

*Supporting Information for*

Enantioselective Synthesis of 2,5-Dihydrobenzo[*b*]azepine Derivatives  
via Iridium-Catalyzed Asymmetric Allylic Amination with  
2-Allylanilines and Ring-Closing-Metathesis Reaction

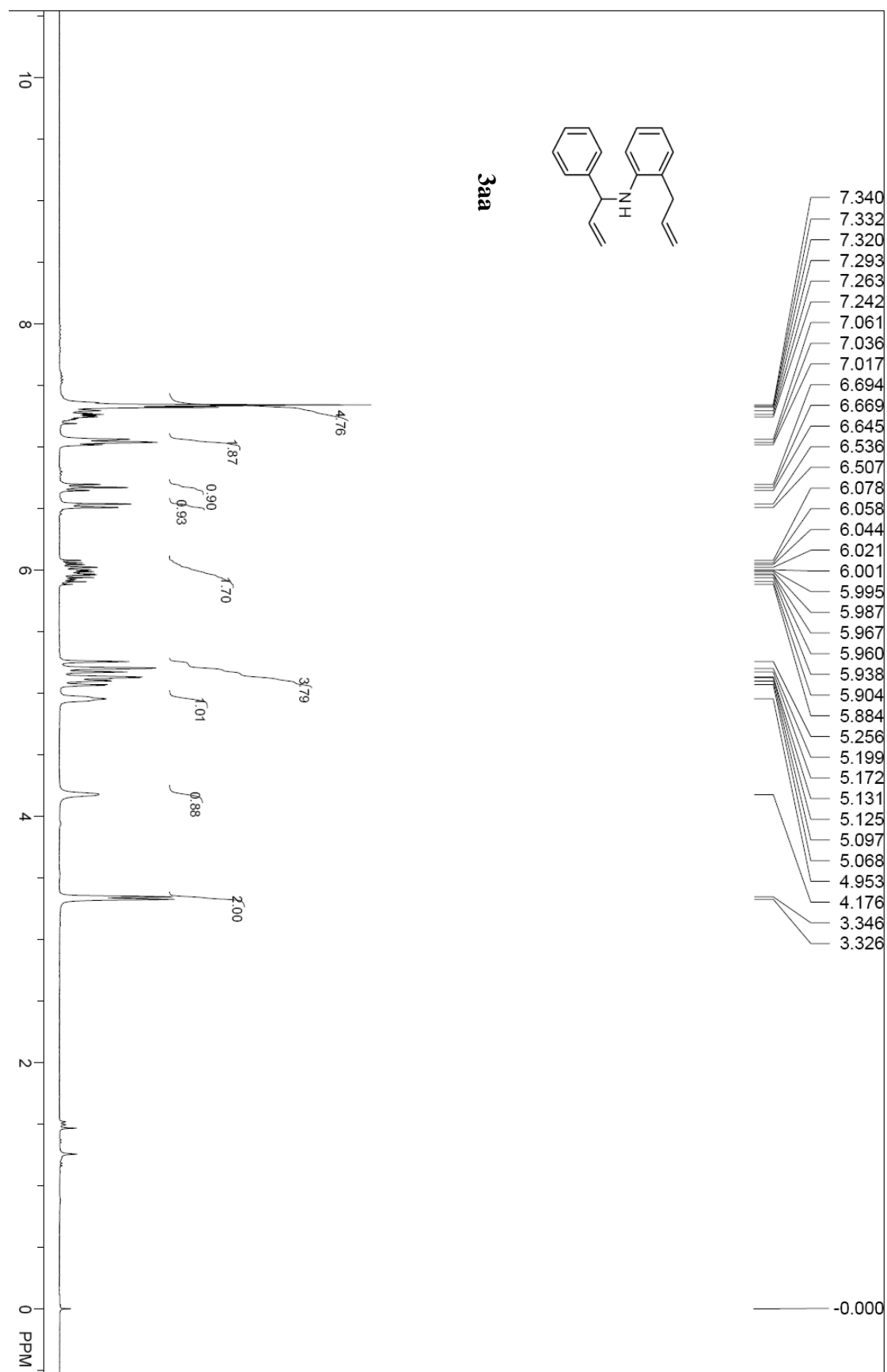
Ke-Yin Ye, Li-Xin Dai and Shu-Li You\*

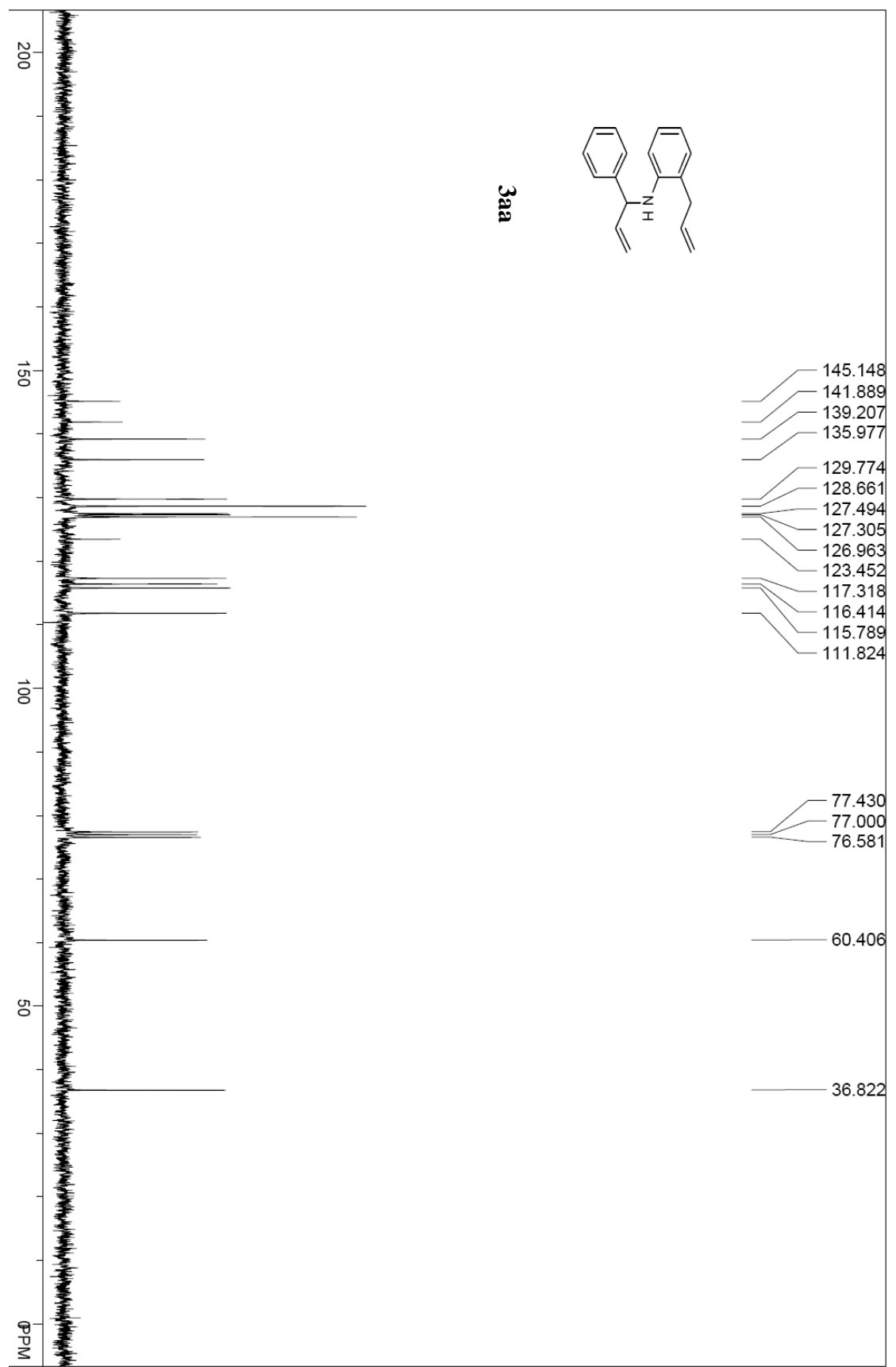
State Key Laboratory of Organometallic Chemistry  
Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences  
345 Lingling Lu, Shanghai 200032, China

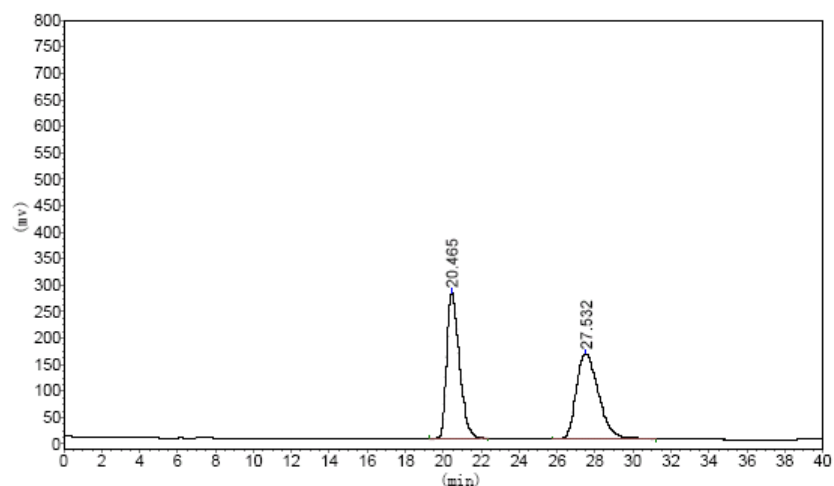
E-mail: [slyou@sioc.ac.cn](mailto:slyou@sioc.ac.cn)

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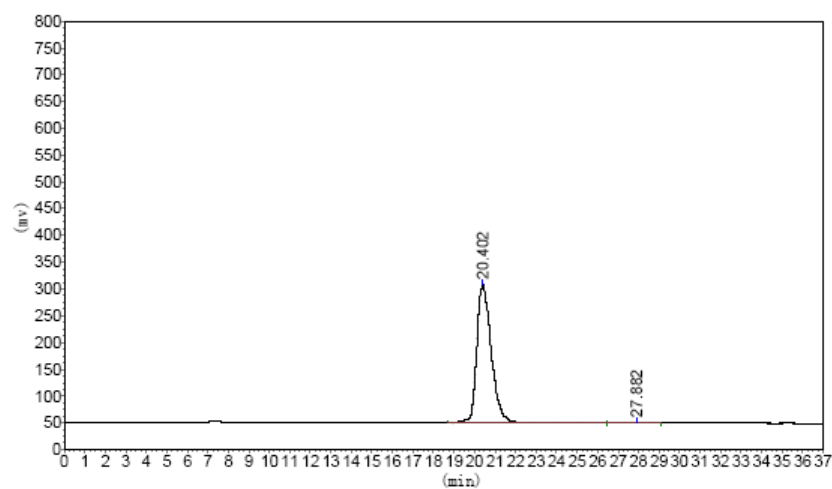
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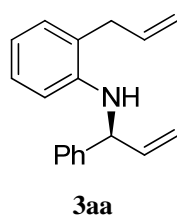


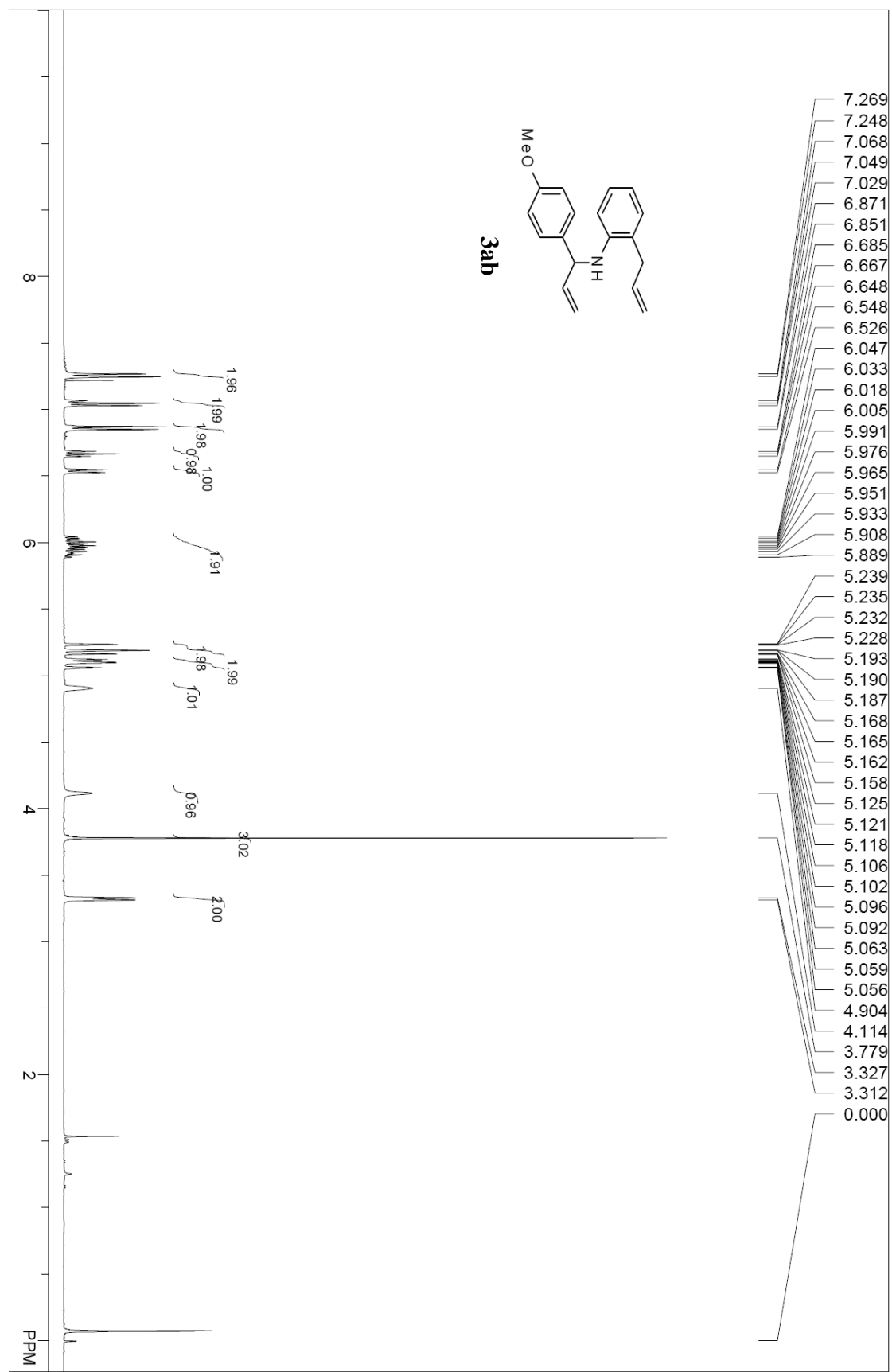


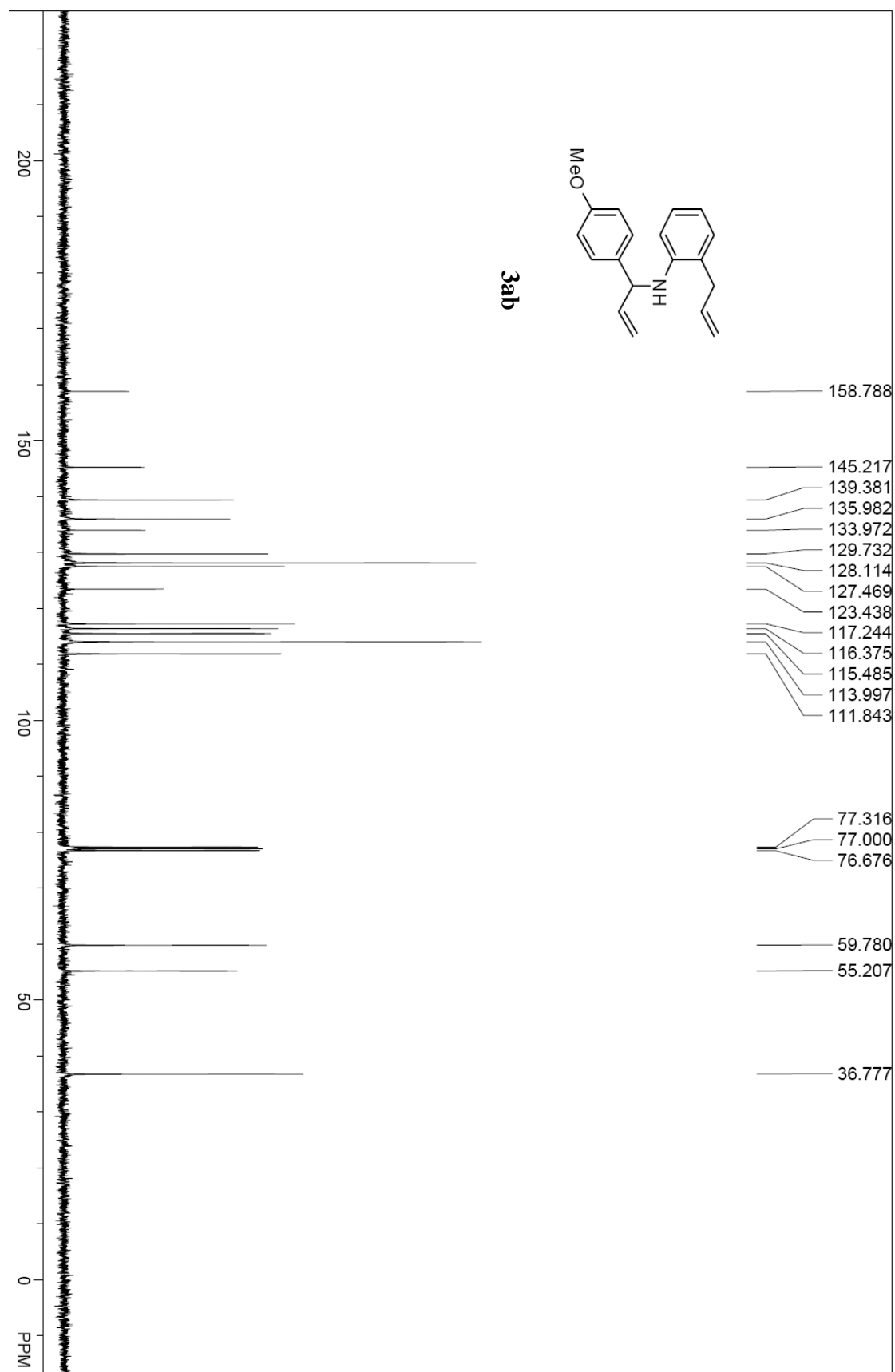
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2	27.532	162010.703	13385504.000	50.7311
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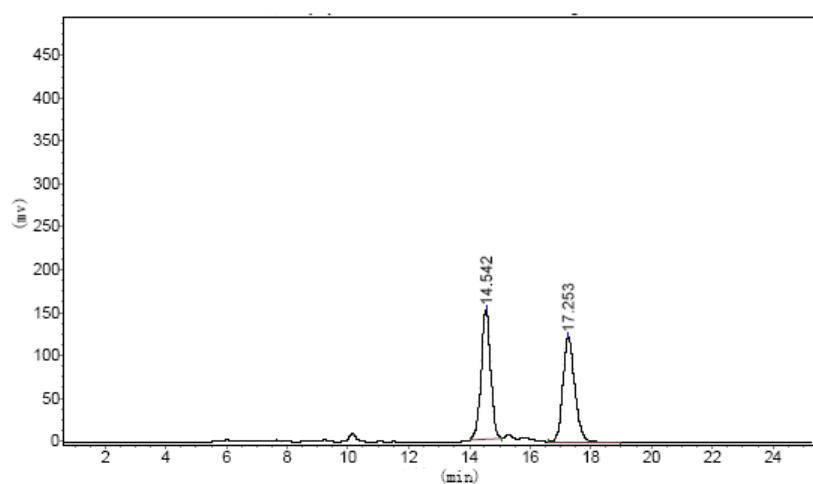


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.402	258282.938	12673854.000	99.3582
2	27.882	1121.163	81869.734	0.6418
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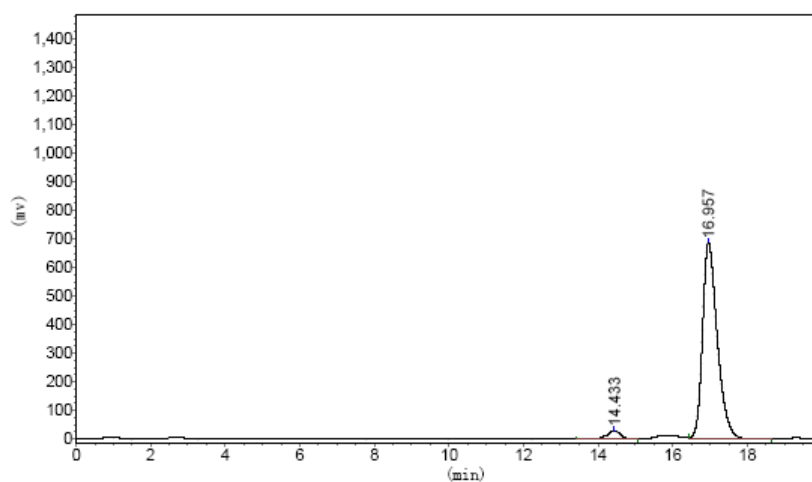




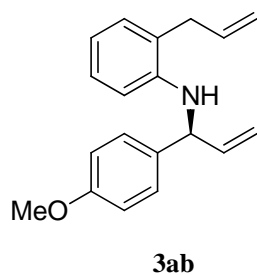


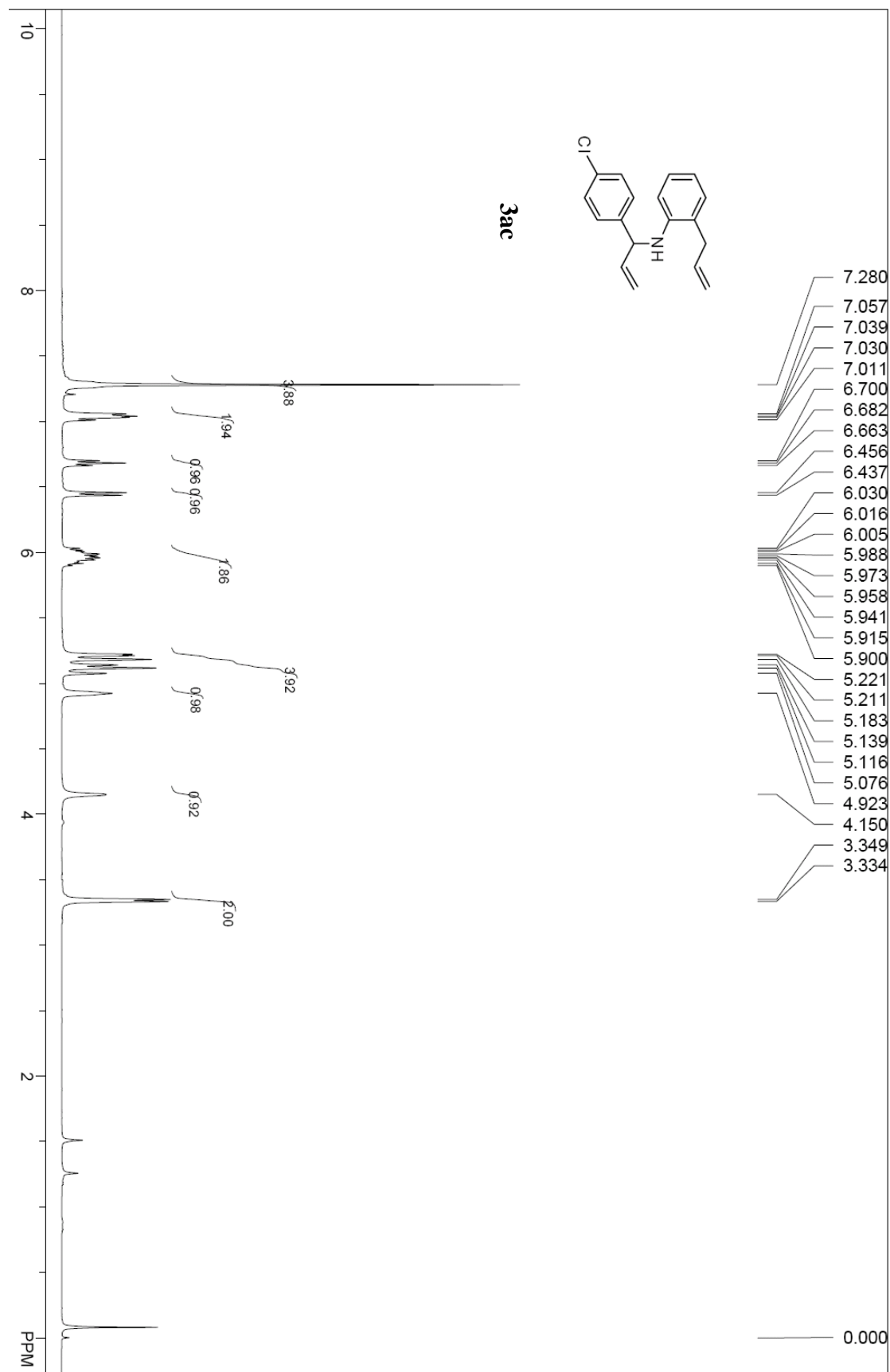


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14.542	150719.859	3260485.500	49.6340
2	17.253	122385.406	3308565.750	50.3660
<b>Total</b>		273105.266	6569051.250	100.0000

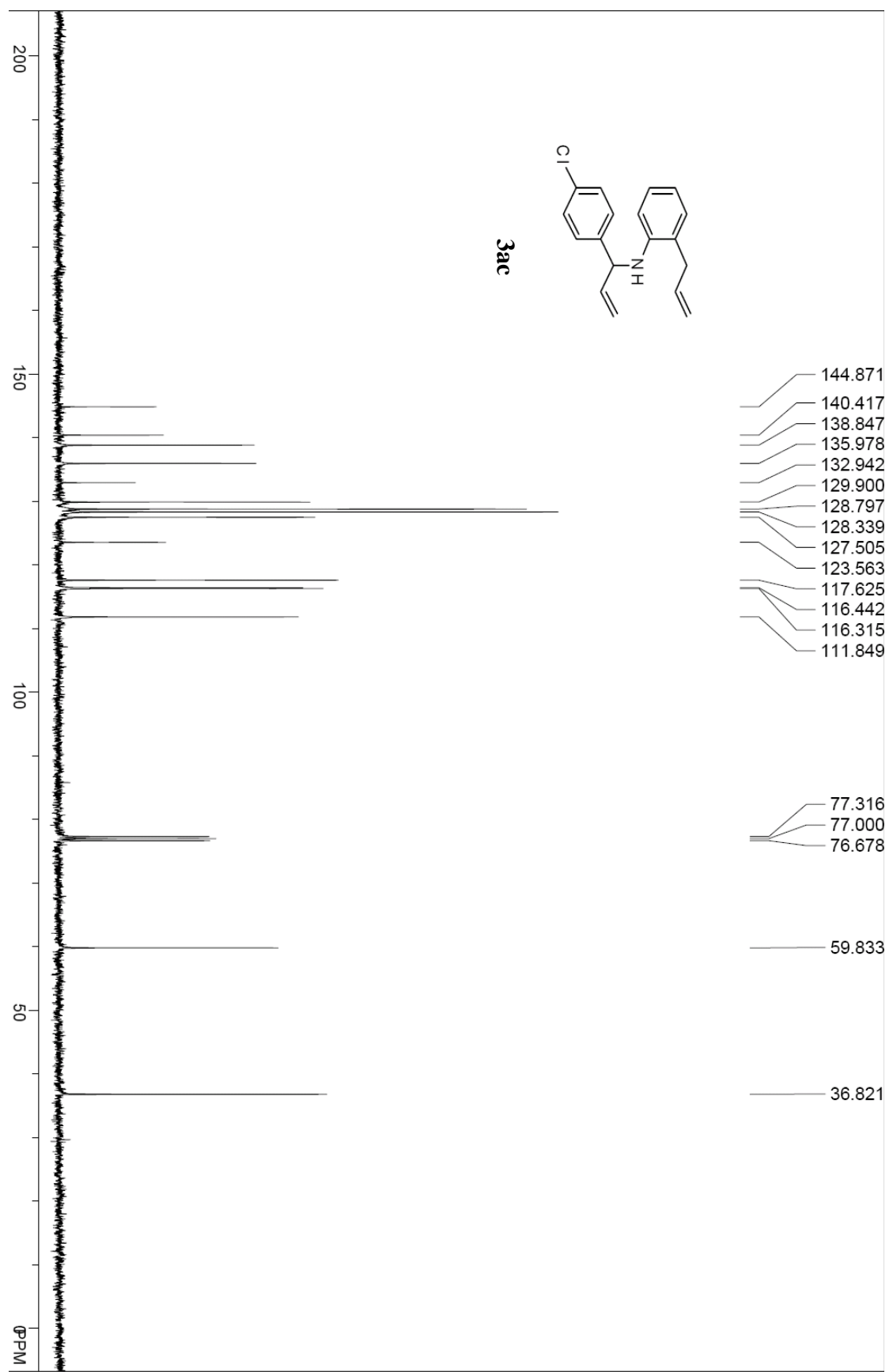


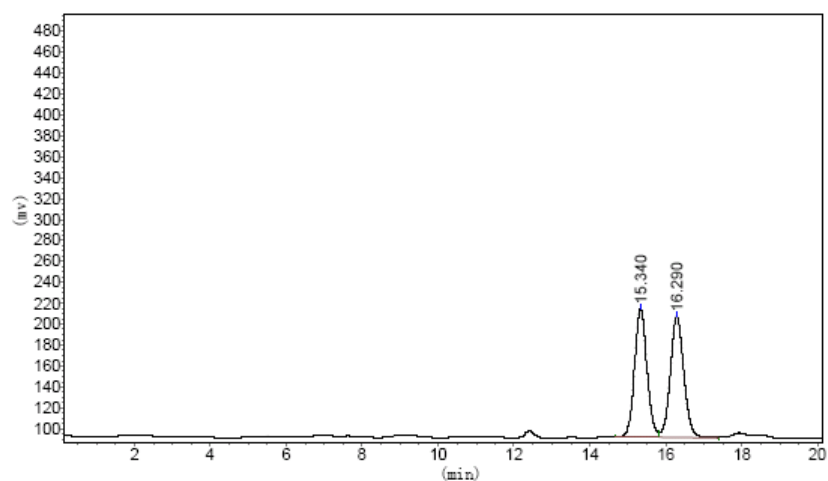
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14.433	29239.289	769032.063	3.8919
2	16.957	689013.813	18991018.000	96.1081
<b>Total</b>		718253.102	19760050.063	100.0000



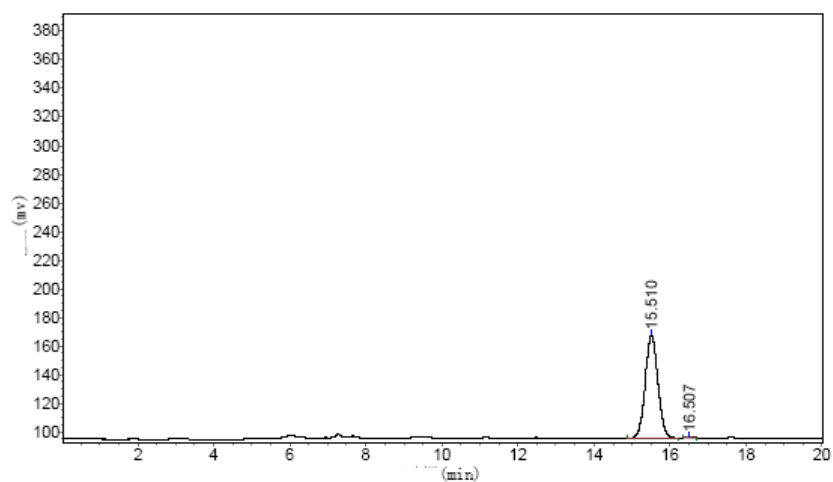




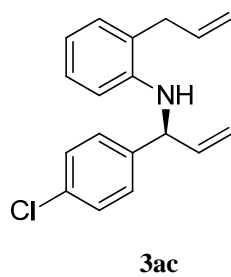


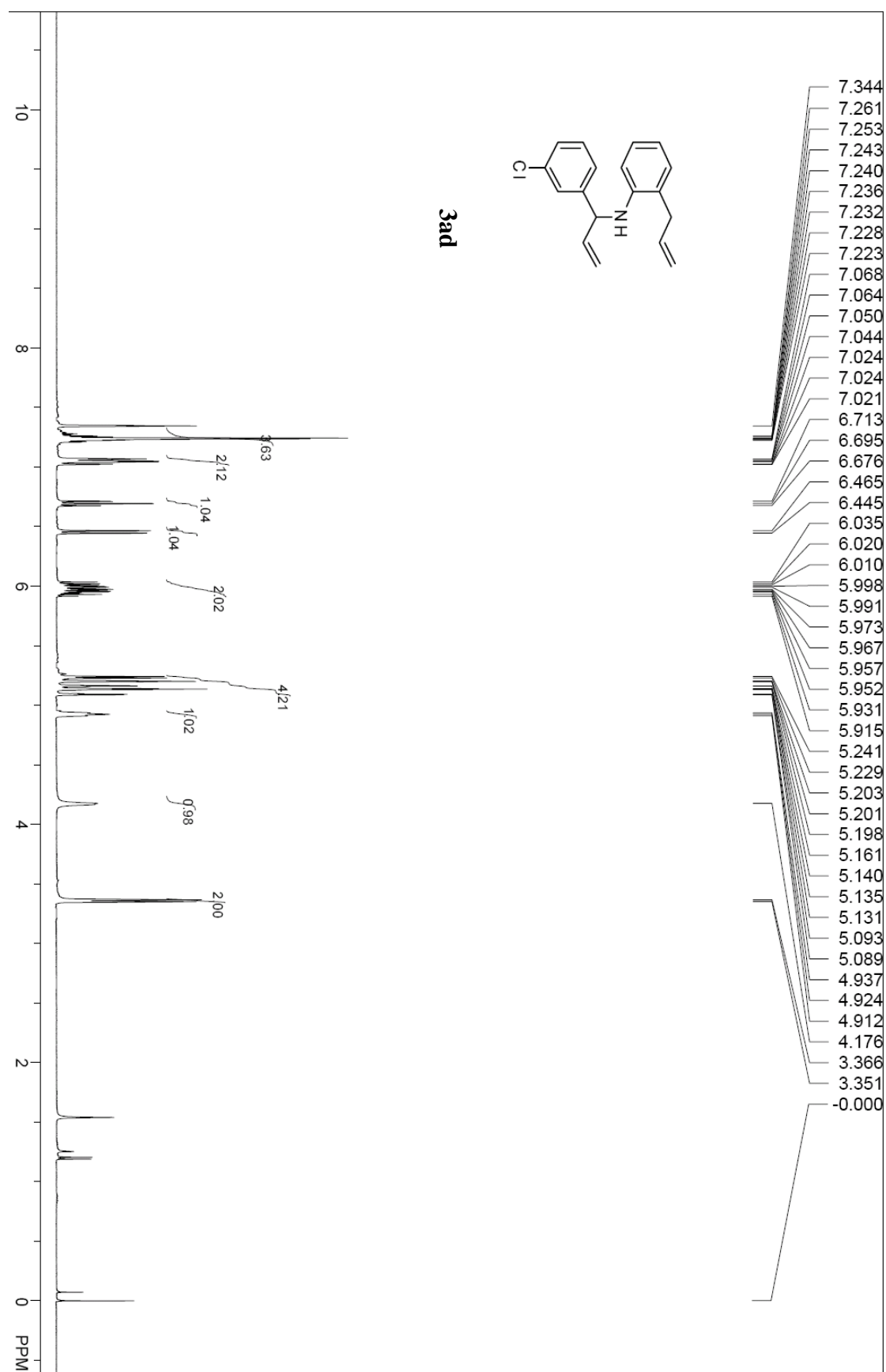


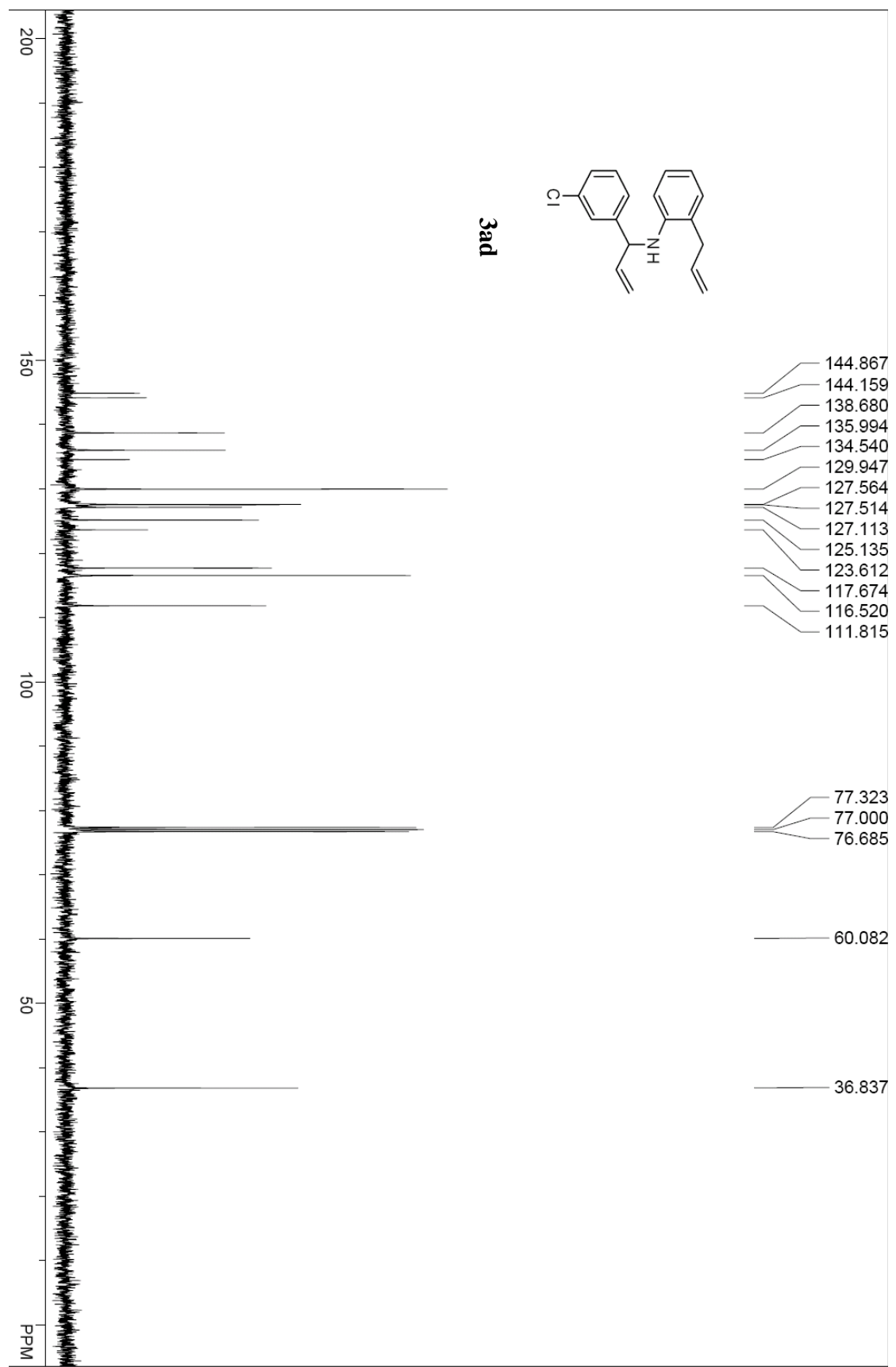
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1	15.340	123440.508	2830994.500	49.7117
2	16.290	116019.320	2863830.500	50.2883
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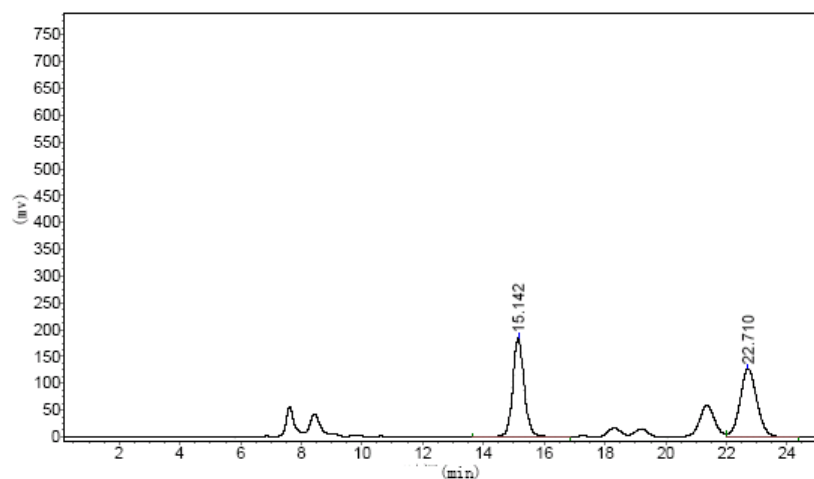


