

Asymmetric Synthesis of Enantioenriched α -Allyl Esters through Pd(BINAPHANE)-Catalysed Allylation of Disubstituted Ketenes

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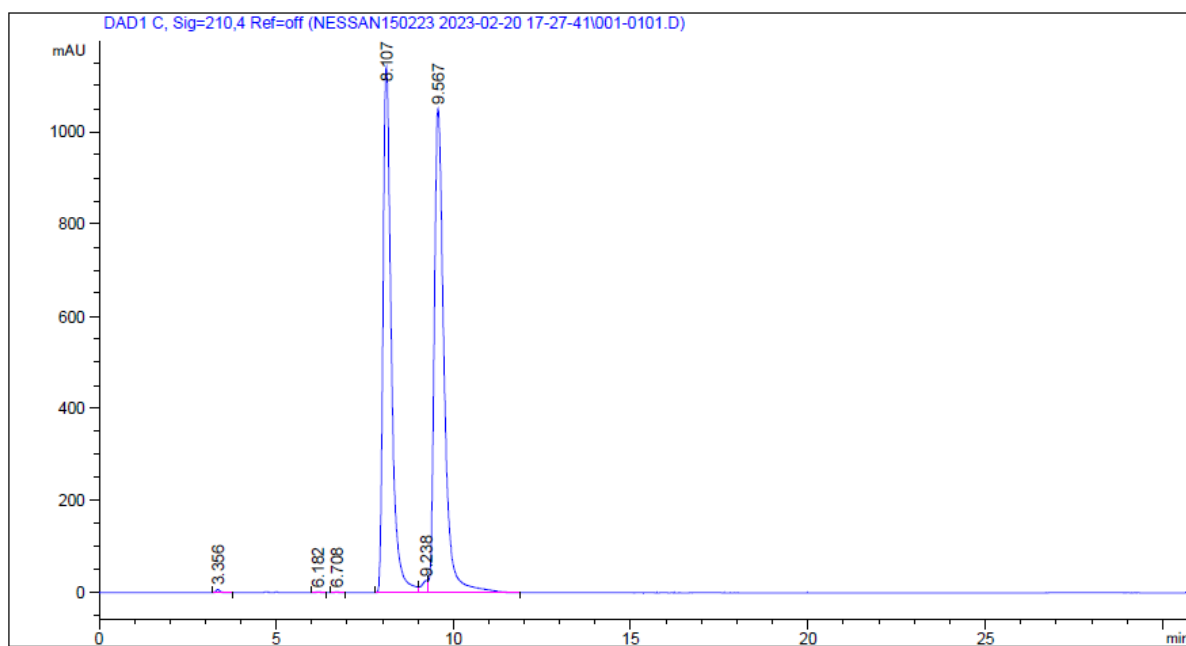
NMR and GC/HPLC spectra

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HPLC of (±)-3i:

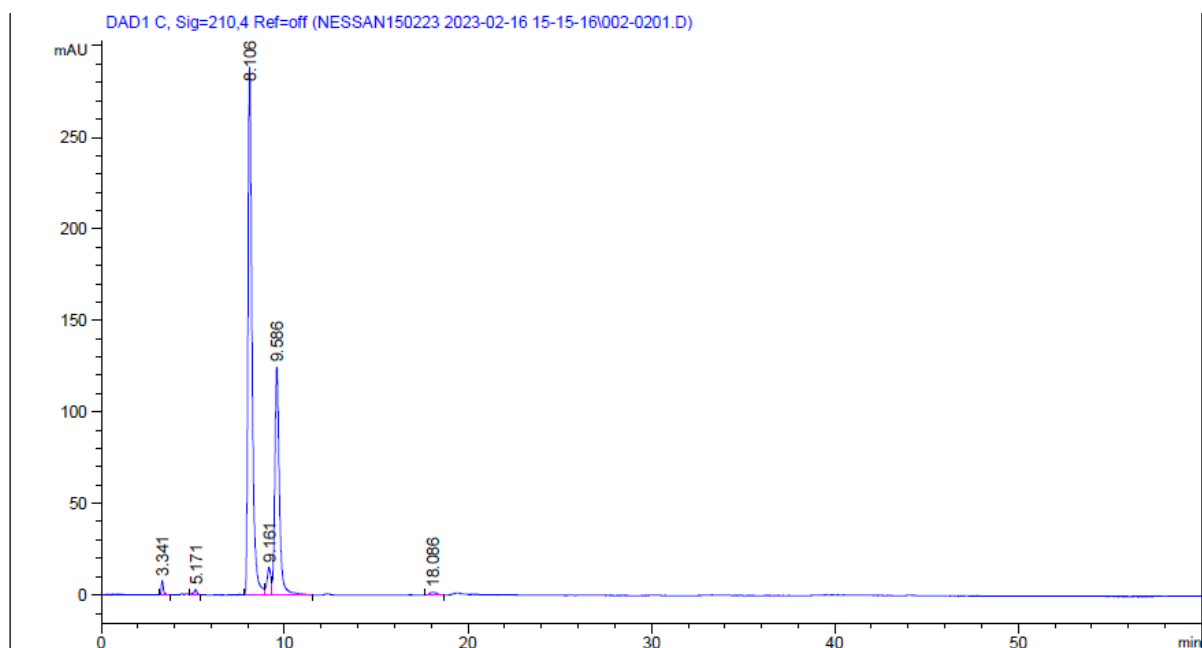


Signal 1: DAD1 C, Sig=210,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.356	BB	0.1070	44.62936	6.42699	0.1140
2	6.182	BB	0.1442	14.27917	1.45929	0.0365
3	6.708	BB	0.1621	11.94839	1.16054	0.0305
4	8.107	BV	0.2481	1.85771e4	1140.04211	47.4430
5	9.238	VV	0.1727	306.72290	26.17441	0.7833
6	9.567	VB	0.2923	2.02020e4	1050.69397	51.5928

Totals : 3.91567e4 2225.95731

HPLC of (+)-**3i**:

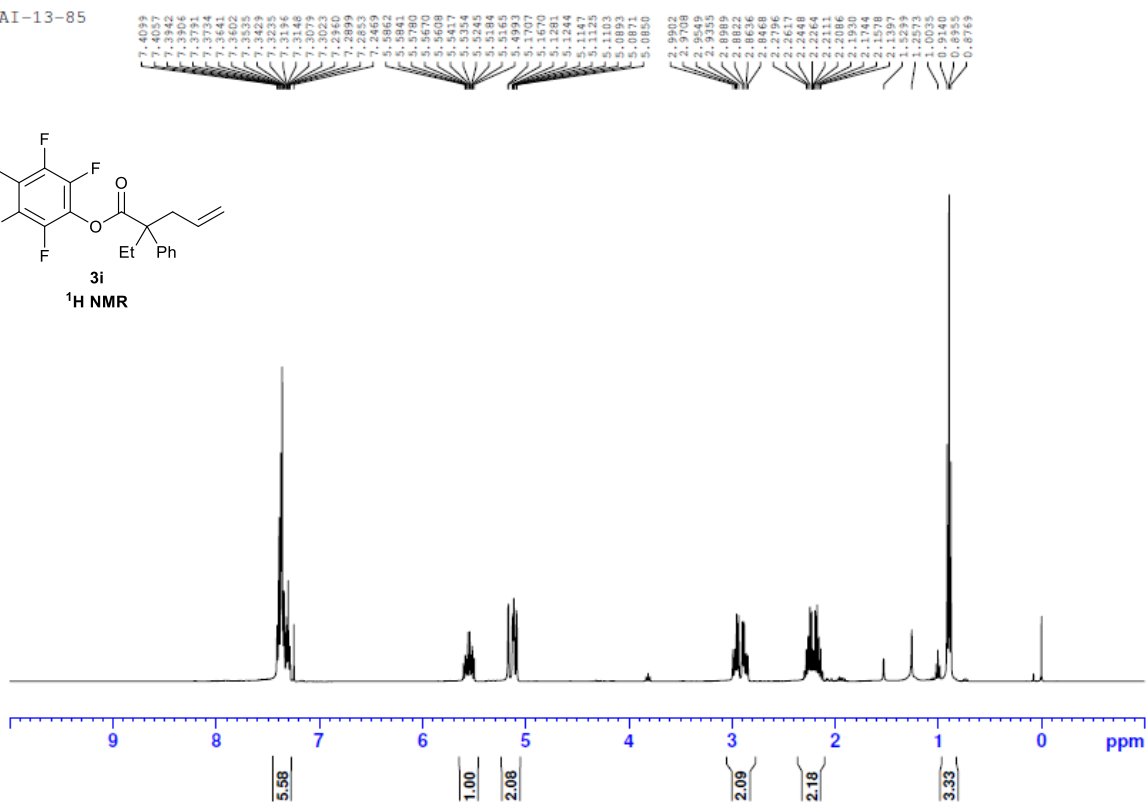
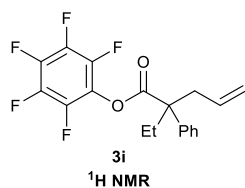


Signal 1: DAD1 C, Sig=210,4 Ref=off

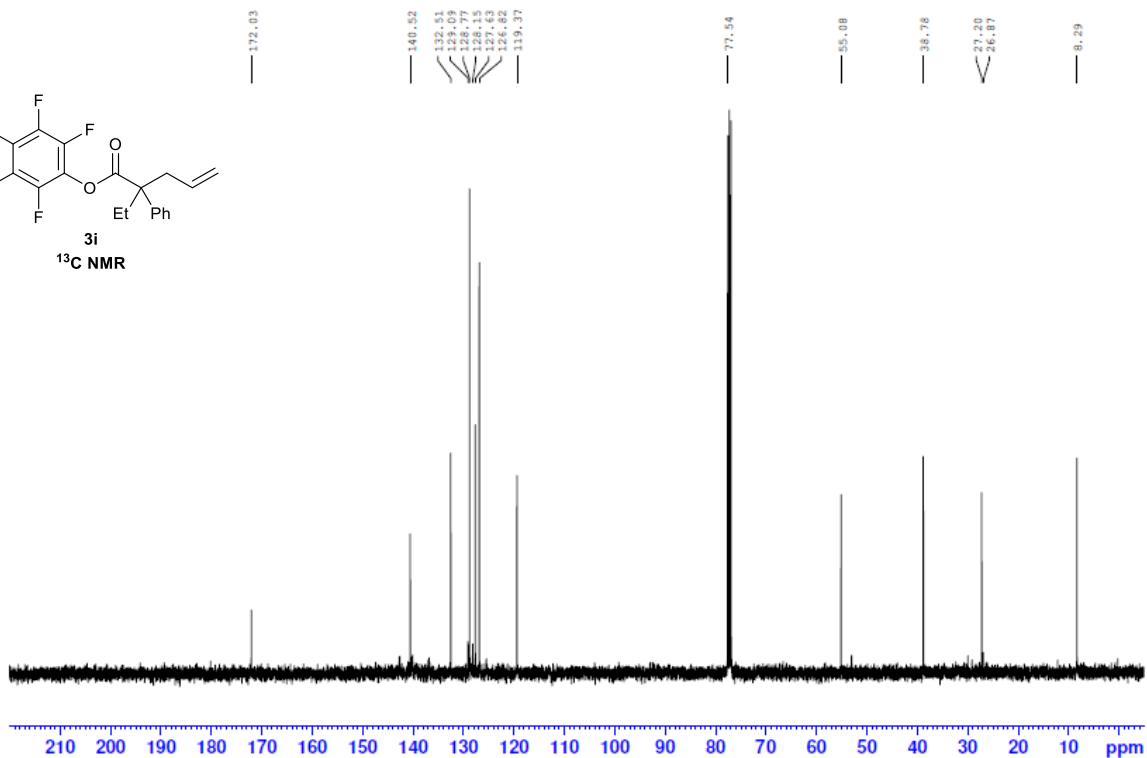
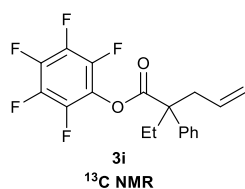
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.341	BB	0.1154	57.99095	7.56438	0.8288
2	5.171	BB	0.1628	33.83868	2.92869	0.4836
3	8.106	BV	0.2314	4436.00781	288.53543	63.4000
4	9.161	VV	0.2307	234.07767	15.27991	3.3455
5	9.586	VB	0.2667	2188.69751	124.77144	31.2812
6	18.086	BB	0.3137	46.24009	1.78814	0.6609

Totals : 6996.85271 440.86799

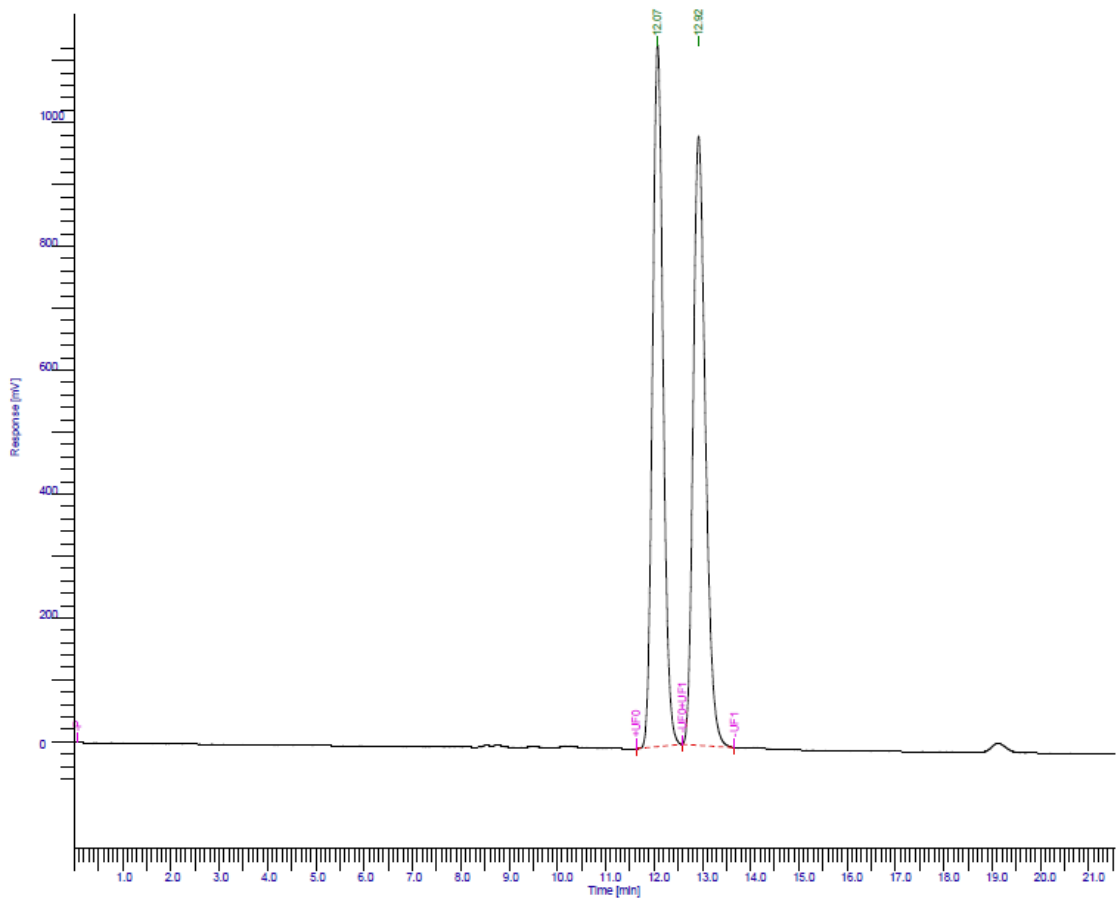
AI-13-85



AI-13-85 13C

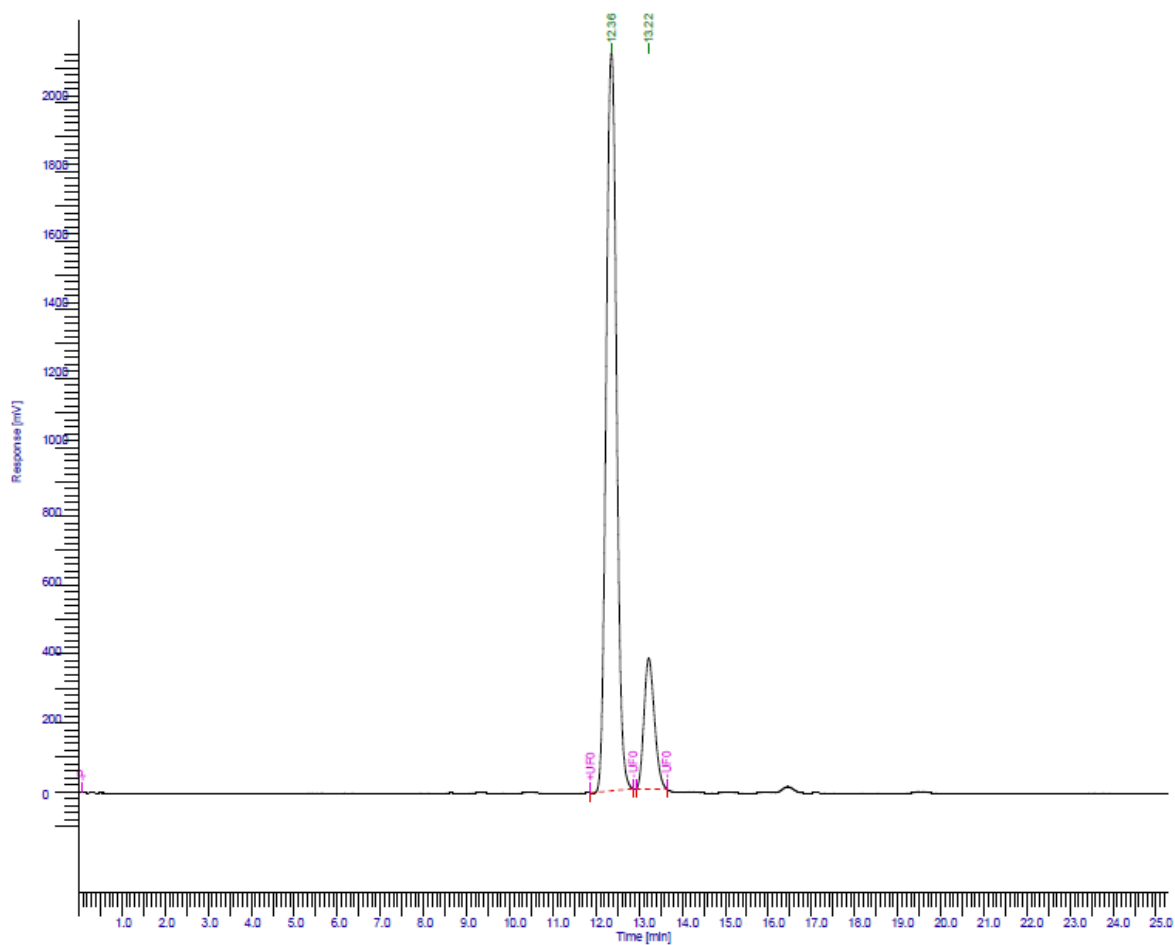


HPLC of (±)-3j



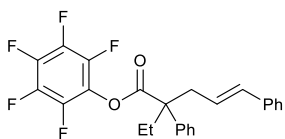
Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.071	17310087.27	1.13e+06	49.96	49.96	*MM	15.2885
2	12.921	17340531.13	983211.52	50.04	50.04	*MM	17.6366
		34650618.40	2.12e+06	100.00	100.00		

HPLC of enantioenriched **3j**:

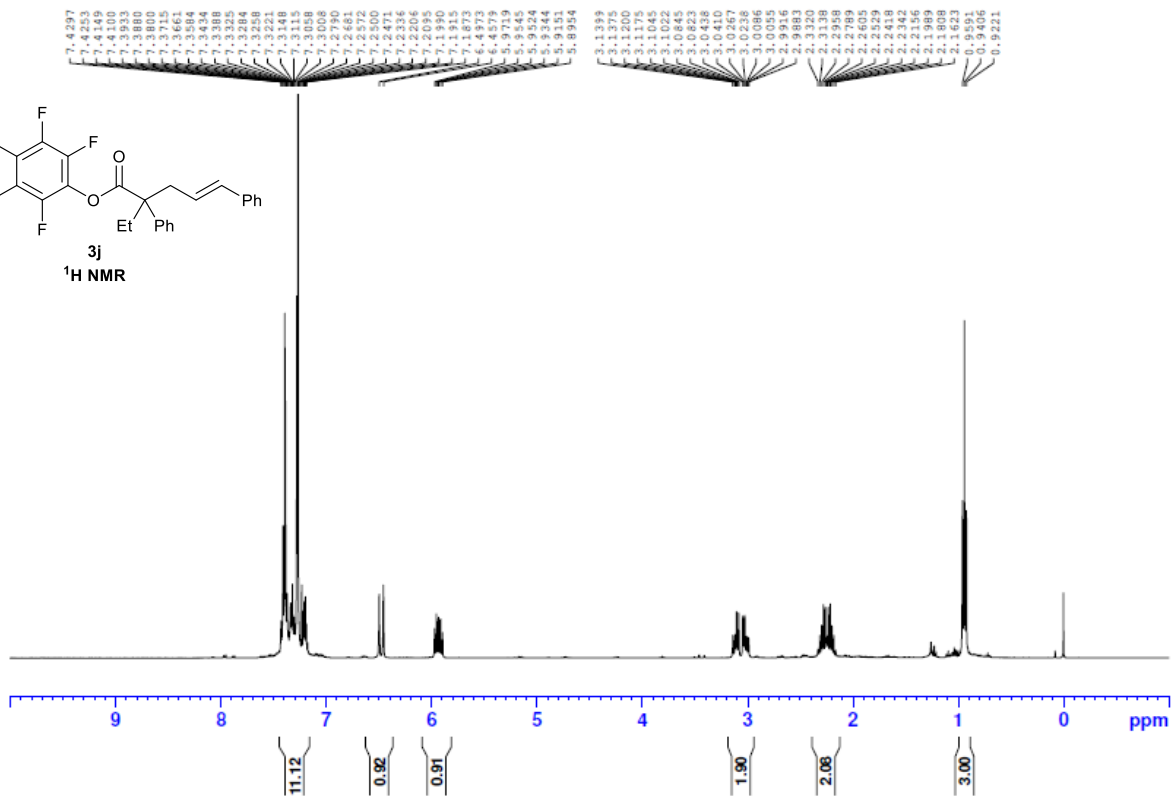


Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.357	35848178.10	2.14e+06	84.88	84.88	*MM	16.7360
2	13.222	6386681.32	378761.45	15.12	15.12	*MM	16.8620
		42234859.42	2.52e+06	100.00	100.00		

