

Lactol in Asymmetric Aldol-Desymmetrization Sequence: Access to Tetrahydro-4*H*-furo[2,3-*b*]pyran-2-one and Tetrahydro-4*H*-furo[2,3-*b*]furan-2-one Derivatives

Ji-Yao Li,[†] Ke-Wei Yu,[‡] Chao-Chao Xie,[†] Yan-Kai Liu^{*,†}

[†]Key Laboratory of Marine Drugs, Chinese Ministry of Education, School of Medicine and Pharmacy, Ocean University of China, and Laboratory for Marine Drugs and Bioproducts of Qingdao National Laboratory for Marine Science and Technology, Qingdao 266003, People's Republic of China

[‡]Jinan Central Hospital Affiliated to Shandong University, Jinan 250013, People's Republic of China

Supporting Information

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1. Optimization of the Reaction Condition

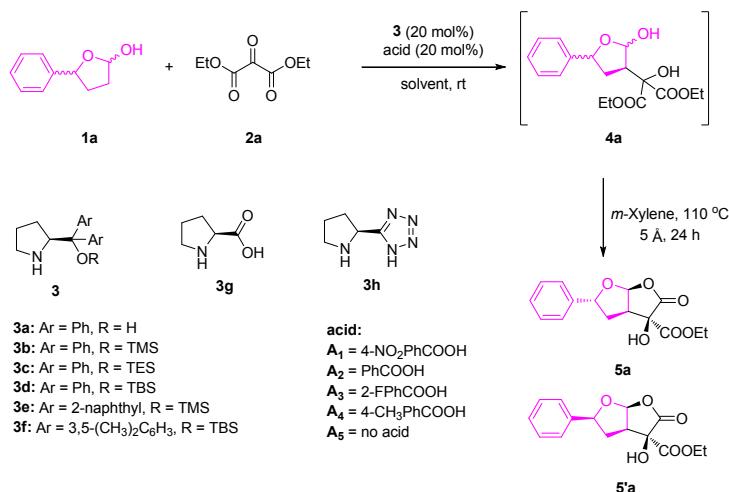


Table 1

Entry	Cat.	Acid	Solvent	Time ^b (h)	Yield ^c (%)	ee ^d (%)		dr ^e
						5a/5'a	5a/5'a	
1 ^f	3a	A ₁	CH ₃ CN	-	-	-	-	-
2	3b	A ₁	CH ₃ CN	15	31/33	>99/96	-/-	-/-
3	3c	A ₁	CH ₃ CN	24	30/32	97/85	-/-	-/-
4	3d	A ₁	CH ₃ CN	15	30/32	91/84	-/-	-/-
5	3e	A ₁	CH ₃ CN	15	27/29	98/96	-/-	-/-
6	3f	A ₁	CH ₃ CN	15	32/33	94/78	-/-	-/-
7	3g	A ₁	CH ₃ CN	48	28/29	-93/-99	-/-	-/-
8	3h	A ₁	CH ₃ CN	>48	trace	-	-/-	-/-
9	3b	A ₂	CH ₃ CN	28	26/25	97/96	-/-	-/-
10	3b	A ₃	CH ₃ CN	24	32/30	98/96	-/-	-/-
11	3b	A ₄	CH ₃ CN	36	23/24	96/98	-/-	-/-
12 ^g	3b	A ₅	CH ₃ CN	-	-/-	-/-	-/-	-/-
13	3b	A ₃	CH ₂ Cl ₂	10	28/27	96/95	2.7:1/-	
14	3b	A ₃	toluene	8	24/25	98/99	1.0:1/-	
15	3b	A ₃	THF	24	29/28	>96/96	35.0:1/-	
16 ^h	3b	A ₃	CH ₃ CN/H ₂ O	12	31/32	>99/98	11.0:1/-	
17 ⁱ	3b	A ₃	CH ₂ Cl ₂ /H ₂ O	12	27/26	98/95	2.5:1/-	

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.36 mmol, 1.2 equiv), **2a** (0.3 mmol, 1.0 equiv) in solvent (0.6 mL) with **3** (20 mol%) and **acid** (20 mol%) at 25 °C. After workup, the mixture was concentrated and the residue was purified by flash chromatography on silica gel to afford **4a**. Then, *m*-Xylene (2.0 mL) and 5 Å (1.0 equiv) were added to the reaction at 110 °C for 24 hours, After full conversion of the second step, the residue was purified by flash chromatography on silica gel. [c] Yield of **5a** and **5'a**. [b] For the first step. [d/e] Determined by Chiral HPLC analysis. [f/g] No reaction. [h/i] 20% H₂O was added. Entry in bold marks optimized conditions.

2. Details of Reaction Conditions Study

Table 2. Screening of catalysts^a

Reaction Scheme:

1a + 2a $\xrightarrow[CH_3CN, rt]{\begin{matrix} \mathbf{3} (20 \text{ mol}\%) \\ \mathbf{A}_1 (20 \text{ mol}\%) \end{matrix}} 4a$

4a $\xrightarrow[m\text{-Xylene, } 110^\circ\text{C}]{5 \text{ \AA}, 24 \text{ h}} \begin{matrix} \mathbf{5a} \\ \mathbf{5}'a \end{matrix}$

Catalysts (3):

- 3a: Ar = Ph, R = H
- 3b: Ar = Ph, R = TMS
- 3c: Ar = Ph, R = TES
- 3d: Ar = Ph, R = TBS
- 3e: Ar = 2-naphthyl, R = TMS
- 3f: Ar = 3,5-(CH₃)₂C₆H₃, R = TBDMS

Compounds (3g, 3h):

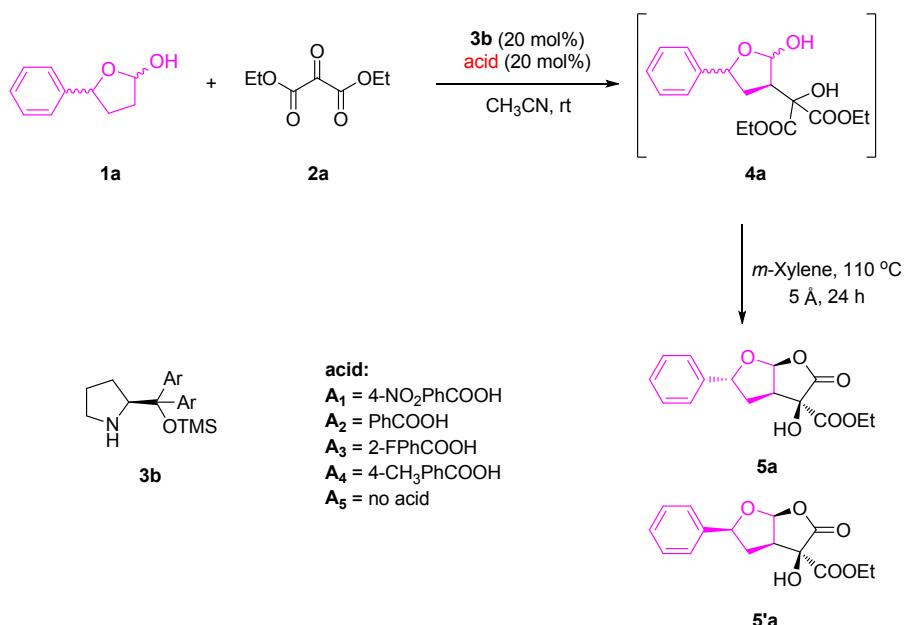
- 3g: N-hydroxy-2-pyrrolidinone
- 3h: 2-(azidomethyl)piperidin-3-one

Table 2: Screening of Catalysts^a

Entry	Cat.	Acid	Solvent	Time ^b (h)	Yield ^c (%)		ee ^d (%)
					5a/5'a	5a/5'a	
1 ^e	3a	A ₁	CH ₃ CN	-	-	-	-/-
2	3b	A ₁	CH ₃ CN	15	31/33	>99/96	
3	3c	A ₁	CH ₃ CN	24	30/32	97/98	
4	3d	A ₁	CH ₃ CN	15	30/32	91/84	
5	3e	A ₁	CH ₃ CN	15	27/29	98/96	
6	3f	A ₁	CH ₃ CN	15	32/33	94/78	
7	3g	A ₁	CH ₃ CN	48	28/29	-93/-99	
8	3h	A ₁	CH ₃ CN	>48	trace	-/-	

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.36 mmol, 1.2 equiv), **2a** (0.3 mmol, 1.0 equiv) in solvent (0.6 mL) with **3** (20 mol%) and **A₁** (20 mol%) at 25 °C. After workup, the mixture was concentrated and the residue was purified by flash chromatography on silica gel to afford **4a**. Then, *m*-xylene (2.0 mL) and 5 Å (1.0 equiv) were added to the reaction at 110 °C for 24 hours, after full conversion of the second step, the residue was purified by flash chromatography on silica gel. [b] For the first step. [c] Yield of **5a** and **5'a**, [d] Determined by Chiral HPLC analysis. [e] No reaction.

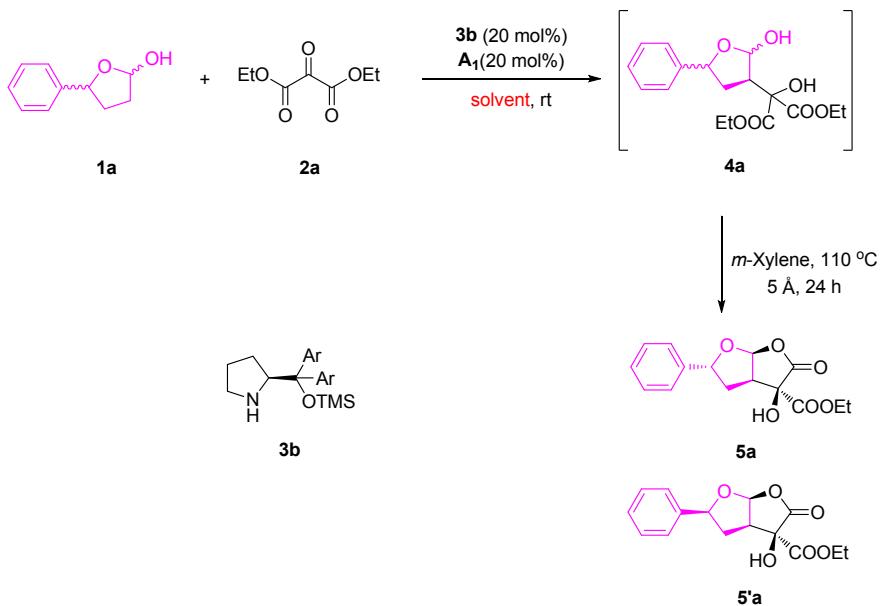
Table 3. Screening of acids^a



Entry	Cat.	Acid	Solvent	Time ^b (h)	Yield ^c (%)		ee ^d (%)
					5a/5'a	5a/5'a	
1	3b	A₁	CH ₃ CN	15	31/33	>99/96	
2	3b	A₂	CH ₃ CN	28	26/25	97/96	
3	3b	A₃	CH ₃ CN	24	32/30	98/96	
4	3b	A₄	CH ₃ CN	36	23/24	96/98	
5 ^e	3b	A₅	CH ₃ CN	-	-/-	-/-	

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.36 mmol, 1.2 equiv), **2a** (0.3 mmol, 1.0 equiv) in solvent (0.6 mL) with **3b** (20 mol%) and **acid** (20 mol%) at 25 °C. After workup, the mixture was concentrated and the residue was purified by flash chromatography on silica gel to afford **4a**. Then, *m*-Xylene (2.0 mL) and 5 Å (1.0 equiv) were added to the reaction at 110 °C for 24 hours, after full conversion of the second step, the residue was purified by flash chromatography on silica gel. [b] For the first step. [c] Yield of **5a** and **5'a**, [d] Determined by Chiral HPLC analysis. [e] No reaction.

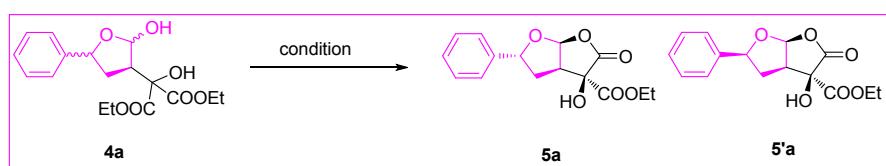
Table 4. Screening of solvents^a



Entry	Cat.	Acid	Solvent	Time ^b (h)	Yield ^c (%)		dr ^e
					5a/5'a	ee ^d (%)	
1	3b	A ₁	CH ₃ CN	15	31/33	>99/96	
2	3b	A ₁	CH ₂ Cl ₂	10	28/27	96/95	2.7:1/-
3	3b	A ₁	toluene	8	24/25	9899	1.0:1/-
4	3b	A ₁	THF	24	29/28	>96/96	35.0:1/-
5 ^f	3b	A ₁	CH ₃ CN/H ₂ O	12	31/32	>99/98	11.0:1/-
6 ^g	3b	A ₁	CH ₂ Cl ₂ /H ₂ O	12	27/26	98/95	2.5:1/-

[a] Unless otherwise specified, all reactions were carried out using **1a** (0.36 mmol, 1.2 equiv), **2a** (0.3 mmol, 1.0 equiv) in solvent (0.6 mL) with **3b** (20 mol%) and **A₁** (20 mol%) at 25 °C. After workup, the mixture was concentrated and the residue was purified by flash chromatography on silica gel to afford **4a**. Then, *m*-xylene (2.0 mL) and 5 Å (1.0 equiv) were added to the reaction at 110 °C for 24 hours, after full conversion of the second step, the residue was purified by flash chromatography on silica gel. [b] For the first step. [c] Yield of **5a** and **5'a**. [d/e] Determined by Chiral HPLC analysis. [f/g] 20 % H₂O was added.

Table 5. Screening of second step



Condition ^a	Time ^b (h)	Yield ^c (%)	
		5a/5'a	5a/5'a
3.0 eq PTSA, DCM, 20 °C	15	25/12	96/90
3.0 eq BF ₃ ·Et ₂ O, DCM, 0 °C	3	mess	-
2.0 eq FeCl ₃ ·6H ₂ O, DCM, 25 °C	5	mess	-
6M HCl : CH ₃ CN 1:1, 40 °C	12	trace	96/90
2.0 eq LiClO ₄ , toluene, 40 °C	>48	-	-
2.0 eq LiClO ₄ , toluene, 110 °C	4	mess	-
0.2 eq PTSA, toluene, 110 °C	4	mess	-
Toluene, 110 °C	24	23/34	99/96
<i>m</i> -Xylene, 110 °C	15	25/33	98/93
<i>m</i> -Xylene, 5 Å, 110 °C	15	31/33	>99/96
1.2 eq DBU, THF, 25 °C	5	-	-

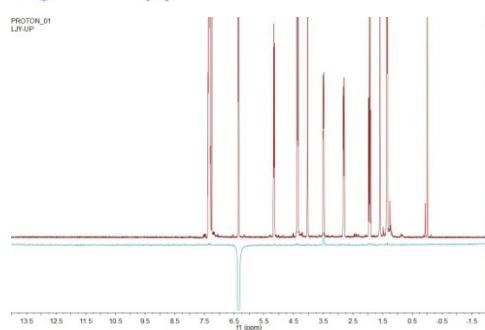
[a] In solvent (1.0 mL) with **4a** (0.1 mmol). [b] For the second step. [c] Yield of **5a** and **5'a**. [d] Determined by Chiral HPLC analysis. DCM = dichloromethane; PTSA = *p*-toluenesulfonic acid; DBU = 1,8-Diazabicyclo[5.4.0]undec-7-ene.

3. The Determination of the Absolute Configuration of Compound 5a/5'd/5h/5'h/5l

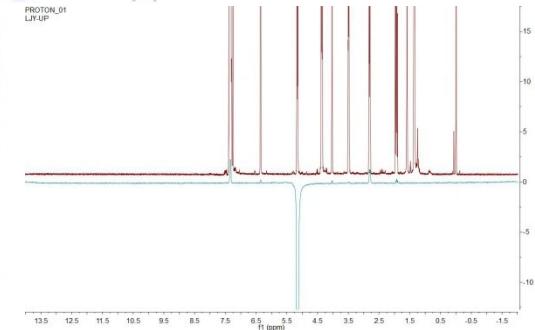
Up Spot 5a:

The determination of the relative configuration of compound 5a by NOE

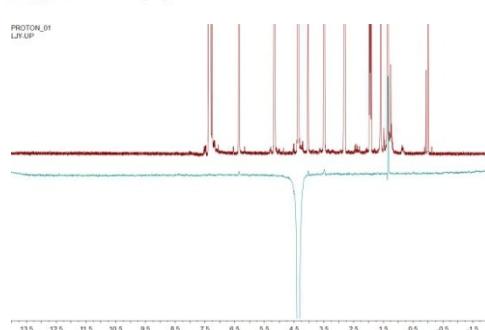
H₃: 6.36 ppm



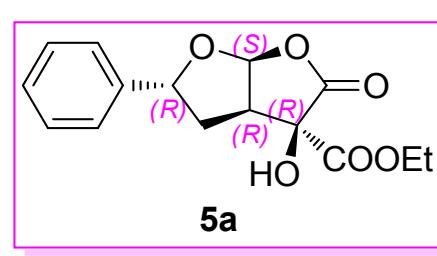
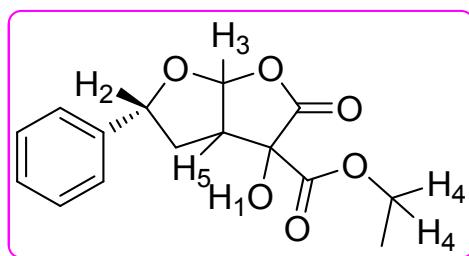
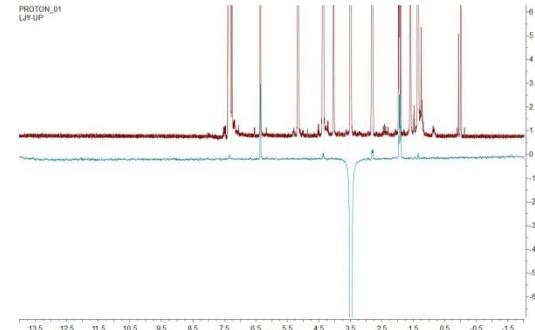
H₂: 5.16 ppm



H₄: 4.36 ppm



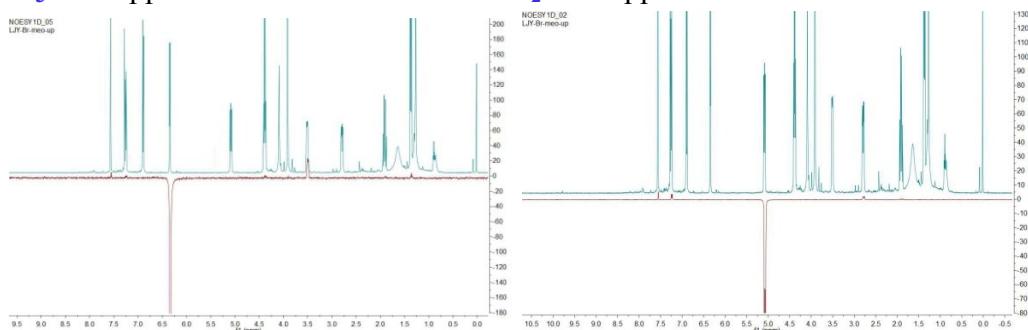
H₅: 3.49 ppm



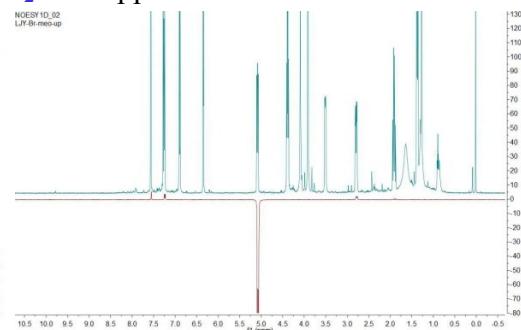
Up Spot 5h:

The determination of the relative configuration of compound 5h by NOE

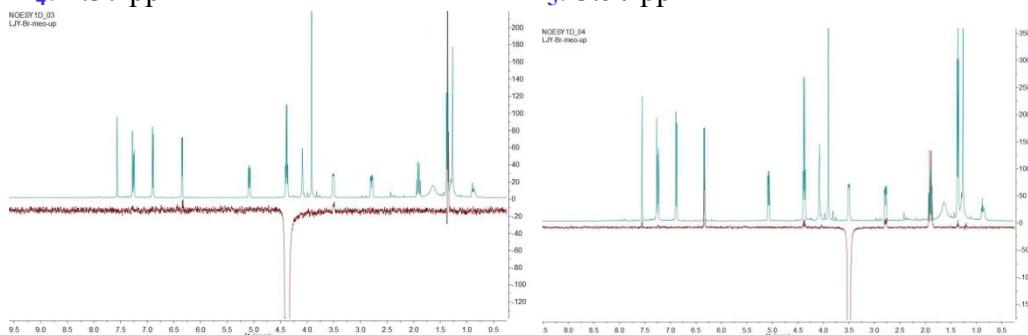
H₃: 6.33 ppm



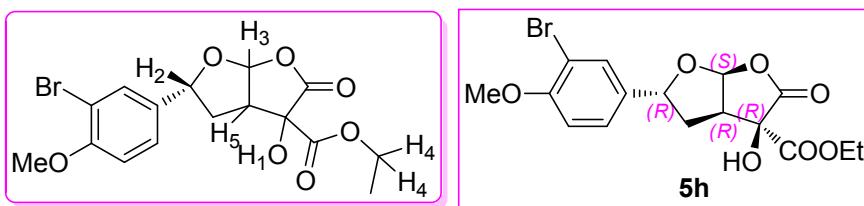
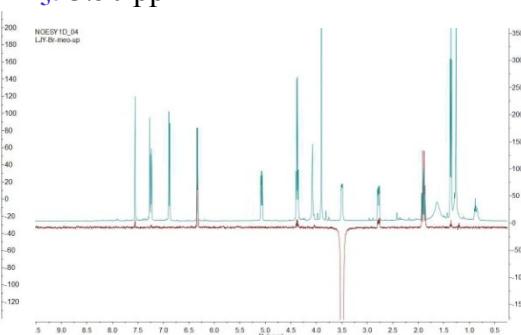
H₂: 5.07 ppm



H₄: 4.37 ppm



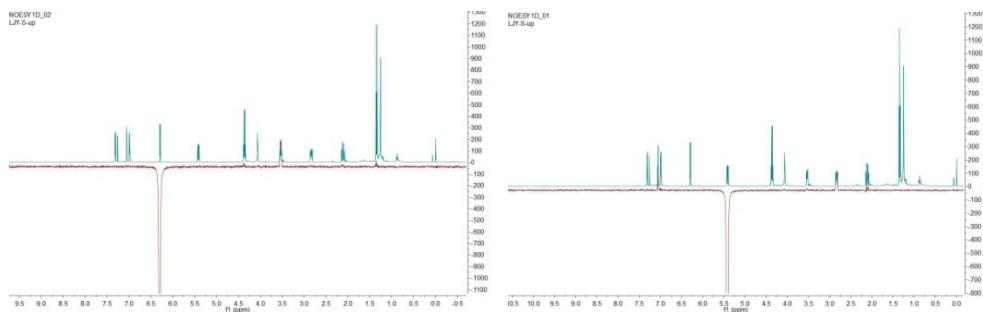
H₅: 3.50 ppm



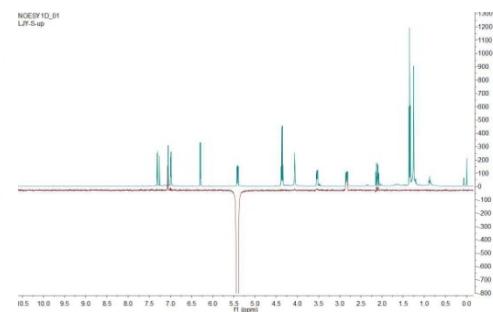
Up Spot 5l:

The determination of the relative configuration of compound 5l by NOE

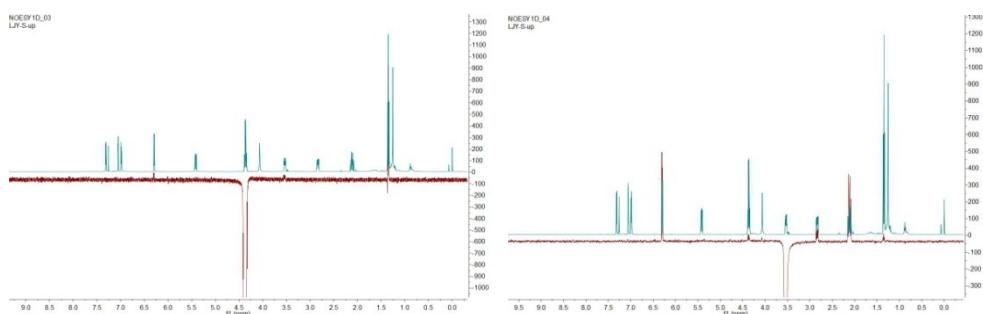
H₃: 6.30 ppm



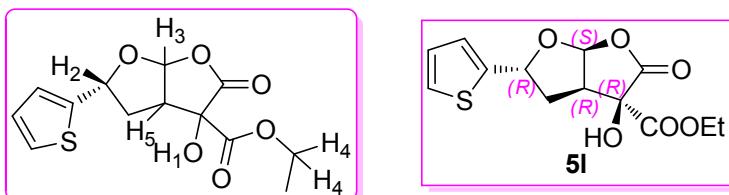
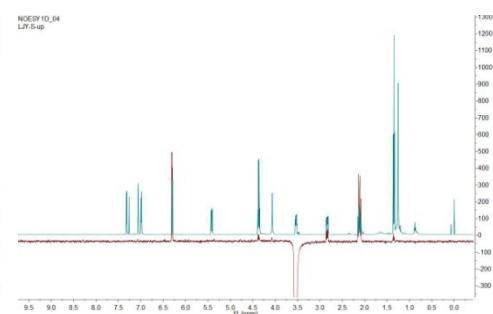
H₂: 5.42 ppm



H₄: 4.37 ppm



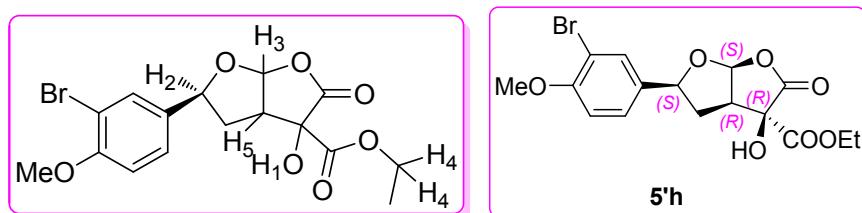
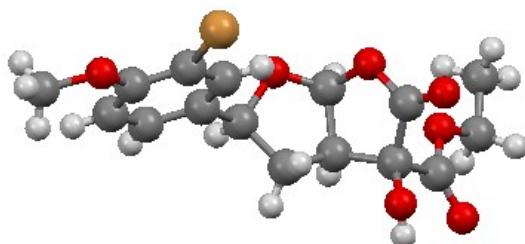
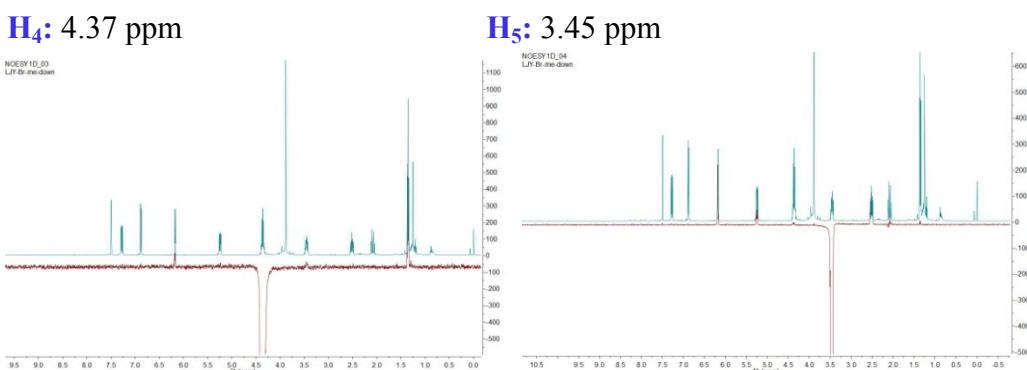
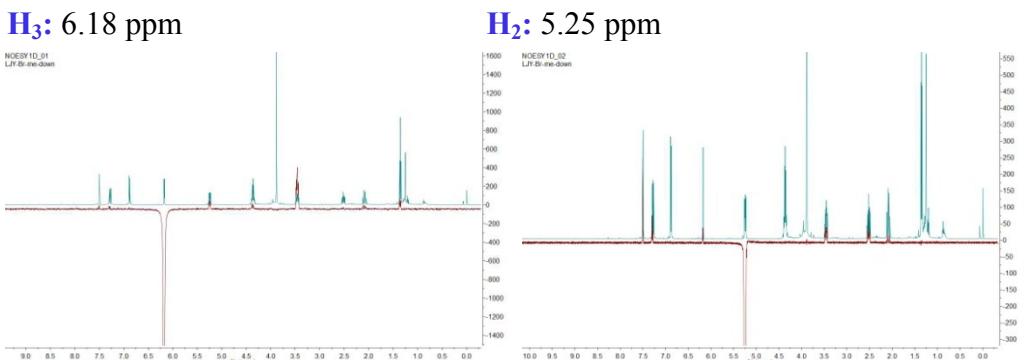
H₅: 3.50 ppm



Down Spot 5'h:

The determination of the absolute configuration of compound 5'h by Single Crystal X-Ray and NOE.

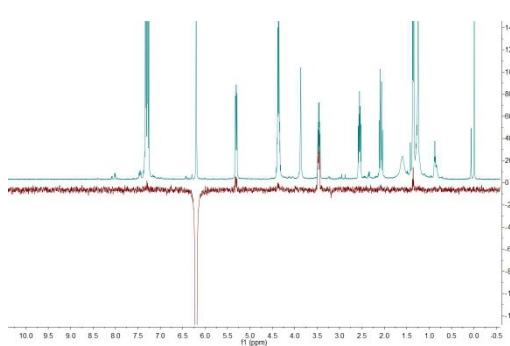
[CCDC 1510140 (5'h) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif].



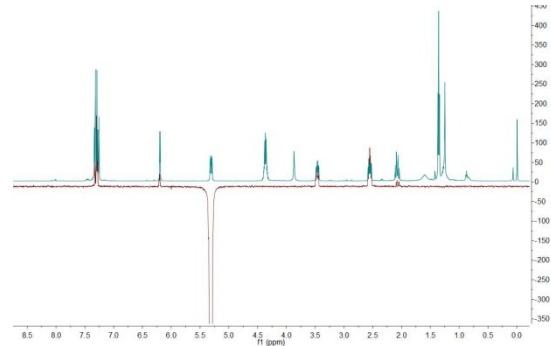
Down Spot 5'd:

The determination of the relative configuration of compound 5'd by NOE

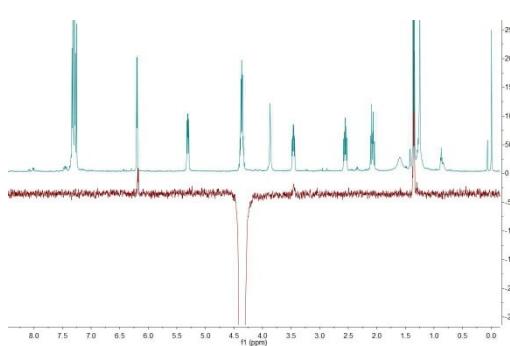
H₃: 6.20 ppm



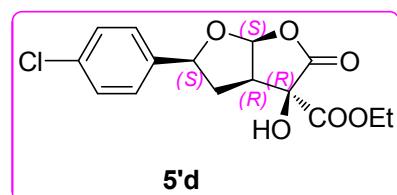
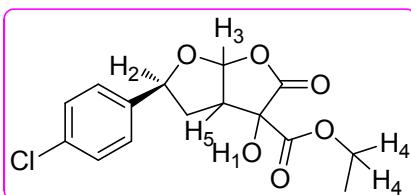
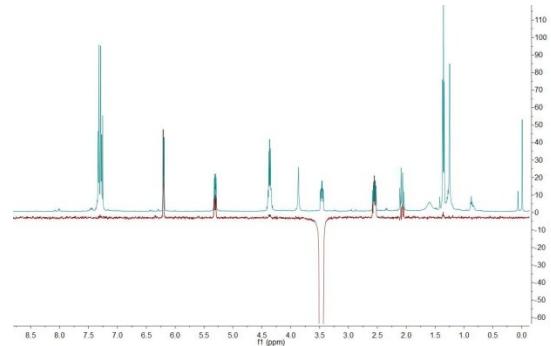
H₂: 5.32 ppm



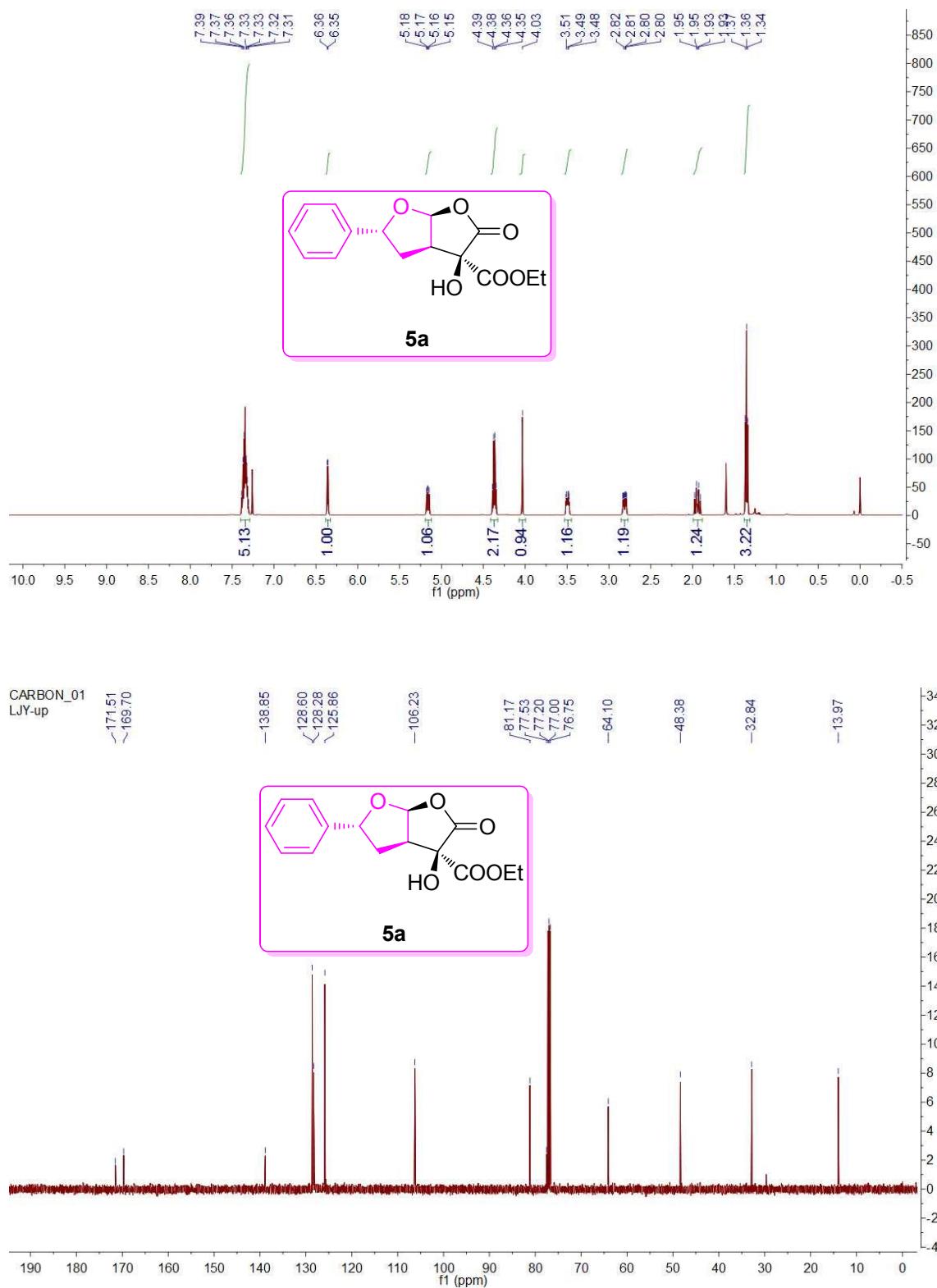
H₄: 4.37 ppm

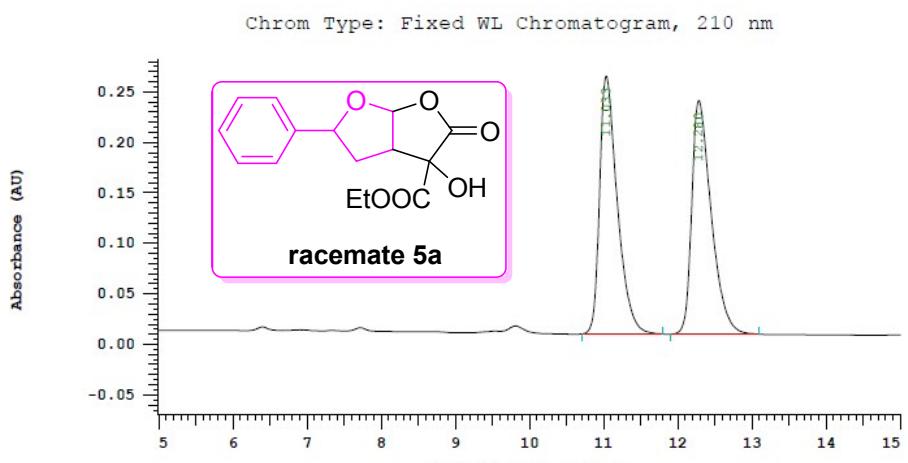


H₅: 3.47 ppm



4. NMR spectra and HPLC Traces



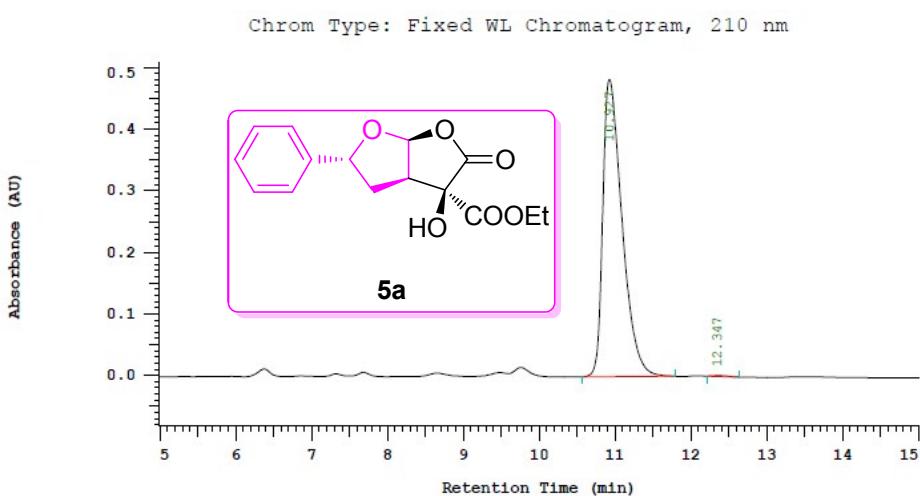


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

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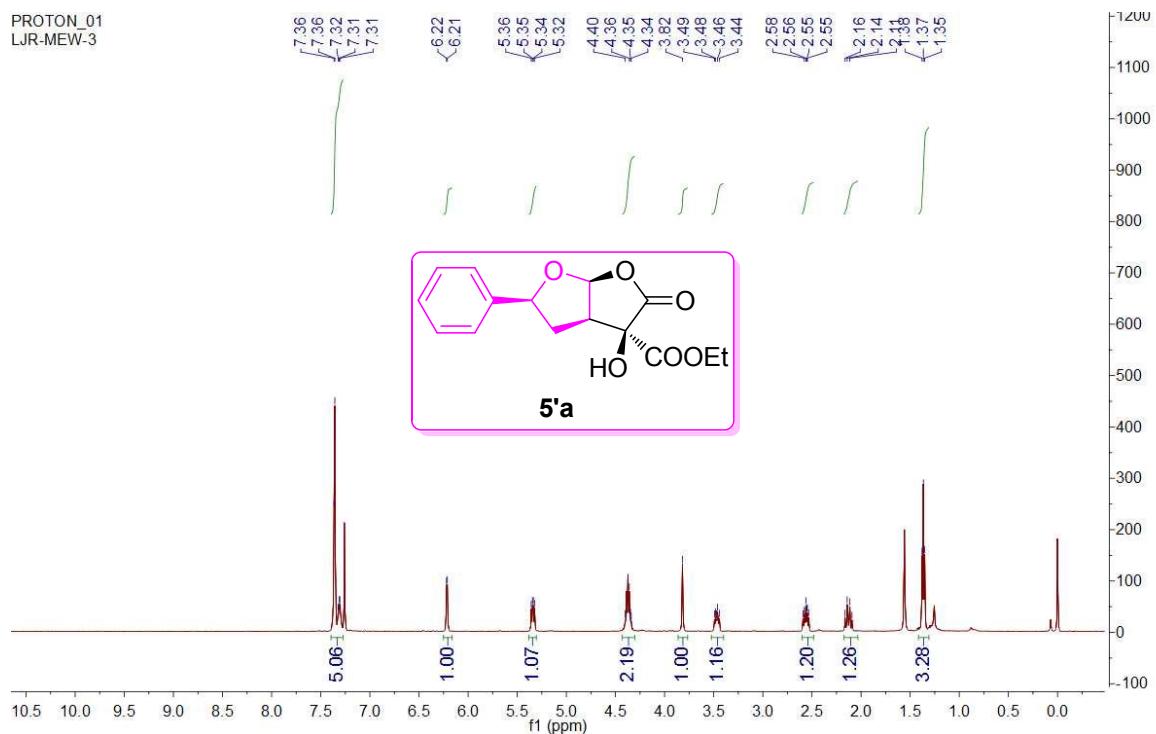
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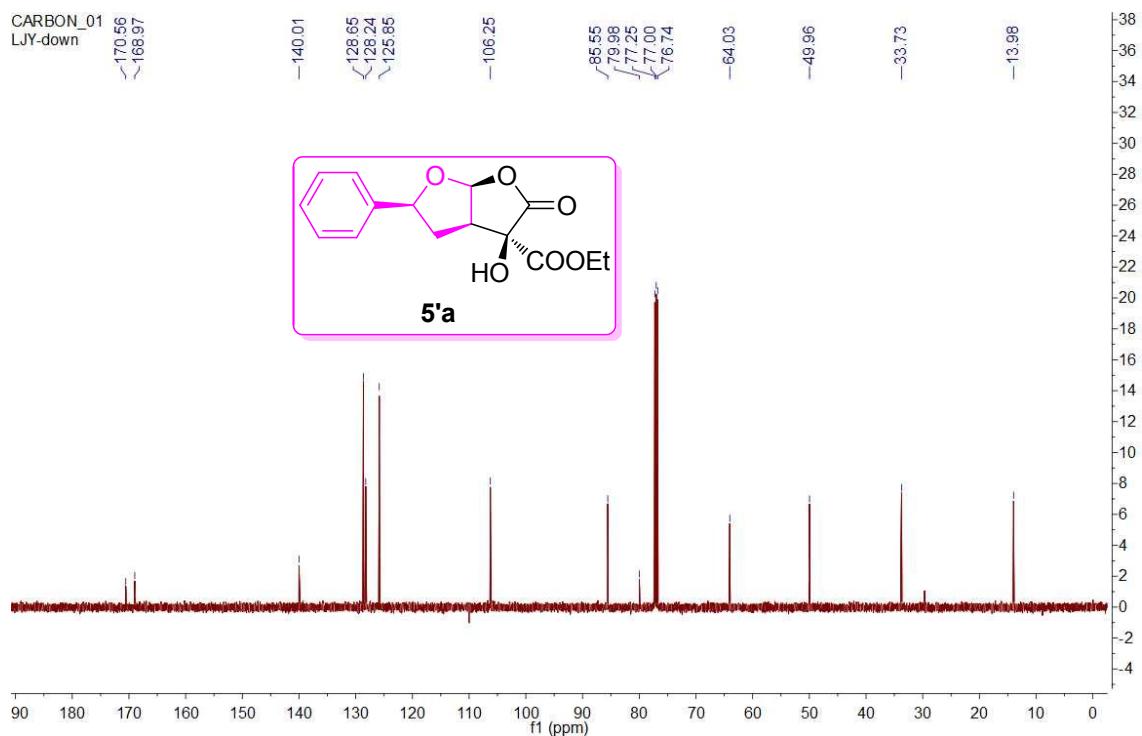
Calculation Method: AREA%

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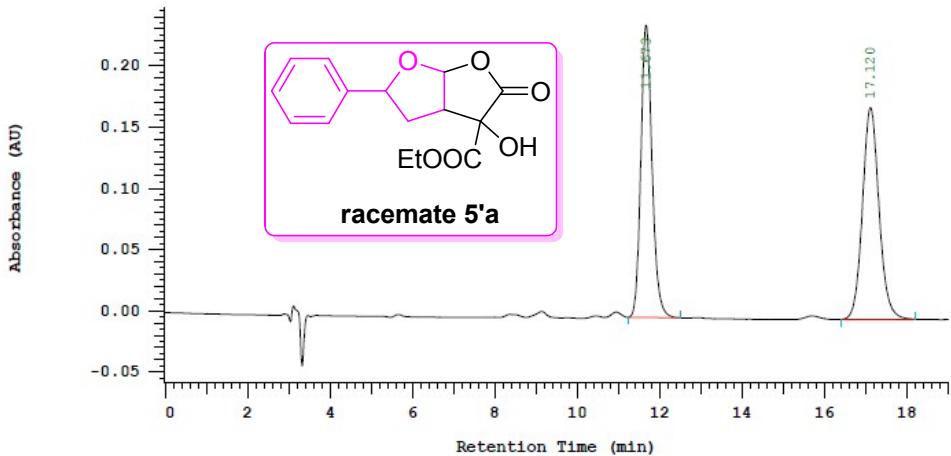
PROTON_01
LJR-MEW-3



