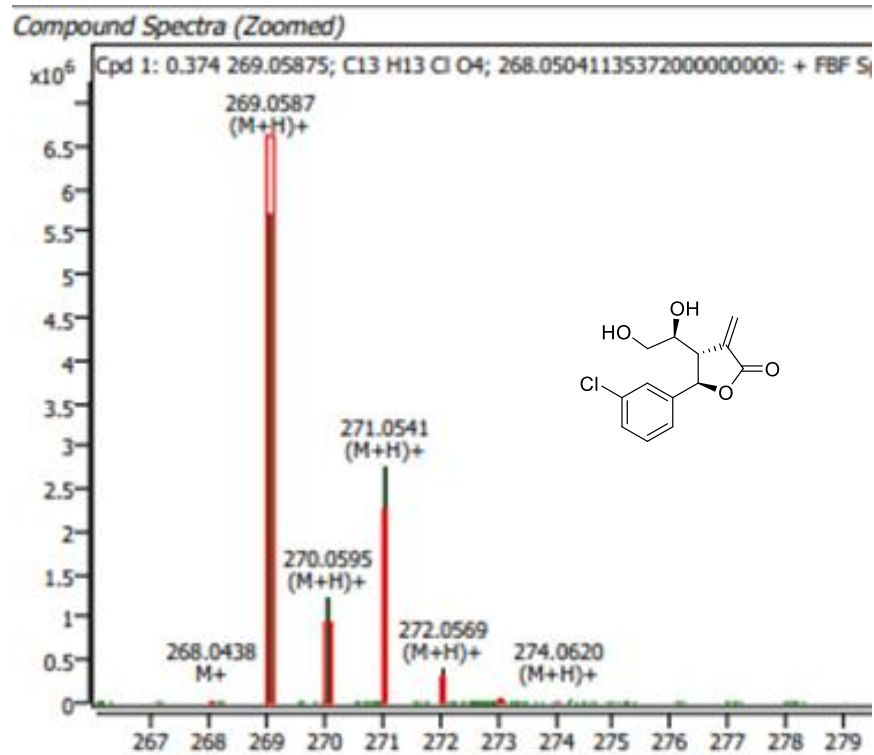
**8f**: HRMS (Q-TOF)  $m/z$ :  $[\text{M} + \text{H}]^+$  Calcd for  $\text{C}_{13}\text{H}_{14}\text{O}_4\text{F}$  253.0871; Found 253.0892.



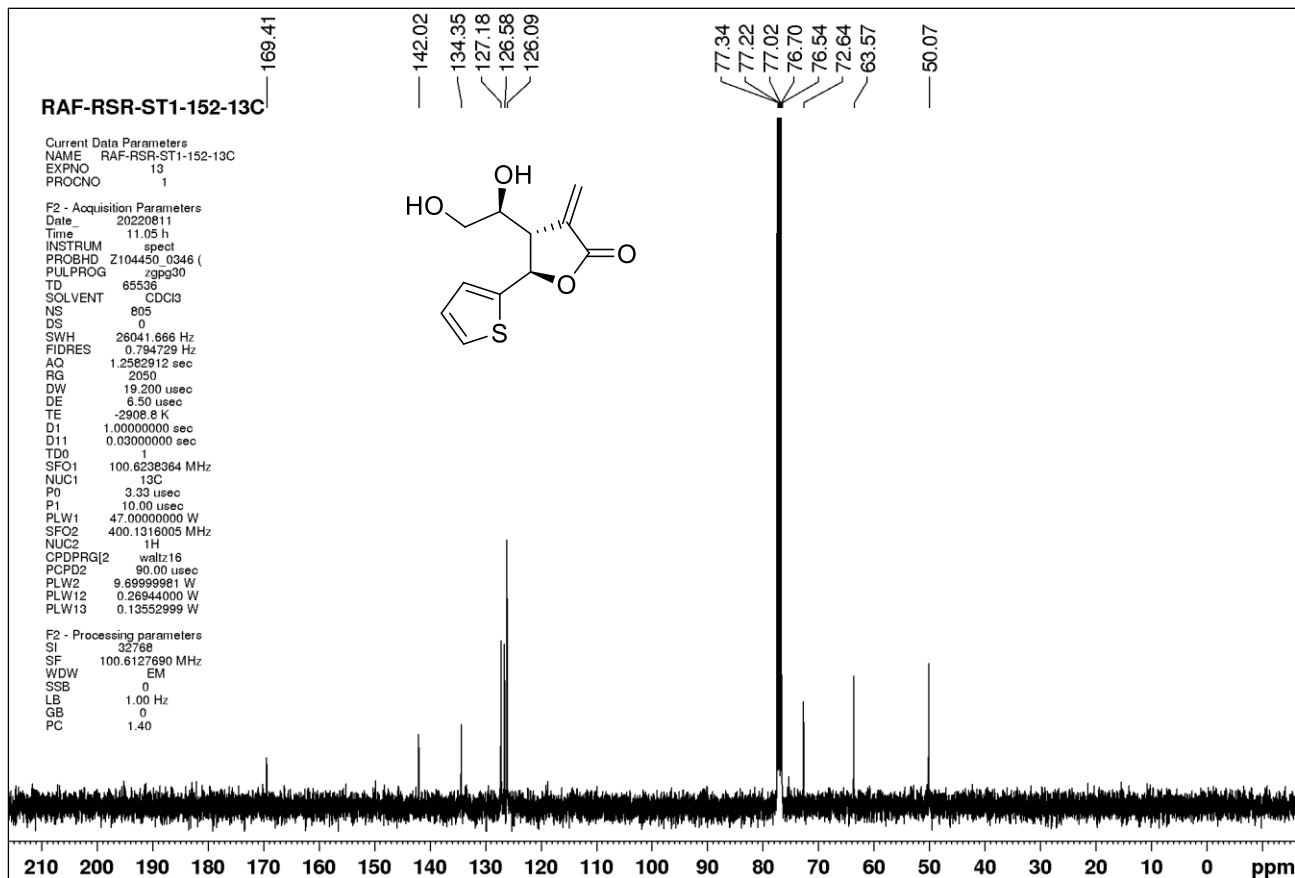
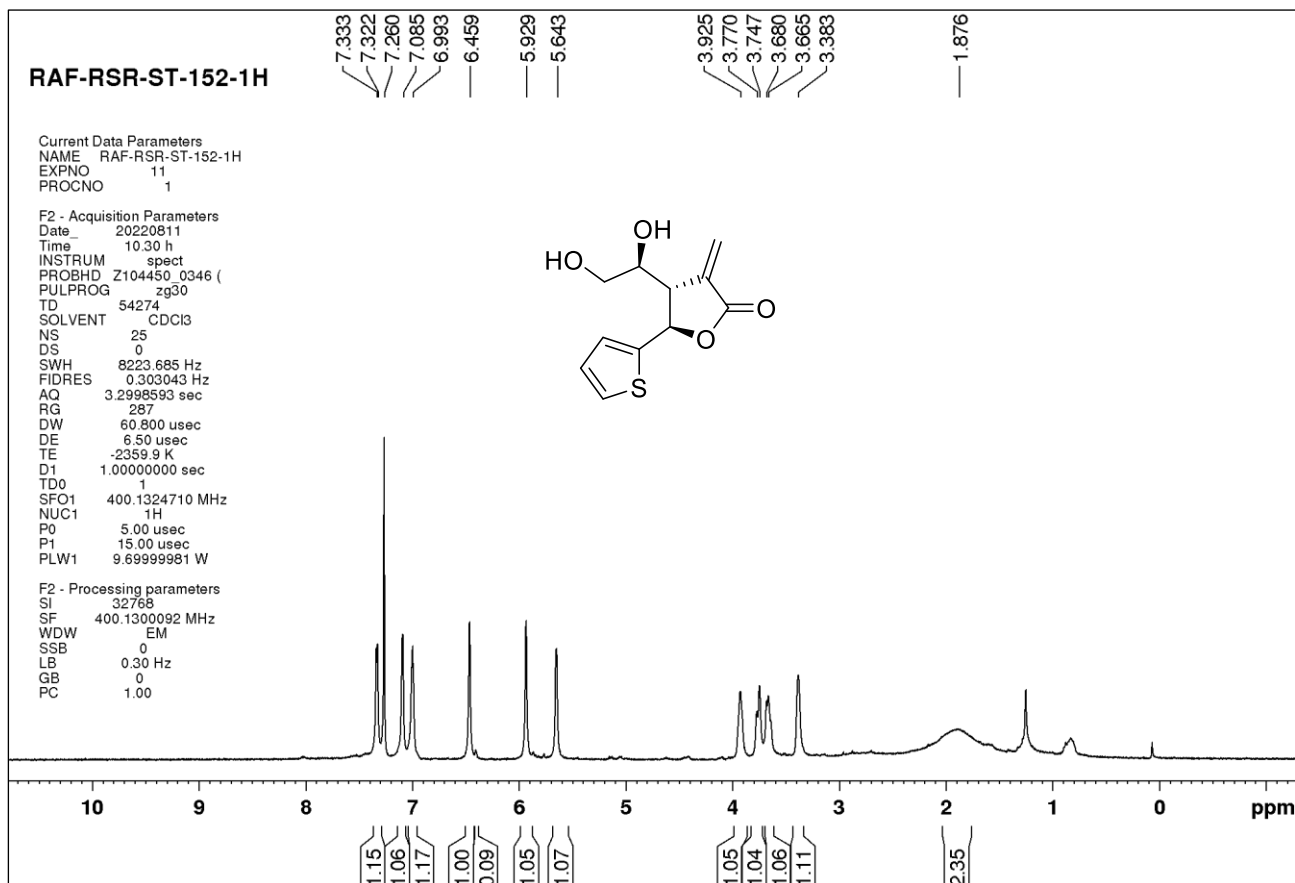
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **8g**



**8g:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{14}ClO_4$  269.0580; Found 269.0587.

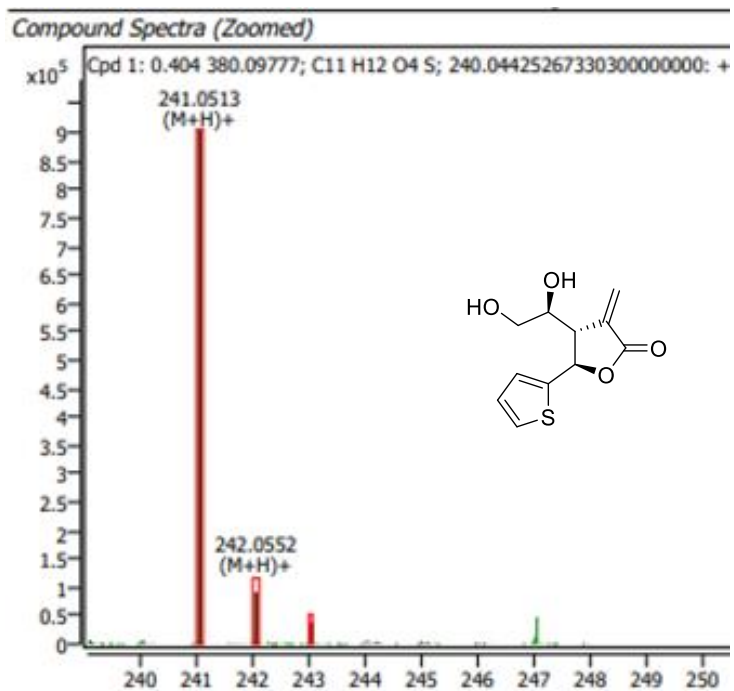


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) of compound **8h**

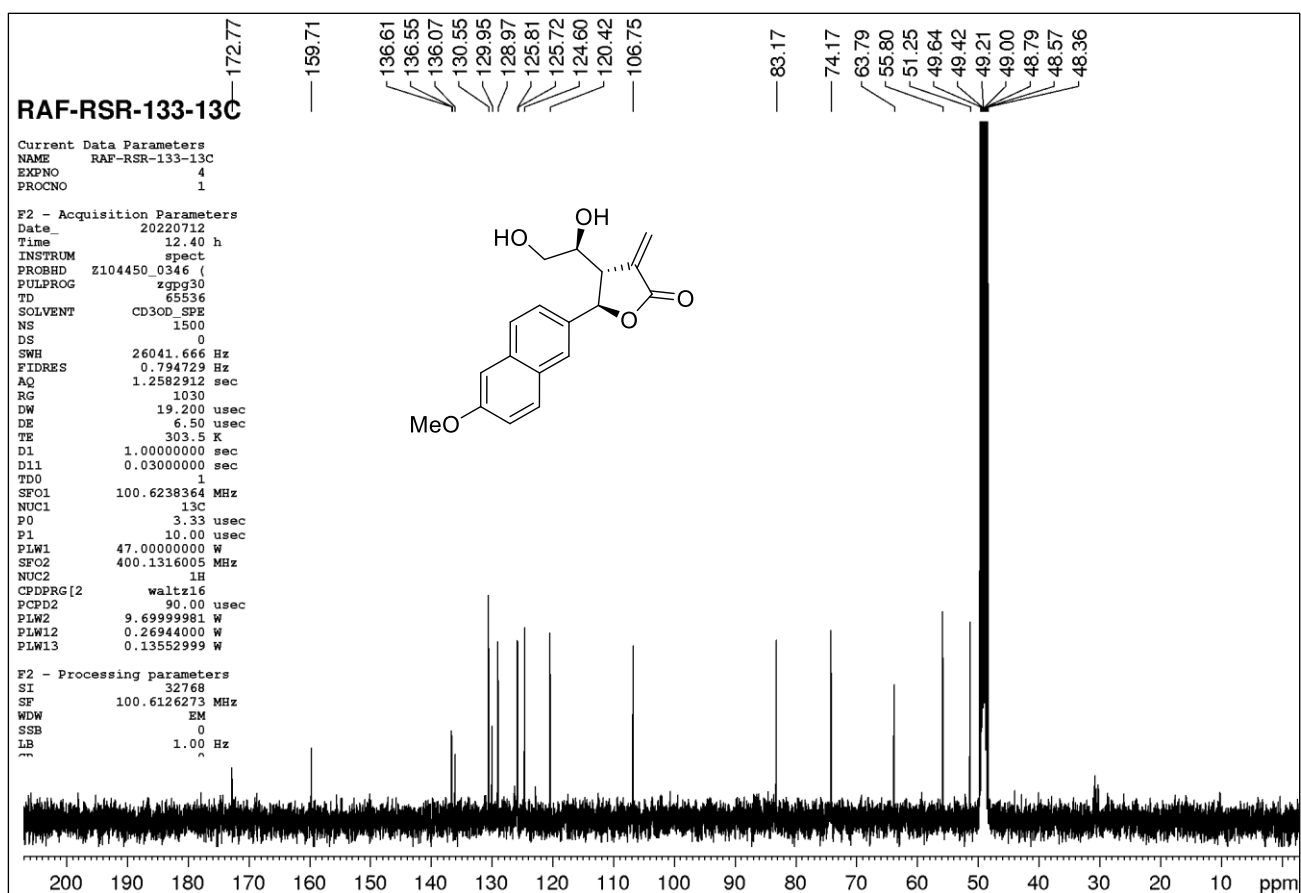
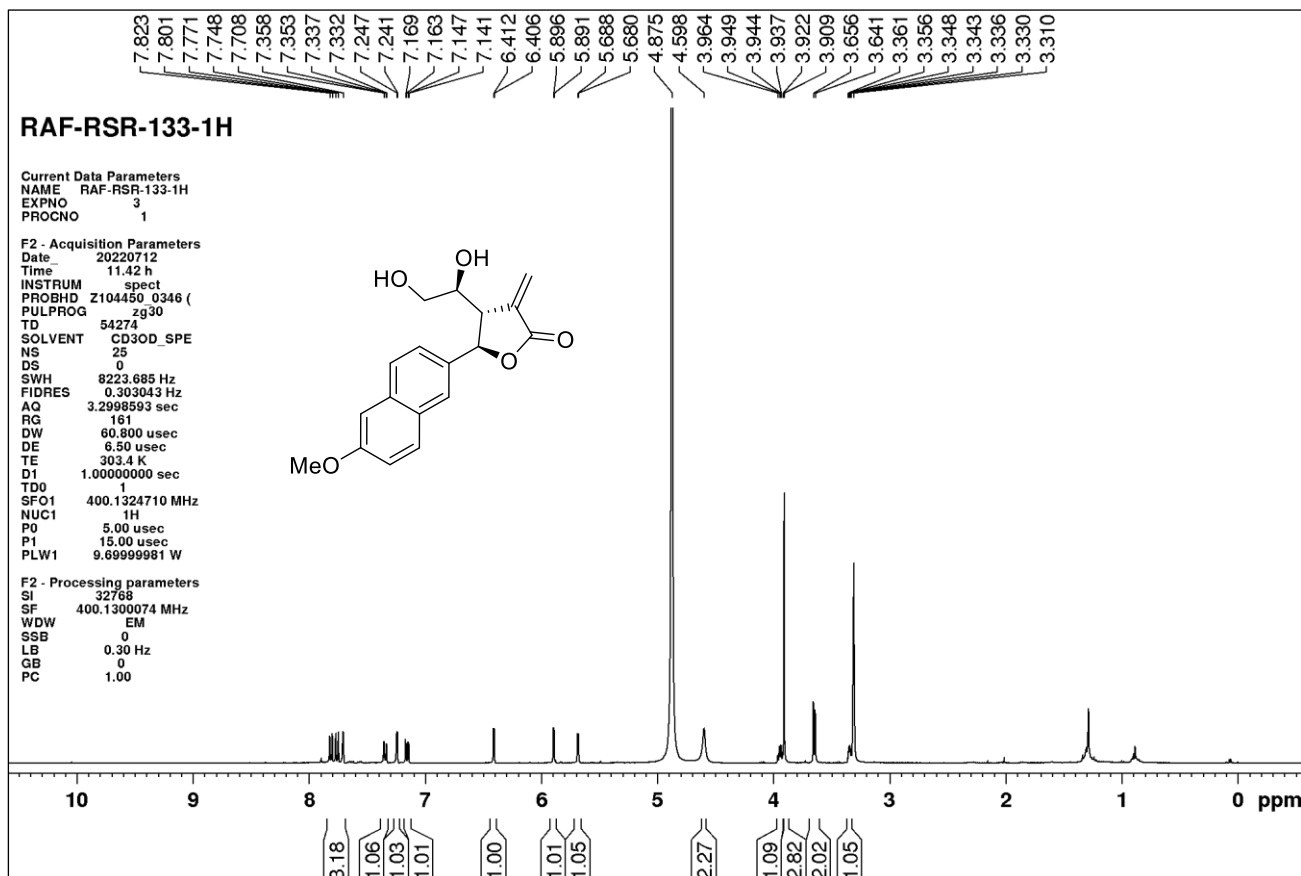




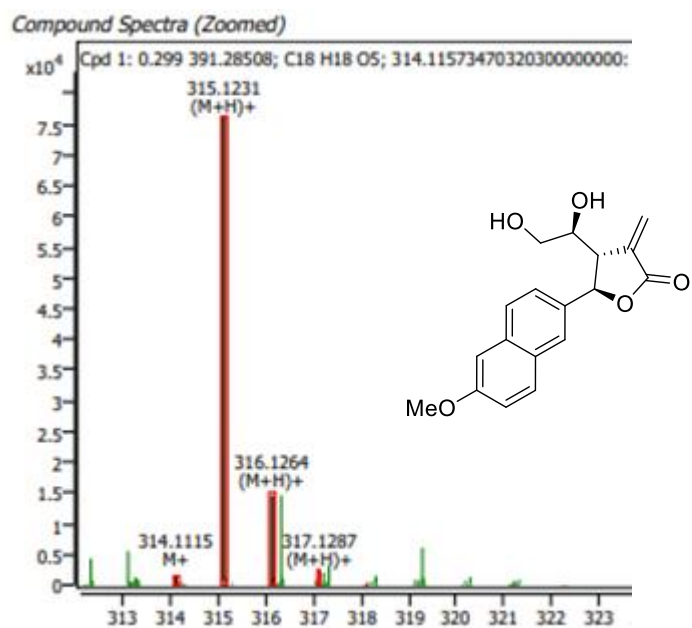
**8h:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{11}H_{13}SO_4$  241.0515; Found 241.0513.



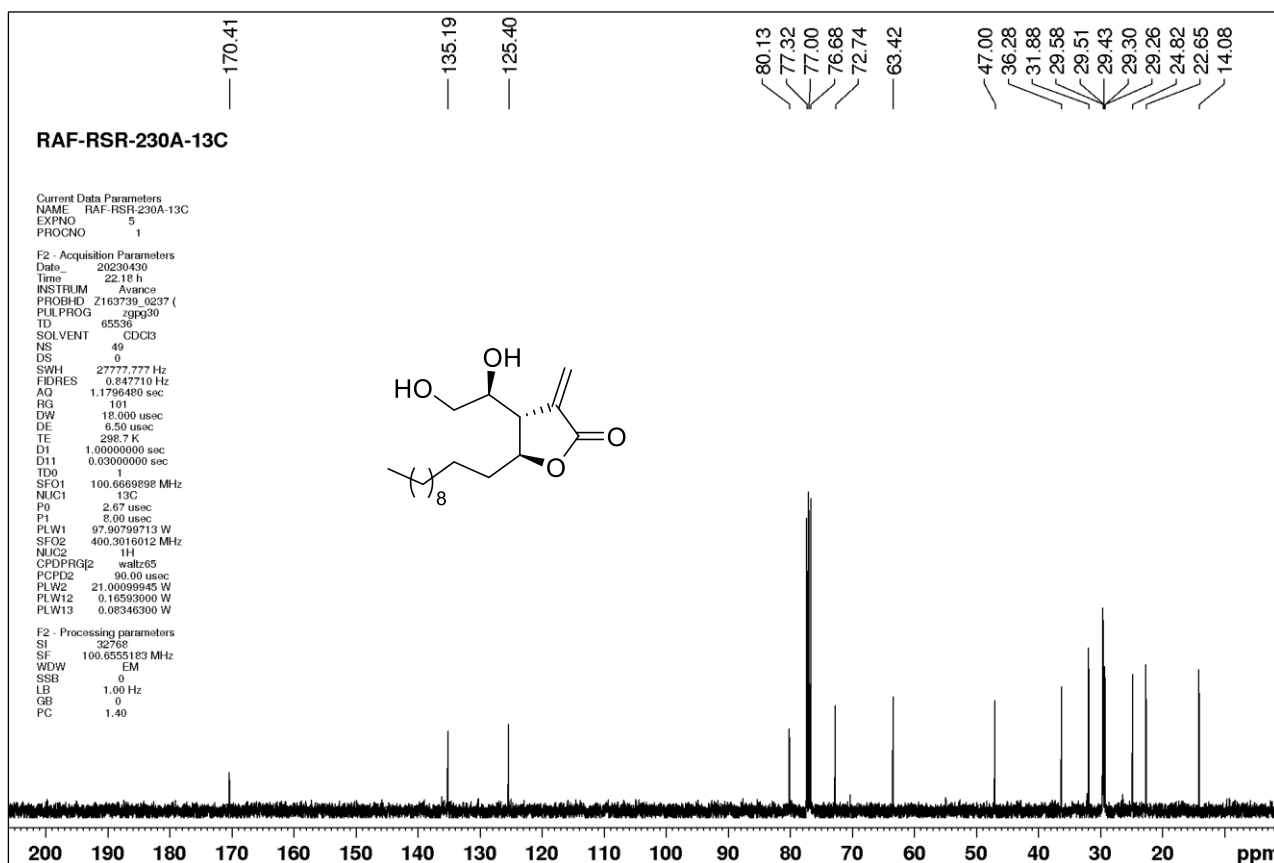
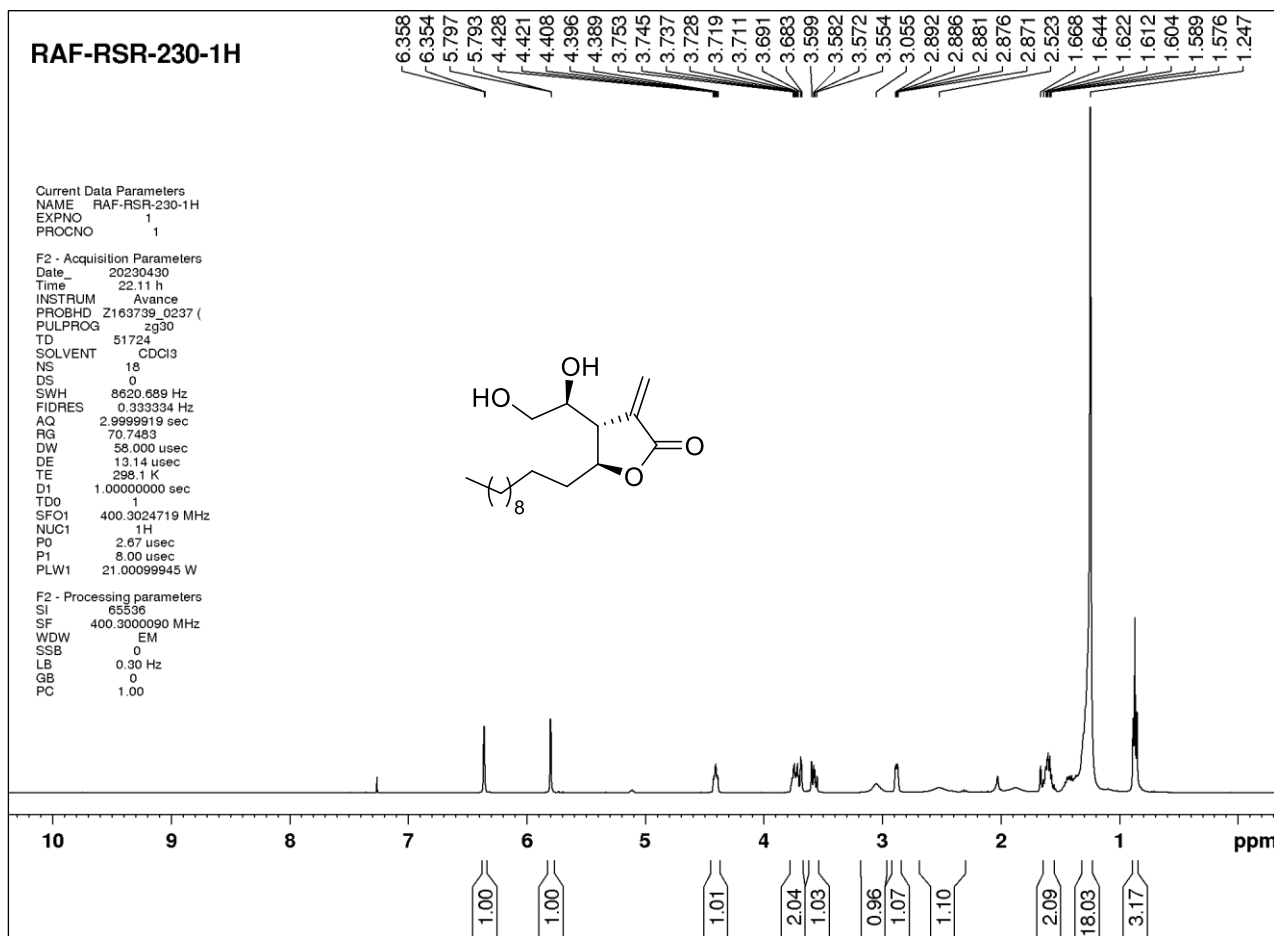
$^1\text{H}$  NMR (400 MHz, MeOH- $d_4$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz, MeOH- $d_4$ ) of compound **8i**



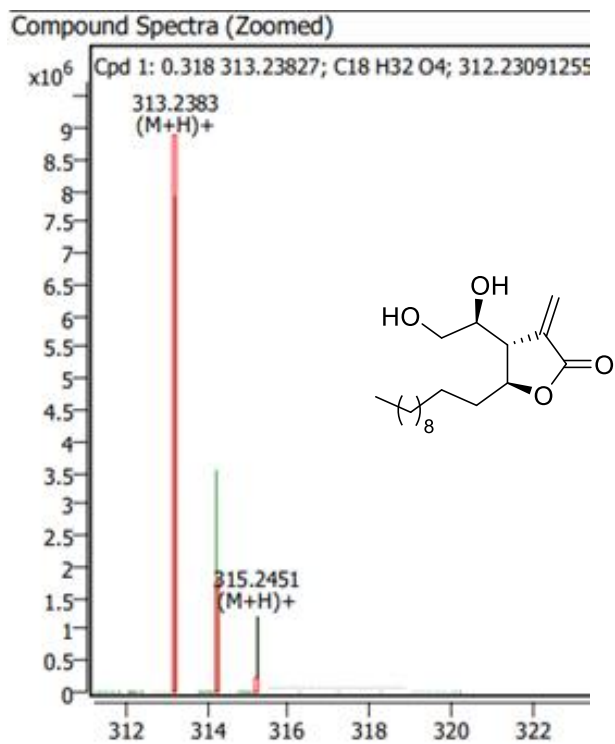
8i: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{18}H_{19}O_5$  315.1231; Found 315.1231.



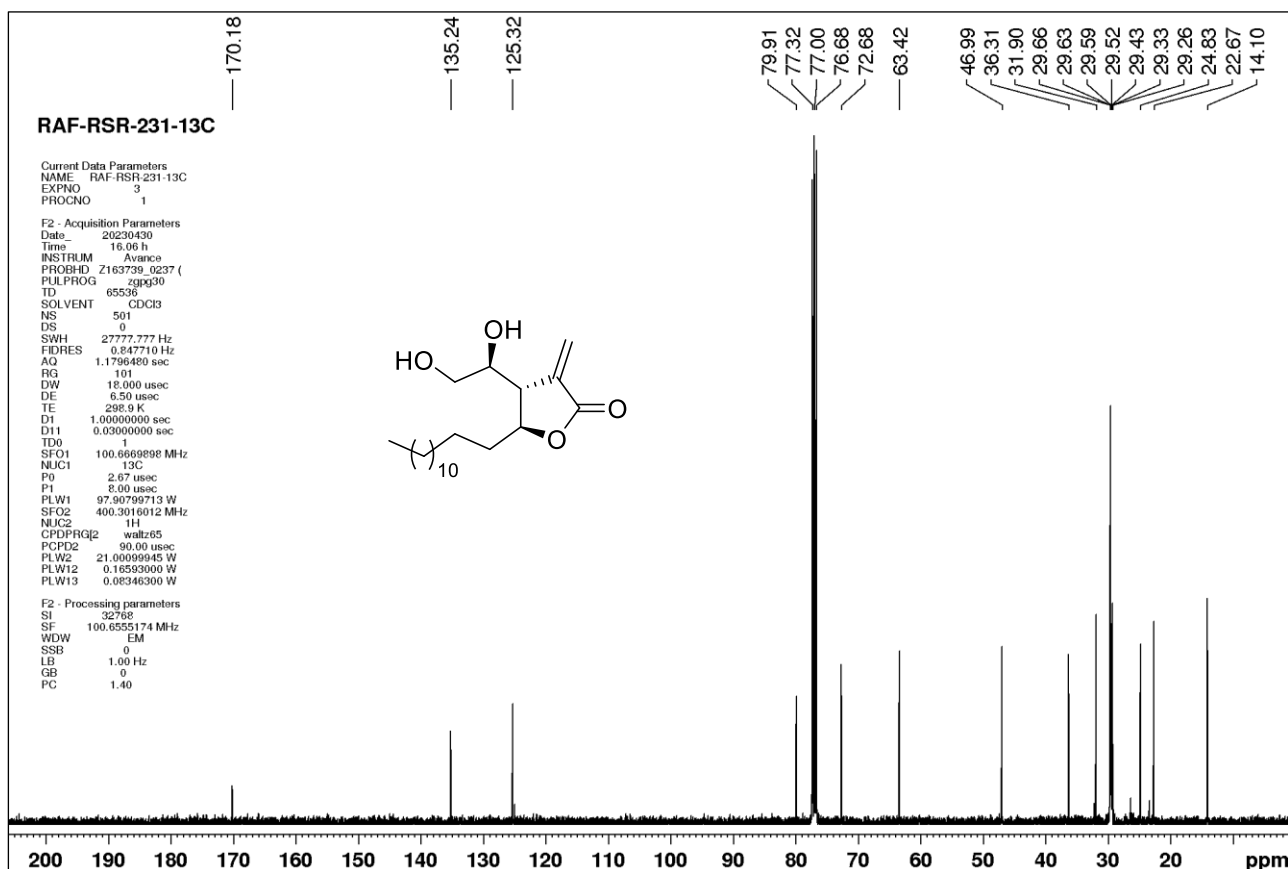
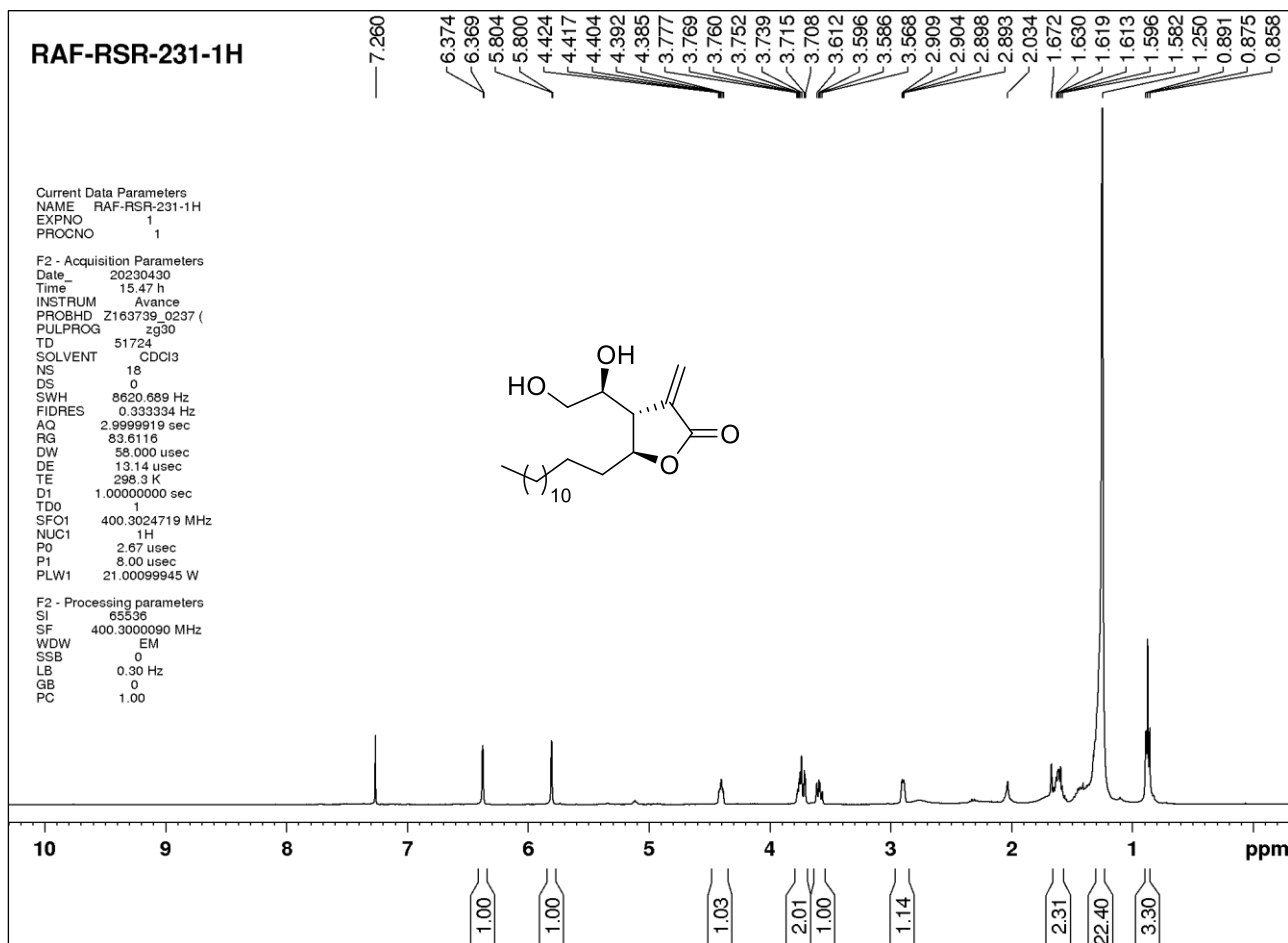
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) of compound **8j**



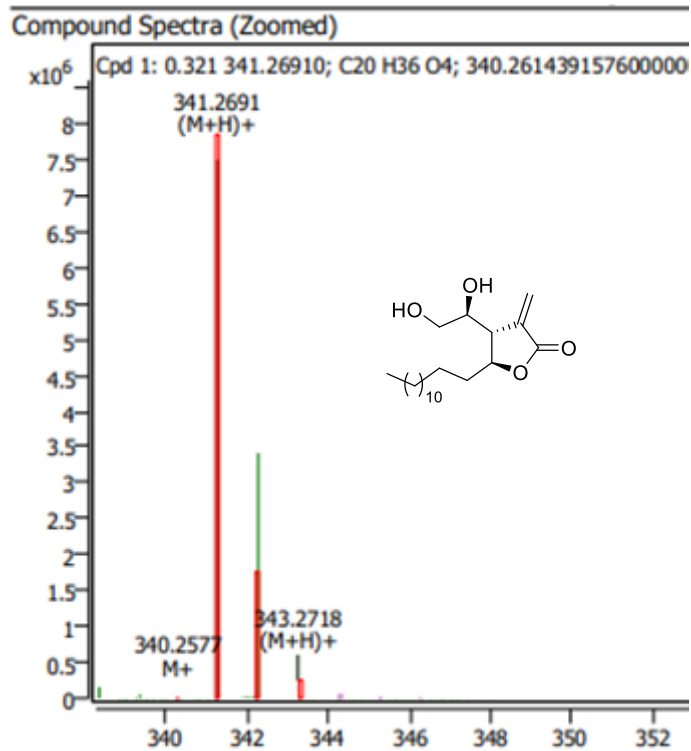
**8j:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{18}H_{33}O_4$  313.2374; Found 313.2383.