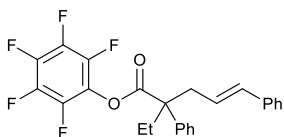
AI-13-88



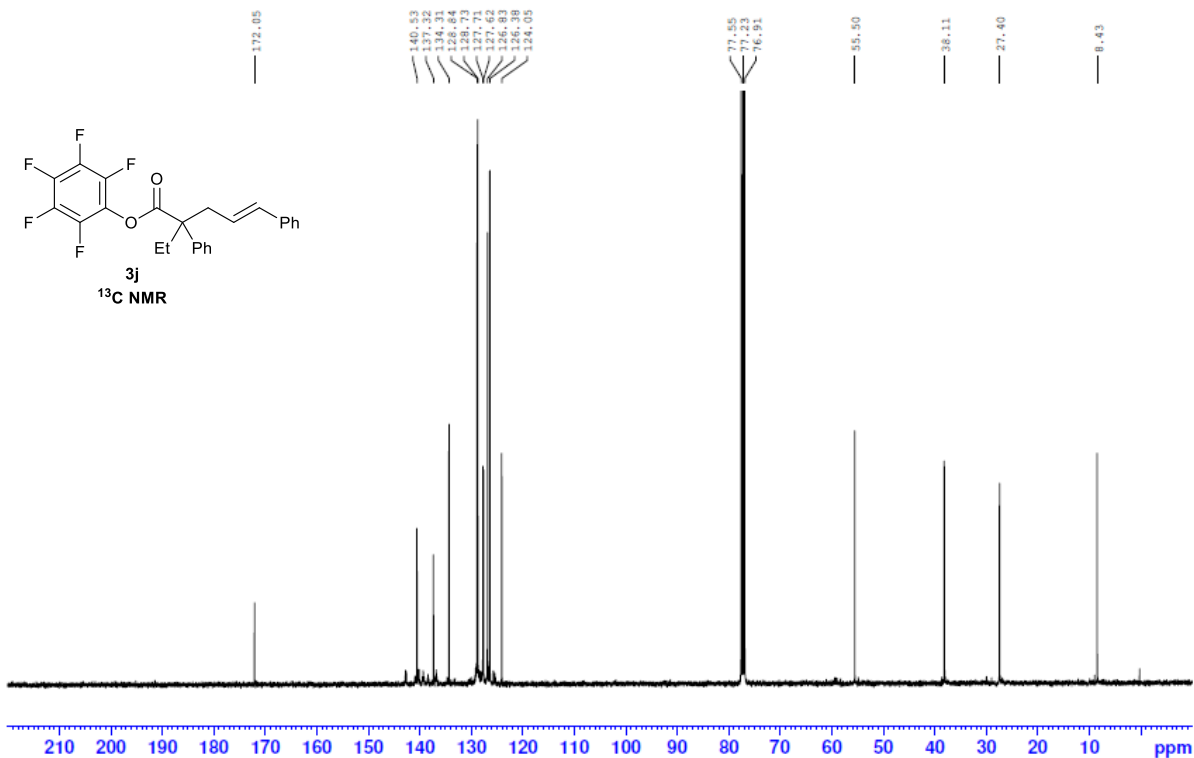
3j
¹H NMR



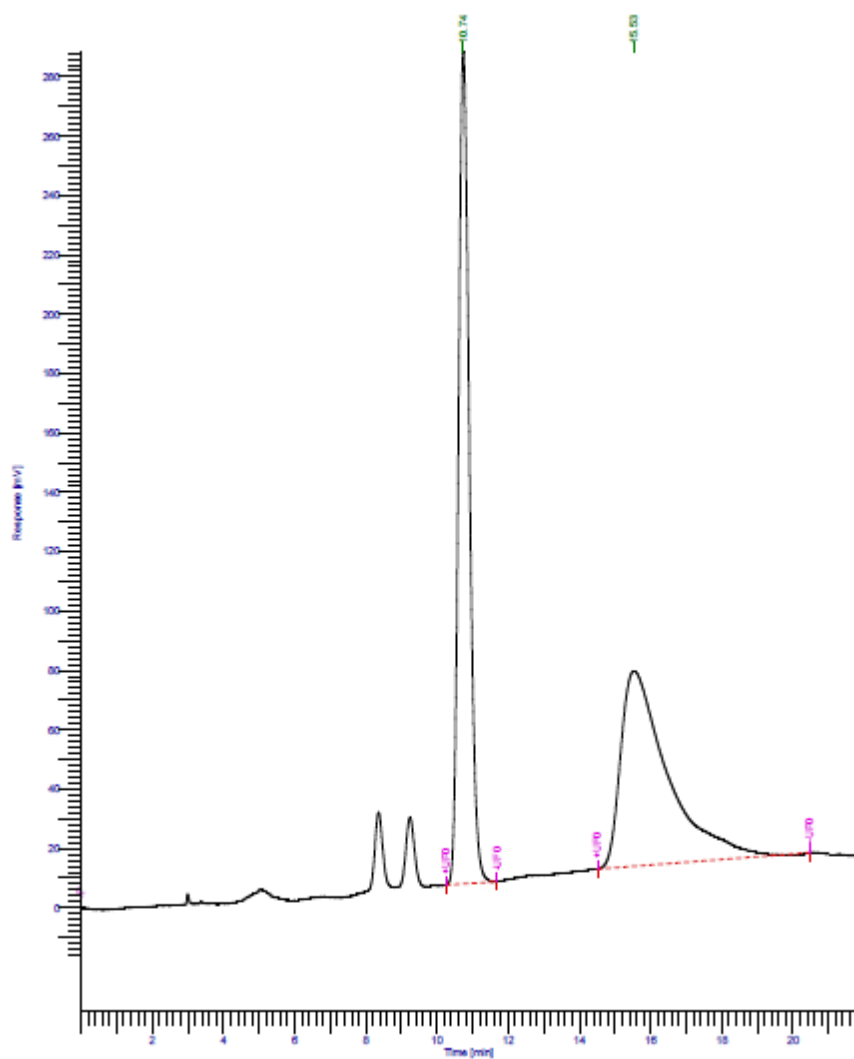
AI-13-88 13C



3j
¹³C NMR

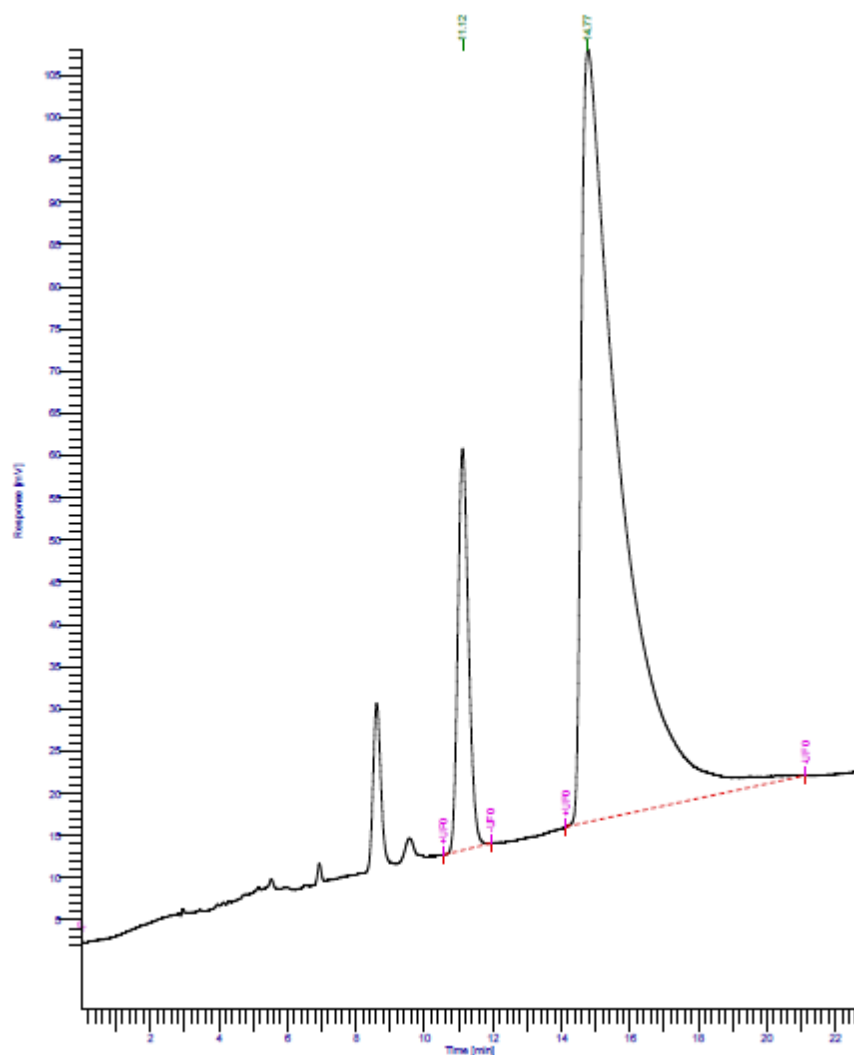


HPLC of (±)-3k:



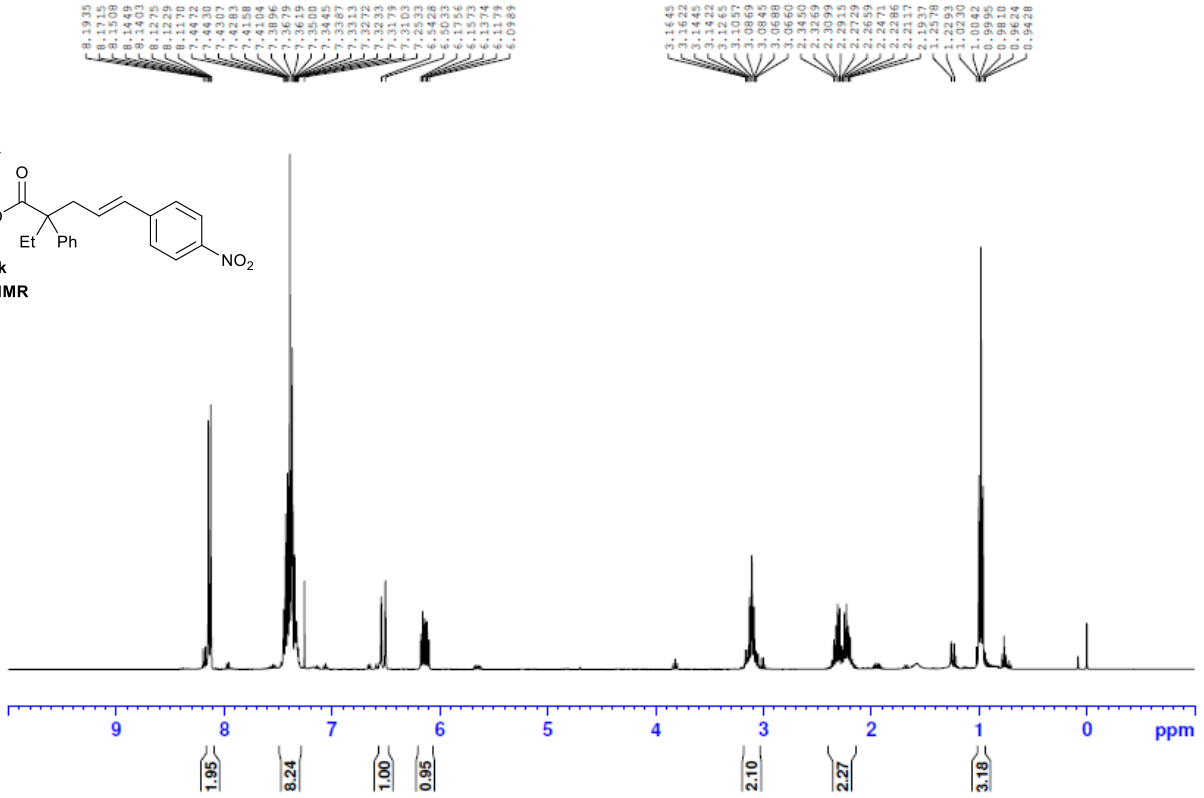
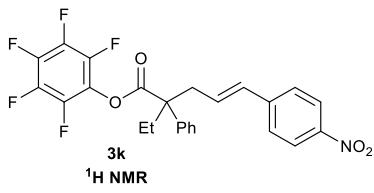
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	10.736	5907024.01	280495.13	49.48	49.48	*MM	21.0593
2	15.532	6030561.63	65766.43	50.52	50.52	*MM	91.6967
		11937585.64	346261.56	100.00	100.00		

HPLC of (-)-3k:

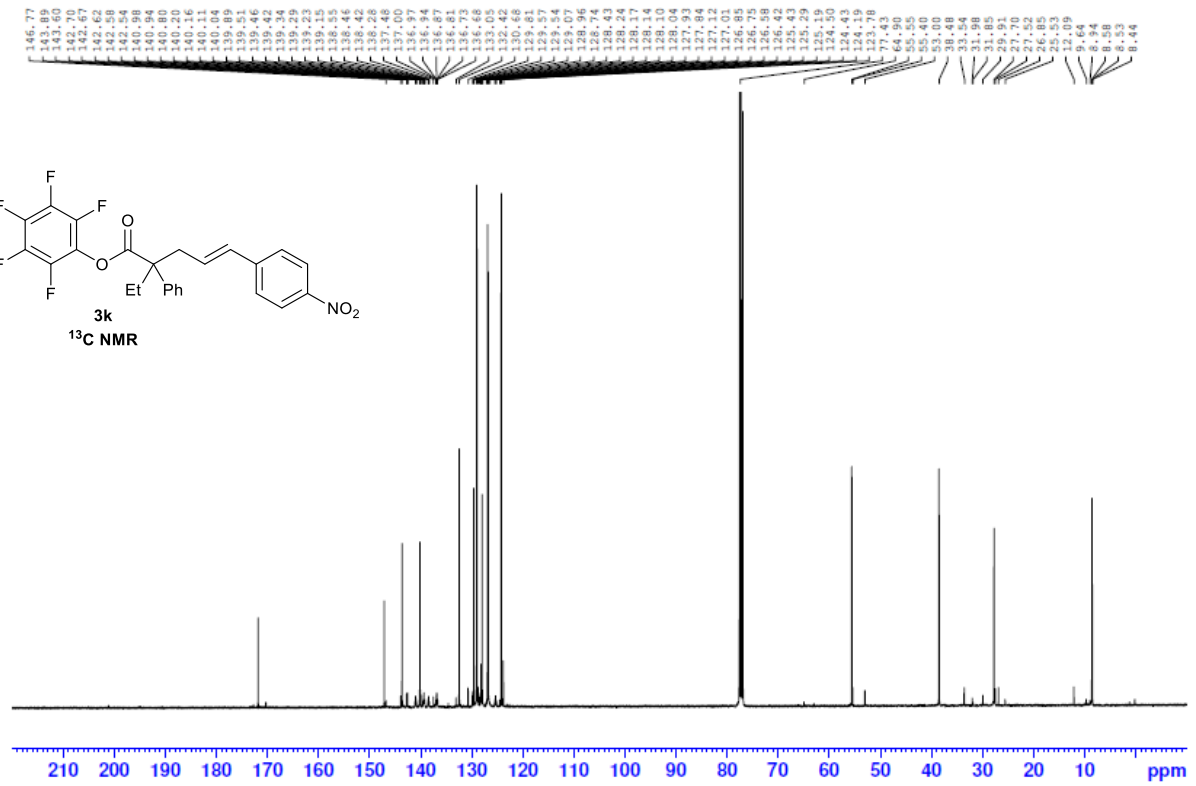
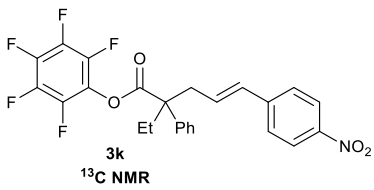


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	11.117	1029251.44	47522.94	12.45	12.45	*MM	21.6580
2	14.769	7240381.33	91500.84	87.55	87.55	*MM	79.1291
		8269632.76	139023.78	100.00	100.00		

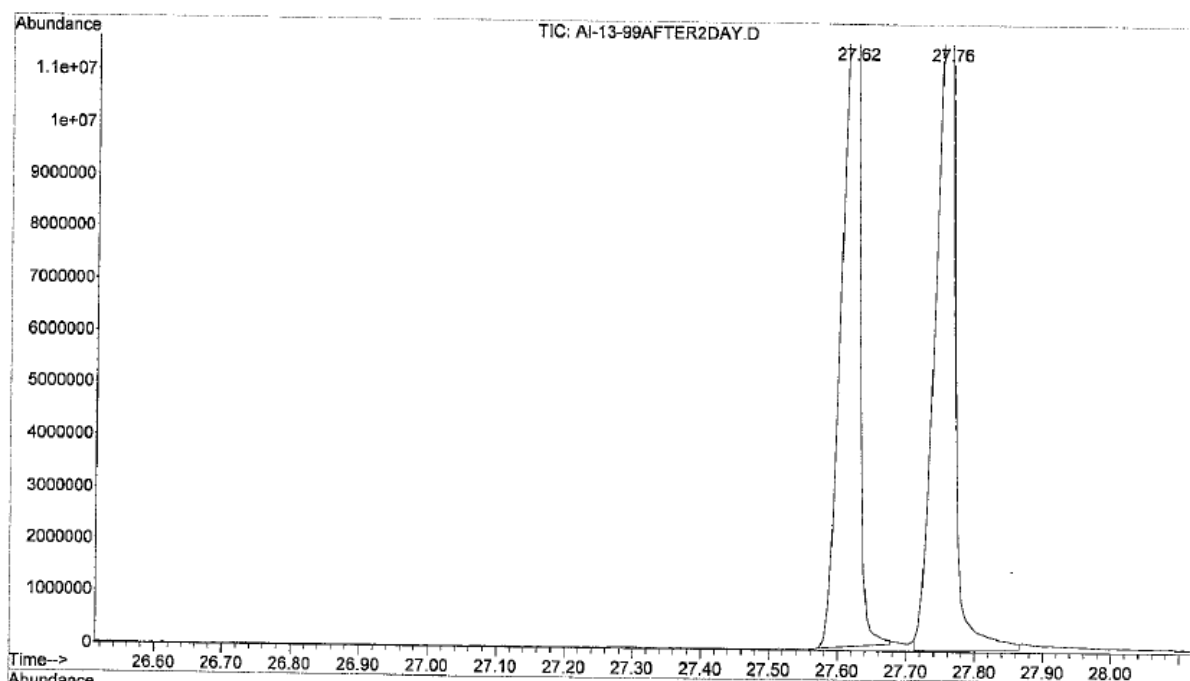
AI-14-15



AI-14-15 13C

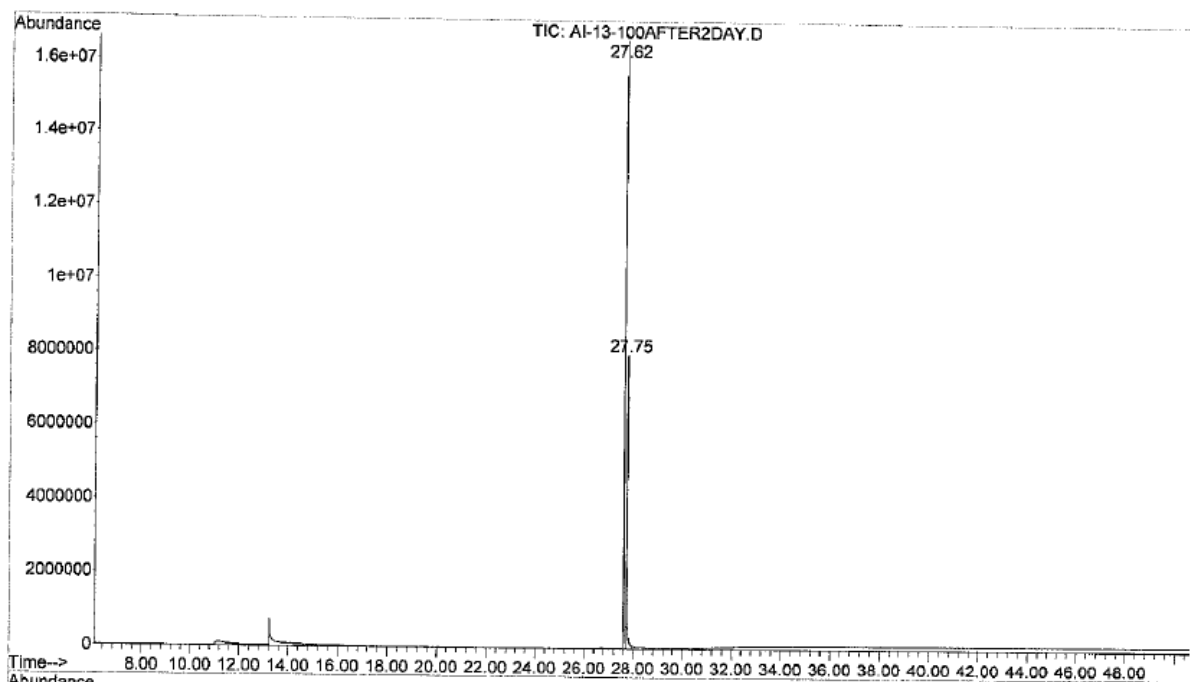


GC trace of amide derivative of (\pm)-**3I** (prepared from (*S*)- α -methylbenzylamine):



