

Supplementary Information for:

**Rhodium-Catalyzed Enantioselective 1,2-Addition of Arylboronic
Acids to Heteroaryl α -Ketoesters for Synthesis of Heteroaromatic
 α -Hydroxy Esters**

Hui Wang, Ting-Shun Zhu, and Ming-Hua Xu*

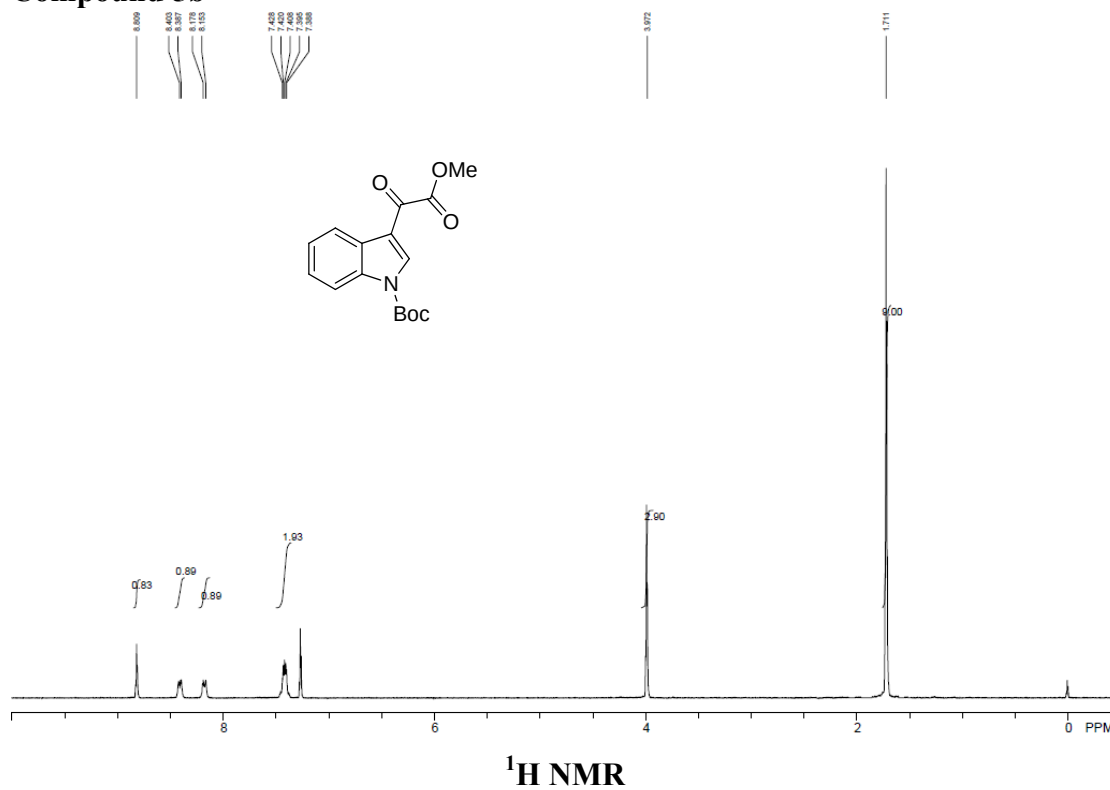
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555 Zuchongzhi Road, Shanghai 201203*

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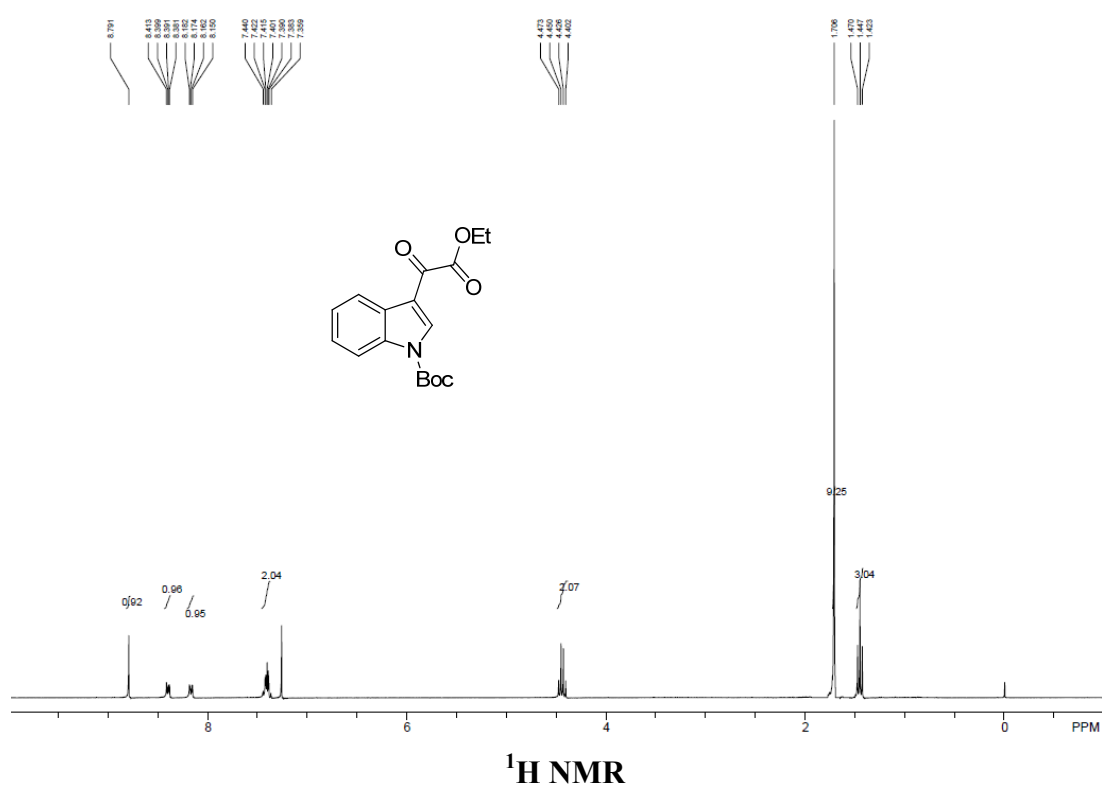
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Compound 5b



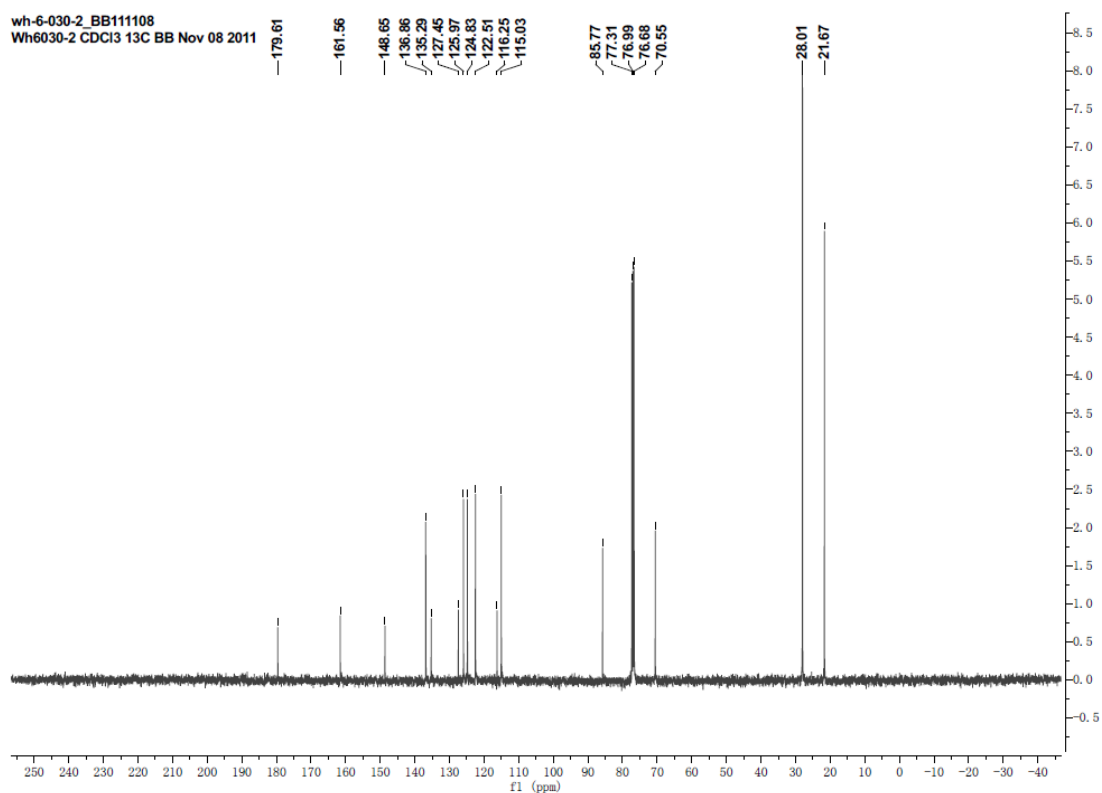
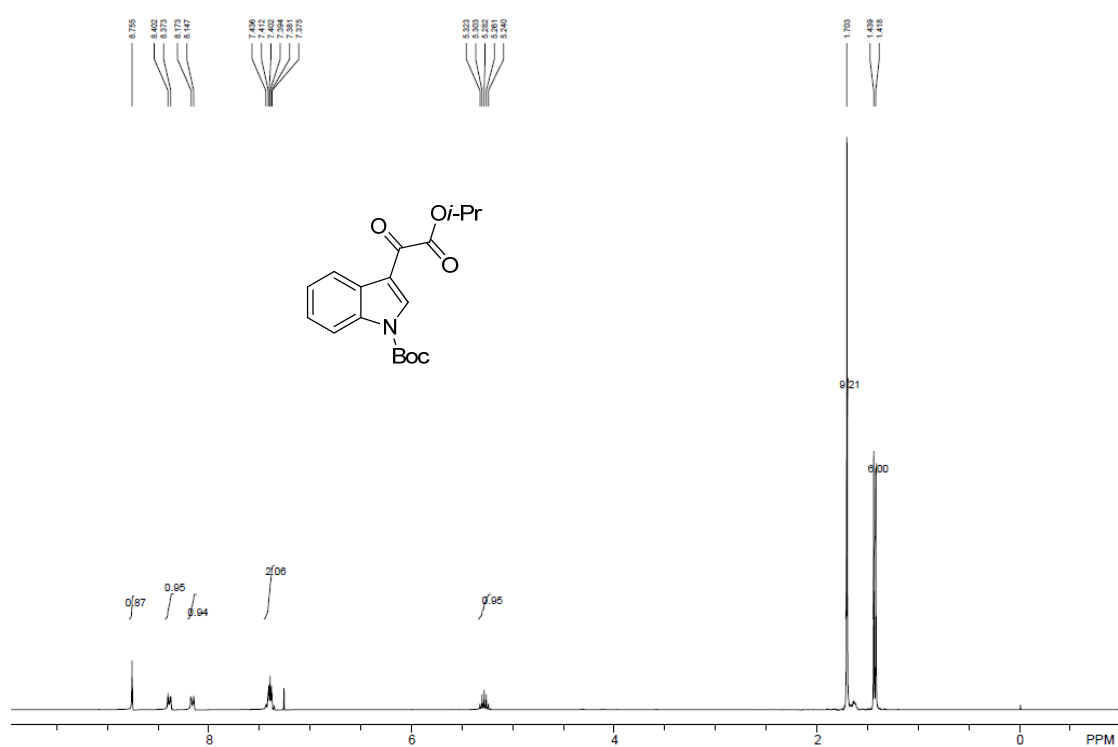
Ref: *J. Am. Chem. Soc.* **2007**, 129, 13794.

Compound 5c

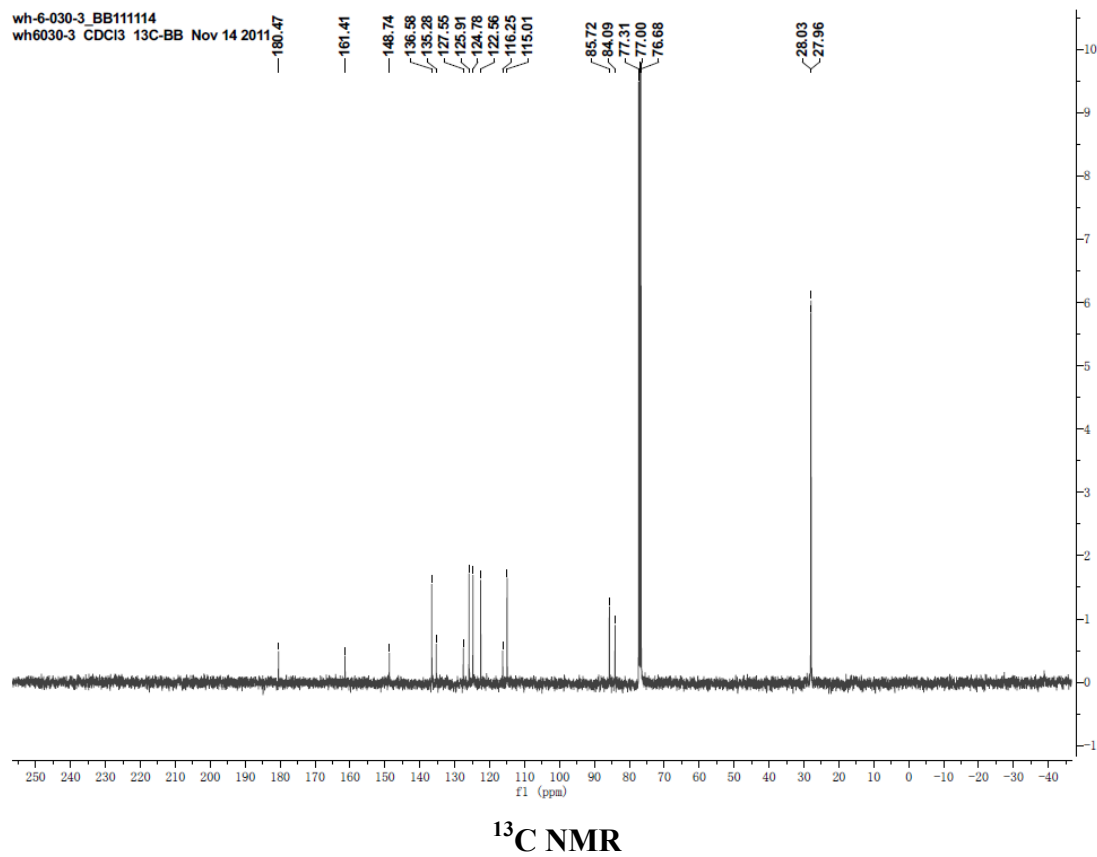
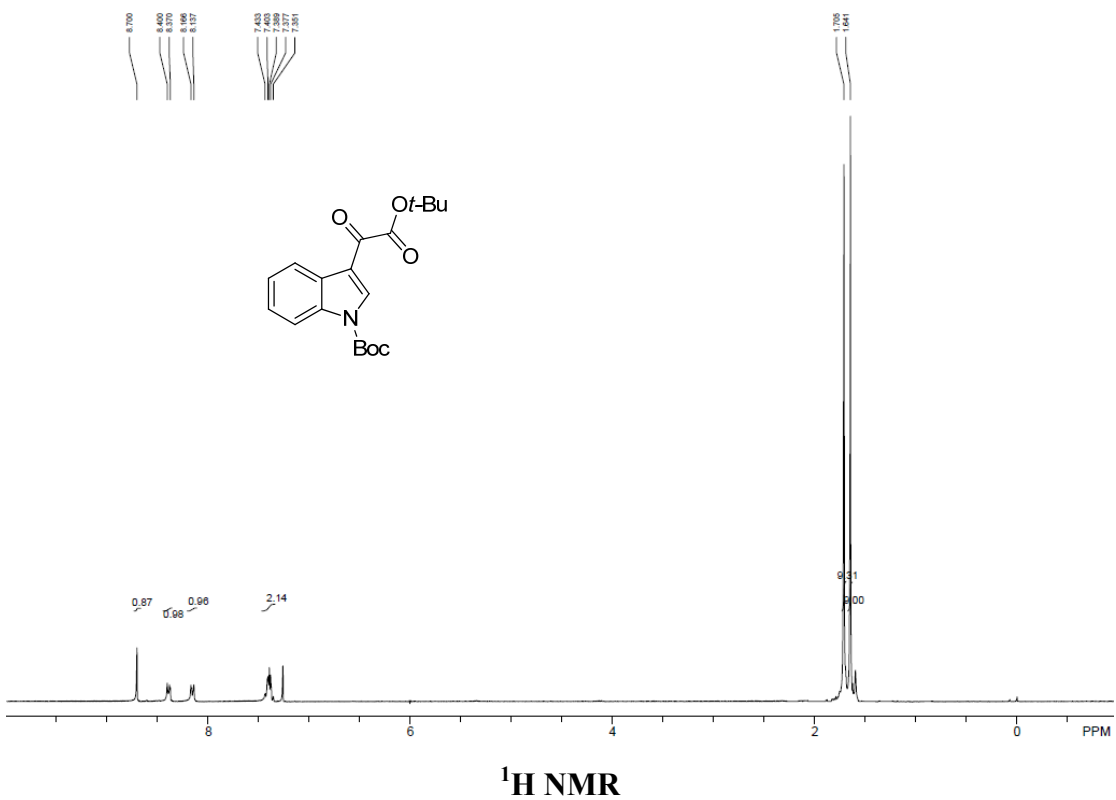


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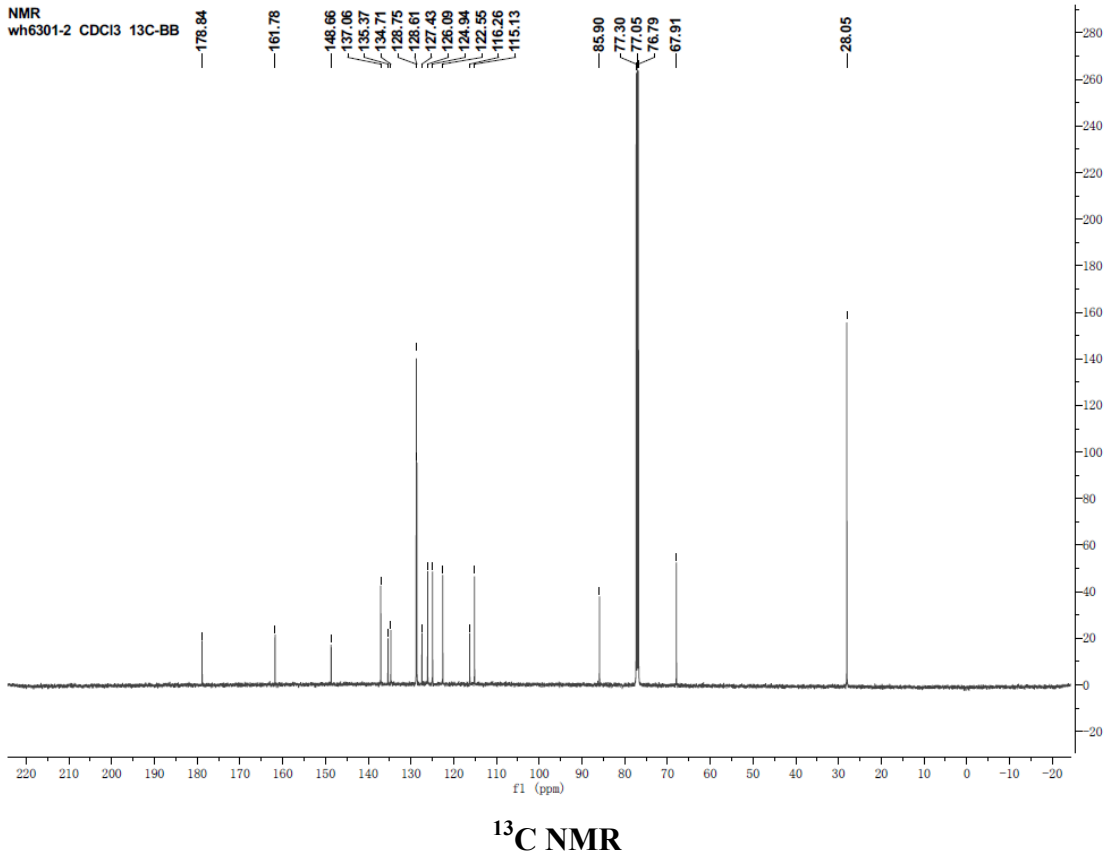
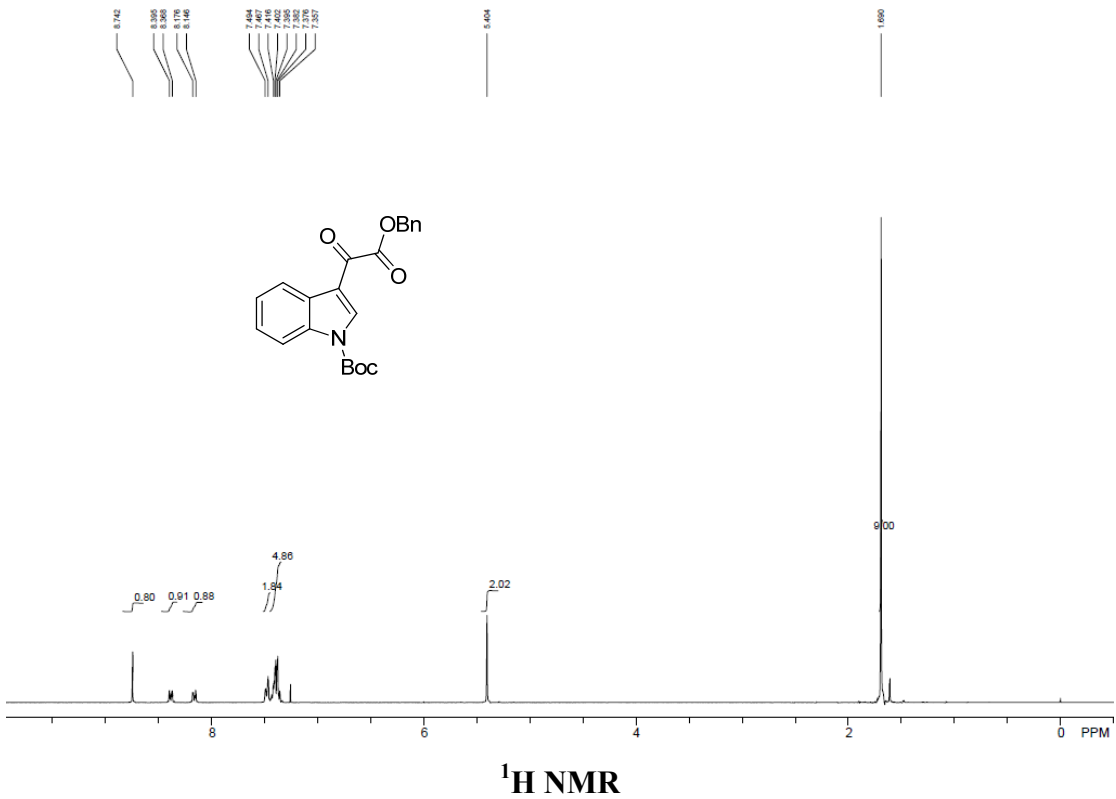
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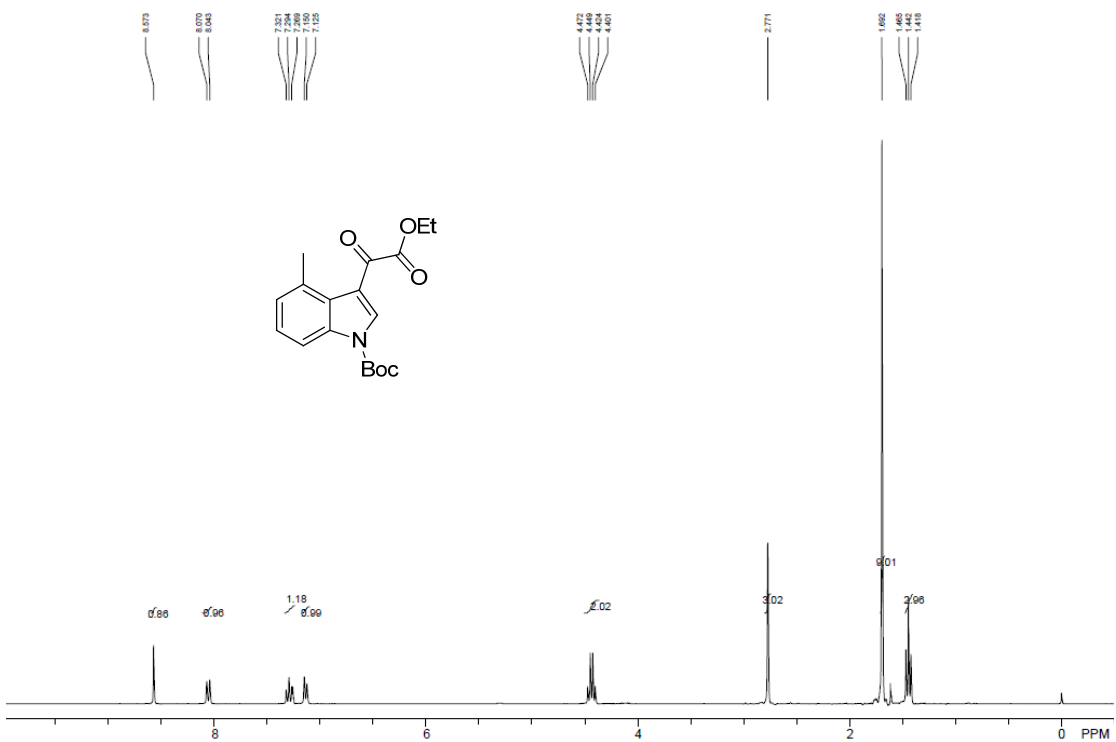
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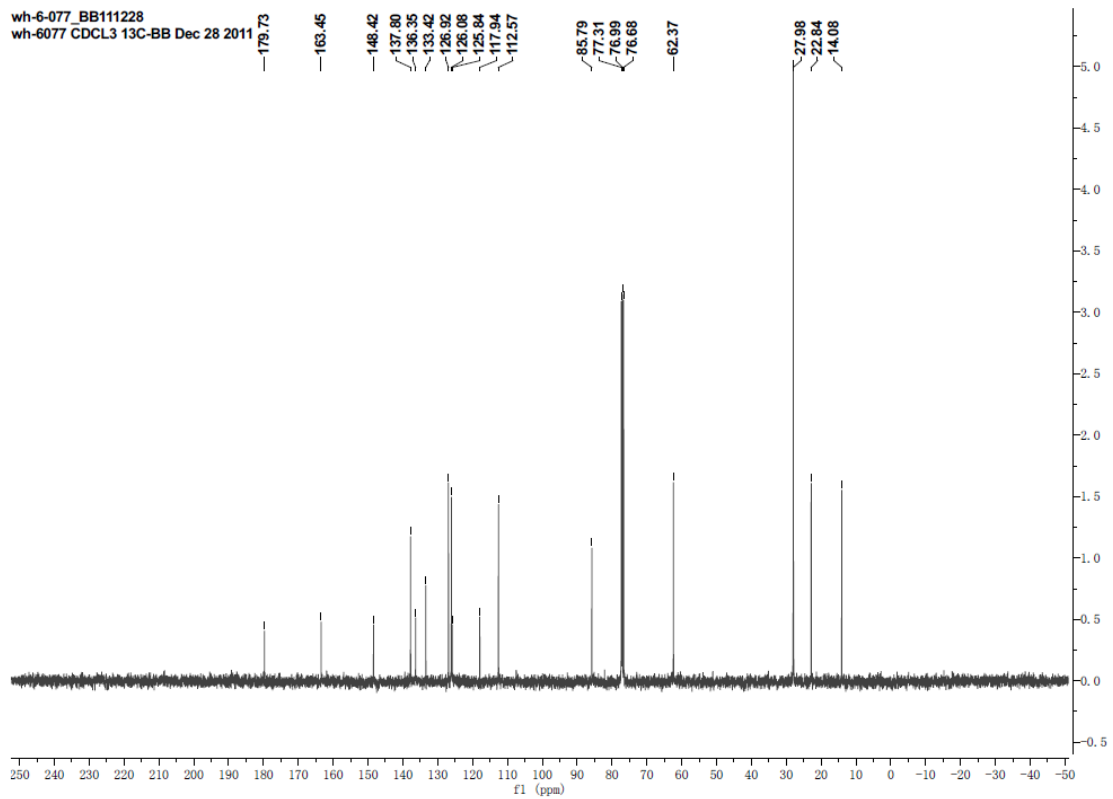
Compound 5f