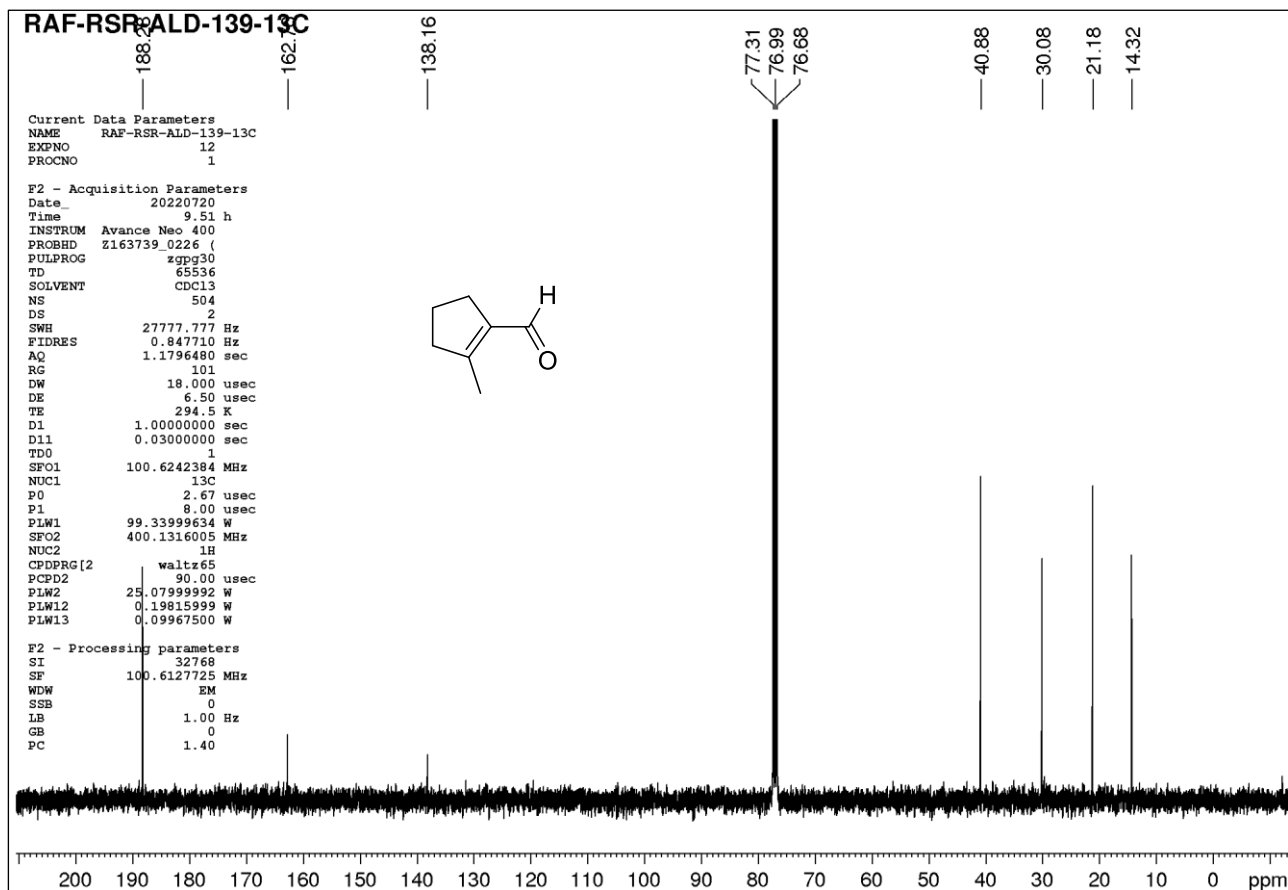
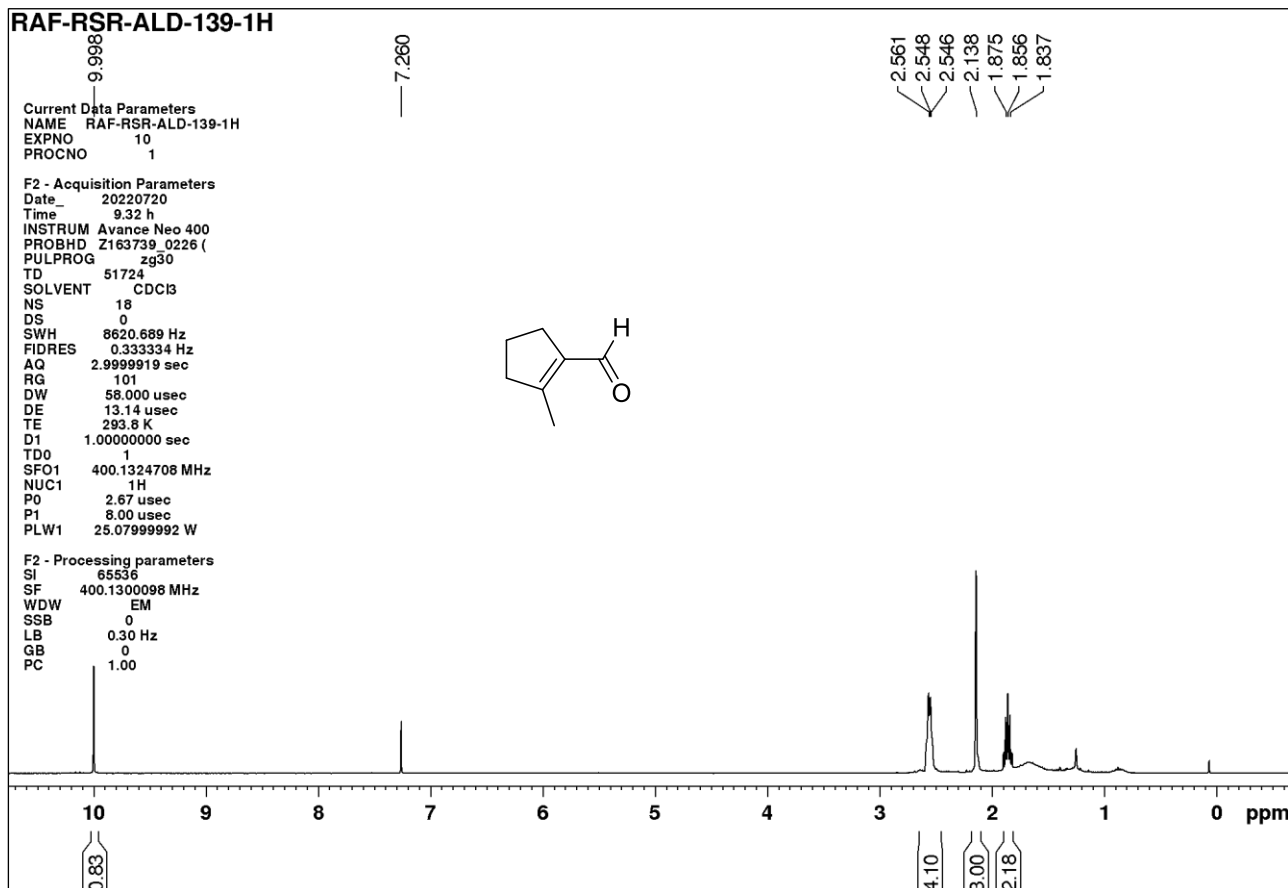
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **8k**



**8k:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{20}H_{37}O_4$  341.2687; Found 341.2691.

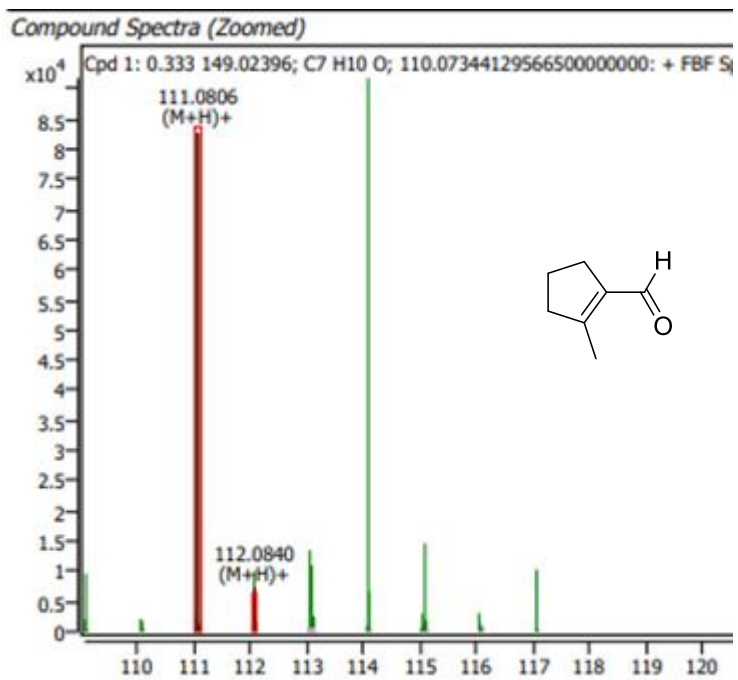


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **11**

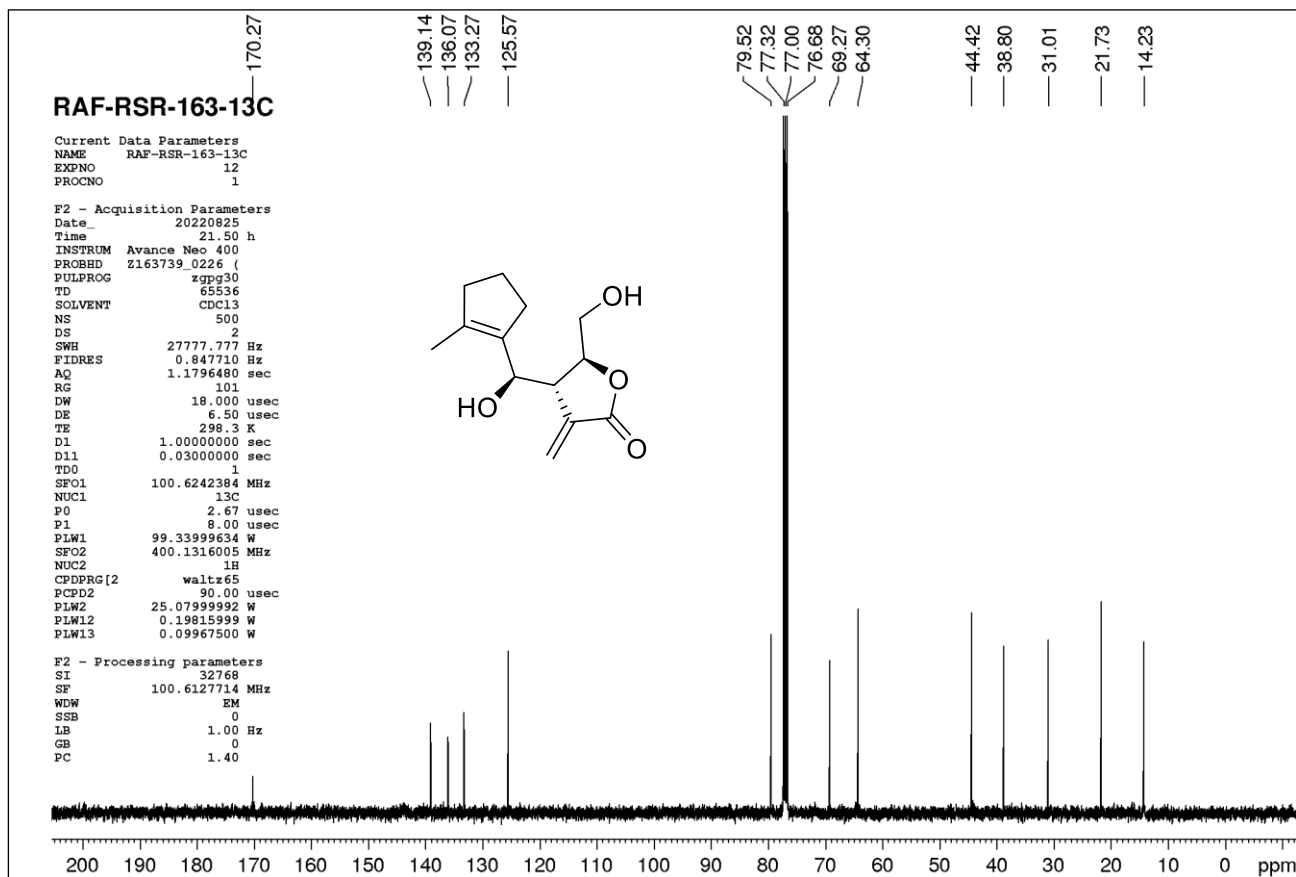
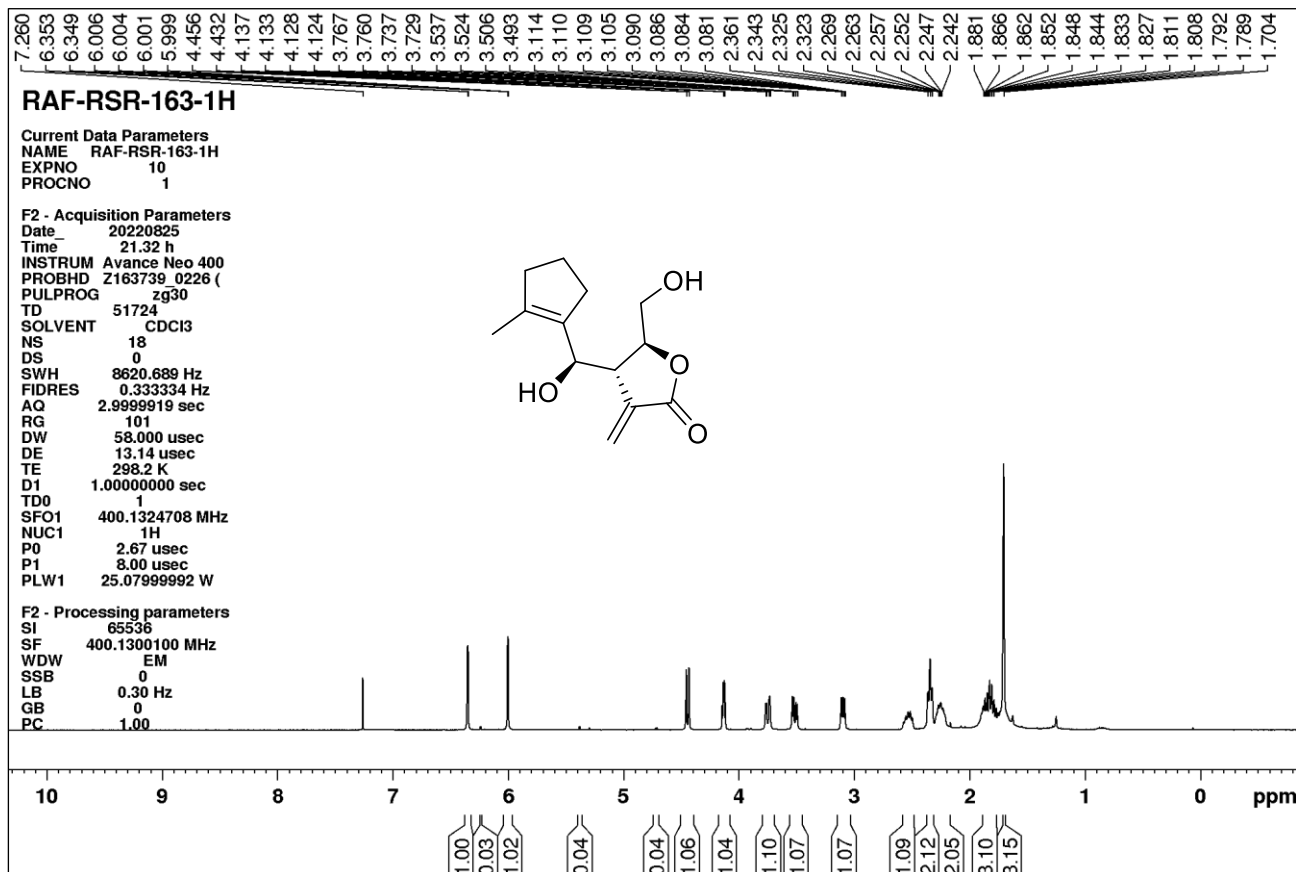




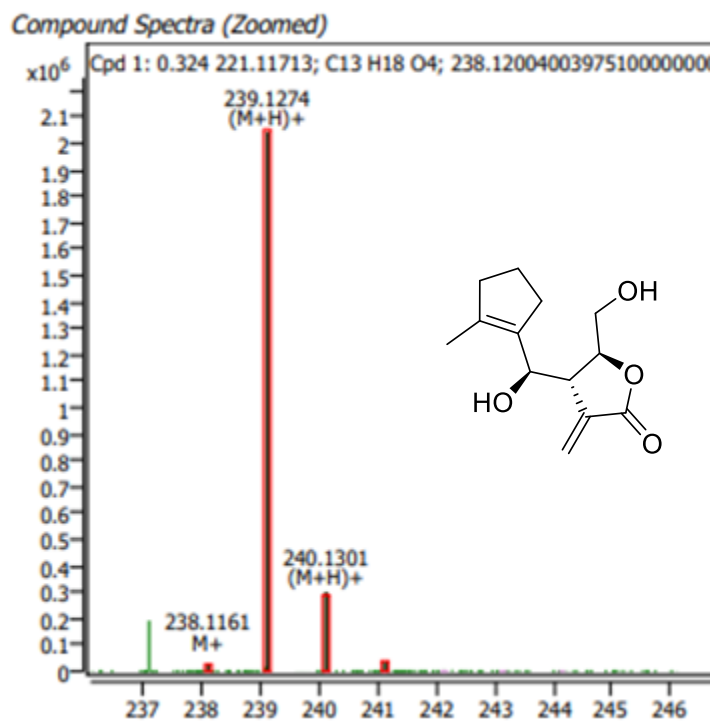
11: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_7H_{11}O$  111.0809; Found 111.0806



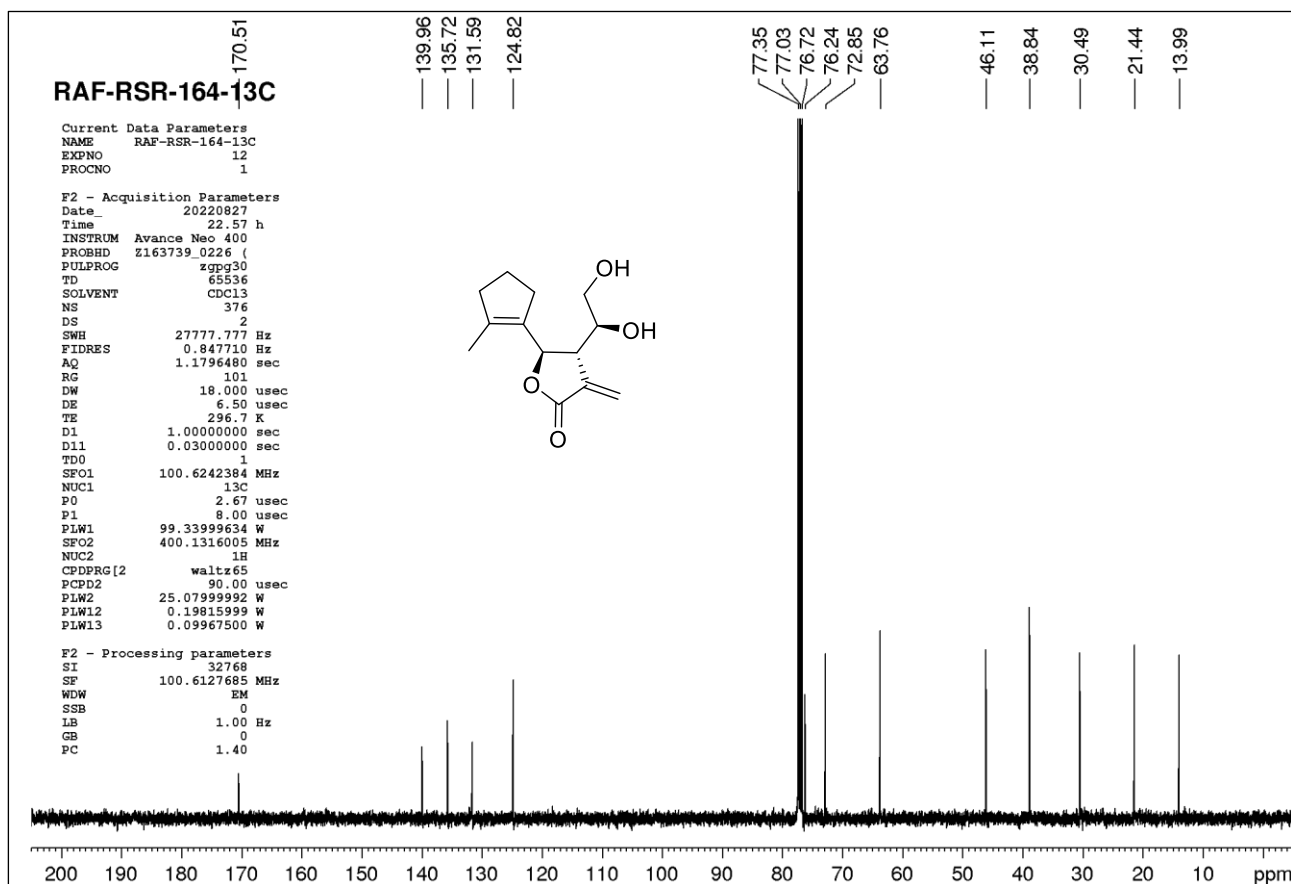
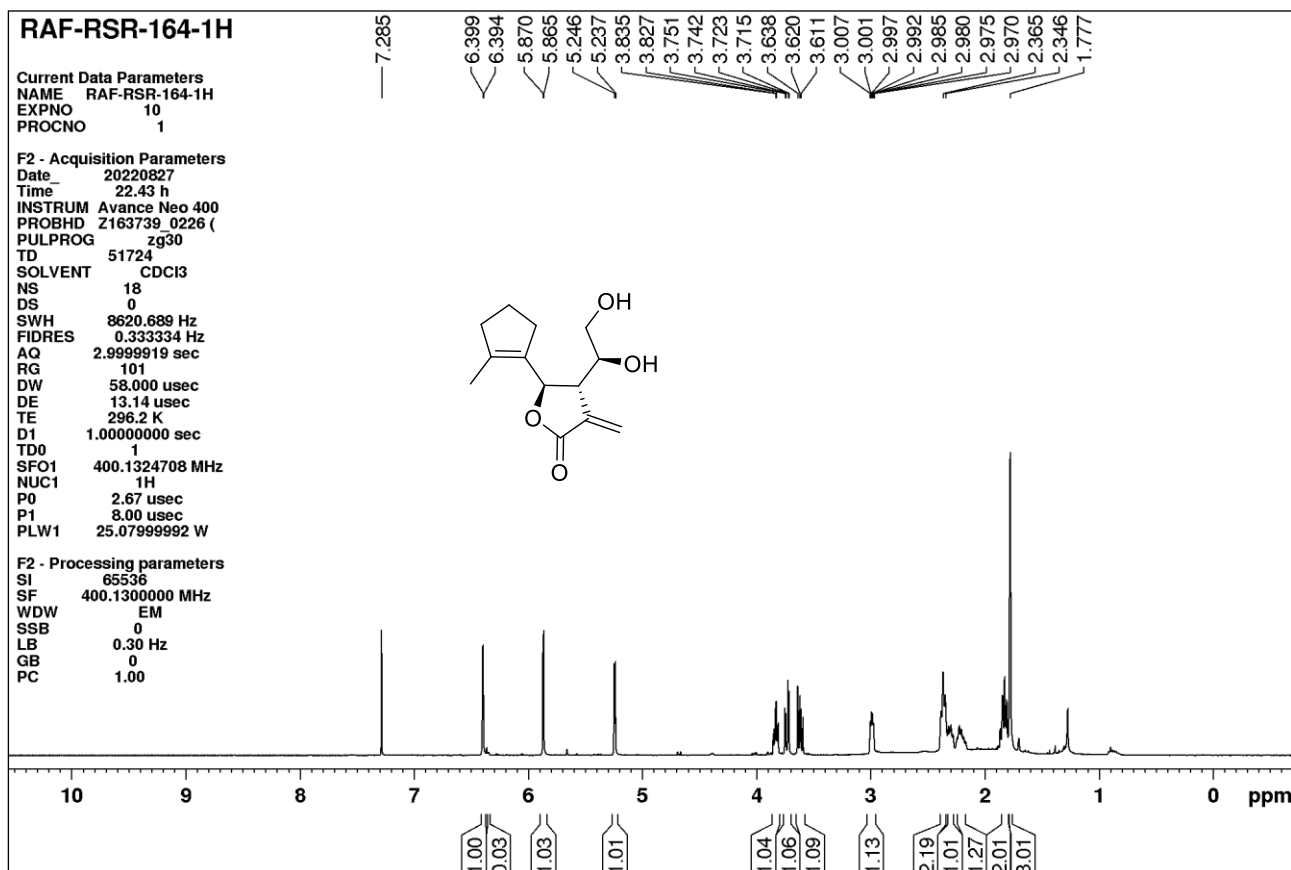
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) of compound **12**



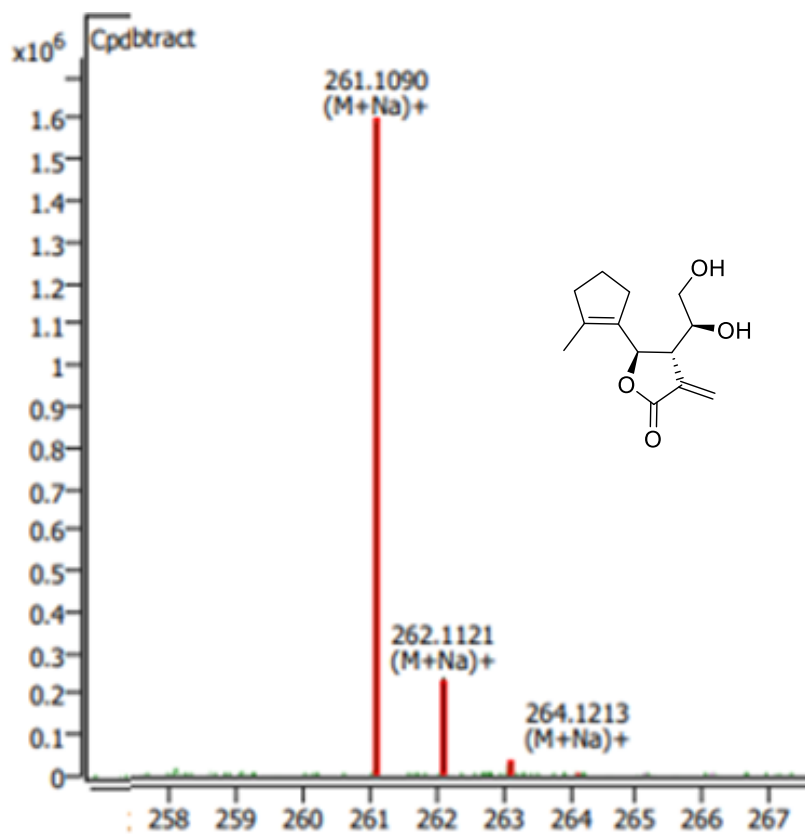
12: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{19}O_4$  239.1278; Found 239.1274.



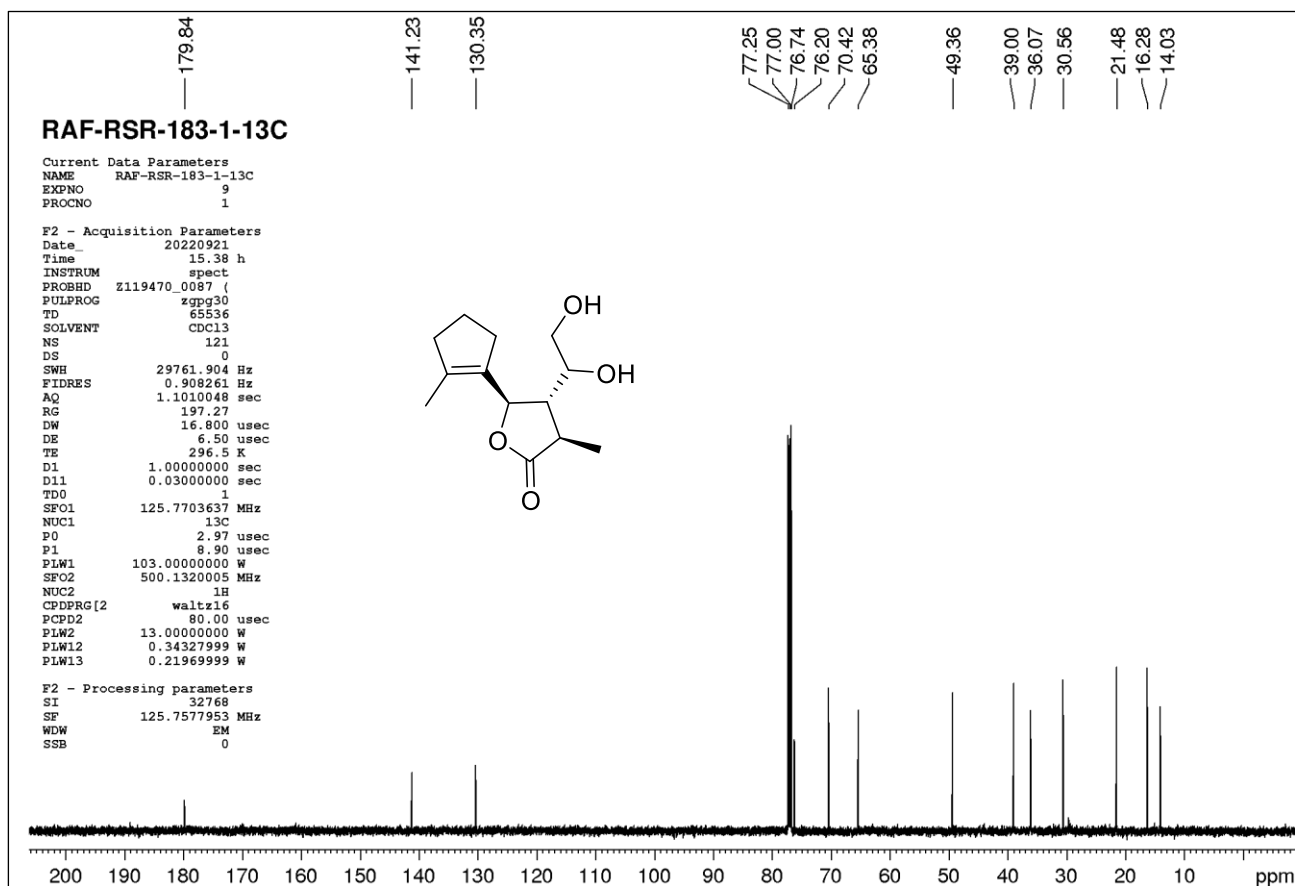
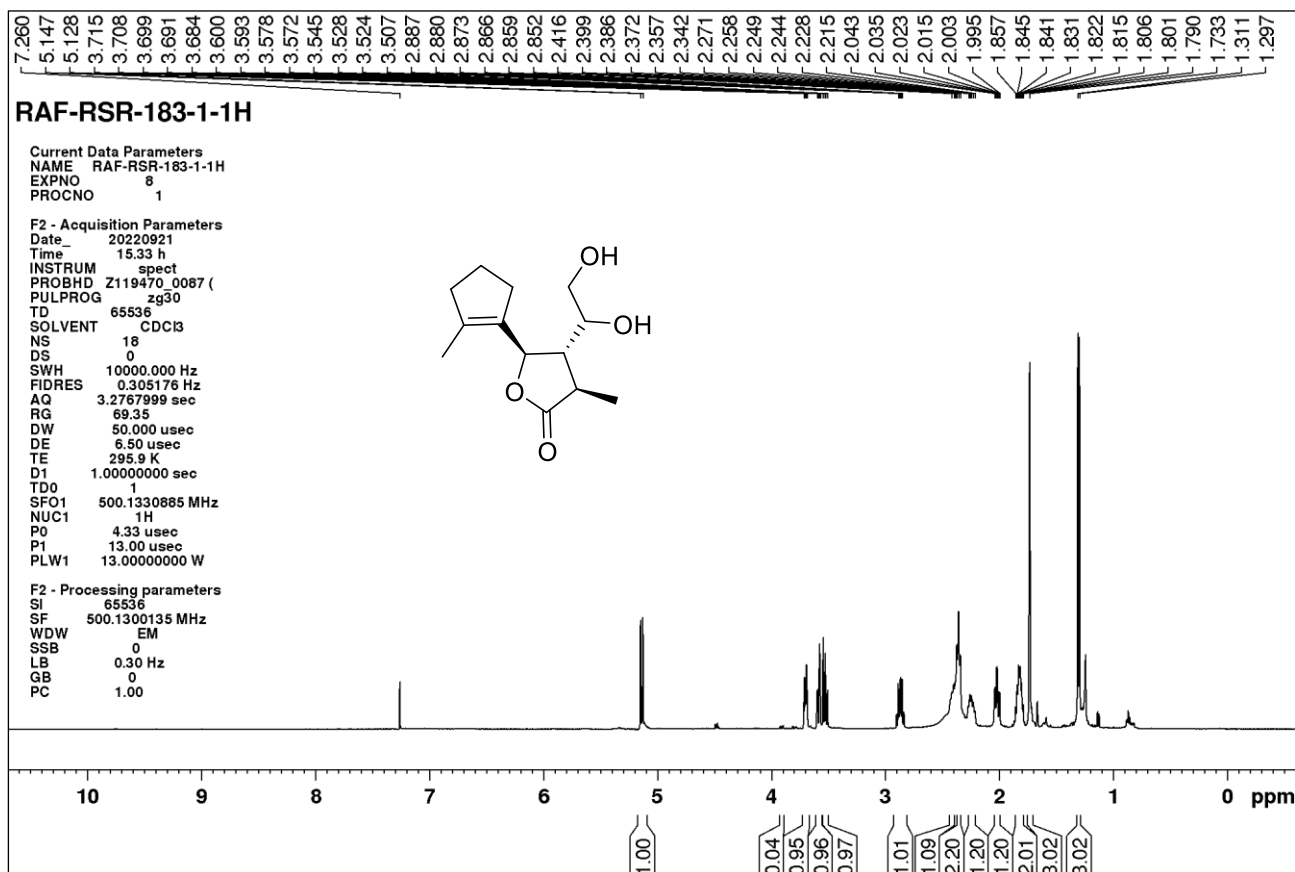
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **13**



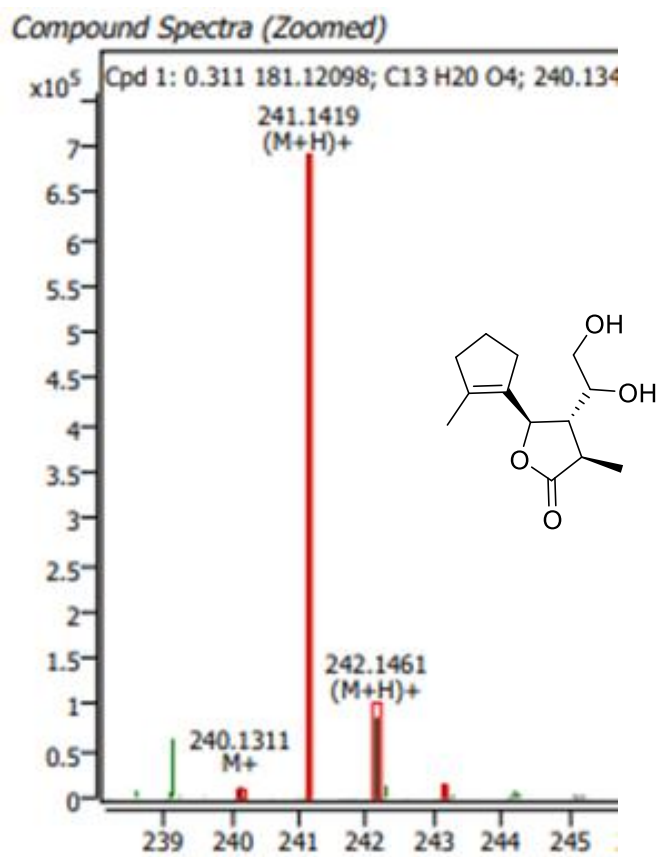
13: HRMS (Q-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{13}H_{18}O_4Na$  261.1098; Found 261.1090.