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.510	73050.242	1708896.000	99.7180
2	16.507	381.041	4831.871	0.2820
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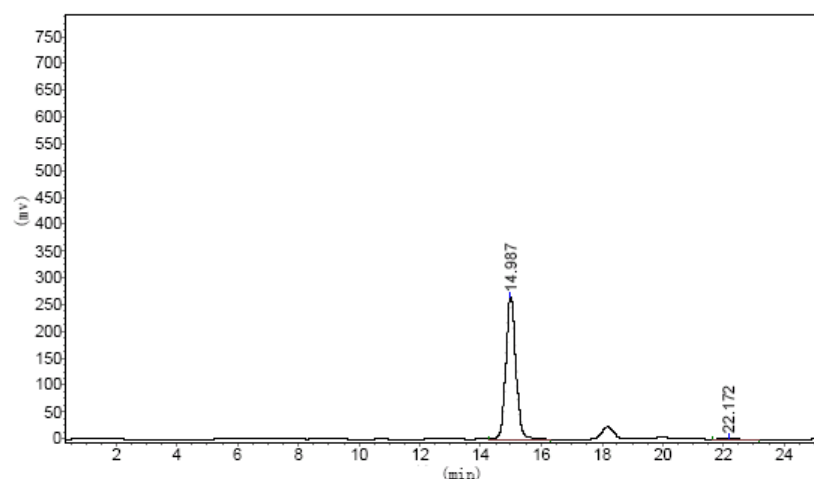




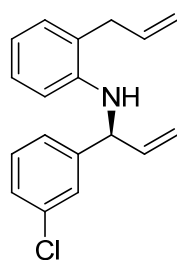




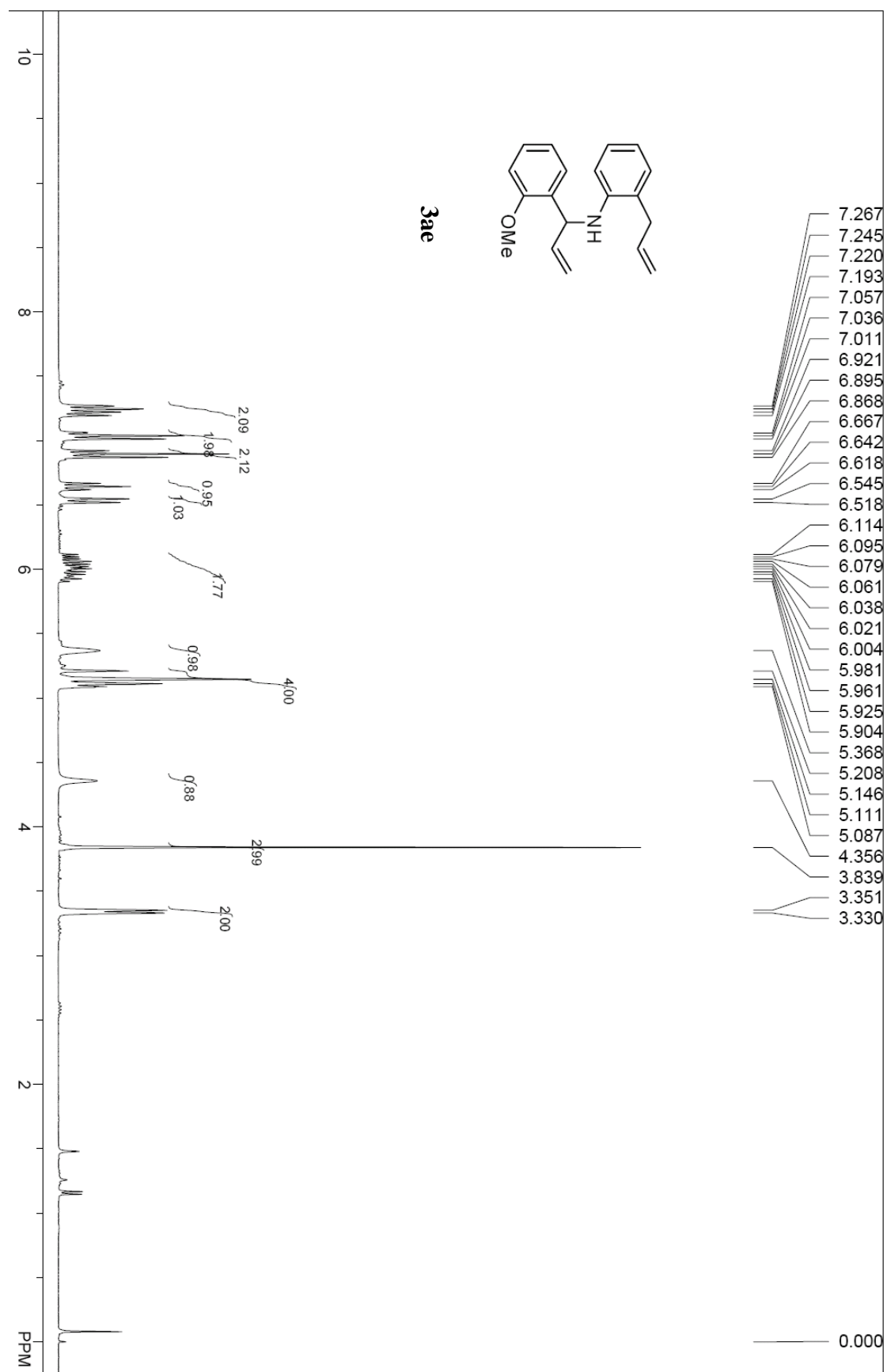
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1	15.142	186180.500	4897187.000	49.5001
2	22.710	128329.188	4996106.500	50.4999
<b>Total</b>		314509.688	9893293.500	100.0000

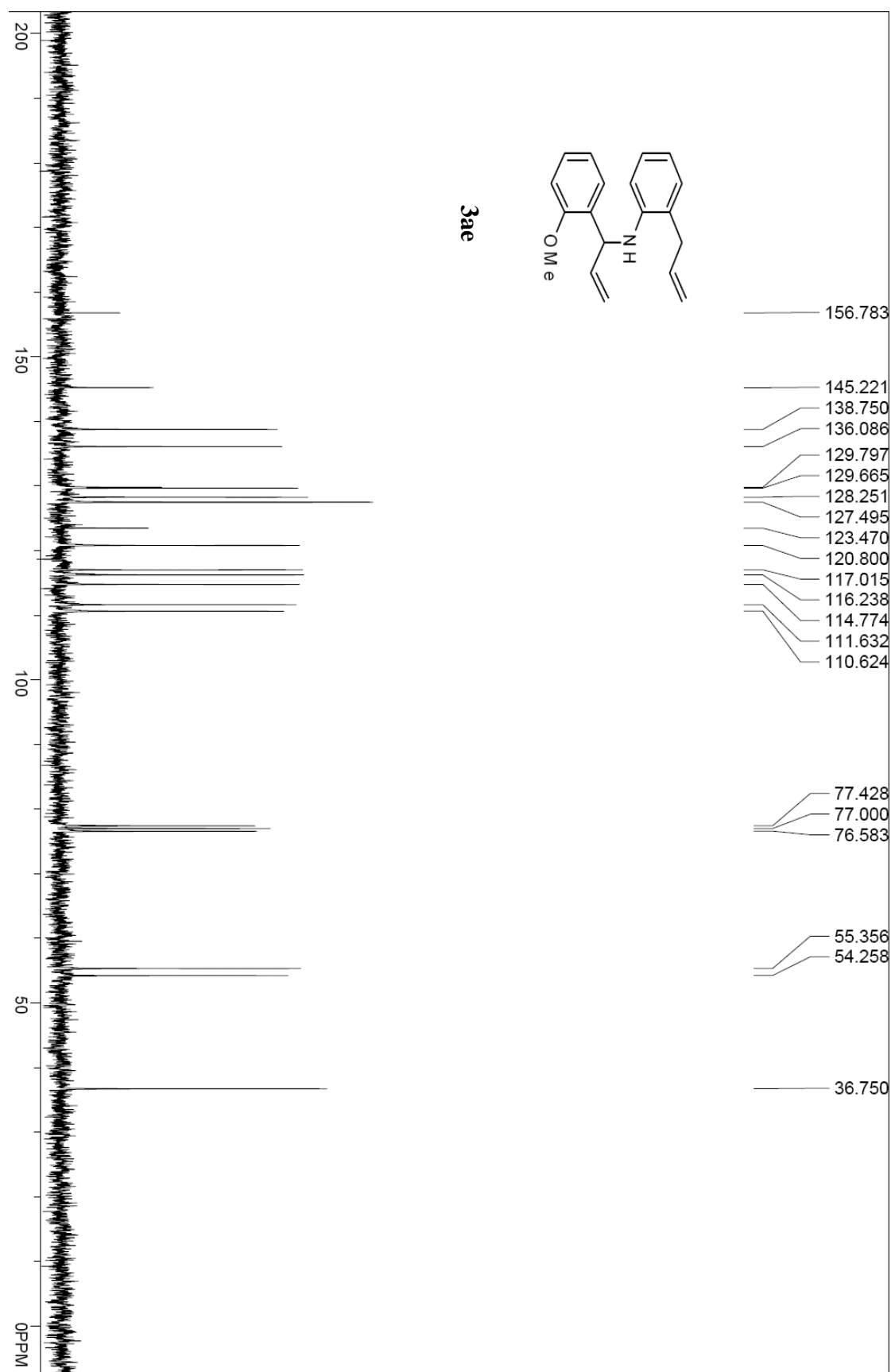


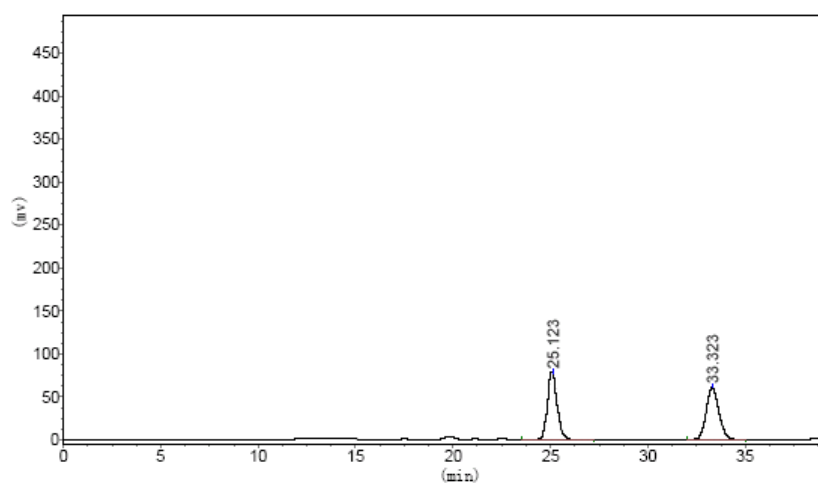
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1	14.987	266473.156	6117143.000	98.8841
2	22.172	2199.713	69029.141	1.1159
<b>Total</b>		268672.870	6186172.141	100.0000



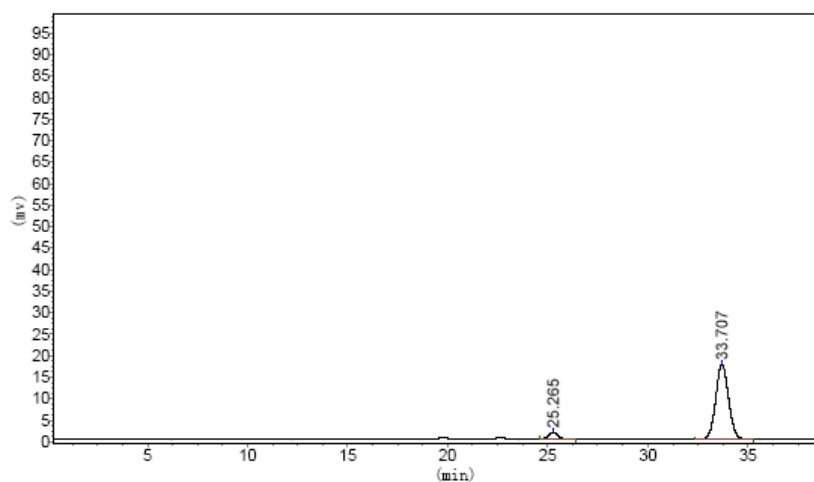
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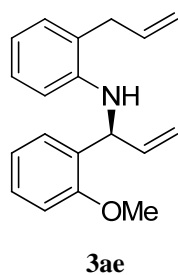




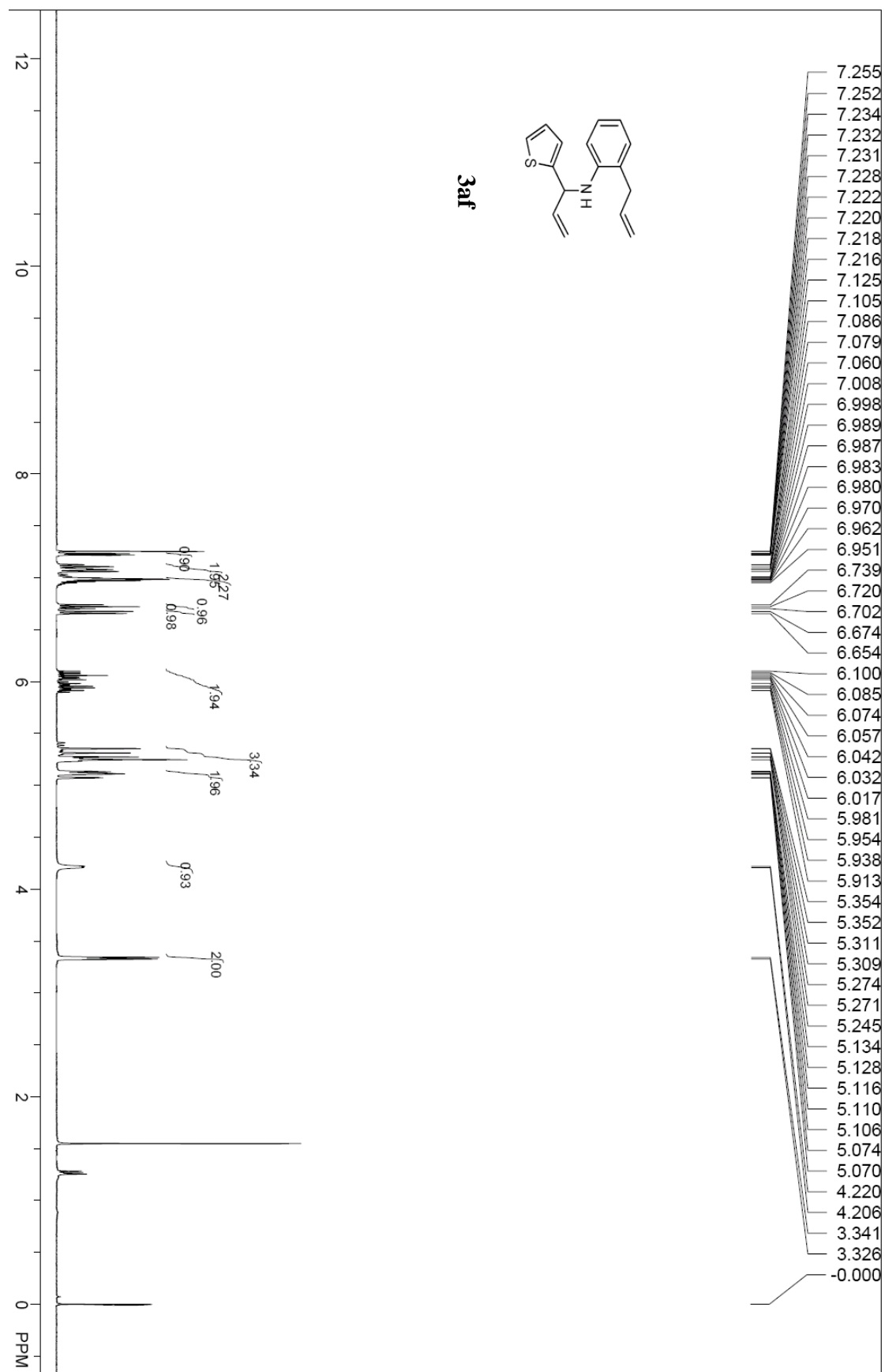
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1	25.123	78588.859	2722438.500	50.0178
2	33.323	60405.891	2720500.000	49.9822
<b>Total</b>		138994.750	5442938.500	100.0000

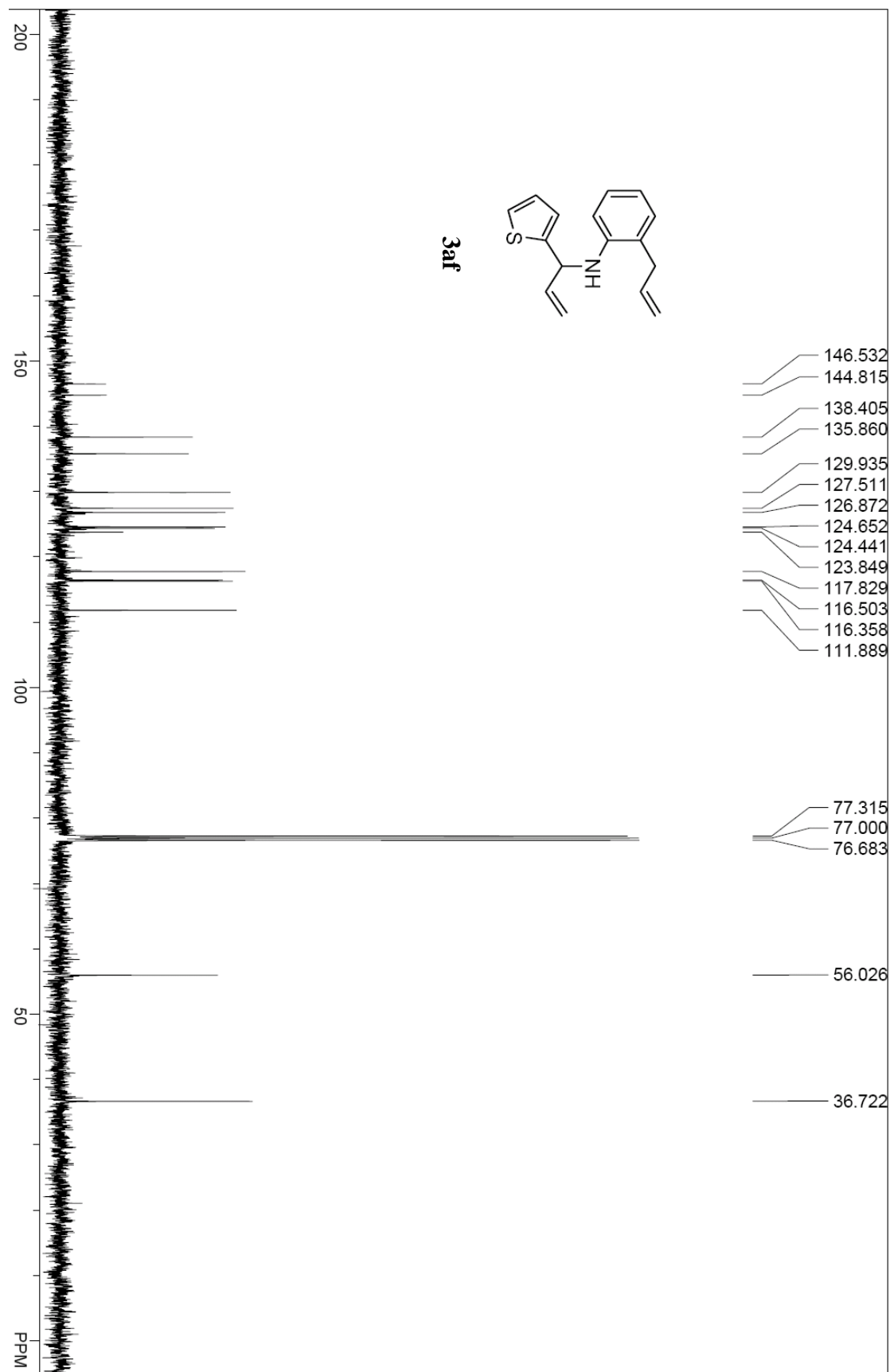


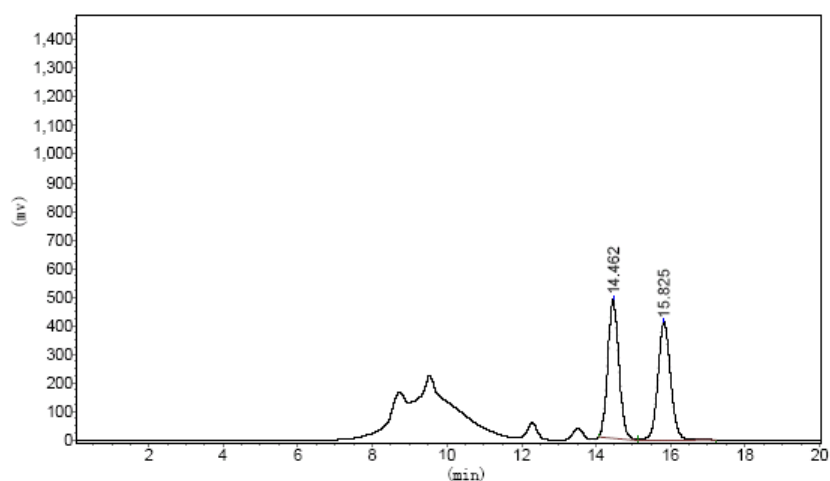
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	25.265	1673.353	57470.957	6.8521
2	33.707	17533.043	781260.563	93.1479
<b>Total</b>		19206.396	838731.520	100.0000



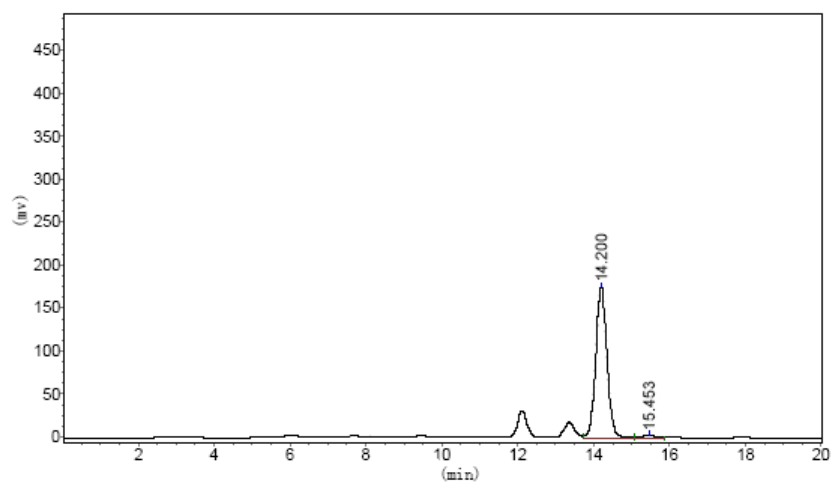




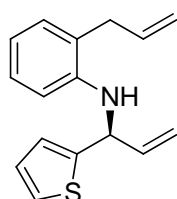




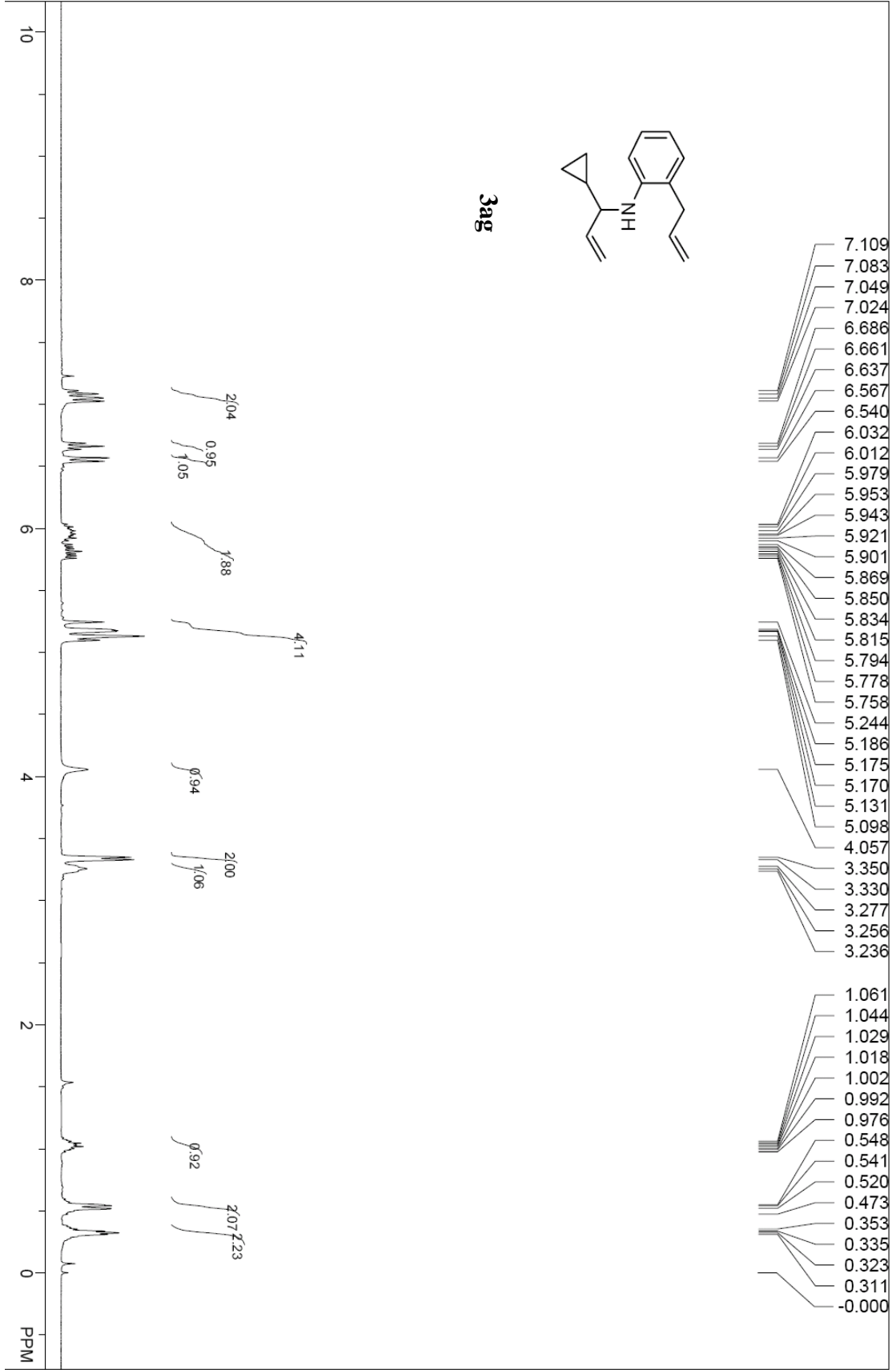
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1	14.462	485043.250	10074307.000	50.5947
2	15.825	412526.250	9837457.000	49.4053
<b>Total</b>		897569.500	19911764.000	100.0000

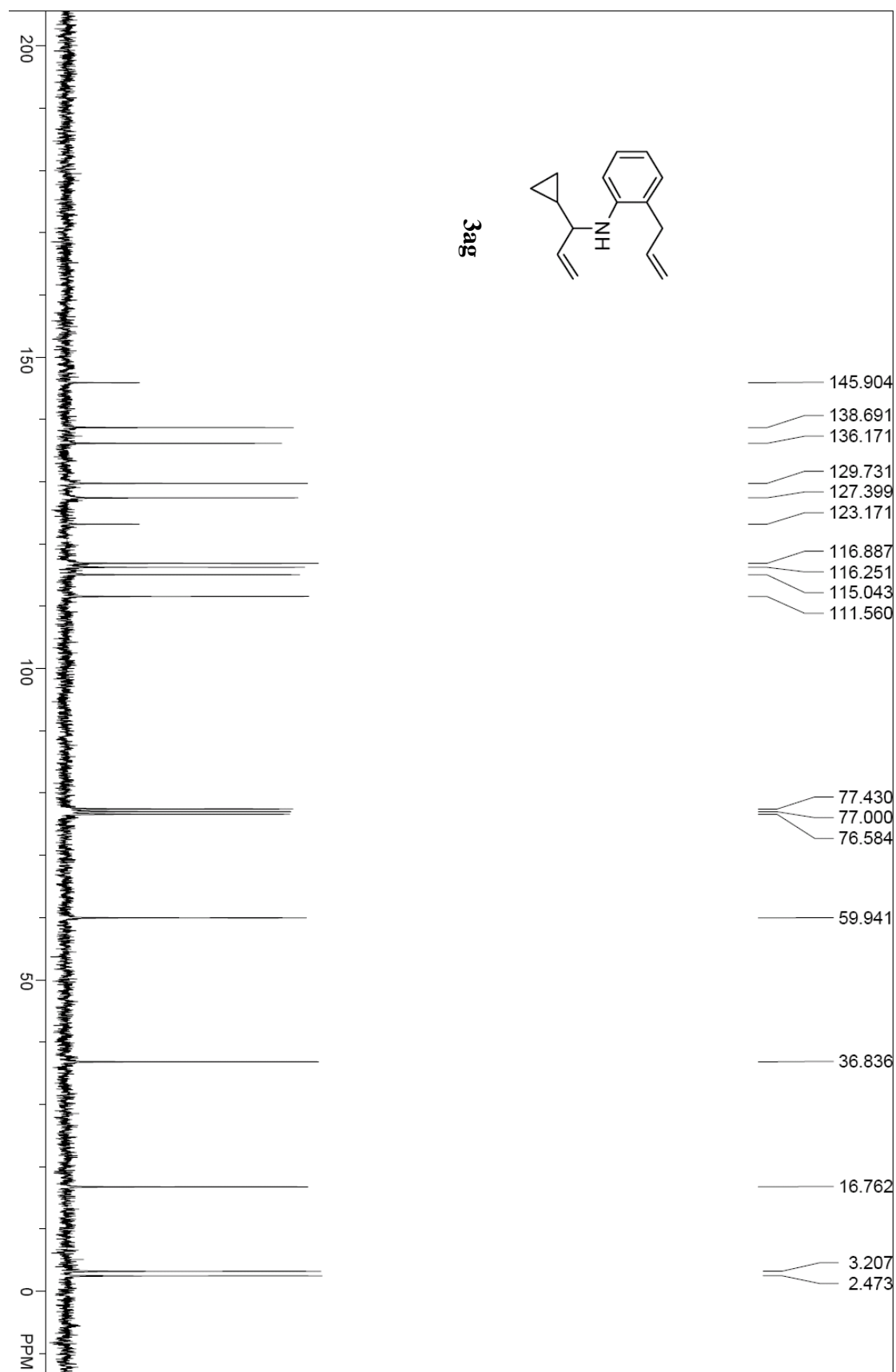


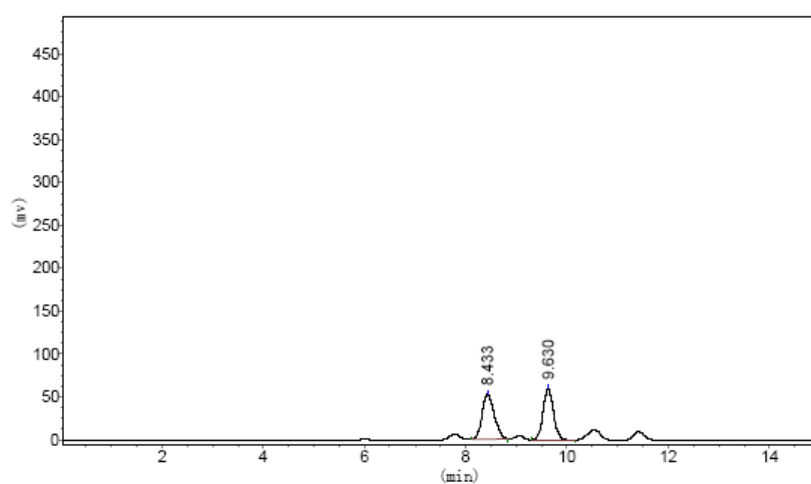
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1	14.200	175743.359	3619483.750	98.0005
2	15.453	2677.976	73846.234	1.9994
<b>Total</b>		178421.336	3693329.984	100.0000



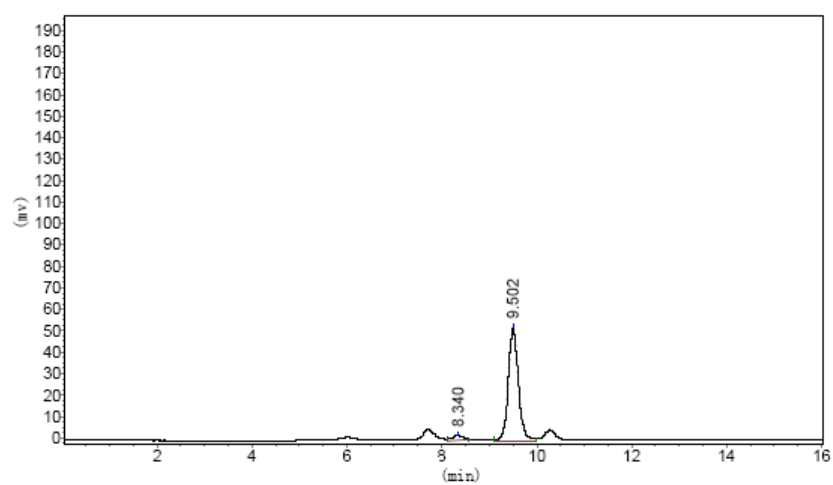
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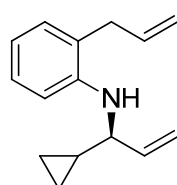




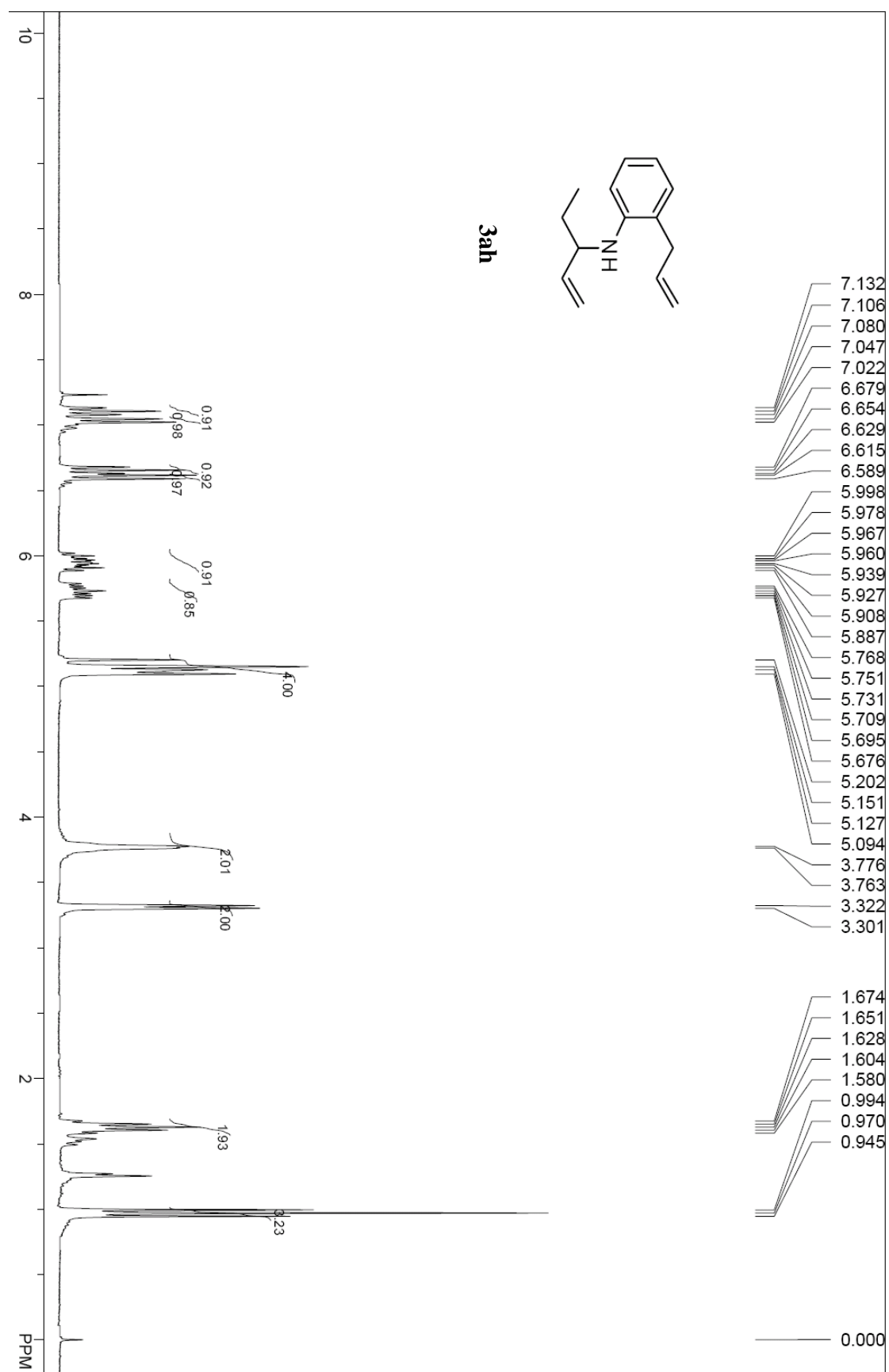
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8.433	52358.723	864757.688	49.2863
2	9.630	60903.676	889801.063	50.7137
<b>Total</b>		113262.398	1754558.750	100.0000

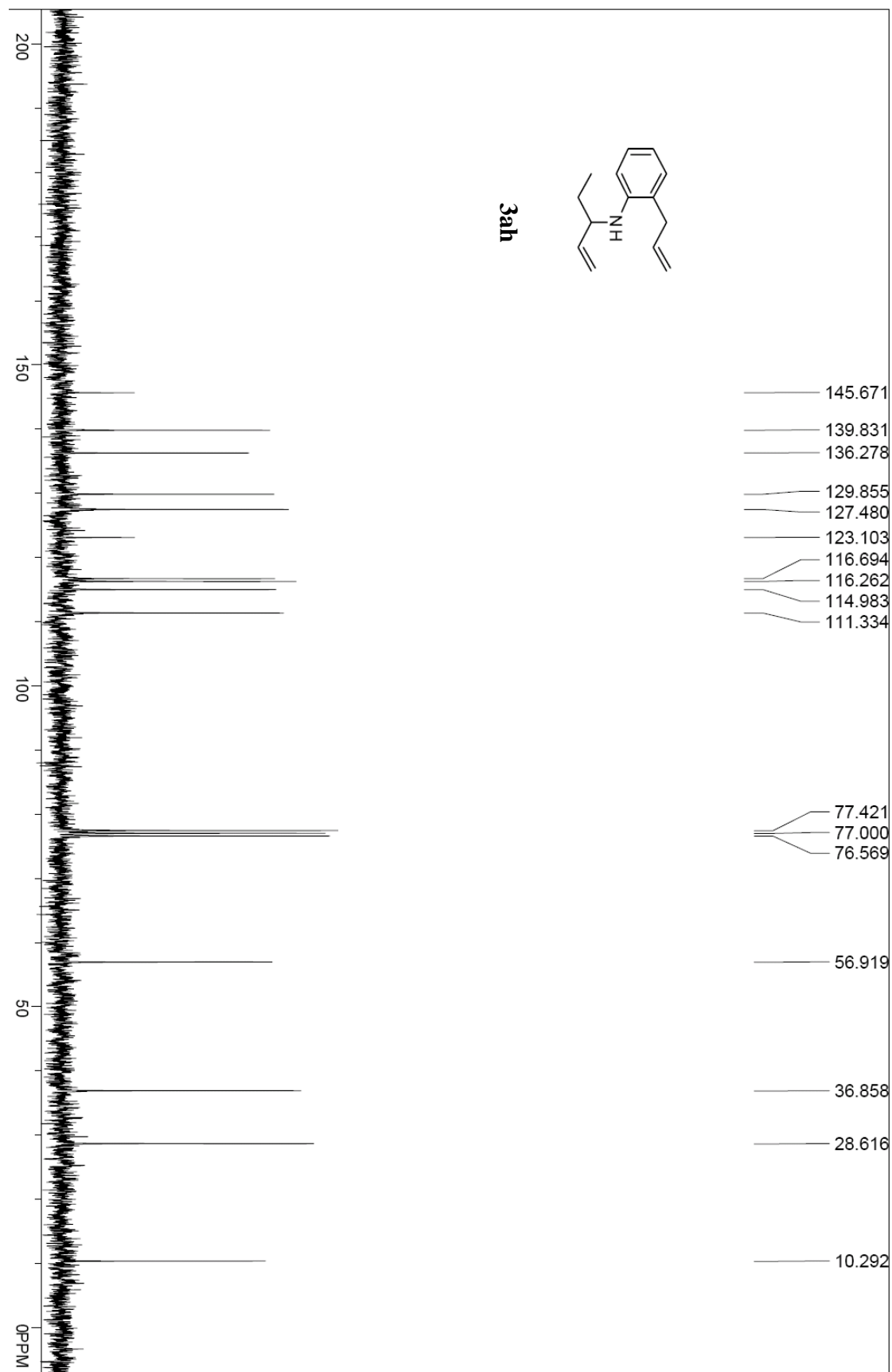


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	8.340	1964.500	32668.006	4.0352
2	9.502	52741.727	776909.750	95.9648
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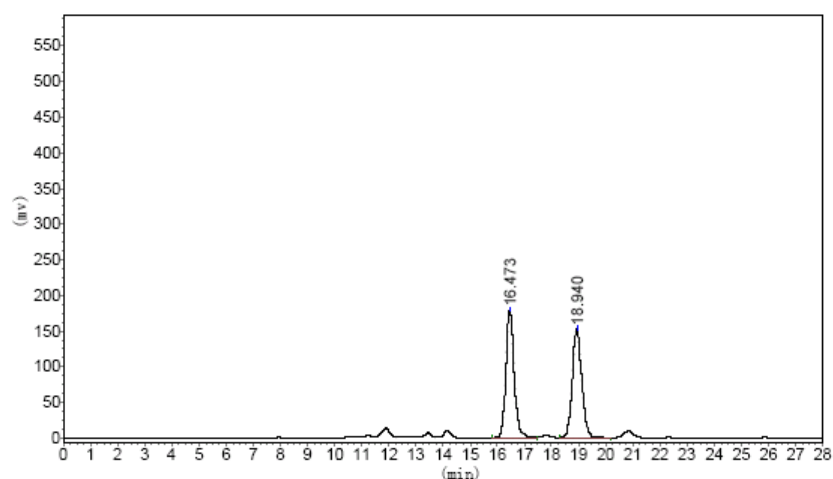