Compound 5h

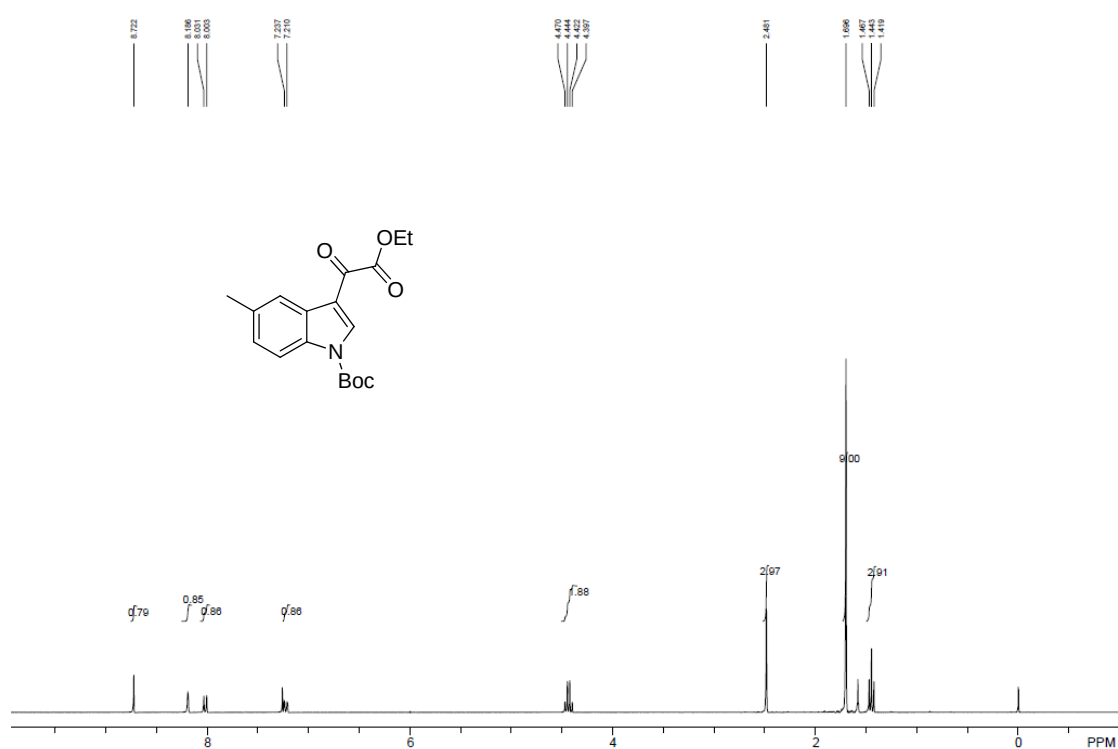


¹H NMR

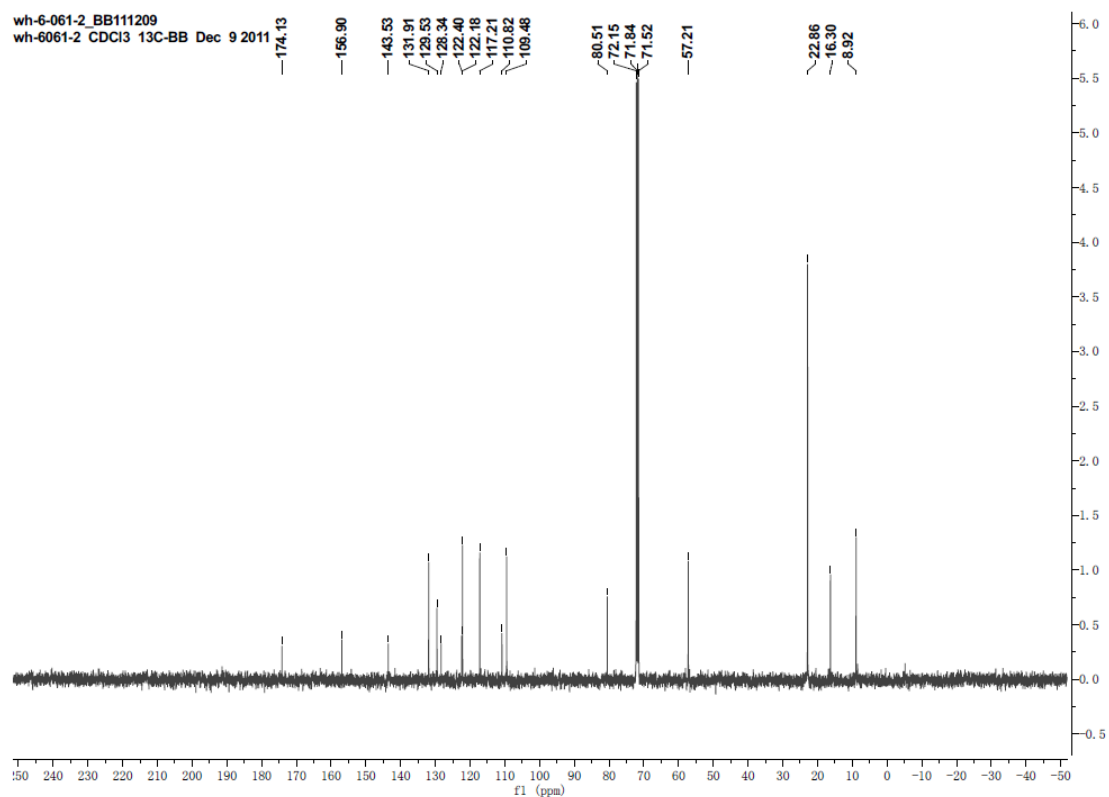


¹³C NMR

Compound 5i

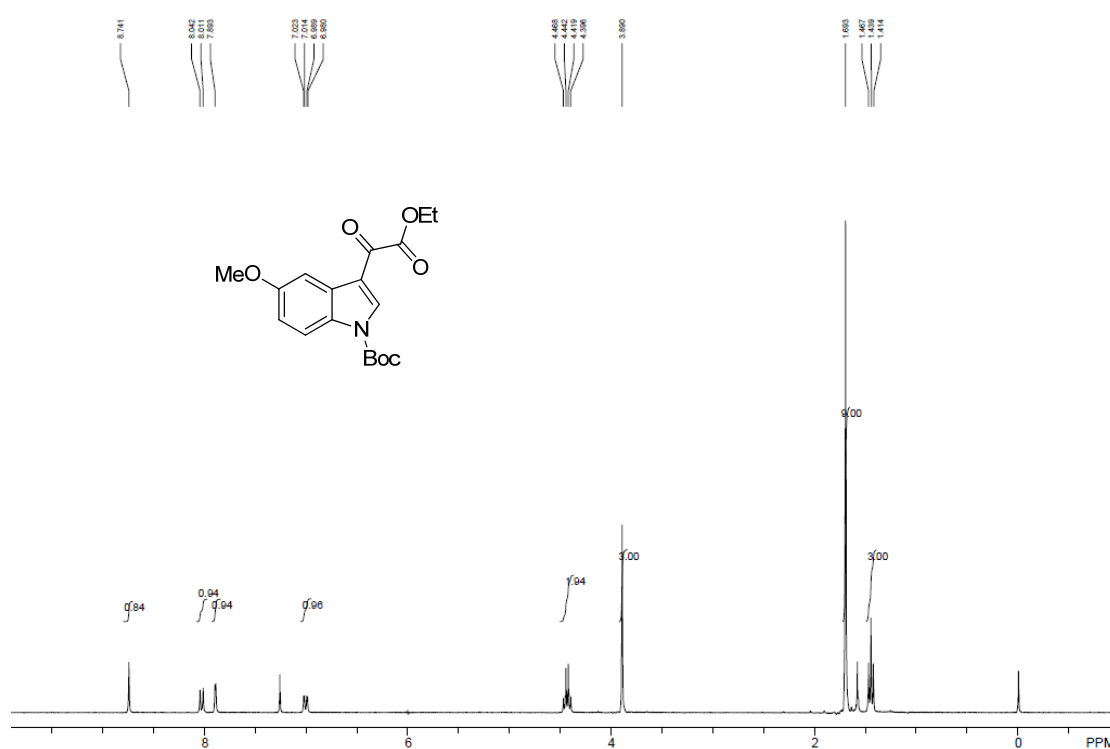


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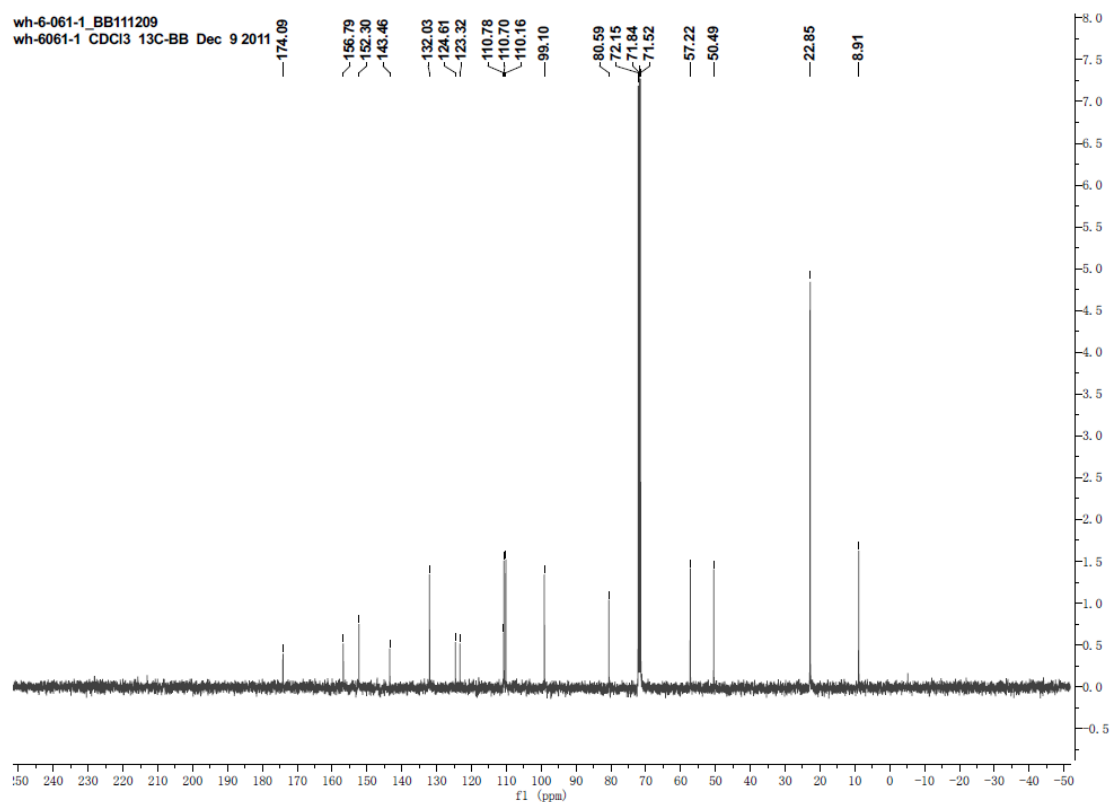


¹³C NMR

Compound 5j

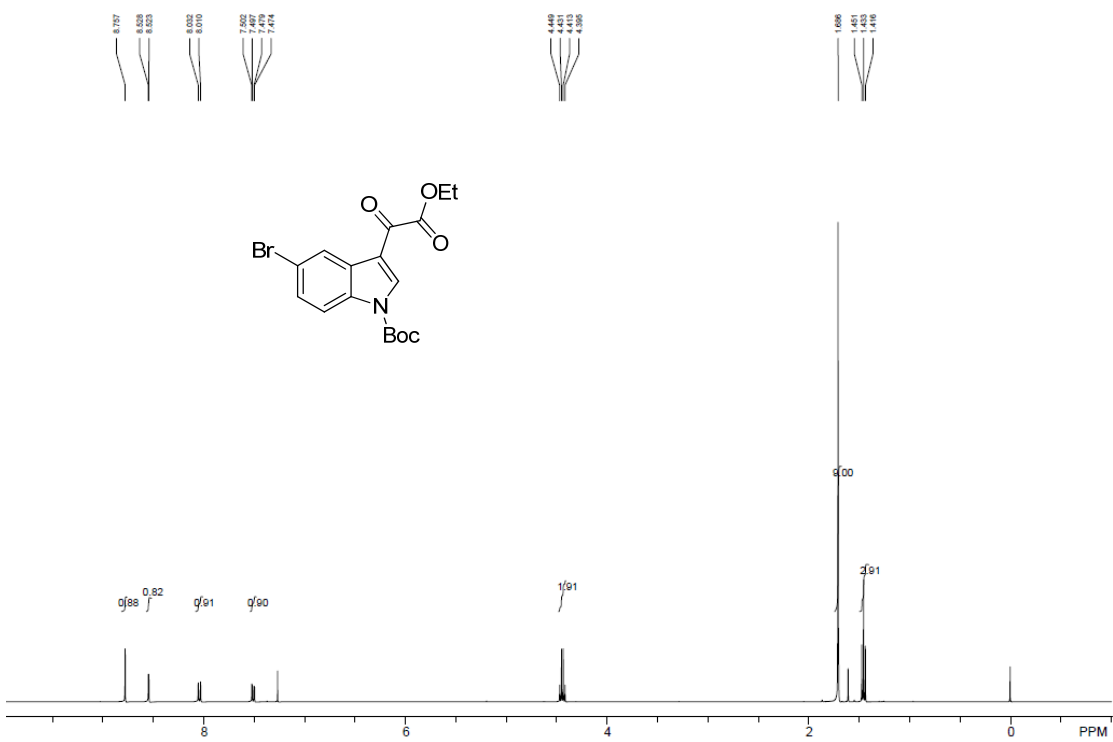


¹H NMR

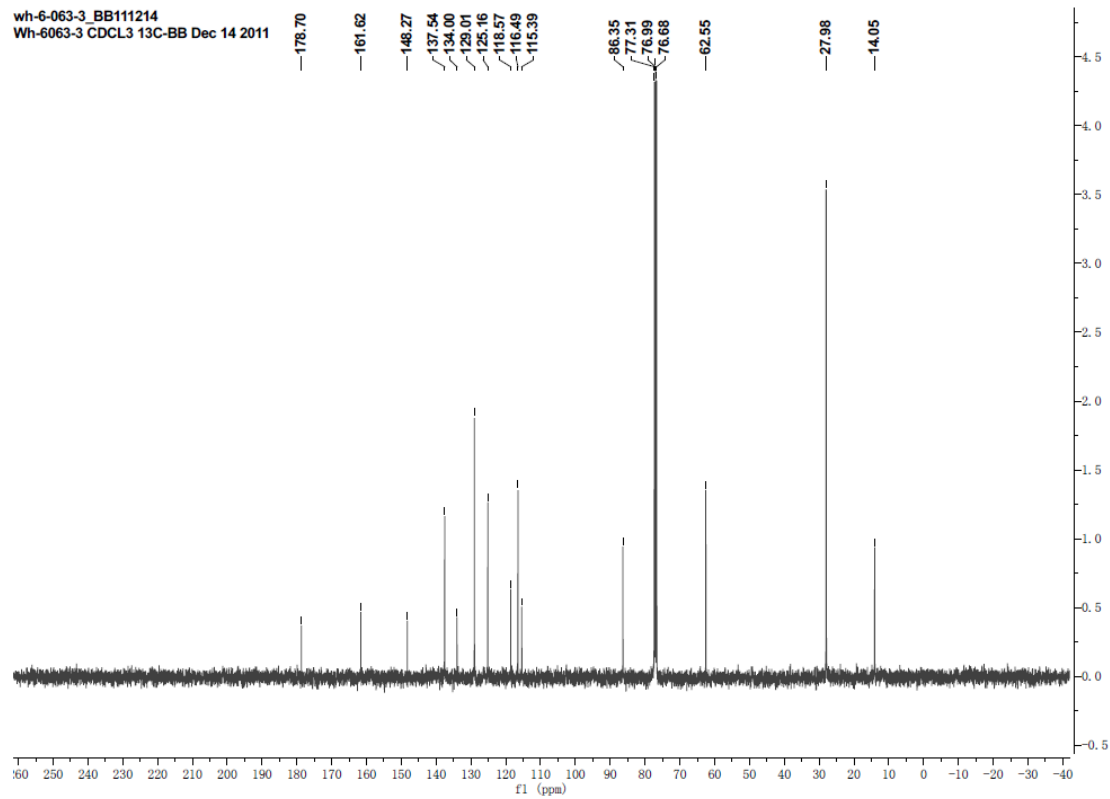


¹³C NMR

Compound 5k

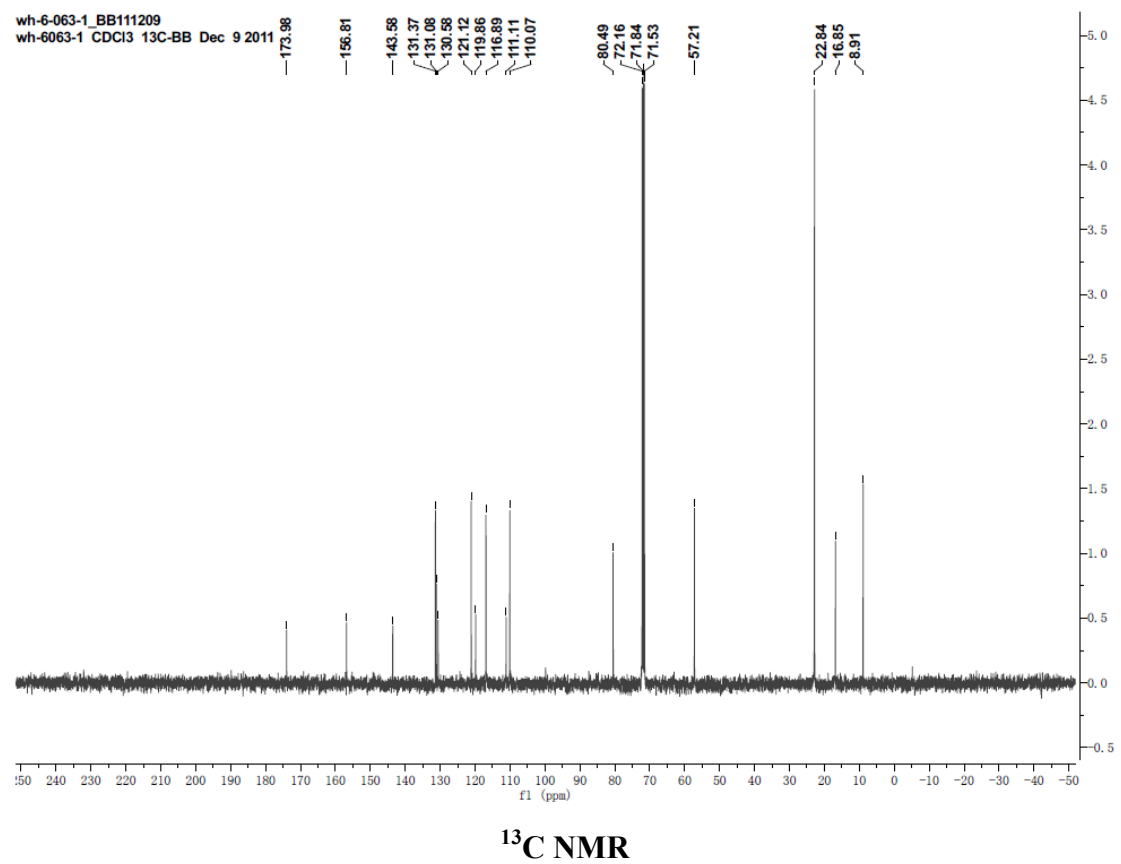
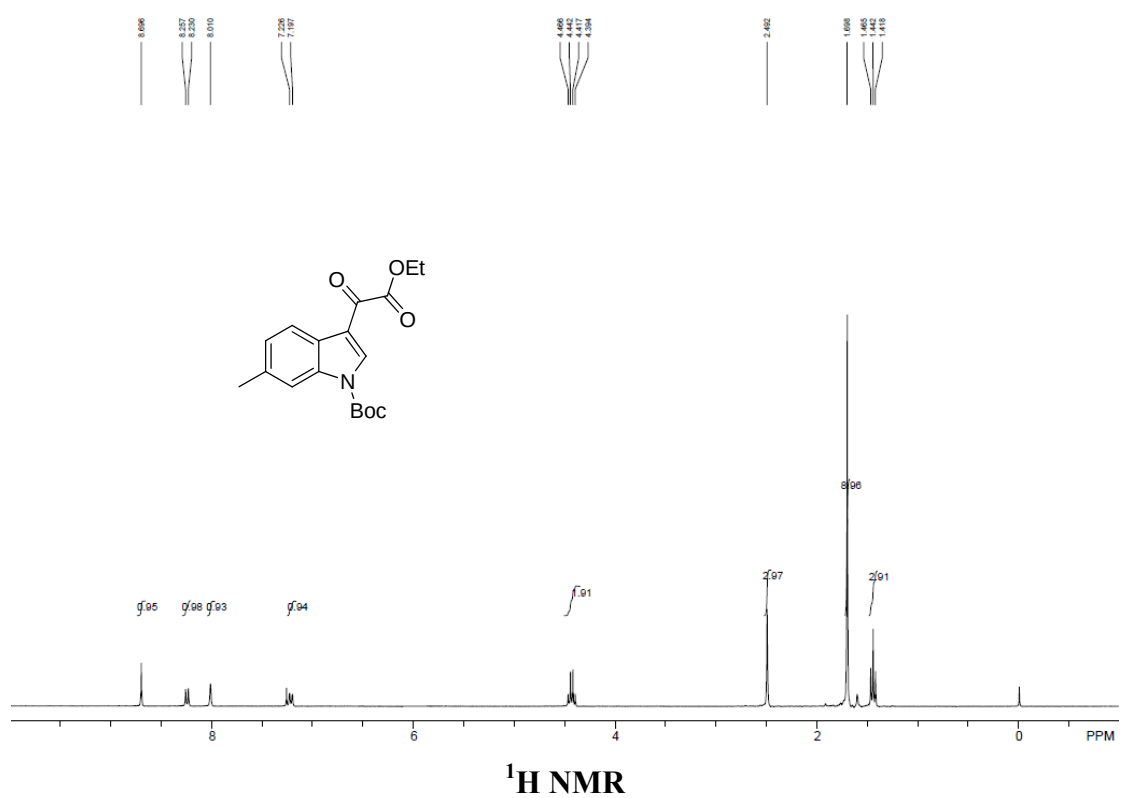


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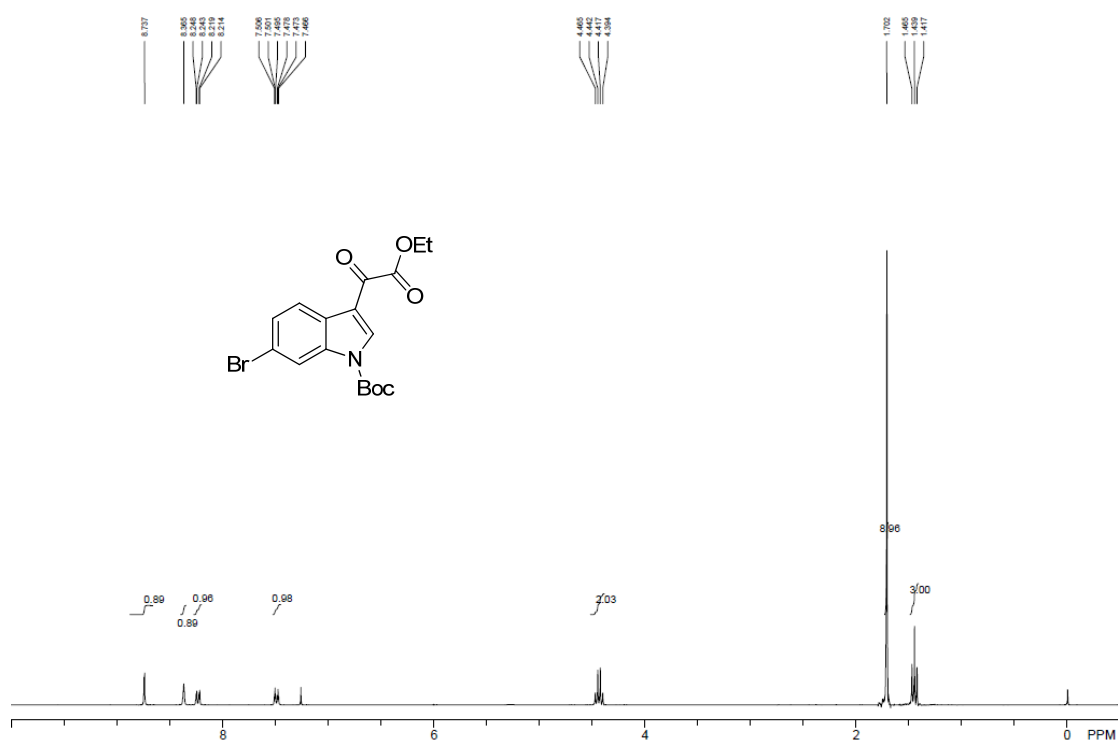


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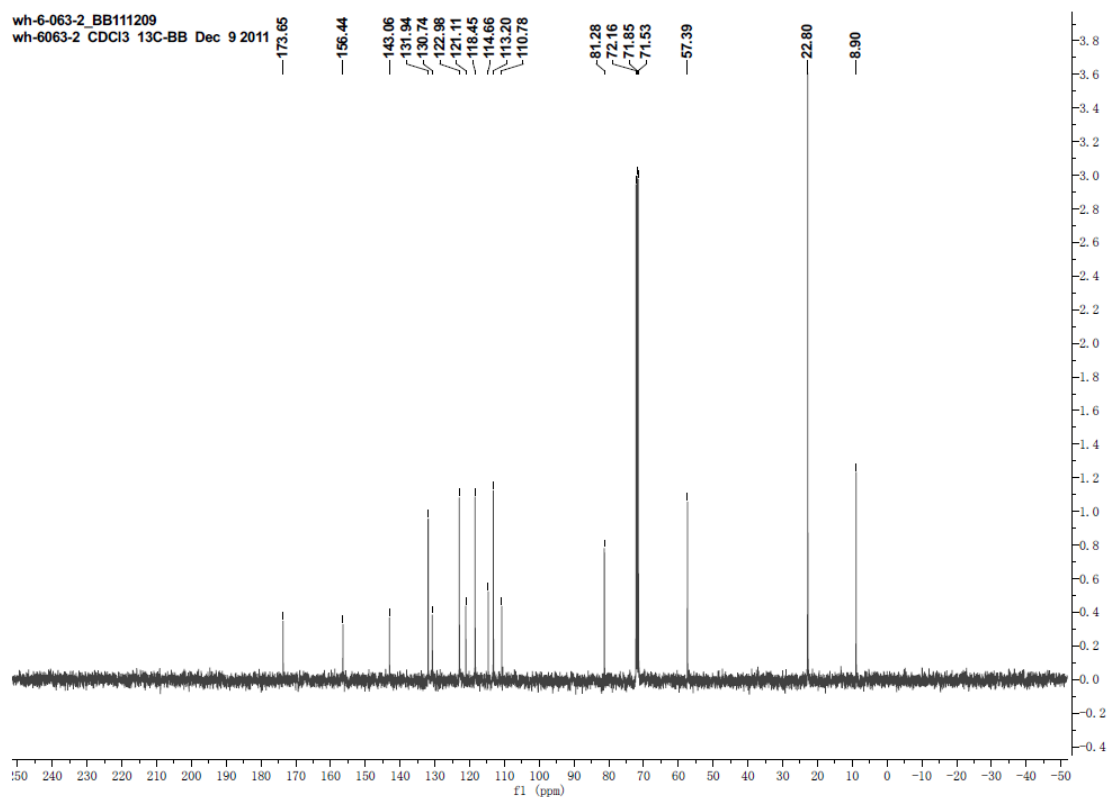
Compound 5l



Compound 5m

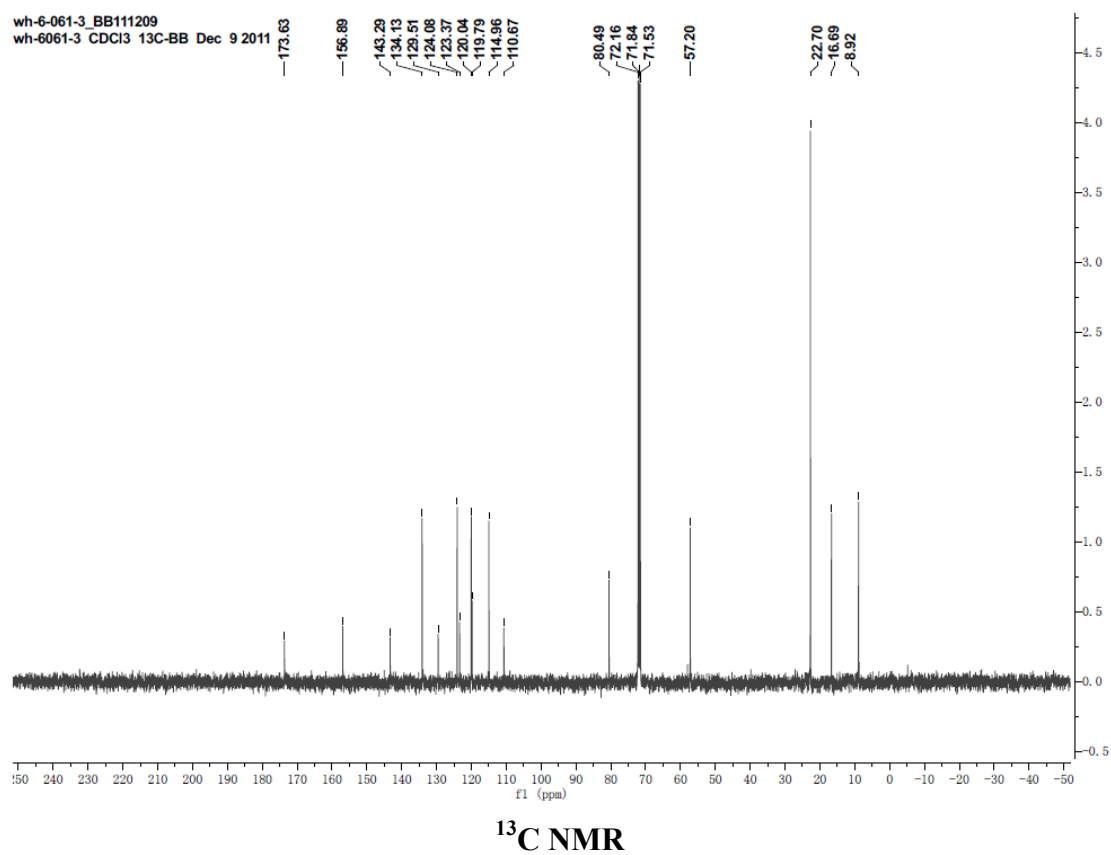
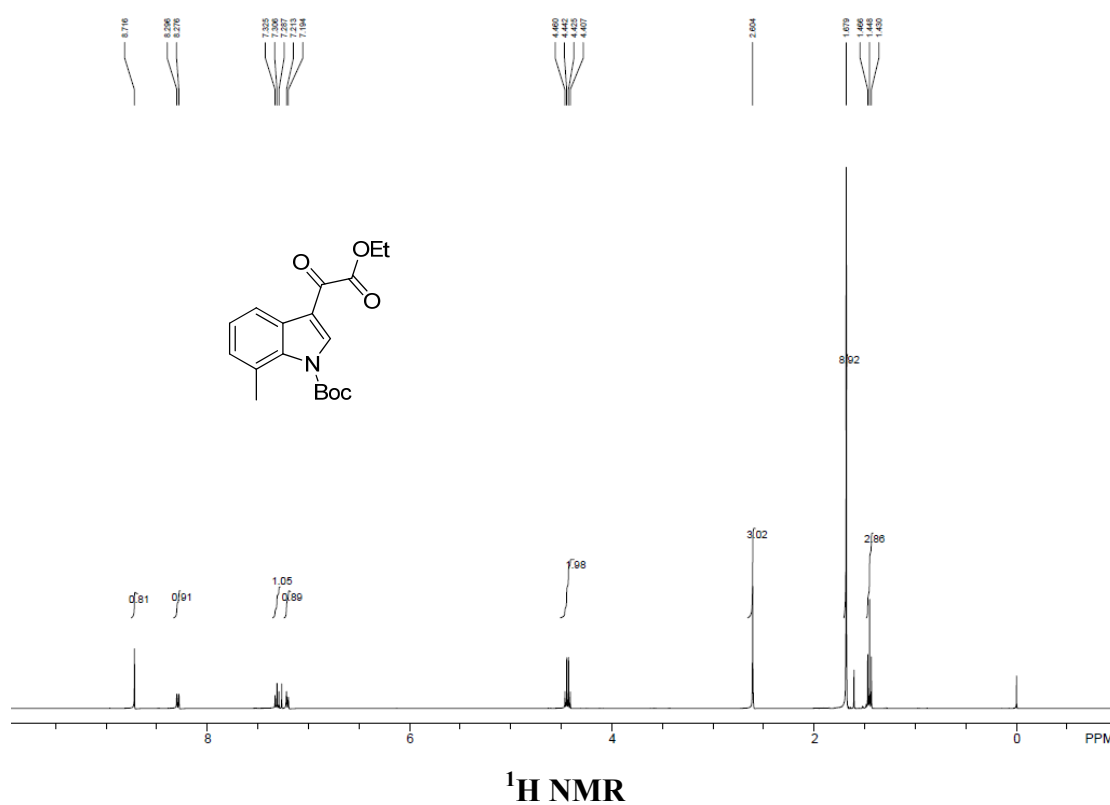


¹H NMR

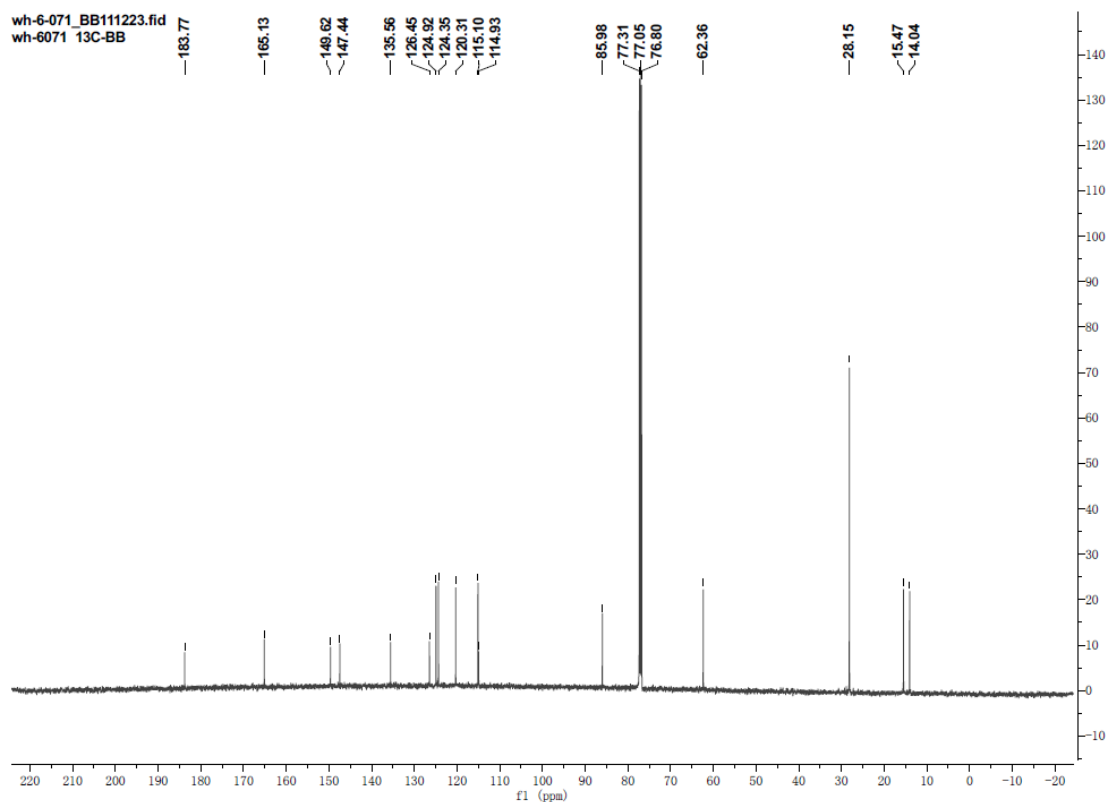
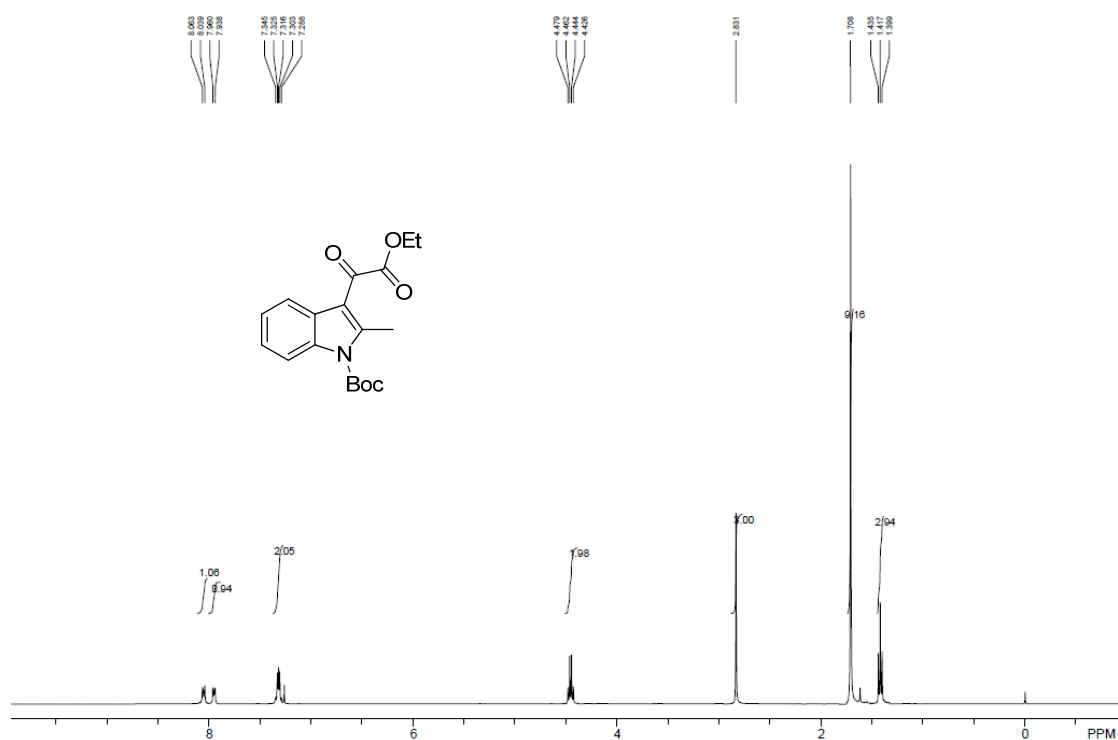


