

Electronic Supplementary Information for:

Development of TsDPEN based Imine-containing Ligands for the Copper-Catalyzed Asymmetric Kinugasa Reaction

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CONTENTS :

1. Detailed results for Figure 2.	S2
2. The structure of the Cu complex optimized by DFT.	S3
3. Copies of HPLC charts	S11
4. Copies of NMR spectra	S30

1. Detailed results for Figure 2.

		L1	L2	L3a	L3b	L3c	L3d
Cu(OAc) ₂	Yield (%)	N.R.	16	88	97	86	80
	<i>cis/trans</i>	-	32.3:1	5.7:1	5.7:1	5.7:1	4.6:1
	<i>ee (cis)</i> (%)	-	9	81	83	78	78
Cu(OTf) ₂	Yield (%)	26	17		90		
	<i>cis/trans</i>	6.7:1	15.7:1		5.3:1		
	<i>ee (cis)</i> (%)	39	27		82		
Cu(ClO ₄) ₂	Yield (%)	13	69		91		
	<i>cis/trans</i>	8.1:1	6.1:1		5.3:1		
	<i>ee (cis)</i> (%)	15	35		82		
CuSO ₄	Yield (%)	N.R.	16		47		
	<i>cis/trans</i>	-	19:1		5.3:1		
	<i>ee (cis)</i> (%)	-	22		82		
CuOAc	Yield (%)	N.R.	30		94		
	<i>cis/trans</i>	-	6.1:1		5.7:1		
	<i>ee (cis)</i> (%)	-	10		82		
CuOTf	Yield (%)	34	31		27		
	<i>cis/trans</i>	5.7:1	19:1		8.1:1		
	<i>ee (cis)</i> (%)	24	36		24		
CuI	Yield (%)	97	95		90		
	<i>cis/trans</i>	4.9:1	5.3:1		4.3:1		
	<i>ee (cis)</i> (%)	0	6		54		

2. The structure of the Cu complex optimized by DFT.

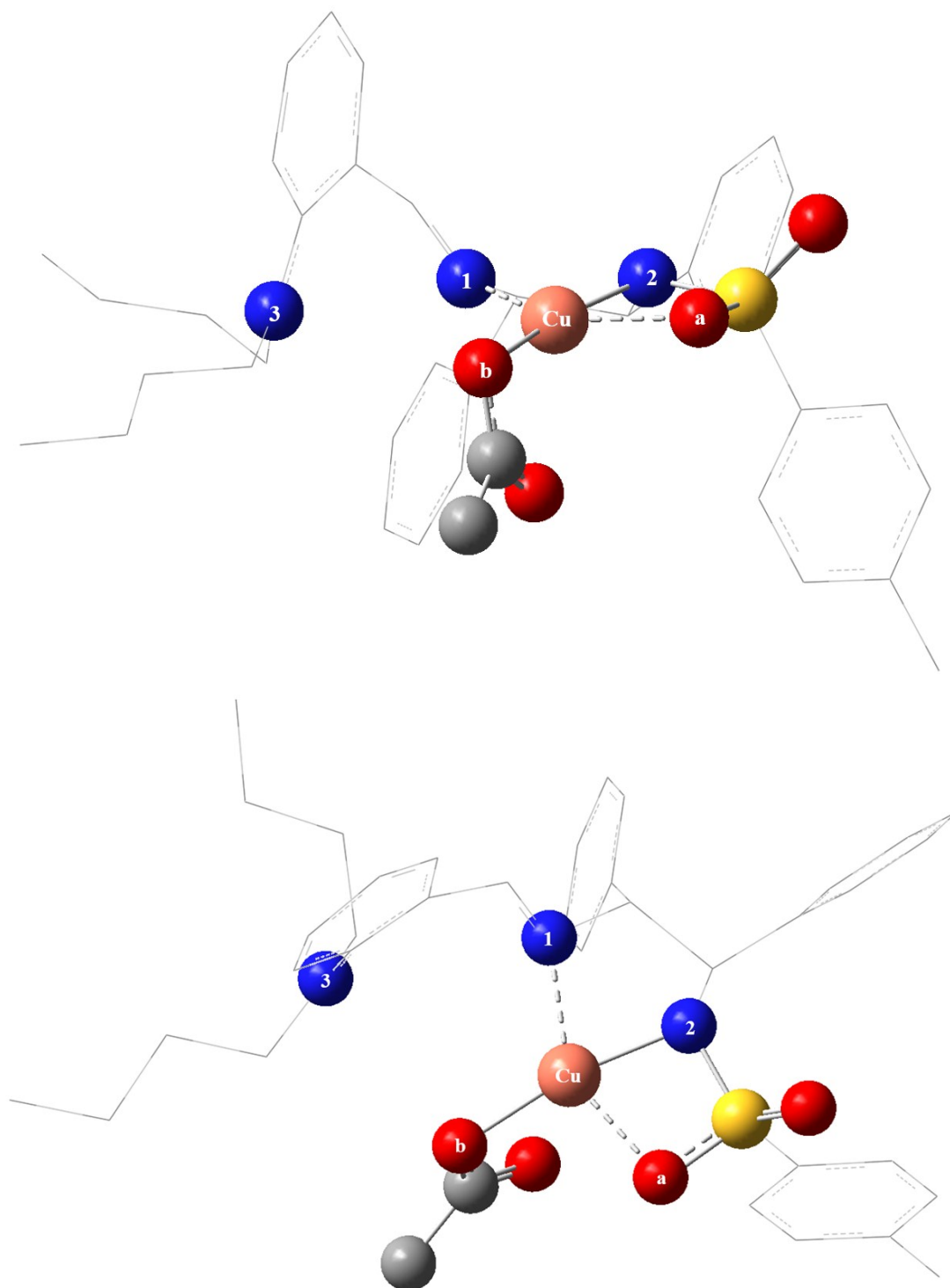


Figure S1. The geometry of Cu/L3b optimized by density functional theory (DFT)

Computational Methods: DFT calculations were carried out using the Gaussian 09 software package^[1]. Considering both the desired precision of structures and available

computer resources, the geometry optimizations were performed using the Becke's three-parameter nonlocal exchange function^[2] and the Lee, Yang, and Parr nonlocal correlation function (LYP)^[3] at a mixed basis set level. The SDD basis set with the associated effective core potential was used for Cu, while the 6-31G(d) basis set^[4] was used for all other atoms (C, H, O, N, S). The final optimized structure of Cu complex was obtained with no imaginary frequencies, which indicates that it is a stable structure. B3LYP energy of this structure is -2535.028607 a.u. after adding the zero-point correction.

Selected bond length (nm)

Cu-N ₁	Cu-N ₂	Cu-N ₃	Cu-O _a	Cu-O _b
0.2124	0.1932	0.3925	0.2196	0.1938

Frequencies for the final optimized structure of Cu complex

Numbers	Frequencies	Numbers	Frequencies	Numbers	Frequencies
1	11.14	91	756.44	181	1394.10
2	13.22	92	761.65	182	1395.47
3	5.48	93	769.91	183	1398.38
4	23.25	94	779.00	184	1400.68
5	26.10	95	799.82	185	1403.91
6	28.92	96	804.20	186	1419.13
7	33.30	97	820.81	187	1423.78
8	35.58	98	829.46	188	1442.07
9	37.00	99	836.32	189	1442.80
10	38.12	100	851.27	190	1443.87
11	43.83	101	854.67	191	1446.64
12	44.89	102	862.79	192	1447.88
13	48.40	103	867.37	193	1448.25
14	53.97	104	868.68	194	1461.04

[1] M. J. Frisch, G. W. , H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox. Gaussian 09, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.

