Electronic Supplementary Information

Self-Association Free Bifunctional Thiourea Organocatalysts: Synthesis of Chiral α-Amino Acids via Dynamic Kinetic Resolution of Racemic Azlactones

Joong Suk Oh,[a] Ji Woong Lee,[a] Tae Hee Ryu,[a] Jae Heon Lee,[a] Choong Eui Song[a,b]*

[a] Department of Chemistry, Sungkyunkwan University, 300 Cheoncheon, Jangan, Suwon, Gyeonggi, 440-746 (Korea);
[b] Department of Energy Science, Sungkyunkwan University, 300 Cheoncheon, Jangan, Suwon, Gyeonggi, 440-746 (Korea)
Fax: (+82) 31-290-7075; E-mail: s1673@skku.edu

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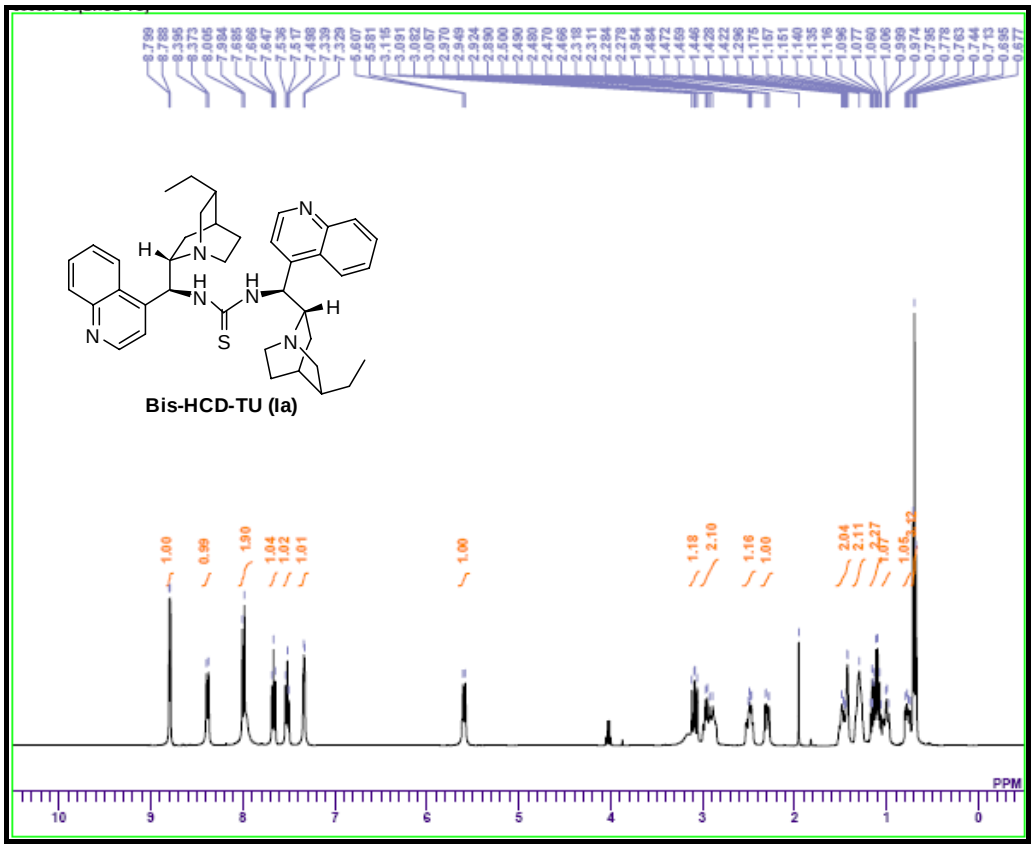
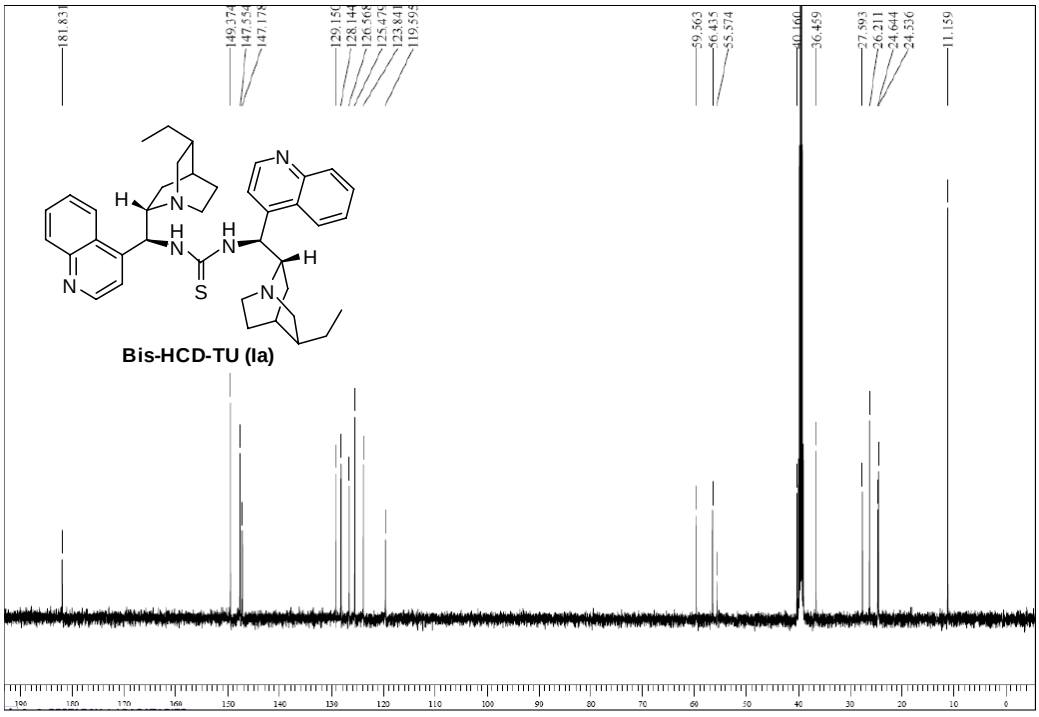
1. General remarks and materials

All chemicals used in this study were obtained from commercial sources and used without further purification. The chromatographic purification of the products was carried out by flash chromatography using Merck silica gel 60 (230–400 mesh). Thin-layer chromatography was carried out on Merck silica gel 60F plates. HPLC analyses were performed on a Varian Pro Star Series instrument equipped with an isostatic pump using a CHIRALCEL OD-H Column (250 × 4.6 mm). The ^{1}H and ^{13}C NMR spectra were recorded on Varian 300, Varian 400 and Varian 500 spectrometers. The IR spectra were obtained using a Bruker Vertex 70 spectrometer with MIRacle Micro ATR accessory. The HRMS spectra were recorded on a Jeol JMS-700 M station. The melting points (Mps) were determined on a Buchi B-540 melting point apparatus and were uncorrected. The optical rotation was measured on a Perkin Elmer Polarimeter 343 plus.

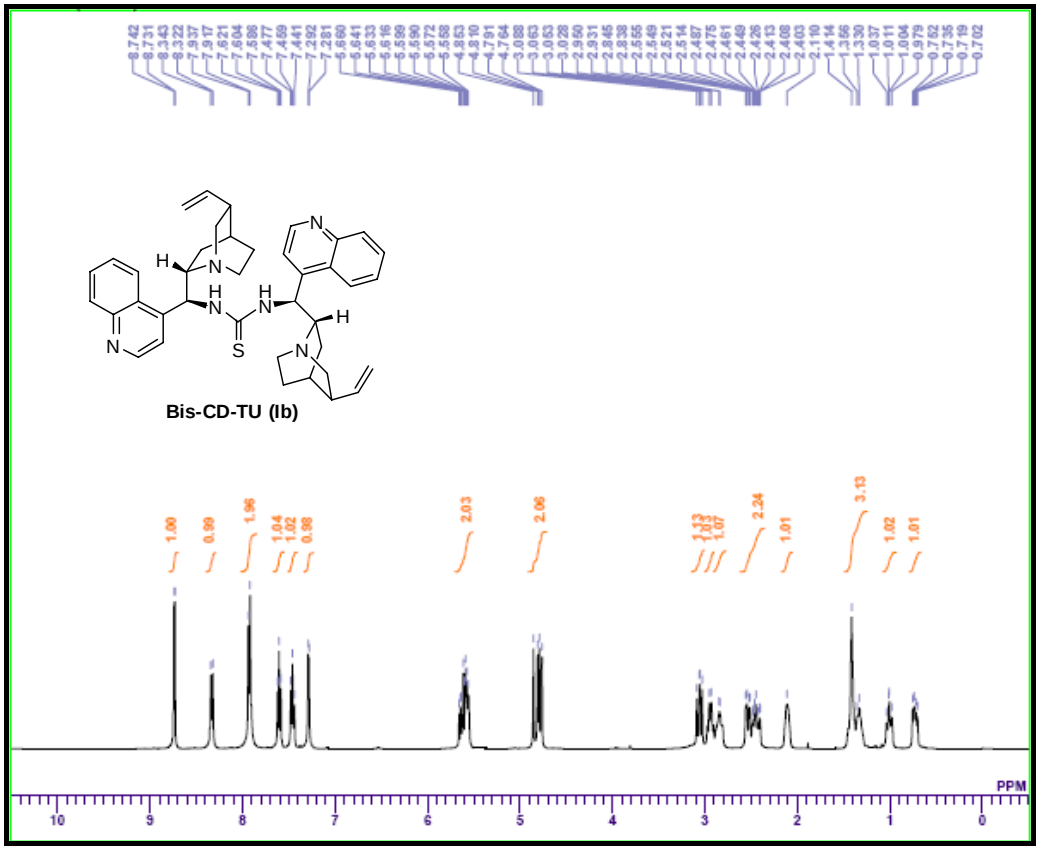
2. ^{1}H and ^{13}C NMR of Cinchona-based catalysts (Ia-d)

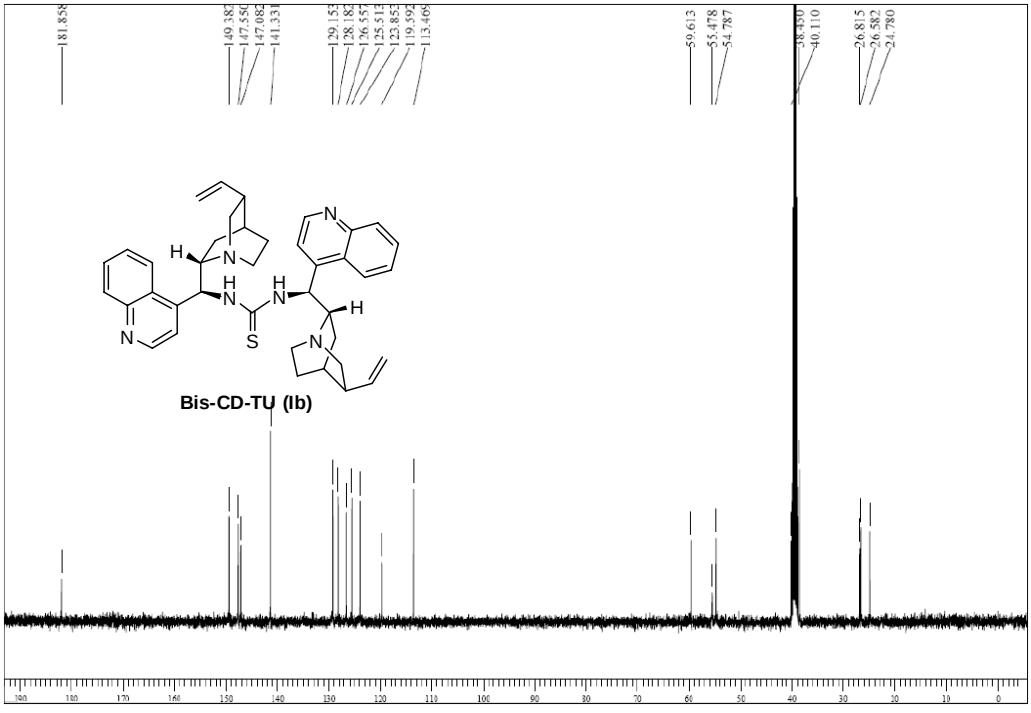
^{1}H and ^{13}C NMR spectra of **Bis-HCD-TU (Ia)**



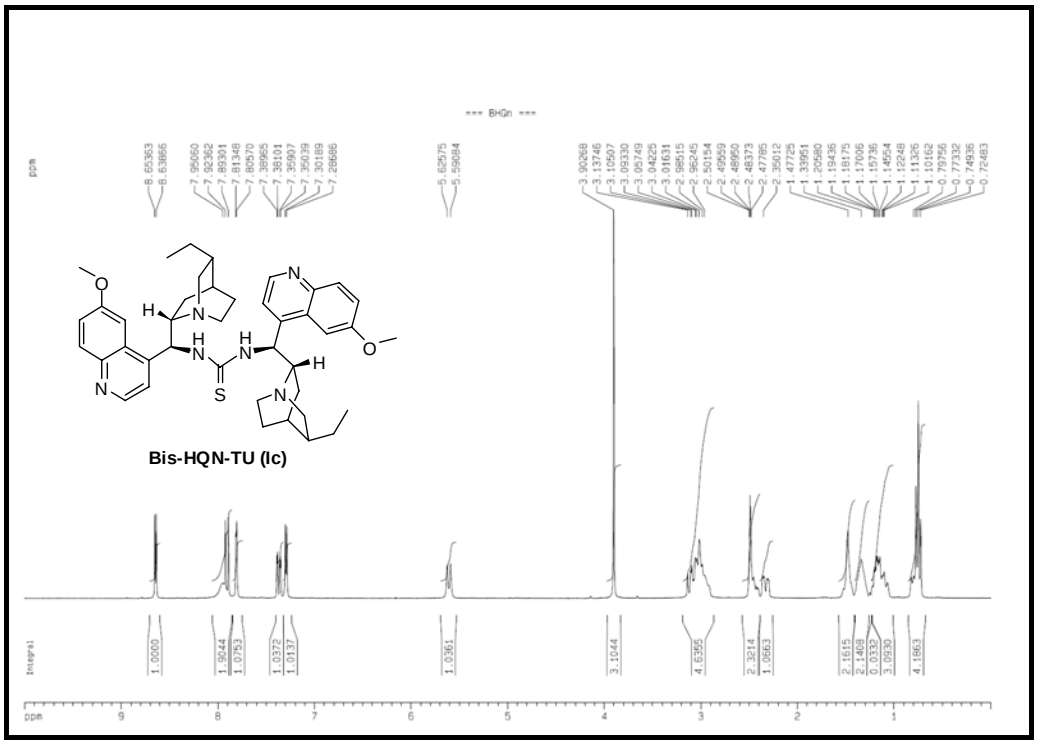


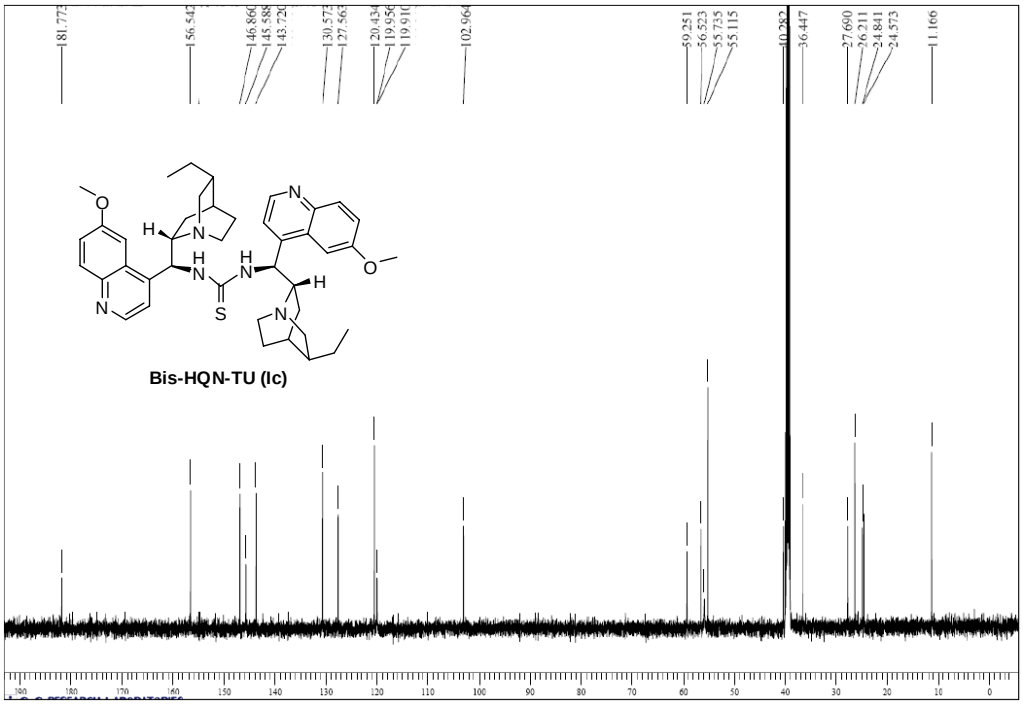
^{1}H and ^{13}C NMR spectra of **Bis-CD-TU (Ib)**



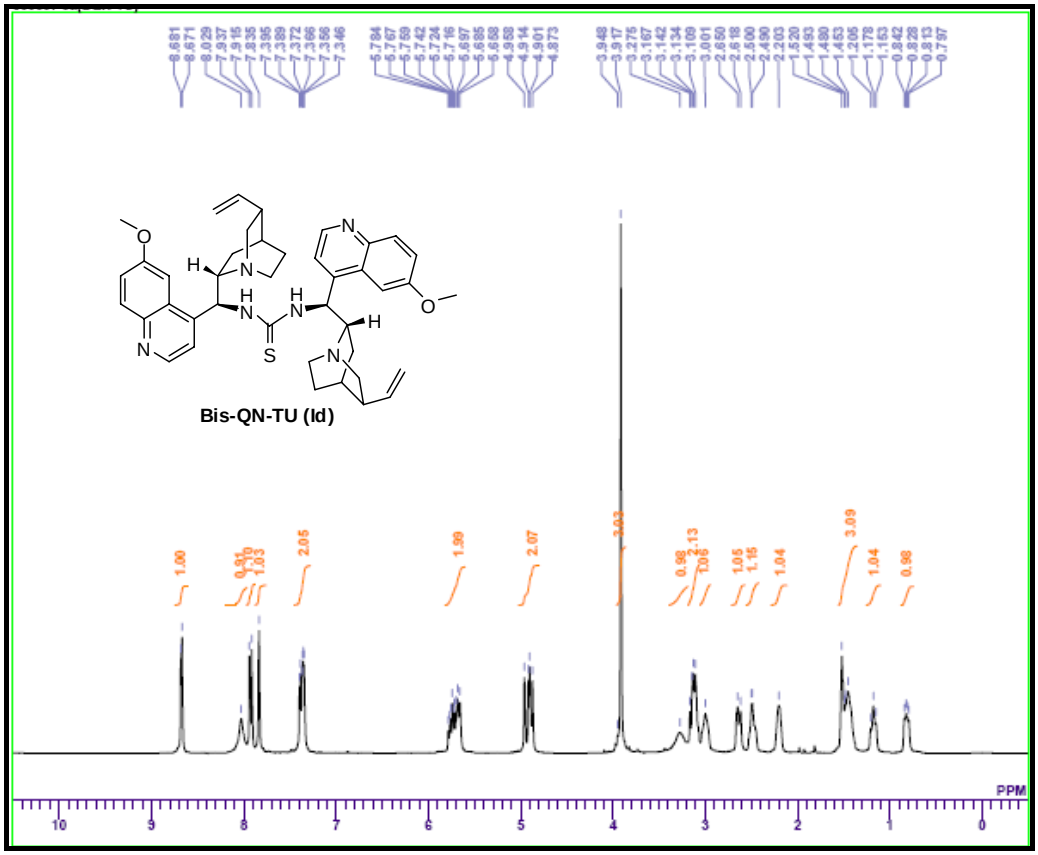


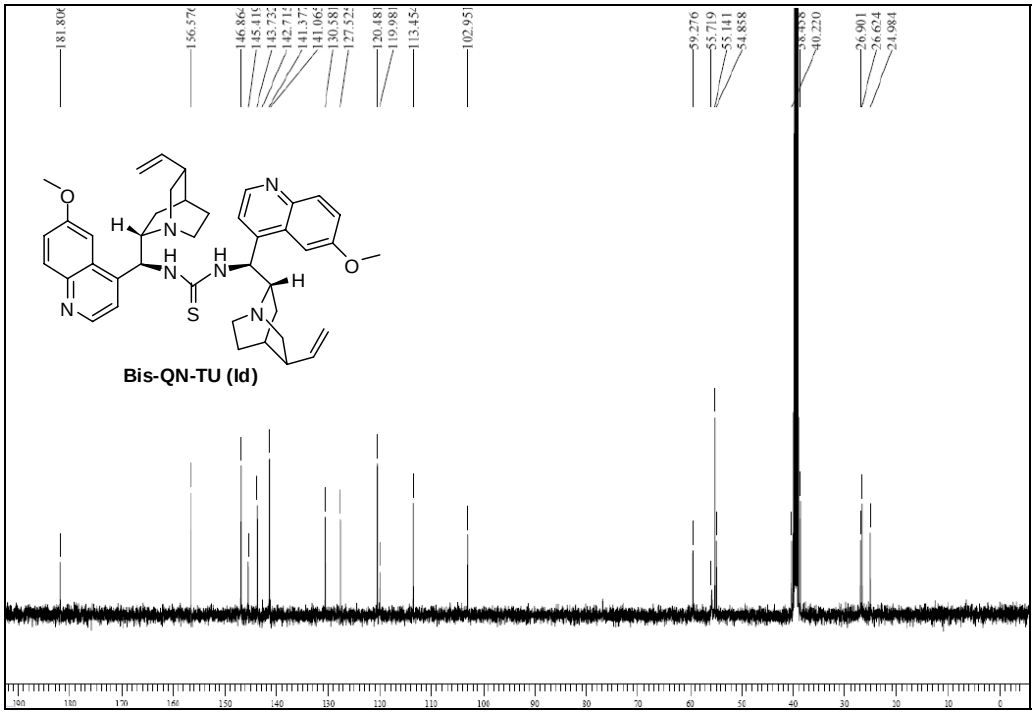
^{1}H and ^{13}C NMR spectra of **Bis-HQn-TU (Ic)**





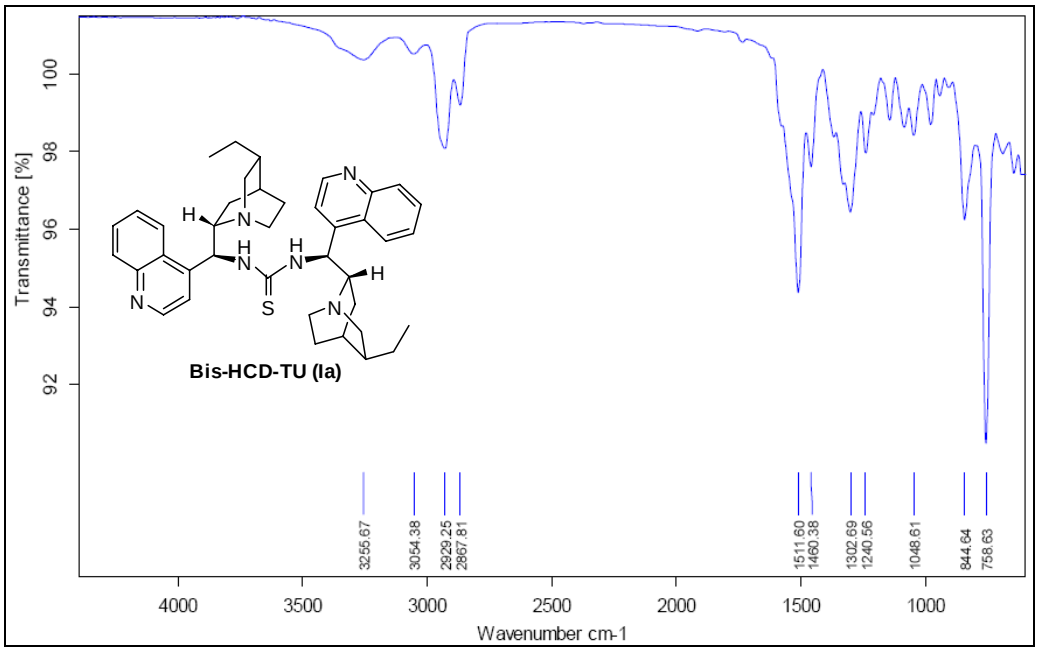
^{1}H, ^{13}C NMR spectra of **Bis-HQn-TU (Id)**