¹³C NMR

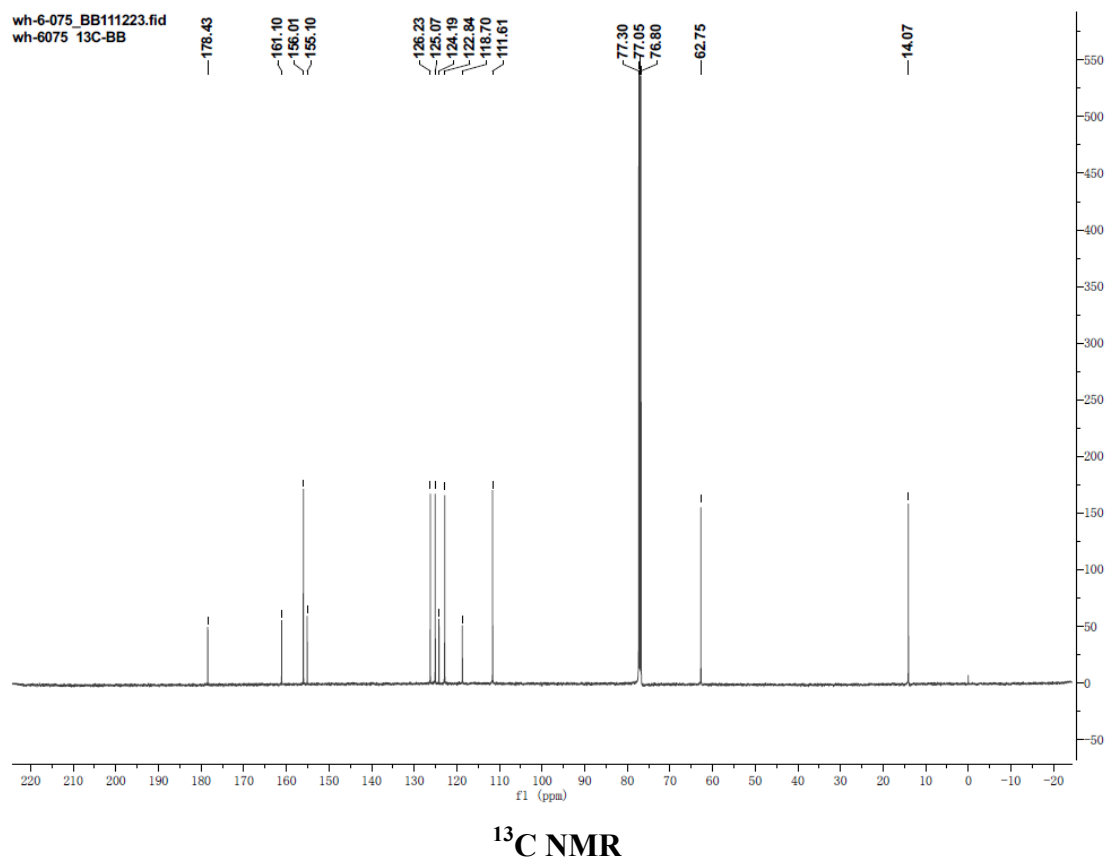
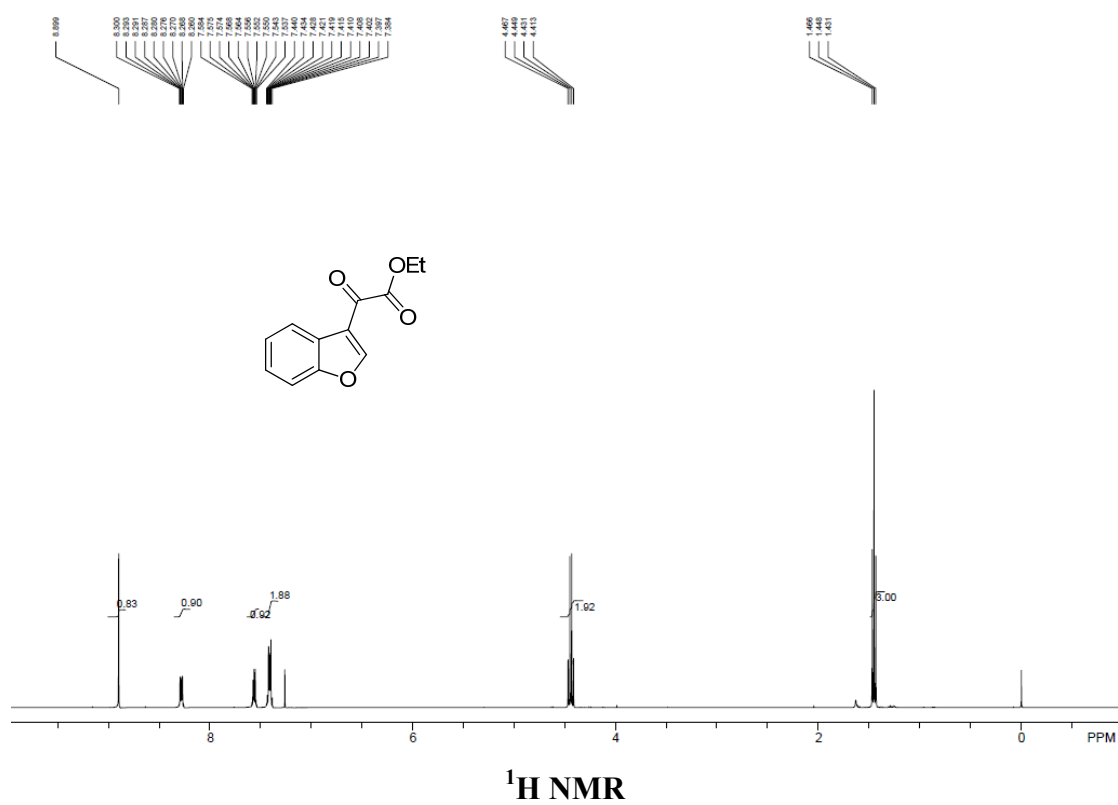
Compound 5n



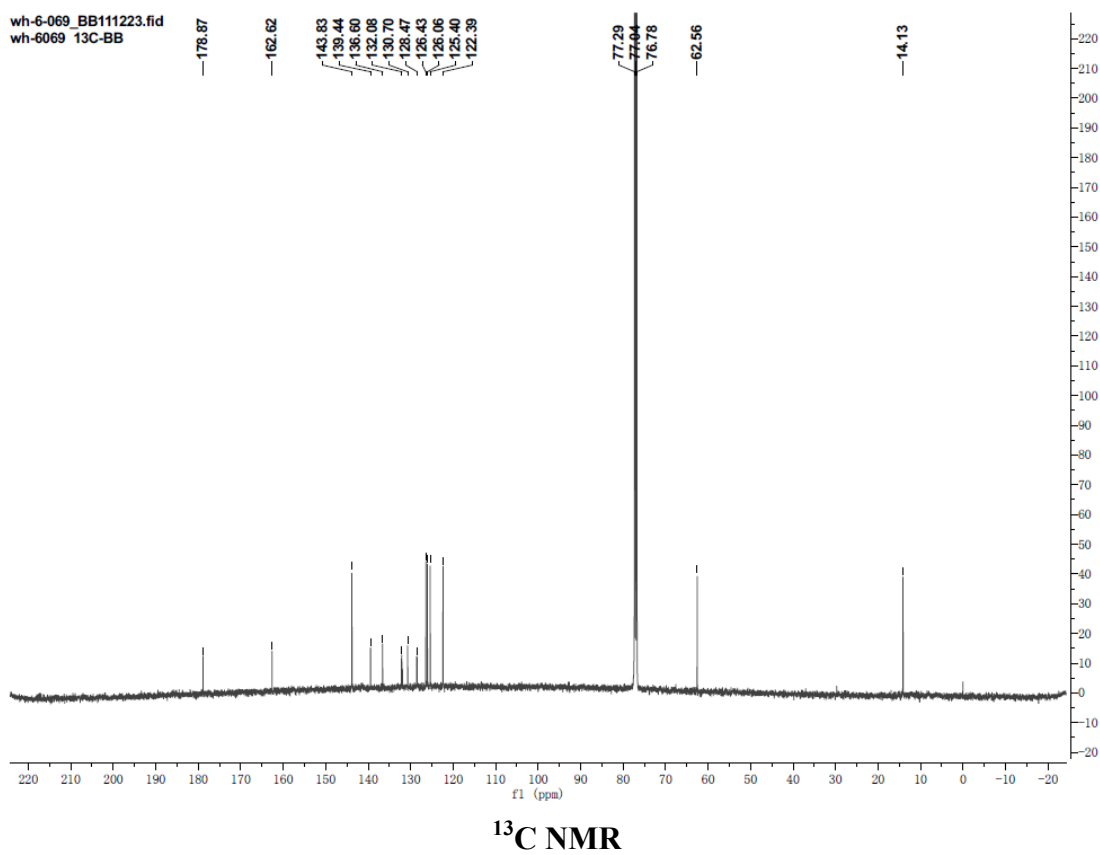
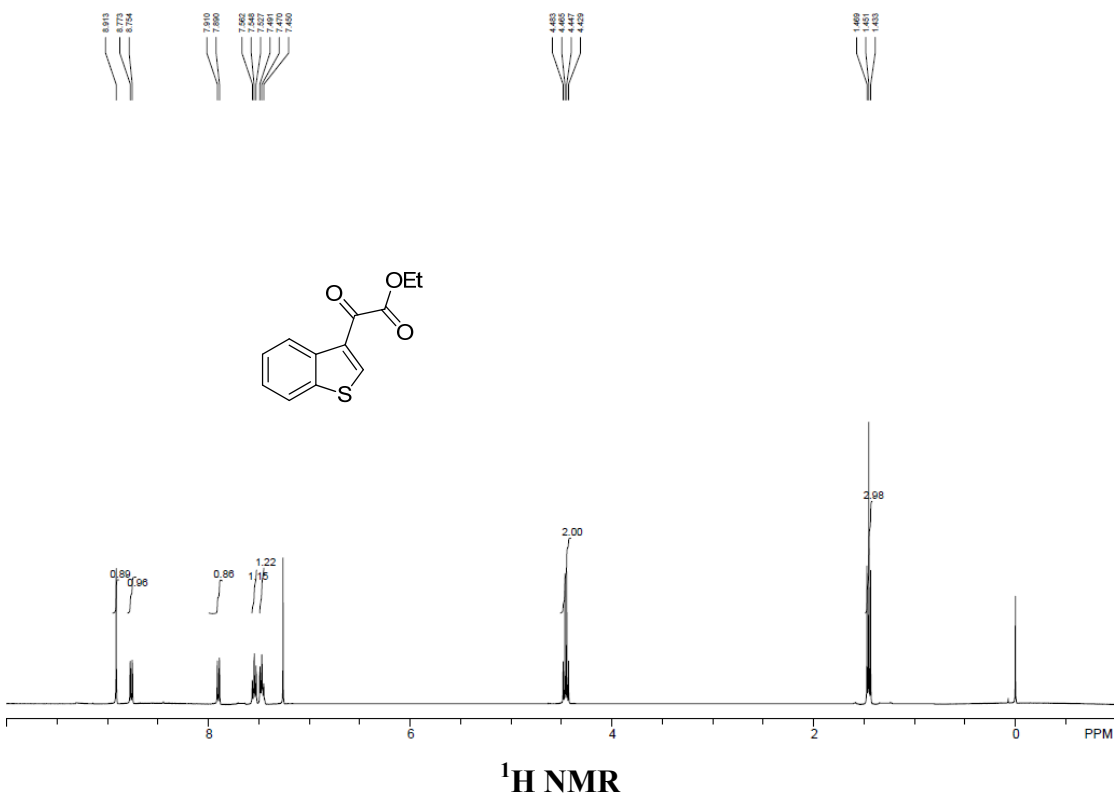
Compound 5o



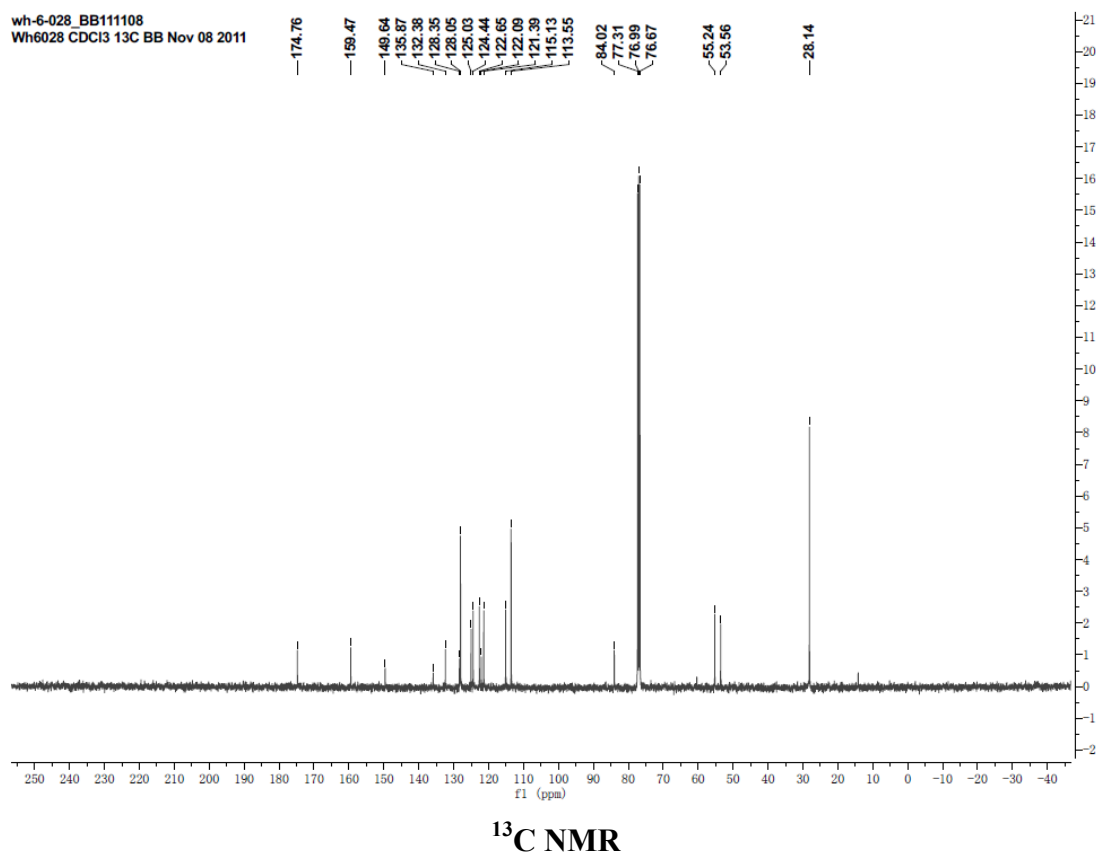
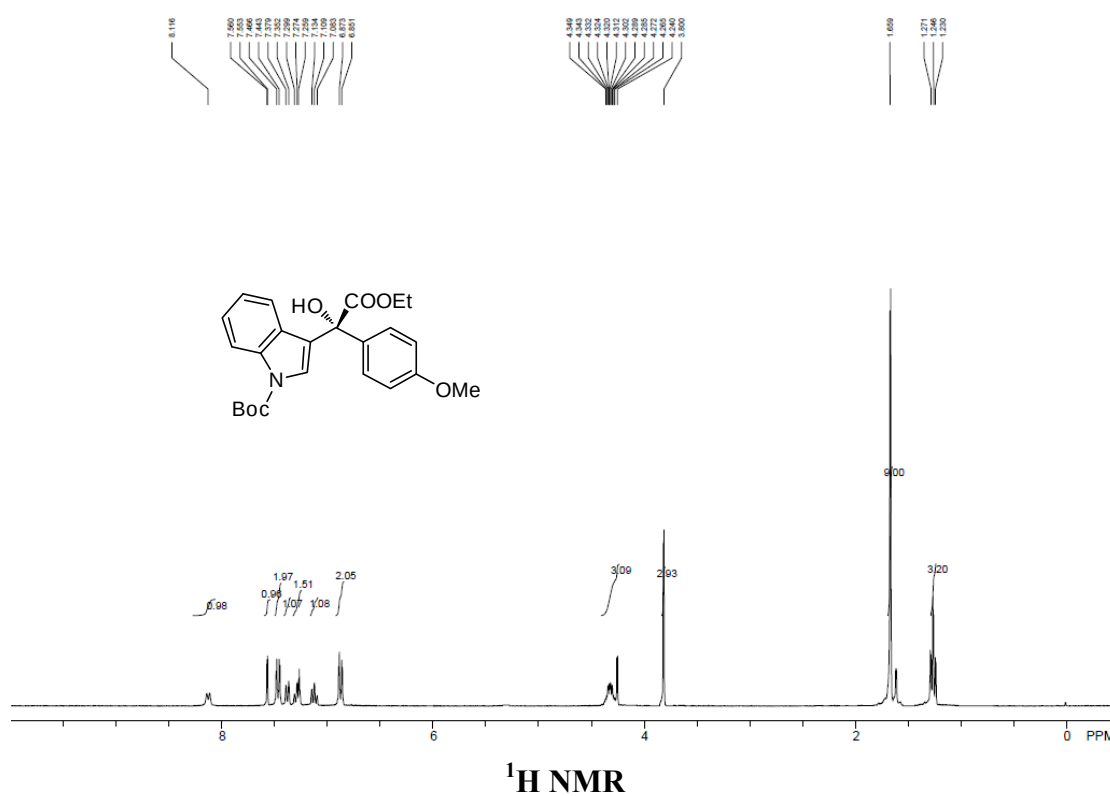
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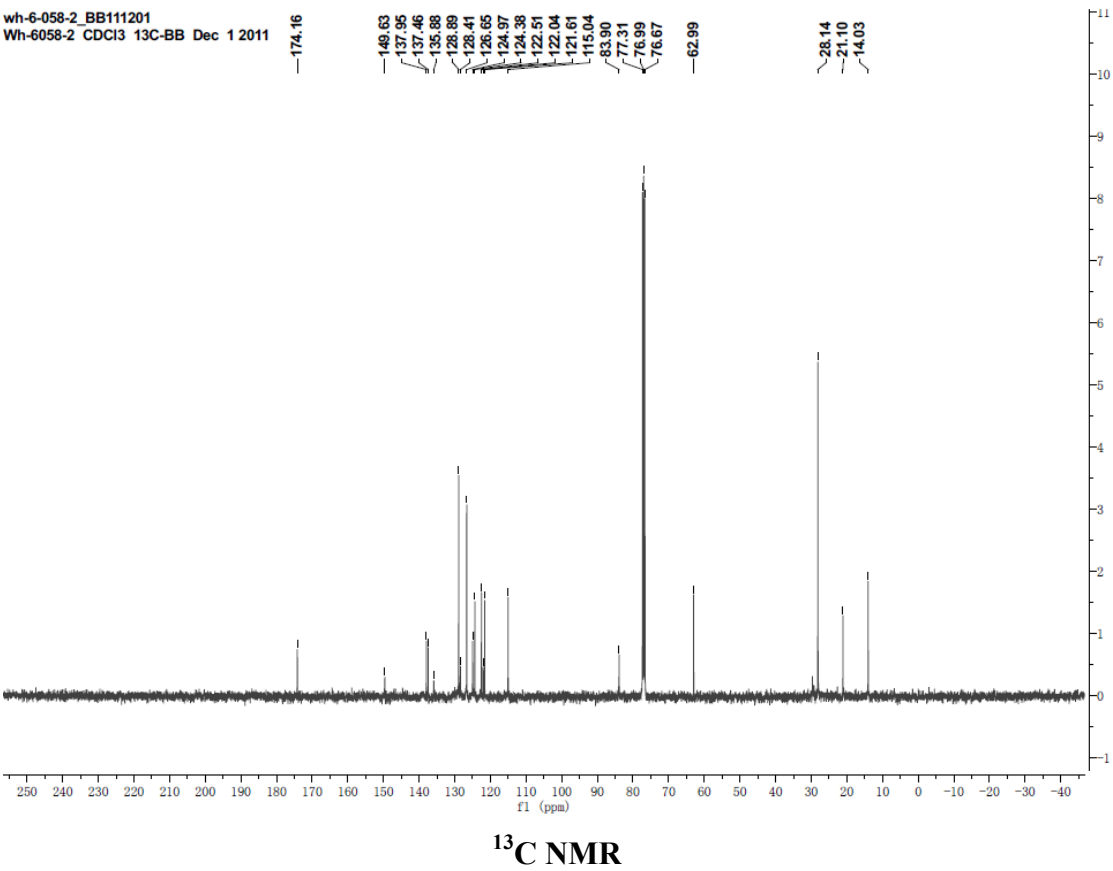
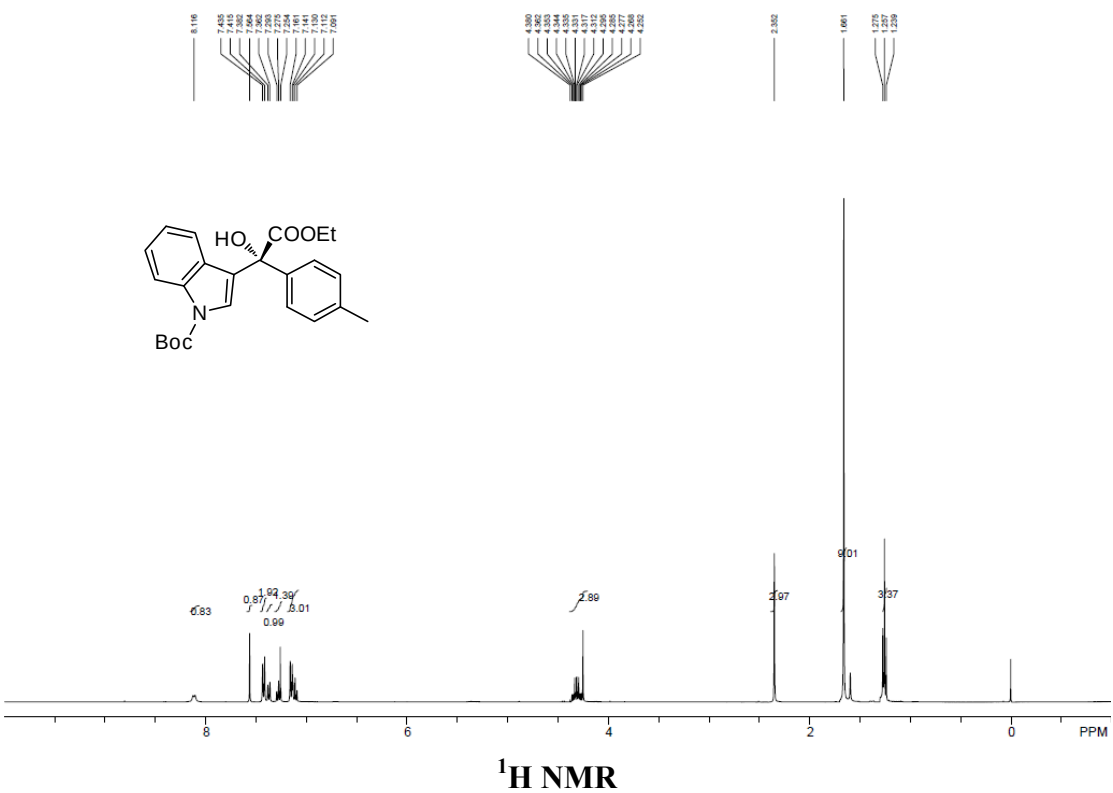
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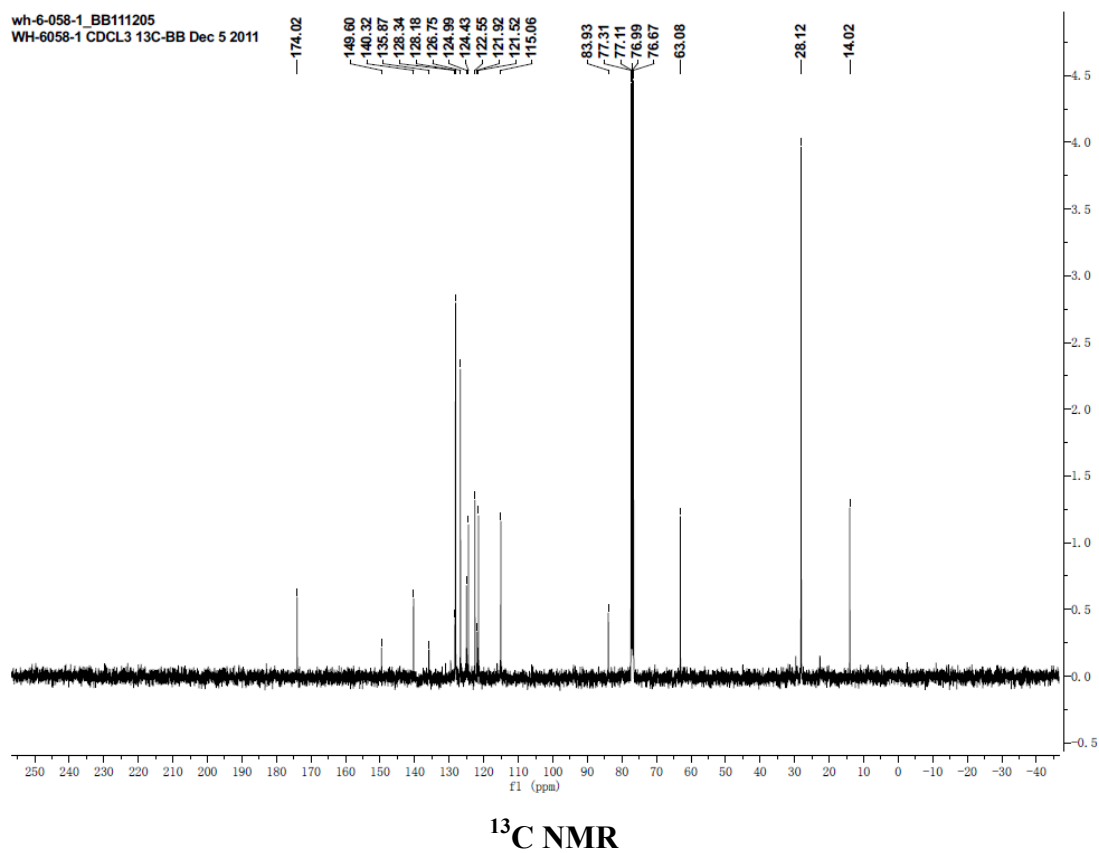
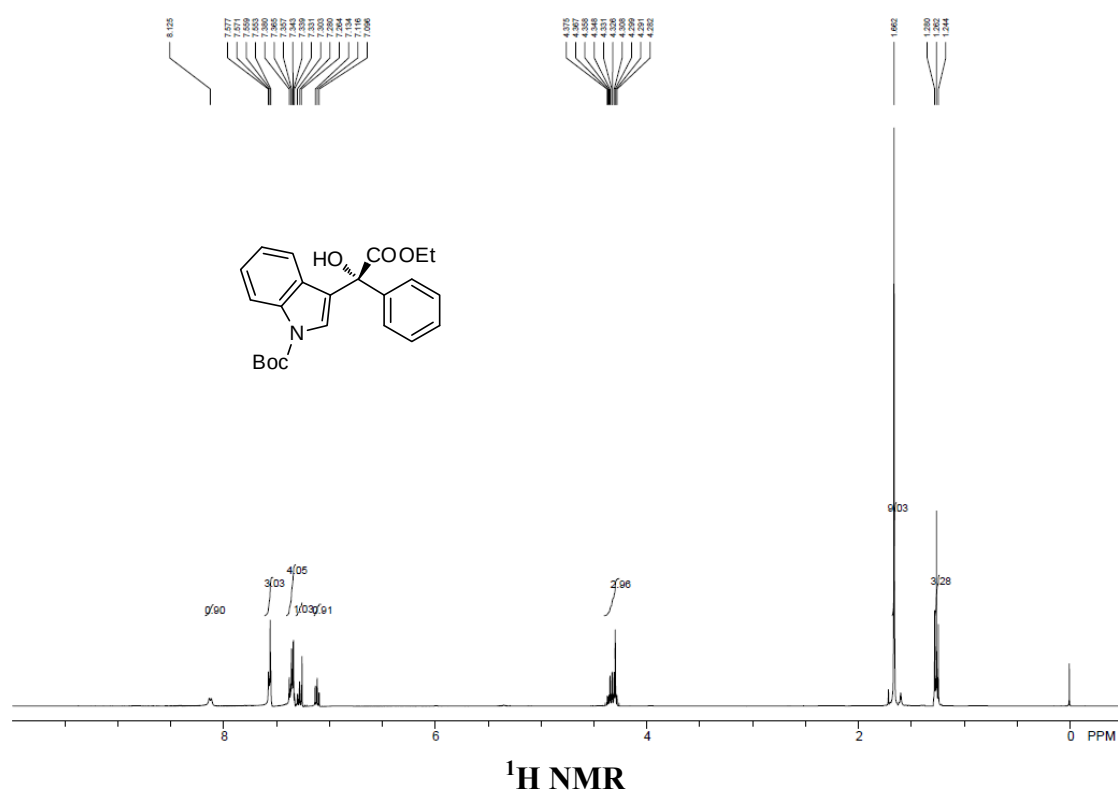
Compound 7c