[2] W. Kohn, A. D. Becke, R. G. Parr, *J. Phys. Chem.* **1996**, *100*, 12974-12980.

[3] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[4] P. C. Hariharan, J. A. Pople, *Theoretica. Chimica. Acta.* **1973**, *28*, 213-222.

15	57.85	105	870.51	195	1493.53
16	62.64	106	876.25	196	1501.62
17	66.40	107	897.03	197	1501.83
18	70.40	108	917.00	198	1502.91
19	73.06	109	929.46	199	1507.87
20	76.52	110	937.24	200	1510.48
21	80.61	111	942.20	201	1516.36
22	89.89	112	943.26	202	1517.93
23	96.66	113	946.46	203	1520.15
24	100.65	114	960.53	204	1521.70
25	106.02	115	972.78	205	1522.46
26	118.23	116	977.66	206	1527.41
27	132.74	117	980.41	207	1530.41
28	141.01	118	982.26	208	1531.85
29	150.19	119	989.53	209	1536.60
30	151.28	120	992.51	210	1538.63
31	162.14	121	996.69	211	1542.95
32	164.18	122	1000.06	212	1545.07
33	183.17	123	1001.54	213	1545.20
34	187.87	124	1003.64	214	1546.99
35	203.47	125	1007.93	215	1558.98
36	206.76	126	1016.18	216	1599.62
37	216.12	127	1017.84	217	1627.12
38	220.09	128	1021.61	218	1638.87
39	232.30	129	1033.16	219	1643.11
40	242.10	130	1034.52	220	1643.58
41	245.98	131	1038.06	221	1655.81
42	253.28	132	1039.15	222	1660.58
43	257.00	133	1041.75	223	1661.73
44	257.47	134	1057.19	224	1661.77
45	274.31	135	1061.28	225	1668.20
46	278.72	136	1063.43	226	3019.13
47	301.59	137	1068.06	227	3024.71
48	315.66	138	1074.99	228	3028.07
49	316.45	139	1077.32	229	3039.33

50	325.14	140	1086.97	230	3041.14
51	340.34	141	1106.83	231	3042.08
52	356.04	142	1110.77	232	3044.12
53	360.70	143	1119.07	233	3044.90
54	375.48	144	1127.33	234	3045.68
55	391.99	145	1137.68	235	3049.58
56	410.98	146	1144.11	236	3049.62
57	416.21	147	1153.09	237	3056.95
58	417.74	148	1154.71	238	3065.01
59	419.71	149	1155.71	239	3068.19
60	425.84	150	1192.06	240	3072.55
61	439.03	151	1193.59	241	3079.59
62	446.77	152	1194.28	242	3089.77
63	469.27	153	1200.58	243	3101.91
64	479.63	154	1209.47	244	3107.26
65	490.61	155	1215.89	245	3109.00
66	501.98	156	1219.24	246	3110.65
67	512.58	157	1220.71	247	3112.41
68	517.59	158	1224.70	248	3114.49
69	538.56	159	1226.10	249	3126.88
70	543.31	160	1234.10	250	3128.69
71	564.78	161	1240.02	251	3131.18
72	573.51	162	1259.17	252	3165.69
73	586.70	163	1264.66	253	3175.70
74	608.08	164	1270.69	254	3179.91
75	616.27	165	1276.61	255	3180.39
76	623.38	166	1297.26	256	3184.47
77	630.90	167	1305.95	257	3188.67
78	636.71	168	1320.33	258	3189.30
79	637.50	169	1326.07	259	3190.32
80	647.59	170	1329.46	260	3191.85
81	654.44	171	1341.05	261	3192.17
82	673.38	172	1342.47	262	3197.91
83	694.73	173	1345.96	263	3200.67
84	711.06	174	1347.31	264	3208.64

85	713.43	175	1356.87	265	3211.08
86	716.24	176	1364.65	266	3216.95
87	719.12	177	1365.66	267	3220.07
88	724.31	178	1369.63	268	3222.42
89	742.95	179	1373.62	269	3236.96
90	751.70	180	1380.11	270	3244.79

Computed energies for the final optimized structure of Cu complex

Energies	Absolute Energy Values (a.u.)
Zero-point correction	0.764186
Thermal correction to Energy	0.812414
Thermal correction to Enthalpy	0.813358
Thermal correction to Gibbs Free Energy	0.673572
Sum of electronic and zero-point Energies	-2535.028607
Sum of electronic and thermal Energies	-2534.980379
Sum of electronic and thermal Enthalpies	-2534.979435
Sum of electronic and thermal Free Energies	-2535.119221

Cartesian coordinates for the final optimized structure of Cu complex

Atoms	Coordinates (Angstroms)		
	X	Y	Z
C	0.72384500	1.70172900	-0.03469100
C	2.05864700	0.89985200	0.25049600
N	-0.45956500	0.93882400	0.44342400
C	3.17853000	1.85878400	0.63707900
C	0.57980000	2.05582400	-1.50652500
N	1.71298900	-0.08121500	1.27418400
C	-1.29611600	1.59599500	1.17539400
C	-2.51150800	1.12231300	1.83363600
C	-2.63287600	1.62560600	3.15276200
C	-3.56102500	1.13800300	4.05283300
C	-4.42915000	0.12732200	3.61655900
C	-4.40194700	-0.31905000	2.30695000
C	-3.48561700	0.19047500	1.34478300
N	-3.62645400	-0.17491400	0.02108100
C	0.41293500	1.05492800	-2.47823000

