

Different hybridized oxygen atoms controlled chemoselective formation of oxocarbenium ion: synthesis of chiral heterocyclic compounds

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Supporting Information

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The Synthesis of Required Bicyclic O,O-Acetal **4** and **4'**

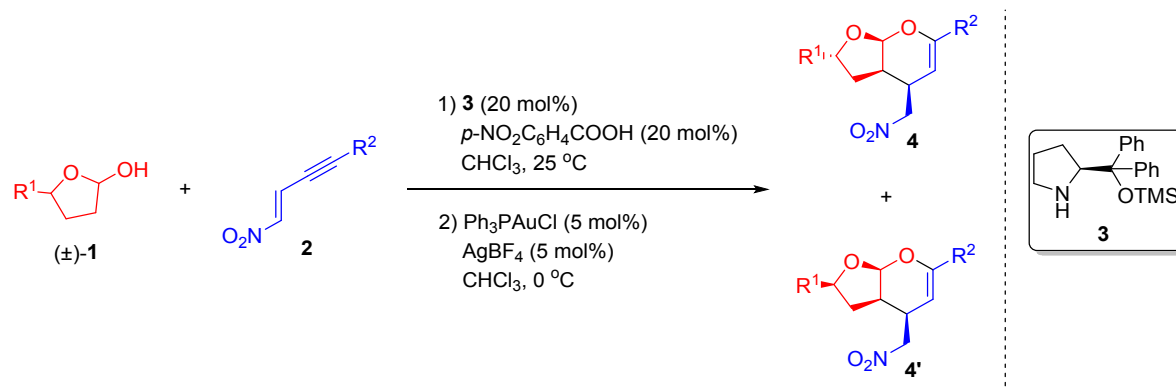


Table 1: ^a

entry	R ¹ /R ²	4 , 4'	yield [%] ^[b]	<i>ee</i> [%] ^[c]	dr ^[d]
			total (4 / 4')	4 / 4'	4 / 4'
1	Ph/Ph	4a , 4'a	77 (37/40)	>99/99	14:1/12:1
2	4-BrC ₆ H ₄ /Ph	4b , 4'b	77 (37/40)	99/98	>20:1/>20:1
3	Me/Ph	4c , 4'c	76 (36/40)	>99/>99	>20:1/13:1
4	2-thienyl/Ph	4d , 4'd	74 (33/41)	>99/>99	>20:1/19:1
5	Ph/4-MeC ₆ H ₄	4e , 4'e	73 (36/37)	>99/>99	>20:1/>20:1
6	Ph/4-FC ₆ H ₄	4f , 4'f	73 (32/41)	>99/>99	>20:1/>20:1
7	Ph/3-MeC ₆ H ₄	4g , 4'g	79 (36/43)	>99/>99	>20:1/15:1
8	Ph/3-thienyl	4h , 4'h	74 (36/38)	99/>99	>20:1/>20:1

^a See the General procedure.

^b The total yield of **4** and **4'**; the values in brackets refer to the yield of pure compounds **4** and **4'**.

^c Determined by HPLC analyses of isolated compounds **4** and **4'** on chiral stationary phases.

^d Determined by ¹H NMR analysis.

General procedure: A glass vial equipped with a magnetic stirring bar was charged with lactols (**±**)-**1** (0.40 mmol), nitroenynes **2** (0.48 mmol), **3** (0.08 mmol) and *p*-NO₂C₆H₄COOH (0.08 mmol) in

CHCl₃ (2 mL) at 25 °C. The resulting reaction mixture was kept under vigorous stirring until the consumption of lactols (**±**)-**1** (monitored by TLC analysis). After completion of the reaction, the solvent was removed under vacuum and the crude product was purified by flash chromatography on silica gel to afford the Michael adducts. Then the obtained products were dissolved in redistilled CHCl₃ (4 mL) under argon environment at 0 °C. Ph₃PAuCl (5 mol%) and AgBF₄ (5 mol%) were added successively. It was hydrolyzed with water and extracted with CH₂Cl₂ when the reaction was complete. The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure. After purified by a flash column chromatography on silica gel using petroleum ether/ethyl acetate (20:1 to 15:1) as eluent, compounds **4** and **4'** were finally obtained.

Ring-Opening of **4** and **4'** by Chemoselective Protonation

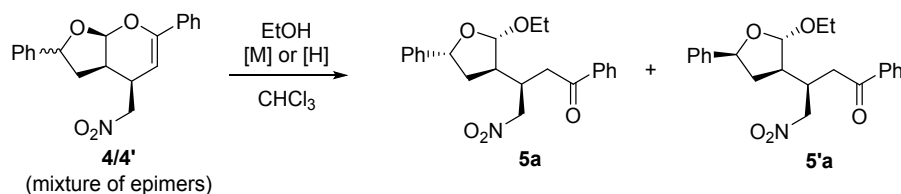


Table 2:^a

entry	catalyst	Time (h)	yield (%) ^b	ee [%] ^c	dr ^d
			total (5a/5'a)	5a/5'a	5a/5'a
1	[Au]	--	--	--	--
2 ^e	[Au]	12 h	87 (43/44)	>99/99	>20:1/14:1
3	[Ag]	6 h	80 (41/39)	99/99	15:1/12:1
4	DPP	--	-	--	-
5	<i>p</i> -TsOH	1 h	93 (46/47)	>99/>99	>20:1/14:1

^a All reactions were performed by the following procedure: **4a/4'a** (0.20 mmol) were dissolved in distilled CHCl₃ (1 mL) at 0 °C. EtOH (0.40 mmol) and corresponding catalysts were added and the reaction was kept at 0 °C until **4a** and **4a'** were consumed completely. The reaction was purified immediately by a flash column chromatography on silica gel to give compounds **5a** and **5'a**.

^b The total yield of **5a** and **5'a**; the values in brackets refer to the yield of isolated pure compounds **5a** and **5'a**.

^c Determined by HPLC analyses of isolated compounds **5a** and **5'a** on chiral stationary phases.

^d Determined by ¹H NMR analysis of the crude reaction mixture.

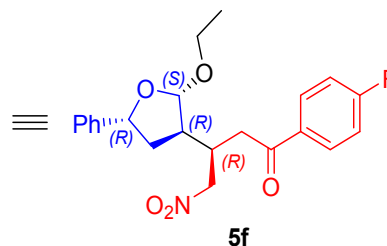
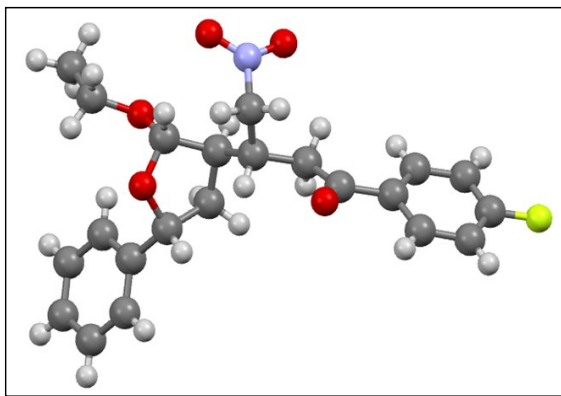
^e AgBF₄ (5 mol%) was added after 2 h. [Au] = Ph₃PAuCl, [Ag] = AgBF₄.

First, we investigated the ring-opening reaction between the mixture of **4a/4'a** and EtOH (2.0 eq). No reaction was observed by using only PPh₃AuCl (5 mol%) as the catalyst (entry 1) in 2h. But when AgBF₄ (5 mol%) was added to the solution, the reaction could occur and generate **5a** and **5'a** in 12 h (entry 2). And then we proved that AgBF₄ (5 mol%) alone could also provide significant turnover (entry 3). Surprisingly, diphenyl hydrogen phosphate (DPP, 20 mol%) showed no catalytic activity in this transformation (entry 4). To our excitement, *p*-toluenesulfonic acid (*p*-TsOH, 20 mol%) showed very high catalytic activity (entry 5), the ring-opening process finished in only 1 h, thus both **5a** and **5'a** were obtained with excellent diastereoselectivity. With these results in hand, we studied the suitability of the substrate for this reaction.

X-ray structure determination

Single Crystal X-Ray Diffraction Data of 5f.

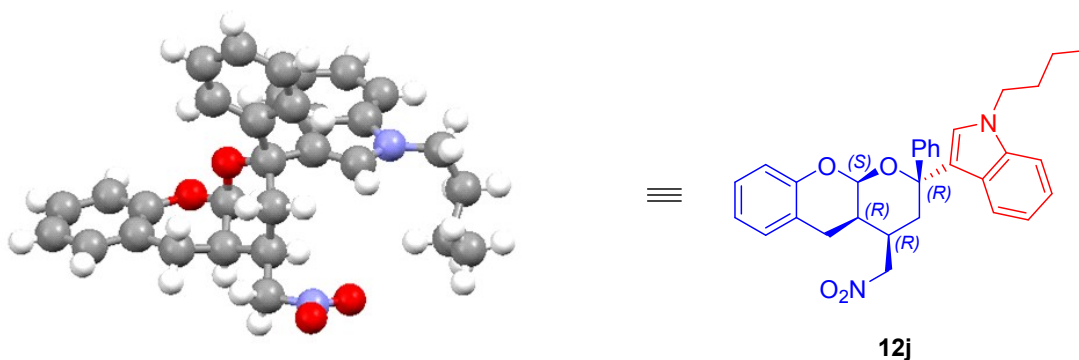
X-ray crystallographic data have been deposited in the Cambridge Crystallographic Data Centre database (http://www.ccdc.cam.ac.uk/data_request/cif.) under accession code CCDC 1506248.



Bond precision:	C-C = 0.0115 Å		Wavelength=0.71073
Cell:	a=7.530 (3)	b=5.649 (2)	c=23.594 (9)
	alpha=90	beta=96.387 (6)	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	997.4 (7)	997.4 (7)	
Space group	P 21	P 1 21 1	
Hall group	P 2yb	P 2yb	
Moiety formula	C22 H24 F N O5	C22 H24 F N O5	
Sum formula	C22 H24 F N O5	C22 H24 F N O5	
Mr	401.42	401.42	
Dx, g cm-3	1.337	1.337	
Z	2	2	
Mu (mm-1)	0.101	0.101	
F000	424.0	424.0	
F000'	424.24		
h, k, lmax	9, 6, 28	9, 6, 28	
Nref	3792 [2103]	3586	
Tmin, Tmax			
Tmin'			
Correction method= Not given			
Data completeness=	1.71/0.95	Theta (max)= 25.680	
R(reflections)=	0.0768 (3463)	wR2(reflections)= 0.2068 (3586)	
S =	1.196	Npar= 264	

Single Crystal X-Ray Diffraction Data of 12j.

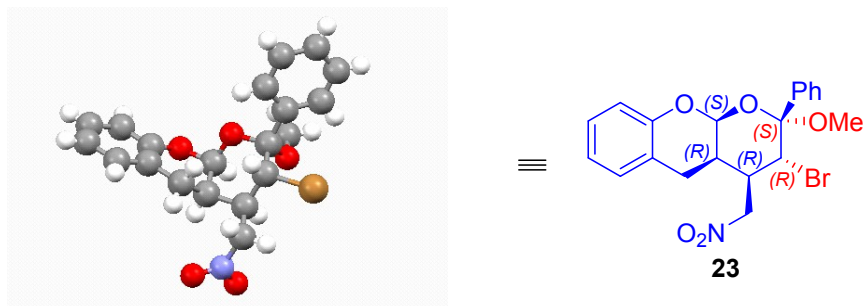
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Bond precision:	C-C = 0.0035 Å	Wavelength=1.54184
Cell:	a=7.9683(3) alpha=90	b=16.3532(6) beta=90
Temperature:	100 K	c=23.8547(9) gamma=90
Volume	Calculated 3108.4(2)	Reported 3108.4(2)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C31 H32 N2 O4, C4 H8 O2	4(C31 H32 N2 O4), 4(C4 H8 O2)
Sum formula	C35 H40 N2 O6	C140 H160 N8 O24
Mr	584.69	2338.75
Dx, g cm ⁻³	1.249	1.249
Z	4	1
Mu (mm ⁻¹)	0.688	0.688
F000	1248.0	1248.0
F000'	1251.79	
h, k, lmax	9, 19, 28	9, 19, 28
Nref	5720 [3249]	5132
Tmin, Tmax		
Tmin'		
Correction method	Not given	
Data completeness	1.58/0.90	Theta(max) = 68.416
R(reflections)	0.0385(4893)	wR2(reflections) = 0.0992(5132)
S	1.030	Npar = 411

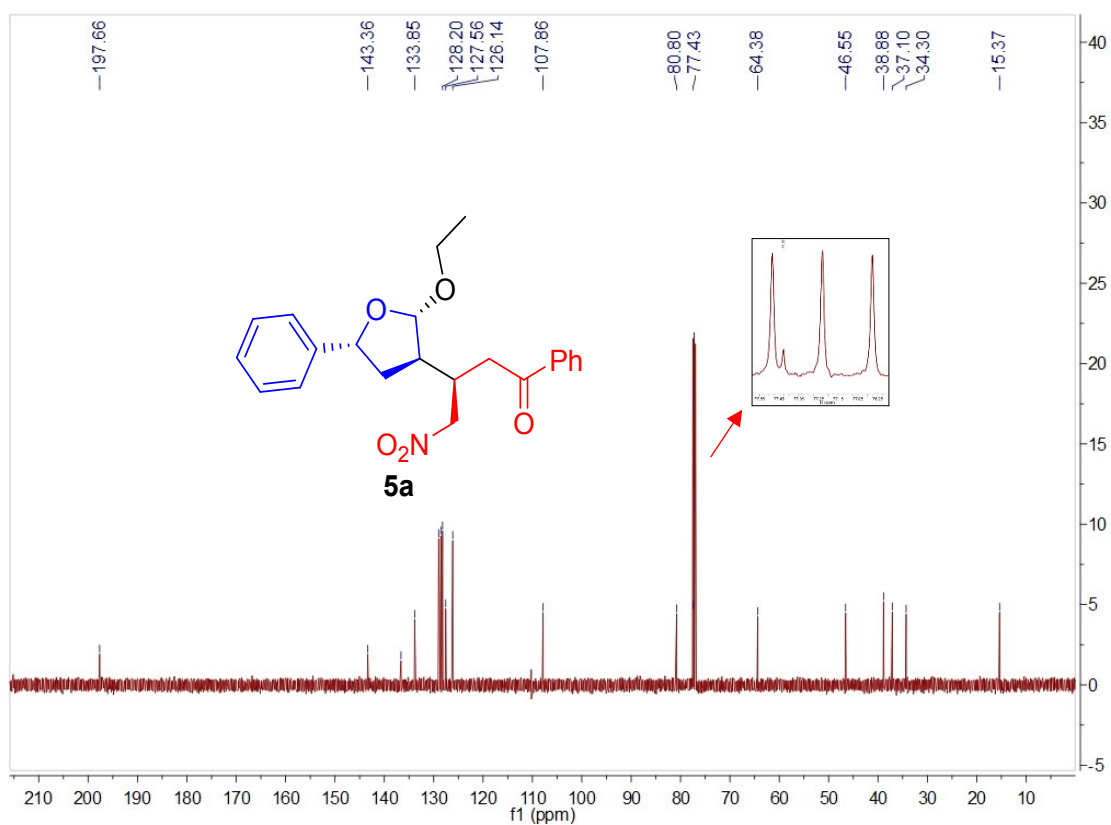
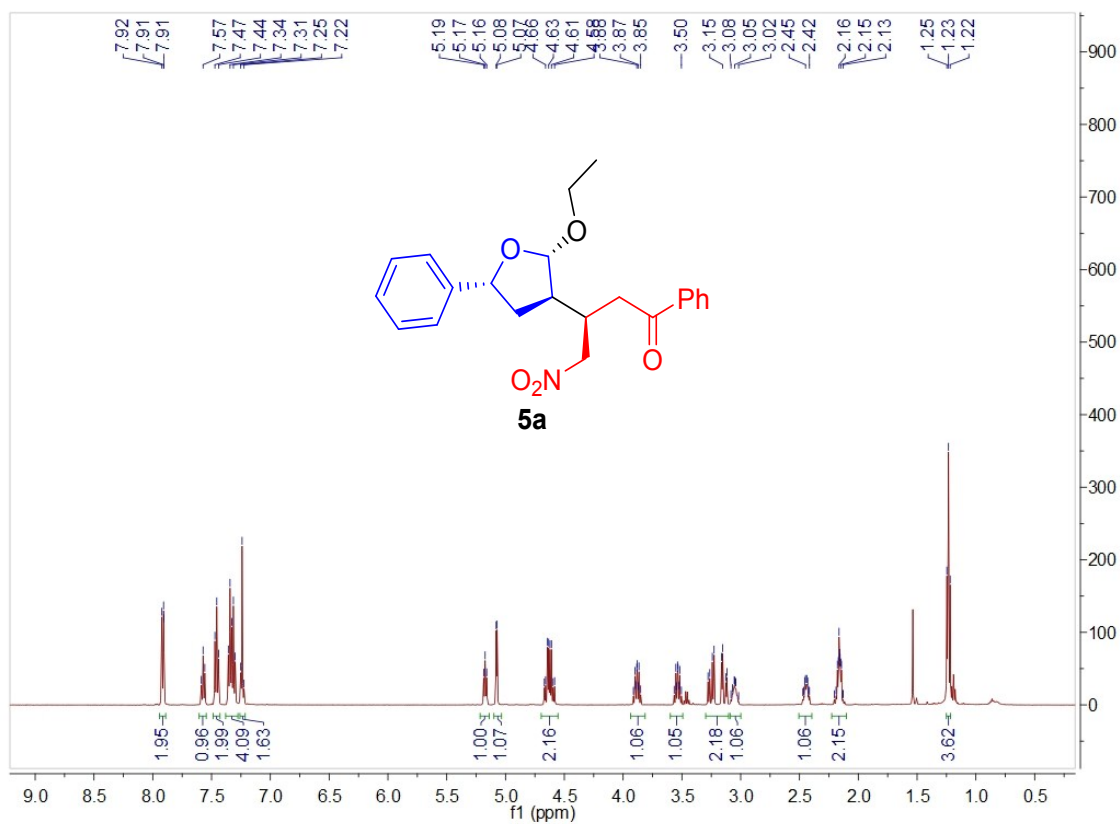
Single Crystal X-Ray Diffraction Data of 23.

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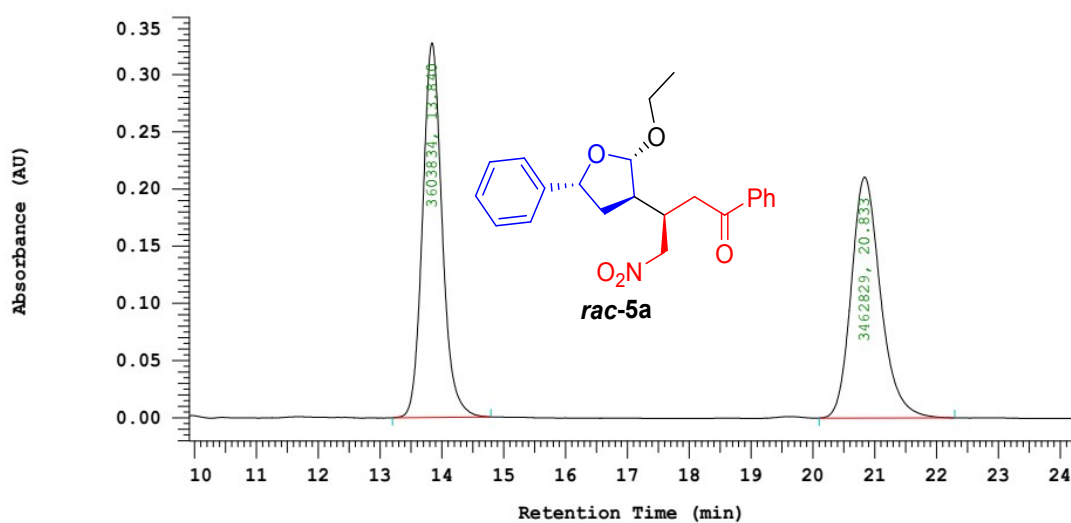


Bond precision:	C-C = 0.0125 Å	Wavelength=0.71073
Cell:	a=6.6706(10) b=25.351(4) c=11.3316(17)	
	alpha=90 beta=89.9000 gamma=90	
Temperature: 293 K		
	Calculated	Reported
Volume	1916.2(5)	1916.2(5)
Space group	P 21	P2(1)
Hall group	P 2yb	P 2yb
Moiety formula	C20 H20 Br N O5	C40 H40 Br2 N2 O10
Sum formula	C20 H20 Br N O5	C40 H40 Br2 N2 O10
Mr	434.27	868.56
Dx, g cm ⁻³	1.505	1.505
Z	4	2
Mu (mm ⁻¹)	2.176	2.176
F000	888.0	888.0
F000'	887.27	
h, k, lmax	7, 30, 13	7, 30, 13
Nref	6740[3453]	6468
Tmin, Tmax	0.599, 0.706	0.612, 0.722
Tmin'	0.575	
Correction method= # Reported T Limits: Tmin=0.612 Tmax=0.722 AbsCorr =		
MULTI-SCAN		
Data completeness= 1.87/0.96	Theta(max)= 25.000	
R(reflections)= 0.0587(5619)	wR2(reflections)= 0.1664(6468)	
S = 1.036	Npar= 490	

NMR spectra and HPLC Traces



Chrom Type: Fixed WL Chromatogram, 210 nm

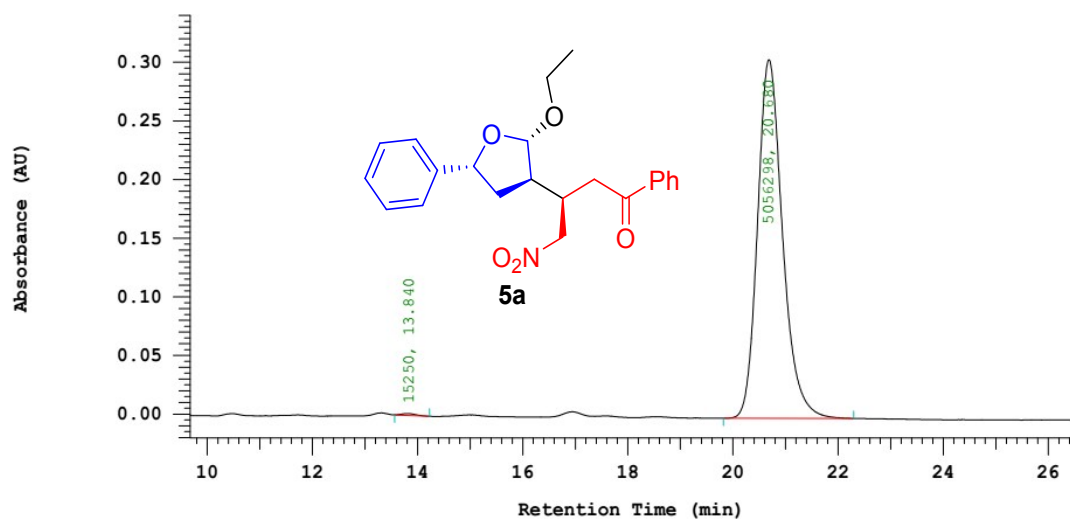


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
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2	20.833	3462829	49.002	BB
		7066663	100.000	

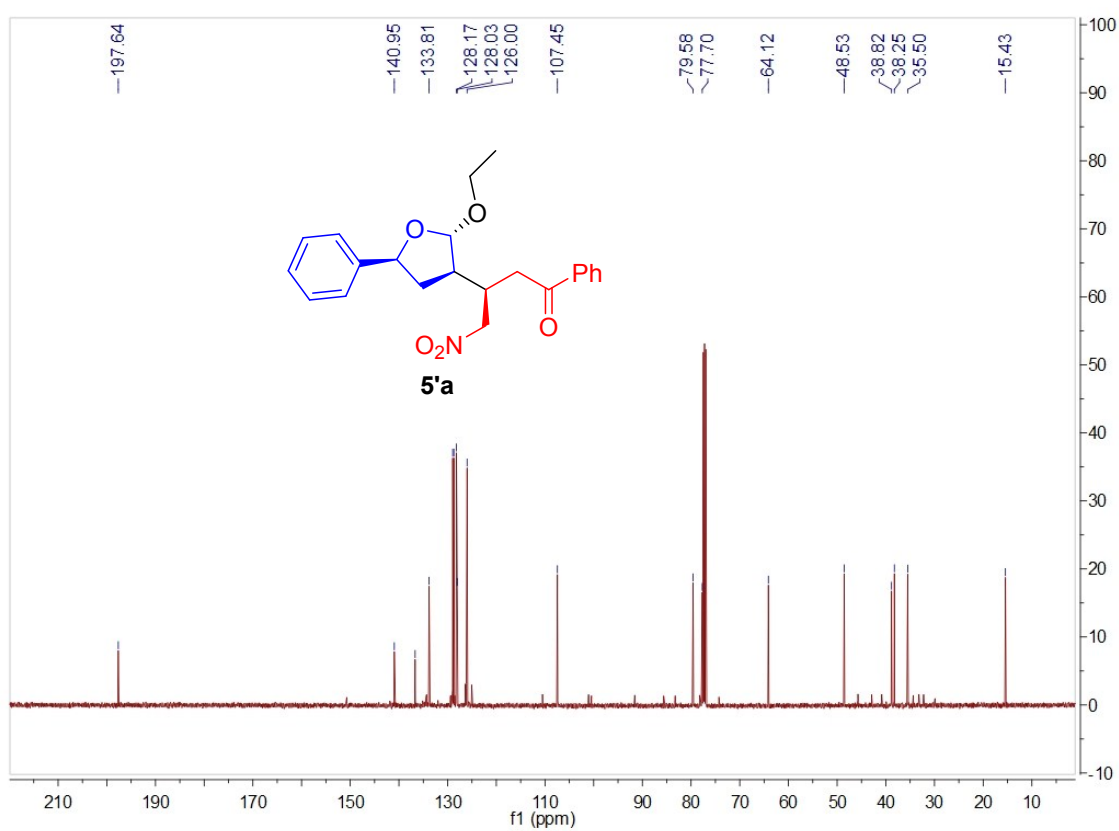
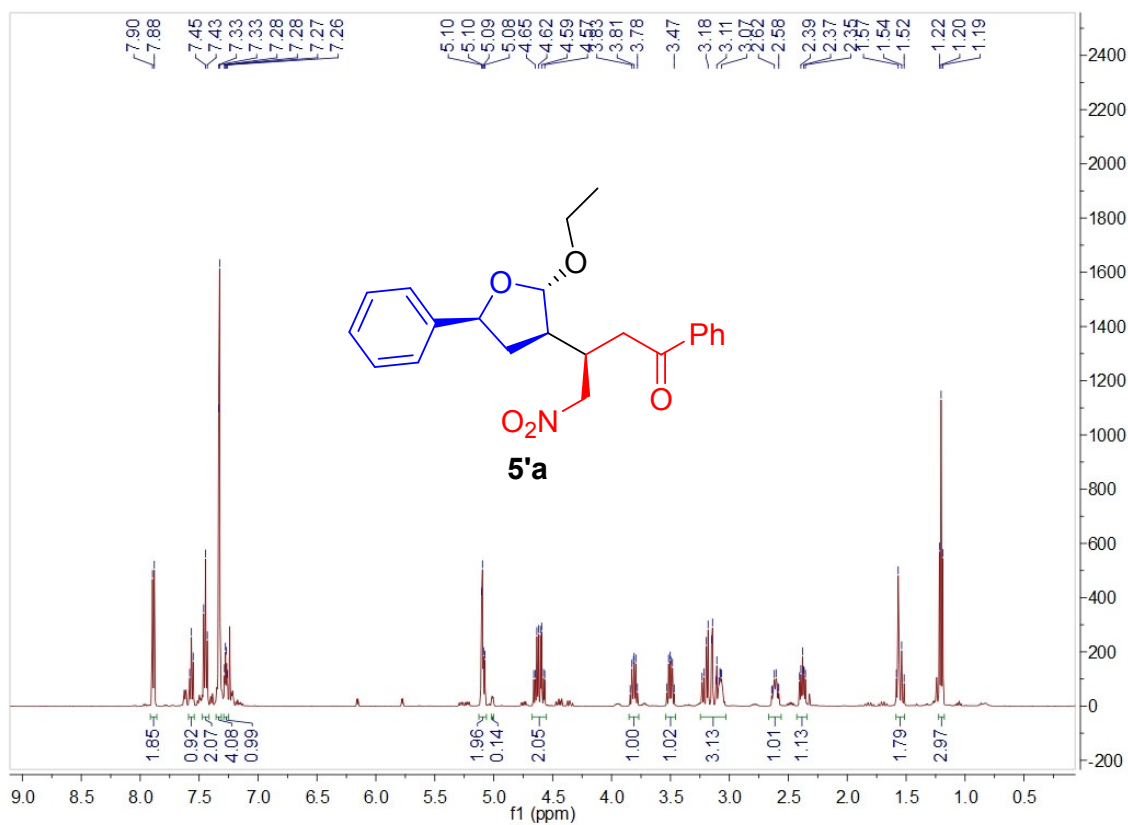
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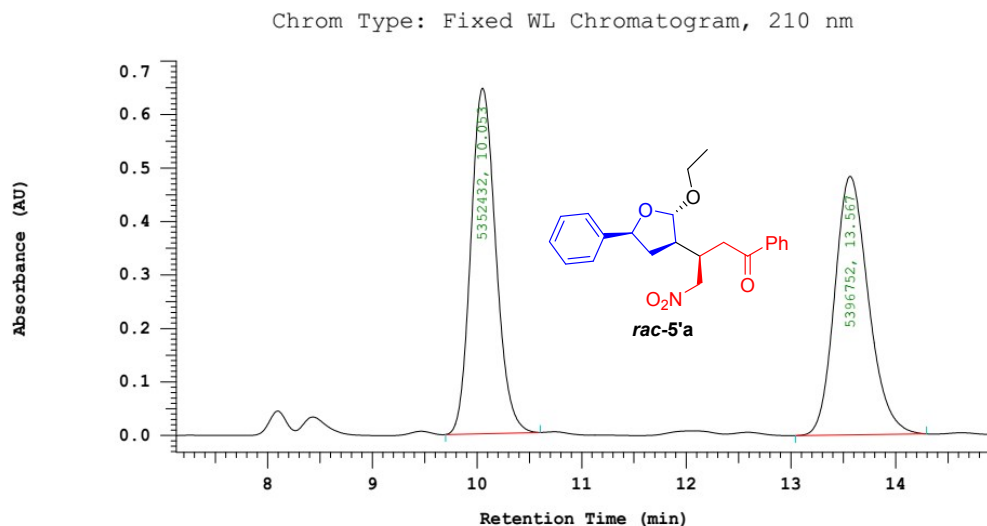


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

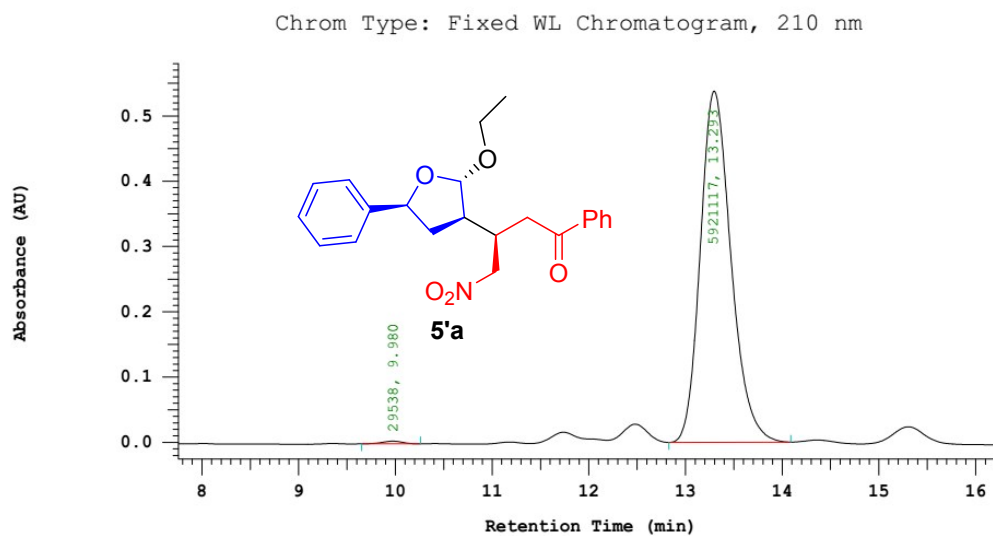
No.	RT	Area	Area %	BC
1	13.840	15250	0.301	BB
2	20.680	5056298	99.699	BB
		5071548	100.000	





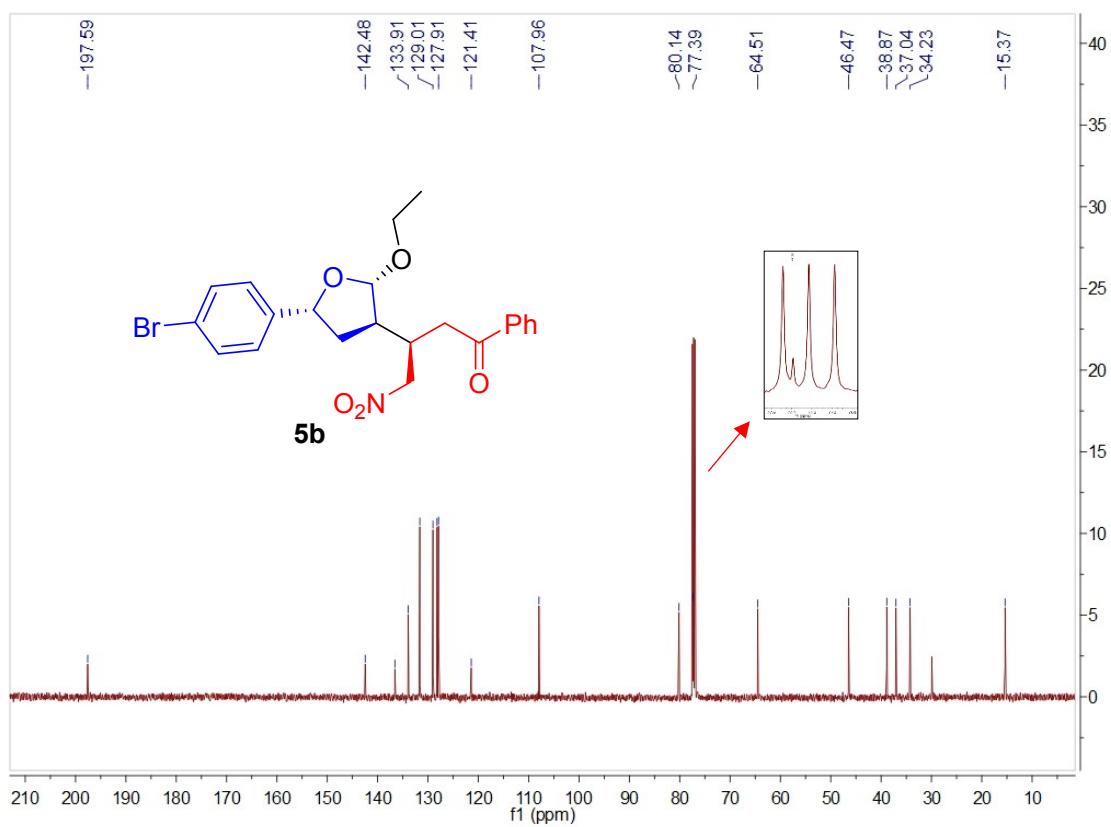
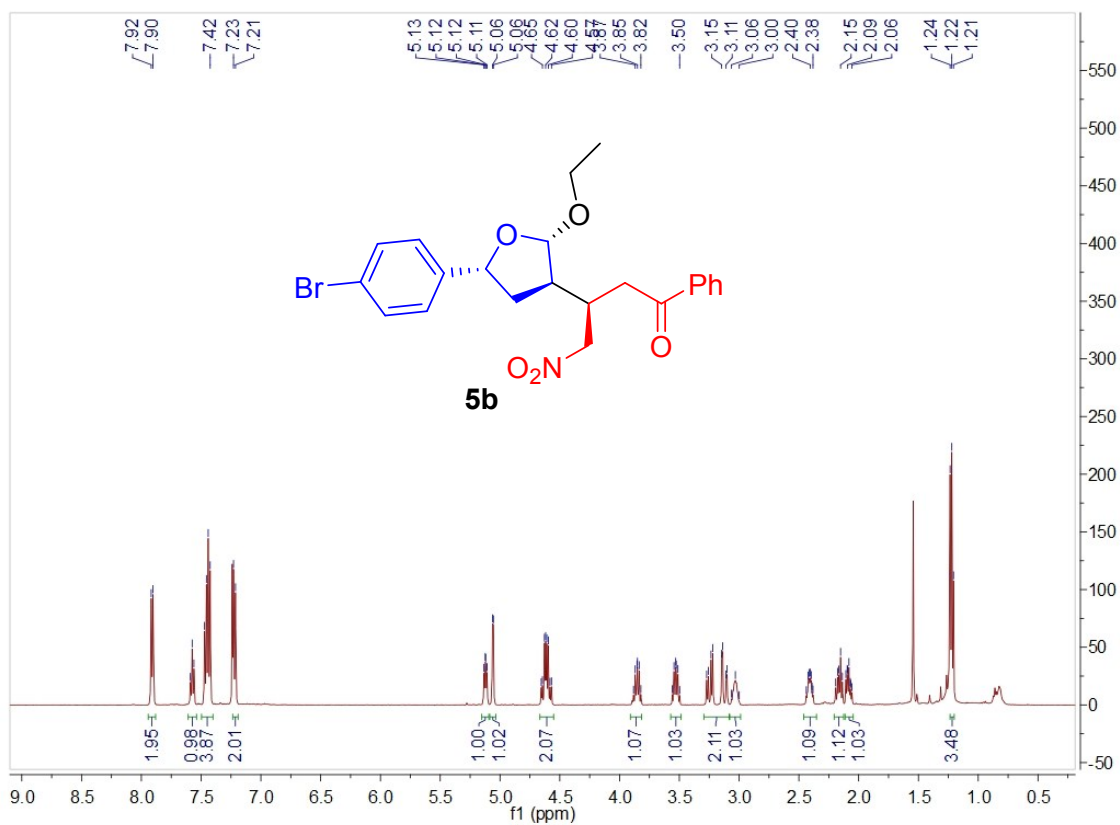
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 Peak Quantitation: AREA
 Calculation Method: AREA%

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1	10.053	5352432	49.794	BB
2	13.567	5396752	50.206	BB
		10749184	100.000	

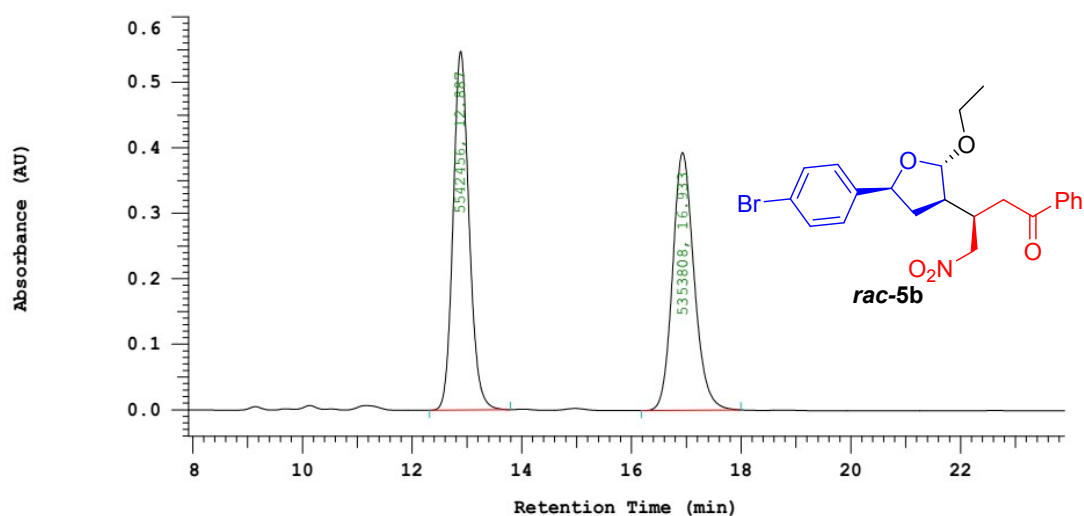


Chrom Type: Fixed WL Chromatogram, 210 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.980	29538	0.496	BB
2	13.293	5921117	99.504	BB
		5950655	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

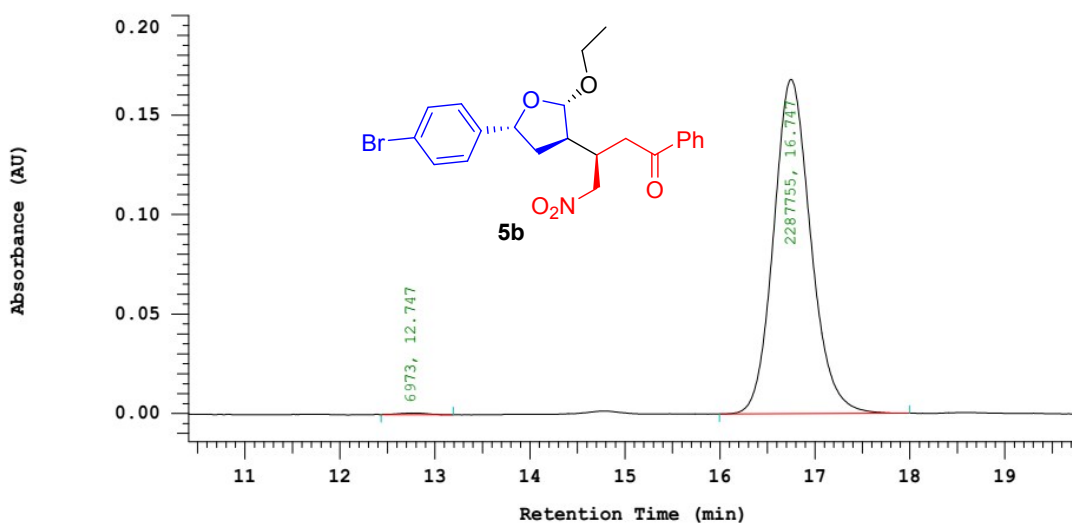


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	12.887	5542456	50.866	BB
2	16.933	5353808	49.134	BB
		10896264	100.000	

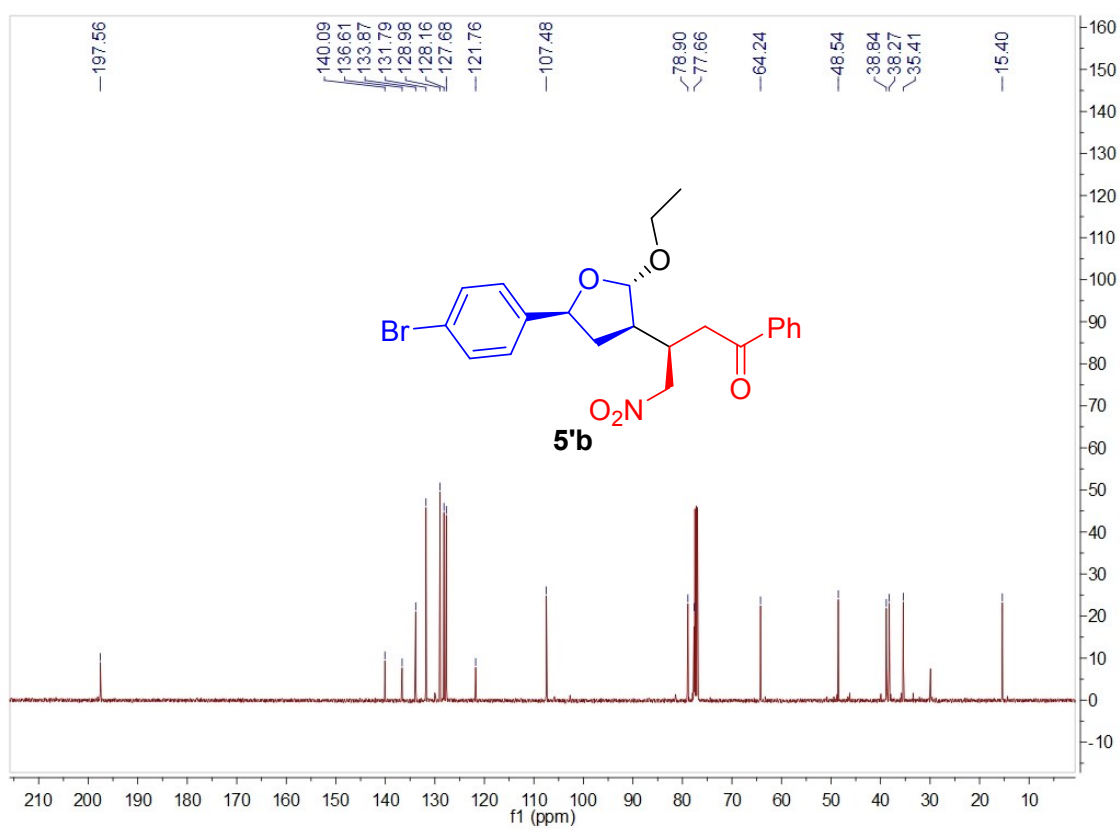
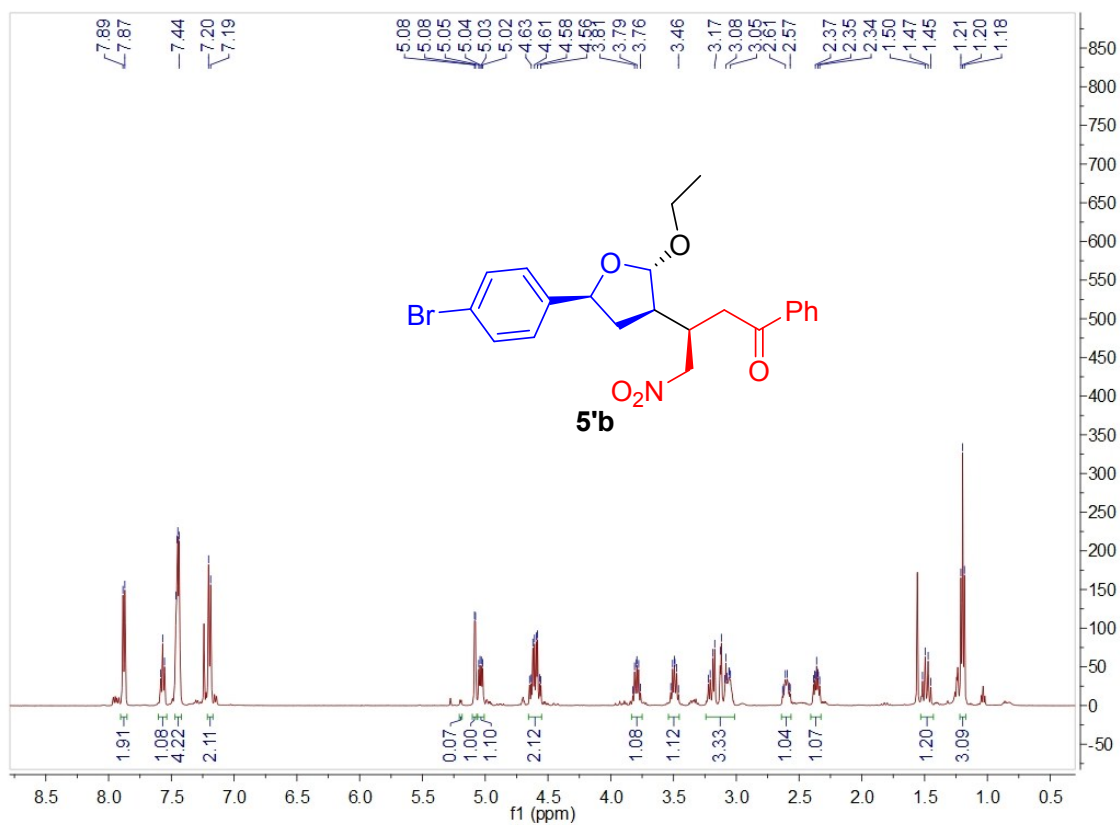
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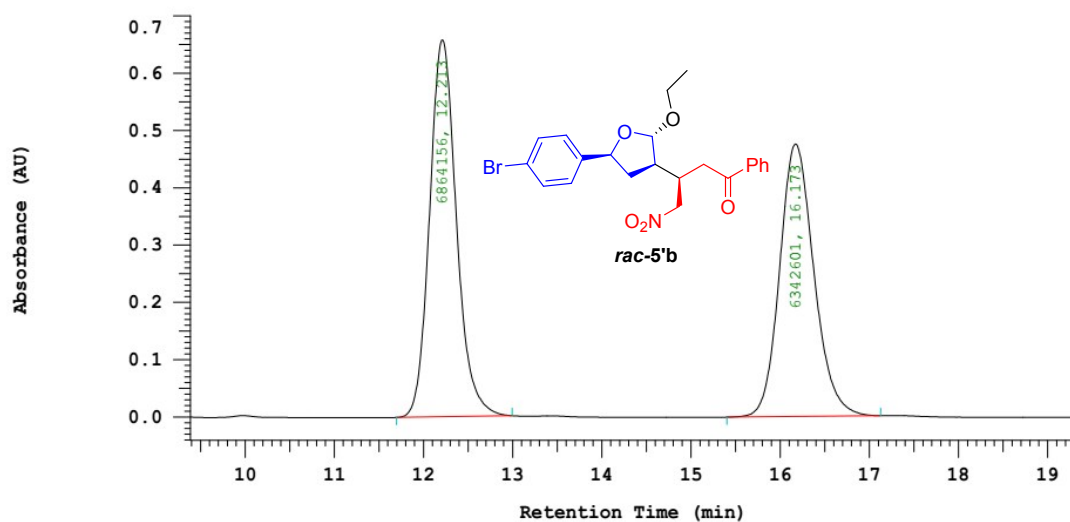
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Peak Quantitation: AREA
Calculation Method: AREA%

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Chrom Type: Fixed WL Chromatogram, 210 nm

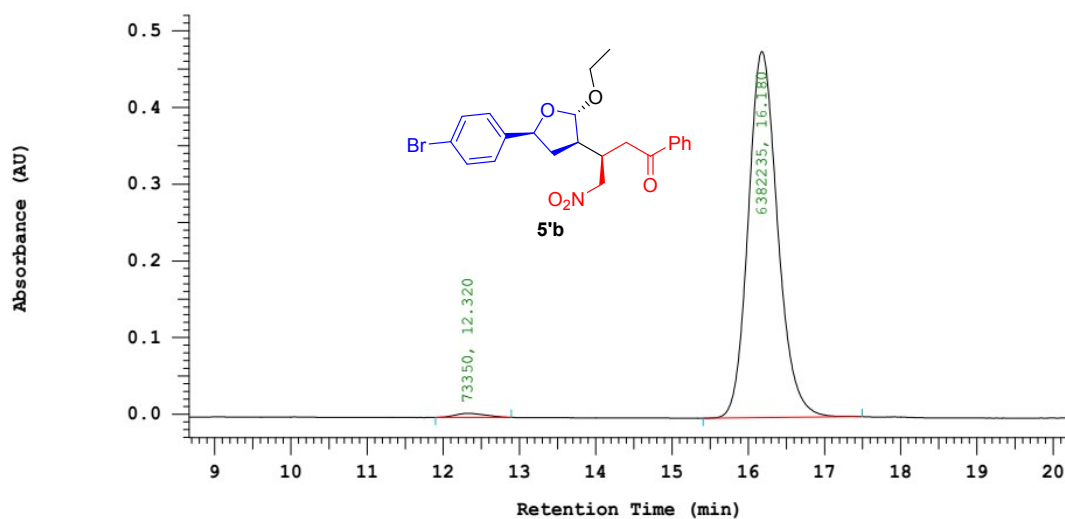


Chrom Type: Fixed WL Chromatogram, 210 nm

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Calculation Method: AREA%

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1	12.213	6864156	51.975	BB
2	16.173	6342601	48.025	BB
		13206757	100.000	

