

Supporting Information

**Cooperative Dinuclear Zinc-Catalyzed Asymmetric Carbonyl-Ene Reaction: A Novel  
Promotion Strategy for Hydrazone**

Wen-Bo Hu, Xixi Song and Min-Can Wang\*

The College of Chemistry and Molecular Engineering, Zhengzhou University, 75 Daxue  
Road, Zhengzhou, Henan 450052, P. R. China

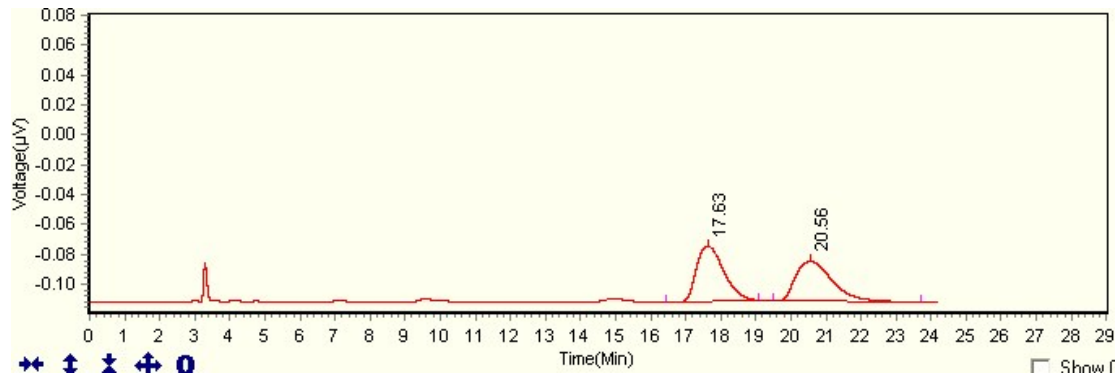
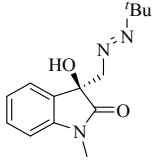
E-mail: wangmincan@zzu.edu.cn

Table of Contents

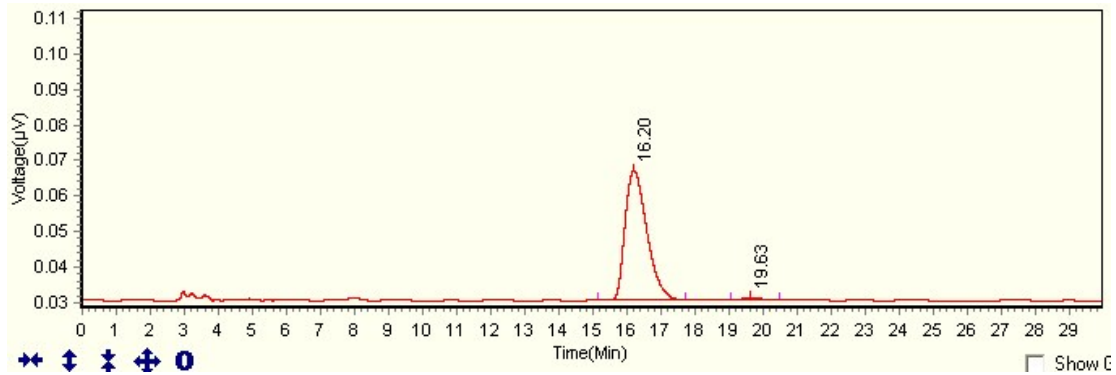
Chiral HPLC Spectra of the Asymmetric Carbonyl-Ene Reaction Products.....	S2
NMR Spectra for the products.....	S20
IR and HRMS Spectra of <b>3ha</b> .....	S43

# Spectra

Chiralpak AS column [hexane/*i*-PrOH (95:5) 1 mL/min]

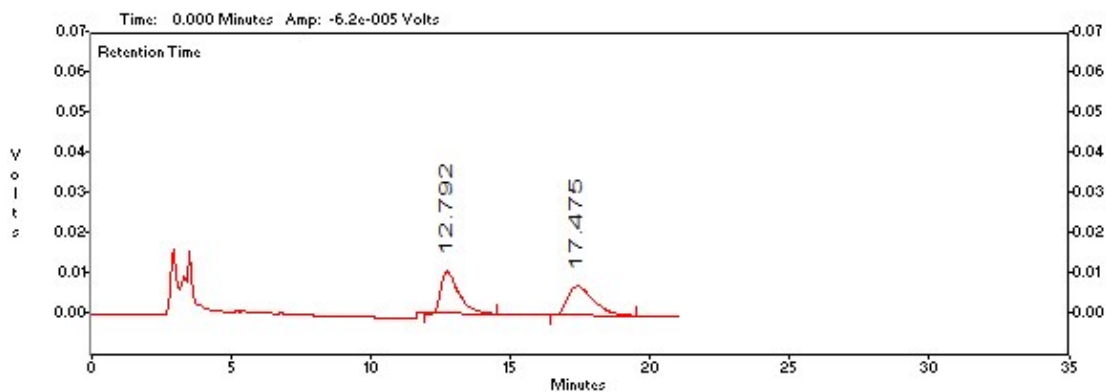
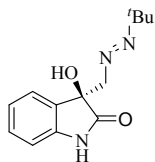


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	17.63	977111	18272	50.67%	2.648
2	20.56	951091	13236	49.33%	4.181
Total		1,928,202	31,508	100.00%	

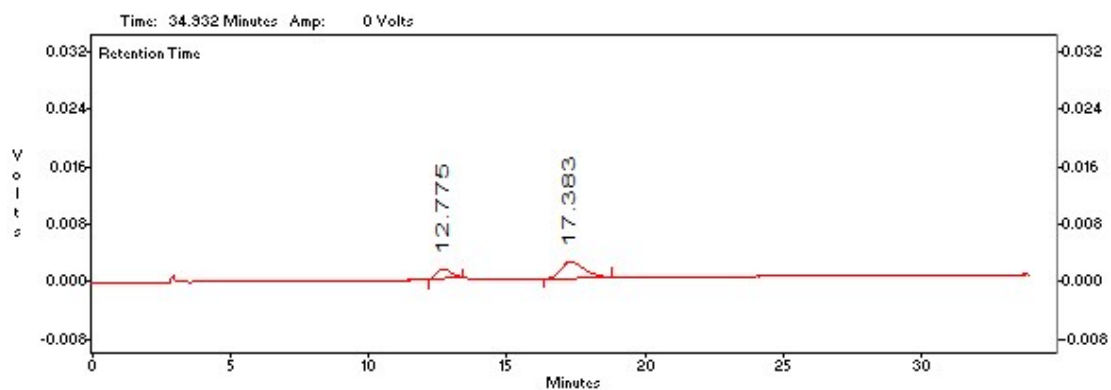


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	16.20	805095	18150	98.50%	2.563
2	19.63	12247	264	1.50%	1.454
Total		817,342	18,414	100.00%	

Chiralpak AS column [hexane/*i*-PrOH (90:10) 1 mL/min]

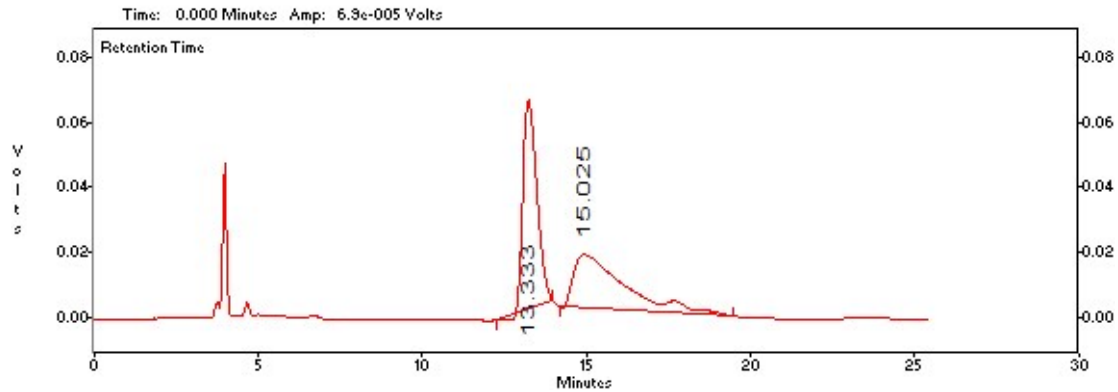
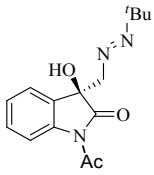


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	12.792	475415	50.540	10506	59.182	MM
2	17.475	465247	49.460	7246	40.818	MM
<b>Totals</b>		<b>940662</b>	<b>100.000</b>	<b>17751</b>	<b>100.000</b>	

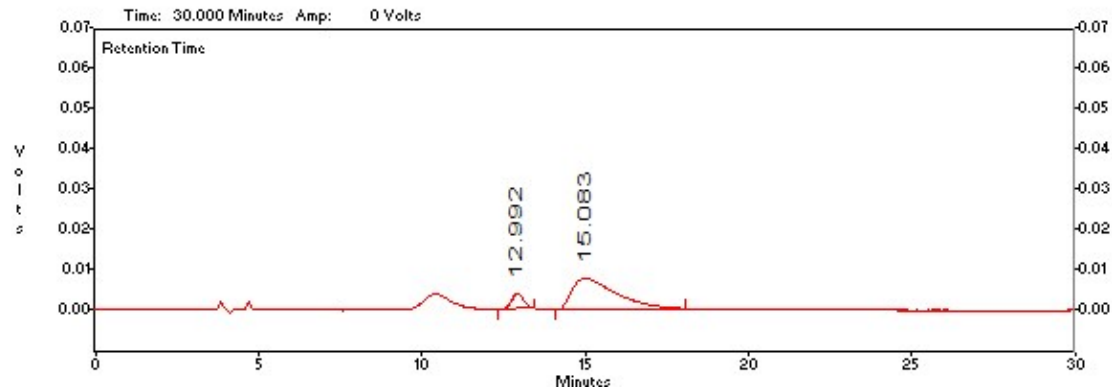


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	12.775	50365	27.349	1375	37.692	MM
2	17.383	133789	72.651	2273	62.308	MM
<b>Totals</b>		<b>184154</b>	<b>100.000</b>	<b>3648</b>	<b>100.000</b>	

Chiralpak AS column [hexane/*i*-PrOH (95:5) 0.8 mL/min]

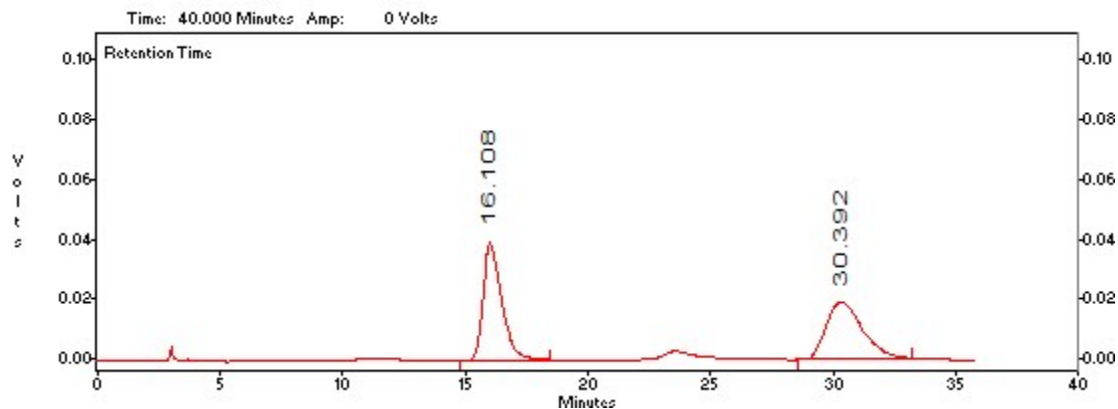
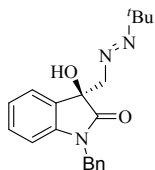


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	13.333	1954842	51.981	64479	79.580	MM
2	15.025	1805812	48.019	16545	20.420	MM
<b>Totals</b>		<b>3760654</b>	<b>100.000</b>	<b>81024</b>	<b>100.000</b>	

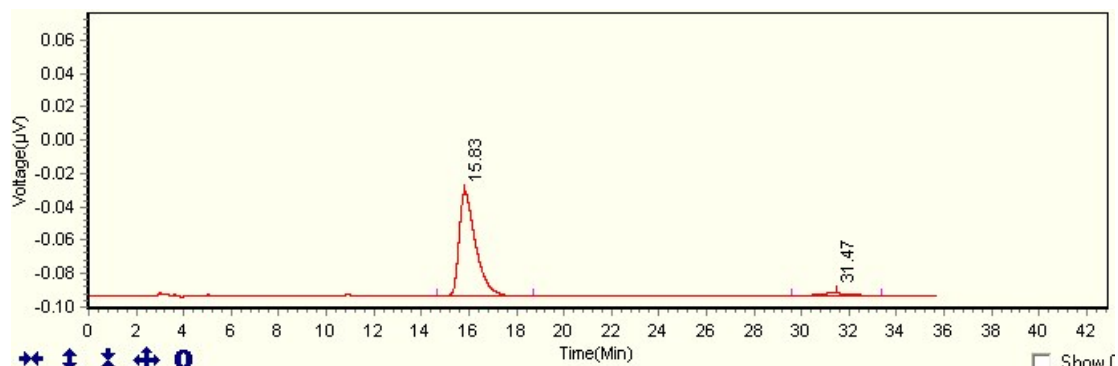


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	12.992	102841	12.540	3741	32.650	MM
2	15.083	717289	87.460	7718	67.350	MM
<b>Totals</b>		<b>820131</b>	<b>100.000</b>	<b>11459</b>	<b>100.000</b>	

Chiralpak AS column [hexane/*i*-PrOH (95:5) 1 mL/min]

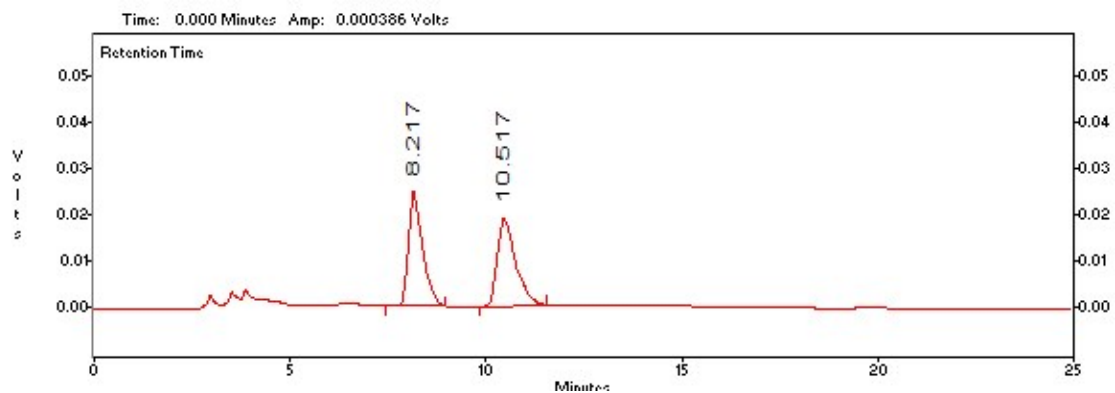
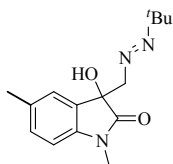


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	16.108	2057421	50.763	39164	66.844	MM
2	30.392	1995568	49.237	19426	33.156	MM
<b>Totals</b>		<b>4052989</b>	<b>100.000</b>	<b>58589</b>	<b>100.000</b>	

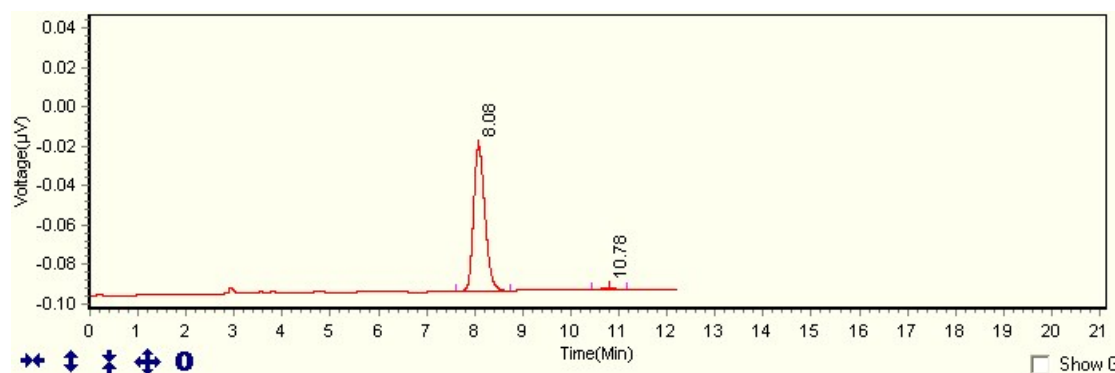


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	15.83	1496903	31116	95.08%	4.048
2	31.47	77506	756	4.92%	3.774
Total		1,574,409	31,872	100.00%	

Chiralpak OD-H column [hexane/*i*-PrOH (95:5) 1 mL/min]

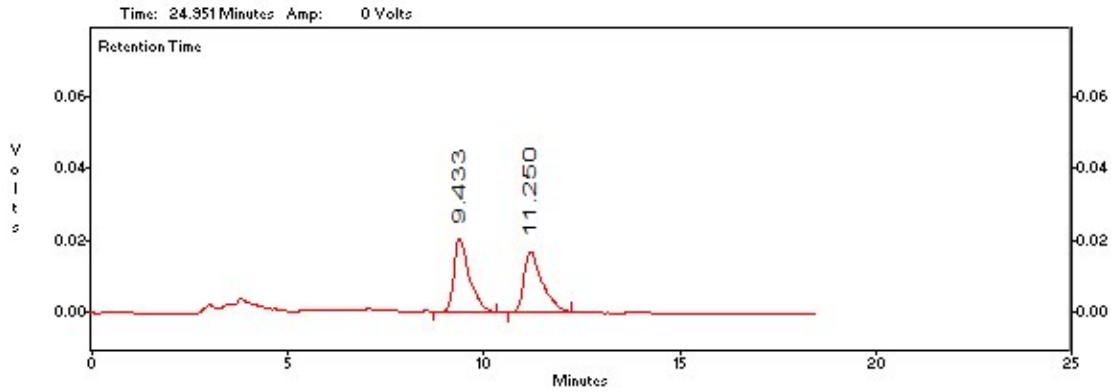
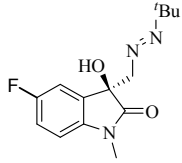


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	8.217	610800	49.912	24733	56.643	MM
2	10.517	612948	50.088	18932	43.357	MM
<b>Totals</b>		<b>1223748</b>	<b>100.000</b>	<b>43664</b>	<b>100.000</b>	

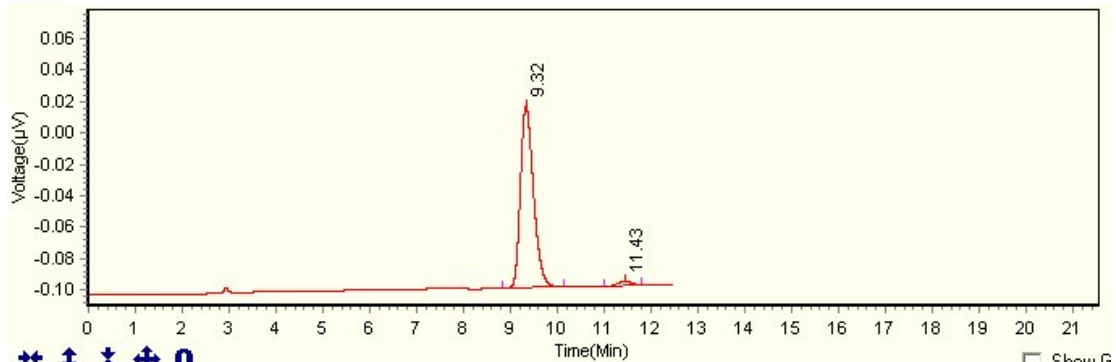


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	8.08	602501	36738	98.02%	1.128
2	10.78	12200	590	1.98%	0.705
Total		614,701	37,328	100.00%	

