

Supporting Information

Stereoselective Convergent Total Synthesis of Oxylipins

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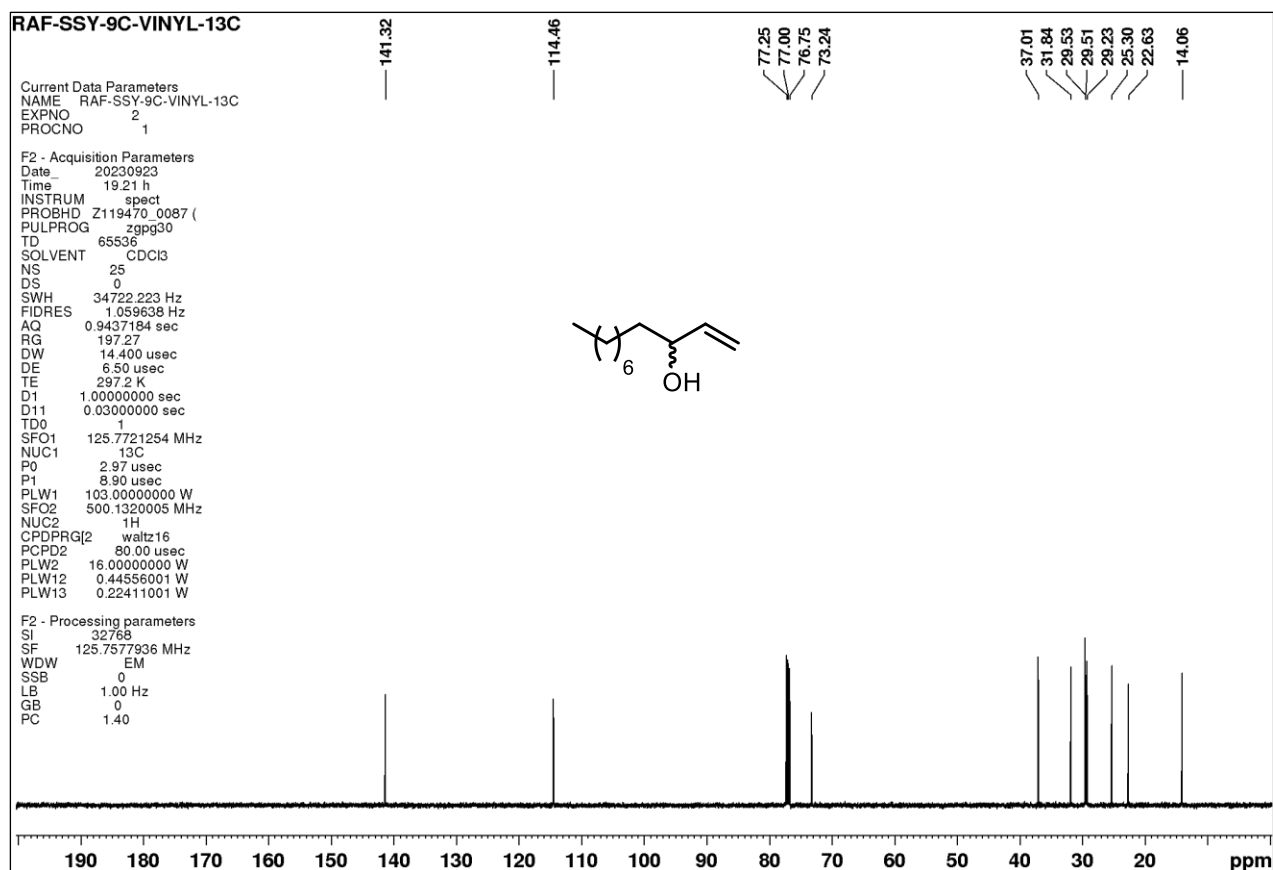
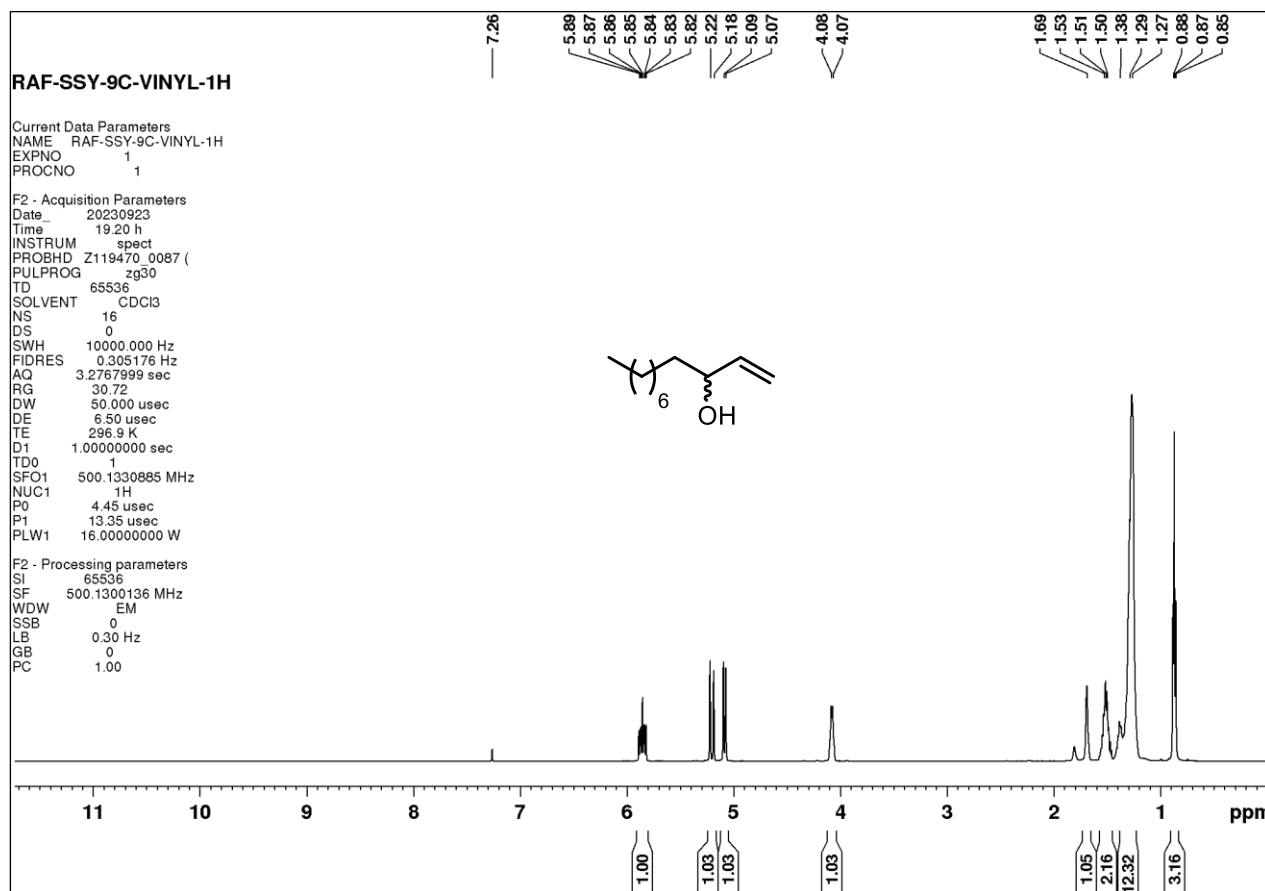
Maharashtra, India

Email: rfernand@chem.iitb.ac.in

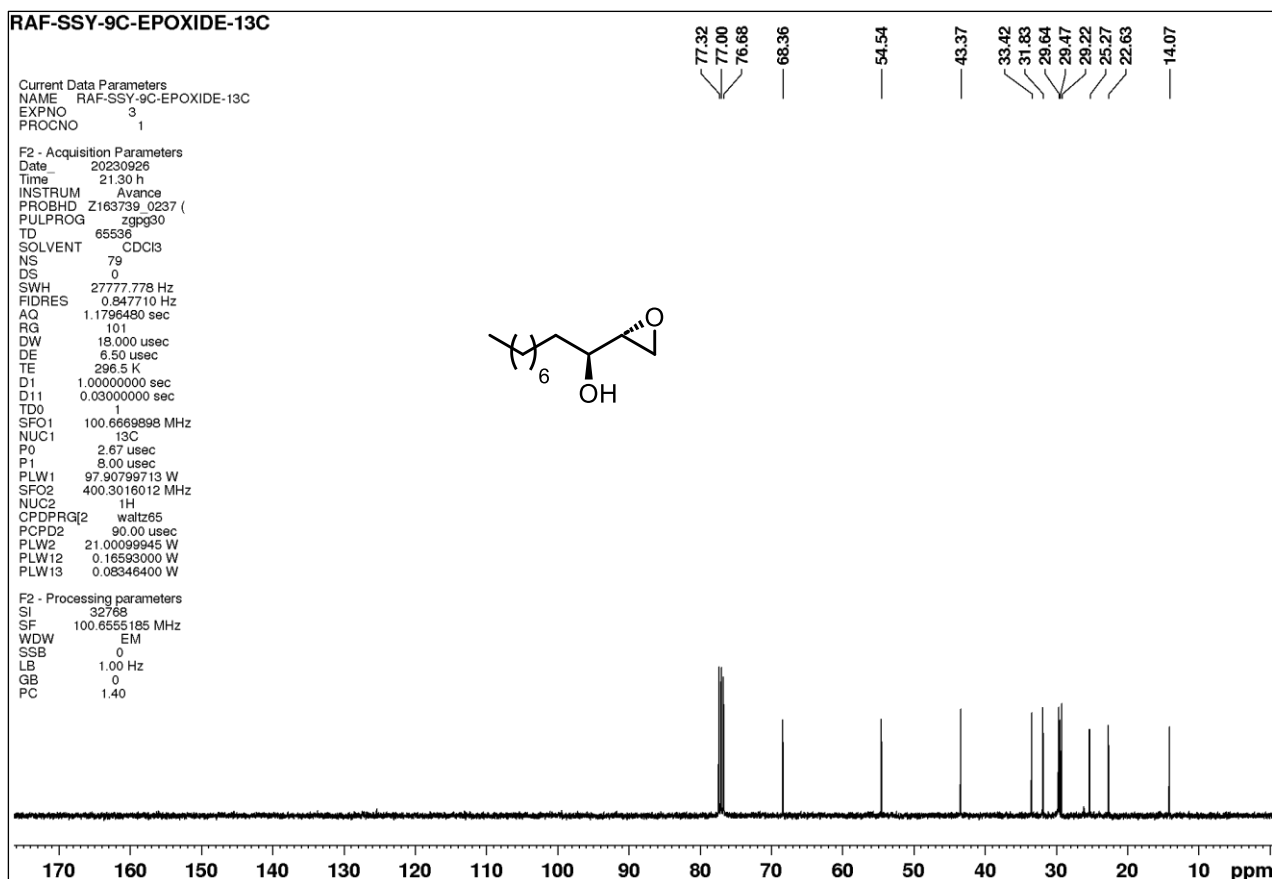
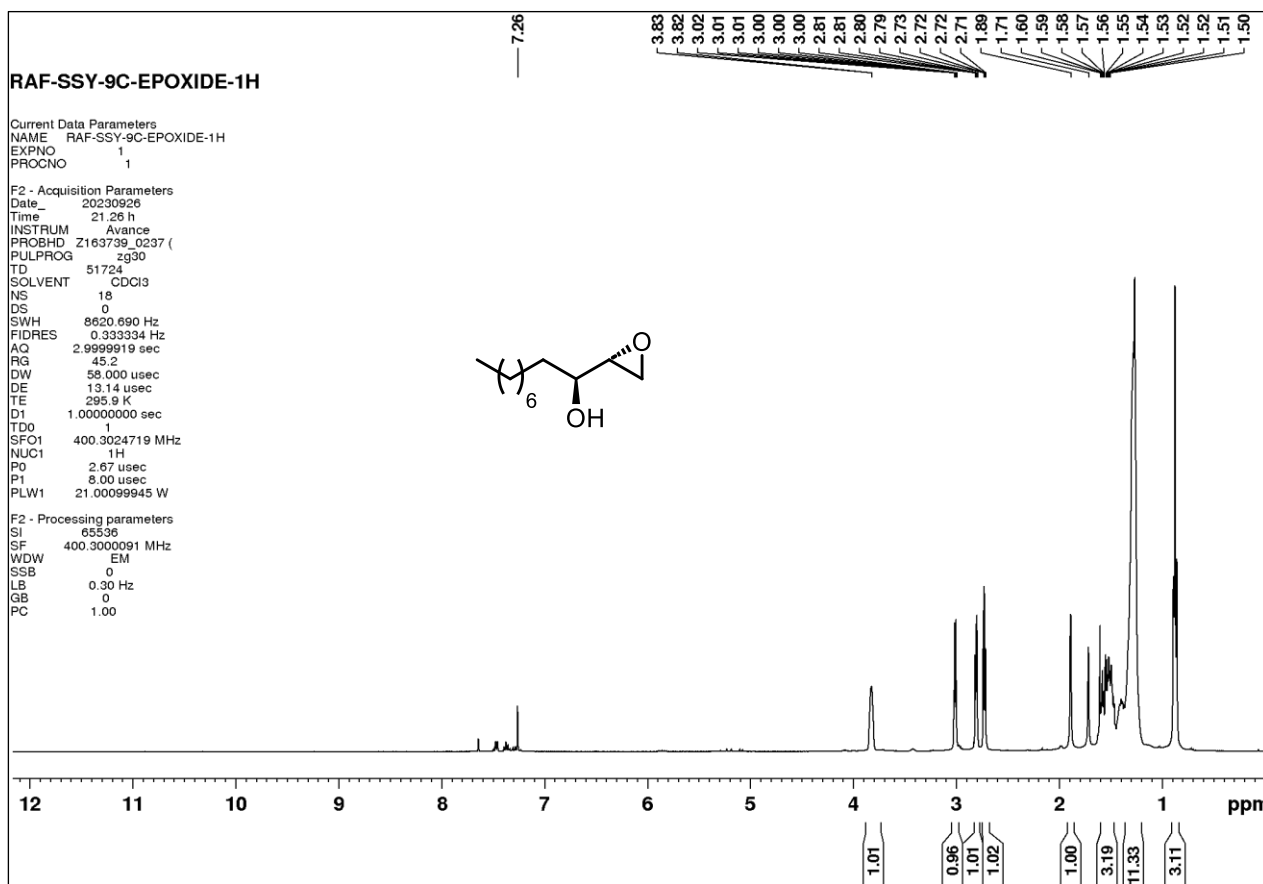
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¹H, ¹³C NMR and HRMS spectral of all compounds S2–S50

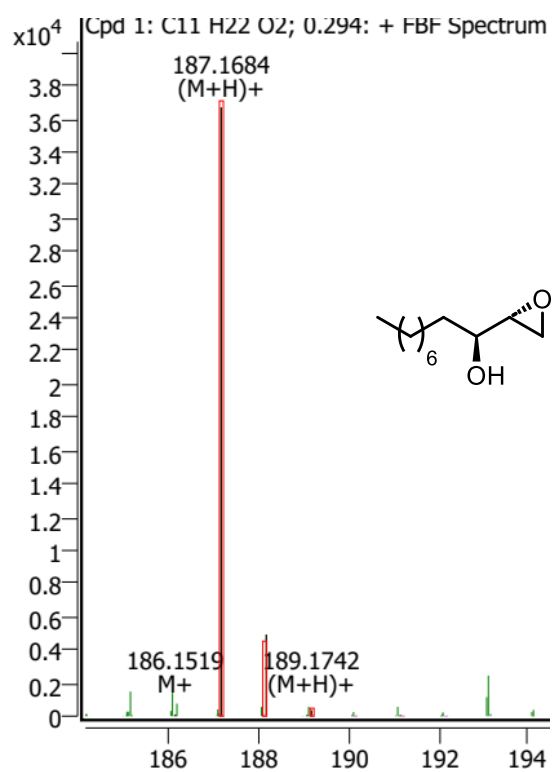
^1H NMR (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of compound **3**



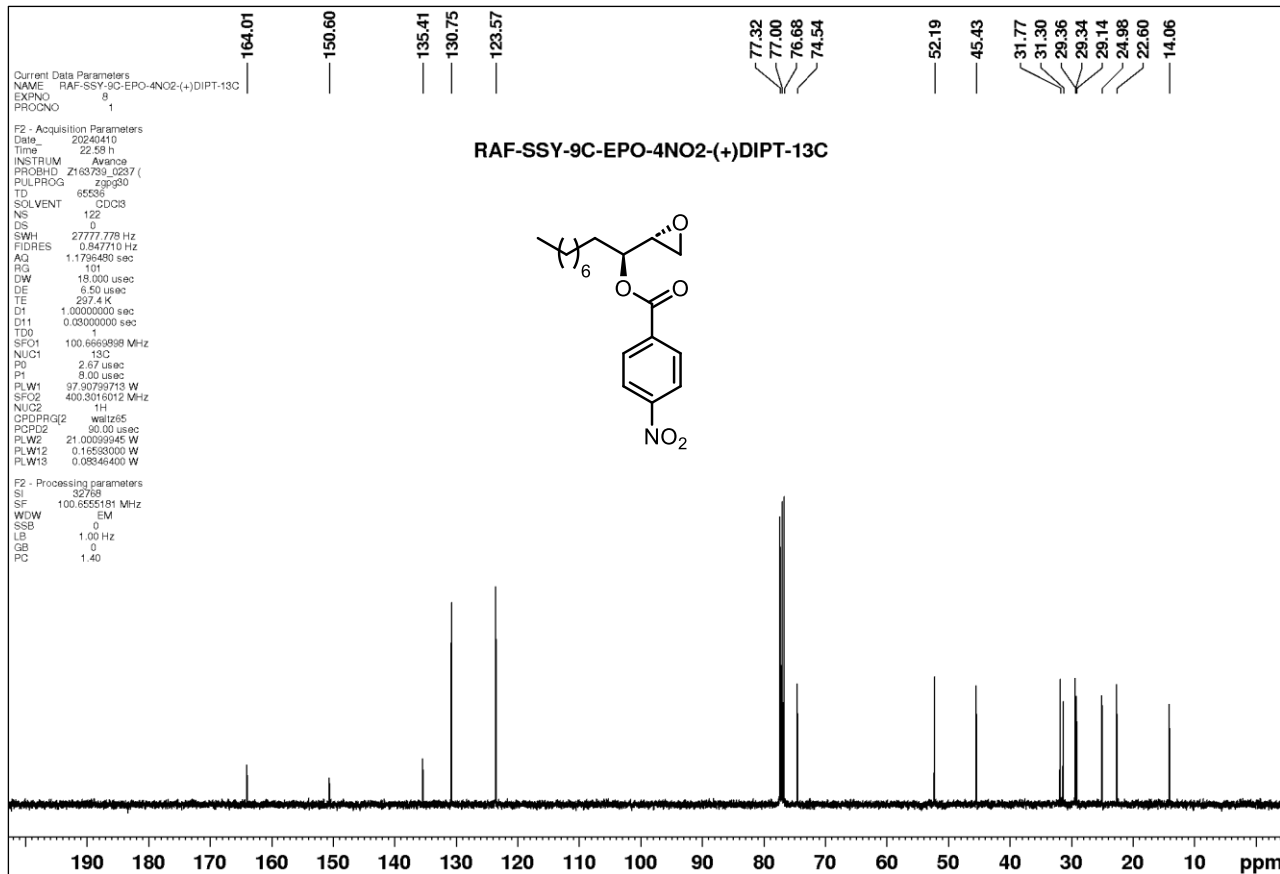
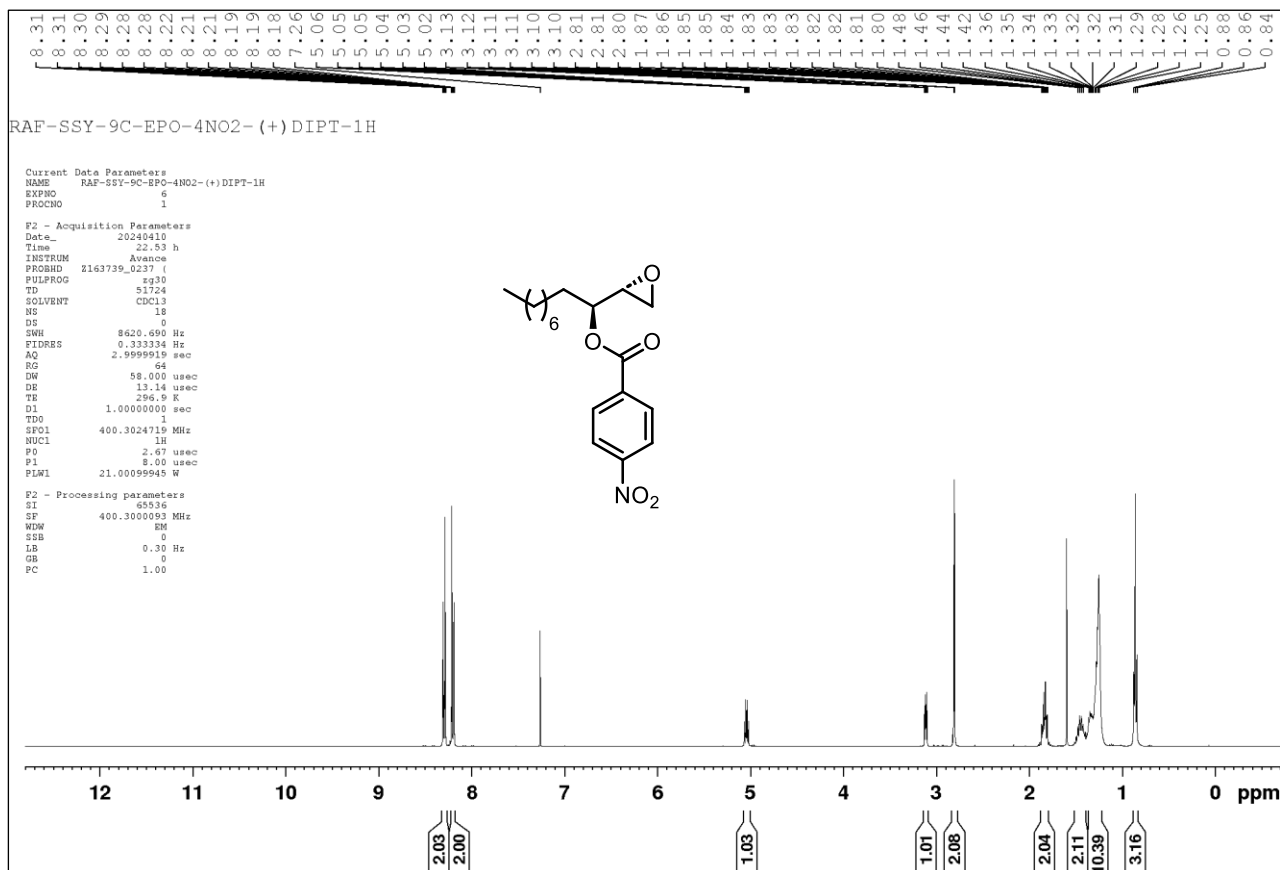
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound **10**



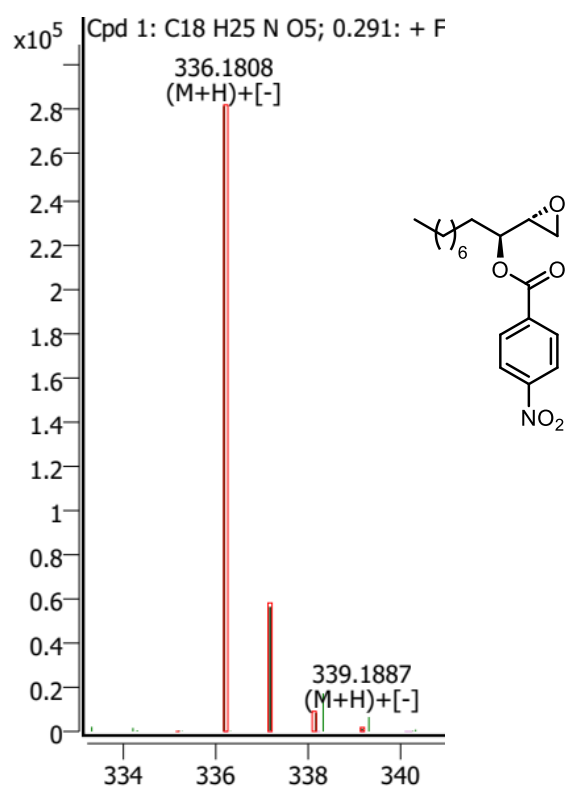
10: HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{11}H_{23}O_2$ 187.1693; Found 187.1684



¹H NMR (400 MHz, CDCl₃) and ¹³C{¹H} NMR (100 MHz, CDCl₃) of compound **10'**

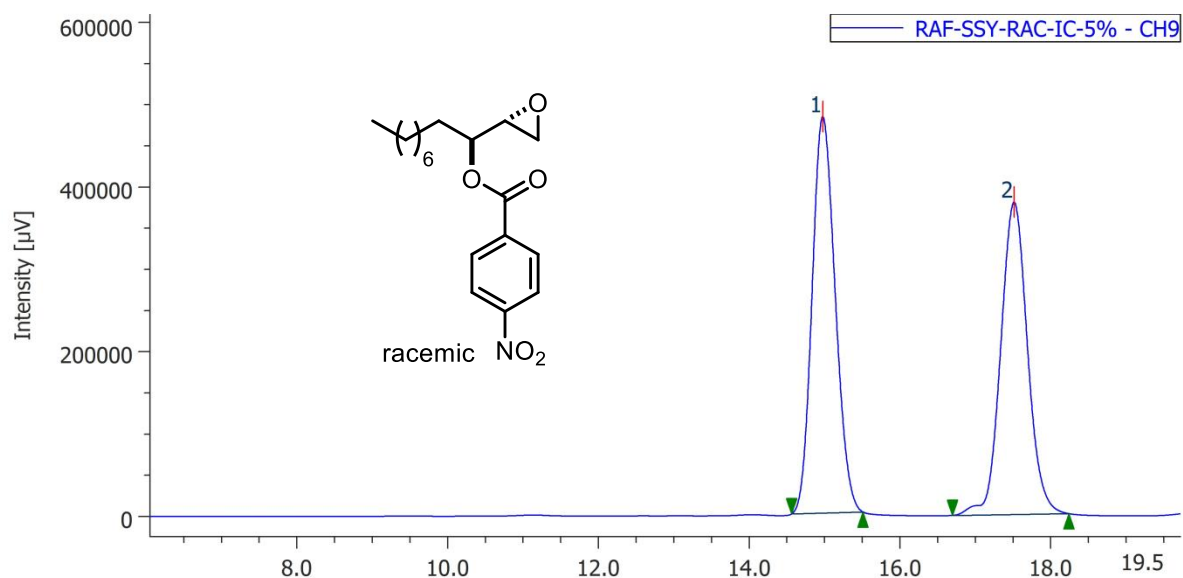


10': HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{18}H_{26}NO_5$ 336.1806; Found 336.1808.

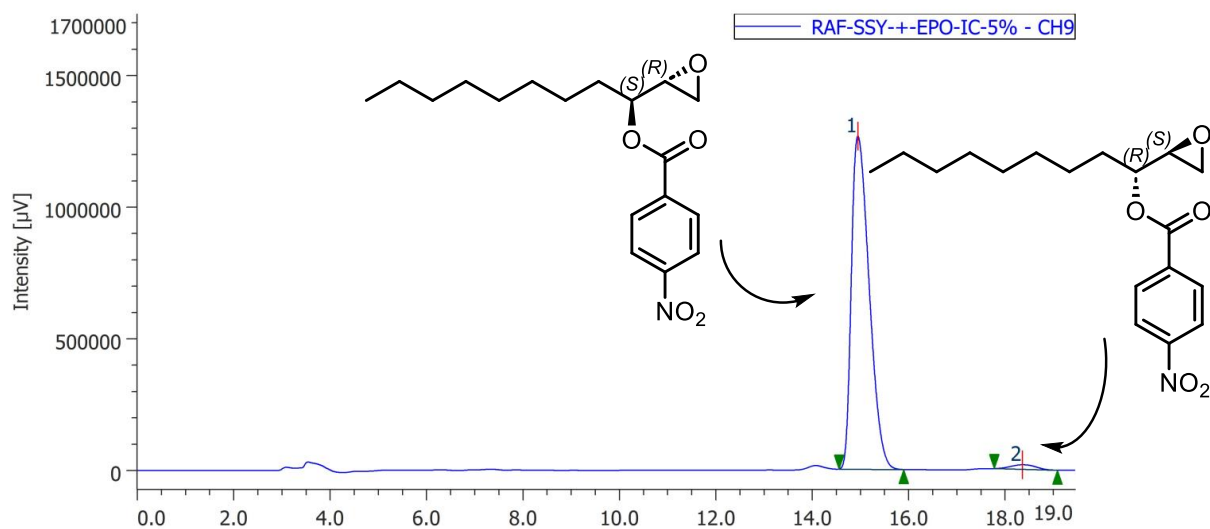


HPLC chromatograms of racemic and chiral **10'** (96% *ee*)

Note: The racemic (bonds shown are relative) required was prepared by manual mixing of the two enantiomers prepared separately. Hence the ratio may not be exactly 50:50.

