

Supporting Information

**Asymmetric amination of α , α -dialkyl substituted aldehydes catalyzed by a
simple chiral primary amino acid and its application to the preparation of a S1P₁
agonist**

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Beijing Key Laboratory of Active Substance Discovery and Druggability Evaluation,
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China

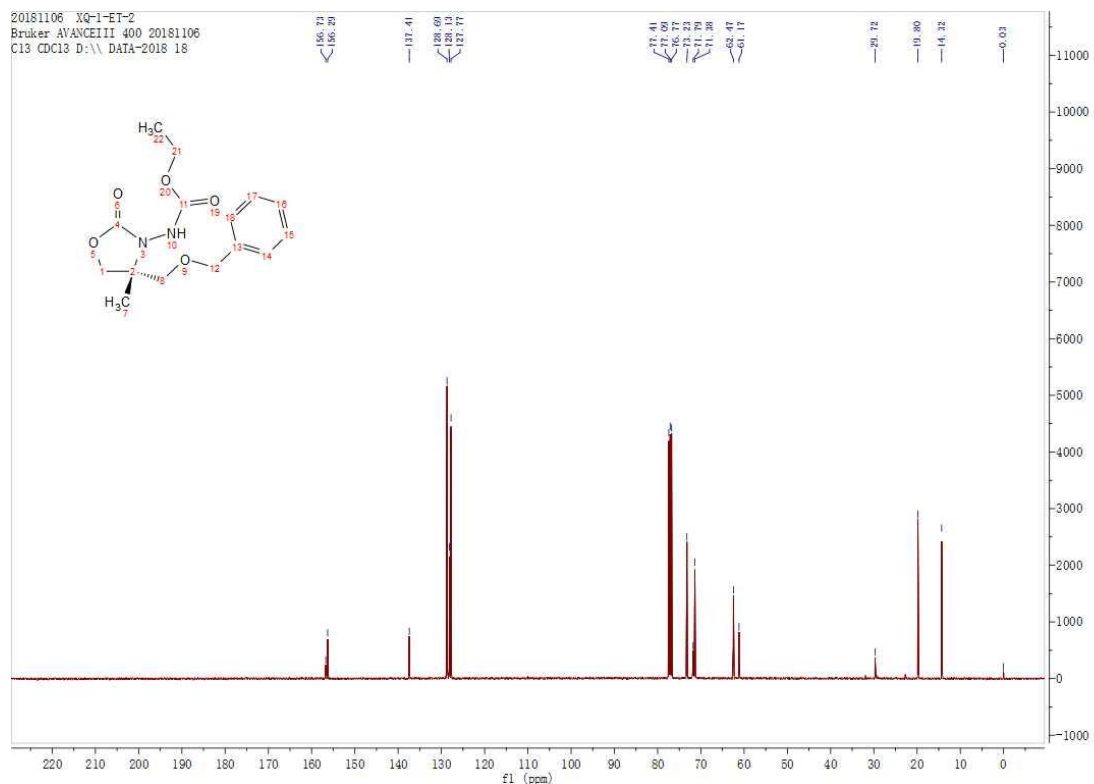
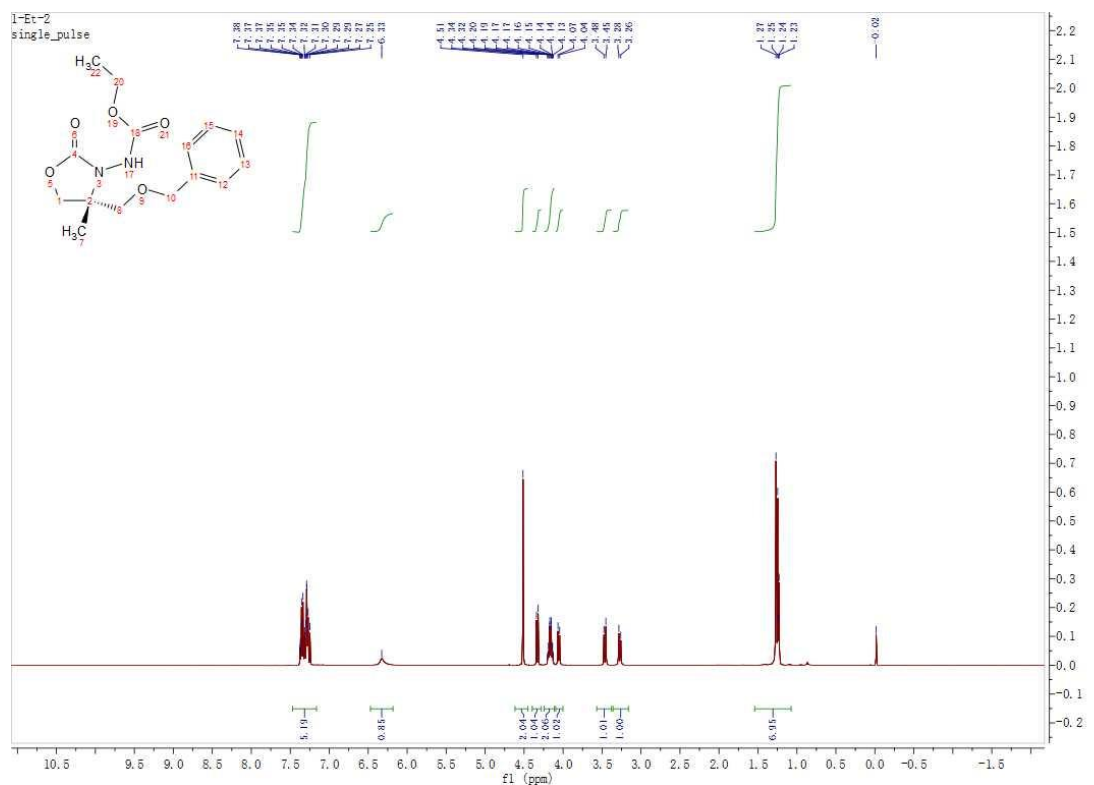
^b Beijing Union Pharmaceutical Factory, PR China

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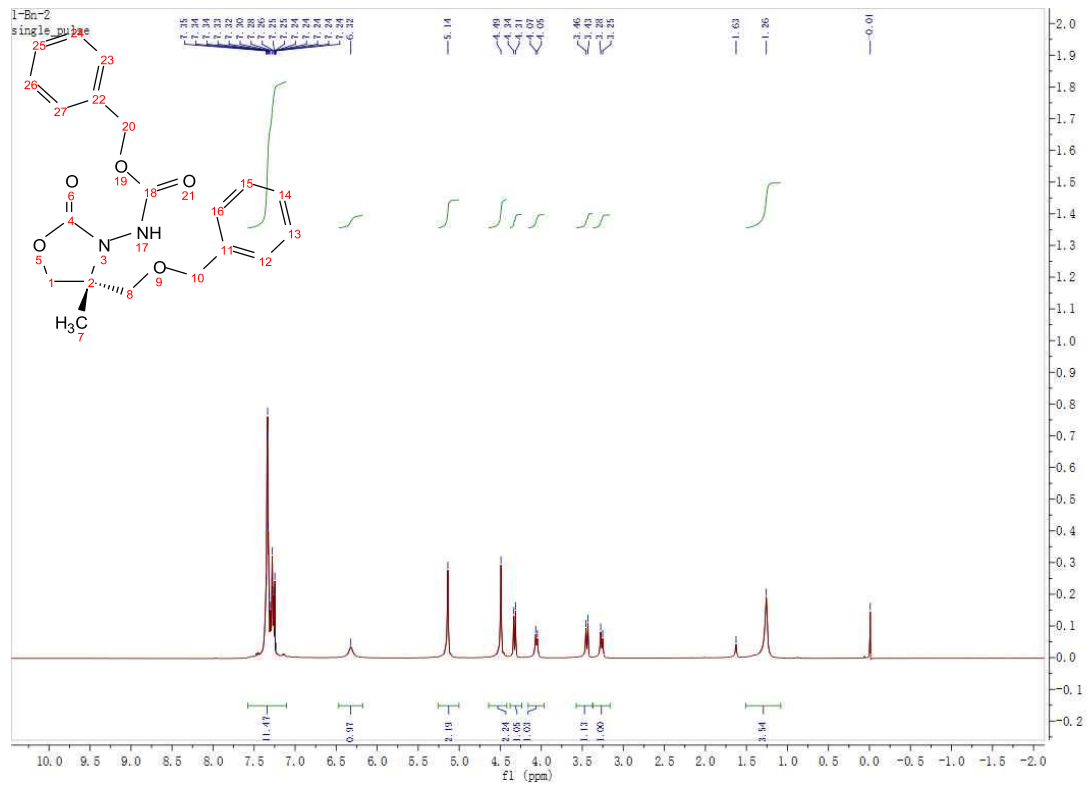
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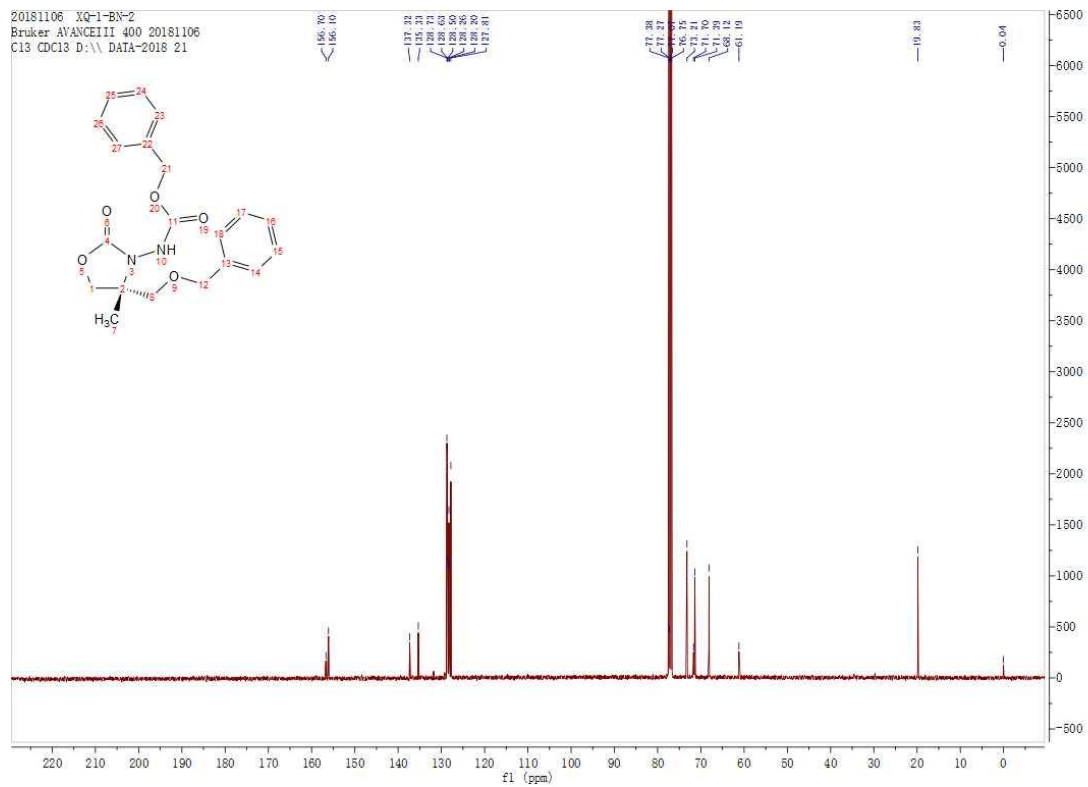
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Selected NMR spectra

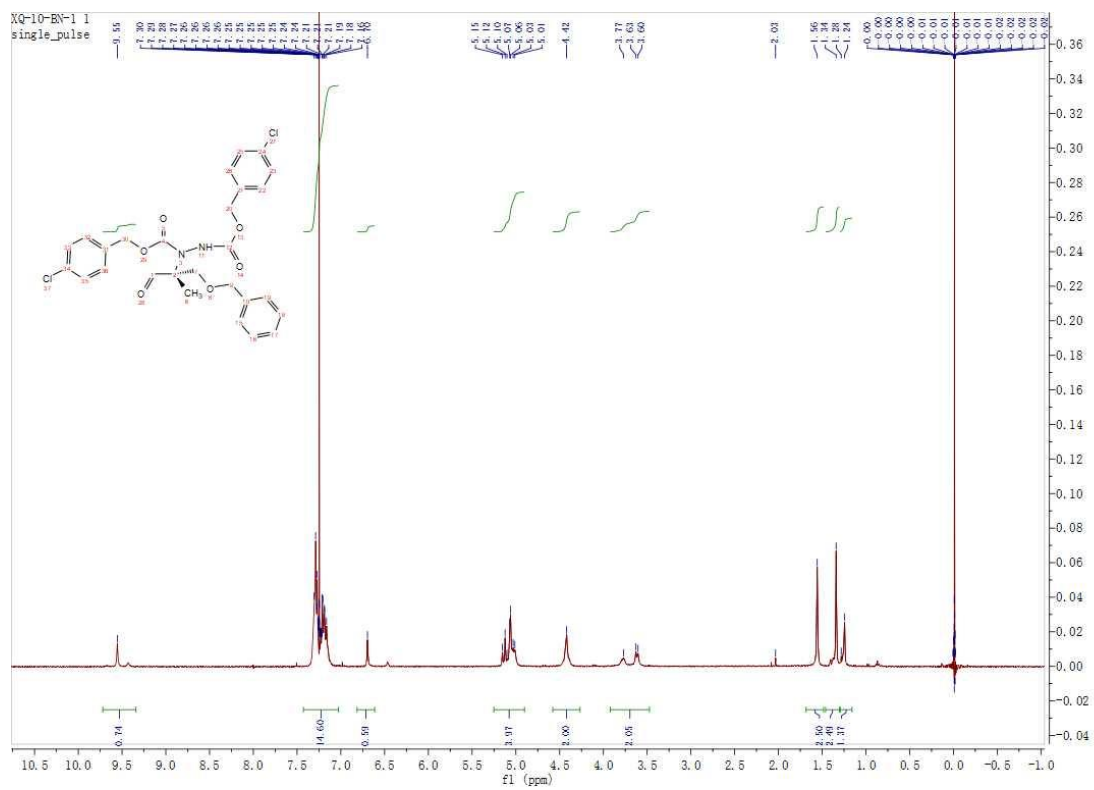


5a-Et

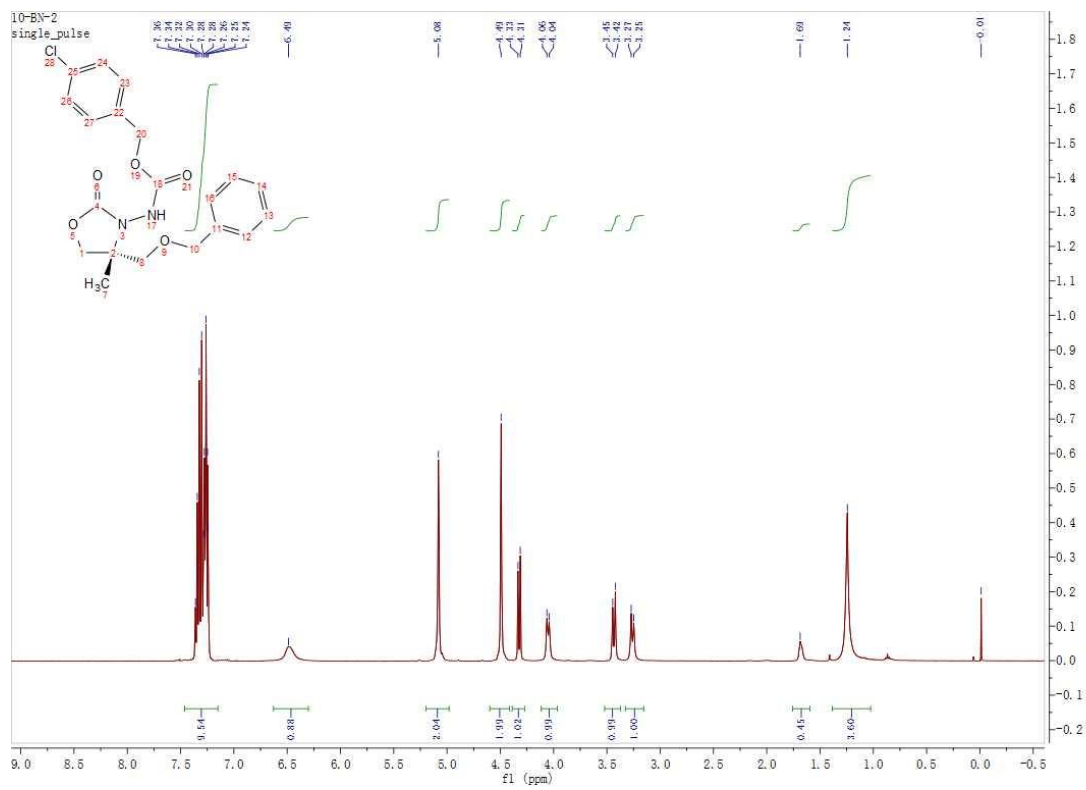


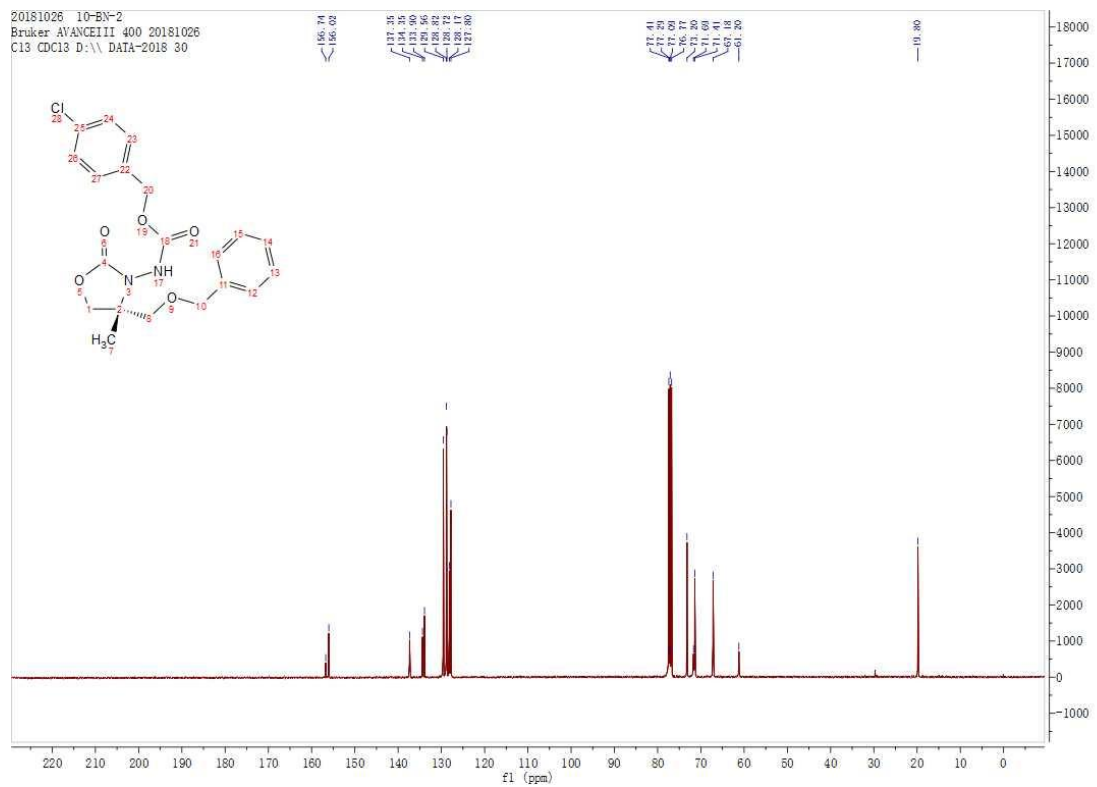


5a-Bn

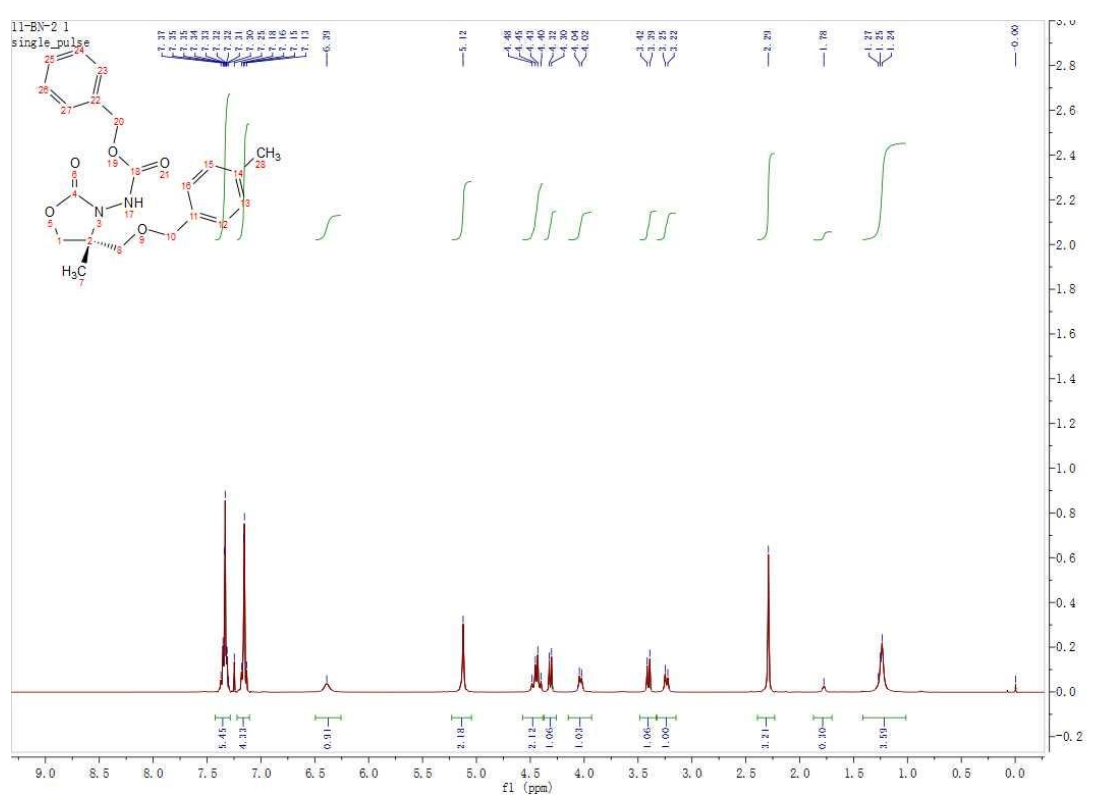


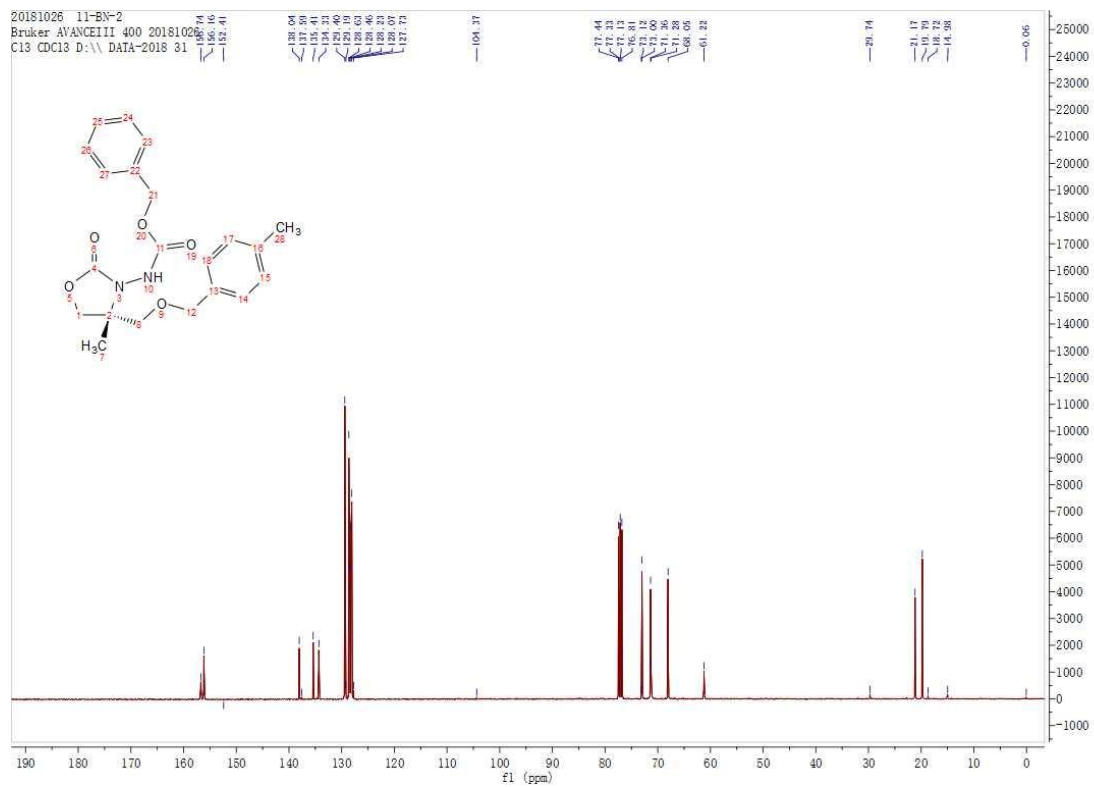
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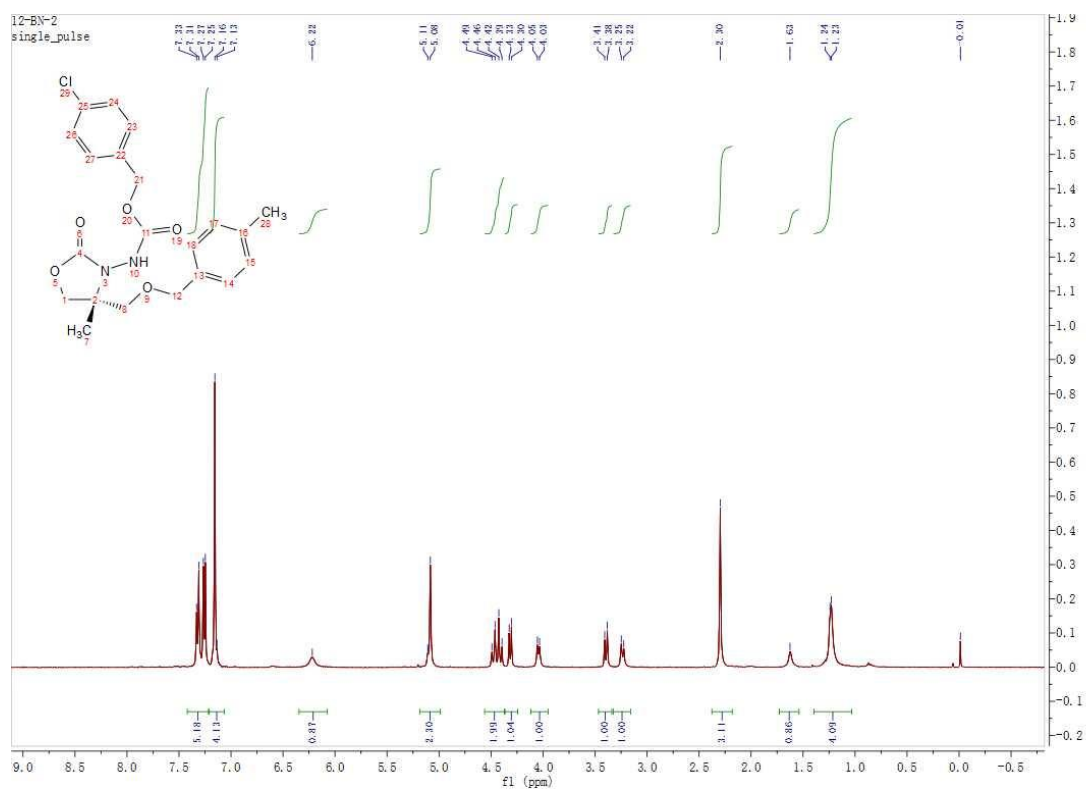


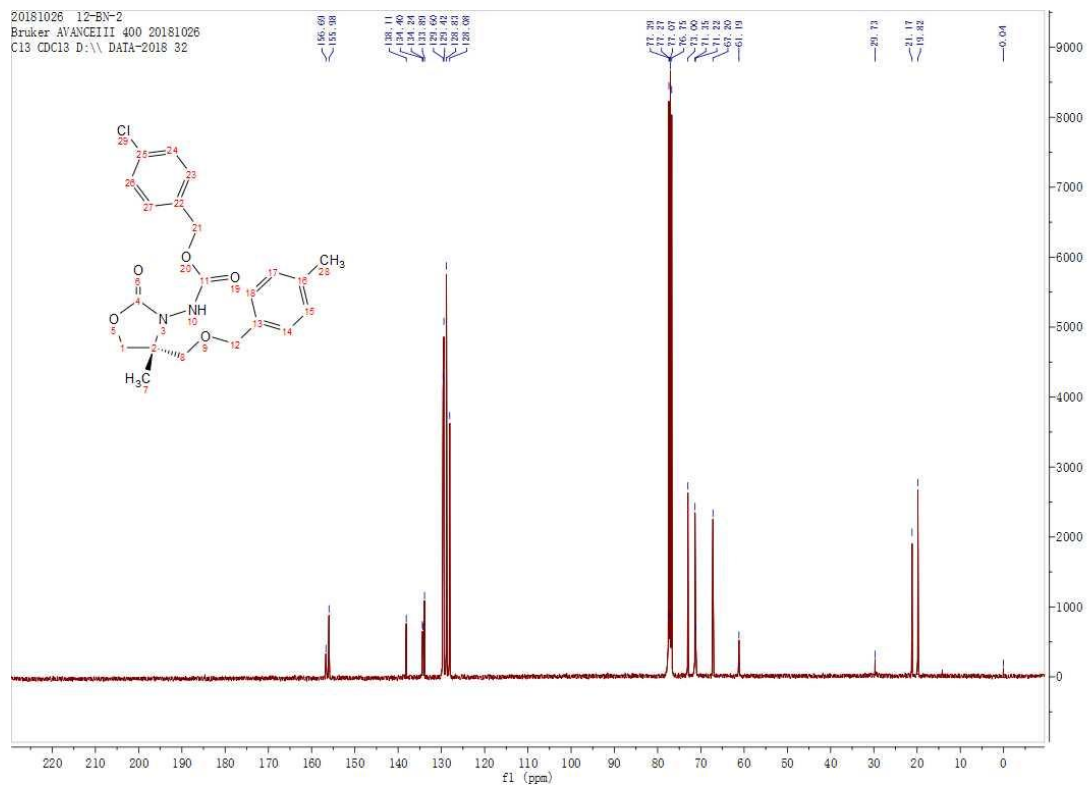
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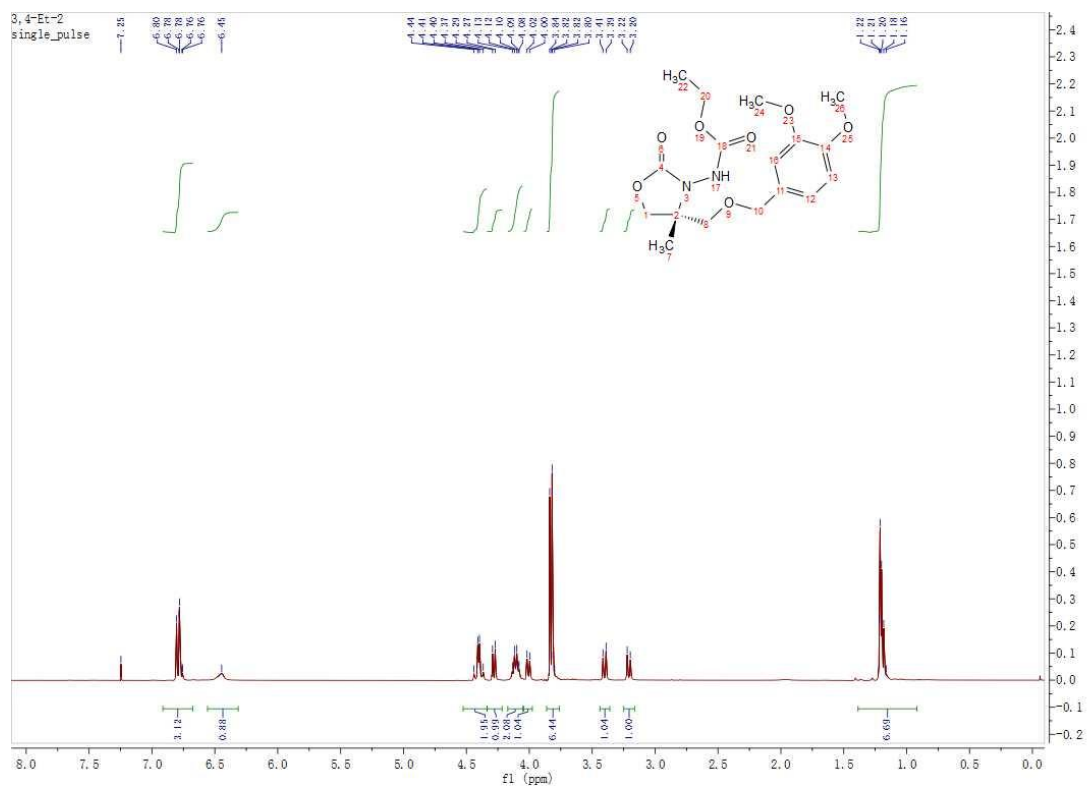