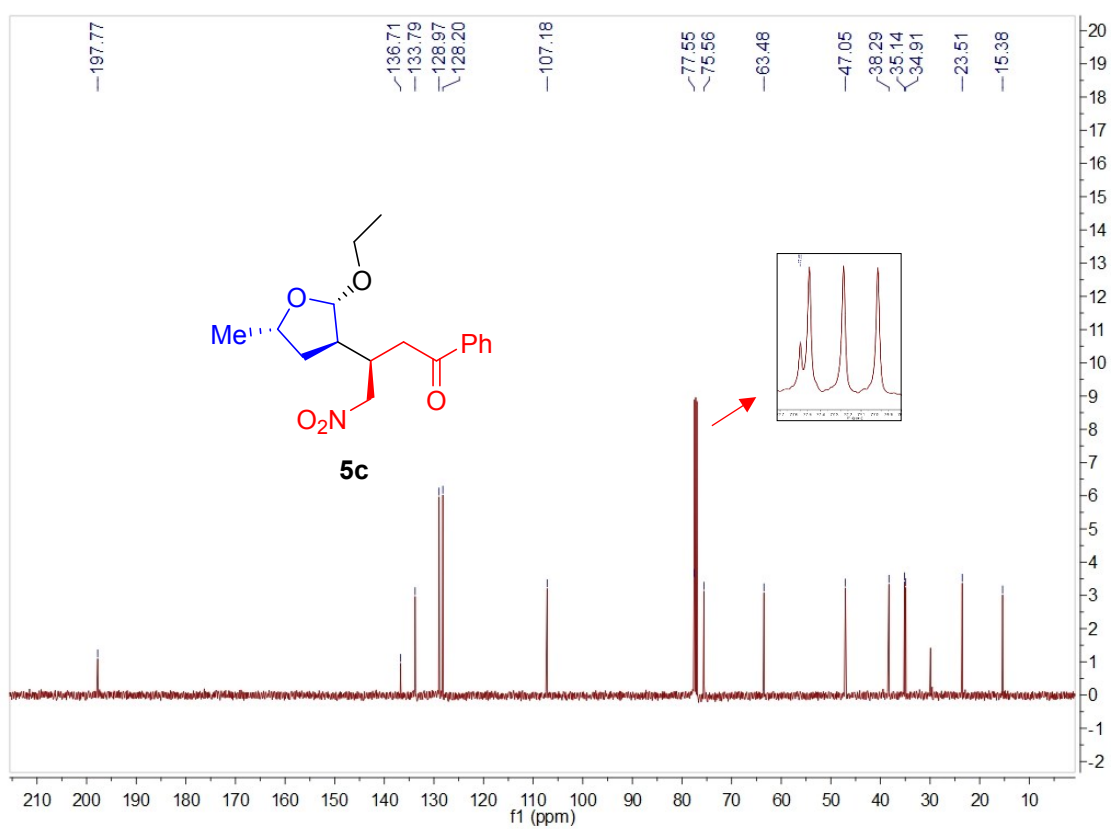
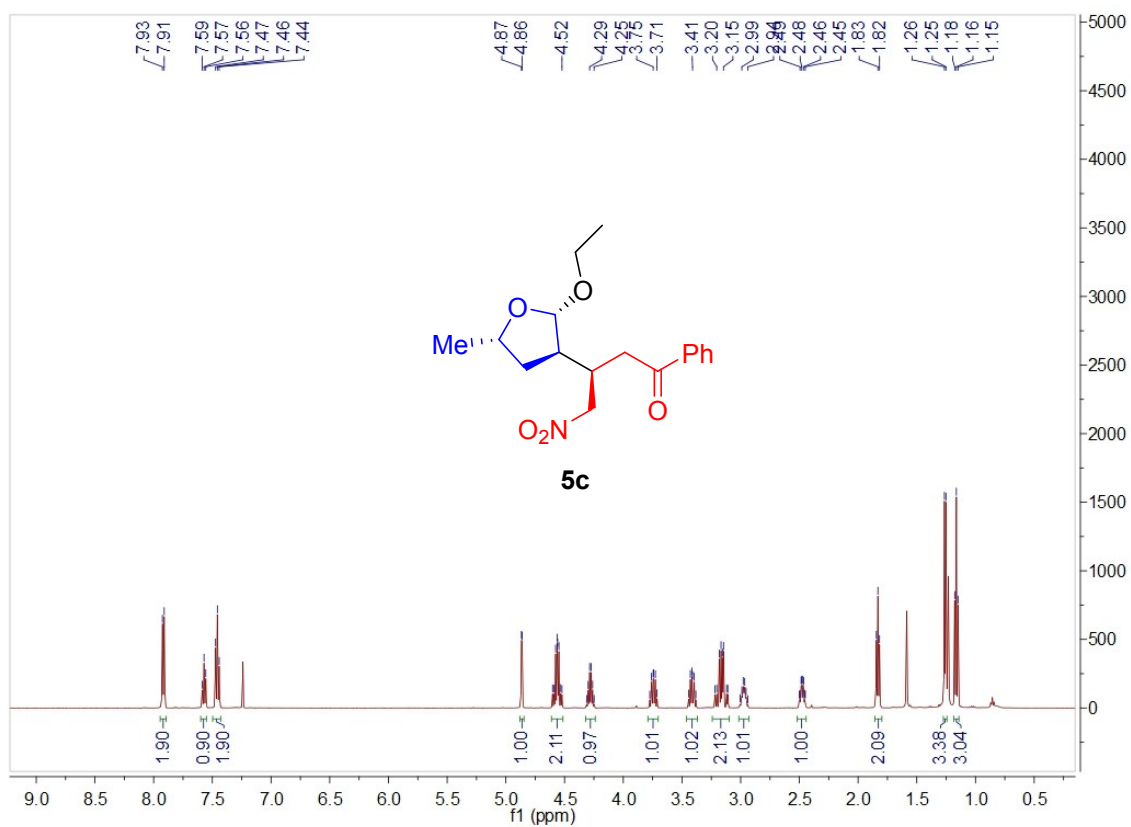
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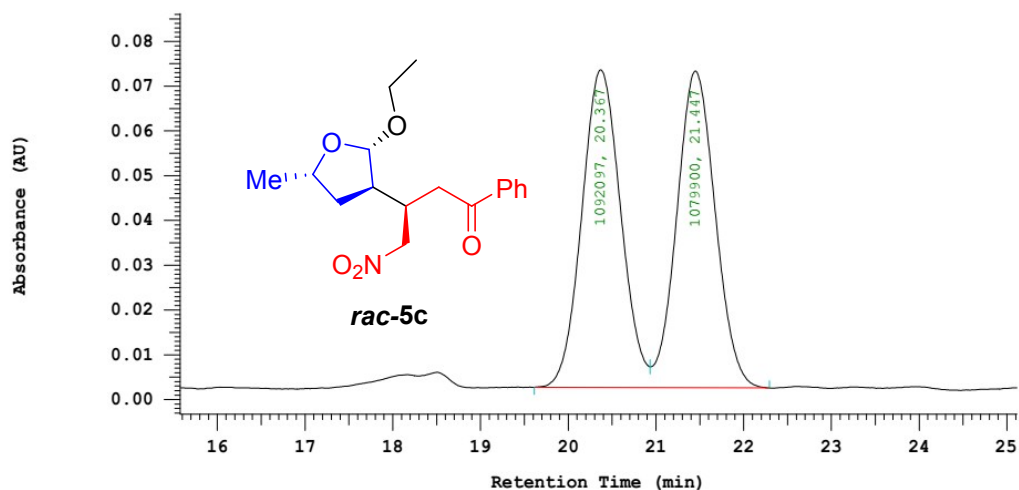
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Peak Quantitation: AREA
Calculation Method: AREA%

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		6455585	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

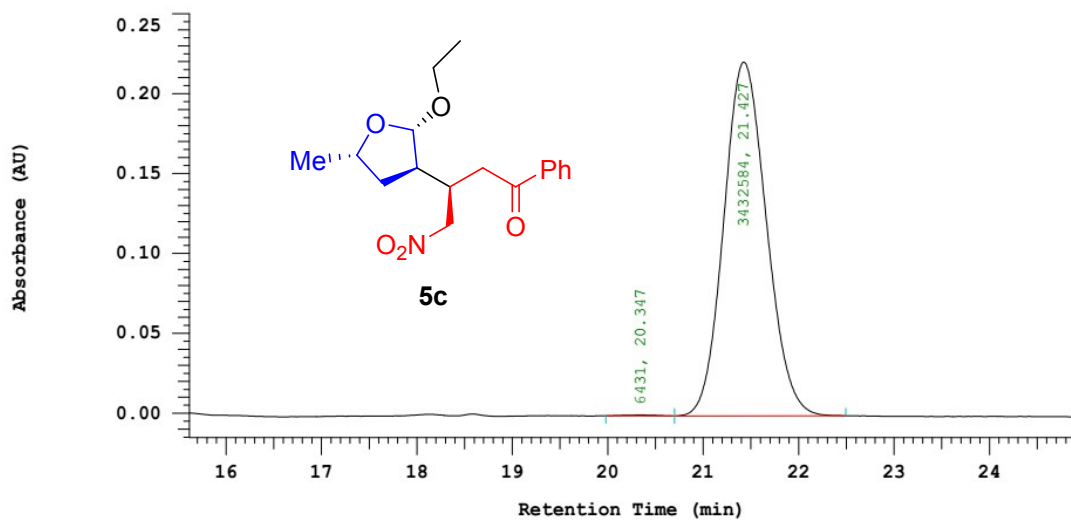


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

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1	20.367	1092097	50.281	BV
2	21.447	1079900	49.719	VB
		2171997	100.000	

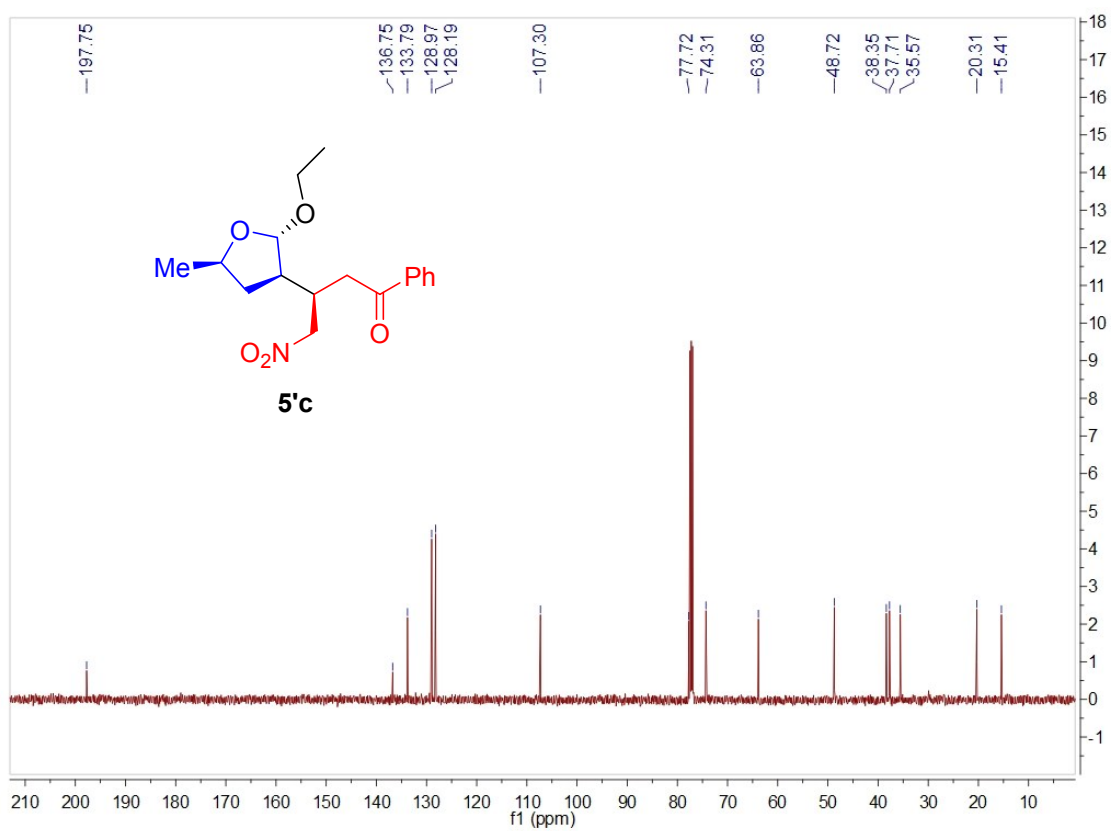
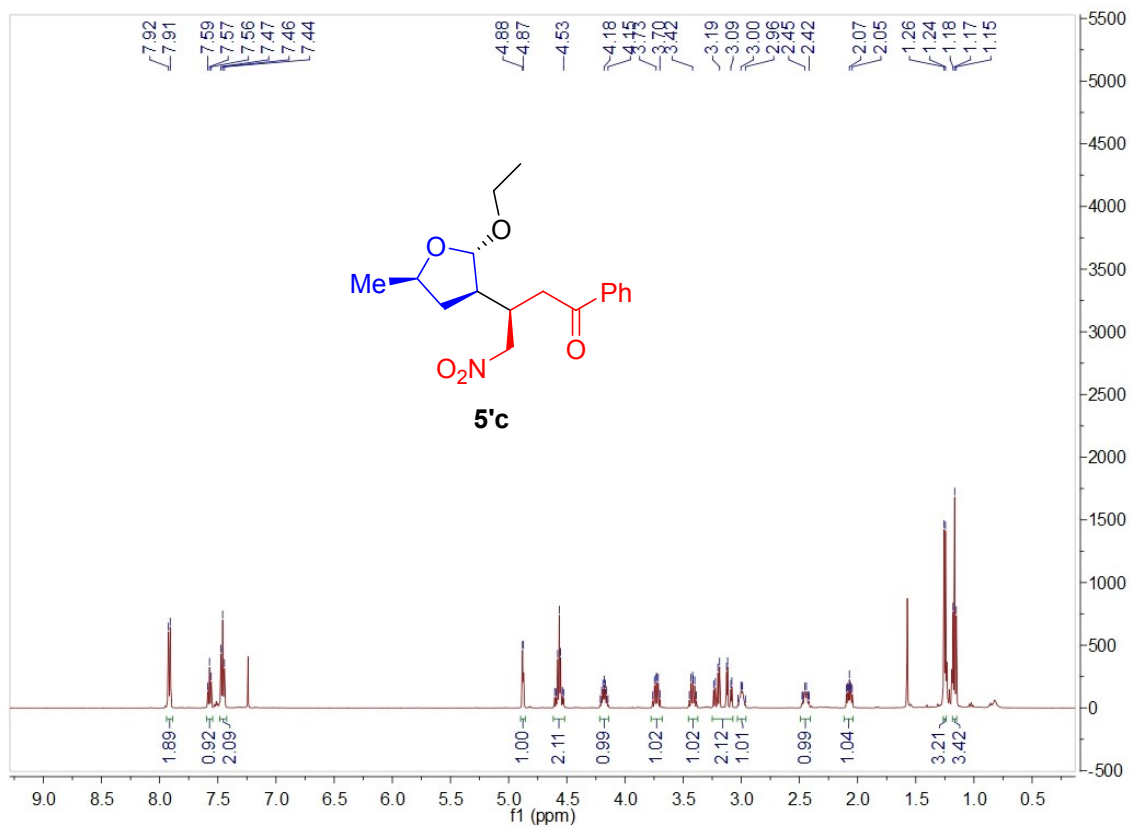
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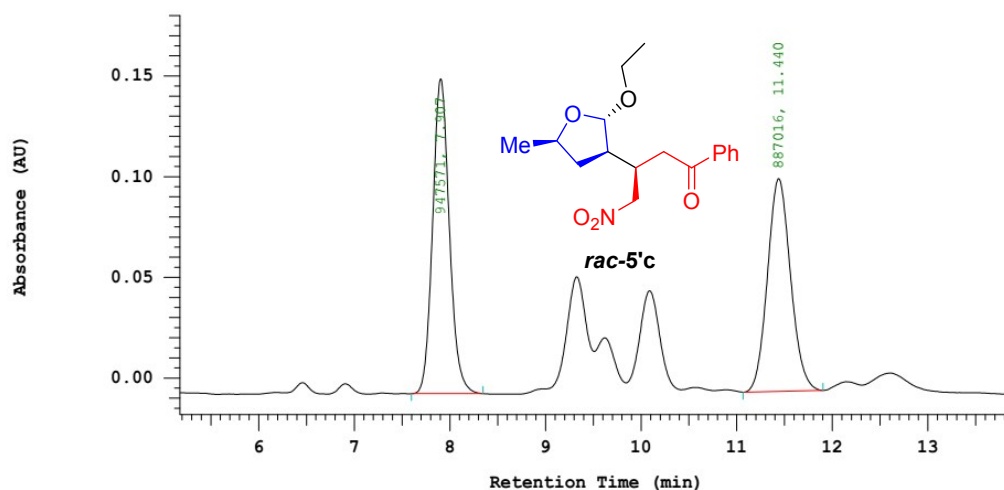
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Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	20.347	6431	0.187	BB
2	21.427	3432584	99.813	BB
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Chrom Type: Fixed WL Chromatogram, 210 nm

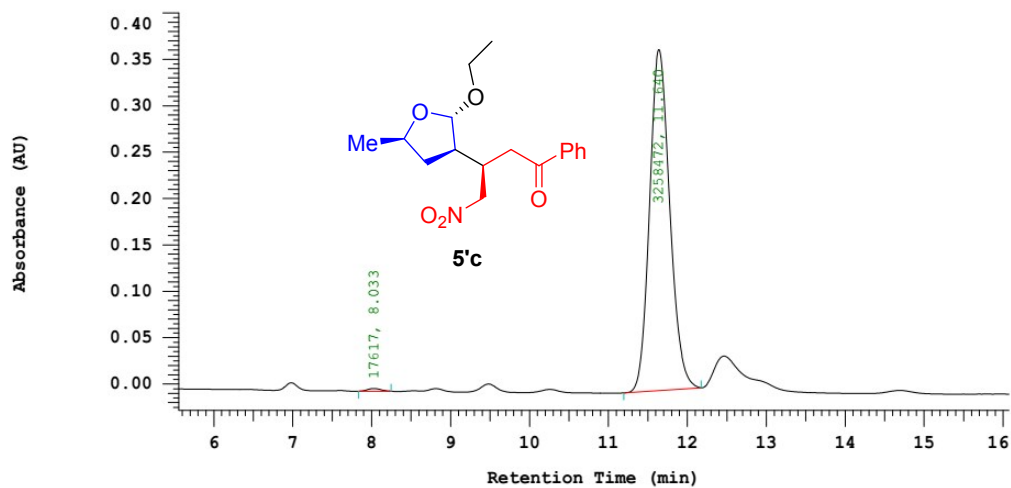


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.907	947571	51.650	BB
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		1834587	100.000	

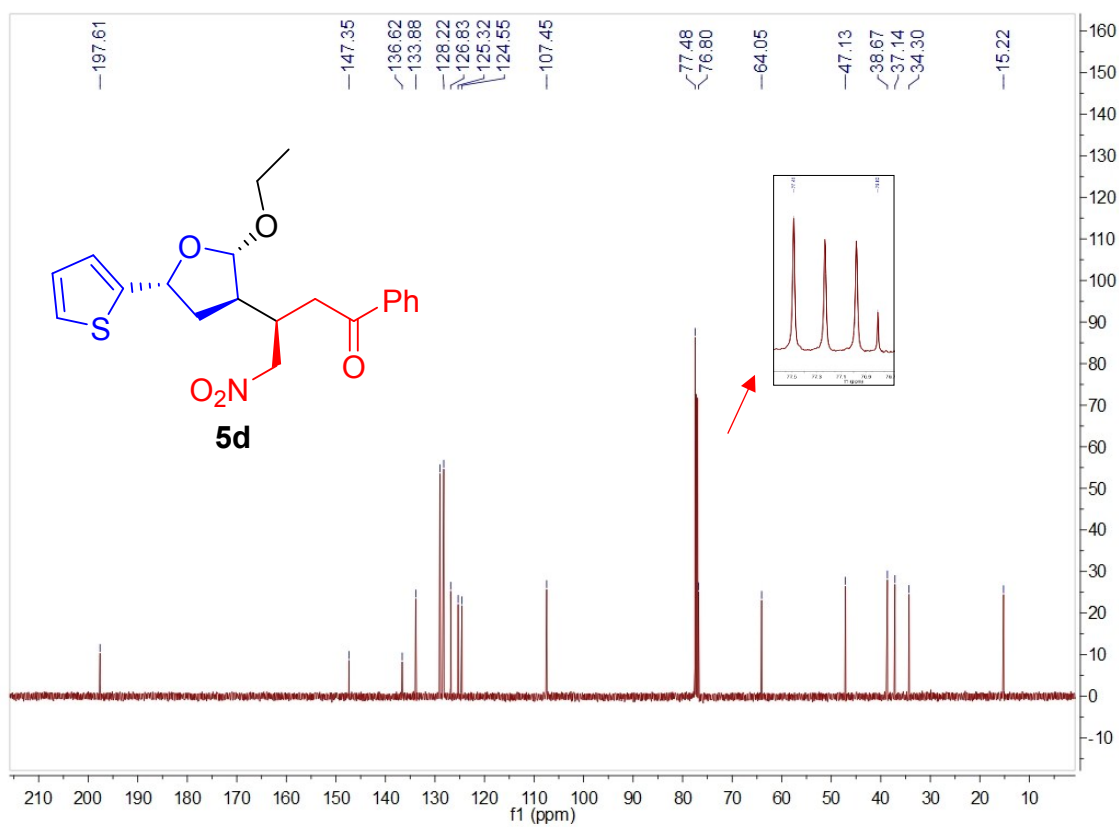
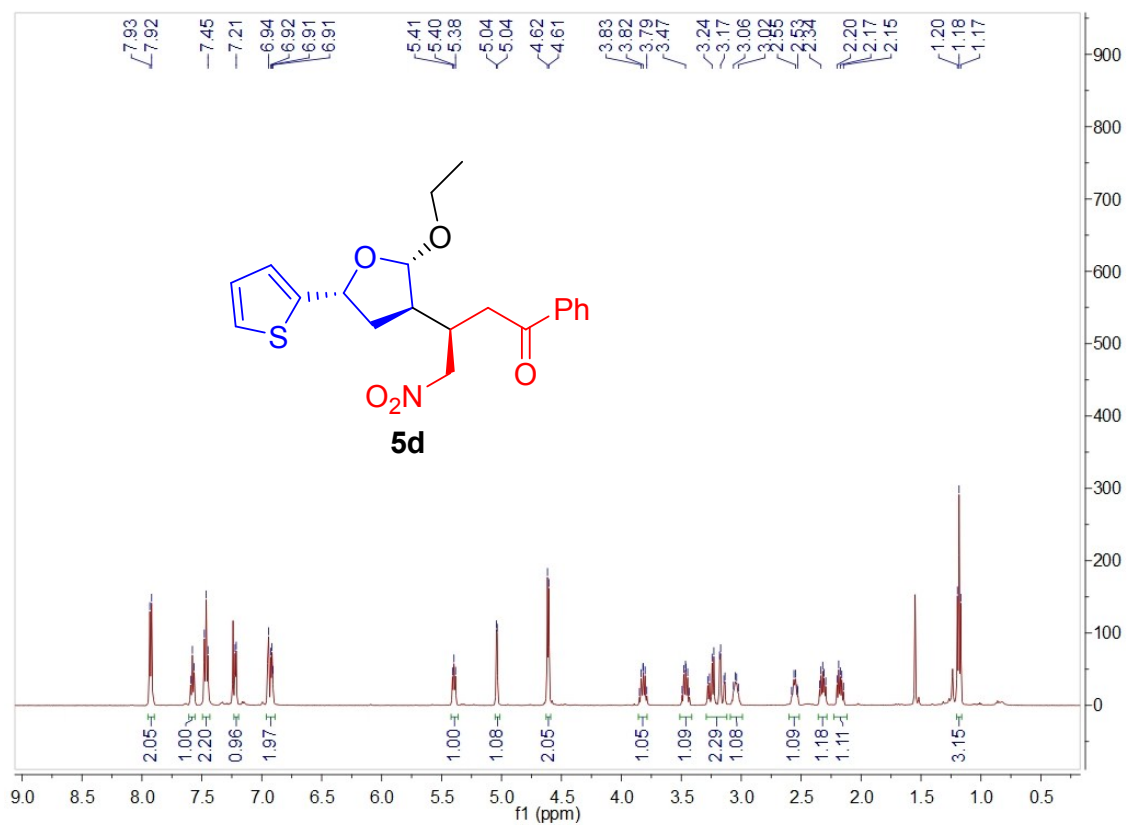
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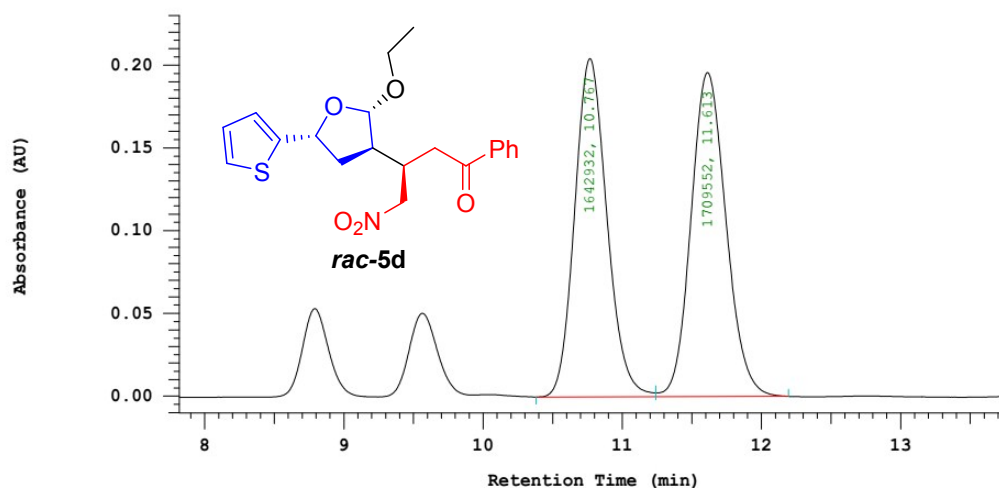
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
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2	11.640	3258472	99.462	BB
		3276089	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

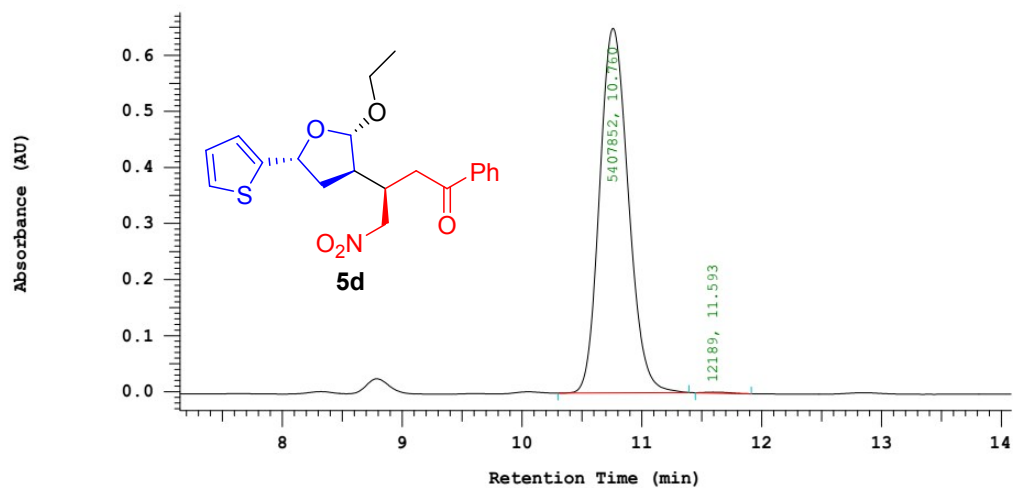


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

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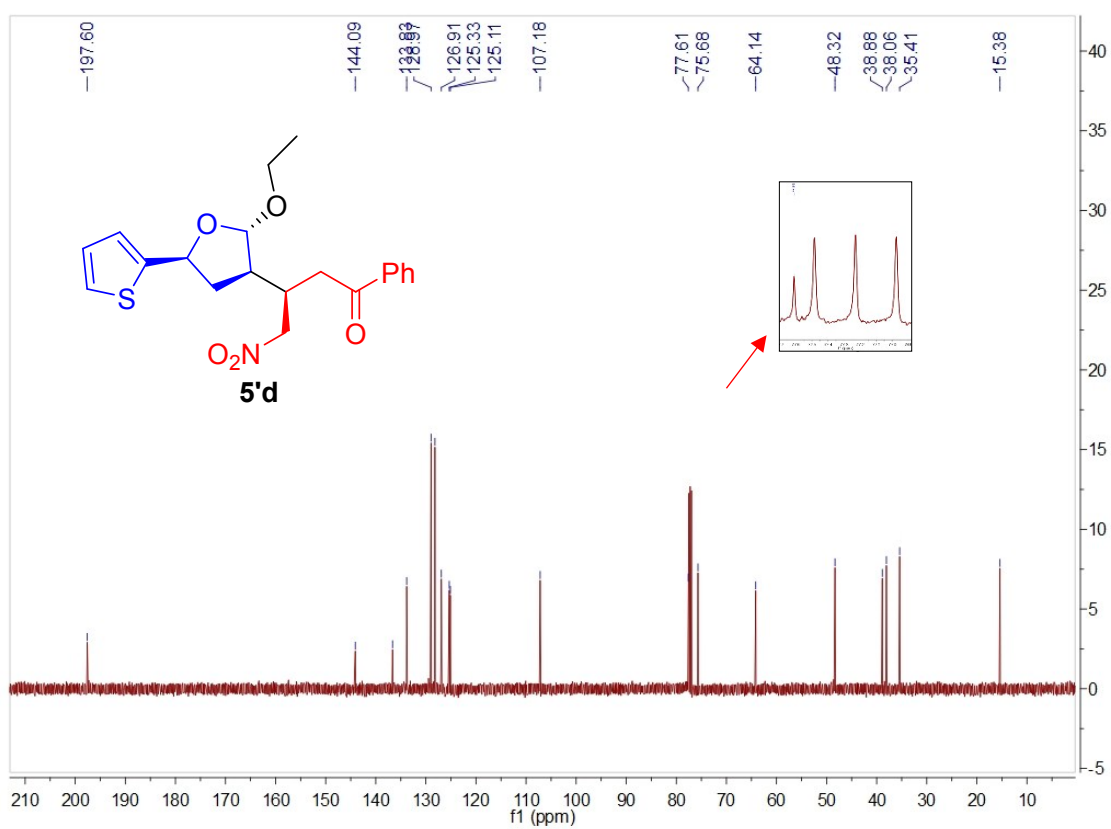
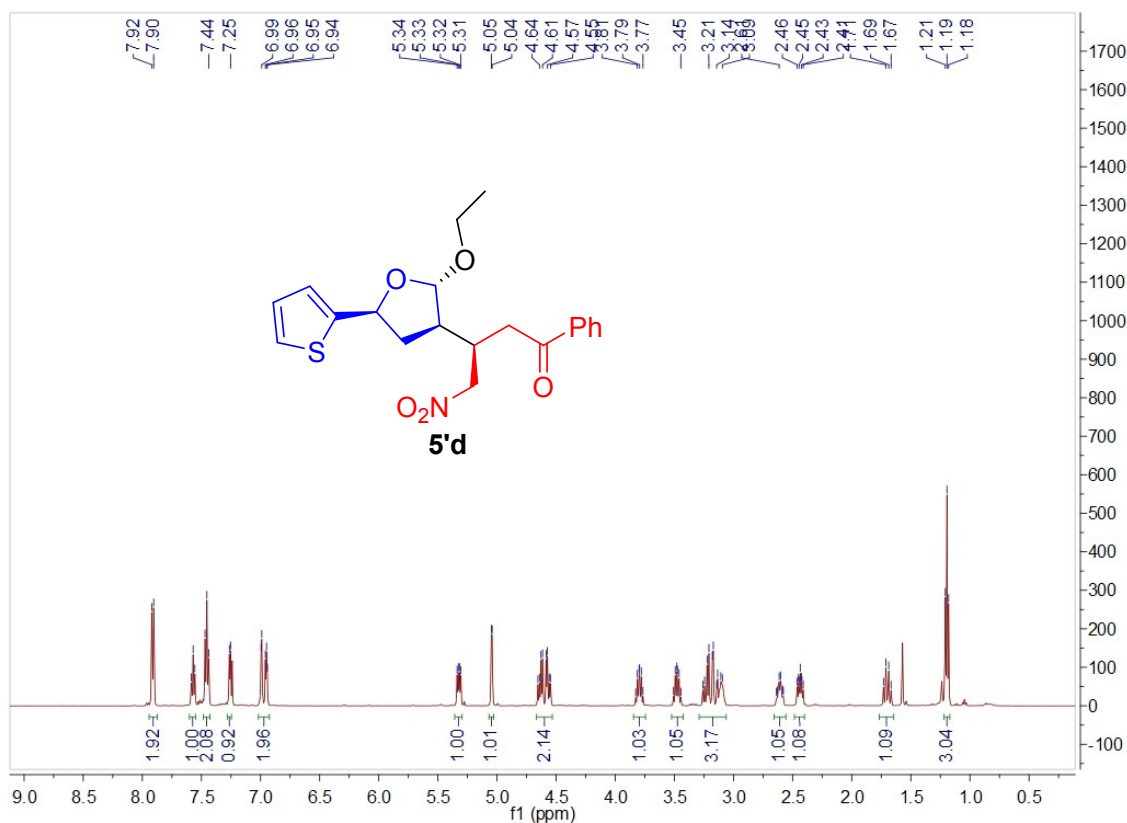
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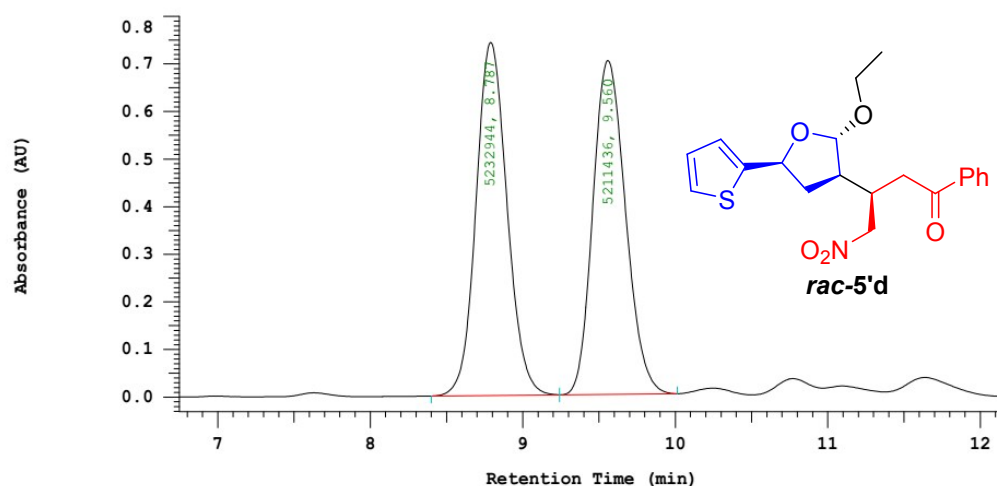
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Peak Quantitation: AREA
Calculation Method: AREA%

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Chrom Type: Fixed WL Chromatogram, 210 nm

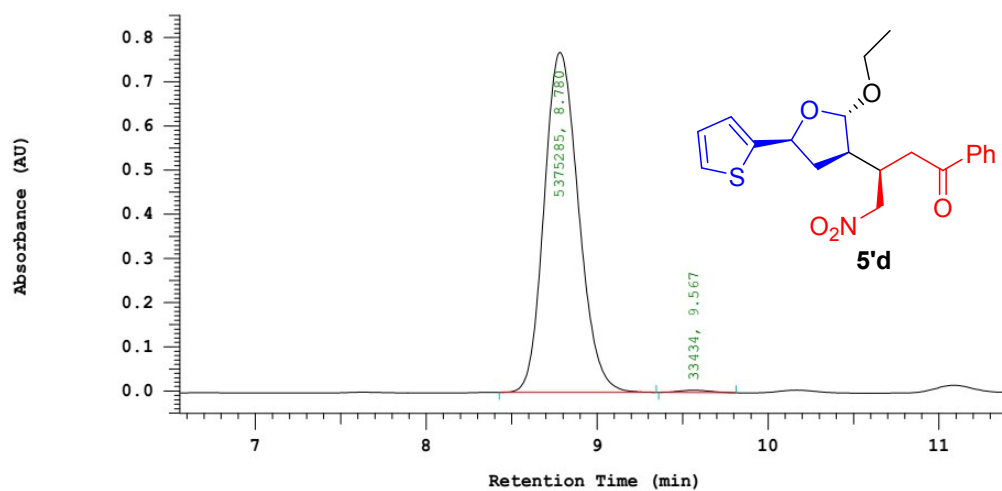


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

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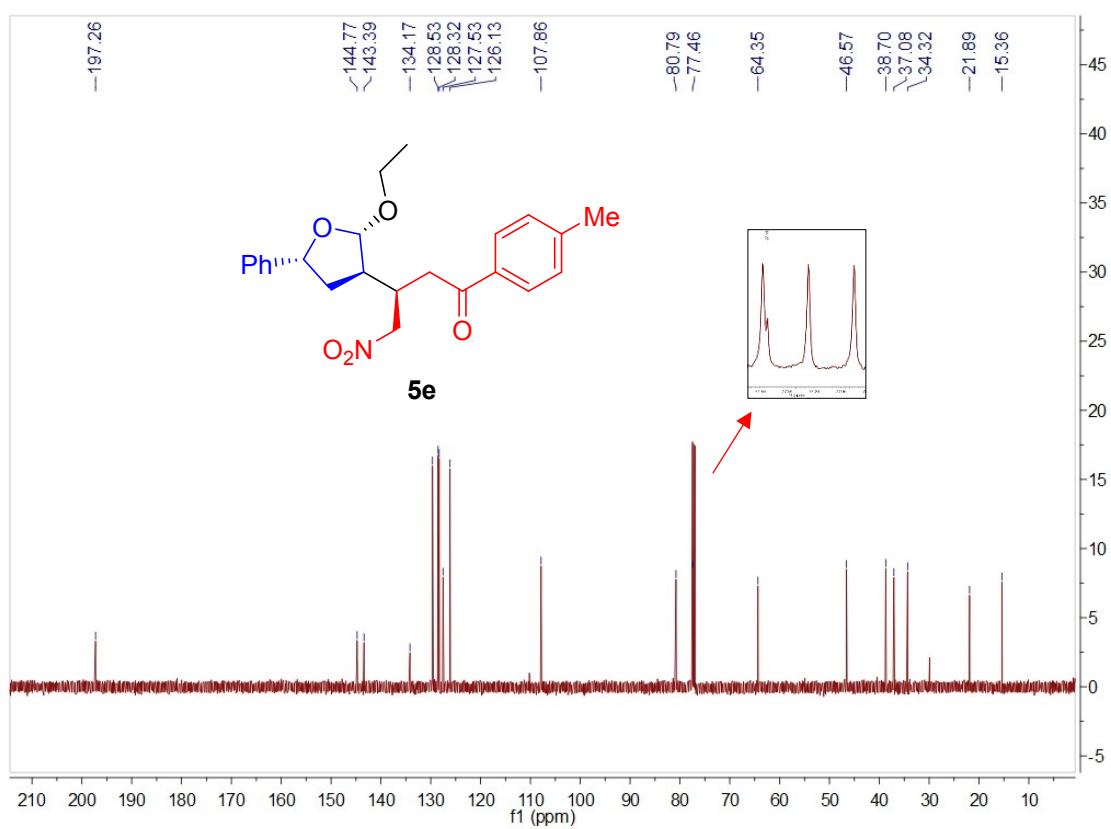
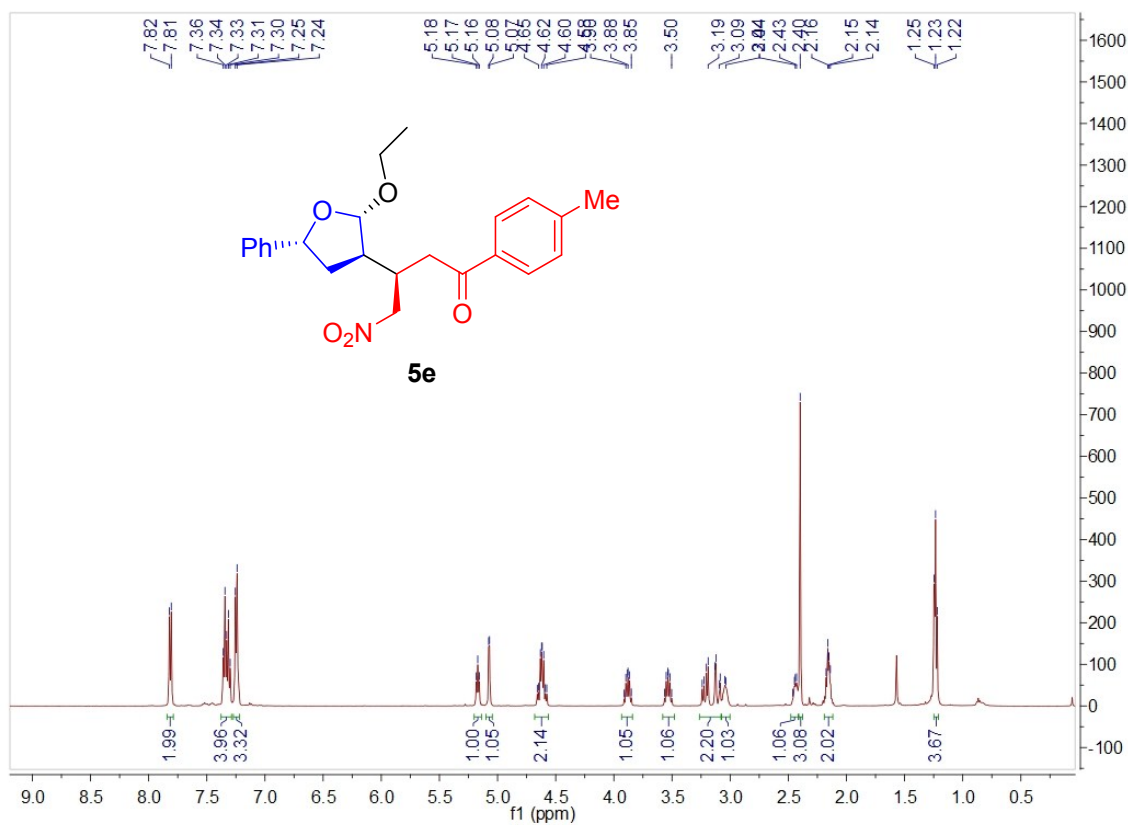
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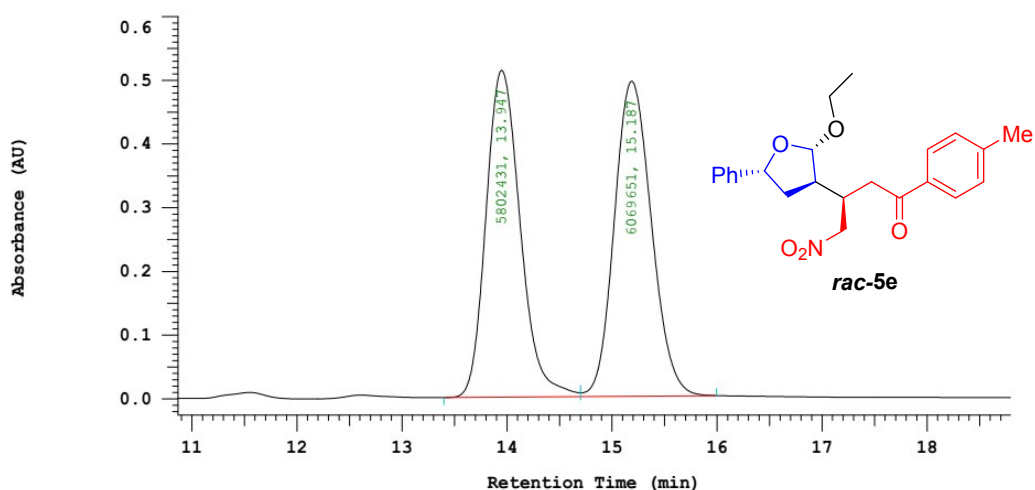
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Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
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2	9.567	33434	0.618	BB
		5408719	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

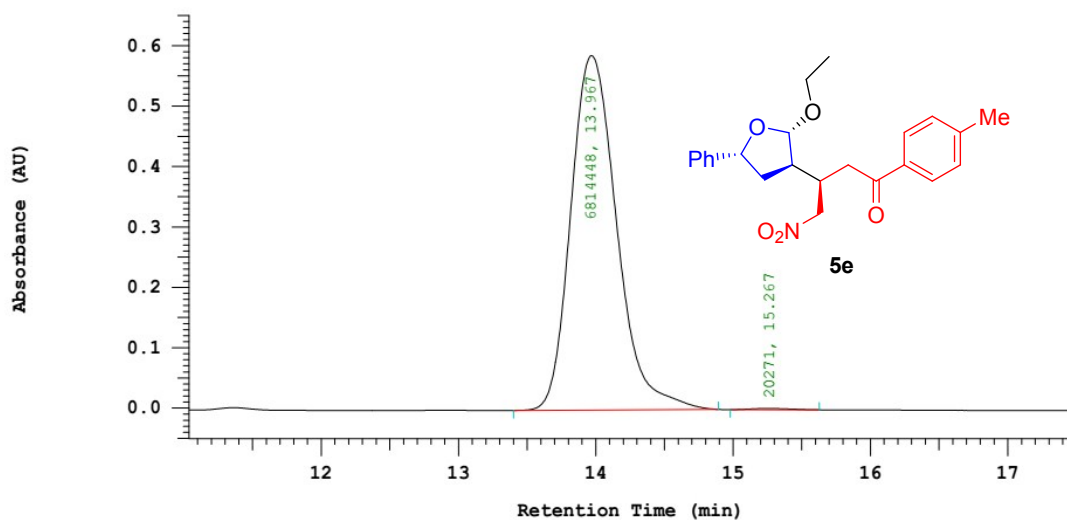


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.947	5802431	48.875	BV
2	15.187	6069651	51.125	VB
		11872082	100.000	

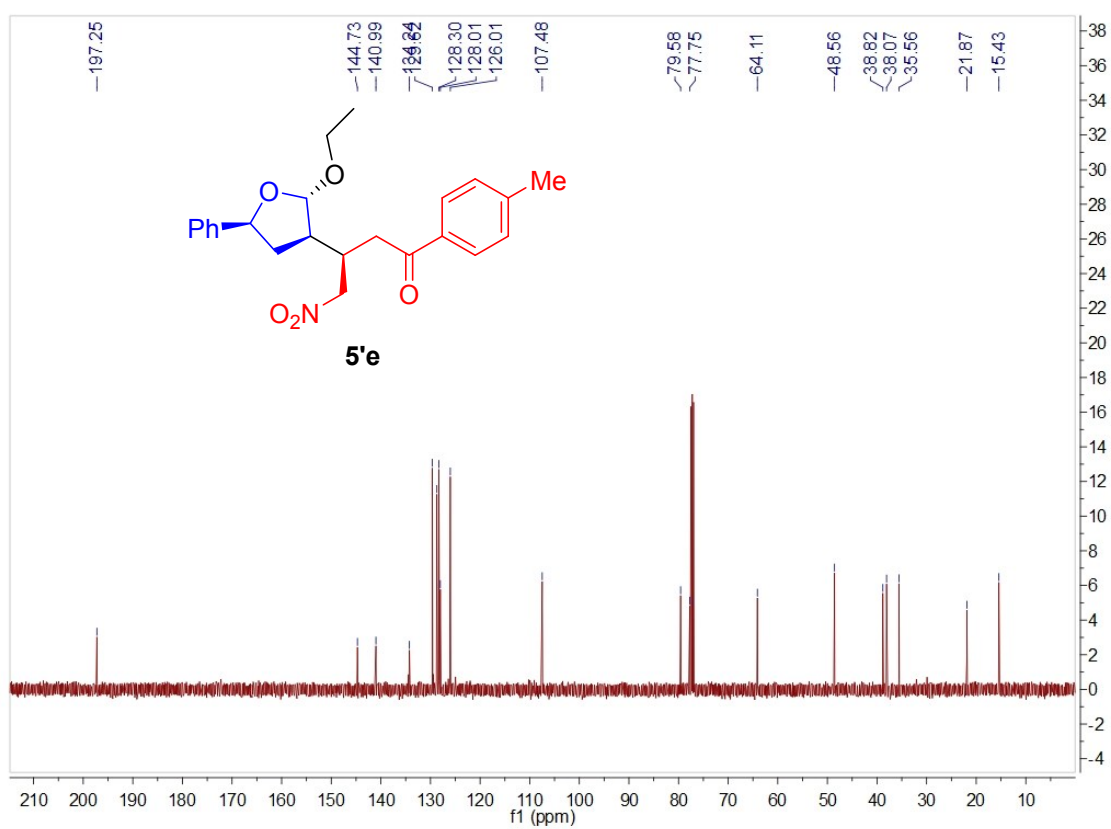
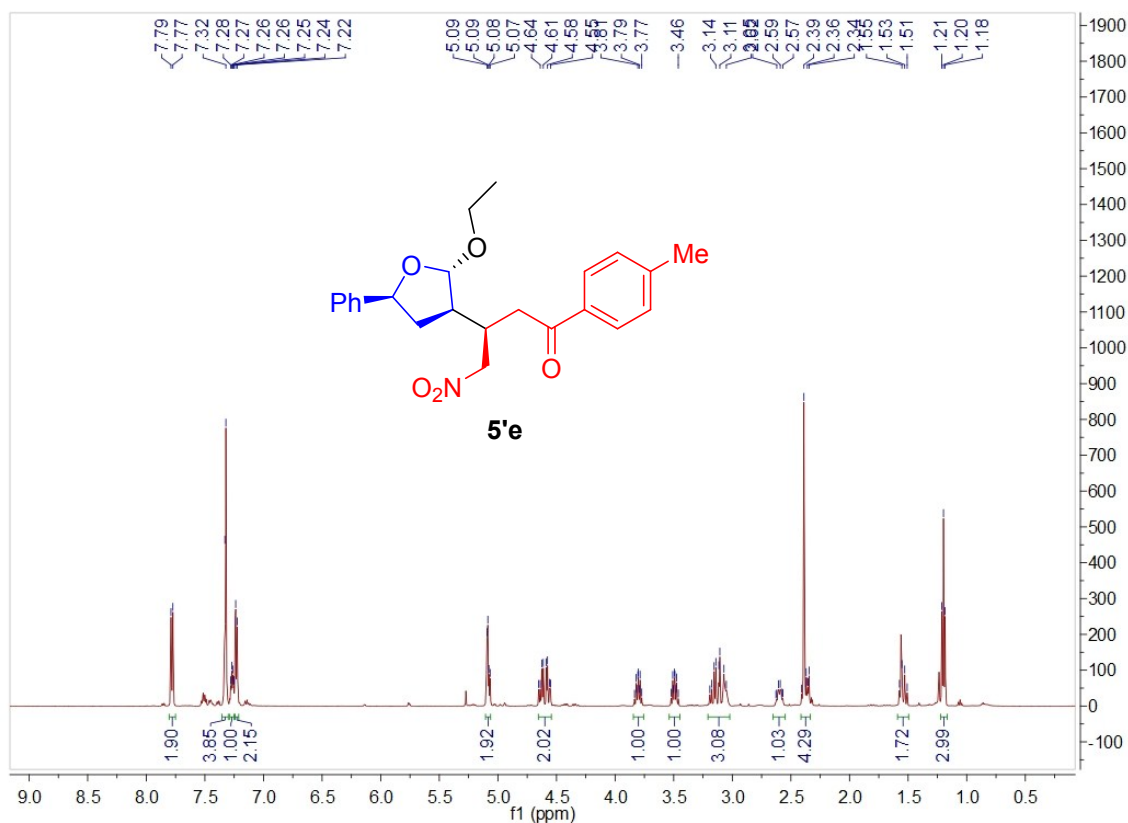
Chrom Type: Fixed WL Chromatogram, 210 nm



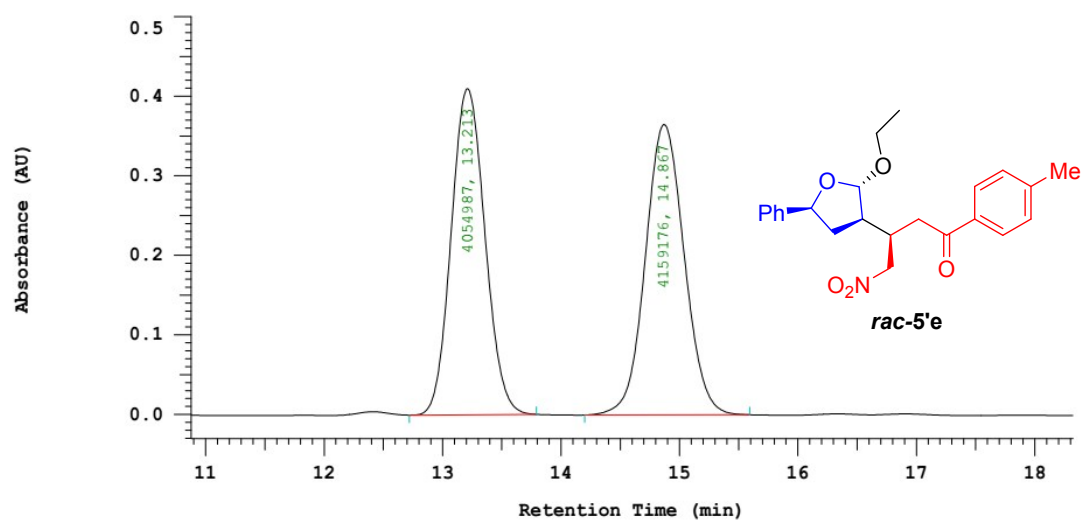
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.967	6814448	99.703	BB
2	15.267	20271	0.297	BB
		6834719	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

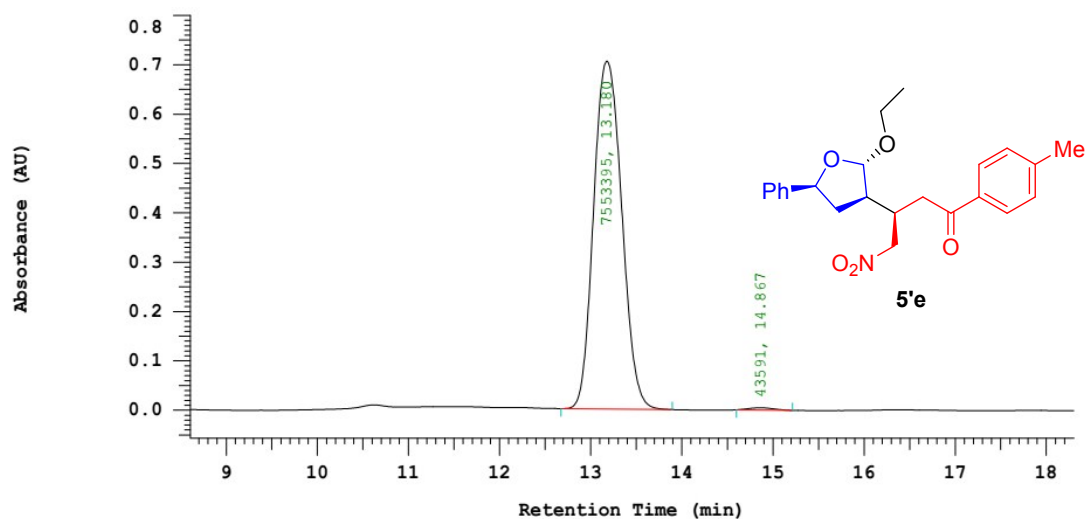


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.213	4054987	49.366	BB
2	14.867	4159176	50.634	BB
		8214163	100.000	