Chiralpak OD-H column [hexane/*i*-PrOH (95:5) 1 mL/min]

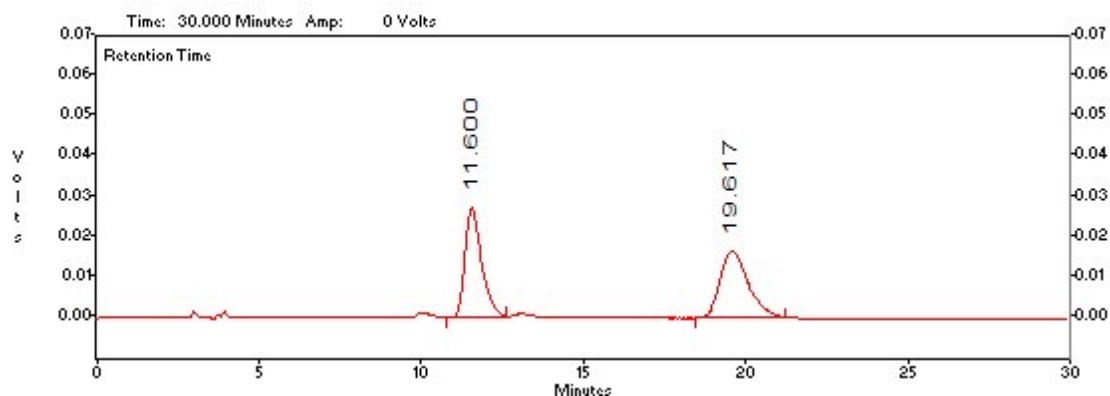
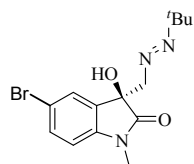


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	9.433	552257	50.660	20344	54.694	MM
2	11.250	537861	49.340	16852	45.306	MM
<b>Totals</b>		<b>1090118</b>	<b>100.000</b>	<b>37196</b>	<b>100.000</b>	

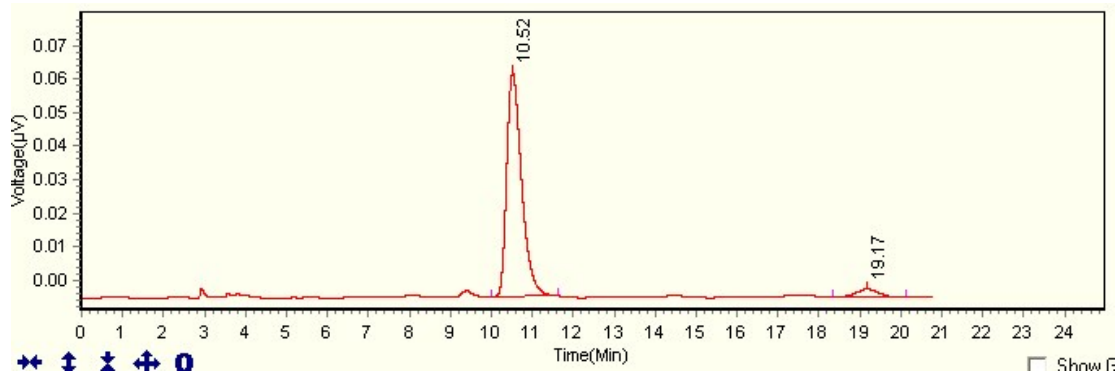


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	9.32	1113886	57691	97.47%	1.34
2	11.43	28885	1416	2.53%	0.766
Total		1,142,771	59,107	100.00%	

Chiralpak OD-H column [hexane/i-PrOH (95:5) 1 mL/min]



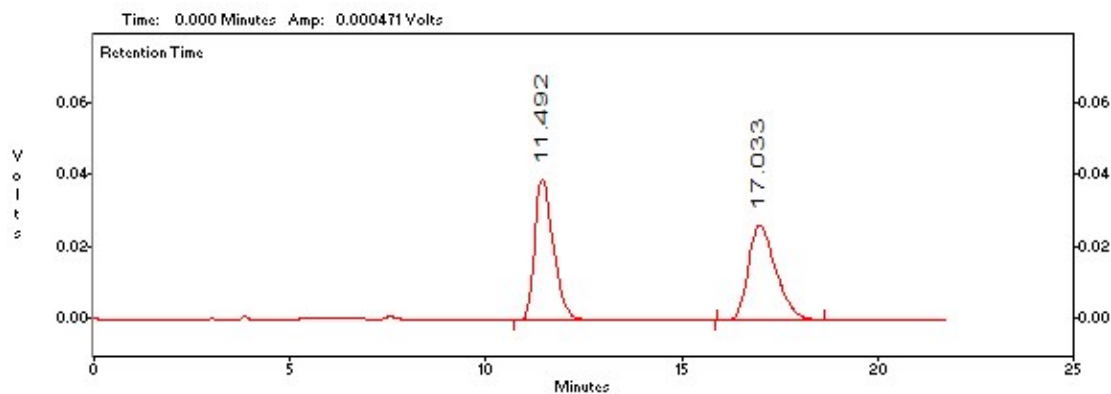
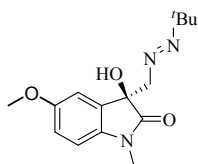
Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	11.600	979378	49.812	27069	62.007	MM
2	19.617	986762	50.188	16586	37.993	MM
<b>Totals</b>		<b>1966140</b>	<b>100.000</b>	<b>43655</b>	<b>100.000</b>	



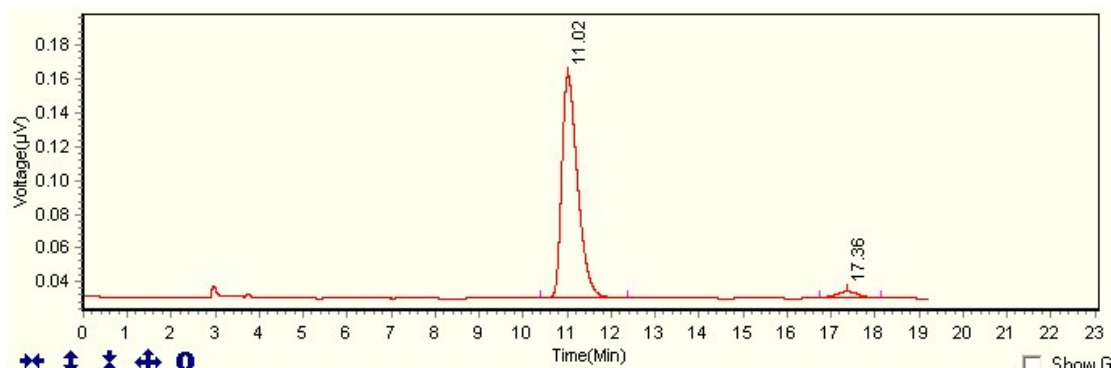
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	10.52	840054	33252	95.22%	1.628
2	19.17	42153	1147	4.78%	1.786
<b>Total</b>		<b>882,207</b>	<b>34,399</b>	<b>100.00%</b>	



Chiralpak OD-H column [hexane/i-PrOH (95:5) 1 mL/min]

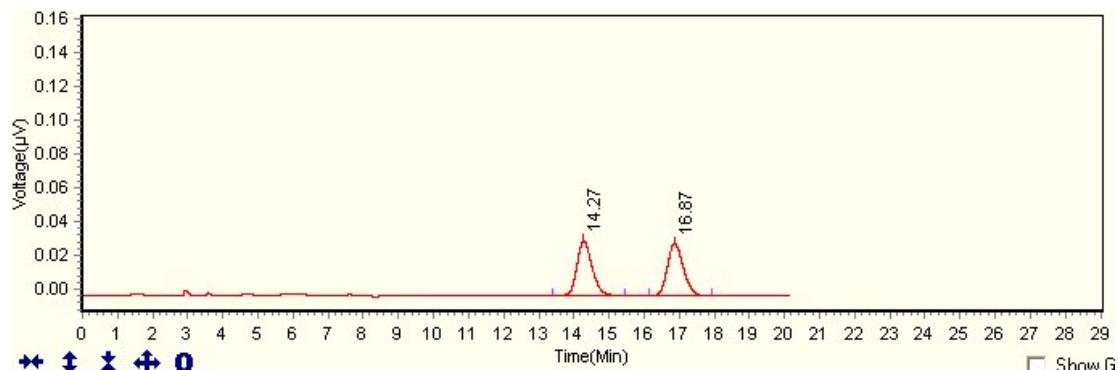
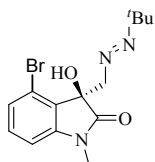


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	11.492	1301086	50.323	39227	59.727	MM
2	17.033	1284407	49.677	26450	40.273	MM
<b>Totals</b>		<b>2585493</b>	<b>100.000</b>	<b>65676</b>	<b>100.000</b>	

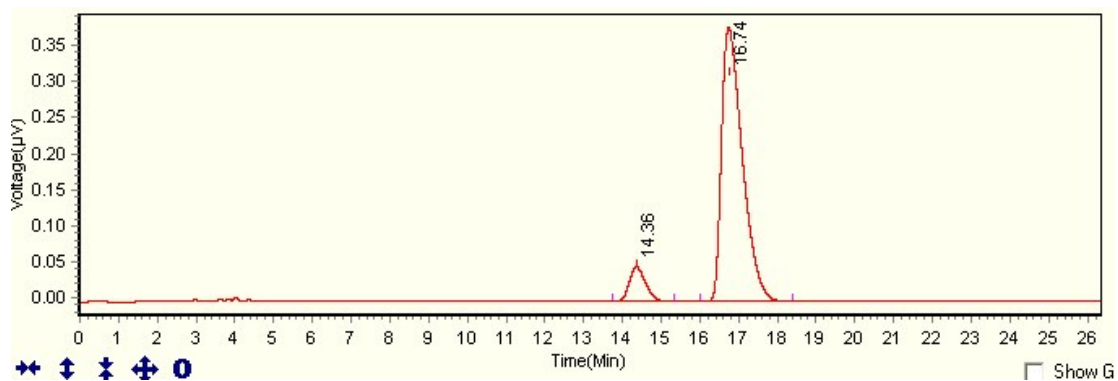


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	11.02	1635304	65765	96.60%	1.983
2	17.36	57488	1757	3.40%	1.395
Total		1,692,792	67,522	100.00%	

Chiralpak OD-H column [hexane/*i*-PrOH (95:5) 1 mL/min]

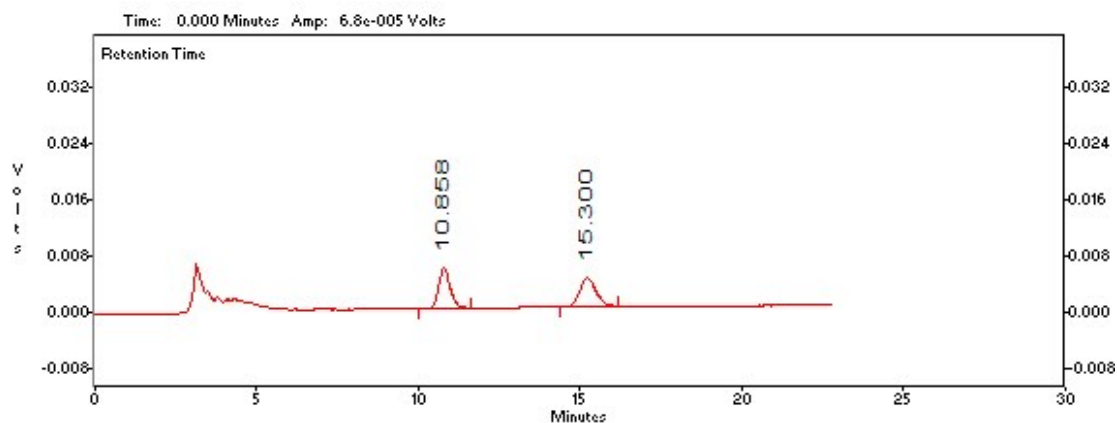
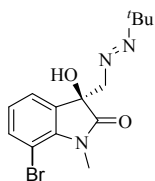


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	14.27	477116	16061	49.69%	2.063
2	16.87	483165	15342	50.31%	1.788
Total		960,281	31,403	100.00%	

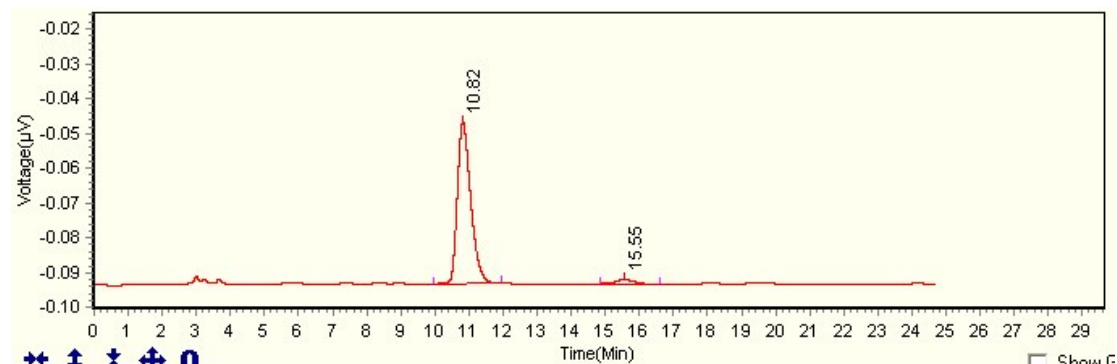


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	14.36	694092	23983	8.93%	1.592
2	16.74	7078537	189575	91.07%	2.388
Total		7,772,629	213,558	100.00%	

Chiralpak AS column [hexane/i-PrOH (95:5) 1 mL/min]

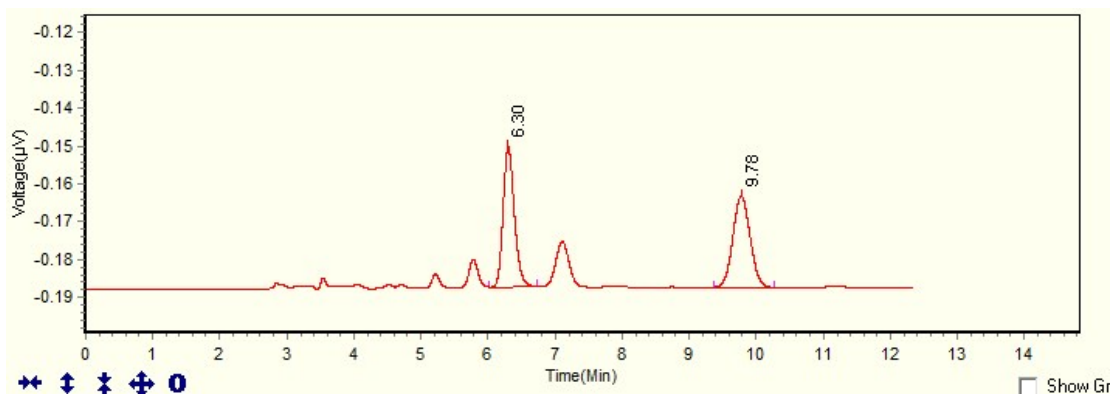
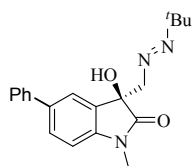


Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	10.858	142893	50.353	5666	58.565	MM
2	15.300	140887	49.647	4009	41.435	MM
<b>Totals</b>		<b>283780</b>	<b>100.000</b>	<b>9675</b>	<b>100.000</b>	

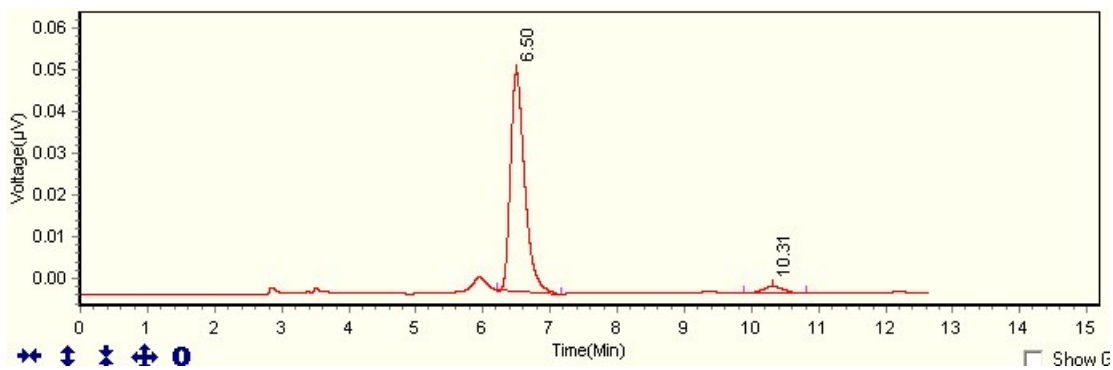


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	10.82	635385	23242	96.91%	1.993
2	15.55	20229	592	3.09%	1.756
Total		655,614	23,834	100.00%	

Chiralpak OD-H column [hexane/i-PrOH (90:10) 1mL/min]

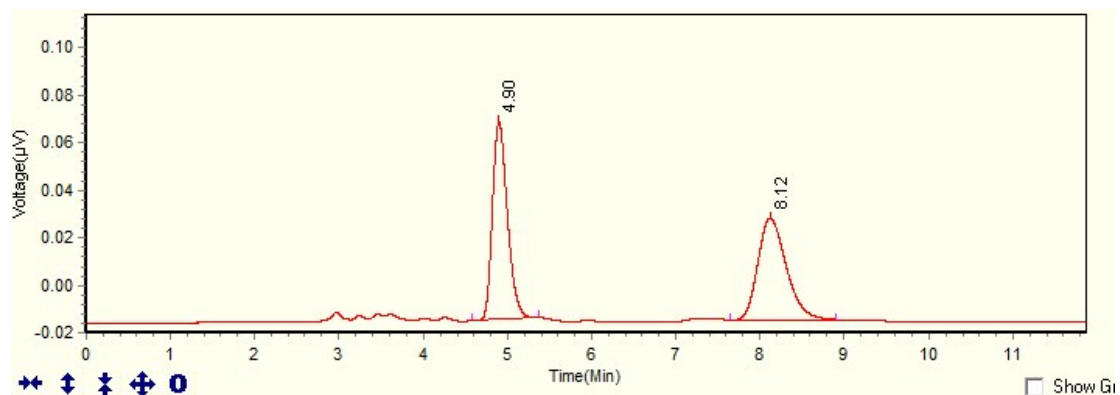
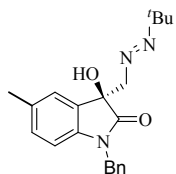


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	6.30	215327	18451	50.00%	0.714
2	9.78	215311	12048	50.00%	0.904
Total		430,638	30,499	100.00%	