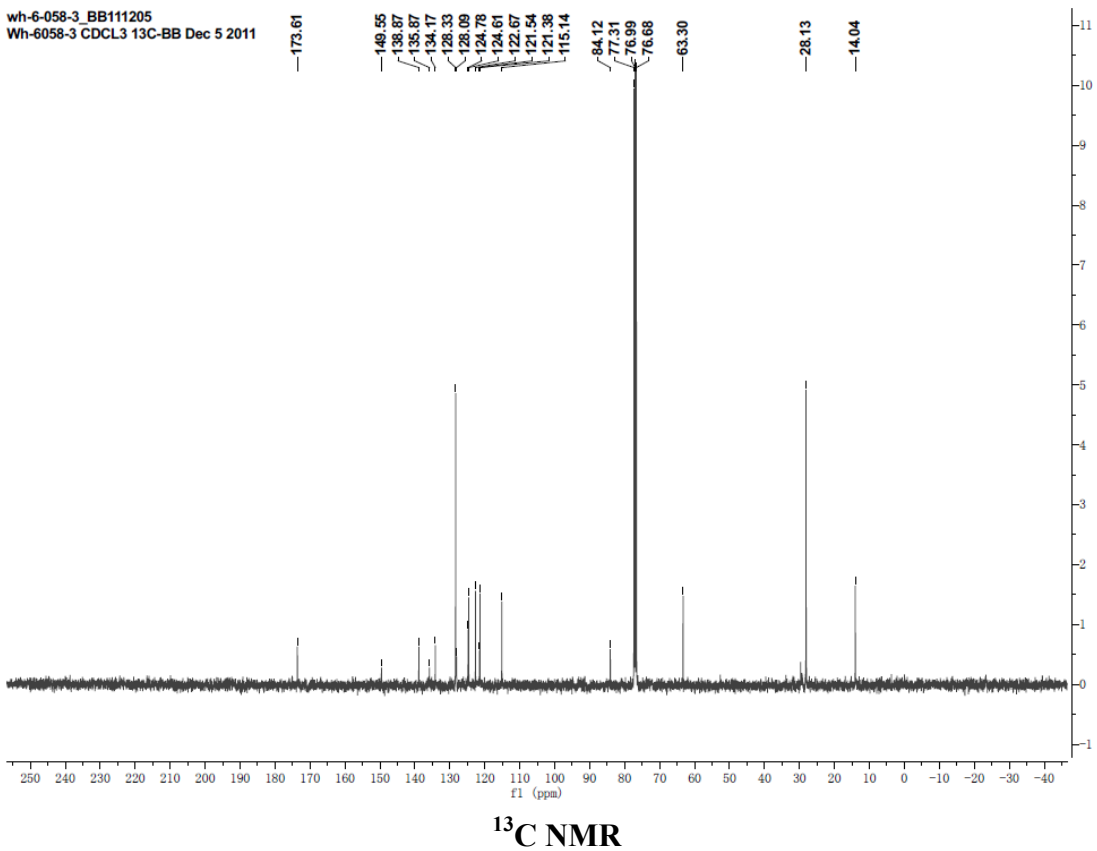
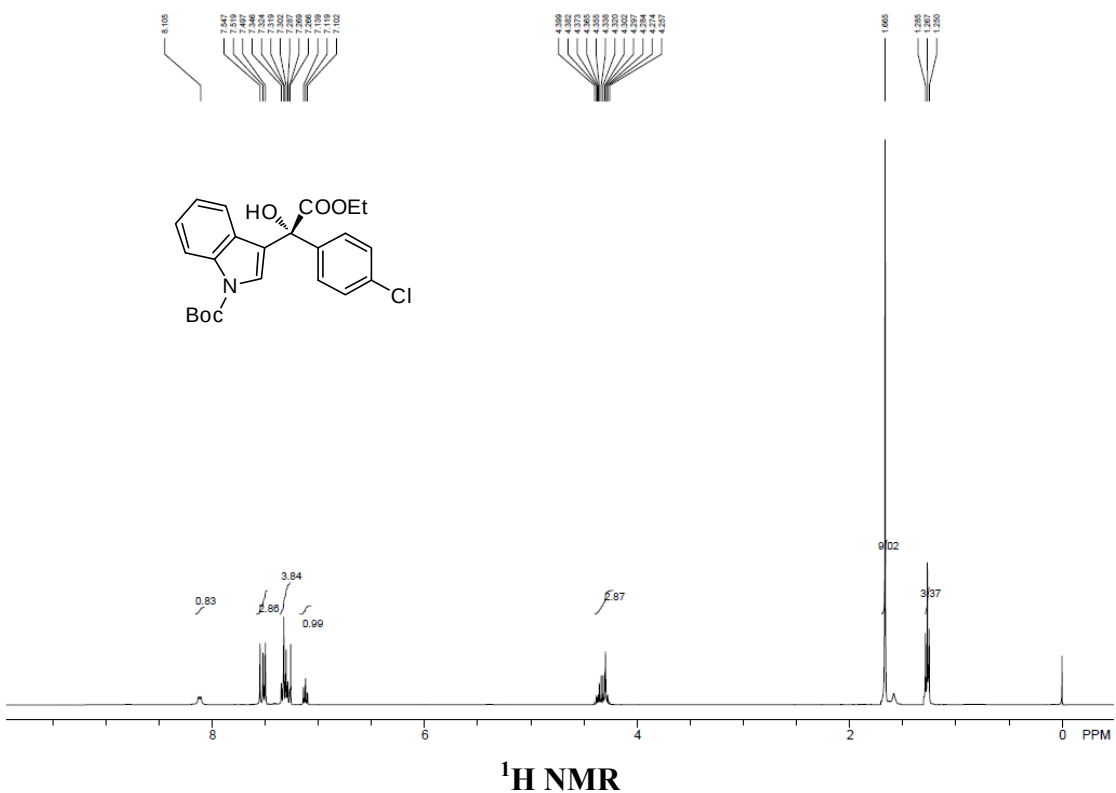
Compound 7h



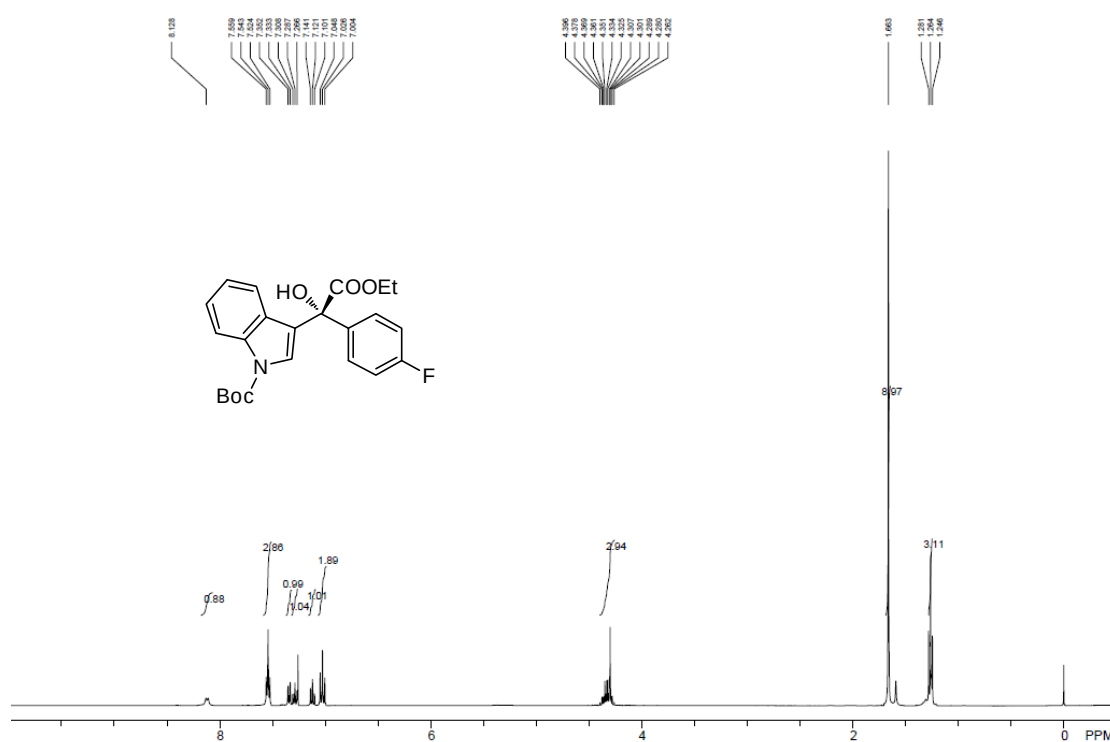
Compound 7i



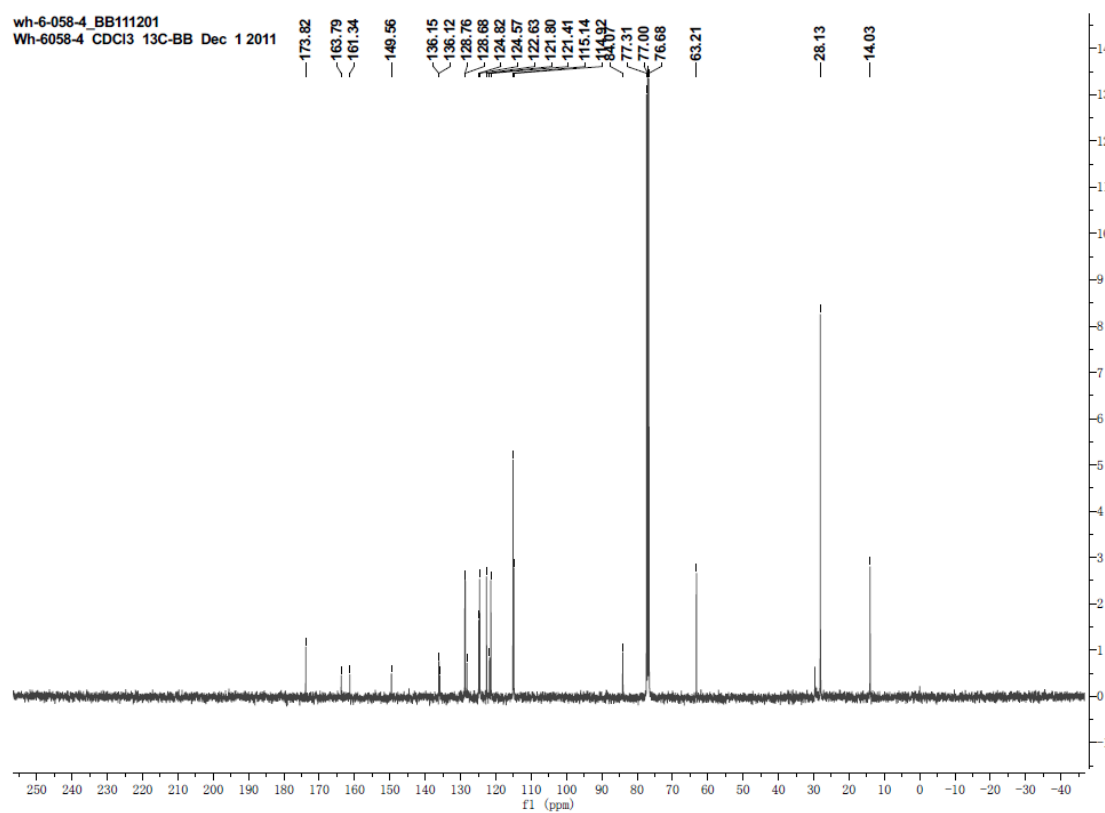
Compound 7j



Compound 7k

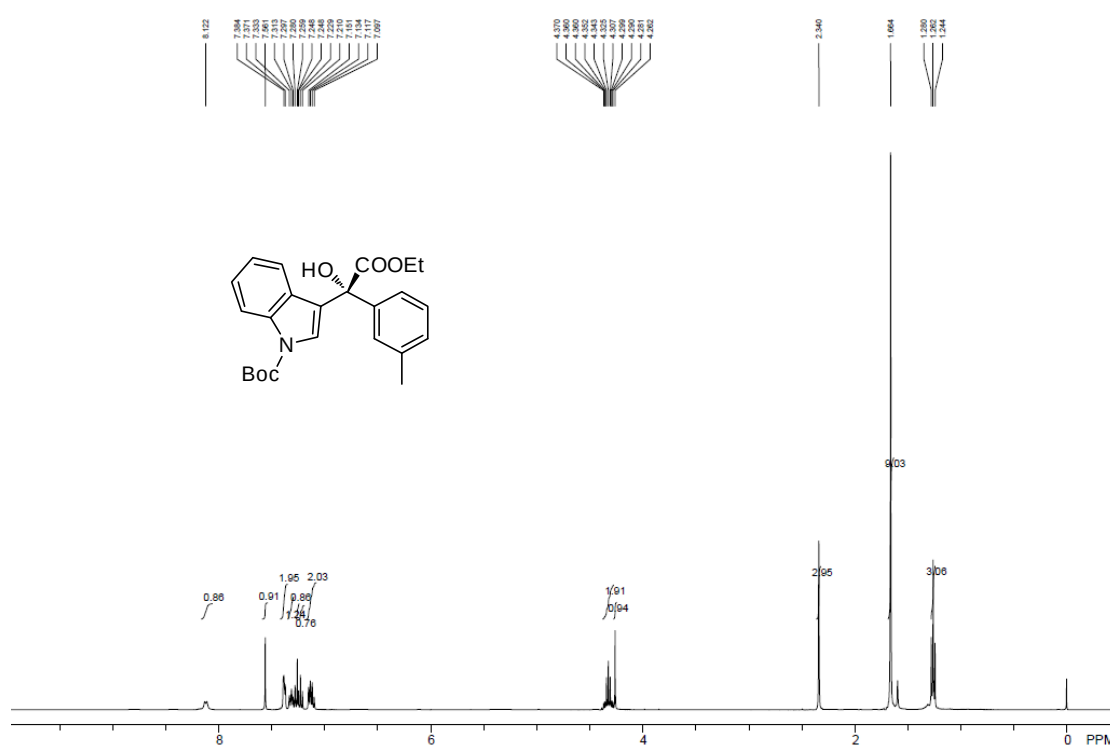


¹H NMR

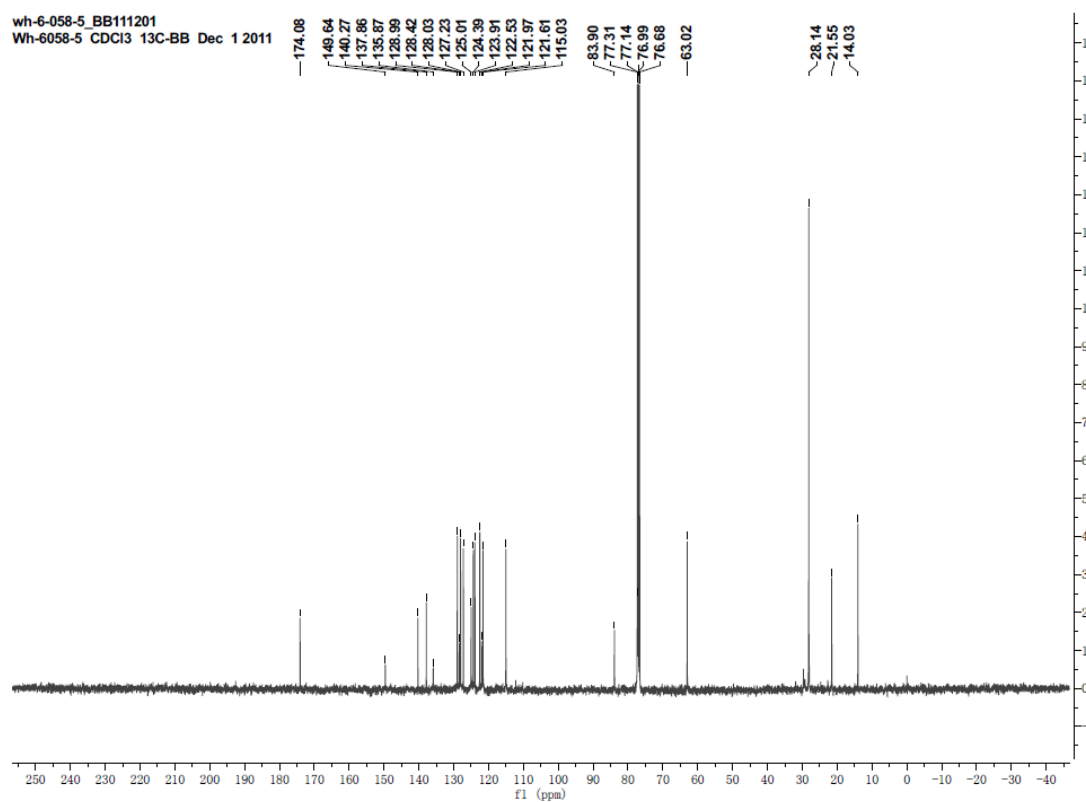


¹³C NMR

Compound 7l

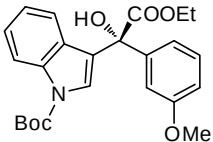
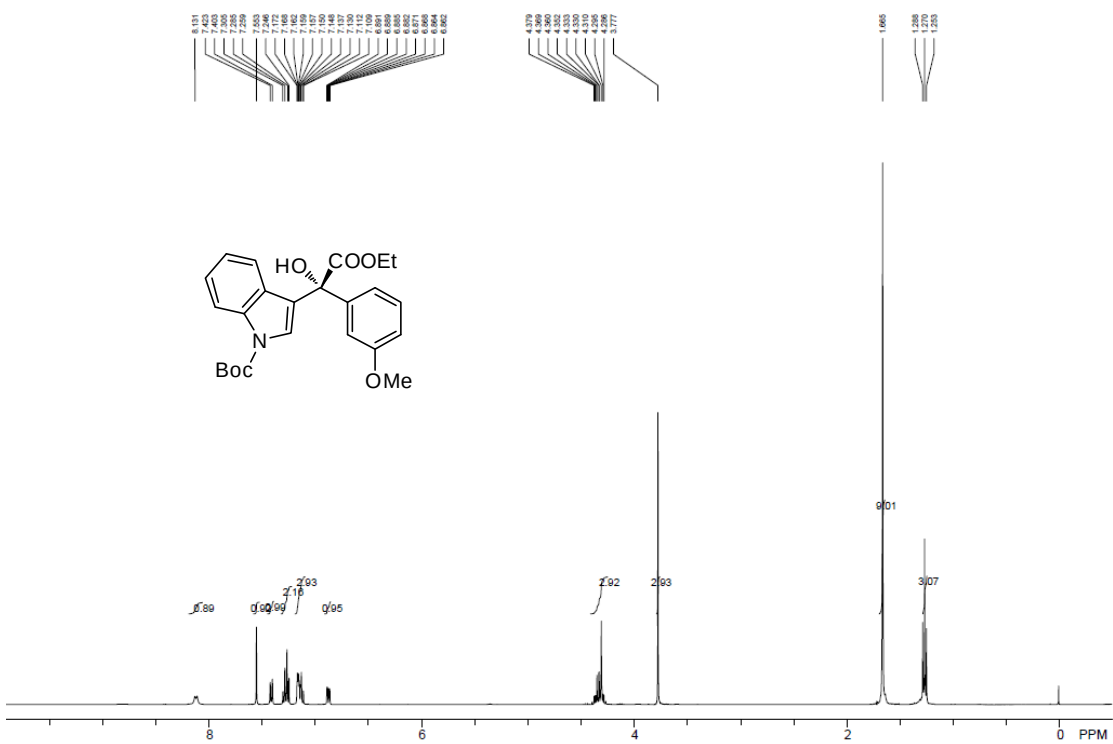


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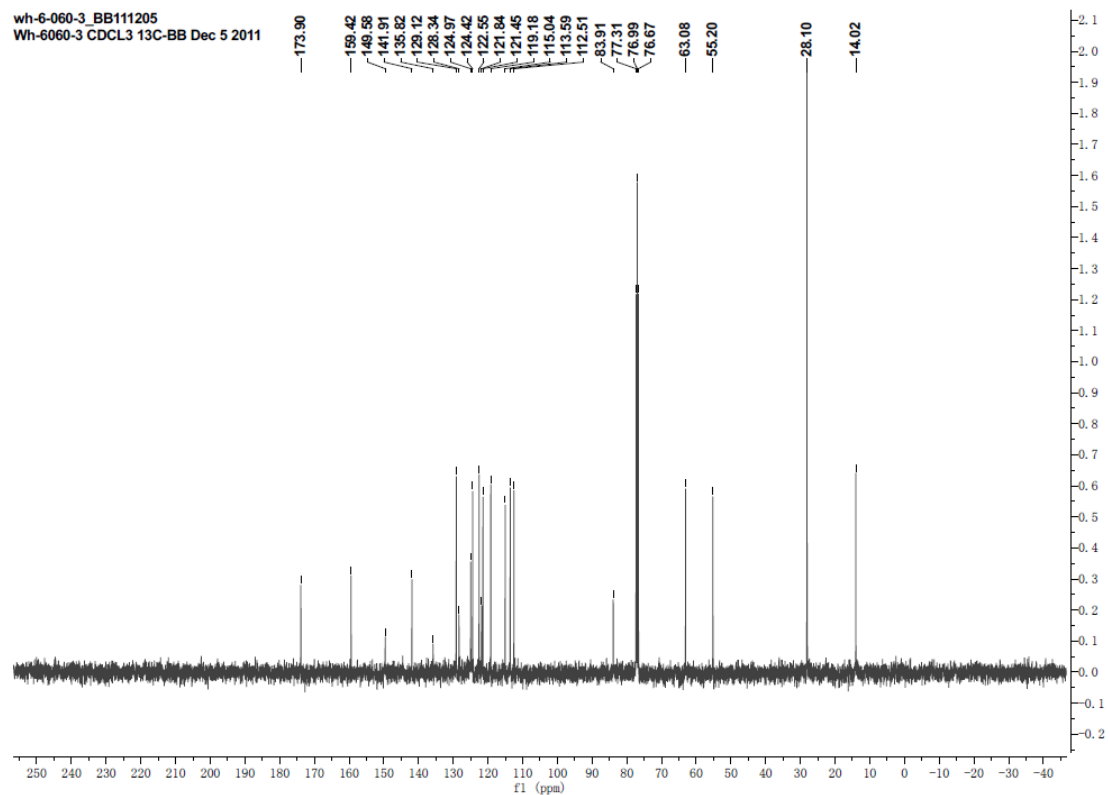


¹³C NMR

Compound 7m

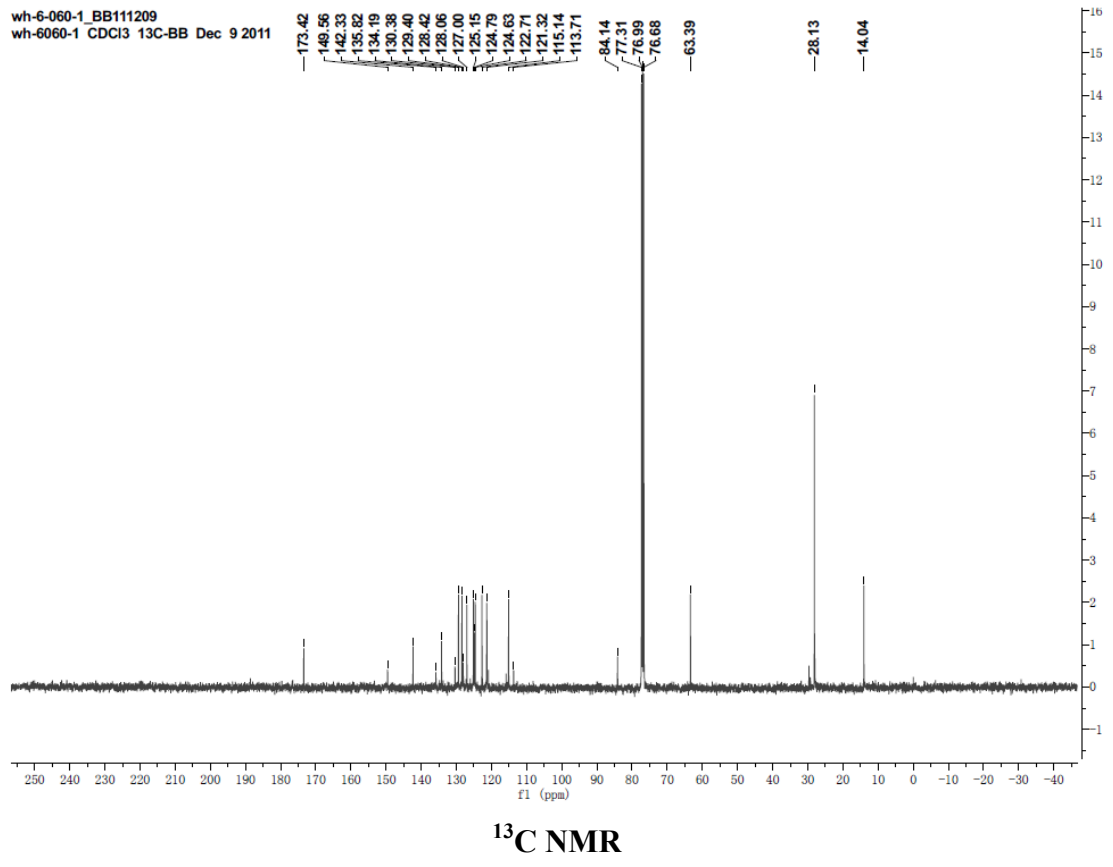
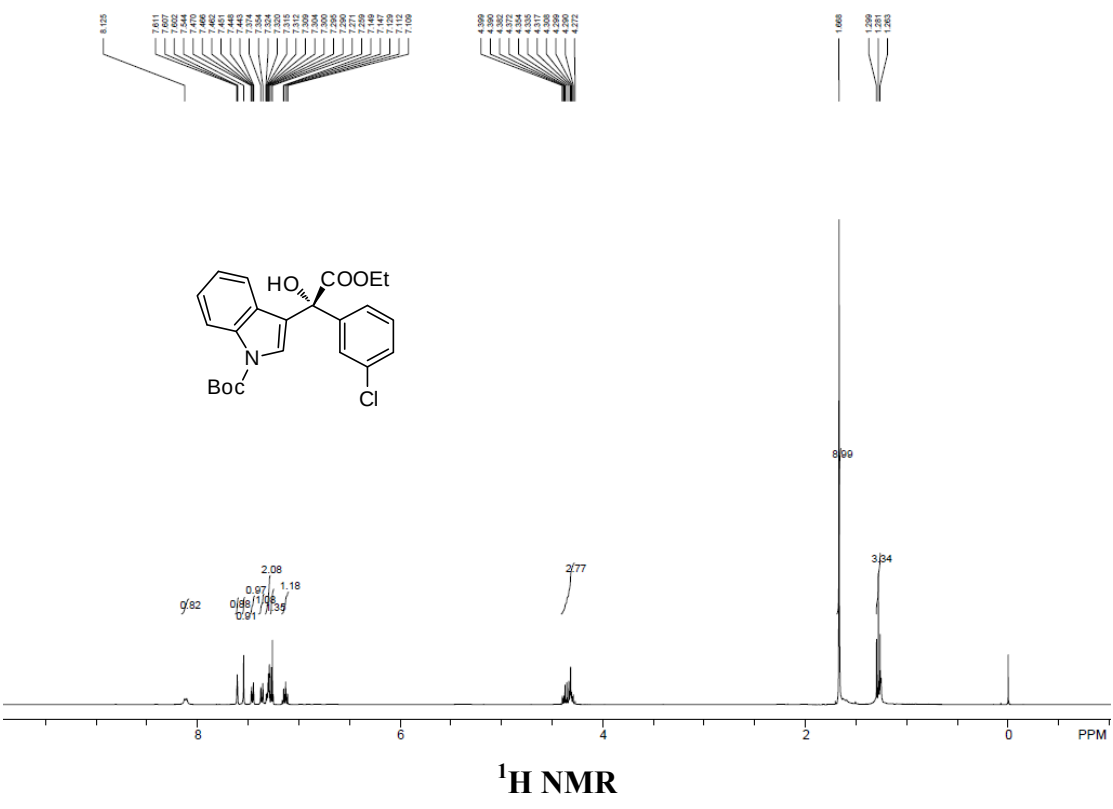


¹H NMR

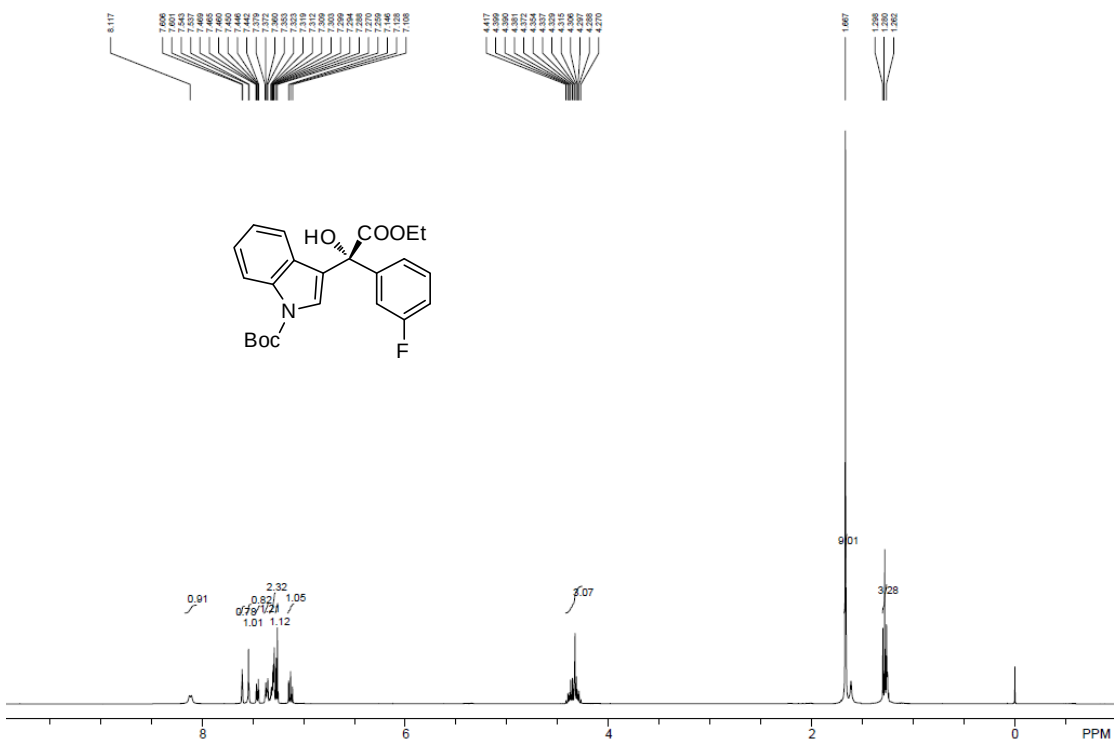


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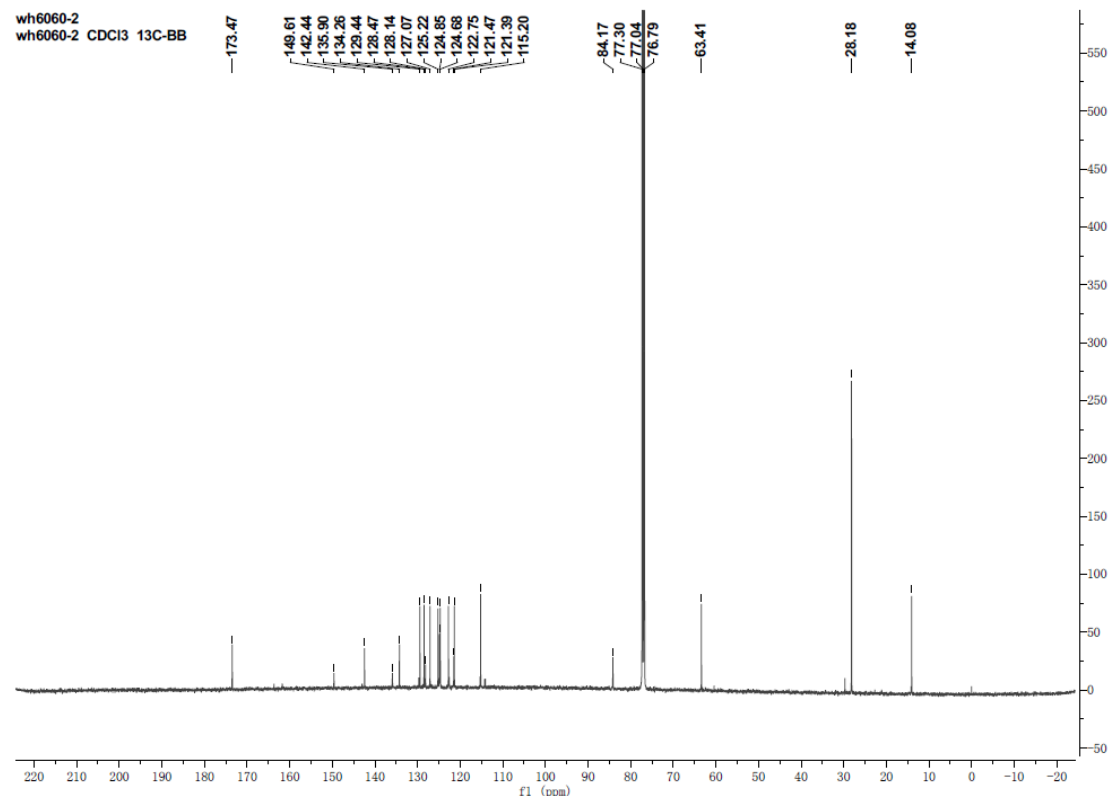
Compound 7n