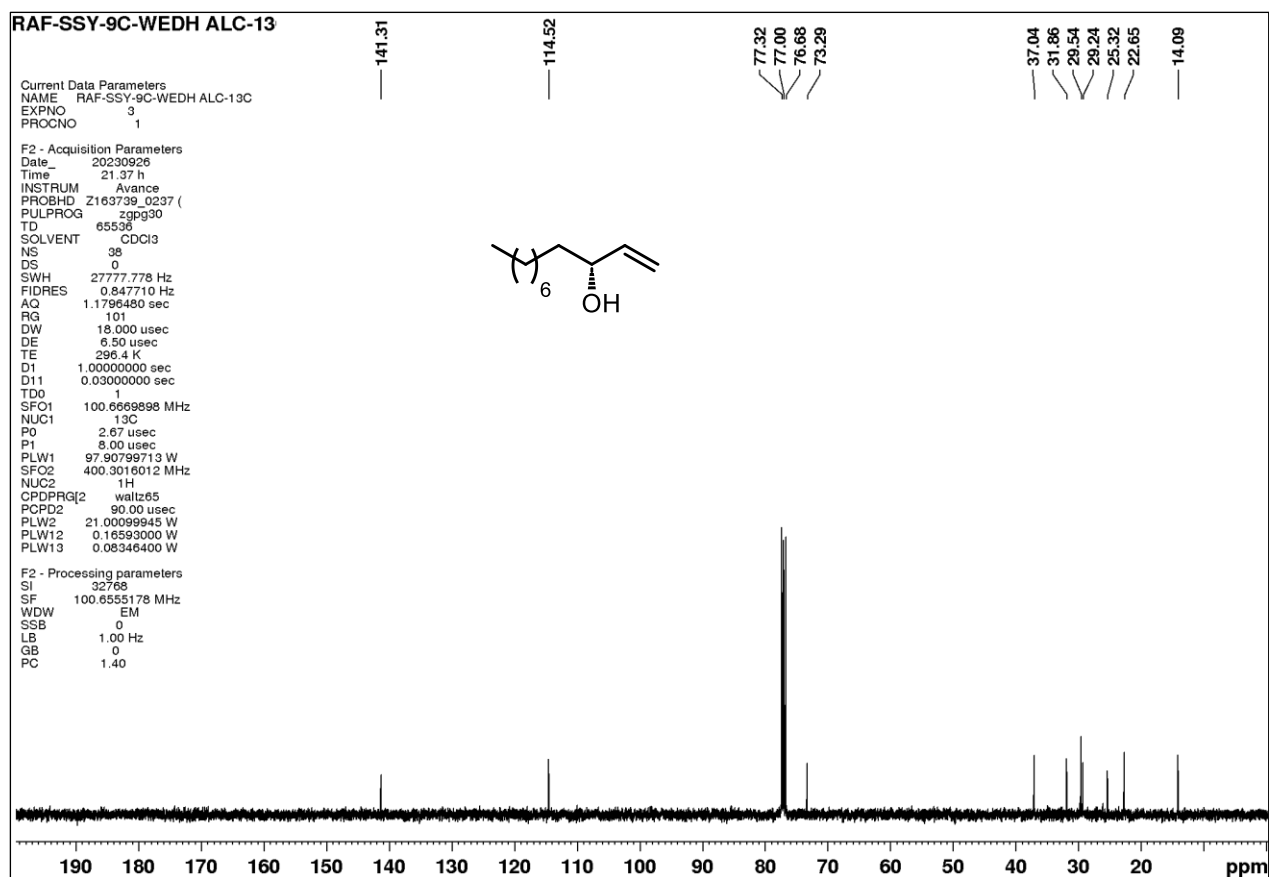
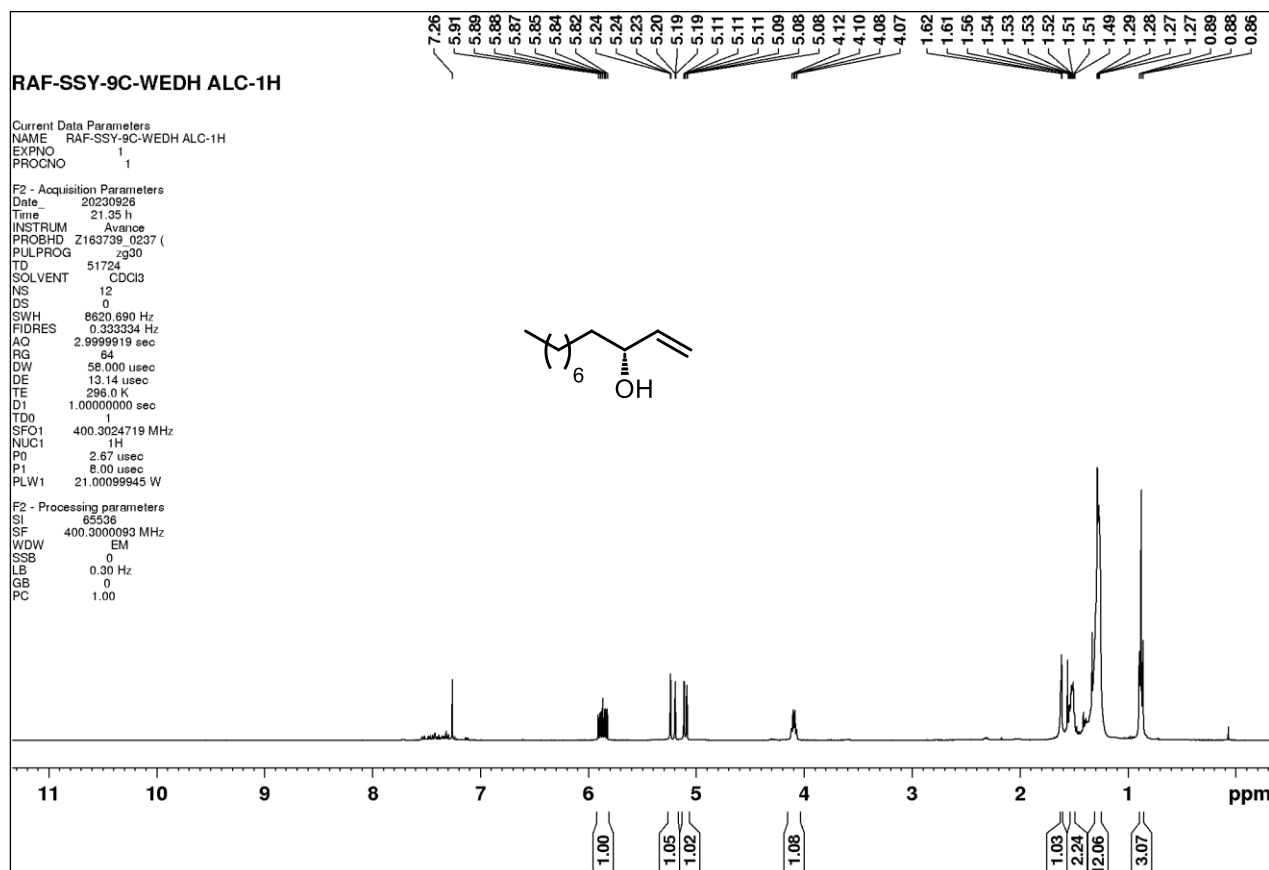


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1	Unknown	9	14.973	10228431	481157	52.192	55.925	N/A	11197	4.226	1.137	
2	Unknown	9	17.510	9369104	379205	47.808	44.075	N/A	12068	N/A	1.077	
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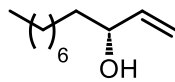
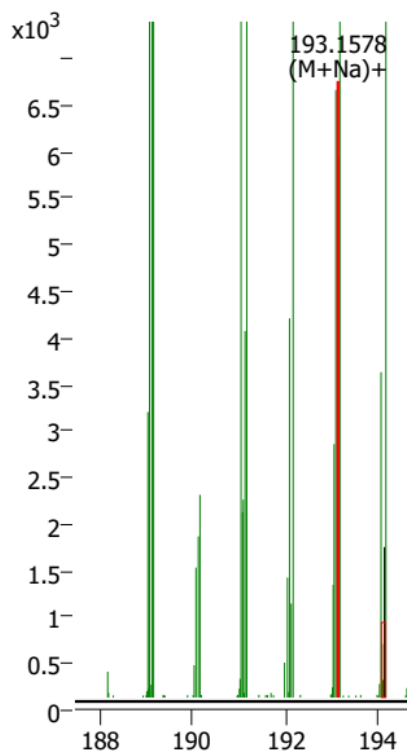


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	14.940	32375922	1264661	98.104	98.650	N/A	7619	4.058	1.540	
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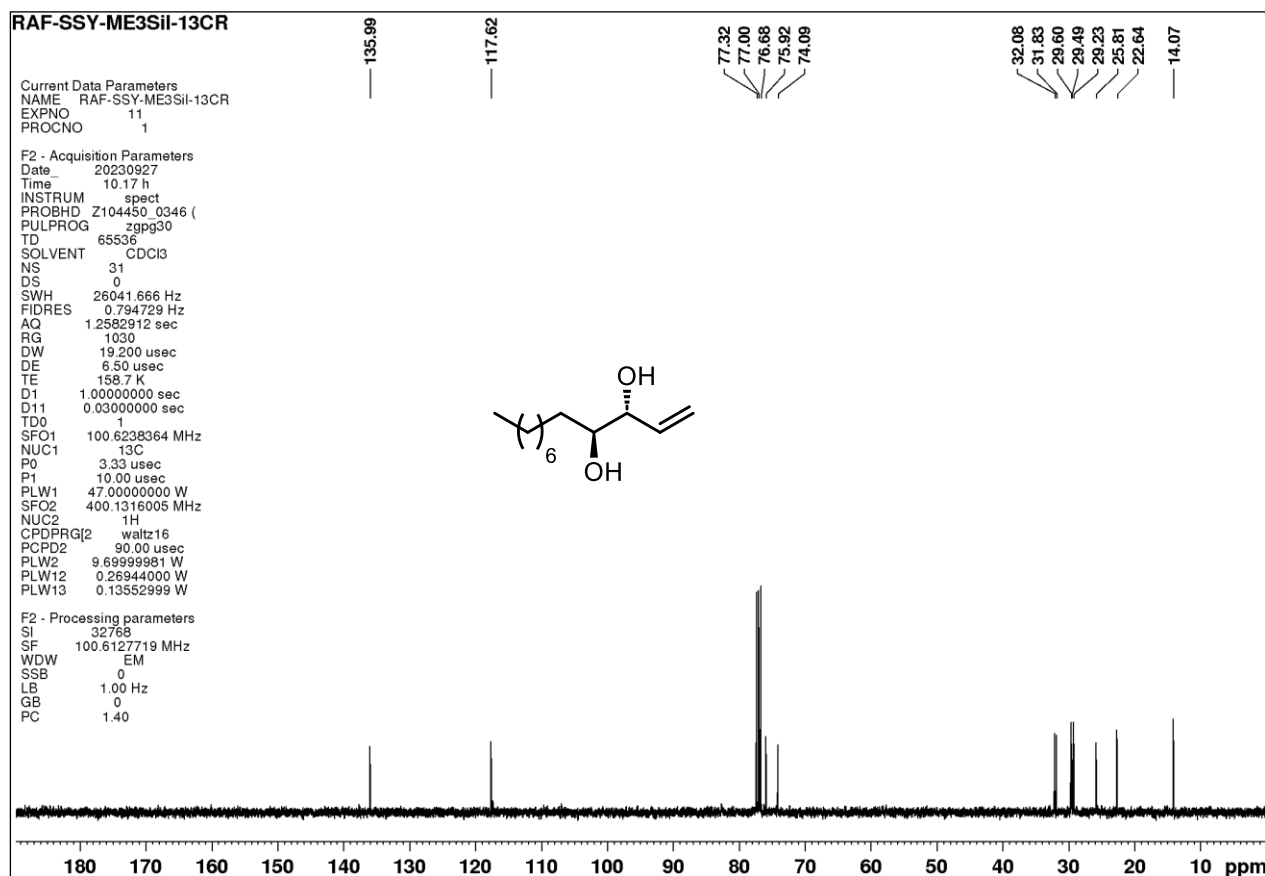
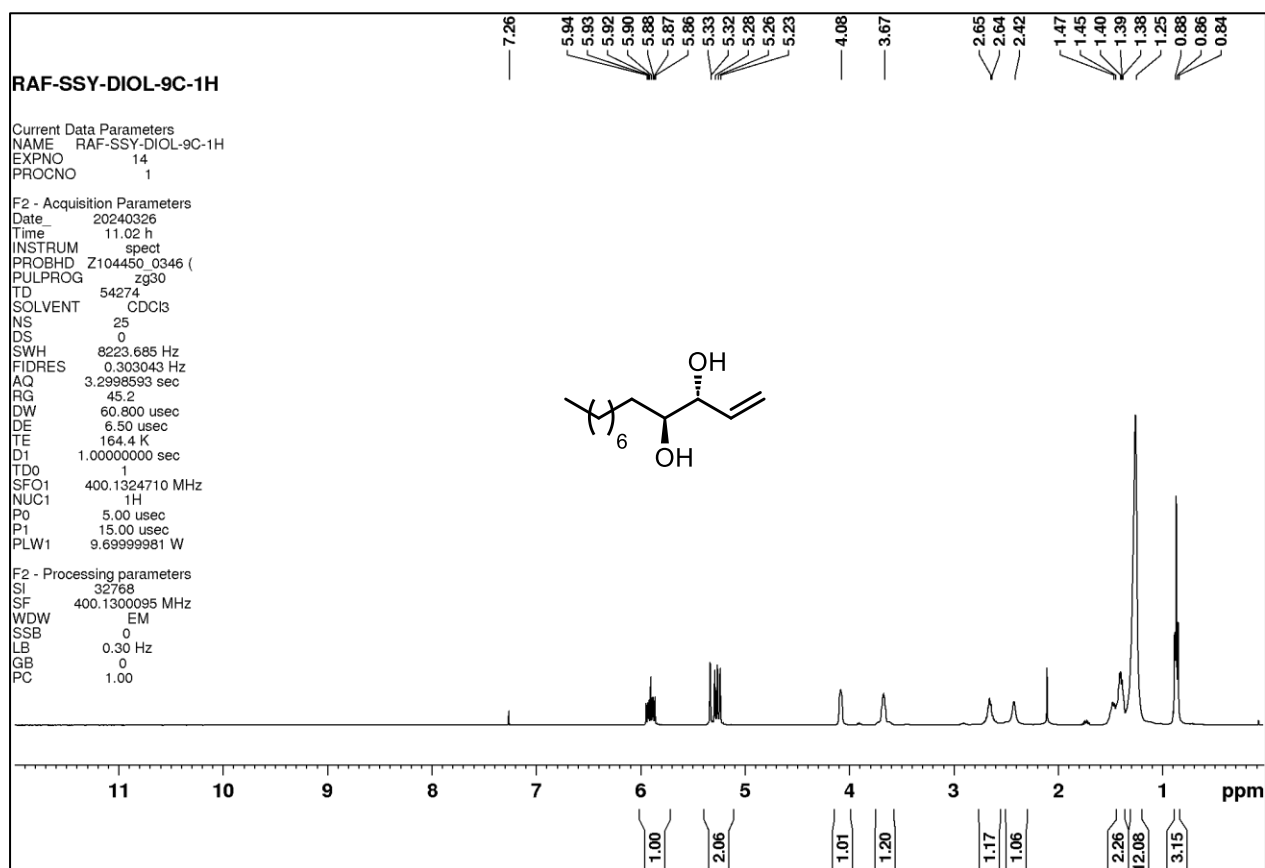
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound **9**



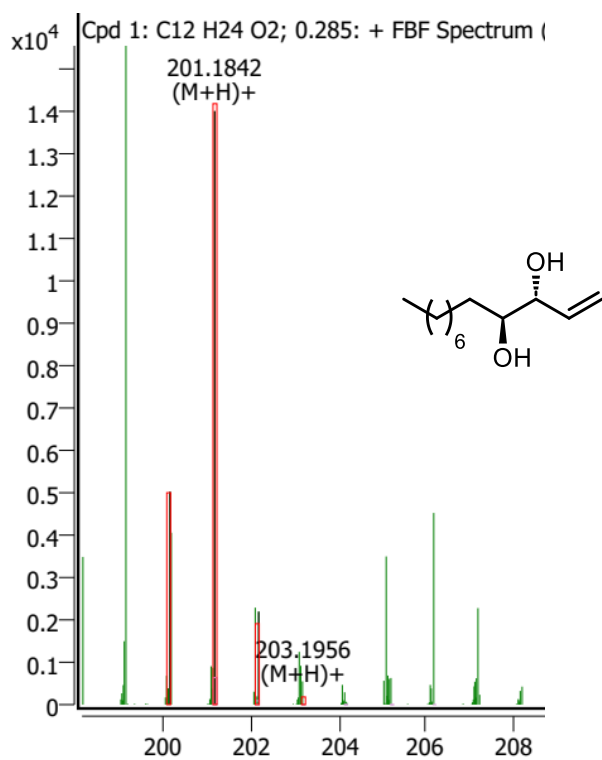
9: HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{11}H_{22}ONa$ 193.1564; Found 193.1578



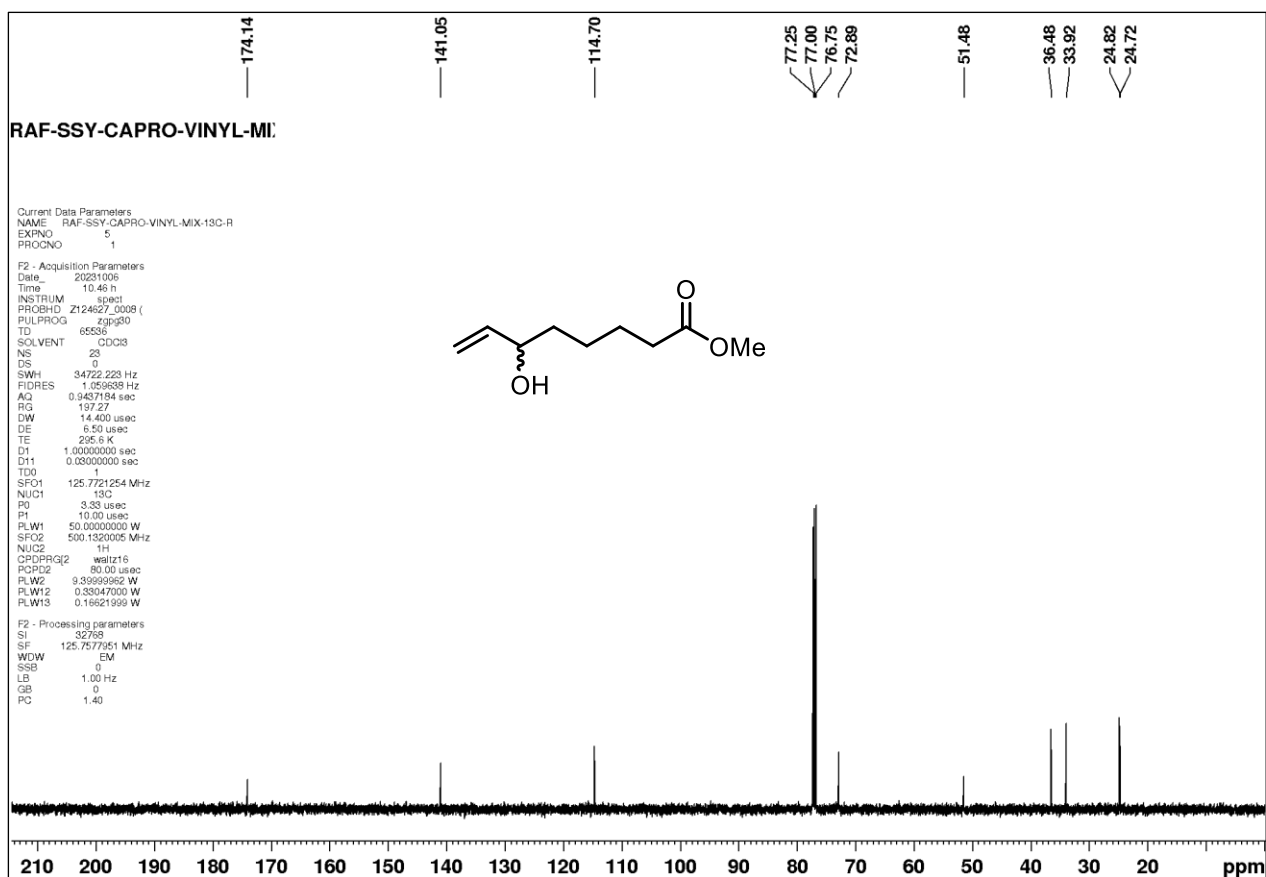
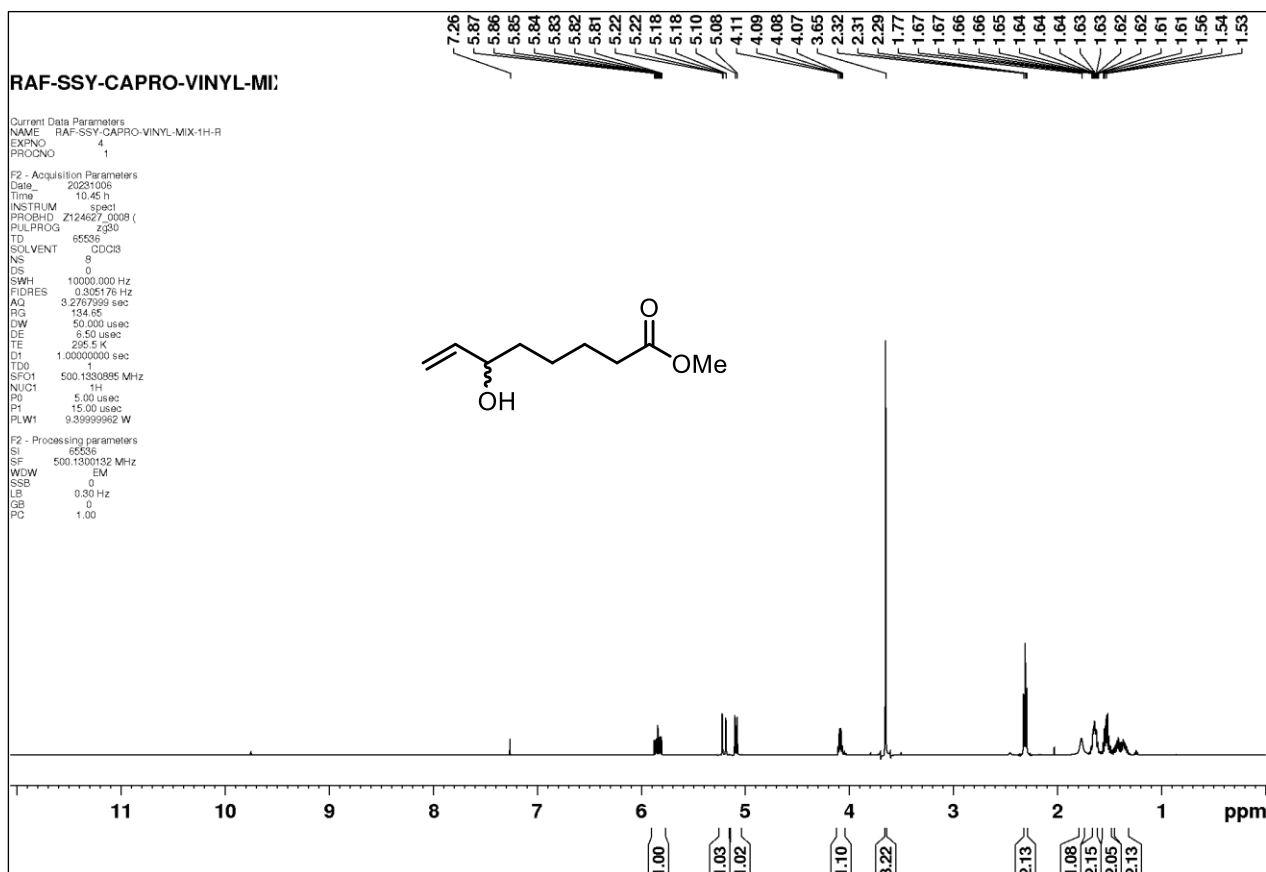
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound **2**



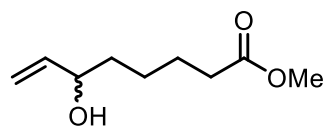
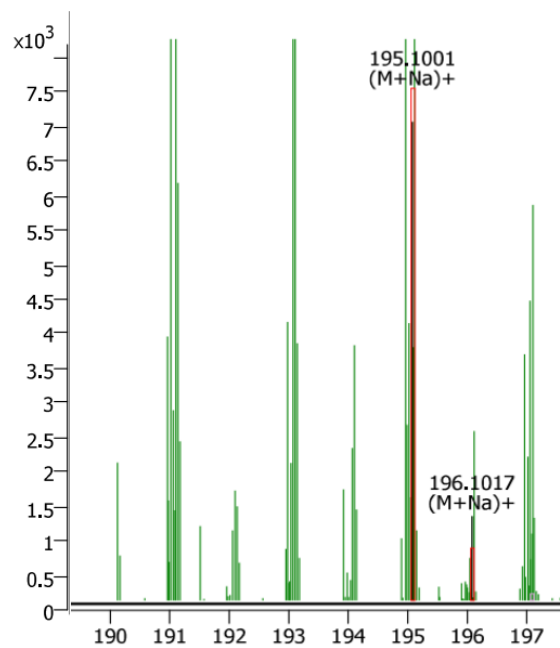
2: HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_{12}H_{25}O_2$ 201.1849; Found 201.1842