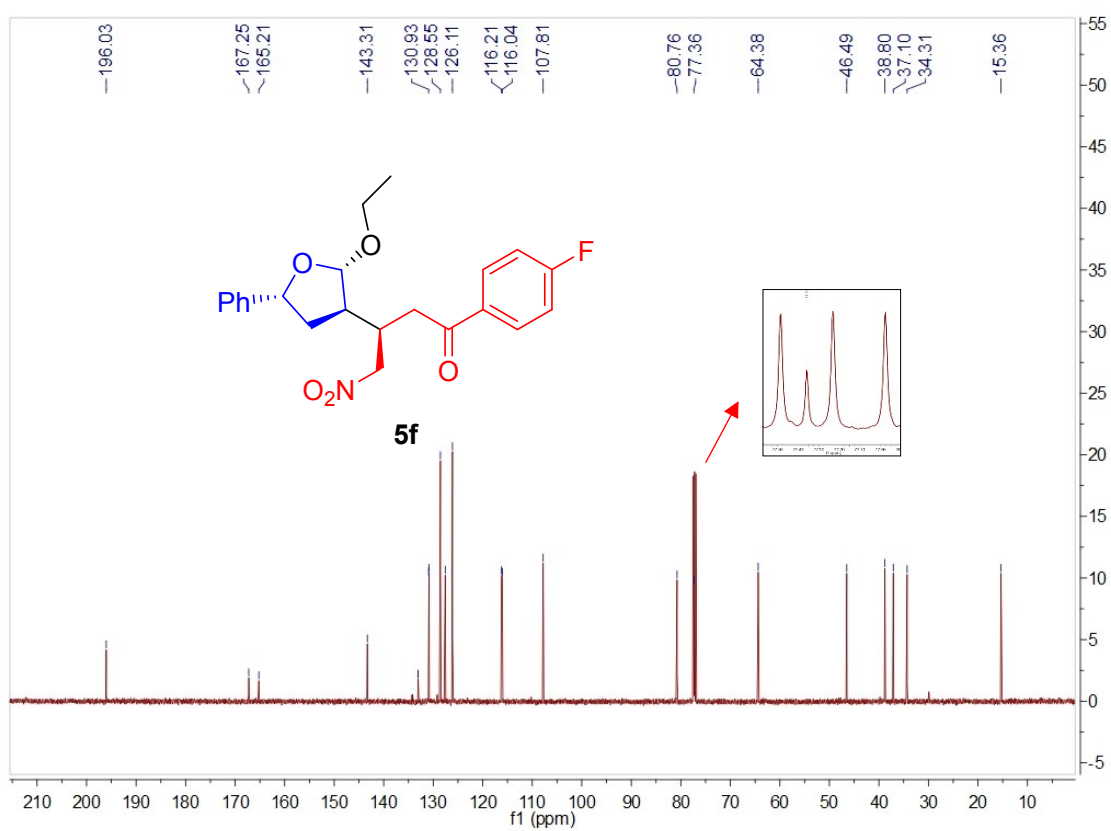
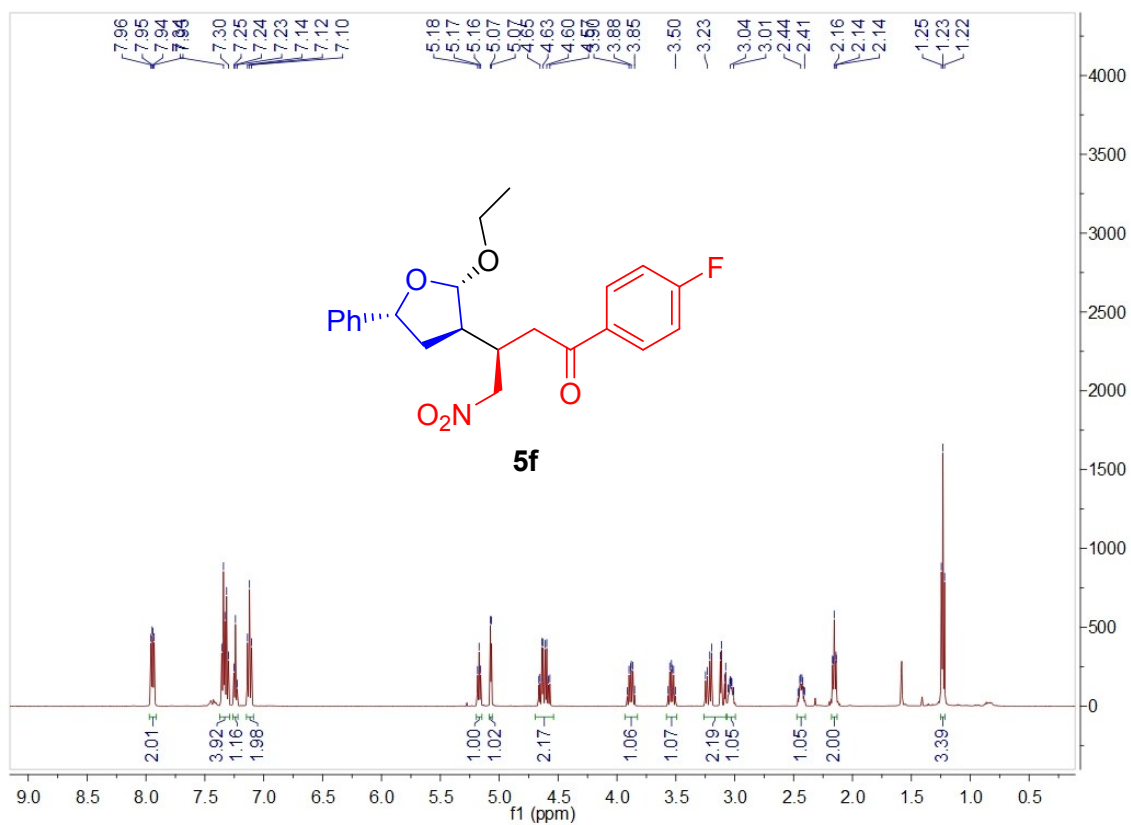
Chrom Type: Fixed WL Chromatogram, 210 nm



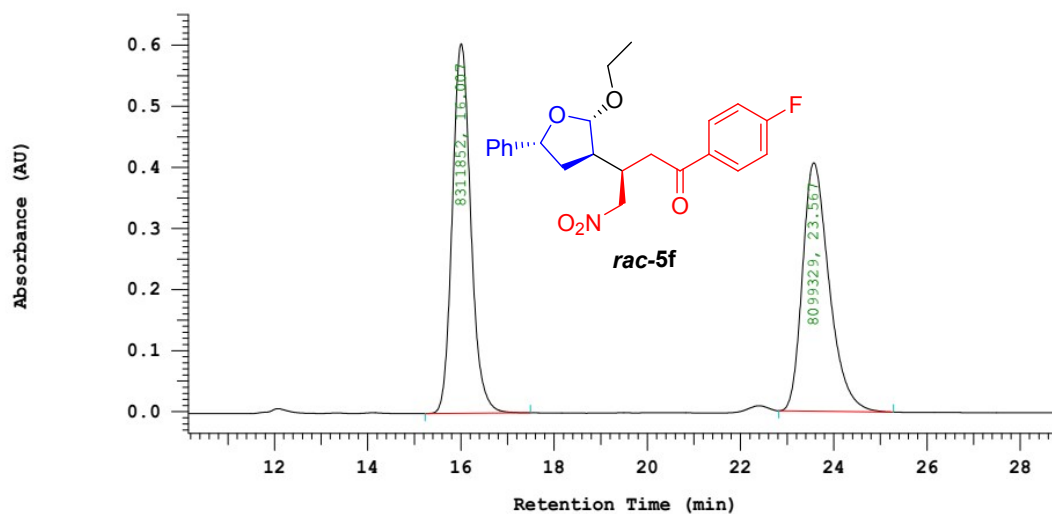
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.180	7553395	99.426	BB
2	14.867	43591	0.574	BB
		7596986	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

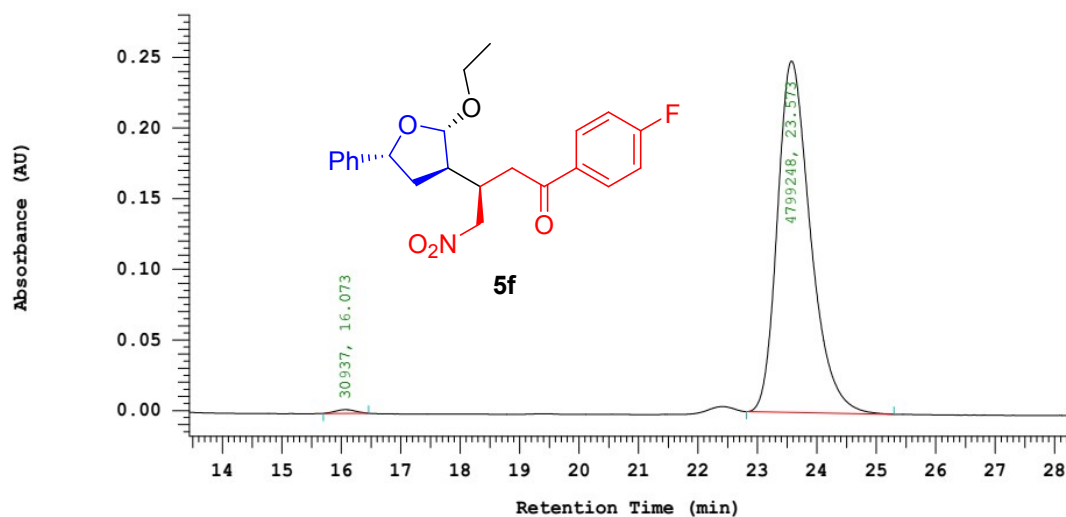


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	16.007	8311852	50.647	BB
2	23.567	8099329	49.353	BB
		16411181	100.000	

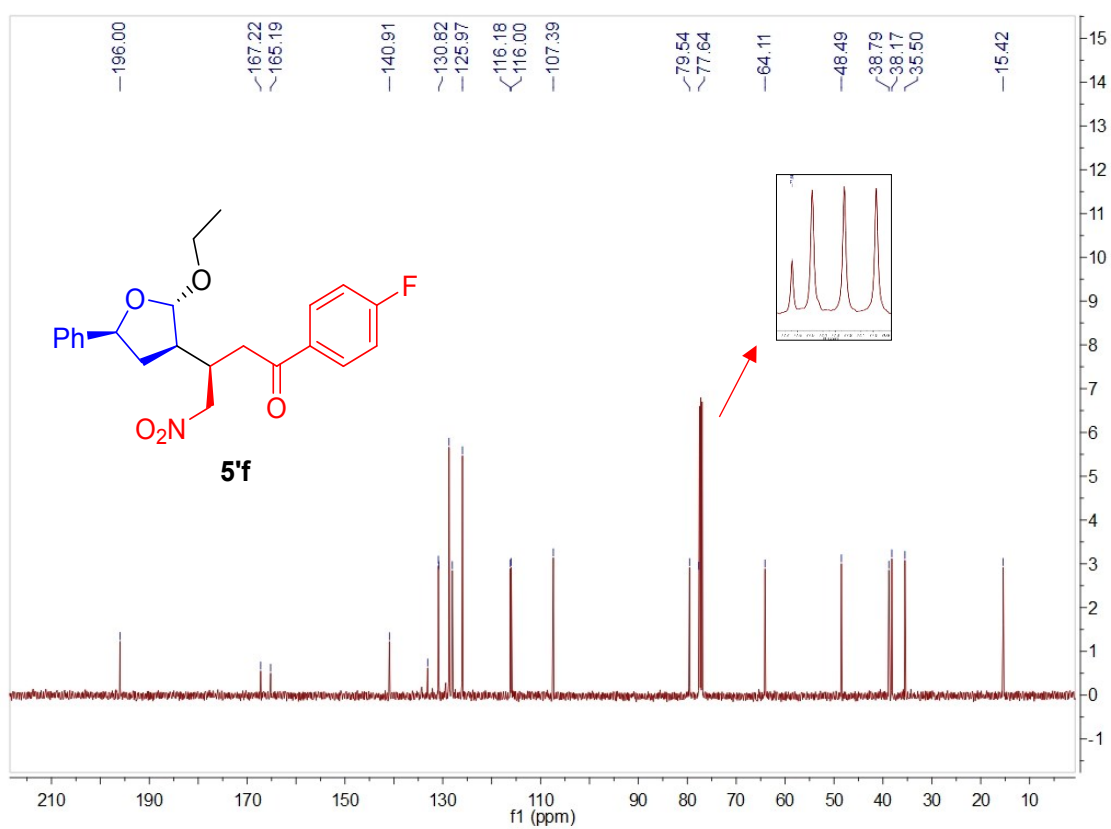
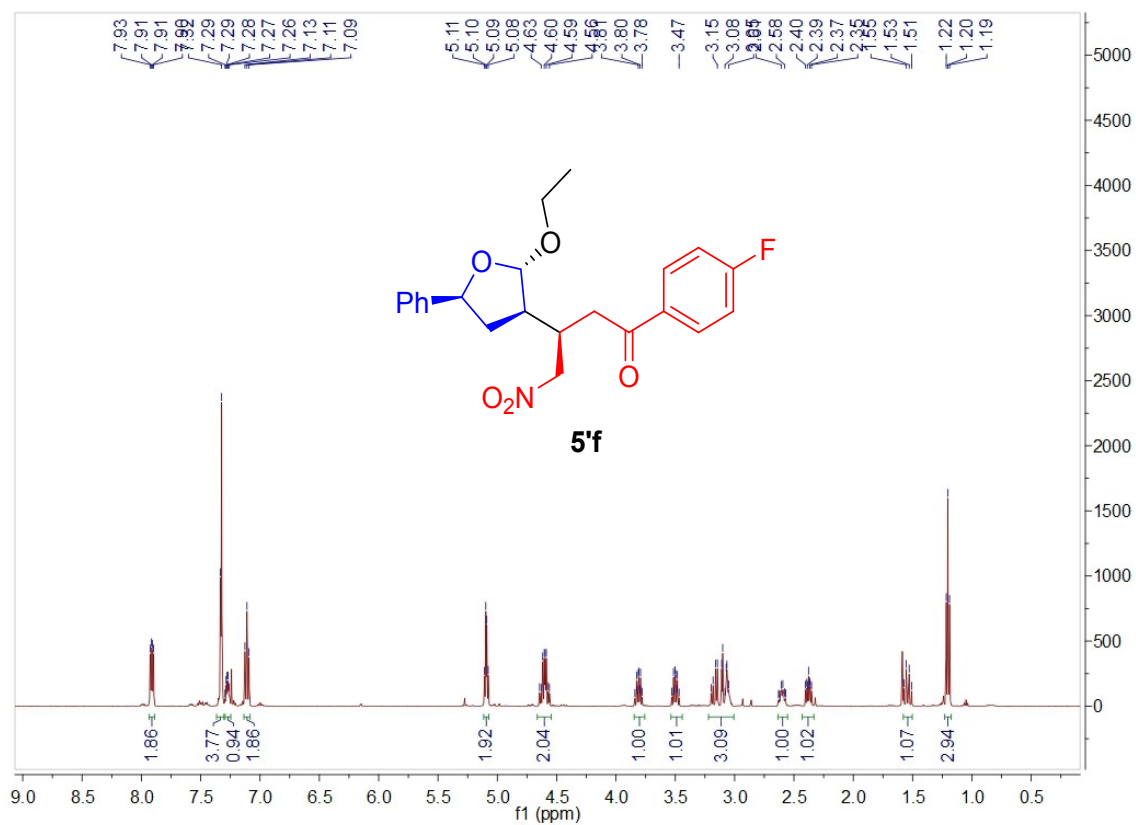
Chrom Type: Fixed WL Chromatogram, 210 nm



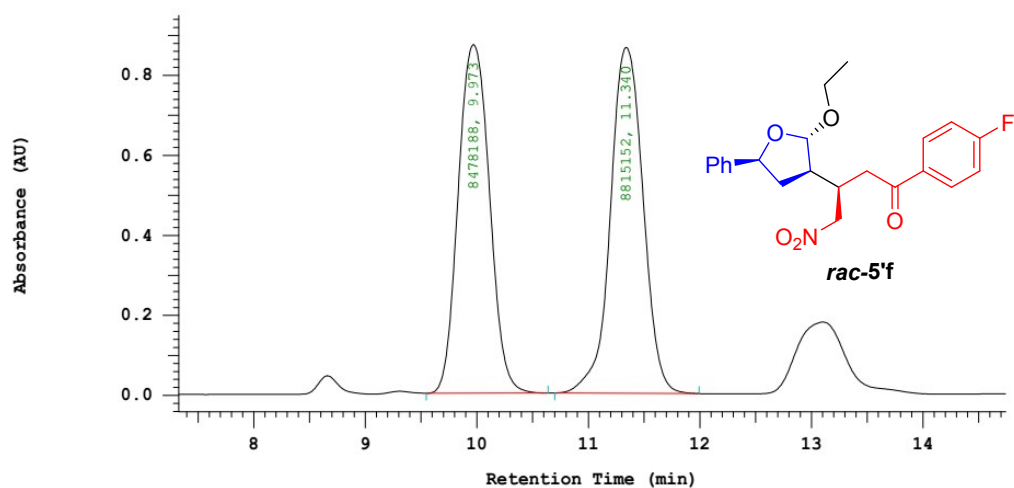
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	16.073	30937	0.641	BB
2	23.573	4799248	99.359	BB
		4830185	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

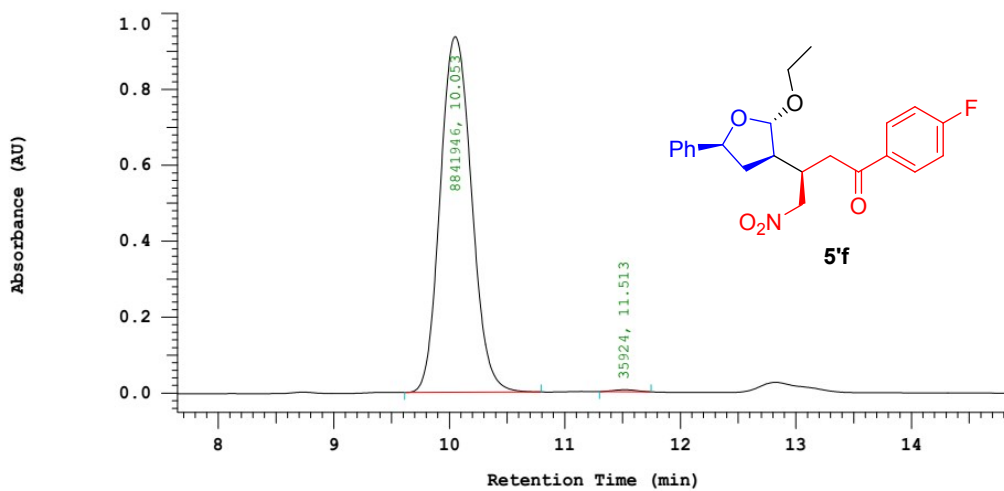


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.973	8478188	49.026	BB
2	11.340	8815152	50.974	BB
		17293340	100.000	

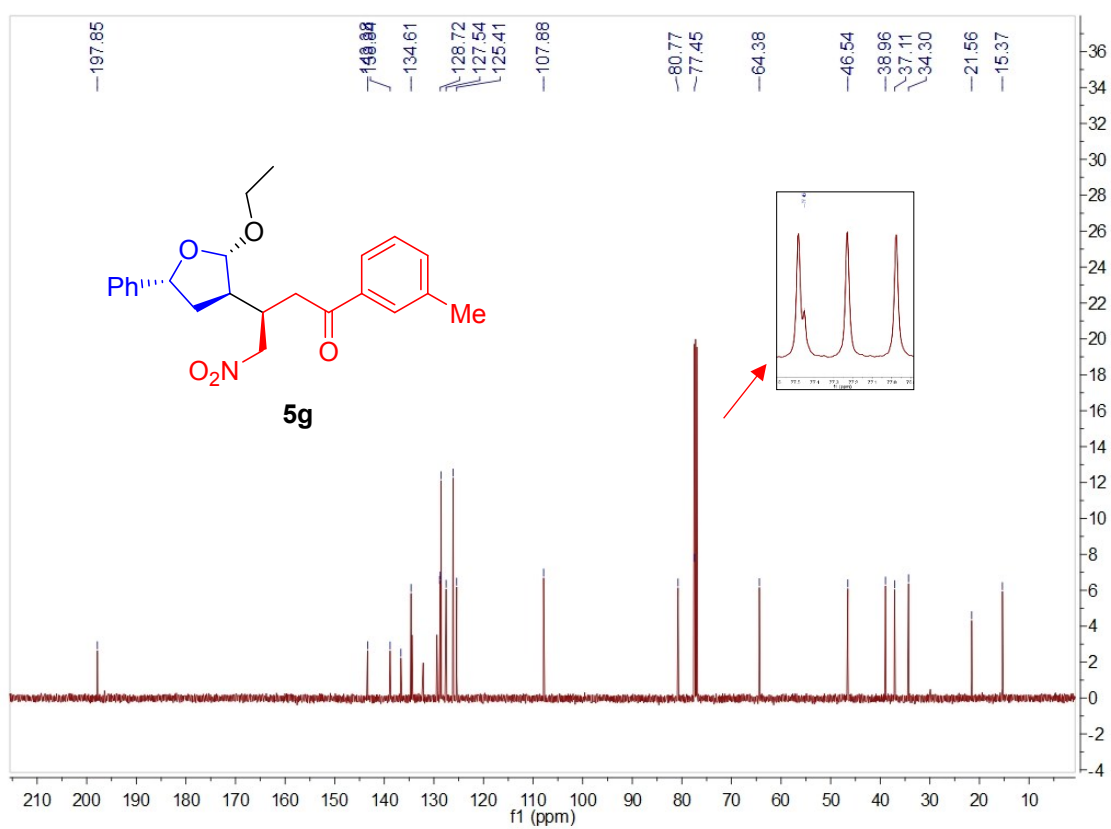
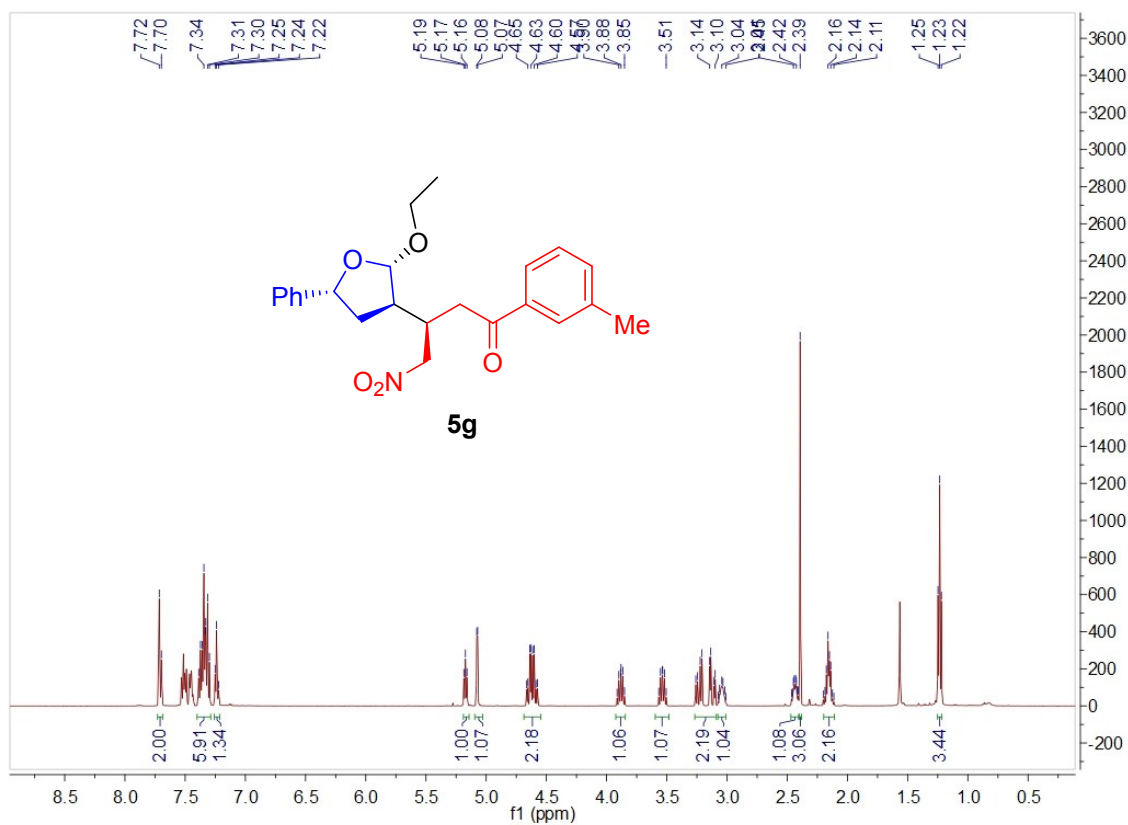
Chrom Type: Fixed WL Chromatogram, 210 nm



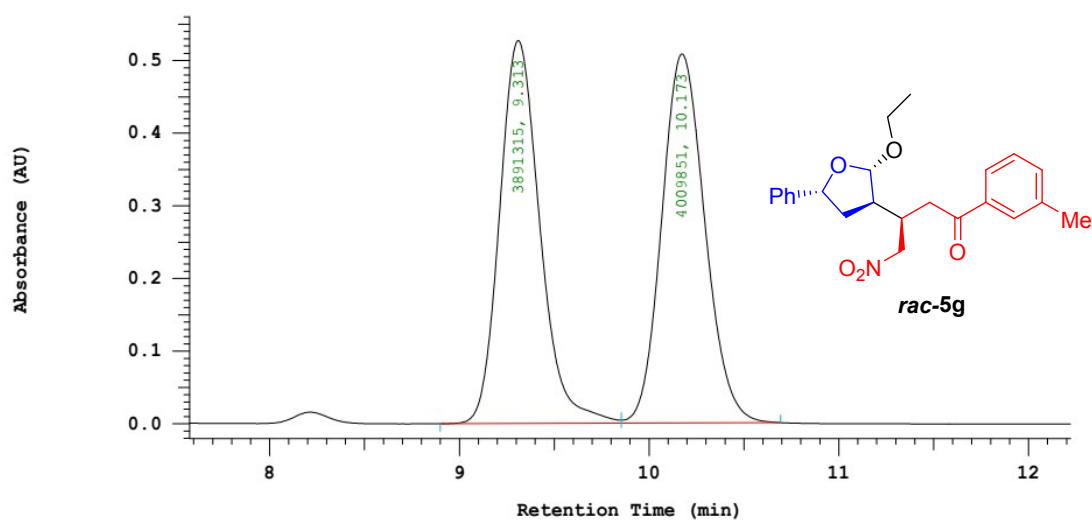
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.053	8841946	99.595	BB
2	11.513	35924	0.405	BB
		8877870	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

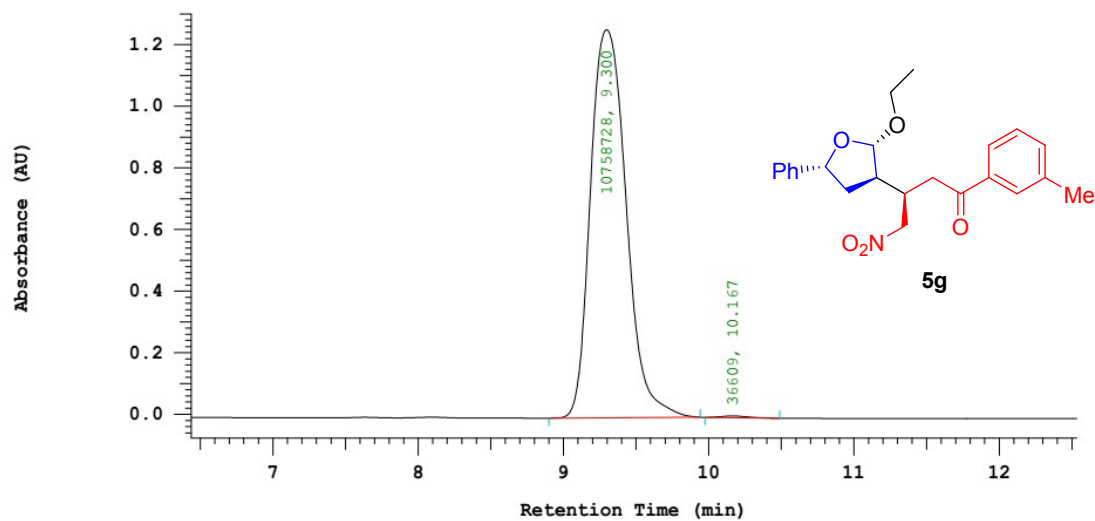


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.313	3891315	49.250	BV
2	10.173	4009851	50.750	VB
		7901166	100.000	

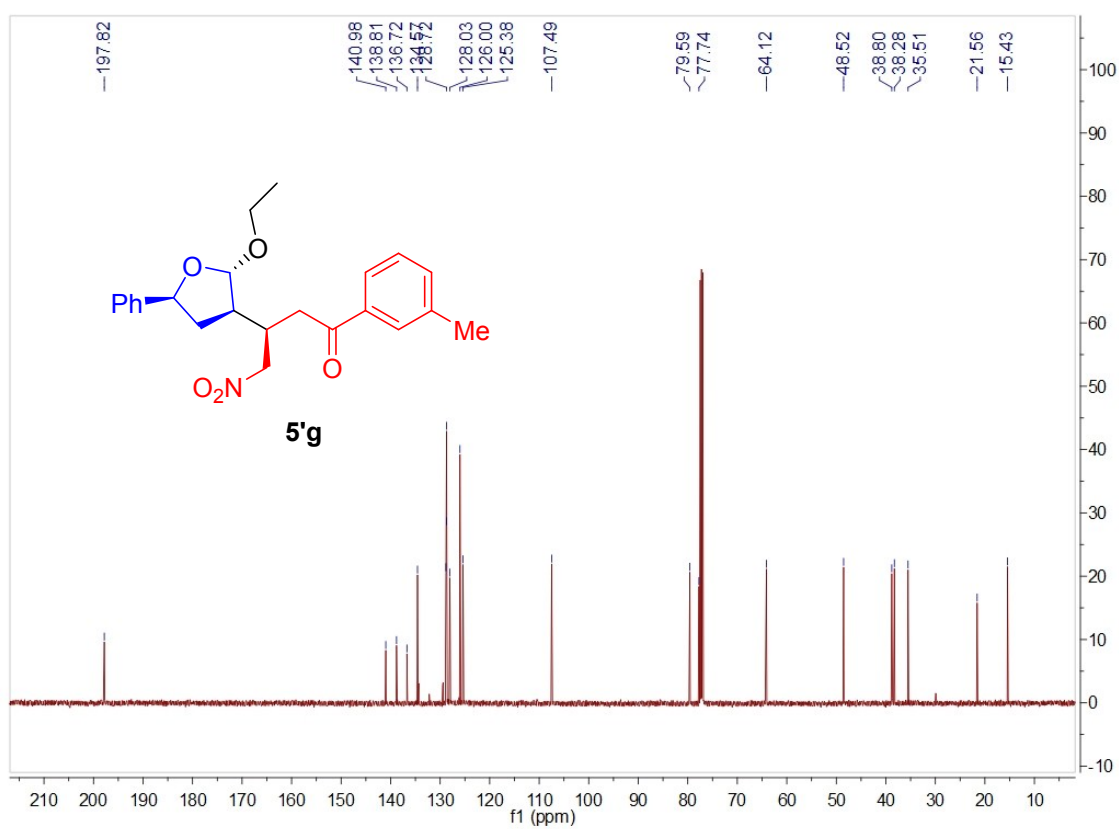
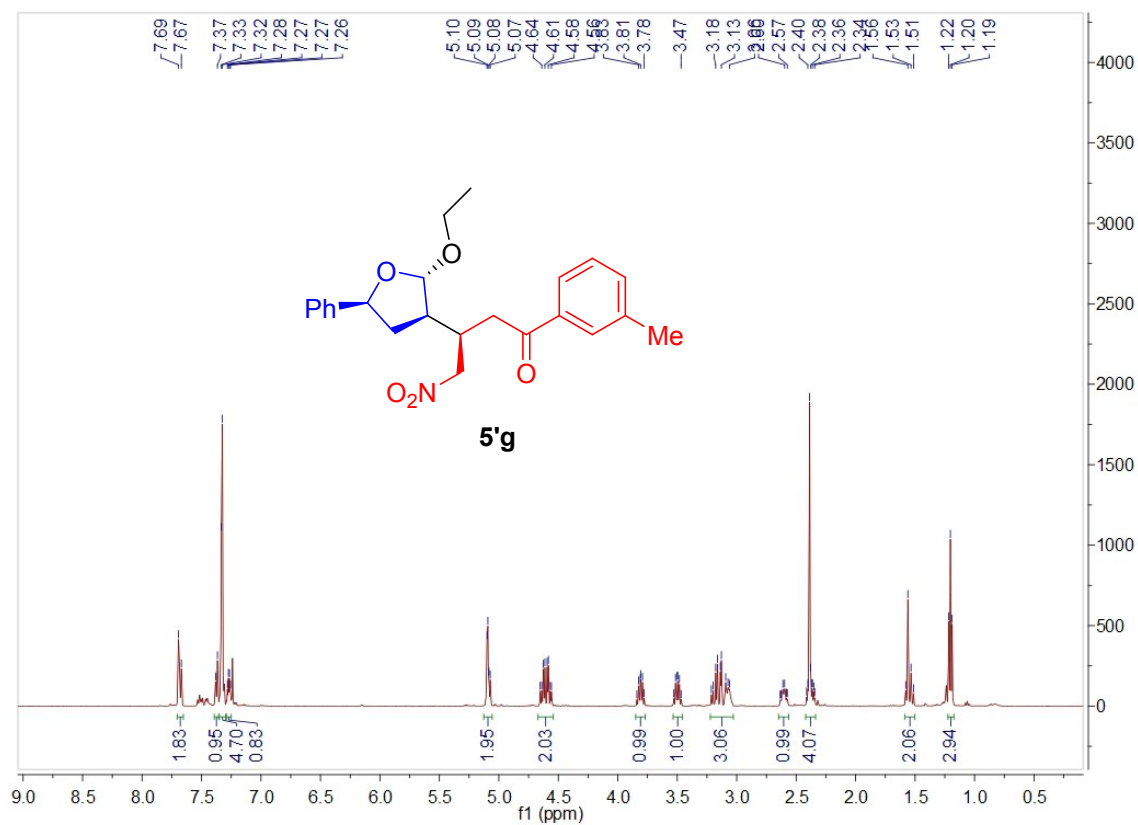
Chrom Type: Fixed WL Chromatogram, 210 nm



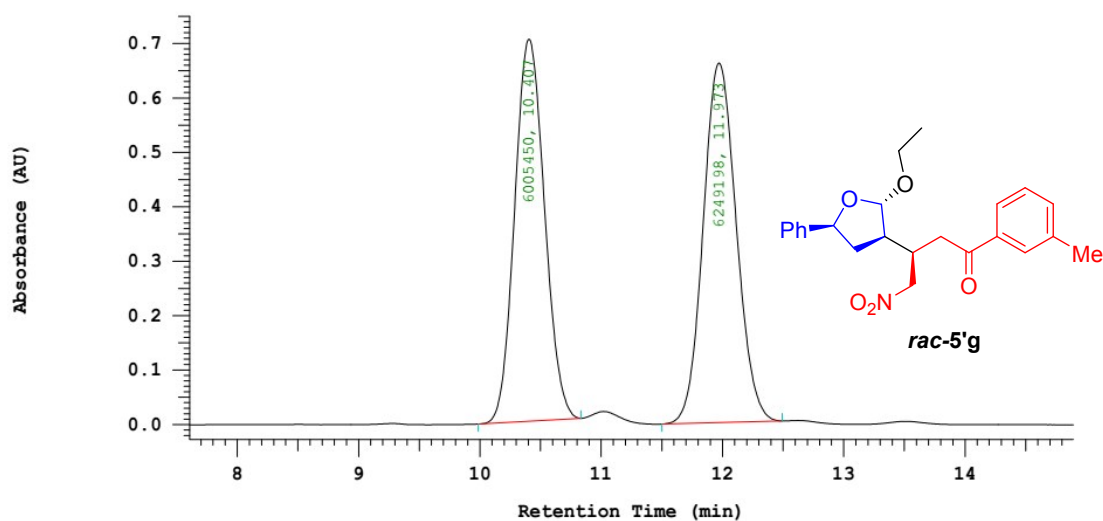
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.300	10758728	99.661	BB
2	10.167	36609	0.339	BB
		10795337	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

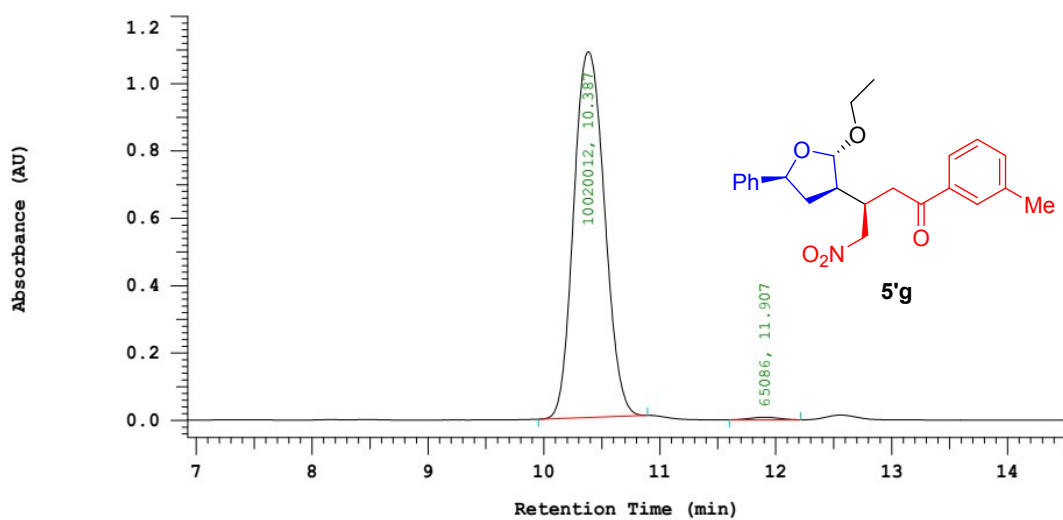


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.407	6005450	49.005	BB
2	11.973	6249198	50.995	BB
12254648			100.000	

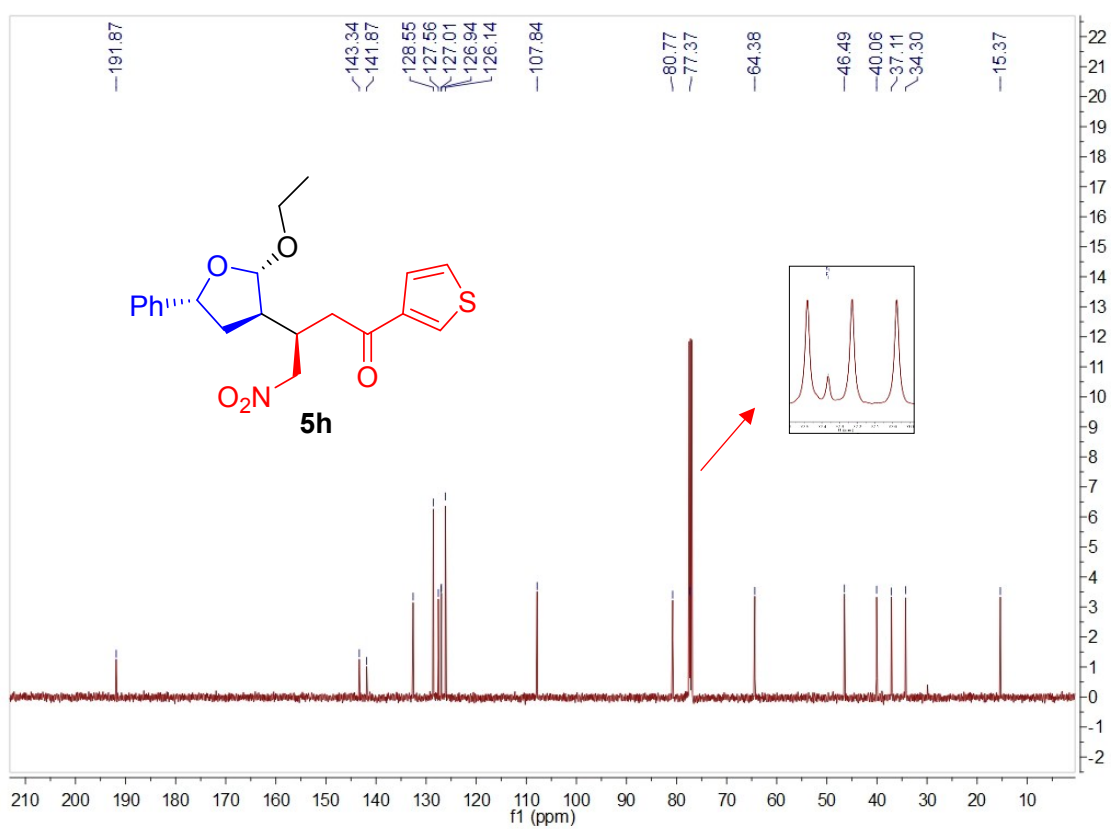
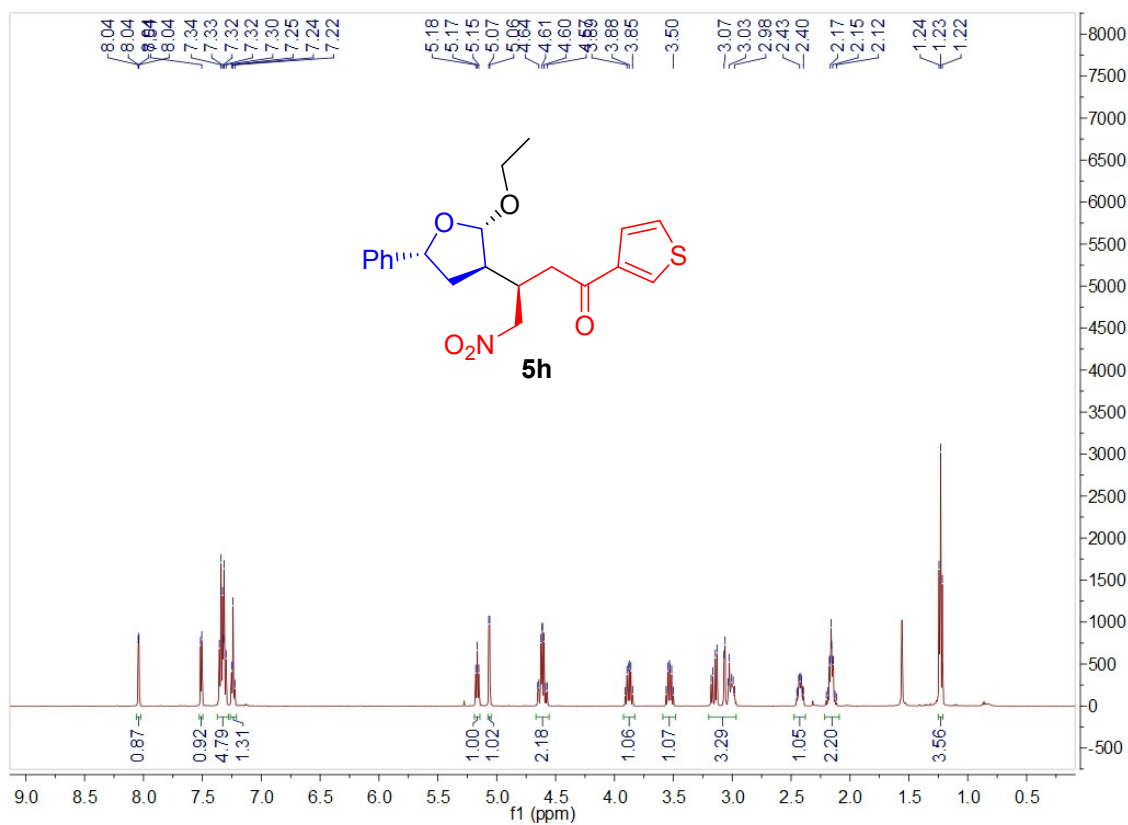
Chrom Type: Fixed WL Chromatogram, 210 nm



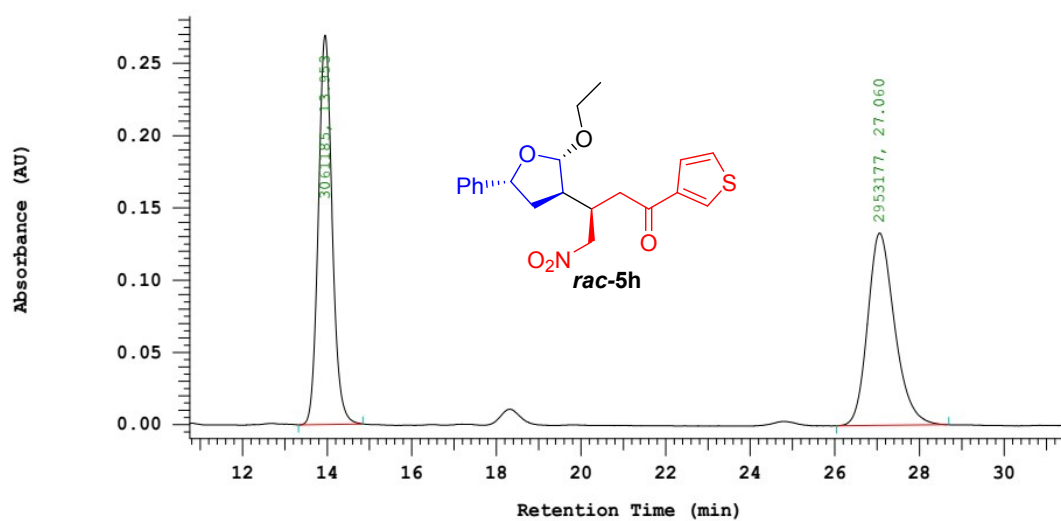
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.387	10020012	99.355	BB
2	11.907	65086	0.645	BB
10085098			100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

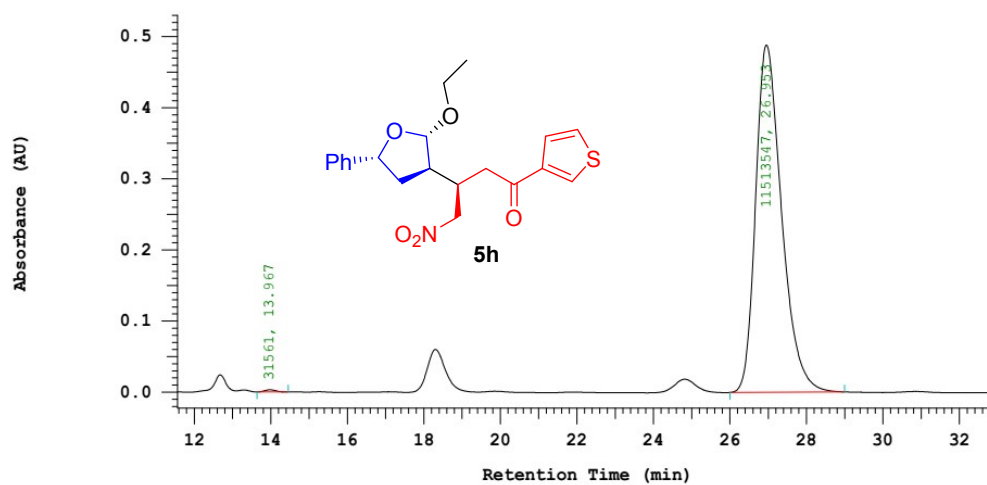


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.953	3061185	50.898	BB
2	27.060	2953177	49.102	BB
		6014362	100.000	

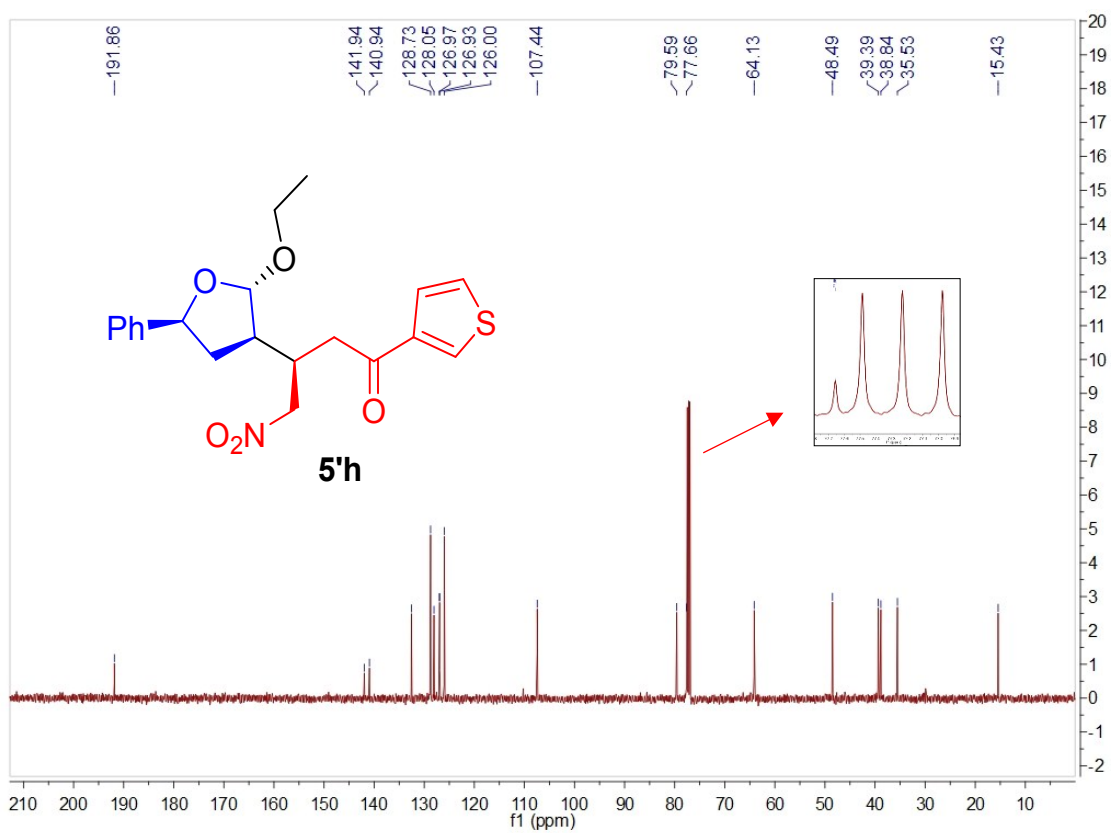
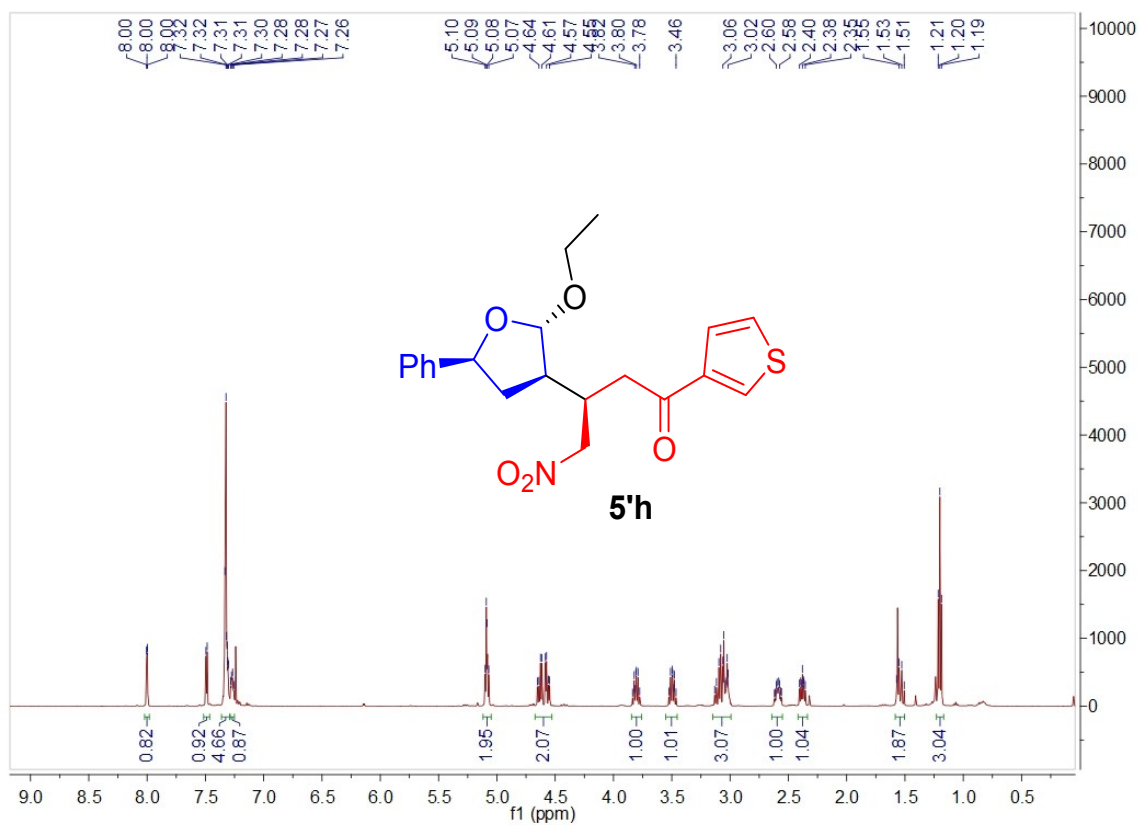
Chrom Type: Fixed WL Chromatogram, 210 nm