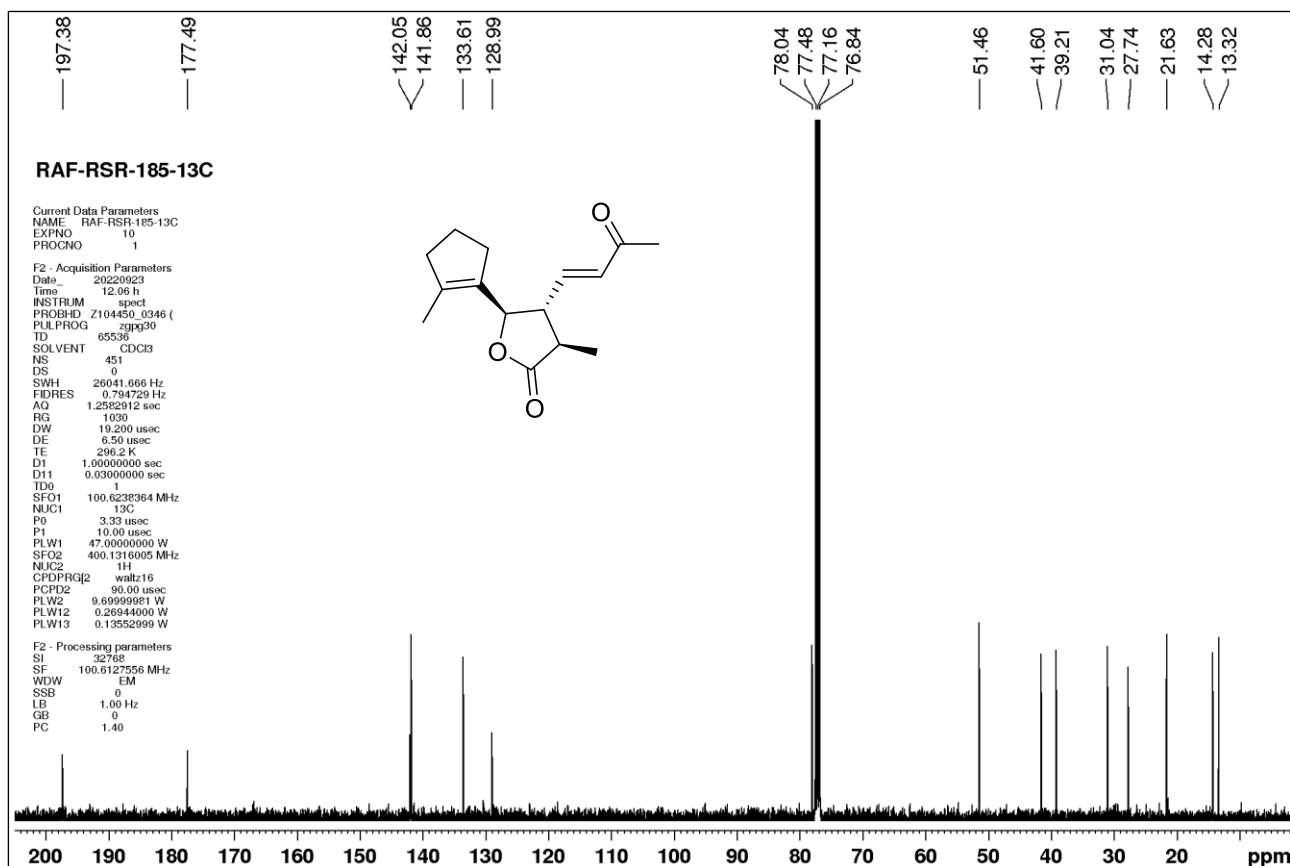
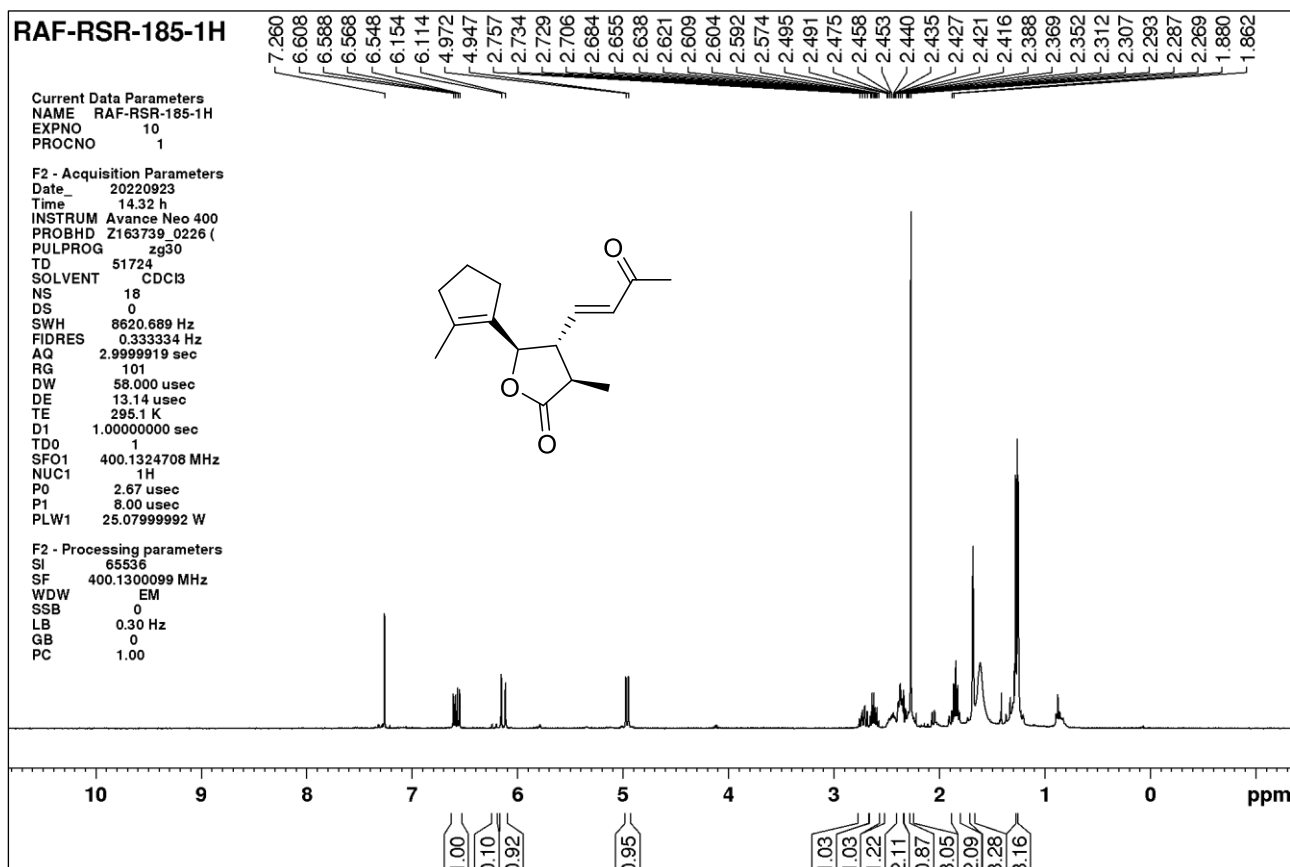
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound **14**



14: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{21}O_4$  241.1433; Found 241.1419.

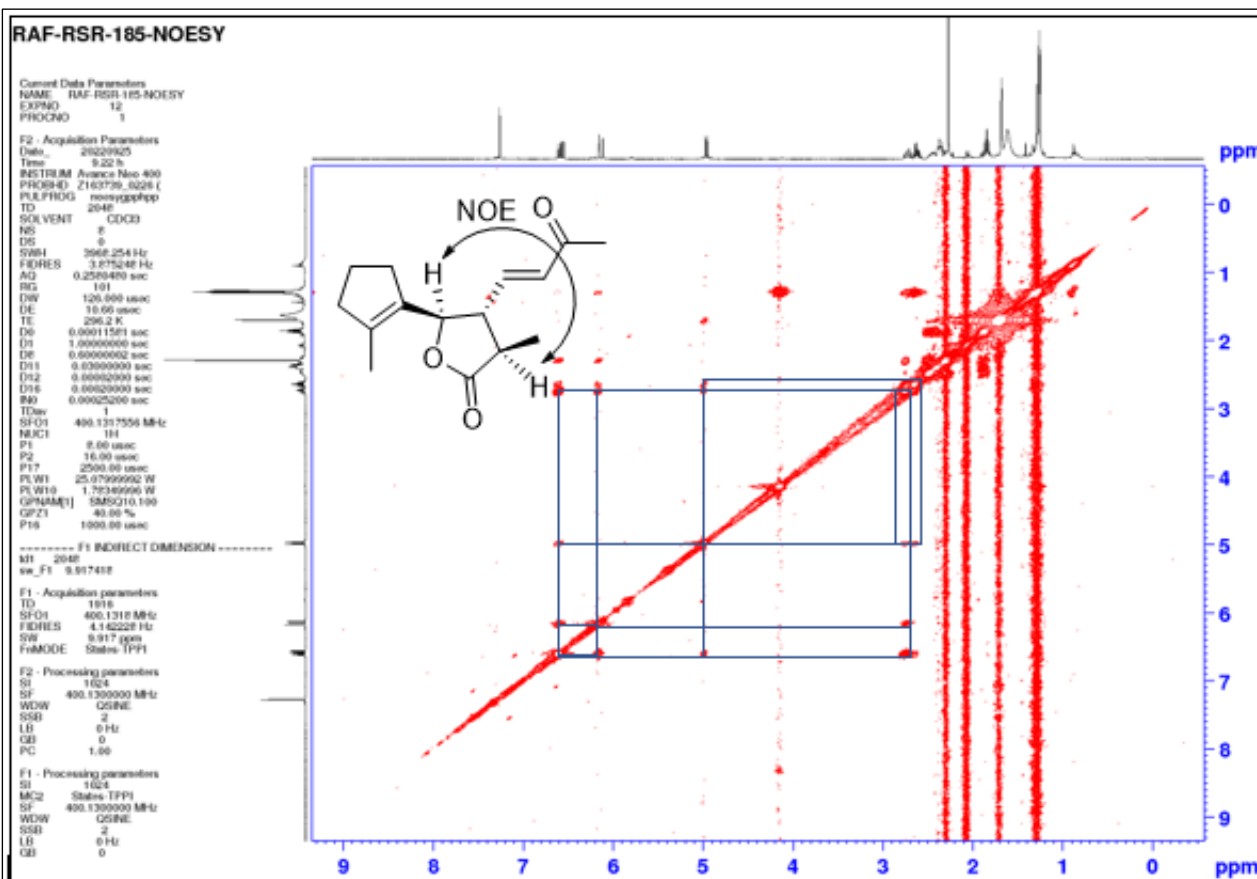
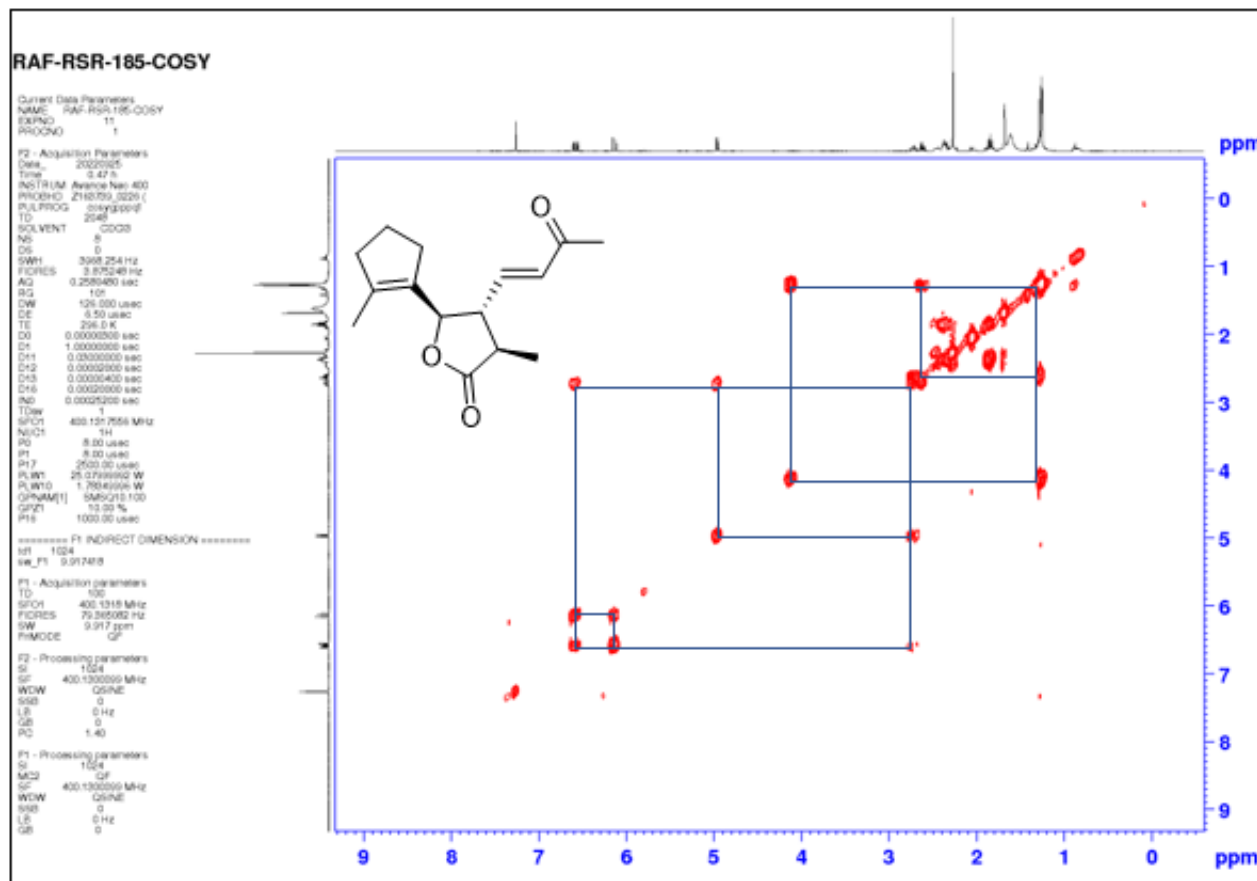


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **16**

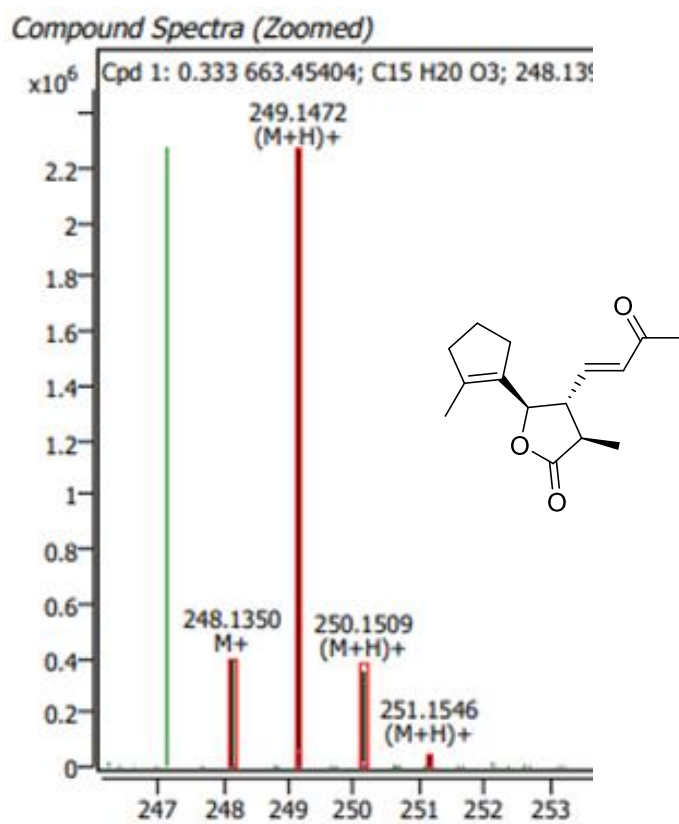




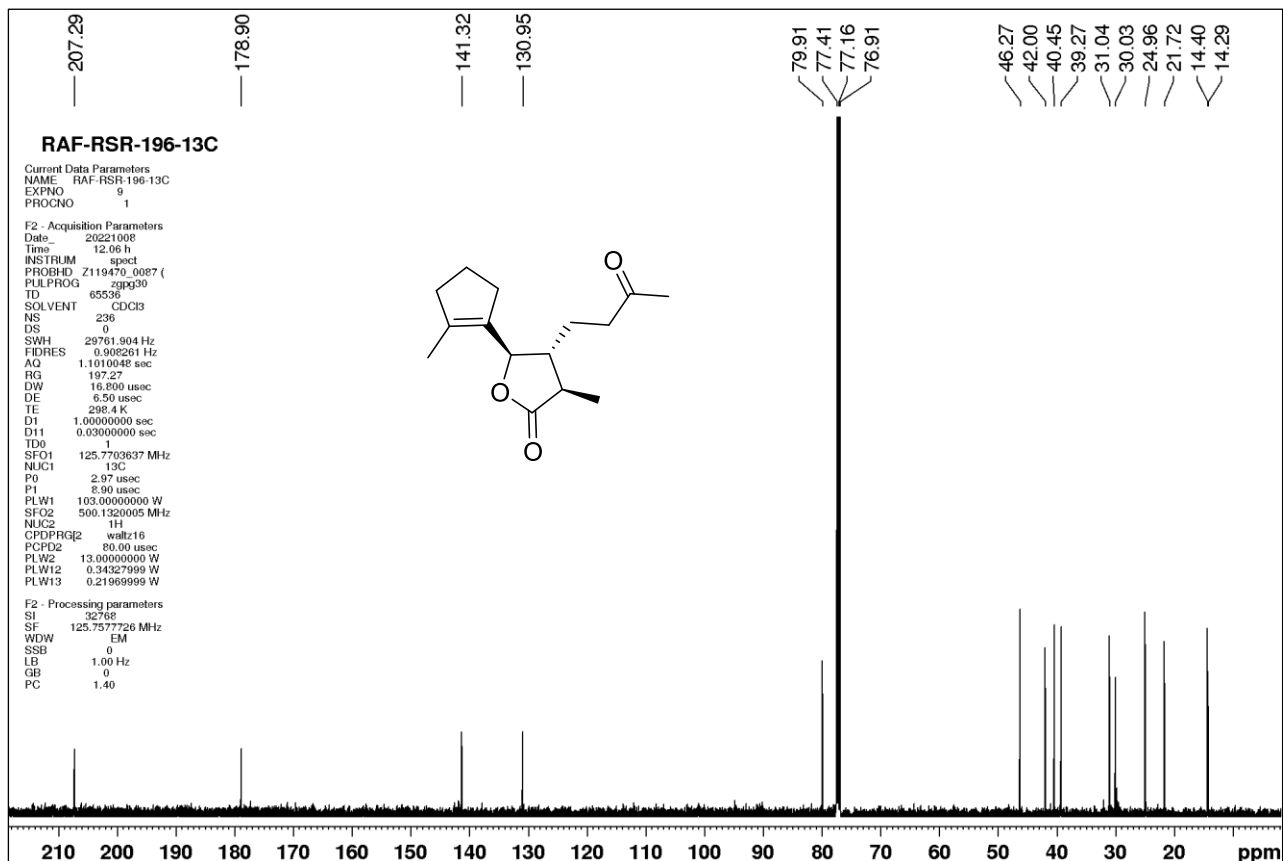
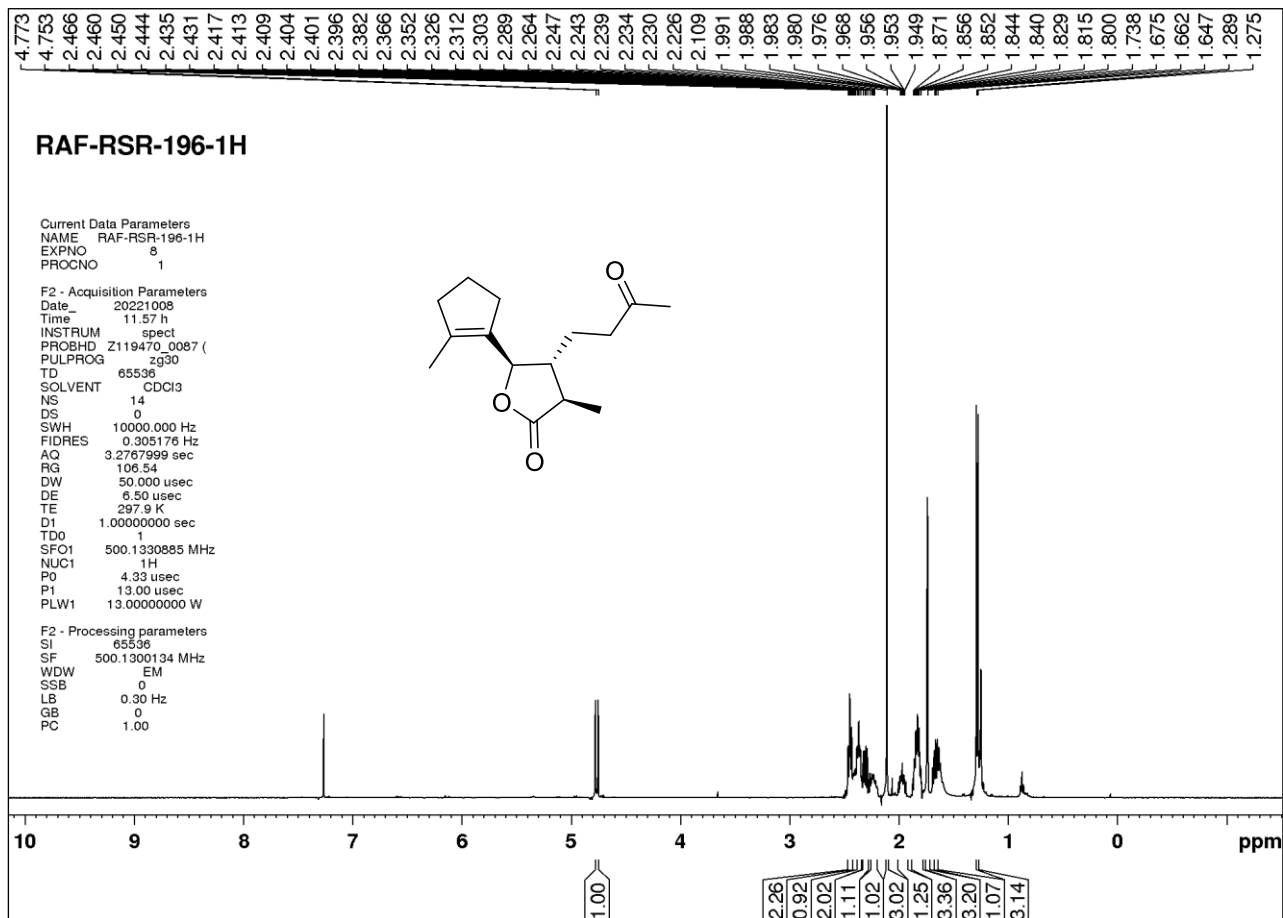
COSY (400 MHz, CDCl<sub>3</sub>) and NOESY (400 MHz, CDCl<sub>3</sub>) of compound **16**



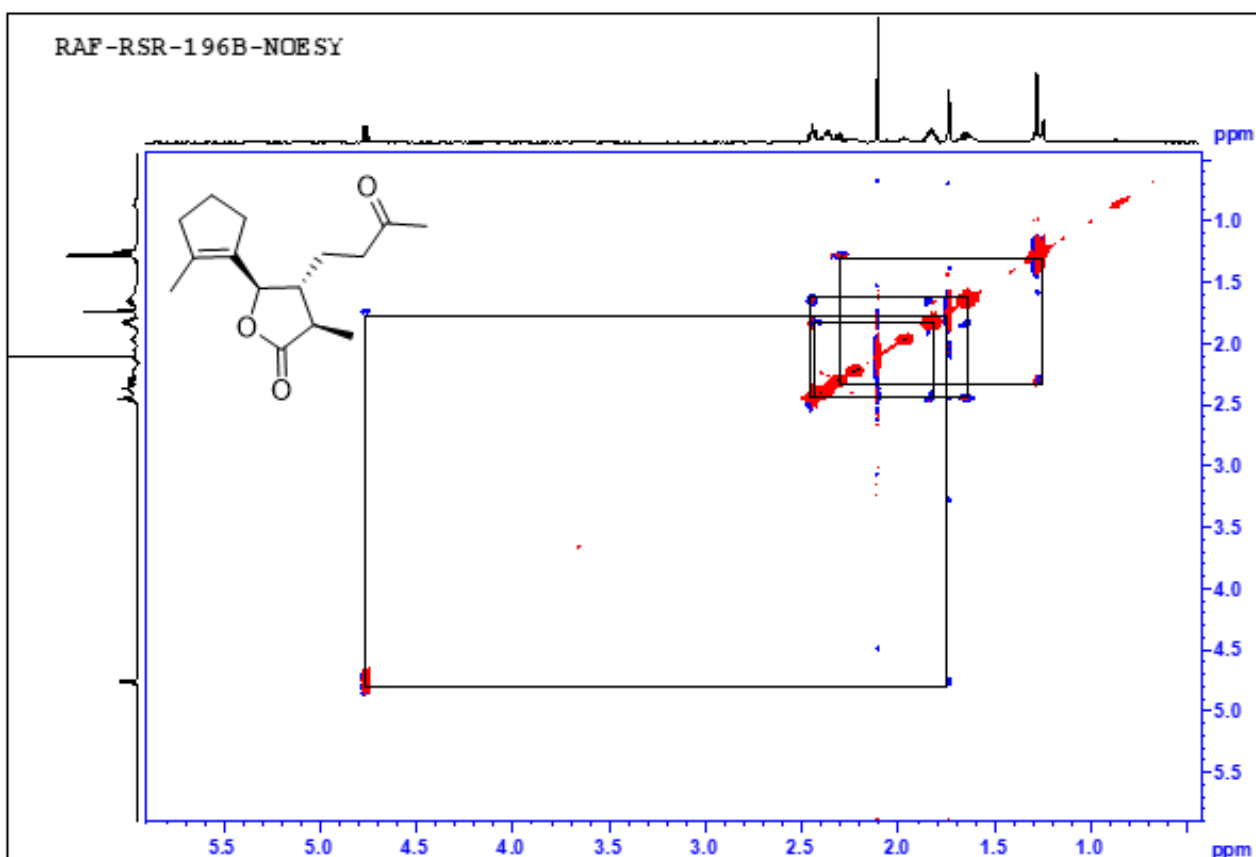
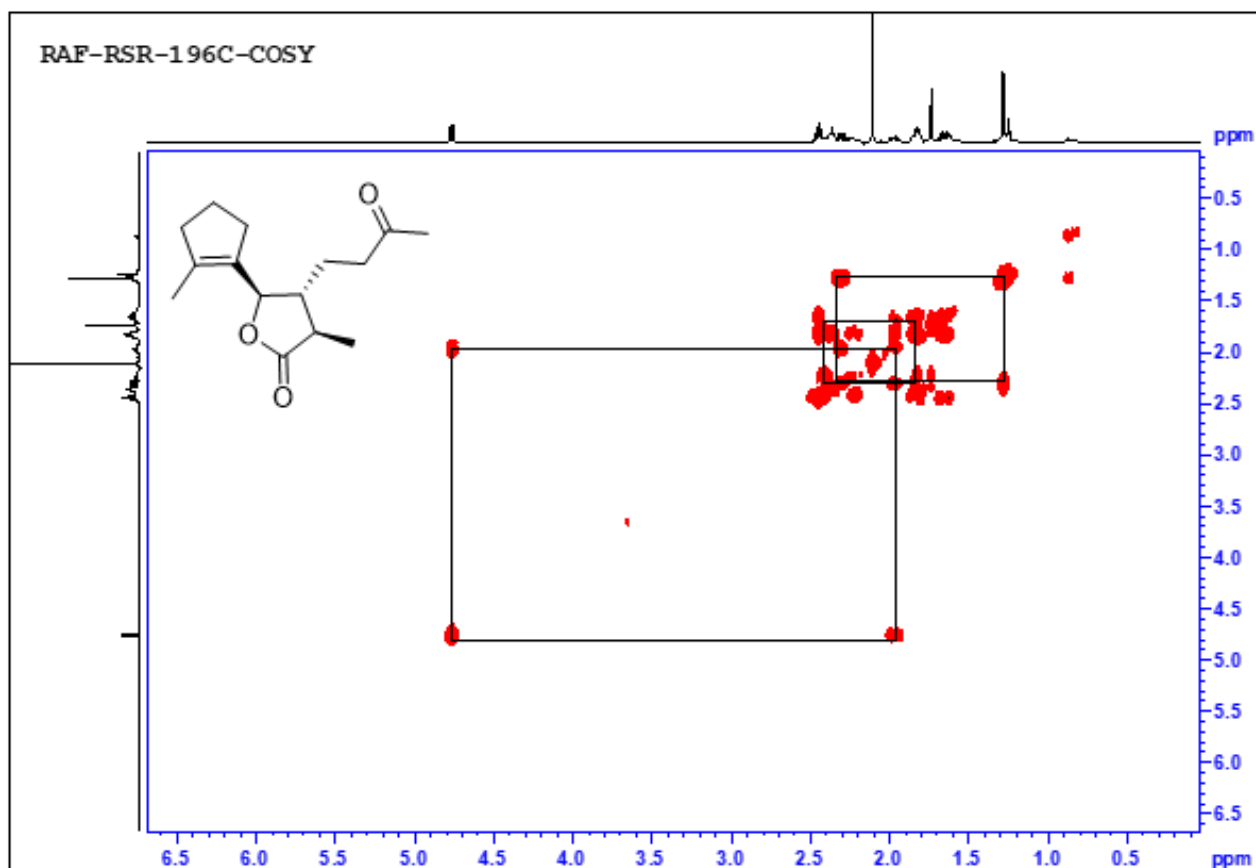
16: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{21}O_3$  249.1486; Found 249.1472.



