

## Supporting Information

### **An enantioselective organocatalyzed aza-Morita–Baylis –Hillman reaction of isatin-derived ketimines with acrolein**

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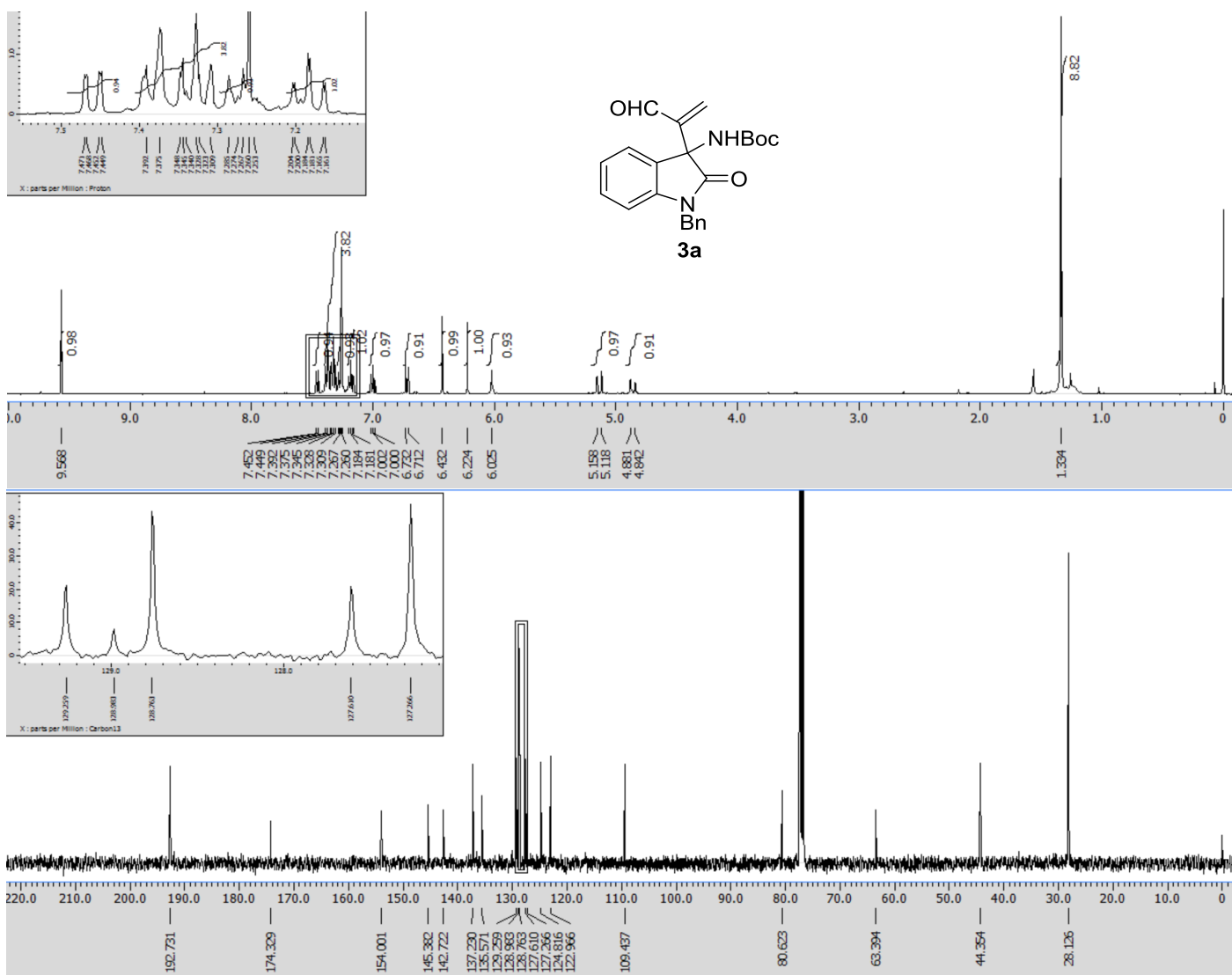
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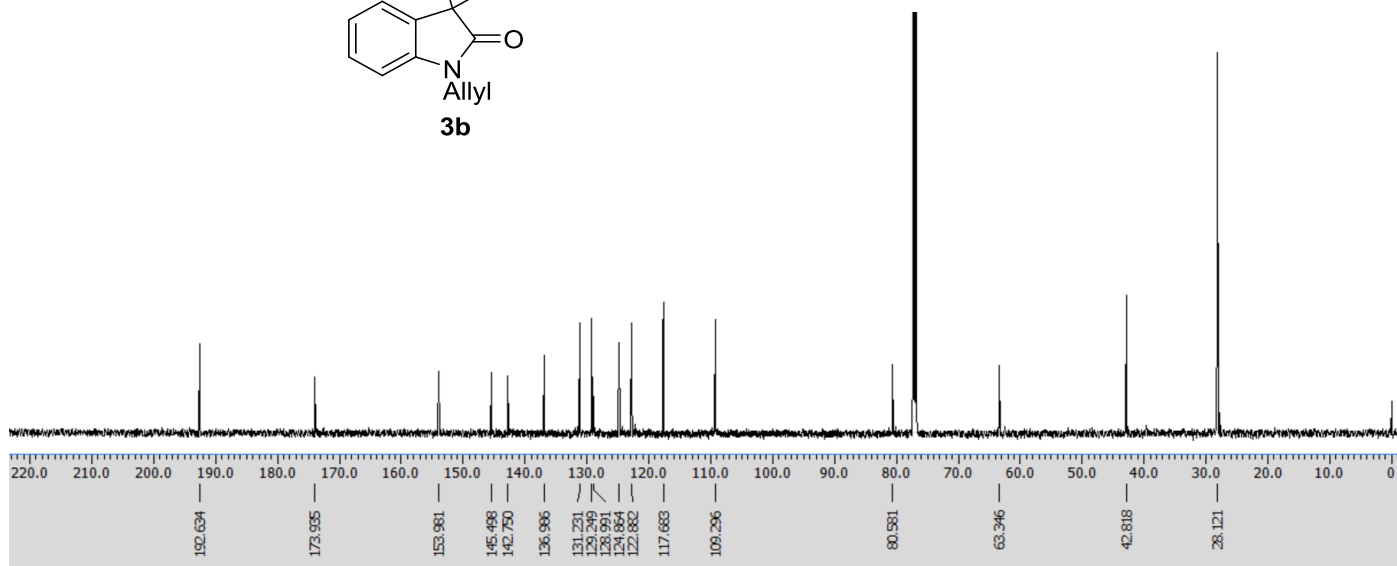
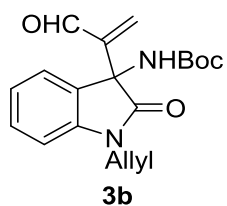
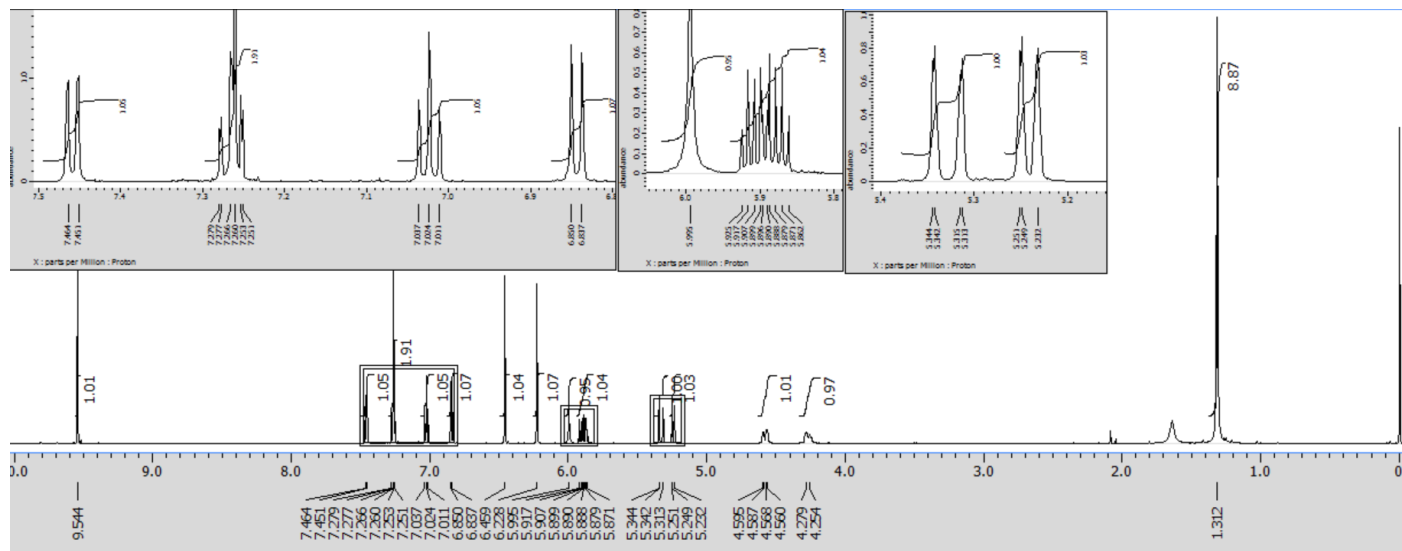
## General information

$^1\text{H}$ -,  $^{13}\text{C}$ -, and  $^{19}\text{F}$ -NMR spectra were recorded with JEOL JMN ECS400 FT NMR, JNM ECA600 FT NMR or Bruker AVANCE II ( $^1\text{H}$ -NMR 400, 600 or 700 MHz,  $^{13}\text{C}$ -NMR 100, 150 or 175 MHz,  $^{19}\text{F}$ -NMR 376 MHz).  $^1\text{H}$ -NMR spectra are reported as follows: chemical shift in ppm relative to the chemical shift of  $\text{CHCl}_3$  at 7.26 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz).  $^{13}\text{C}$ -NMR spectra reported in ppm relative to the central line of triplet for  $\text{CDCl}_3$  at 77 ppm.  $\text{CF}_3\text{CO}_2\text{H}$  used as external standards for  $^{19}\text{F}$ -NMR. FT-MS spectra were obtained with LTQ Orbitrap XL (Thermo Fisher Scientific). ESI-MS spectra were obtained with JMS-T100LC (JEOL). FAB-MS spectra were obtained with JMS-700 (JEOL). Optical rotations were measured with JASCO P-1030 polarimeter. HPLC analyses were performed on a JASCO HPLC system (JASCO PU 980 pump and UV-975 UV/Vis detector) using a mixture of hexane and 2-propanol as eluents. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR4100). Column chromatography on  $\text{SiO}_2$  was performed with Kanto Silica Gel 60 (40-100  $\mu\text{m}$ ). Commercially available organic and inorganic compounds were used without further purification. *N*-*tert*-butoxycarbonyl (Boc) protected ketimines **1** were prepared following the reported procedures.<sup>1</sup> The product **3i** was identical in all respects with reported in the literature.<sup>2</sup>

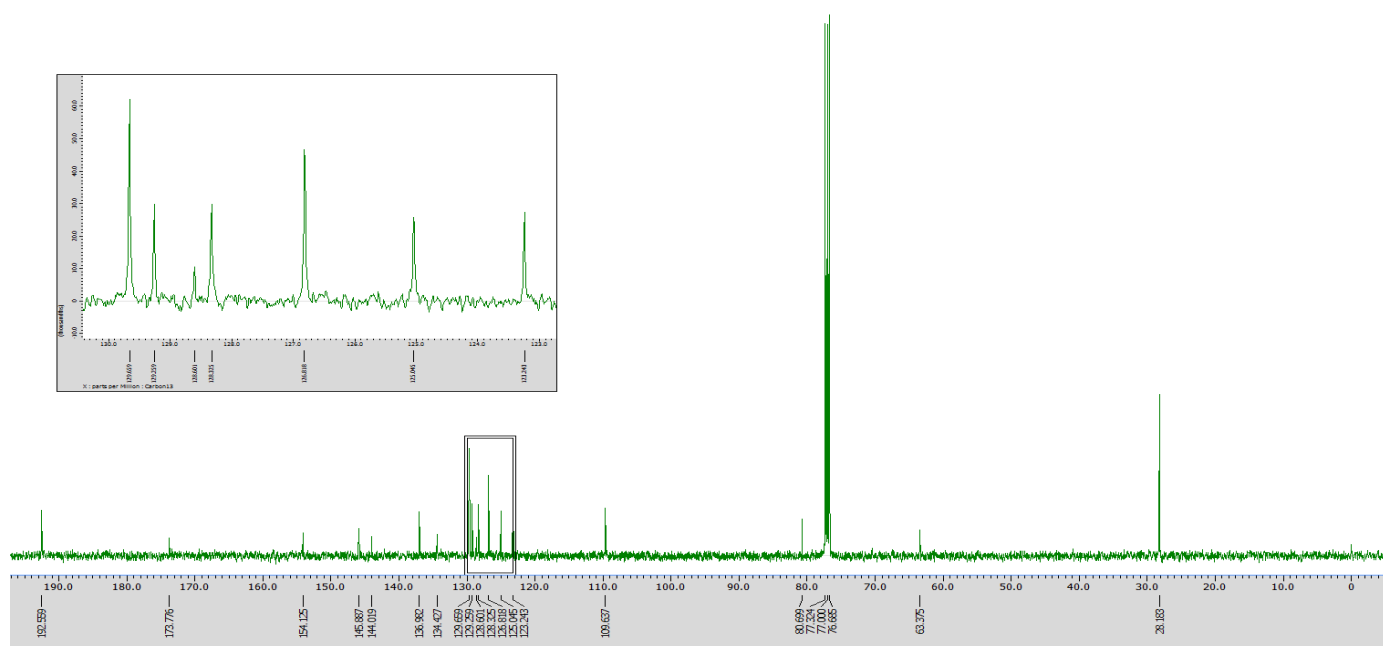
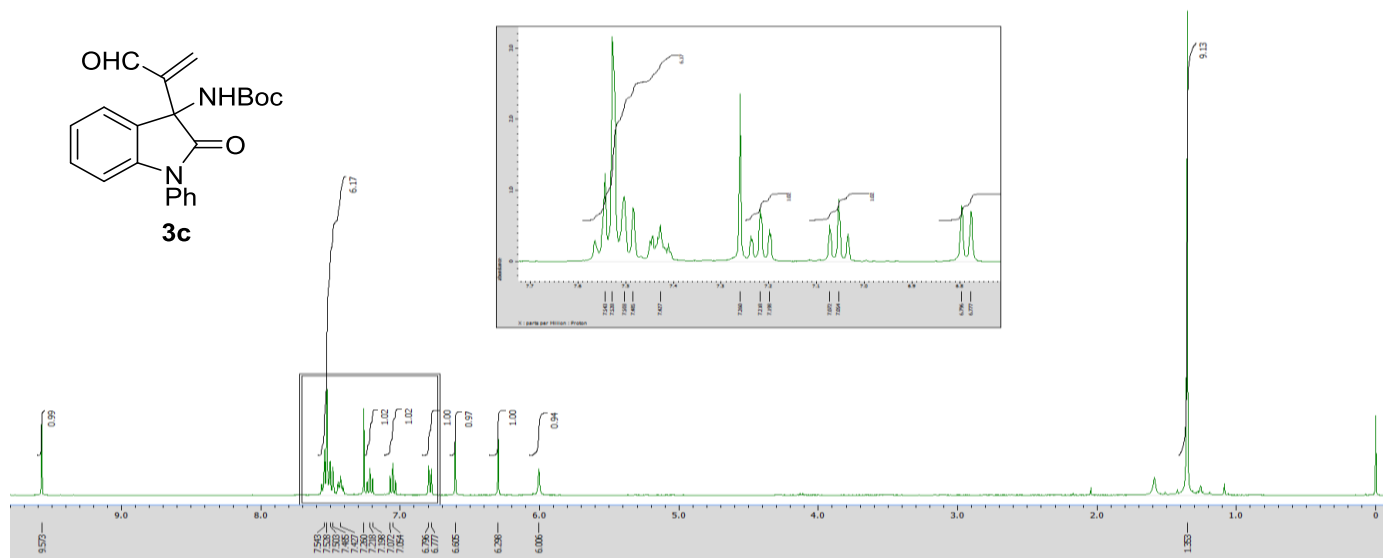
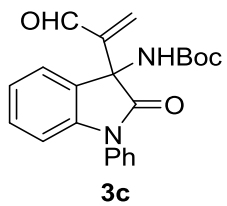
## $^1\text{H}$ and $^{13}\text{C}$ -NMR spectra of **3a**