Compound 7o

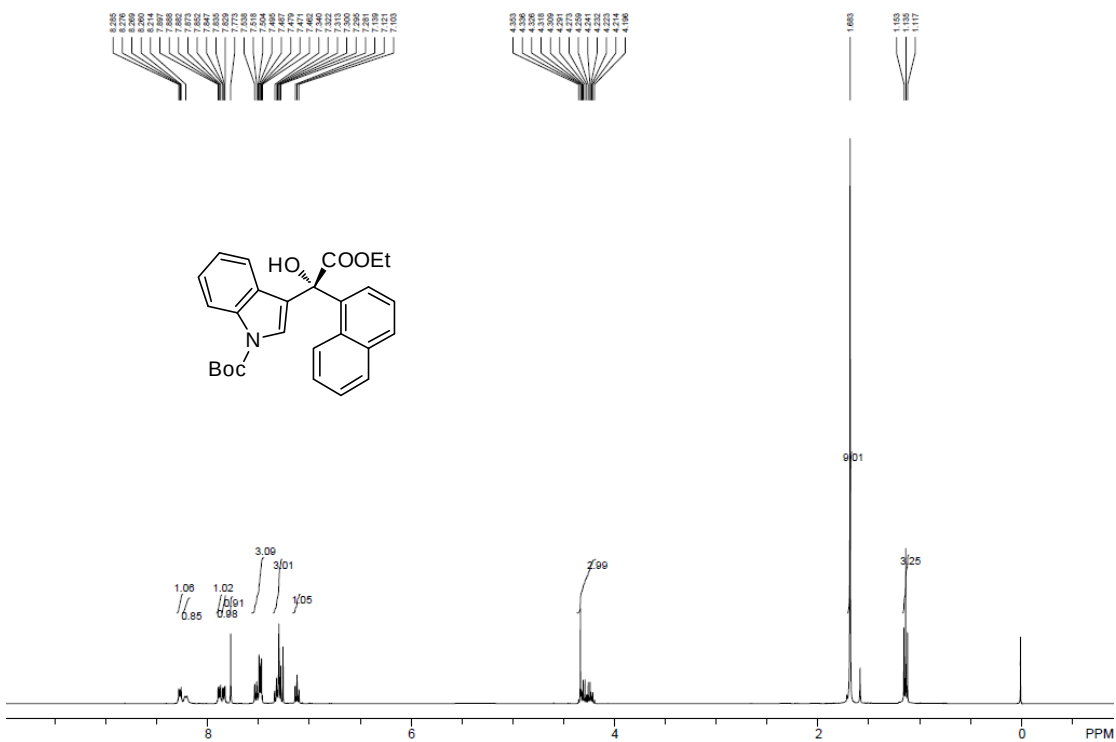


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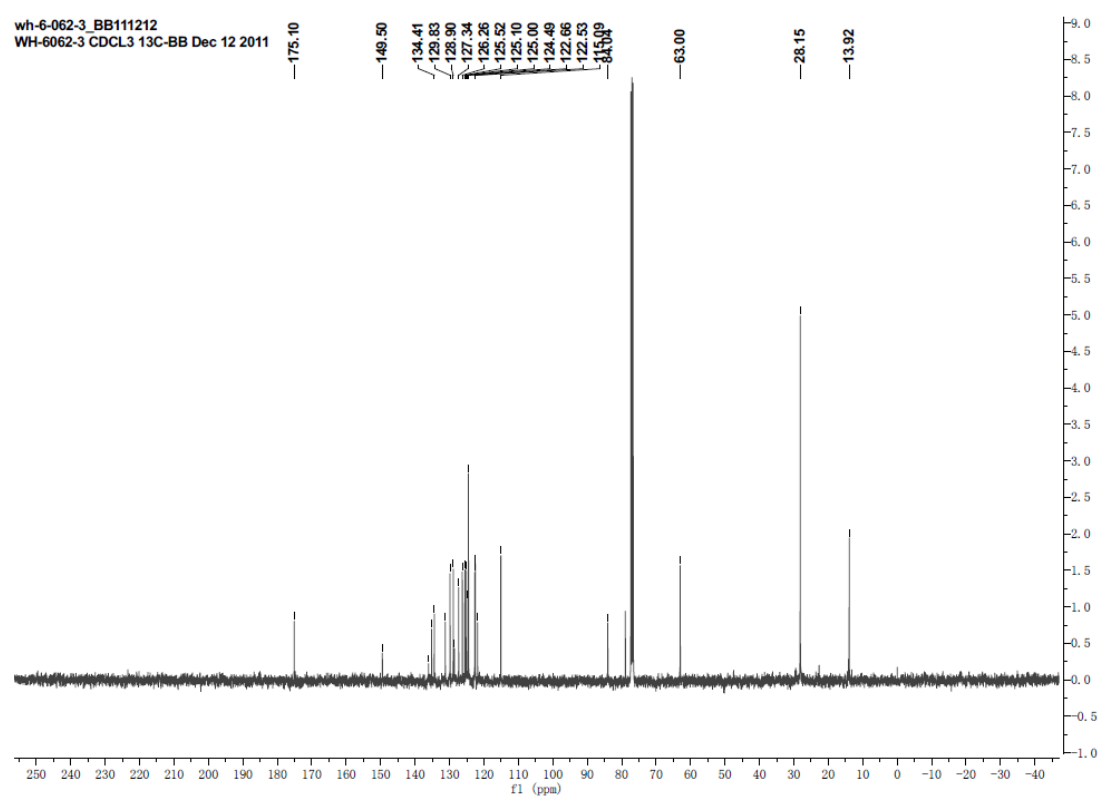


¹³C NMR

Compound 7p

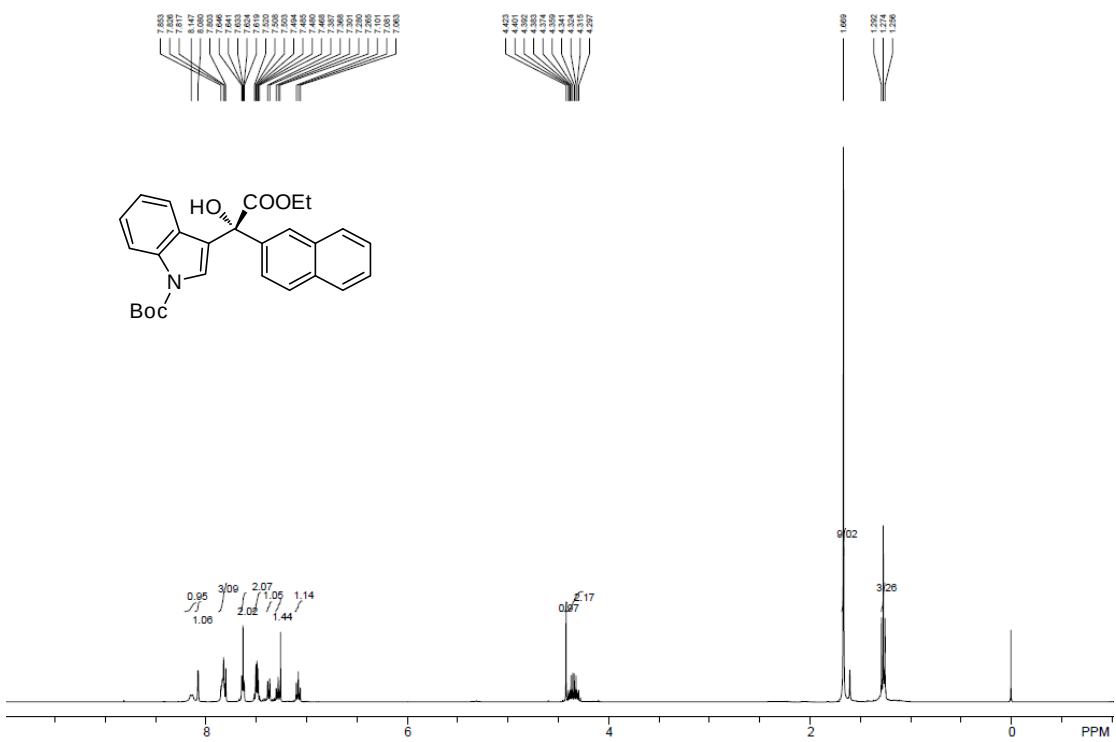


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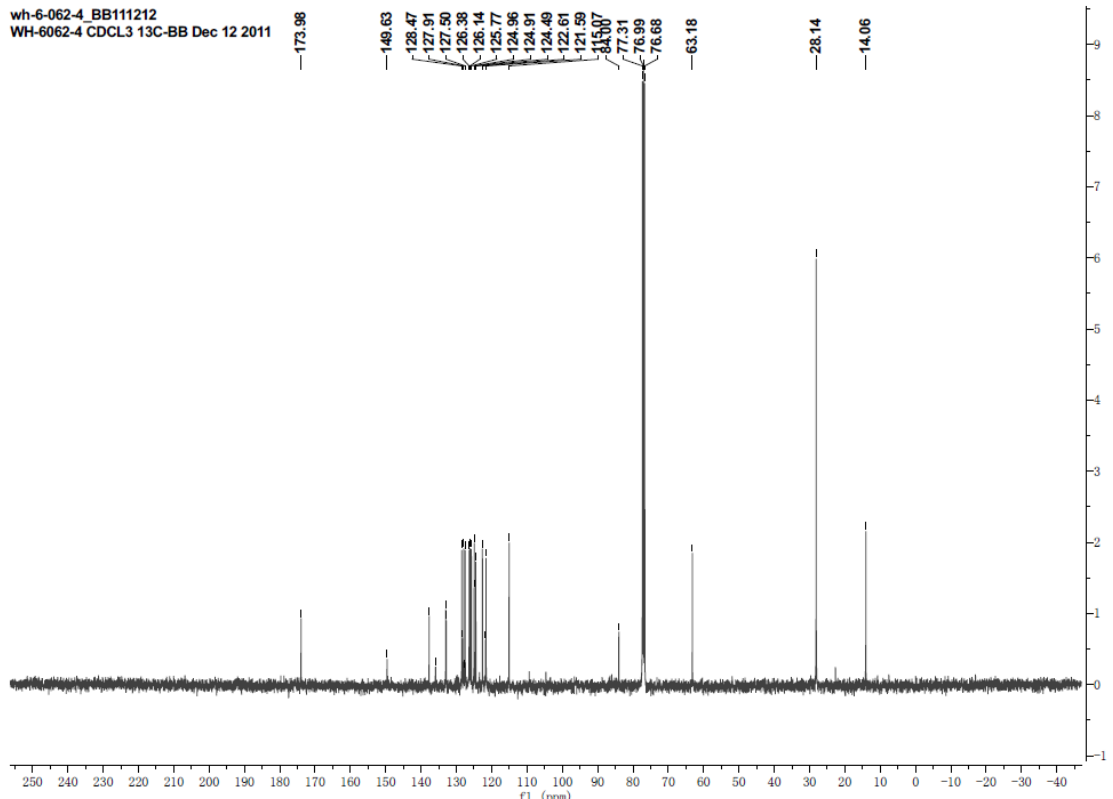


¹³C NMR

Compound 7q

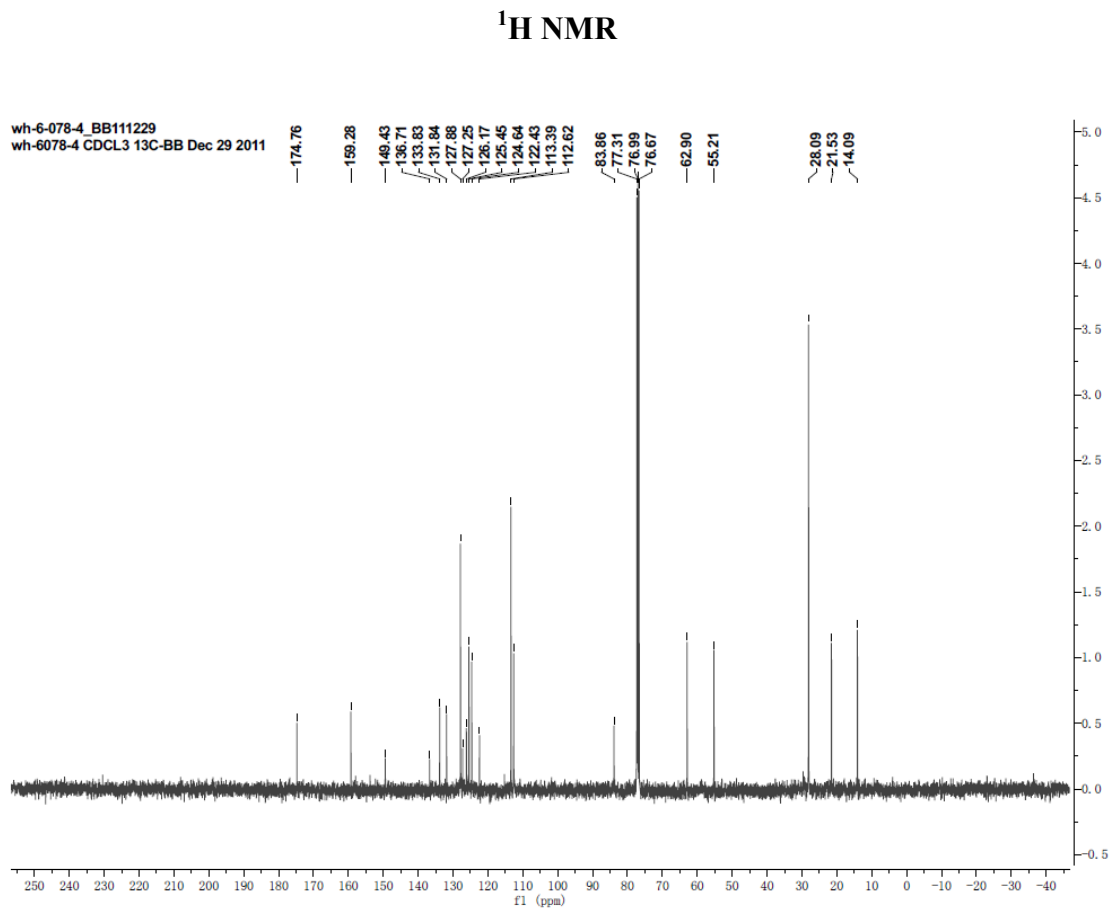
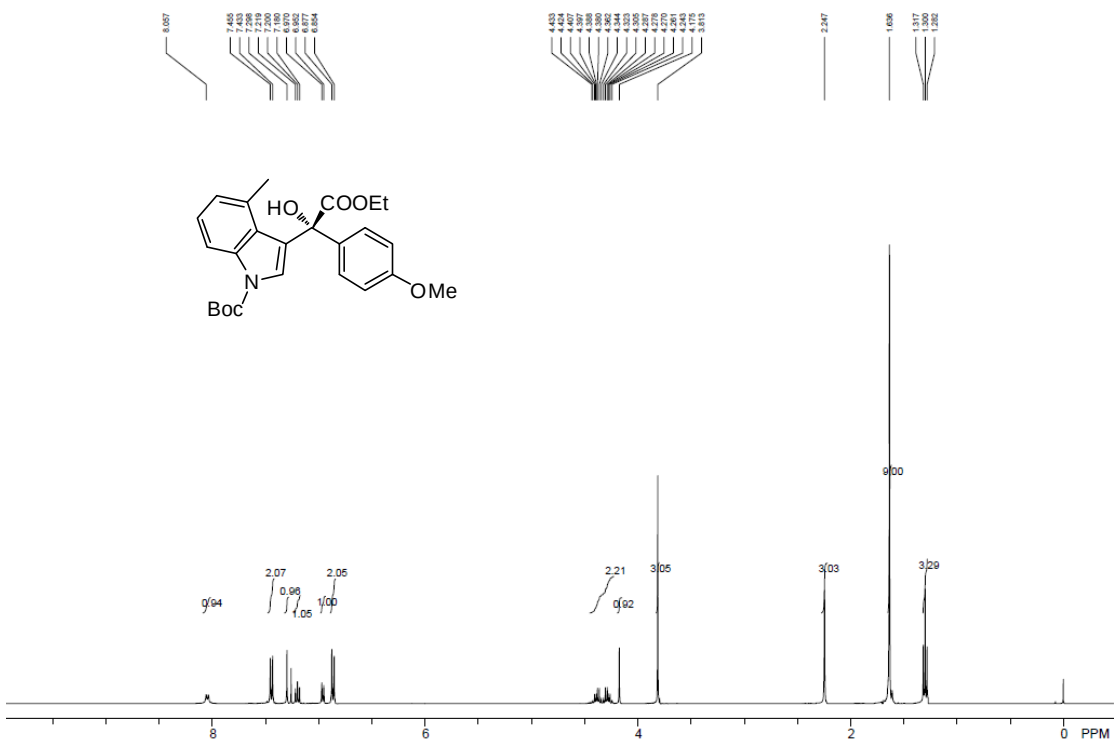


¹H NMR



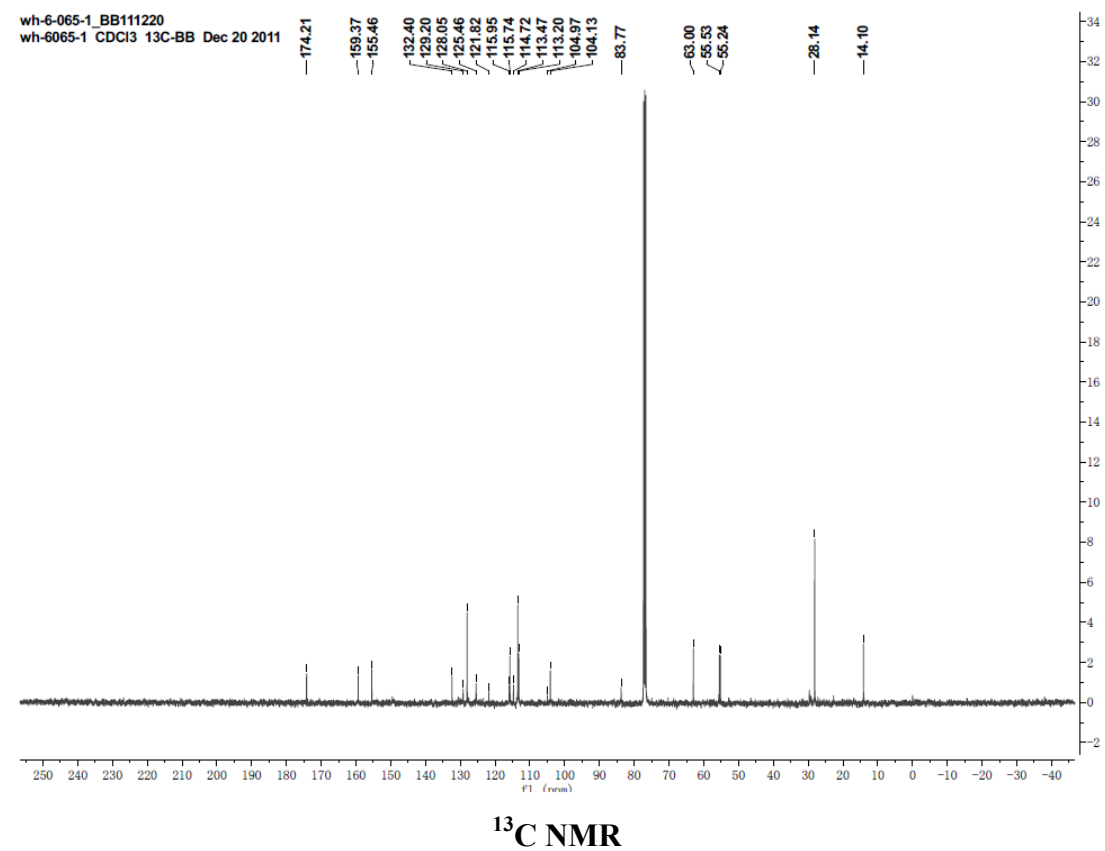
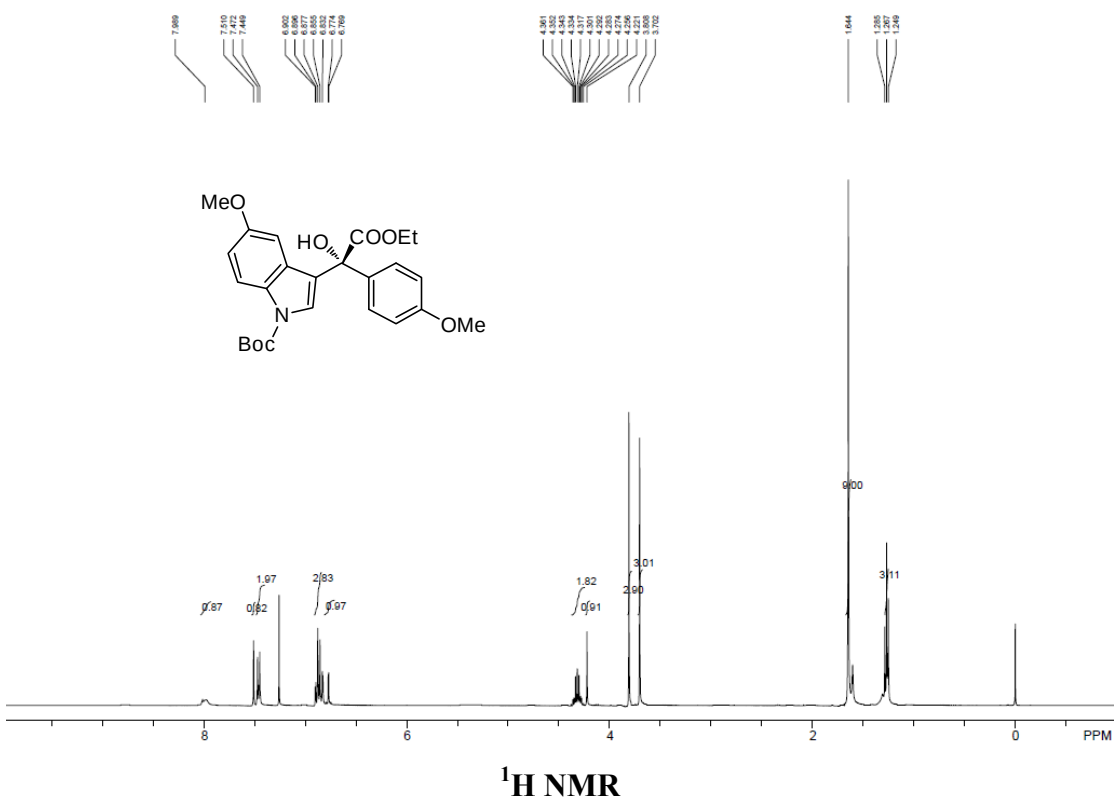
¹³C NMR

Compound 7r

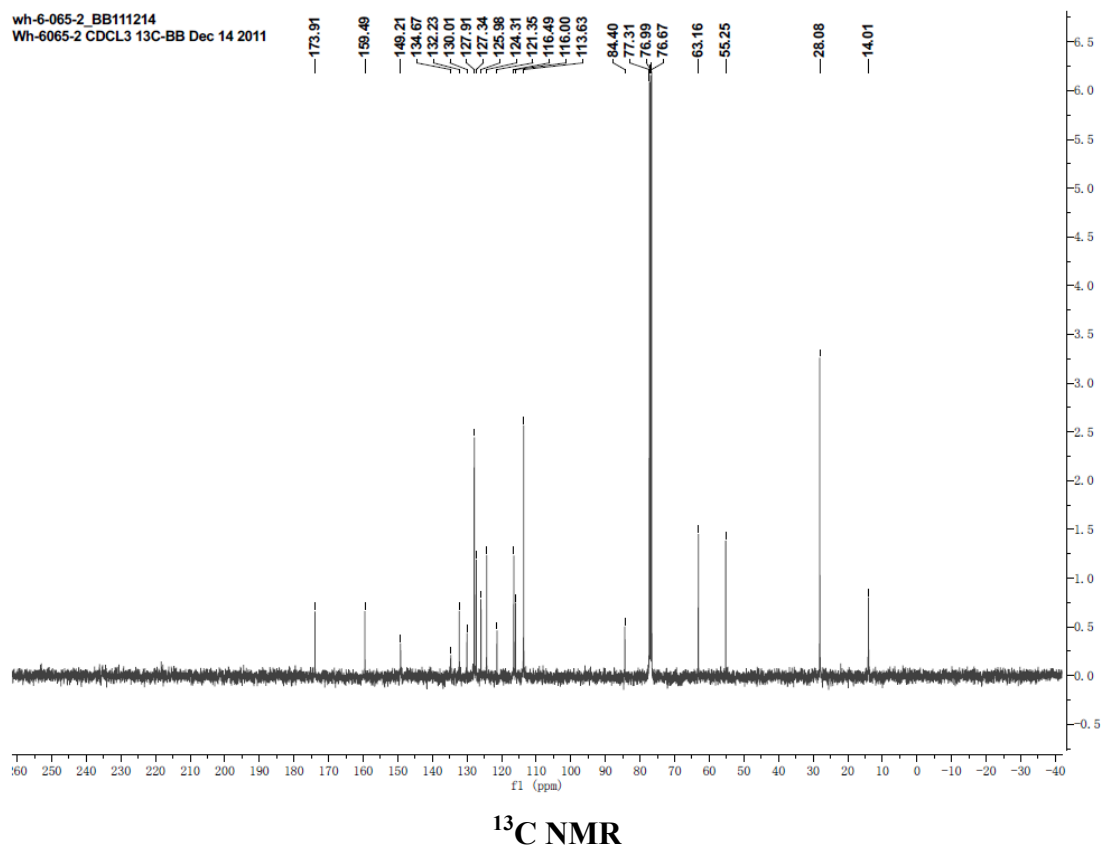
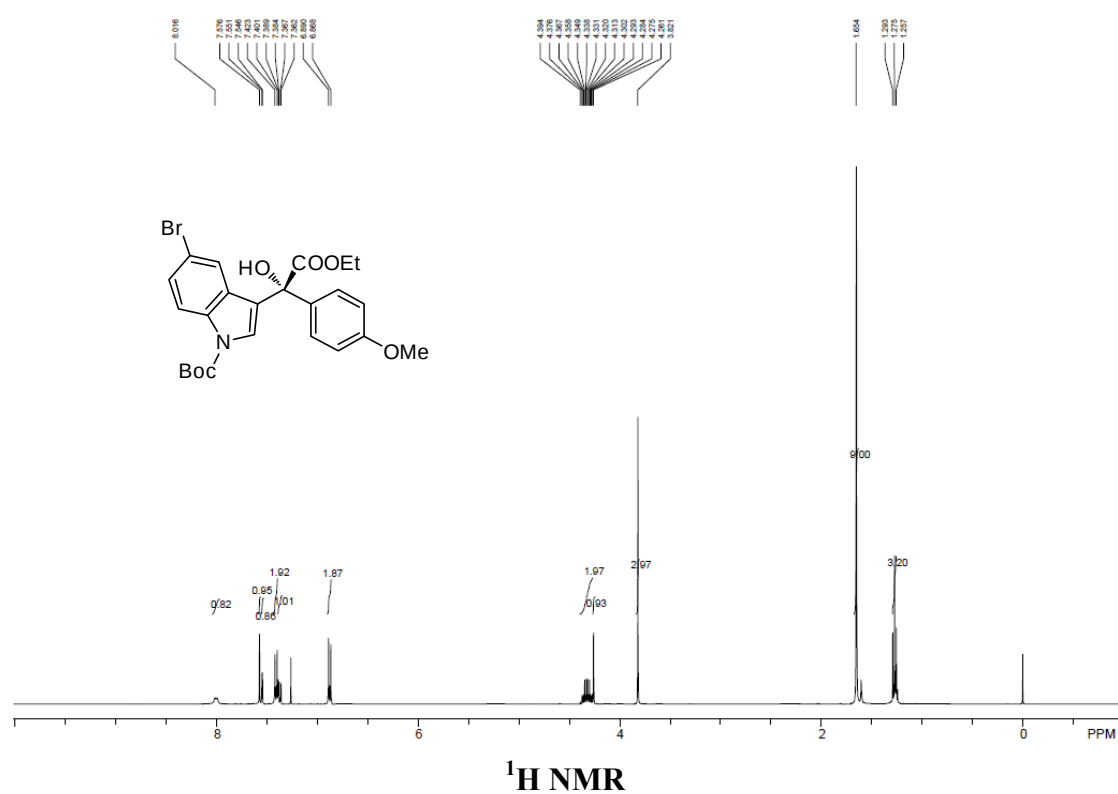