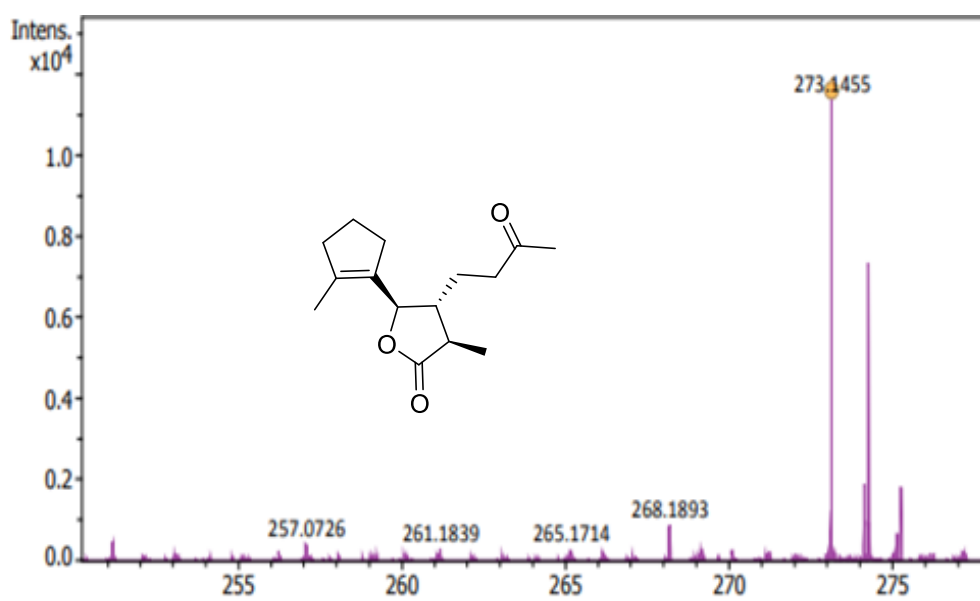
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound 17



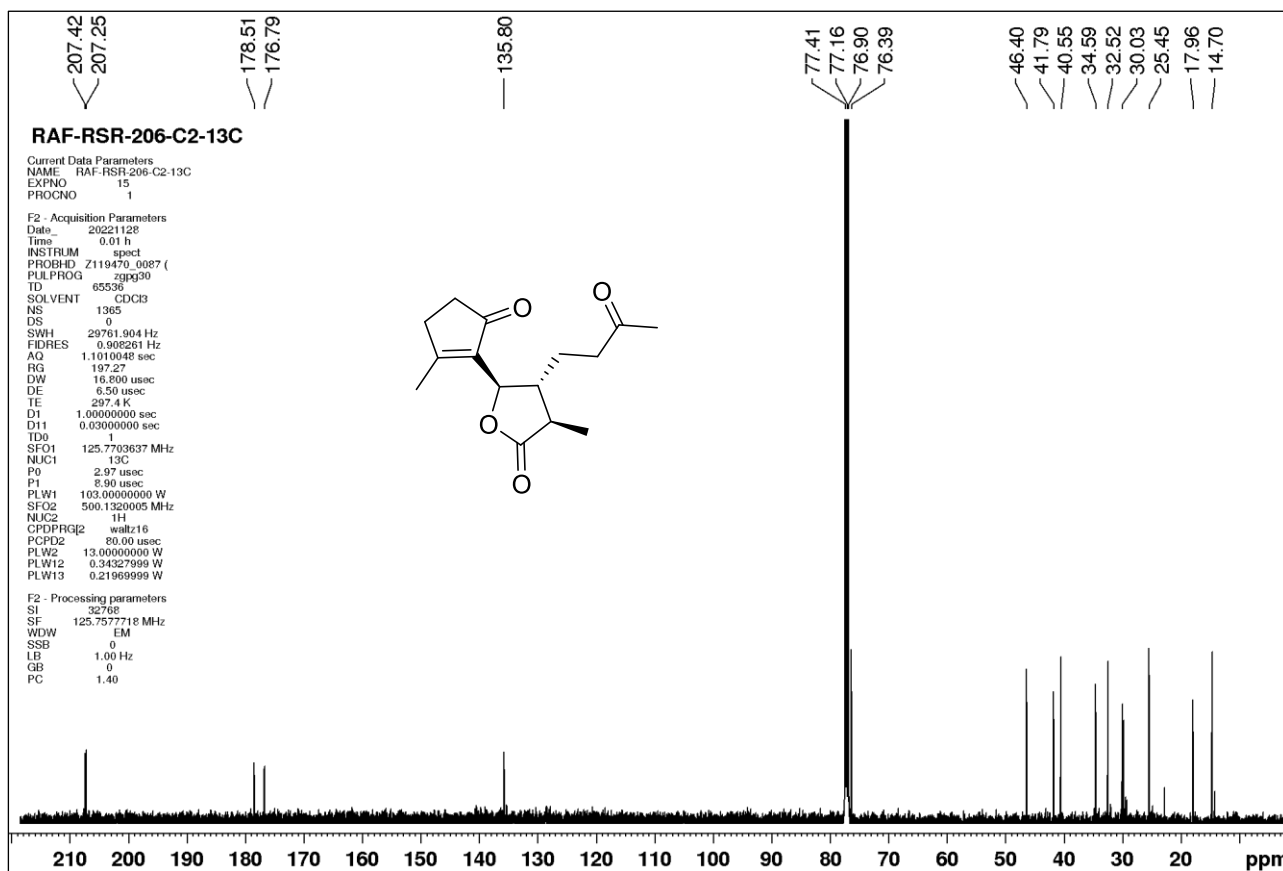
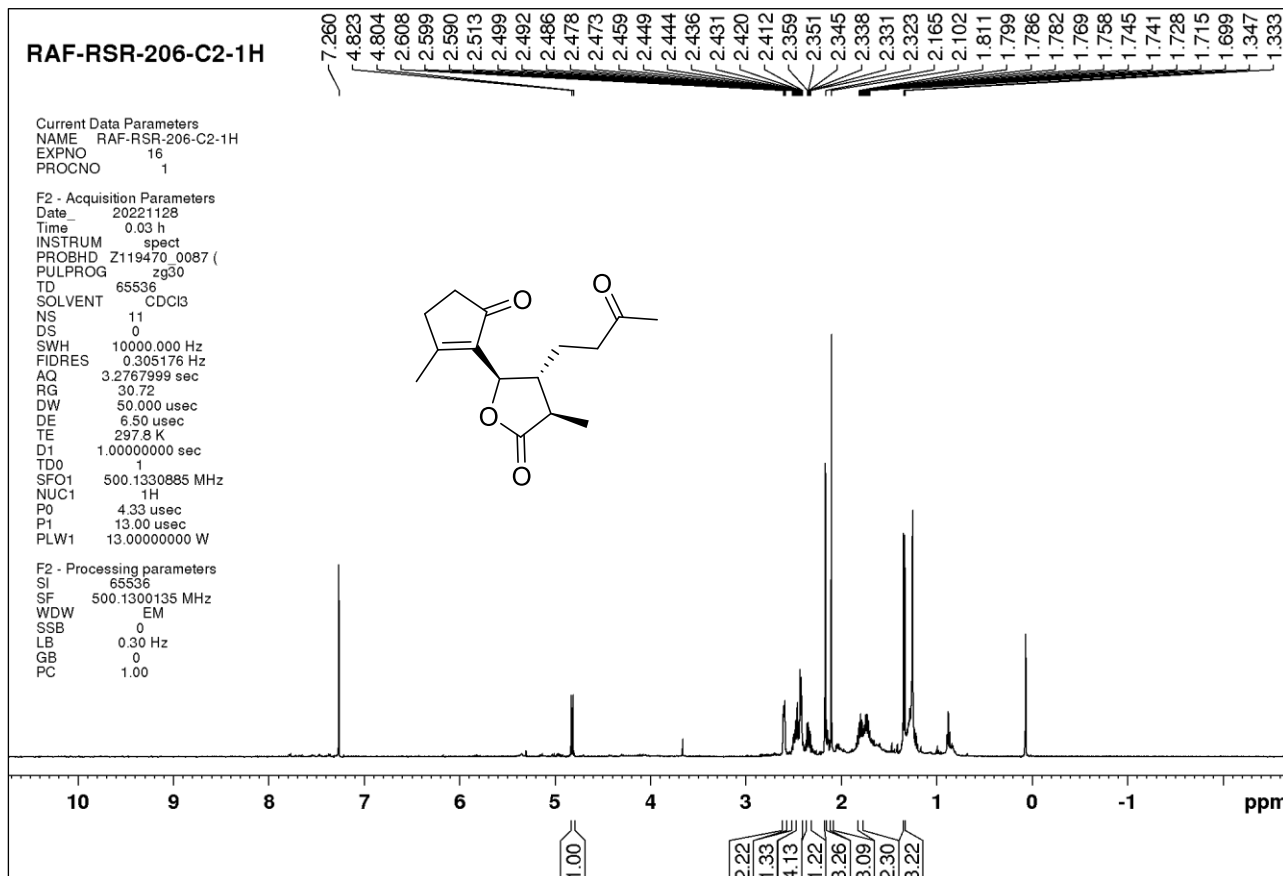
COSY (400 MHz, CDCl<sub>3</sub>) and NOESY (400 MHz, CDCl<sub>3</sub>) of compound **17**



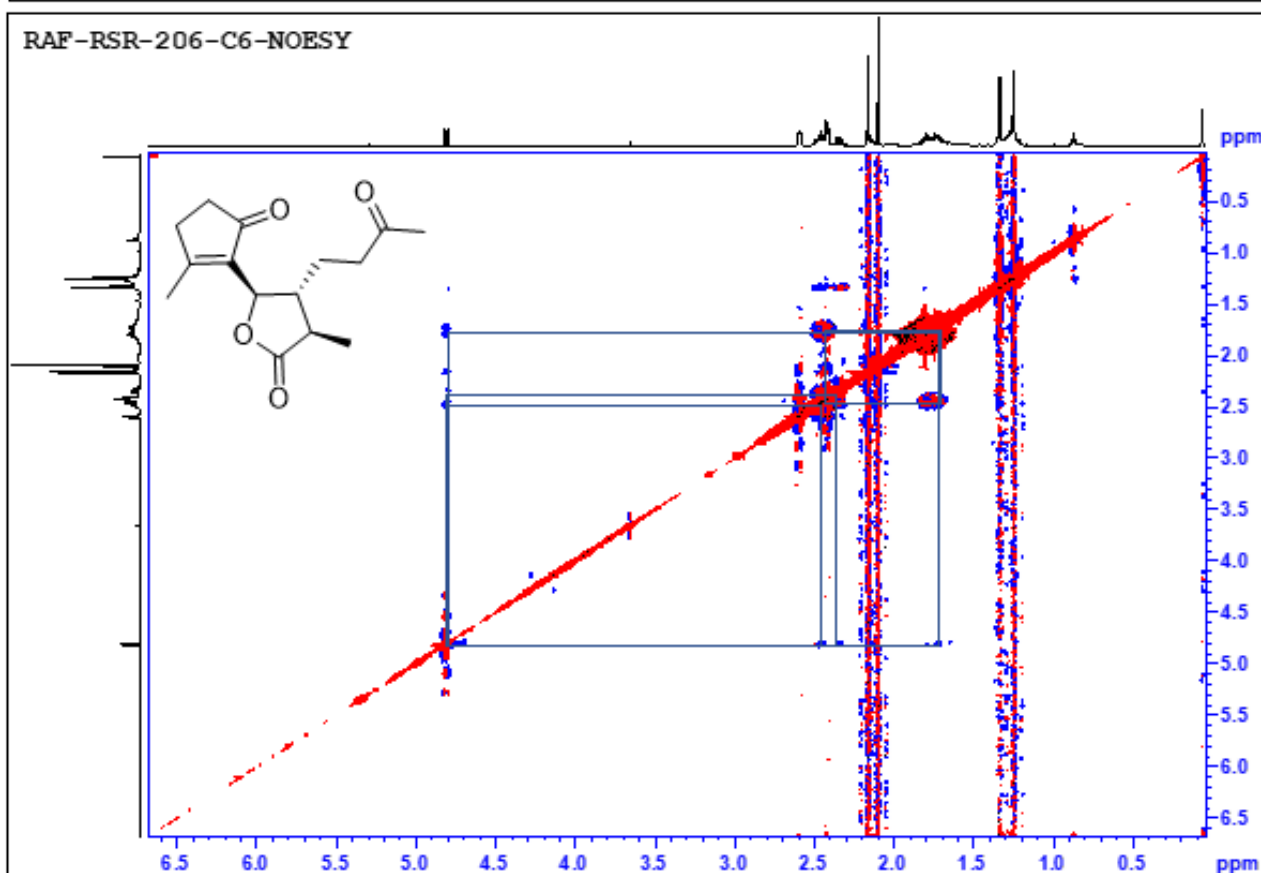
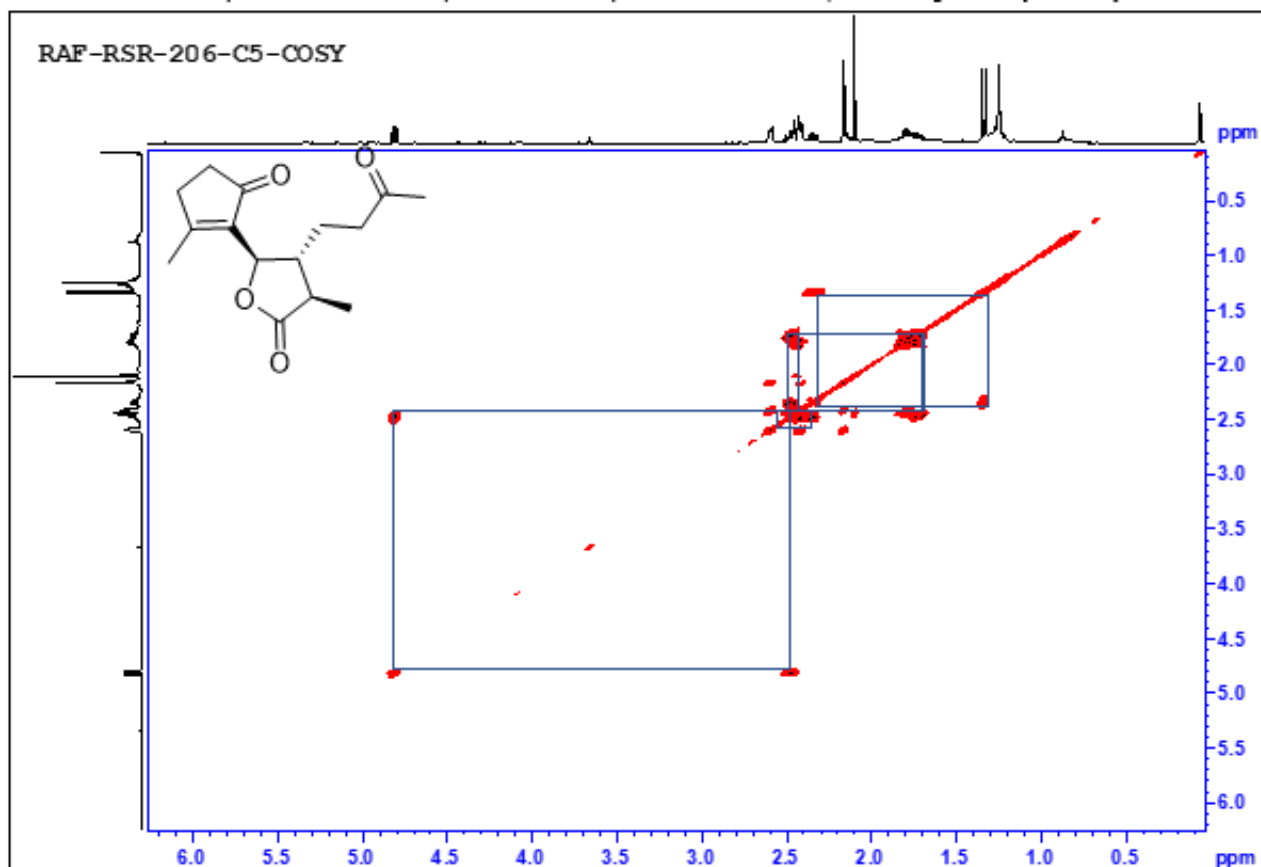
17: HRMS (ESI-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{15}H_{22}O_3Na$  273.1461; Found 273.1455.



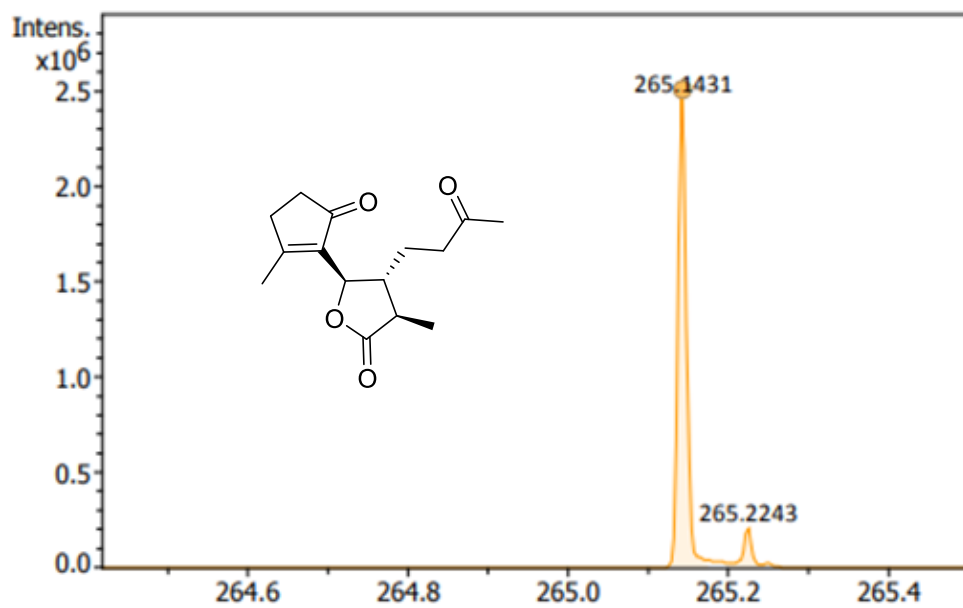
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) of compound *ent-2a*



COSY (400 MHz, CDCl<sub>3</sub>) and NOESY (400 MHz, CDCl<sub>3</sub>) of compound *ent-2a*

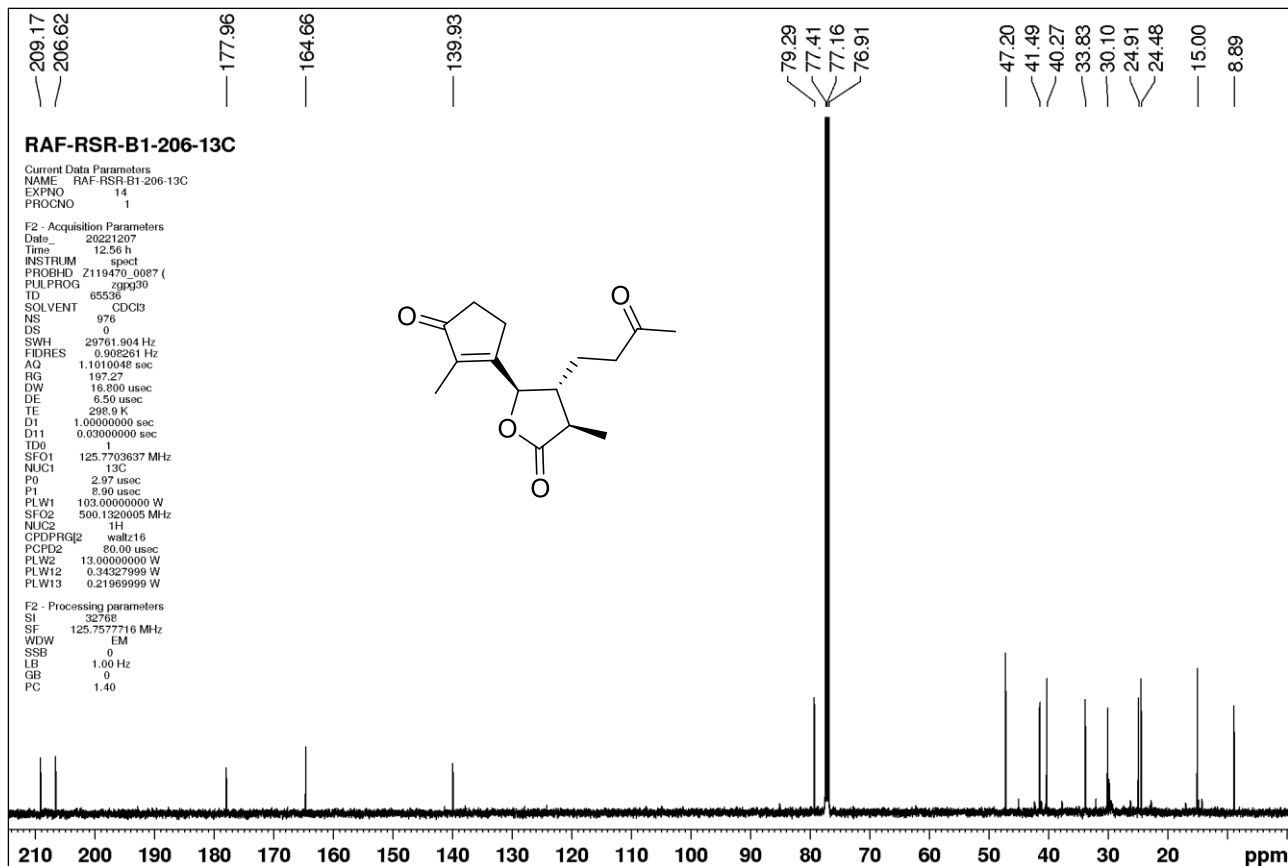
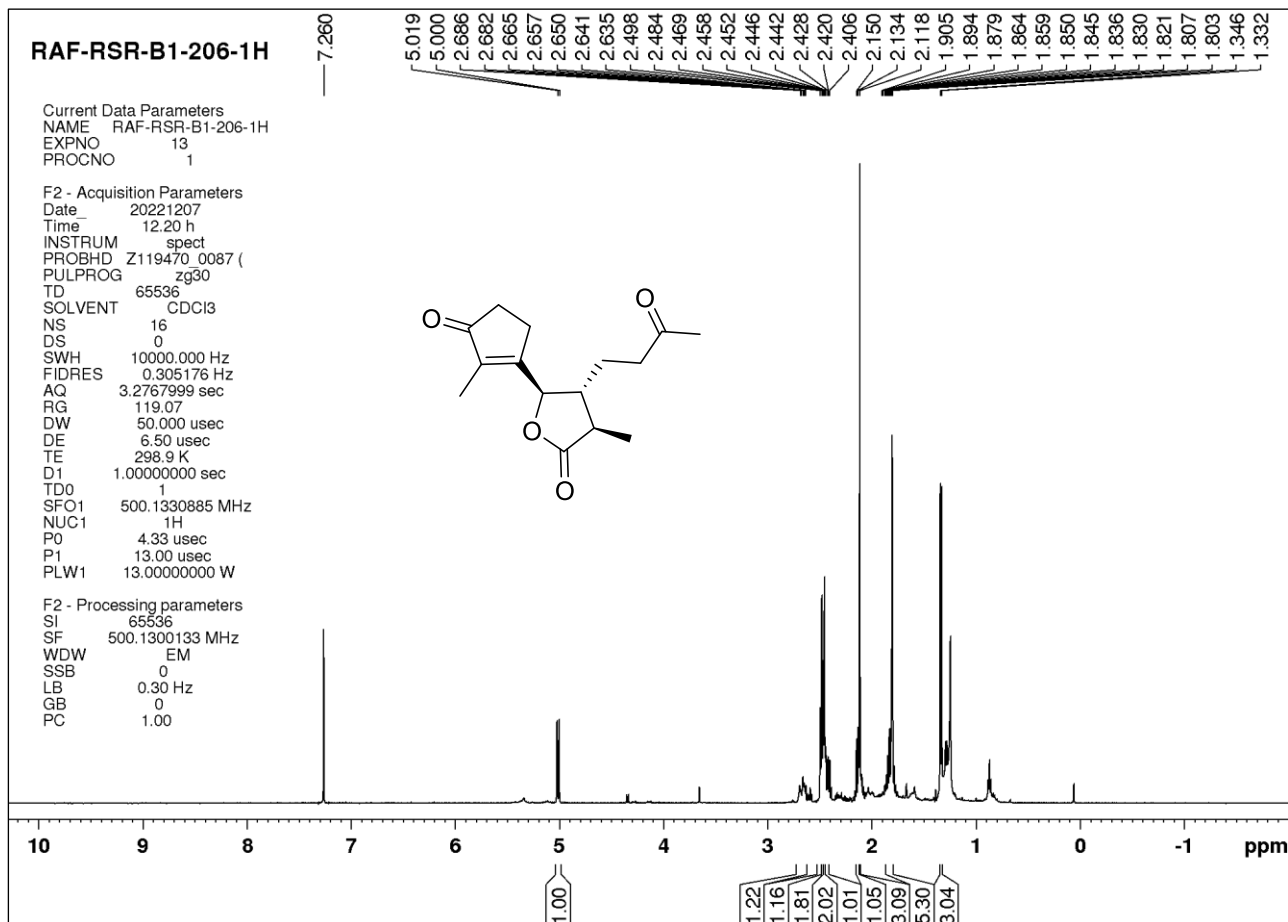


*ent*-**2a**: HRMS (ESI-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{21}O_4$  265.1435; Found 265.1431.

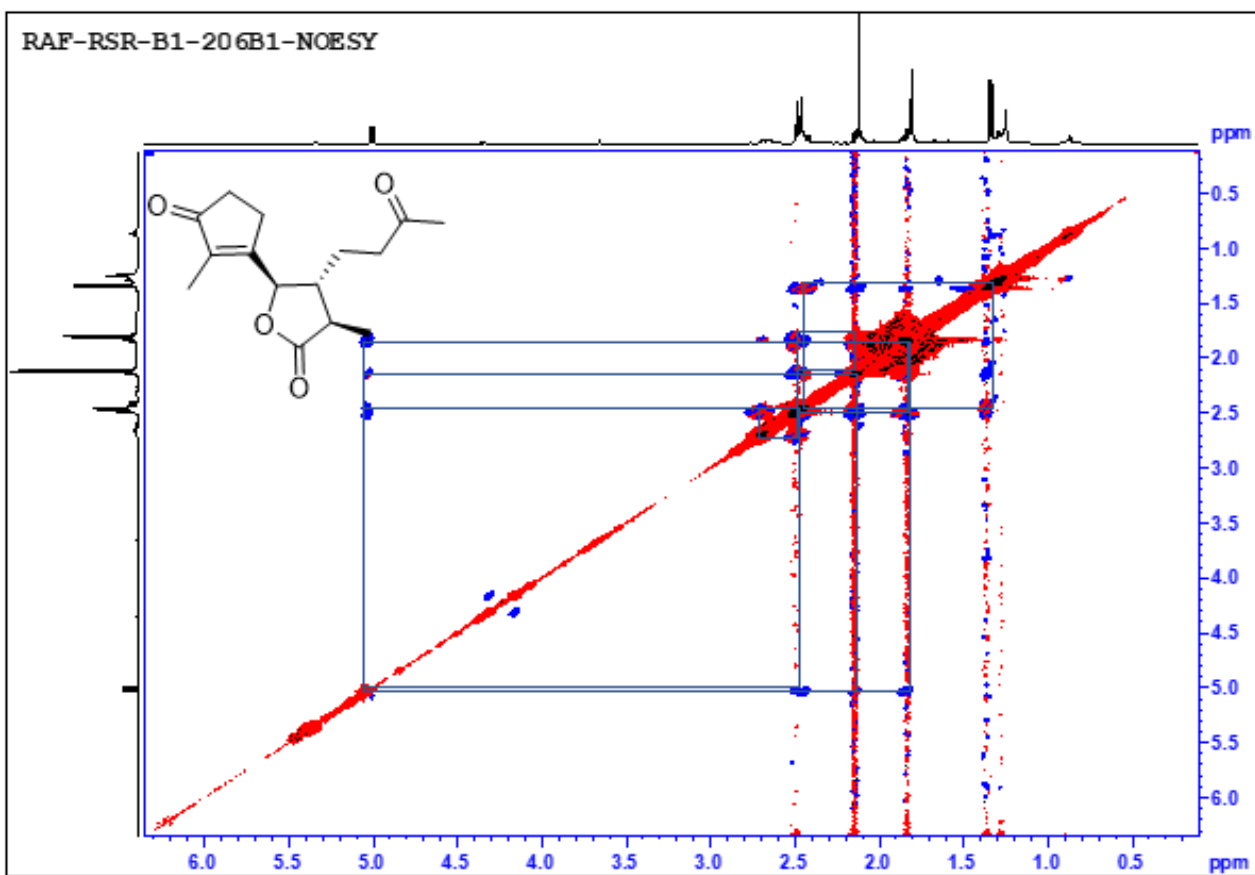
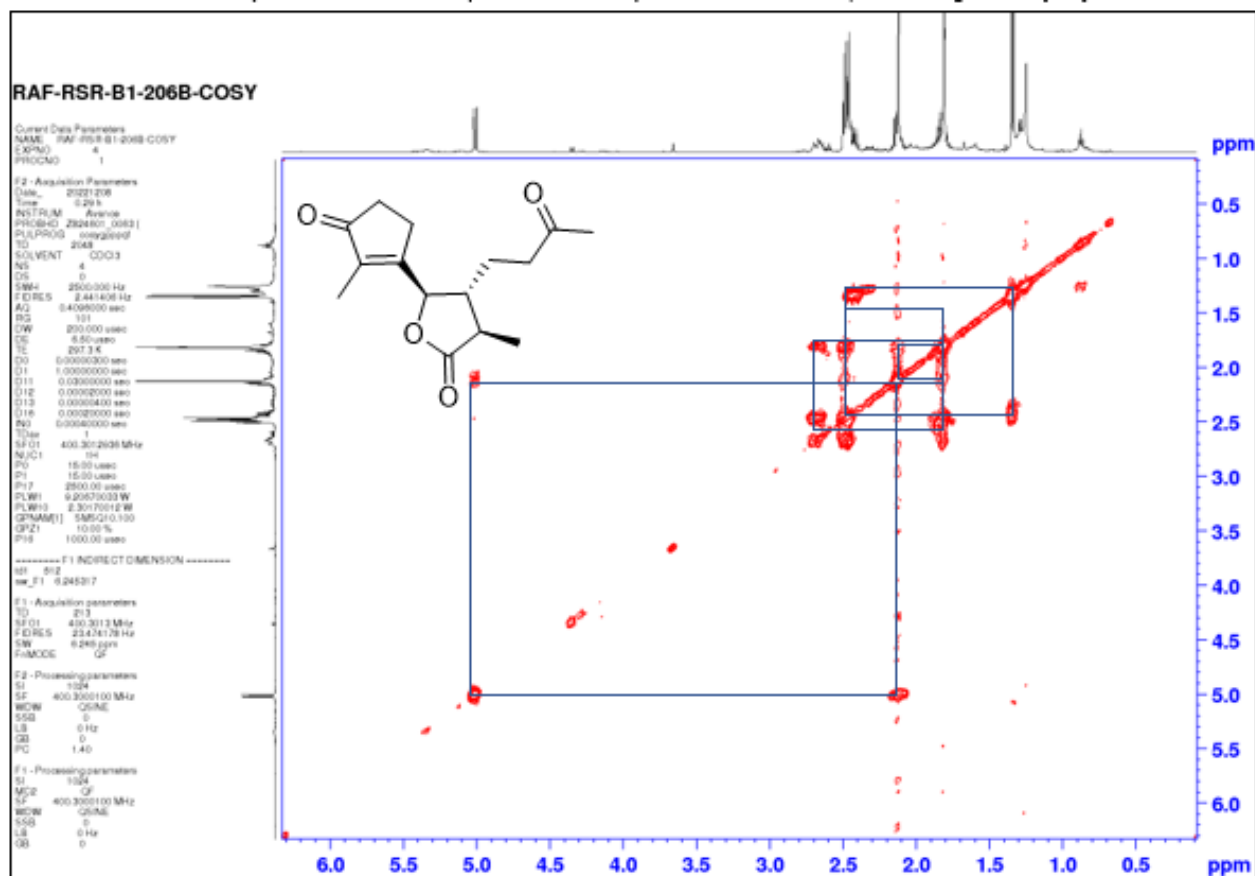




<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) of compound **18**

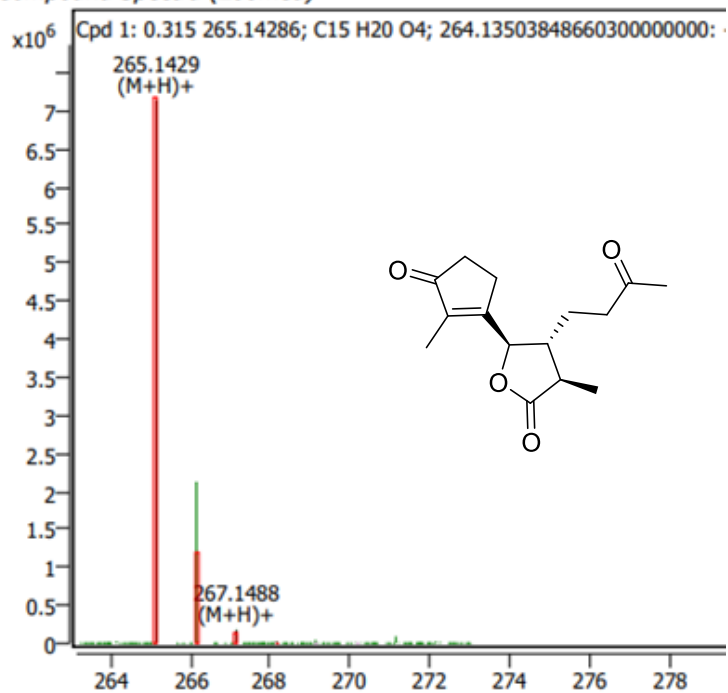


COSY (400 MHz, CDCl<sub>3</sub>) and NOESY (400 MHz, CDCl<sub>3</sub>) of compound **18**

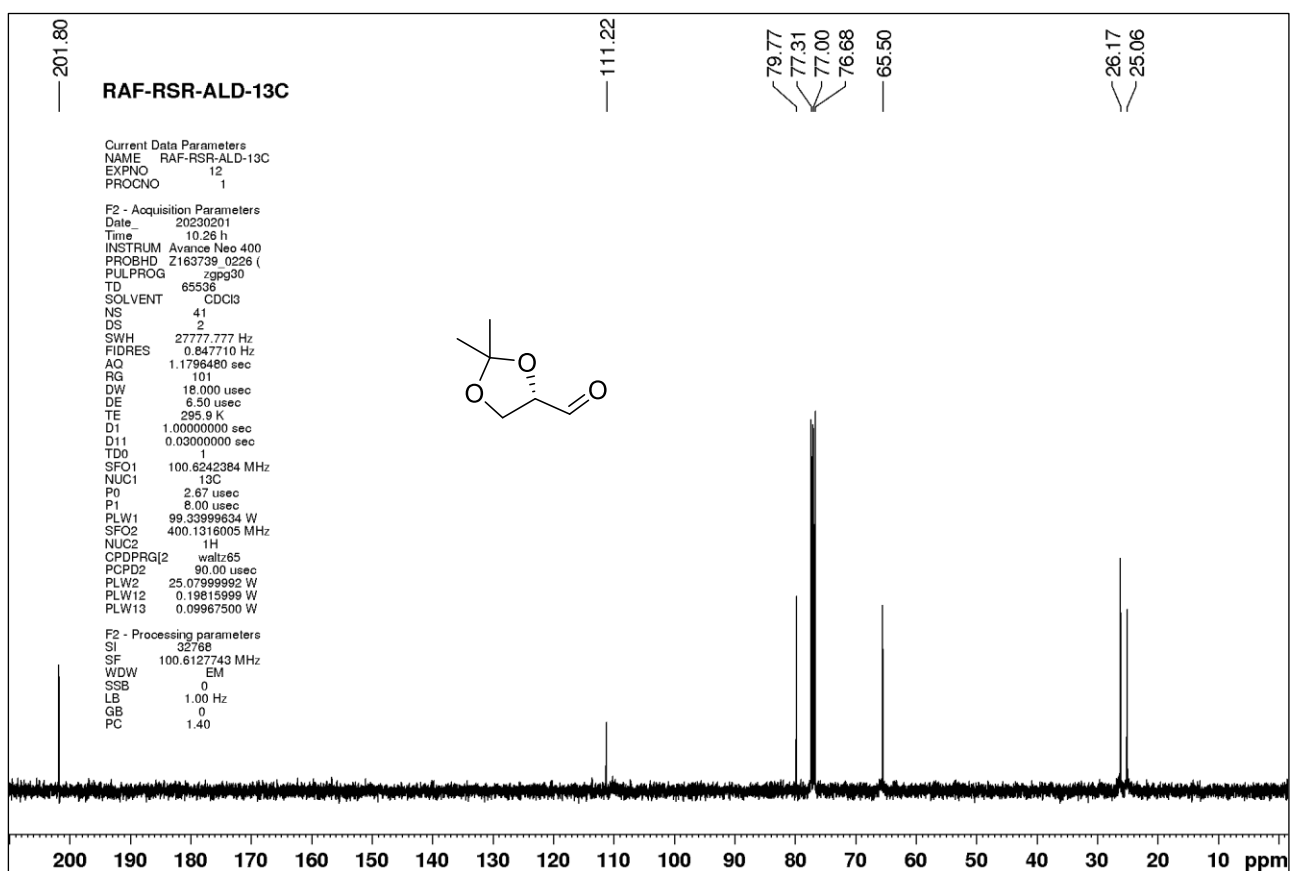
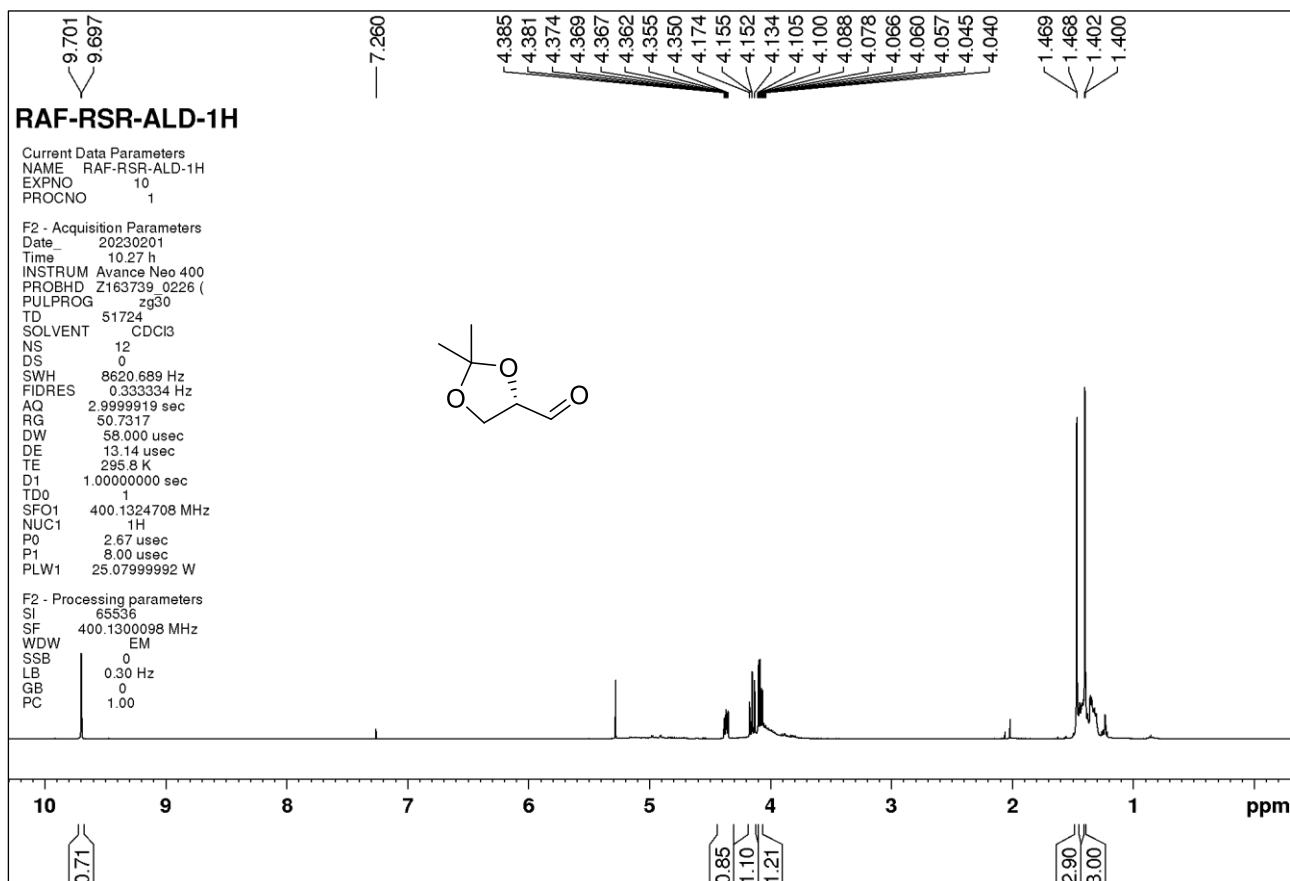


18: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{21}O_4$  265.1435; Found 265.1429.