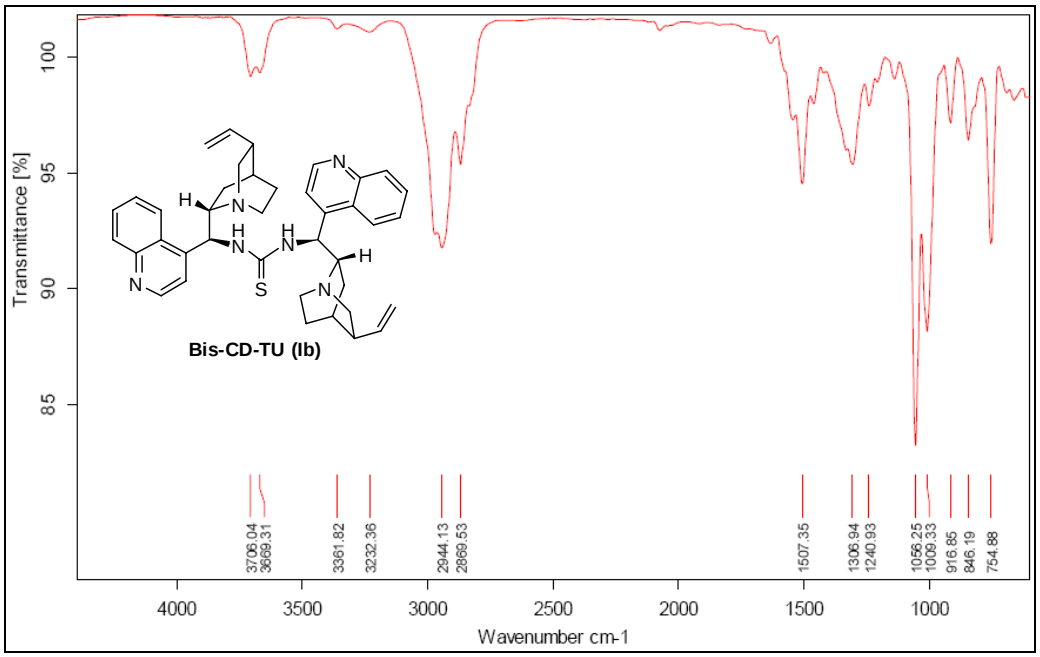


3. IR spectra of Cinchona-based catalysts (Ia-d)

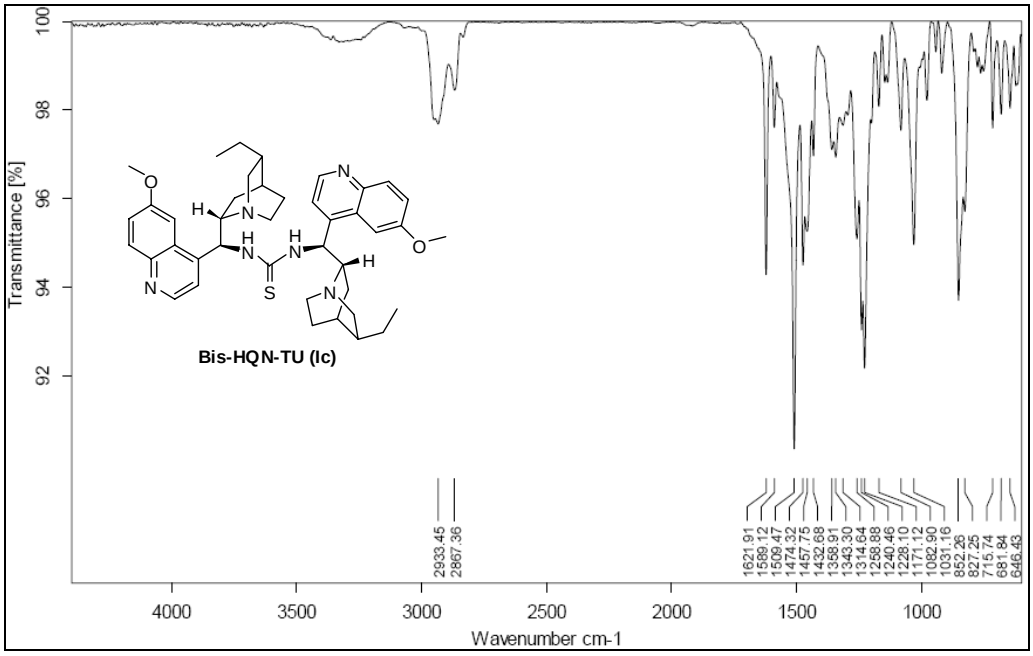
IR spectrum of **Bis-HCD-TU (Ia)**



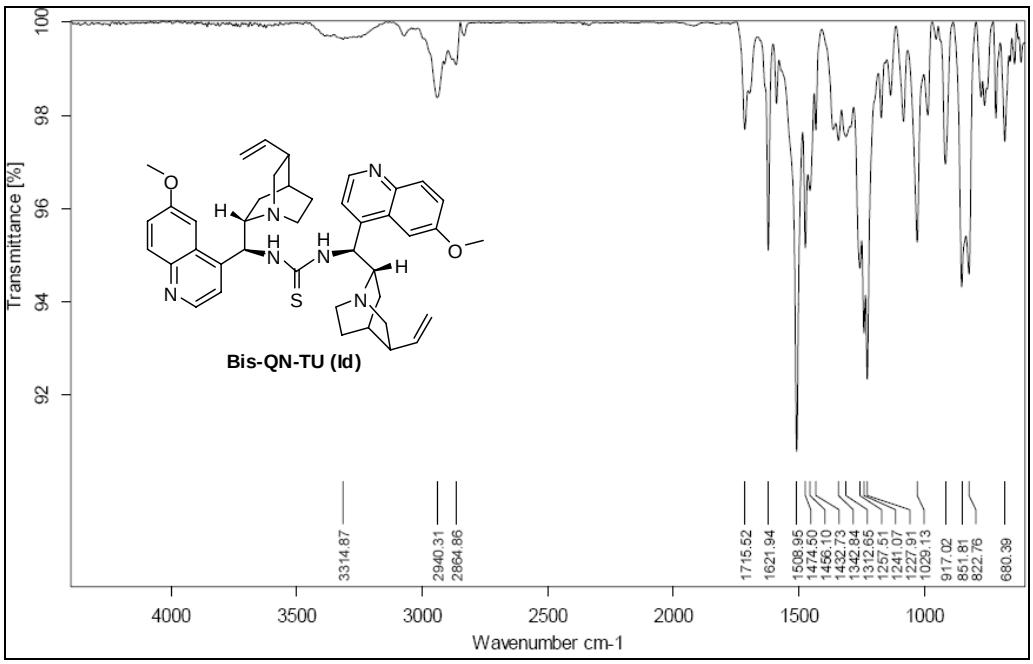
IR spectrum of **Bis-CD-TU (Ib)**



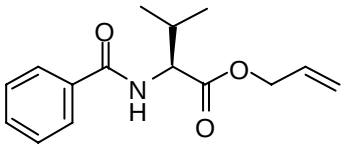
IR spectrum of **Bis-HQN-TU (Ic)**



IR spectrum of **Bis-QN-TU (Id)**

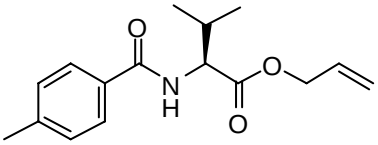


4. Analytical data of products



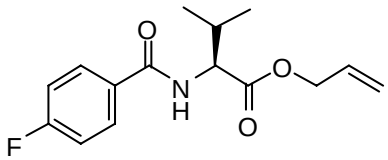
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 (d, *J* = 6.8 , 3H), 1.01 (d, *J* = 6.8 , 3H), 2.26–2.34 (m, 1H), 4.60–4.71 (m, 2H), 4.81 (dd, *J* = 4.8 and 8.4 Hz, 1H), 5.26 (dd, *J* = 10.4 and 1.2 Hz, 1H), 5.35 (dq, *J* = 16.8 and 1.2 Hz, 1H), 5.85–5.97 (sym.m, 1H), 6.86 (br d, *J* = 8.8 Hz, 1H), 7.38–7.43 (m, 2H), 7.46–7.51 (m, 1H), 7.78–7.83 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.84, 18.96, 21.35, 31.47, 57.19, 65.70, 118.77, 126.83, 128.92, 130.95, 131.27, 141.82, 166.94, 171.66.

Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 5.7 min, t_S =9.1 min.



^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (d, *J* = 6.8 , 3H), 1.01 (d, *J* = 6.8 , 3H), 2.25–2.34 (m, 1H), 2.38 (s, 3H), 4.59-4.71 (m, 2H), 4.81 (dd, *J* = 4.8 and 8.8 Hz, 1H), 5.26 (dq, *J* = 10 and 1.2 Hz, 1H), 5.35 (dq, *J* = 16.8 and 1.2 Hz, 1H), 5.86-6.00 (sym.m, 1H), 6.78 (br d, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8 Hz, 2H), 7.71 (d, *J* = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.84, 18.96, 21.35, 31.47, 57.19, 65.70, 118.77, 126.83, 128.92, 130.95, 131.27, 141.82, 166.94, 171.66.

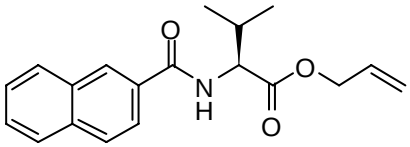
Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 5.0 min, t_S =12.8 min.



^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (d, *J*=7.2 Hz, 3H), 1.01 (d, *J*=7.2 Hz, 3H), 2.25–2.36(sym.m, 1H), 4.66–4.69 (m, 2H), 4.79 (dd, *J*=4.9 Hz and *J*=8.6 Hz, 1H), 5.26 (dq, *J* = 10 and 1.2 Hz, 1H), 5.35 (dq, *J* = 16.8 and 1.2 Hz, 1H), 5.87–6.97 (sym.m, 1H), 6.92(d, *J* = 8.8 Hz, 1H), 7.04–7.11 (m, 2H), 7.79–7.85(m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ^{13}C NMR

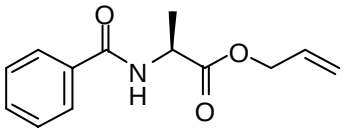
(500 MHz, $CDCl_3$) δ 17.86, 18.94, 31.51, 57.48, 65.89, 115.51 (d, ^2J (C–C-F) = 21.6 Hz), 119.01, 129.36 (d, ^3J (C–C-C-F) = 8.88 Hz), 130.26 (d, ^4J (C-C-C-C-F) = 3.0 Hz), 131.42, 164.76 (d, ^1J (C-F) = 250.6 Hz), 166.20, 171.81.

Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 5.0 min, t_S =12.8 min.



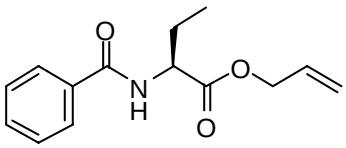
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 (d, J = 7.2 Hz, 3H), 1.05 (d, J = 7.2 Hz, 3H), 2.28–2.39 (sym.m, 1H), 4.64–4.73 (m, 2H), 4.89 (dd, J = 4.8 and 8.8 Hz, 1H), 5.27 (d, J = 10.4, 1H), 5.37 (d, J = 17.6 Hz, 1H), 5.88–5.99 (sym.m, 1H), 6.92 (br d, J = 8.4 Hz, 1H), 7.49-7.57 (m, 2H), 7.83-7.91 (m, 4H), 8.31 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.98, 19.01, 31.65, 57.42, 65.90, 118.97, 123.44, 126.60, 127.40, 127.55, 128.30, 128.76, 131.08, 131.30, 132.32, 134.60, 167.14, 171.78.

Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 10.1 min, t_S =16.6 min.



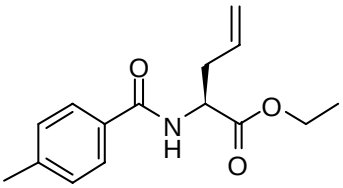
^{1}H NMR (300 MHz, $CDCl_3$) δ 1.53 (d, J = 7.2 Hz, 3H), 4.66 (d, J = 5.7 Hz, 2H), 4.83 (p, J = 7.2 Hz, 1H), 5.26 (dd, J = 1.2 and 10.5 Hz, 1H), 5.34 (dd, J = 17.1 and 1.2 Hz, 1H), 5.87-6.00 (sym m., 1H), 7.02 (br d, J = 6.7 Hz, 1H), 7.37–7.51 (m, 3H), 7.78–7.81 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.96, 26.10, 26.29, 32.57, 33.44, 34.19, 40.34, 50.52, 65.91, 118.78, 127.01, 128.52, 131.50, 131.66, 133.89, 167.03, 173.03.

Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 8.6 min, t_S =14.2 min.



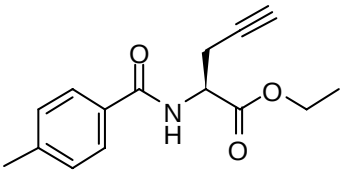
^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, *J* = 7.5 Hz, 3H), 1.85 (td, *J* = 7.1 Hz and 14.1 Hz, 1H), 1.96-2.10 (m, 1H), 4.62–4.74 (m, 2H), 4.77-4.84 (m, 1H), 5.28 (dd, *J* = 10.5 and 1.2 Hz, 1H), 5.36 (dq, *J* = 17.2 and 1.4 Hz, 1H), 5.85-5.98 (sym.m, 1H), 6.82 (br d, *J* = 7.4 Hz, 1H), 7.40–7.53 (m, 3H), 7.79–7.82 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 9.46, 25.73, 53.57, 65.98, 118.95, 126.98, 128.53, 131.42, 131.67, 133.92, 166.98, 172.26.

Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 7.1 min, t_S =14.4 min.



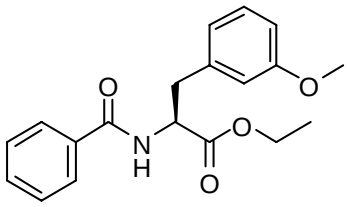
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.0 Hz, 3H), 2.40 (s, 3H), 2.59–2.65 (m, 1H), 2.69-2.75 (m, 1H), 4.19-4.29 (m, 2H), 4.87 (td, *J* = 5.6 Hz and 7.6 Hz, 1H), 5.16-5.19 (m, 1H), 5.71–5.80 (sym.m, 1H), 6.67 (d, *J* = 6.8 Hz, 1H), 7.22–7.25 (m, 2H), 7.67–7.72 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 14.16, 21.37, 36.61, 51.92, 61.49, 119.11, 126.97, 129.14, 131.14, 132.27, 142.06, 166.73, 171.82.

Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 5.8 min, t_S =9.3 min.



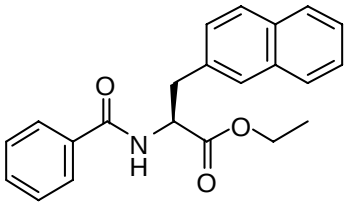
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.32 (t, *J* = 7.1 Hz, 3H), 2.40 (t, *J* = 2.6 Hz, 1H), 2.40 (s, 3H), 2.86 (ddd, *J* = 17.0 Hz and *J* = 4.3 Hz and *J* = 2.7 Hz, $1H_A$ of AB-spin system), 2.91 (ddd, *J* = 17.0 Hz and *J* = 4.3 Hz and *J* = 2.7 Hz, $1H_B$ of AB-spin system), 4.23–4.28 (m, 1H), 4.29-4.33 (m, 1H), 4.92 (td, *J* = 4.6 Hz and *J* = 7.7 Hz, 1H), 6.98 (d, *J* = 7.3 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) 14.13, 21.42, 22.58, 50.94, 61.97, 71.53, 78.53, 127.09, 129.21, 130.93, 142.29, 166.83, 170.47.

Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 7.8 min, t_S =10.5 min.



^{1}H NMR (300 MHz, $CDCl_3$) δ 1.29 (t, *J* = 7.2 Hz, 3H), 3.21 (dd, *J* = 13.6 Hz and 5.3 Hz, $1H_A$ of AB-spin system), 3.27 (dd, *J* = 13.6 Hz and 5.3 Hz, $1H_A$ of AB-spin system), 3.73 (s, 3H), 4.22 (dd, *J* = 14.1 and 7.3 Hz, 2H), 5.06 (td, *J* = 7.5 and 5.6 Hz, 1H), 6.61 (d, *J* = 7.3 Hz, 1H), 6.76 (m, 3H), 7.20 (m, 1H), 7.42 (m, 2H), 7.51 (m, 1H), 7.74 (m, 2H) ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.13, 37.89, 53.51, 55.14, 61.65, 112.68, 114.90, 121.70, 126.97, 128.59, 129.52, 131.75, 133.95, 137.38, 159.67, 166.75, 171.53.

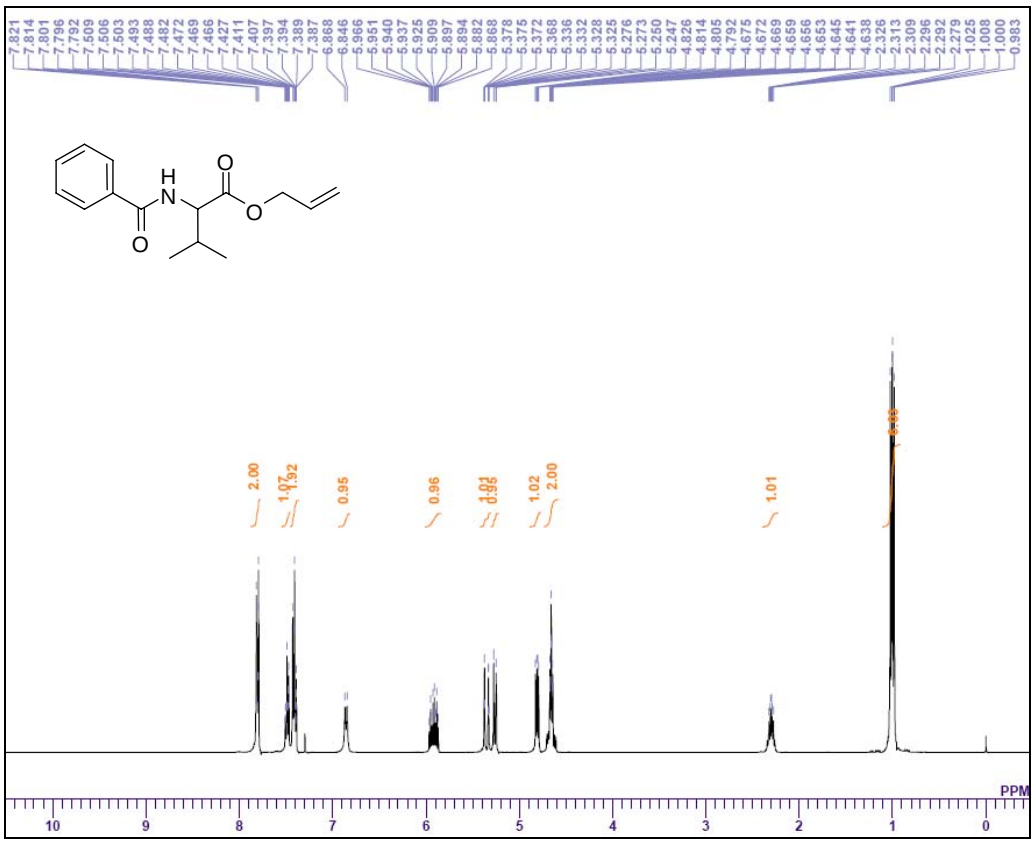
Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 10.5 min, t_S =13.0 min.

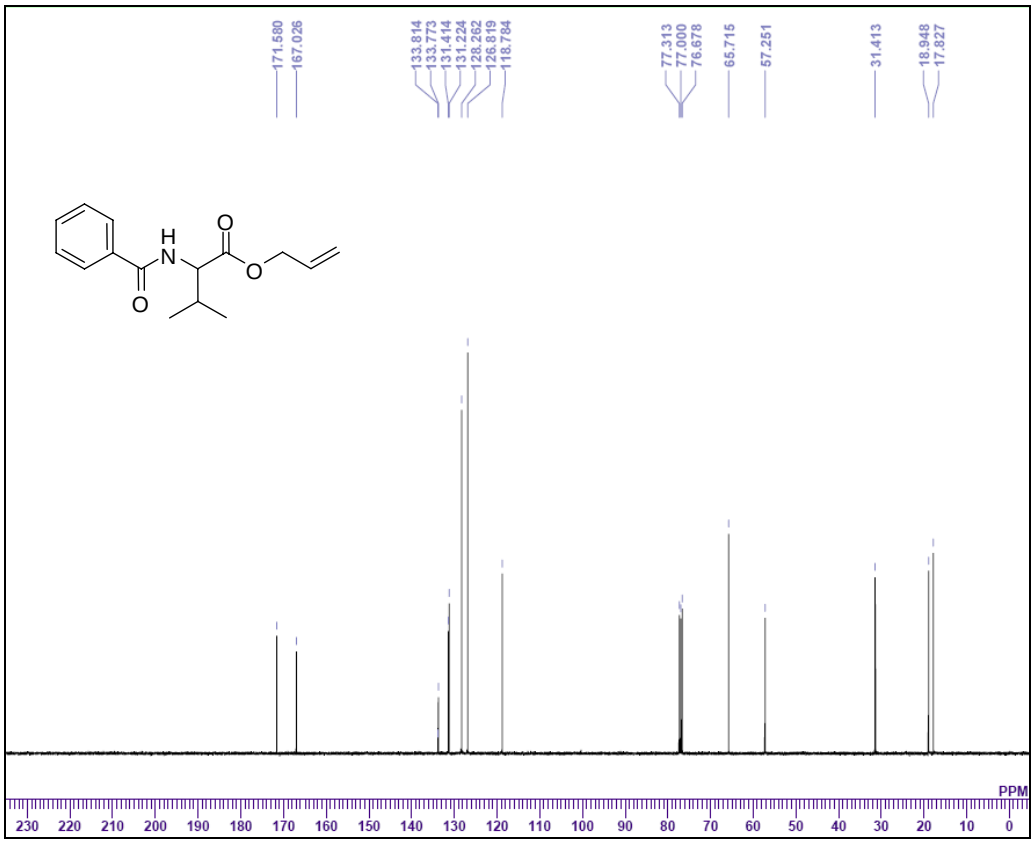


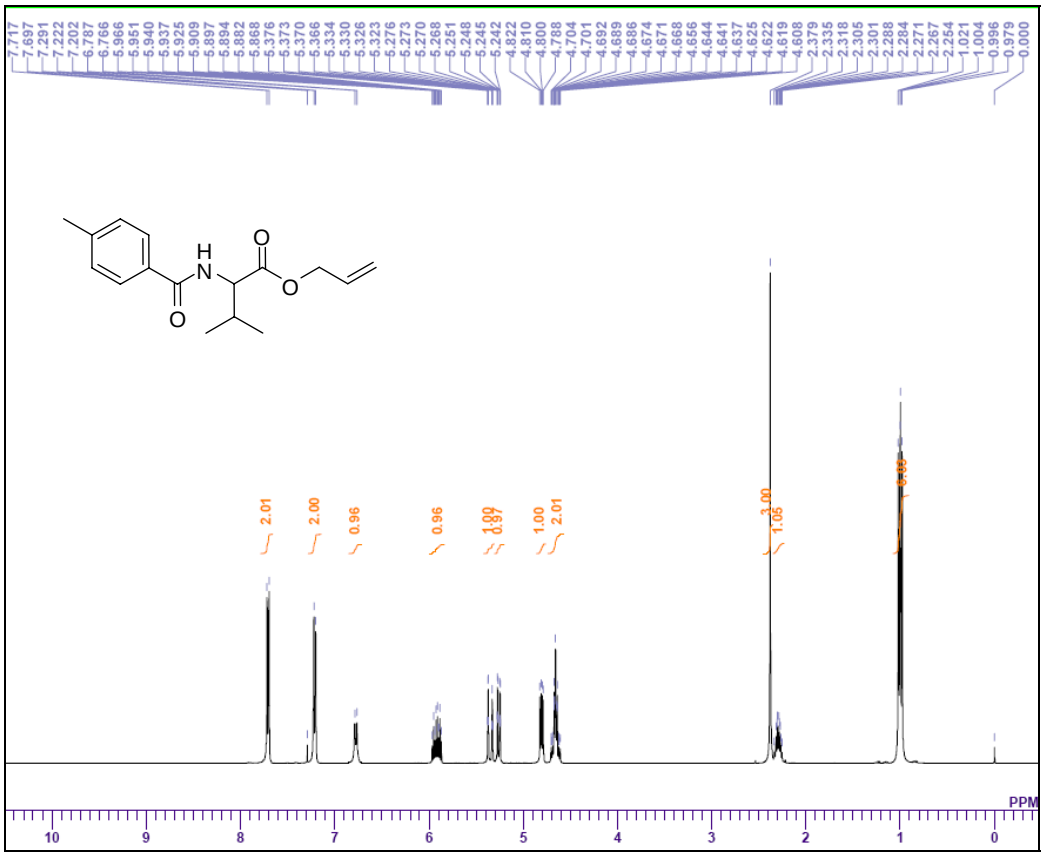
^{1}H NMR (500 MHz, $CDCl_3$) δ 1.18 (t, *J* = 7.1 Hz, 3H), 3.36 (dd, *J* = 13.9 Hz and 5.8 Hz, $1H_A$ of AB-spin system), 2.92 (dd, *J* = 13.9 Hz and 5.8 Hz, $1H_B$ of AB-spin system),, 4.11-4.20 (m, 2H), 5.13(td, *J* = 5.9 and 7.4 Hz, 1H), 6.90 (br d, *J* = 7.3 Hz, 1H), 7.27–7.32(m, 3H), 7.38–7.42 (m, 3H), 7.59 (br s, 1H), 7.69–7.76 (m, 5H) ^{13}C NMR (125 MHz, $CDCl_3$) 13.91, 37.80, 53.55, 61.39, 125.50, 125.94, 126.84, 127.26, 127.30, 127.44, 127.93, 127.96, 128.31, 131.46, 132.28, 133.21, 133.44, 133.71, 166.81, 171.44.