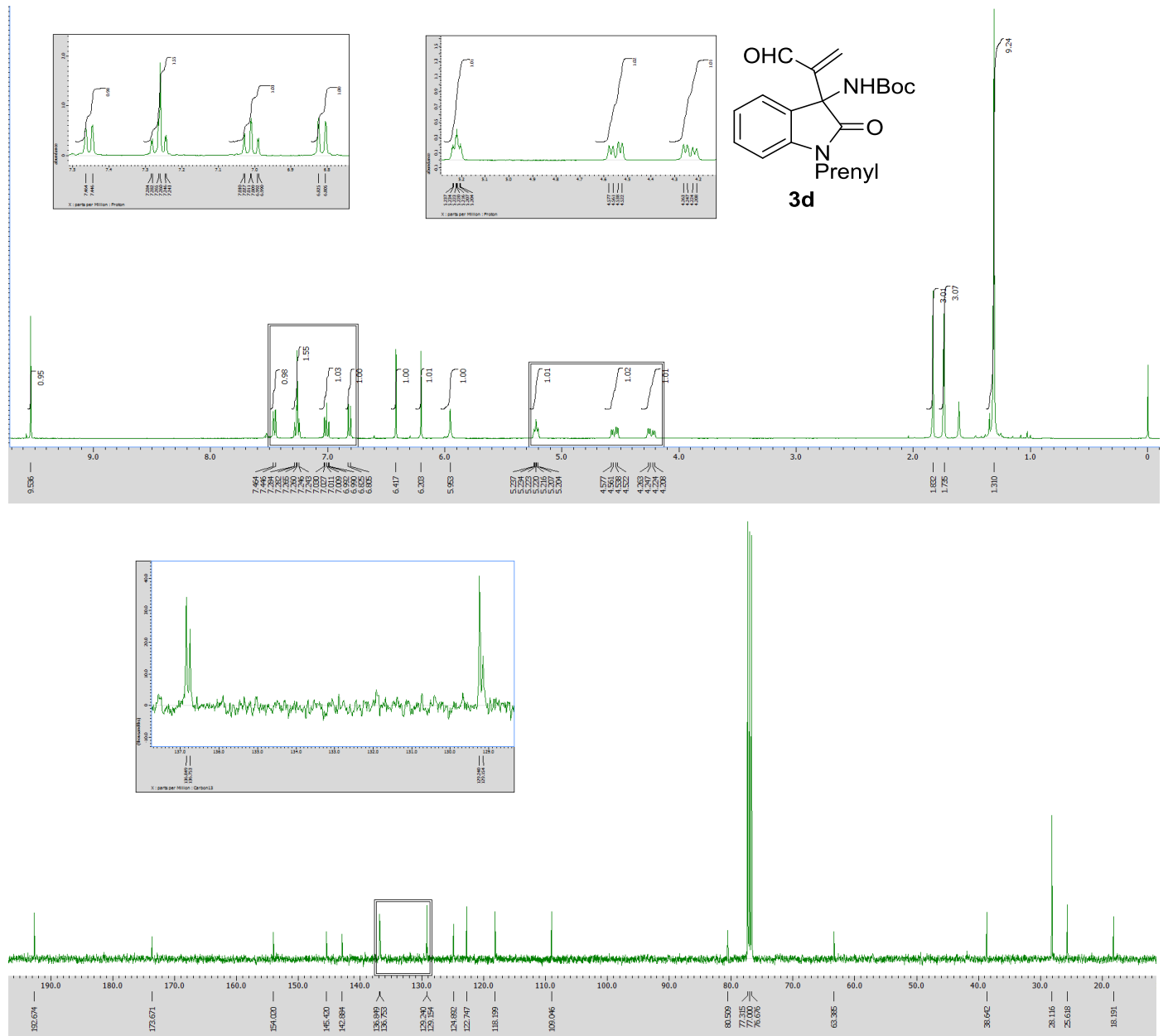
$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of **3b**



<sup>1</sup>H and <sup>13</sup>C-NMR spectra of 3c

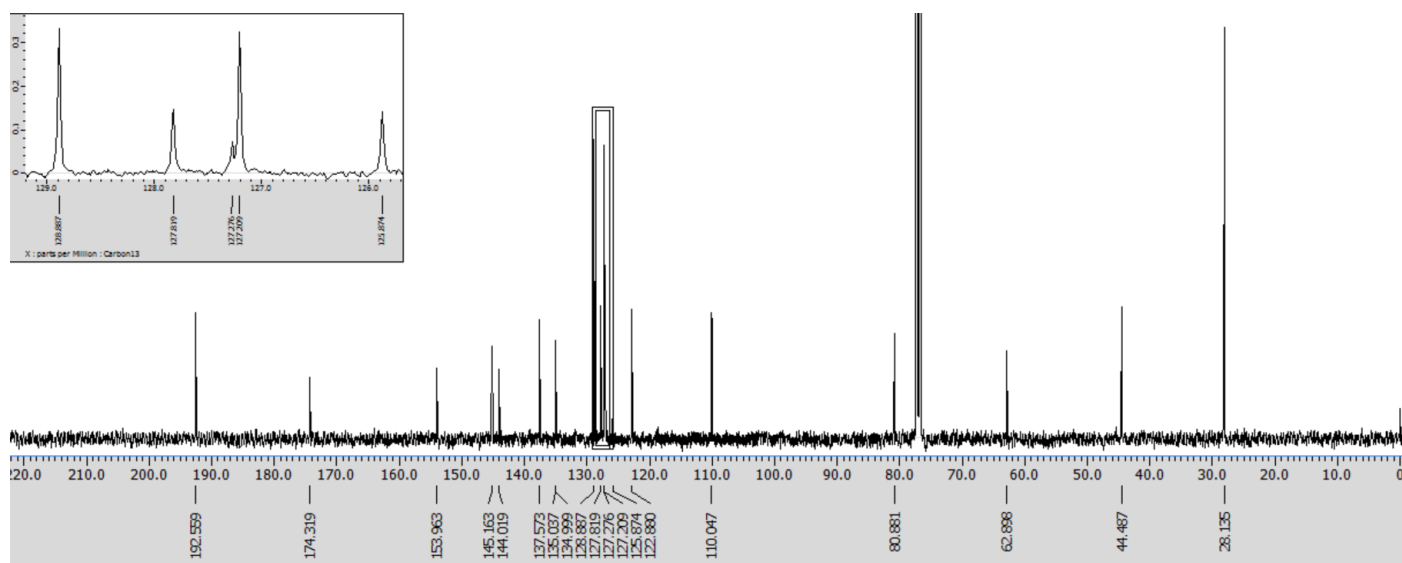
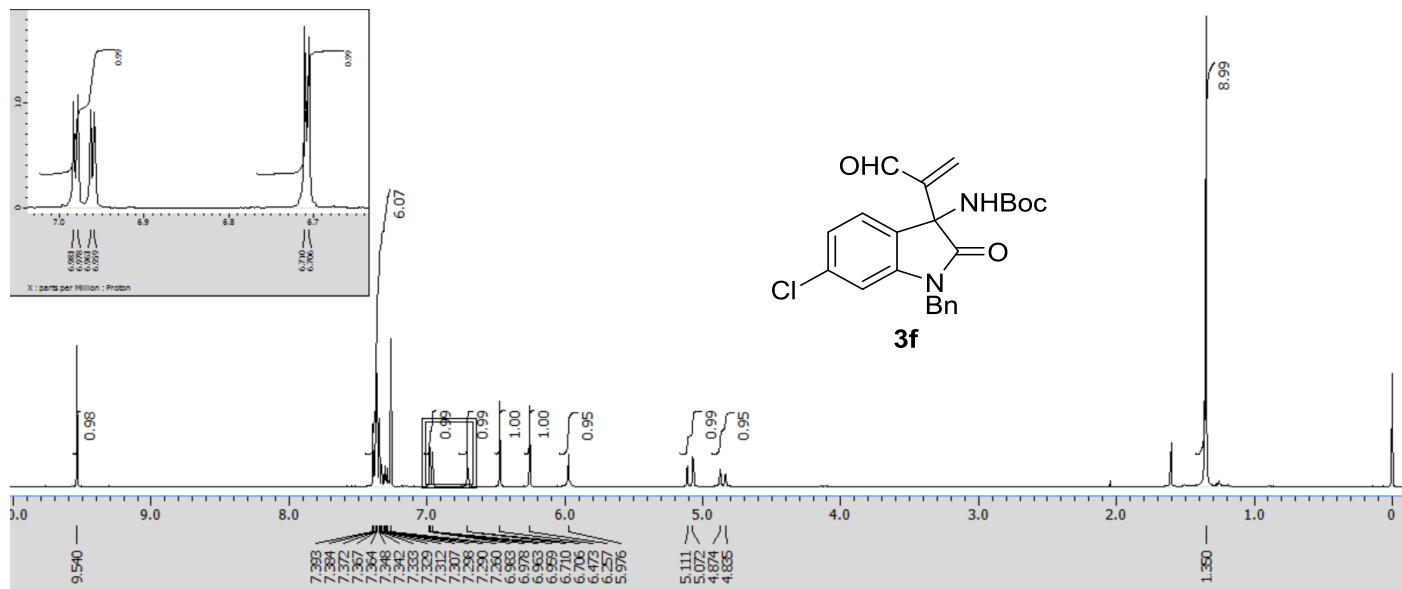


$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of **3d**

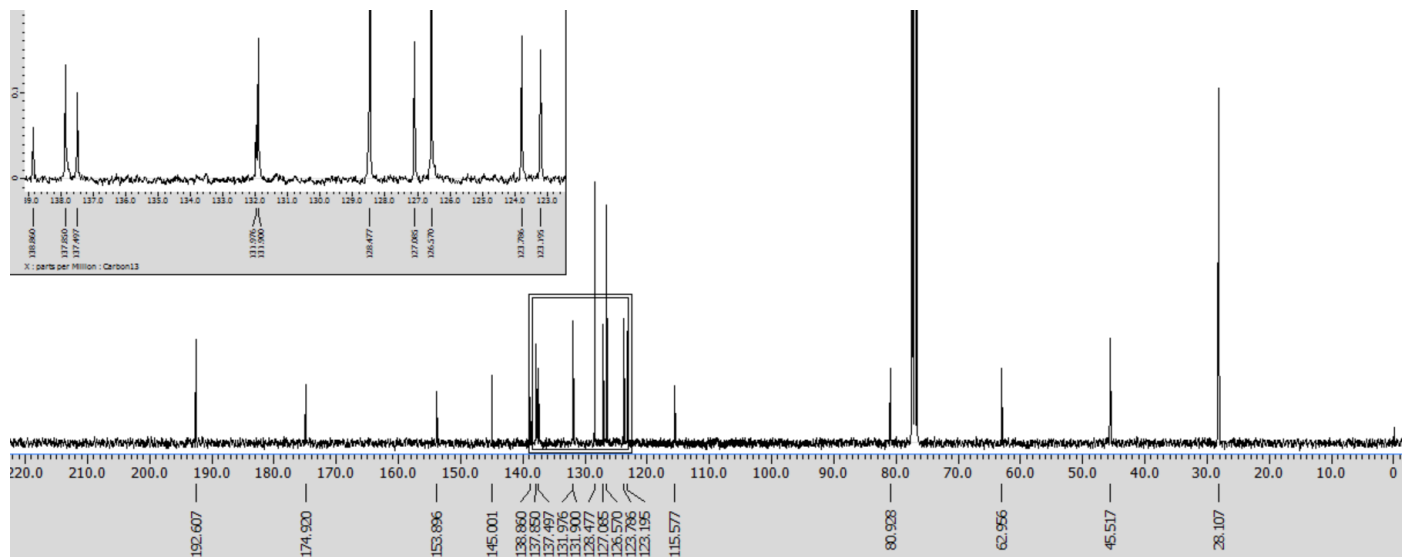
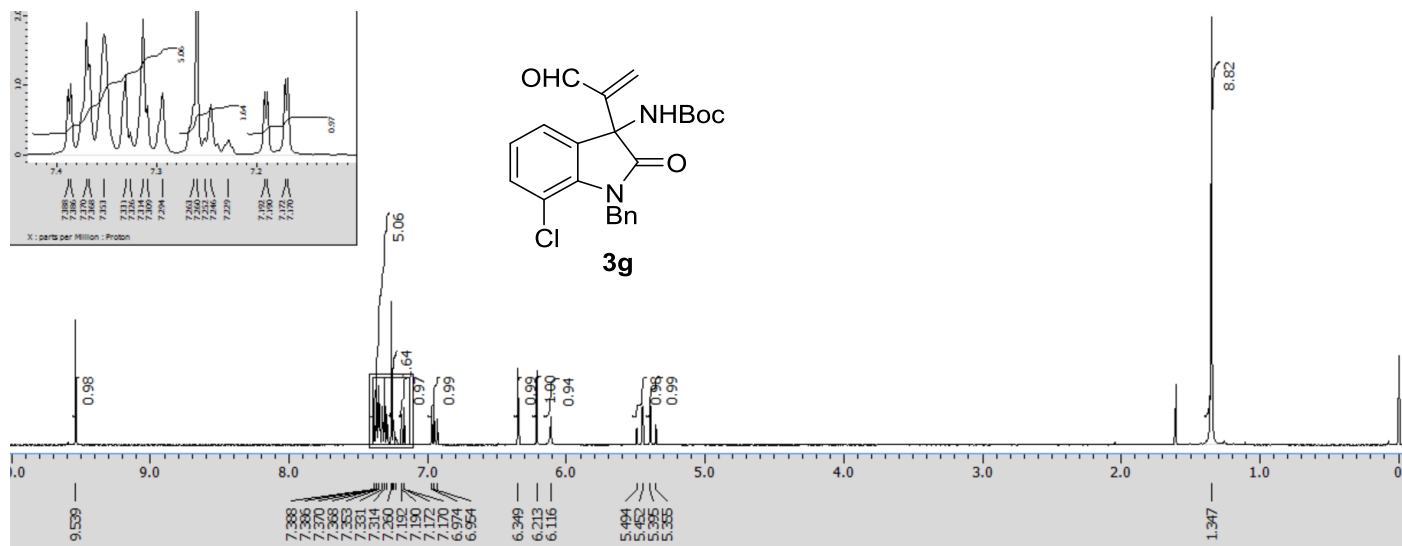




<sup>1</sup>H and <sup>13</sup>C-NMR spectra of 3f

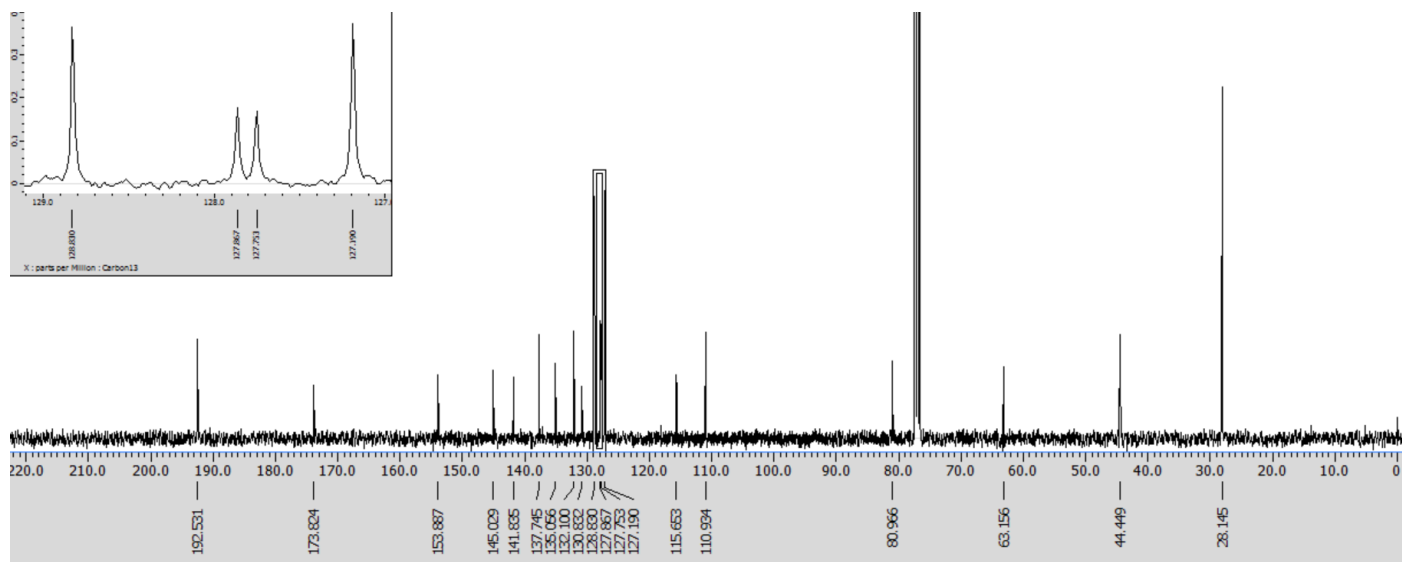
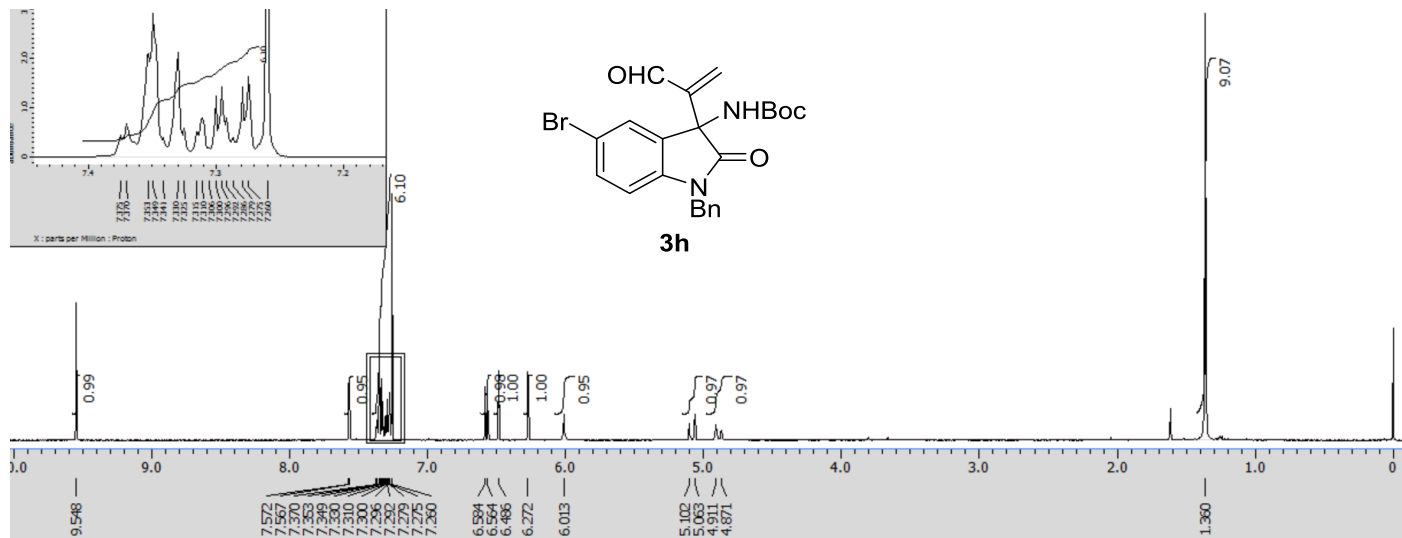