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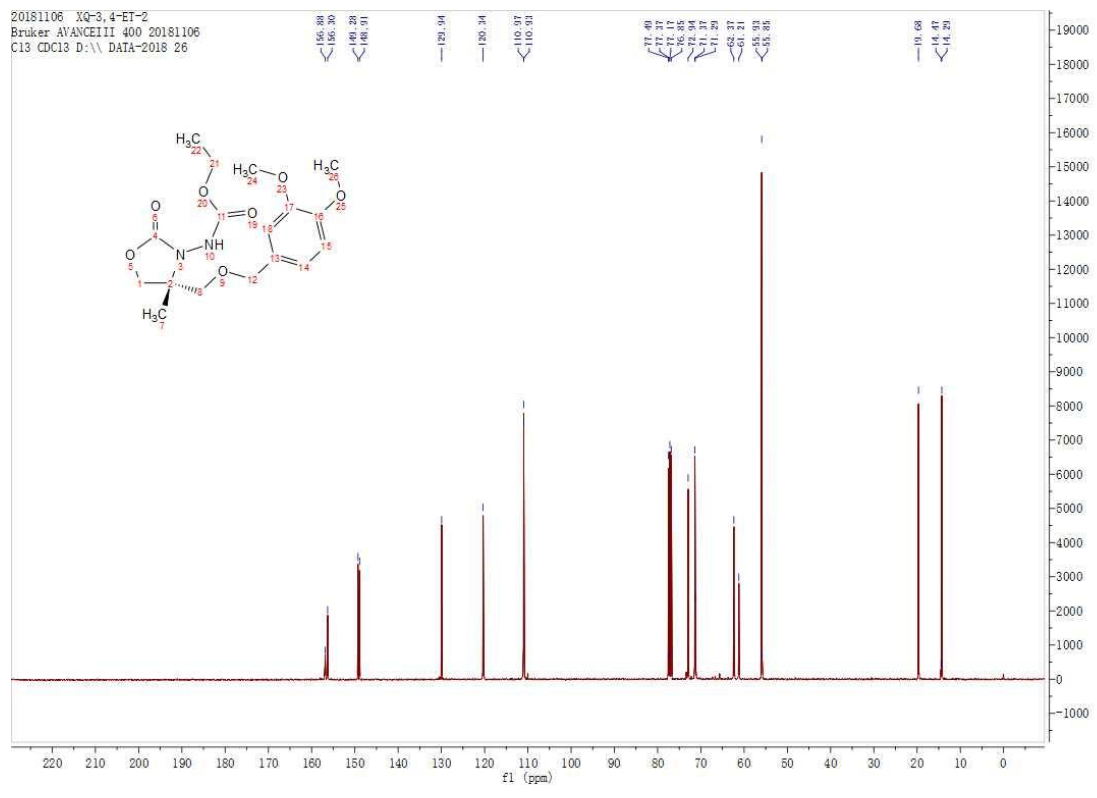




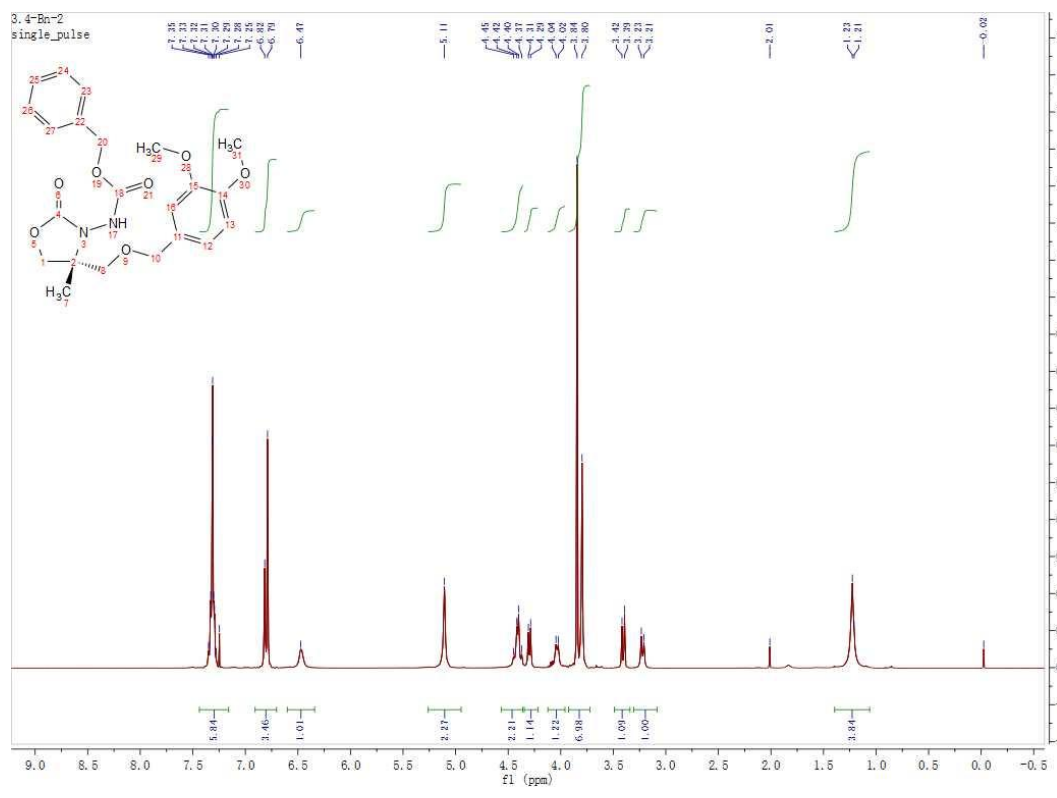
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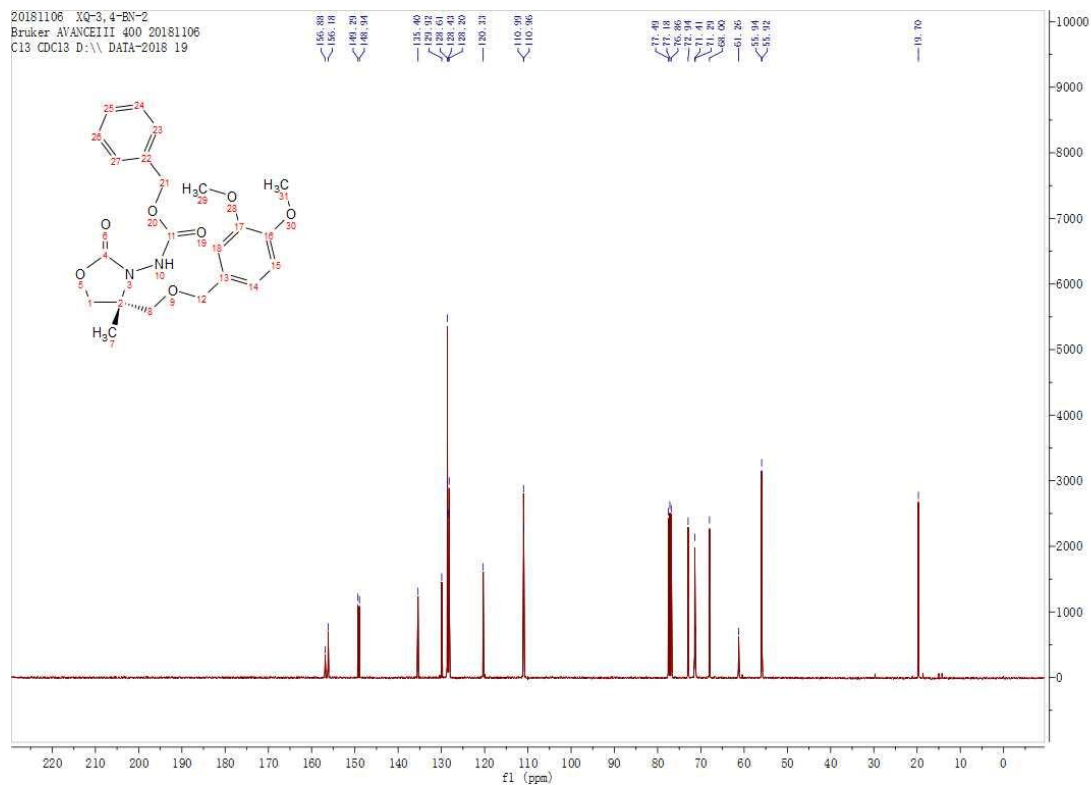


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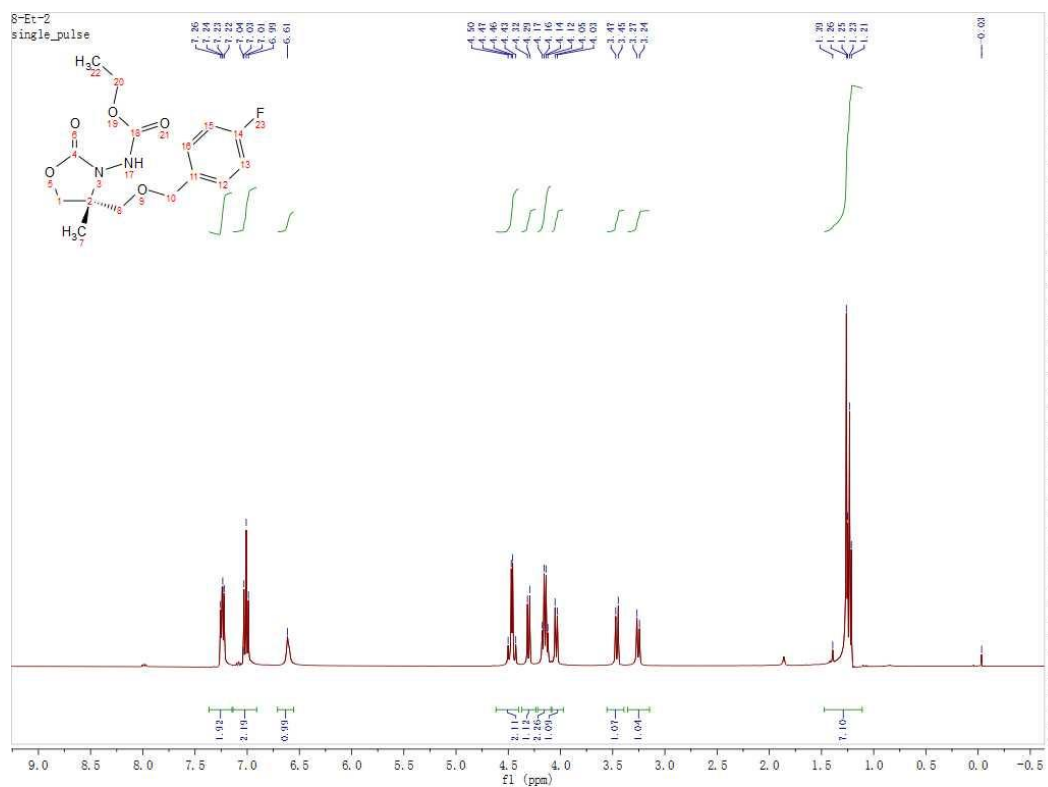


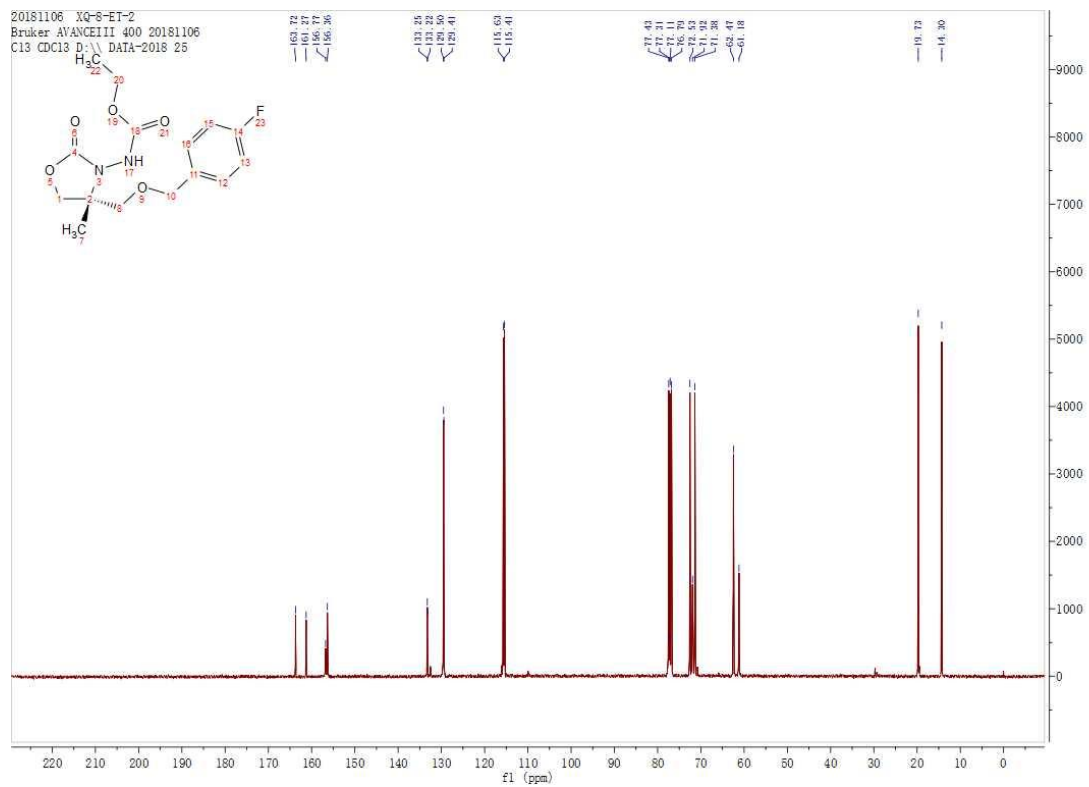
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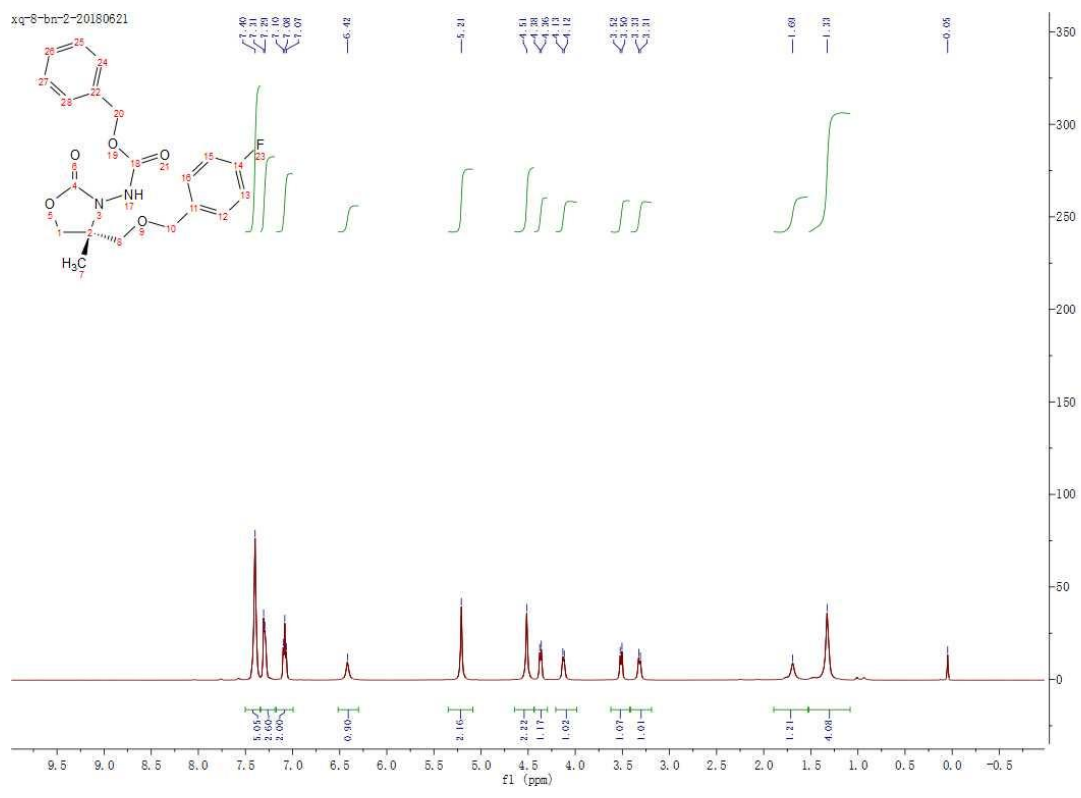


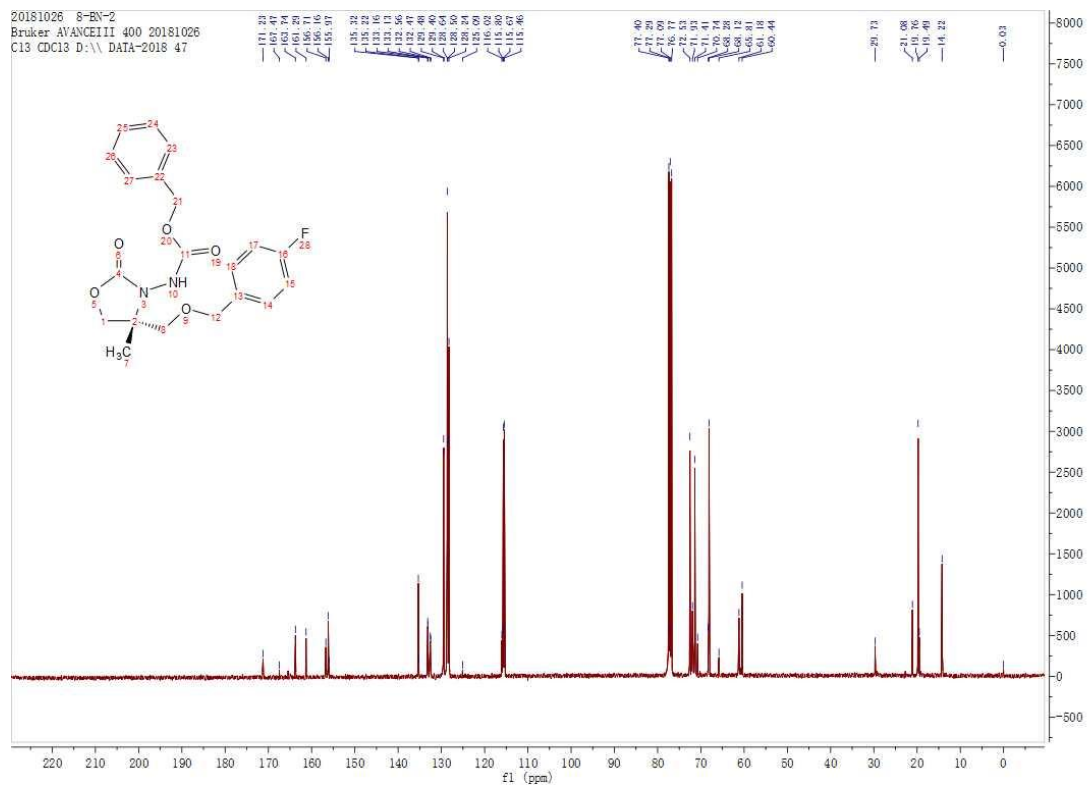
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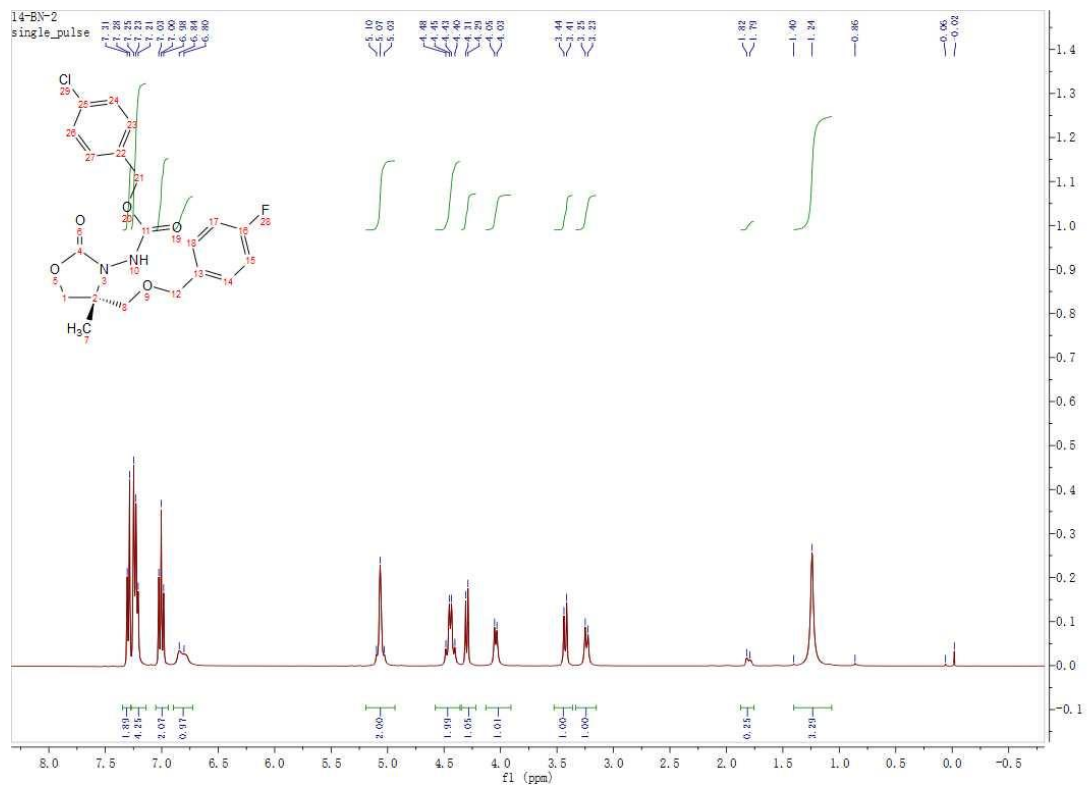


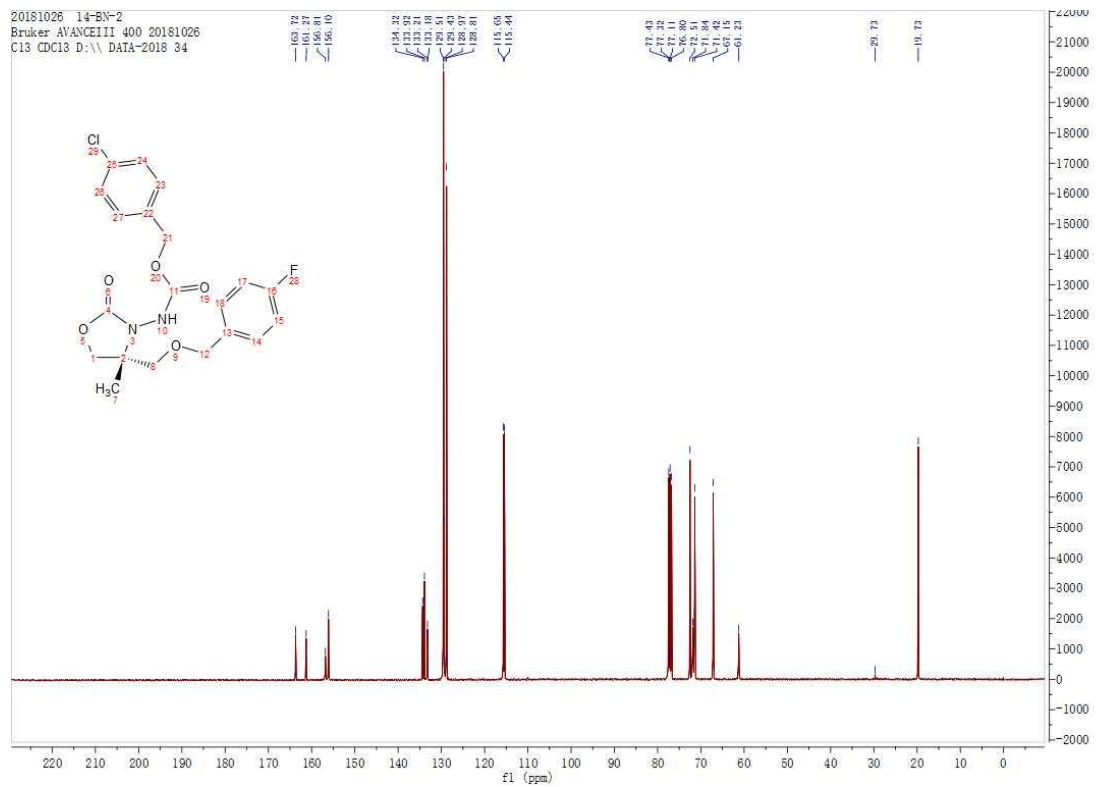
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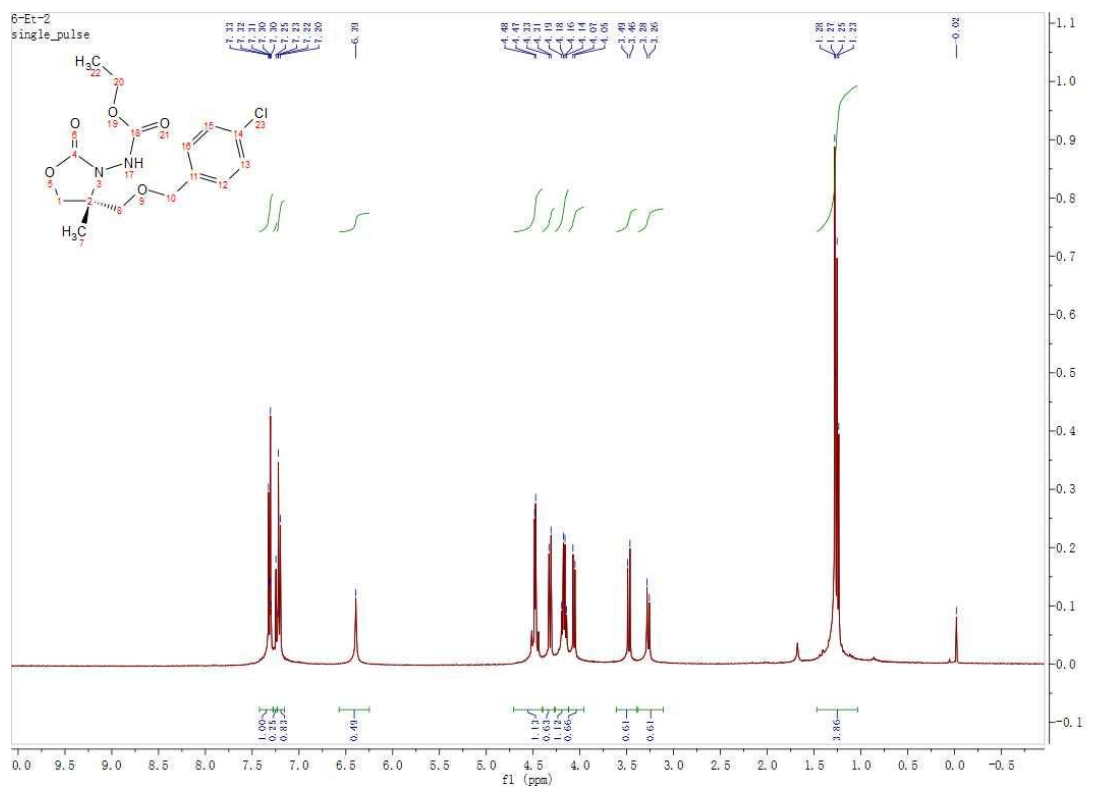