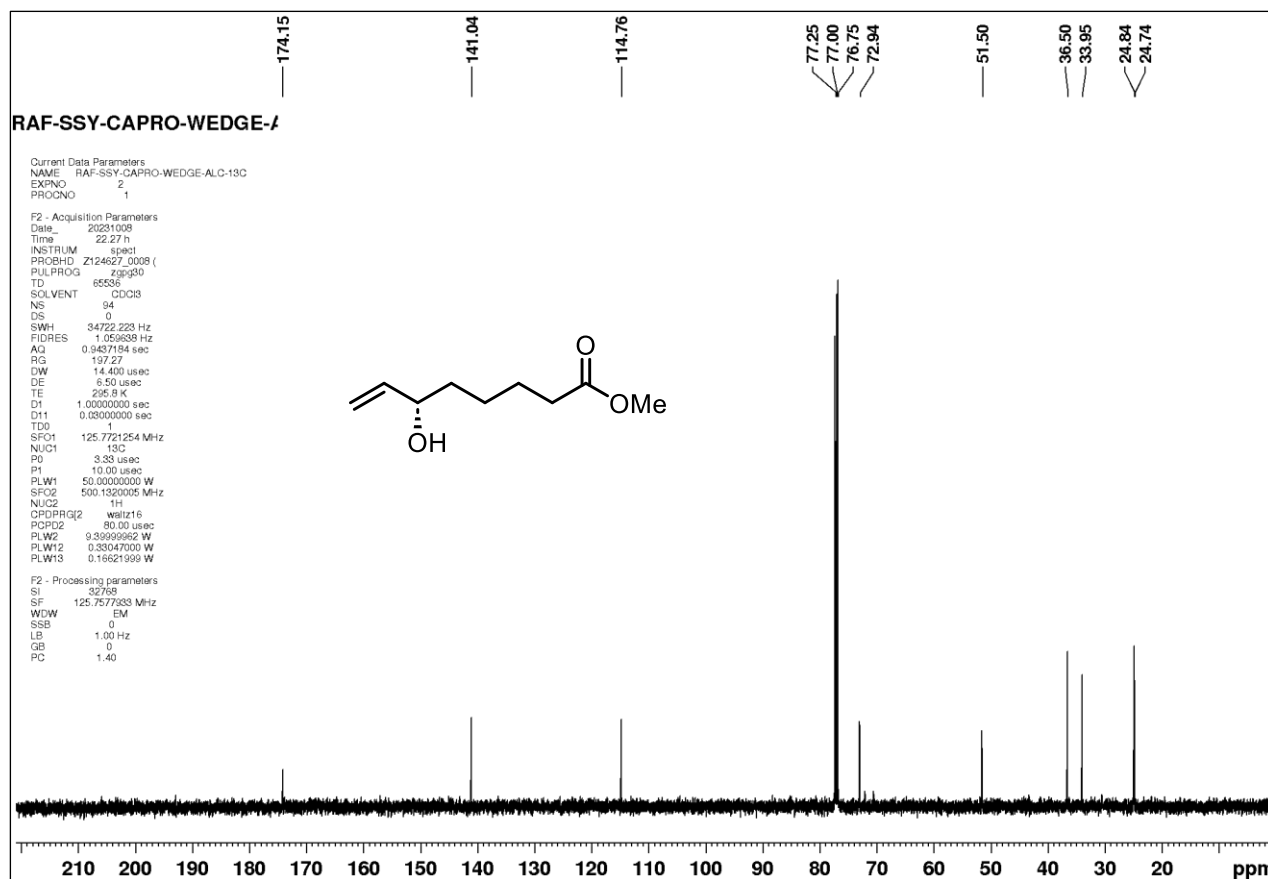
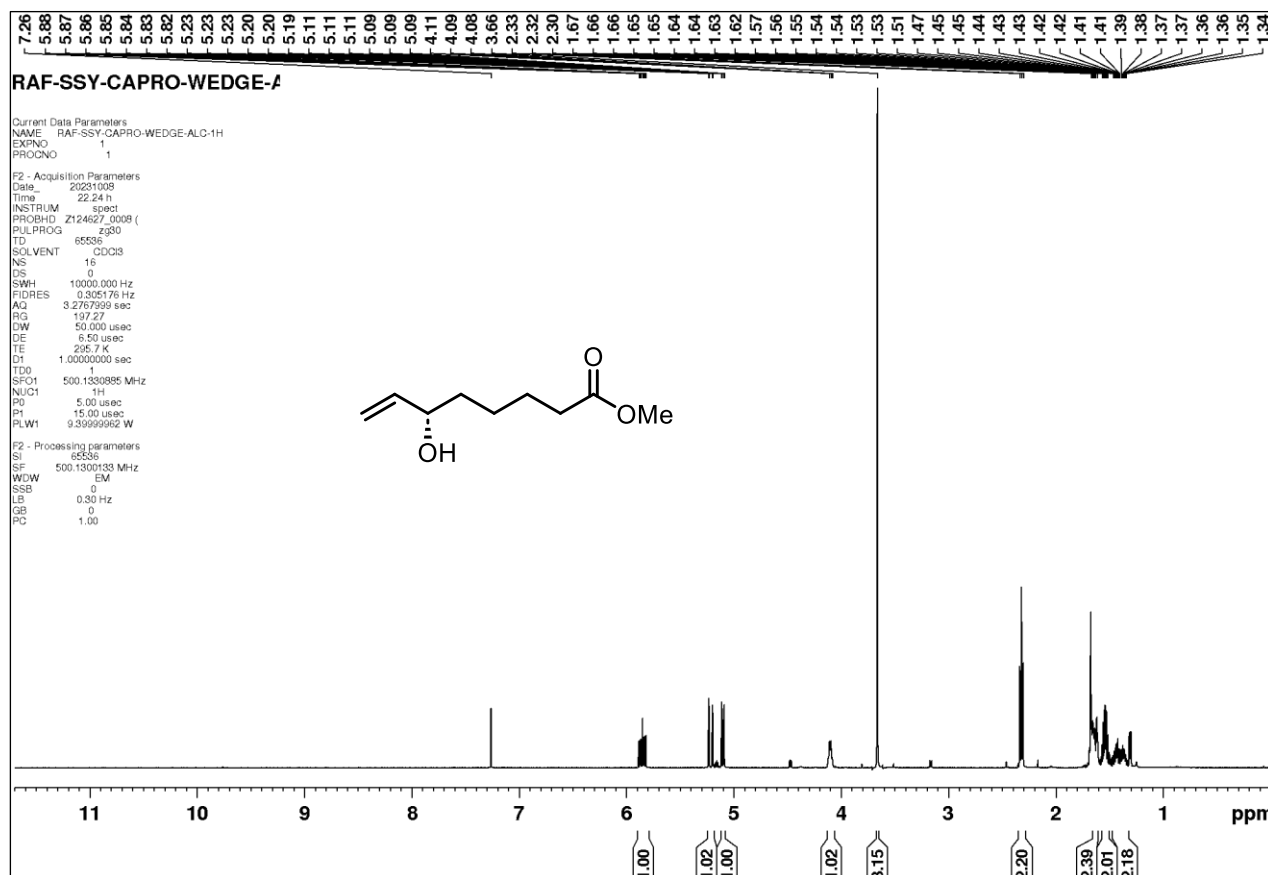
^1H NMR (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of compound **11**



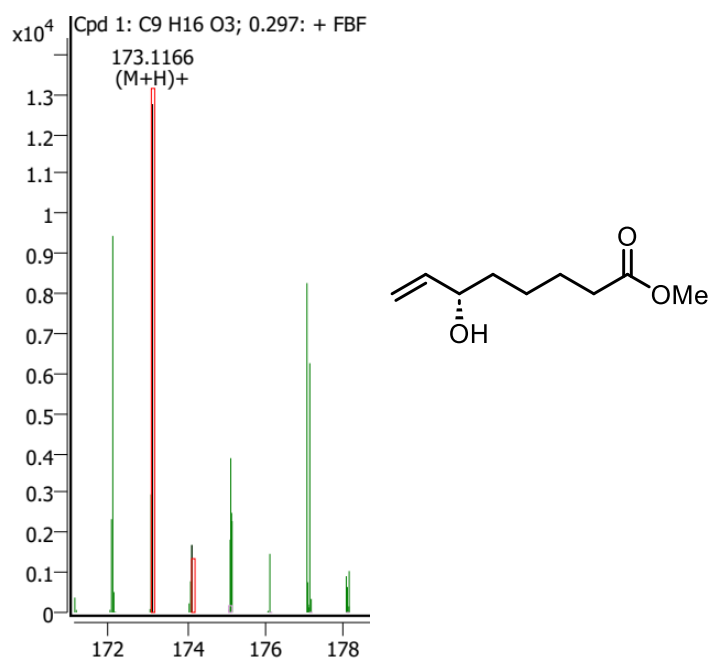
11: HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_9H_{16}O_3Na$ 195.0992; Found 195.1001



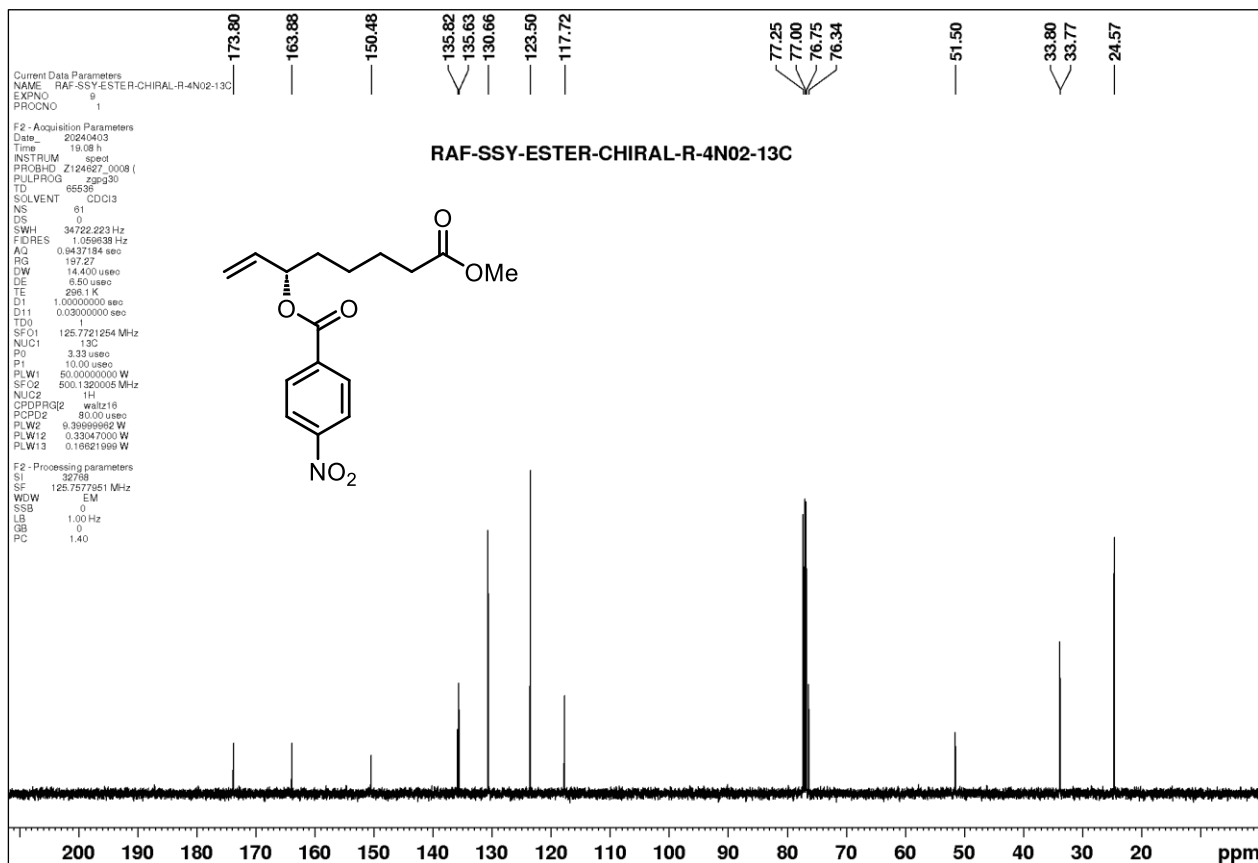
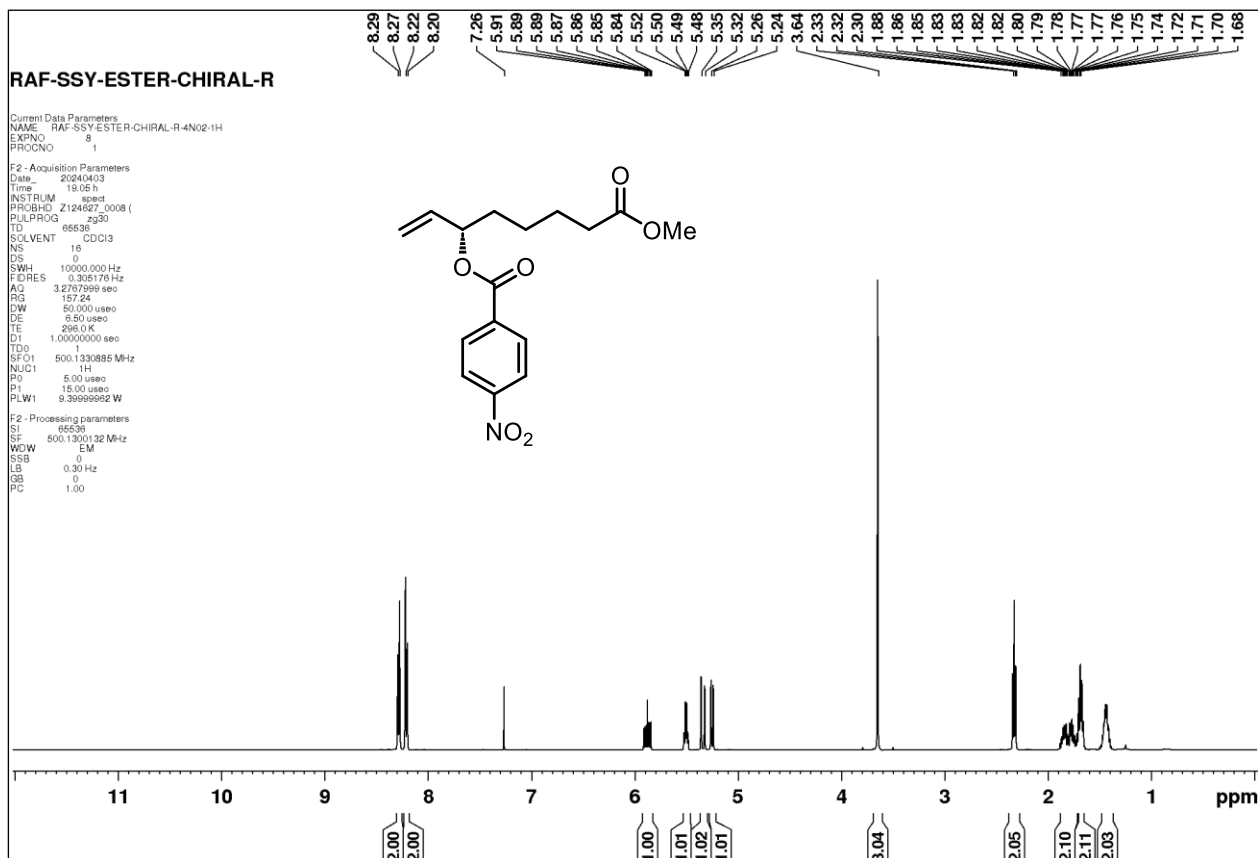
¹H NMR (500 MHz, CDCl₃) and ¹³C{¹H} NMR (125 MHz, CDCl₃) of compound 4



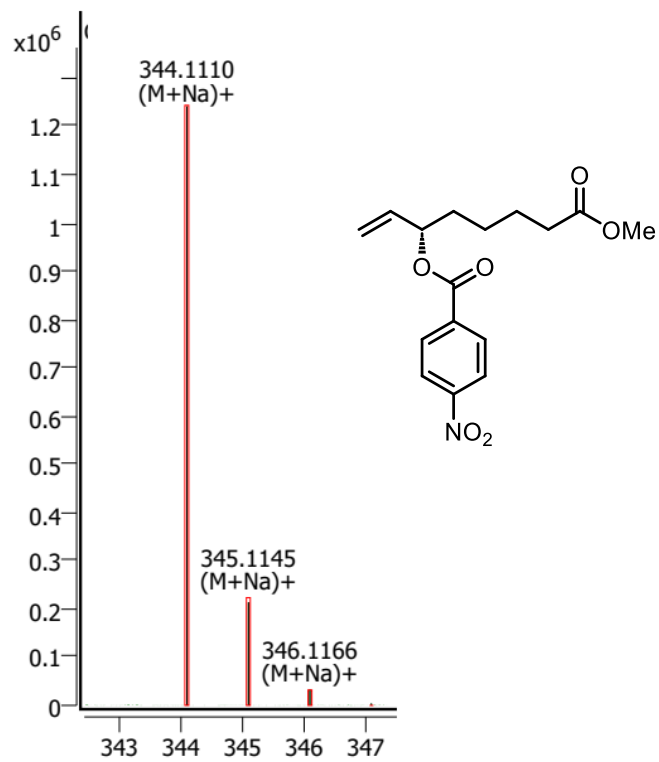
4: HRMS (ESI-TOF) m/z : $[M + H]^+$ calcd for $C_9H_{17}O_3$ 173.1173; Found 173.1166



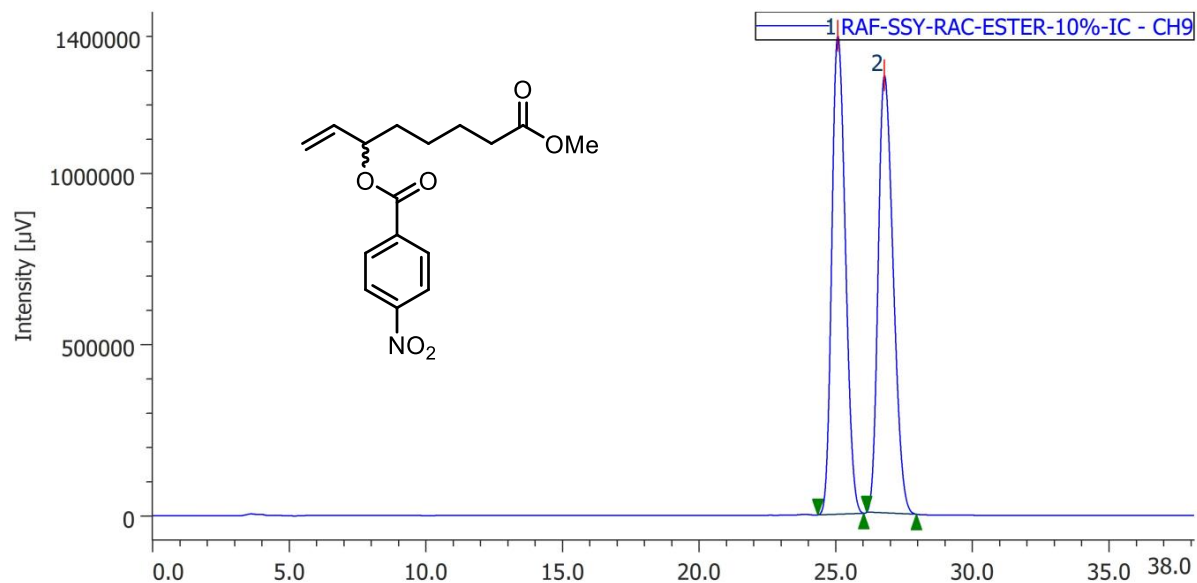
^1H NMR (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of compound 4'



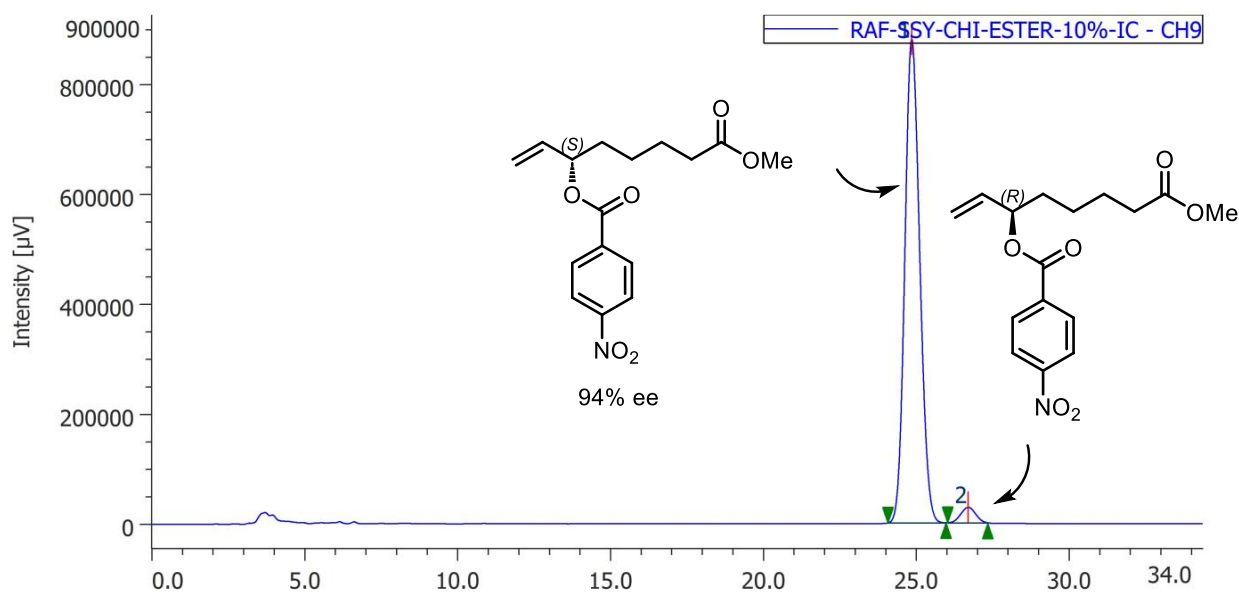
4': HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{16}H_{19}NO_6Na$ 344.1105; Found 344.1110.



HPLC chromatograms of racemic and chiral 4' (94% ee)

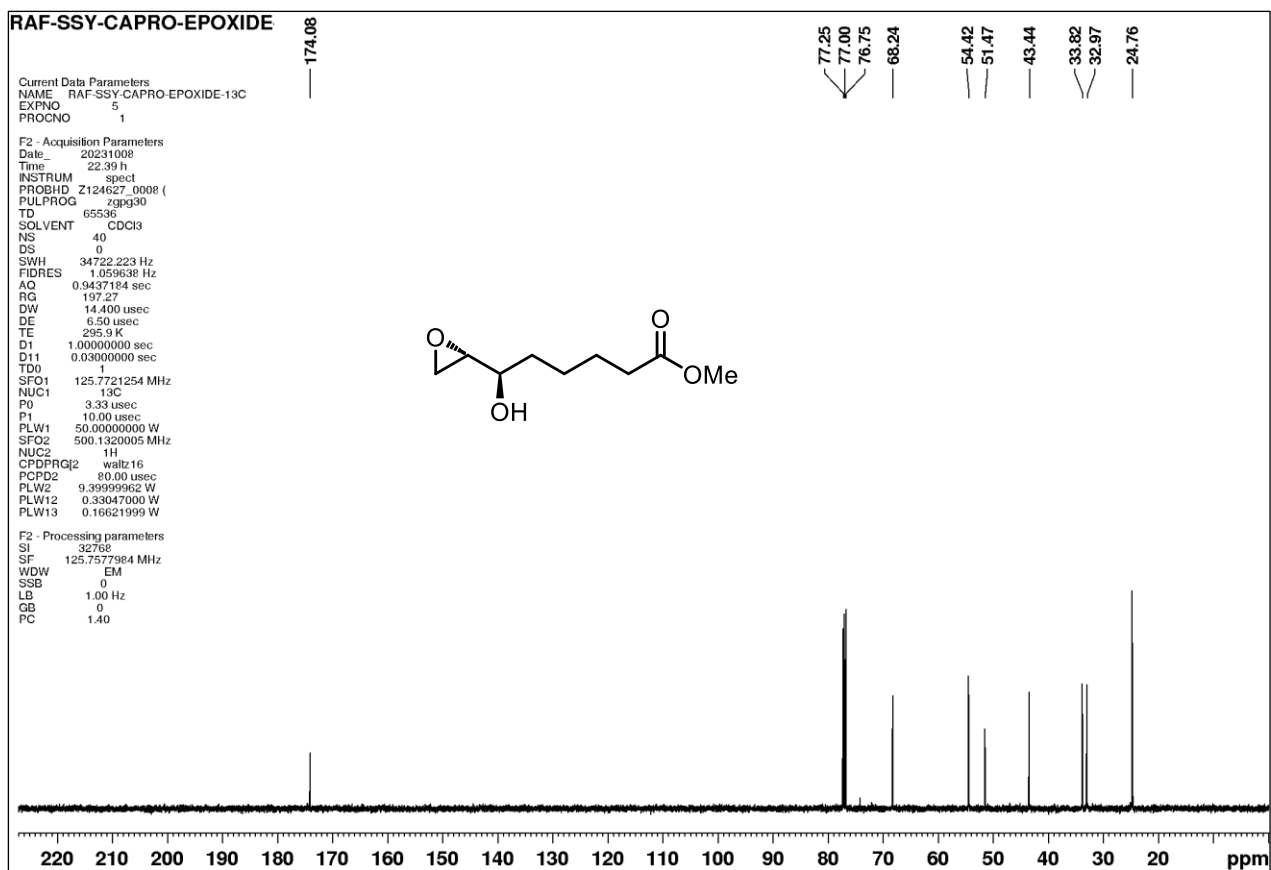
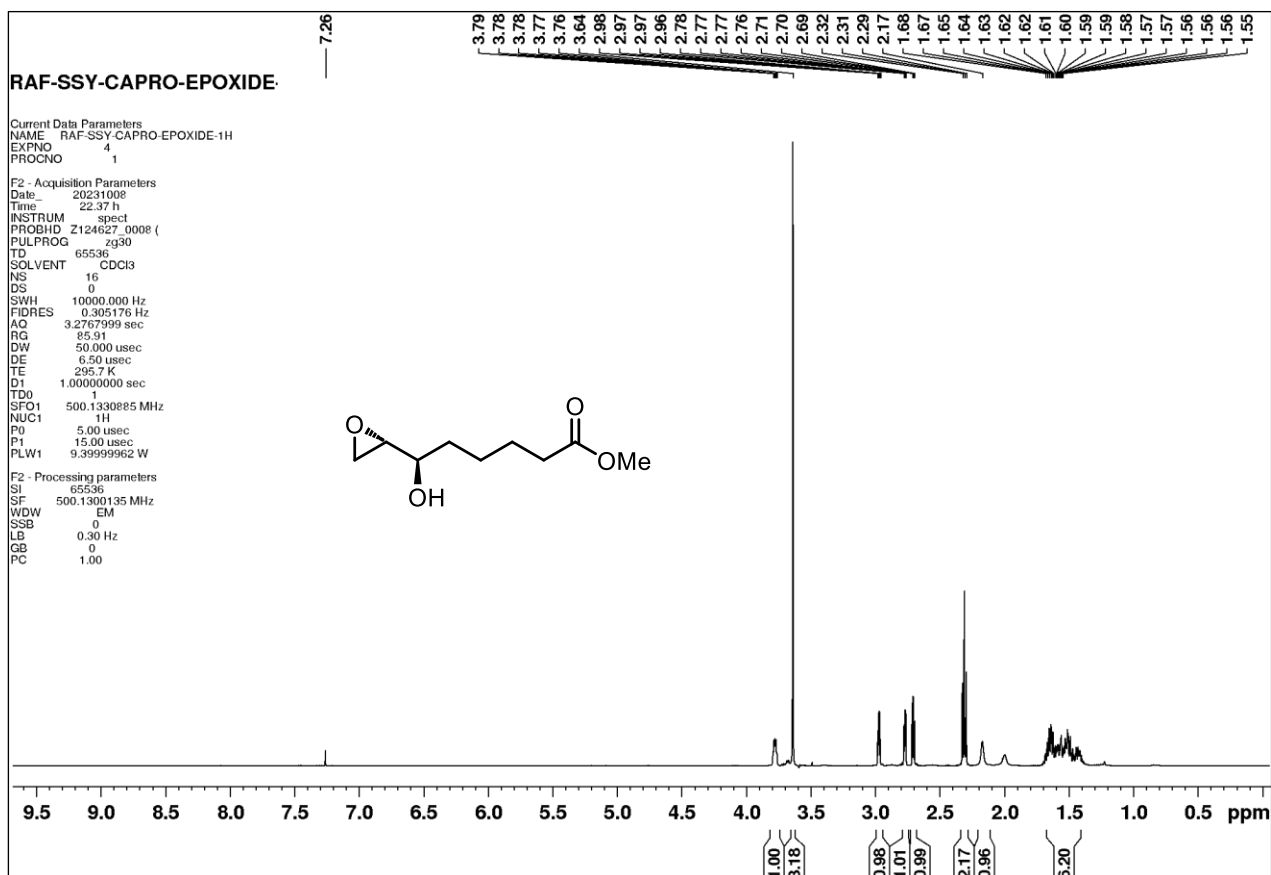


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	25.067	48352659	1395861	49.757	52.240	N/A	11697	1.756	1.183	
2	Unknown	9	26.773	48824788	1276138	50.243	47.760	N/A	10978	N/A	1.273	
Total				97177447	2671999			0.00000				