# <sup>1</sup>H and <sup>13</sup>C-NMR spectra of 3g

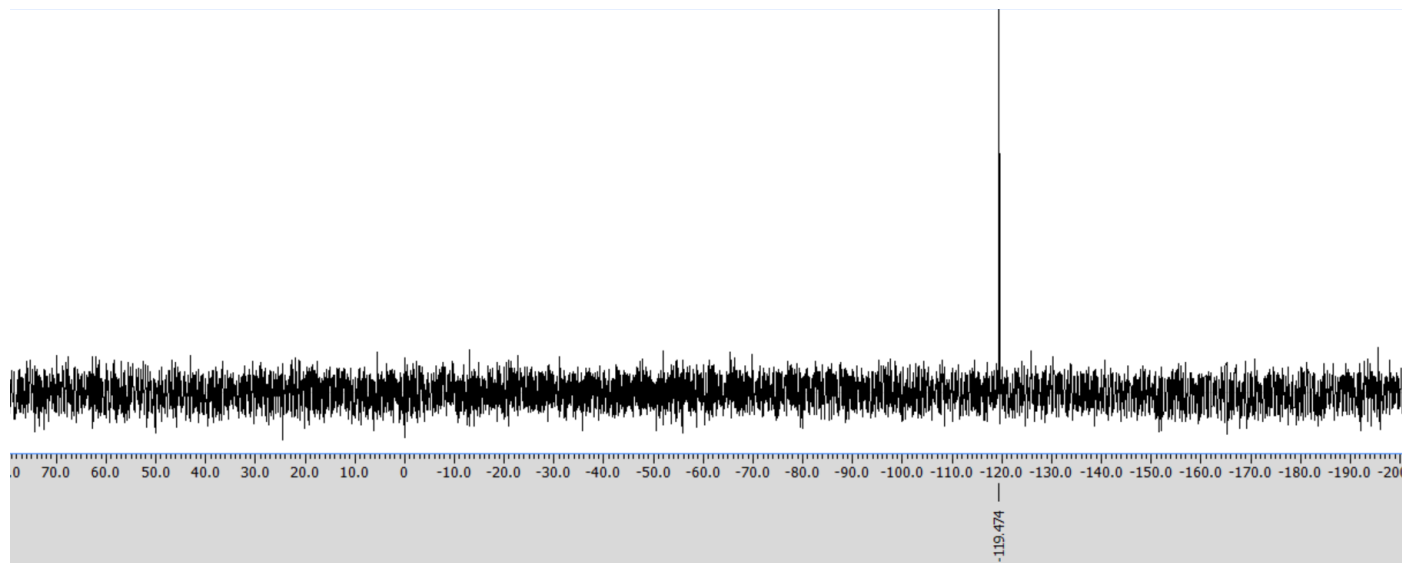
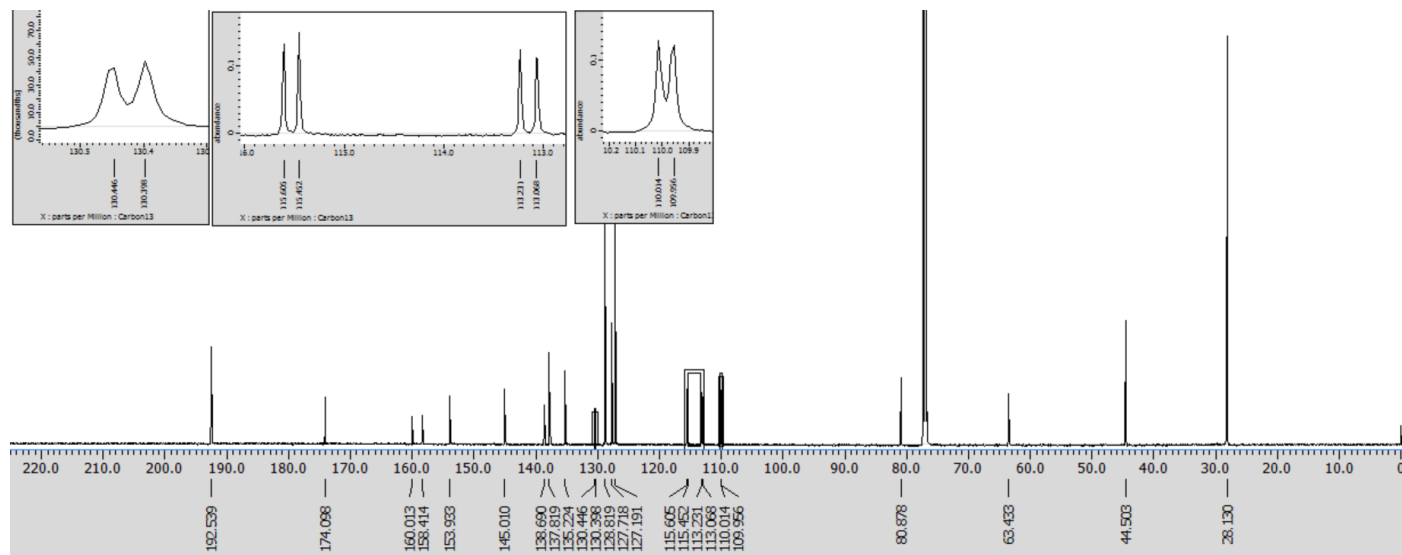
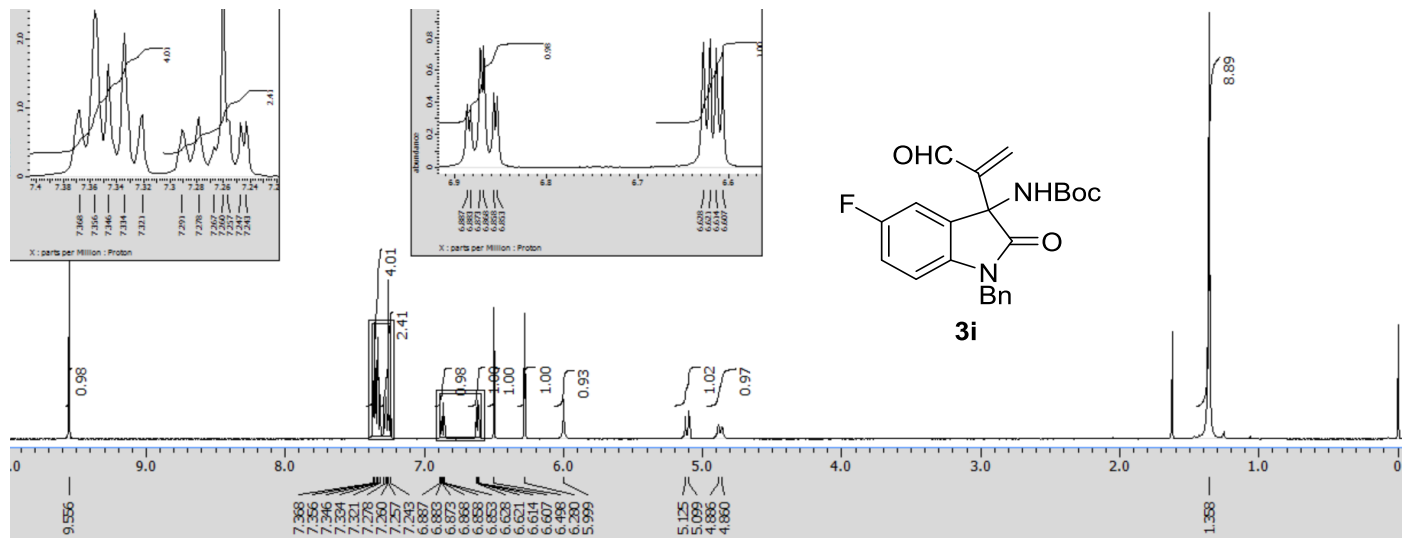




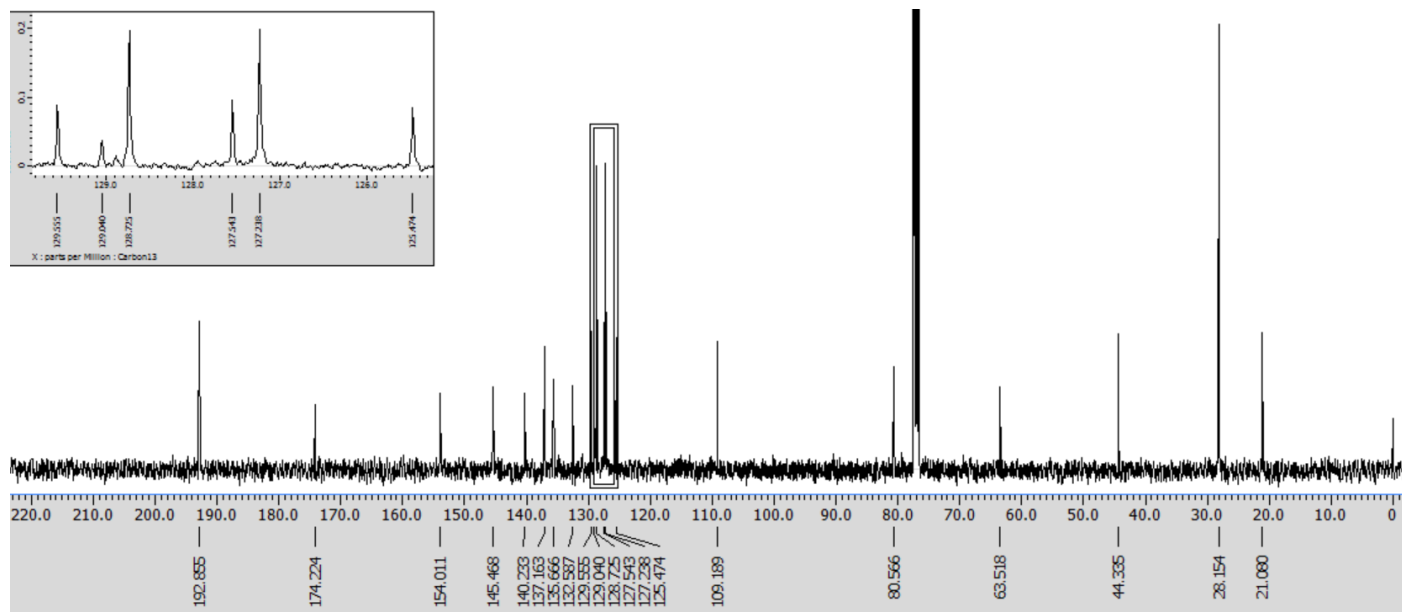
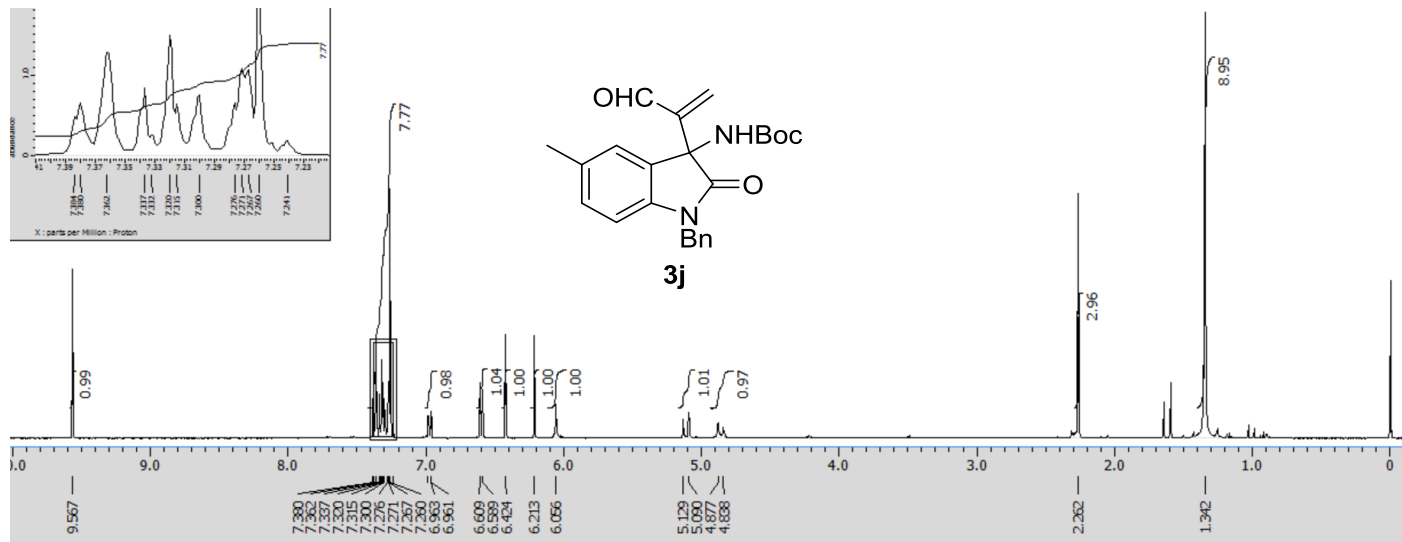
<sup>1</sup>H and <sup>13</sup>C-NMR spectra of 3h



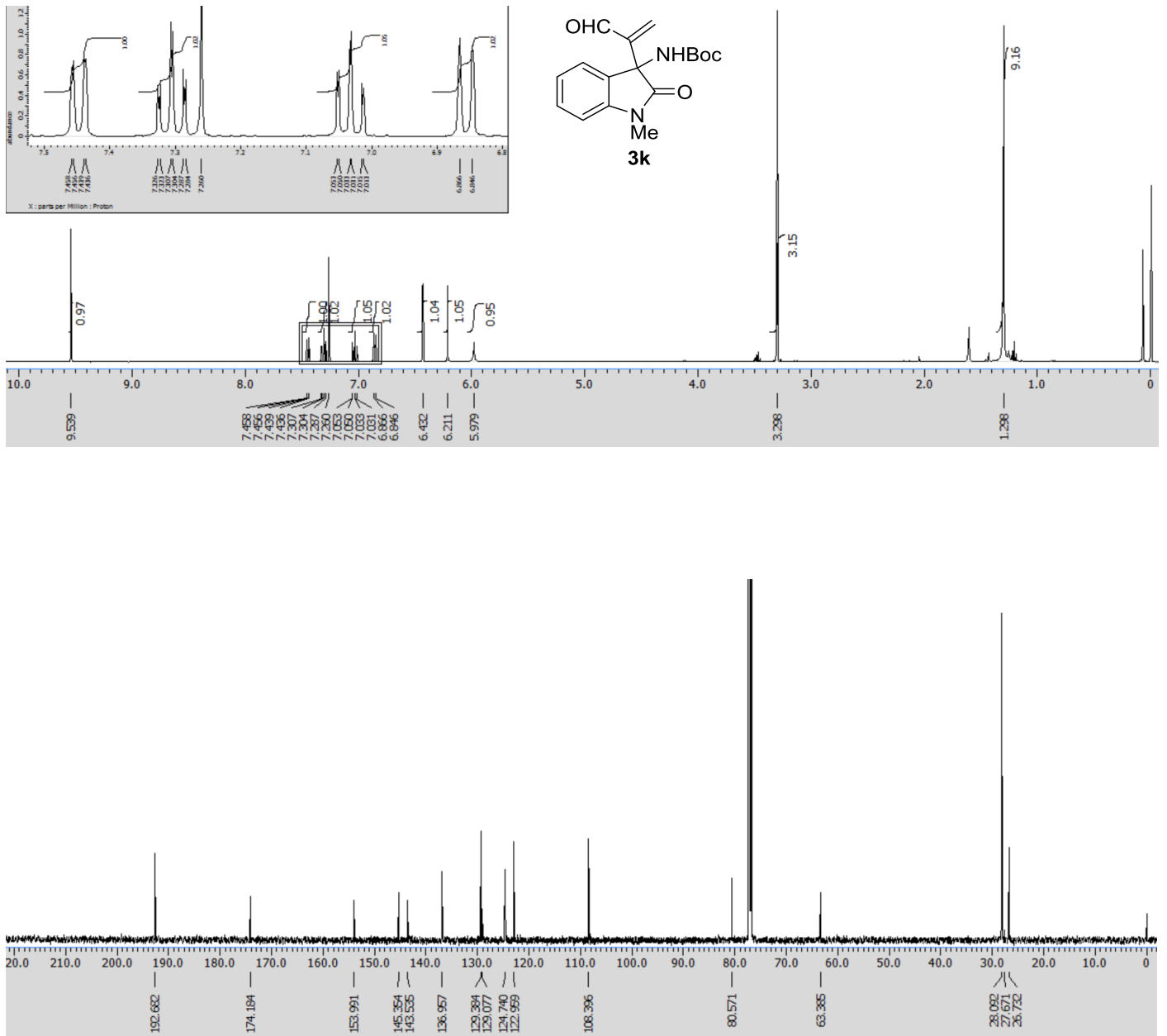
$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ -NMR spectra of **3i**