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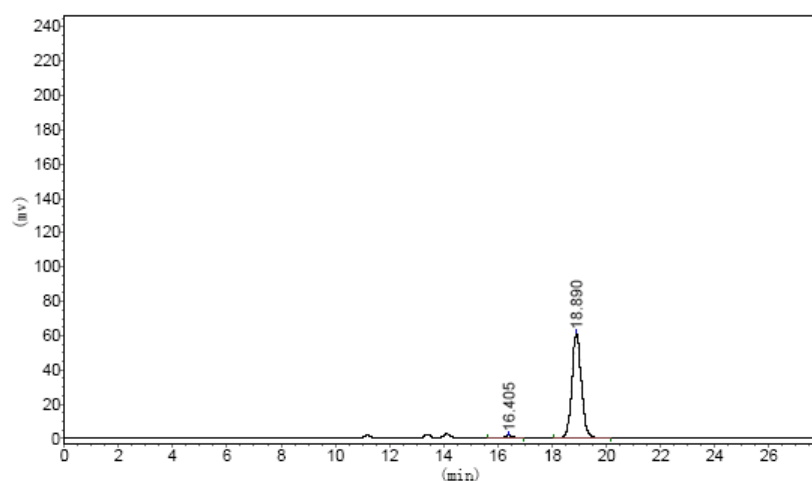




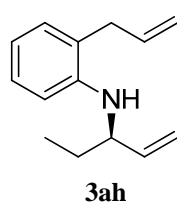


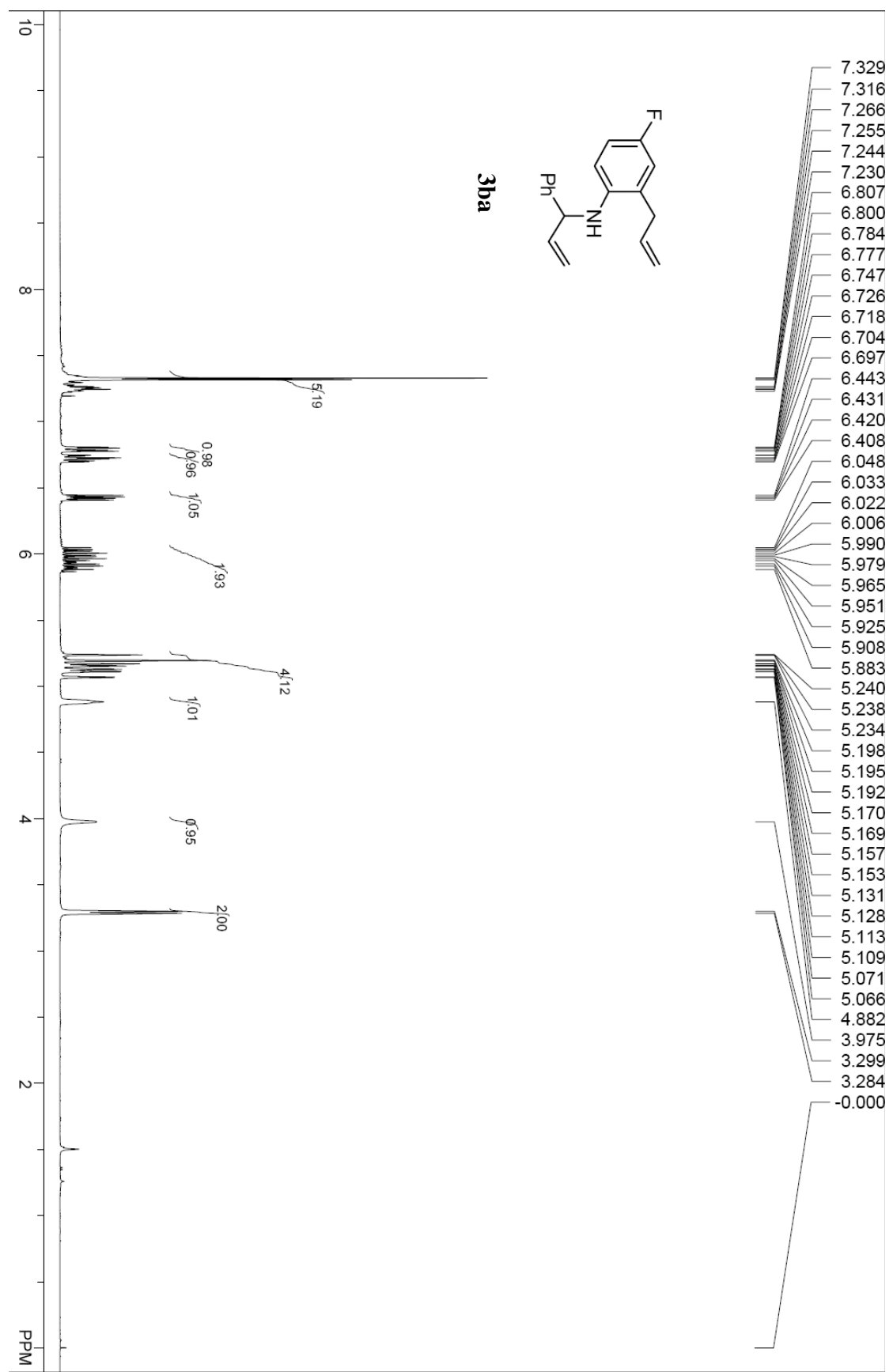


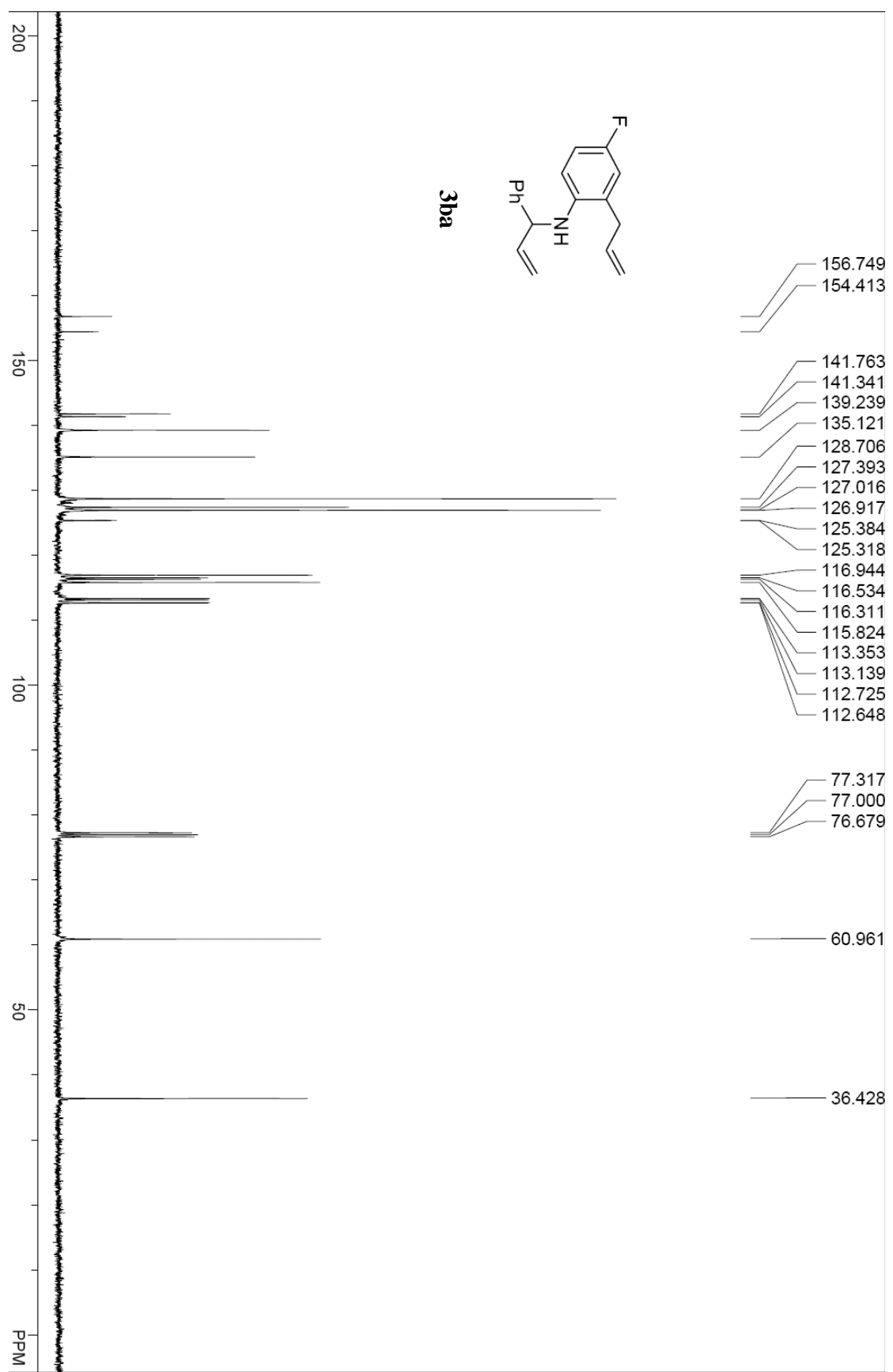
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.473	177380.438	3816072.750	50.4848
2	18.940	151656.359	3742776.000	49.5152
<b>Total</b>		329036.797	7558848.750	100.0000

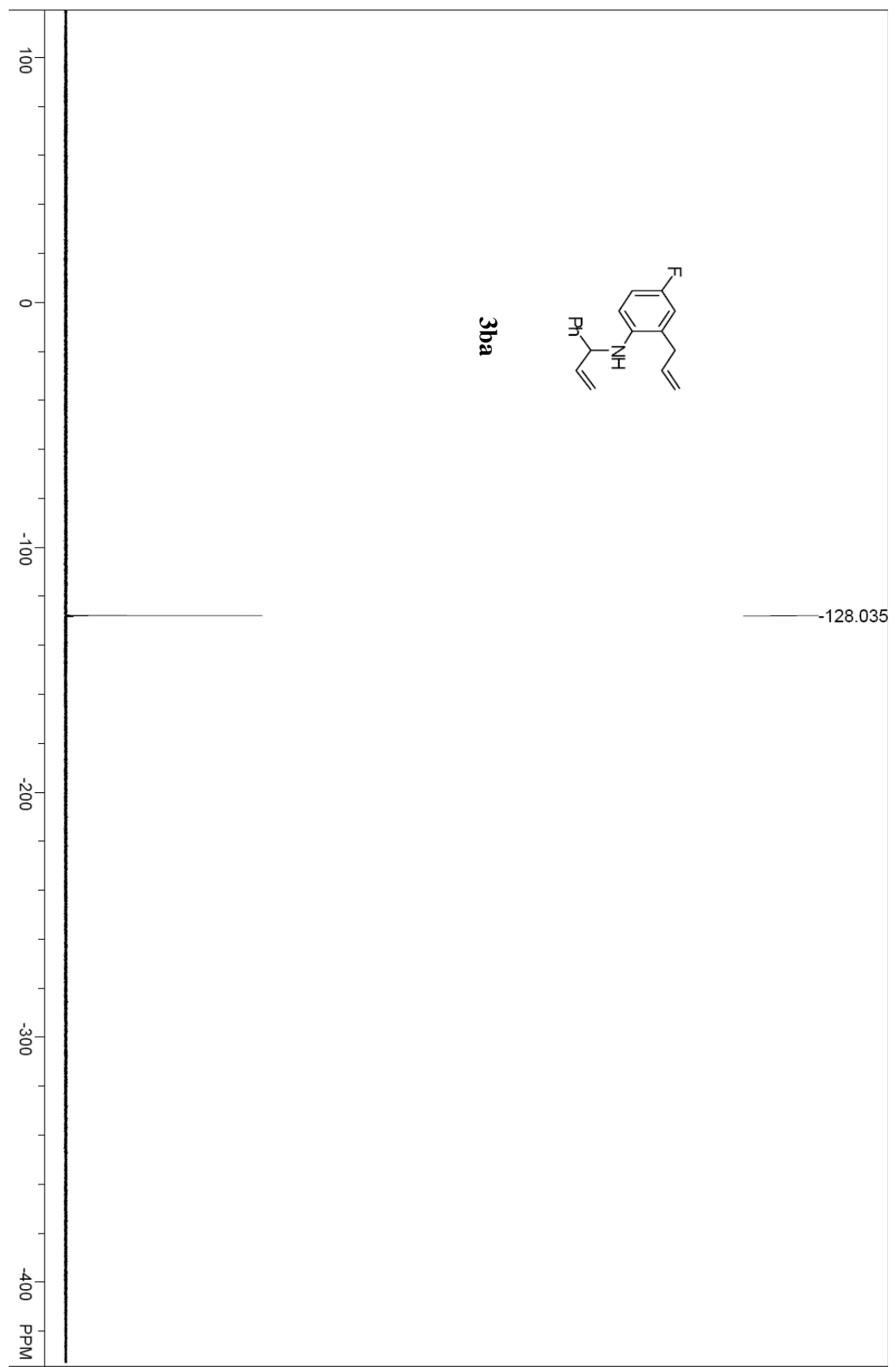


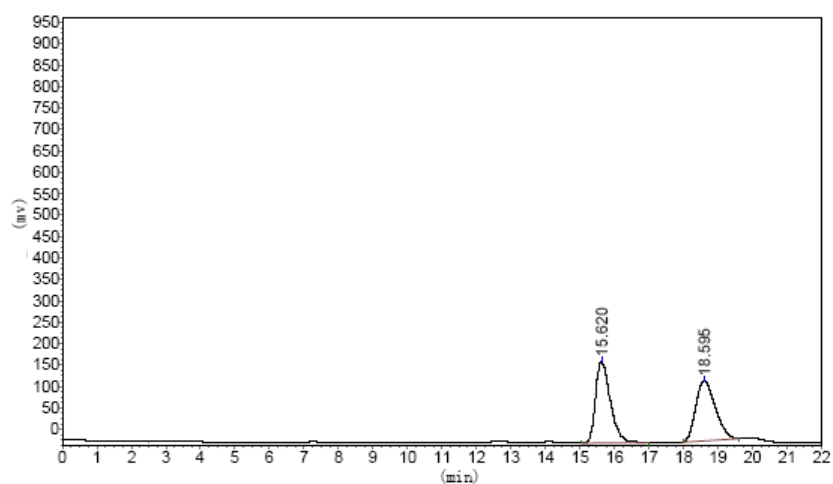
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.405	1484.579	30940.600	2.0434
2	18.890	61130.469	1483197.625	97.9566
<b>Total</b>		62615.048	1514138.225	100.0000



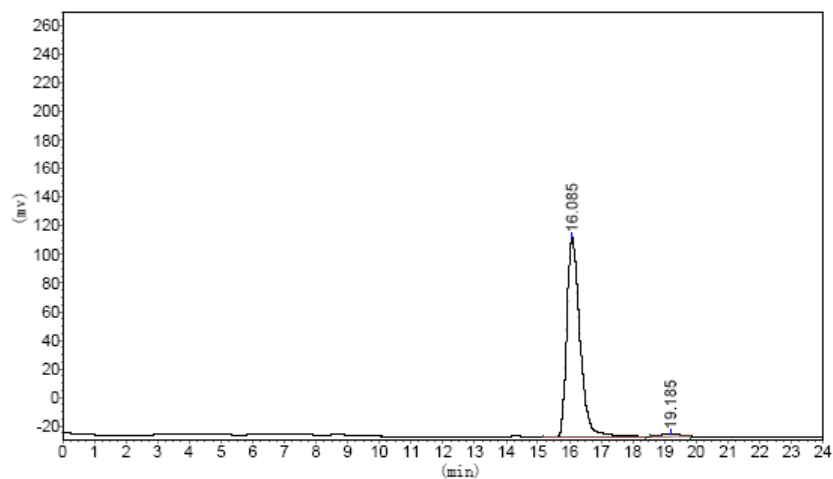




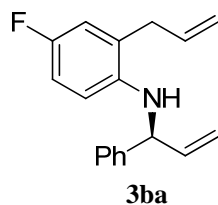


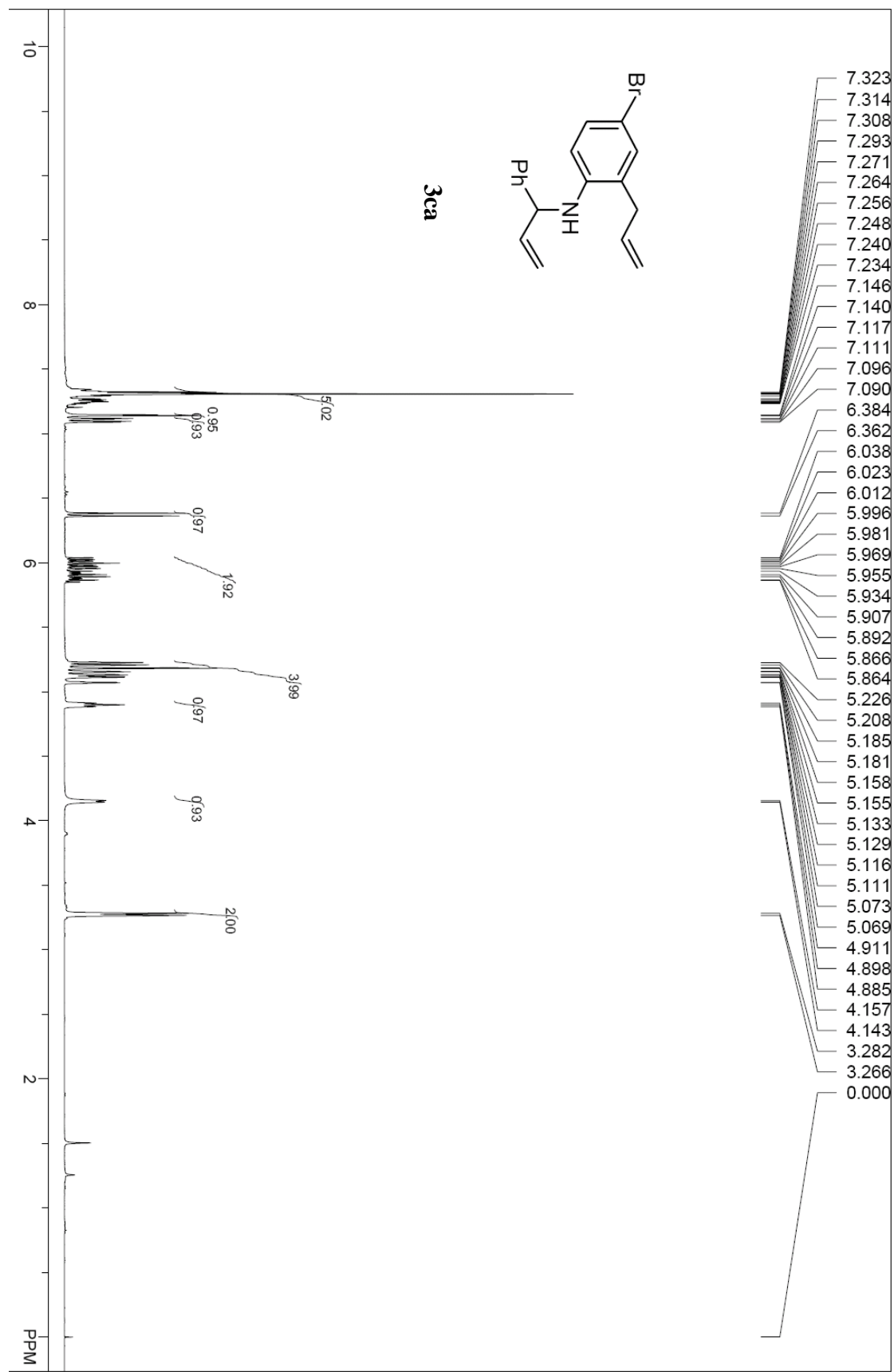


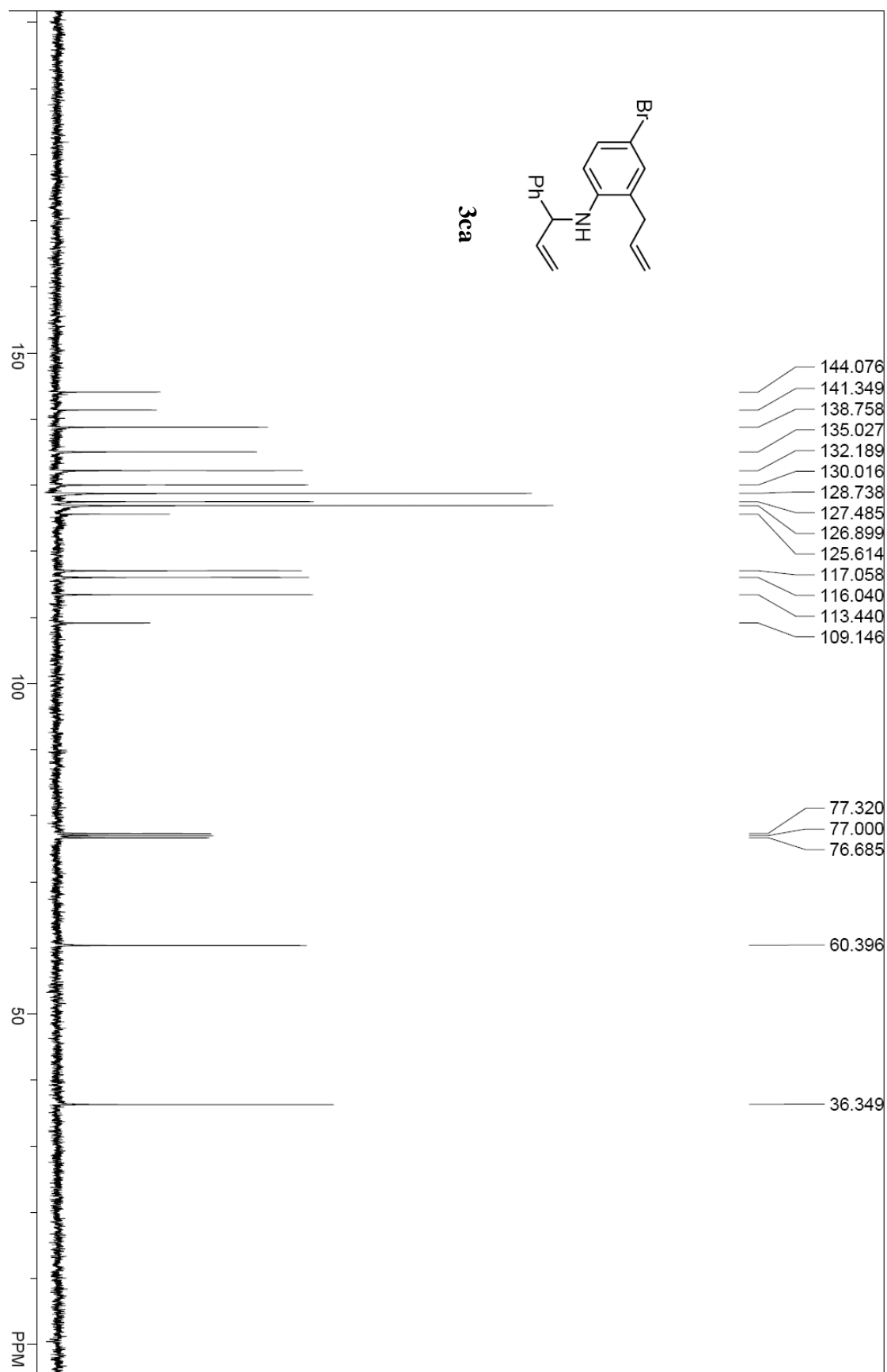
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1	15.620	191571.453	5674707.000	50.8229
2	18.595	139703.031	5490951.500	49.1771
Total		331274.484	11165658.500	100.0000

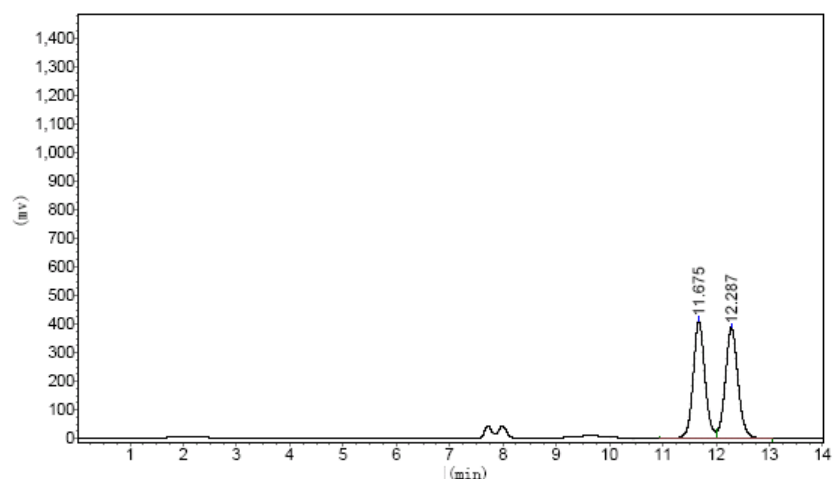


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1	16.085	140581.094	4101513.000	98.3618
2	19.185	1704.326	68310.688	1.6382
Total		142285.420	4169823.688	100.0000

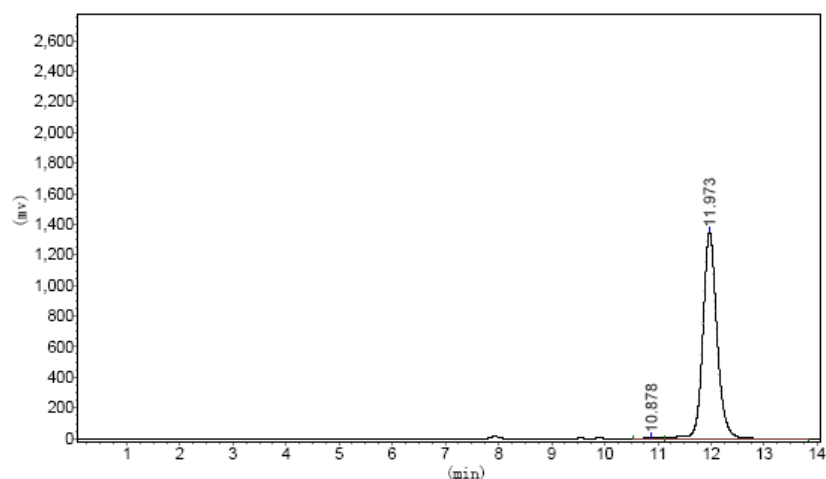




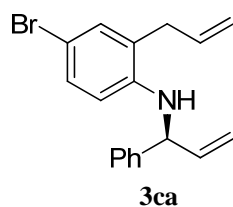




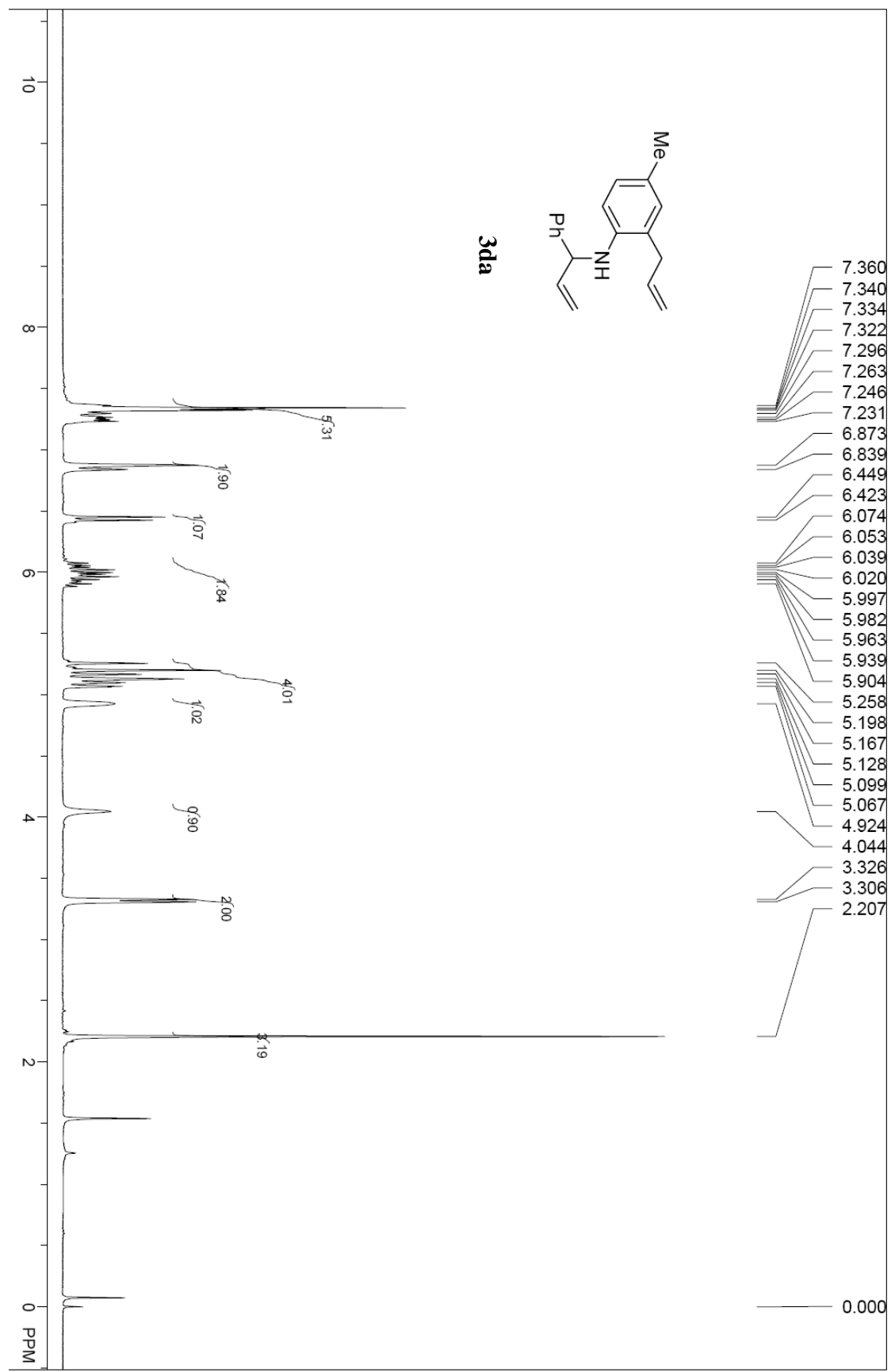
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.675	412172.156	6348433.000	49.5251
2	12.287	389329.781	6470176.500	50.4749
<b>Total</b>		801501.938	12818609.500	100.0000

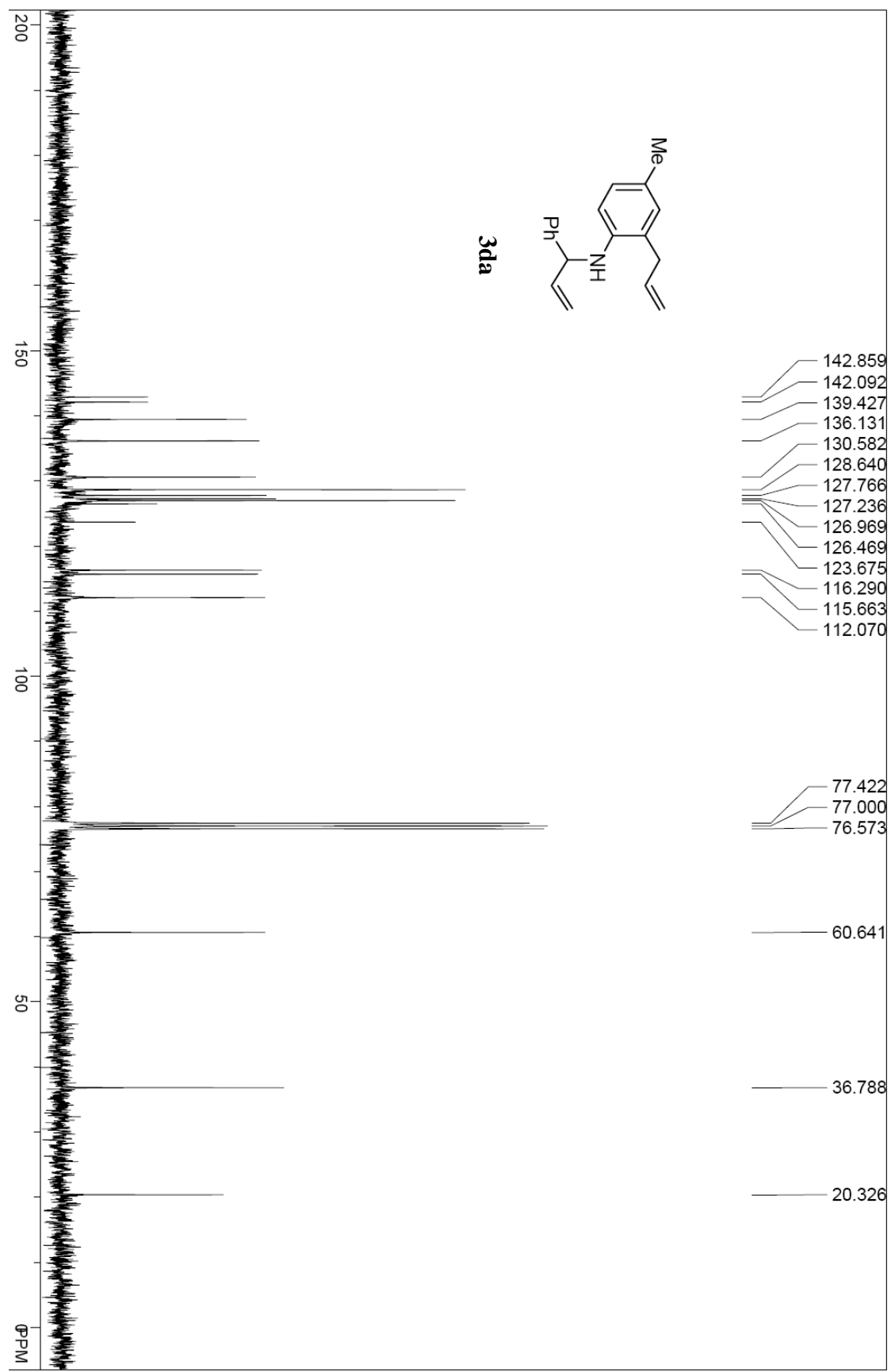


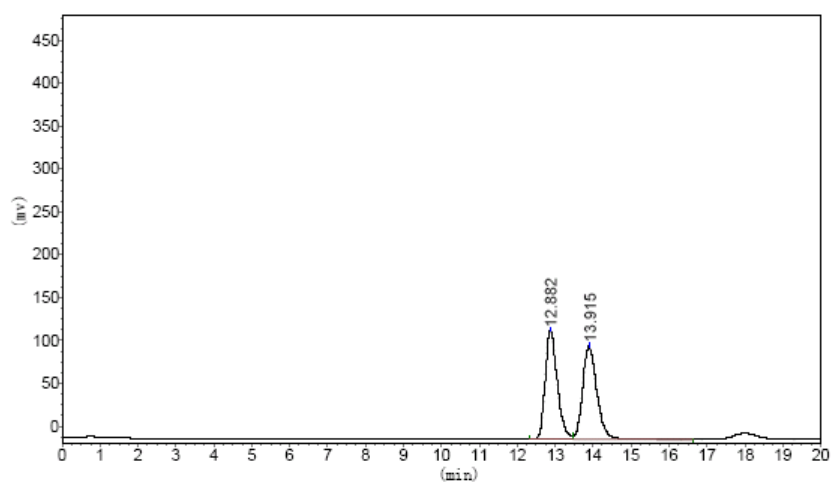
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1	10.878	11124.292	173172.359	0.6874
2	11.973	1353801.000	25017372.000	99.3126
<b>Total</b>		1364925.292	25190544.359	100.0000



