

*Supporting Information*

**Ru-Catalyzed Asymmetric Hydrogenation of  $\delta$ -Keto Weinreb Amides:  
Enantioselective Synthesis of (+)-Centrolobine**

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Shanghai 200240, China

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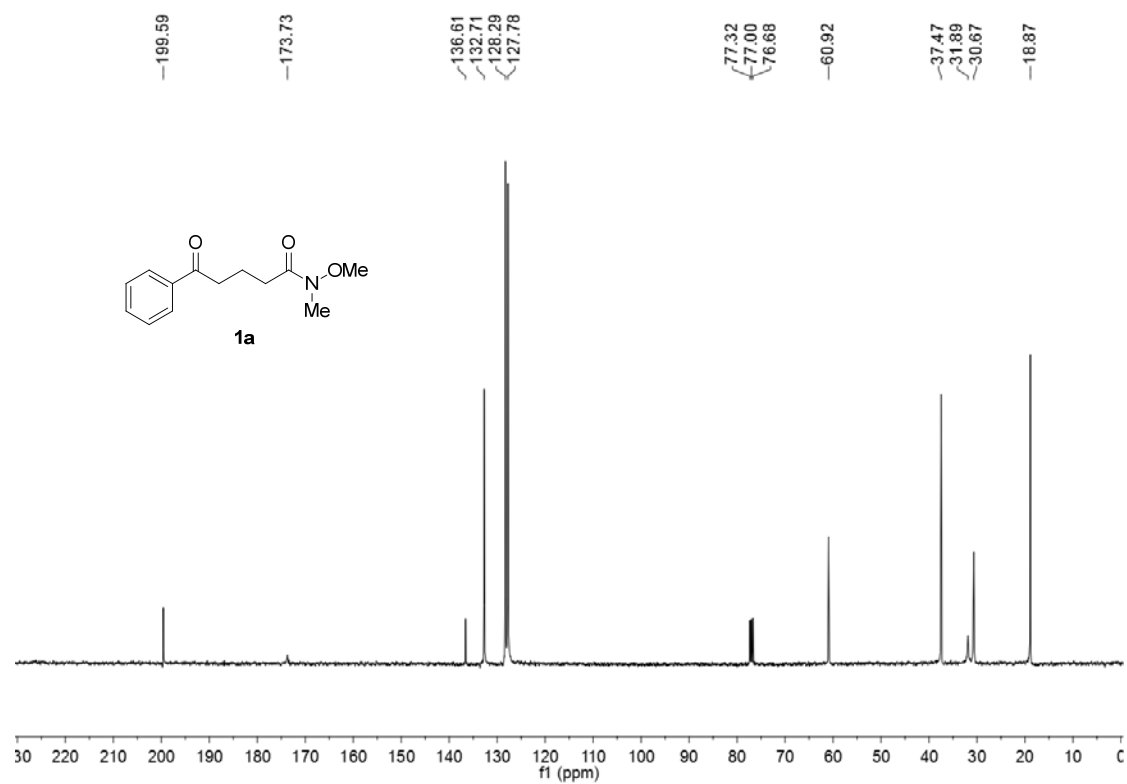
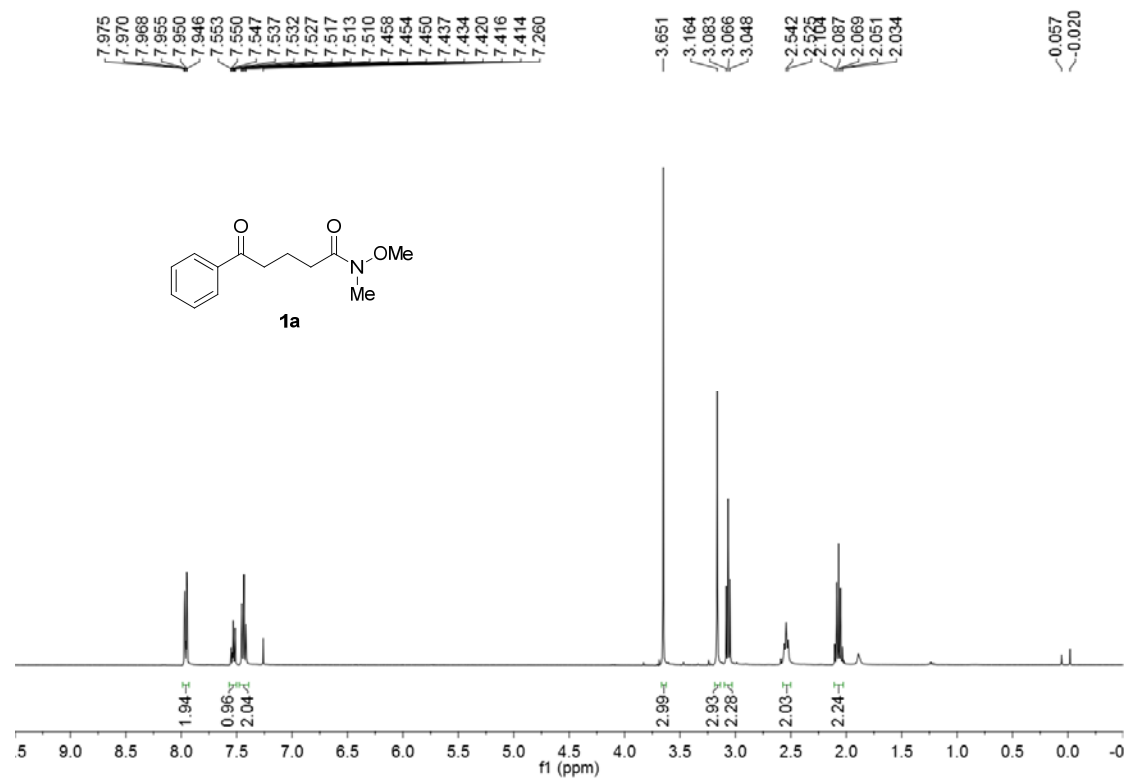
[zhaoguo@sjtu.edu.cn](mailto:zhaoguo@sjtu.edu.cn)

**Table of Contents**

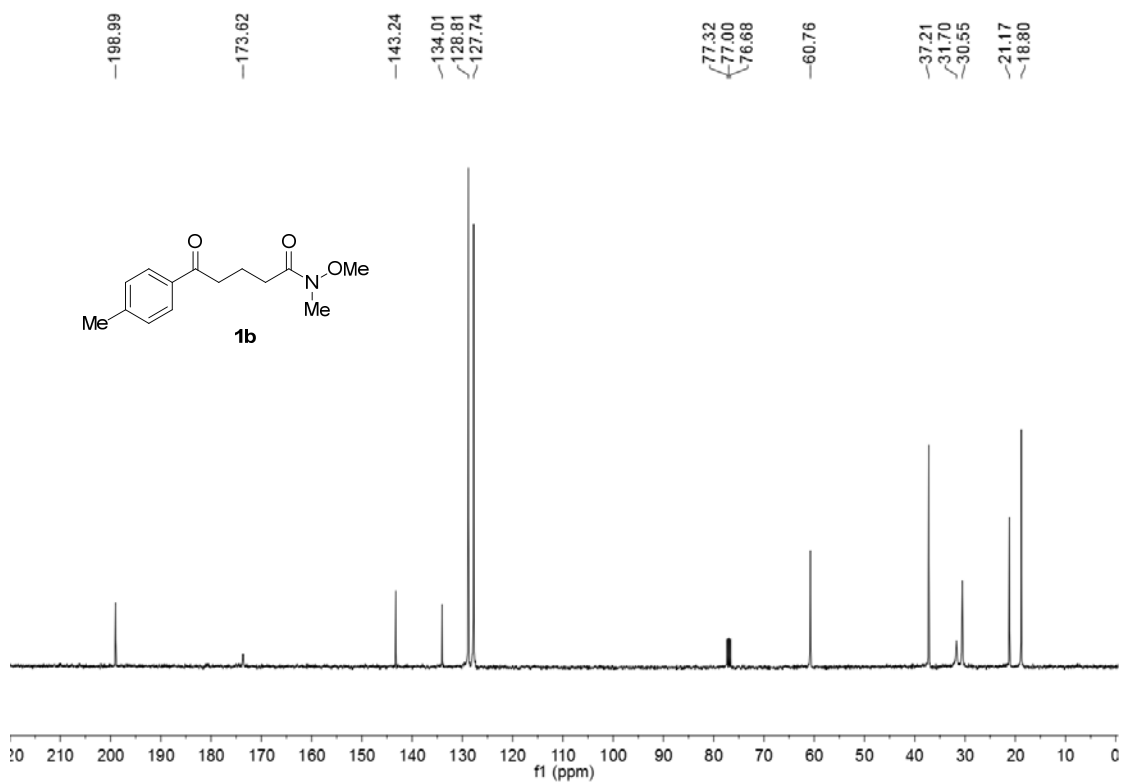
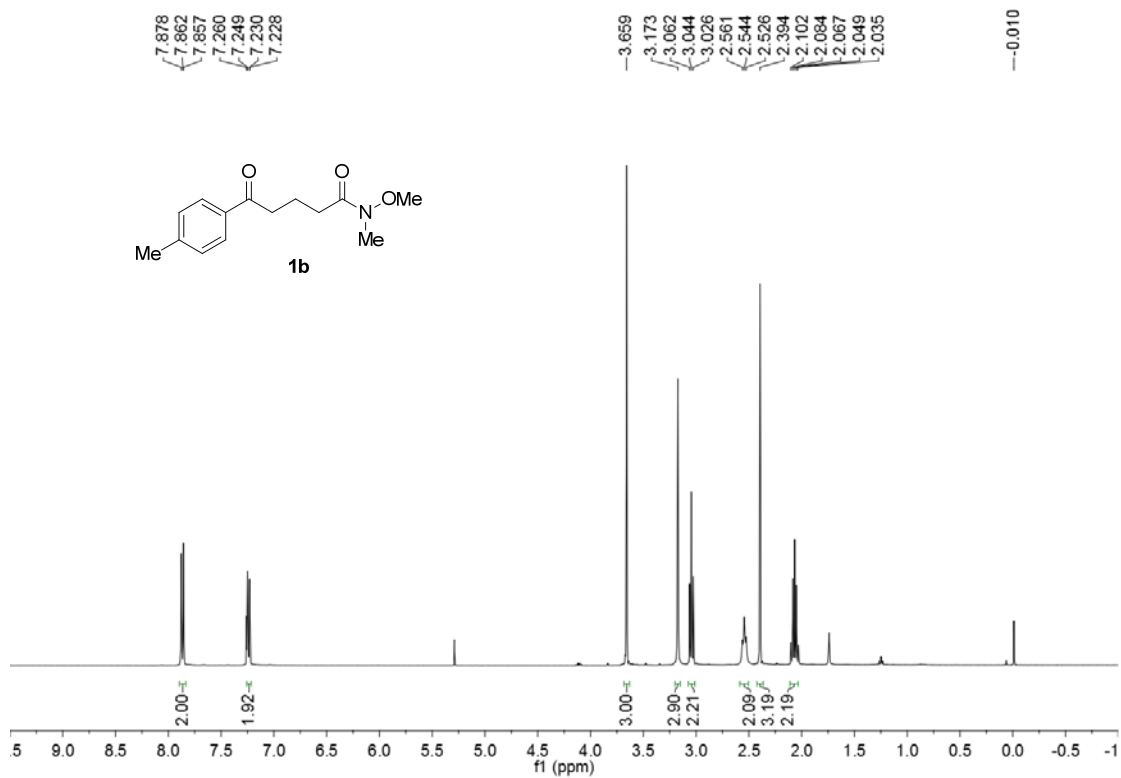
<b>NMR data for compounds 1, 2.....</b>	<b>S2</b>
<b>HPLC for racemic and chiral compounds 2.....</b>	<b>S32</b>

Copy of NMR spectra for 1, 2

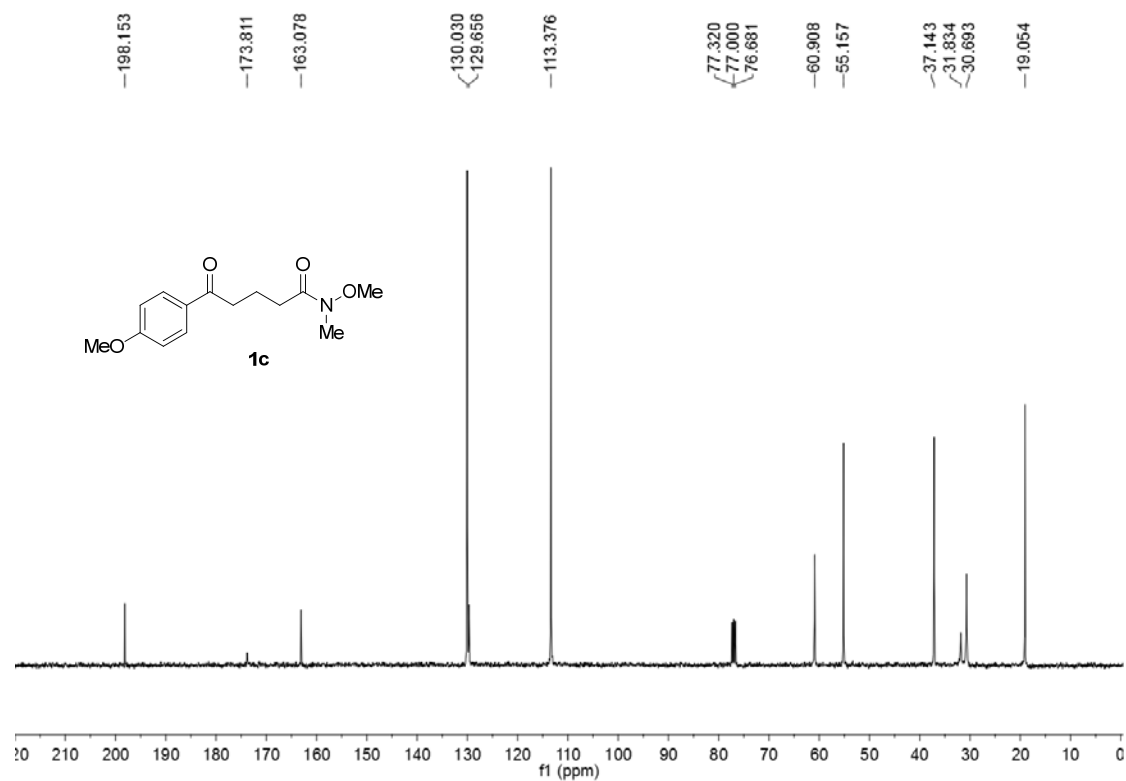
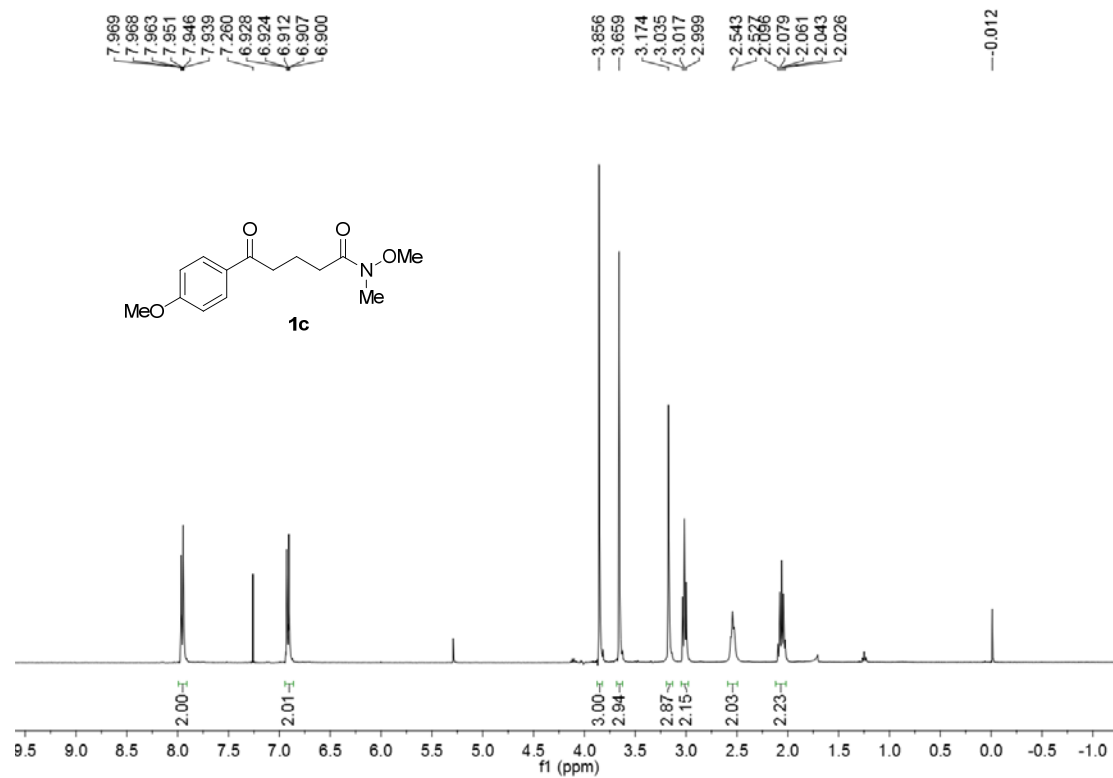
*N*-Methoxy-*N*-methyl-5-oxo-5-phenylpentanamide, (1a)



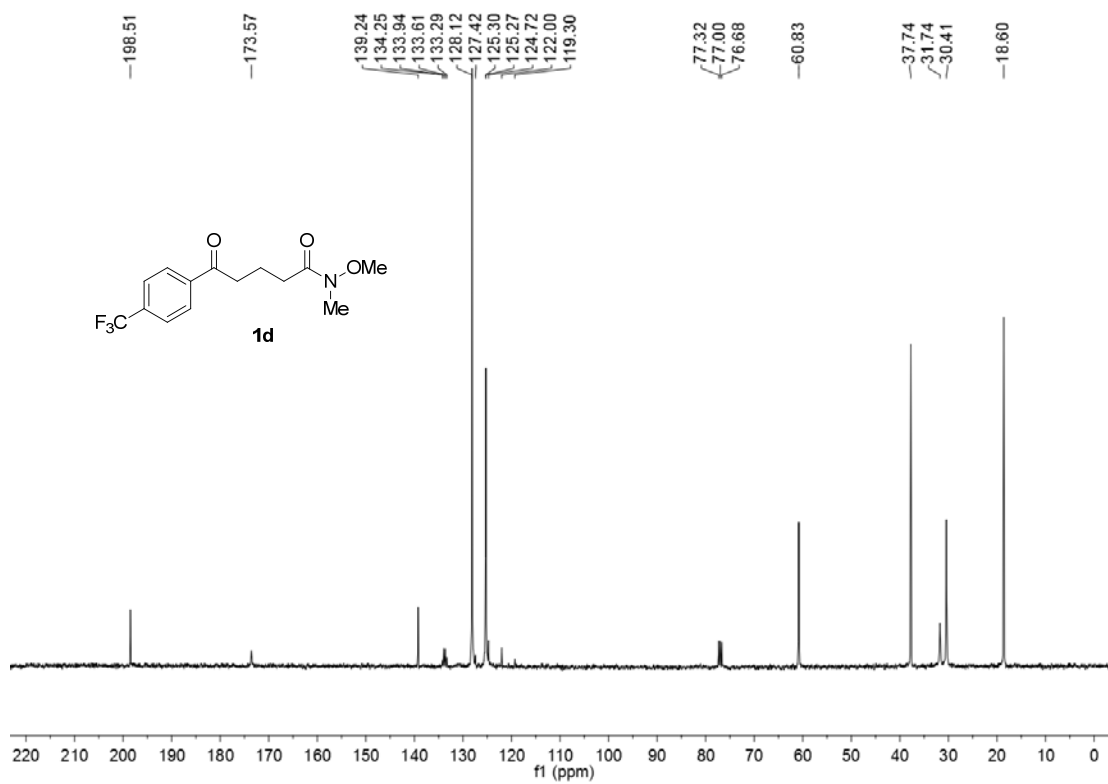
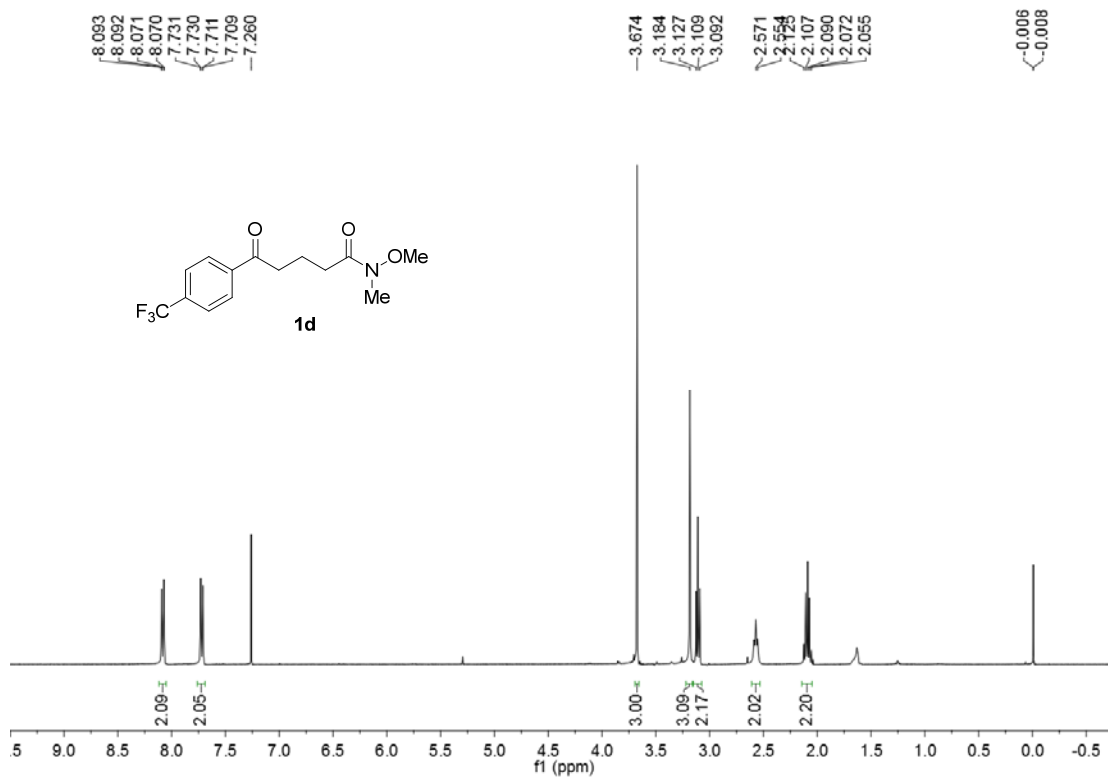
***N*-Methoxy-*N*-methyl-5-oxo-5-(*p*-tolyl)pentanamide, (1b)**



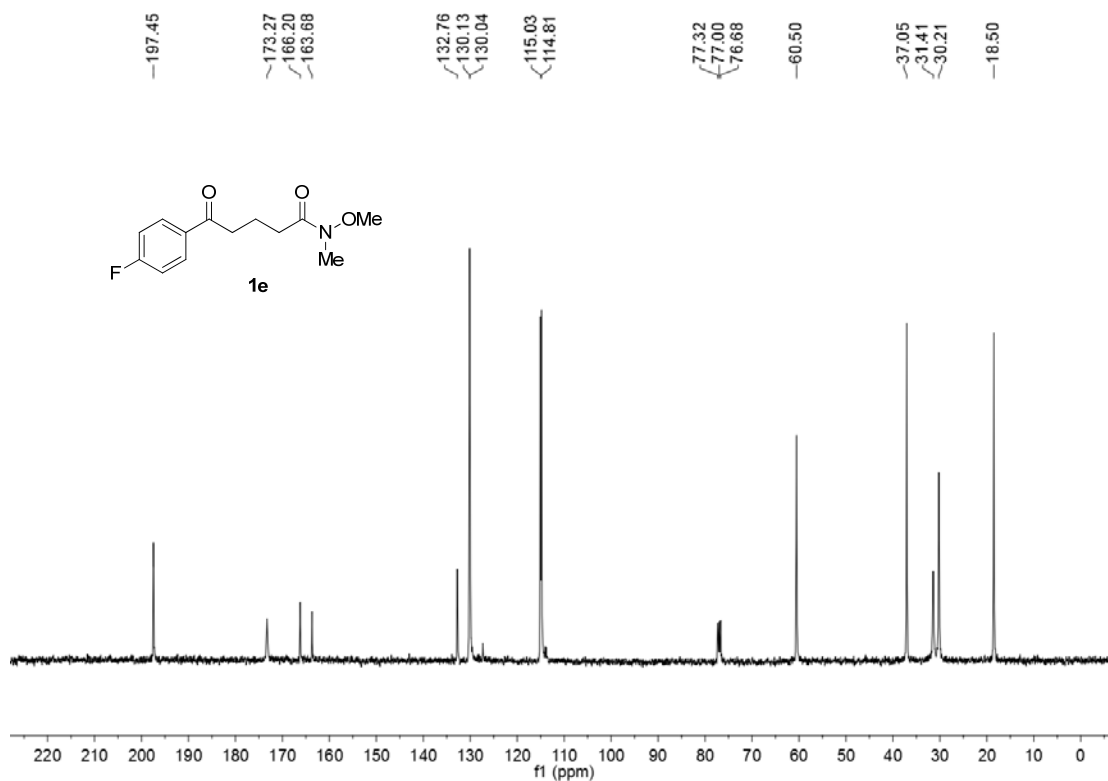
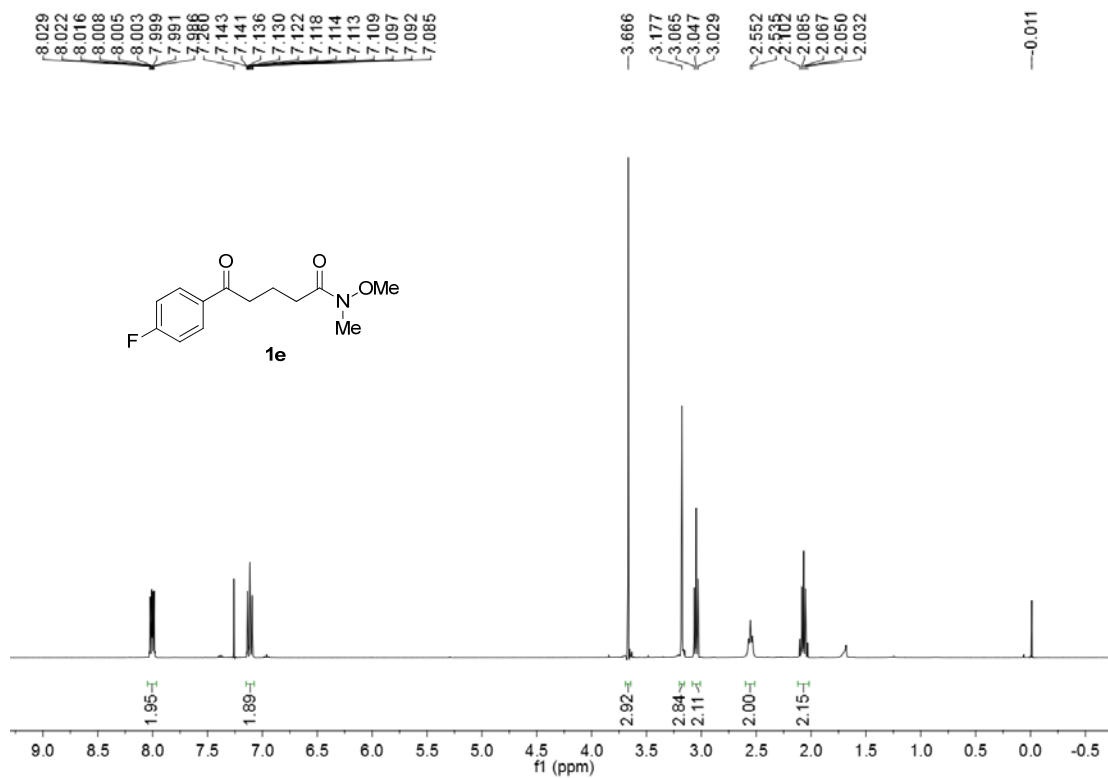
***N*-Methoxy-*N*-methyl-5-oxo-5-(4-methoxyphenyl)pentanamide, (1c)**