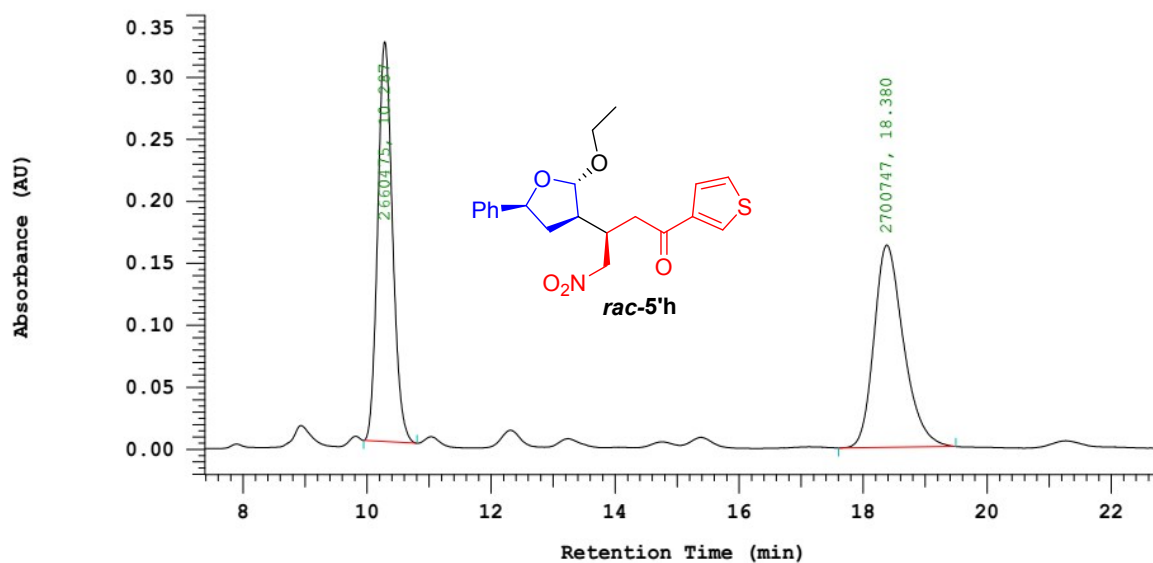
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.967	31561	0.273	BB
2	26.953	11513547	99.727	BB
		11545108	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm



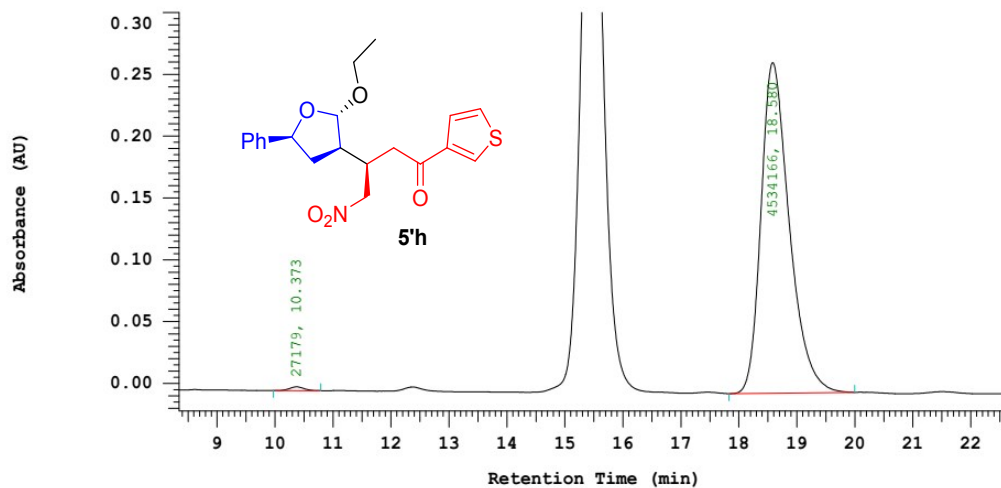
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.287	2660475	49.624	BB
2	18.380	2700747	50.376	BB
		5361222	100.000	

Chrom Type: Fixed WL Chromatogram, 210 nm

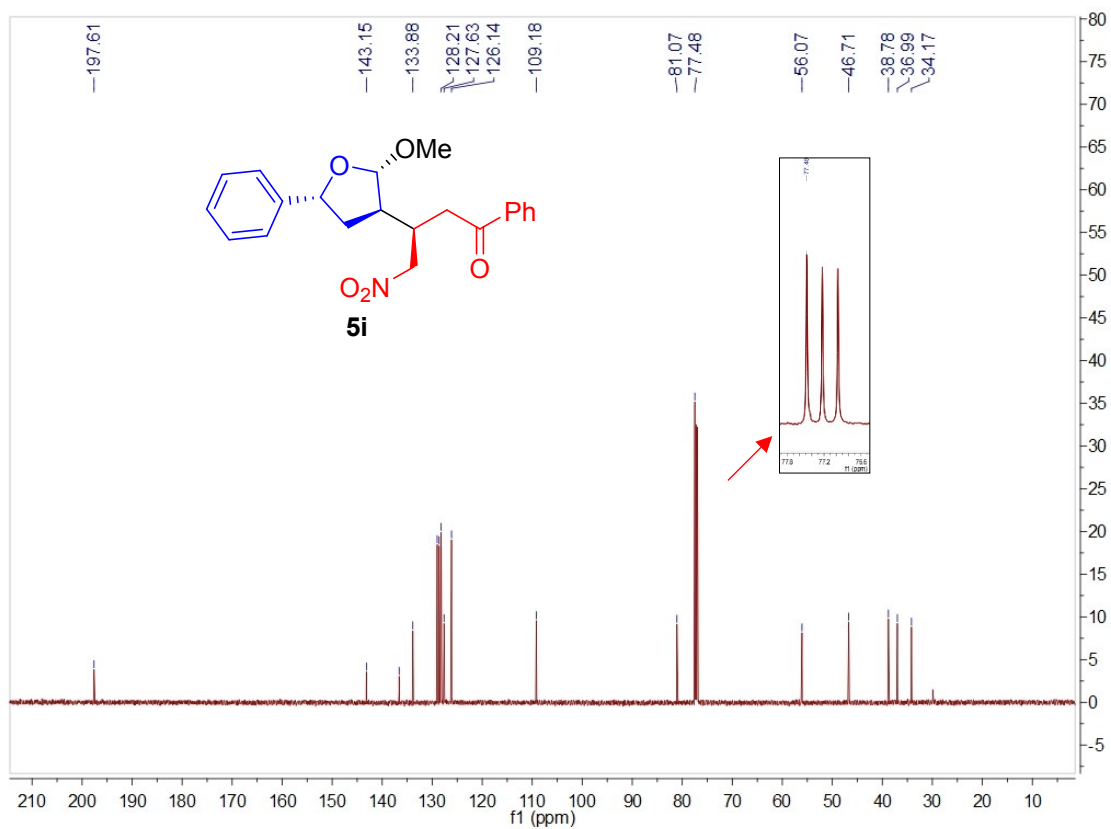
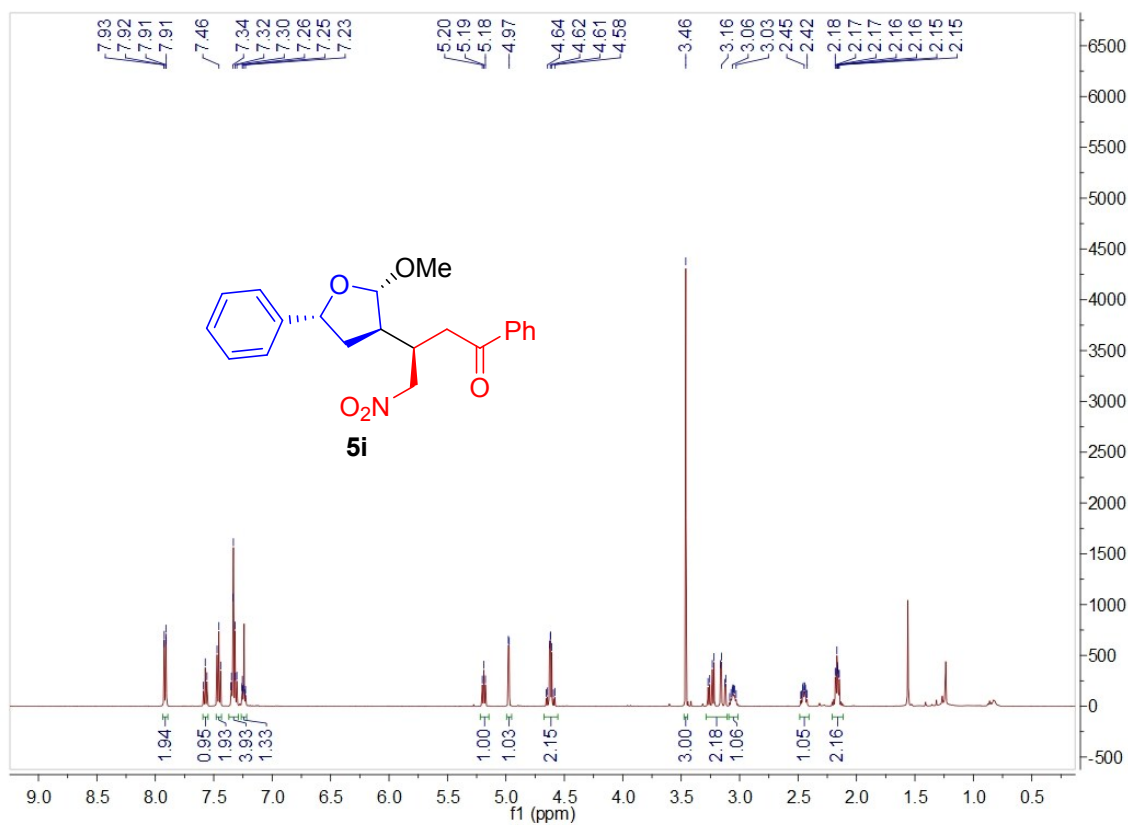


Chrom Type: Fixed WL Chromatogram, 210 nm

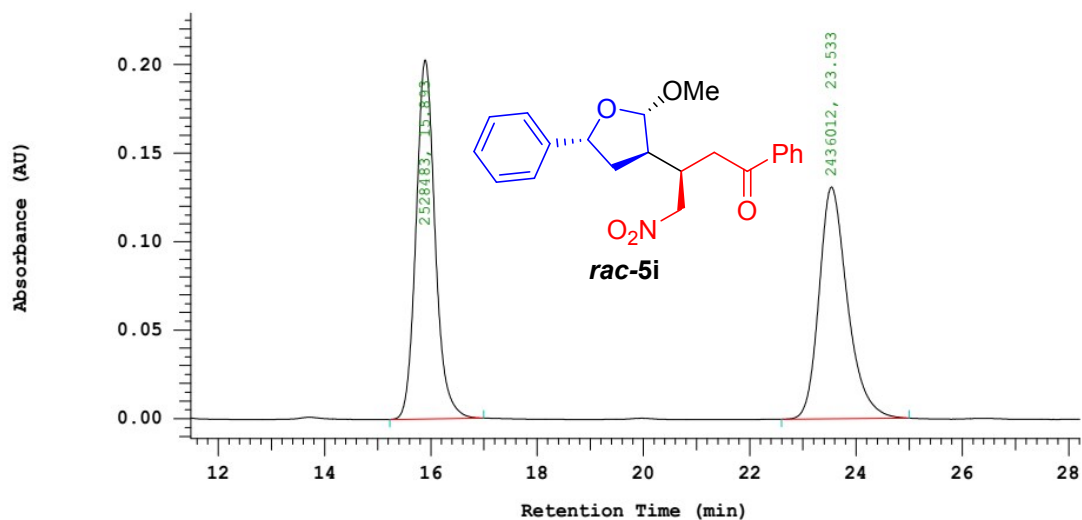
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.373	27179	0.596	BB
2	18.580	4534166	99.404	BB
		4561345	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

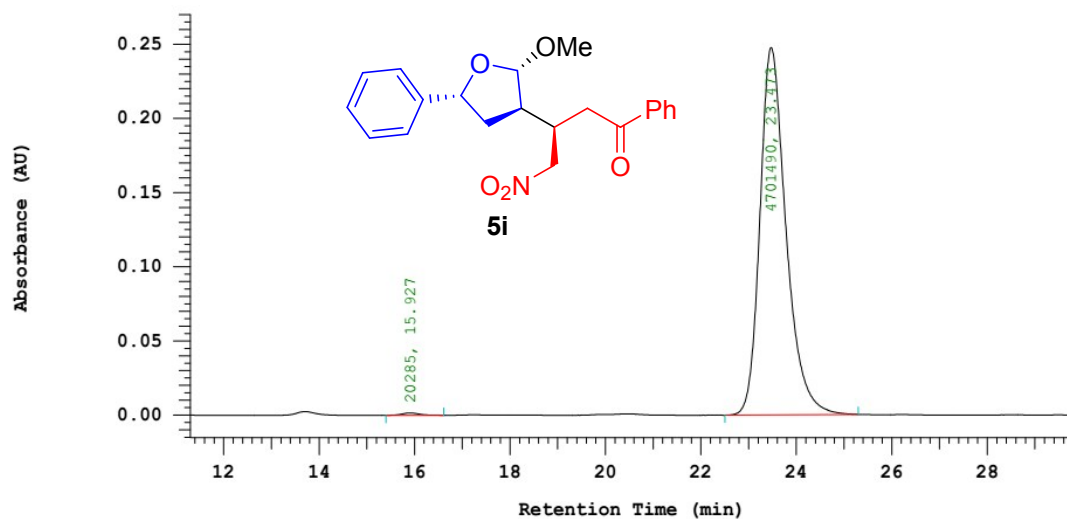


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.893	2528483	50.931	BB
2	23.533	2436012	49.069	BB
		4964495	100.000	

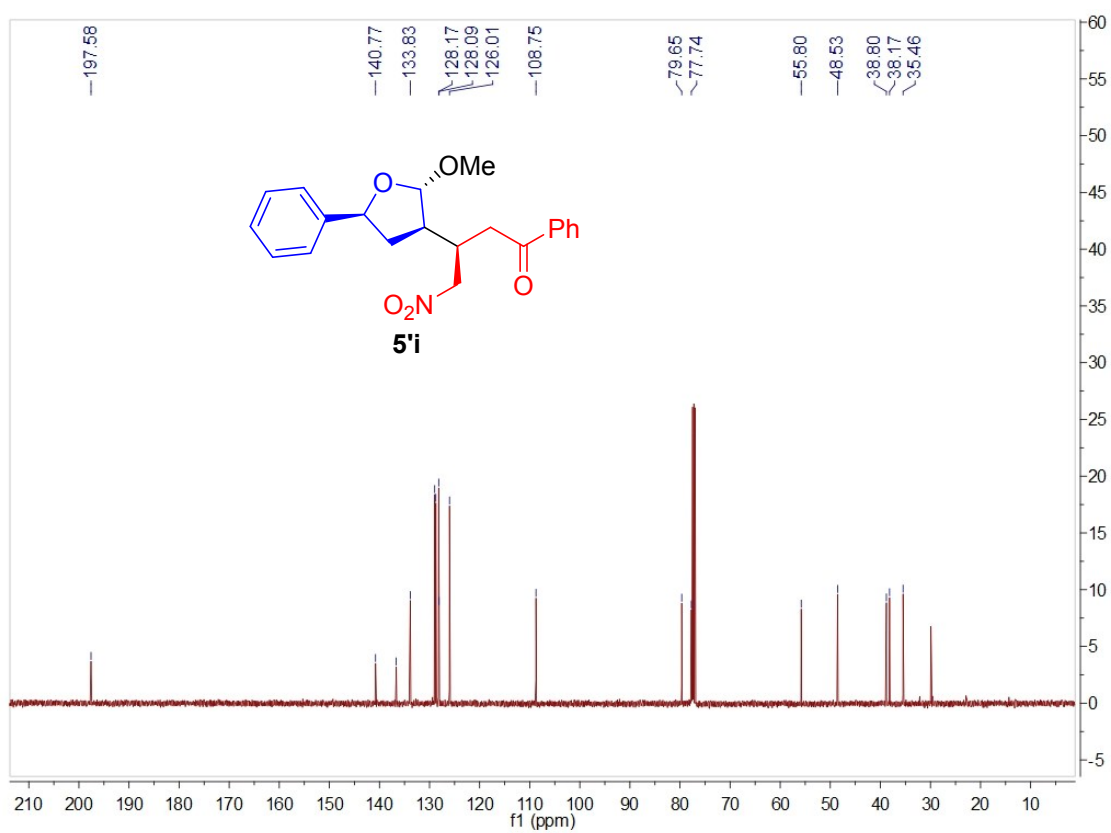
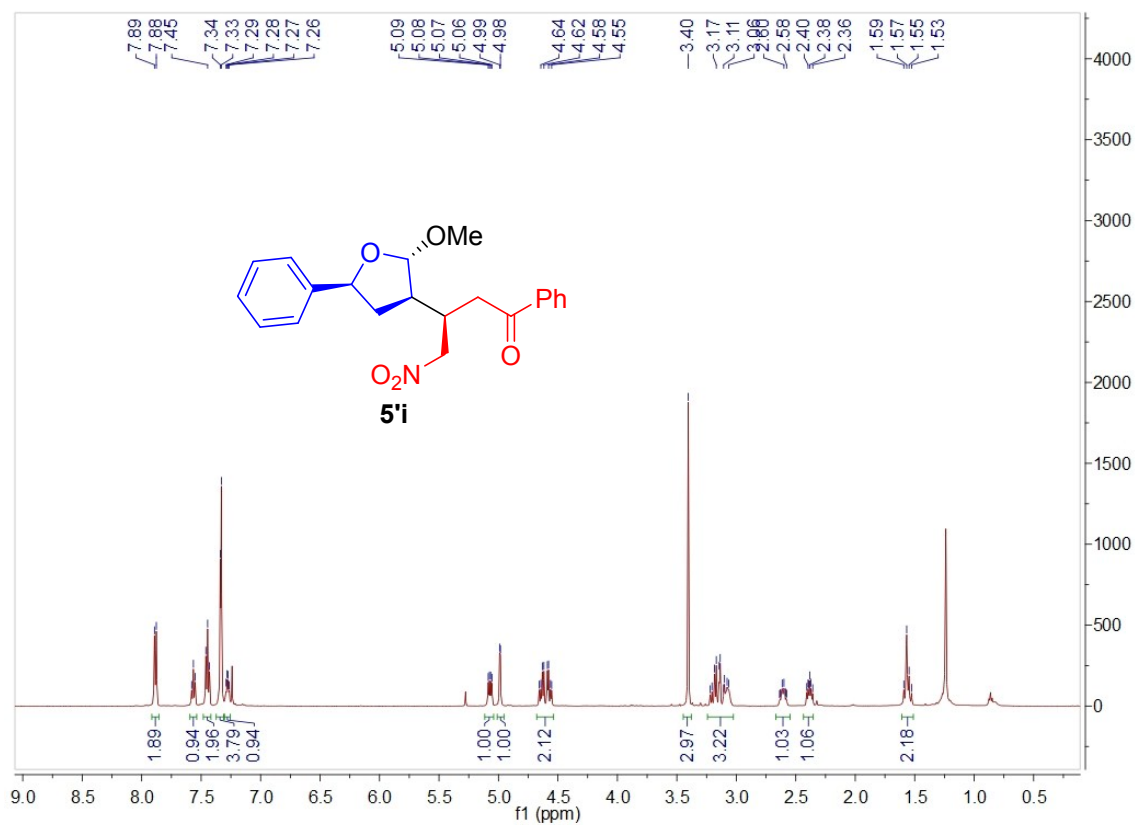
Chrom Type: Fixed WL Chromatogram, 210 nm



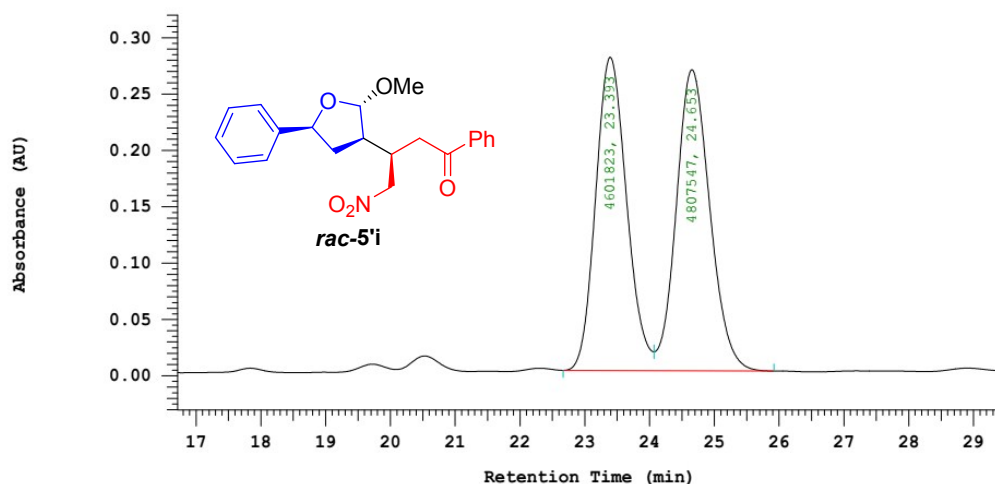
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.927	20285	0.430	BB
2	23.473	4701490	99.570	BB
		4721775	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

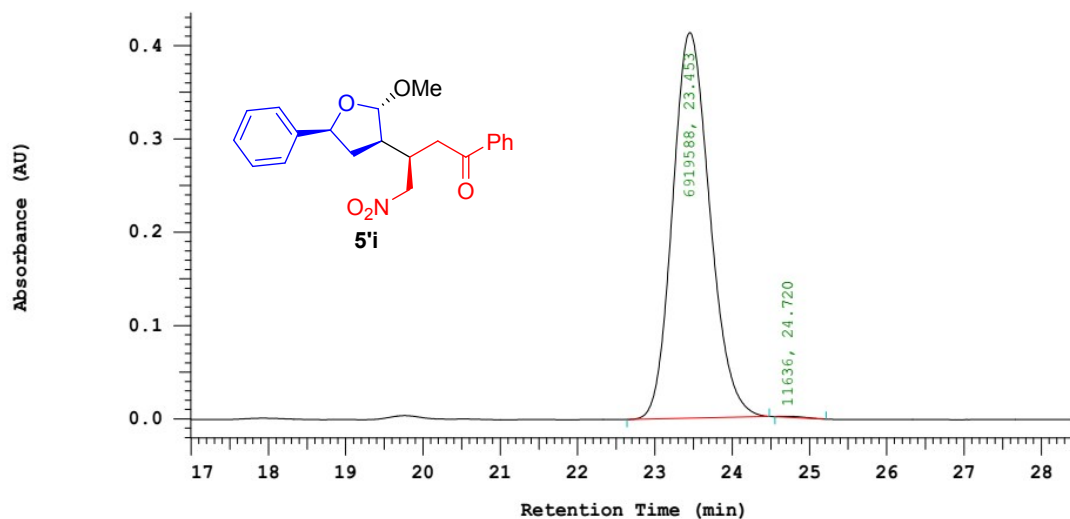


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	23.393	4601823	48.907	BV
2	24.653	4807547	51.093	VB
		9409370	100.000	

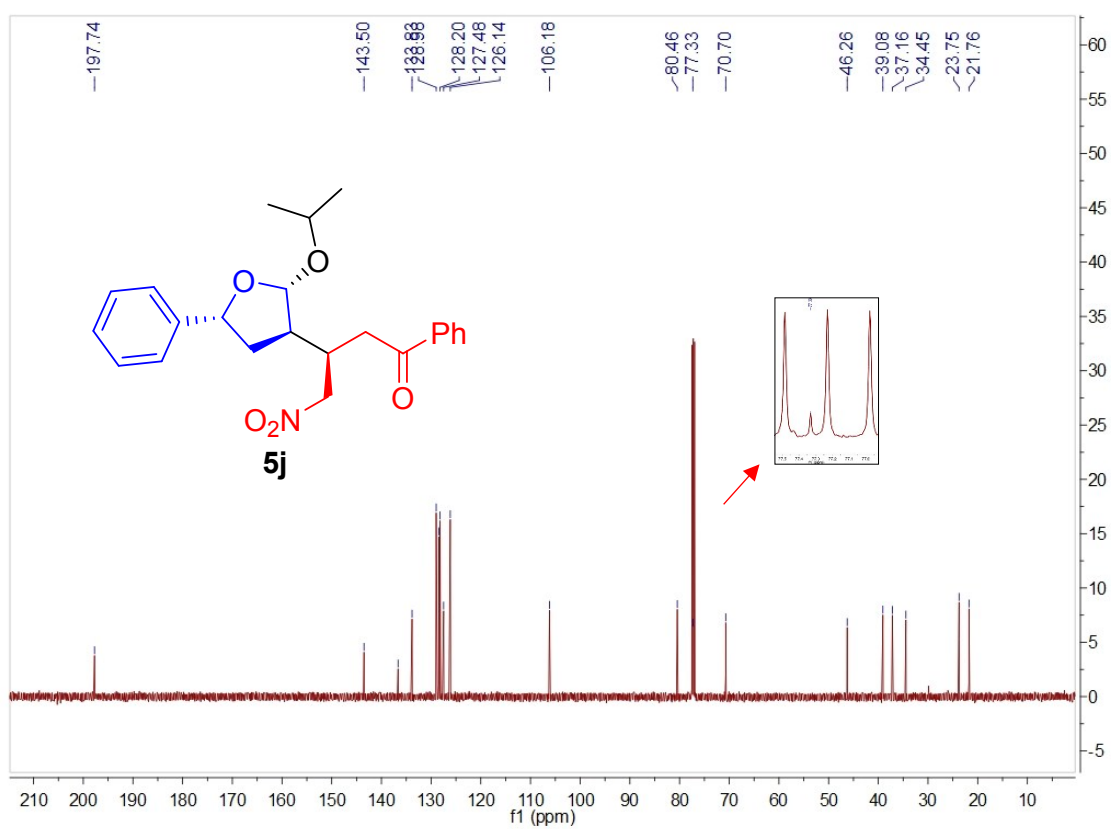
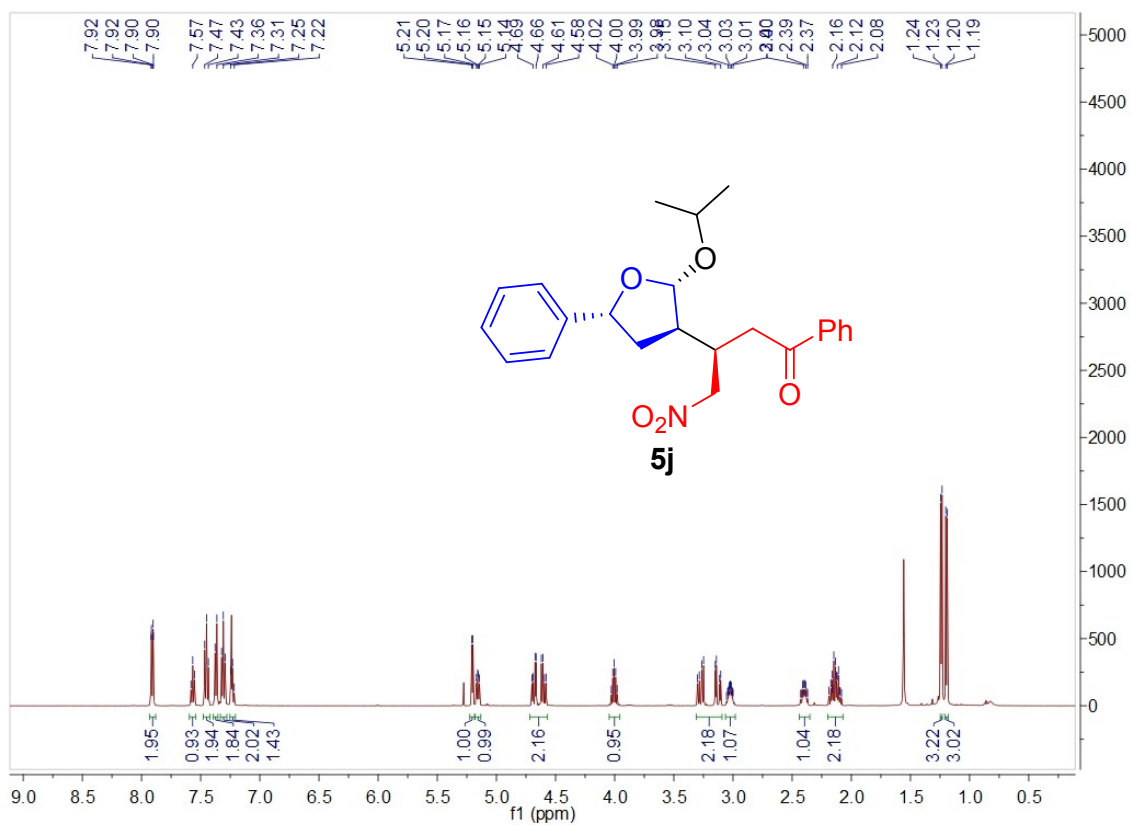
Chrom Type: Fixed WL Chromatogram, 210 nm



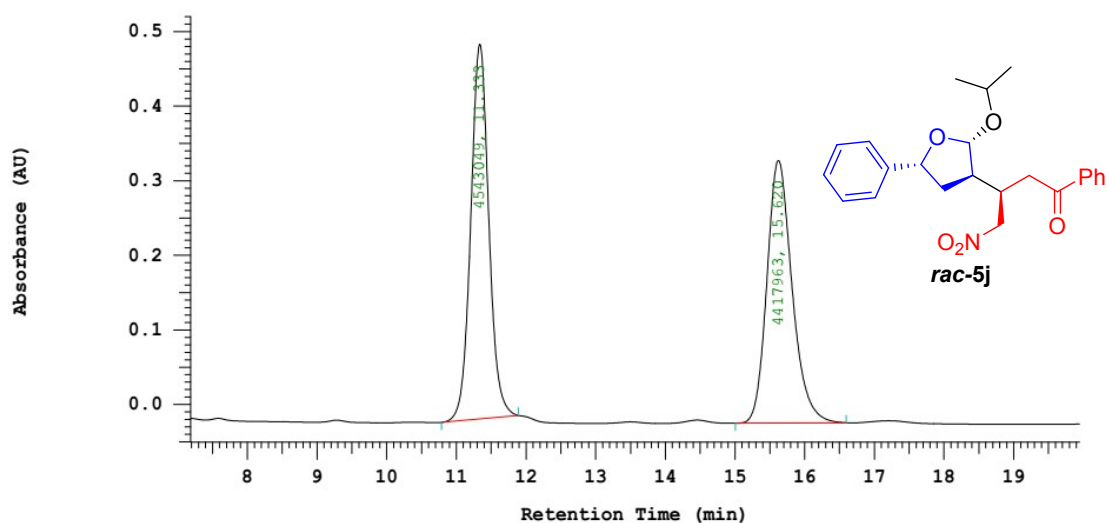
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	23.453	6919588	99.832	BB
2	24.720	11636	0.168	BB
		6931224	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

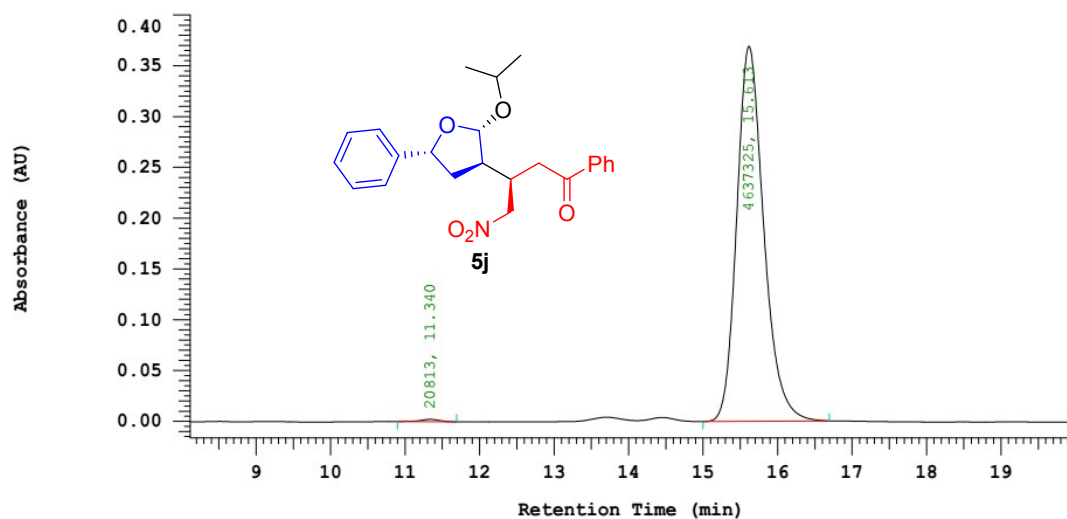


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.333	4543049	50.698	BB
2	15.620	4417963	49.302	BB
		8961012	100.000	

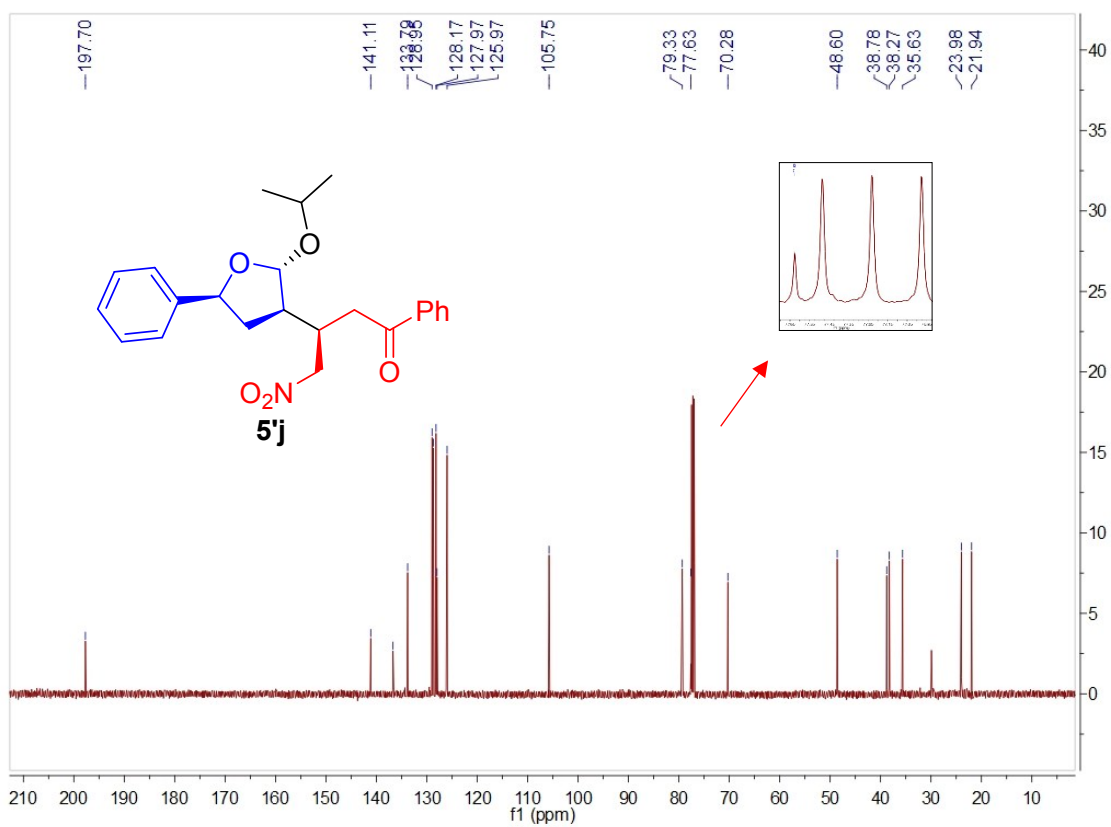
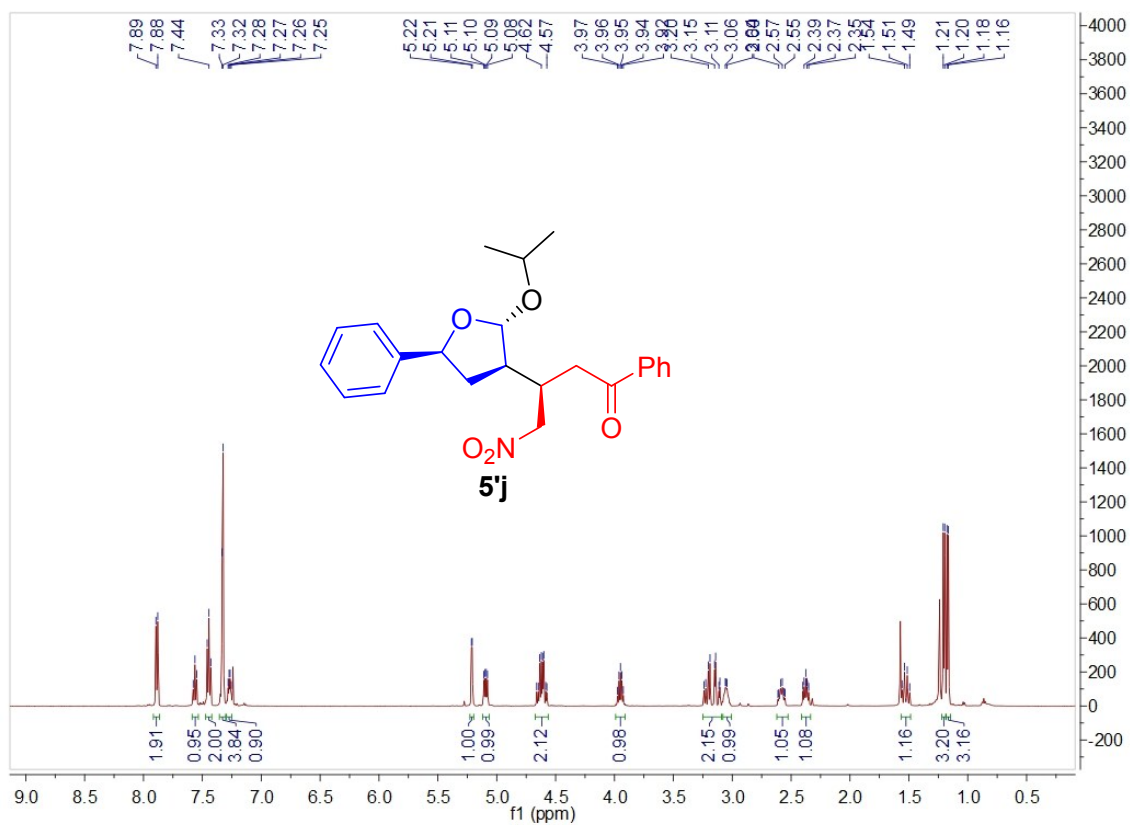
Chrom Type: Fixed WL Chromatogram, 210 nm



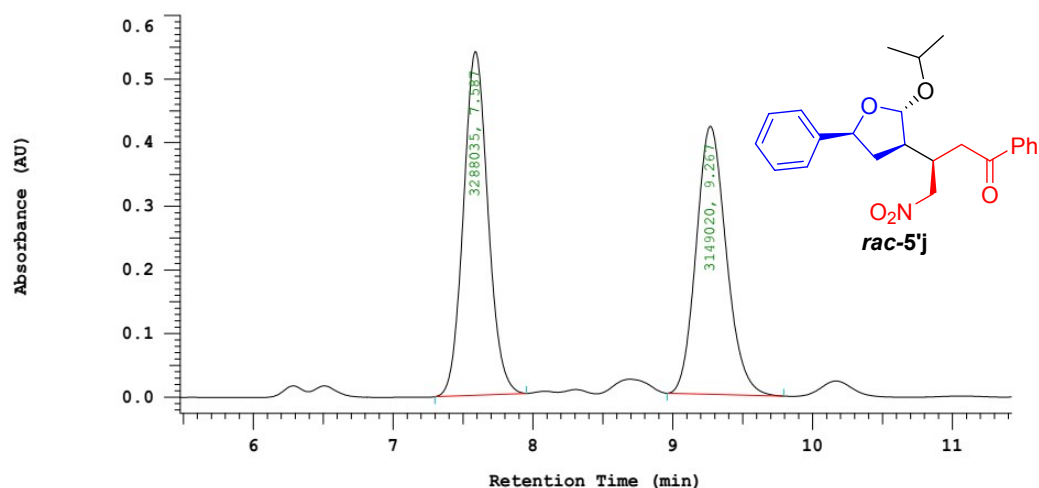
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	11.340	20813	0.447	BB
2	15.613	4637325	99.553	BB
		4658138	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

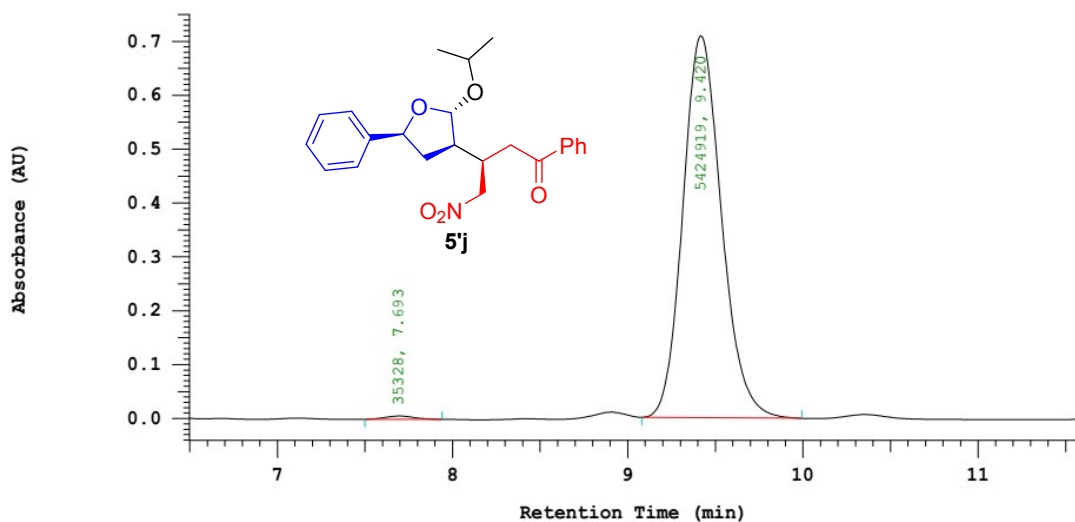


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.587	3288035	51.080	BB
2	9.267	3149020	48.920	BB
		6437055	100.000	

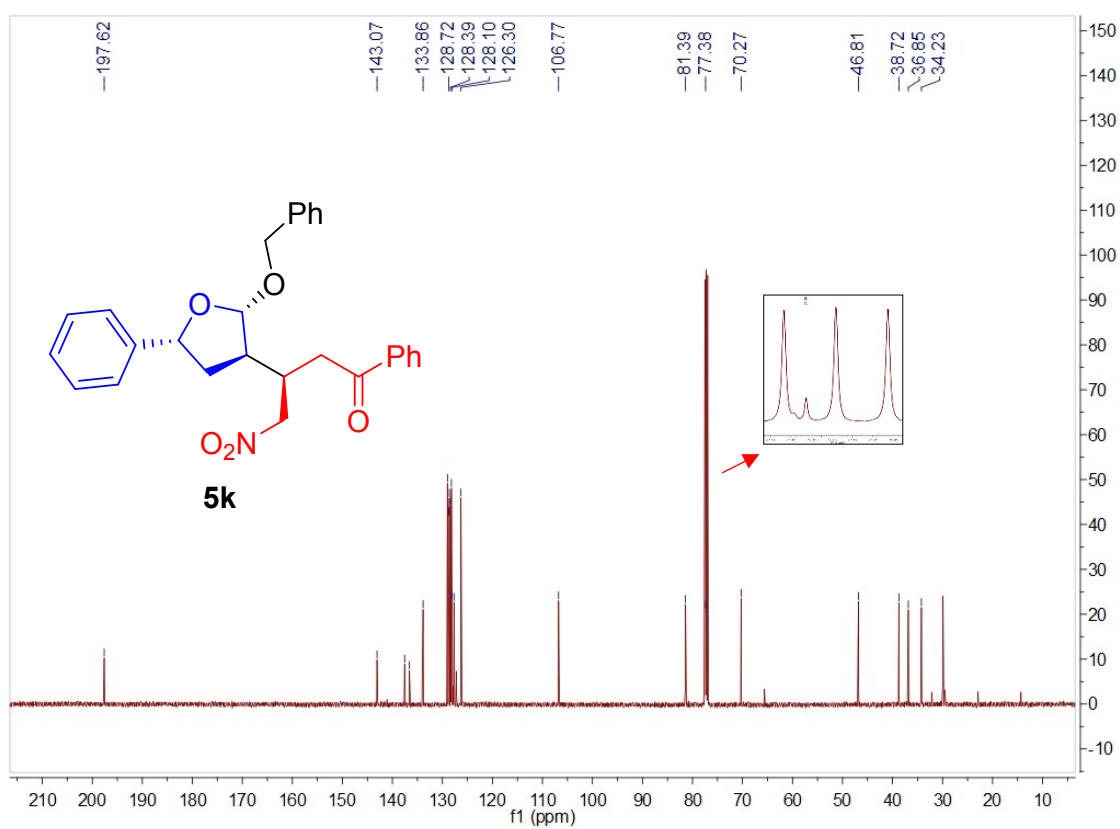
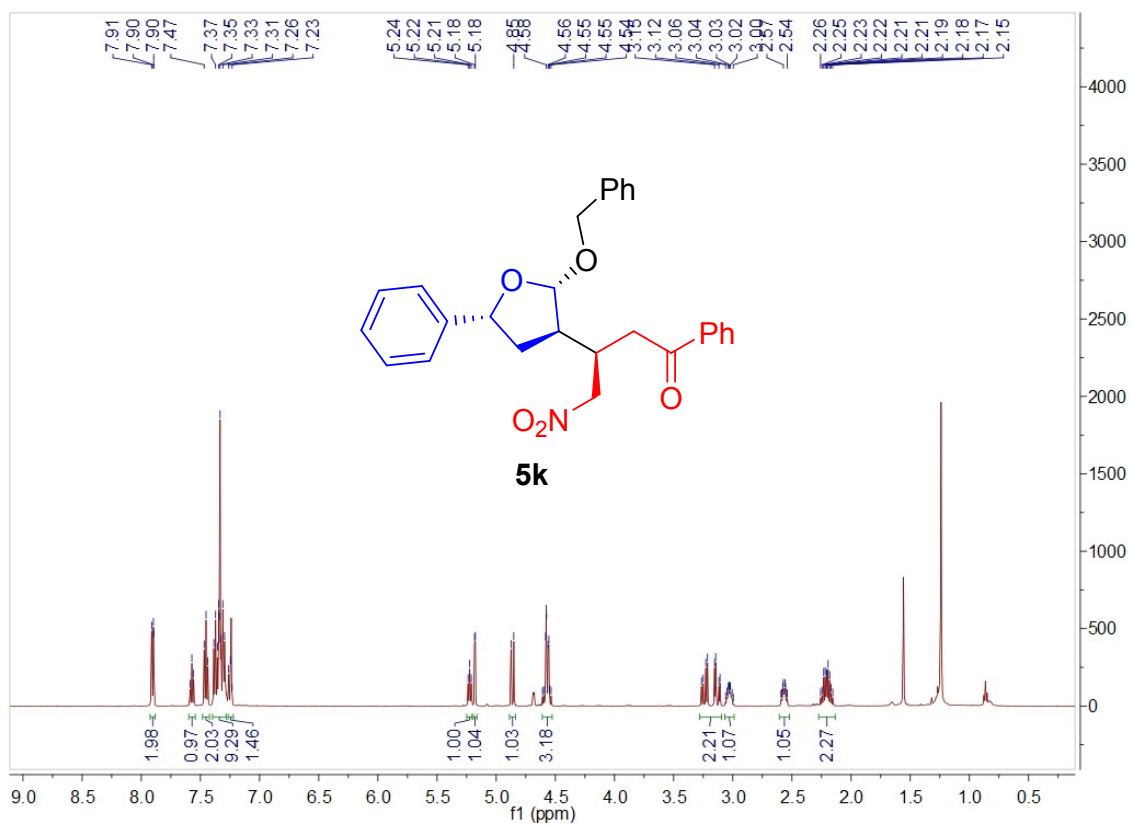
Chrom Type: Fixed WL Chromatogram, 210 nm



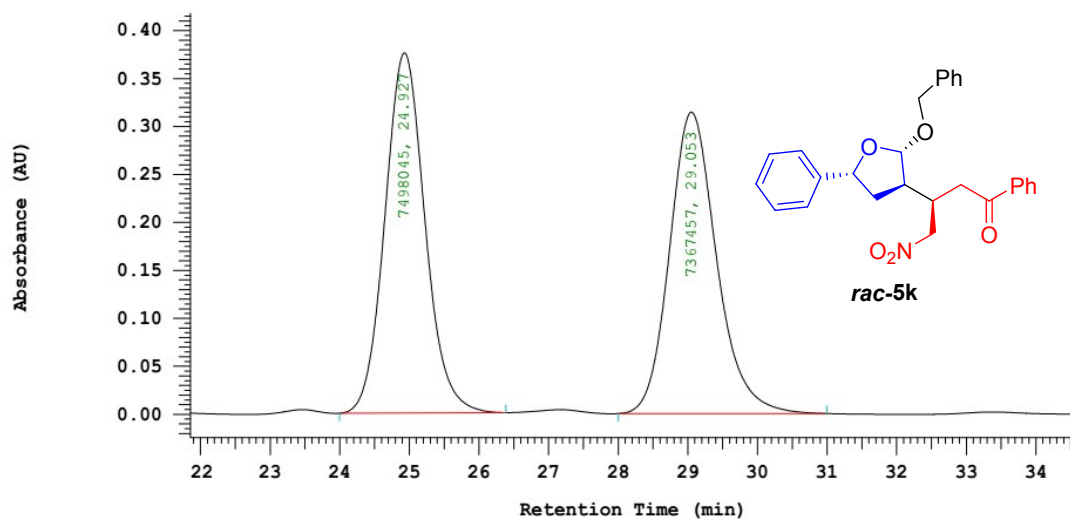
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.693	35328	0.647	BB
2	9.420	5424919	99.353	BB
		5460247	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

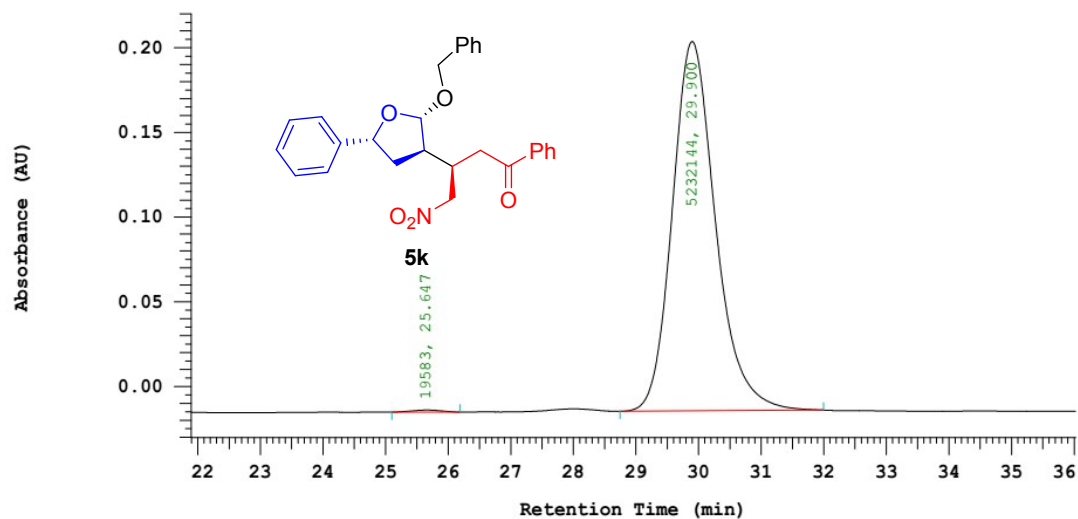


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	24.927	7498045	50.439	BB
2	29.053	7367457	49.561	BB
		14865502	100.000	