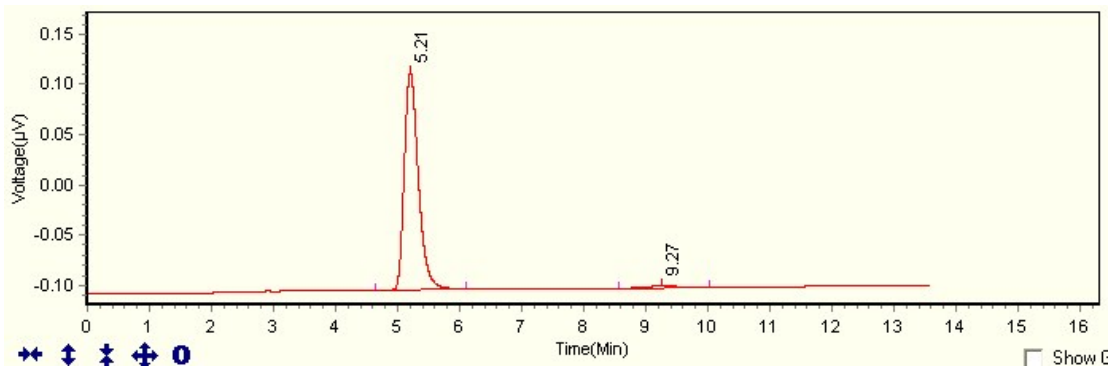


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	6.50	391663	26448	95.87%	0.966
2	10.31	16869	795	4.13%	0.941
Total		408,532	27,243	100.00%	

Chiralpak AS column [hexane/i-PrOH (80:20) 1 mL/min]

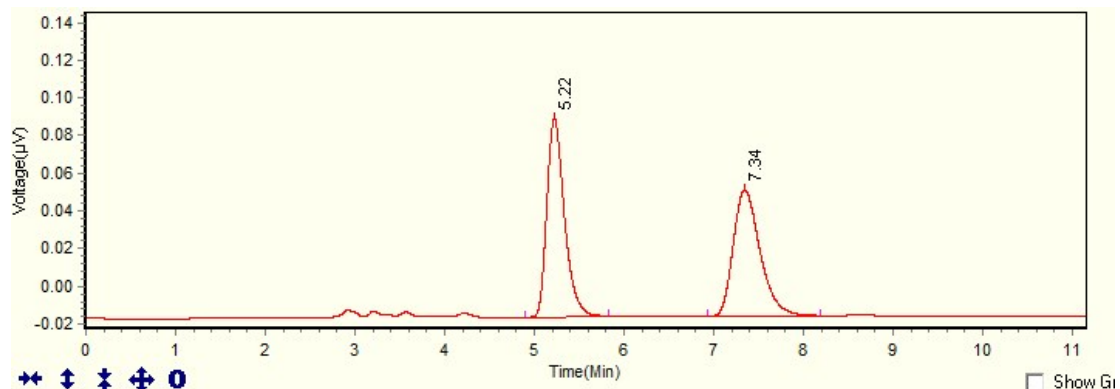
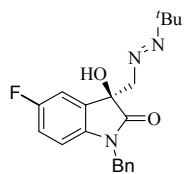


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	4.90	512584	41621	50.54%	0.794
2	8.12	501609	21446	49.46%	1.255
Total		1,014,193	63,067	100.00%	

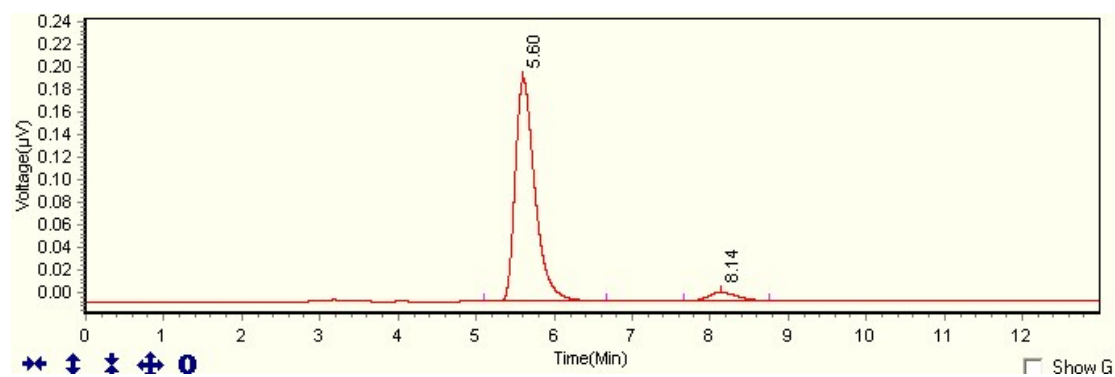


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	5.21	1712510	108236	98.35%	1.463
2	9.27	28700	907	1.65%	1.462
Total		1,741,210	109,143	100.00%	

Chiralpak AS column [hexane/i-PrOH (80:20) 1 mL/min]

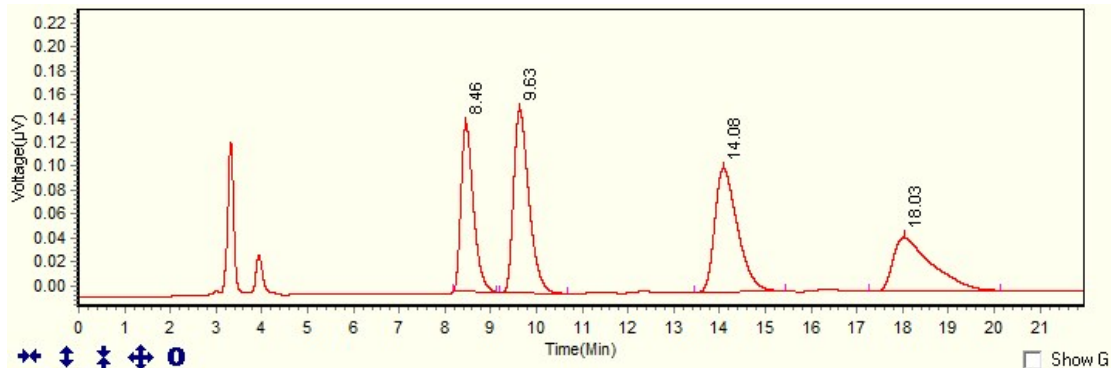
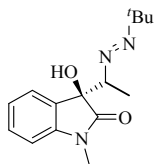


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	5.22	713879	52500	50.50%	0.931
2	7.34	699777	33516	49.50%	1.258
Total		1,413,656	86,016	100.00%	

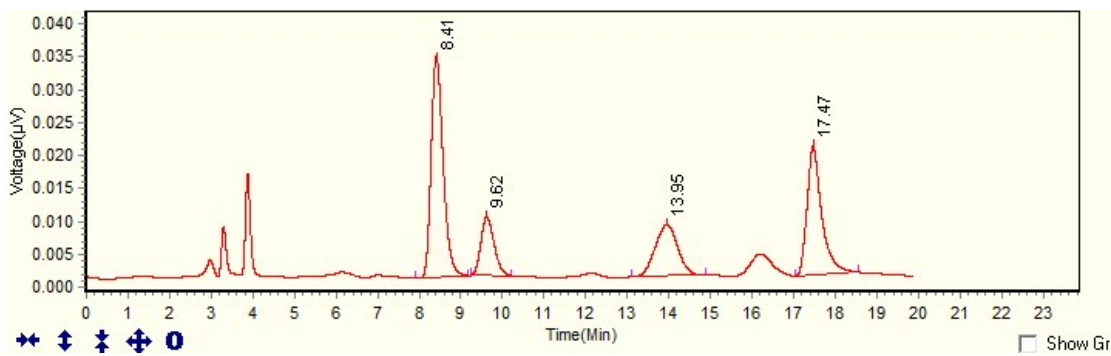


No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	5.60	1713108	98008	94.68%	1.561
2	8.14	96185	3763	5.32%	1.091
Total		1,809,293	101,771	100.00%	

Chiralpak AS column [hexane/i-PrOH (95:5) 1 mL/min]

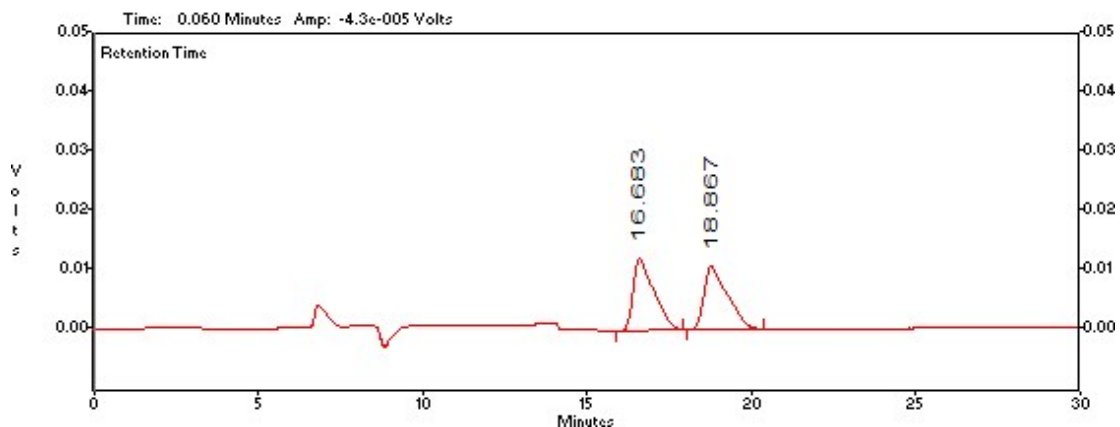
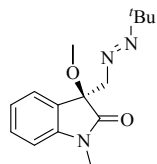


No.	Retention Time	PeakArea	Peak Height	PeakArea(%)	Peak Width
1	8.46	1325568	70069	21.30%	0.933
2	9.63	1792352	76791	28.80%	1.46
3	14.08	1795835	51954	28.86%	1.987
4	18.03	1309296	22449	21.04%	2.879
Total		6,223,051	221,263	100.00%	

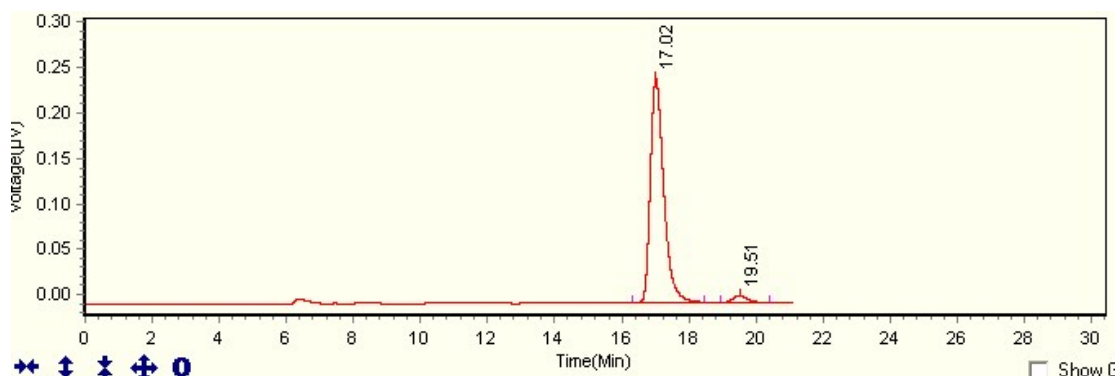


No.	Retention Time	PeakArea	Peak Height	PeakArea(%)	Peak Width
1	8.41	334659	16801	40.84%	1.262
2	9.62	97856	4434	11.94%	0.965
3	13.95	146399	3908	17.86%	1.782
4	17.47	240570	9781	29.36%	1.522
Total		819,484	34,924	100.00%	

Chiralpak OD-H column [hexane/i-PrOH (98:2) 0.5 mL/min]



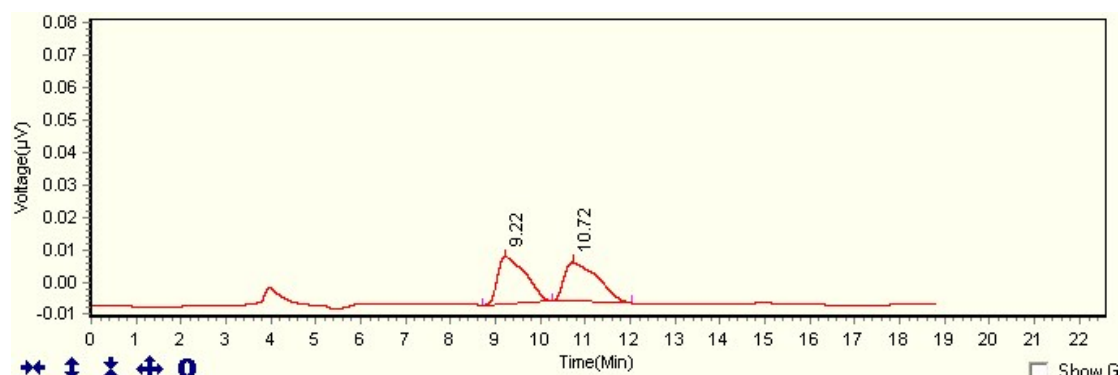
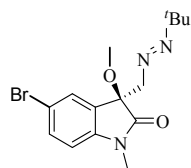
Pkno	Ret. Time	Area	Area%	Height	Height%	Flags
1	16.683	513346	50.293	12245	53.796	MM
2	18.867	507356	49.707	10517	46.204	MM
<b>Totals</b>		<b>1020702</b>	<b>100.000</b>	<b>22761</b>	<b>100.000</b>	



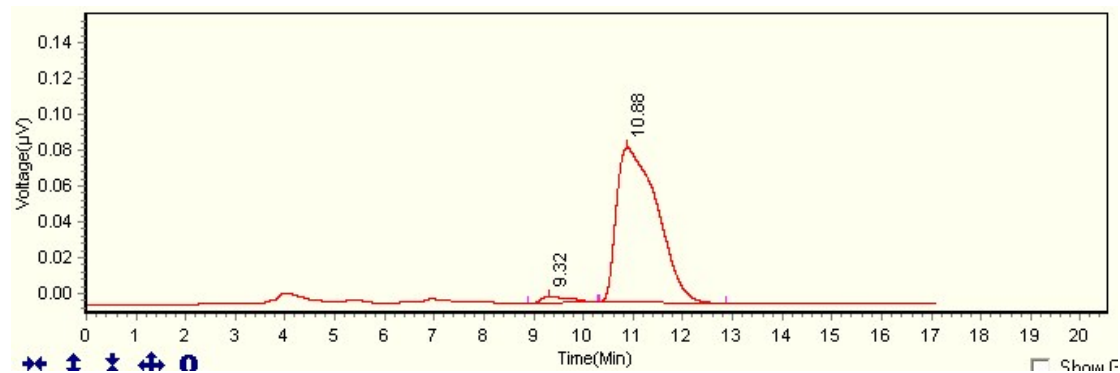
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	17.02	3404109	122700	96.84%	2.143
2	19.51	111209	3721	3.16%	1.461
Total		3,515,318	126,421	100.00%	



Chiralpak AD column [hexane/*i*-PrOH (98:2) 0.8 mL/min]



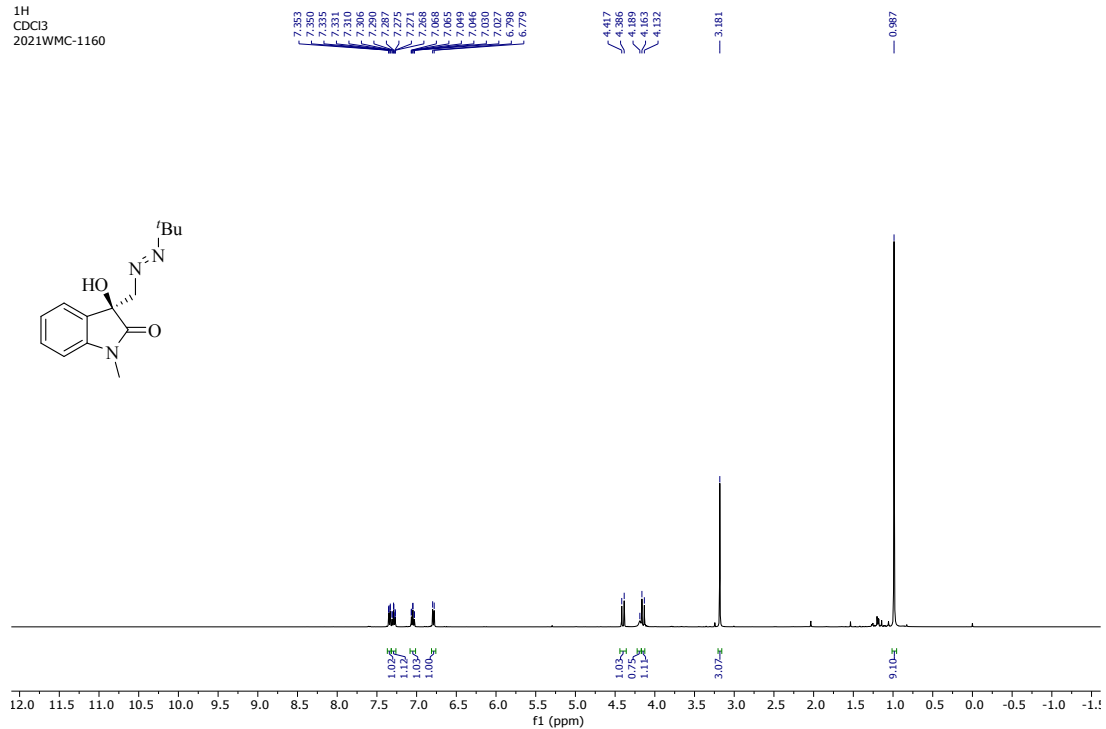
No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	10.72	317550	6100	50.48%	1.771
2	9.22	311501	7248	49.52%	1.555
Total		629,051	13,348	100.00%	



No.	Retention Time	Peak Area	Peak Height	Peak Area(%)	Peak Width
1	9.32	77393	1815	3.03%	1.404
2	10.88	2478637	43408	96.97%	2.548
Total		2,556,030	45,223	100.00%	

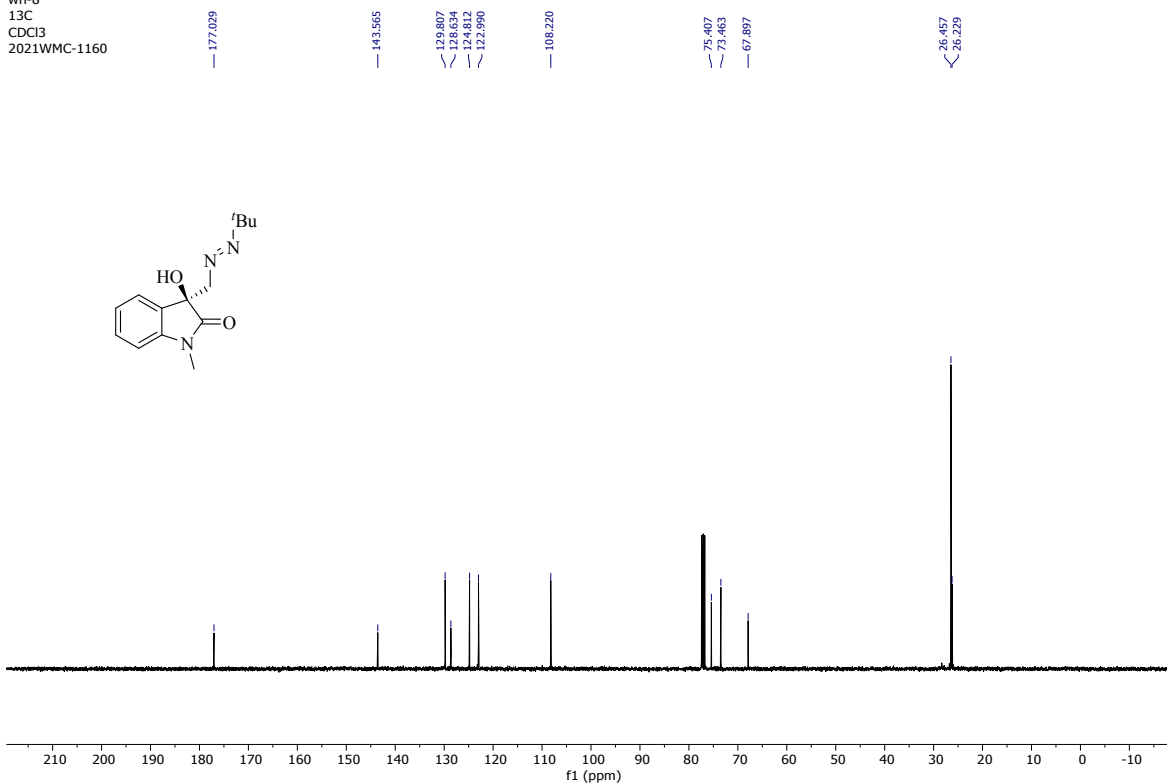
<sup>1</sup>H NMR spectrum of **3aa** (CDCl<sub>3</sub>, 400 MHz)