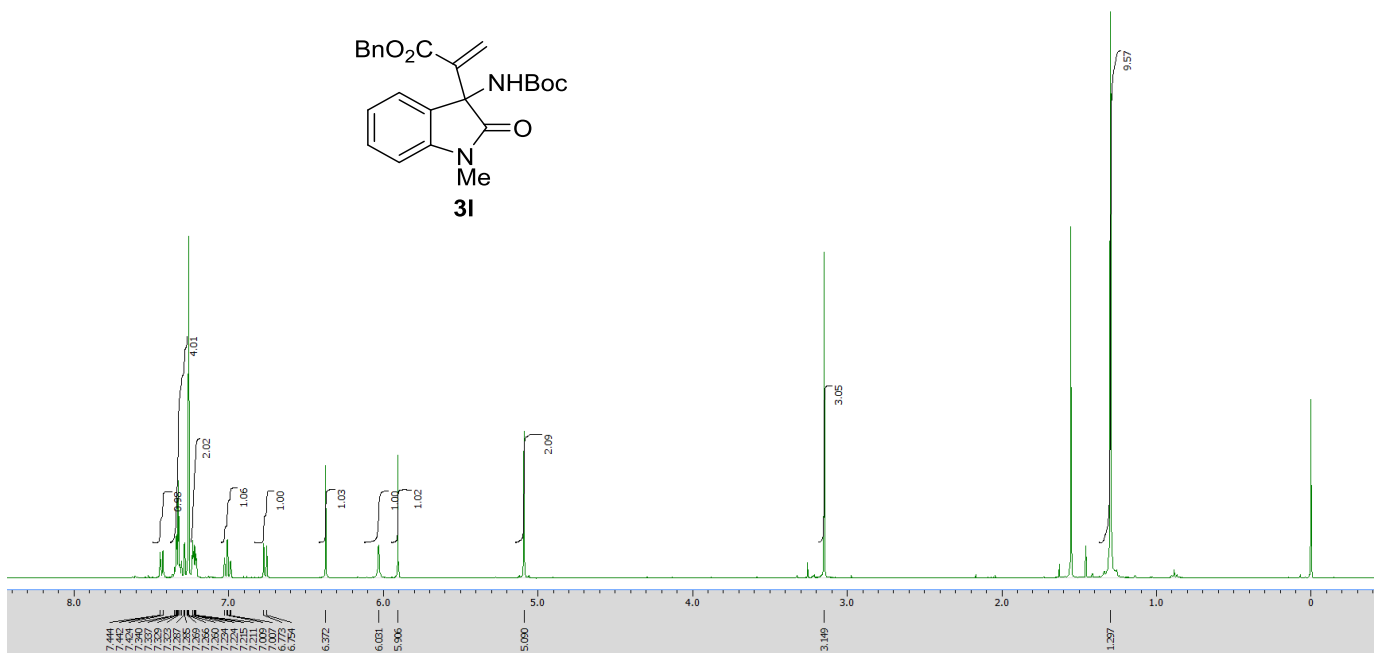
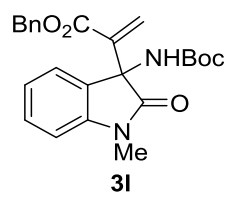
<sup>1</sup>H and <sup>13</sup>C-NMR spectra of 3j



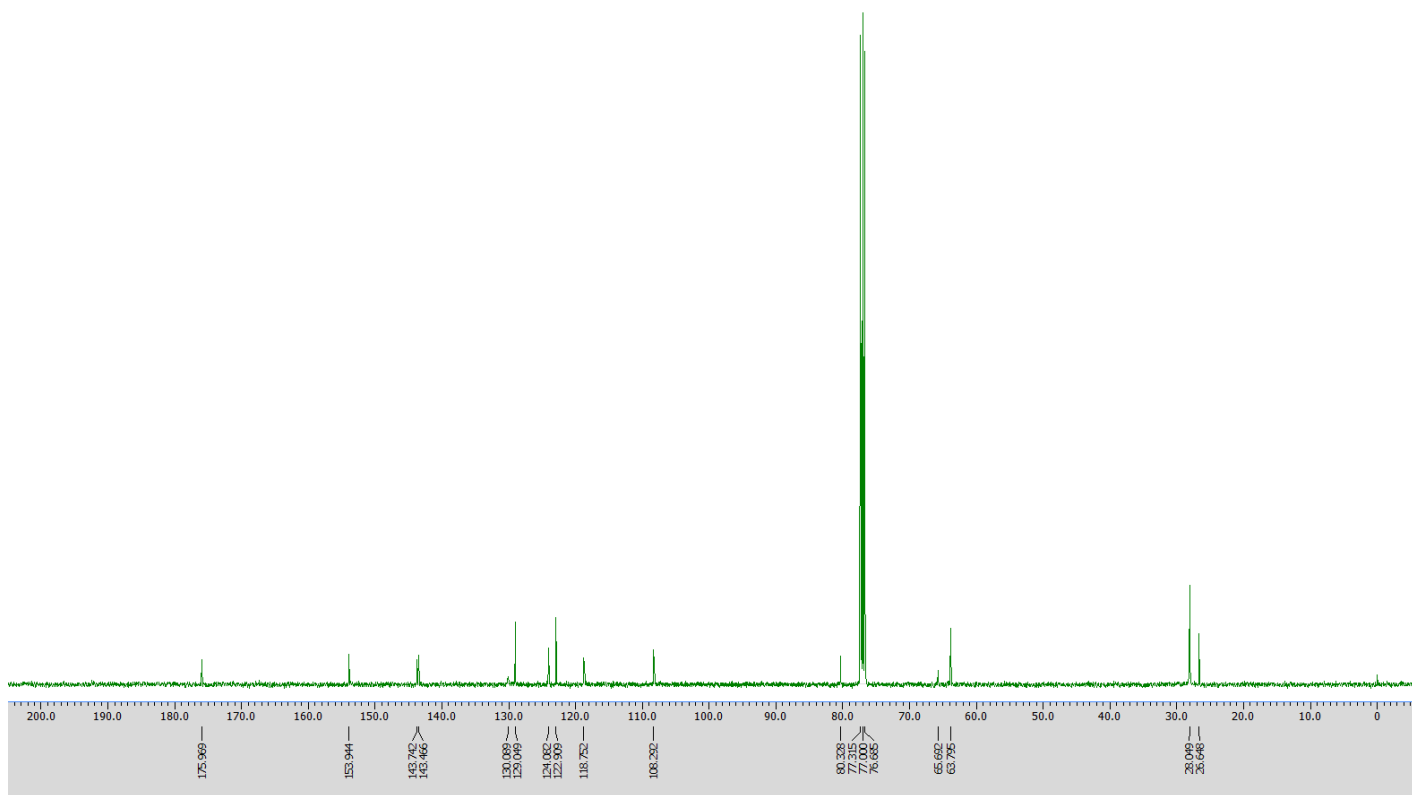
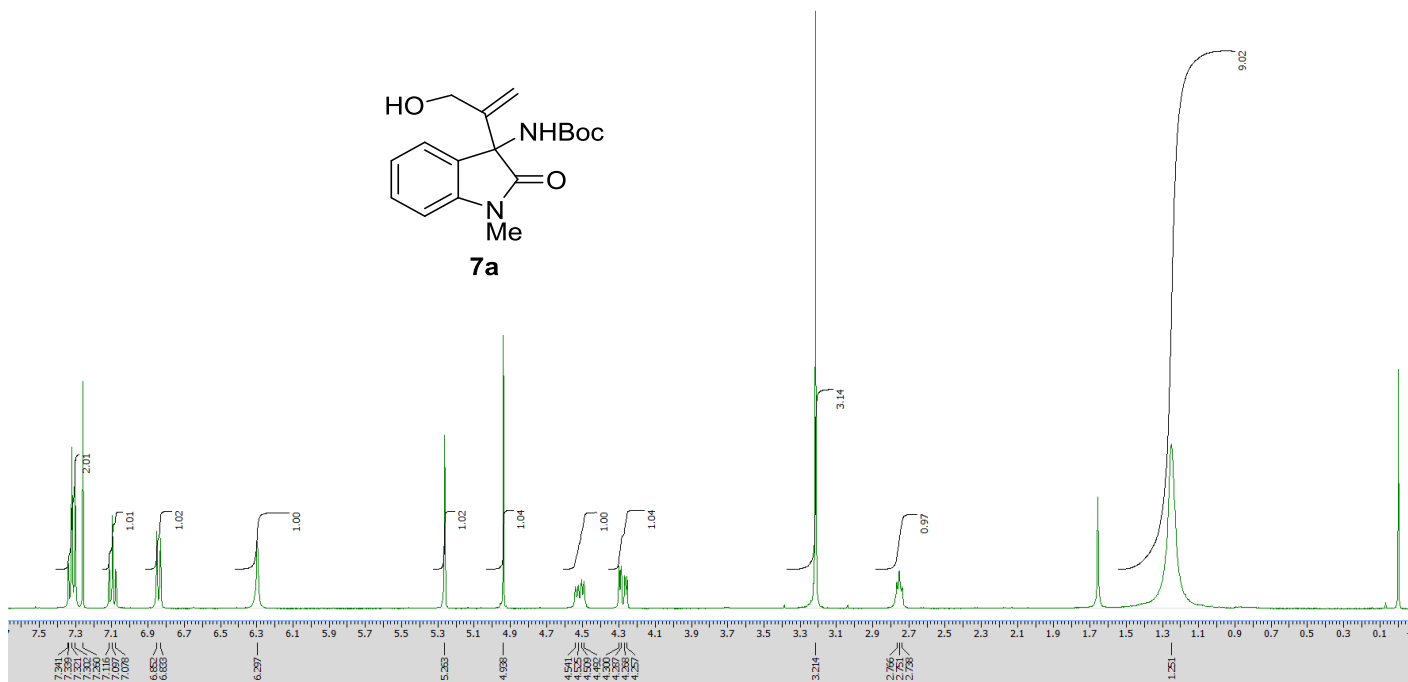
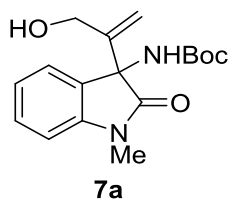
$^1\text{H}$  and  $^{13}\text{C}$ -NMR spectra of **3k**



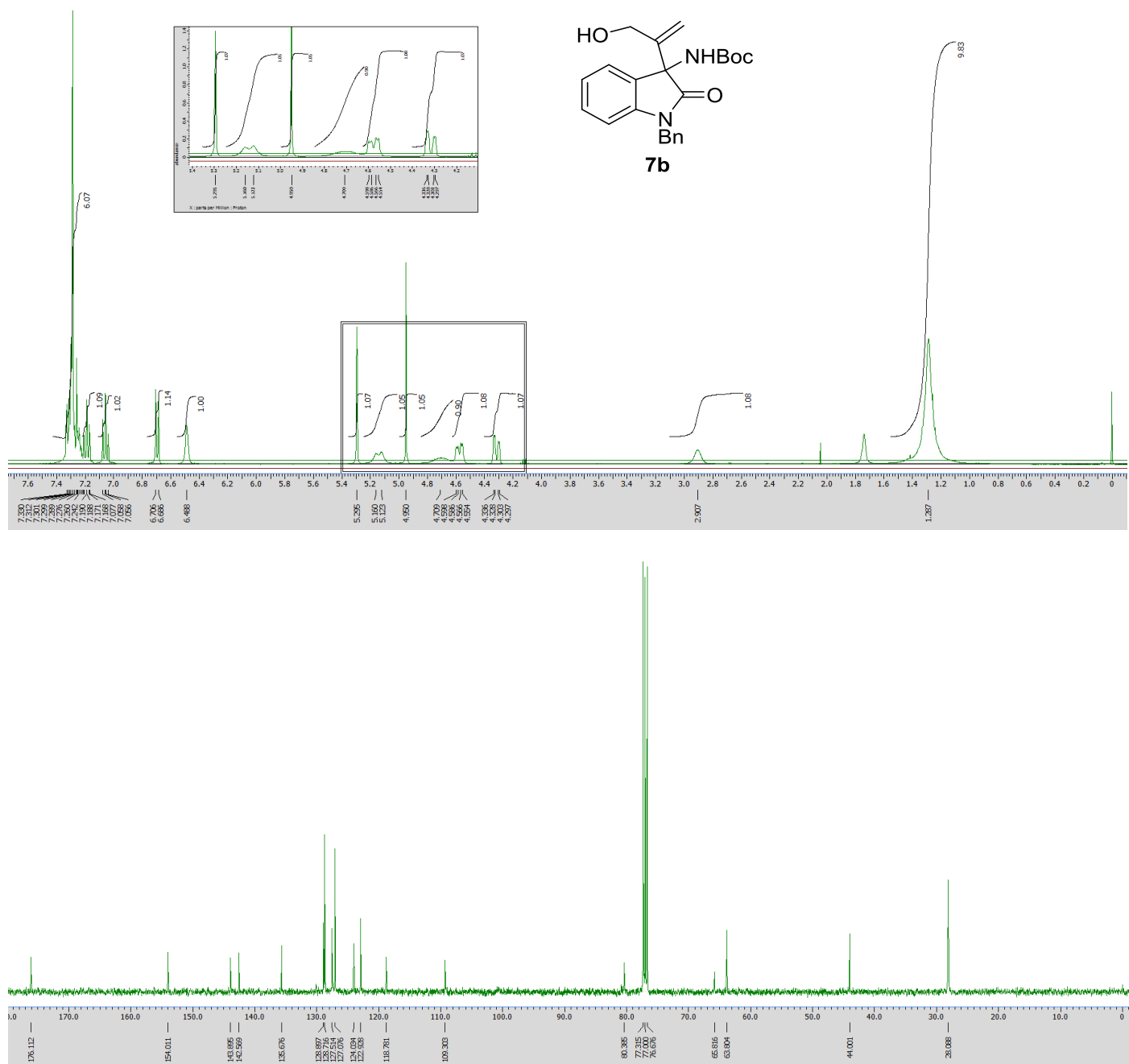
<sup>1</sup>H-NMR spectrum of 3I



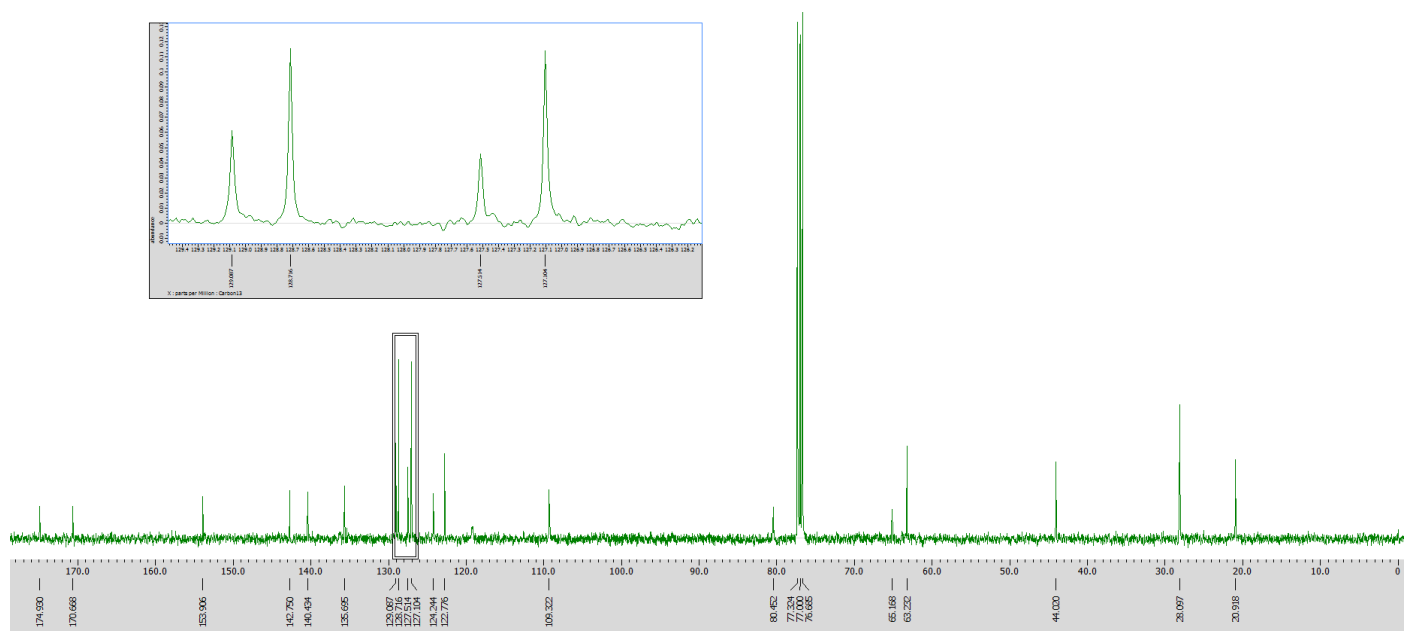
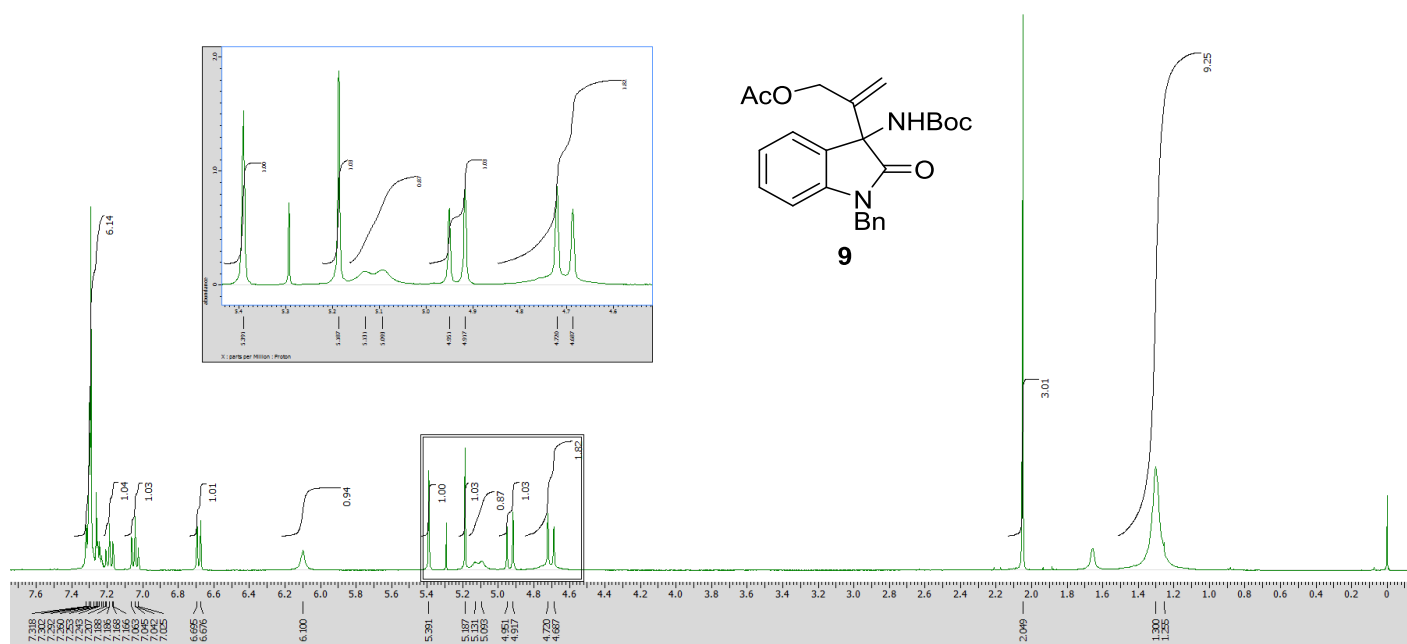
<sup>1</sup>H and <sup>13</sup>C-NMR spectra of 7a