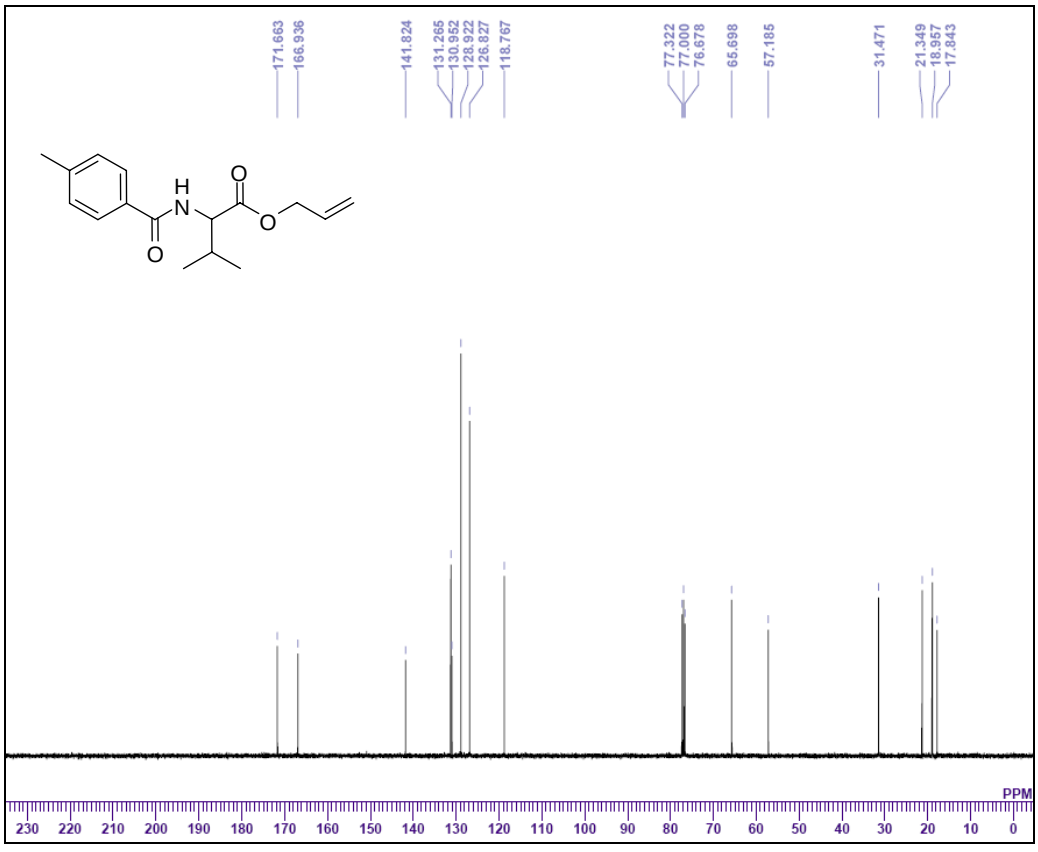
Enantiomeric excess was determined by using HPLC analysis: CHIRALPAK OD-H; Hexane: Isopropyl alcohol=90:10; flow rate: 1.0 mL/min; 220 nm; t_R = 12.1 min, t_S =14.8 min.

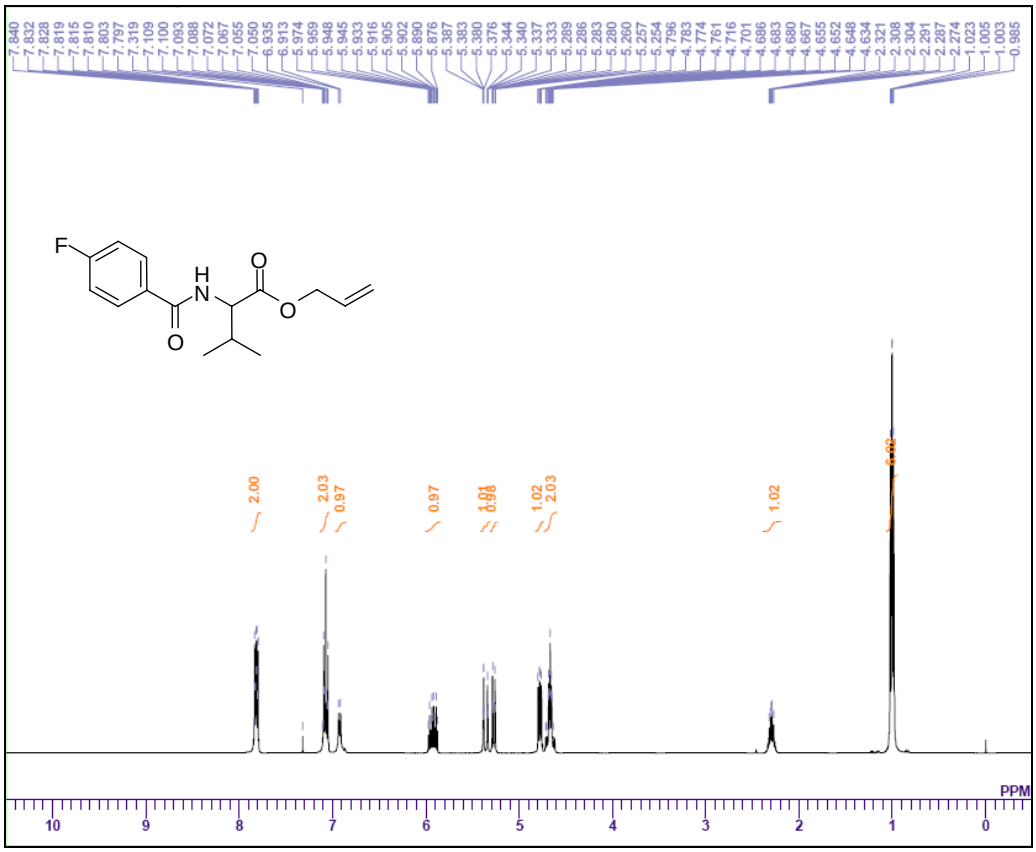
5. NMR Spectra for *N*-acylated-α-amino acid esters