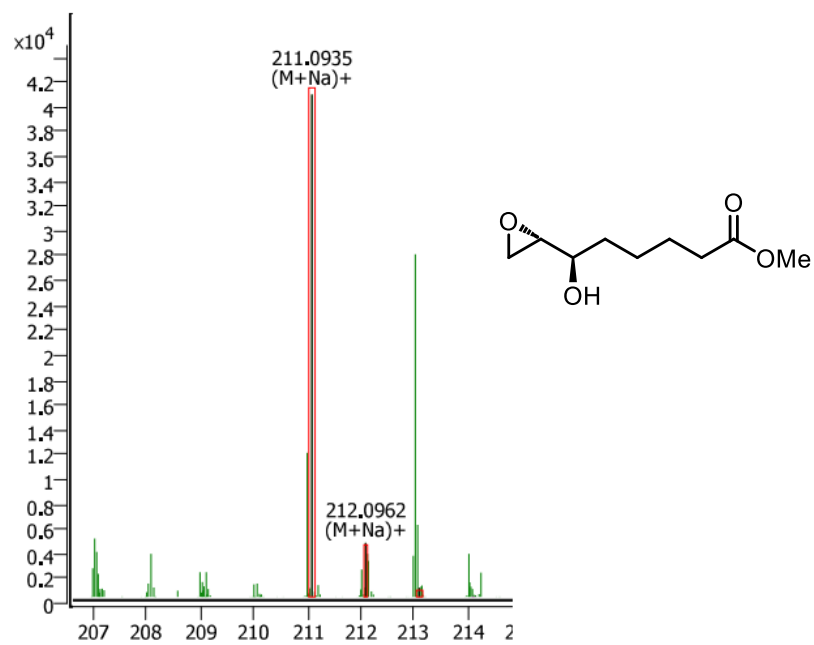


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	24.840	29863019	880024	96.870	96.886	N/A	12212	2.030	1.126	
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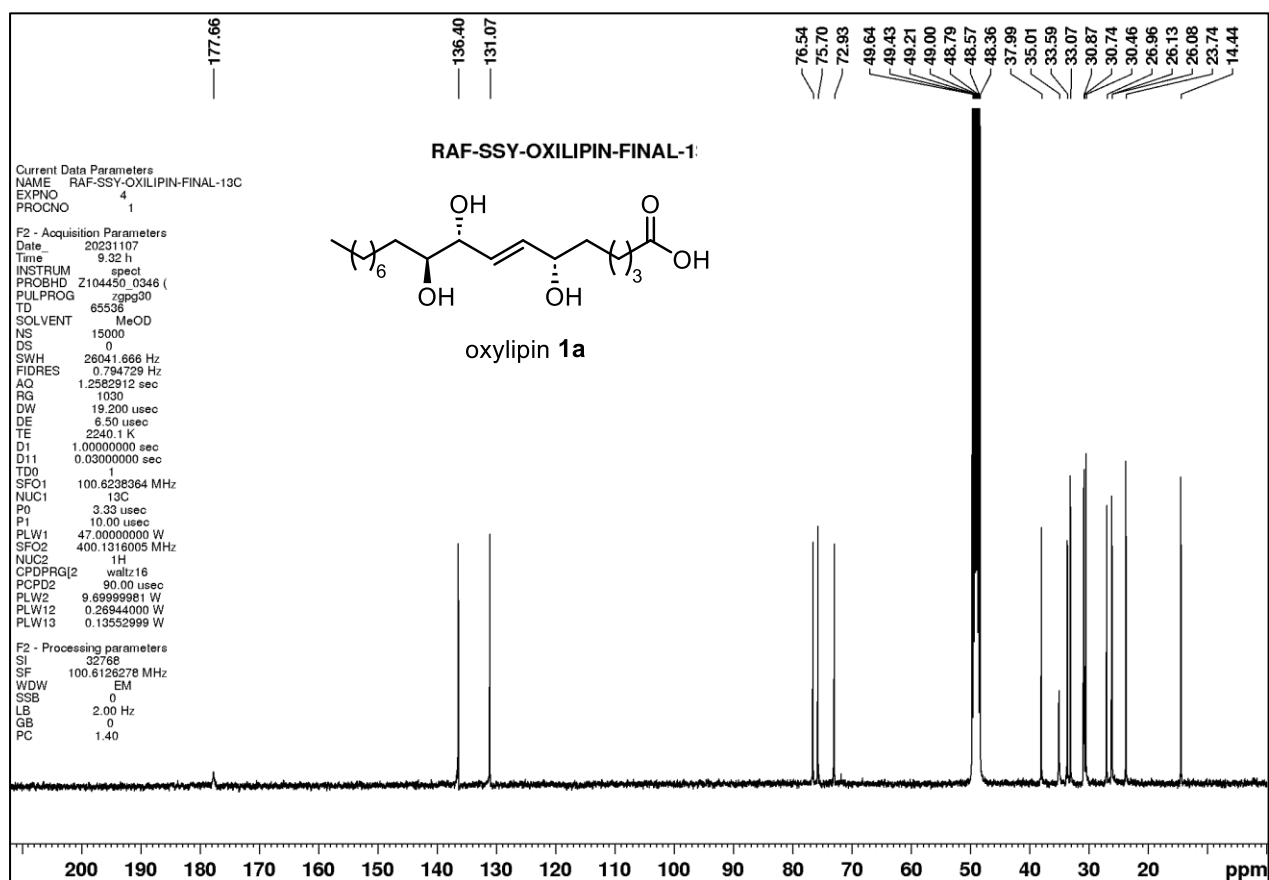
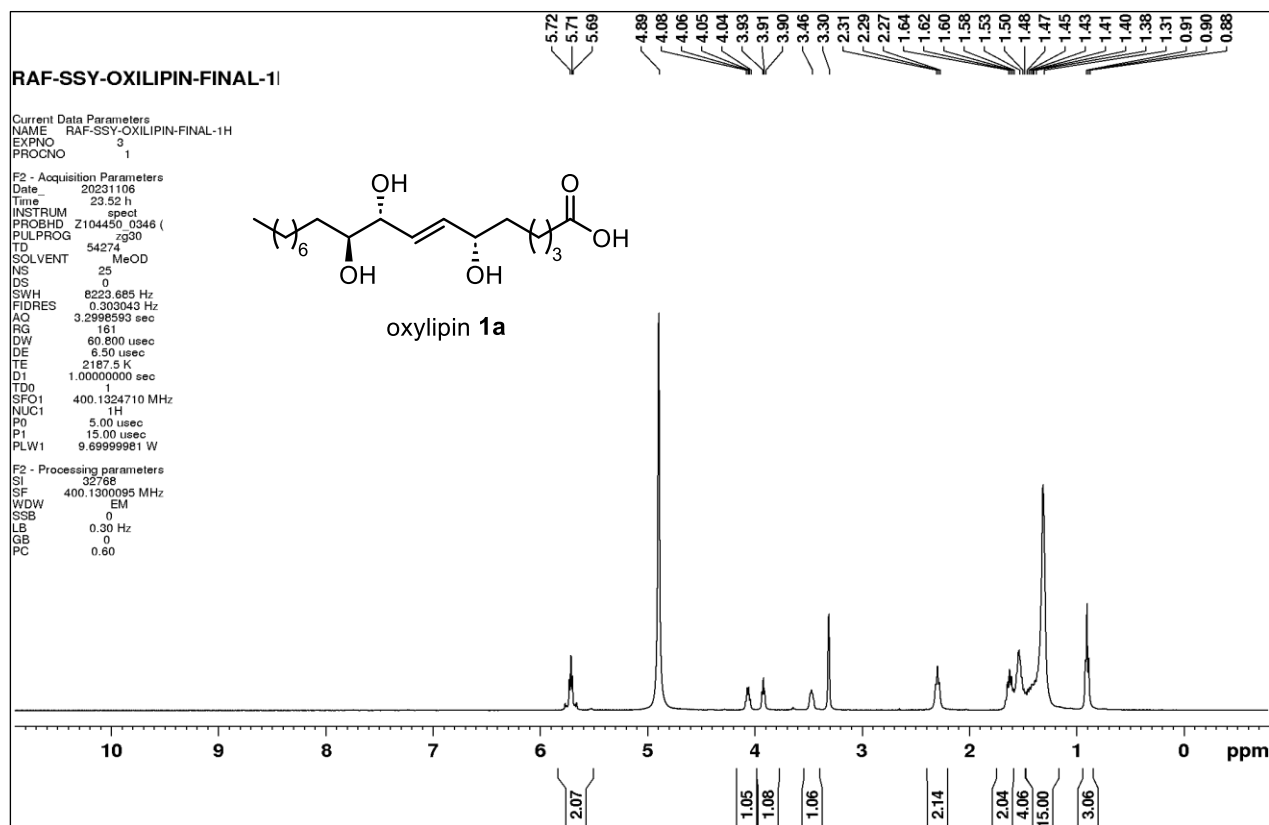
^1H NMR (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, CDCl_3) of compound **12**



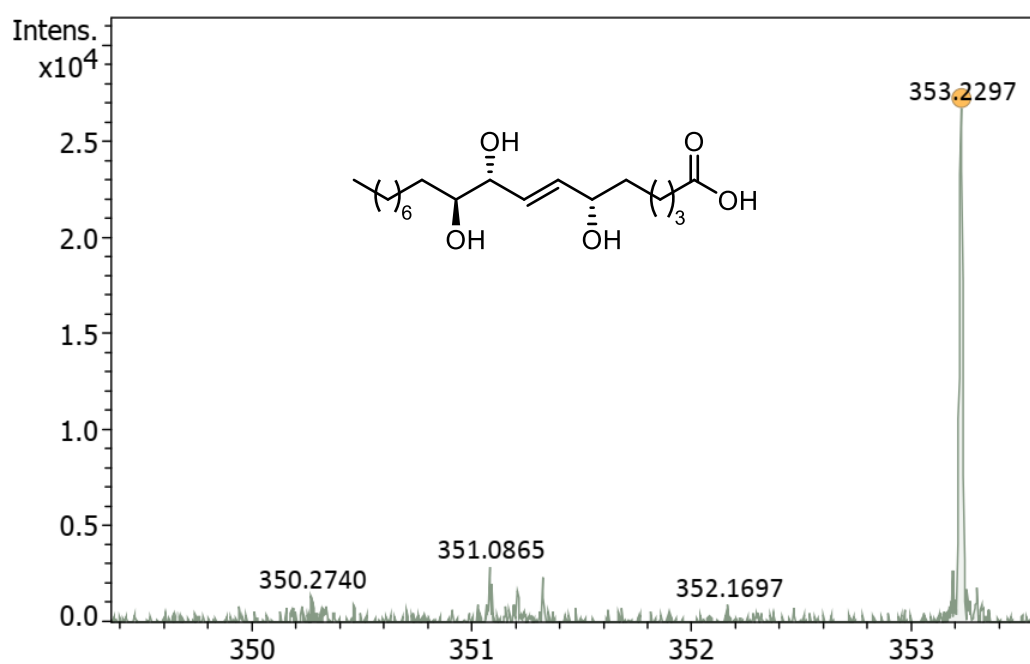
12: HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_9H_{16}O_4Na$ 211.0941; Found 211.0935



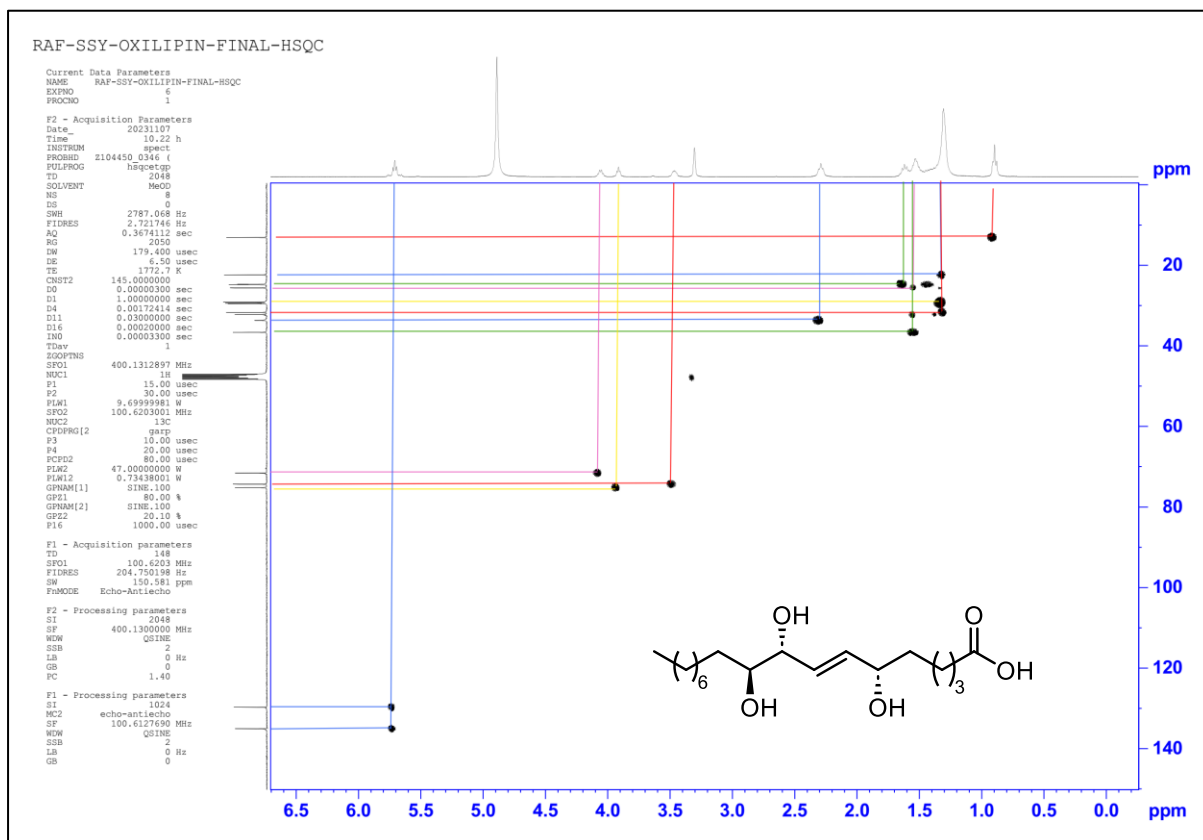
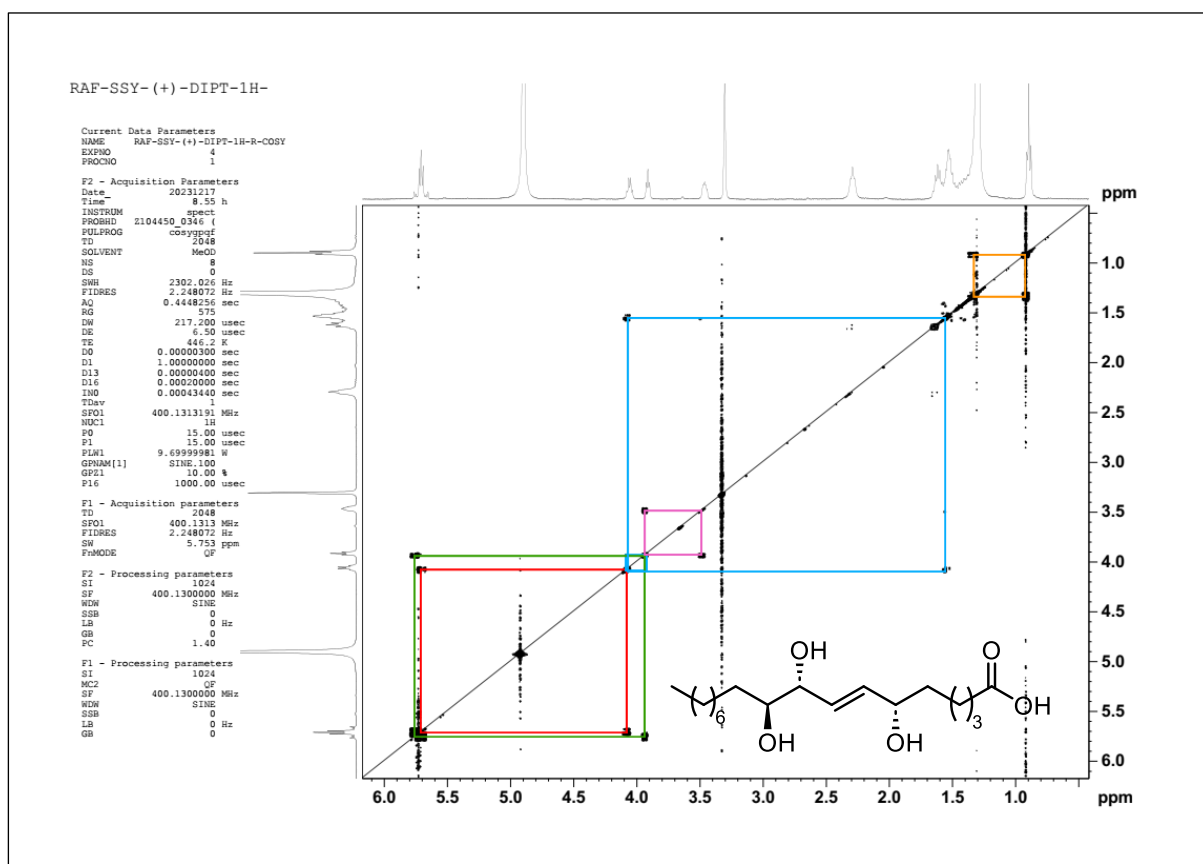
^1H NMR (400 MHz, CD_3OD) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) of compound **1a**



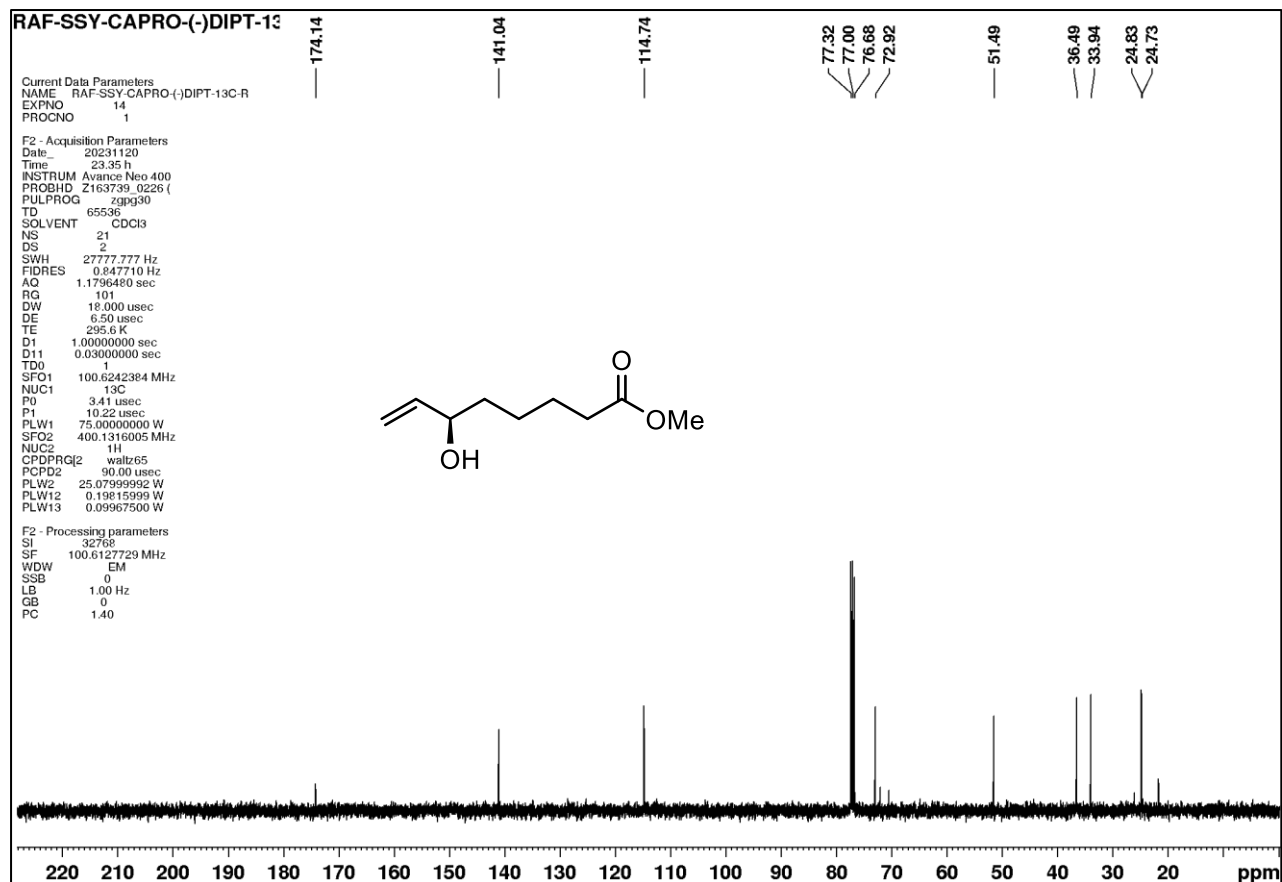
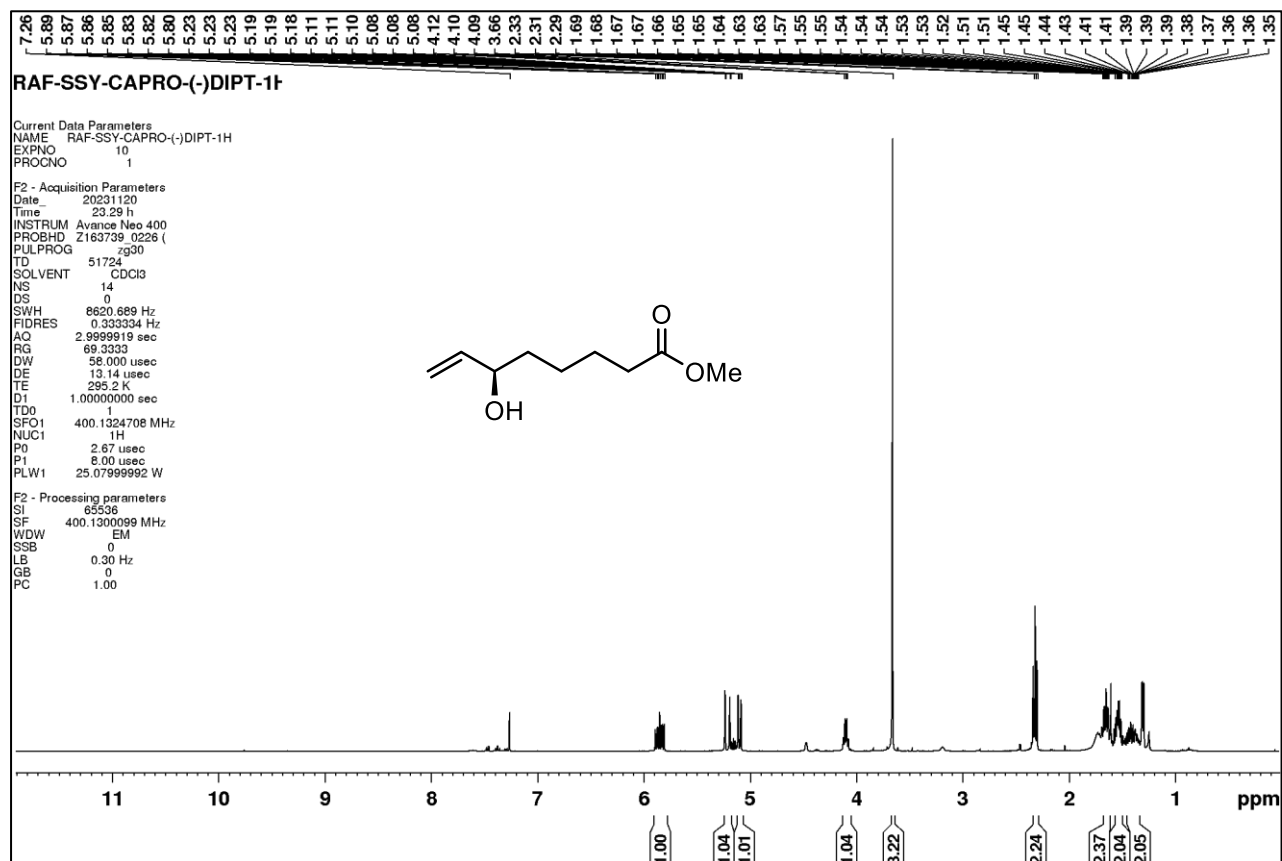
1a: HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{18}H_{34}O_5Na$ 353.2298; Found 353.2297



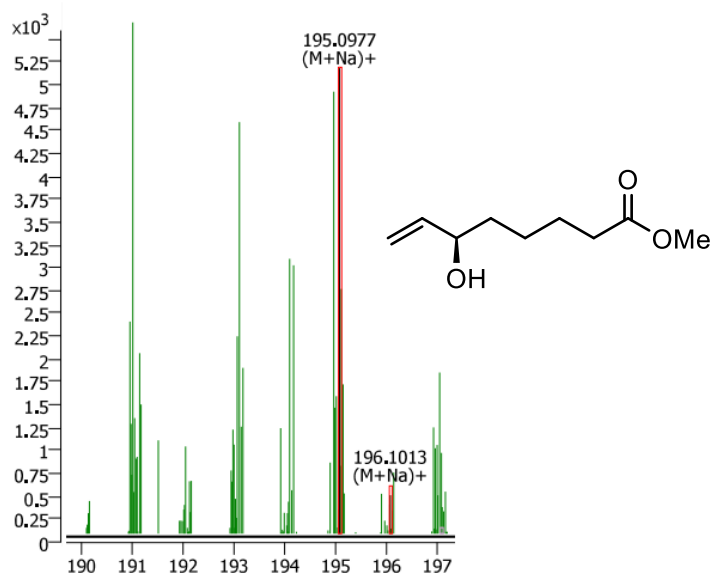
COSY and HSQC of Compound 1a



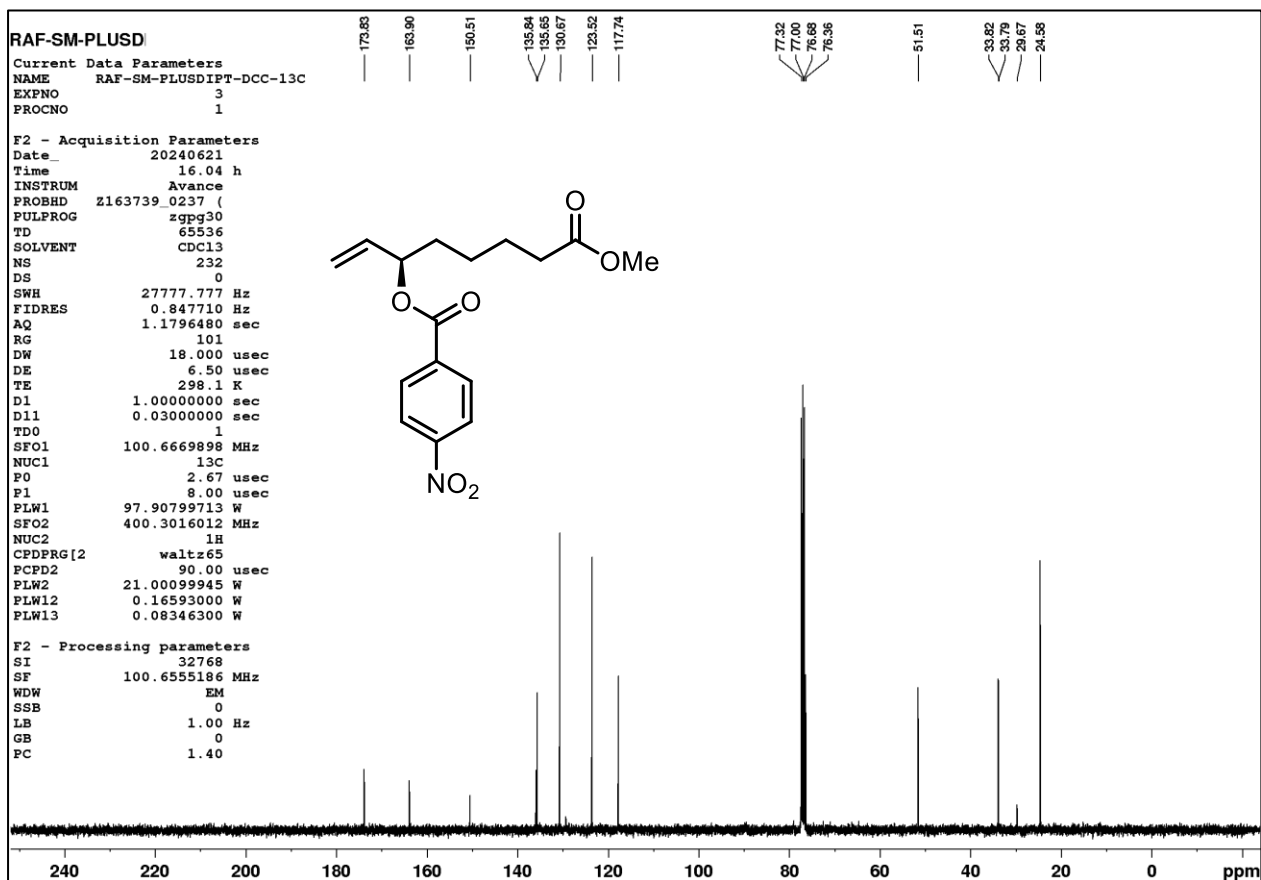
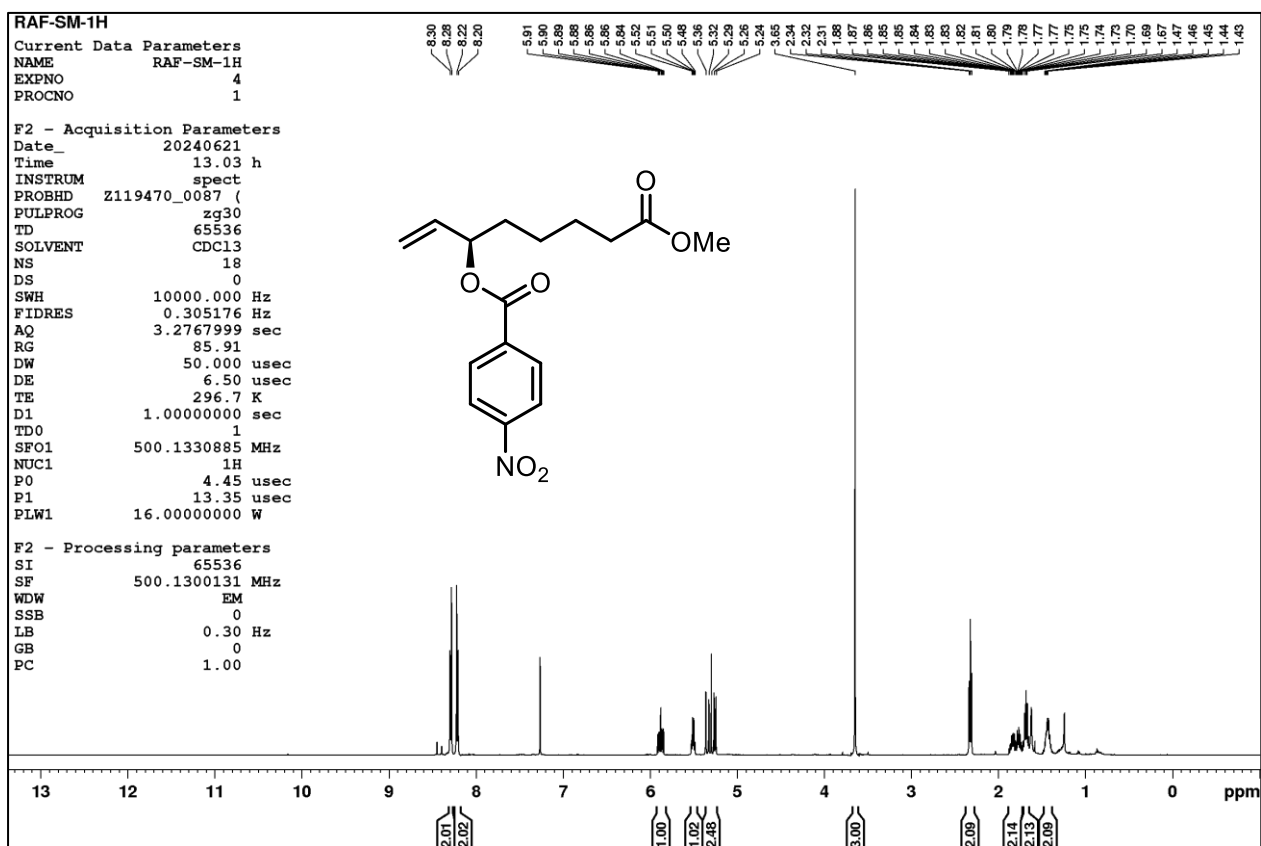
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound *ent-4*