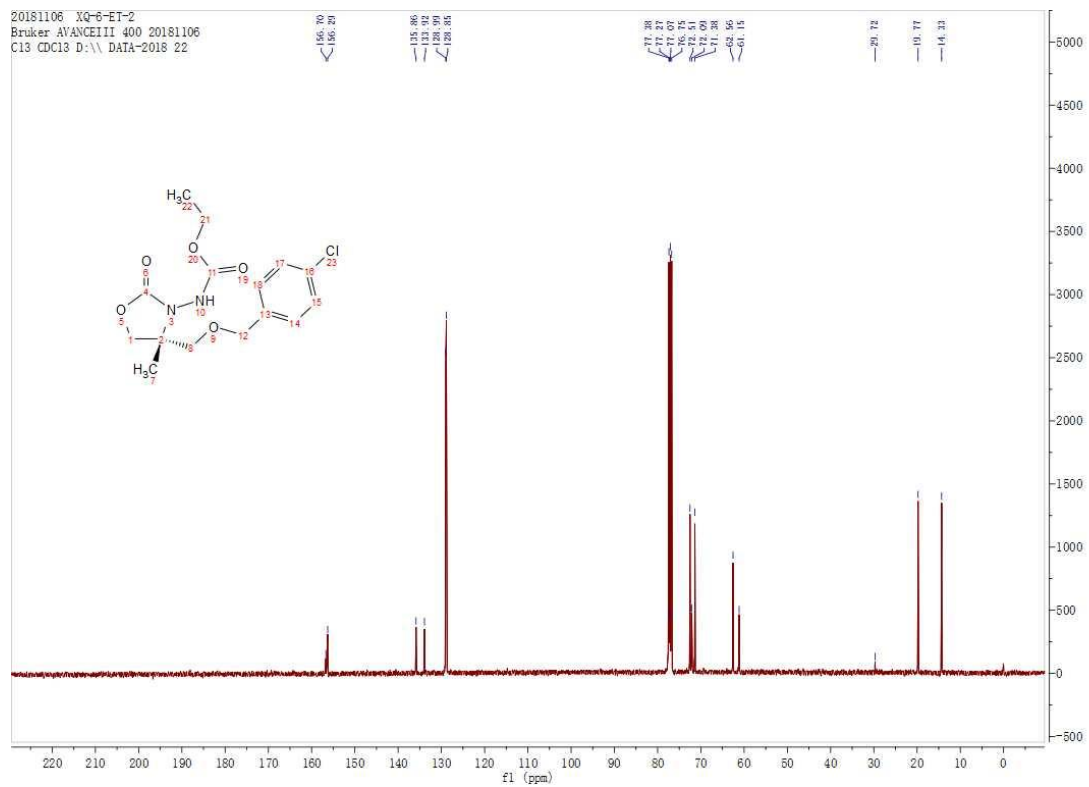
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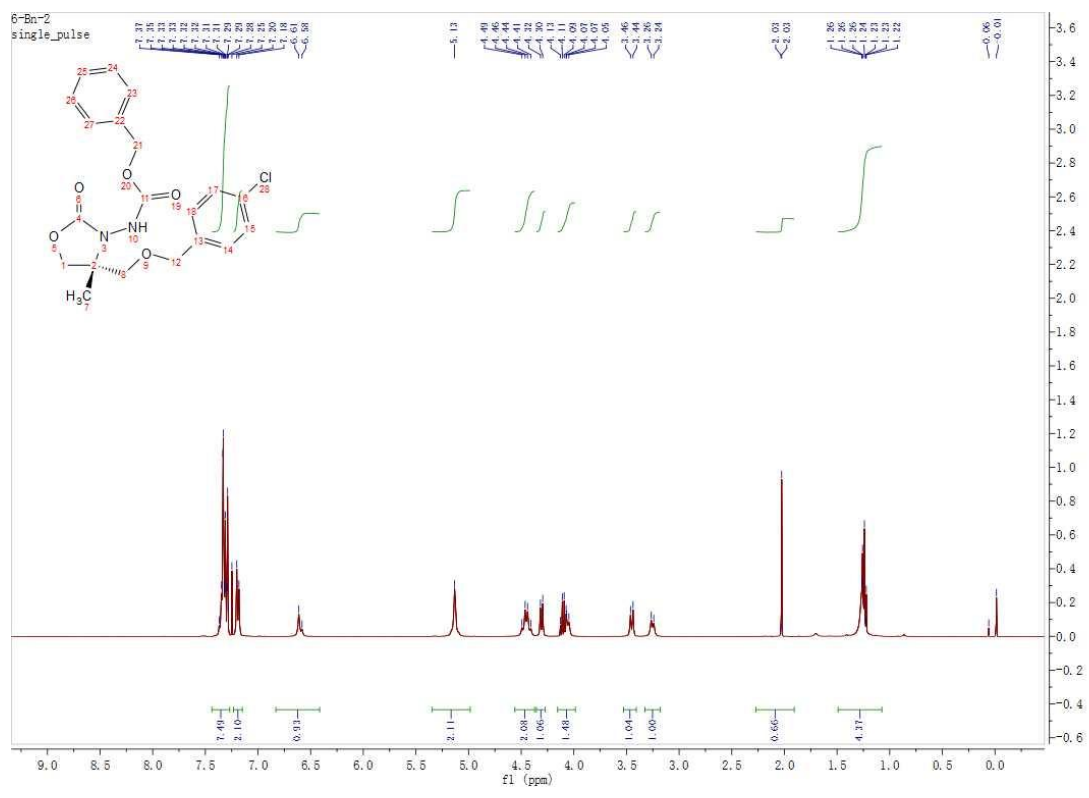


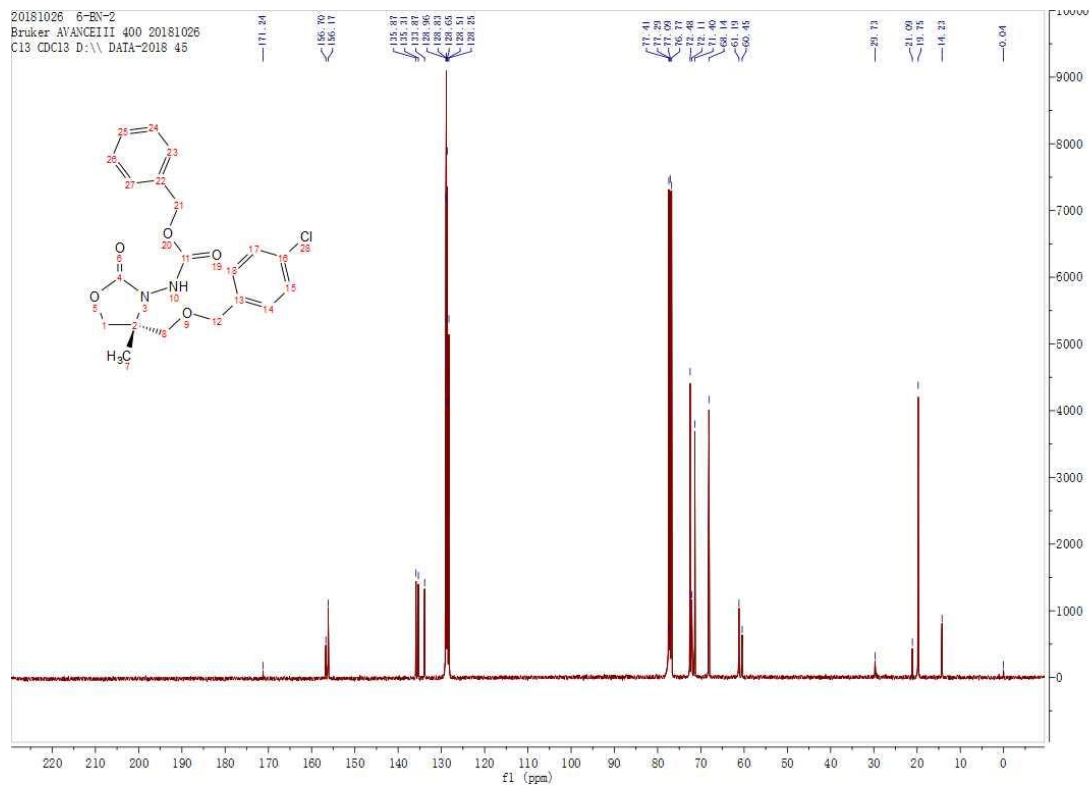
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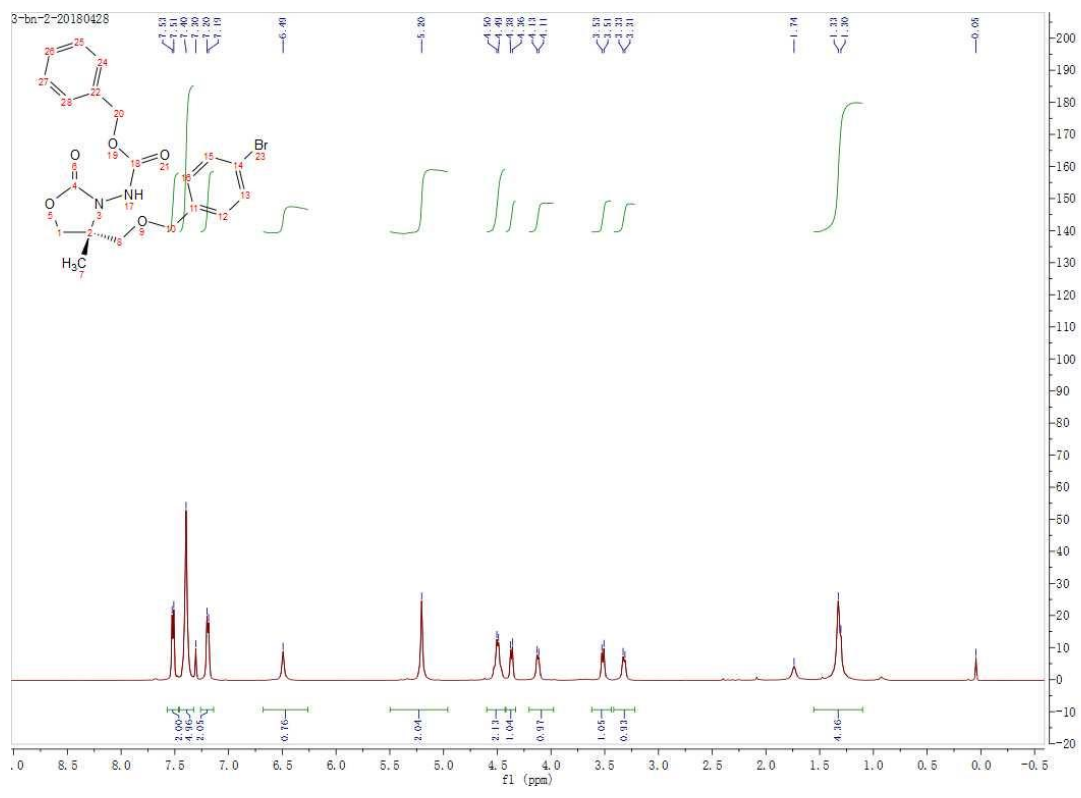


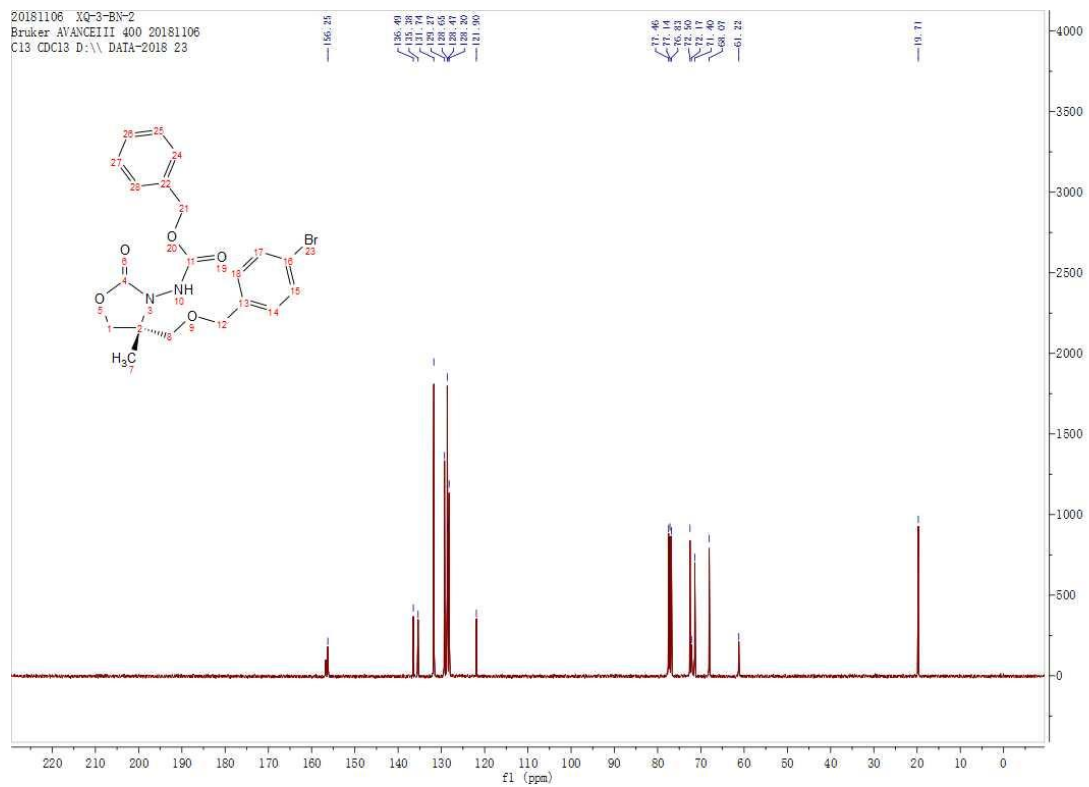
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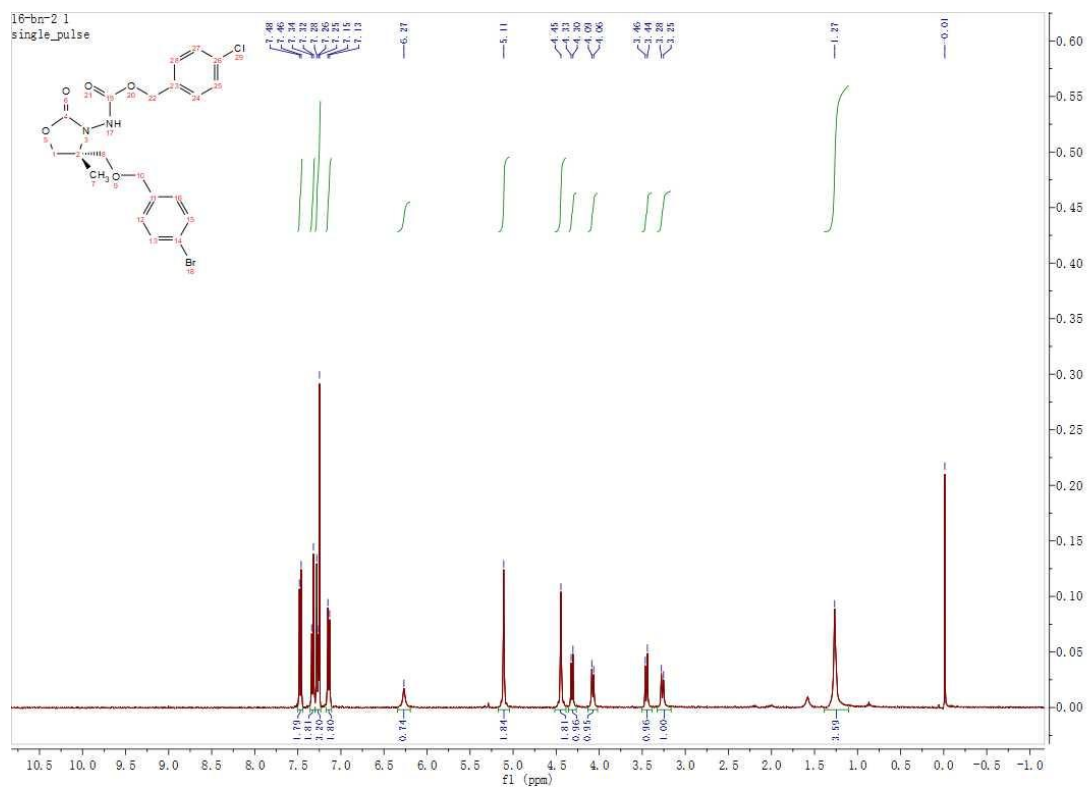


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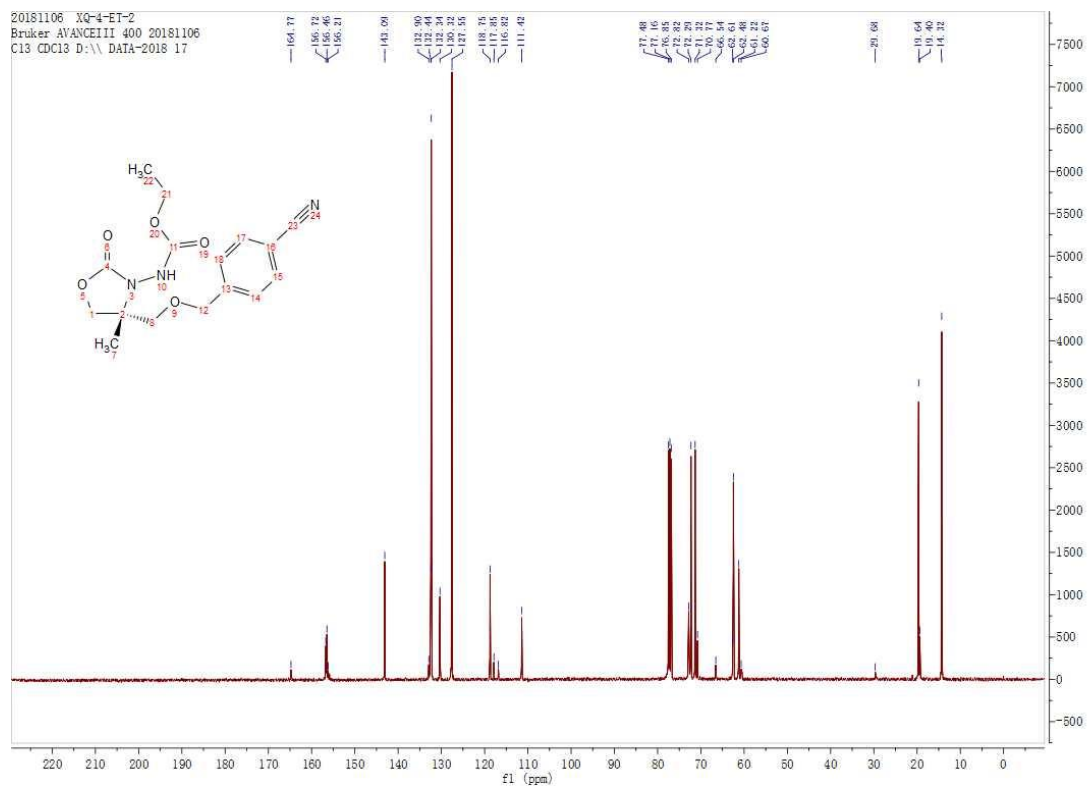
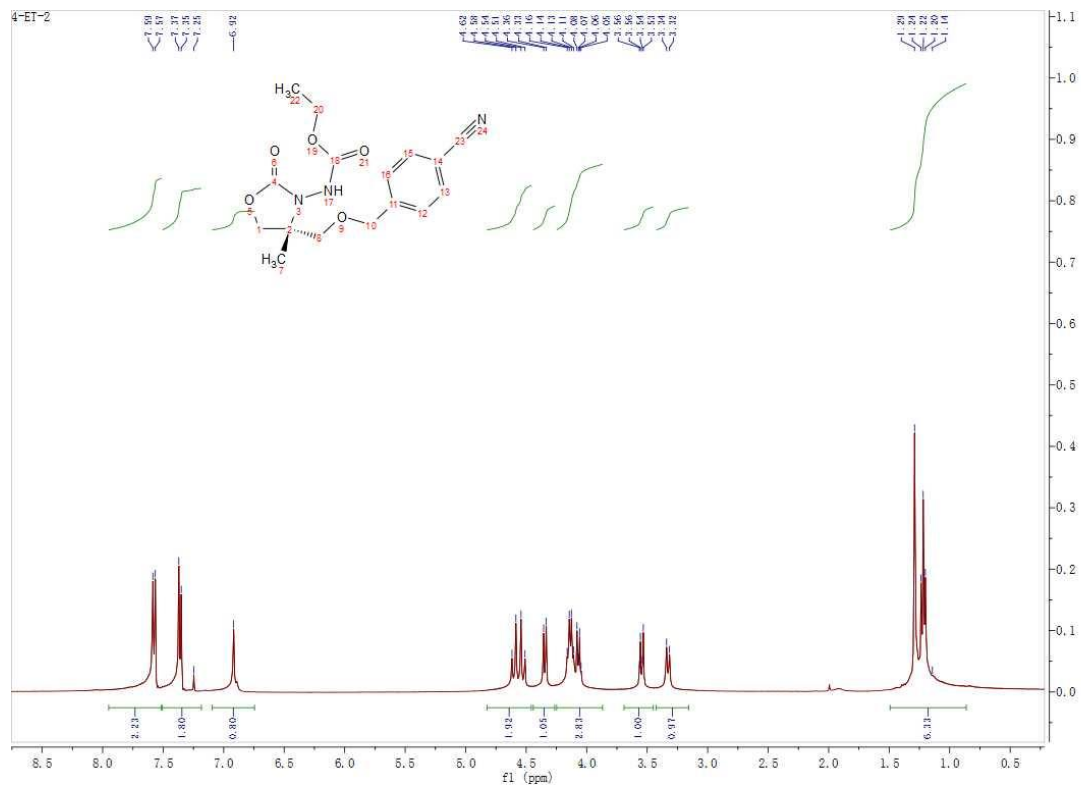