2021WMC.1160.fid  
wh-8  
1H  
CDCl<sub>3</sub>  
2021WMC-1160



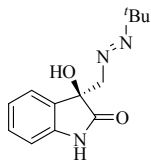
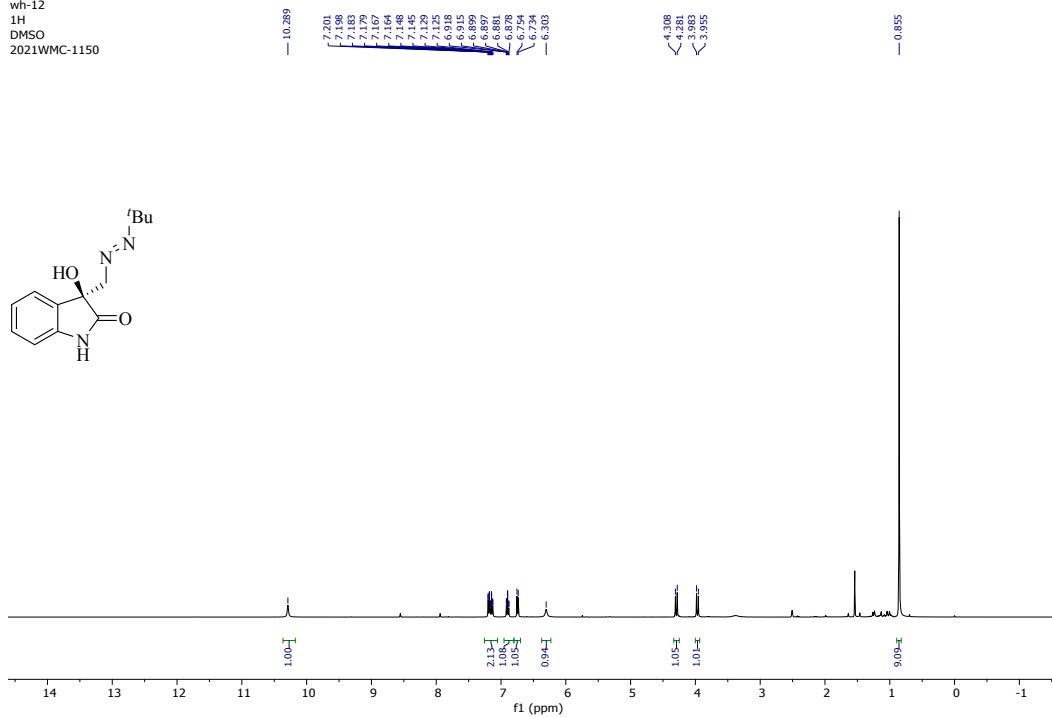
<sup>13</sup>C NMR spectrum of **3aa** (CDCl<sub>3</sub>, 100 MHz)

2021WMC.1161.fid  
wh-8  
13C  
CDCl<sub>3</sub>  
2021WMC-1160



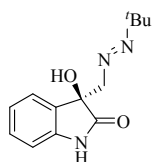
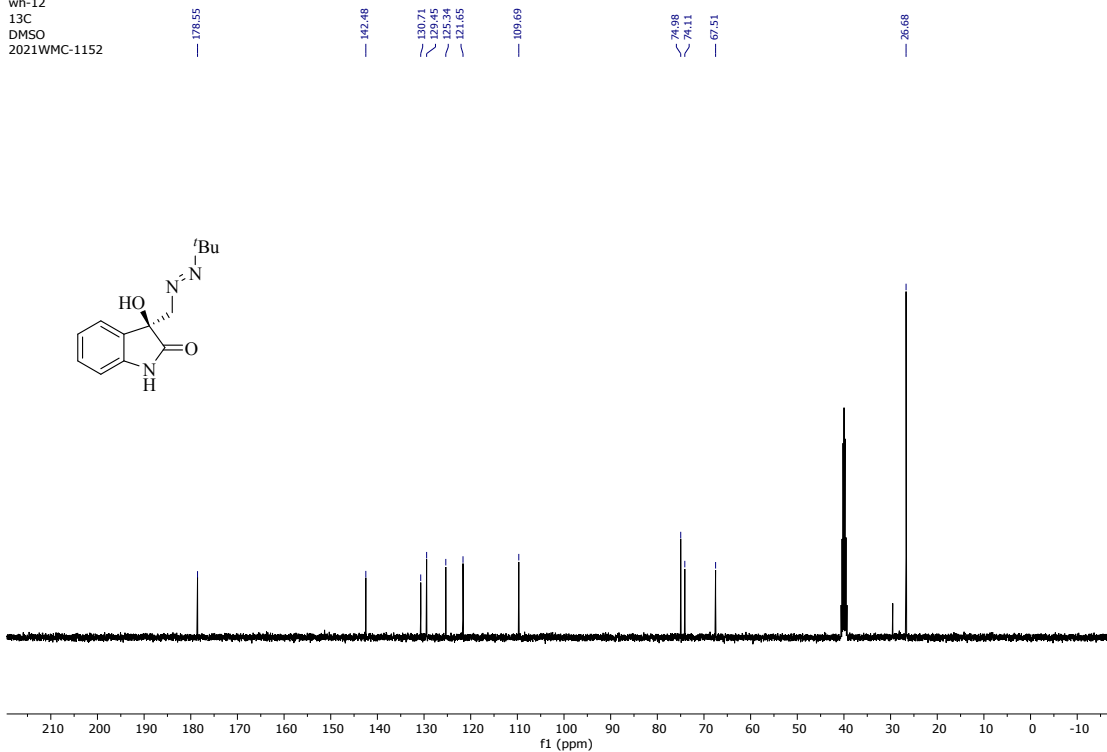
<sup>1</sup>H NMR spectrum of **3ba** (DMSO-d, 400 MHz)

2021WMC.1150.fid  
wh-12  
1H  
DMSO  
2021WMC-1150



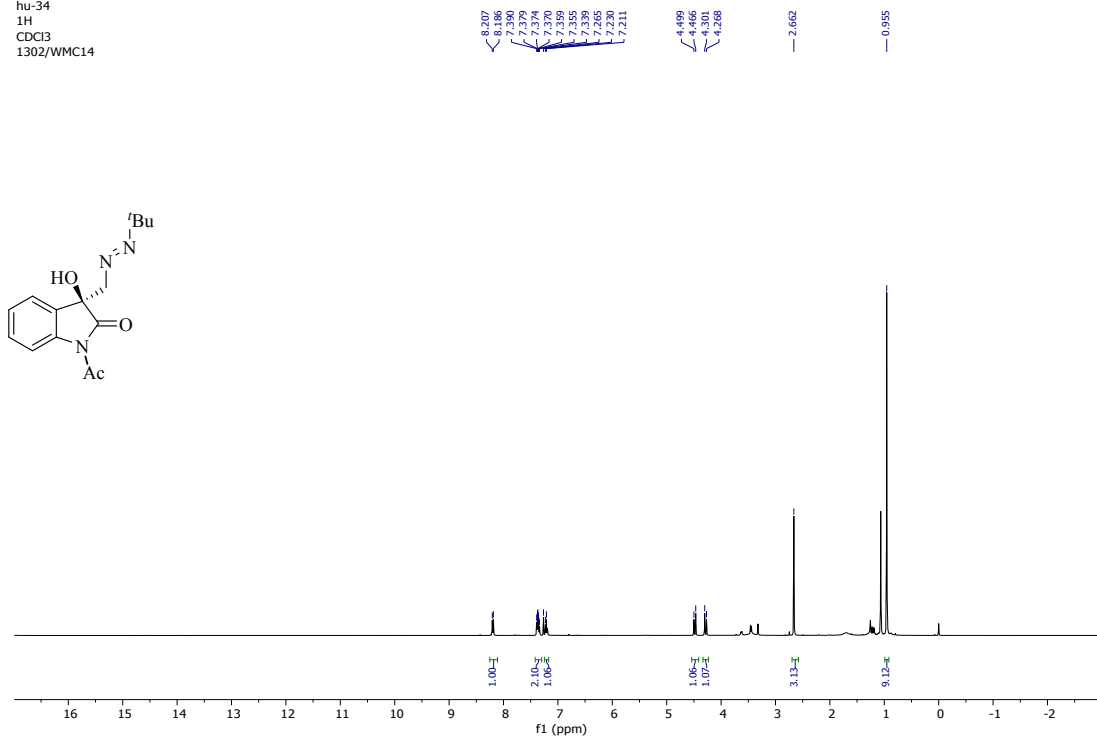
<sup>13</sup>C NMR spectrum of **3ba** (DMSO-d, 100 MHz)

2021WMC.1152.fid  
wh-12  
13C  
DMSO  
2021WMC-1152



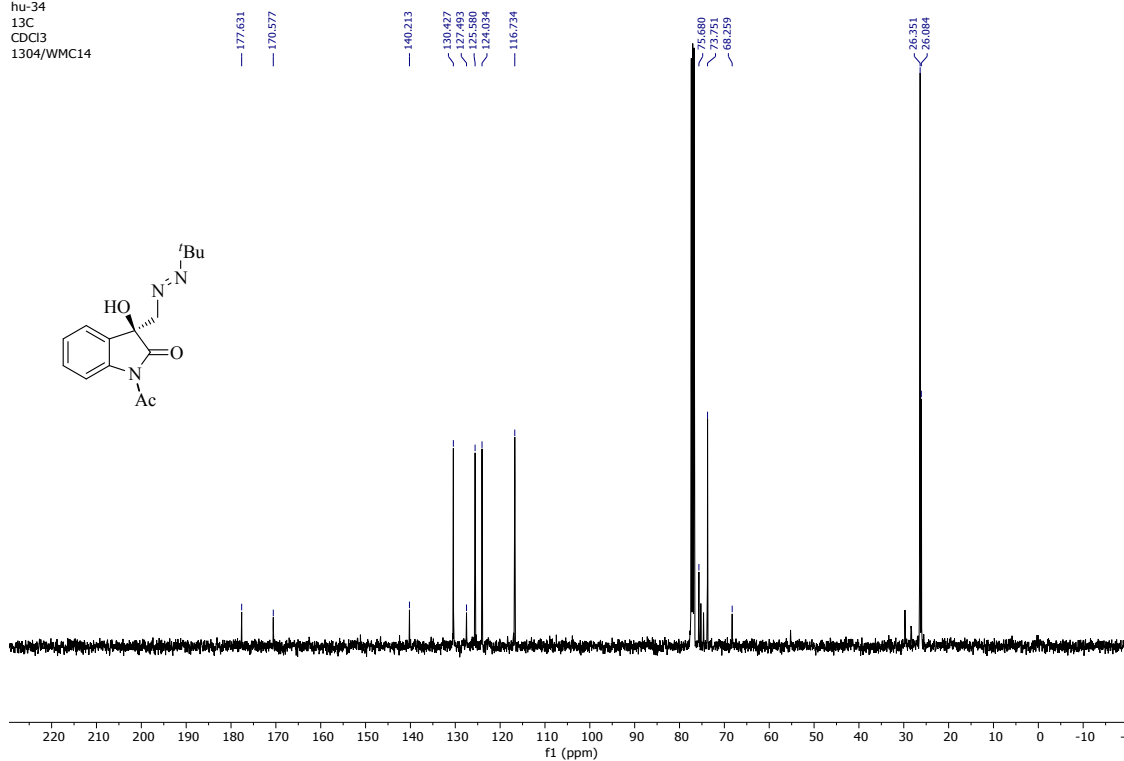
<sup>1</sup>H NMR spectrum of **3a** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1301-1304.1302.fid  
hu-34  
1H  
CDCl3  
1302/WMC14



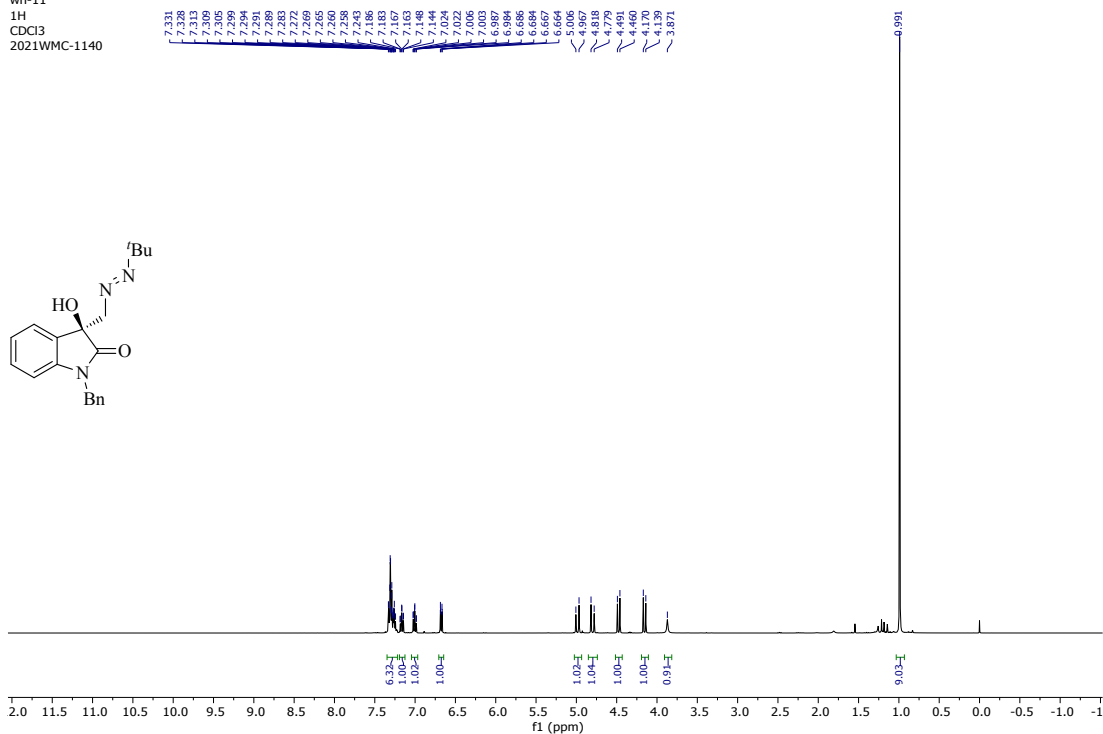
<sup>13</sup>C NMR spectrum of **3a** (CDCl<sub>3</sub>, 100 MHz)

WMC14-1305-1306.1305.fid  
hu-34  
13C  
CDCl3  
1304/WMC14



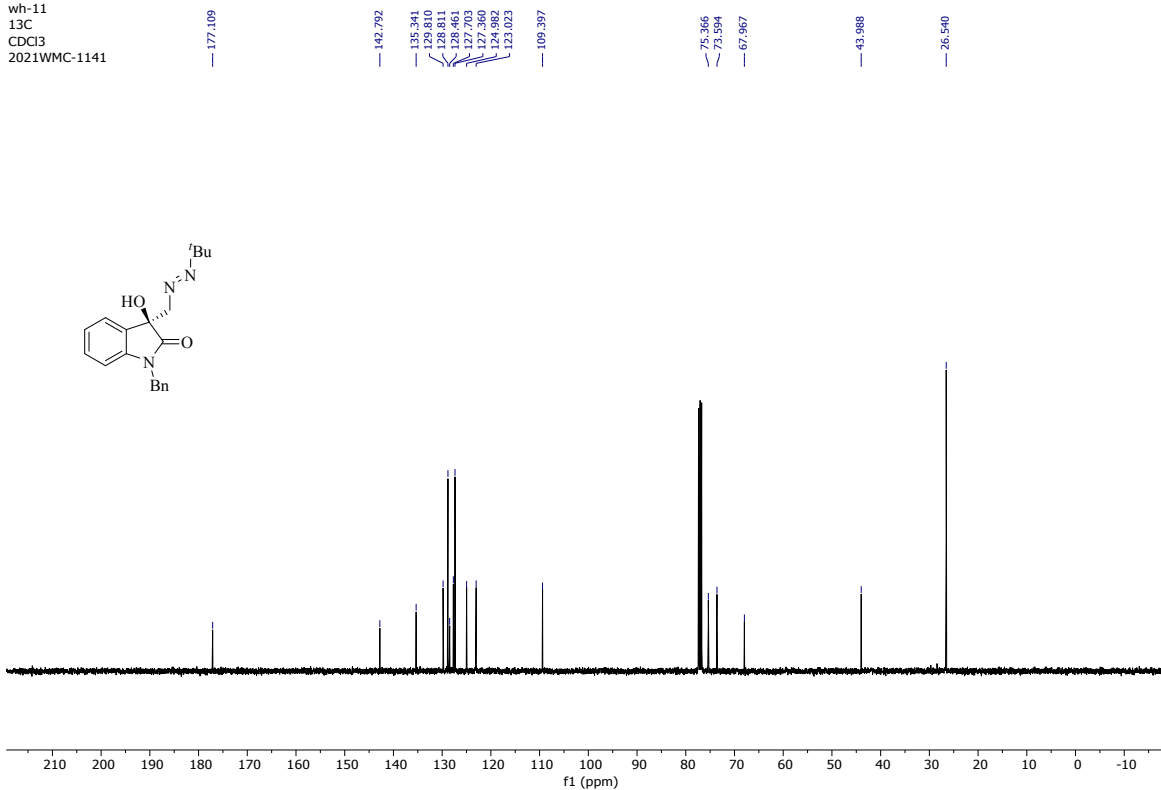
<sup>1</sup>H NMR spectrum of **3da** (CDCl<sub>3</sub>, 400 MHz)

2021WMC.1140.fid  
wh-11  
CDCl<sub>3</sub>  
2021WMC-1140



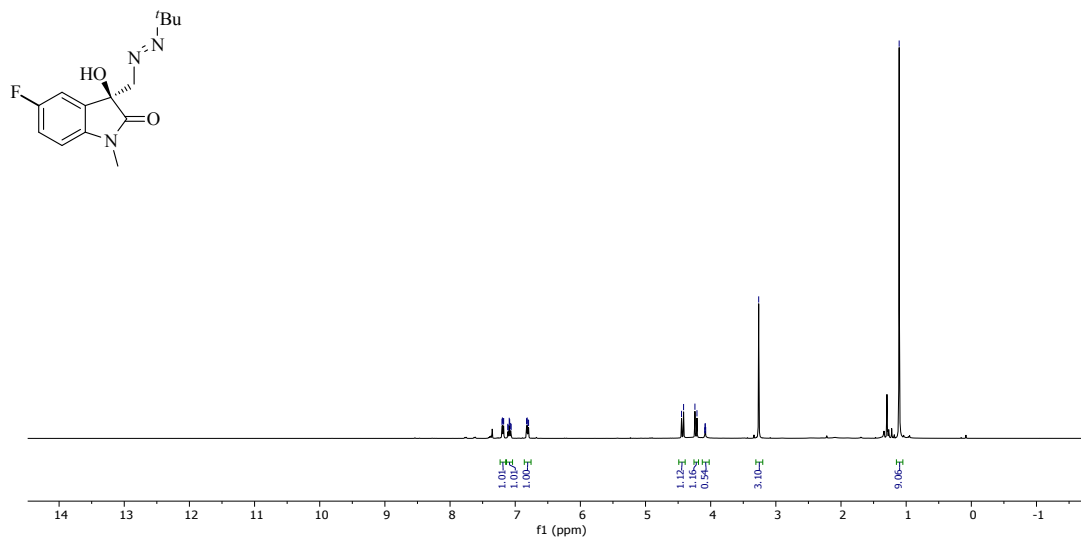
<sup>13</sup>C NMR spectrum of **3da** (CDCl<sub>3</sub>, 100 MHz)