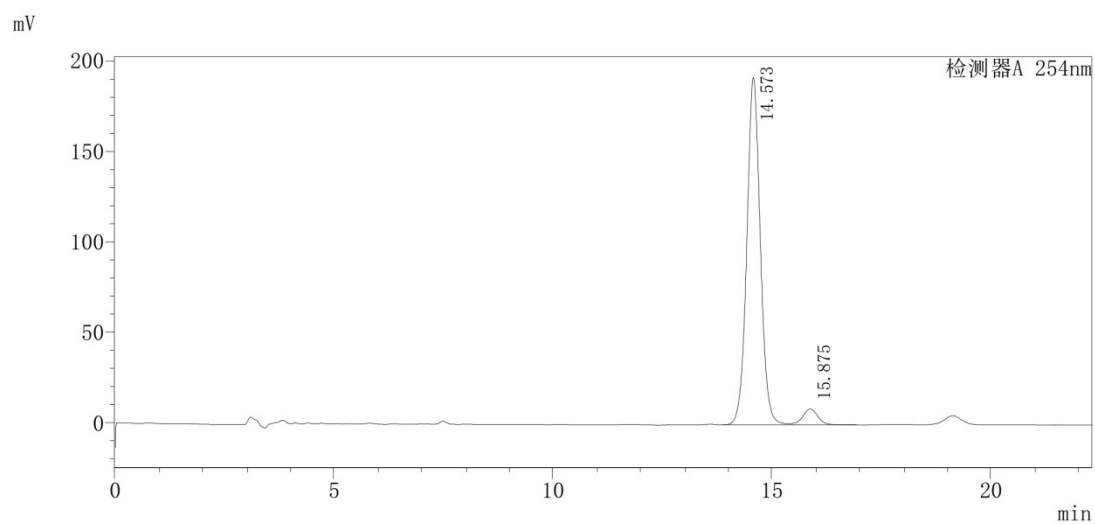
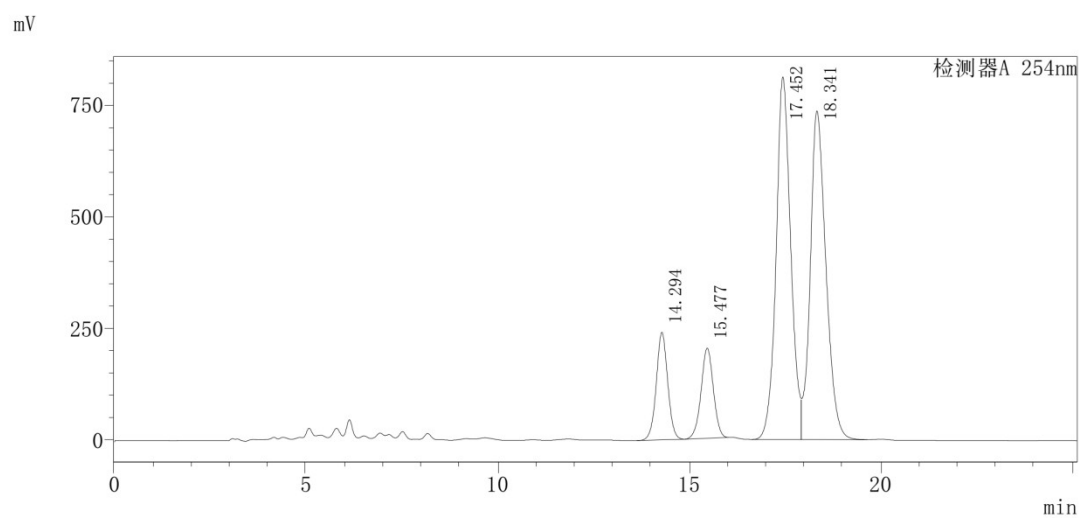
C	0.28447600	1.39834400	-3.82414500
C	0.32710000	2.73859900	-4.22004800
C	0.49715100	3.73669700	-3.26054200
C	0.61964900	3.39497900	-1.91109500
C	3.39302800	2.22320700	1.97293700
C	4.39091200	3.14209500	2.30124200
C	5.18245500	3.71144600	1.30102700
C	4.97666000	3.34962700	-0.03181800
C	3.98312000	2.42563400	-0.36020800
C	-4.28008200	-1.44103800	-0.32764700
C	-5.76299300	-1.33290800	-0.71887500
C	-6.36678200	-2.69630100	-1.08330300
C	-7.83910600	-2.60925500	-1.49891100
C	-3.13273300	0.61542500	-1.11362100
C	-3.55790500	2.09221800	-1.14623500
C	-5.07075700	2.33000200	-1.23818100
C	-5.43115200	3.81766300	-1.31189200
S	2.65667300	-1.35328600	1.69262000
O	1.57902700	-2.41552800	1.76977800
O	3.47403700	-1.12830600	2.88877500
C	3.77203100	-1.79861500	0.35879300
C	3.27990400	-2.40586400	-0.80123000
C	4.17548800	-2.72269900	-1.82181800
C	5.54614100	-2.44964500	-1.70477100
C	6.00665200	-1.83578800	-0.53118600
C	5.13100000	-1.50731600	0.50148300
C	6.50779800	-2.83362100	-2.80431100
H	0.77814700	2.63466700	0.53948200
H	2.34985400	0.40299000	-0.68563900
H	-1.03422600	2.63231700	1.42931400
H	-1.91958400	2.38144900	3.47512000
H	-3.60640100	1.51864500	5.06793300
H	-5.16575000	-0.29031400	4.29816800
H	-5.14265500	-1.04523400	1.99808800
H	0.37173400	0.00877900	-2.18239800

H	0.15232100	0.61520700	-4.56615700
H	0.22976100	3.00137900	-5.27012400
H	0.53413300	4.78135200	-3.55806800
H	0.75414400	4.17640400	-1.16684600
H	2.79416200	1.76085600	2.75111300
H	4.55461000	3.40765500	3.34243800
H	5.96050200	4.42501900	1.55947200
H	5.59414500	3.77949500	-0.81635100
H	3.83192200	2.13978800	-1.39834400
H	-4.14532900	-2.14084300	0.50070700
H	-3.72110400	-1.87153000	-1.16708200
H	-5.86637500	-0.64786600	-1.57122400
H	-6.33508300	-0.88212100	0.10289400
H	-6.26803300	-3.37944900	-0.22759700
H	-5.78245200	-3.14597700	-1.89892400
H	-8.24116400	-3.59679800	-1.75184900
H	-7.96540200	-1.96255200	-2.37585900
H	-8.45504500	-2.19513200	-0.69125600
H	-3.53495500	0.13288300	-2.00994300
H	-2.04242700	0.54359600	-1.18715800
H	-3.06088900	2.53944900	-2.01833100
H	-3.16680600	2.62791400	-0.27288400
H	-5.56665500	1.87627700	-0.37098200
H	-5.46648400	1.81392200	-2.12488600
H	-6.51538000	3.96282200	-1.37938000
H	-4.97523600	4.29473800	-2.18834100
H	-5.07861600	4.35435700	-0.42238500
H	2.22158300	-2.62332400	-0.91152000
H	3.79915600	-3.19506200	-2.72603900
H	7.06530500	-1.61299300	-0.42209200
H	5.48881300	-1.04222800	1.41335900
H	7.36239200	-2.15013100	-2.84764900
H	6.01866200	-2.83169900	-3.78397500
H	6.90703300	-3.84368600	-2.64130100
Cu	0.10251200	-1.06659300	0.86209400

O	-1.31516600	-2.34505100	0.52913200
C	-0.91555600	-2.81525400	-0.60522300
O	0.02970100	-2.29473800	-1.24234600
C	-1.59902800	-4.06530800	-1.12382900
H	-2.59051400	-4.19441200	-0.68489800
H	-1.66182000	-4.03946300	-2.21504500
H	-0.98711300	-4.93189200	-0.84556400