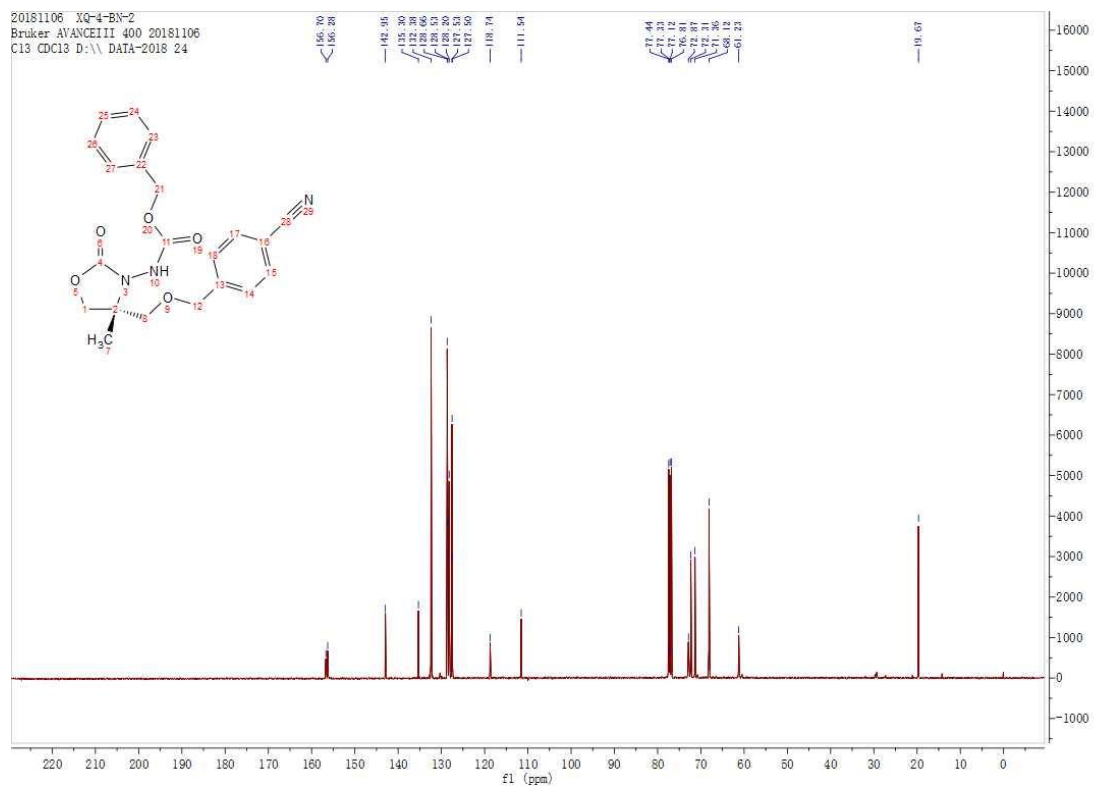
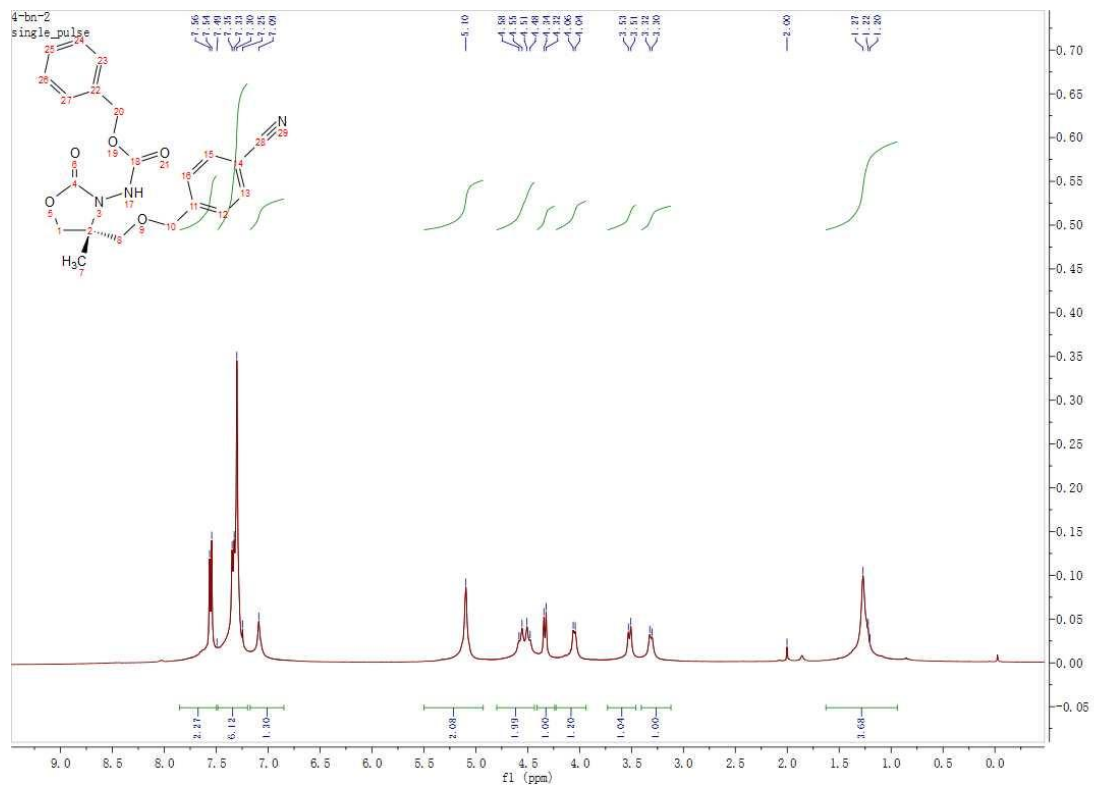
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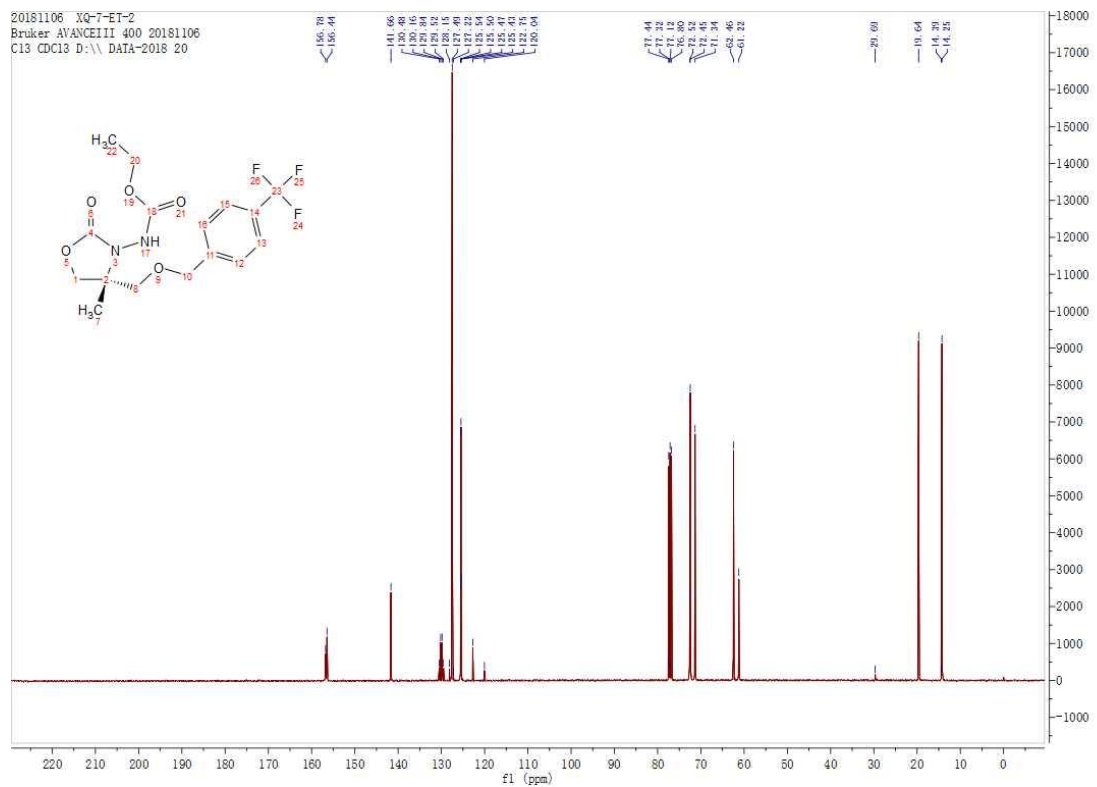
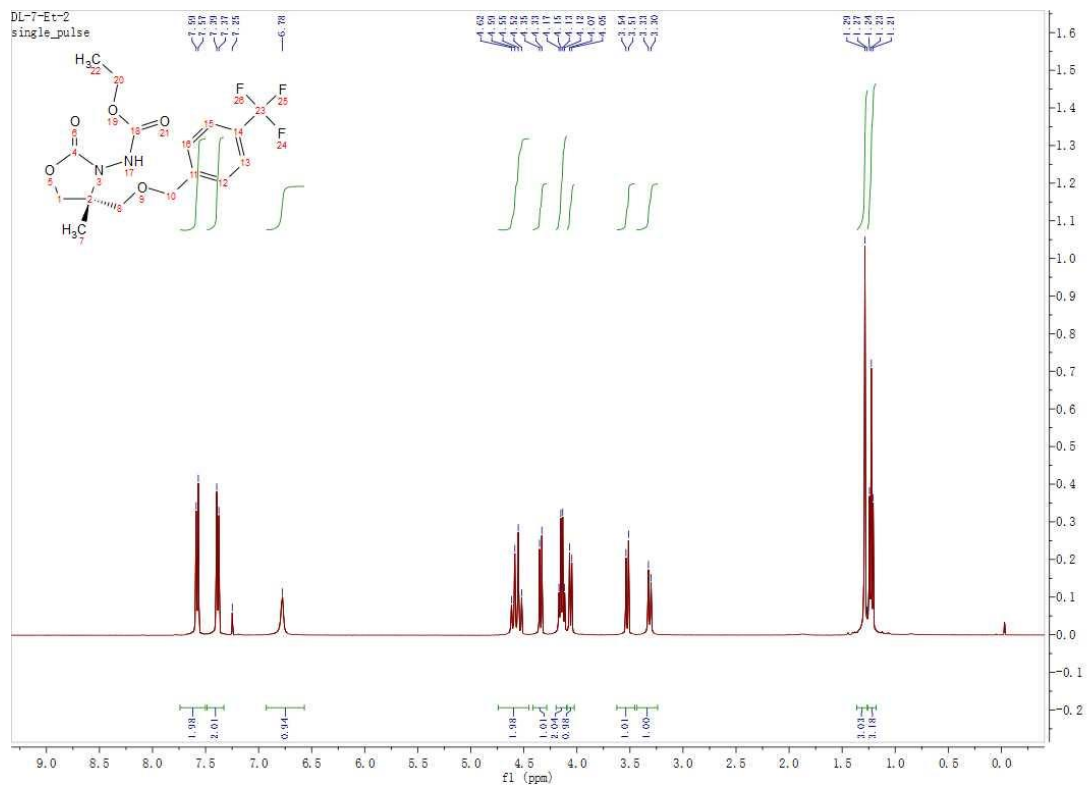
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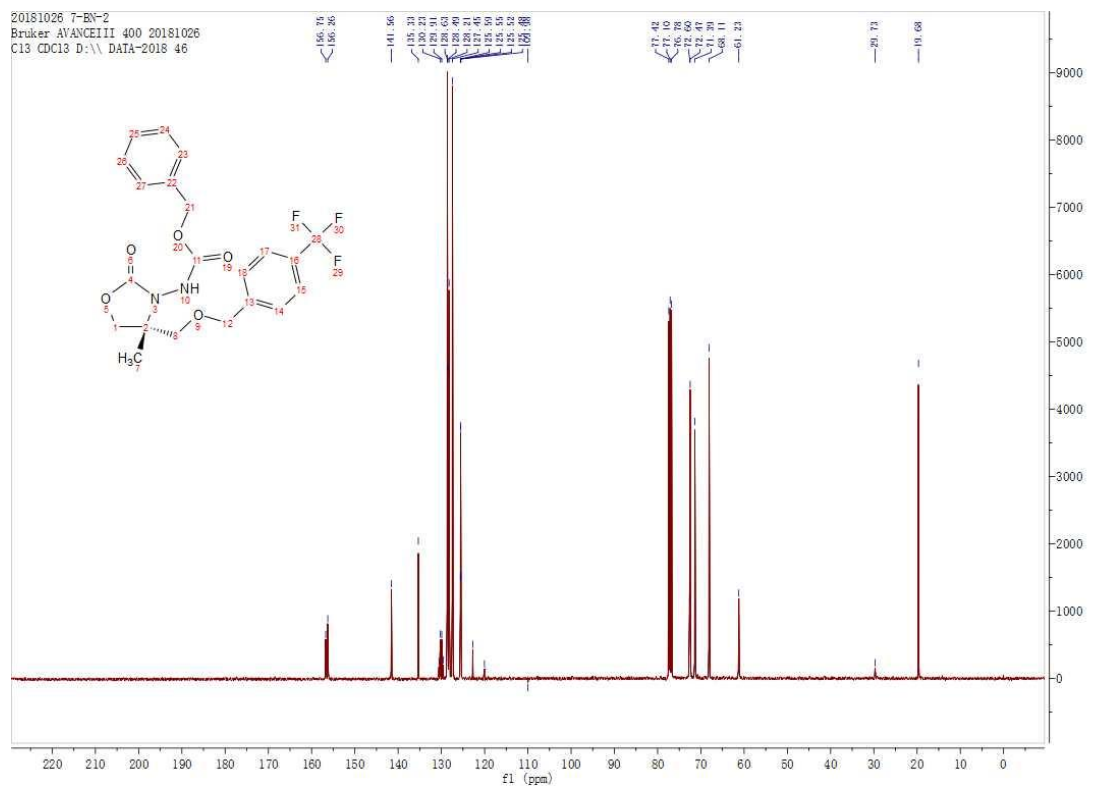
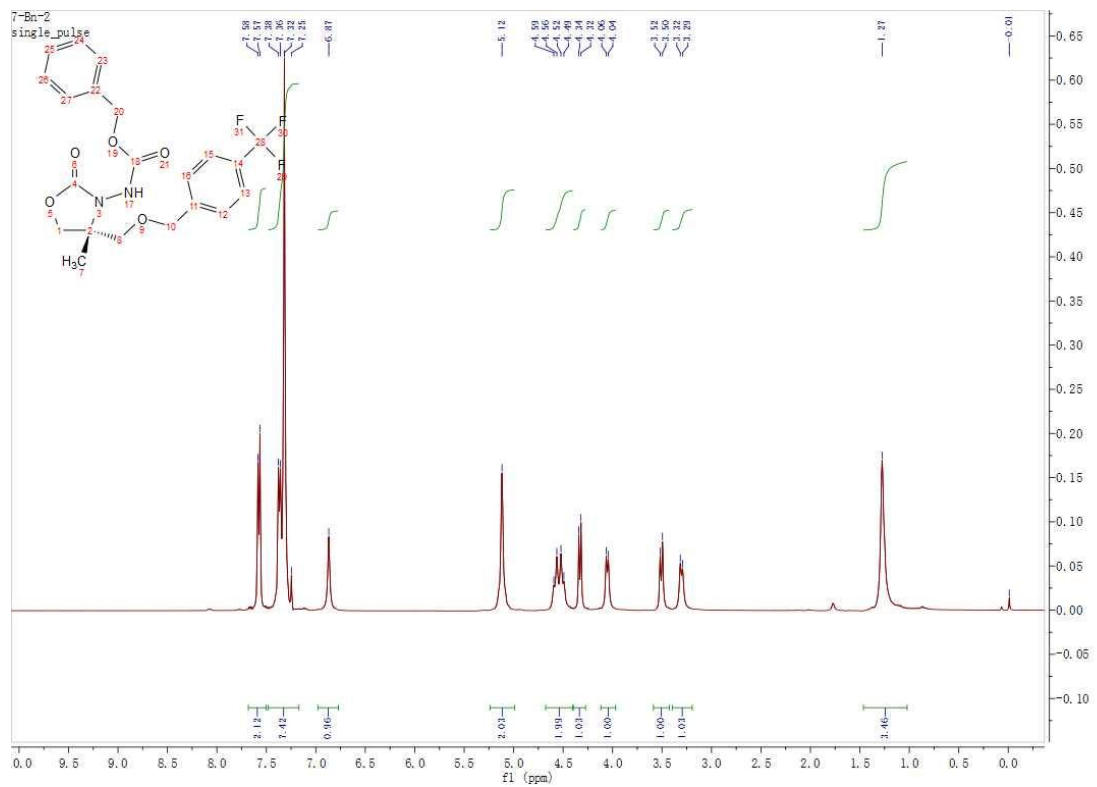
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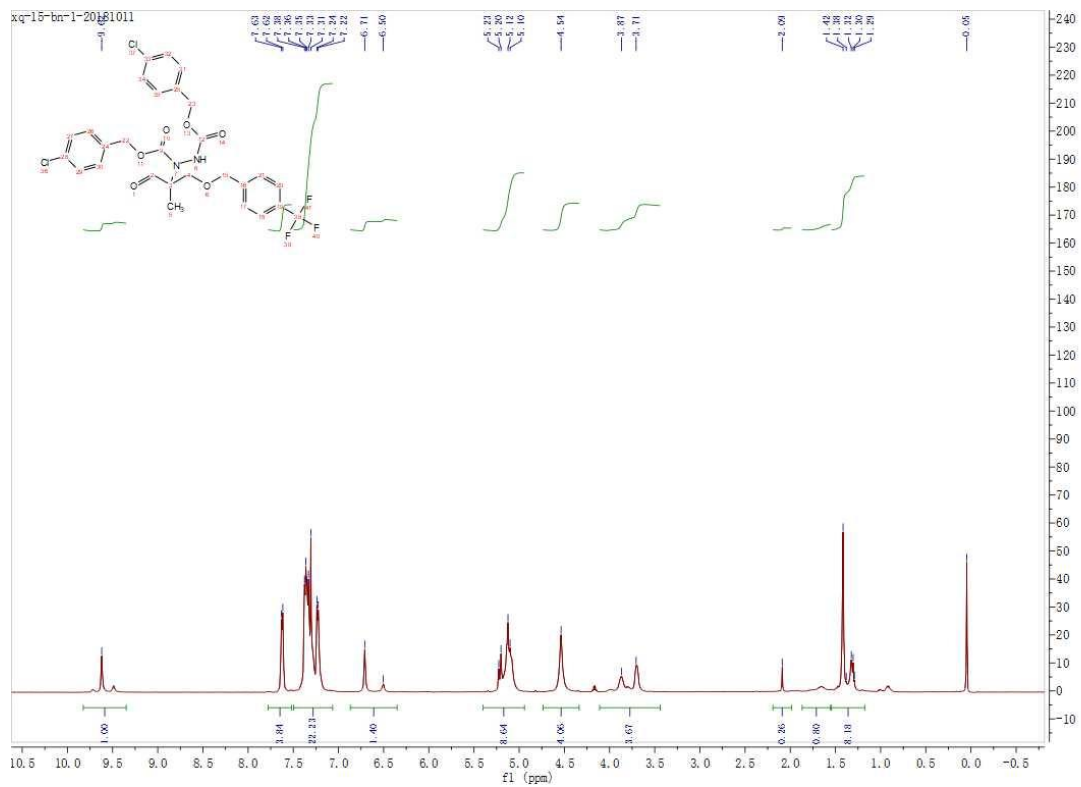
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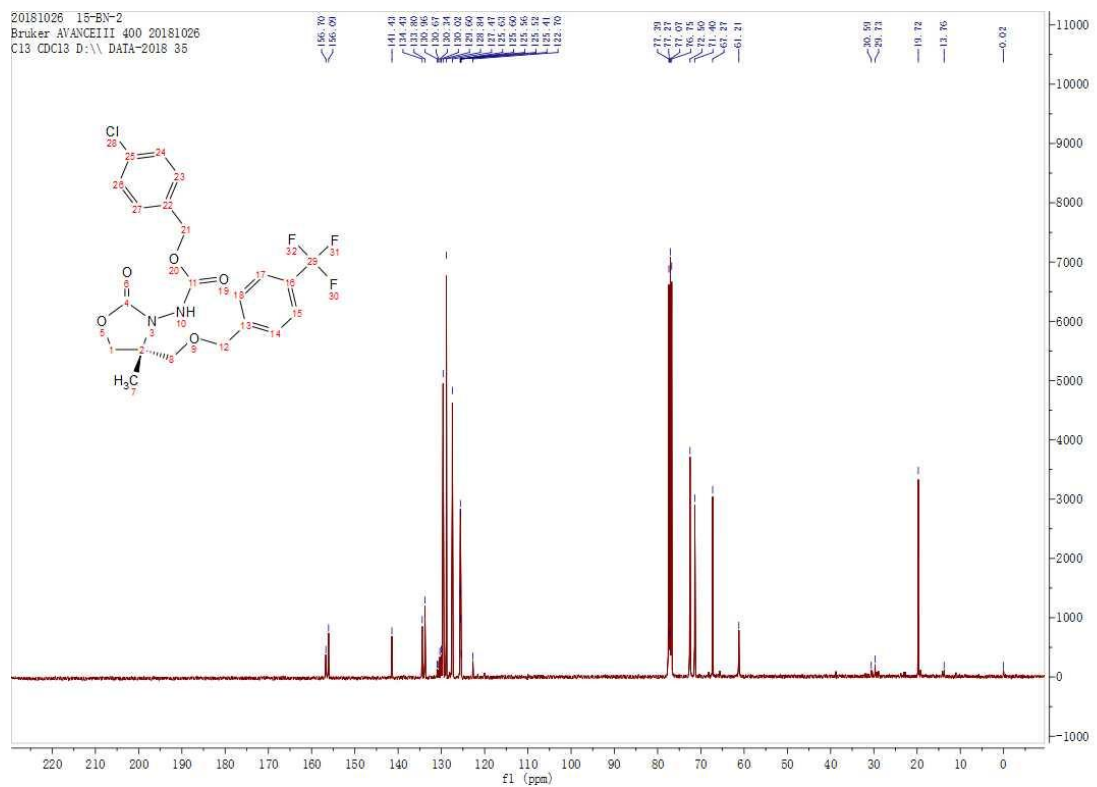
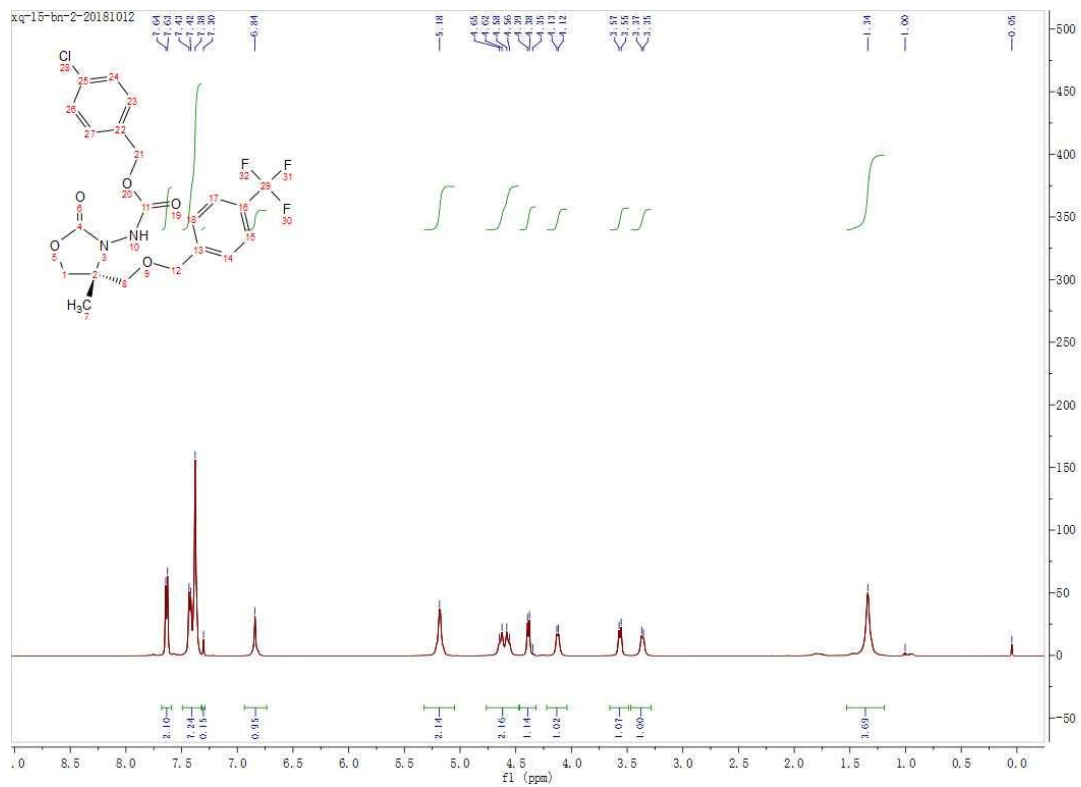
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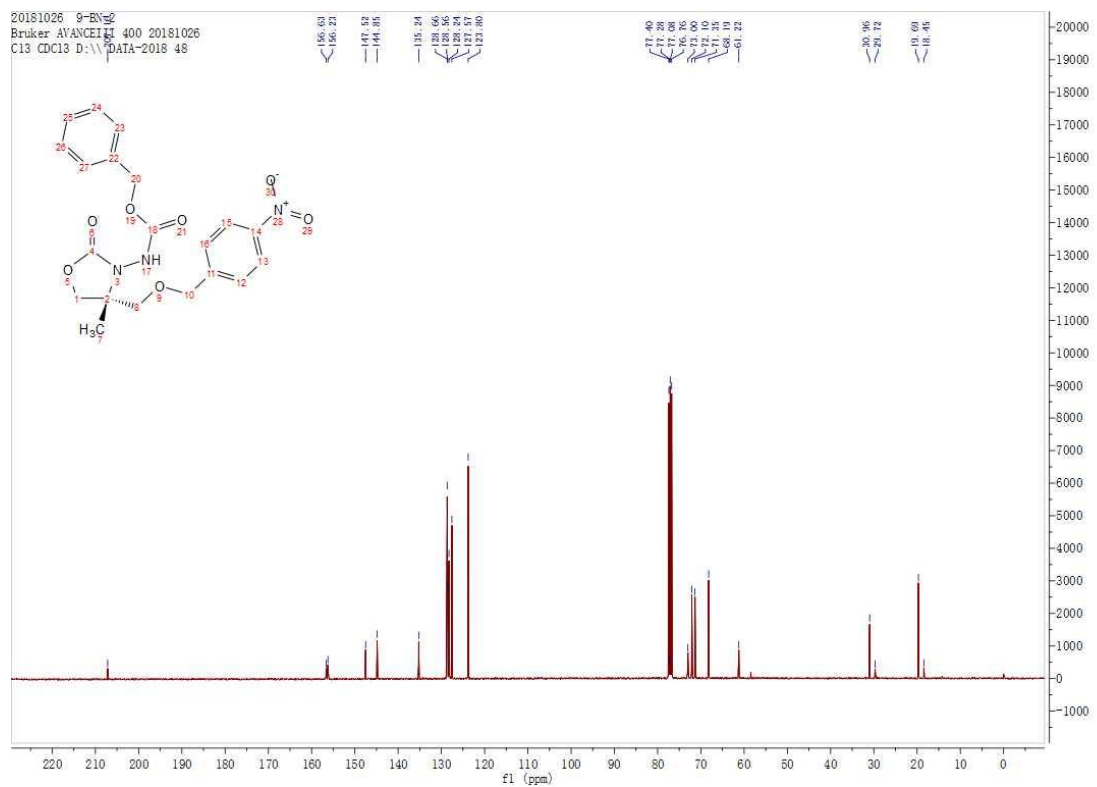
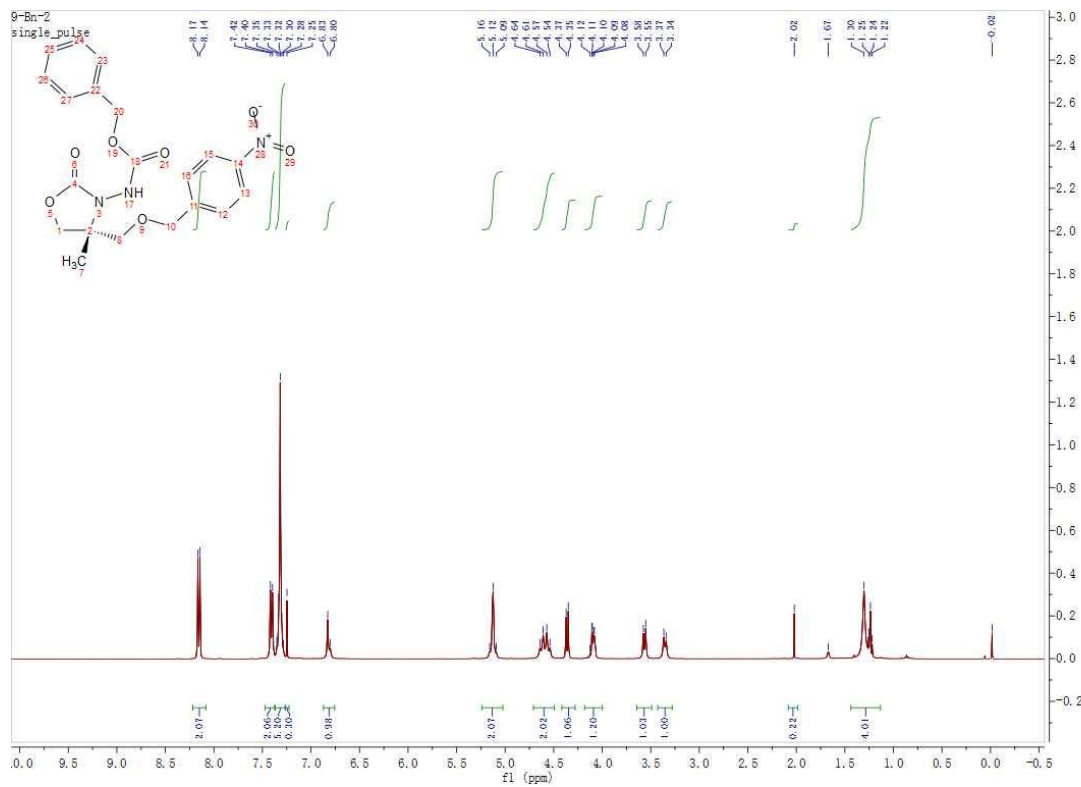
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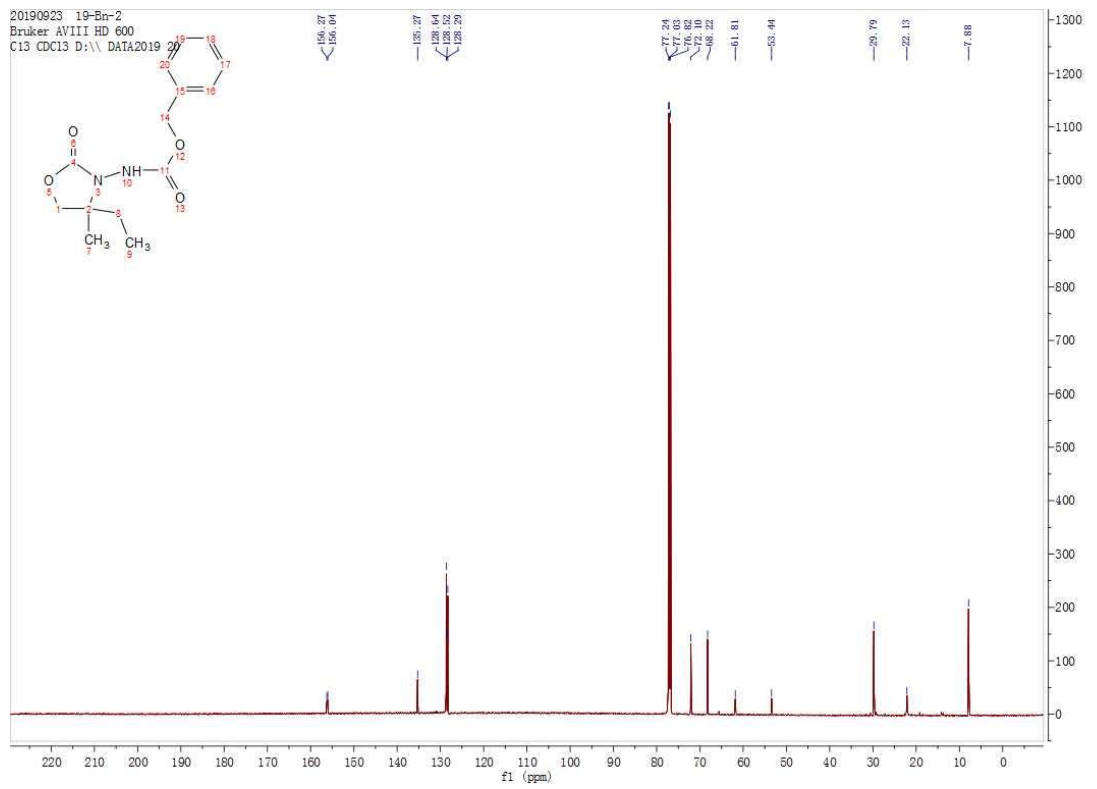
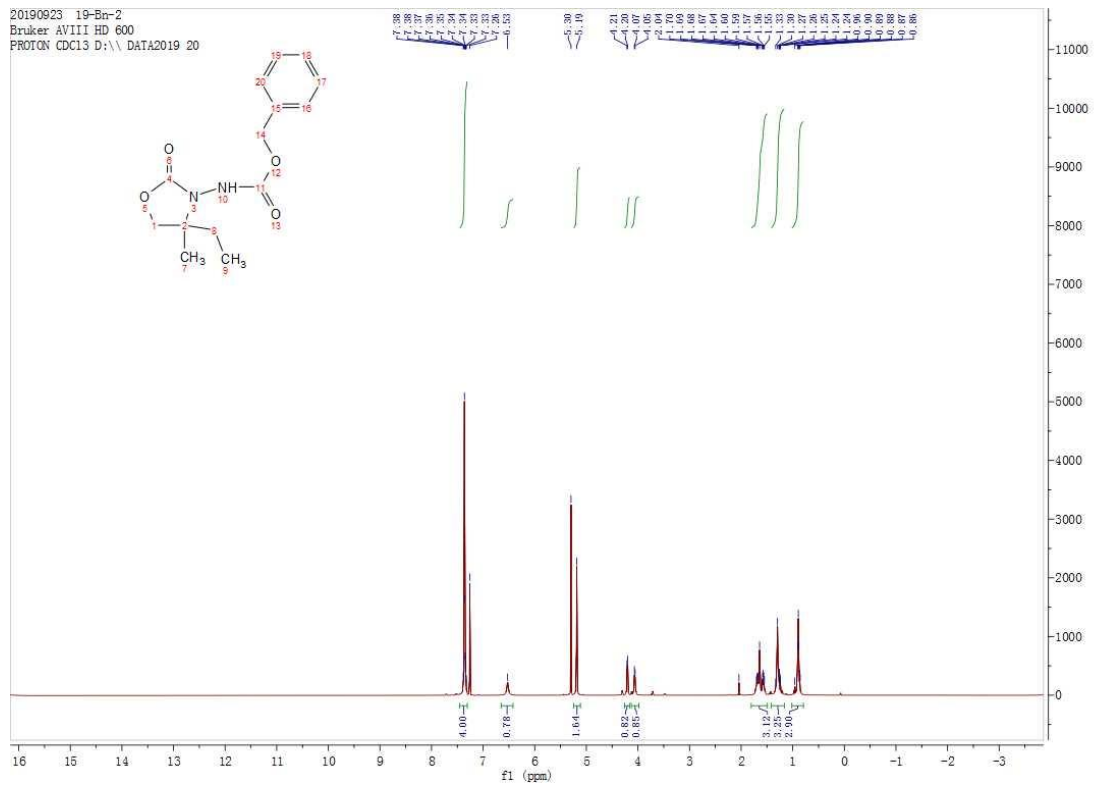
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5h-p-ClBn

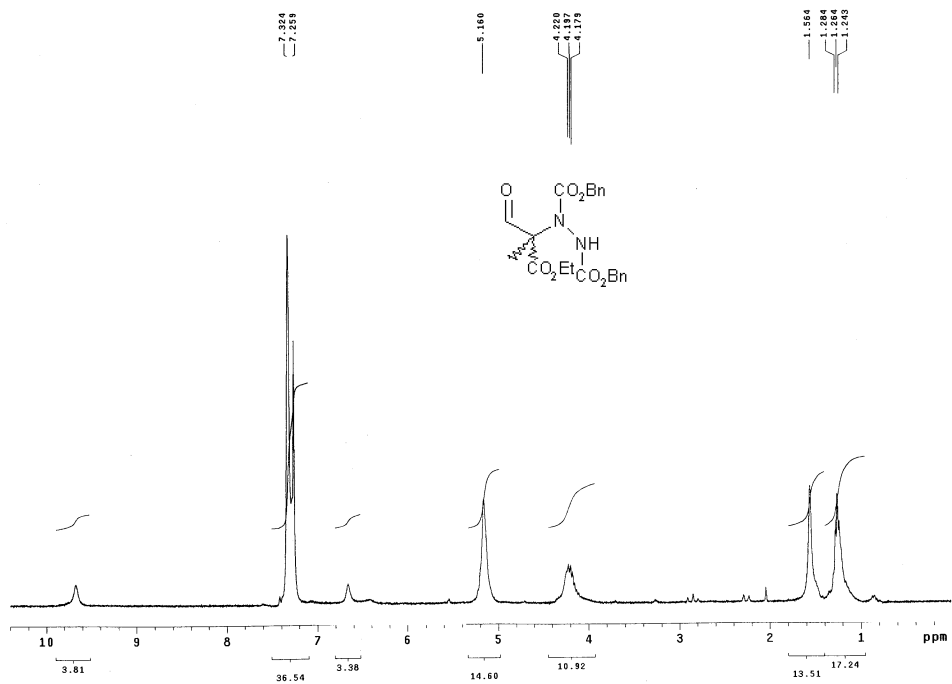


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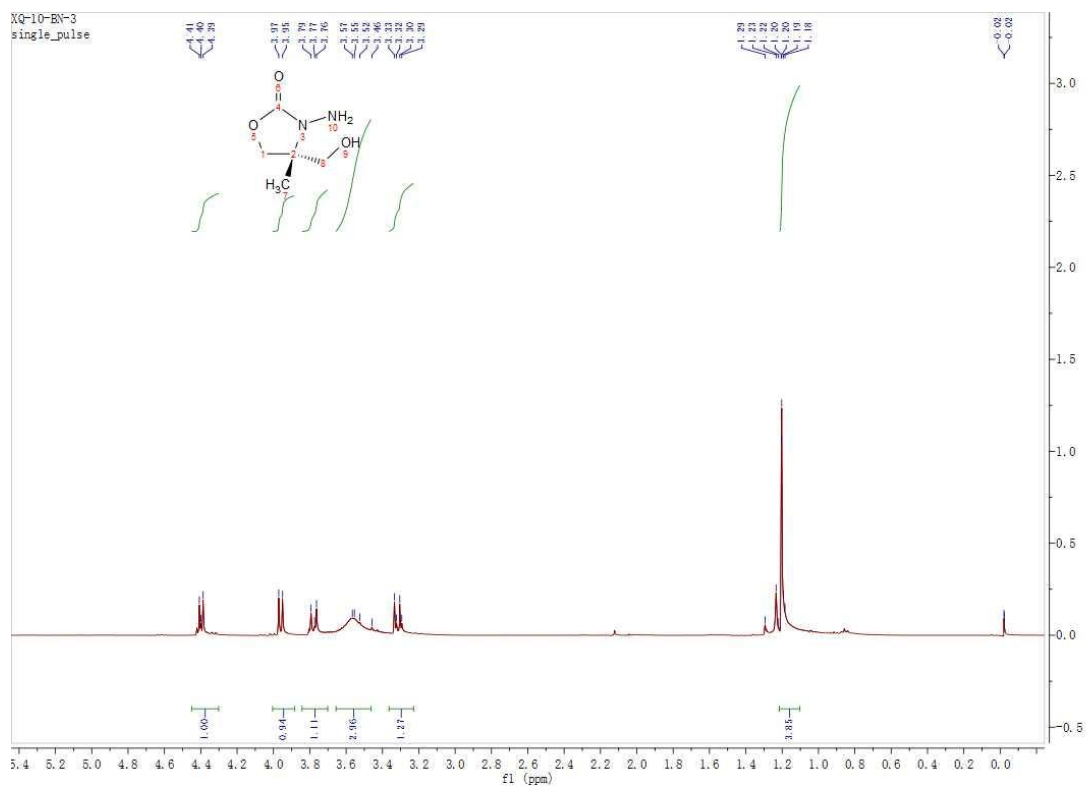