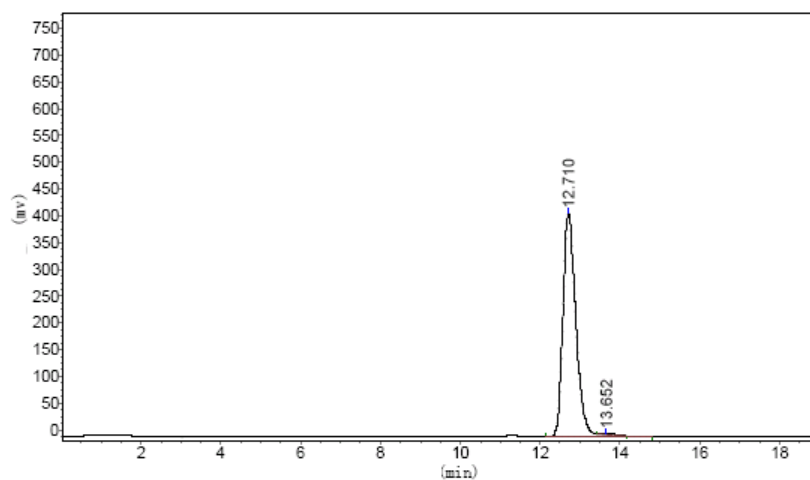




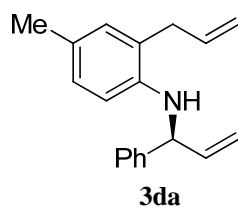


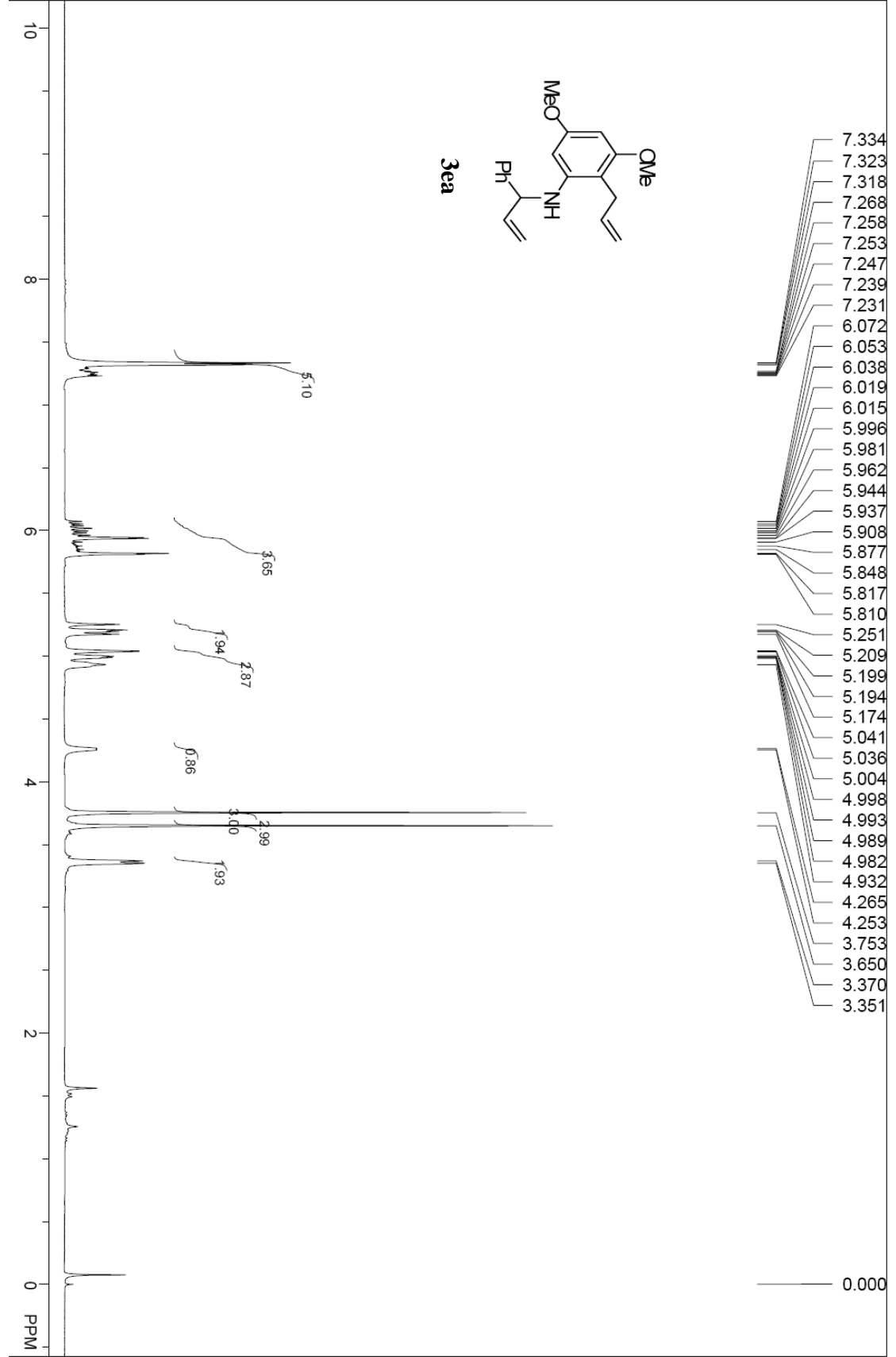


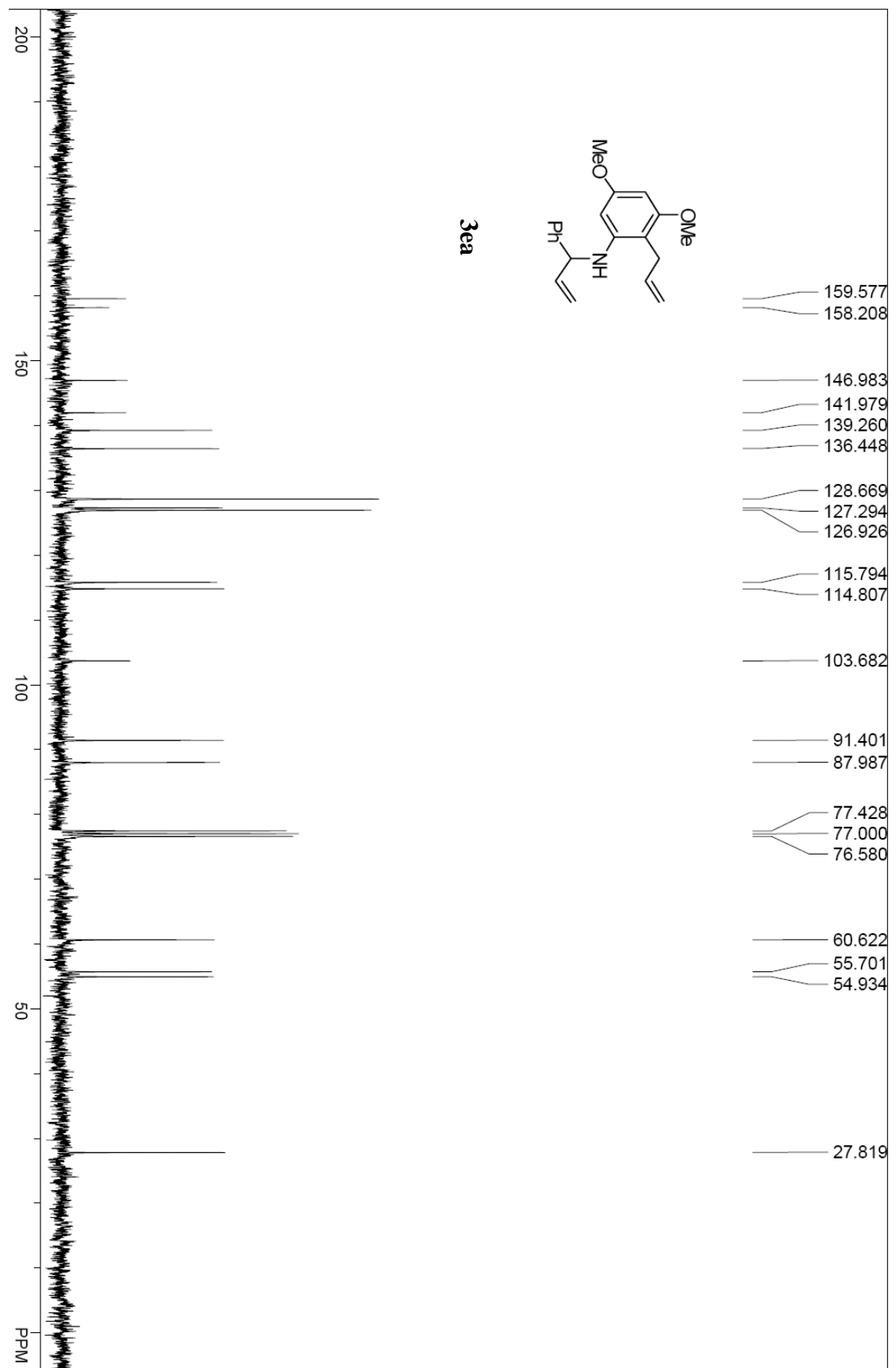
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.882	125628.461	2798852.250	49.7356
2	13.915	108350.445	2828612.250	50.2644
<b>Total</b>		233978.906	5627464.500	100.0000

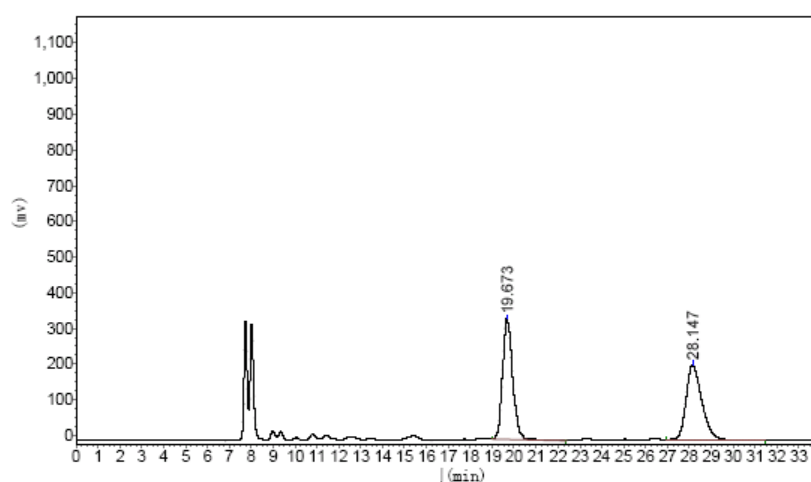


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.710	417236.594	9490659.000	99.3569
2	13.652	2860.412	61431.402	0.6431
<b>Total</b>		420097.006	9552090.402	100.0000

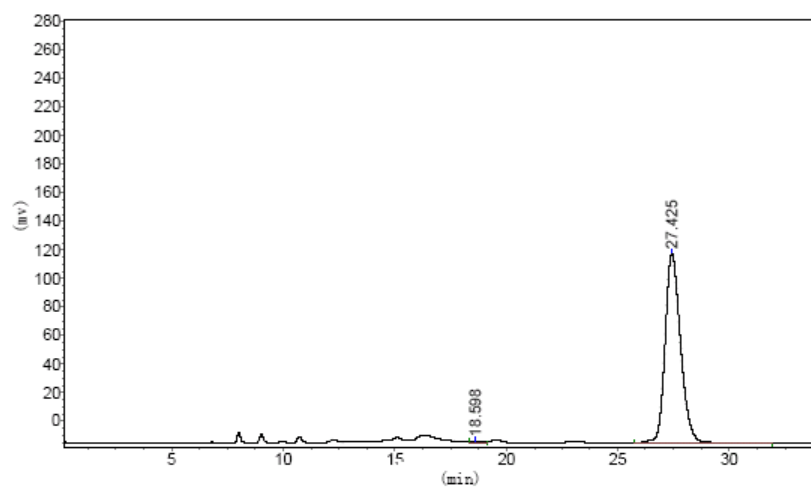




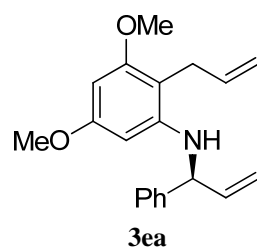


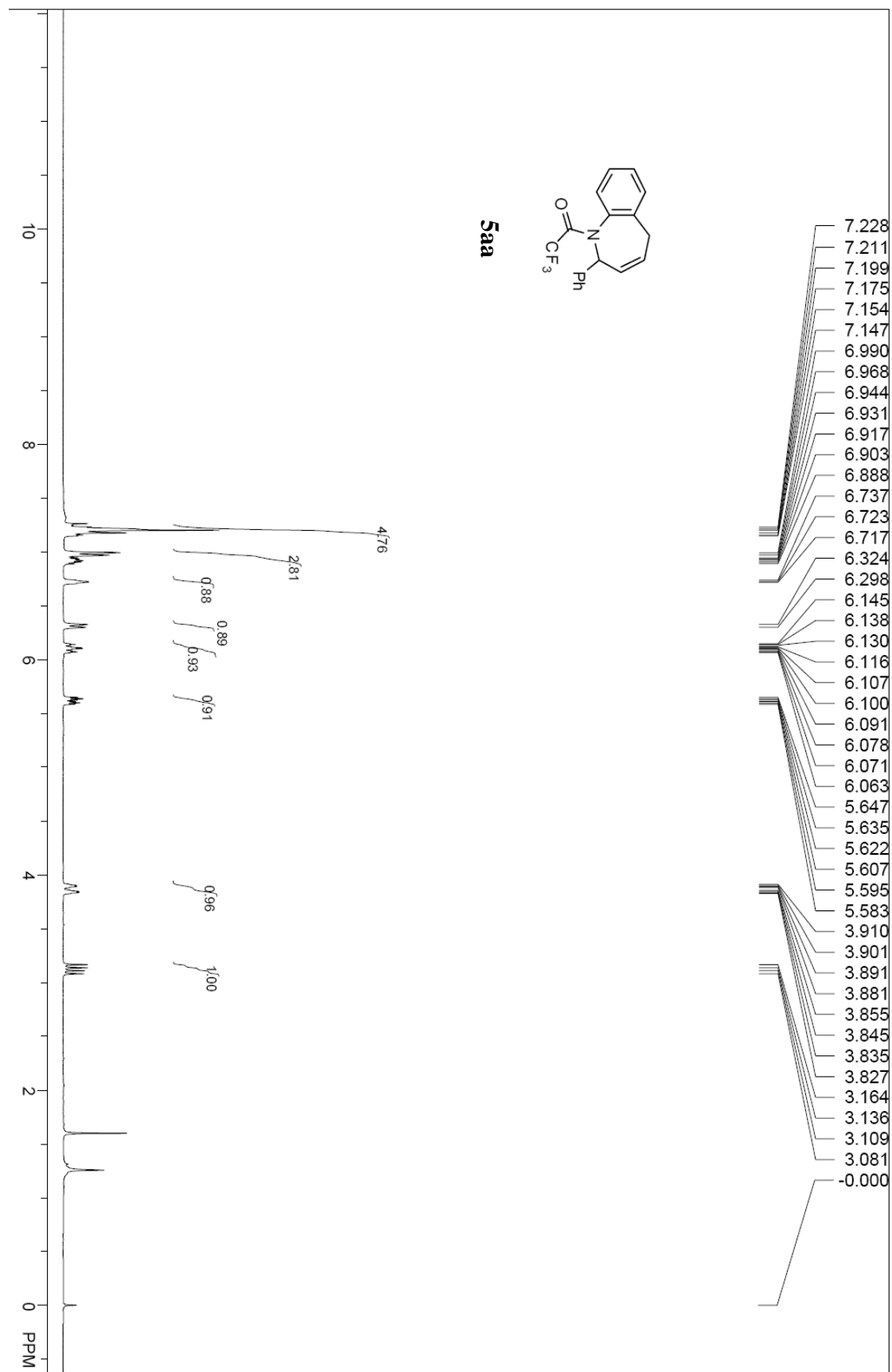


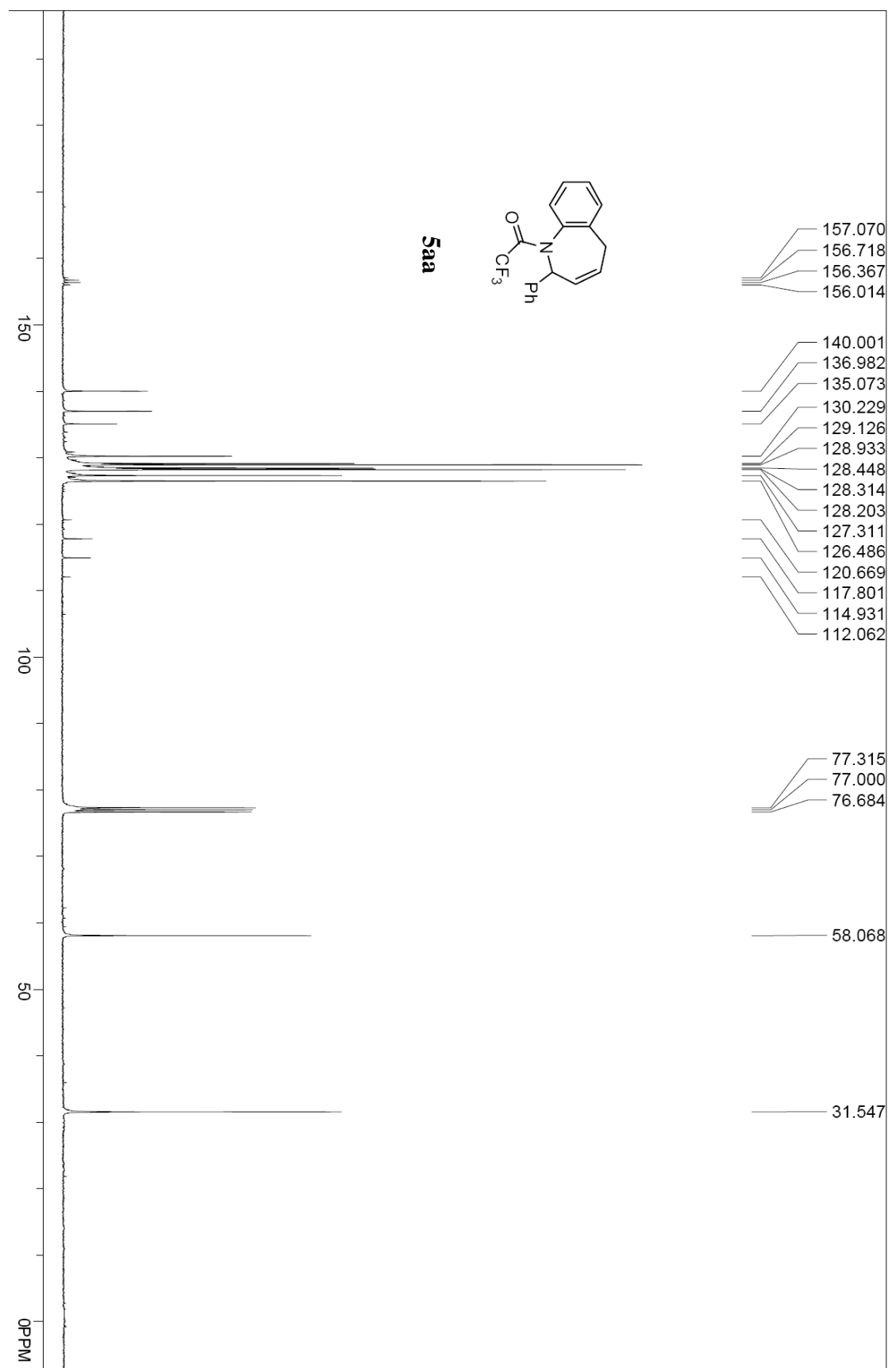
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19.673	337682.938	10956902.000	50.2637
2	28.147	212913.719	10841945.000	49.7363
<b>Total</b>		550596.656	21798847.000	100.0000



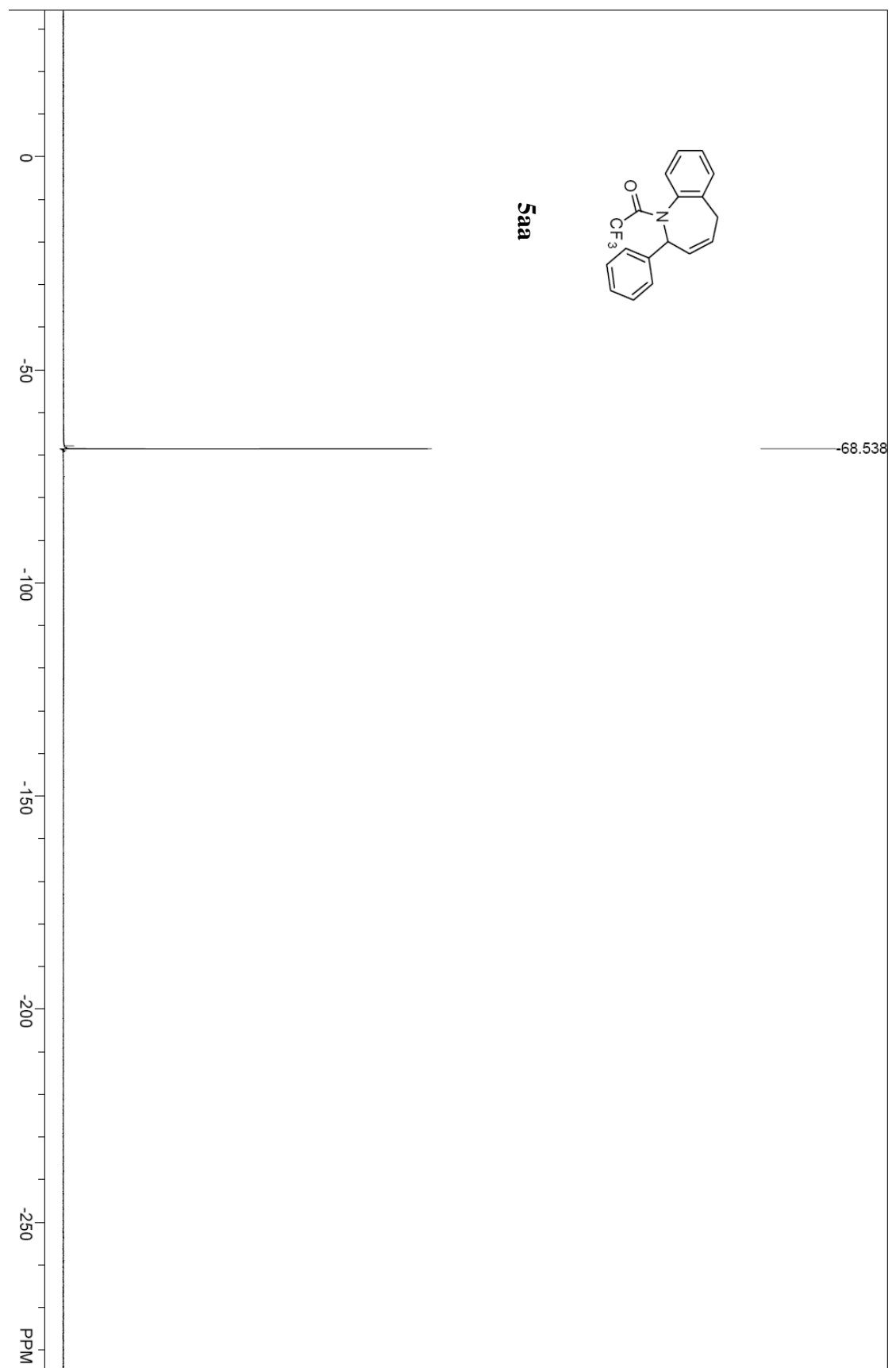
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	18.598	1157.174	48323.477	0.7448
2	27.425	133242.250	6439970.500	99.2552
<b>Total</b>		134399.424	6488293.977	100.0000

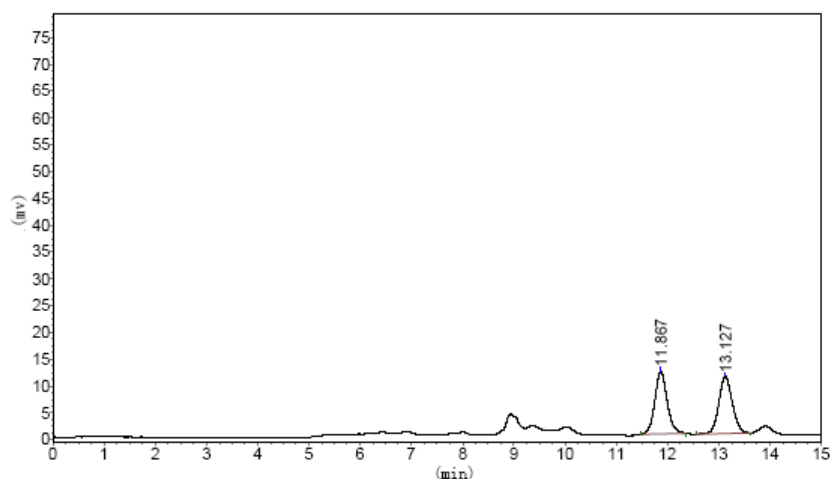




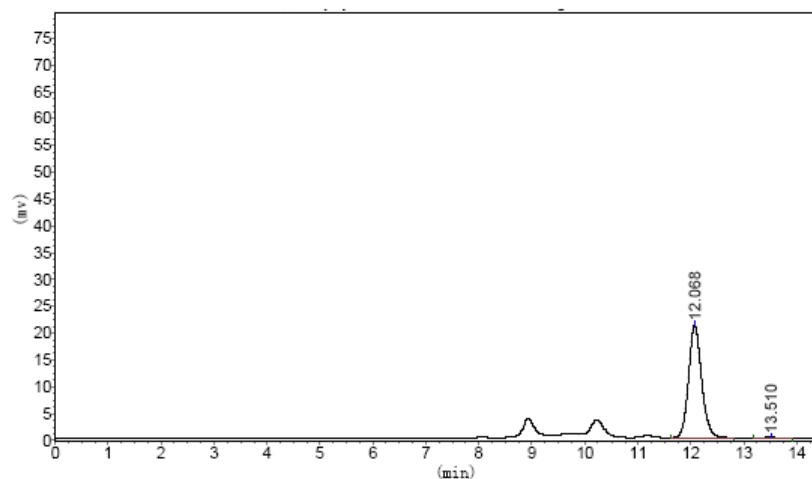




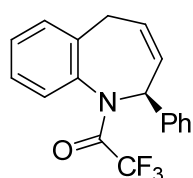




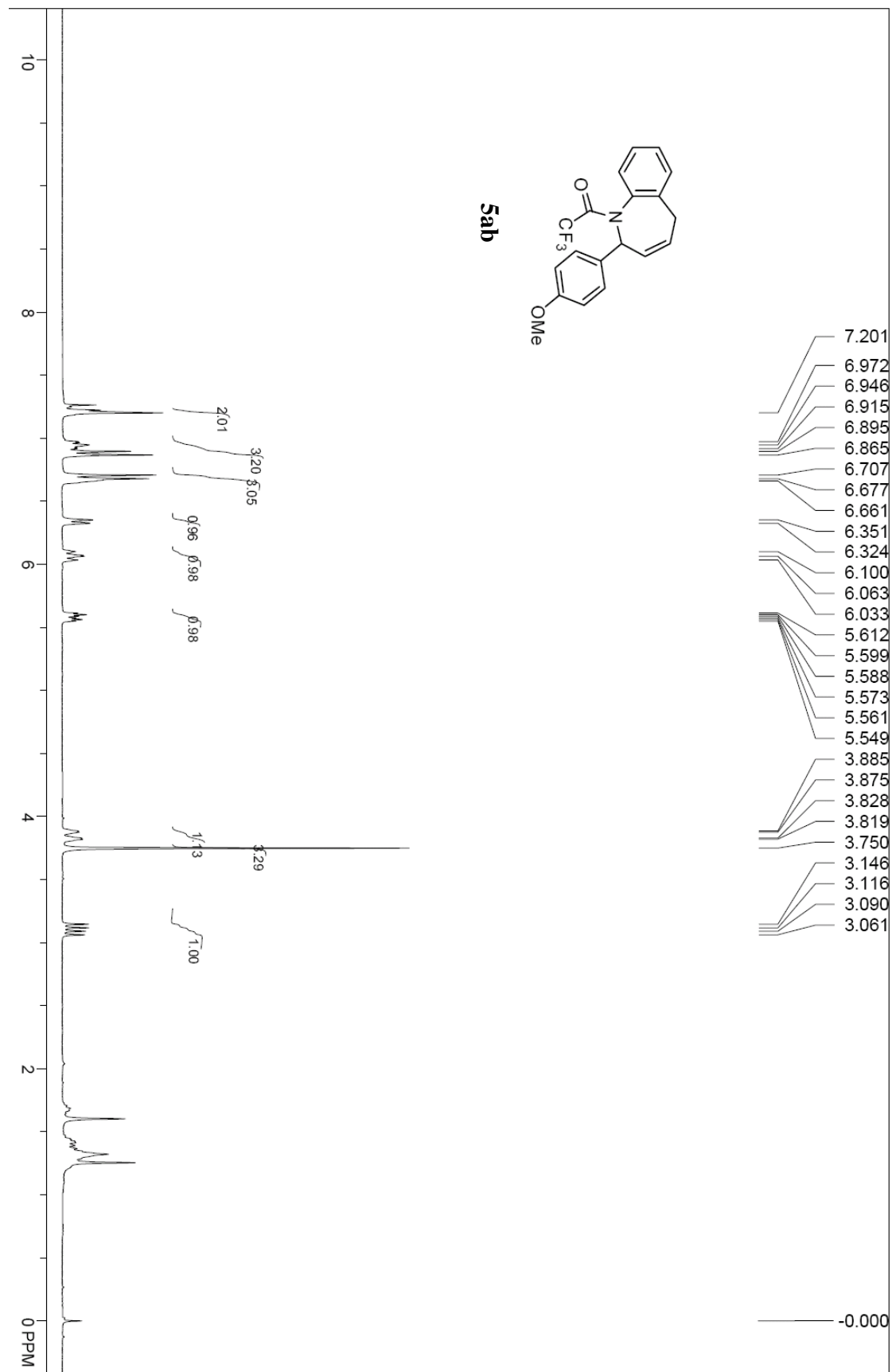
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.867	11641.022	195216.031	50.1069
2	13.127	10604.977	194382.813	49.8931
<b>Total</b>		22245.999	389598.844	100.0000

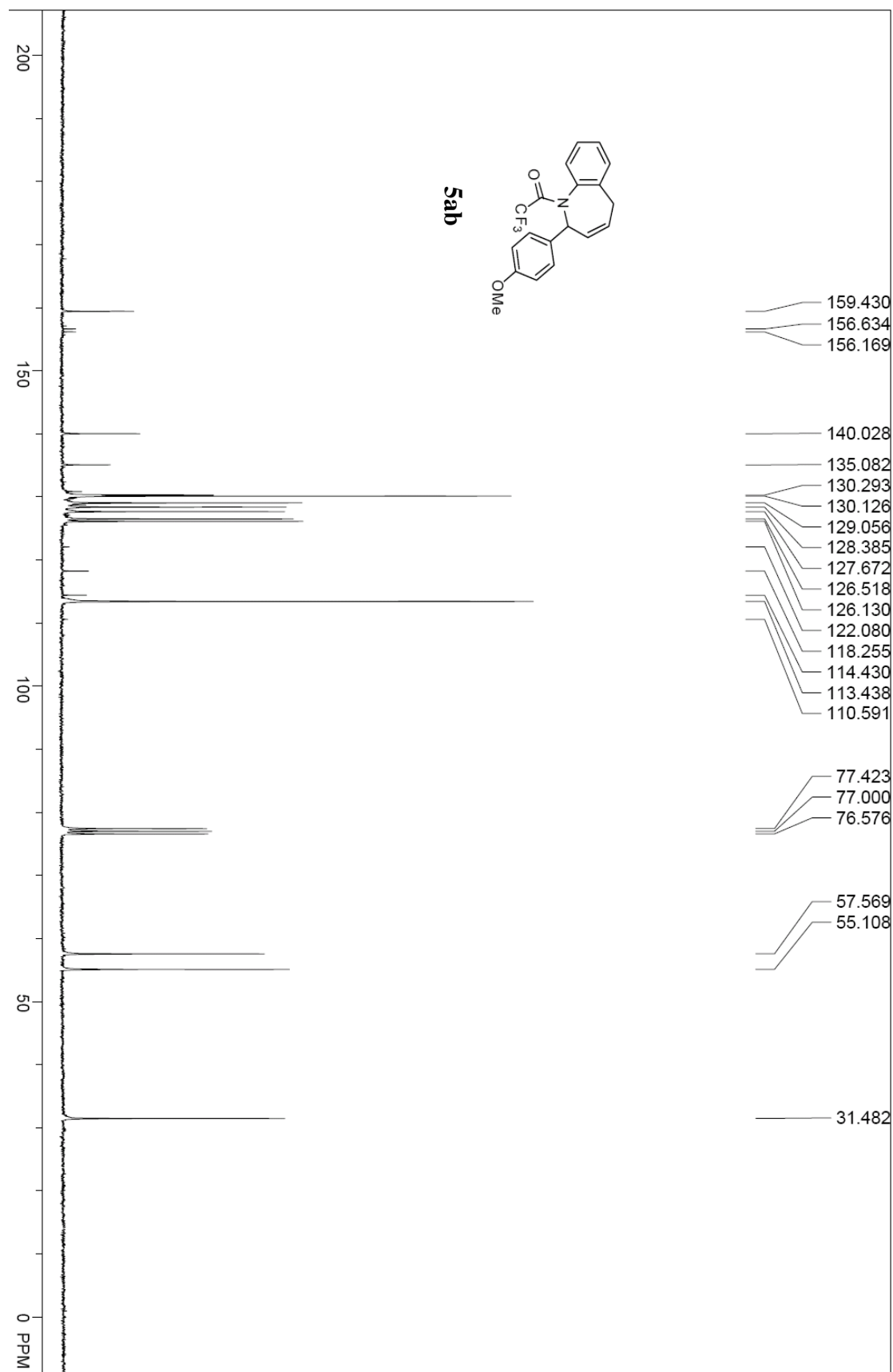


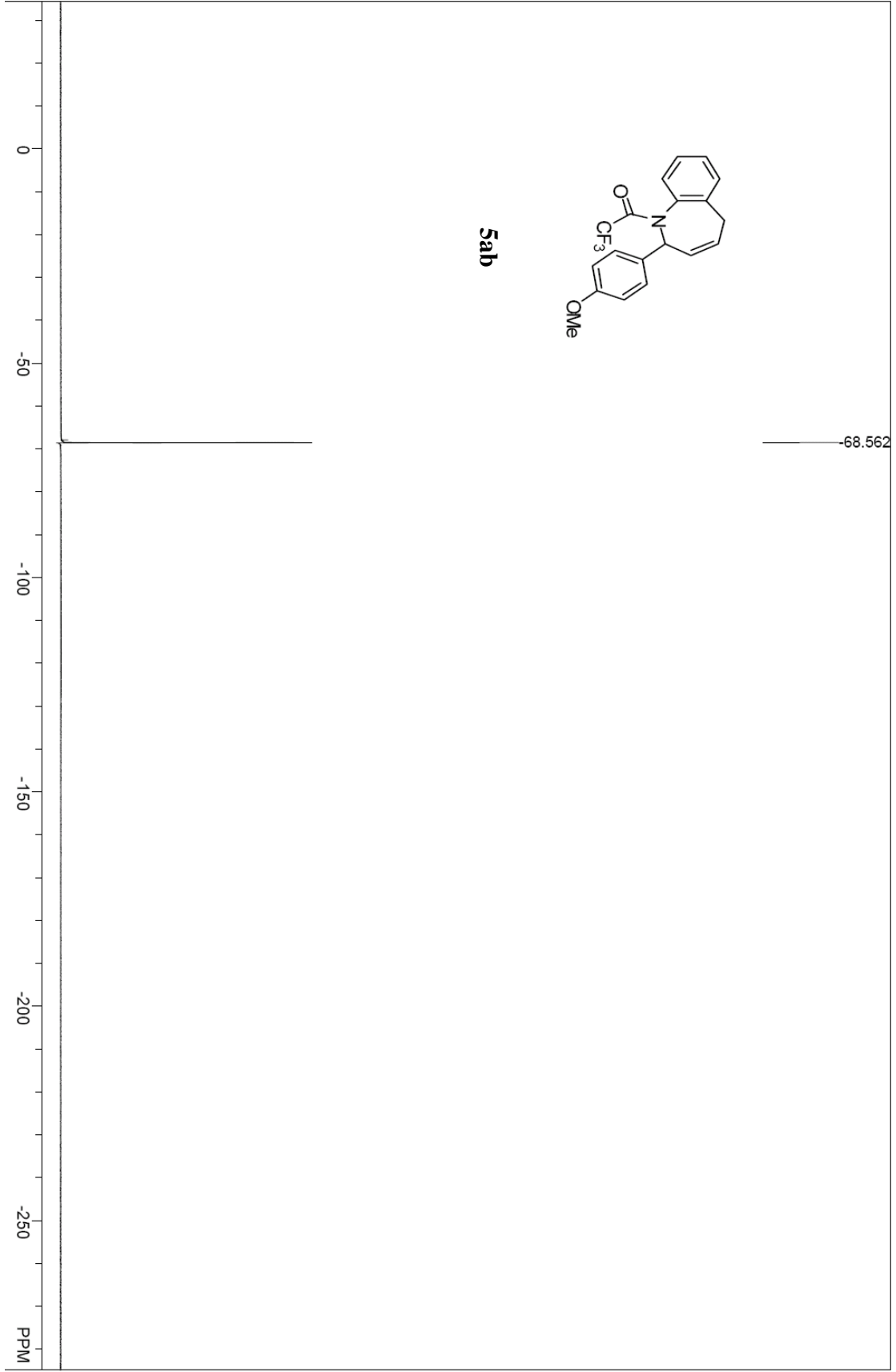
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.068	20985.512	360599.625	99.2648
2	13.510	142.966	2670.801	0.7352
<b>Total</b>		21128.478	363270.426	100.0000

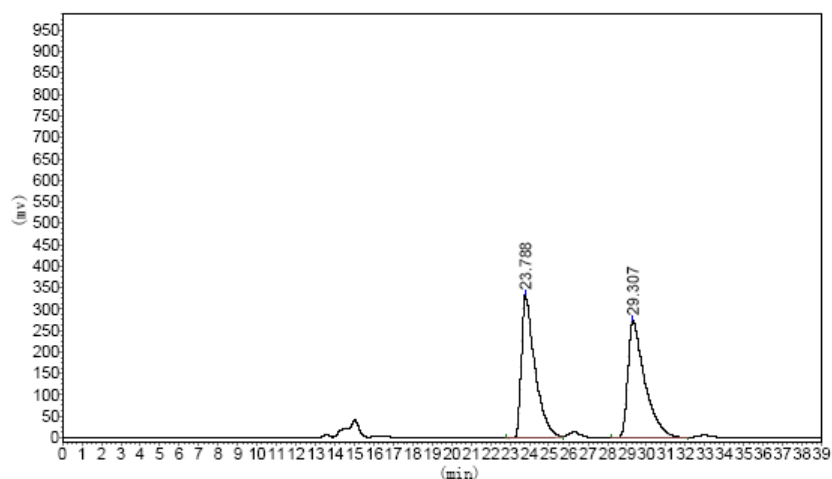


**5aa**

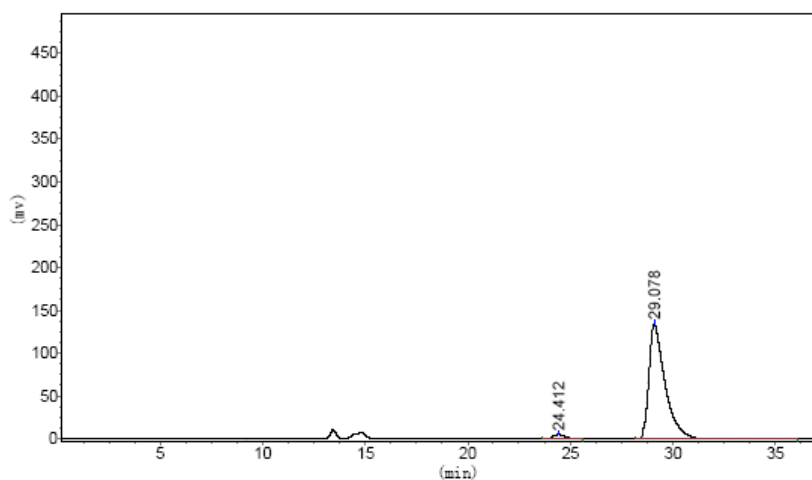




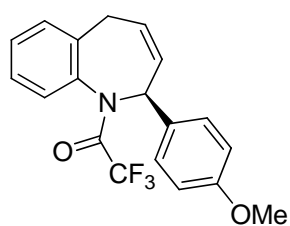




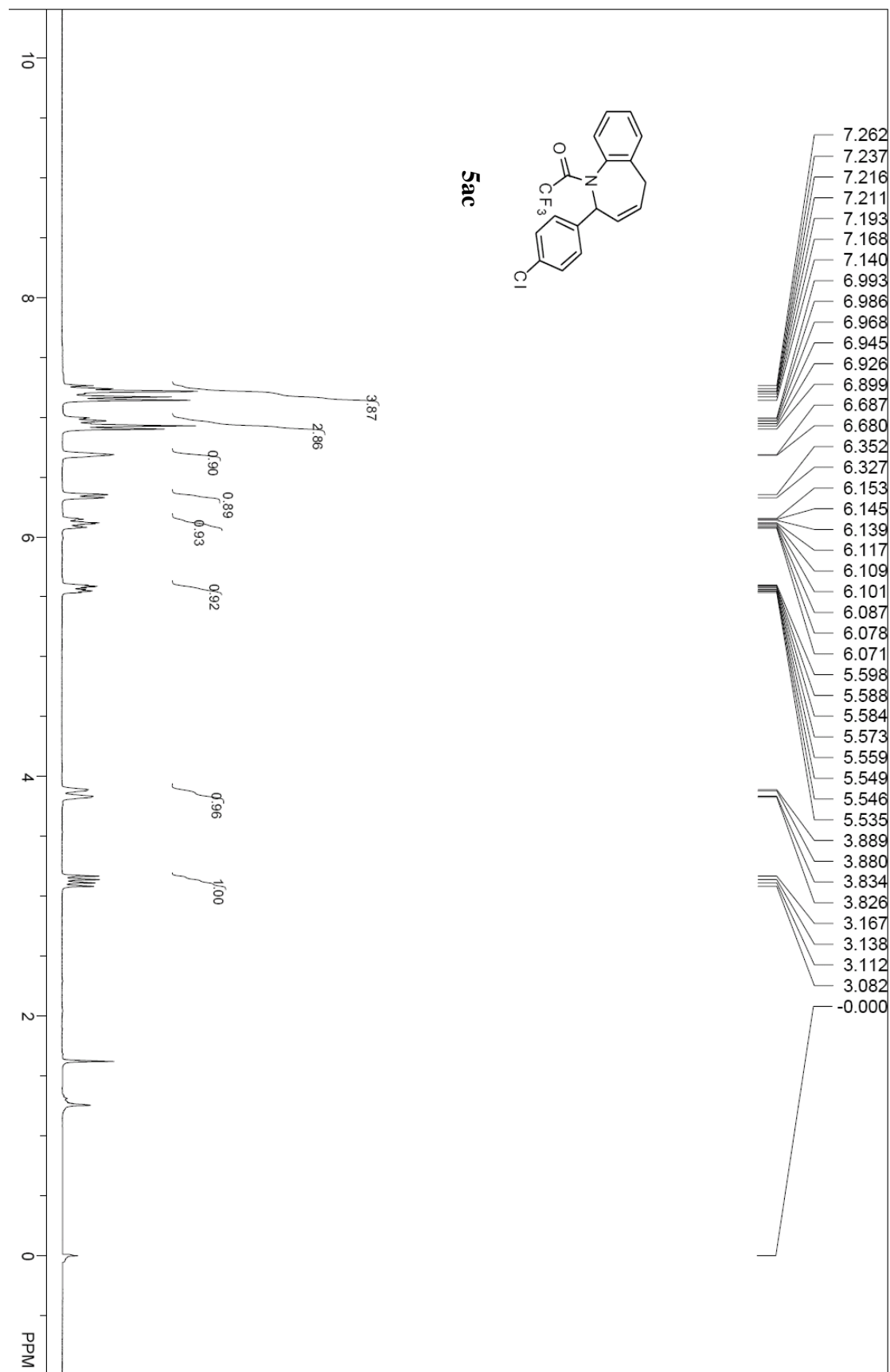
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	23.788	331863.688	16011273.000	49.6831
2	29.307	272951.500	16215536.000	50.3169
<b>Total</b>		604815.188	32226809.000	100.0000