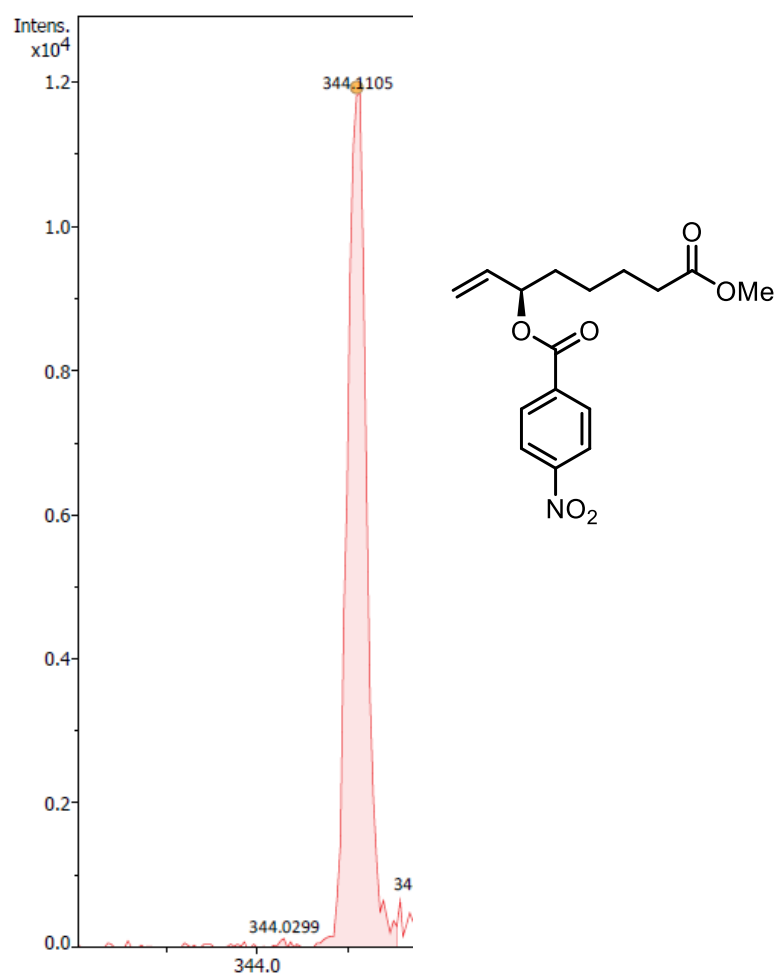
ent-4: HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_9H_{16}O_3Na$ 195.0992; Found 195.0977



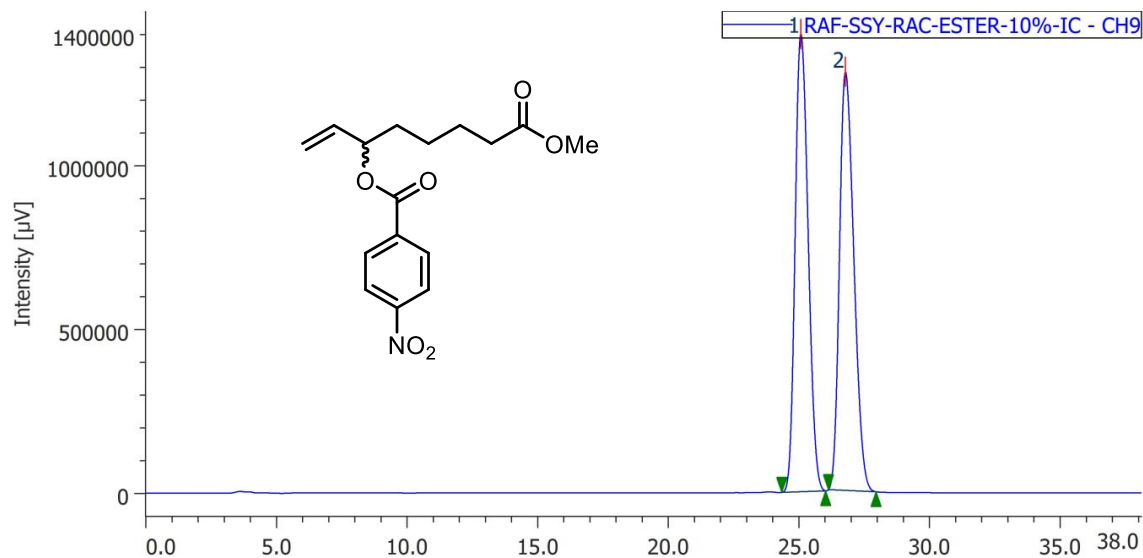
^1H NMR (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound *ent-4'*



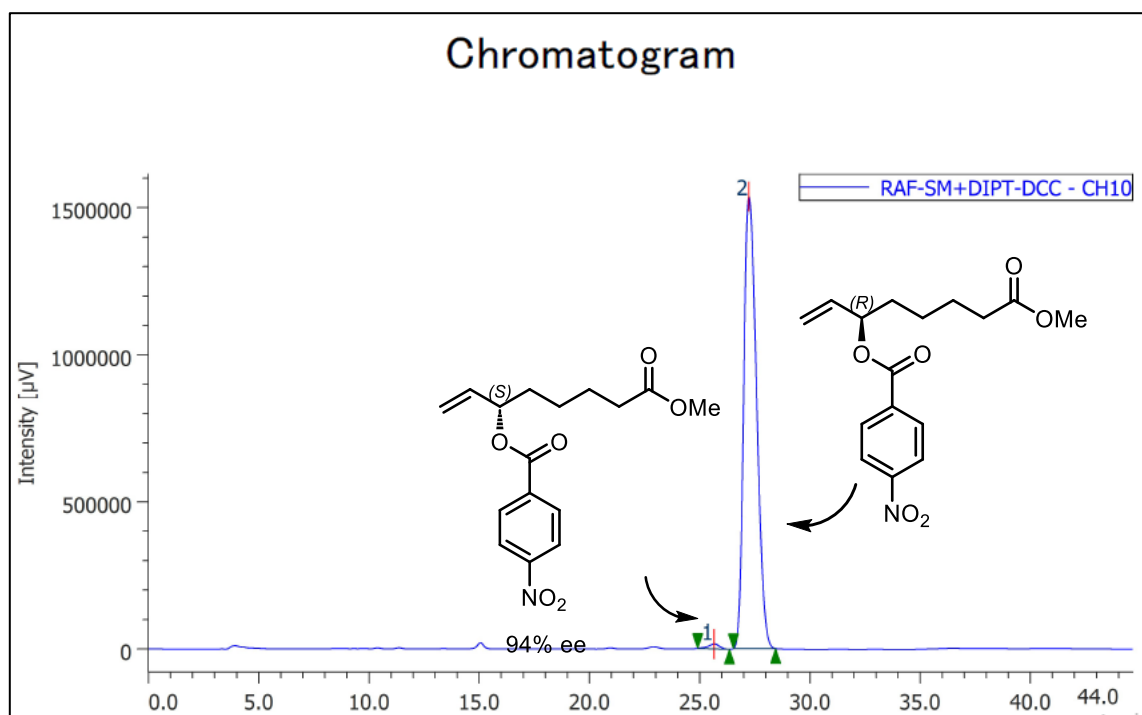
ent-4': HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{16}H_{19}NO_6Na$ 344.1105; Found 344.1105.



HPLC chromatograms of racemic and chiral *ent*-4' (98% *ee*)

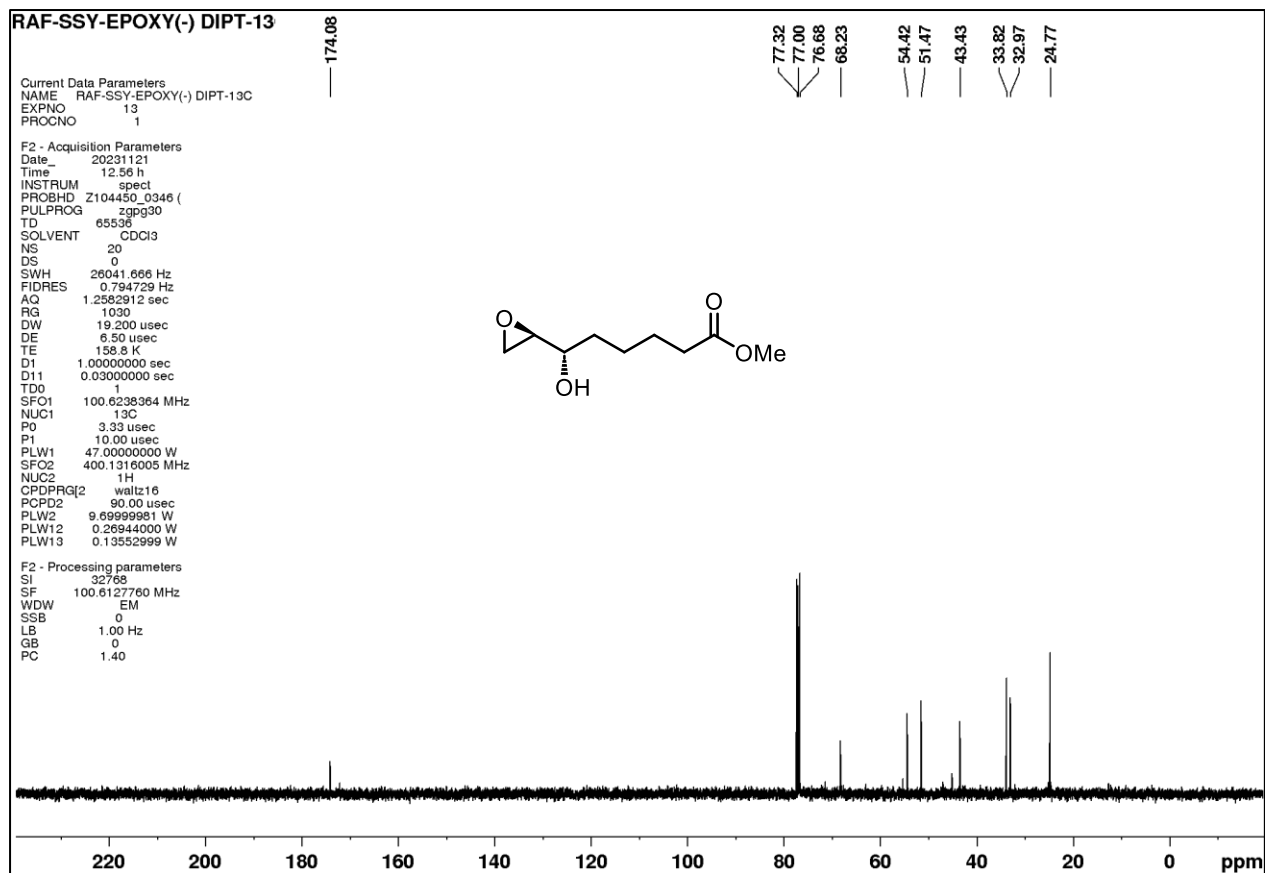
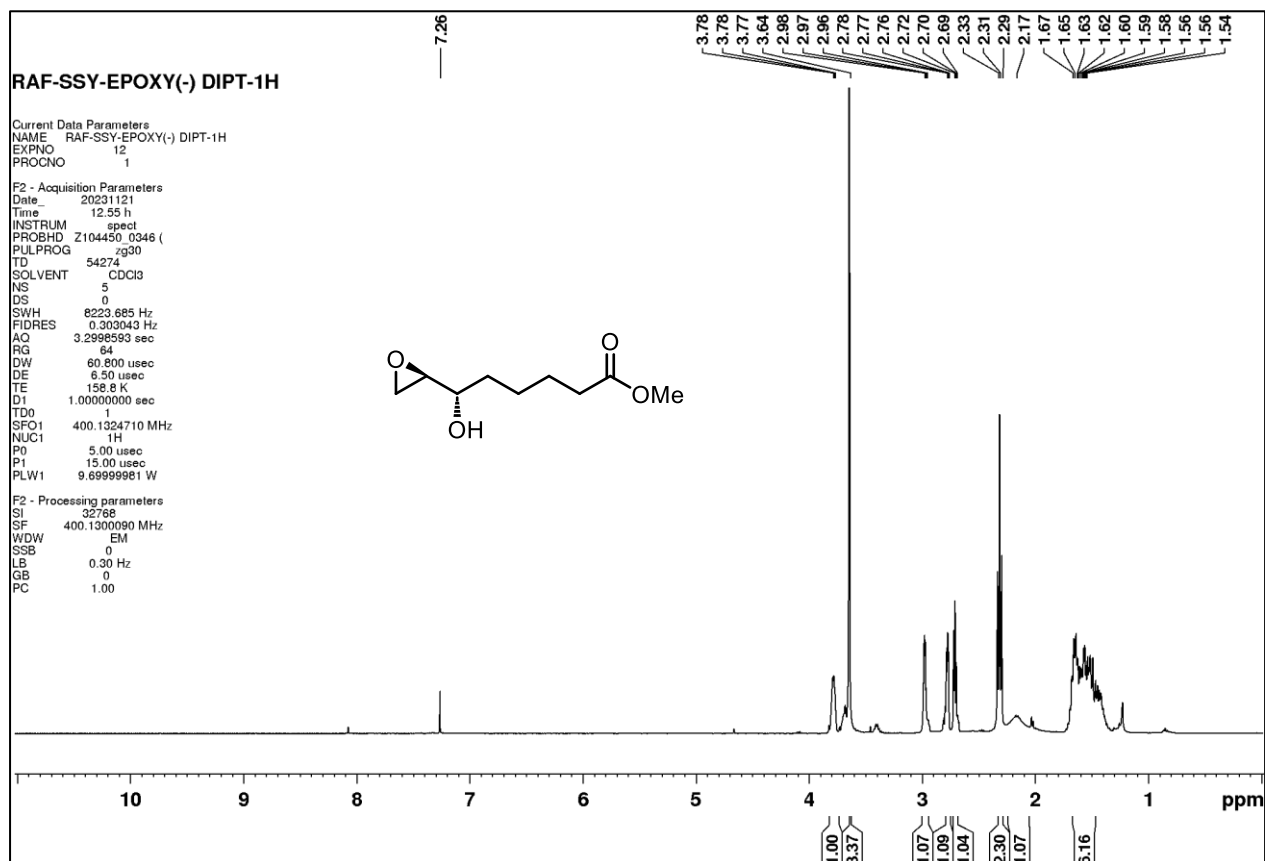


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	25.067	48352659	1395861	49.757	52.240	N/A	11697	1.756	1.183	
2	Unknown	9	26.773	48824788	1276138	50.243	47.760	N/A	10978	N/A	1.273	
Total				97177447	2671999			0.00000				

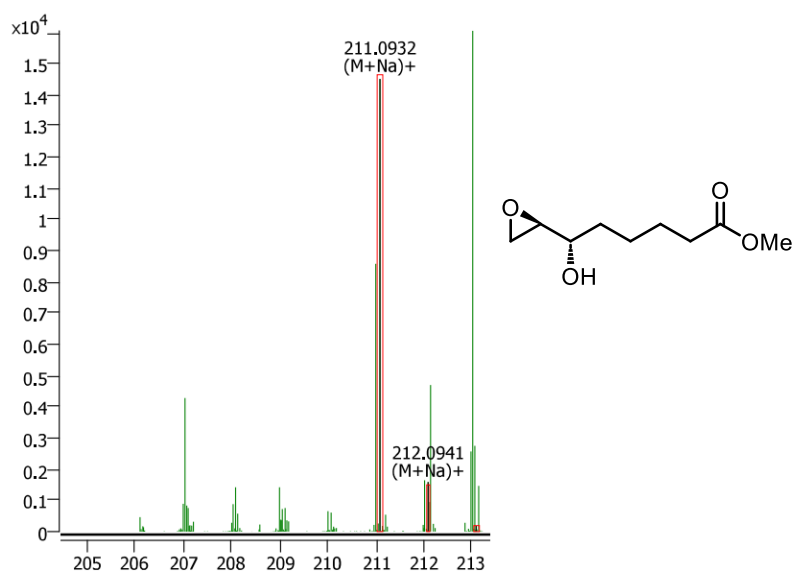


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	10	25.643	589132	16427	0.943	1.059	N/A	11981	1.572	0.882	
2	Unknown	10	27.227	61891887	1534747	99.057	98.941	N/A	10112	N/A	1.298	
Total				62481019	1551174			0.00000				

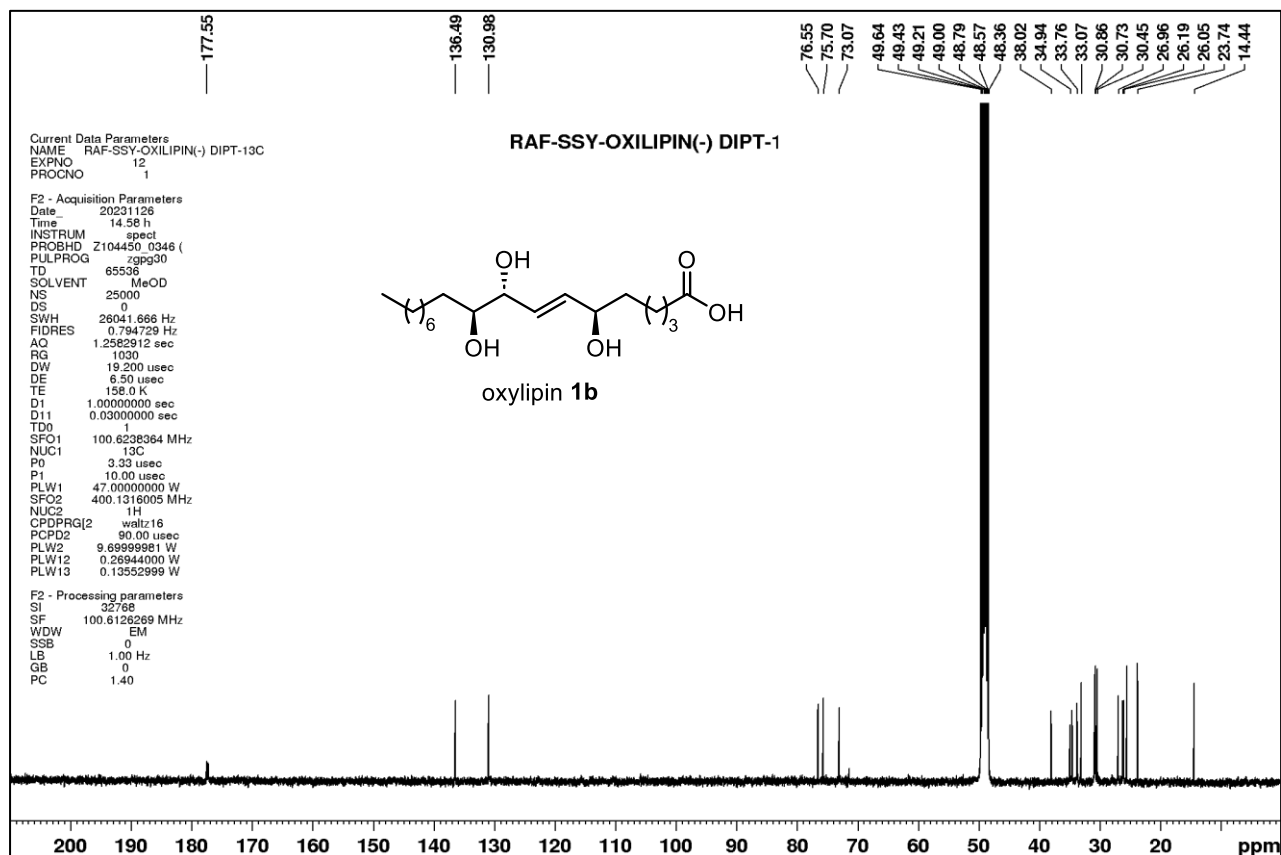
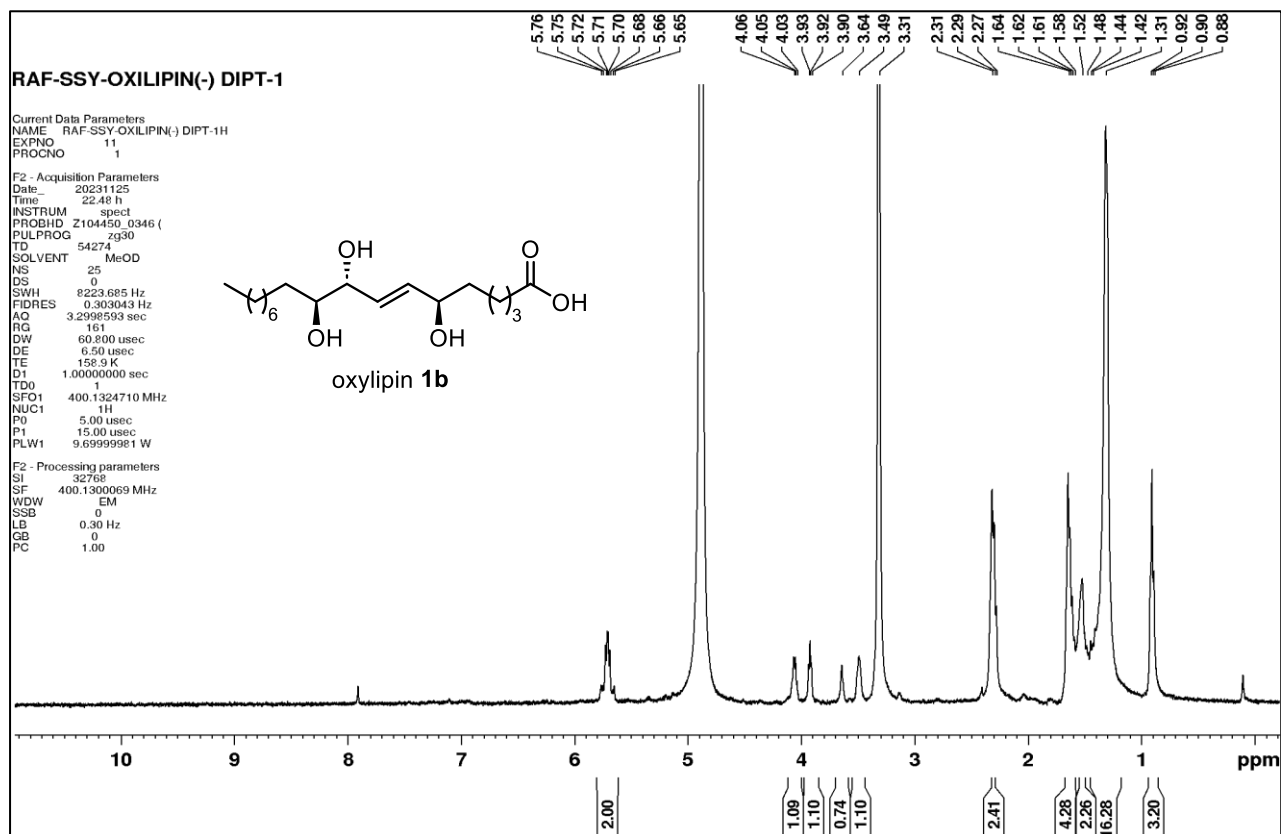
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound *ent*-12



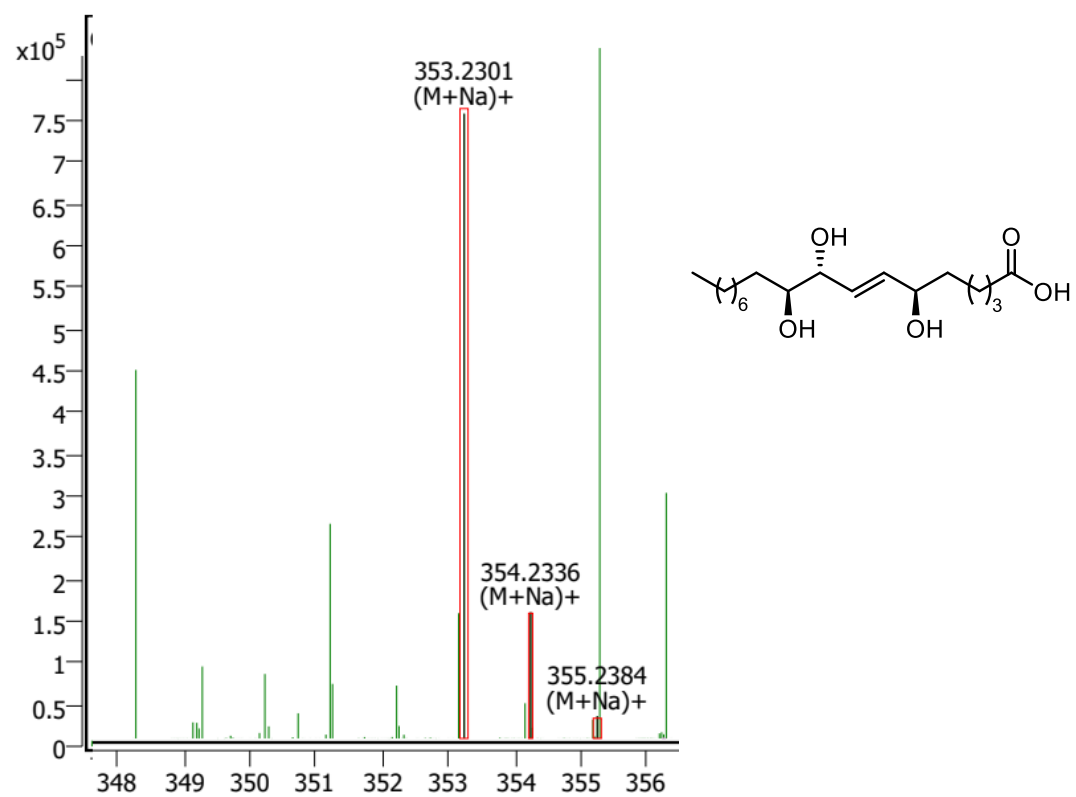
ent-**12**: HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_9H_{16}O_4Na$ 211.0941; Found 211.0932