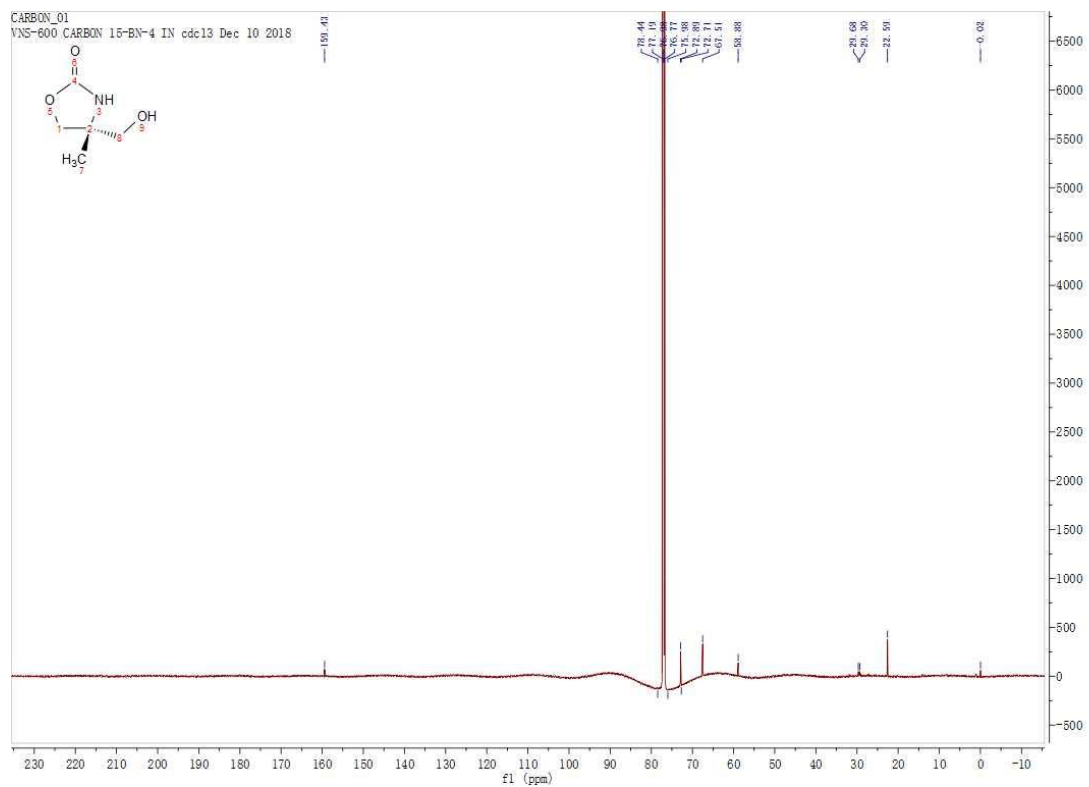
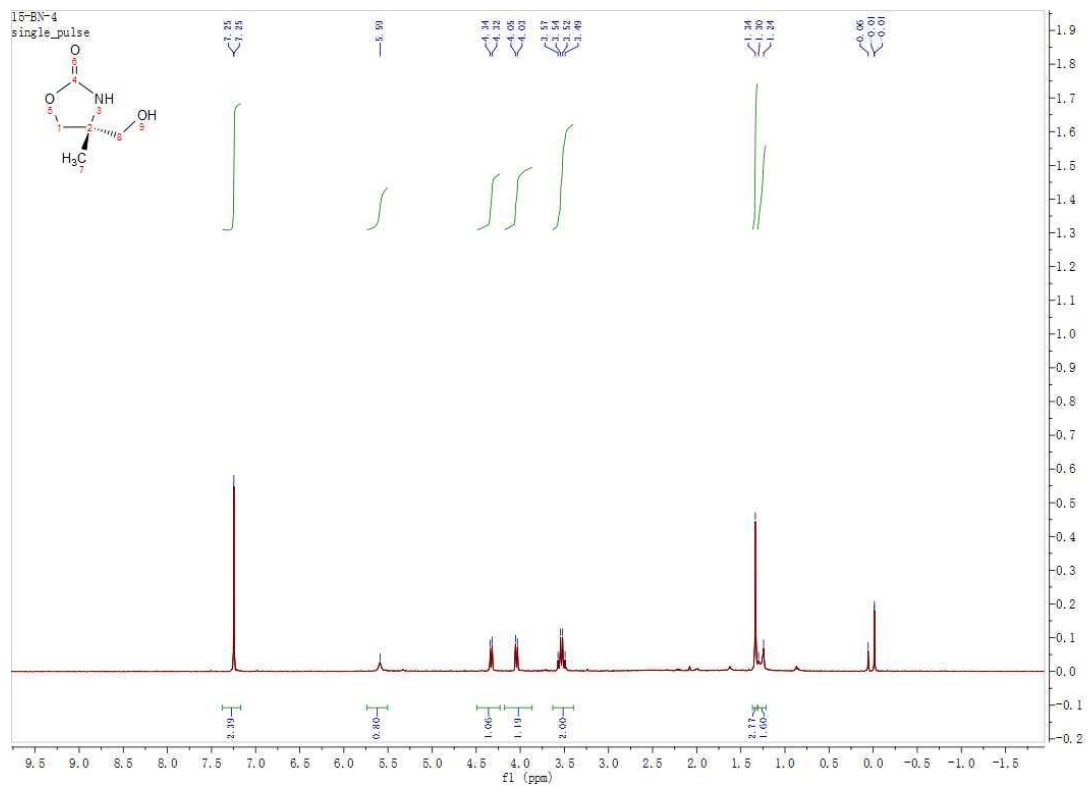
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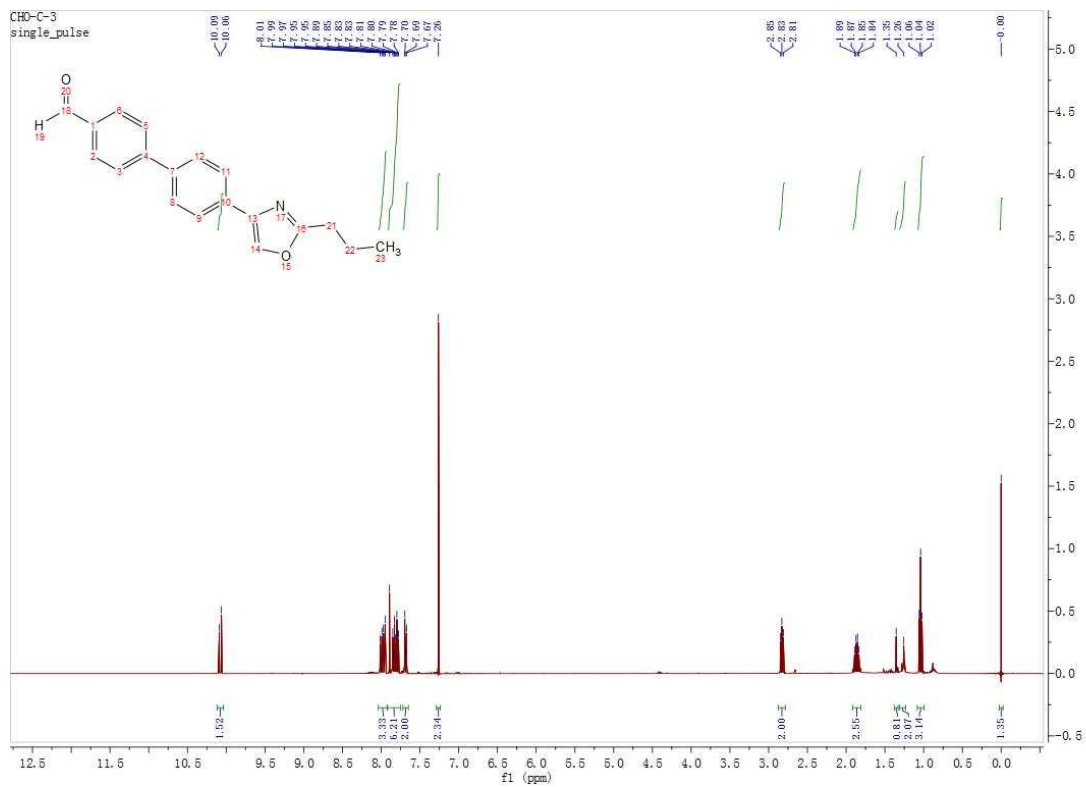
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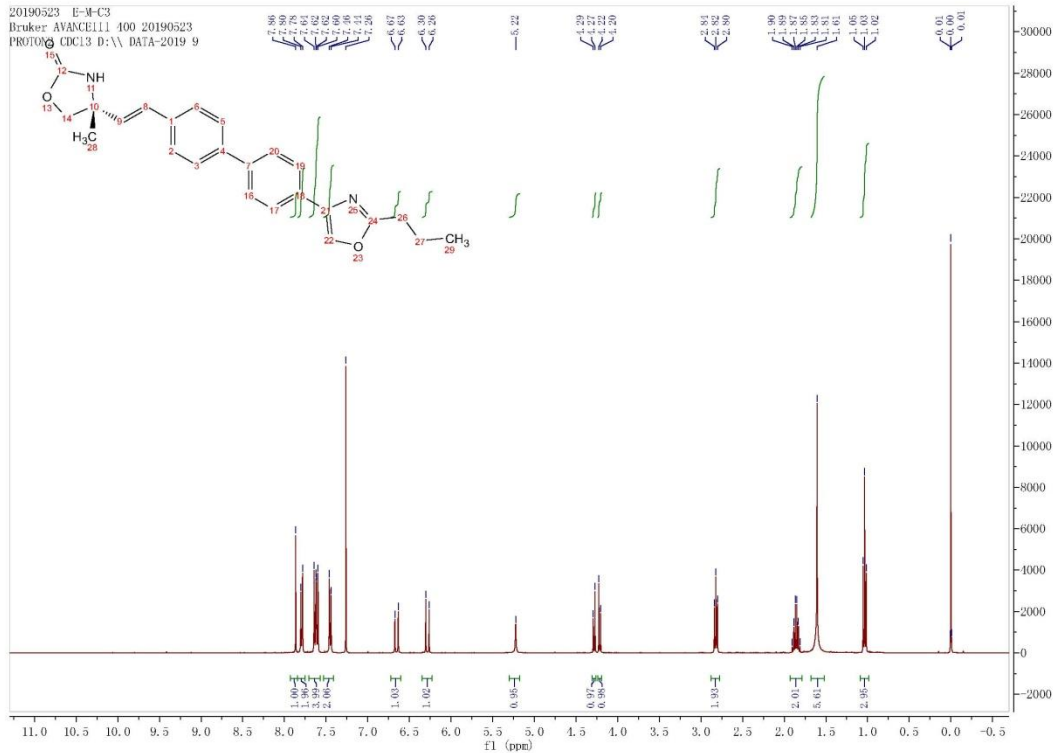


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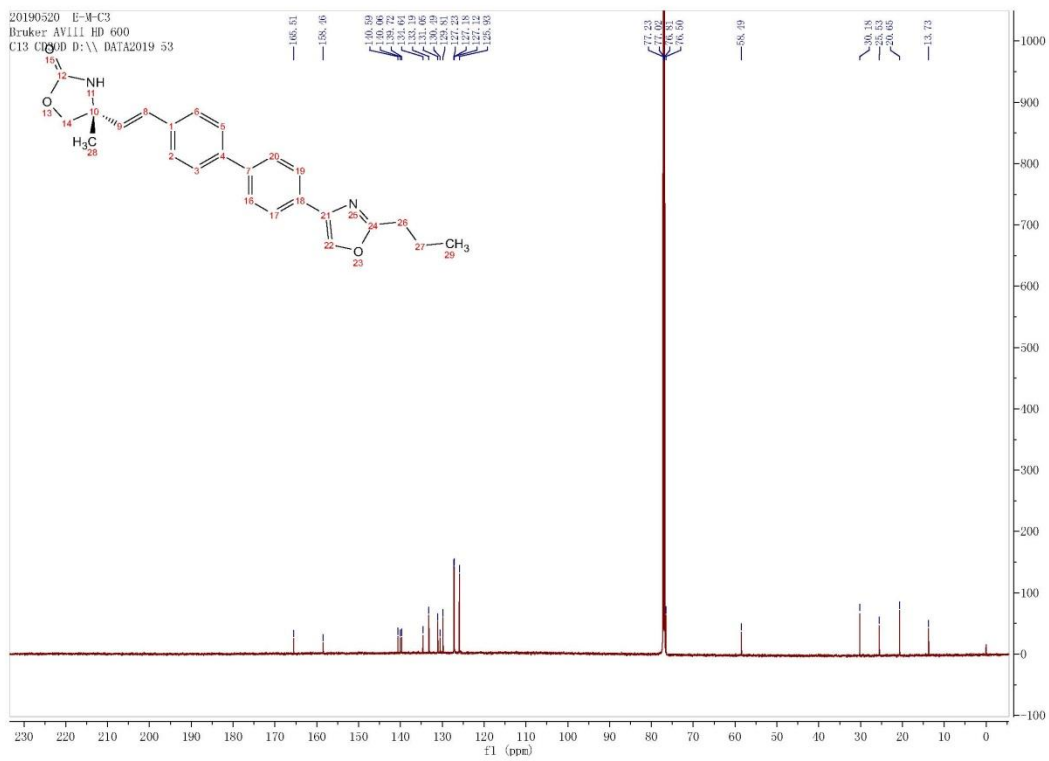




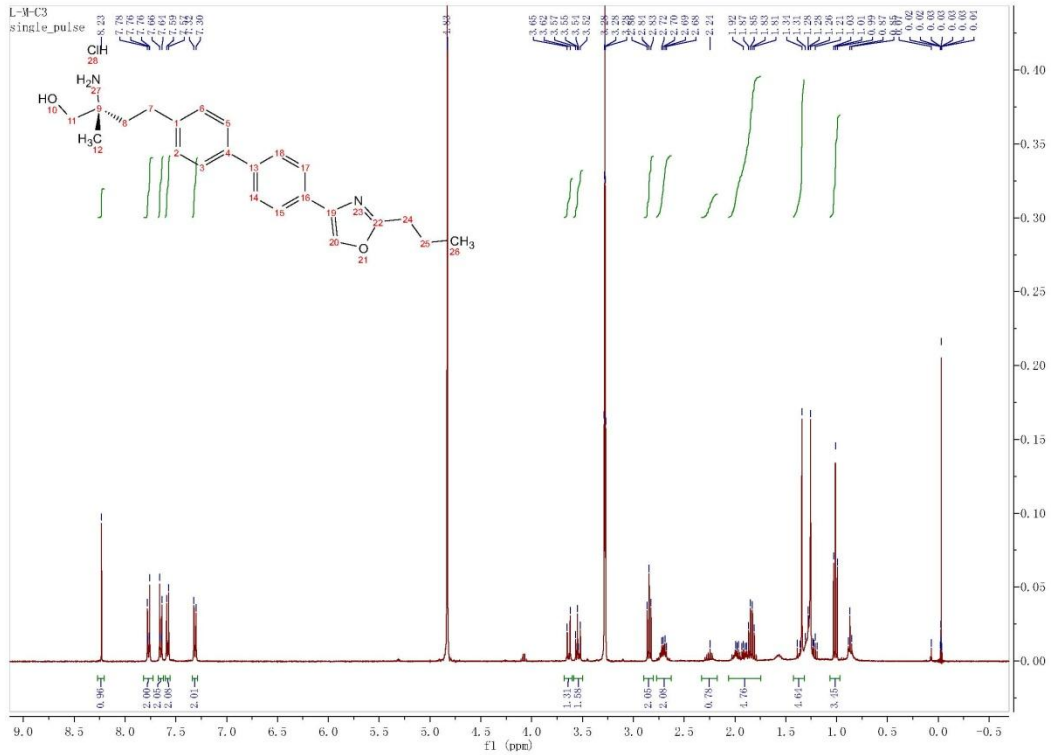




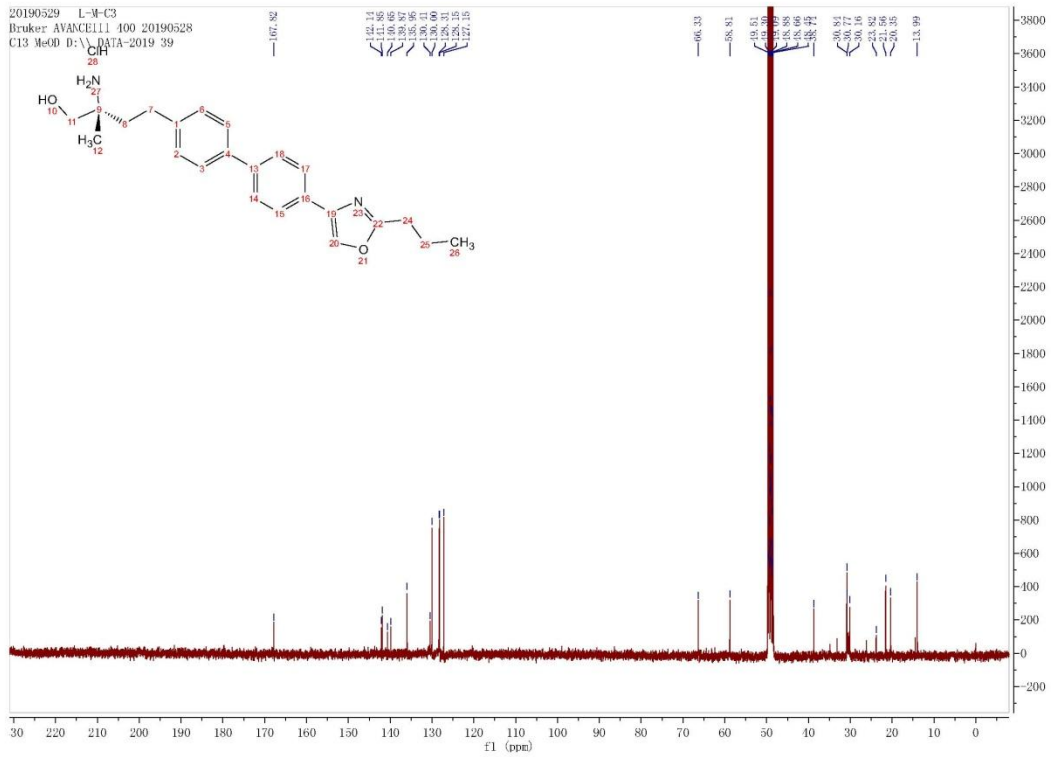
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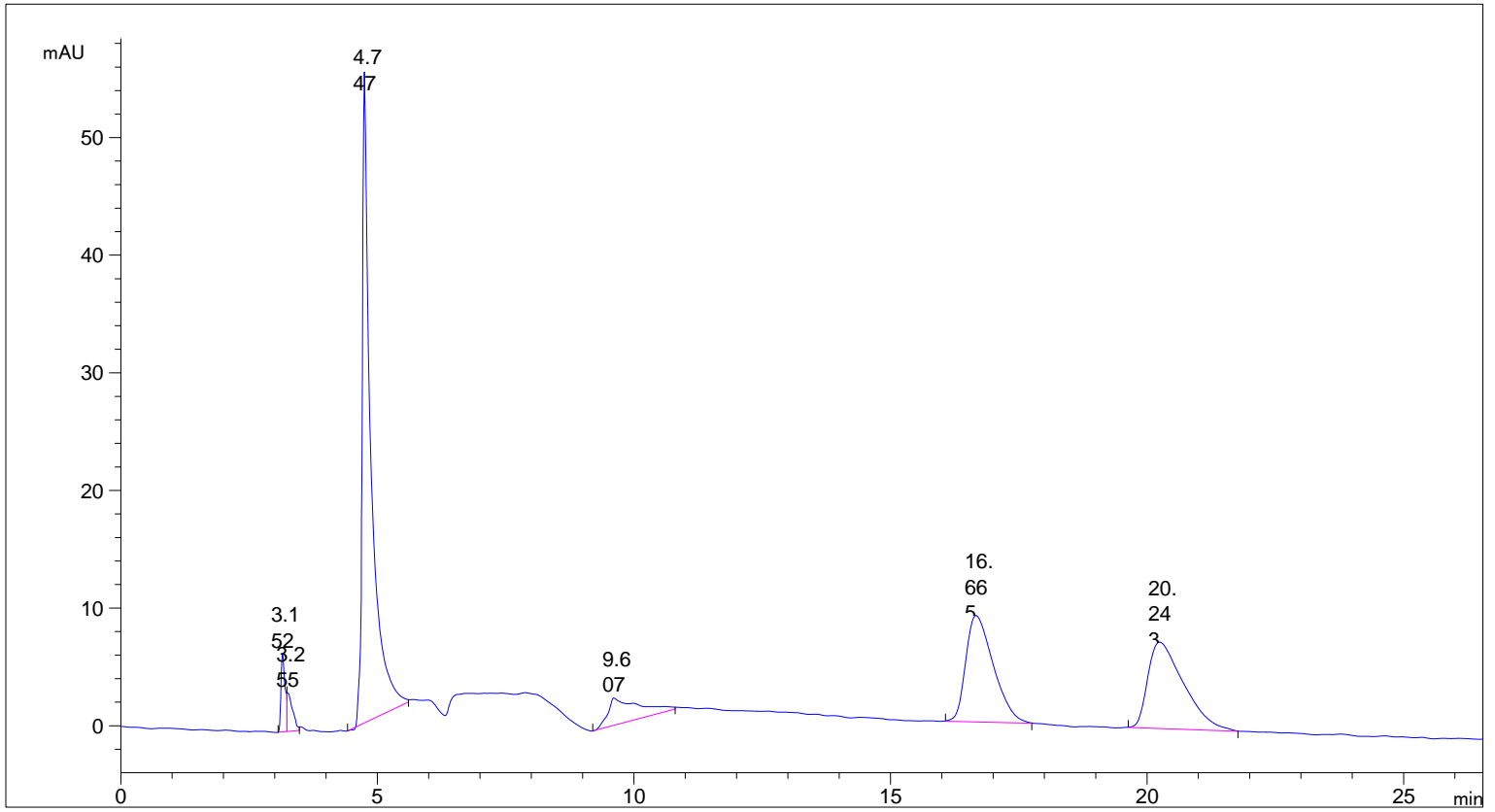
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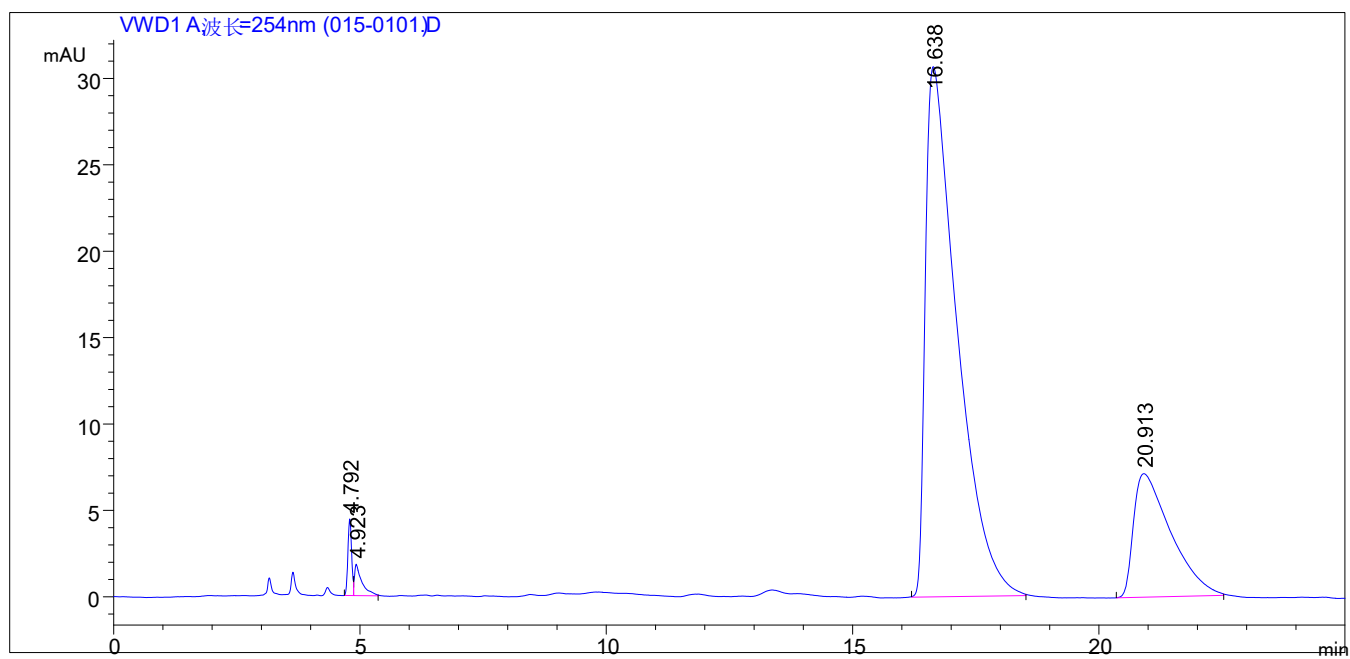


Compound 5a-Et dl



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	16.665	9.05899	338.79767	22.4580
2	20.243	7.34823	356.26523	23.6159

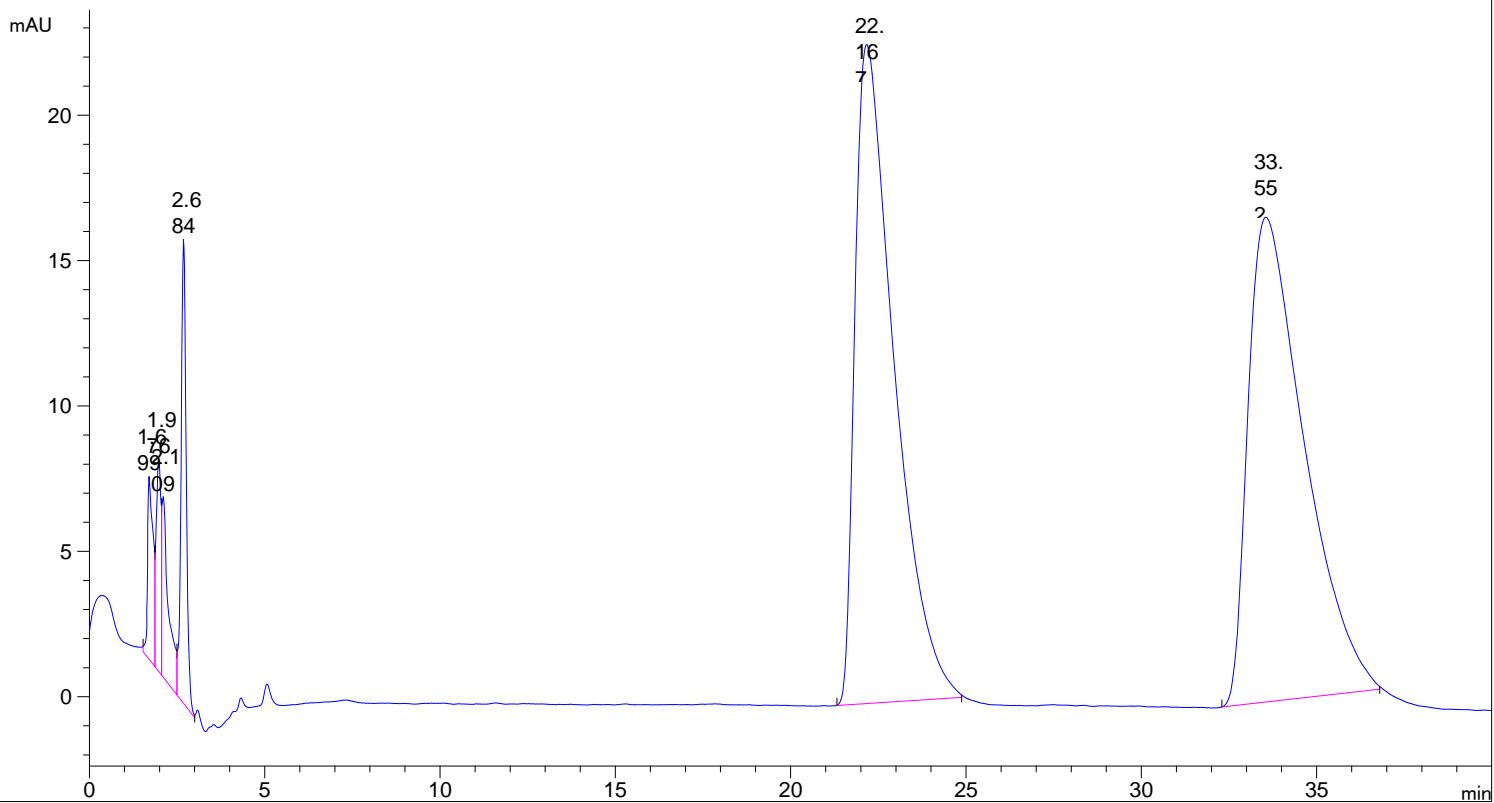
Compound 5a-Et



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	16.638	30.68669	1372.30359	76.6872
2	20.913	7.14394	374.98001	20.9547