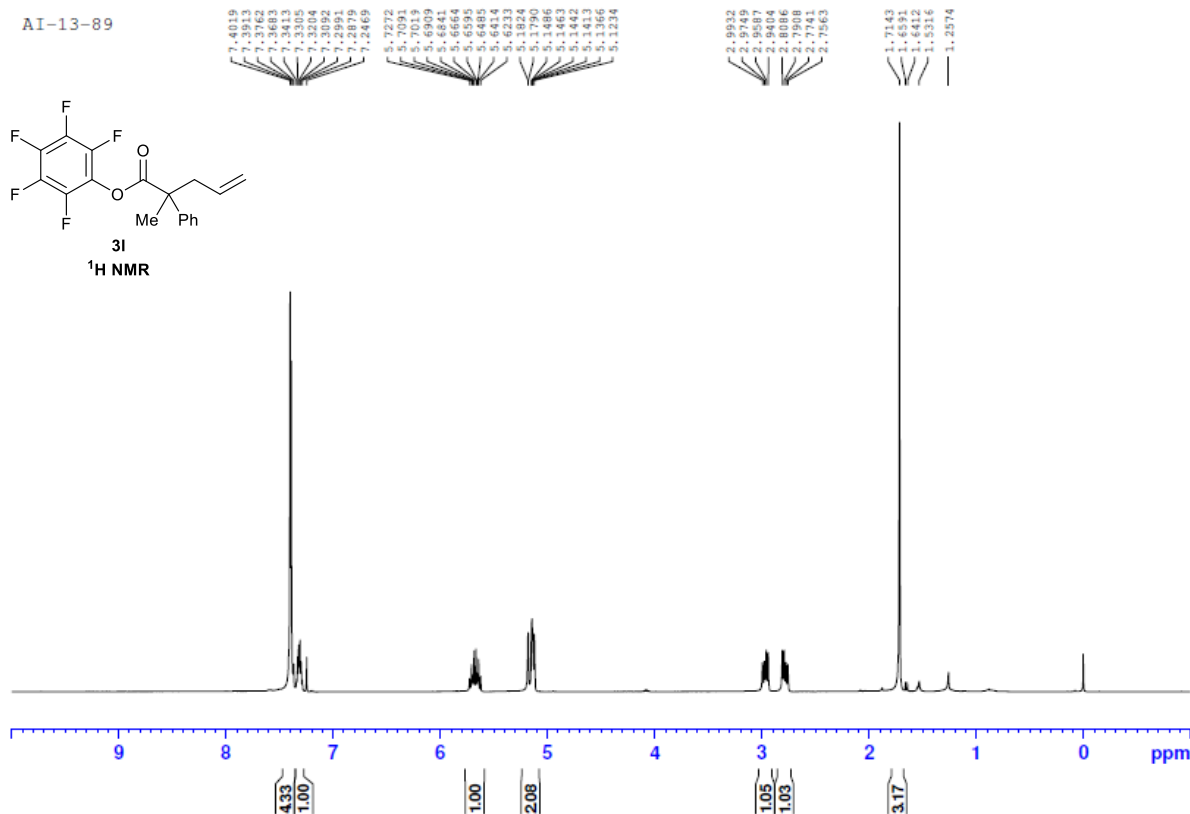
peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	27.620	3759	3767	3782	rM	15281015	26109439	97.36%	49.331%
2	27.757	3783	3791	3810	rM	14194216	26817656	100.00%	50.669%

GC-MS trace of amide derivative of ($-$)-**3I** (prepared from (*S*)- α -methylbenzylamine):

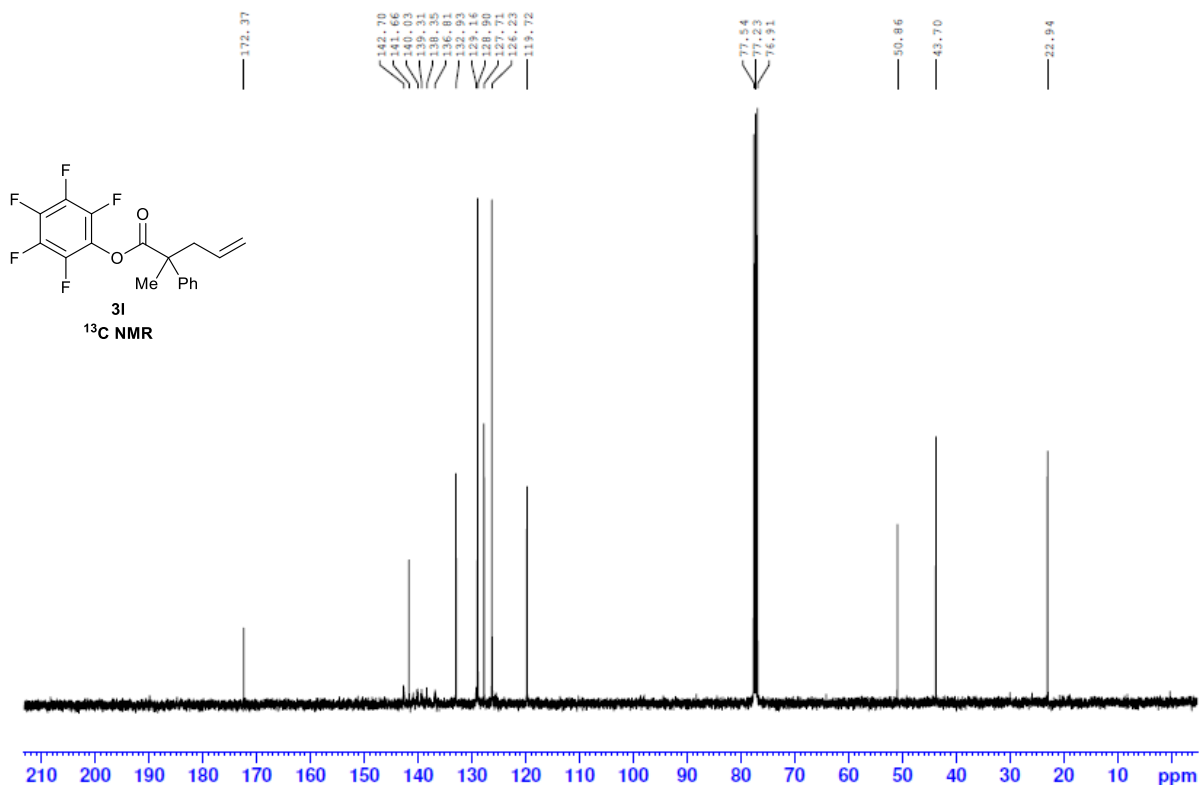


peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	27.623	3758	3768	3782	rM	16581250	30662709	100.00%	66.812%
2	27.749	3782	3790	3822	rM	7960735	15231306	49.67%	33.188%

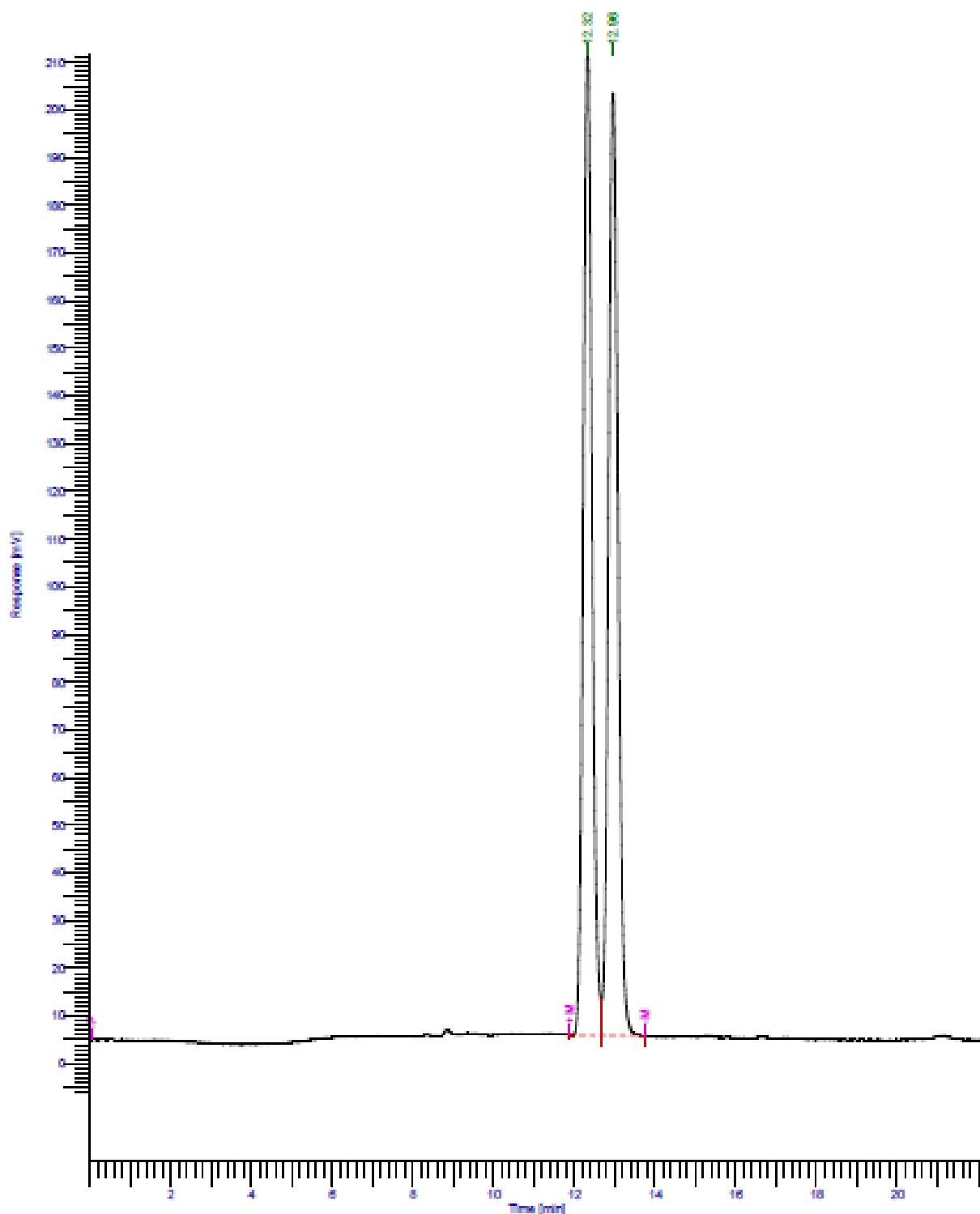
AI-13-89



AI-13-89 13C

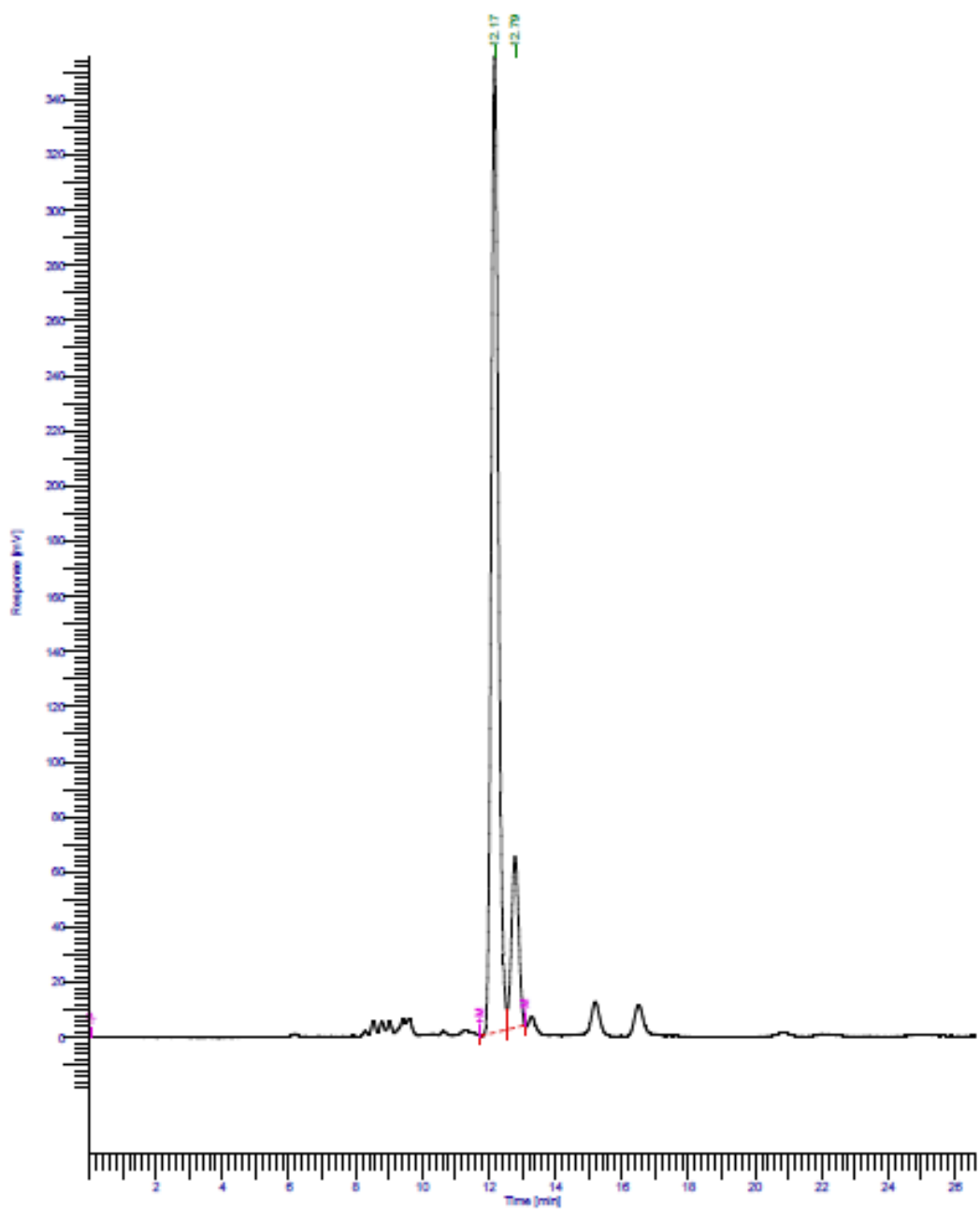


HPLC of (±)-3m:



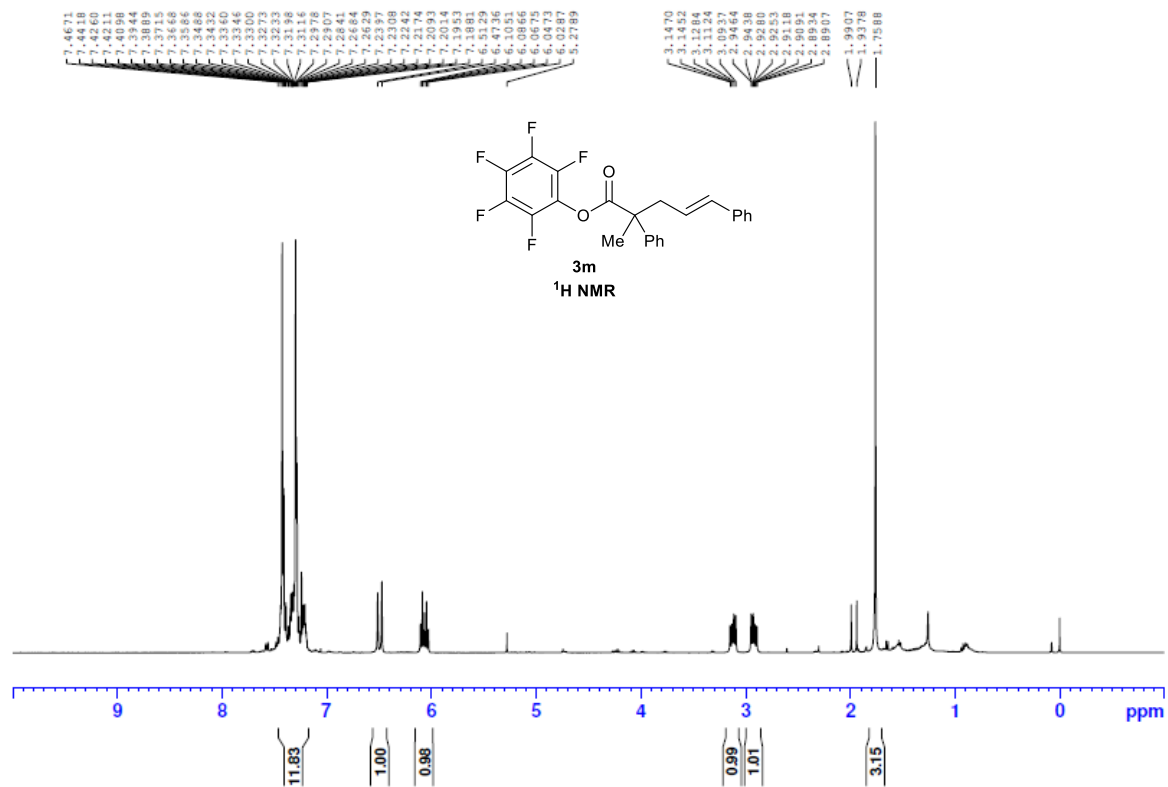
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.323	3127200.80	205806.64	49.57	49.57	*BV	15.1948
2	12.959	3181137.04	197572.39	50.43	50.43	*VB	16.1011
		6308337.84	403379.03	100.00	100.00		

HPLC of (+)-3m:

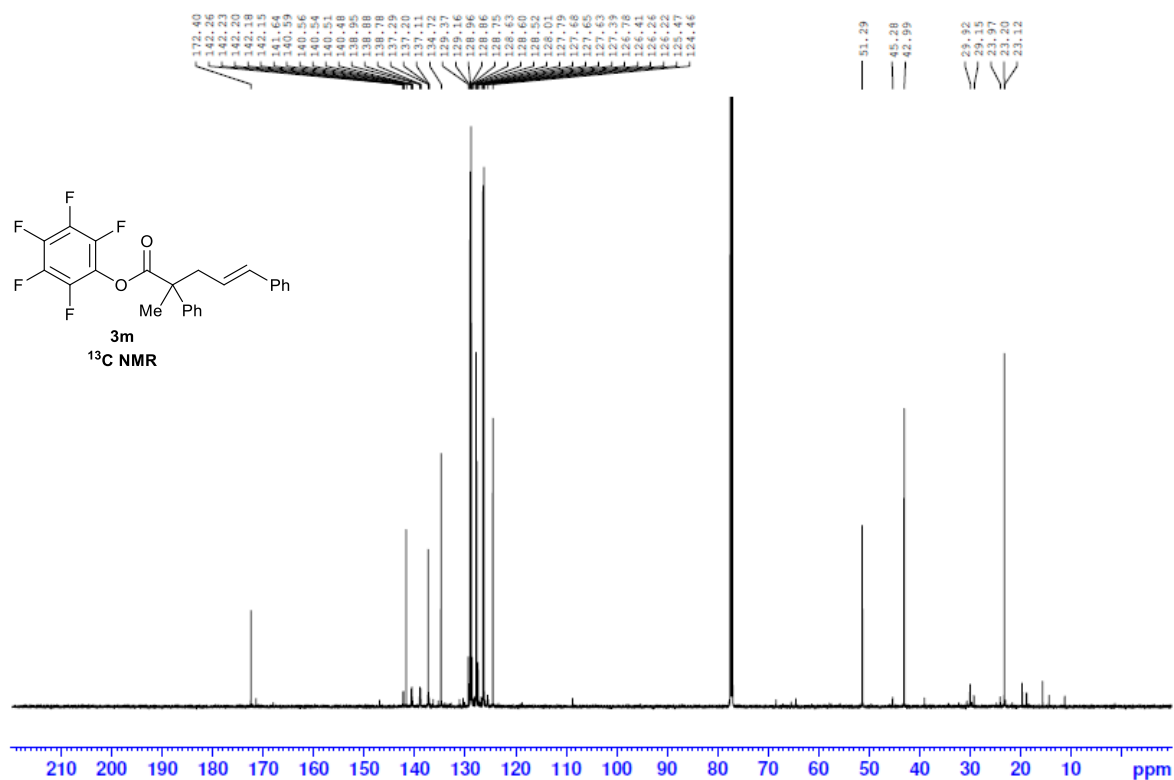


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.173	5355255.06	354070.50	85.09	85.09	*BV	15.1248
2	12.788	938265.71	62034.14	14.91	14.91	*VB	15.1250
		6293520.77	416104.64	100.00	100.00		

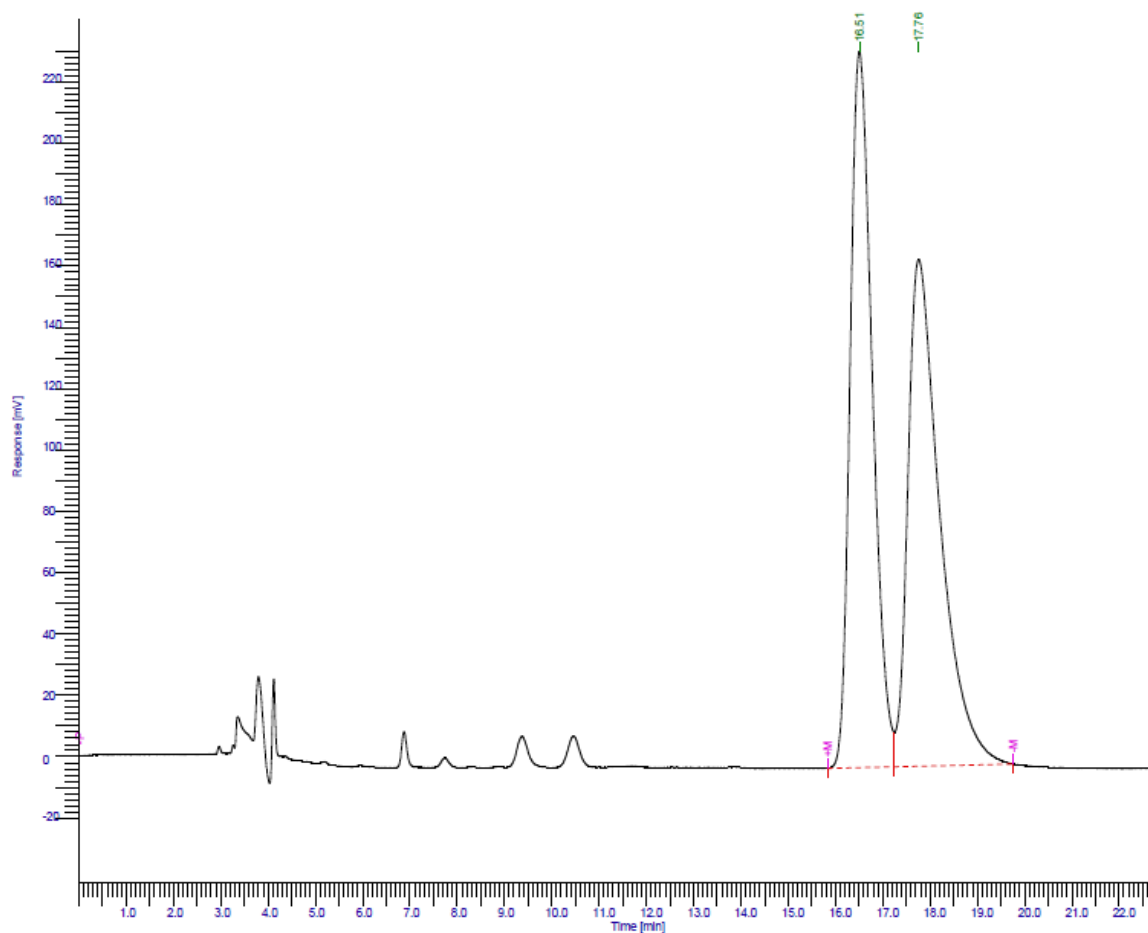
AI-13-94



N123 AI13-94

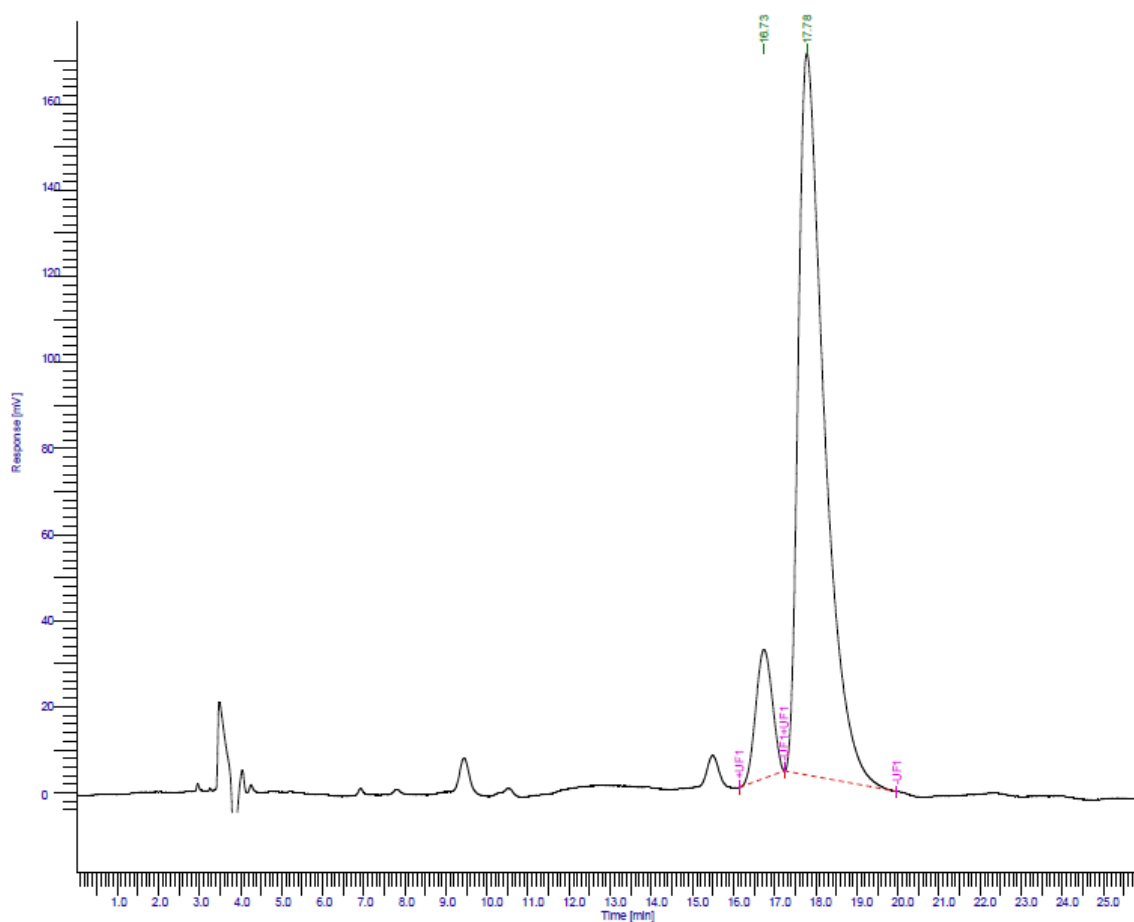


HPLC of (±)-3n:



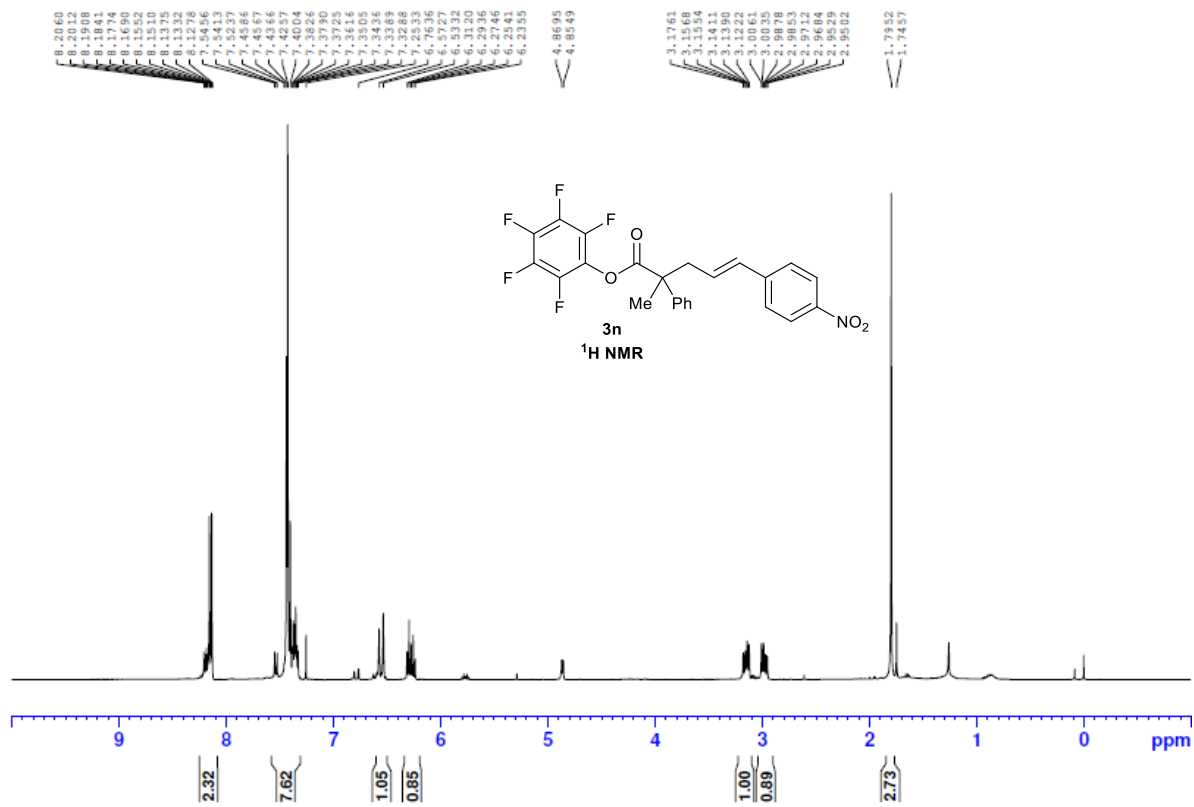
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	16.506	7636857.91	233694.52	49.47	49.47	*BV	32.6788
2	17.760	7800626.79	165369.00	50.53	50.53	*VB	47.1710
		15437484.70	399063.53	100.00	100.00		

HPLC of (+)-3n:

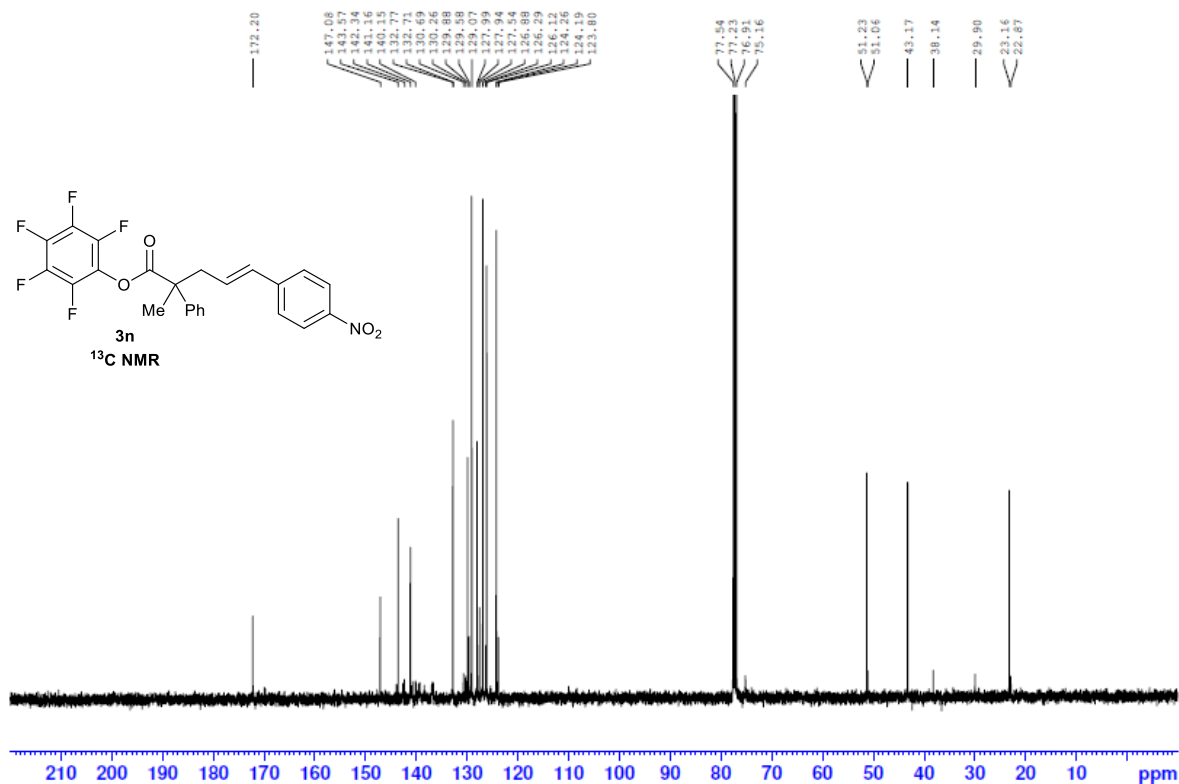


Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	16.735	839160.41	29970.34	10.20	10.20	*MM	27.9997
2	17.783	7390619.41	167798.52	89.80	89.80	*MM	44.0446
		8229779.83	197768.86	100.00	100.00		

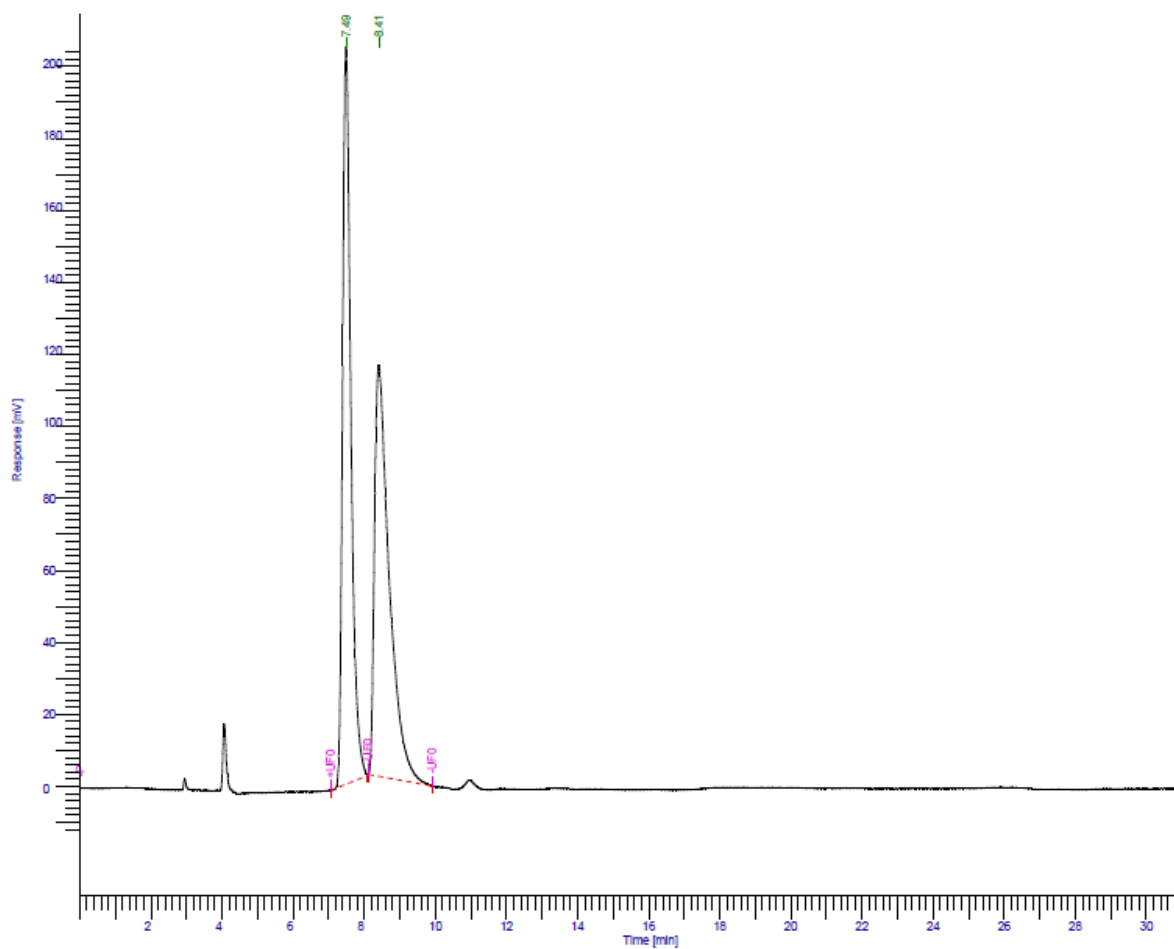
AI-14-47



AI-14-47 13C

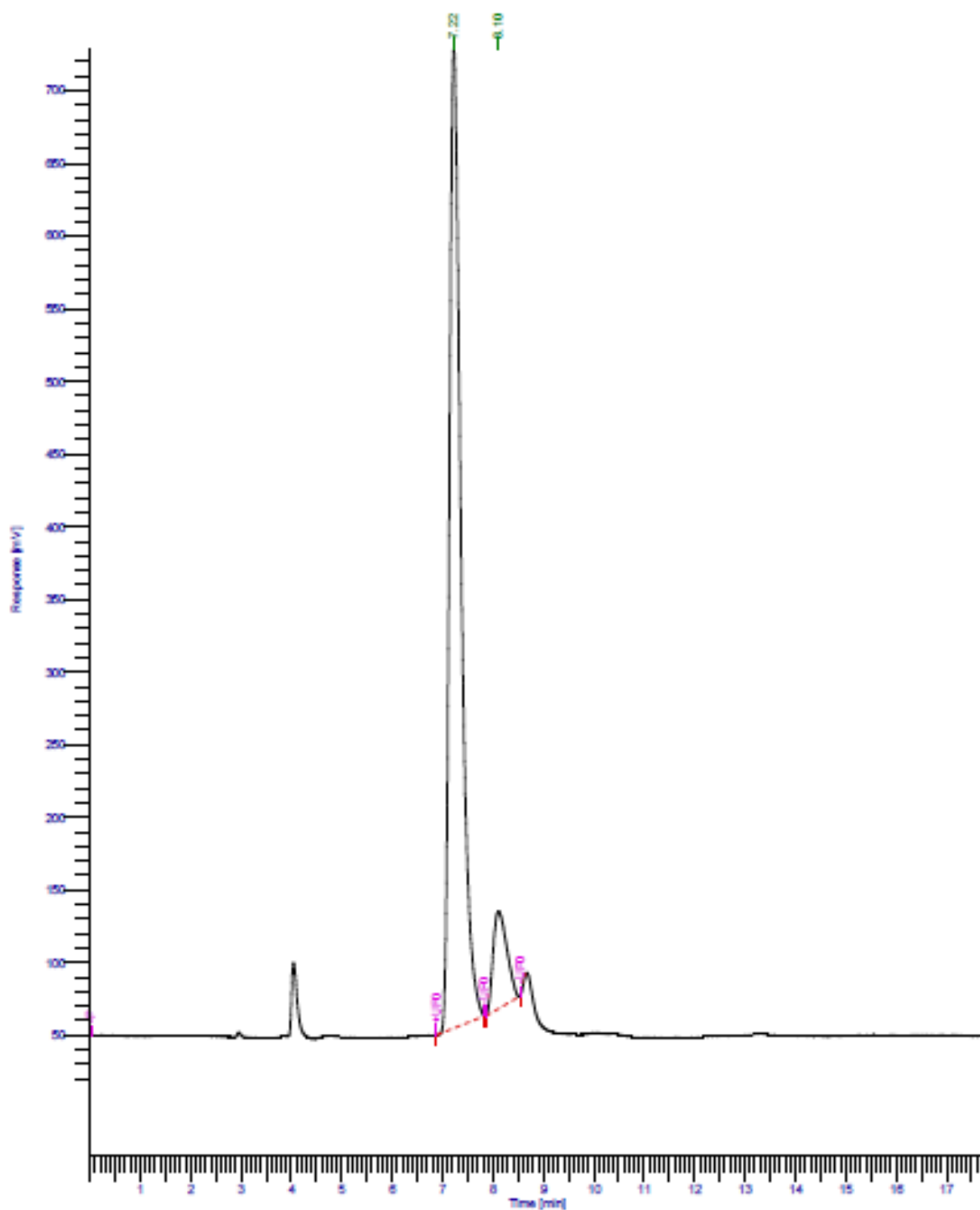


HPLC of (±)-3p:



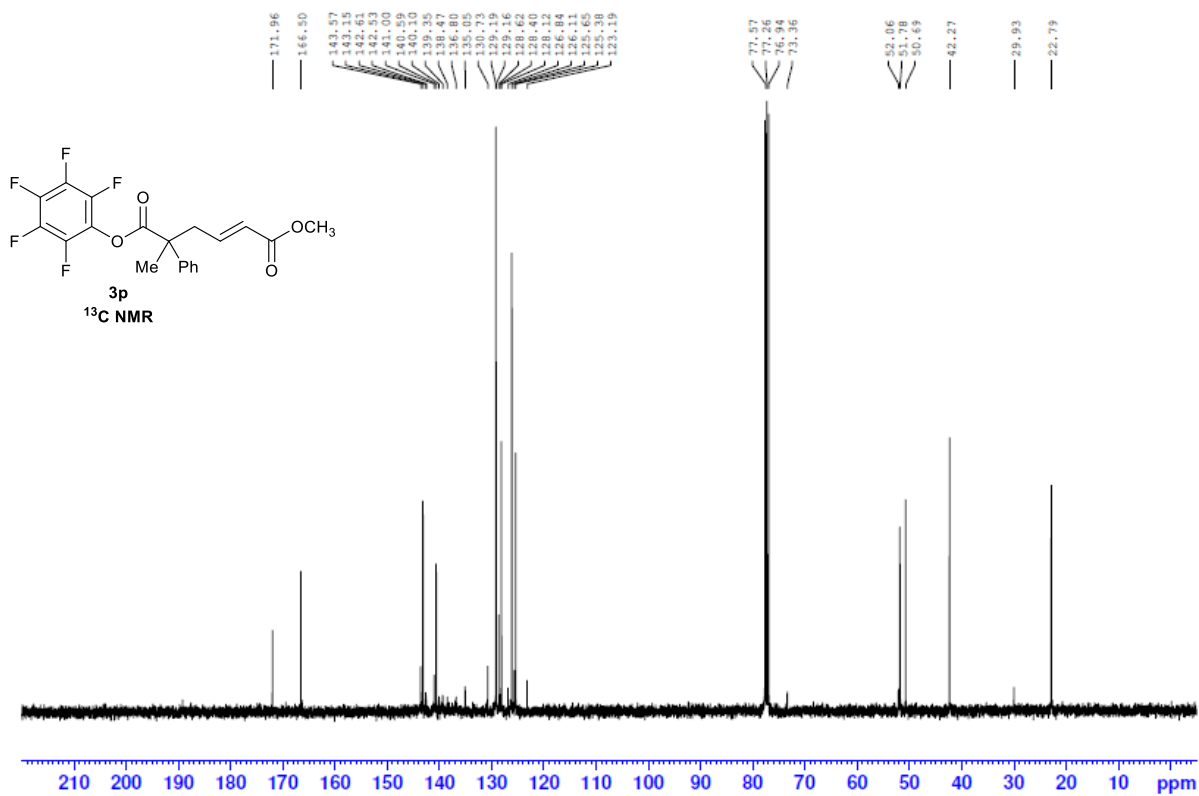
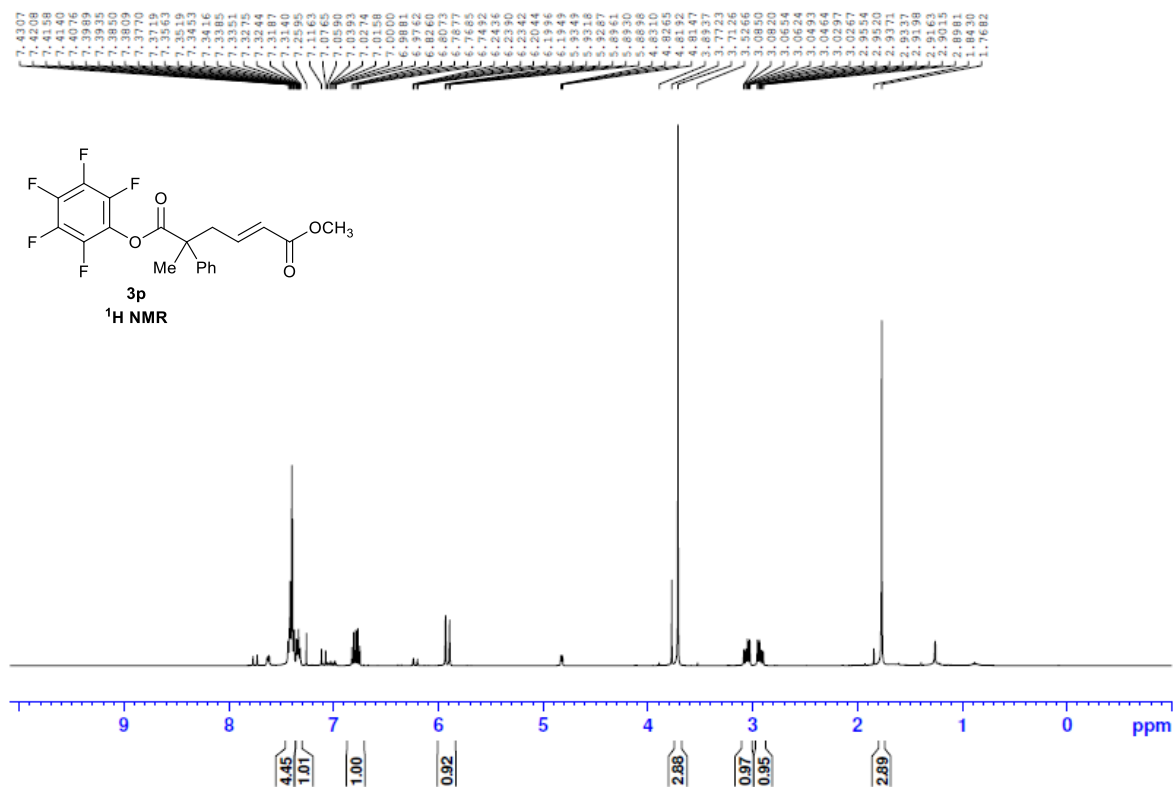
Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.487	3312559.31	204864.77	50.16	50.16	*MM	16.1695
2	8.411	3290998.37	113966.89	49.84	49.84	*MM	28.8768
		6603557.68	318831.66	100.00	100.00		