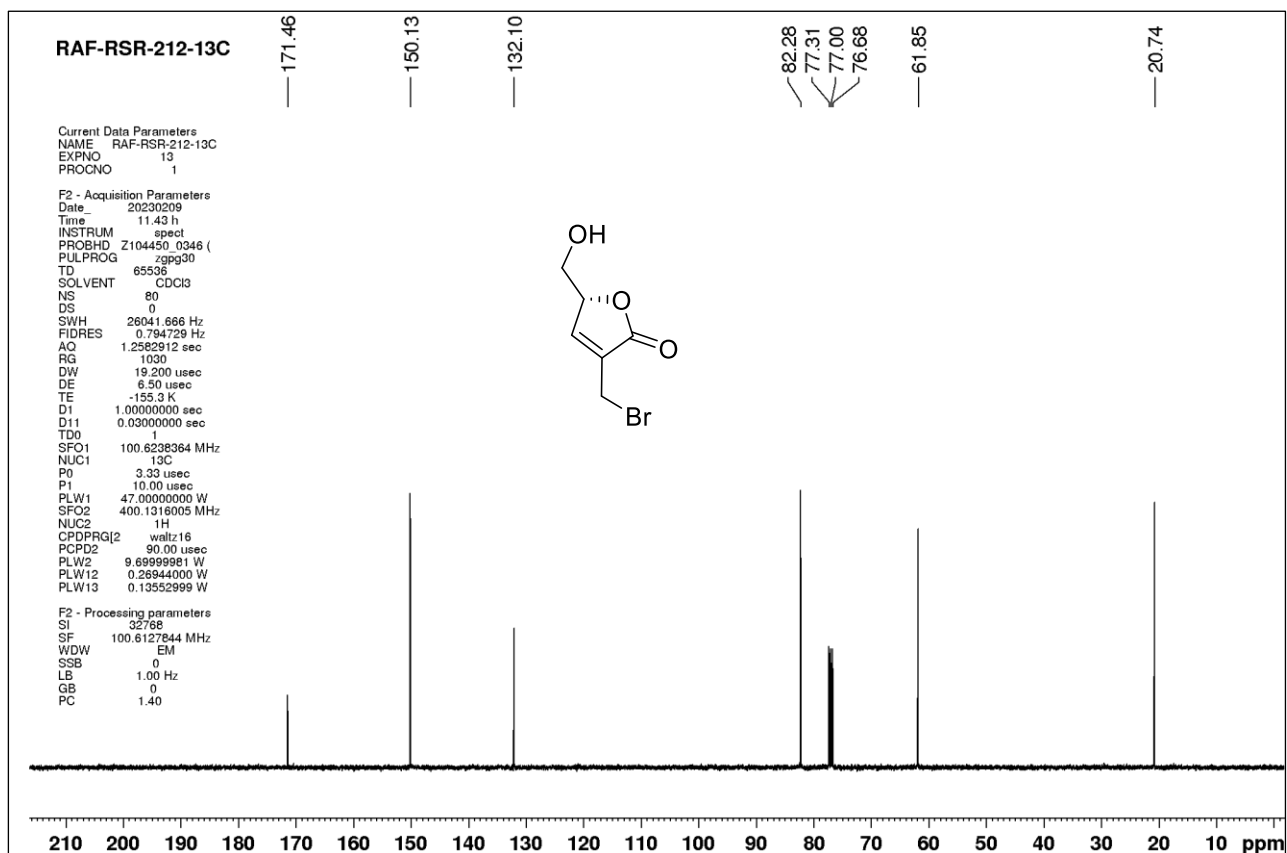
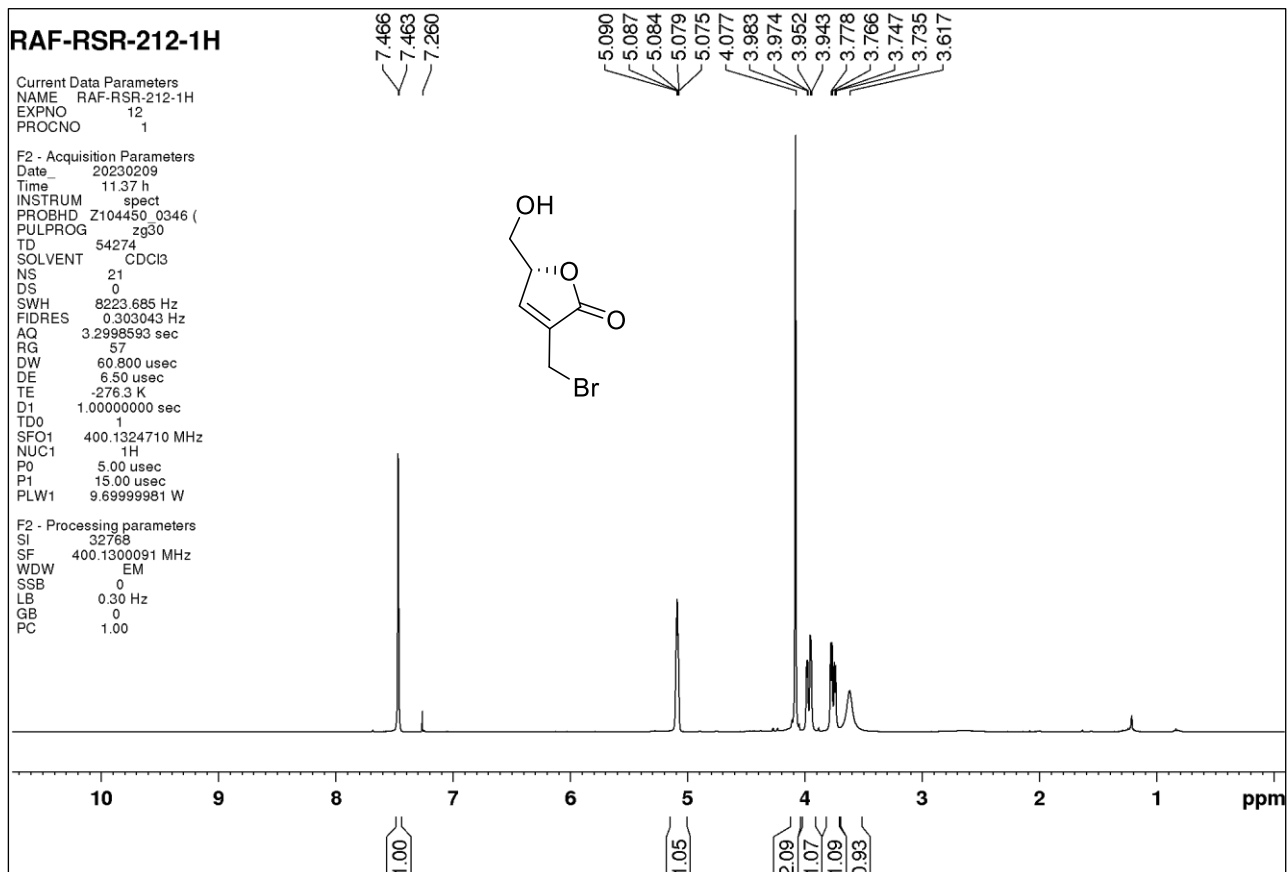
Compound Spectra (Zoomed)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **20**

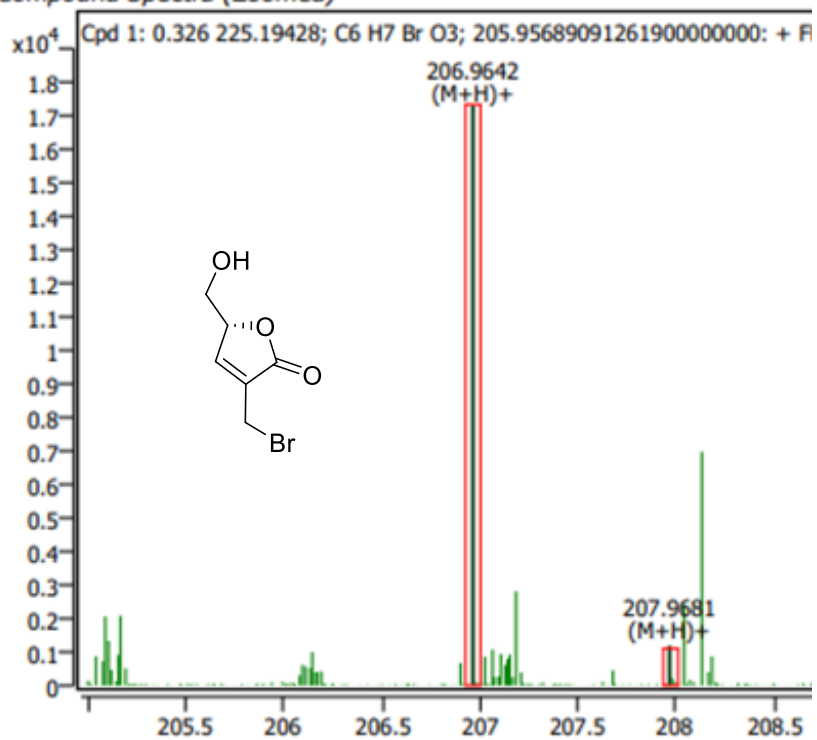


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound *ent*-**3b**

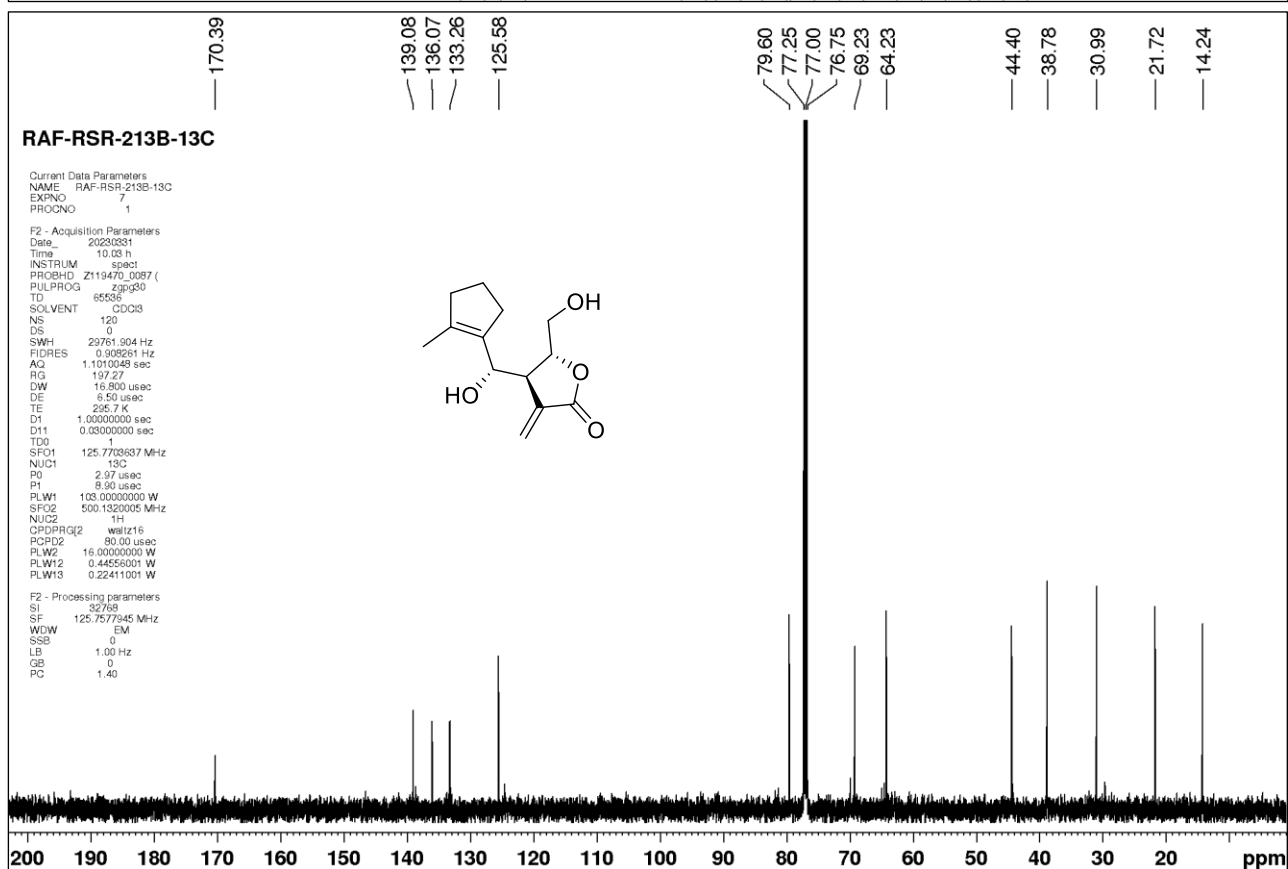
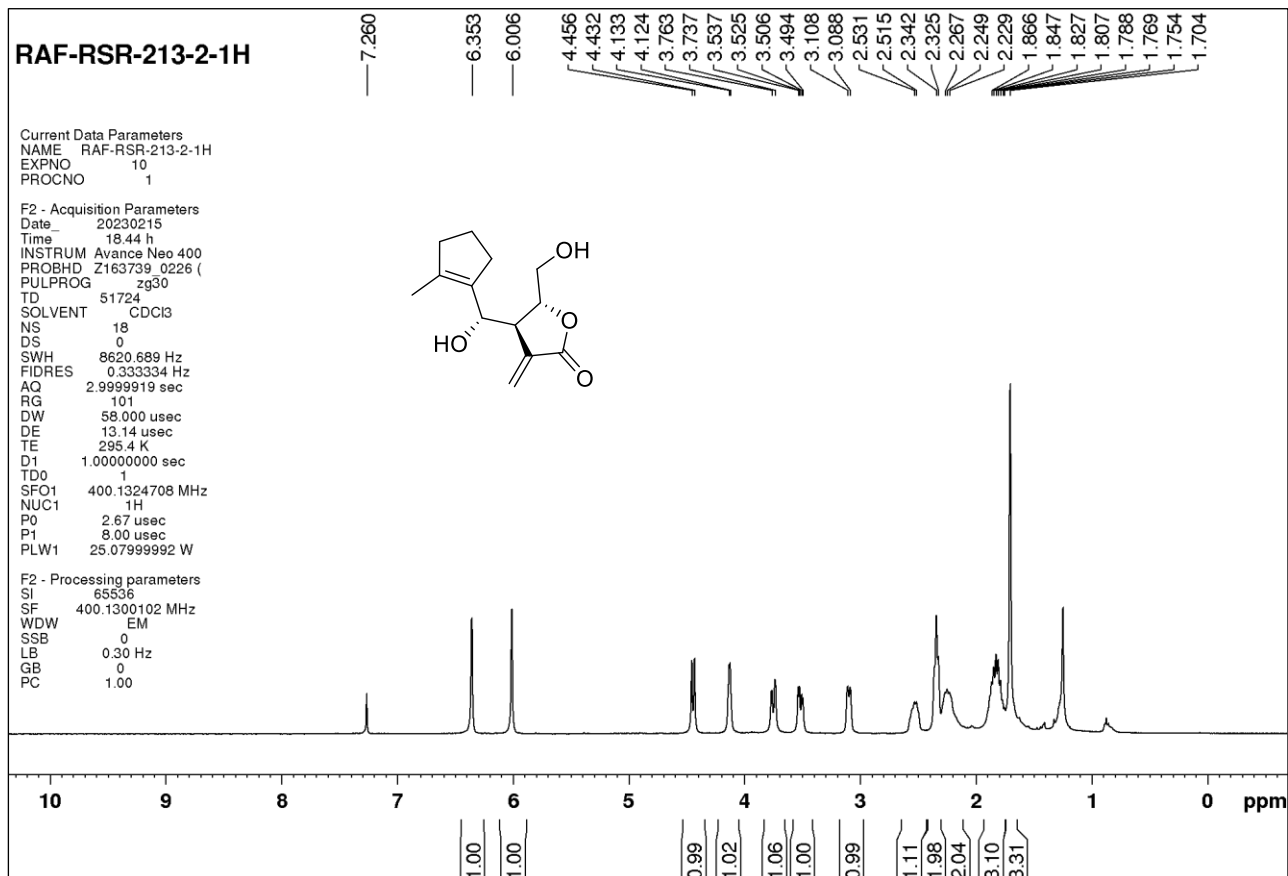


*ent*-**3b**: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_6H_8O_3Br$  206.9648; Found 206.9642.

Compound Spectra (Zoomed)

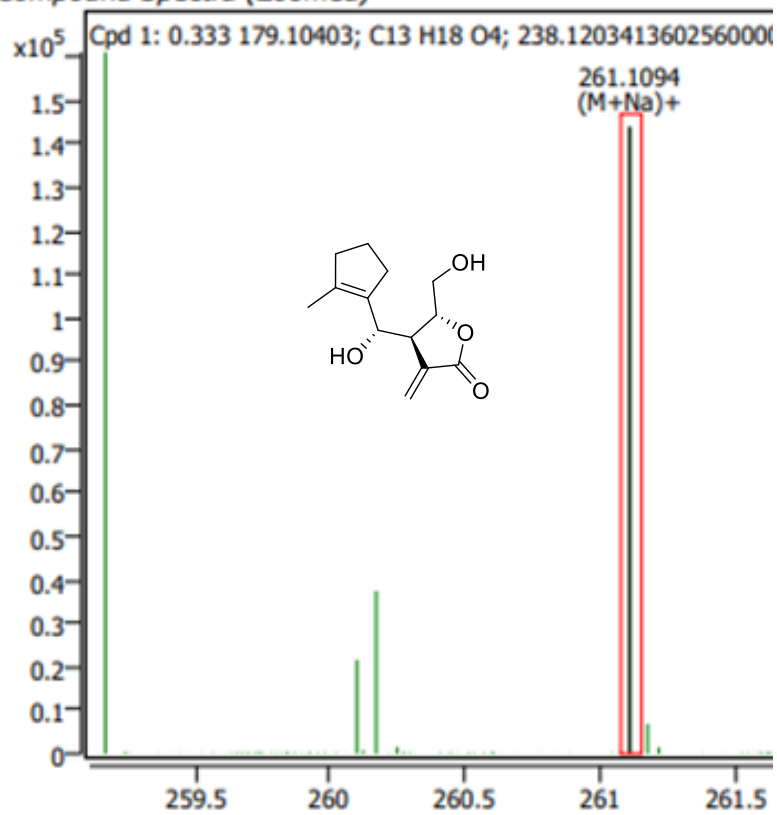


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) of compound *ent-12*



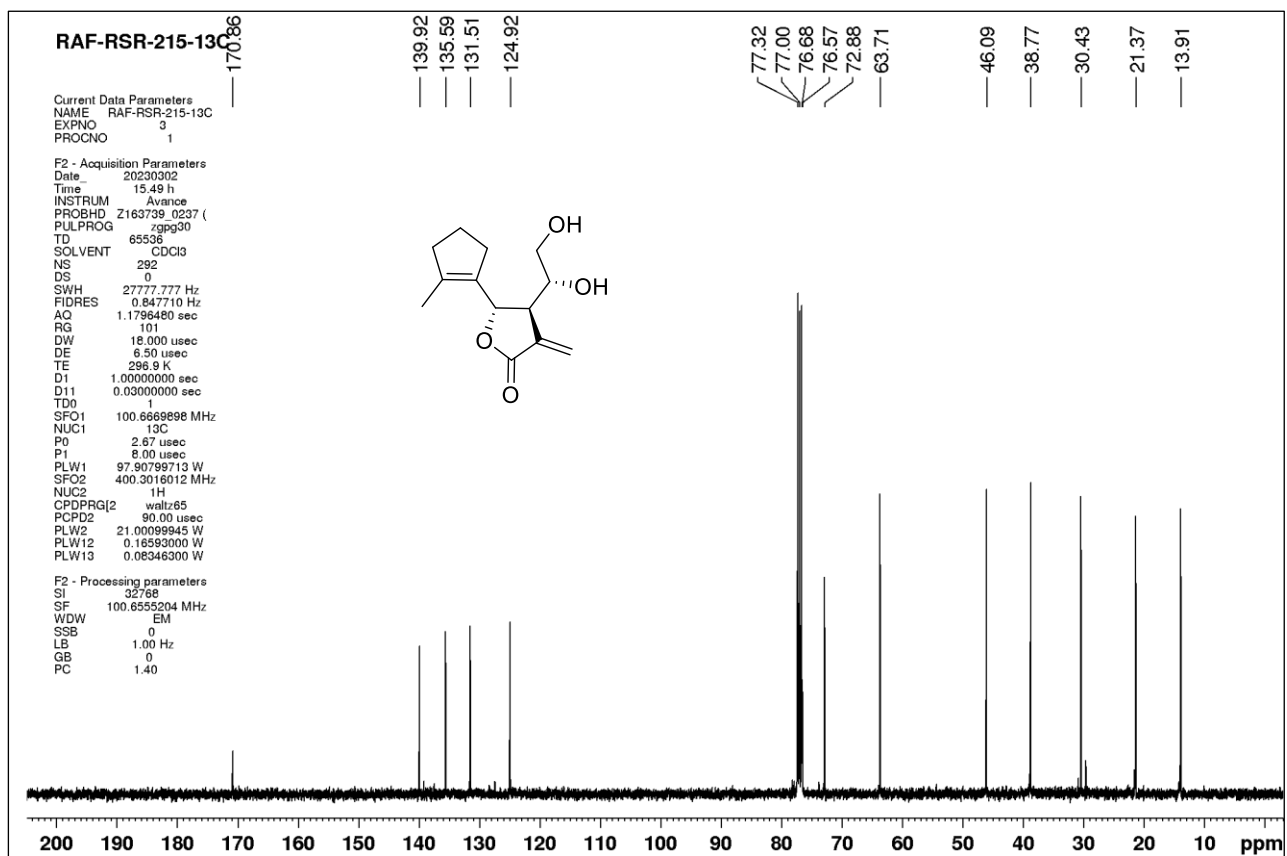
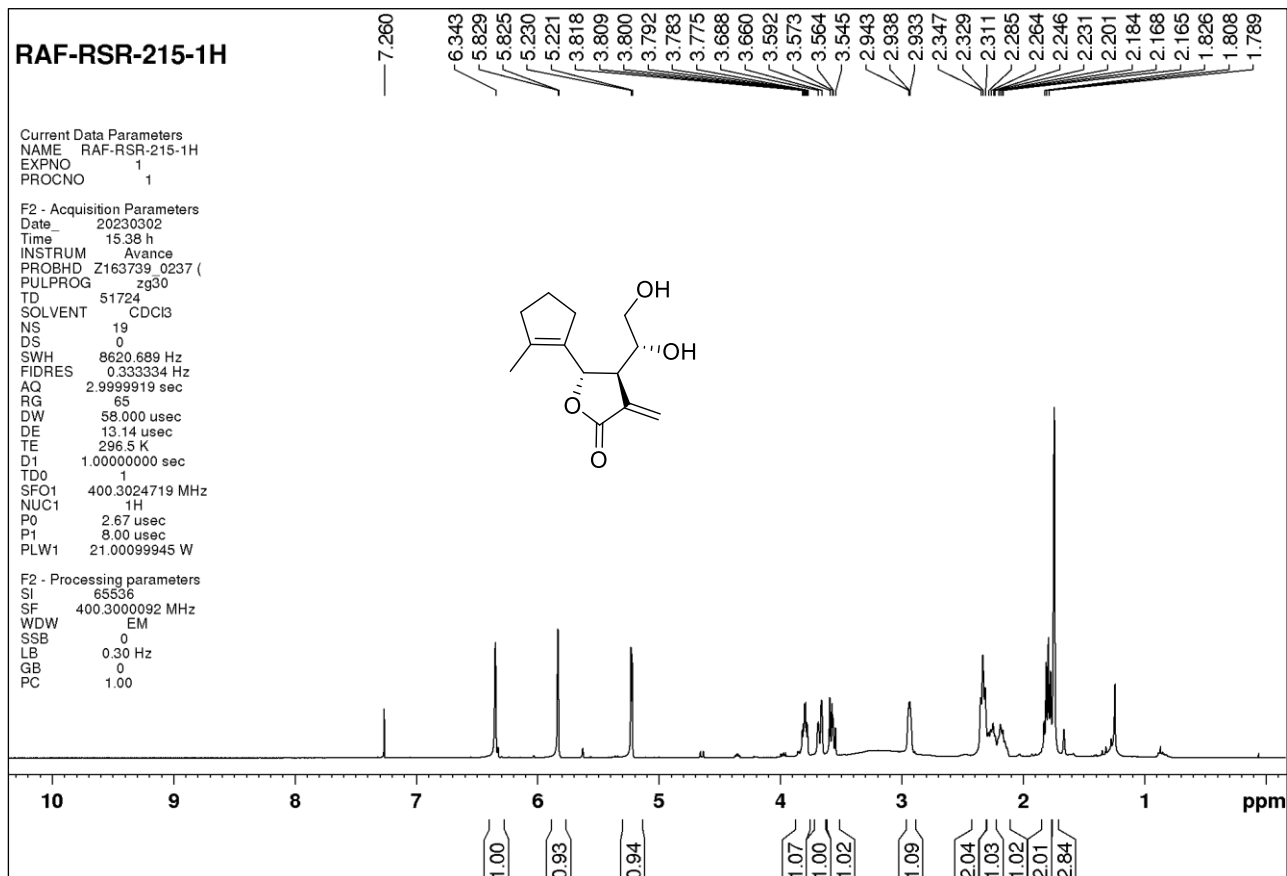
*ent*-**12**: HRMS (Q-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{13}H_{18}O_4Na$  261.1098; Found 261.1094.

Compound Spectra (Zoomed)

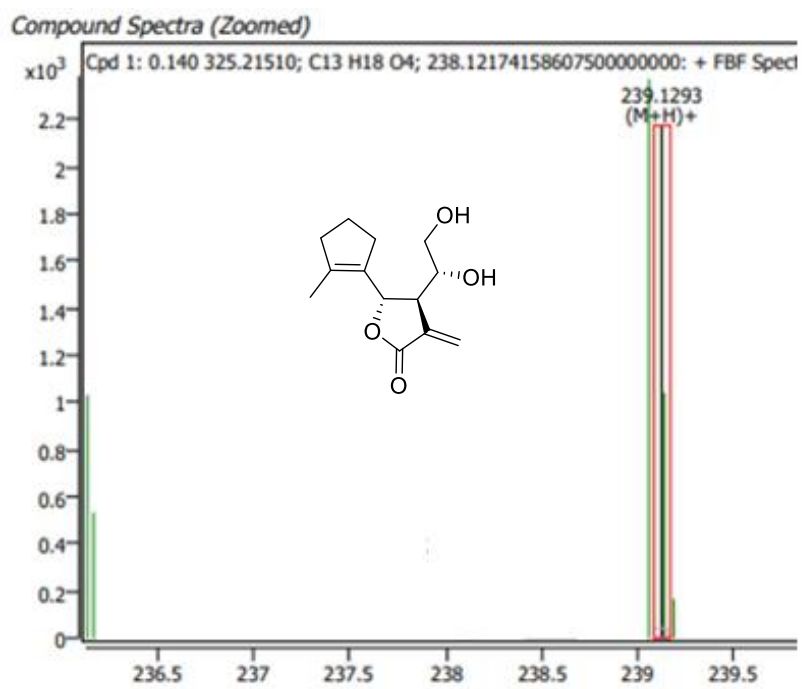




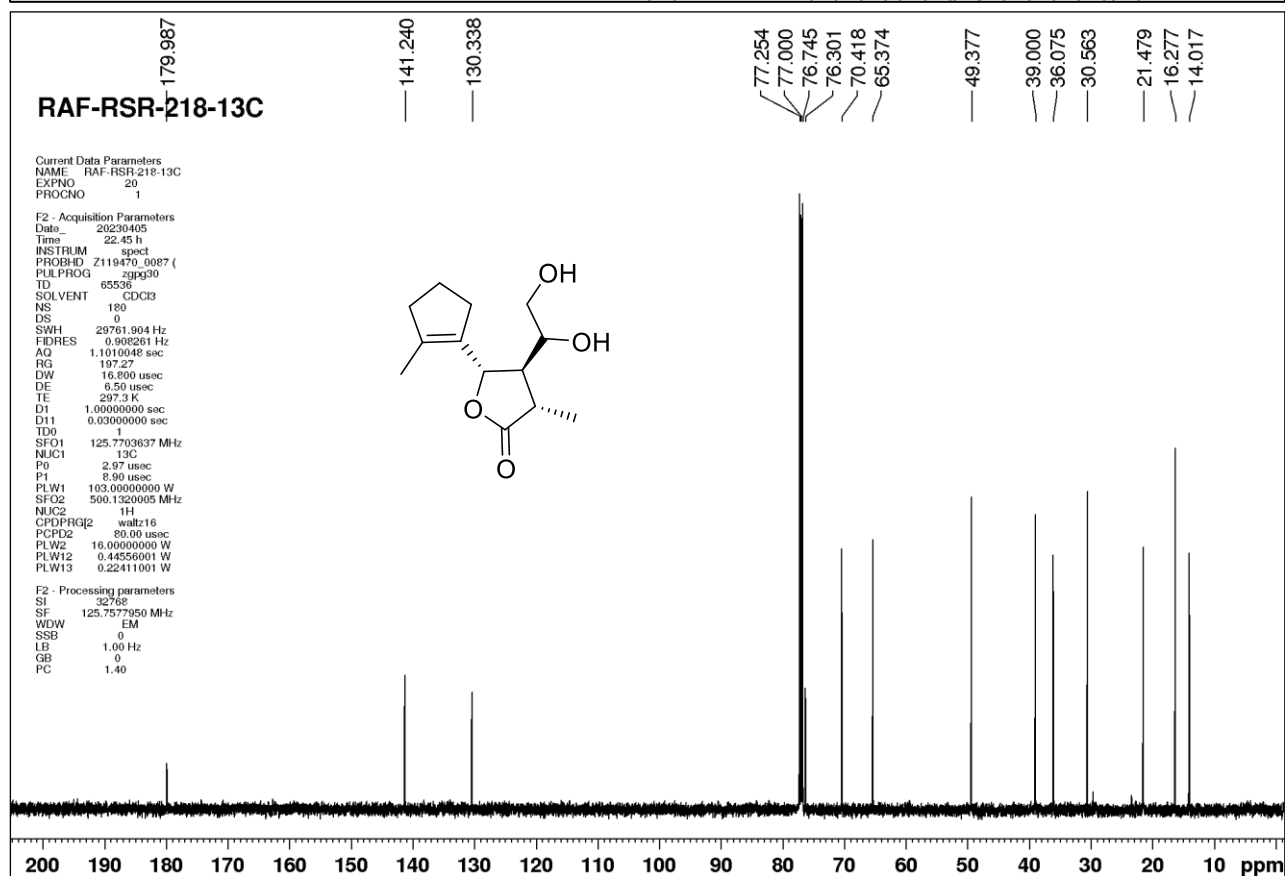
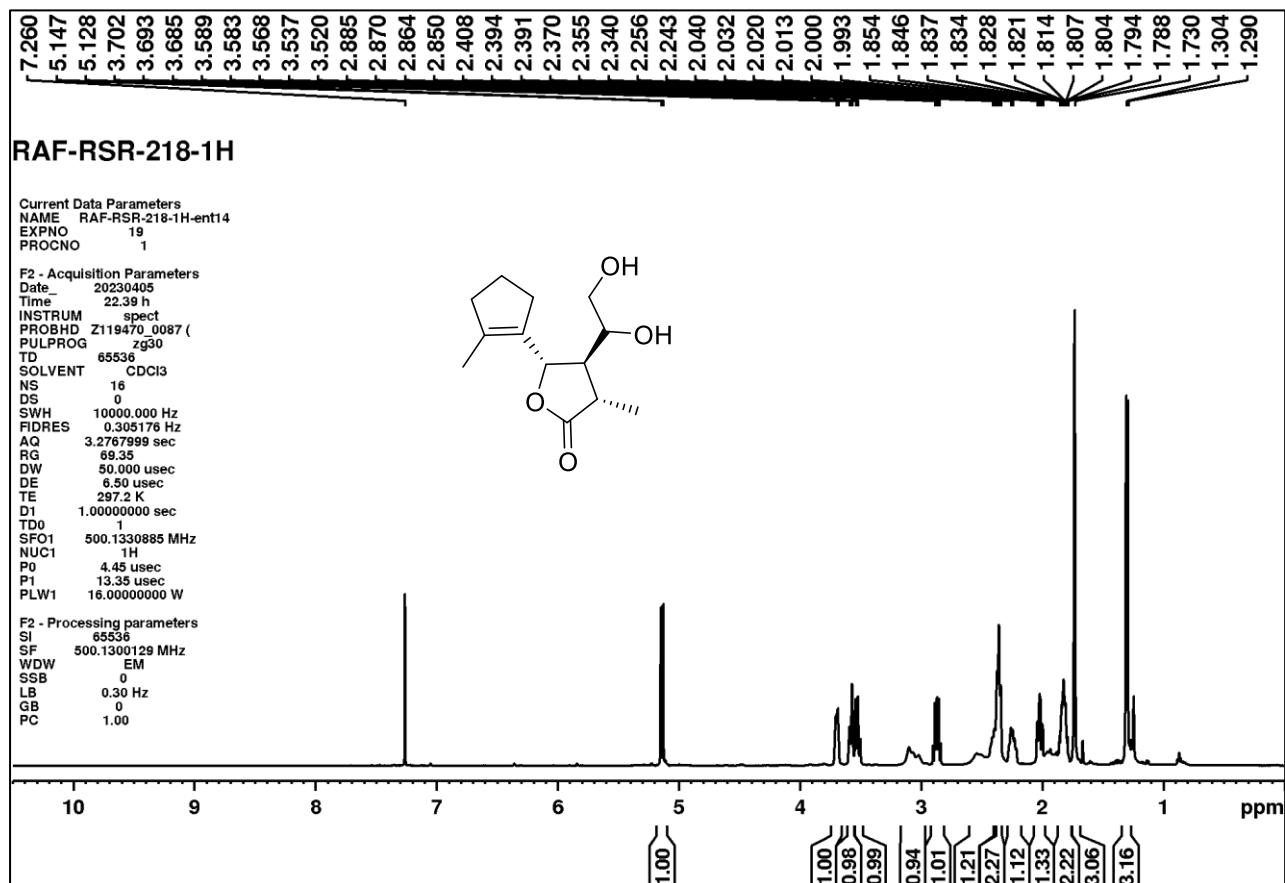
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) of compound *ent*-13