CARBON_01
LJY-down
-170.56
-168.97



Chrom Type: Fixed WL Chromatogram, 210 nm

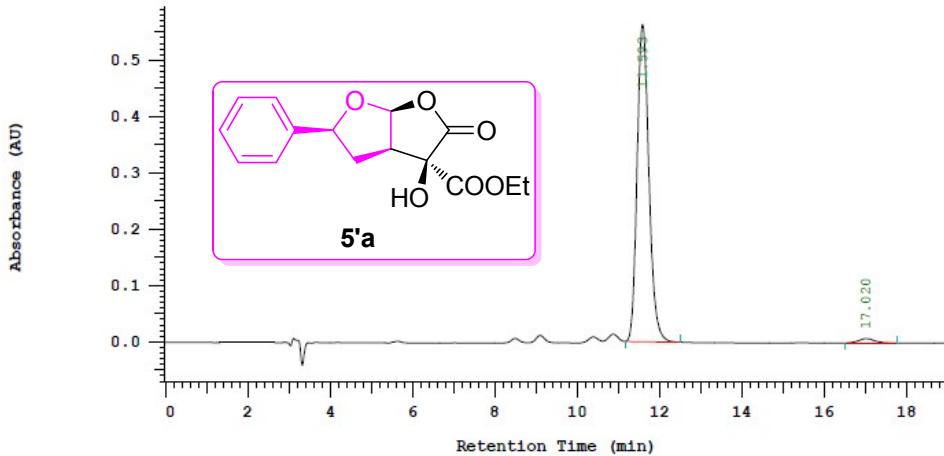


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

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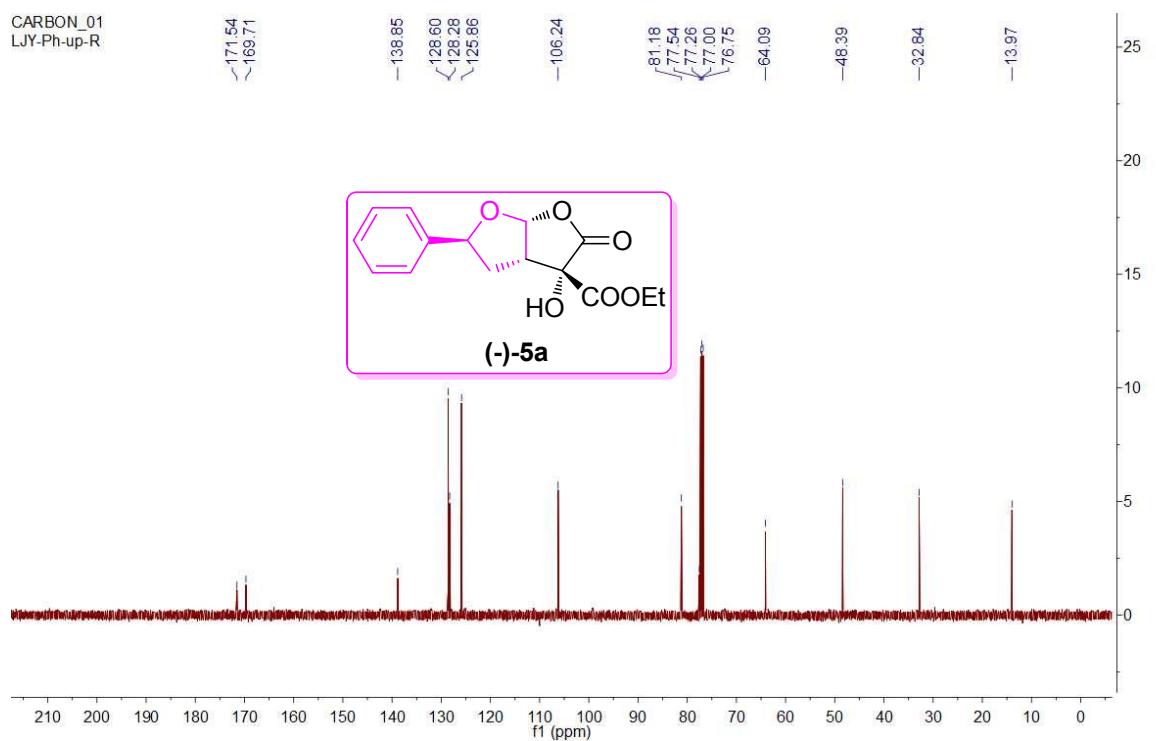
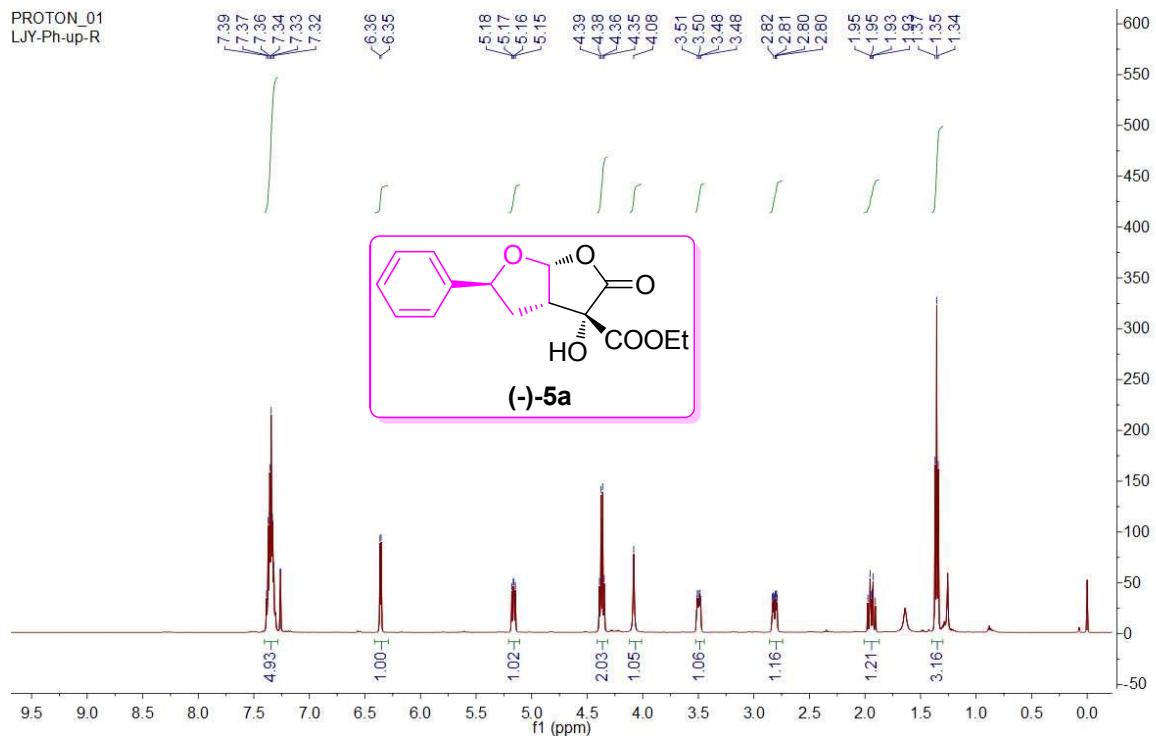
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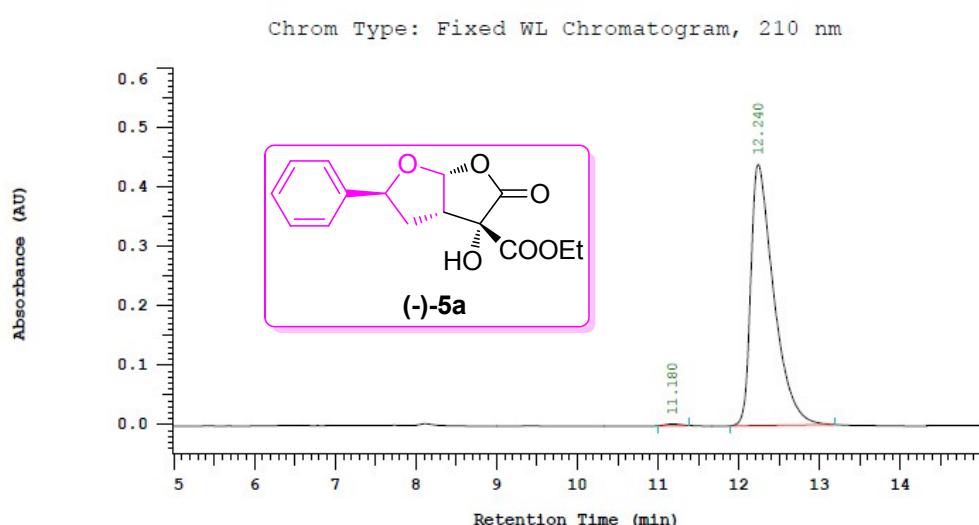
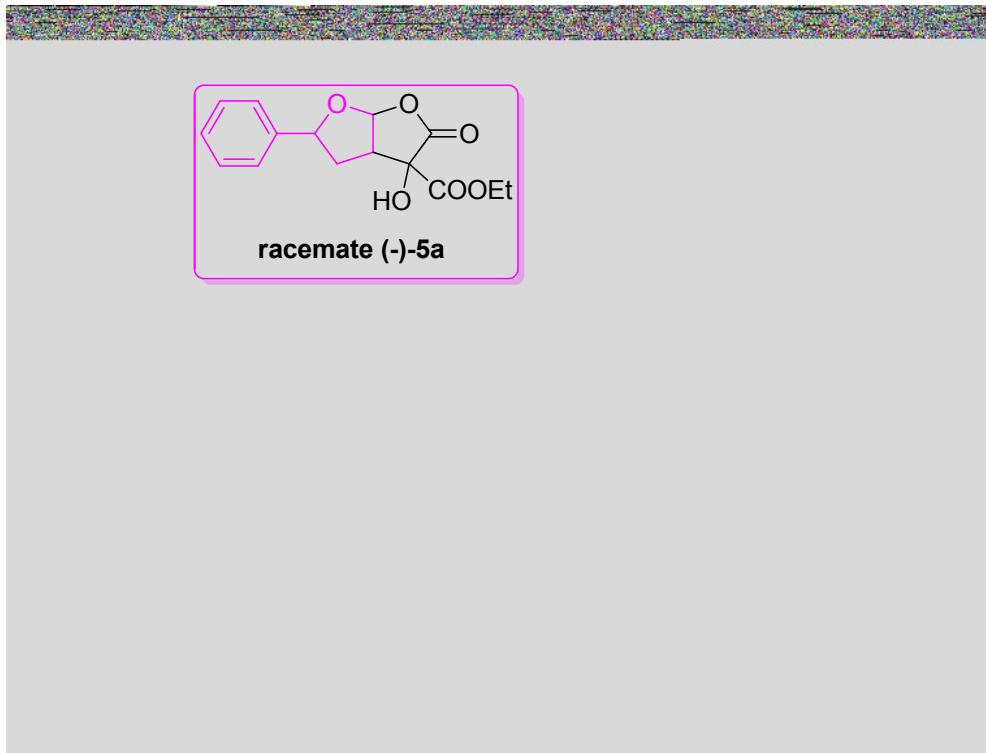


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

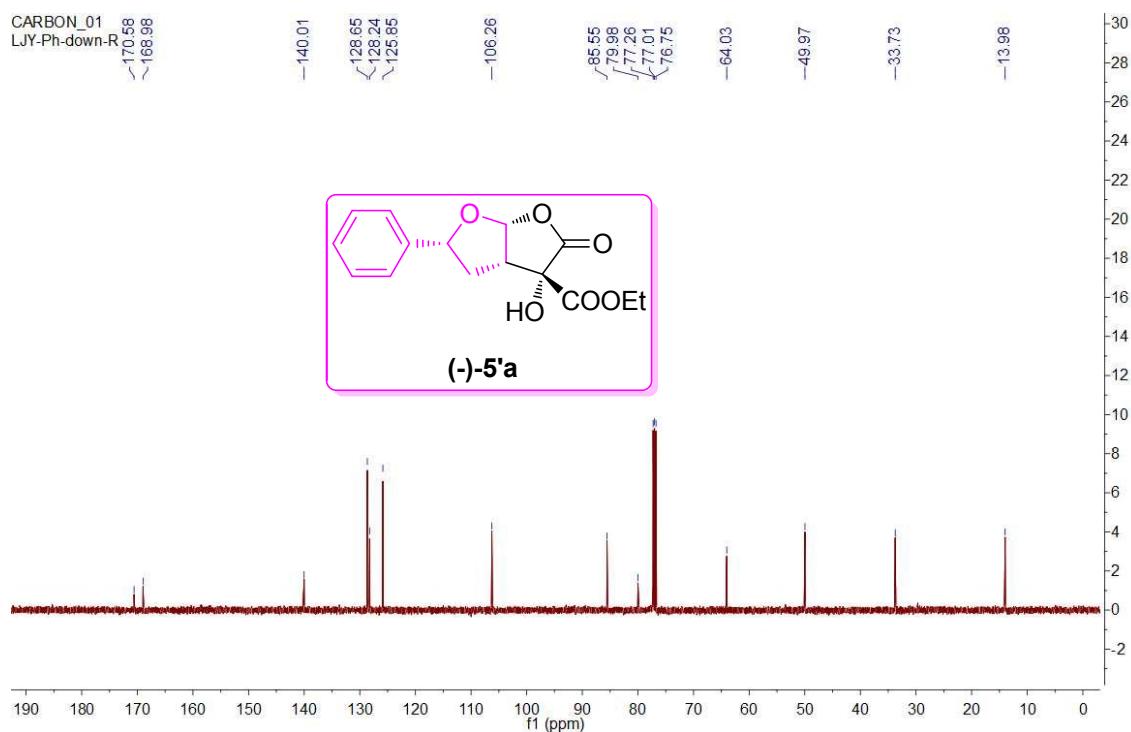
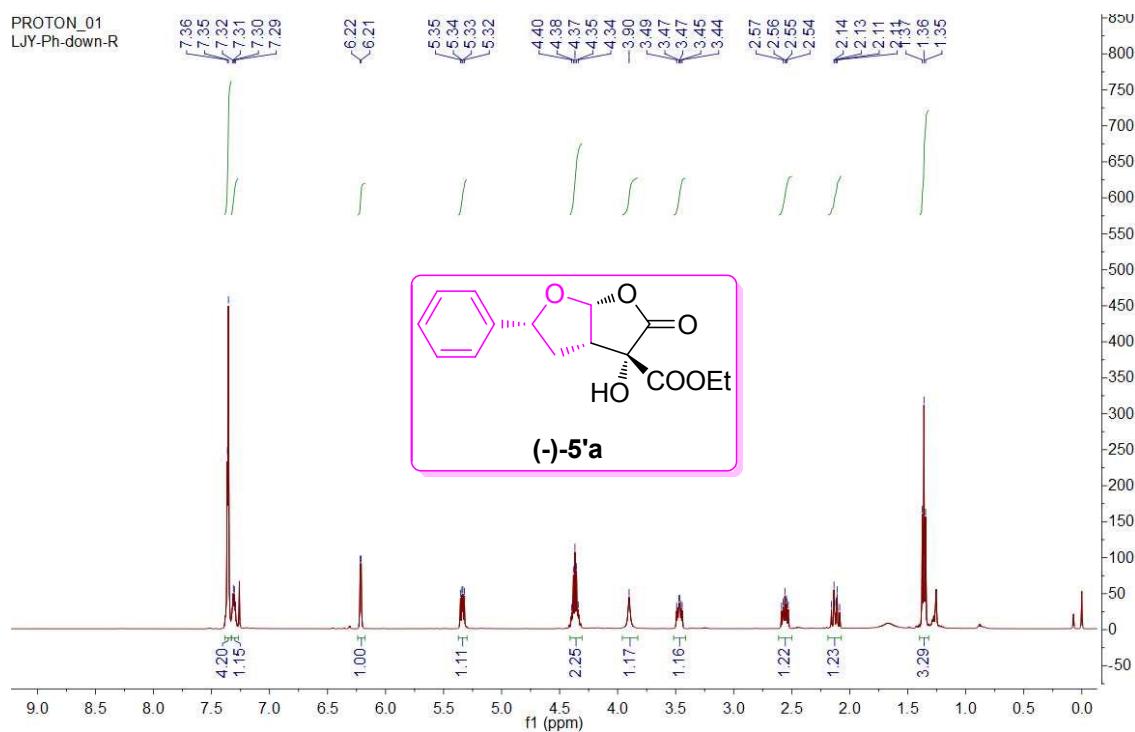
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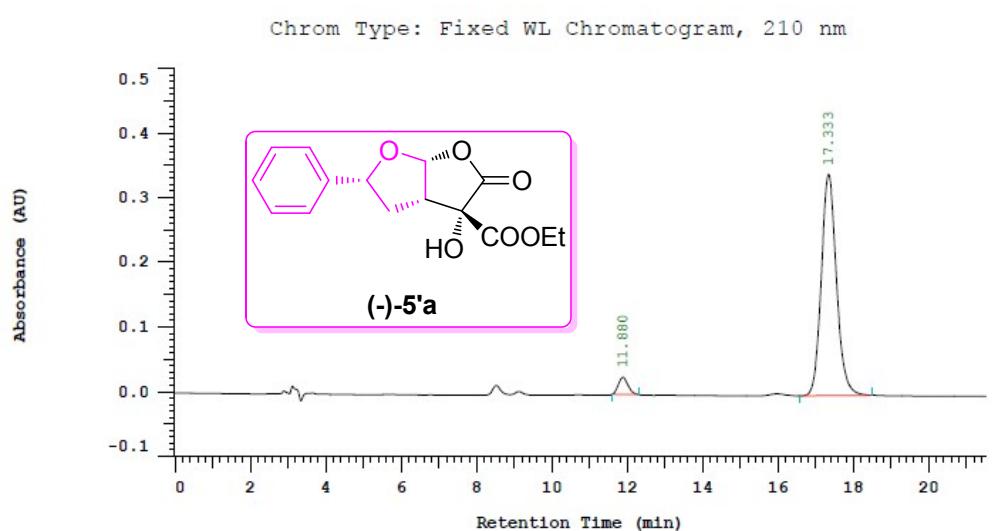
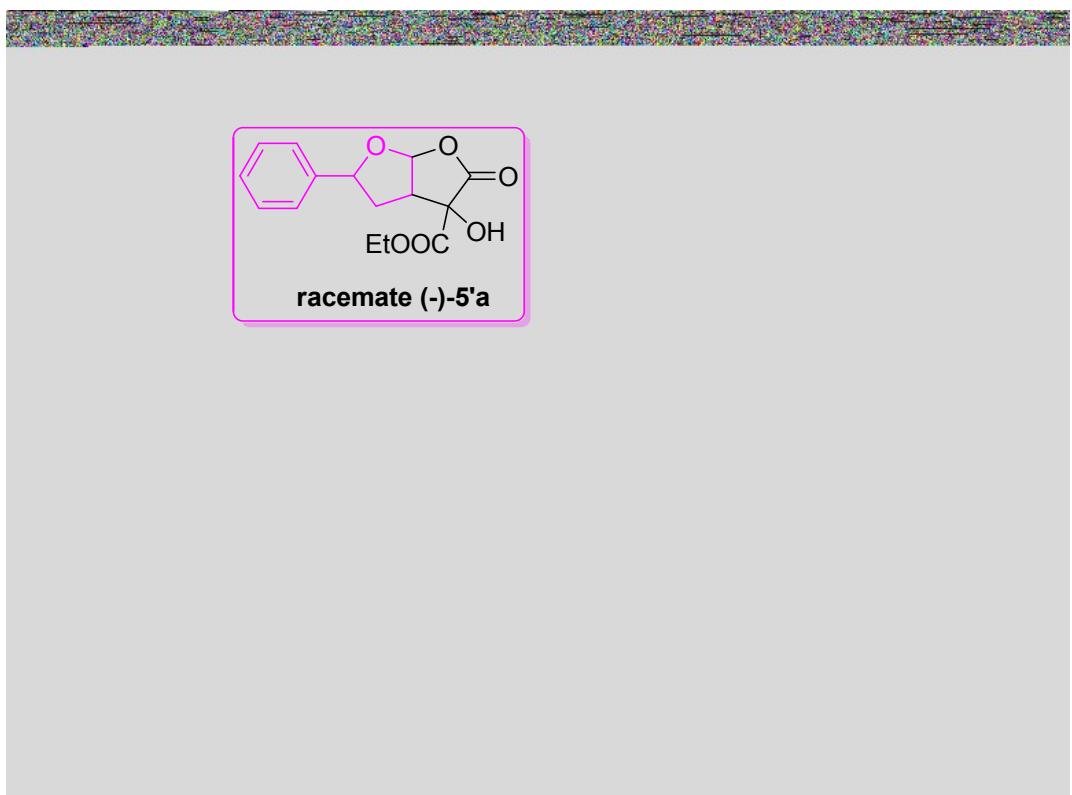




Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

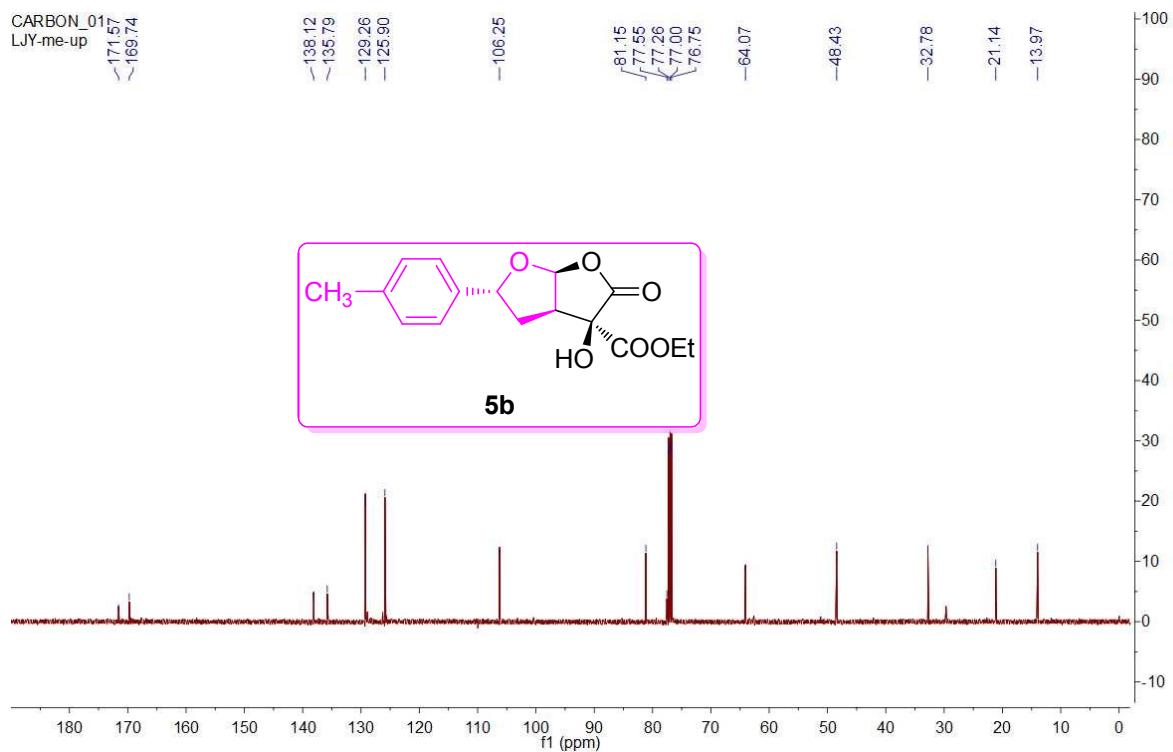
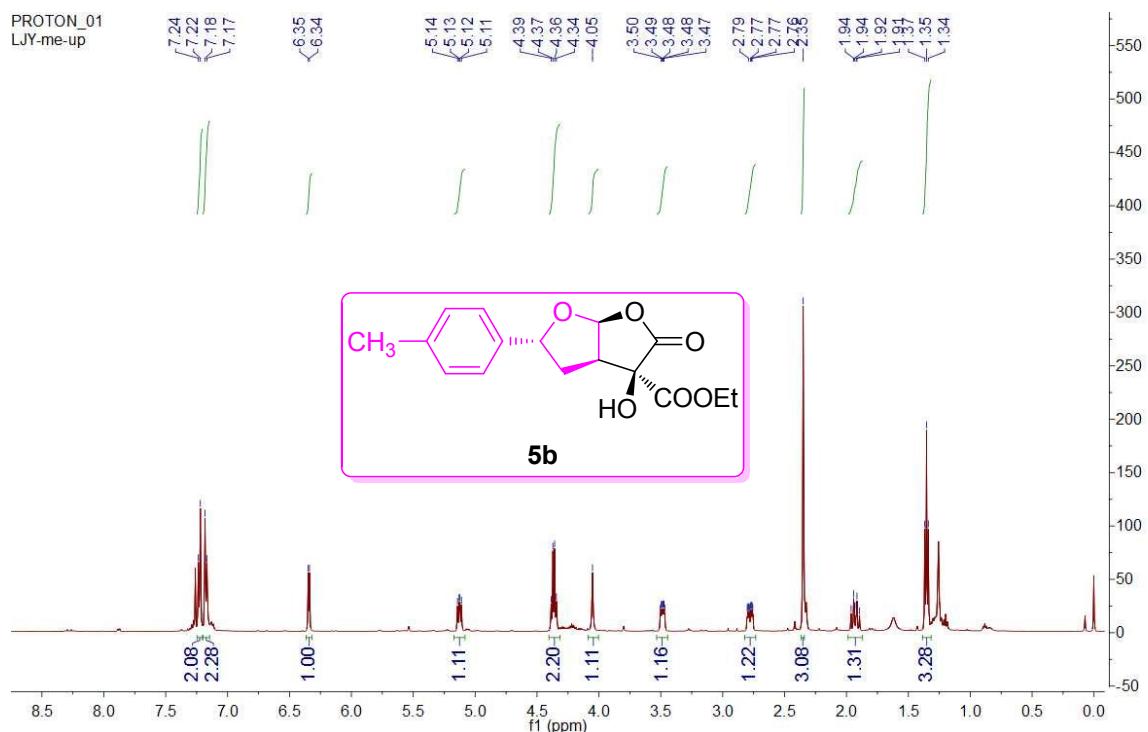
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4369395			100.000	



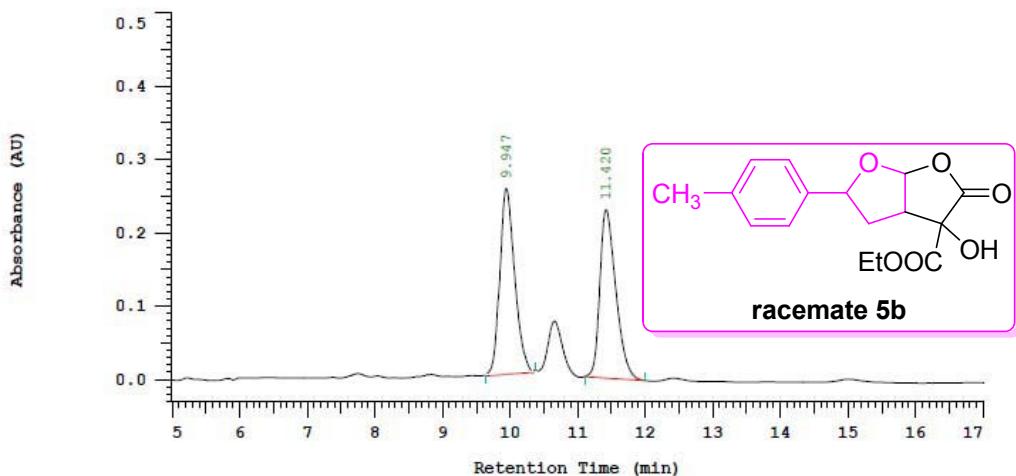


Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.880	235022	4.705	BB
2	17.333	4760370	95.295	BB
4995392			100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

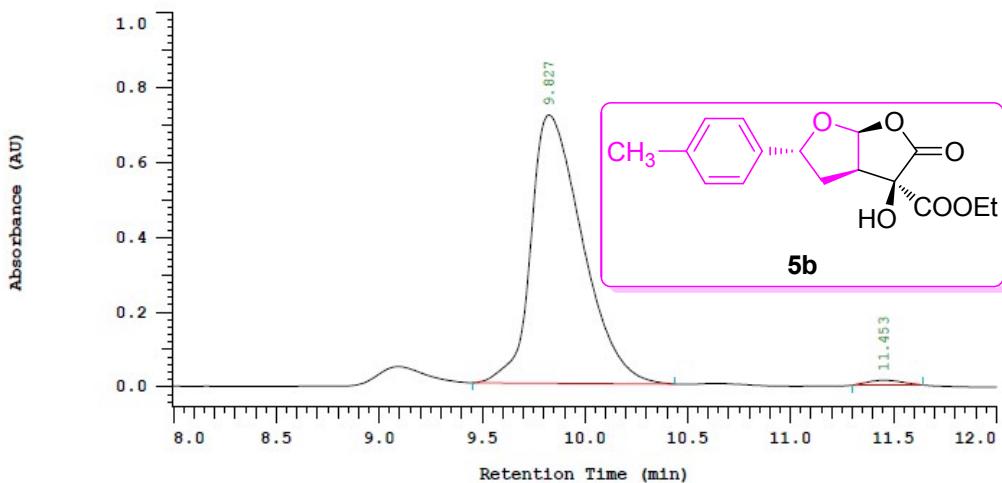


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.947	5069200	48.425	BB
2	11.420	5399088	51.575	BB
10468288		100.000		

Chrom Type: Fixed WL Chromatogram, 210 nm

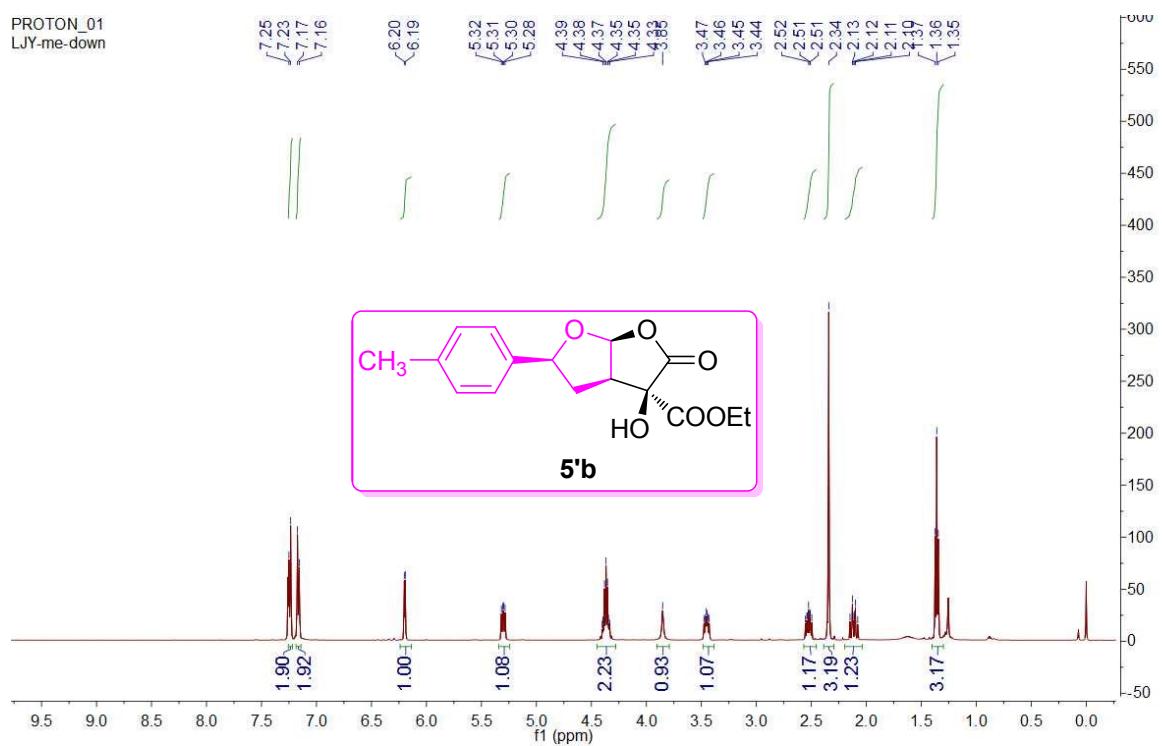


Chrom Type: Fixed WL Chromatogram, 210 nm

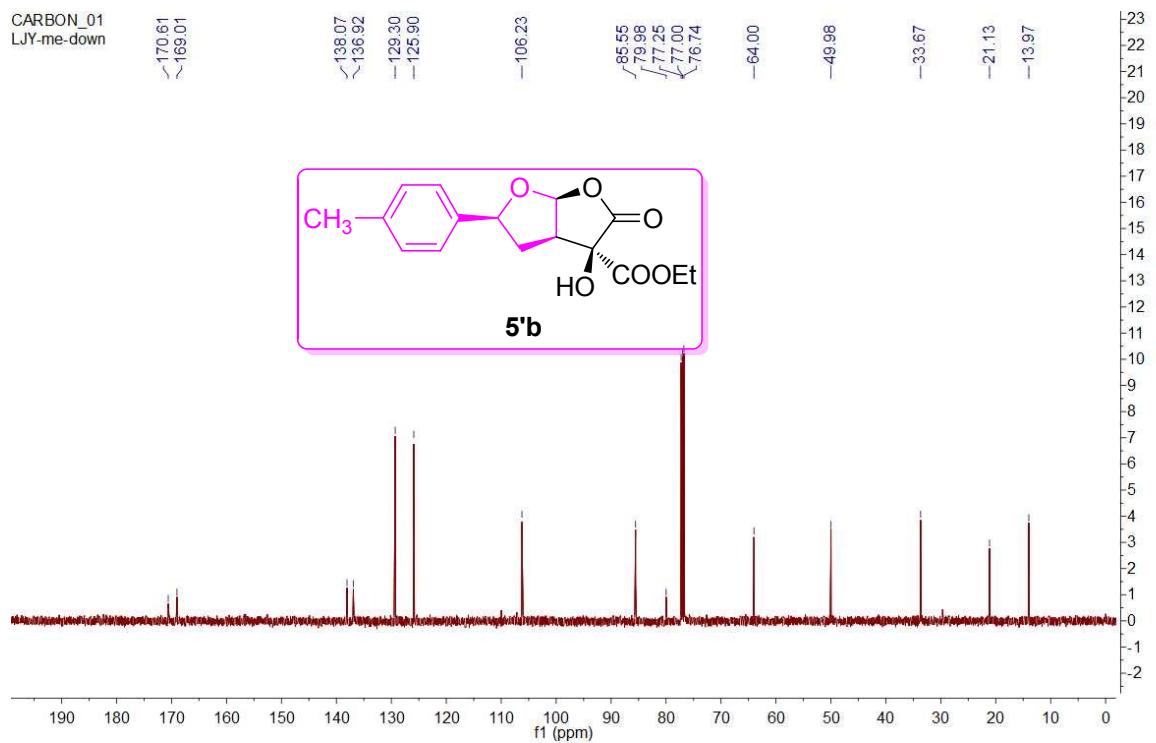
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.827	6243921	98.849	BB
2	11.453	72692	1.151	BB
6316613		100.000		

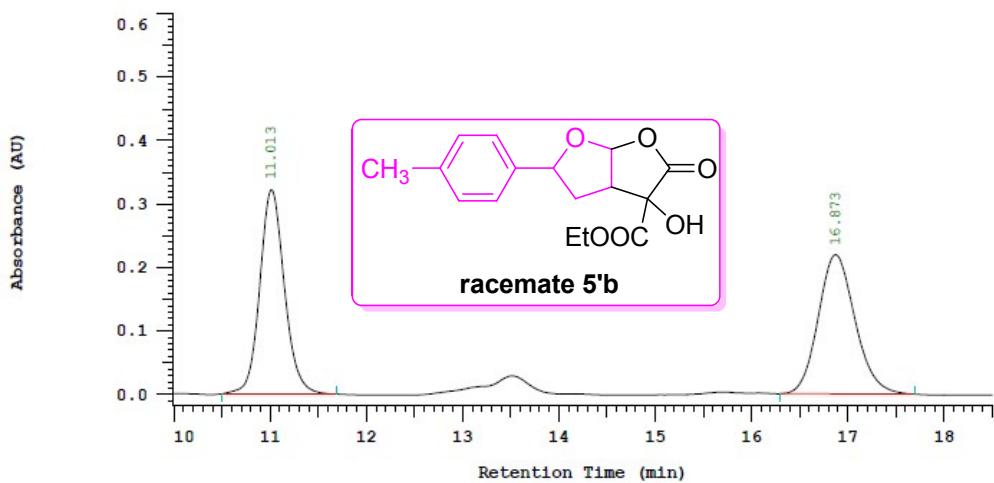
PROTON_01
LJY-me-down



CARBON_01
LJY-me-down



Chrom Type: Fixed WL Chromatogram, 210 nm

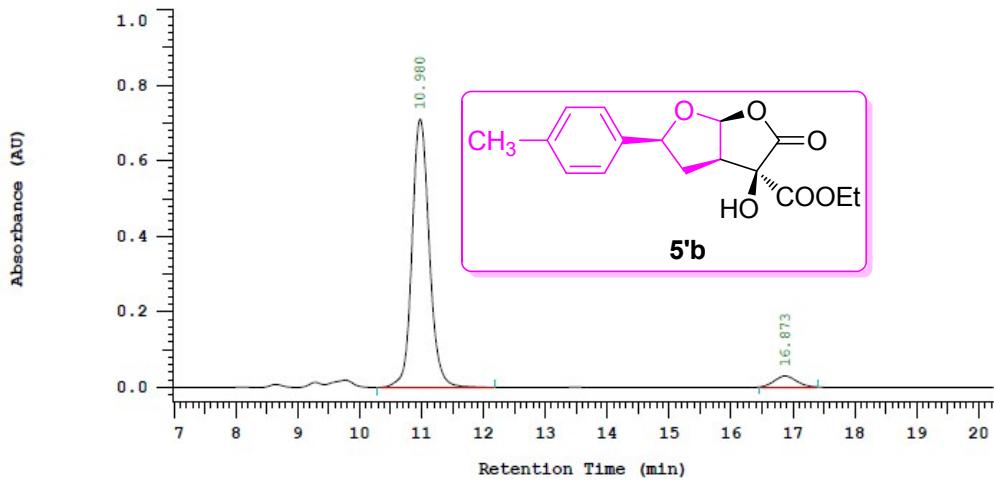


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.013	2864116	49.590	BB
2	16.873	2911456	50.410	BB
		5775572	100.000	

Chrom Type: Fixed WL Chromatogram, 210 nm

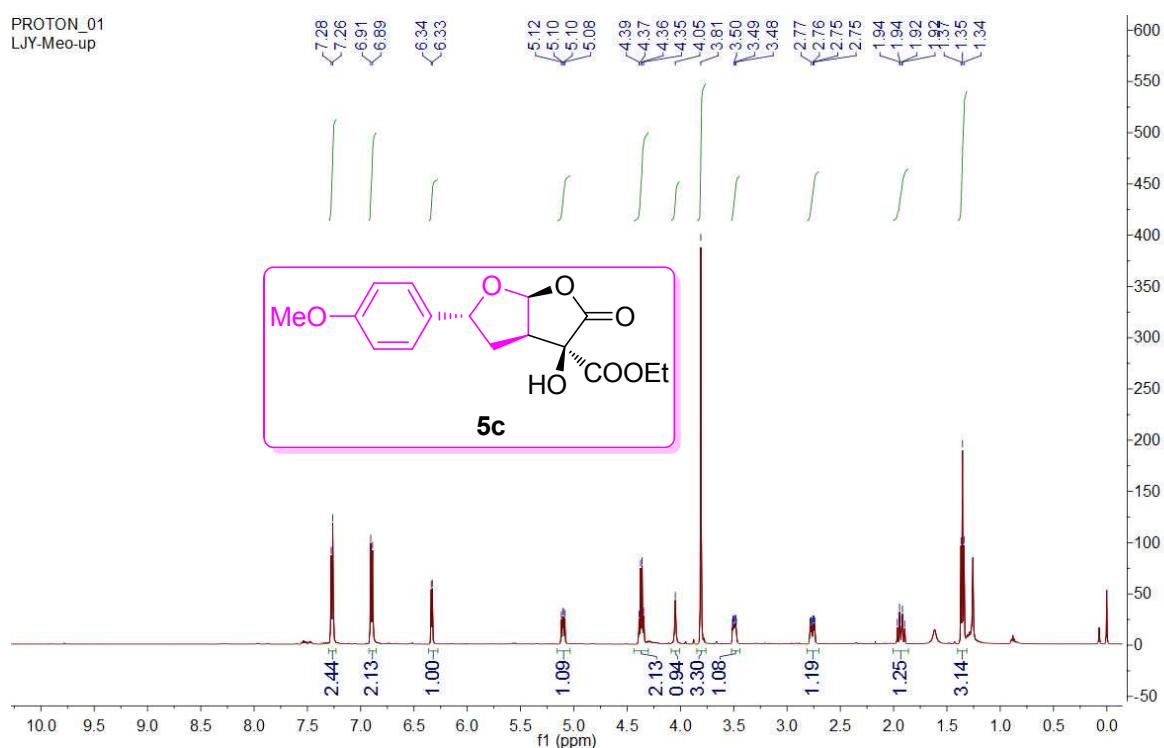


Chrom Type: Fixed WL Chromatogram, 210 nm

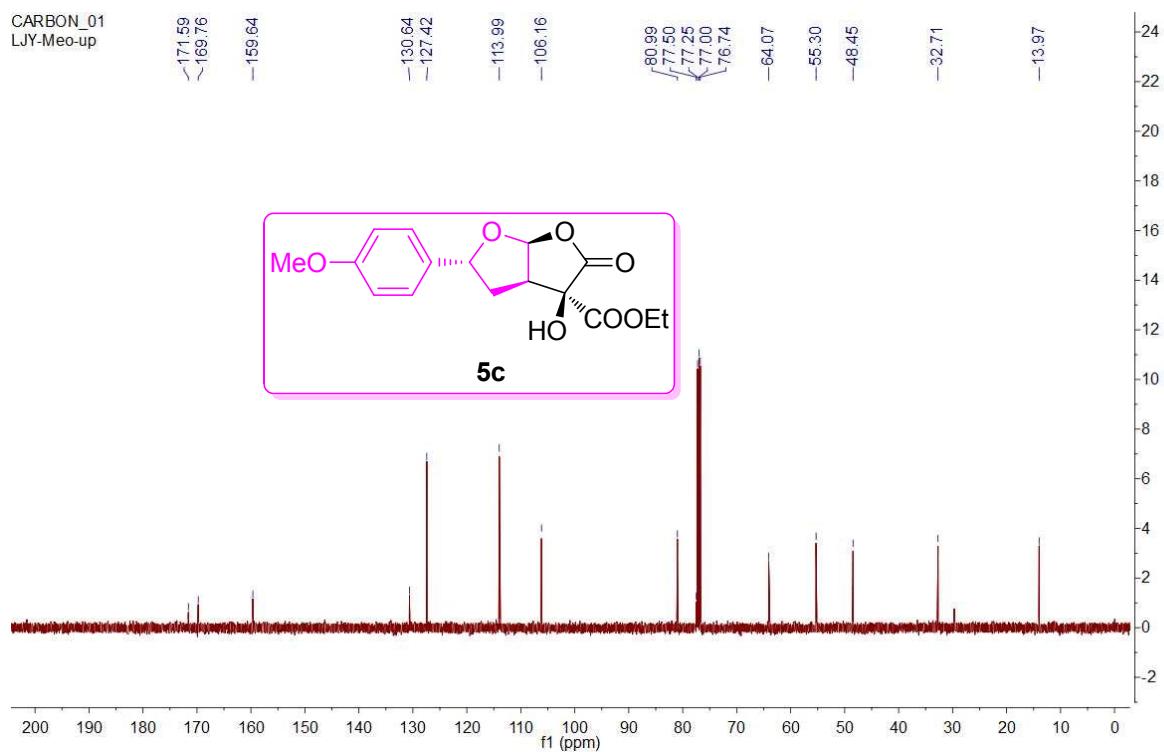
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.980	6854928	95.068	BB
2	16.873	355656	4.932	BB
		7210584	100.000	

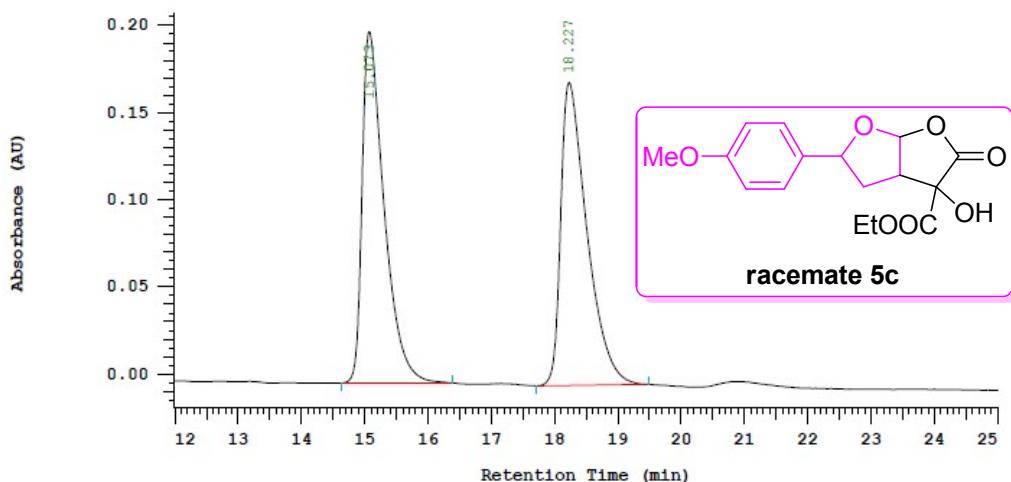
PROTON_01
LJY-Meo-up



CARBON_01
LJY-Meo-up



Chrom Type: Fixed WL Chromatogram, 210 nm

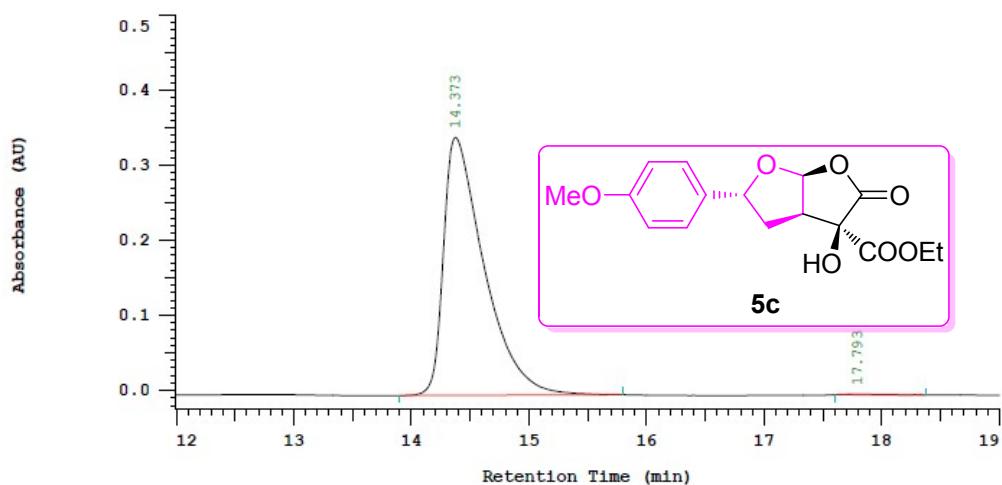


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.073	2424158	49.268	BB
2	18.227	2496186	50.732	BB
4920344		100.000		