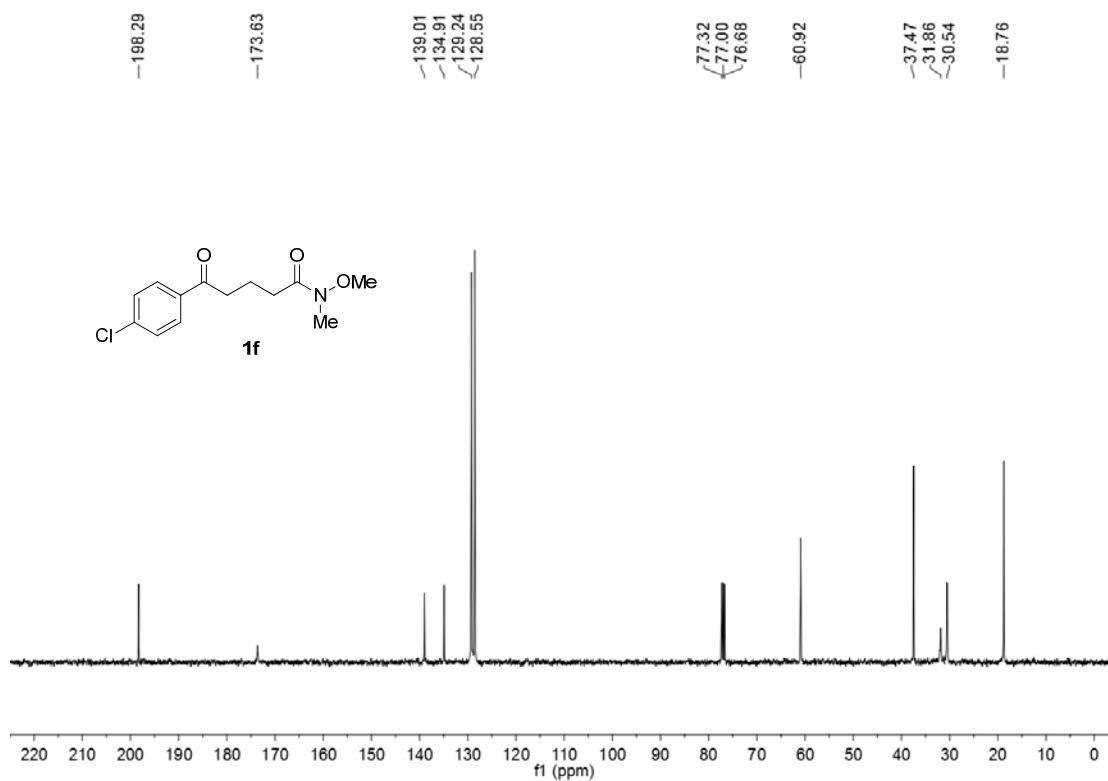
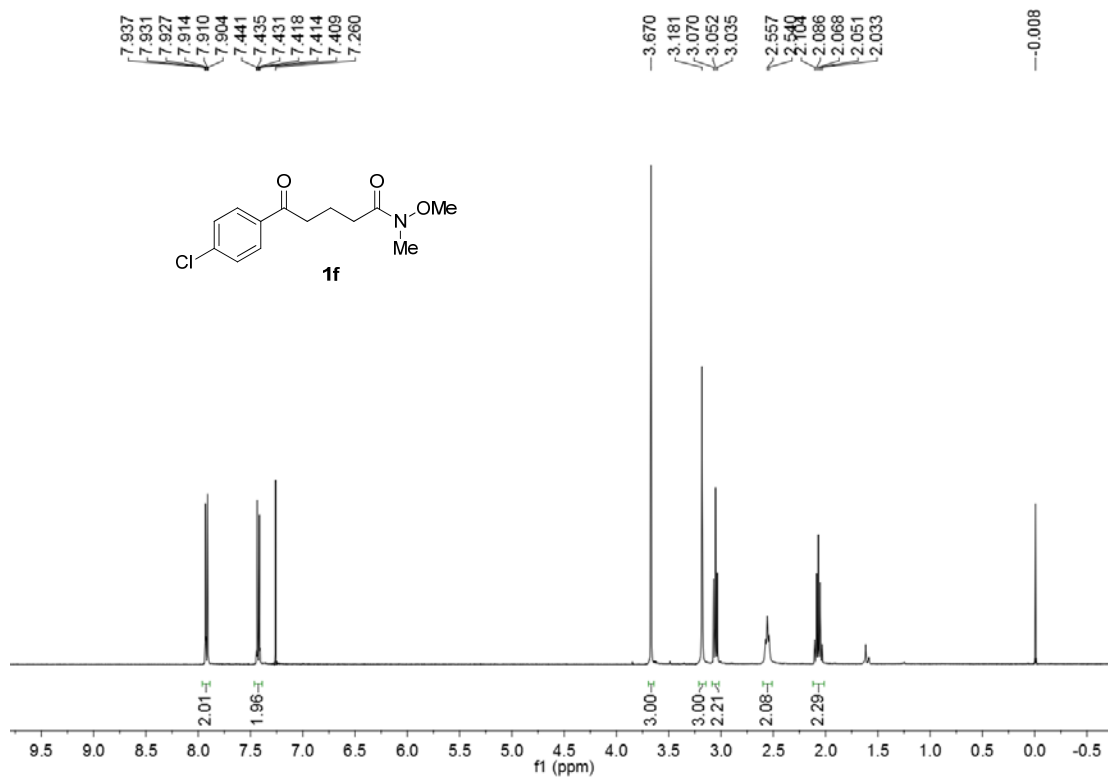
***N*-Methoxy-*N*-methyl-5-oxo-5-(4-(trifluoromethyl)phenyl)pentanamide, (1d)**



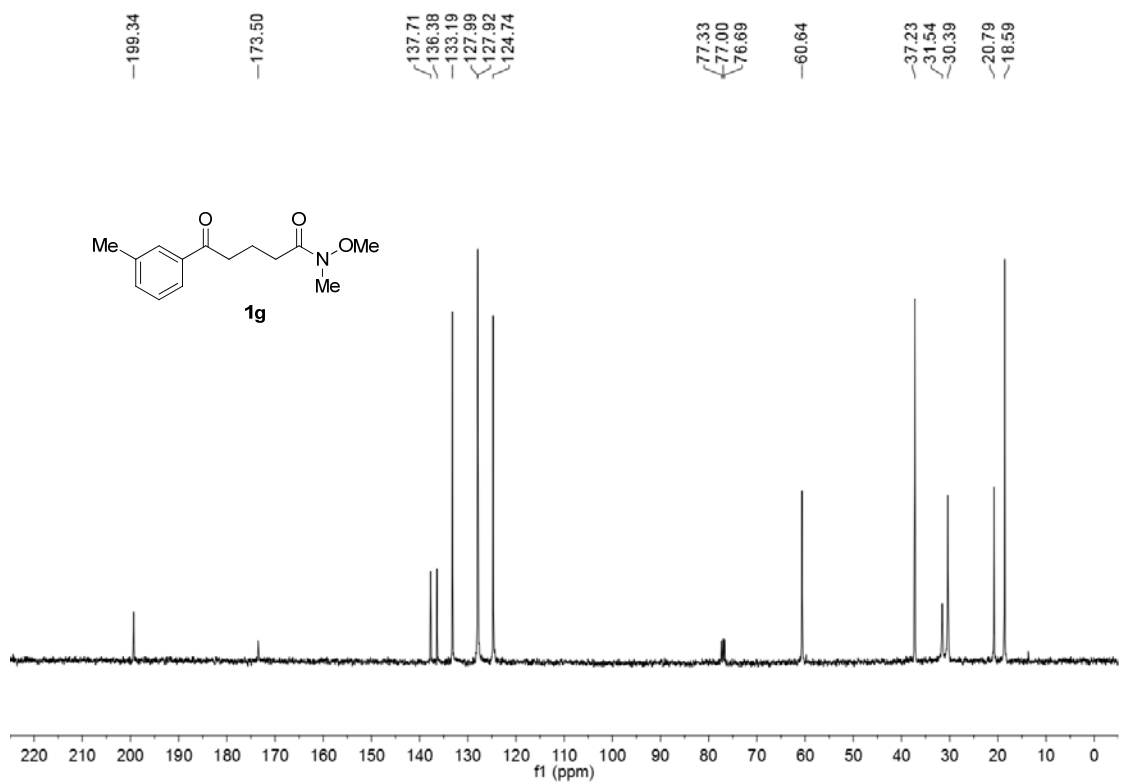
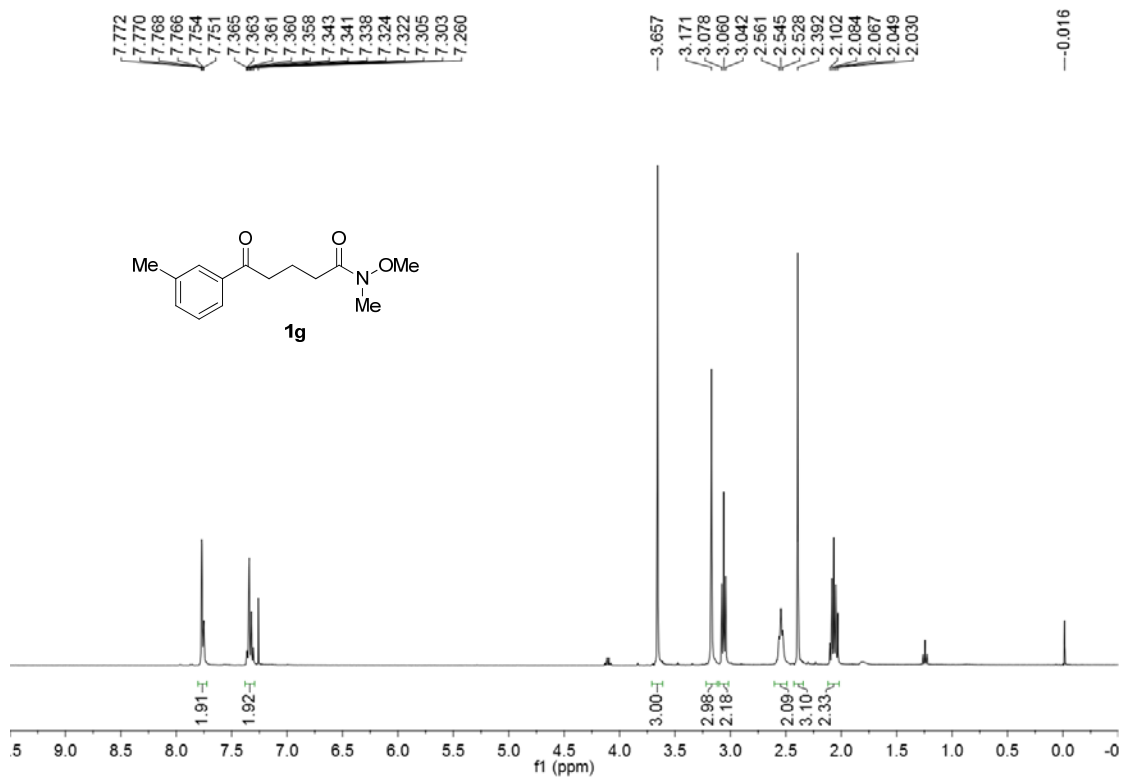
***N*-Methoxy-*N*-methyl-5-oxo-5-(4-fluorophenyl)pentanamide, (1e)**



***N*-Methoxy-*N*-methyl-5-oxo-5-(4-chlorophenyl)pentanamide, (1f)**

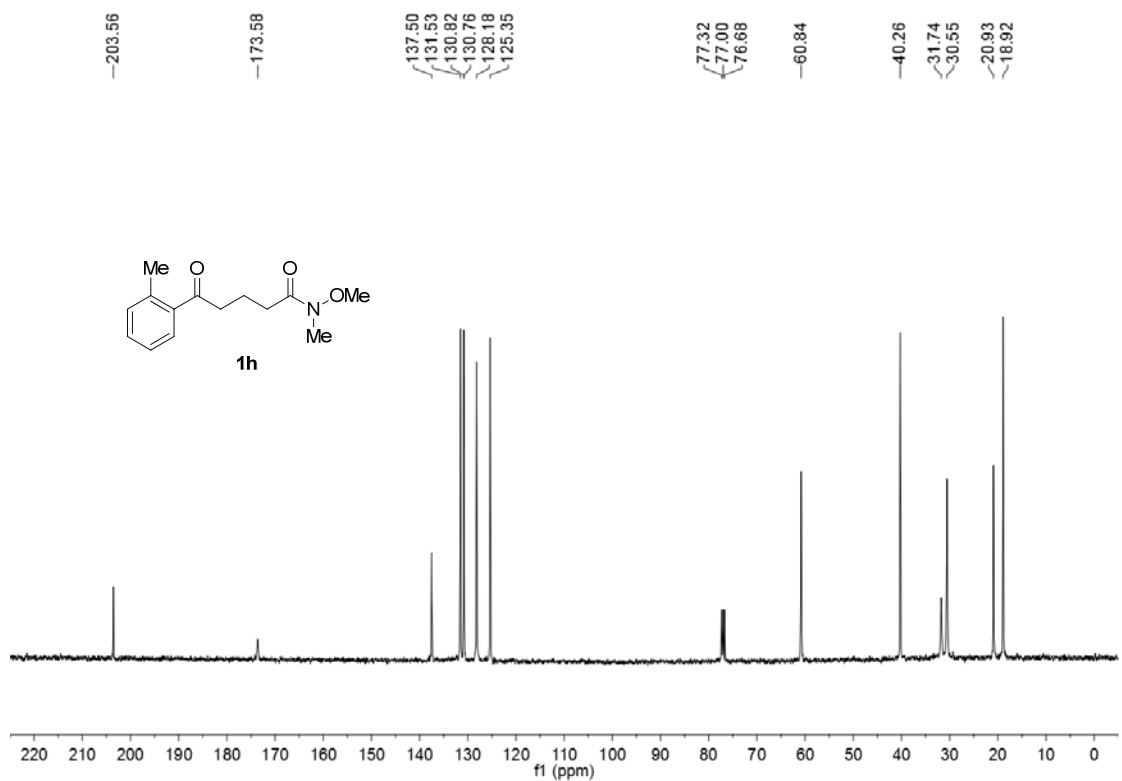
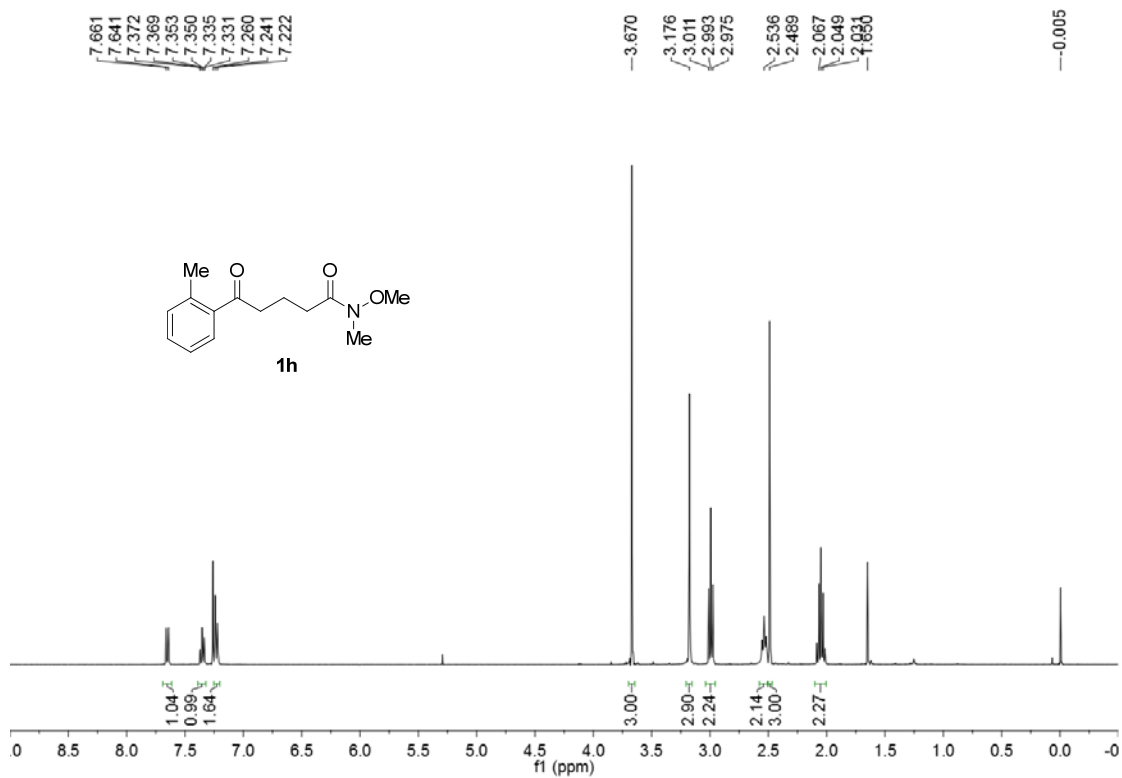


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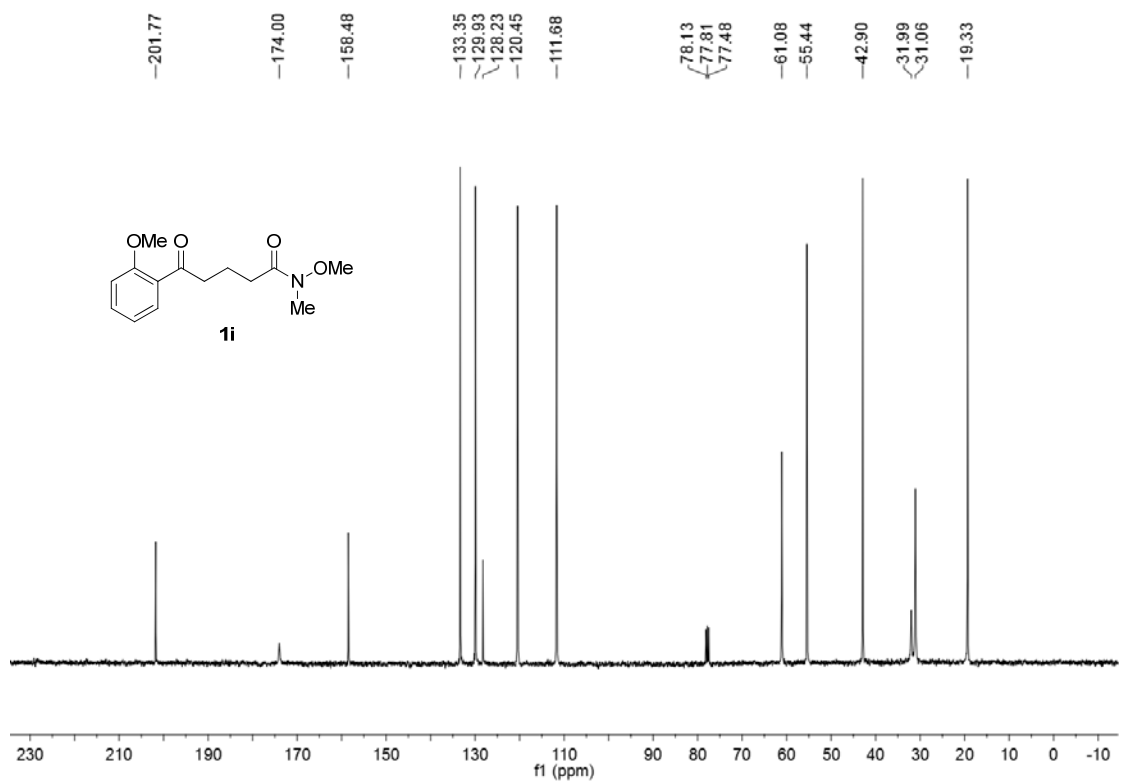
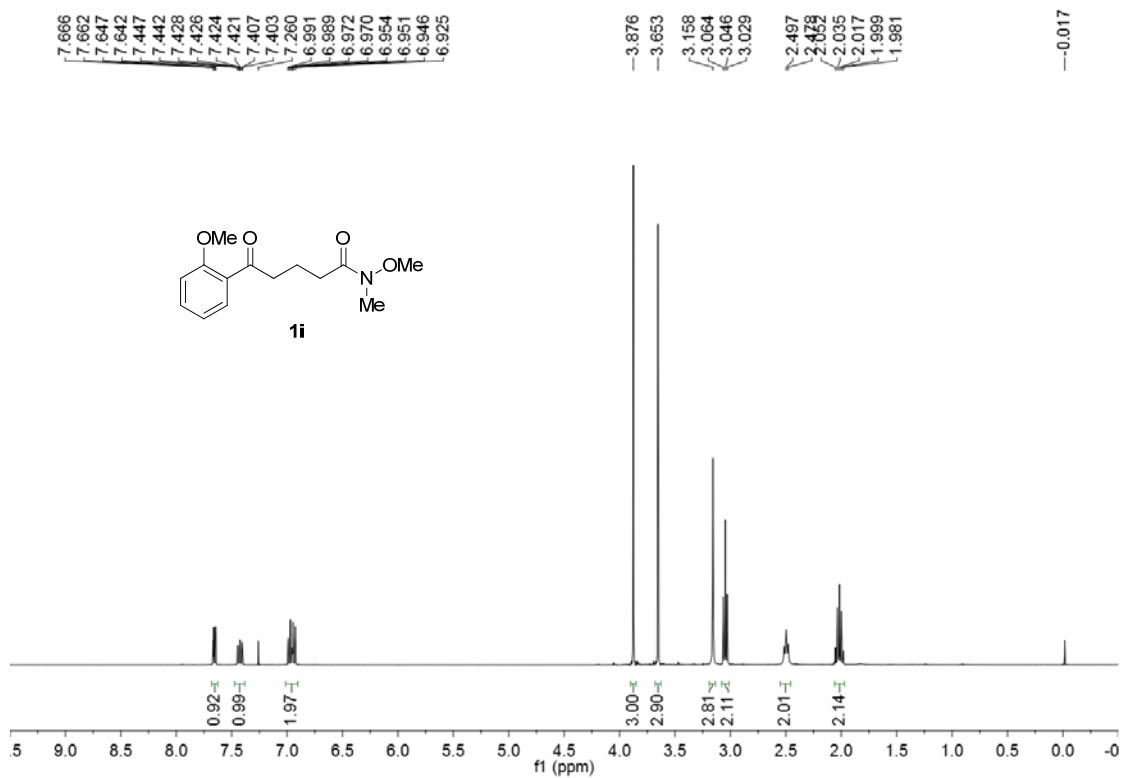