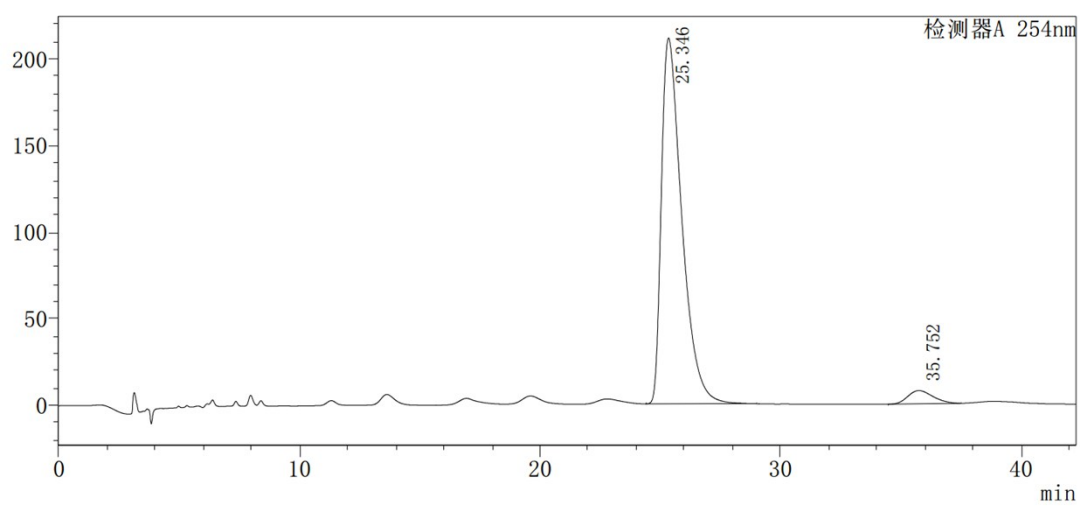
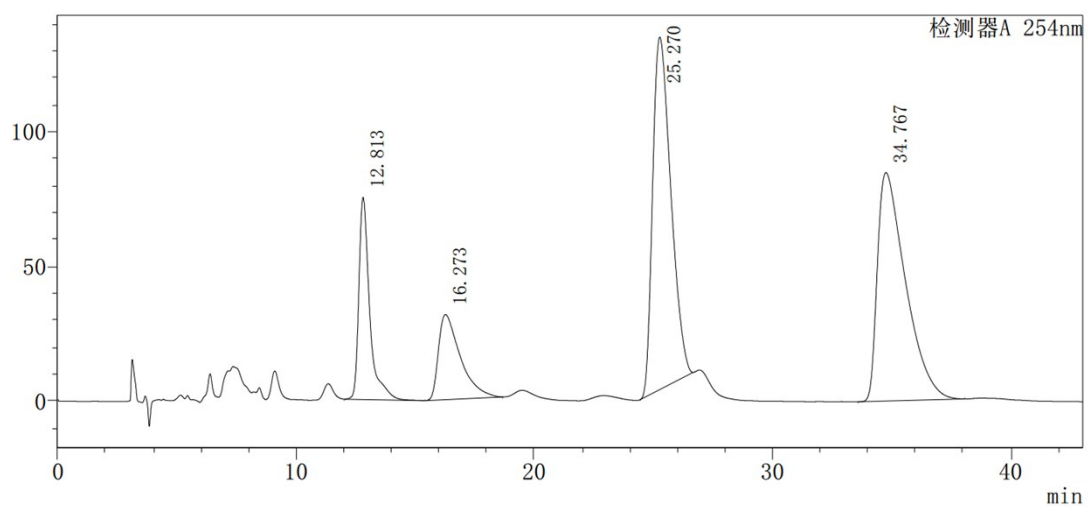
3. Copies of HPLC charts

(1) 3a (IA)



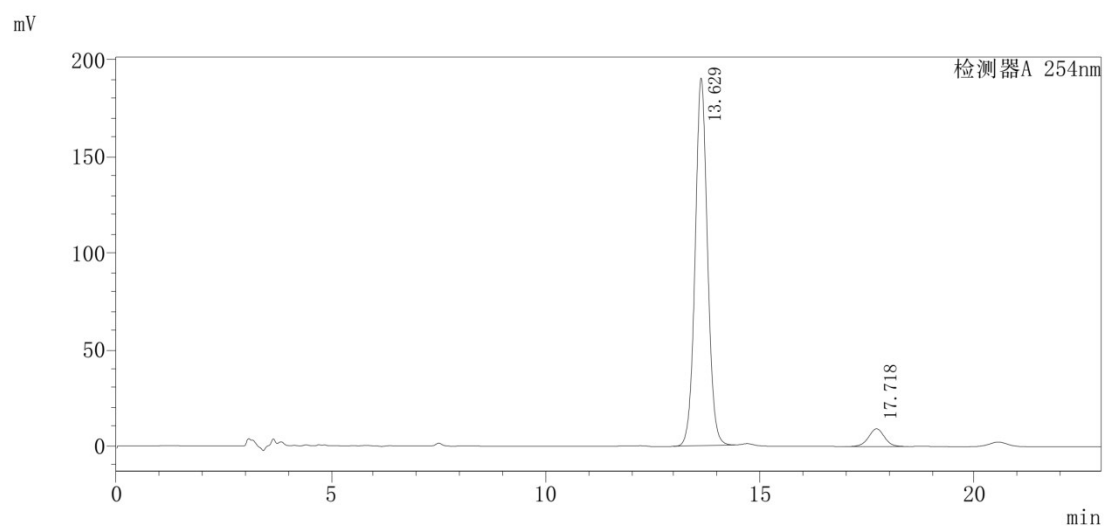
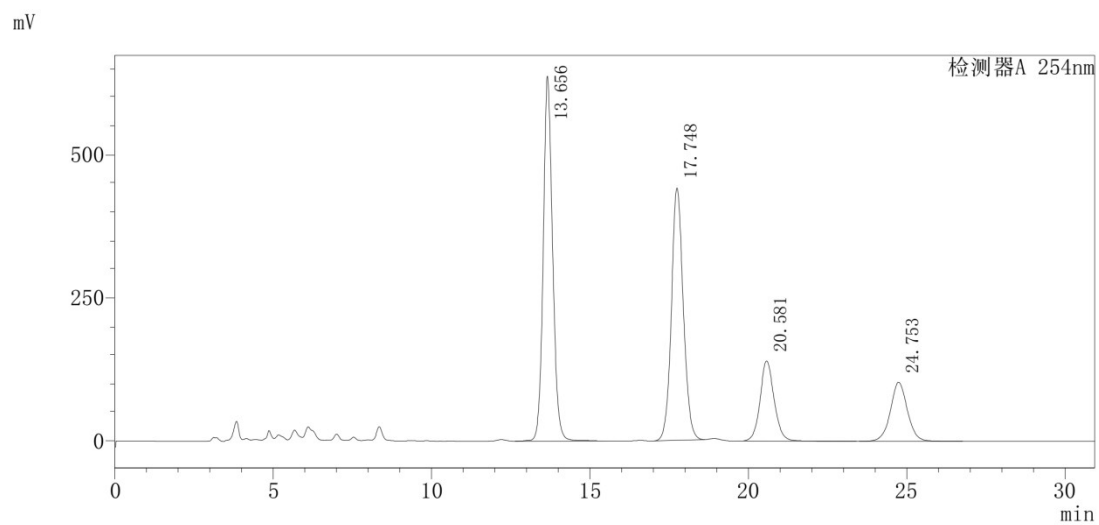
Peak#	Ret Time	Area	Height	Area%
1	14.573	4100906	191625	95.025
2	15.875	214685	8832	4.975

(2) 3a (OD-H)



Peak#	Ret Time	Area	Height	Area%
1	25.346	12467002	211151	95.732
2	35.752	555830	7662	4.268