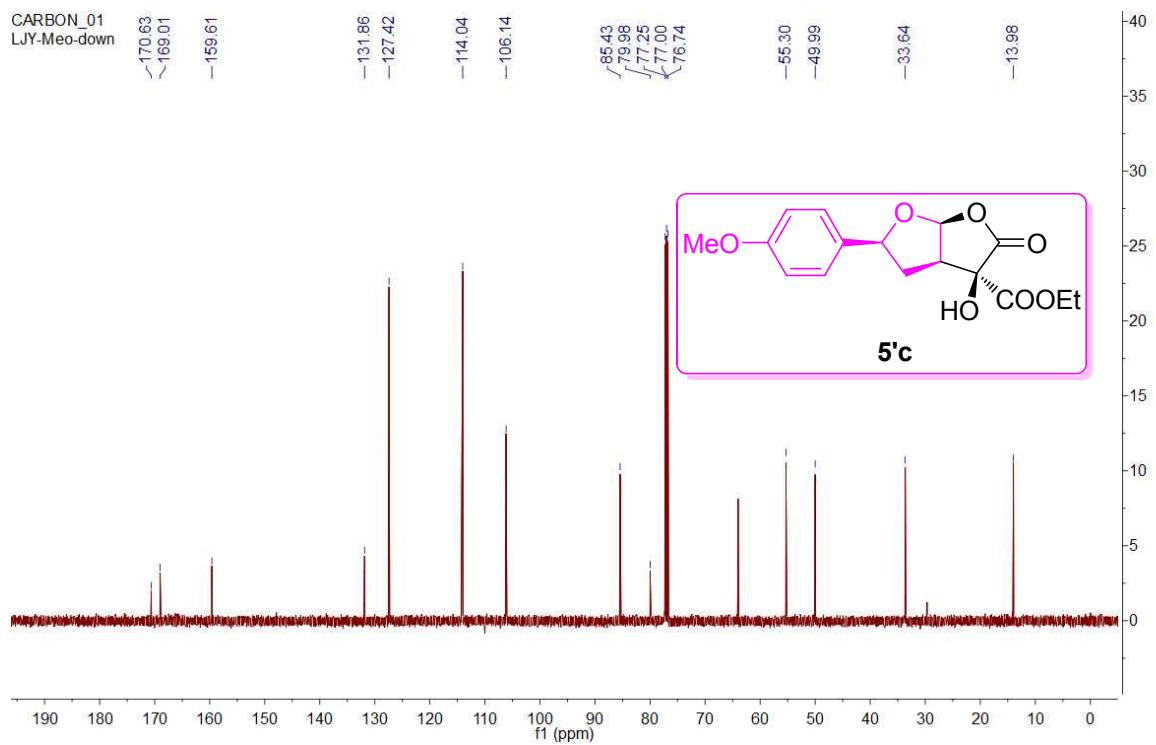
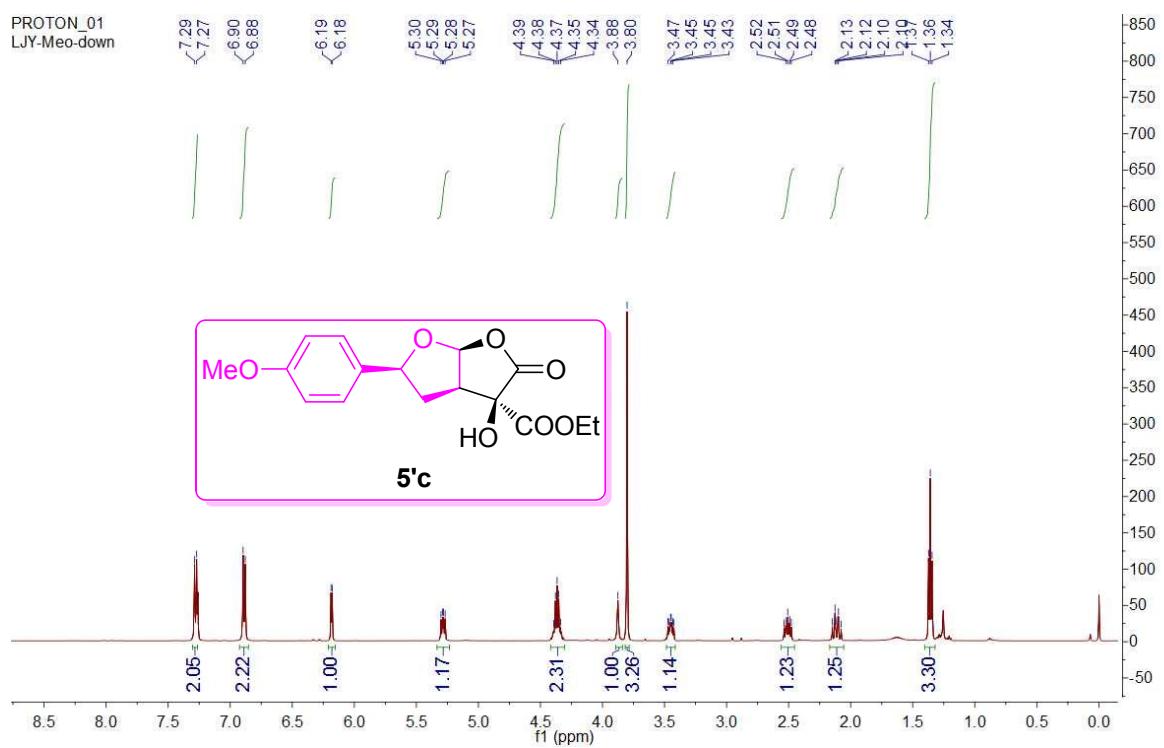
Chrom Type: Fixed WL Chromatogram, 210 nm

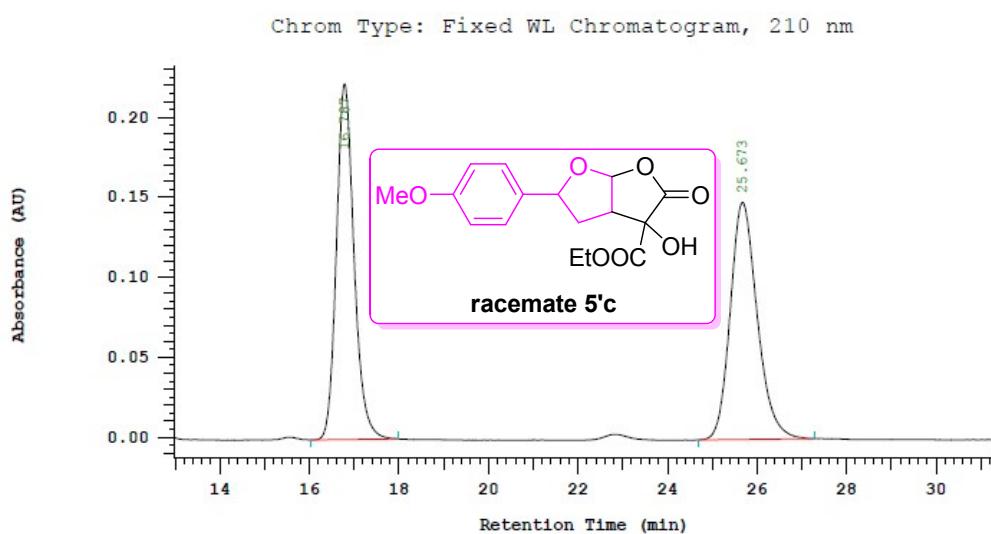


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

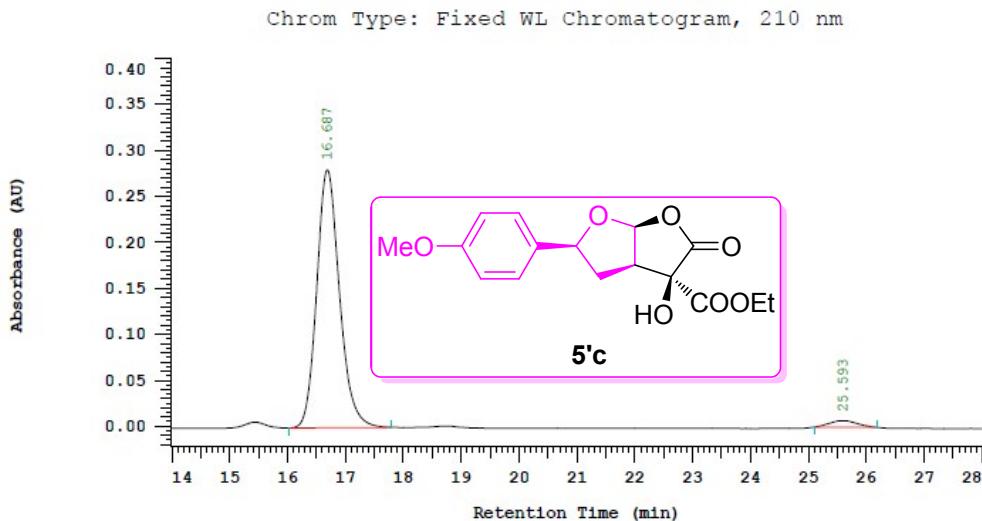
No.	RT	Area	Area %	BC
1	14.373	4134039	99.792	BB
2	17.793	8628	0.208	BB
4142667		100.000		





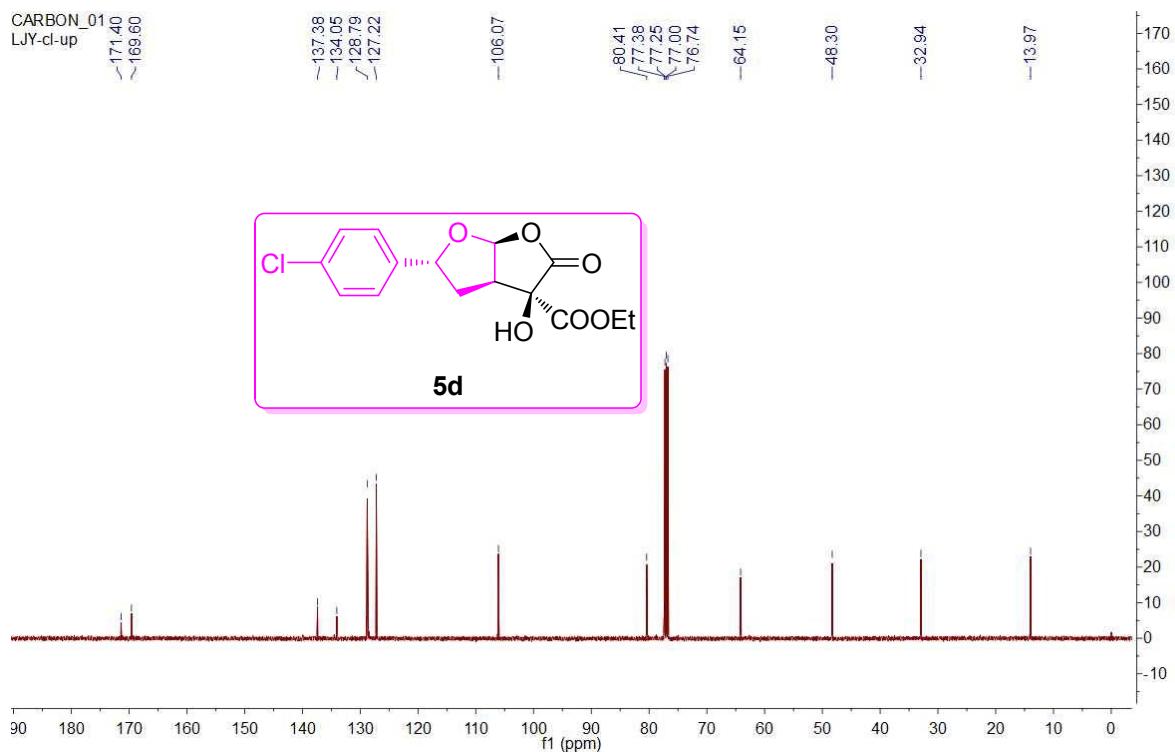
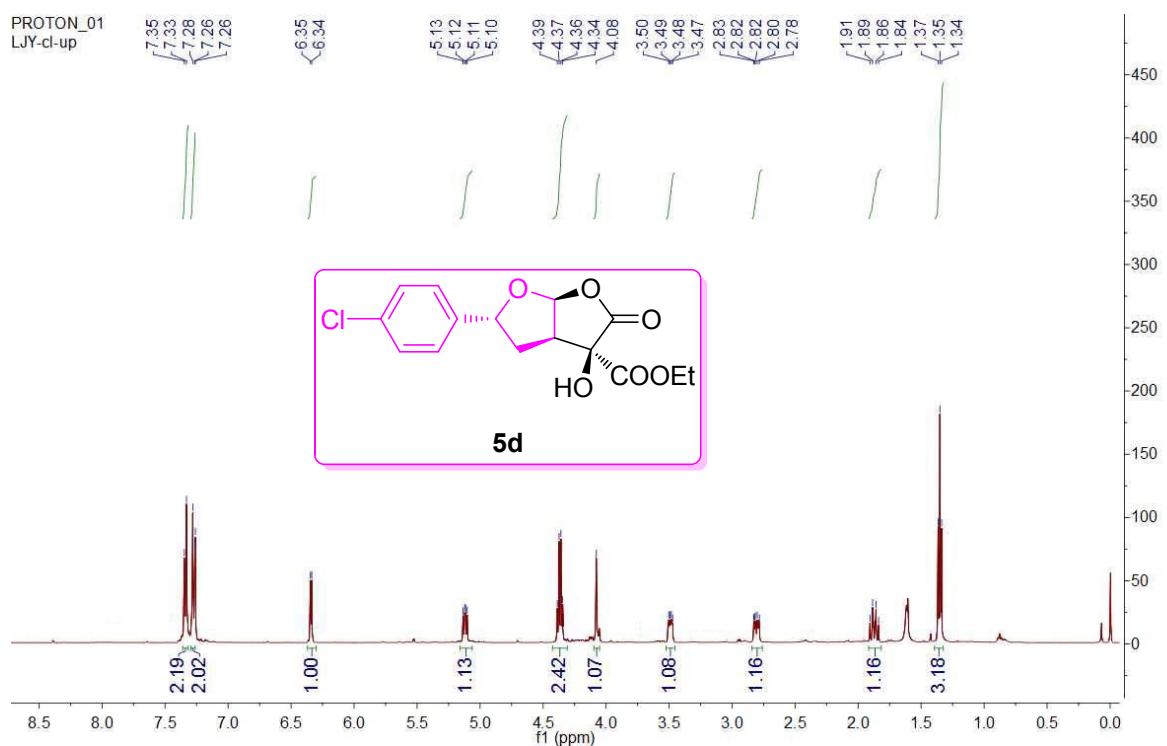
Chrom Type: Fixed WL Chromatogram, 210 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	16.787	3050218	49.608	BB
2	25.673	3098479	50.392	BB
		6148697	100.000	

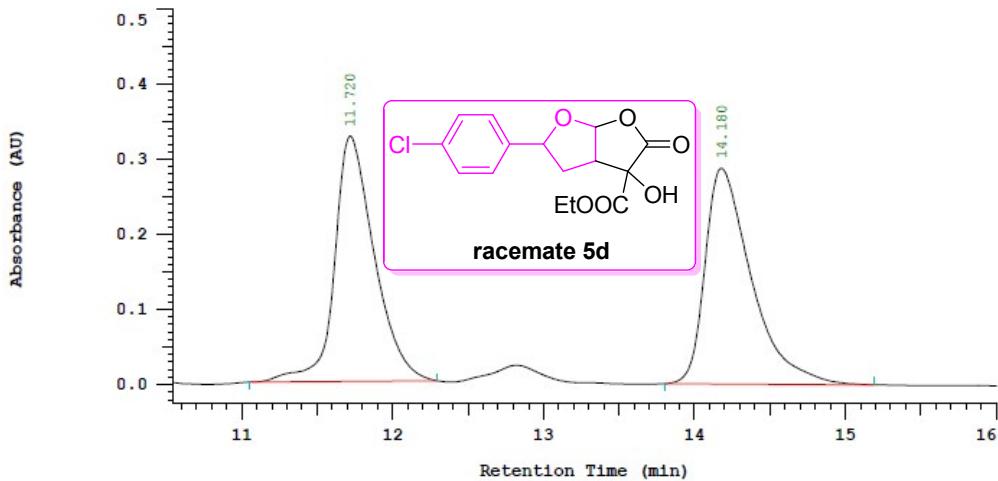


Chrom Type: Fixed WL Chromatogram, 210 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	16.687	3829228	96.955	BB
2	25.593	120247	3.045	BB
		3949475	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

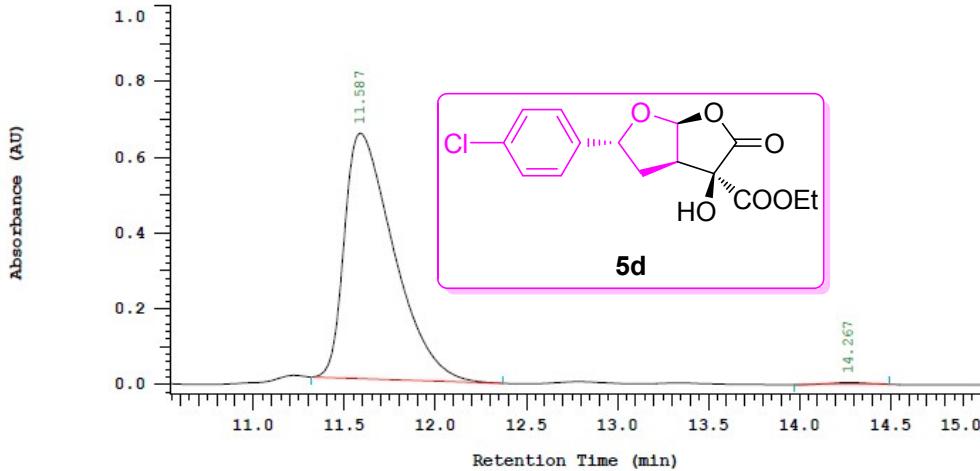


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.720	2993813	49.431	BB
2	14.180	3062715	50.569	BB
		6056528	100.000	

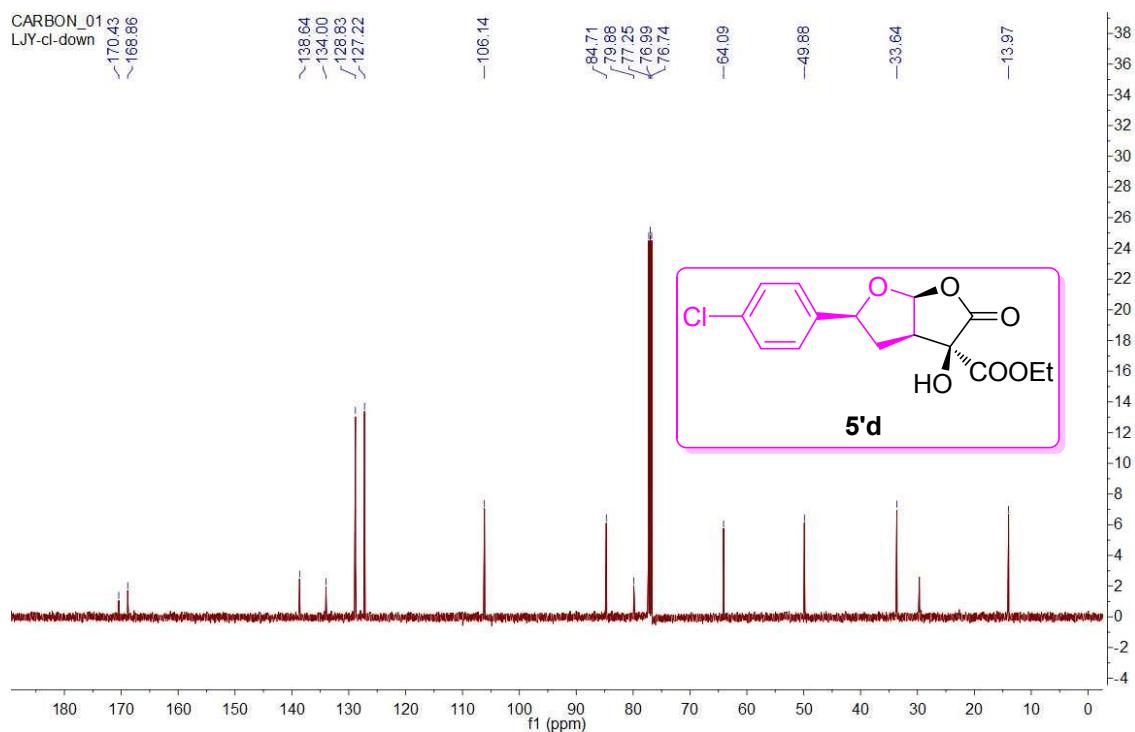
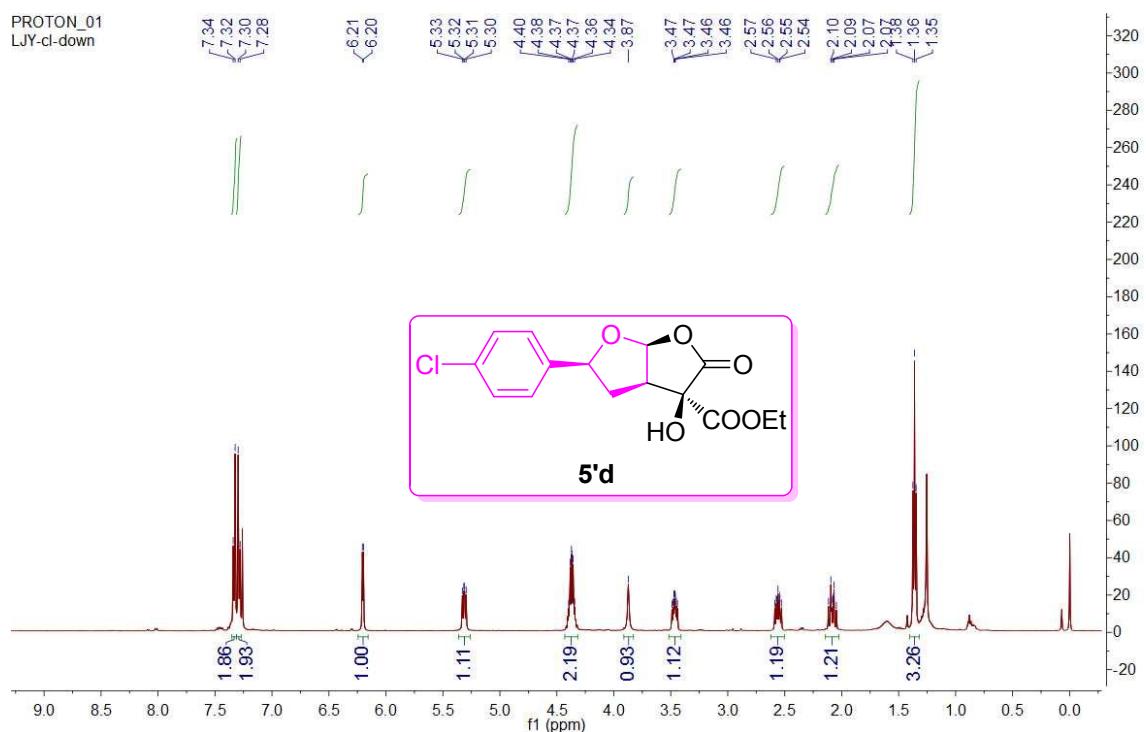
Chrom Type: Fixed WL Chromatogram, 210 nm



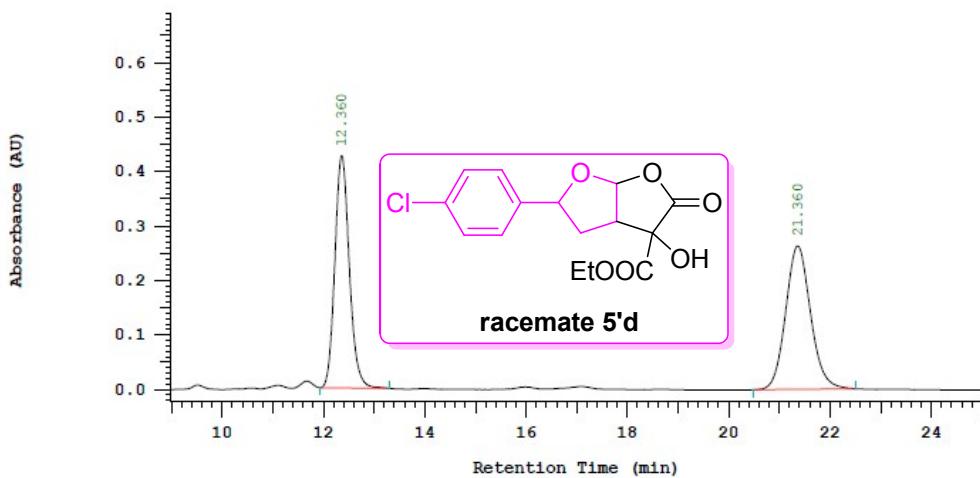
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.587	6114418	99.422	BB
2	14.267	35568	0.578	BB
		6149986	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

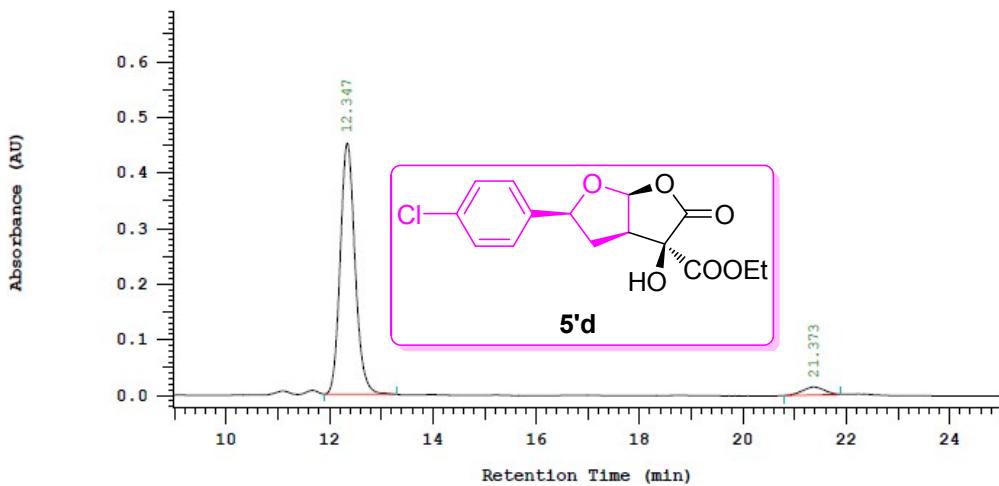


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.360	4236575	48.531	BB
2	21.360	4492996	51.469	BB
		8729571	100.000	

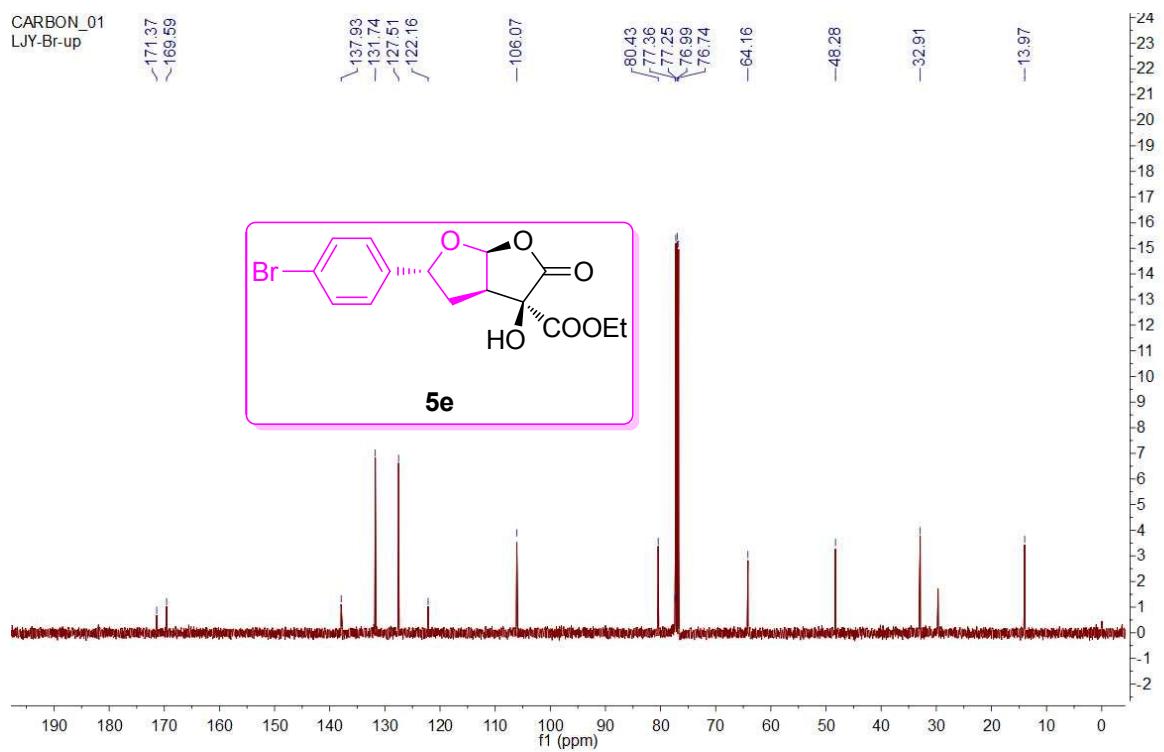
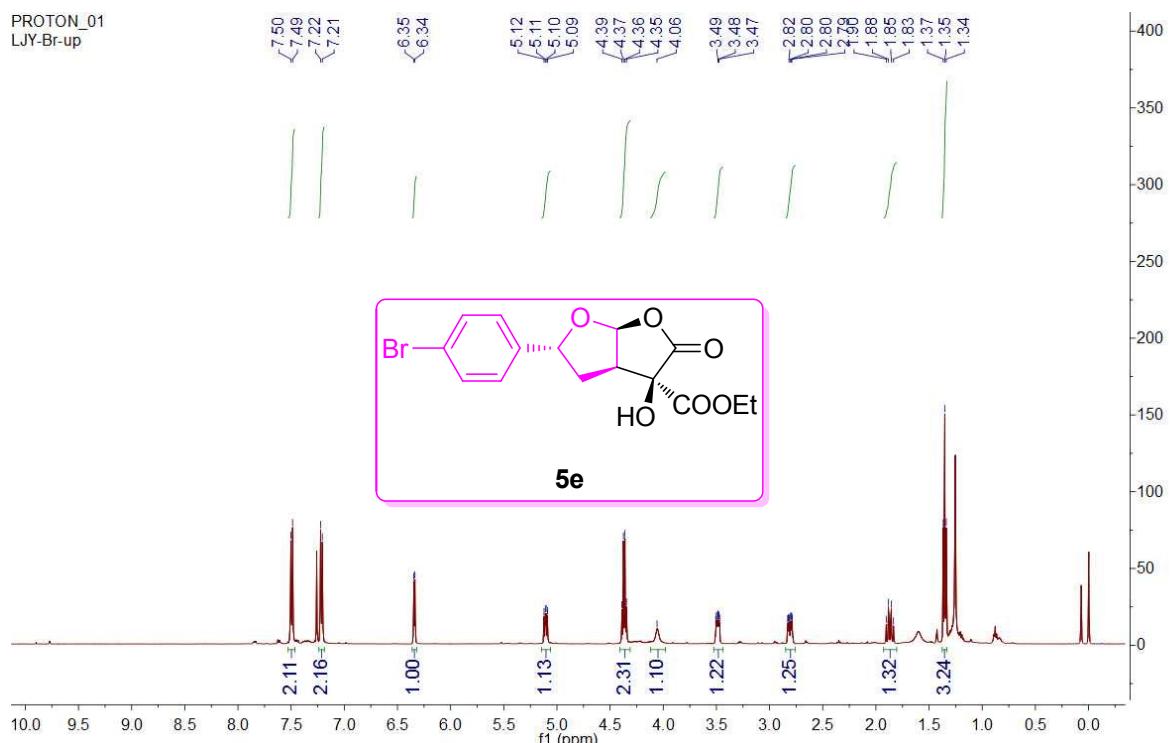
Chrom Type: Fixed WL Chromatogram, 210 nm



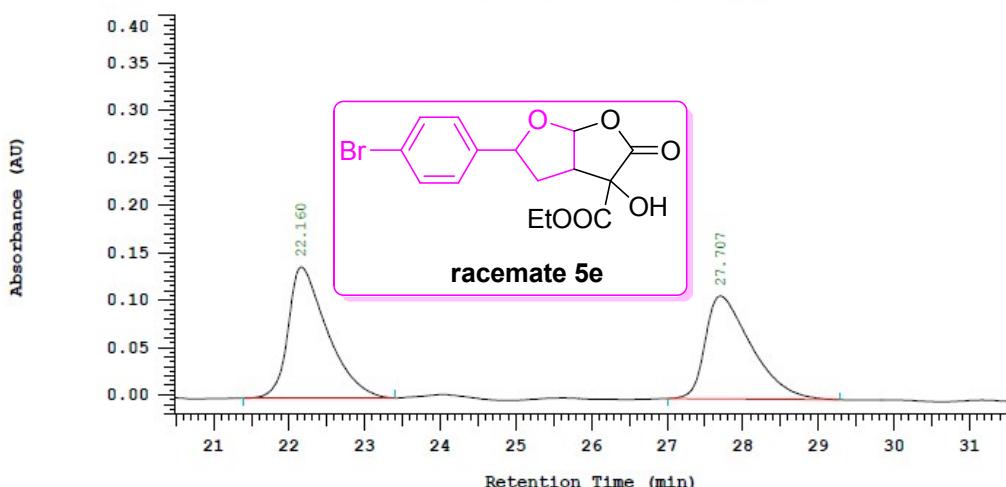
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.347	4507033	95.577	BB
2	21.373	208582	4.423	BB
		4715615	100.000	



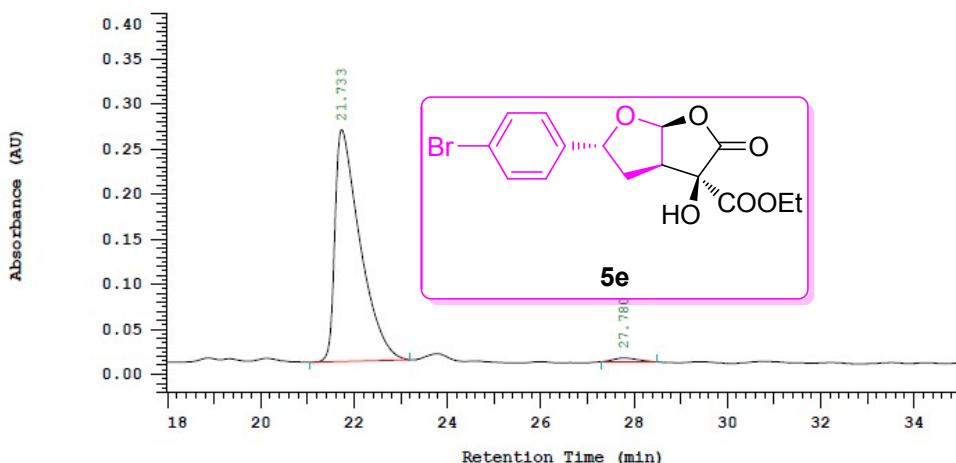
Chrom Type: Fixed WL Chromatogram, 210 nm



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

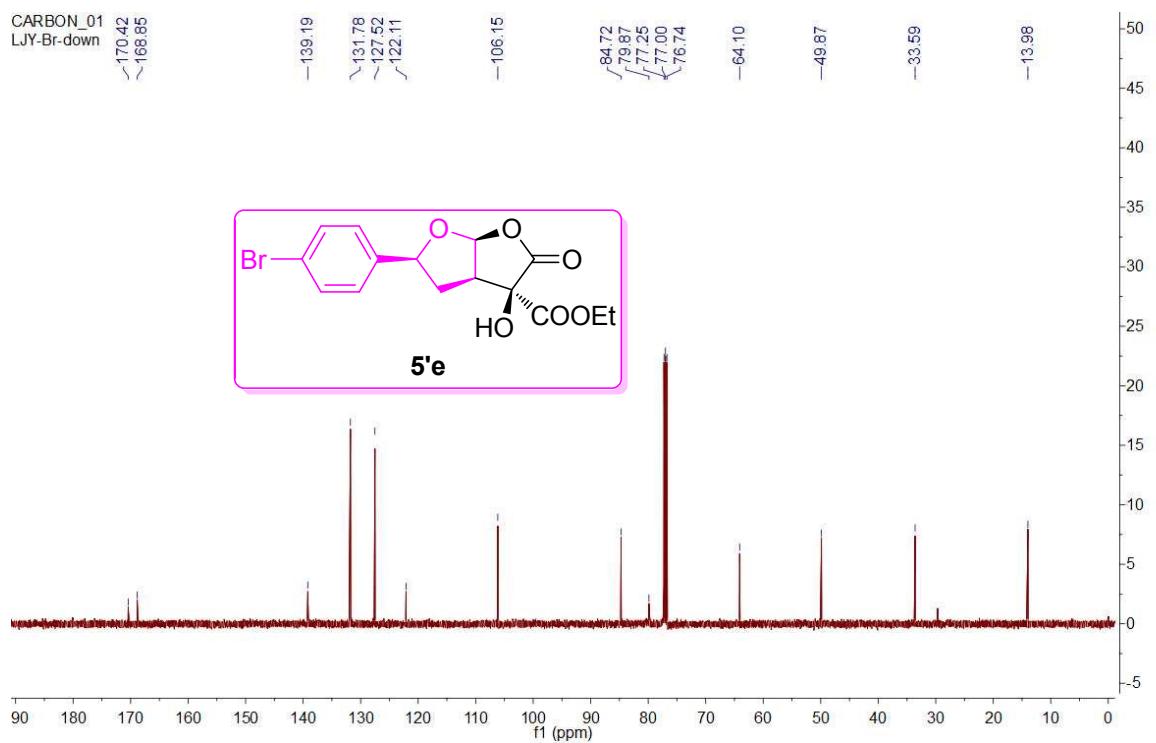
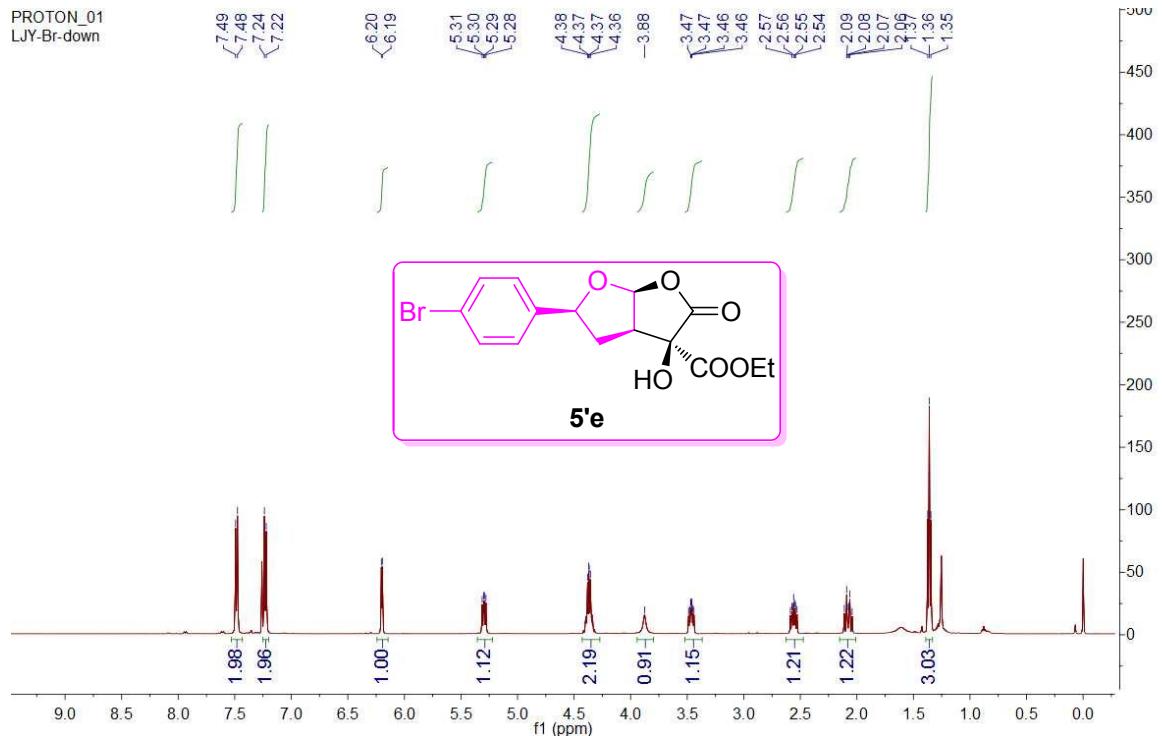
No.	RT	Area	Area %	BC
1	22.160	2484514	52.008	BB
2	27.707	2292666	47.992	BB
		4777180	100.000	

Chrom Type: Fixed WL Chromatogram, 210 nm

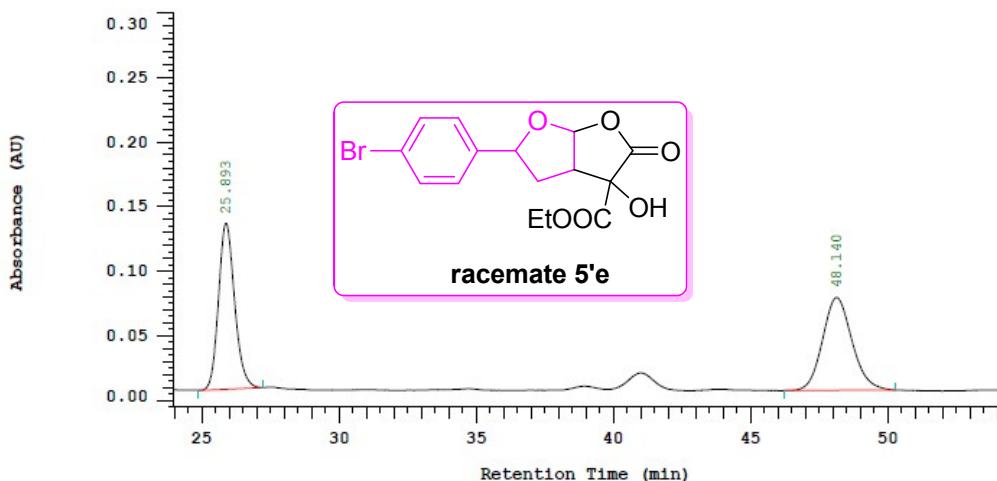


Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	21.733	4817629	98.446	BB
2	27.780	76072	1.554	BB
		4893701	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

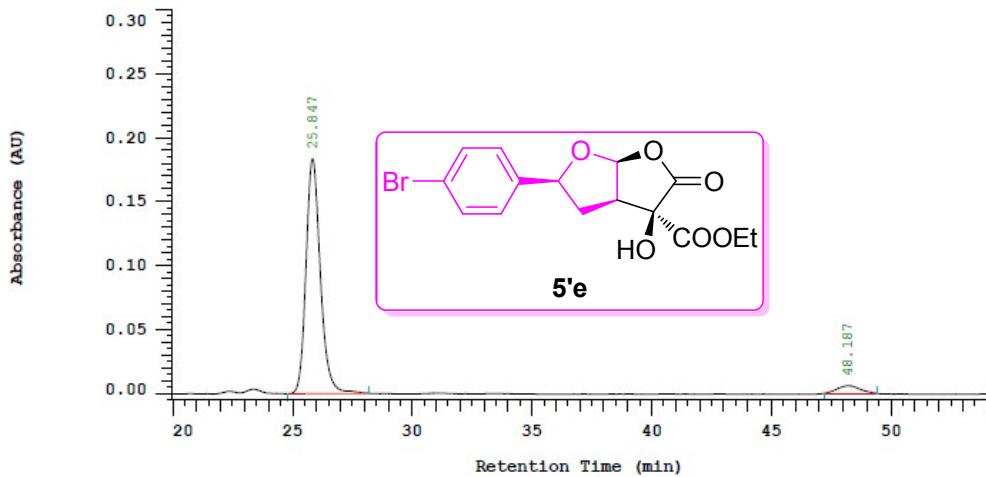


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	25.893	2604697	49.380	BB
2	48.140	2670089	50.620	BB
		5274786	100.000	