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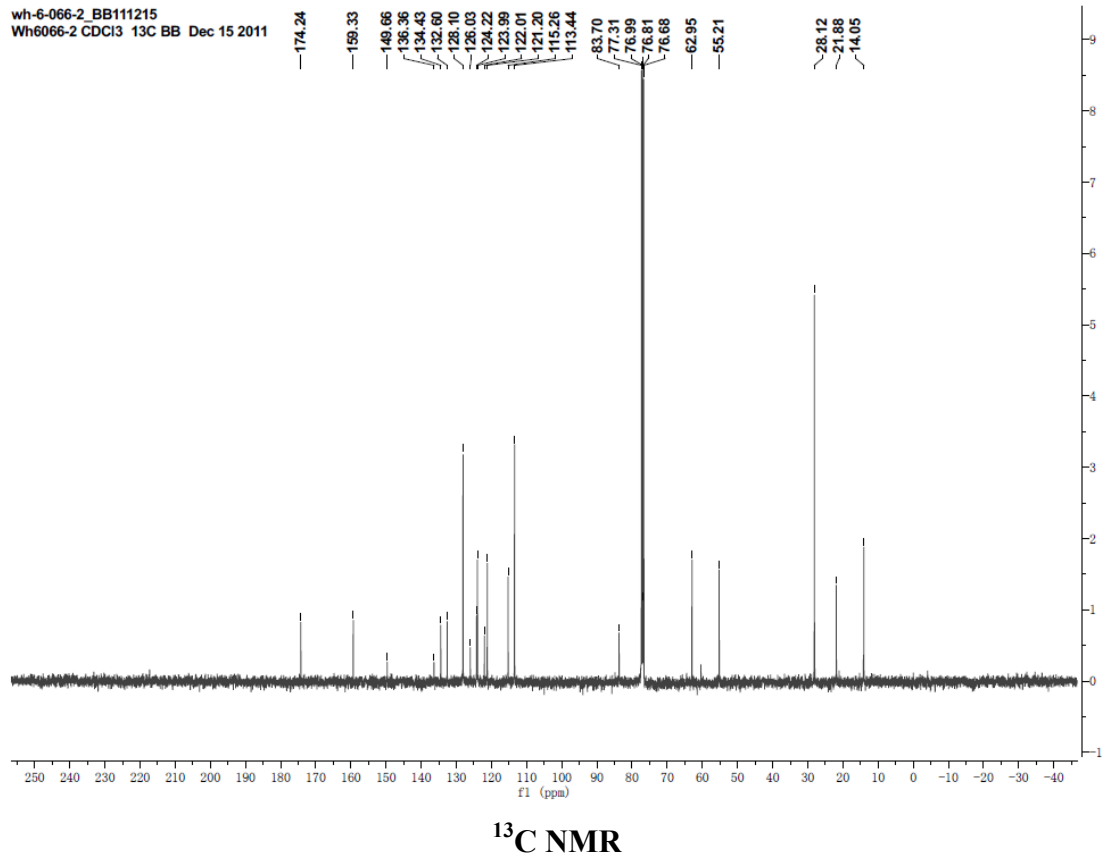
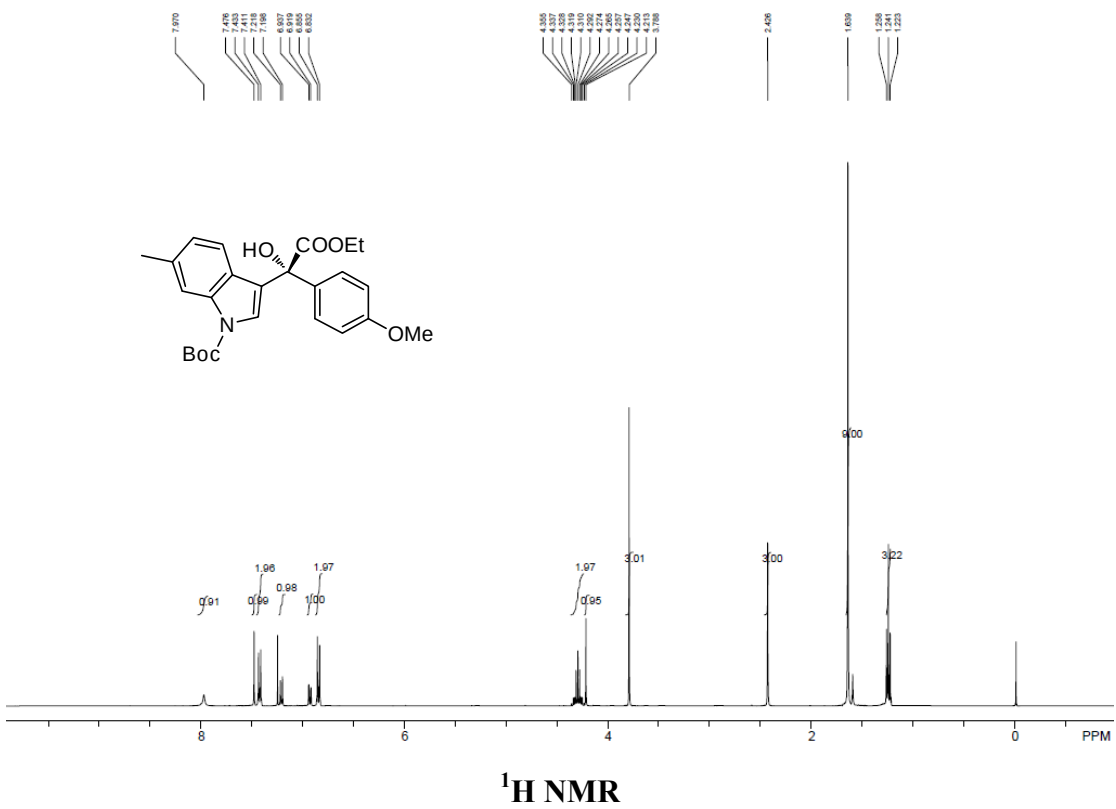
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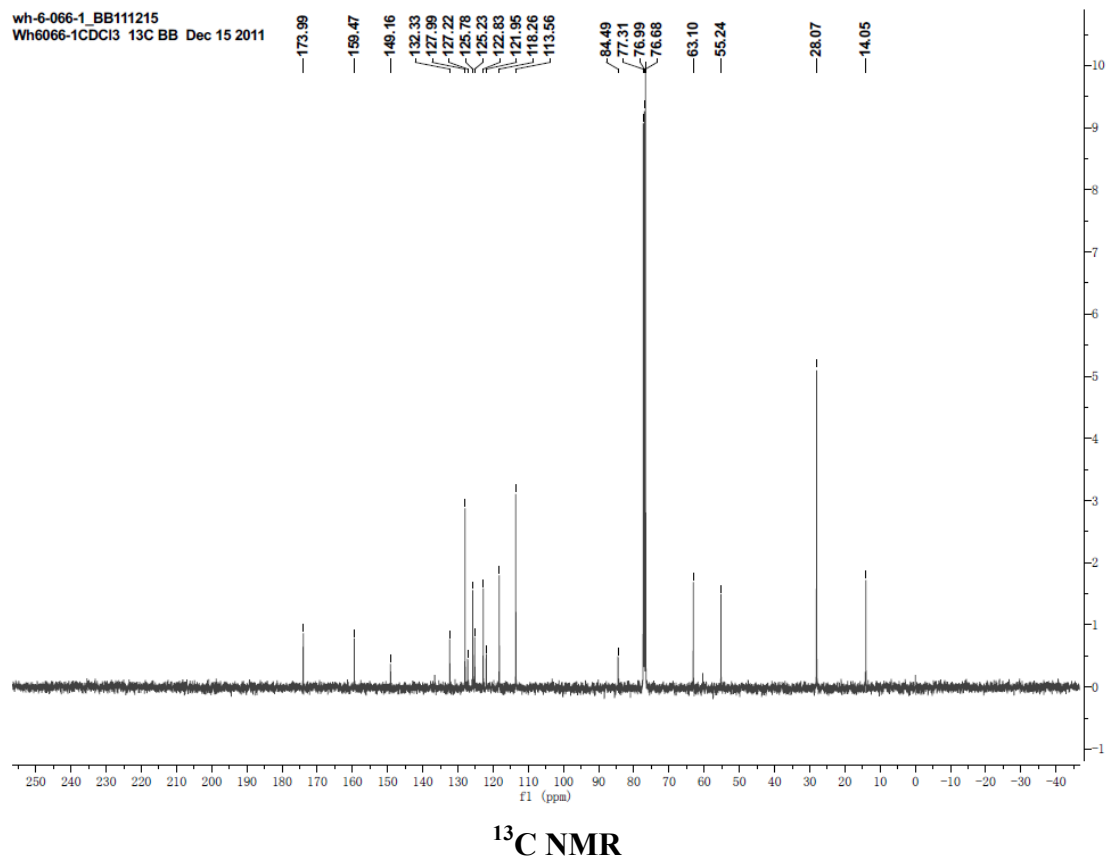
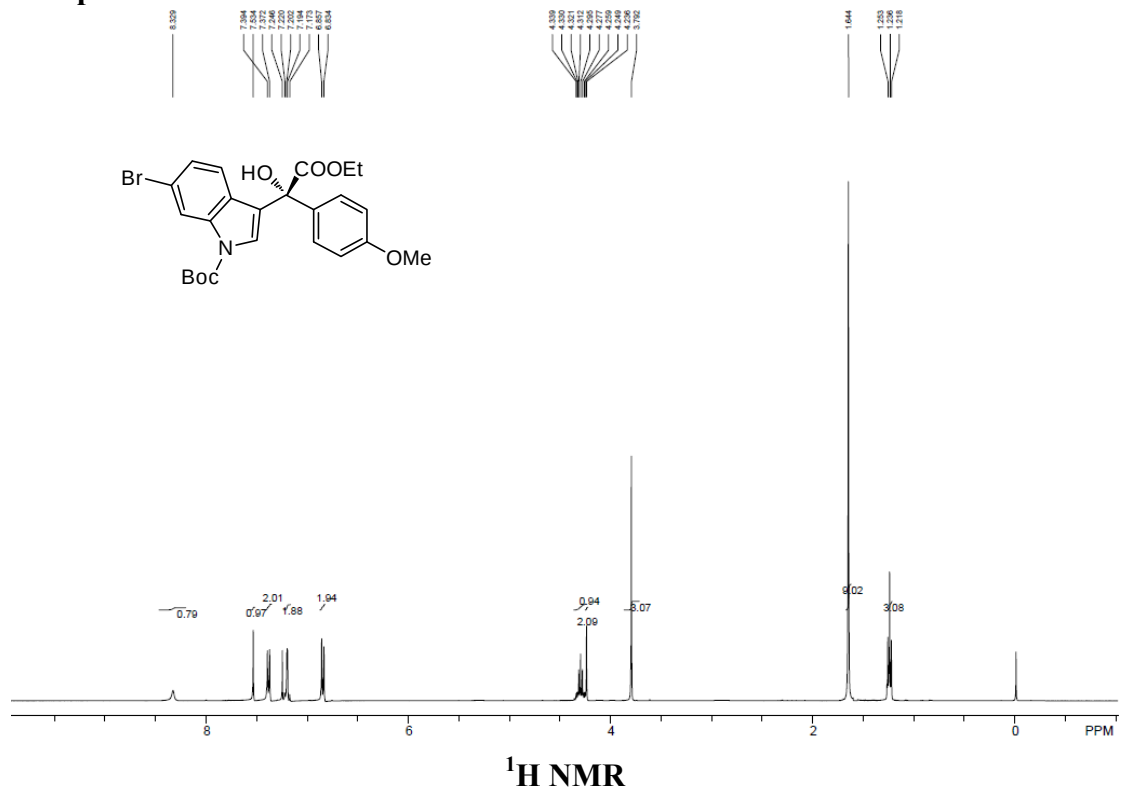
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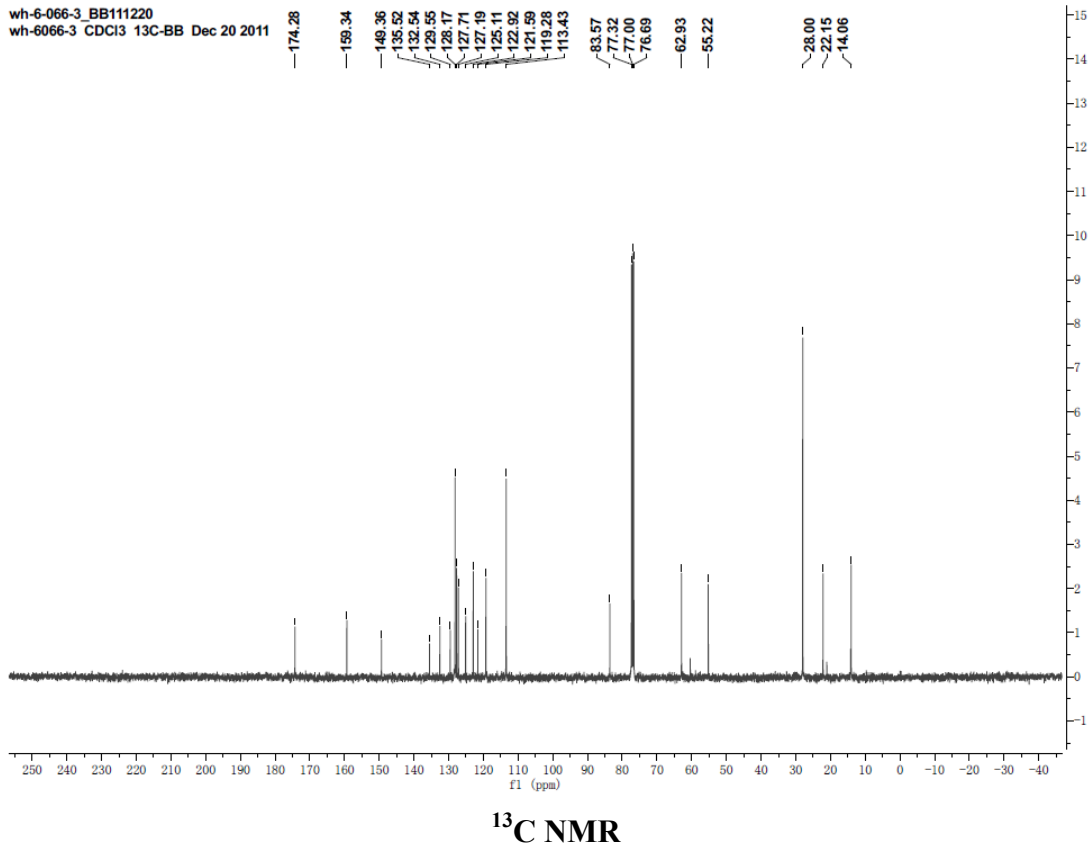
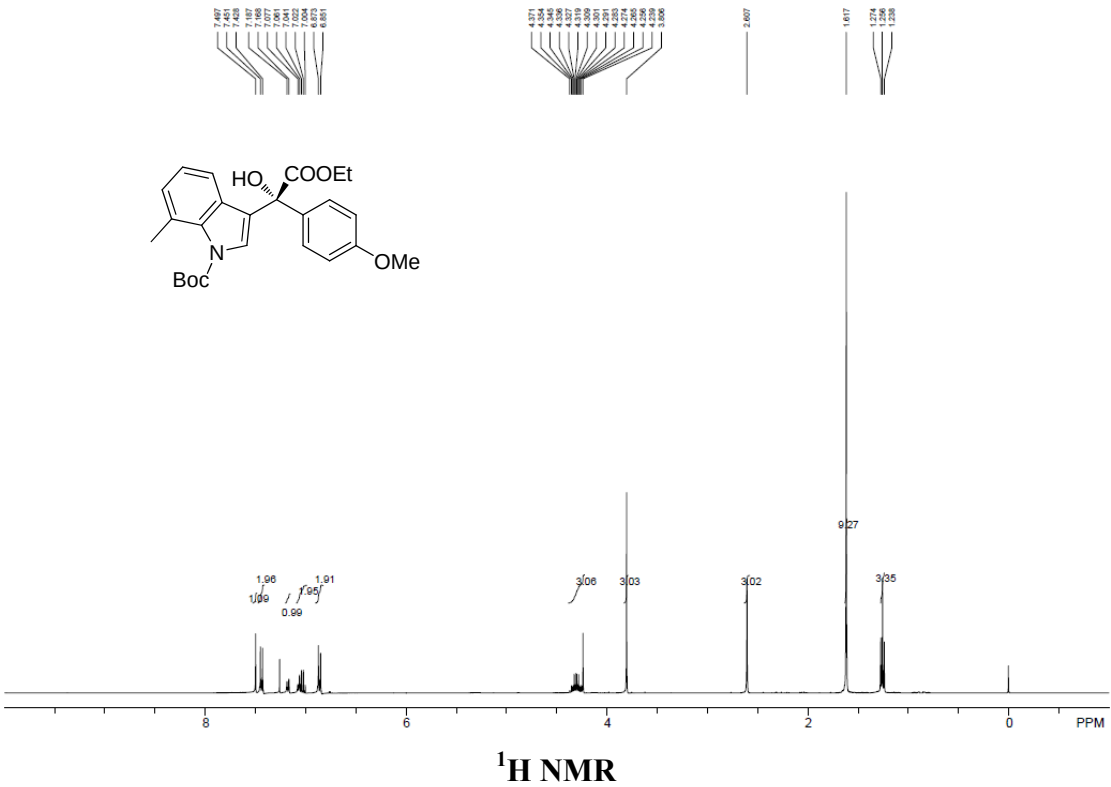
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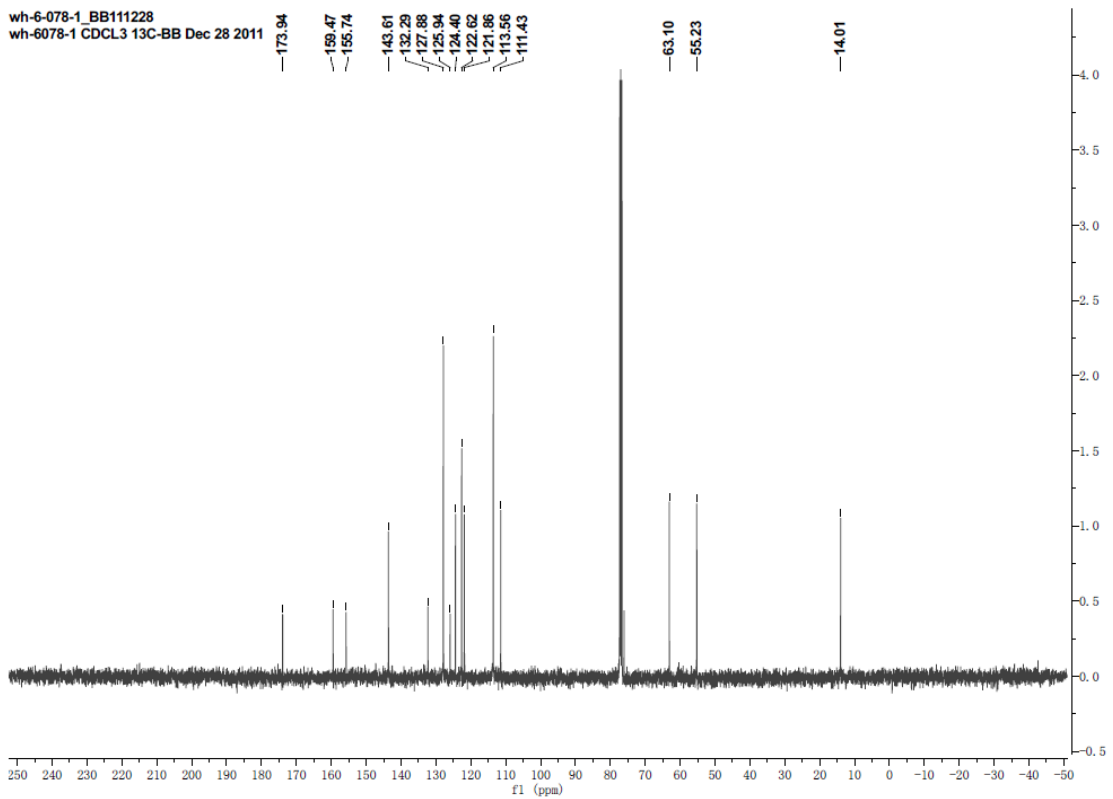
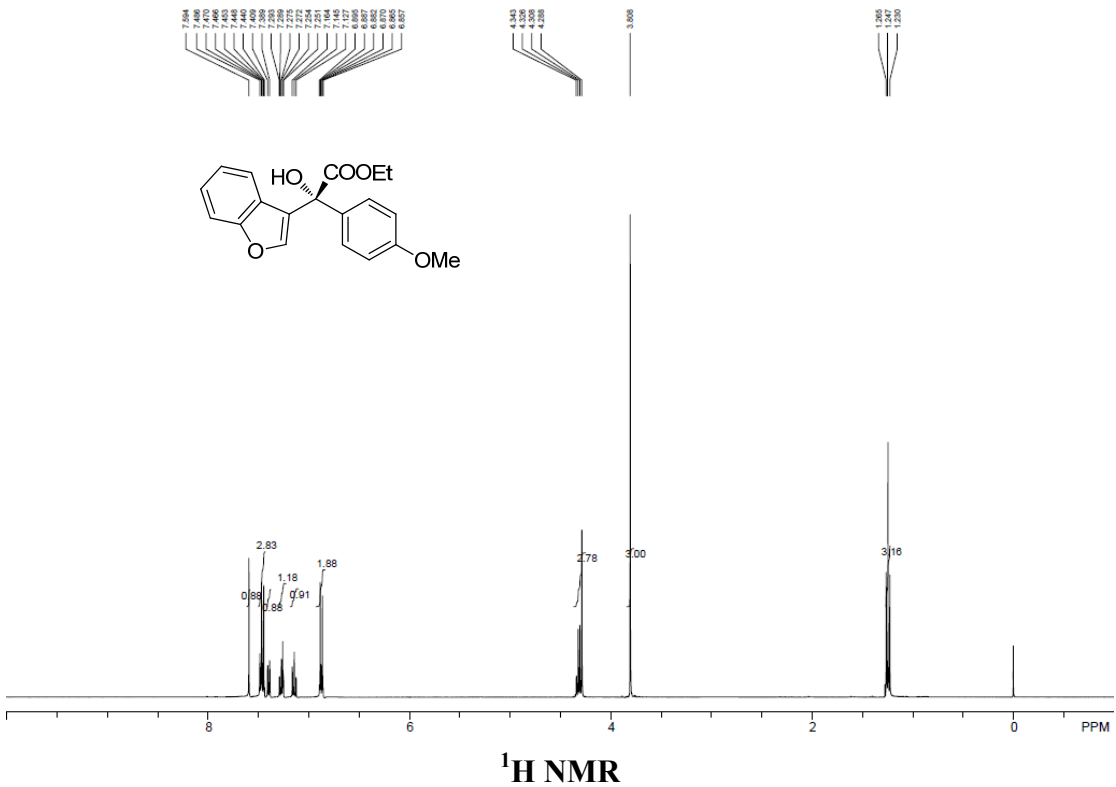
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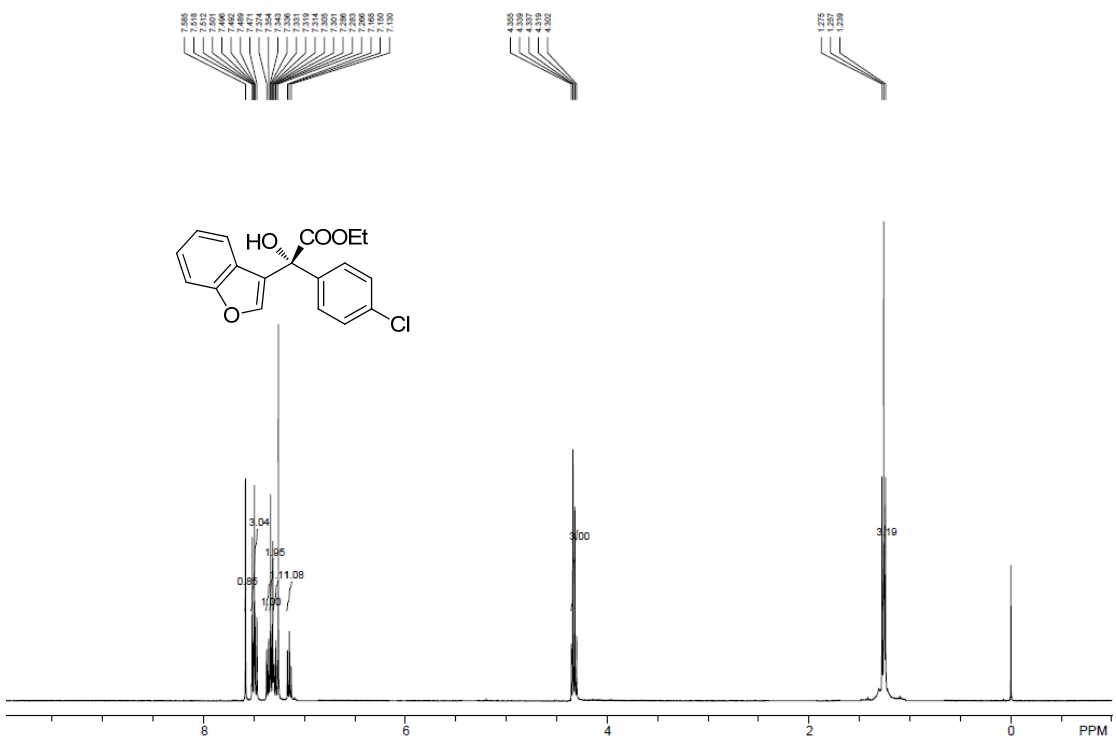
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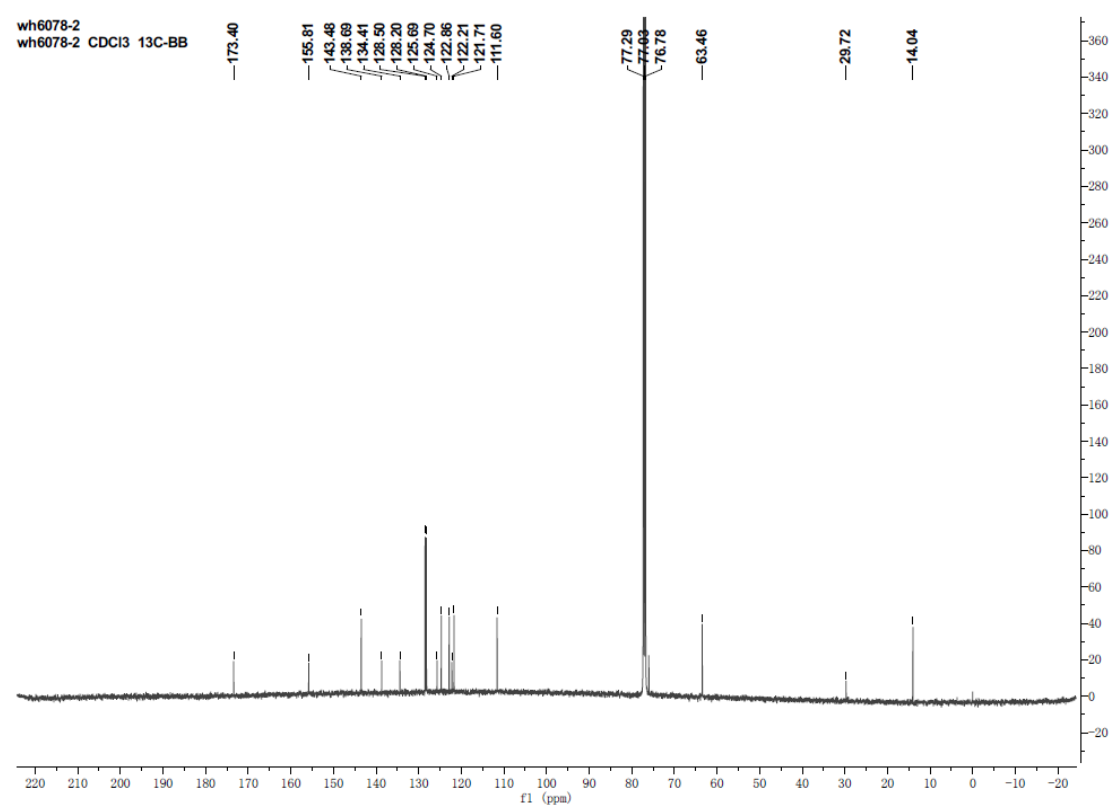
Compound 8a



Compound 8b

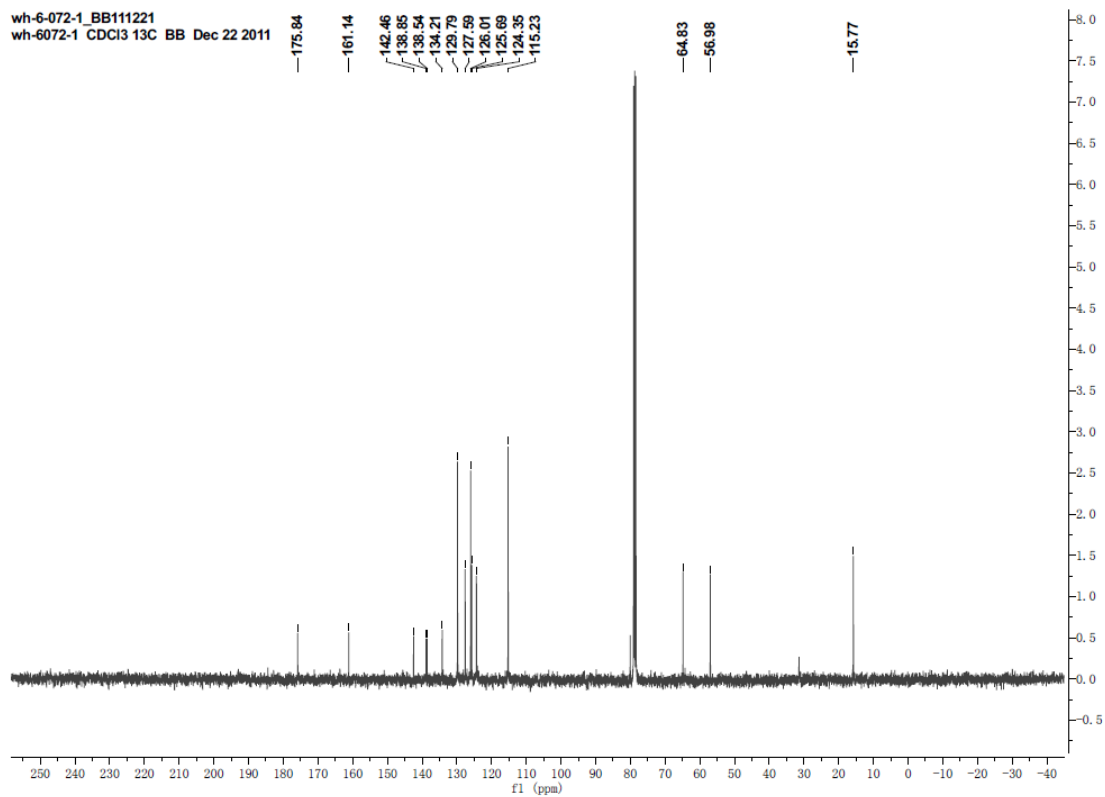
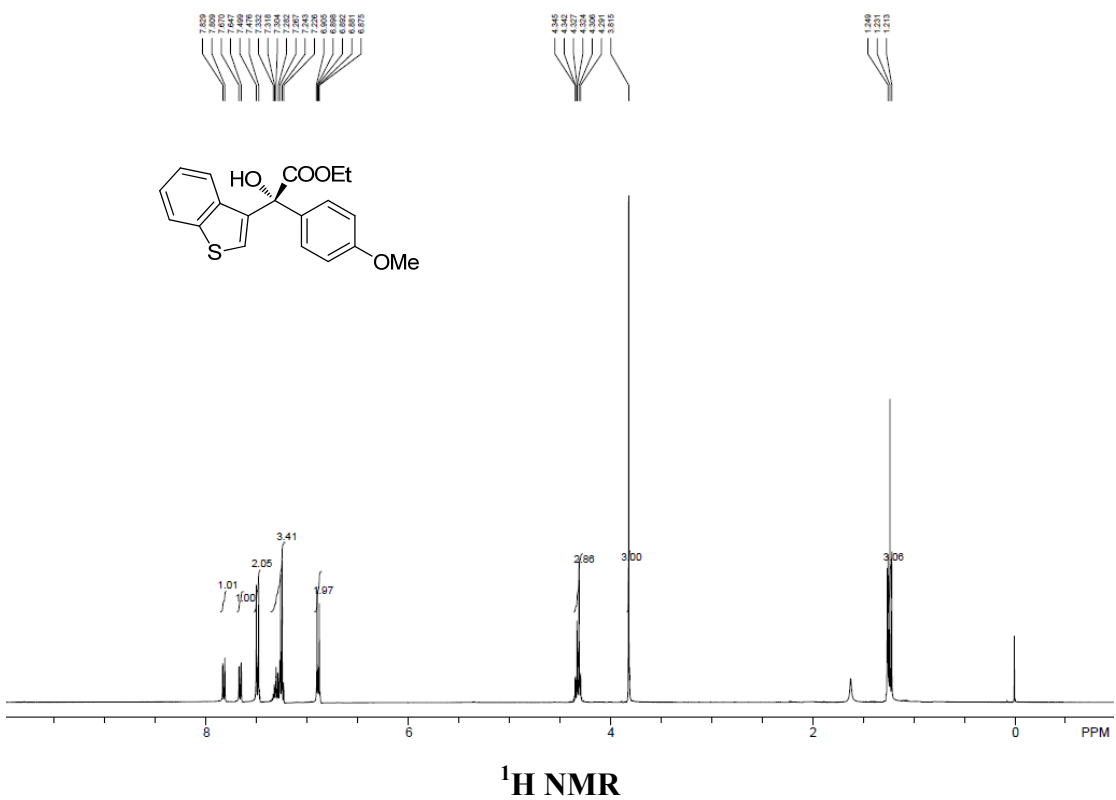


¹H NMR



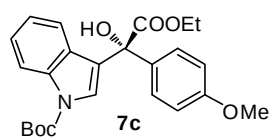
¹³C NMR

Compound 9

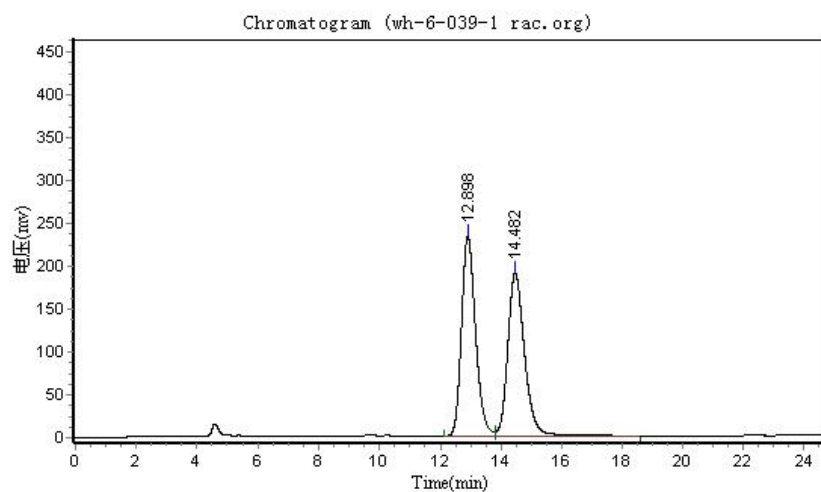


¹³C NMR

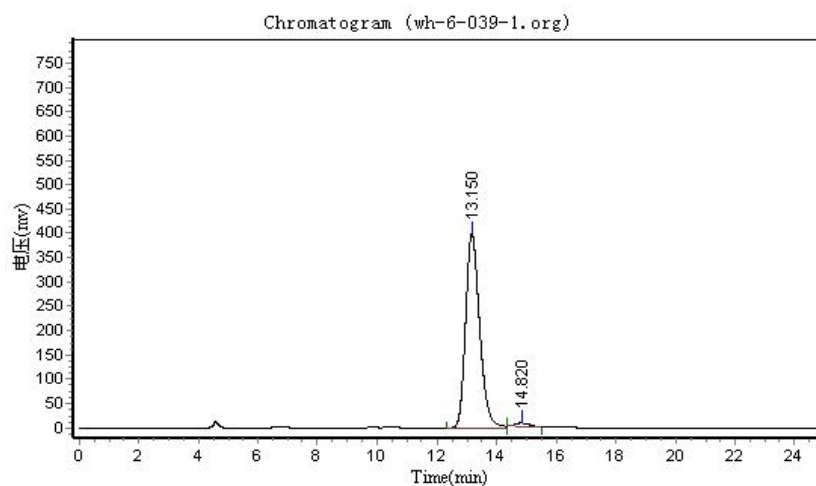
HPLC Spectra of addition products



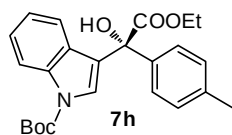
HPLC: Chiral OD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 13.2 min
(major), 14.8 min.