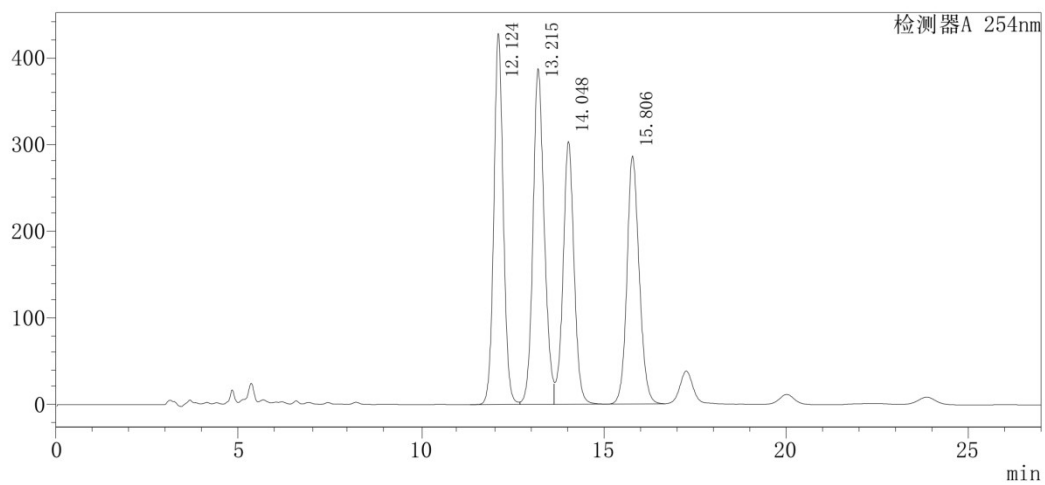
(3) 3b



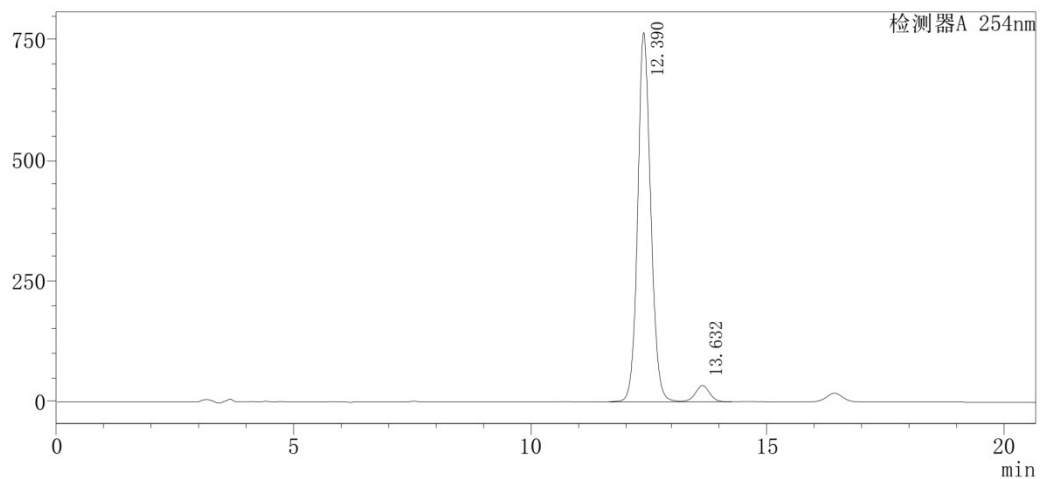
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1	13.629	3819985	190618	94.166
2	17.718	236657	9211	5.834

(4) 3c

mV

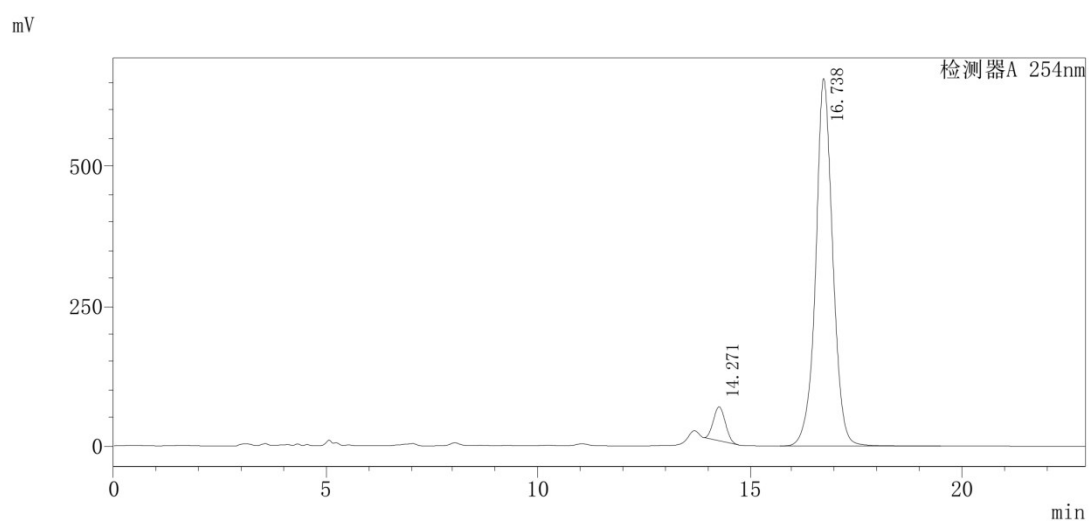
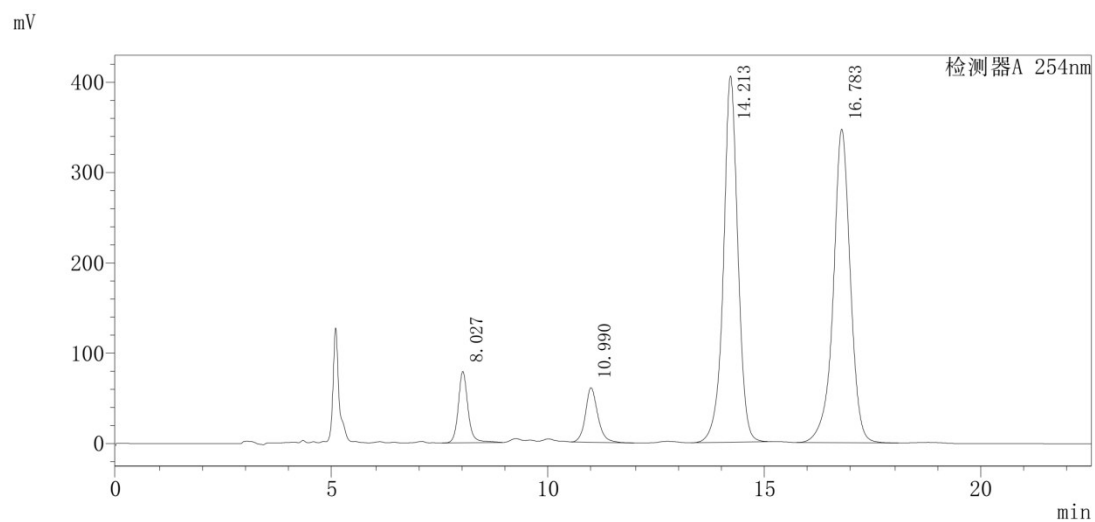