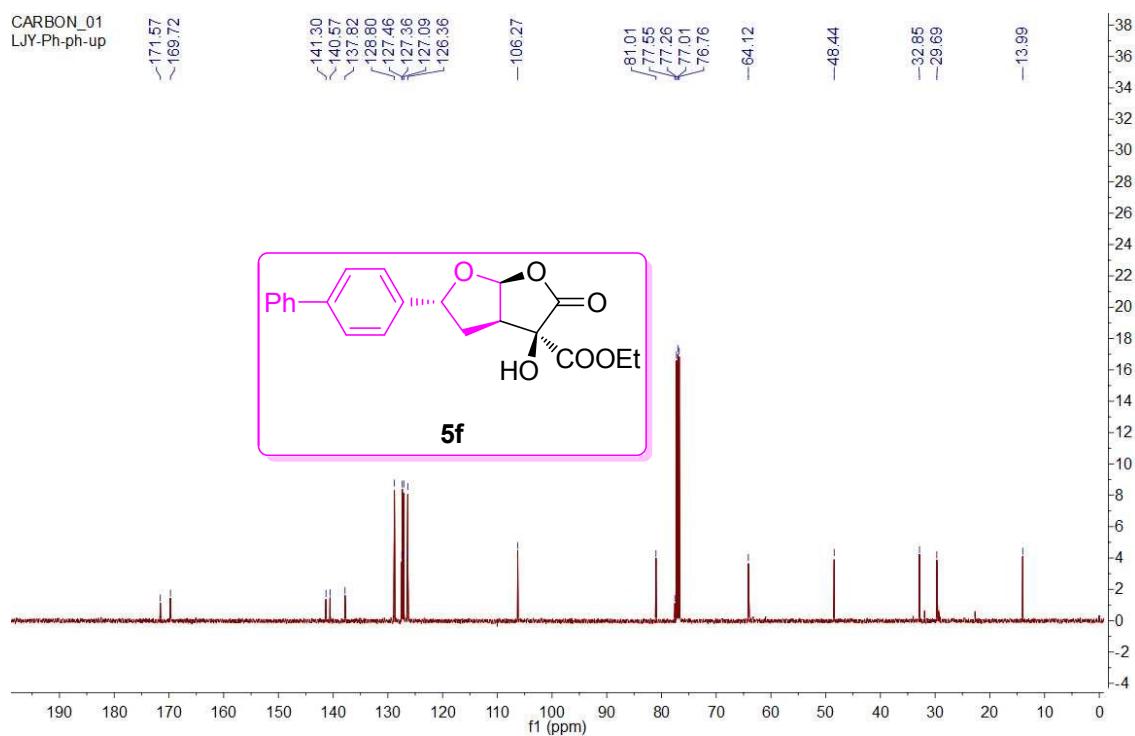
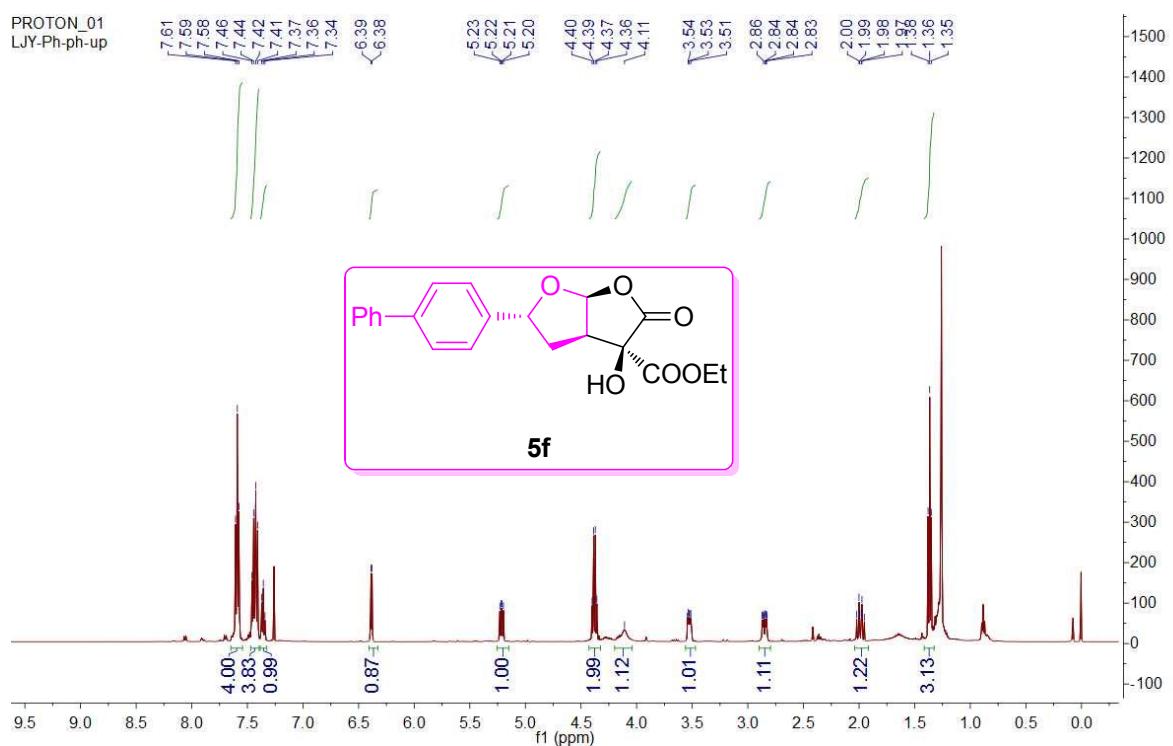
Chrom Type: Fixed WL Chromatogram, 210 nm



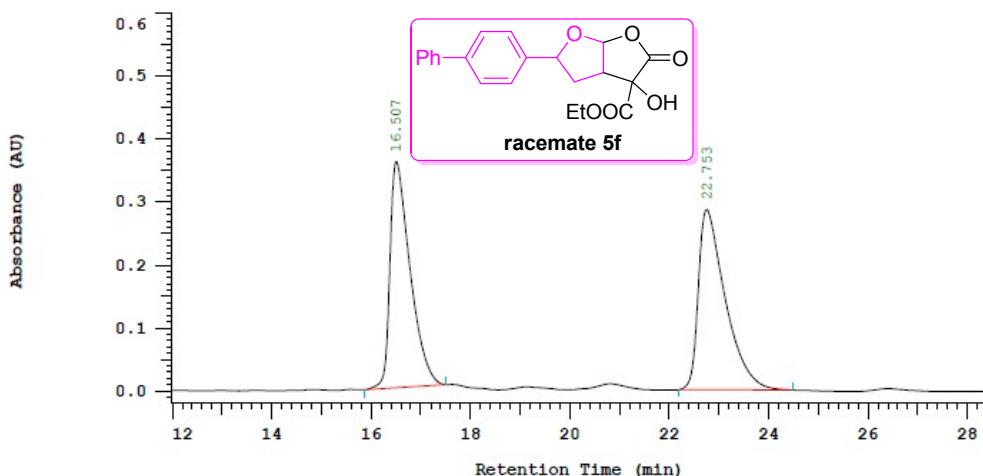
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	25.847	3804105	95.051	BB
2	48.187	198060	4.949	BB
		4002165	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

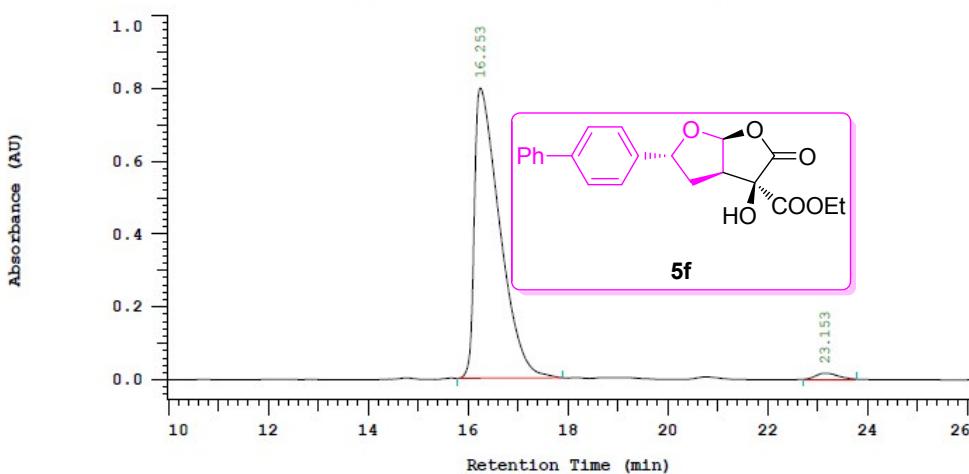


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	16.507	5069276	48.425	BB
2	22.753	5399022	51.575	BB
10468298		100.000		

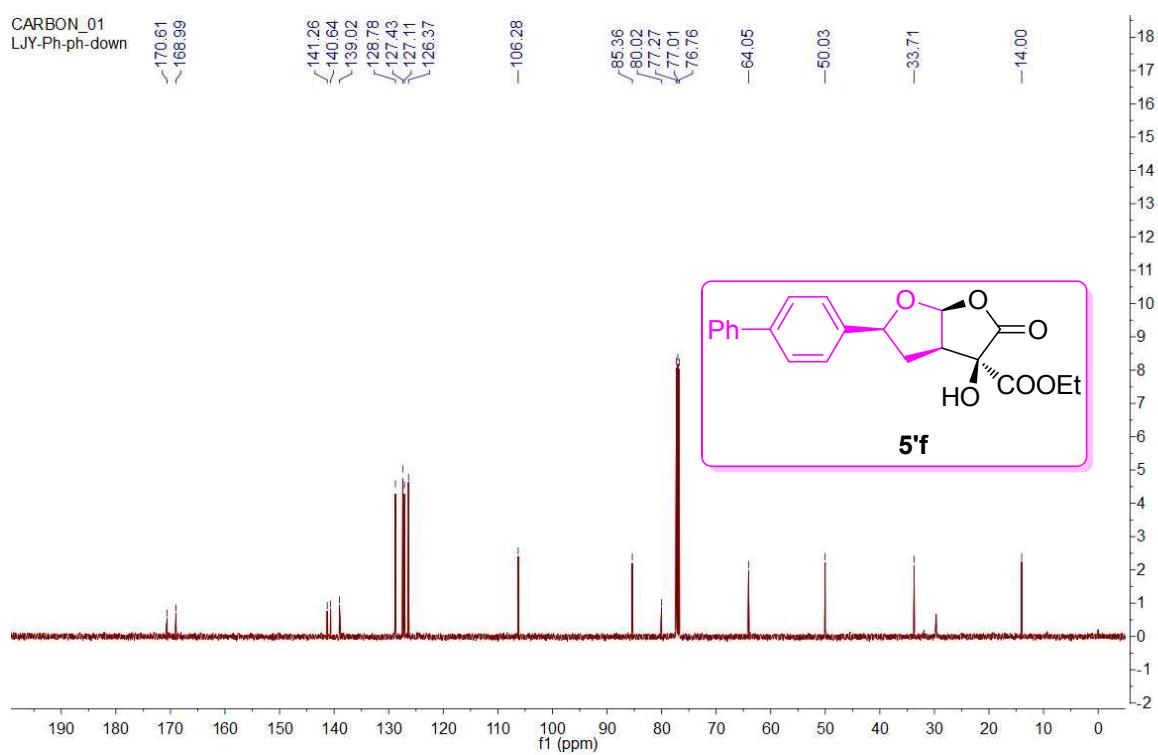
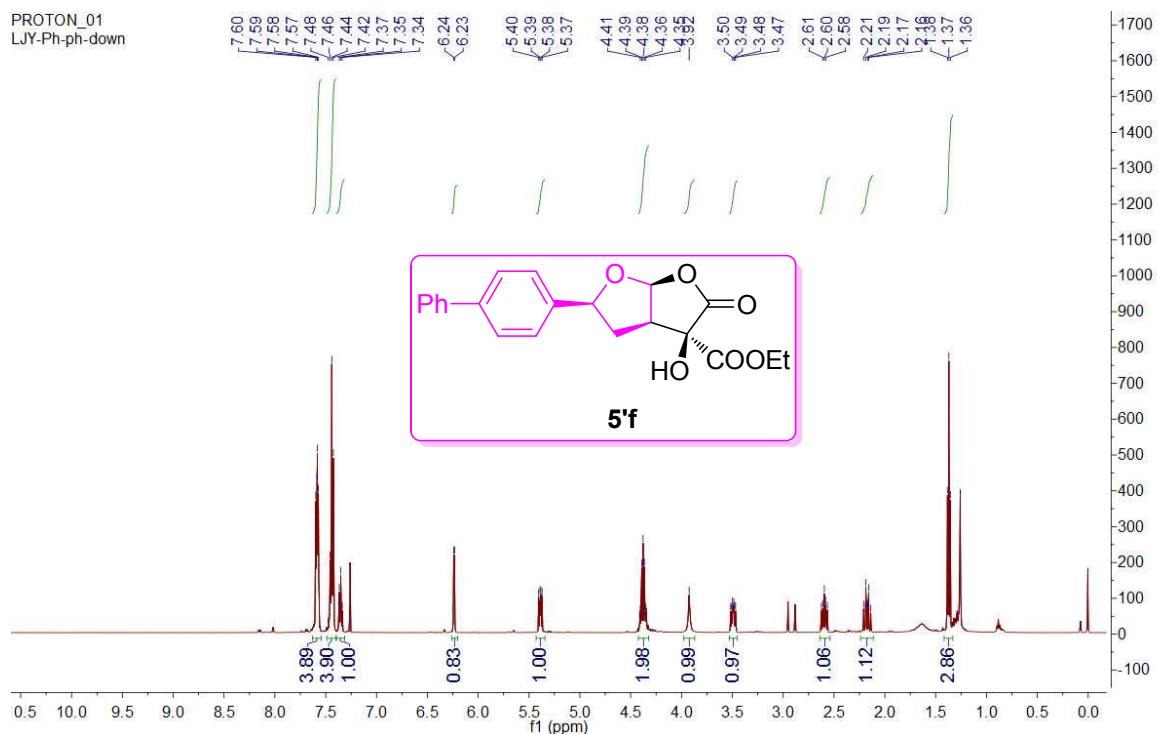
Chrom Type: Fixed WL Chromatogram, 210 nm



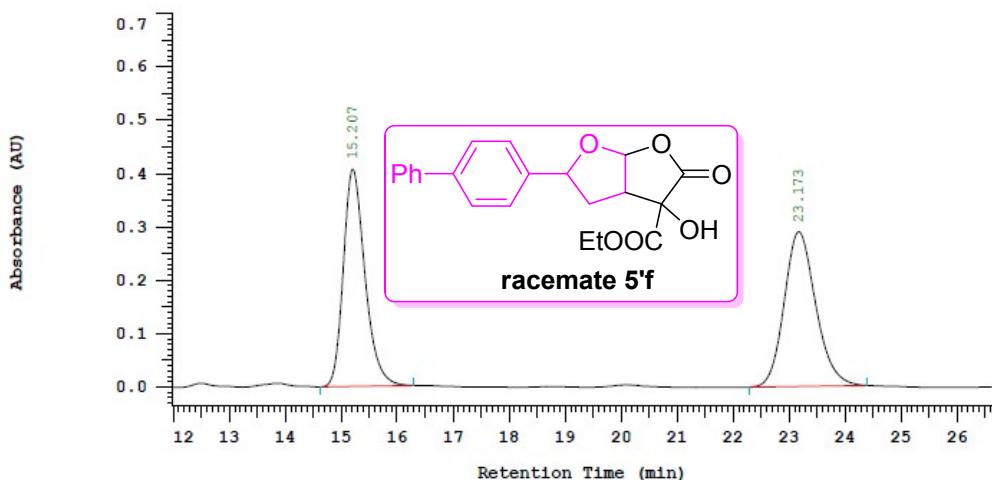
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	16.253	14030490	98.201	BB
2	23.153	257078	1.799	BB
14287568		100.000		



Chrom Type: Fixed WL Chromatogram, 210 nm

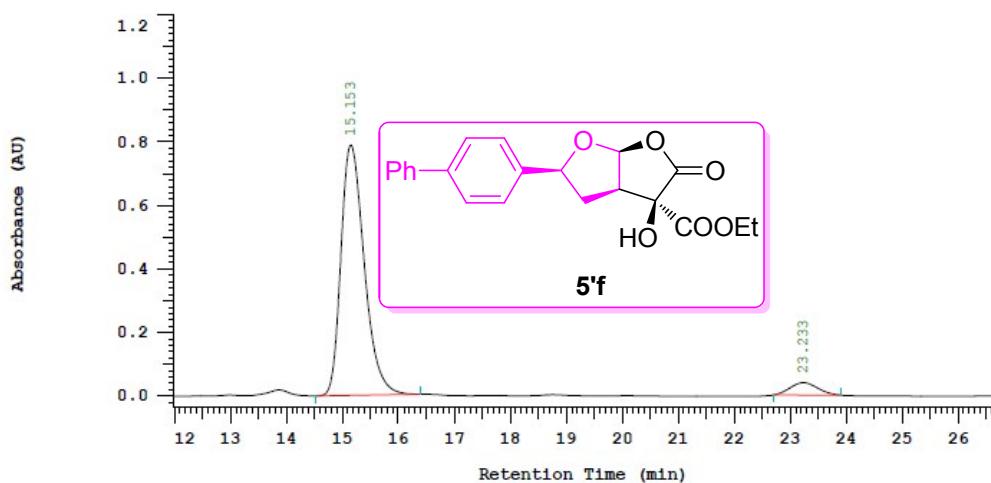


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.207	5464139	49.091	BB
2	23.173	5666438	50.909	BB
		11130577	100.000	

Chrom Type: Fixed WL Chromatogram, 210 nm

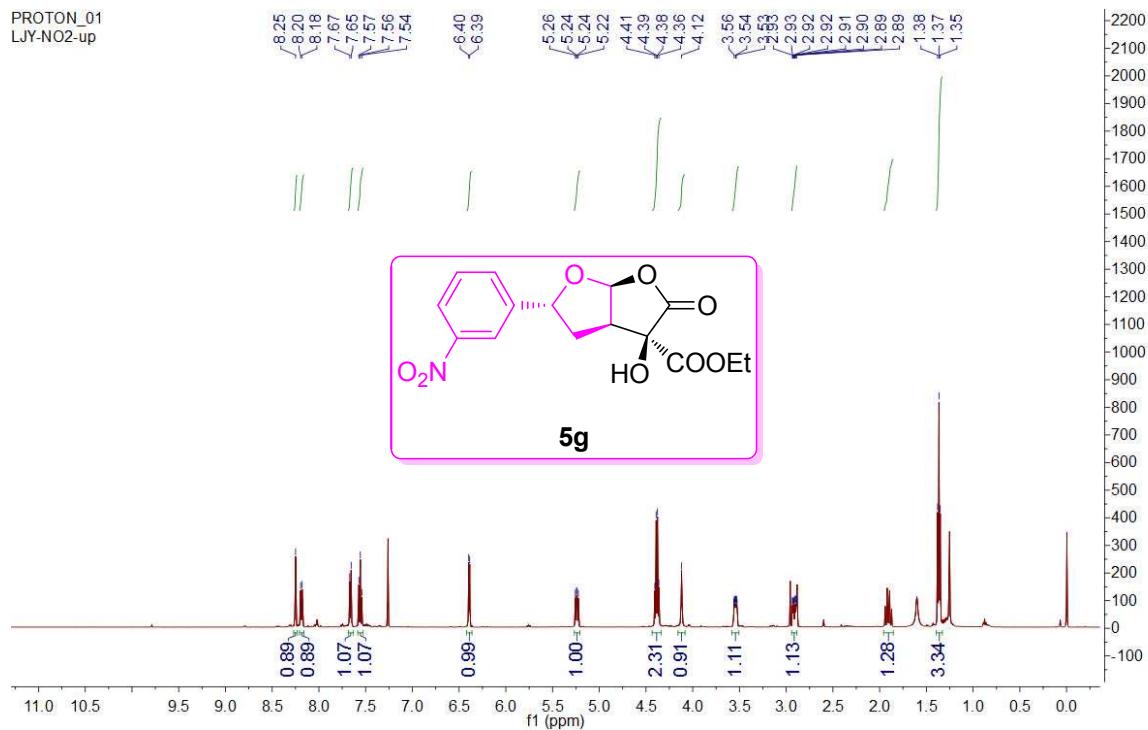


Chrom Type: Fixed WL Chromatogram, 210 nm

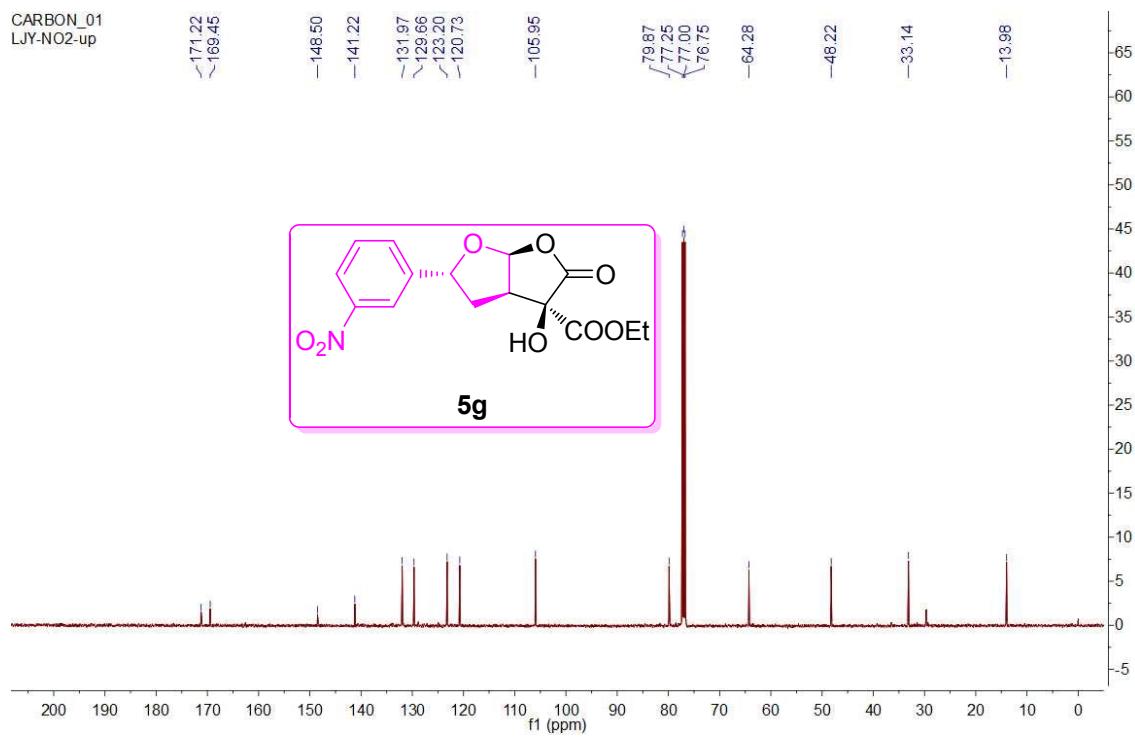
Peak Quantitation: AREA
Calculation Method: AREA%

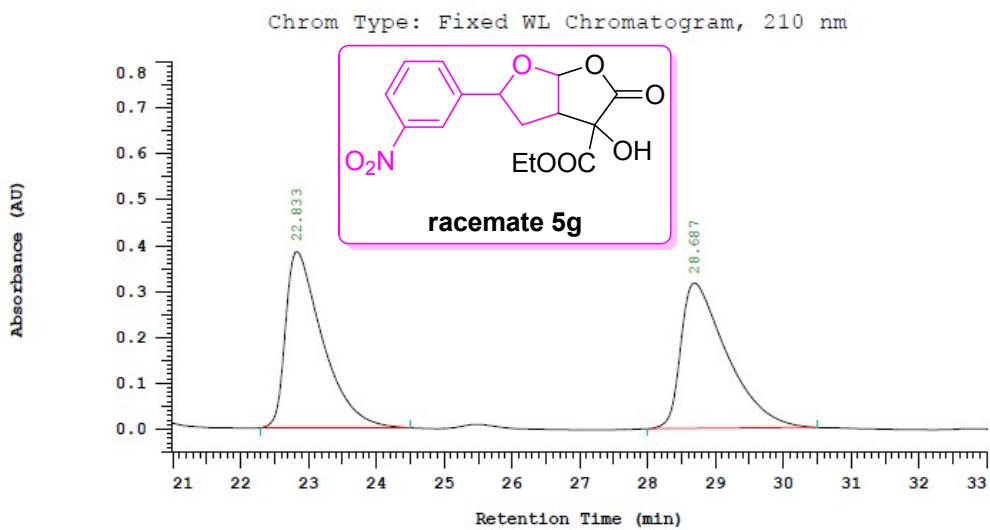
No.	RT	Area	Area %	BC
1	15.153	11431783	94.457	BB
2	23.233	670907	5.543	BB
		12102690	100.000	

PROTON_01
LJY-NO2-up



CARBON_01
LJY-NO2-up



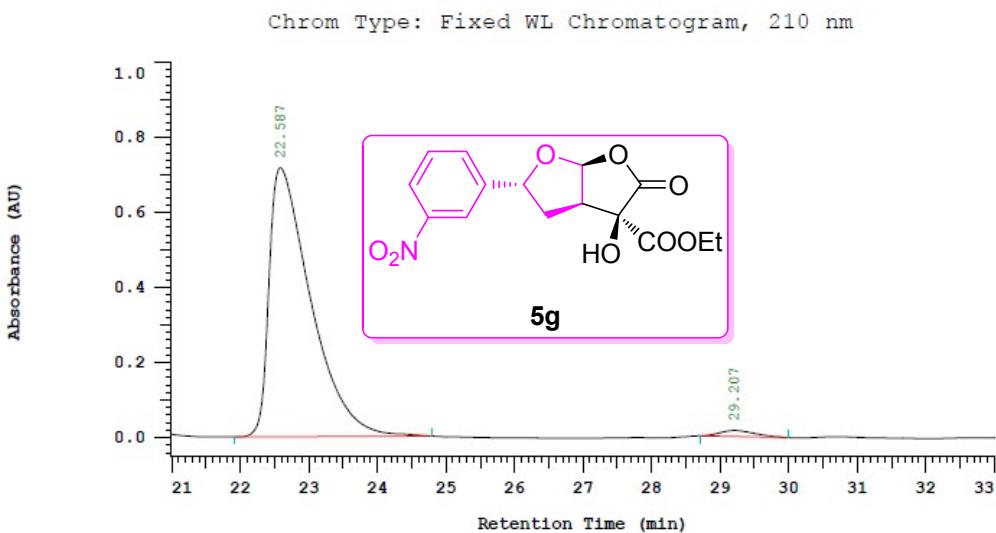


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	22.833	7272795	49.279	BB
2	28.687	7485505	50.721	BB
		14758300	100.000	

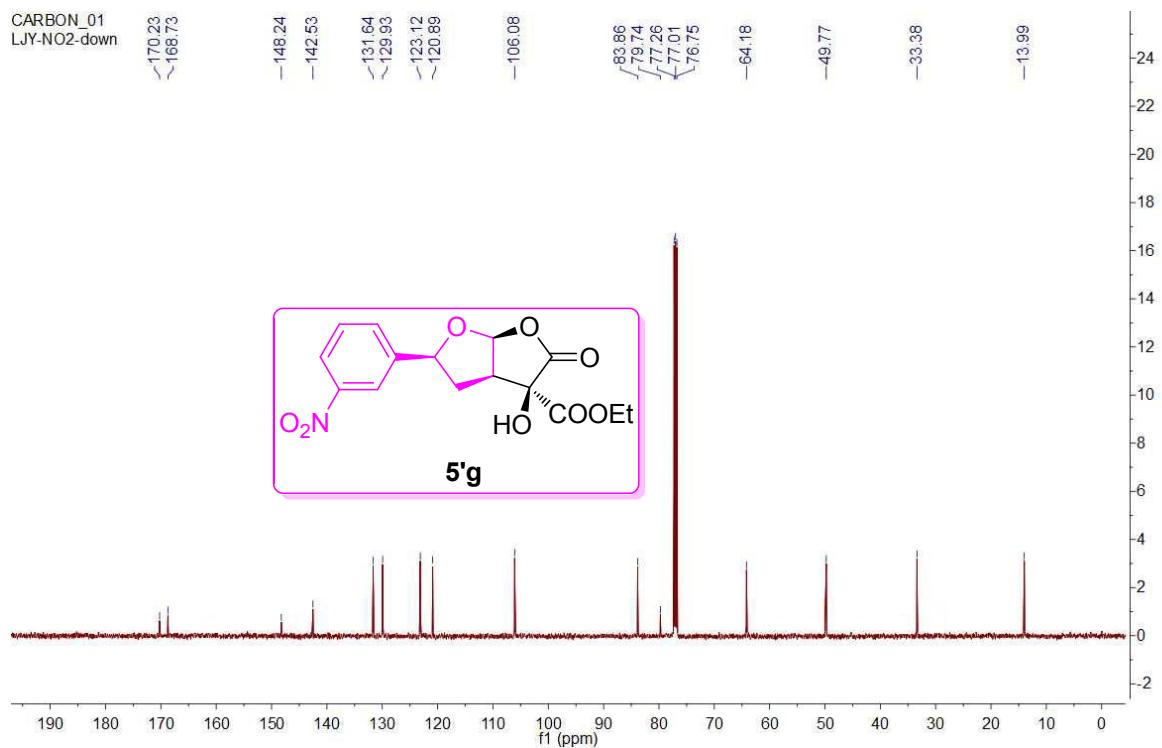
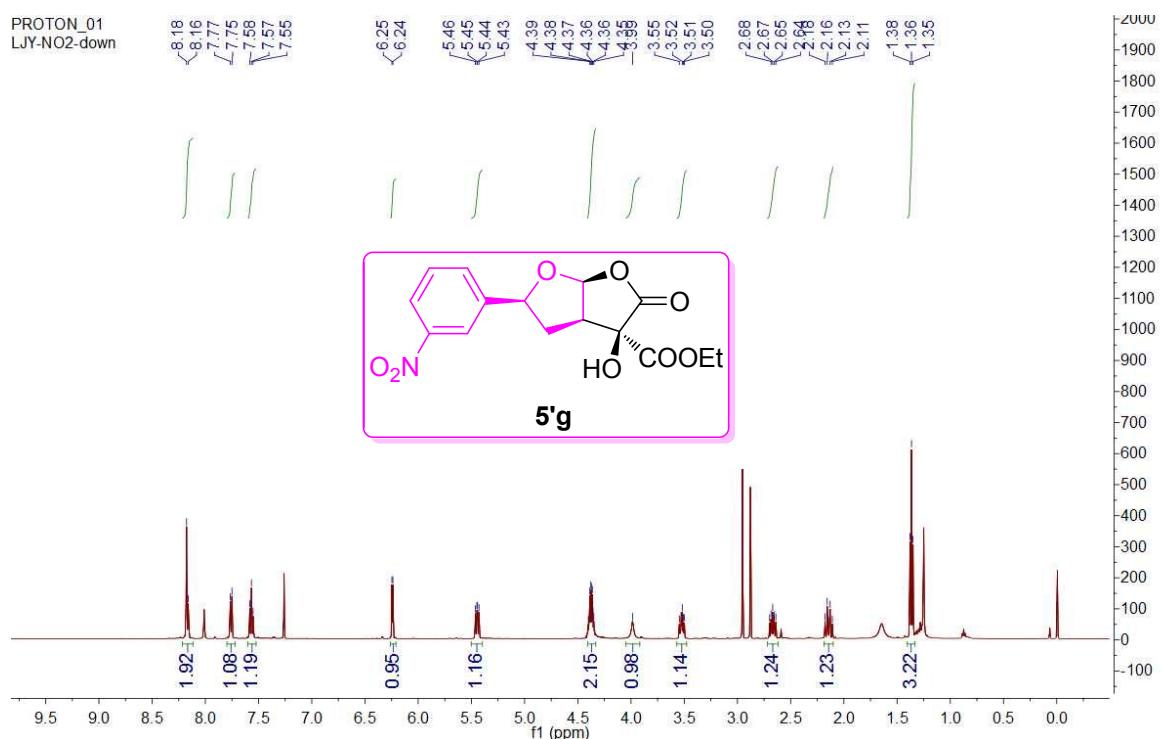


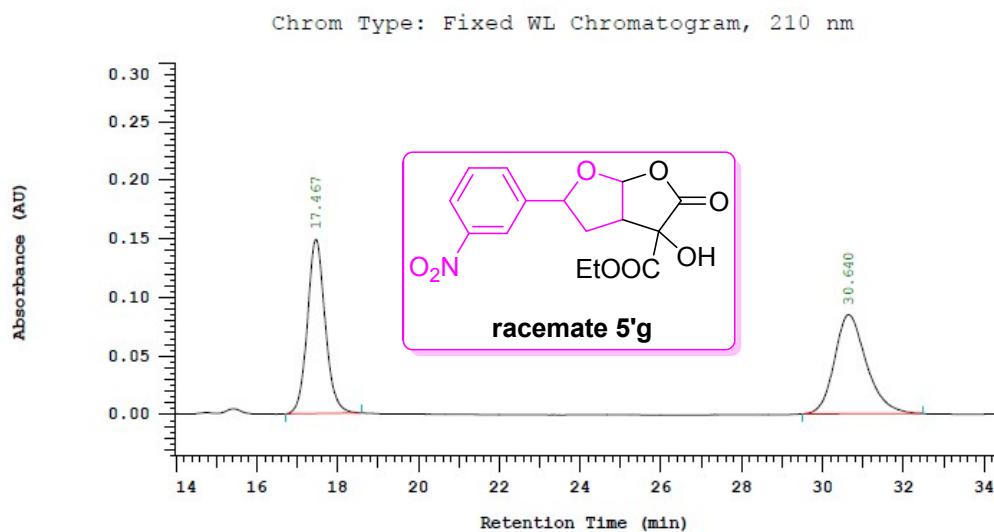
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	22.587	15156526	98.145	BB
2	29.207	286518	1.855	BB
		15443044	100.000	



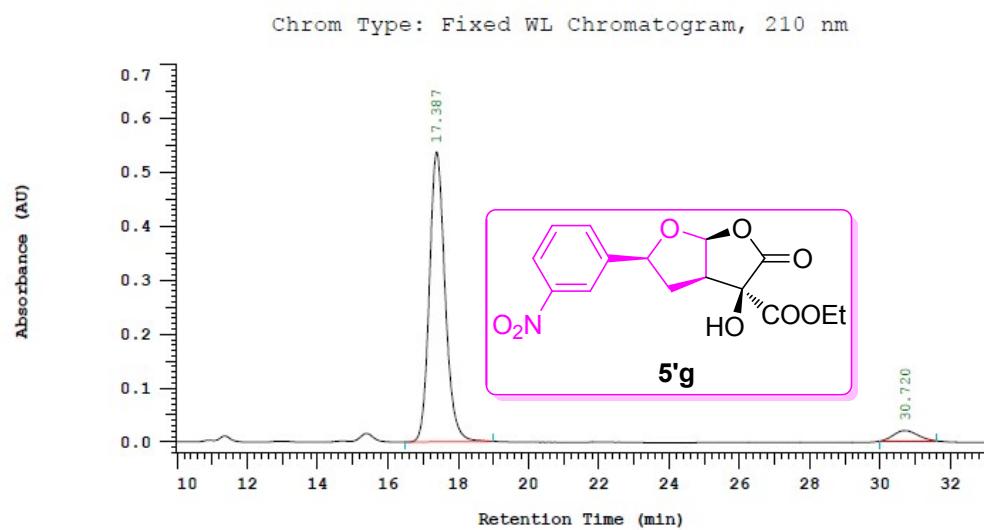


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	17.467	2272576	49.450	BB
2	30.640	2323147	50.550	BB
		4595723	100.000	

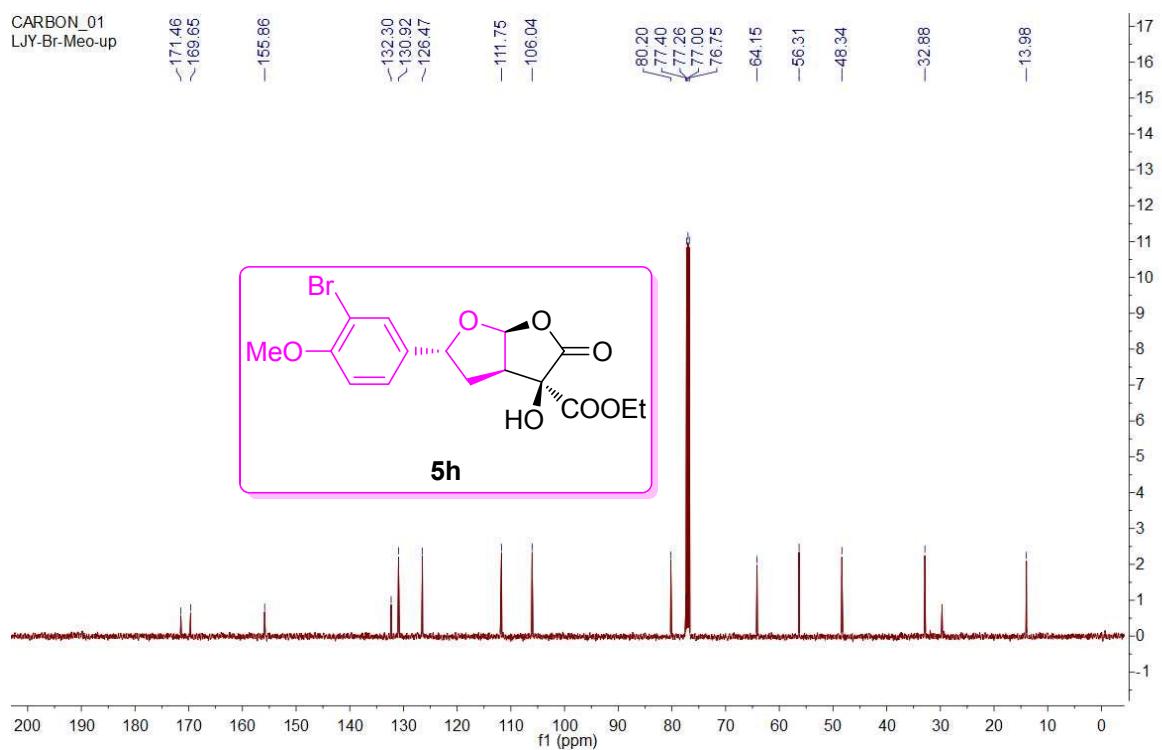
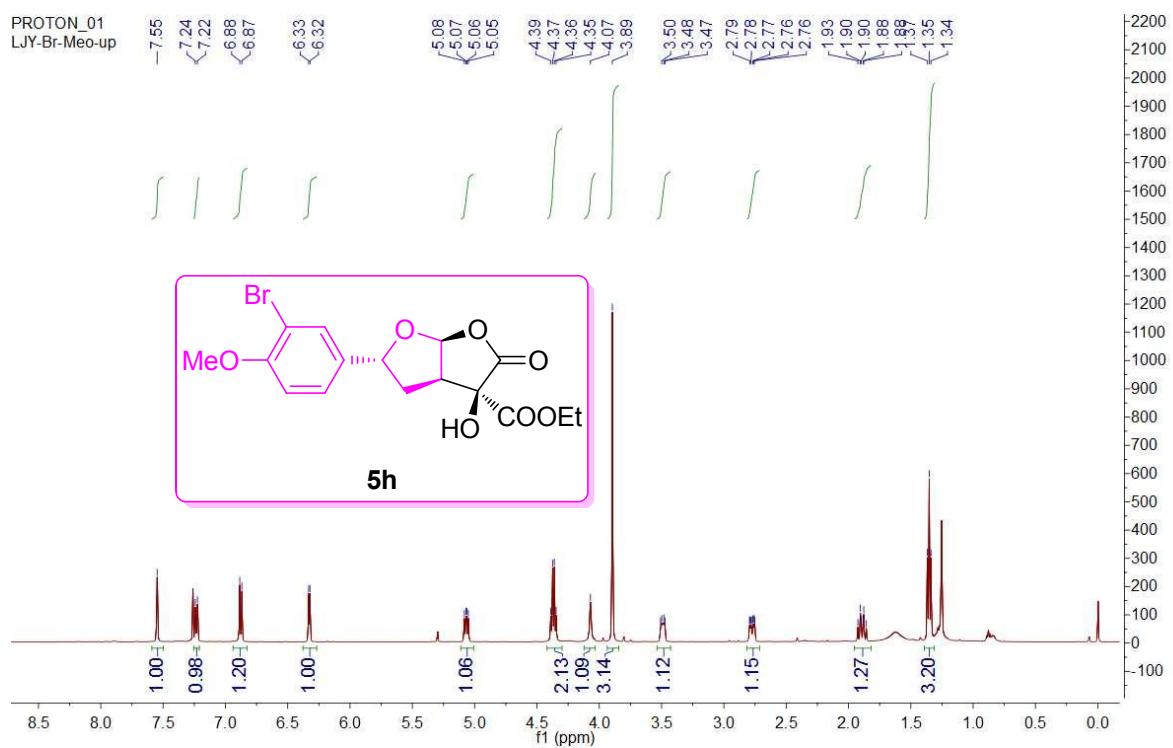


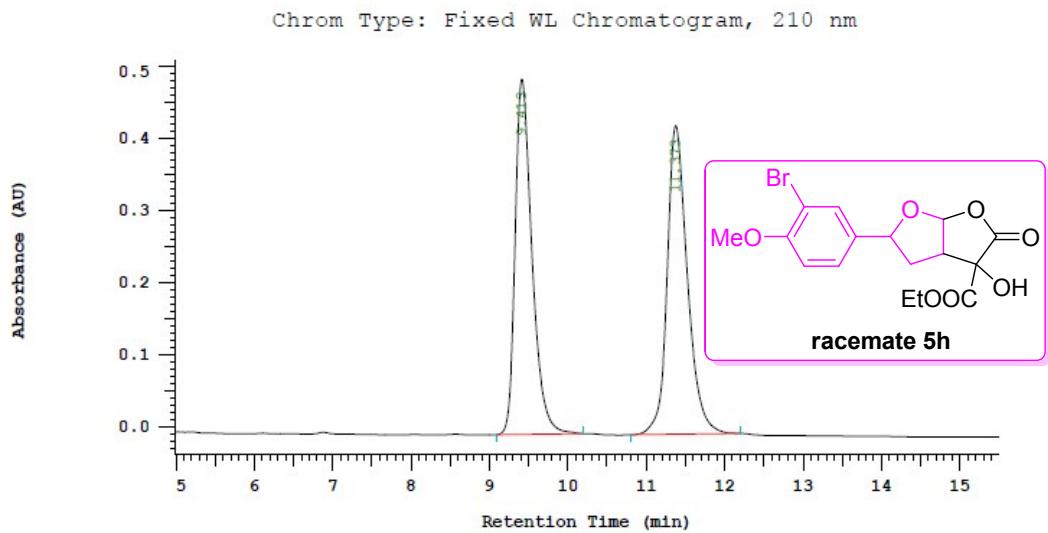
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	17.387	8351667	94.779	BB
2	30.720	460081	5.221	BB
		8811748	100.000	



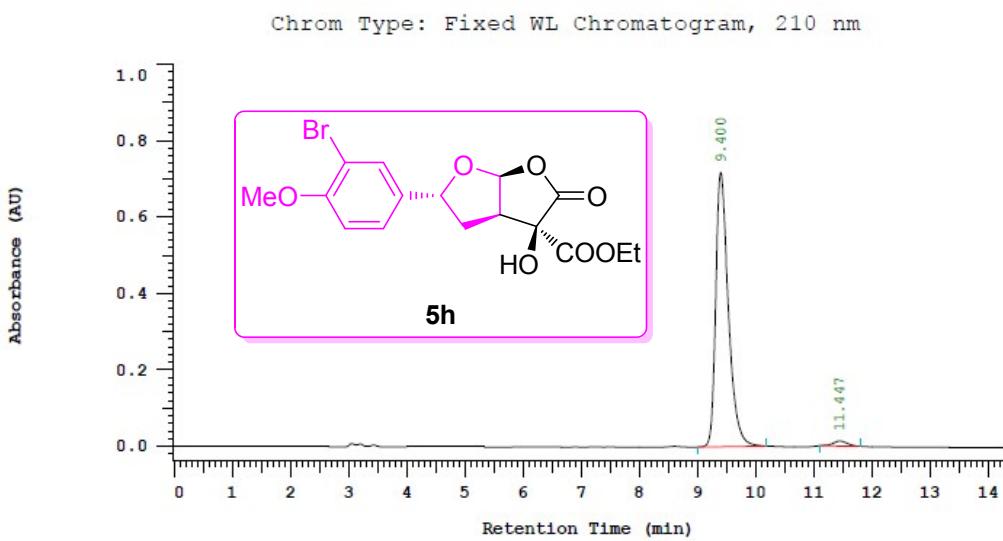


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.413	3650086	48.835	BB
2	11.373	3824252	51.165	BB
		7474338	100.000	

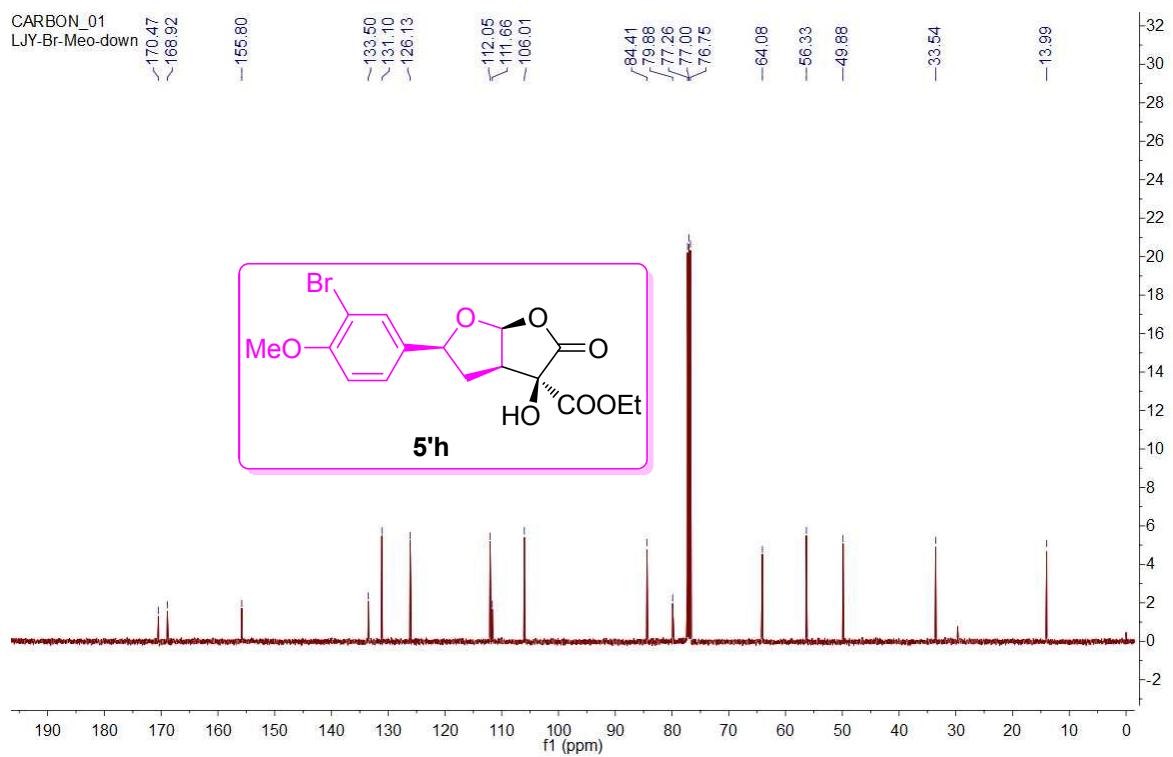
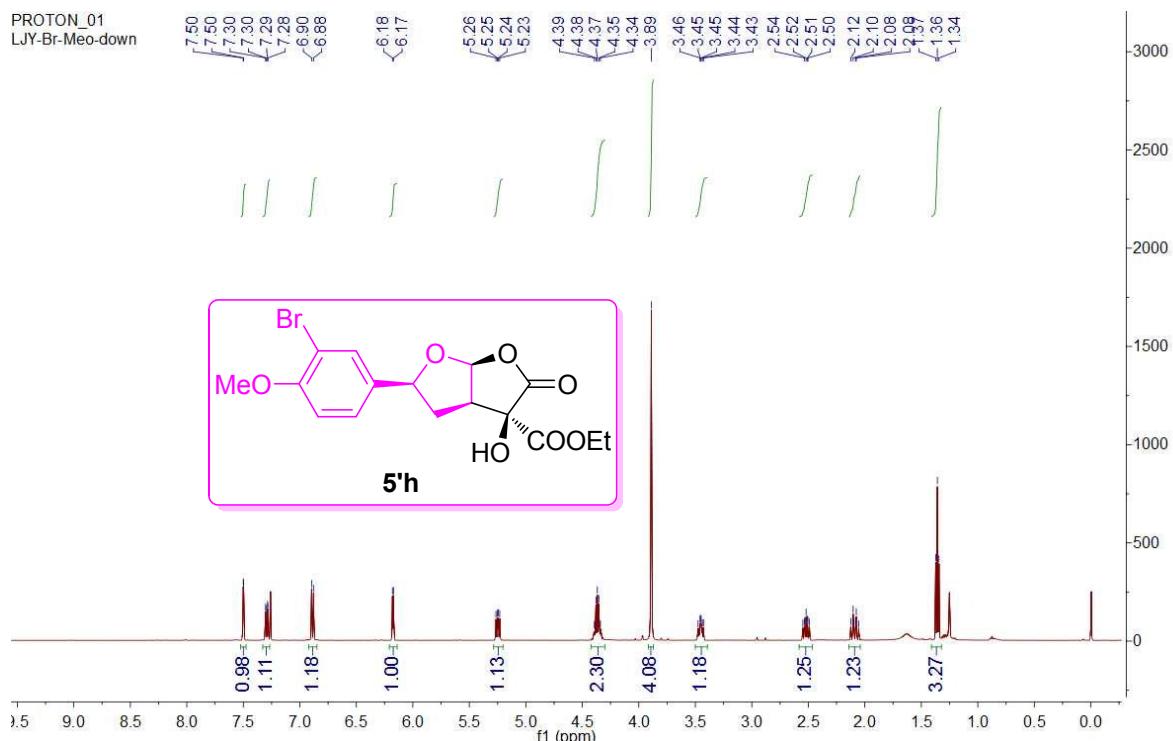