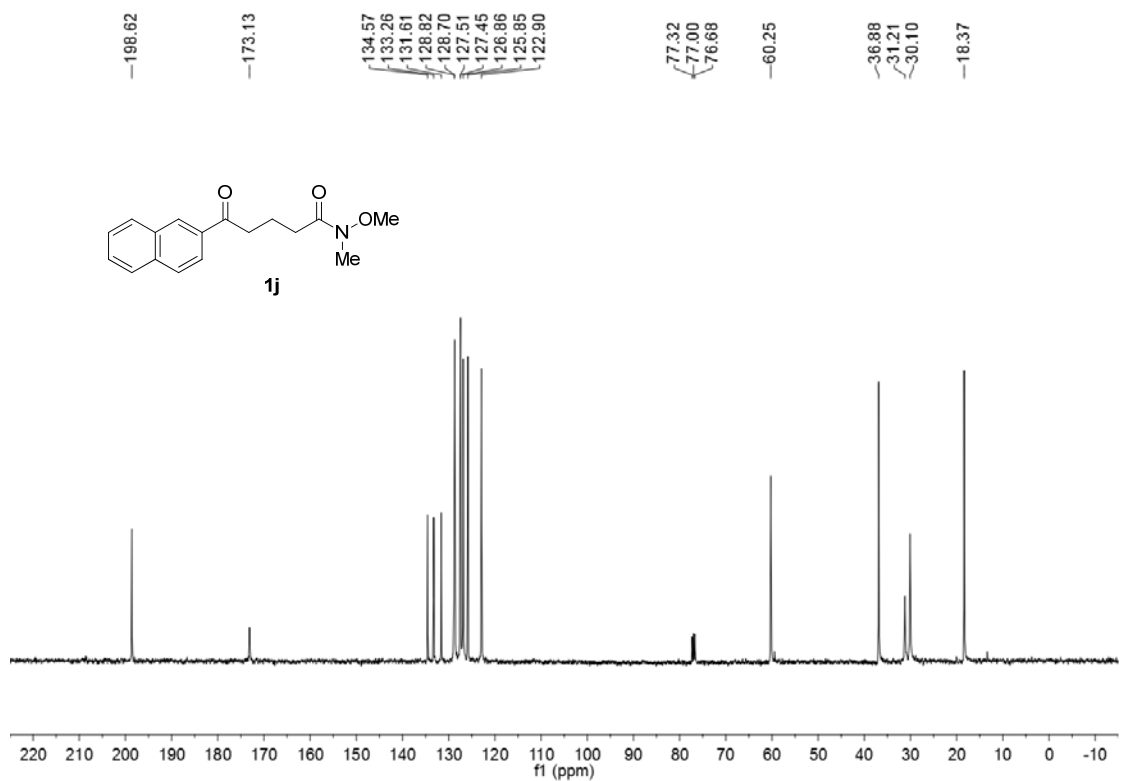
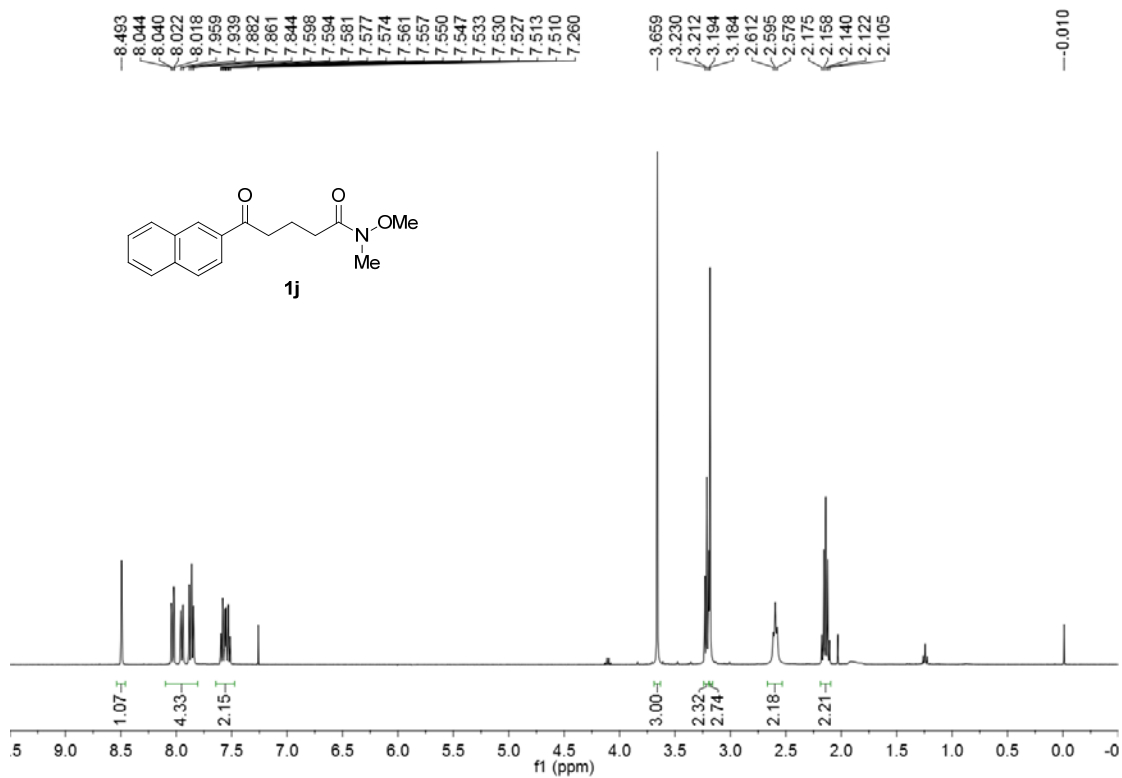
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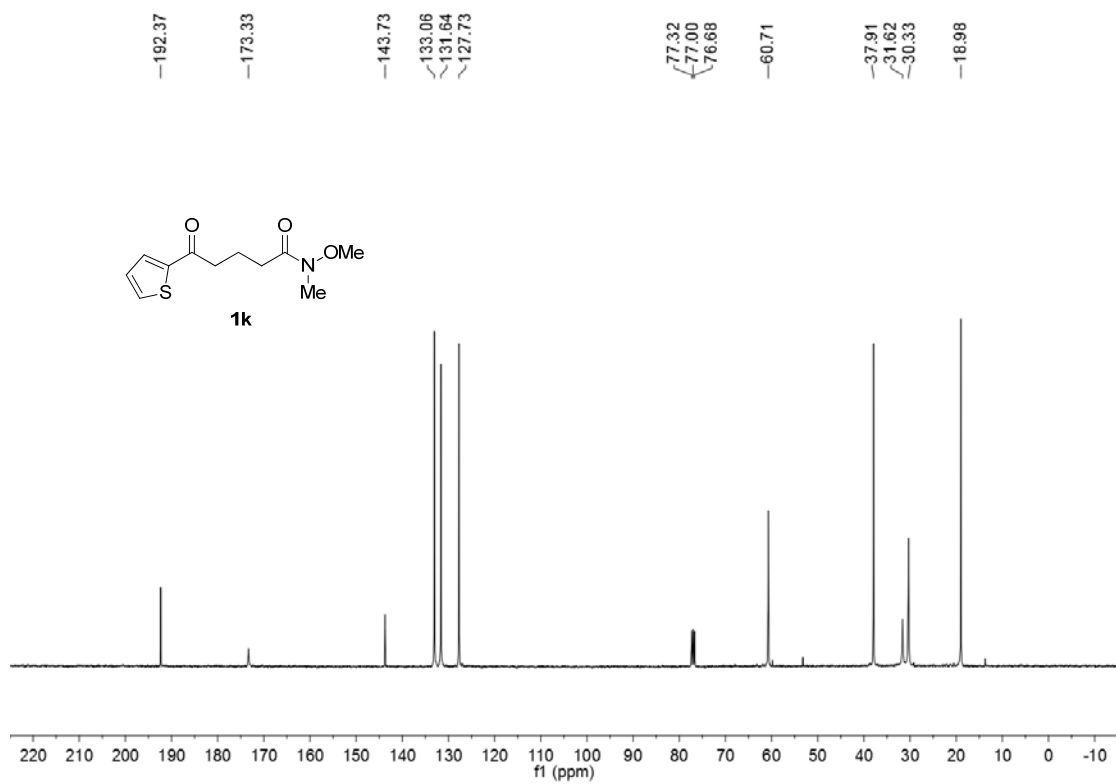
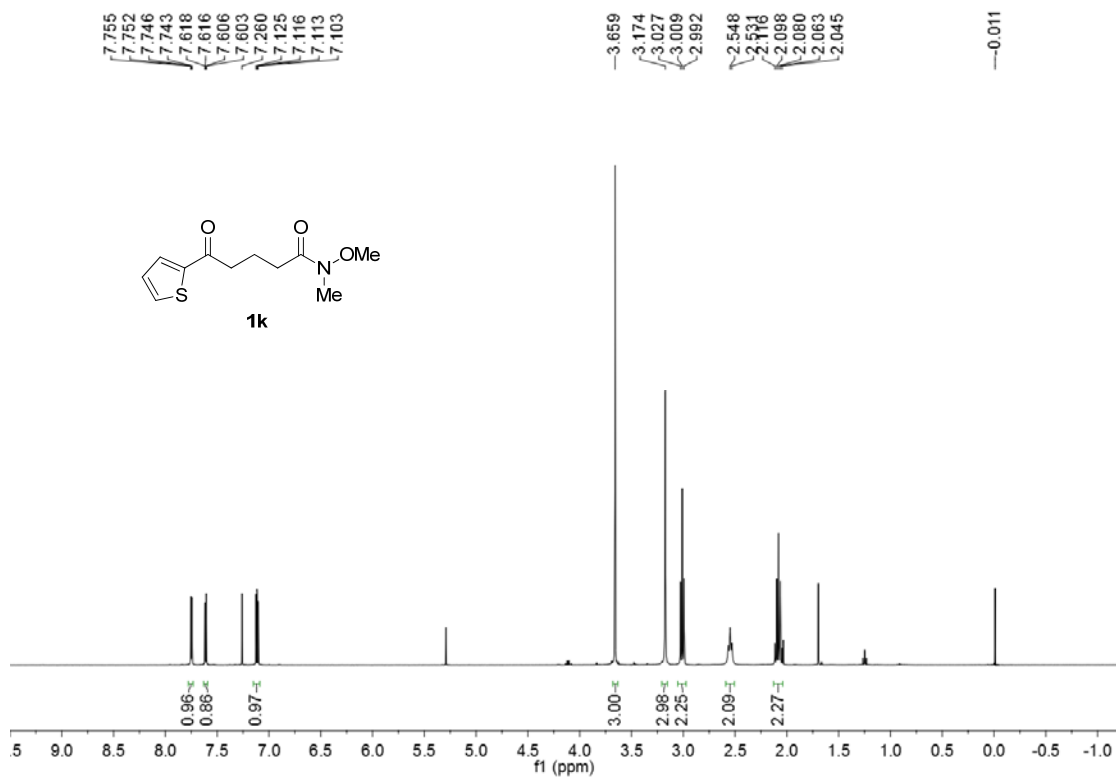
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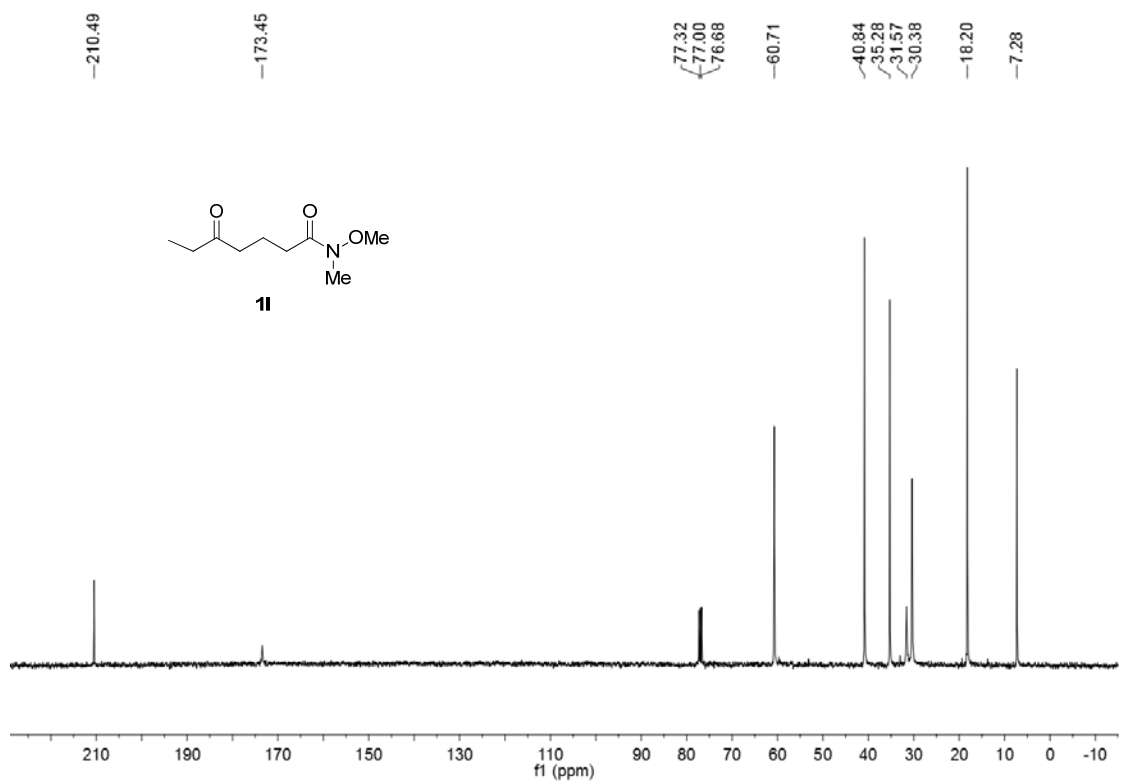
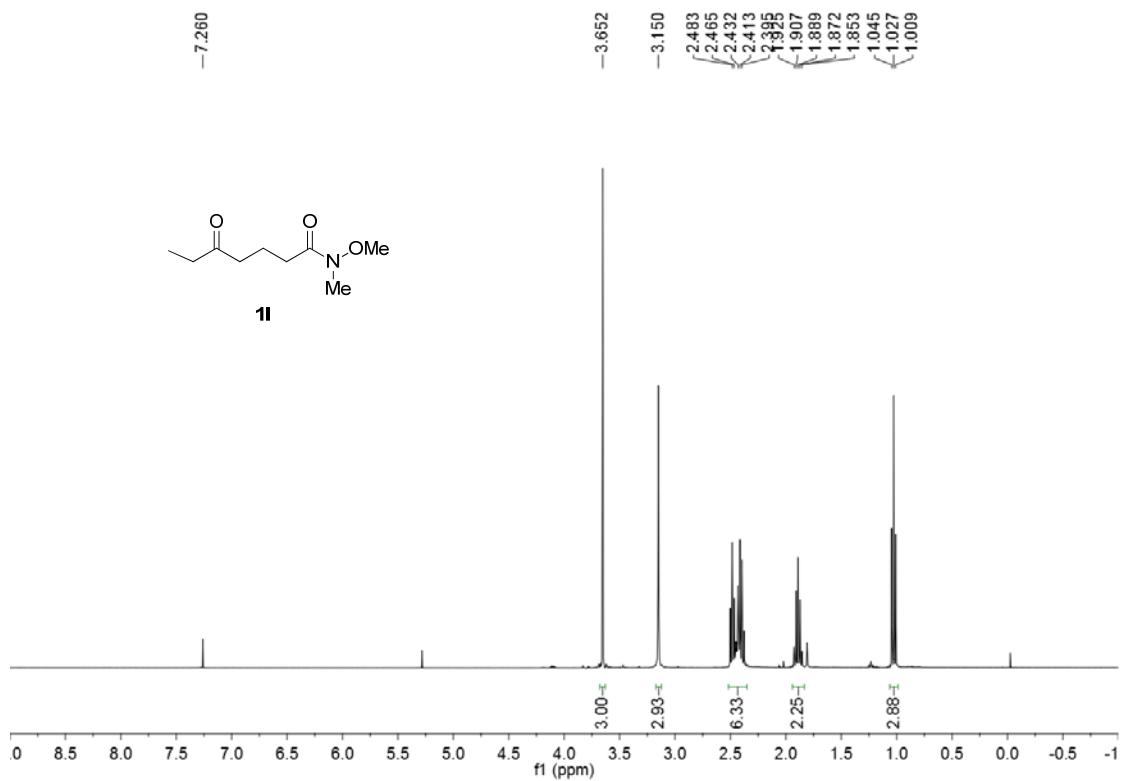
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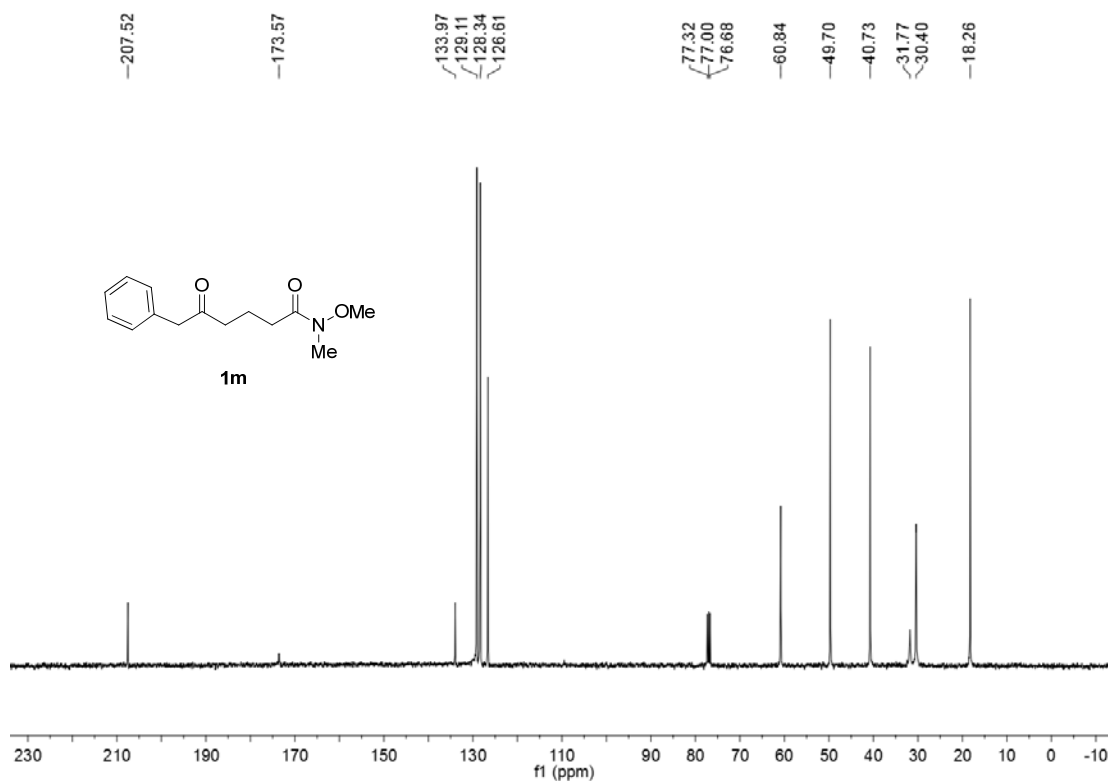
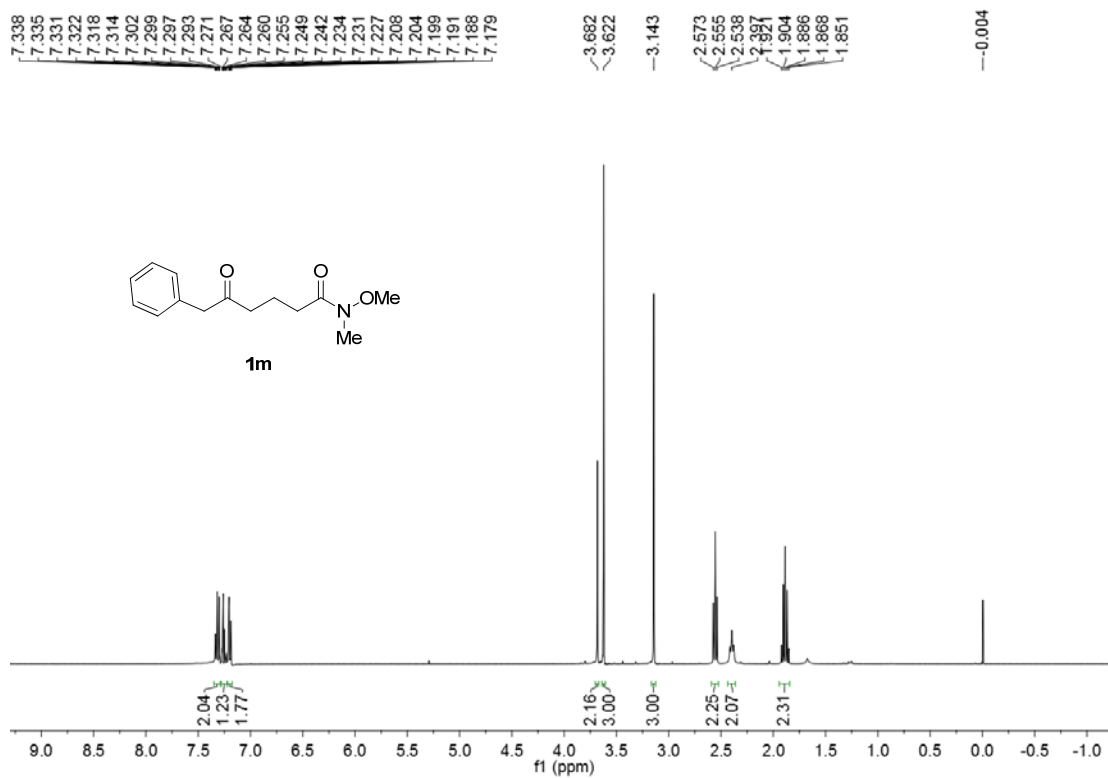
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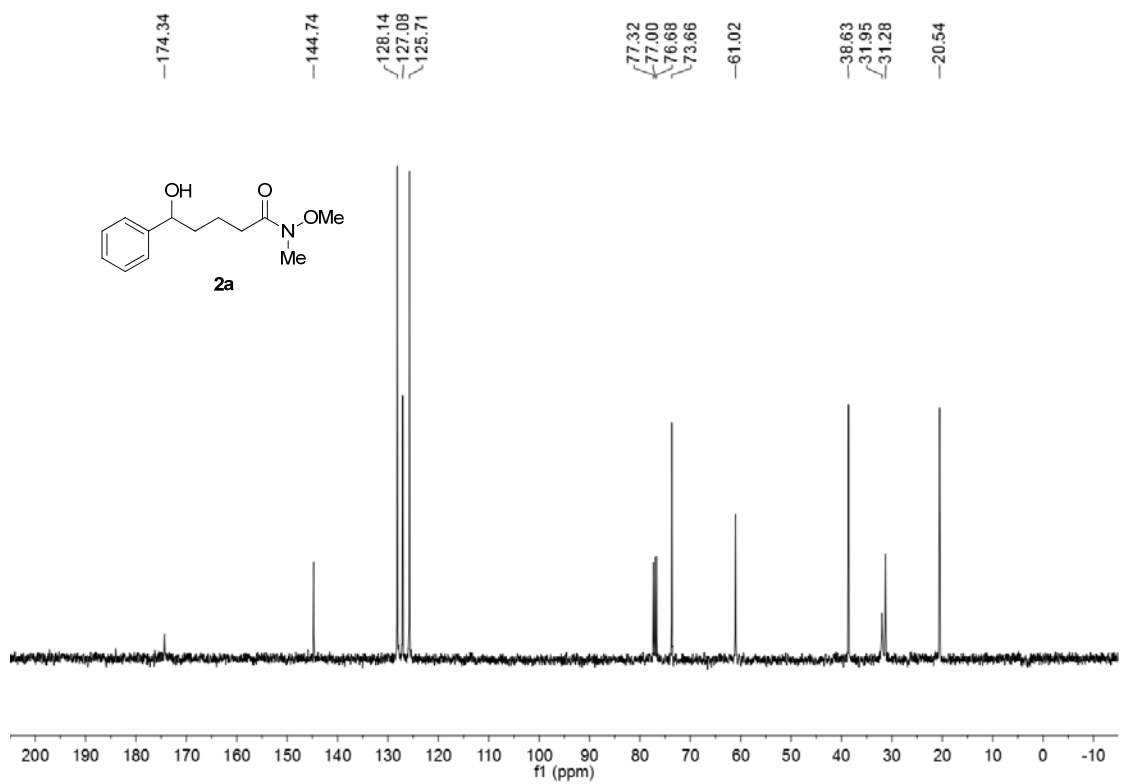
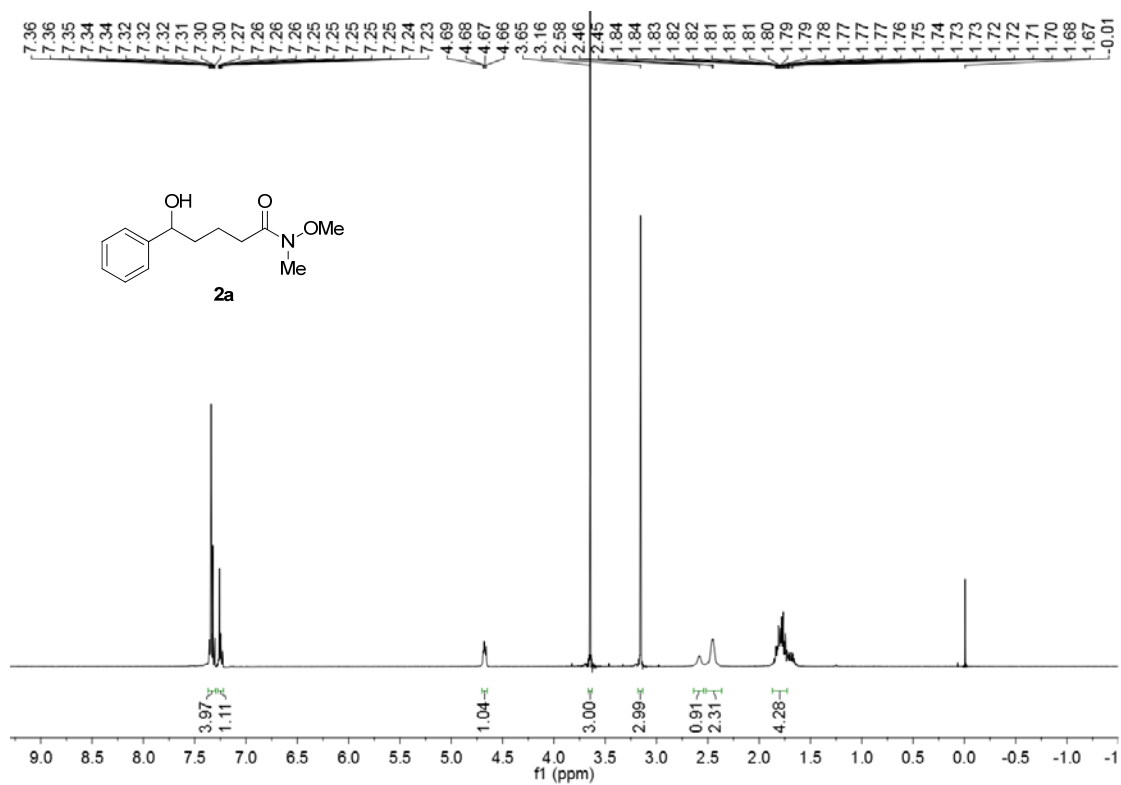
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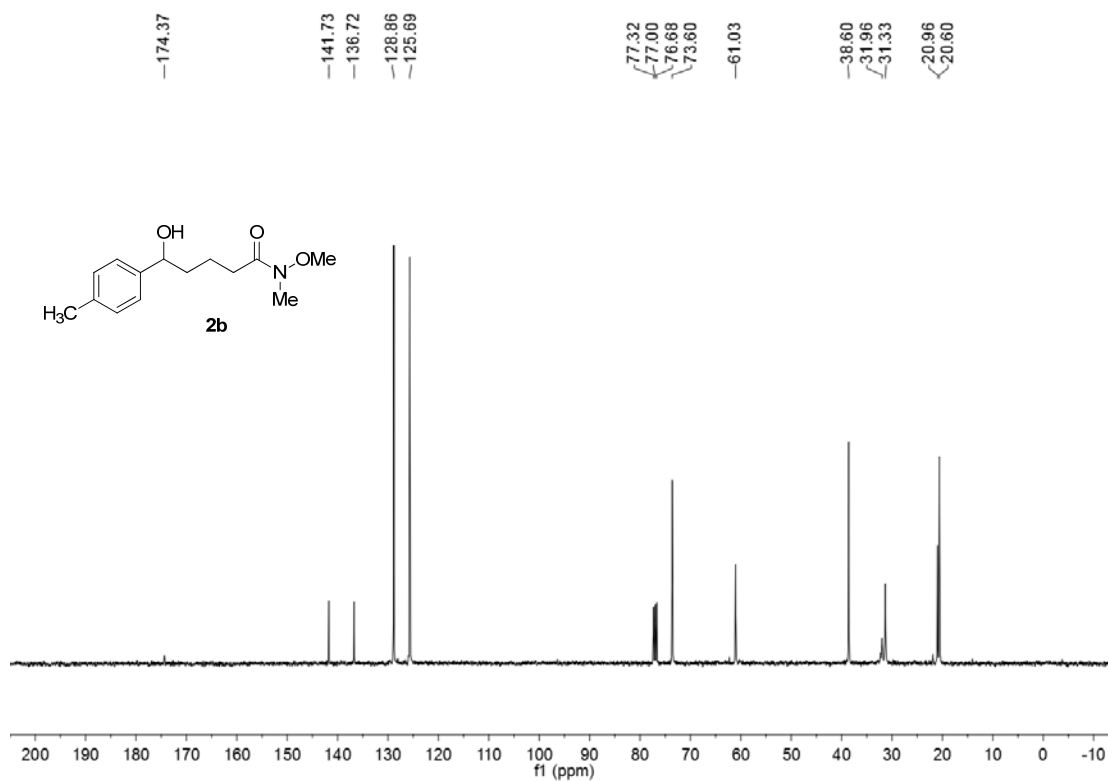
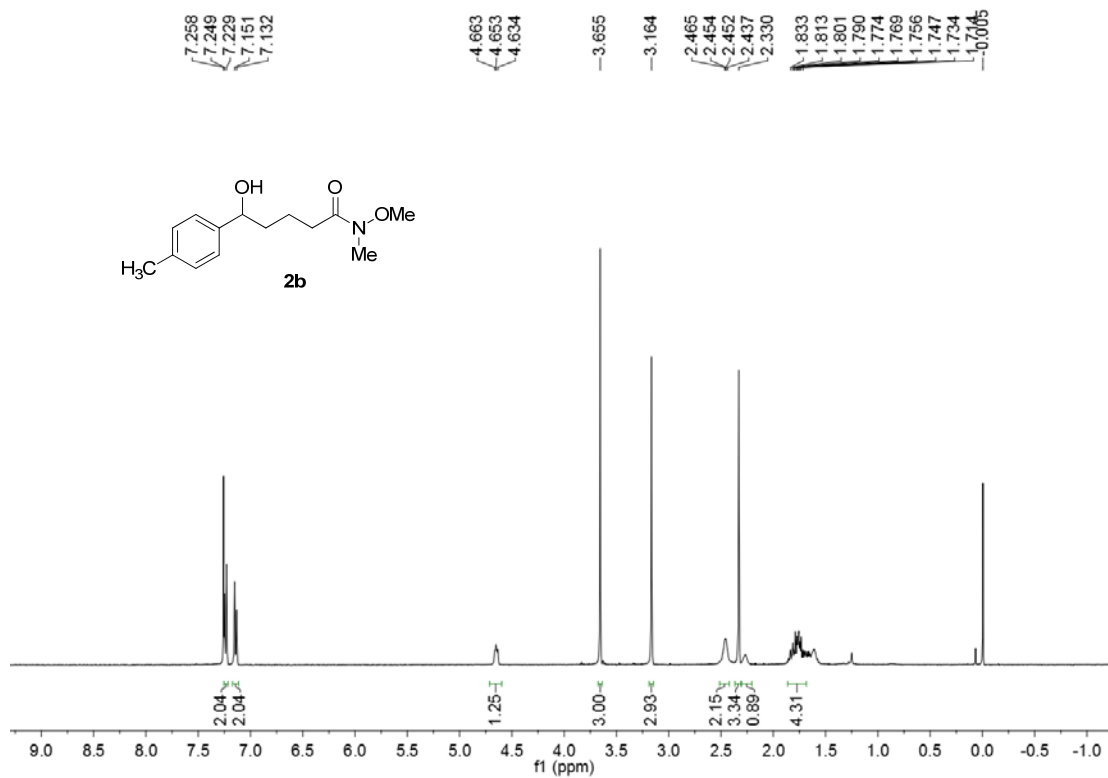
***N*-Methoxy-*N*-methyl-5-oxo-6-phenylhexanamide, (1m)**



**5-Hydroxy-N-methoxy-N-methyl-5-phenylpentanamide, (2a)**

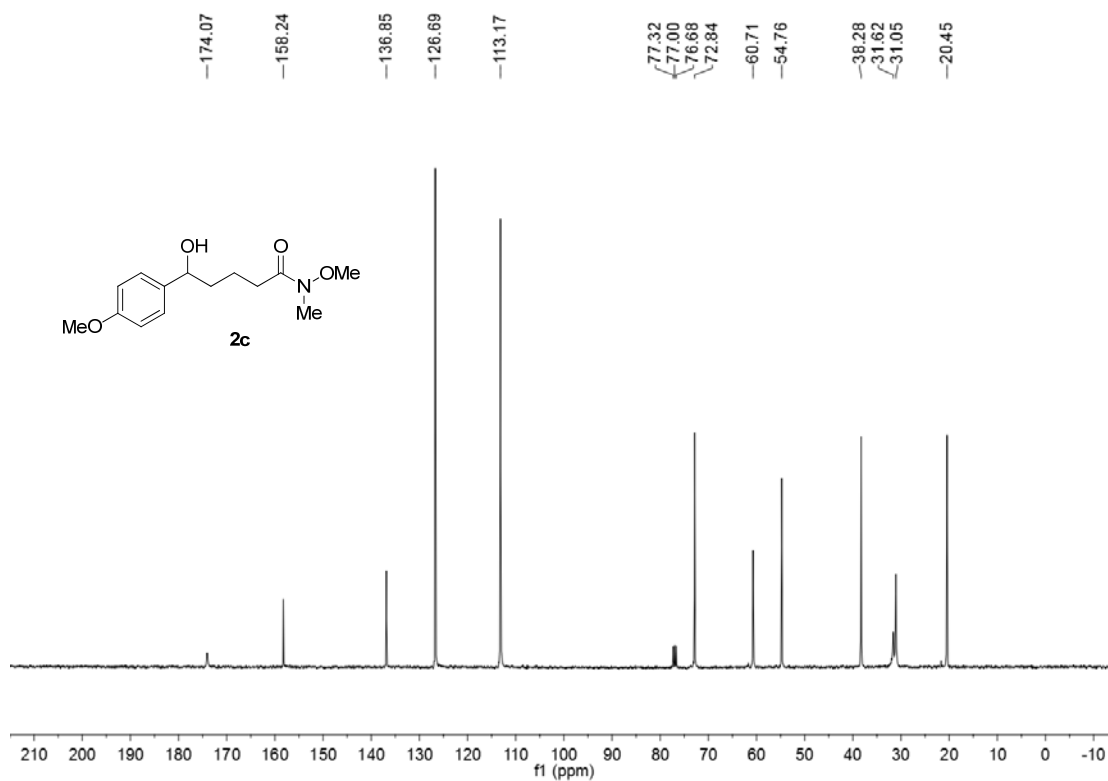
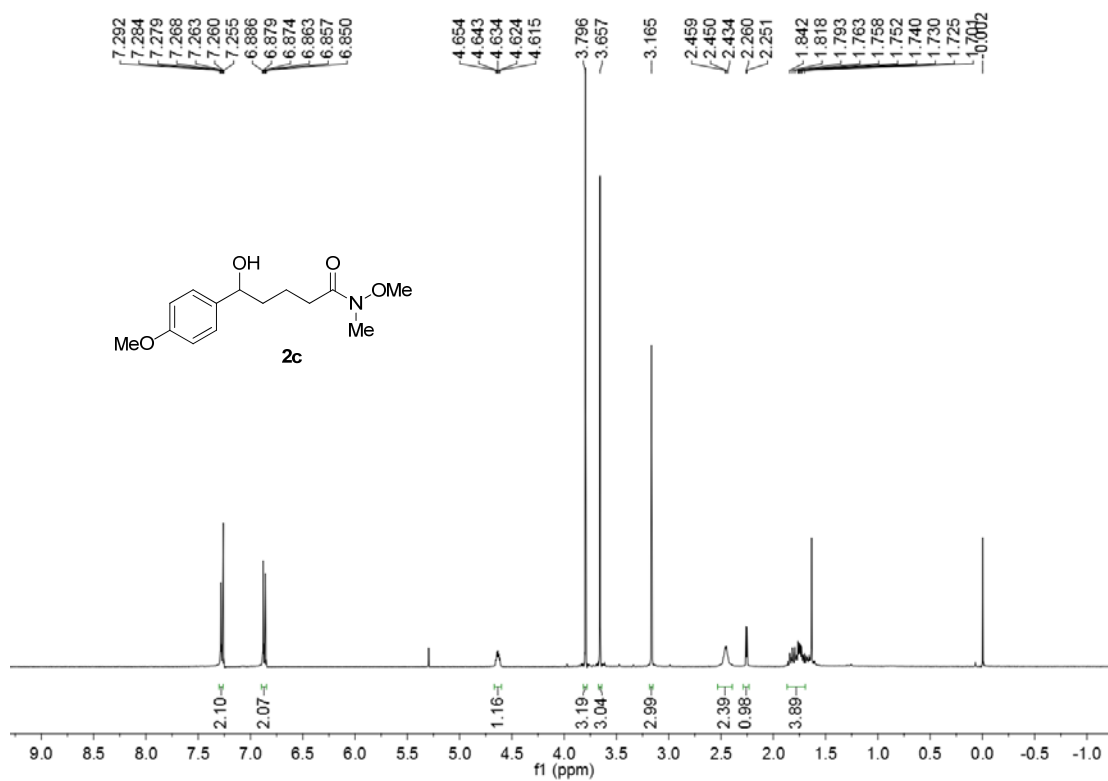