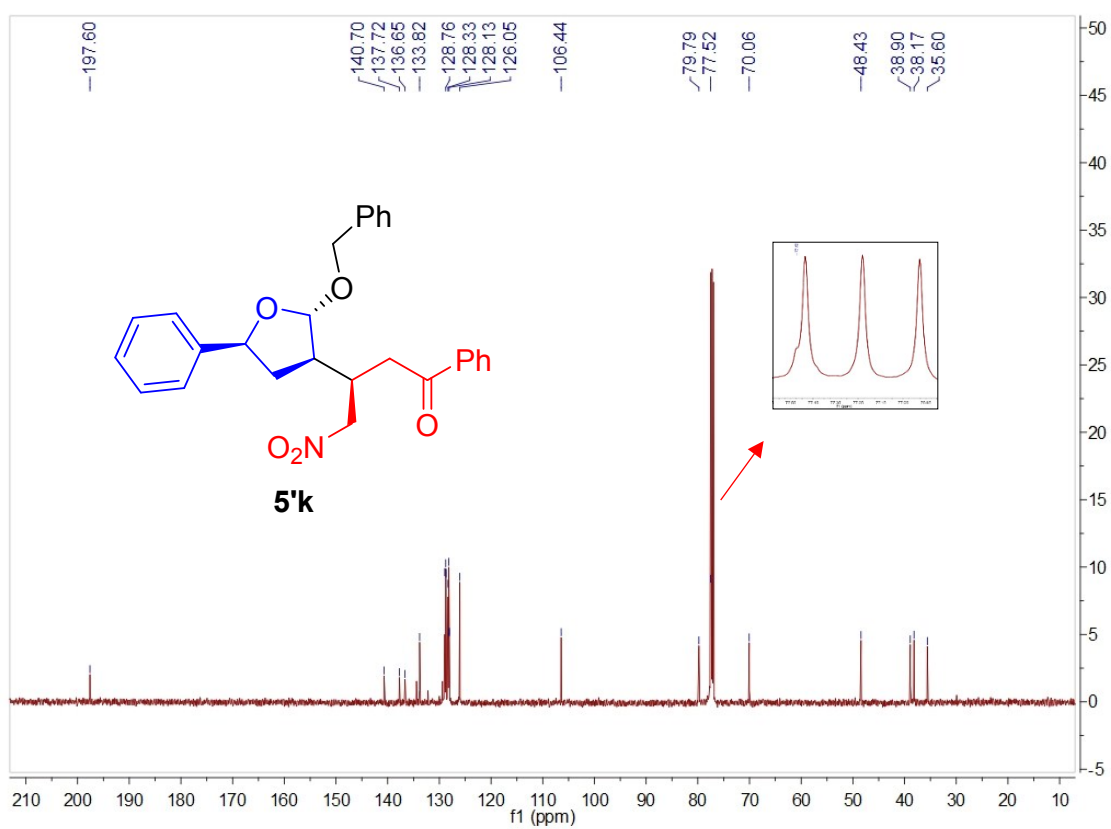
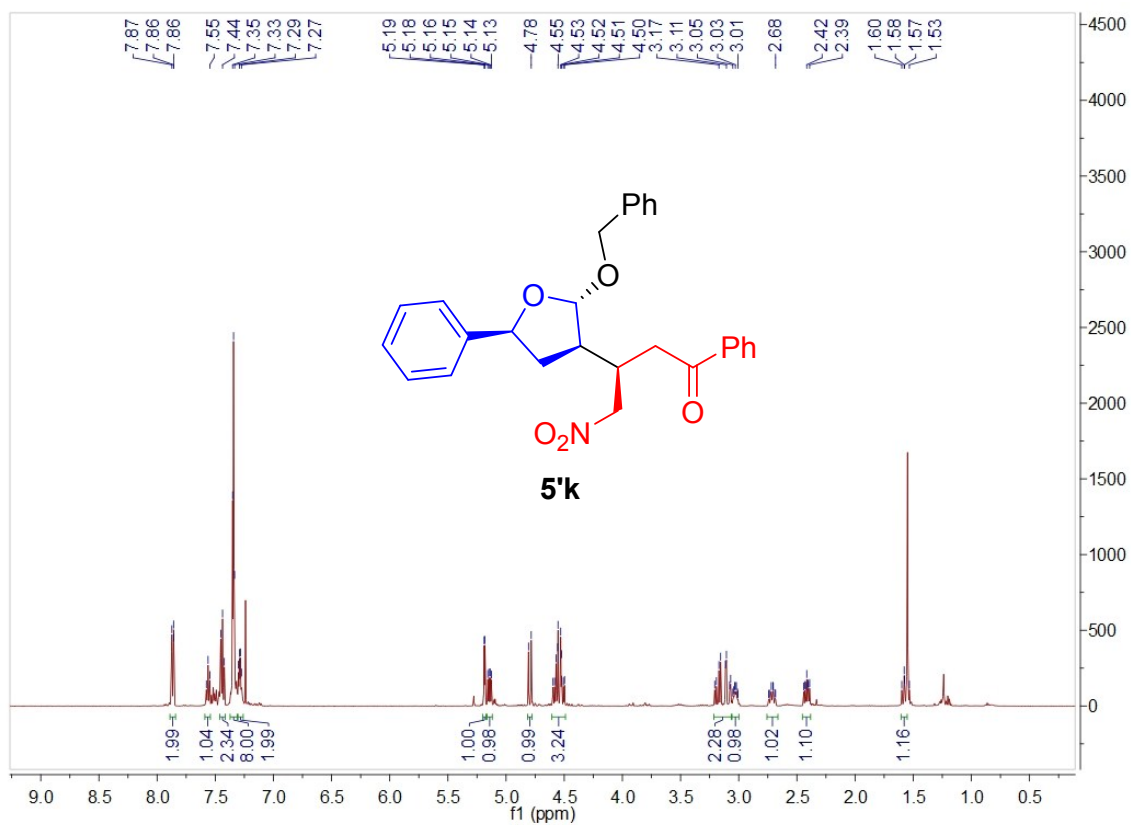
Chrom Type: Fixed WL Chromatogram, 210 nm



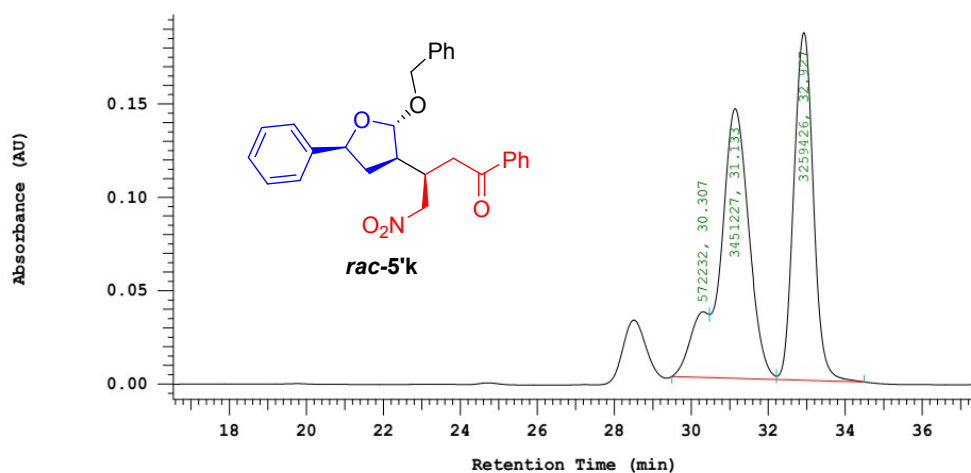
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	25.647	19583	0.373	BB
2	29.900	5232144	99.627	BB
		5251727	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

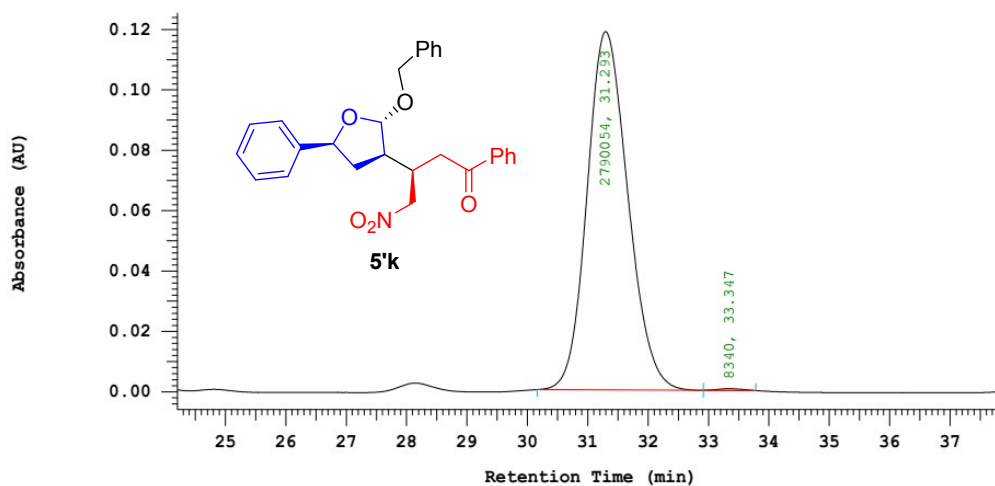


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	30.307	572232	7.857	BV
2	31.133	3451227	47.388	VV
3	32.927	3259426	44.755	VB
		7282885	100.000	

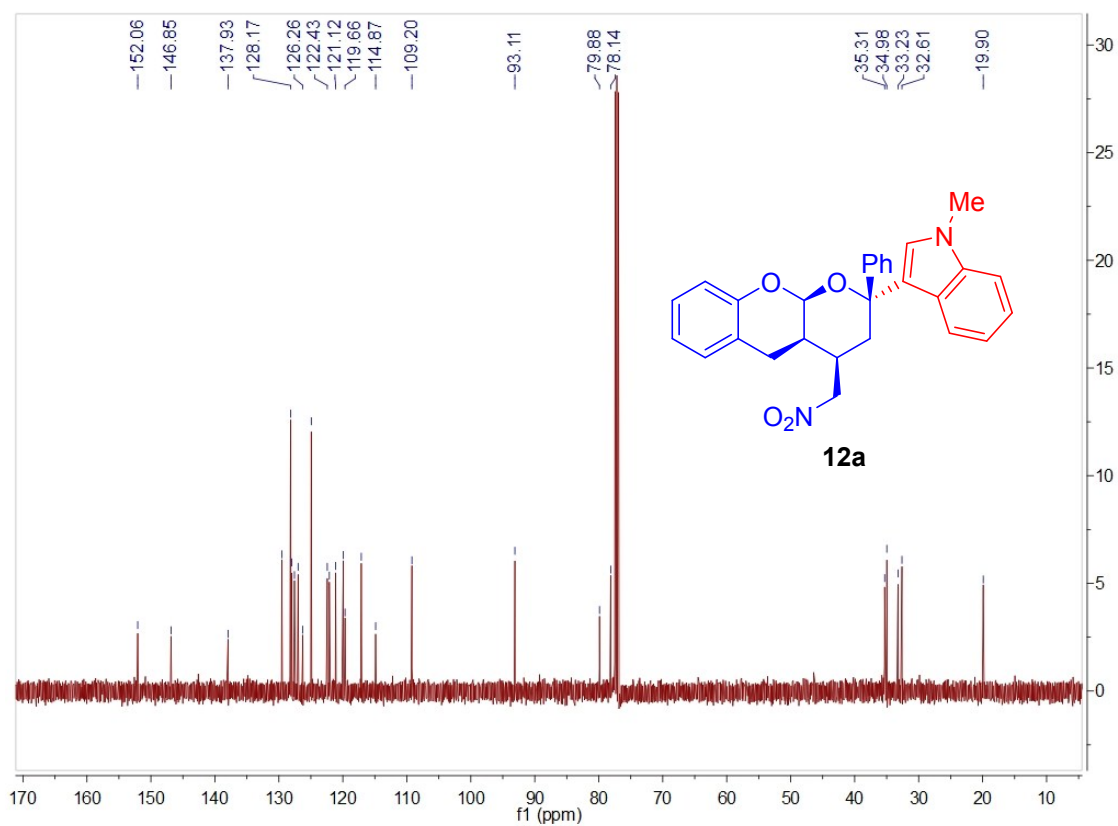
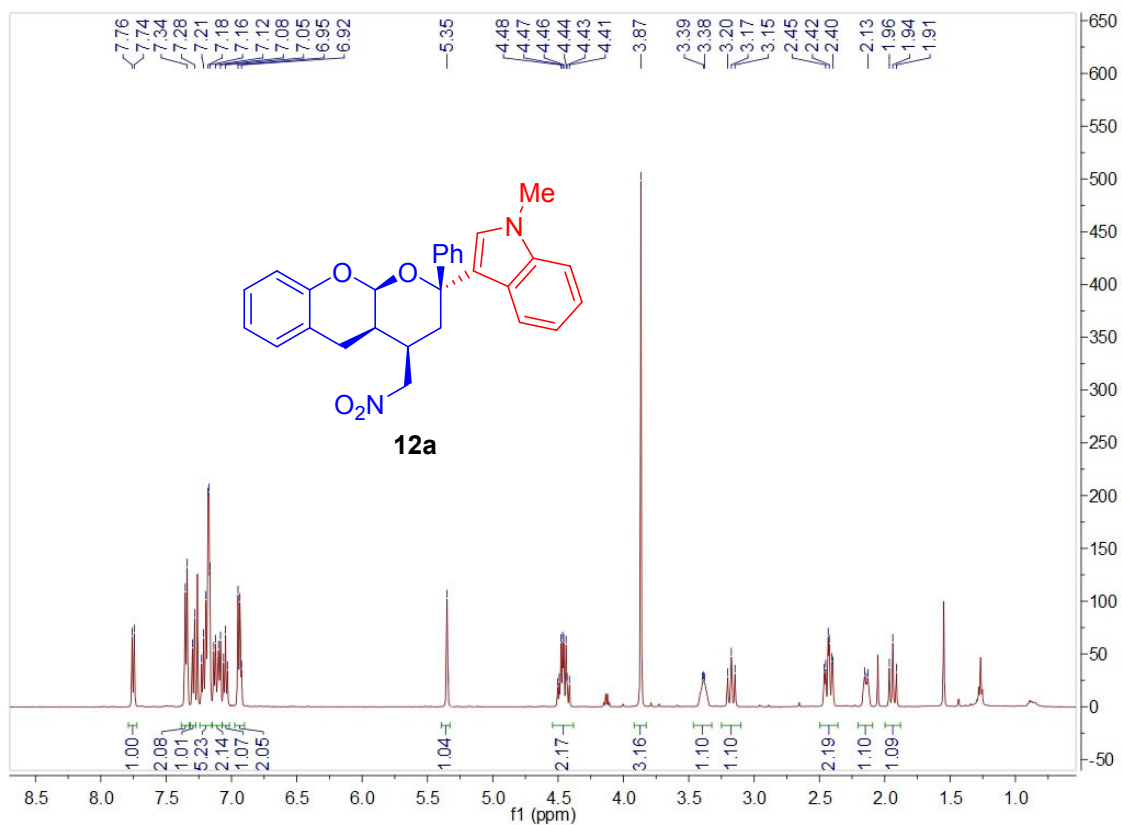
Chrom Type: Fixed WL Chromatogram, 230 nm



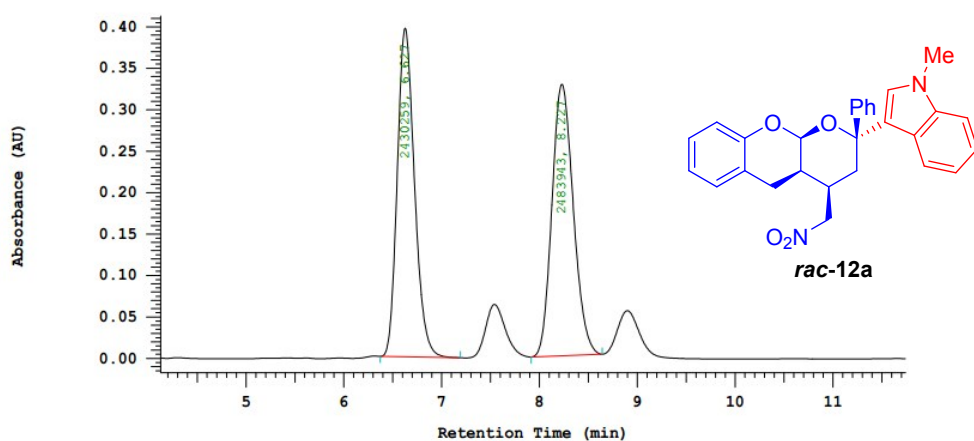
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	31.293	2790054	99.702	BB
2	33.347	8340	0.298	TBB
		2798394	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm



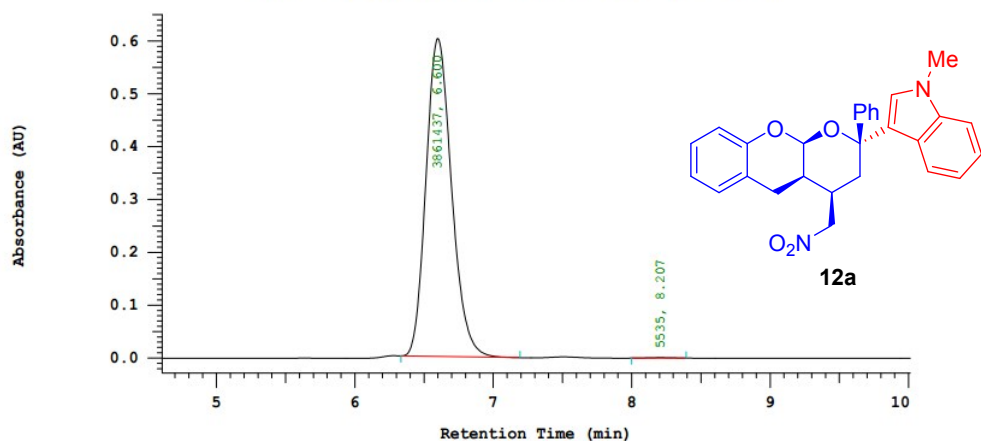
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.627	2430259	49.454	BB
2	8.227	2483943	50.546	BB
		4914202	100.000	

Chrom Type: Fixed WL Chromatogram, 230 nm

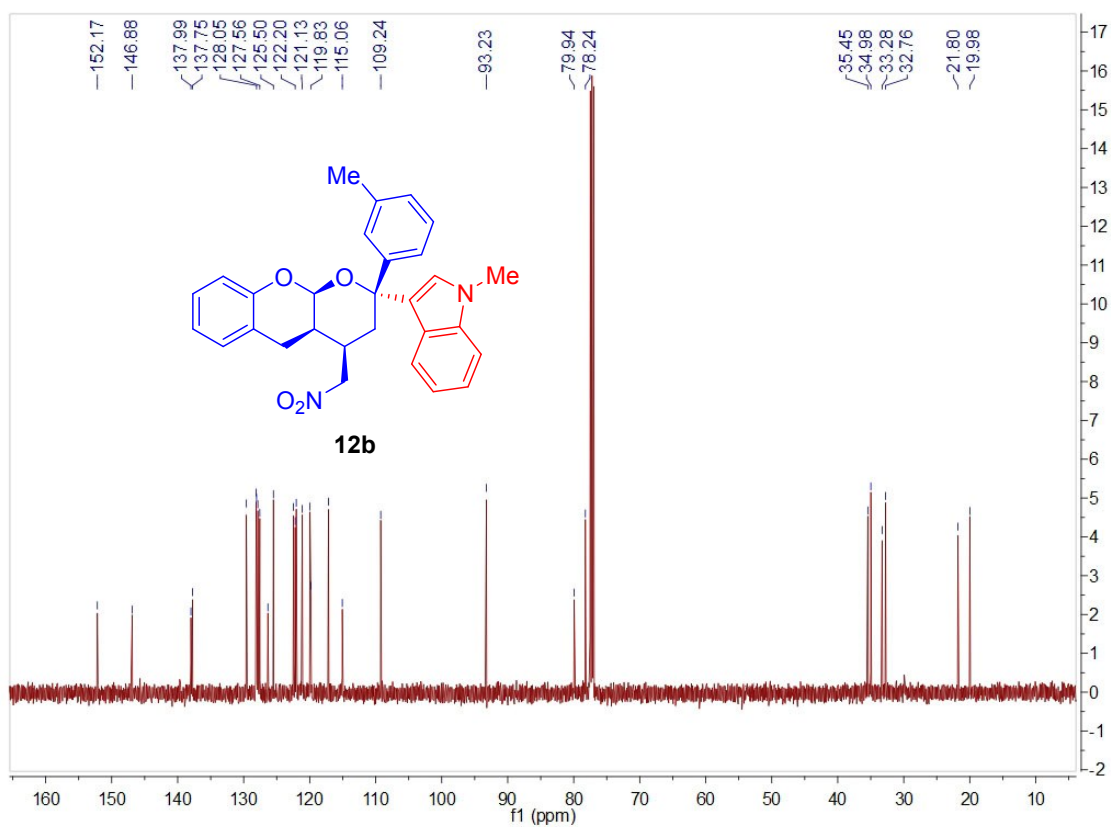
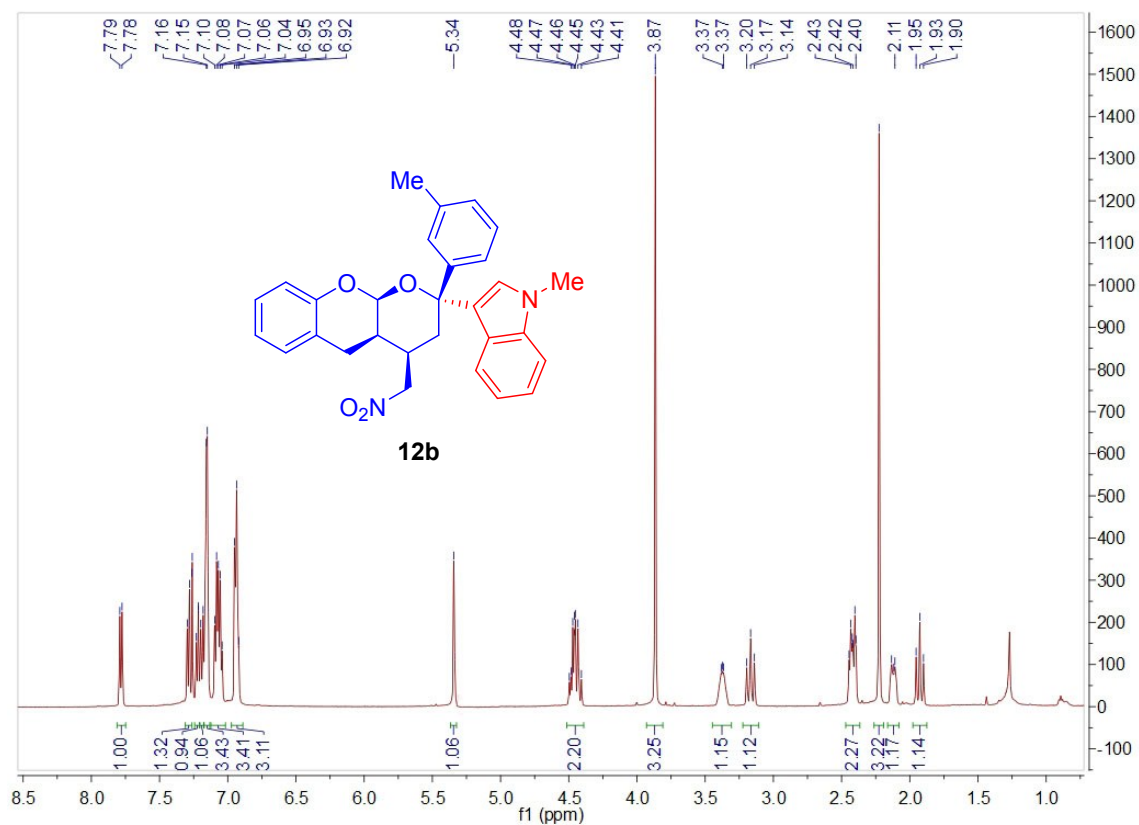


Chrom Type: Fixed WL Chromatogram, 230 nm

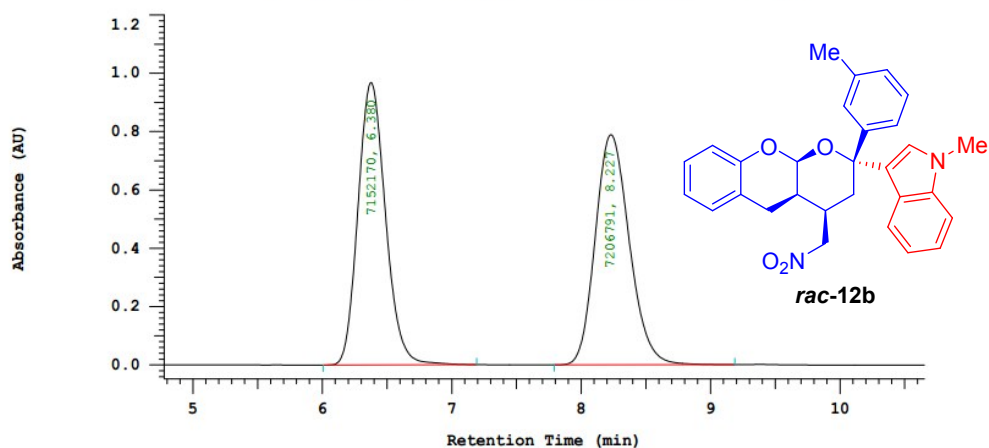
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.600	3861437	99.857	BB
2	8.207	5535	0.143	BB
		3866972	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

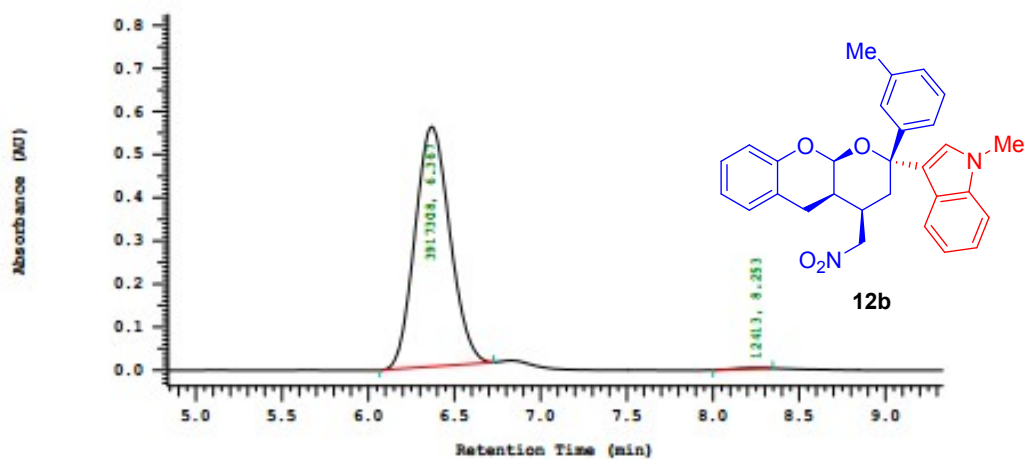


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.380	7152170	49.810	BB
2	8.227	7206791	50.190	BB
		14358961	100.000	

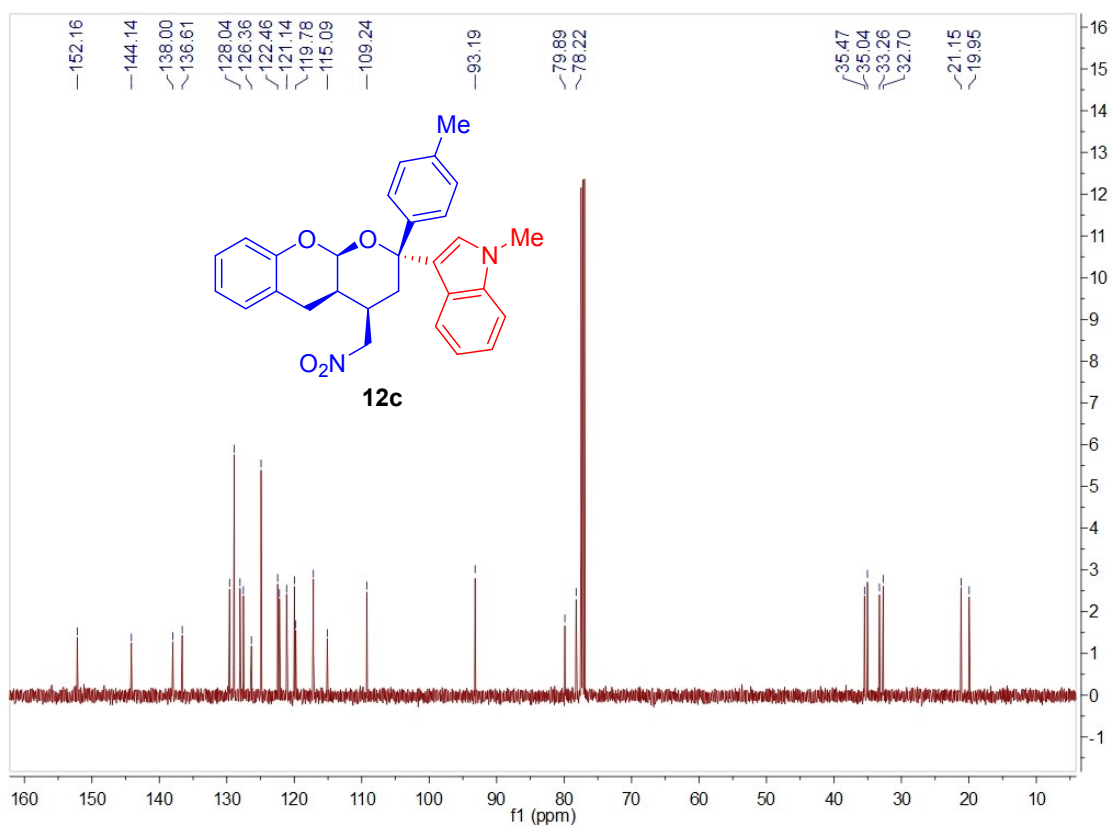
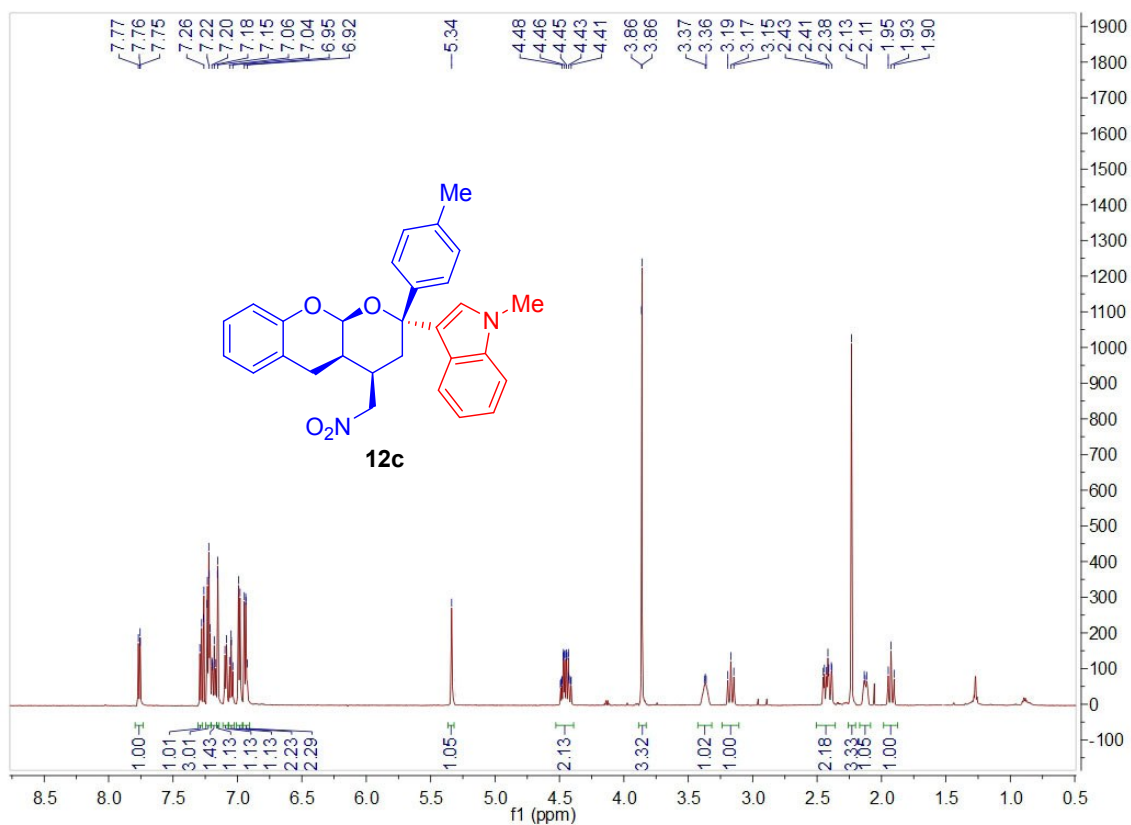
Chrom Type: Fixed WL Chromatogram, 230 nm

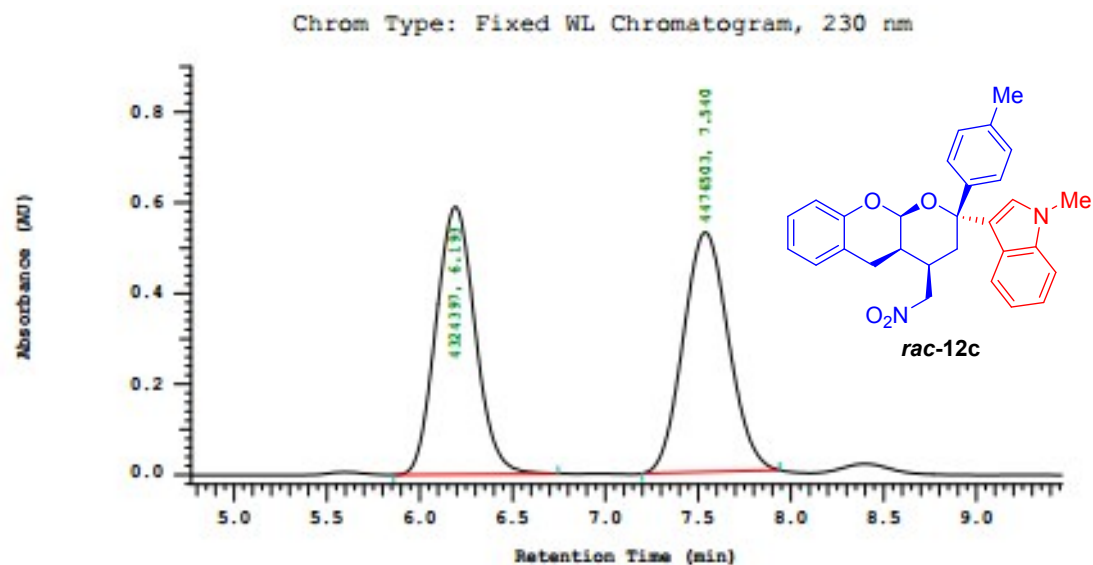


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.367	3917308	99.684	BB
2	8.253	12413	0.316	BB
		3929721	100.000	



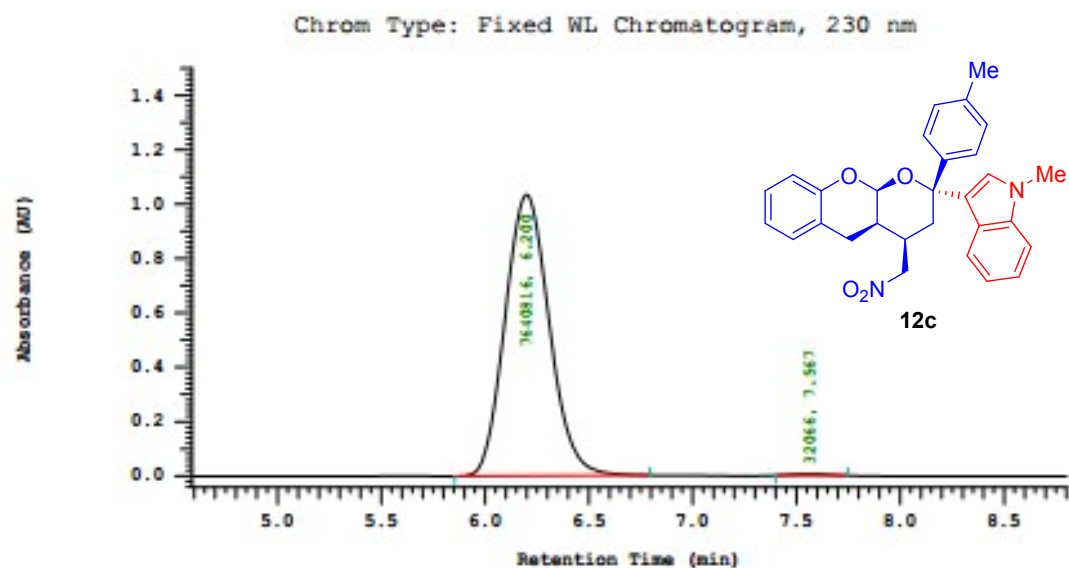


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.193	4324397	49.136	BB
2	7.540	4476503	50.864	BB
		8800900	100.000	

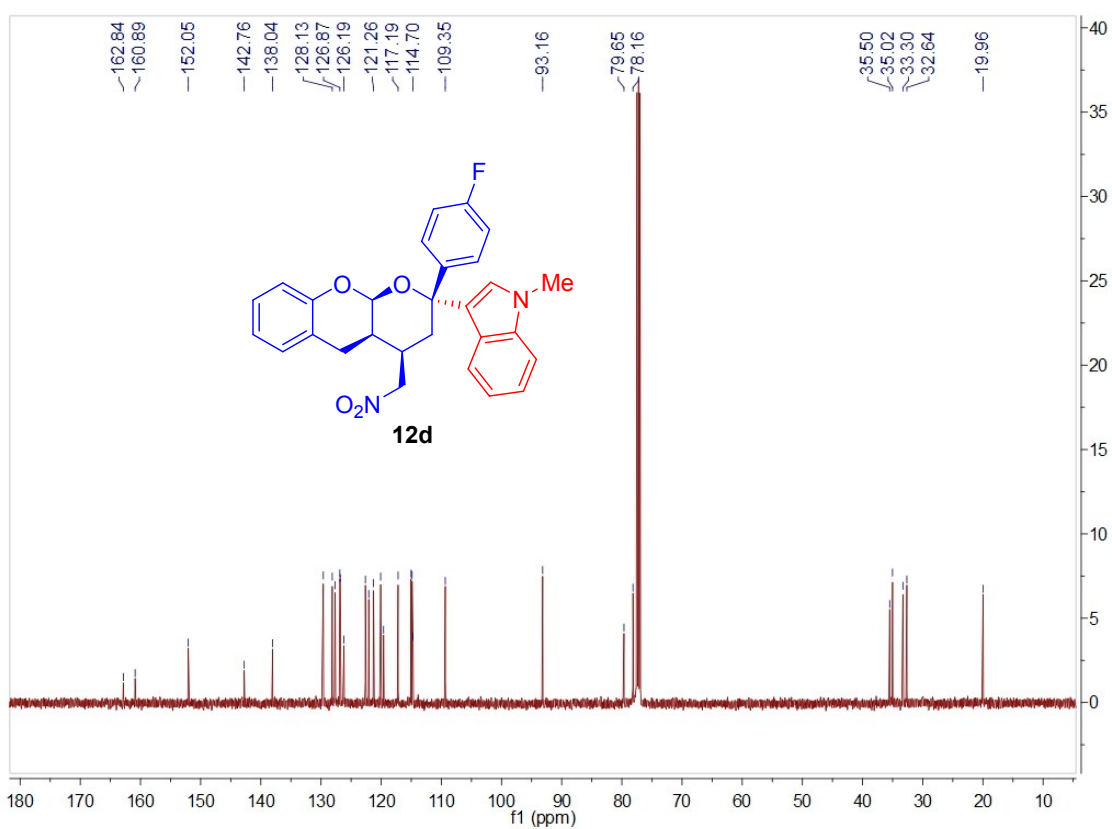
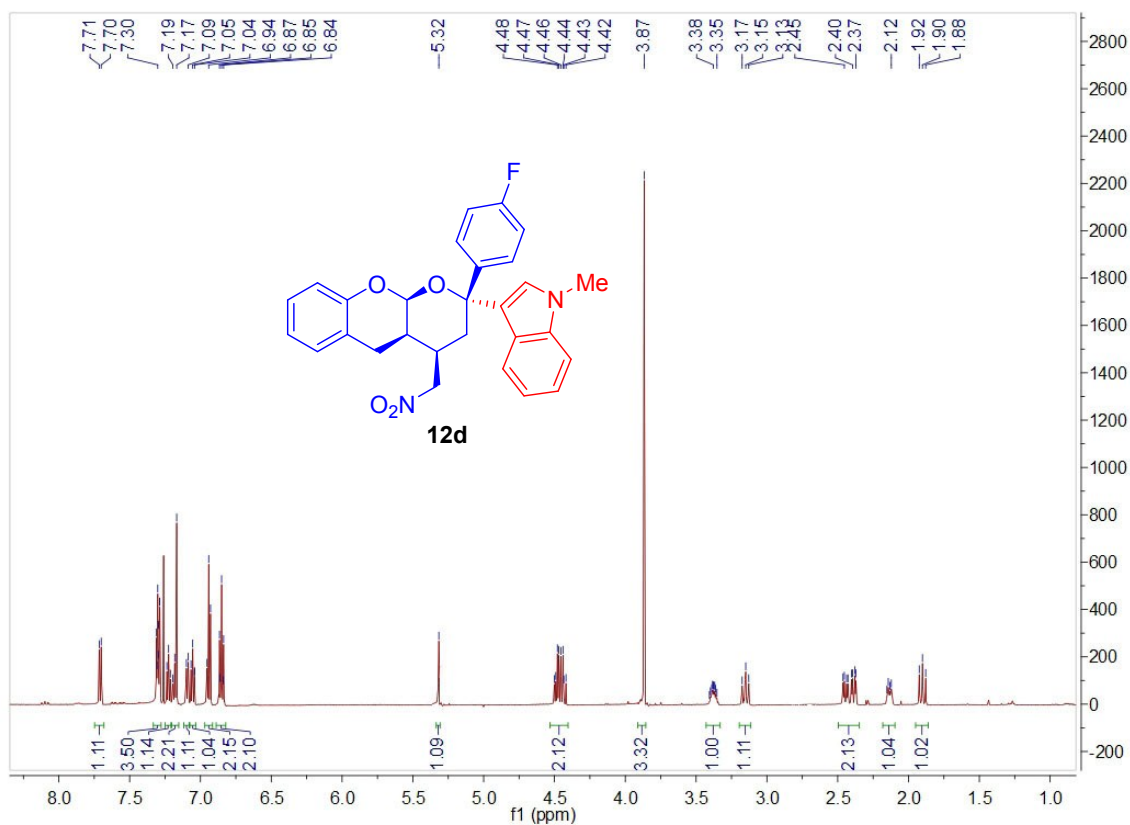


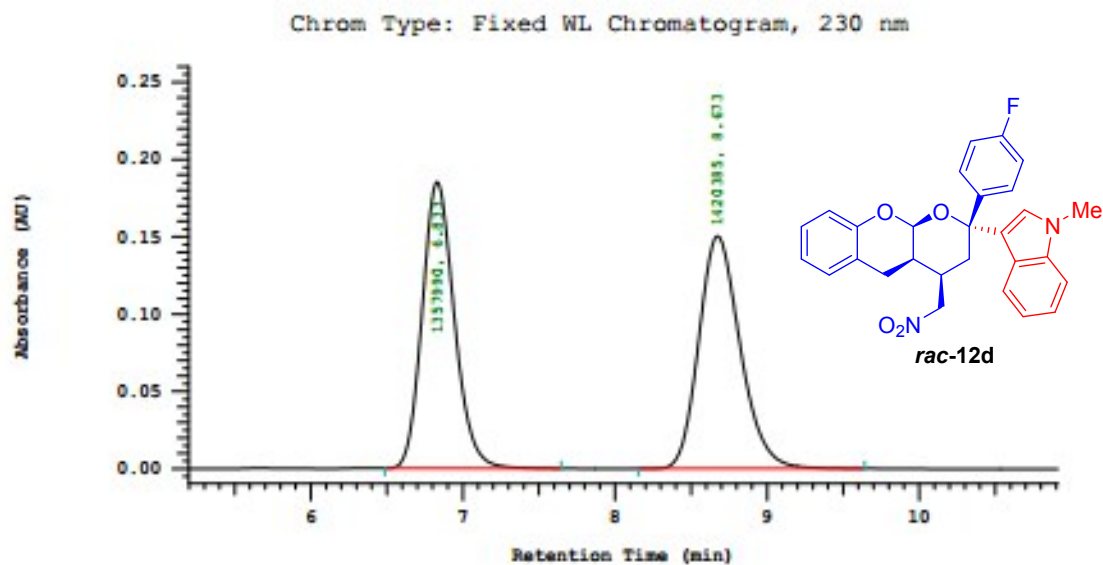
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.200	7640816	99.582	BB
2	7.567	32066	0.418	BB
		7672882	100.000	



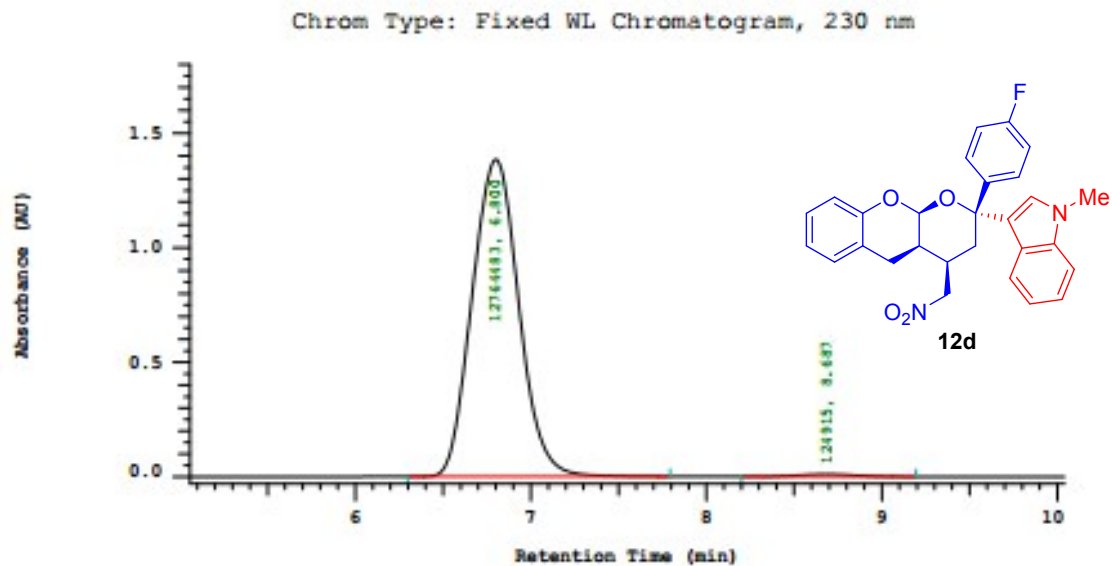


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.833	1357990	48.877	BB
2	8.673	1420385	51.123	BB
		2778375	100.000	

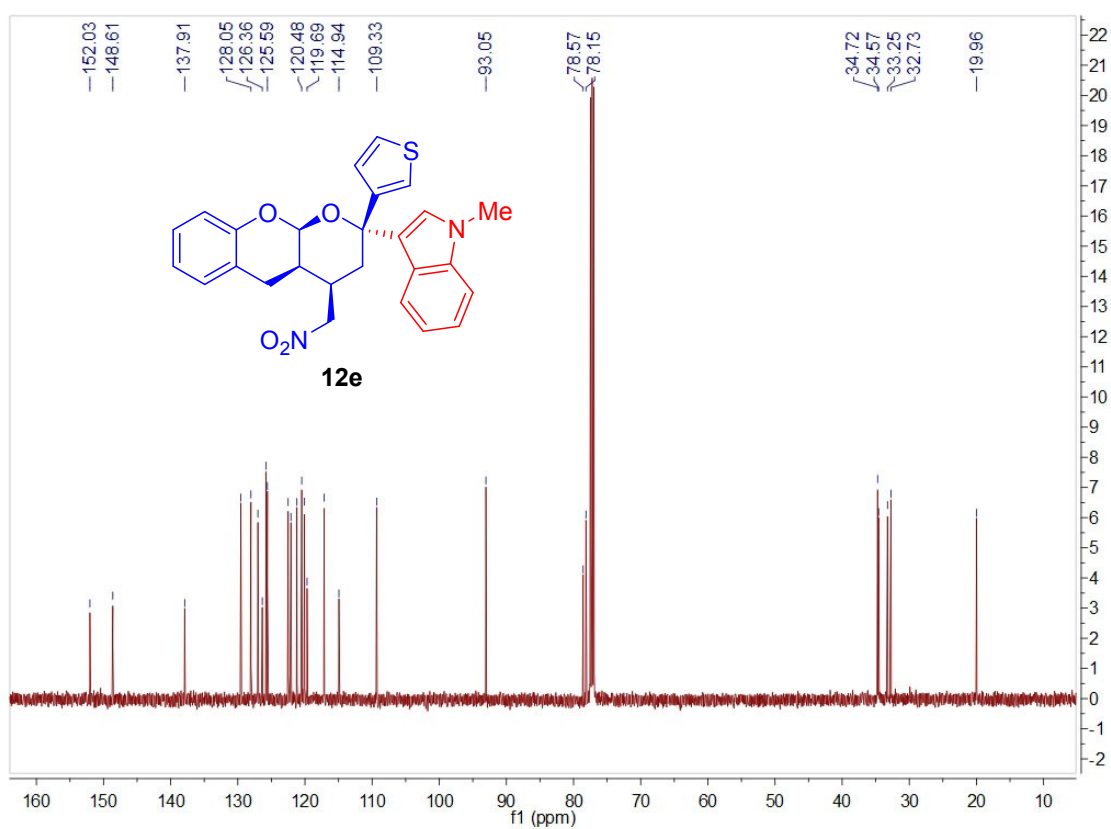
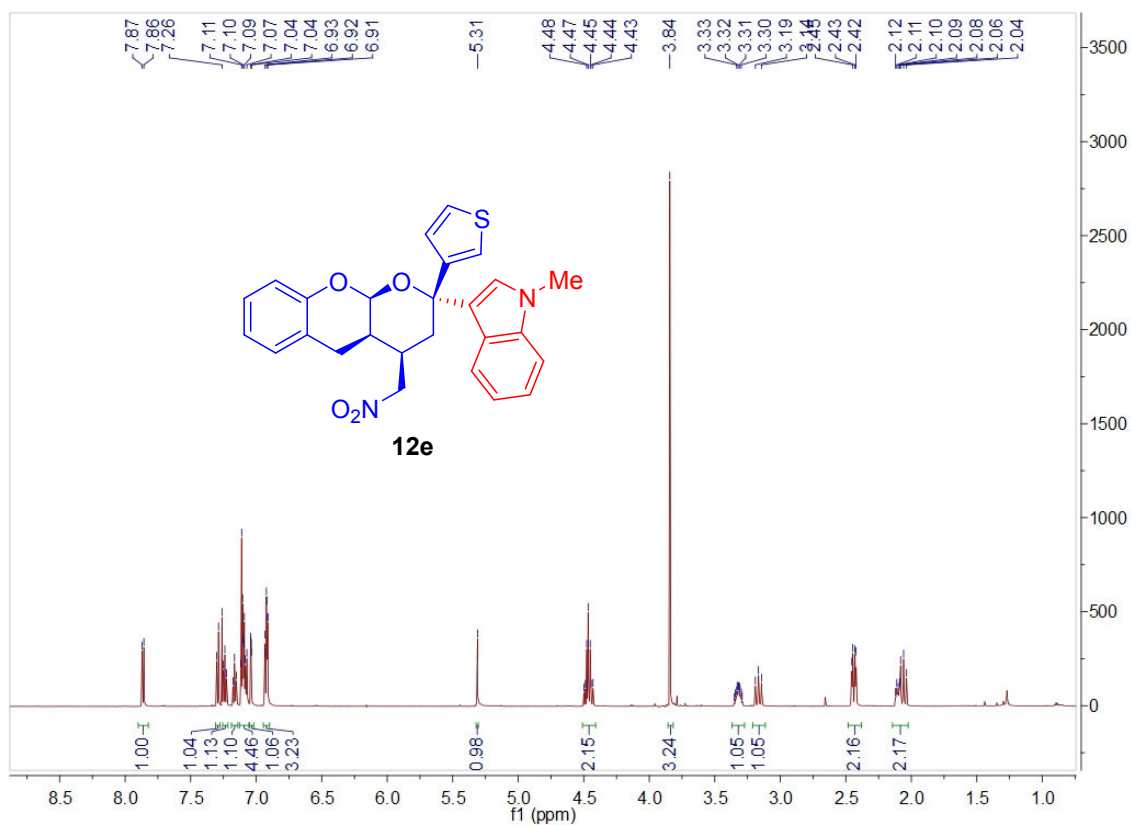


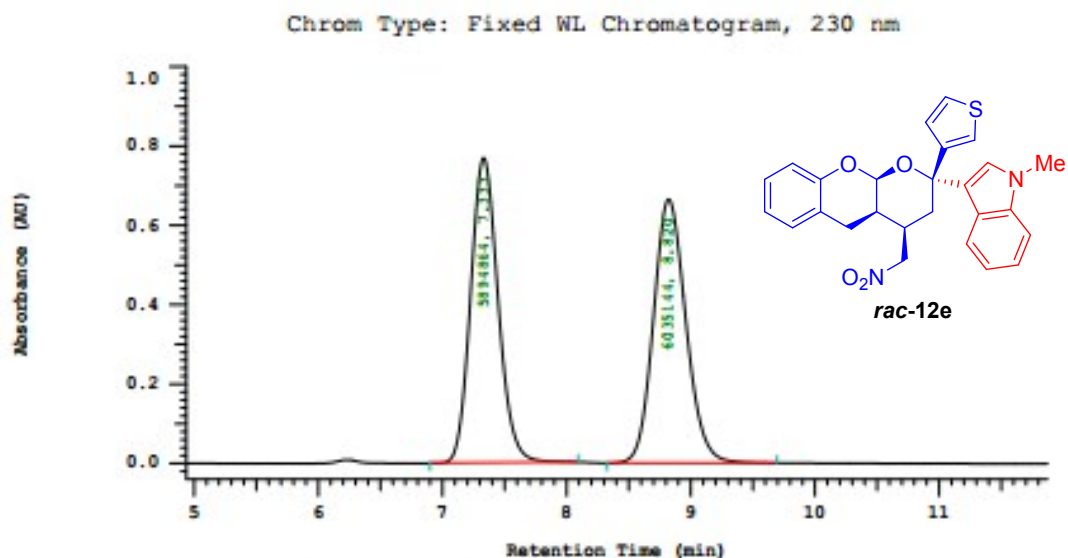
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.800	12764483	99.031	BB
2	8.687	124915	0.969	BB
		12889398	100.000	



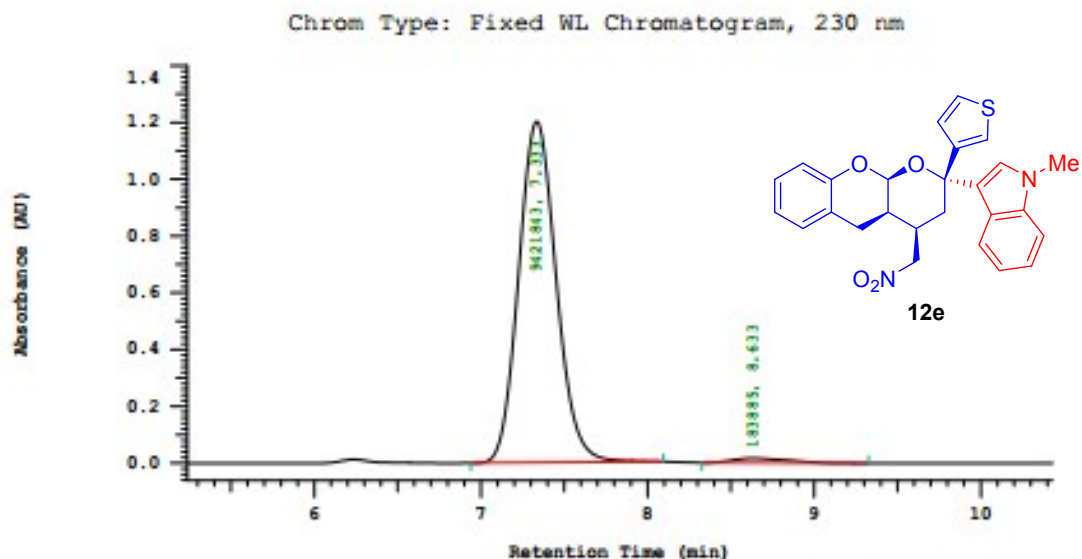


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.333	5894864	49.412	BB
2	8.820	6035144	50.588	BB
		11930008	100.000	