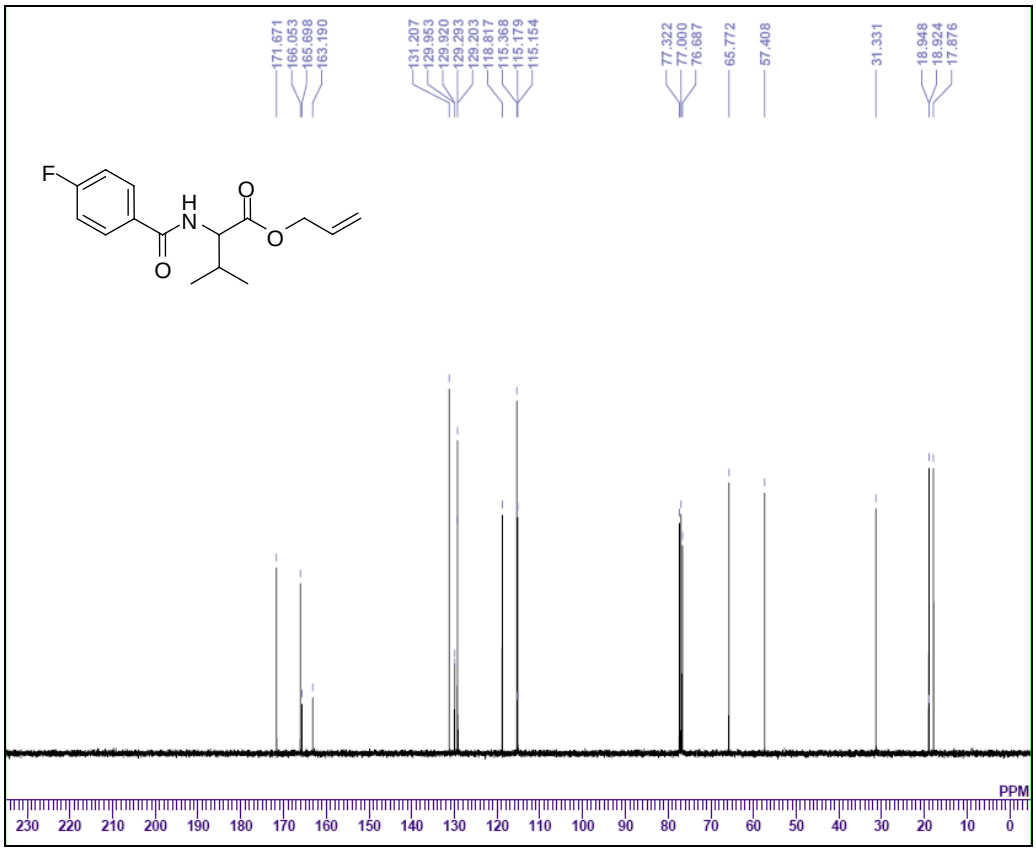


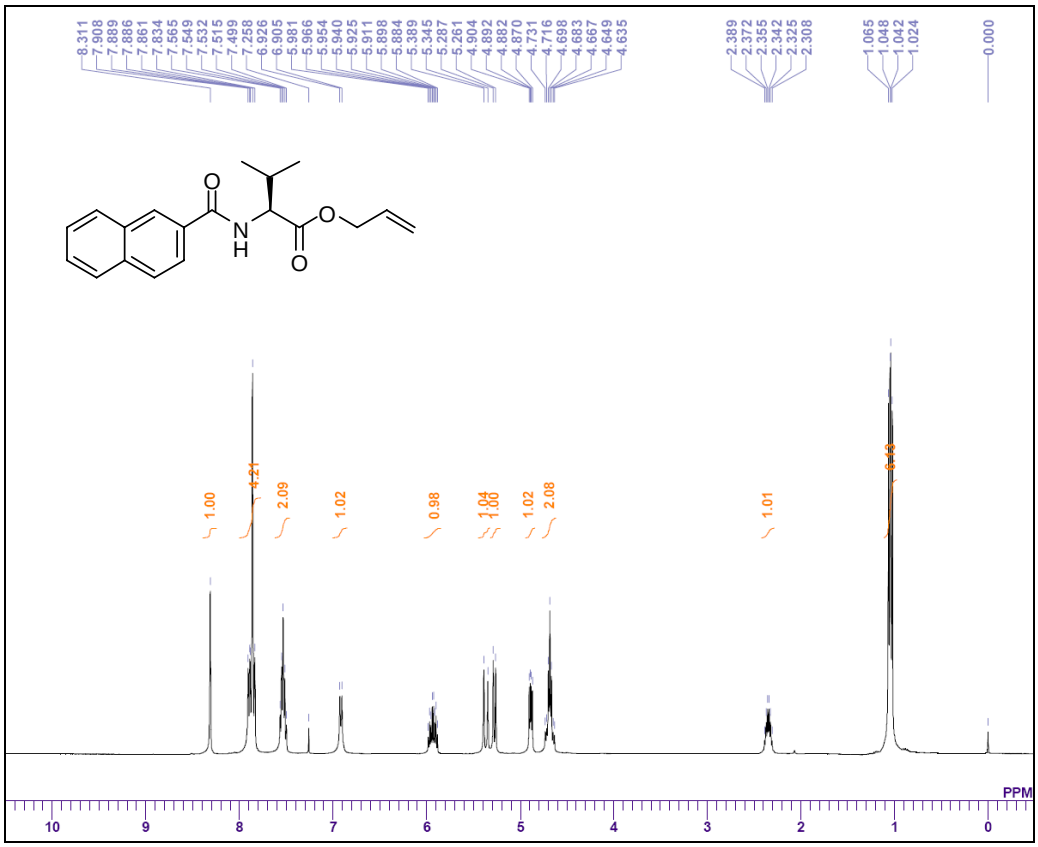


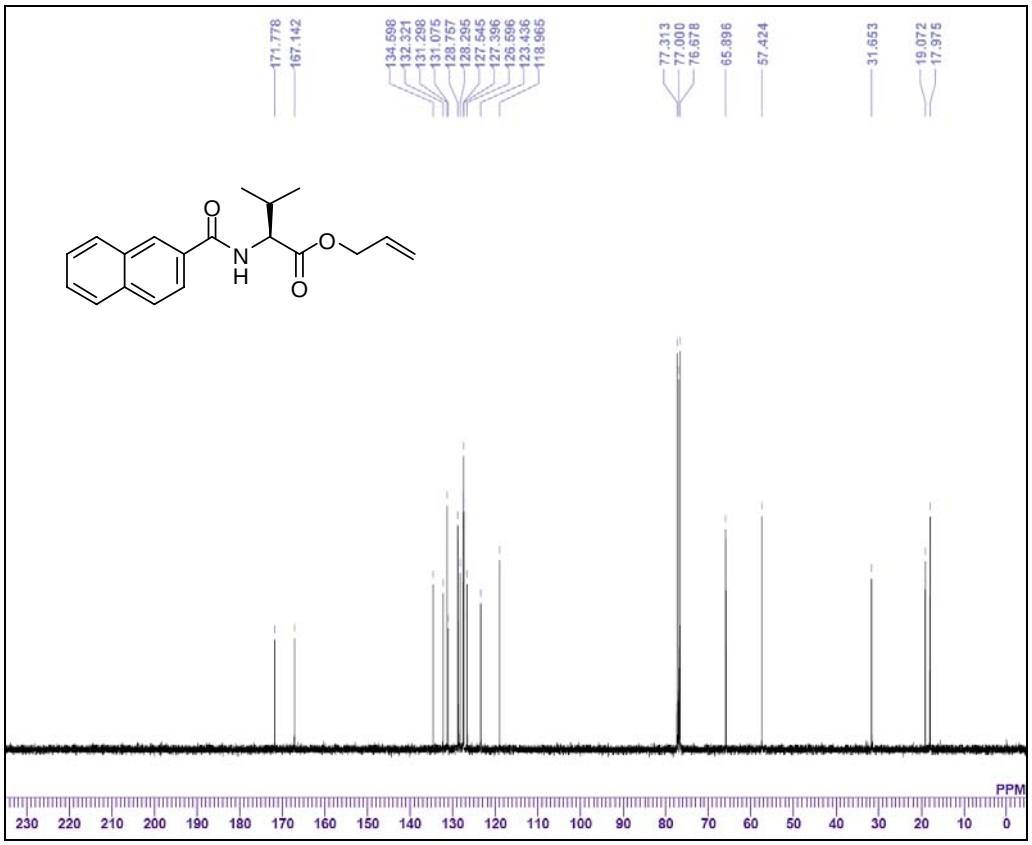


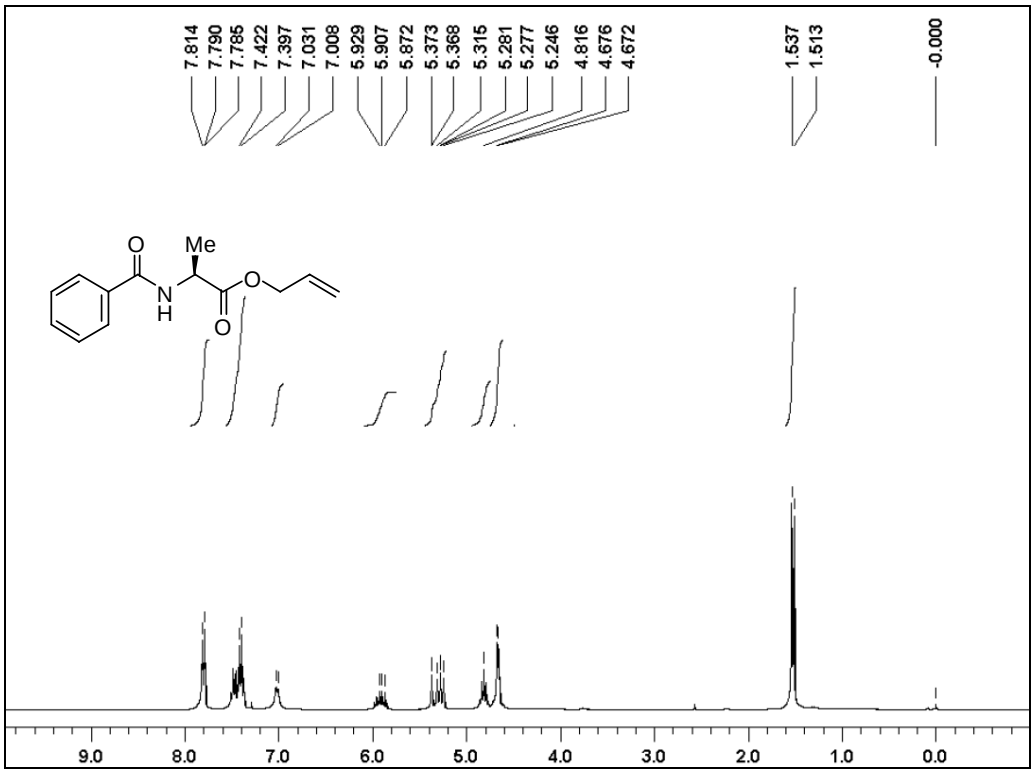


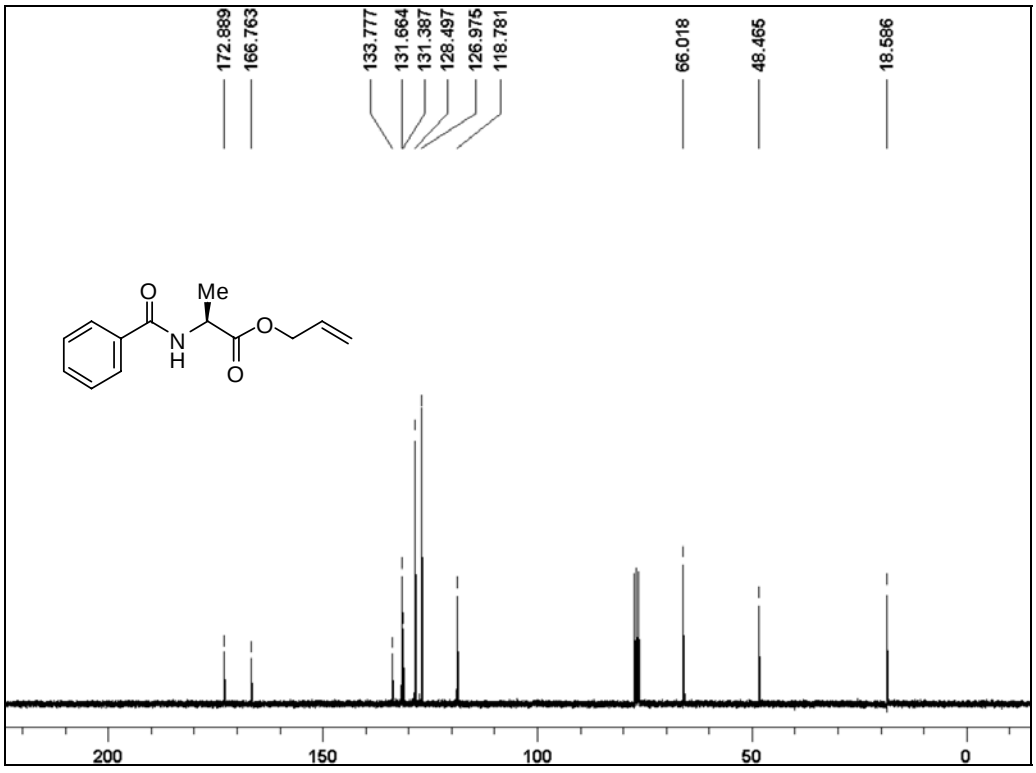


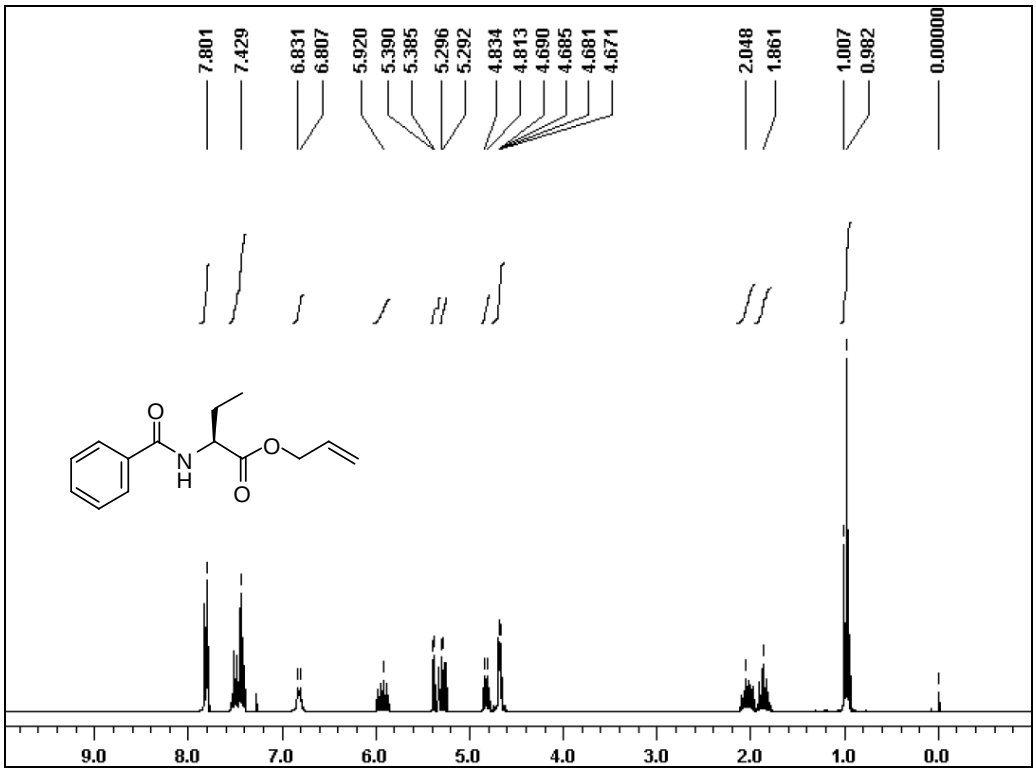


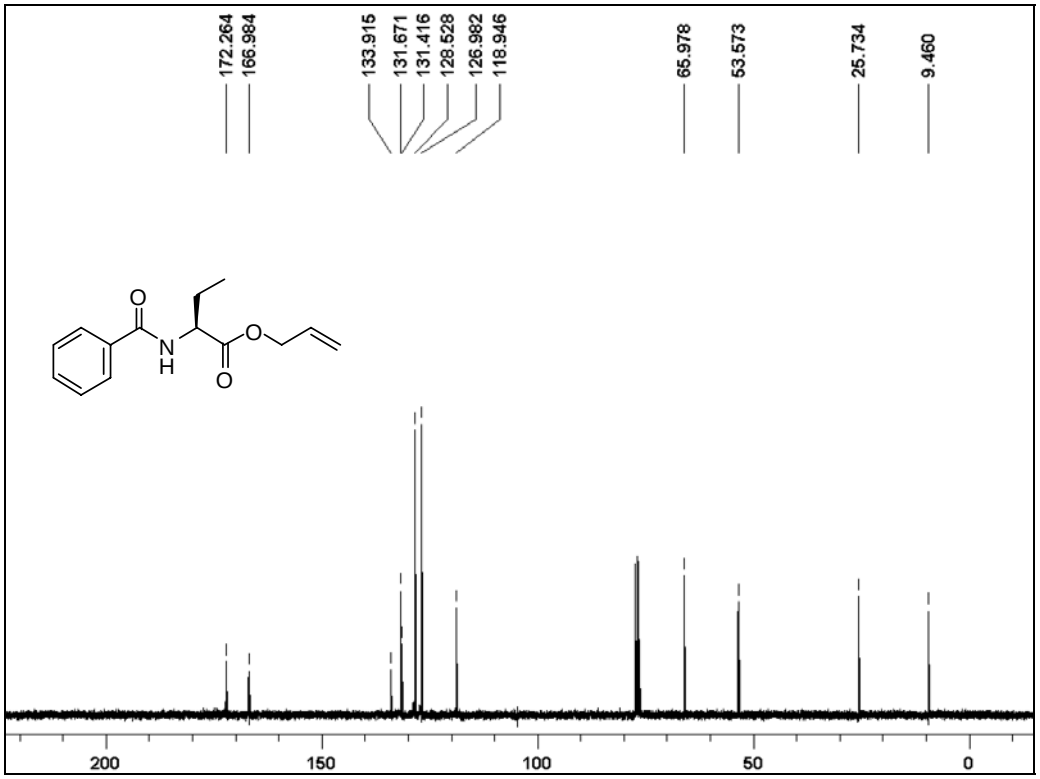


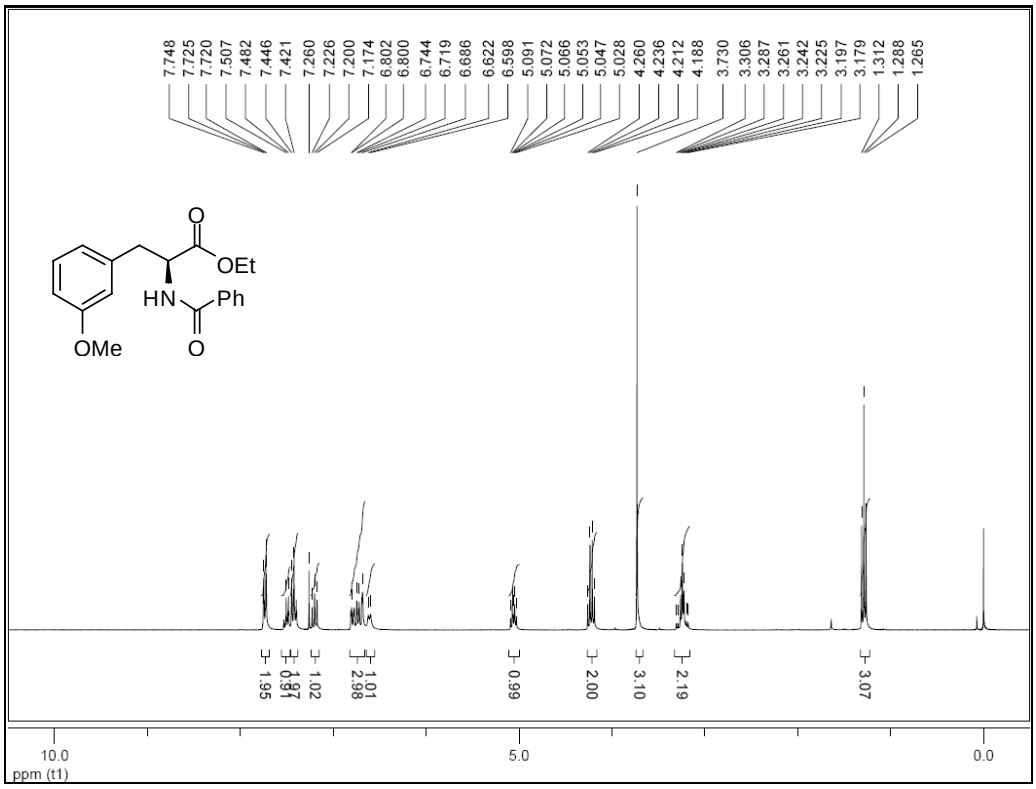


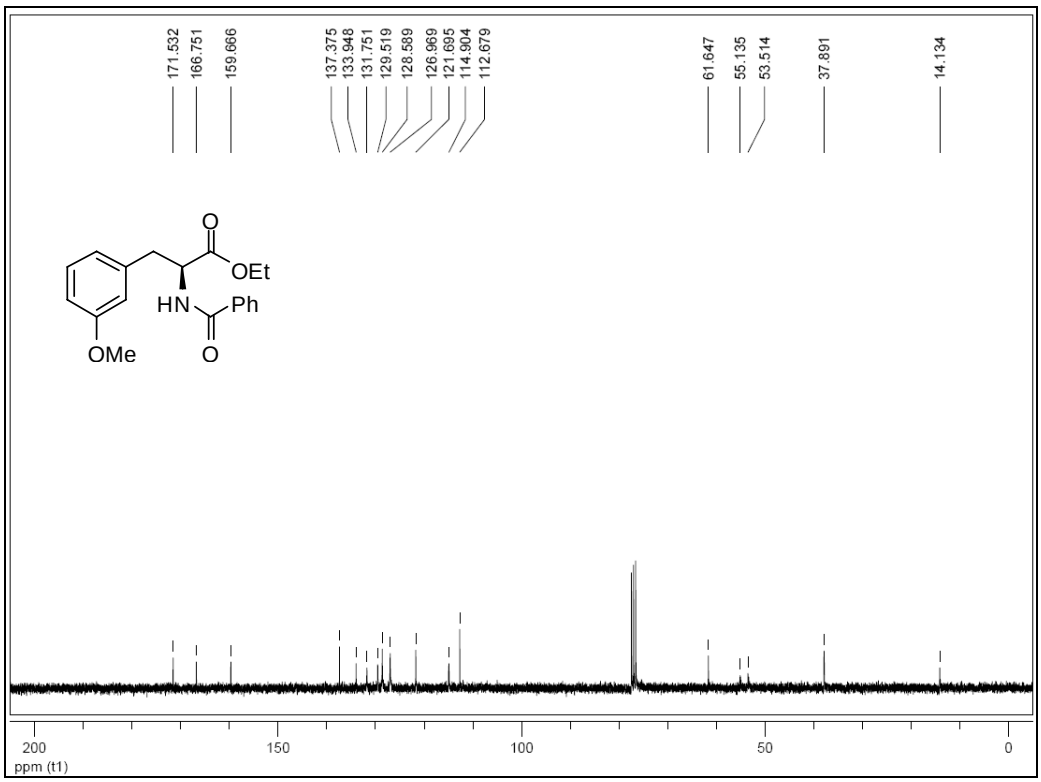


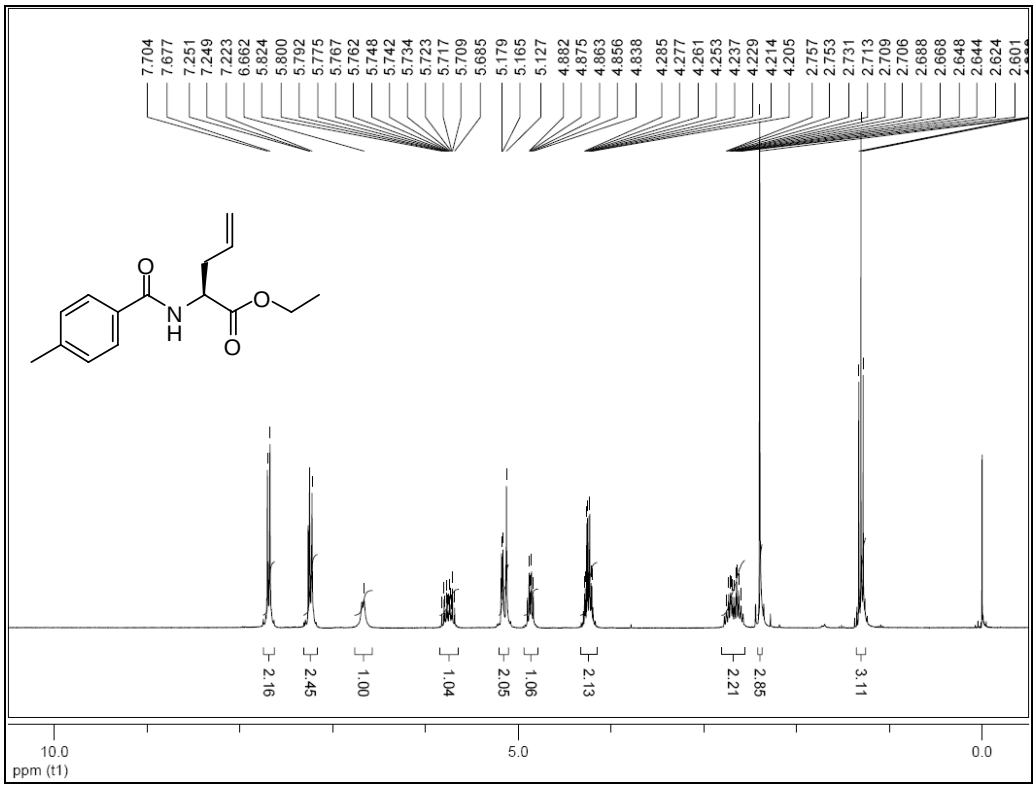


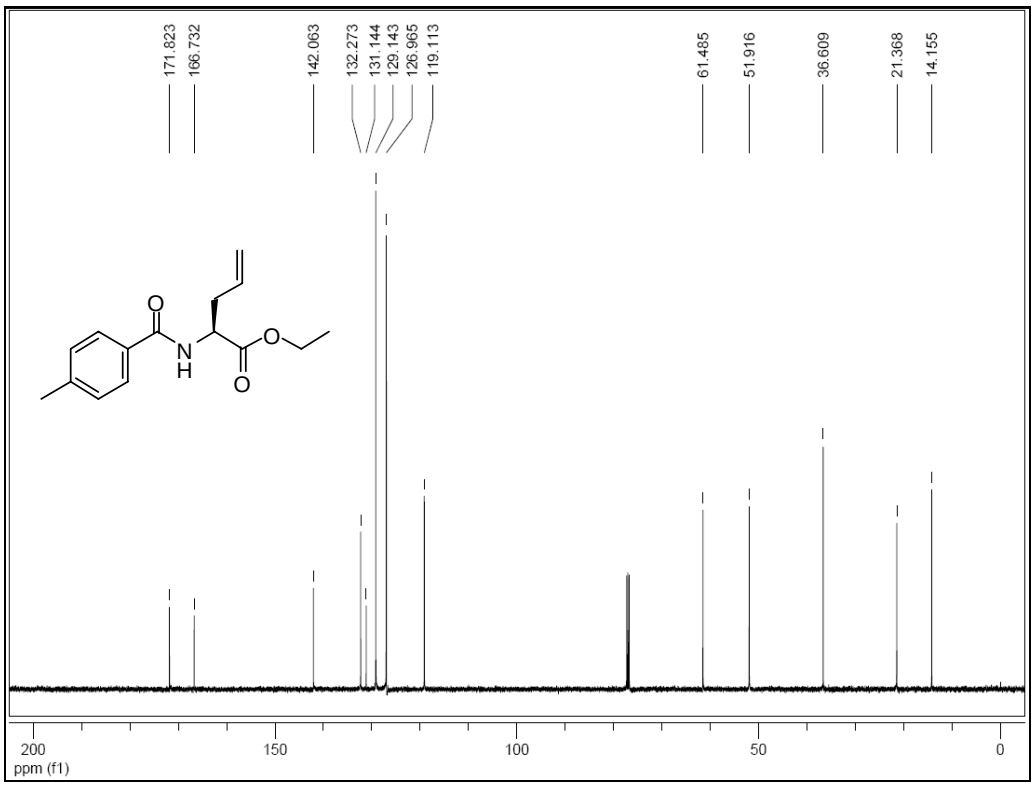


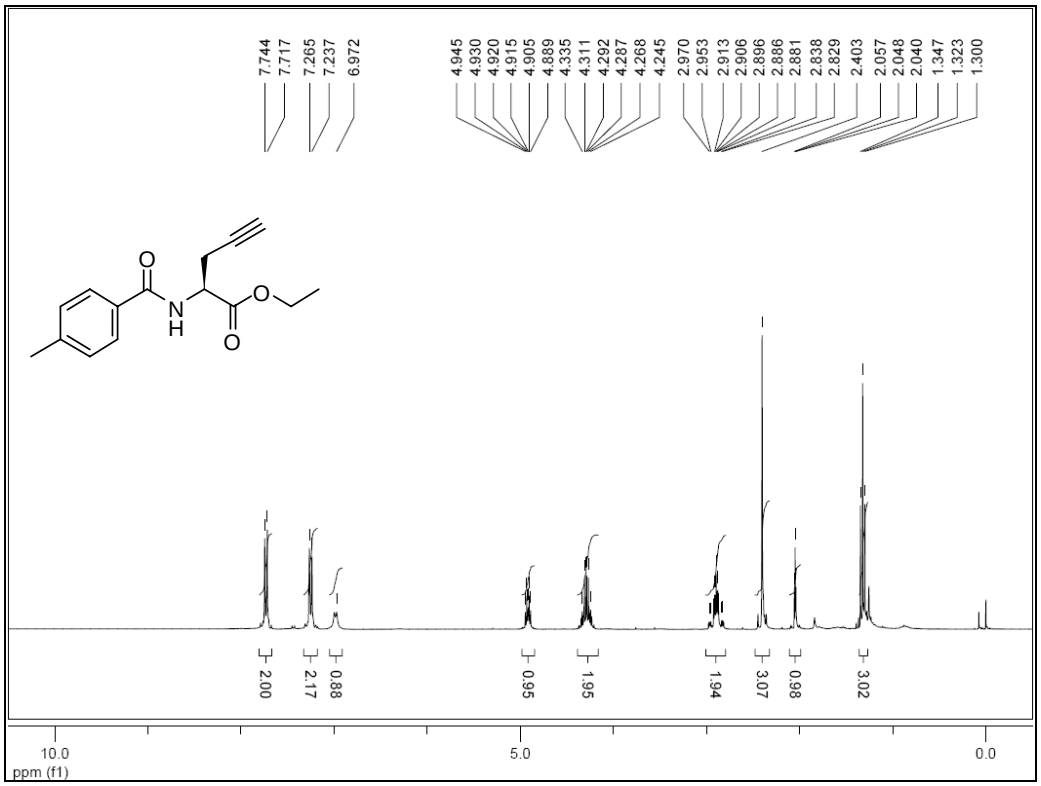


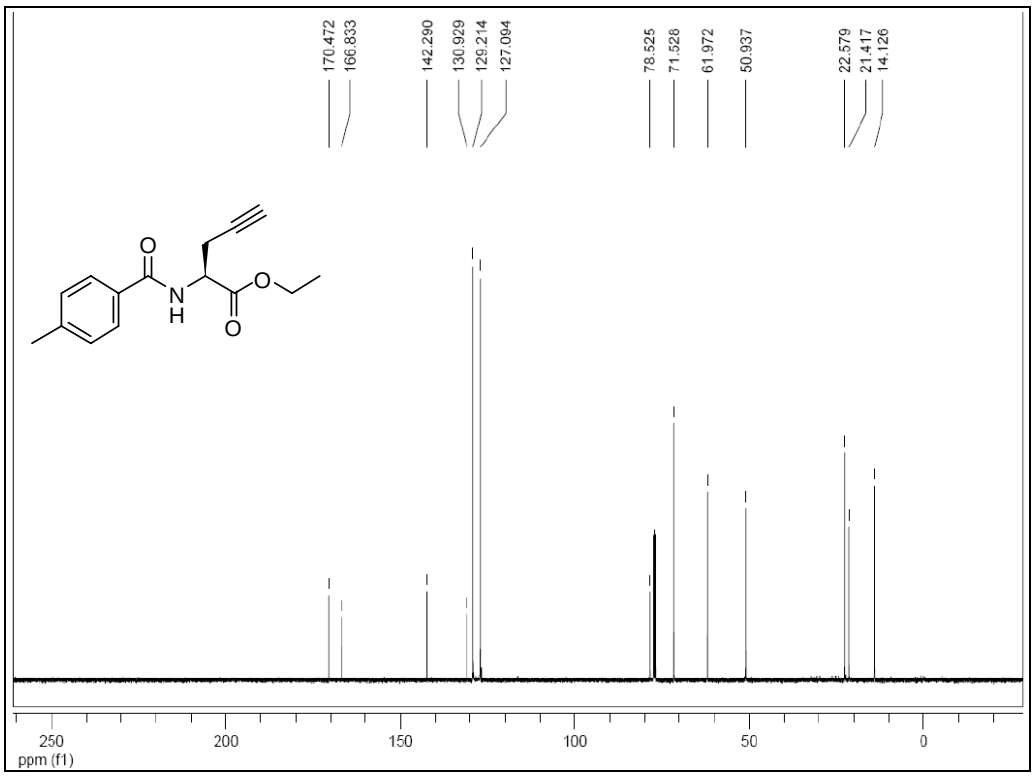


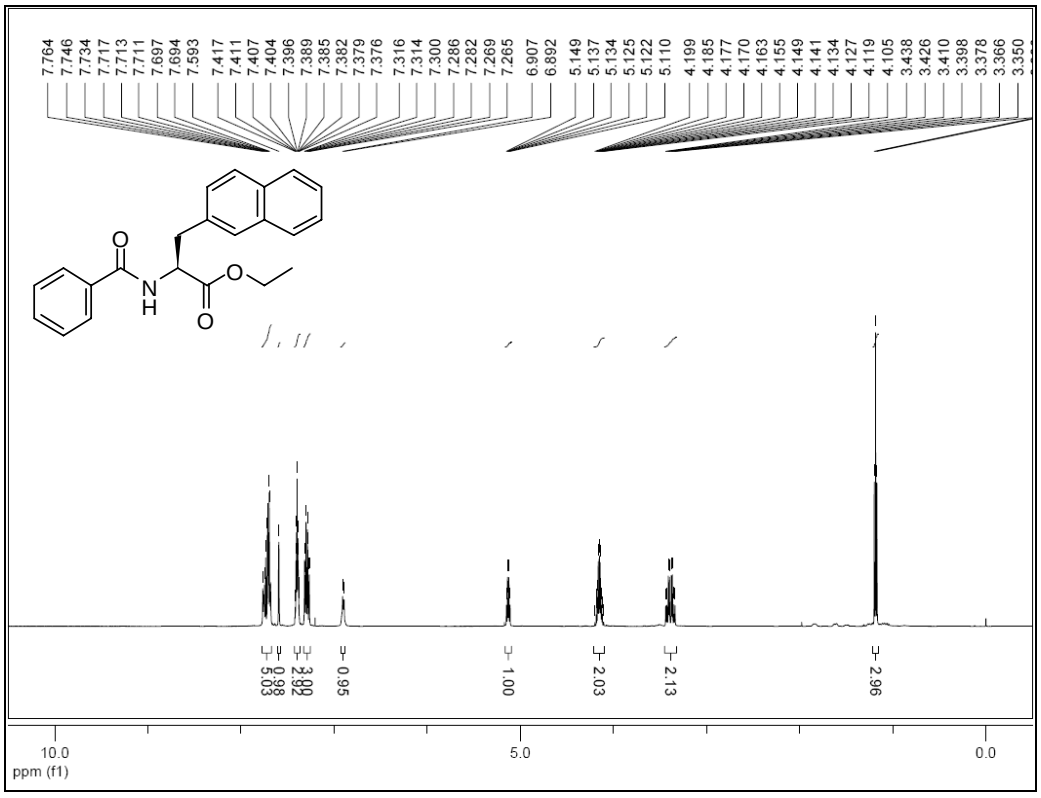


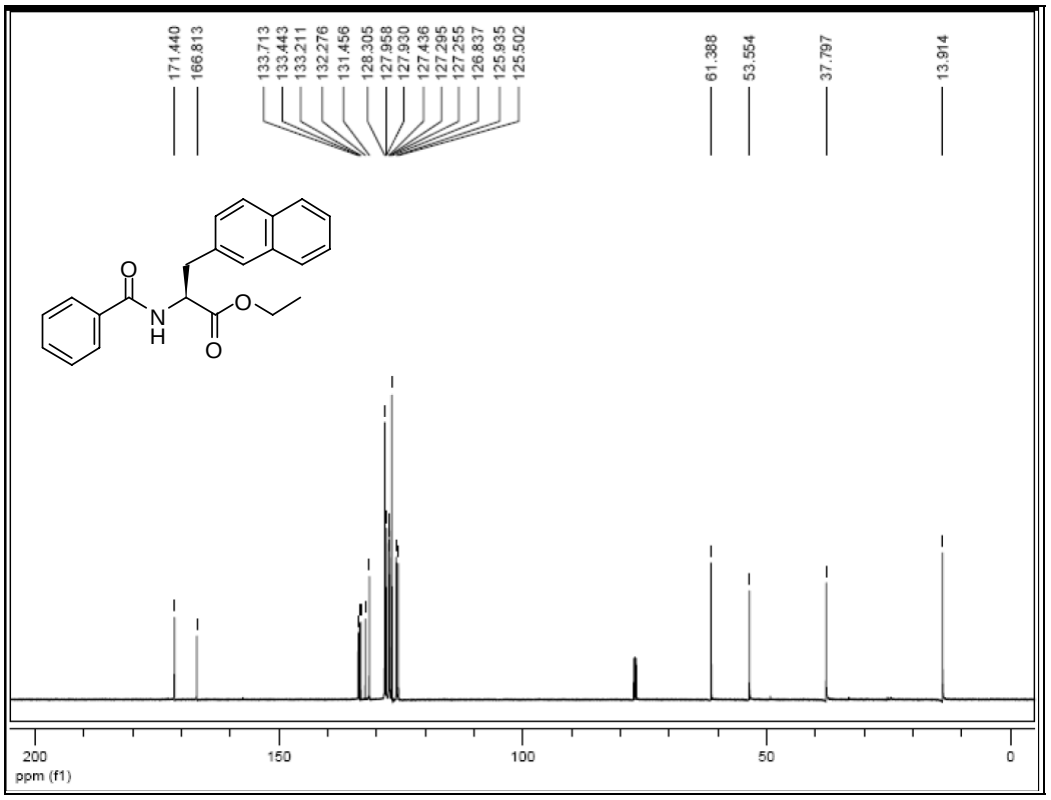












5. HPLC spectra of *N*-acylated-α-amino acid esters

Table 1. Entry 1 (racemic sample)