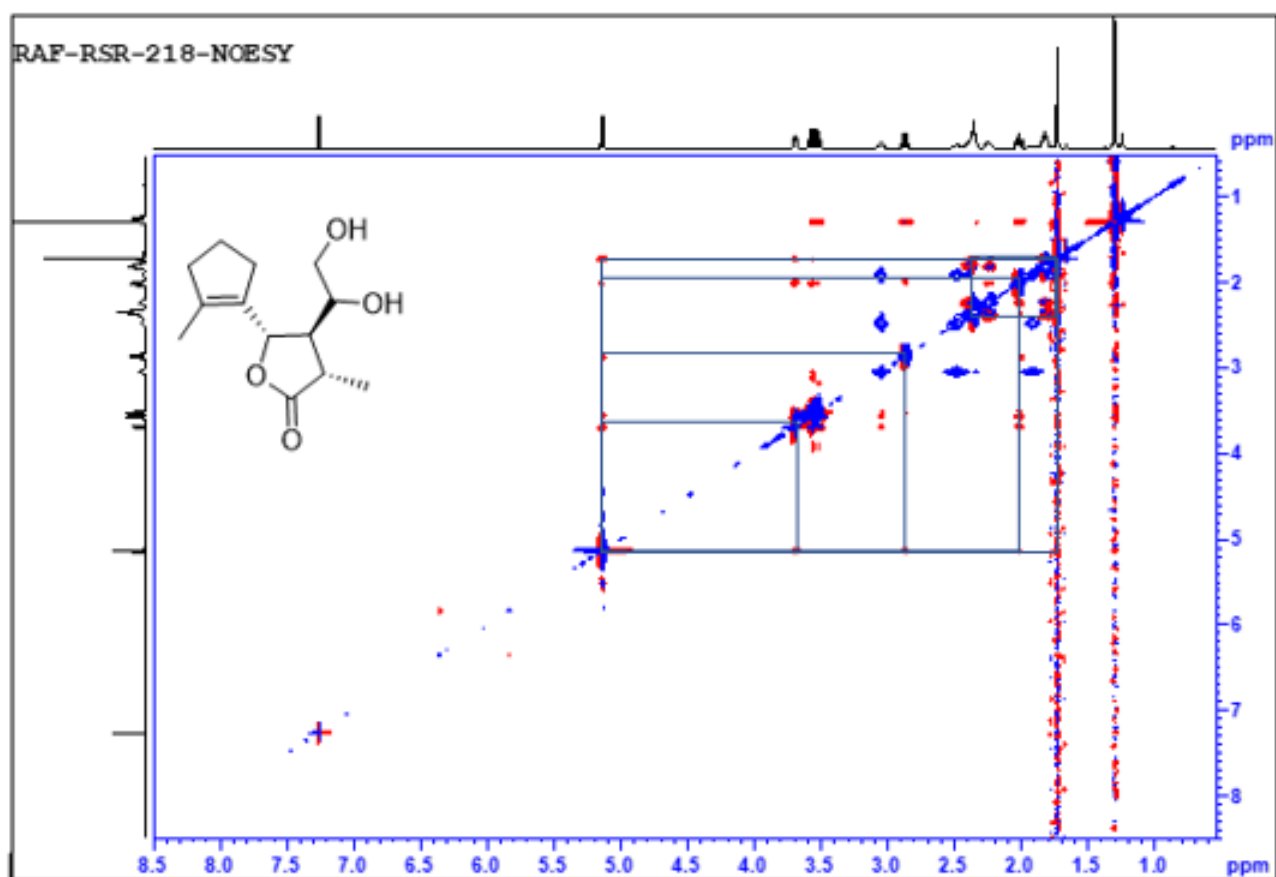
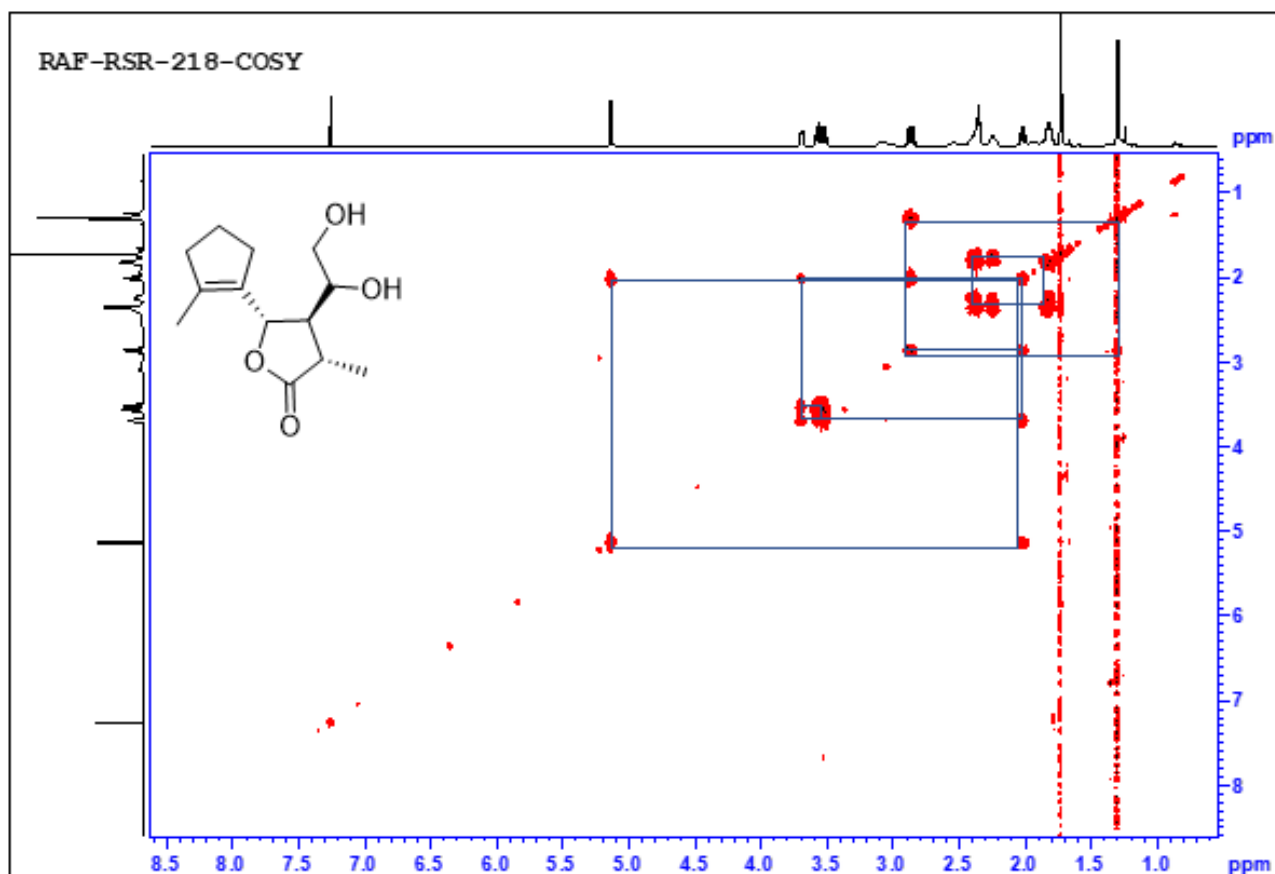
*ent*-**13**: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{13}H_{19}O_4$  239.1278; Found 239.1293.



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) of compound *ent*-14

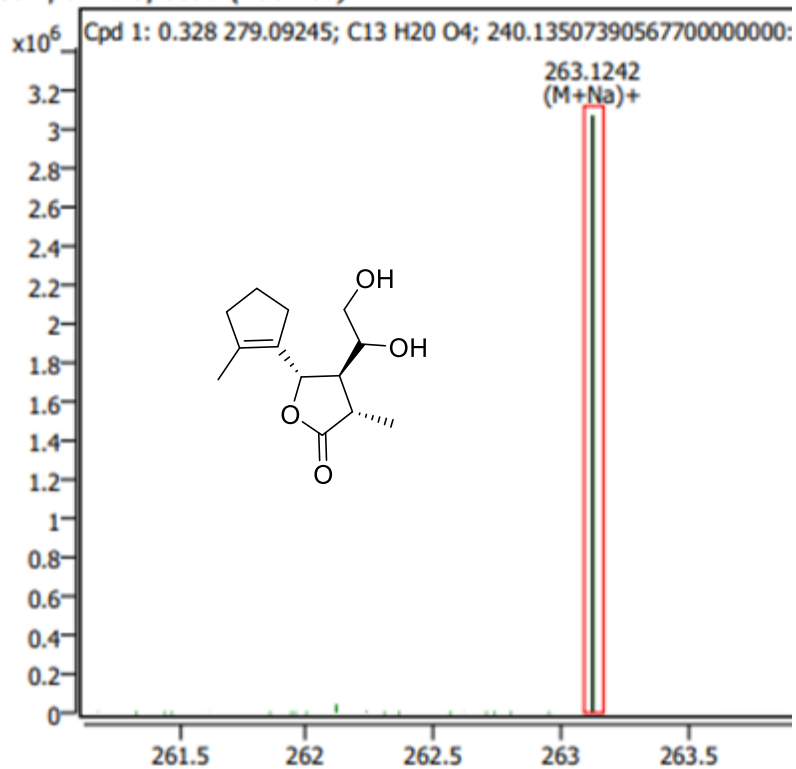


COSY (400 MHz, CDCl<sub>3</sub>) and NOESY (400 MHz, CDCl<sub>3</sub>) of compound *ent*-14

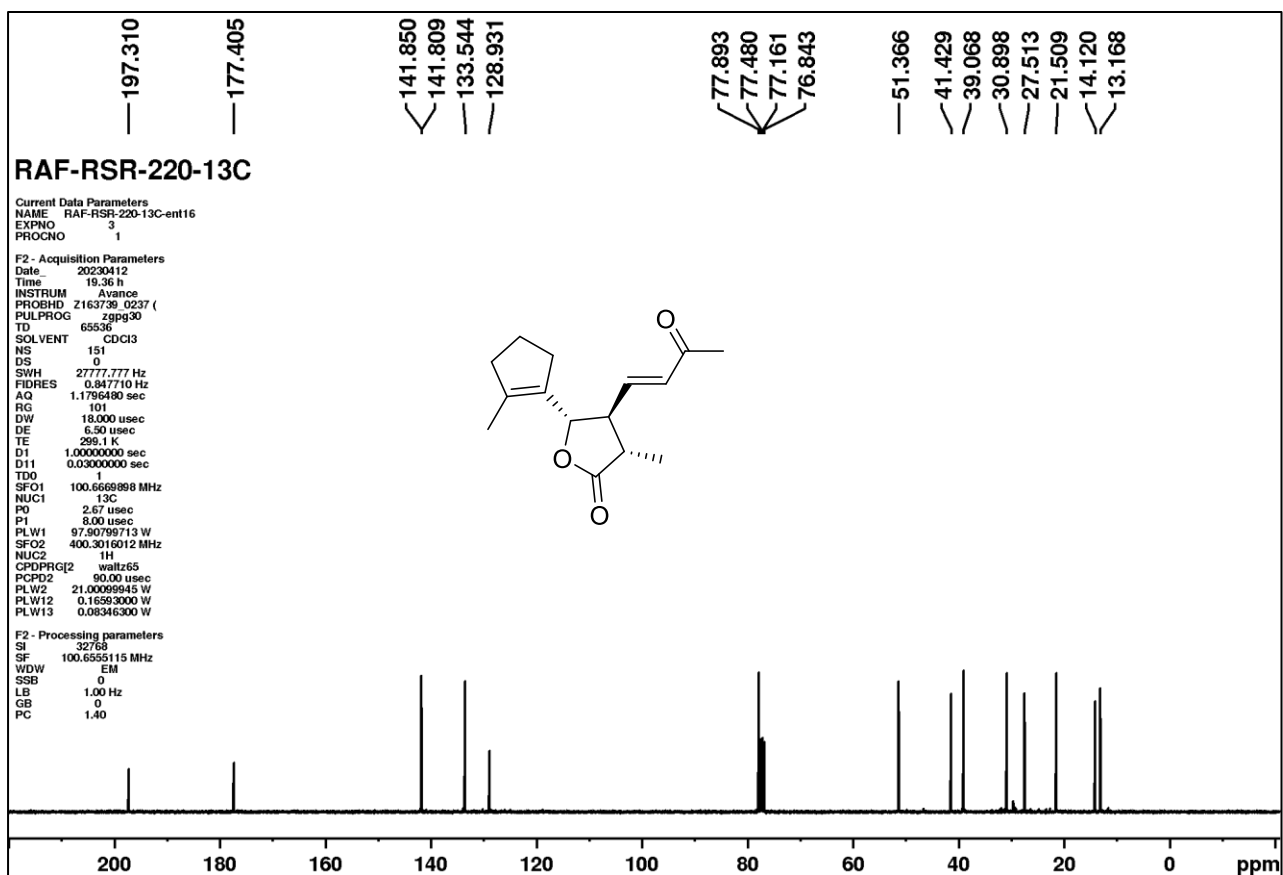
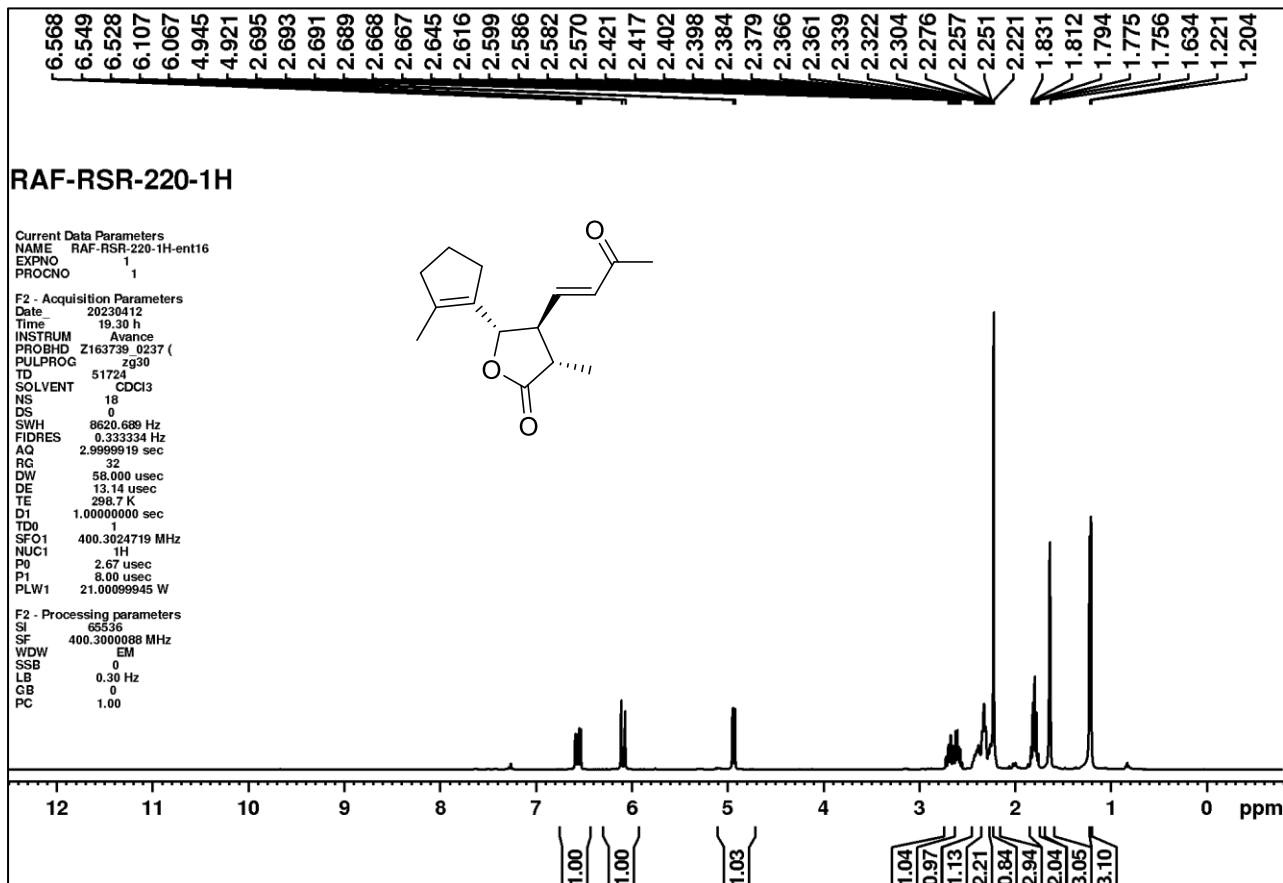


*ent*-14: HRMS (Q-TOF)  $m/z$ :  $[M + Na]^+$  Calcd for  $C_{13}H_{20}O_4Na$  263.1254; Found 263.1242.

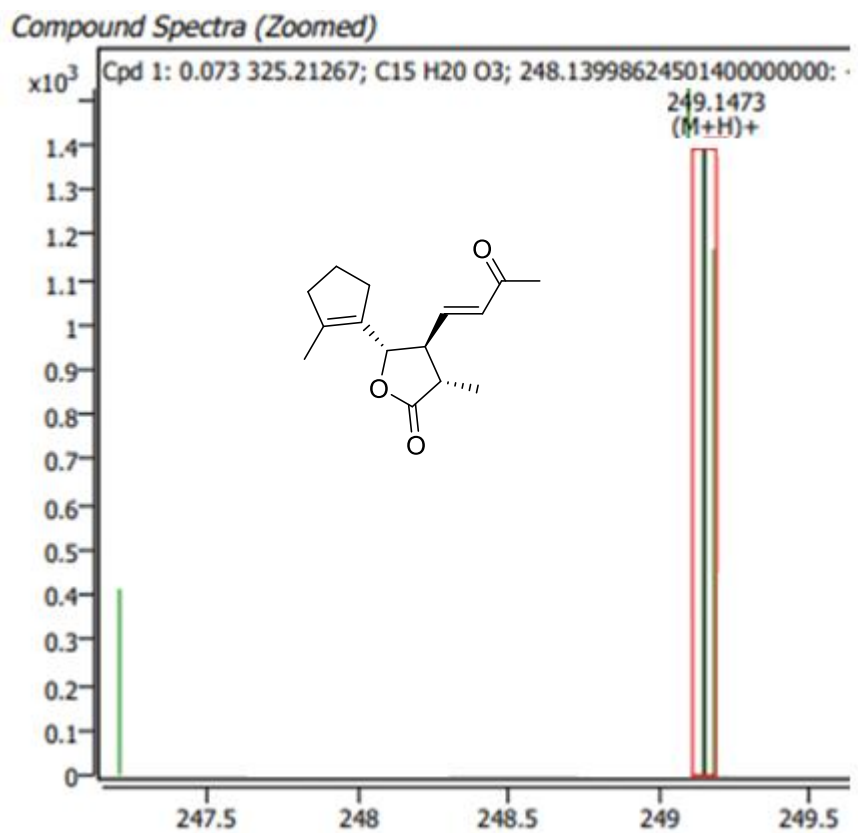
Compound Spectra (Zoomed)



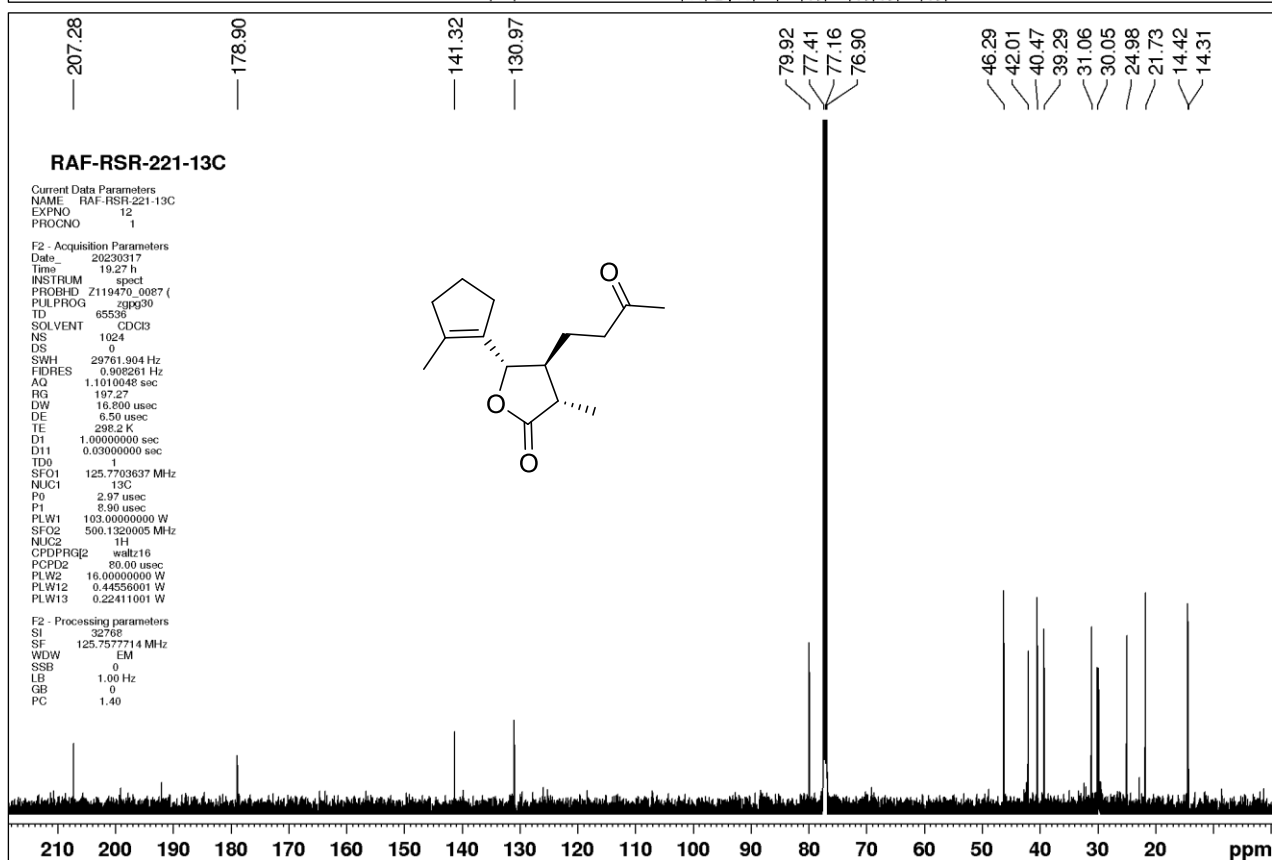
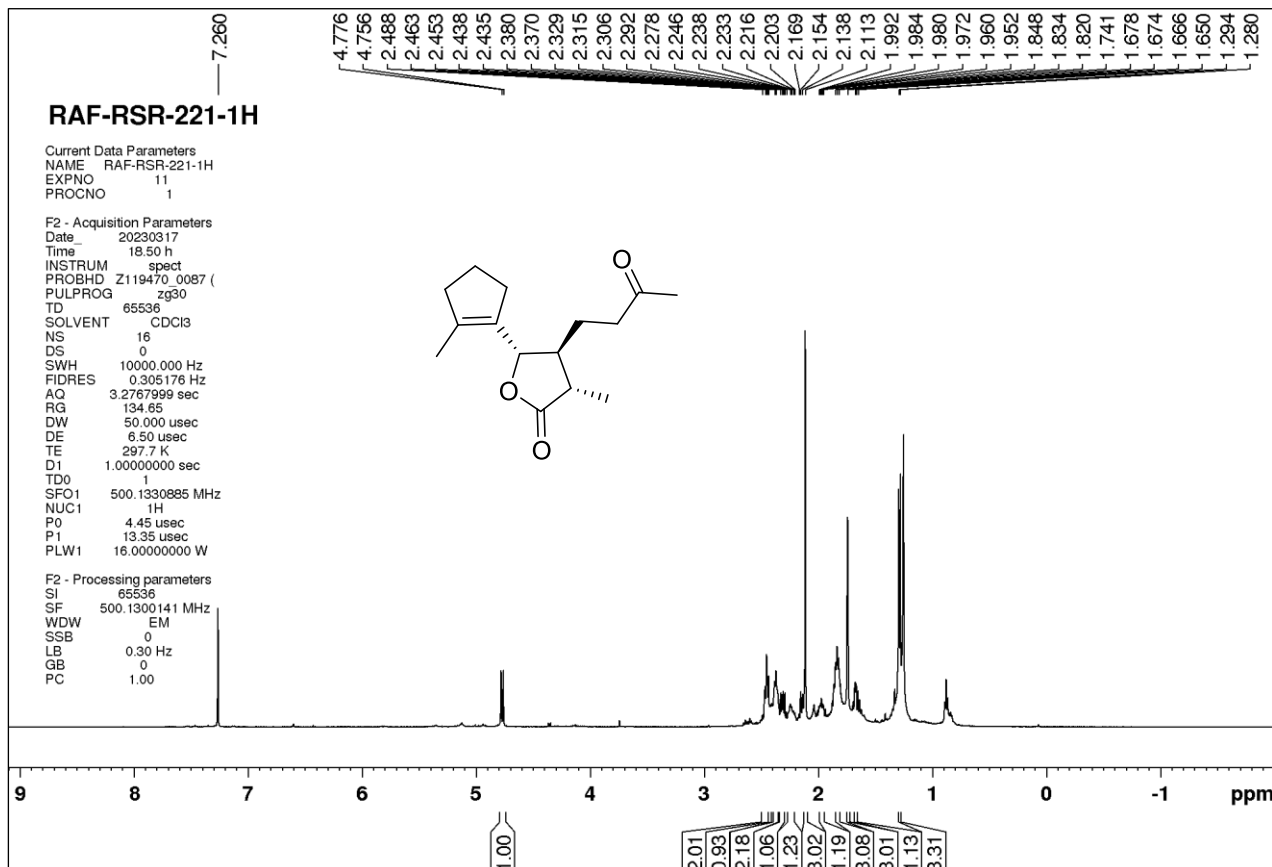
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>) of compound *ent-16*



*ent*-16: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{21}O_3$  249.1486; Found 249.1473.



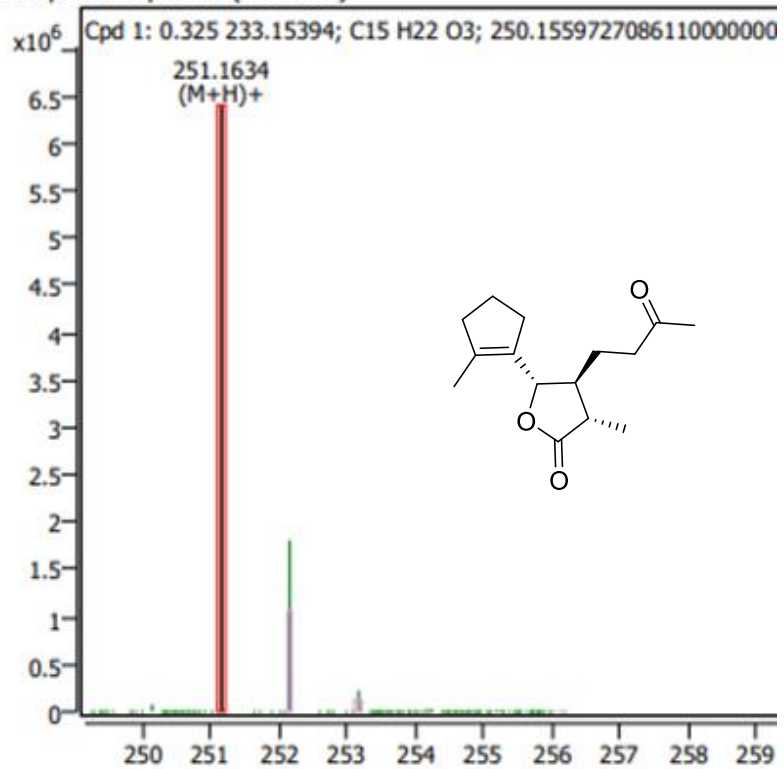
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C{<sup>1</sup>H} NMR (125 MHz, CDCl<sub>3</sub>) of compound *ent-17*



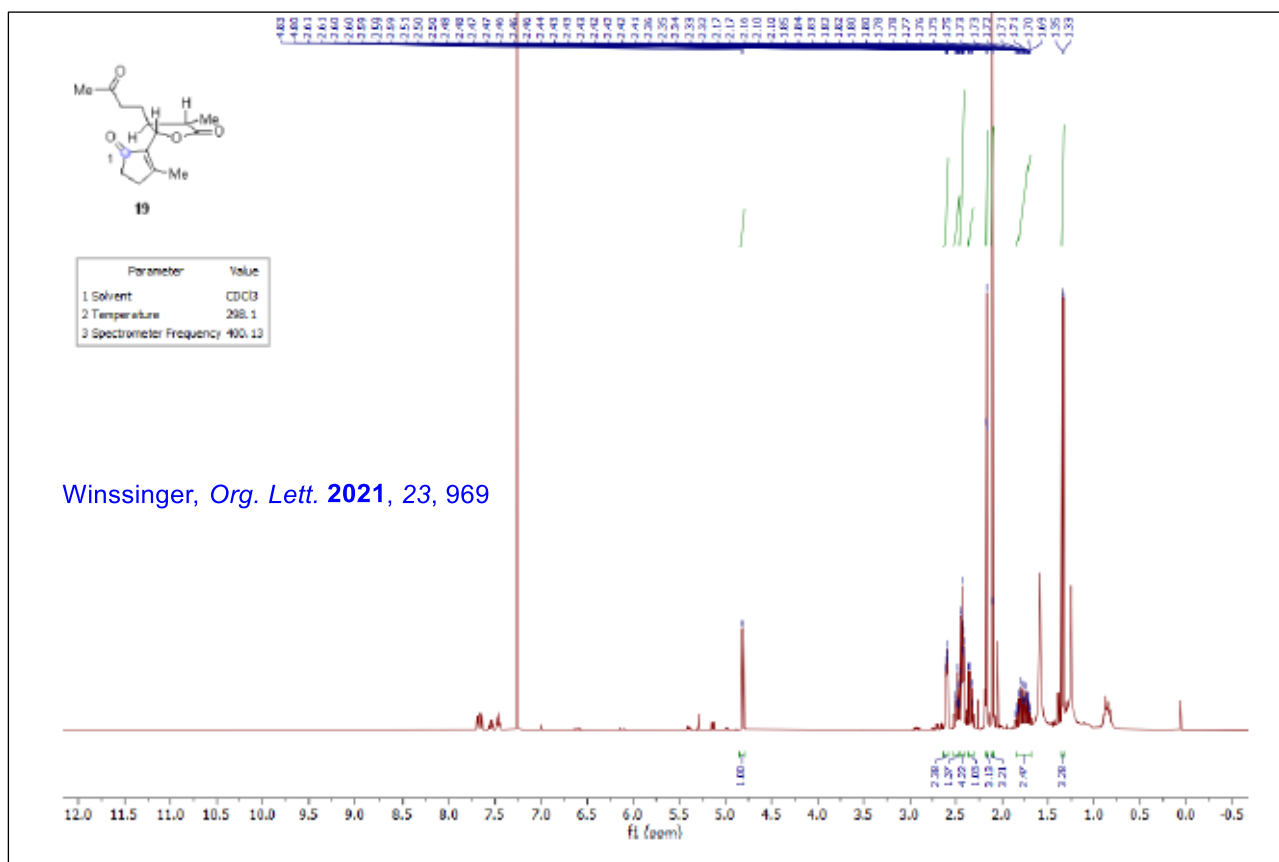
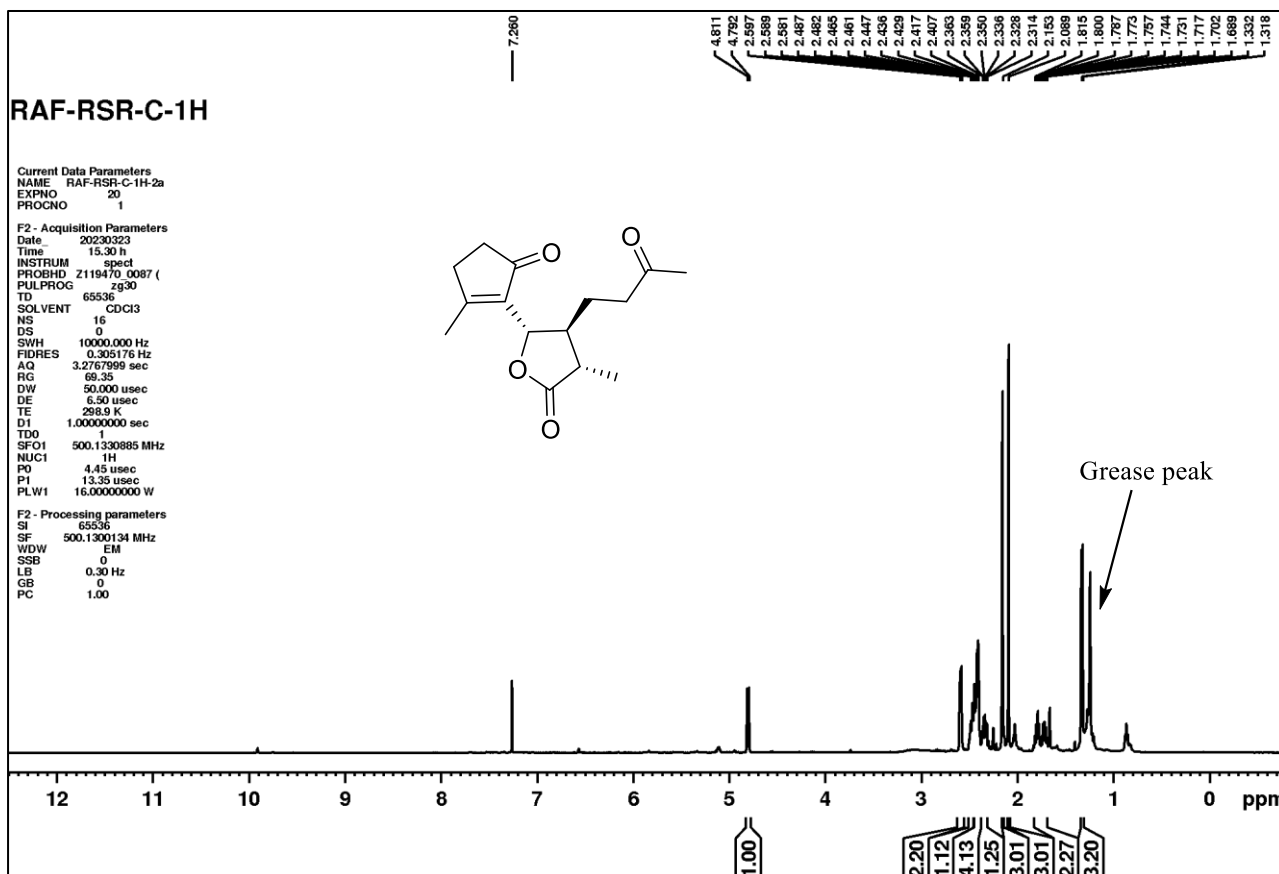


*ent*-17: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{23}O_3$  251.1642; Found 251.1634.