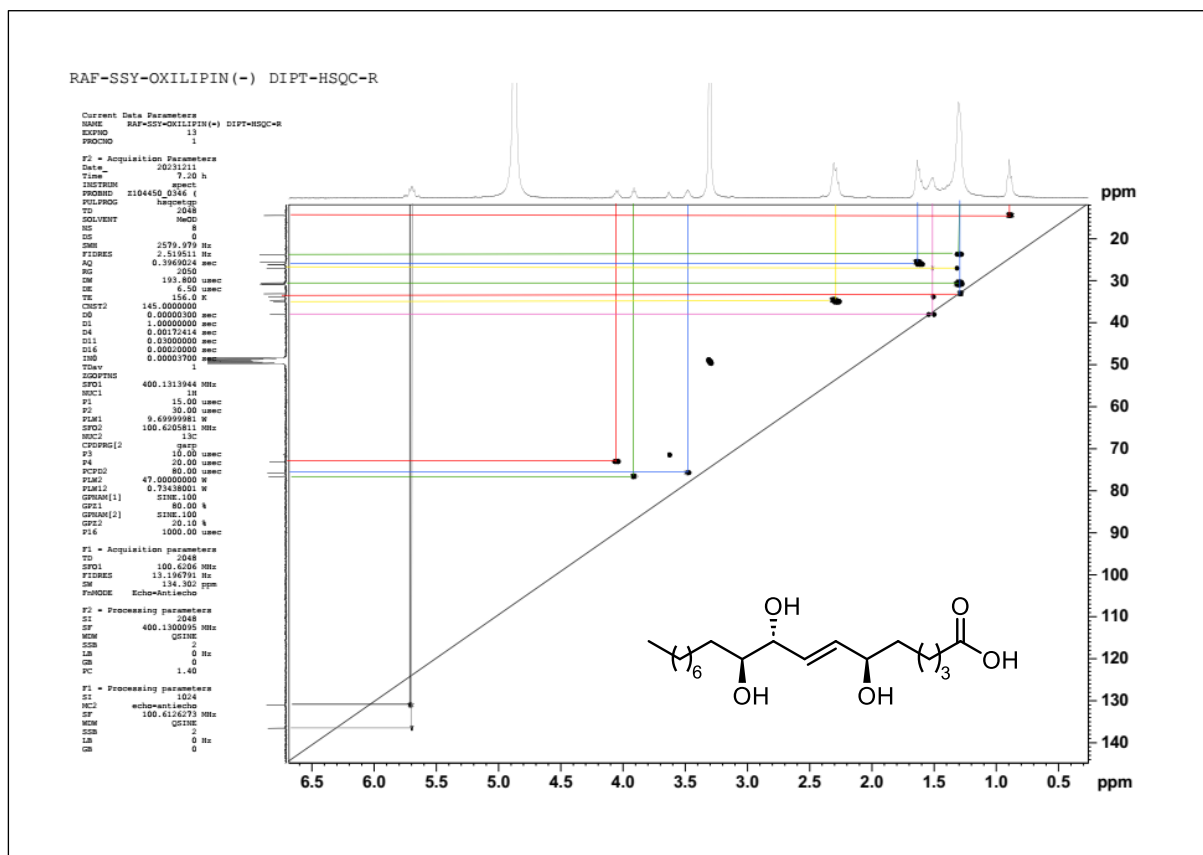
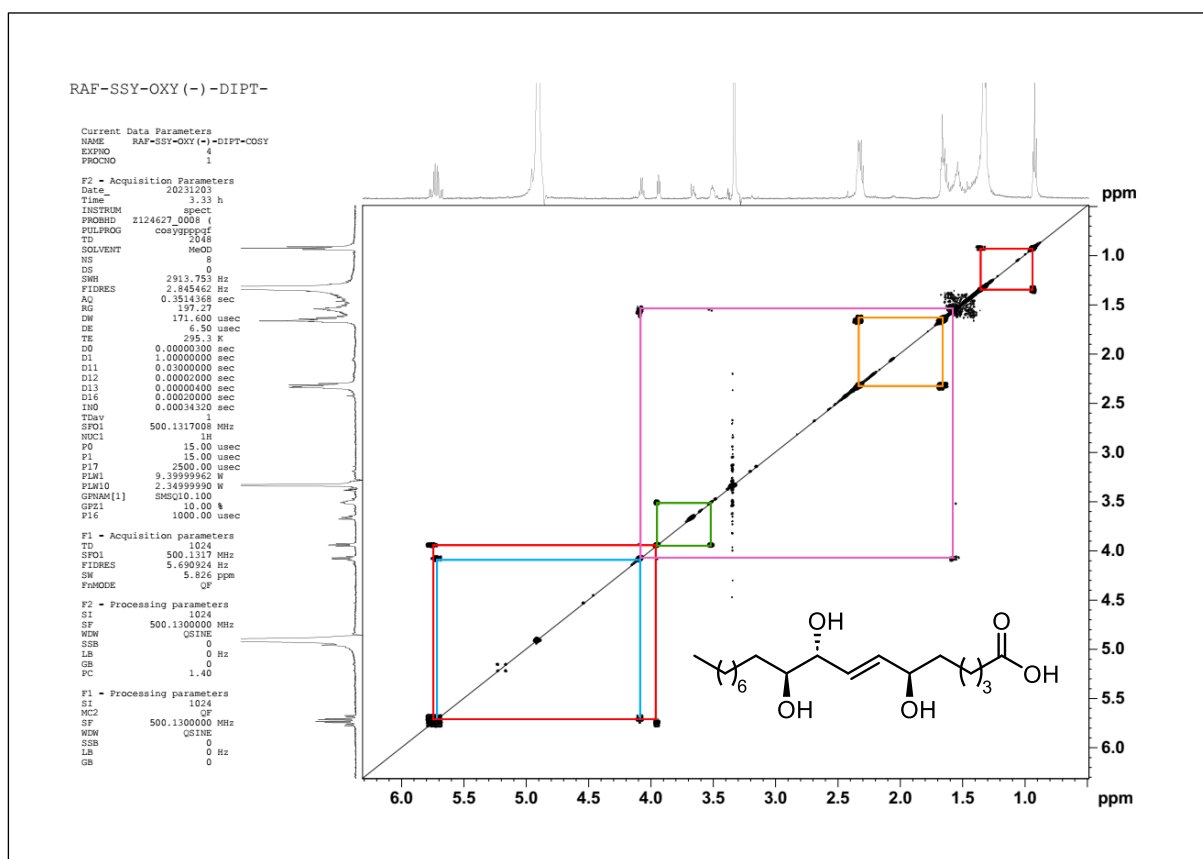
^1H NMR (400 MHz, CD_3OD) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) of compound **1b**



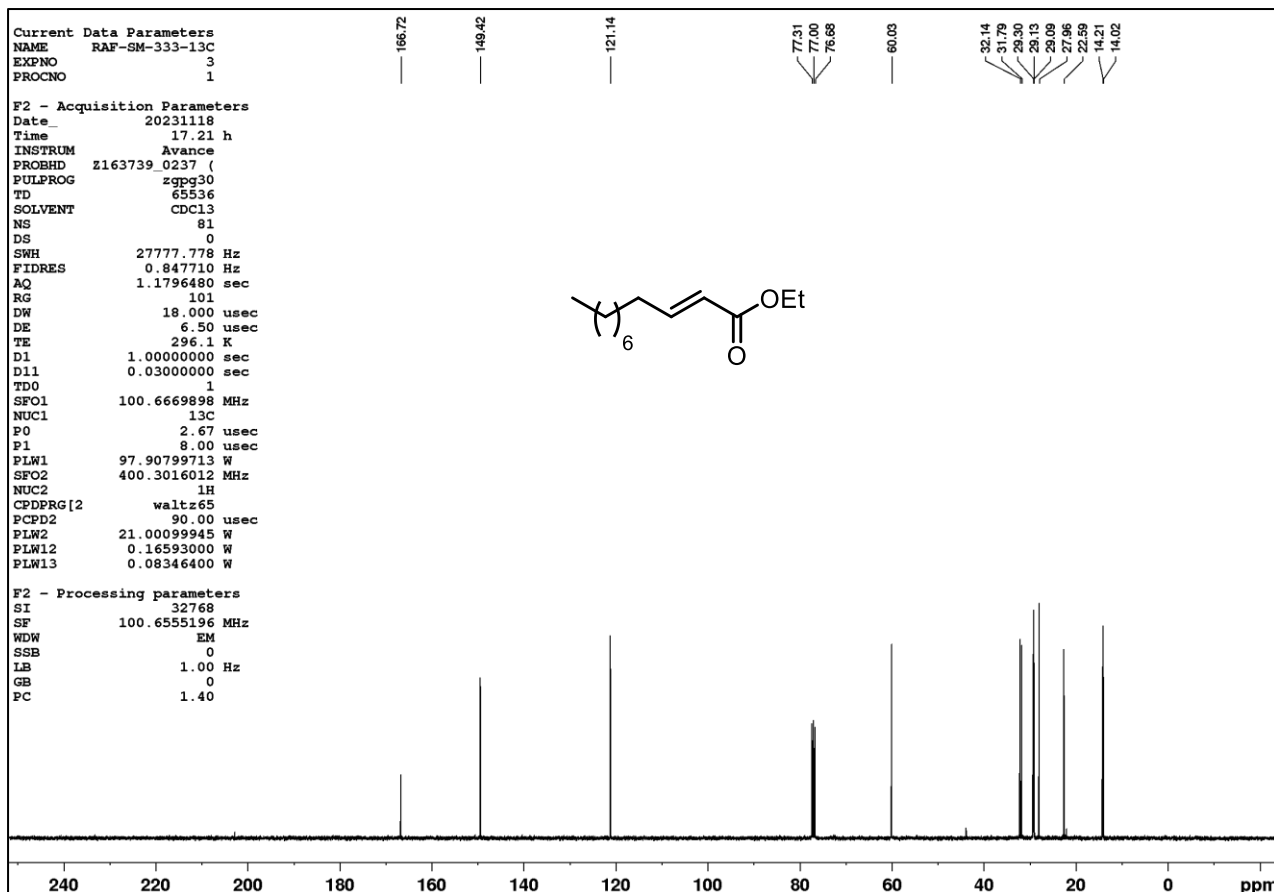
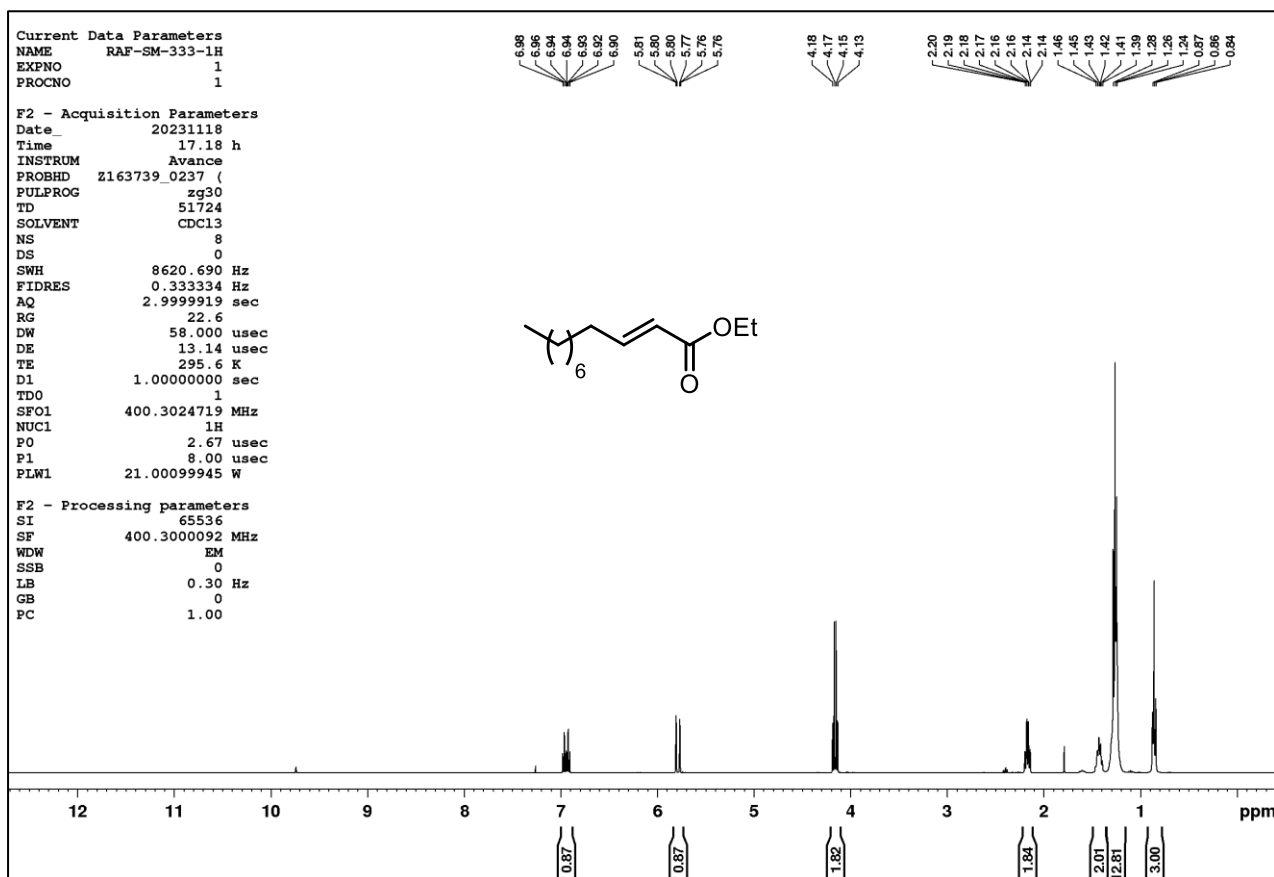
1b: HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{18}H_{34}O_5Na$ 353.2298; Found 353.2301



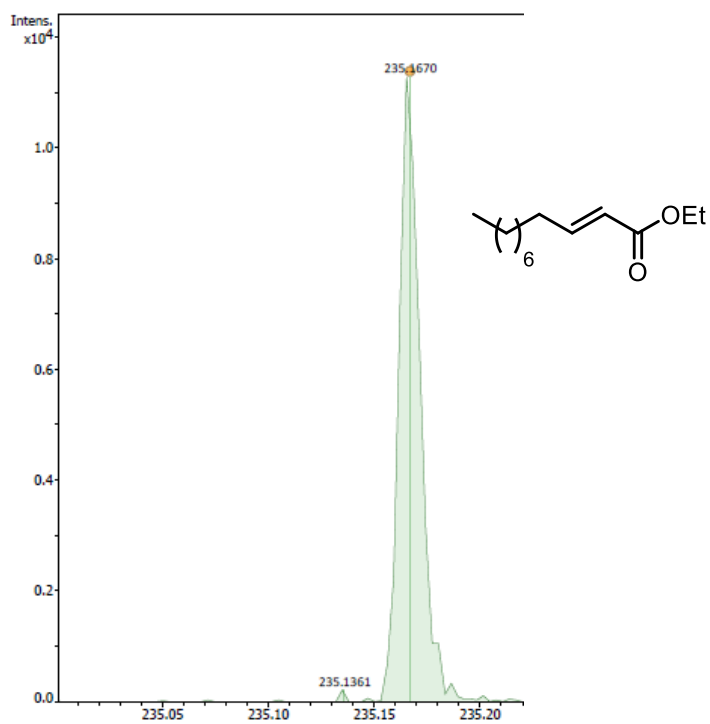
COSY and HSQC of compound 1b



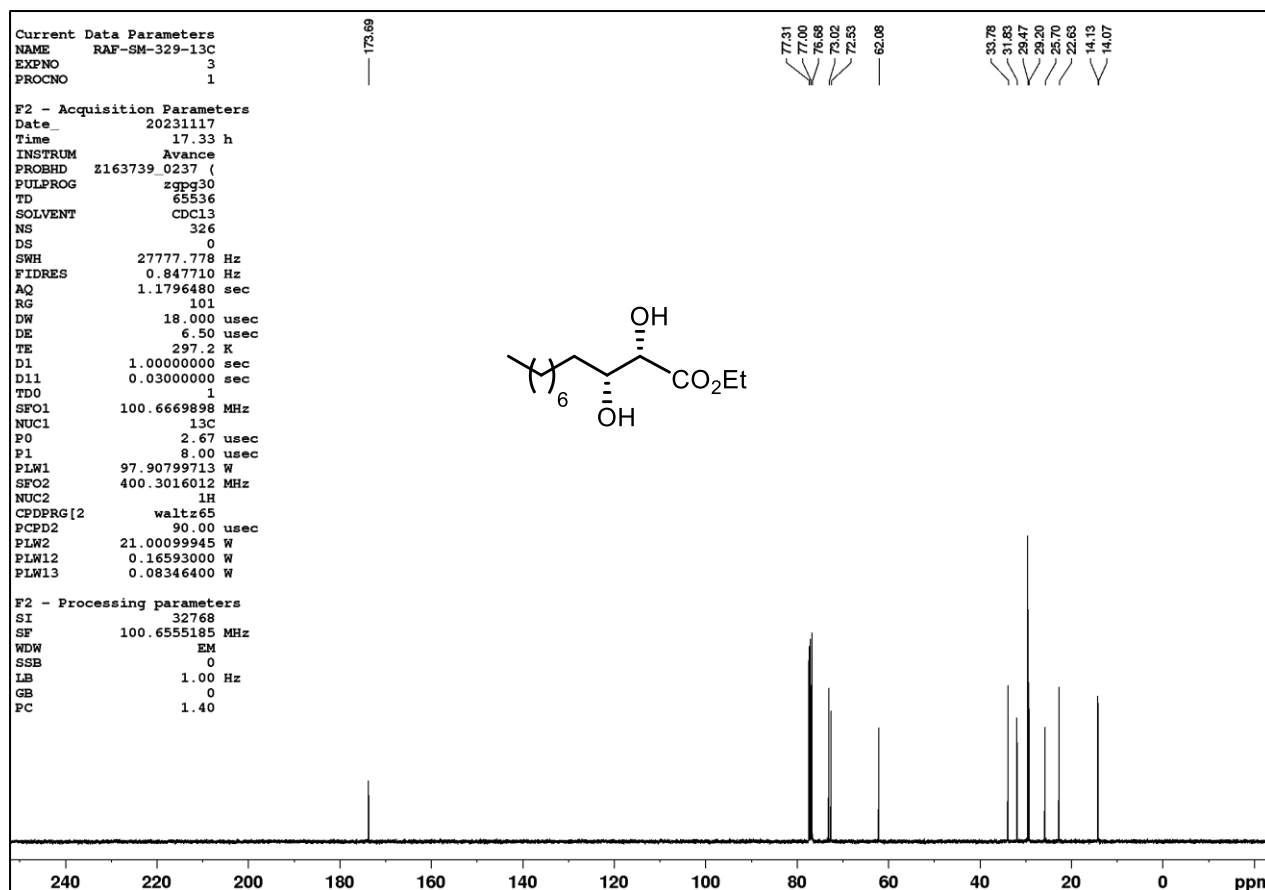
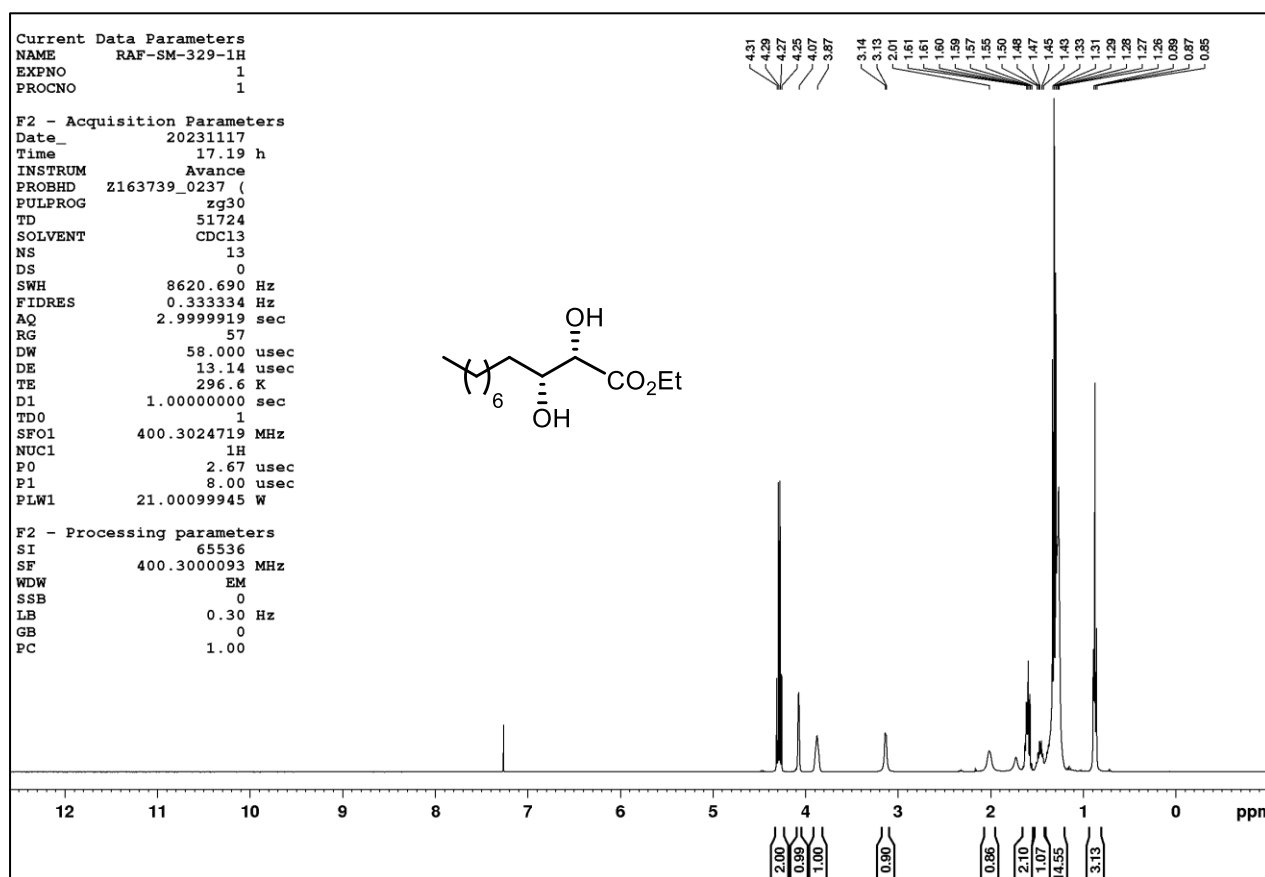
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound 7



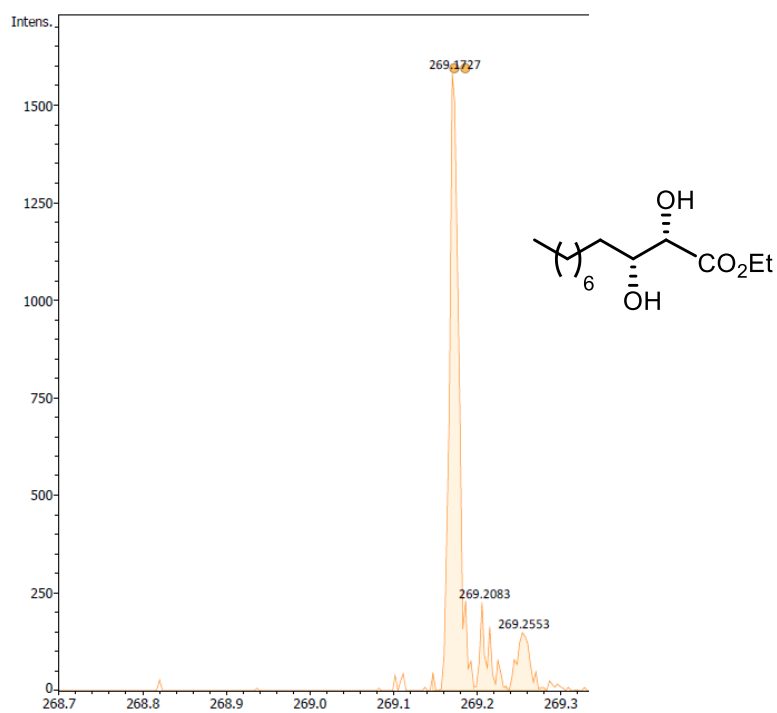
7: HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $C_{13}H_{24}O_2Na$ 235.1669; Found 235.1670.