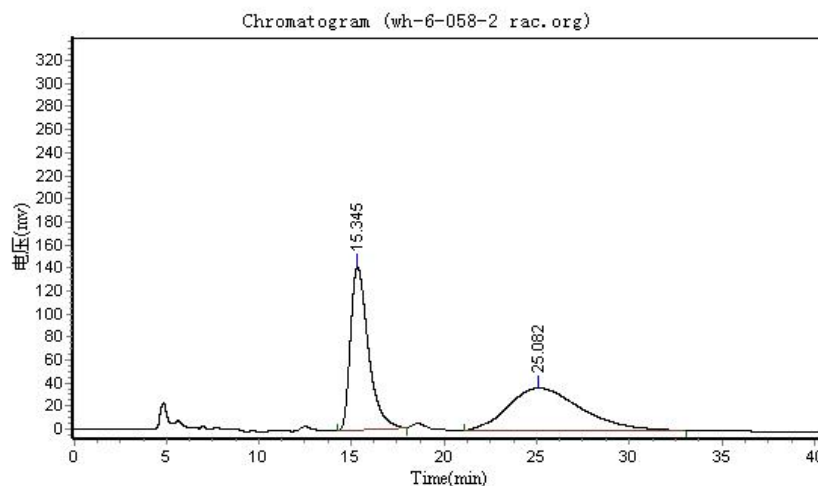
Results					
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1		12.898	231917.141	7466808.000	50.5607
2		14.482	190115.438	7301197.000	49.4393
Total			422032.578	14768005.000	100.0000



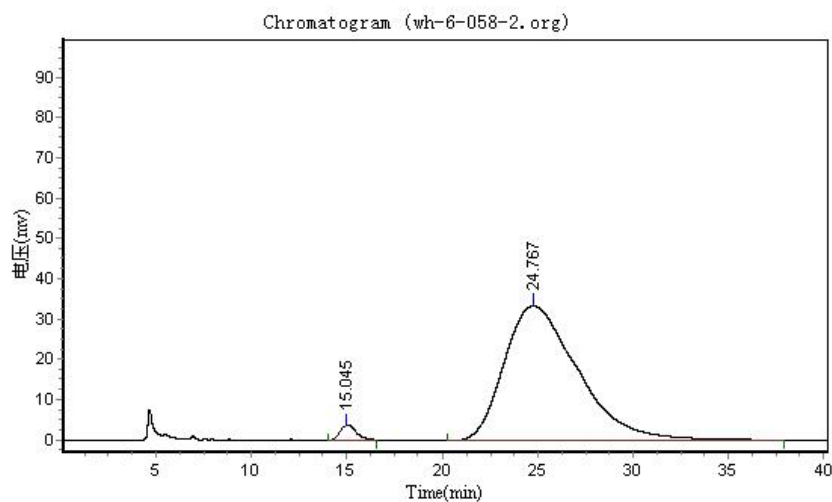
Results					
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1		13.150	399320.594	13093110.000	98.2327
2		14.820	7118.925	235560.328	1.7673
Total			406439.519	13328670.328	100.0000



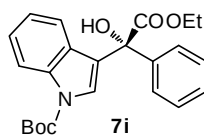
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hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 15.0 min,
24.8 min (major).



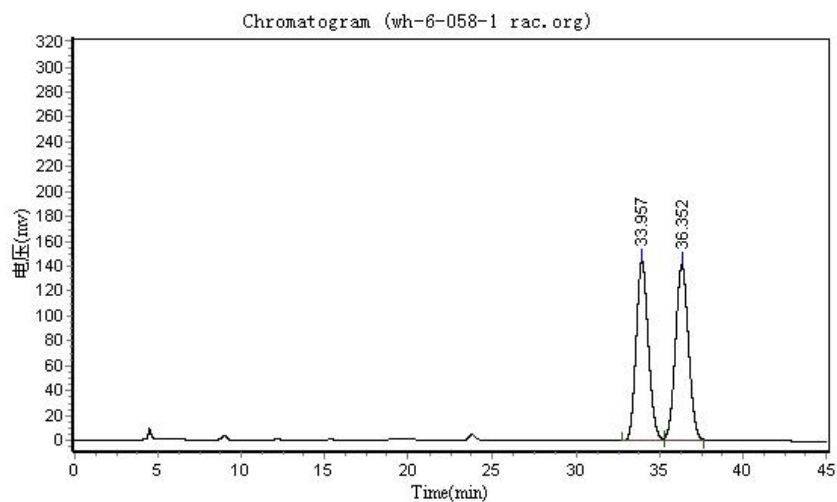
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.345	141286.719	9443678.000	48.4526
2		25.082	36831.230	10046853.000	51.5474
Total			178117.949	19490531.000	100.0000



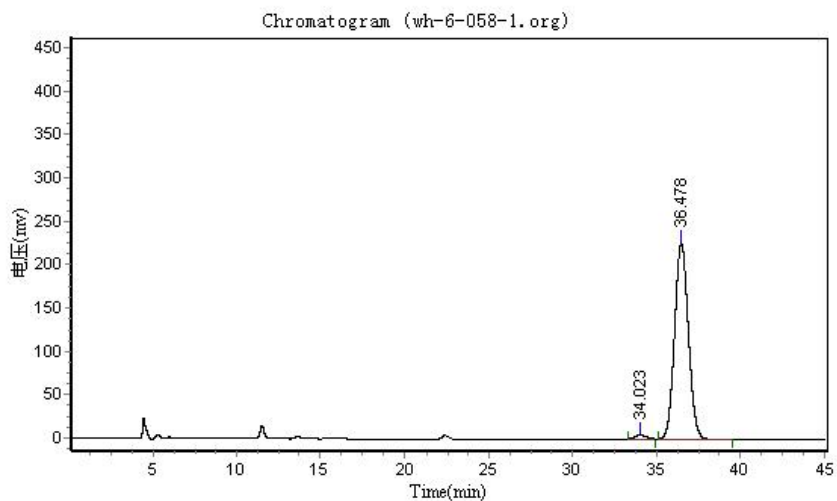
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		15.045	3583.752	225475.797	2.4394
2		24.767	33489.500	9017467.000	97.5606
Total			37073.252	9242942.797	100.0000



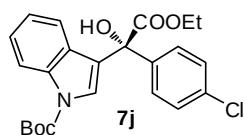
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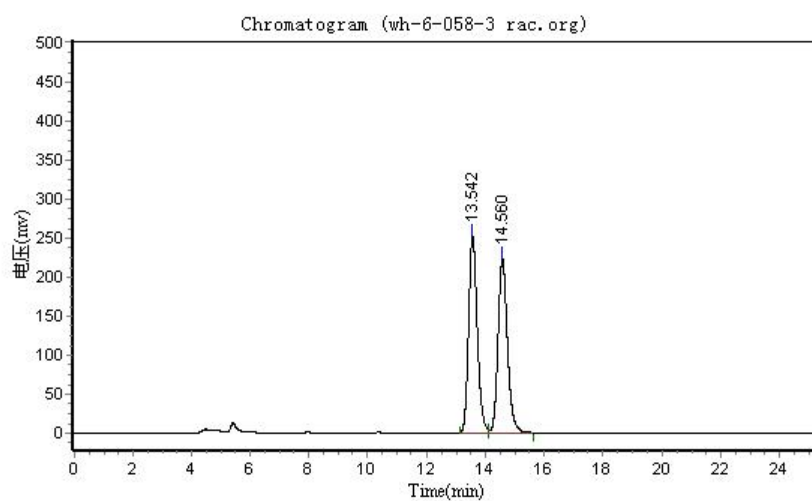
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		33.957	144609.938	7335114.500	48.9829
2		36.352	141154.734	7639731.000	51.0171
Total			285764.672	14974845.500	100.0000



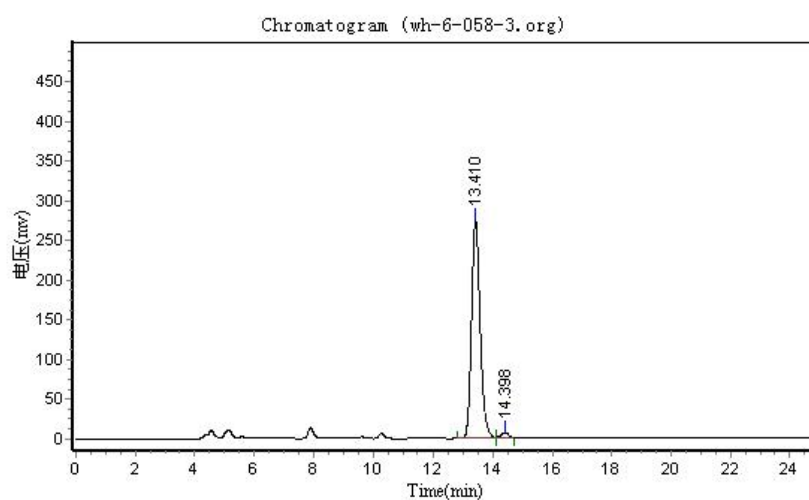
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		34.023	3914.201	189341.906	1.4356
2		36.478	226425.313	12999857.000	98.5644
Total			230339.514	13189198.906	100.0000



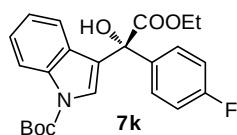
HPLC: Chiral AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 13.4 min (major), 14.4 min.



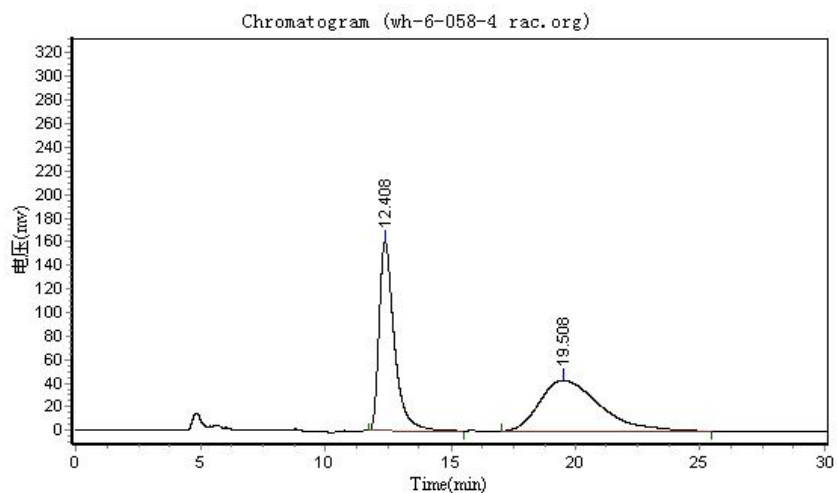
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.542	251561.672	5196427.000	51.0387
2		14.560	223097.656	4984911.500	48.9613
Total			474659.328	10181338.500	100.0000



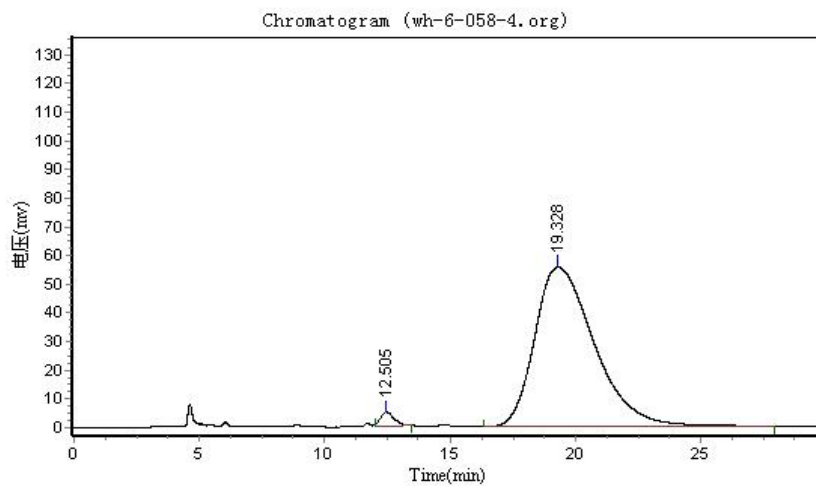
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.410	273807.438	5511221.500	98.1535
2		14.398	5959.715	103679.883	1.8465
Total			279767.153	5614901.383	100.0000



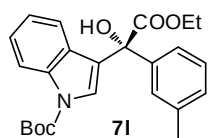
HPLC: Chiral AY-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 12.5 min,
19.3 min (major).



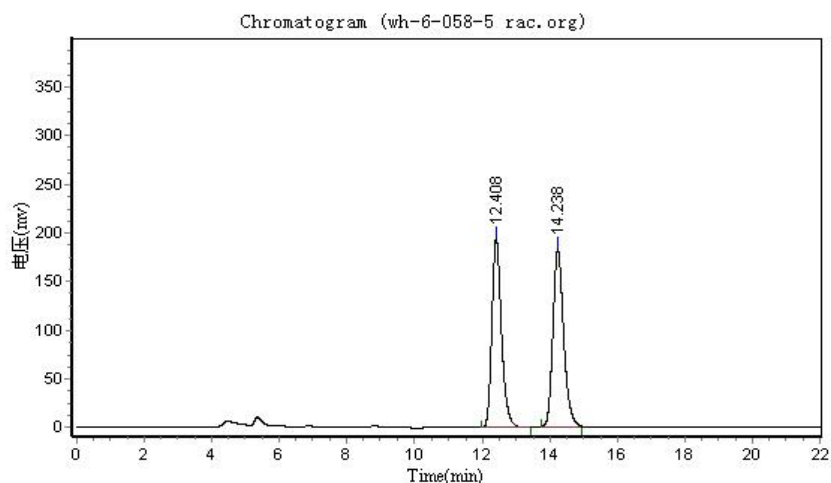
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.408	159722.938	6769234.000	48.2960
2		19.508	42933.813	7246892.500	51.7040
Total			202656.750	14016126.500	100.0000



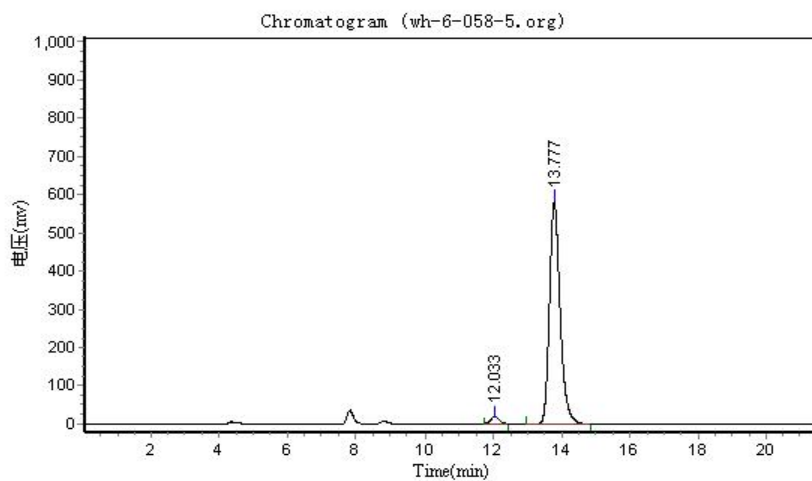
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.505	4894.856	187583.969	1.9939
2		19.328	55404.266	9220194.000	98.0061
Total			60299.122	9407777.969	100.0000



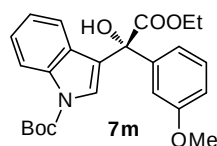
HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 12.0 min,
13.8 min (major).



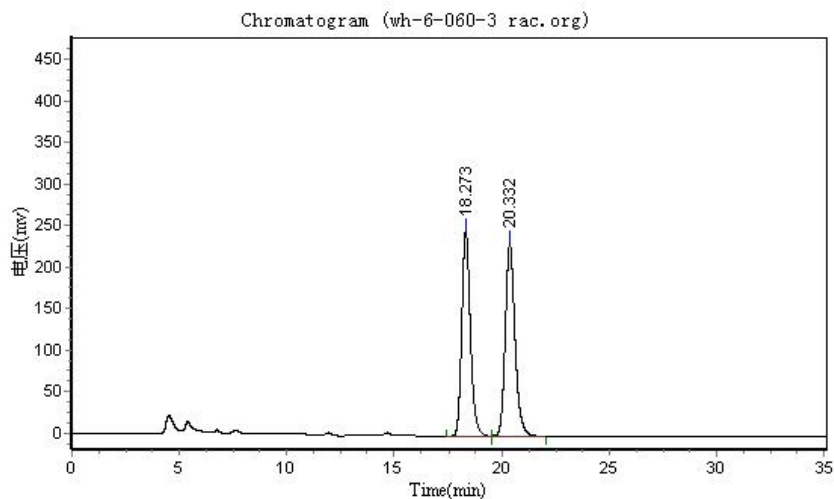
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.408	194186.859	3845206.000	48.8118
2		14.238	182121.016	4032410.250	51.1882
Total			376307.875	7877616.250	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.033	18863.607	332191.688	2.5729
2		13.777	580244.250	12579209.000	97.4271
Total			599107.857	12911400.688	100.0000

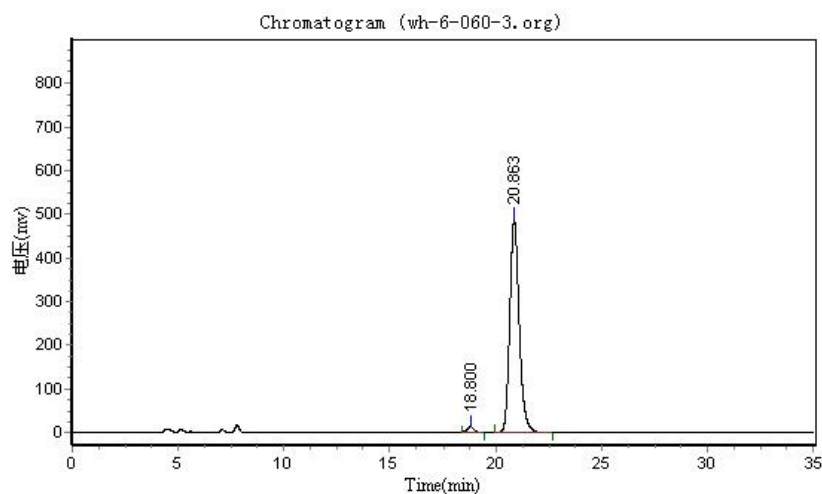


HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 18.8 min,
20.9 min (major).



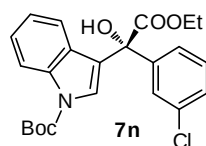
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.273	246883.672	6898140.500	48.7305
2		20.332	230951.250	7257549.500	51.2695
Total			477834.922	14155690.000	100.0000

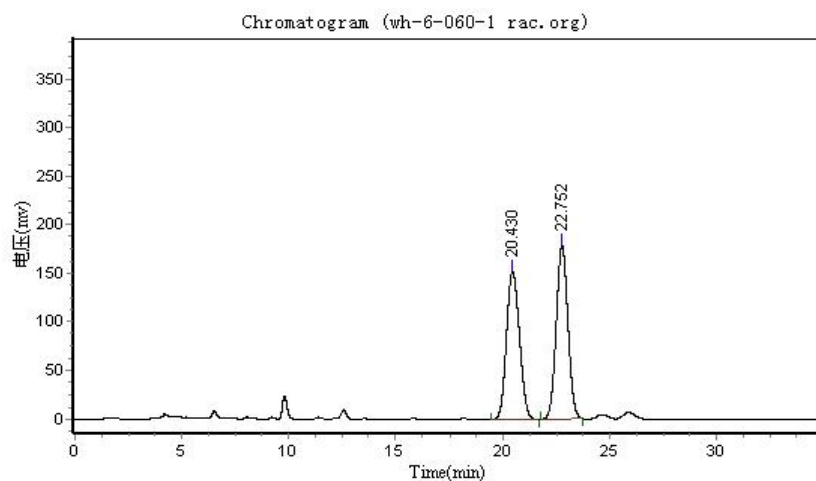


Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.800	12257.471	316662.813	2.0539
2		20.863	486501.938	15101237.000	97.9461
Total			498759.408	15417899.813	100.0000

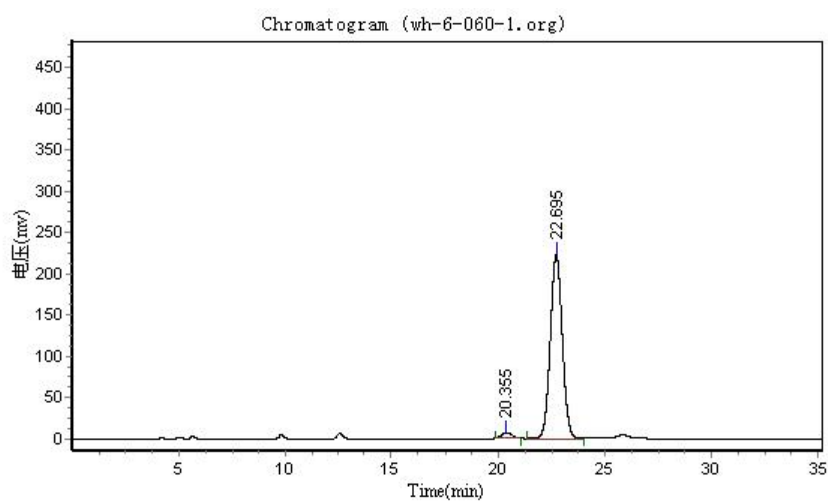


HPLC: Chiral AD-3 column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 20.4 min, 22.7 min (major).



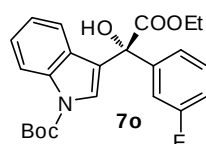
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.430	152461.984	6454008.500	48.6696
2		22.752	178671.250	6806840.500	51.3304
Total			331133.234	13260849.000	100.0000

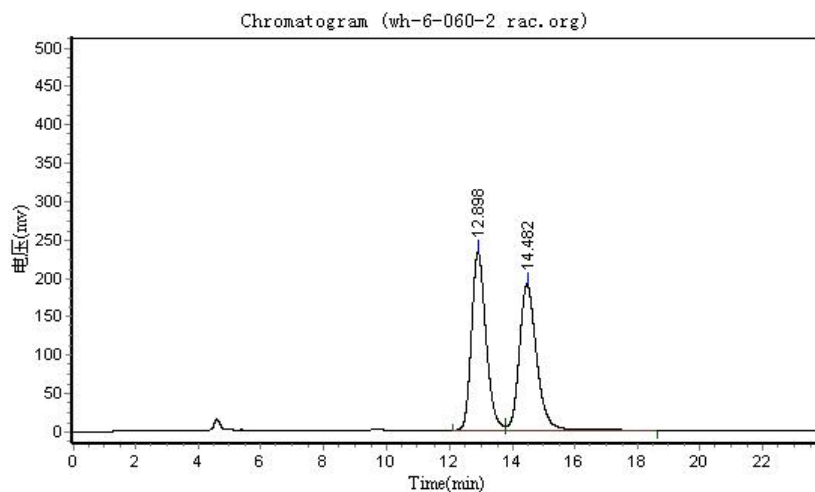


Results

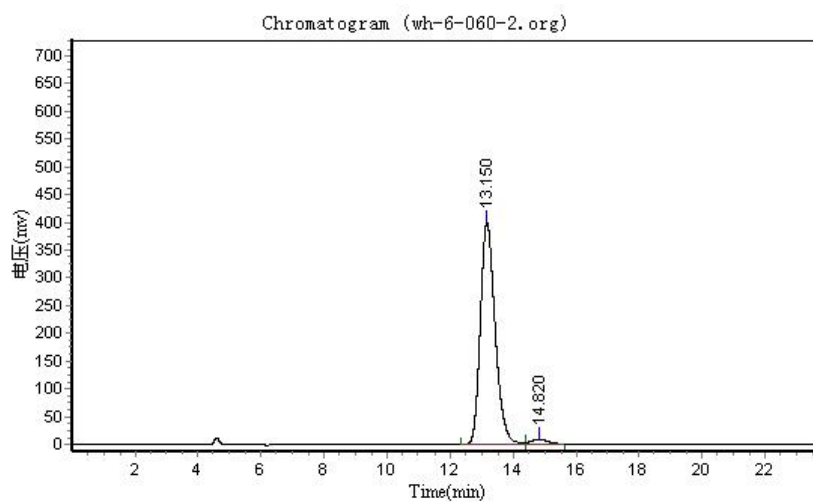
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.355	6153.459	227872.641	2.5336
2		22.695	223767.500	8766025.000	97.4664
Total			229920.959	8993897.641	100.0000



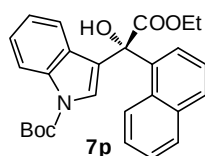
HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 13.2 min
(major), 14.8 min.



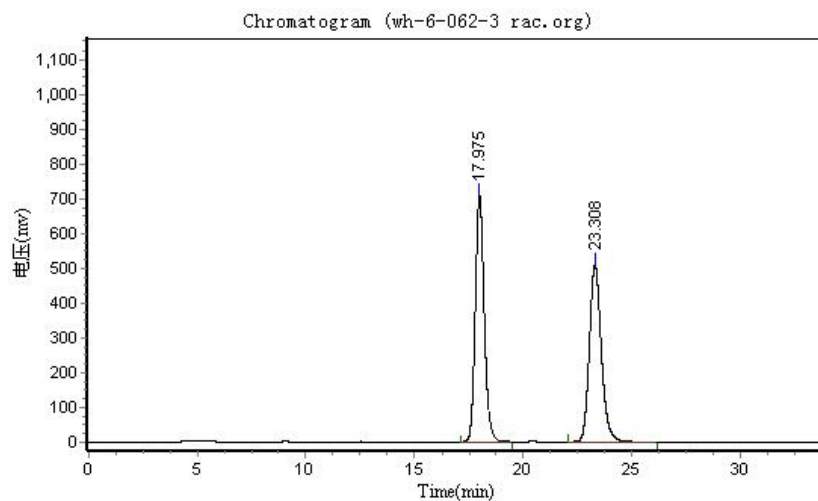
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		12.898	231917.141	7466808.000	50.5607
2		14.482	190115.438	7301197.000	49.4393
Total			422032.578	14768005.000	100.0000



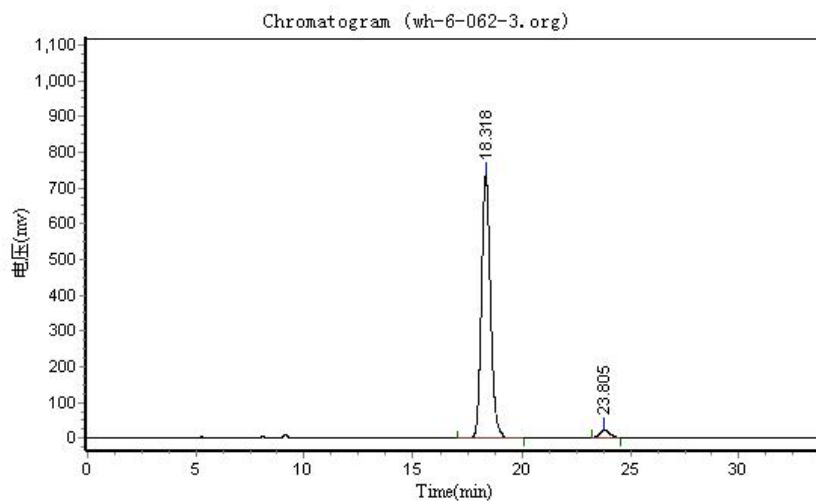
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		13.150	399202.000	13091184.000	97.4940
2		14.820	8912.592	336498.844	2.5060
Total			408114.592	13427682.844	100.0000



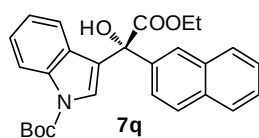
HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 18.3 min
(major), 23.8 min.



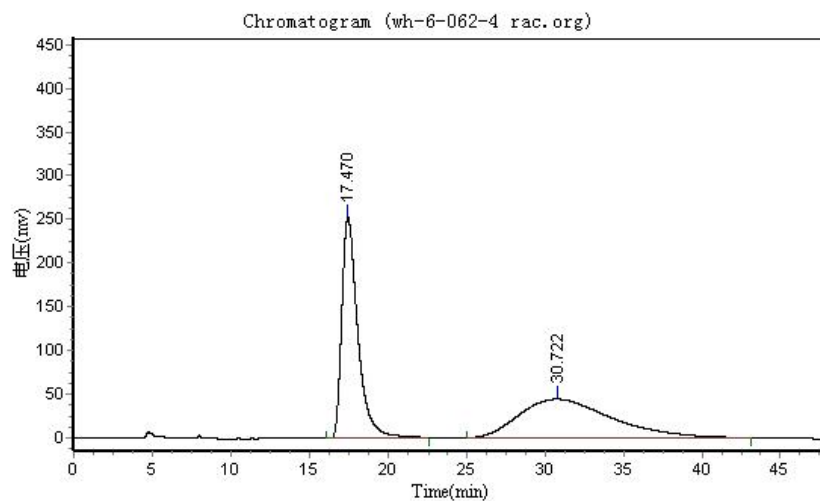
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.975	707916.875	20374940.000	51.0666
2		23.308	510124.563	19523840.000	48.9334
Total			1218041.438	39898780.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.318	736470.188	21494402.000	96.7805
2		23.805	20478.057	715028.500	3.2195
Total			756948.244	22209430.500	100.0000

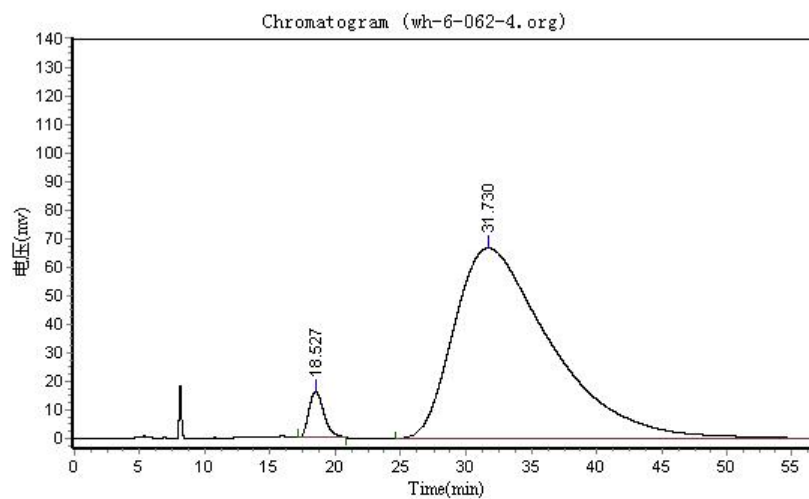


HPLC: Chiral AY-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 18.5 min,
31.7 min (major).



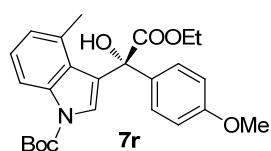
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.470	252166.063	18213576.000	50.4556
2		30.722	43978.117	17884630.000	49.5444
Total			296144.180	36098206.000	100.0000

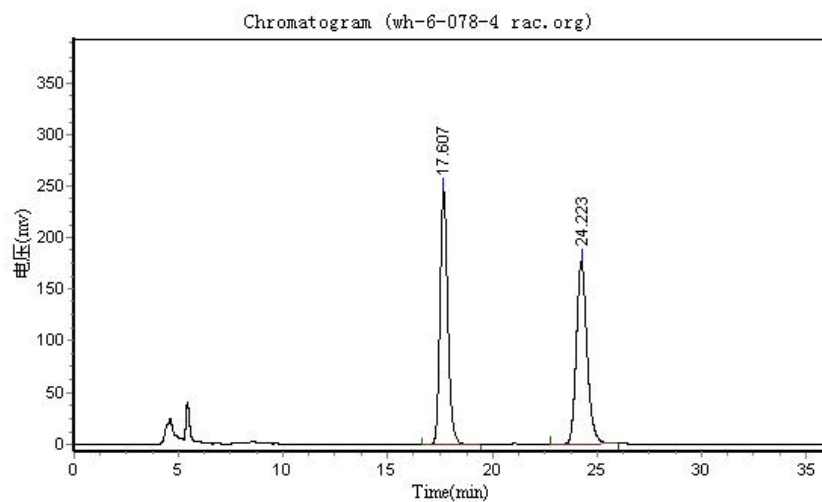


Results

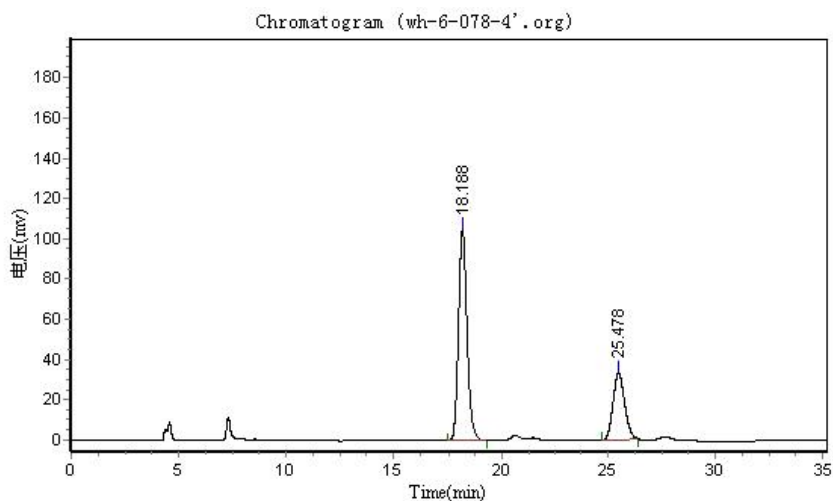
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.527	16061.068	1305872.625	3.6148
2		31.730	66926.469	34820088.000	96.3852
Total			82987.537	36125960.625	100.0000



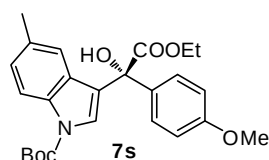
HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 18.2
min, 25.5 min (major).