mV



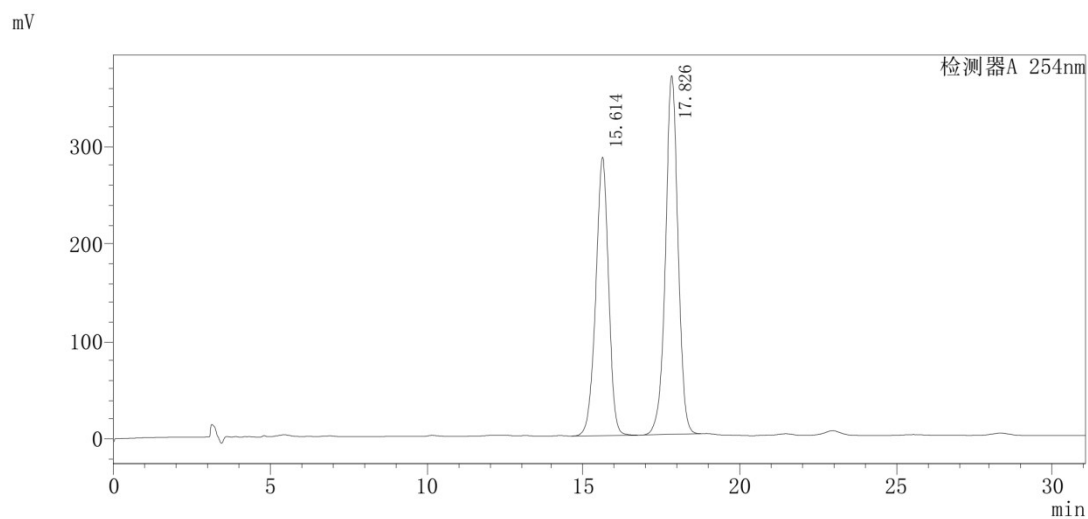
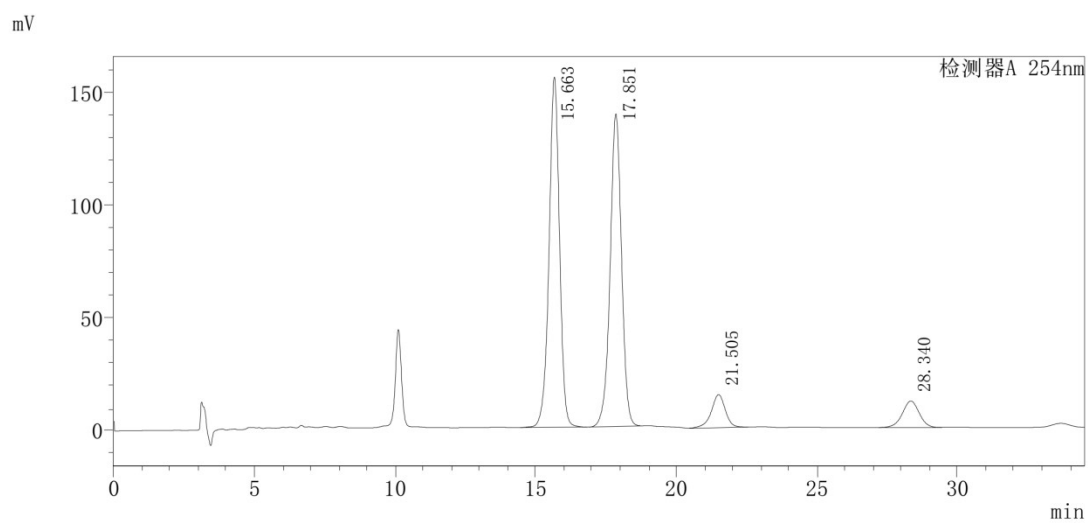
Peak#	Ret Time	Area	Height	Area%
1	12.390	14678413	764645	95.296
2	13.632	724563	34144	4.704

(5) 3d



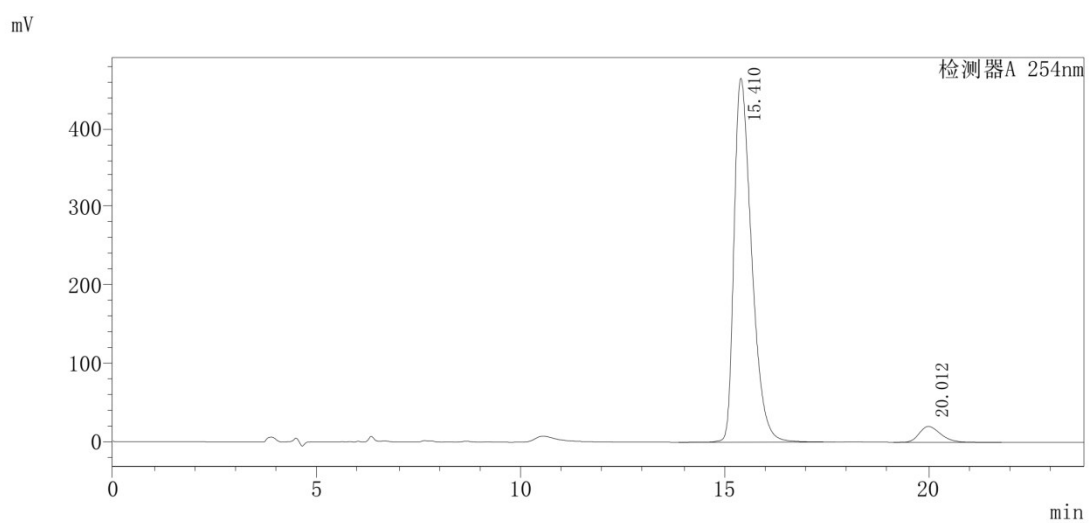
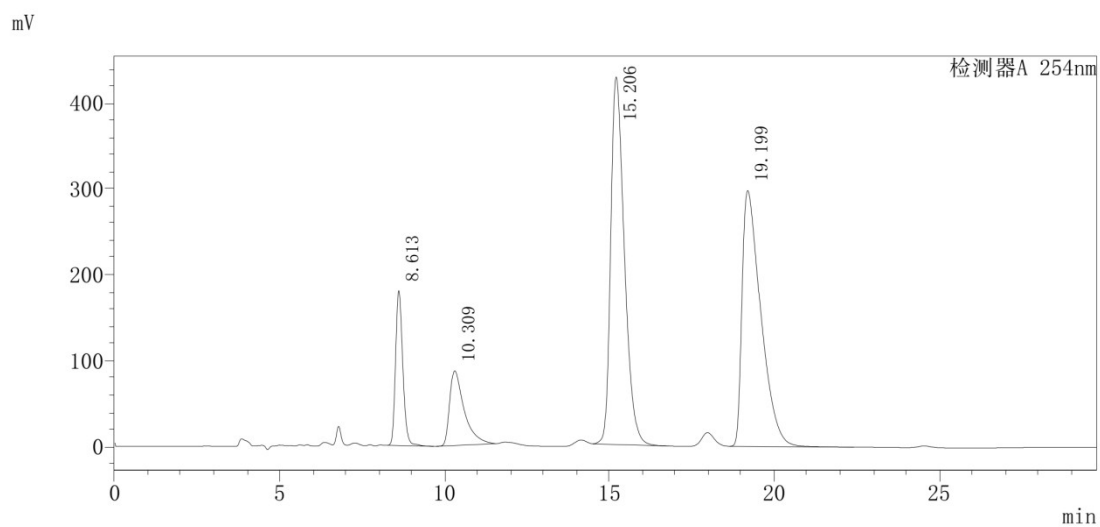
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1	14.271	1191493	60832	6.078
2	16.738	18410285	657520	93.922