**5-Hydroxy-N-methoxy-N-methyl-5-(p-tolyl)pentanamide, (2b)**

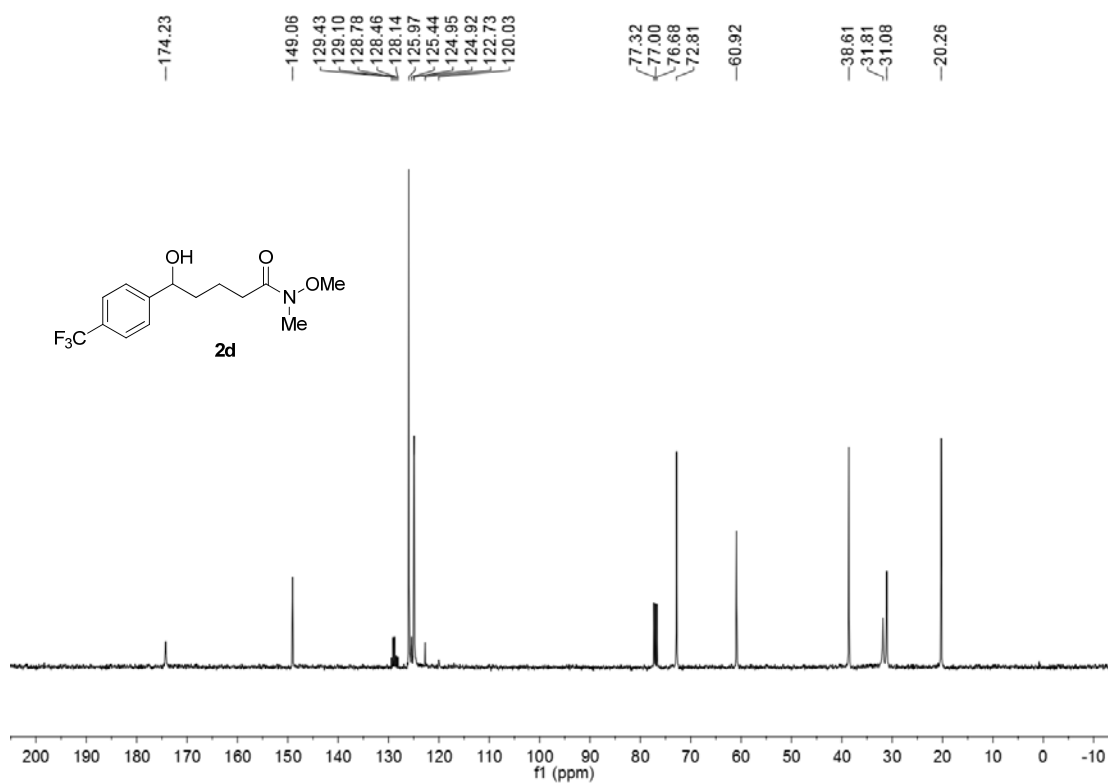
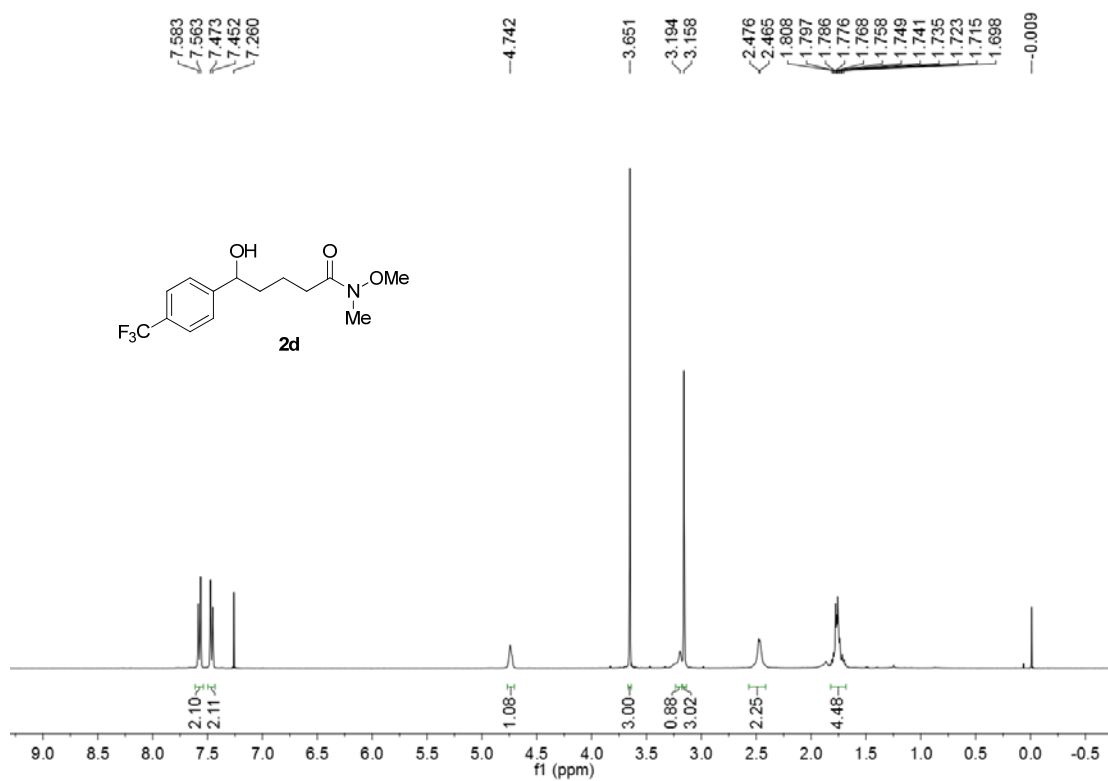




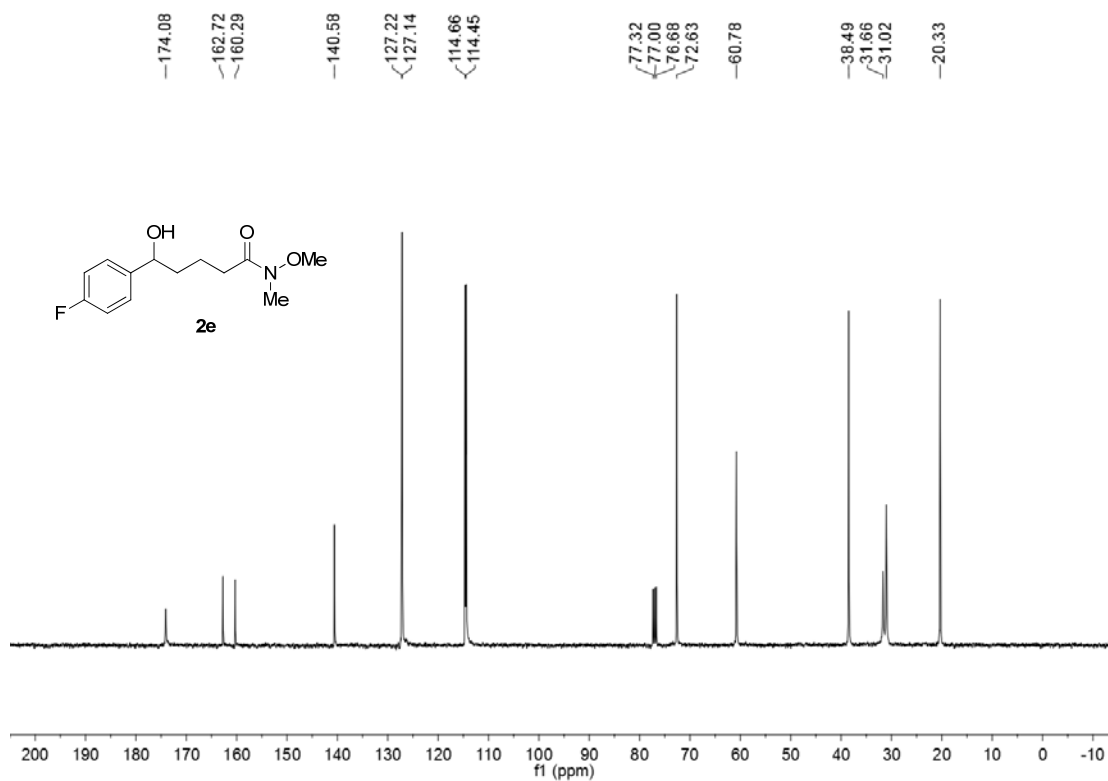
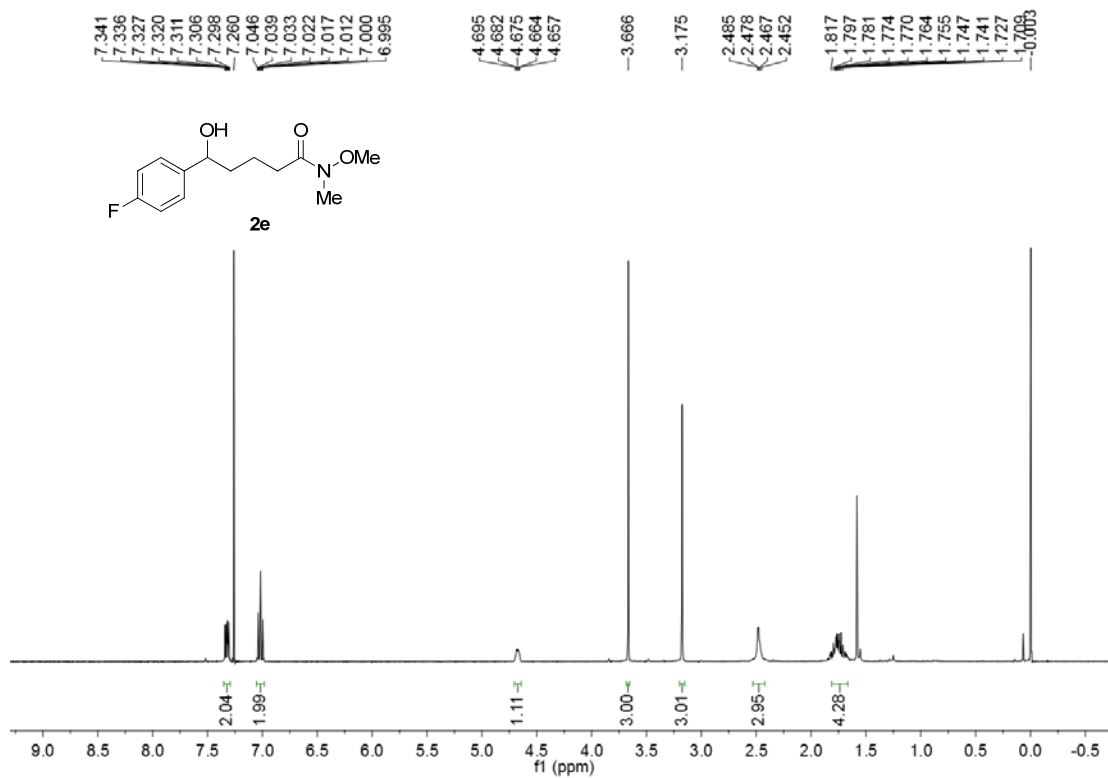
5-Hydroxy-N-methoxy-N-methyl-5-(4-methoxyphenyl)pentanamide, (2c)



### 5-Hydroxy-N-methoxy-N-methyl-5-(4-(trifluoromethyl)phenyl)pentanamide, (2d)

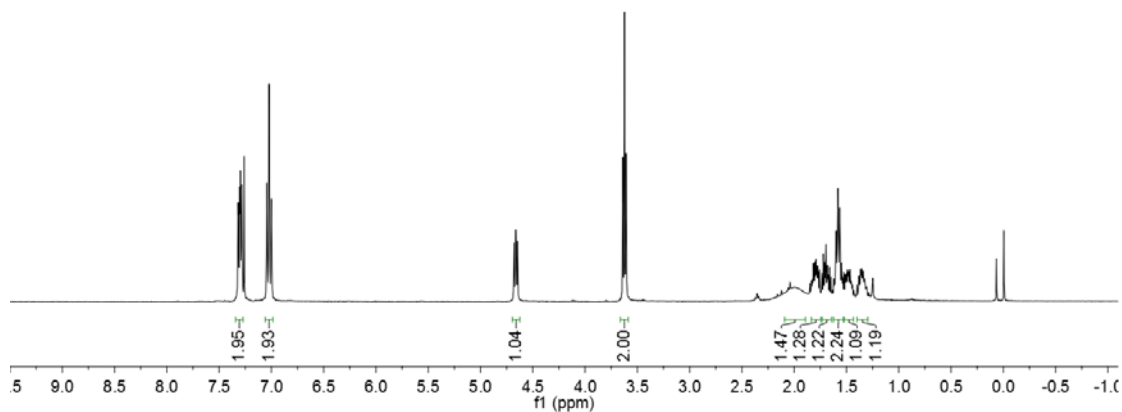
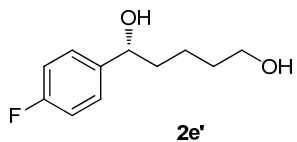


5-Hydroxy-N-methoxy-N-methyl-5-(4-fluorophenyl)pentanamide, (2e)

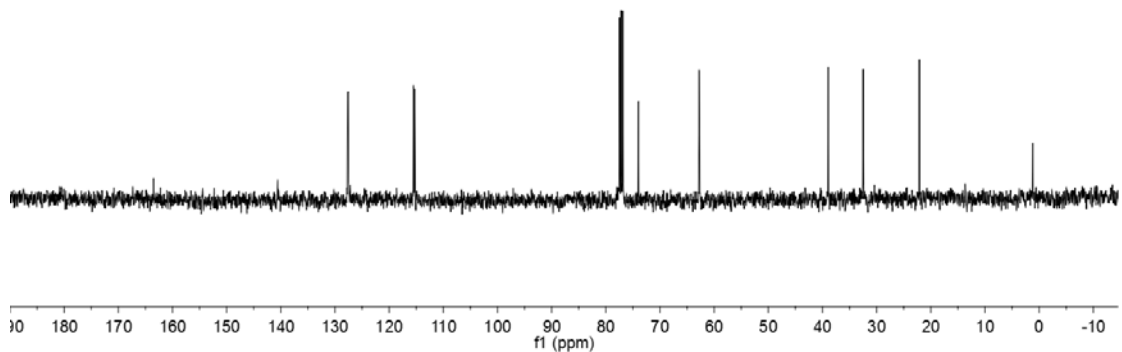
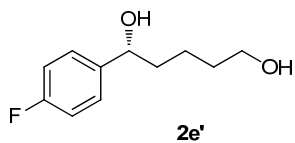


**1-(4-Fluorophenyl)pentane-1,5-diol, (2e')**

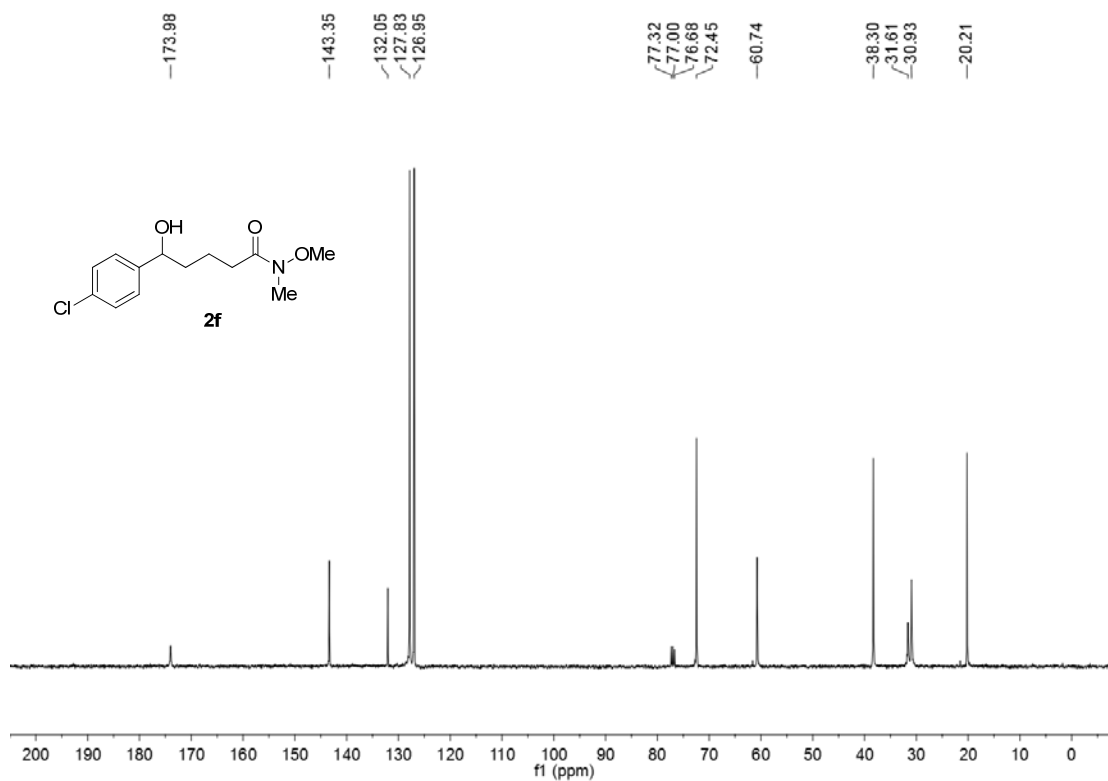
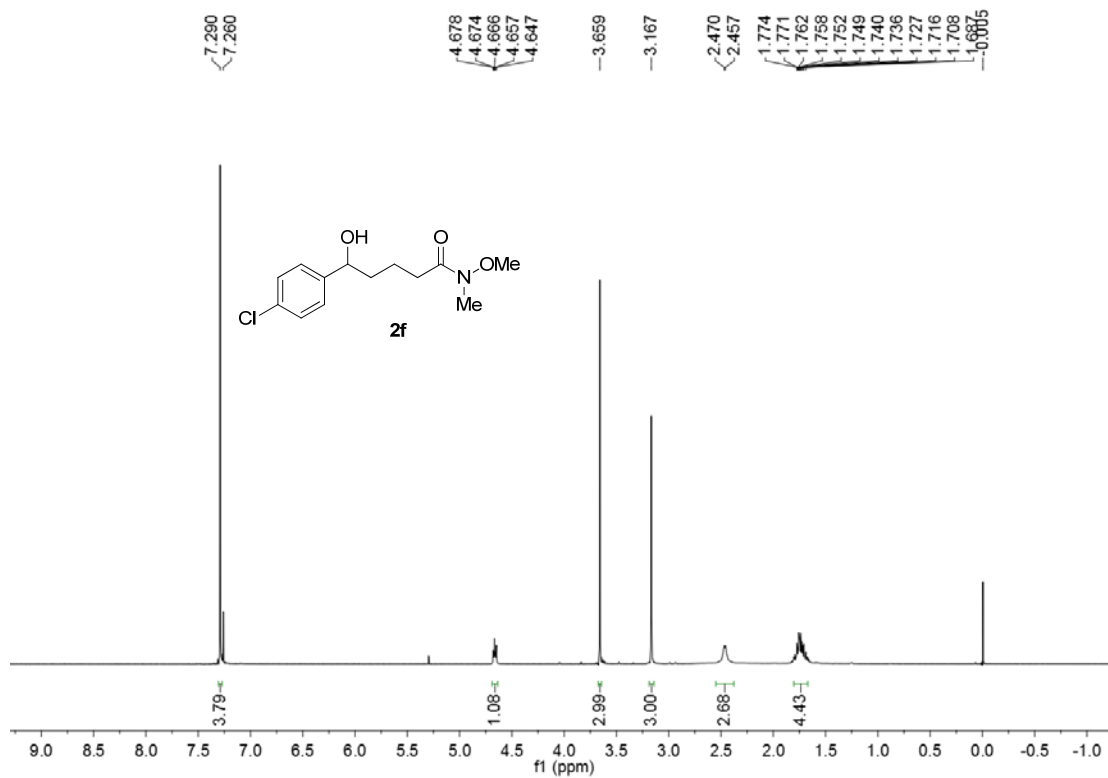
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4.647  
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3.623  
3.607  
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1.662  
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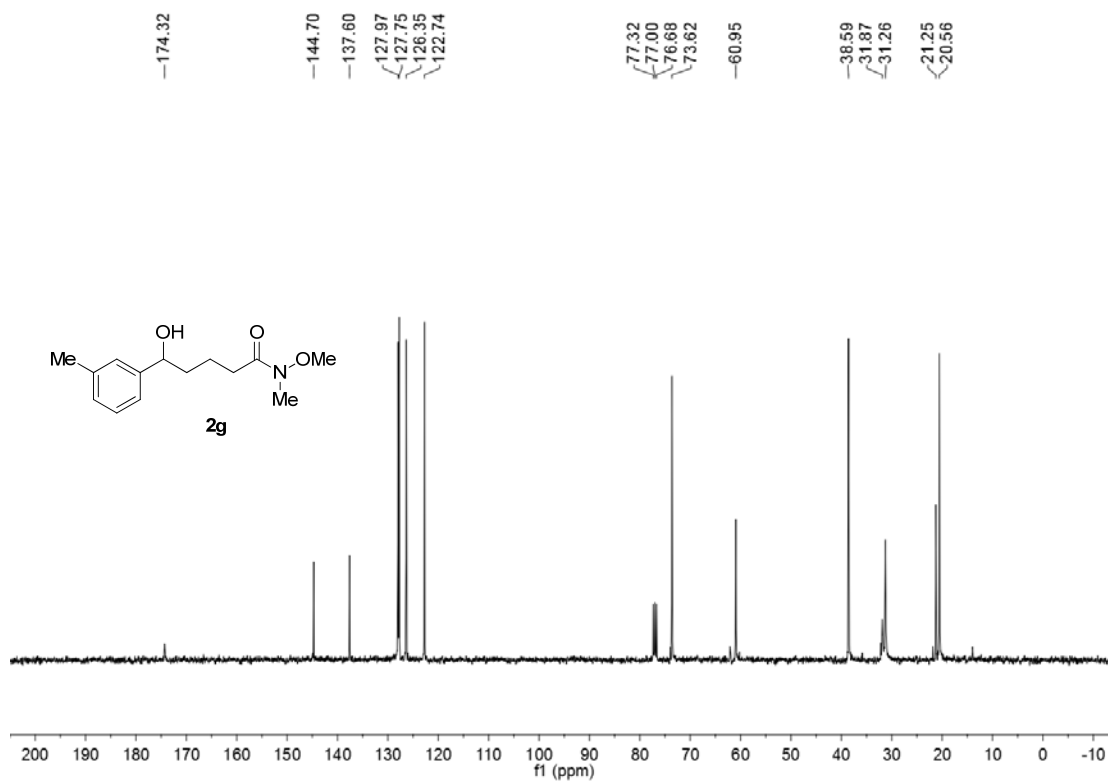
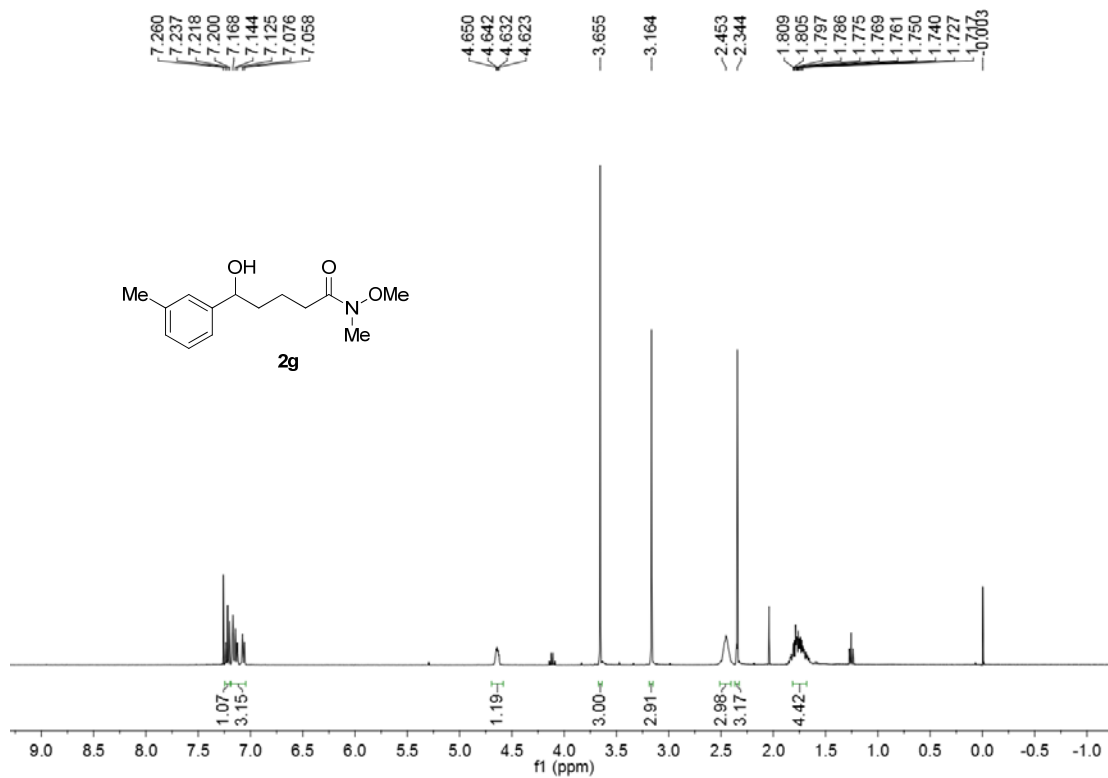
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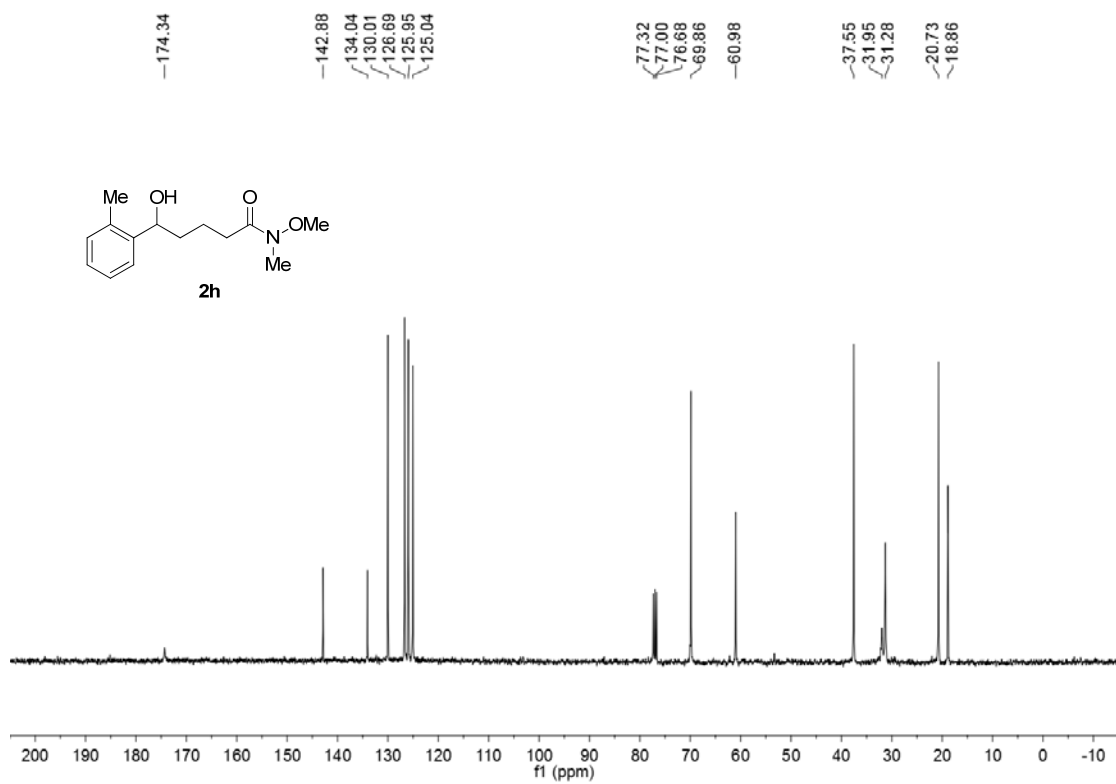
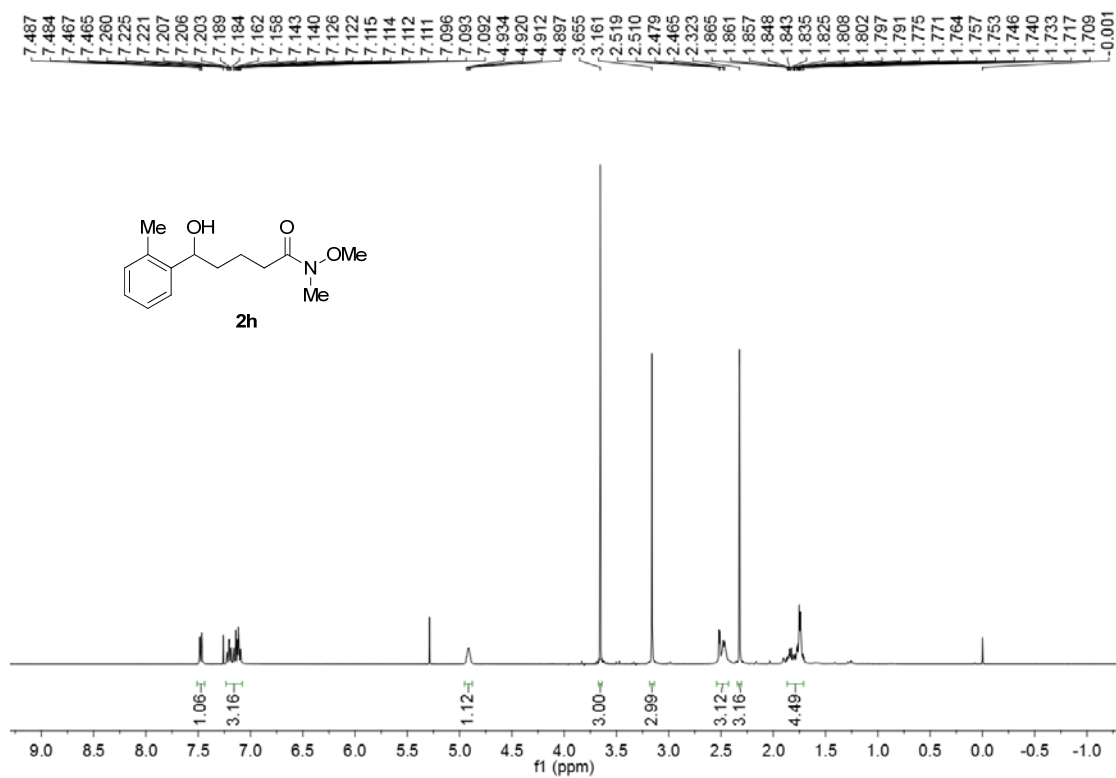
5-Hydroxy-N-methoxy-N-methyl-5-(4-chlorophenyl)pentanamide, (2f)