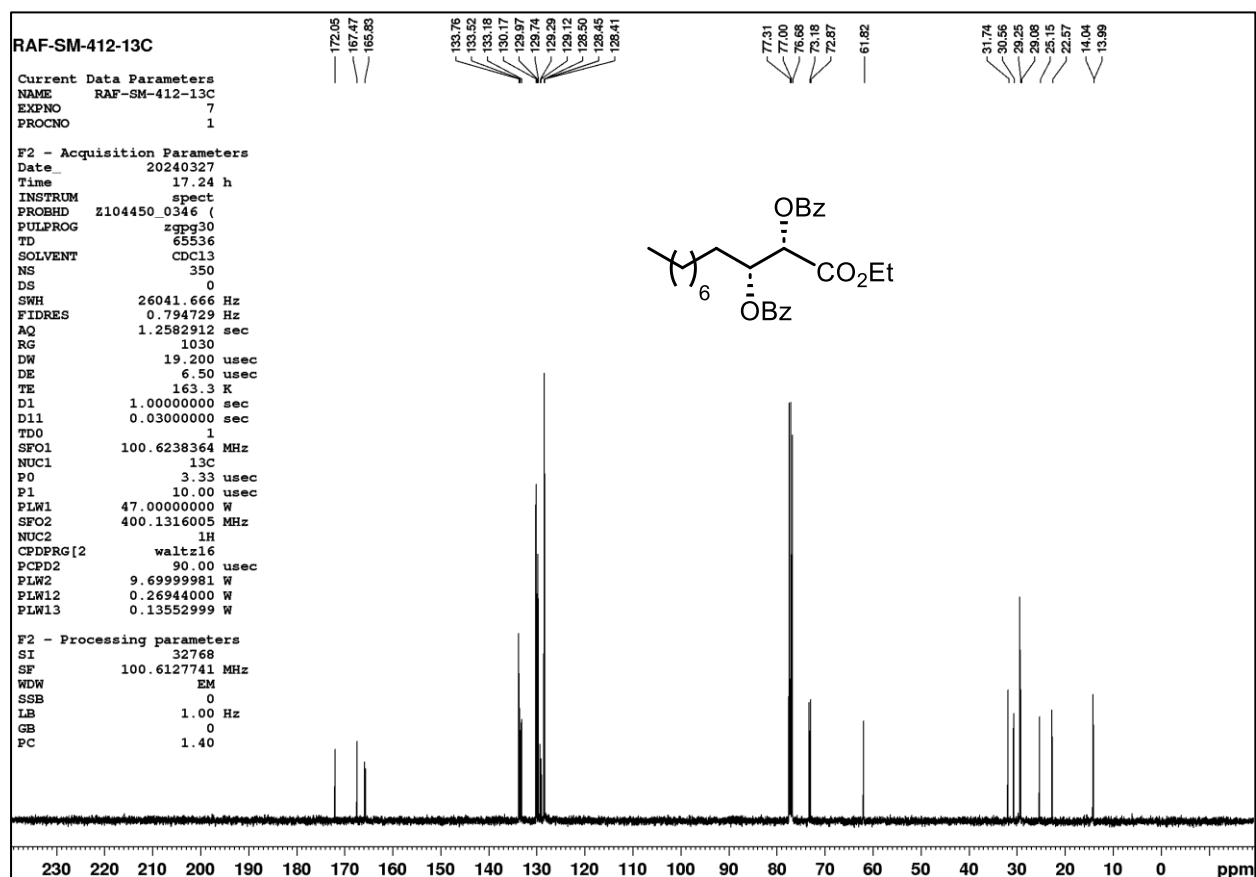
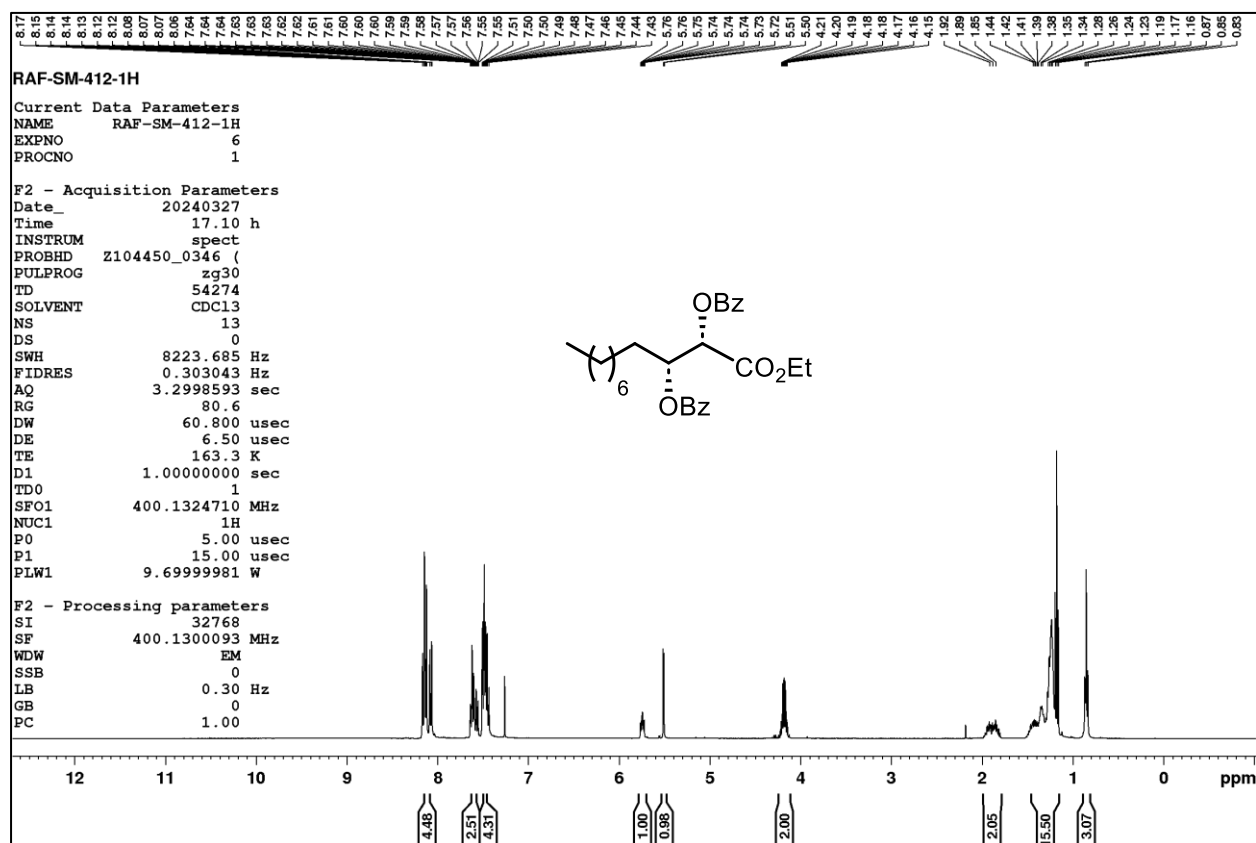
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound **13**



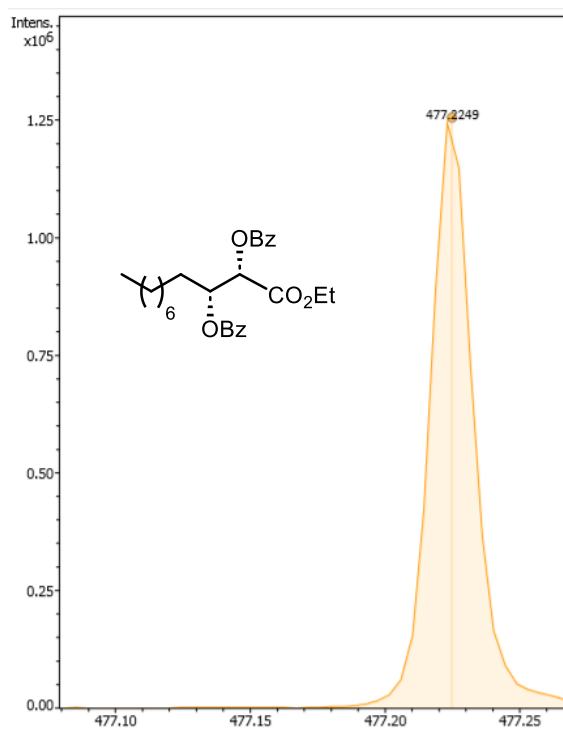
13: HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $C_{13}H_{26}O_4Na$ 269.1723; Found 269.1727



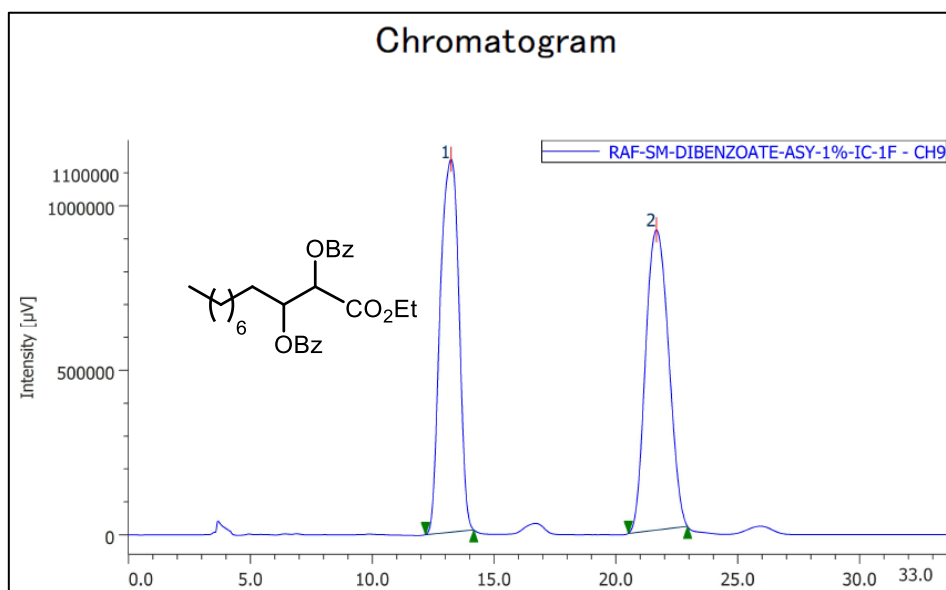
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound **13'**



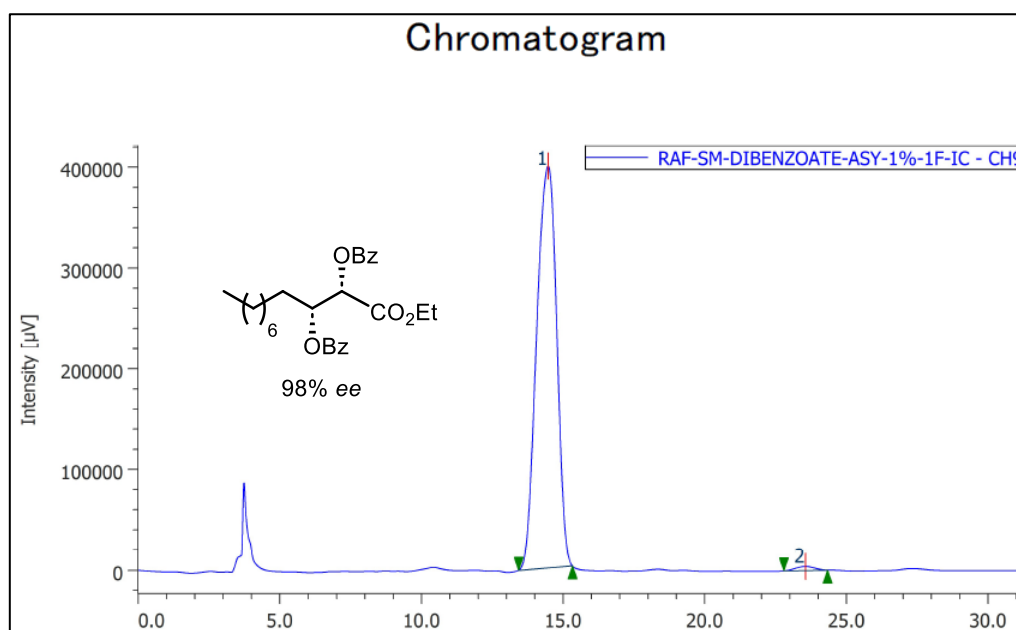
13': HRMS (ESI-TOF) m/z : $[M + Na]^+$ calcd for $C_{27}H_{34}NaO_6$ 477.2248; Found 477.2249.



HPLC chromatograms of racemic and chiral **13'**

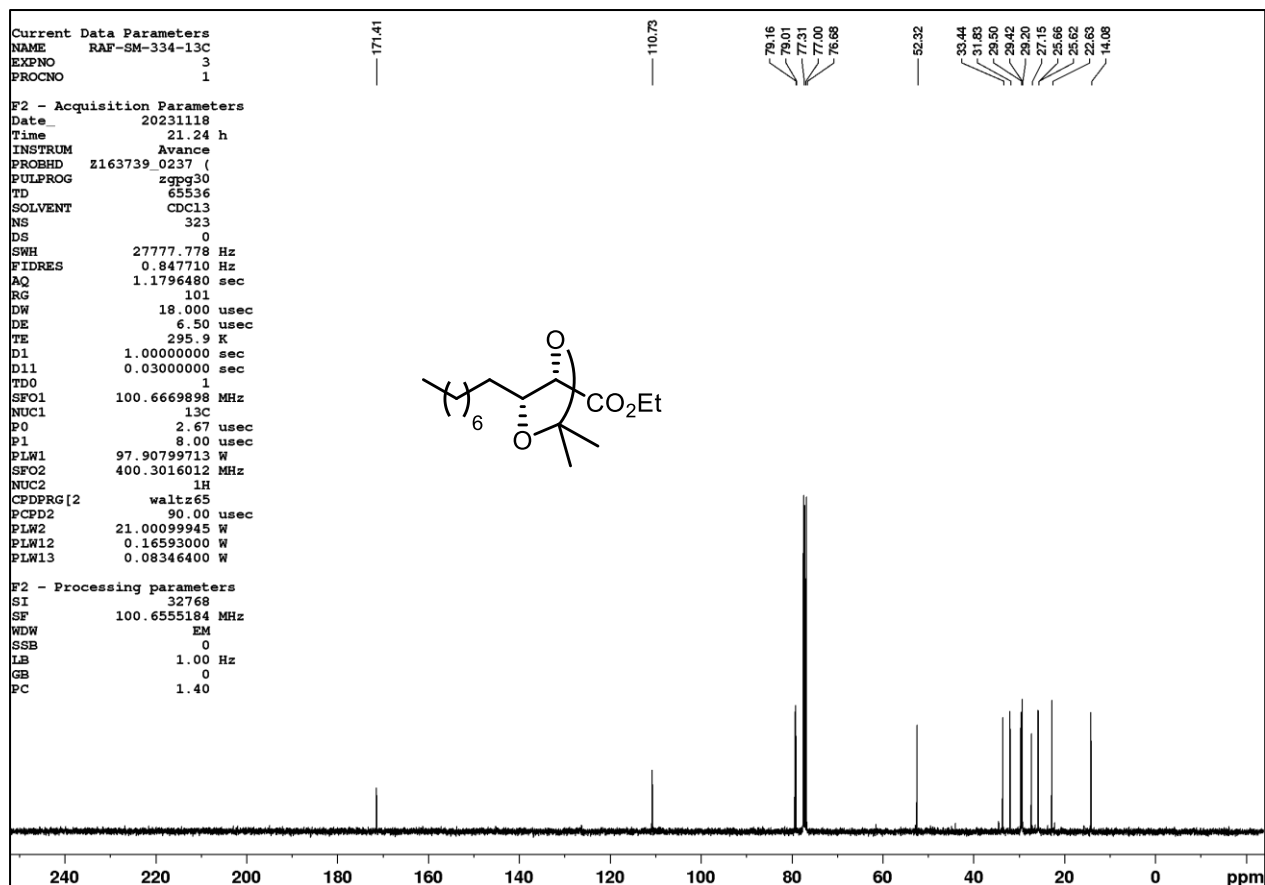
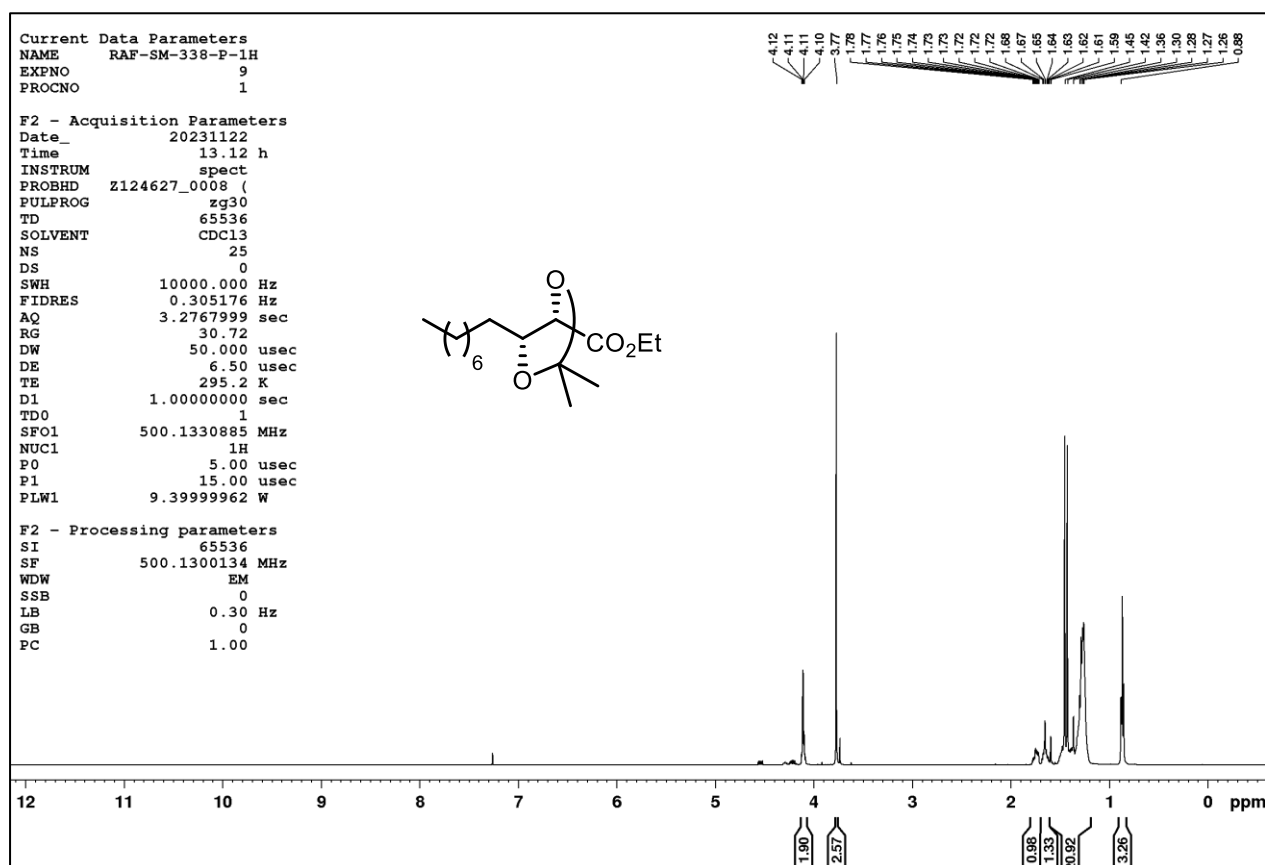


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	13.233	60237946	1132379	50.146	55.394	N/A	1242	5.087	0.927	
2	Unknown	9	21.657	59886137	911843	49.854	44.606	N/A	2269	N/A	1.098	
Total				120124083	2044222			0.00000				

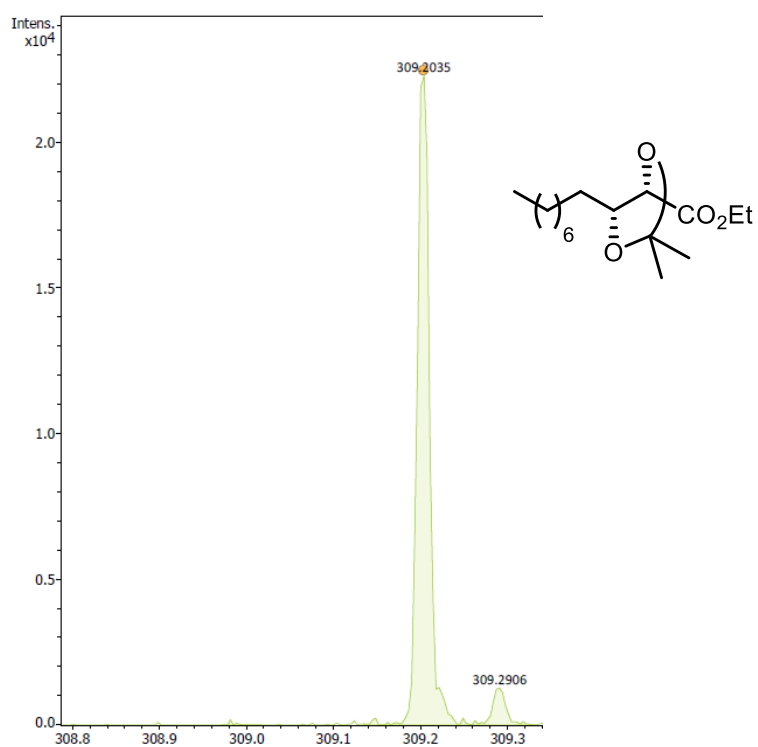


#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	14.467	19530235	398402	99.040	98.973	N/A	1800	6.910	0.913	
2	Unknown	9	23.547	189258	4135	0.960	1.027	N/A	5490	N/A	0.979	
Total				19719493	402537			0.00000				

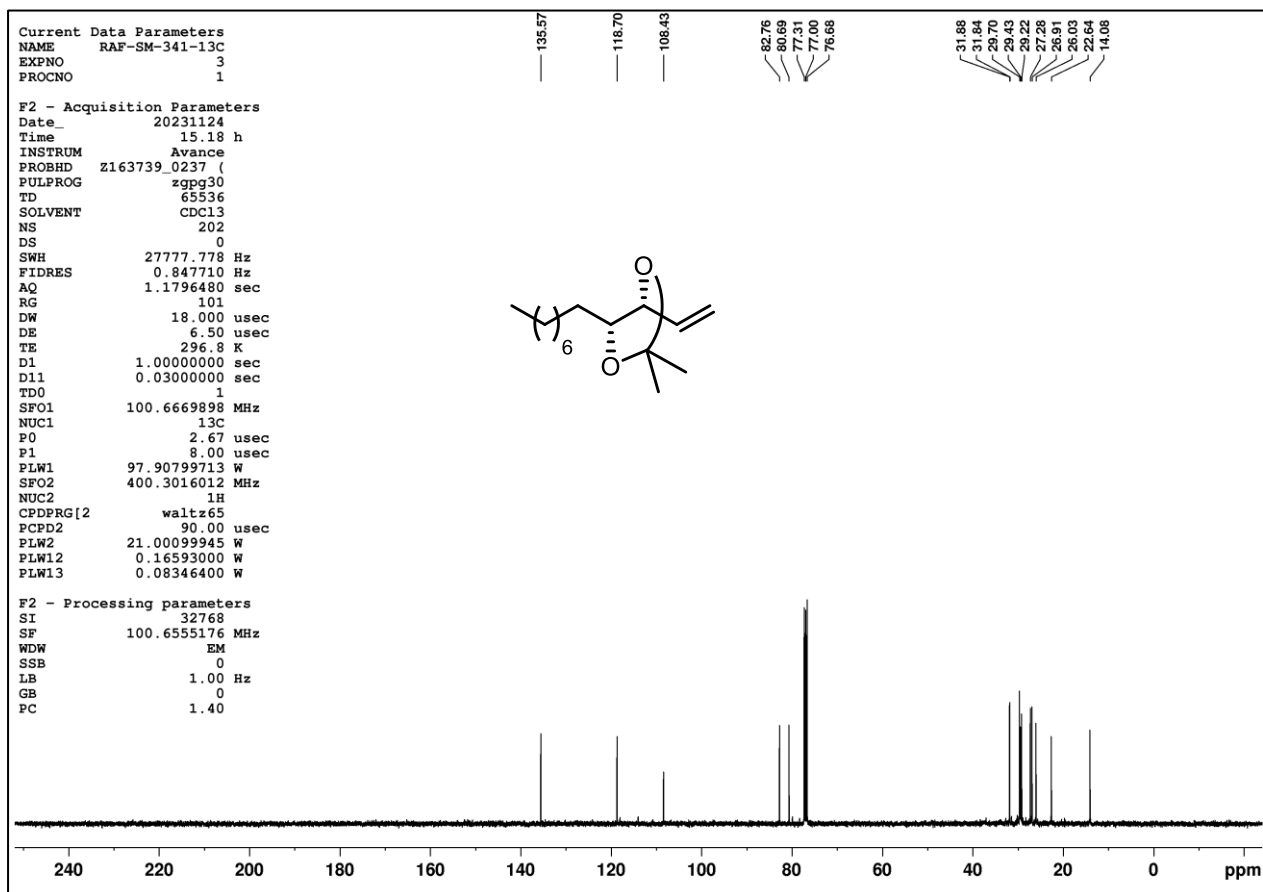
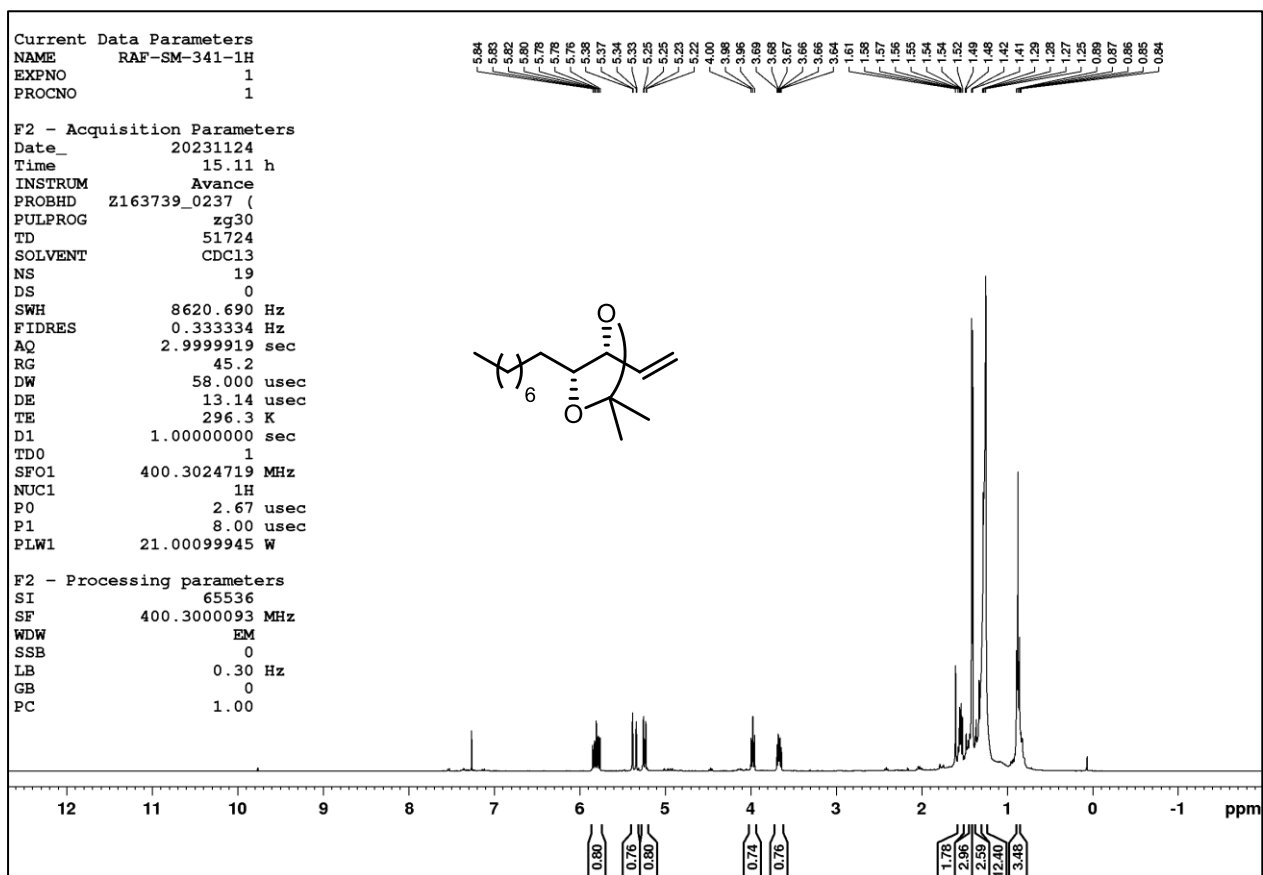
^1H NMR (500 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound **14**



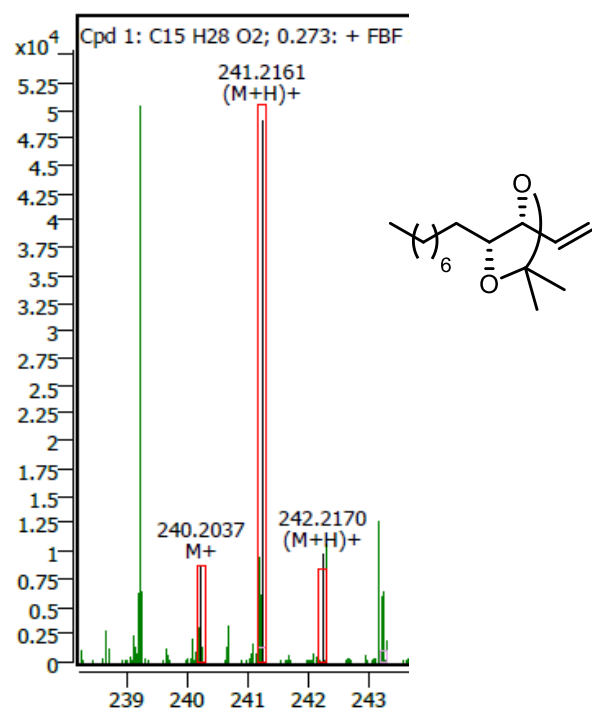
14: HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $C_{16}H_{30}O_4Na$ 309.2036; Found 309.2035