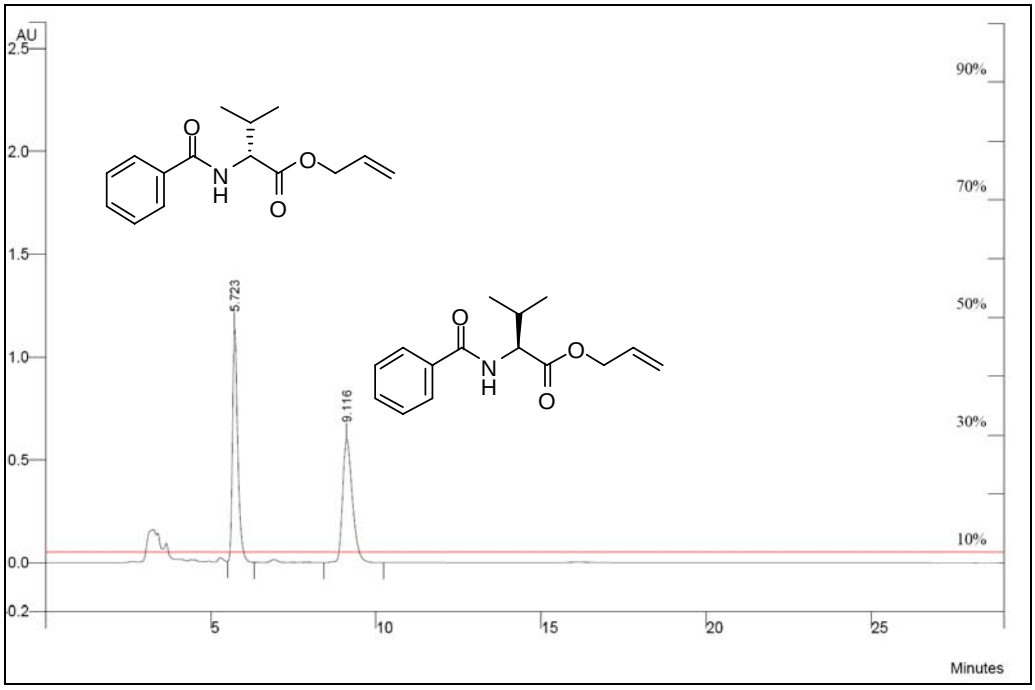
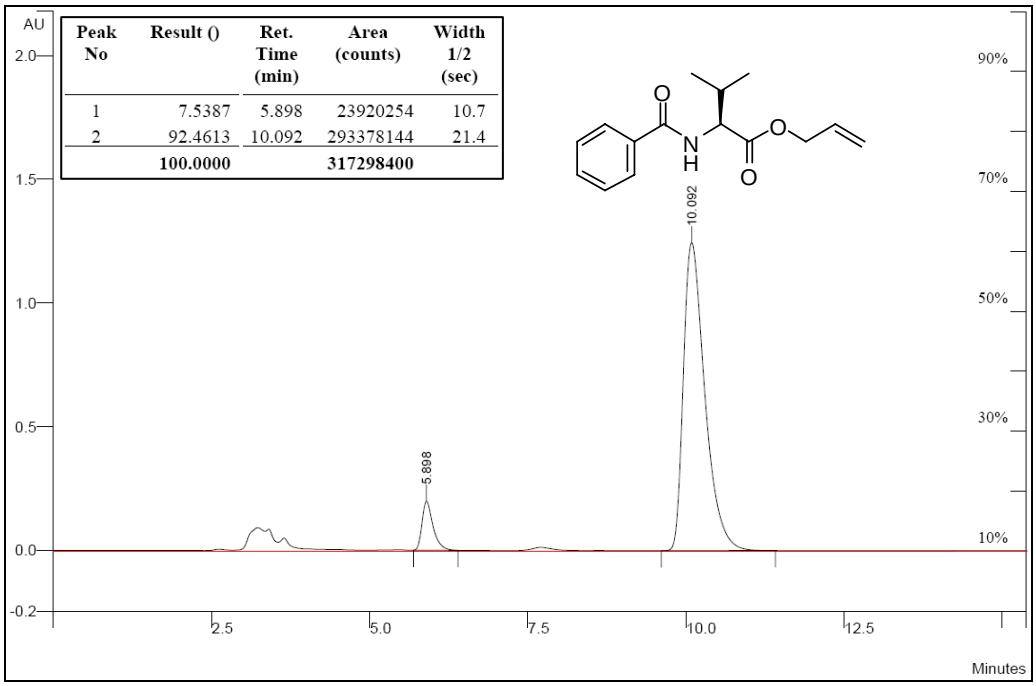
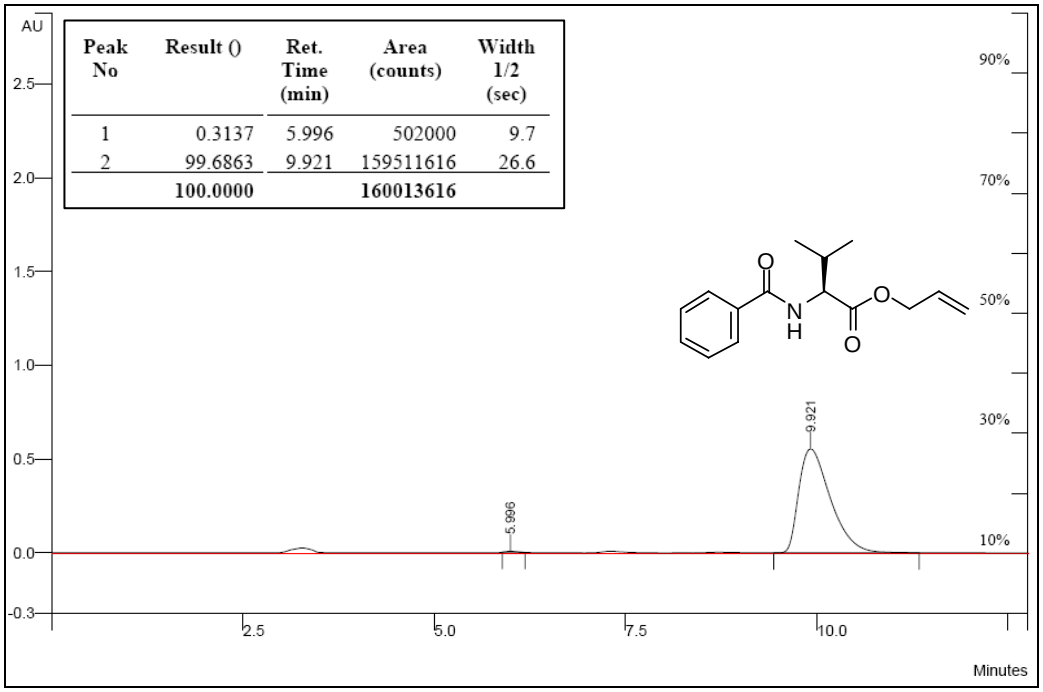


Table 1. Entry 1 (before recrystallization)



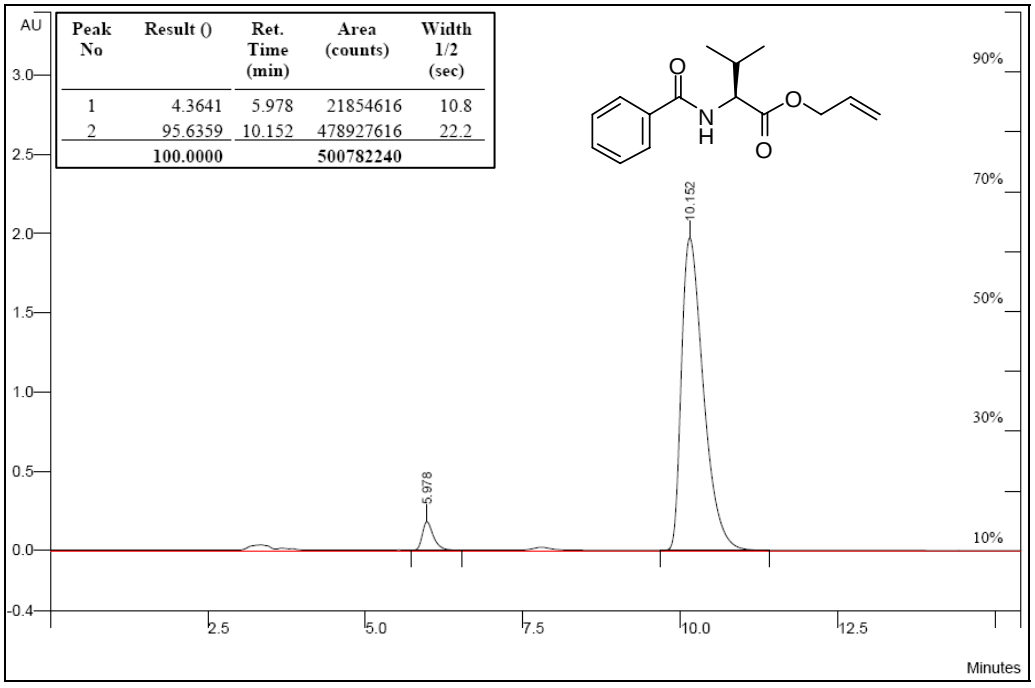
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	7.5387	5.898	23920254	10.7
2	92.4613	10.092	293378144	21.4
	100.0000		**317298400**	

Table 1. Entry 1 (after recrystallization)



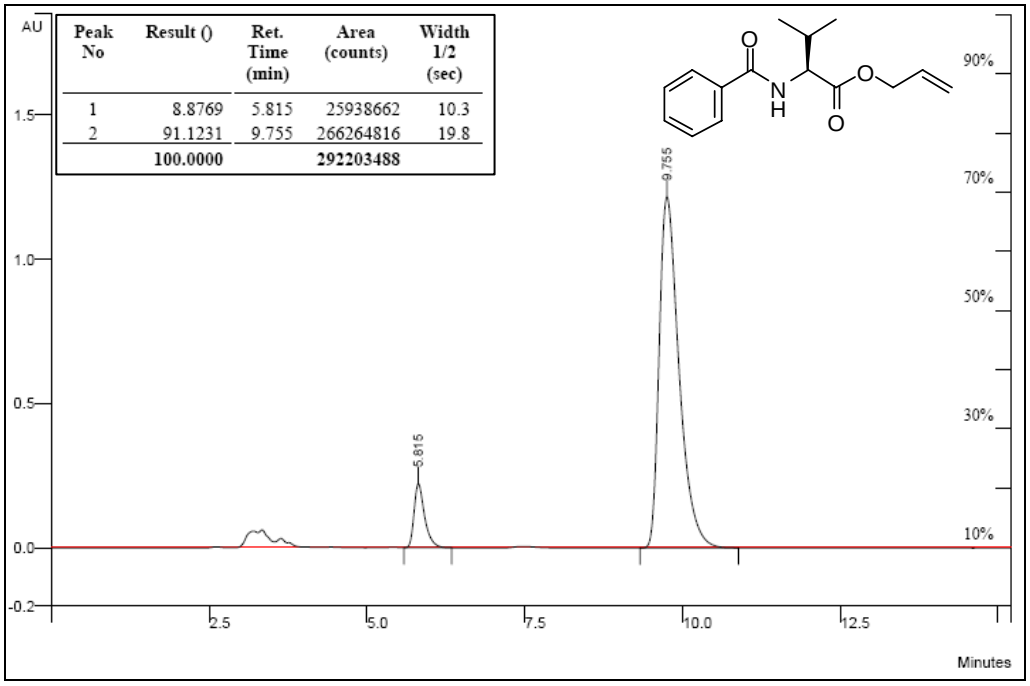
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	0.3137	5.996	502000	9.7
2	99.6863	9.921	159511616	26.6
	100.0000		**160013616**	

Table 1. Entry 2



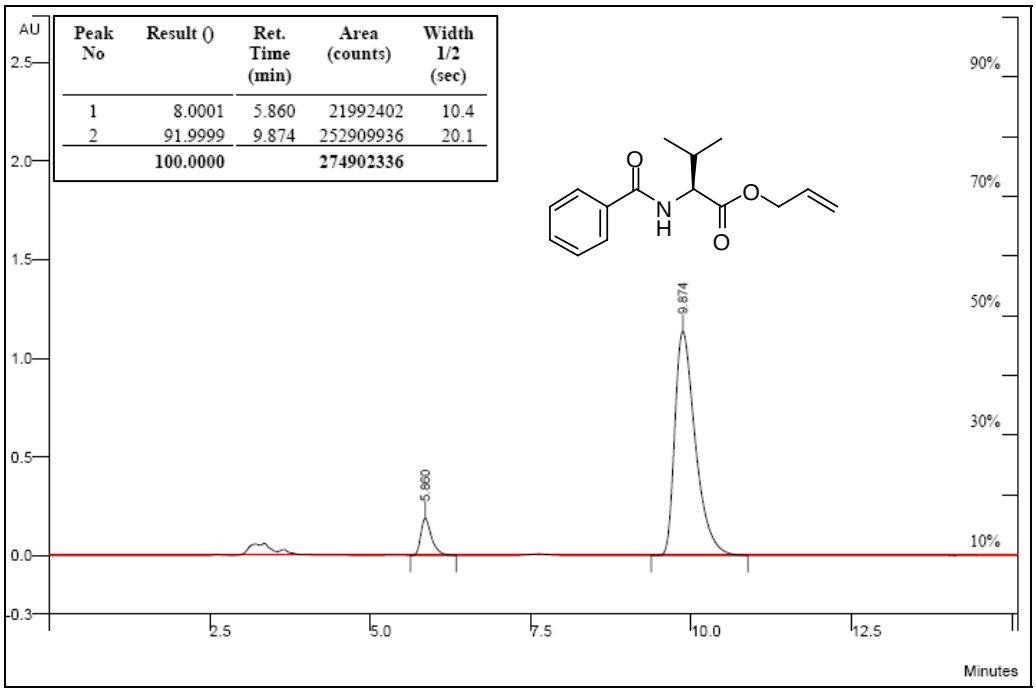
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	4.3641	5.978	21854616	10.8
2	95.6359	10.152	478927616	22.2
	100.0000		**500782240**	

Table 1. Entry 3



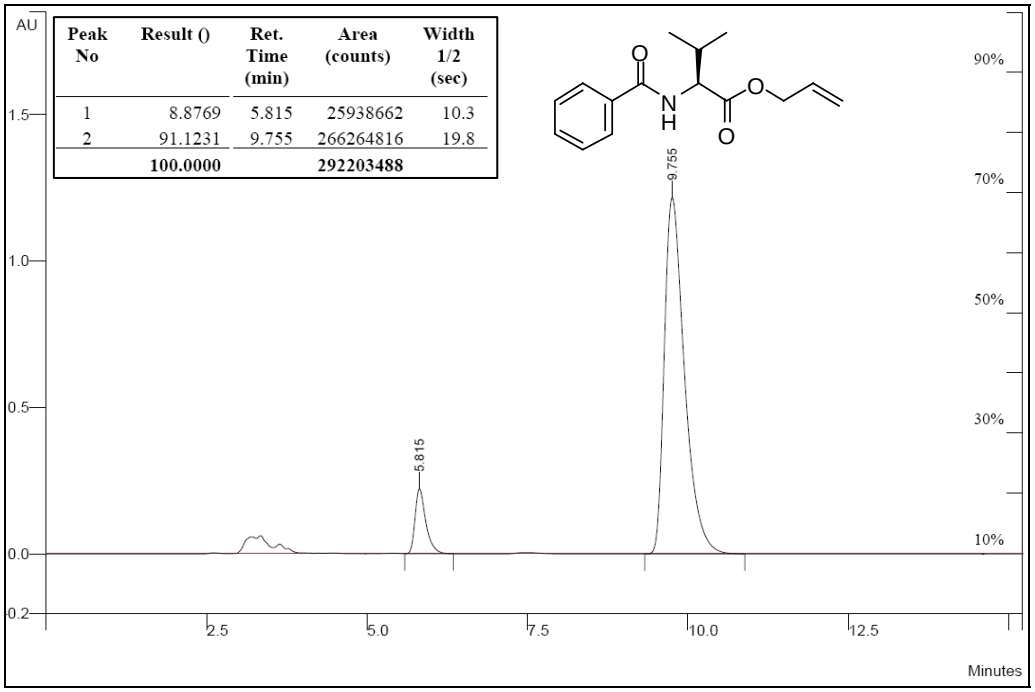
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	8.8769	5.815	25938662	10.3
2	91.1231	9.755	266264816	19.8
	100.0000		**292203488**	

Table 1. Entry 4



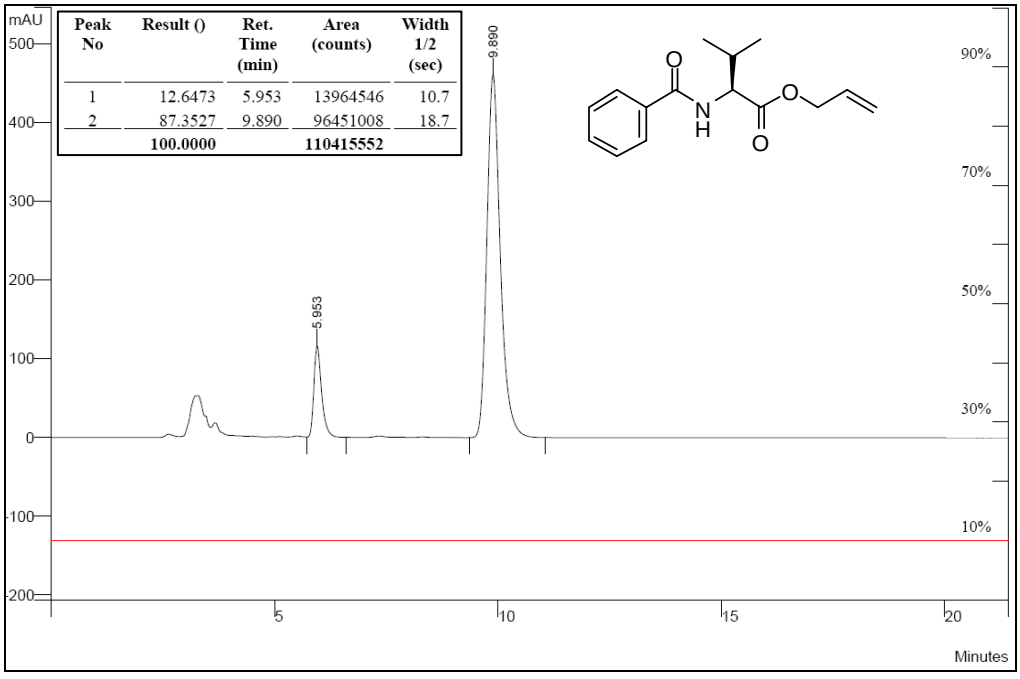
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	8.0001	5.860	21992402	10.4
2	91.9999	9.874	252909936	20.1
	100.0000		**274902336**	

Table 1. Entry 5



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	8.8769	5.815	25938662	10.3
2	91.1231	9.755	266264816	19.8
	100.0000		**292203488**	

Table 1. Entry 6



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	12.6473	5.953	13964546	10.7
2	87.3527	9.890	96451008	18.7
	100.0000		**110415552**	

Table 2. Entry 1 (racemic sample)

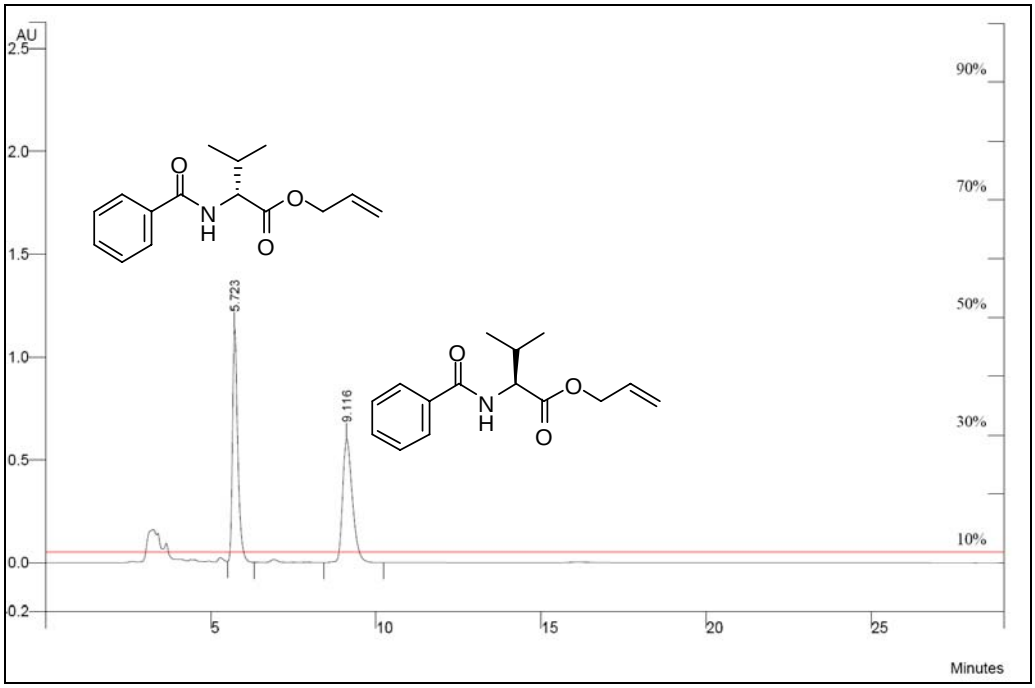


Table 2. Entry 1

Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	4.9205	5.668	14004628	10.9
2	95.0795	9.208	270612448	20.5
	100.0000		**284617088**	