(6) 3e



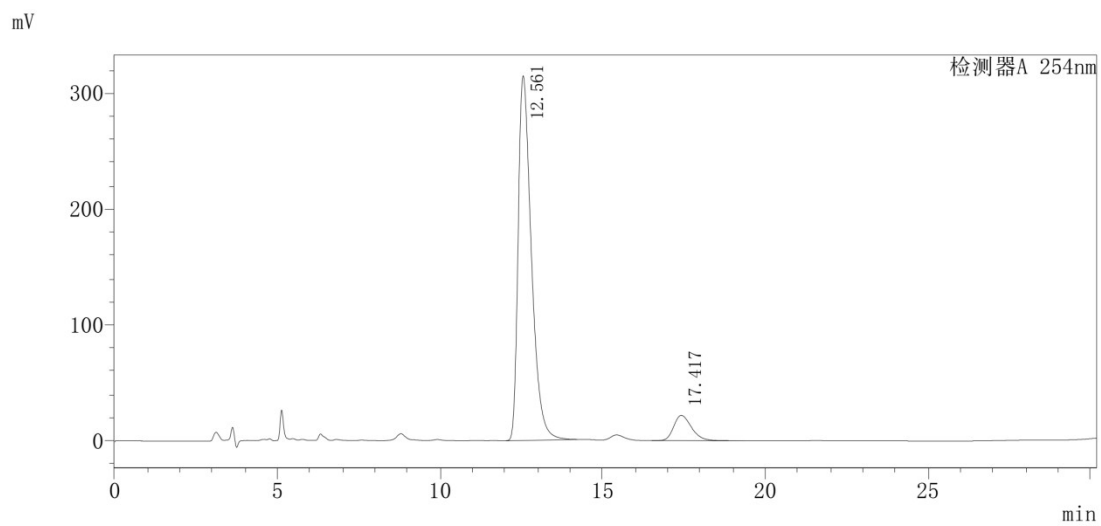
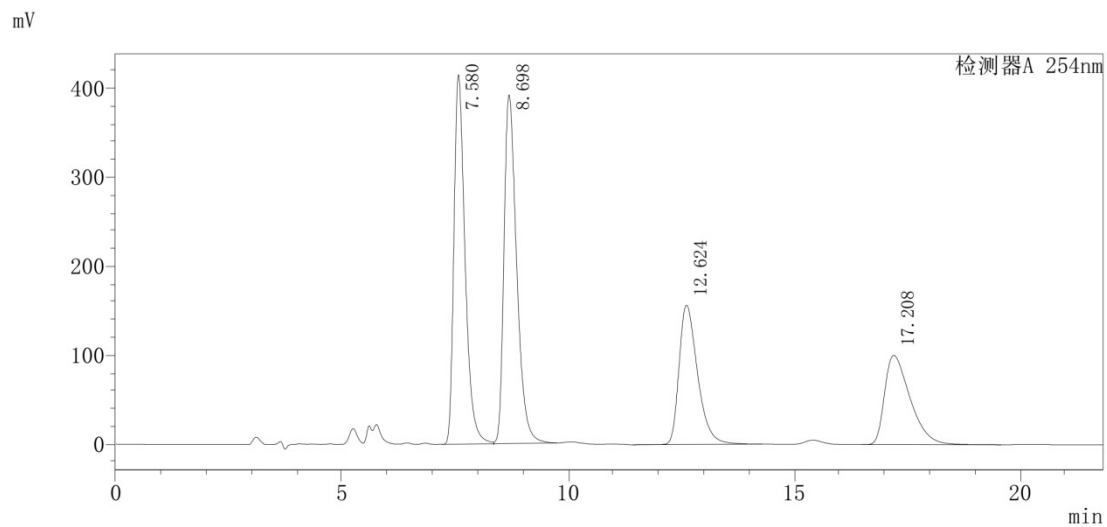
Peak#	Ret Time	Area	Height	Area%
1	15.614	8142939	285874	44.234
2	17.826	10265661	368278	55.766

(7) 3f



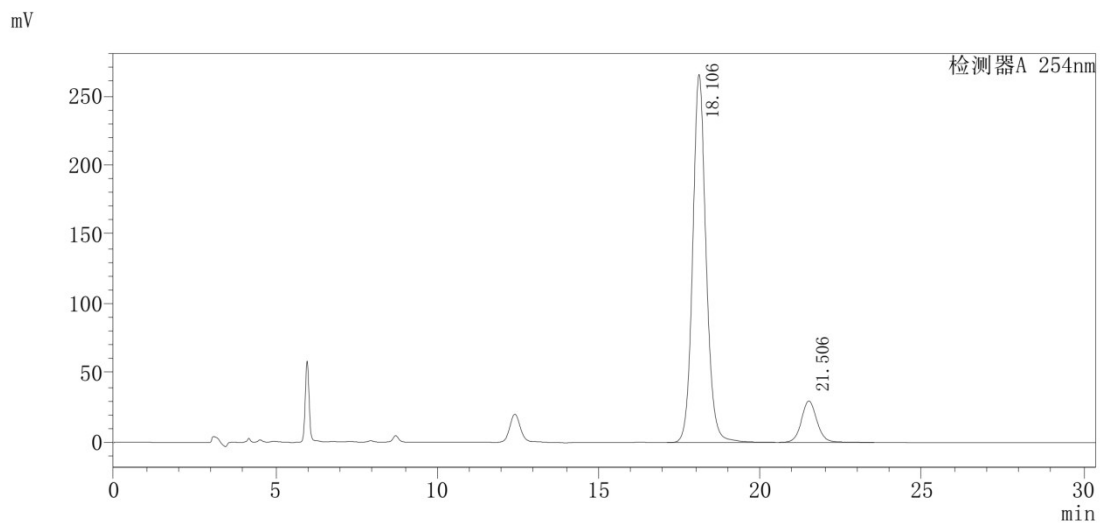
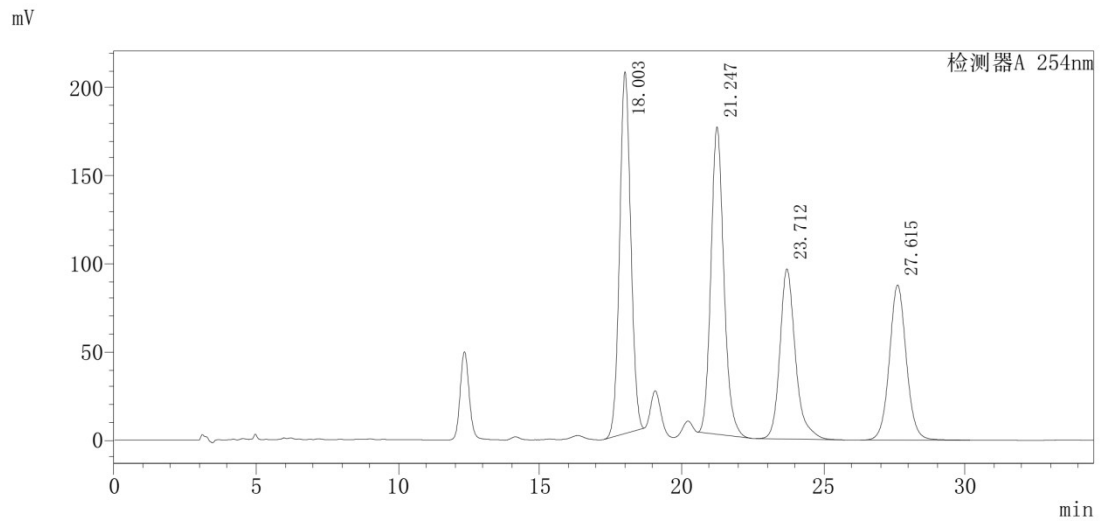
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1	15.410	14000548	465391	94.959
2	20.012	743287	20270	5.041