Chrom Type: Fixed WL Chromatogram, 210 nm

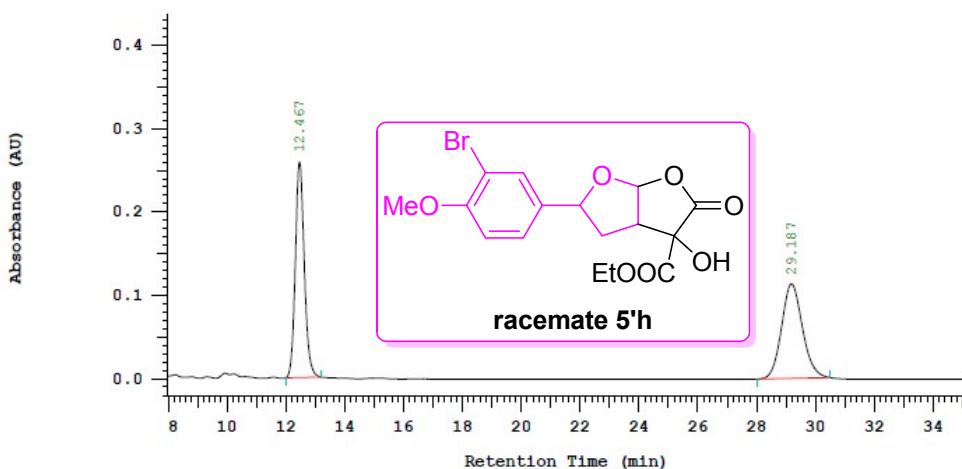
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.400	5422723	97.985	BB
2	11.447	111522	2.015	BB
		5534245	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

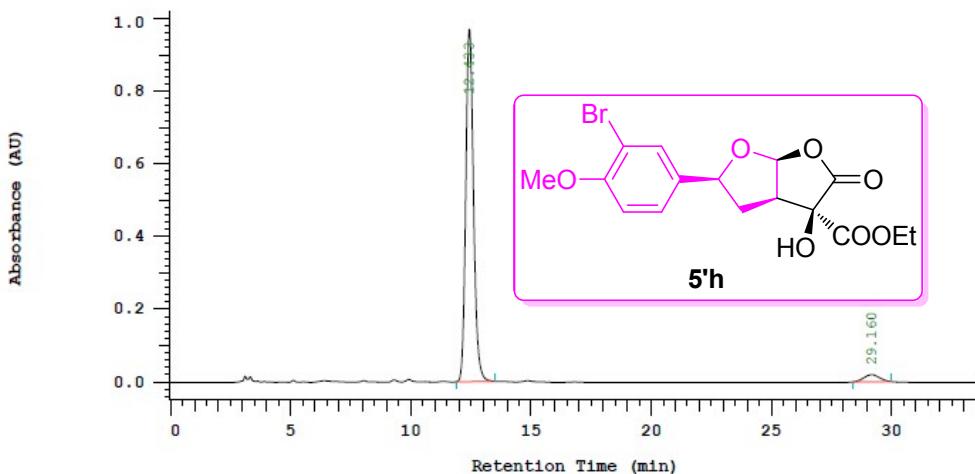


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.467	2729667	49.414	BB
2	29.187	2794356	50.586	BB
5524023		100.000		

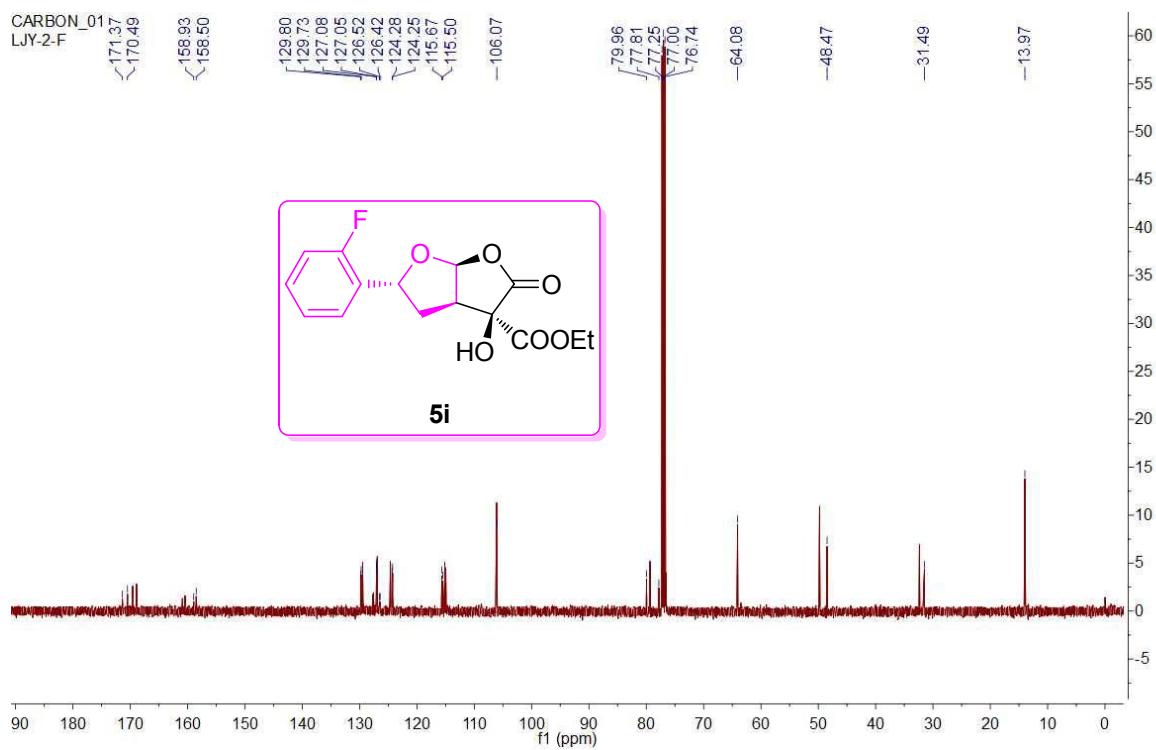
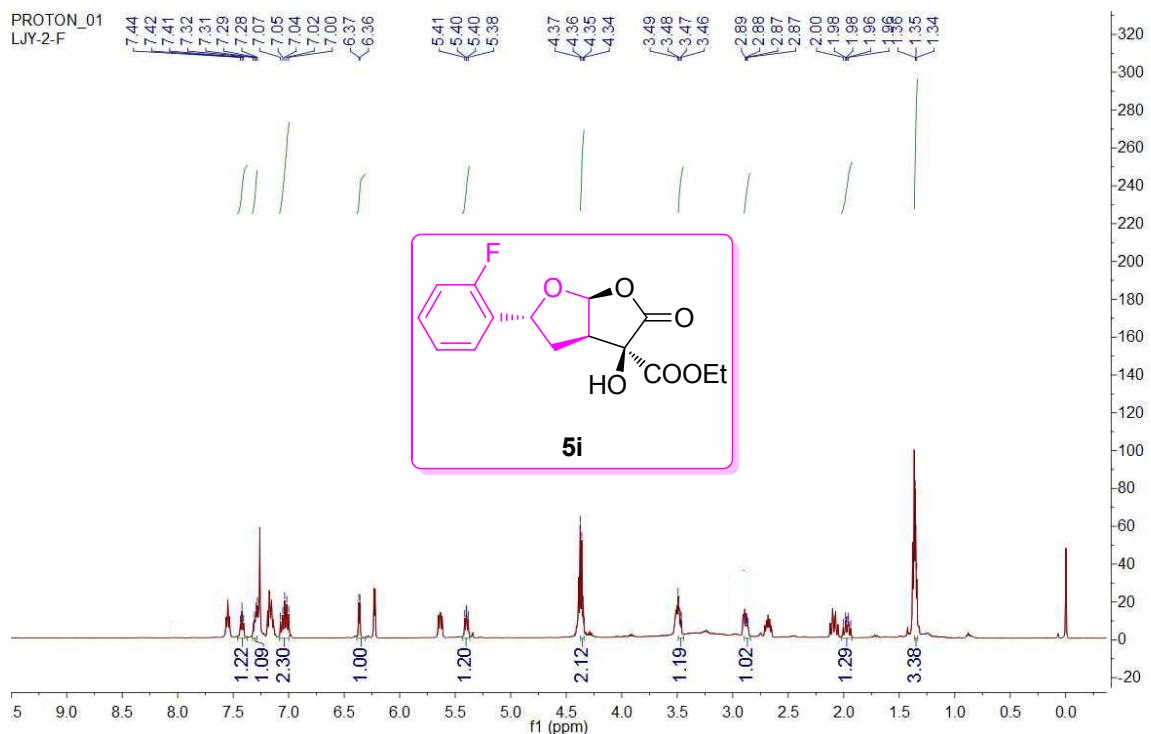
Chrom Type: Fixed WL Chromatogram, 210 nm



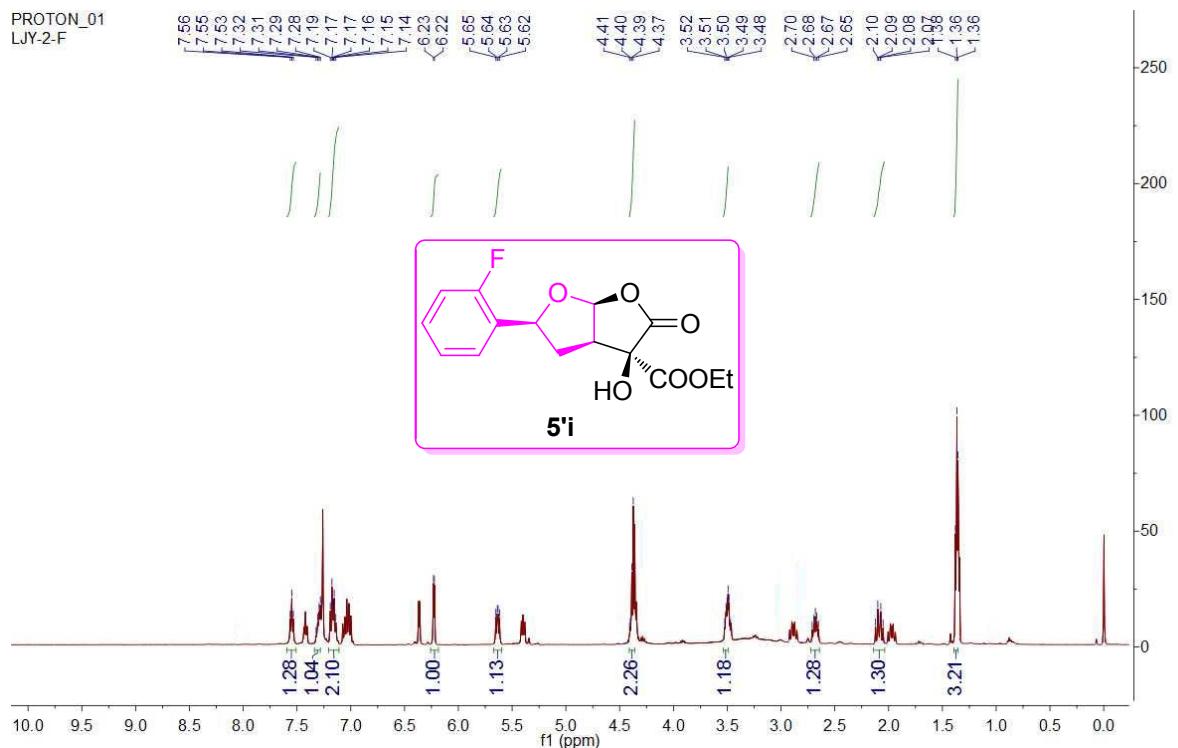
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

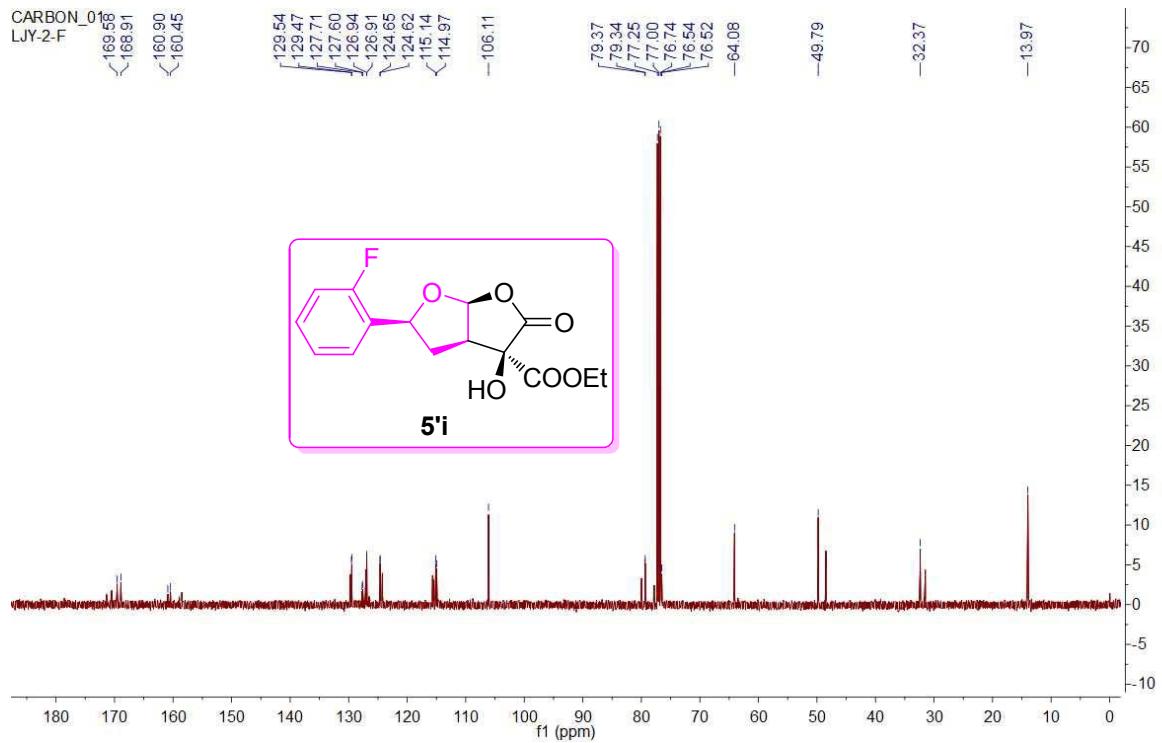
No.	RT	Area	Area %	BC
1	12.433	10701449	96.084	BB
2	29.160	436147	3.916	BB
11137596		100.000		

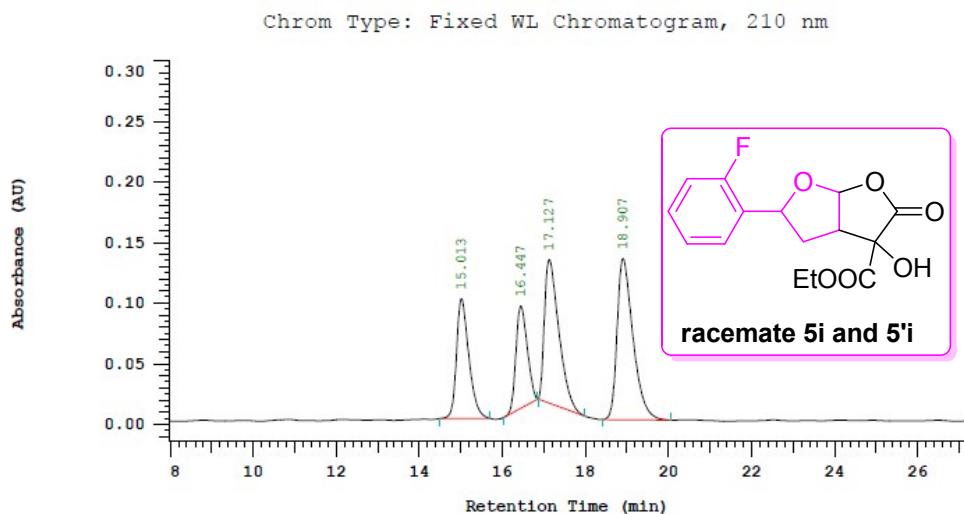


PROTON_01
LYY-2-F



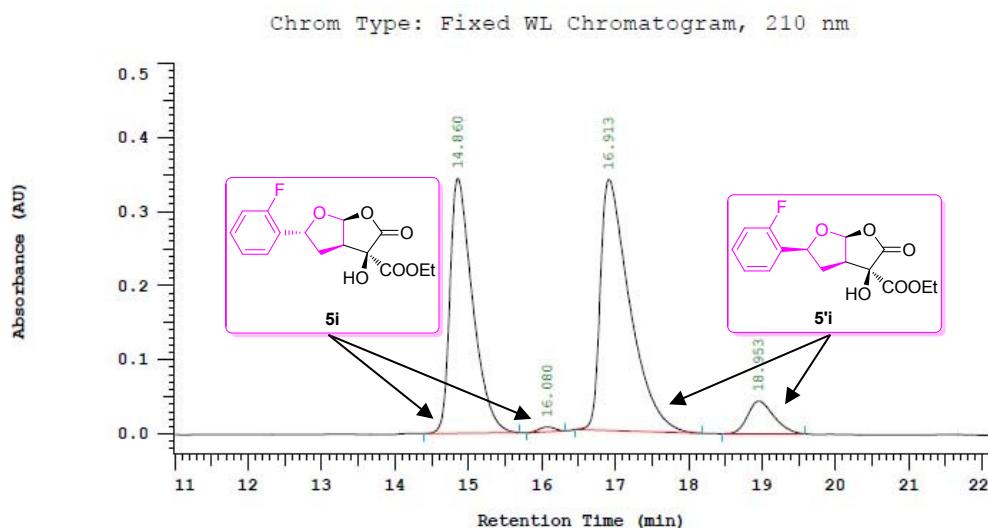
CARBON_01
LYY-2-F





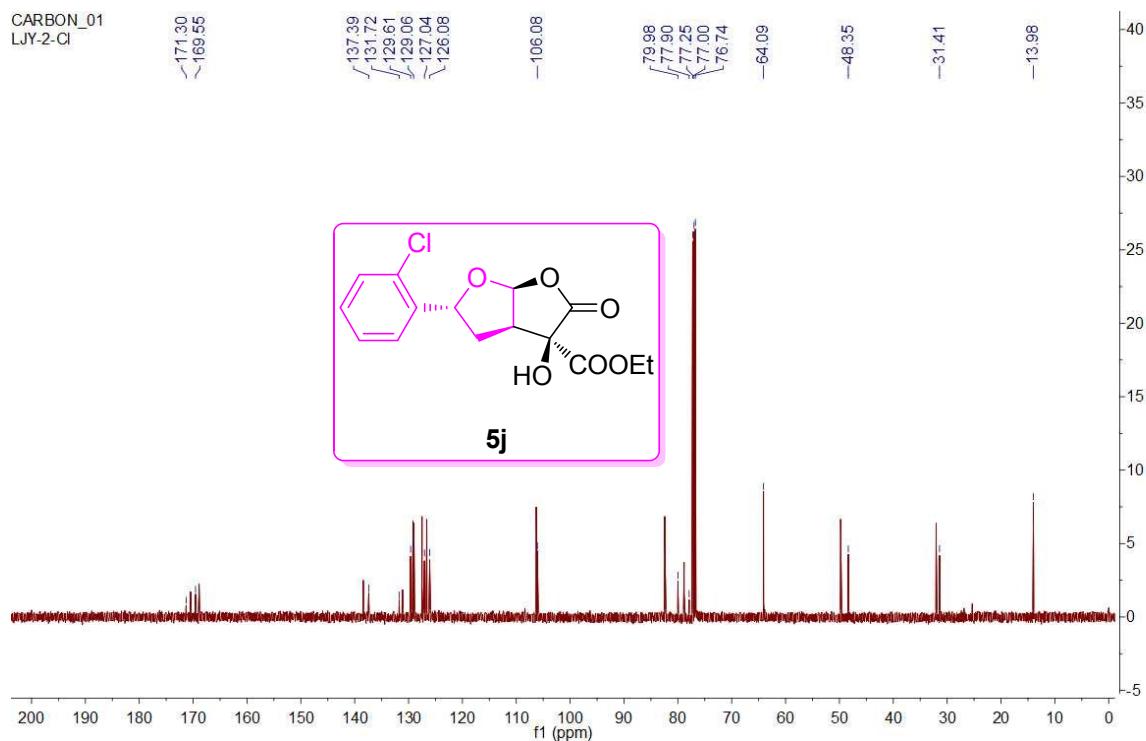
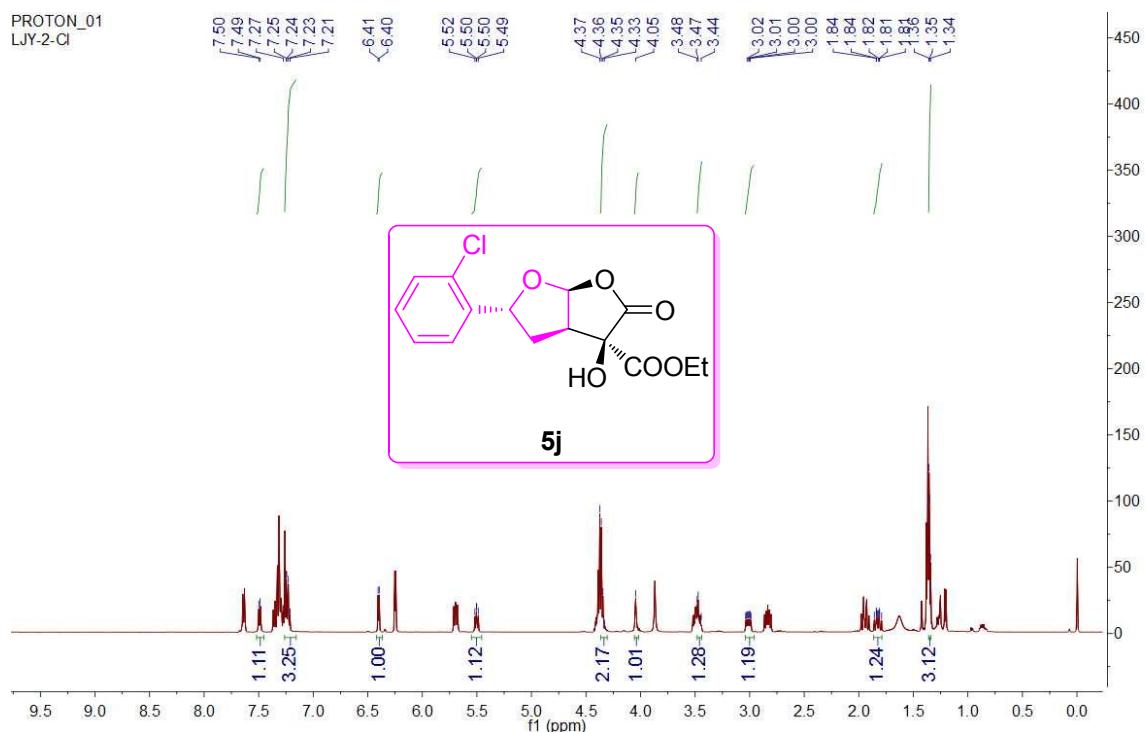
Chrom Type: Fixed WL Chromatogram, 210 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

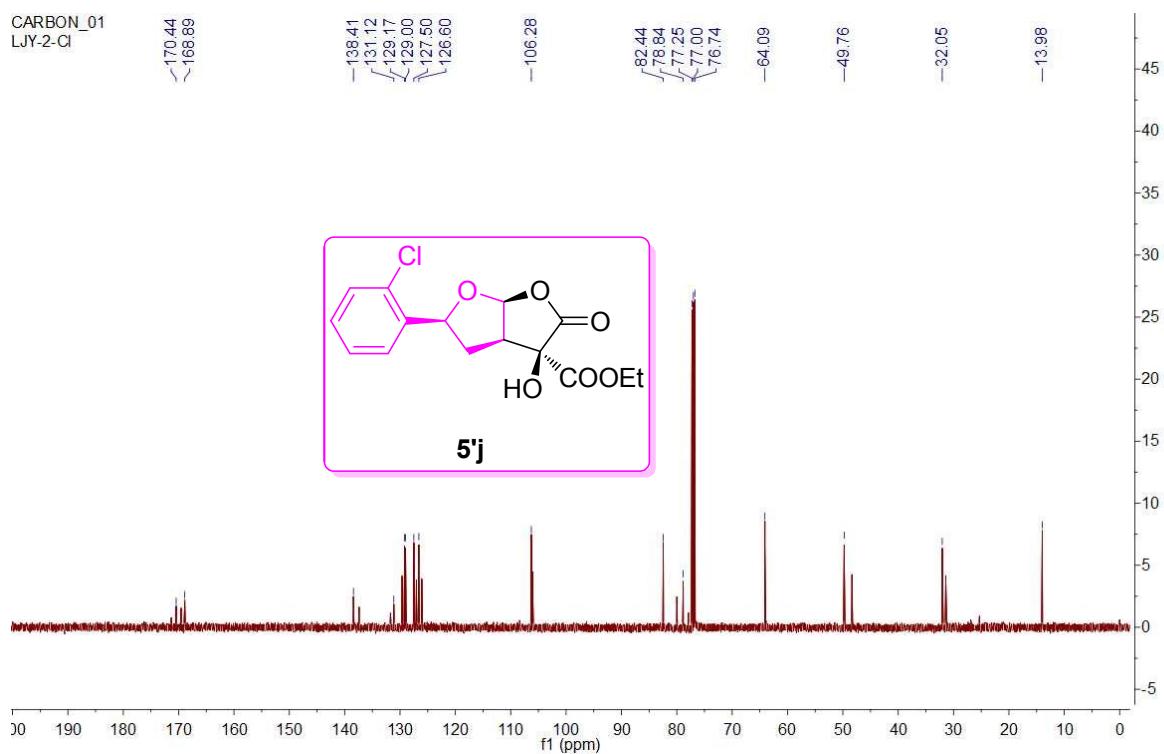
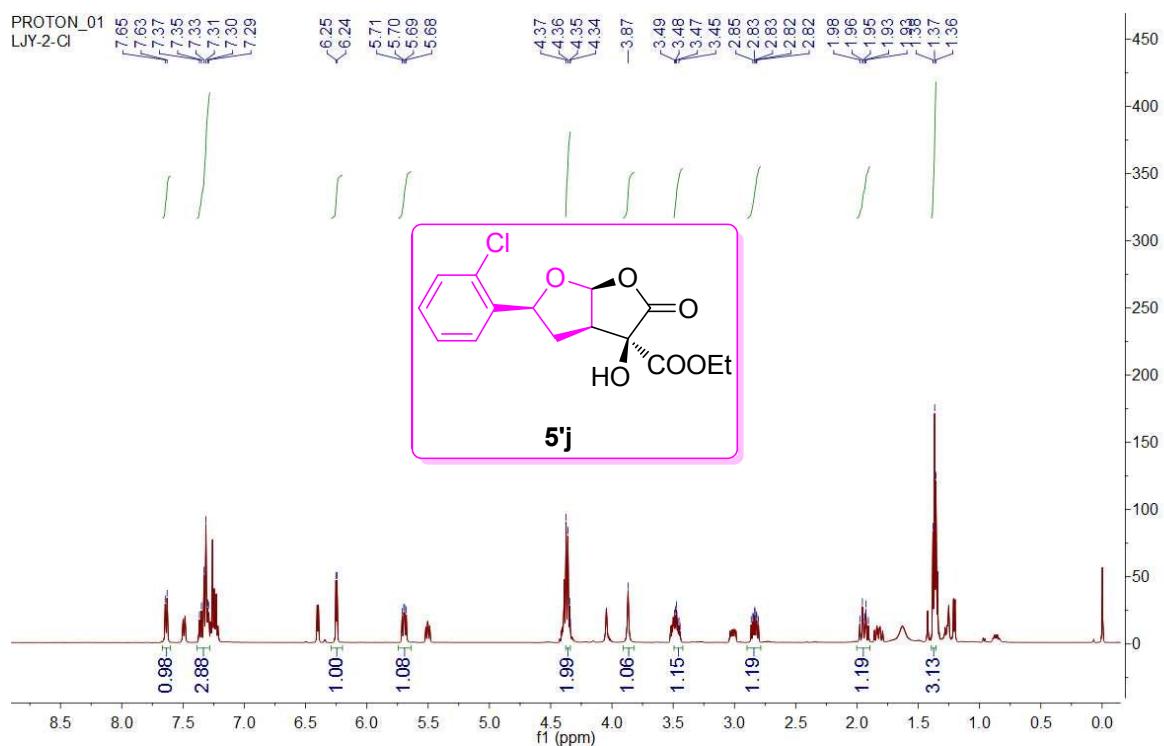
No.	RT	Area	Area %	BC
1	15.013	1020620	20.323	BB
2	16.447	800844	15.947	BB
3	17.127	1432071	28.516	BB
4	18.907	1768395	35.213	BB
		5021930	100.000	

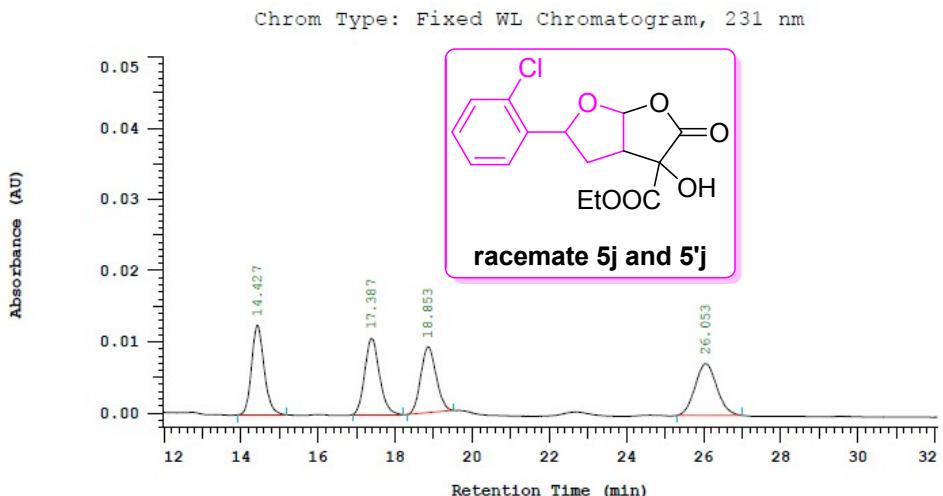


Chrom Type: Fixed WL Chromatogram, 210 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	14.860	3684739	42.681	BB
2	16.080	47227	0.547	BB
3	16.913	4693643	54.368	BB
4	18.953	207509	2.404	BB
		8633118	100.000	

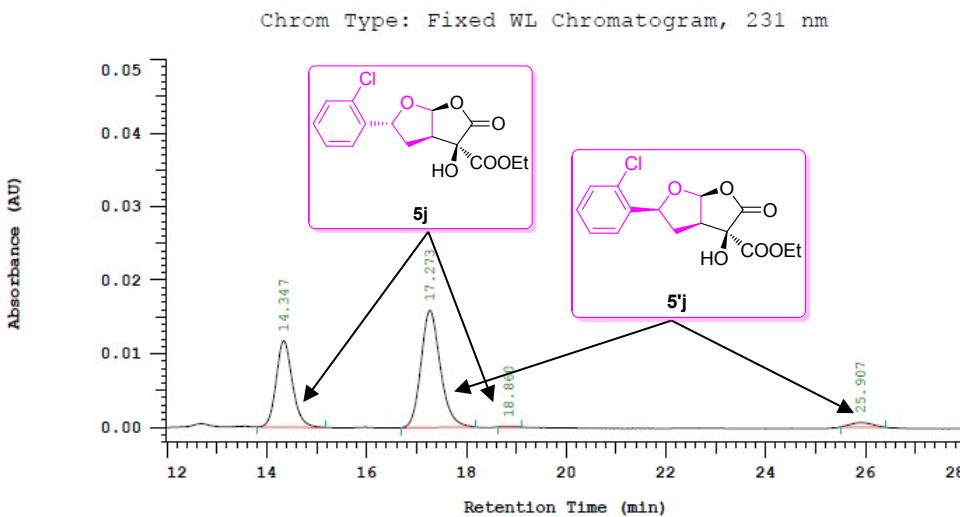






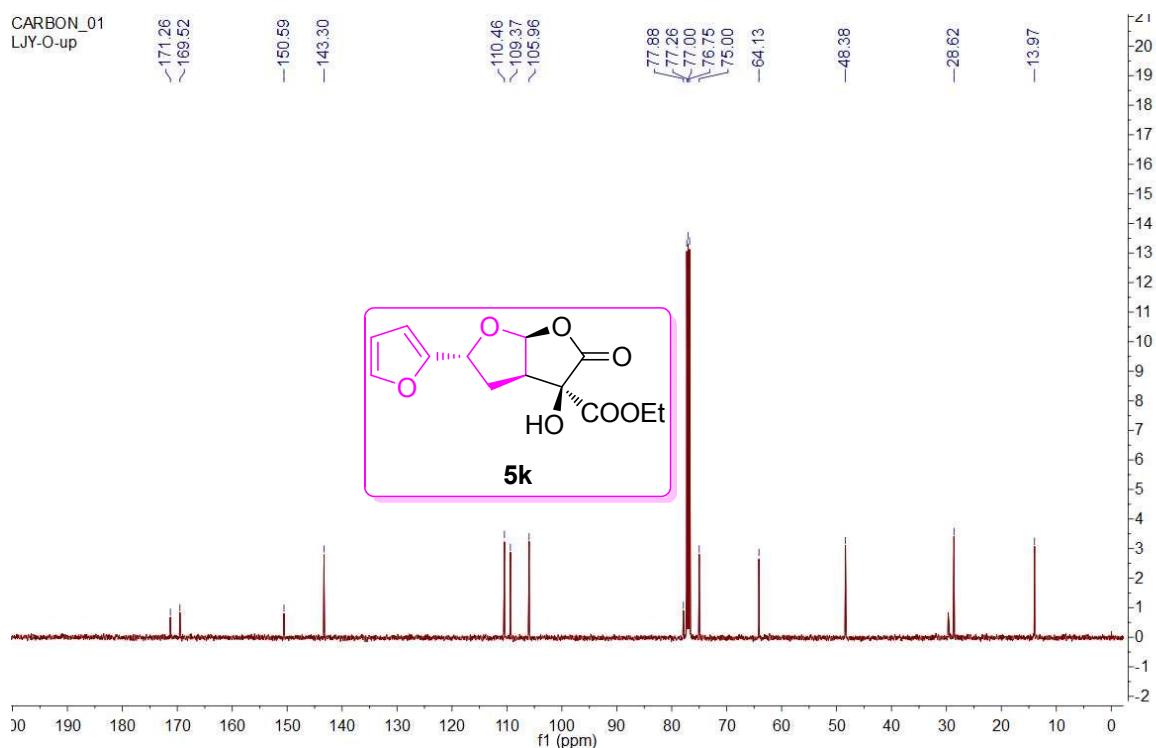
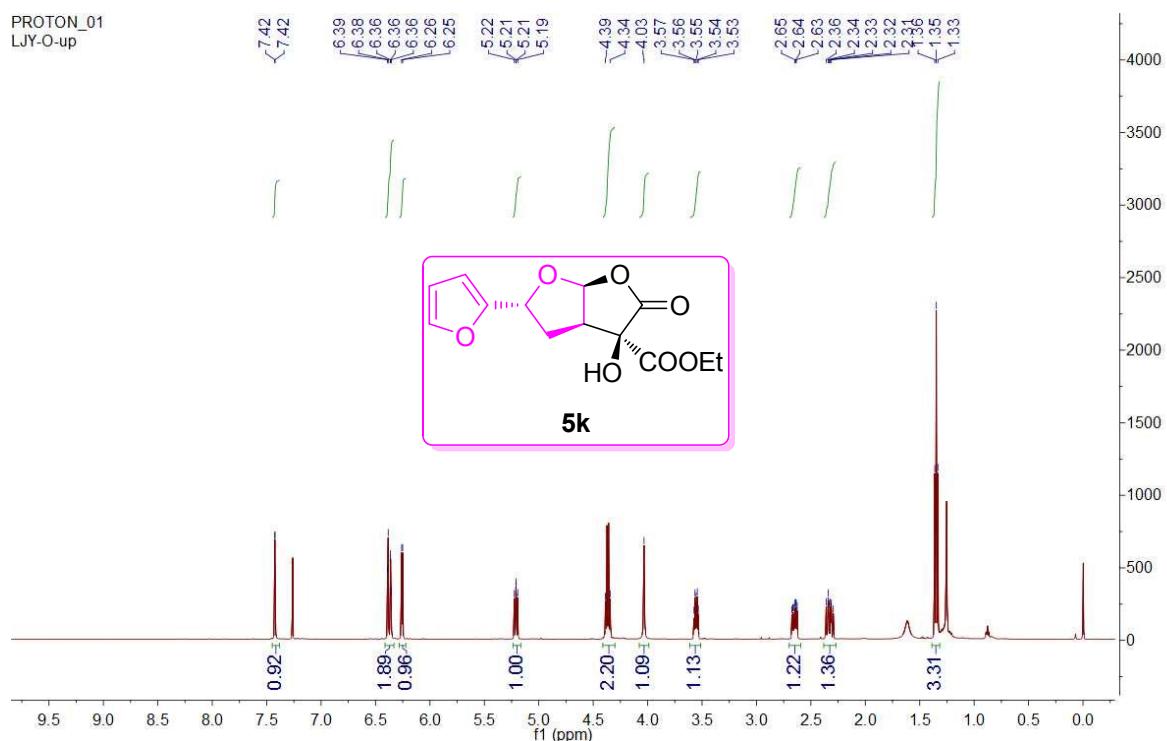
Chrom Type: Fixed WL Chromatogram, 231 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

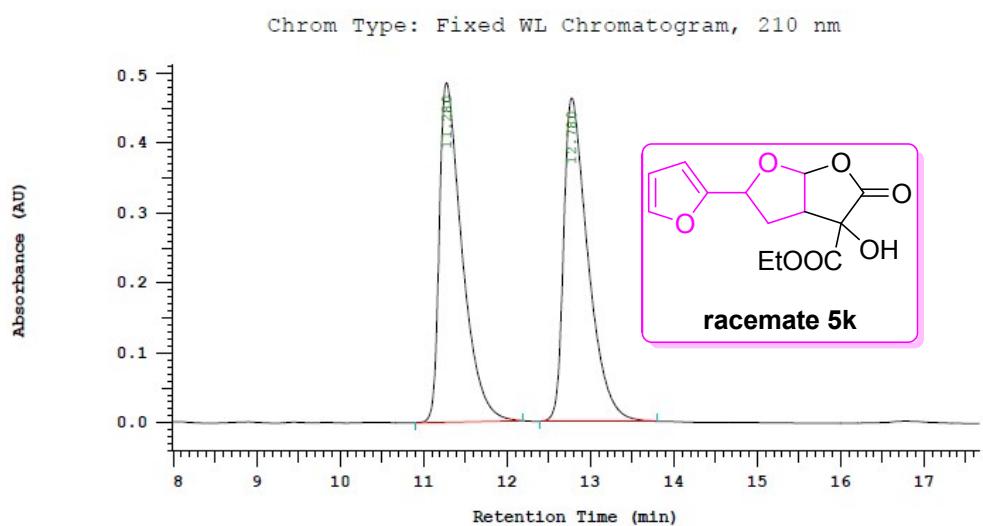
No.	RT	Area	Area %	BC
1	14.427	142500	25.634	BB
2	17.387	142696	25.669	BB
3	18.853	128099	23.044	BB
4	26.053	142604	25.653	BB
		555899	100.000	



Chrom Type: Fixed WL Chromatogram, 231 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	14.347	132951	37.074	BB
2	17.273	215910	60.208	BB
3	18.860	623	0.174	BB
4	25.907	9125	2.545	BB
		358609	100.000	



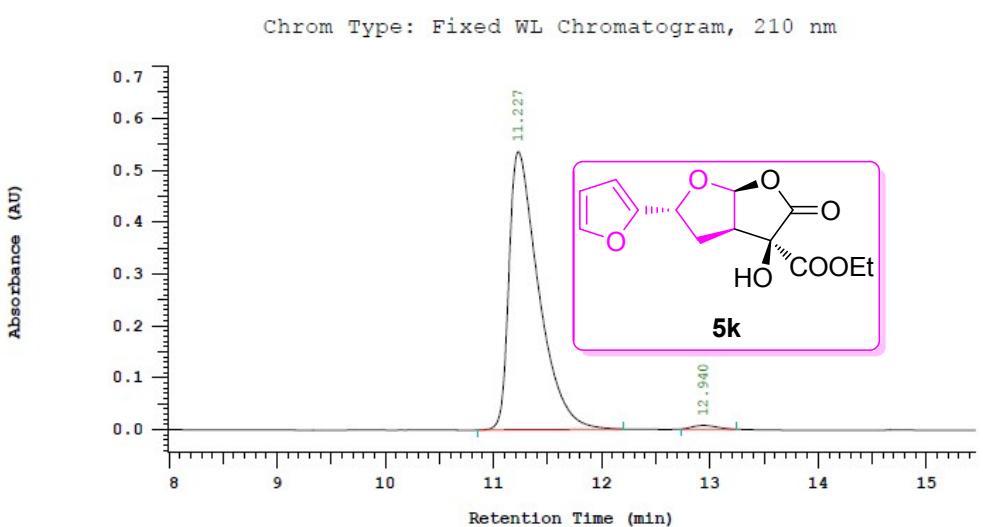


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.280	4605844	49.480	BB
2	12.780	4702667	50.520	BB
		9308511	100.000	