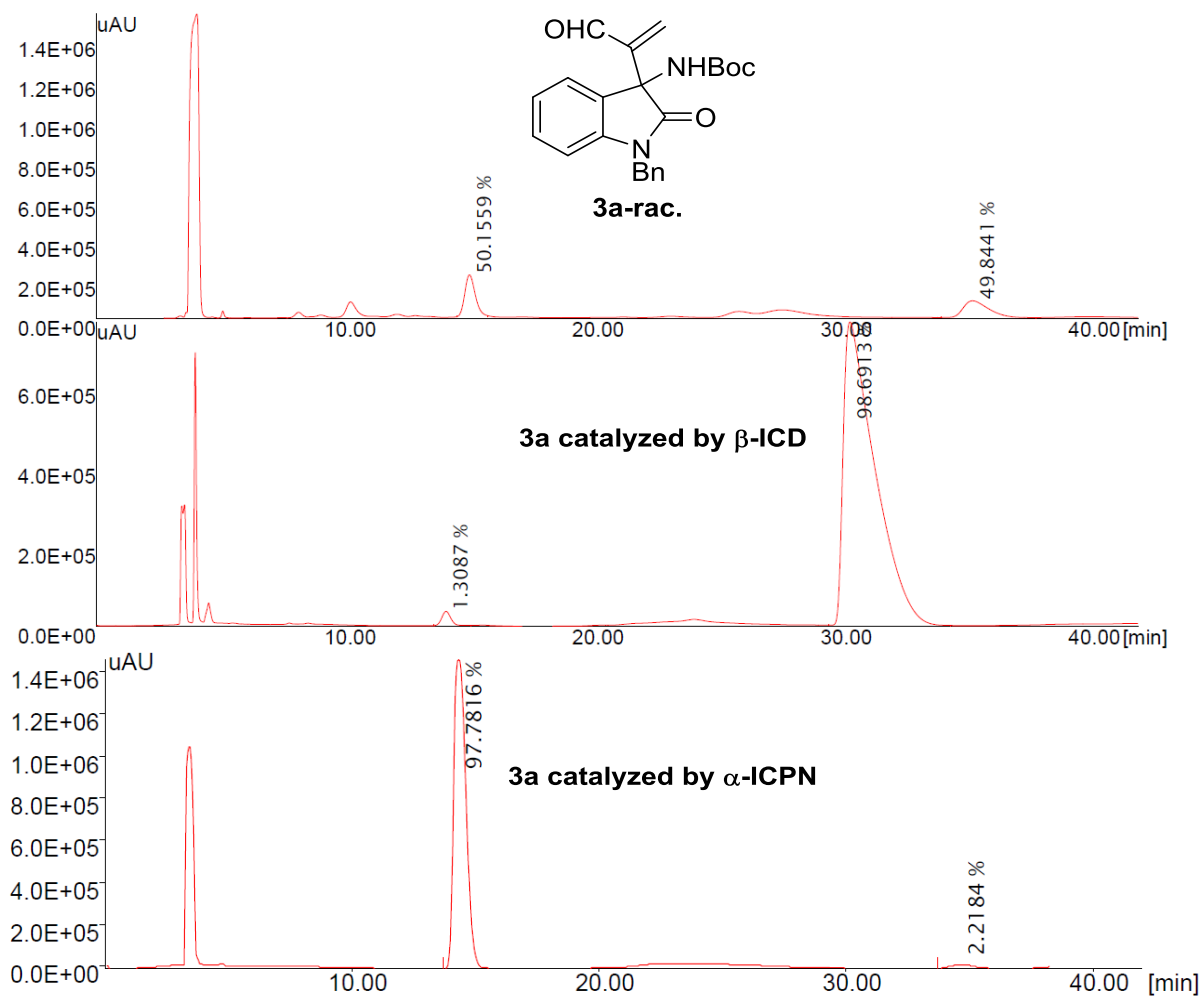
<sup>1</sup>H and <sup>13</sup>C-NMR spectra of 7b

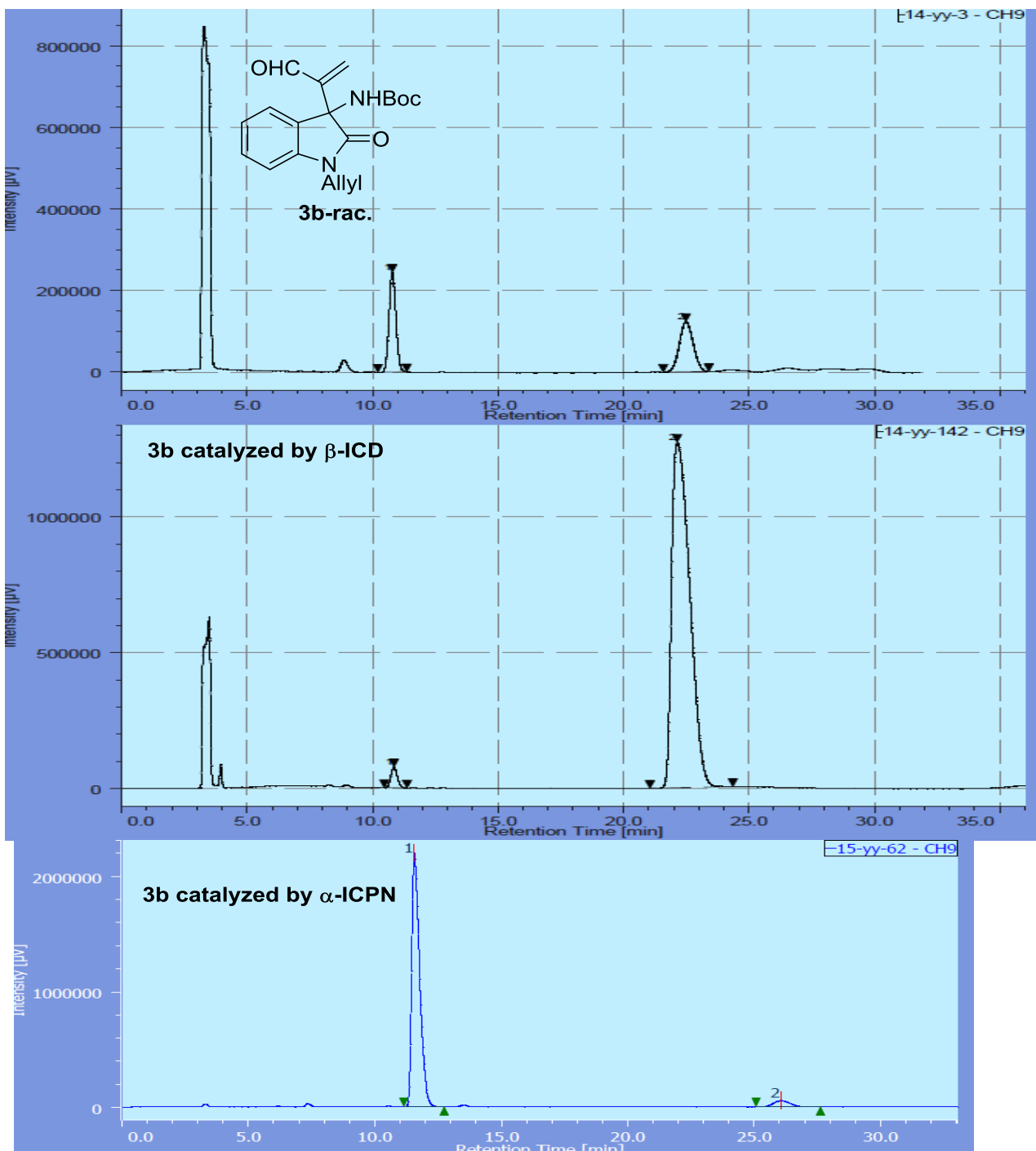


<sup>1</sup>H and <sup>13</sup>C-NMR spectra of 9









Channel & Peak Information Table

Chromatogram Name 14-yy-3-CH9

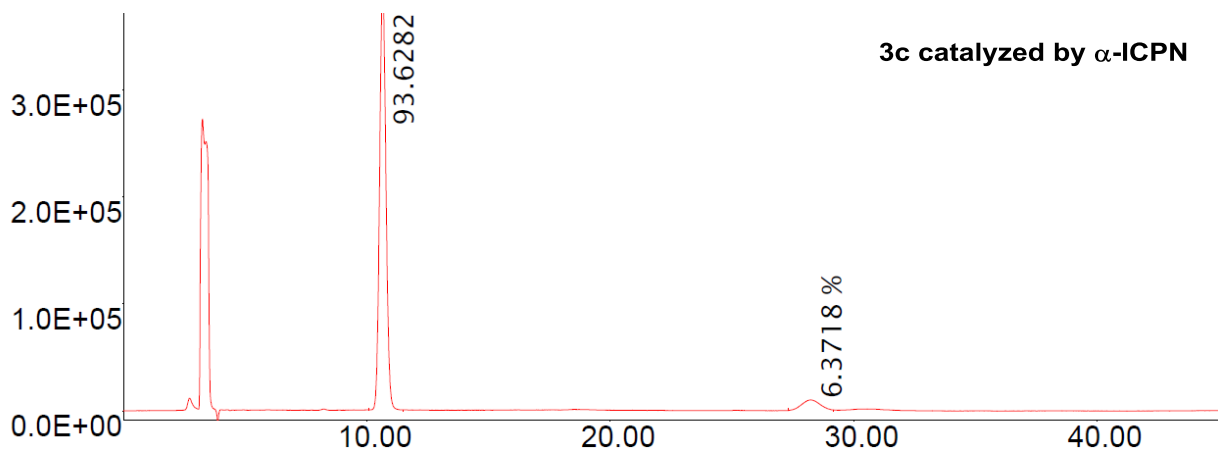
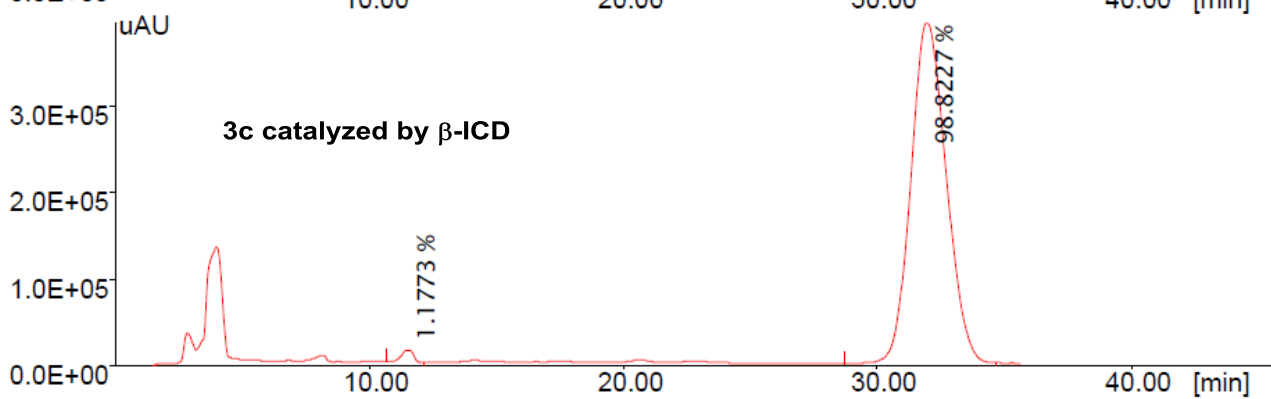
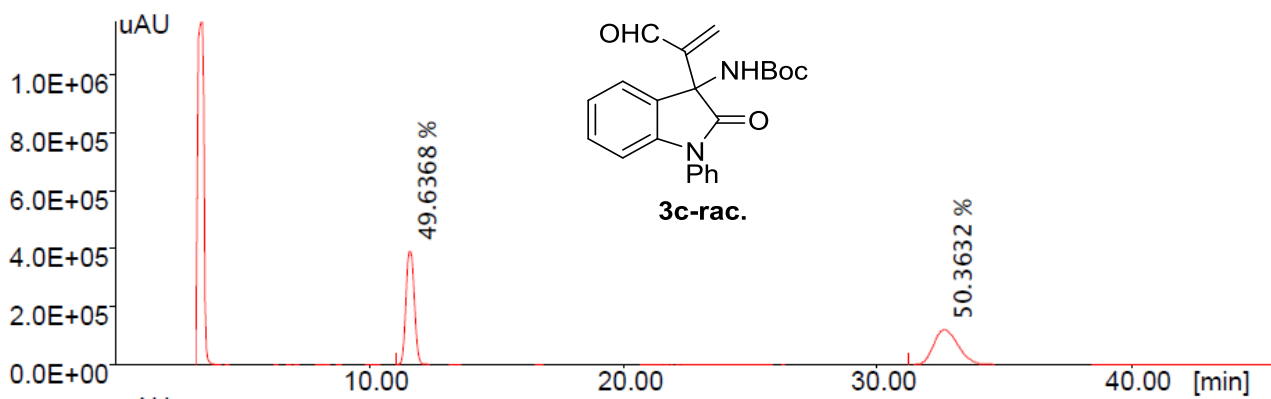
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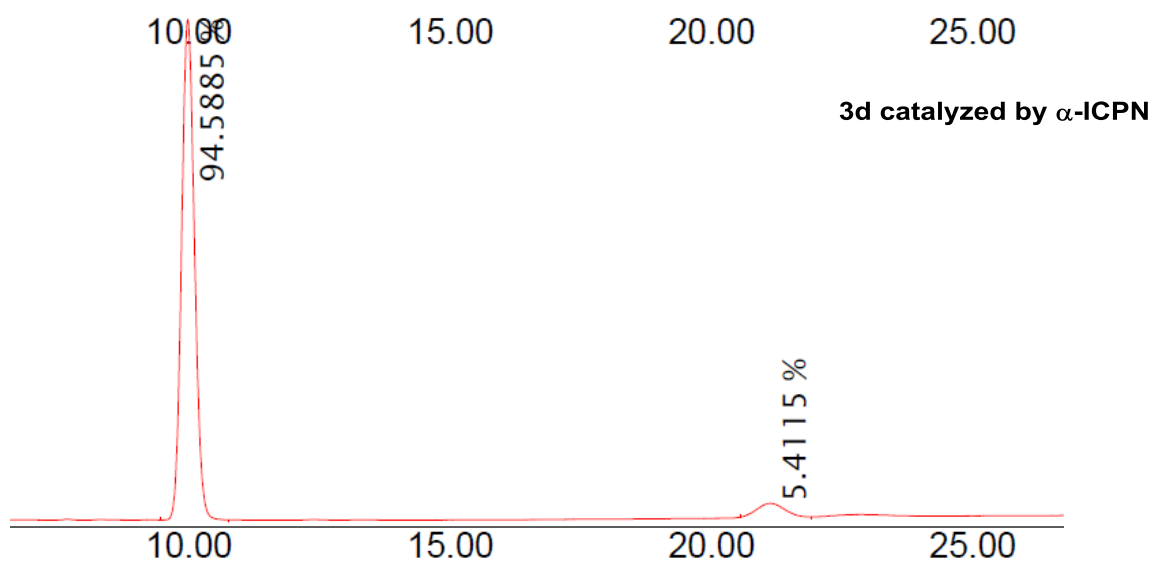
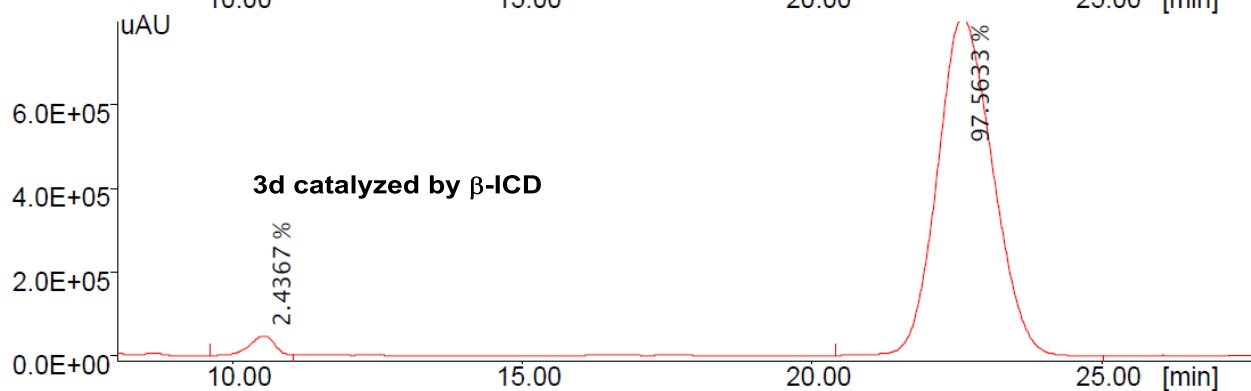
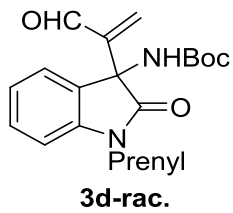
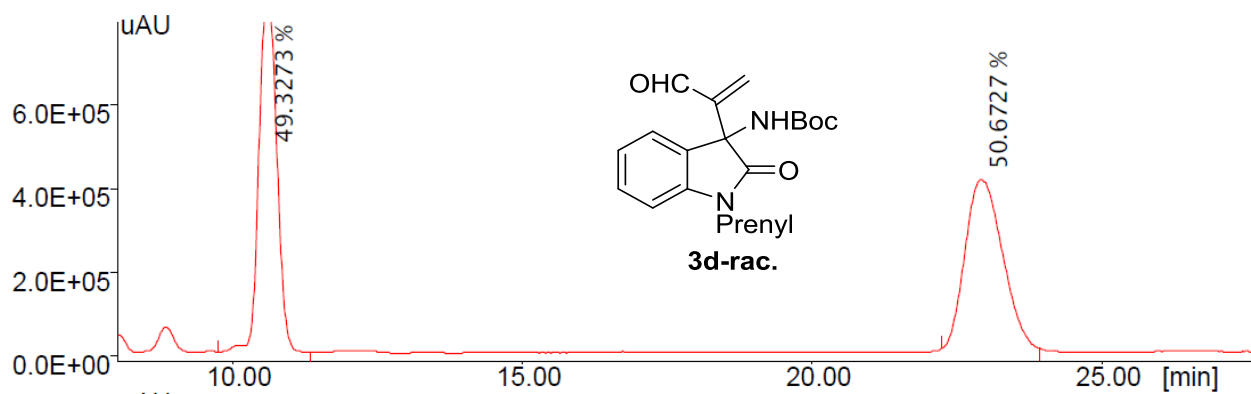
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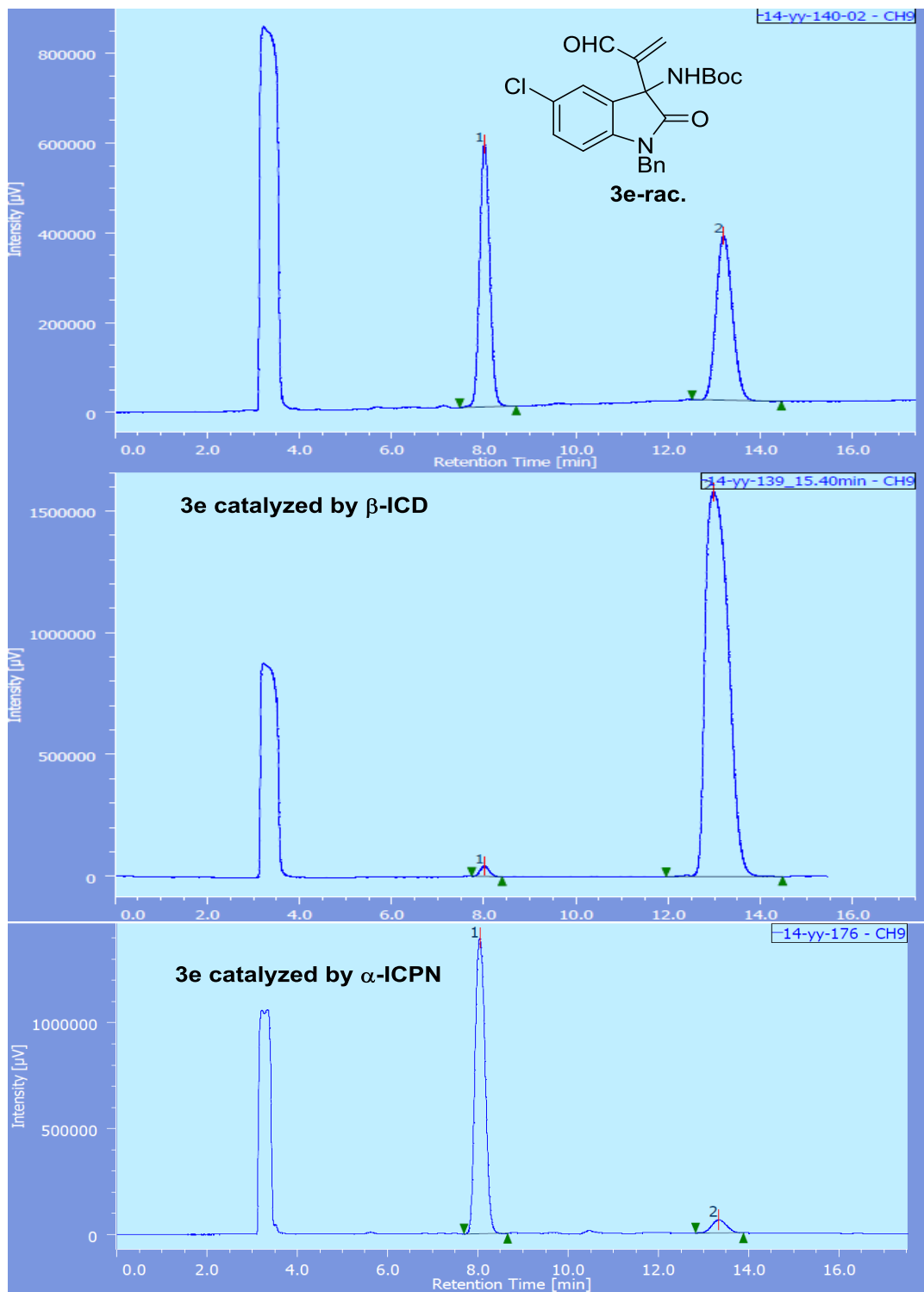
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1	Unknown	9	10.778	4733012	244565	49.926	66.499	N/A	7023	15.198	1.089	
2	Unknown	9	22.487	4747119	123209	50.074	33.501	N/A	7619	N/A	1.049	