2021WMC.1141.fid  
wh-11  
13C  
CDCl<sub>3</sub>  
2021WMC-1141



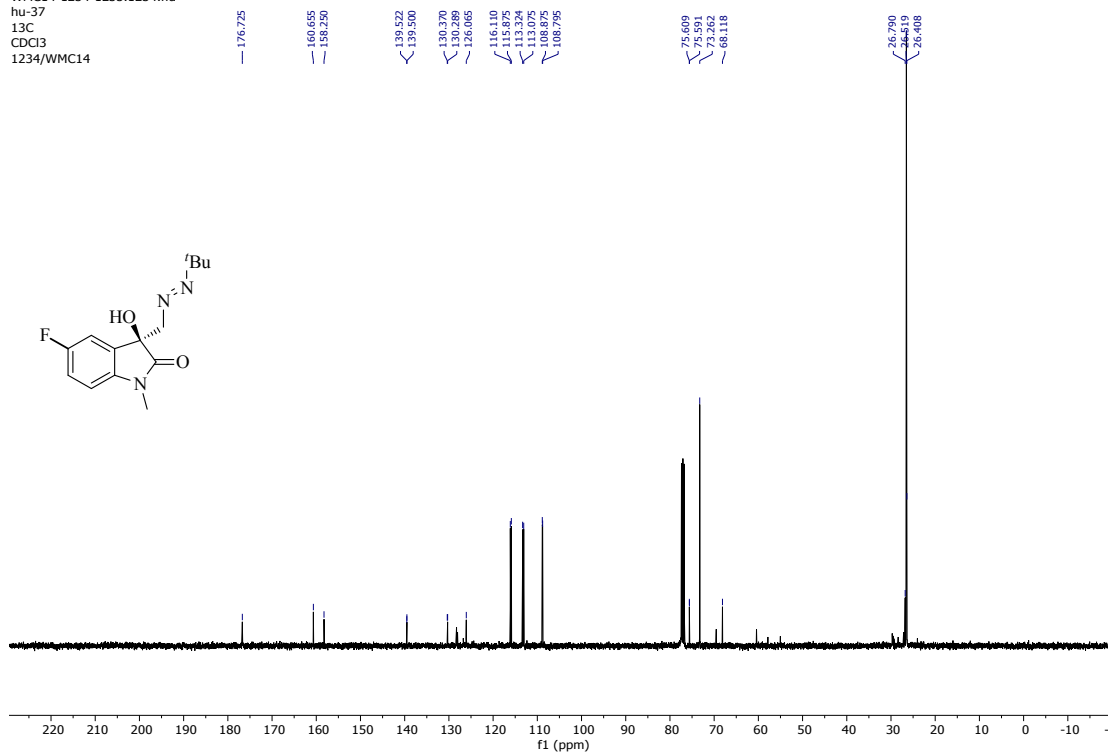
<sup>1</sup>H NMR spectrum of **3ea** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1231-1233.1232.fid  
hu-37  
1H  
CDCl3  
1232/WMC08



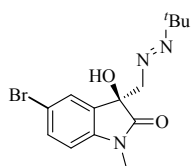
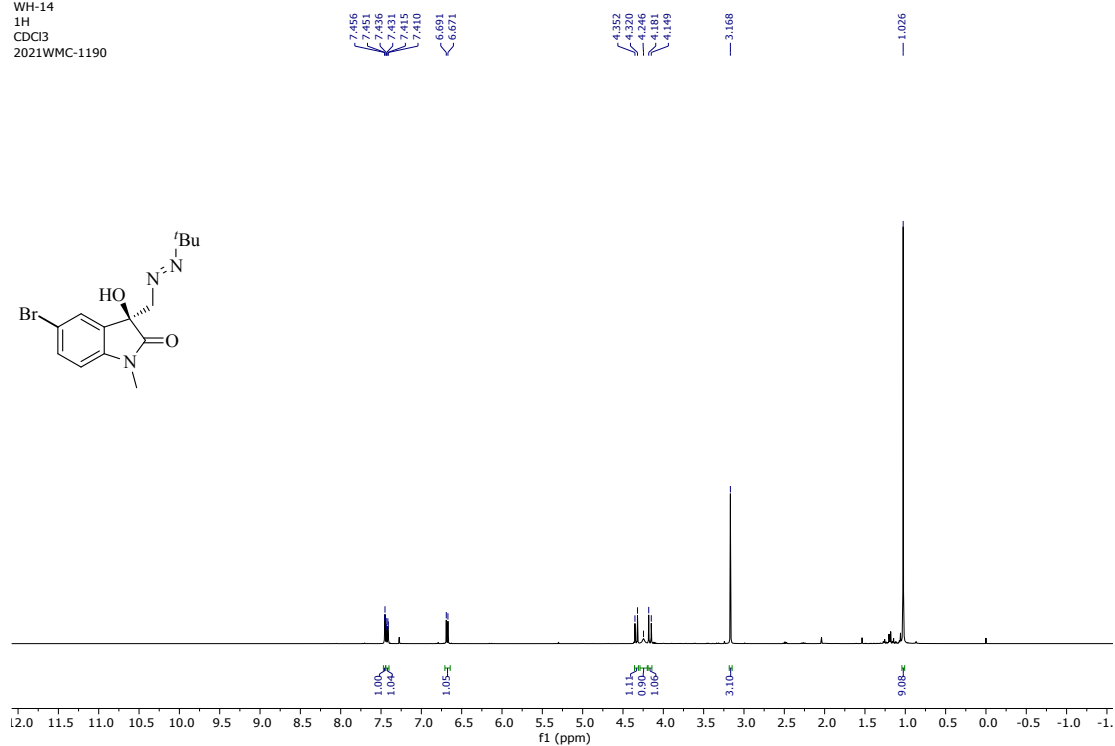
<sup>13</sup>C NMR spectrum of **3ea** (CDCl<sub>3</sub>, 100 MHz)

WMC14-1234-1235.1234.fid  
hu-37  
13C  
CDCl3  
1234/WMC14



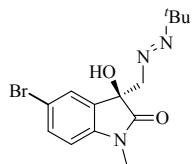
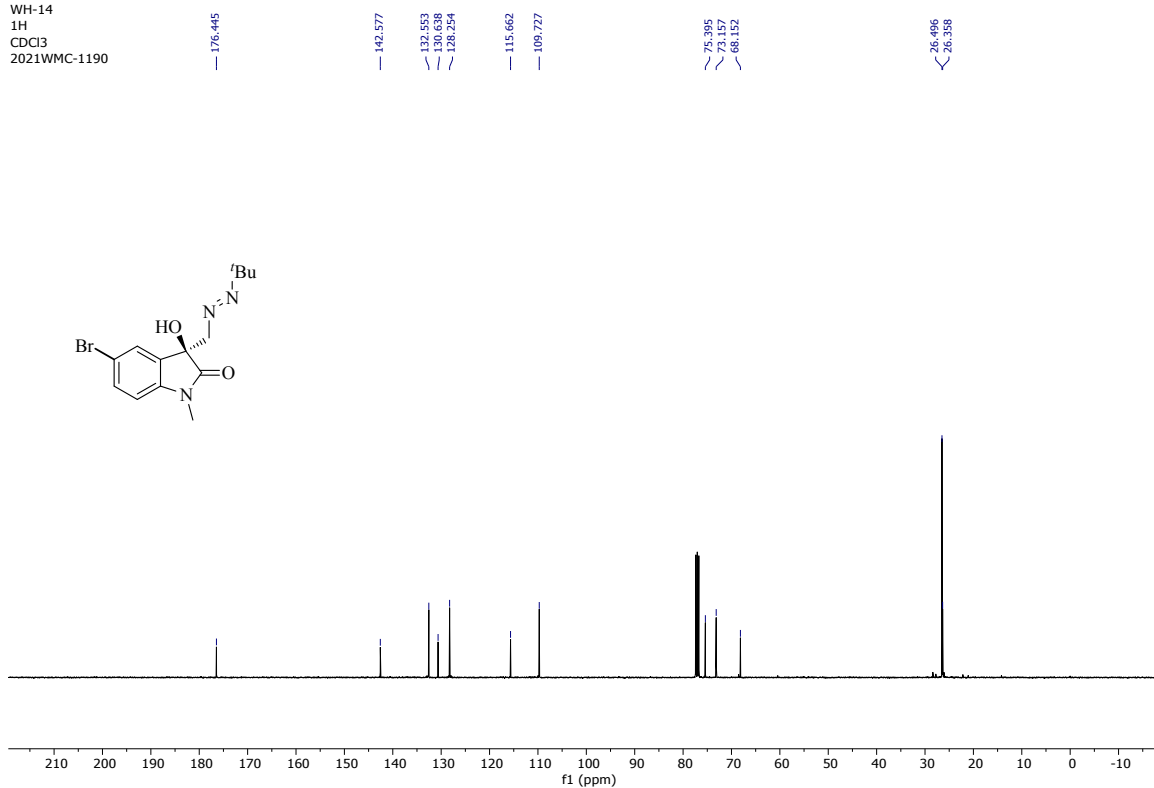
<sup>1</sup>H NMR spectrum of **3fa** (CDCl<sub>3</sub>, 400 MHz)

2021WMC.1190.fid  
WH-14  
1H  
CDCl<sub>3</sub>  
2021WMC-1190



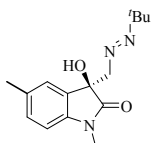
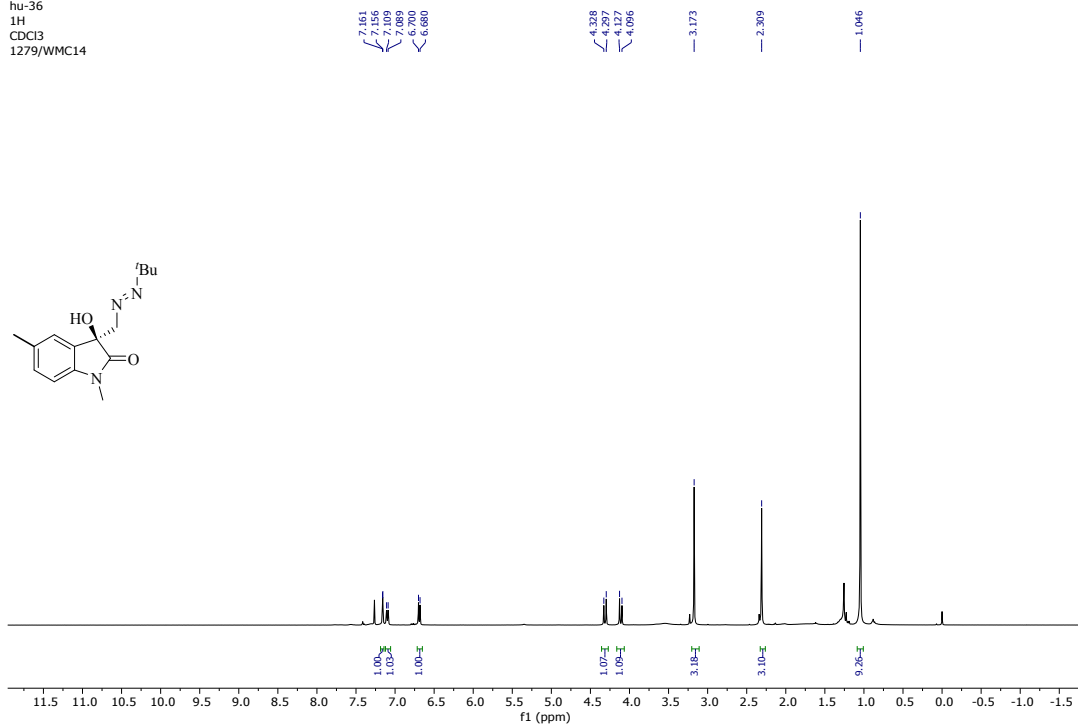
<sup>13</sup>C NMR spectrum of **3fa** (CDCl<sub>3</sub>, 100 MHz)

2021WMC.1191.fid  
WH-14  
1H  
CDCl<sub>3</sub>  
2021WMC-1190



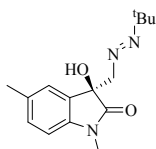
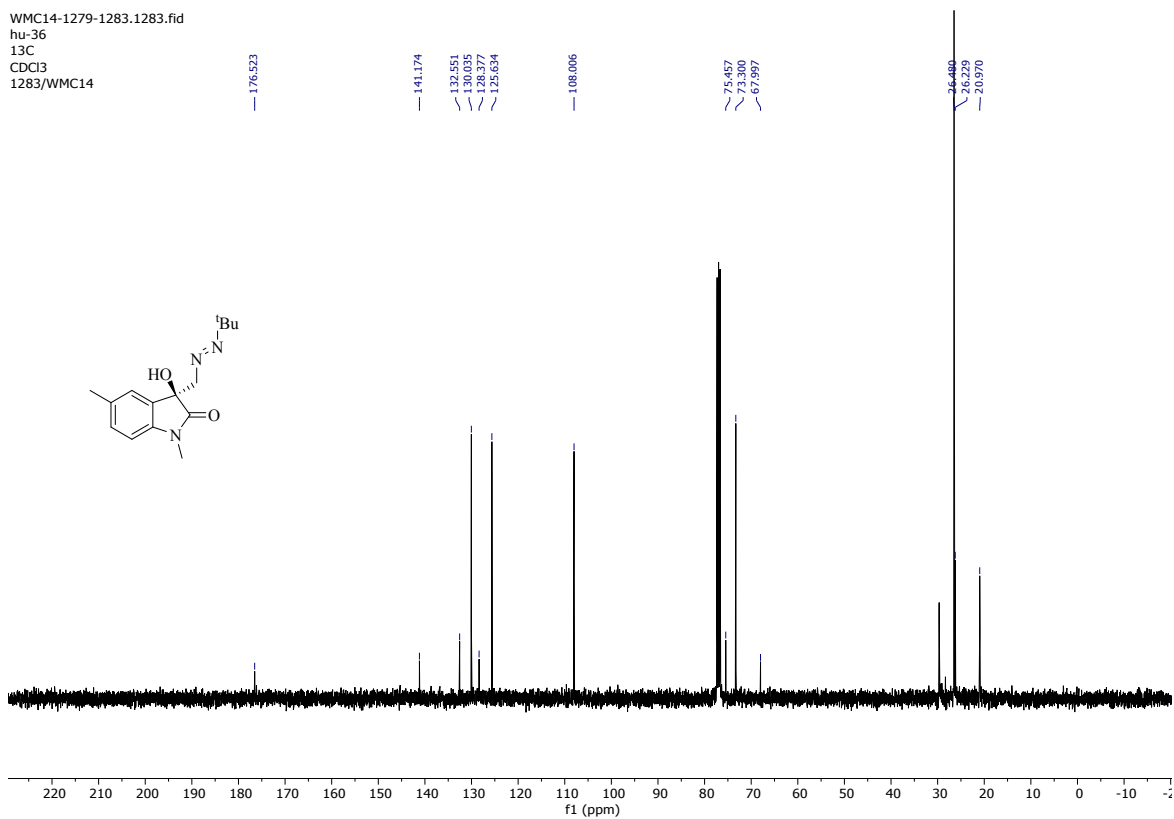
### $^1\text{H}$ NMR spectrum of **3ga** ( $\text{CDCl}_3$ , 400 MHz)

WMC14-1279-1283.1279.fid  
hu-36  
1H  
CDCl3  
1279/WMC14



### $^{13}\text{C}$ NMR spectrum of **3ga** ( $\text{CDCl}_3$ , 100 MHz)

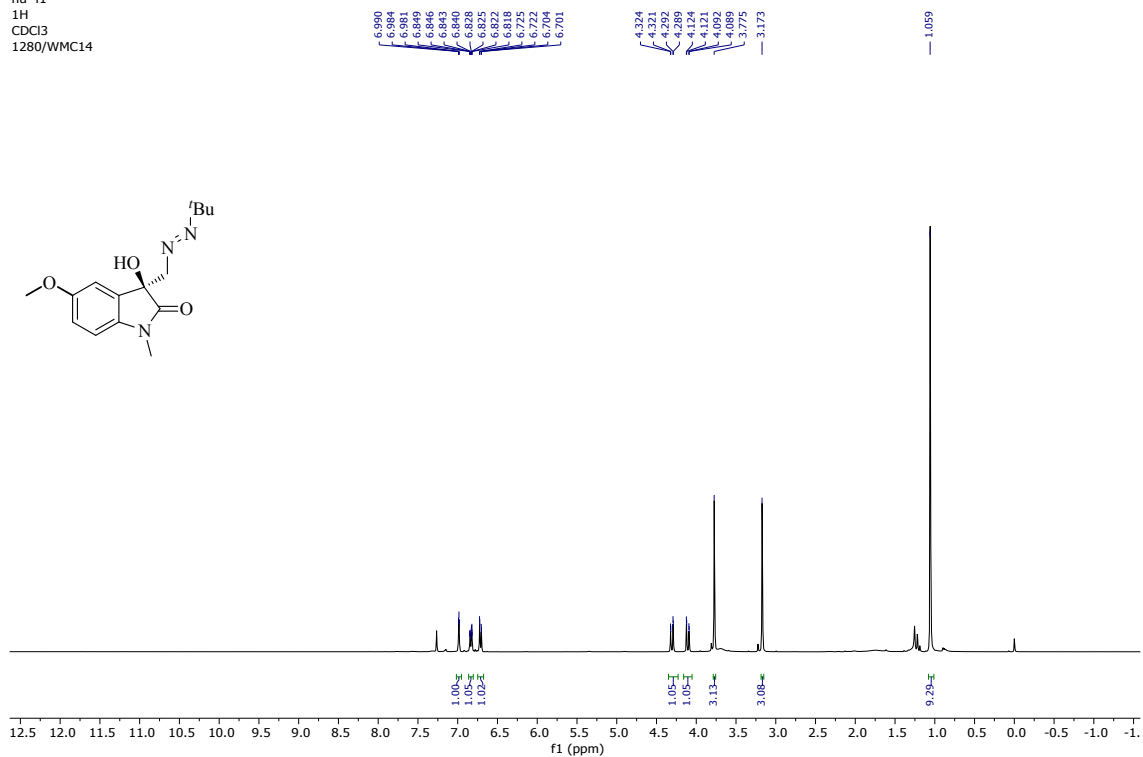
WMC14-1279-1283.1283.fid  
hu-36  
13C  
CDCl3  
1283/WMC14