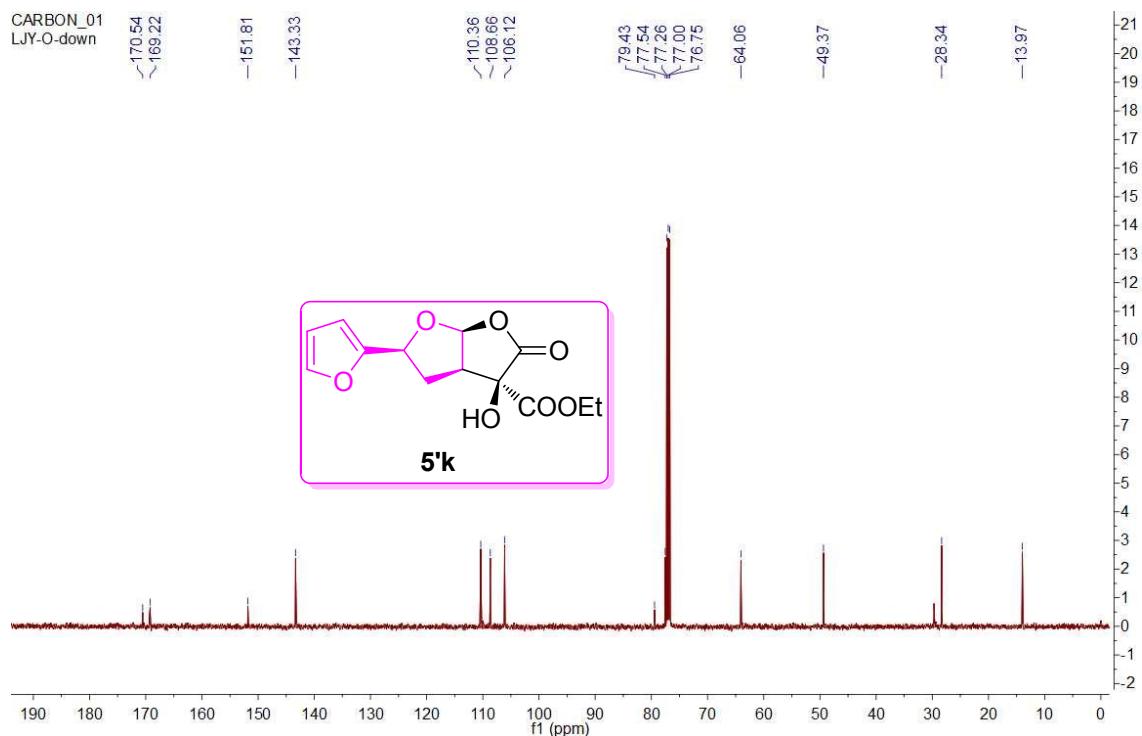
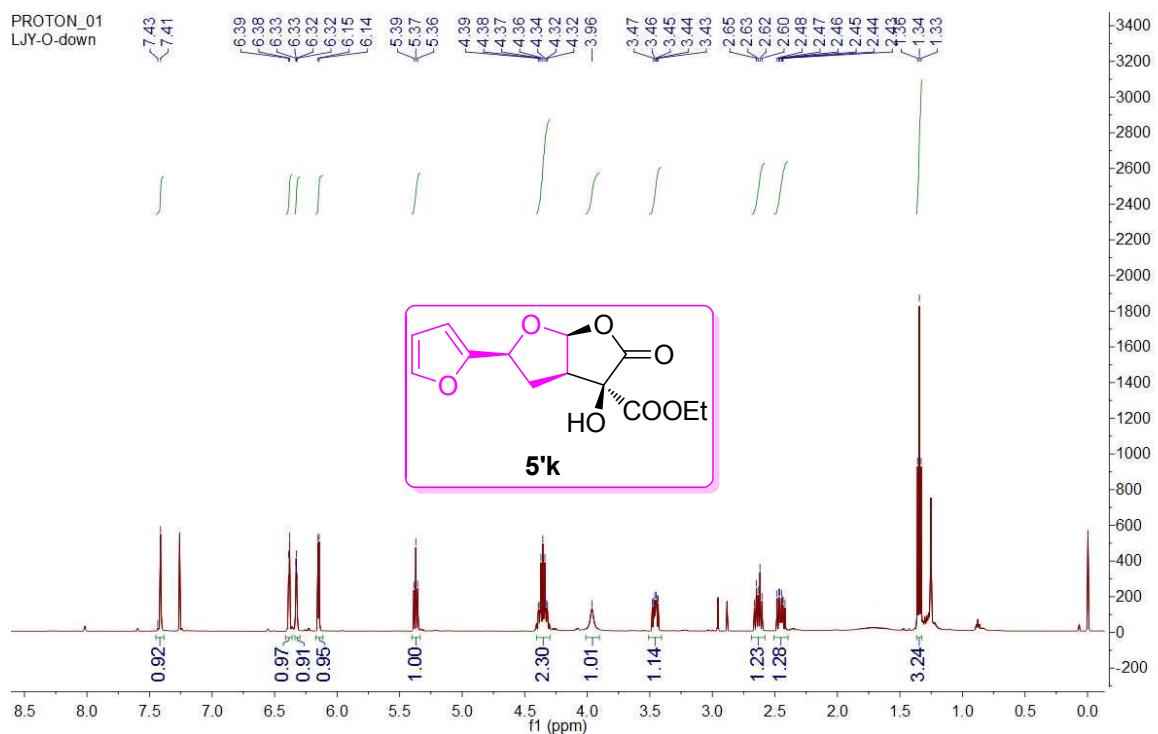


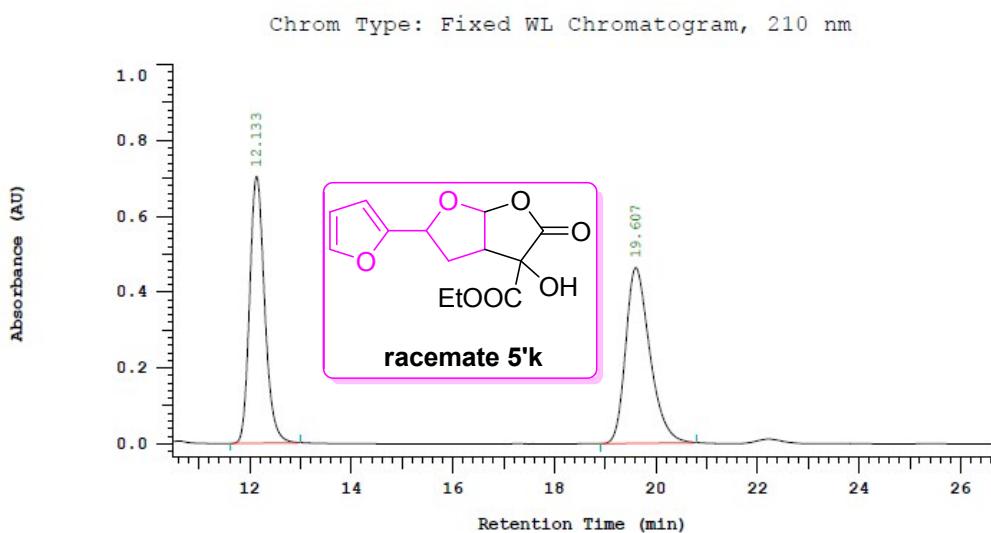
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.227	5103152	98.949	BB
2	12.940	54181	1.051	BB
		5157333	100.000	



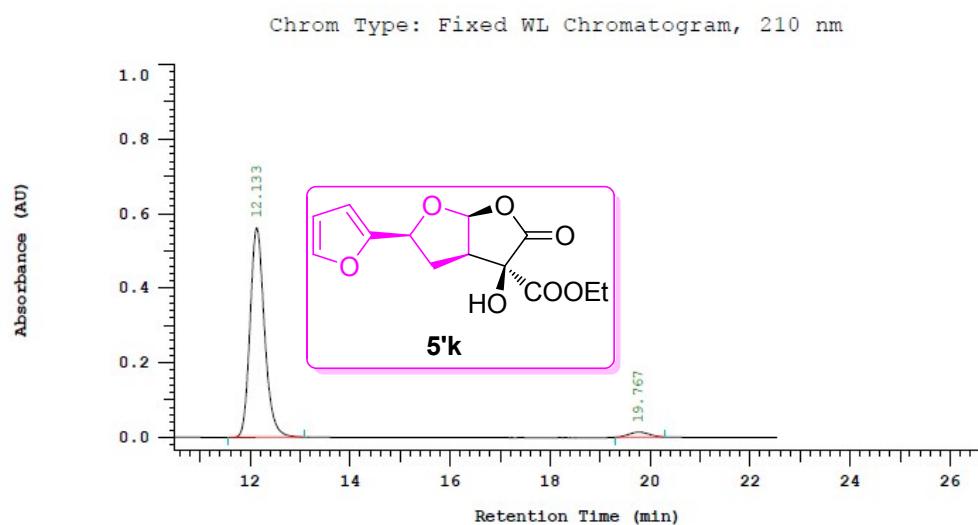


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.133	7255588	48.600	BB
2	19.607	7673651	51.400	BB
14929239		100.000		

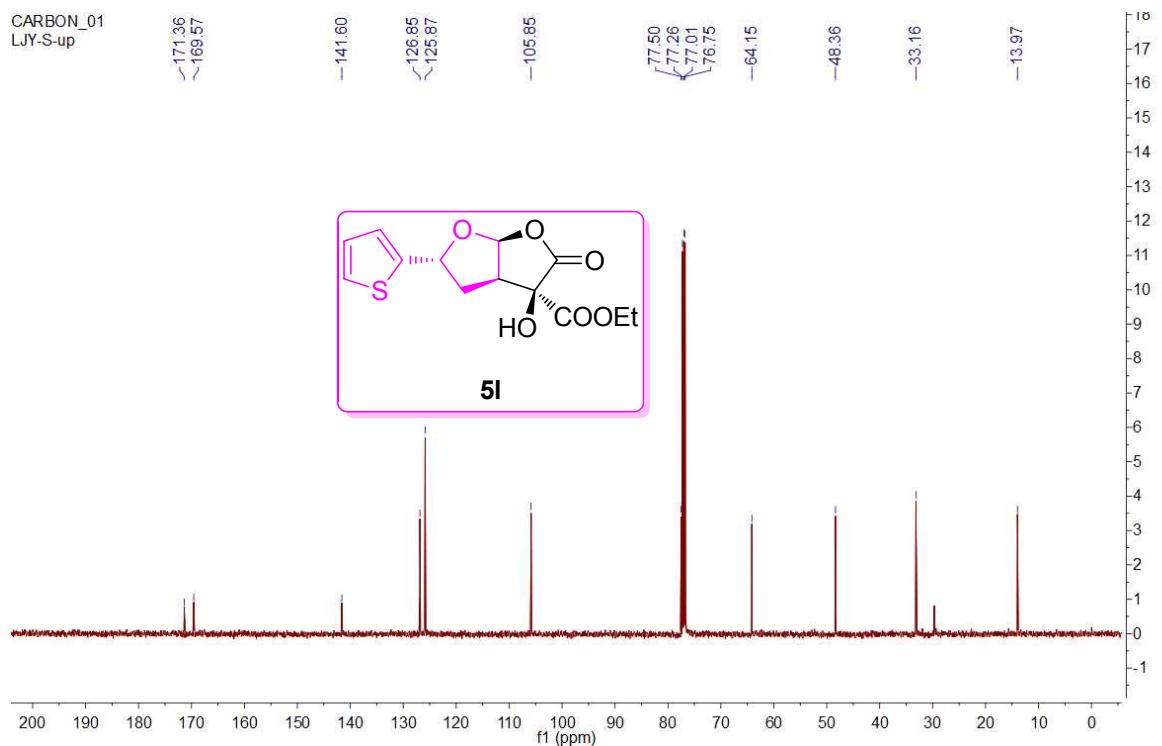
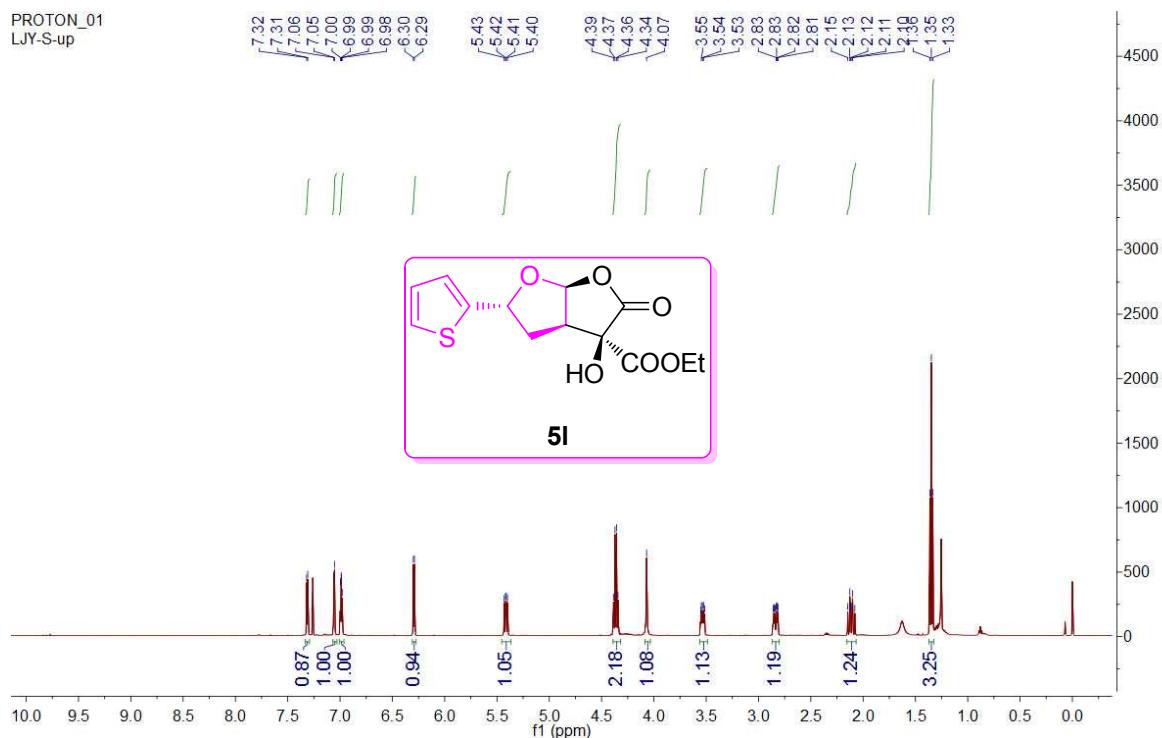


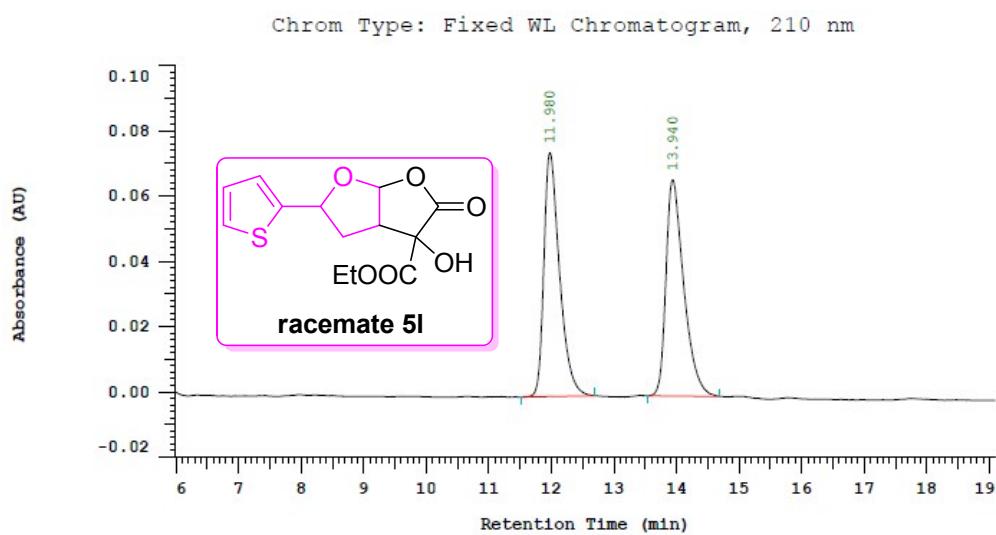
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

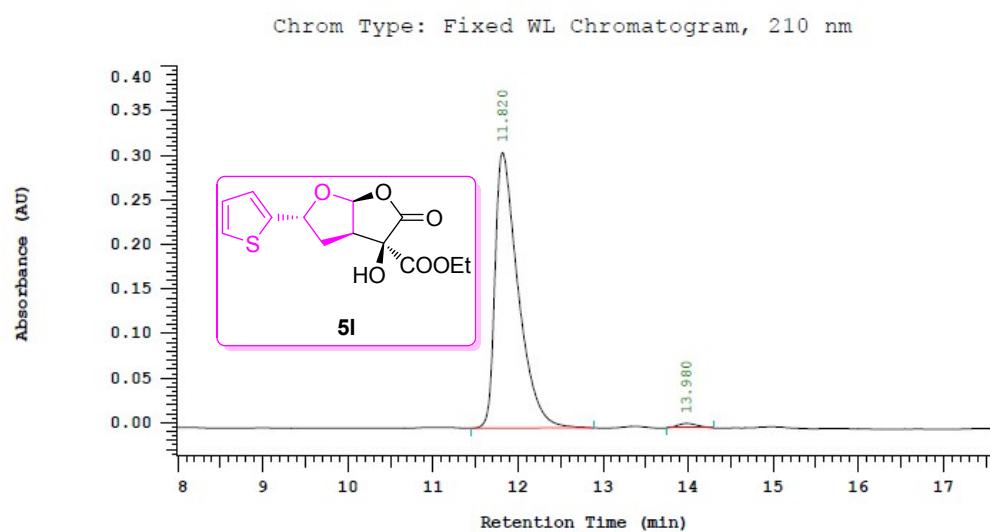
No.	RT	Area	Area %	BC
1	12.133	5671060	96.728	BB
2	19.767	191856	3.272	BB
5862916		100.000		





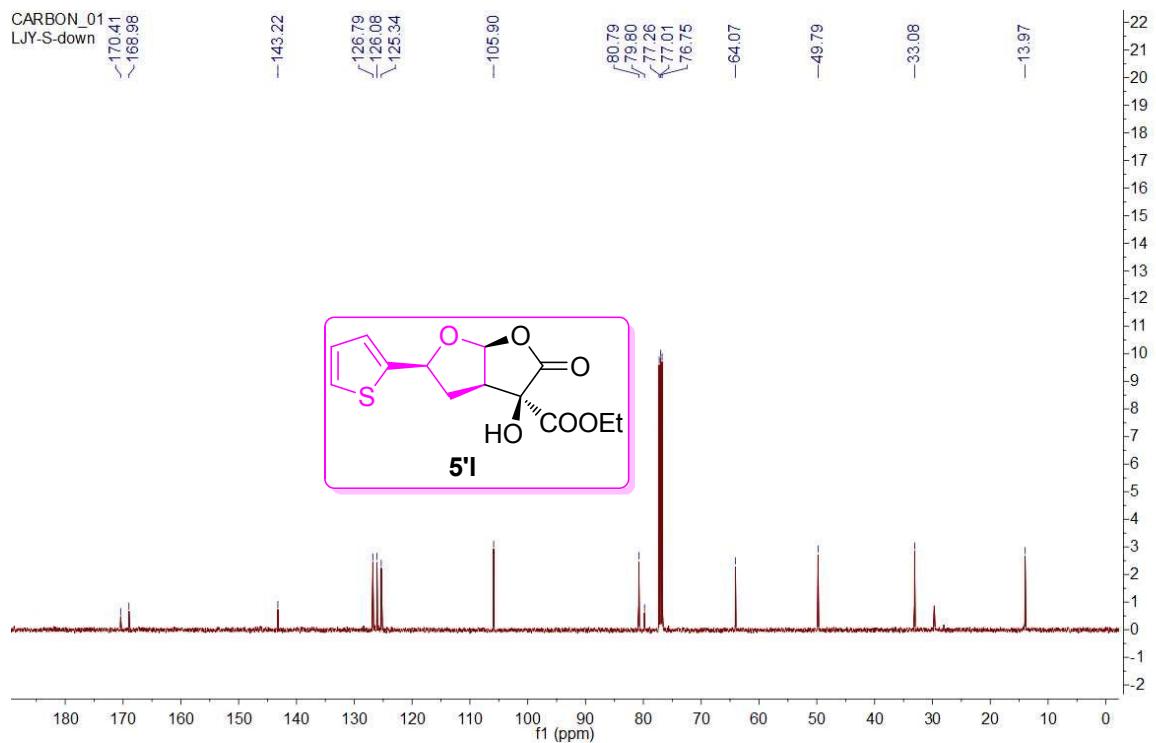
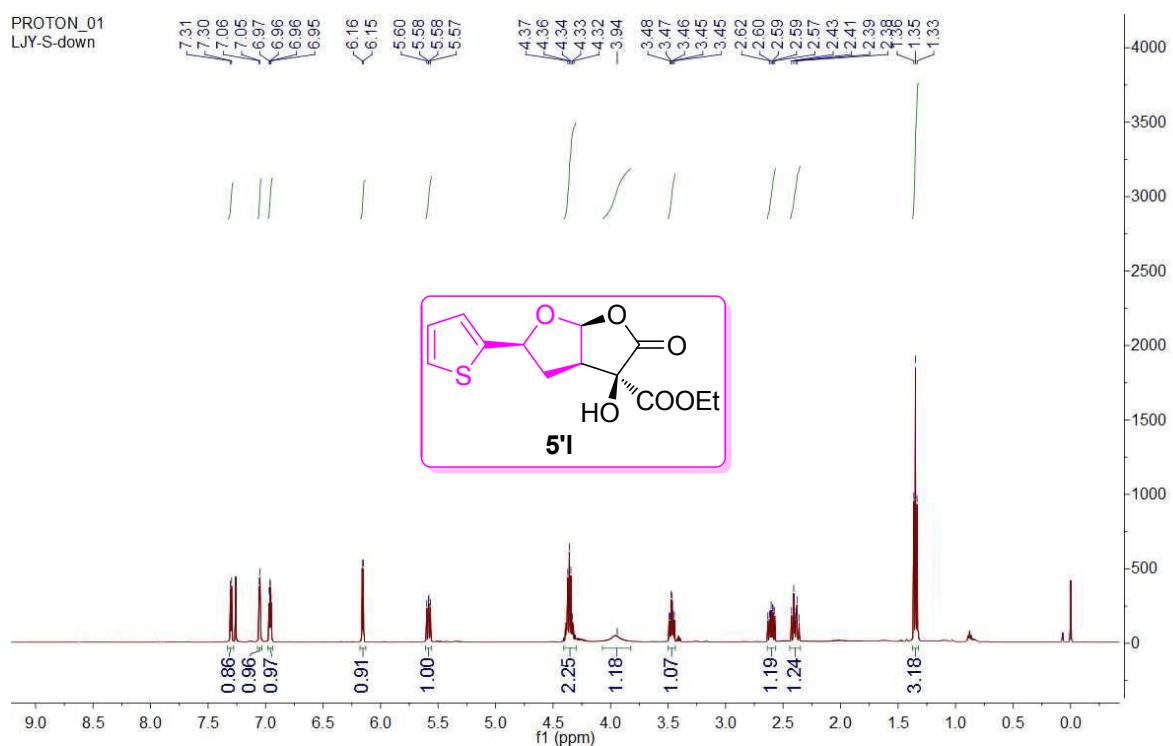
Chrom Type: Fixed WL Chromatogram, 210 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.980	646666	49.585	BB
2	13.940	657486	50.415	BB
		1304152	100.000	

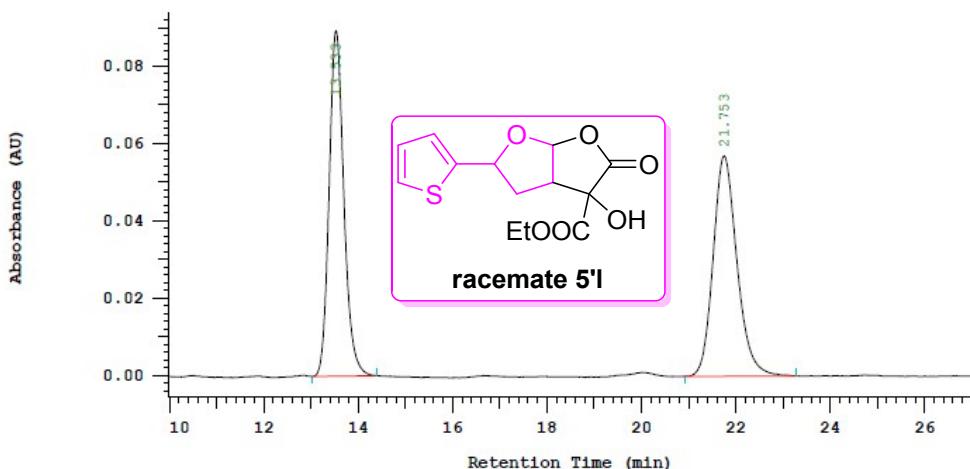


Chrom Type: Fixed WL Chromatogram, 210 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.820	2917415	98.642	BB
2	13.980	40158	1.358	BB
		2957573	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

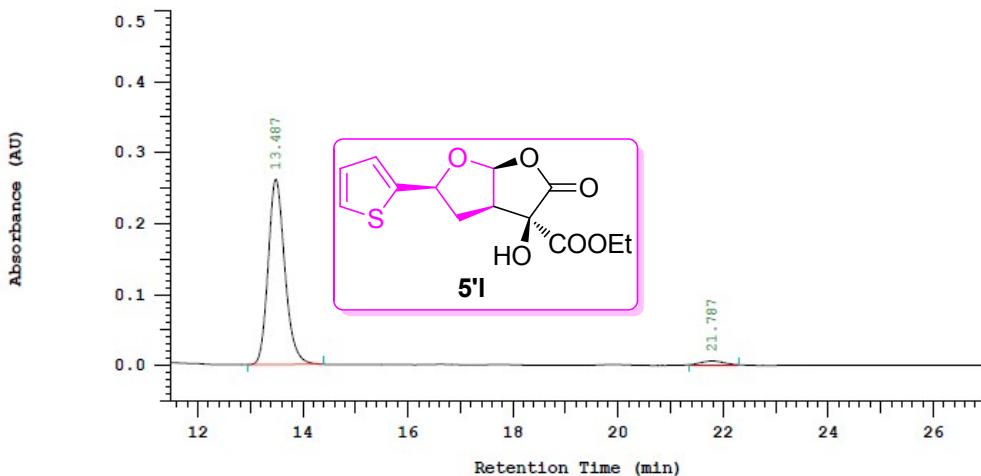


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.533	970318	49.276	BB
2	21.753	998836	50.724	BB
1969154			100.000	

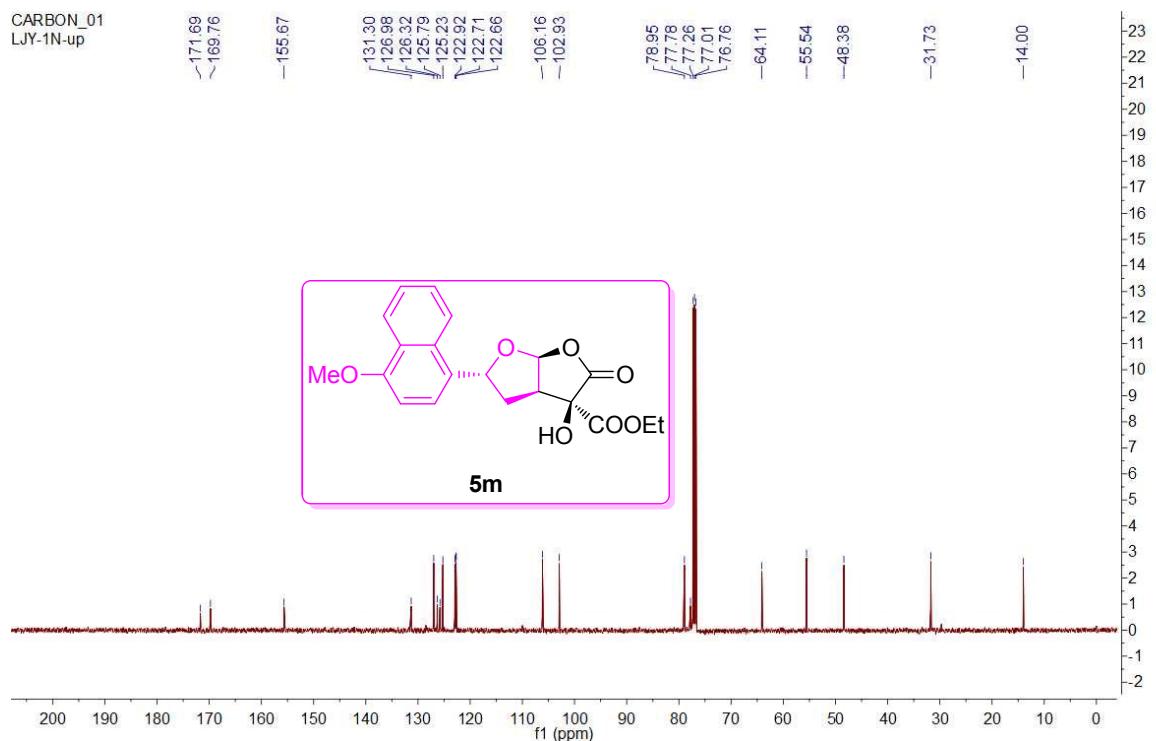
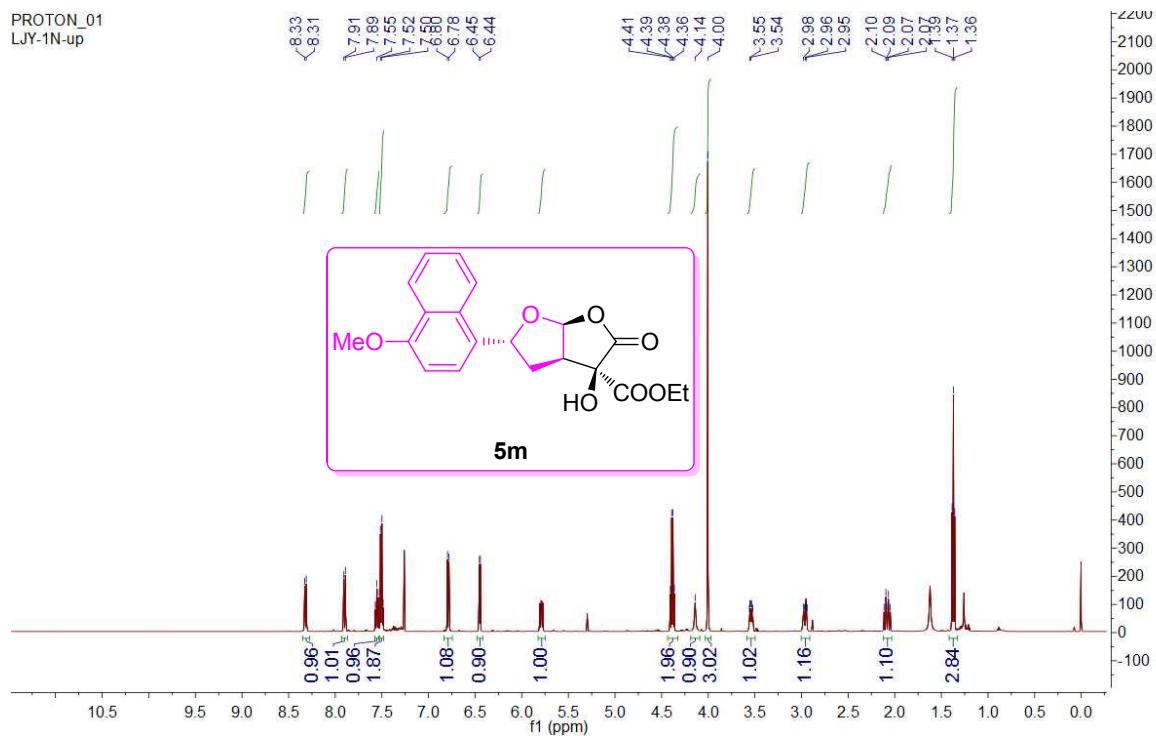
Chrom Type: Fixed WL Chromatogram, 210 nm

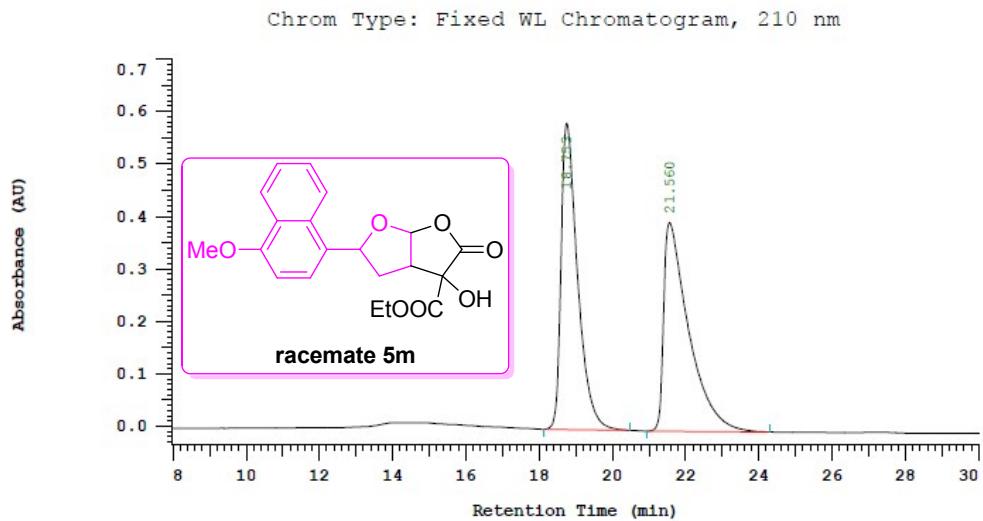


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.487	2868748	97.381	BB
2	21.787	77156	2.619	BB
2945904			100.000	





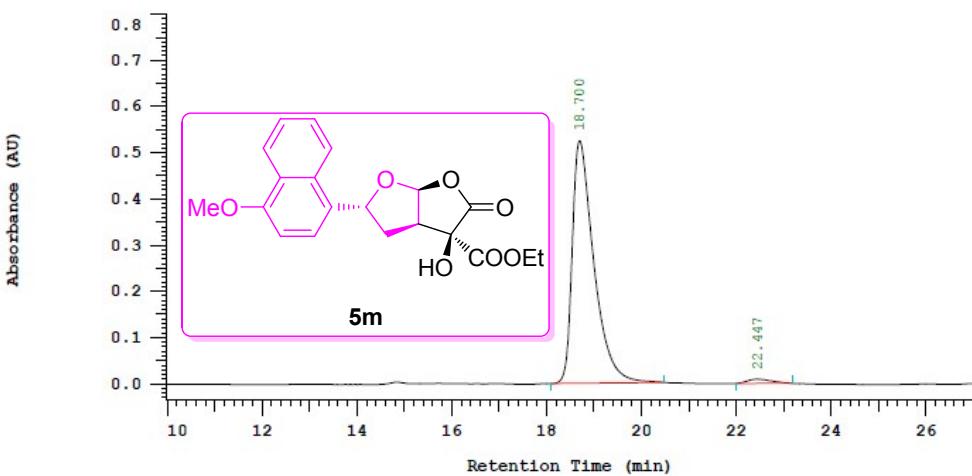
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.753	9178247	49.345	BB
2	21.560	9421936	50.655	BB
18600183		100.000		

Chrom Type: Fixed WL Chromatogram, 210 nm

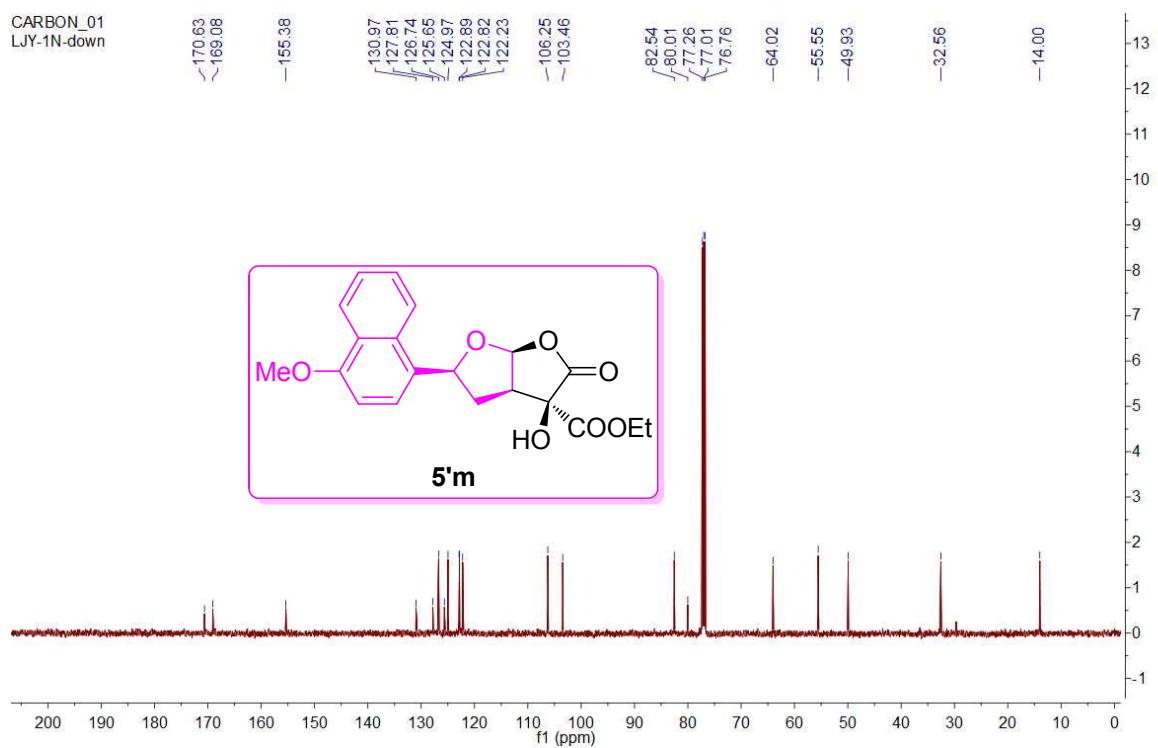
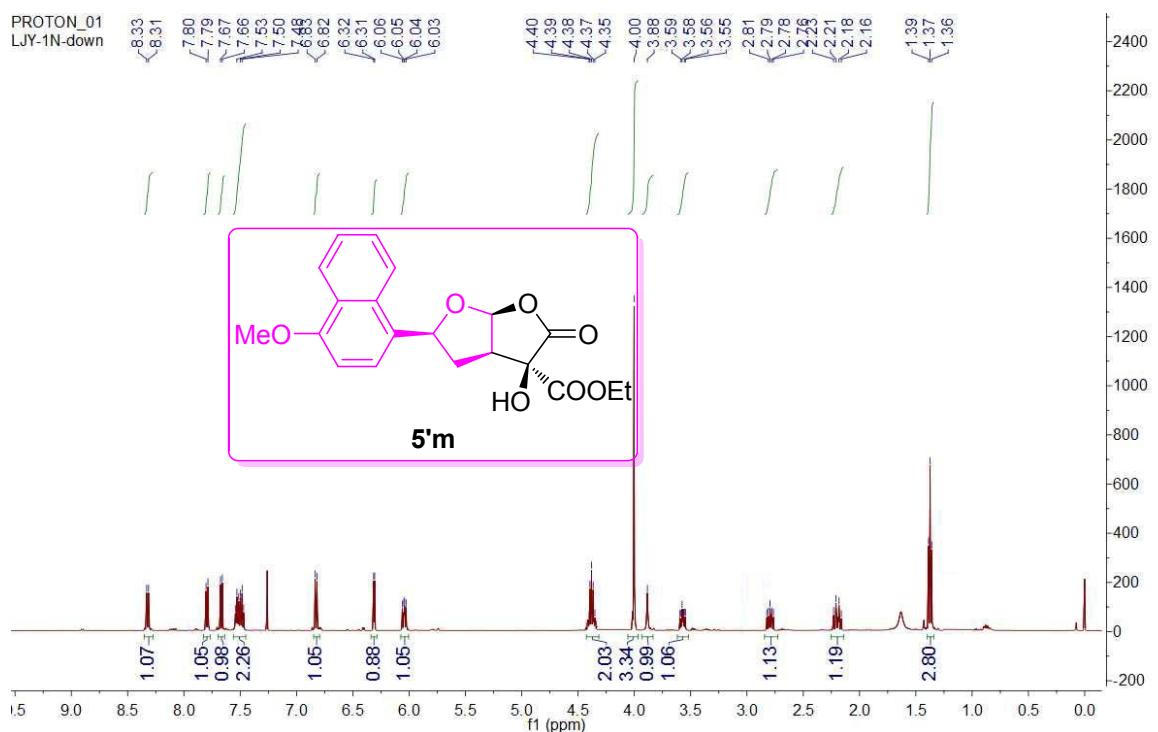


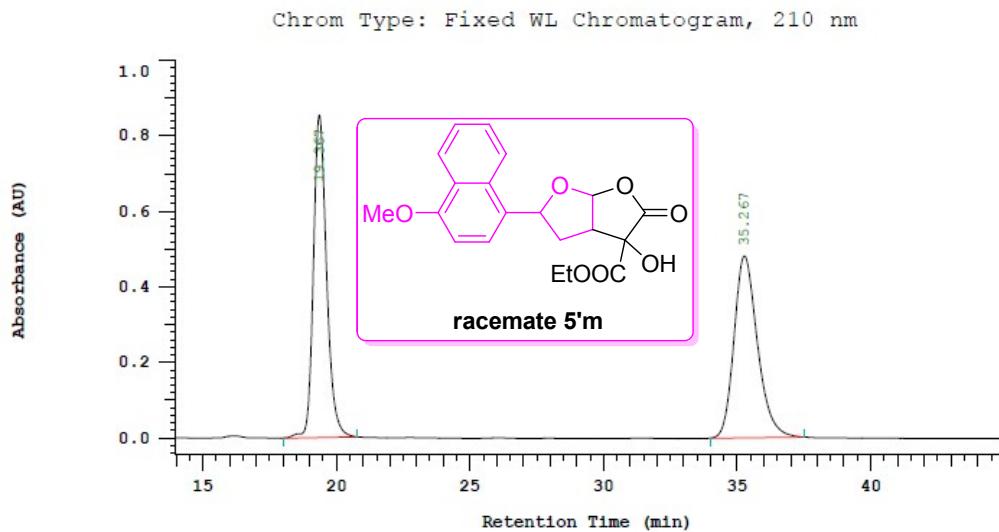
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.700	8299237	98.088	BB
2	22.447	161740	1.912	BB
8460977		100.000		



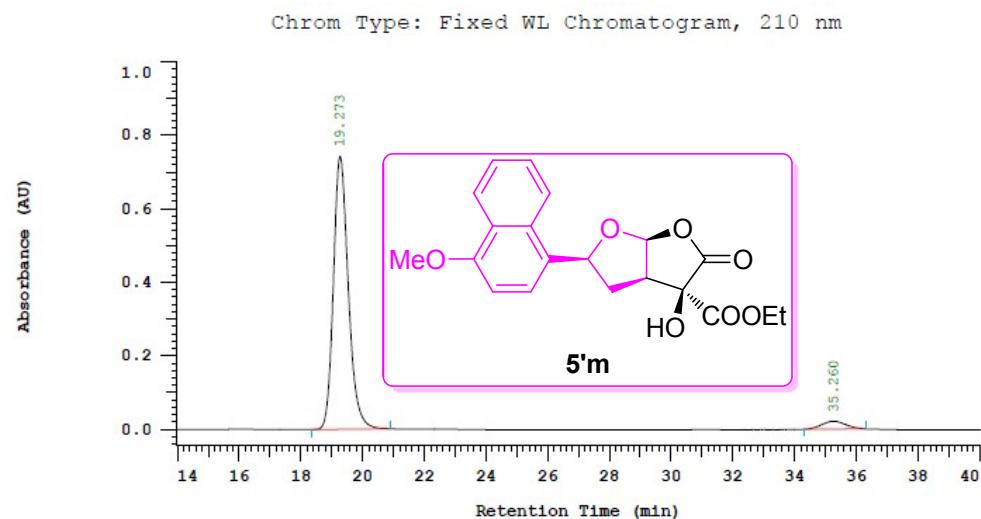


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	19.367	14509425	49.834	BB
2	35.267	14605921	50.166	BB
		29115346	100.000	

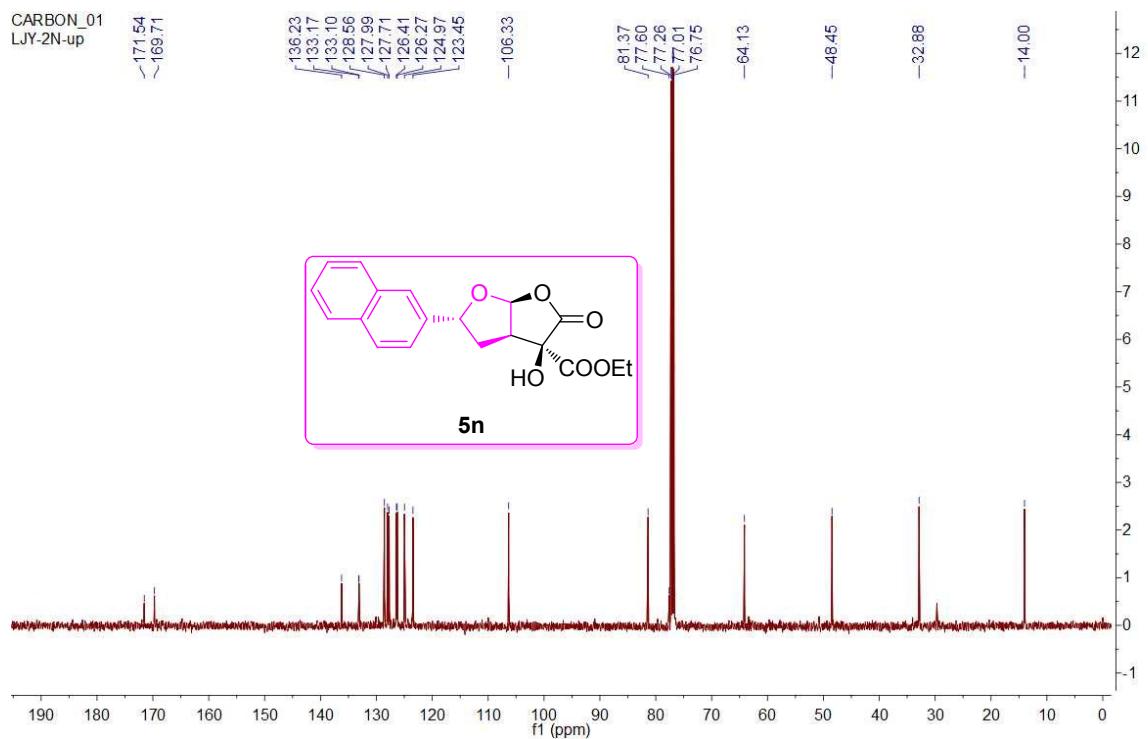
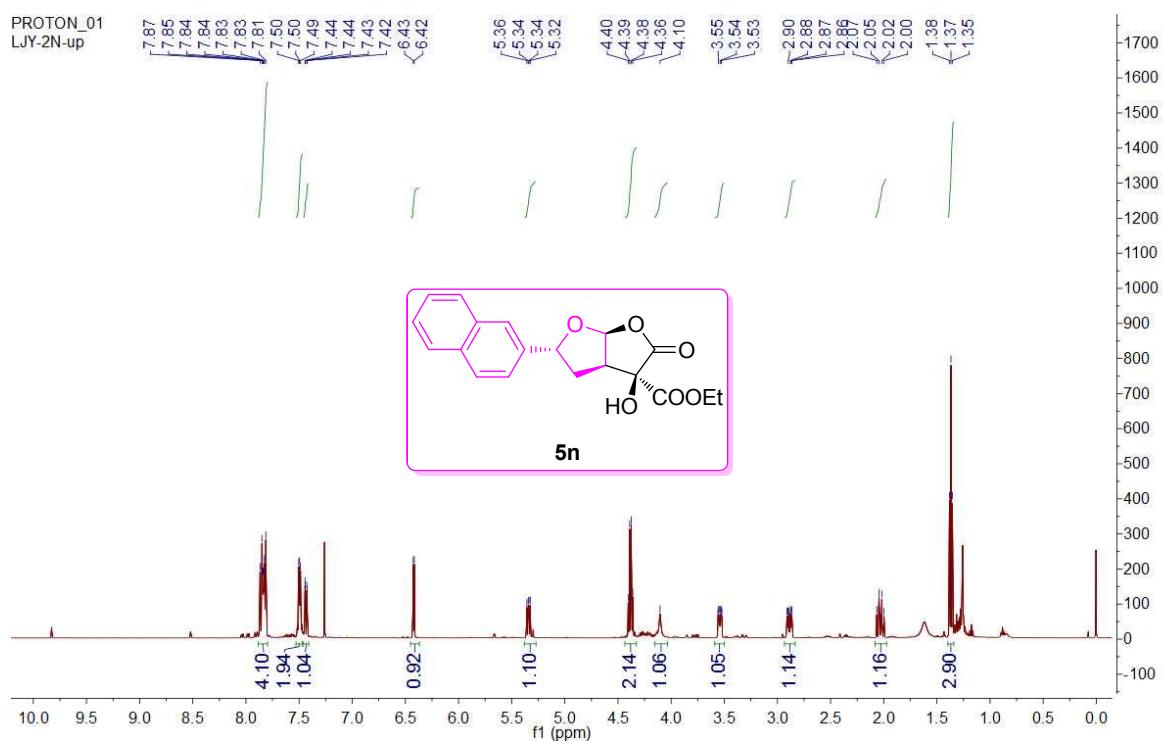