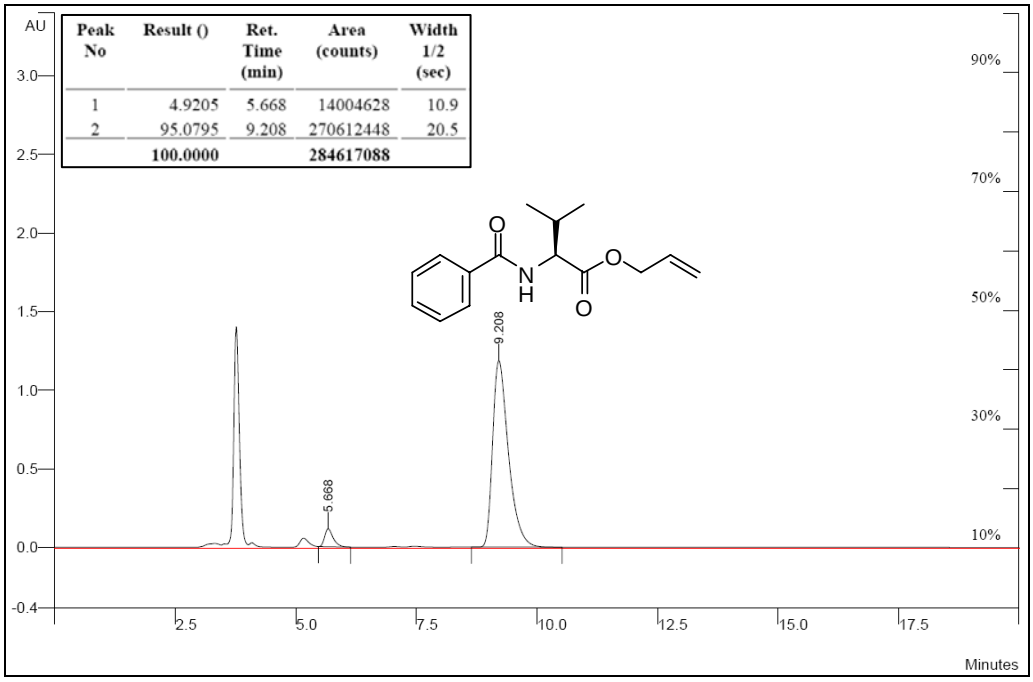
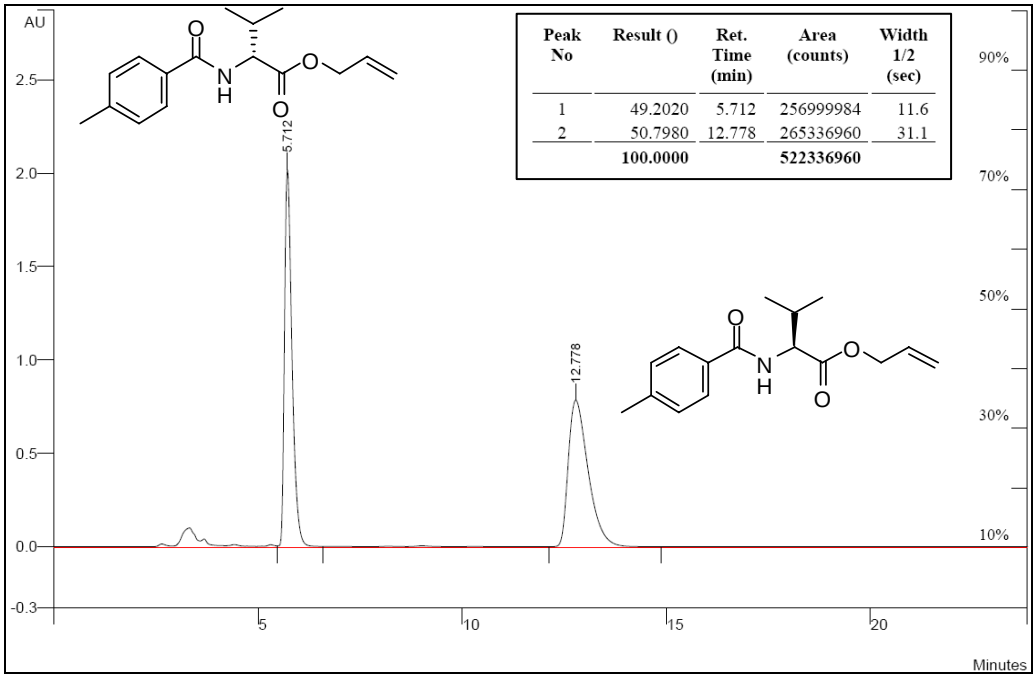
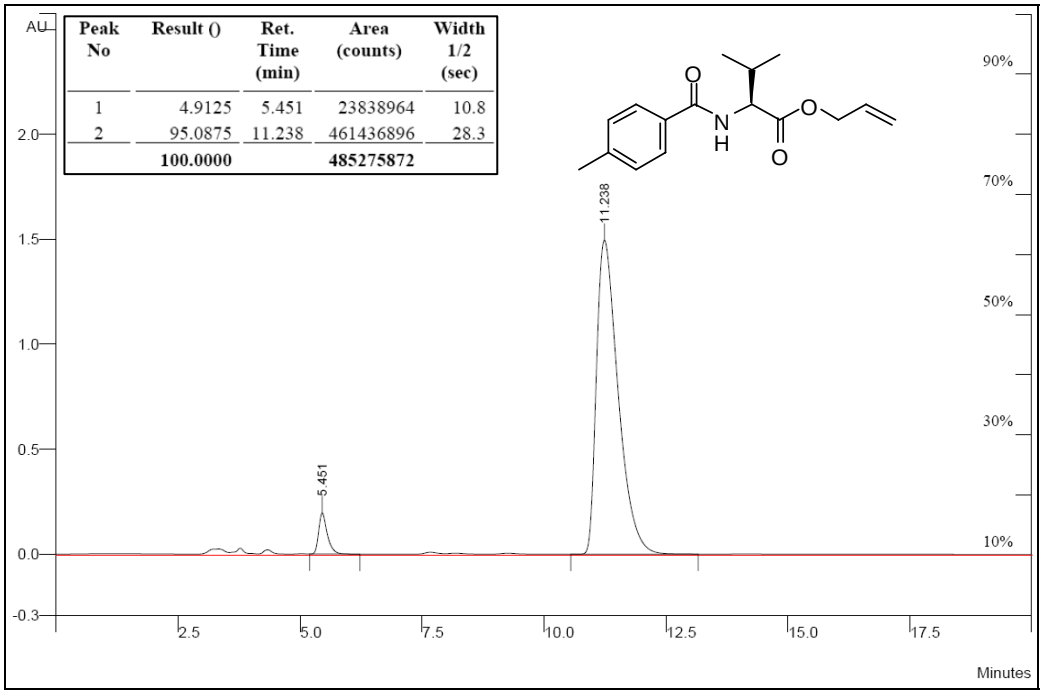


Table 2. Entry 2 (racemic sample)



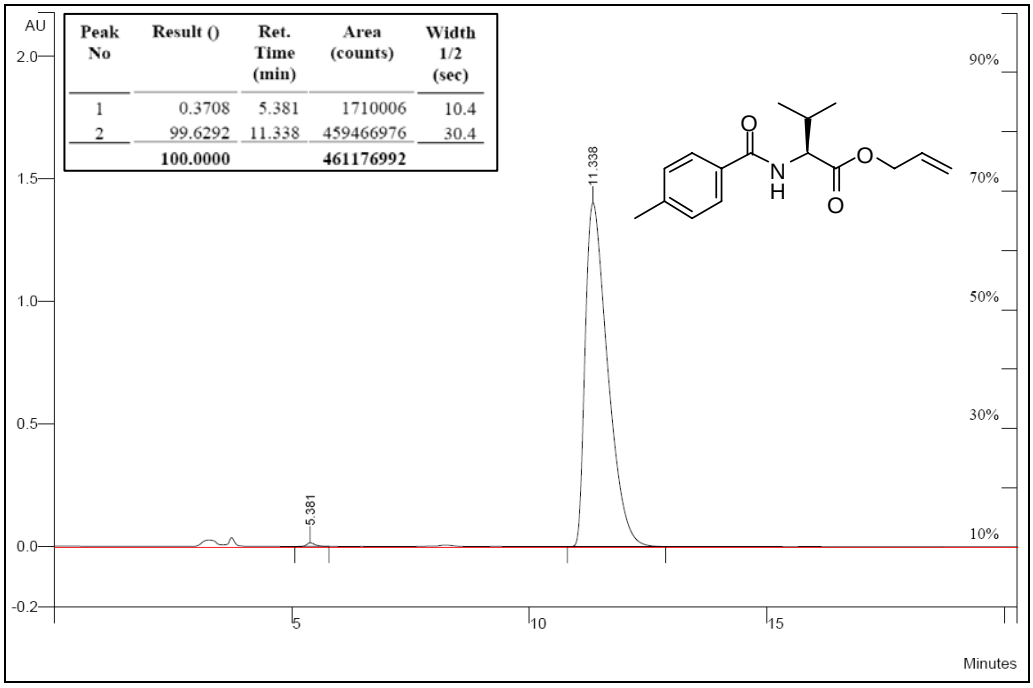
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.2020	5.712	256999984	11.6
2	50.7980	12.778	265336960	31.1
	100.0000		**522336960**	

Table 2. Entry 2 (before recrystallization)



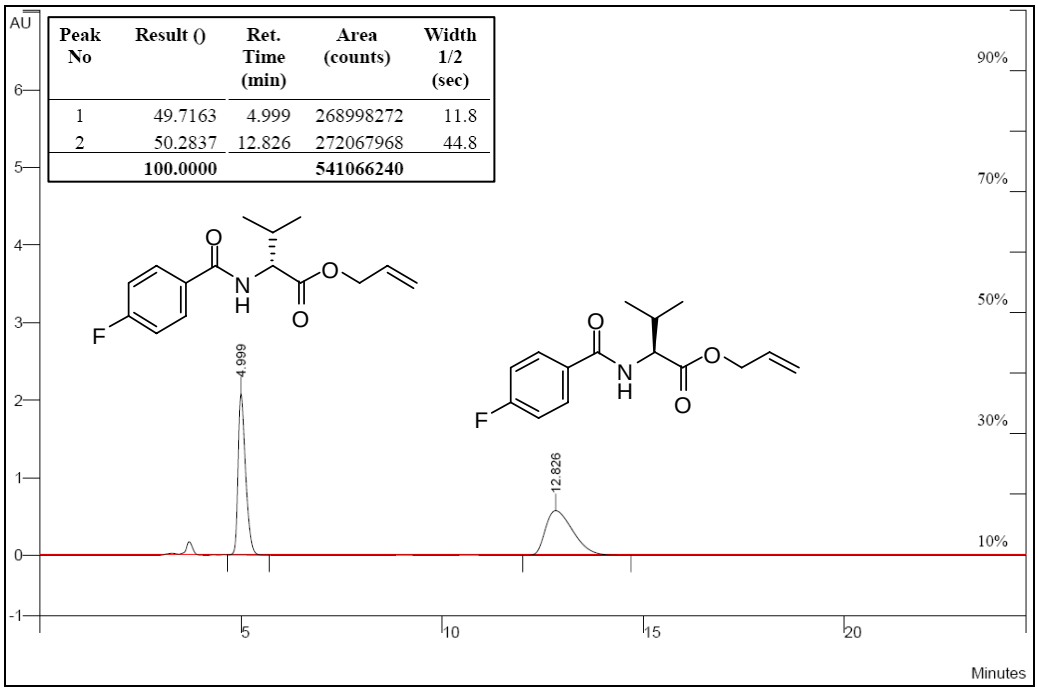
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	4.9125	5.451	23838964	10.8
2	95.0875	11.238	461436896	28.3
	100.0000		**485275872**	

Table 2. Entry 2 (after recrystallization)



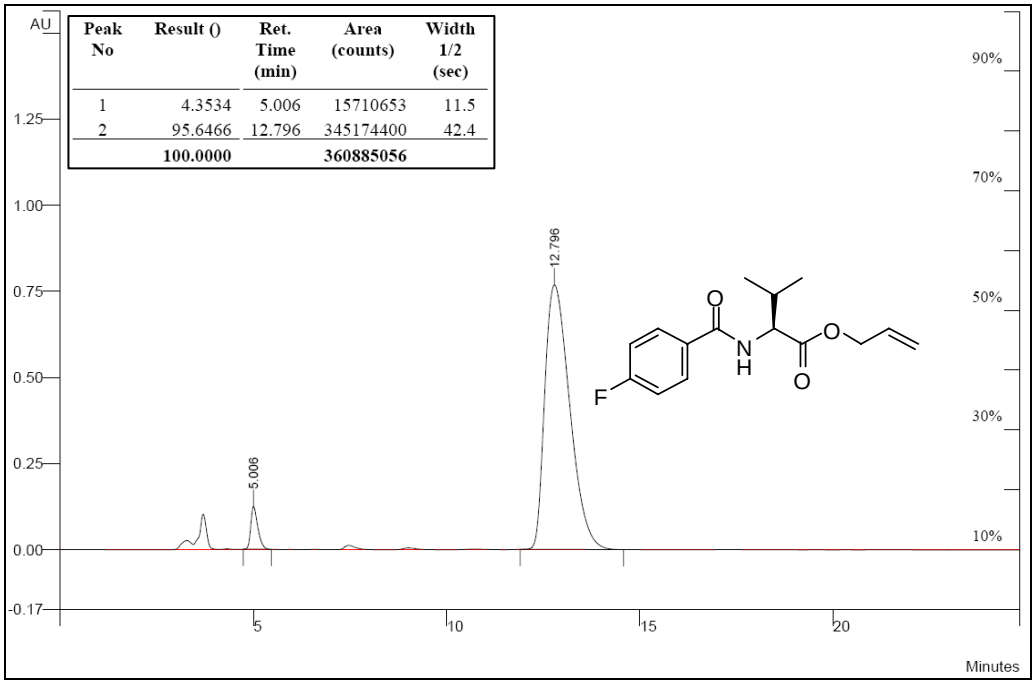
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	0.3708	5.381	1710006	10.4
2	99.6292	11.338	459466976	30.4
	100.0000		**461176992**	

Table 2. Entry 3 (racemic sample)



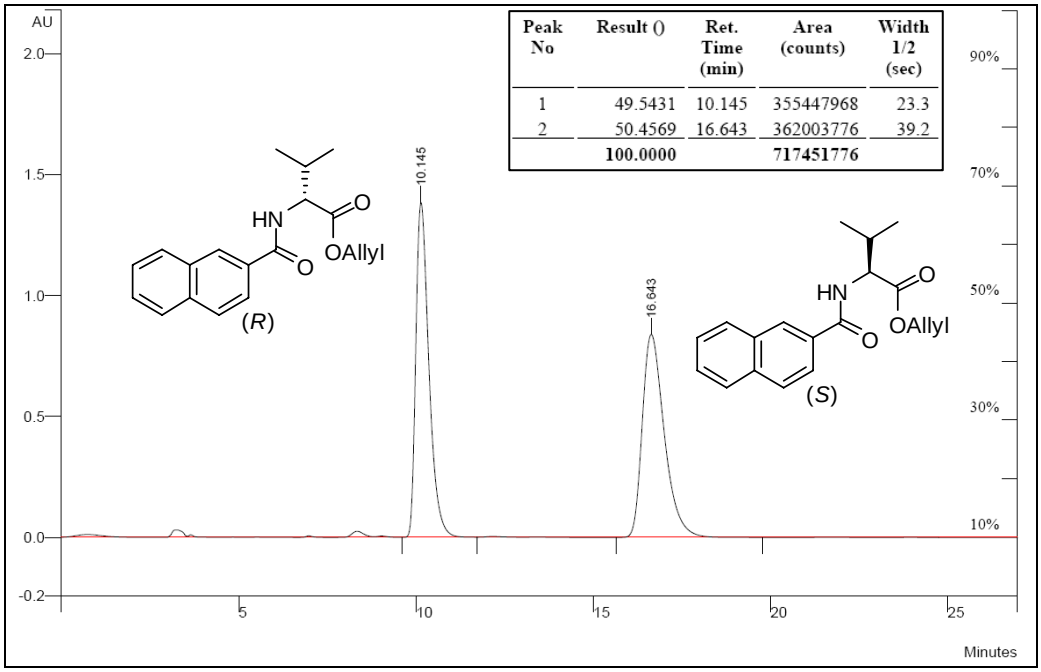
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.7163	4.999	268998272	11.8
2	50.2837	12.826	272067968	44.8
	100.0000		**541066240**	

Table 2. Entry 3



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	4.3534	5.006	15710653	11.5
2	95.6466	12.796	345174400	42.4
	100.0000		**360885056**	

Table 2. Entry 4 (racemic sample)



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.5431	10.145	355447968	23.3
2	50.4569	16.643	362003776	39.2
	100.0000		**717451776**	

Table 2. Entry 4 (before recrystallization)

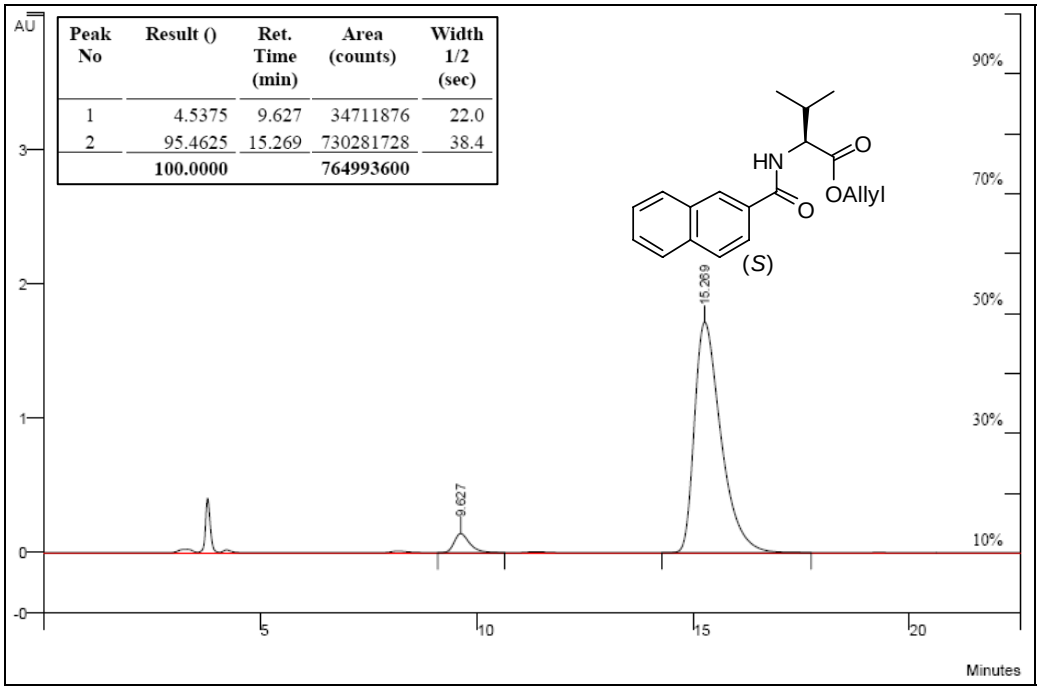


Table 2. Entry 4 (after recrystallization)

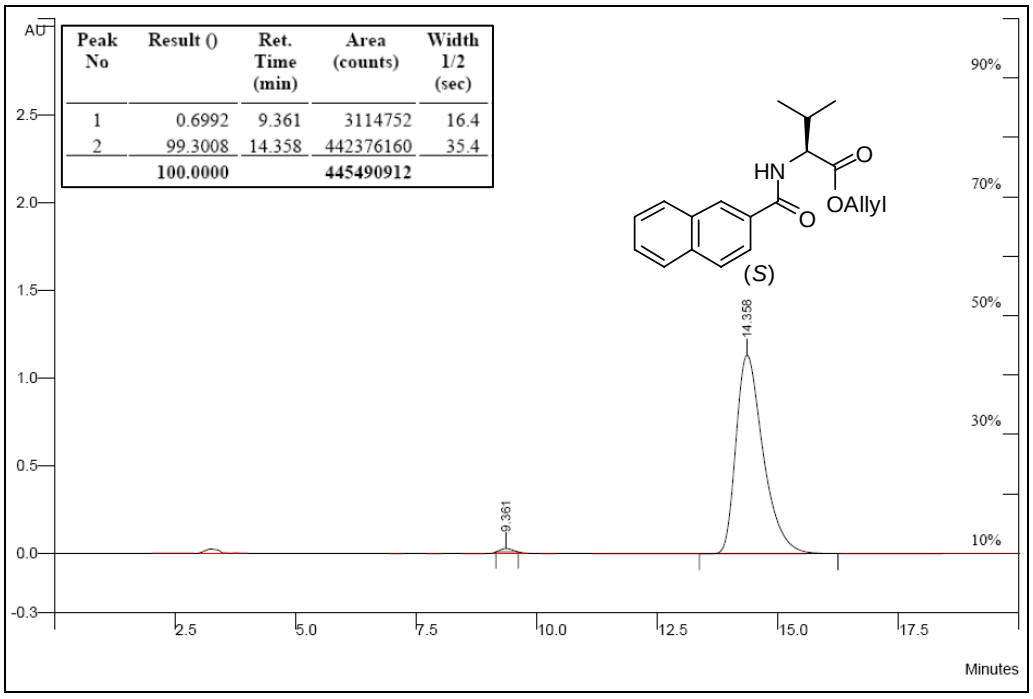
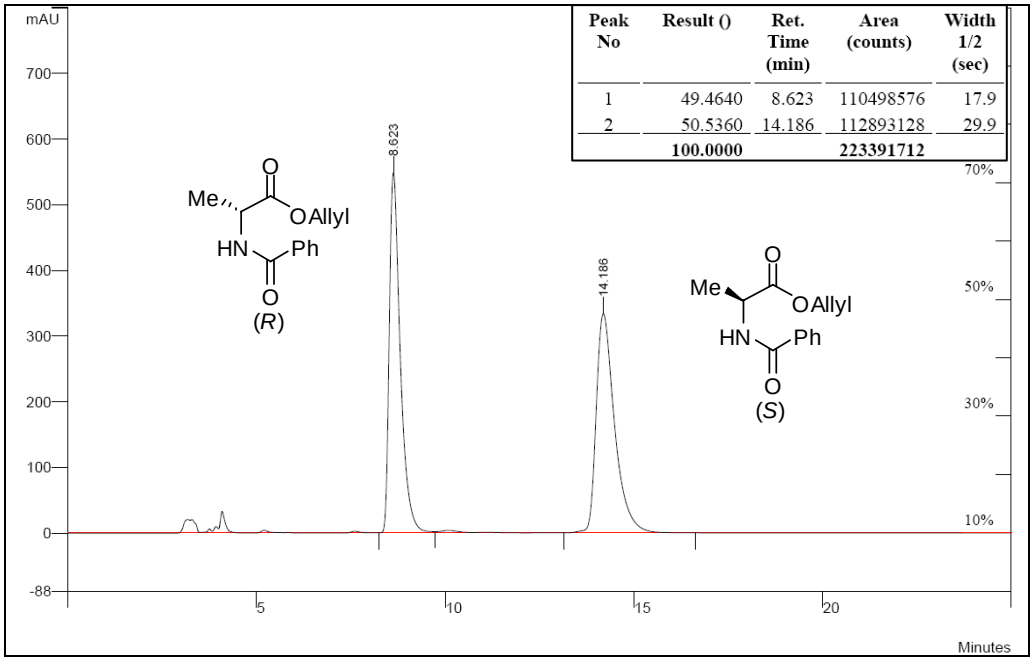
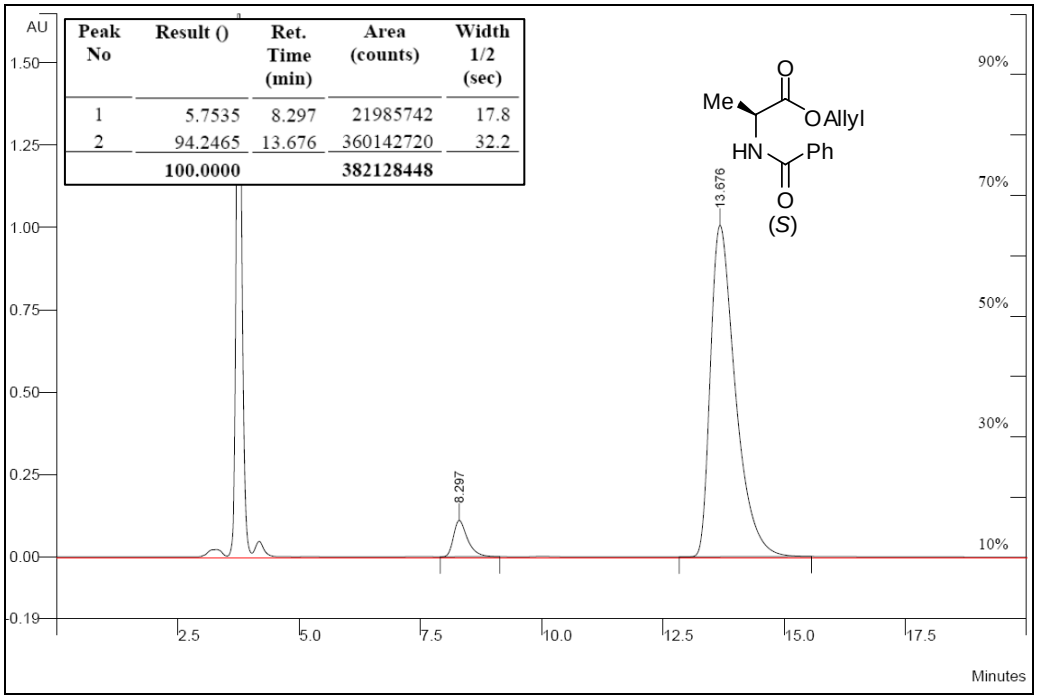