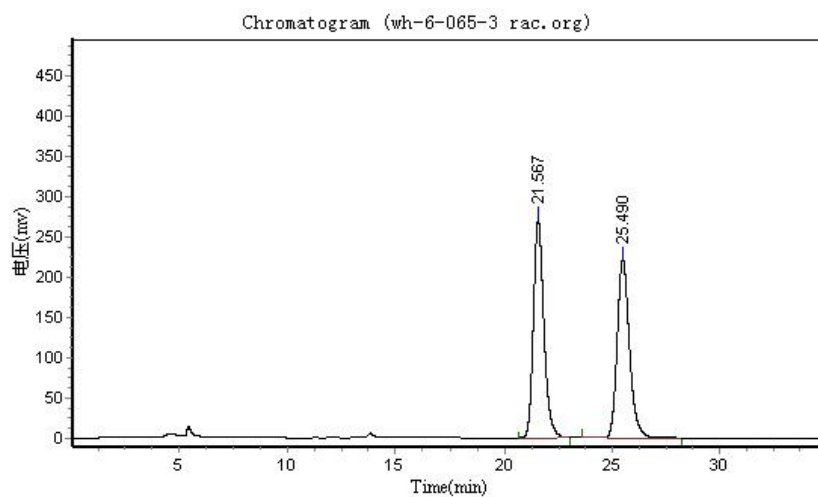
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		17.607	245444.875	6394880.500	50.1603
2		24.223	177053.859	6354007.000	49.8397
Total			422498.734	12748887.500	100.0000



Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		18.188	104826.984	2908213.000	70.0644
2		25.478	32995.590	1242557.625	29.9356
Total			137822.574	4150770.625	100.0000

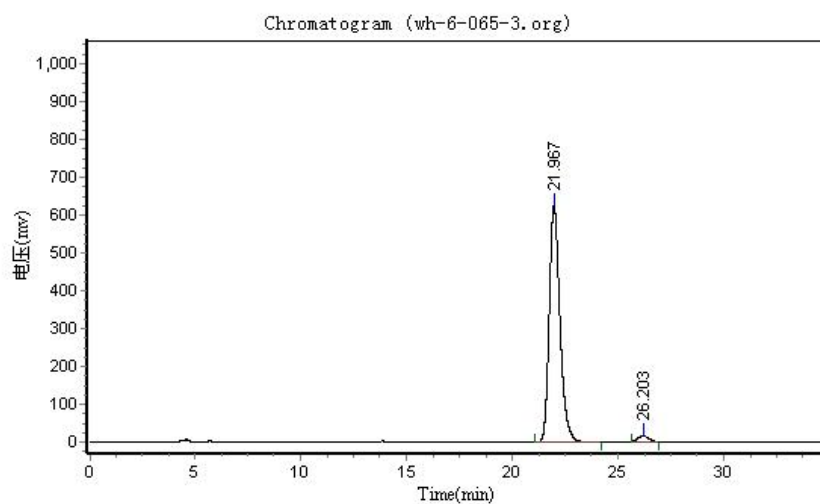


HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 22.0
min (major), 26.2 min.



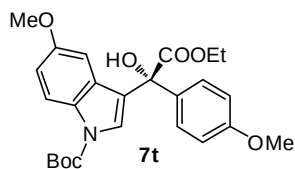
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.567	271203.250	9152229.000	51.1540
2		25.490	222727.016	8739308.000	48.8460
Total			493930.266	17891537.000	100.0000

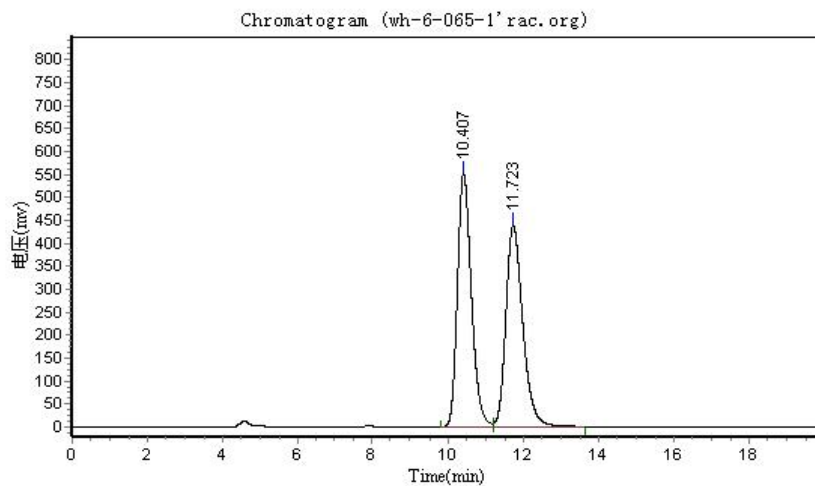


Results

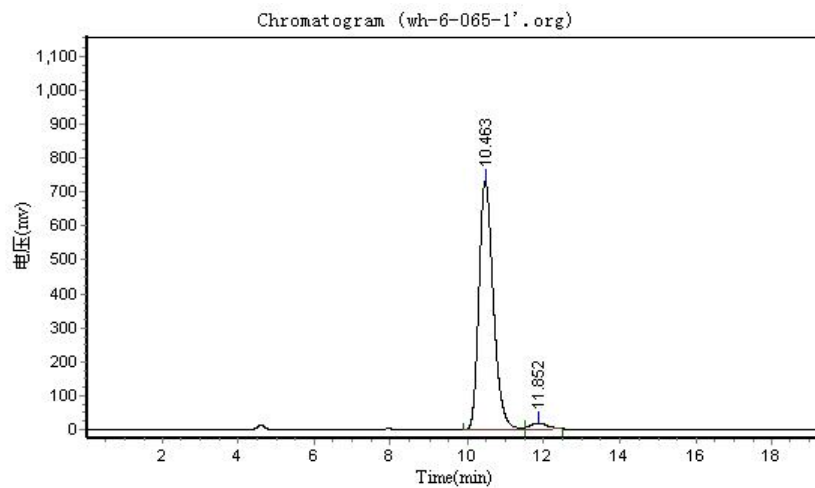
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.967	625787.563	22203192.000	97.5024
2		26.203	15611.470	568749.750	2.4976
Total			641399.032	22771941.750	100.0000



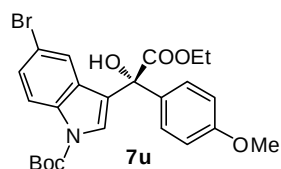
HPLC: Chiral OD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 10.5
min (major), 11.9 min.



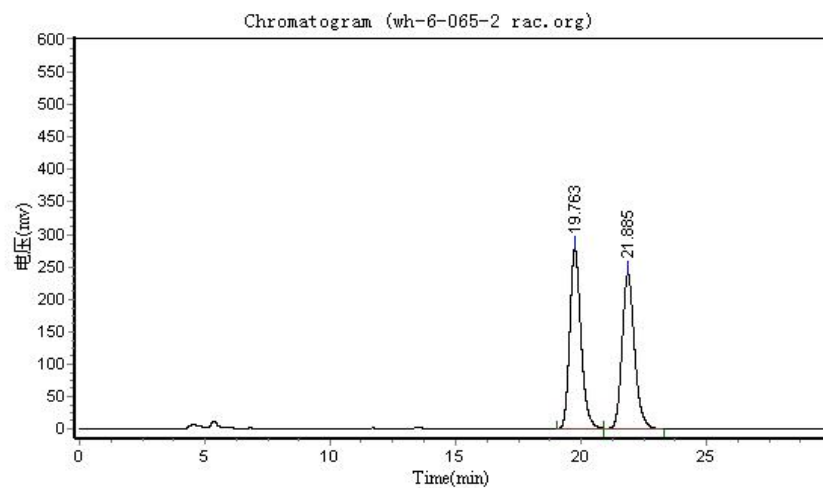
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.407	552319.438	14293880.000	50.7830
2		11.723	439494.531	13853115.000	49.2170
Total			991813.969	28146995.000	100.0000



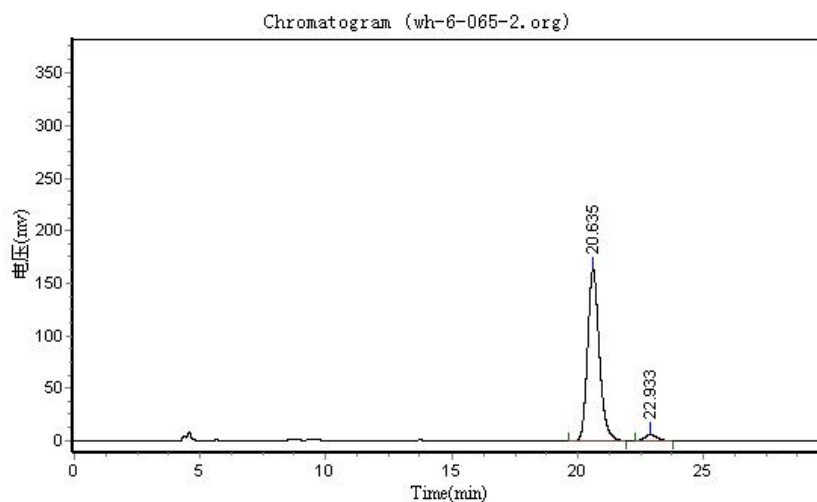
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		10.463	731769.125	19189656.000	97.3074
2		11.852	17280.615	530994.063	2.6926
Total			749049.740	19720650.063	100.0000



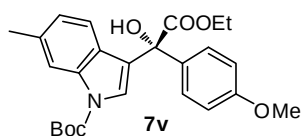
HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 20.6
min (major), 22.9 min.



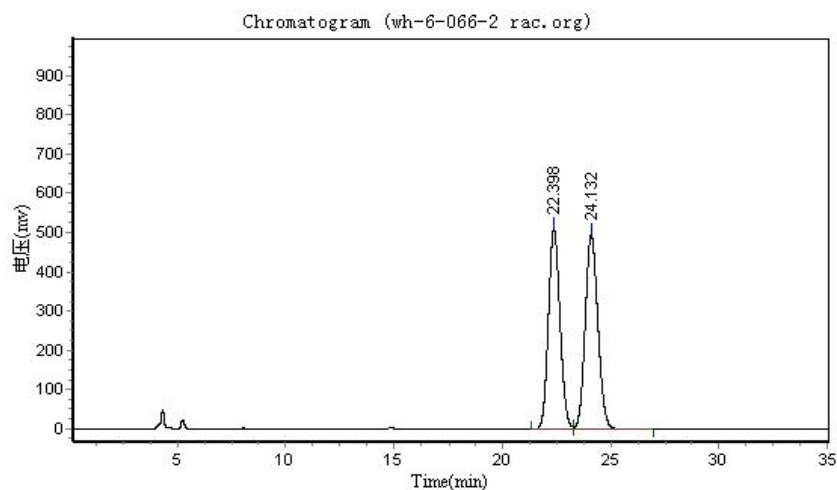
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.763	279430.531	8740759.000	51.1275
2		21.885	239286.922	8355243.000	48.8725
Total			518717.453	17096002.000	100.0000



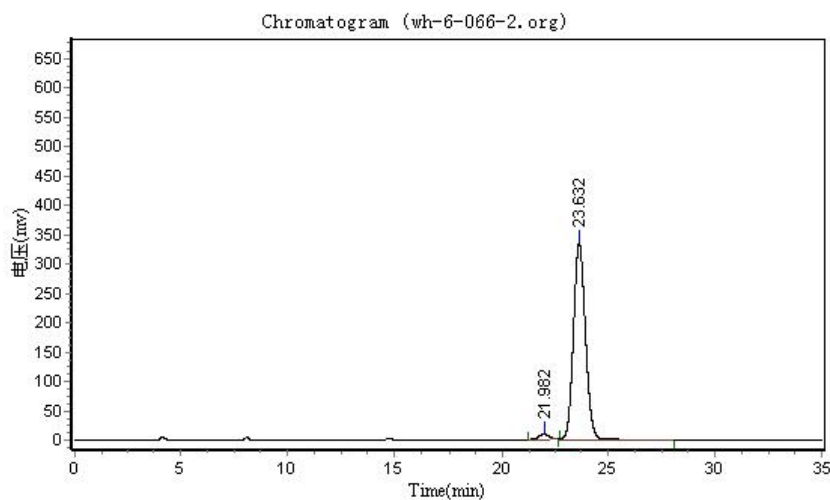
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.635	163634.156	5313189.500	96.2867
2		22.933	6008.081	204905.188	3.7133
Total			169642.237	5518094.688	100.0000



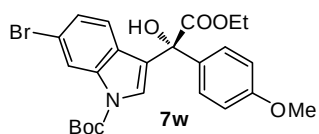
HPLC: Chiral AD-3 column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 22.0
min, 23.6 min (major).



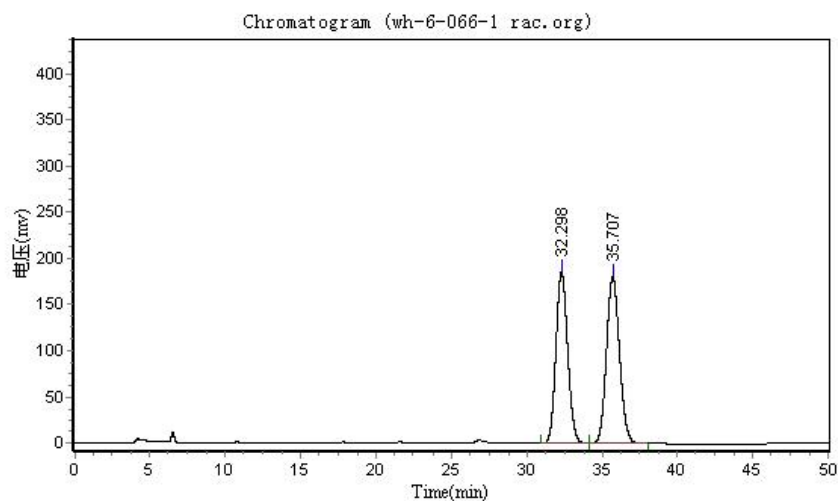
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		22.398	509610.406	19002340.000	48.4645
2		24.132	494448.906	20206418.000	51.5355
Total			1004059.313	39208758.000	100.0000



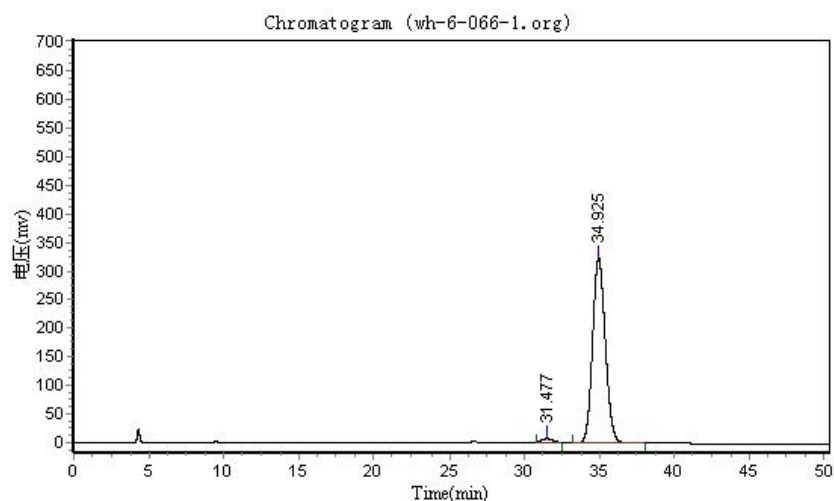
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.982	8190.545	280780.188	2.1083
2		23.632	333971.906	13036778.000	97.8917
Total			342162.451	13317558.188	100.0000



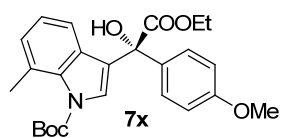
HPLC: Chiral AD-3 column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 95/5; flow = 0.7 mL/min; Retention time: 31.5
min, 34.9 min (major).



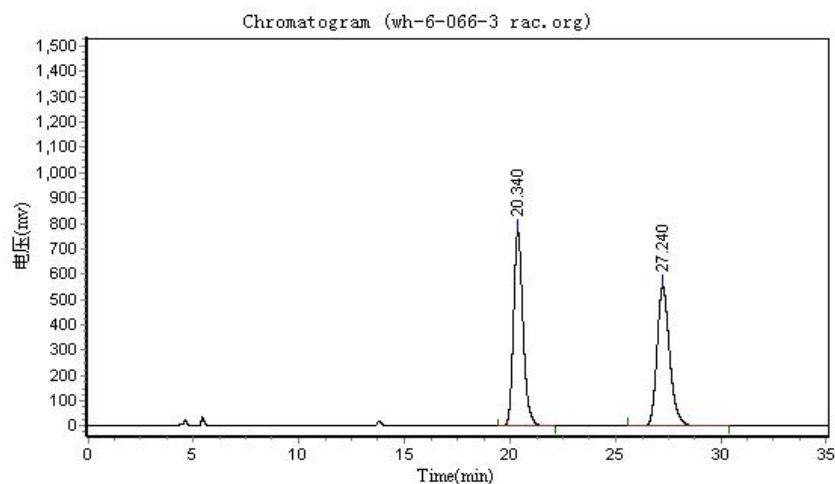
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		32.298	186261.875	10102366.000	48.0543
2		35.707	180707.047	10920457.000	51.9457
Total			366968.922	21022823.000	100.0000



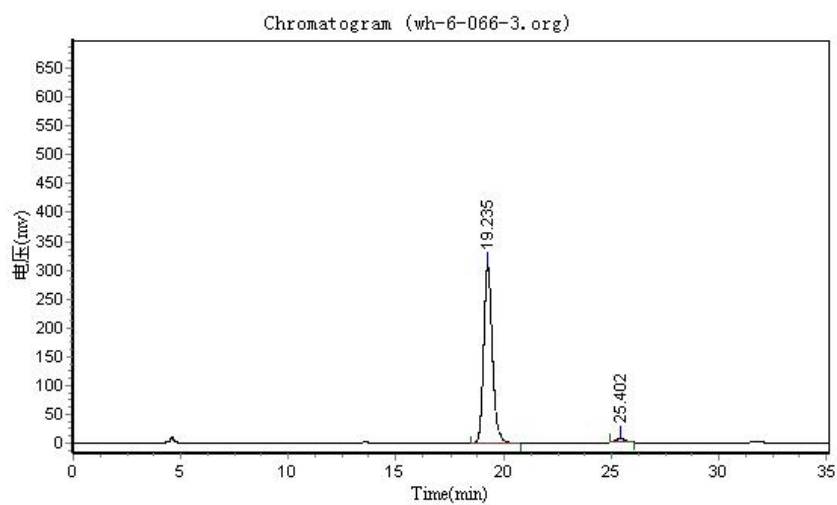
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.477	6503.438	312856.250	1.6154
2		34.925	323242.938	19054146.000	98.3846
Total			329746.375	19367002.250	100.0000



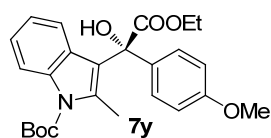
HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 19.2
min (major), 25.4 min.



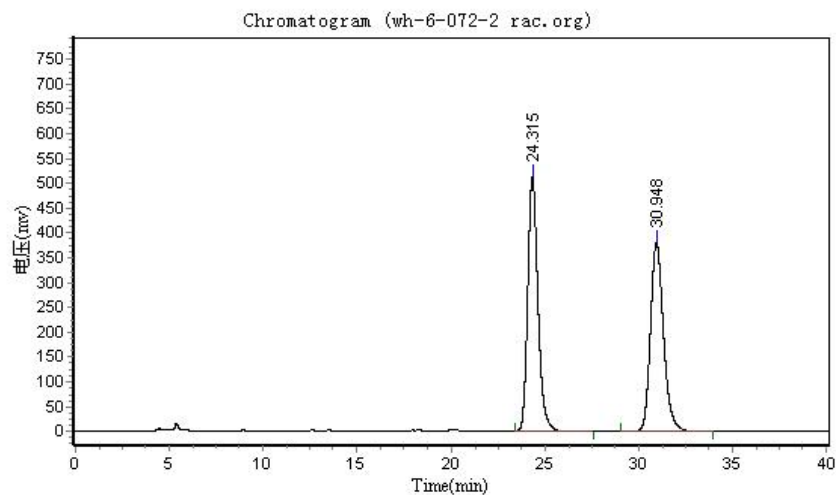
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.340	770687.813	24297822.000	51.3004
2		27.240	548000.063	23066022.000	48.6996
Total			1318687.875	47363844.000	100.0000



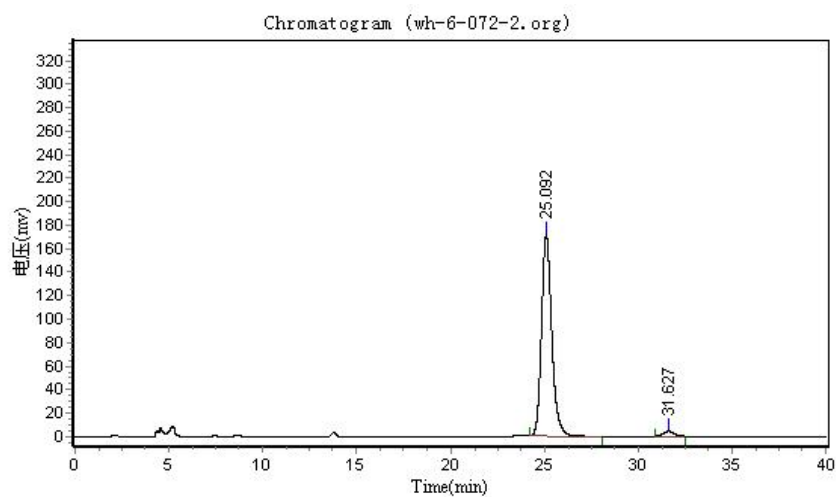
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		19.235	307948.000	8652165.000	97.7773
2		25.402	6077.532	196685.906	2.2227
Total			314025.532	8848850.906	100.0000



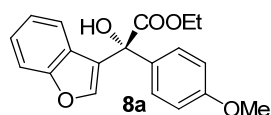
HPLC: Chiral AD-H column (250 mm); detected at 220 nm; hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 25.1 min (major), 31.6 min.



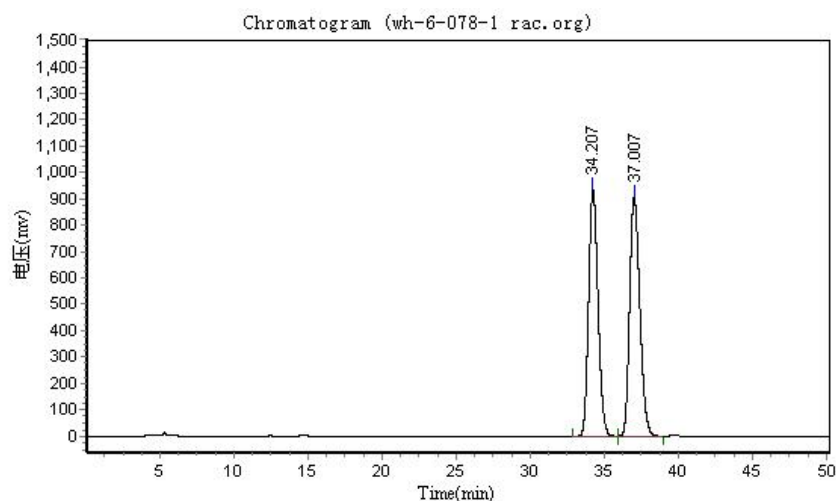
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		24.315	512743.531	19479172.000	51.4579
2		30.948	380394.469	18375440.000	48.5421
Total			893138.000	37854612.000	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		25.092	170946.531	6447280.500	97.3638
2		31.627	4099.743	174566.594	2.6362
Total			175046.274	6621847.094	100.0000

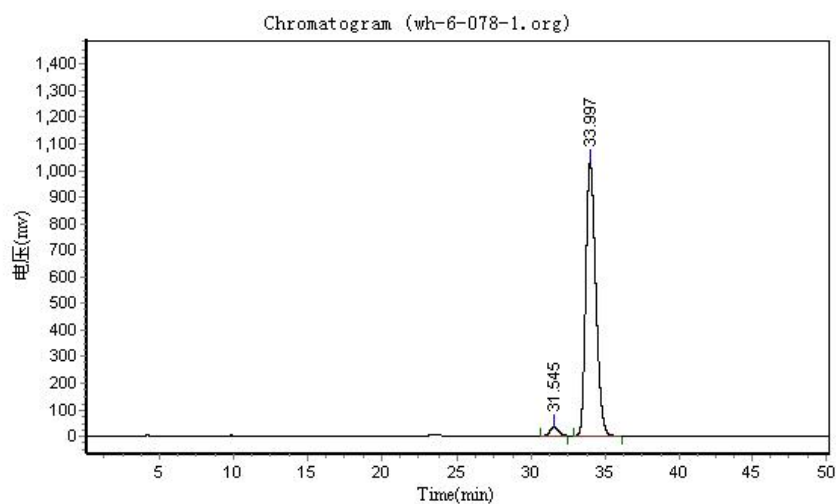


HPLC: Chiral AD-3 column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 31.5
min, 34.0 min (major).



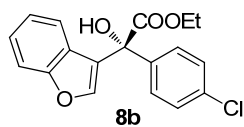
Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		34.207	935473.438	41376732.000	48.7740
2		37.007	906581.500	43456884.000	51.2260
Total			1842054.938	84833616.000	100.0000

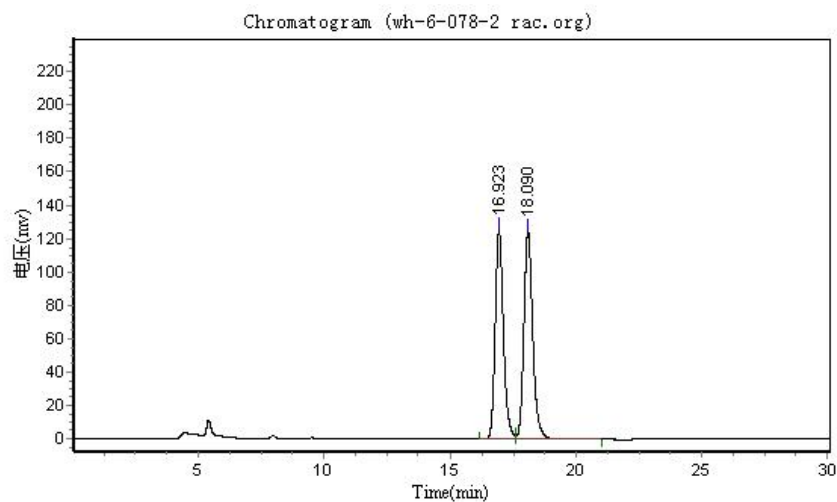


Results

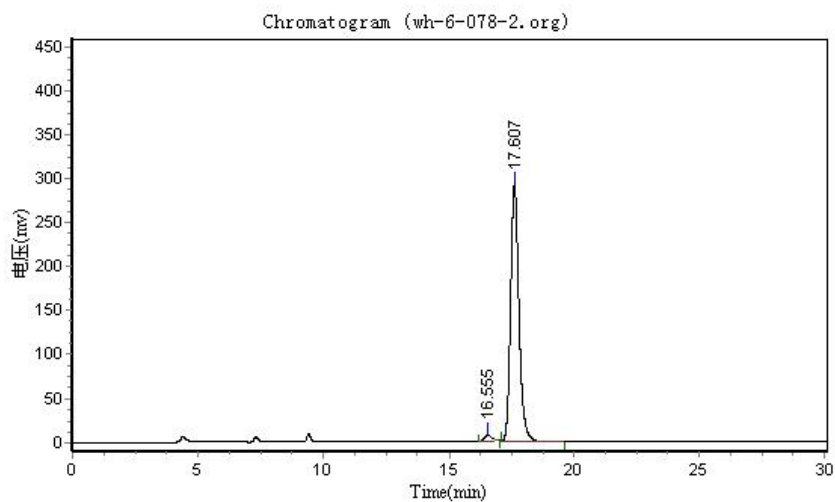
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		31.545	33266.191	1351037.375	2.7146
2		33.997	1030835.500	48418704.000	97.2854
Total			1064101.691	49769741.375	100.0000



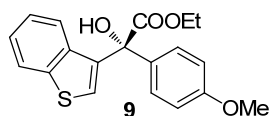
HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 90/10; flow = 0.7 mL/min; Retention time: 16.6 min,
17.6 min (major).



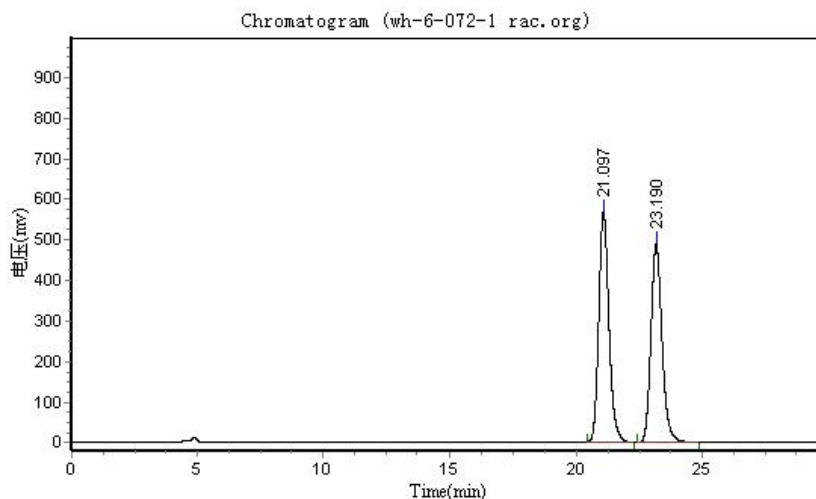
Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.923	124832.367	2848753.500	48.1647
2		18.090	124496.977	3063850.750	51.8353
Total			249329.344	5914604.250	100.0000



Results					
Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		16.555	7877.304	163062.891	2.3354
2		17.607	292237.813	6819104.000	97.6646
Total			300115.116	6982166.891	100.0000

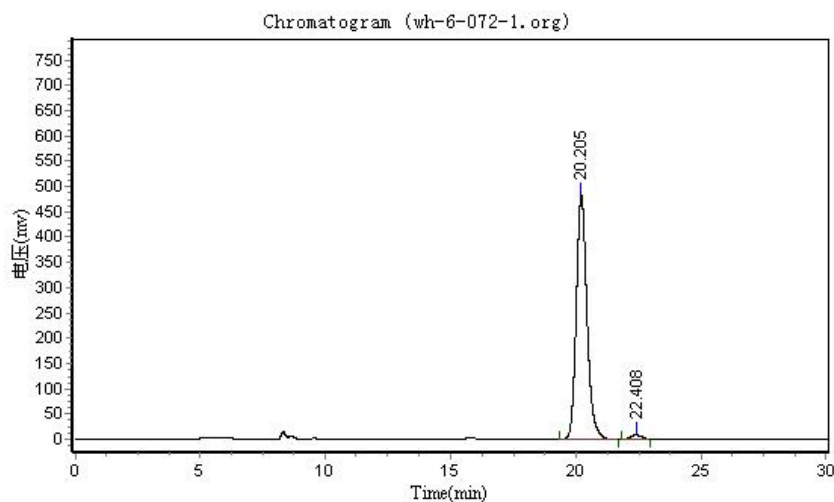


HPLC: Chiral AD-H column (250 mm); detected at 220 nm;
hexane/*i*-propanol = 80/20; flow = 0.7 mL/min; Retention time: 20.2
(major) min, 22.4 min.



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		21.097	567572.438	15981700.000	51.4759
2		23.190	489374.594	15065269.000	48.5241
Total			1056947.031	31046969.000	100.0000



Results

Peak No.	Peak ID	Ret Time	Height	Area	Conc.
1		20.205	484225.938	14405610.000	98.3224
2		22.408	8087.751	245788.859	1.6776
Total			492313.689	14651398.859	100.0000