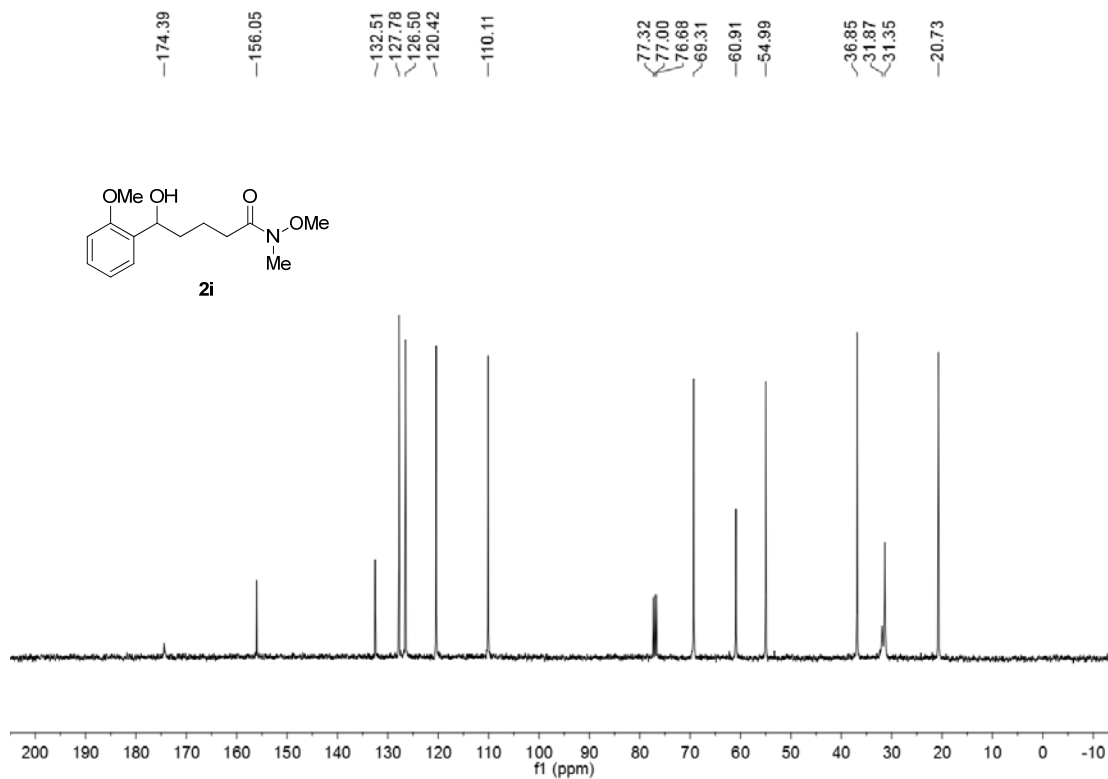
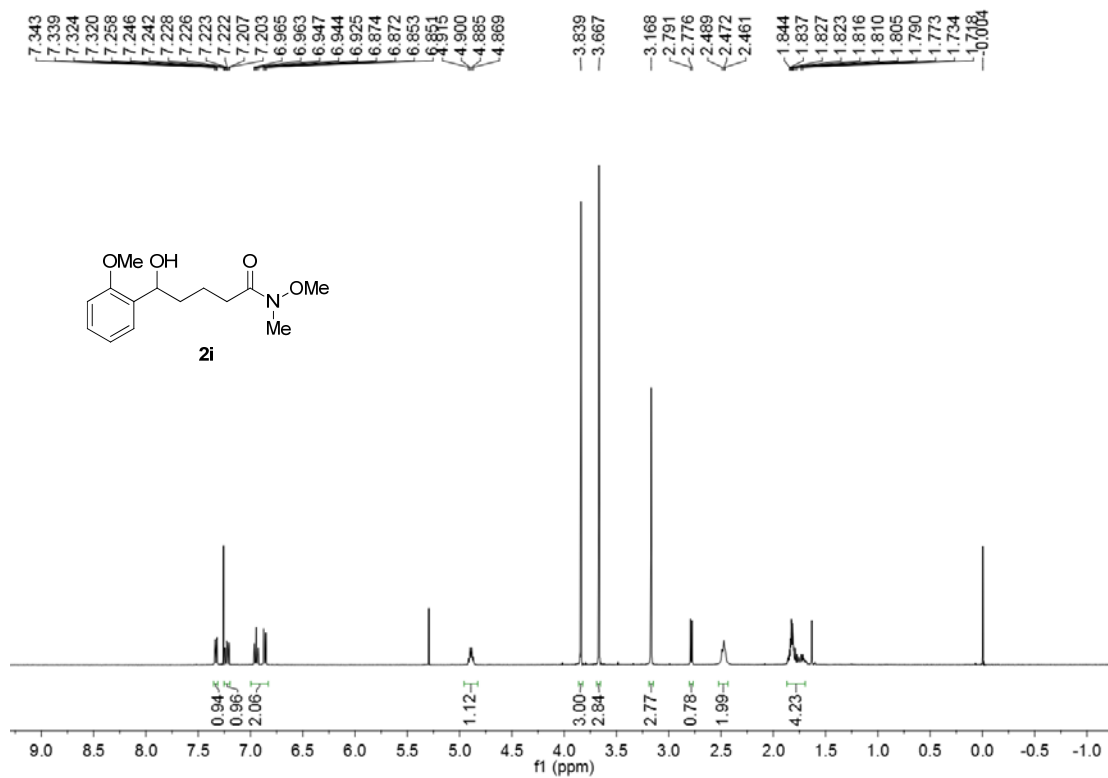
**5-Hydroxy-N-methoxy-N-methyl-5-(m-tolyl)pentanamide, (2g)**



**5-Hydroxy-N-methoxy-N-methyl-5-(o-tolyl)pentanamide, (2h)**

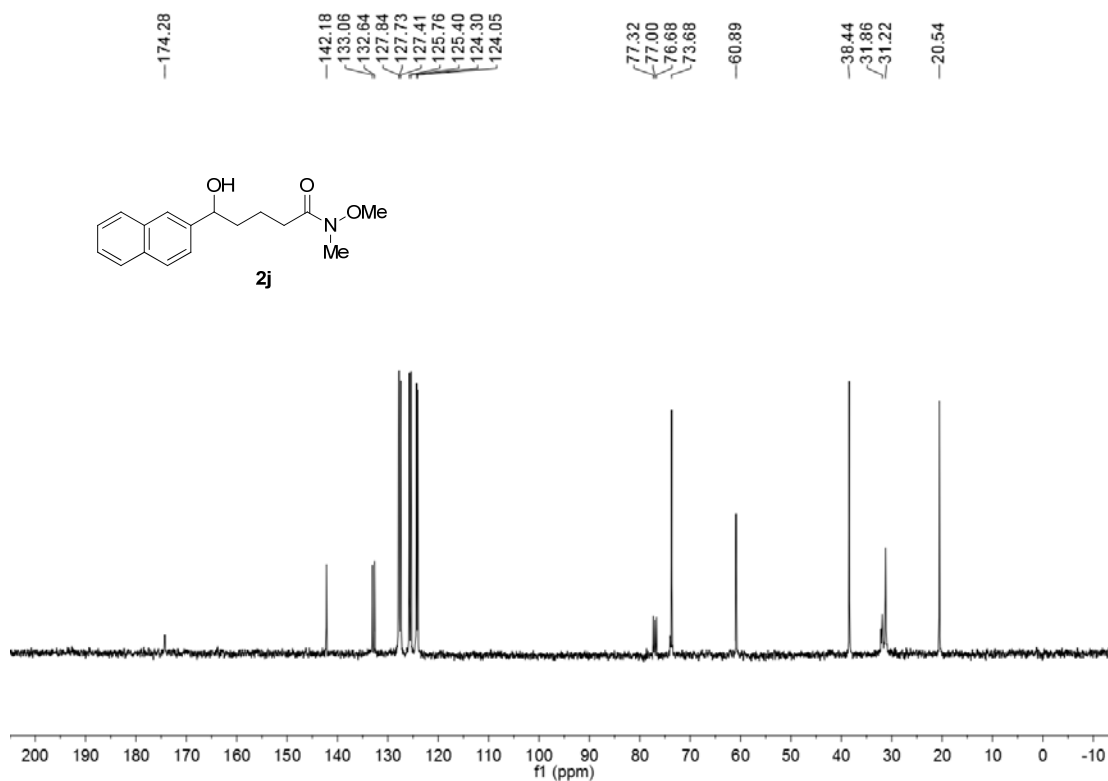
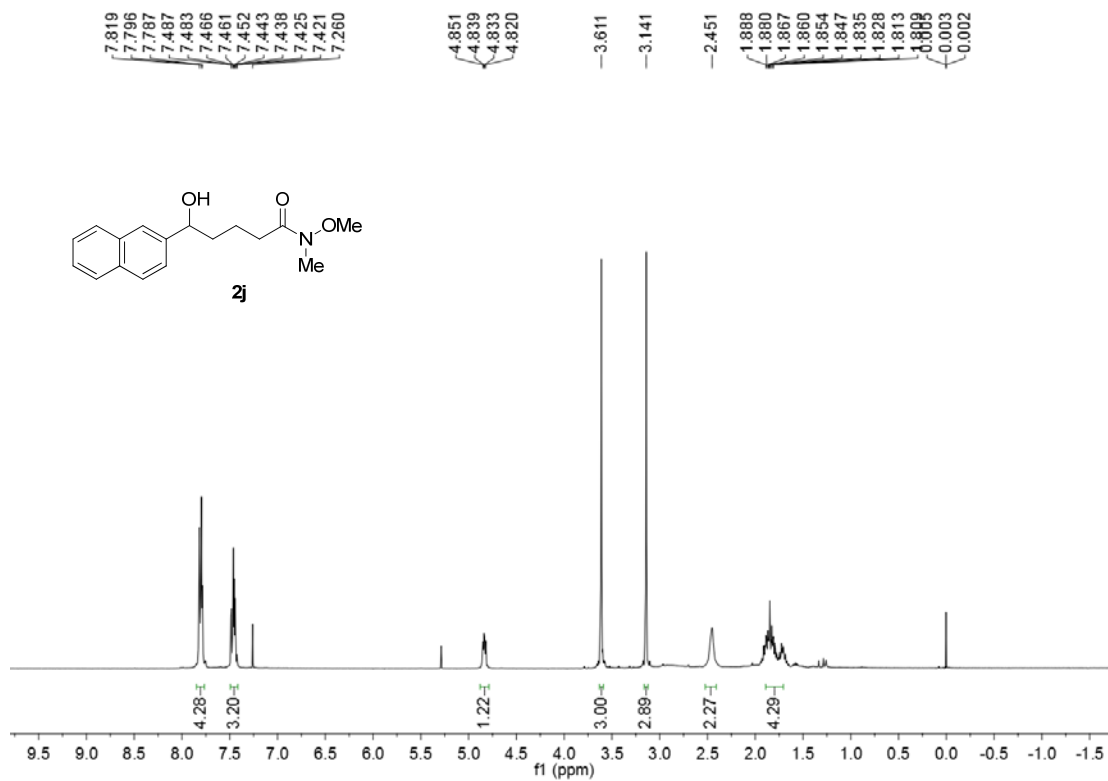


5-Hydroxy-N-methoxy-N-methyl-5-(2-methoxyphenyl)pentanamide, (2i)

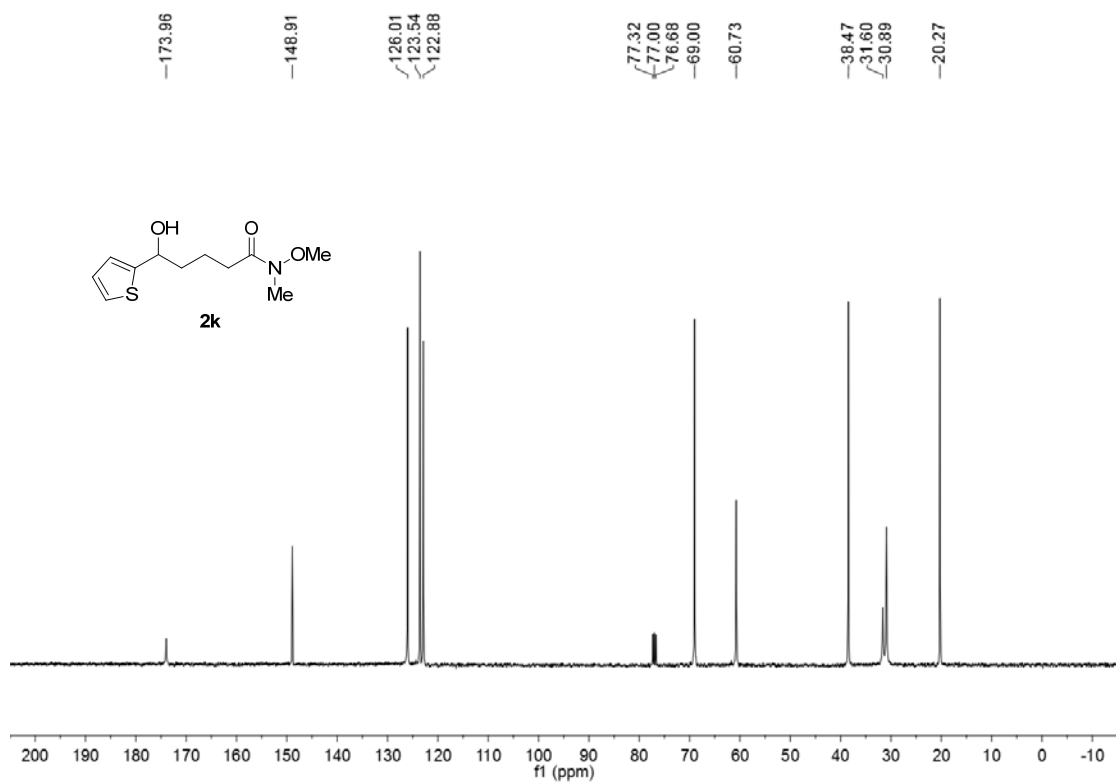
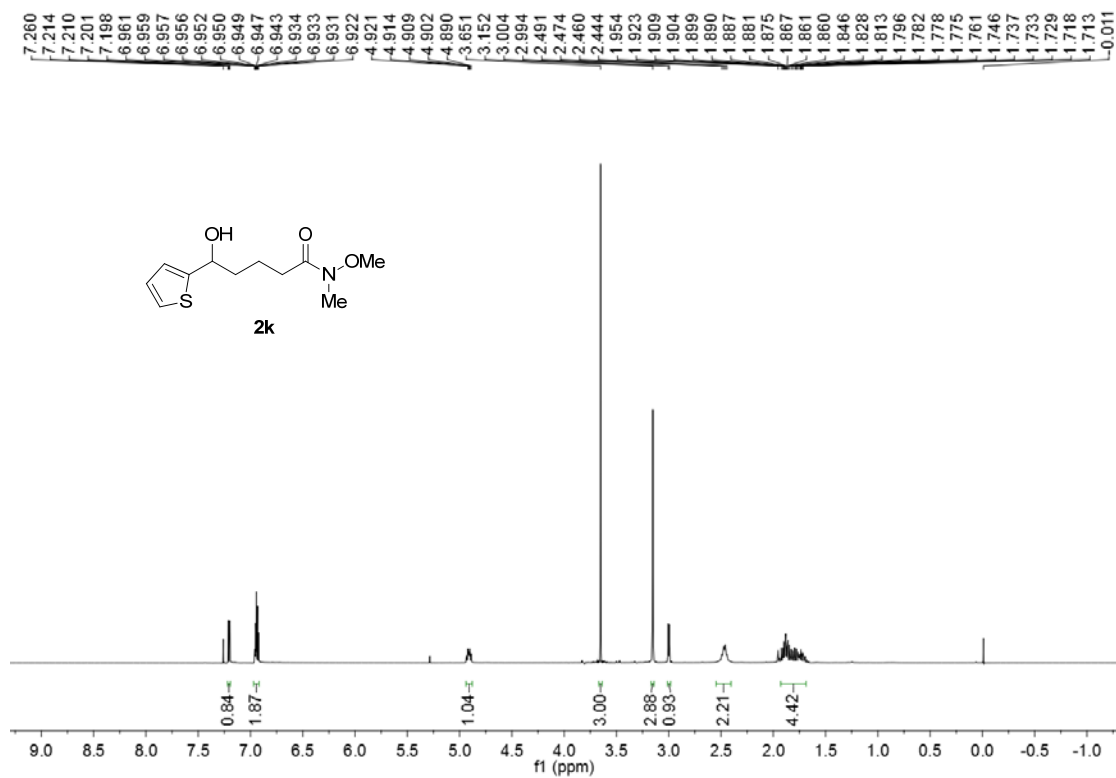




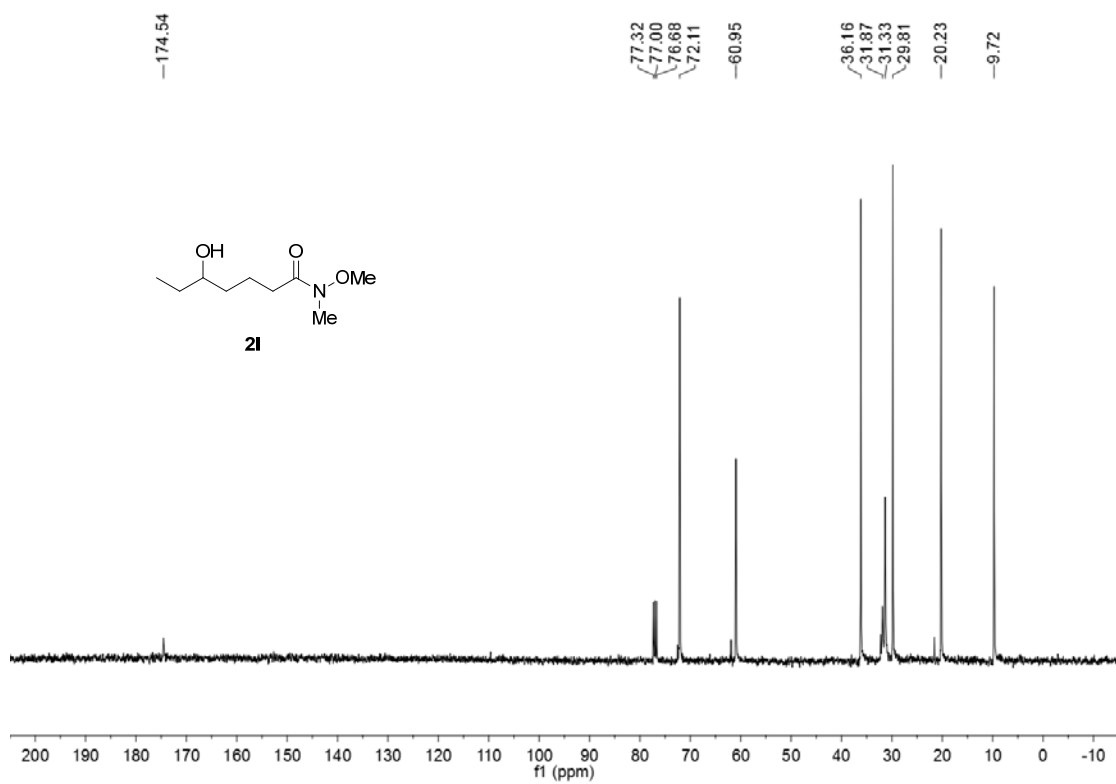
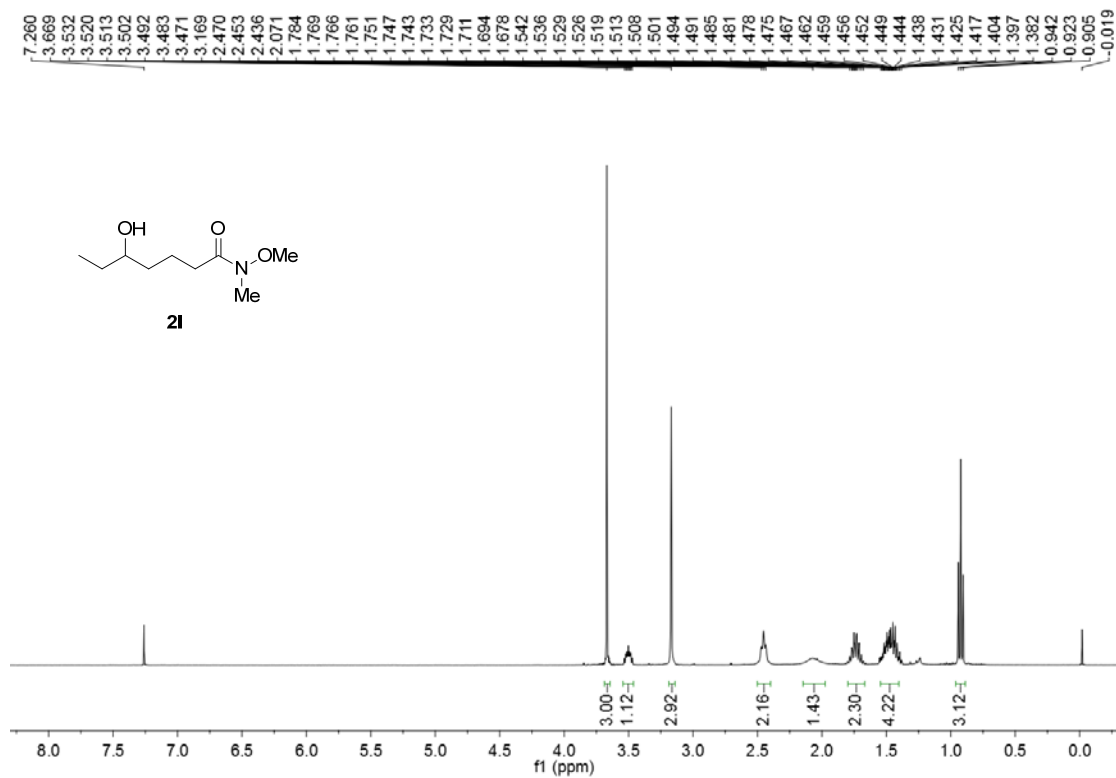
5-Hydroxy-N-methoxy-N-methyl-5-(naphthalen-2-yl)pentanamide, (2j)



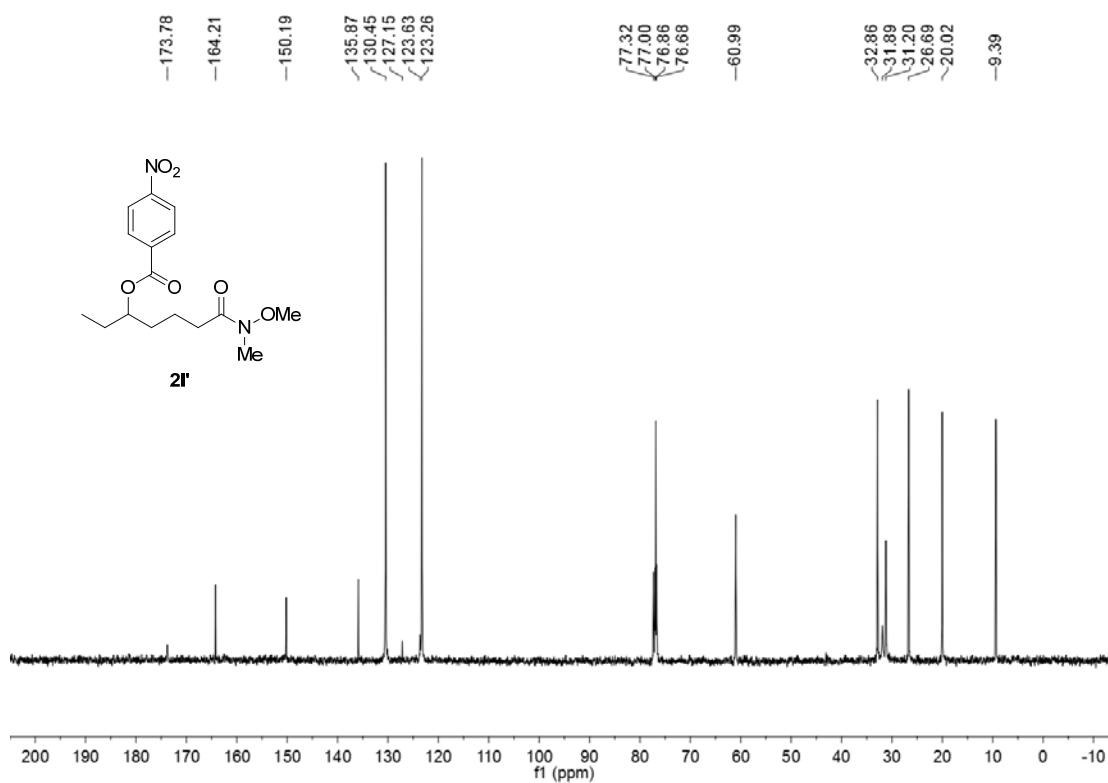
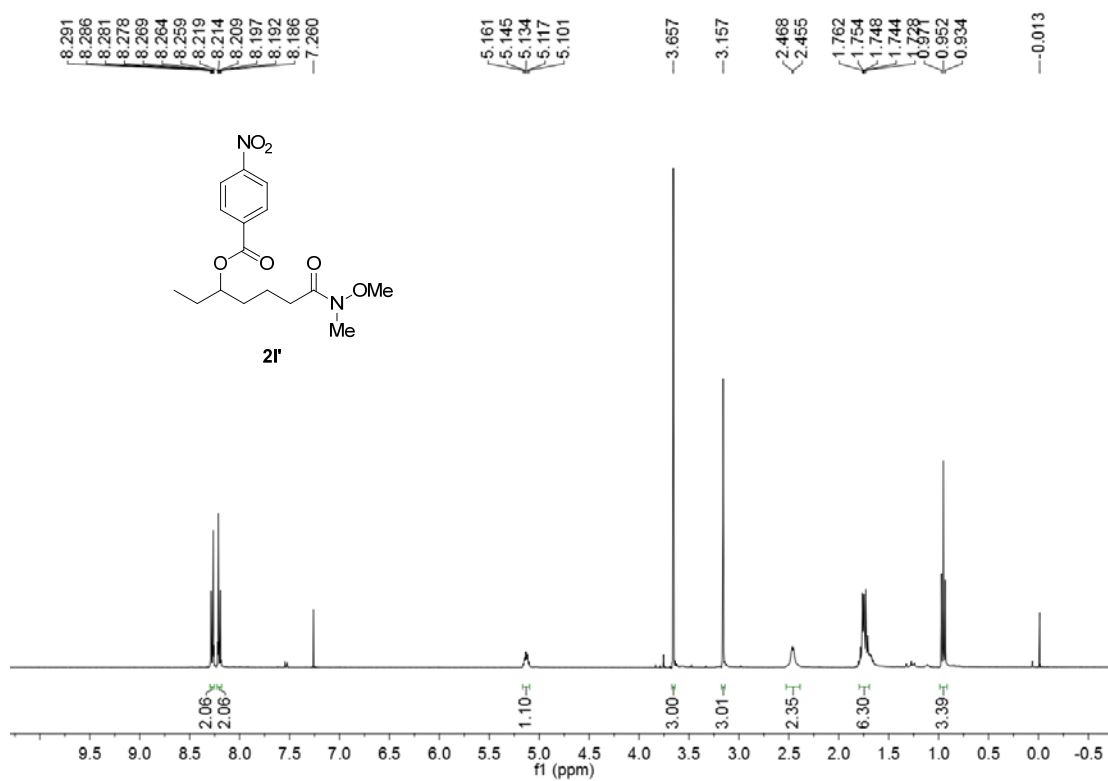
5-Hydroxy-N-methoxy-N-methyl-5-(thiophen-2-yl)pentanamide, (2k)



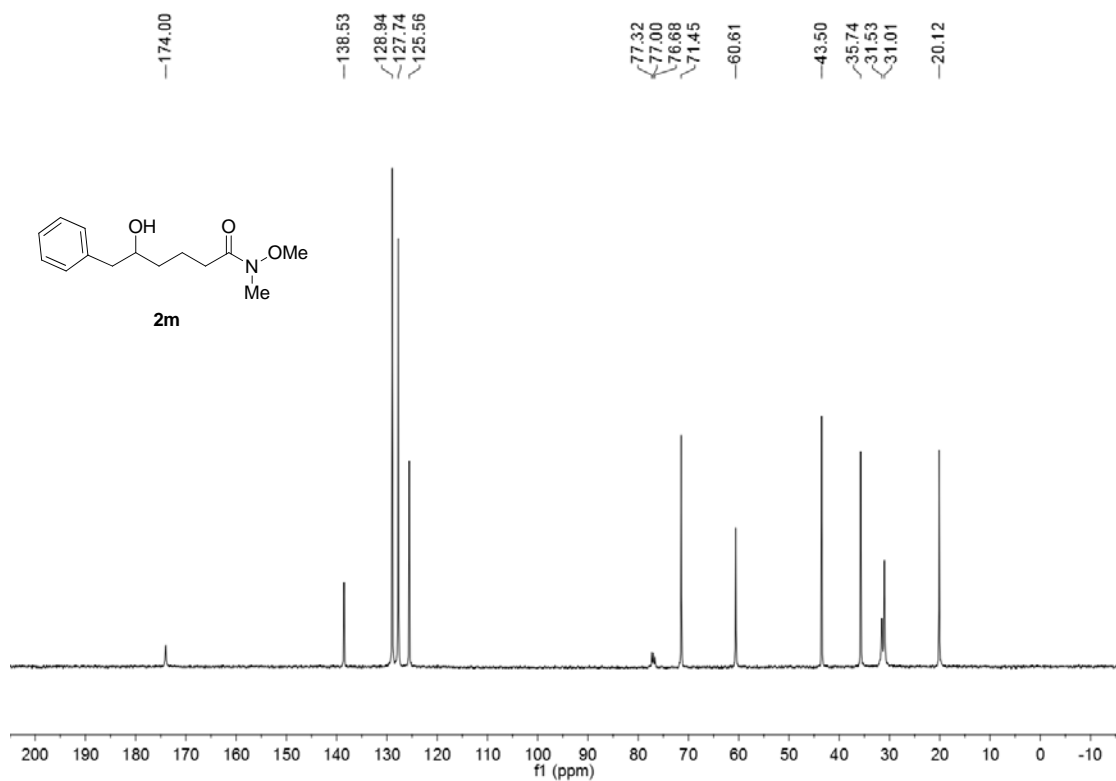
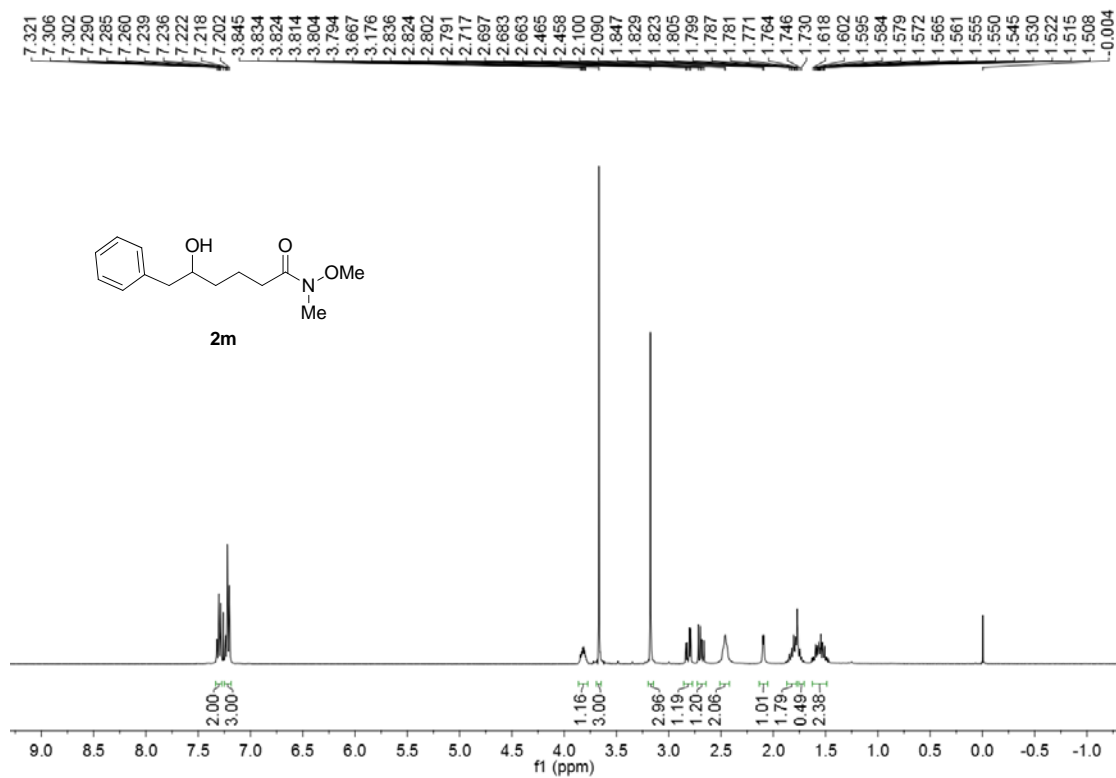
5-Hydroxy-N-methoxy-N-methylheptanamide, (2I)