Table 2. Entry 5 (racemic sample)



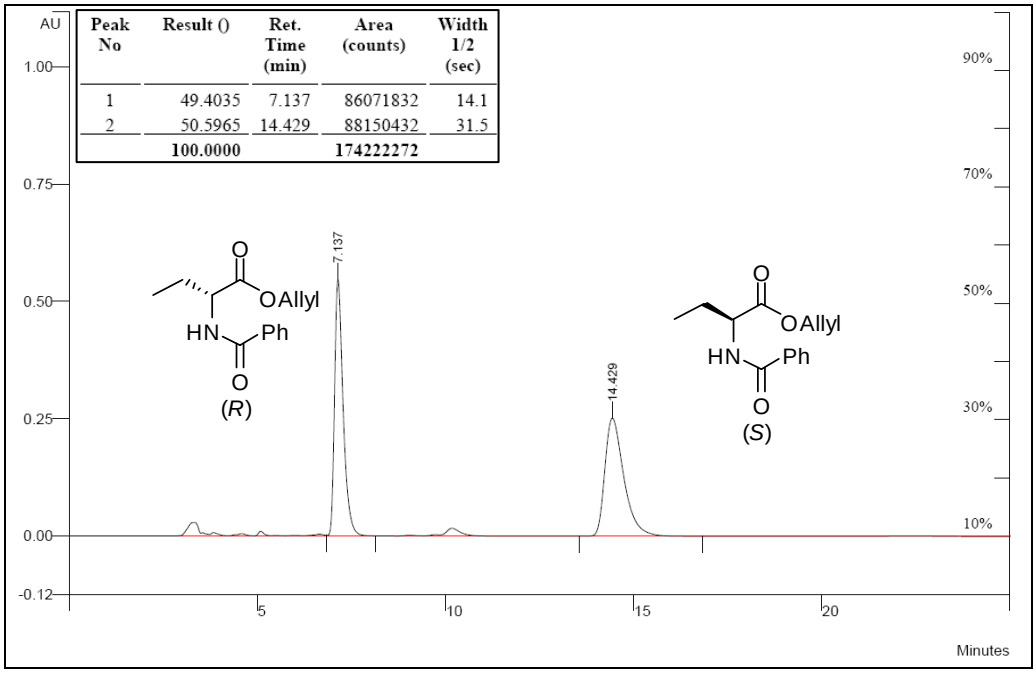
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.4640	8.623	110498576	17.9
2	50.5360	14.186	112893128	29.9
	100.0000		**223391712**	

Table 2. Entry 5



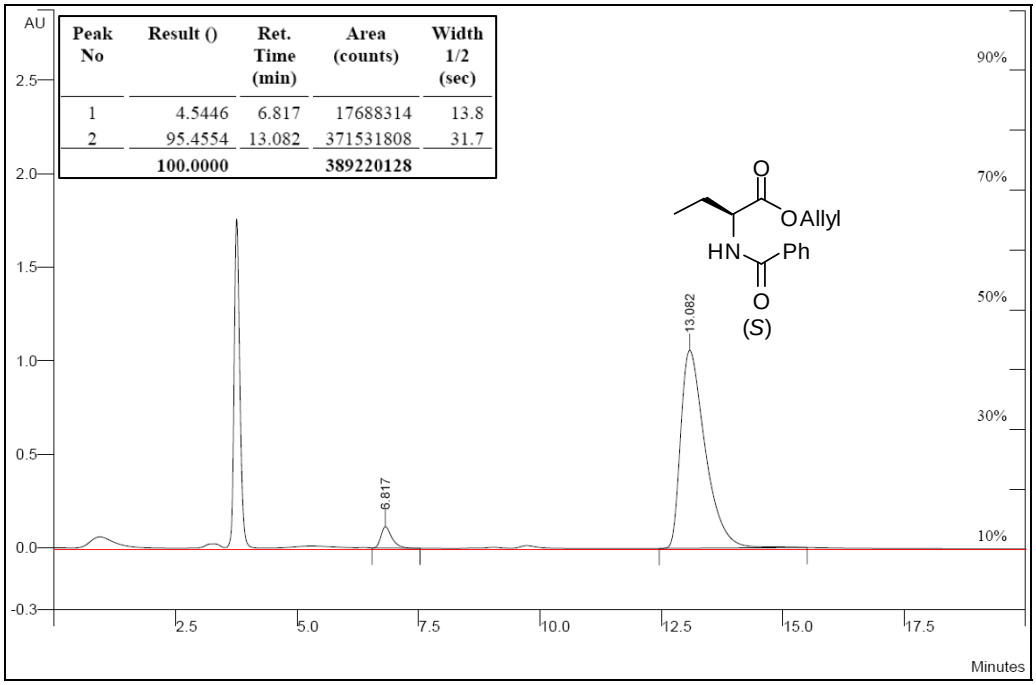
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	5.7535	8.297	21985742	17.8
2	94.2465	13.676	360142720	32.2
	100.0000		**382128448**	

Table 2. Entry 6 (racemic sample)



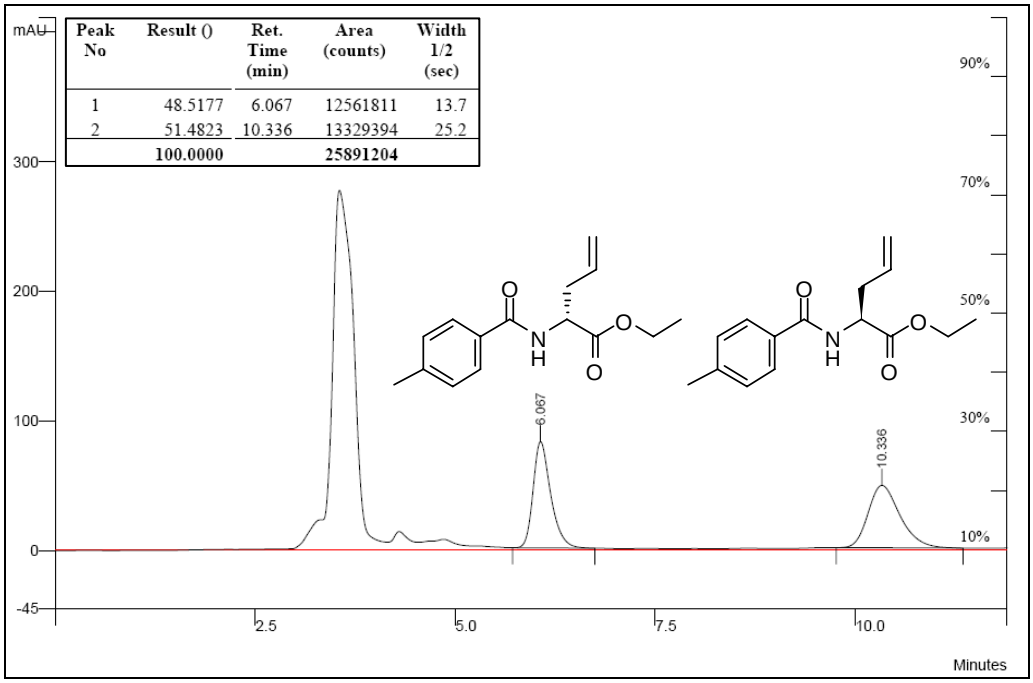
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.4035	7.137	86071832	14.1
2	50.5965	14.429	88150432	31.5
	100.0000		**174222272**	

Table 2. Entry 6



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	4.5446	6.817	17688314	13.8
2	95.4554	13.082	371531808	31.7
	100.0000		**389220128**	

Table 2. Entry 7 (racemic sample)



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	48.5177	6.067	12561811	13.7
2	51.4823	10.336	13329394	25.2
	100.0000		**25891204**	

Table 2. Entry 7 (before recrystallization)

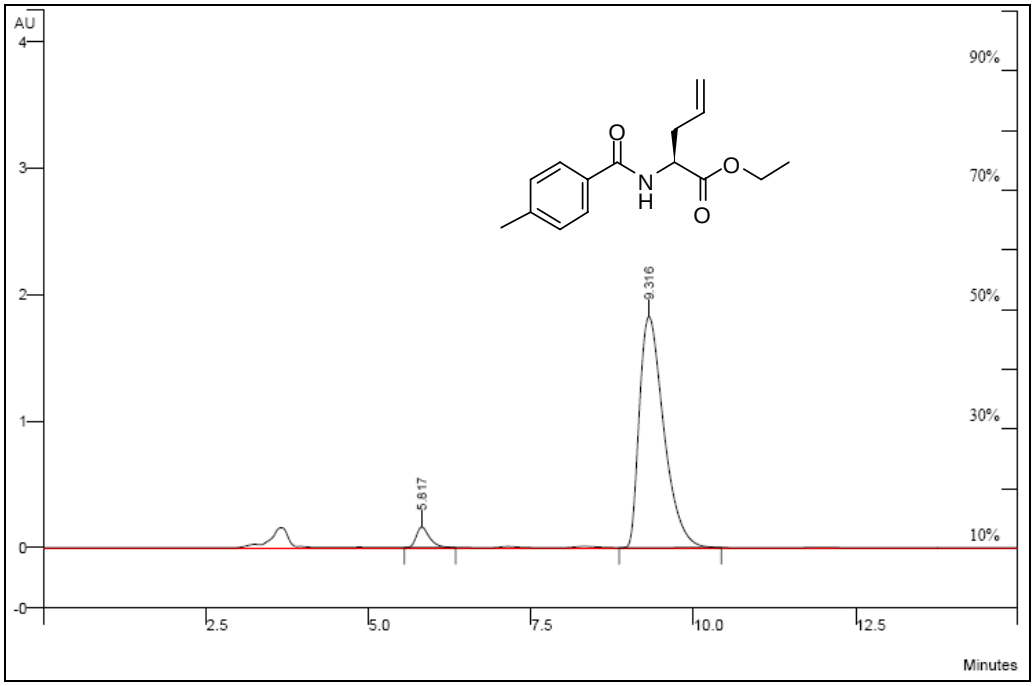
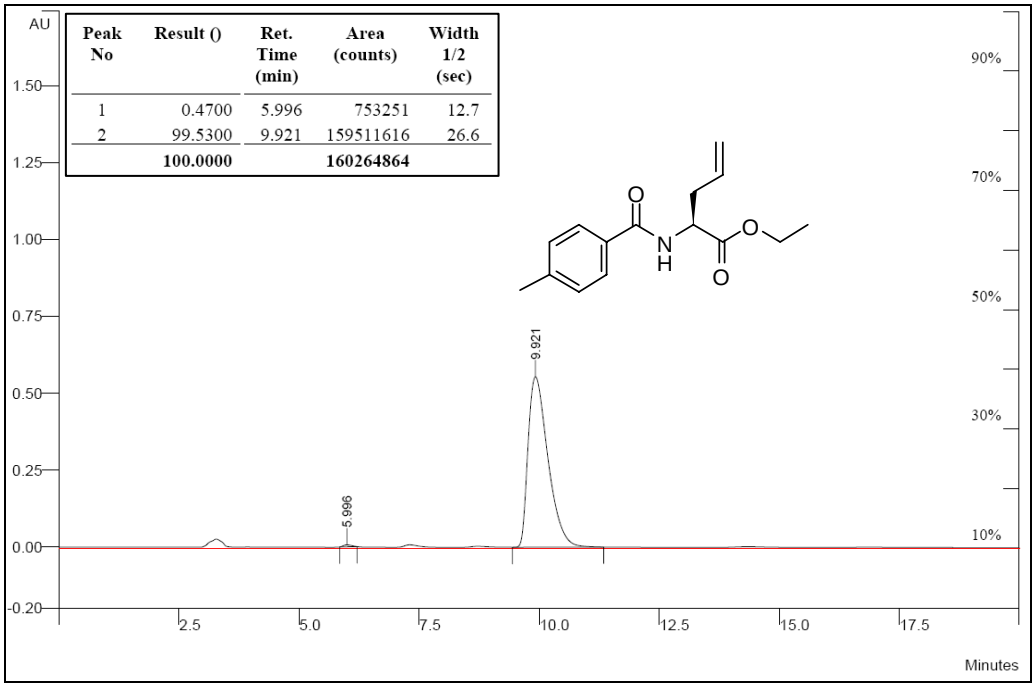
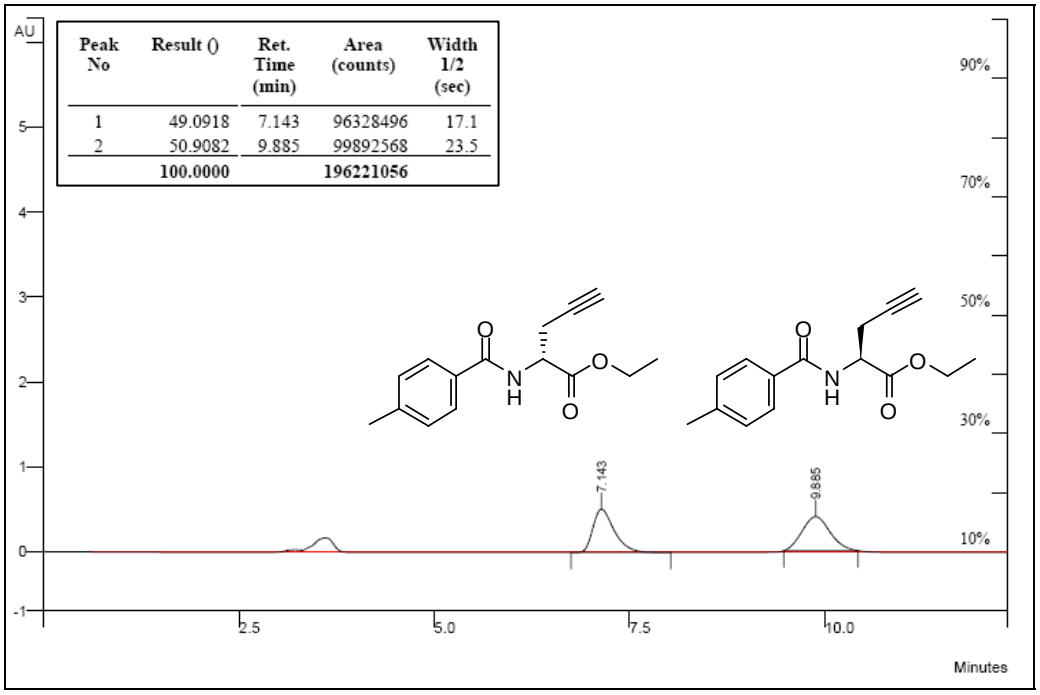


Table 2. Entry 7 (after recrystallization)



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	0.4700	5.996	753251	12.7
2	99.5300	9.921	159511616	26.6
	100.0000		**160264864**	

Table 2. Entry 8 (racemic sample)



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	49.0918	7.143	96328496	17.1
2	50.9082	9.885	99892568	23.5
	100.0000		**196221056**	

Table 2. Entry 8 (before recrystallization)

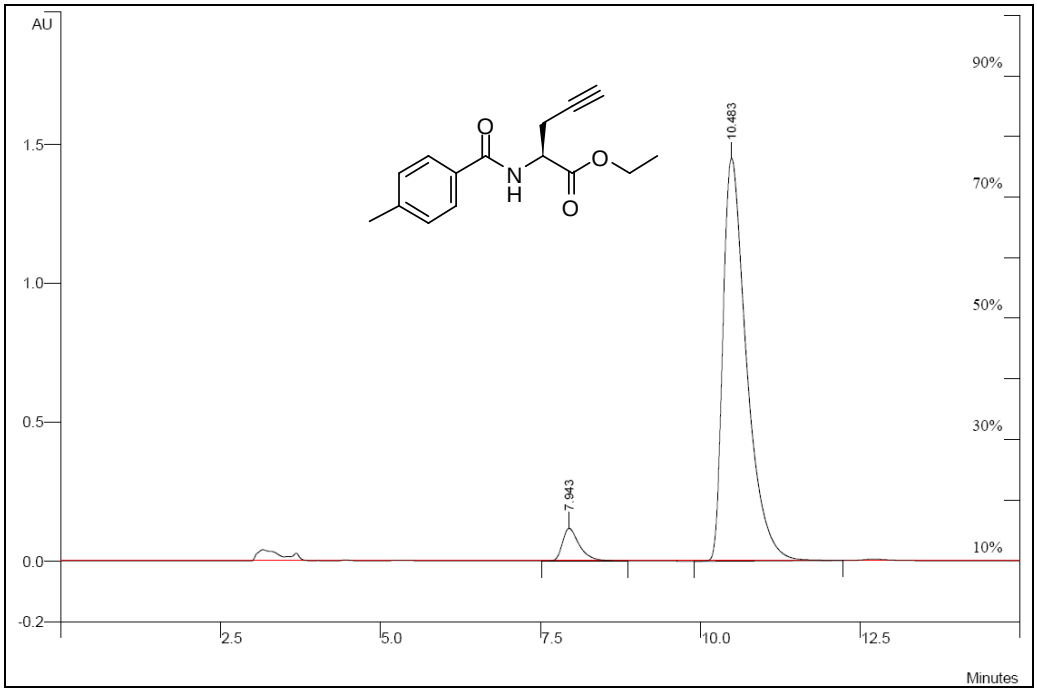
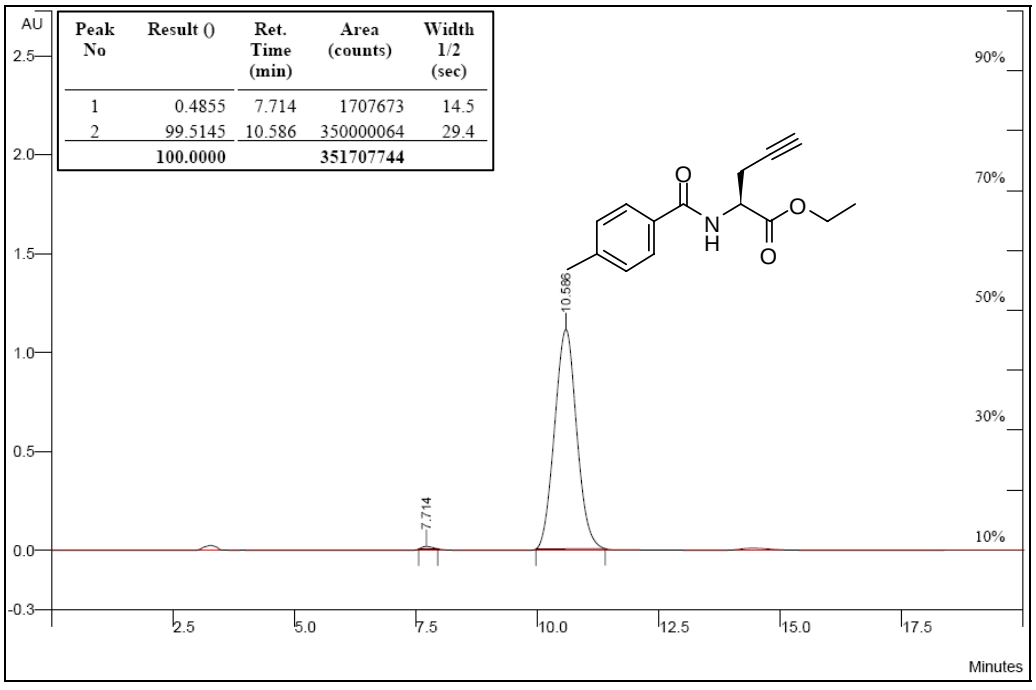


Table 2. Entry 8 (after recrystallization)



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	0.4855	7.714	1707673	14.5
2	99.5145	10.586	350000064	29.4
	100.0000		**351707744**	

Table 2. Entry 9 (racemic sample)

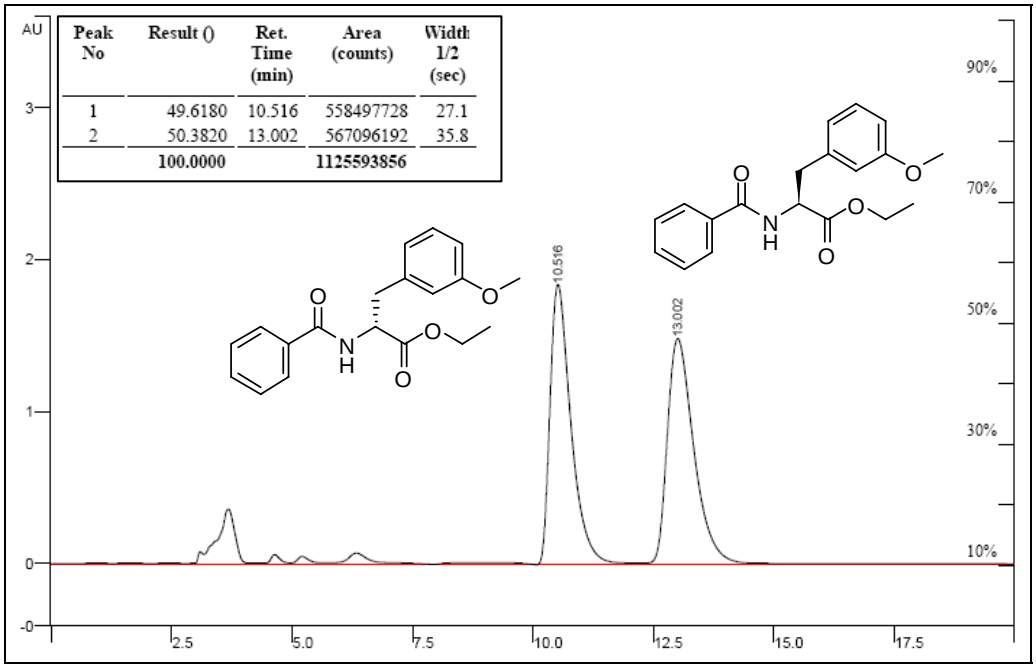


Table 2. Entry 9 (before recrystallization)

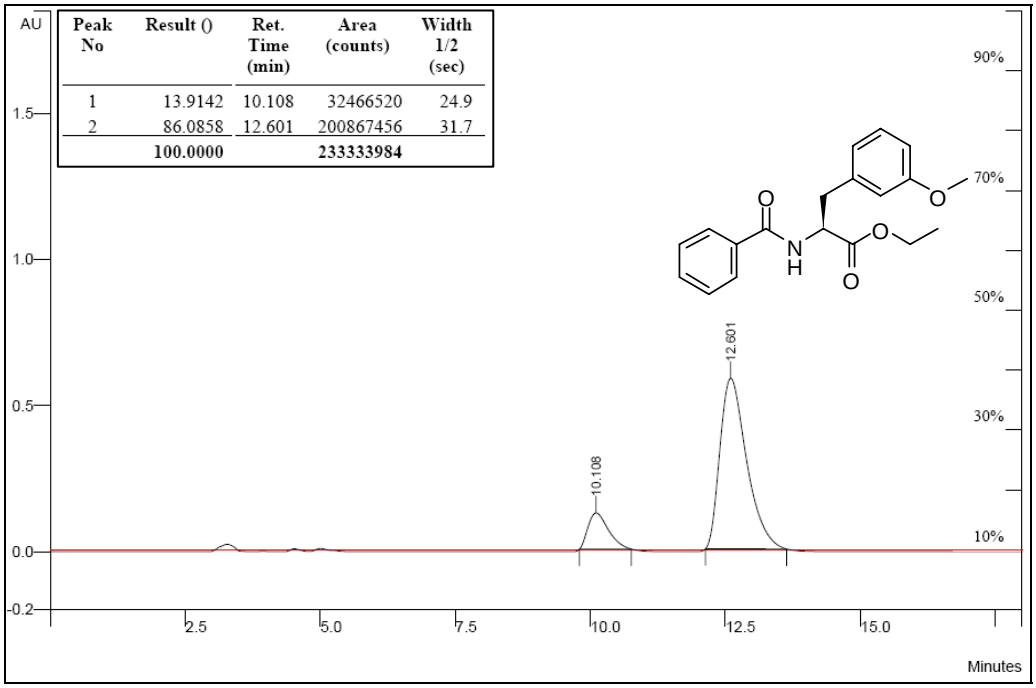


Table 2. Entry 9 (after recrystallization)

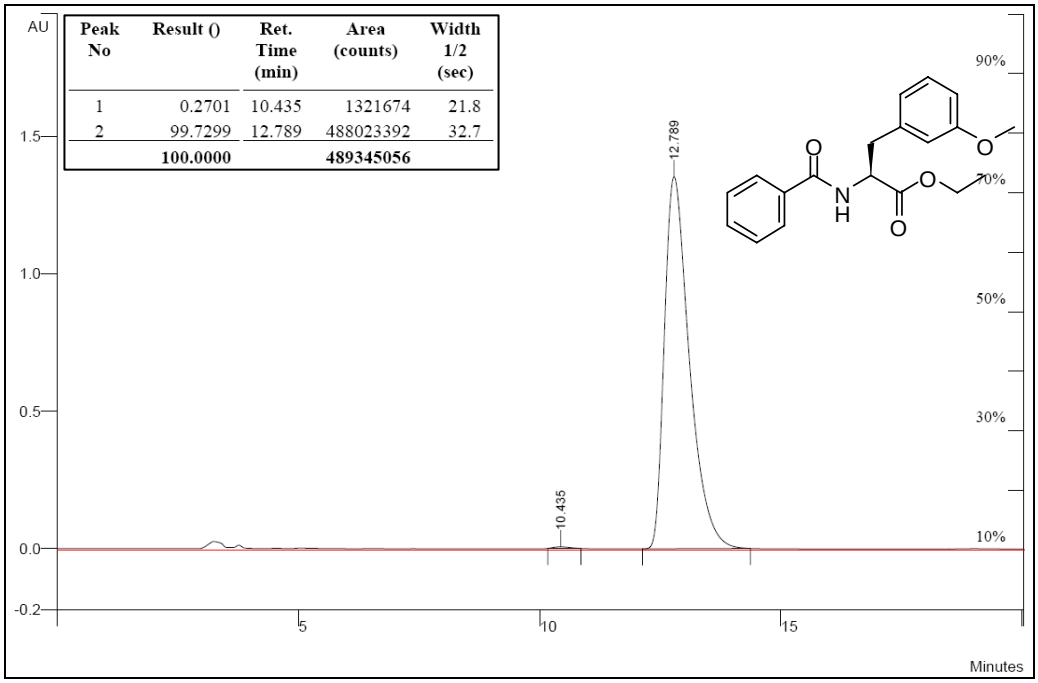


Table 2. Entry 10 (racemic sample)

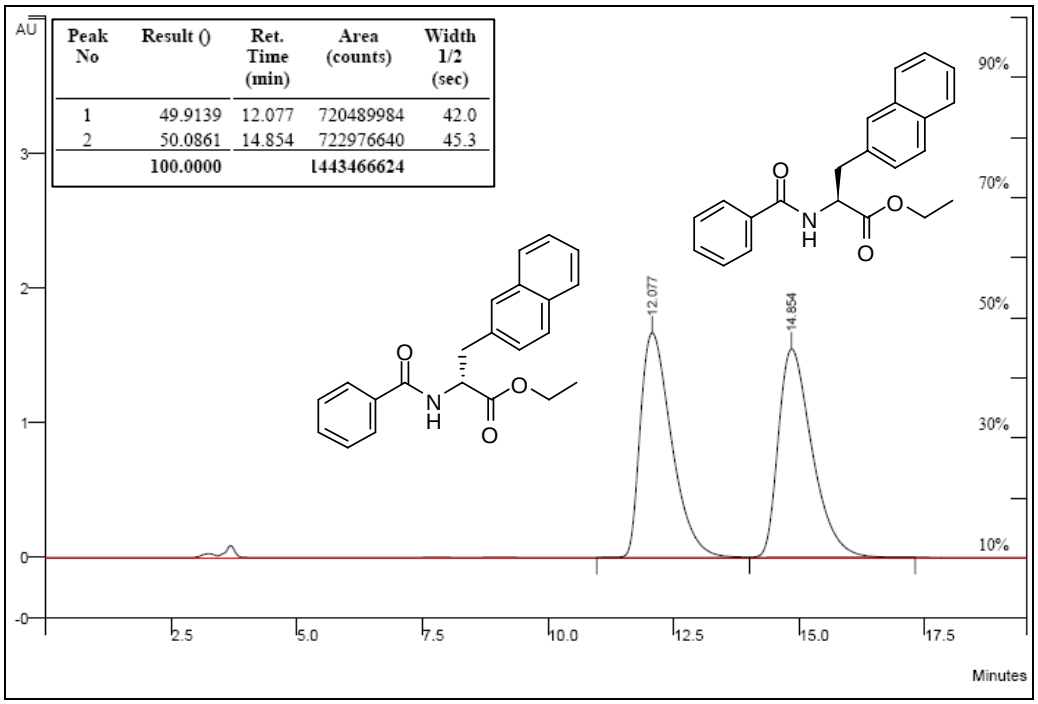
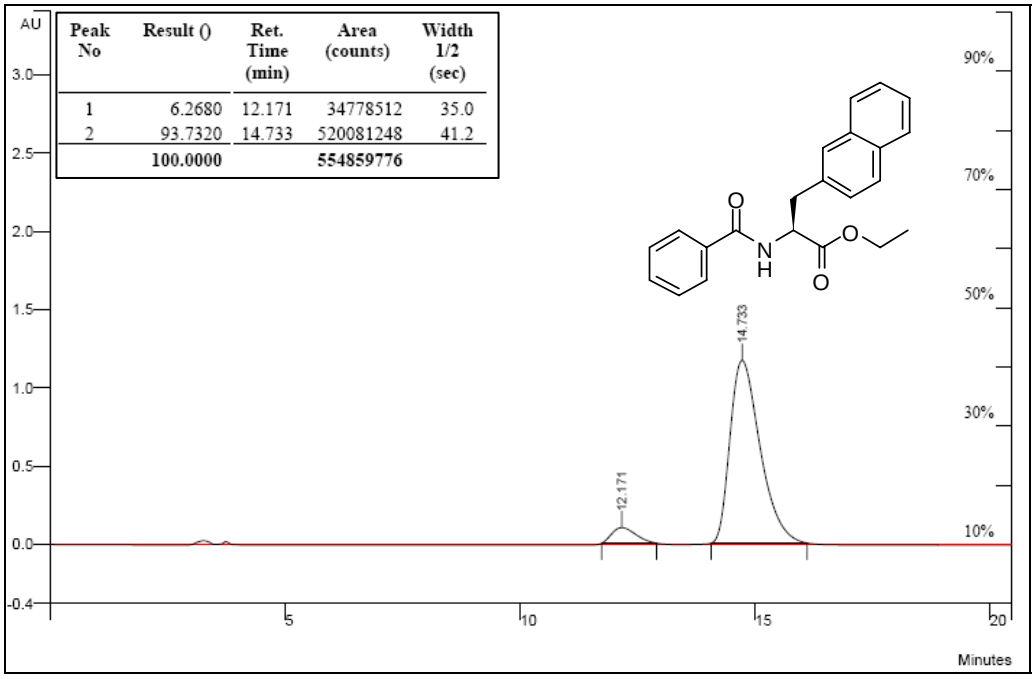
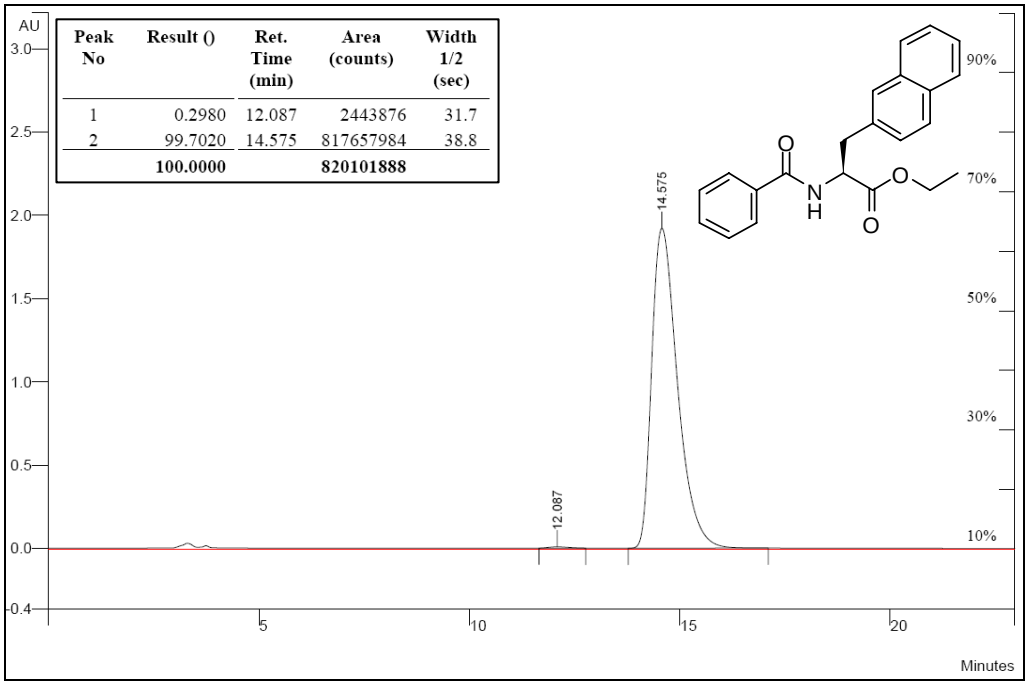


Table 2. Entry 10 (before recrystallization)



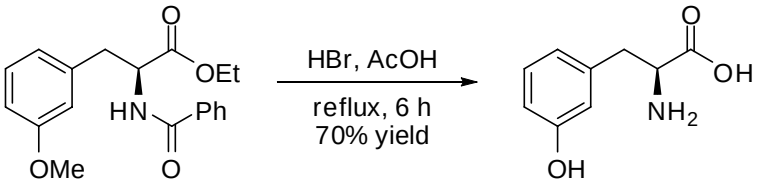
Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	6.2680	12.171	34778512	35.0
2	93.7320	14.733	520081248	41.2
	100.0000		**554859776**	

Table 2. Entry 10 (after recrystallization)



Peak No	Result ()	Ret. Time (min)	Area (counts)	Width 1/2 (sec)
1	0.2980	12.087	2443876	31.7
2	99.7020	14.575	817657984	38.8
	100.0000		**820101888**	

6. Multigram-scale synthesis of L-*m*-tyrosine by hydrolysis of 2i



2i
>99% ee
(4.37 g scale)

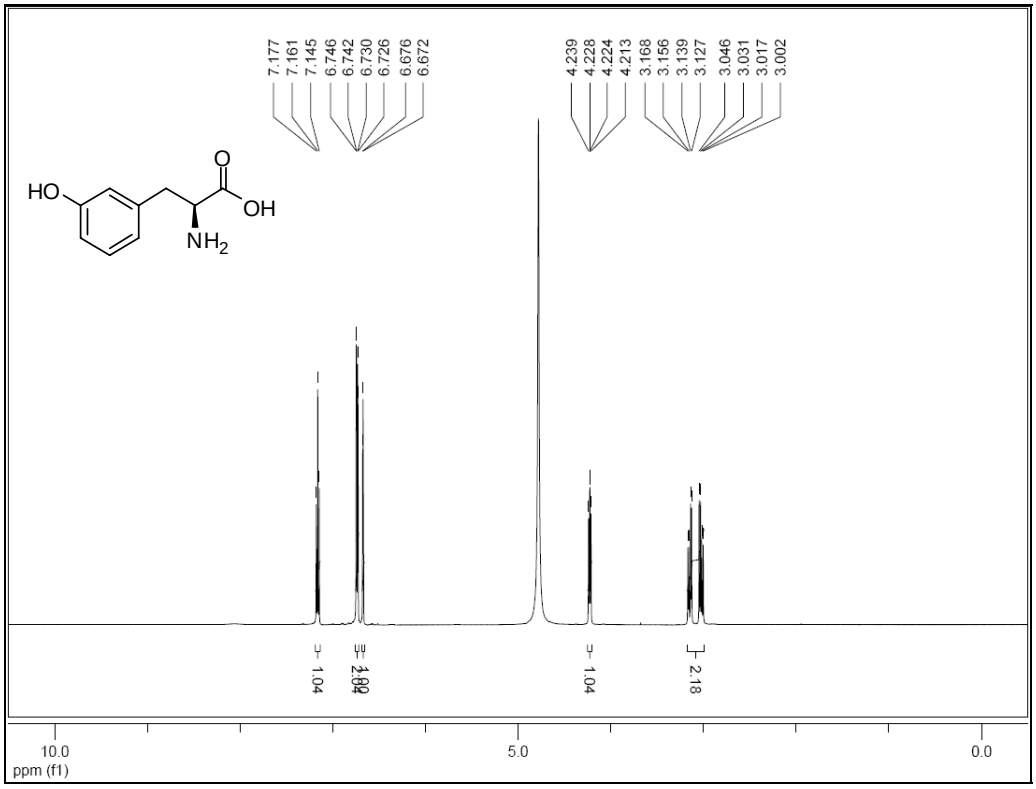
L-*m*-tyrosine
(99.1% ee)

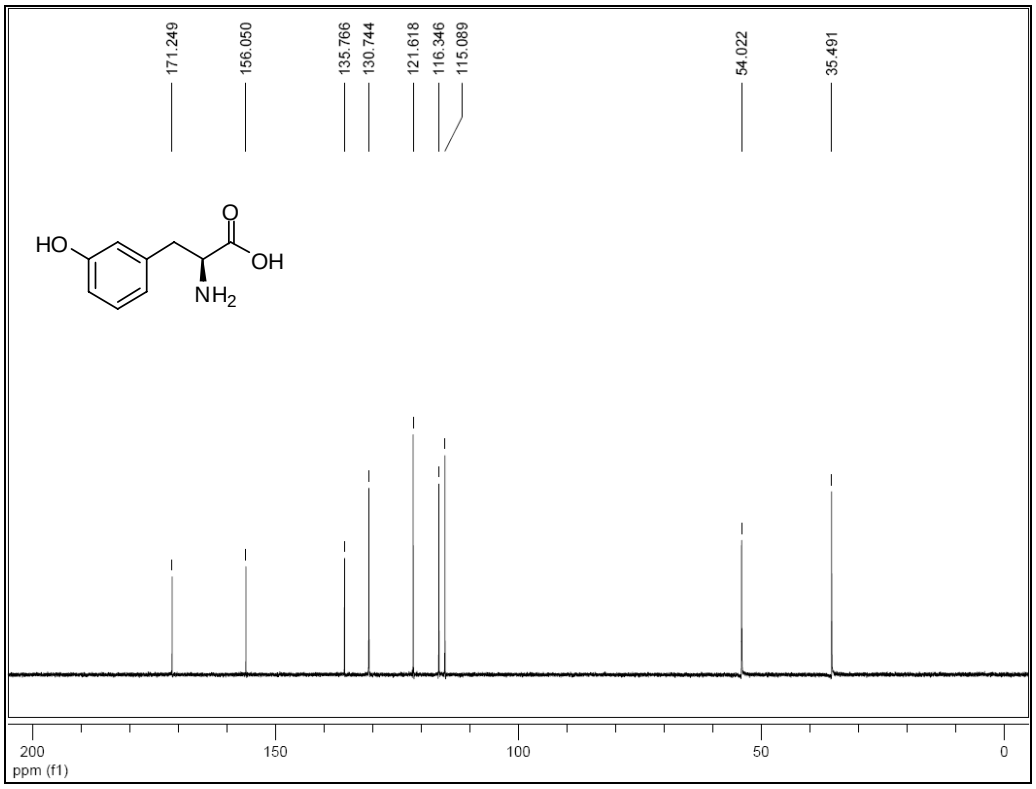
A suspension of **2i** (4.34 g, 13.35 mmol) in mixture of HBr (8 mL) and AcOH (8 mL) was refluxed for 6 h, followed by complete evaporation of the liquid. The residue was redissolved in water (12 mL), and extracted with CH_2Cl_2 (12 mL X 2). The pH of the aqueous layer was then adjusted to 5.5-6 by adding 4 N NaOH solution. The precipitate formed was filtered and dried in vacuo to yield L-*m*-tyrosine (1.7 g, 70%) as colorless crystals.

^{1}H NMR (500 MHz, D_2O, DCl) δ 3.02 (dd, J = 14.5 Hz and 7.5 Hz, $1H_A$ of AB-spin system), 3.15 (dd, J = 14.5 Hz and 7.5 Hz, $1H_B$ of AB-spin system) 3.79 (dd, J = 5.5 and 7.5 Hz, 1H), 6.67-6.77 (m, 3H), 7.14-7.18 (m, 1H); ^{13}C NMR (125 MHz, D_2O, DCl) δ 35.49, 54.02, 115.09, 116.35, 121.62, 130.74, 135.77, 156.05, 171.25.

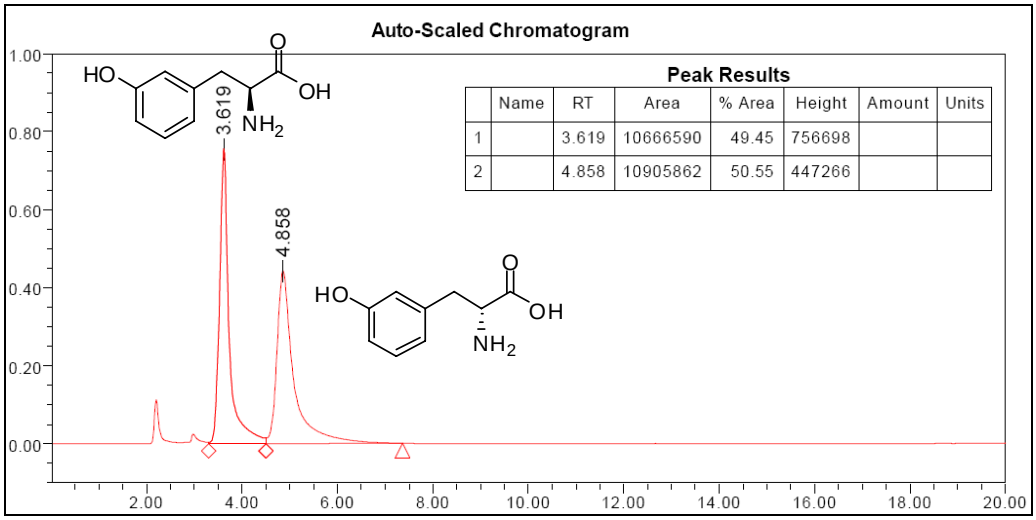
Enantiomeric excess was determined by using HPLC analysis: ChiroSil RCA-51002546, 250*4.6mm (5um); : 80% MeOH & 20%, 10mM $HClO_4$ in H_2O; flow rate: 1.0 mL/min; 220 nm; t_s = 3.9 min, t_r =5.5 min.

^{1}H and ^{13}C NMR spectra of (*S*)-m-tyrosine



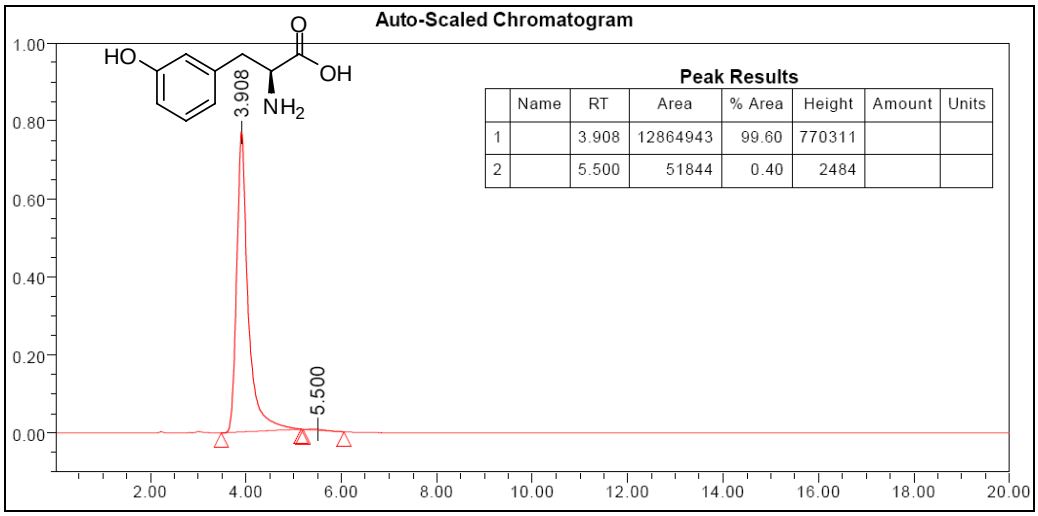


HPLC Spectrum of racemic m-tyrosine



	Name	RT	Area	% Area	Height	Amount	Units
1		3.619	10666590	49.45	756698		
2		4.858	10905862	50.55	447266		

HPLC Spectrum of (*S*)-m-tyrosine (Scheme 1)



	Name	RT	Area	% Area	Height	Amount	Units
1		3.908	12864943	99.60	770311		
2		5.500	51844	0.40	2484		

7. Crystal data for the compound Bis-Cd-TU(Ib)·C_7H_8.

Identification code	ma	
Empirical formula	$C_{46}H_{52}N_6S$	
Formula weight	721.00	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 11.6327(11) Å	α = 90°.
	b = 11.6667(10) Å	β = 104.810(4)°.
	c = 15.0995(13) Å	γ = 90°.
Volume	1981.2(3) Å^3	
Z	2	
Density (calculated)	1.209 Mg/m^3	
Absorption coefficient	0.122 mm^{-1}	
F(000)	772	
Crystal size	0.46 × 0.40 × 0.36 mm^3	
Theta range for data collection	2.23 to 28.59°.	
Index ranges	$-11 \le h \le 15$, $-15 \le k \le 15$, $-20 \le l \le 19$	
Reflections collected	28496	
Independent reflections	9417 [R(int) = 0.0227]	
Completeness to theta = 28.59°	95.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9573 and 0.9459	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9417/1/444	
Goodness-of-fit on F^2	1.026	
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0684, $wR2$ = 0.1819	
R indices (all data)	$R1$ = 0.1018, $wR2$ = 0.2095	
Absolute structure parameter	0.90(10)	
Largest diff. peak and hole	0.643 and −0.401 e·Å^{-3}	

8. References

1. J. Ye, D. J. Dixon, P. S. Hynes, *Chem. Commun*. 2005, 4481-4483.
2. J. Liang, J. C. Ruble and G. C. Fu, *J. Org. Chem*. 1998, **63**, 3154-3155.