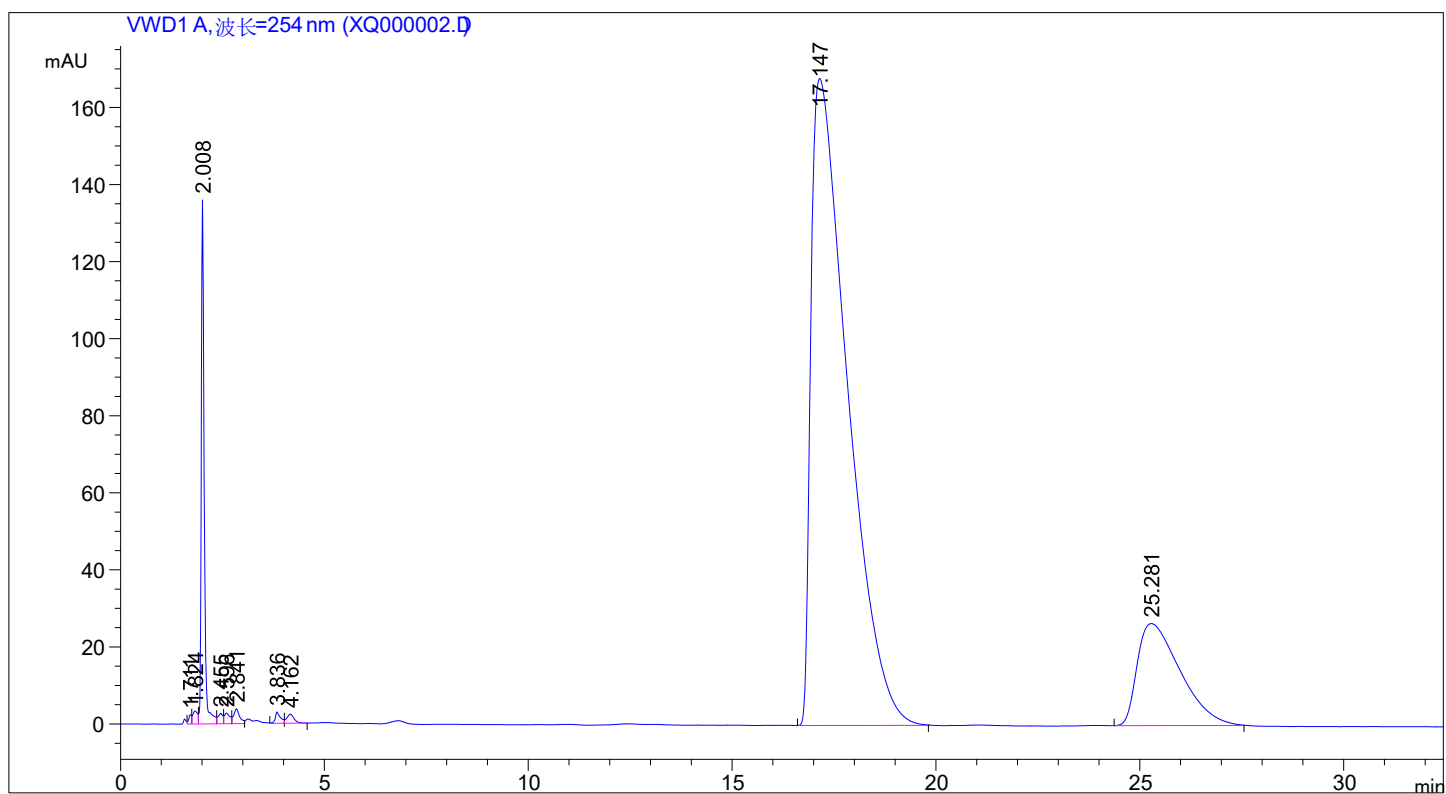
Compound **5a-Bn dl**

VWD1 A, 波长=254 nm (013-0101.D)



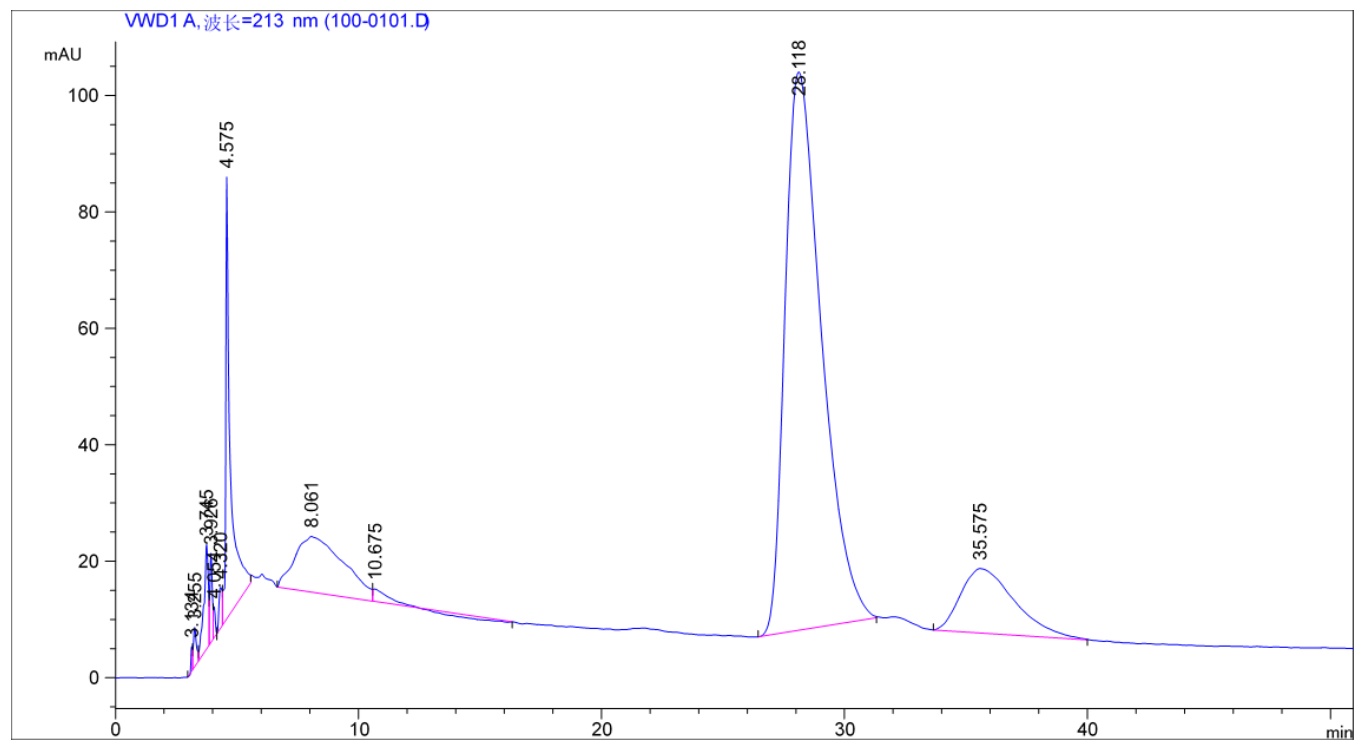
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1	22.167	22.66112	1768.23779	44.0888
2	33.552	16.67373	1859.02771	46.3526

Compound **5a-Bn**

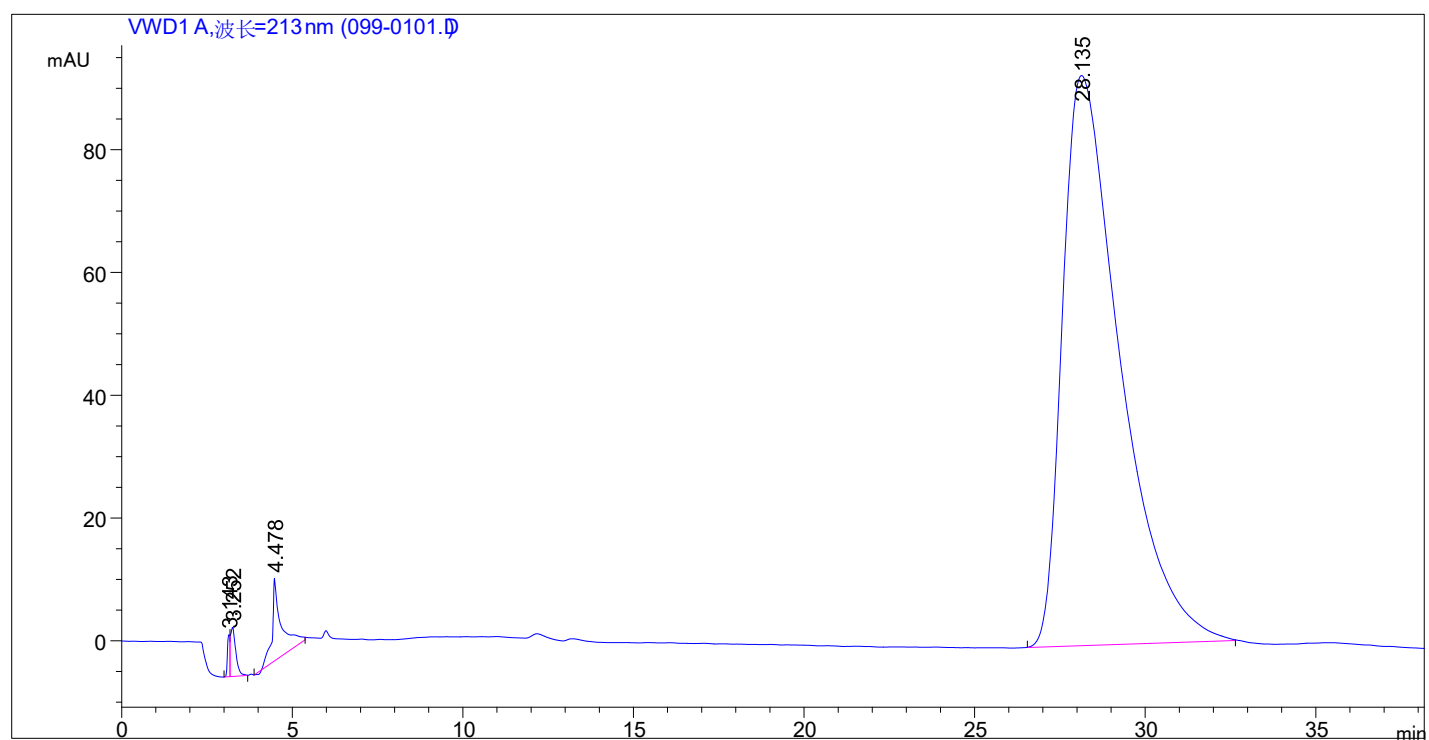


Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	17.147	167.86404	1.04715e4	78.9290
2	25.281	26.47453	1936.24060	14.5945

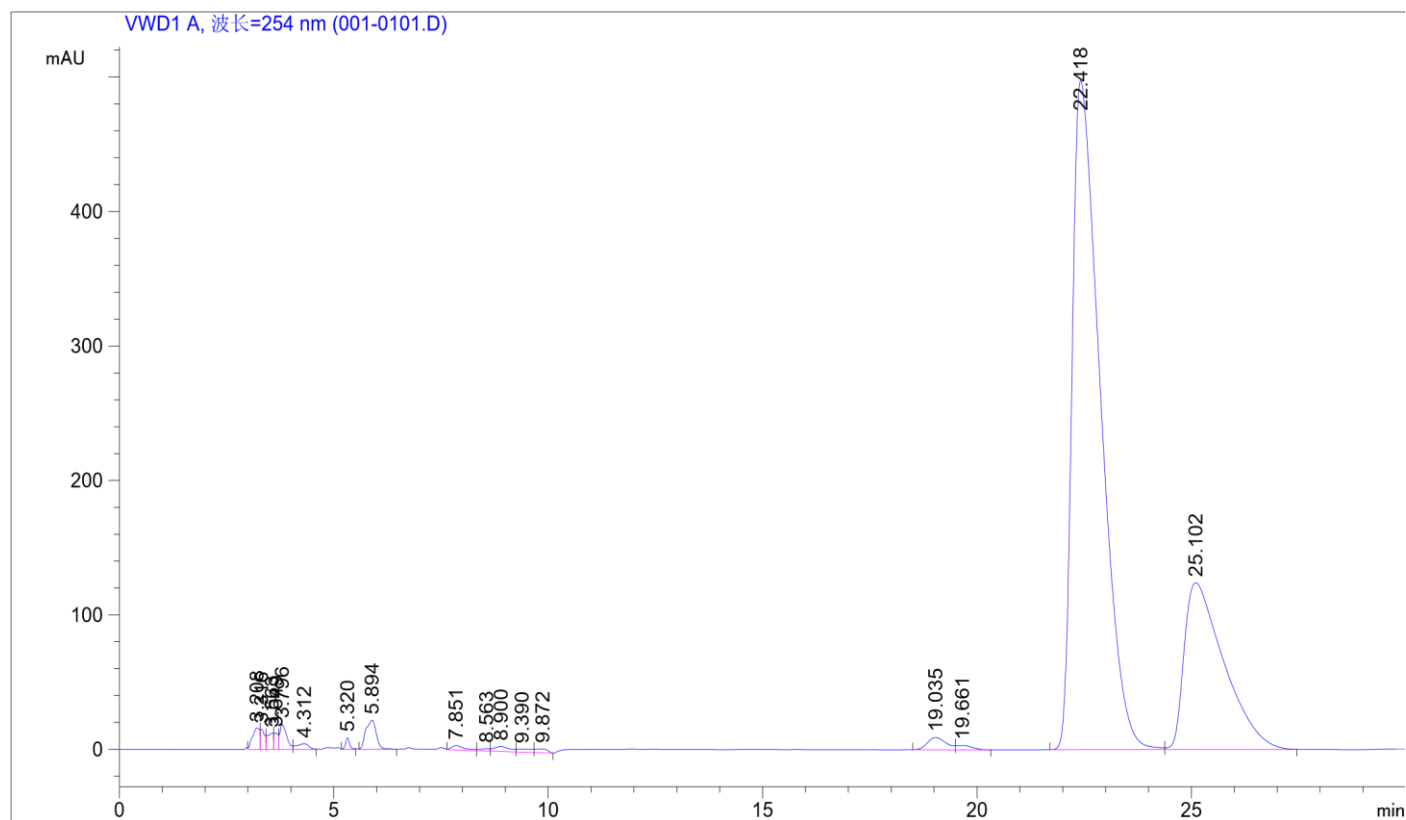
Compound **5a-p-CIBn**



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	28.118	95.91936	9999.09766	68.4824
2	35.575	11.02750	1705.92249	11.6836

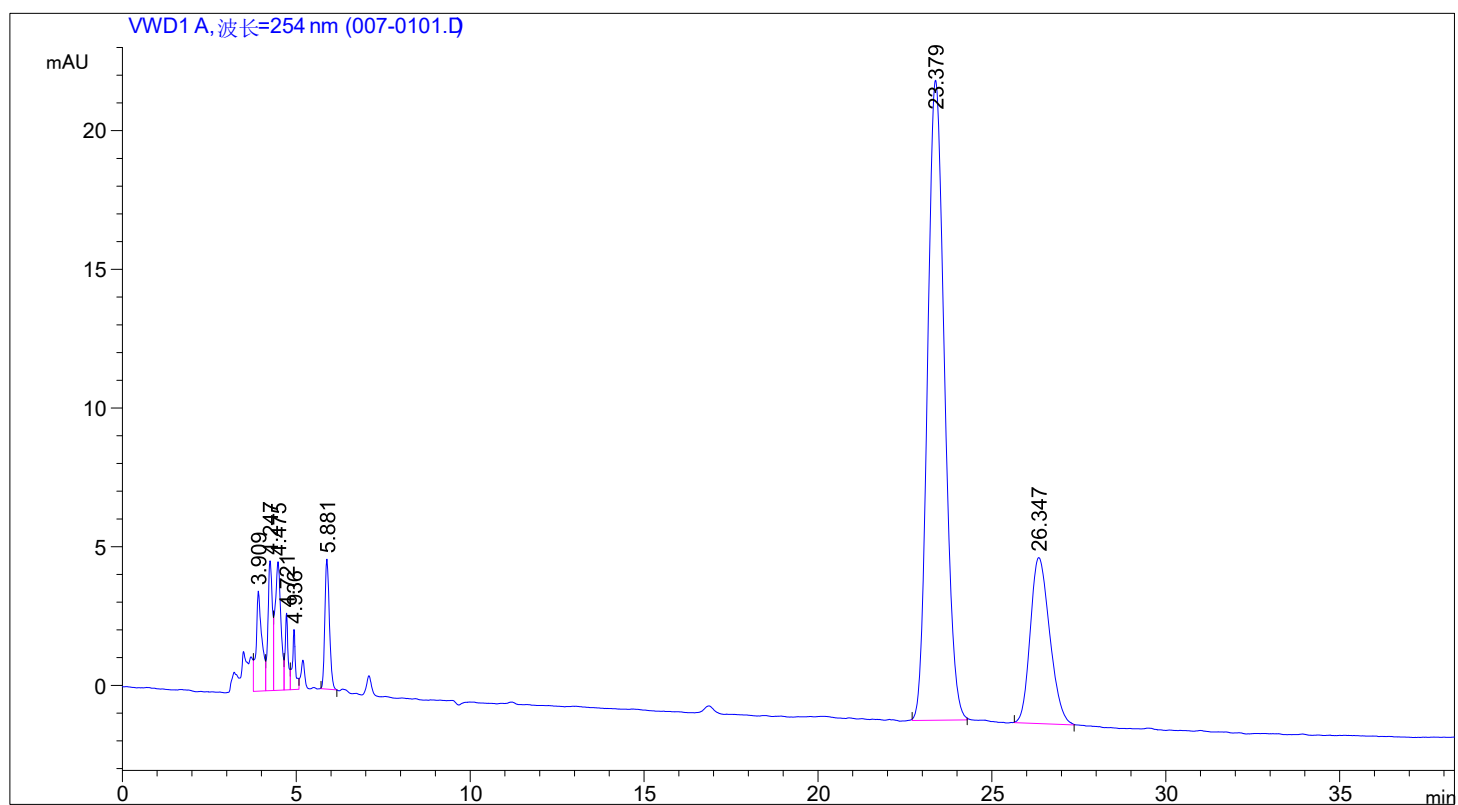


Compound **5b-Bn**



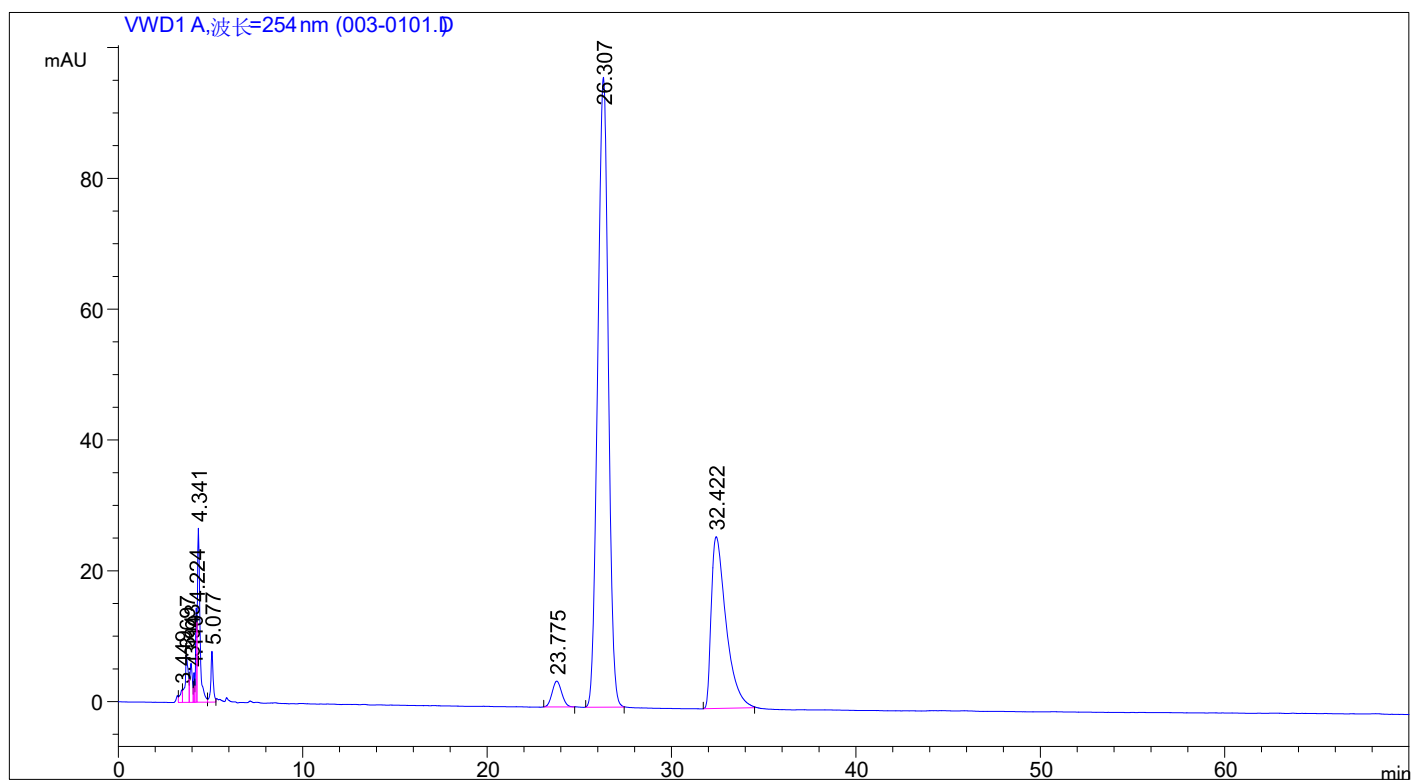
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1	22.418	497.77283	2.26849e4	69.6756
2	25.102	124.07160	7985.82617	24.5282

Compound **5b-p-CIBn**



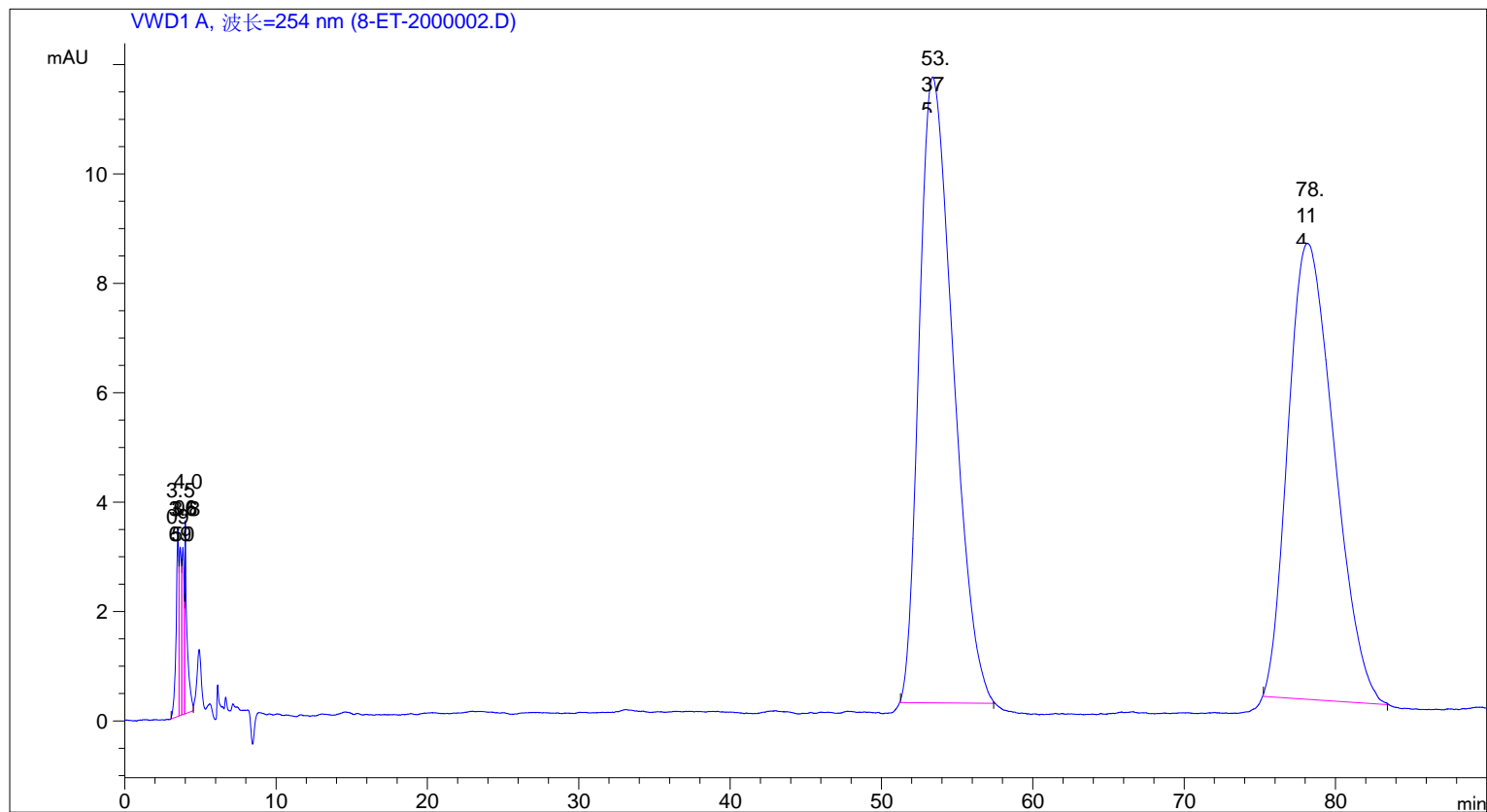
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1	23.379	23.07633	779.43982	63.7475
2	26.347	5.98660	232.08263	18.9812

Compound **5c-Bn**



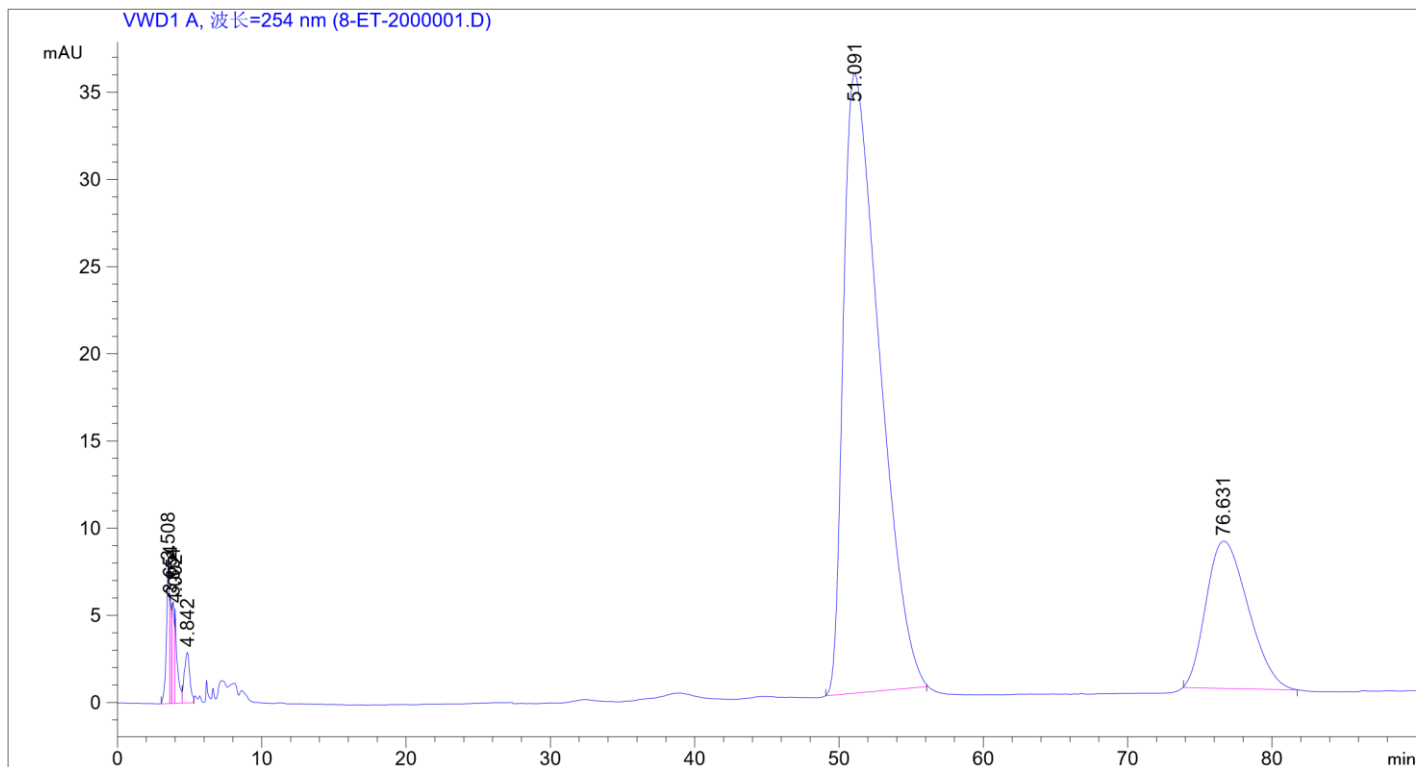
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1	26.307	96.30007	3828.54517	63.6508
2	32.422	26.26961	1466.70081	24.3844

Compound **5d-Et dl**



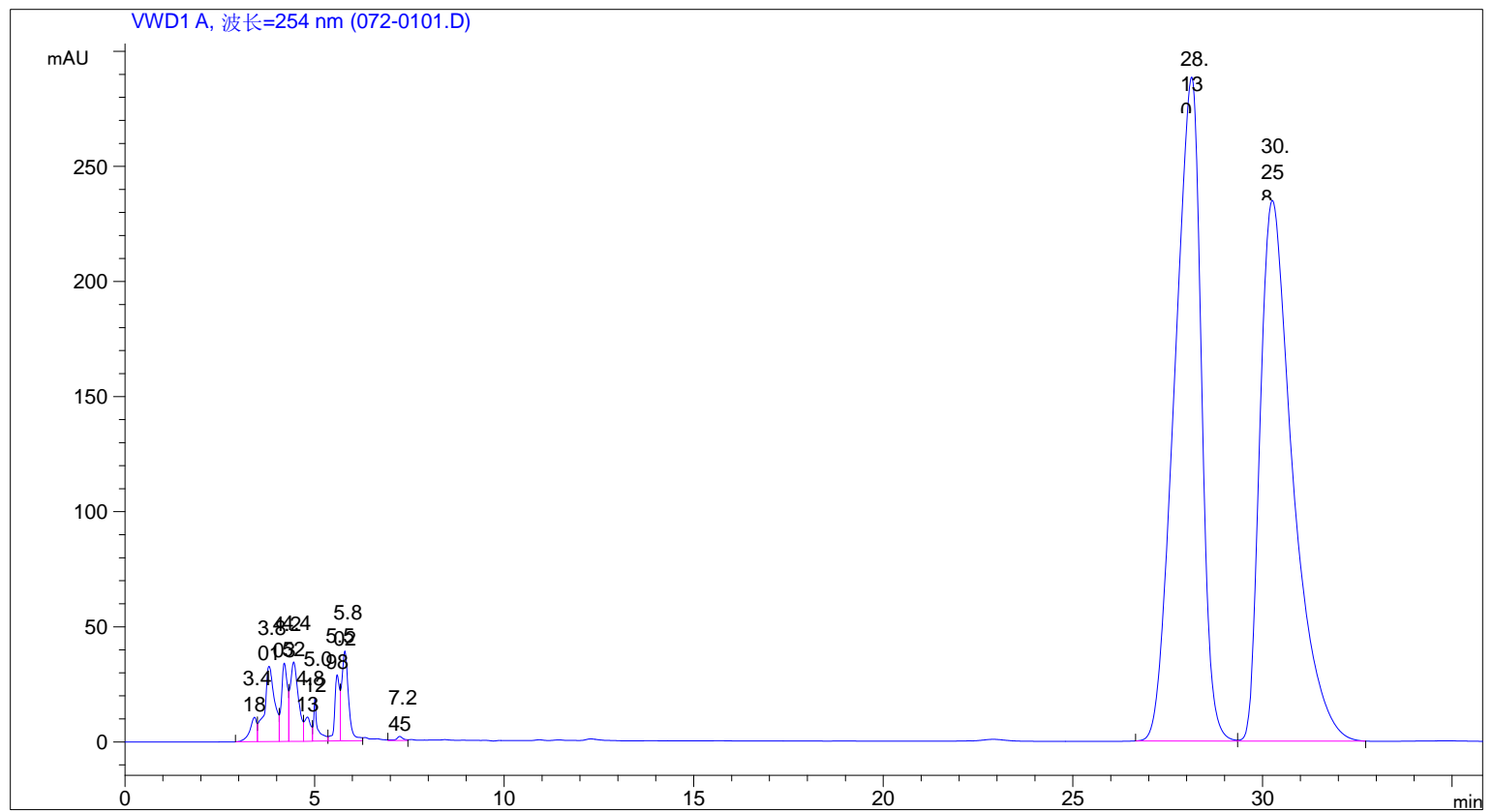
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1	53.375	11.44293	1787.11304	48.4324
2	78.114	8.33517	1763.58191	47.7947