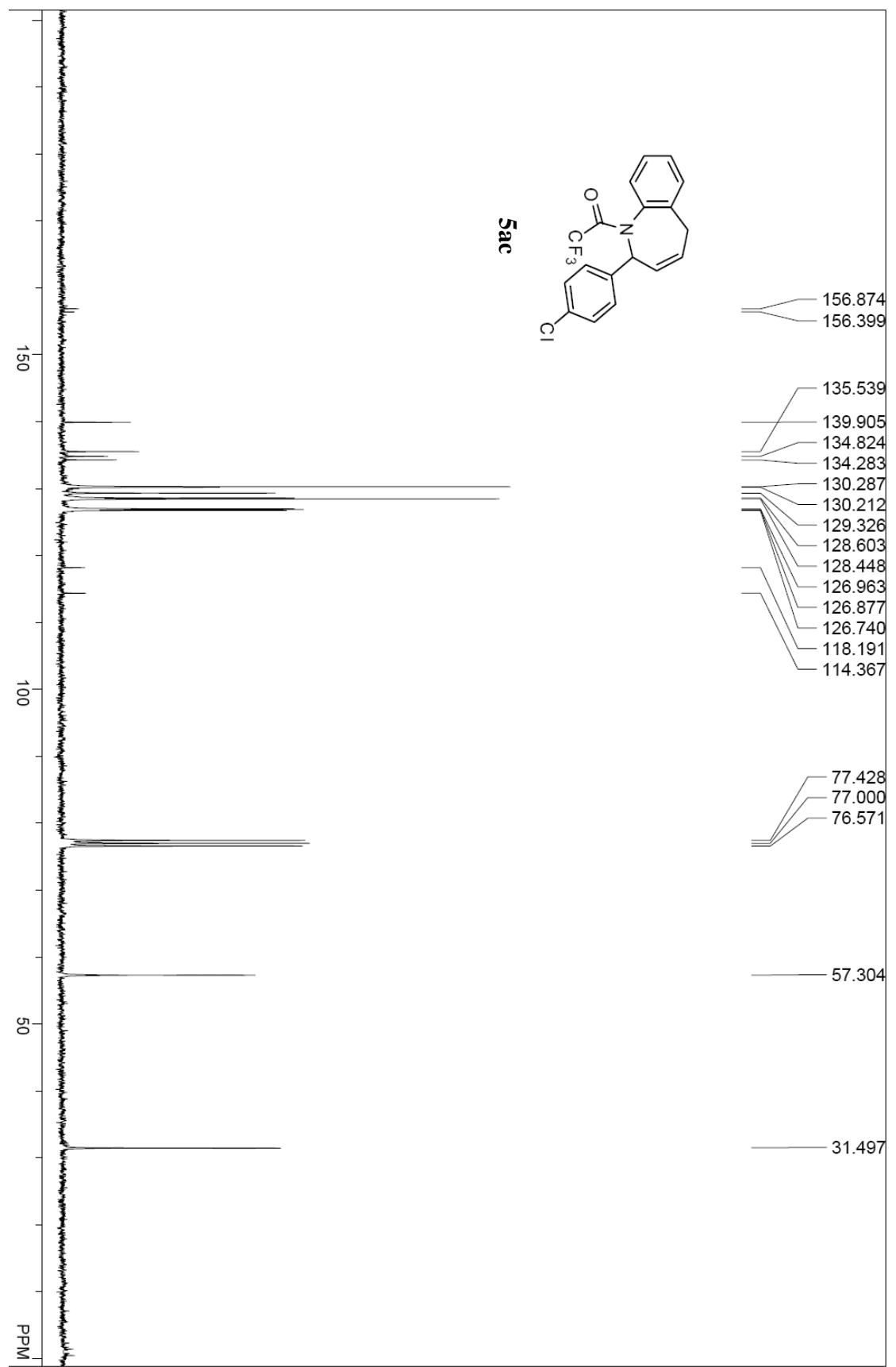


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	24.412	5295.873	210808.516	2.8044
2	29.078	134167.641	7306175.500	97.1956
<b>Total</b>		139463.514	7516984.016	100.0000

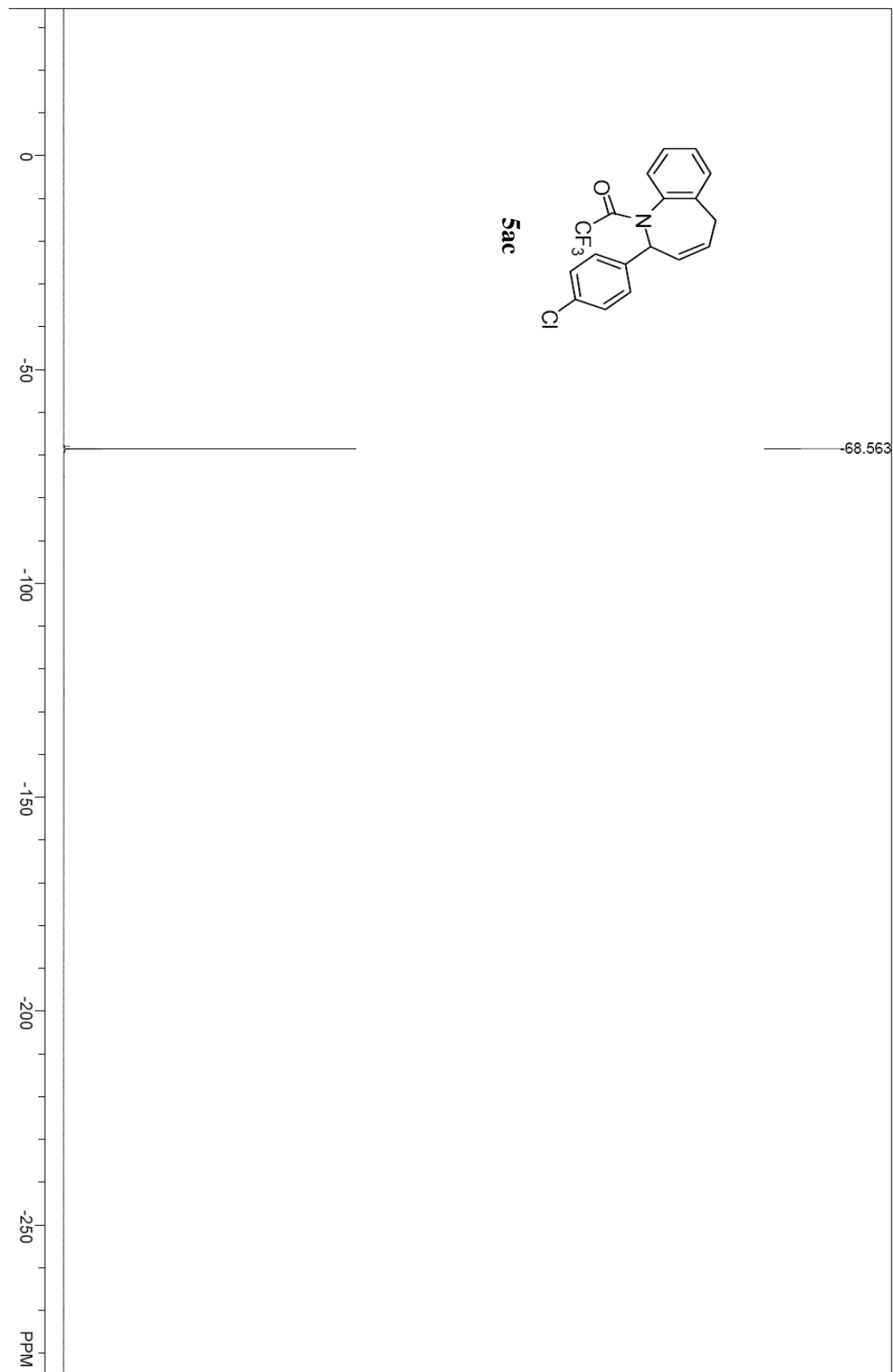


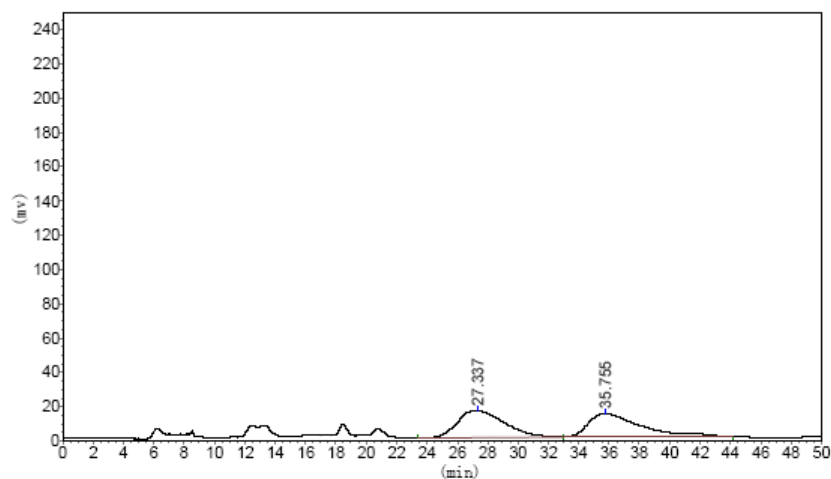
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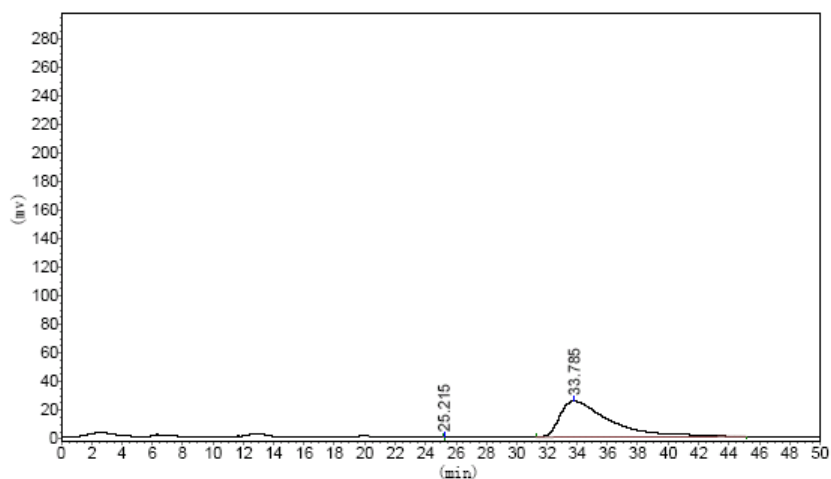




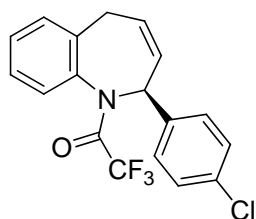




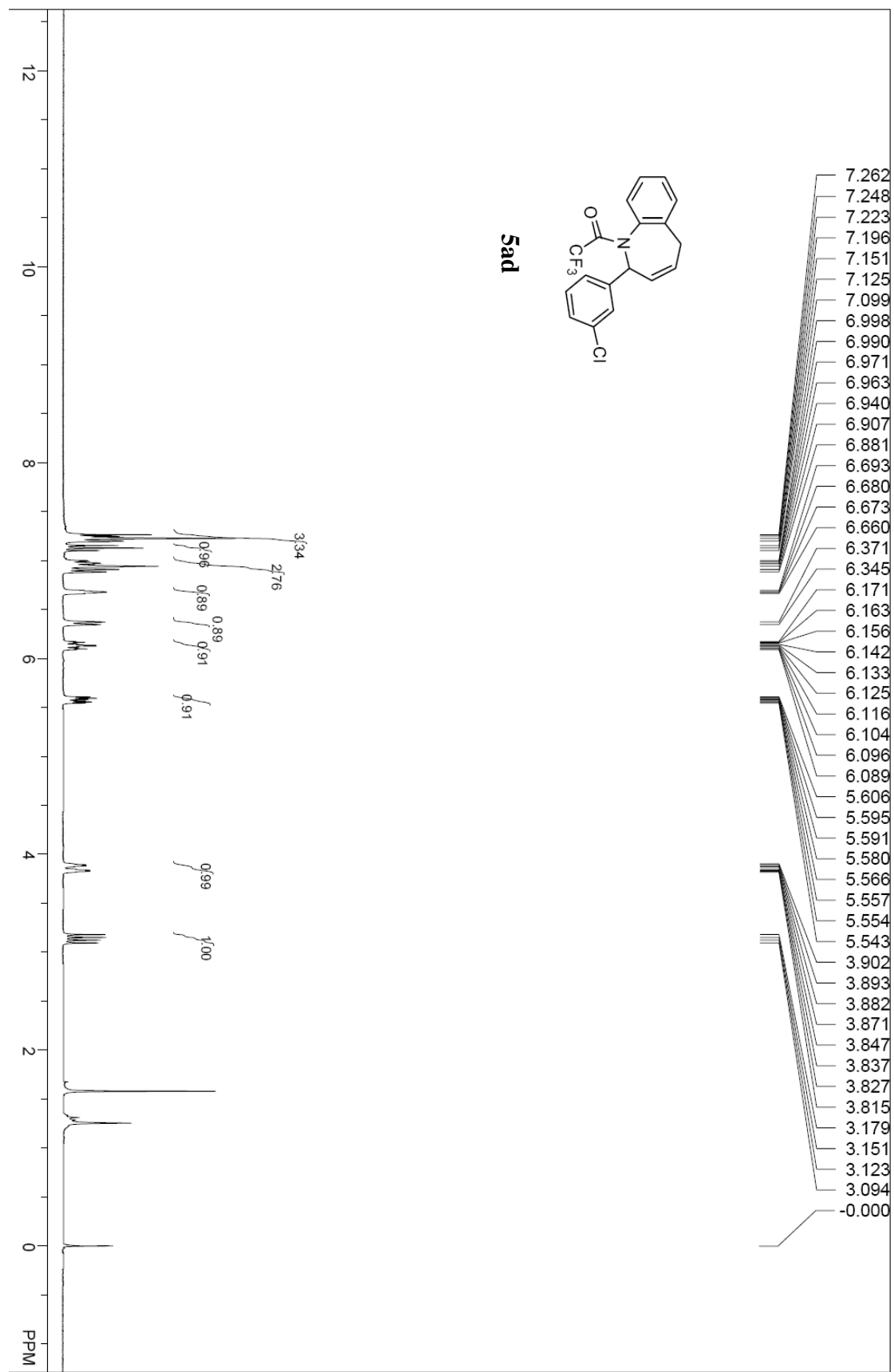
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	27.337	15430.995	3321529.250	50.2740
2	35.755	13475.431	3285324.250	49.7260
Total		28906.426	6606853.500	100.0000

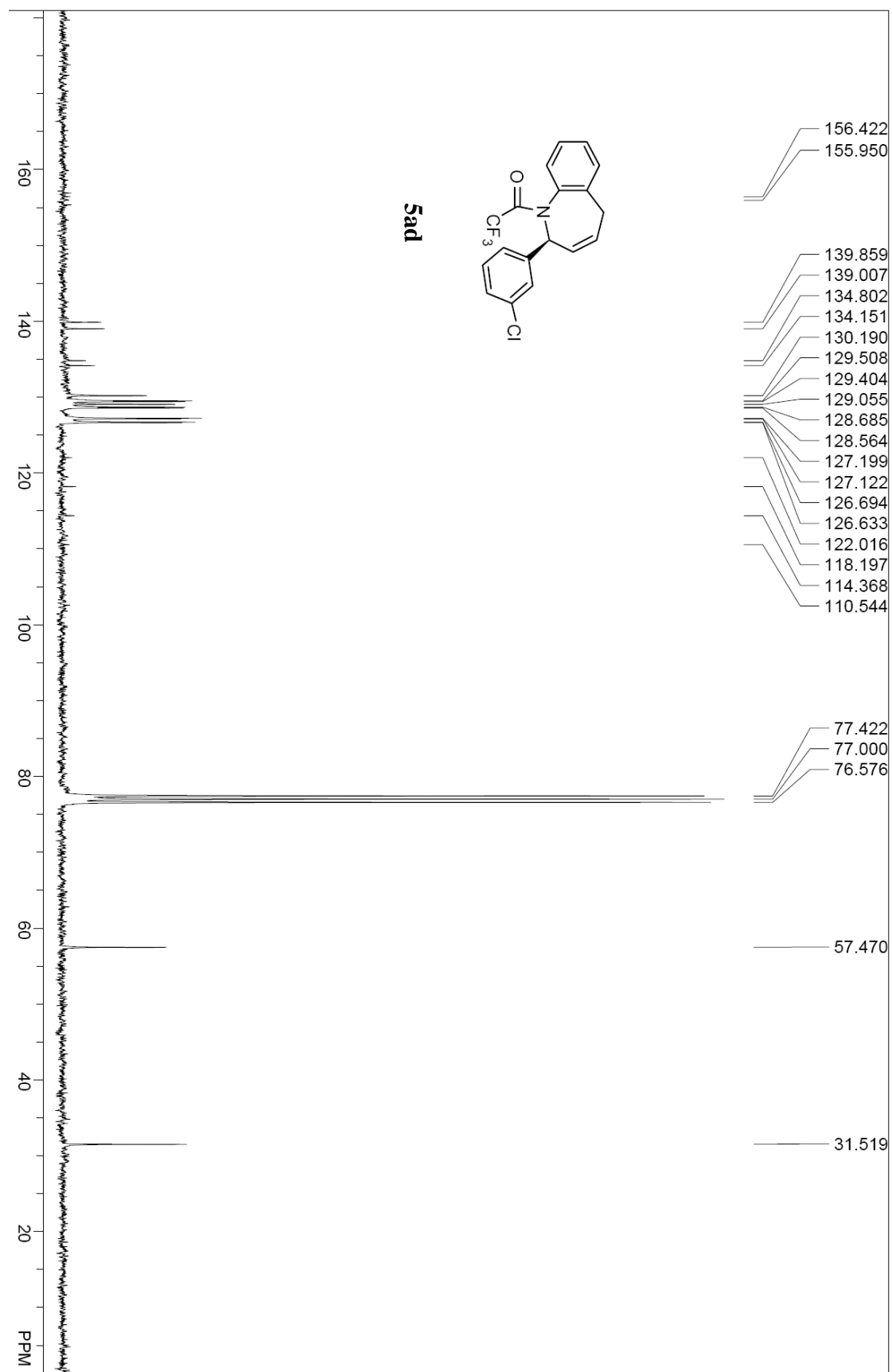


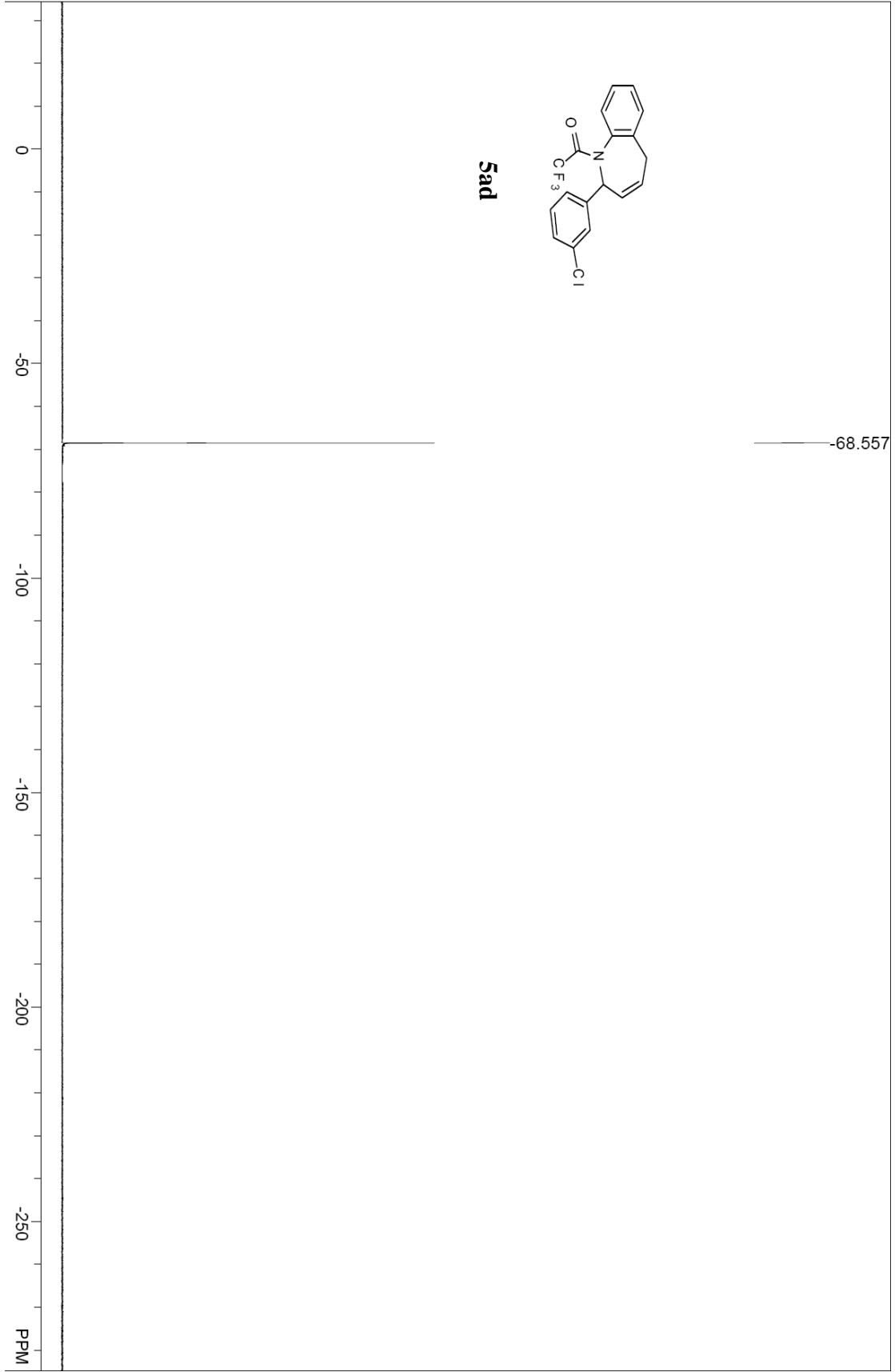
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	25.215	3.536	5.300	0.0001
2	33.785	24985.793	5648578.000	99.9999
Total		24989.329	5648583.300	100.0000

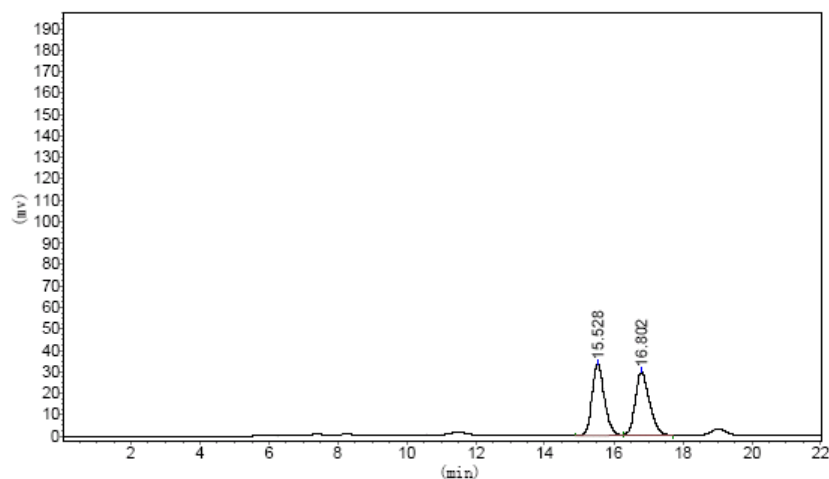


5ac

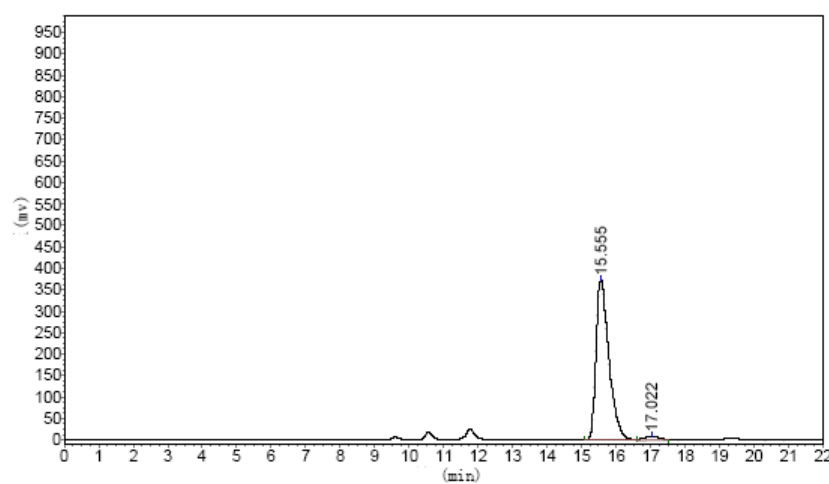




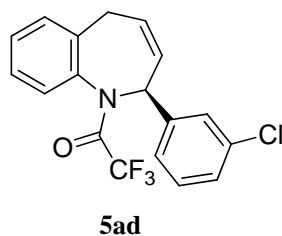


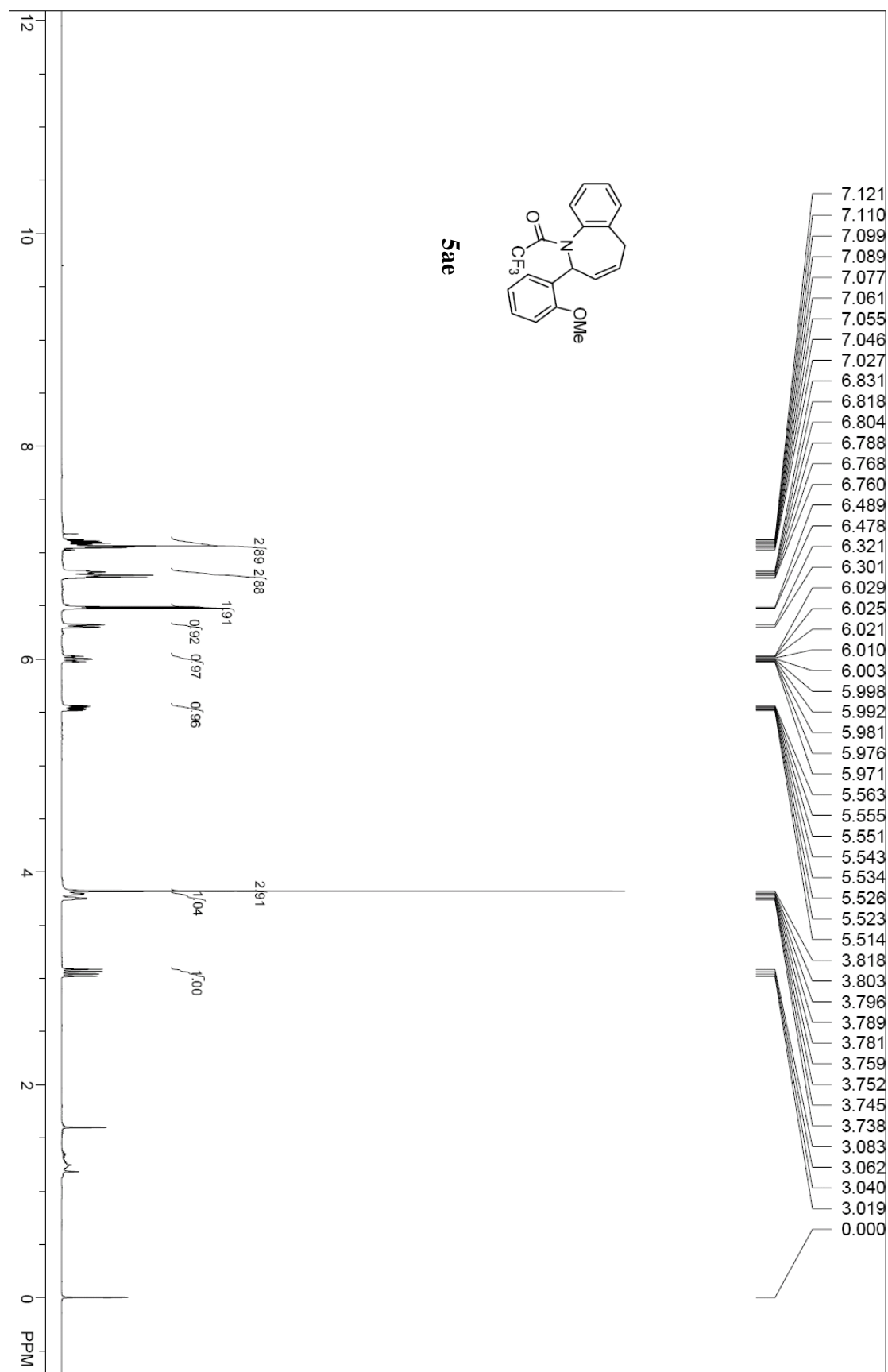


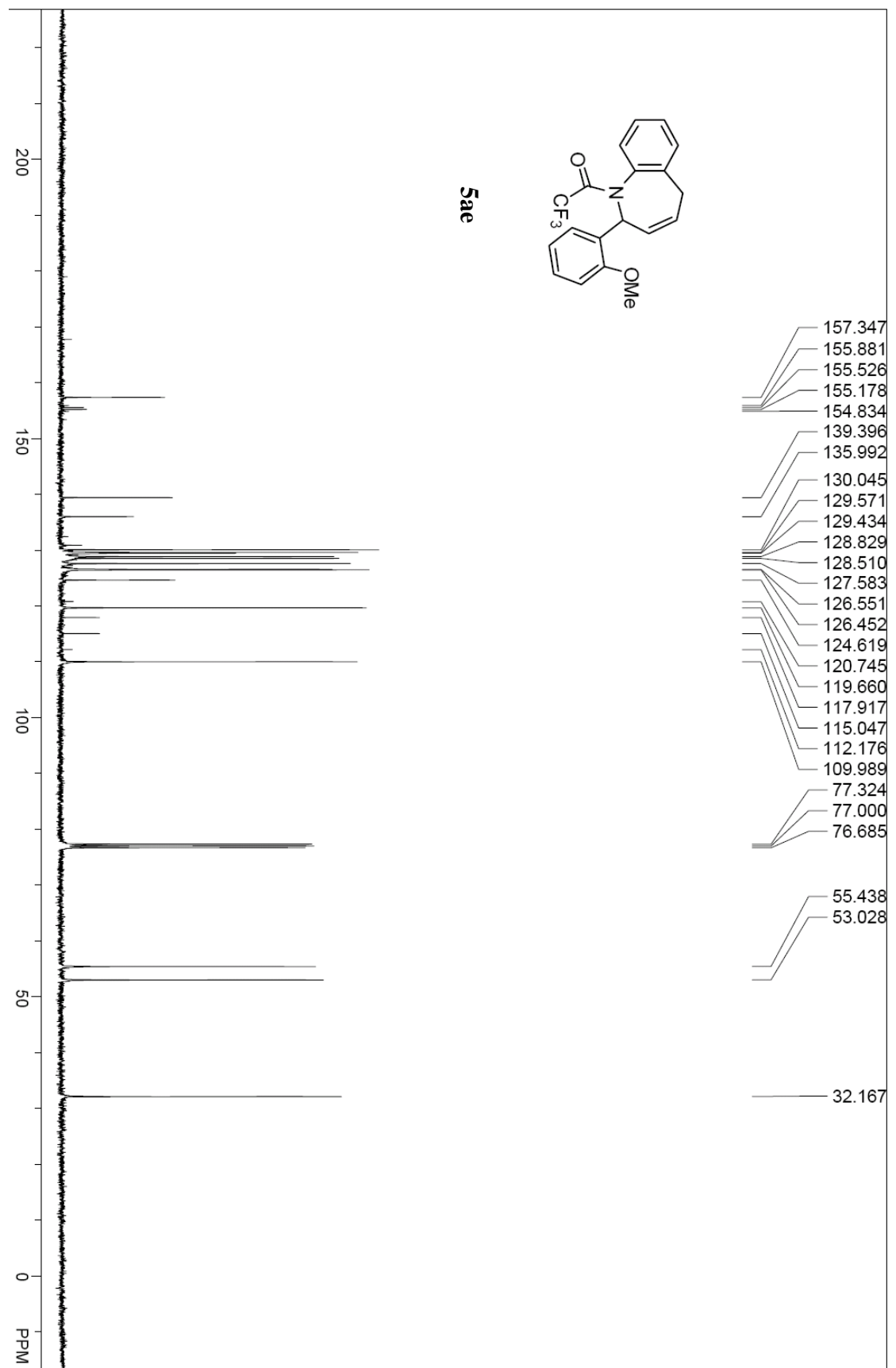
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.528	33271.367	830023.563	49.7740
2	16.802	29326.799	837560.313	50.2260
<b>Total</b>		62598.166	1667583.875	100.0000



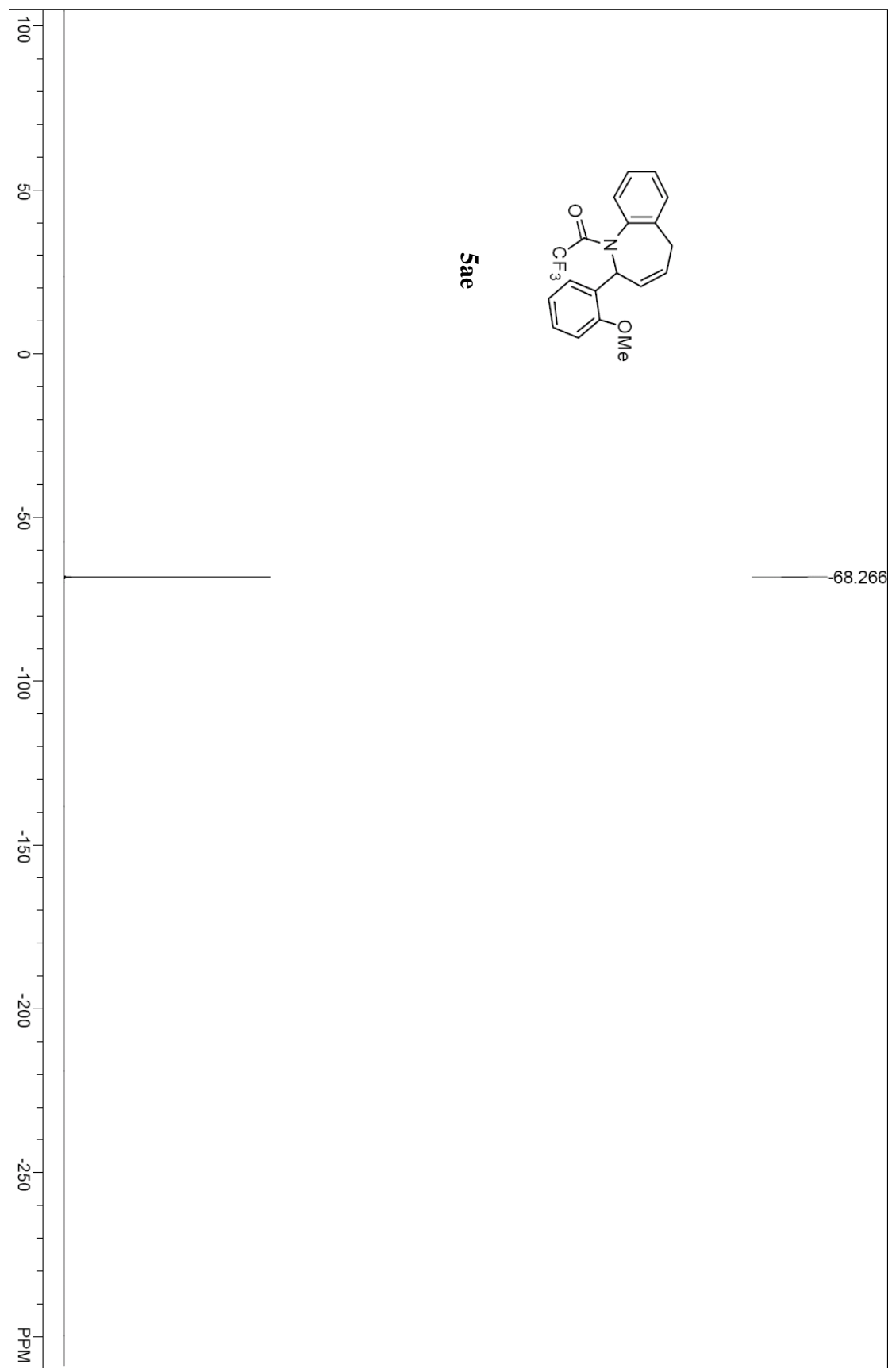
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.555	373401.938	9730737.000	97.5010
2	17.022	8559.526	249401.438	2.4990
<b>Total</b>		381961.464	9980138.438	100.0000

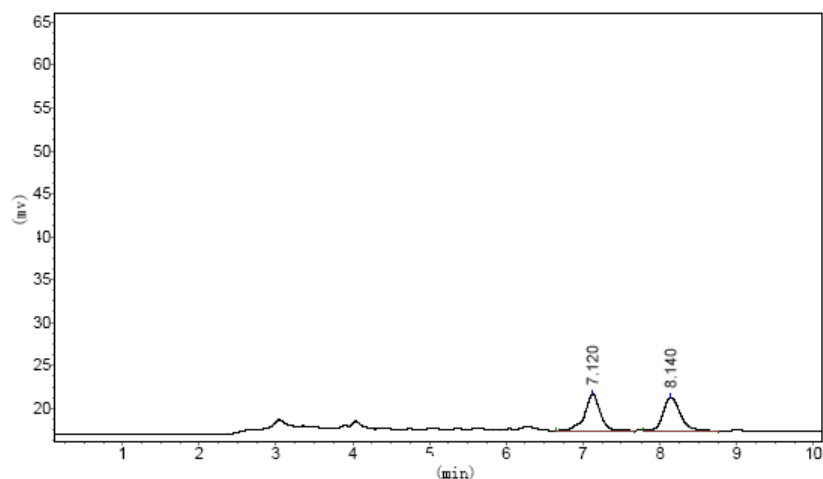




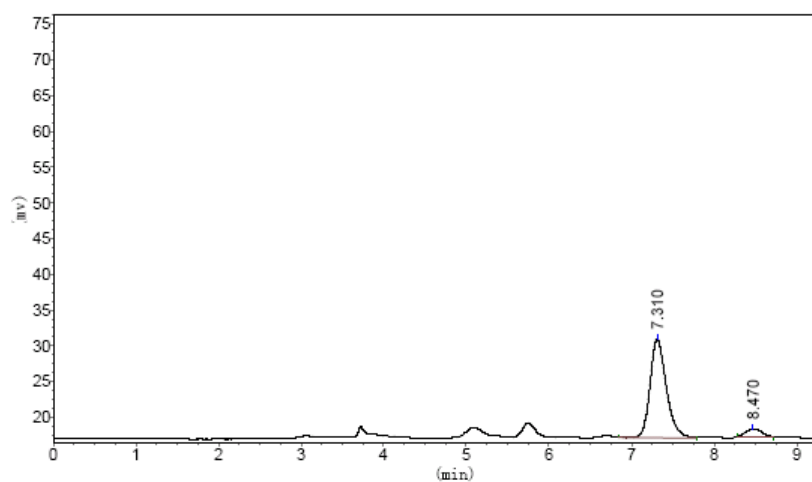




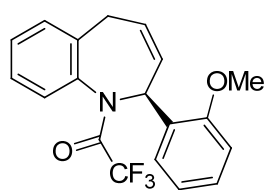




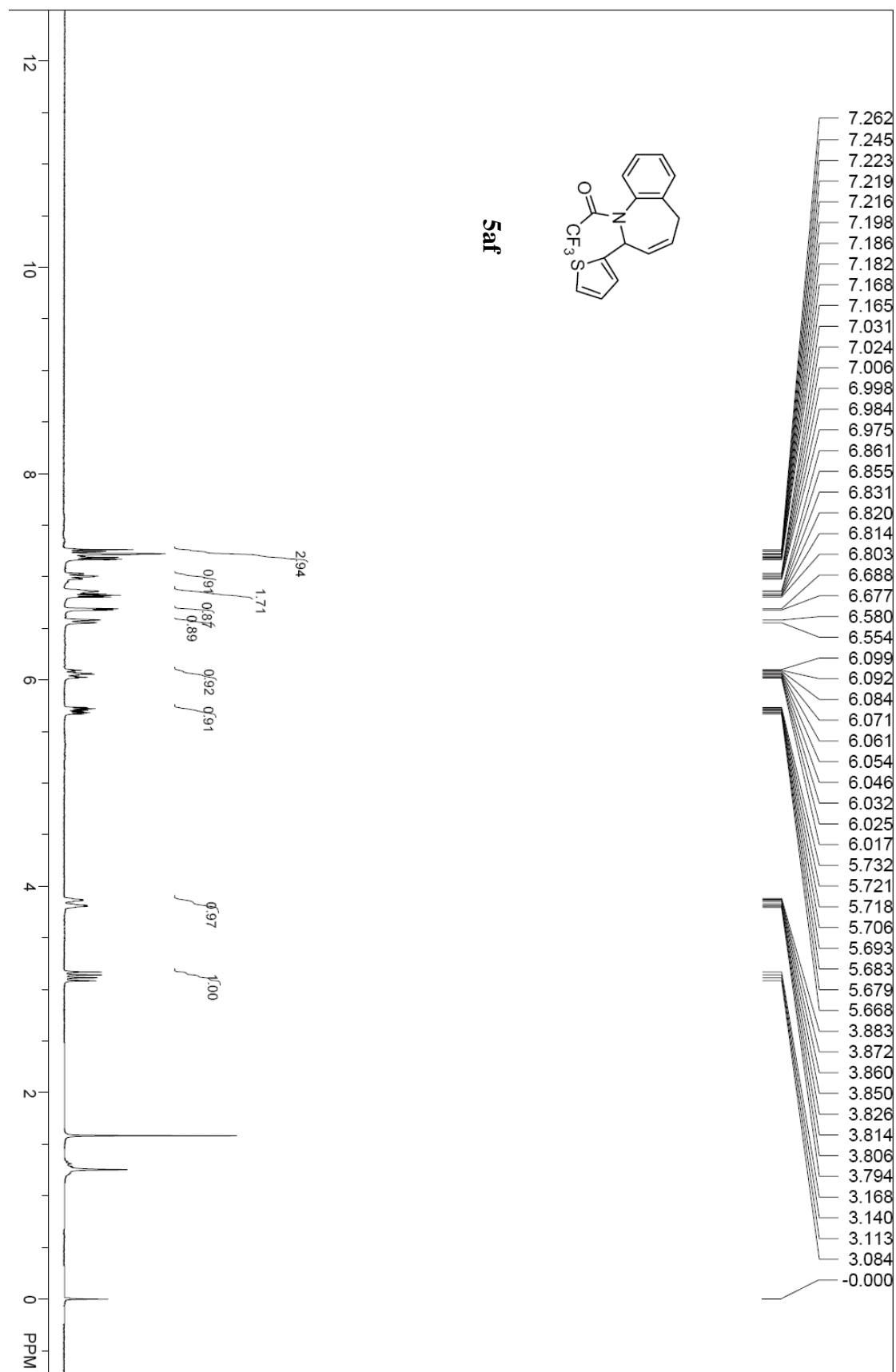
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.120	4243.009	58932.770	49.5709
2	8.140	3871.097	59953.141	50.4291
<b>Total</b>		8114.107	118885.910	100.0000