Chrom Type: Fixed WL Chromatogram, 210 nm

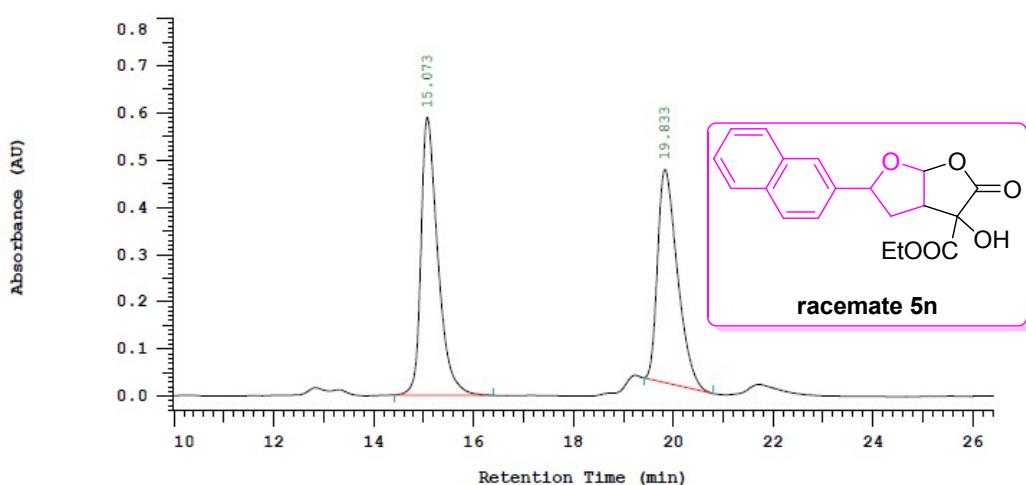
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	19.273	12406667	95.494	BB
2	35.260	585392	4.506	BB
		12992059	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

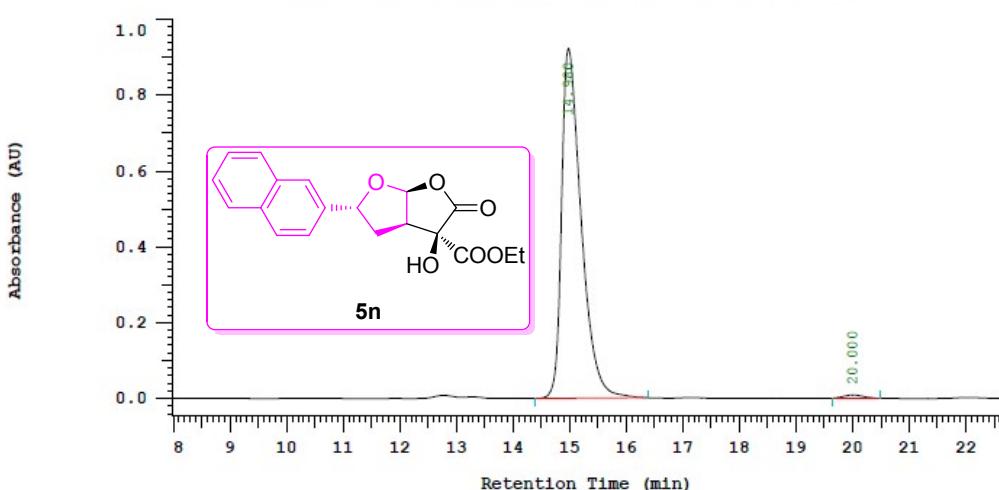


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.073	6909830	52.426	BB
2	19.833	6270288	47.574	BB
13180118			100.000	

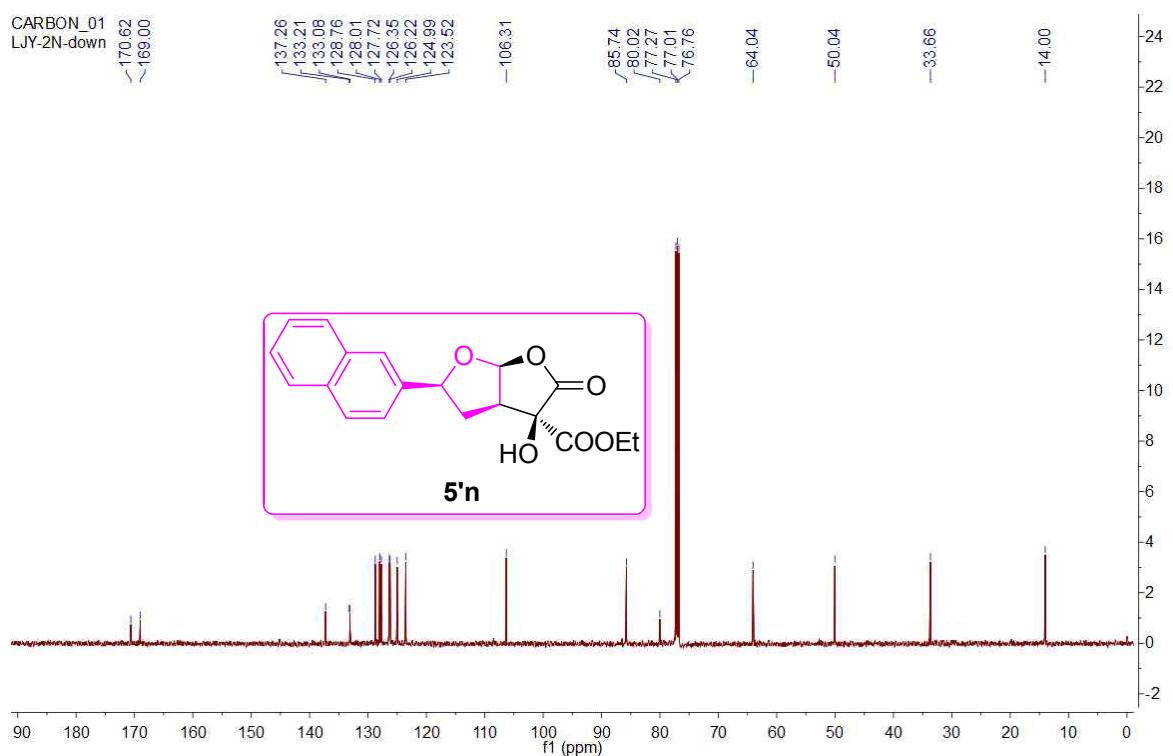
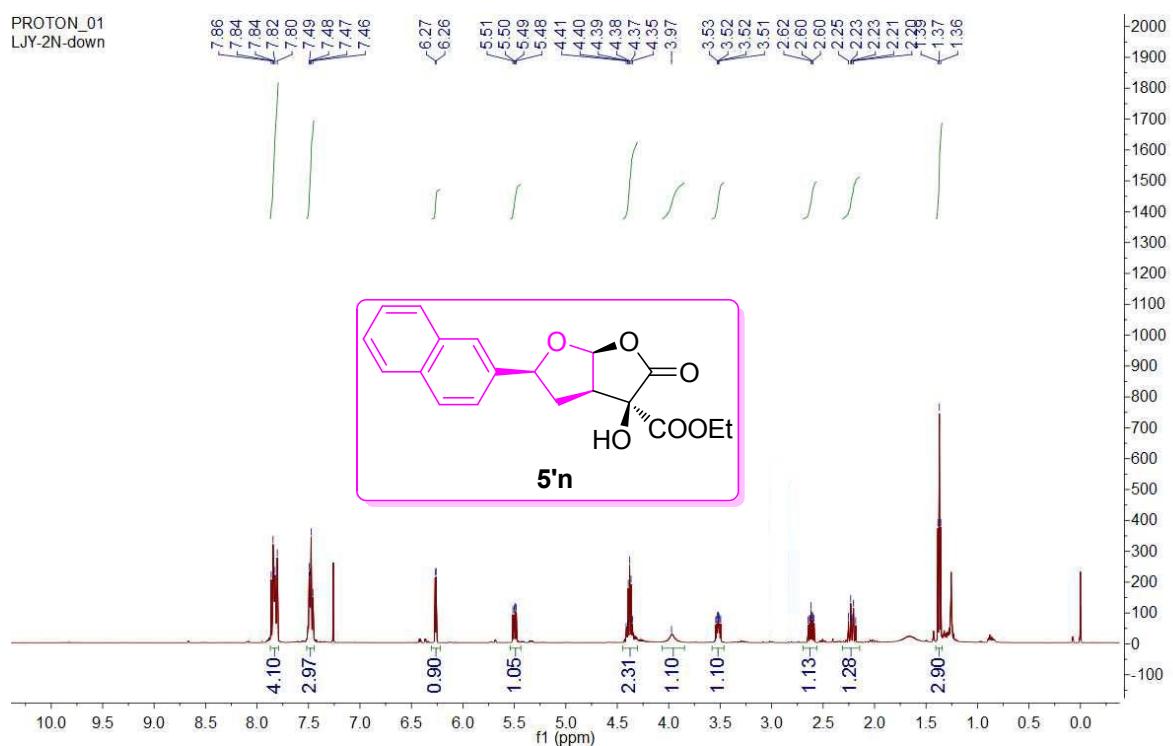
Chrom Type: Fixed WL Chromatogram, 210 nm



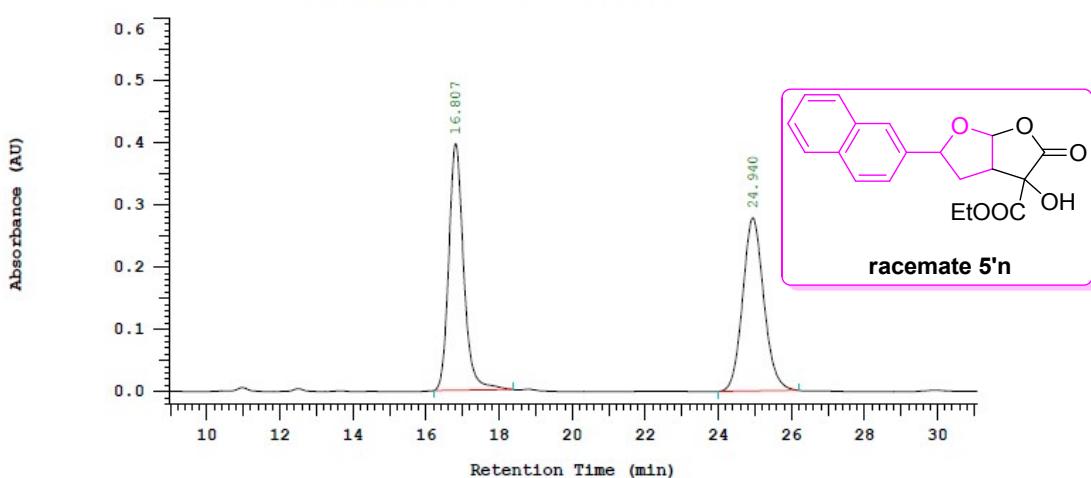
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	14.980	11095870	99.103	BB
2	20.000	100414	0.897	BB
11196284			100.000	



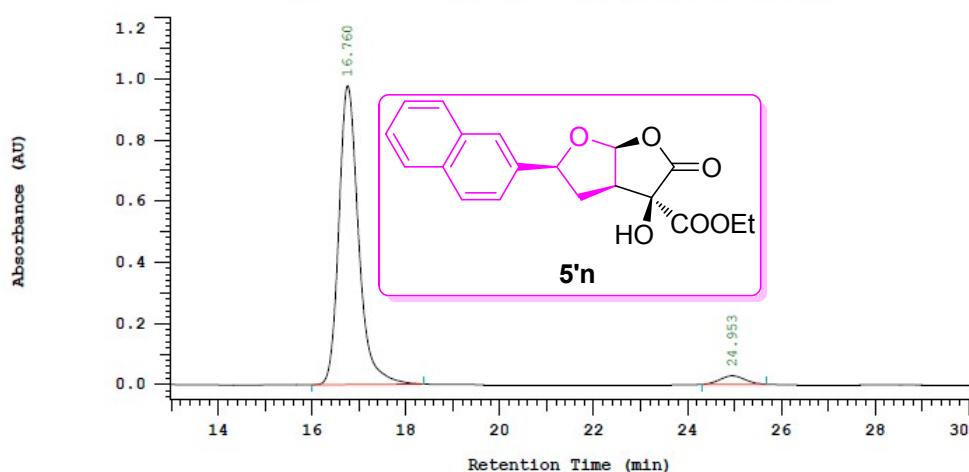
Chrom Type: Fixed WL Chromatogram, 210 nm



Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

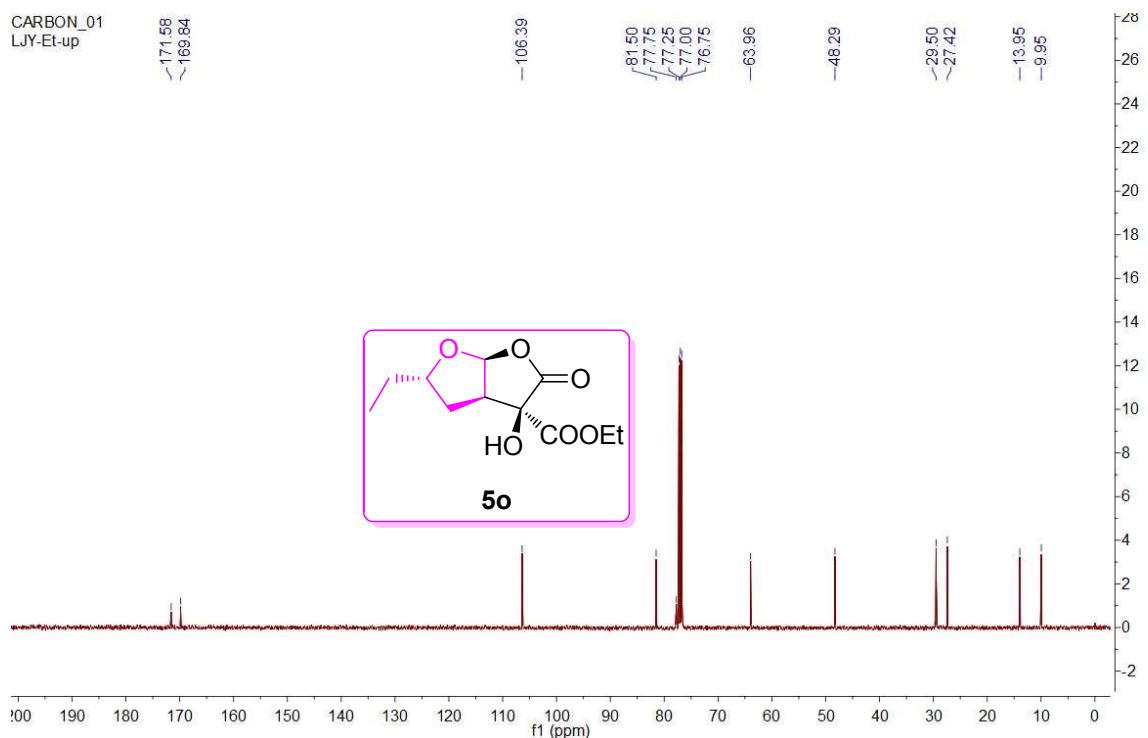
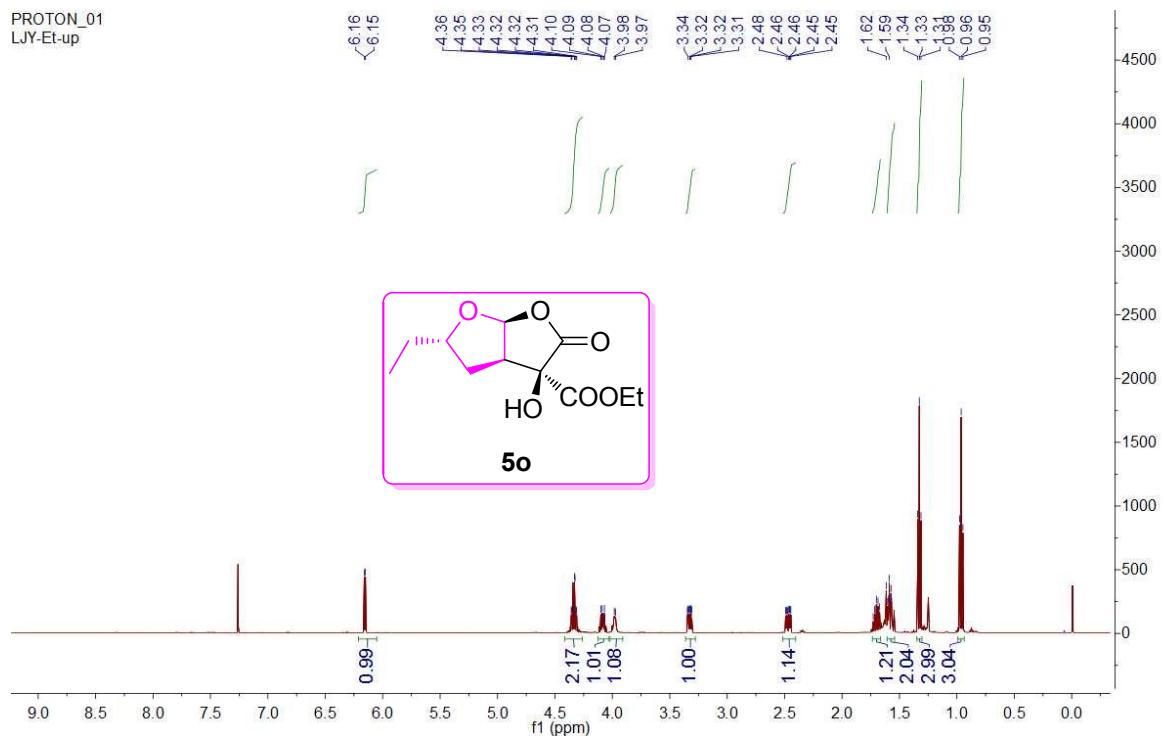
No.	RT	Area	Area %	BC
1	16.807	5585612	49.880	BB
2	24.940	5612455	50.120	BB
11198067		100.000		

Chrom Type: Fixed WL Chromatogram, 210 nm

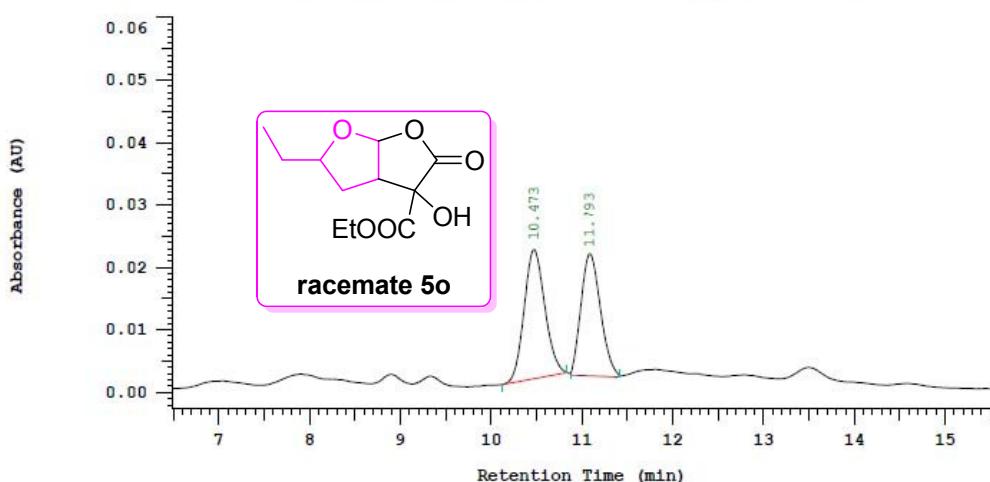


Chrom Type: Fixed WL Chromatogram, 210 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	16.760	14269208	96.468	BB
2	24.953	522513	3.532	BB
14791721		100.000		



Chrom Type: Fixed WL Chromatogram, 210 nm

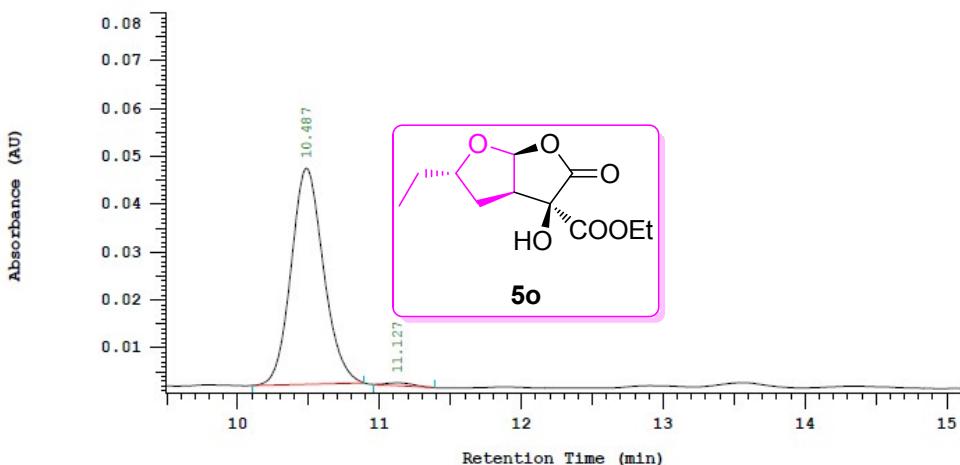


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.473	163671	49.941	BB
2	11.193	164056	50.059	BB
327727		100.000		

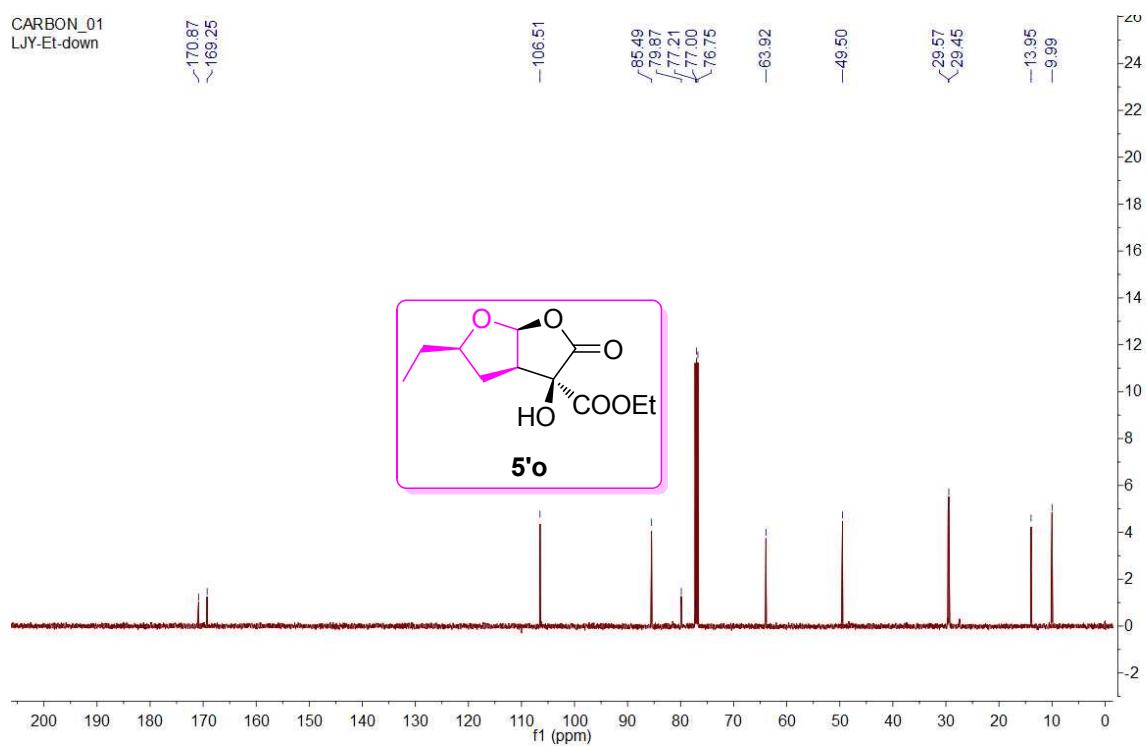
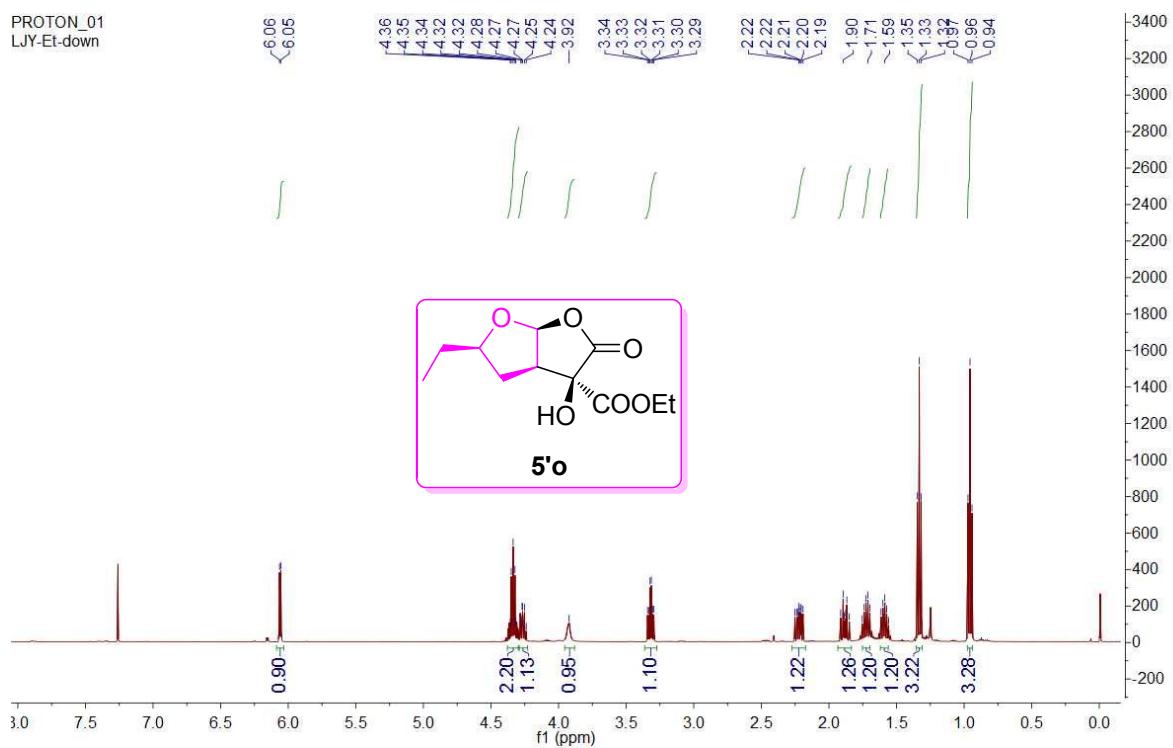
Chrom Type: Fixed WL Chromatogram, 210 nm



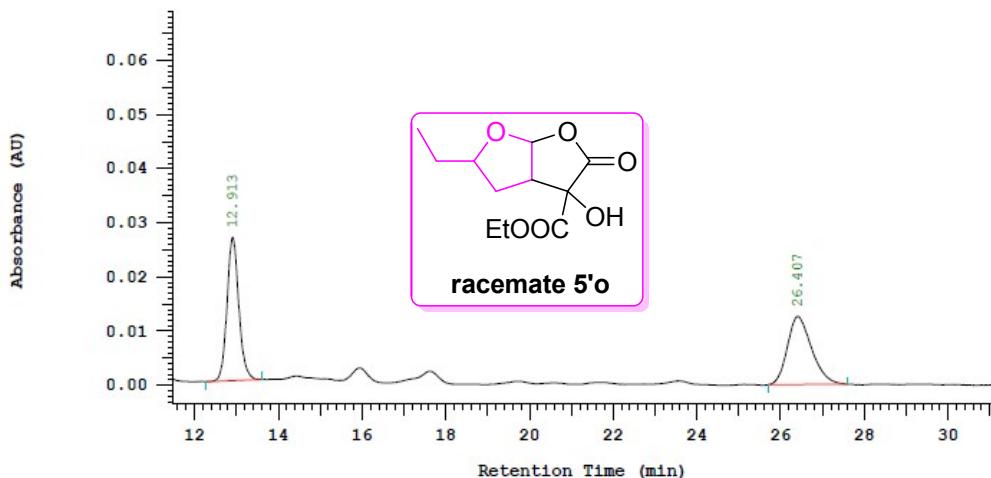
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.487	358532	98.846	BB
2	11.127	4185	1.154	BB
362717		100.000		



Chrom Type: Fixed WL Chromatogram, 210 nm

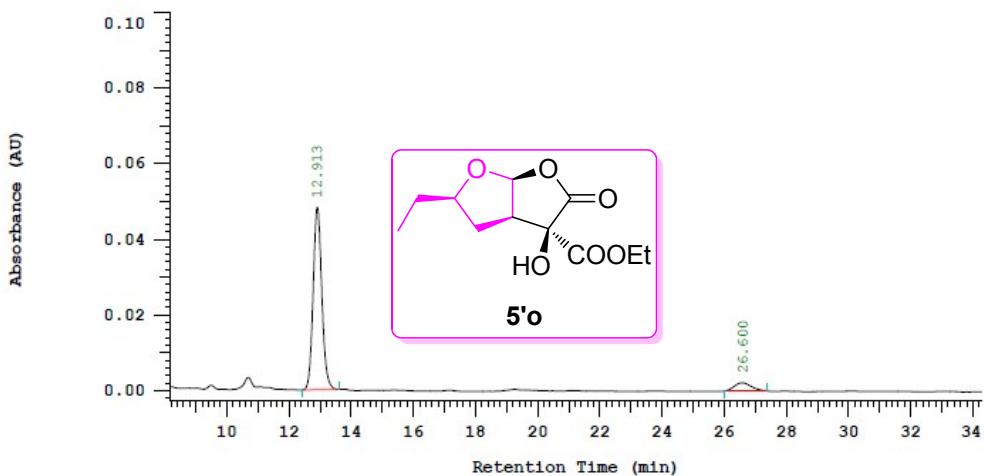


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.913	258154	50.552	BB
2	26.407	252517	49.448	BB
Total			510671	100.000

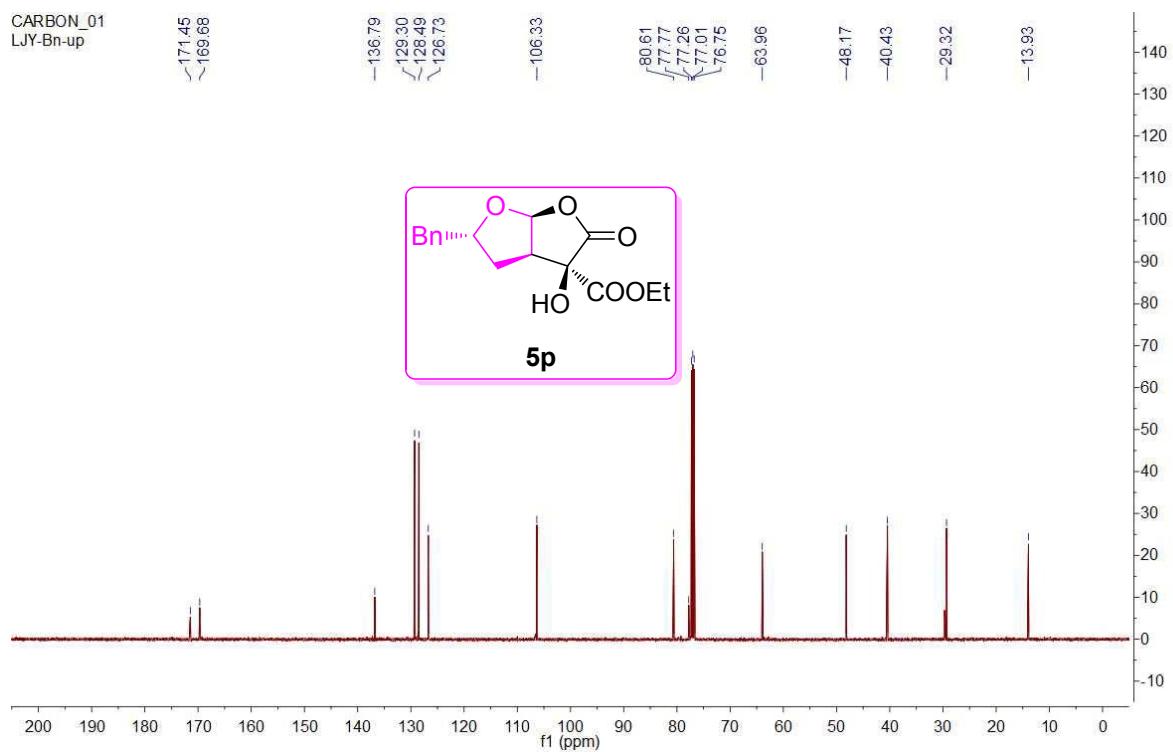
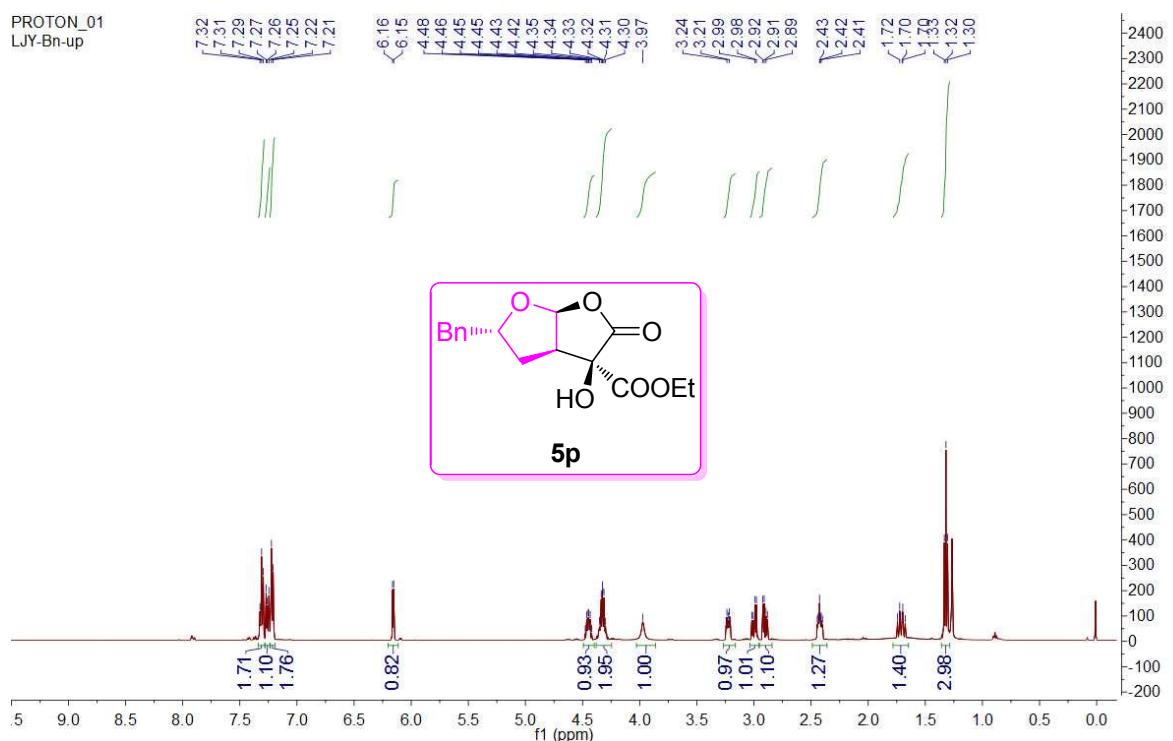
Chrom Type: Fixed WL Chromatogram, 210 nm



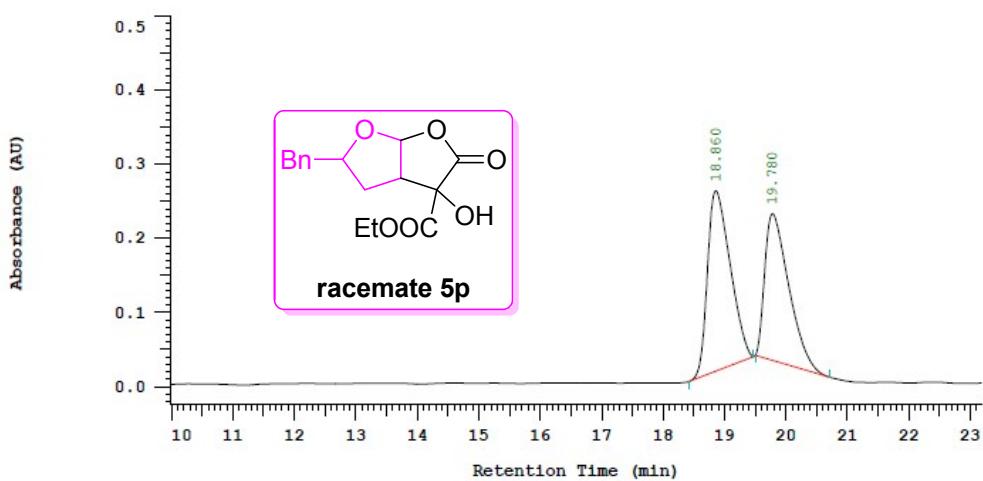
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.913	463645	91.770	BB
2	26.600	41579	8.230	BB
Total			505224	100.000



Chrom Type: Fixed WL Chromatogram, 210 nm

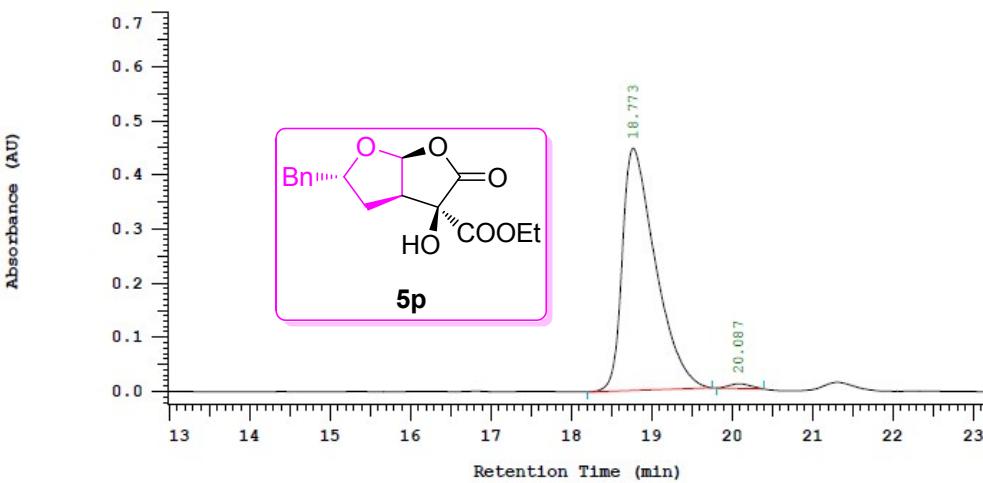


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.860	3112573	53.531	BB
2	19.780	2701940	46.469	BB
5814513		100.000		

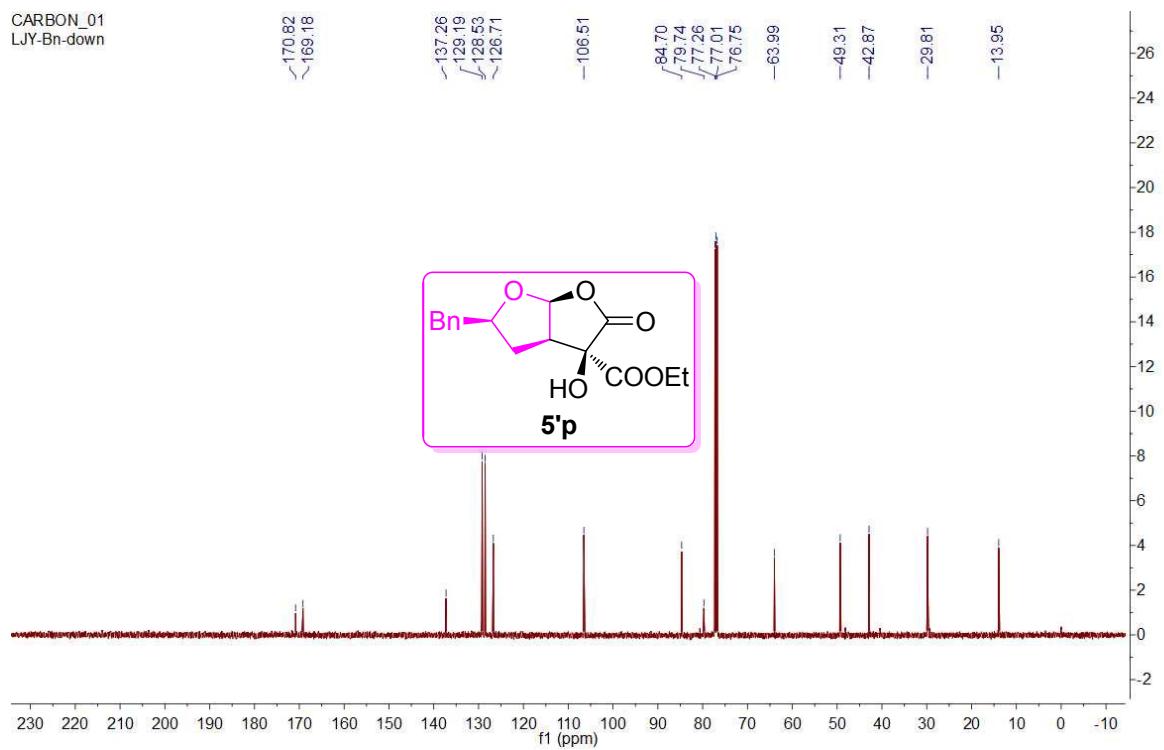
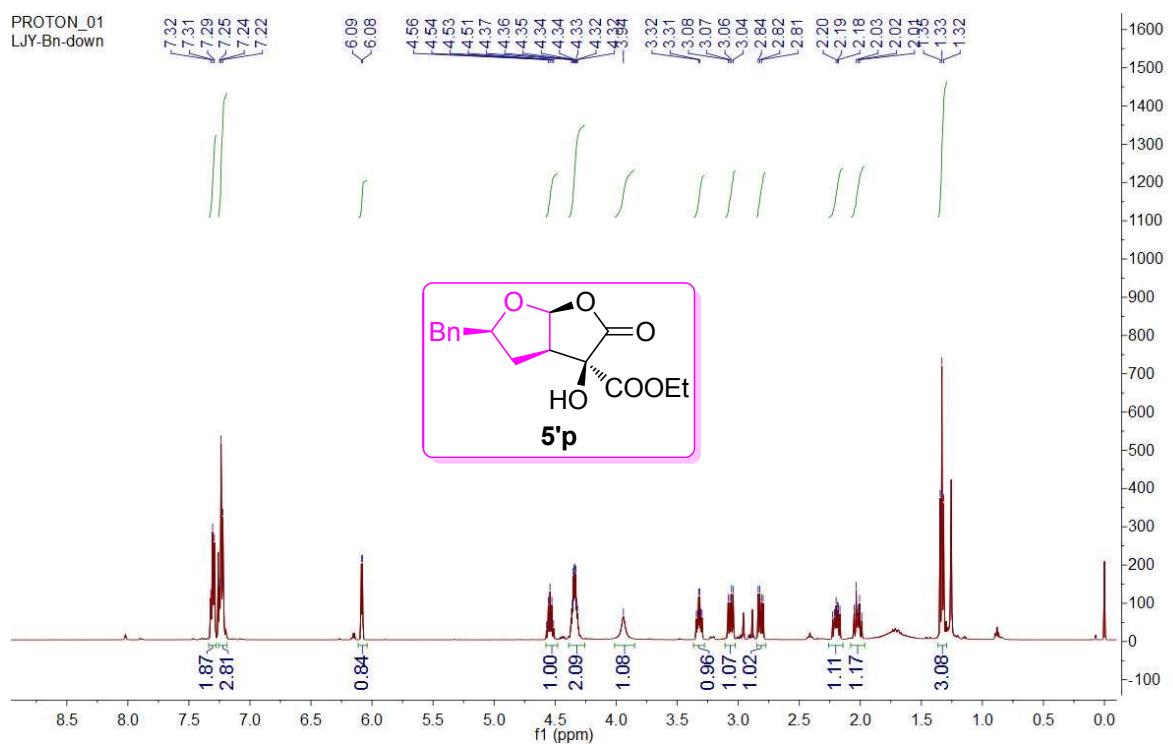
Chrom Type: Fixed WL Chromatogram, 210 nm



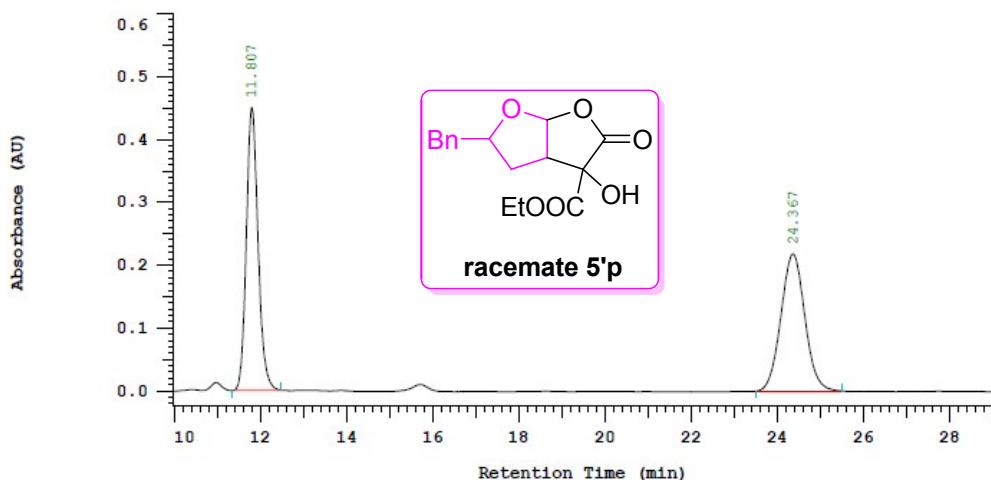
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.773	6419059	98.743	BB
2	20.087	81730	1.257	BB
6500789		100.000		



