

## SUPPORTING INFORMATION

# Readily Available Chiral Benzimidazoles-Derived Guanidines as Organocatalysts in the Asymmetric $\alpha$ -Amination of 1,3-Dicarbonyl Compounds

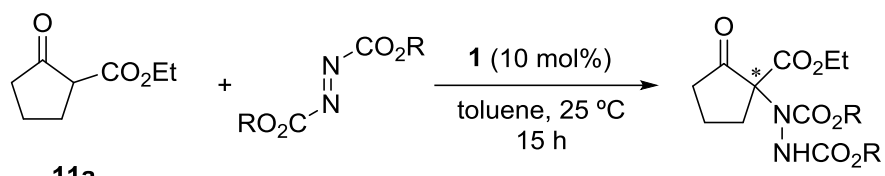
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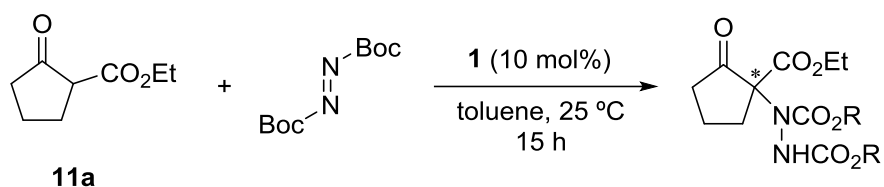
Azodicarboxylate tests and NLE experiments	2
$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Catalysts	3
$^1\text{H}$ NMR Spectra of Chiral Amination Products	13
HPLC Chromatograms of Chiral Amination Products	19

## Azodicarboxylate tests

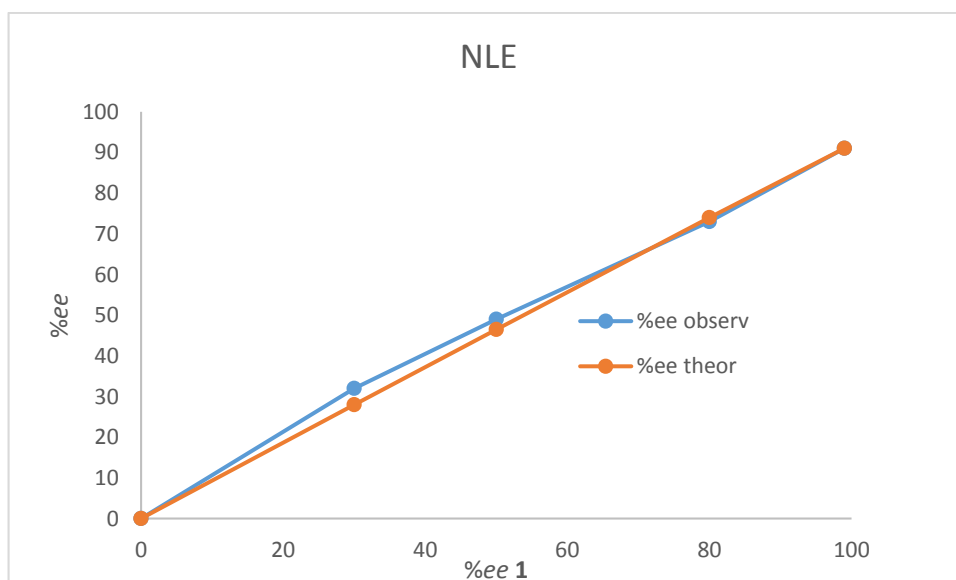


R = Et, >95% conv. 55% ee  
R = Bn,  $\approx$ 70% conv. 64% ee

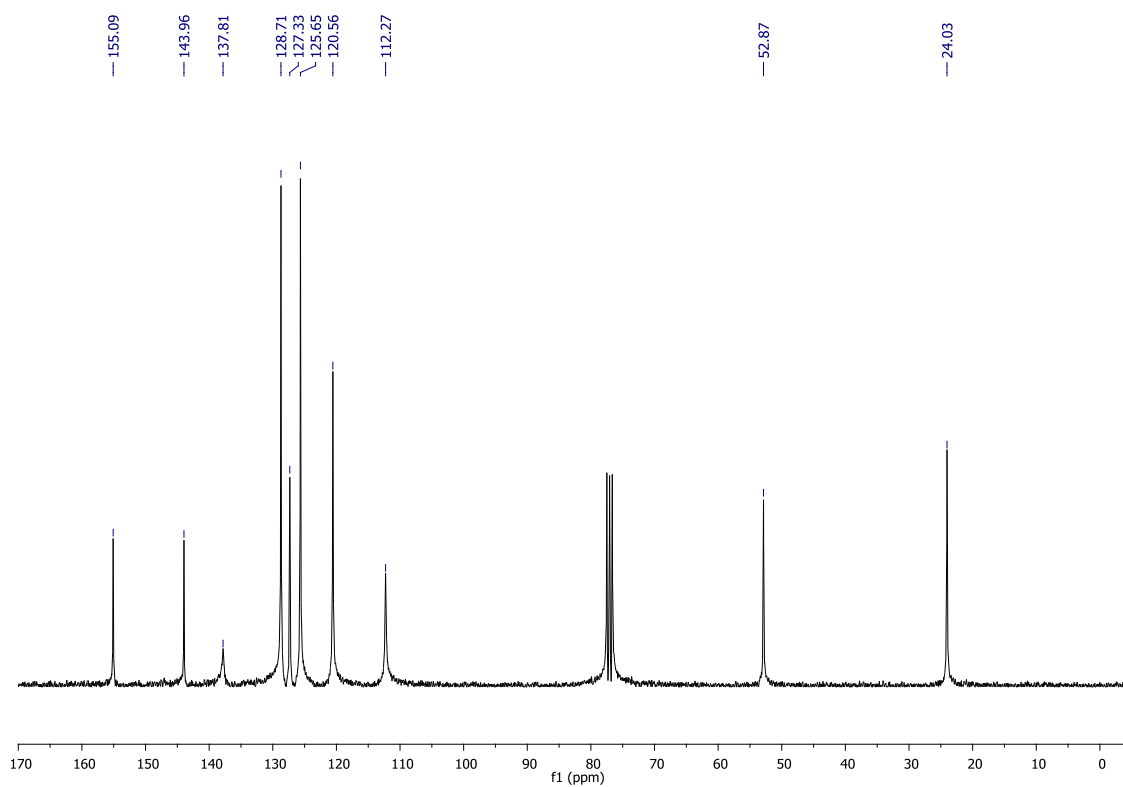
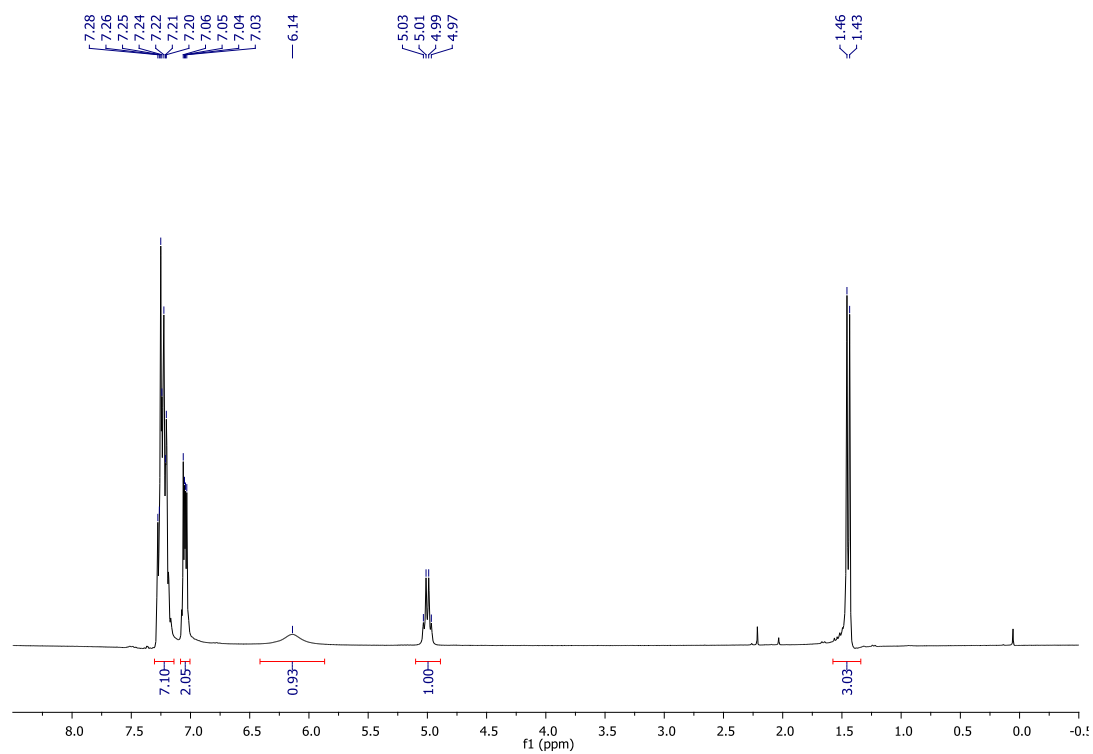
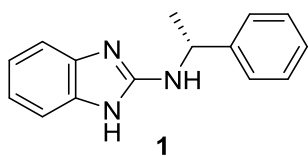
## Non Linear Effects Experiments

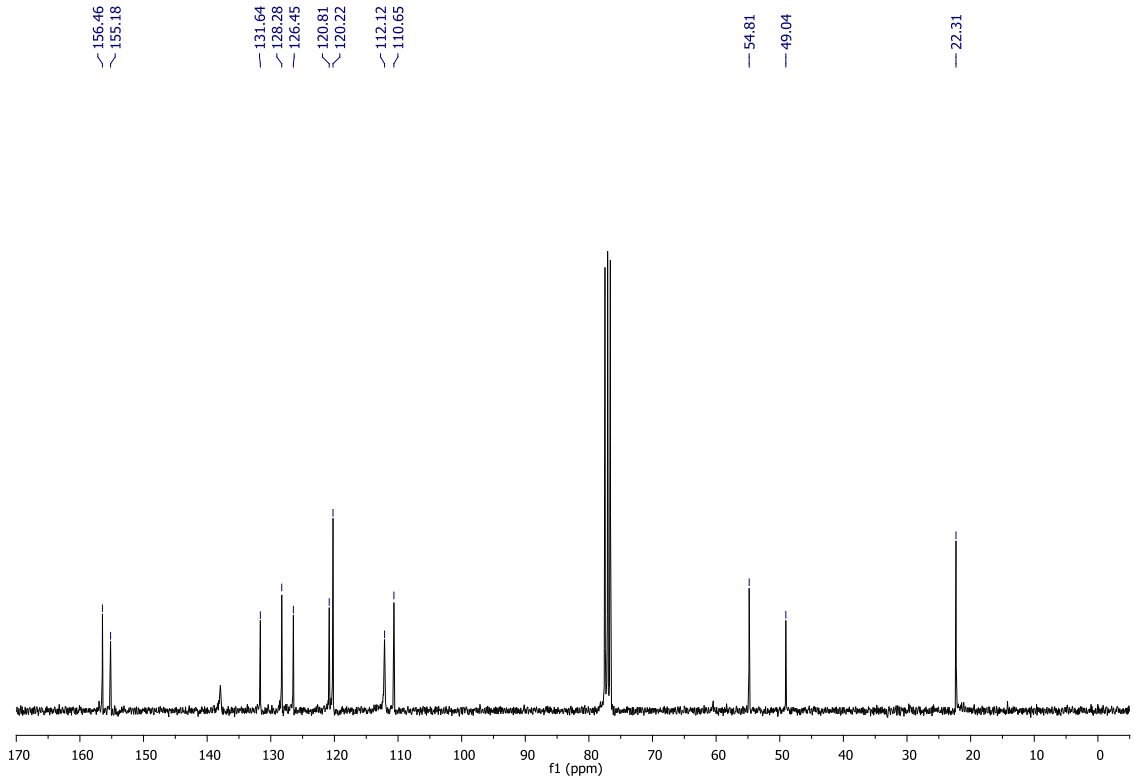
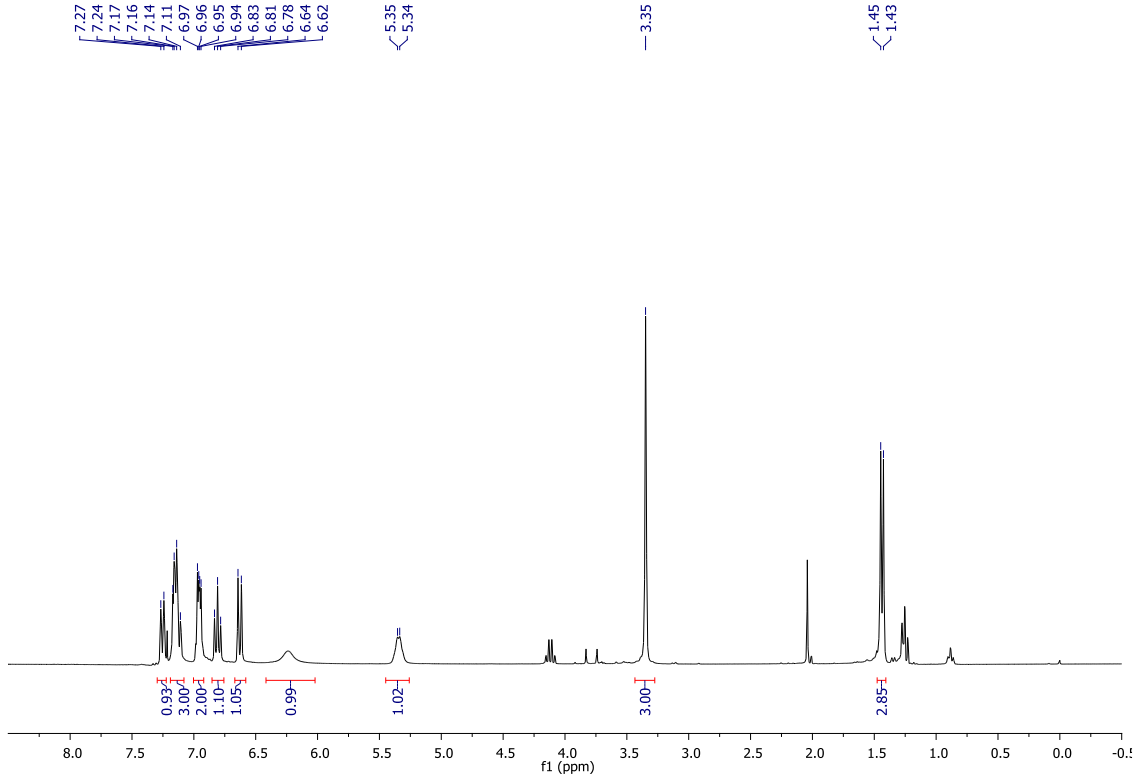
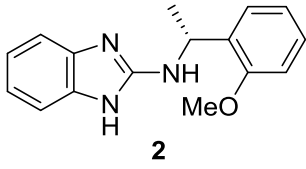


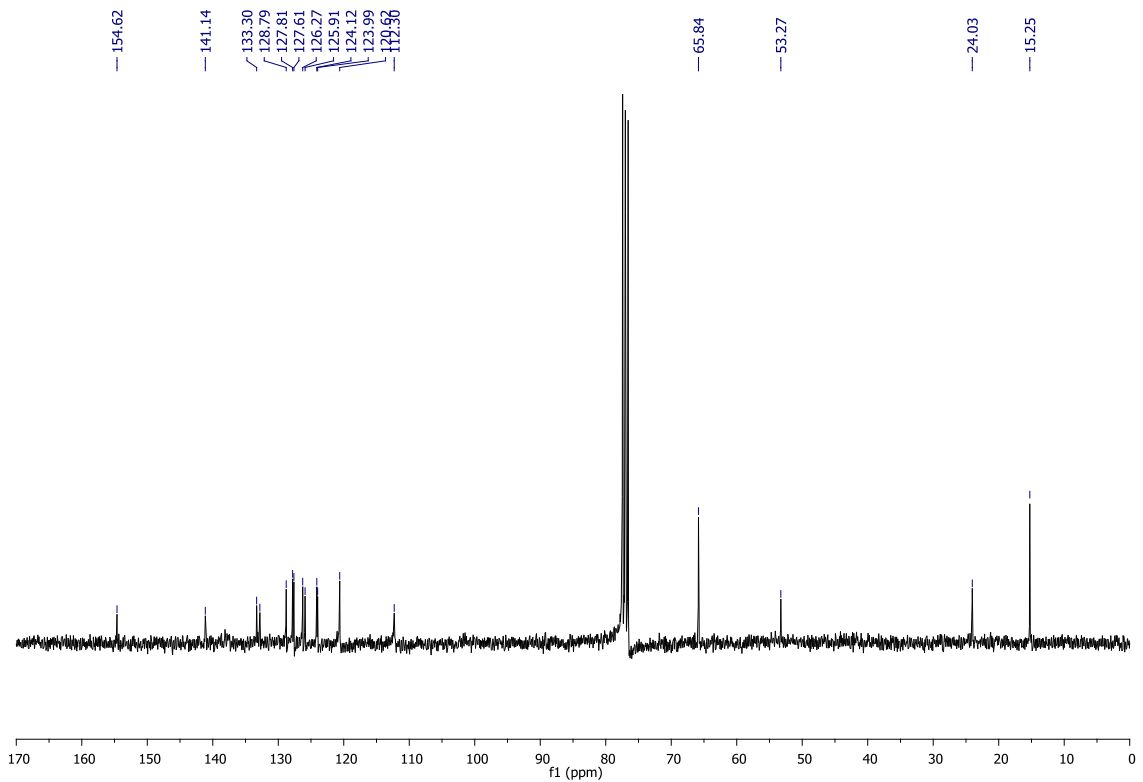
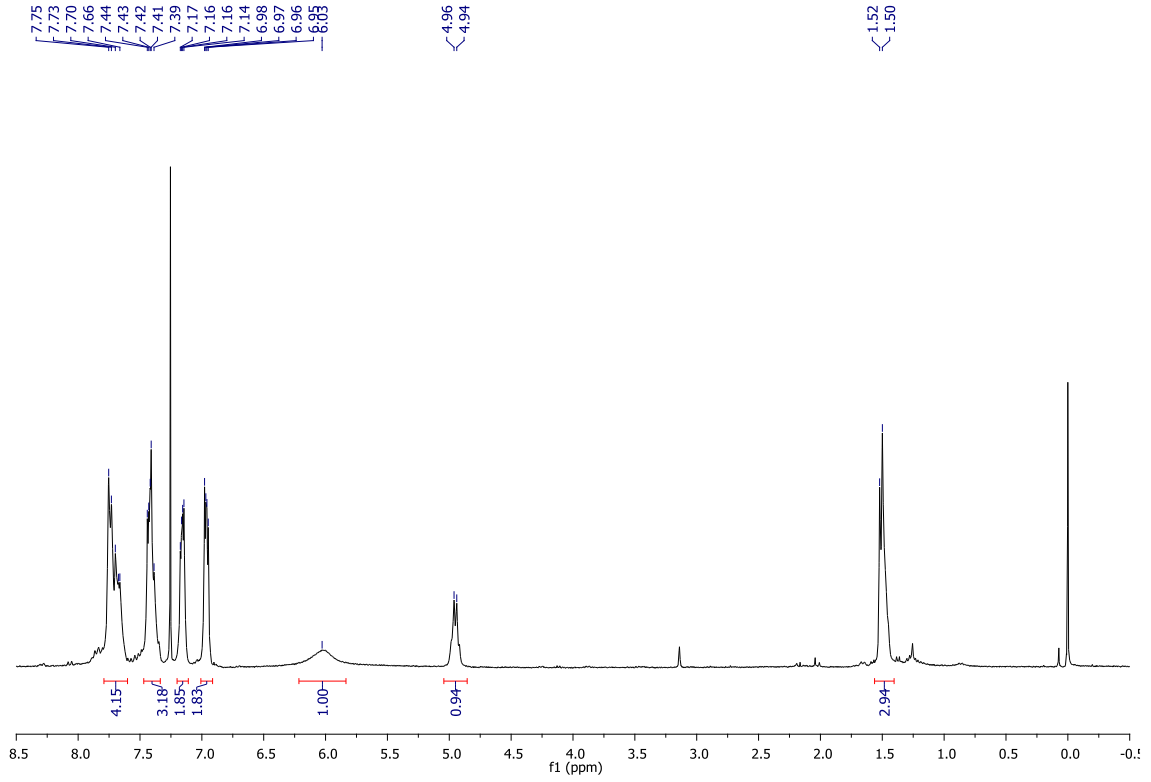
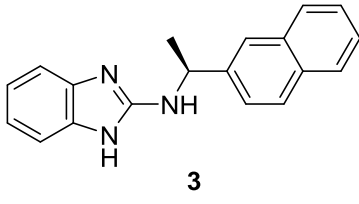
%ee 1	%ee theor.	%ee observ.
0	0	0
30	28	33
50	46.5	49
80	74	73
99	91	91