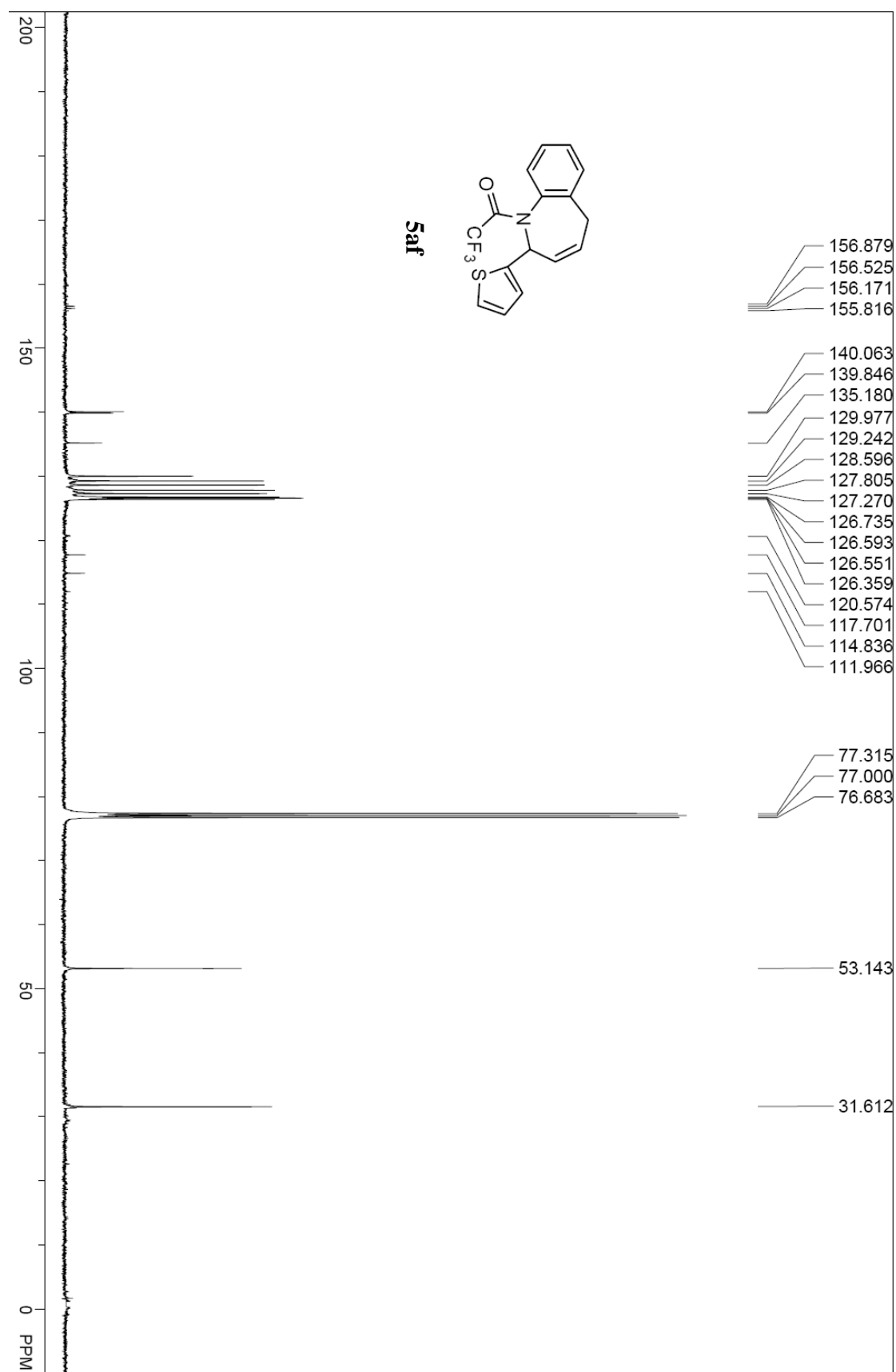


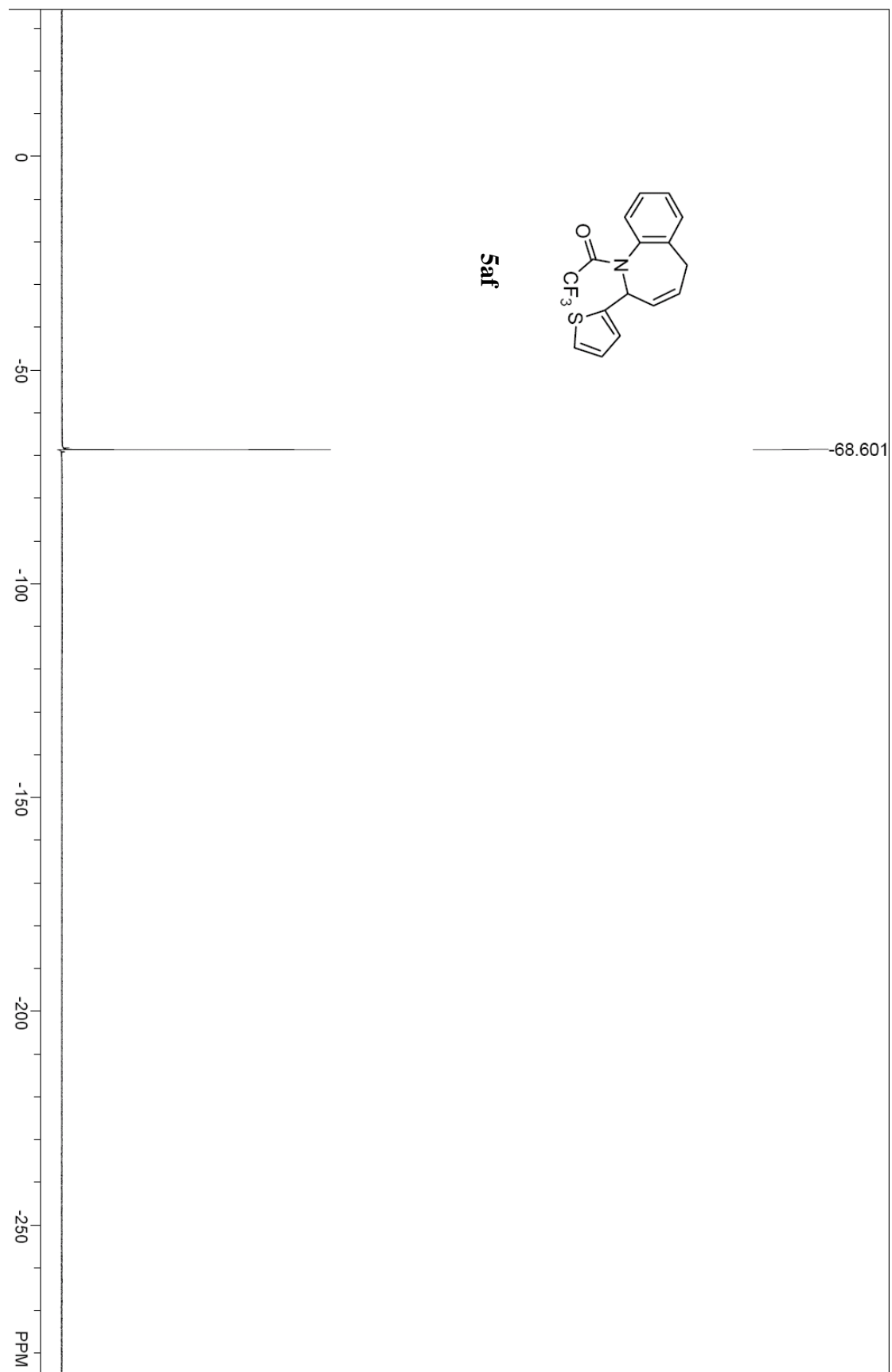
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.310	13829.887	187826.266	92.3047
2	8.470	1130.246	15658.754	7.6953
<b>Total</b>		14960.132	203485.020	100.0000

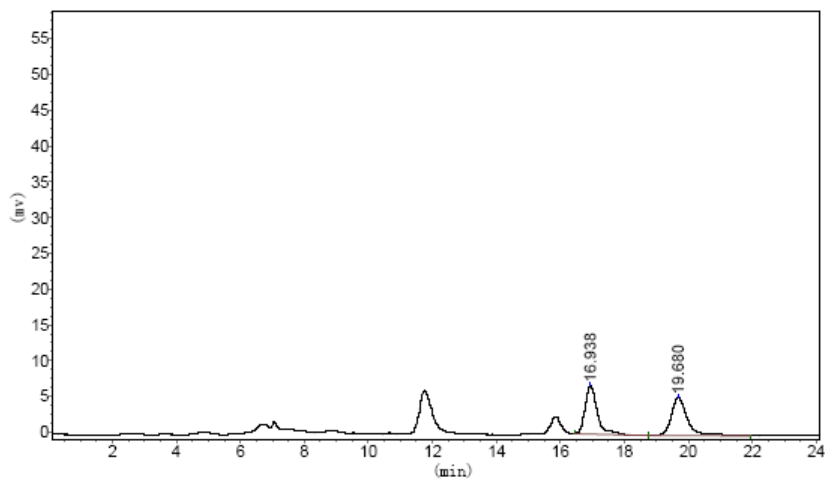


**5ae**

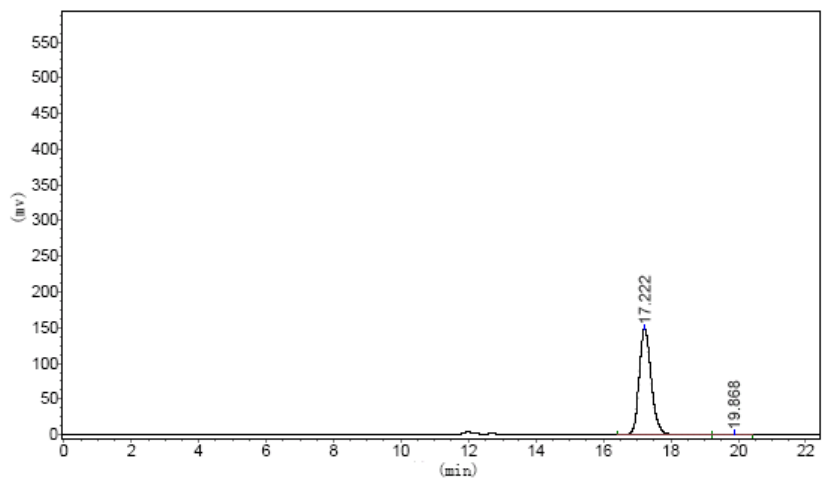




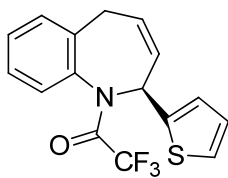




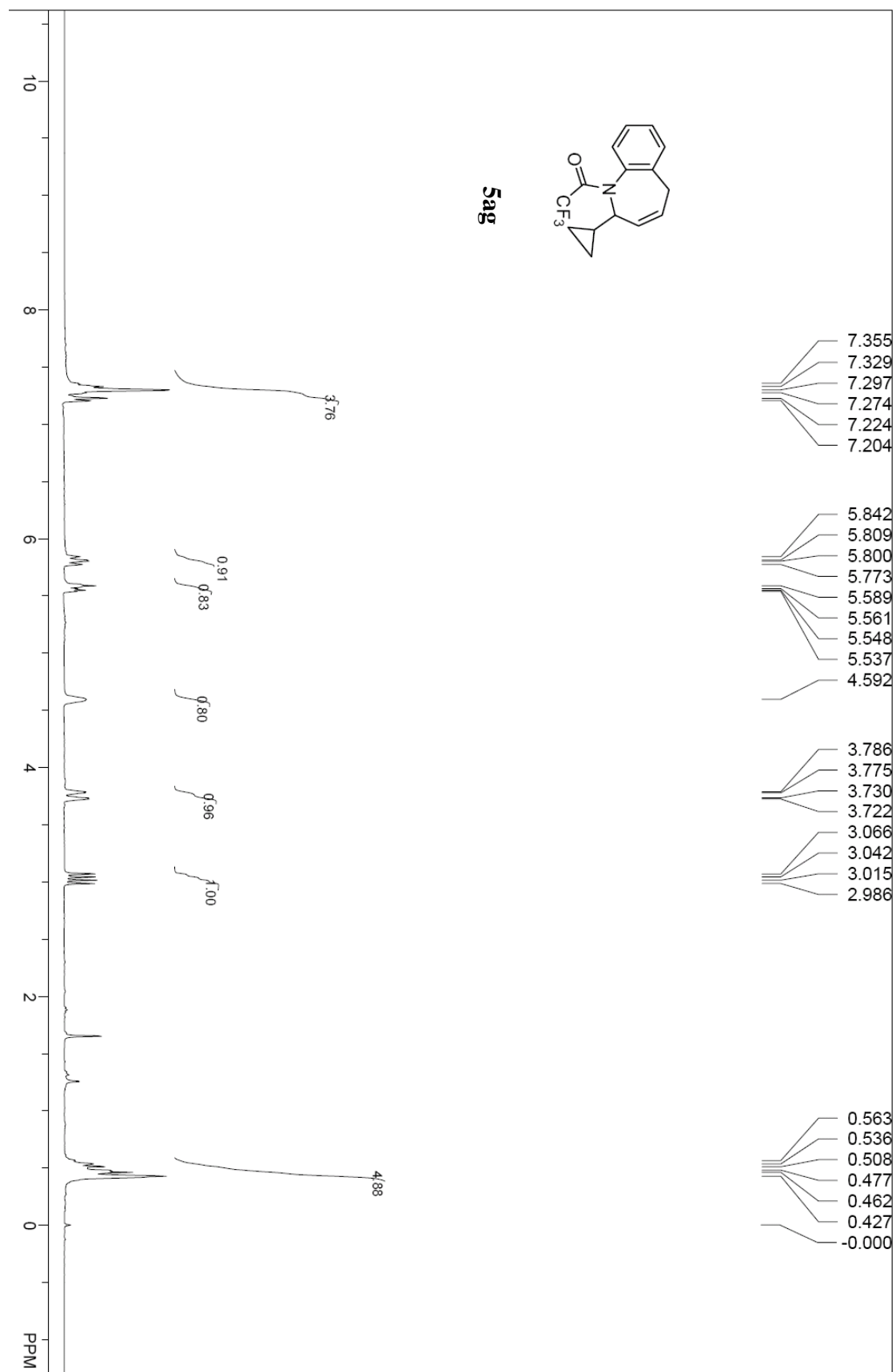
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.938	6731.577	180746.656	49.5487
2	19.680	5231.145	184039.000	50.4513
Total		11962.722	364785.656	100.0000

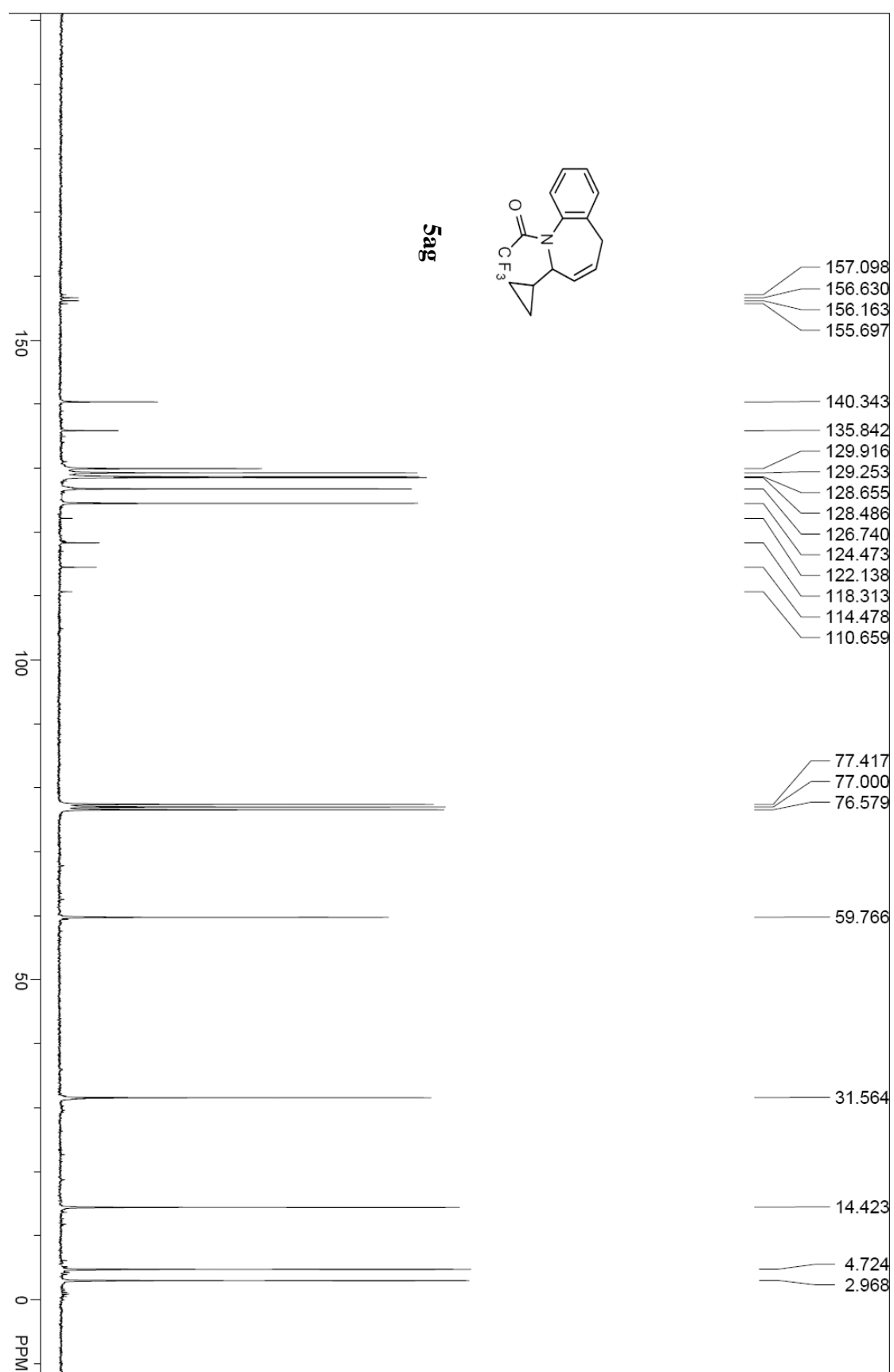


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17.222	148243.609	3678706.500	99.0384
2	19.868	1080.624	35716.863	0.9616
Total		149324.233	3714423.363	100.0000

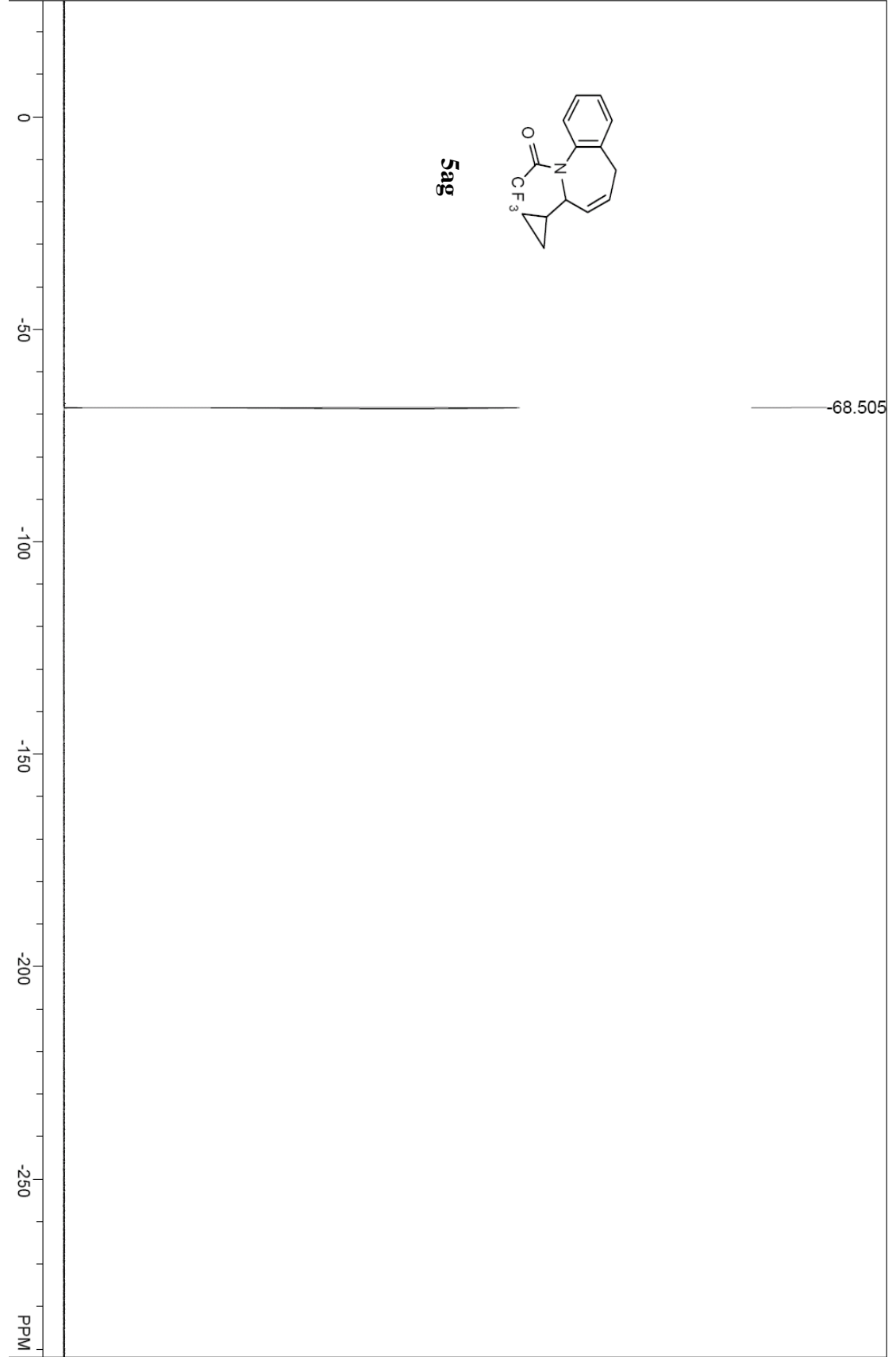


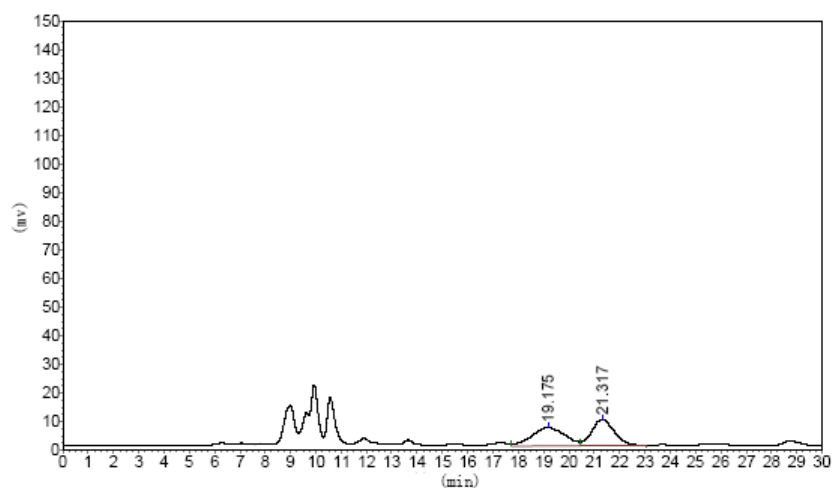
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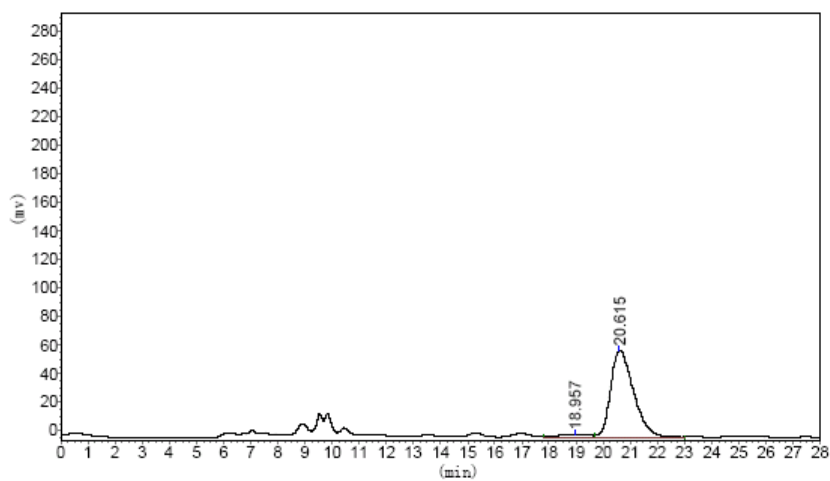




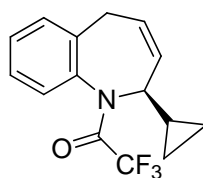




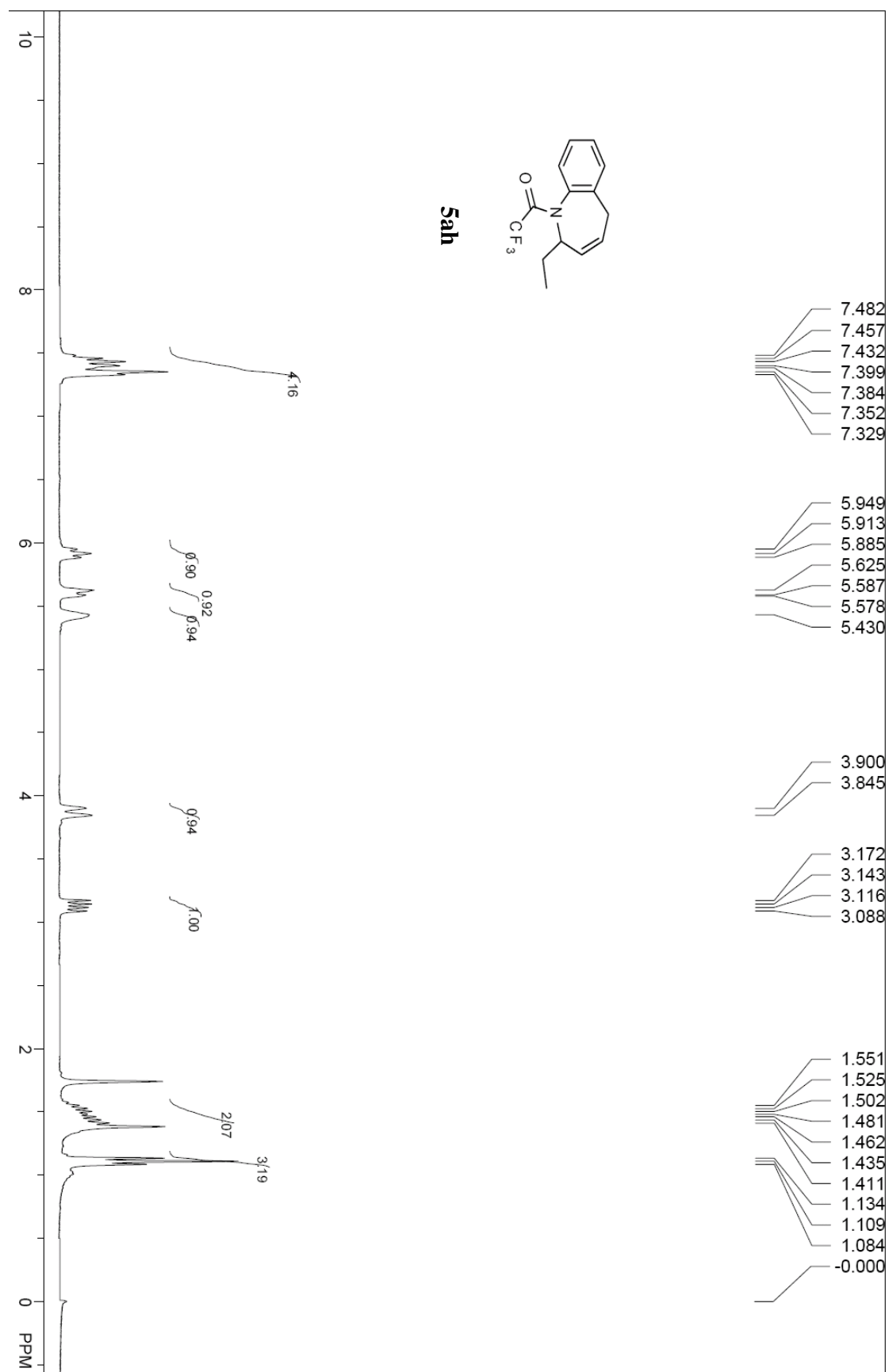
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19.175	6374.385	571938.438	49.9952
2	21.317	9244.735	572047.375	50.0048
<b>Total</b>		15619.120	1143985.813	100.0000

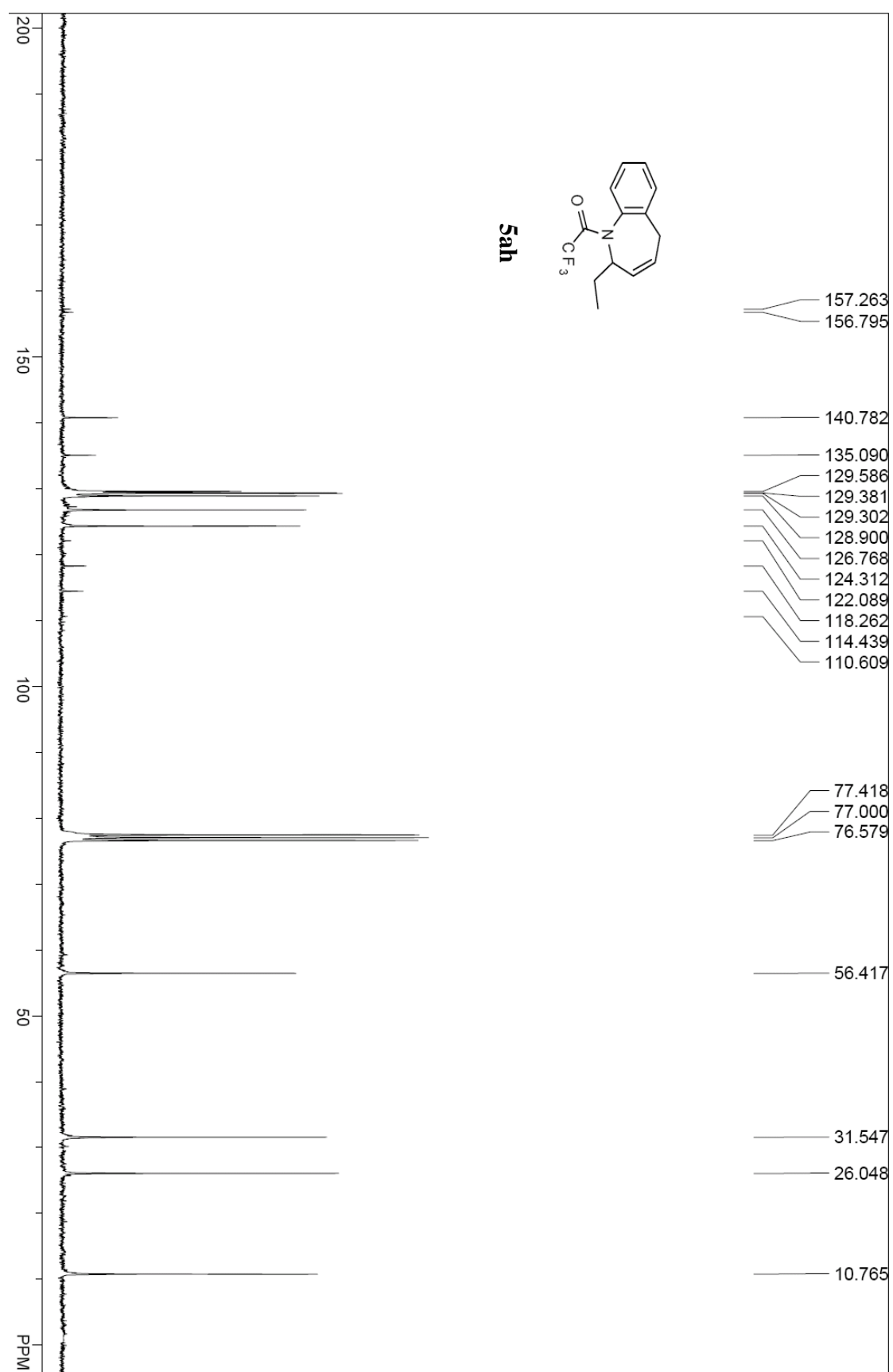


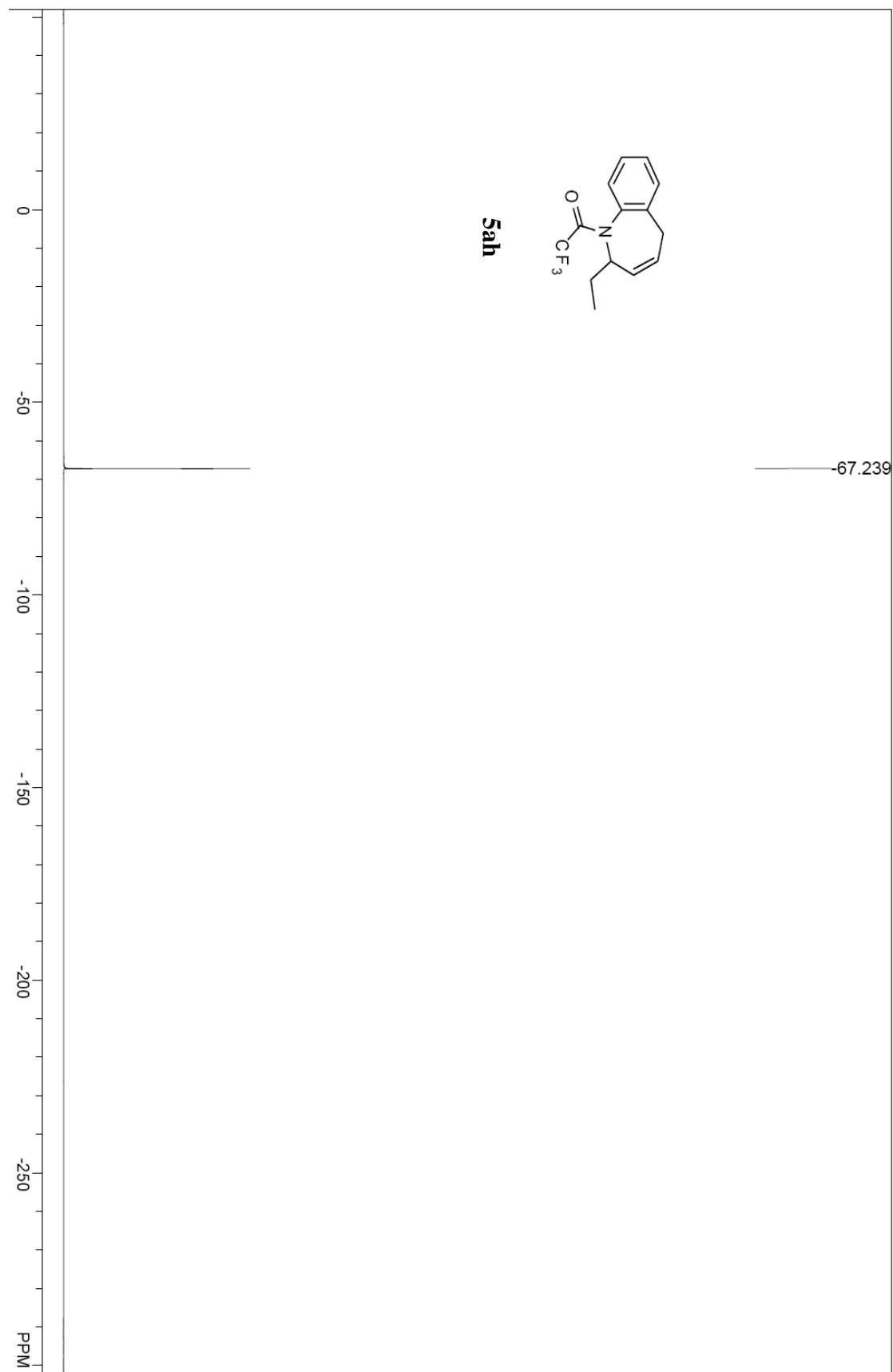
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	18.957	2103.497	150087.969	4.0359
2	20.615	60875.430	3568704.250	95.9641
<b>Total</b>		62978.926	3718792.219	100.0000