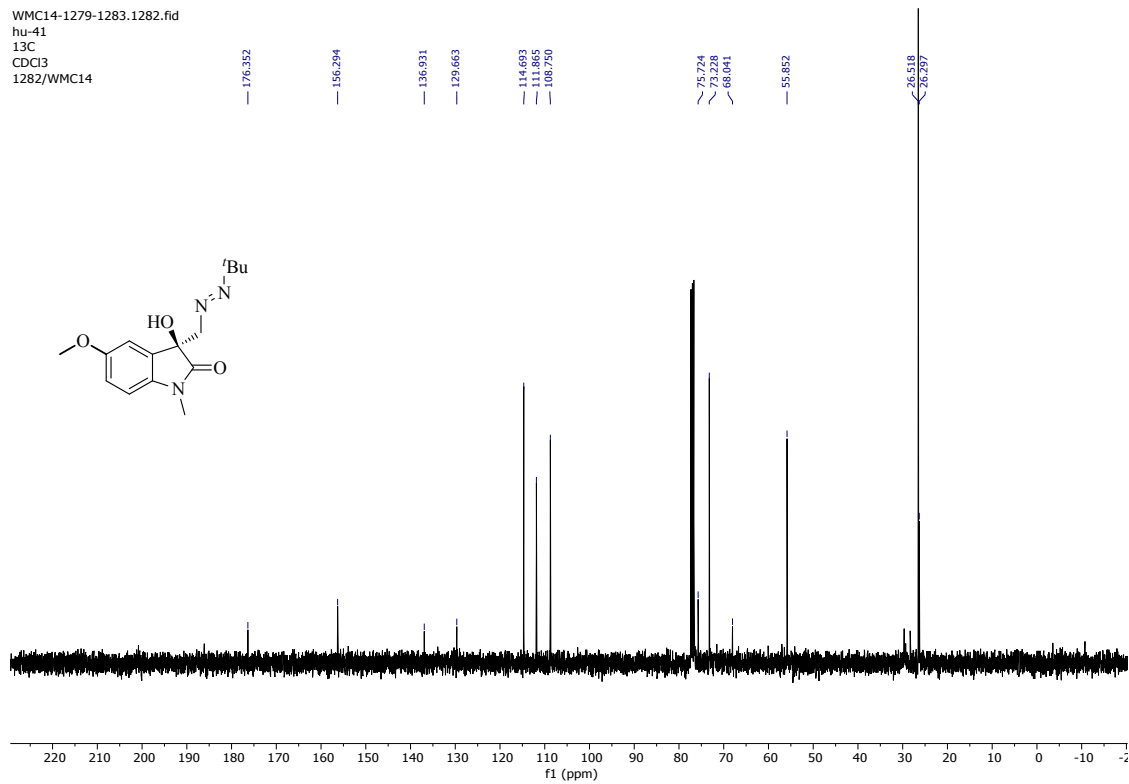
<sup>1</sup>H NMR spectrum of **3ha** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1279-1283.1280.fid  
hu-41  
1H  
CDCl<sub>3</sub>  
1280/WMC14



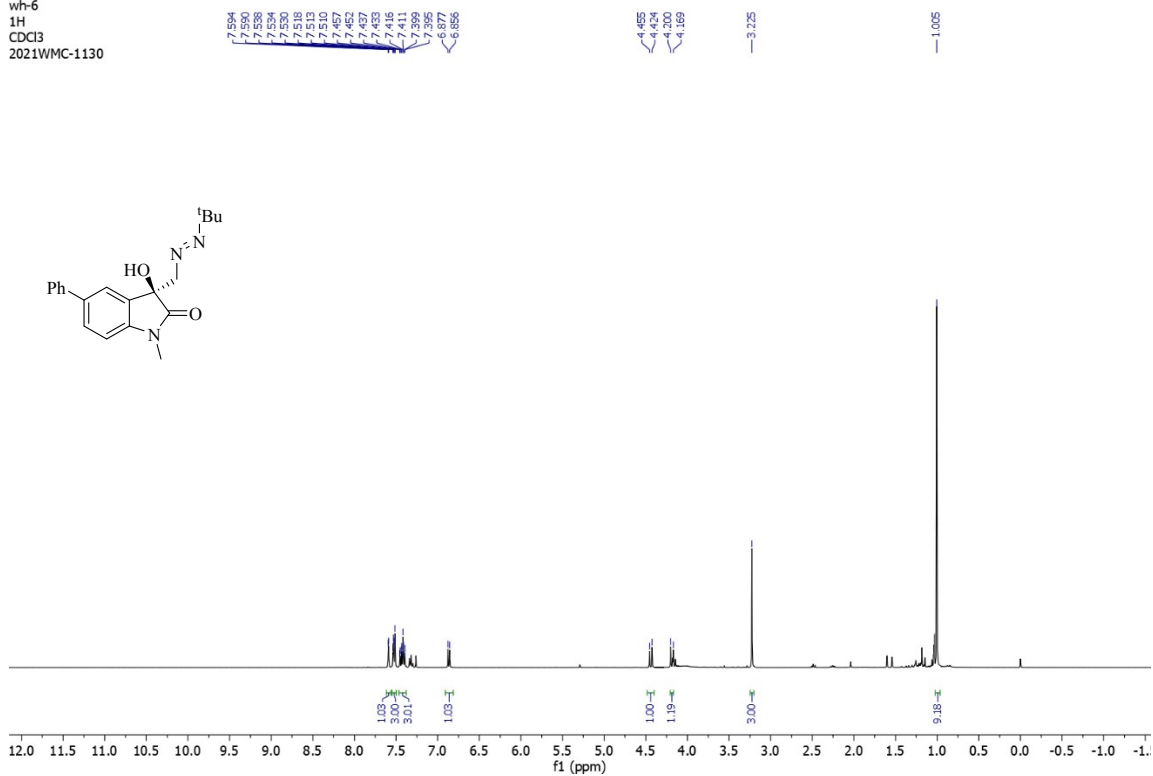
<sup>13</sup>C NMR spectrum of **3ha** (CDCl<sub>3</sub>, 100 MHz)

WMC14-1279-1283.1282.fid  
hu-41  
13C  
CDCl<sub>3</sub>  
1282/WMC14



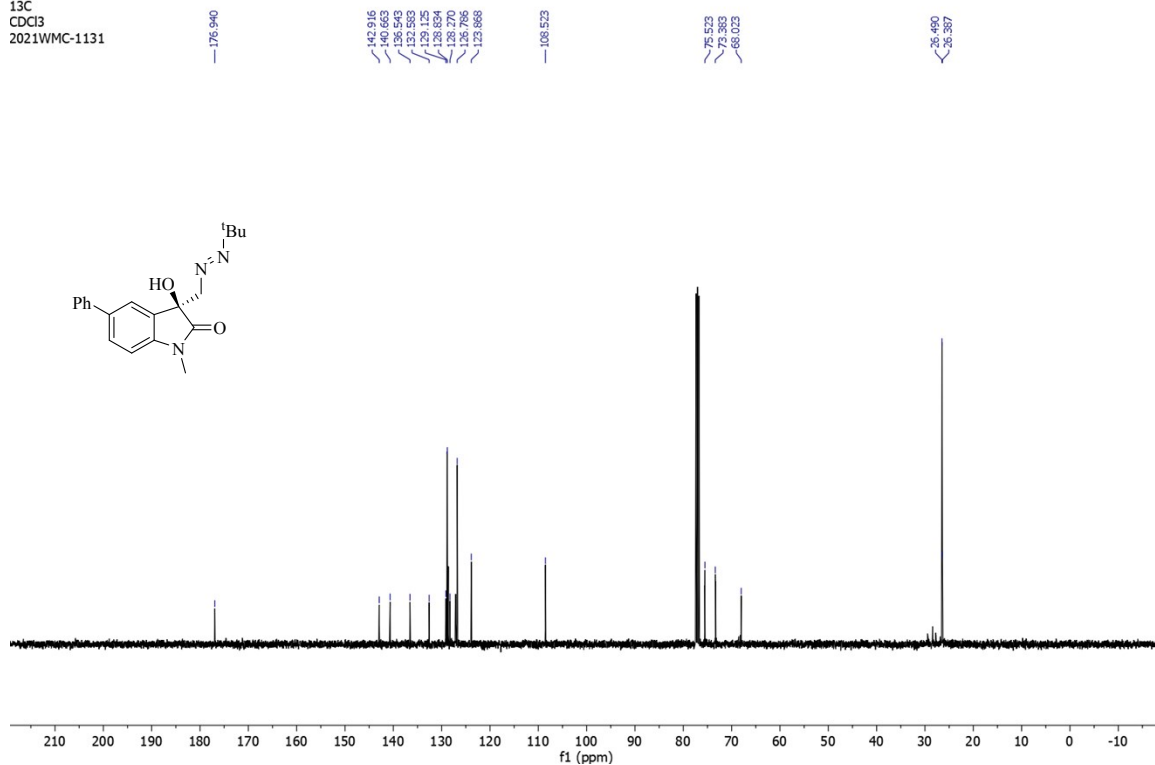
<sup>1</sup>H NMR spectrum of **3ia** (CDCl<sub>3</sub>, 400 MHz)

2021WMC.1130.fid  
wh-6  
1H  
CDCl3  
2021WMC-1130



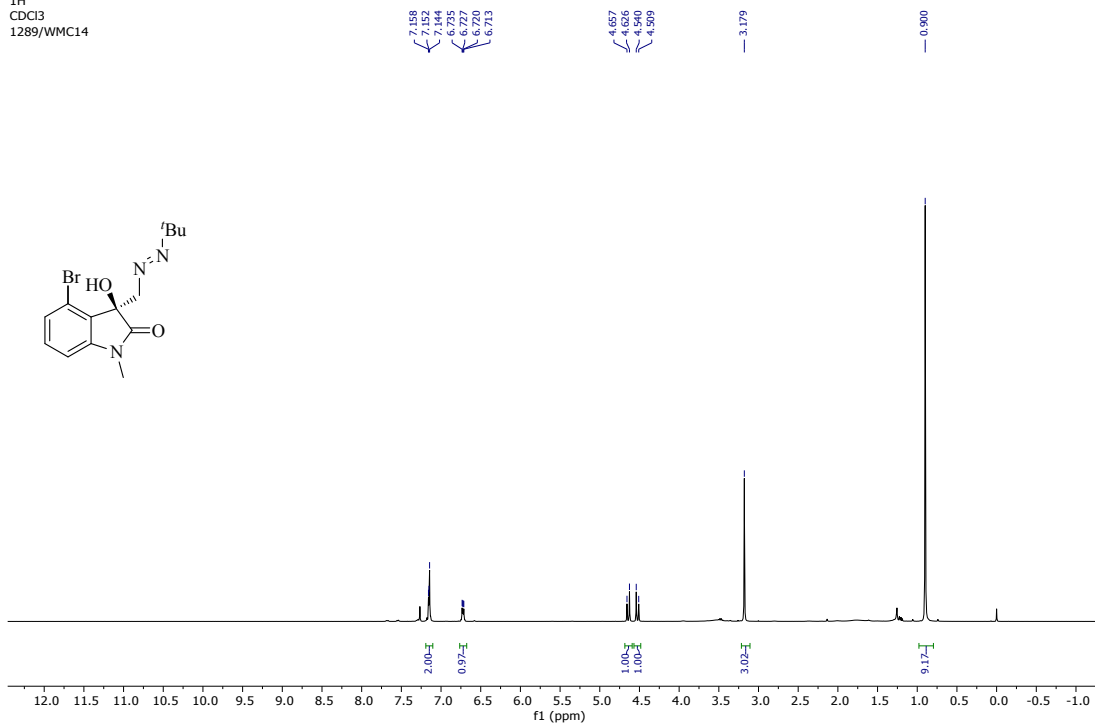
<sup>13</sup>C NMR spectrum of **3ia** (CDCl<sub>3</sub>, 100 MHz)

2021WMC.1131.fid  
wh-6  
13C  
CDCl3  
2021WMC-1131



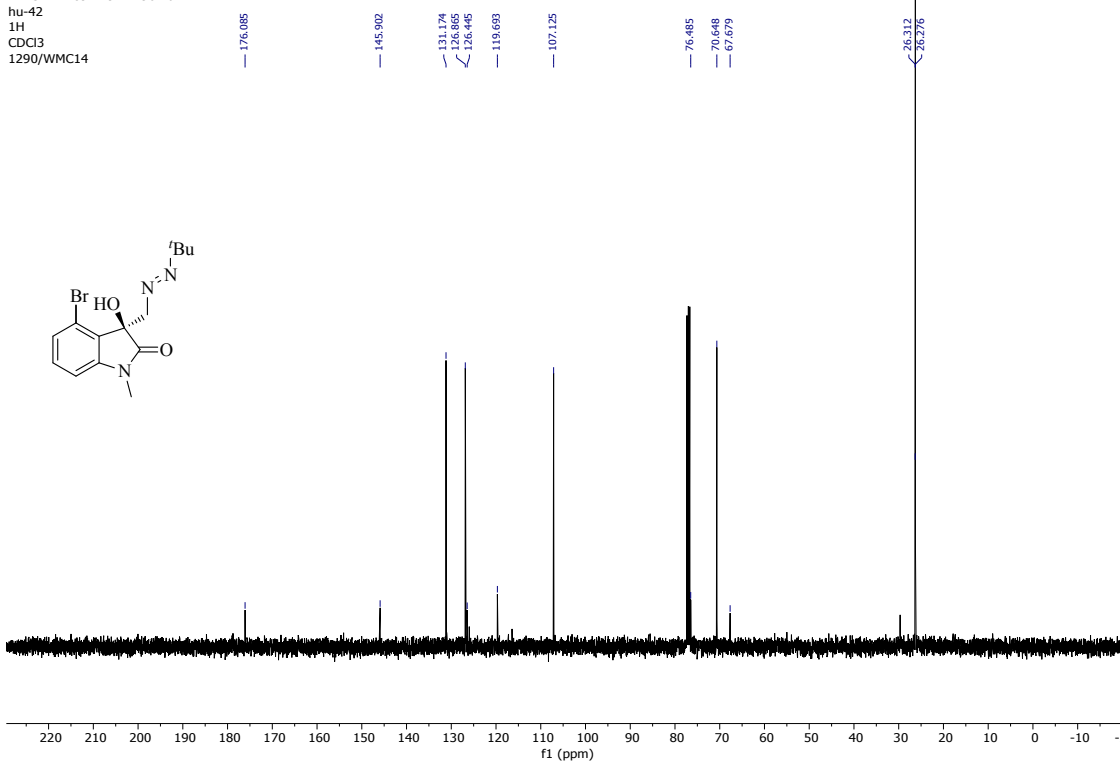
<sup>1</sup>H NMR spectrum of **3ja** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1289-1294.1289.fid  
hu-42  
1H  
CDCl<sub>3</sub>  
1289/WMC14



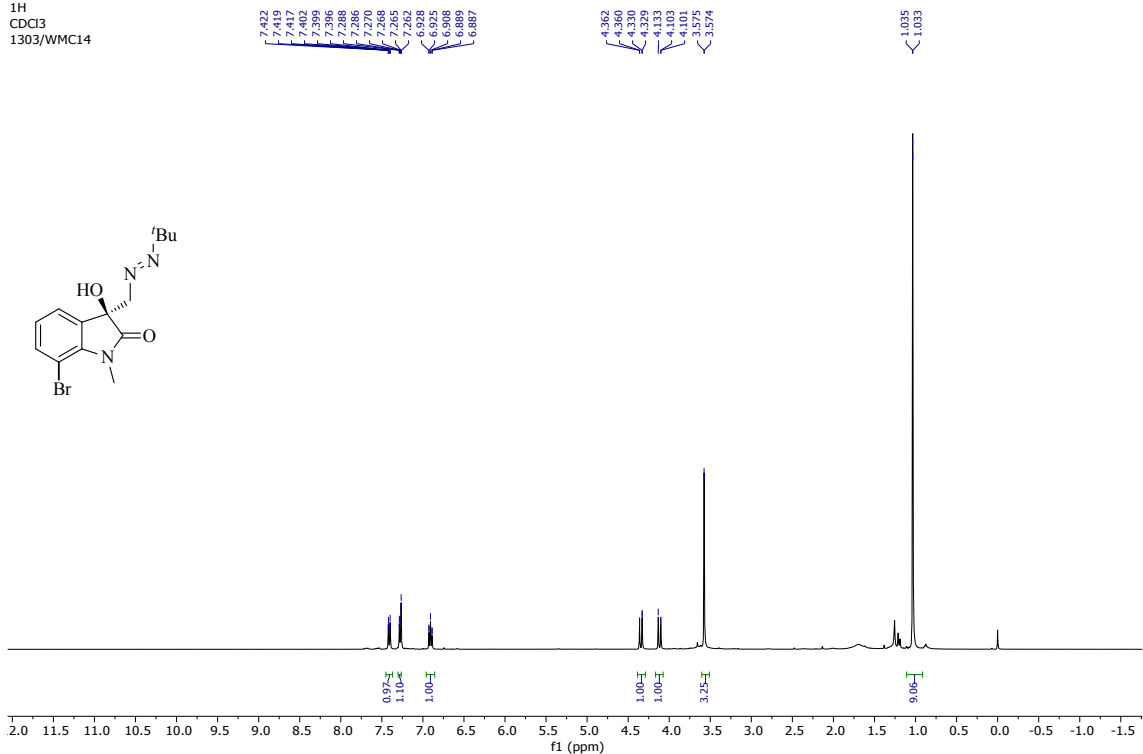
<sup>13</sup>C NMR spectrum of **3ja** (CDCl<sub>3</sub>, 100 MHz)

WMC14-1289-1294.1290.fid  
hu-42  
1H  
CDCl<sub>3</sub>  
1290/WMC14



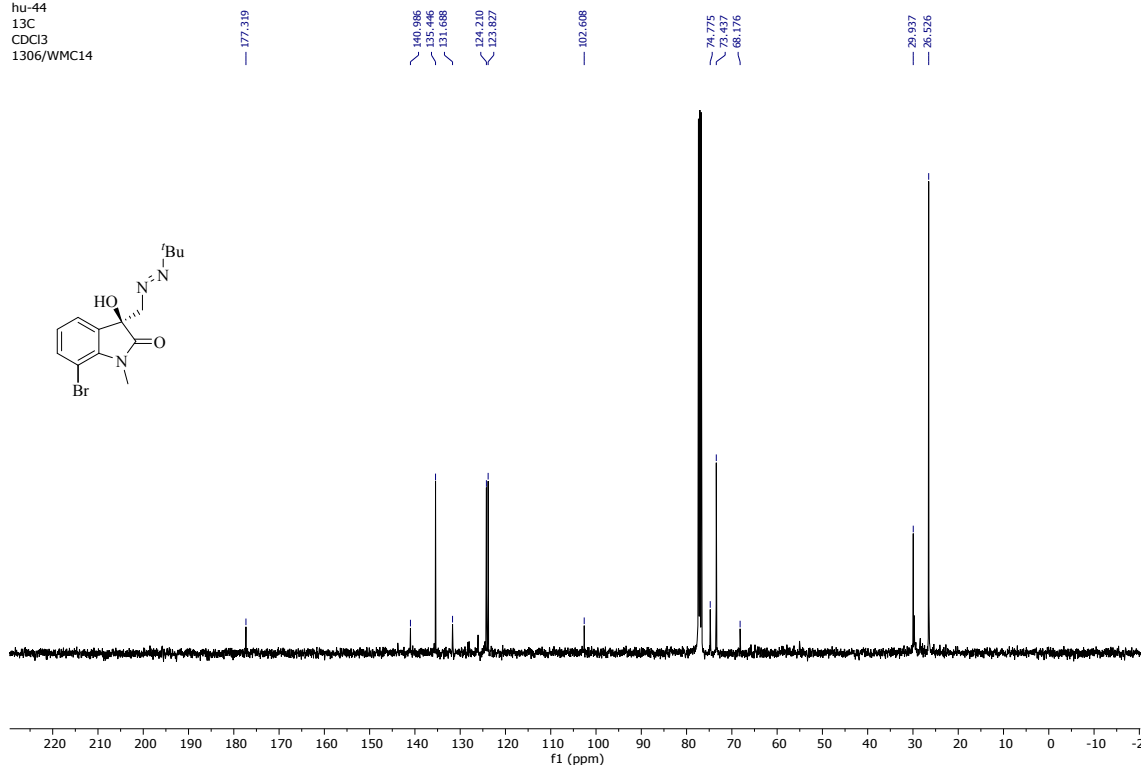
<sup>1</sup>H NMR spectrum of **3ka** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1301-1304.1303.fid  
hu-44  
1H  
CDCl<sub>3</sub>  
1303/WMC14