Compound Spectra (Zoomed)

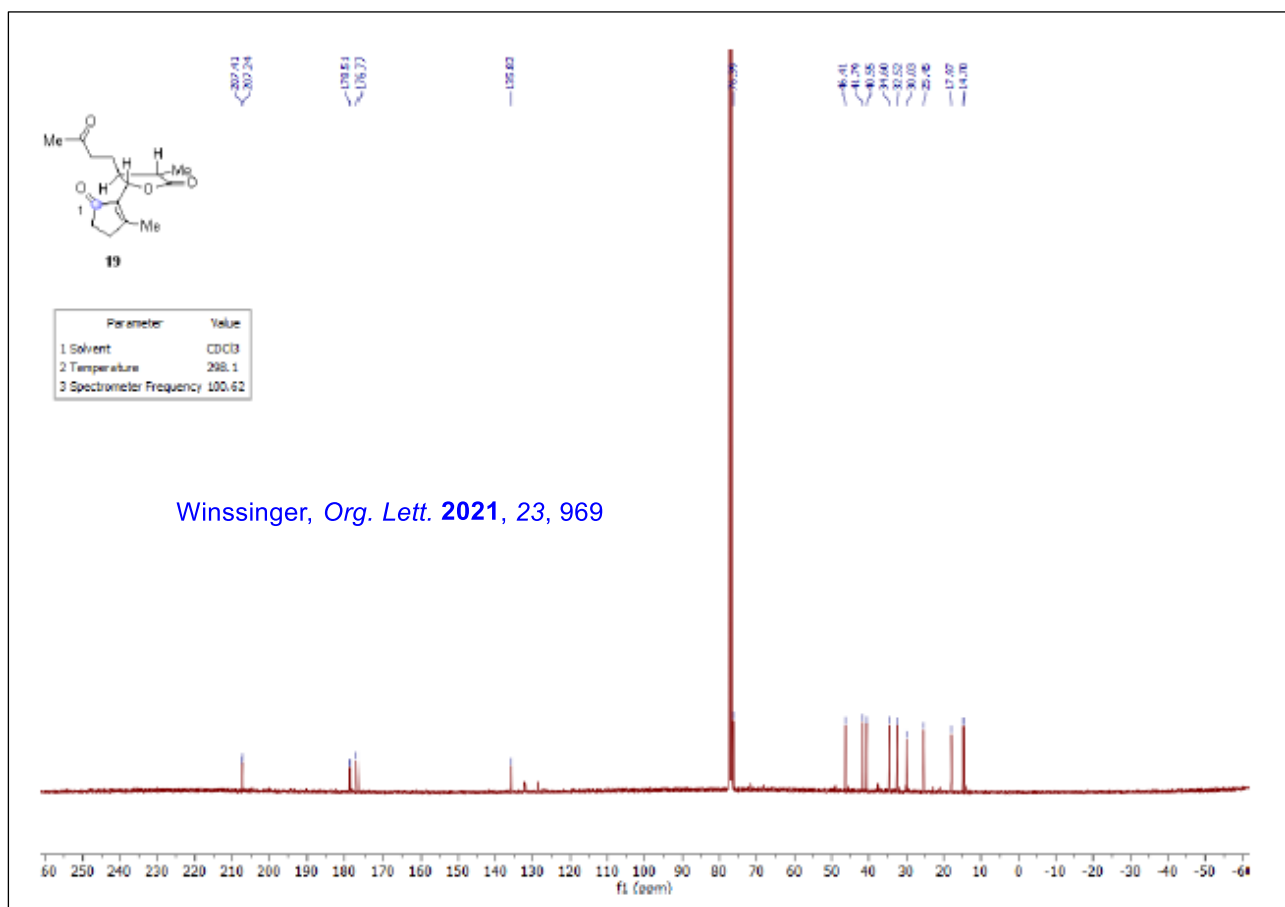
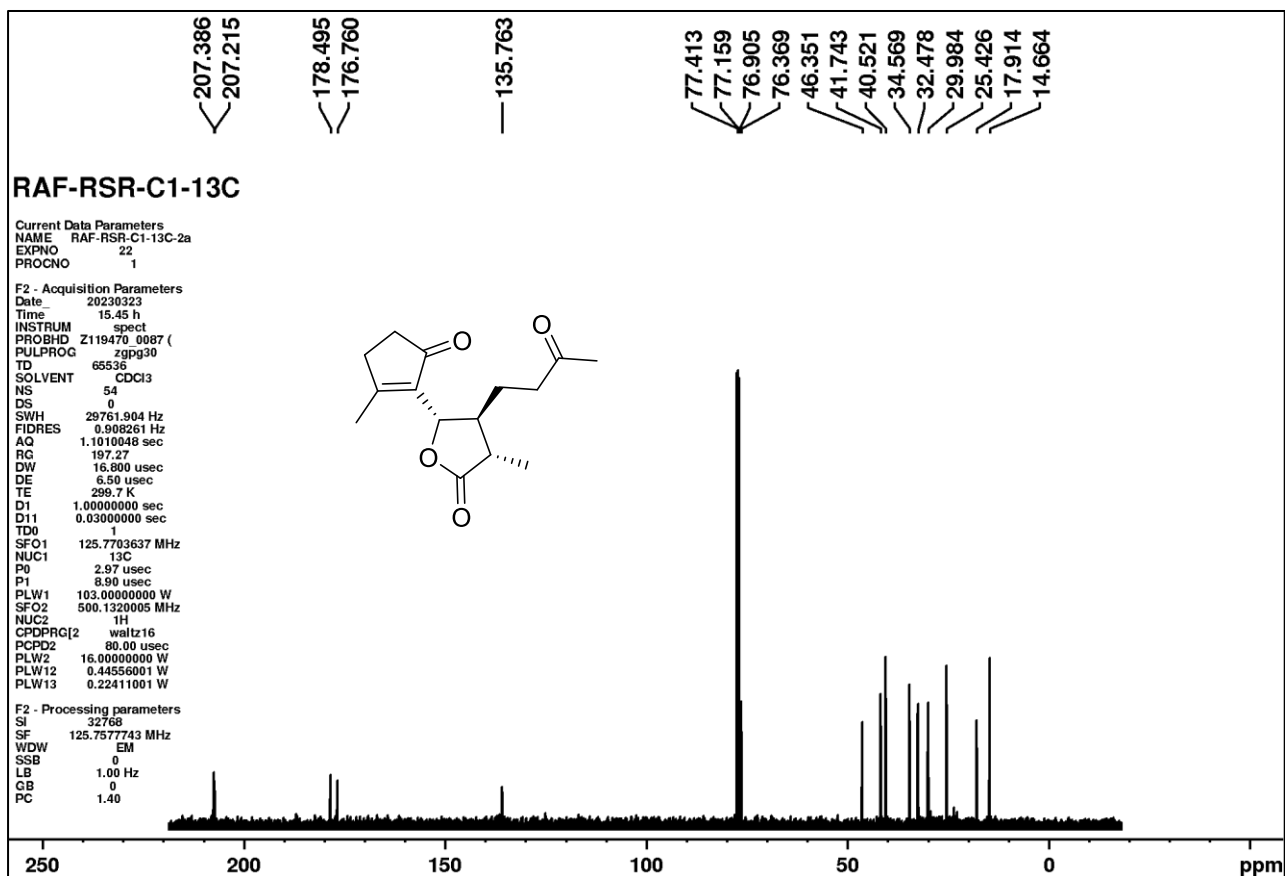


<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) of compound **2a** and reported spectra of (±)-**2a**



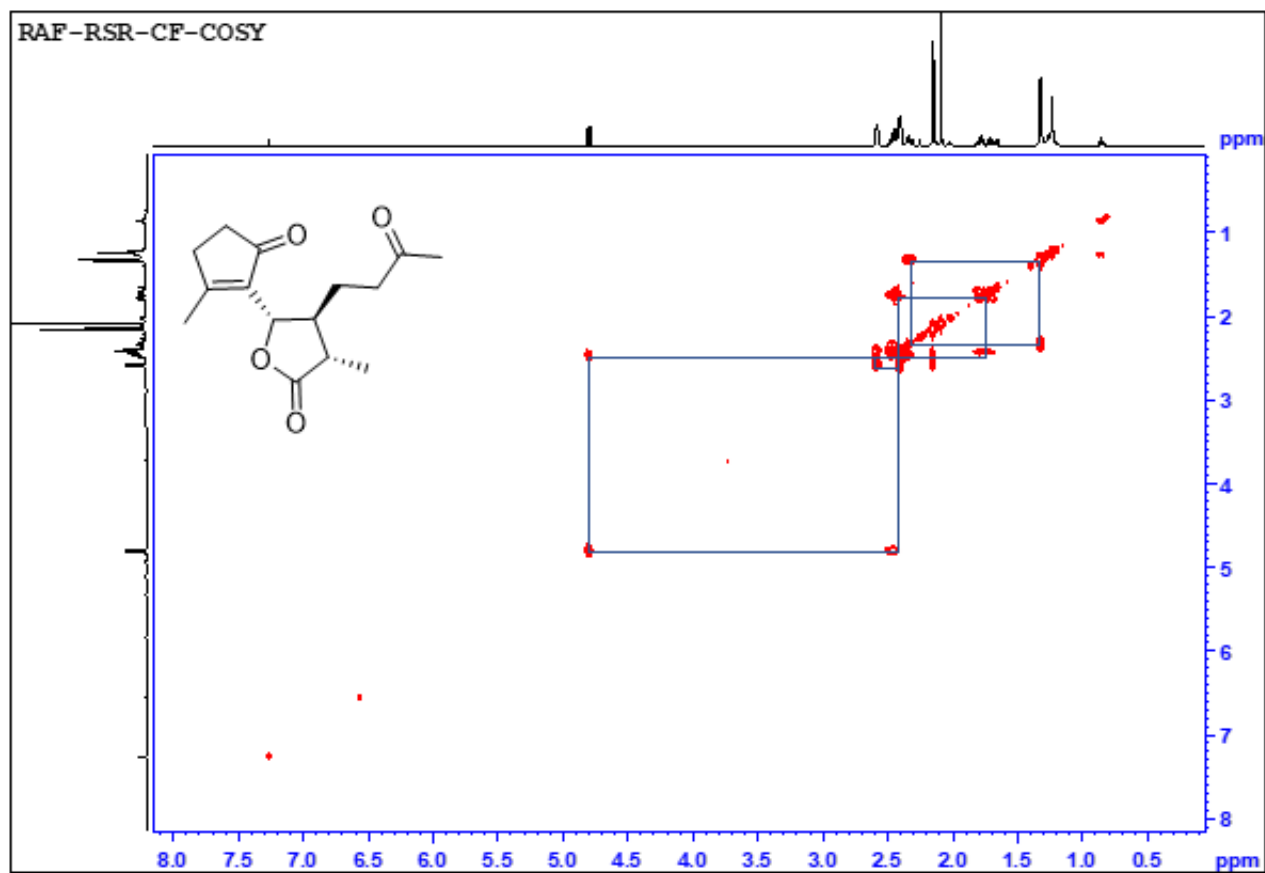
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$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of compound **2a** and reported spectra of ( $\pm$ )-**2a**

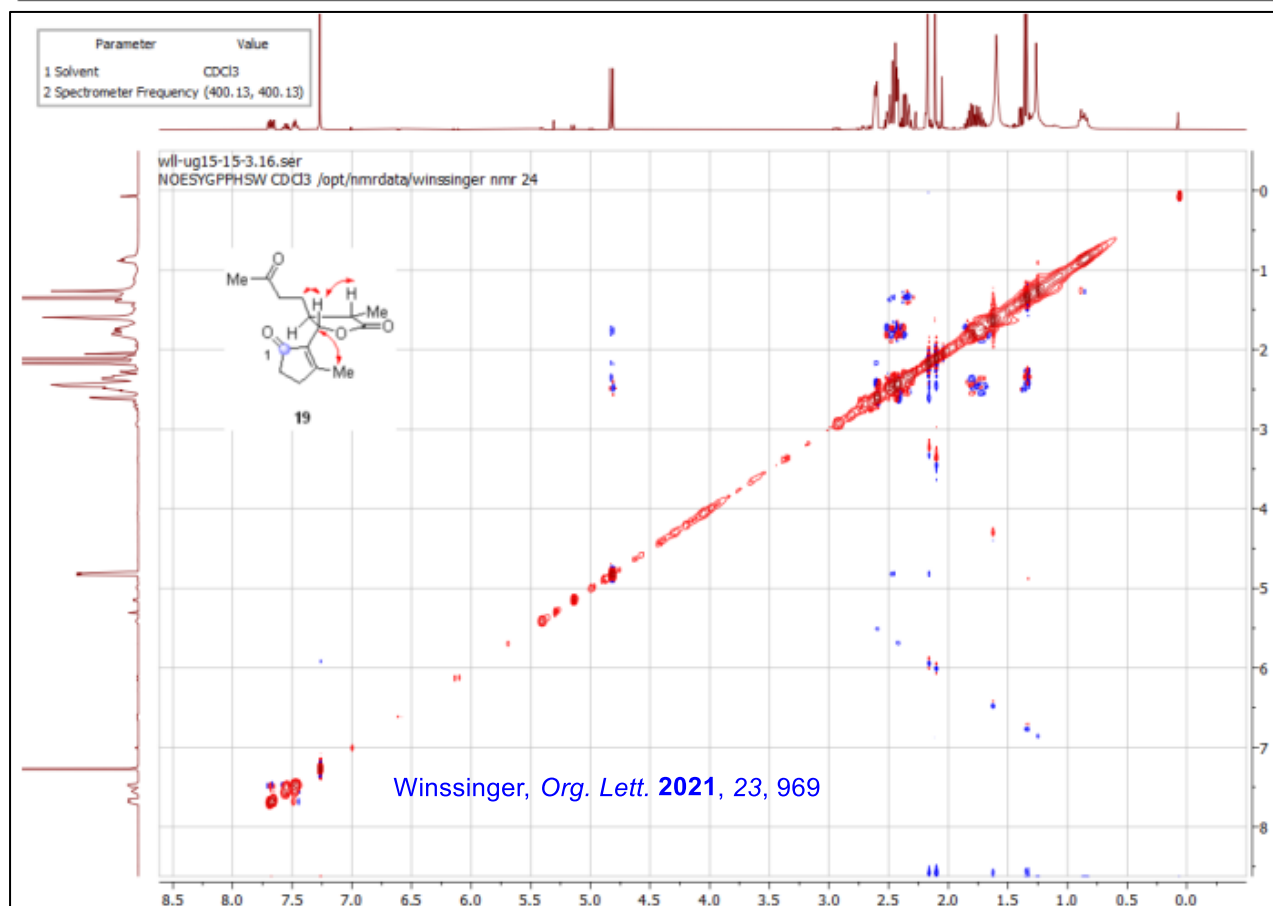
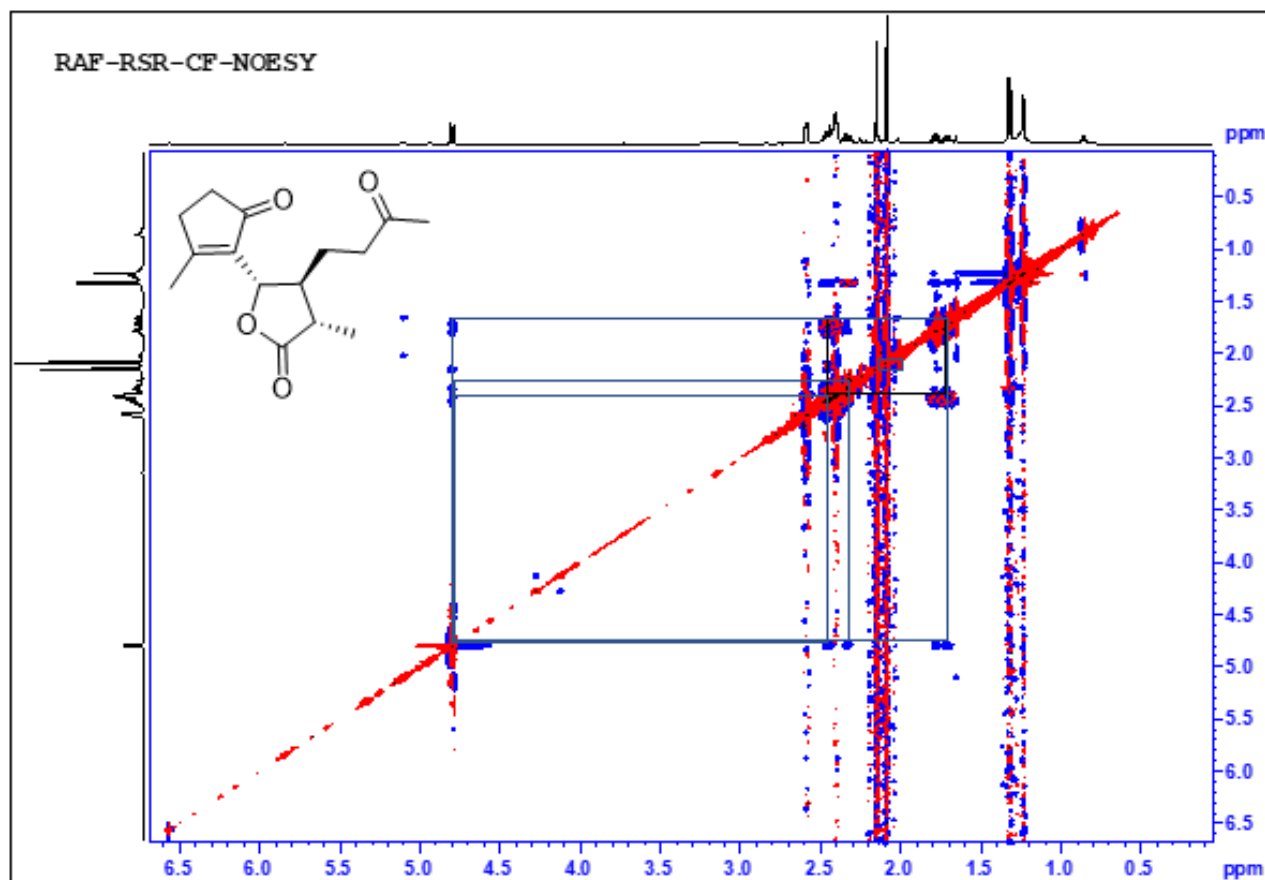


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COSY (400 MHz, CDCl<sub>3</sub>) of compound **2a** and reported spectra of (±)-**2a**

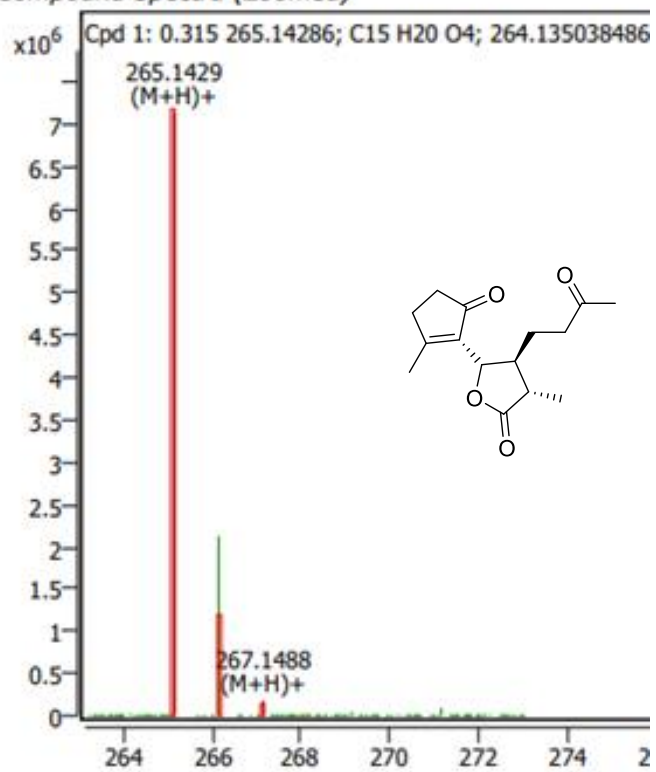


NOESY (400 MHz, CDCl<sub>3</sub>) of compound **2a** and reported spectra of (±)-**2a**

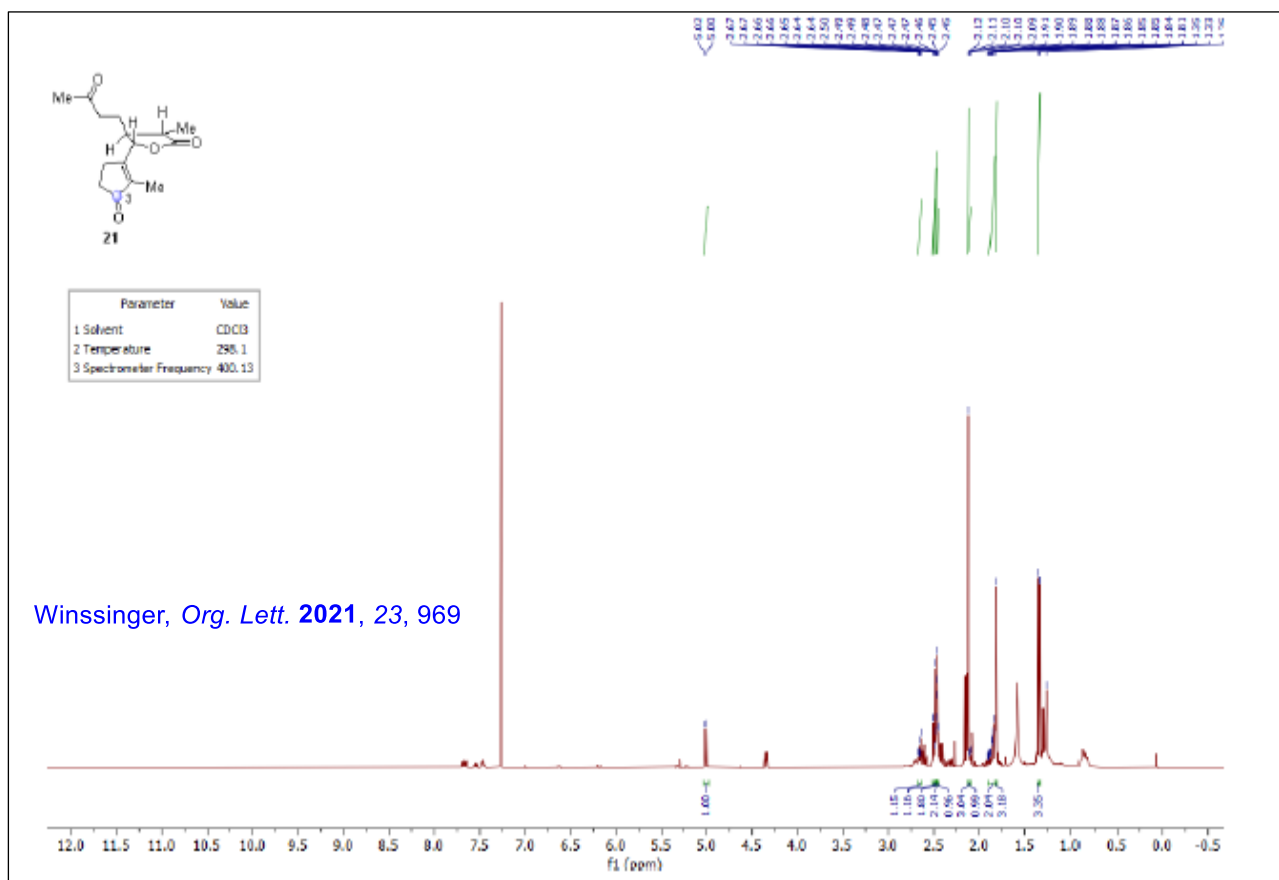
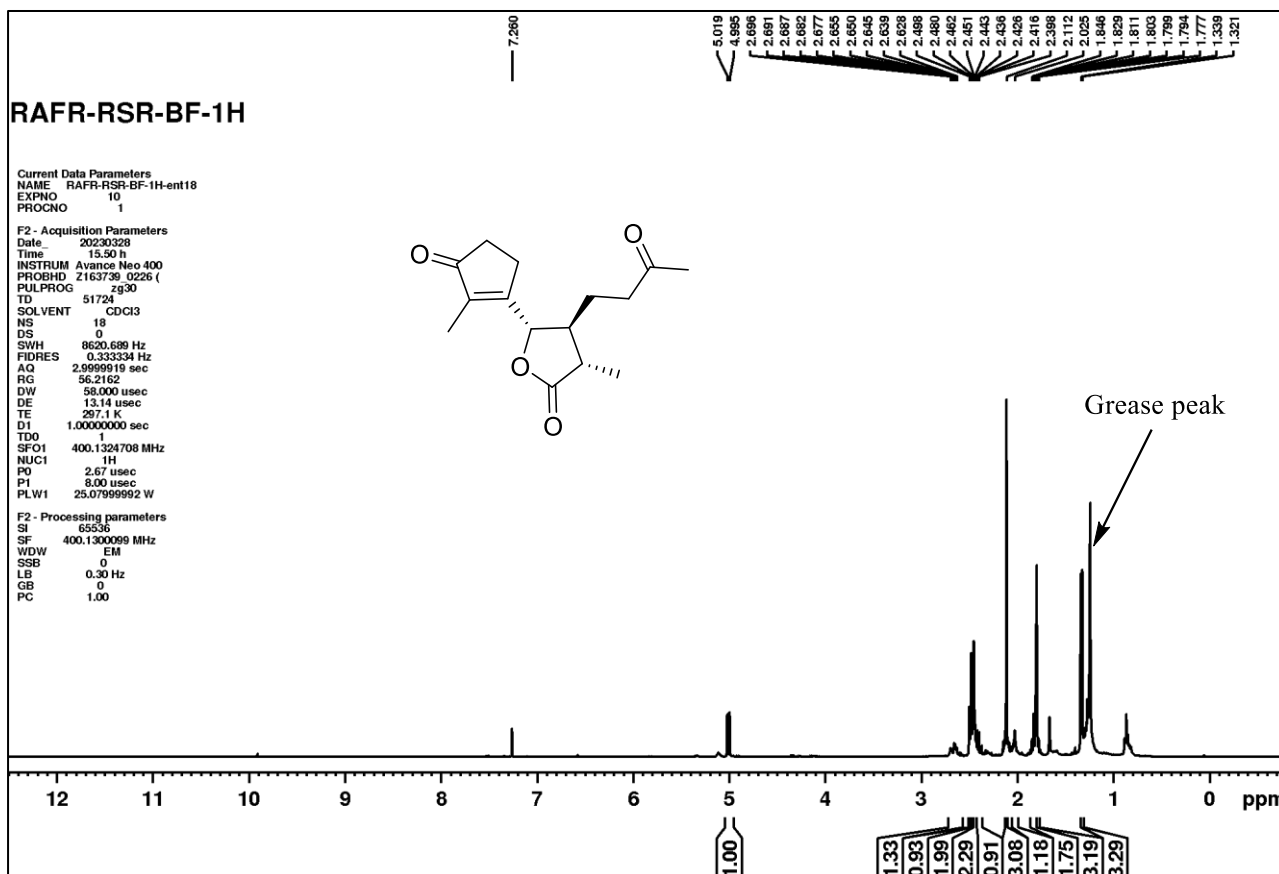


**2a:** HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{21}O_4$  265.1435; Found 265.1429.

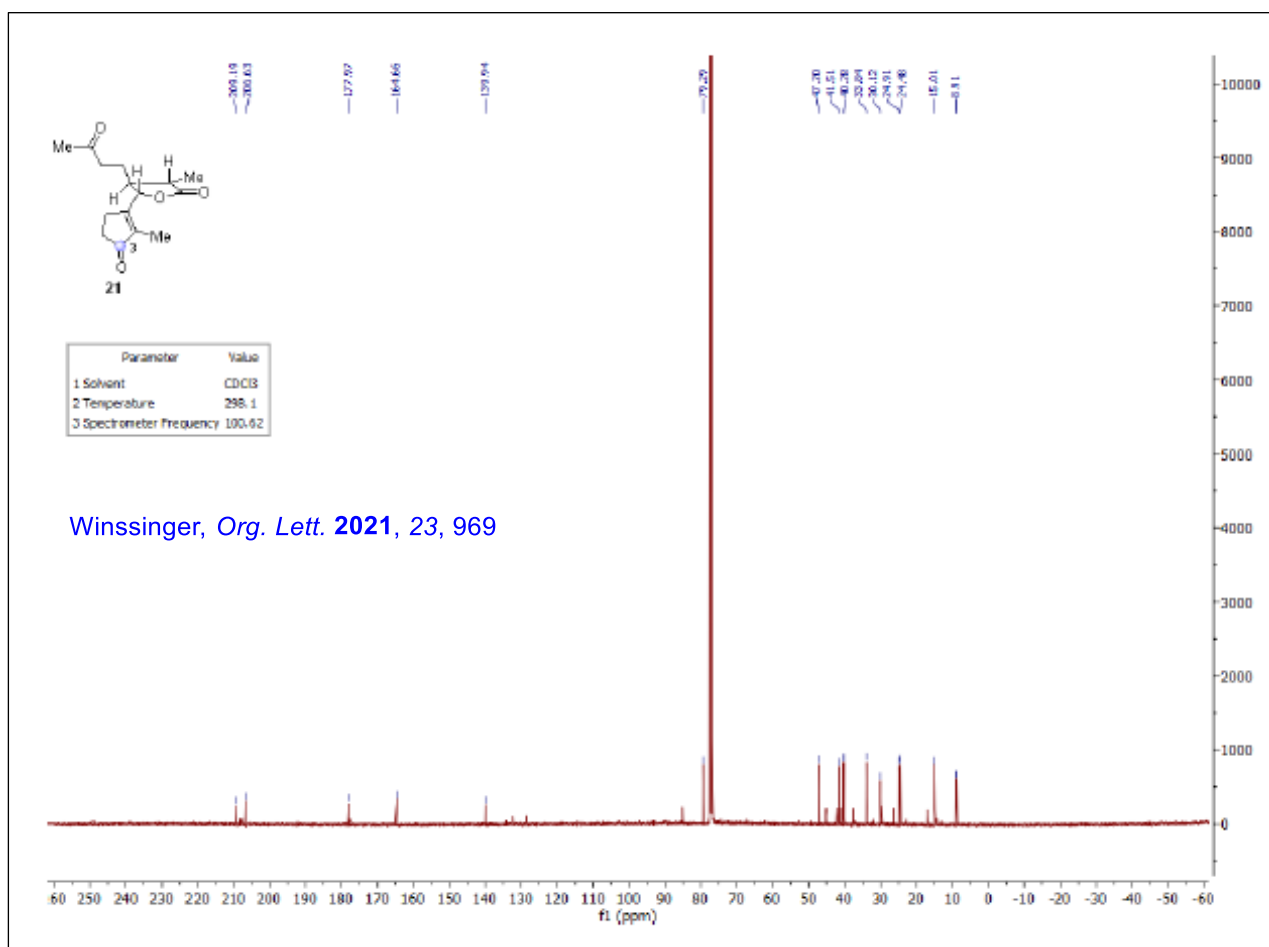
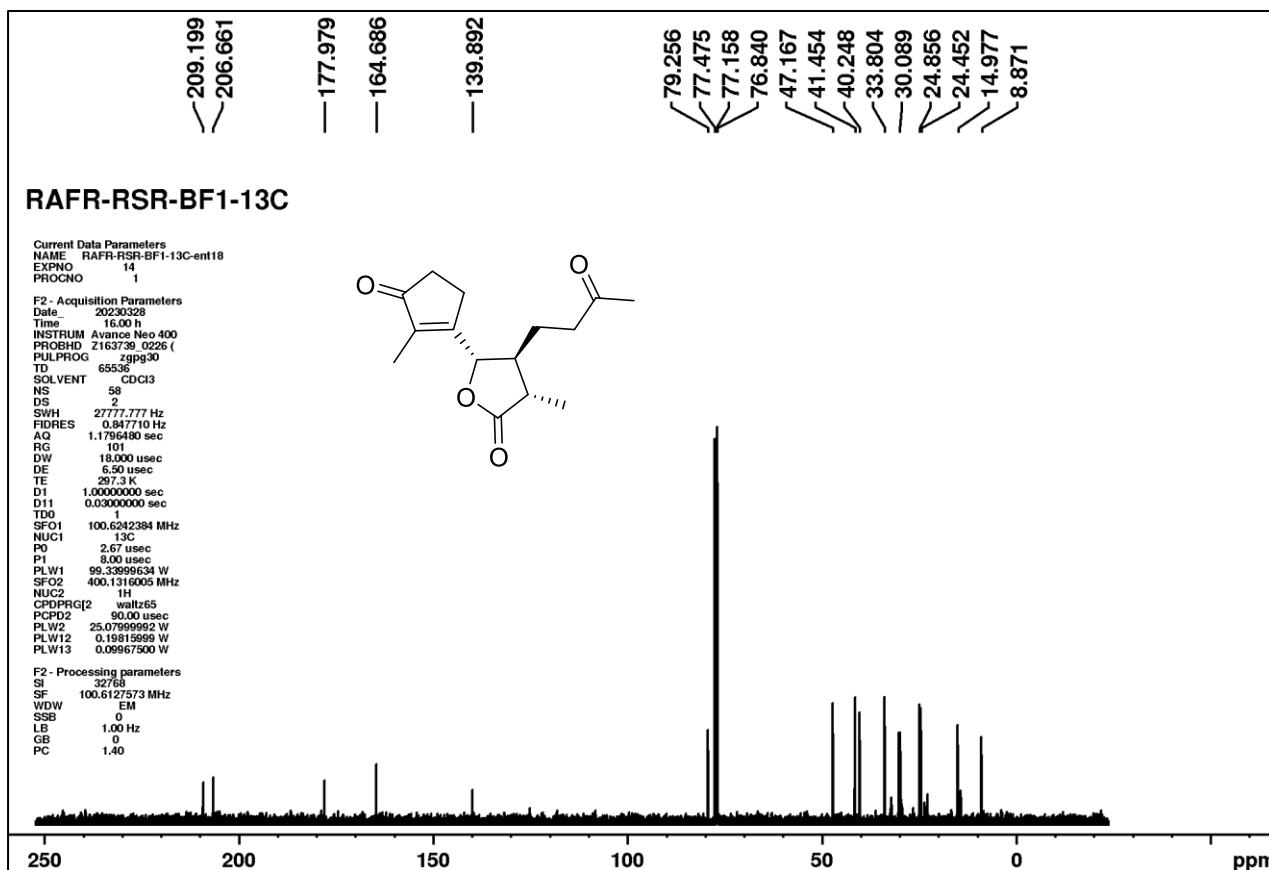
Compound Spectra (Zoomed)



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of compound *ent*-**18** and reported spectra of (±)-**18**