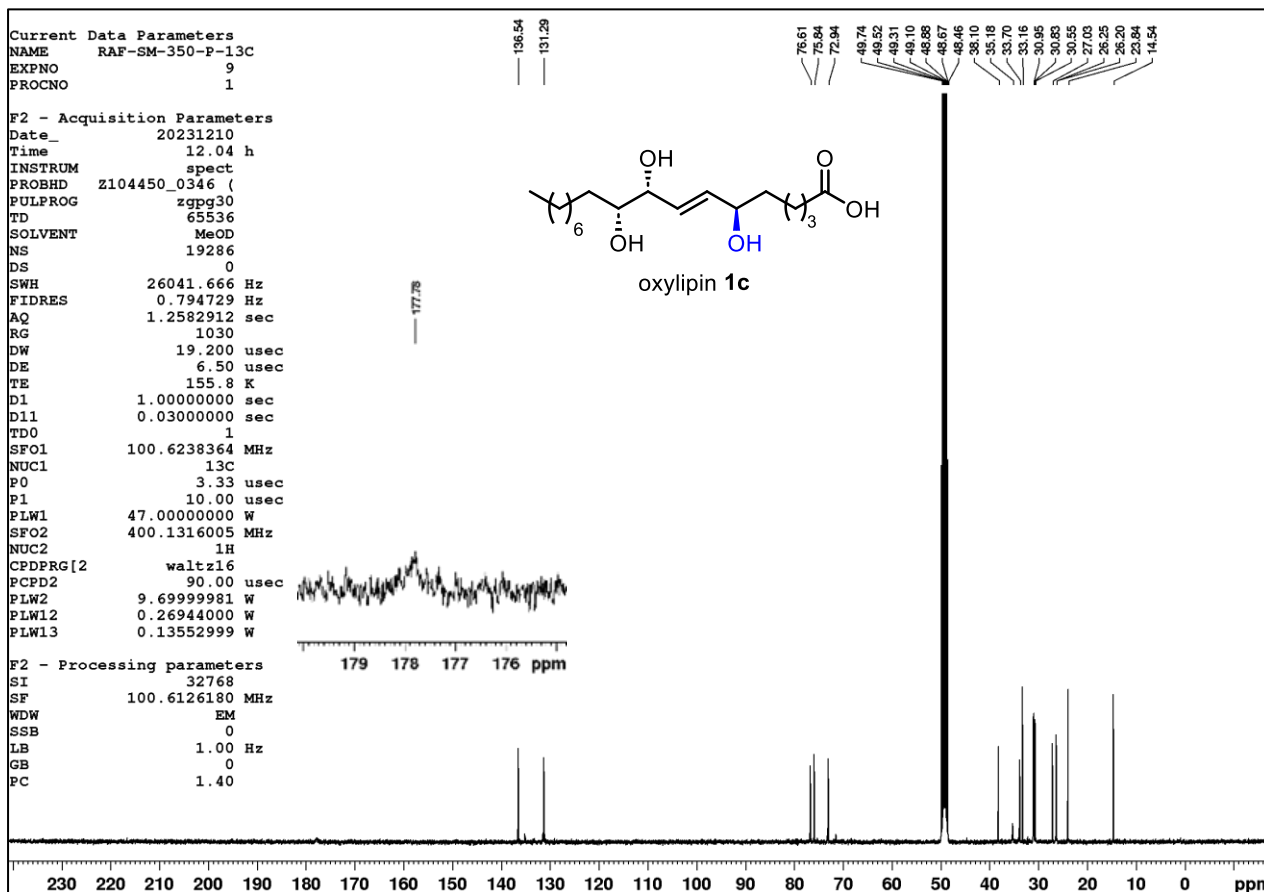
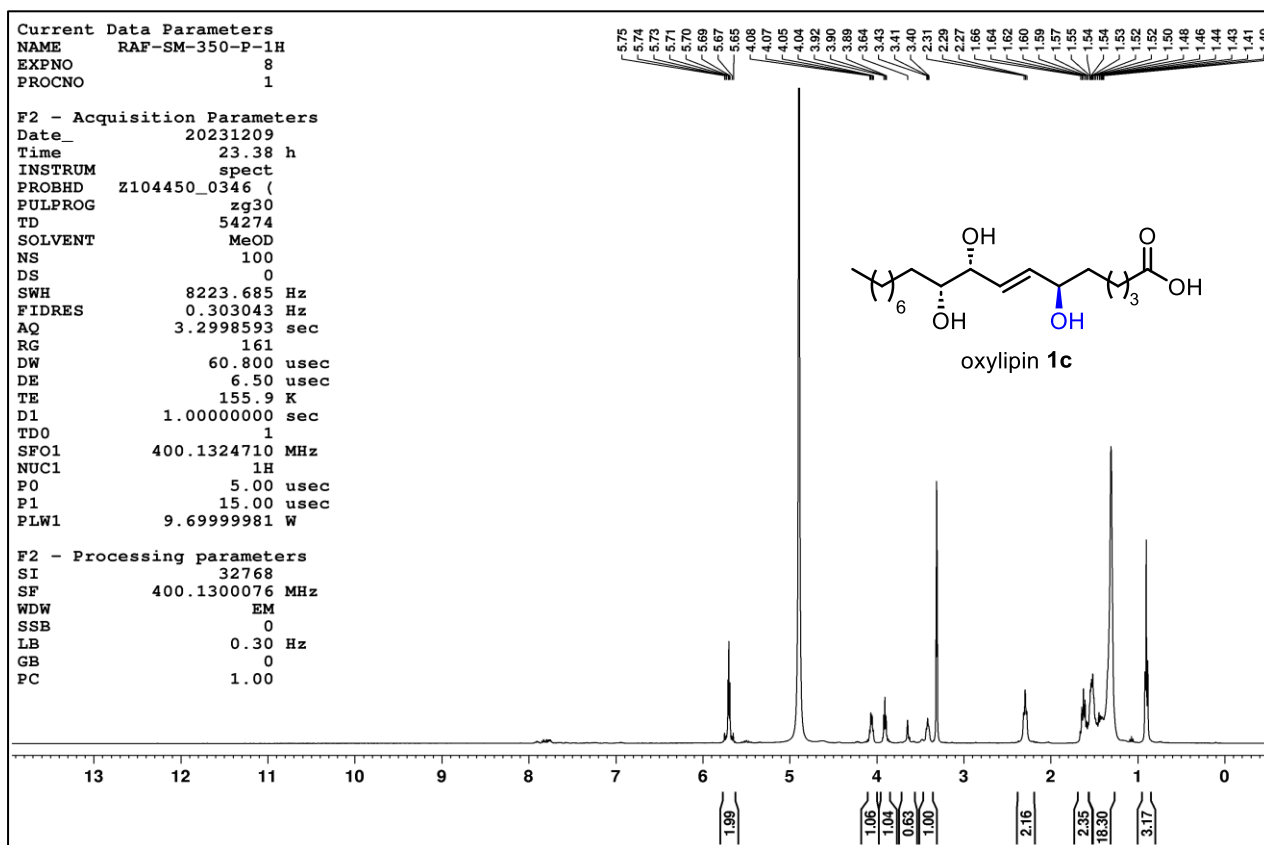
^1H NMR (400 MHz, CDCl_3) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3) of compound 6



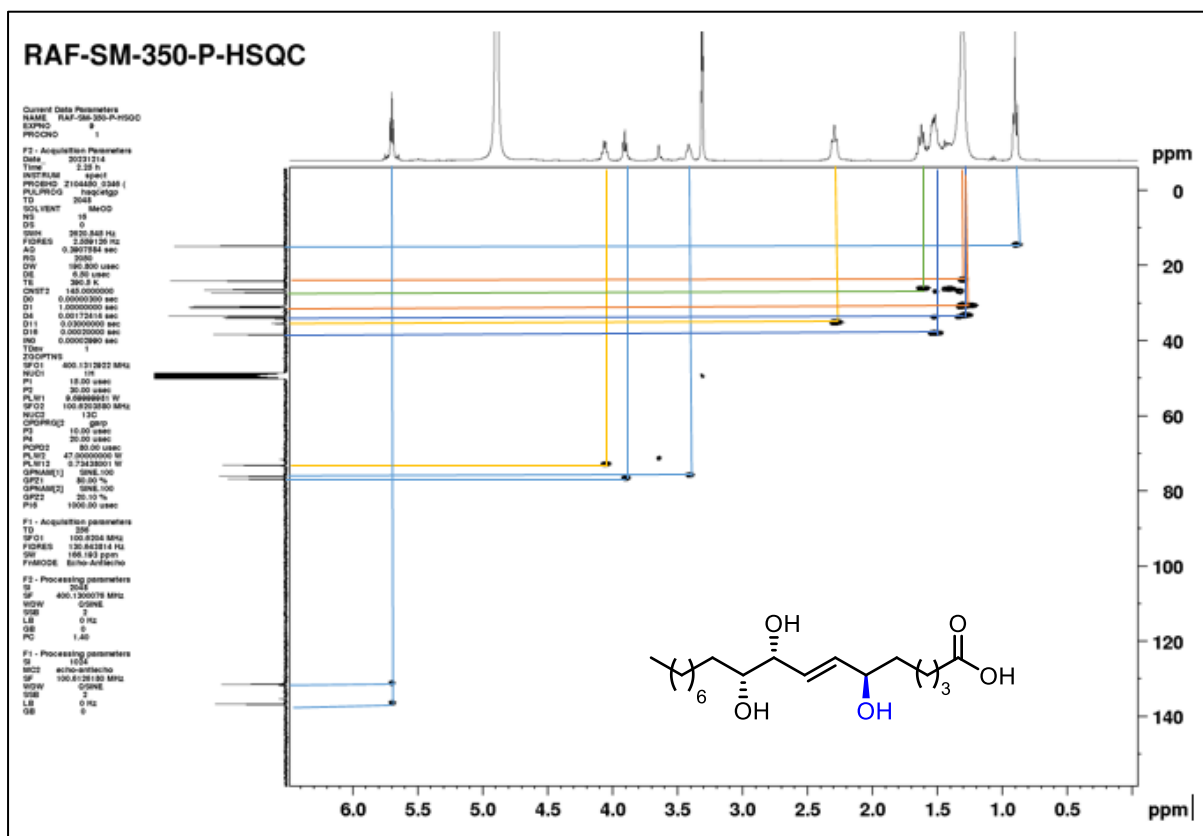
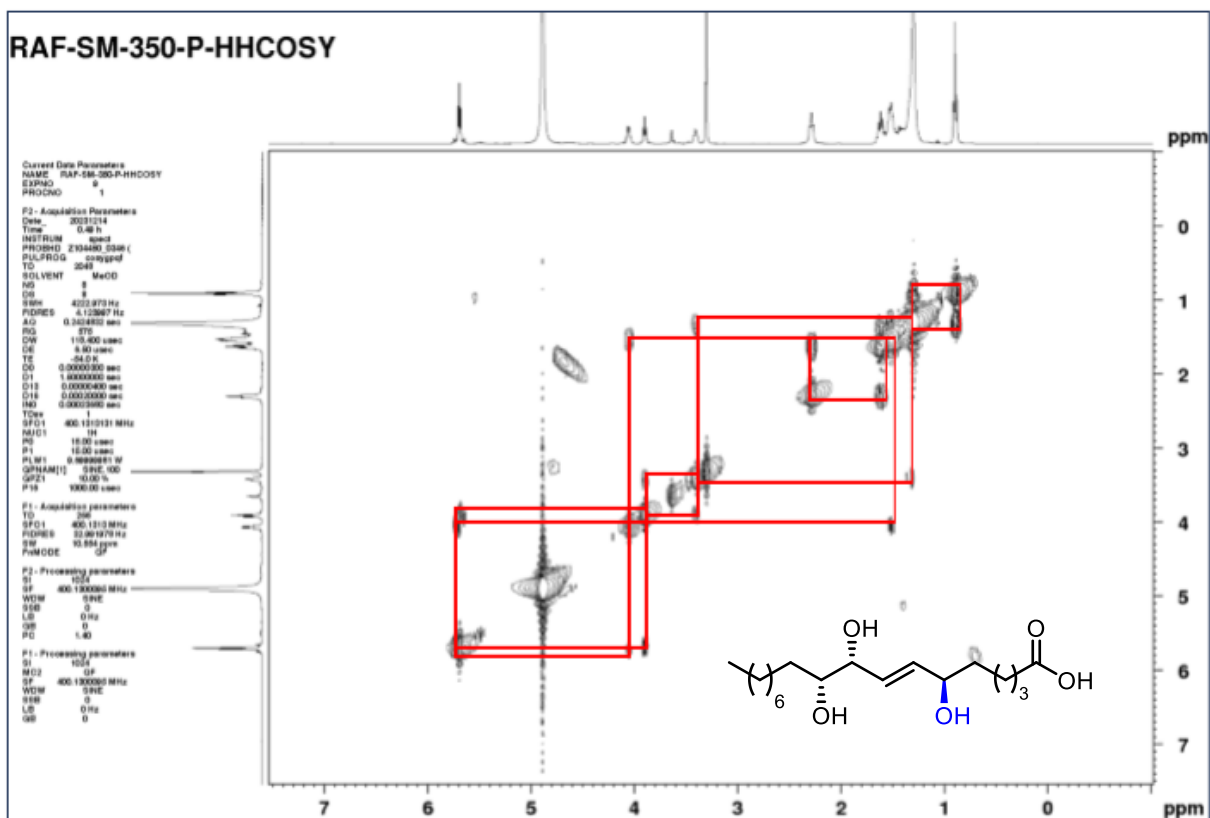
6: HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $C_{15}H_{29}O_2$ 241.2162; Found 241.2161



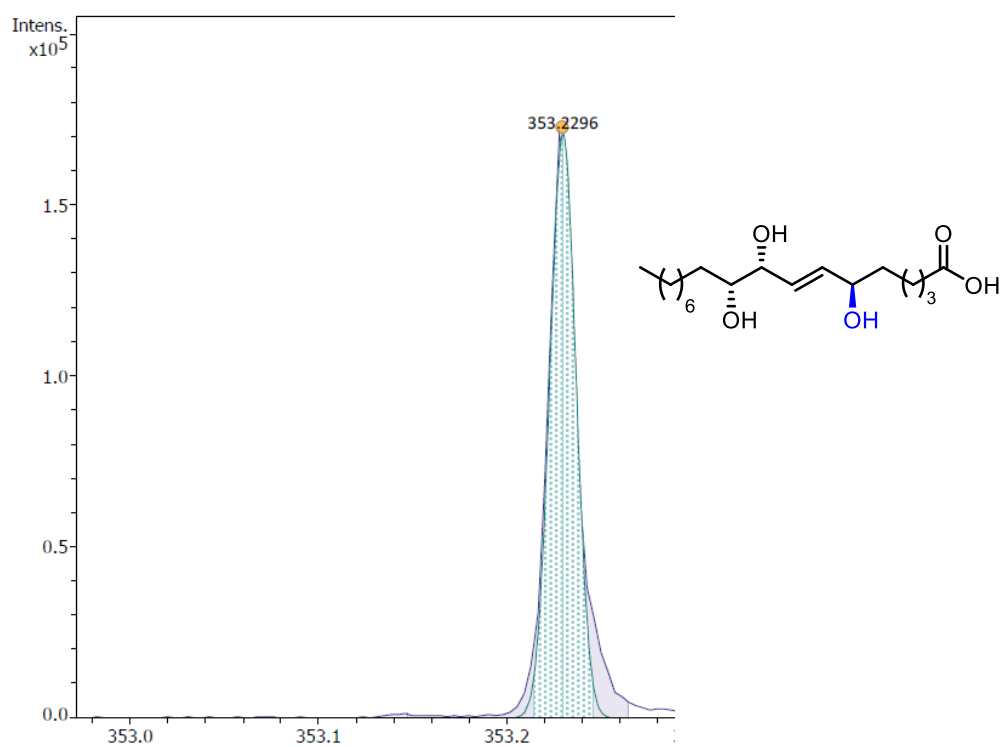
^1H NMR (400 MHz, CD_3OD) and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD_3OD) spectra of compound **1c**



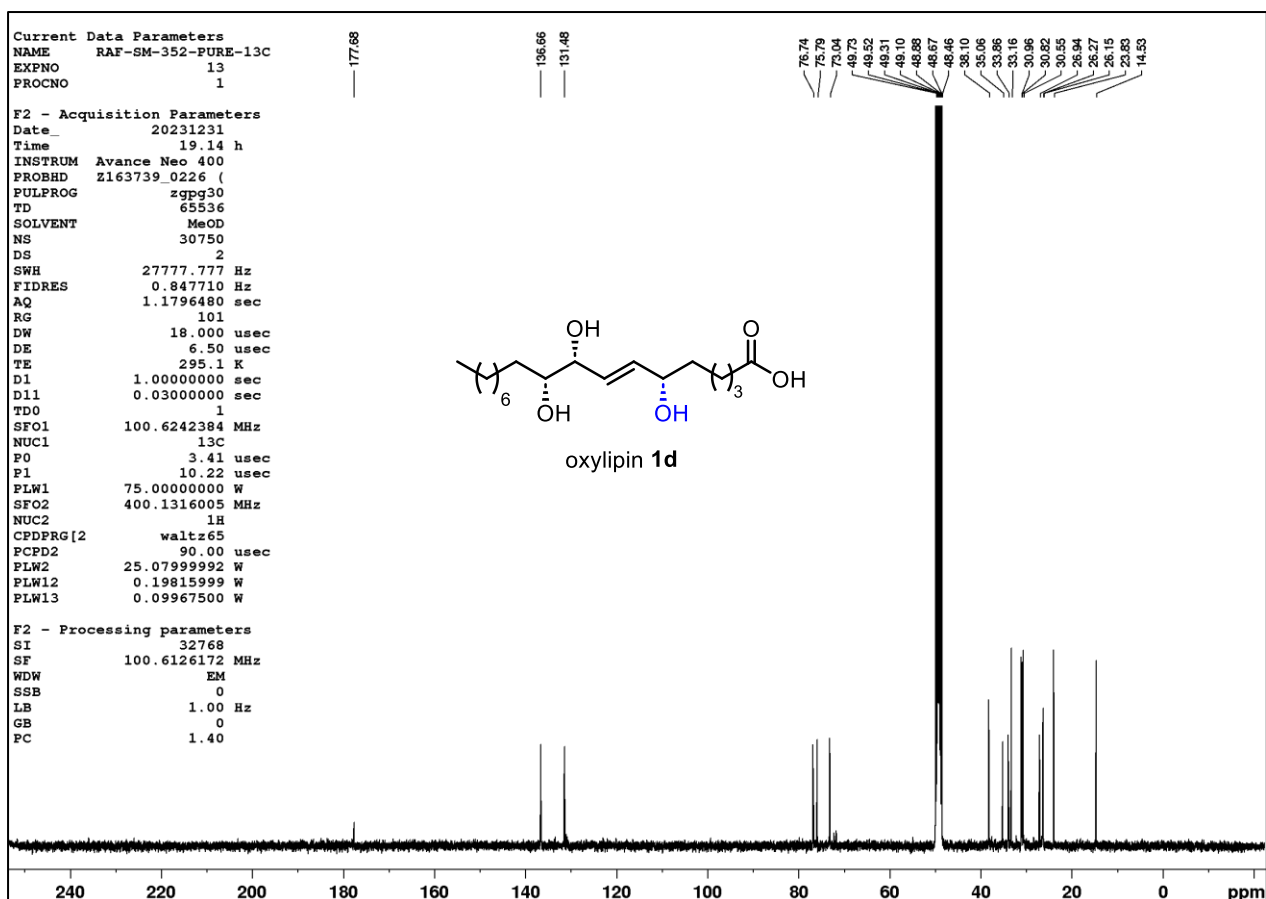
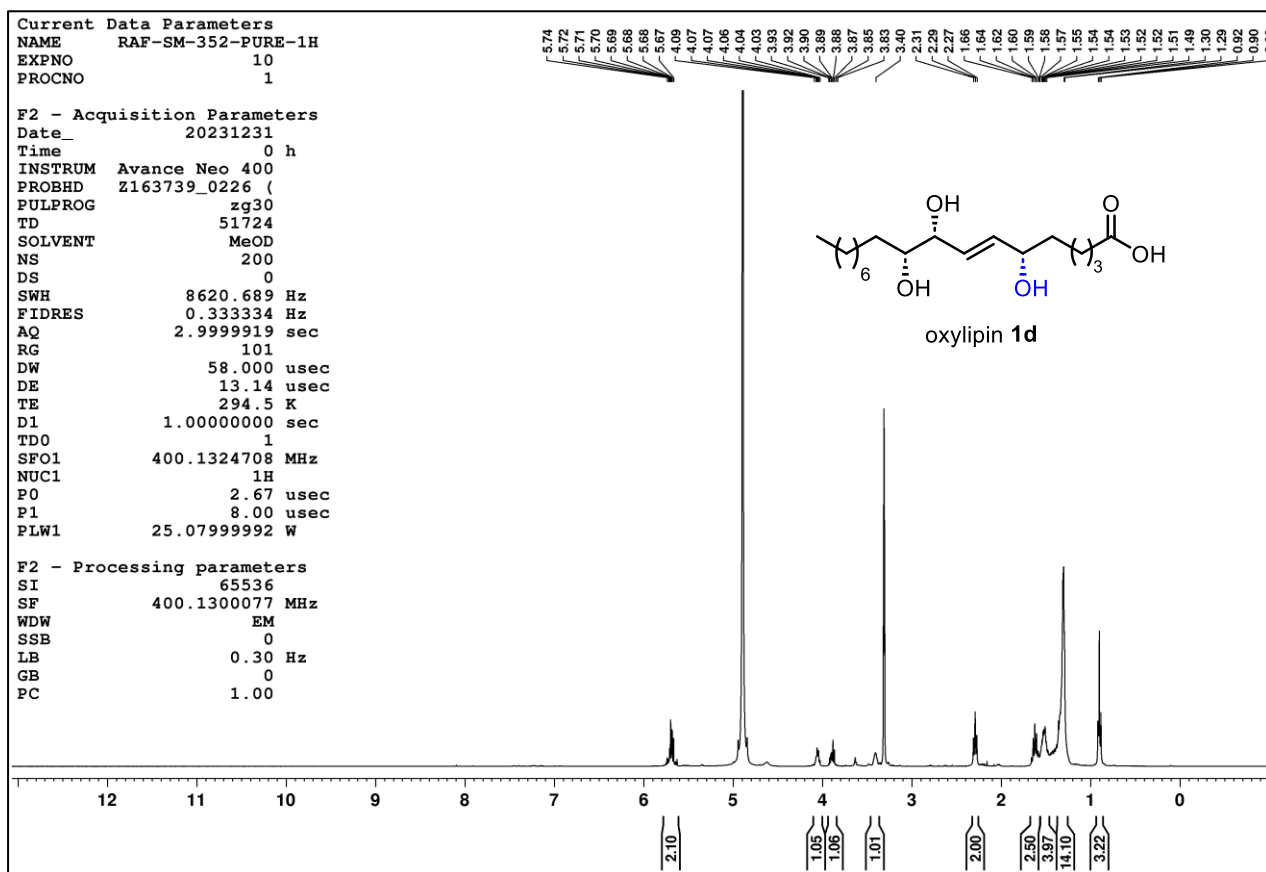
COSY and HSQC of compound 1c



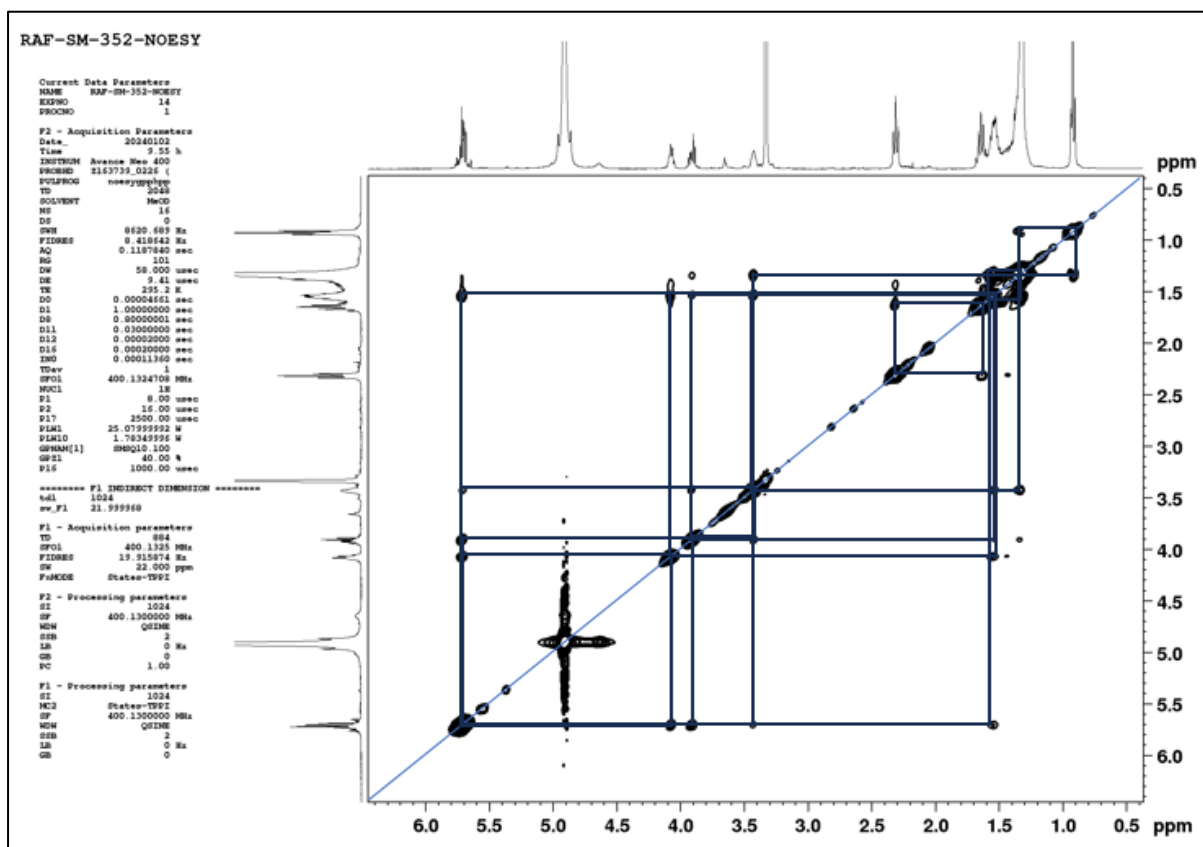
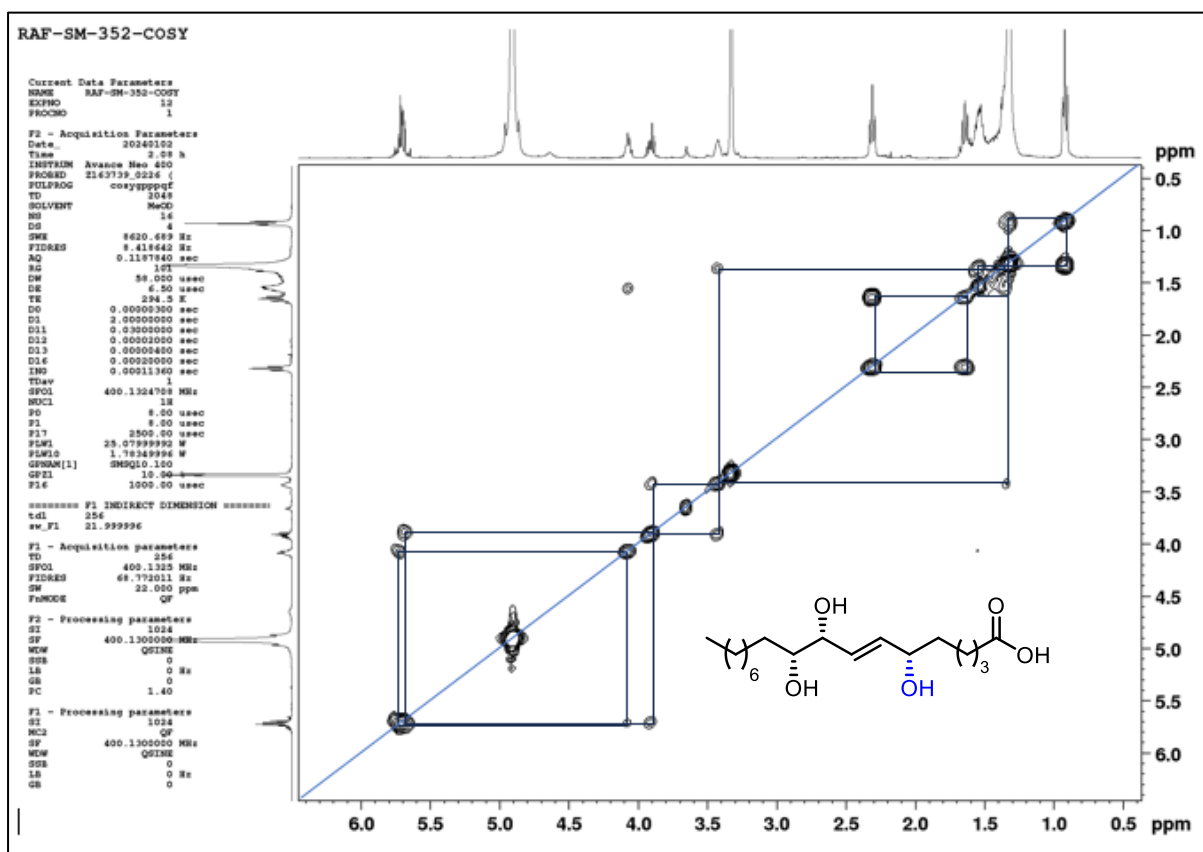
1c: HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $C_{18}H_{34}O_5Na$ 353.2298; Found 353.2296



H NMR (400 MHz, CD₃OD) and ¹³C{¹H} NMR (100 MHz, CD₃OD) spectra of compound **1d**



COSY and NOESY of compound 1d



1d: HRMS (ESI-TOF) m/z : $[M + Na]^+$ Calcd for $C_{18}H_{34}O_5Na$ 353.2298; Found 353.2302