#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	10.843	1376400	76833	2.120	5.697	N/A	8365	12.221	1.090	
2	Unknown	9	22.135	63557090	1271909	97.880	94.303	N/A	4125	N/A	1.784	

#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	11.558	47935917	2198716	95.058	97.629	N/A	6488	16.157	1.724	
2	Unknown	9	26.042	2492148	53391	4.942	2.371	N/A	7247	N/A	1.194	







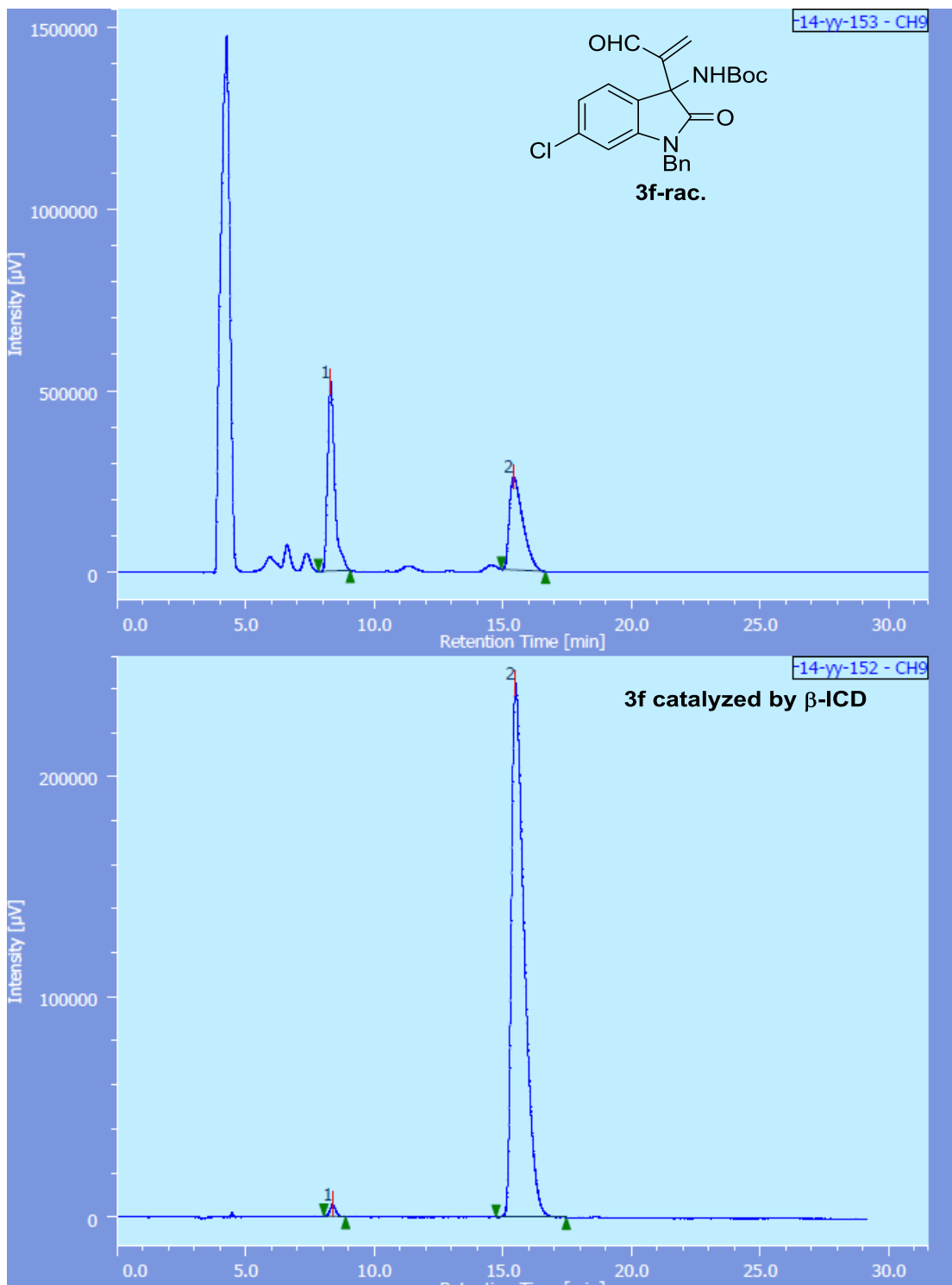
Channel & Peak Information Table

Chromatogram Name 14-yy-140-02-CH9

Sample Name

Channel Name 208.0nm

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2	Unknown	9	13.198	8950168	366255	50.175	38.475	N/A	6574	N/A	1.124	
#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.007	583931	42691	1.058	2.630	N/A	7601	7.452	1.075	
2	Unknown	9	12.977	54609934	1580470	98.942	97.370	N/A	2863	N/A	1.513	
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1	Unknown	9	8.040	21673511	1393702	93.712	95.725	N/A	5698	10.110	1.110	
2	Unknown	9	13.325	1454370	62238	6.288	4.275	N/A	7338	N/A	1.073	



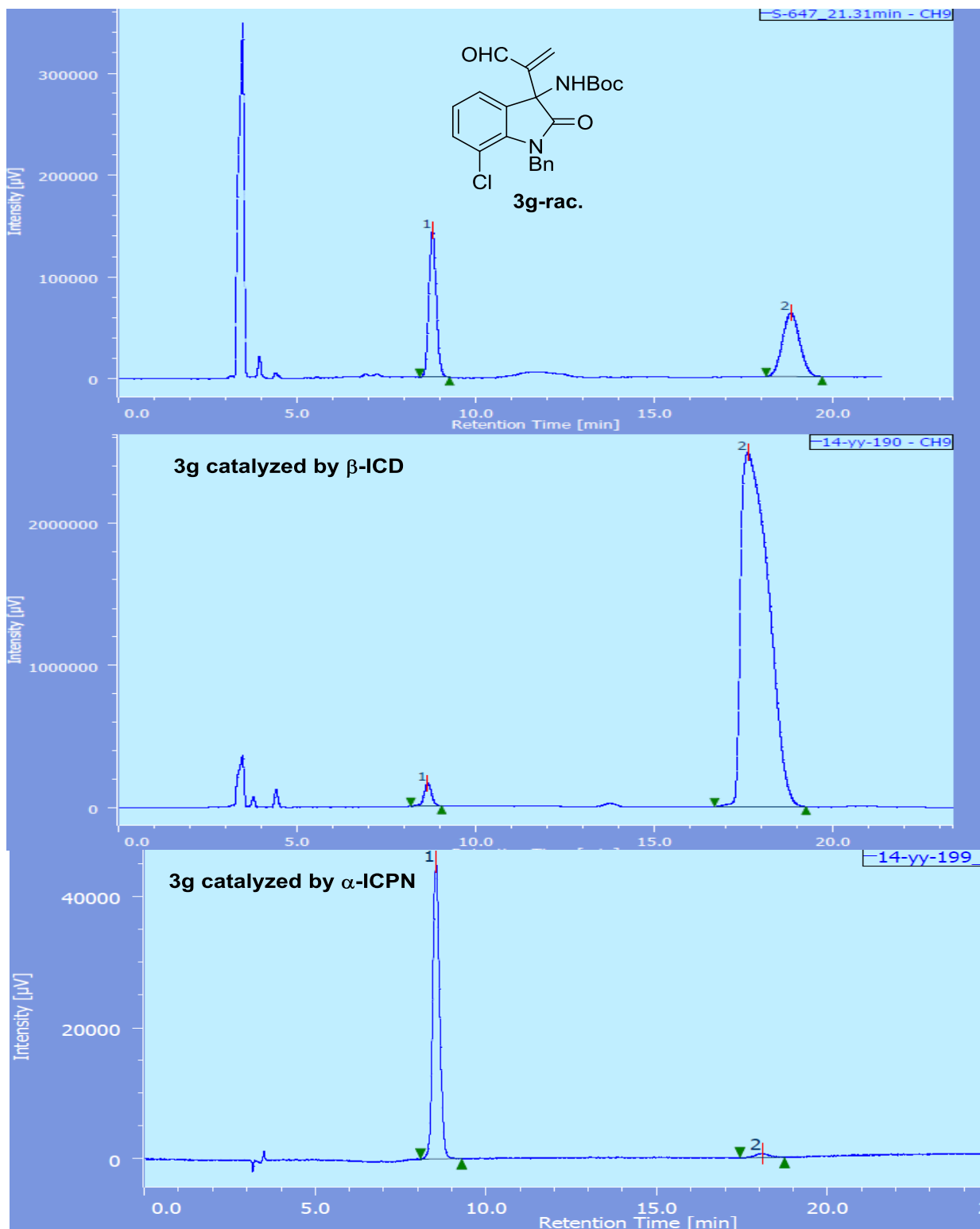
Channel & Peak Information Table

Chromatogram Name 14-yy-153-CH9

Sample Name

Channel Name 263.0nm

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1	Unknown	9	8.300	10081193	520572	51.860	67.012	N/A	4880	9.935	1.619	
2	Unknown	9	15.417	9358182	256265	48.140	32.988	N/A	4116	N/A	1.853	
#	Peak Name	CH	tR [min]	Area [ $\mu$ V-sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.385	83870	5414	0.986	2.184	N/A	6910	10.925	1.070	
2	Unknown	9	15.493	8421449	242513	99.014	97.816	N/A	4728	N/A	1.814	



Channel & Peak Information Table

Chromatogram Name S-647\_21.31min-CH9

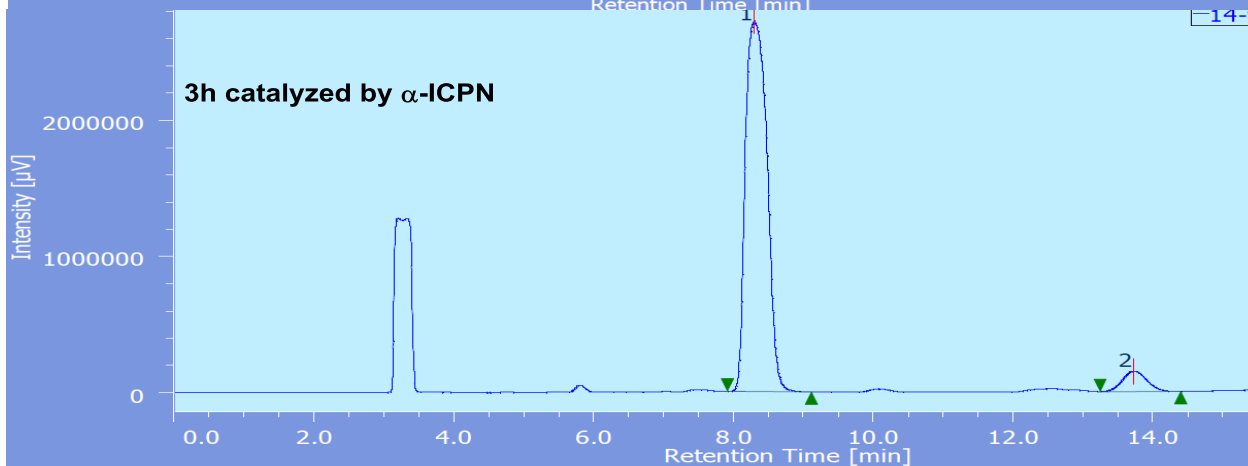
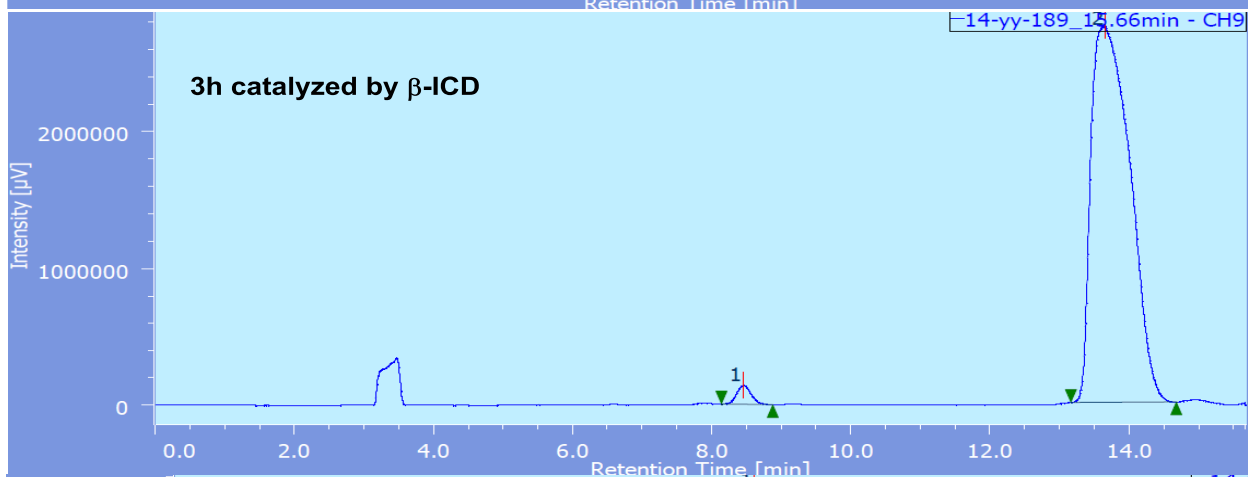
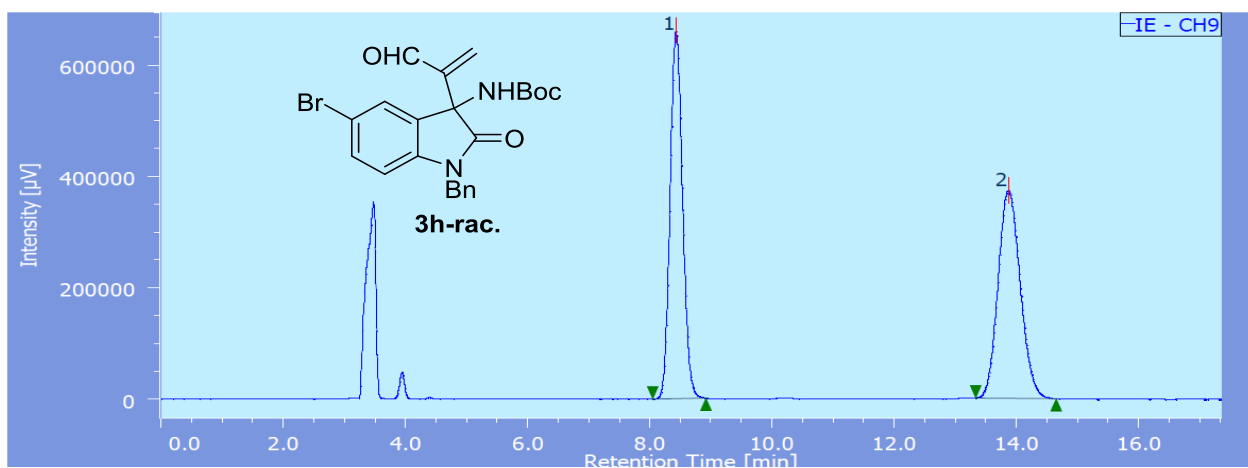
Sample Name