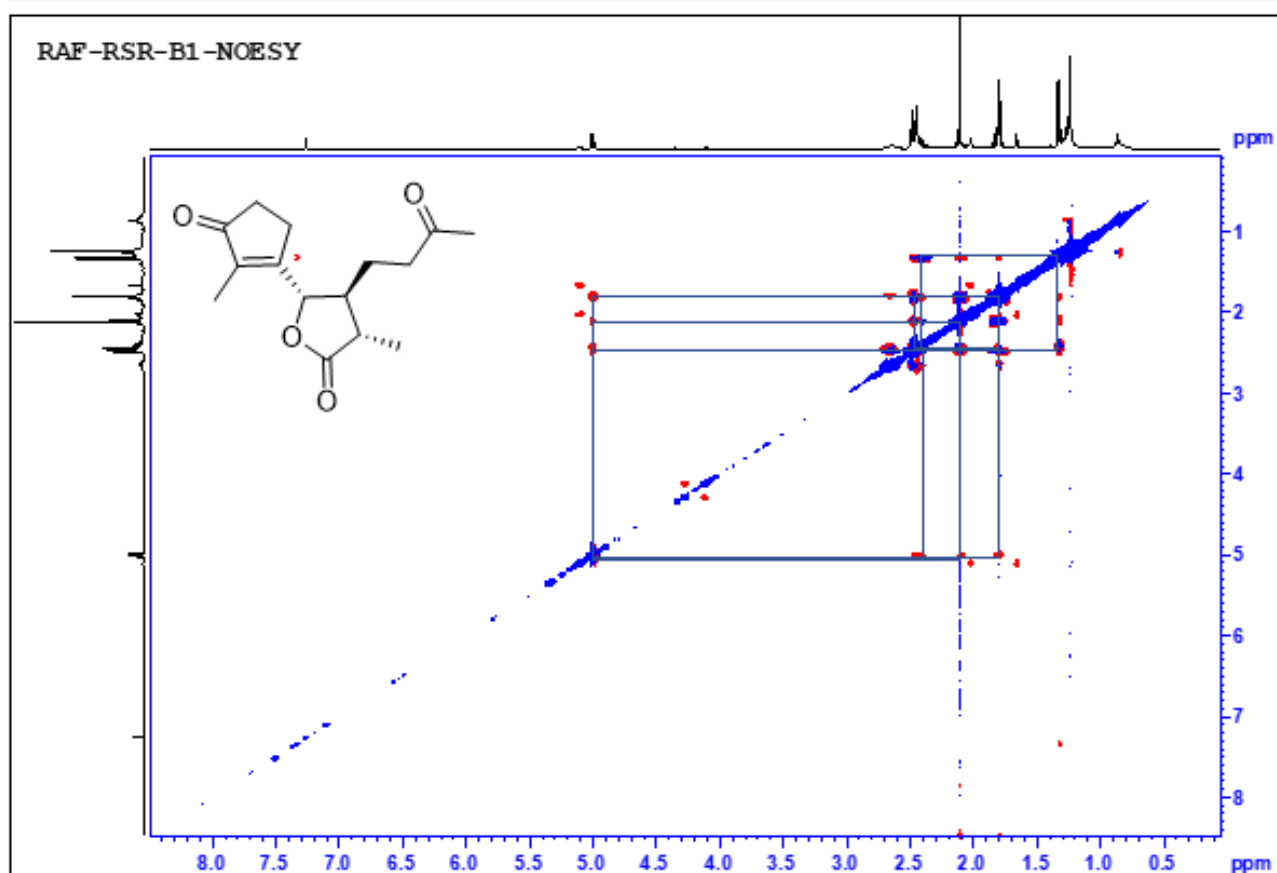
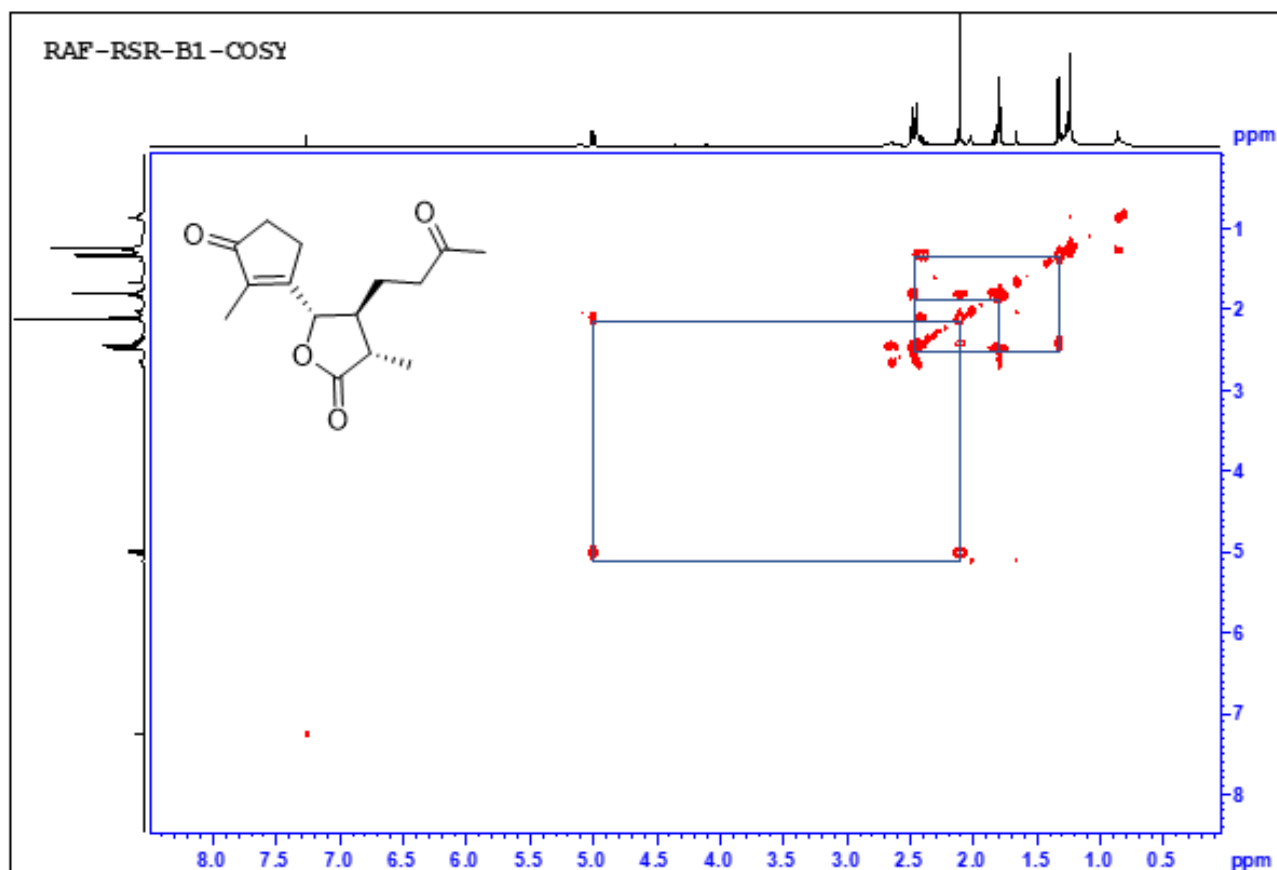


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound *ent*-**18** and reported spectra of ( $\pm$ )-**18**

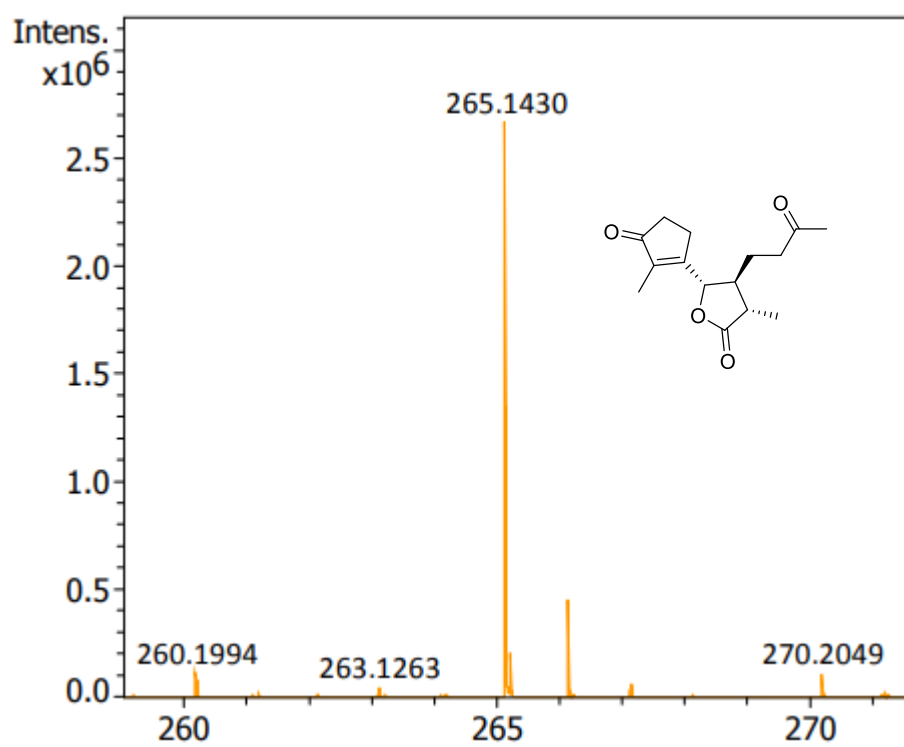




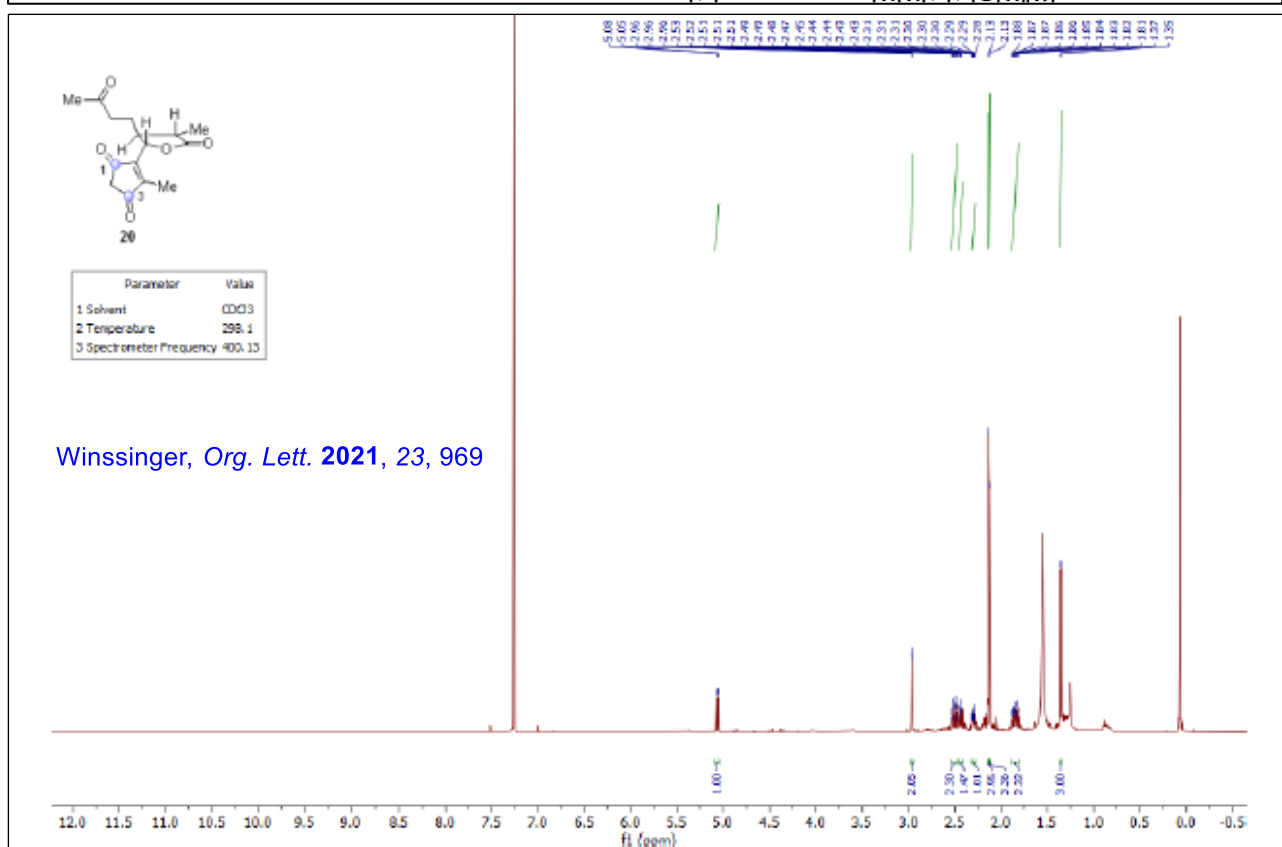
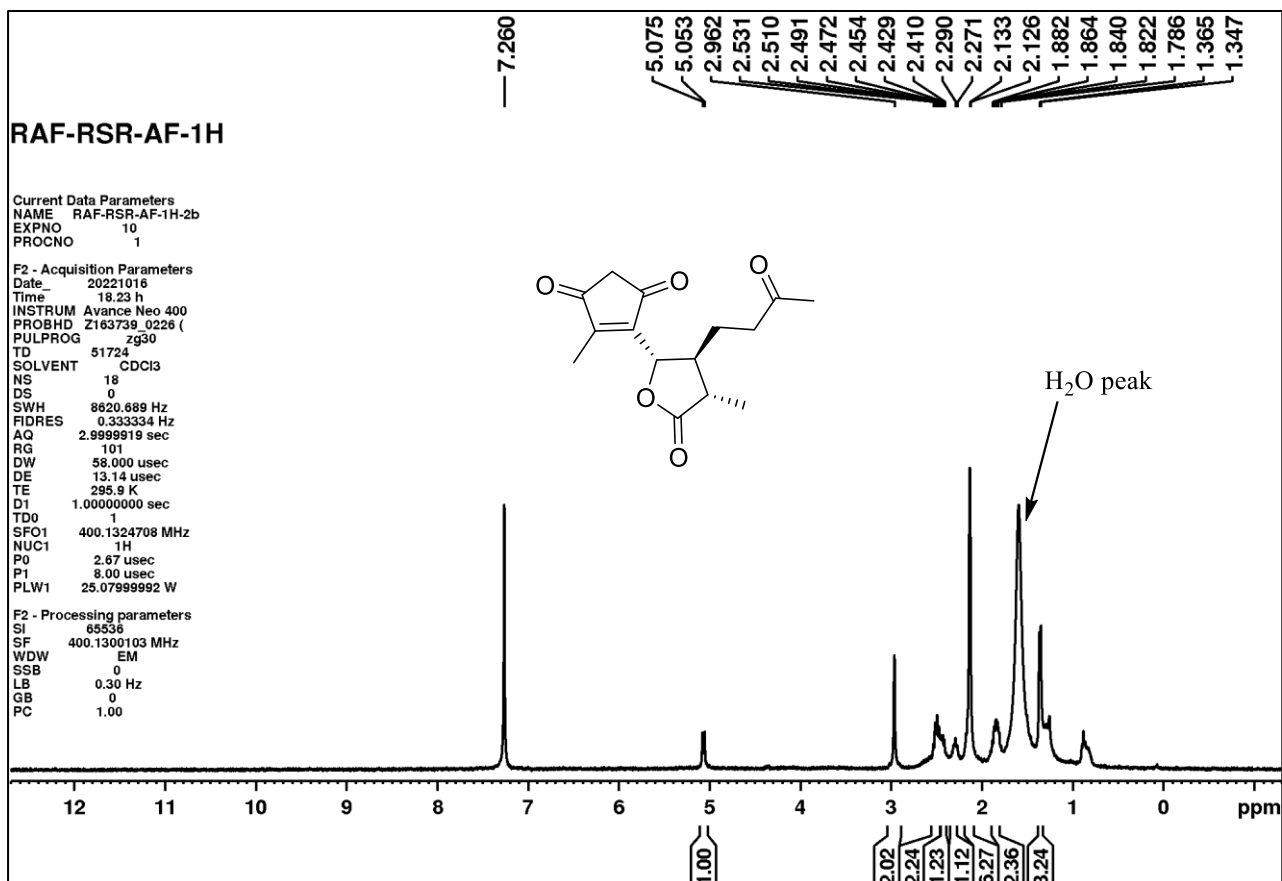
COSY (400 MHz, CDCl<sub>3</sub>) and NOESY (400 MHz, CDCl<sub>3</sub>) of compound *ent-18*



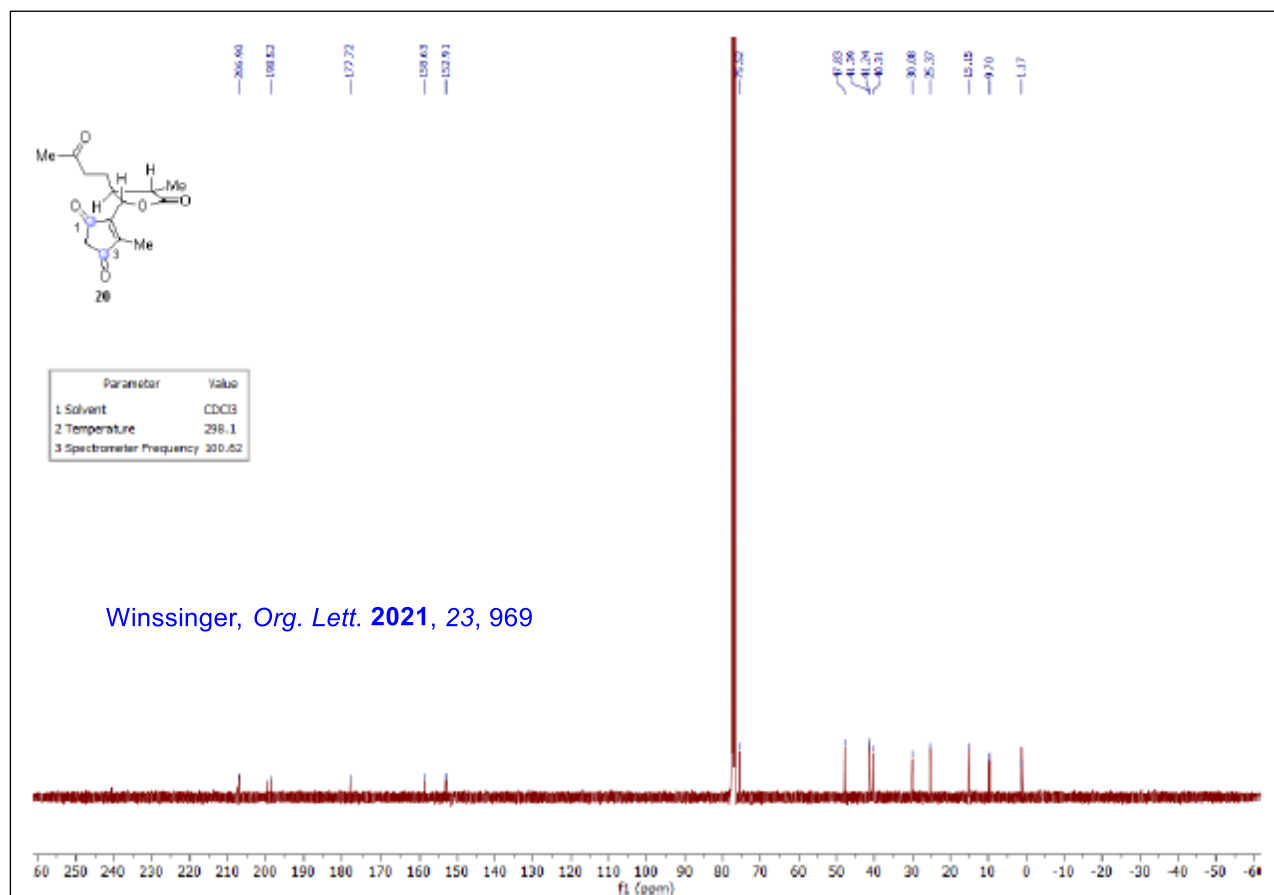
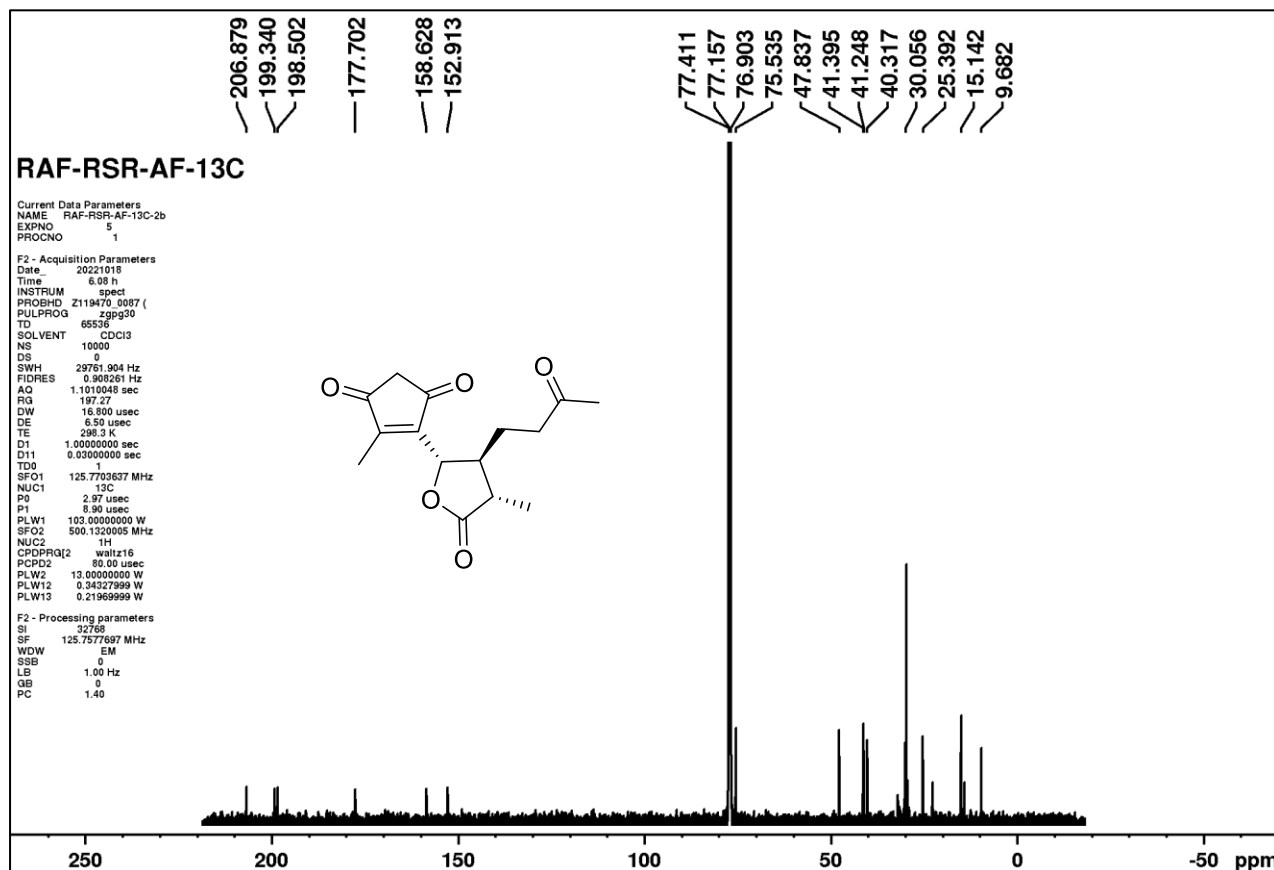
*ent*-**18**: HRMS (Q-TOF)  $m/z$ :  $[M + H]^+$  Calcd for  $C_{15}H_{21}O_4$  265.1435; Found 265.1430.



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) of compound **2b** and reported spectra of ( $\pm$ )-**2b**

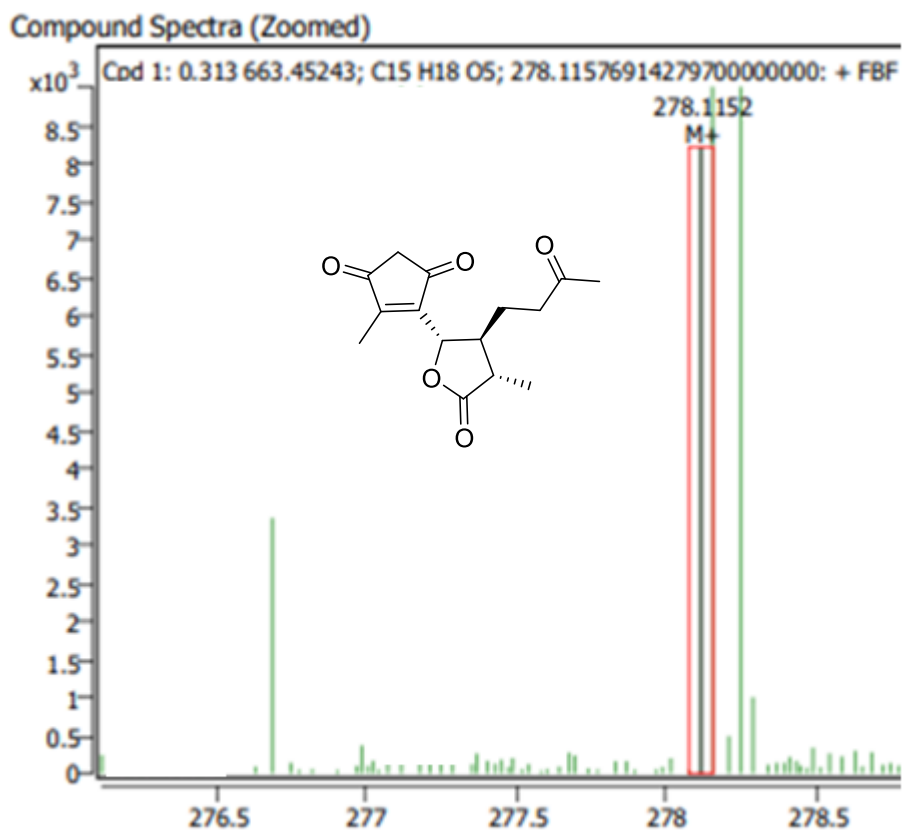


$^{13}\text{C}\{^1\text{H}\}$  NMR (125 MHz,  $\text{CDCl}_3$ ) of **2b** and reported spectra of ( $\pm$ )-**2b**

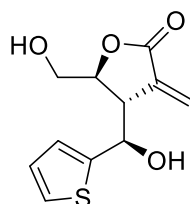
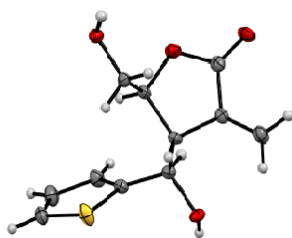


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**2b:** HRMS (Q-TOF)  $m/z$ :  $[M]^+$  Calcd for  $C_{15}H_{18}O_5$  278.1150; Found 278.1152.



## X-Ray Data of 7h



**Sample preparation:** A solution of compound **7h** (10 mg) in  $\text{CDCl}_3$  (0.5 mL) was placed in a vial (10 mL). The vial was closed with cap and kept at room temperature for 24 h. Then, colourless prisms were observed.

**Crystal measurement:** X-ray crystal structures were determined with a Bruker Single Crystal Kappa Apex II diffractometer. Thermal ellipsoids are drawn at 50% probability level.

**Table S1.** Crystallographic Information for Compound **7h**

<b>CCDC</b>	<b>2267170</b>
Empirical formula	$\text{C}_{11}\text{H}_{12}\text{O}_4\text{S}$
Formula weight	240.27
Temperature/K	150.00(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/&	8.5447(4)
b/&	10.2606(5)
c/&	12.5052(5)
n/°	90
§/°	90
y/°	90
Volume/& <sup>3</sup>	1096.38(9)
Z	4
Pcalc C	1.456
Jt <sup>1</sup>	0.290
F(000)	504.0
Crystal size/mm <sup>3</sup>	0.205 0.15 0.096
Radiation	MoK $\alpha$ (X = 0.71073)
2 $\theta$ - range for data collection/°	5.136 to 66.826
Index ranges	-12 $\bar{n}$ h $\bar{n}$ 13, -14 $\bar{n}$ k $\bar{n}$ 12, -19 $\bar{n}$ l $\bar{n}$ 14
Reflections collected	12004
Independent reflections	3579 [R <sub>int</sub> ' 0.05509 R <sub>sigma</sub> ' 0.0616]
Data/restraints/parameters	3579/0/147
Goodness-of-fit on F <sup>2</sup>	0.966
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>i</sub> 0.0405, wR <sub>2</sub> ' 0.0874
Final R indexes [all data]	R <sub>i</sub> ' 0.0552, wR <sub>2</sub> ' 0.0998

Largest diff. peak/hole / e Å <sup>-3</sup>	0.27/-0.33
Flack parameter	0.06(5)

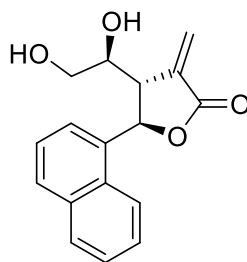
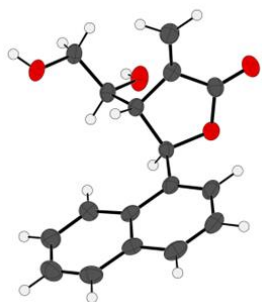
**Table S2.** Bond lengths for **7h**

Atom Atom	Length/Å	Atom Atom	Length/ Å
S1C8	1.727(2)	C3 C2	1.479(3)
S1C11	1.712(2)	C8 C9	1.368(3)
O3C6	1.432(3)	C4 C2	1.508(3)
O2C3	1.355(3)	C4 C5	1.539(3)
O2C5	1.462(2)	C2 C1	1.329(3)
O4C7	1.438(2)	C5 C6	1.512(3)
O1C3	1.209(3)	C9 C10	1.420(3)
C7C8	1.499(3)	C11 C10	1.354 (3)
C7C4	1.542(3)		

**Table S3.** Bond Angles for **7h**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C11	S1	C8	92.35(11)	C2	C4	C5	102.15(17)
C3	O2	C5	110.66(16)	C5	C4	C7	112.49(17)
O4	C7	C8	111.97(17)	C3	C2	C4	107.35(18)
O4	C7	C4	106.33(16)	C1	C2	C3	122.0(2)
C8	C7	C4	113.28(16)	C1	C2	C4	130.7(2)
O2	C3	C2	109.66(18)	O2	C5	C4	106.31(15)
O1	C3	O2	121.1(2)	O2	C5	C6	109.92(17)
O1	C3	C2	129.2(2)	C6	C5	C4	112.06(17)
C7	C8	S1	122.21(16)	O3	C6	C5	109.07(17)
C9	C8	S1	110.38(16)	C8	C9	C10	112.9(2)
C9	C8	C7	127.40(19)	C10	C11	S1	111.41(17)
C2	C4	C7	111.12(16)	C11	C10	C9	113.0(2)

## X-Ray Data of 8a



**Sample preparation:** A solution of compound **8a** (10 mg) in  $\text{CDCl}_3$  (0.5 mL) was placed in a vial (10 mL). The vial was closed with cap and kept at room temperature for 24 h. Then, colourless prisms were observed.

**Crystal measurement:** X-ray crystal structures were determined with a Bruker Single Crystal Kappa Apex II diffractometer. Thermal ellipsoids are drawn at 50% probability level.

**Table S4.** Crystallographic Information for Compound **8a**

<b>CCDC</b>	<b>2270886</b>
Empirical formula	$\text{C}_{17}\text{H}_{16}\text{O}_4$
Formula weight	284.30
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	5.1299(4)
b/Å	14.7848(10)
c/Å	9.1241(6)
$\alpha/^\circ$	90
$\beta/^\circ$	90.366(7)
$\gamma/^\circ$	90
Volume/Å <sup>3</sup>	692.00(8)
Z	2
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.364
$\mu/\text{mm}^{-1}$	0.097
F(000)	300.0
Crystal size/mm <sup>3</sup>	0.16 × 0.15 × 0.11
Radiation	$\text{MoK}\alpha$ ( $\lambda = 0.71073$ )
2 $\theta$ range for data collection/ $^\circ$	5.246 to 49.978
Index ranges	$-6 \leq h \leq 6, -17 \leq k \leq 17, -10 \leq l \leq 10$
Reflections collected	7550
Independent reflections	2381 [ $R_{\text{int}} = 0.0684, R_{\text{sigma}} = 0.0611$ ]
Data/restraints/parameters	2381/1/192
Goodness-of-fit on $F^2$	1.054
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0436, wR_2 = 0.1038$
Final R indexes [all data]	$R_1 = 0.0482, wR_2 = 0.1073$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.21/-0.17
Flack parameter	0.6(10)



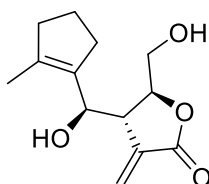
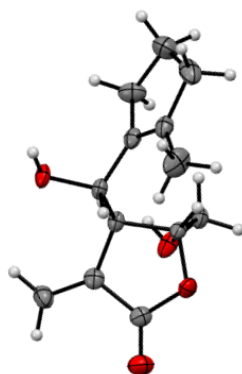
**Table S5.** Bond lengths for **8a**

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O001	C00A	1.433(4)	C009	C00B	1.553(5)
O002	C008	1.341(4)	C009	C00H	1.493(5)
O002	C00B	1.462(4)	C00C	C00G	1.432(5)
O003	C005	1.429(4)	C00C	C00I	1.417(6)
O004	C008	1.216(4)	C00C	C00L	1.420(6)
C005	C009	1.531(5)	C00D	C00H	1.326(5)
C005	C00A	1.522(5)	C00E	C00F	1.376(5)
C006	C007	1.365(5)	C00E	C00K	1.412(6)
C006	C00B	1.514(5)	C00F	C00G	1.415(5)
C006	C00G	1.435(5)	C00I	C00K	1.353(6)
C007	C00J	1.422(5)	C00J	C00L	1.352(6)
C008	C00H	1.481(5)			

**Table S6.** Bond Angles for **8a**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C008	O002	C00B	110.8(3)	C006	C00B	C009	113.4(3)
O003	C005	C009	106.1(3)	C00I	C00C	C00G	119.0(4)
O003	C005	C00A	109.3(3)	C00I	C00C	C00L	122.0(4)
C00A	C005	C009	114.5(3)	C00L	C00C	C00G	119.0(4)
C007	C006	C00B	122.2(3)	C00F	C00E	C00K	120.3(4)
C007	C006	C00G	119.5(3)	C00E	C00F	C00G	121.3(3)
C00G	C006	C00B	118.2(3)	C00C	C00G	C006	119.1(3)
C006	C007	C00J	121.0(4)	C00F	C00G	C006	123.0(3)
O002	C008	C00H	109.7(3)	C00F	C00G	C00C	117.9(3)
O004	C008	O002	120.5(3)	C008	C00H	C009	107.0(3)
O004	C008	C00H	129.8(3)	C00D	C00H	C008	122.6(3)
C005	C009	C00B	111.2(3)	C00D	C00H	C009	130.3(3)
C00H	C009	C005	111.9(3)	C00K	C00I	C00C	121.6(4)
C00H	C009	C00B	101.5(3)	C00L	C00J	C007	120.8(4)
O001	C00A	C005	109.0(3)	C00I	C00K	C00E	119.9(4)
O002	C00B	C006	110.3(3)	C00J	C00L	C00C	120.6(4)
O002	C00B	C009	105.5(2)				

## X-Ray Data of 12



**Sample preparation:** A solution of compound **12** (20 mg) in the mixture of petroleum ether and CH<sub>2</sub>Cl<sub>2</sub> (5:1) was placed in a vial (10 mL). The vial was closed with cap and kept at room temperature for 24 h. Then, colourless prisms were observed.

**Crystal measurement:** X-ray crystal structures were determined with a Bruker Single Crystal Kappa Apex II diffractometer. Thermal ellipsoids are drawn at 50% probability level.

**Table S7.** Crystallographic Information for Compound **12**

<b>CCDC</b>	<b>2235974</b>
Empirical formula	C <sub>13</sub> H <sub>18</sub> O <sub>4</sub>
Formula weight	238.285
Temperature/K	150.15
Crystal system	monoclinic
Space group	P2 <sub>1</sub>
a/&	7.5355(3)
b/&	7.5626(2)
c/&	11.2958(3)
n/°	90
§/°	103.257(3)
y/°	90
Volume/& <sup>3</sup>	626.57(4)
Z	2
Pcalc <sup>c</sup>	1.263
Jt <sup>1</sup>	0.093
F(000)	256.2
Crystal size/mm <sup>3</sup>	0.2 • 0.106 0.089
Radiation	Mo Ko (Z = 0.71073)
2θ- range for data collection/°	3.7 to 49.98
Index ranges	-11 ñ h ñ 10, -12 S k ñ 11, -18 ñ l ñ 17
Reflections collected	17844
Independent reflections	2191 [R <sub>int</sub> ' 0•14879 R <sub>sigma</sub> ' 0•0978]
Data/restraints/parameters	2191/1/157
Goodness-of-fit on F <sup>2</sup>	1.048
Final R indexes [I >= 2σ(I)]	R <sub>i</sub> 0.0493, wR <sub>2</sub> ' 0.1294
Final R indexes [all data]	R <sub>i</sub> ' 0.0525, wR <sub>2</sub> ' 0.1341

Largest diff. peak/hole / e Å <sup>-3</sup>	0.21/-0.23
Flack parameter	0.3(9)

**Table S8.** Bond lengths for **12**

Atom Atom	Length/Å	Atom Atom	Length/Å
O001 COOC	1.434(3)	C007 C009	1.321(3)
O002C00D	1.447(3)	C008 C00D	1.539(3)
O003C005	1.451(3)	COOACO0B	1.336(3)
O003 C006	1.347(3)	COOACO0D	1.493(3)
O004C006	1.203(3)	COOACO0E	1.5064)
C001C008	1.544(3)	CO0BCO0F	1.4974)
C005 COOC	1.504(3)	CO0BCO0G	1.5004)
C006 C007	1.487(3)	CO0ECO0H	1.5254)
C007 C008	1.498(3)	CO0GCO0H	1.5235)

**Table S9.** Bond Angles for **12**

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C006	O003	C005	111.52 (17)	C00D	C00A	C00B	126.8 (2)
C008	C005	O003	106.25 (17)	C00E	C00A	C00B	111.9 (2)
C00C	C005	O003	108.97 (18)	C00E	C00A	C00D	121.3 (2)
C00C	C005	C008	113.35 (17)	C00F	C00B	C00A	127.9 (2)
O004	C006	C003	121.5 (2)	C00G	C00B	C00A	111.7 (2)
C007	C006	C003	109.5 (2)	C00G	C00B	C00F	120.4 (2)
C007	C006	C004	129.0 (2)	C005	C00C	C001	111.11 (18)
C008	C007	C006	107.58 (19)	C008	C00D	C002	104.85 (15)
C009	C007	C006	121.4 (2)	C00A	C00D	C002	111.11 (18)
C009	C007	C008	131.0 (2)	C00A	C00D	C008	114.01 (19)
C007	C008	C005	103.00 (18)	C00H	C00E	C00A	104.1 (2)
C00D	C008	C005	113.67 (17)	C00H	C00G	C00B	104.6 (2)
C00D	C008	C007	113.14 (18)	C00G	C00H	C00E	107.1 (2)