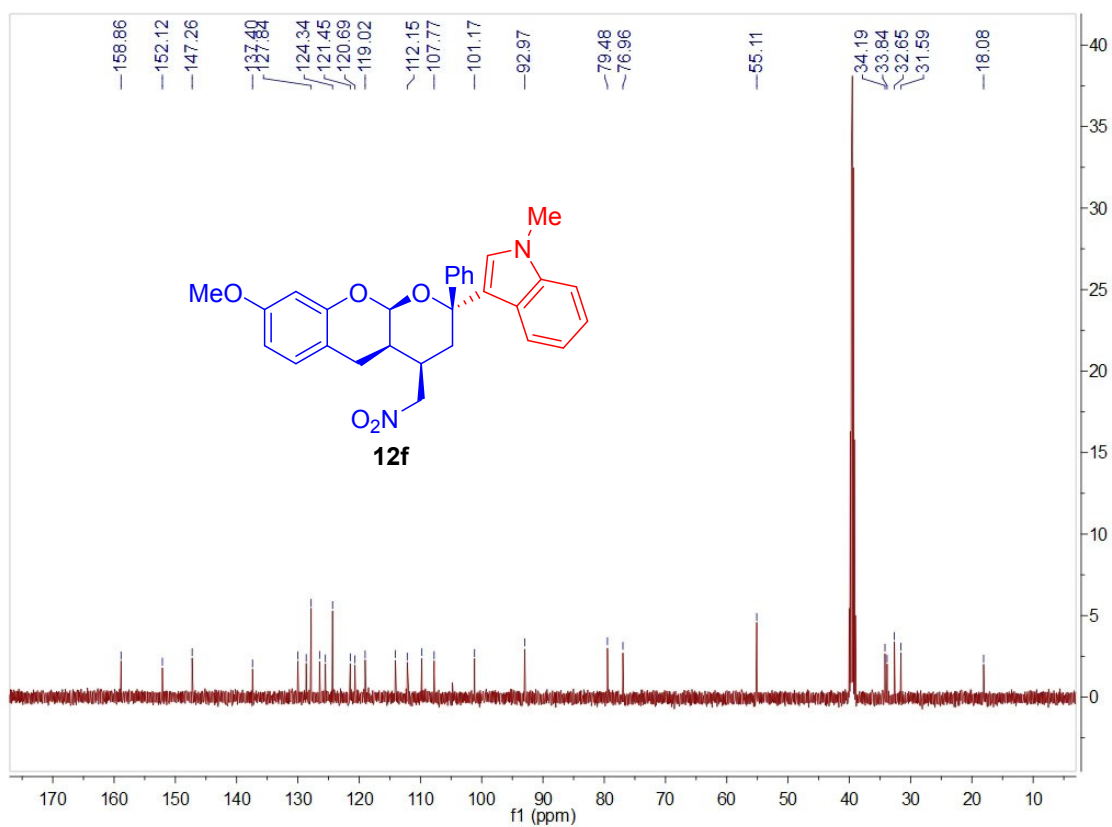
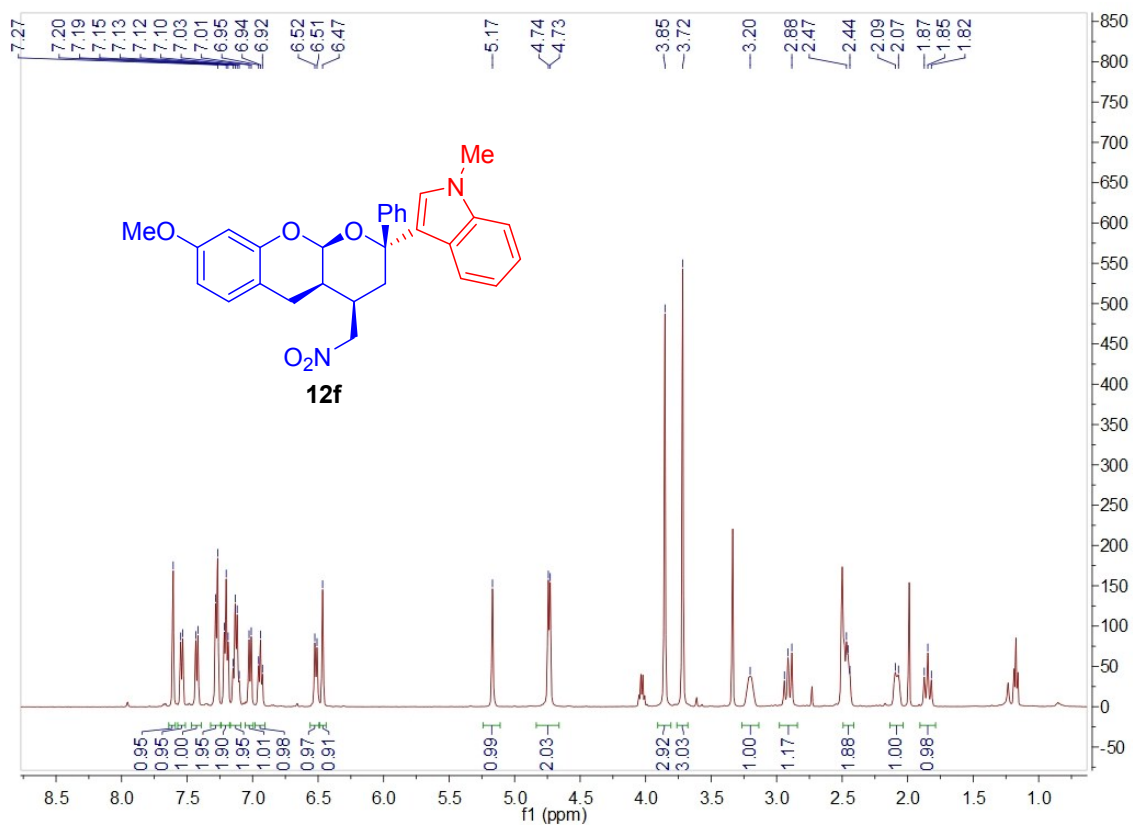


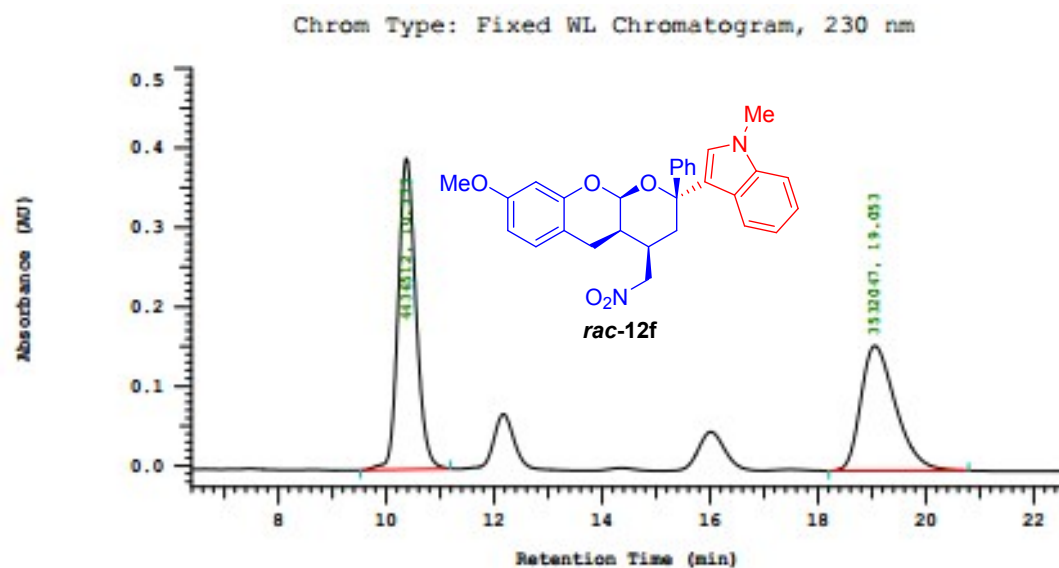
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

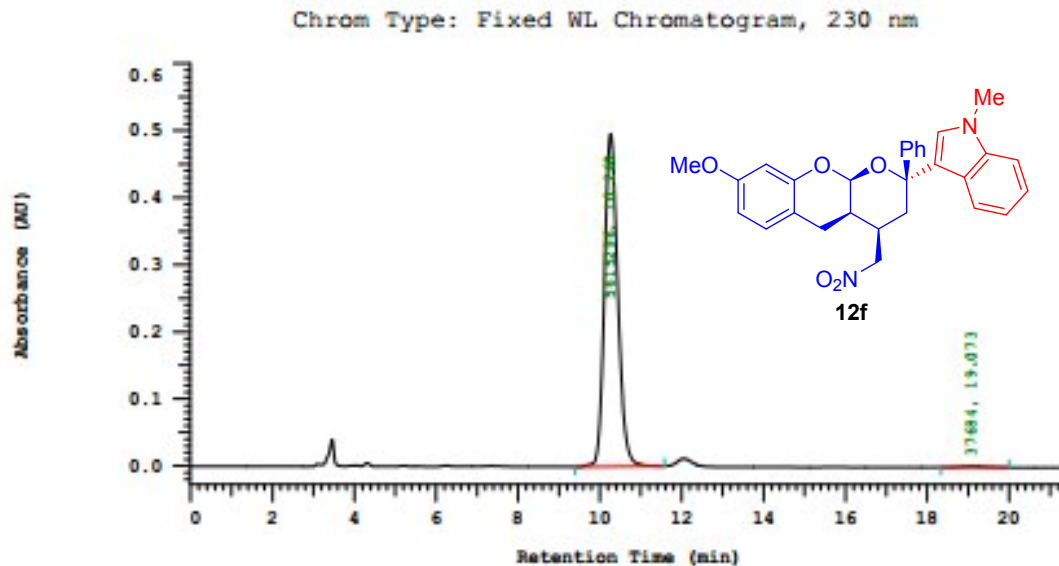
No.	RT	Area	Area %	BC
1	7.333	9421843	98.086	BB
2	8.633	183885	1.914	BB
		9605728	100.000	





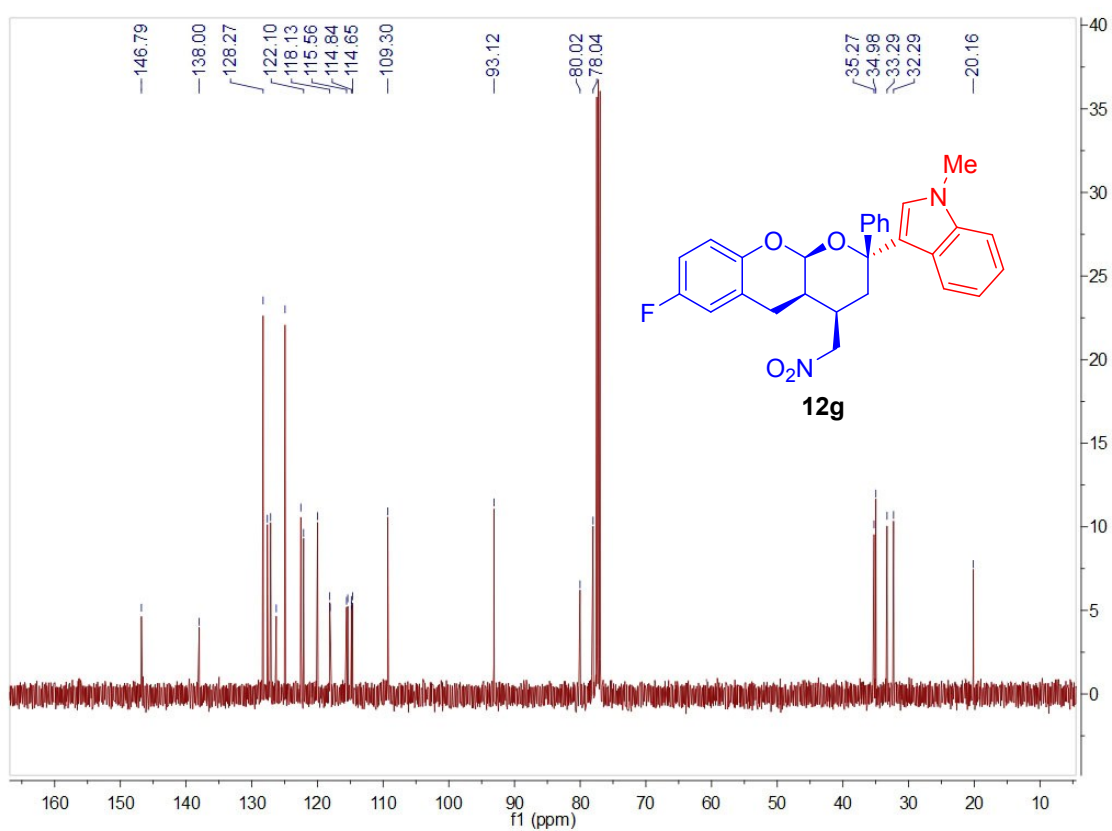
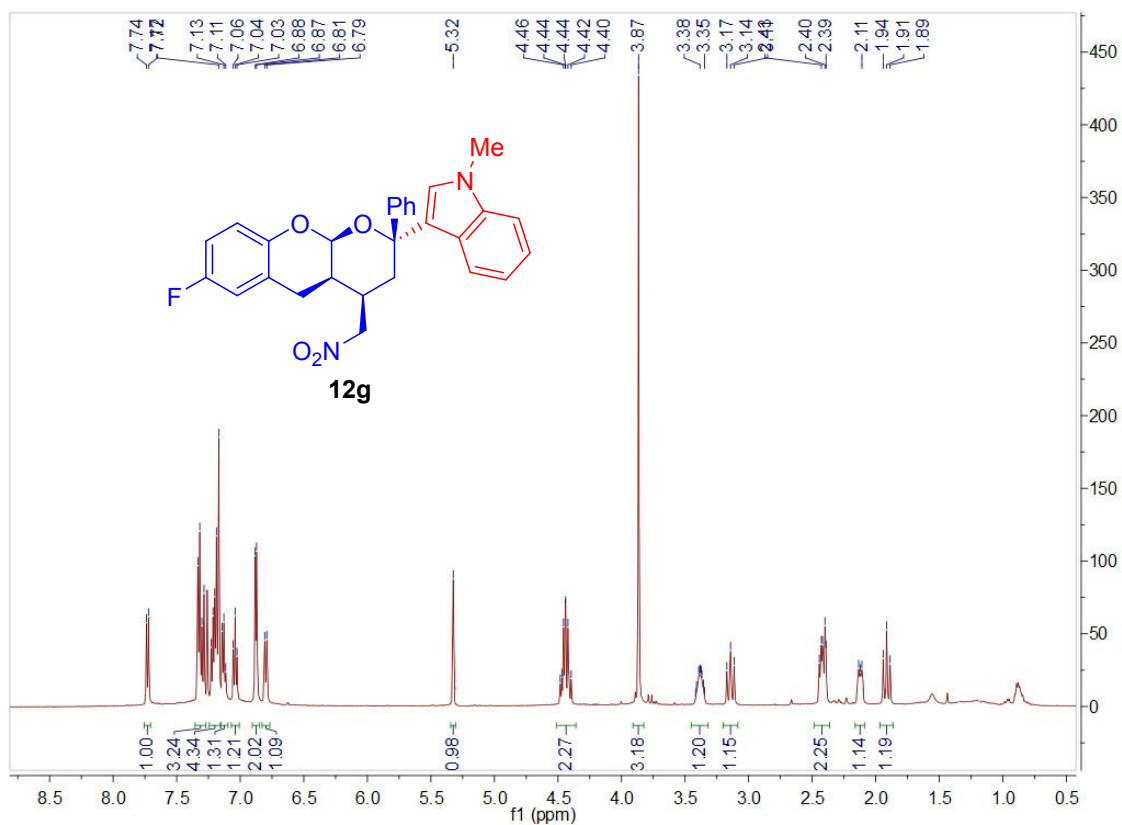
Chrom Type: Fixed WL Chromatogram, 230 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.373	4436512	55.675	BB
2	19.053	3532047	44.325	BB
		7968559	100.000	

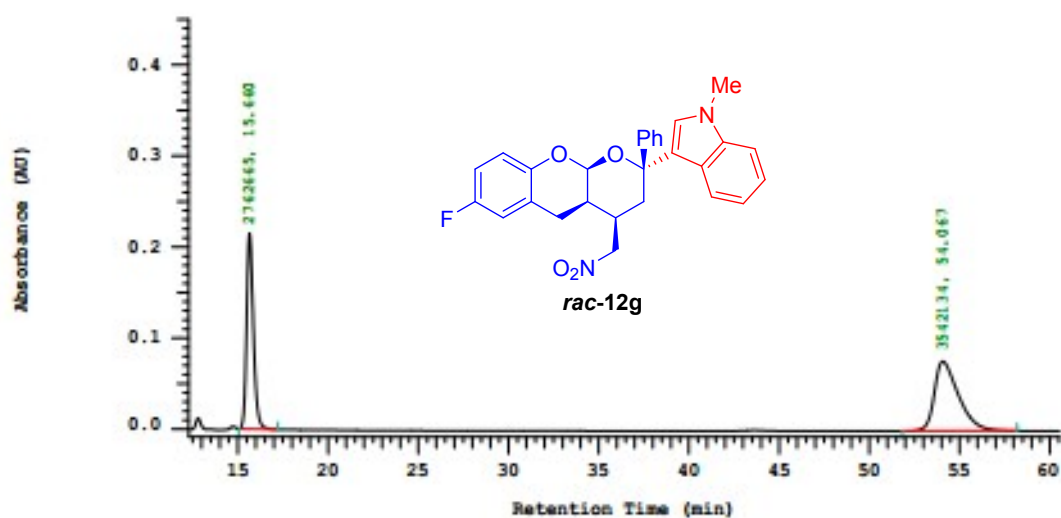


Chrom Type: Fixed WL Chromatogram, 230 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	10.260	5615296	99.333	BB
2	19.073	37684	0.667	BB
		5652980	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

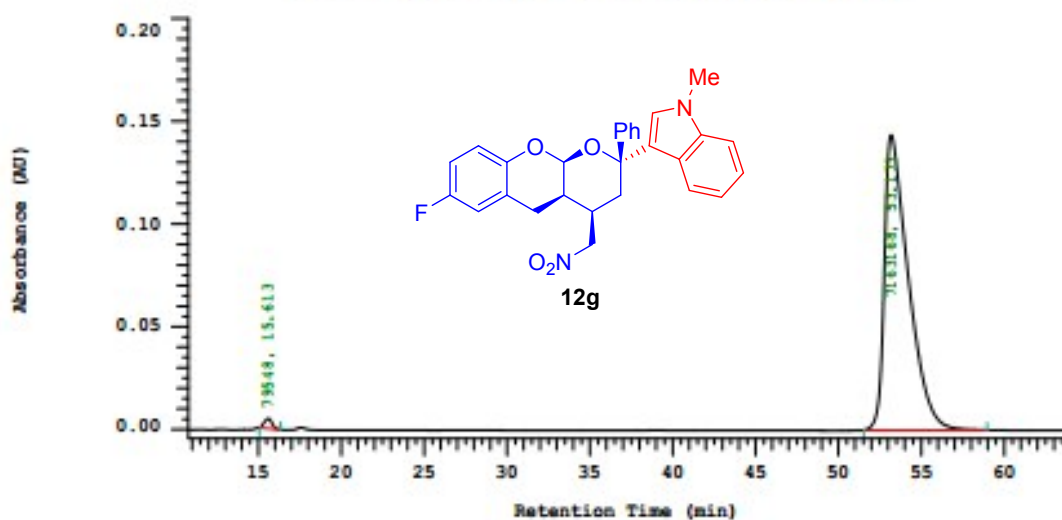


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.660	2762665	43.818	BB
2	54.067	3542134	56.182	BB
		6304799	100.000	

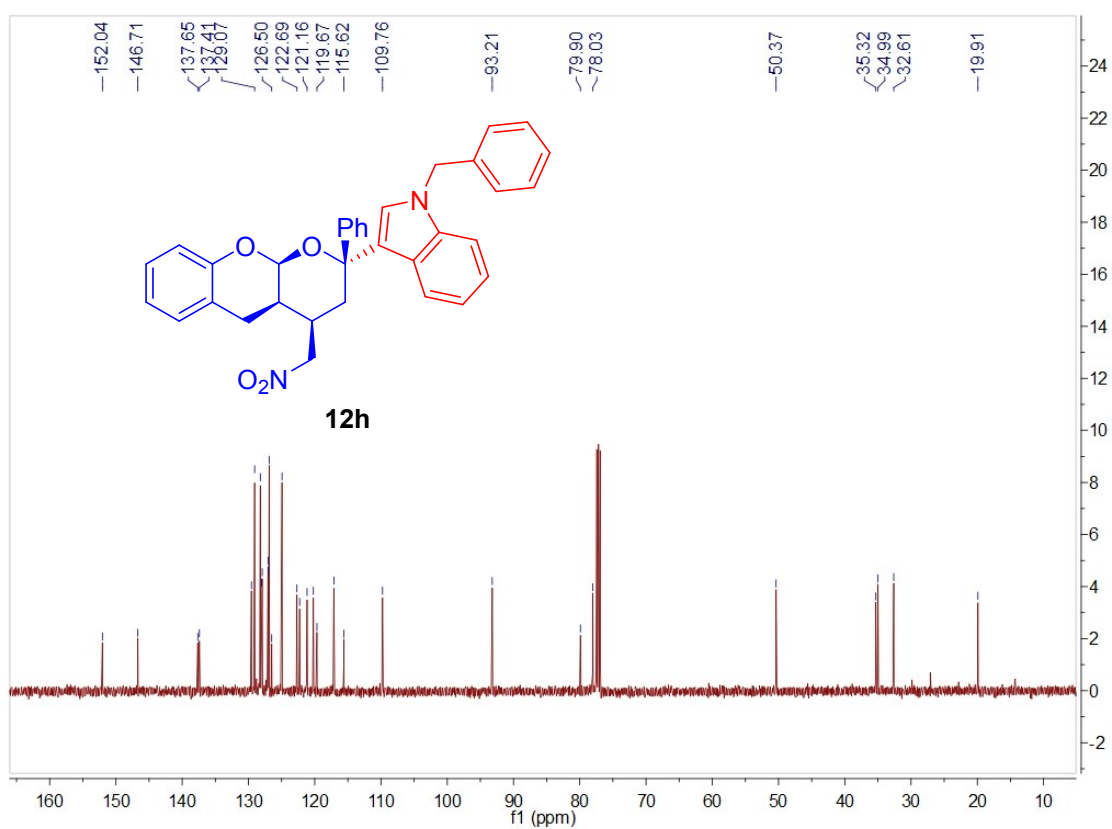
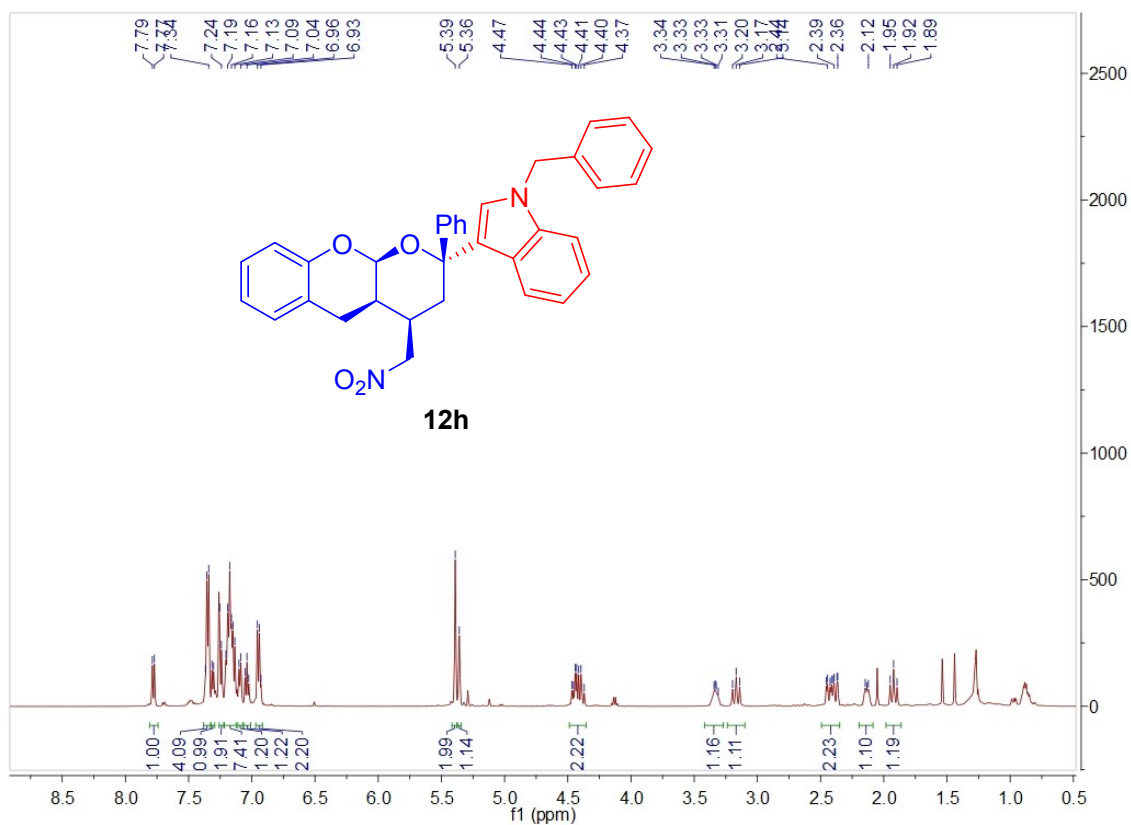
Chrom Type: Fixed WL Chromatogram, 230 nm



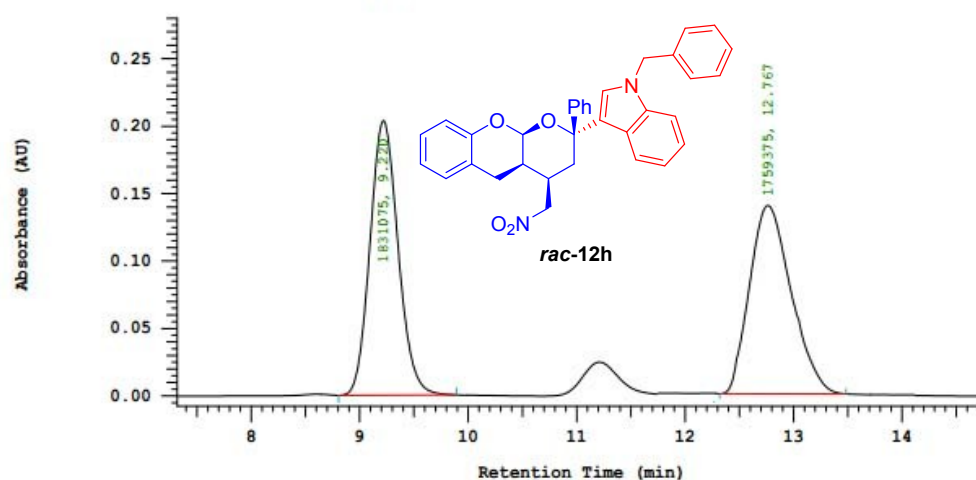
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	15.613	79548	1.098	BB
2	53.173	7163168	98.902	BB
		7242716	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

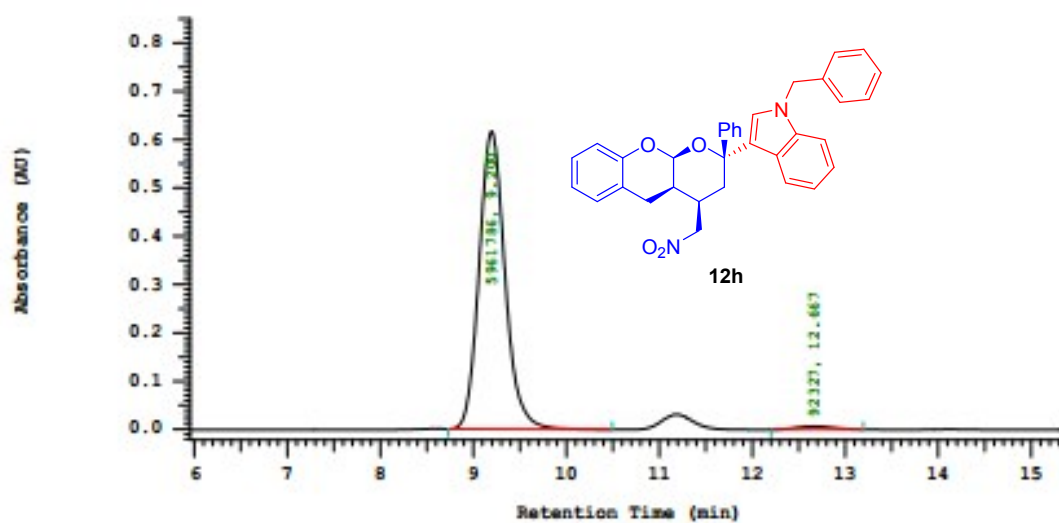


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.220	1831075	50.998	BB
2	12.767	1759375	49.002	BB
		3590450	100.000	

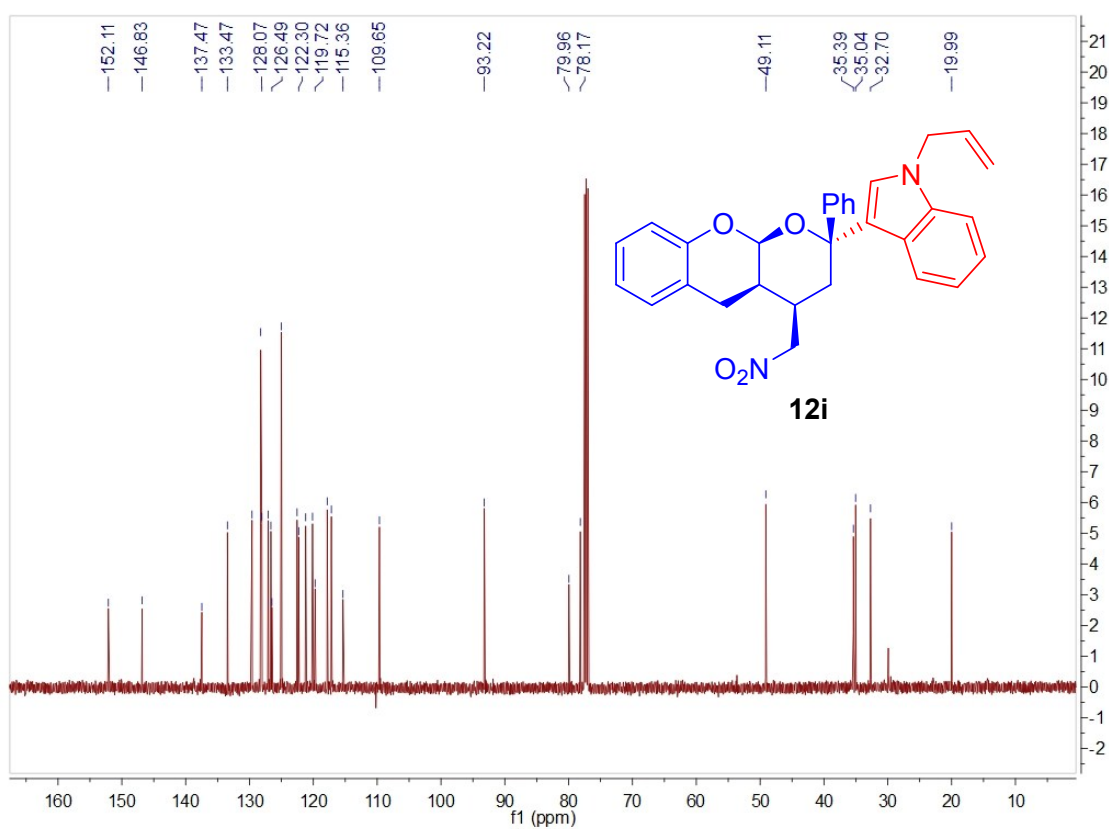
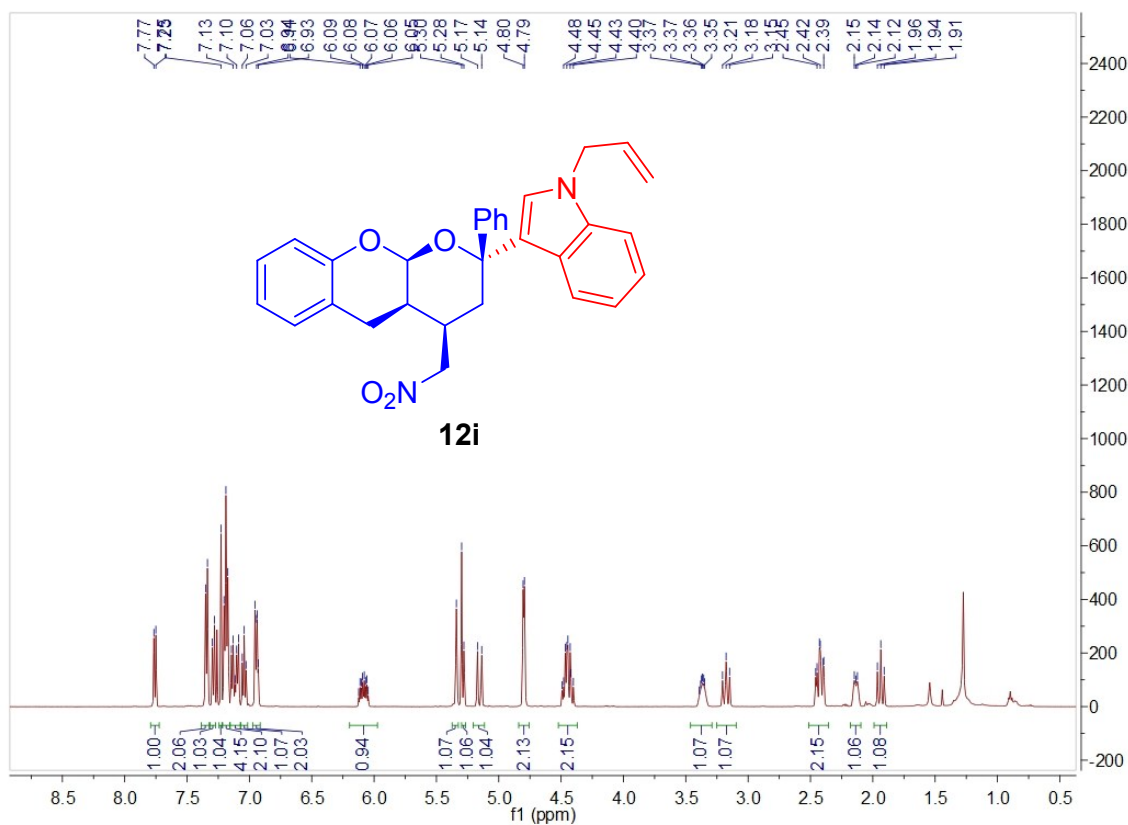
Chrom Type: Fixed WL Chromatogram, 230 nm



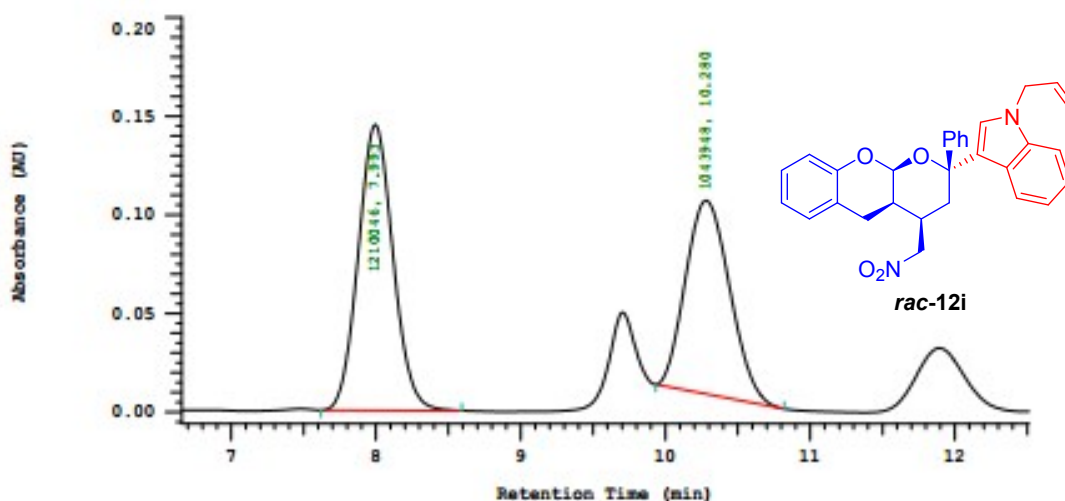
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.200	5961786	98.475	BB
2	12.667	92327	1.525	BB
		6054113	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

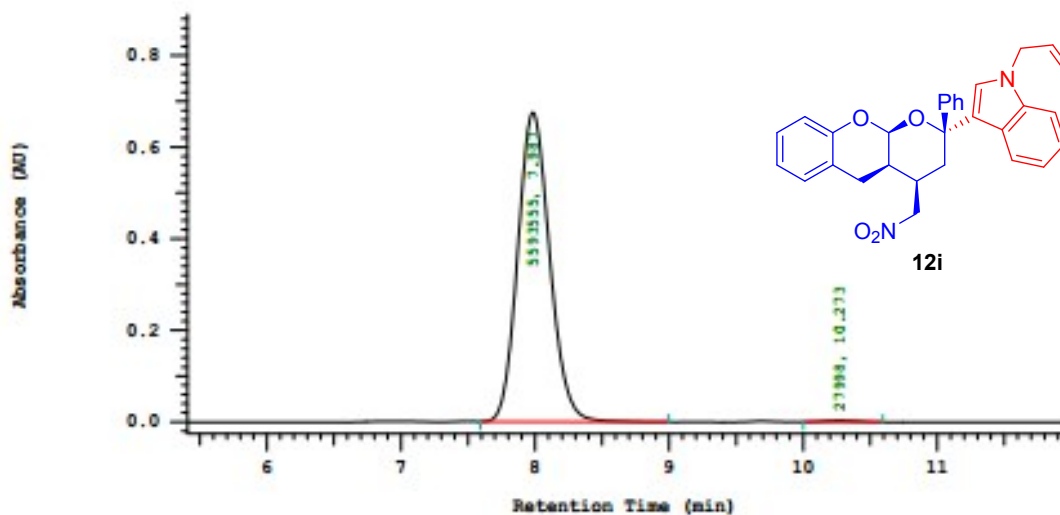


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.993	1210046	53.685	BB
2	10.280	1043948	46.315	BB
		2253994	100.000	

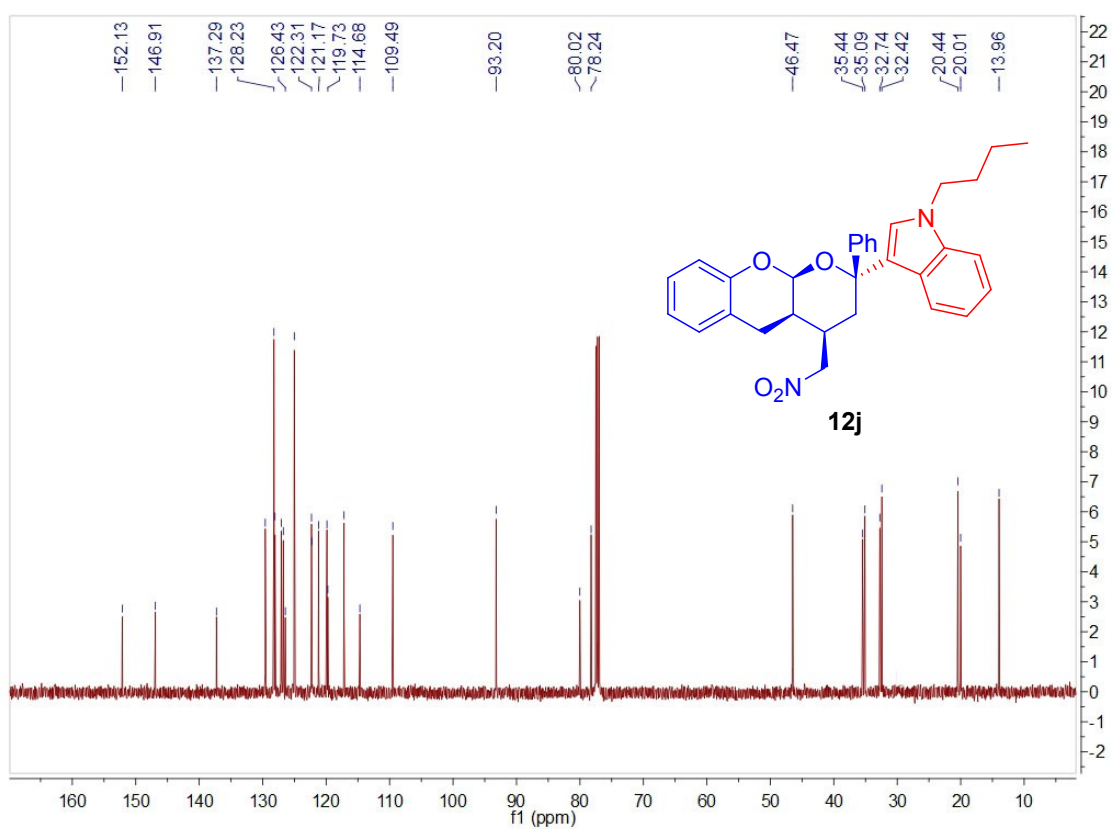
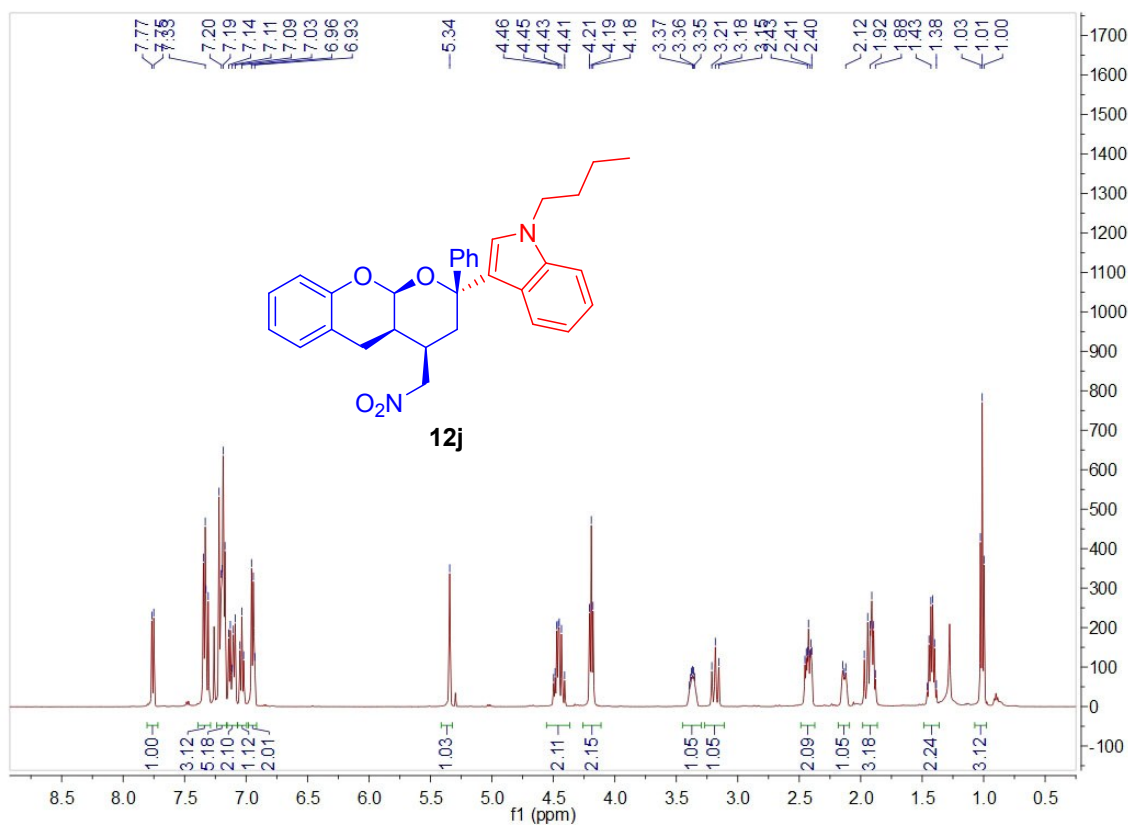
Chrom Type: Fixed WL Chromatogram, 230 nm

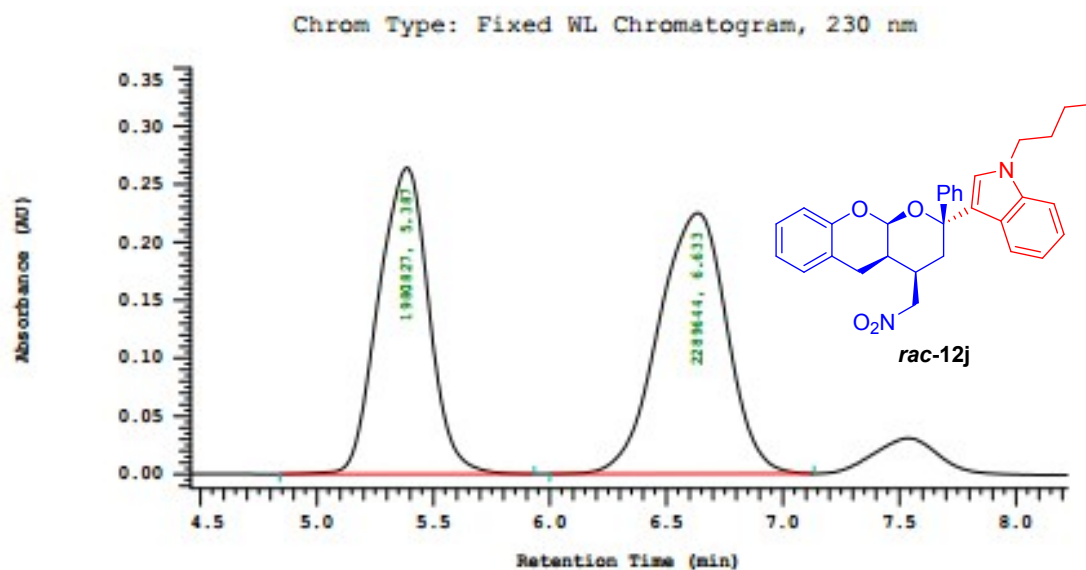


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.987	5593555	99.502	BB
2	10.273	27998	0.498	BB
		5621553	100.000	



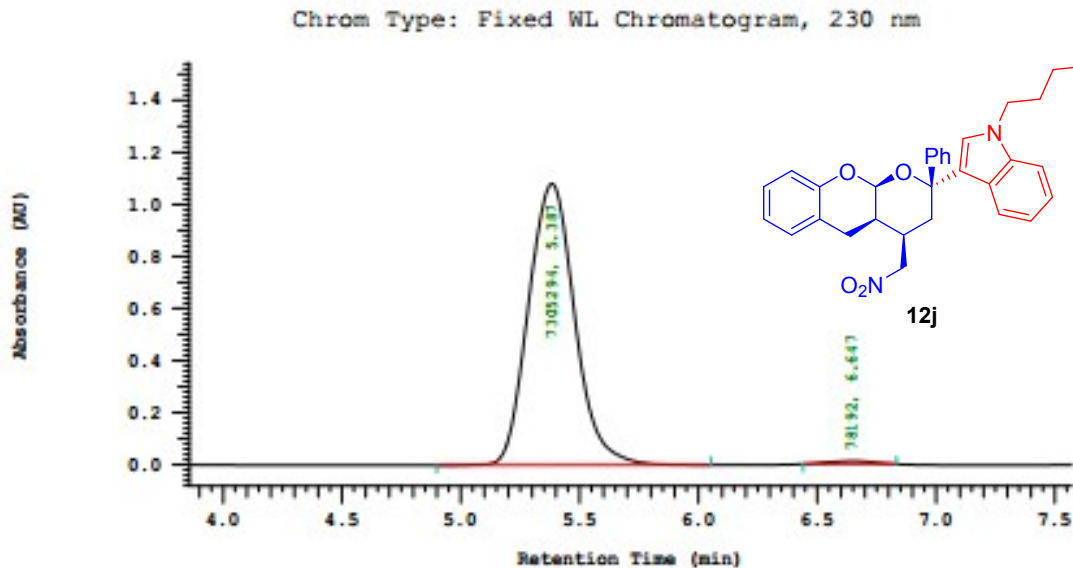


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	5.387	1980827	46.384	BB
2	6.633	2289644	53.616	BB
		4270471	100.000	

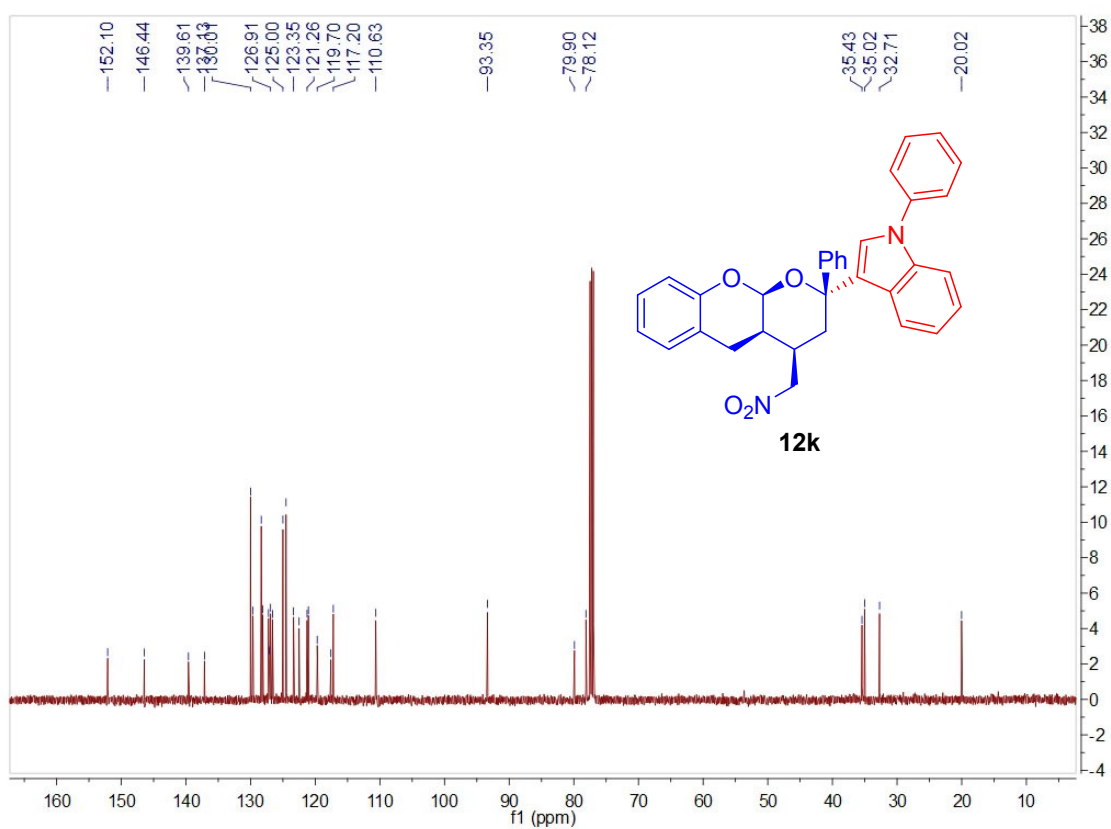
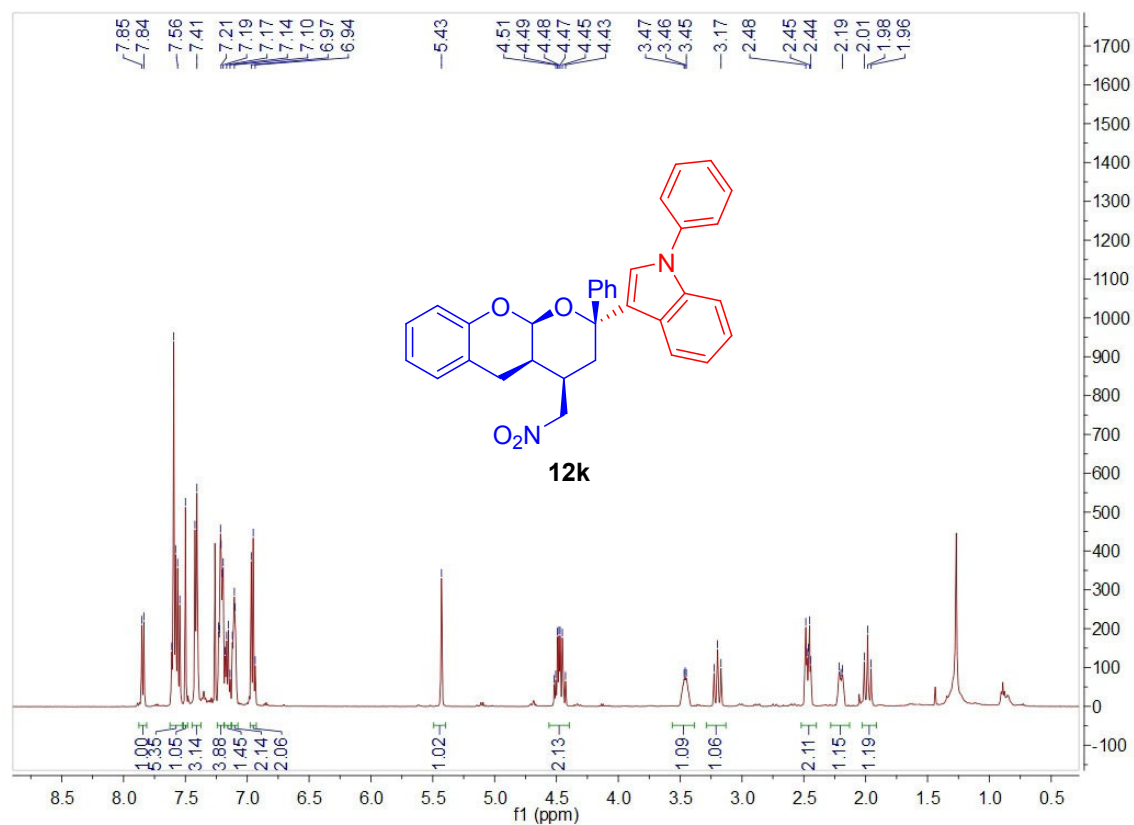