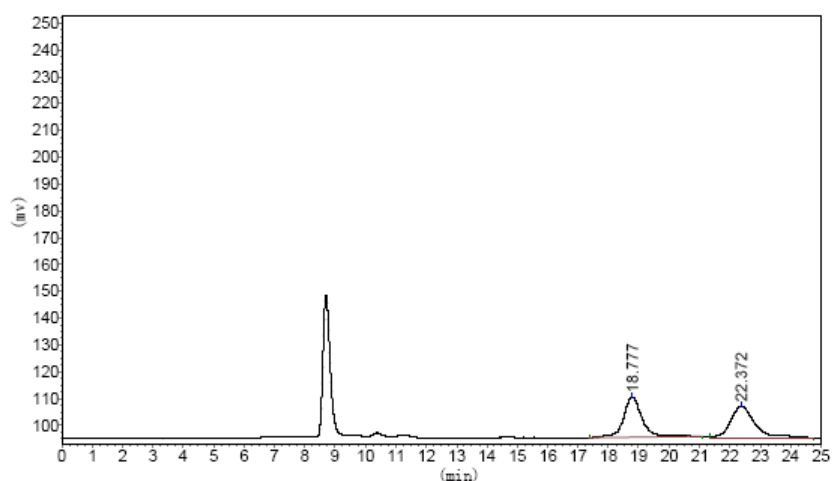


**5ag**

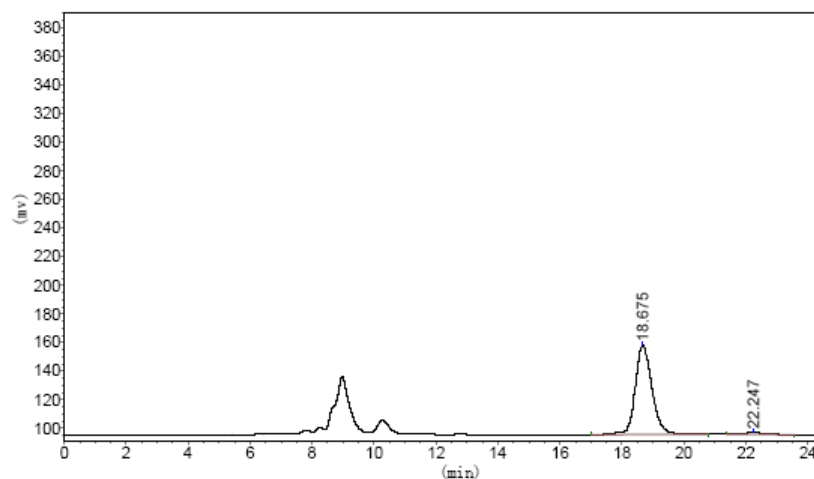




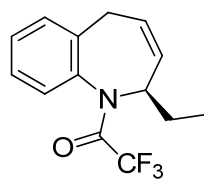




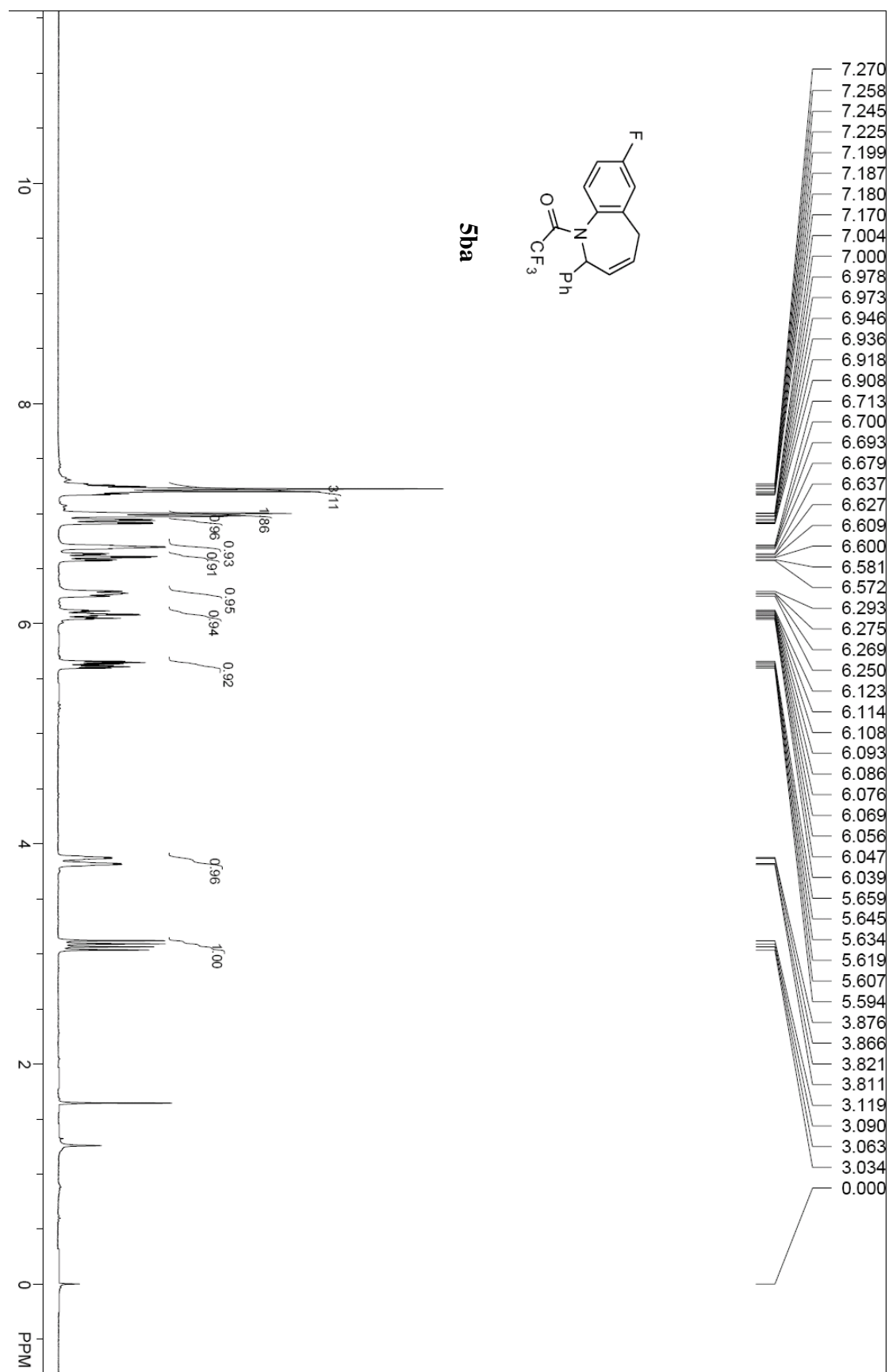
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	18.777	14906.413	637398.188	49.2962
2	22.372	11757.163	655597.938	50.7038
<b>Total</b>		26663.576	1292996.125	100.0000

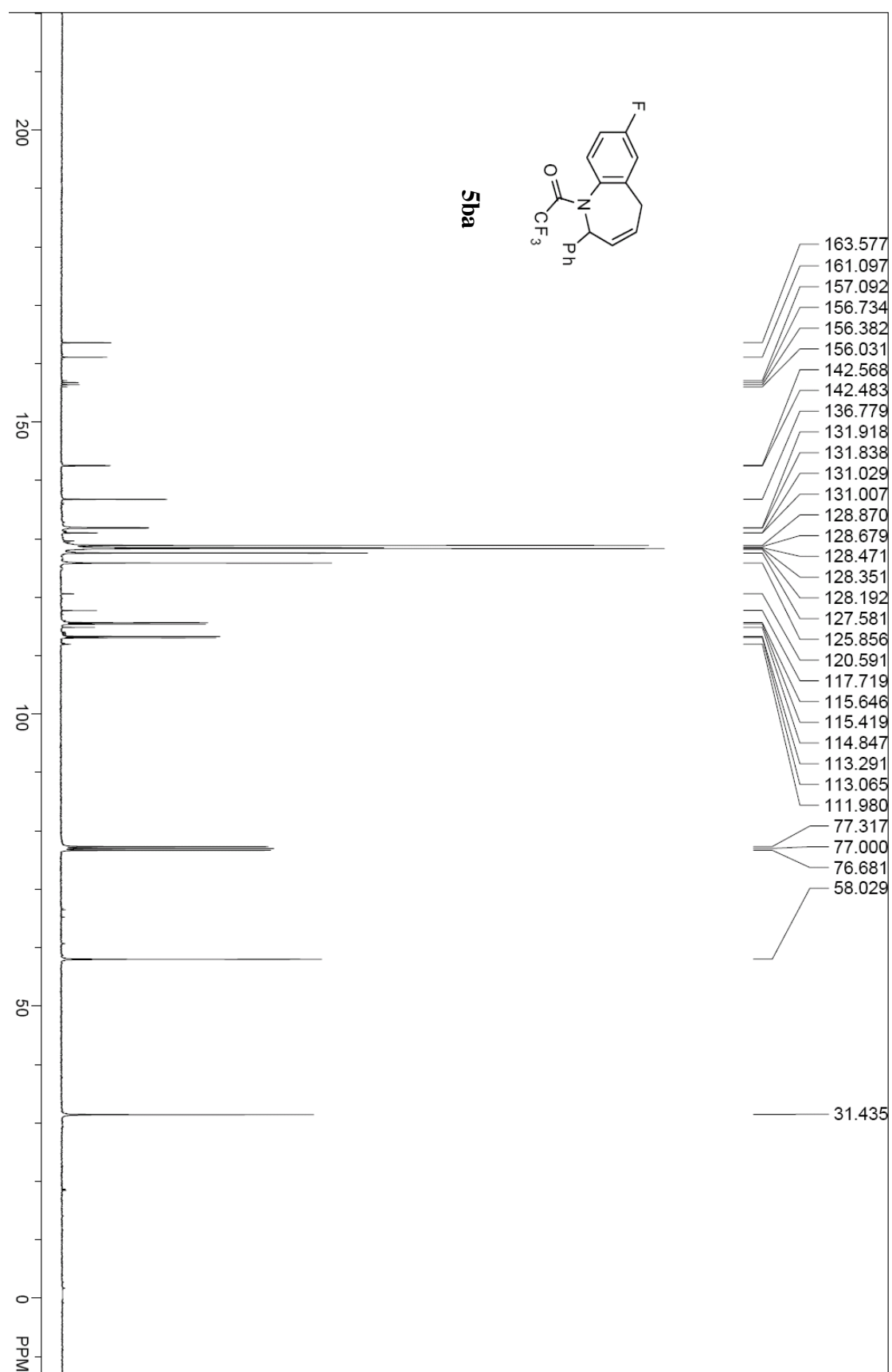


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	18.675	62381.570	2346107.750	97.3678
2	22.247	1275.824	63423.055	2.6322
<b>Total</b>		63657.394	2409530.805	100.0000
		26663.576	1292996.125	100.0000

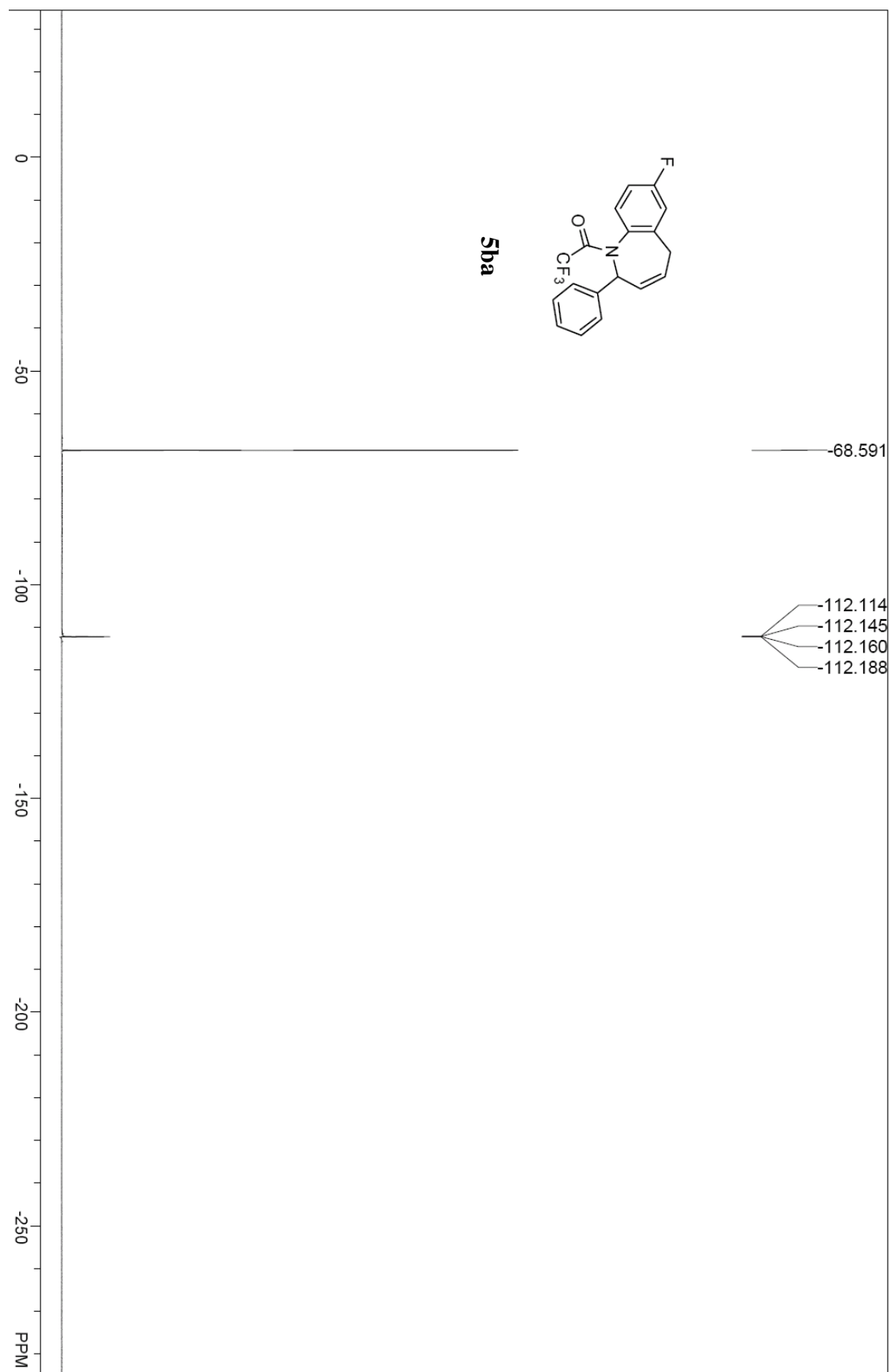


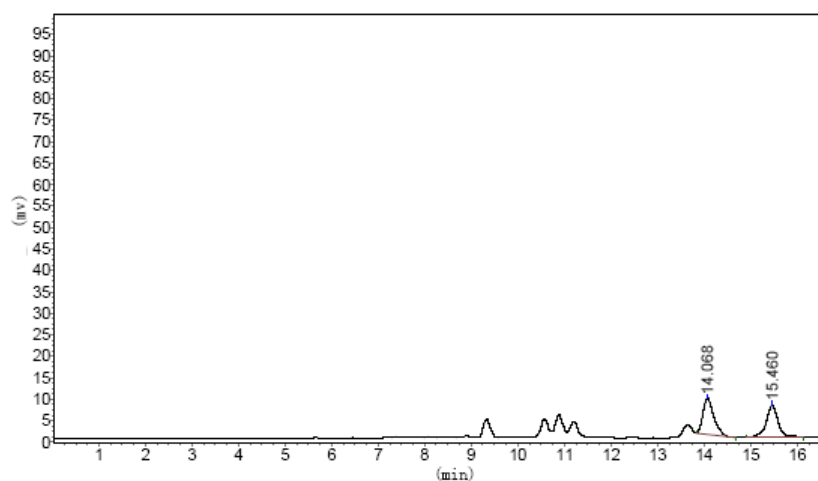
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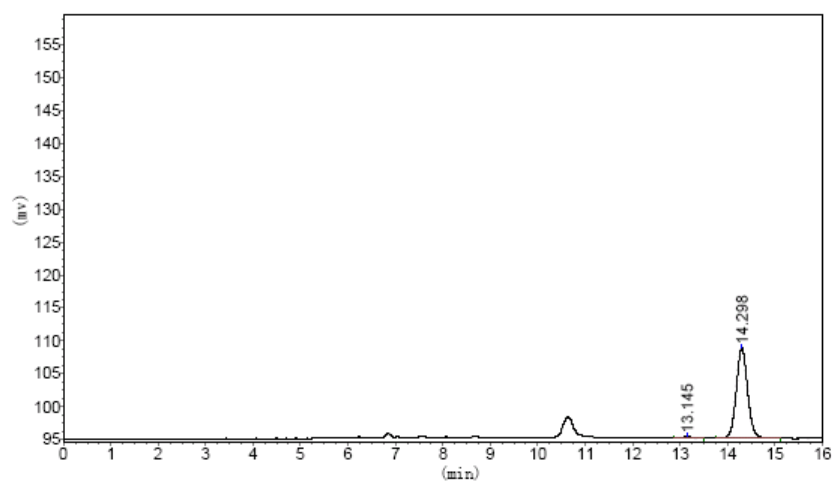




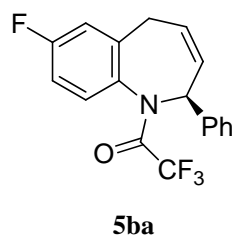


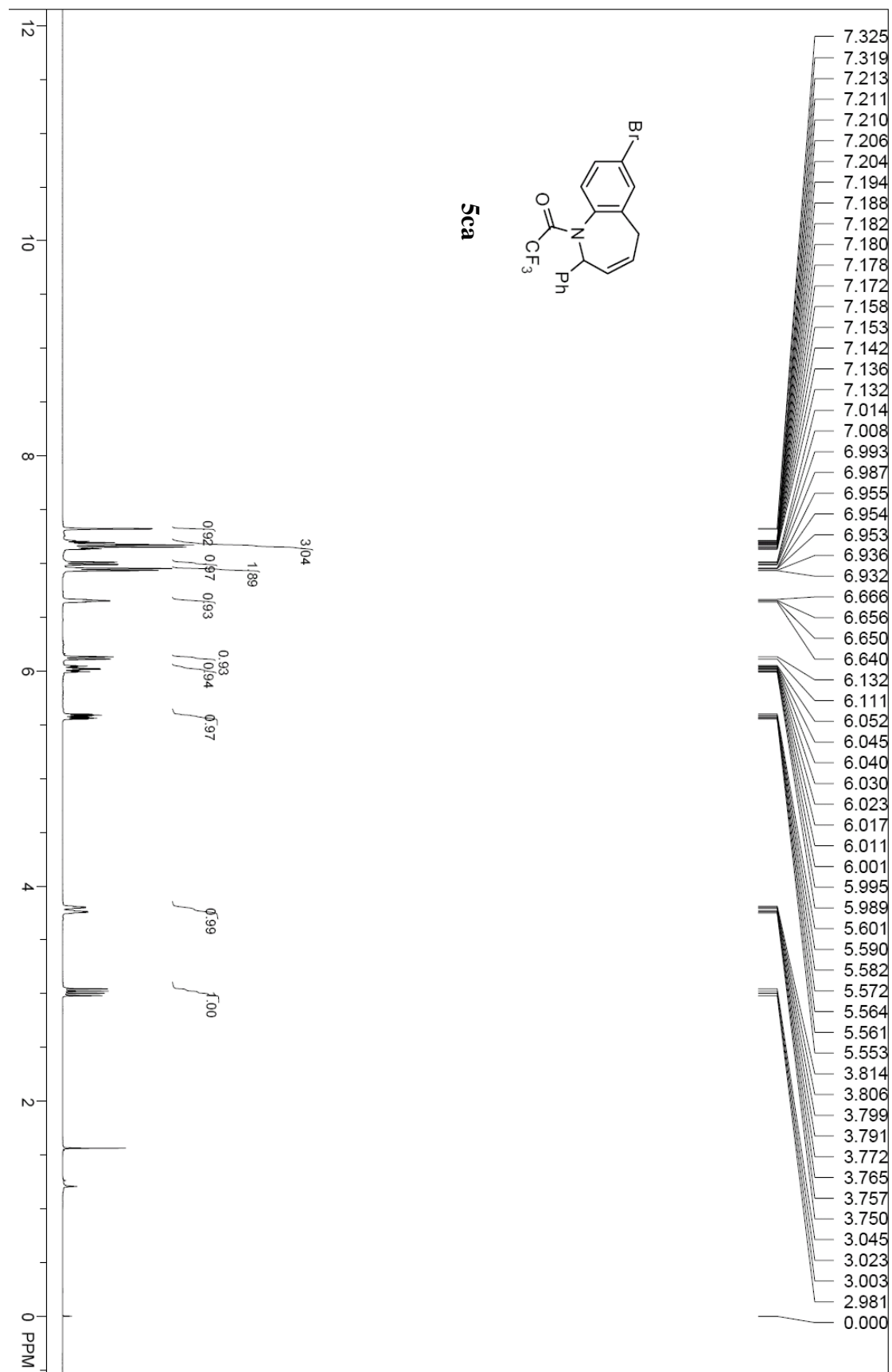


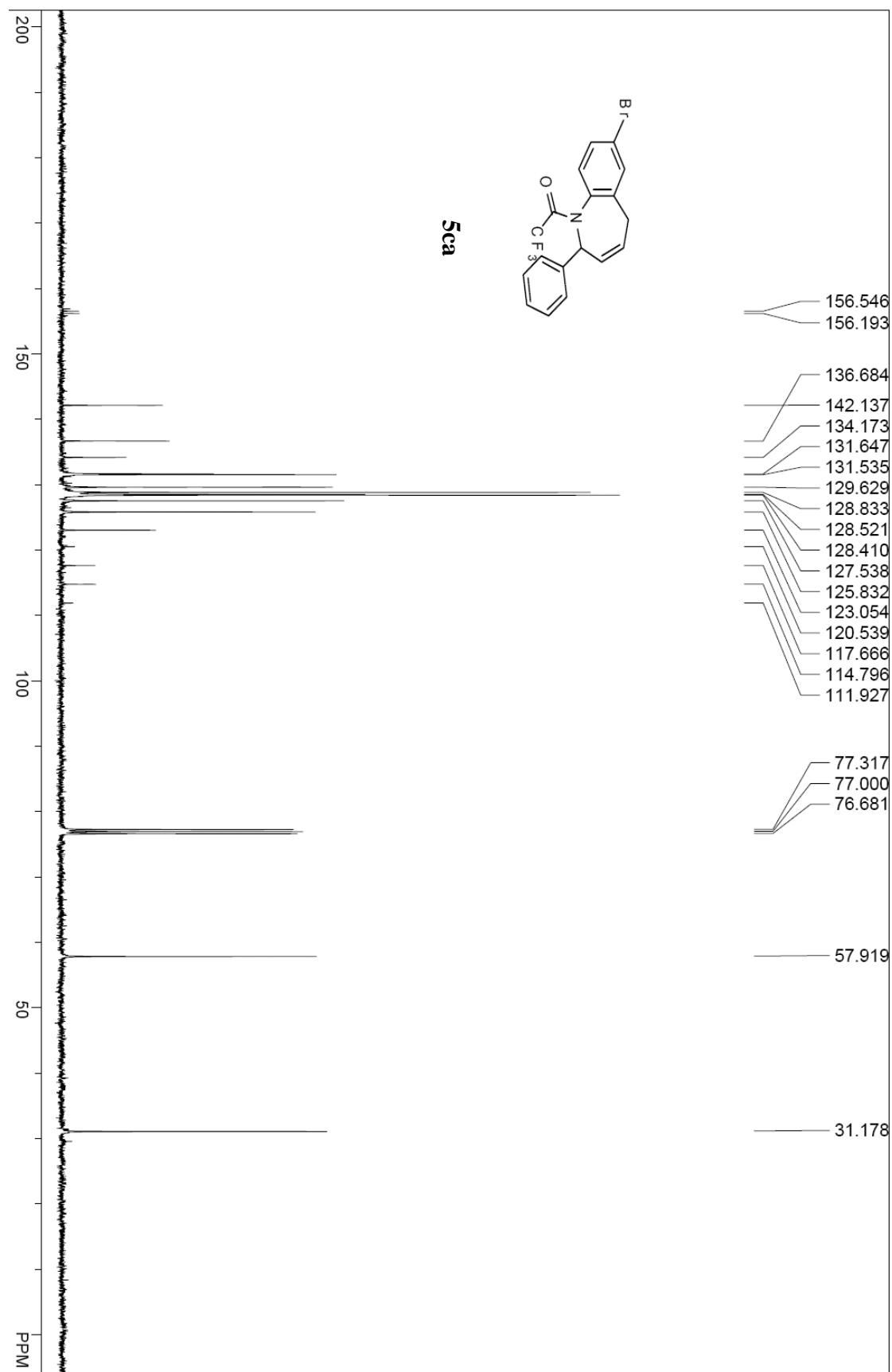
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	14.068	8404.836	135836.344	49.2466
2	15.460	7514.309	139992.797	50.7534
<b>Total</b>		15919.145	275829.141	100.0000

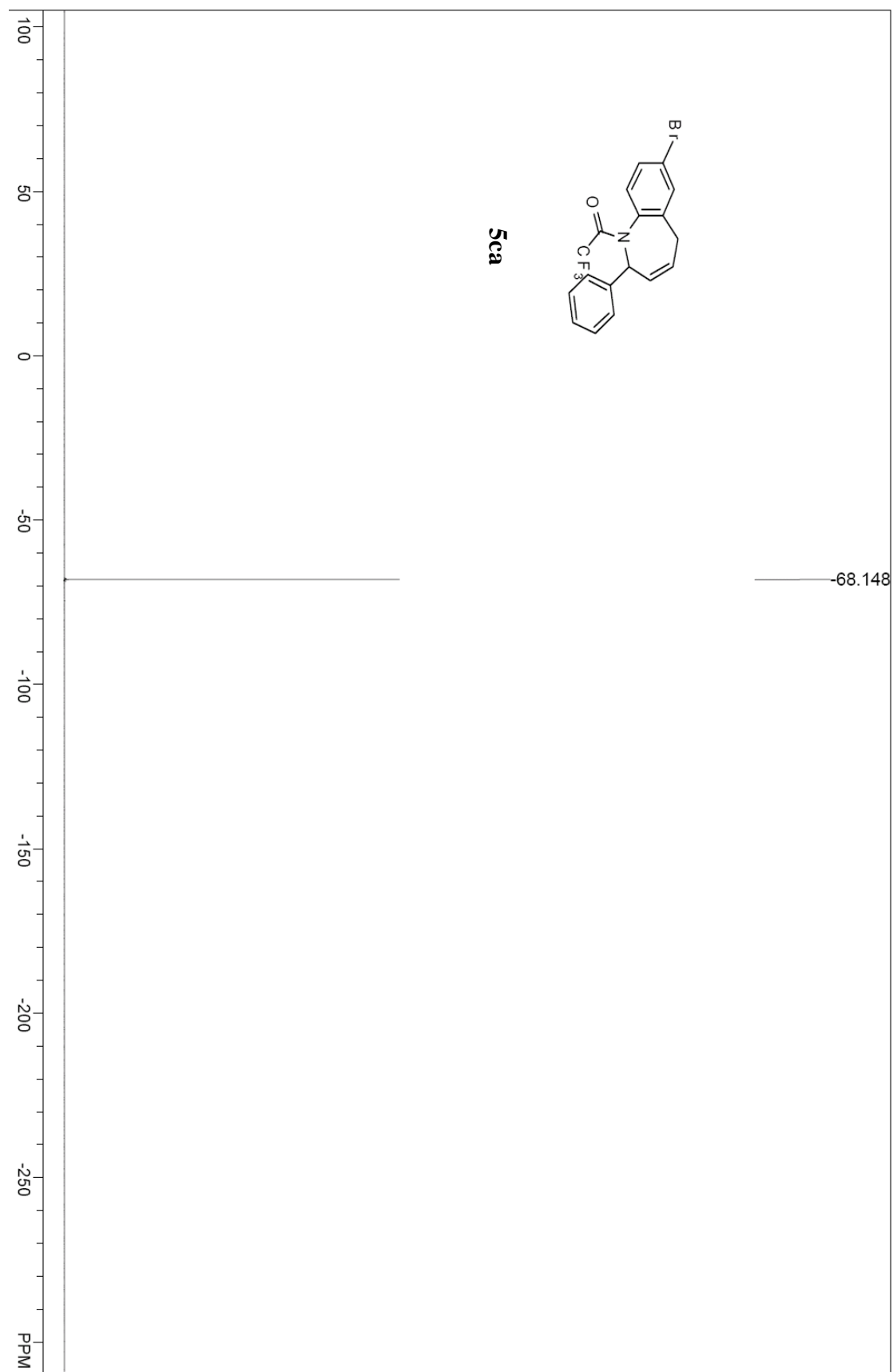


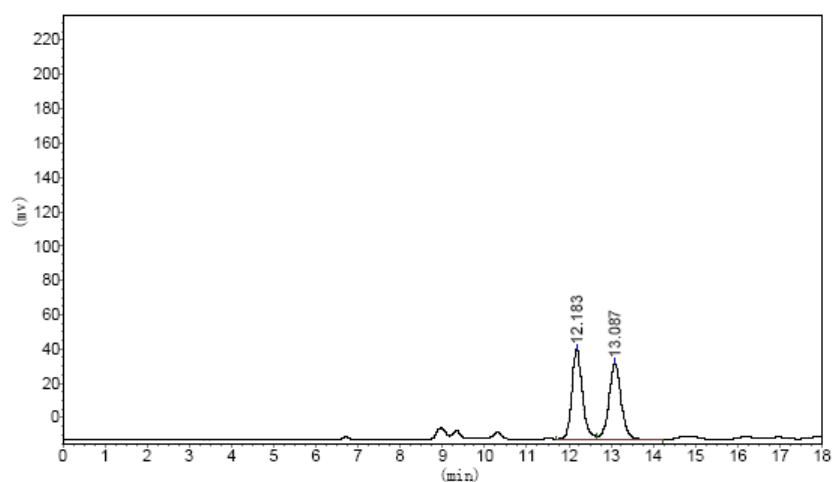
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.145	263.153	3746.624	1.6139
2	14.298	13697.196	228402.406	98.3861
<b>Total</b>		13960.349	232149.030	100.0000



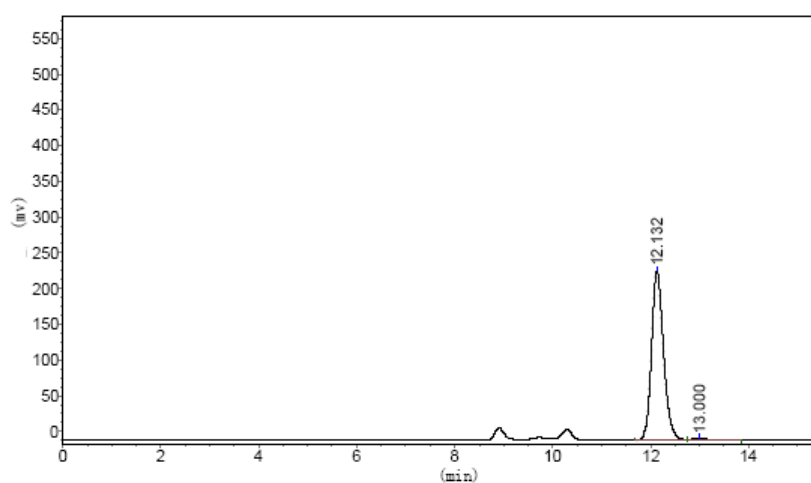




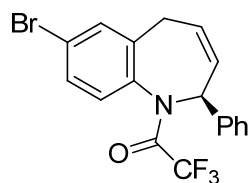




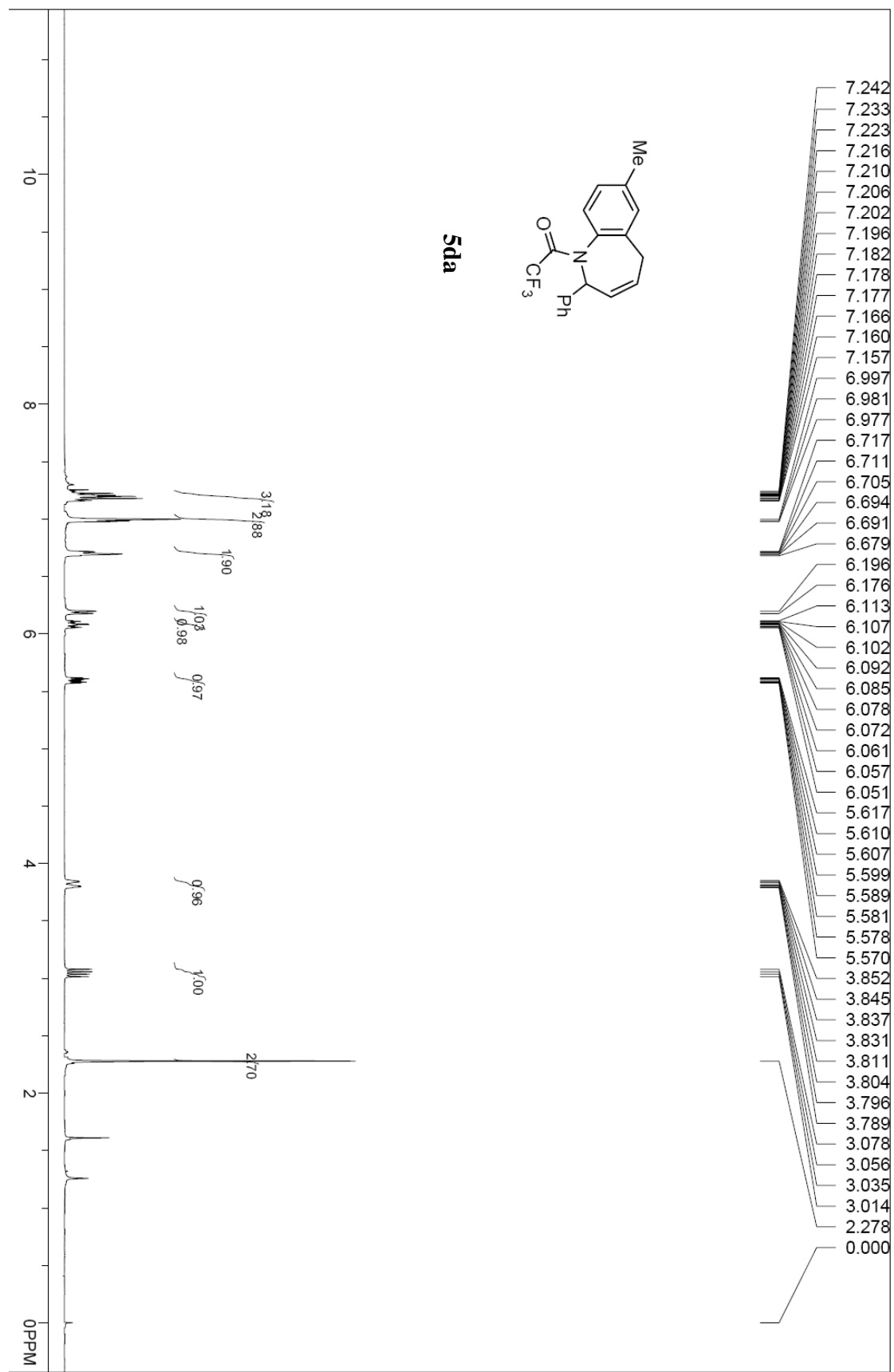
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.183	52729.680	922707.563	50.7469
2	13.087	44555.078	895546.125	49.2531
Total		97284.758	1818253.688	100.0000

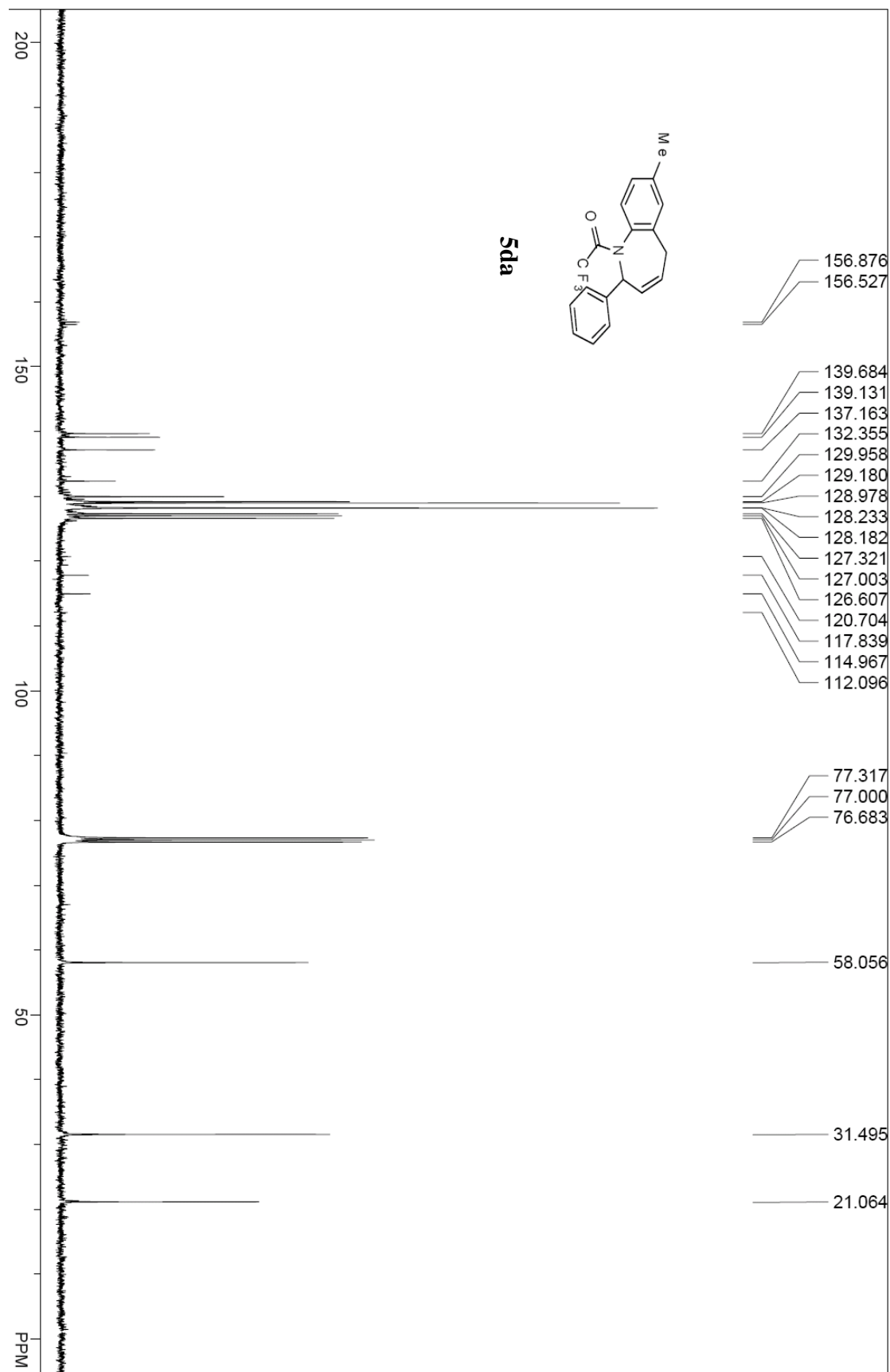


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.132	237533.656	4067913.500	98.3538
2	13.000	3348.846	68087.547	1.6462
Total		240882.502	4136001.047	100.0000

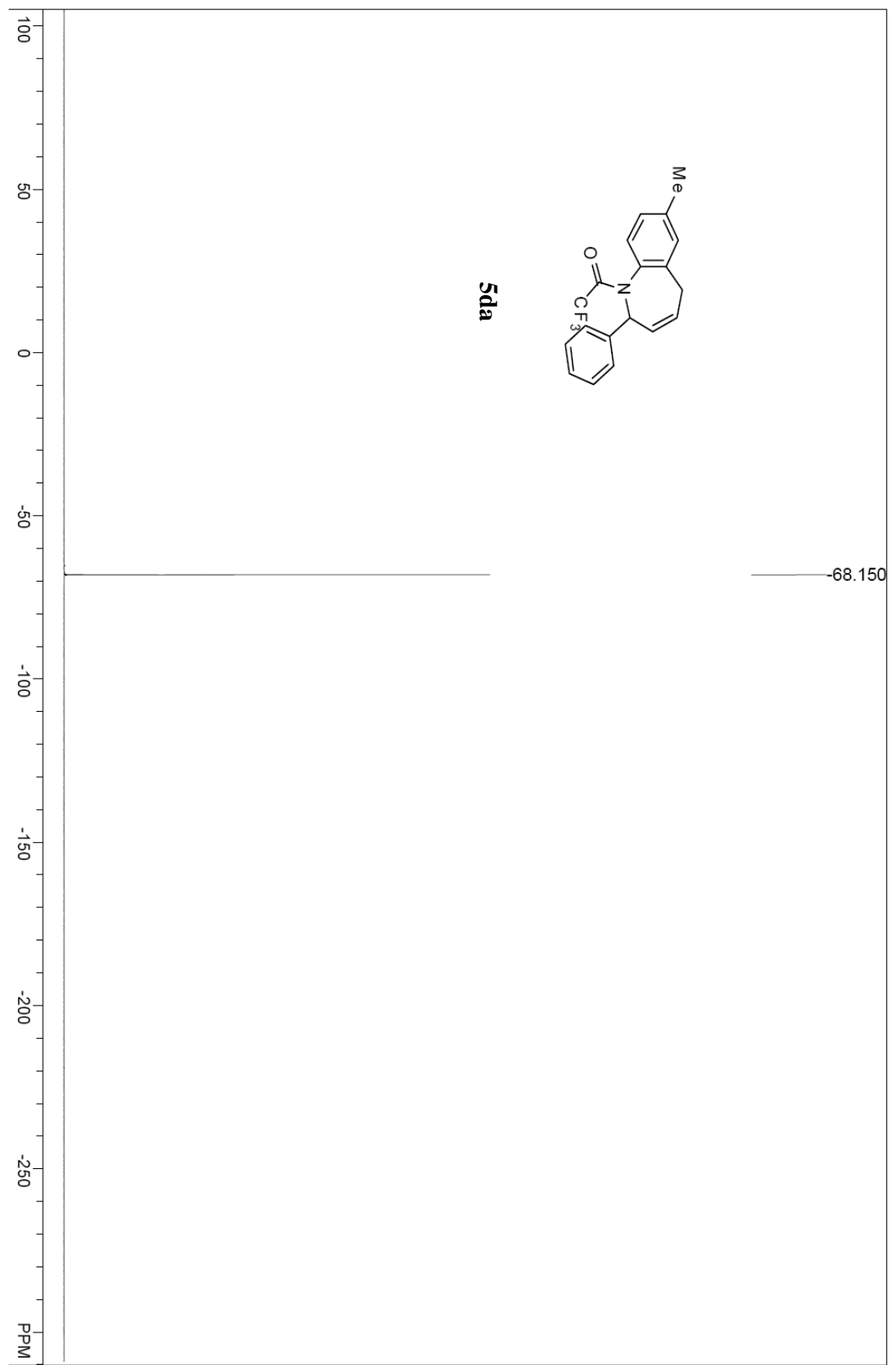


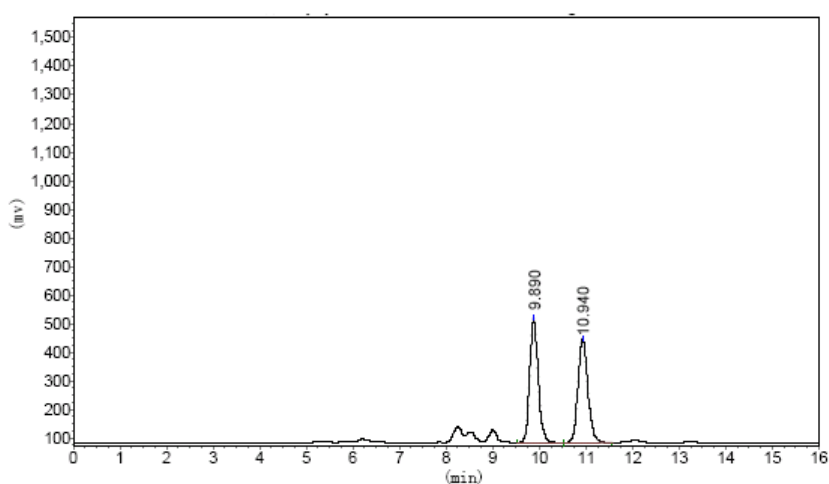
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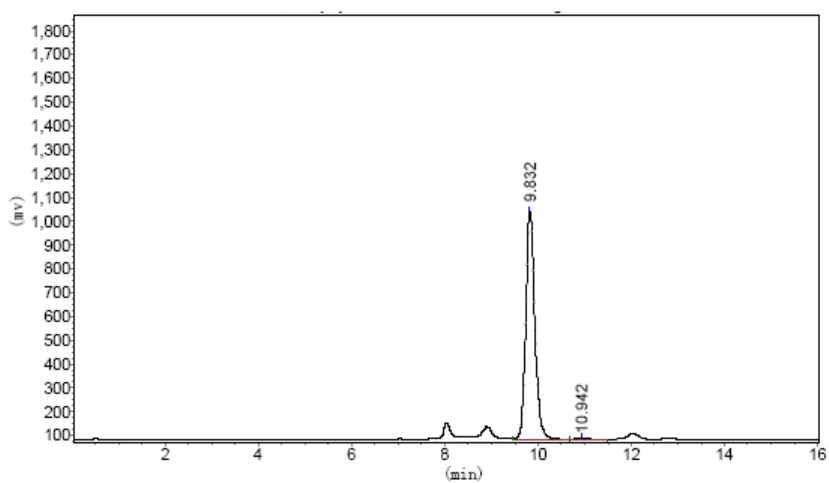