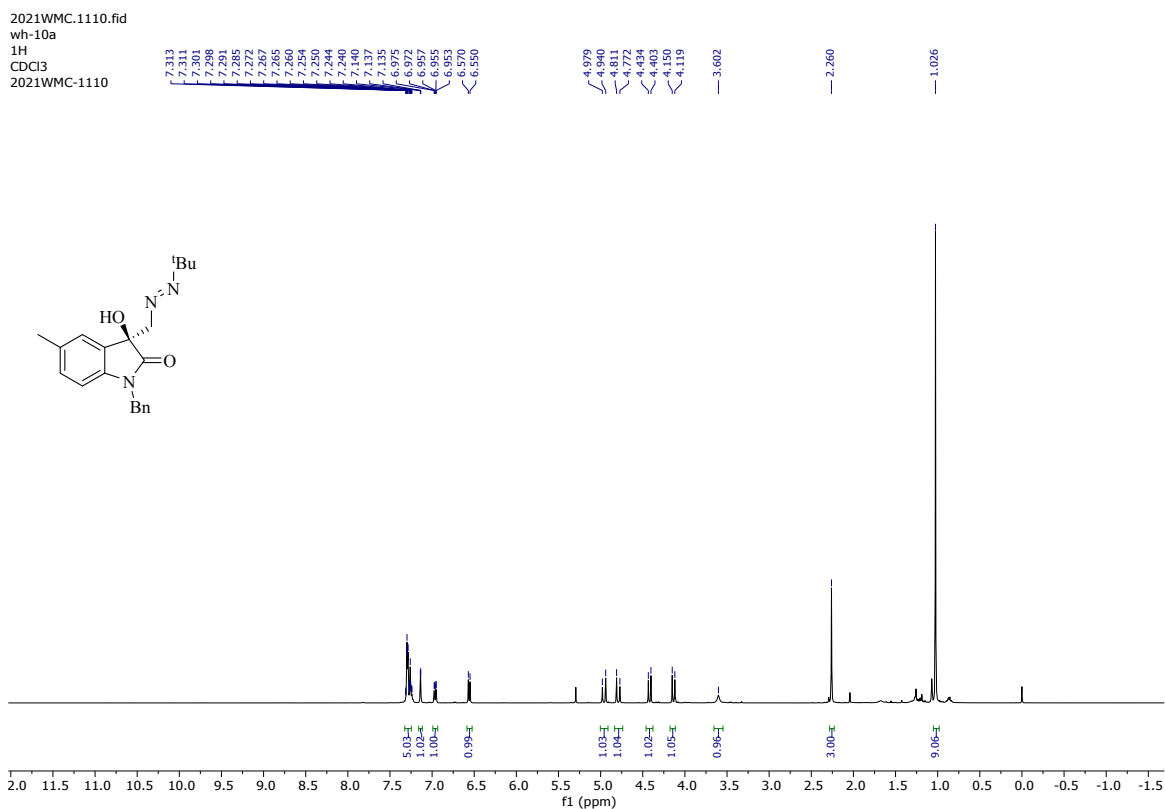


<sup>13</sup>C NMR spectrum of **3ka** (CDCl<sub>3</sub>, 100 MHz)

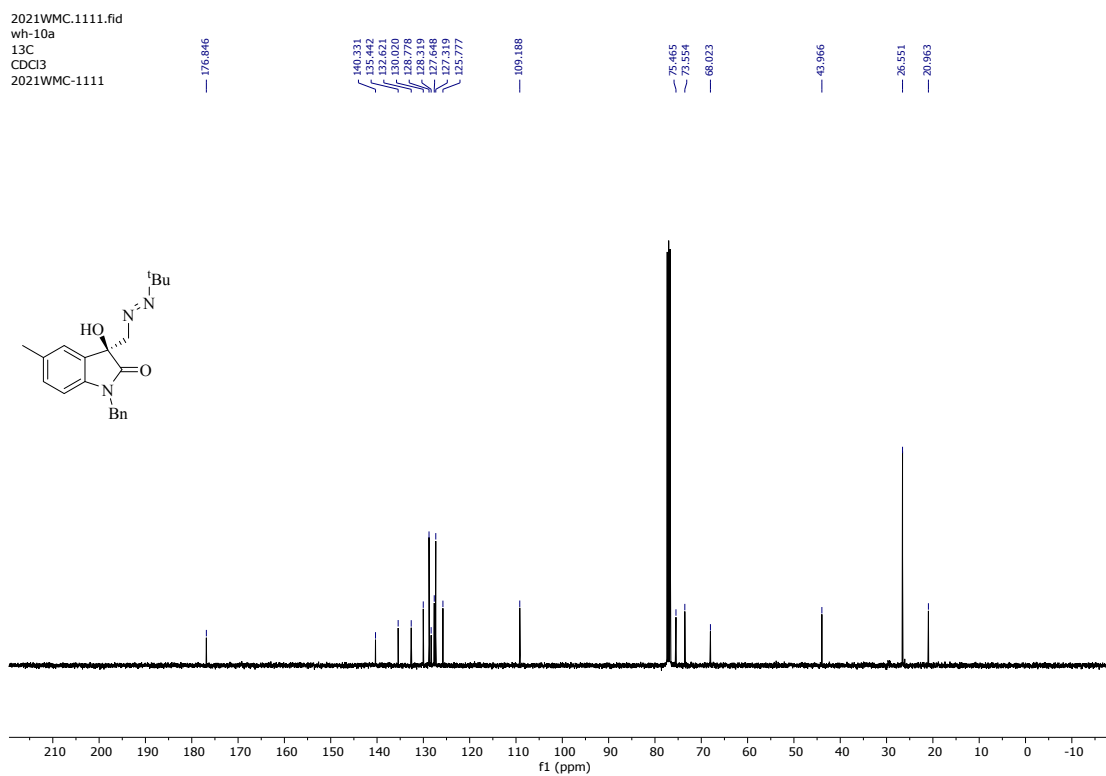
WMC14-1305-1306.1306.fid  
hu-44  
13C  
CDCl<sub>3</sub>  
1306/WMC14



### <sup>1</sup>H NMR spectrum of **3a** (CDCl<sub>3</sub>, 400 MHz)

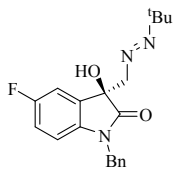
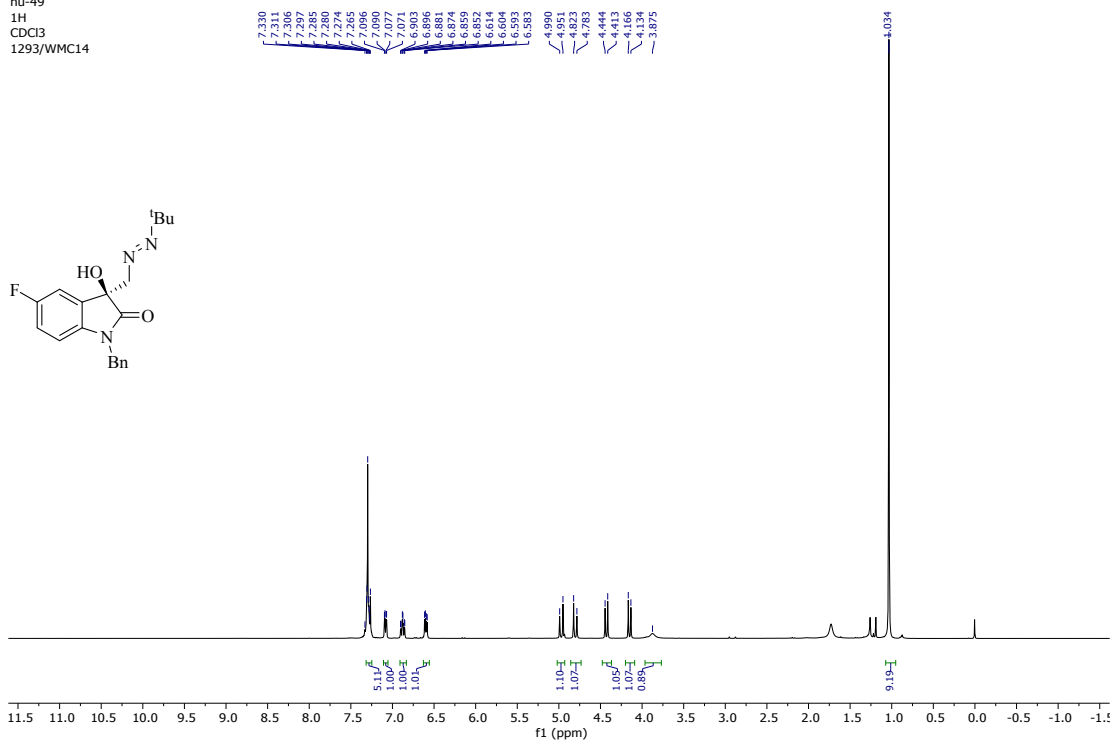


### <sup>13</sup>C NMR spectrum of **3a** (CDCl<sub>3</sub>, 100 MHz)



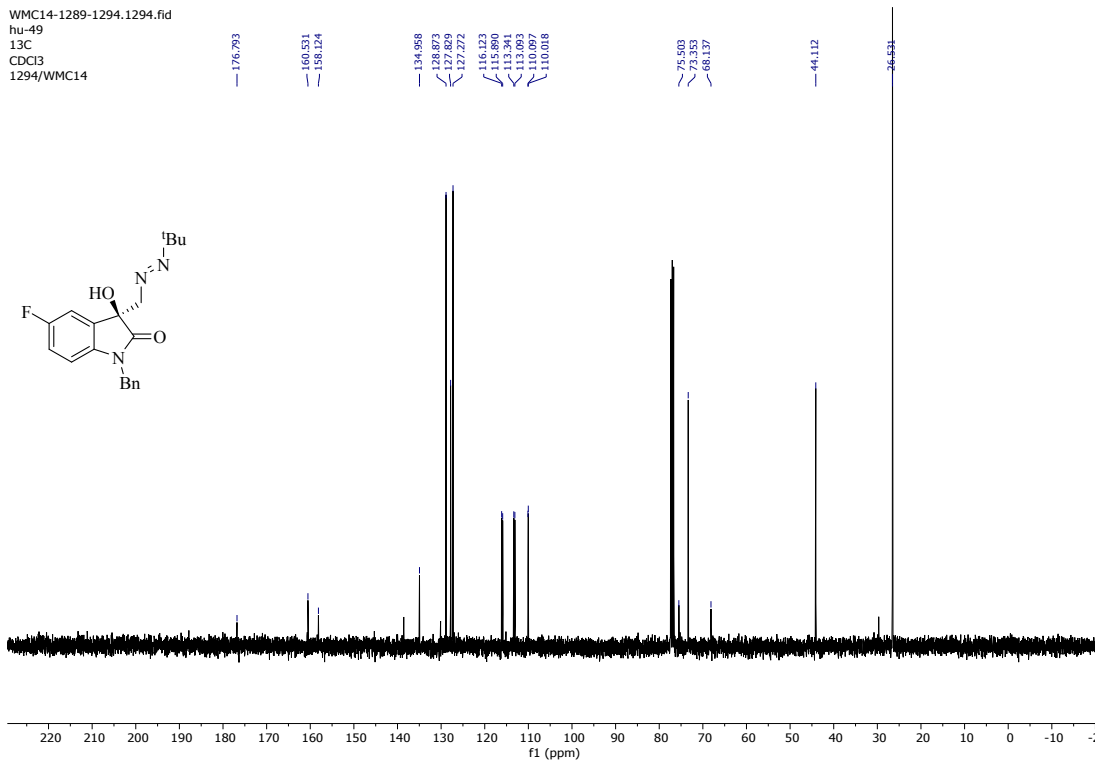
### <sup>1</sup>H NMR spectrum of **3ma** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1289-1294.1293.fid  
hu-49  
1H  
CDCl<sub>3</sub>  
1293/WMC14



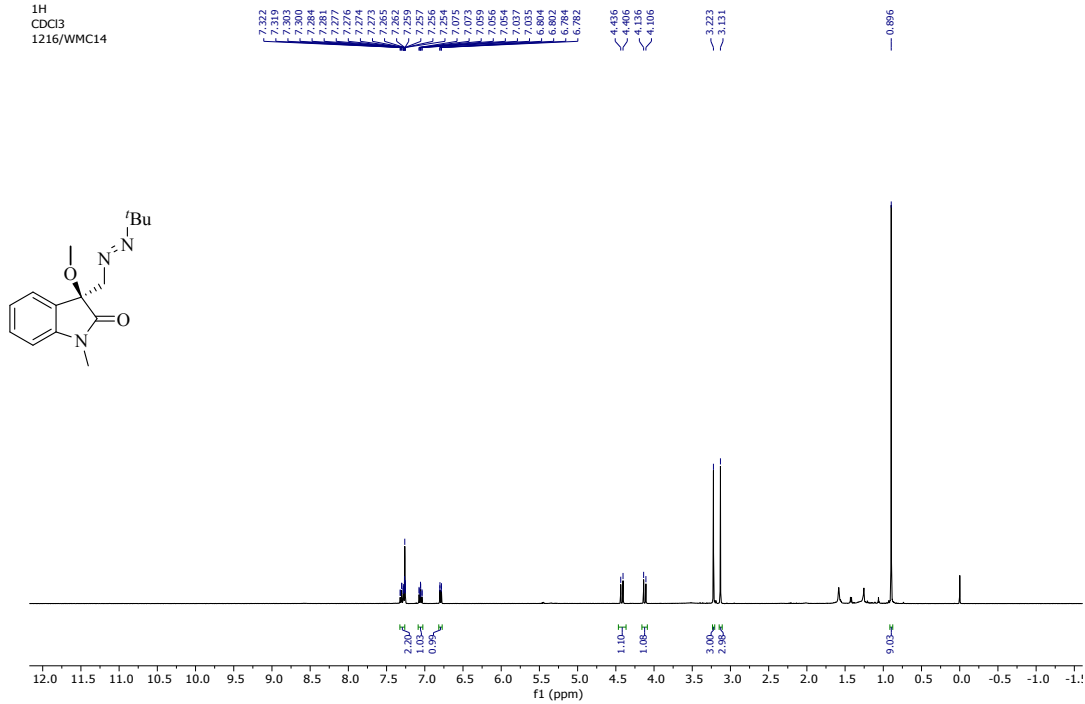
### <sup>13</sup>C NMR spectrum of **3ma** (CDCl<sub>3</sub>, 100 MHz)

WMC14-1289-1294.1294.fid  
hu-49  
13C  
CDCl<sub>3</sub>  
1294/WMC14



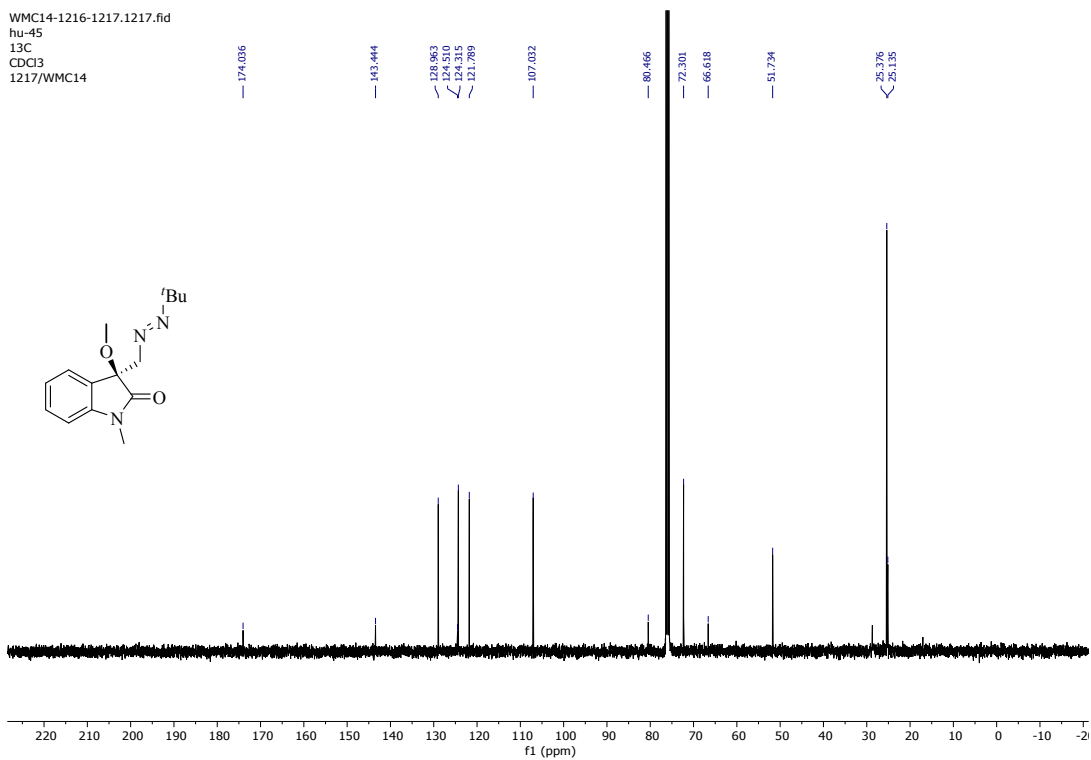
<sup>1</sup>H NMR spectrum of **4a** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1216-1217.1216.fid  
hu-45  
1H  
CDCl3  
1216/WMC14



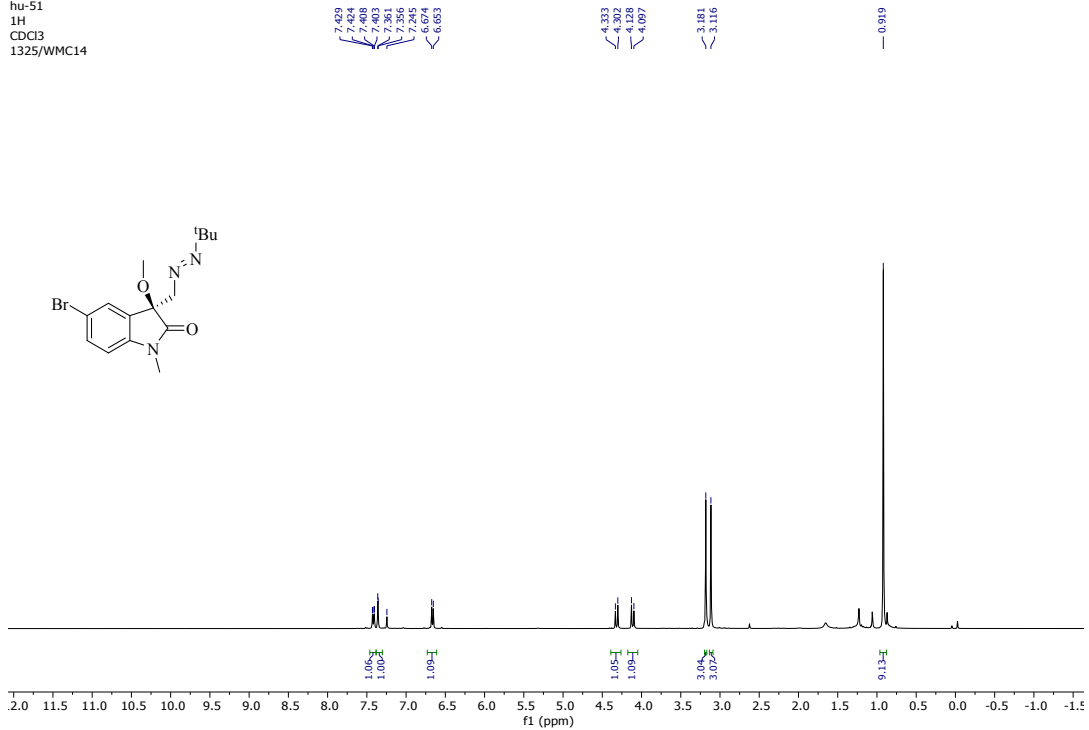
<sup>13</sup>C NMR spectrum of **4a** (CDCl<sub>3</sub>, 100 MHz)