Chrom Type: Fixed WL Chromatogram, 230 nm

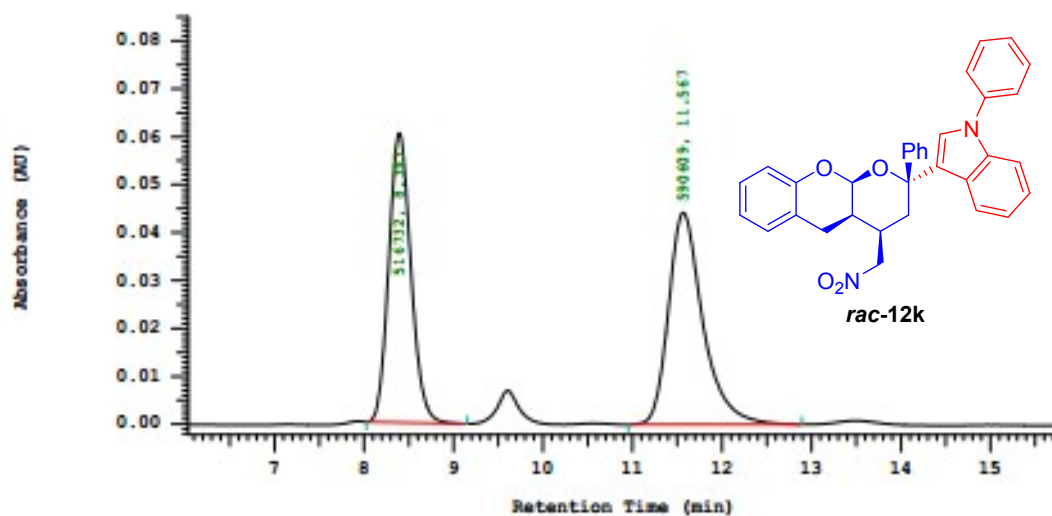
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	5.387	7305294	98.941	BB
2	6.647	78192	1.059	BB
		7383486	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

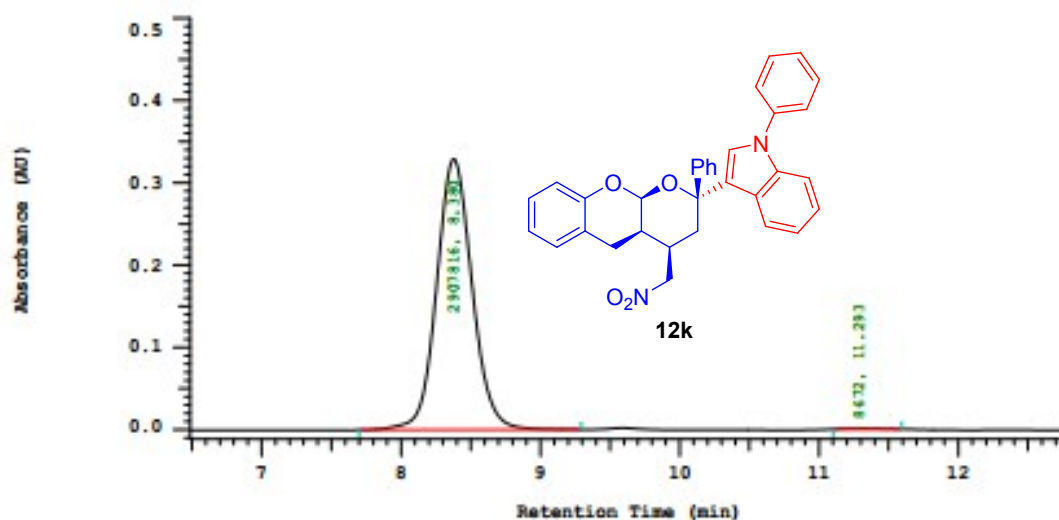


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	8.393	516732	46.664	BB
2	11.567	590609	53.336	BB
		1107341	100.000	

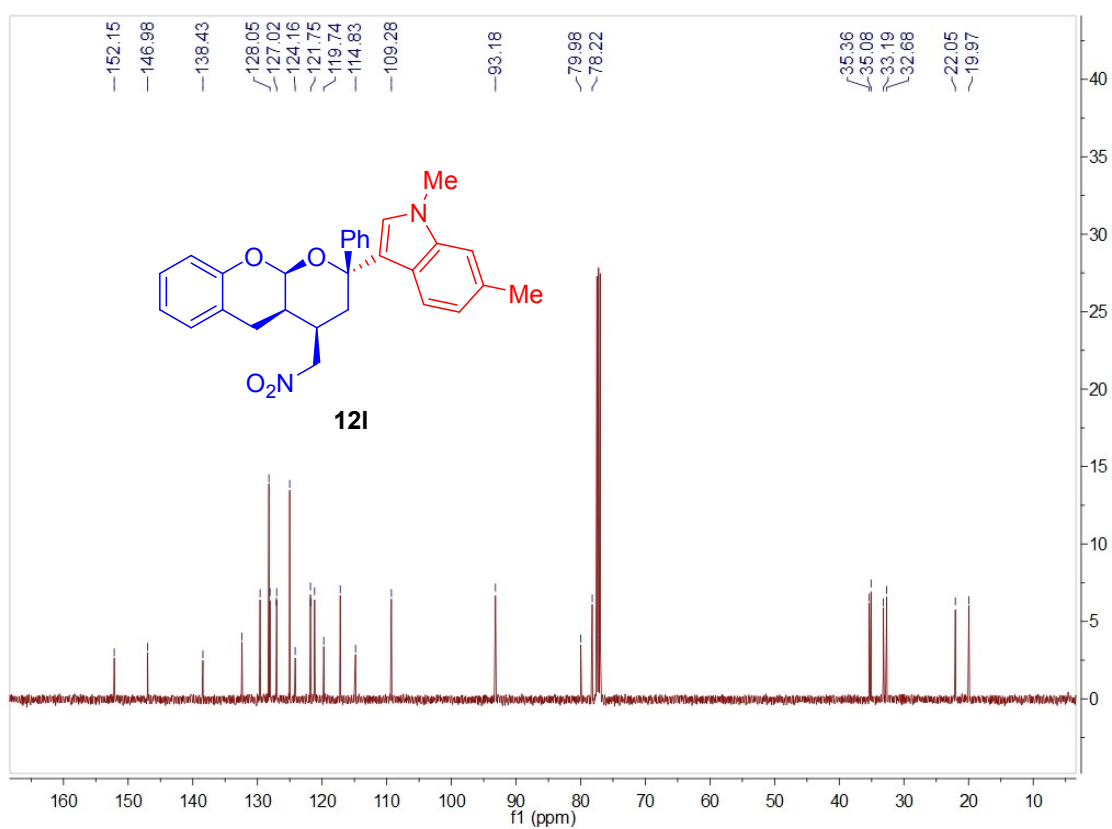
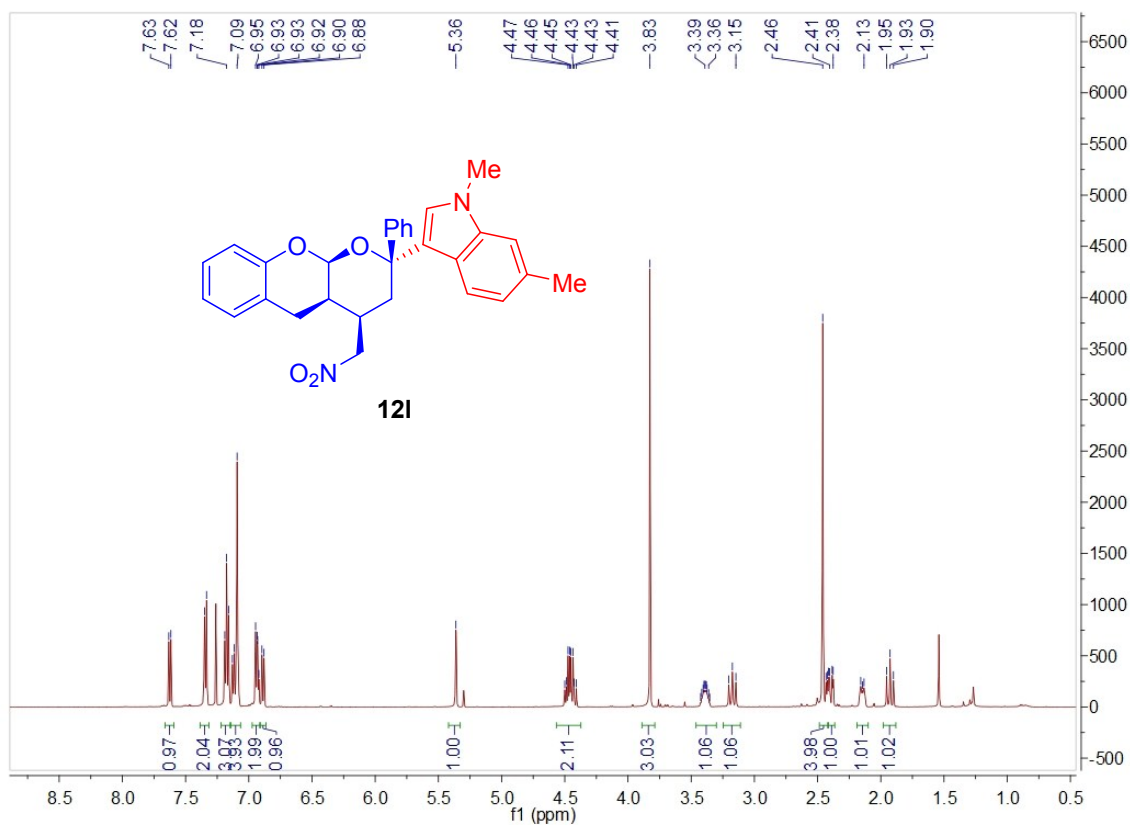
Chrom Type: Fixed WL Chromatogram, 230 nm

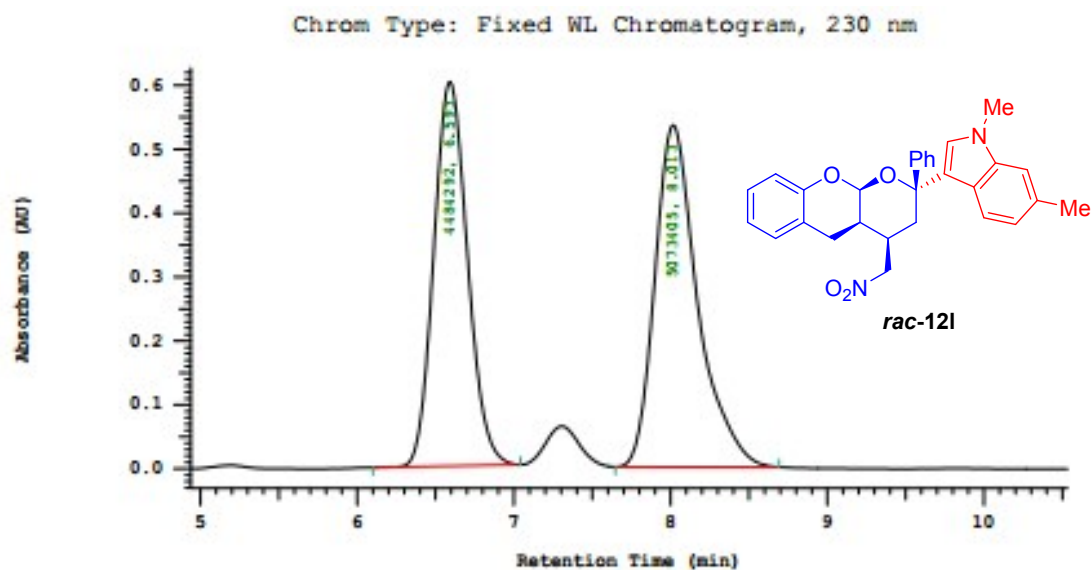


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

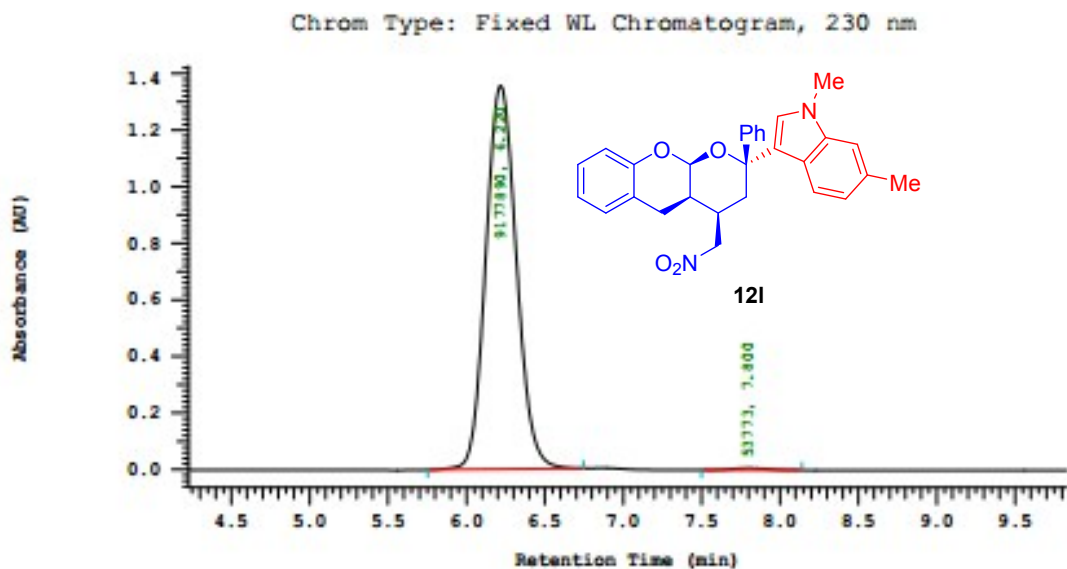
No.	RT	Area	Area %	BC
1	8.380	2907816	99.703	BB
2	11.293	8672	0.297	BB
		2916488	100.000	





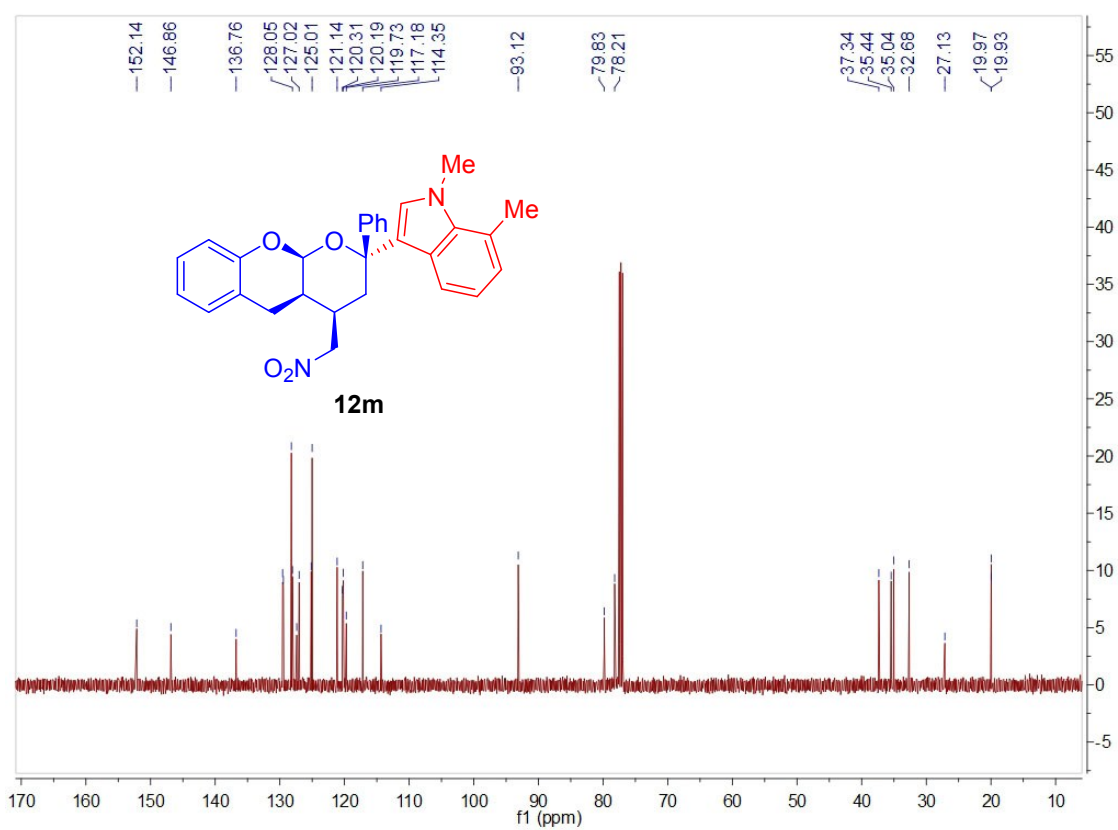
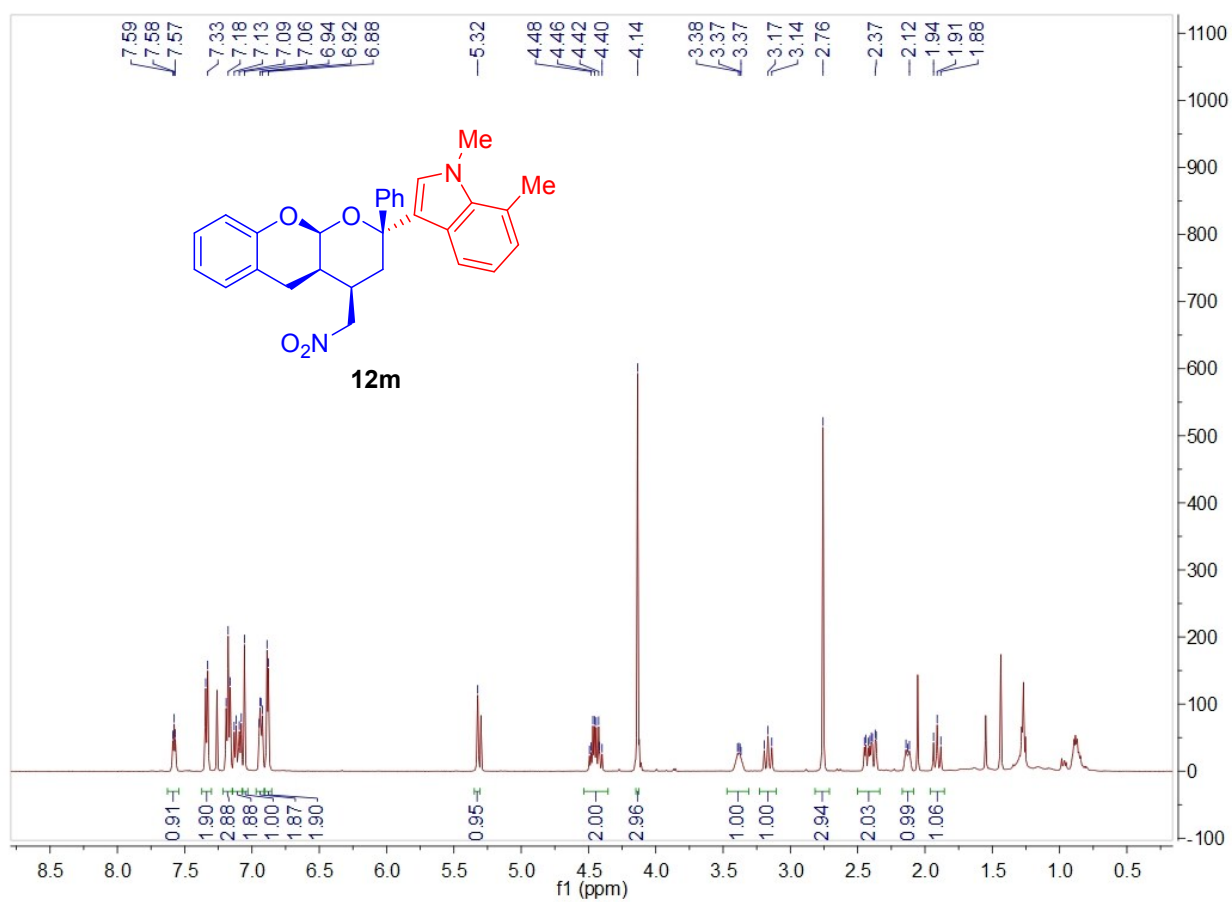
Chrom Type: Fixed WL Chromatogram, 230 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.593	4484292	46.918	BB
2	8.013	5073405	53.082	BB
		9557697	100.000	

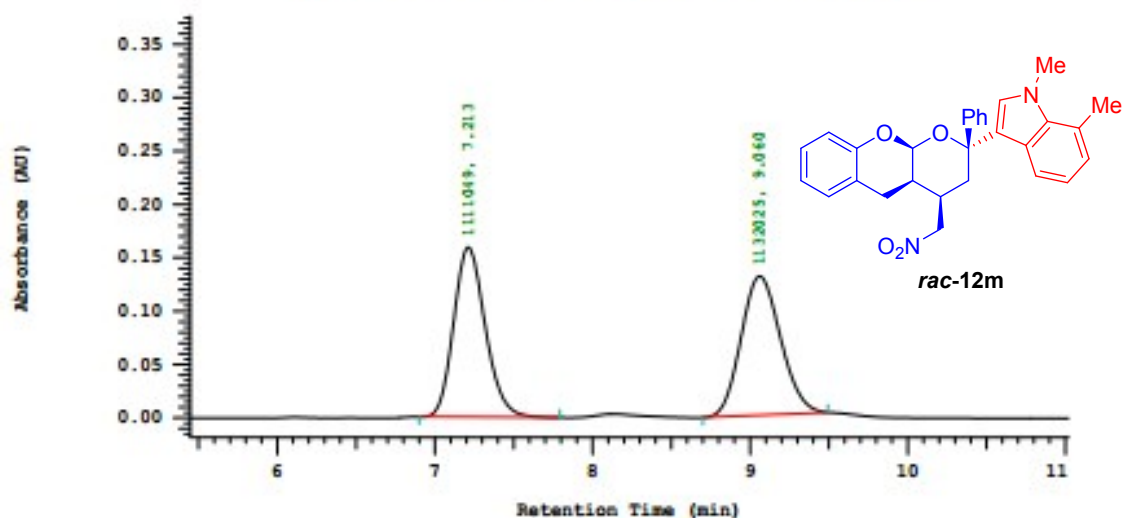


Chrom Type: Fixed WL Chromatogram, 230 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.220	9177890	99.418	BB
2	7.800	53773	0.582	BB
		9231663	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

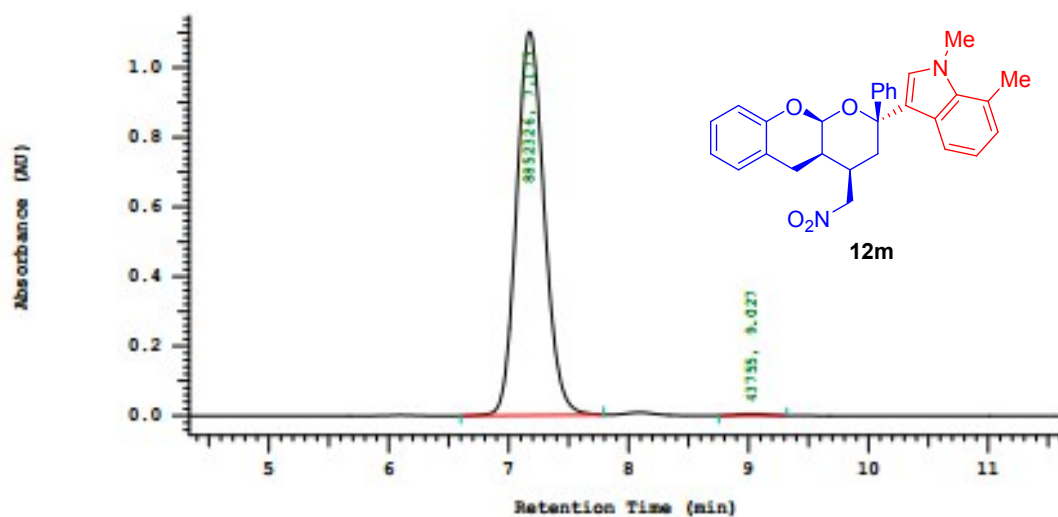


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.213	1111049	49.532	BB
2	9.060	1132025	50.468	BB
		2243074	100.000	

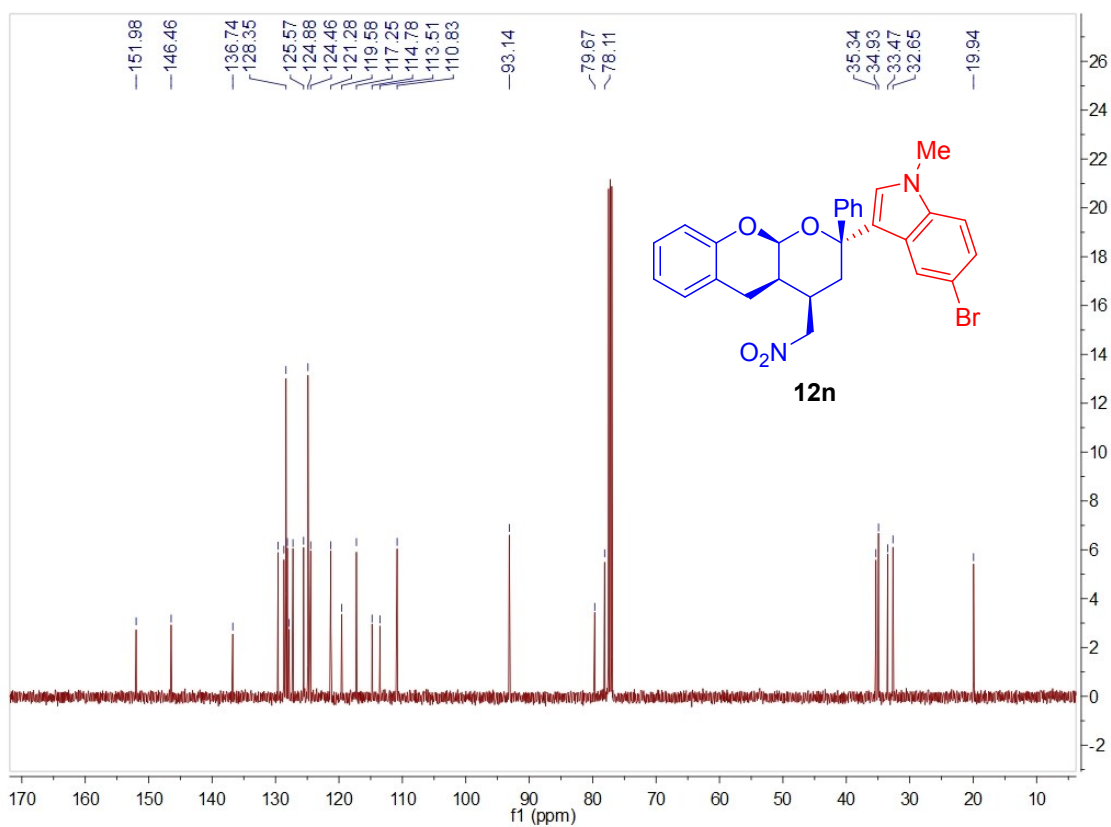
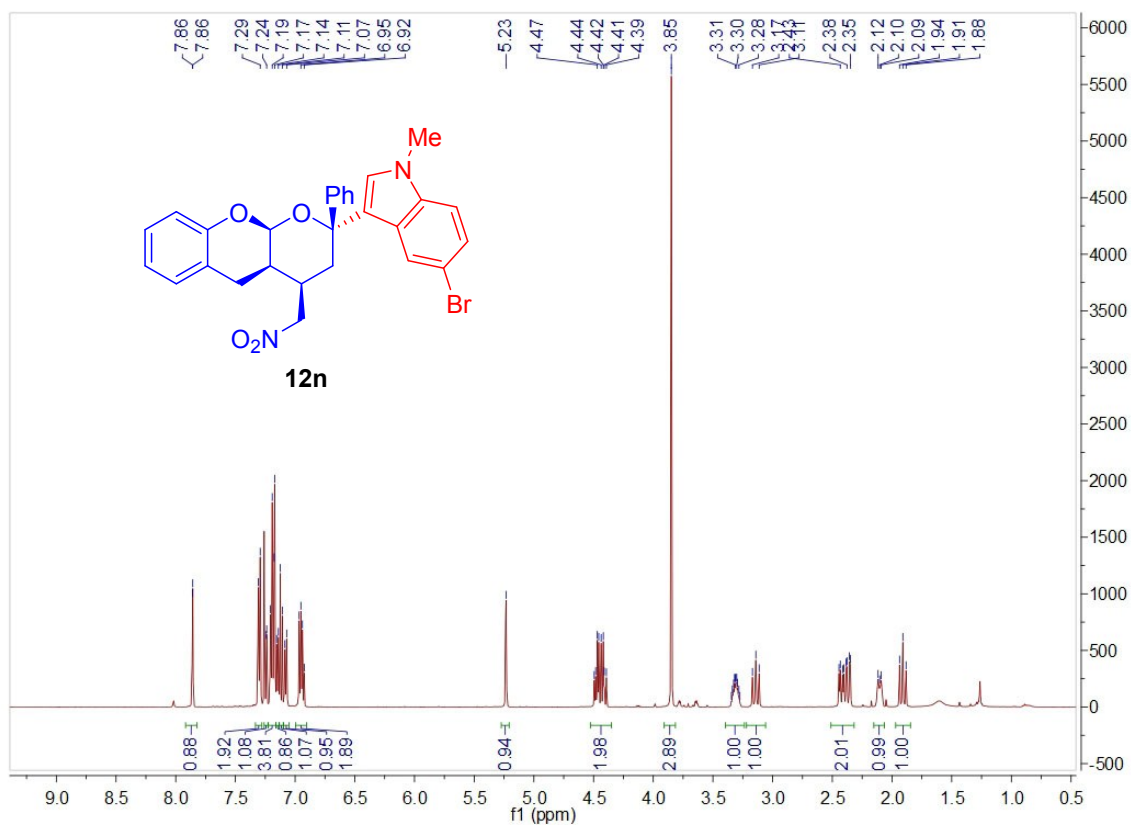
Chrom Type: Fixed WL Chromatogram, 230 nm



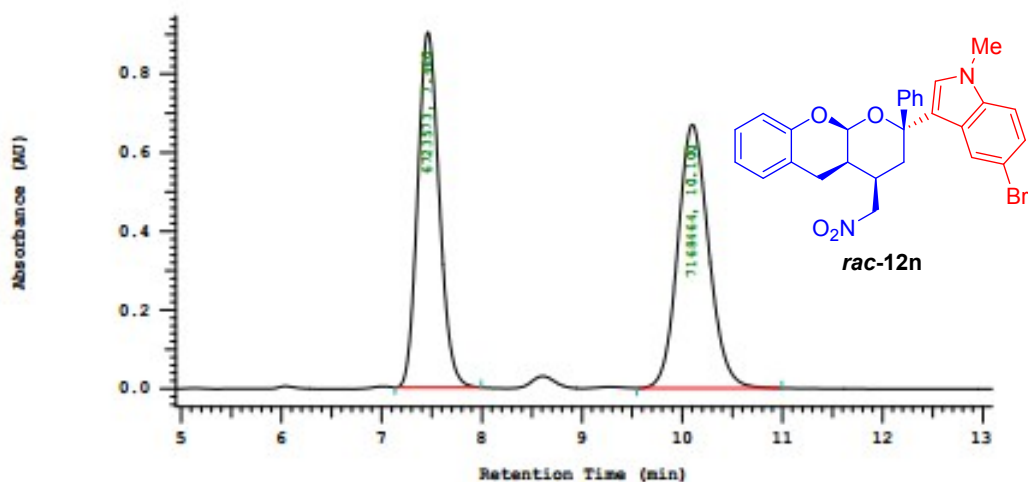
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.173	8852326	99.508	BB
2	9.027	43755	0.492	BB
		8896081	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm



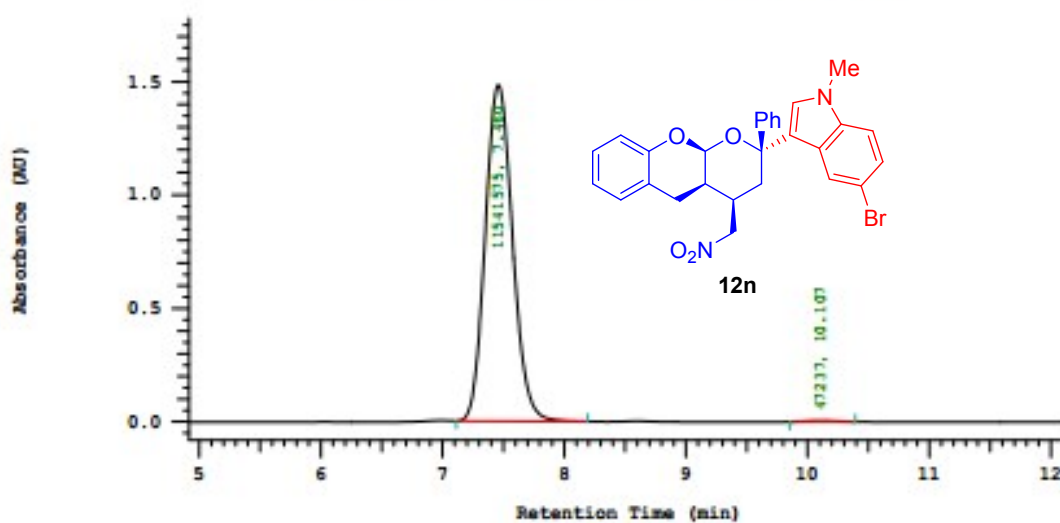
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.460	6723573	48.399	BB
2	10.100	7168464	51.601	BB
		13892037	100.000	

Chrom Type: Fixed WL Chromatogram, 230 nm

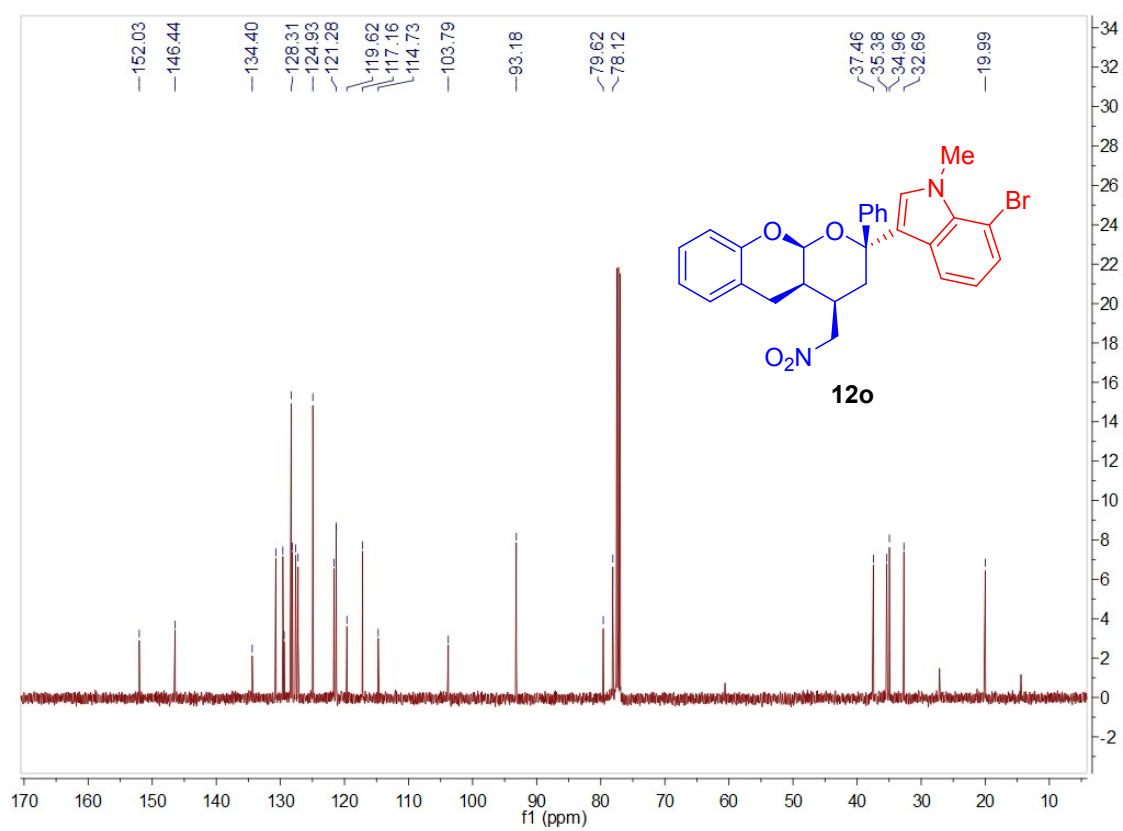
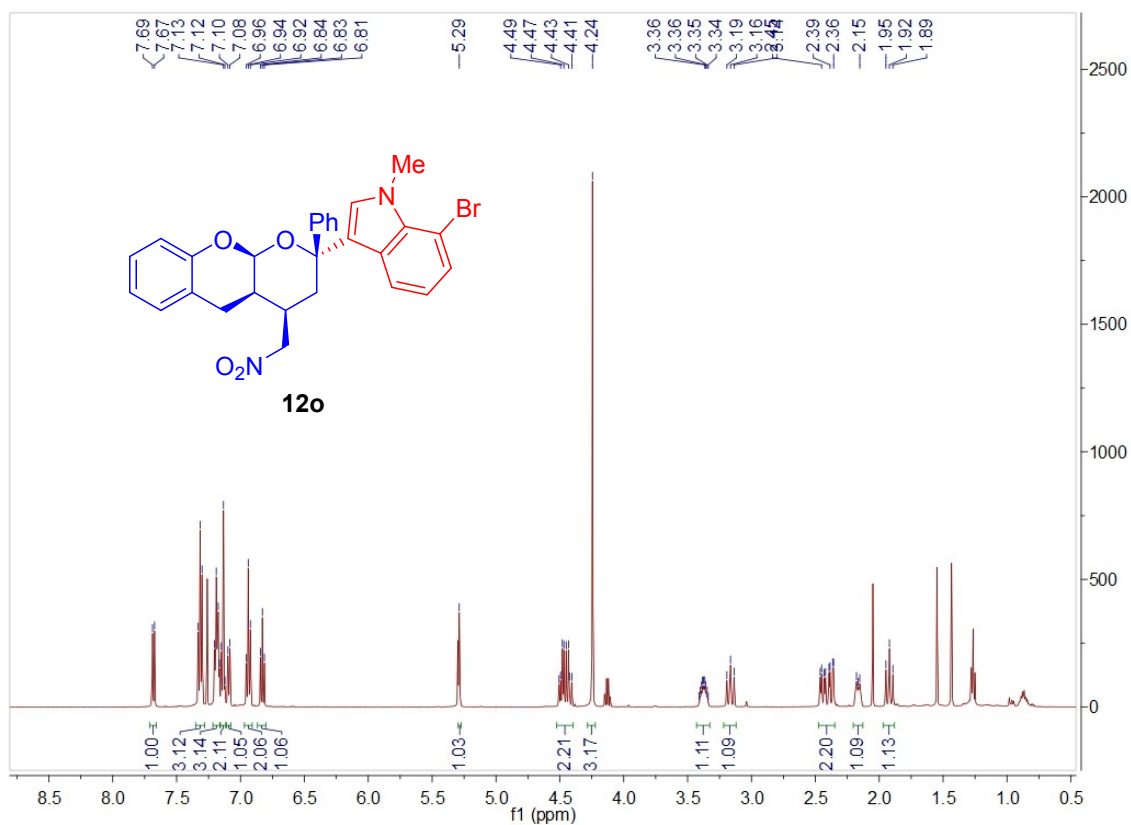


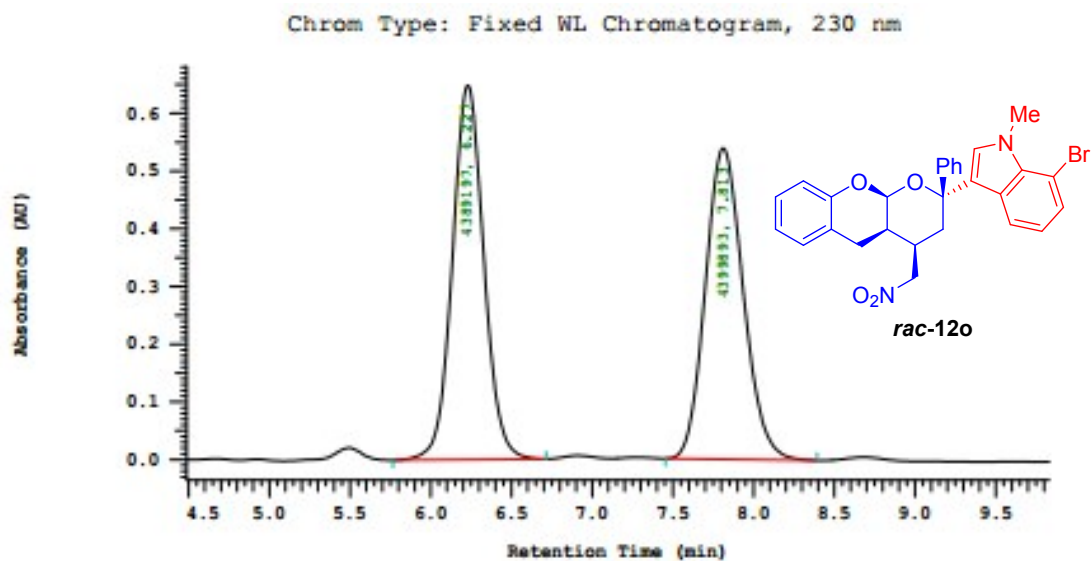
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	7.460	11541575	99.592	BB
2	10.107	47237	0.408	BB
		11588812	100.000	



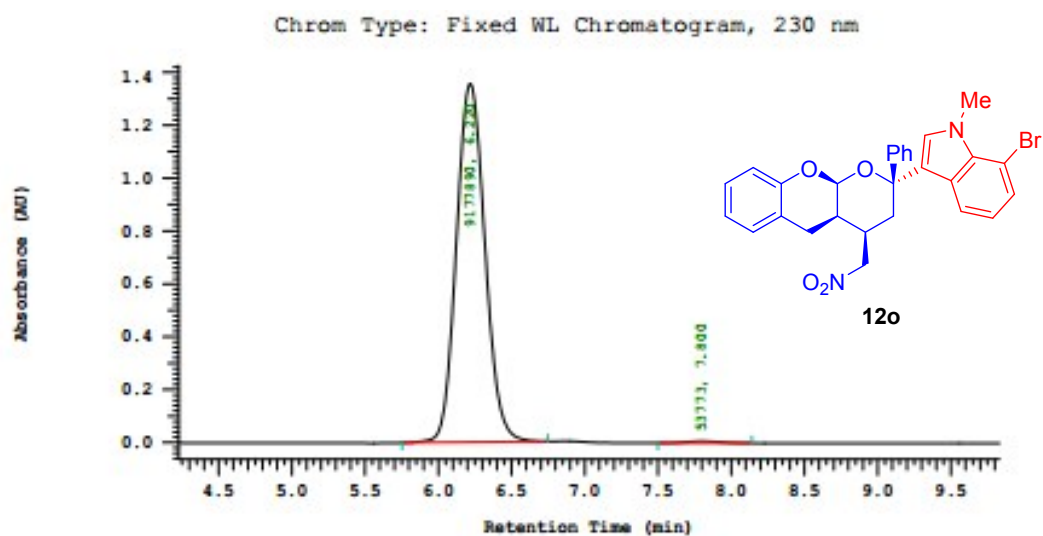


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.227	4389197	49.939	BB
2	7.813	4399893	50.061	BB
		8789090	100.000	

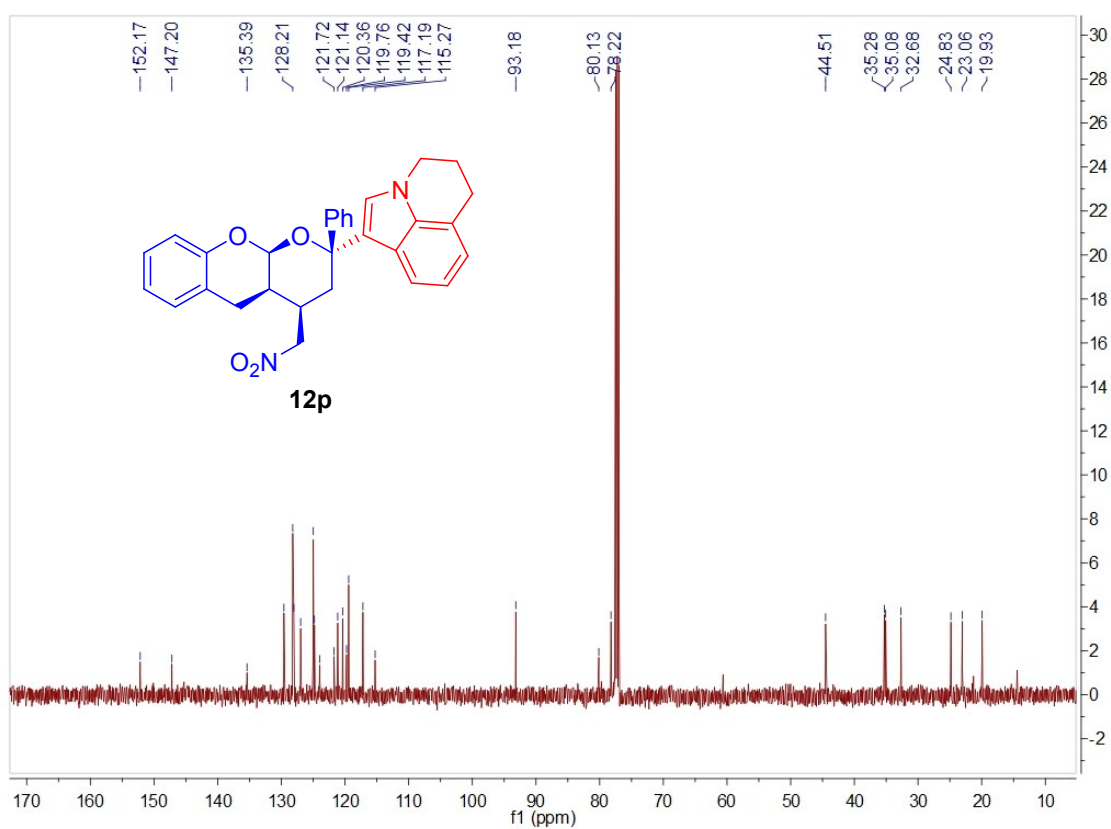
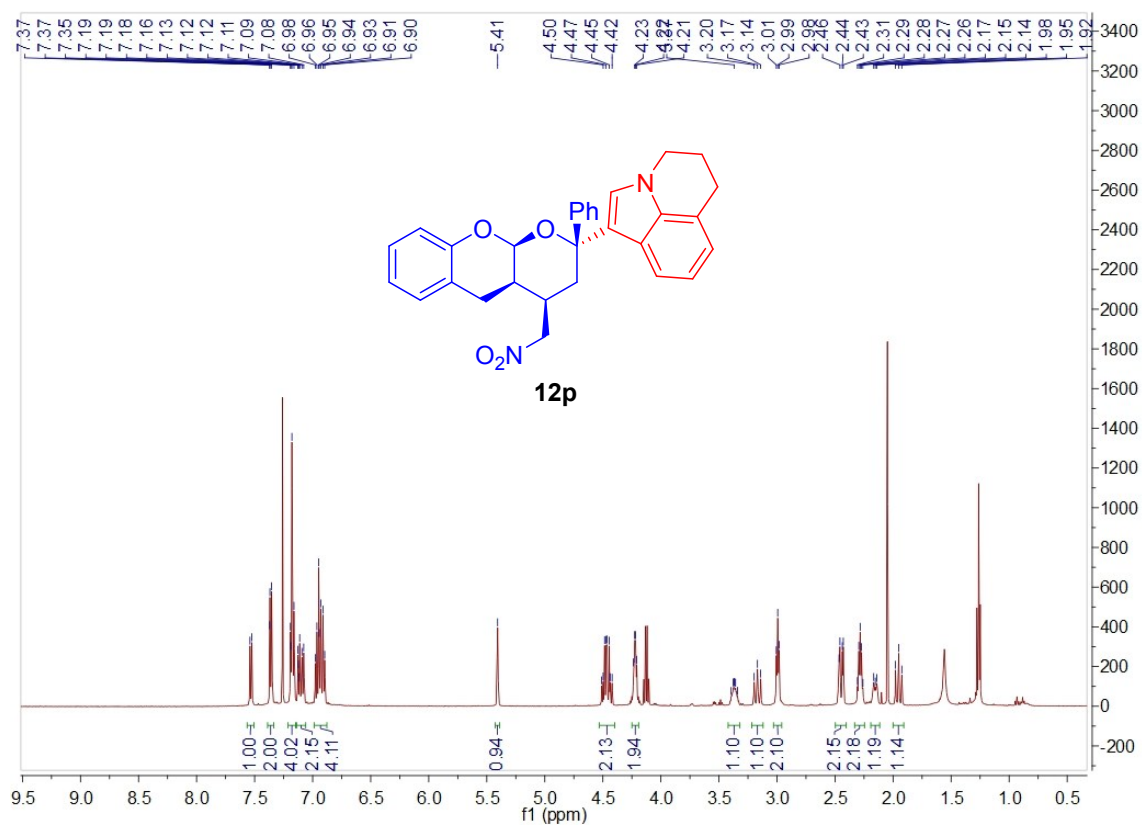


Chrom Type: Fixed WL Chromatogram, 230 nm

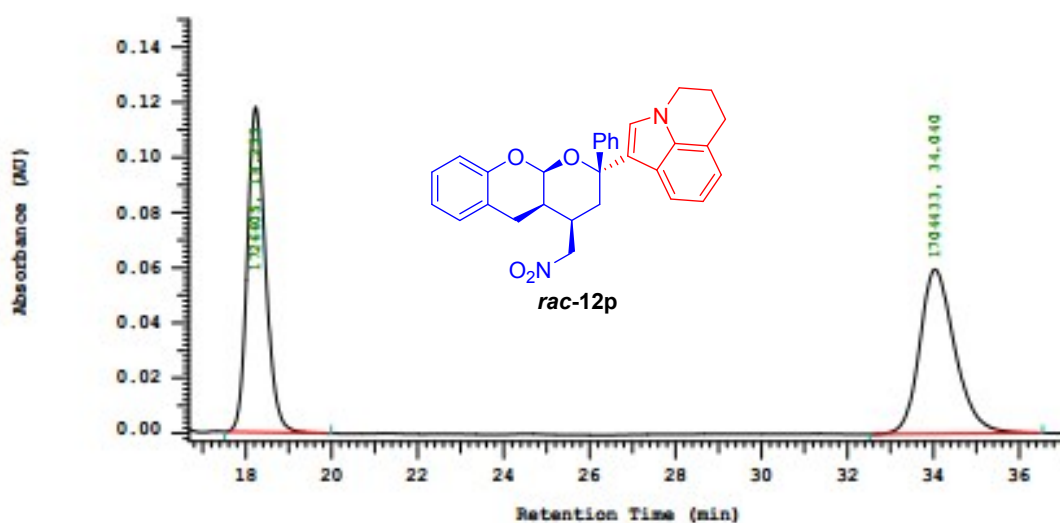
Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.220	9177890	99.418	BB
2	7.800	53773	0.582	BB
		9231663	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

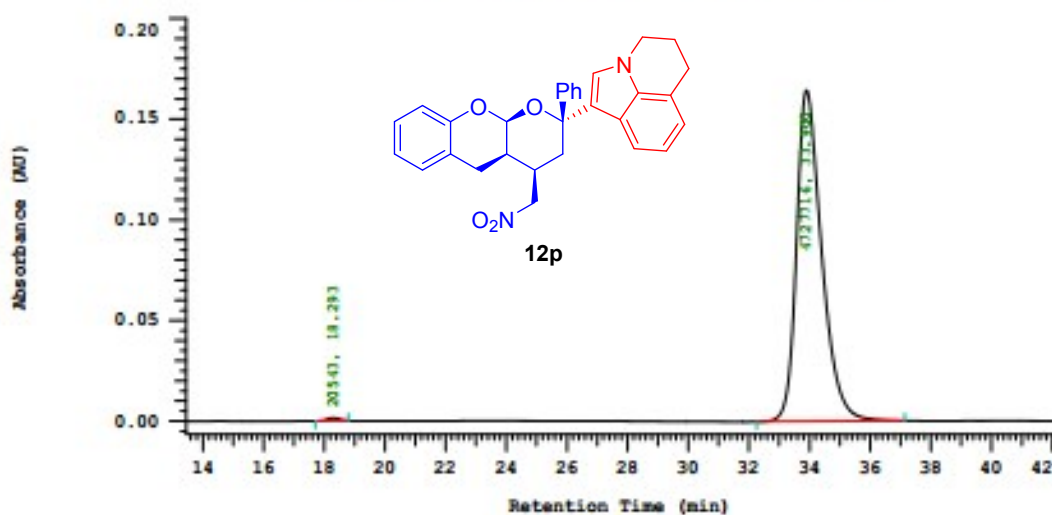


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.233	1726605	50.323	BB
2	34.040	1704433	49.677	BB
		3431038	100.000	