Channel Name 216.0nm

#	Peak Name	CH	tR [min]	Area [ $\mu$ V·sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.788	2068866	143692	49.749	69.710	N/A	8554	15.821	1.073	
2	Unknown	9	18.807	2089717	62437	50.251	30.290	N/A	7148	N/A	1.071	

#	Peak Name	CH	tR [min]	Area [ $\mu$ V·sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.657	2308681	159928	1.699	6.036	N/A	8755	9.396	0.946	
2	Unknown	9	17.608	133554537	2489508	98.301	93.964	N/A	2090	N/A	2.165	

#	Peak Name	CH	tR [min]	Area [ $\mu$ V·sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.528	640251	45244	97.008	98.652	N/A	8592	15.509	1.144	
2	Unknown	9	18.083	19738	618	2.991	1.348	N/A	6953	N/A	0.996	



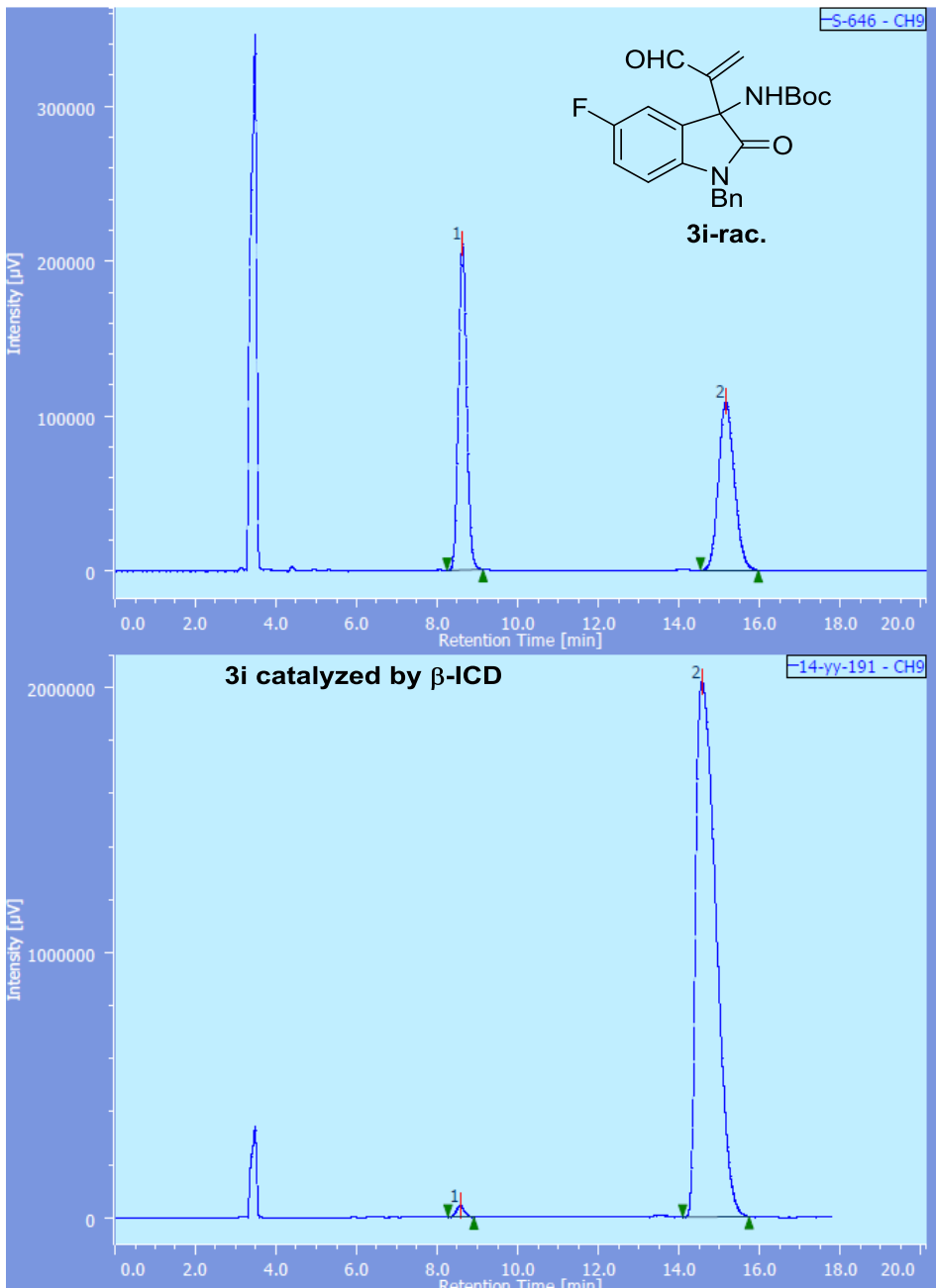
Channel & Peak Information Table

Chromatogram Name IE-CH9  
 Sample Name  
 Channel Name 216.0nm  
 Sampling Interval 100 [msec]  
 Peak Method (Manual)

Formula  
 Decision

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.427	9337402	659899	49.794	63.905	N/A	8124	10.451	1.091	
2	Unknown	9	13.863	9414652	372727	50.206	36.095	N/A	6865	N/A	1.119	
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.453	1995395	137903	1.836	4.778	N/A	7776	6.908	1.076	
2	Unknown	9	13.648	106688405	2748102	98.164	95.222	N/A	2357	N/A	1.587	
#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.292	58229023	2719780	94.114	94.763	N/A	2944	8.647	1.292	
2	Unknown	9	13.723	3641449	150319	5.886	5.237	N/A	7166	N/A	1.087	





Channel & Peak Information Table

Chromatogram Name S-646-CH9

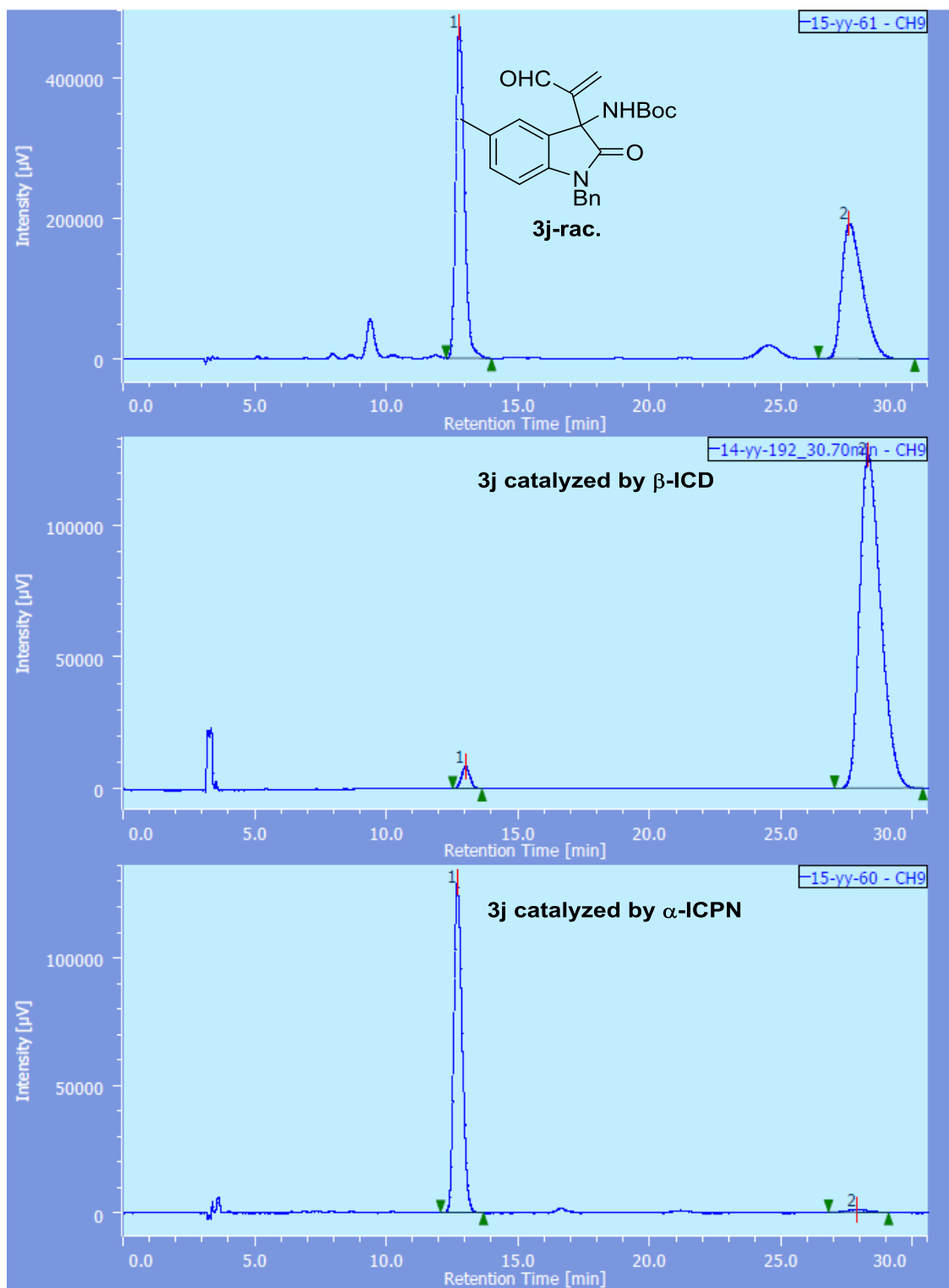
Sample Name

Channel Name 216.0nm

#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.620	3008063	210652	50.125	65.906	N/A	8387	11.866	1.086	
2	Unknown	9	15.150	2993081	108975	49.875	34.094	N/A	6948	N/A	1.128	

#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.563	590808	42101	0.844	2.044	N/A	8525	9.156	1.056	
2	Unknown	9	14.557	69370352	2017750	99.156	97.956	N/A	3824	N/A	1.873	



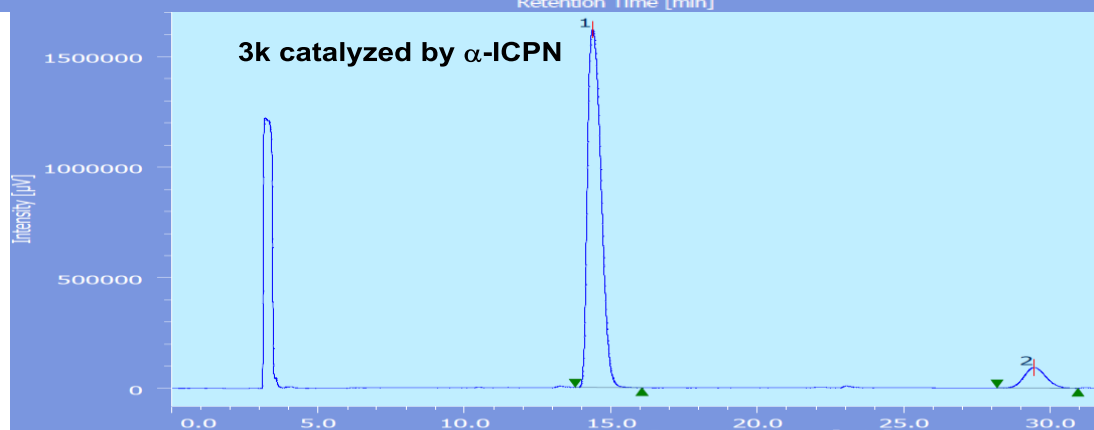
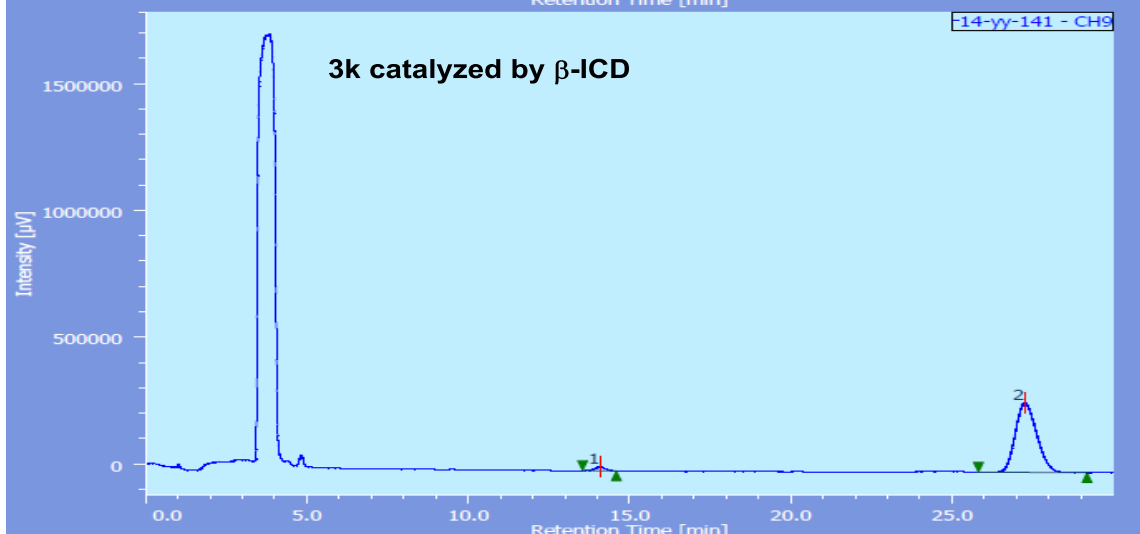
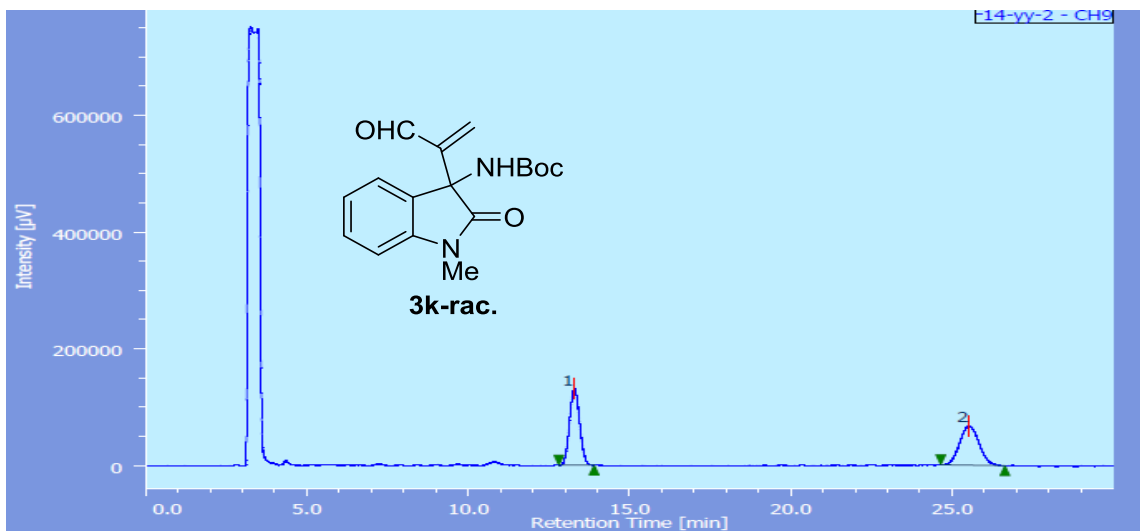
Channel & Peak Information Table

Chromatogram Name 15-yy-61-CH9

Sample Name

Channel Name 262.0nm

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1	Unknown	9	12.783	10811241	470211	50.481	70.947	N/A	7337	14.477	1.236	
2	Unknown	9	27.588	10605103	192552	49.519	29.053	N/A	5762	N/A	1.531	
#	Peak Name	CH	tR [min]	Area [ $\mu$ V $\cdot$ sec]	Height [ $\mu$ V]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	13.010	814668	36084	2.656	6.406	N/A	7402	14.558	1.044	
2	Unknown	9	28.297	29855422	527168	97.344	93.594	N/A	5688	N/A	1.368	
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1	Unknown	9	12.705	2851721	129506	97.766	99.109	N/A	7680	14.680	1.224	
2	Unknown	9	27.900	65176	1164	2.234	0.891	N/A	5566	N/A	1.197	