HPLC of (+)-3p:

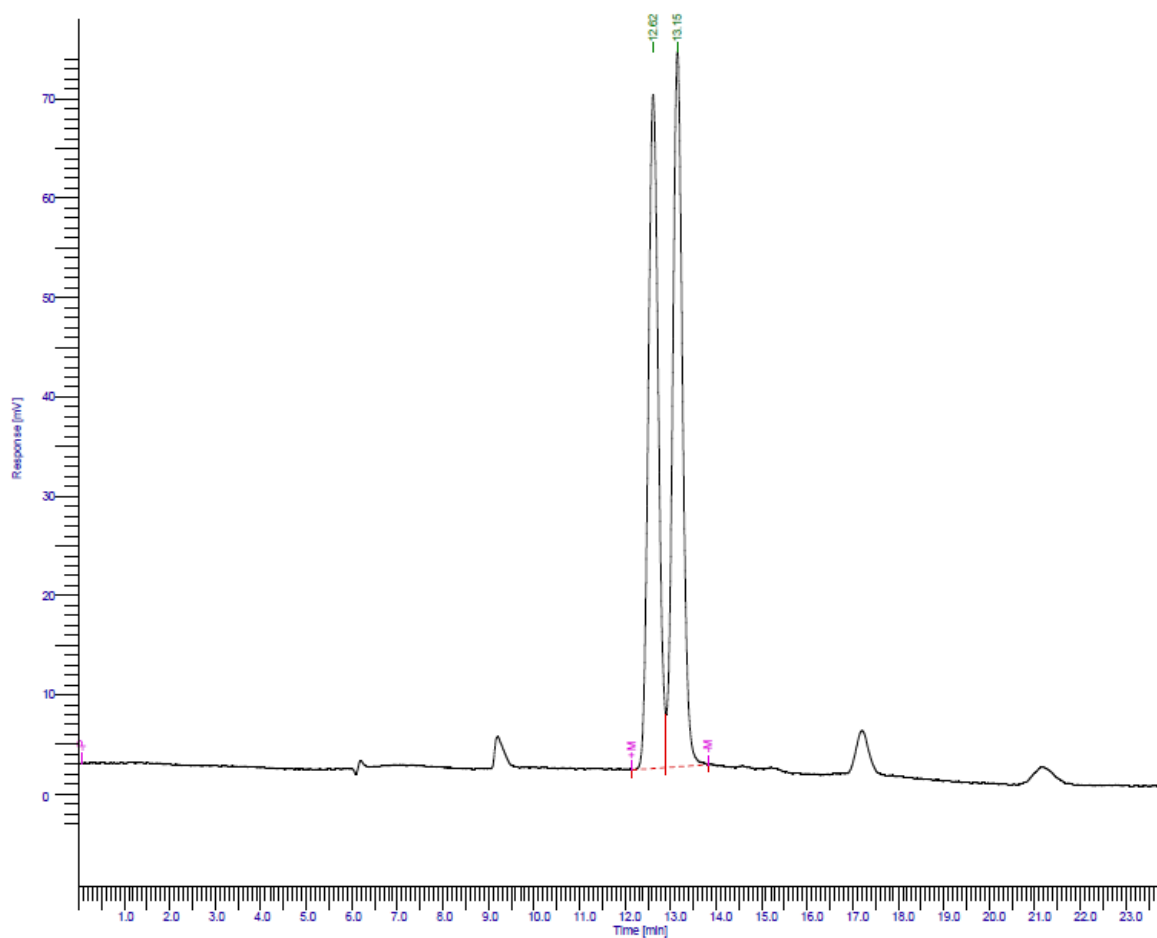


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.223	10721234.21	674224.94	89.37	89.37	*MM	15.9016
2	8.103	1275780.71	67078.26	10.63	10.63	*MM	19.0193
		11997014.93	741303.20	100.00	100.00		

AI-14-53

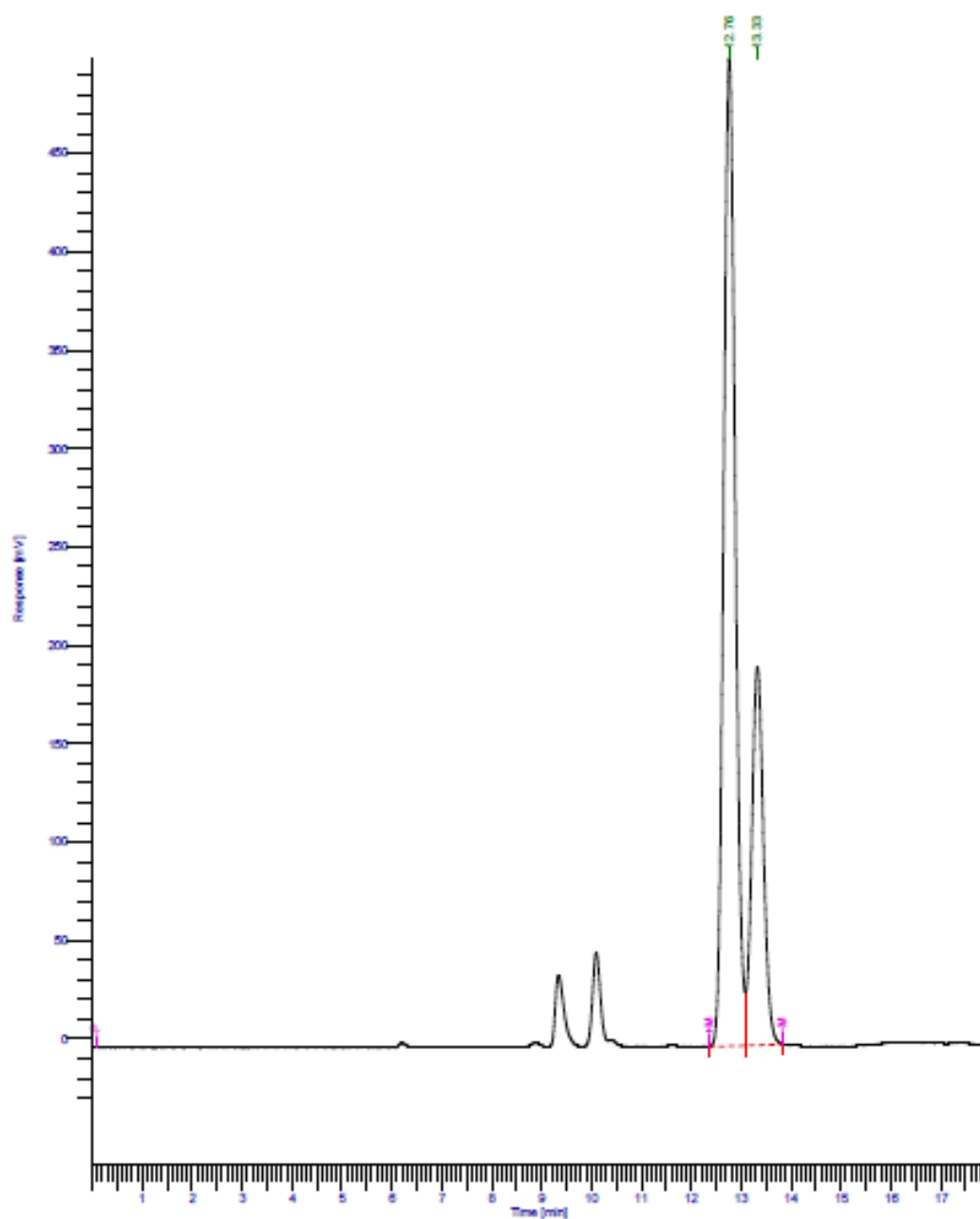


HPLC of (±)-3q:



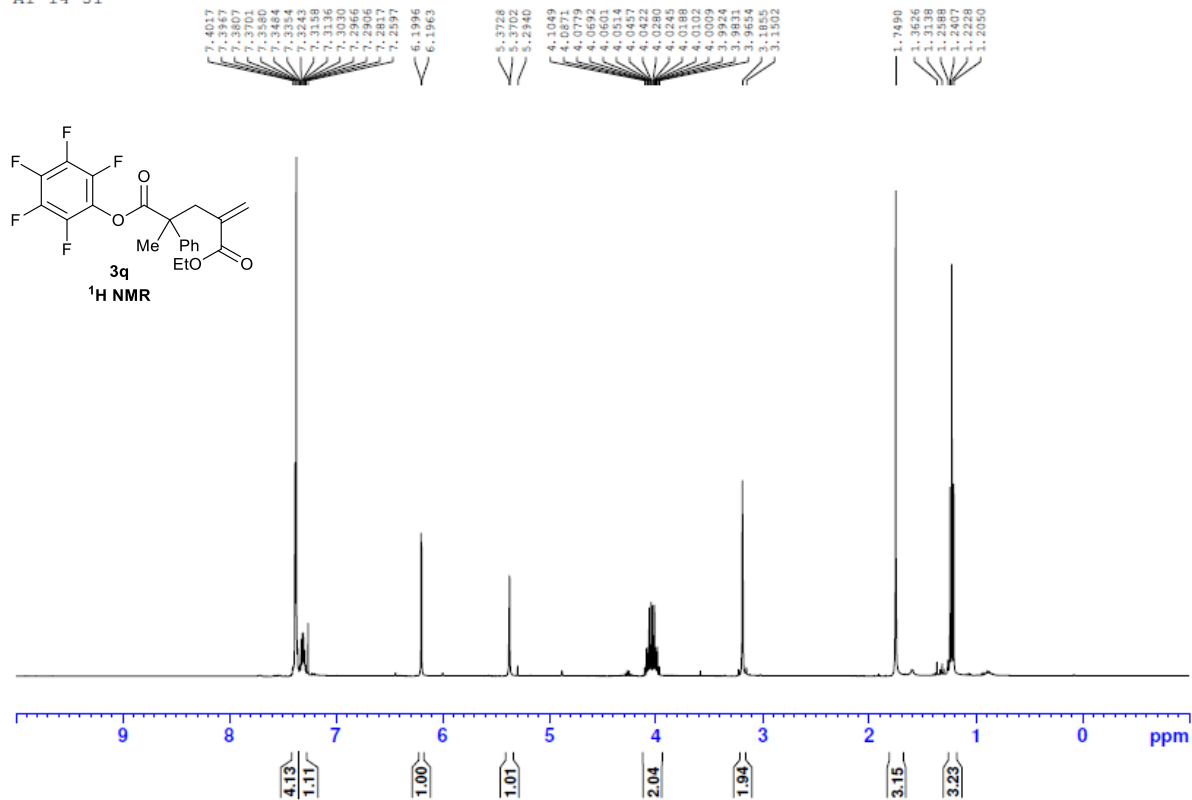
Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.616	1047703.05	67870.06	49.06	49.06	*BV	15.4369
2	13.151	1087765.22	72024.96	50.94	50.94	*VB	15.1026
		2135468.26	139895.02	100.00	100.00		

HPLC of (+)-3q:

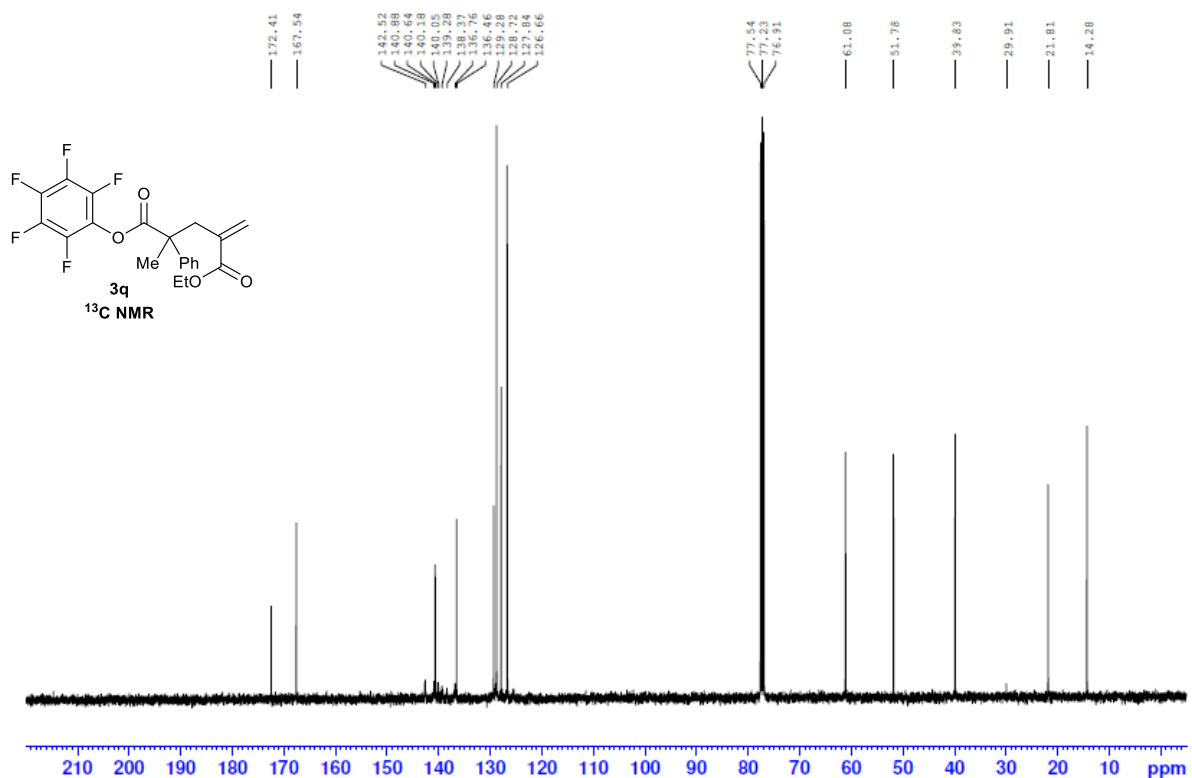


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.761	8141396.14	502015.32	72.20	72.20	*BV	16.2174
2	13.325	3134919.55	191985.73	27.80	27.80	*VB	16.3289
		11276315.69	694001.06	100.00	100.00		

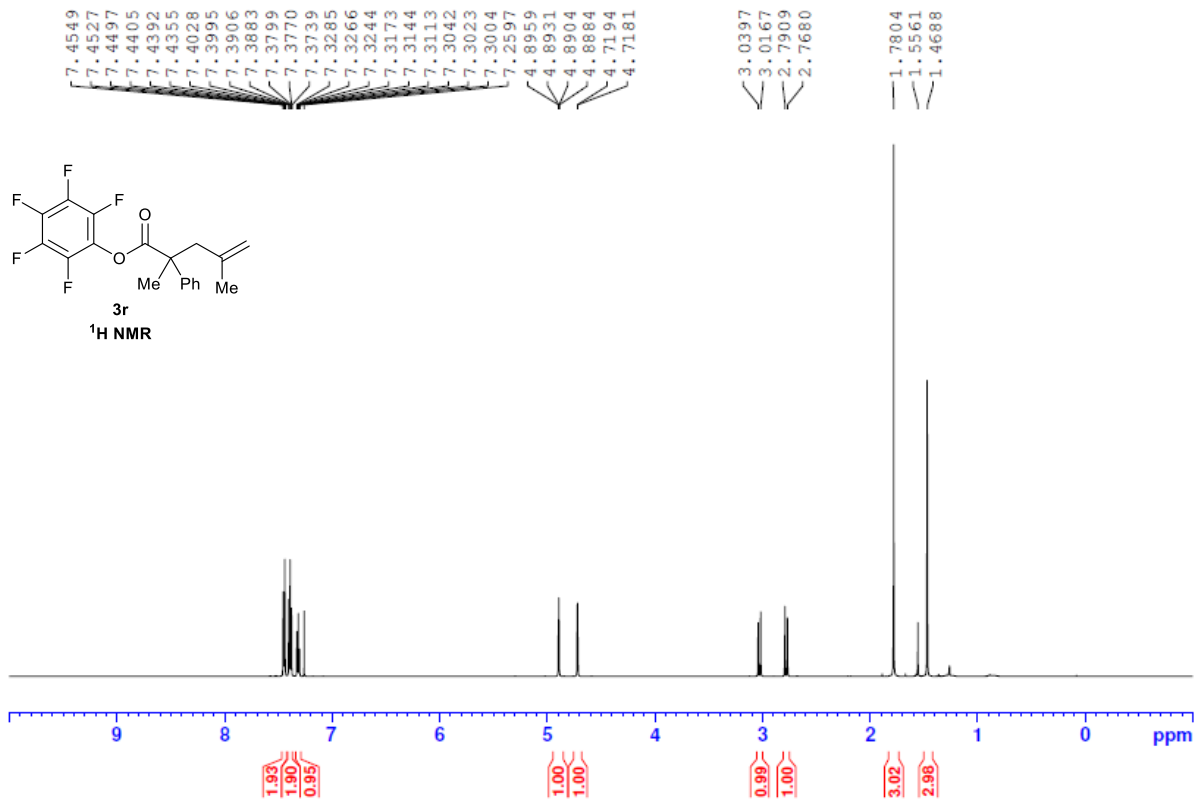
AI-14-51



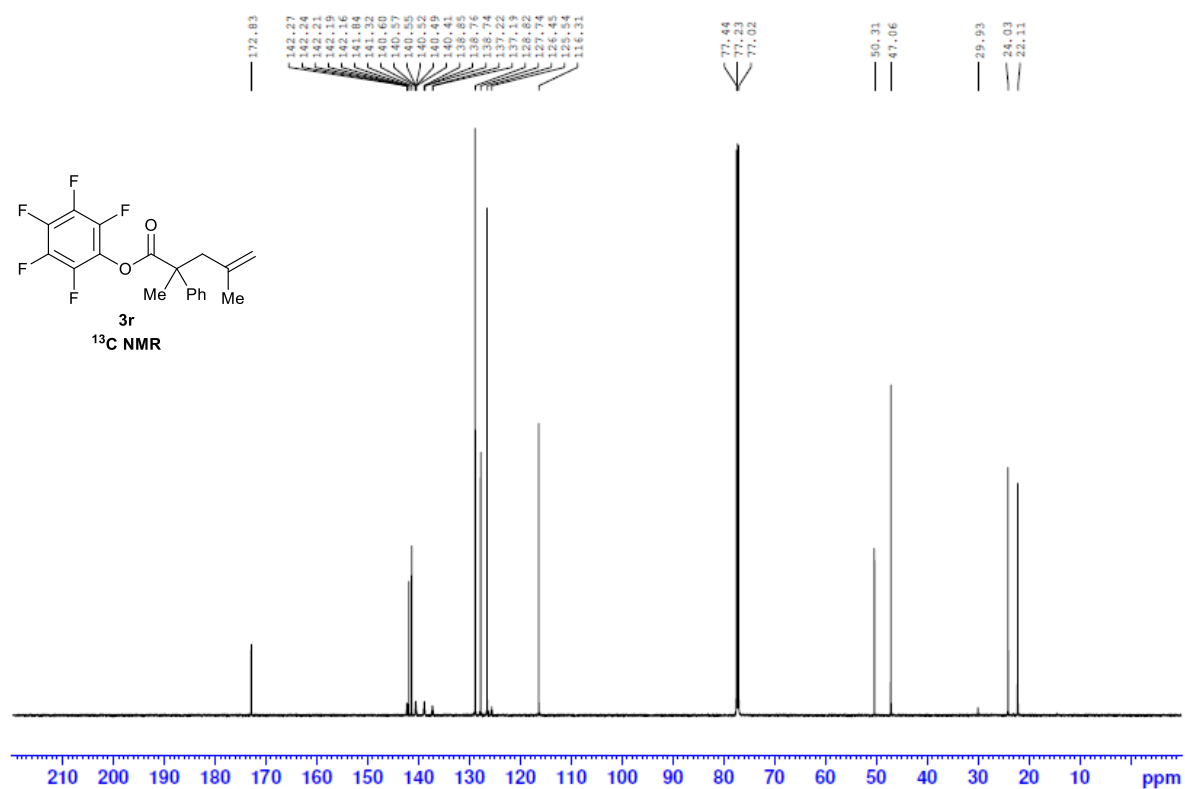
AI-14-51 13C



N123 AI13-97

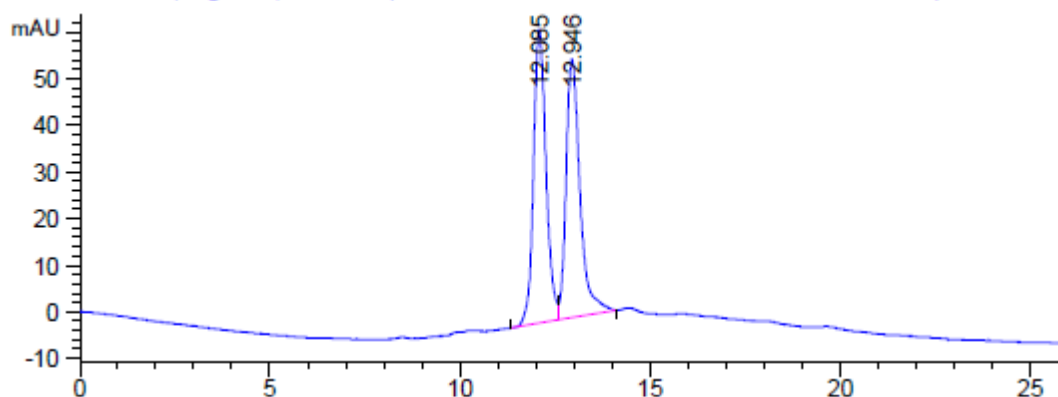


N123 AI13-97

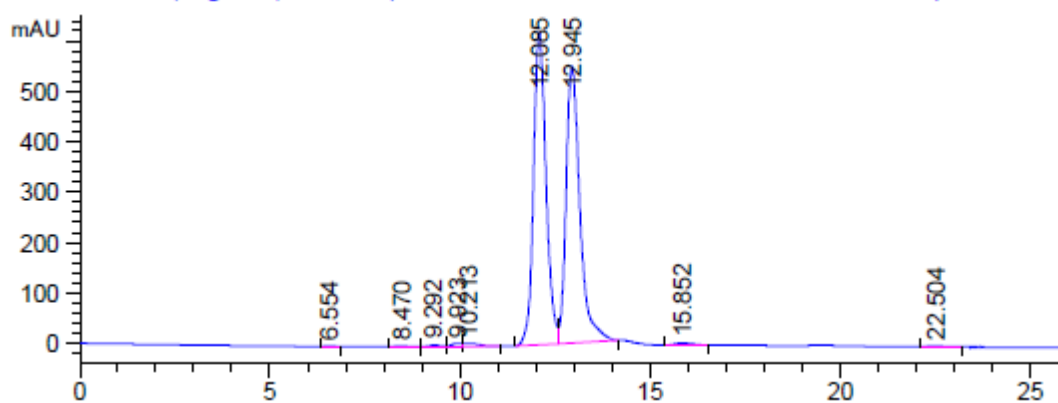


HPLC of (±)-3s:

DAD1 A, Sig=254,4 Ref=off (NESSAN150223 2023-02-23 17-48-16\001-0101.D)



DAD1 B, Sig=225,4 Ref=off (NESSAN150223 2023-02-23 17-48-16\001-0101.D)

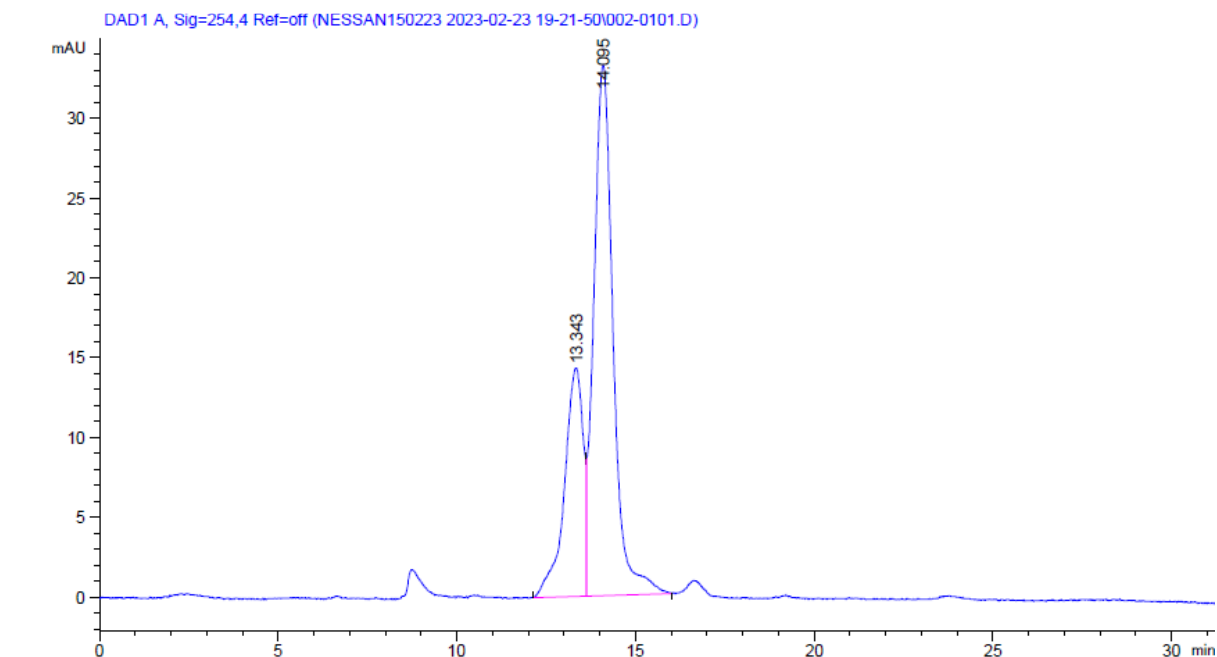


Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.085	BV	0.3522	1444.82642	62.86125	37.9977
2	12.946	VB	0.3881	1415.11243	55.38816	37.2162
3	30.425	BB	0.6422	496.19916	9.12730	13.0496
4	40.865	BBA	0.6233	446.26981	8.57286	11.7365

Totals : 3802.40781 135.94958

HPLC of (-)-3s:

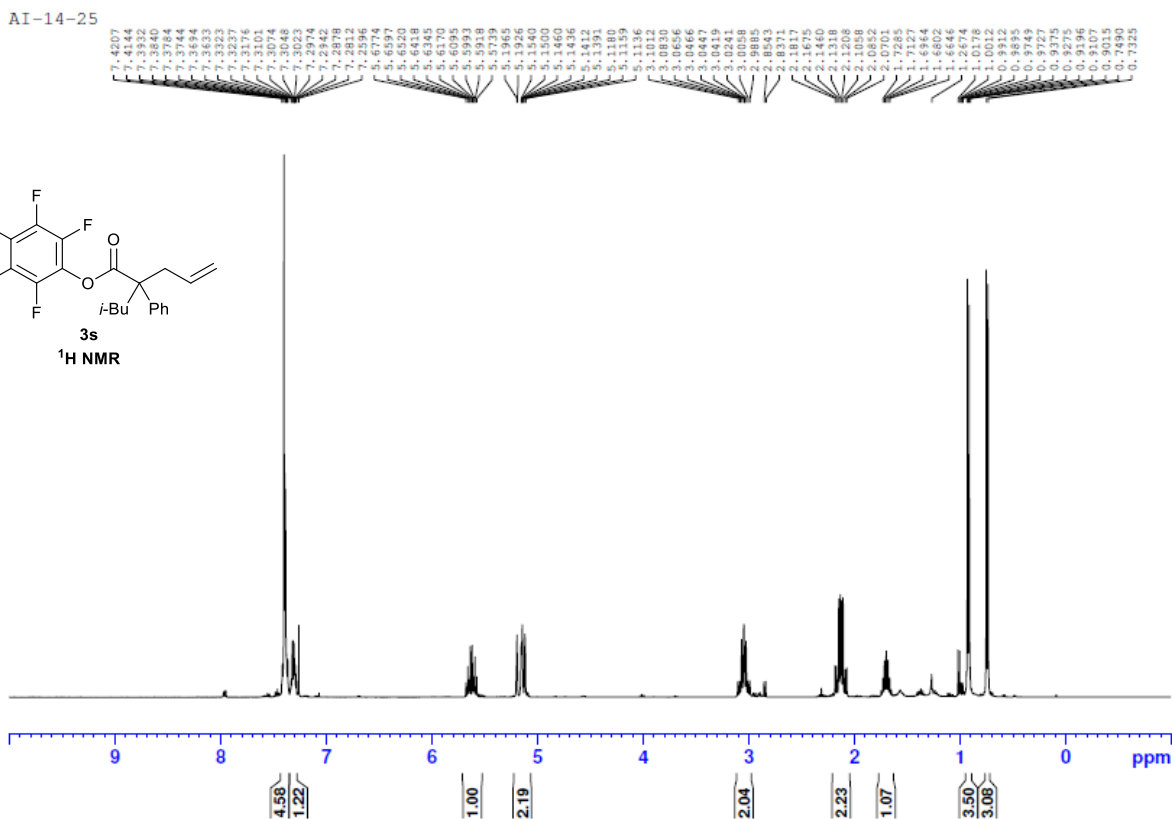
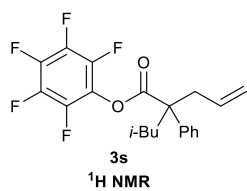


Signal 1: DAD1 A, Sig=254,4 Ref=off

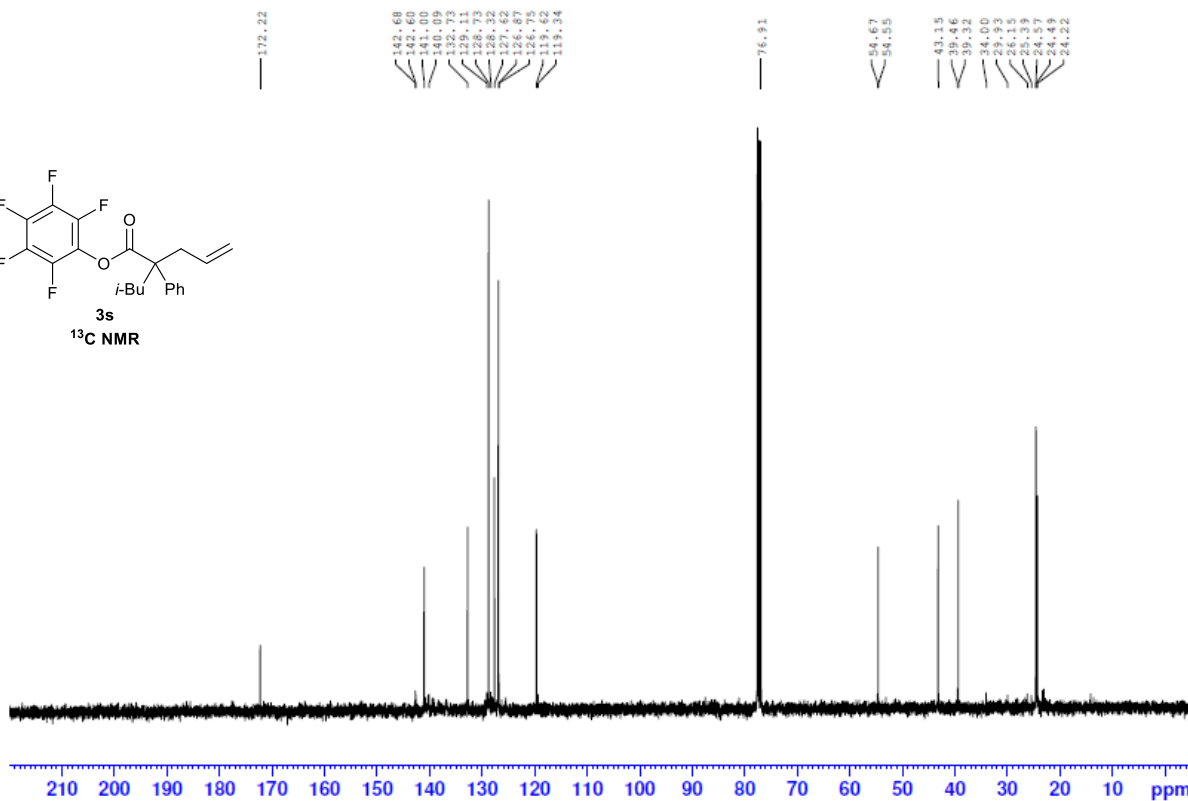
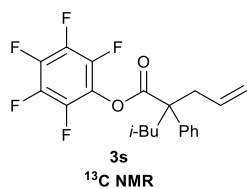
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.343	BV	0.4815	521.22314	14.29210	29.3481
2	14.095	VB	0.5607	1254.77966	33.21686	70.6519

Totals : 1776.00281 47.50896

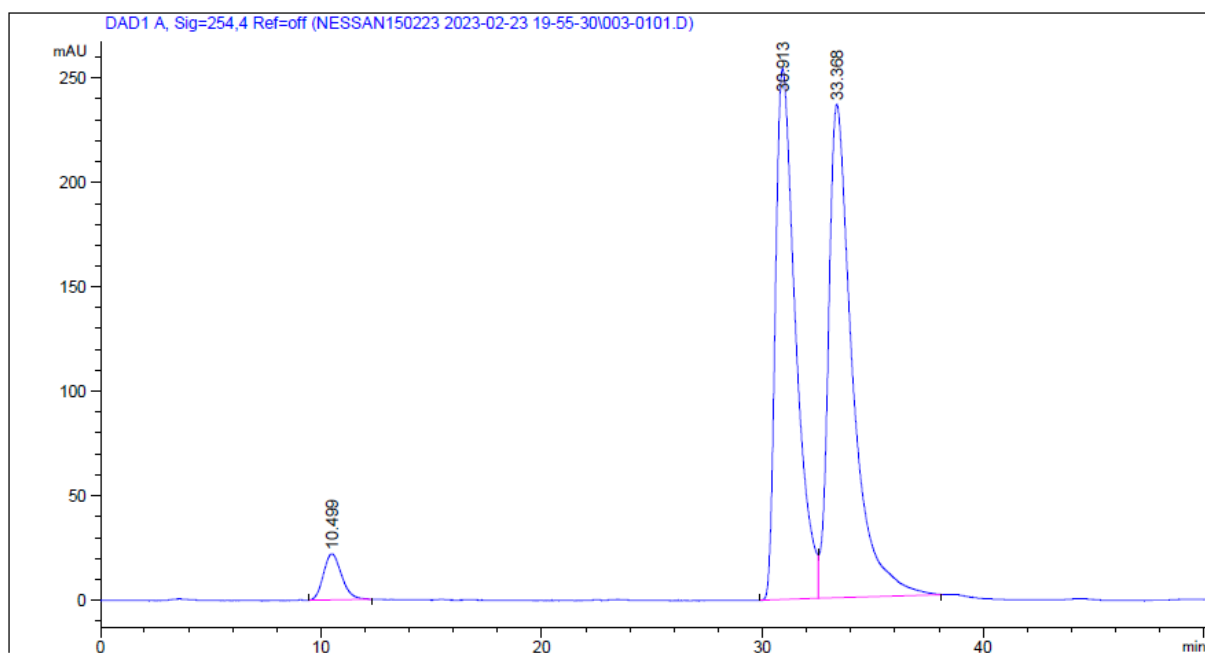
AI-14-25



AI-14-25 13C



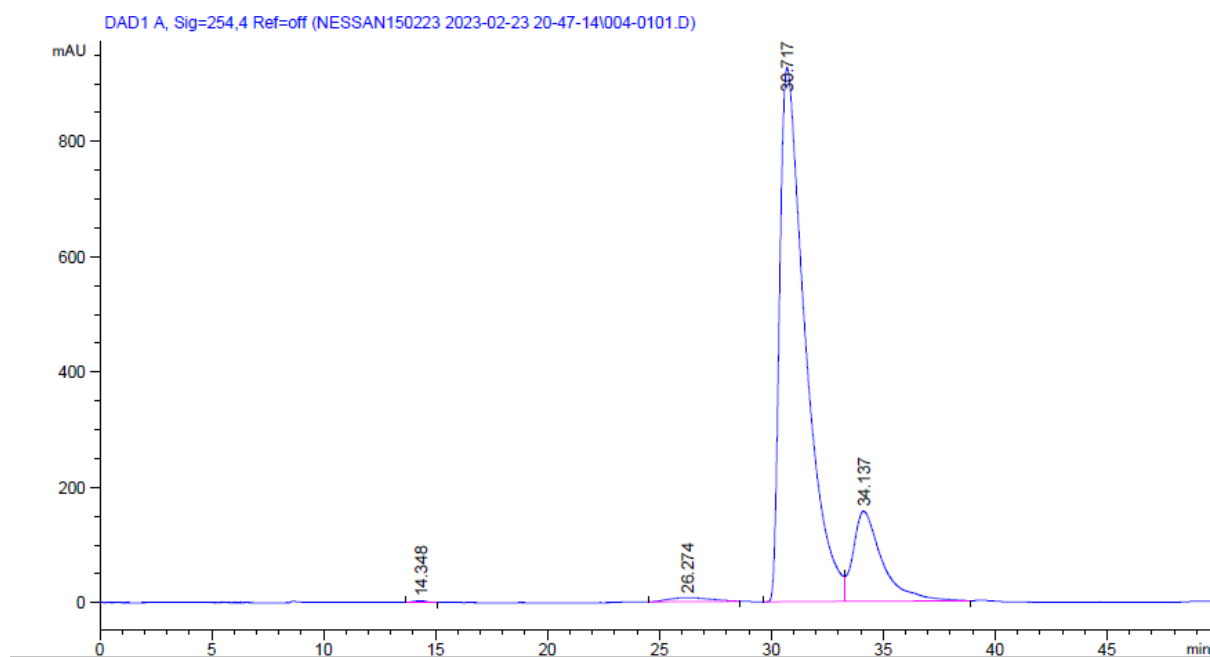
HPLC of (±)-3t:



Signal 1: DAD1 A, Sig=254,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.499	BB	0.7713	1253.76489	21.98618	3.5586
2	30.913	BV	0.9330	1.61216e4	254.49852	45.7578
3	33.368	VB	1.0855	1.78571e4	236.34566	50.6836
Totals :				3.52324e4	512.83036	

HPLC of (+)-3t:

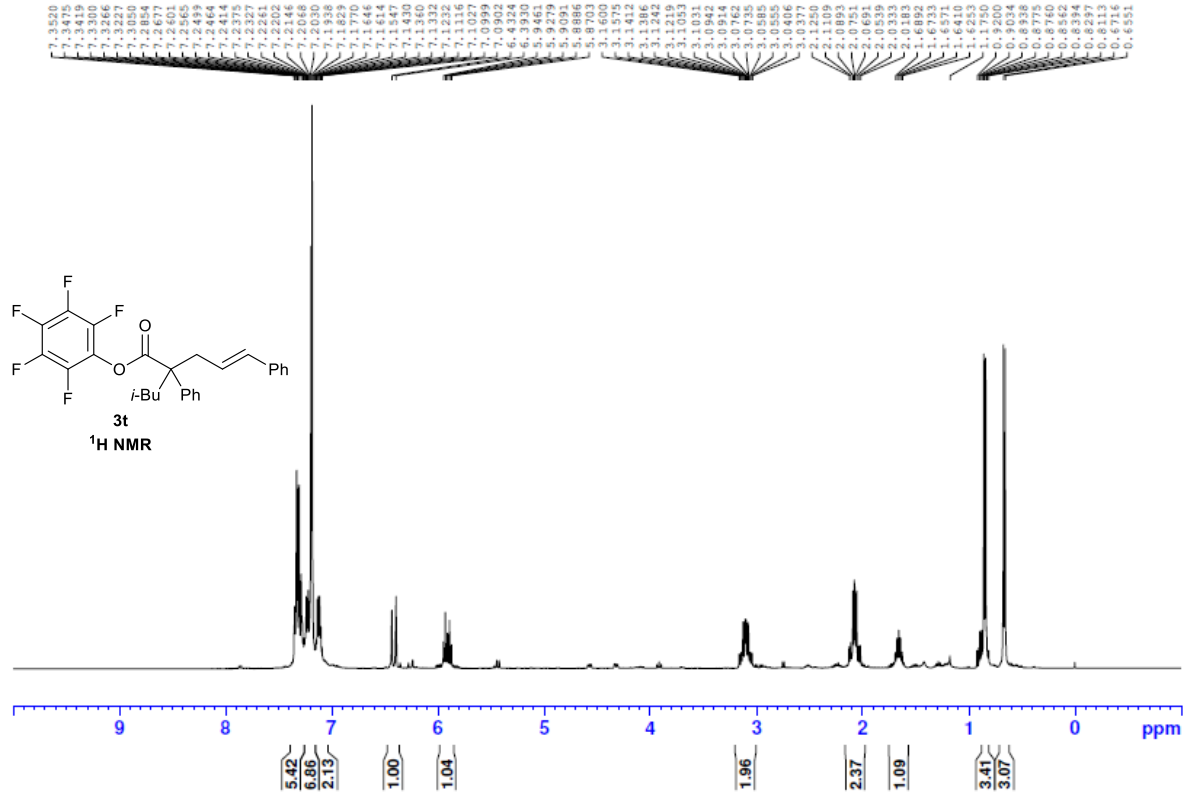


Signal 1: DAD1 A, Sig=254,4 Ref=off

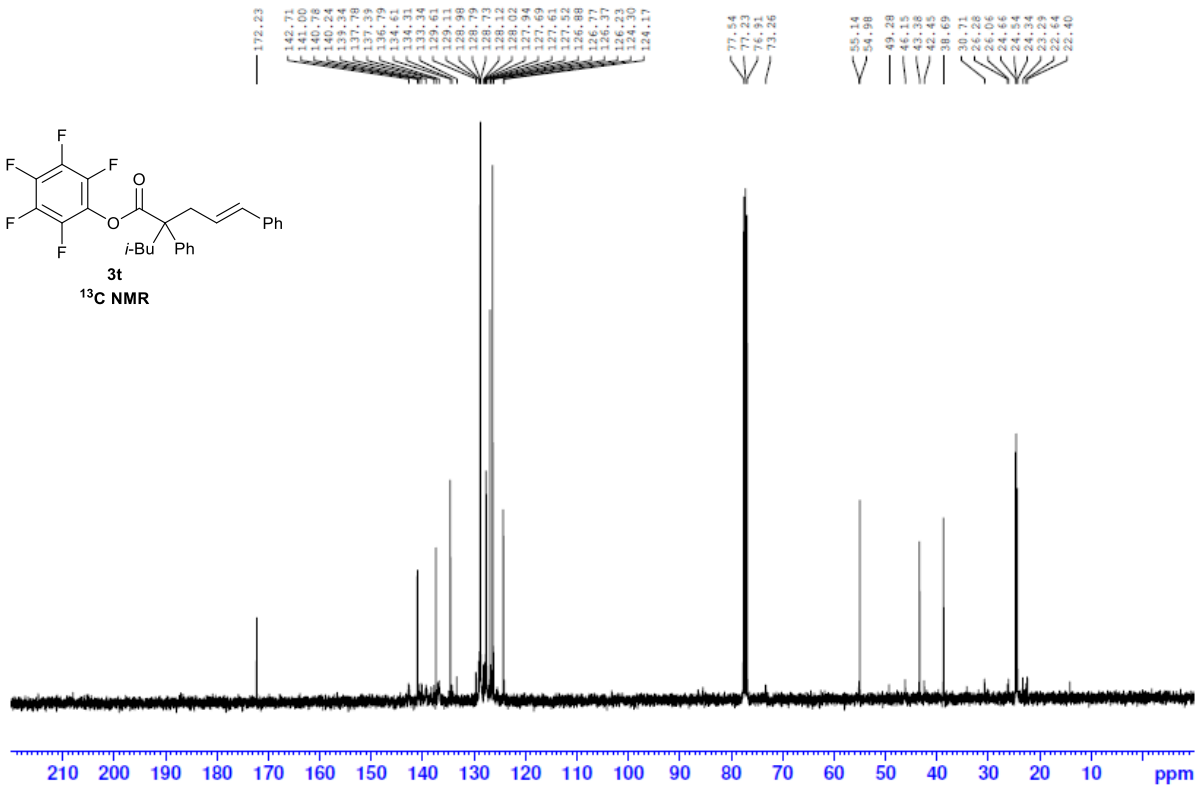
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.348	BB	0.4477	110.85670	2.95449	0.1254
2	26.274	BB	1.4780	864.31897	6.85980	0.9774
3	30.717	BV	1.1107	7.33043e4	926.83331	82.8962
4	34.137	VB	1.2717	1.41495e4	156.36760	16.0010

Totals : 8.84290e4 1093.01520

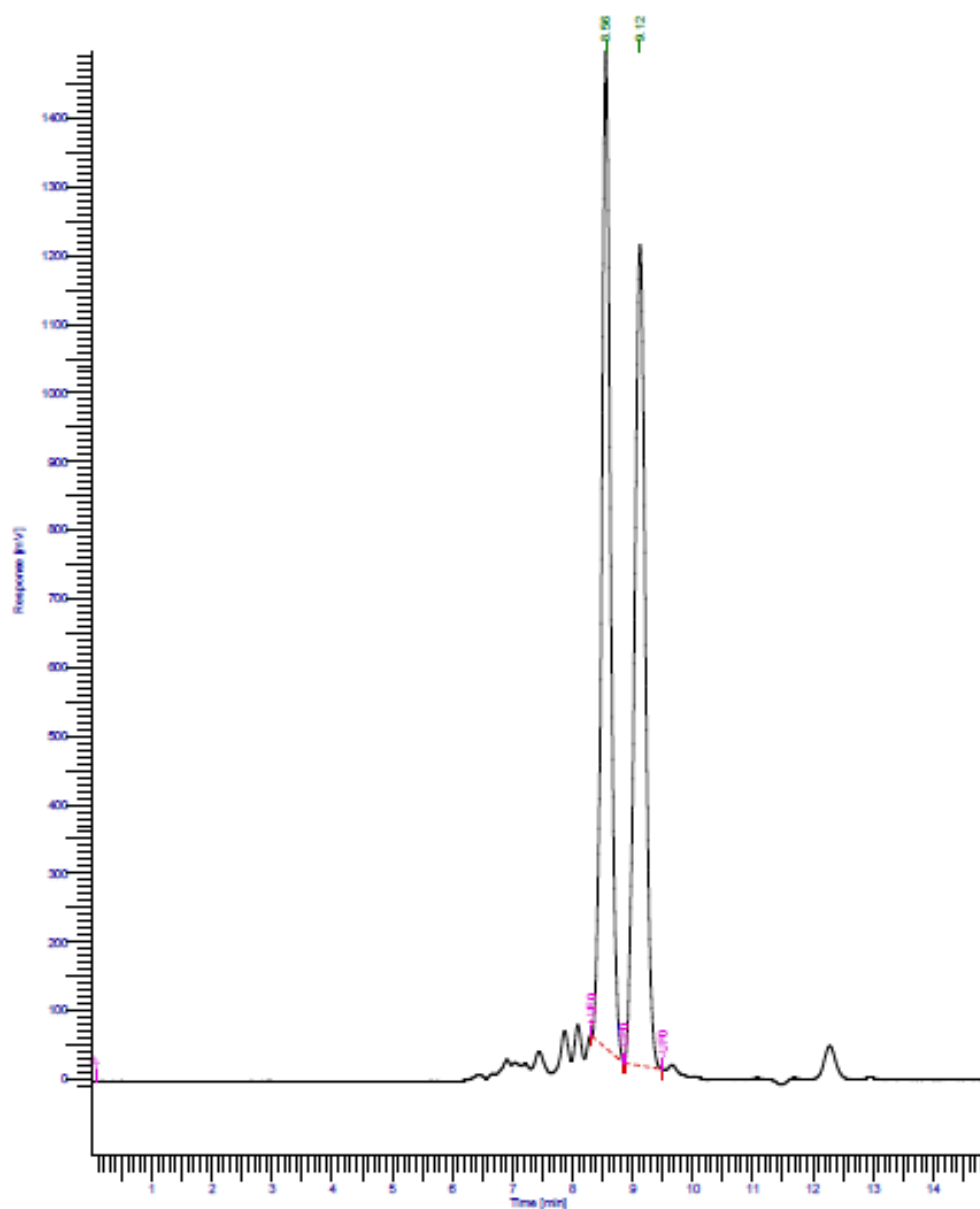
AI-14-23



AI-13-23 13C

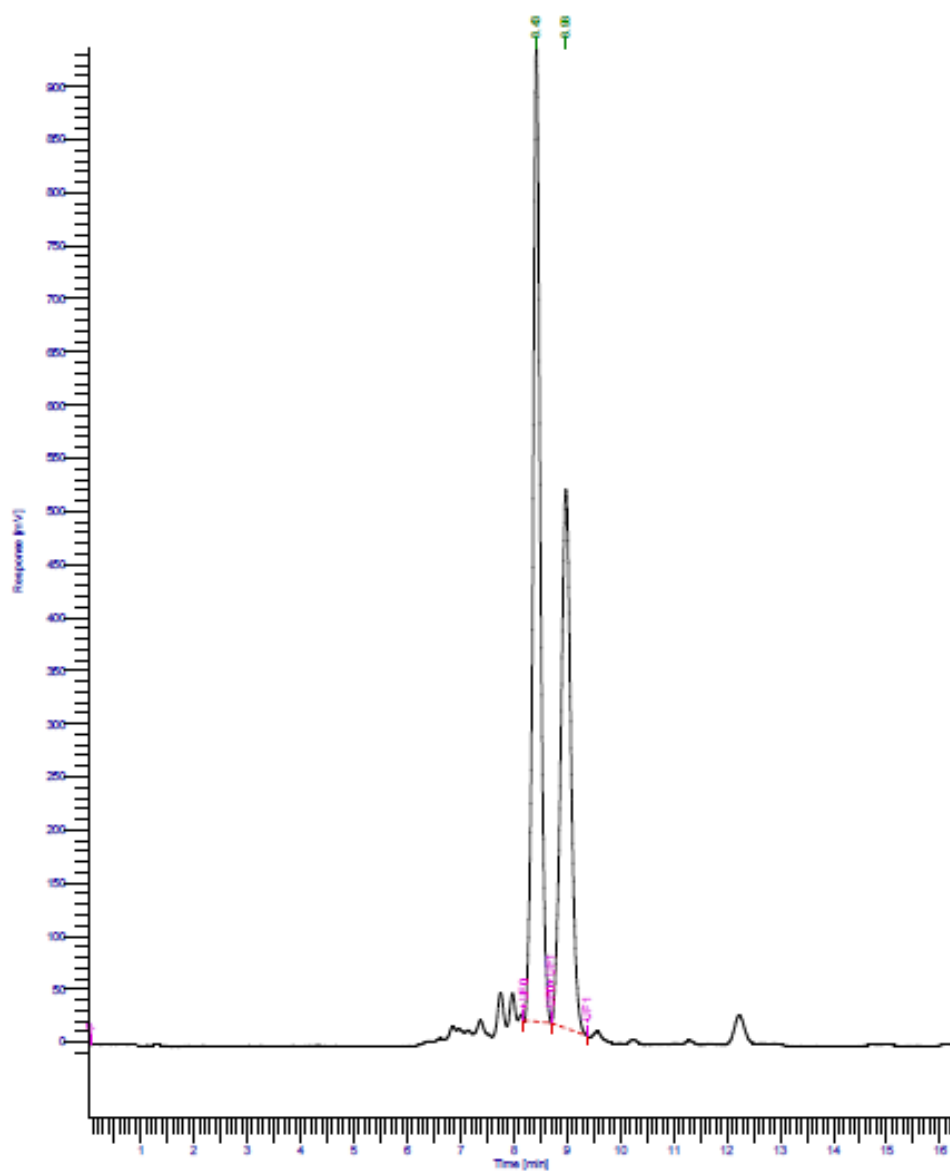


HPLC of (±)-3u:



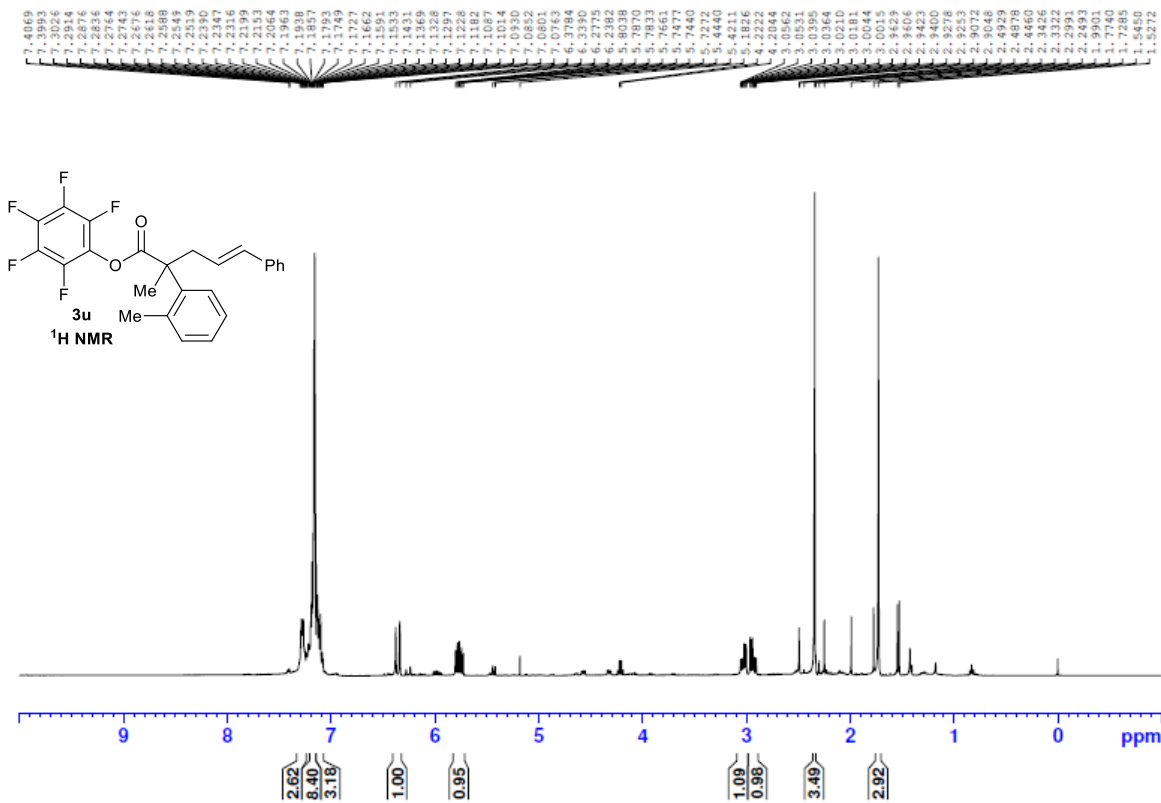
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	8.558	14898360.13	1.45e+06	50.00	50.00	*MM	10.2544
2	9.123	14896665.77	1.20e+06	50.00	50.00	*MM	12.4589
		29795025.90	2.65e+06	100.00	100.00		

HPLC of enantioenriched **3u**:

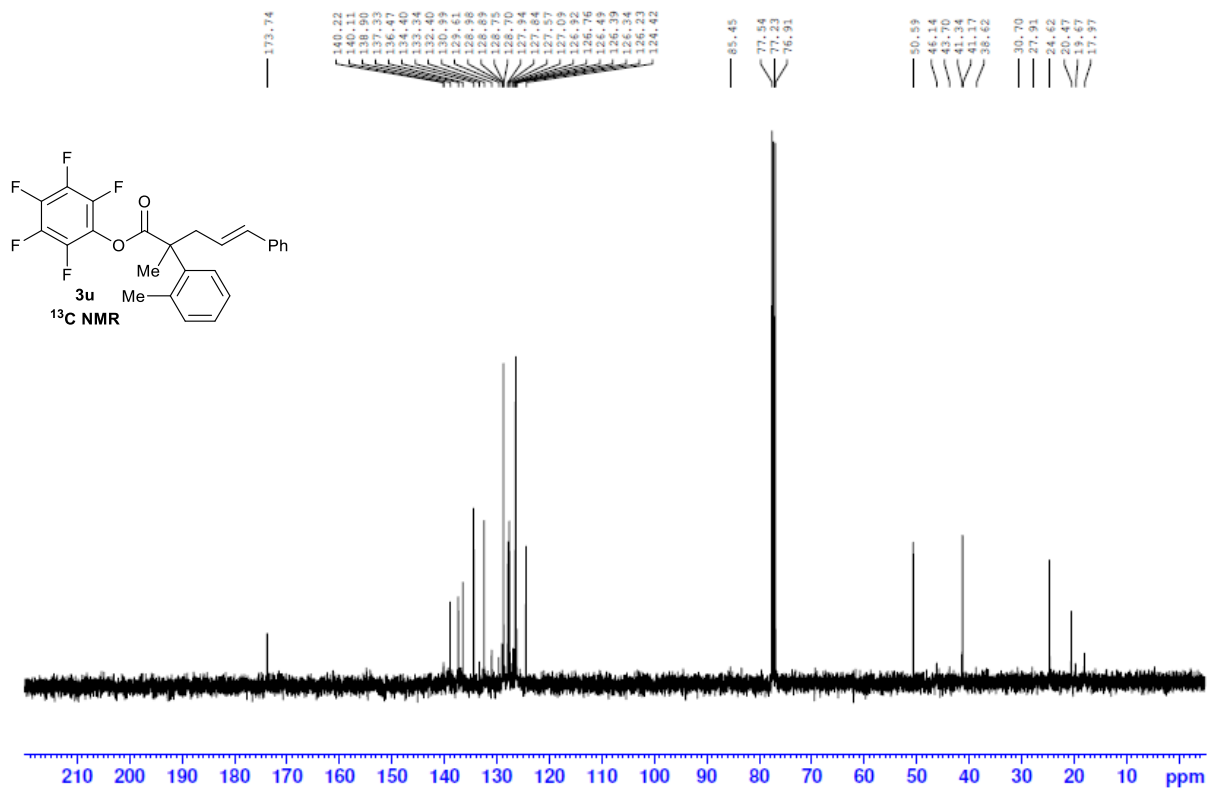


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	8.426	8868226.34	917258.63	56.98	56.98	*MM	9.6682
2	8.983	6694931.12	507332.59	43.02	43.02	*MM	13.1963
		15563157.46	1.42e+06	100.00	100.00		

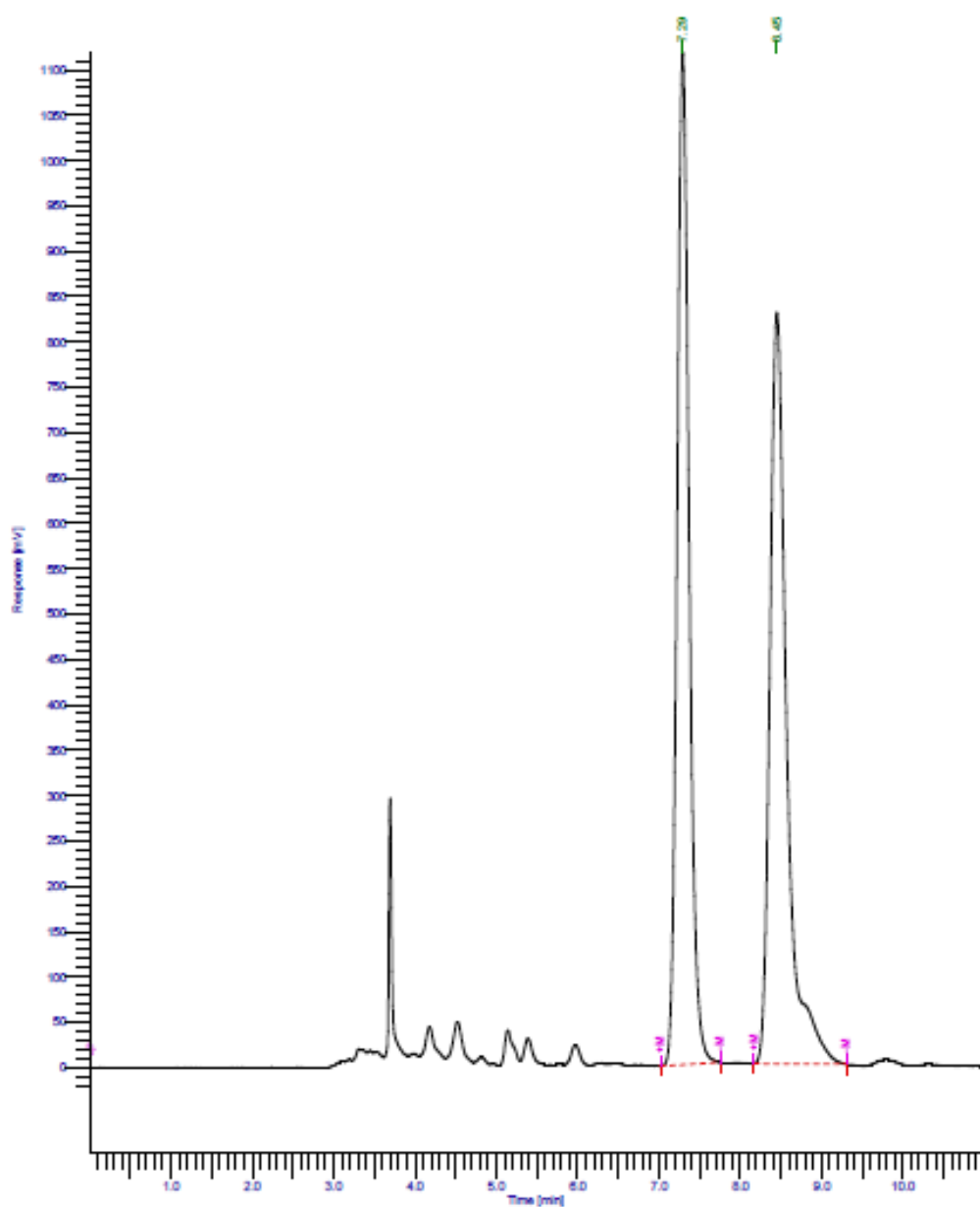
AI-14-43



AI-13-43 13C

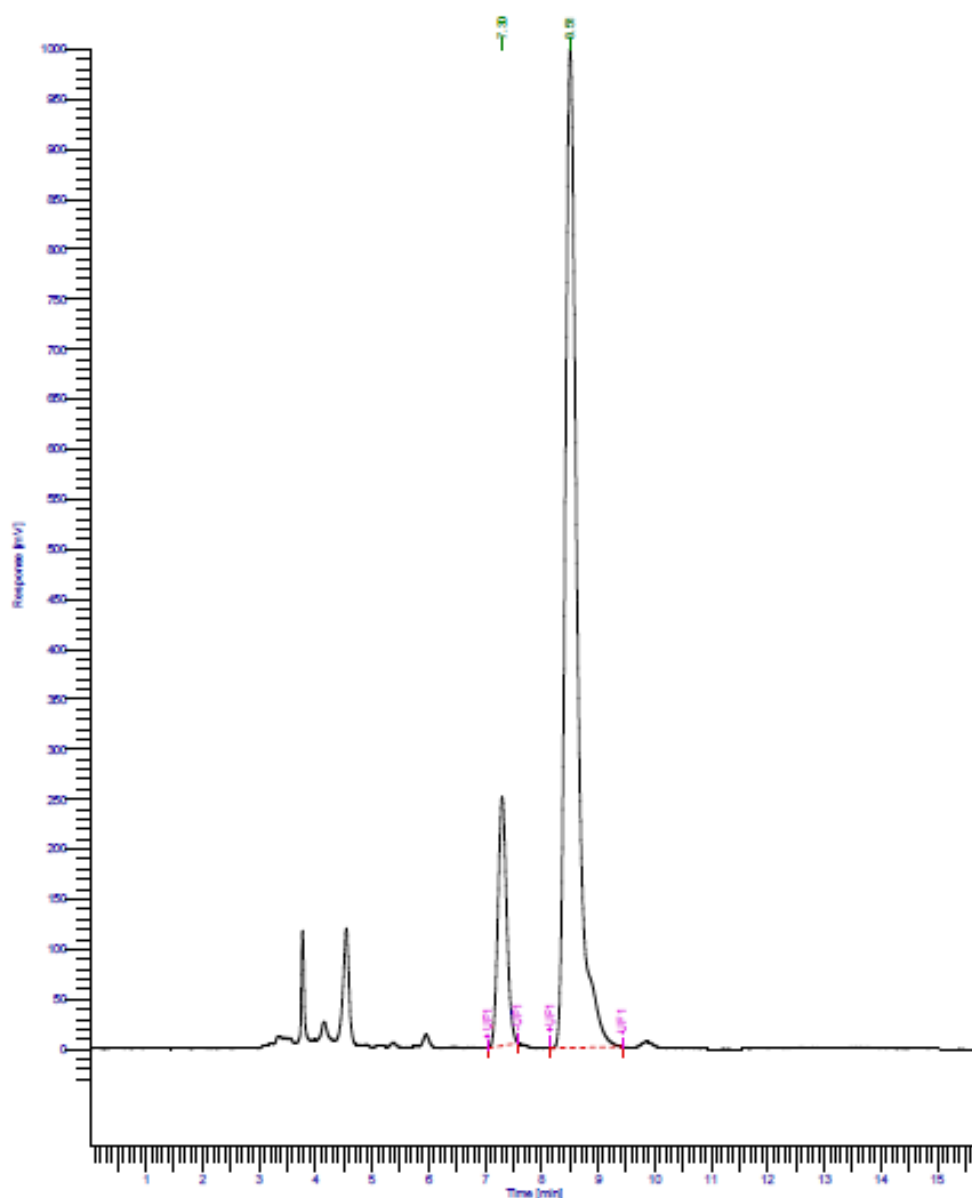


HPLC of (±)-3v:



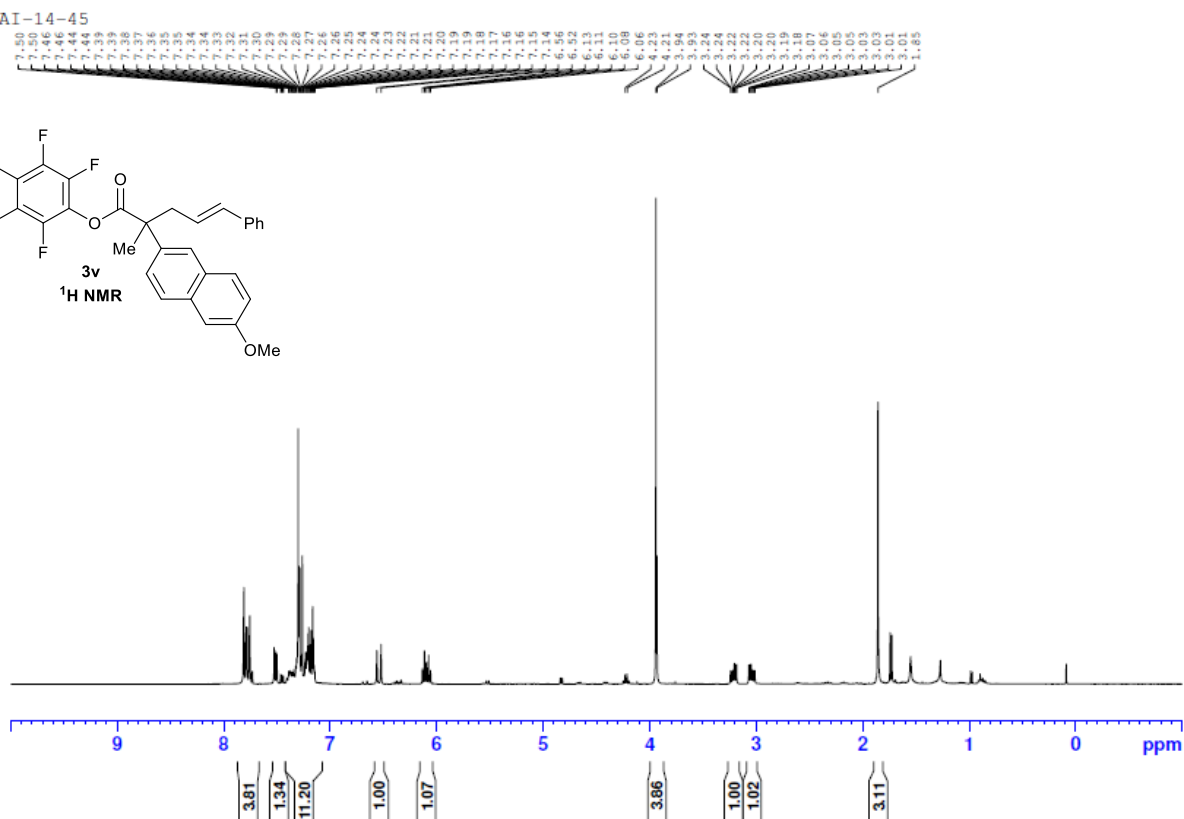
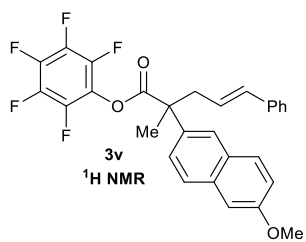
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.291	11510187.71	1.12e+06	49.15	49.15	*BB	10.3037
2	8.450	11909563.88	828391.72	50.85	50.85	*BB	14.3767
		23419751.60	1.95e+06	100.00	100.00		

HPLC of (+)-**3v**:

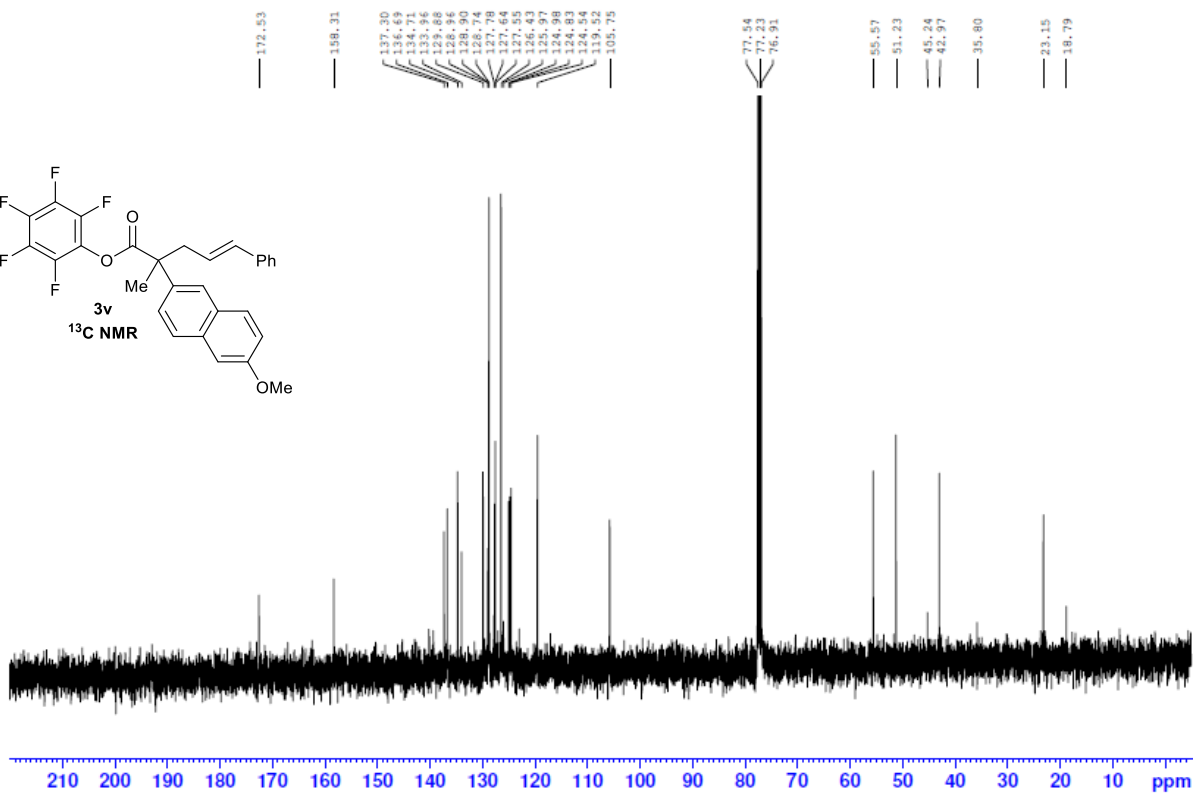
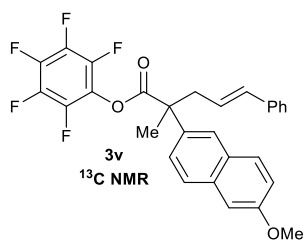


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.304	2669943.60	248753.77	15.44	15.44	*MM	10.7333
2	8.507	14623834.84	998752.93	84.56	84.56	*MM	14.6421
		17293778.43	1.25e+06	100.00	100.00		

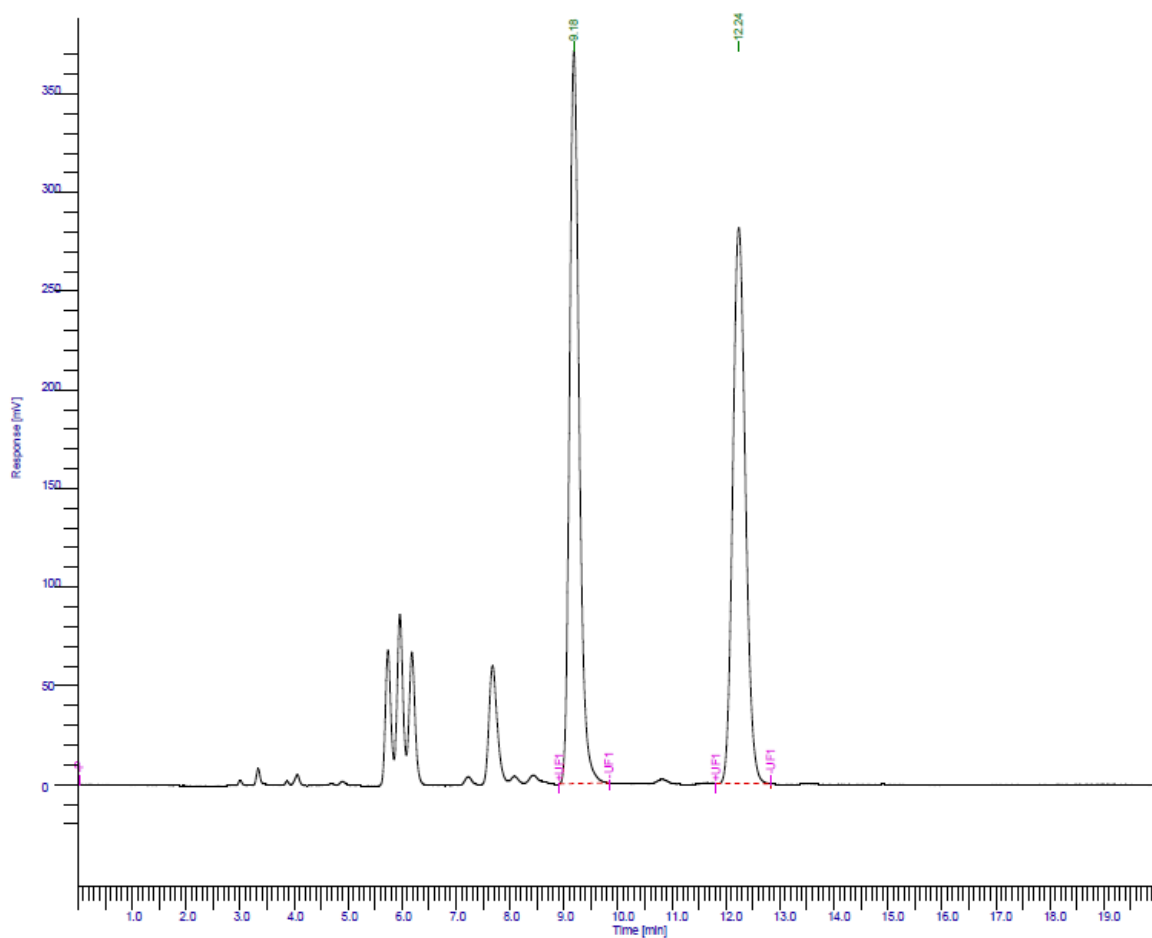
AI-14-45



AI-14-45 13C

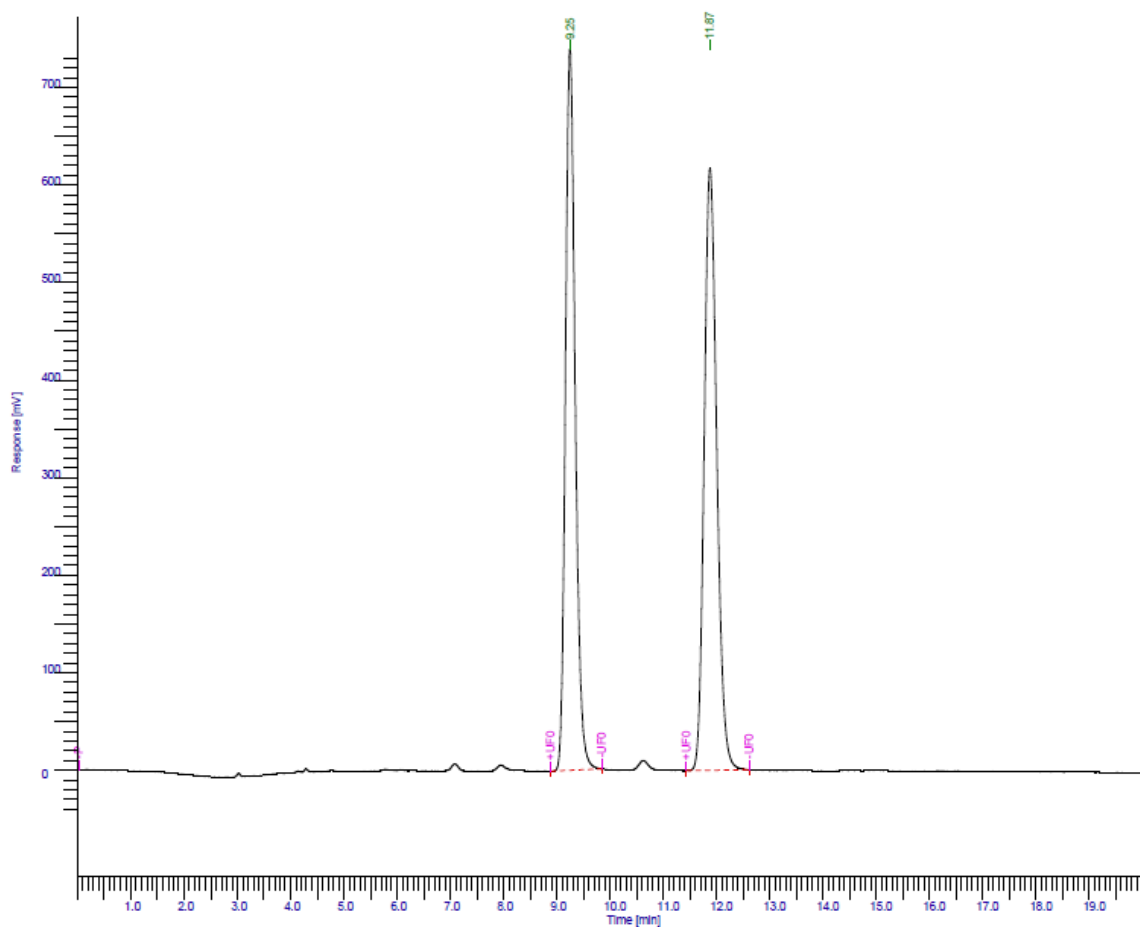


HPLC of (±)-3w:



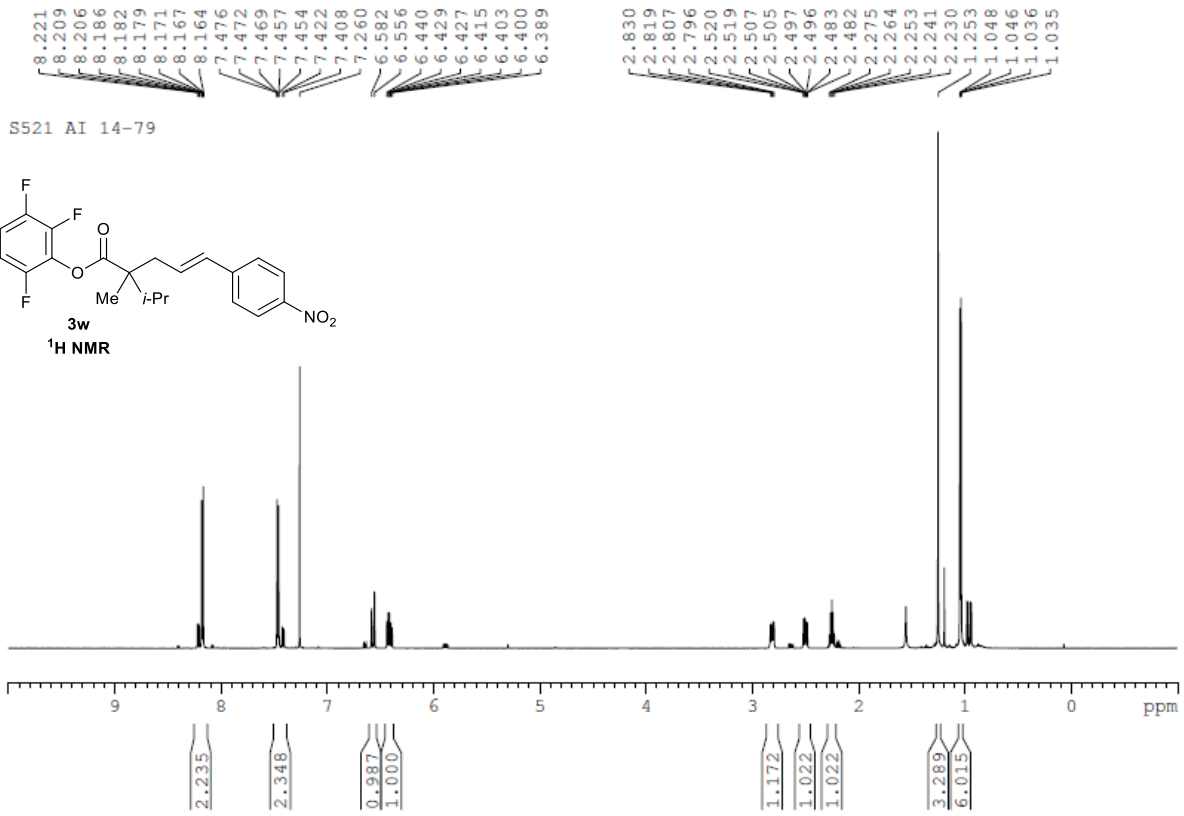
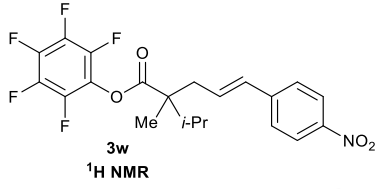
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	9.181	4618201.68	371453.09	50.40	50.40	*MM	12.4328
2	12.239	4545394.99	281707.42	49.60	49.60	*MM	16.1352
		9163596.66	653160.51	100.00	100.00		

HPLC of enantioenriched **3w**:

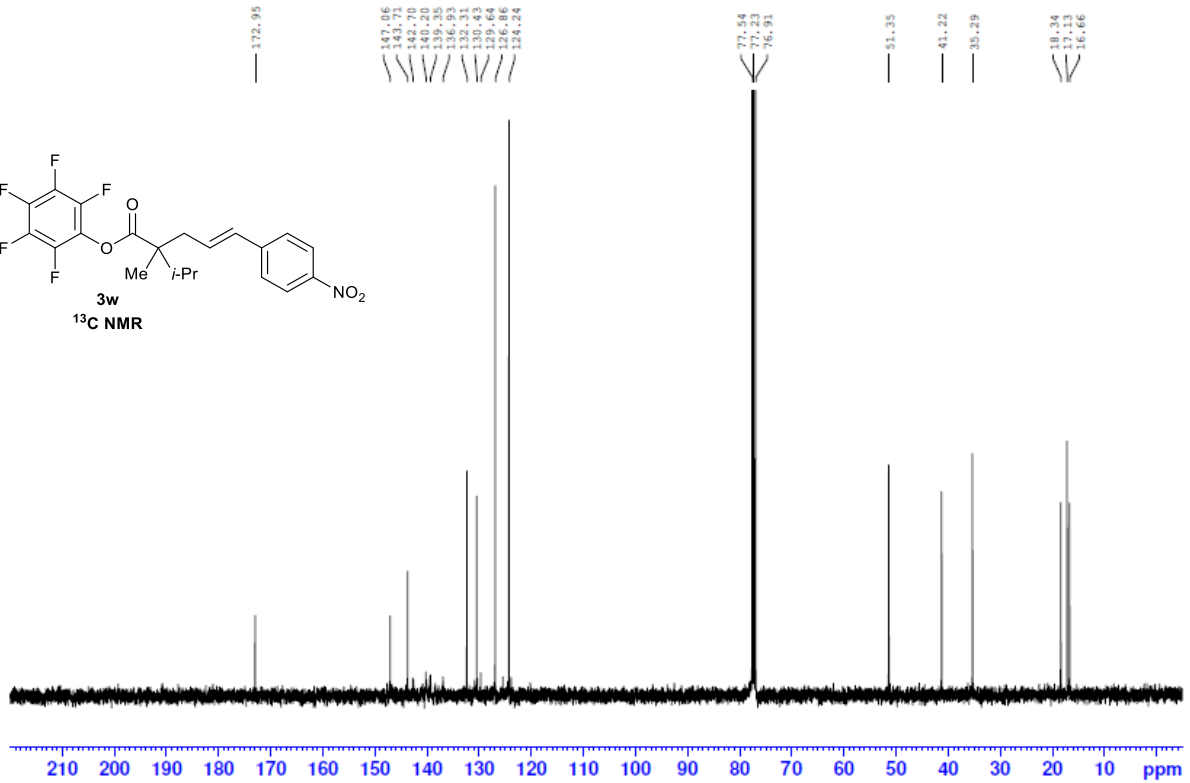
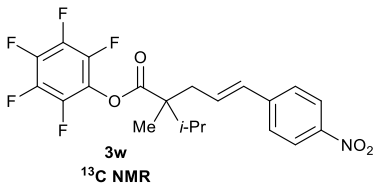


Peak #	Time [min]	Area [$\mu\text{V}\cdot\text{s}$]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	9.247	9439367.62	738986.58	48.28	48.28	*MM	12.7734
2	11.873	10113408.05	616990.69	51.72	51.72	*MM	16.3915
		19552775.67	1.36e+06	100.00	100.00		

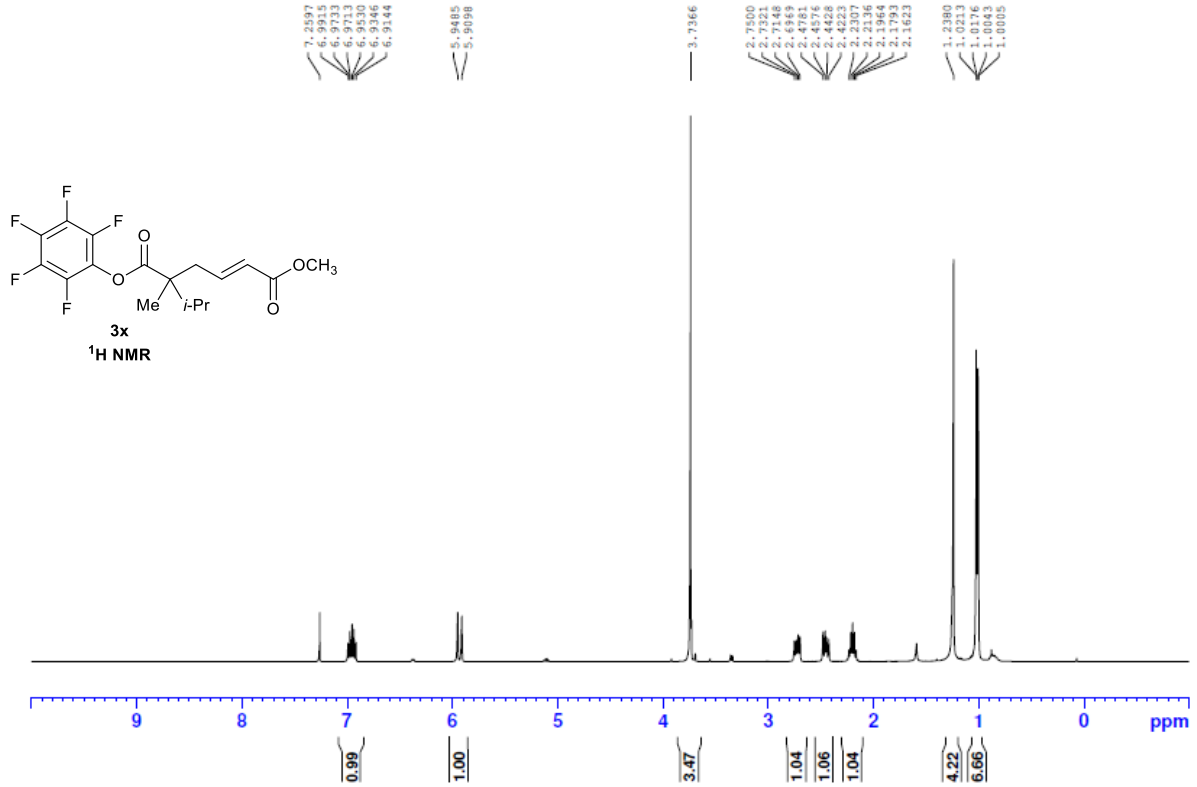
S521 AI 14-79



AI-14-79 13C



AI-14-80



AI-13-80 13C