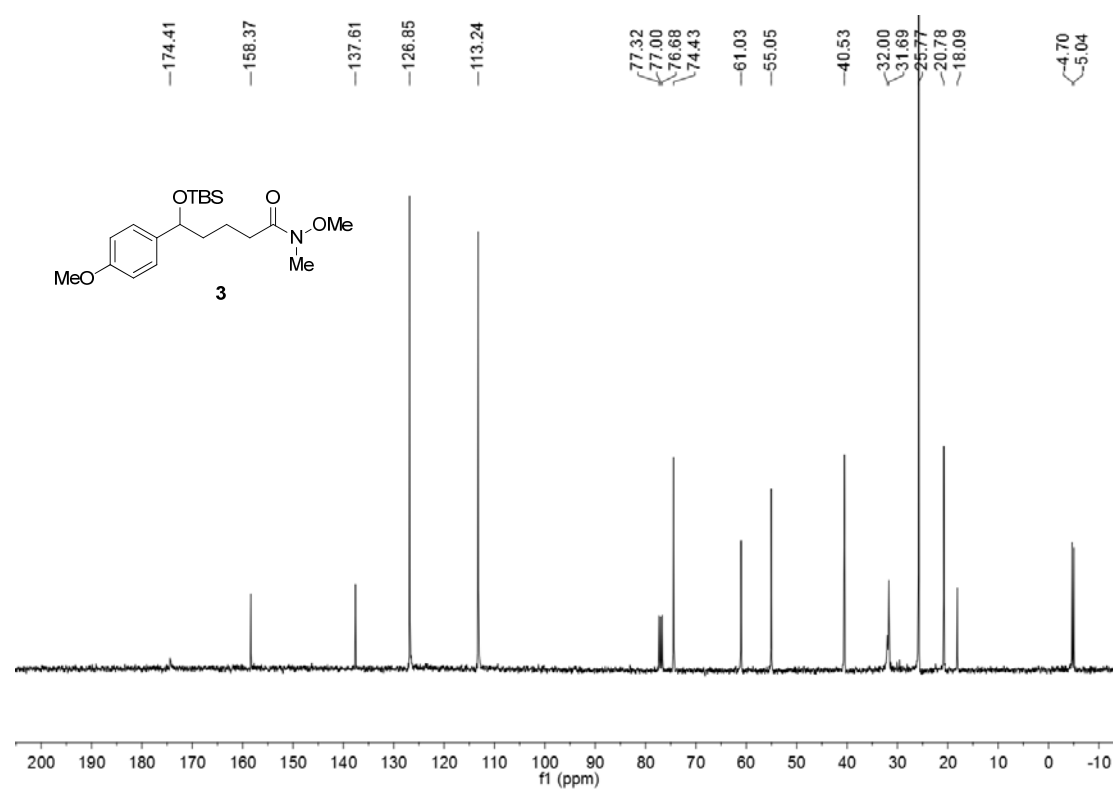
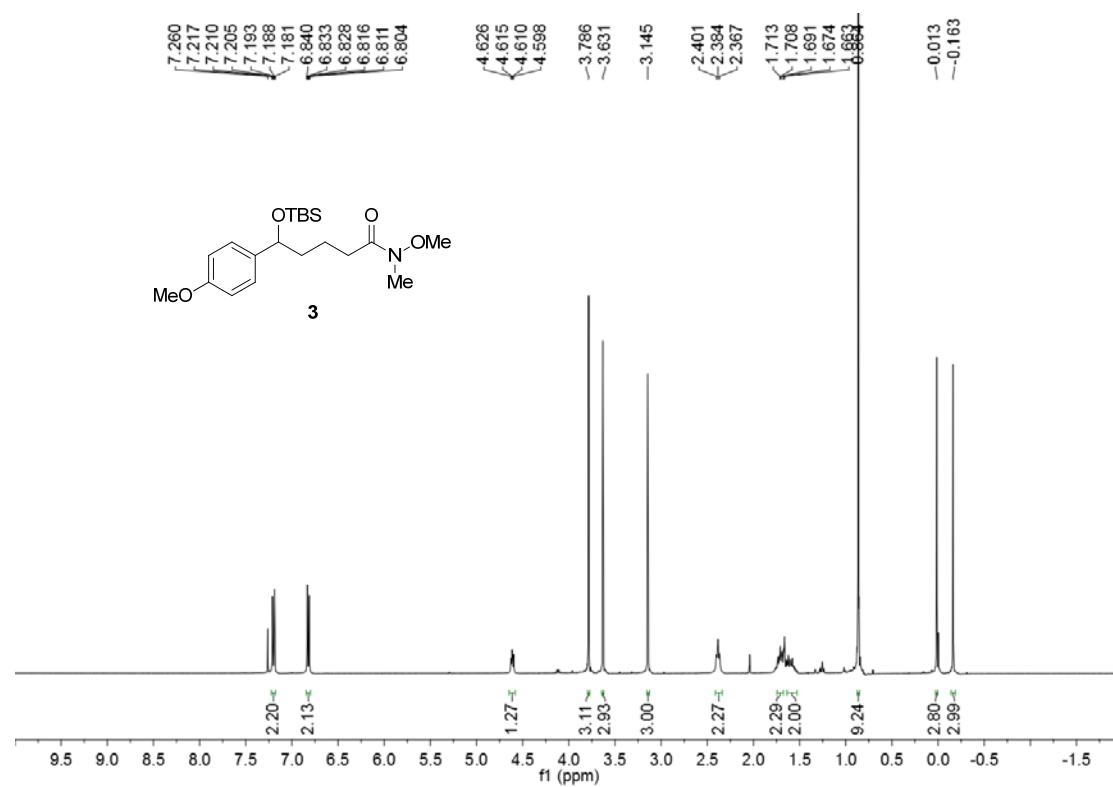
7-(methoxy(methyl)amino)-7-oxoheptan-3-yl-4-nitrobenzoate, (2I')



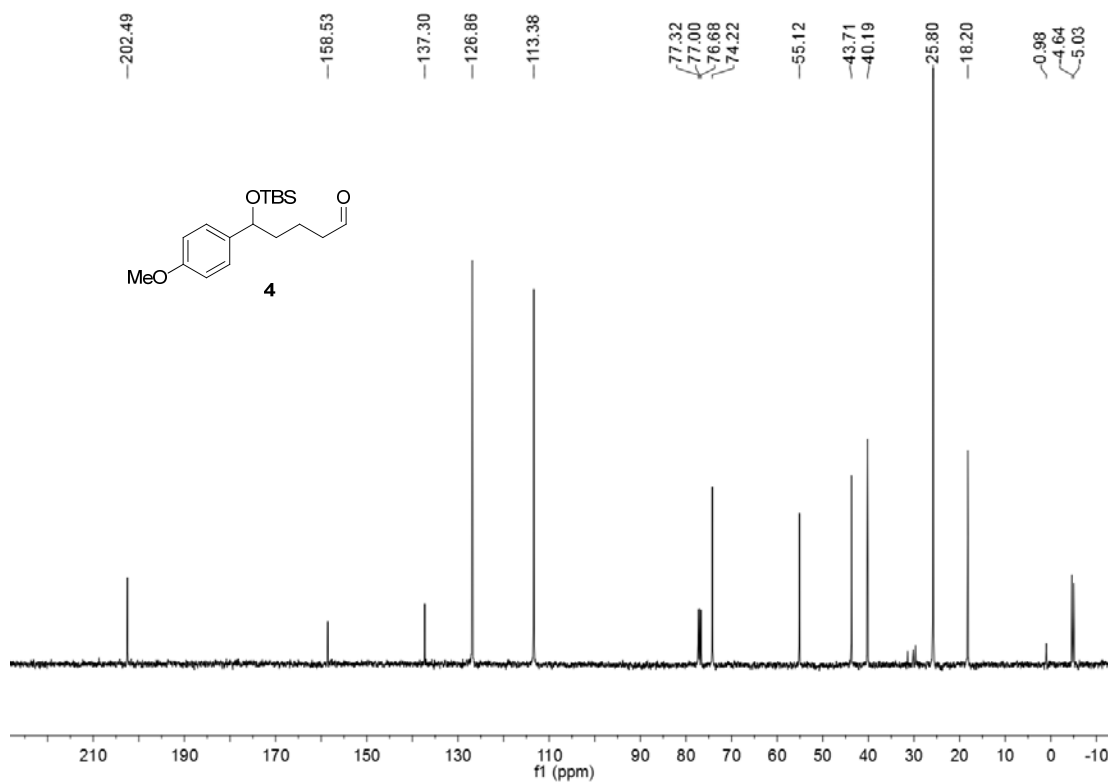
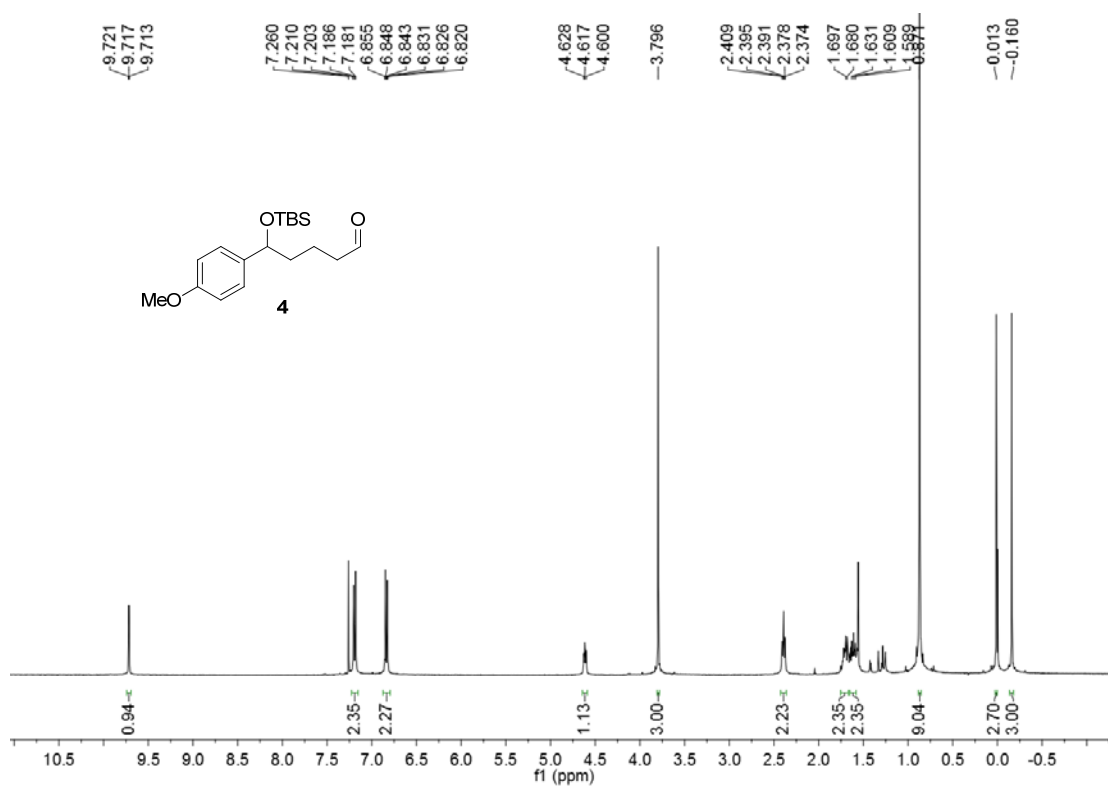
**5-Hydroxy-N-methoxy-N-methyl-6-phenylhexanamide, (2m)**



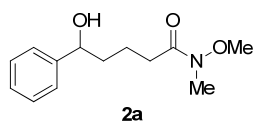
5-((Tert-butyldimethylsilyl)oxy)-*N*-methoxy-5-(4-methoxyphenyl)-*N*-methylpentanamide, (3)



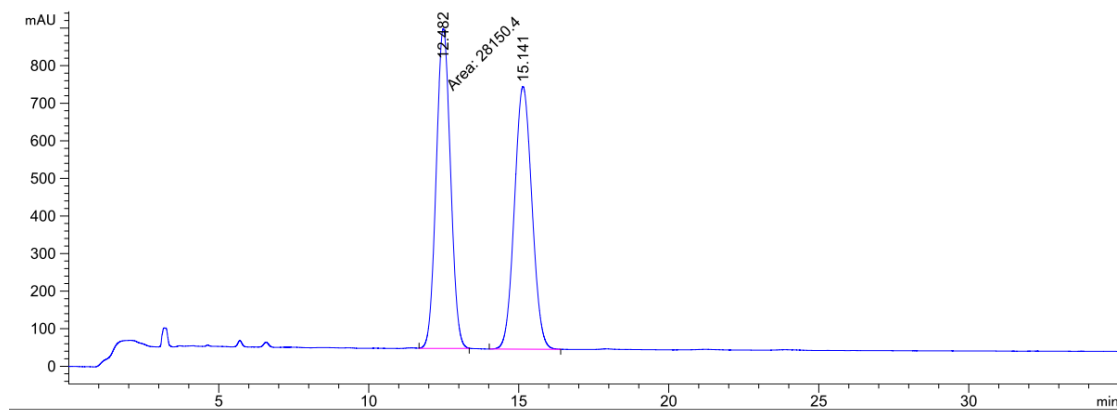
5-((Tert-butyldimethylsilyl)oxy)-5-(4-methoxyphenyl)pentanal, (4)



## HPLC copies for racemic and chiral compounds

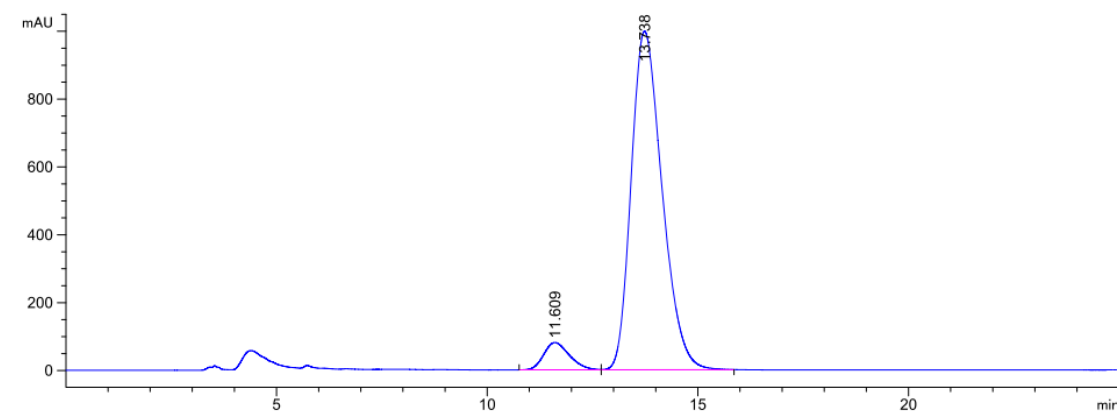


### Racemate:



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.482	MM	0.5512	2.81504e4	851.17047	49.8349
2	15.141	BV	0.4834	2.83370e4	699.06165	50.1651

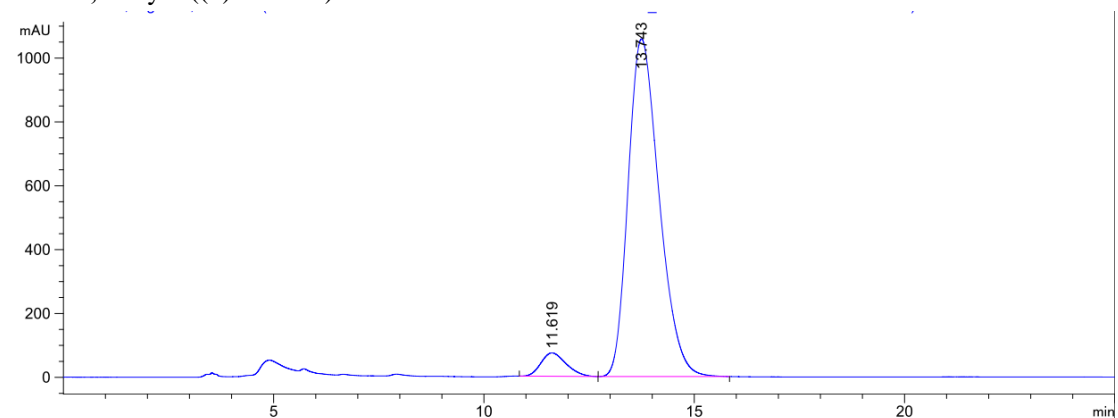
### Table 1, entry 1 ((S)-SunPhos)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.609	BV	0.4935	3398.32056	80.50650	6.2591
2	13.738	VV	0.6007	5.08957e4	997.64655	93.7409

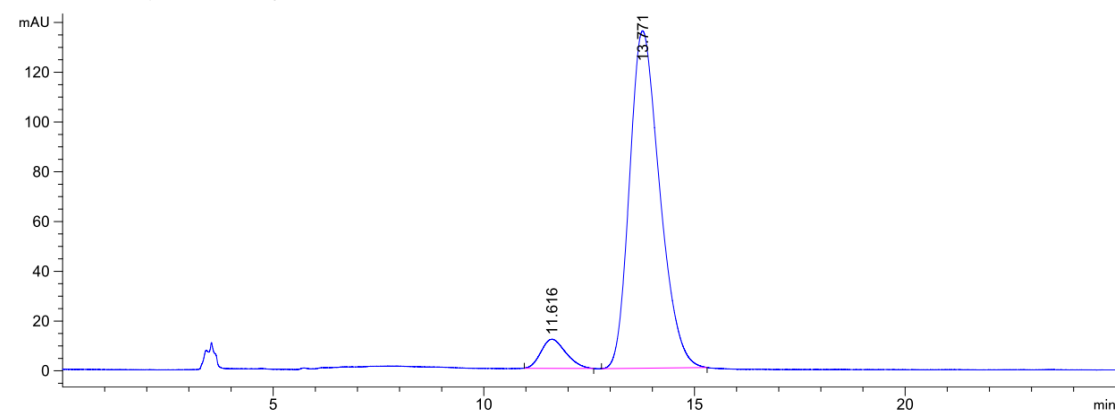


**Table 1, entry 2 ((S)-BINAP)**



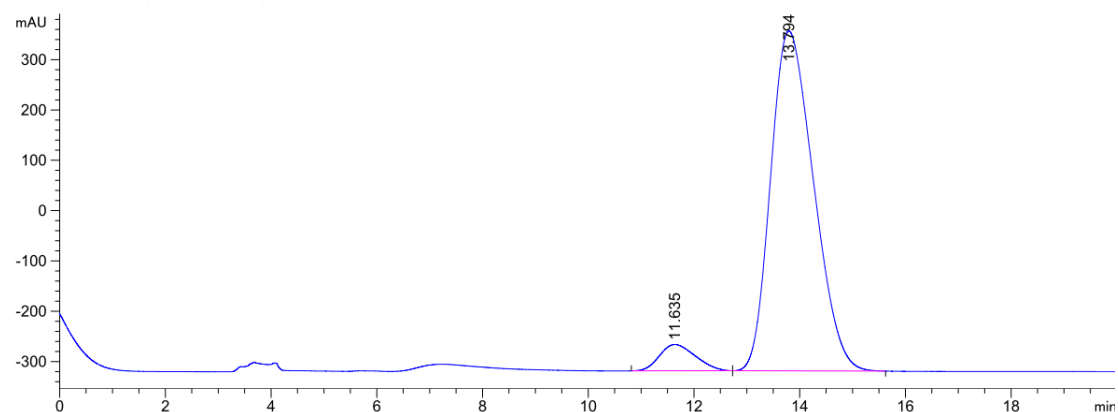
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.619	BB	0.4881	3050.62744	73.29433	5.3319
2	13.743	BV	0.6006	5.41645e4	1057.33960	94.6681

**Table 1, entry 3 ((S)-SegPhos)**



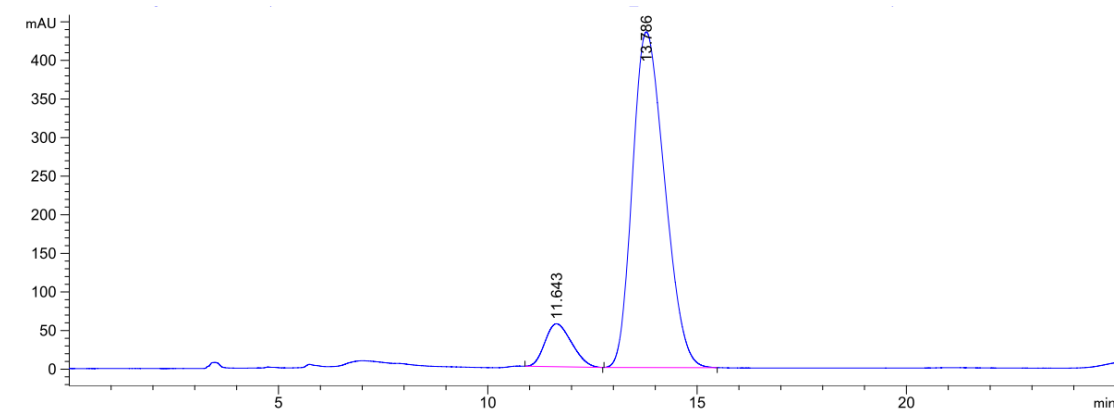
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.616	BB	0.4809	479.56158	11.71870	6.6460
2	13.771	BB	0.5814	6736.17920	135.64049	93.3540

**Table 1, entry 4 ((S)-SynPhos)**



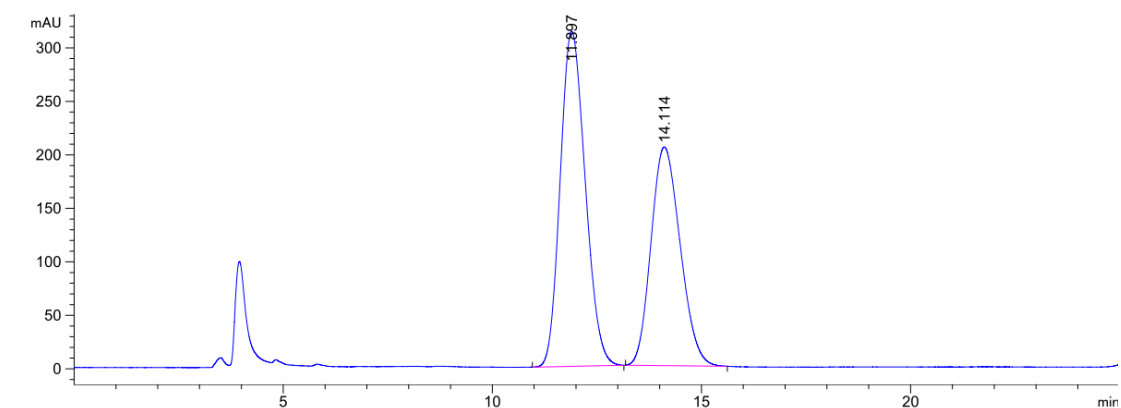
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.635	BB	0.5508	2458.96313	52.22245	6.0759
2	13.794	BB	0.6591	3.80119e4	675.40698	93.9241

**Table 1, entry 5 ((S)-C3-TunePhos)**



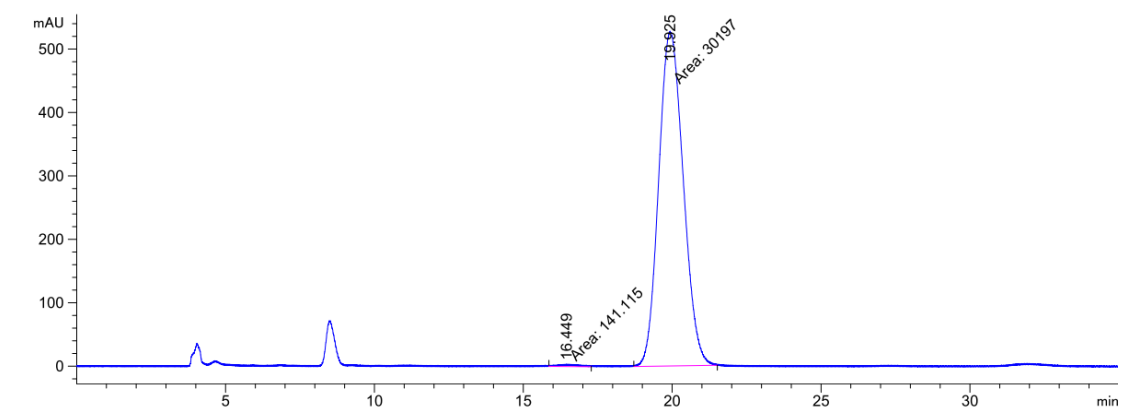
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.643	BB	0.5188	2462.34229	55.69004	9.5893
2	13.786	BV	0.6274	2.32157e4	434.81445	90.4107

**Table 1, entry 6 ((R)-4-Me-SunPhos)**



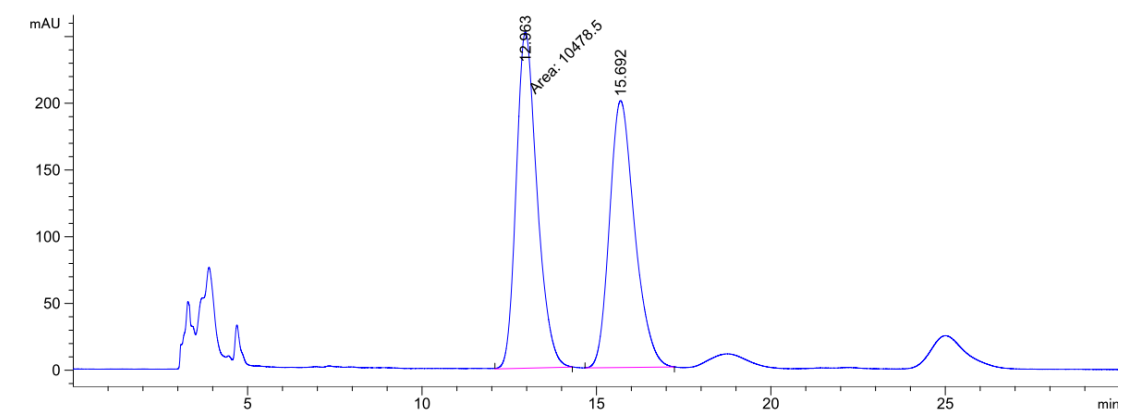
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.897	BB	0.4853	1.29900e4	313.23044	56.7127
2	14.114	BB	0.5710	9914.89746	204.38637	43.2873

**Table 1, entry 7 ((S)-3,5-(CH<sub>3</sub>)<sub>2</sub>-SunPhos)**



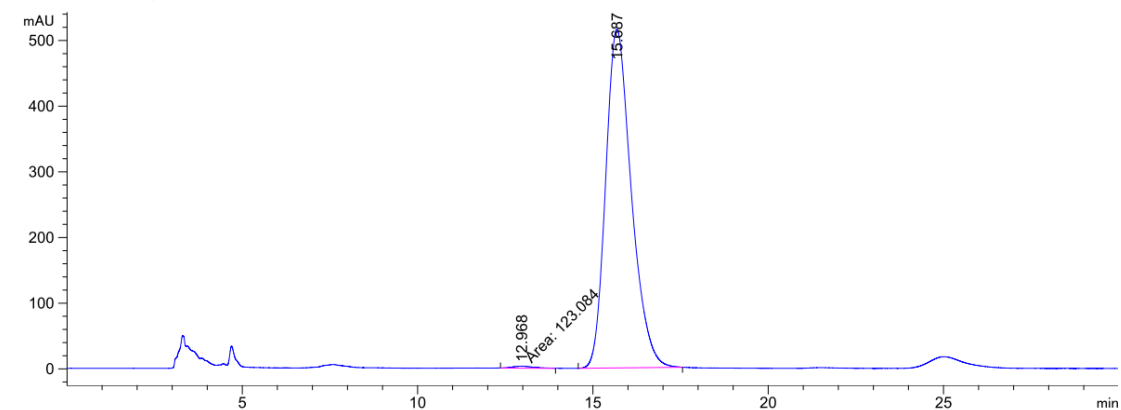
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.449	MM	0.6348	141.11485	3.70516	0.4651
2	19.925	MM	0.9535	3.01970e4	527.82813	99.5349