Channel & Peak Information Table

Chromatogram Name 14-yy-2-CH9

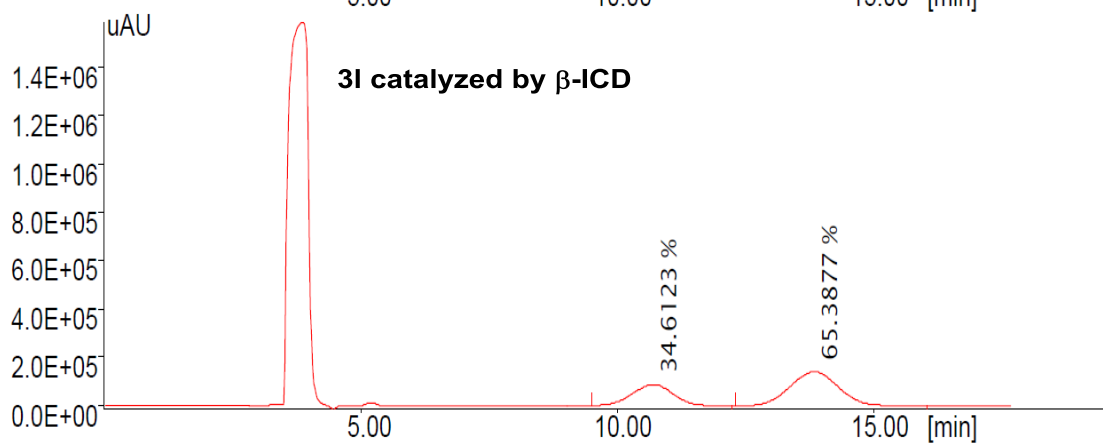
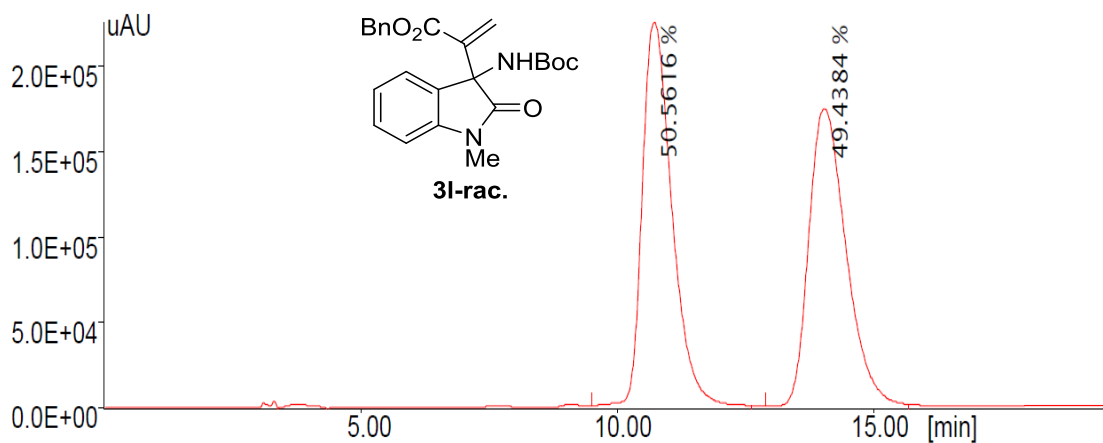
Sample Name

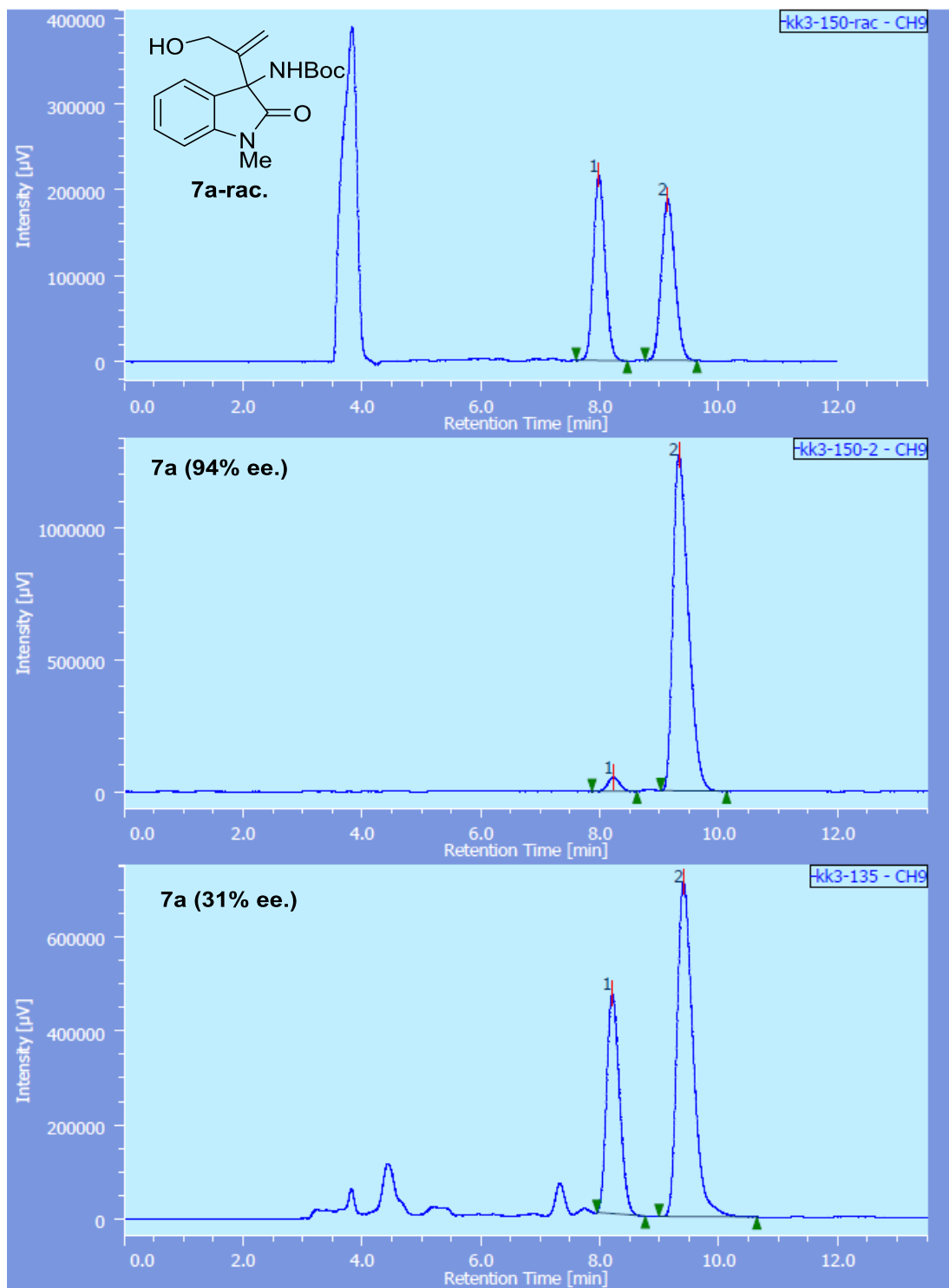
Channel Name 216.0nm

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	13.318	2260001	103073	50.217	66.049	N/A	8528	14.441	1.095	
2	Unknown	9	25.610	2240490	52982	49.783	33.951	N/A	8220	N/A	1.066	

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	14.078	359915	15274	2.748	5.278	N/A	8201	14.237	1.004	
2	Unknown	9	27.240	12738927	274099	97.252	94.722	N/A	7821	N/A	1.187	

#	Peak Name	CH	tR [min]	Area [µV·sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	14.373	51912065	1617280	91.408	94.560	N/A	4262	13.331	1.462	
2	Unknown	9	29.442	4879330	93050	8.592	5.440	N/A	7220	N/A	1.105	





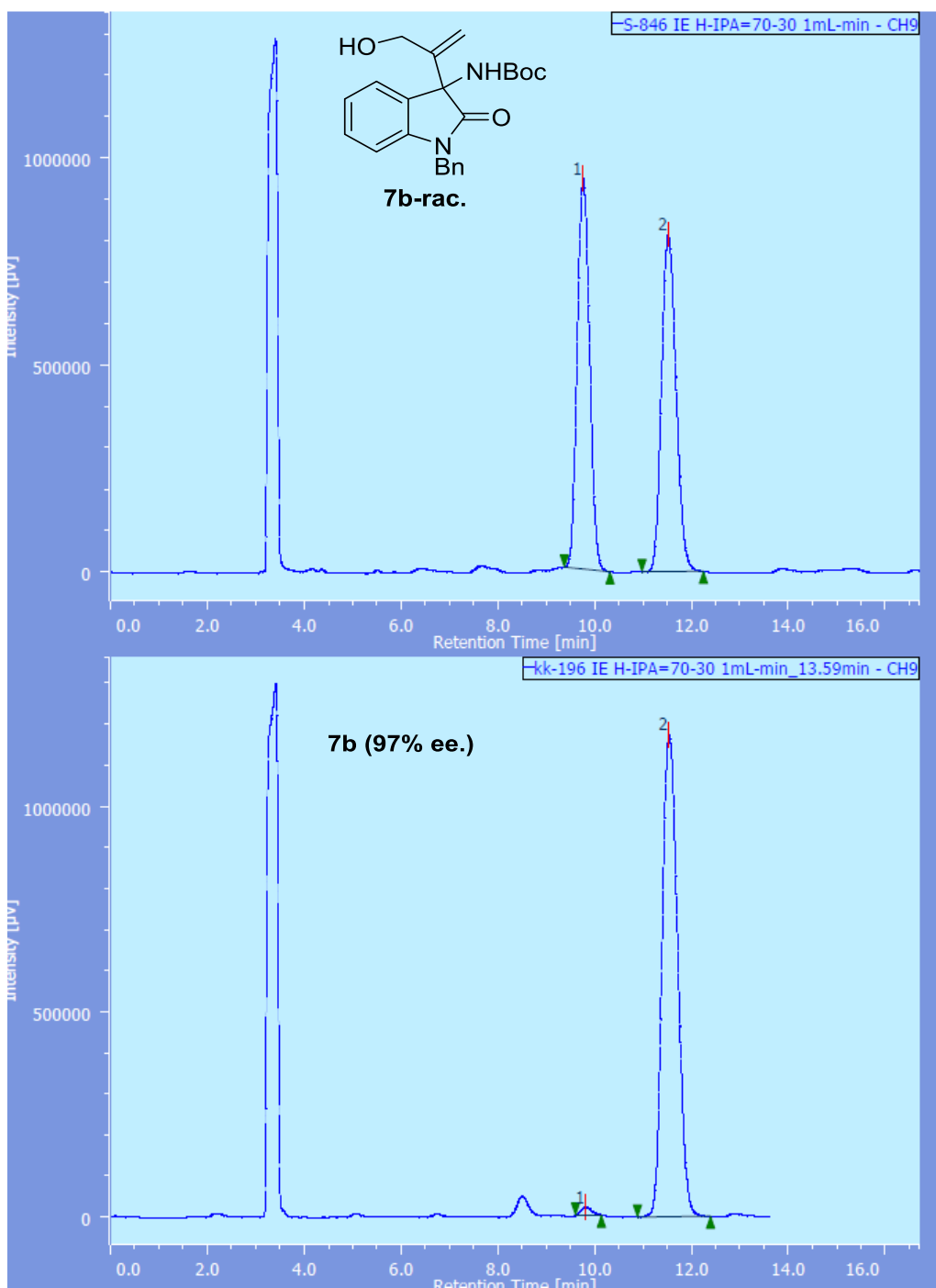
Channel & Peak Information Table

Chromatogram Name kk3-150-rac-CH9

Sample Name kk3-150-rac

Channel Name 240.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	7.980	2959143	216311	49.861	53.576	N/A	7845	2.976	1.126	
2	Unknown	9	9.138	2975637	187432	50.139	46.424	N/A	7568	N/A	1.130	
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.225	753173	53731	3.186	4.051	N/A	7722	2.596	1.077	
2	Unknown	9	9.325	22884591	1272600	96.814	95.949	N/A	6158	N/A	1.458	
#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	8.207	7053465	467825	34.636	39.645	N/A	6670	2.729	1.215	
2	Unknown	9	9.405	13311203	712218	65.364	60.355	N/A	6180	N/A	1.402	



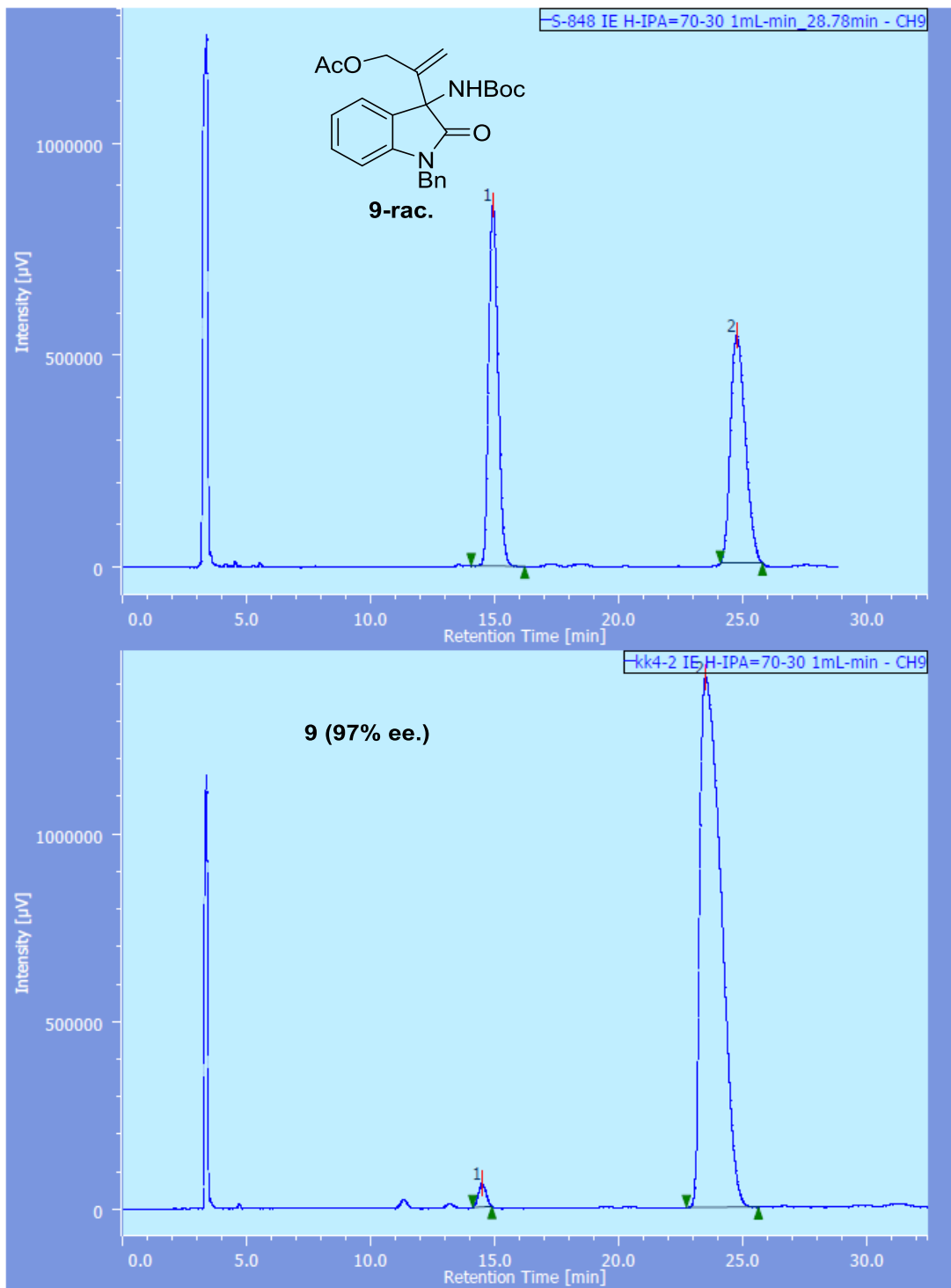
#	Peak Name	CH	tR [min]	Area [µV-sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	9.758	16756510	943503	49.708	53.695	N/A	6652	3.401	1.087	
2	Unknown	9	11.512	16953113	813656	50.292	46.305	N/A	6880	N/A	1.154	

Chromatogram Name kk-196 IE H-IPA=70-30 1mL-min\_13.59min-CH9

Sample Name

Channel Name 214.0nm

#	Peak Name	CH	tR [min]	Area [µV-sec]	Height [µV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	9.810	320605	19943	1.219	1.671	N/A	8002	3.333	1.244	
2	Unknown	9	11.528	25987902	1173906	98.781	98.329	N/A	6001	N/A	1.184	



#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	14.930	22374162	850134	49.685	61.305	N/A	7284	10.736	1.207	
2	Unknown	9	24.760	22658295	536584	50.315	38.695	N/A	7596	N/A	1.264	

Chromatogram Name kk4-2 IE H-IPA=70-30 1mL-min-CH9

Sample Name

Channel Name 210.0nm

#	Peak Name	CH	tR [min]	Area [μV·sec]	Height [μV]	Area%	Height%	Quantity	NTP	Resolution	Symmetry Factor	Warning
1	Unknown	9	14.497	1381919	62360	1.638	4.229	N/A	9143	7.999	1.040	
2	Unknown	9	23.497	82959729	1412225	98.362	95.771	N/A	3245	N/A	2.047	

## References

1. F.-L. Hu, Y. Wei, M. Shi, S. Pindi and G. Li, *Org. Biomol. Chem.*, 2013, **11**, 1921.
2. X. Zhao, T.-Z. Li, J.-Y. Qian, F. Sha and X.-Y. Wu, *Org. Biomol. Chem.*, 2014, **12**, 8072.