WMC14-1216-1217.1217.fid  
hu-45  
13C  
CDCl3  
1217/WMC14



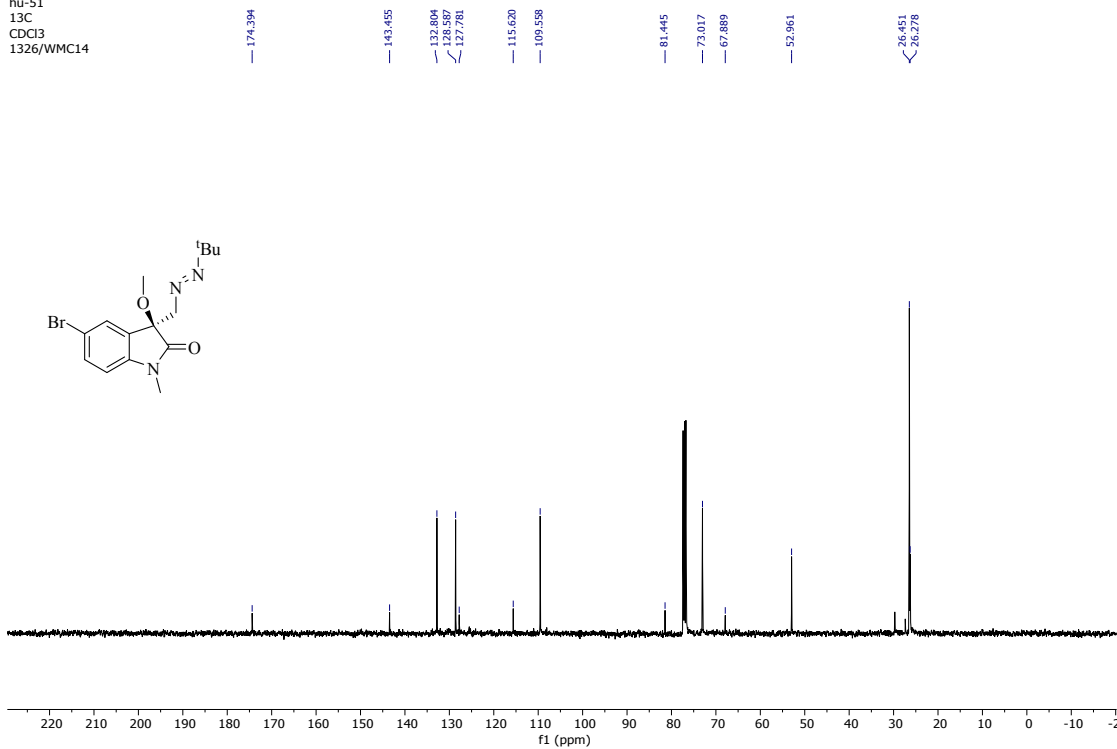
<sup>1</sup>H NMR spectrum of **4h** (CDCl<sub>3</sub>, 400 MHz)

WMC14-1325-1326.1325.fid  
hu-51  
1H  
CDCl3  
1325/WMC14



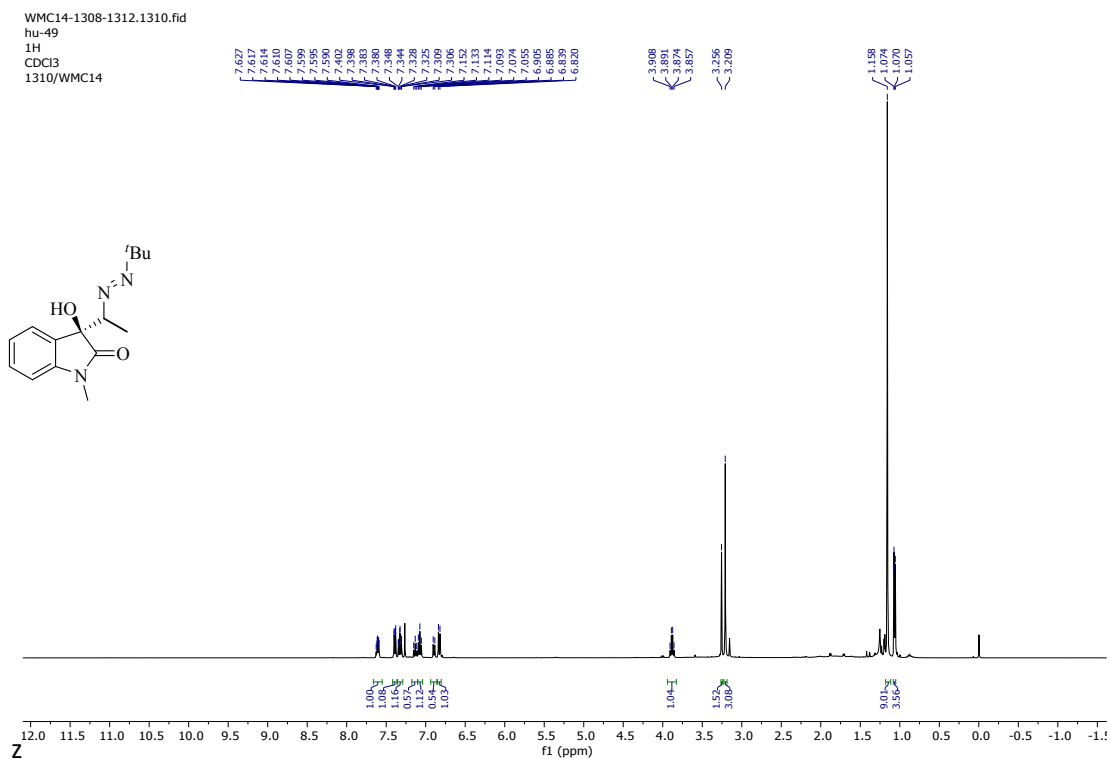
<sup>13</sup>C NMR spectrum of **4h** (CDCl<sub>3</sub>, 100 MHz)

WMC14-1325-1326.1326.fid  
hu-51  
13C  
CDCl3  
1326/WMC14

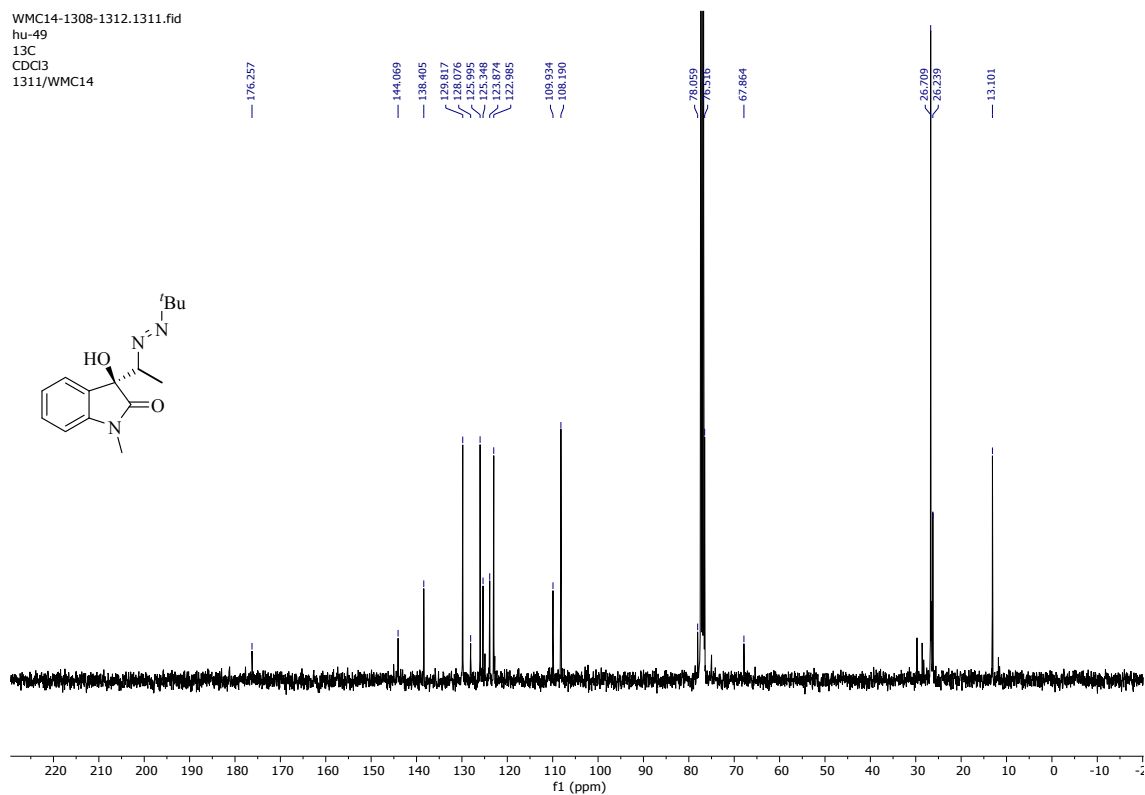




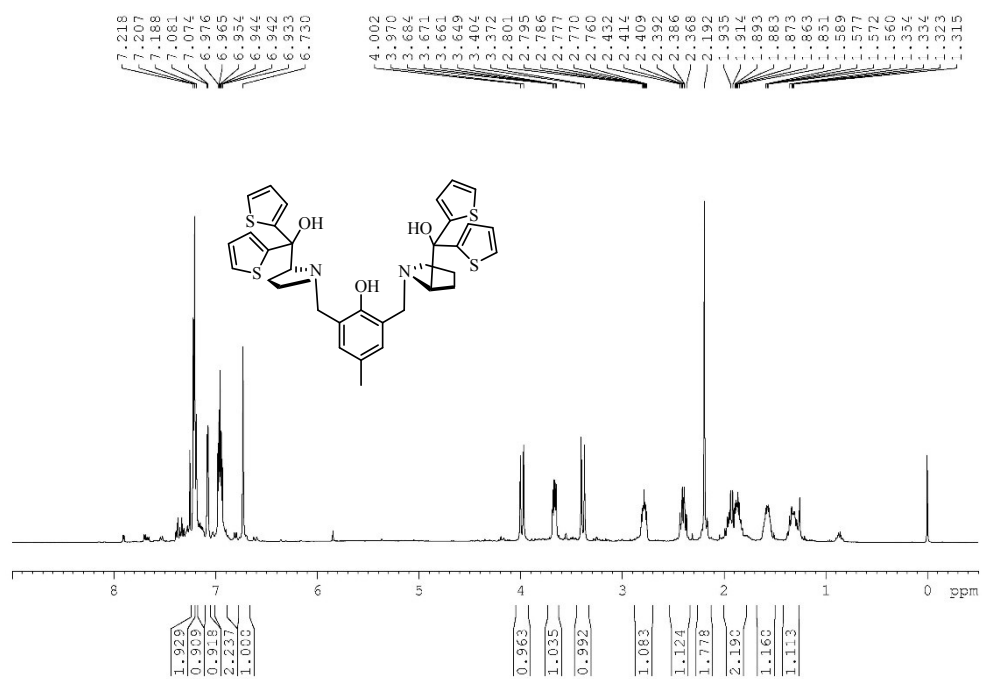
<sup>1</sup>H NMR spectrum of **3ab** (CDCl<sub>3</sub>, 400 MHz)



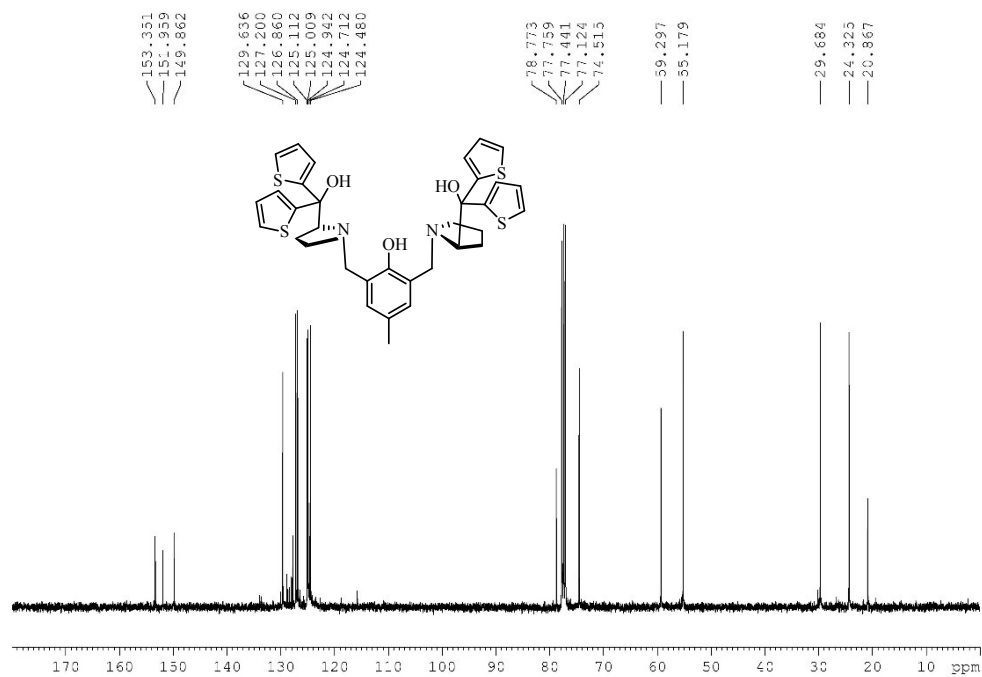
<sup>13</sup>C NMR spectrum of **3ab** (CDCl<sub>3</sub>, 100 MHz)



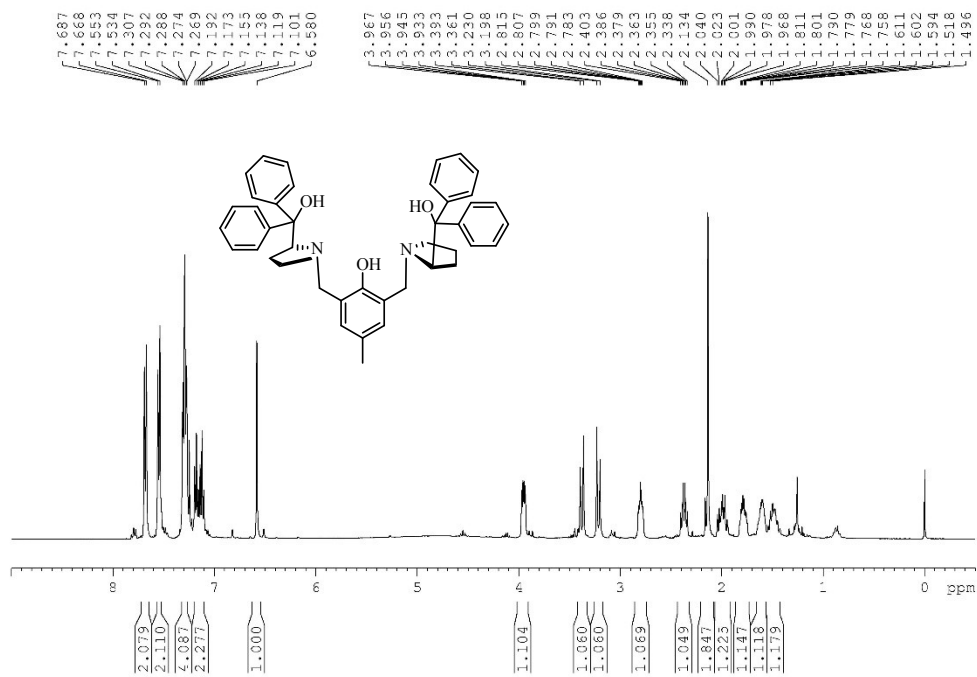
<sup>1</sup>H NMR spectrum of **L<sub>4</sub>** (CDCl<sub>3</sub>, 400 MHz)



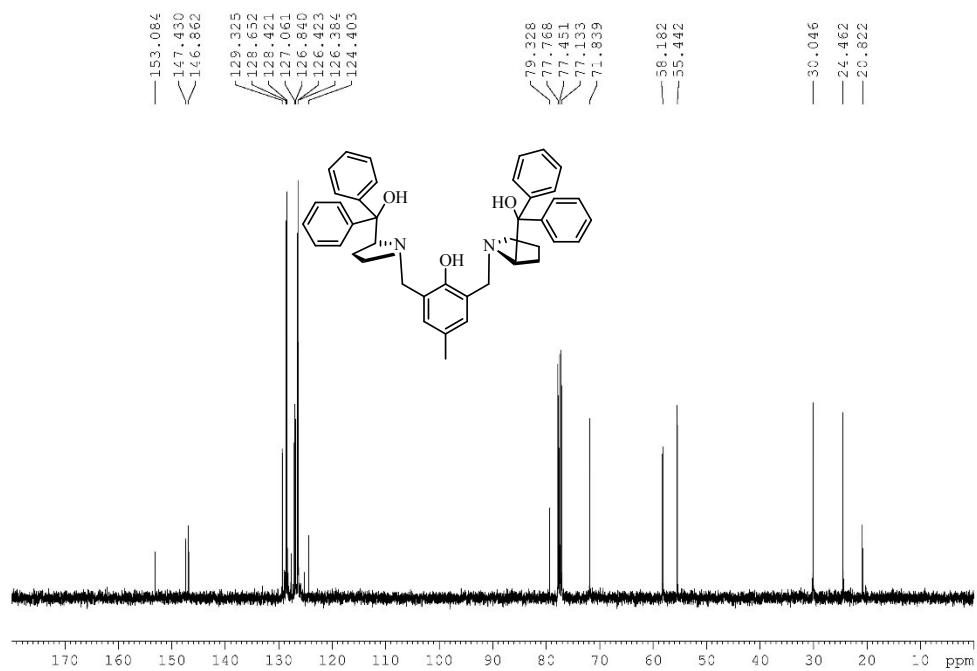
<sup>13</sup>C NMR spectrum of L<sub>4</sub> (CDCl<sub>3</sub>, 100 MHz)



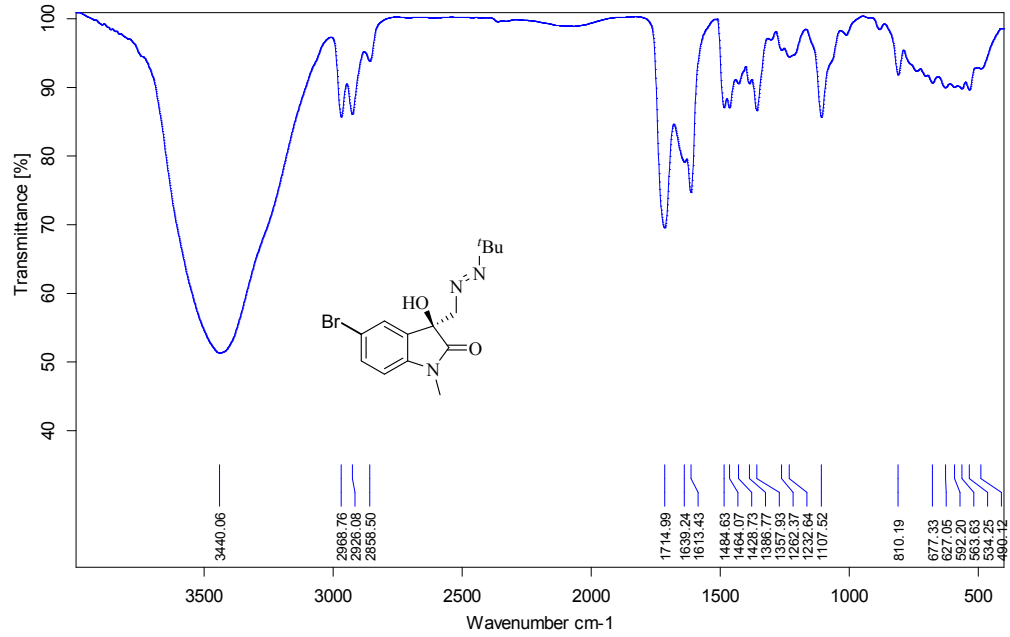
<sup>1</sup>H NMR spectrum of L<sub>2</sub> (CDCl<sub>3</sub>, 400 MHz)



<sup>13</sup>C NMR spectrum of **L2** (CDCl<sub>3</sub>, 100 MHz)



IR spectra:



Page 1/1

HRMS spectra:

