

Enantioselective Synthesis of 2-Indolyl Methanamine Derivatives Through Disulfonimides-Catalyzed Friedel–Crafts C2-Alkylation of 3-Substituted Indoles with Imines

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Supporting Information

X-ray Crystal Analysis of 4i	S2
Syntheses of 3-Substituted Indole Substrates	S3
Copies of ¹H NMR and ¹³C NMR Spectra	S4
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X-ray Crystal Analysis of the Major Diastereomer 4i

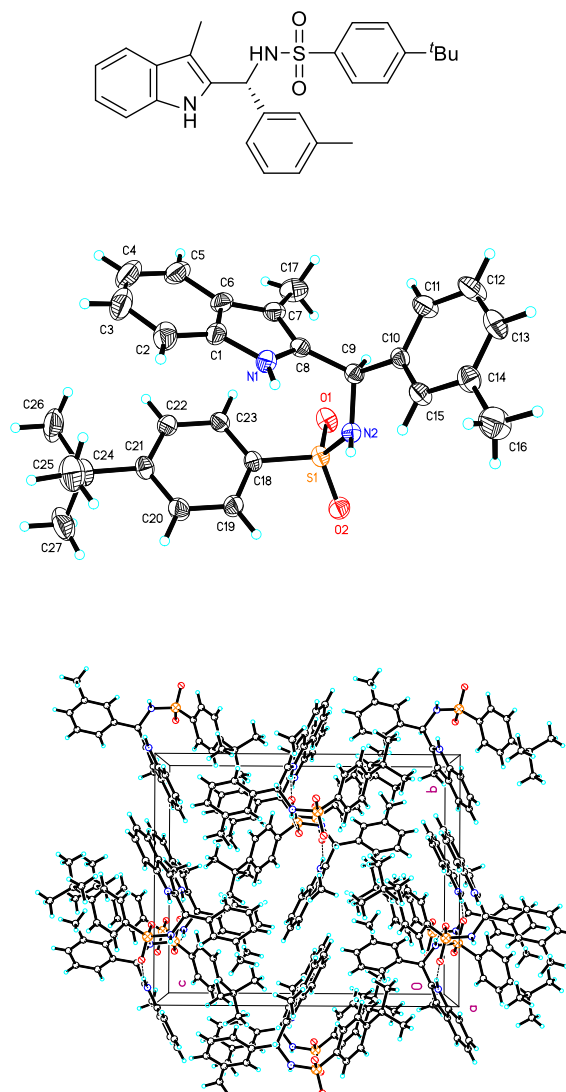


Table 1. Crystal data and structure refinement for mo_dd21073_0m.

Identification code	mo_dd21073_0m	
Empirical formula	C ₂₇ H ₃₀ N ₂ O ₂ S	
Formula weight	446.59	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 9.4321(3) Å	α = 90°.
	b = 14.6668(5) Å	β = 90°.
	c = 17.7584(6) Å	γ = 90°.
Volume	2456.67(14) Å ³	

Z	4
Density (calculated)	1.207 Mg/m ³
Absorption coefficient	0.157 mm ⁻¹
F(000)	952
Crystal size	0.200 x 0.150 x 0.120 mm ³
Theta range for data collection	2.445 to 25.996°.
Index ranges	-11<=h<=11, -18<=k<=16, -21<=l<=18
Reflections collected	12262
Independent reflections	4775 [R(int) = 0.0224]
Completeness to theta = 25.242°	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6390
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4775 / 0 / 298
Goodness-of-fit on F ²	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0338, wR2 = 0.0831
R indices (all data)	R1 = 0.0393, wR2 = 0.0871
Absolute structure parameter	0.00(2)
Extinction coefficient	n/a
Largest diff. peak and hole	0.124 and -0.184 e.Å ⁻³

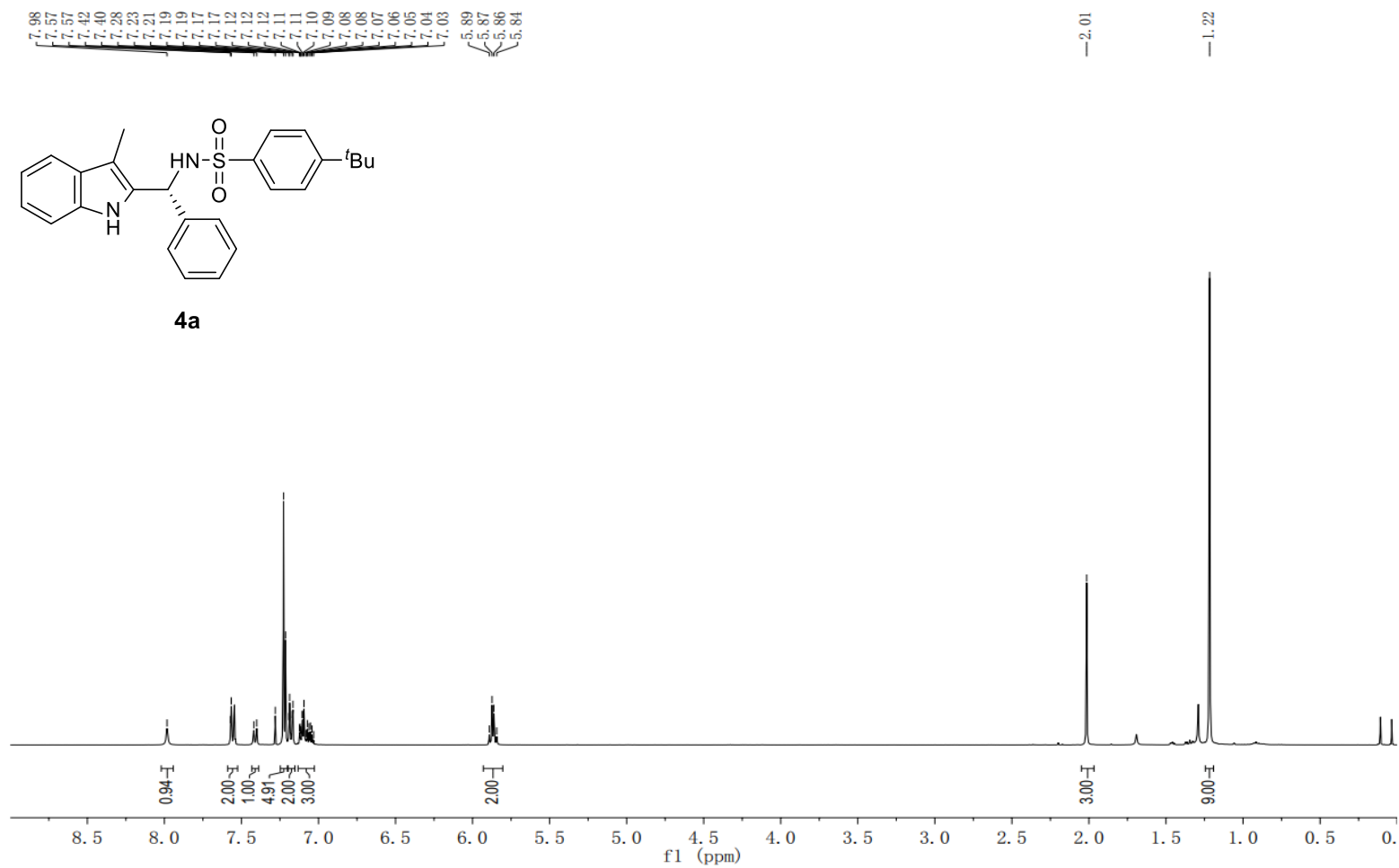
Syntheses of 3-Substituted Indole Substrates

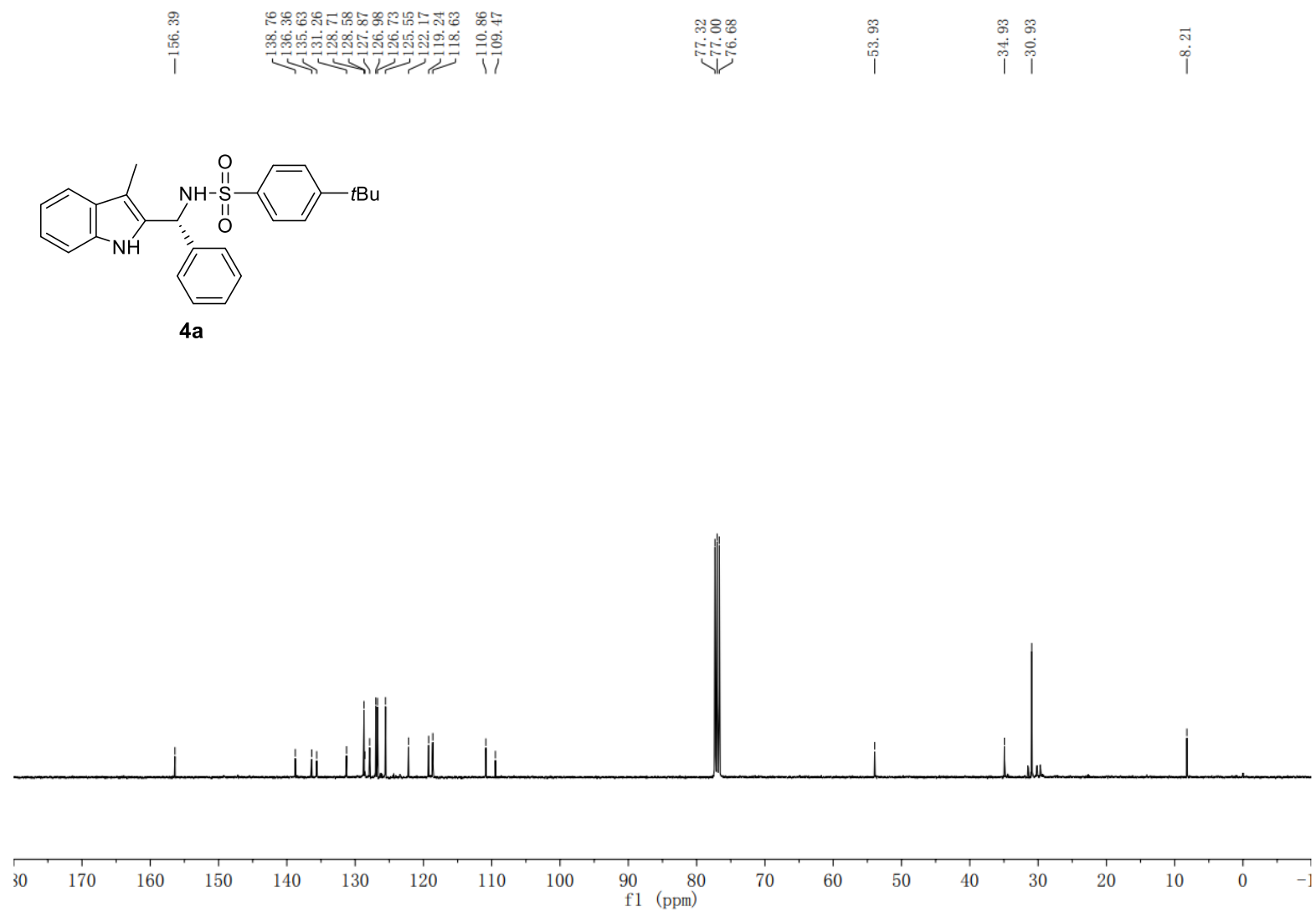
3-methyl indole was purchased, other 3-substituted indoles was prepared following literature procedure.¹⁻⁴ Their characterization data were in accordance with those reported in the literature. Catalysts **1a-g** were prepared following literature procedure.⁵⁻⁶

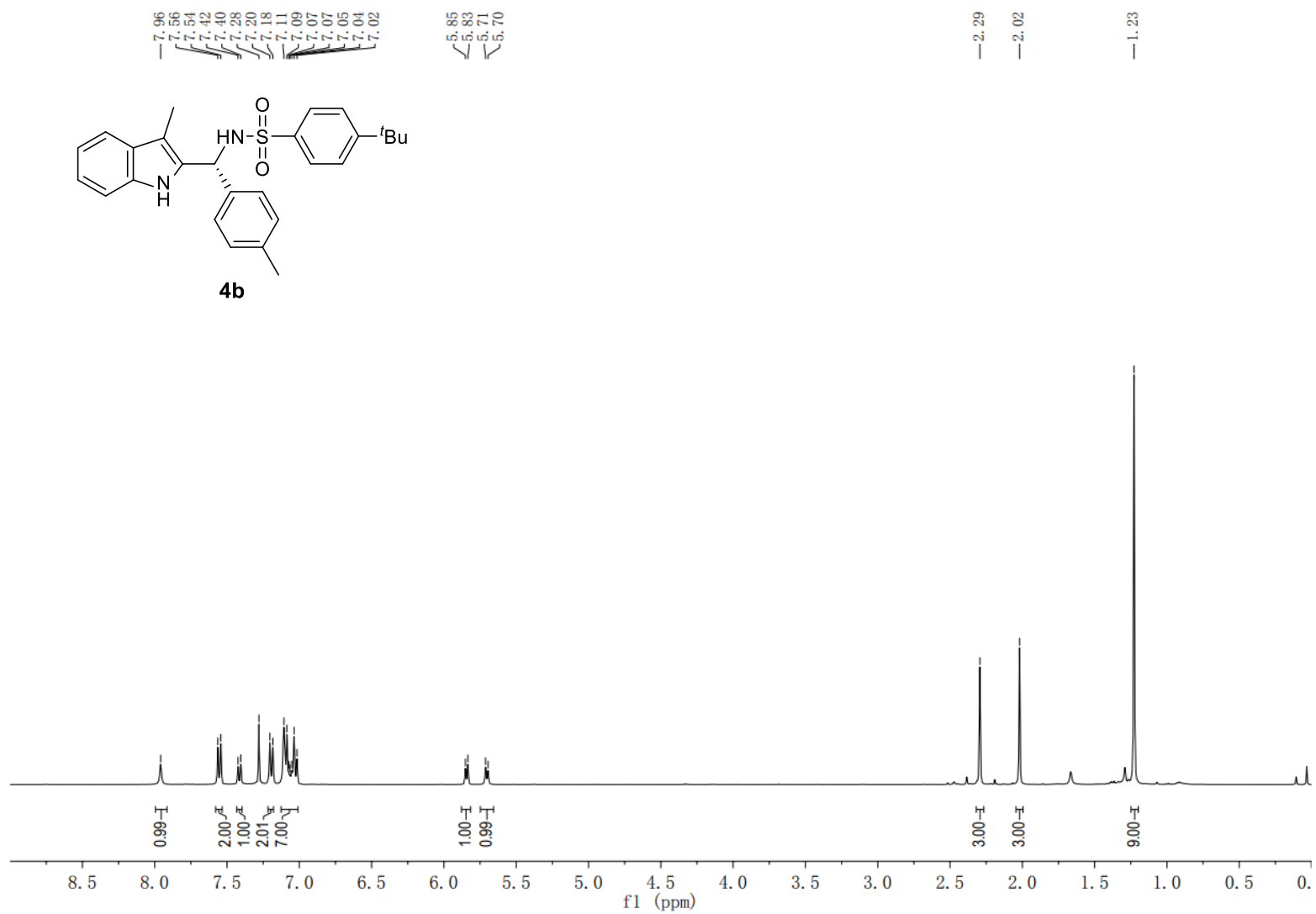
References

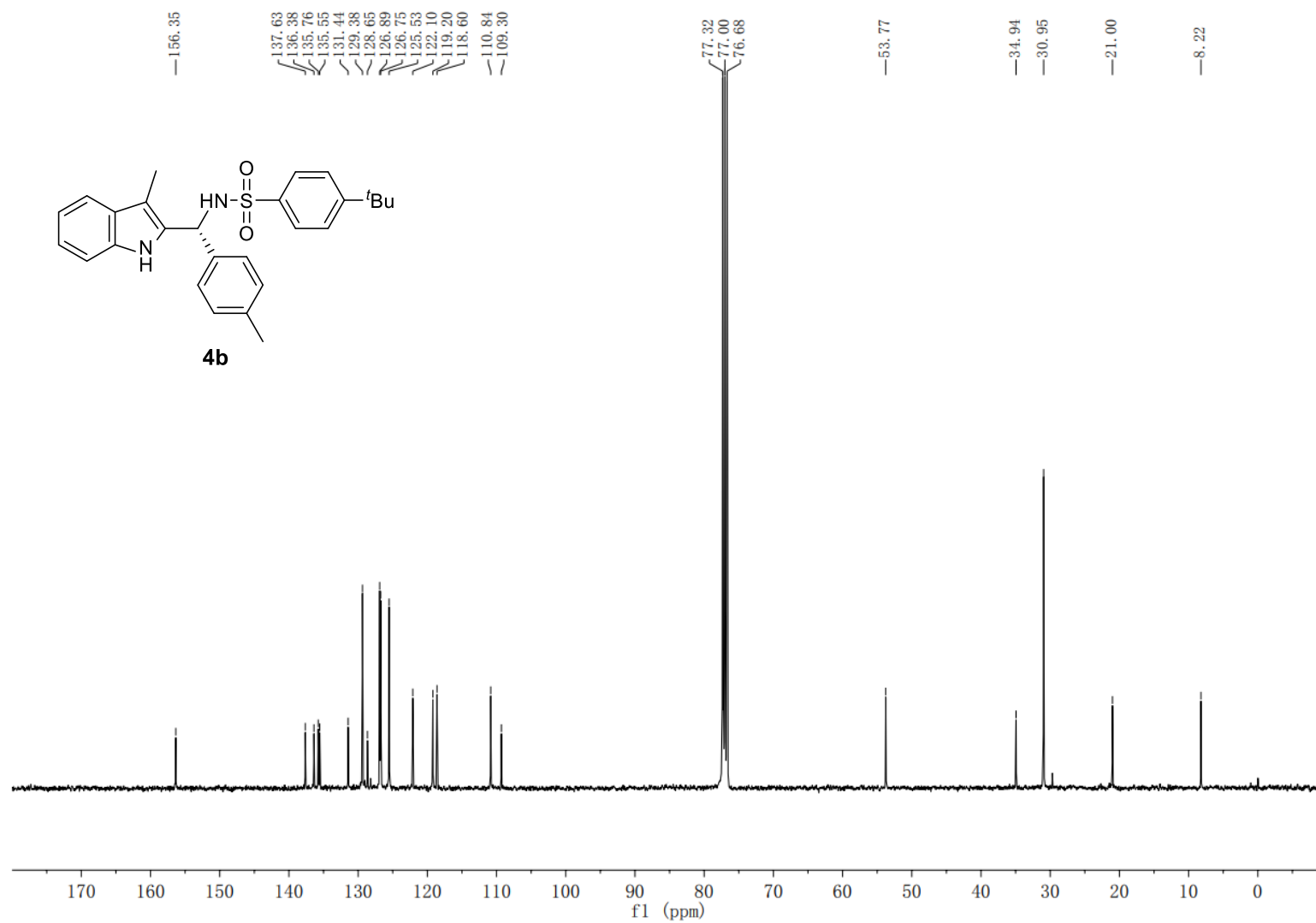
- (1) Y. -L. Hu, D. Fang, D.-S. Li, *Catal. Lett.* 2016, **146**, 968-976.
- (2) C. -L. Song, X. Dong, C.-W. Chiang, A.-W. Lei, *ACS. Catal.* 2018, **8**, 2195-2199.
- (3) M. S. P. Correia, C. Ballet, H. Meistermann, L. P. Conway, D. Globisch, *Bioorg. Med. Chem.* 2019, **27**, 955-962.
- (4) Z.-H. Zhang, V. Smal, P. Retailleau, A. Voituriez, G. Frison, A. Marinetti, X. Guinchard, *J. Am. Chem. Soc.* 2020, **142**, 3797-3805.
- (5) H. He, L.-Y. Chen, W.-Y. Wong, W.-H. Chan, A. W. M. Lee, *Eur. J. Org. Chem.* 2010, 4181-4184.
- (6) L.-Y. Chen, H. He, W. H. Chan, A. W. M. Lee, *J. Org. Chem.* 2011, **76**, 7141-7147.

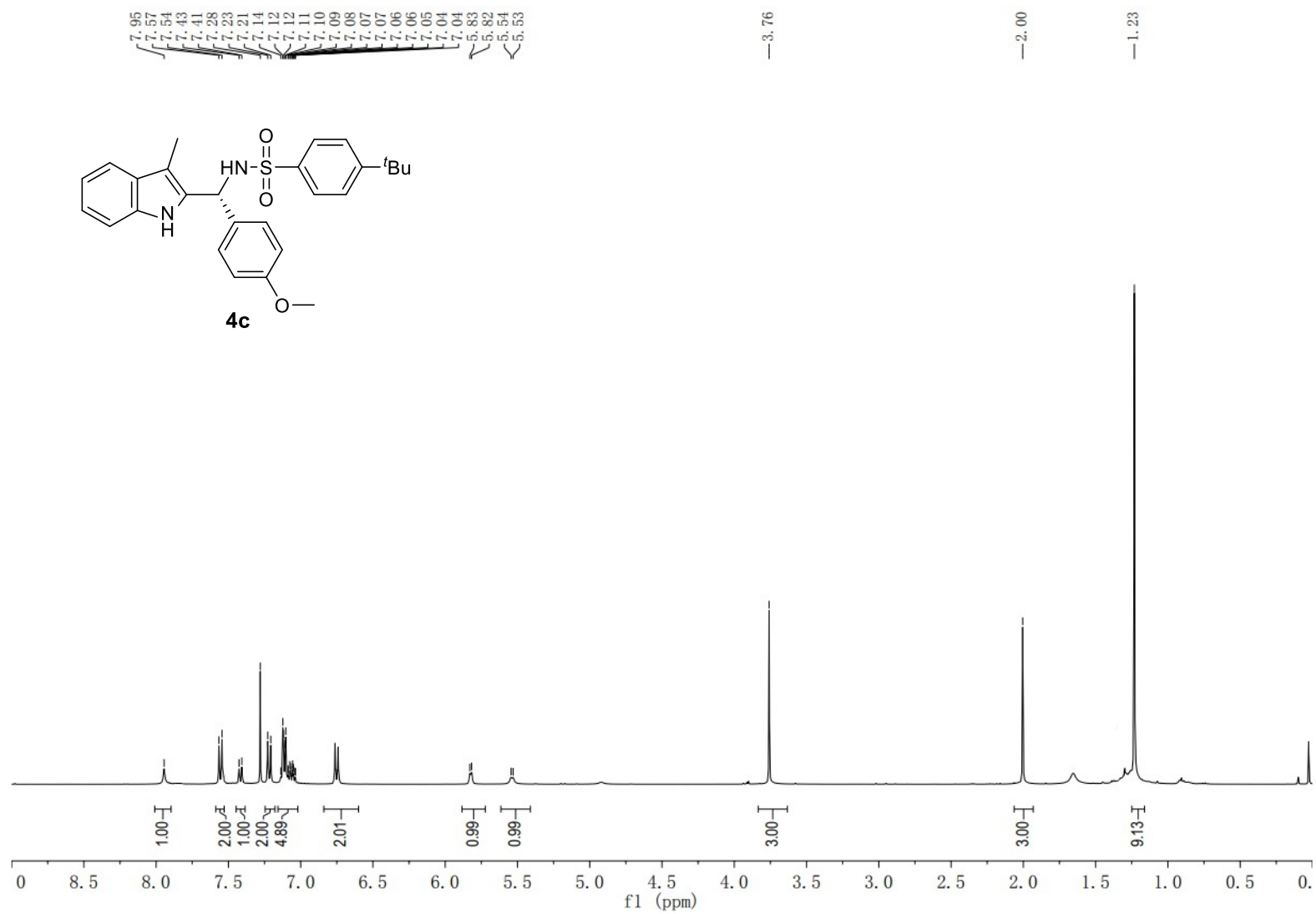
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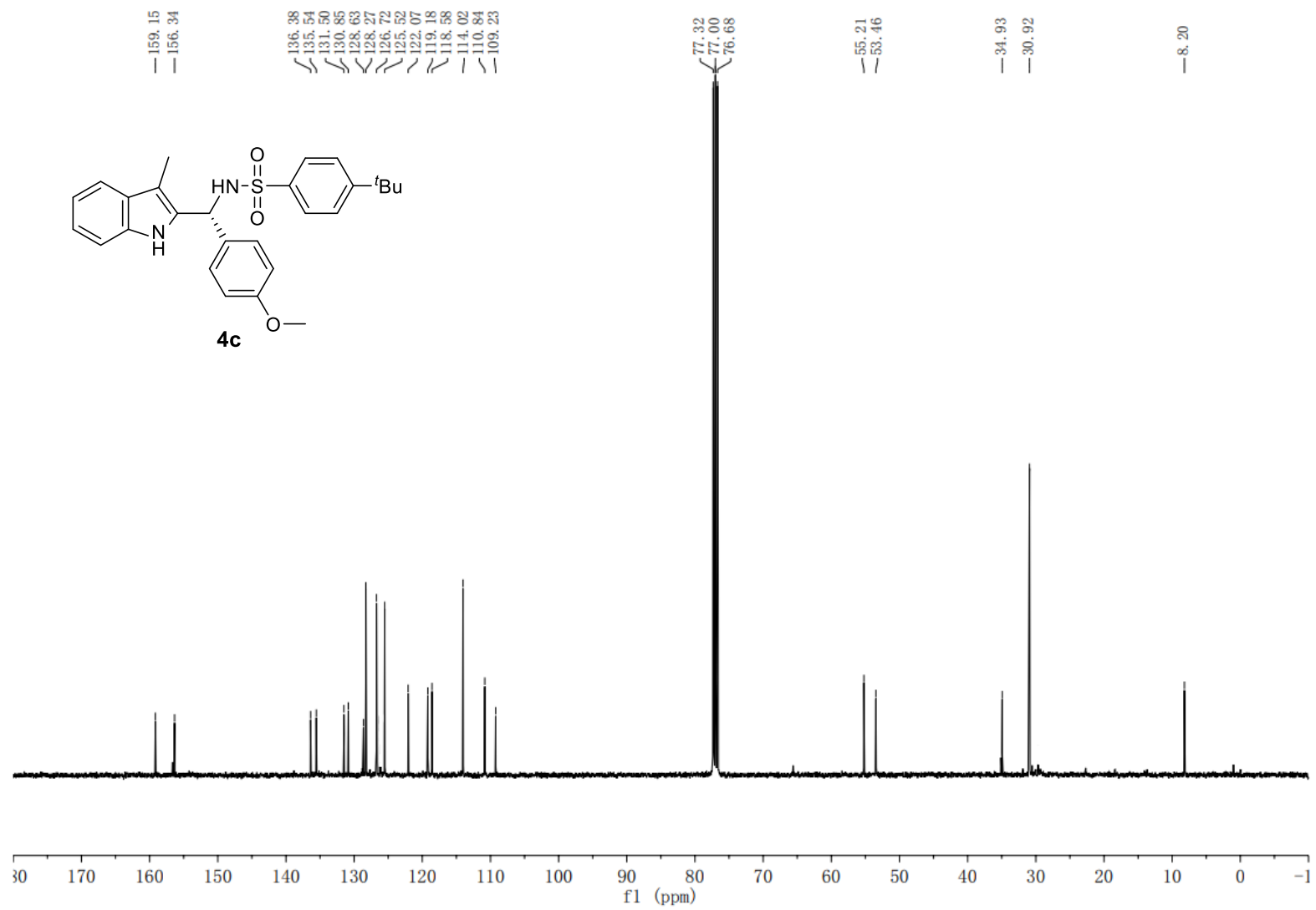


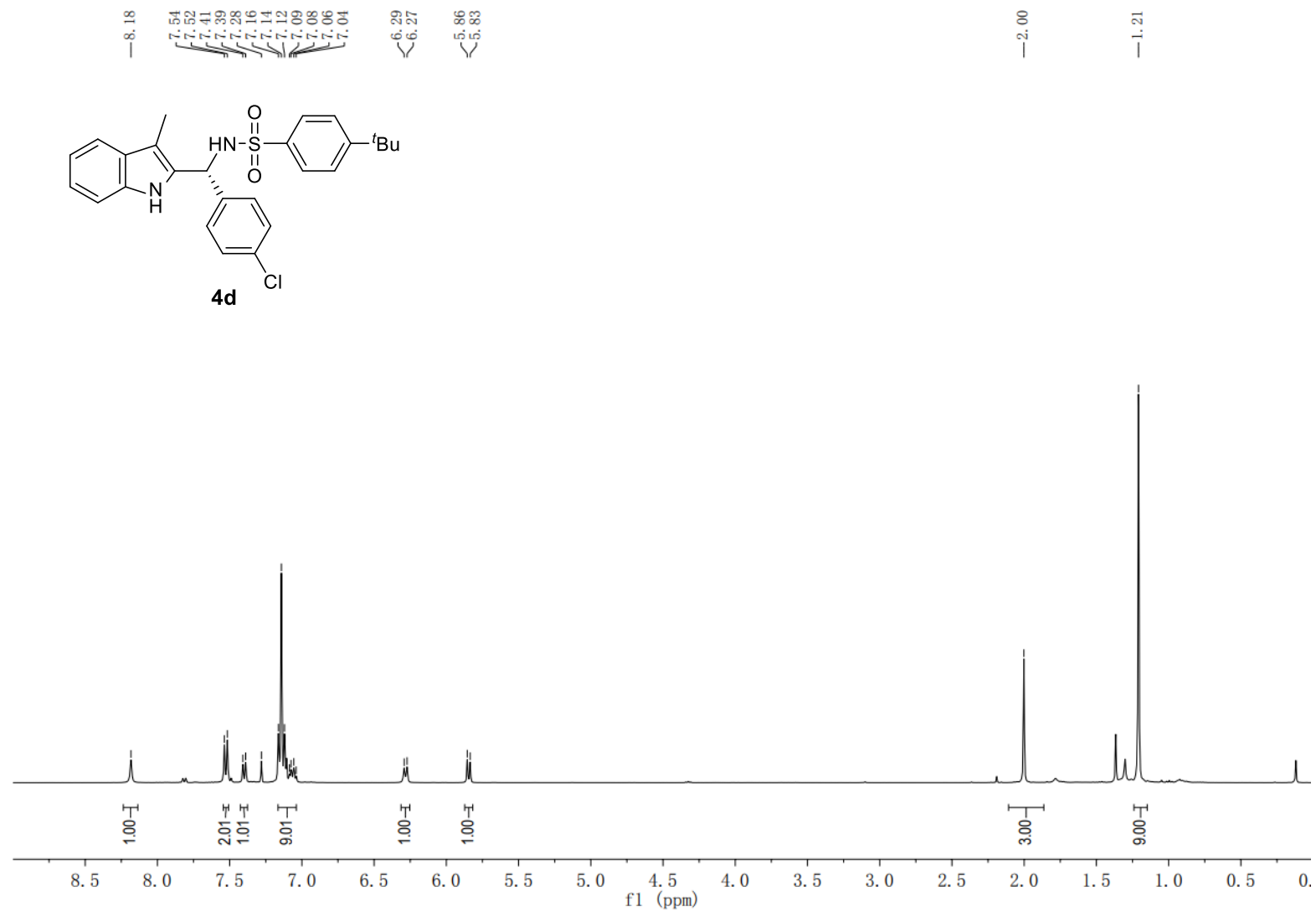


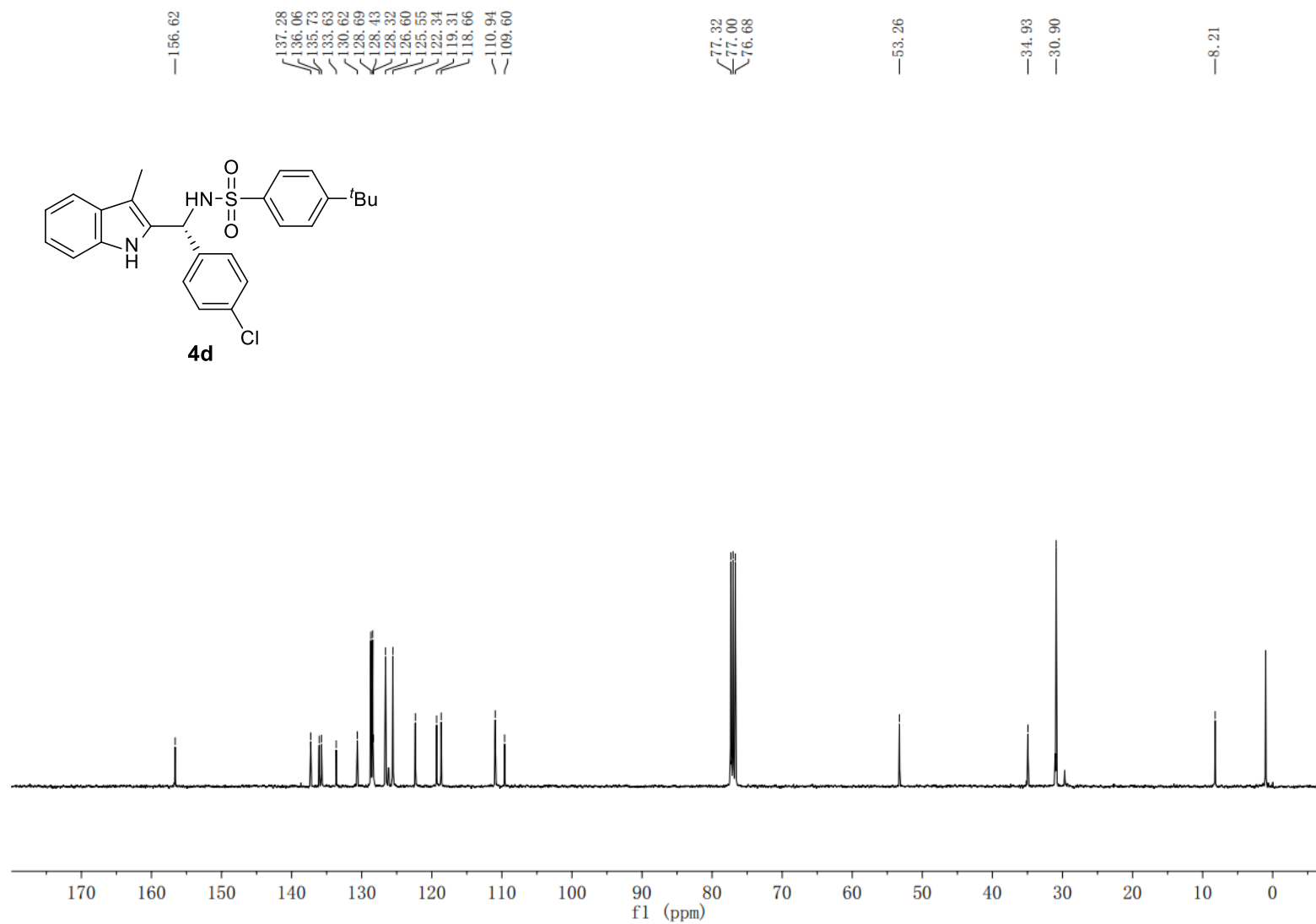


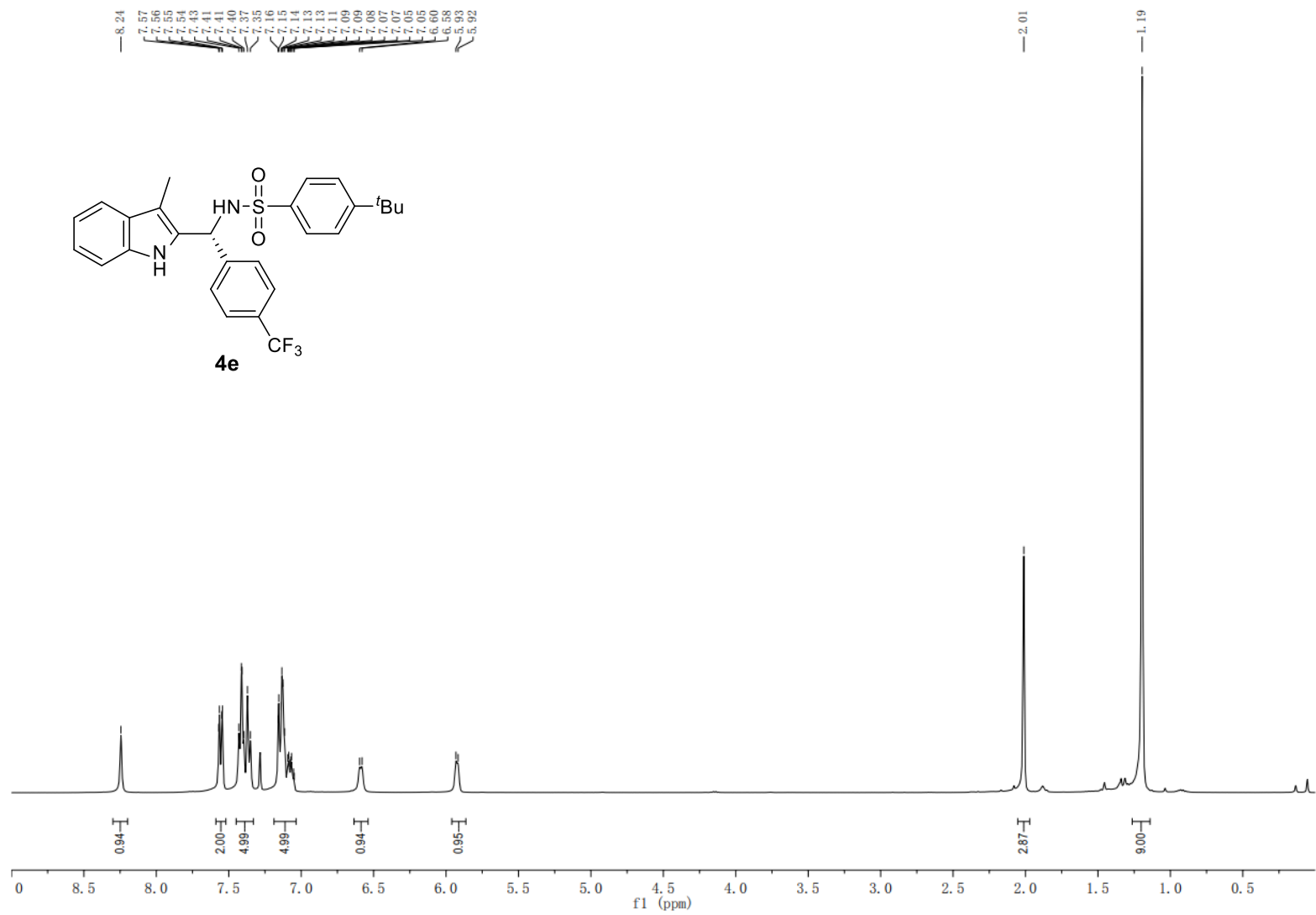


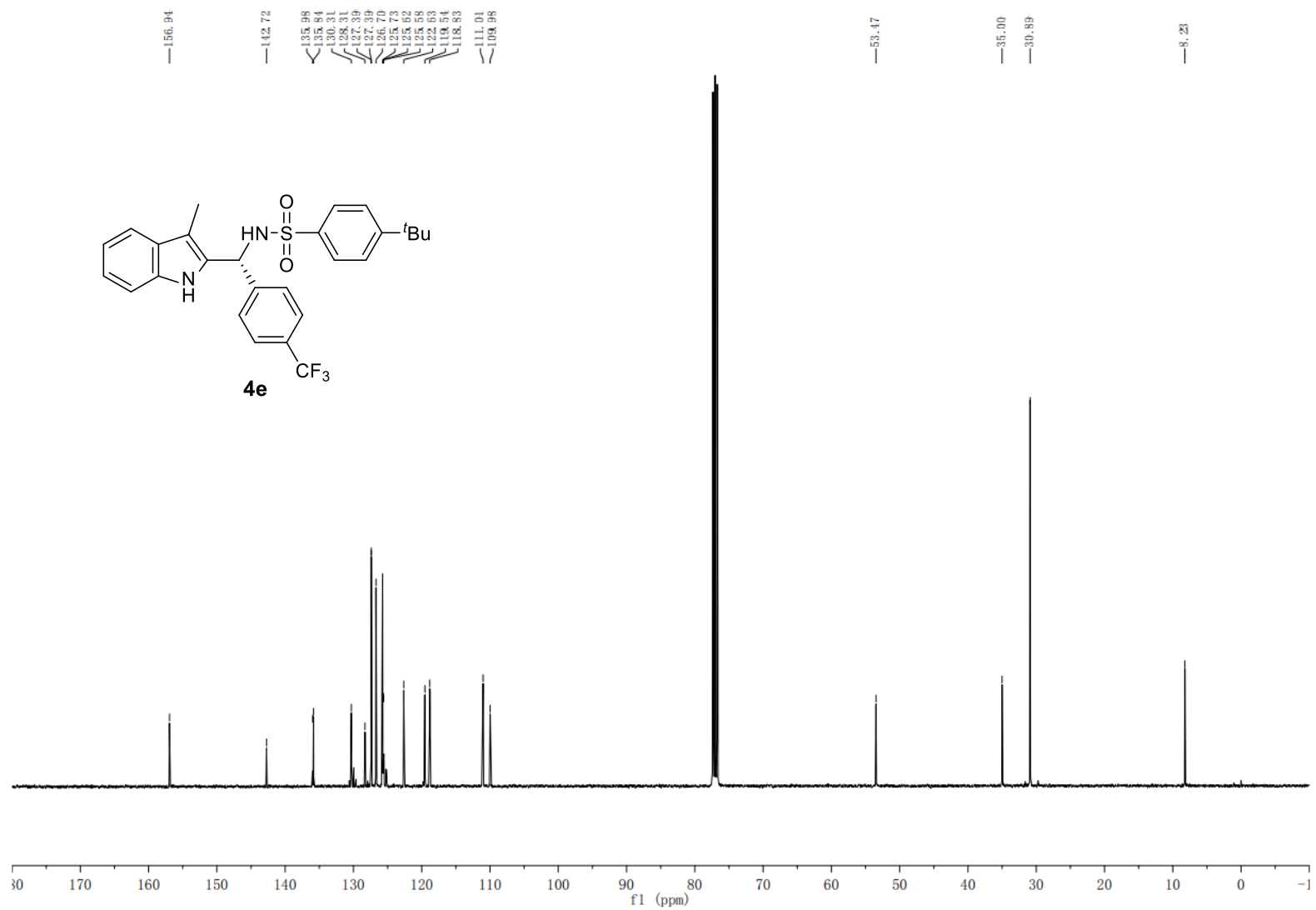


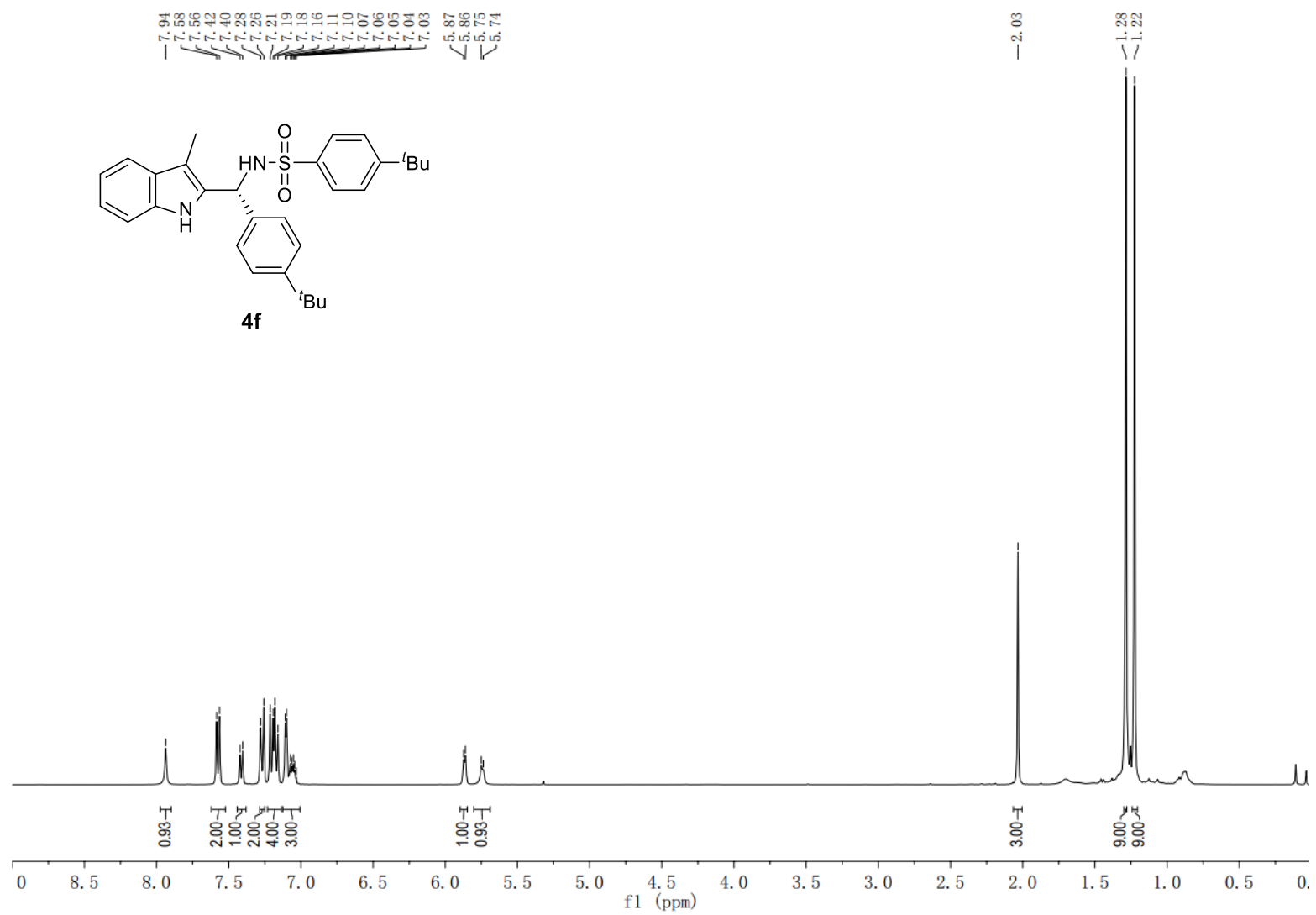


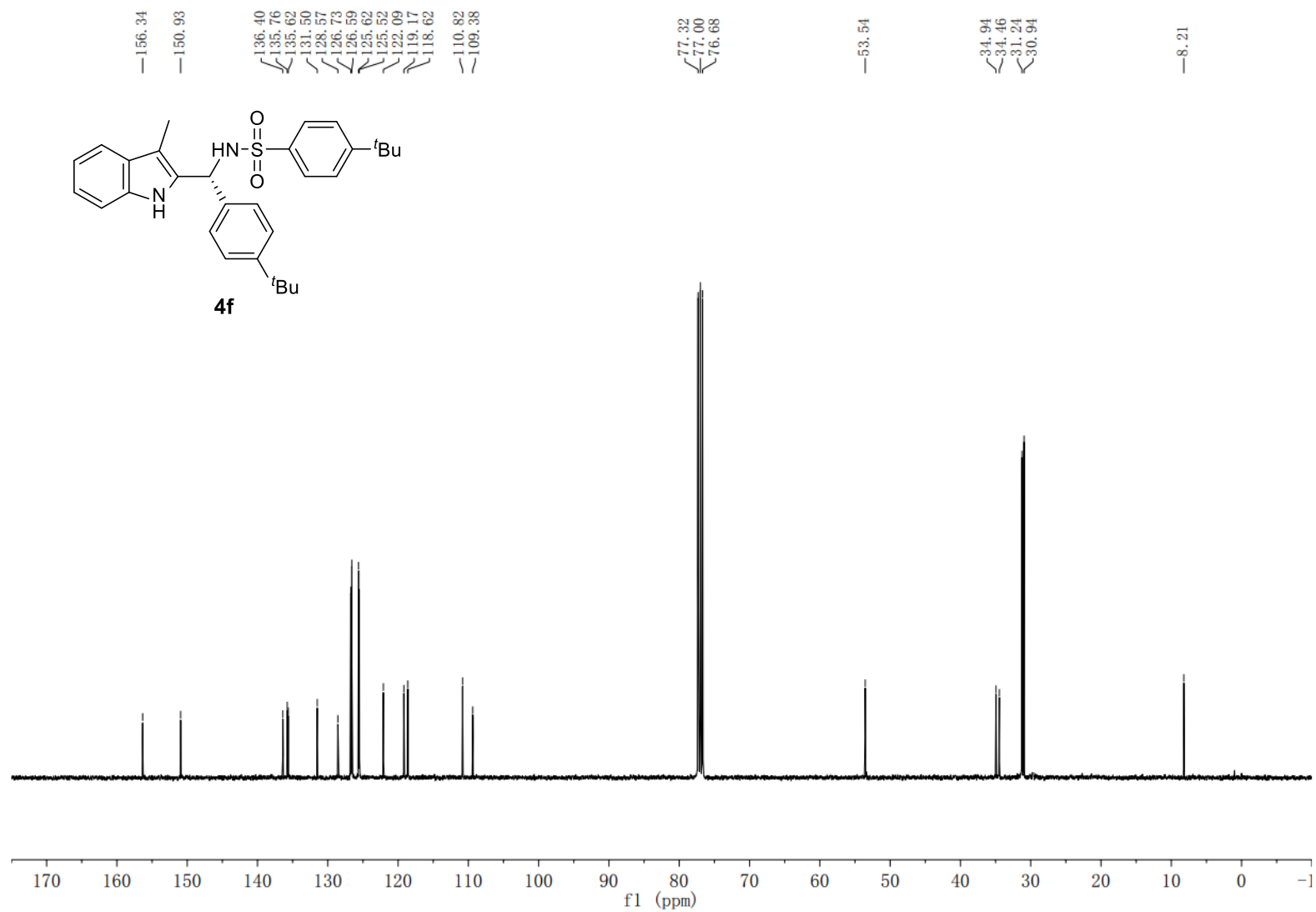


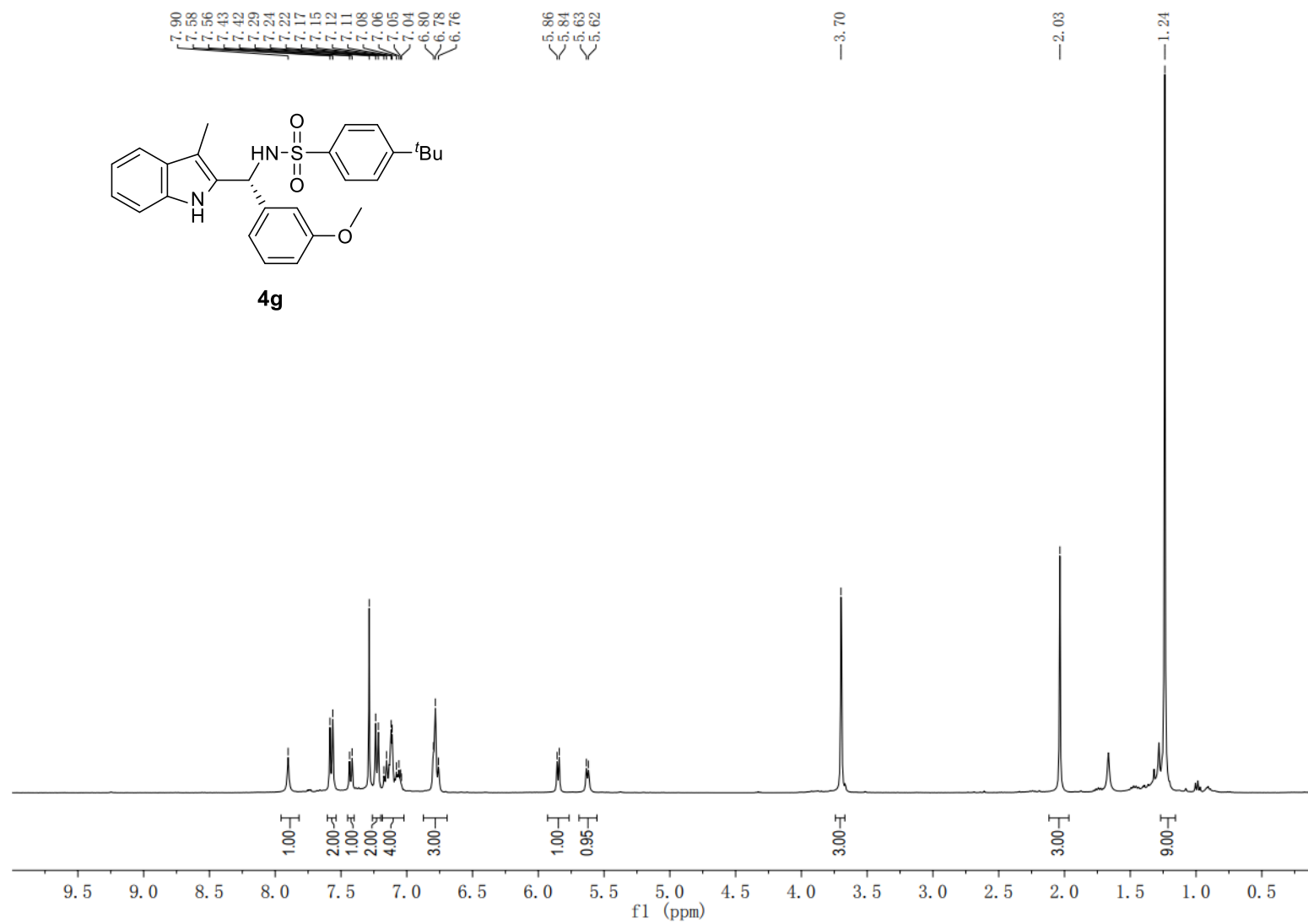


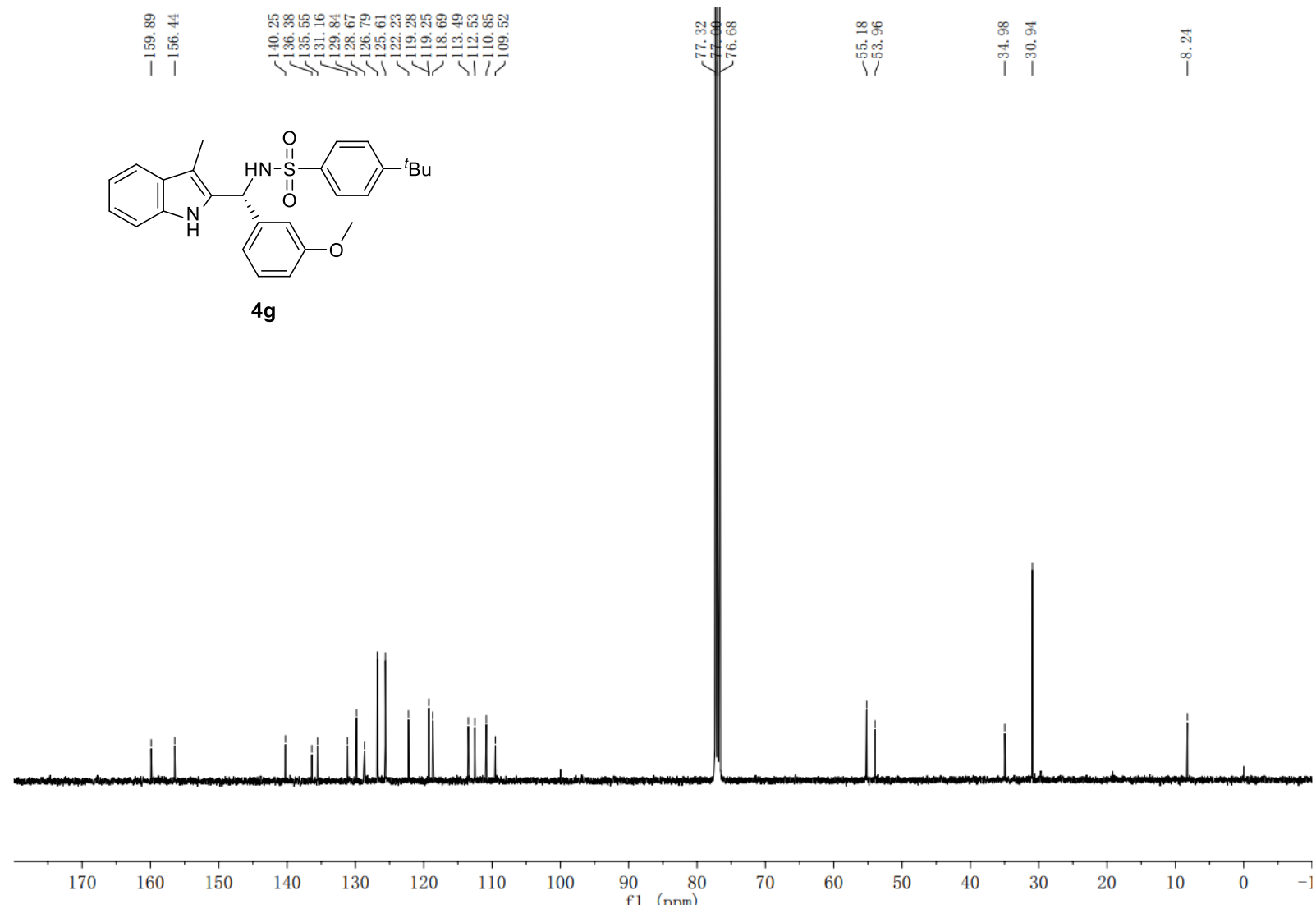


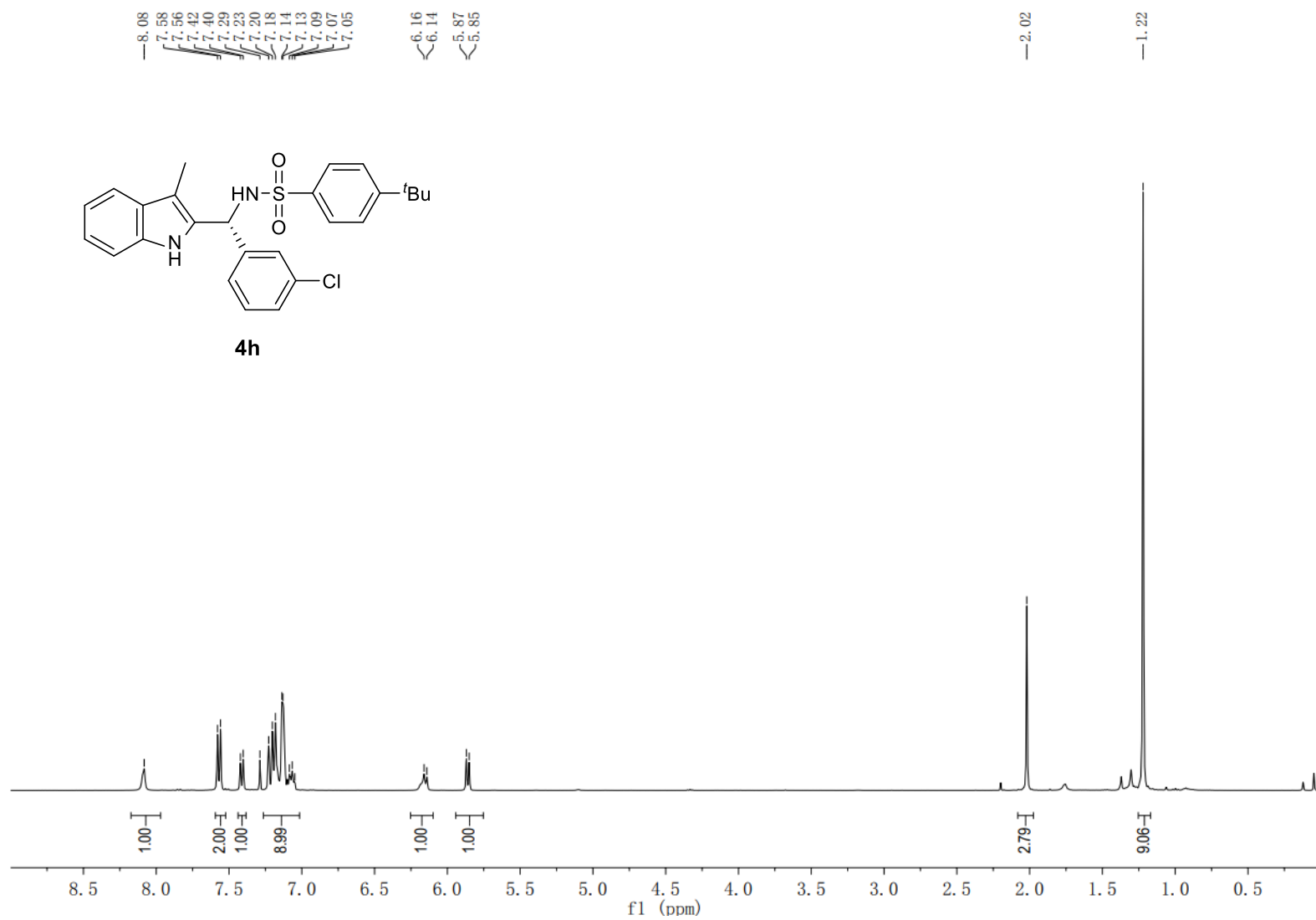


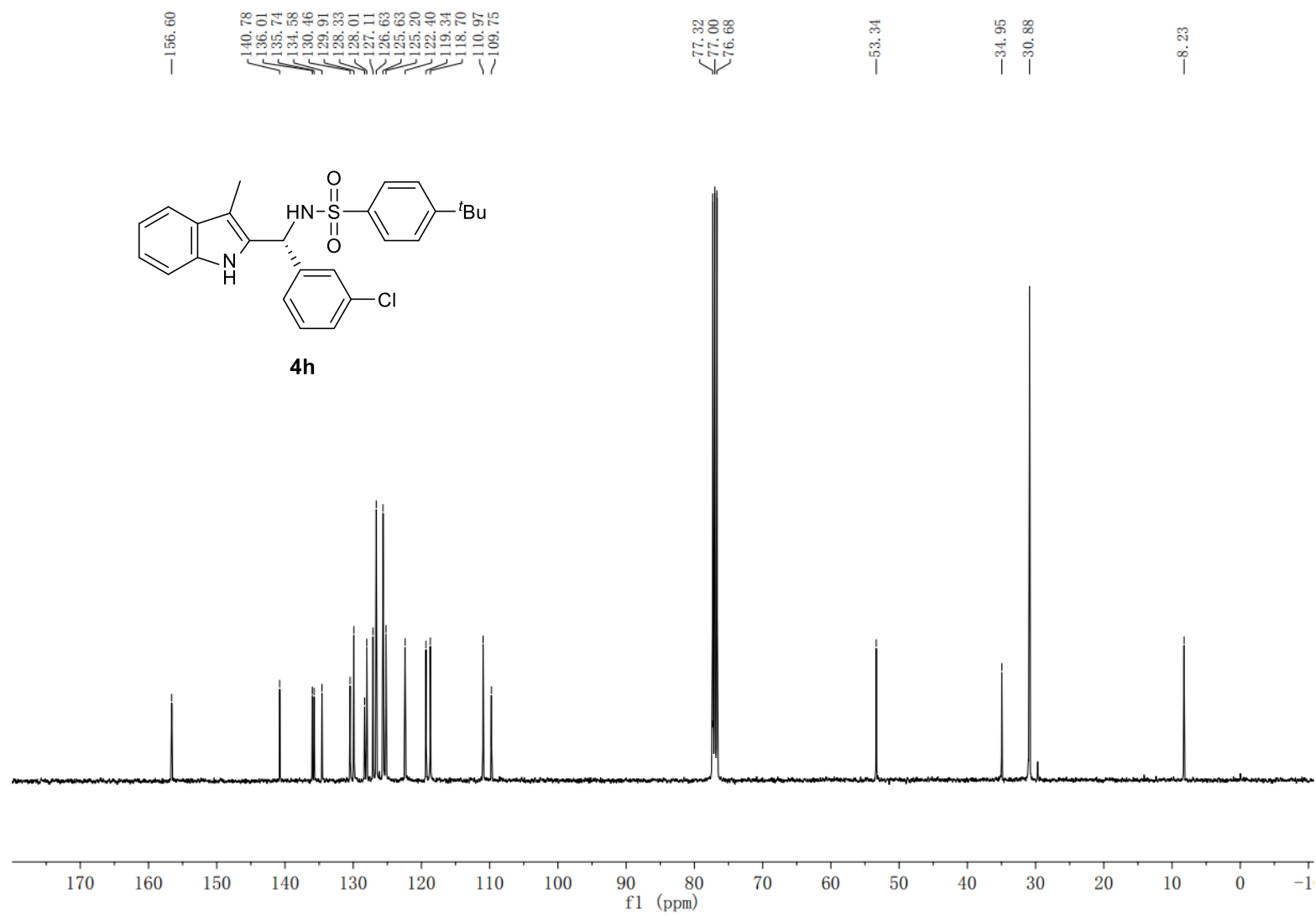


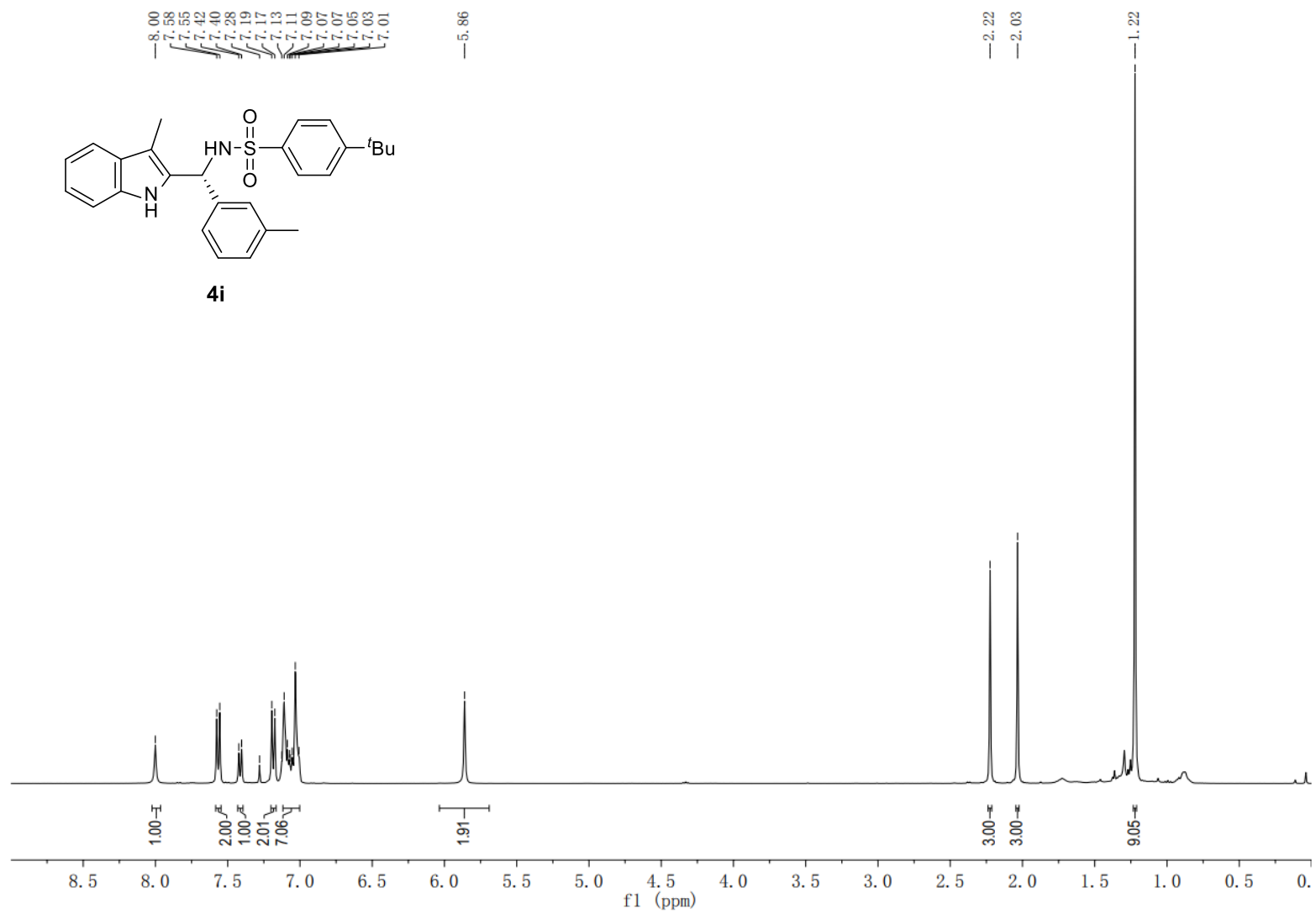


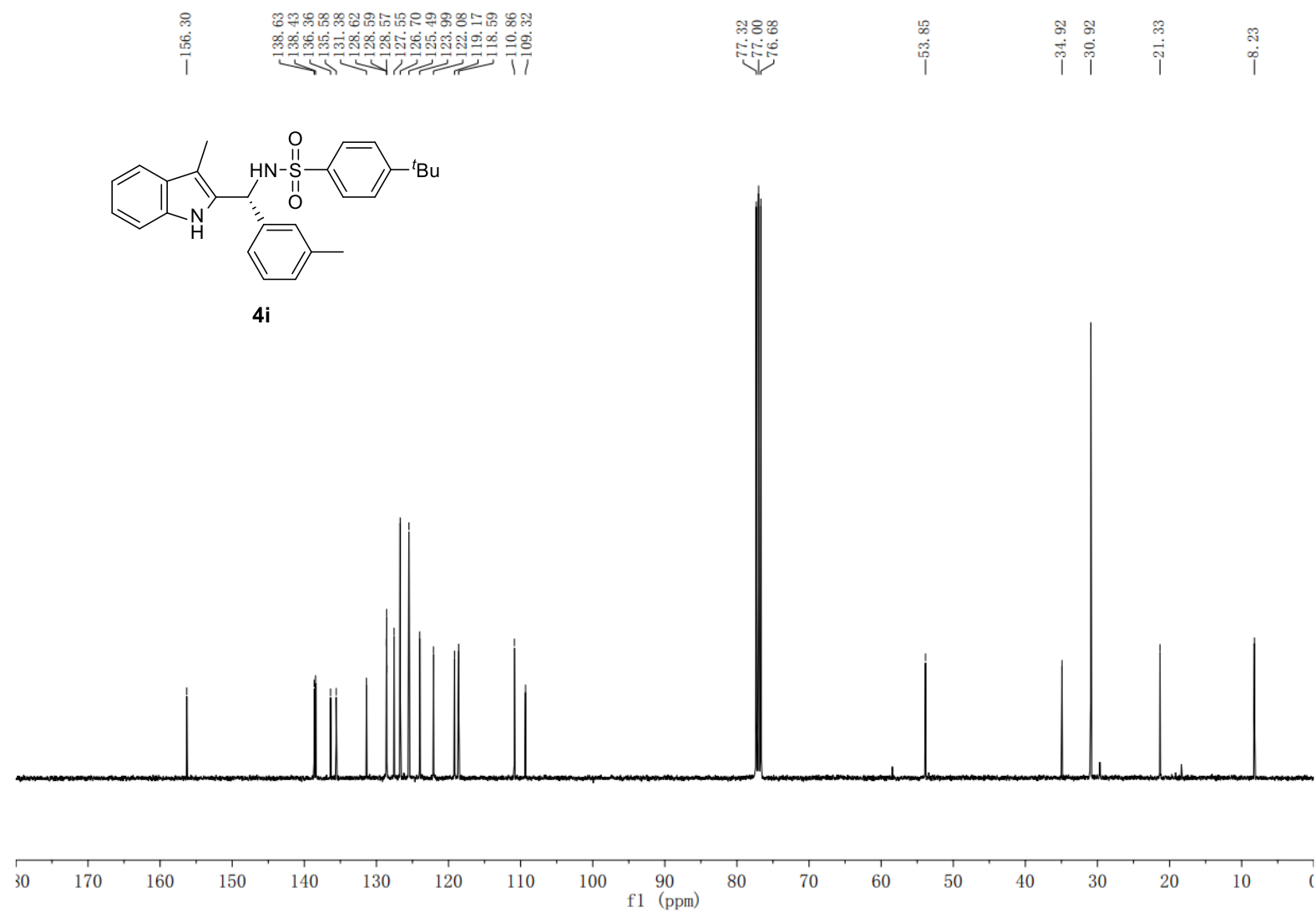


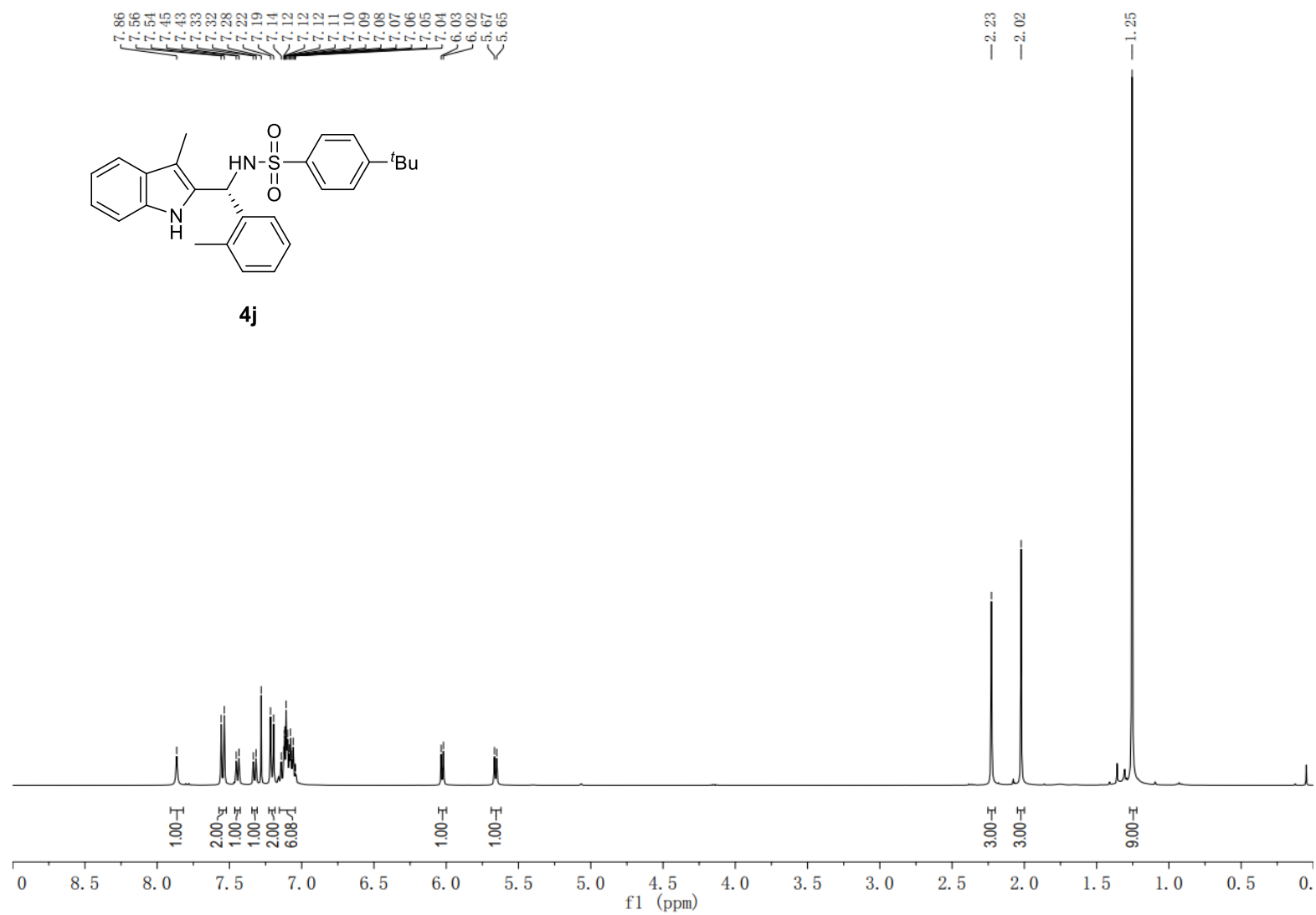


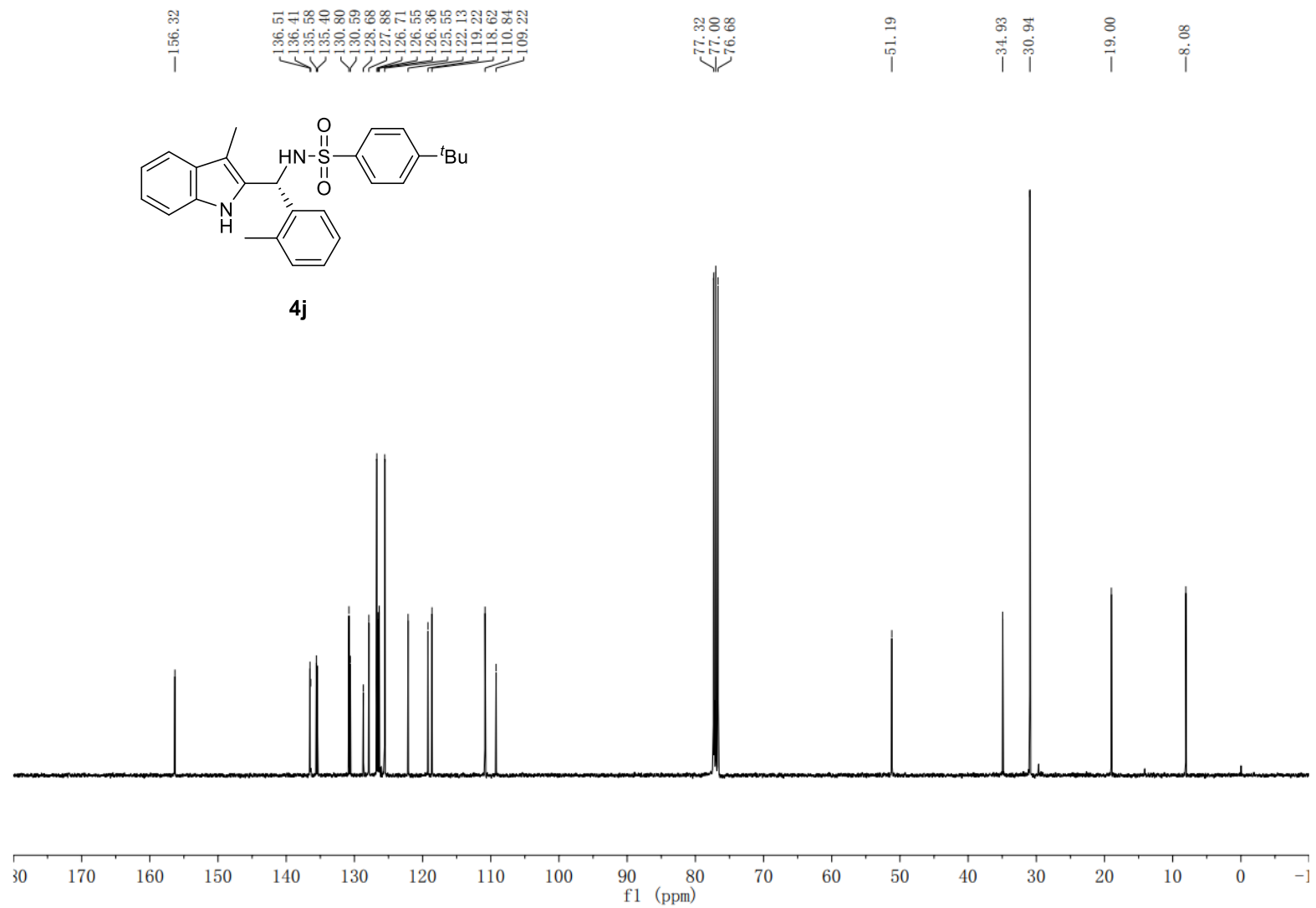


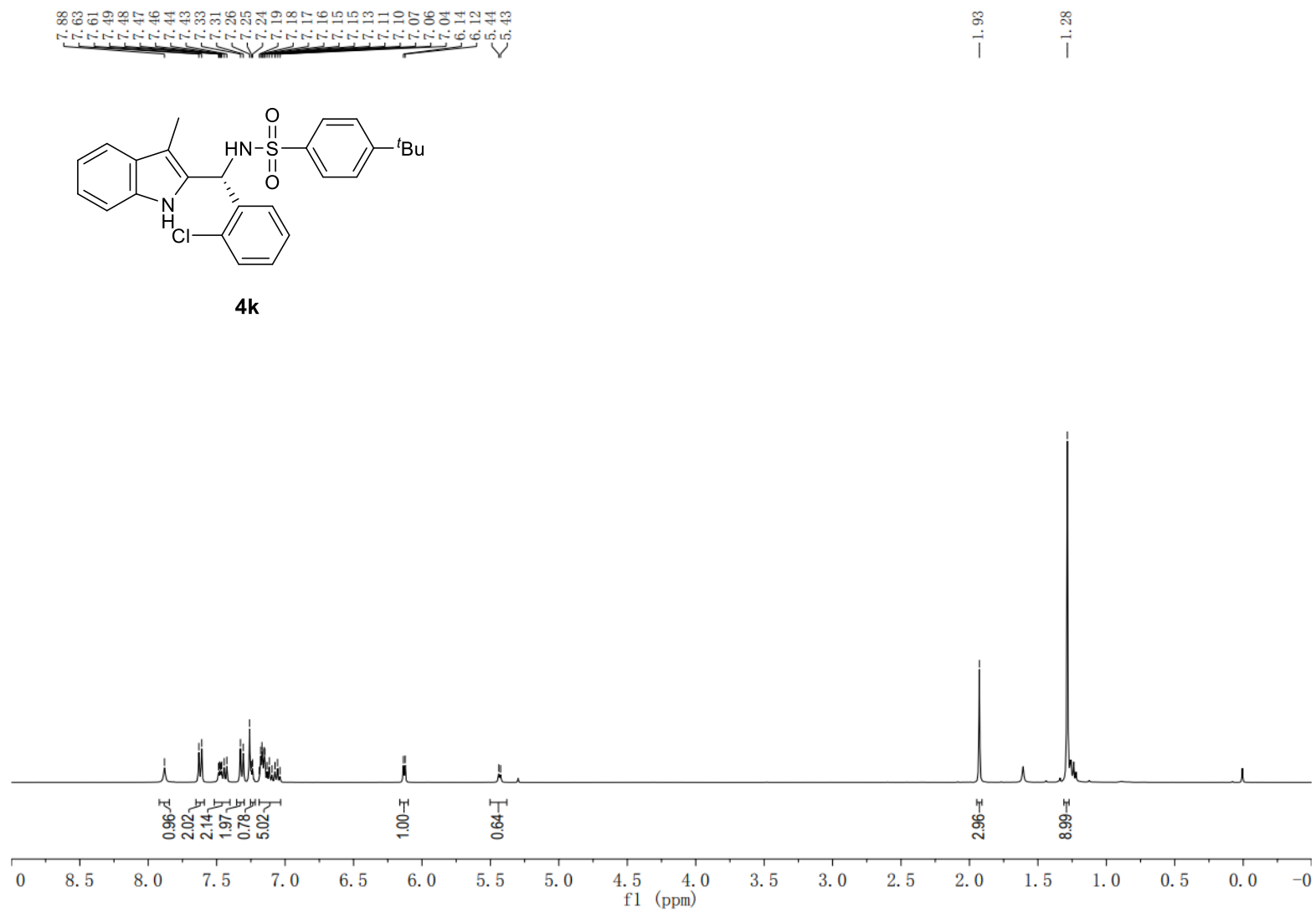


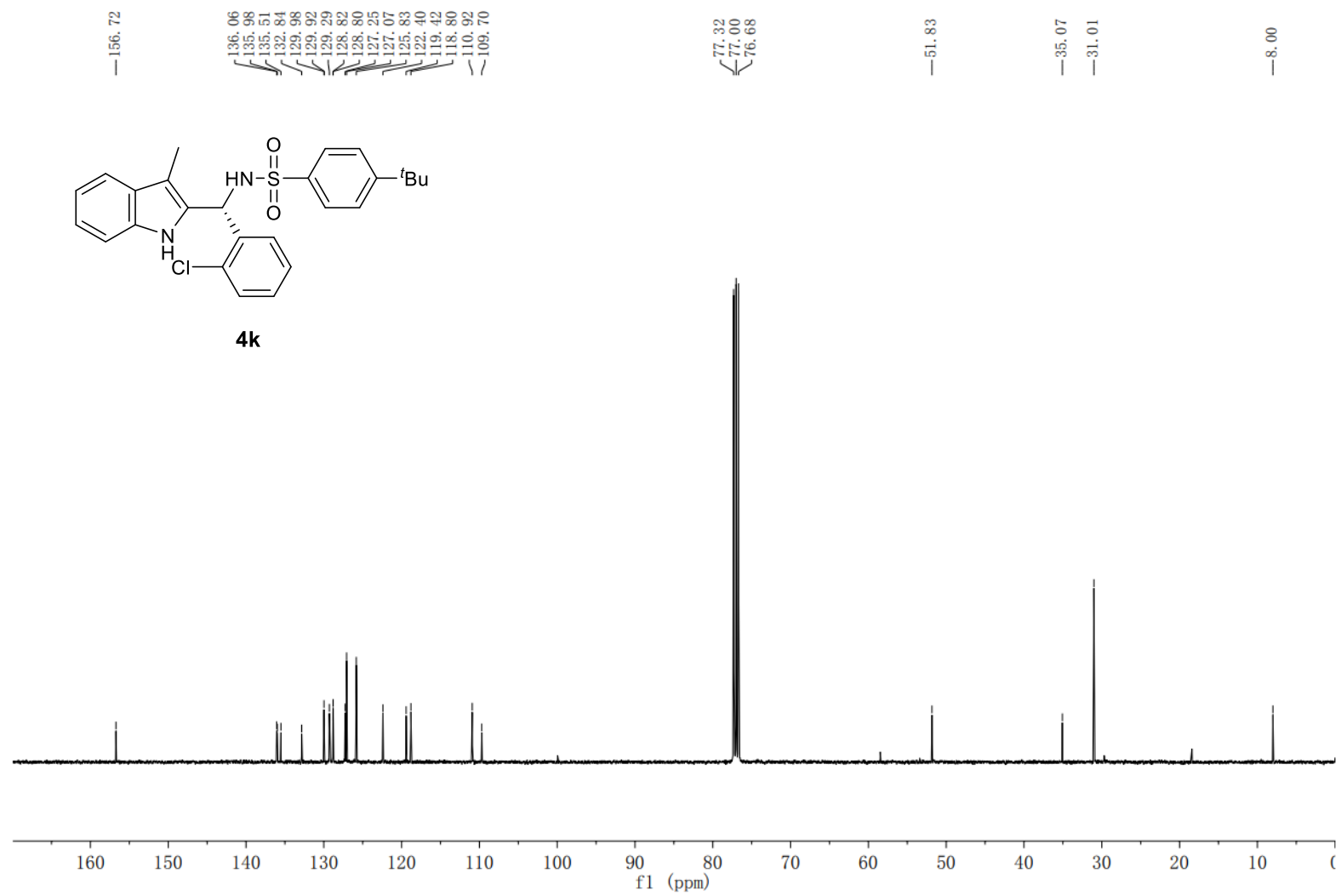


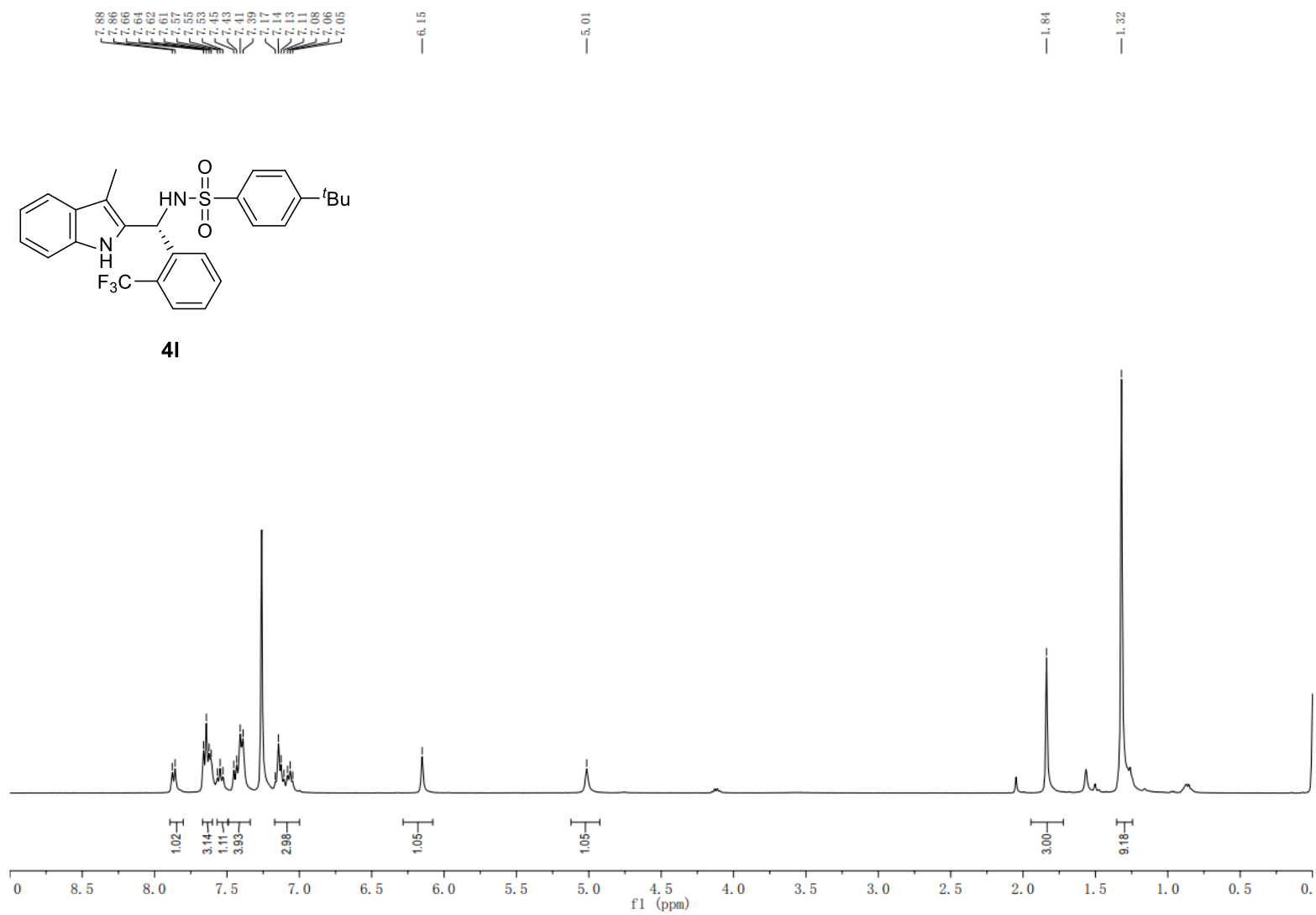


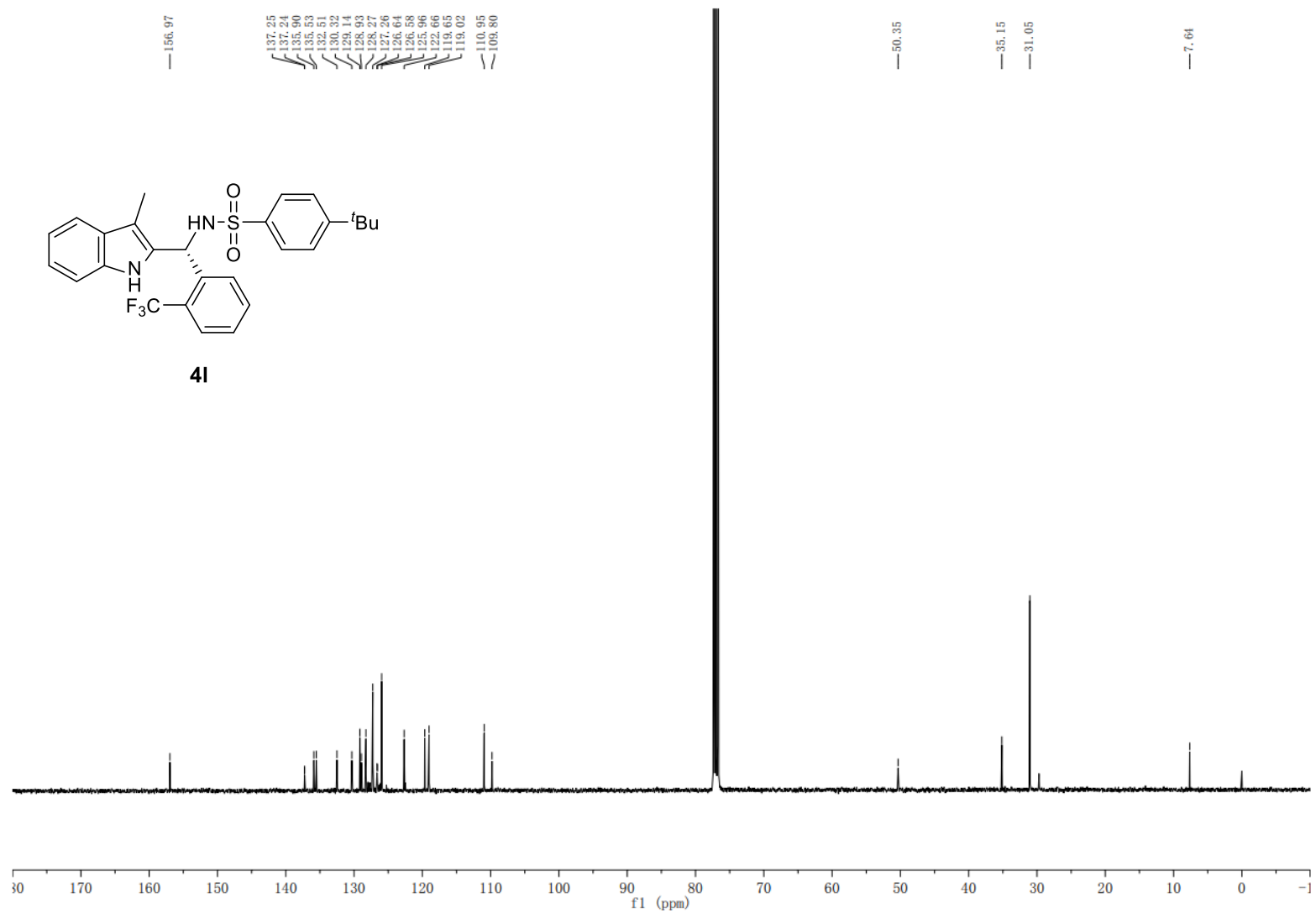


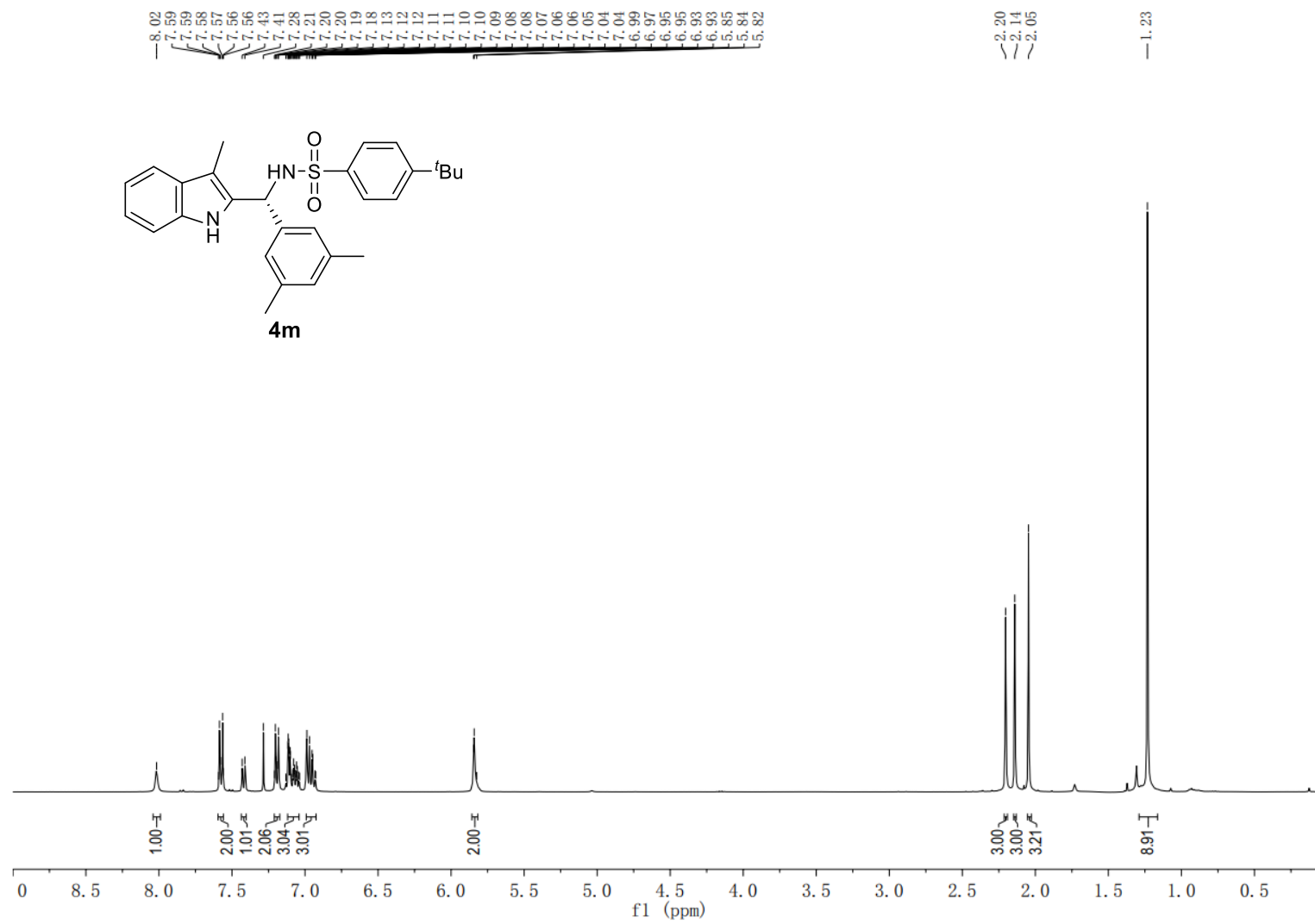


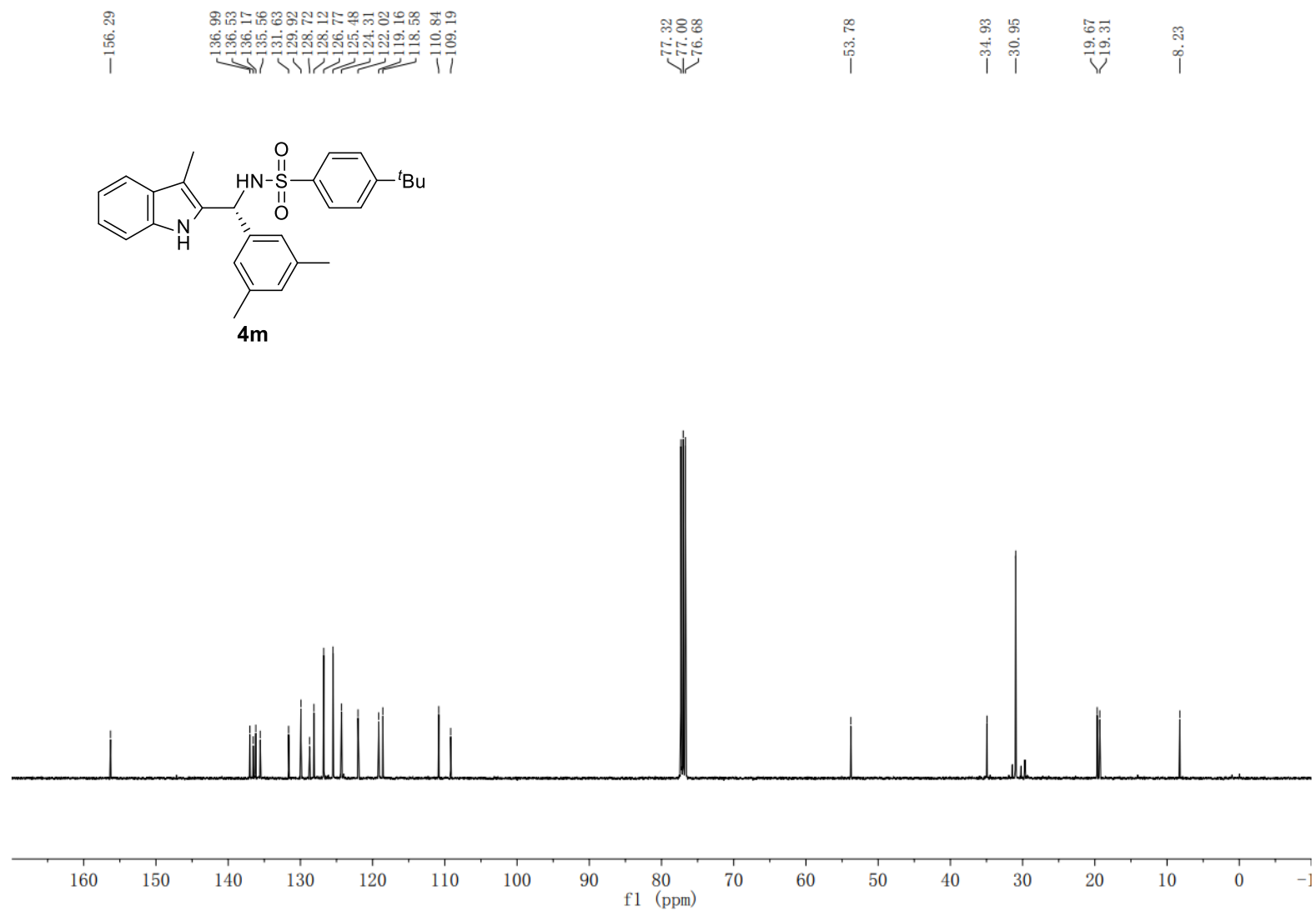


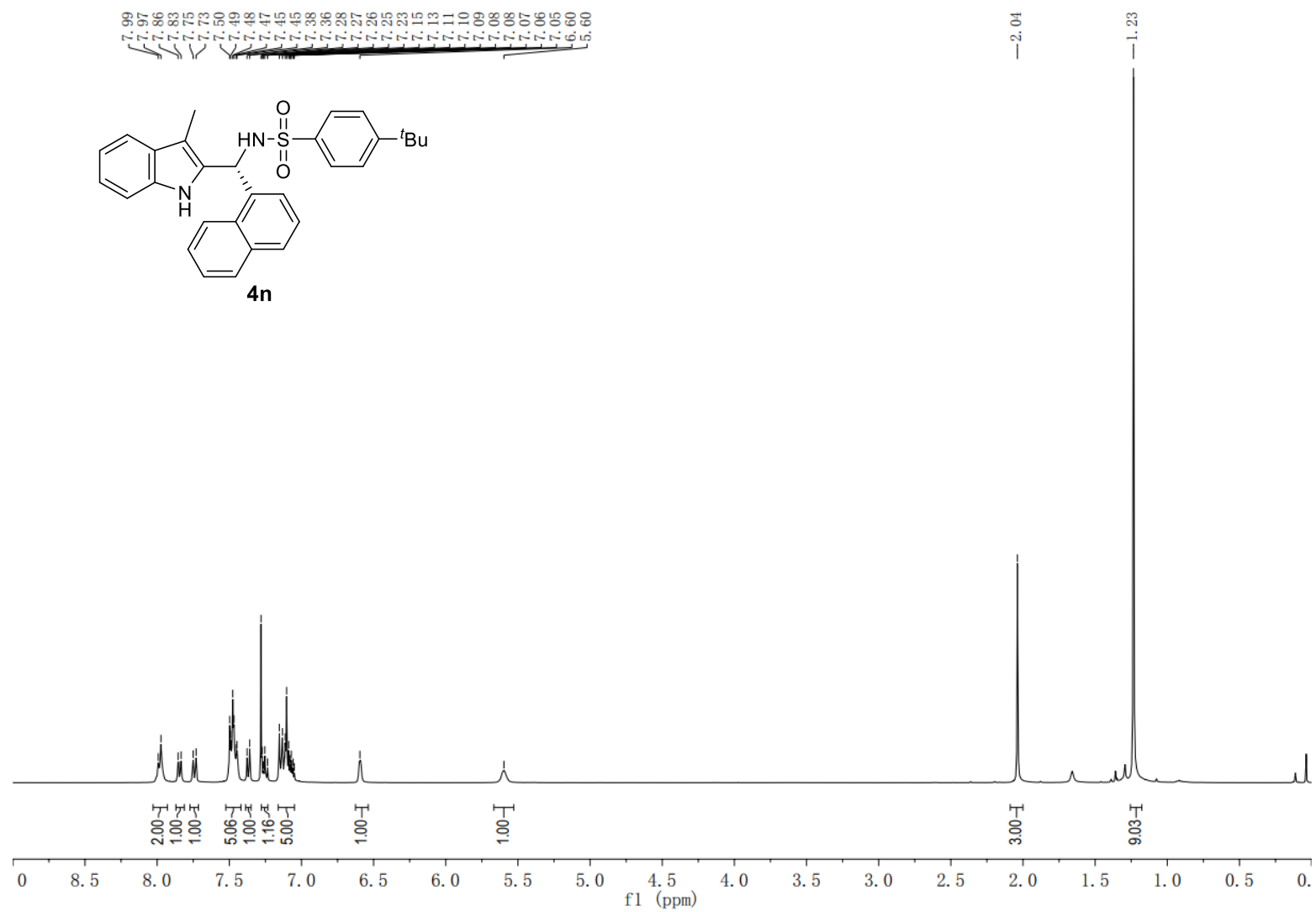


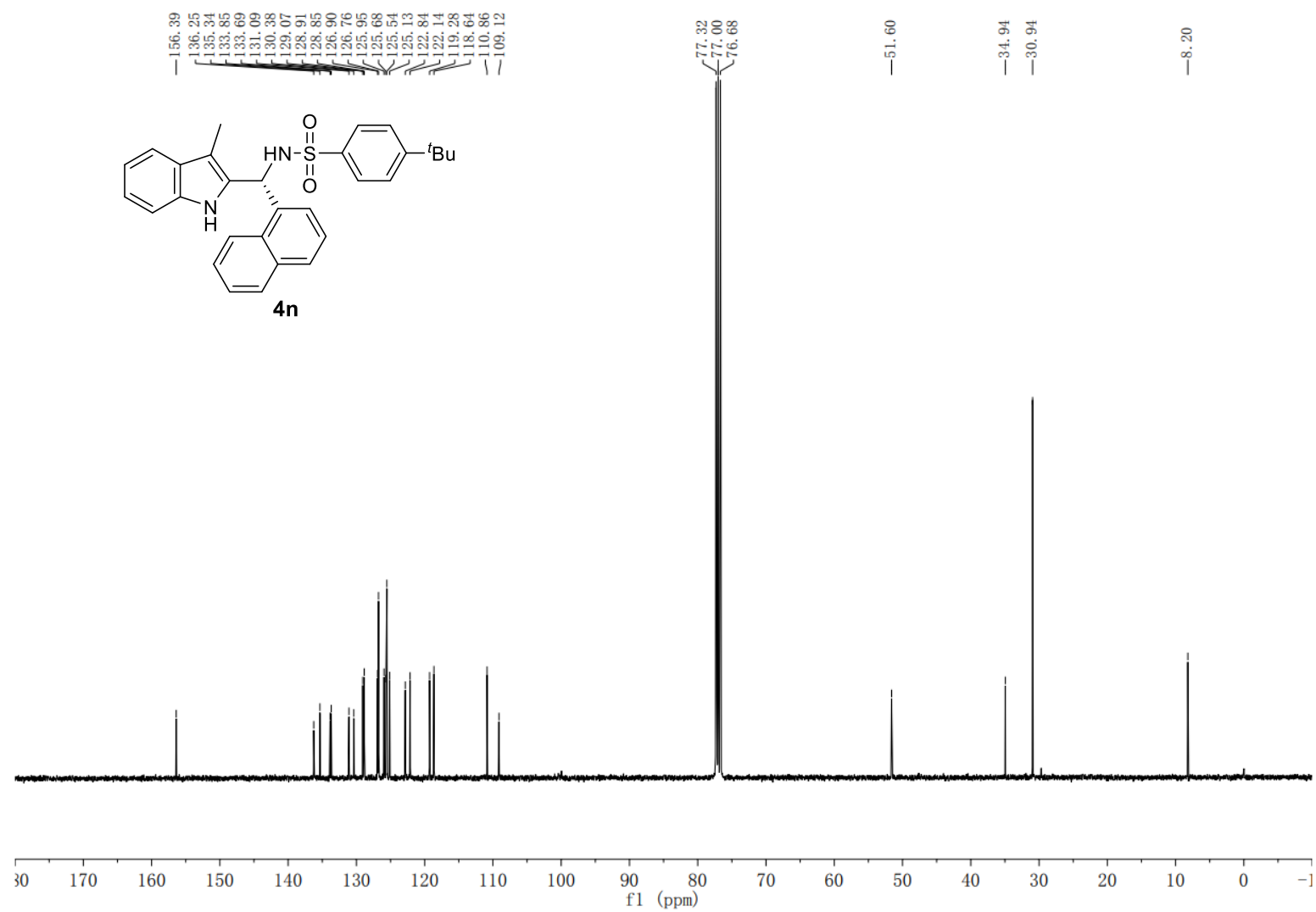


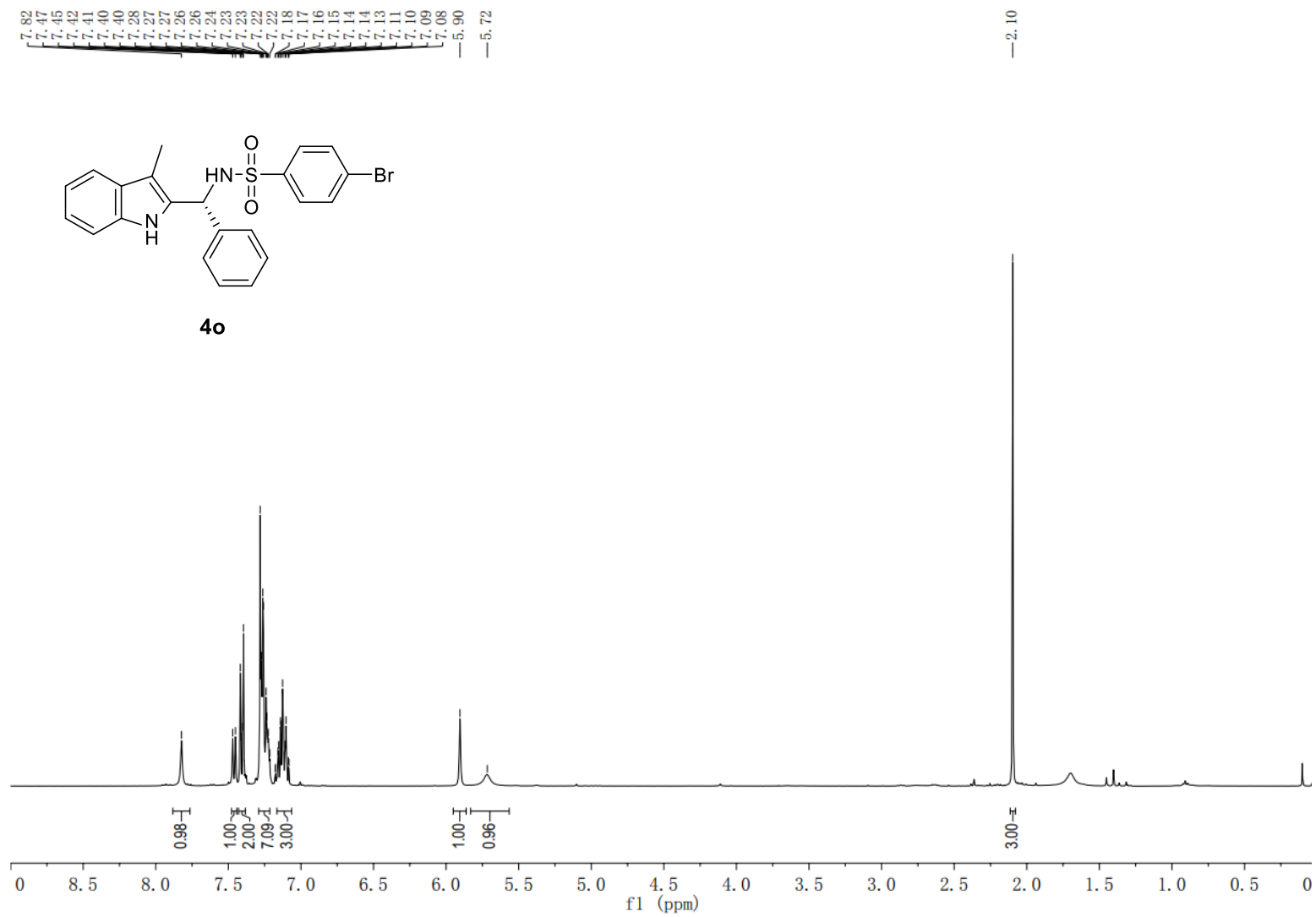


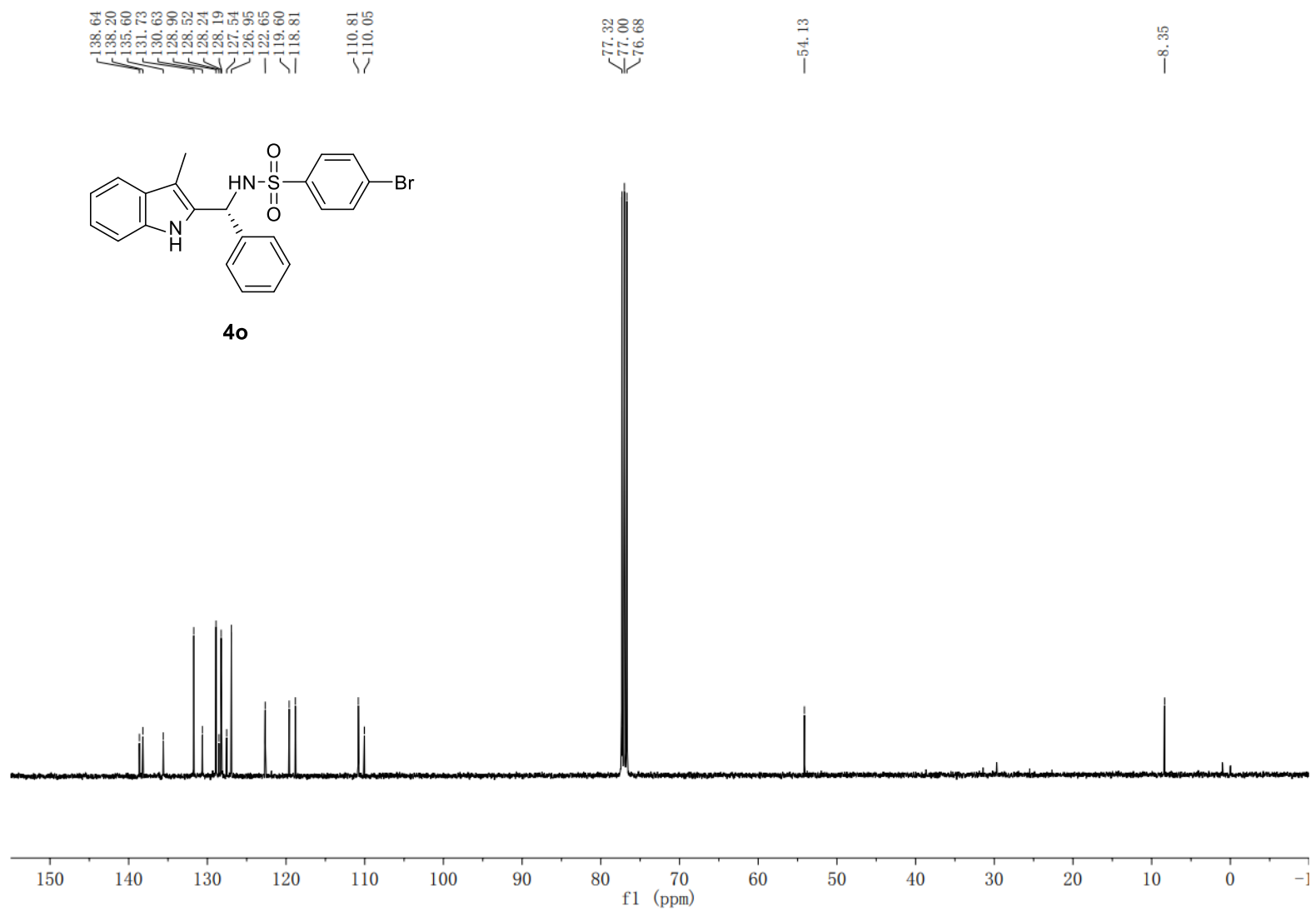


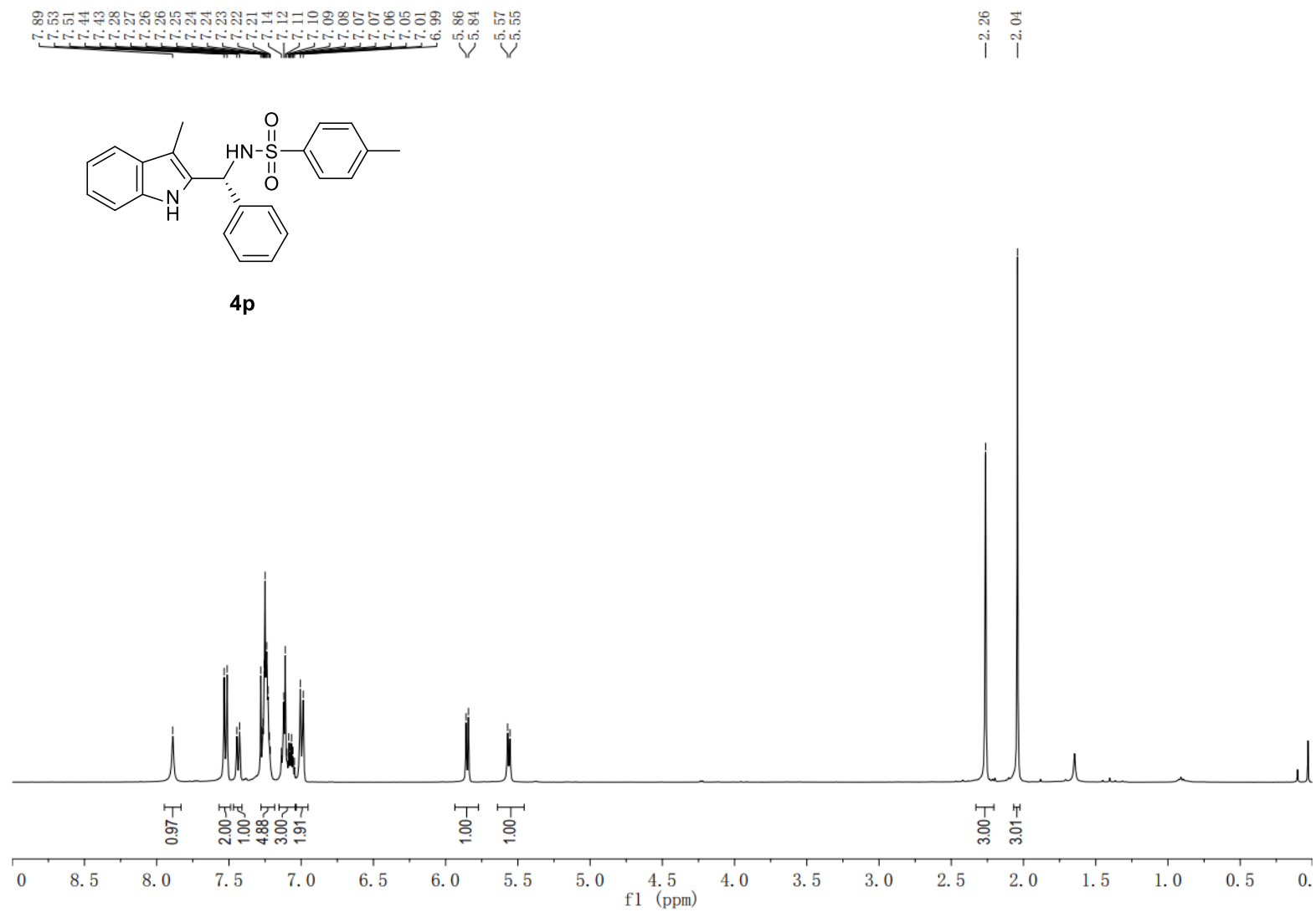


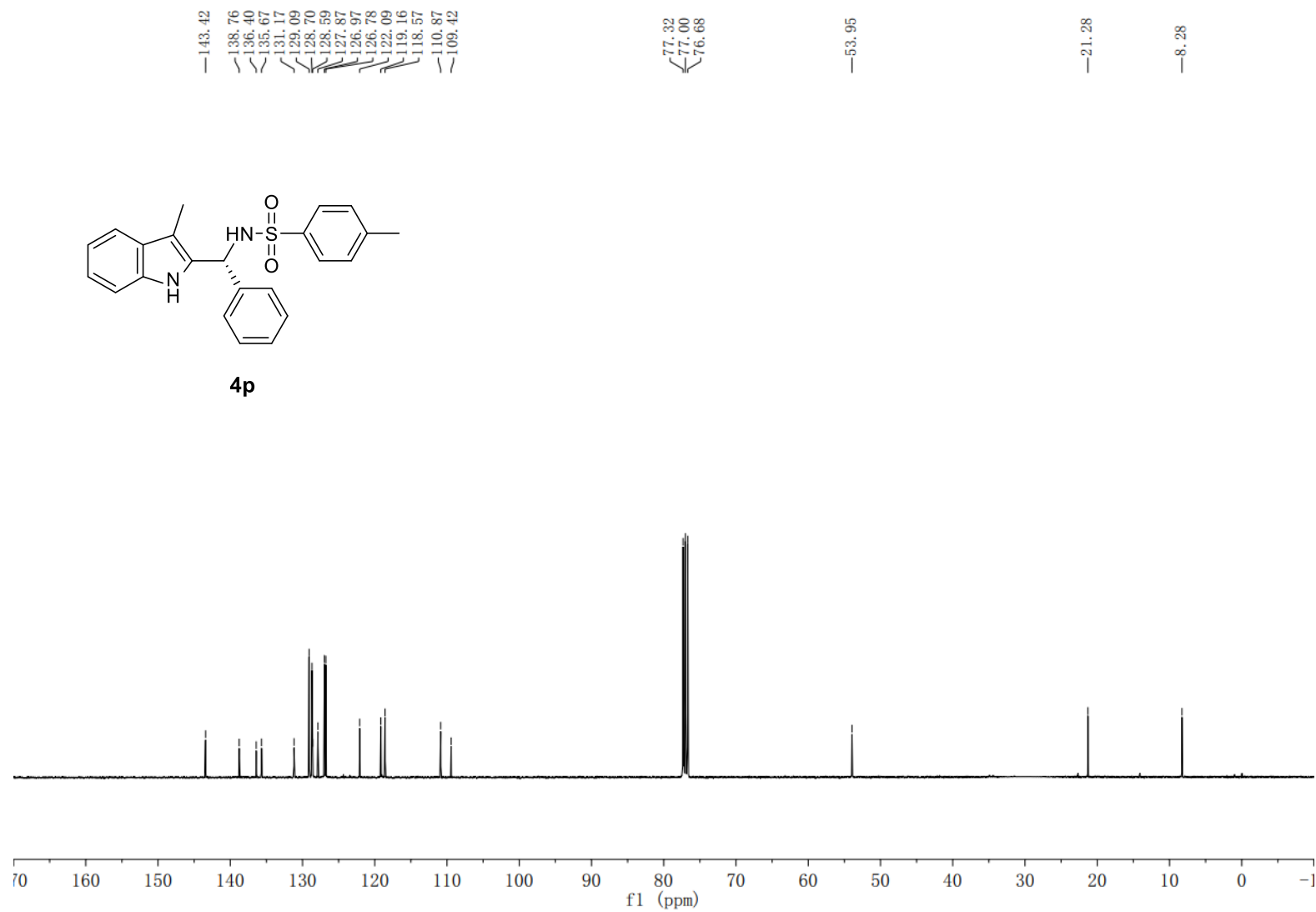


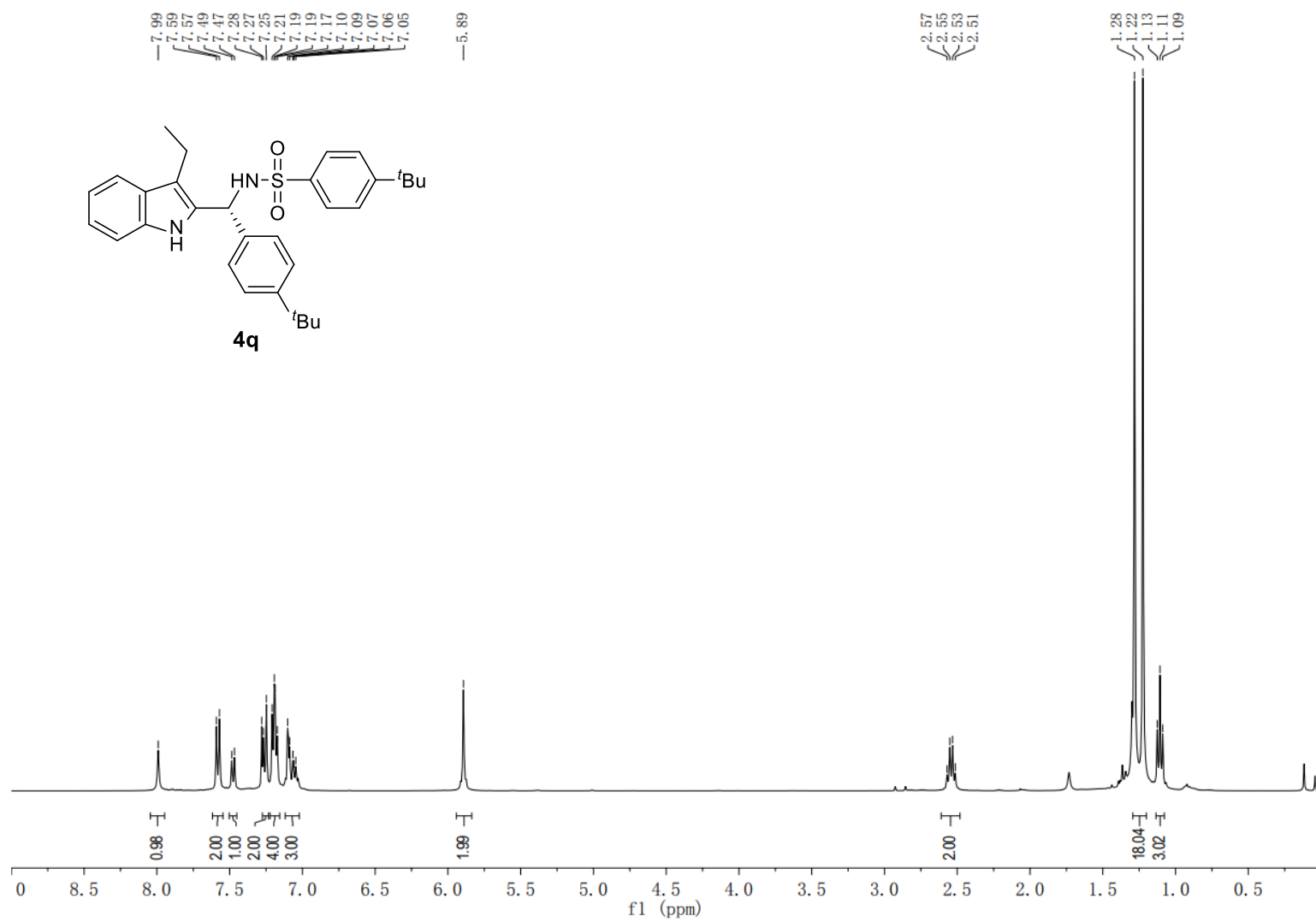


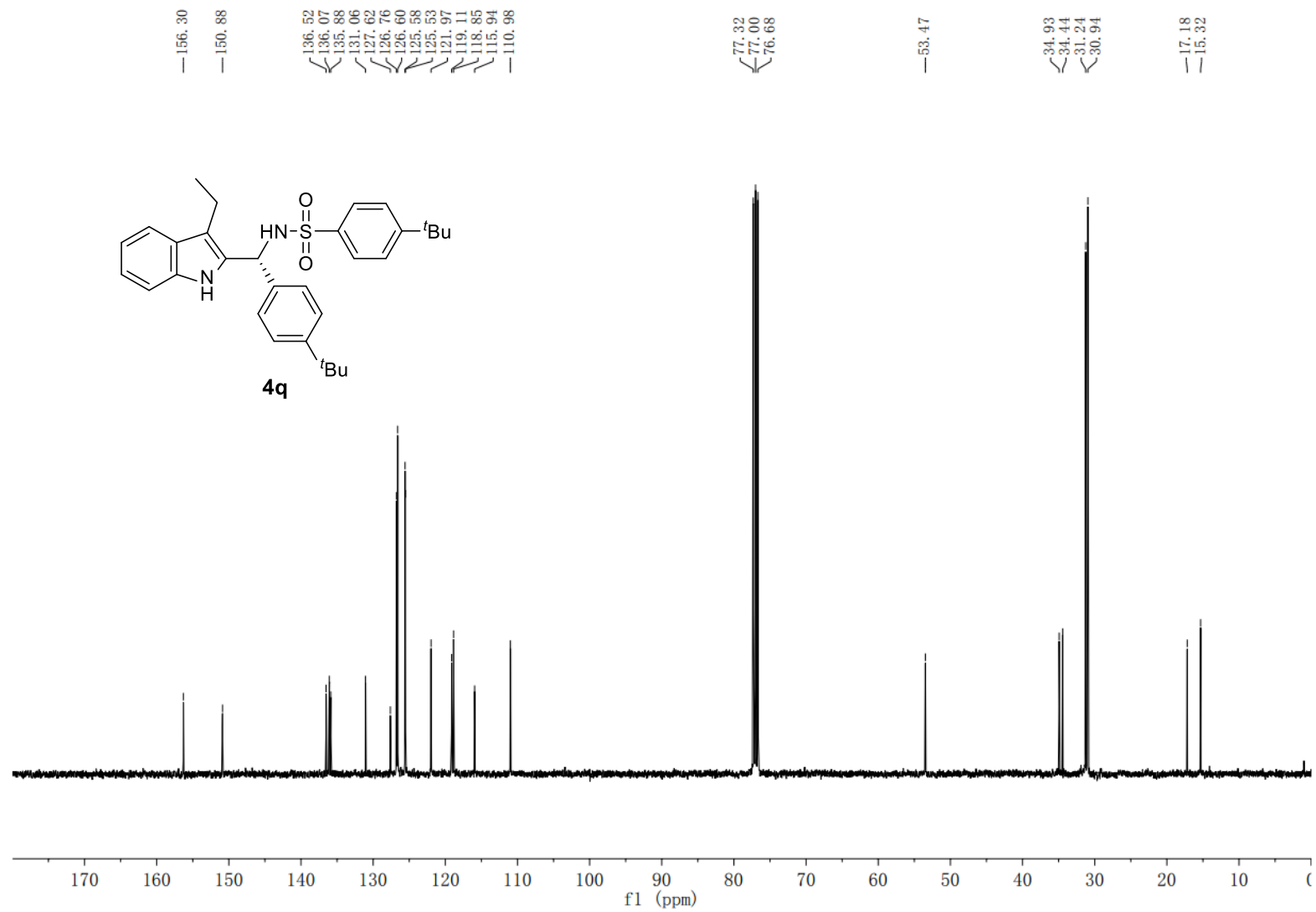


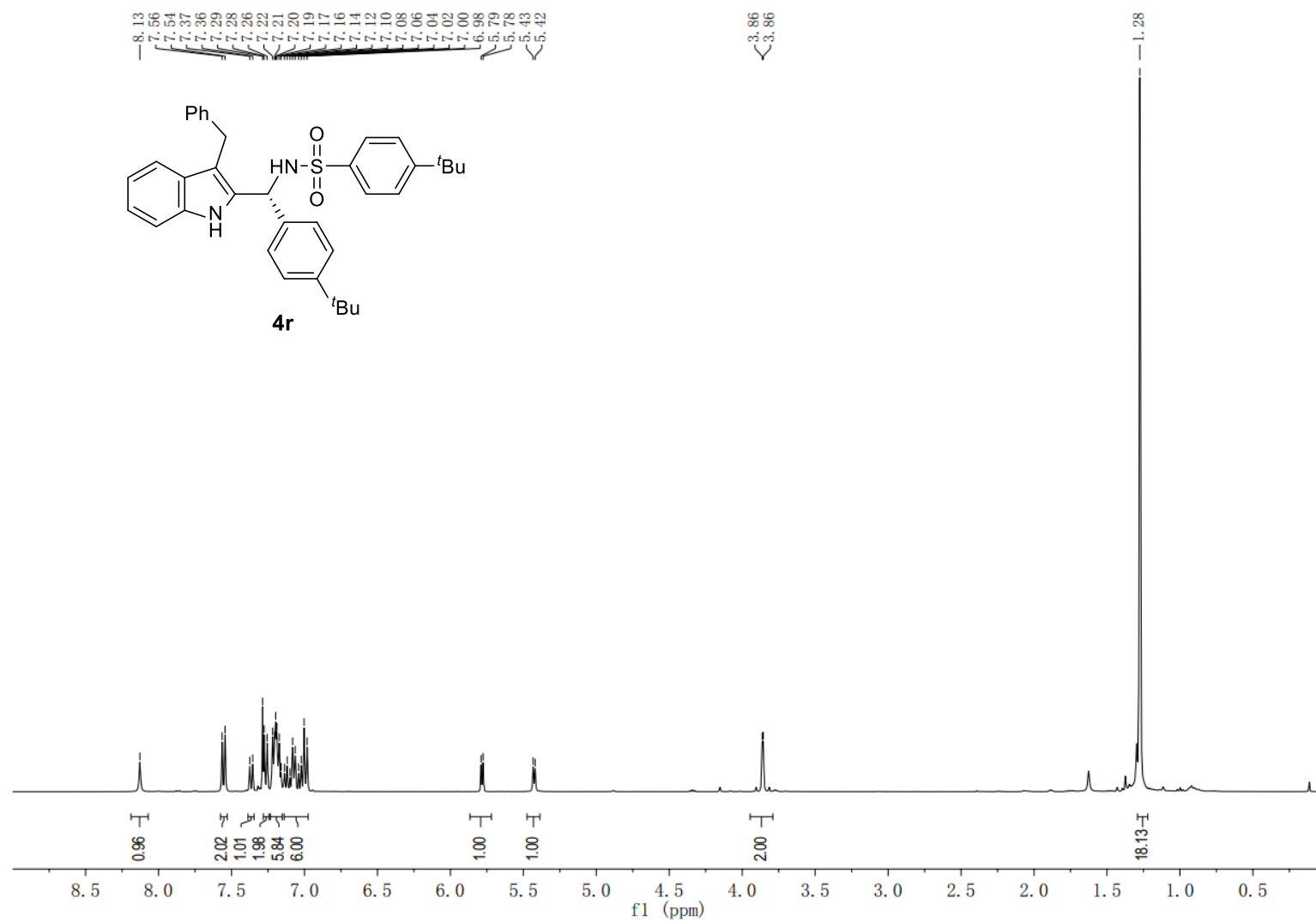


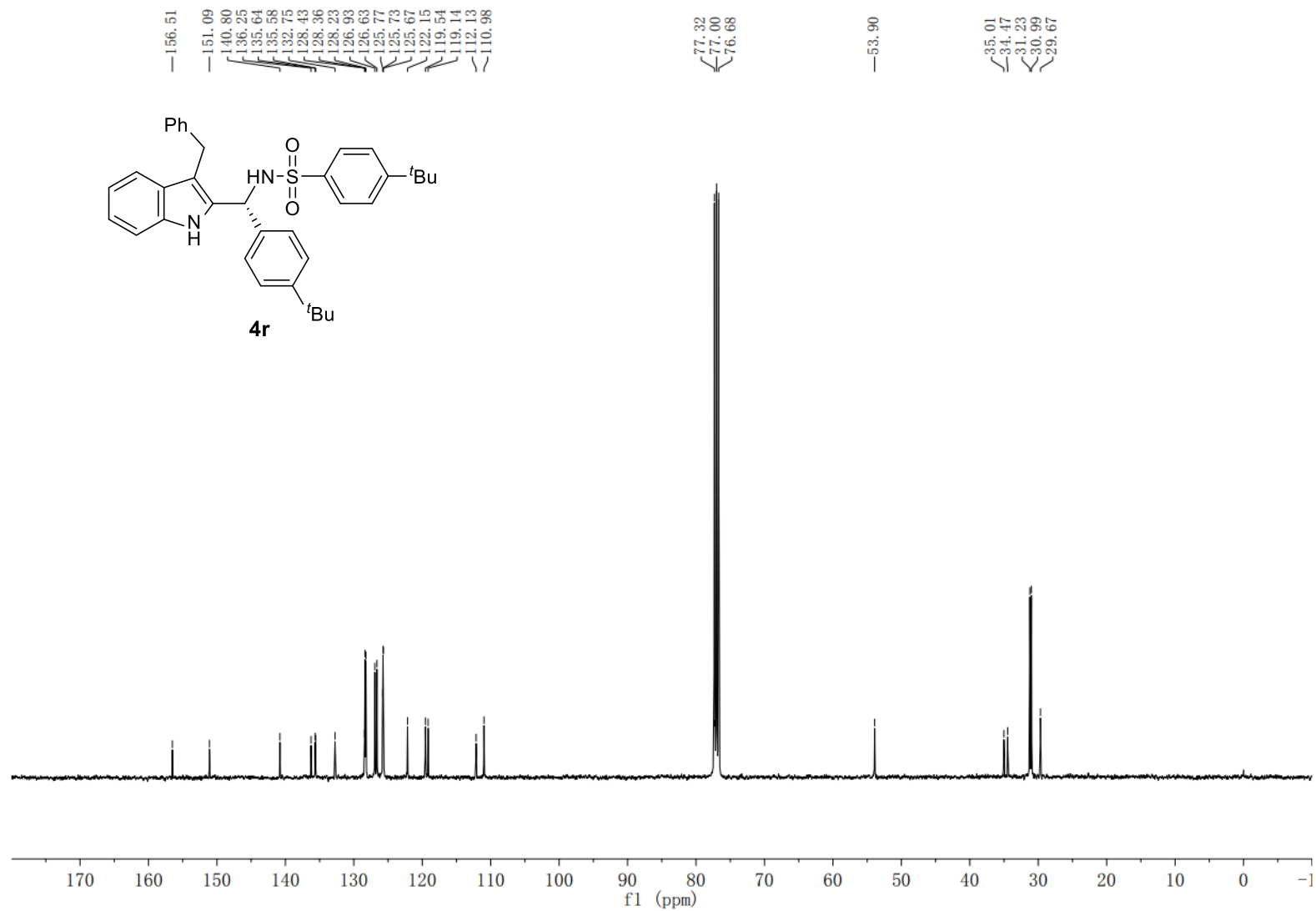


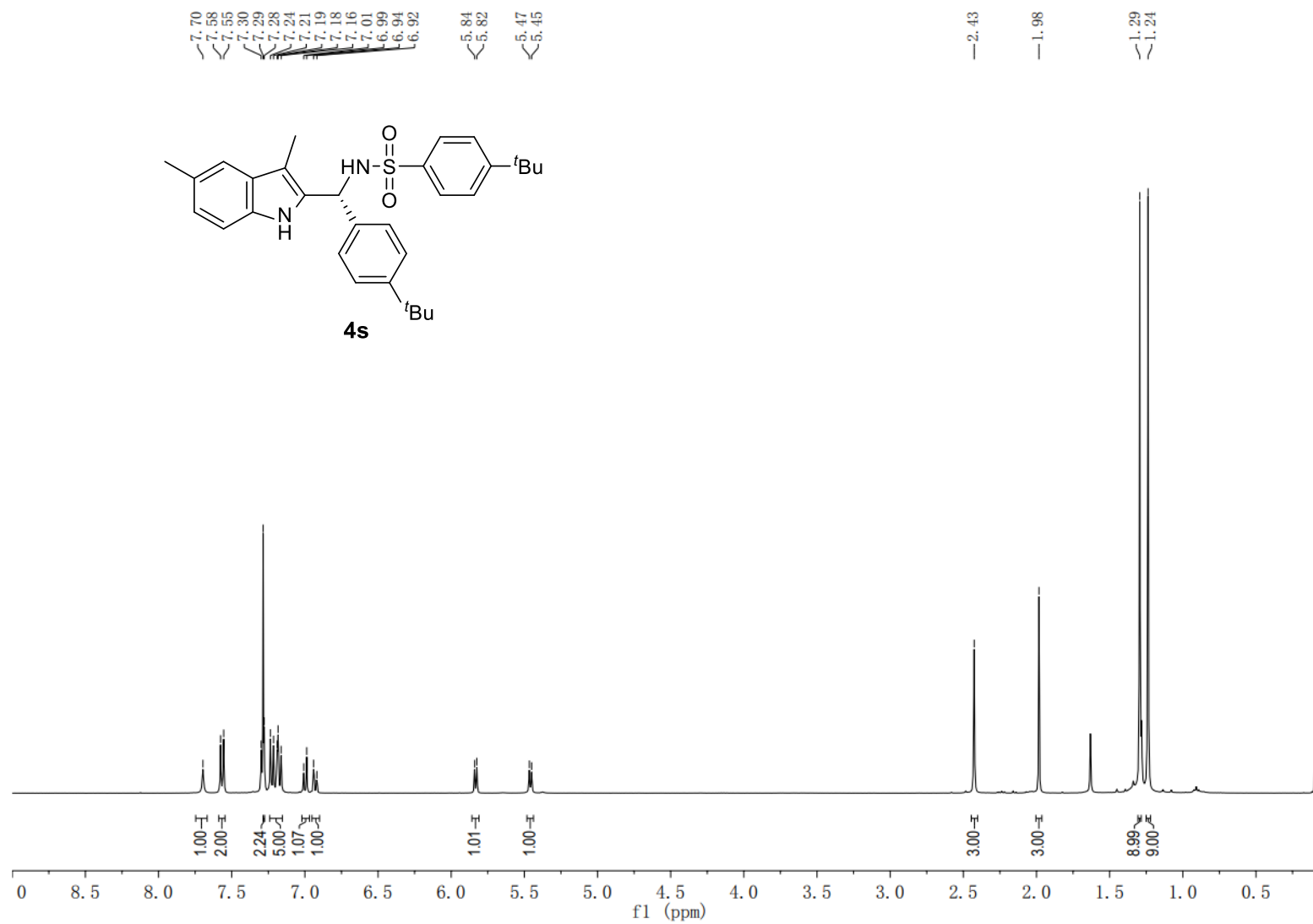


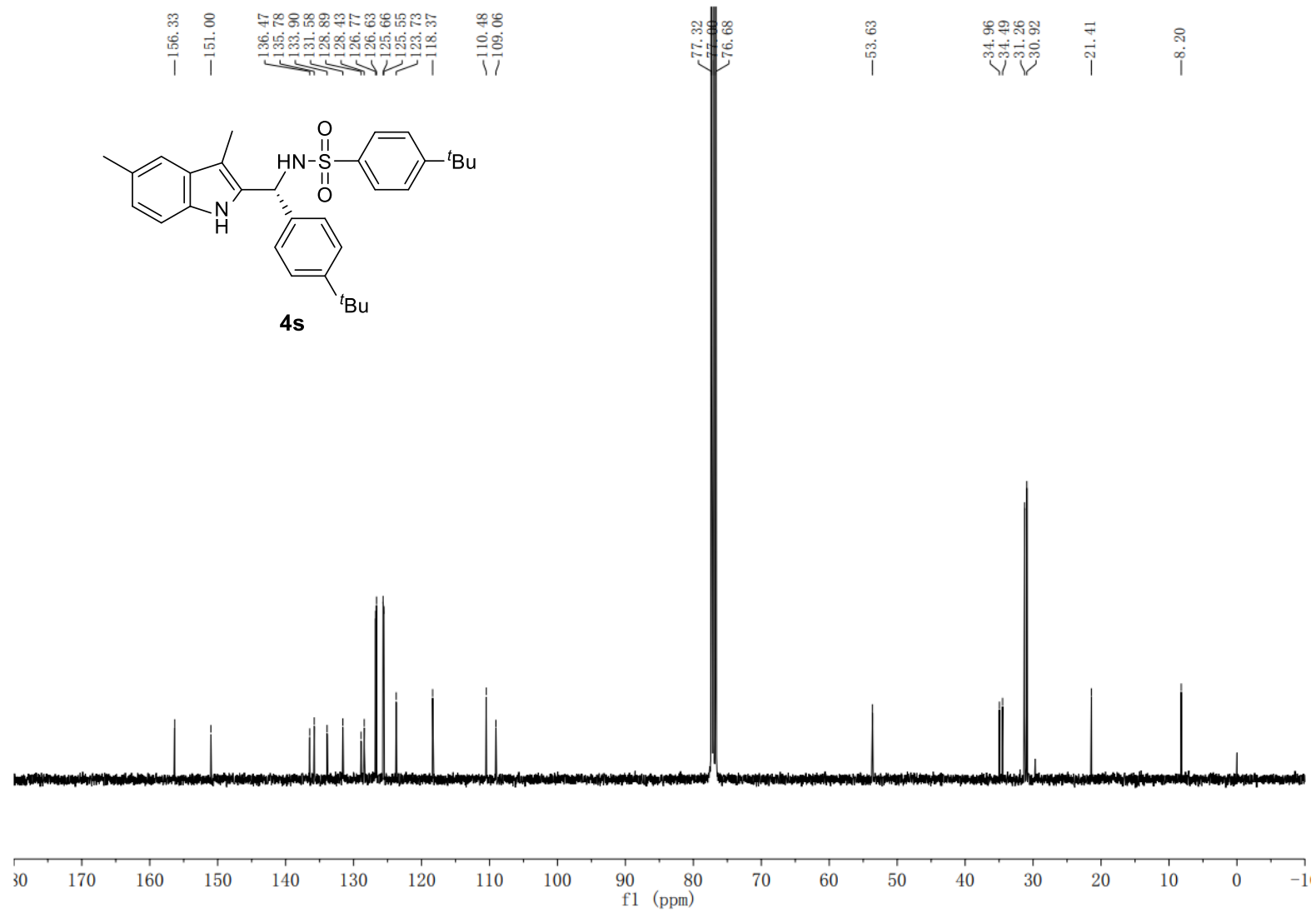


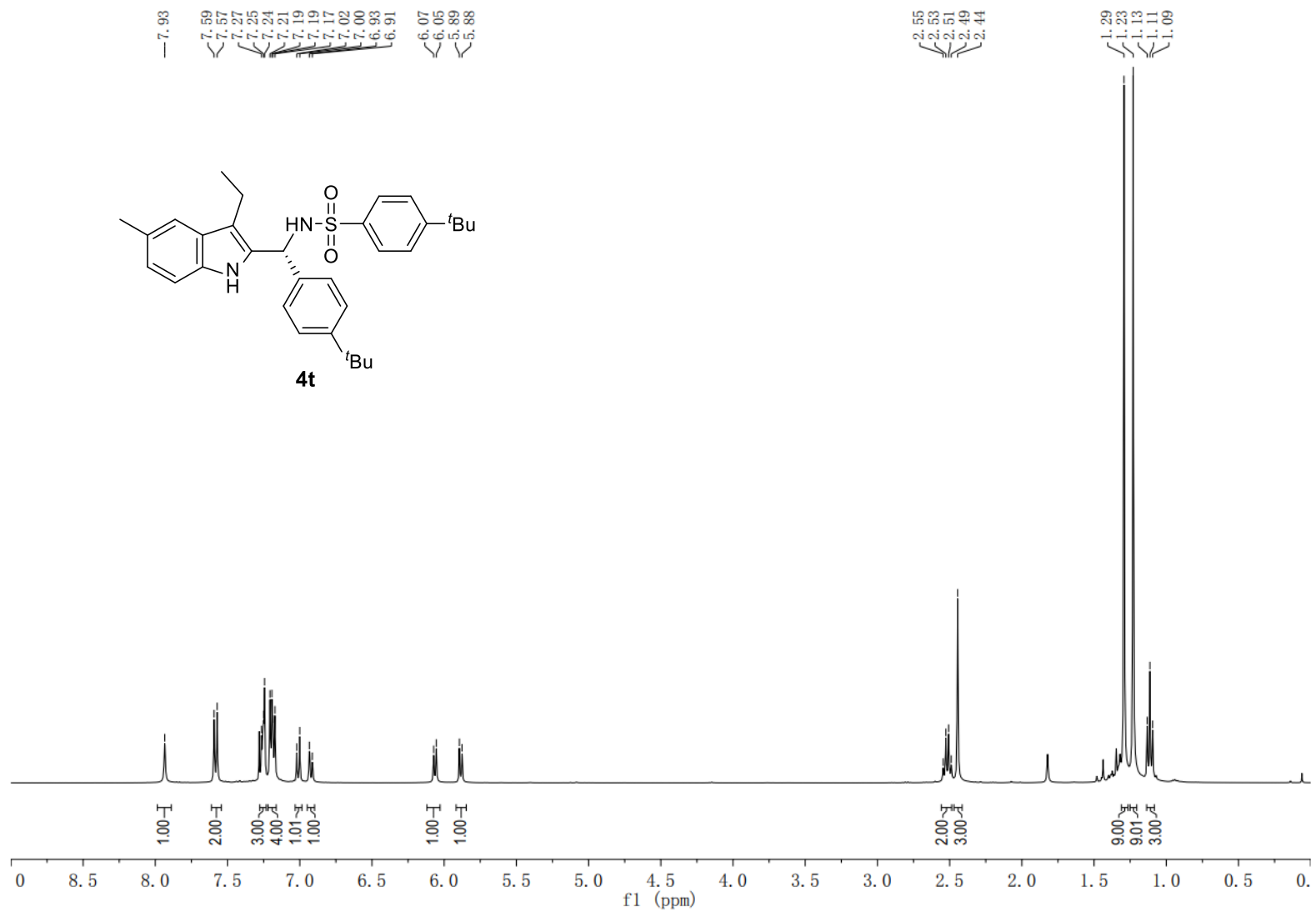


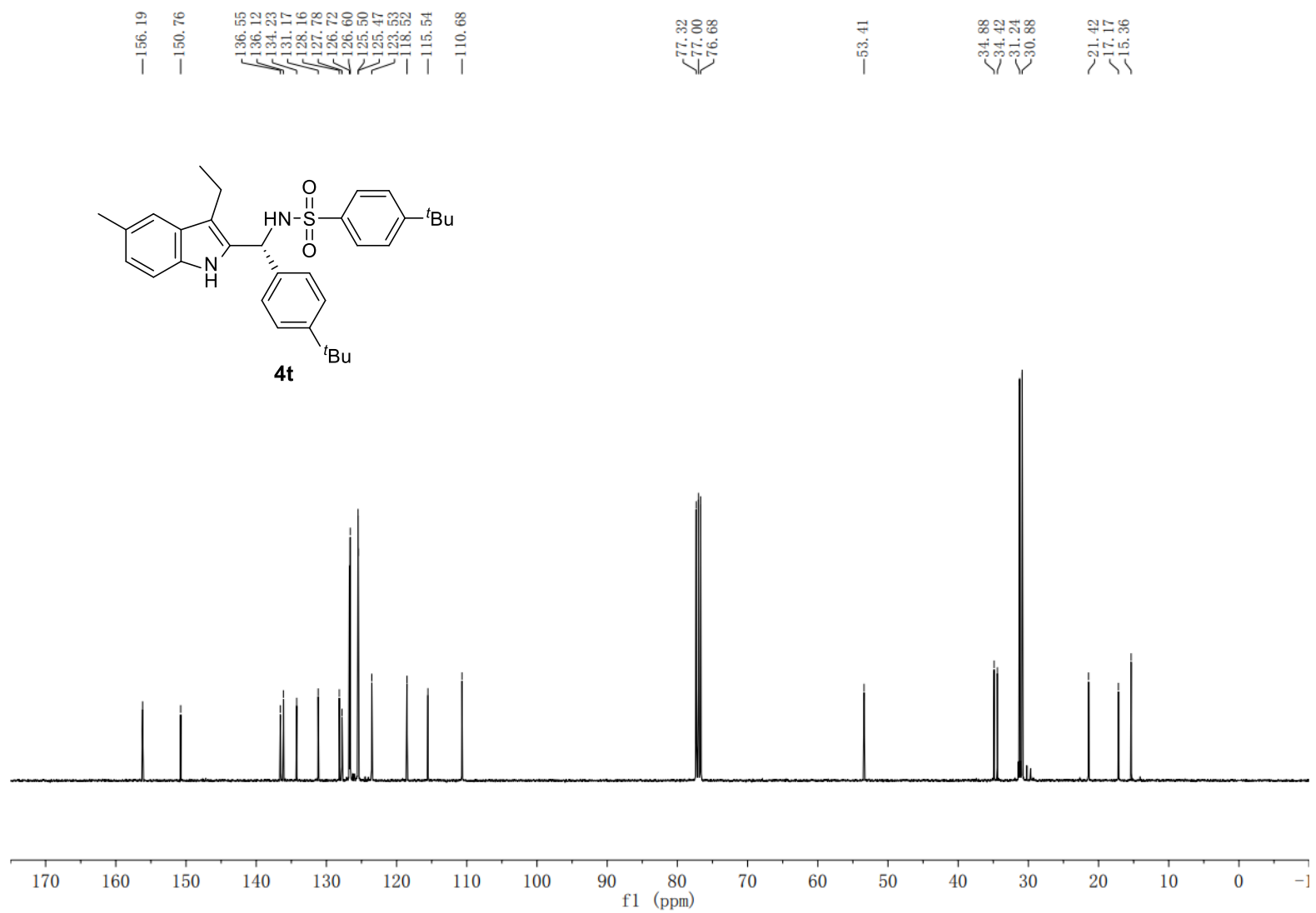


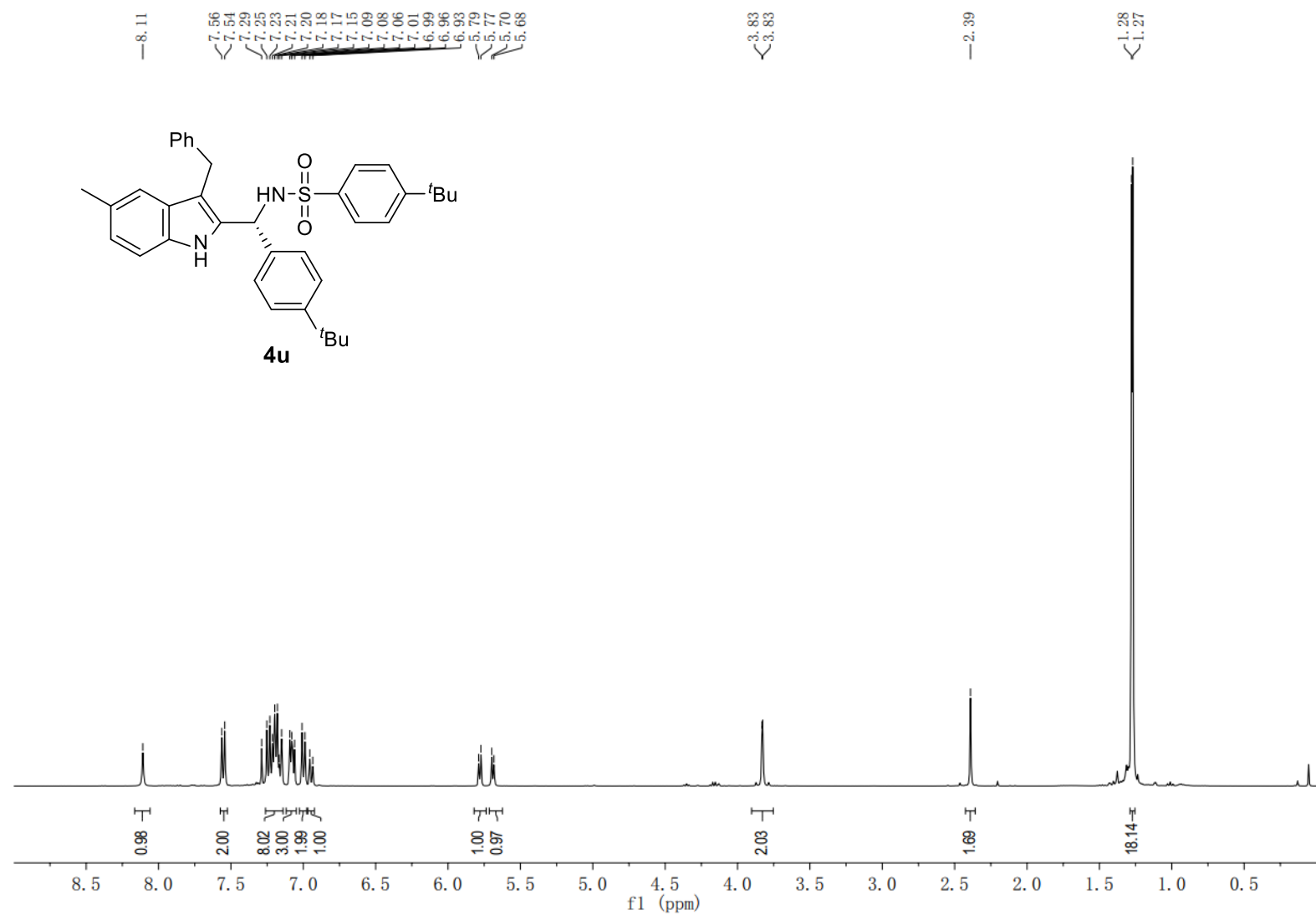


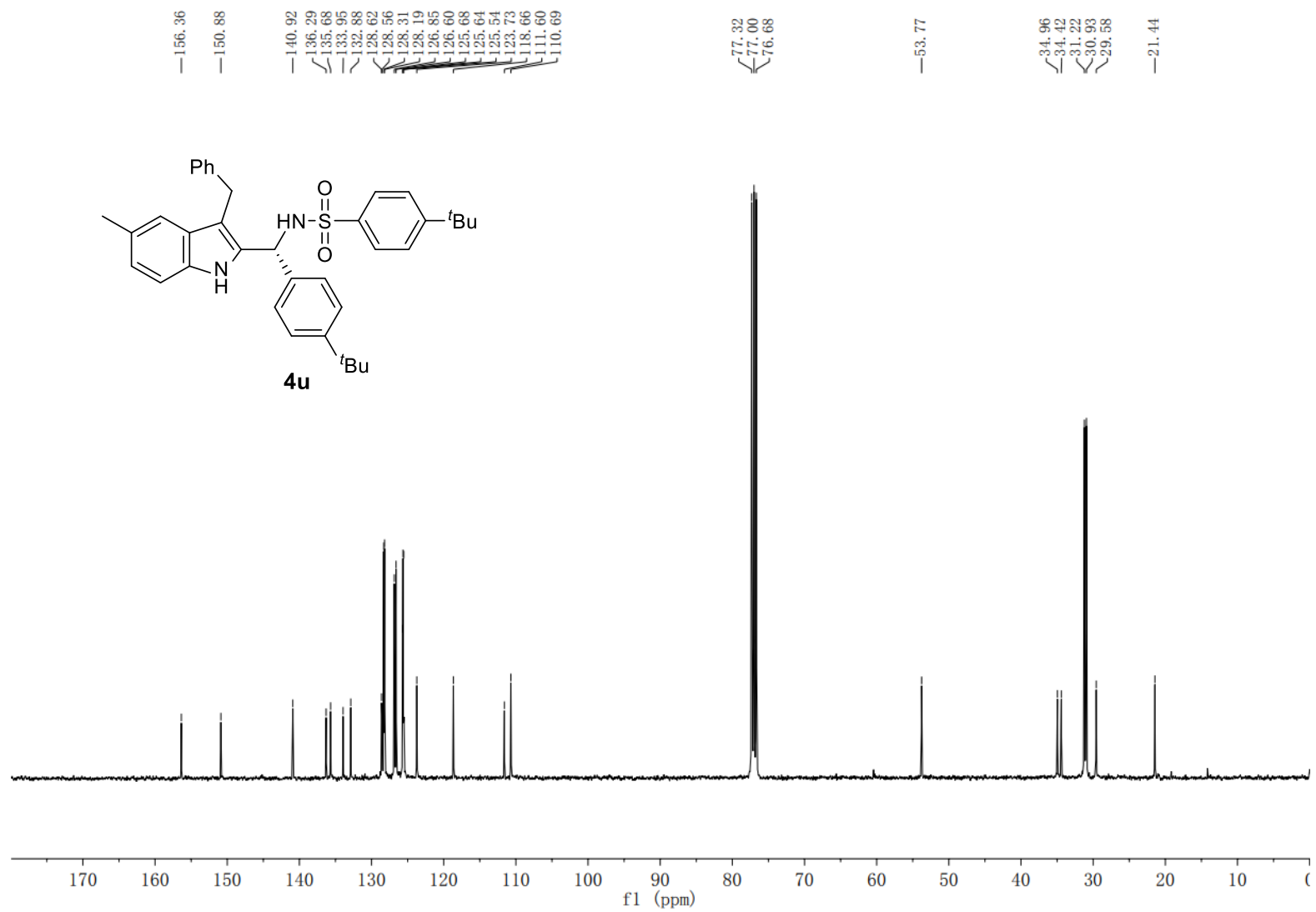


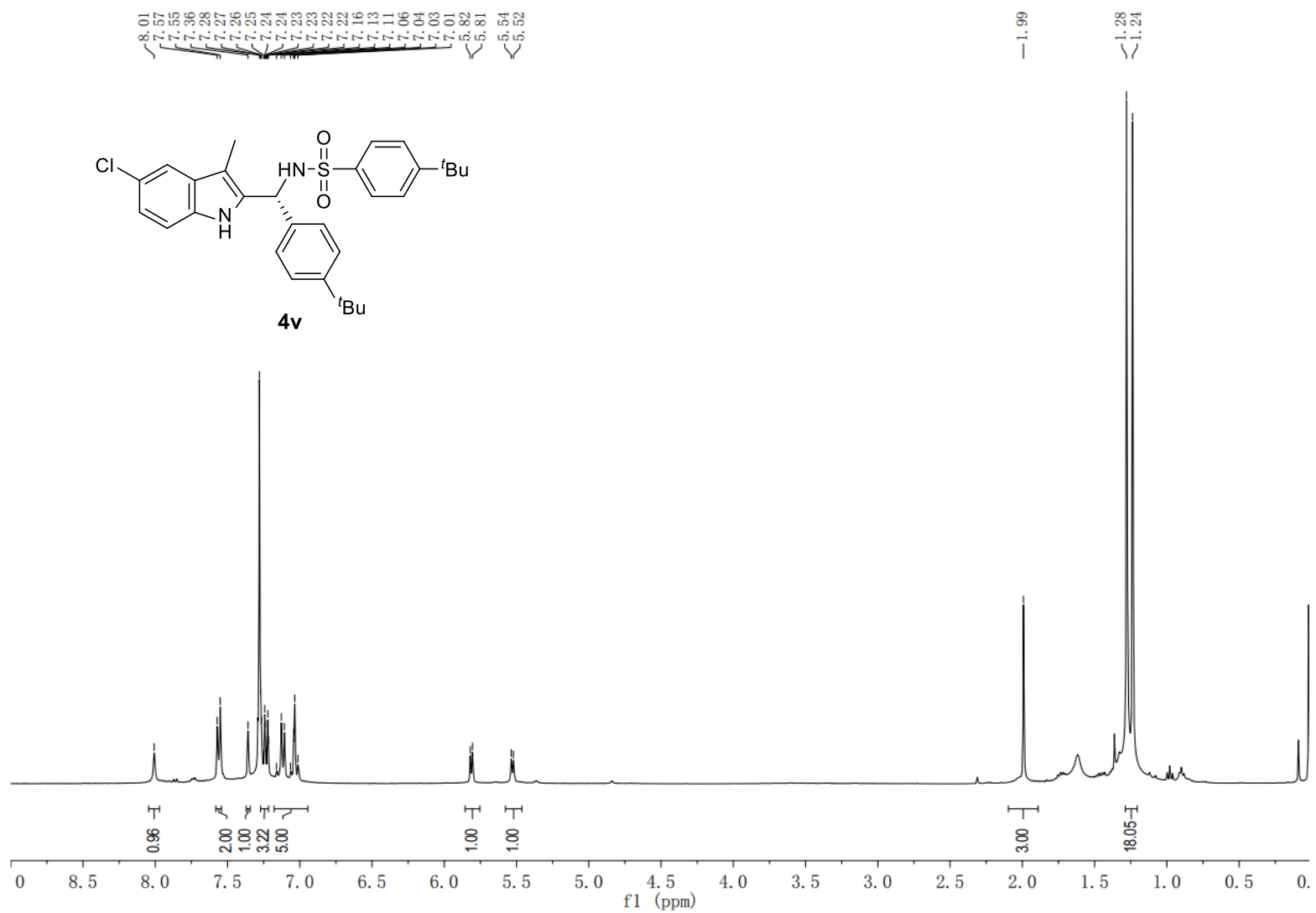


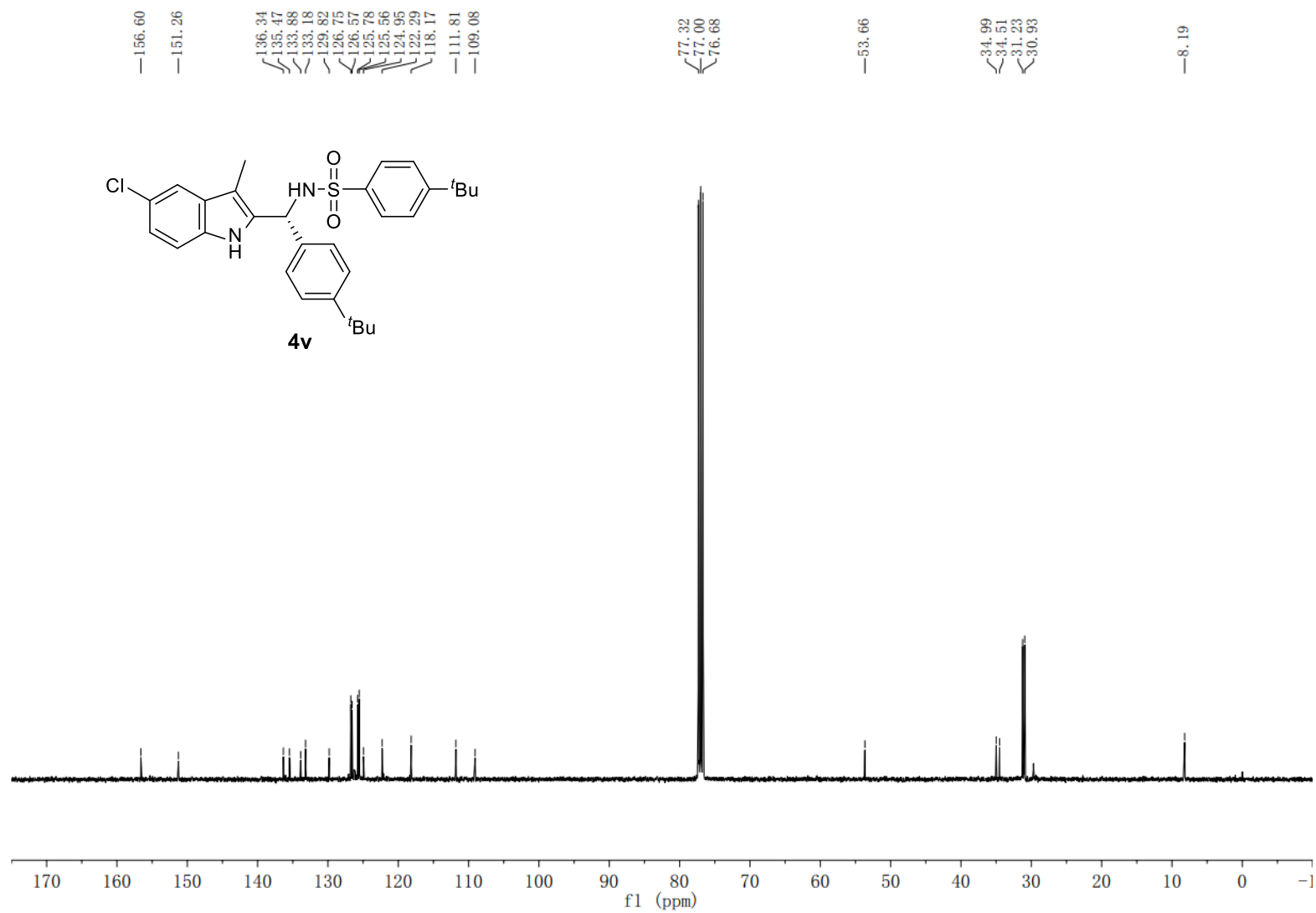


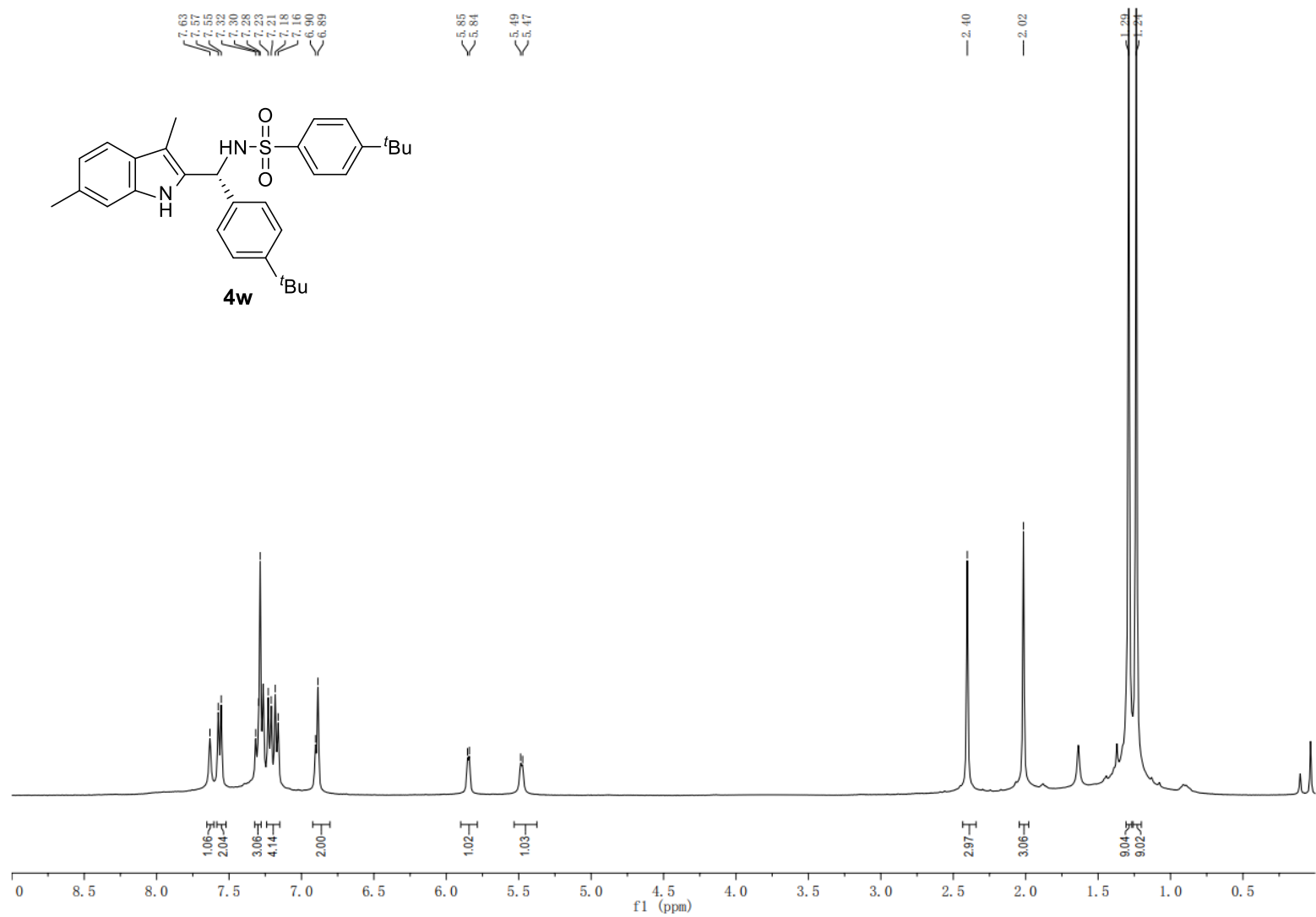


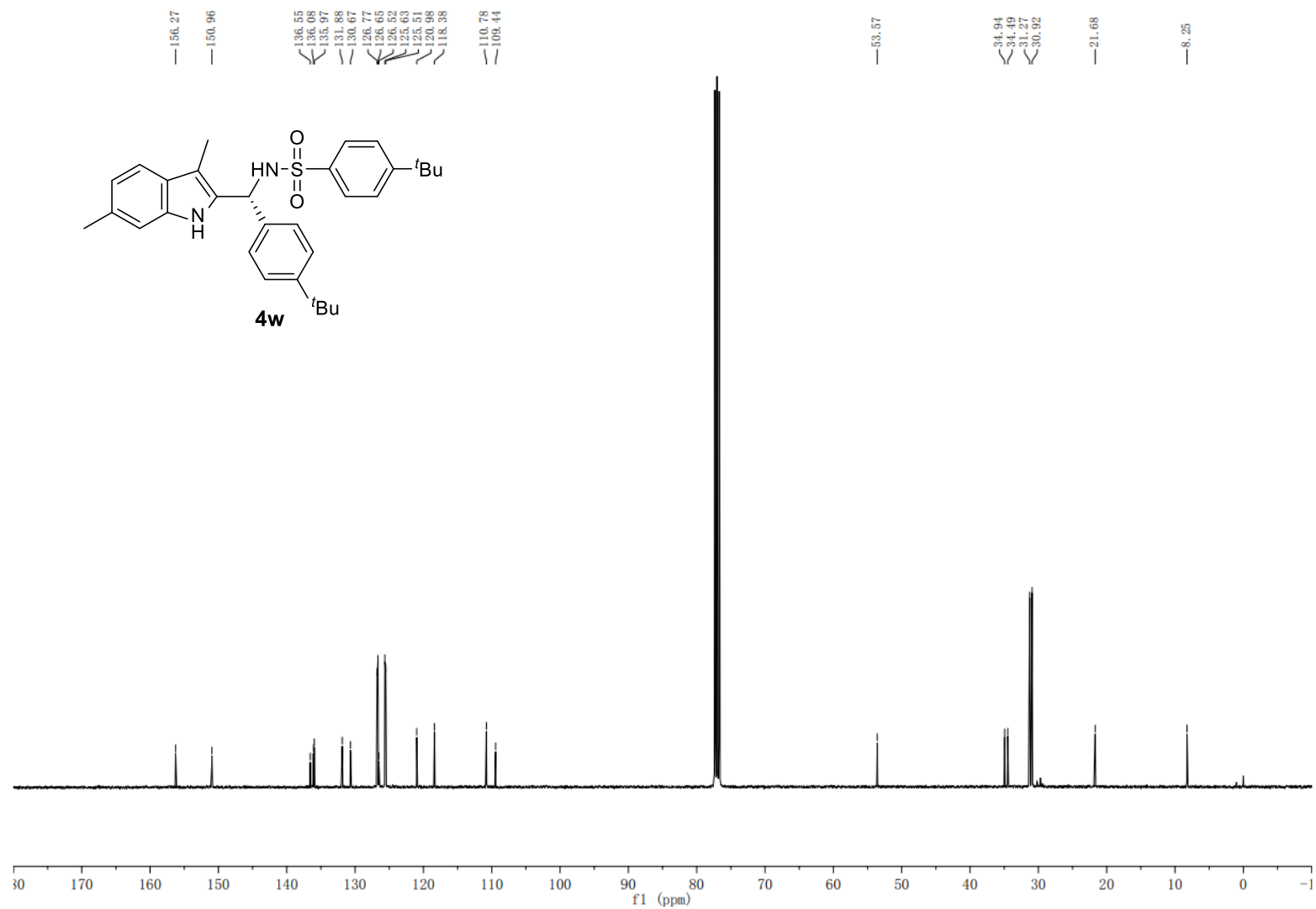


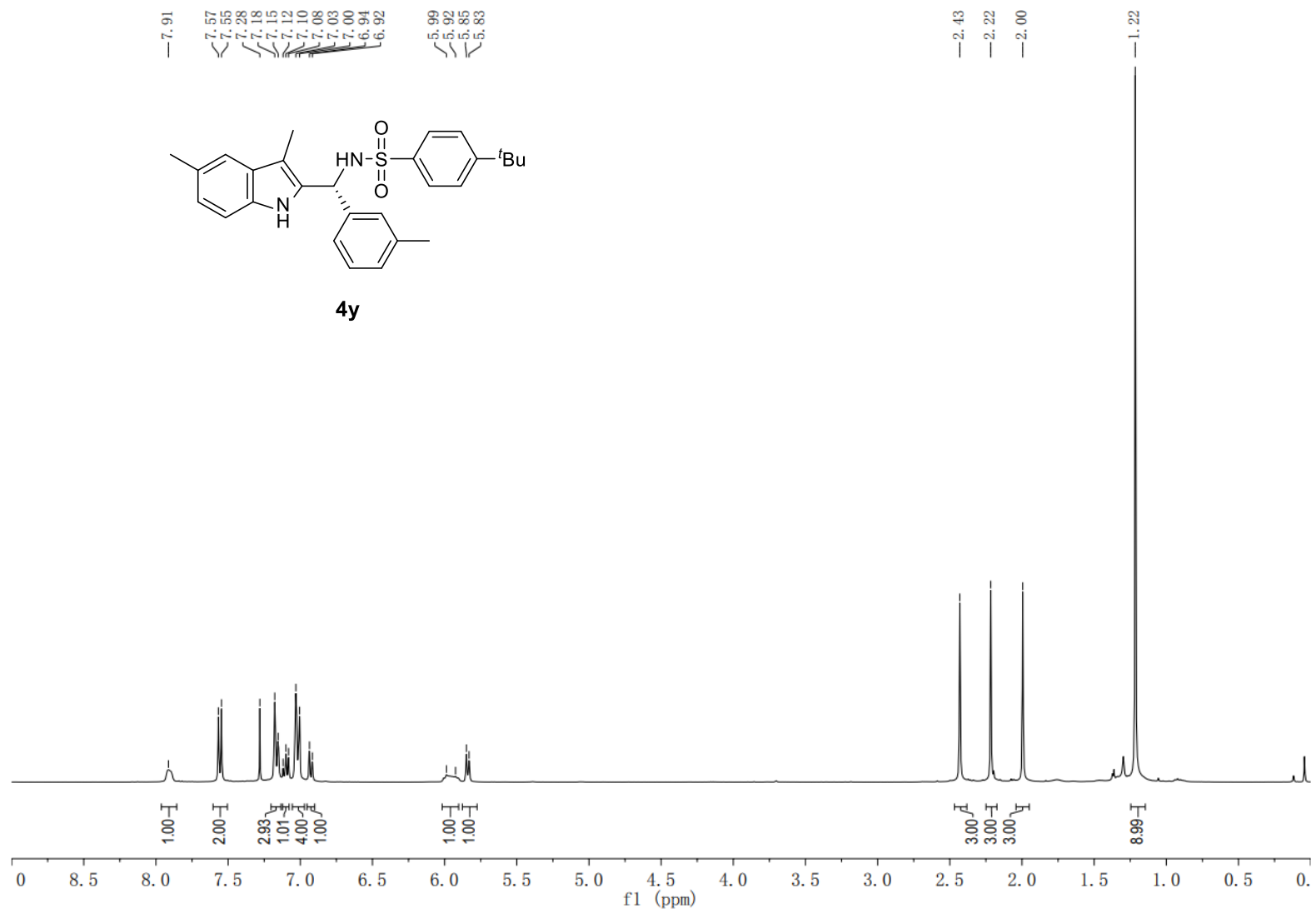


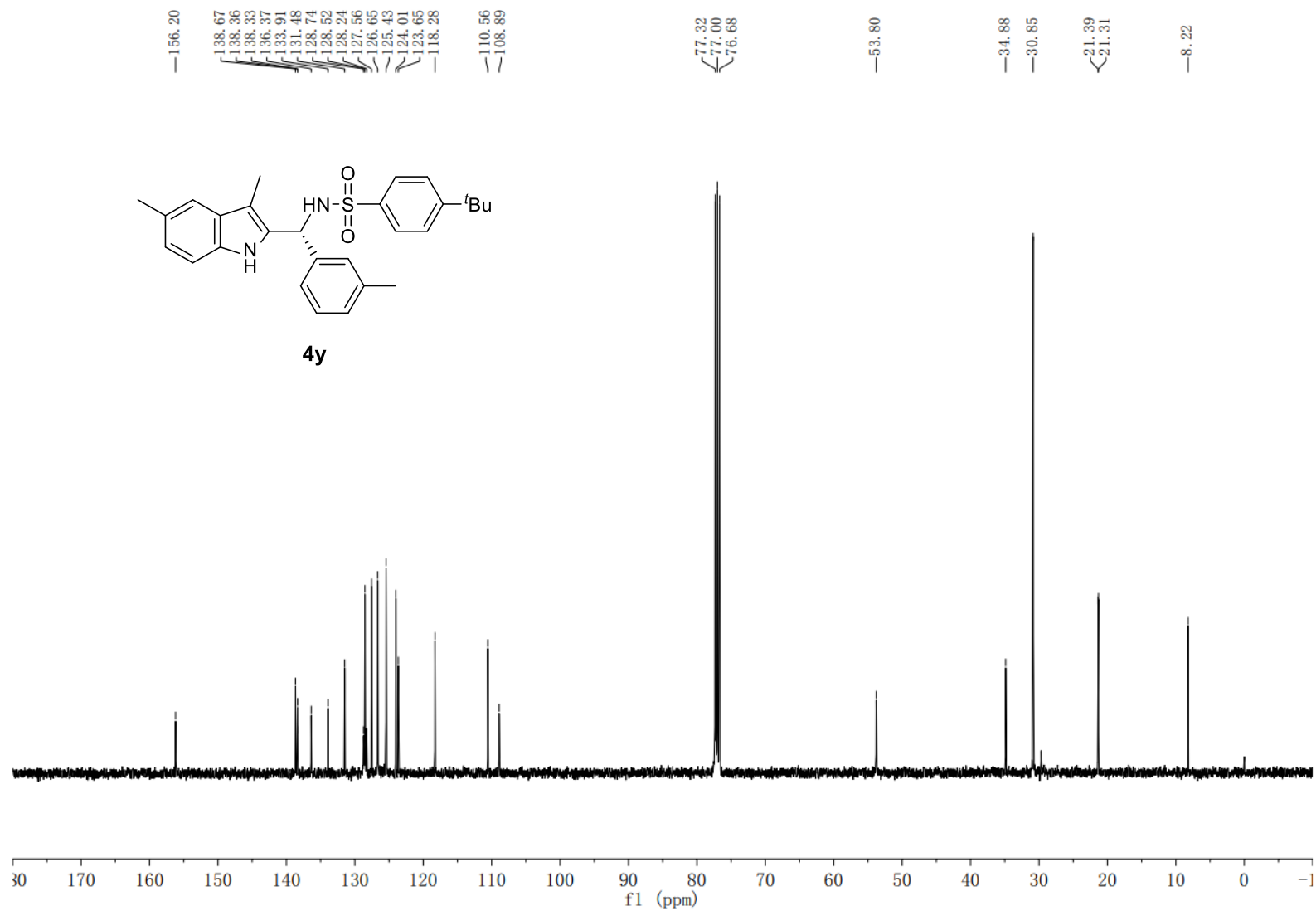


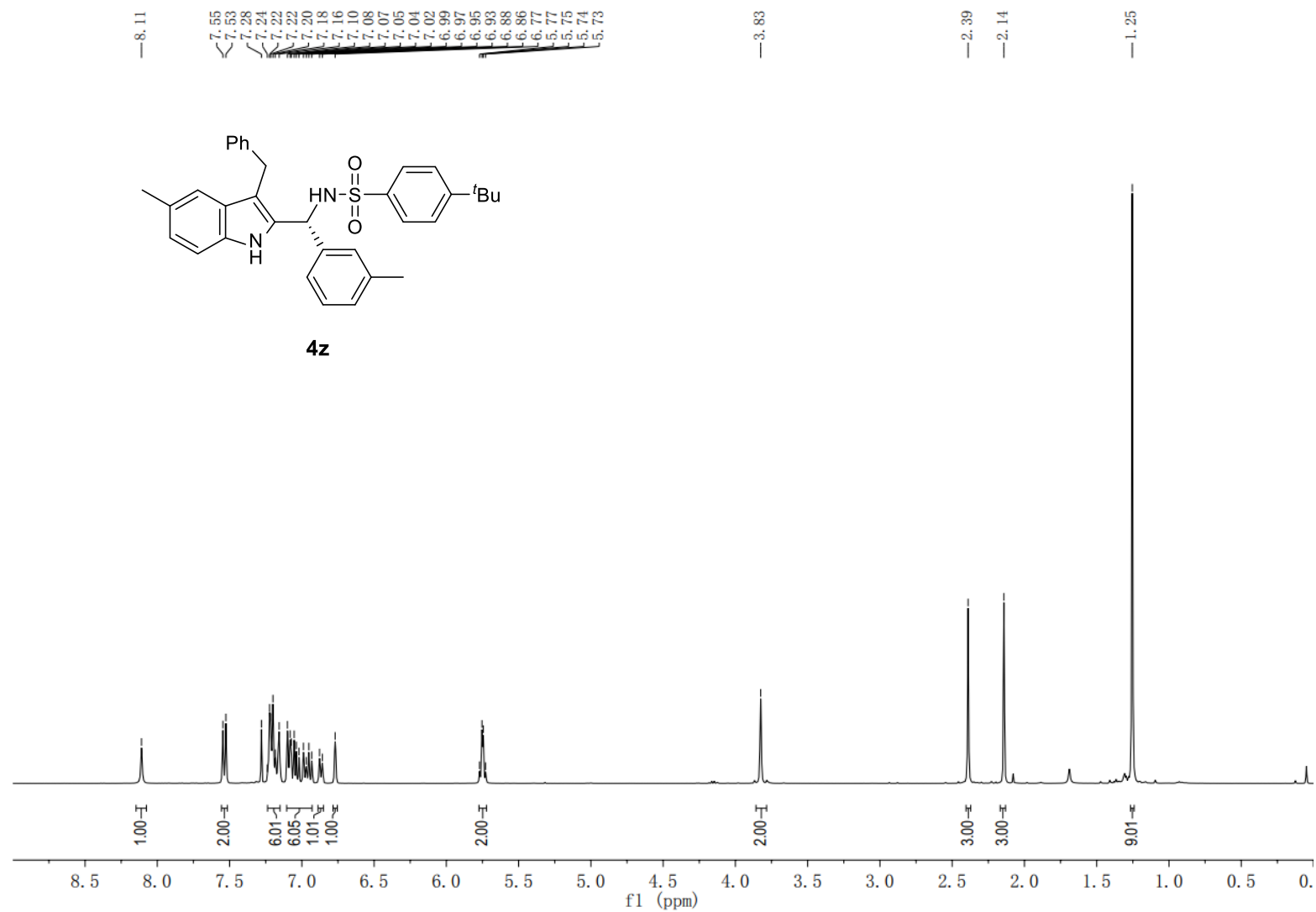


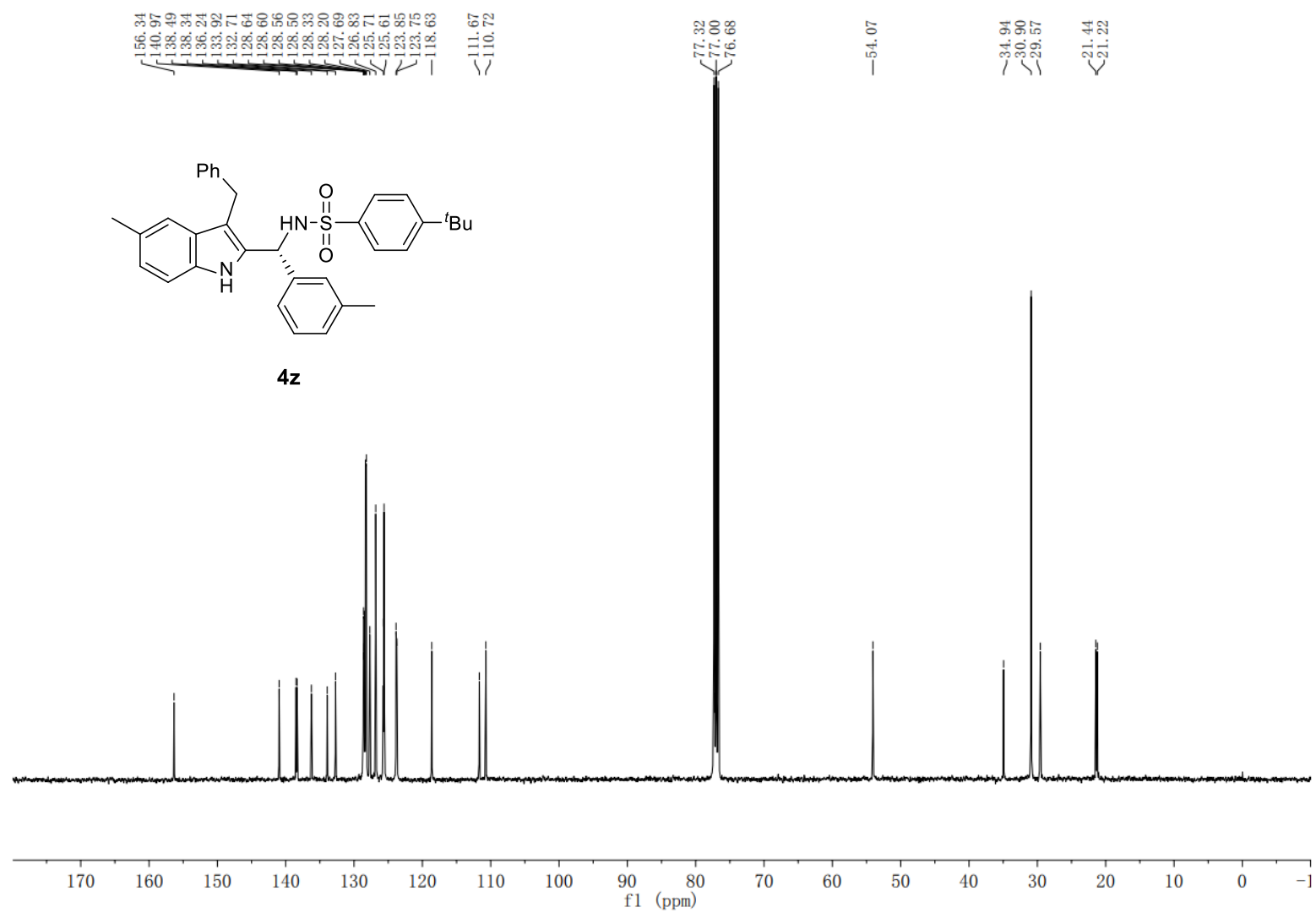


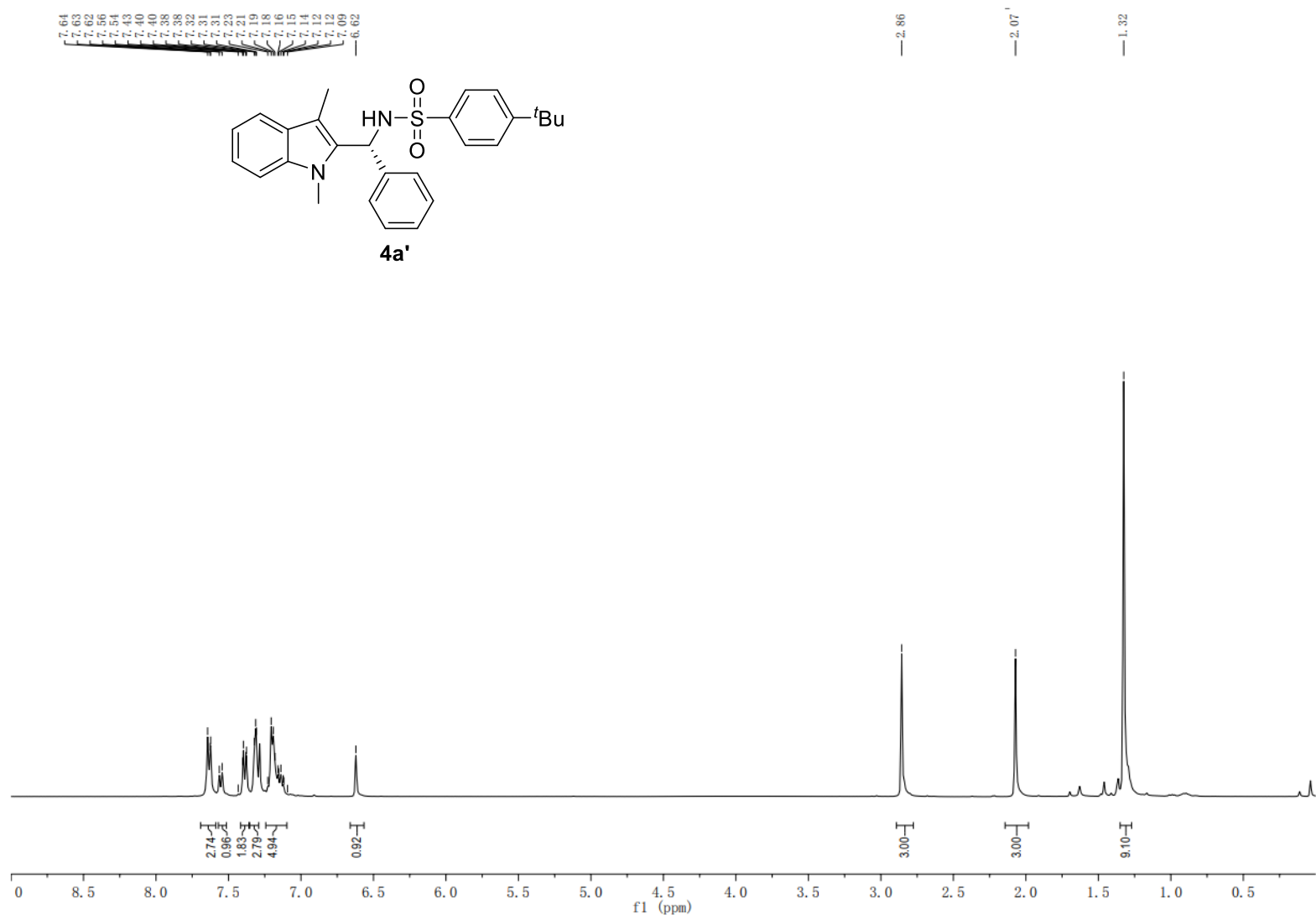


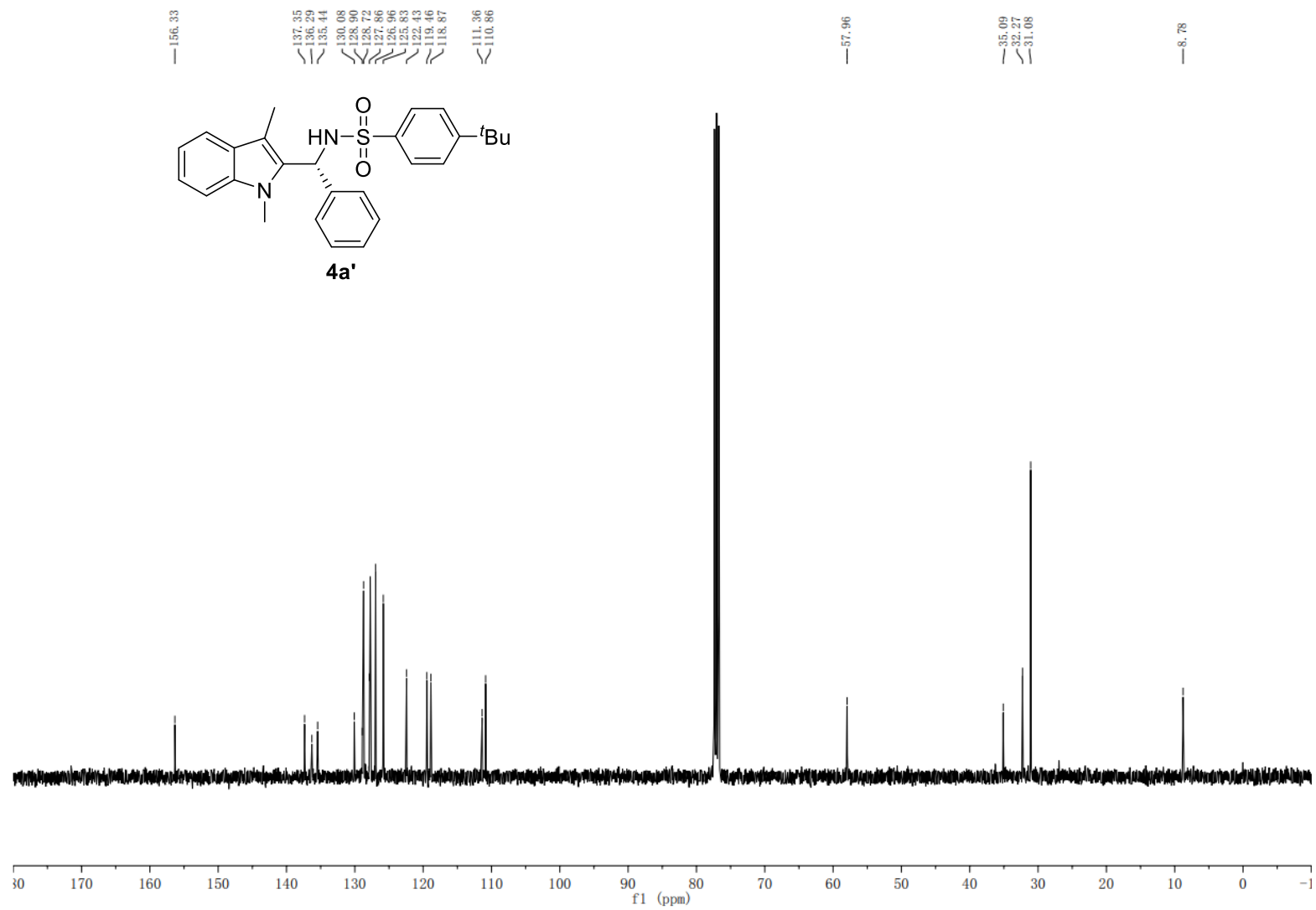






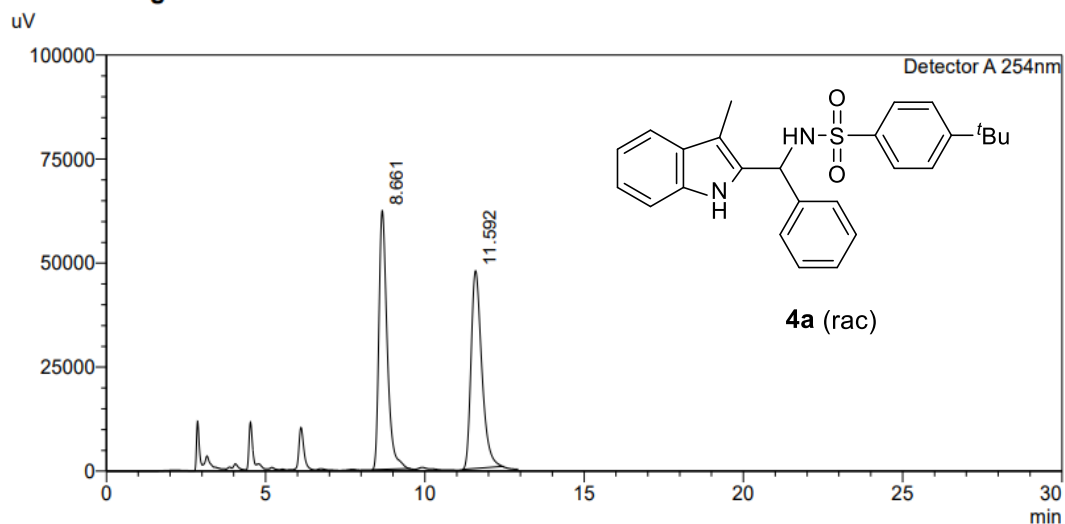






Copies of HPLC Spectra

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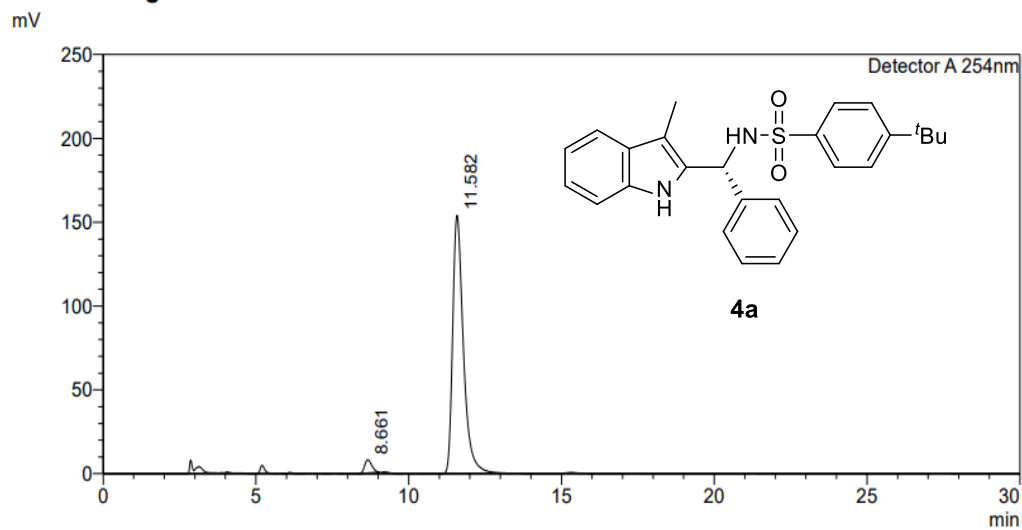


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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.661	1128900	62184	50.180		M	
2	11.592	1120813	47536	49.820		M	
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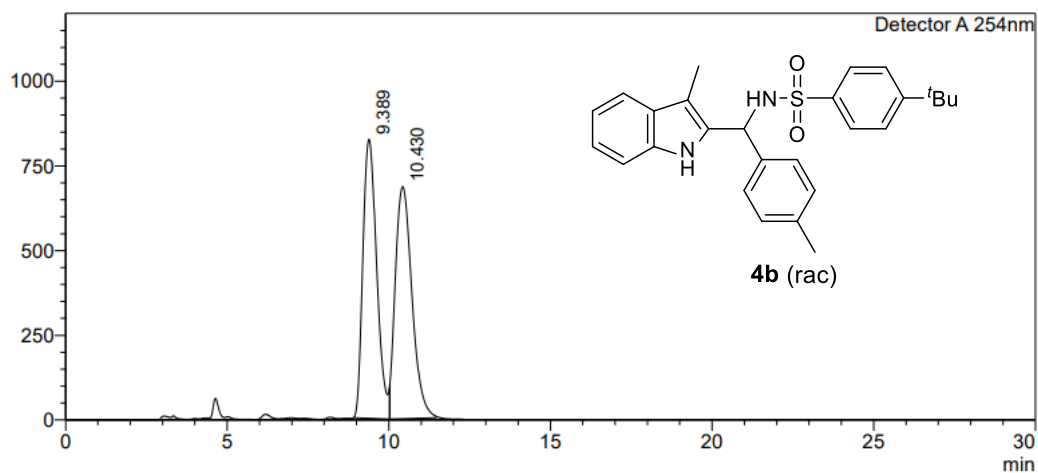
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.661	127672	7866	3.288		M	
2	11.582	3754880	153780	96.712		M	
Total		3882551	161646				

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mV



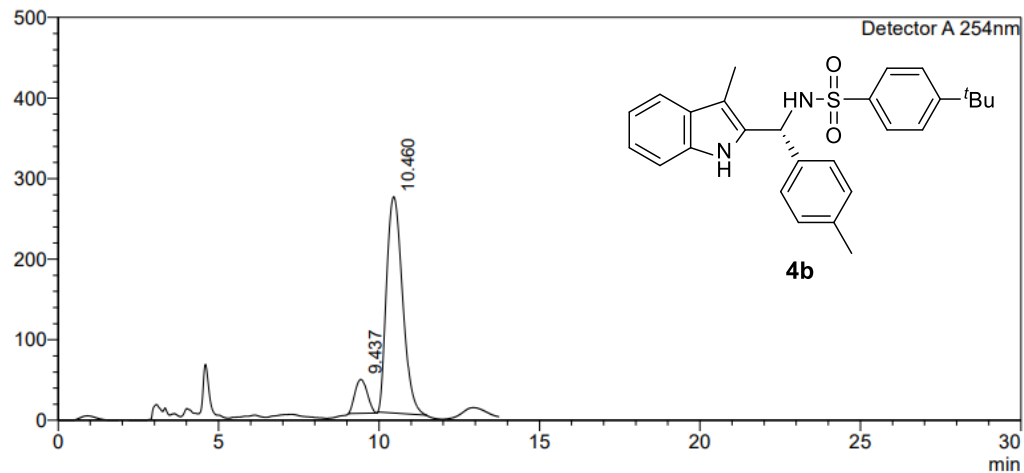
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Detector A 254nm

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1	9.389	24363594	823769	49.759		M	
2	10.430	24600028	685353	50.241		M	
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mV



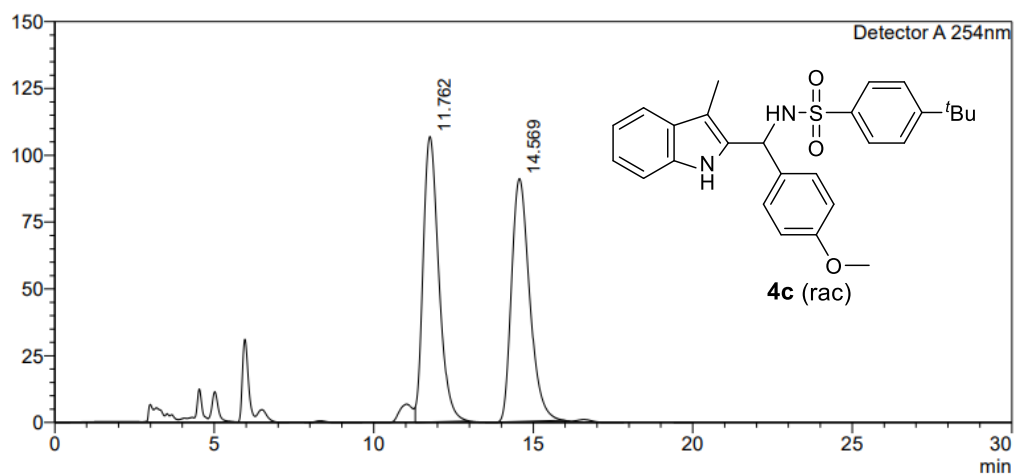
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.437	1106956	42102	10.587		M	
2	10.460	9348502	268540	89.413		M	
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mV



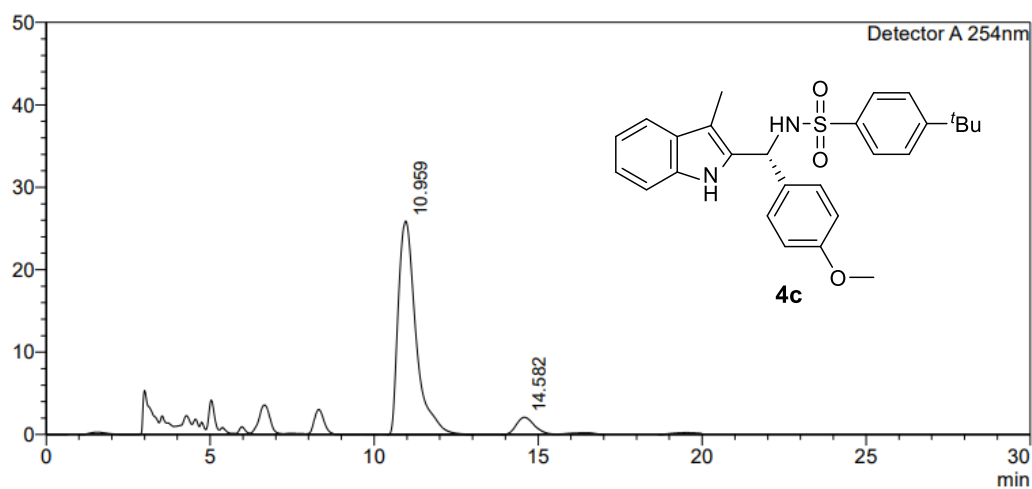
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.762	3636258	106760	50.356		M	
2	14.569	3584884	90895	49.644		M	
Total		7221143	197656				

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mV

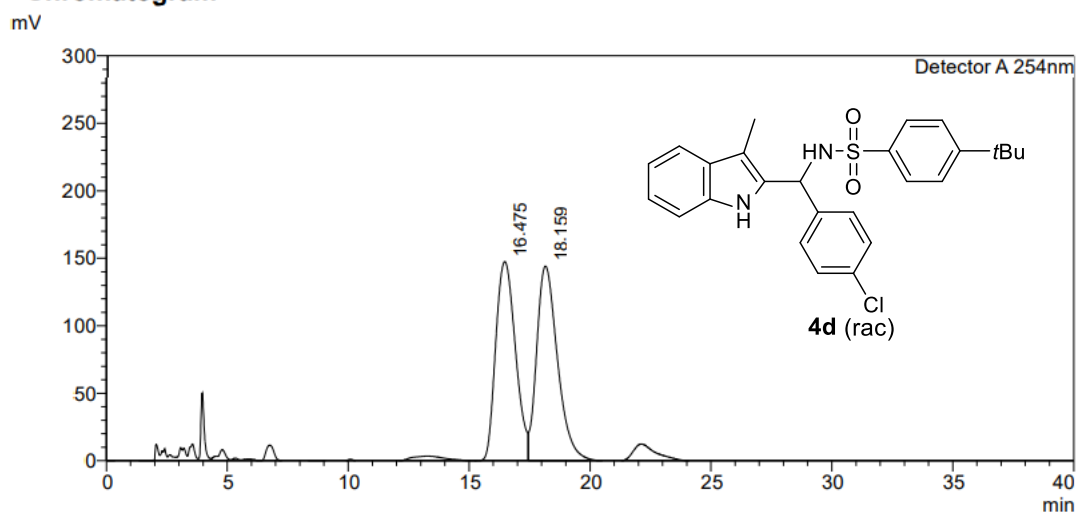


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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.959	965366	25870	91.975			
2	14.582	84236	2125	8.025			
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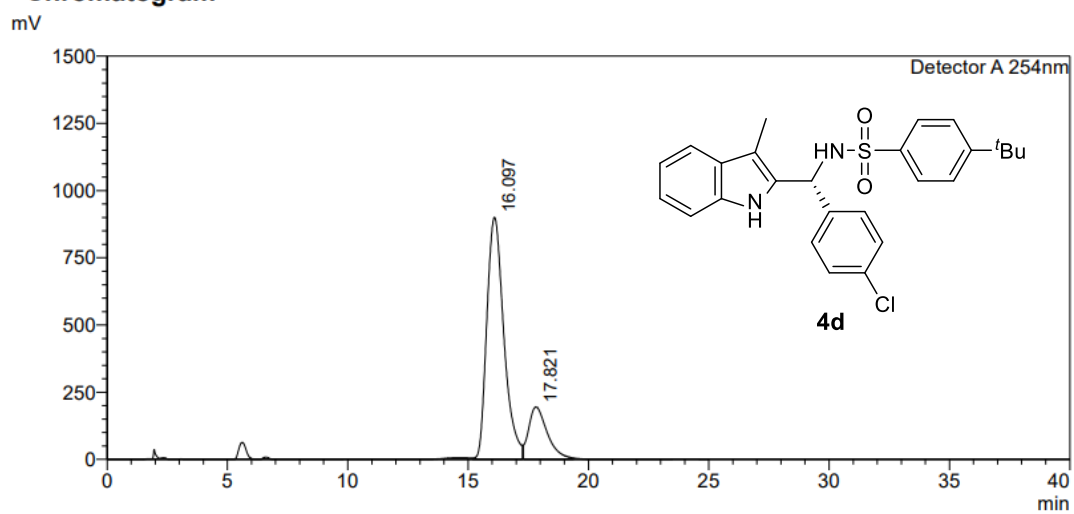


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.475	8450949	148230	49.510			
2	18.159	8618191	144222	50.490		M	
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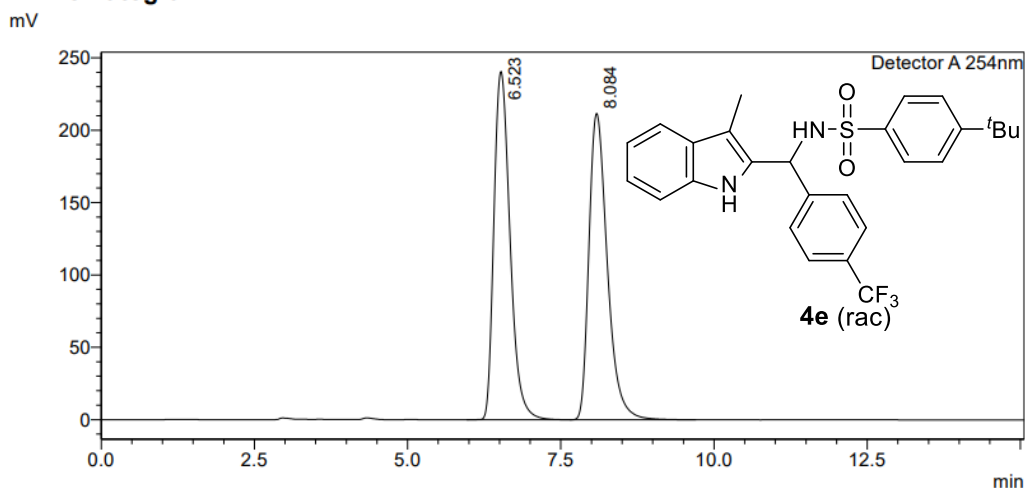


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.097	44357393	900919	80.716			
2	17.821	10597392	195815	19.284		M	
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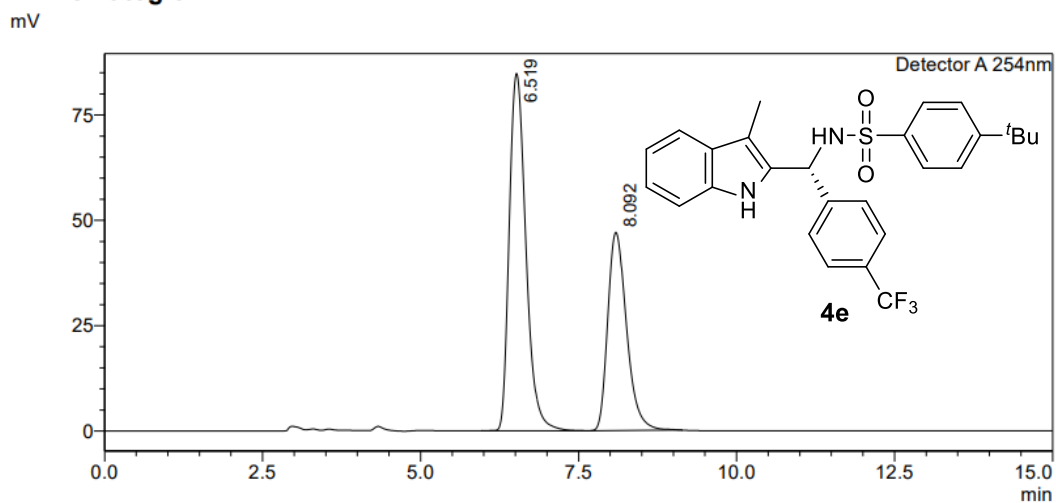


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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.523	4414048	240529	49.961			
2	8.084	4420953	211675	50.039		V	
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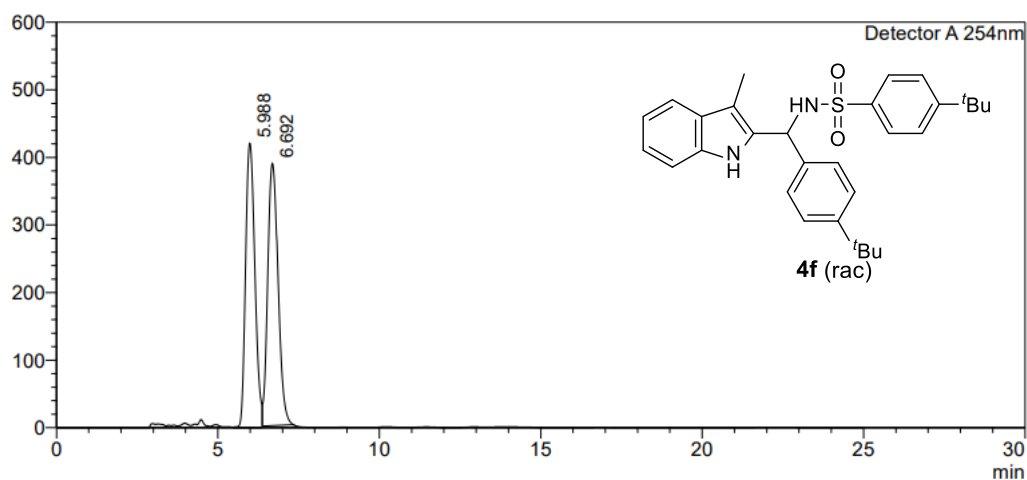
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.519	1560310	84768	61.577			
2	8.092	973605	47024	38.423		M	
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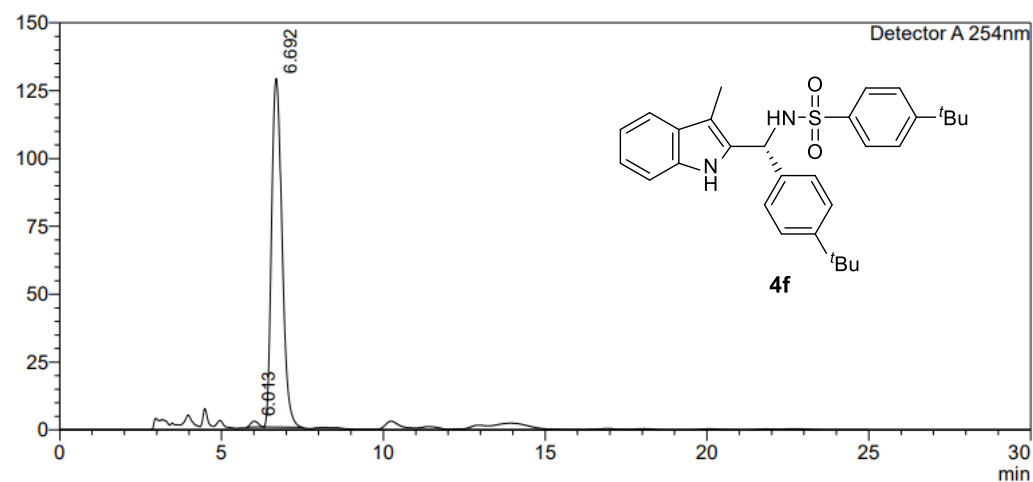
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Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.988	8507833	421411	49.752			
2	6.692	8592786	387889	50.248		M	
Total		17100619	809301				

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mV

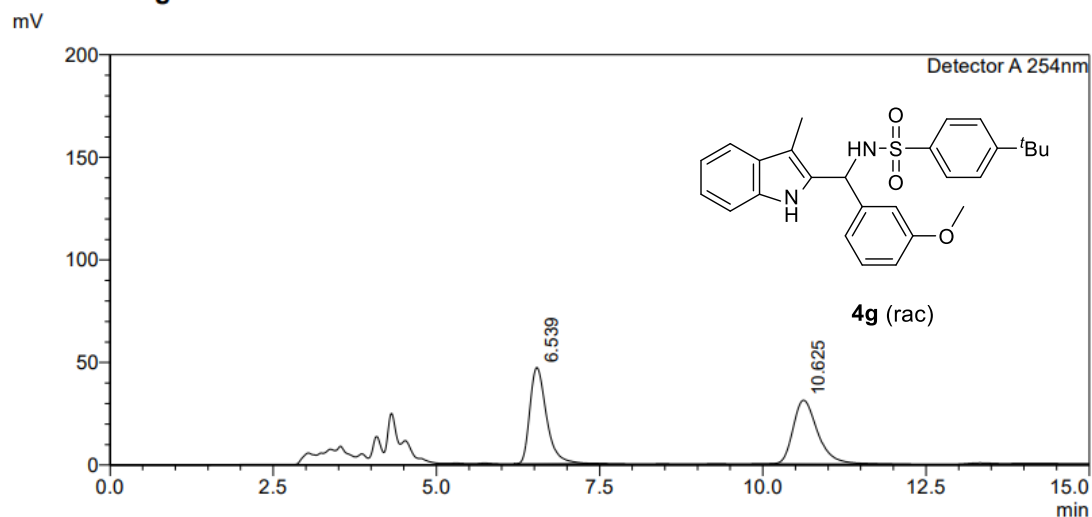


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.013	32764	2102	1.130		M	
2	6.692	2866304	128407	98.870		M	
Total		2899068	130509				

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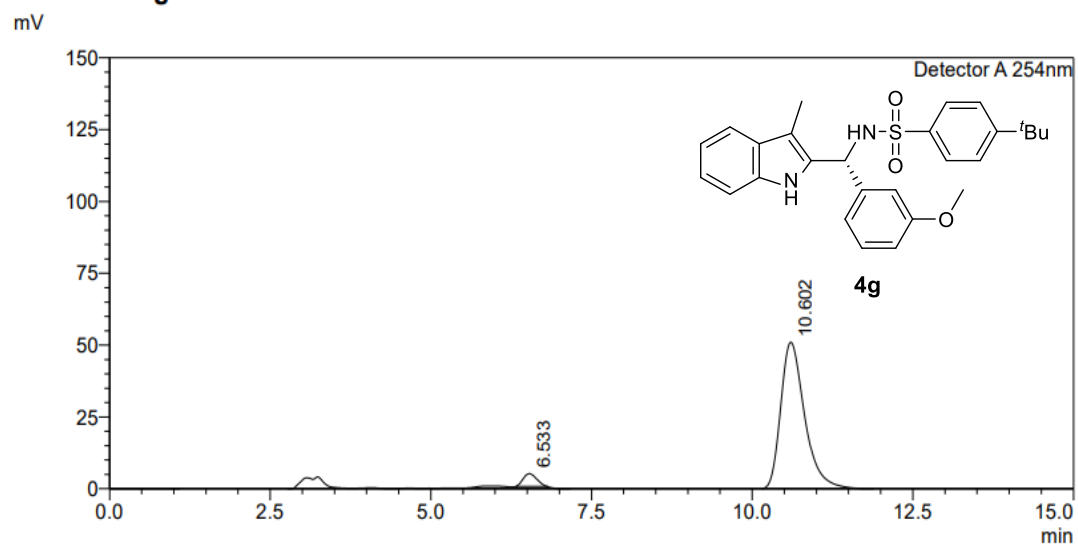


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.539	840319	46919	50.517			
2	10.625	823129	31136	49.483			
Total		1663448	78055				

<Chromatogram>



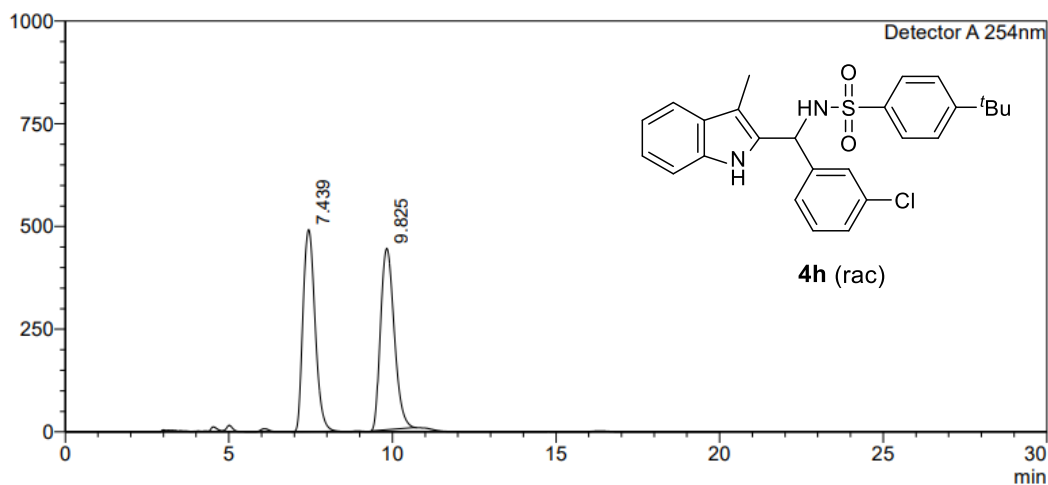
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.533	65812	4444	4.659		M	
2	10.602	1346804	51227	95.341			
Total		1412616	55670				

<Chromatogram>

mV



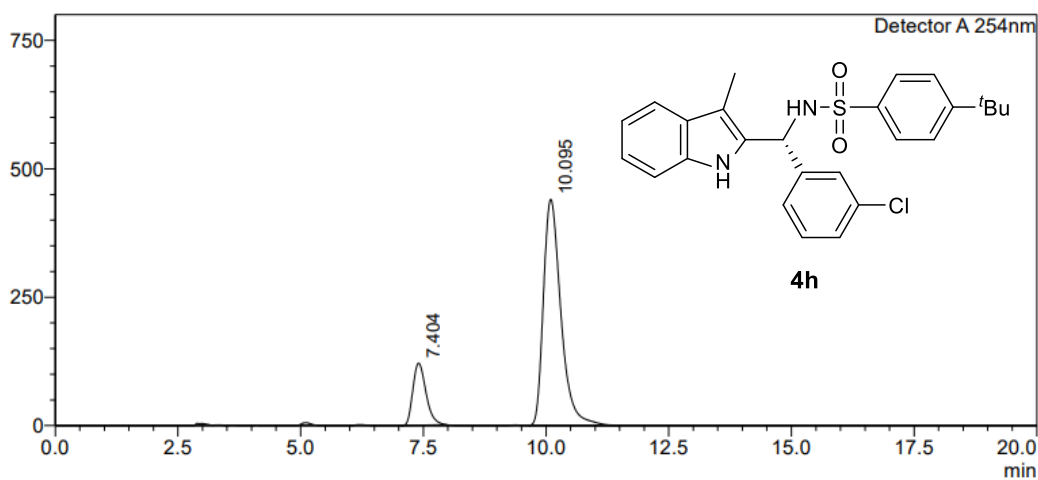
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.439	12723406	491048	49.677		M	
2	9.825	12888876	441379	50.323		M	
Total		25612283	932427				

<Chromatogram>

mV

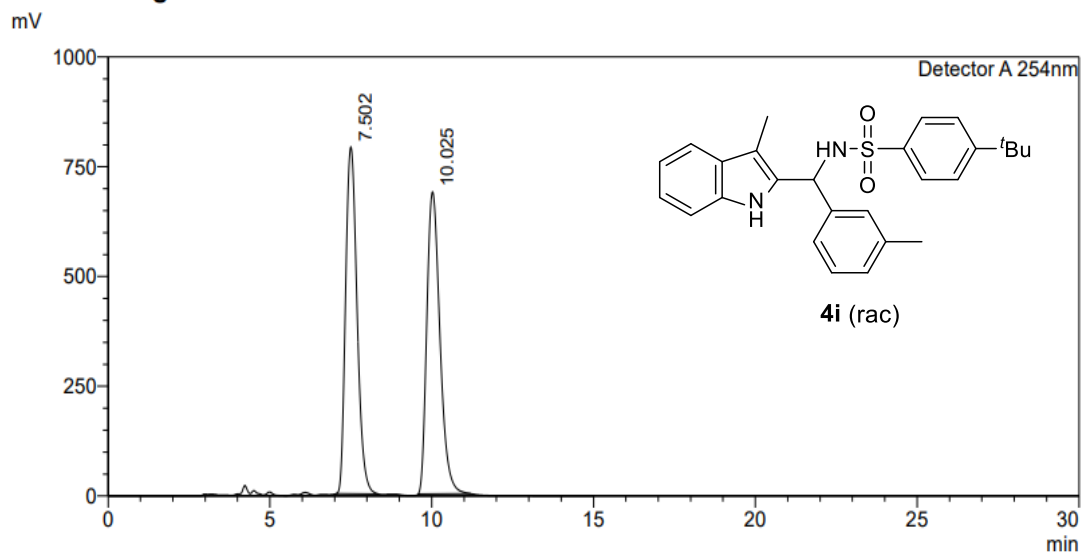


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.404	2245794	120742	17.085		M	
2	10.095	10899209	440154	82.915		M	
Total		13145003	560896				

<Chromatogram>

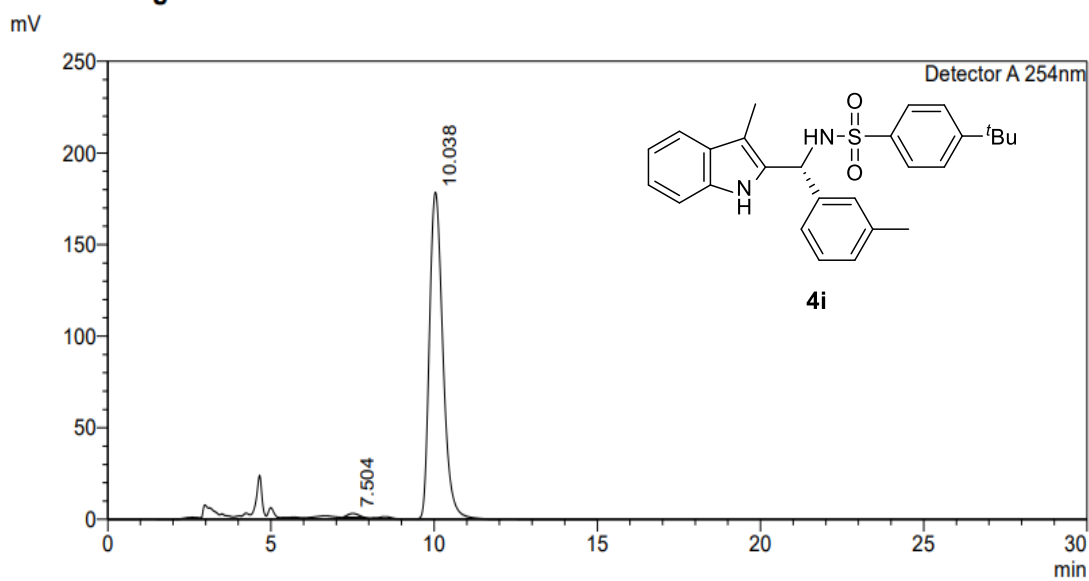


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.502	19466457	789751	50.069		M	
2	10.025	19412447	687685	49.931		M	
Total		38878905	1477436				

<Chromatogram>

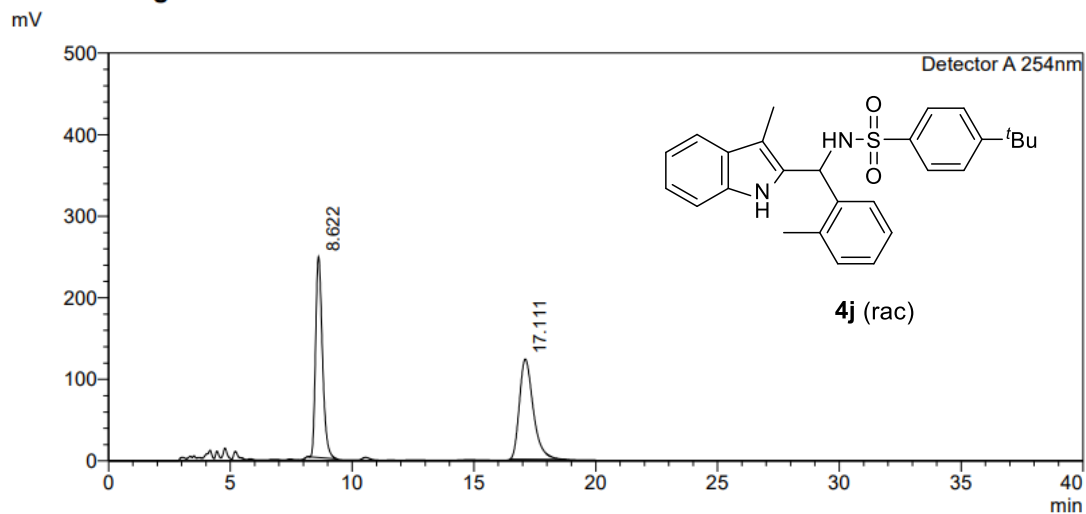


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.504	43765	1978	0.851		M	
2	10.038	5099312	178229	99.149		M	
Total		5143077	180207				

<Chromatogram>

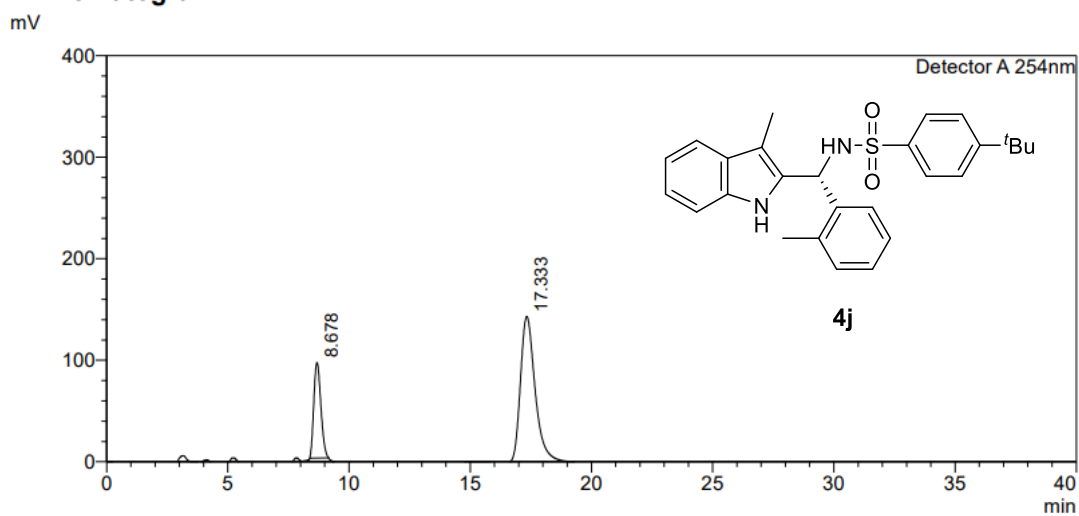


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.622	4797057	246295	49.745		M	
2	17.111	4846278	122818	50.255		M	
Total		9643335	369113				

<Chromatogram>



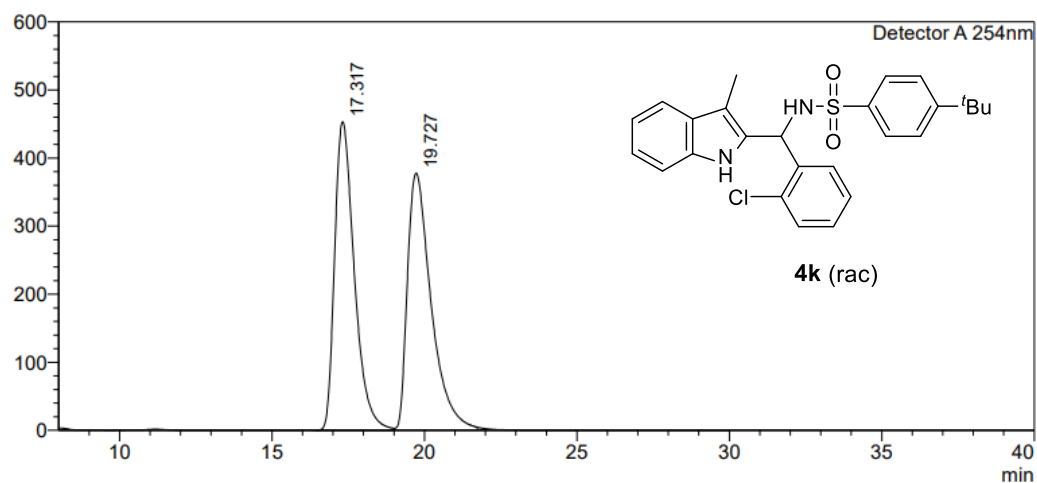
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.678	1902850	94163	23.564		M	
2	17.333	6172266	144234	76.436			
Total		8075116	238397				

<Chromatogram>

mV



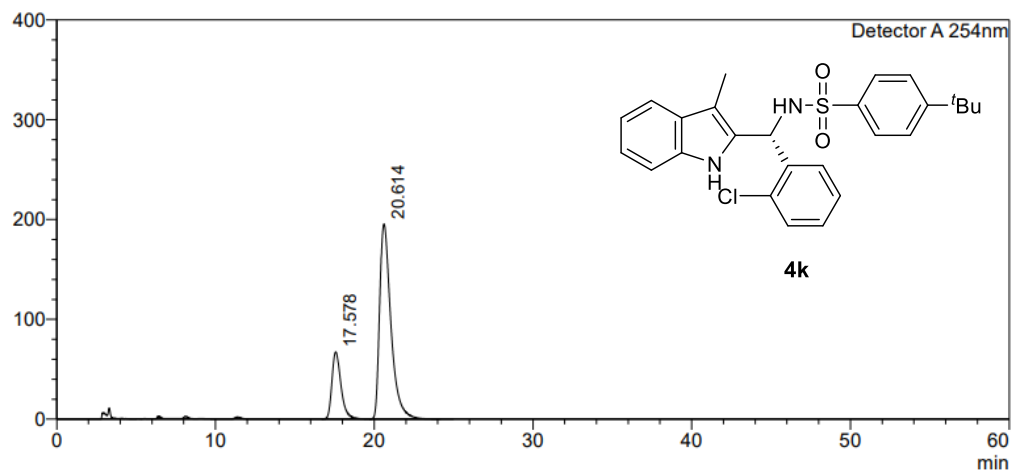
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.317	20339655	453218	49.630			
2	19.727	20642965	379021	50.370		M	
Total		40982621	832239				

<Chromatogram>

mV



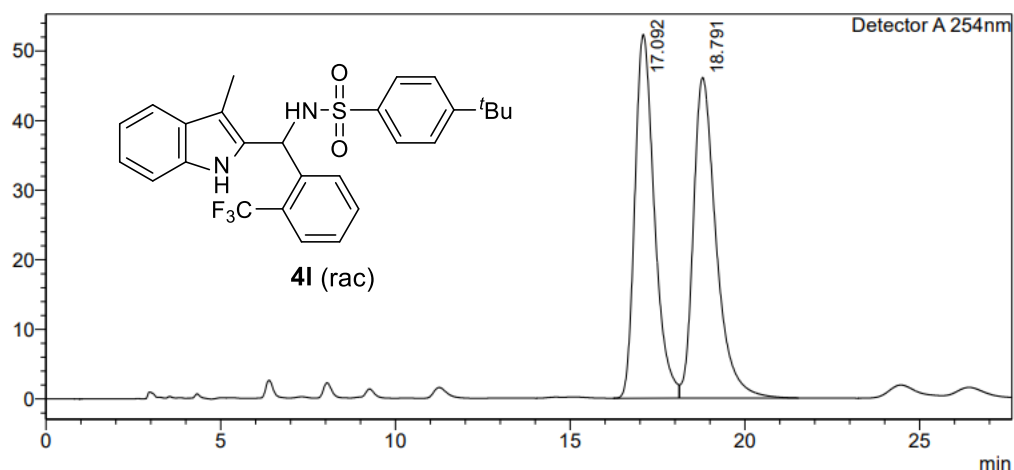
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.578	2666656	67374	21.651			
2	20.614	9649865	195499	78.349		V	
Total		12316521	262873				

<Chromatogram>

mV



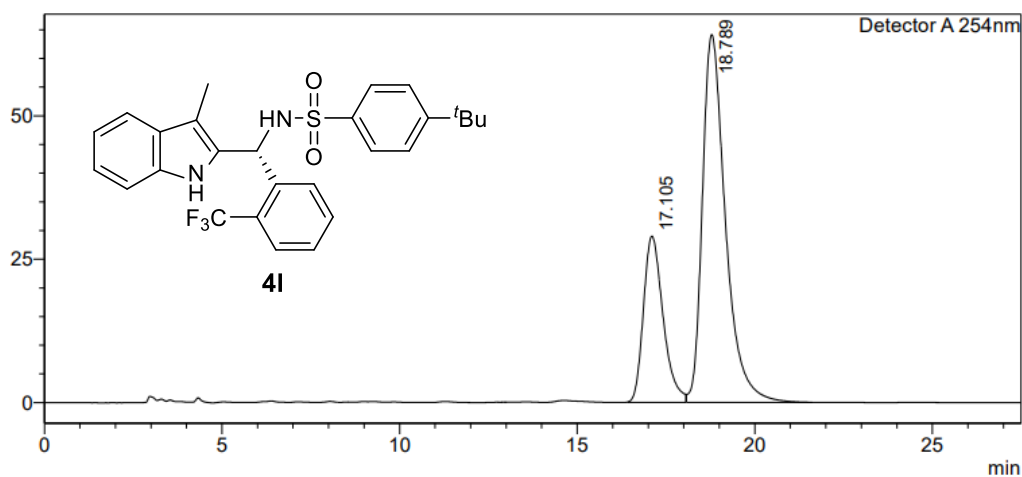
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.092	2021725	52254	49.208			
2	18.791	2086825	46063	50.792		V	
Total		4108550	98317				

<Chromatogram>

mV

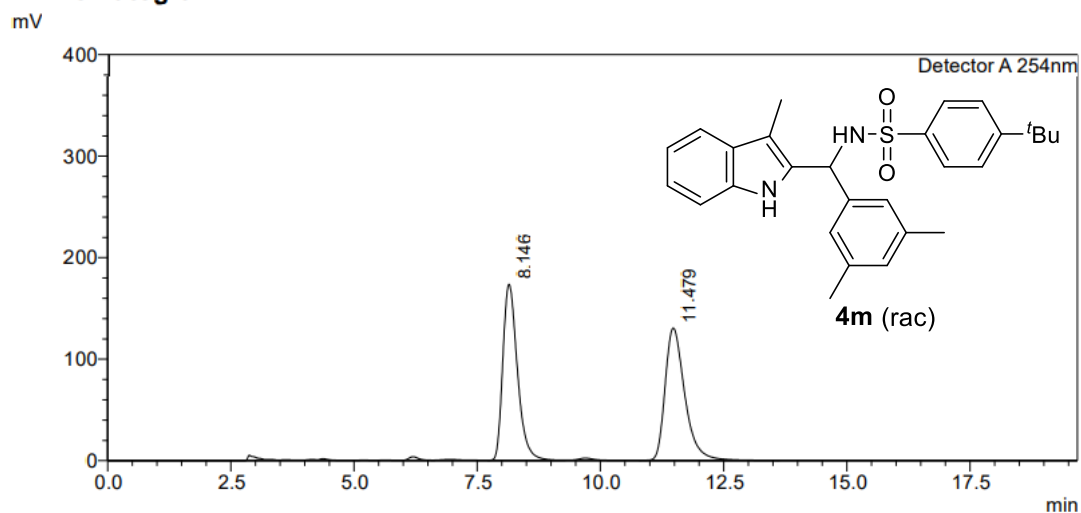


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.105	1117601	28987	27.838		M	
2	18.789	2897030	64094	72.162			
Total		4014631	93082				

<Chromatogram>

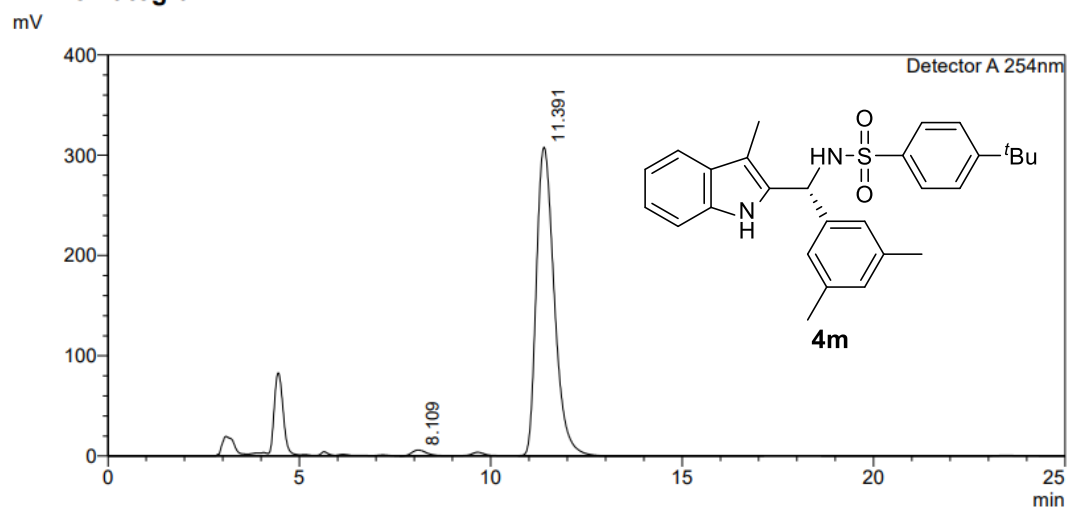


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.146	3580653	173543	49.834			
2	11.479	3604476	130191	50.166			
Total		7185129	303734				

<Chromatogram>



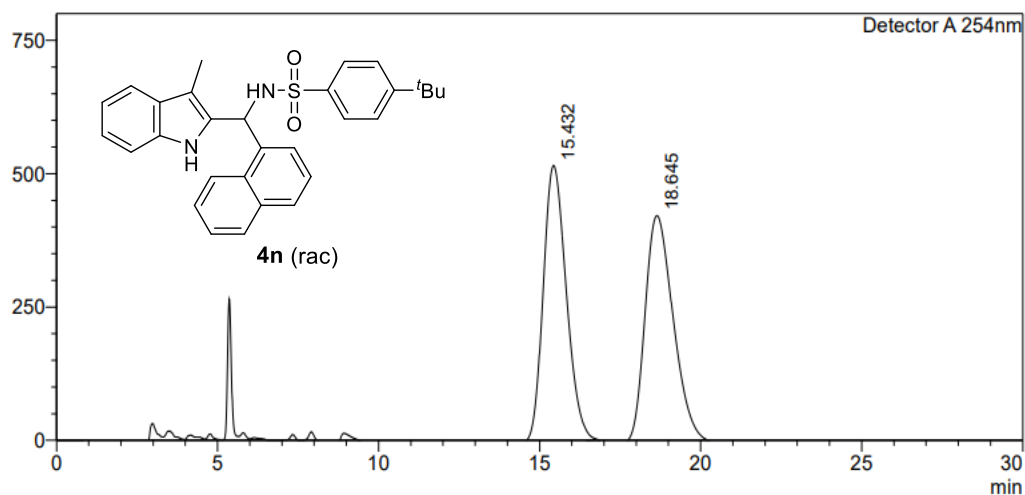
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.109	153888	5754	1.507			
2	11.391	10054603	308083	98.493			
Total		10208491	313837				

<Chromatogram>

mV



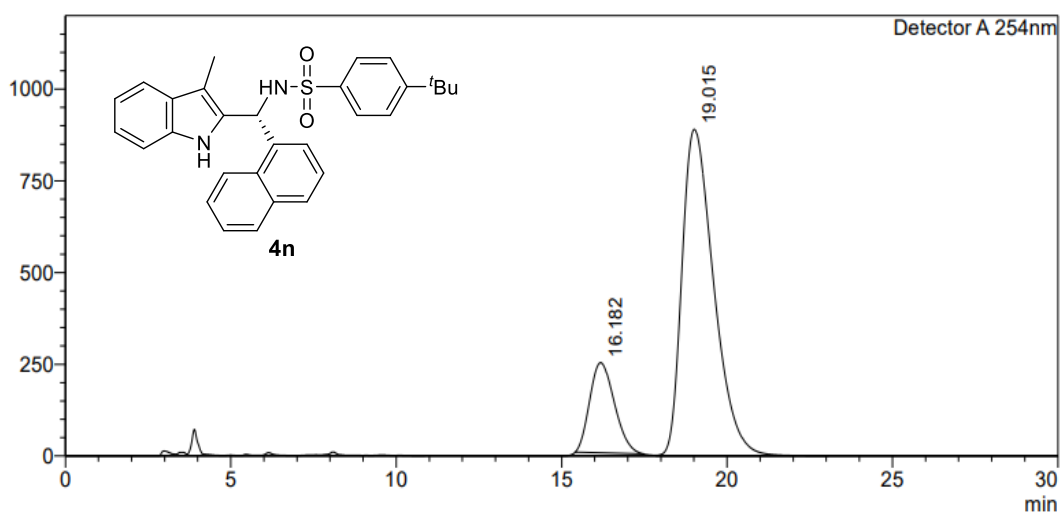
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.432	25658547	516778	49.901		M	
2	18.645	25760306	424256	50.099		M	
Total		51418853	941033				

<Chromatogram>

mV



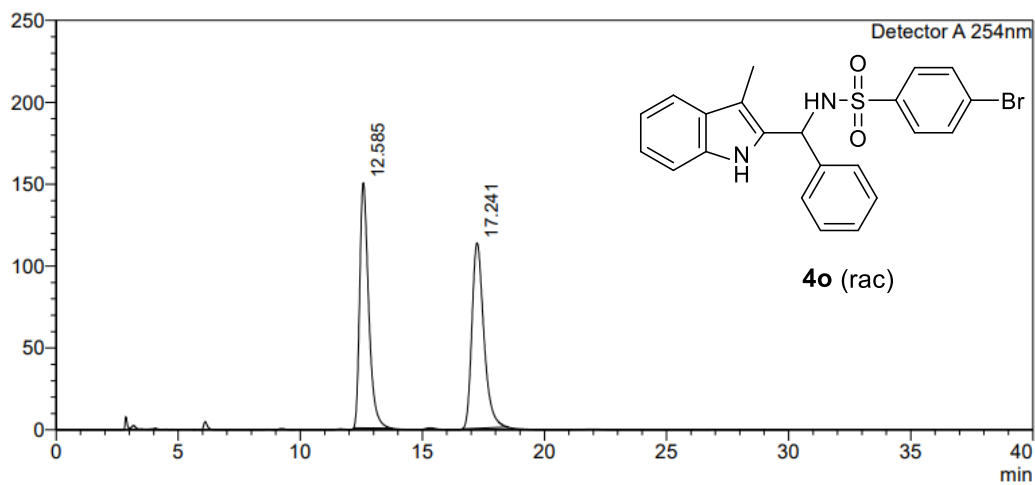
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.182	12791990	245814	17.735		M	
2	19.015	59336281	889954	82.265		M	
Total		72128271	1135767				

<Chromatogram>

mV



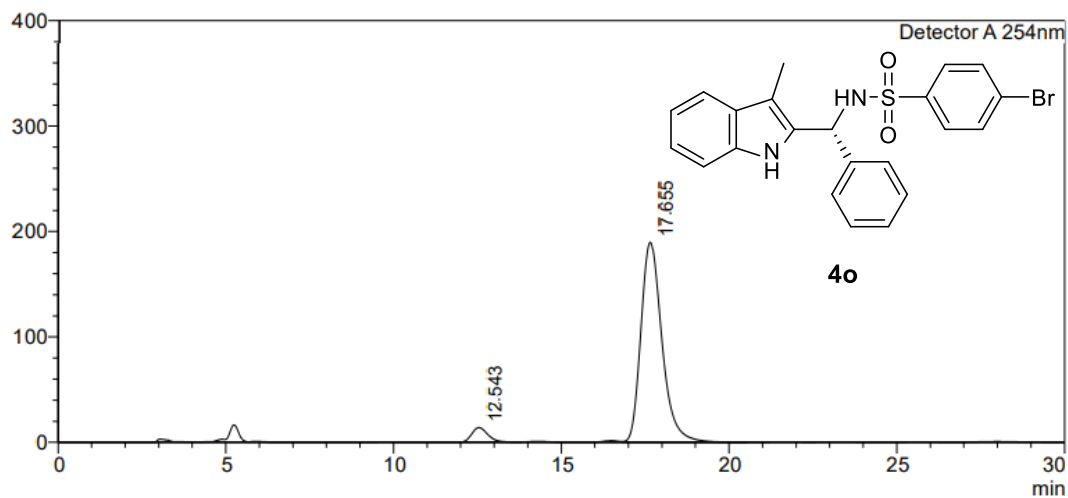
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.585	3819779	149588	49.806		M	
2	17.241	3849548	113227	50.194		M	
Total		7669327	262815				

<Chromatogram>

mV



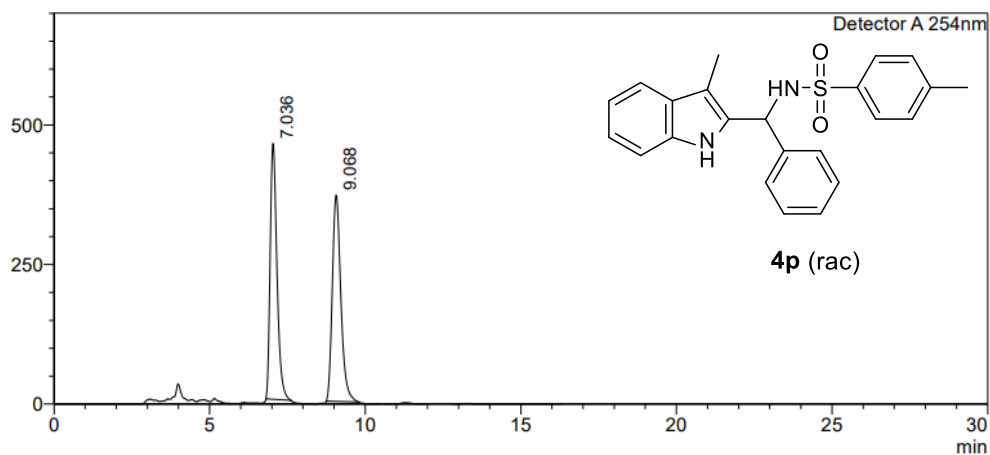
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.543	437257	13578	5.027		M	
2	17.655	8261421	189611	94.973			
Total		8698678	203188				

<Chromatogram>

mV



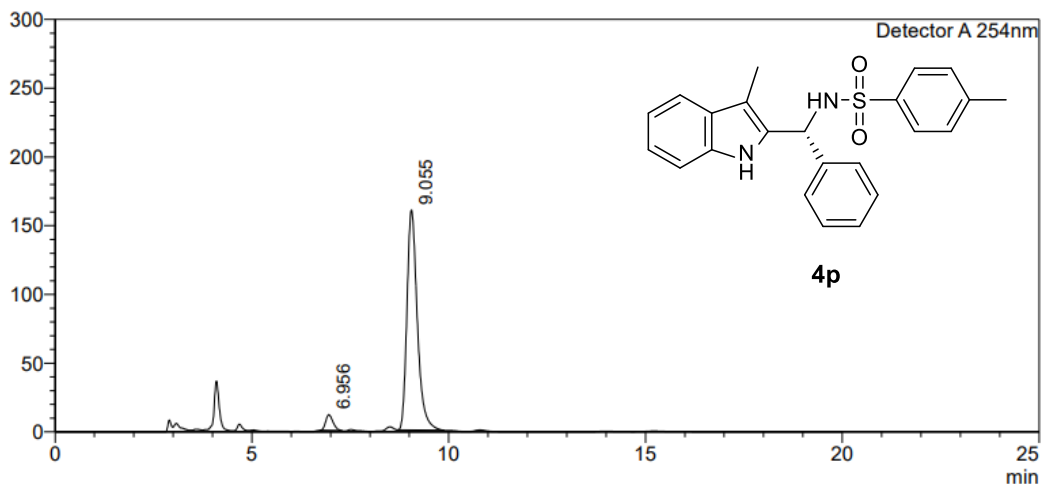
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.036	6960595	458111	49.662		M	
2	9.068	7055306	369343	50.338		M	
Total		14015901	827454				

<Chromatogram>

mV



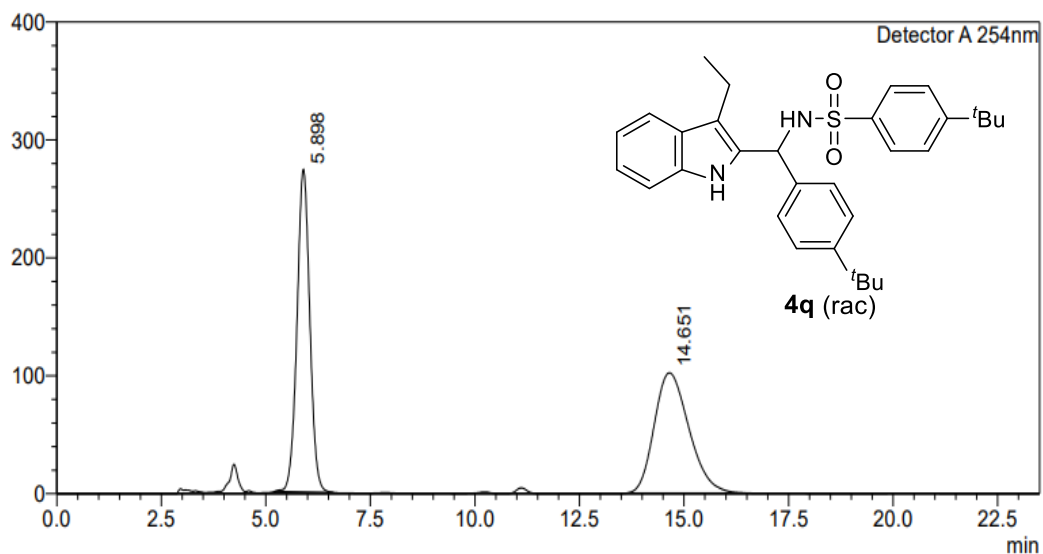
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.956	146143	11323	4.750		M	
2	9.055	2930431	160006	95.250		M	
Total		3076574	171329				

<Chromatogram>

mV



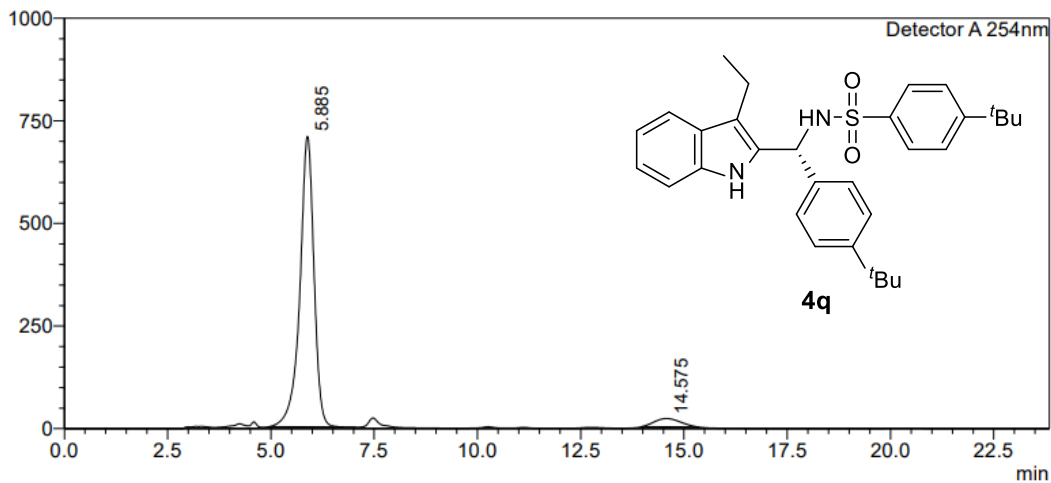
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.898	5803967	273391	49.728		M	
2	14.651	5867423	101895	50.272		M	
Total		11671391	375286				

<Chromatogram>

mV



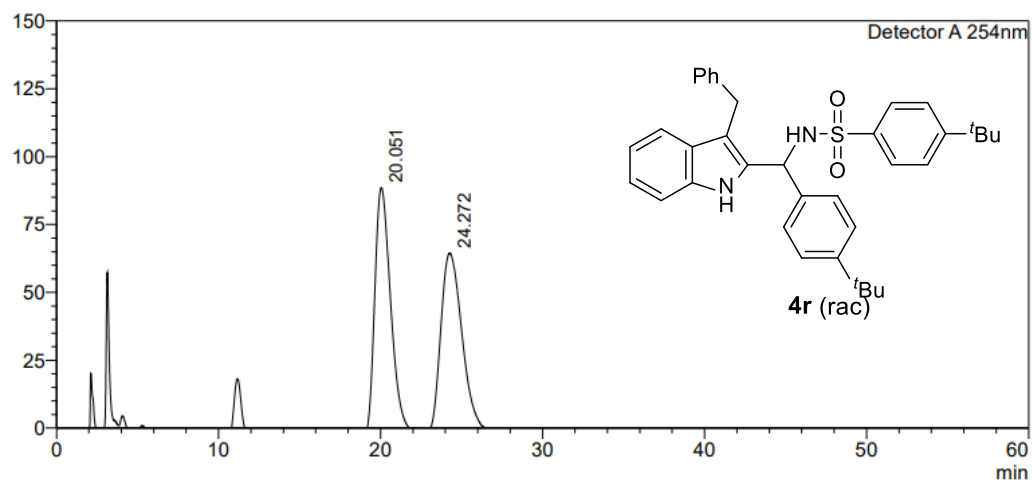
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.885	16806228	707575	95.101		M	
2	14.575	865805	19997	4.899		M	
Total		17672033	727573				

<Chromatogram>

mV



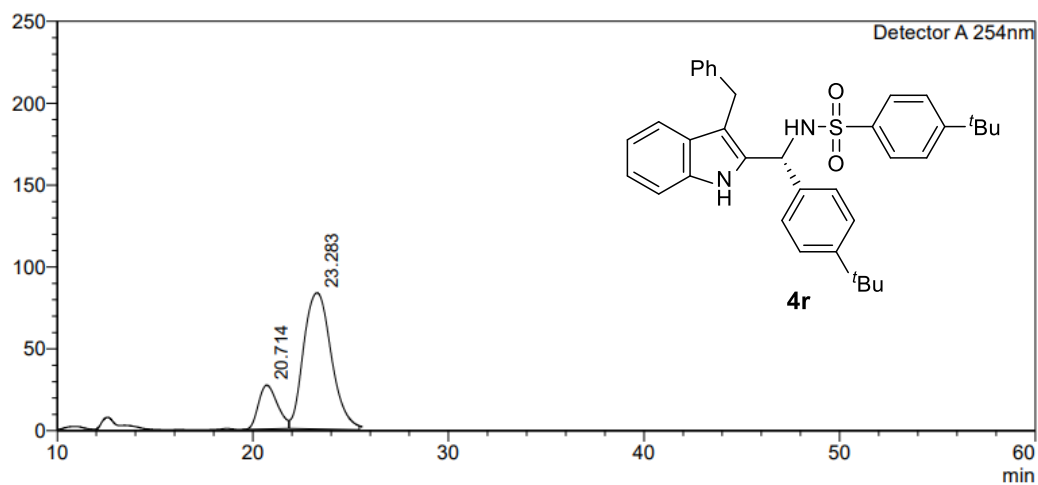
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.051	6321581	91383	49.938			
2	24.272	6337236	67263	50.062		V	
Total		12658817	158647				

<Chromatogram>

mV



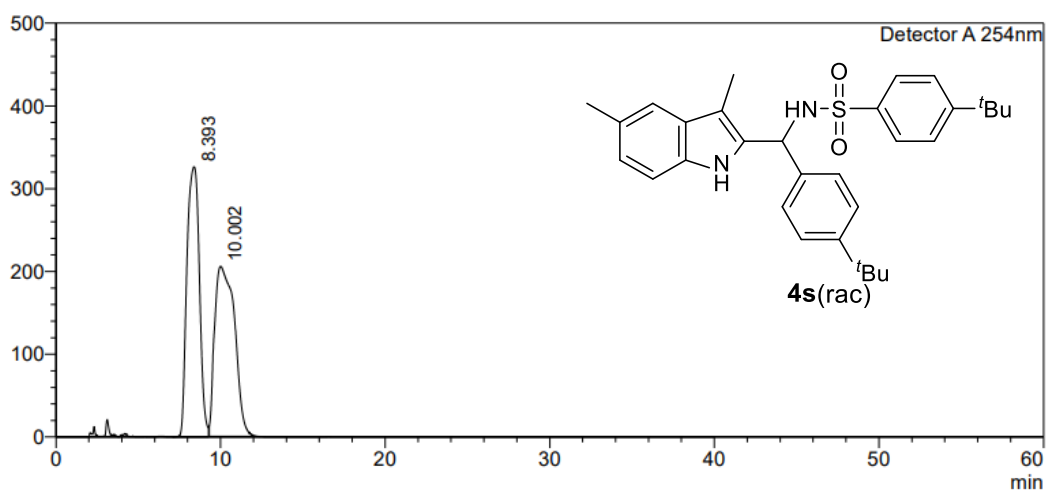
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.714	1807023	26839	18.016			
2	23.283	8223092	83169	81.984		M	
Total		10030115	110008				

<Chromatogram>

mV



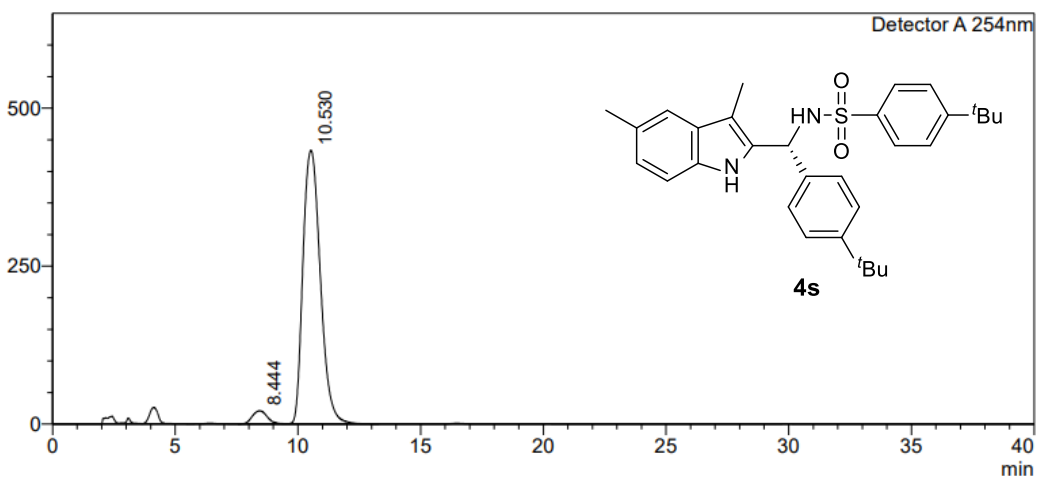
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.393	17172496	326349	49.934			
2	10.002	17217983	205277	50.066		M	
Total		34390479	531627				

<Chromatogram>

mV

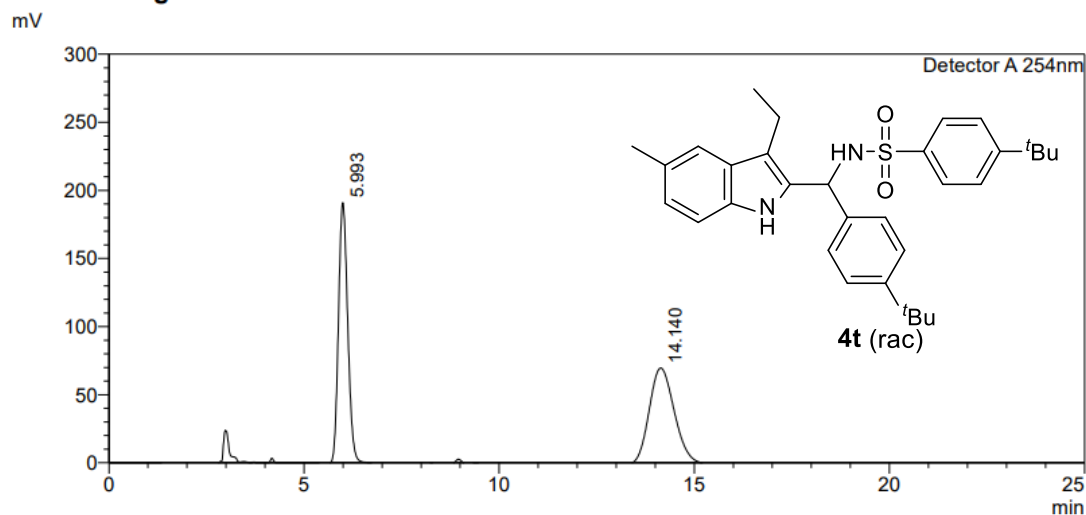


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.444	877806	20704	3.950			
2	10.530	21344485	433215	96.050		V	
Total		22222291	453918				

<Chromatogram>

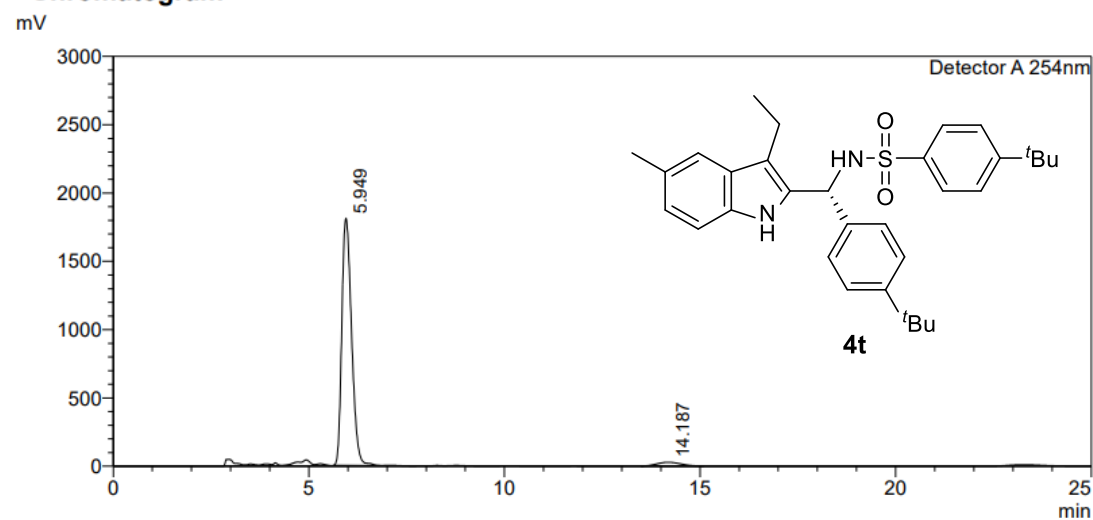


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.993	3162267	191407	49.825			
2	14.140	3184522	70668	50.175		M	
Total		6346789	262075				

<Chromatogram>

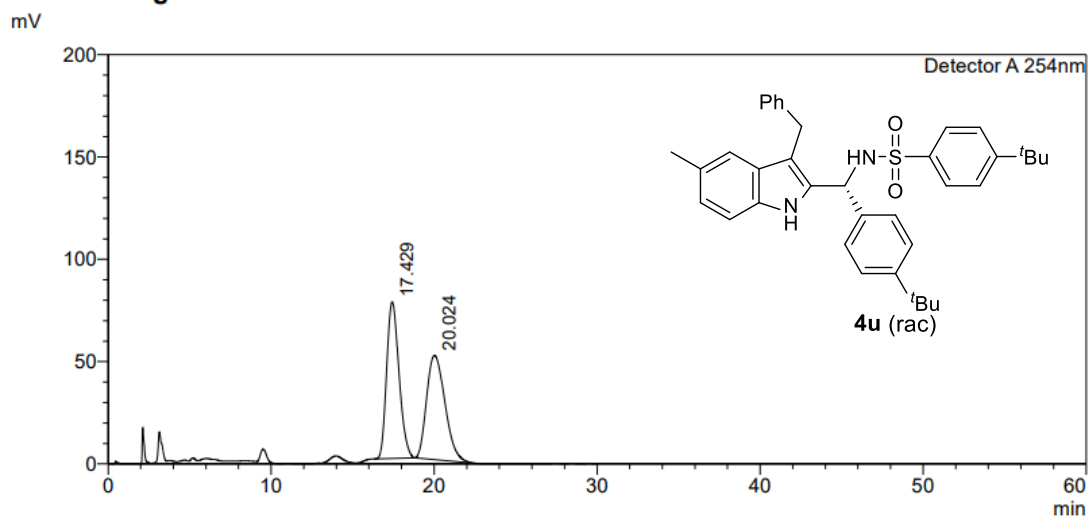


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.949	31292990	1806573	96.310		M	
2	14.187	1199073	27998	3.690		M	
Total		32492064	1834570				

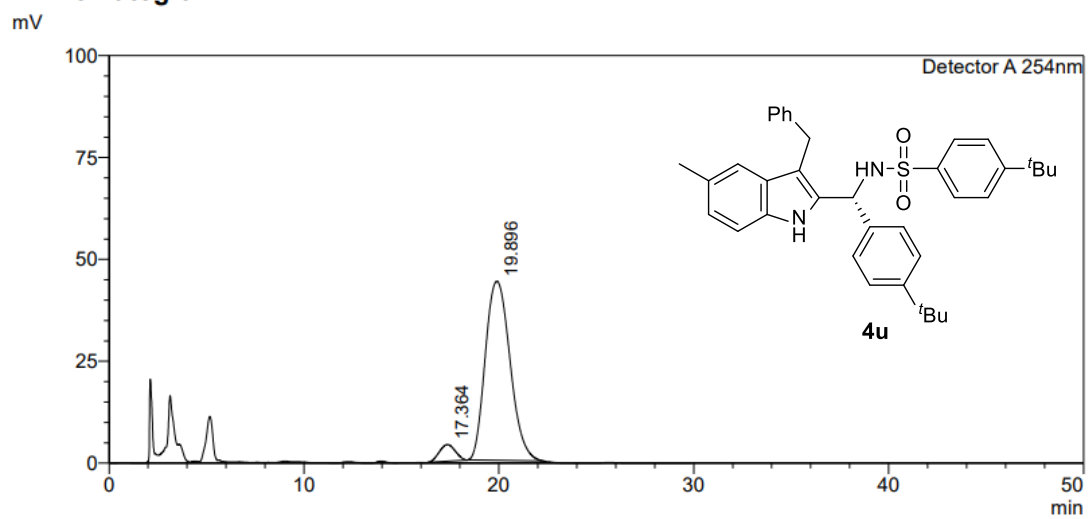
<Chromatogram>



<Peak Table>

Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.429	4027933	76549	50.173		M	
2	20.024	4000111	50973	49.827		M	
Total		8028044	127522				

<Chromatogram>

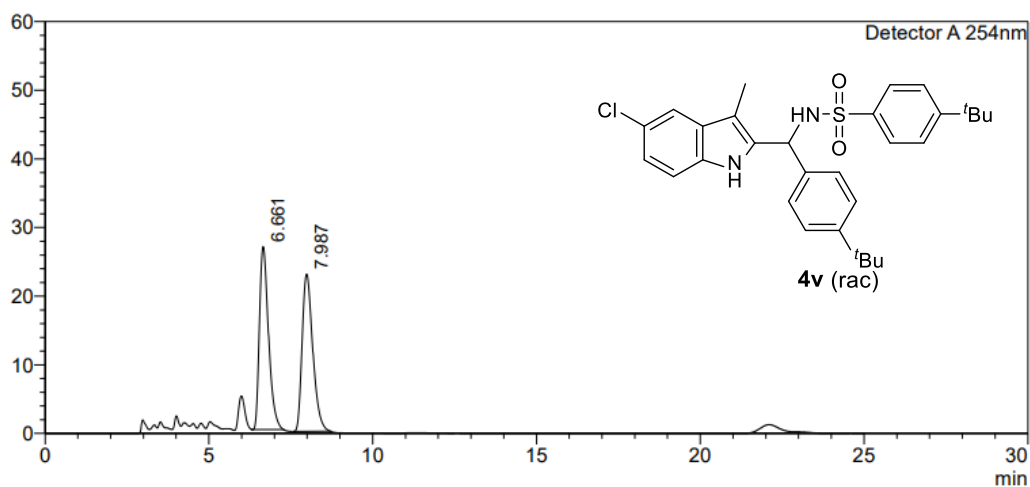


<Peak Table>

Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.364	231179	4072	5.624		M	
2	19.896	3879687	43925	94.376		M	
Total		4110866	47997				

<Chromatogram>

mV



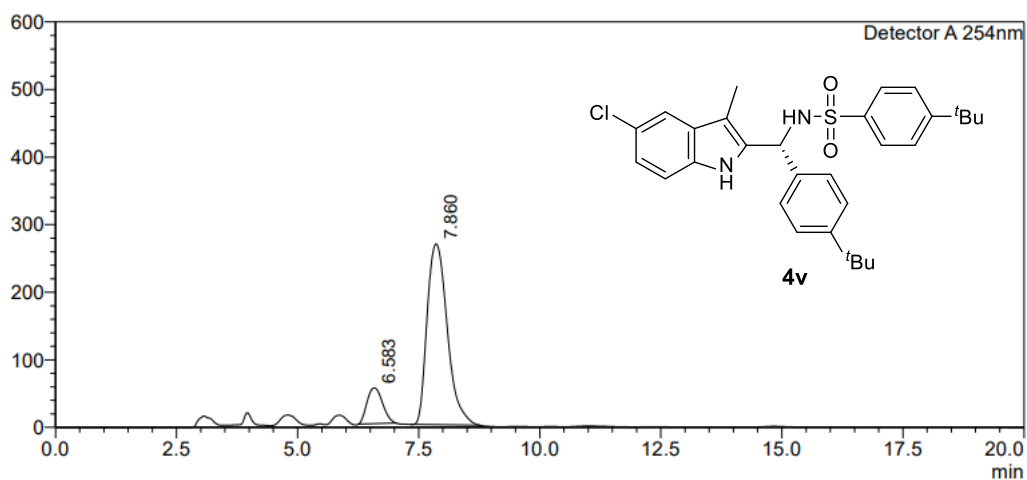
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.661	510393	26608	49.724		M	
2	7.987	516052	22926	50.276		M	
Total		1026445	49534				

<Chromatogram>

mV



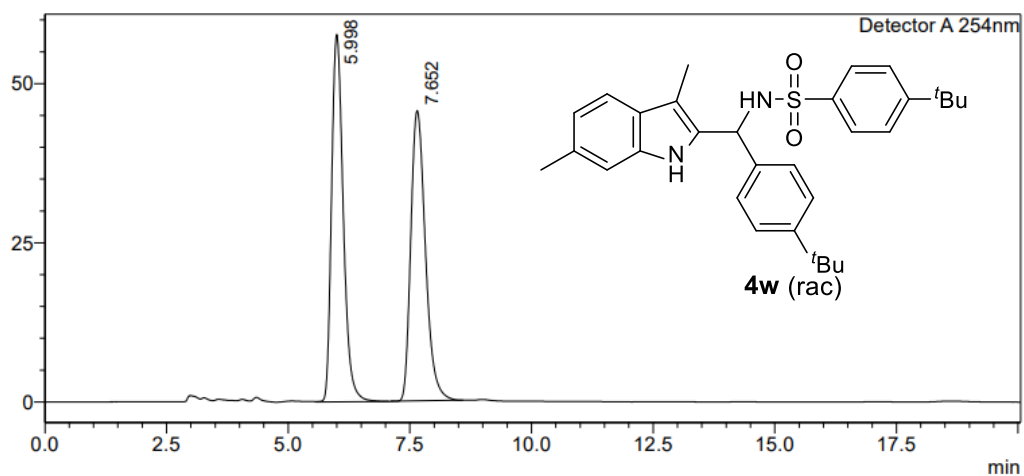
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.583	1185163	53049	13.237		M	
2	7.860	7768545	267504	86.763		M	
Total		8953708	320554				

<Chromatogram>

mV



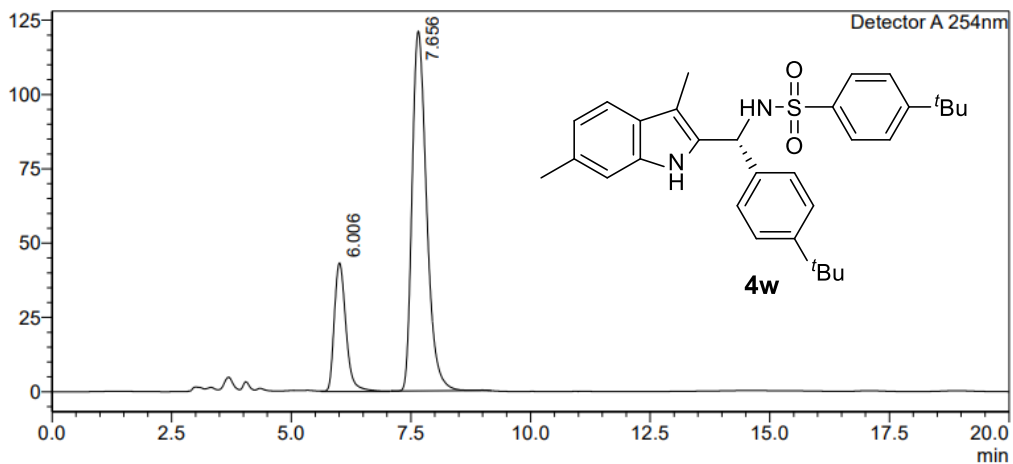
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.998	963955	57646	50.364			
2	7.652	950025	45616	49.636			
Total		1913980	103262				

<Chromatogram>

mV



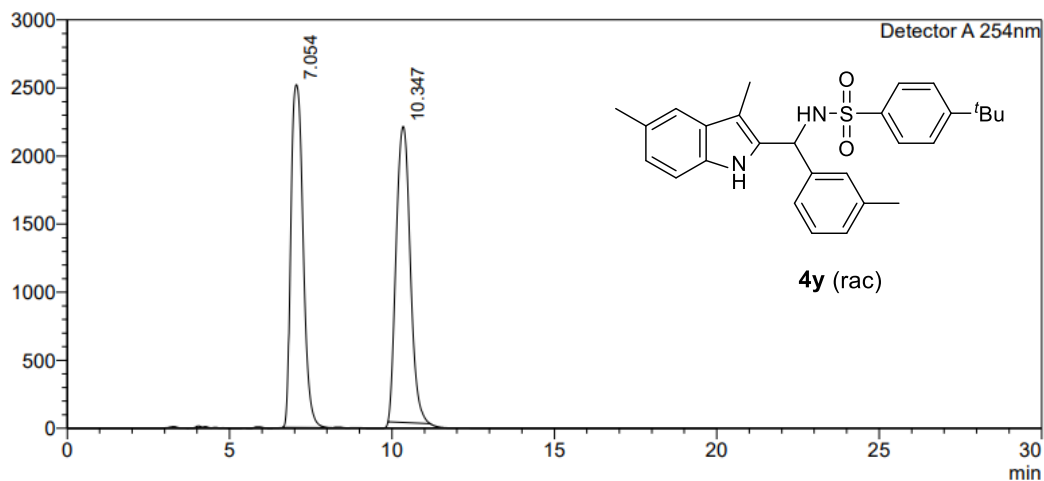
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.006	739163	43297	22.432			
2	7.656	2555937	121028	77.568		M	
Total		3295100	164325				

<Chromatogram>

mV



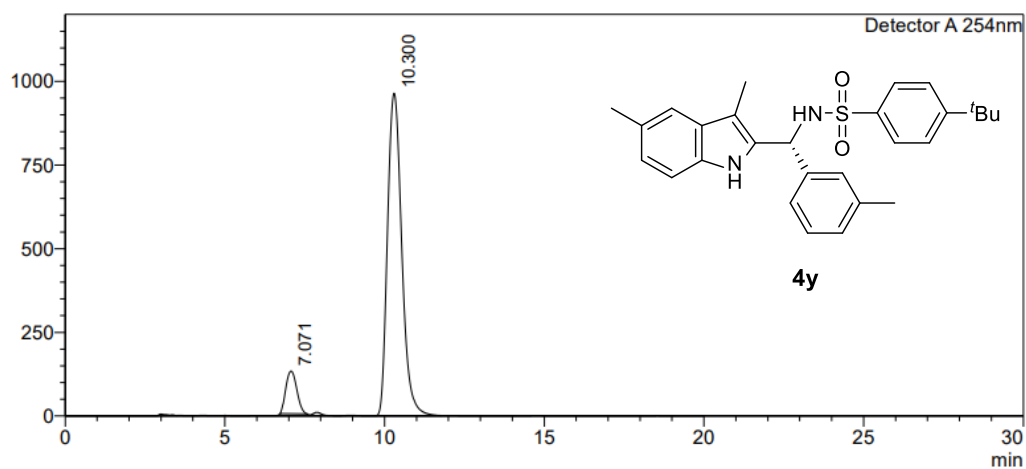
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.054	65676335	2517889	49.929		M	
2	10.347	65864049	2173190	50.071		M	
Total		131540384	4691079				

<Chromatogram>

mV



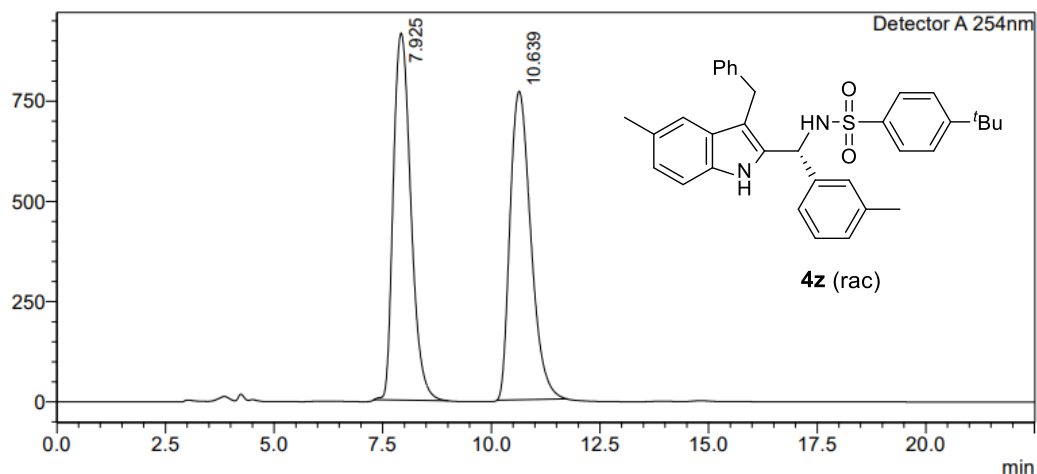
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.071	3013615	126872	9.153		M	
2	10.300	29910455	963728	90.847		M	
Total		32924070	1090599				

<Chromatogram>

mV



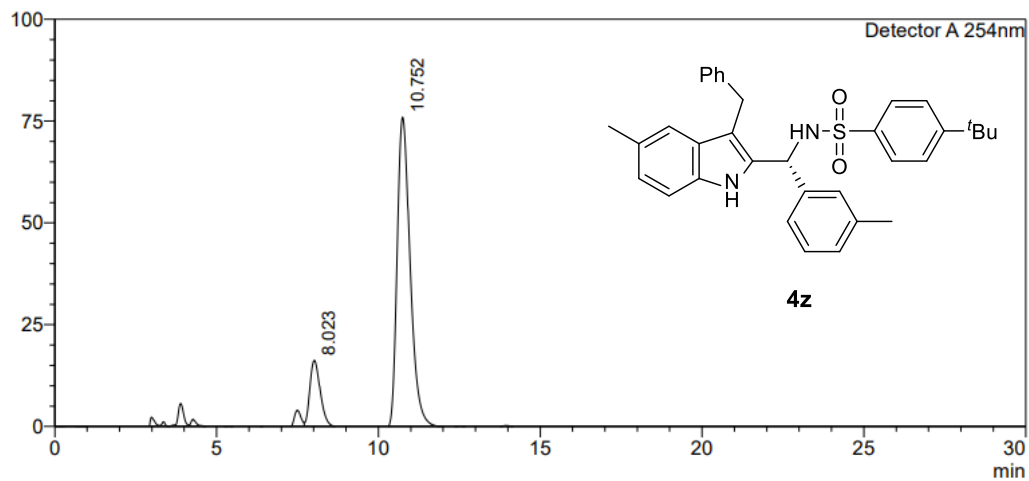
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.925	25712301	914834	50.127		M	
2	10.639	25581722	768991	49.873		M	
Total		51294023	1683825				

<Chromatogram>

mV



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.023	377450	16508	15.144			
2	10.752	2114940	76158	84.856		M	
Total		2492390	92666				