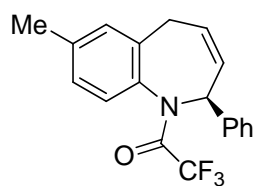




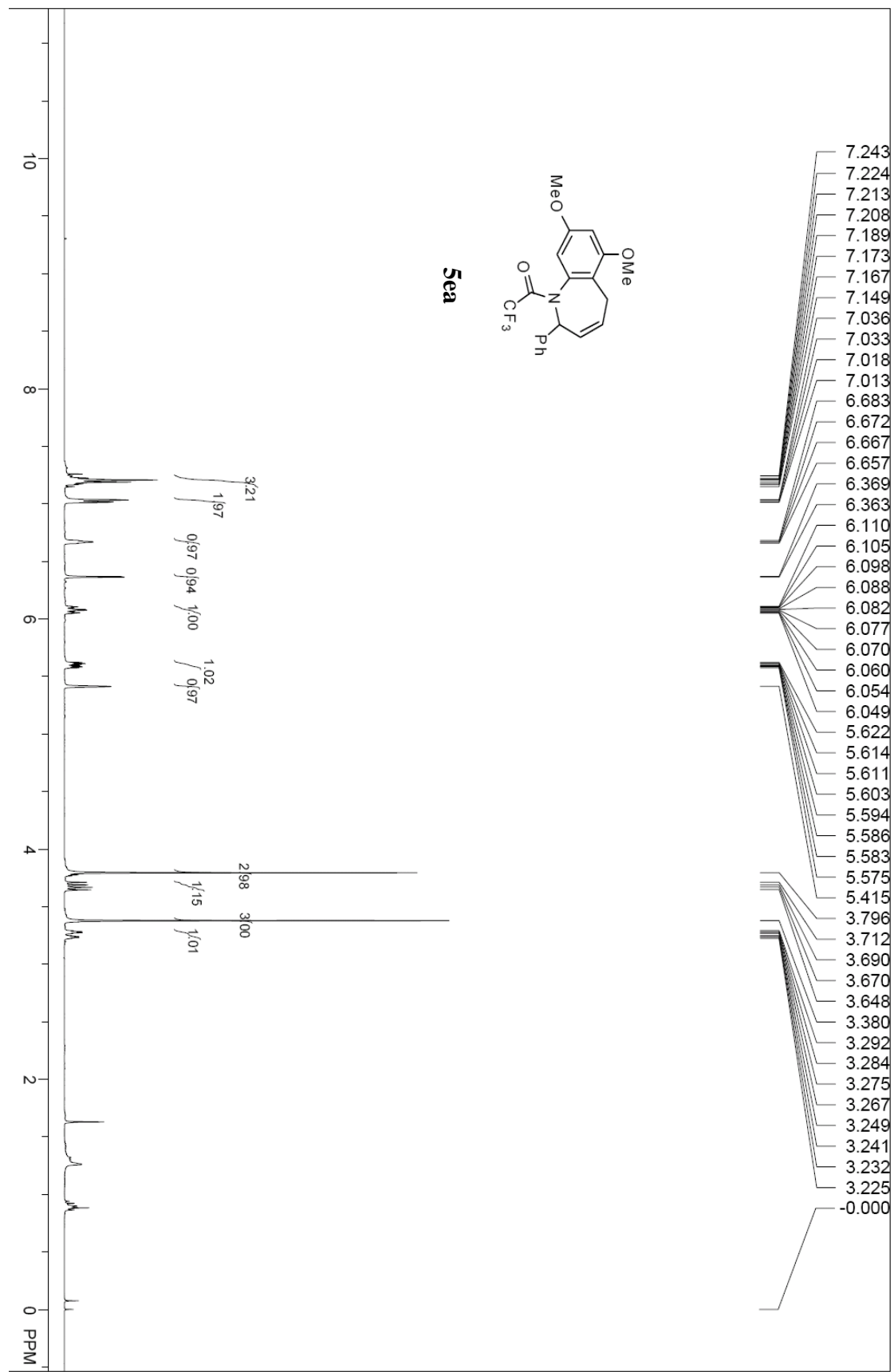
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.890	436080.188	5653919.000	50.6839
2	10.940	363155.188	5501343.000	49.3161
<b>Total</b>		799235.375	11155262.000	100.0000

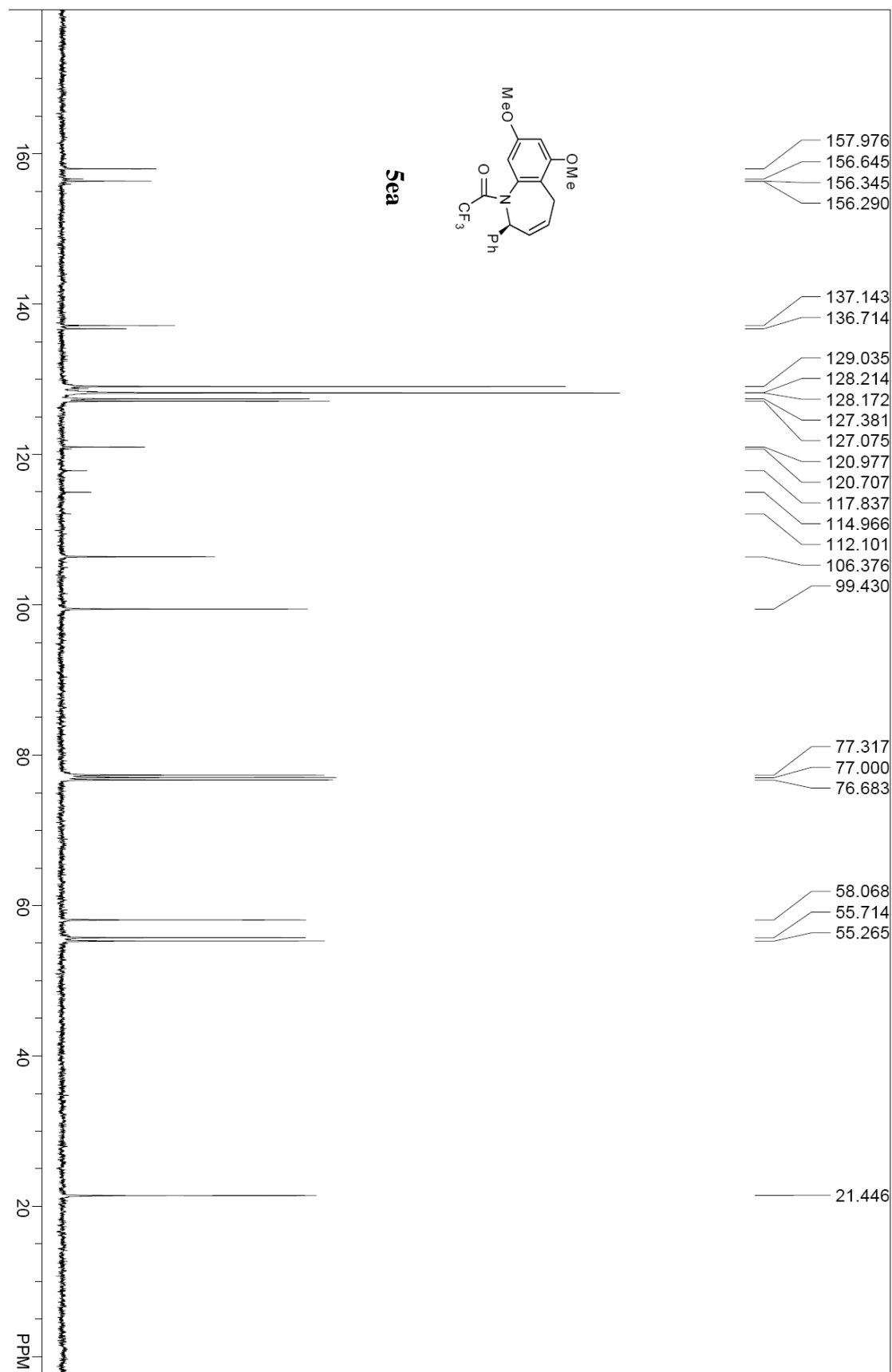


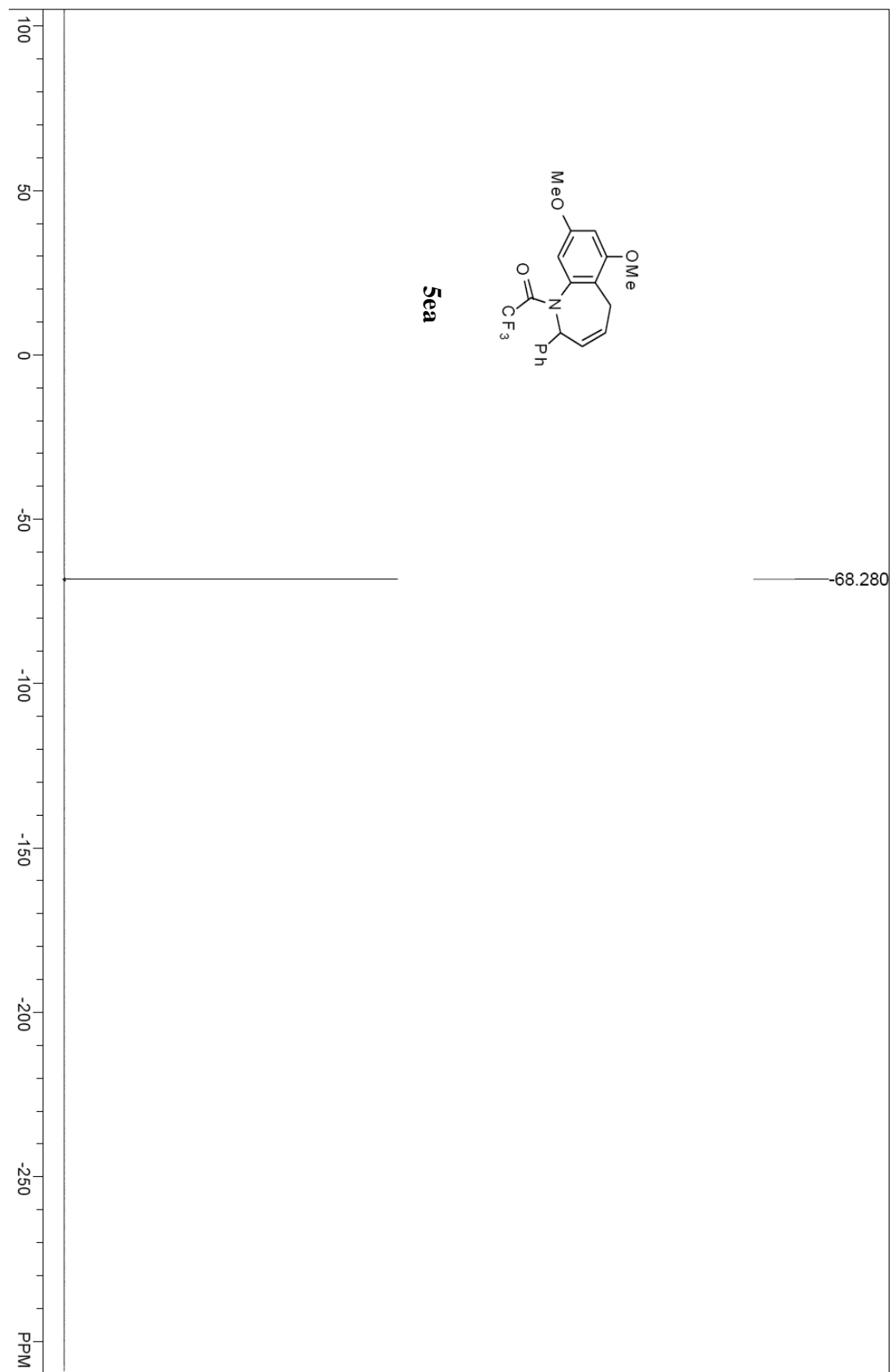
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	9.832	961566.938	13082614.000	98.7814
2	10.942	8498.422	161395.188	1.2186
<b>Total</b>		970065.359	13244009.188	100.0000

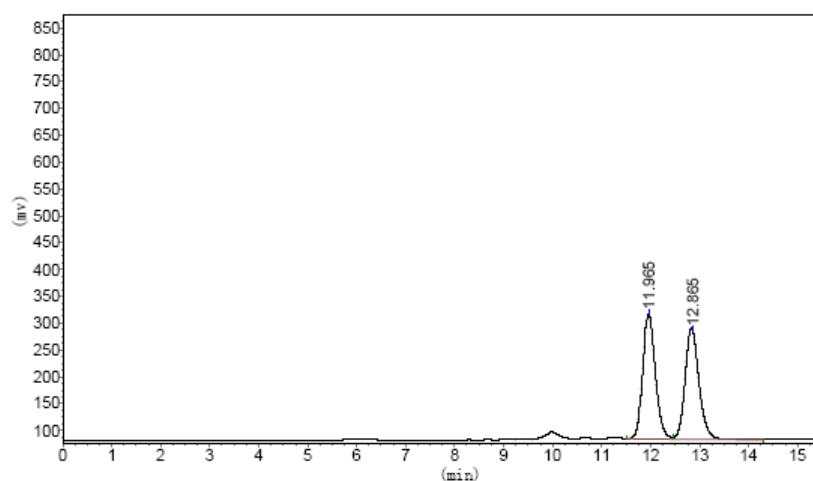


**5da**

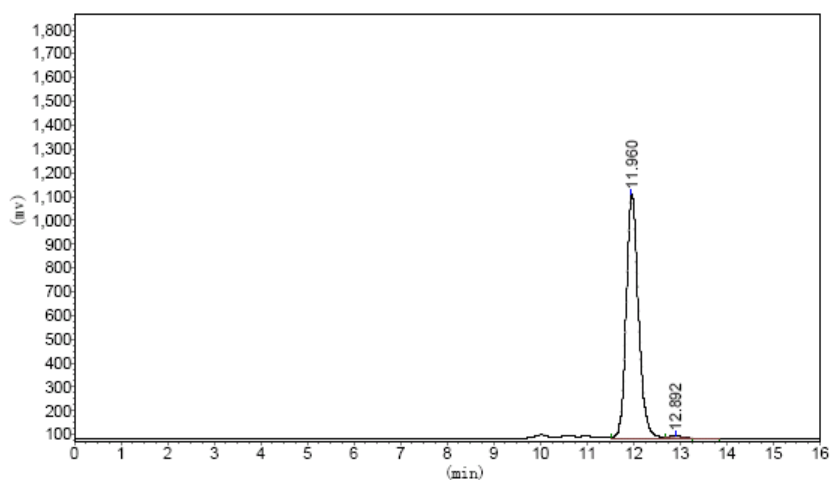




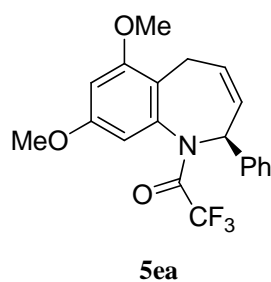


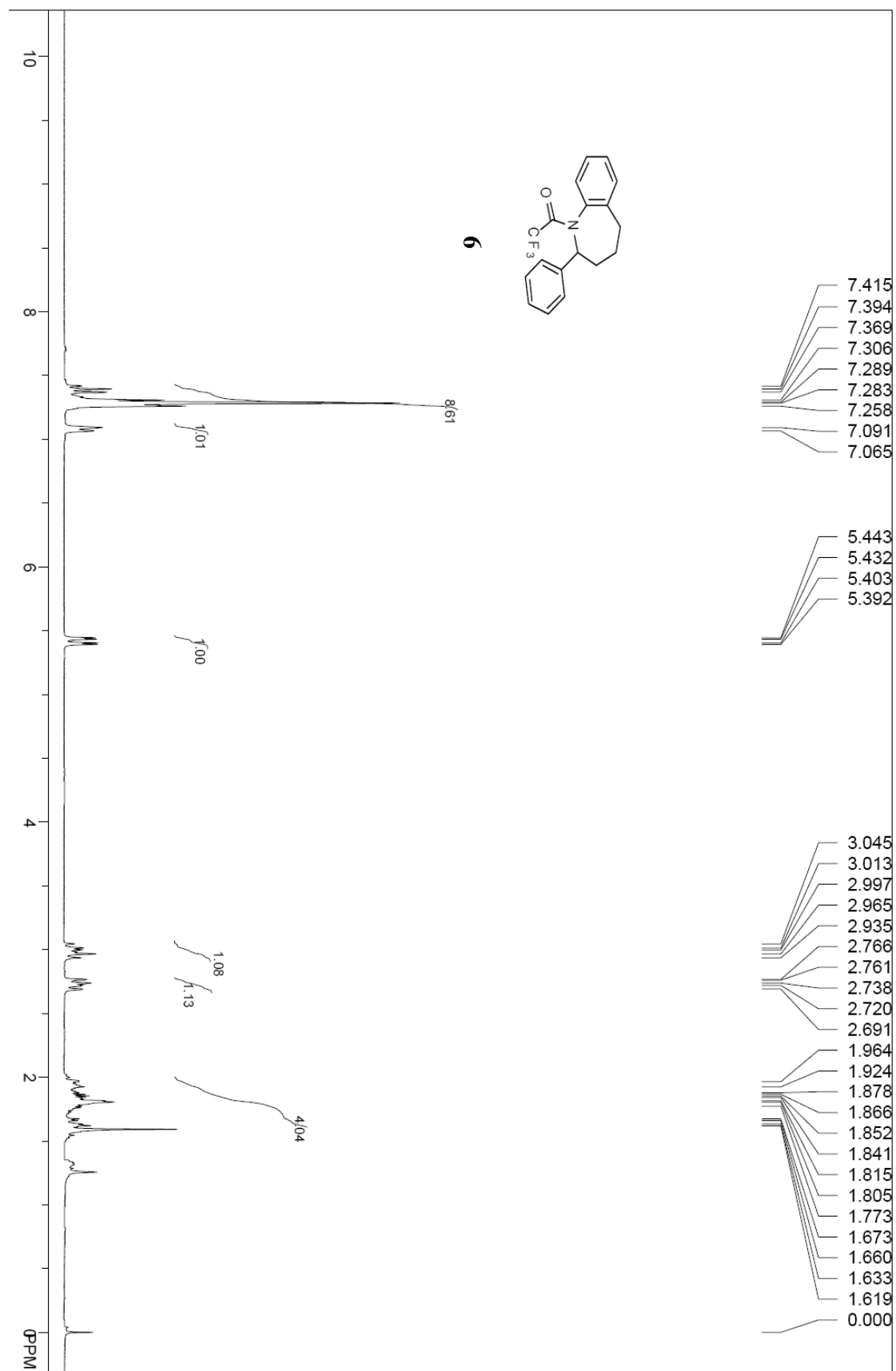


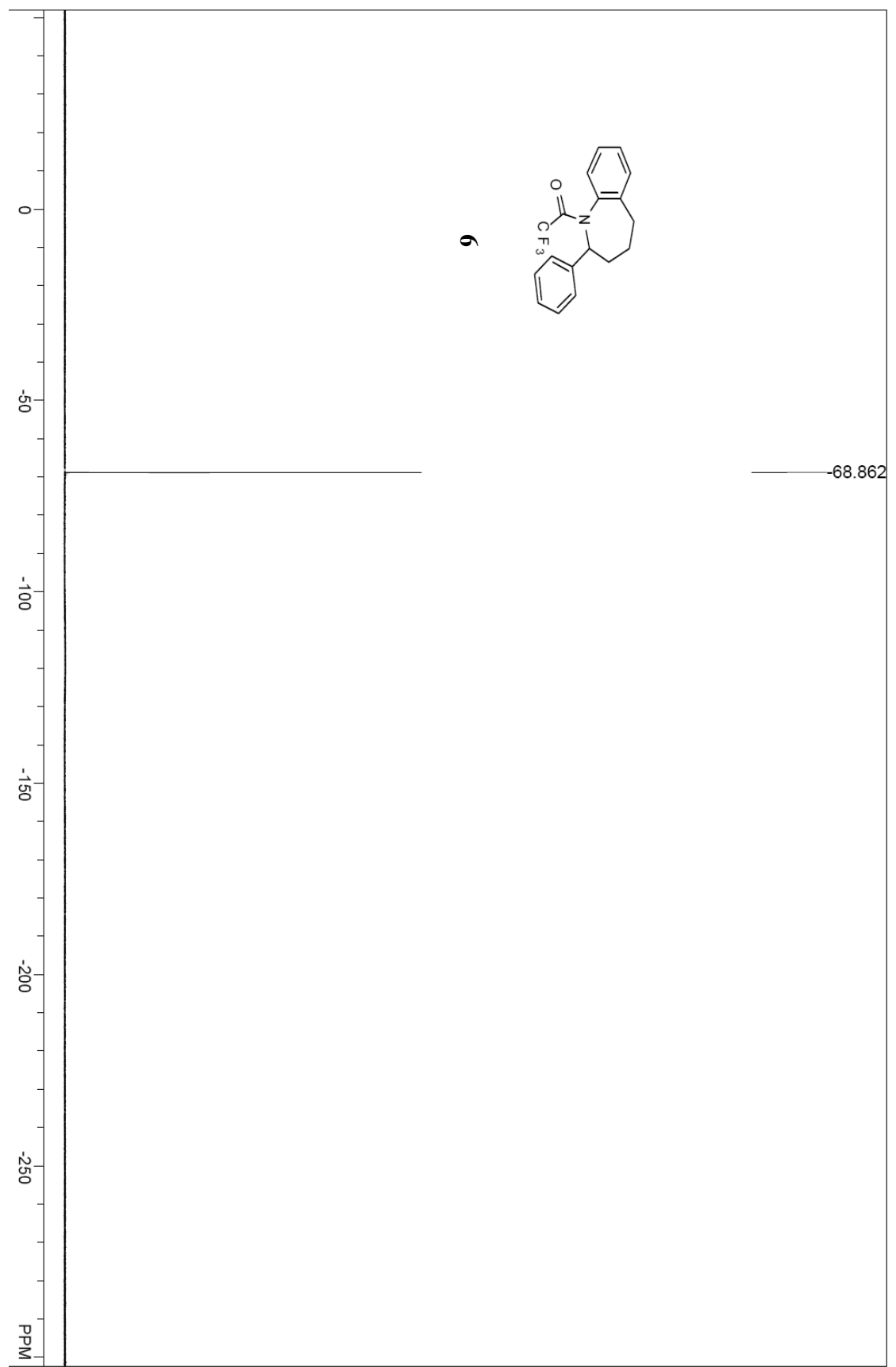
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.965	233040.766	4263858.000	50.6365
2	12.865	207159.047	4156664.750	49.3635
<b>Total</b>		440199.813	8420522.750	100.0000



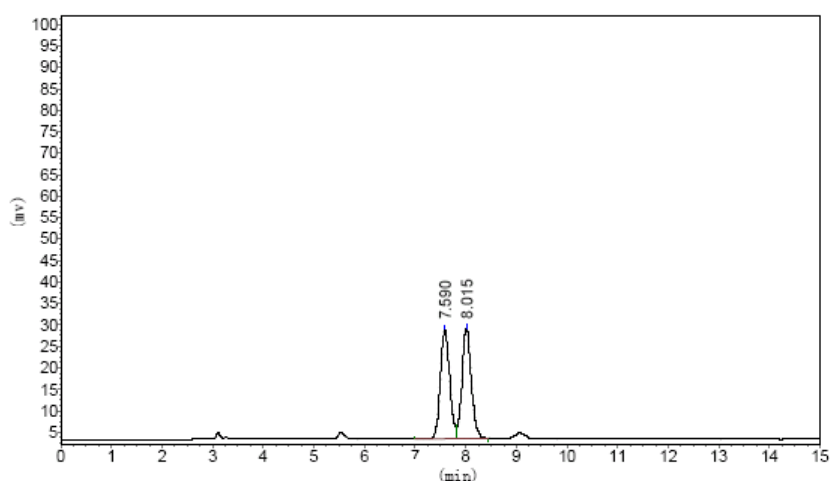
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.960	1028453.063	19056458.000	99.3293
2	12.892	7947.363	128667.750	0.6707
<b>Total</b>		1036400.426	19185125.750	100.0000



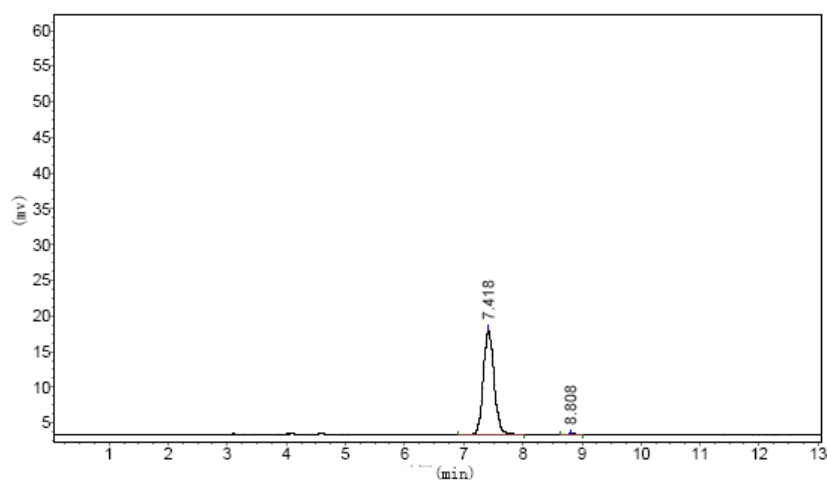




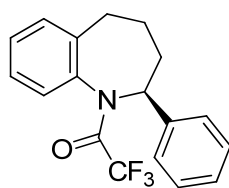




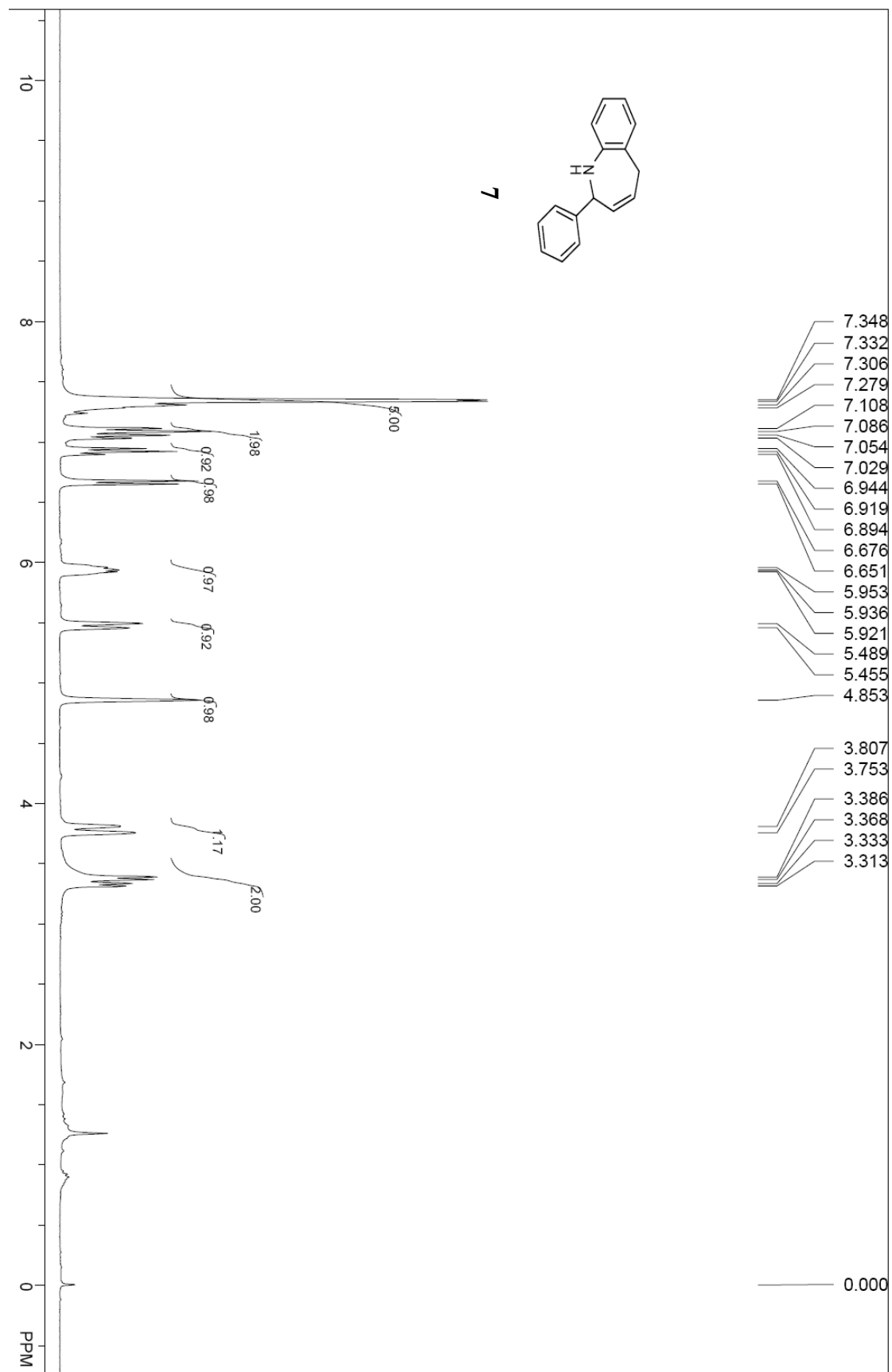
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.590	25437.852	327374.219	50.0403
2	8.015	25617.674	326846.844	49.9597
<b>Total</b>		51055.525	654221.063	100.0000

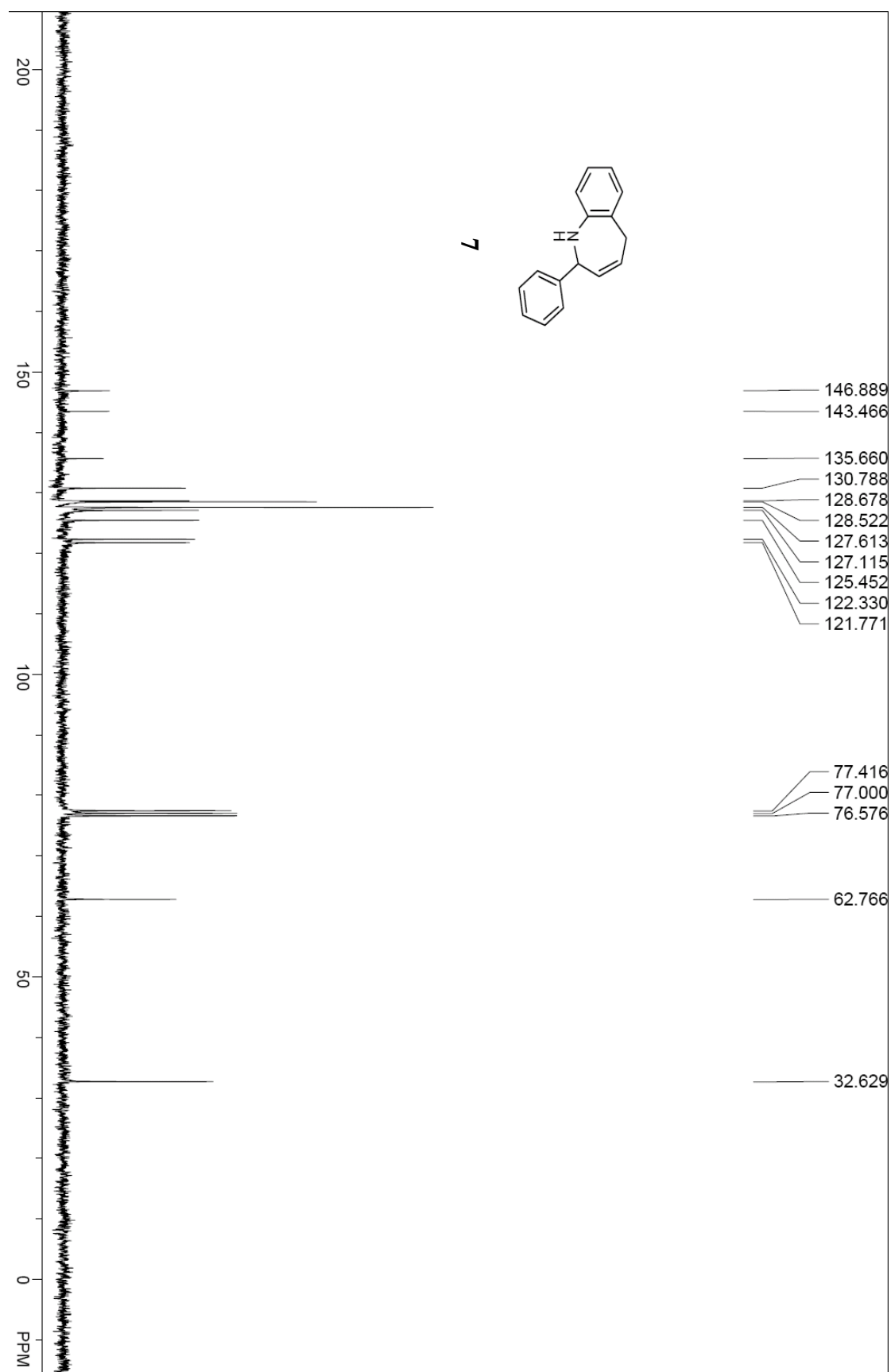


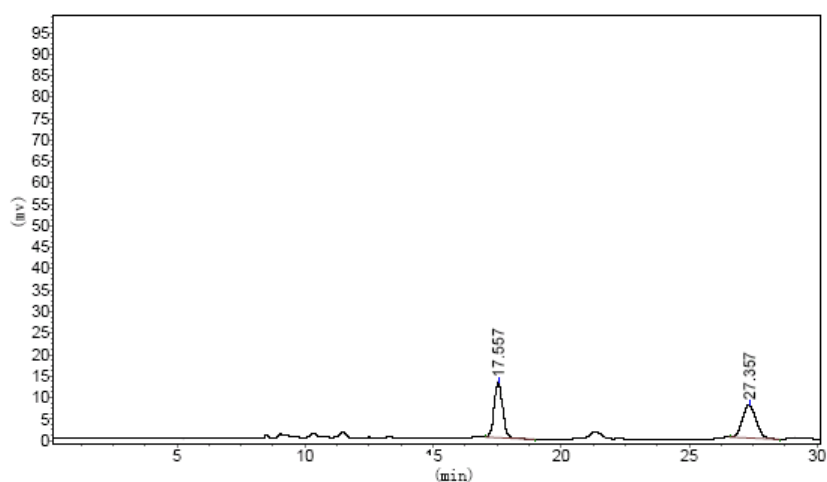
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	7.418	14692.846	186368.797	99.3313
2	8.808	101.029	1254.557	0.6687
<b>Total</b>		14793.875	187623.354	100.0000



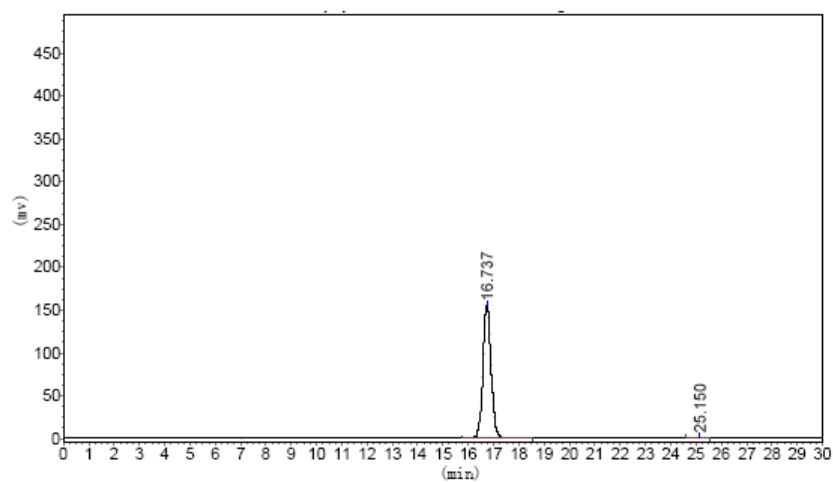
6



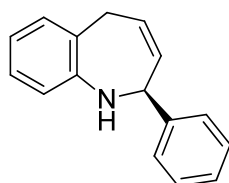




Peak No.	R. Time	Peak Height	Peak Area	Percent
1	17.557	13213.888	314068.531	50.3326
2	27.357	7945.072	309918.094	49.6674
<b>Total</b>		21158.960	623986.625	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.737	155285.125	3490408.000	99.4191
2	25.150	719.275	20394.299	0.5809
<b>Total</b>		156004.400	3510802.299	100.0000



7

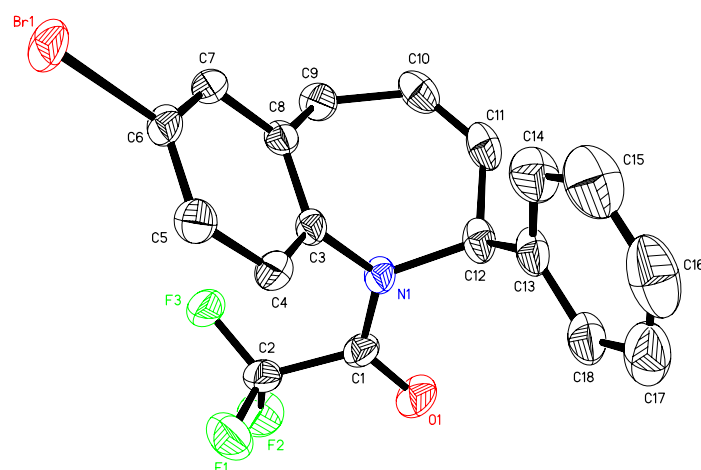


Table 1. Crystal data and structure refinement for (*S*)-**5ca**

Identification code	[CCDC 859342]
Empirical formula	C <sub>18</sub> H <sub>13</sub> Br F <sub>3</sub> N O
Formula weight	396.20
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 8.2256(14) Å    alpha = 90 deg. b = 11.0205(18) Å    beta = 90 deg. c = 18.212(3) Å    gamma = 90 deg.
Volume	1650.9(5) Å <sup>3</sup>
Z, Calculated density	4, 1.594 Mg/m <sup>3</sup>
Absorption coefficient	2.525 mm <sup>-1</sup>
F(000)	792
Crystal size	0.369 x 0.311 x 0.257 mm
Theta range for data collection	2.16 to 25.99 deg.
Limiting indices	-10 ≤ h ≤ 9, -13 ≤ k ≤ 11, -21 ≤ l ≤ 22
Reflections collected / unique	8973 / 3202 [R(int) = 0.0275]
Completeness to theta = 25.99	99.7 %
Absorption correction	Empirical
Max. and min. transmission	1.00000 and 0.57501
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	3202 / 5 / 218
Goodness-of-fit on F <sup>2</sup>	1.038
Final R indices [I > 2sigma(I)]	R1 = 0.0302, wR2 = 0.0719
R indices (all data)	R1 = 0.0382, wR2 = 0.0751
Absolute structure parameter	0.022(8)
Extinction coefficient	0.0035(7)
Largest diff. peak and hole	0.389 and -0.259 e.Å <sup>-3</sup>