**Table 2, entry 1 (in MeOH)**



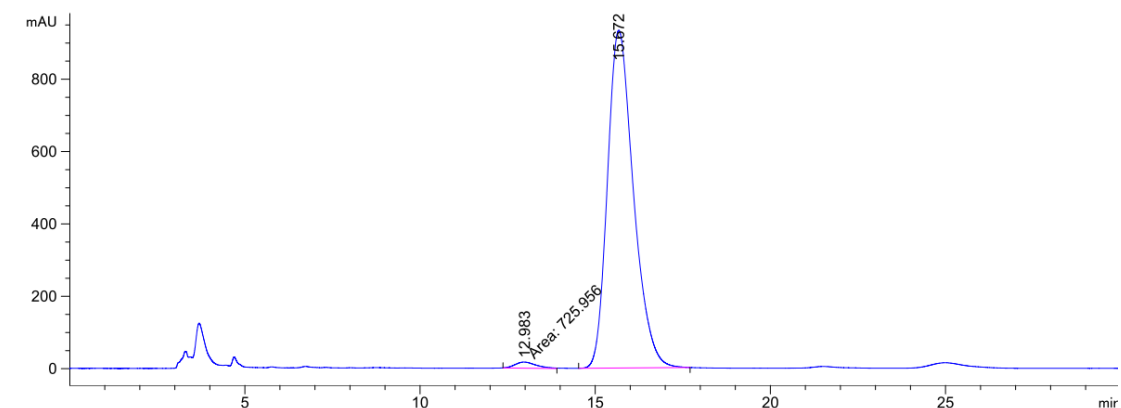
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.963	MM	0.6934	1.04785e4	251.88022	51.1177
2	15.692	BB	0.5861	1.00203e4	199.95497	48.8823

**Table 2, entry 2 (in EtOH)**



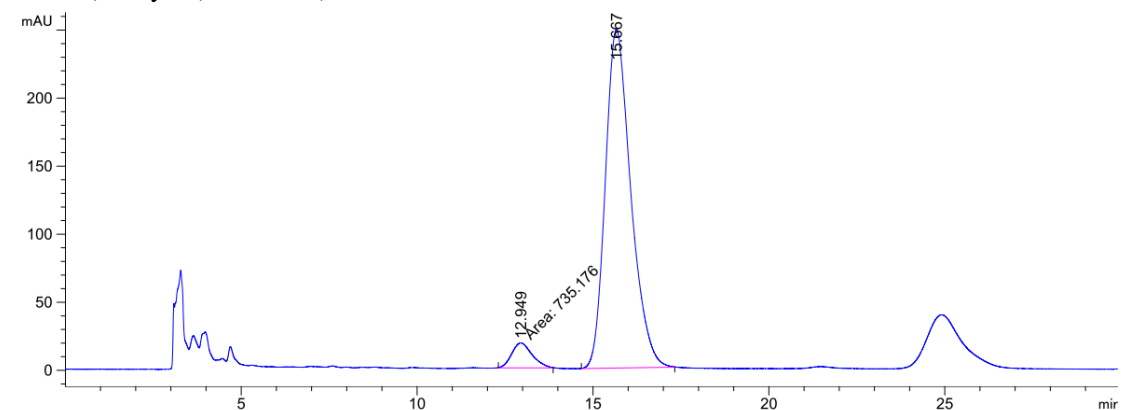
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.968	MM	0.6758	123.08389	3.03547	0.4676
2	15.687	BB	0.6007	2.62014e4	515.32111	99.5324

**Table 2, entry 3 (in DCM)**



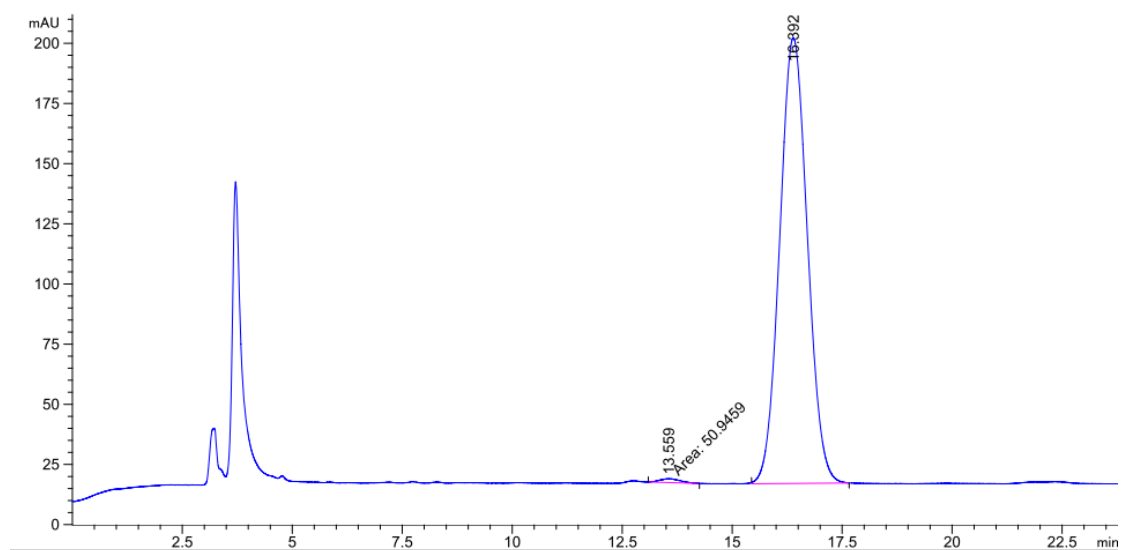
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.983	MM	0.7079	725.95599	17.09226	1.4859
2	15.672	BB	0.6032	4.81319e4	933.26086	98.5141

**Table 2, entry 5 (in Toluene)**



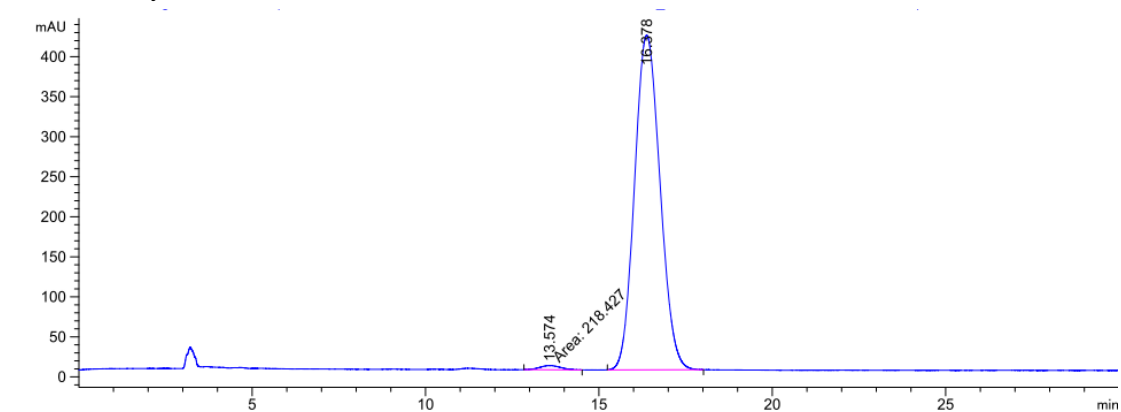
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.949	MM	0.6682	735.17566	18.33700	5.5444
2	15.667	VV	0.5927	1.25245e4	248.61723	94.4556

**Table 2, entry 6 (KOH)**

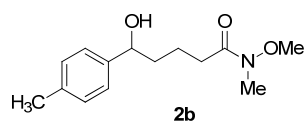


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.559	MM	0.5337	50.94591	1.59098	0.6256
2	16.392	VB	0.5149	8092.37549	185.17209	99.3744

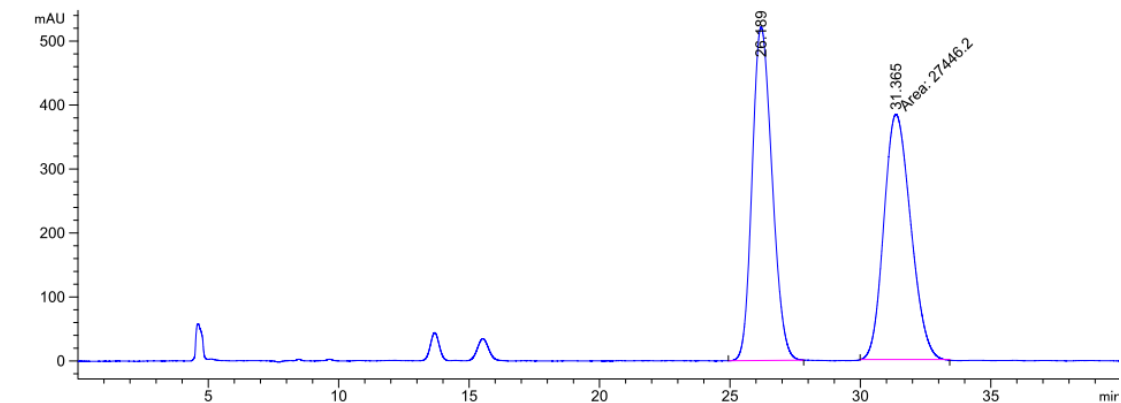
**Table 2, entry 7 (K<sub>2</sub>CO<sub>3</sub>)**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.574	MM	0.6881	218.42688	5.29096	1.0142
2	16.378	VB	0.5977	2.13195e4	417.89914	98.9858

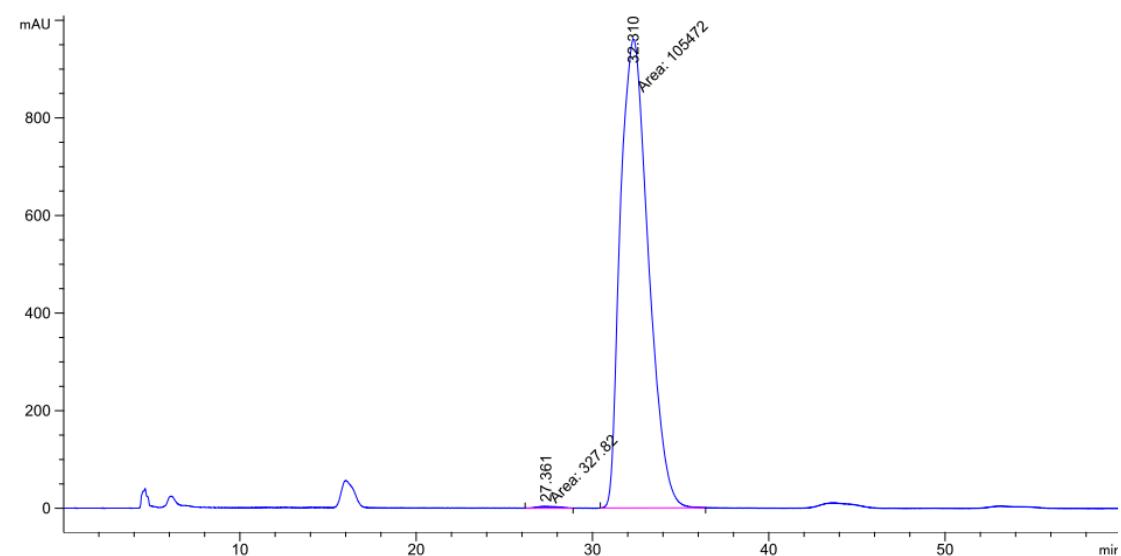


**Racemate:**

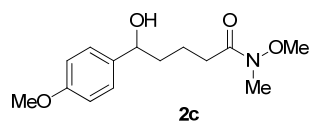


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.189	BV	0.6225	2.76972e4	521.15942	50.2276
2	31.365	MM	1.1931	2.74462e4	383.40515	49.7724

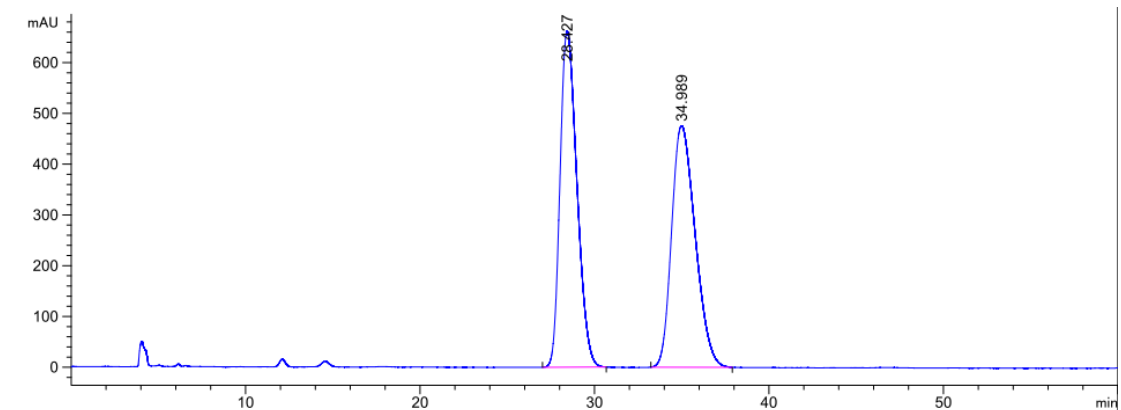
**Table 2, entry 2**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.361	MM	1.3368	327.82010	4.08701	0.3099
2	32.310	MM	1.8302	1.05472e5	960.46600	99.6901

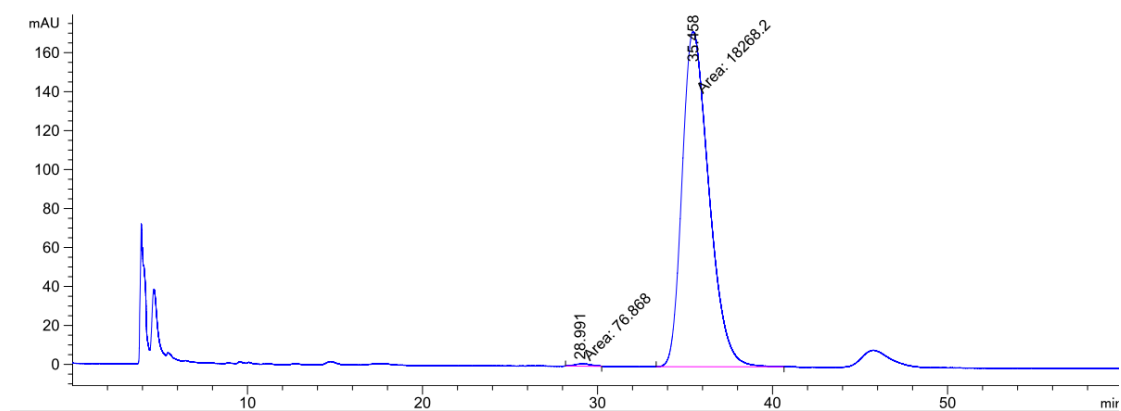


**Racemate:**



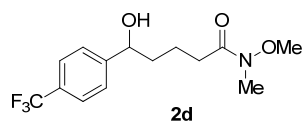
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.427	BB	0.7868	4.45591e4	661.98914	49.9994
2	34.989	BB	1.0944	4.45602e4	475.66702	50.0006

**Table 2, entry 3**

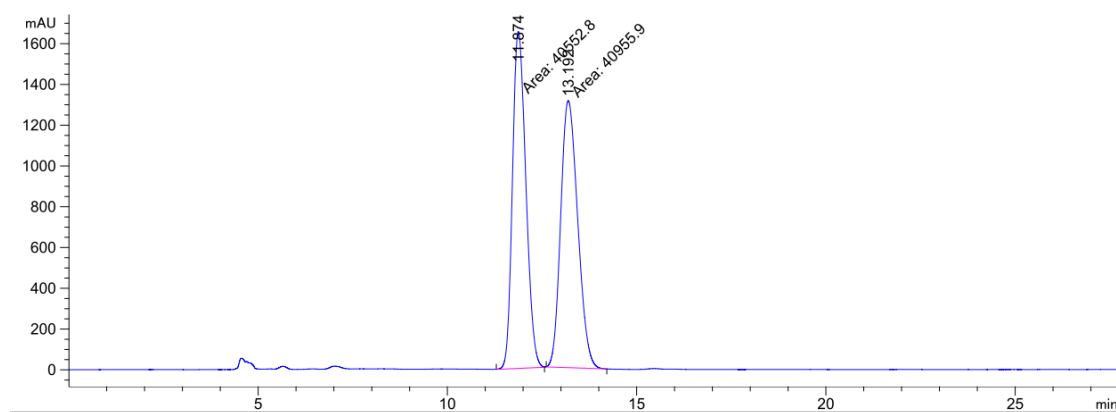


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.991	MM	1.0898	76.86803	1.17553	0.4190
2	35.458	MM	1.7699	1.82682e4	172.03104	99.5810



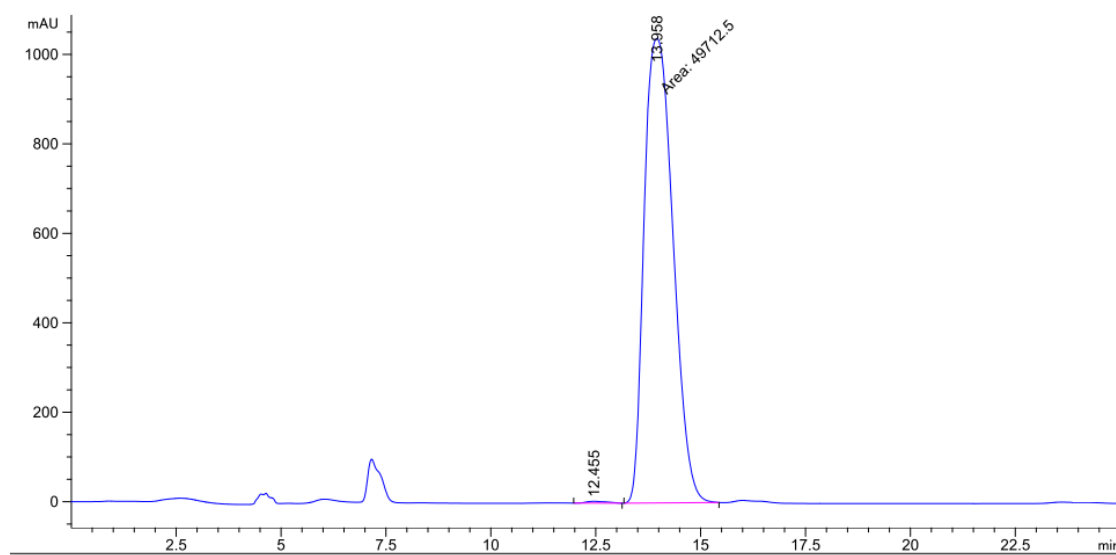


**Racemate:**

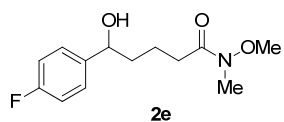


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.874	MM	0.4091	4.05528e4	1652.03357	49.7527
2	13.192	MM	0.5210	4.09559e4	1310.16724	50.2473

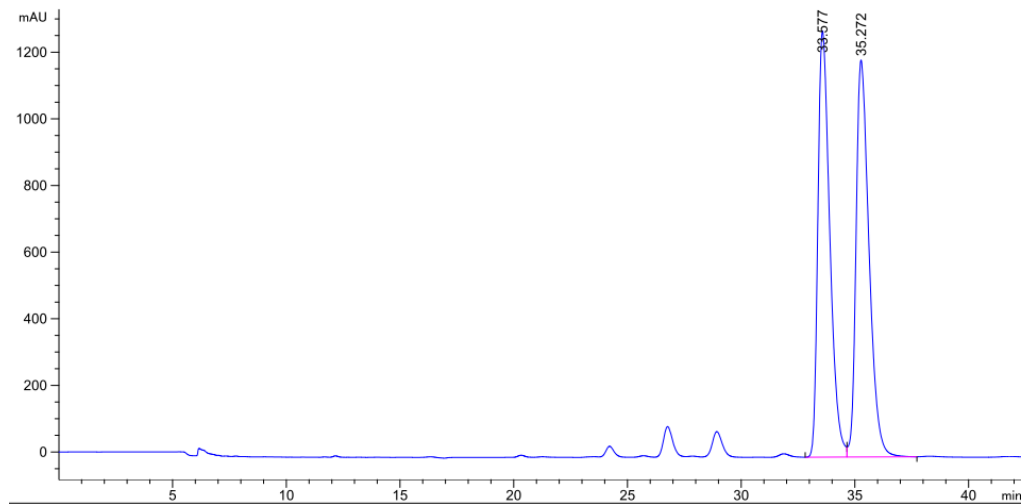
**Table 2, entry 4**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.455	BB	0.4619	134.57985	3.96566	0.2700
2	13.958	MM	0.7979	4.97125e4	1038.34863	99.7300

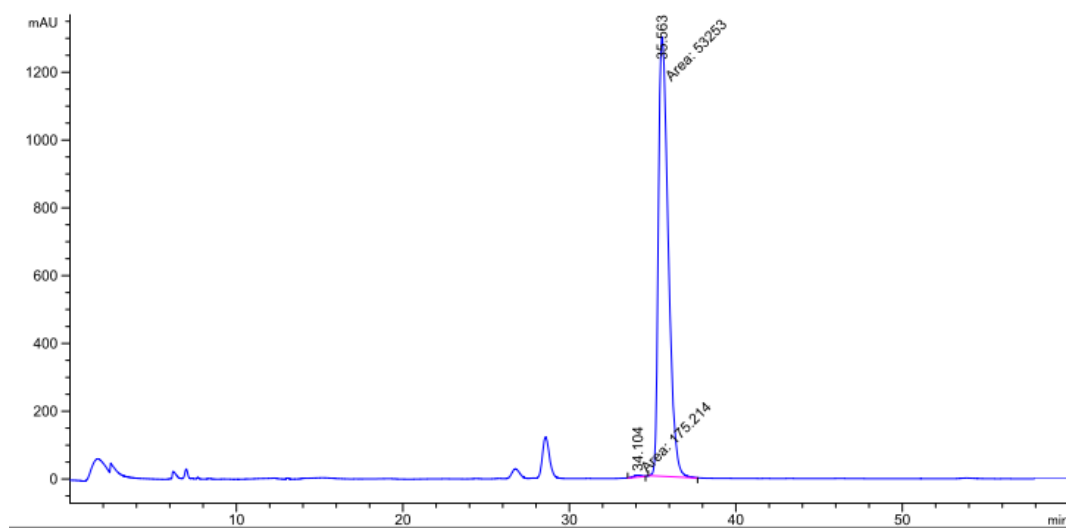


**Racemate:**

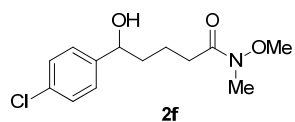


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	33.577	BV	0.5520	4.65062e4	1279.50391	49.5689
2	35.272	VB	0.6074	4.73151e4	1191.26733	50.4311

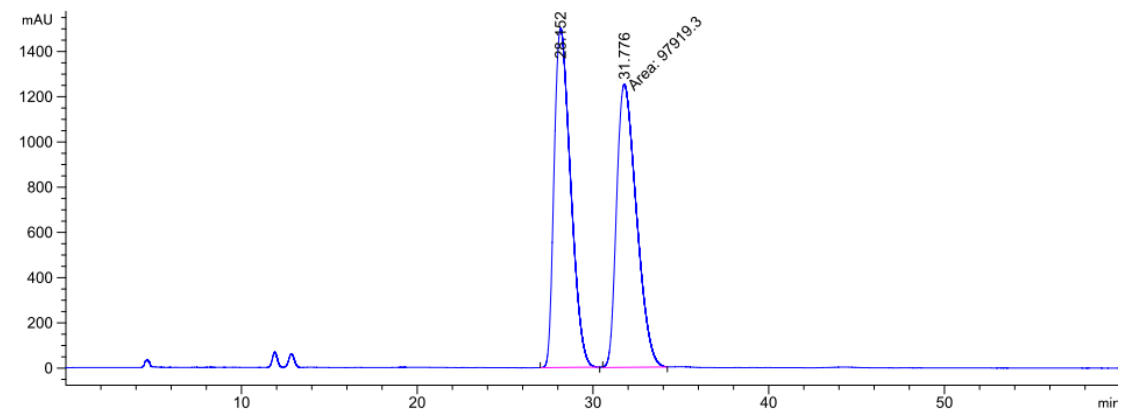
**Table 2, entry 5**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	34.104	MM	0.5641	175.21384	5.17634	0.3279
2	35.563	MM	0.6847	5.32530e4	1296.24536	99.6721

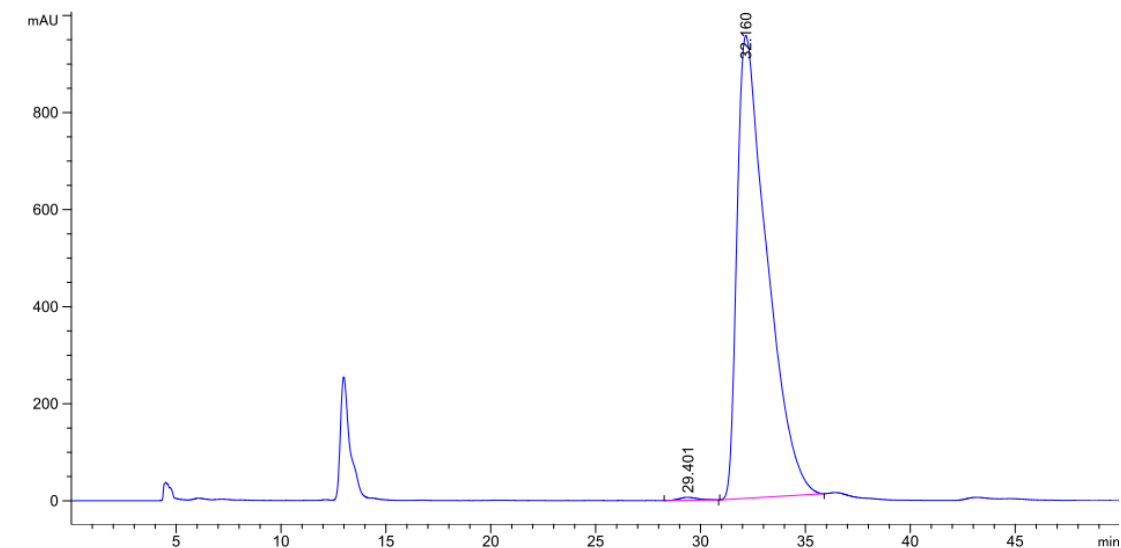


**Racemate:**

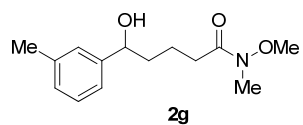


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.152	BB	0.7609	9.76372e4	1500.01270	49.9279
2	31.776	MM	1.3024	9.79193e4	1253.03162	50.0721

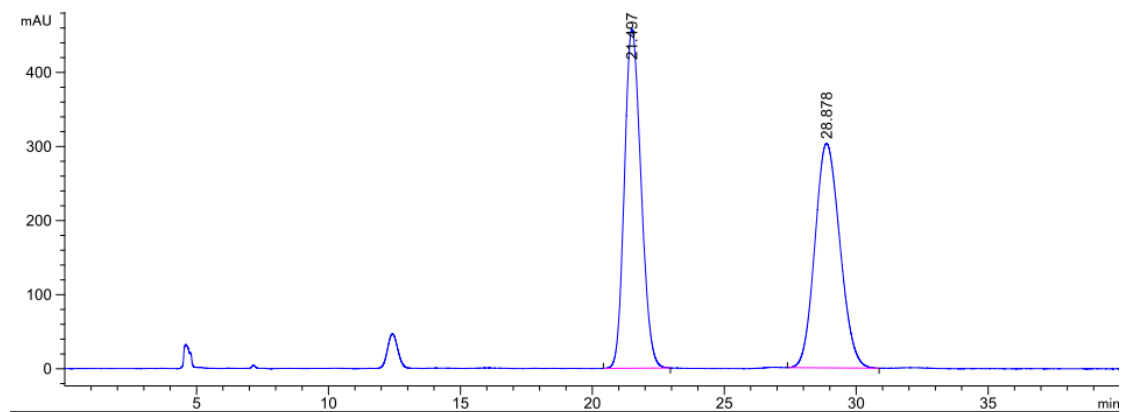
**Table 2, entry 6**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.401	BB	0.7512	386.18127	6.11175	0.4073
2	32.160	BB	1.4107	9.44200e4	954.01752	99.5927

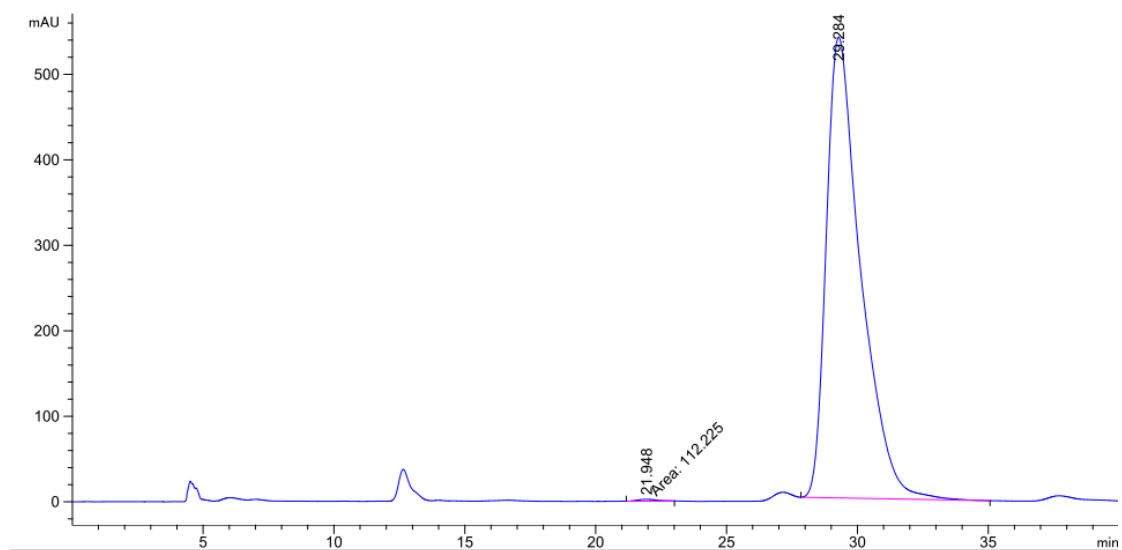


**Racemate:**

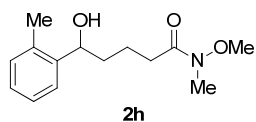


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.497	BB	0.5147	2.00242e4	457.48560	50.0787
2	28.878	BB	0.7706	1.99613e4	303.01355	49.9213

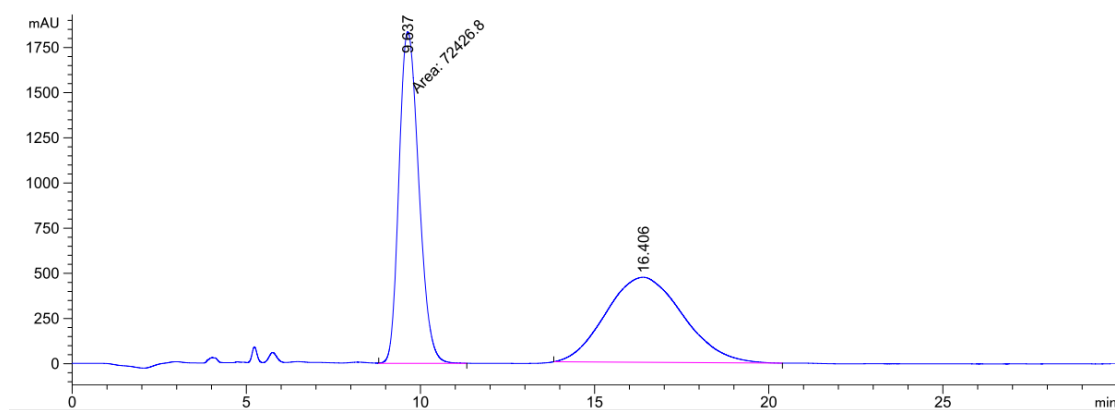
**Table 2, entry 7**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.948	MM	0.8636	112.22507	2.16594	0.2274
2	29.284	BB	1.3377	4.92308e4	538.95801	99.7726

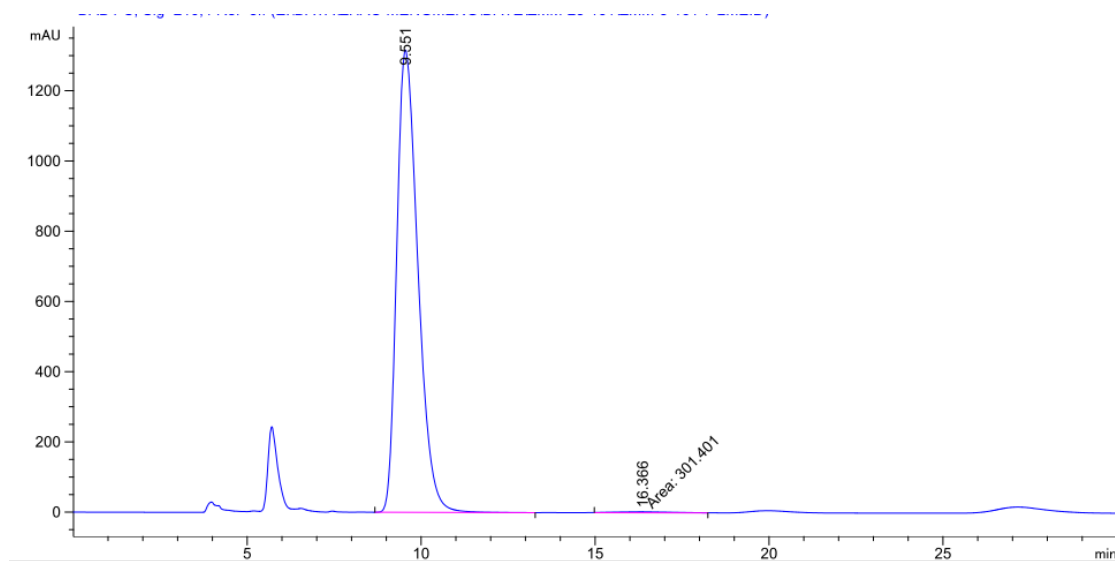


**Racemate:**

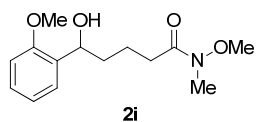


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.637	MM	0.6574	7.24268e4	1836.13538	50.0540
2	16.406	BB	1.7954	7.22705e4	470.81250	49.9460

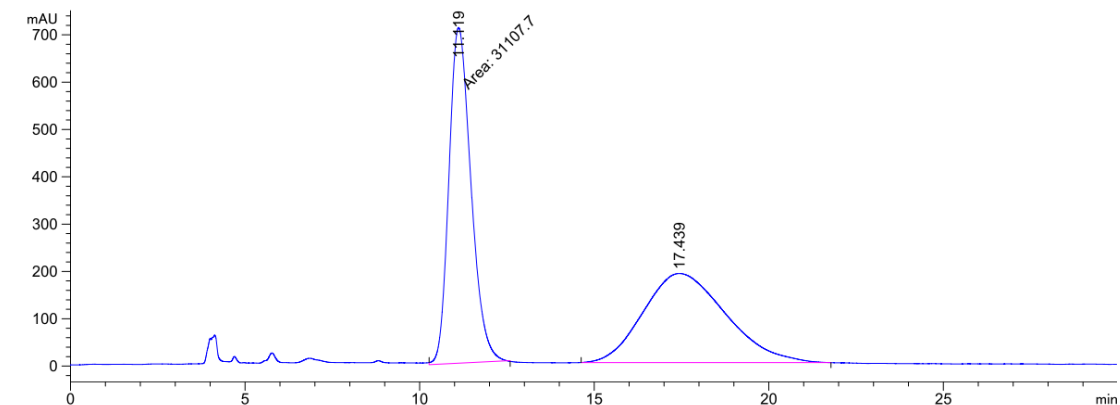
**Table 2, entry 8**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.551	BB	0.6580	5.57344e4	1316.32678	99.4621
2	16.366	MM	1.8959	301.40085	2.64952	0.5379

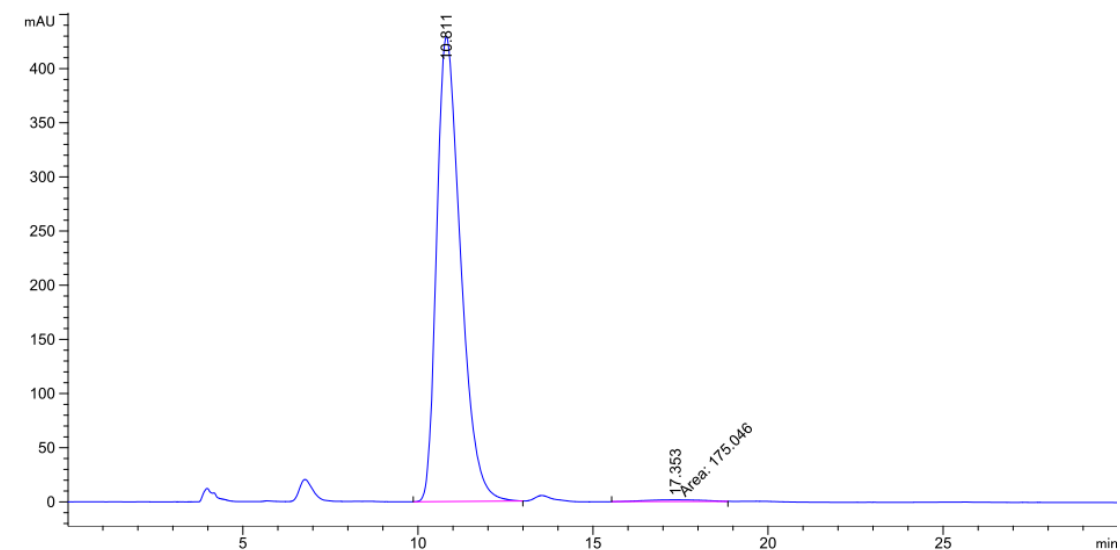


**Racemate:**

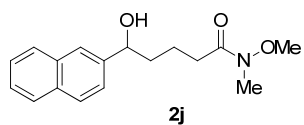


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.119	MM	0.7309	3.11077e4	709.32831	50.1771
2	17.439	BB	1.9184	3.08882e4	188.14160	49.8229

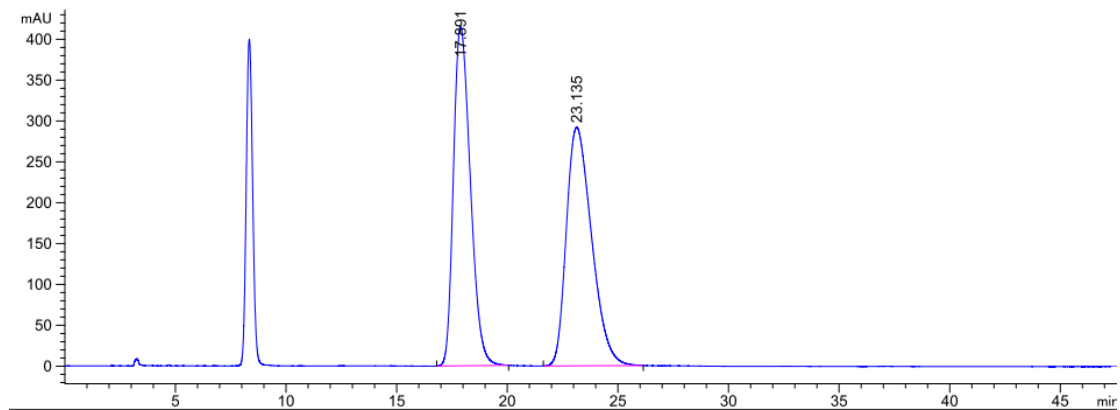
**Table 2, entry 9**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.811	BB	0.7327	2.04167e4	429.38998	99.1499
2	17.353	MM	1.8700	175.04645	1.56011	0.8501

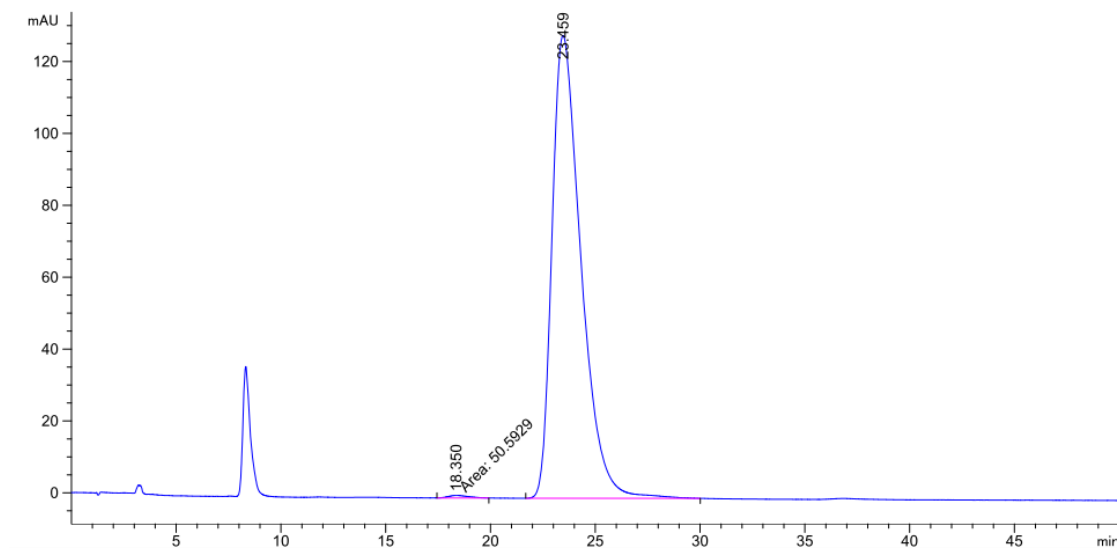


**Racemate:**

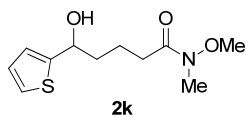


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.891	BB	0.6251	2.20414e4	414.69690	48.7723
2	23.135	BB	0.9274	2.31510e4	291.86533	51.2277

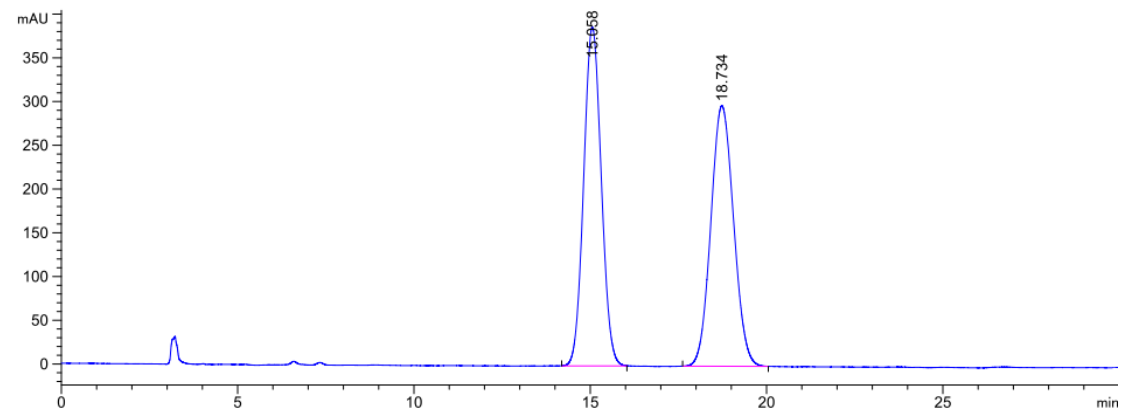
**Table 2, entry 10**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.350	MM	1.1487	50.59293	7.34071e-1	0.4076
2	23.459	BB	1.4259	1.23612e4	128.77695	99.5924

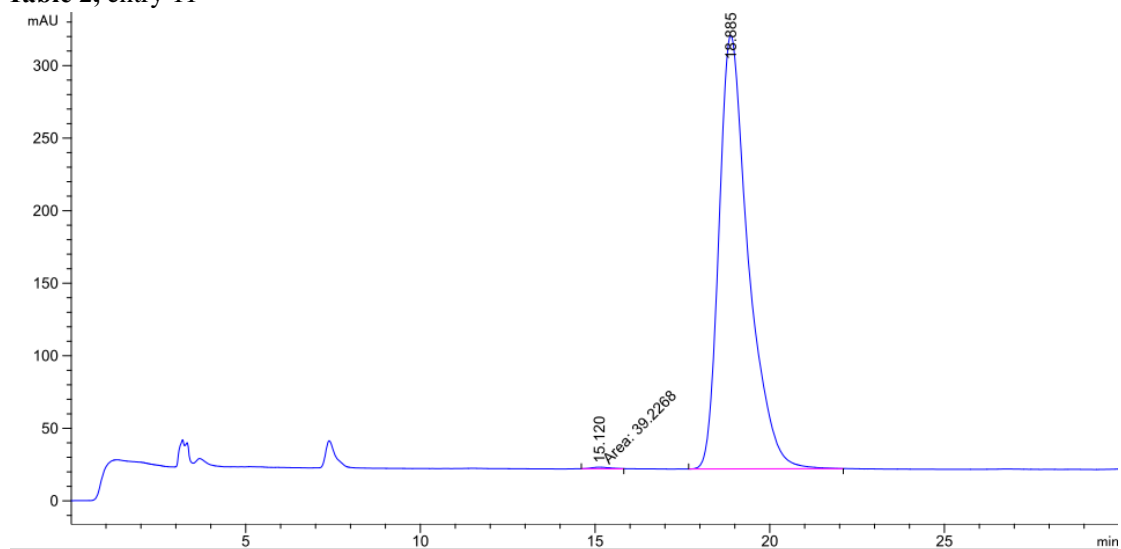


**Racemate:**



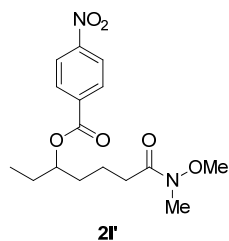
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.058	BV	0.4448	1.33962e4	387.01572	50.0359
2	18.734	VB	0.5295	1.33770e4	297.82297	49.9641

**Table 2, entry 11**

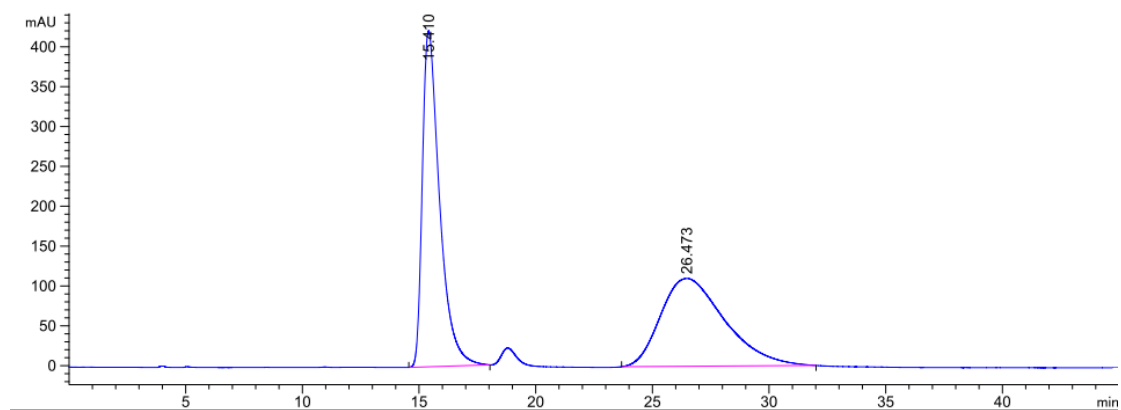


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.120	MM	0.6186	39.22677	1.05686	0.2246
2	18.885	BB	0.8687	1.74249e4	298.66132	99.7754



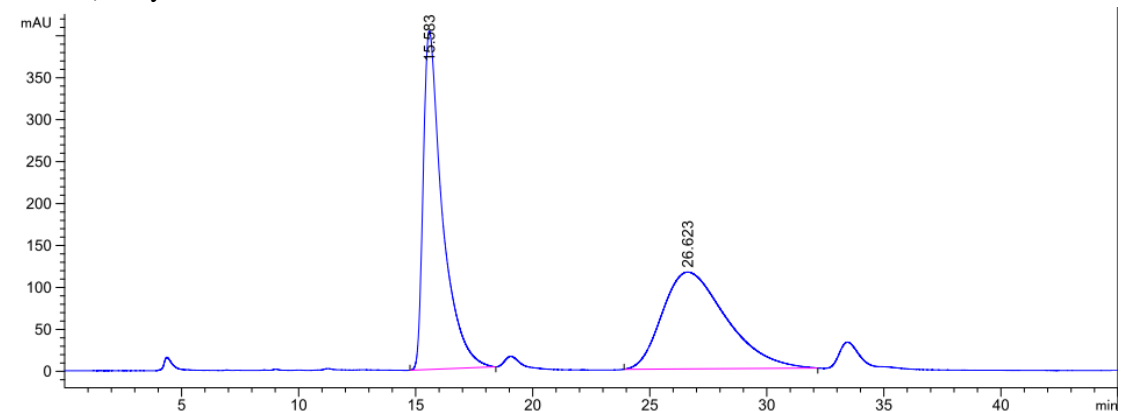


**Racemate:**

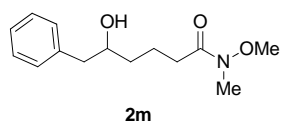


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.410	BB	0.6964	2.16257e4	421.65881	50.7358
2	26.473	BB	2.2266	2.09984e4	110.24780	49.2642

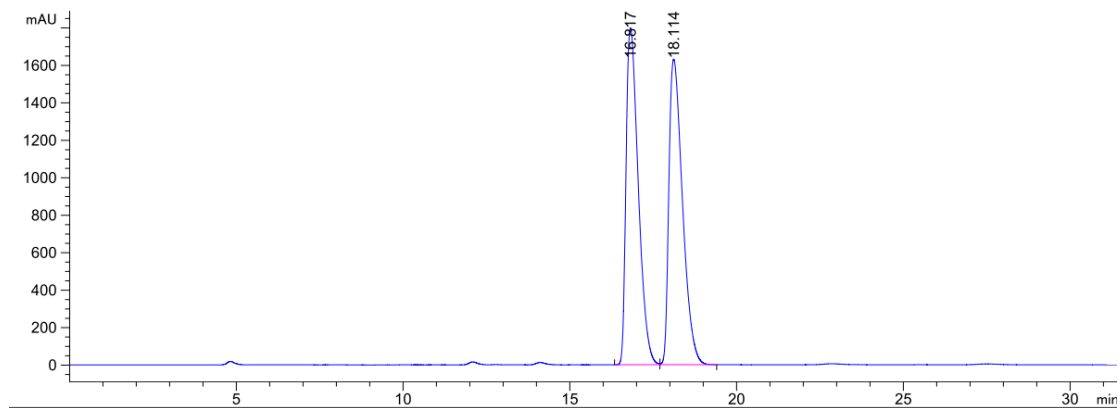
**Table 2, entry 12**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.583	BB	0.6819	2.29917e4	403.13541	51.2803
2	26.623	BB	2.2096	2.18437e4	115.41436	48.7197

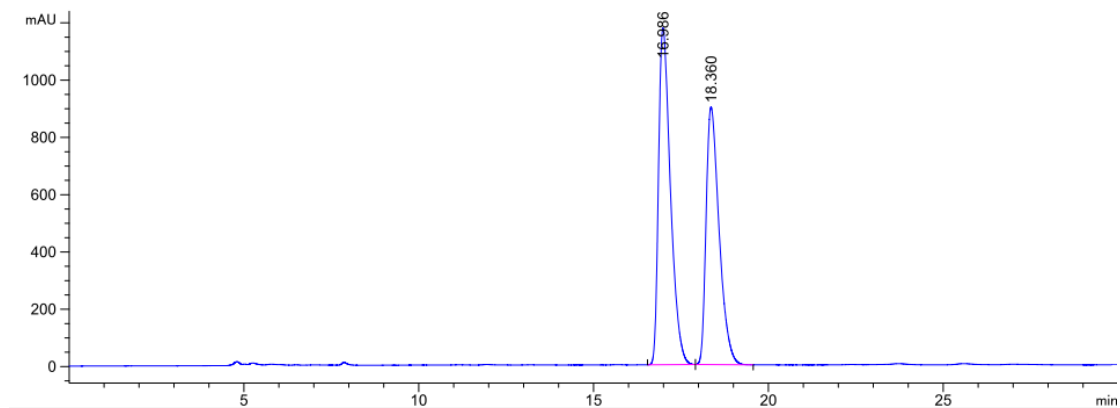


**Racemate:**

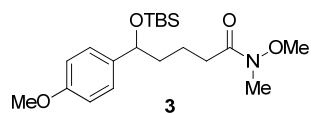


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.817	VV	0.3033	4.57359e4	1798.02917	49.7662
2	18.114	VB	0.3352	4.61655e4	1630.97144	50.2338

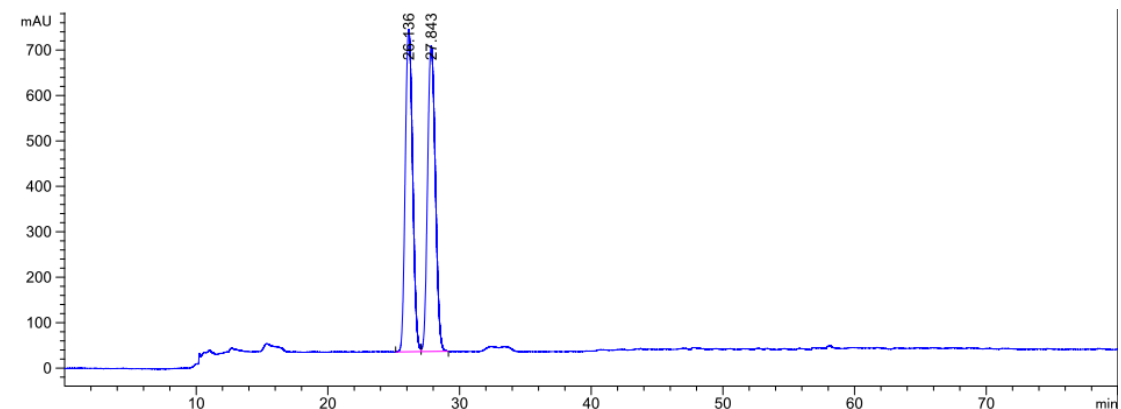
**Table 2, entry 13**



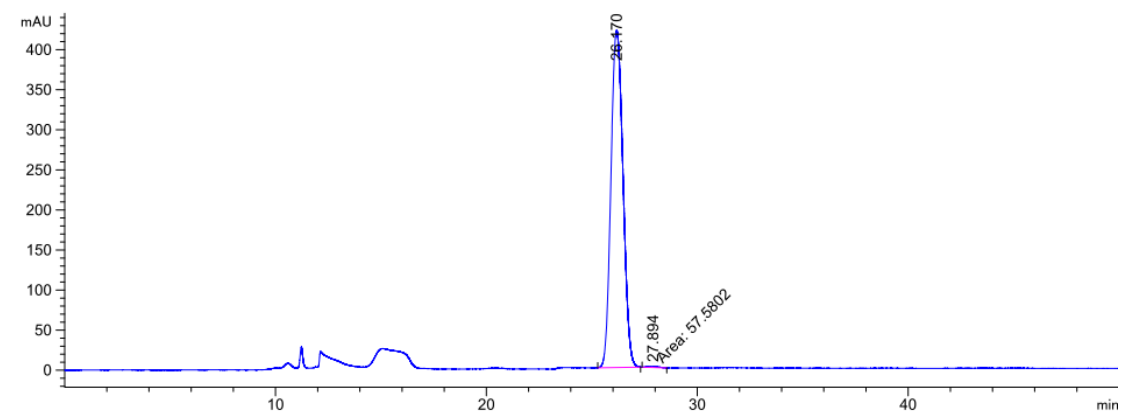
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.986	BB	0.3355	2.77965e4	1175.04883	54.4364
2	18.360	BB	0.3644	2.32658e4	898.98187	45.5636



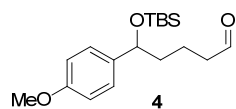
**Racemate:**



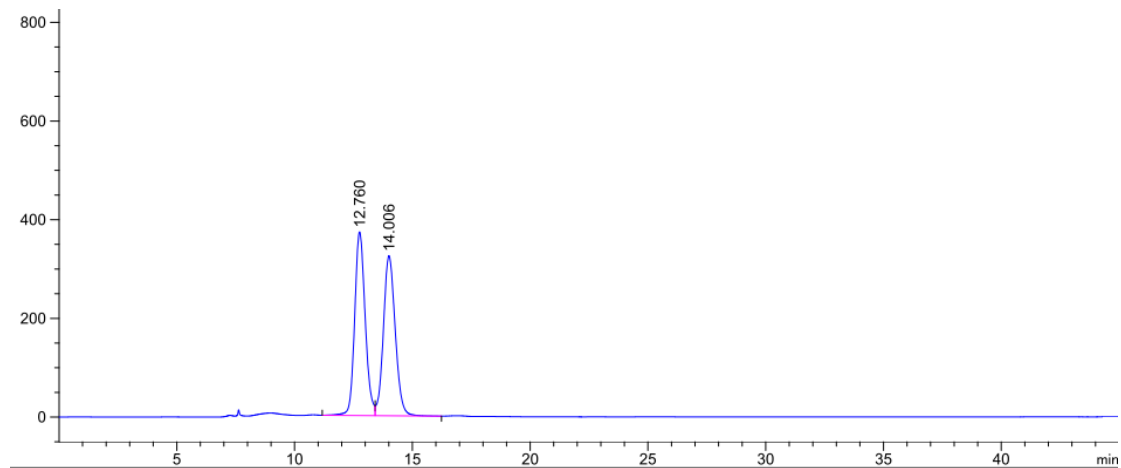
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.136	BV	0.4571	2.75571e4	708.78668	49.9571
2	27.843	VB	0.4811	2.76044e4	672.24316	50.0429



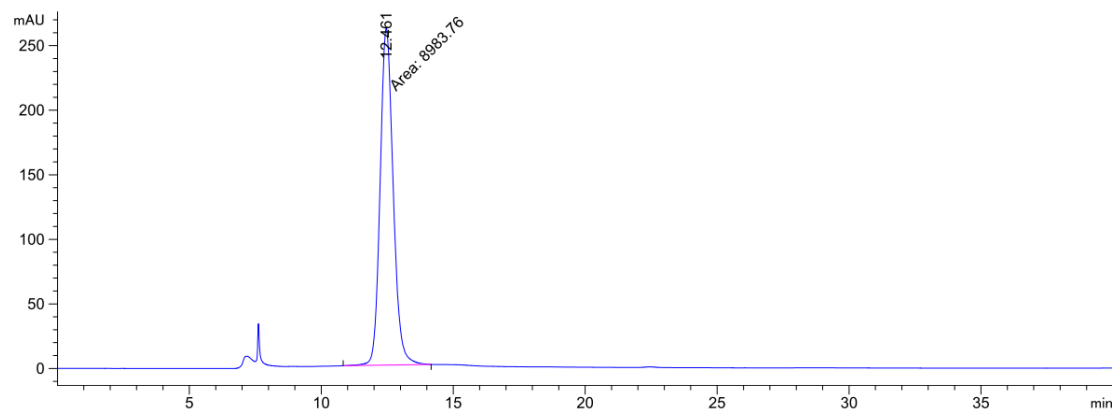
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.170	VV	0.4647	1.66698e4	420.80594	99.6558
2	27.894	MM	0.6219	57.58016	1.54314	0.3442



**Racemate:**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.760	BV	0.4619	1.15473e4	372.28629	50.4611
2	14.006	VB	0.5118	1.13362e4	324.31754	49.5389



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.461	MM	0.5746	8983.75684	260.57510	100.0000