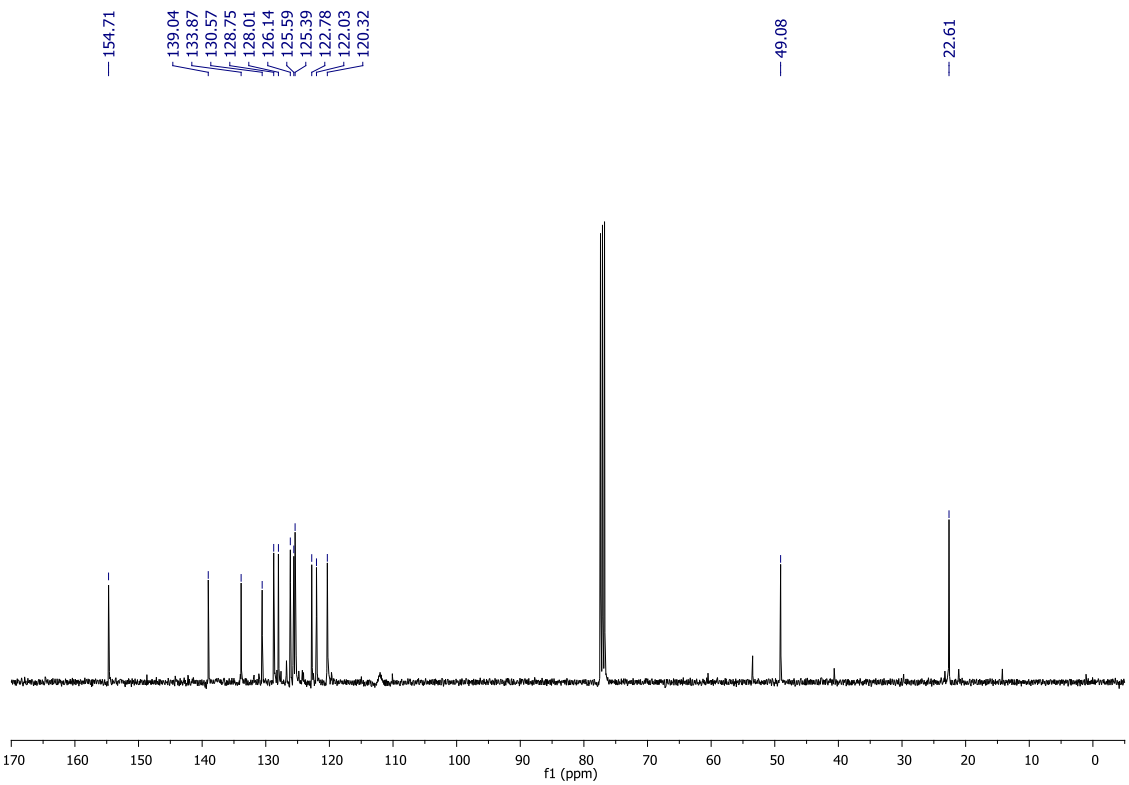
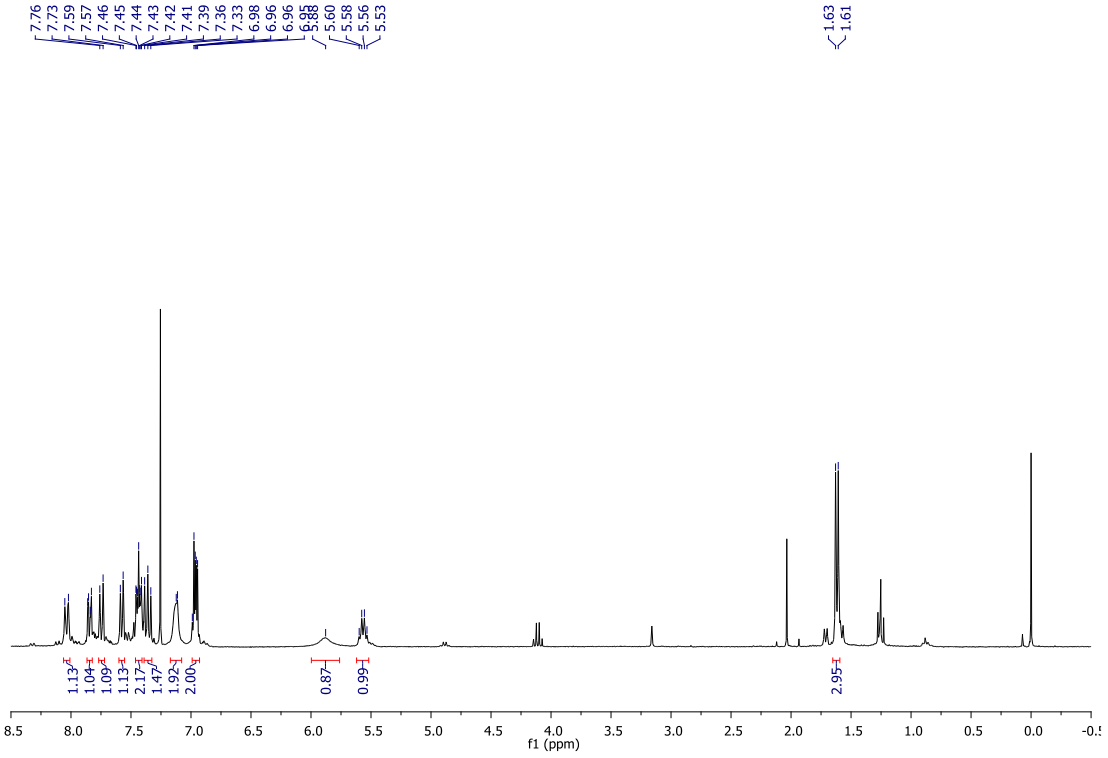
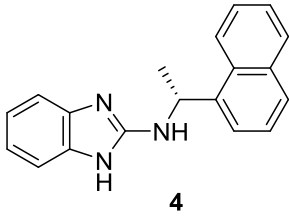


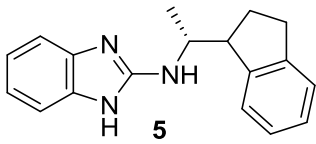
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Catalysts



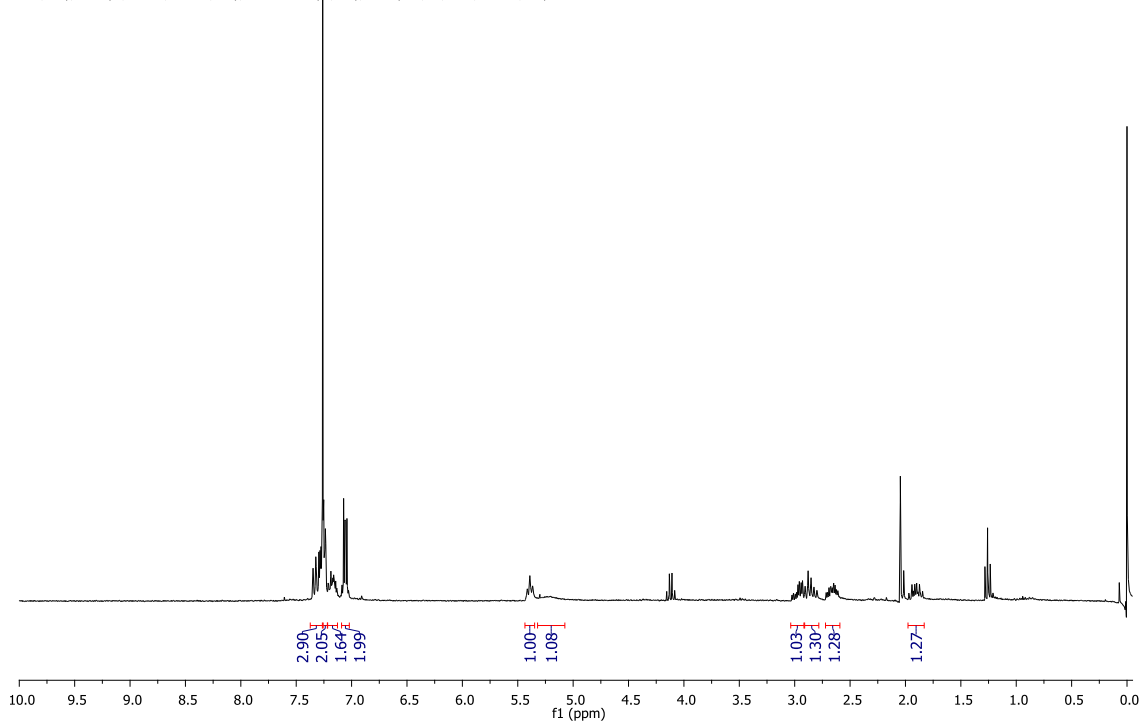




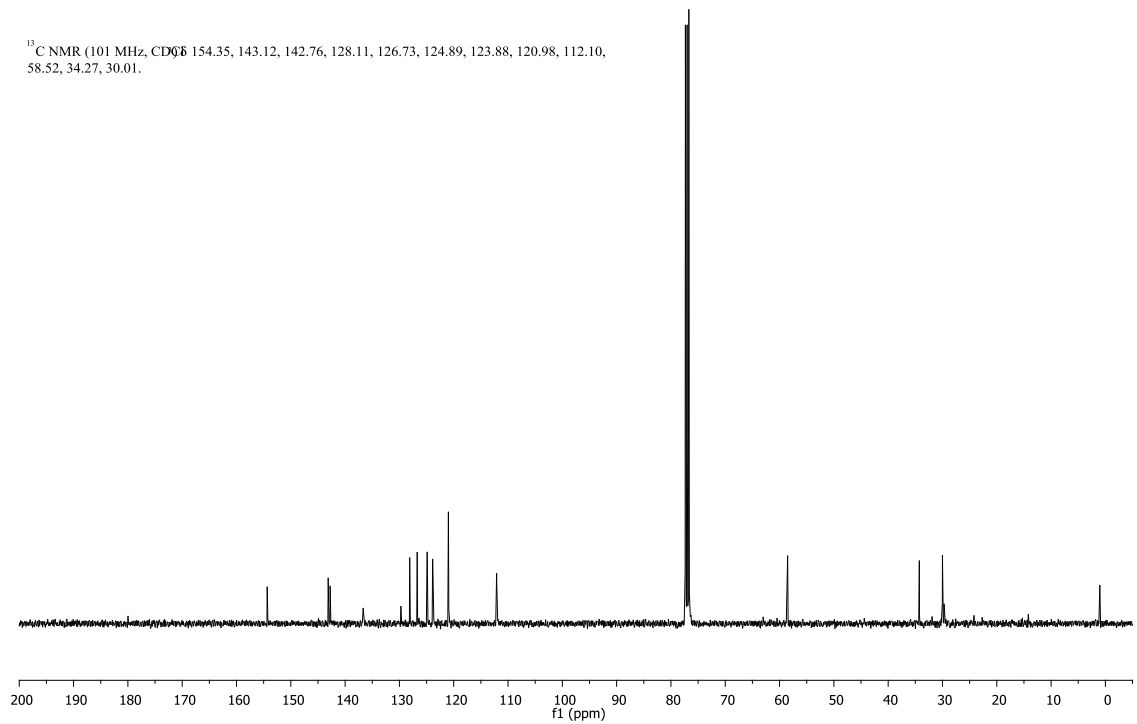


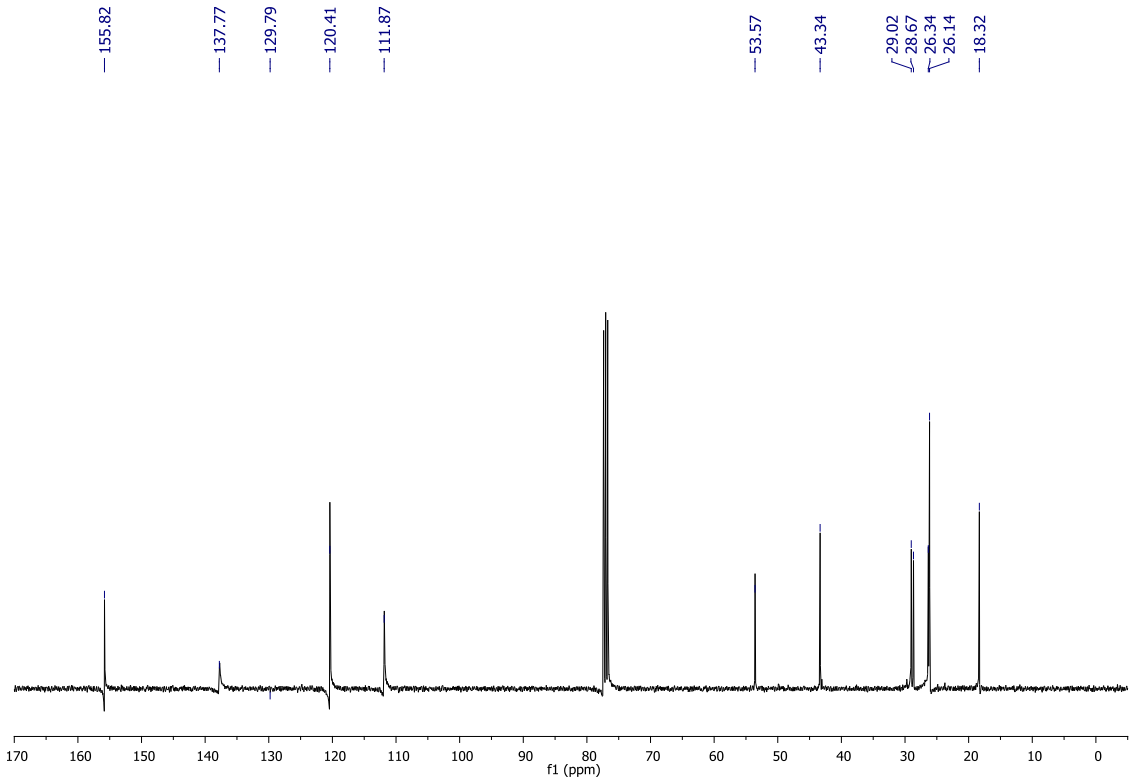
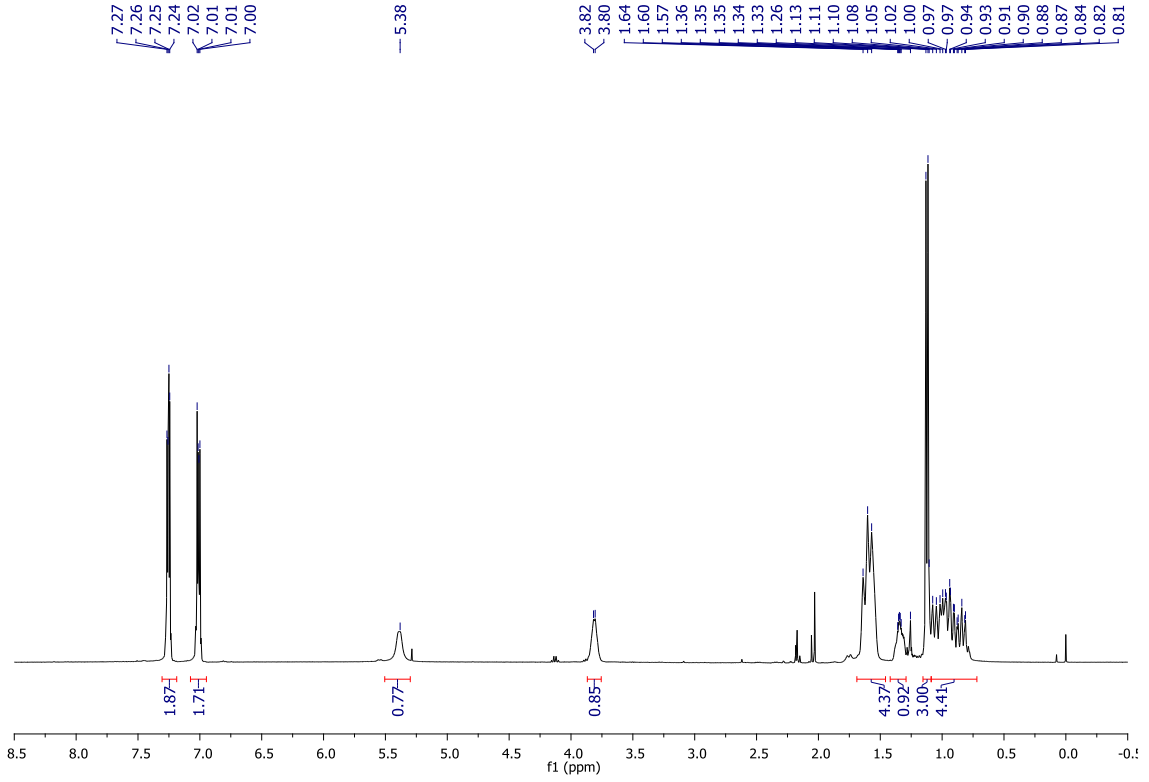
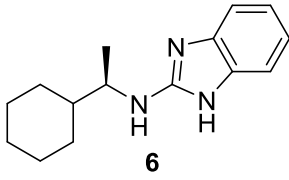


<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 7.37 – 7.26 (m, 9H), 7.26 – 7.22 (m, 6H), 7.17 (ddd, 2.9, 8.1, 2.2 Hz, 5H), 7.09 – 7.02 (m, 6H), 5.39 (t, 7.1 Hz, 3H), 5.27 (d, 20.1 Hz, 3H), 2.98 (dd, 12.3, 8.8, 3.9 Hz, 3H), 2.85 (dt, 15.8, 8.0 Hz, 4H), 2.72 – 2.59 (m, 4H), 1.91 (ddd, 6.0, 12.8, 8.4 Hz, 4H).

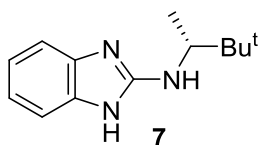


<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) 154.35, 143.12, 142.76, 128.11, 126.73, 124.89, 123.88, 120.98, 112.10, 58.52, 34.27, 30.01.

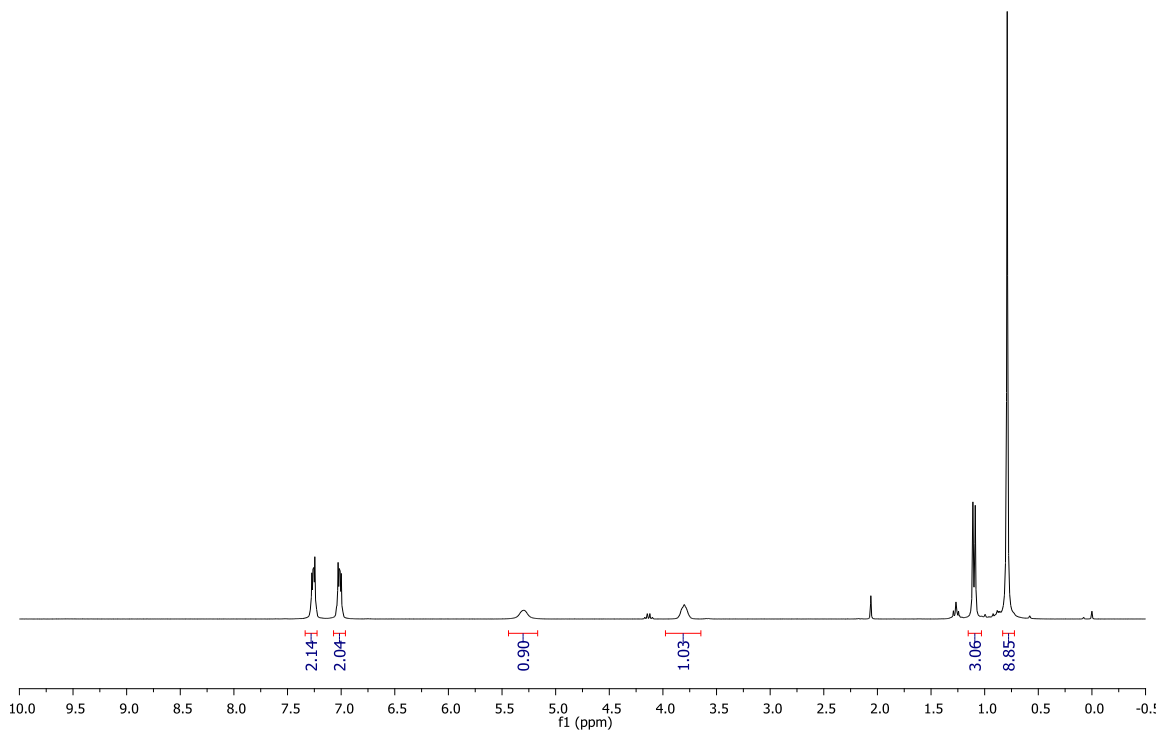




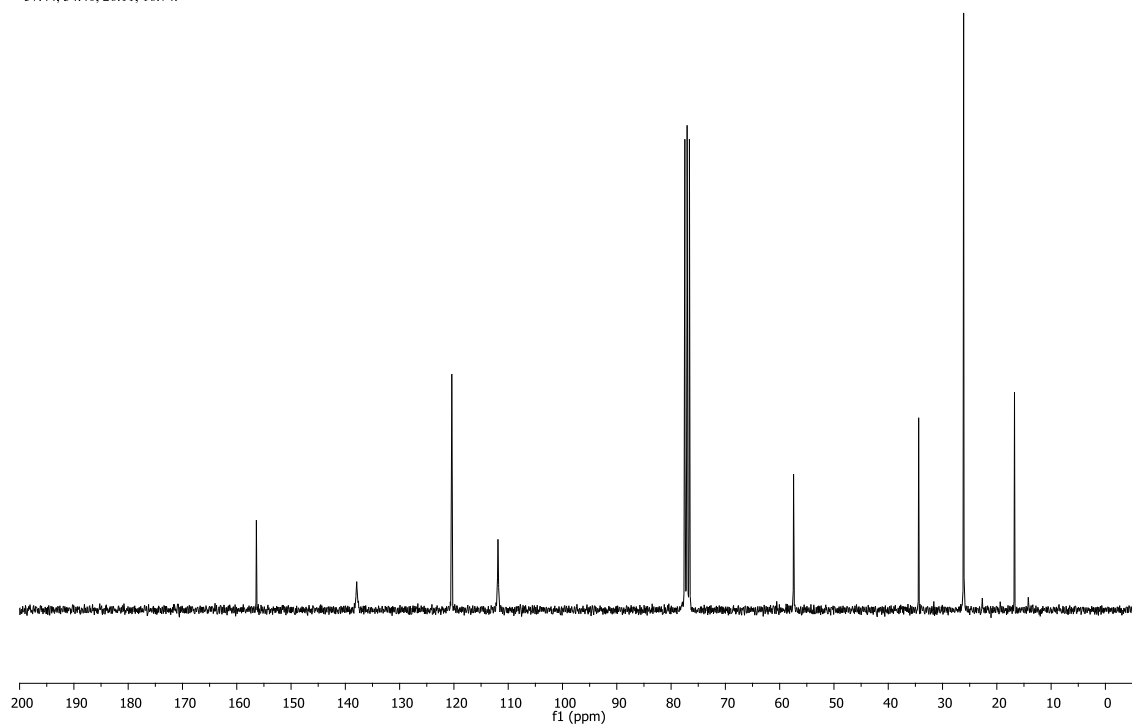


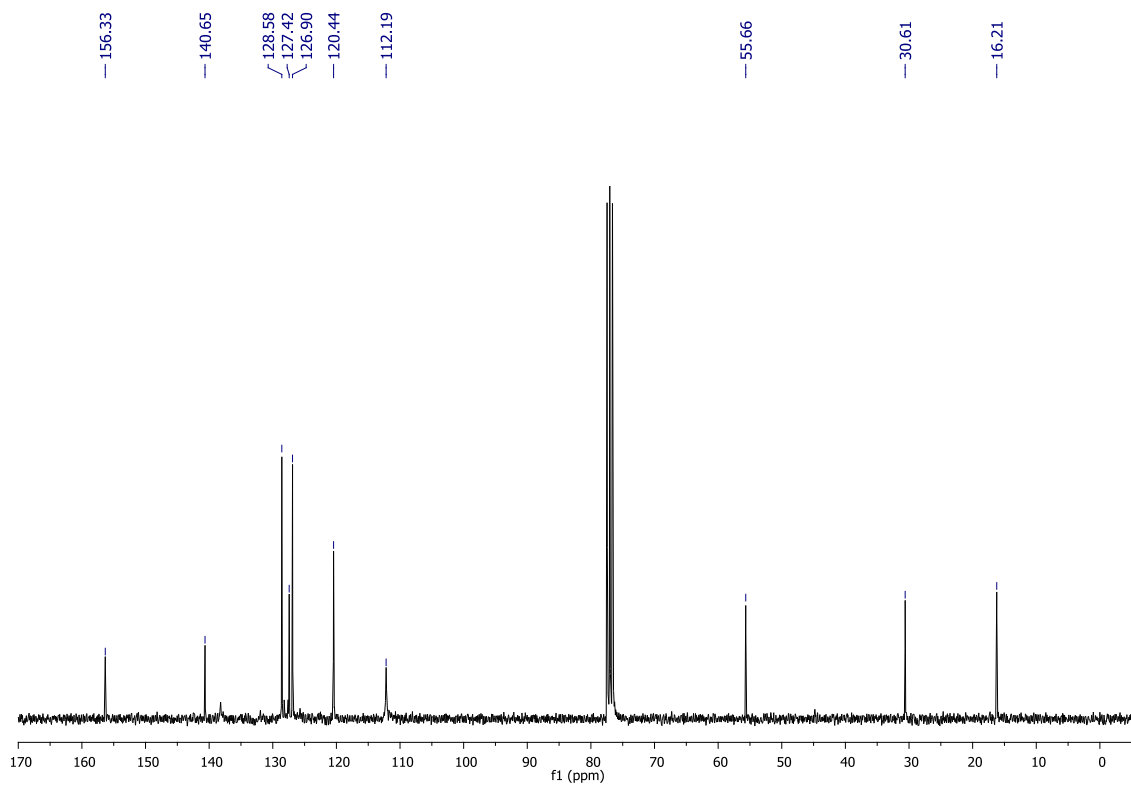
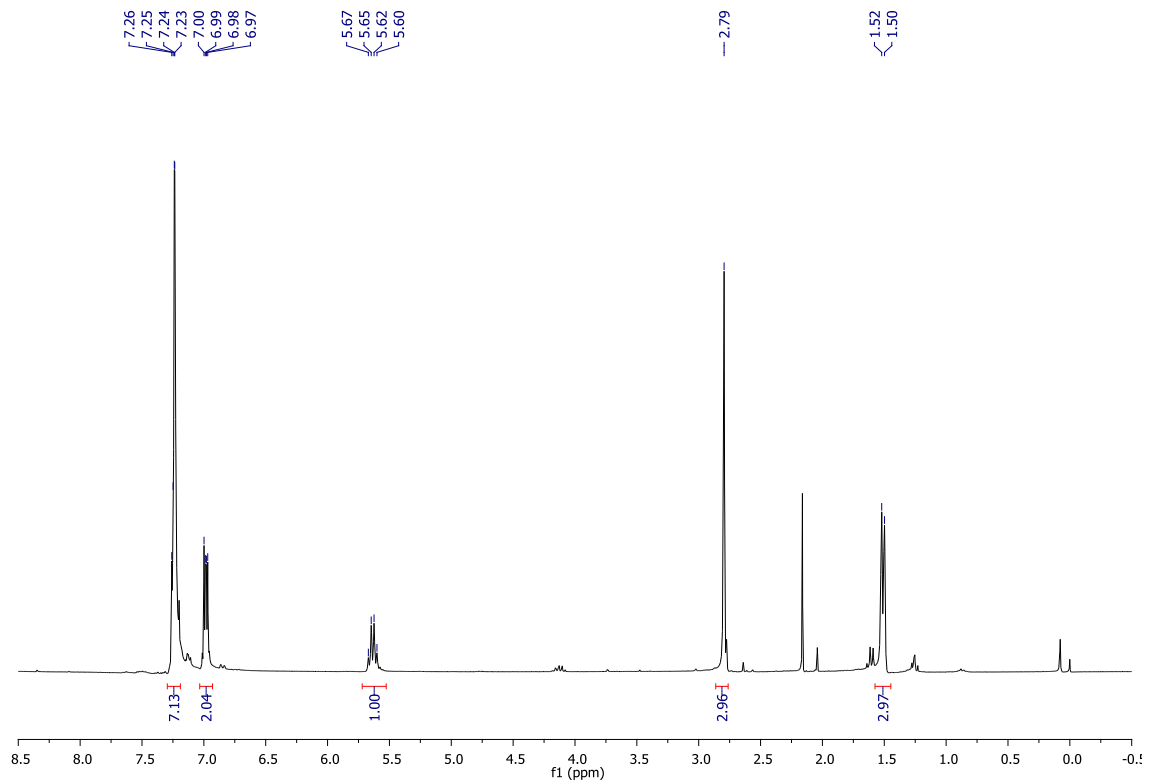
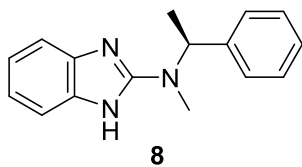


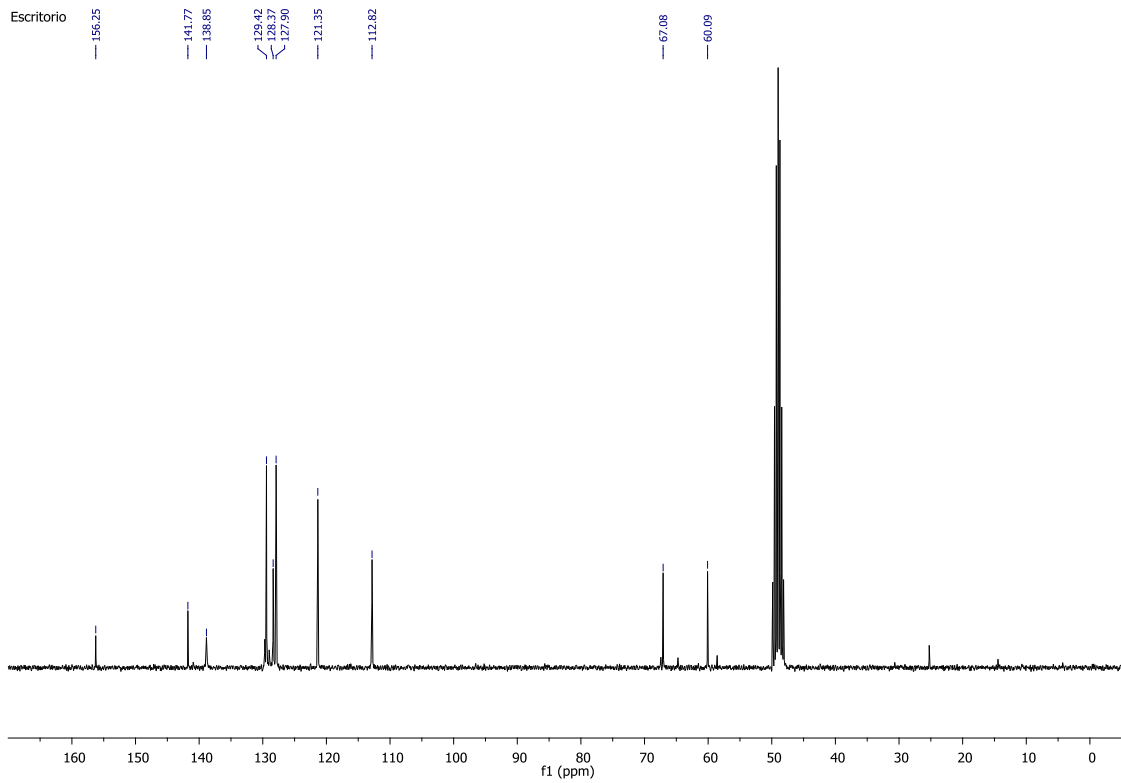
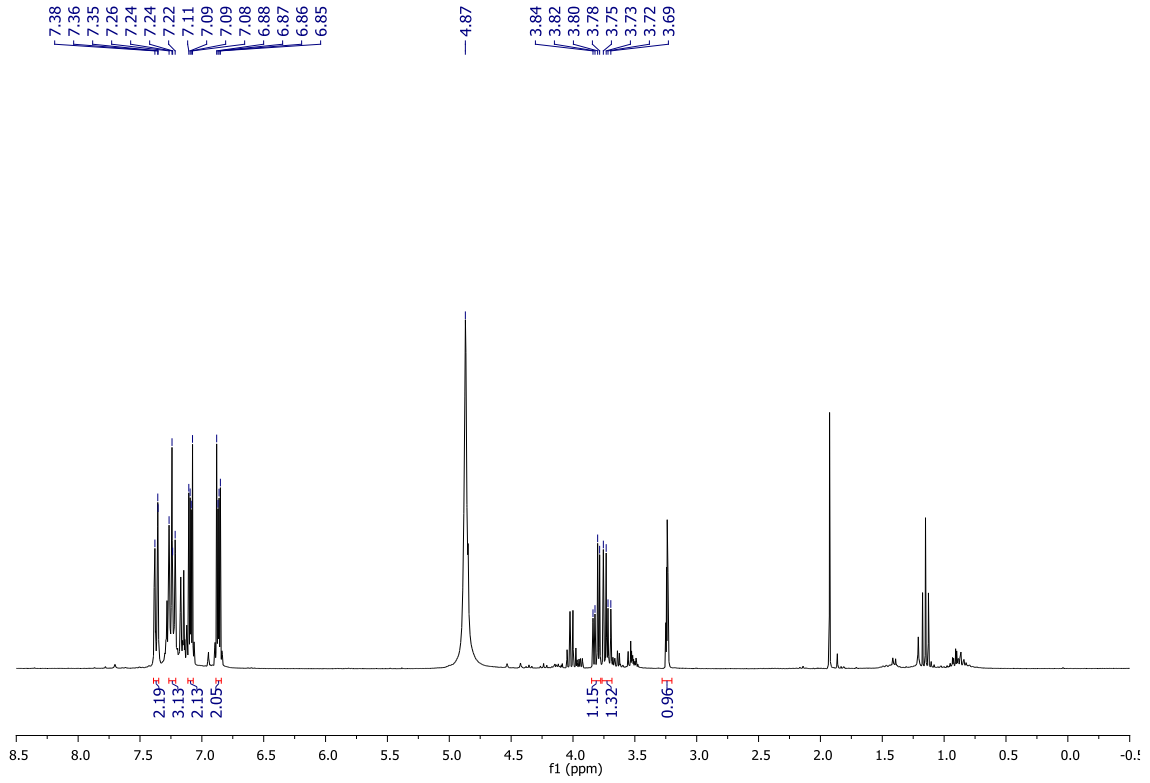
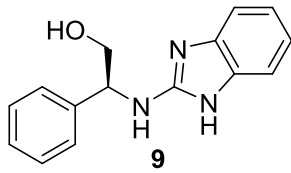
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) 7.25 (td, *J* = 6.1, 2.6 Hz, 2H), 7.01 (dt, *J* = 10.2, 5.1 Hz, 2H), 5.31 (s, 1H), 3.80 (s, 1H), 1.08 (t, *J* = 11.8 Hz, 3H), 0.79 (s, 9H).

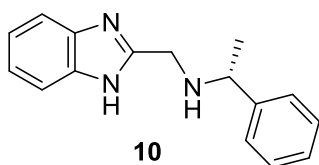


<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 156.39, 120.39, 111.88, 57.44, 34.40, 26.11, 16.74.

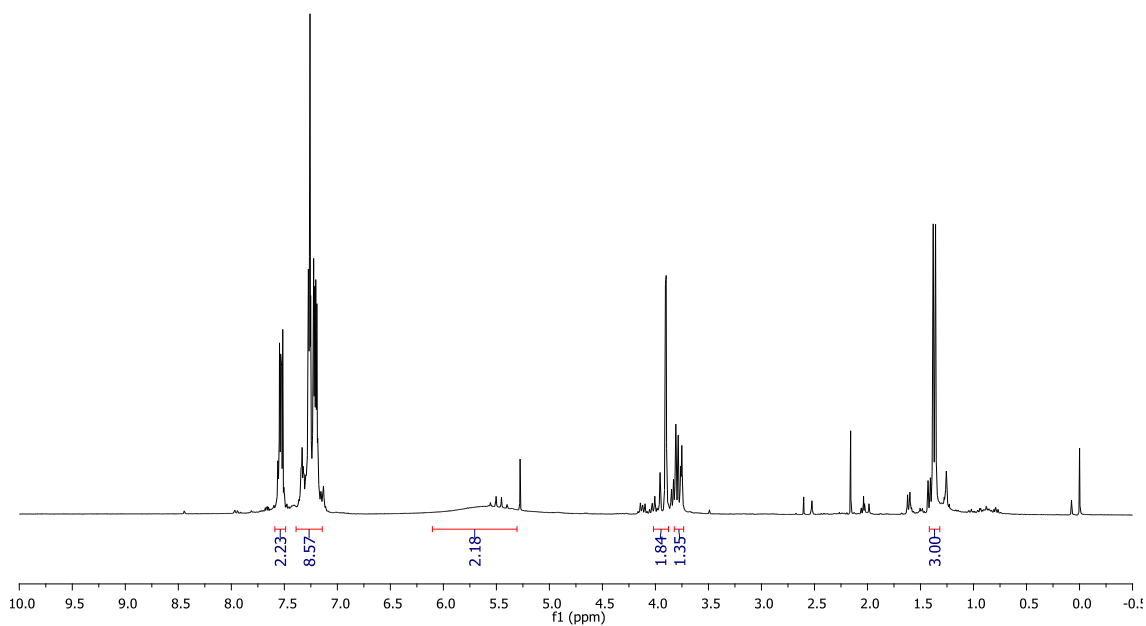




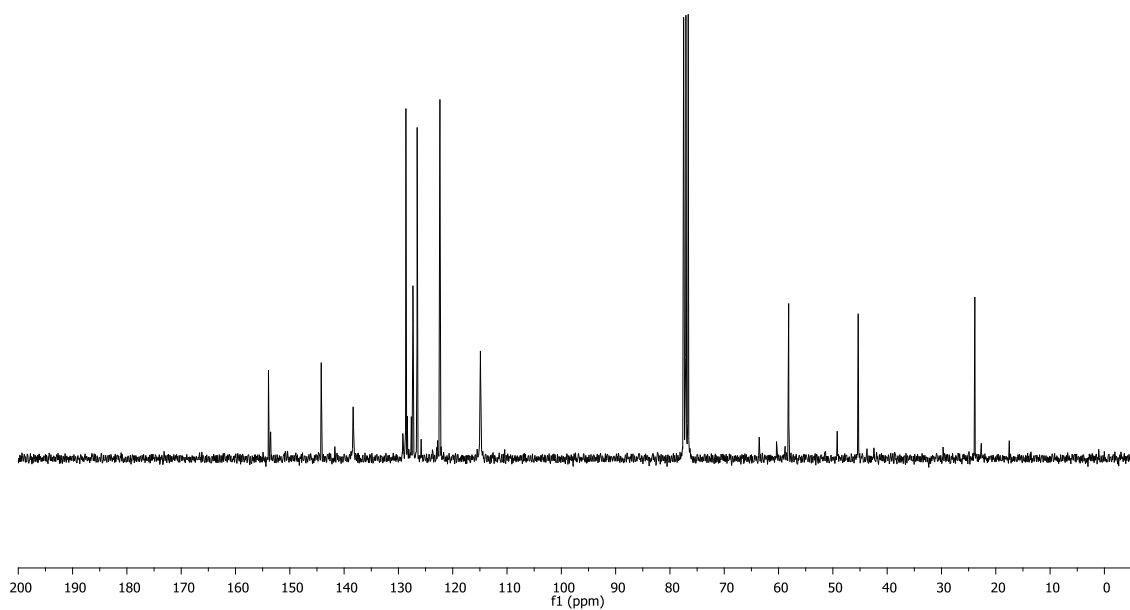




<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.59 – 7.49 (m, 5H), 7.39 – 7.14 (m, 19H), 3.90 (d, = 2.1 Hz, 4H), 3.76 (d, = 3.3 Hz, 3H), 1.37 (d, = 6.6 Hz, 7H).

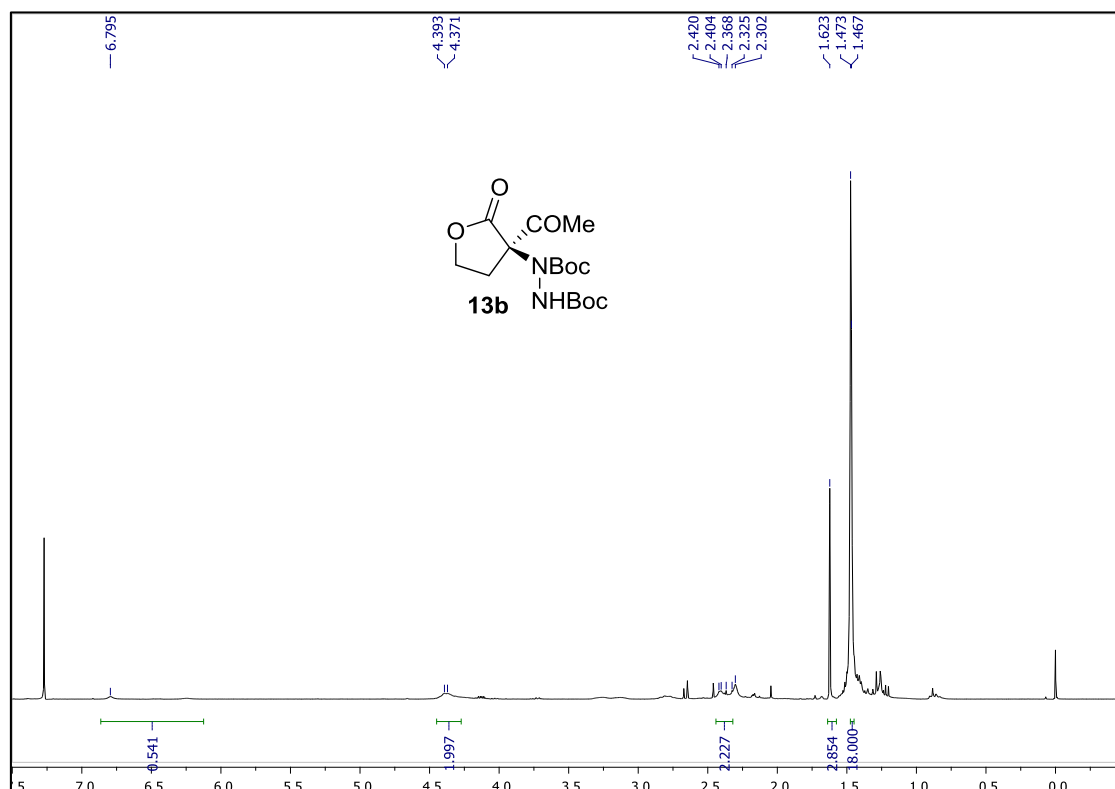
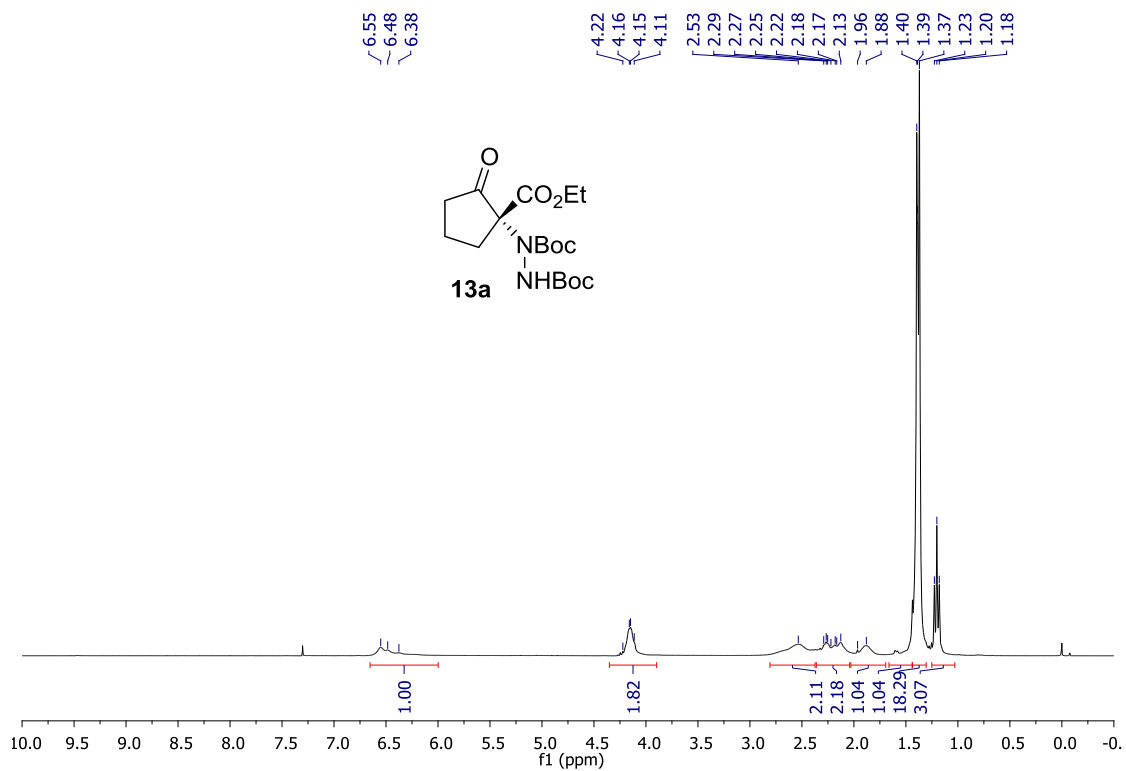


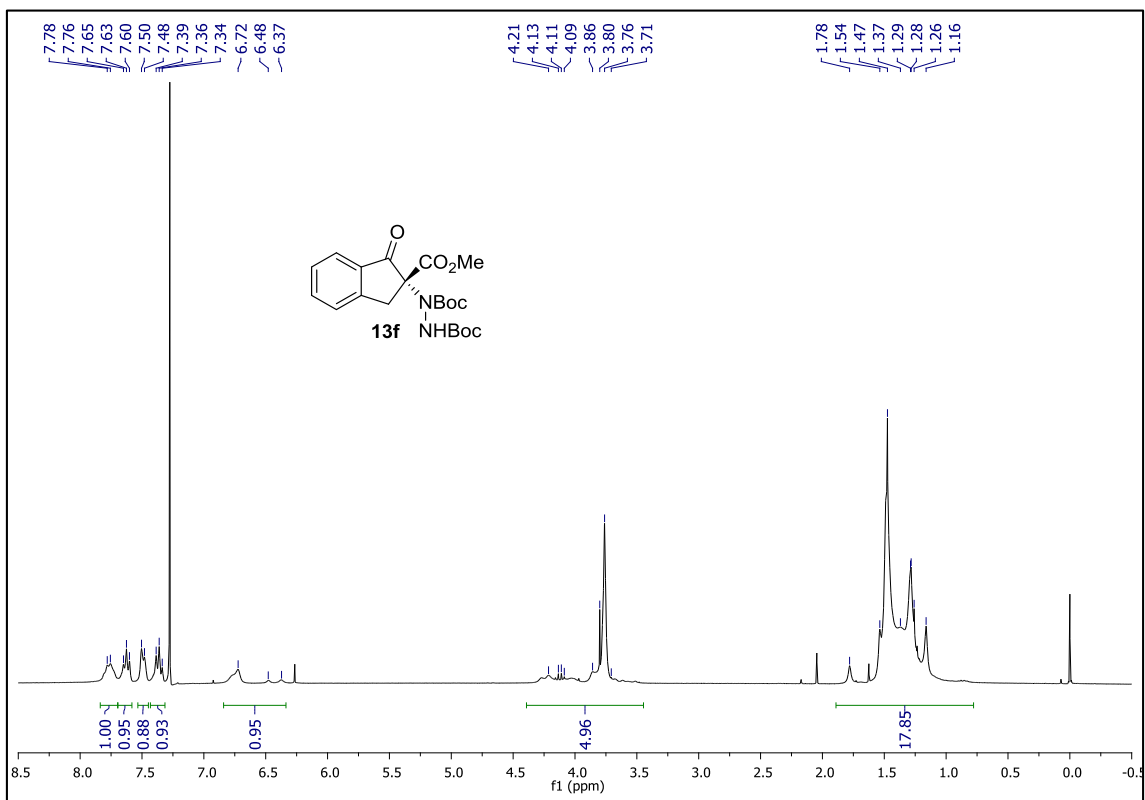
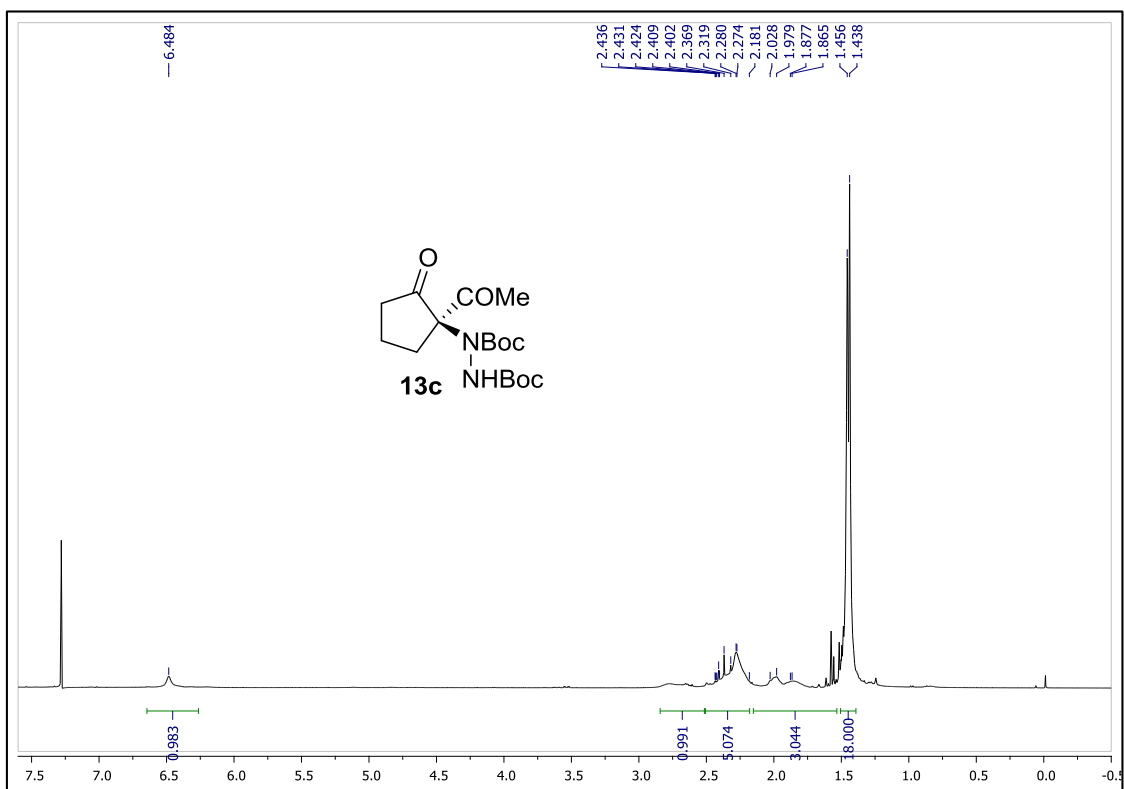
<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 153.93, 144.21, 138.34, 128.62, 127.33, 126.55, 122.36, 114.90, 77.48, 77.06, 76.64, 58.14, 45.34, 23.86.

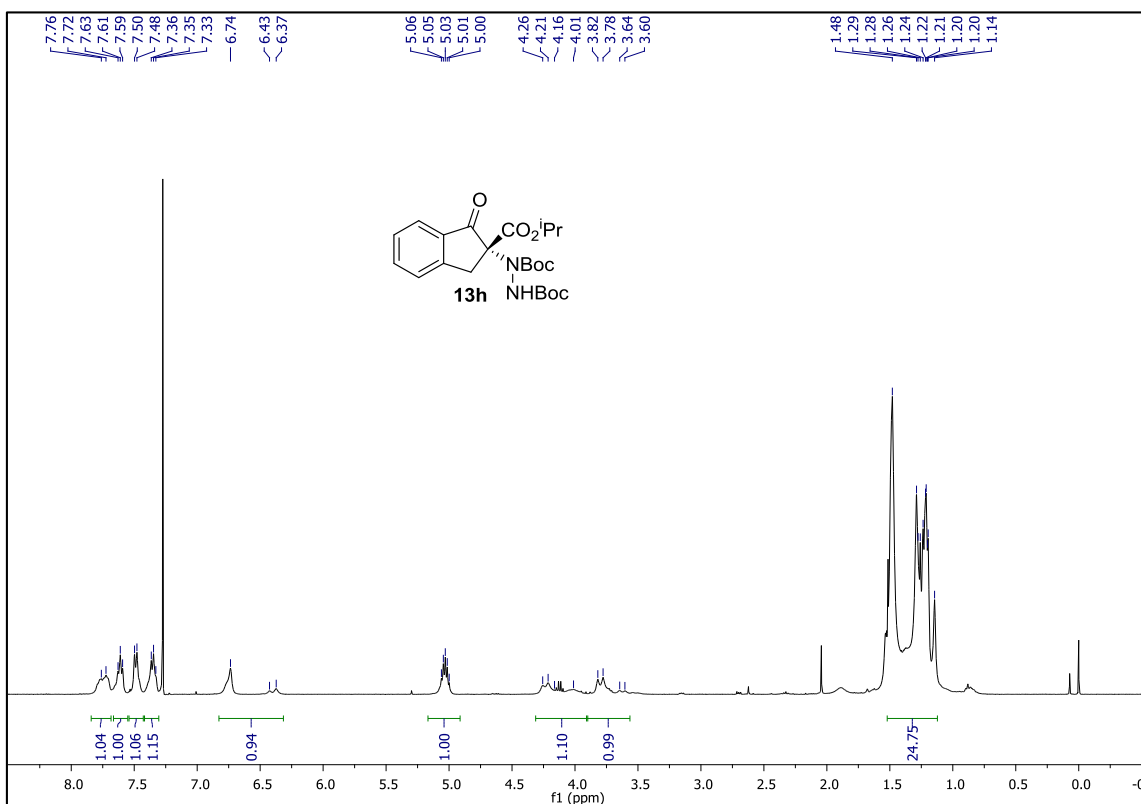
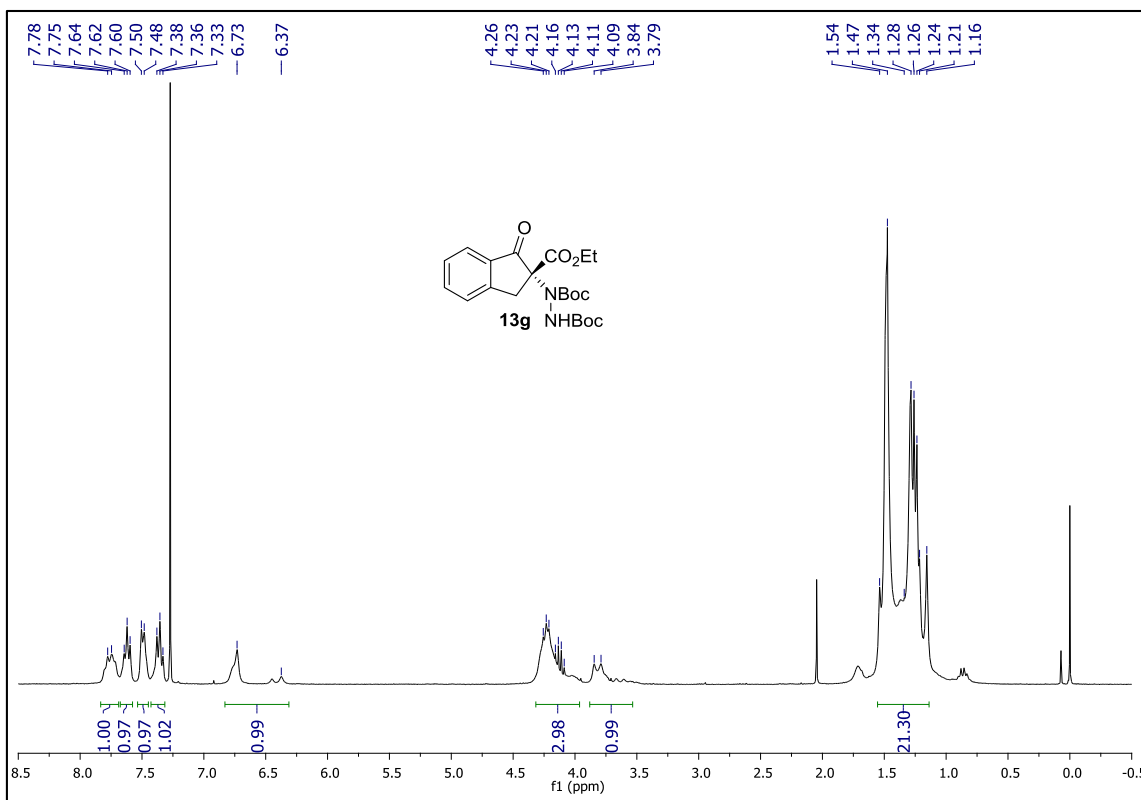


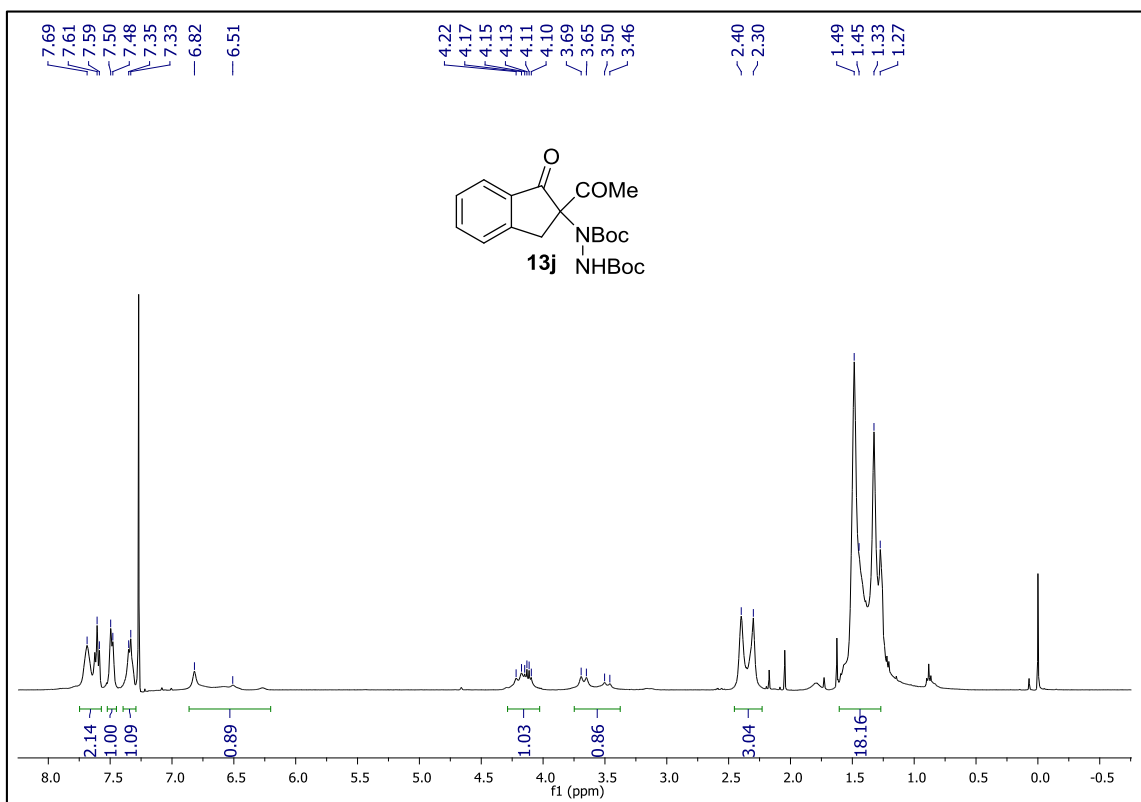
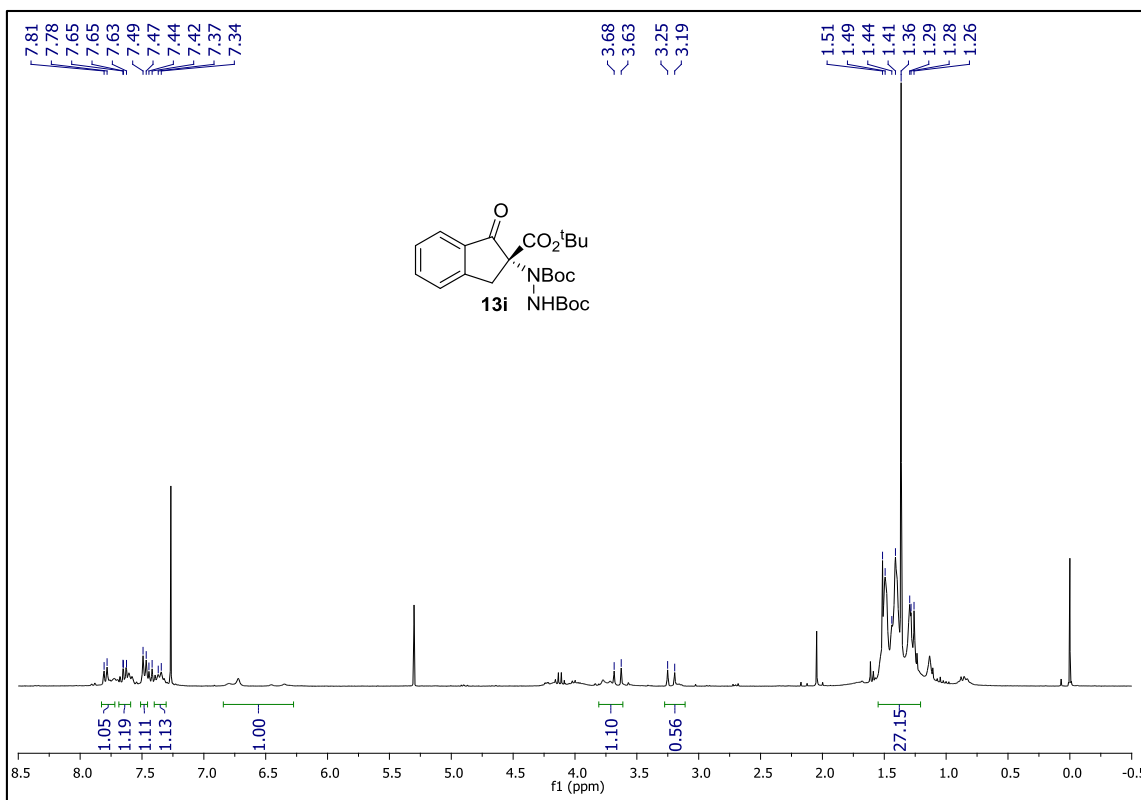
# <sup>1</sup>H NMR Spectra of Chiral Amination Products

Only copy of <sup>1</sup>H NMR of those enantioenriched products ( $\geq 20\%$  ee) are provided.

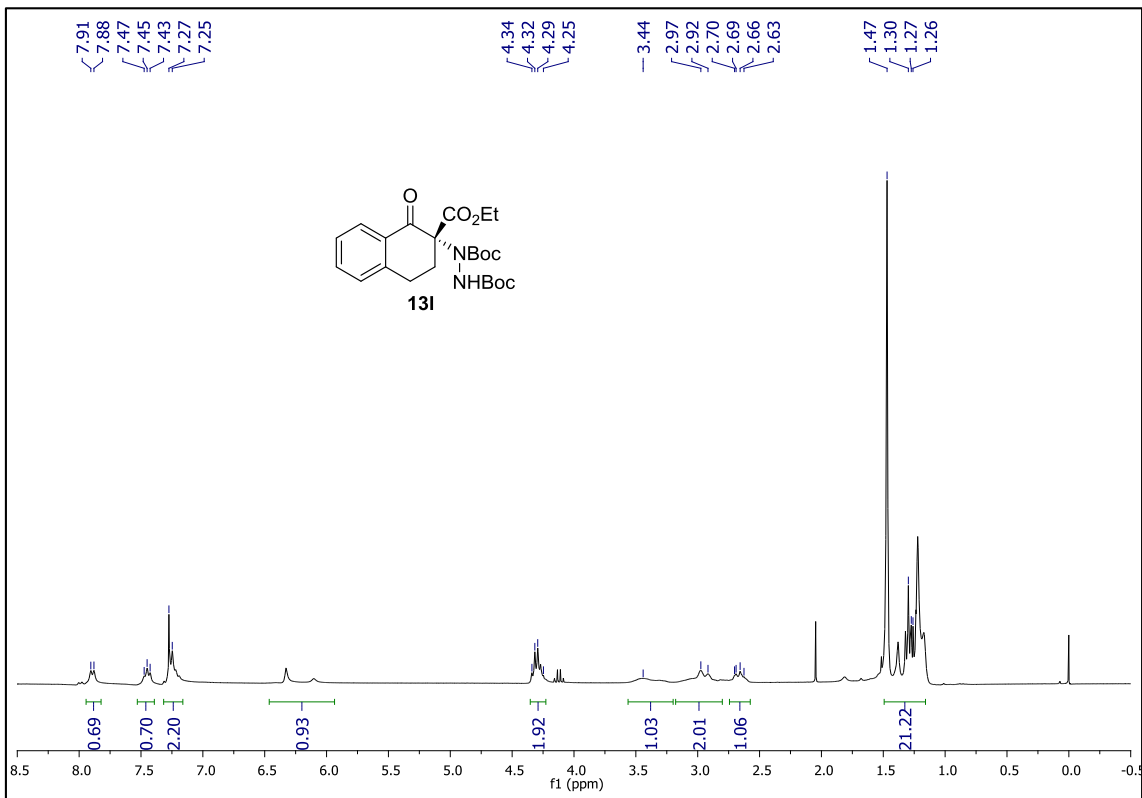
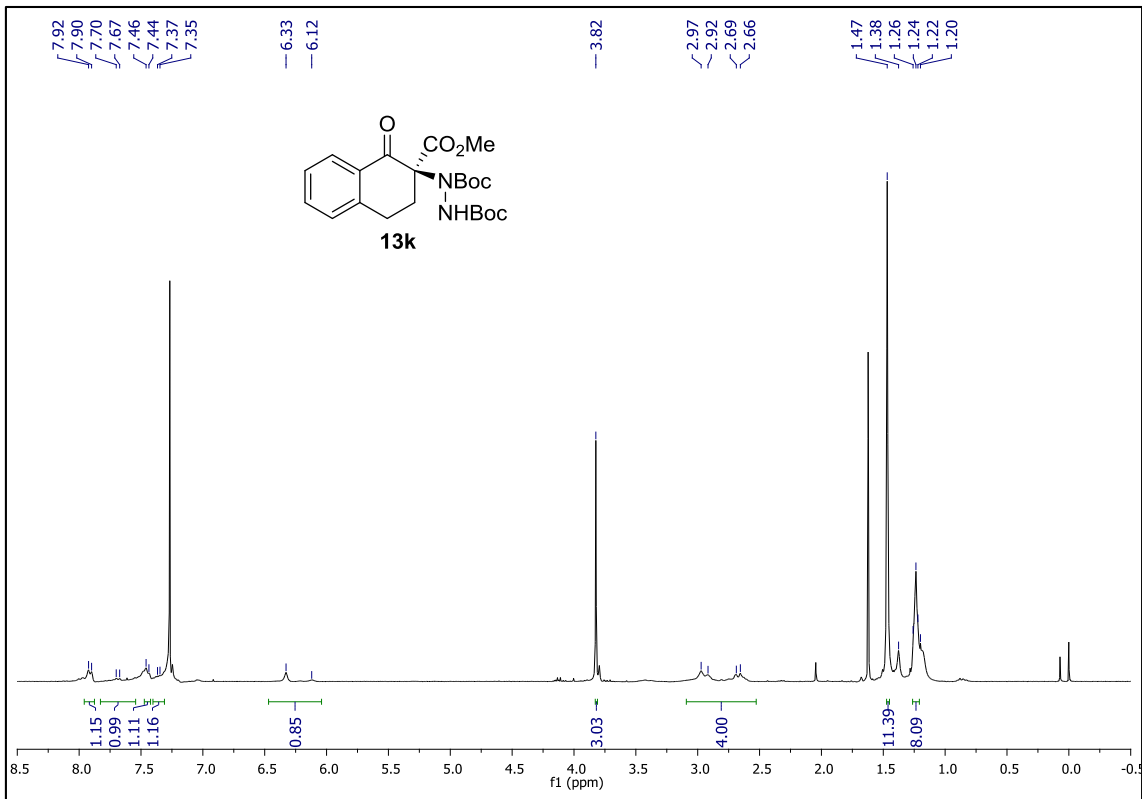


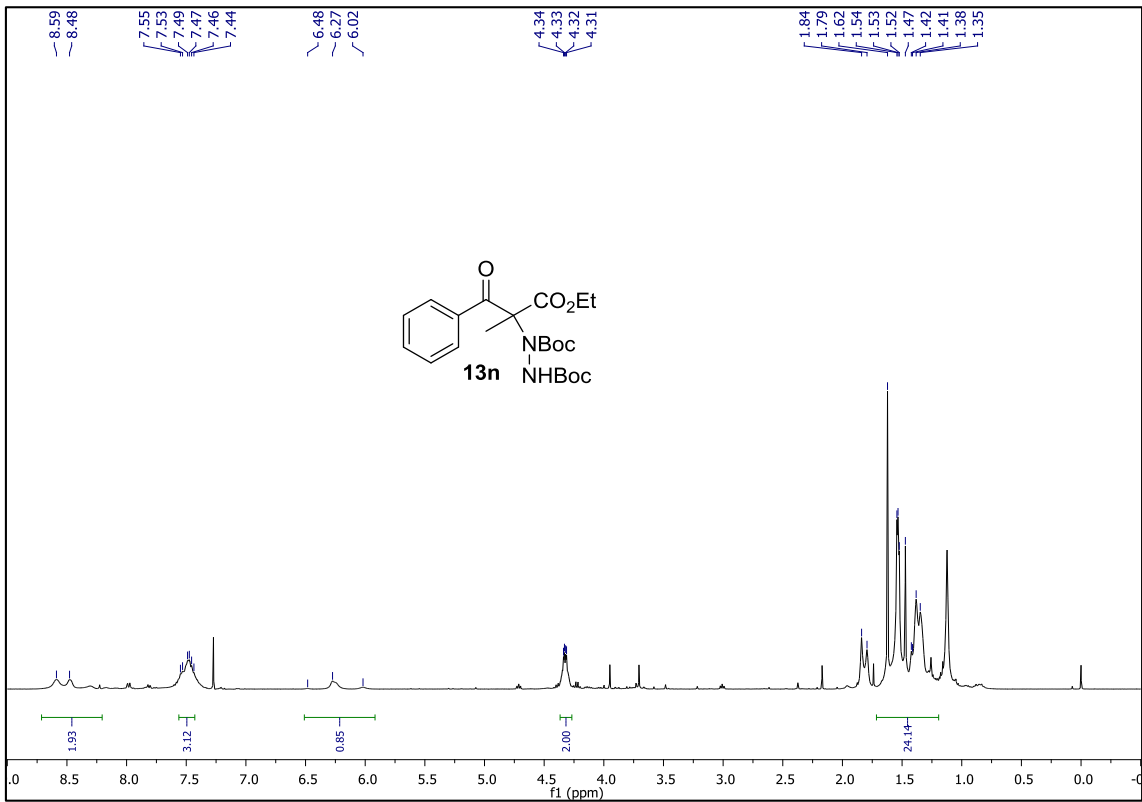
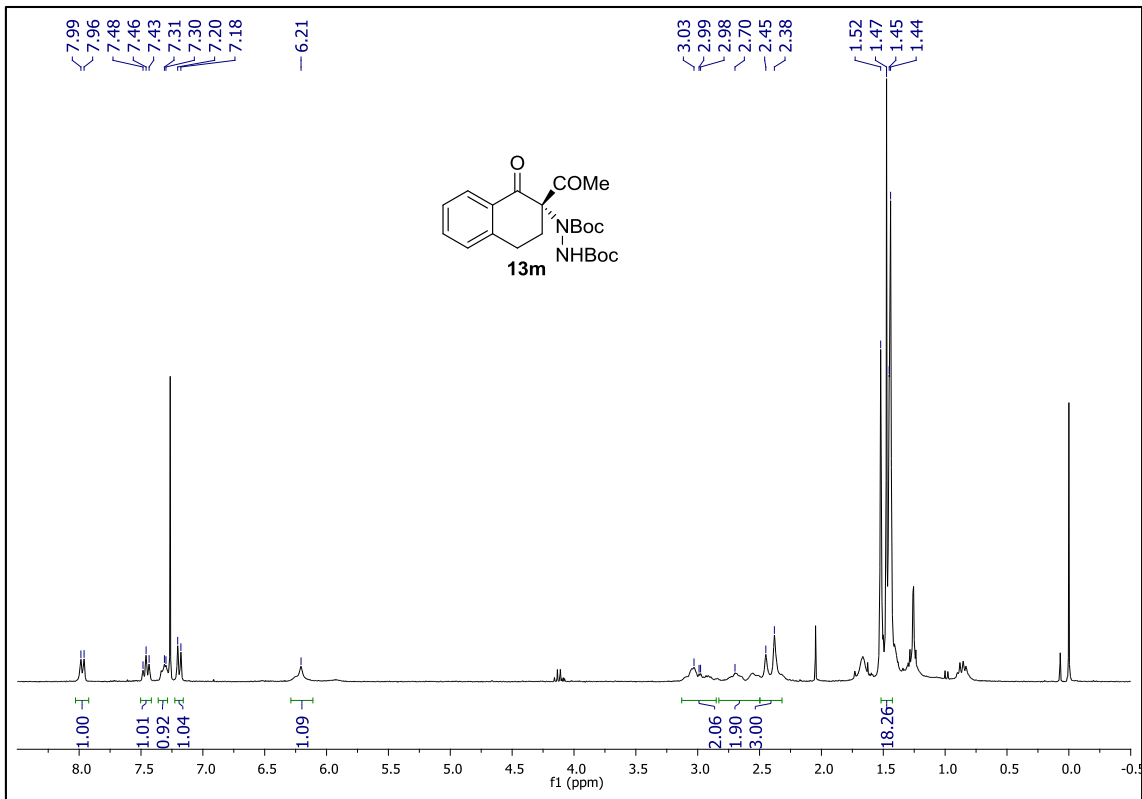






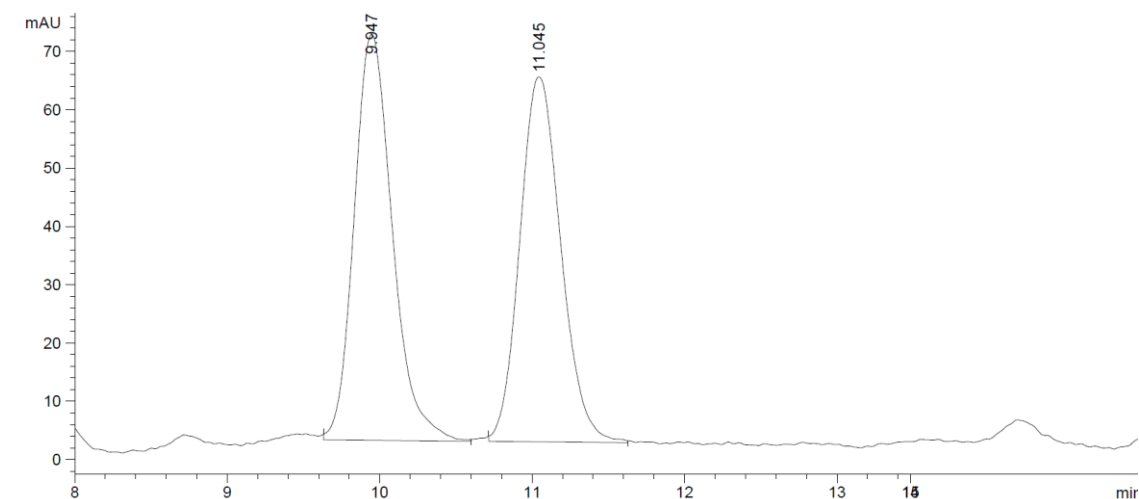
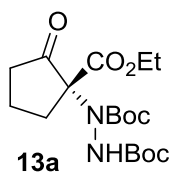




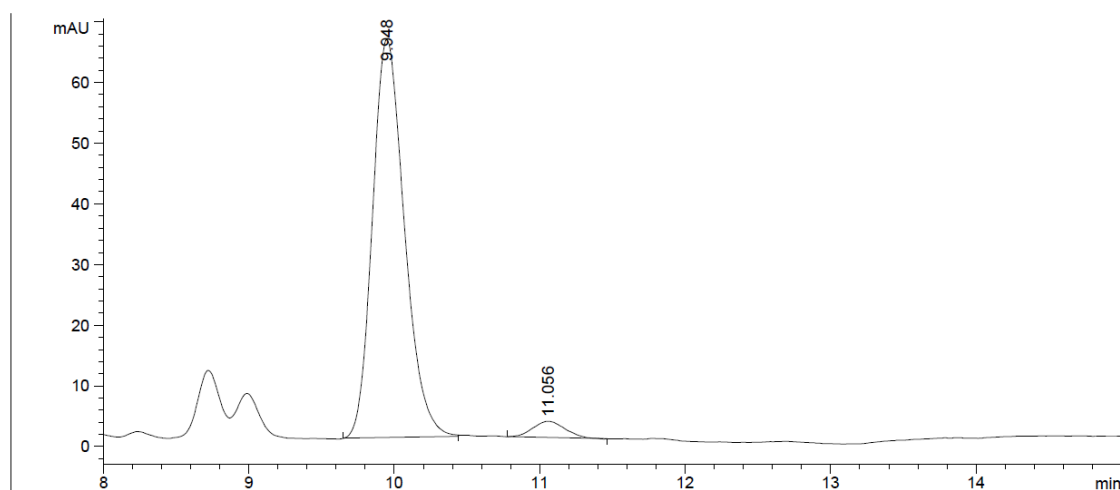


## HPLC Chromatograms of Chiral Amination Products

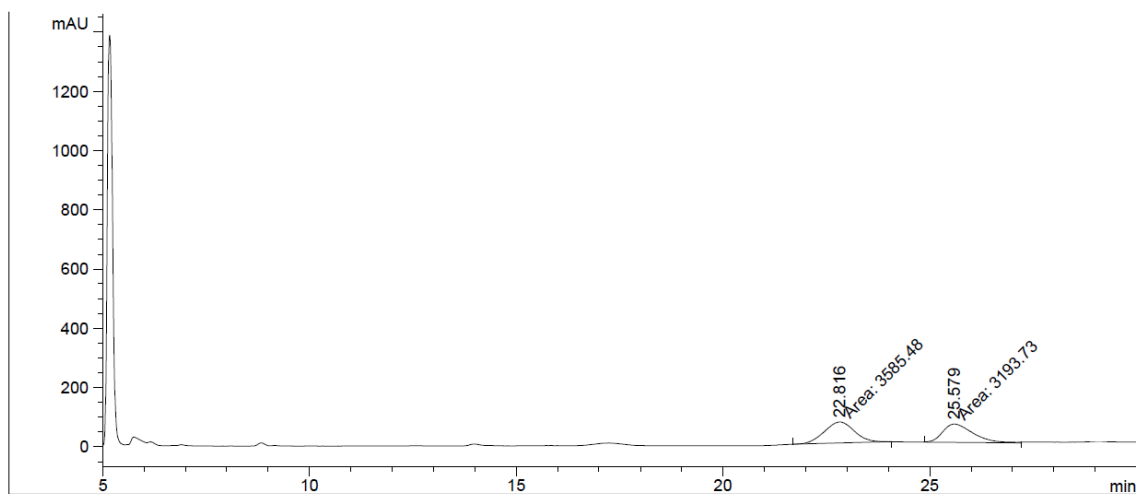
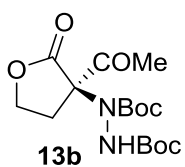
Only copy of HPLC charts of those enantioenriched products ( $\geq 20\%$  *ee*) are provided.



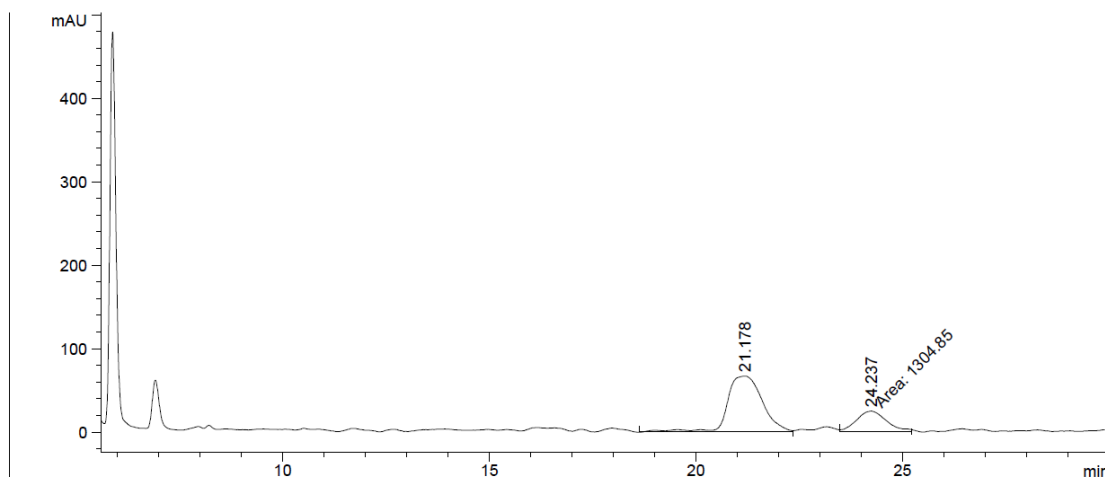
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.947	BB	0.2676	1215.31445	69.62508	50.9333
2	11.045	BB	0.2902	1170.77722	62.59072	49.0667



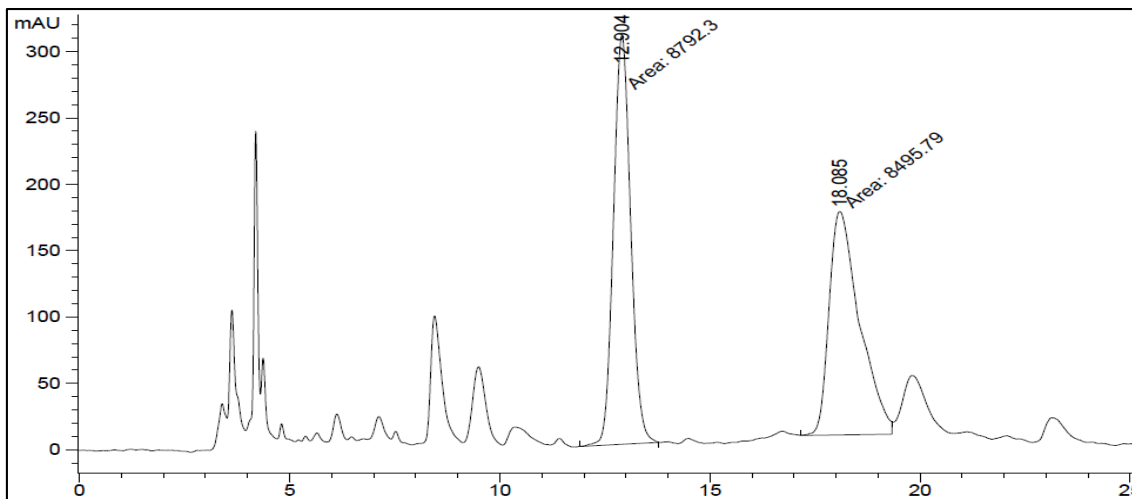
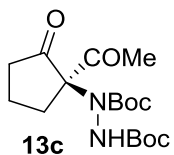
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.948	PB	0.2363	1002.44684	65.58751	96.0346
2	11.056	PP	0.2359	41.39199	2.68403	3.9654



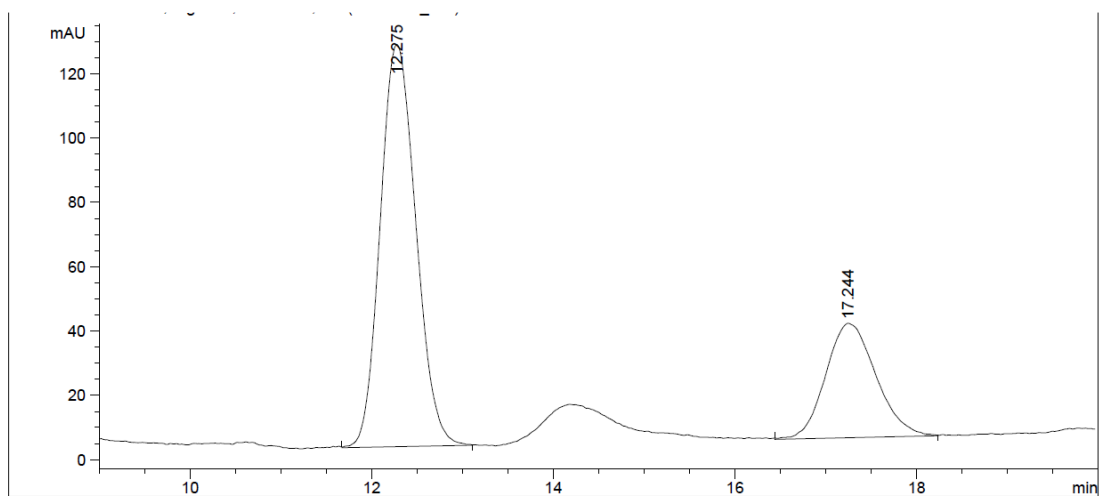
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.816	MM	0.8439	3585.48389	70.81393	52.8894
2	25.579	MM	0.8556	3193.72705	62.21344	47.1106



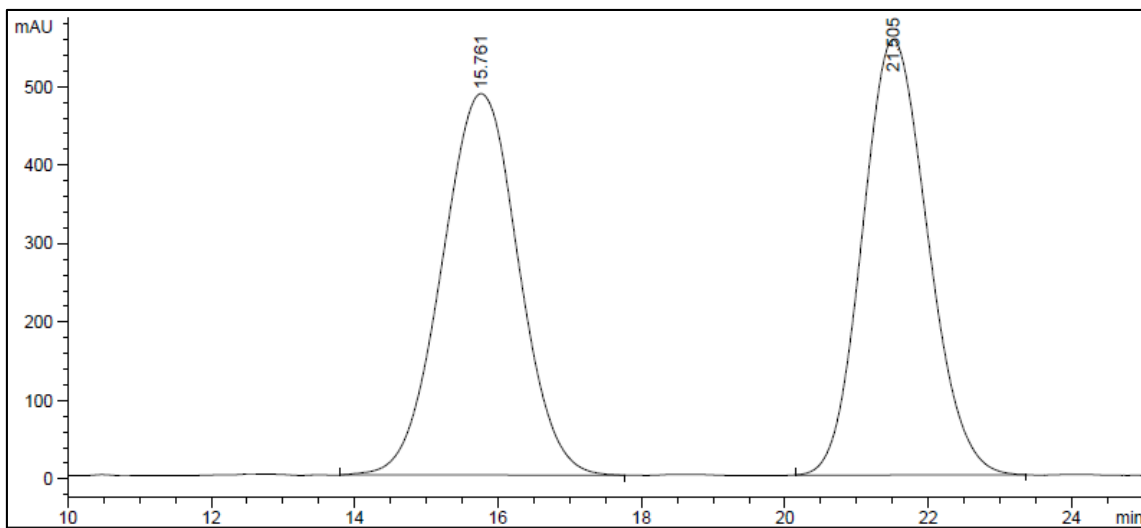
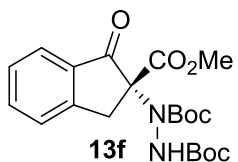
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.178	VV	0.8528	4010.31909	67.14988	75.4504
2	24.237	MF	0.8654	1304.85059	25.12862	24.5496



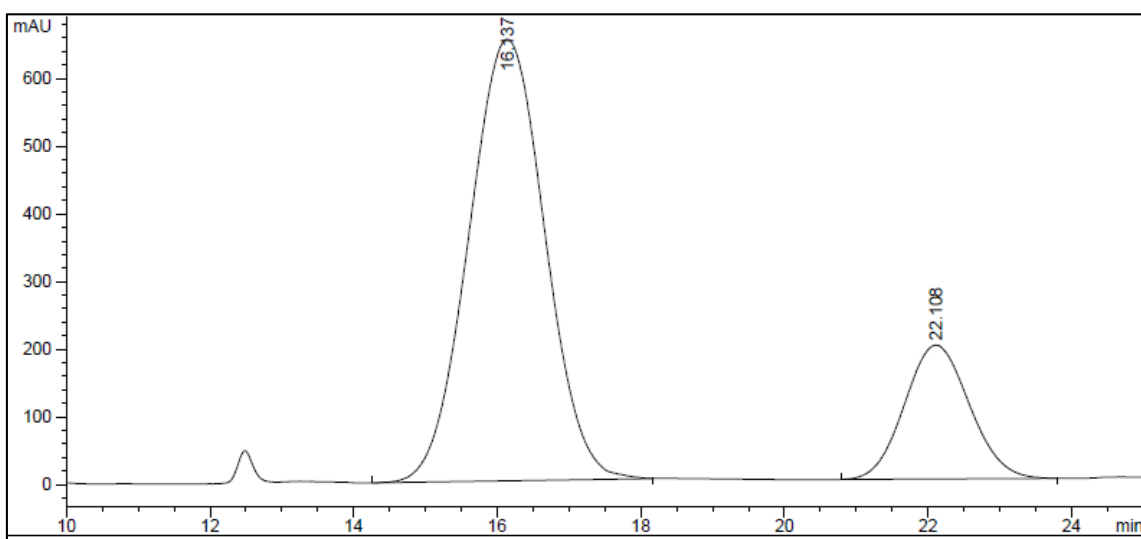
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1	12.904	MM	0.4756	8792.30173	308.11707	50.8576
2	18.085	MF	0.8410	8495.78906	168.36839	49.1424



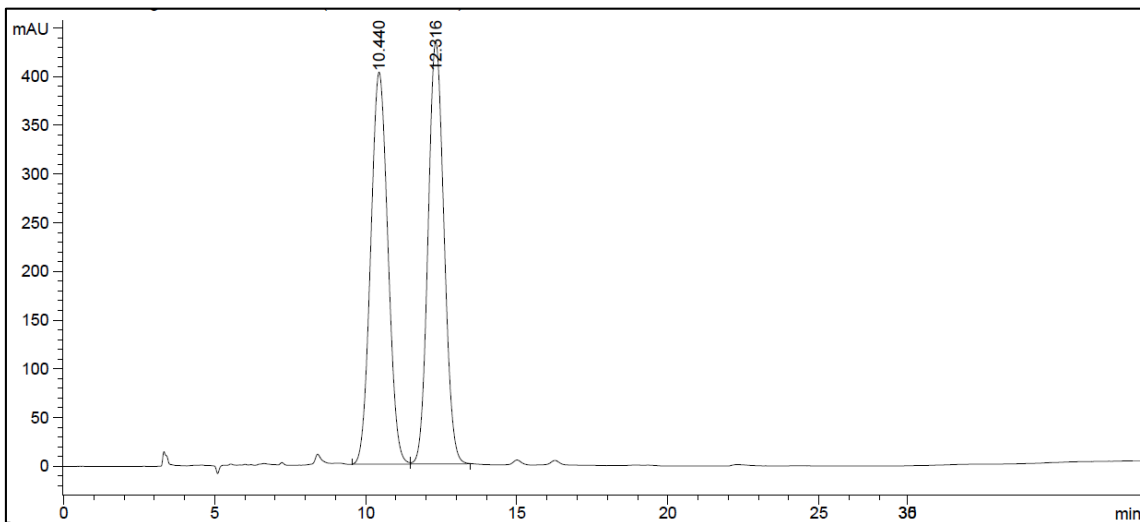
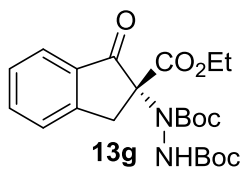
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1	12.275	VB	0.4244	3415.51733	125.14387	71.3517
2	17.244	BV	0.4829	1371.36121	35.63898	28.6483



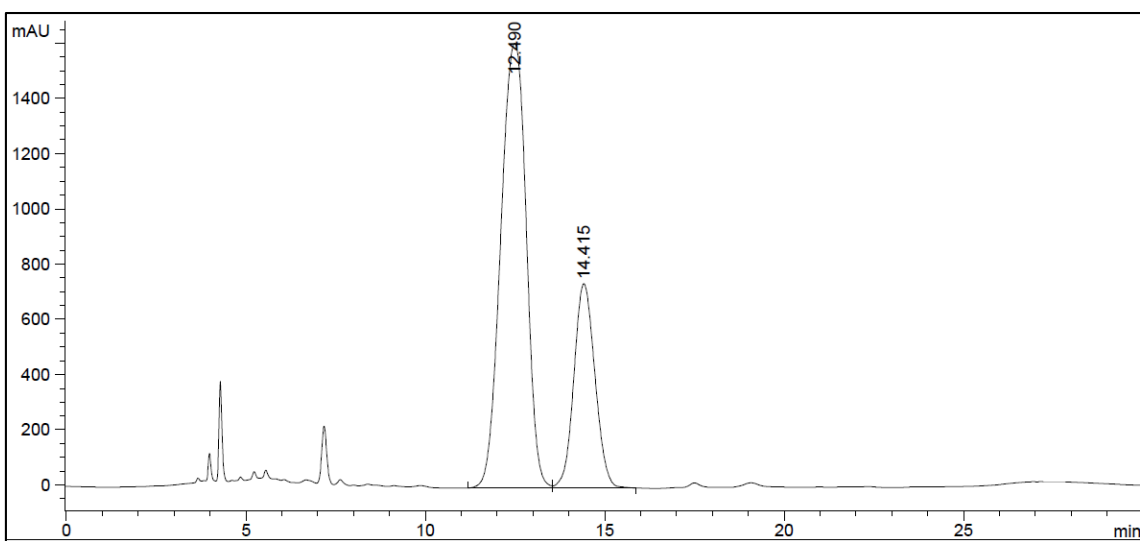
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	15.761	BB	1.1321	36074.2	485.95621	50.6380
2	21.505	BB	0.9834	35165.2	554.86438	49.3620



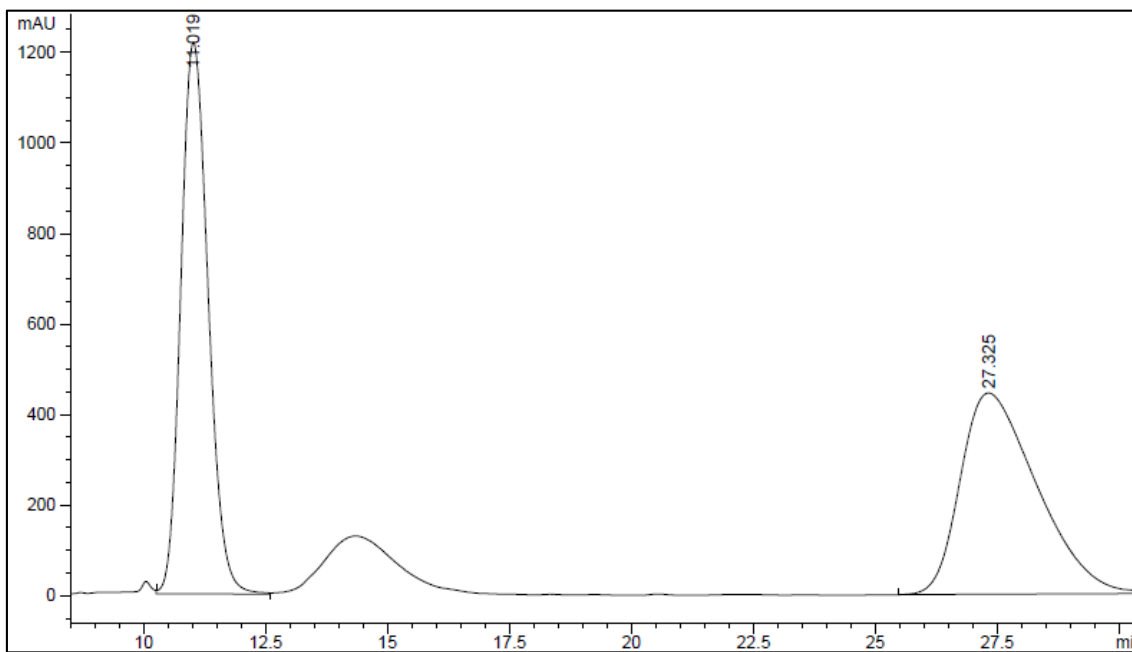
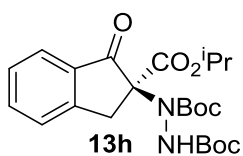
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1	16.137	PB	1.1152	48044.7	652.38928	79.4215
2	22.108	BB	0.9621	12448.6	197.84103	20.5785



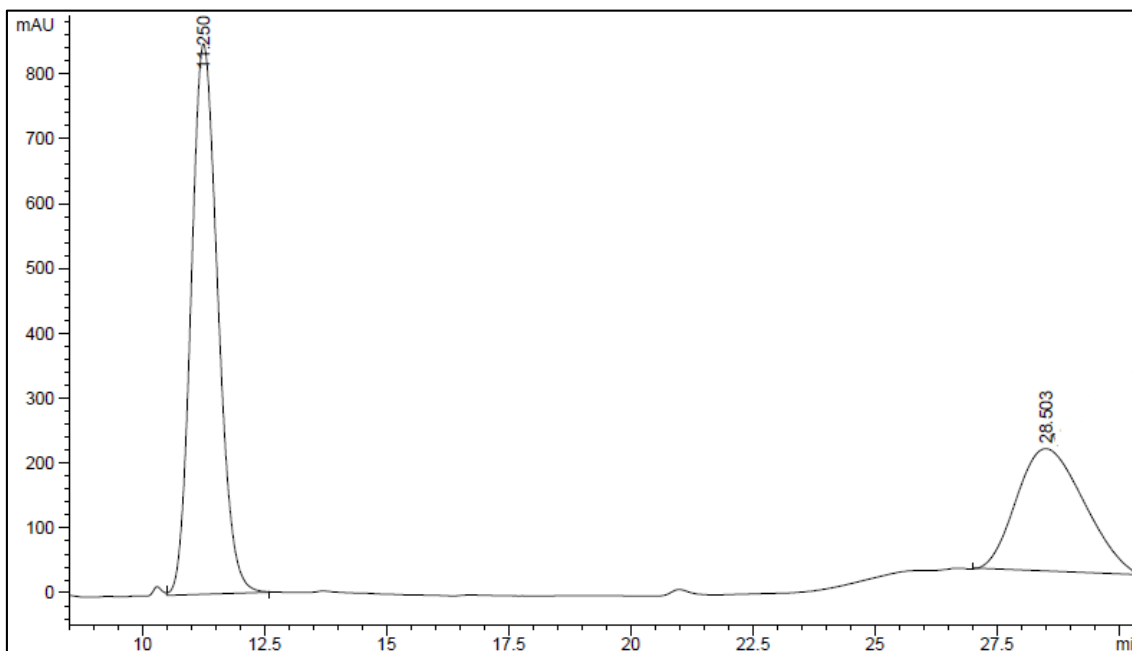
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1	10.440	PV	0.6243	15943.6	402.39029	50.0770
2	12.316	VB	0.5780	15894.5	433.22595	49.9230



Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	12.490	BV	0.7864	79290.0	1610.40979	72.3872
2	14.415	VB	0.6226	30245.9	740.44135	27.6128

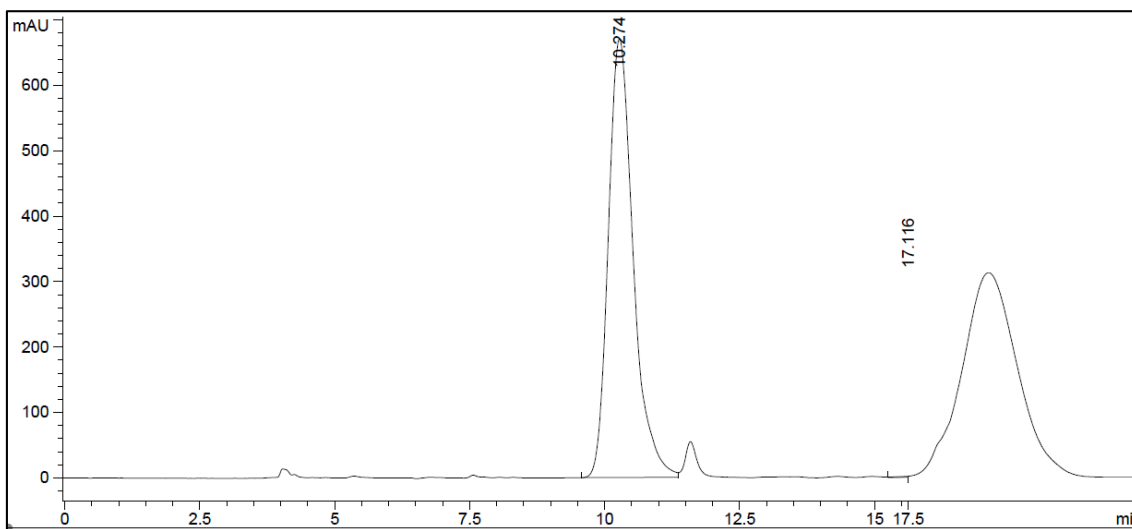
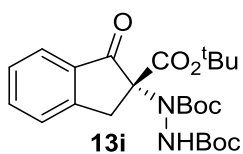


Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	11.019	VB	0.6069	47501.5	1218.22546	49.4937
2	27.325	BB	1.4925	48473.3	444.40399	50.5063

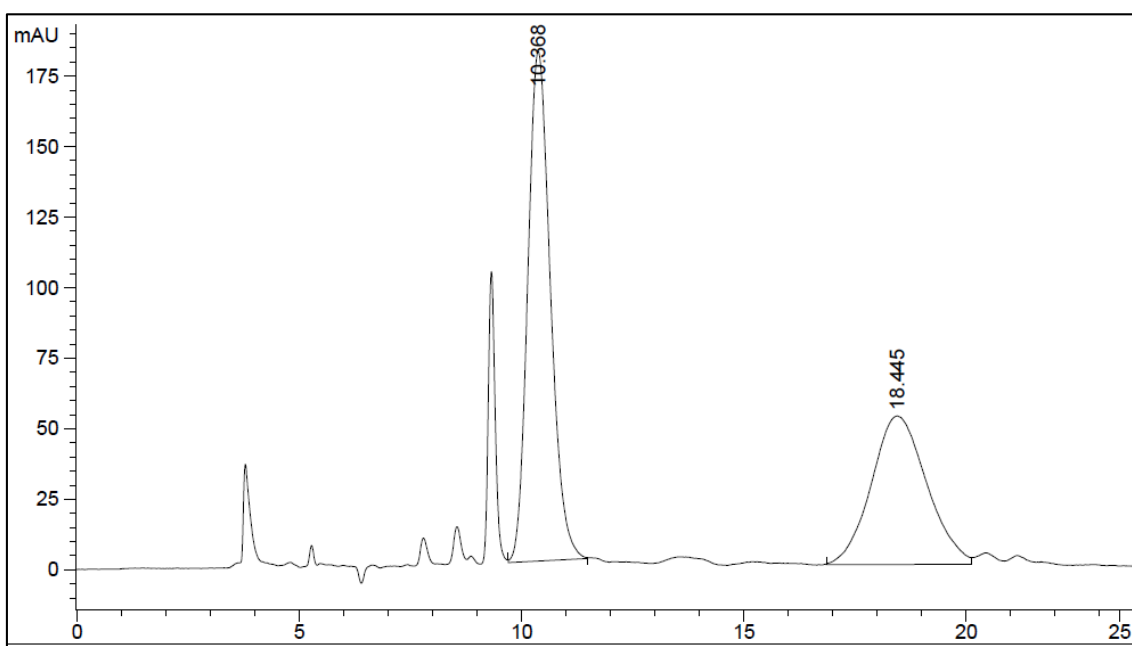


Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	11.250	VB	0.5807	32205.2	848.79523	64.0901
2	28.503	MM	1.5953	18044.7	188.52483	35.9099

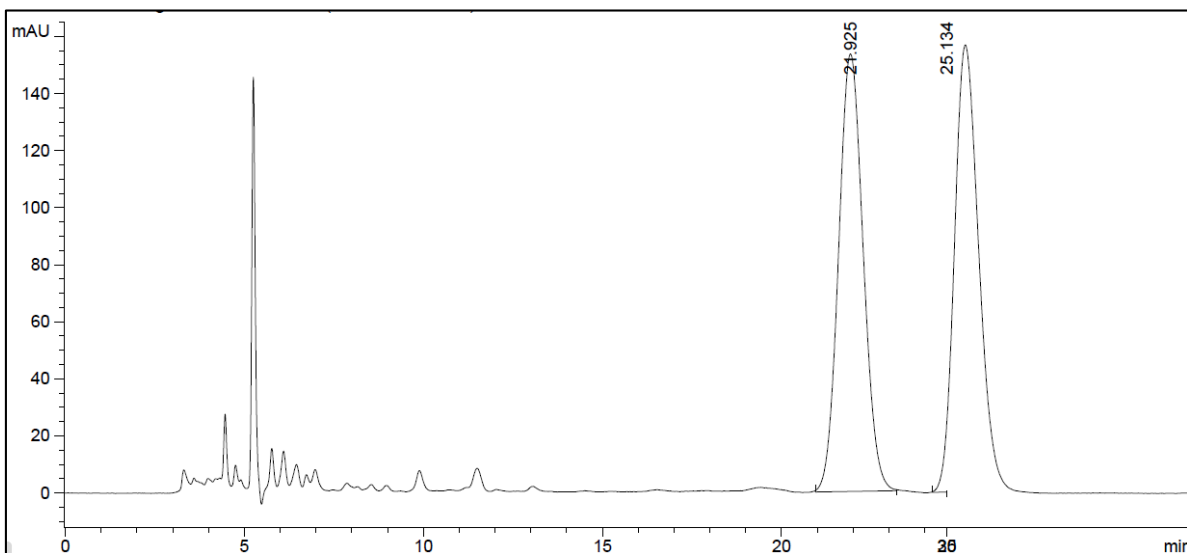
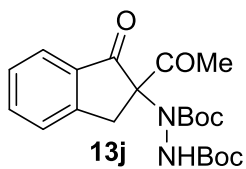




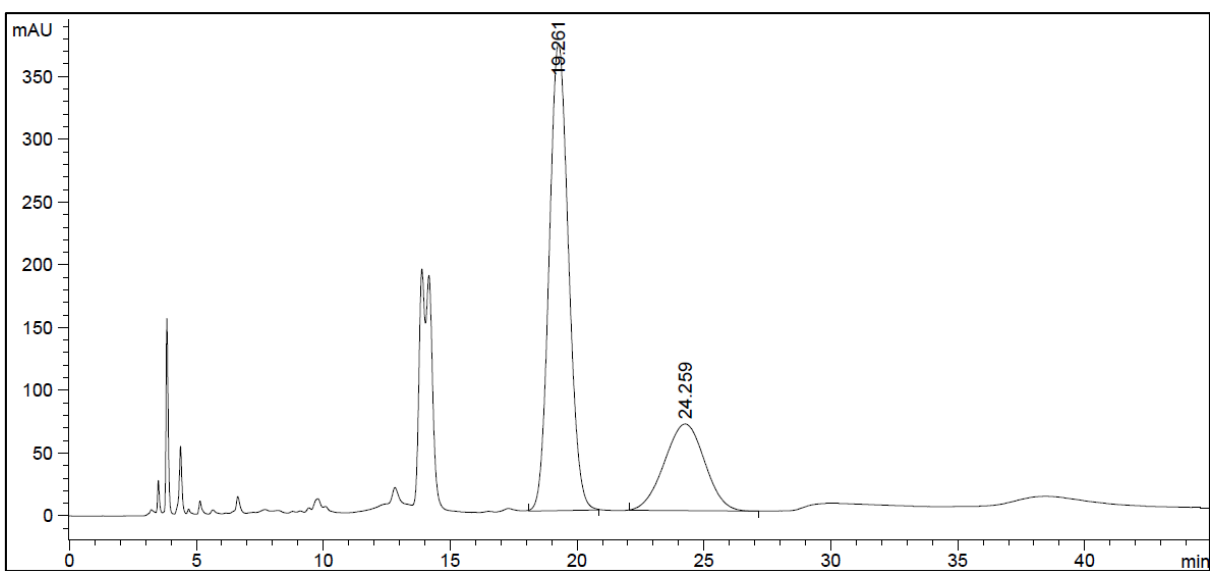
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	10.274	PV	0.4926	21531.9	670.54132	48.981
2	17.116	VB	1.0154	22427.8	313.21094	51.019



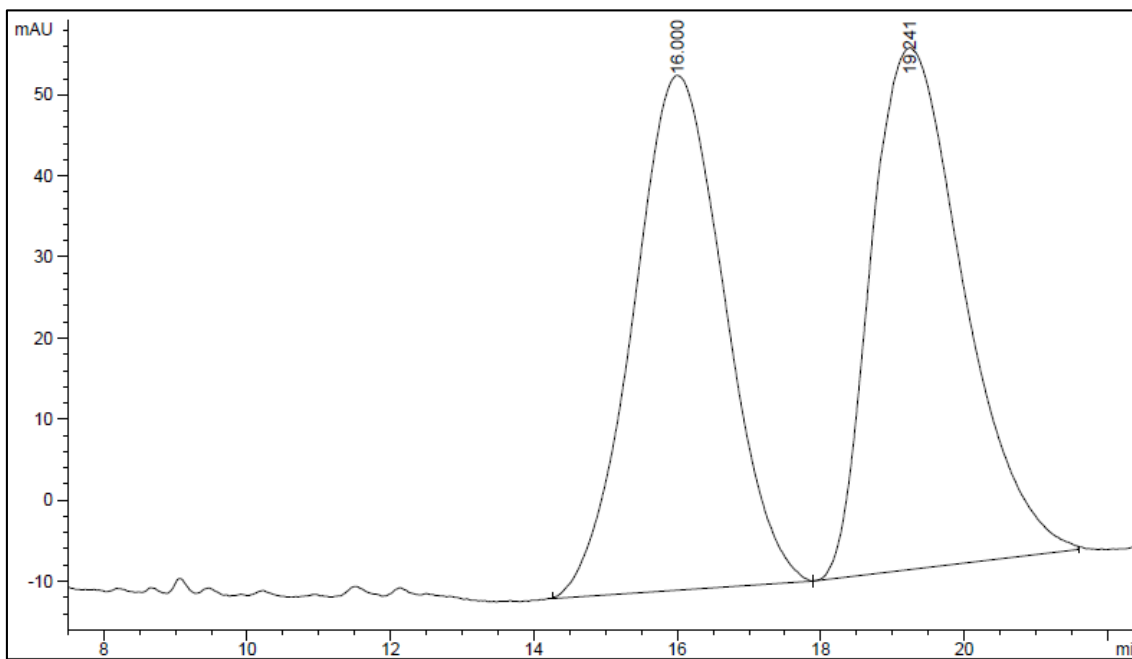
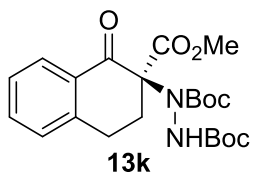
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	10.368	VB	0.5407	6396.97754	180.82336	58.3856
2	18.445	BV	1.0255	4559.45264	52.69088	41.6144



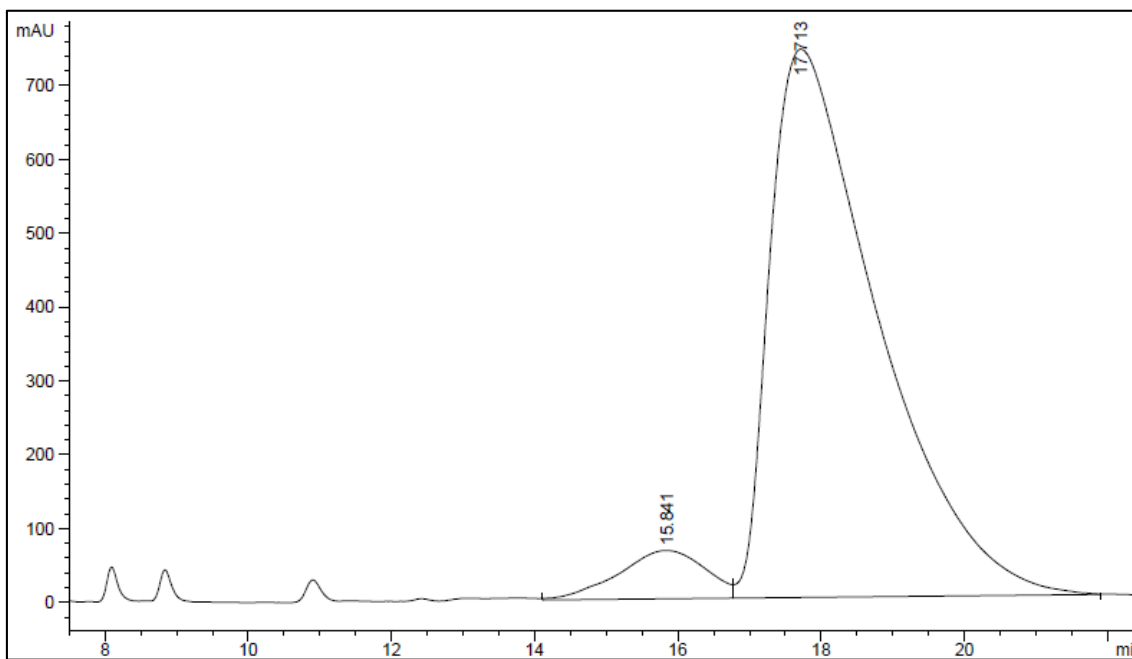
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	21.925	BB	0.7406	7315.40381	153.34898	49.8468
2	25.134	BB	0.7197	7360.36768	156.77203	50.1532



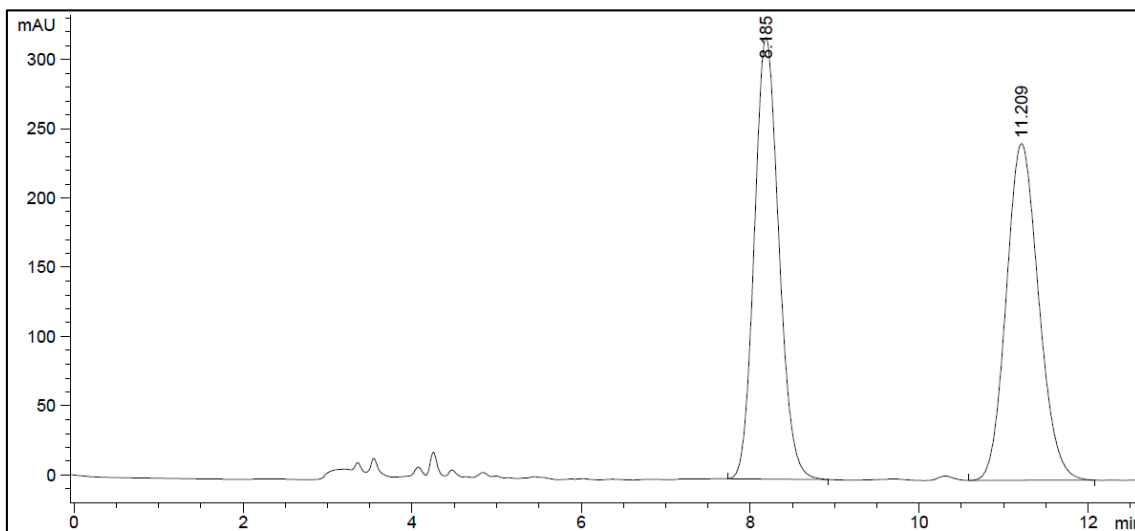
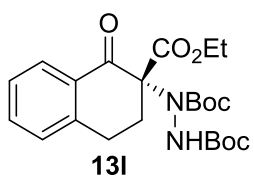
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	19.261	BB	0.8255	19711.1	372.43018	72.0580
2	24.259	BP	1.4129	7643.38232	69.07708	27.9420



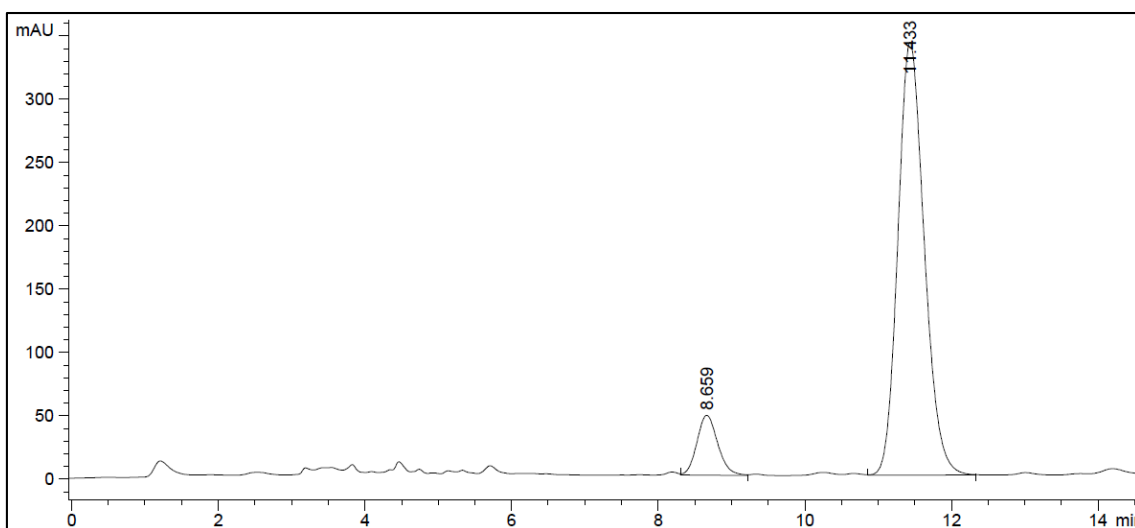
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	16.000	BP	1.0754	5612.87598	63.48714	49.2383
2	19.241	VB	1.0711	5786.52686	64.35174	50.7617



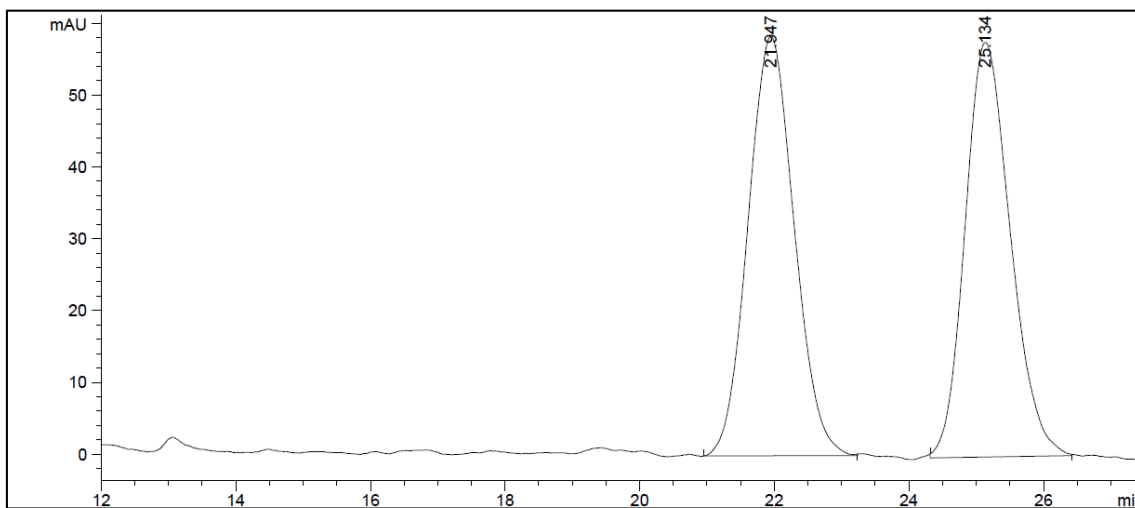
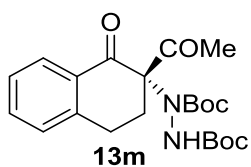
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	15.841	BV	1.0726	5508.57031	56.67299	6.6035
2	17.713	VB	1.4819	77910.1	742.65242	93.3965



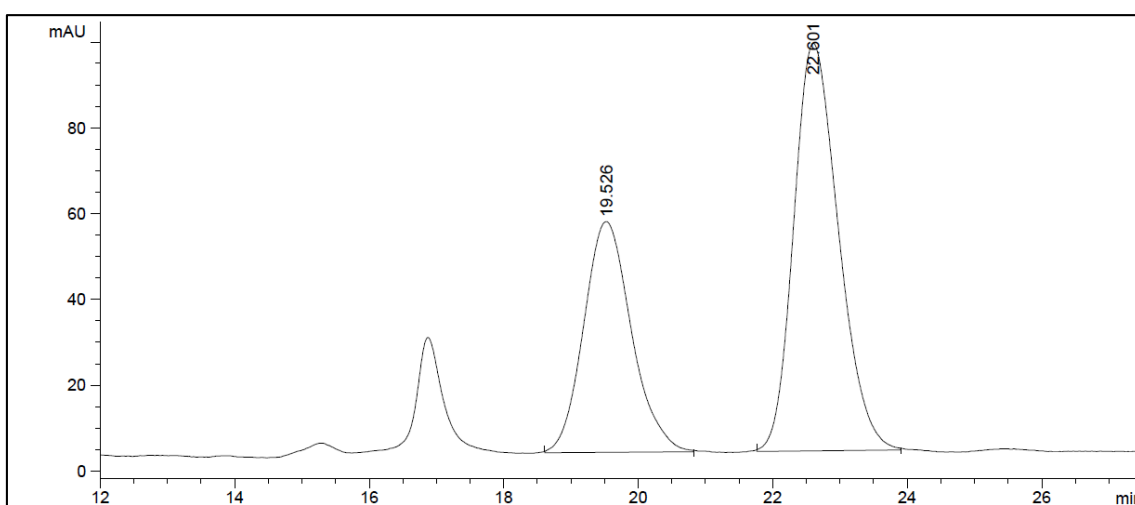
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	8.185	BB	0.3109	6422.34766	318.93024	49.7649
2	11.209	VB	0.4161	6483.03906	24.11255	50.2351



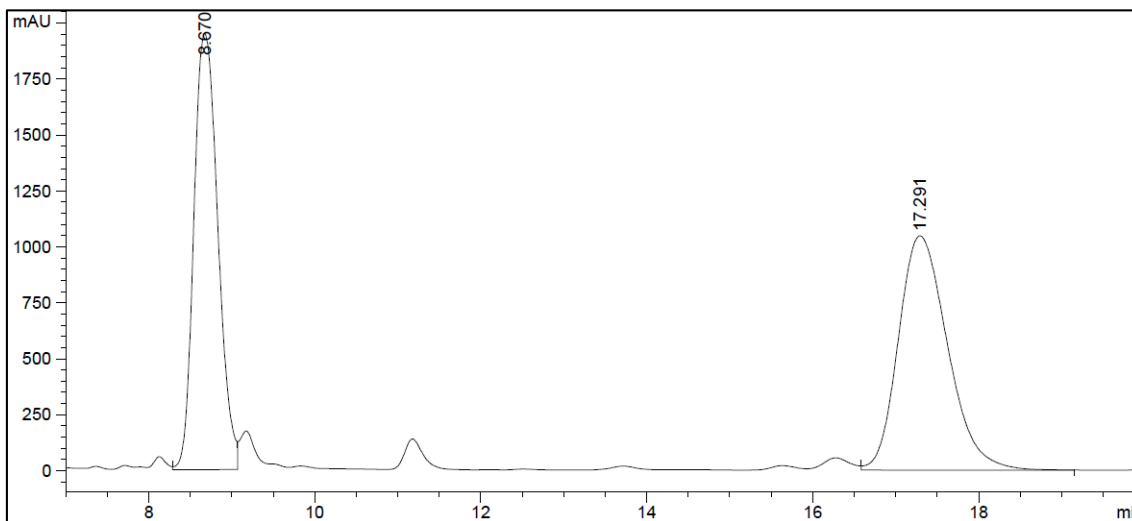
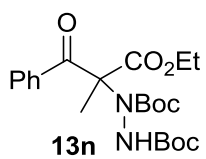
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	8.659	VB	0.3025	936.74677	47.40308	9.8867
2	11.433	VB	0.3874	8538.04395	341.81696	90.1133



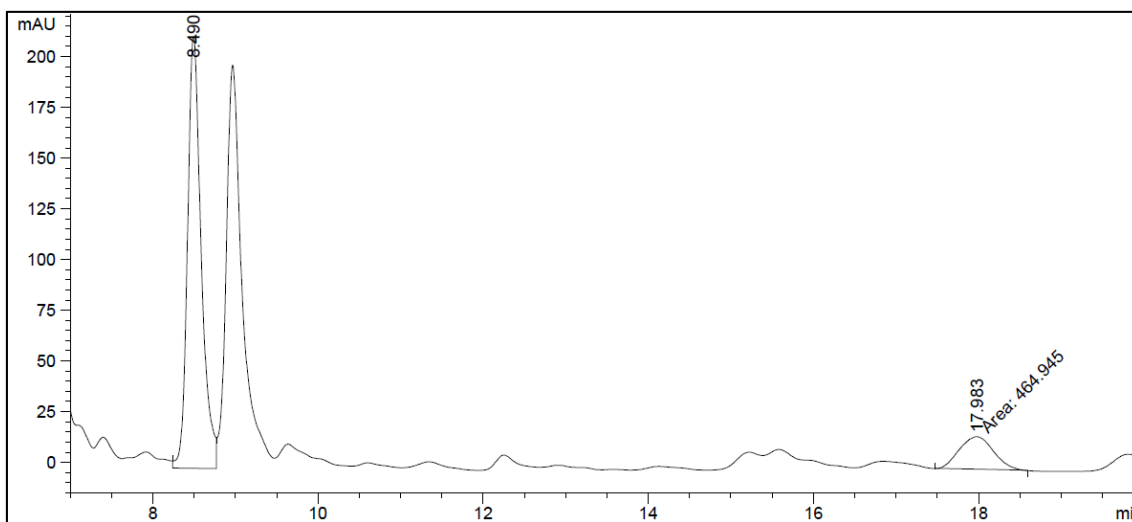
Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	21.947	PB	0.7343	2783.85034	58.38541	50.7383
2	25.134	BB	0.7101	2702.83691	57.74236	49.2617



Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	19.526	BB	0.7467	2650.56055	53.80379	37.6096
2	22.601	BB	0.7137	4396.99707	95.05746	62.3904



Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	8.670	VV	0.3188	39240.3	1949.99158	47.5930
2	17.291	VB	0.6450	43209.4	1047.99988	52.4070



Peak	Ret. Time (min)	Type	Width	Area (mAU*s)	Heigh (mAU)	Area (%)
1	8.490	VV	0.1727	2460.12964	213.02098	84.1049
2	17.983	MM	0.4817	464.94467	16.08597	15.8951