Compound 5d-Et



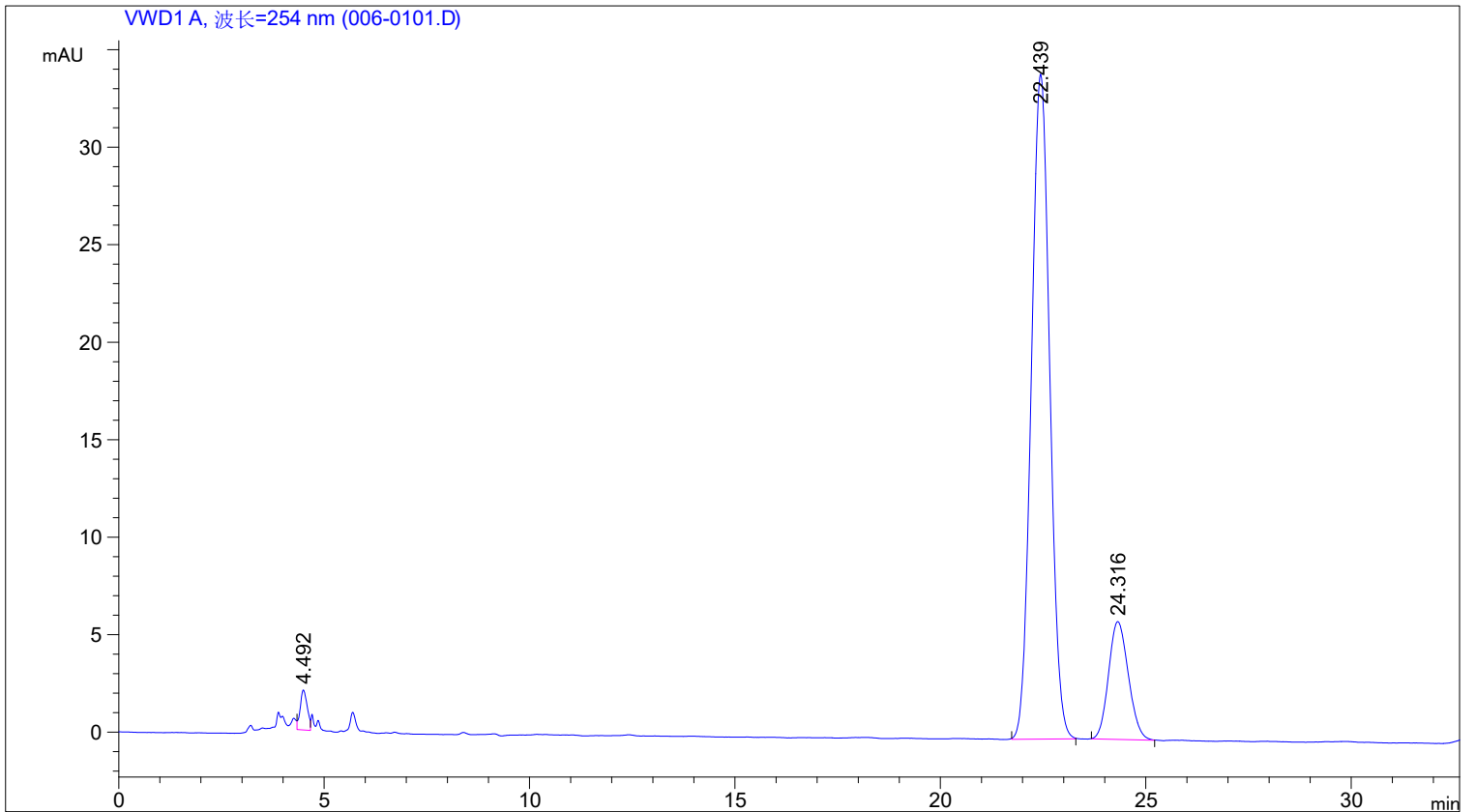
Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Acar [%]
1	51.091	35.53398	6166.01953	74.7797
2	76.631	8.44297	1714.03906	20.7874

Compound **5d-Bn dl**



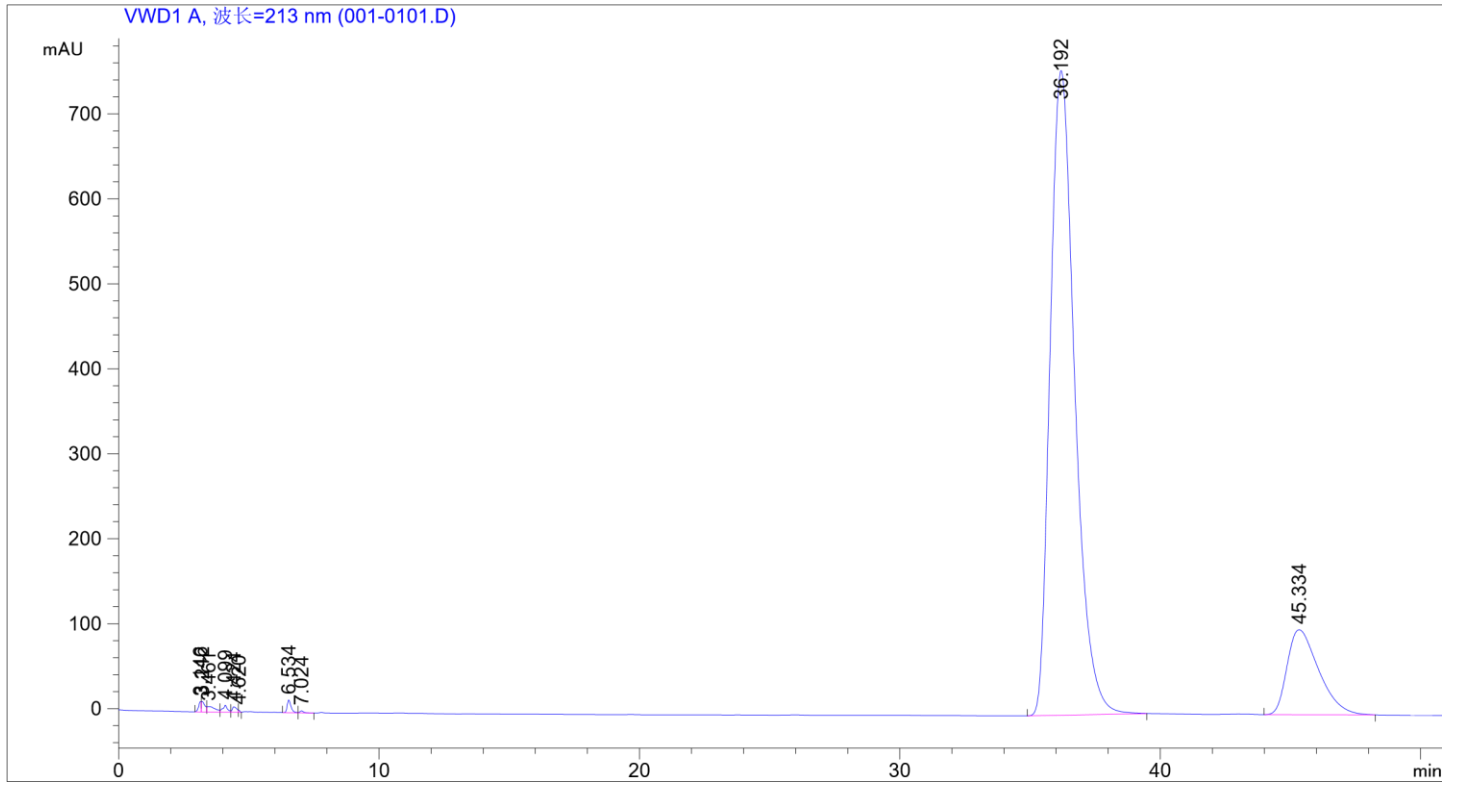
Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	28.130	288.49295	1.40625e4	45.6043
2	30.258	234.95171	1.41093e4	45.7559

Compound **5d-Bn**



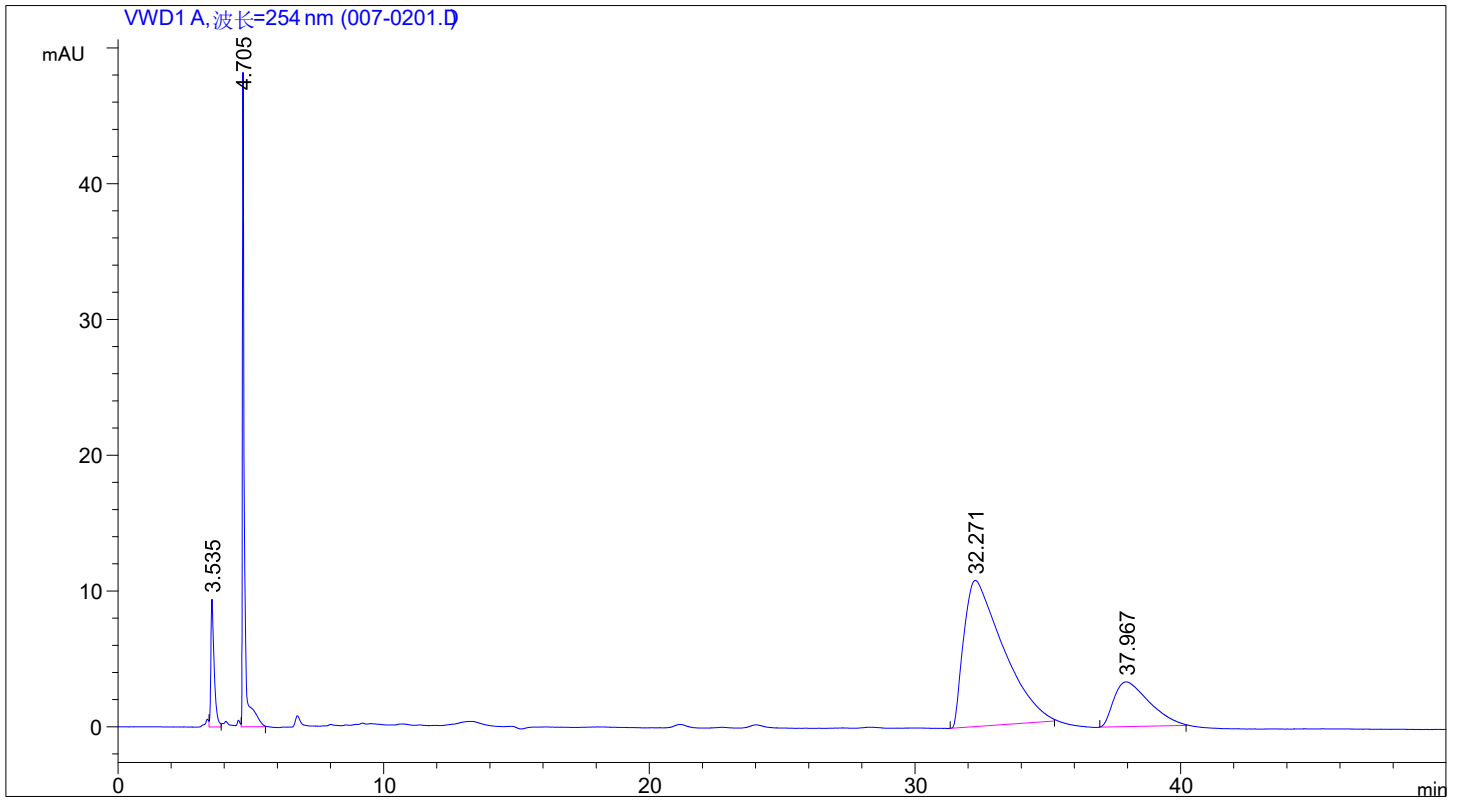
Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	22.439	34.10795	1060.89453	82.4073
2	24.316	6.04603	201.99294	15.6902

Compound **5d-p-CIBn**



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	36.192	758.66632	4.96948e4	84.4757
2	45.334	100.00033	8434.26563	14.3373

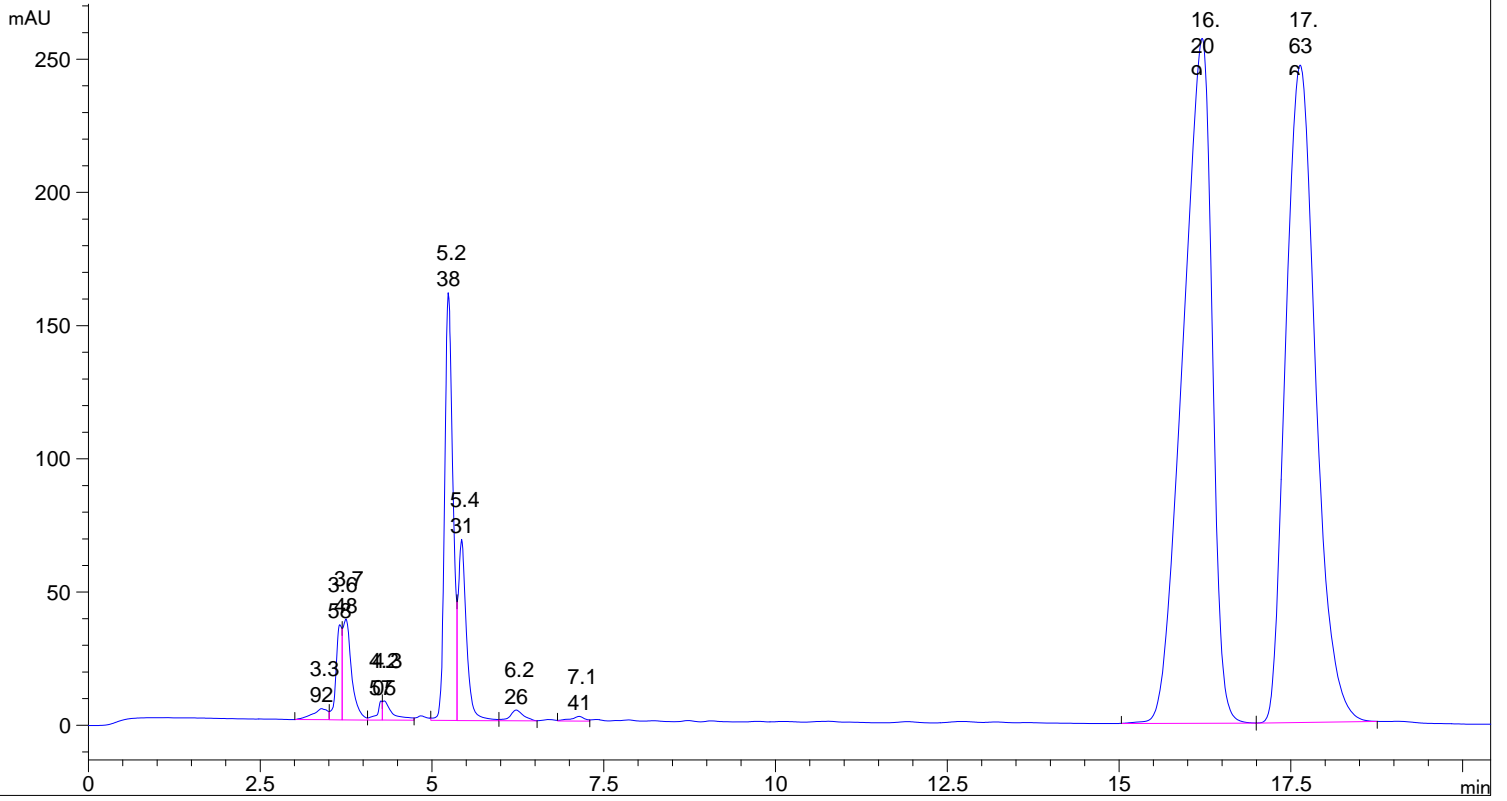
Compound 5e-Et



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	32.271	10.76539	1109.67090	63.9755
2	37.967	3.29769	305.14505	17.5924

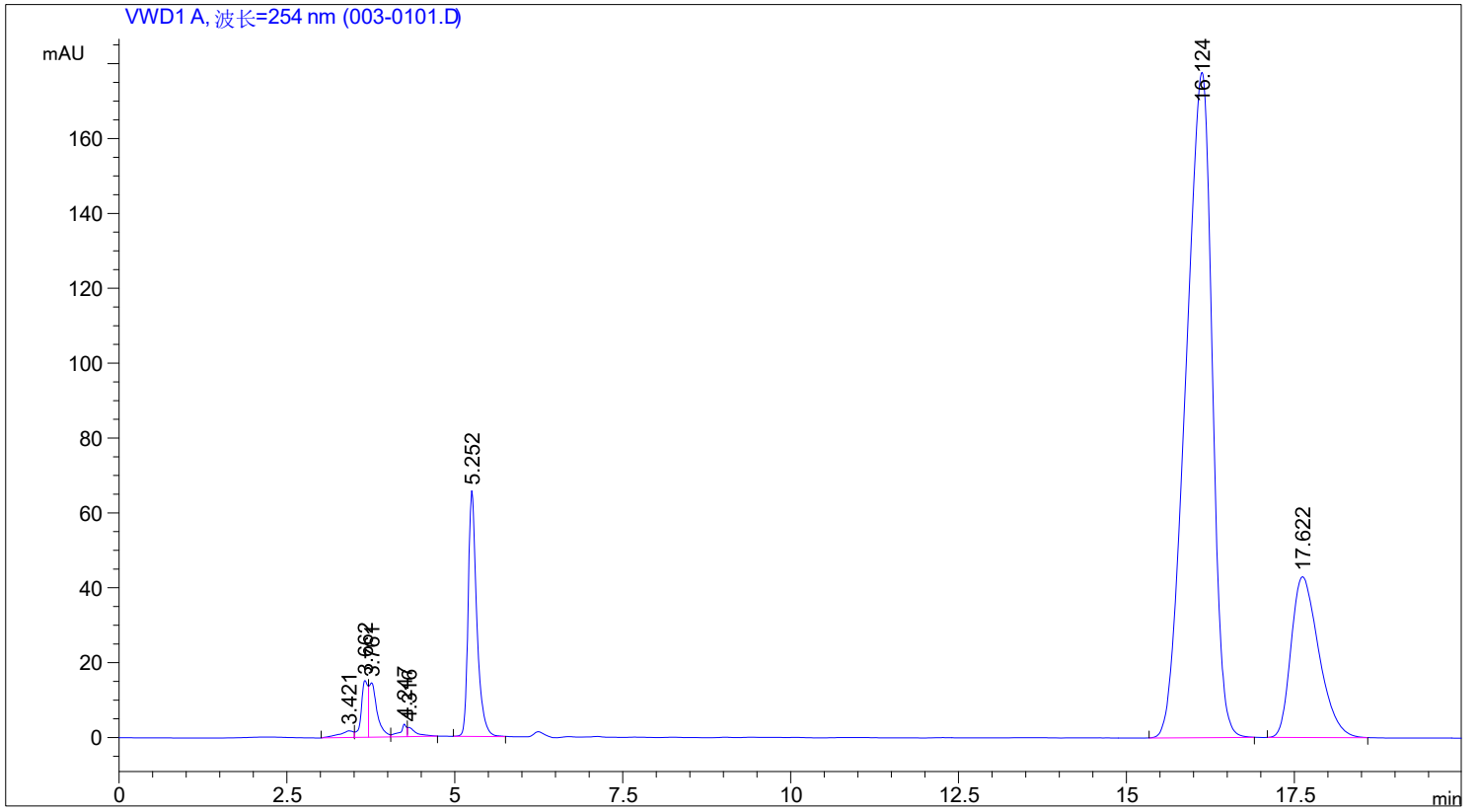
Compound **5e-Bn dl**

VWD1 A, 波长=254 nm (001-0101.D)



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	16.209	257.02286	7578.80127	42.6564
2	17.636	246.73605	7490.40723	42.1588

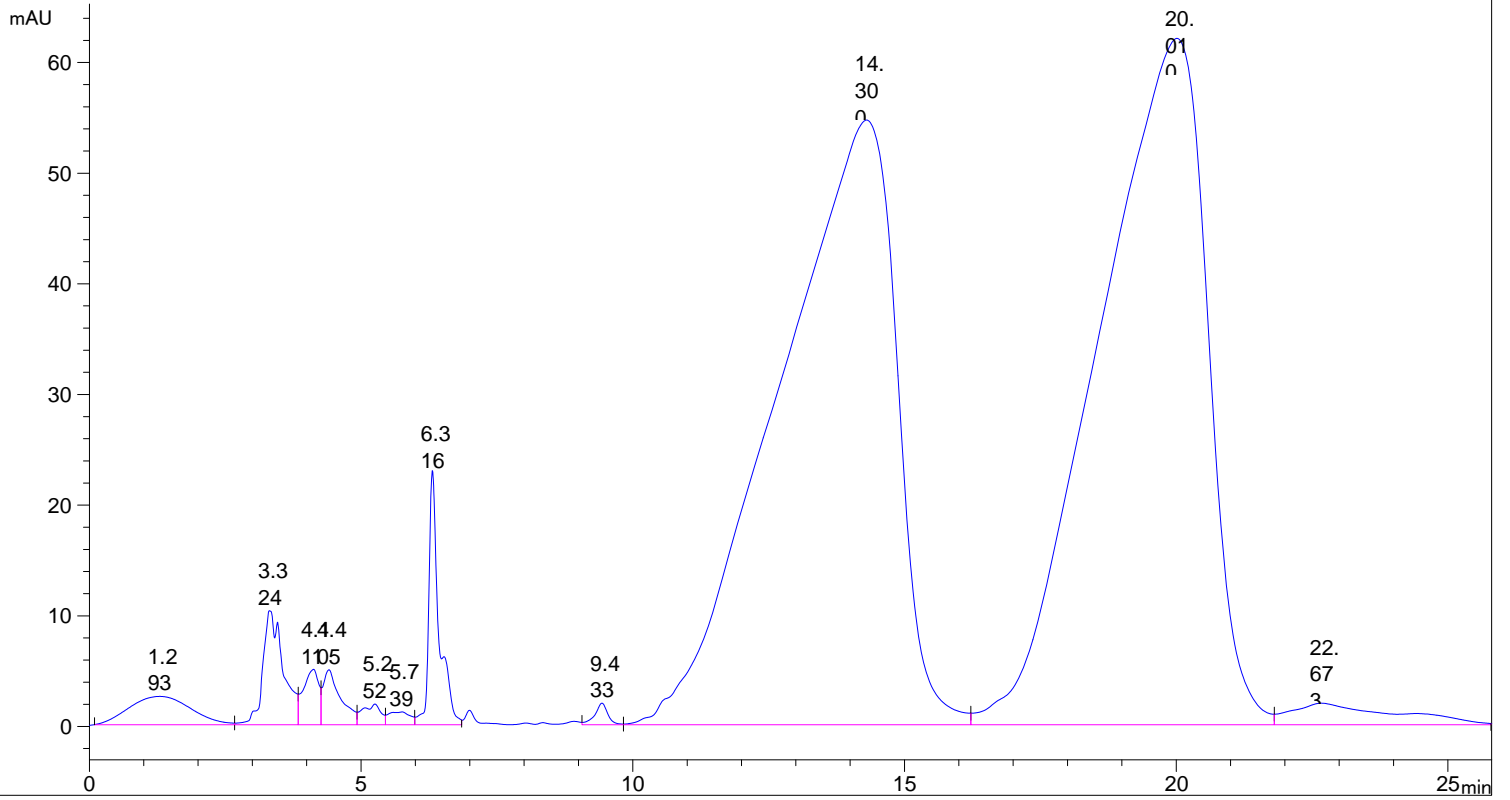
Compound **5e-Bn**



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	16.124	177.72337	4824.42041	69.4815
2	17.622	42.93740	1236.37244	17.8063

Compound **5f-Bn dl**

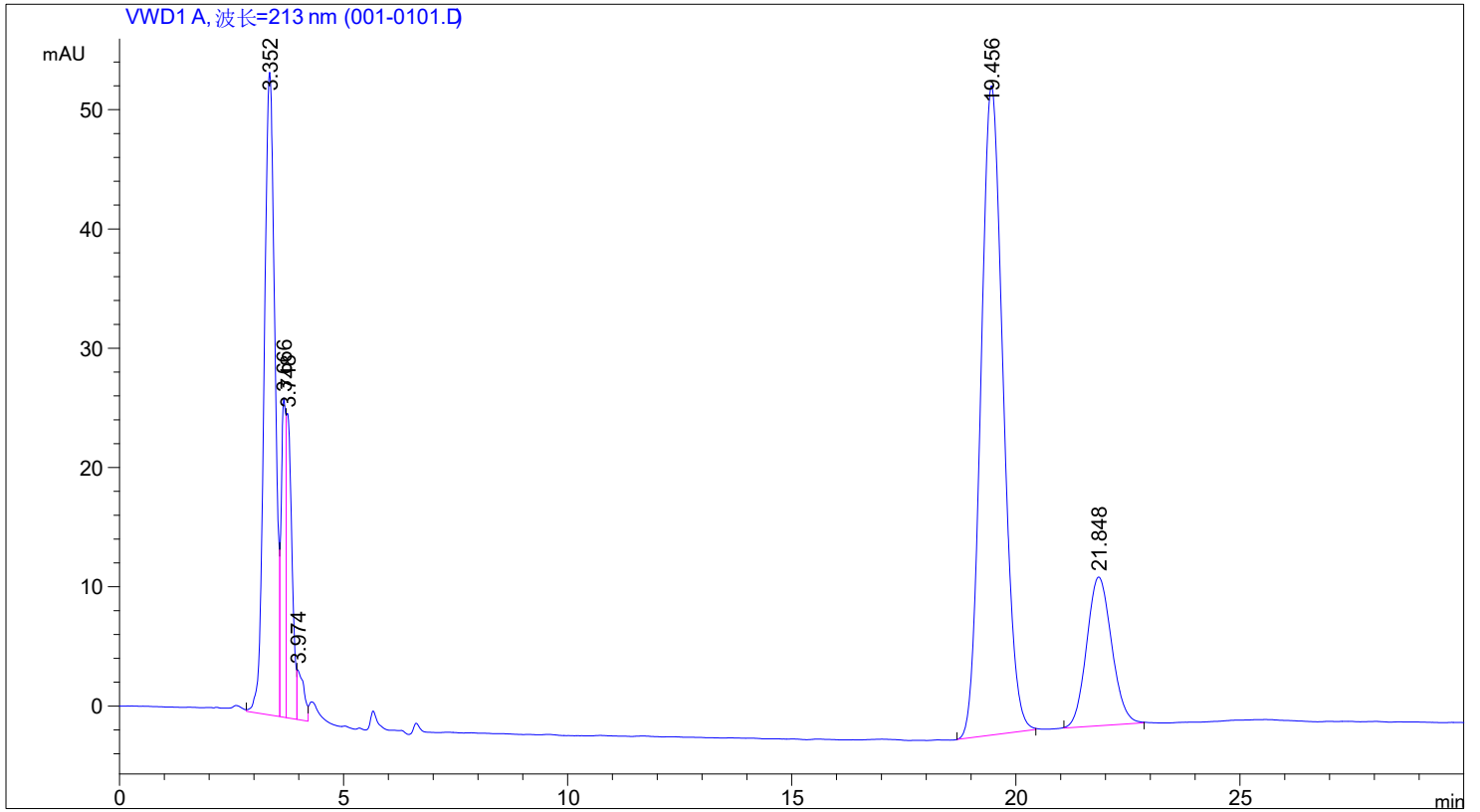
VWD1 A, 波长=254 nm (DEF_LC 2006-01-27 04-37-11\041-0101.D)



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	14.300	54.62917	8240.16113	45.2494
2	20.010	62.01163	8626.79785	47.3726

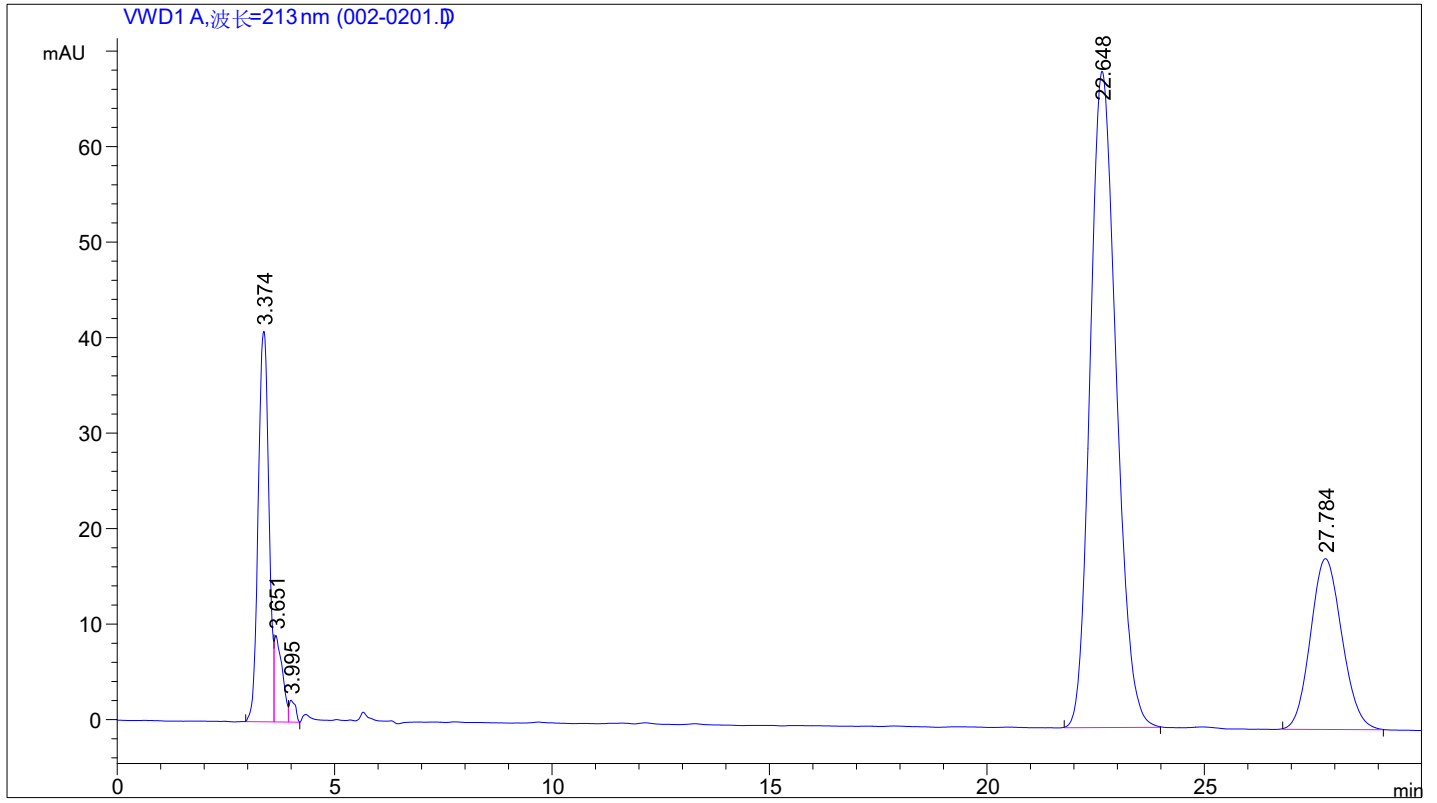
Compound **5f-Bn**

VWD1 A, 波长=213 nm (001-0101.D)