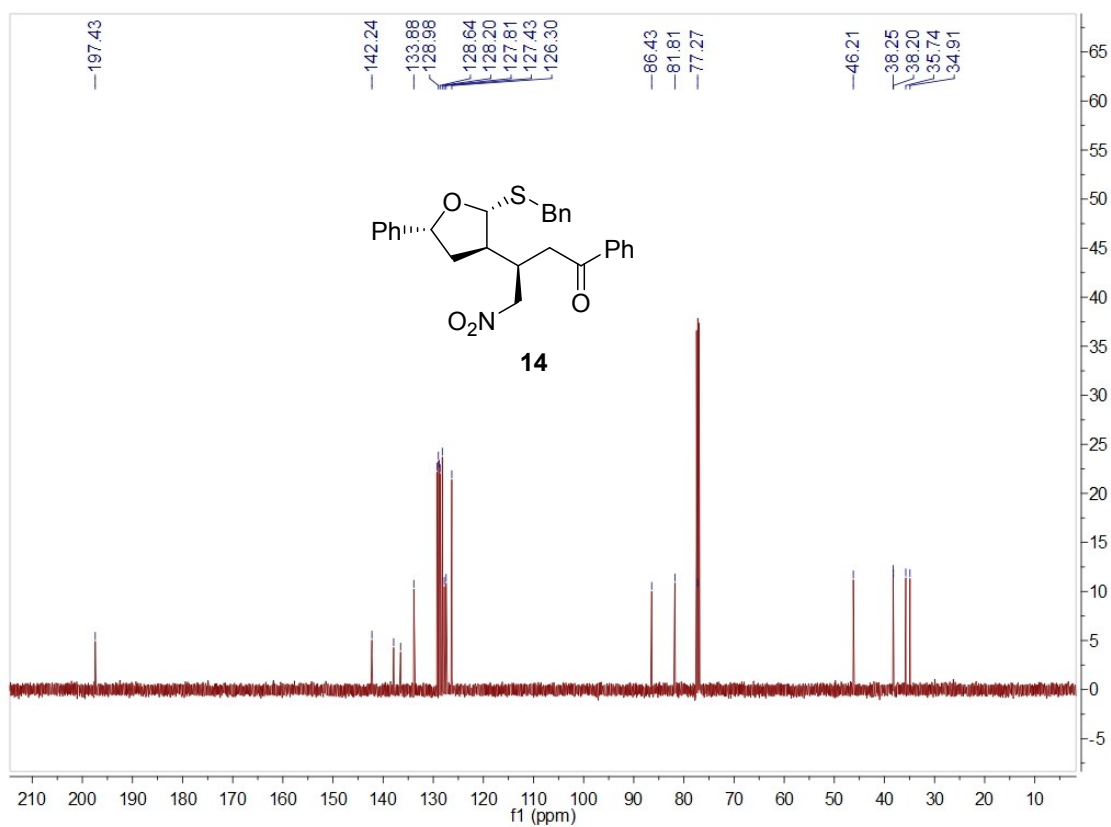
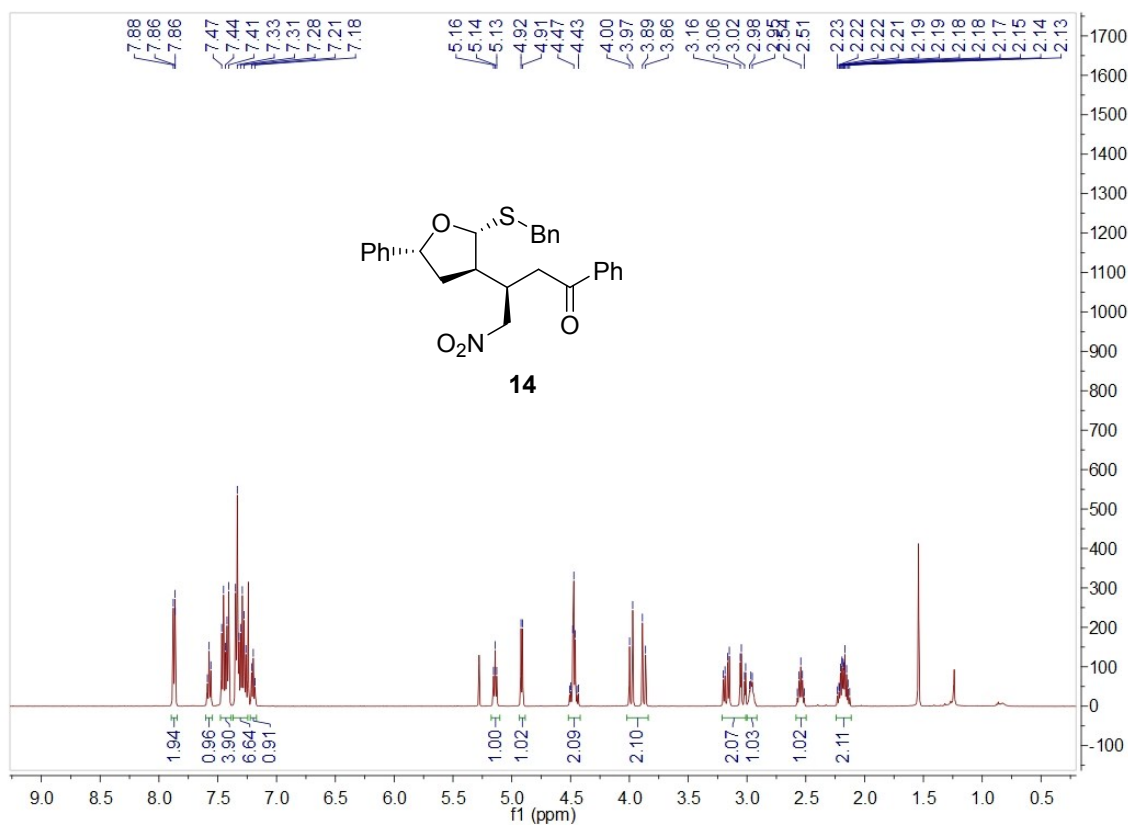
Chrom Type: Fixed WL Chromatogram, 230 nm



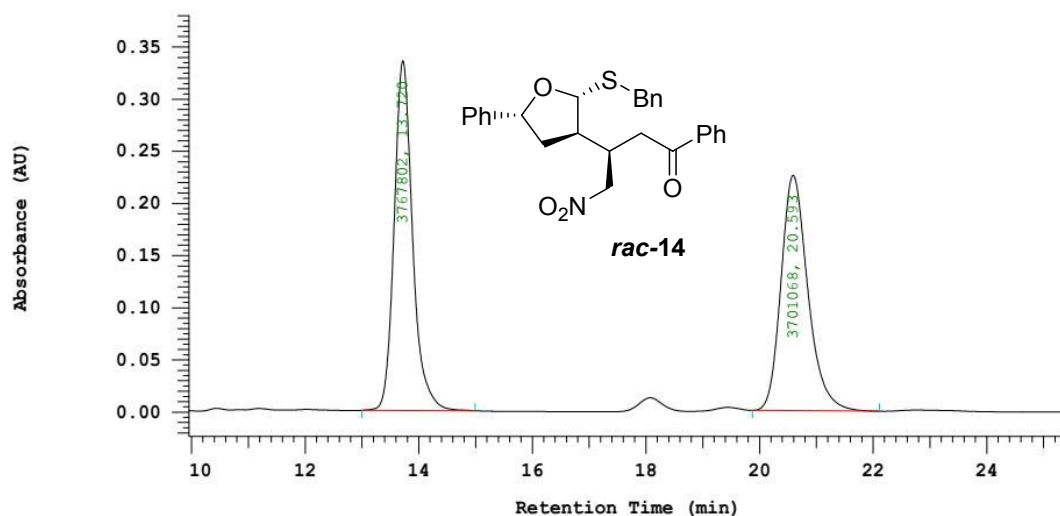
Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.293	20543	0.433	BB
2	33.900	4727716	99.567	BB
		4748259	100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

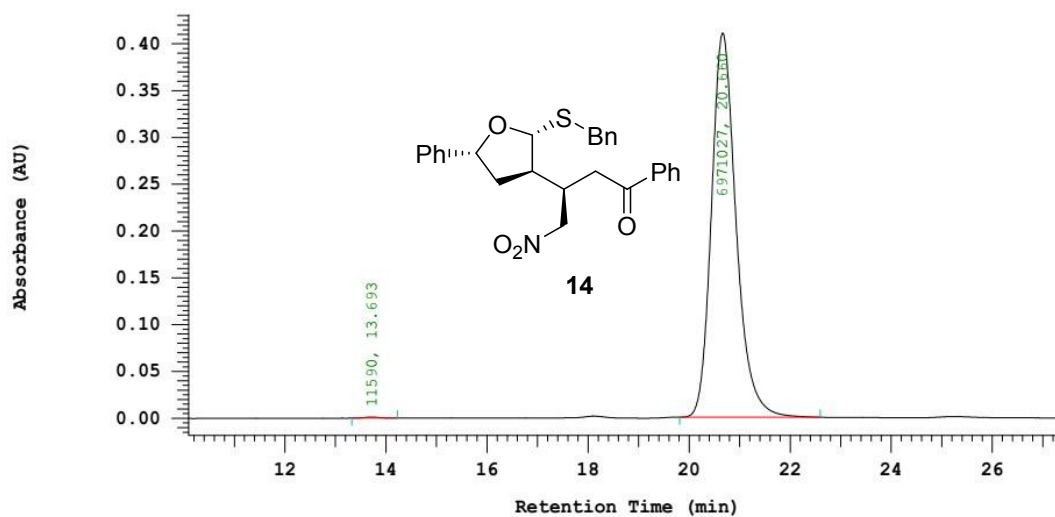


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.720	3767802	50.447	BB
2	20.593	3701068	49.553	BB
7468870			100.000	

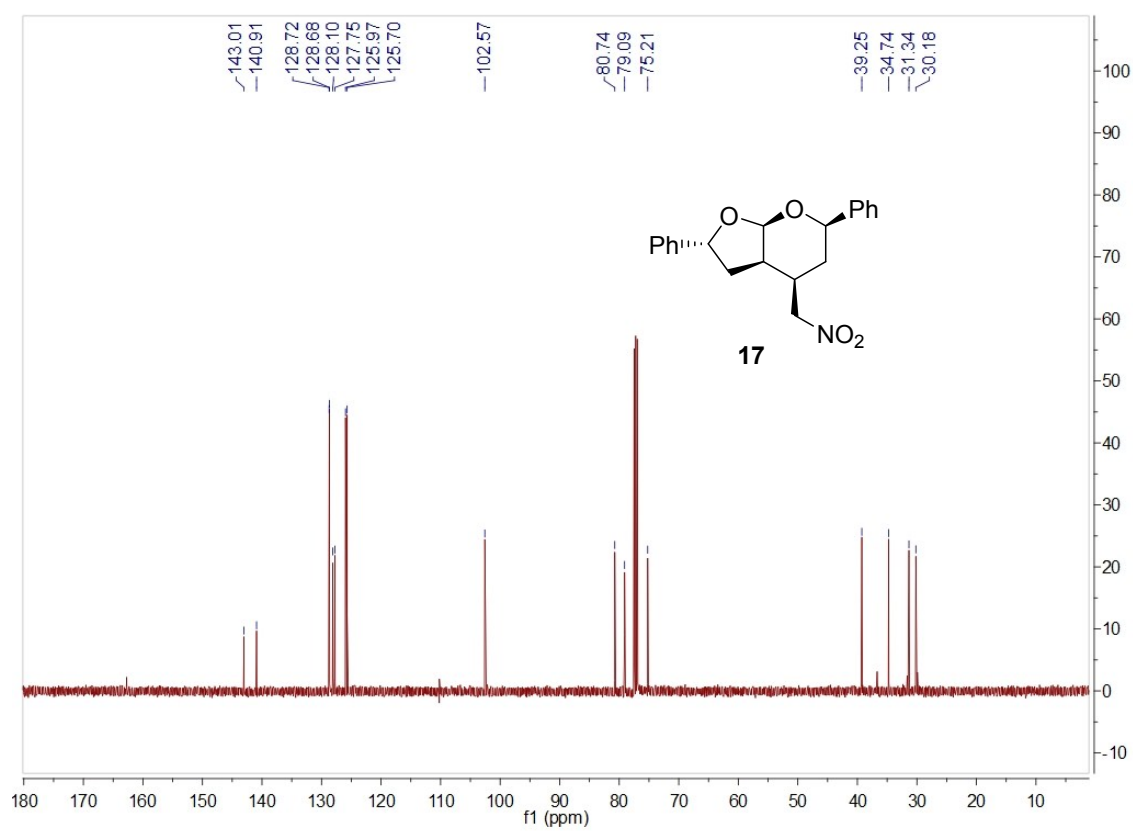
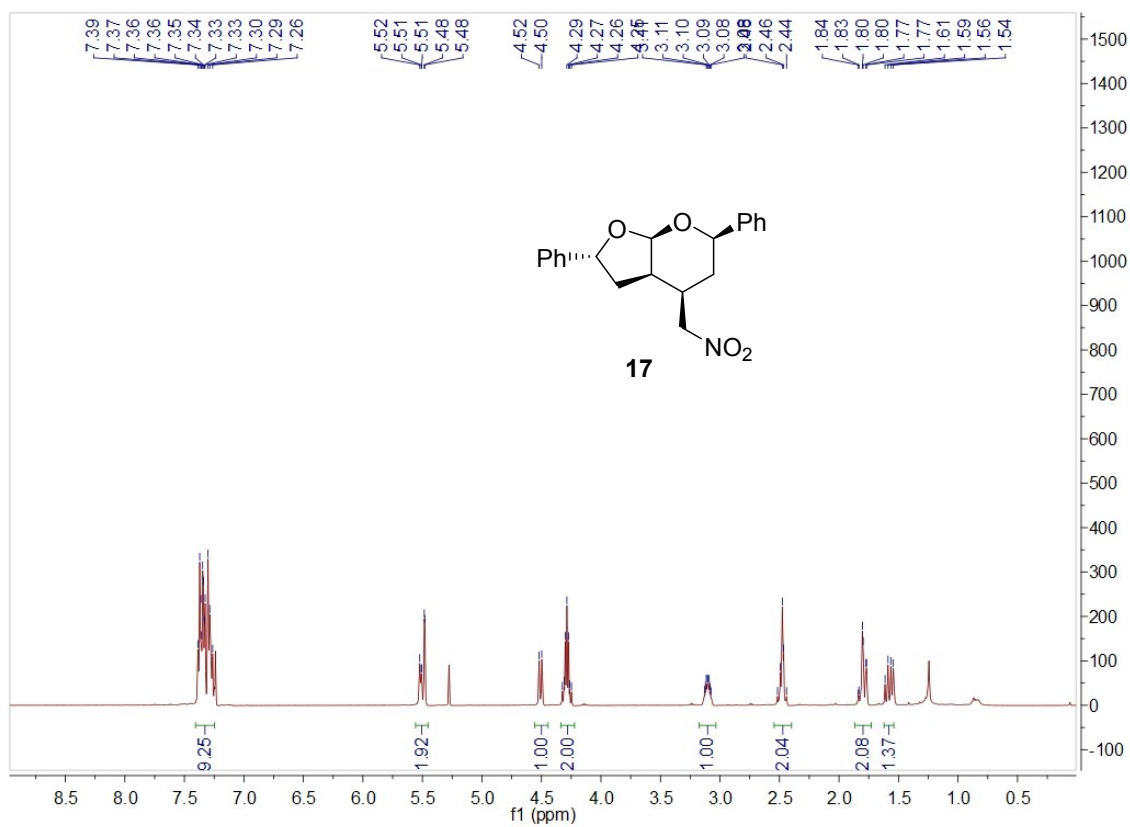
Chrom Type: Fixed WL Chromatogram, 210 nm



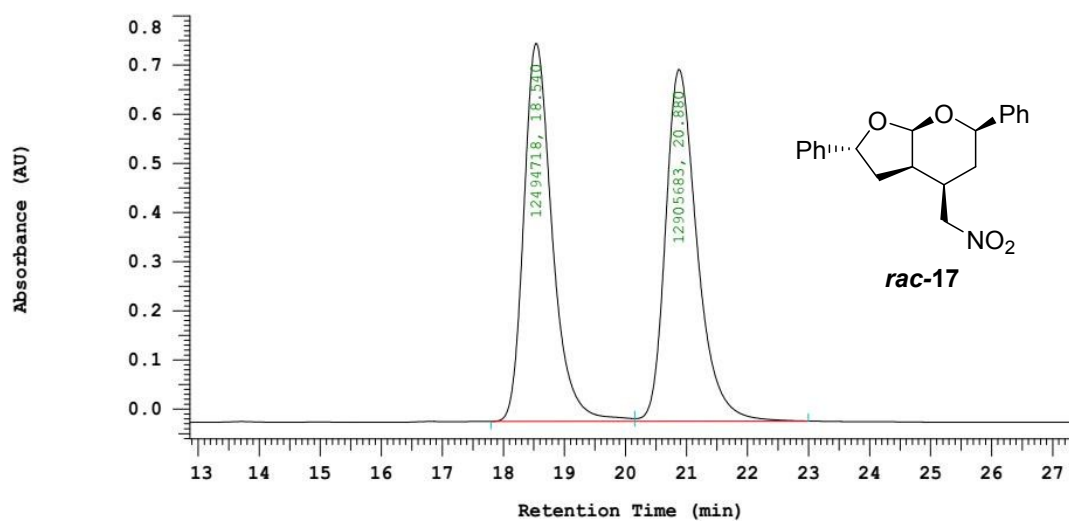
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	13.693	11590	0.166	BB
2	20.660	6971027	99.834	BB
6982617			100.000	



Chrom Type: Fixed WL Chromatogram, 210 nm

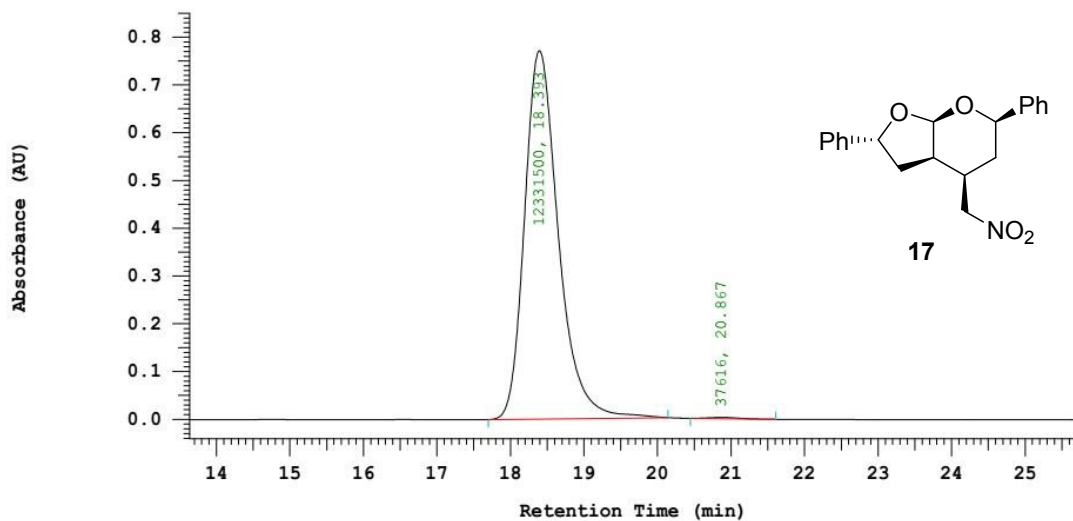


Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.540	12494718	49.191	BV
2	20.880	12905683	50.809	VB
		25400401	100.000	

Chrom Type: Fixed WL Chromatogram, 210 nm

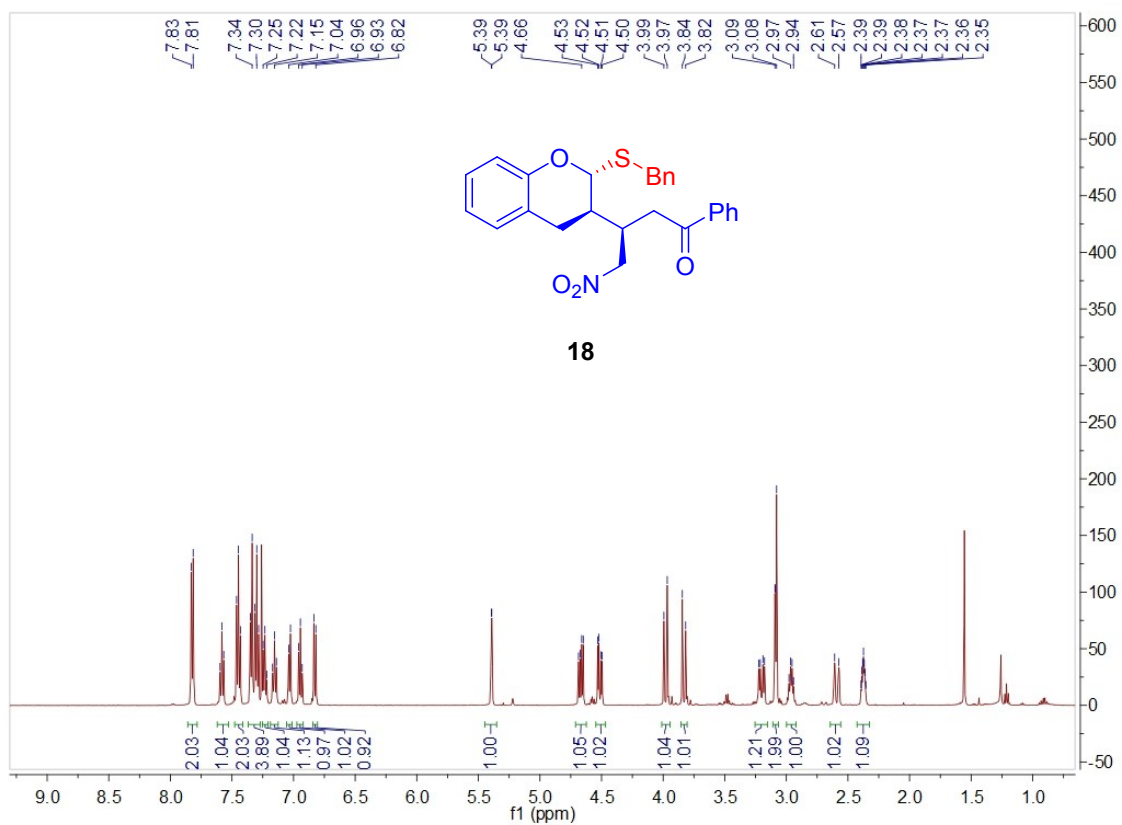
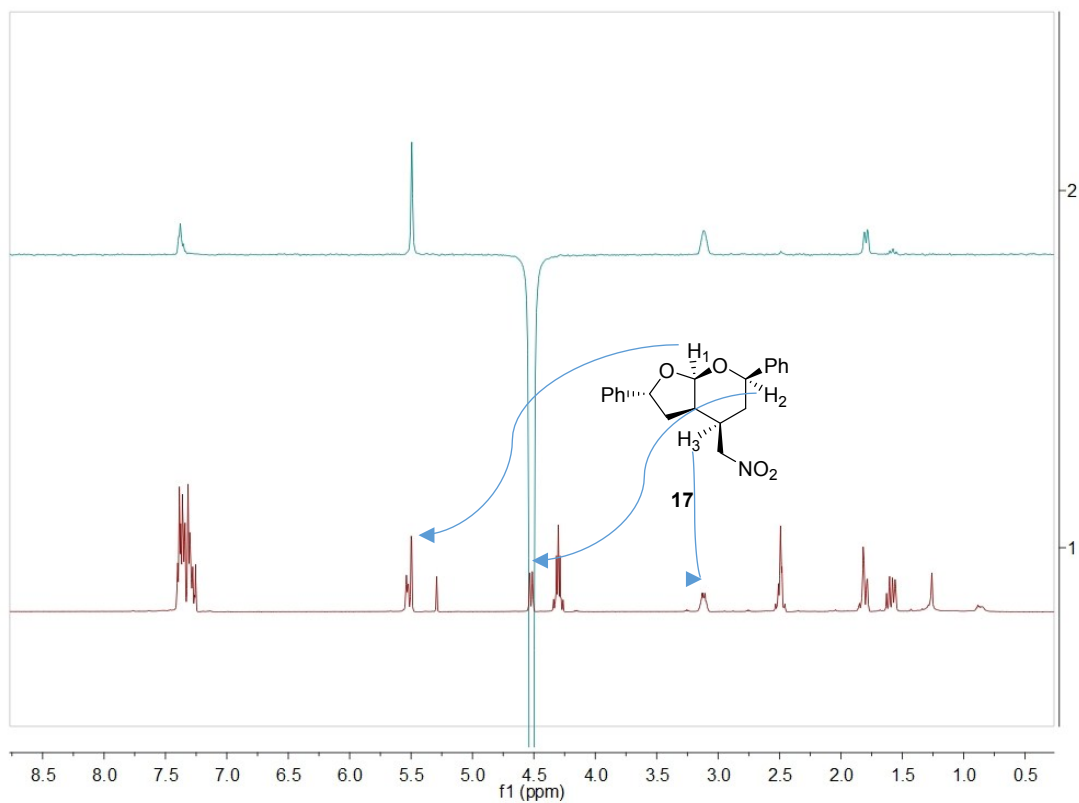


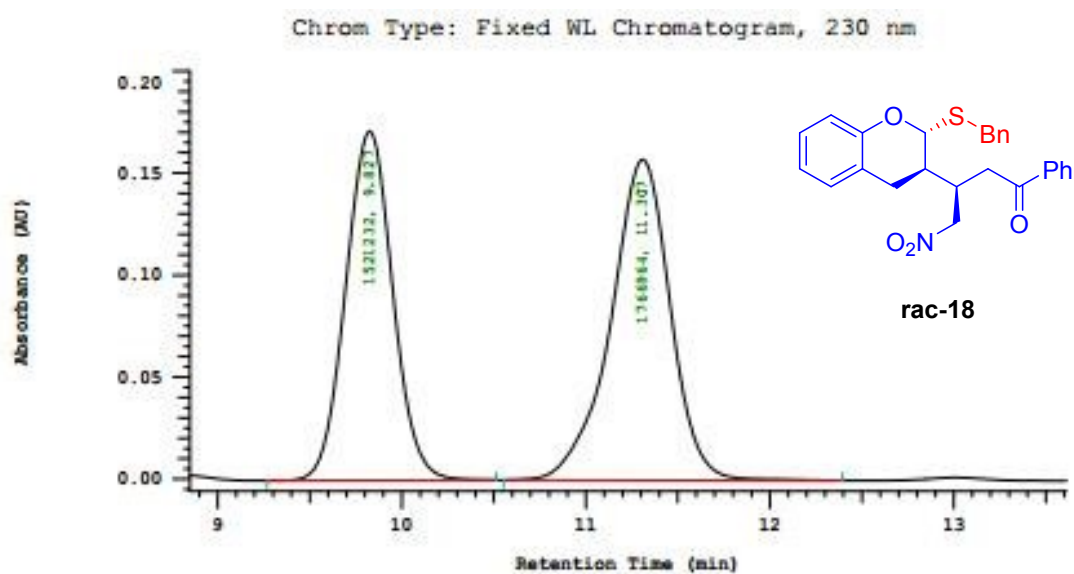
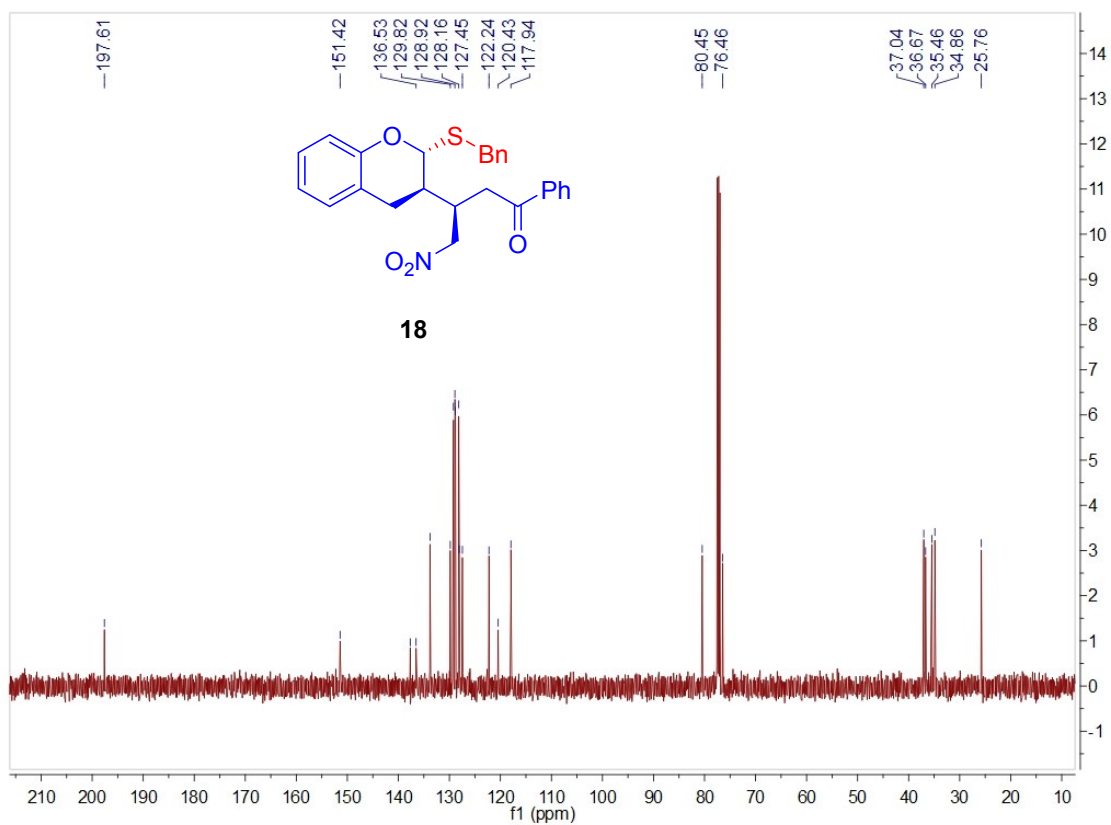
Chrom Type: Fixed WL Chromatogram, 210 nm

Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	18.393	12331500	99.696	BB
2	20.867	37616	0.304	BB
		12369116	100.000	

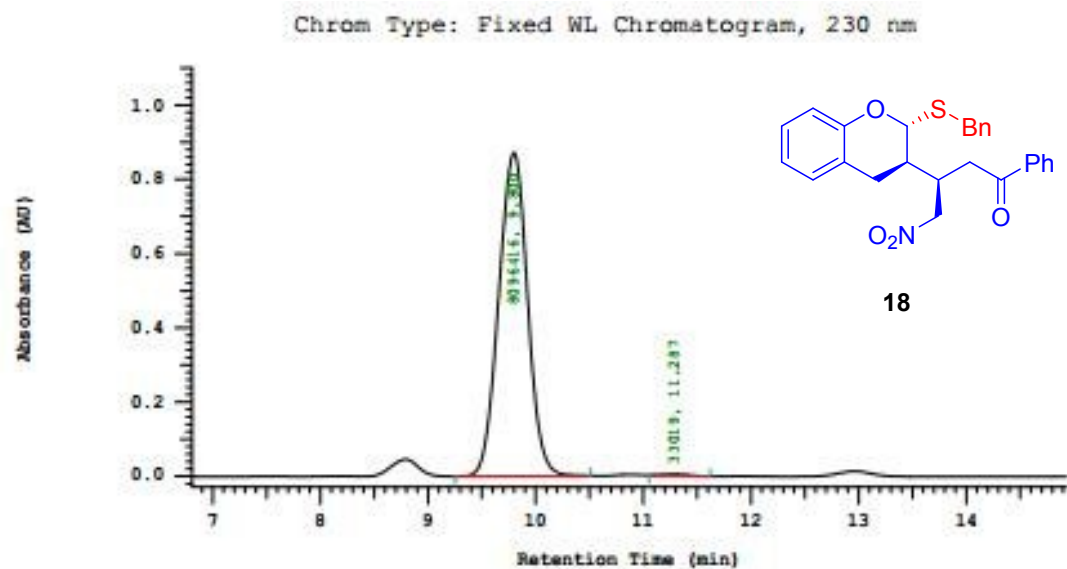
NOE spectra of **17**





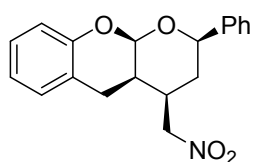
Chrom Type: Fixed WL Chromatogram, 230 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

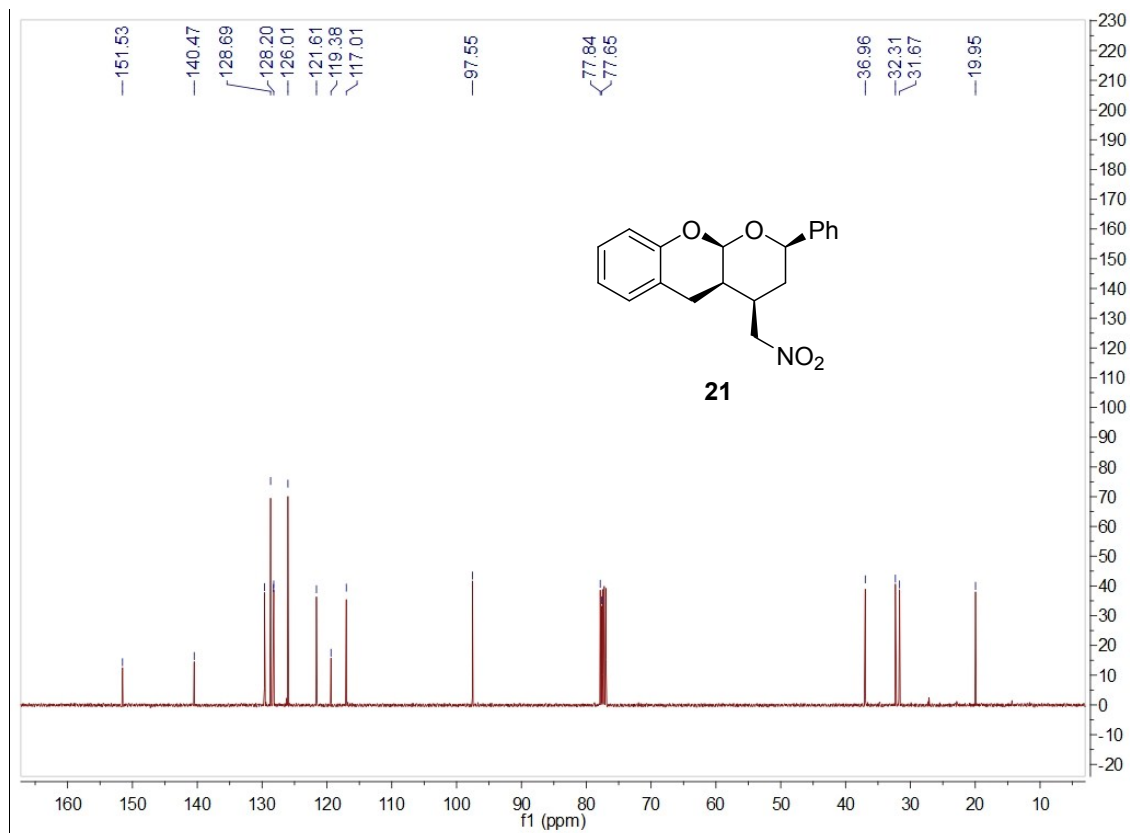
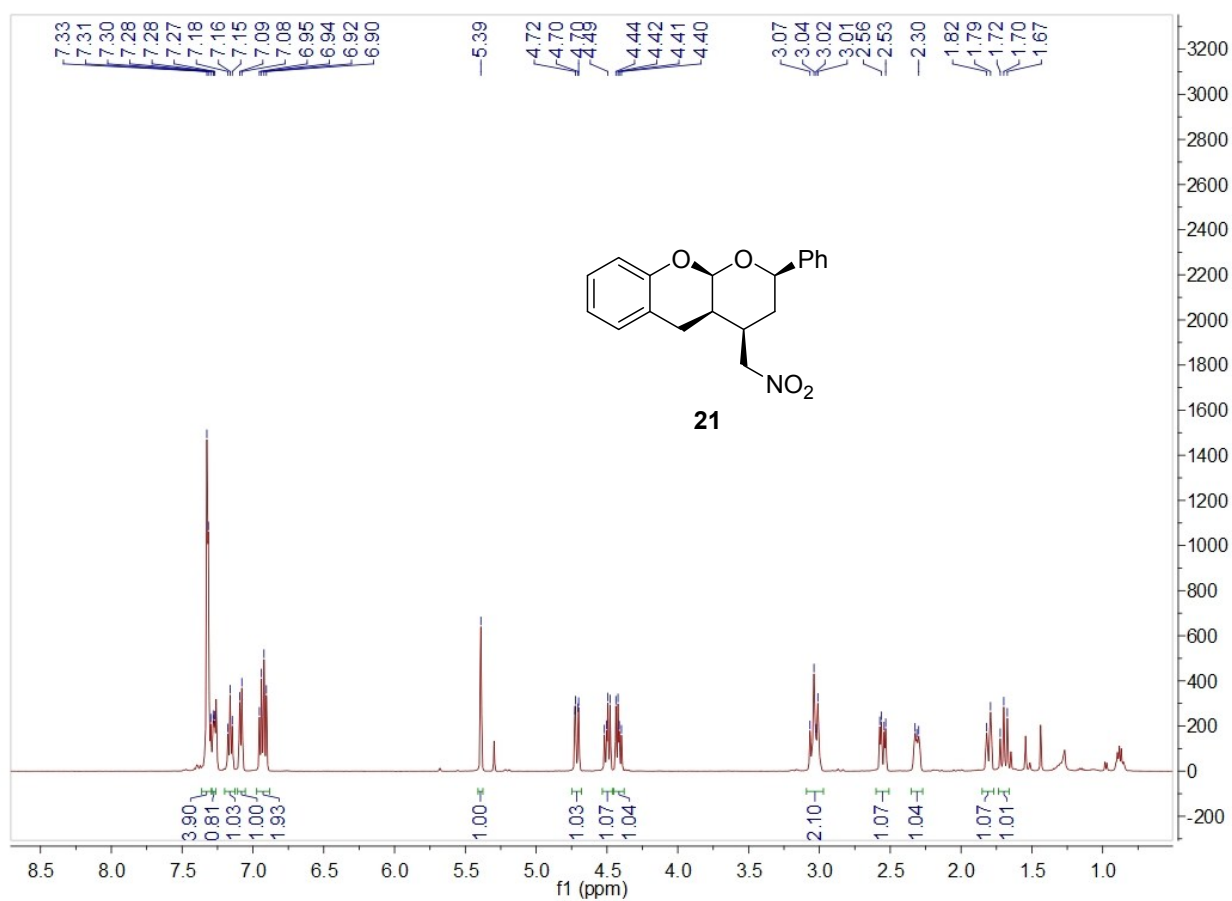
No.	RT	Area	Area %	BC
1	9.827	1521232	46.263	BB
2	11.307	1766964	53.737	BB
		3288196	100.000	

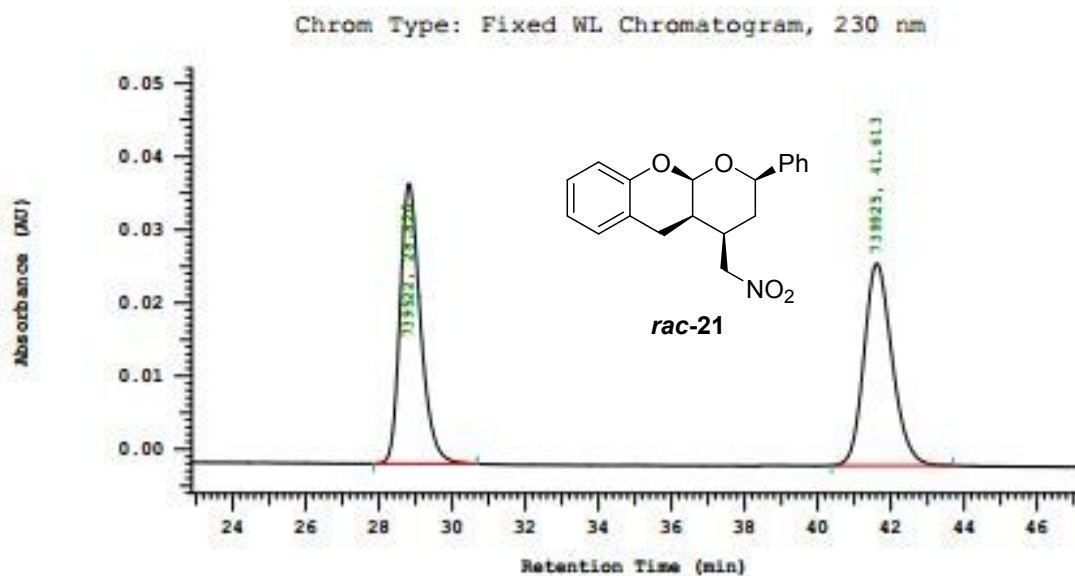


Chrom Type: Fixed WL Chromatogram, 230 nm
 Peak Quantitation: AREA
 Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	9.800	8096416	99.594	BB
2	11.287	33019	0.406	BB
		8129435	100.000	

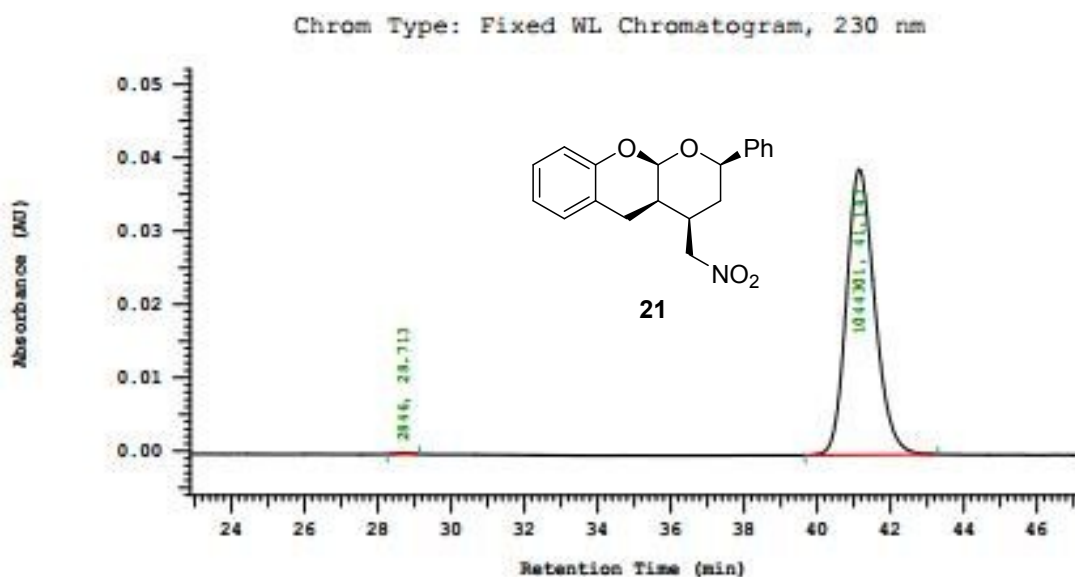






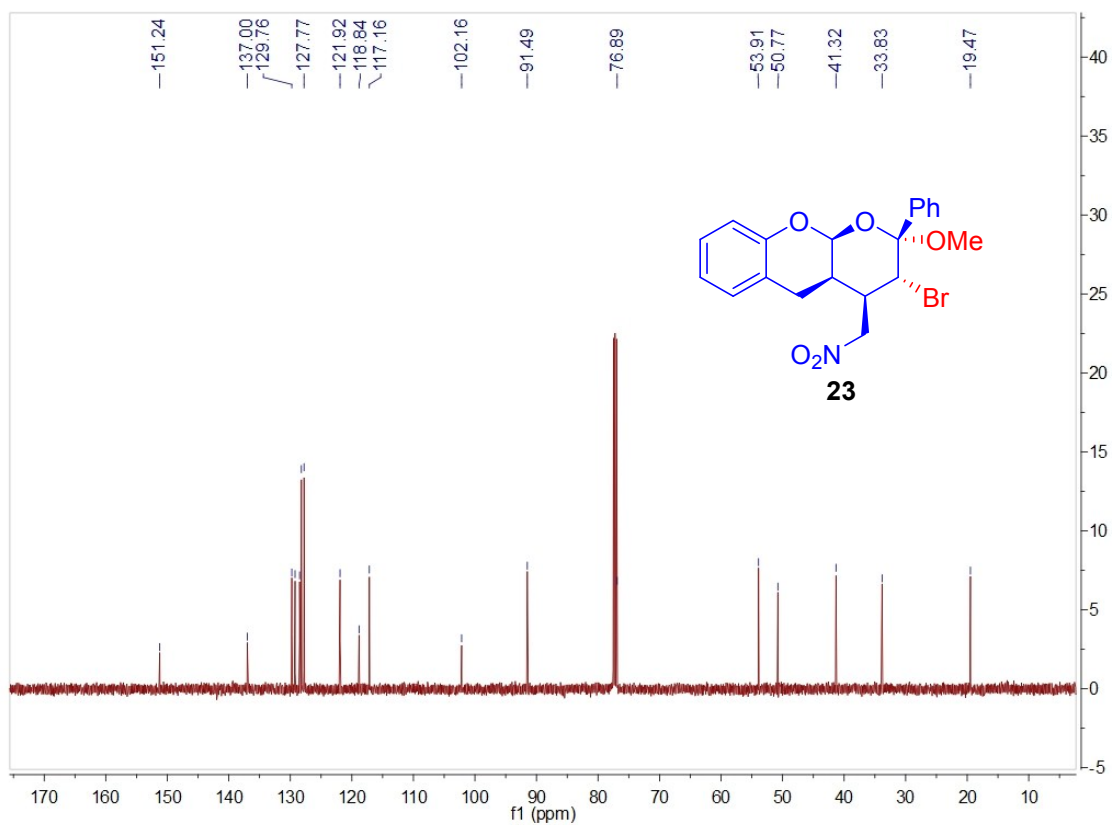
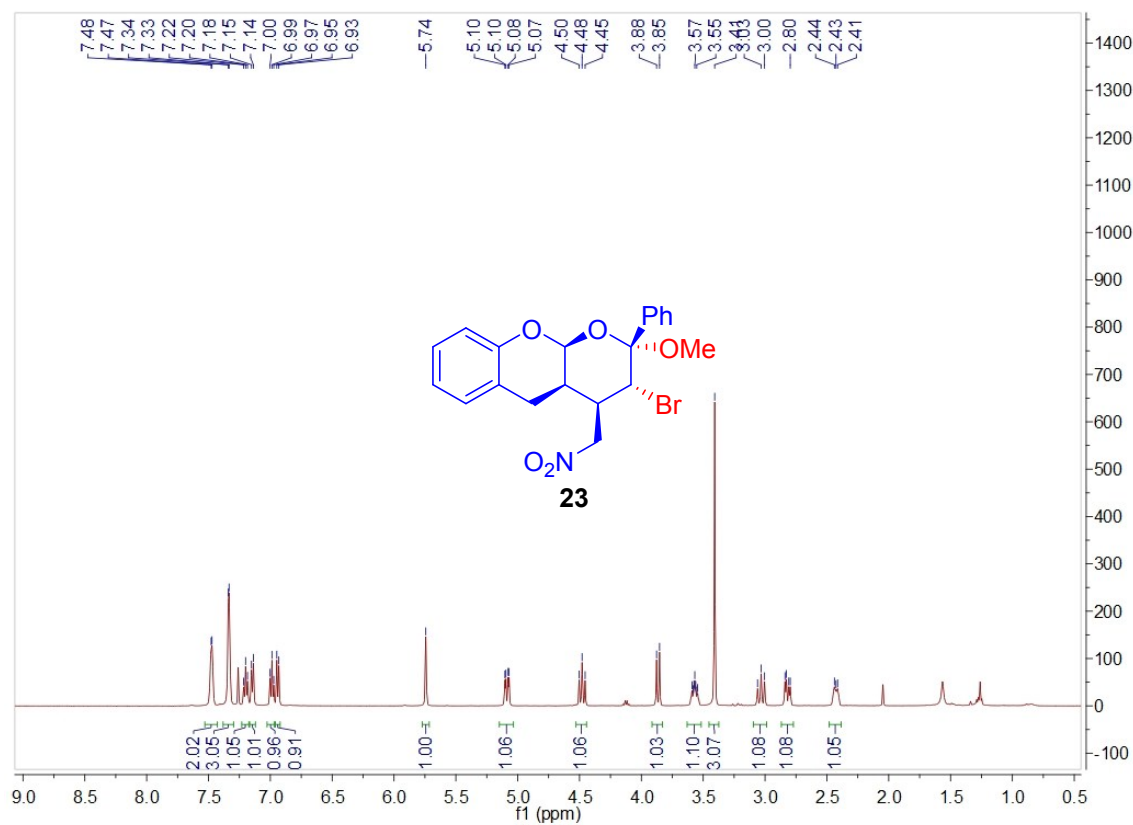
Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

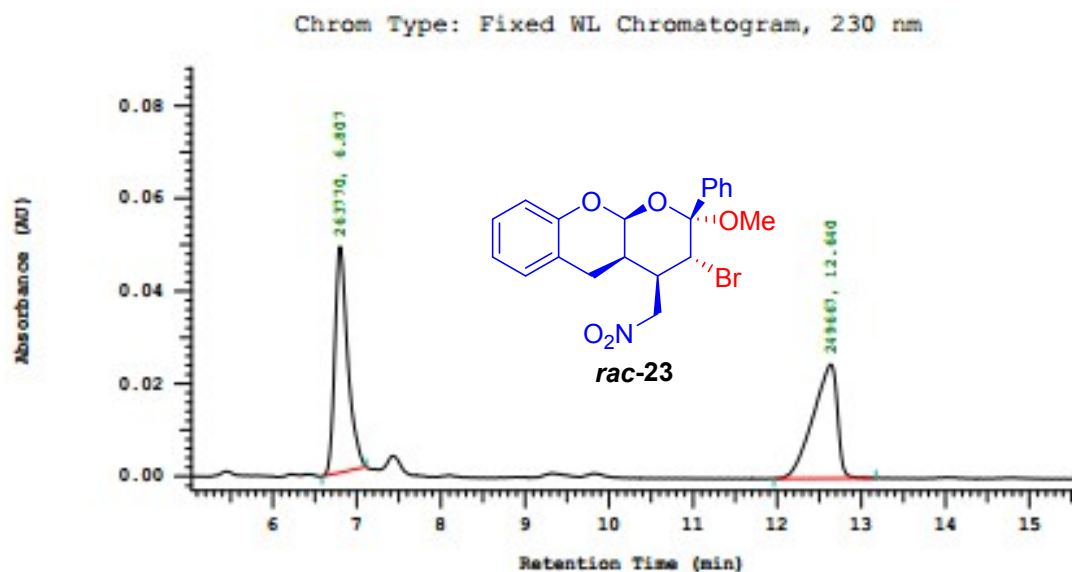
No.	RT	Area	Area %	BC
1	28.820	739522	49.986	BB
2	41.613	739925	50.014	BB
		1479447	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm
Peak Quantitation: AREA
Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	28.713	2846	0.272	BB
2	41.147	1044301	99.728	BB
		1047147	100.000	



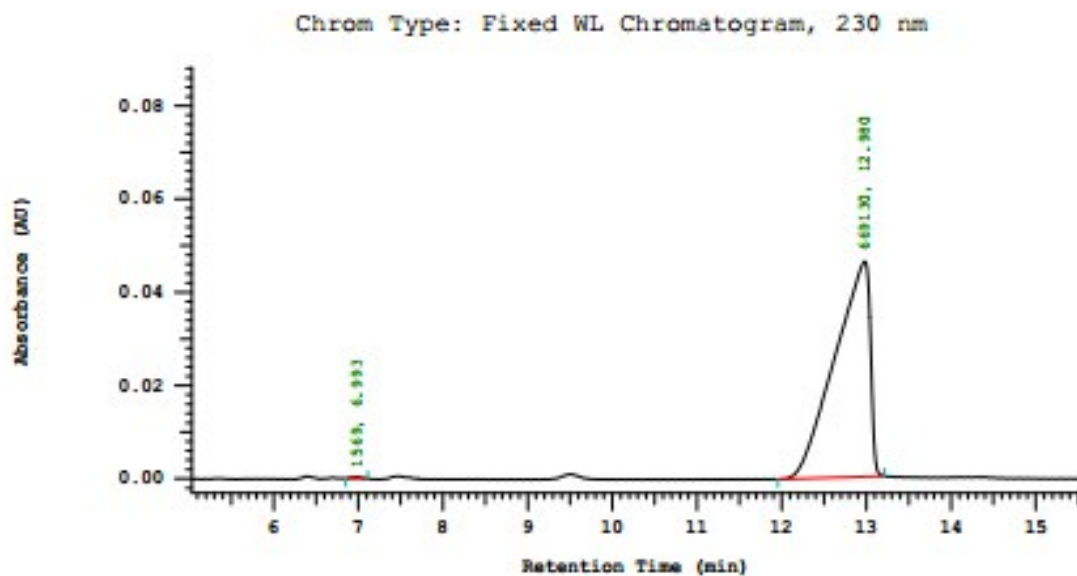


Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.807	263770	51.373	BB
2	12.640	249667	48.627	BB
		513437	100.000	



Chrom Type: Fixed WL Chromatogram, 230 nm

Peak Quantitation: AREA

Calculation Method: AREA%

No.	RT	Area	Area %	BC
1	6.993	1569	0.234	BB
2	12.980	669130	99.766	BB
		670699	100.000	