Chrom Type: Fixed WL Chromatogram, 210 nm

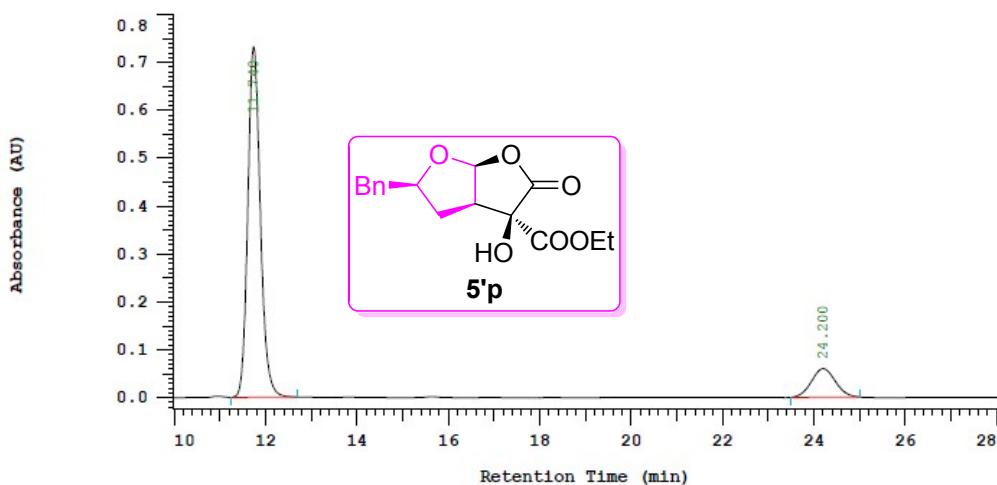


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.807	4262755	50.369	BB
2	24.367	4200225	49.631	BB
8462980		100.000		

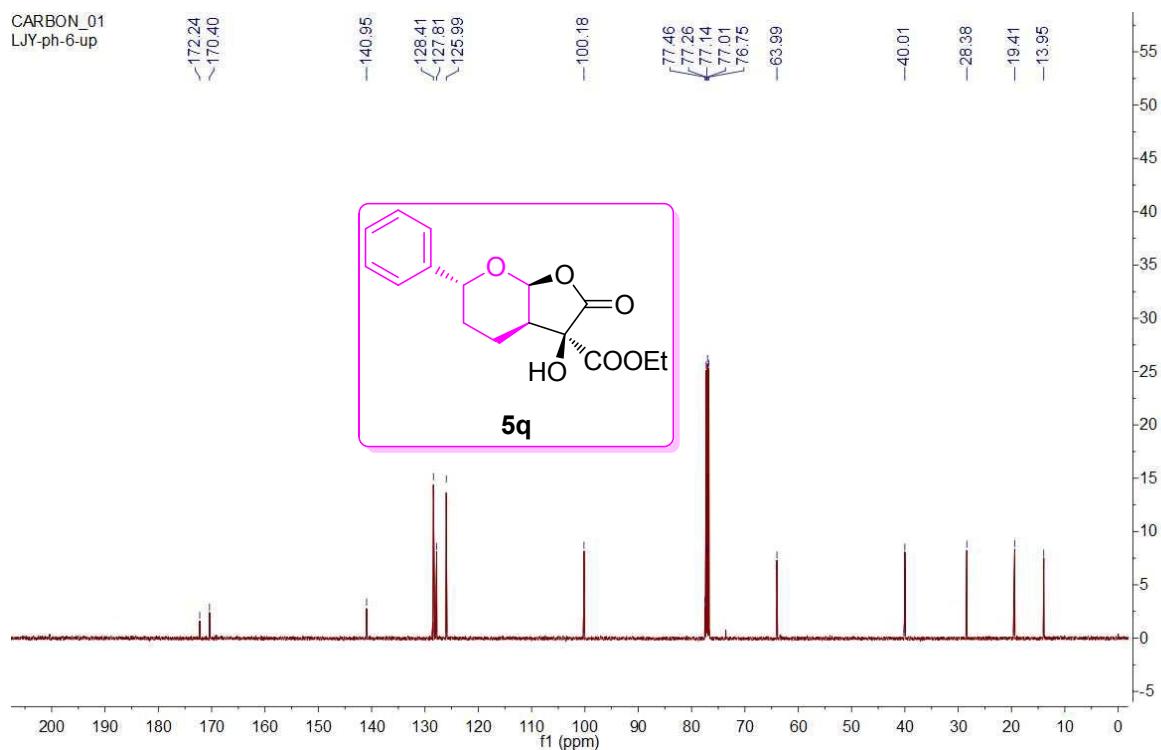
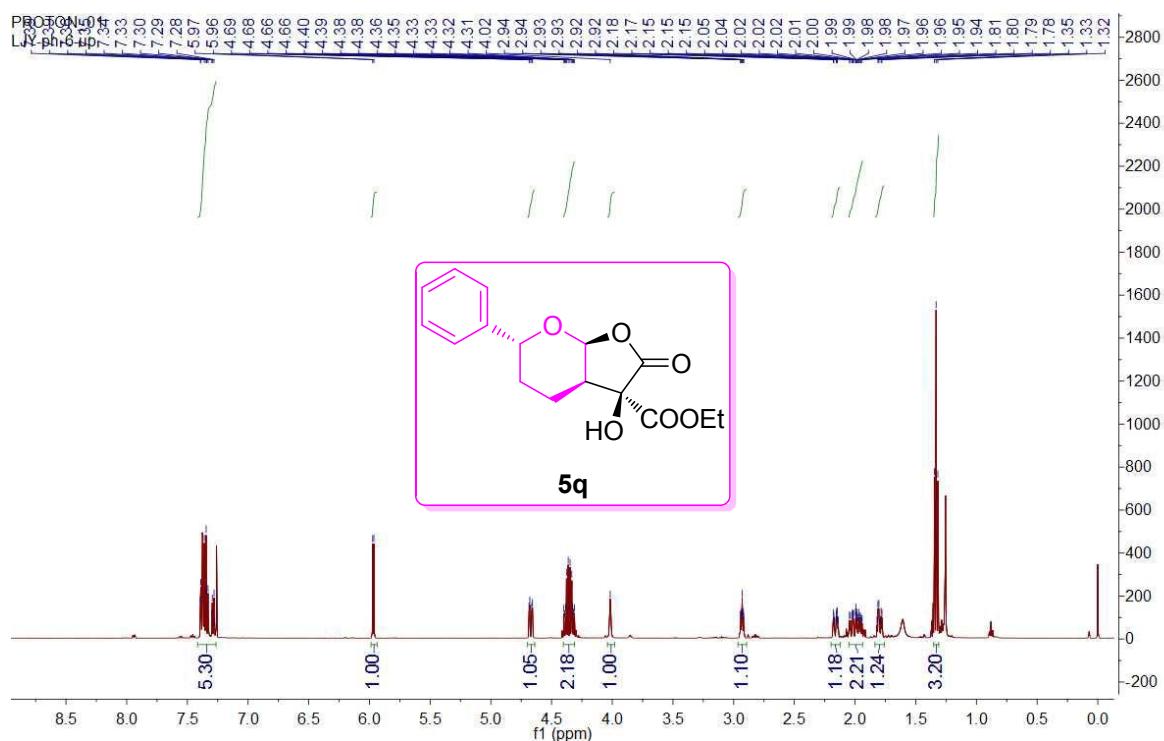
Chrom Type: Fixed WL Chromatogram, 210 nm



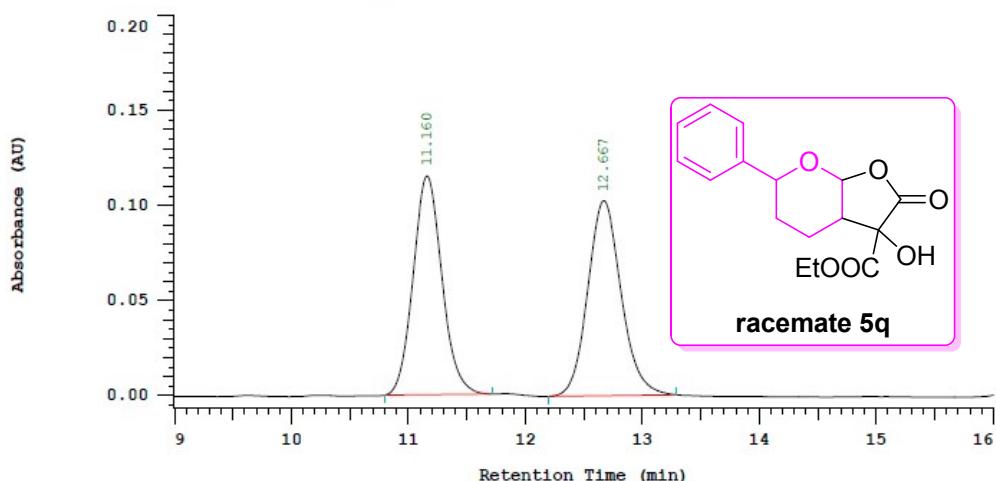
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.740	6985527	86.575	BB
2	24.200	1083226	13.425	BB
8068753		100.000		



Chrom Type: Fixed WL Chromatogram, 210 nm



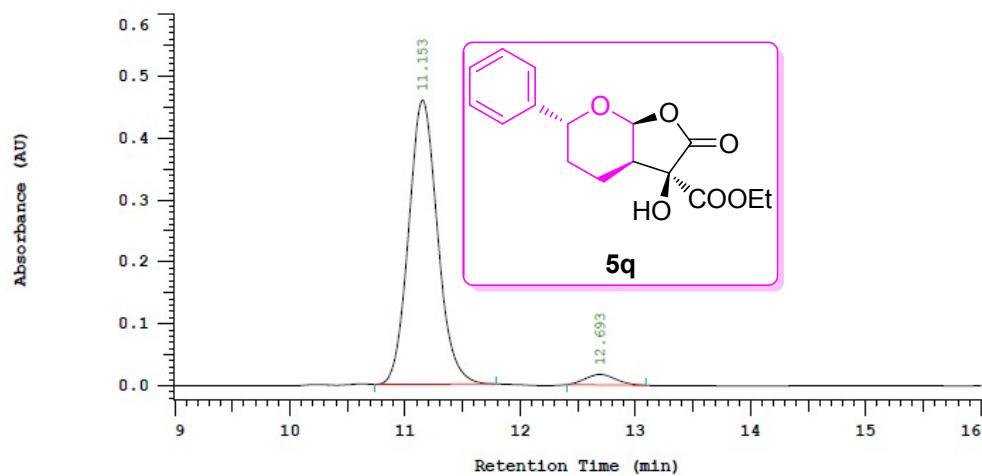
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.160	984584	49.233	BB
2	12.667	1015258	50.767	BB
		1999842	100.000	

Chrom Type: Fixed WL Chromatogram, 210 nm

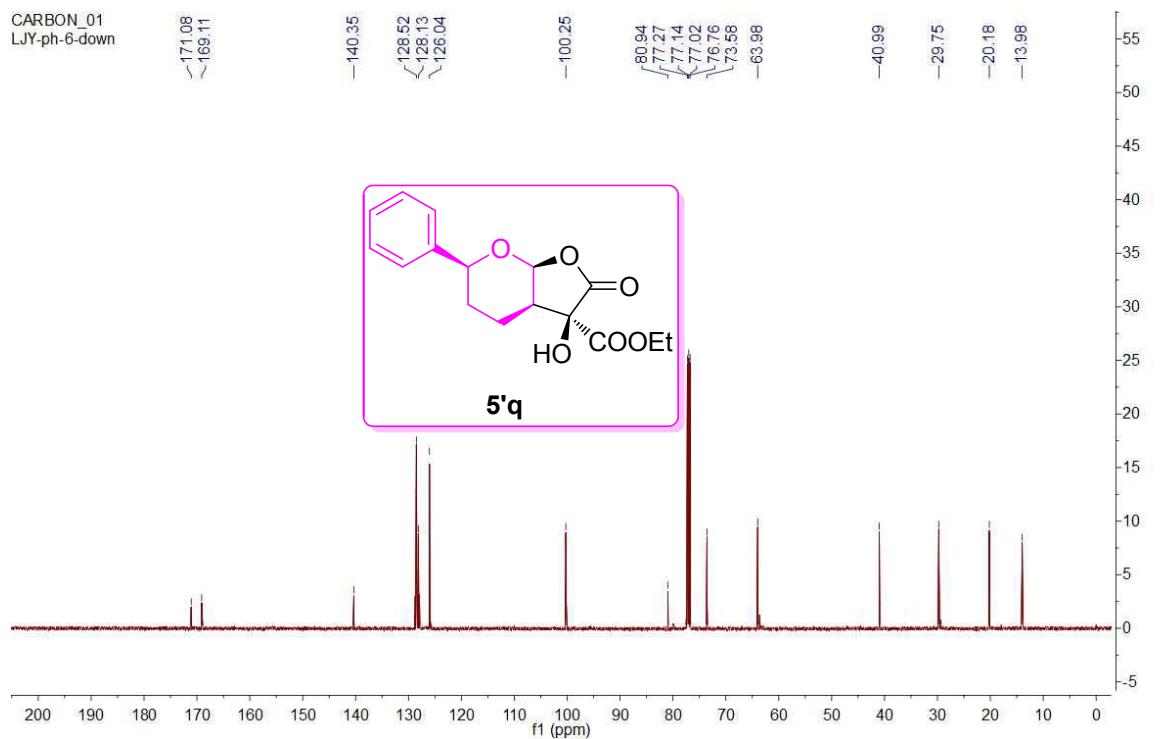
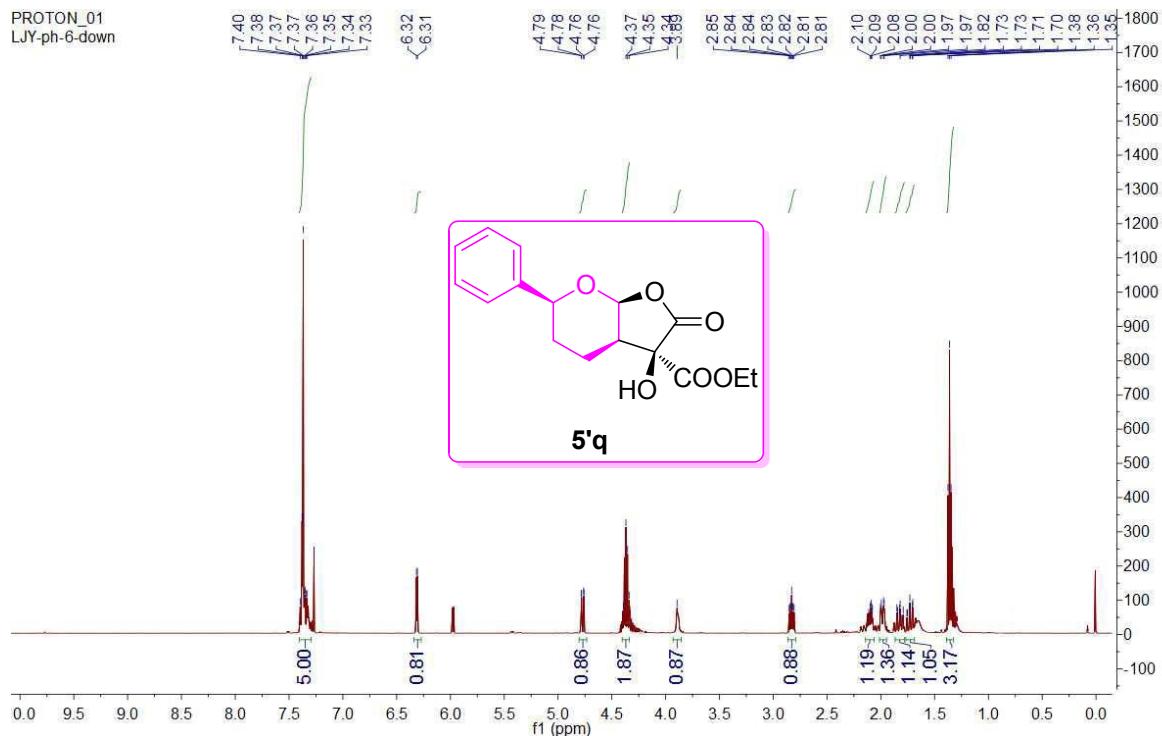


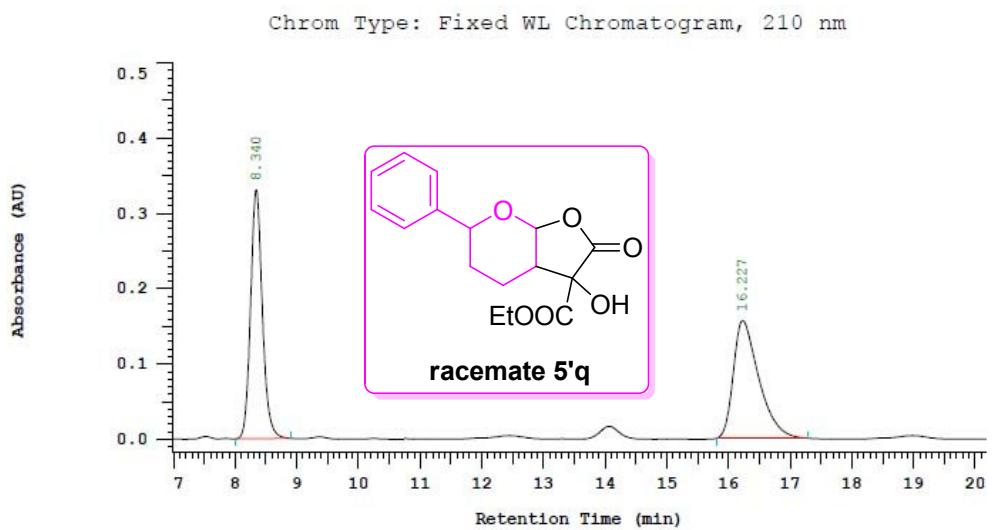
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.153	3997333	96.222	BB
2	12.693	156932	3.778	BB
		4154265	100.000	



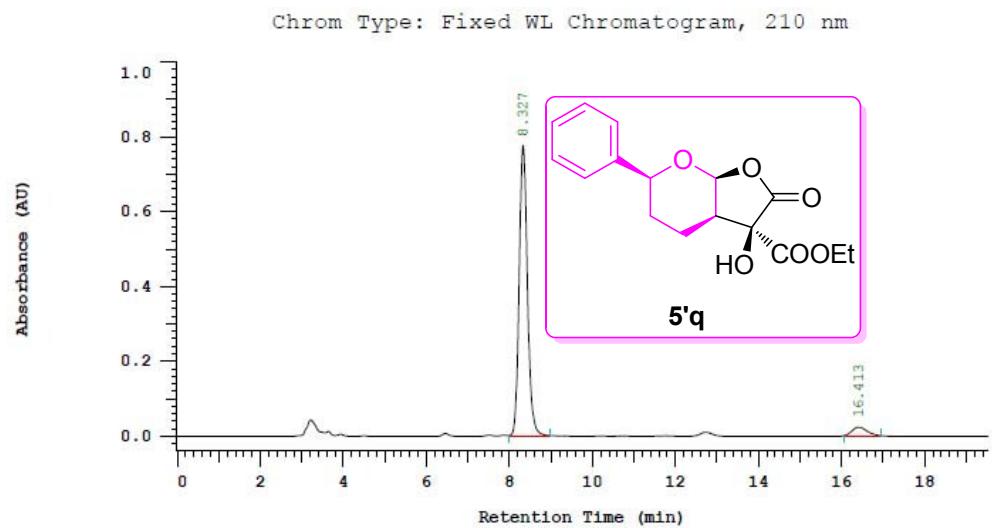


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.340	2204411	49.549	BB
2	16.227	2244542	50.451	BB
		4448953	100.000	

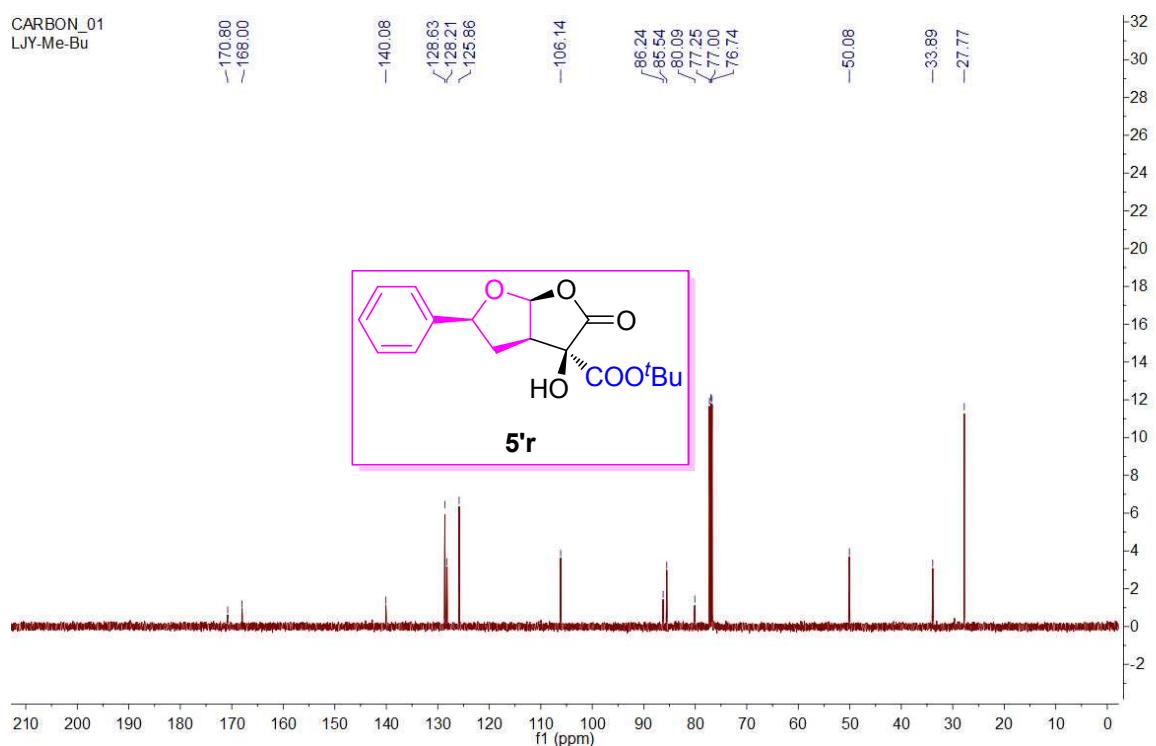
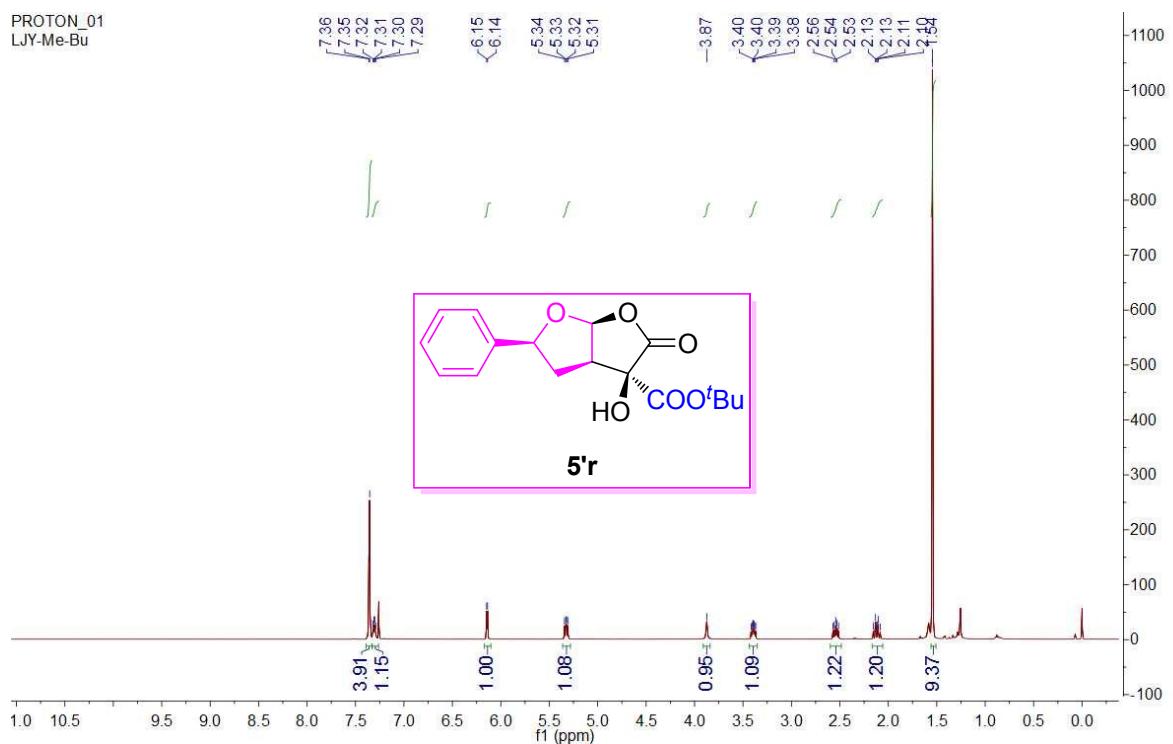


Chrom Type: Fixed WL Chromatogram, 210 nm

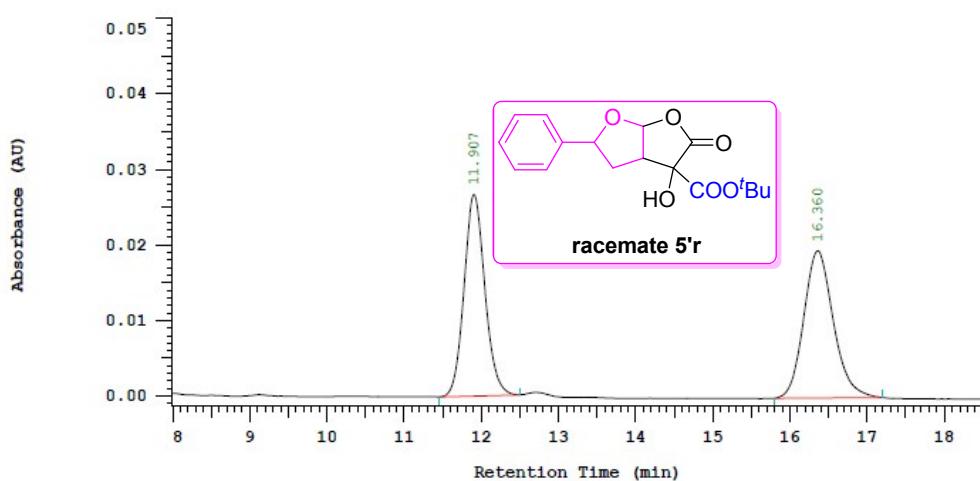
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.327	5326867	94.997	BB
2	16.413	280518	5.003	BB
		5607385	100.000	



Chrom Type: Fixed WL Chromatogram, 231 nm

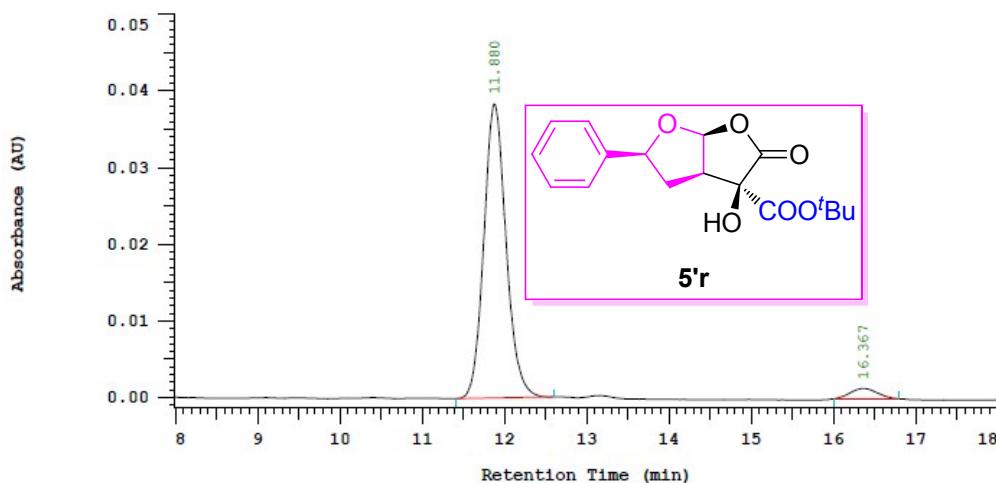


Chrom Type: Fixed WL Chromatogram, 231 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.907	249943	49.096	BB
2	16.360	259144	50.904	BB
		509087	100.000	

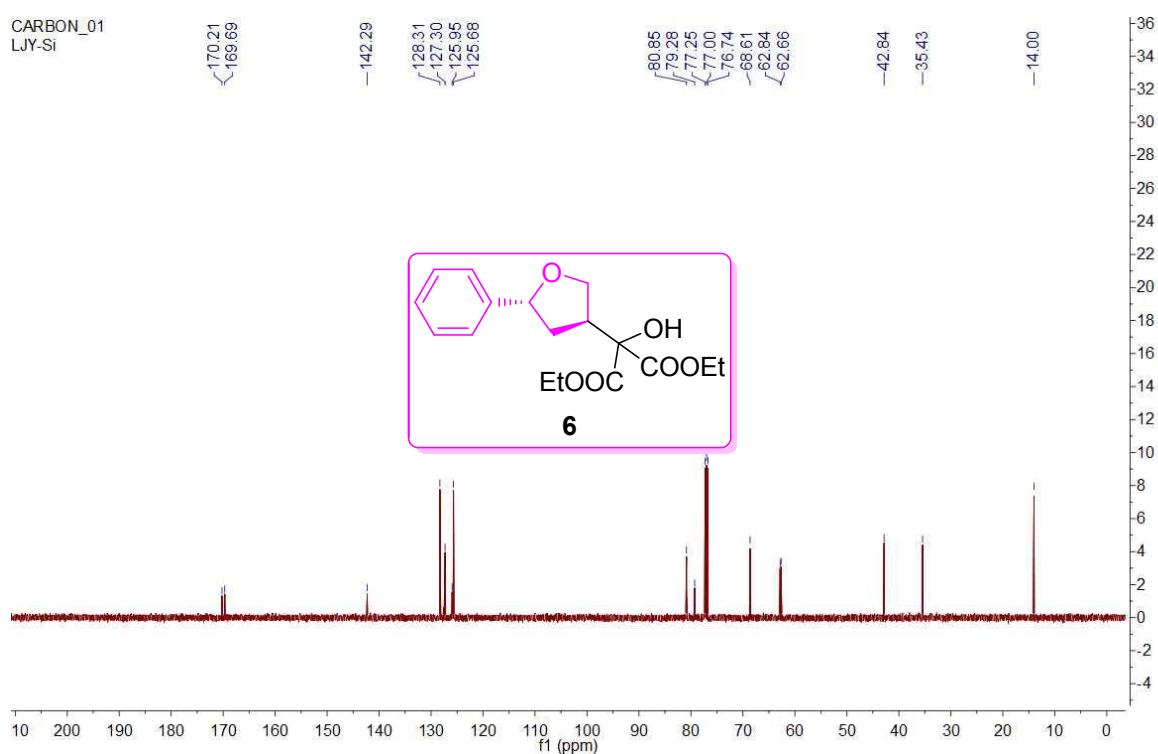
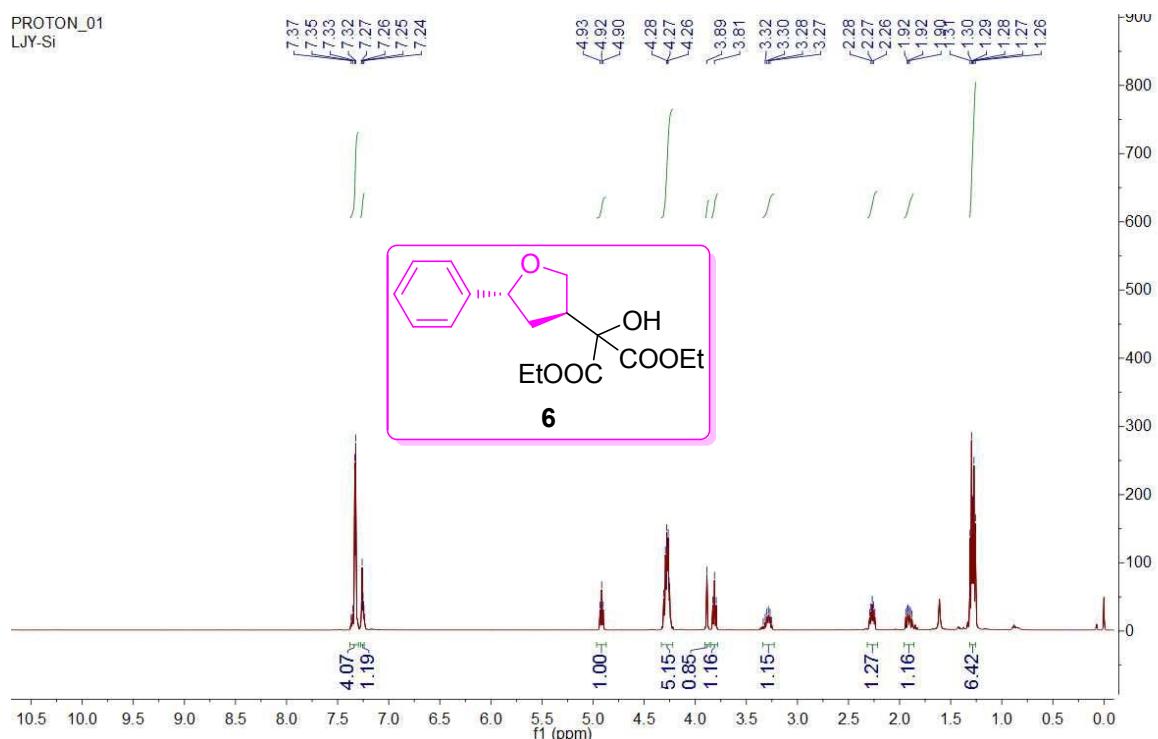
Chrom Type: Fixed WL Chromatogram, 231 nm

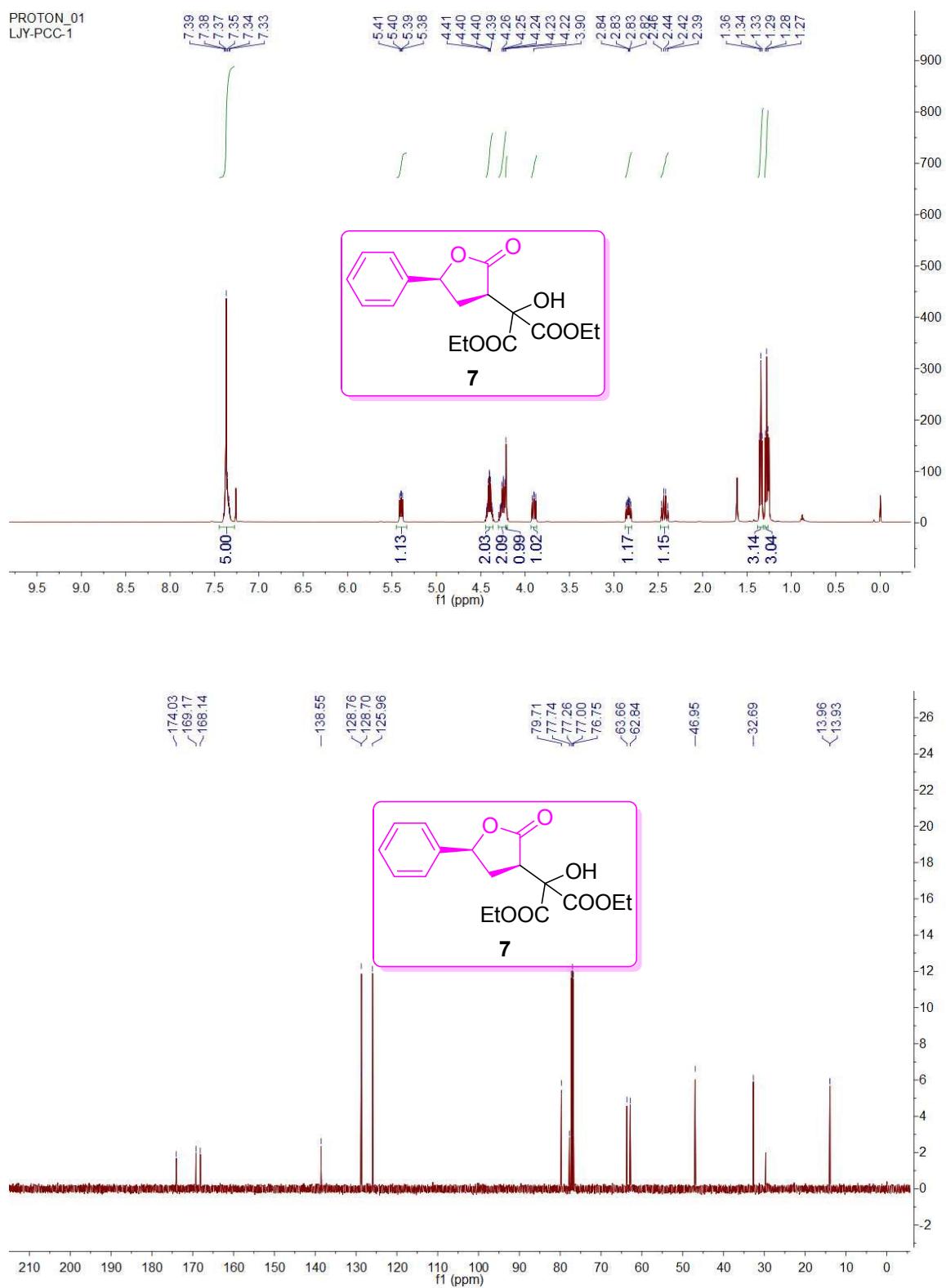


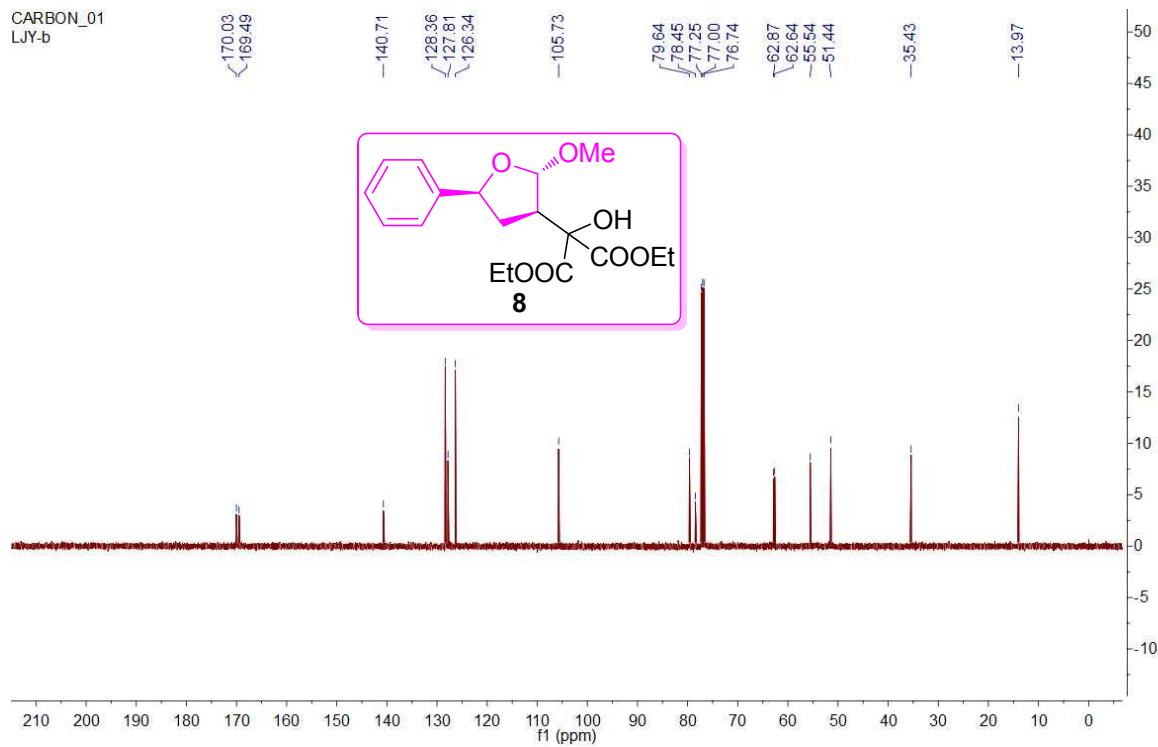
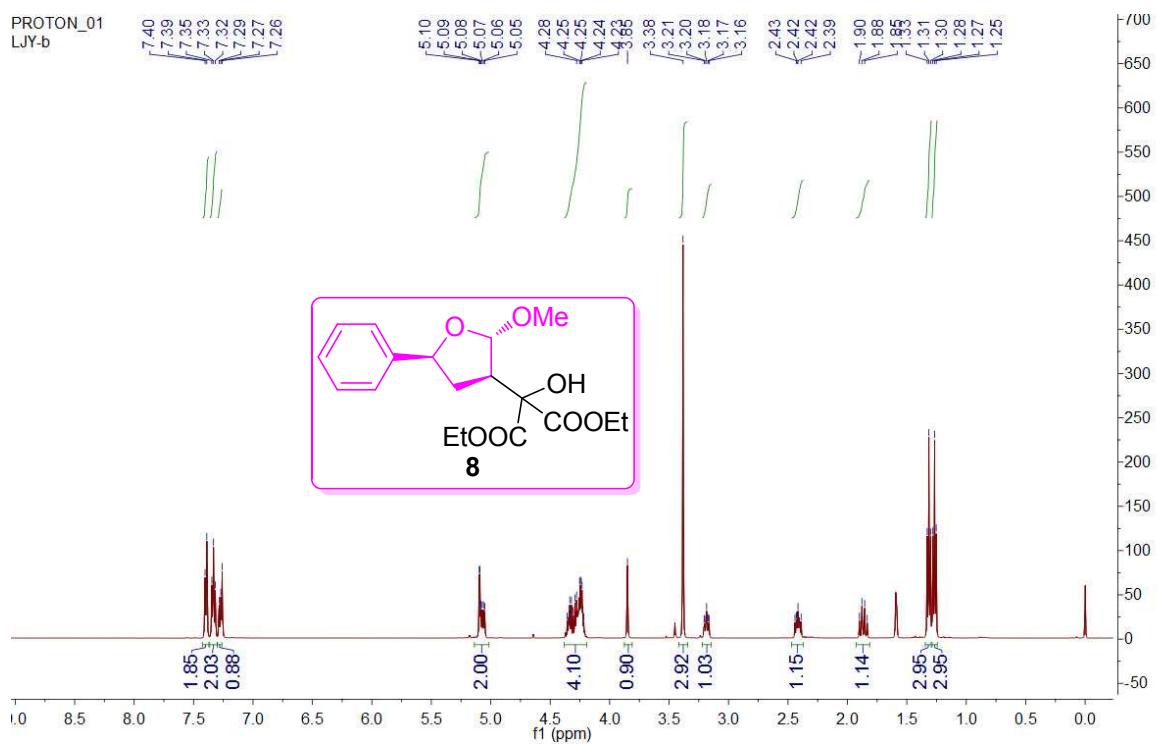
Chrom Type: Fixed WL Chromatogram, 231 nm

Peak Quantitation: AREA
Calculation Method: AREA%

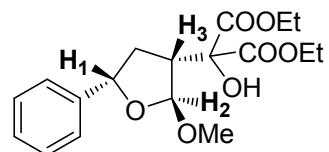
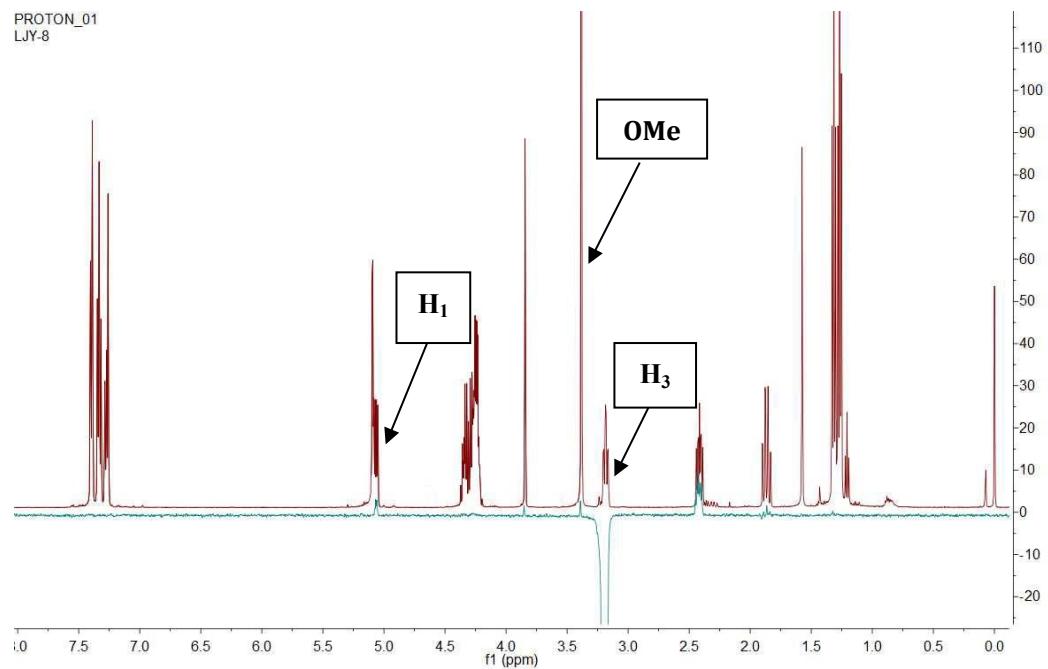
No.	RT	Area	Area %	BC
1	11.880	360490	95.824	BB
2	16.367	15710	4.176	BB
		376200	100.000	







The determination of the absolute configuration of compound 8 by NOE



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