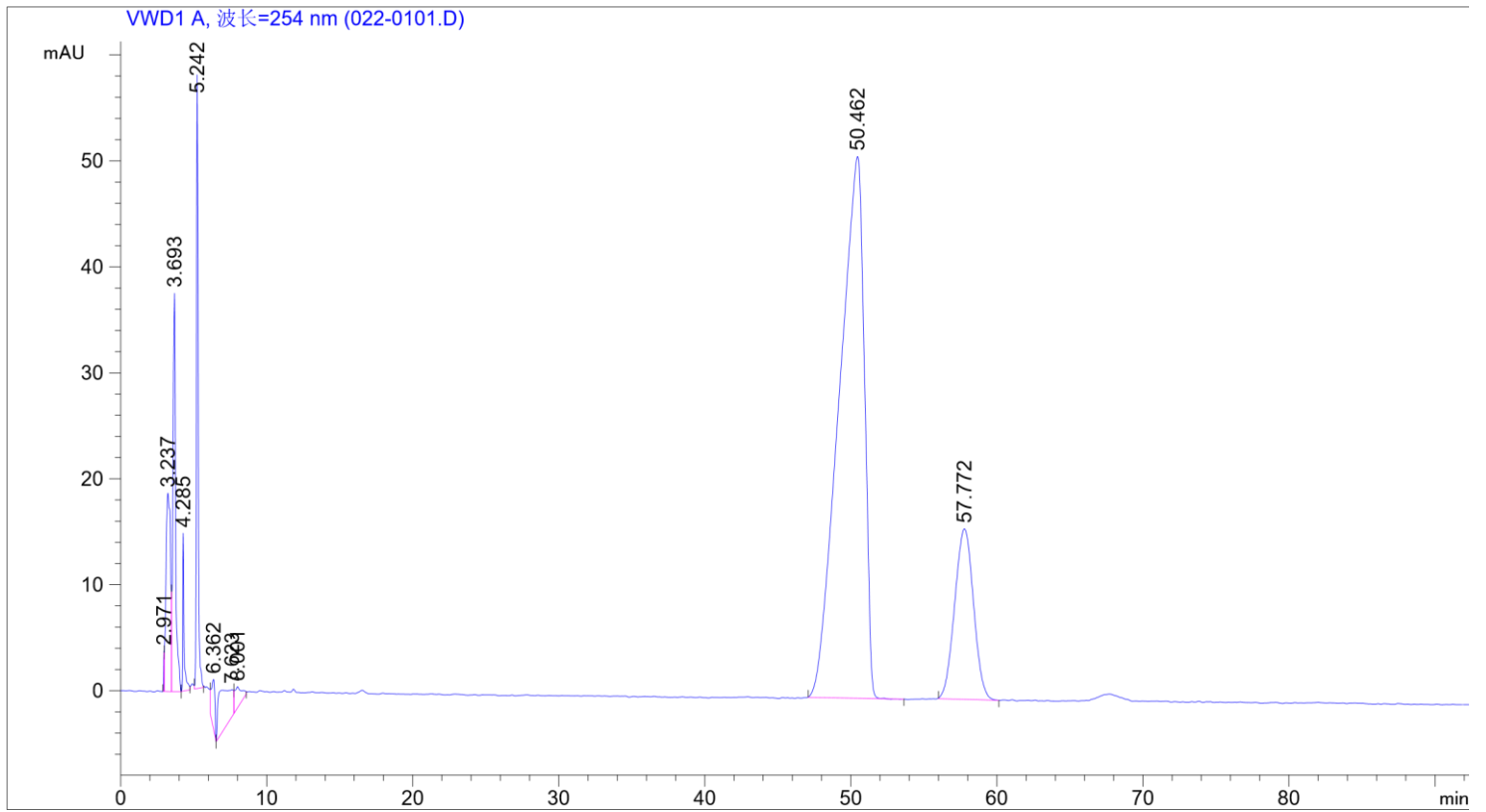
Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	19.456	54.43020	1869.71924	50.3427
2	21.848	12.47171	481.57748	12.9666

Compound **5f-p-CIBn**



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	22.648	68.70069	2864.91846	62.3241
2	27.784	17.8804	899.32349	19.5641

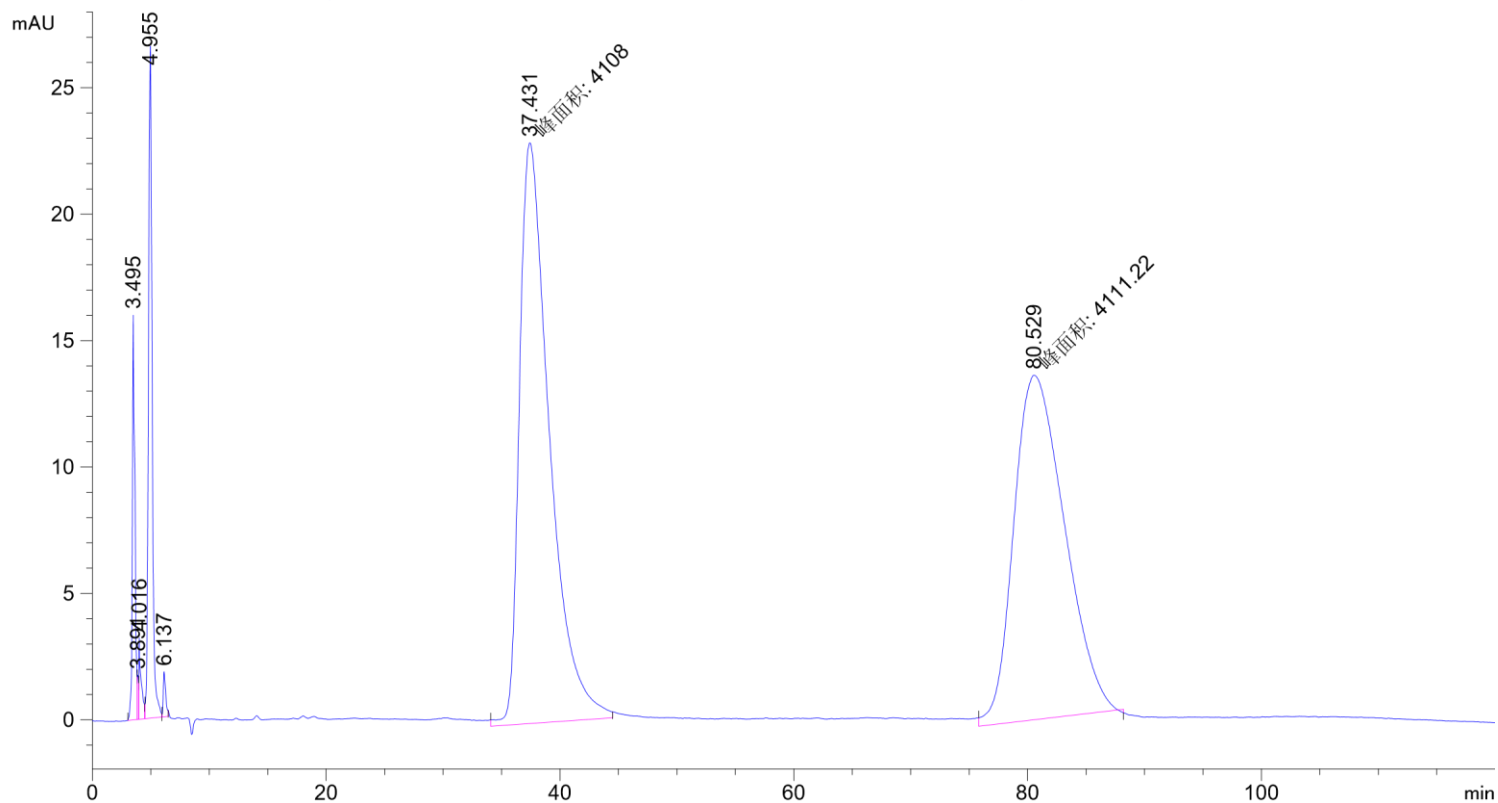
Compound **5g-p-CIBn**



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	50.462	51.12057	6106.41260	64.8842
2	57.772	16.08788	1445.99084	15.3645

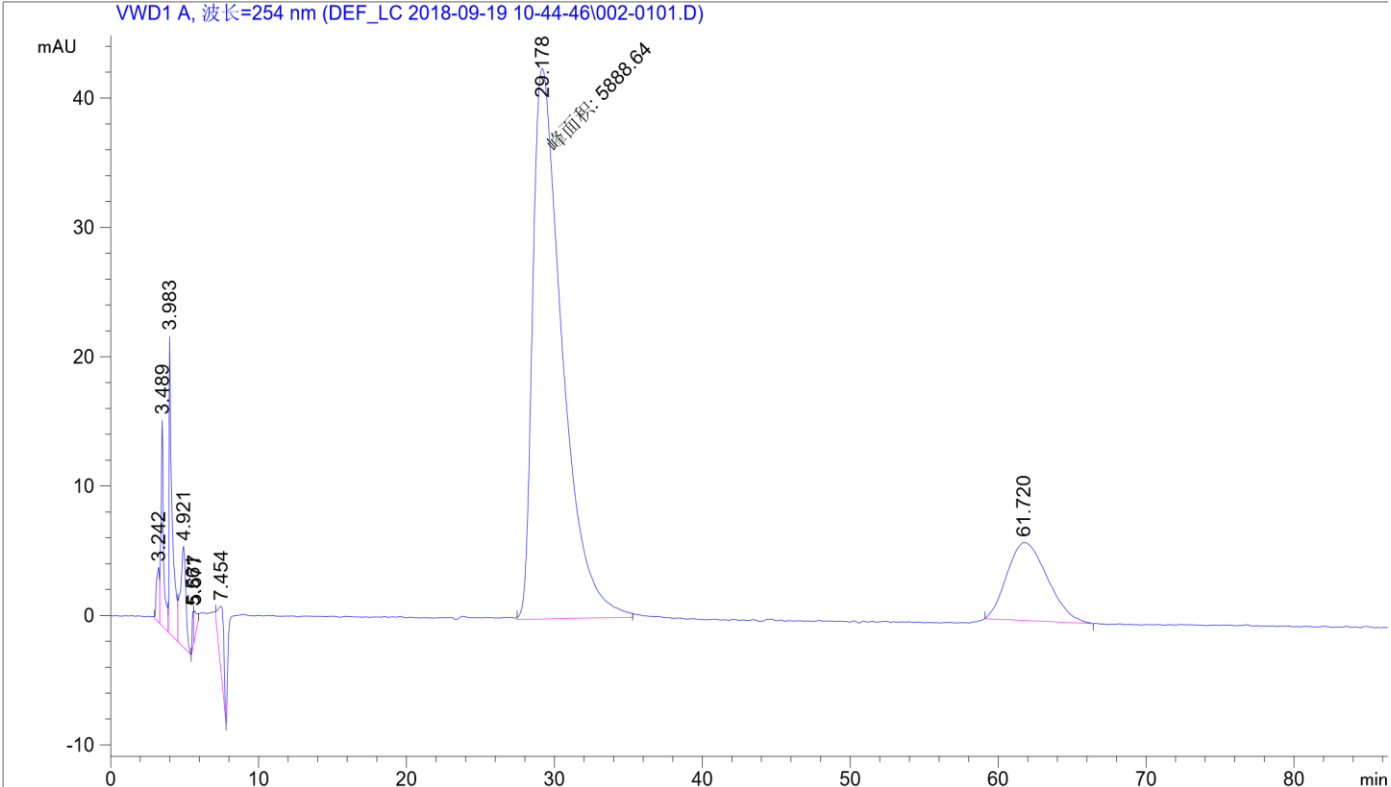
Compound **5h-Bn dl**

VWD1 A, 波长=254 nm (C:\CHEM32\1\DATA\XQ\DEF_LC 2018-07-11 17-39-26\8-ET-2000001.D)



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	37.431	22.96922	4107.99951	44.9871
2	80.529	13.63098	4111.21924	45.0223

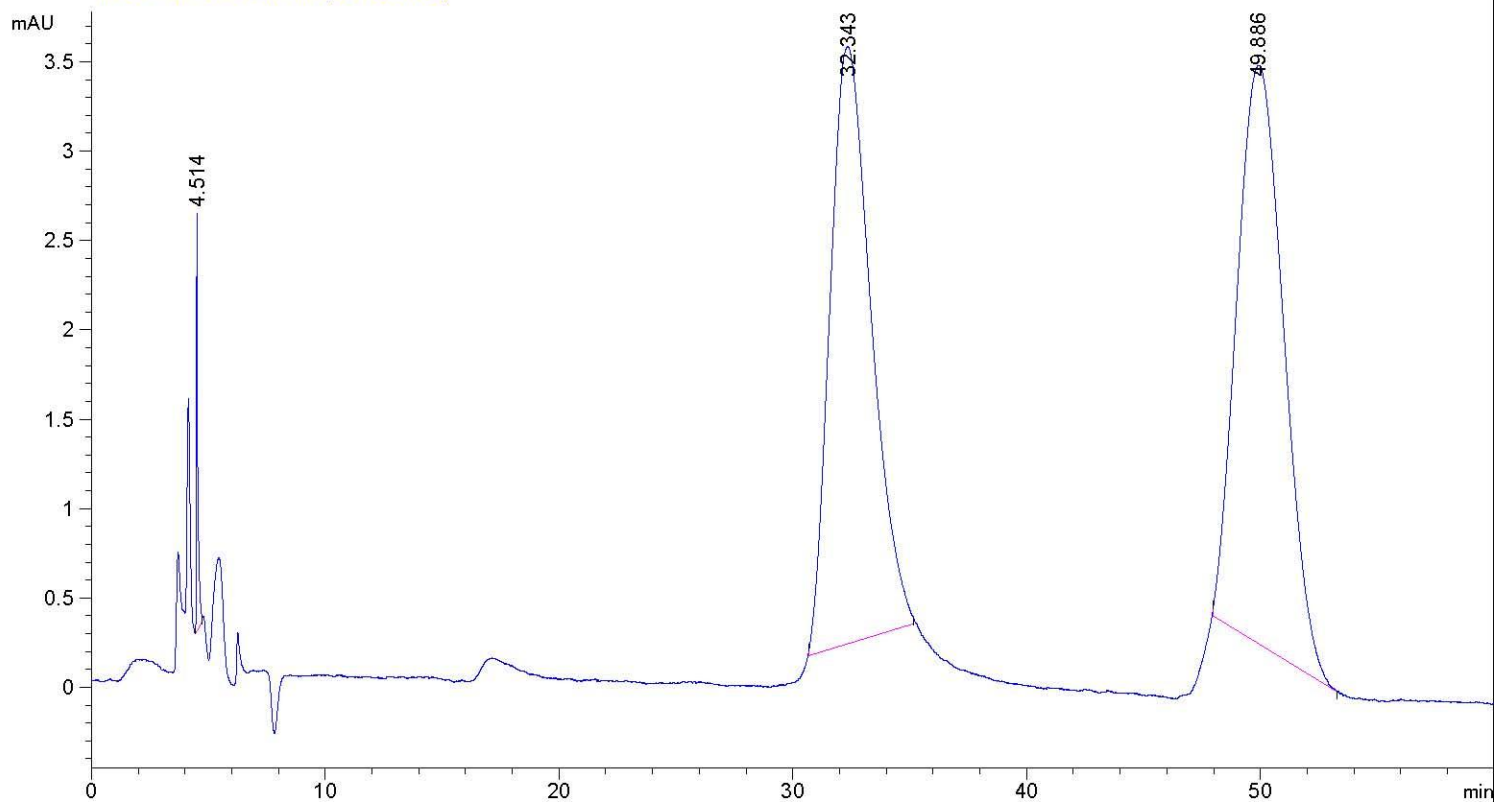
Compound **5h-Bn**



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	29.178	42.57212	5888.64355	73.7024
2	61.720	6.01482	1146.58789	14.3507

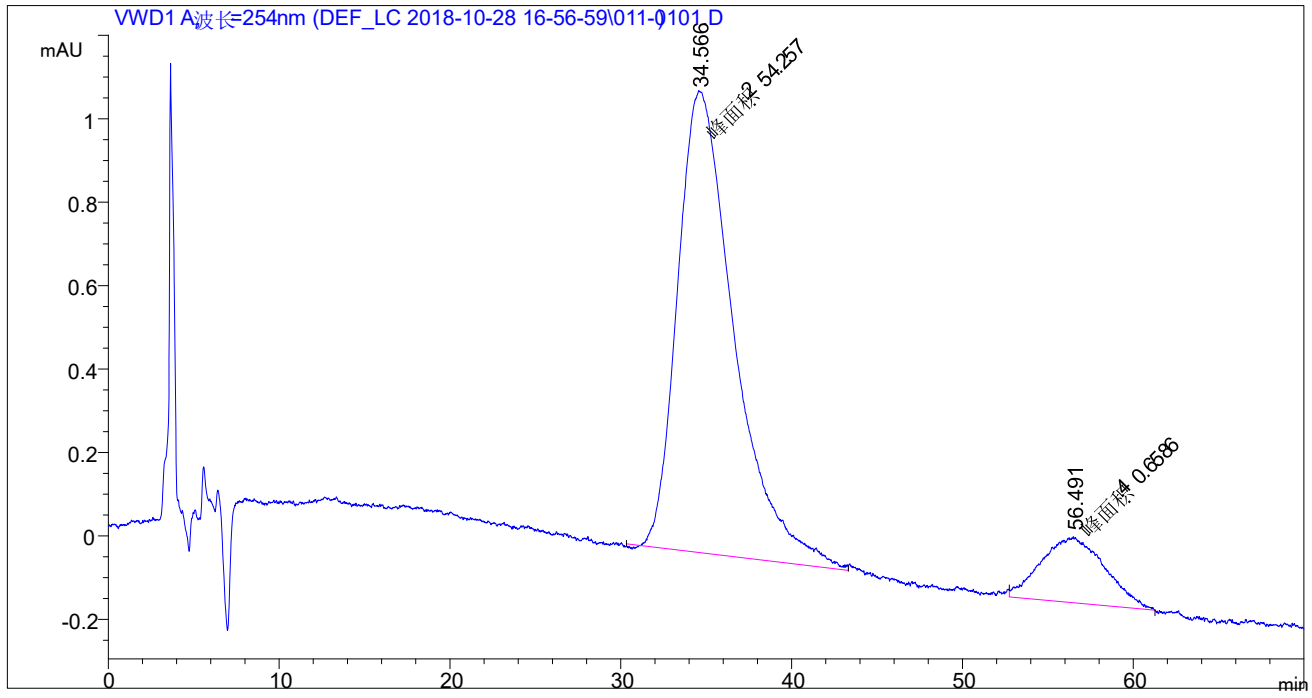
Compound **5h-p-CIBn dl**

VWD1 A, 波长=254 nm (001-0201.D)

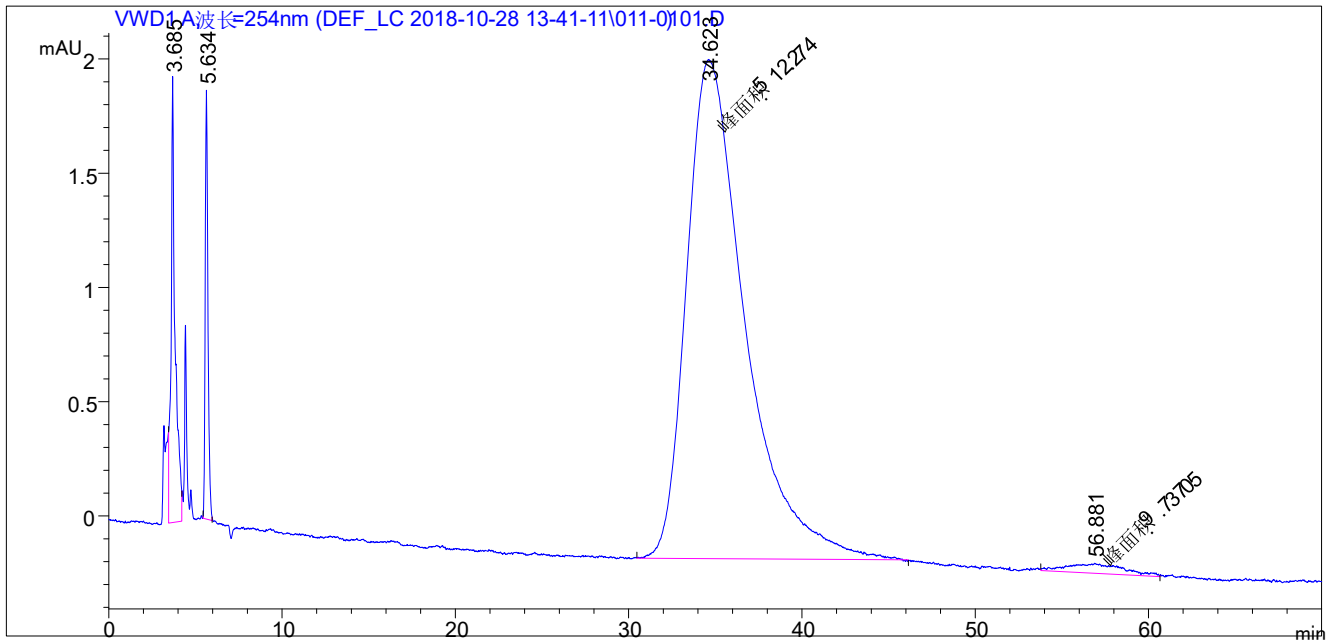


Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	32.343	3.34417	408.73773	47.1587
2	49.886	3.23238	448.21954	51.7140

Compound **5h-p-CIBn**



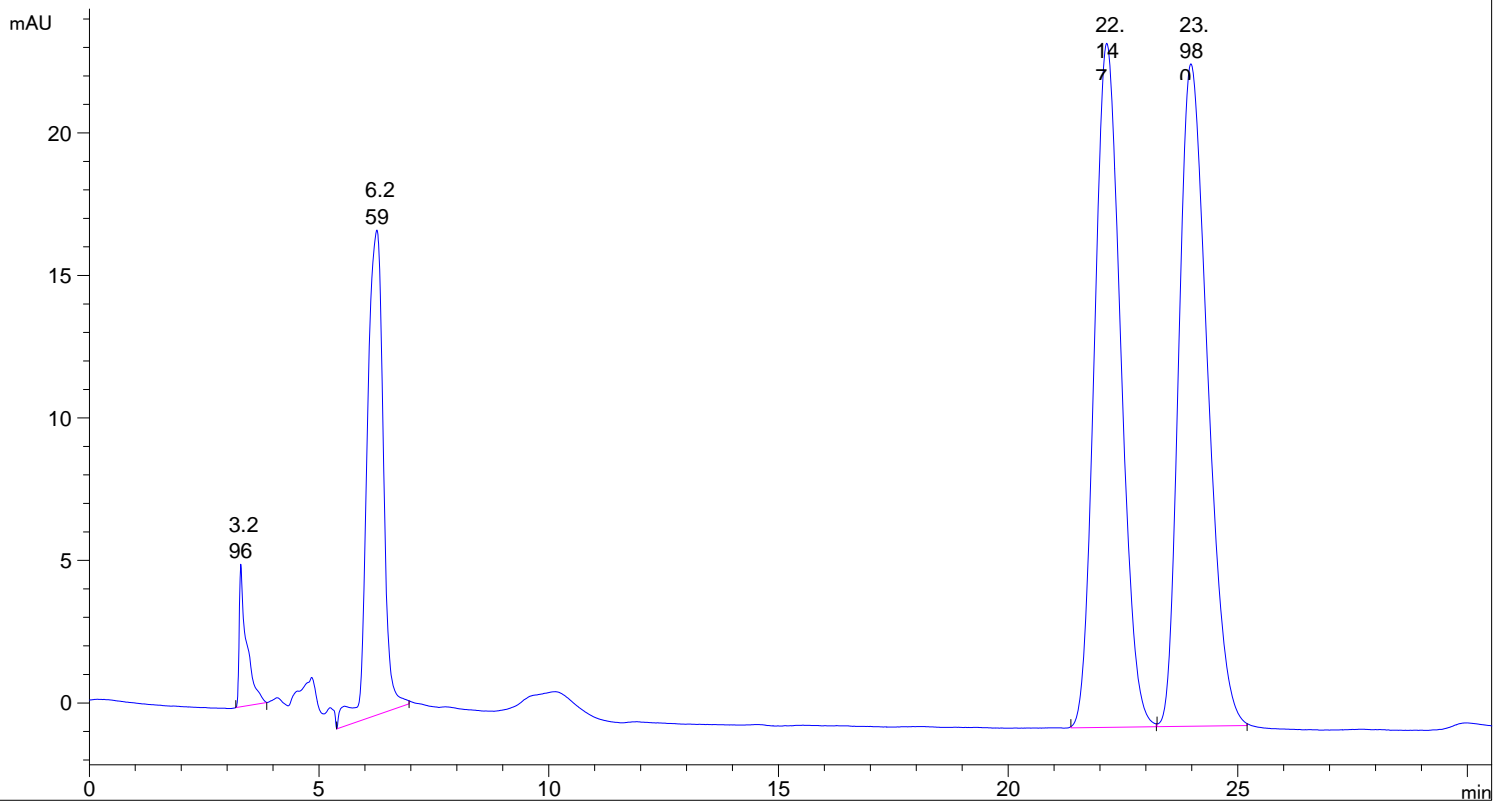
Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	34.566	1.10731	254.25696	86.2135
2	56.491	1.58646e-1	40.65862	13.7865



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	34.623	2.18480	512.27380	89.1234
2	56.881	4.43100e-2	9.73705	1.6940

Compound **5l-Bn dl**

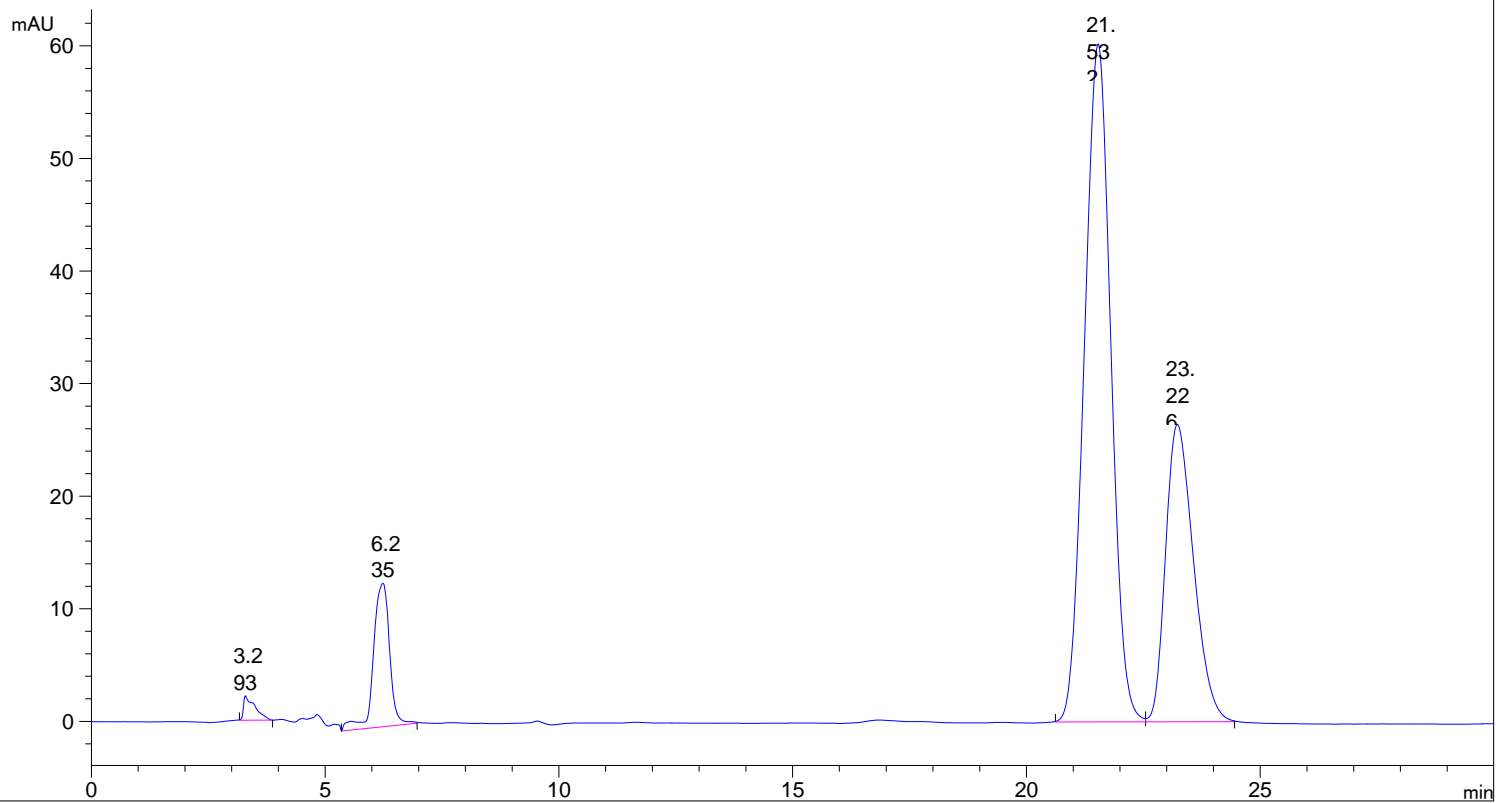
VWD1 A, 波长=254 nm (002-0101.D)



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	22.147	24.00043	958.59290	39.2928
2	23.980	23.24430	1006.06158	41.2385

Compound 5I-Bn Cat

VWD1 A, 波长=254 nm (001-0101.D)



Peak	Ret Time [min]	Height [mV*sec]	Area [mV]	Aear [%]
1	21.532	60.22359	2365.11938	62.0958
2	23.226	26.42085	1097.69263	28.8198