(8) 3g



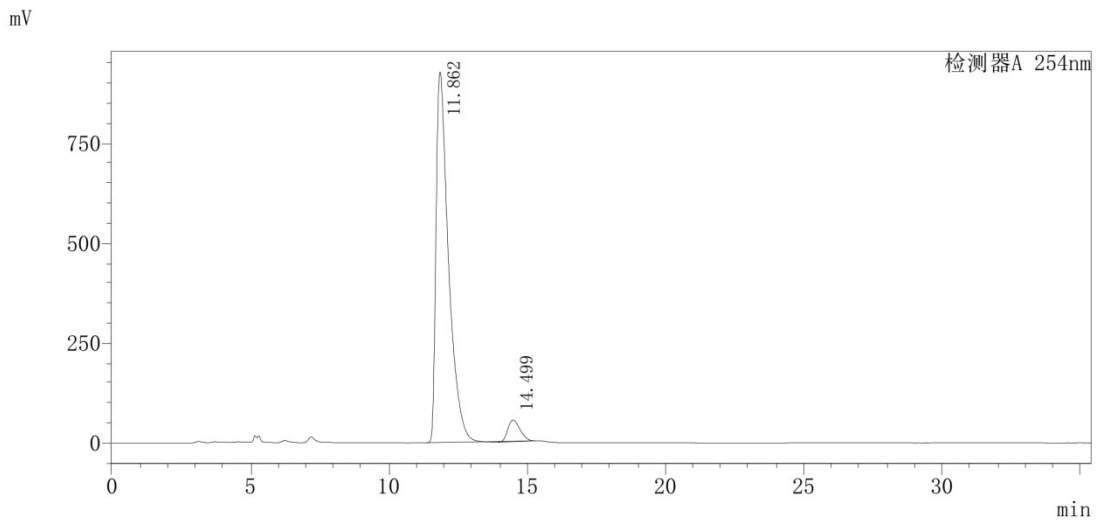
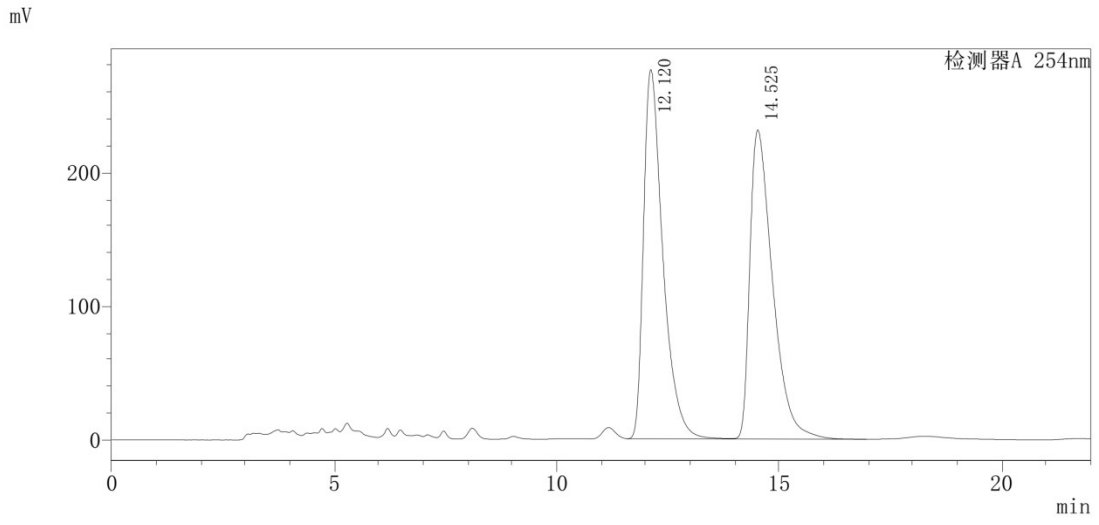
Peak#	Ret Time	Area	Height	Area%
1	12.561	8932603	314200	91.431
2	17.417	837217	21828	8.569

(9) 3h



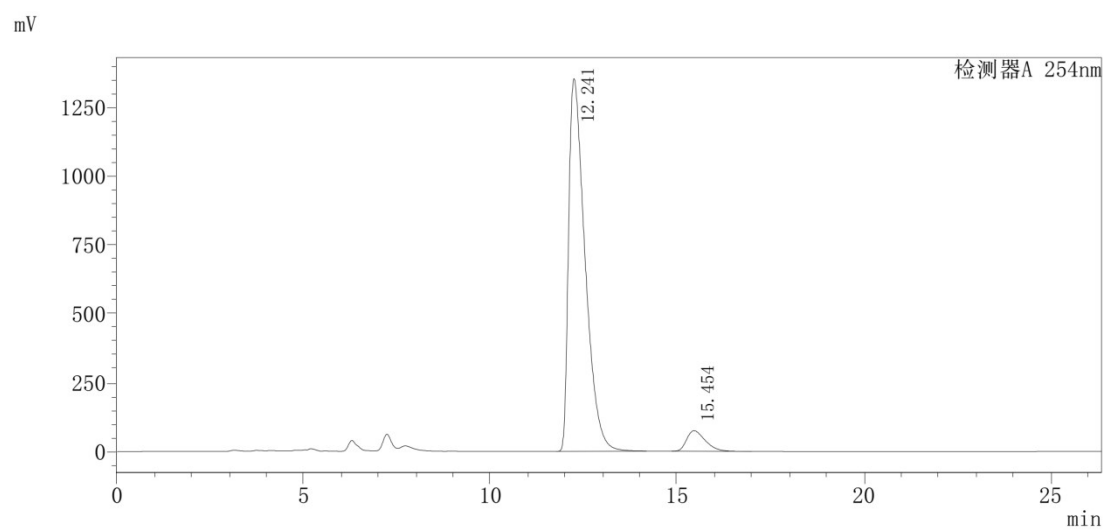
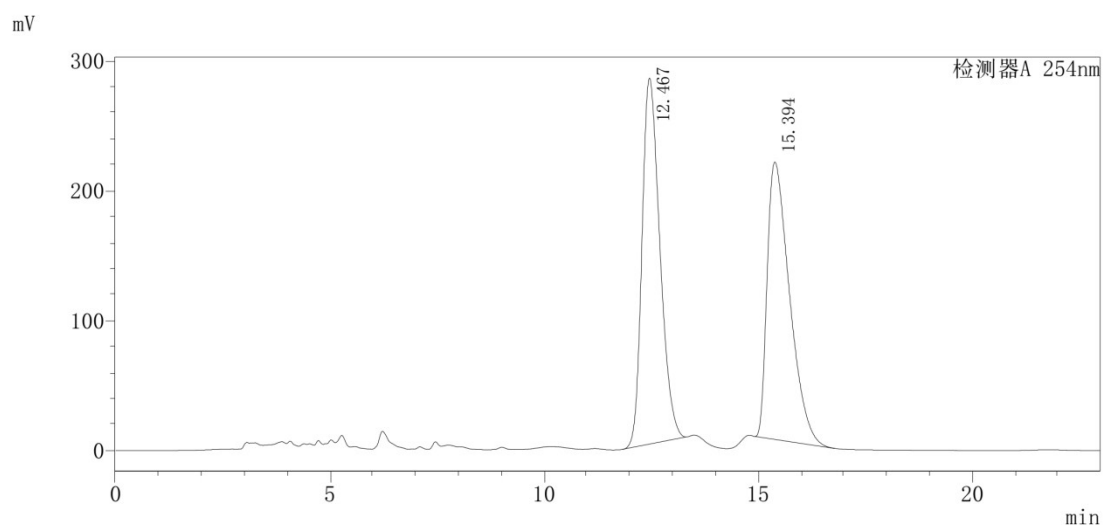
Peak#	Ret Time	Area	Height	Area%
1	18.106	7676384	265600	88.528
2	21.506	994743	29839	11.472

(10) 3i



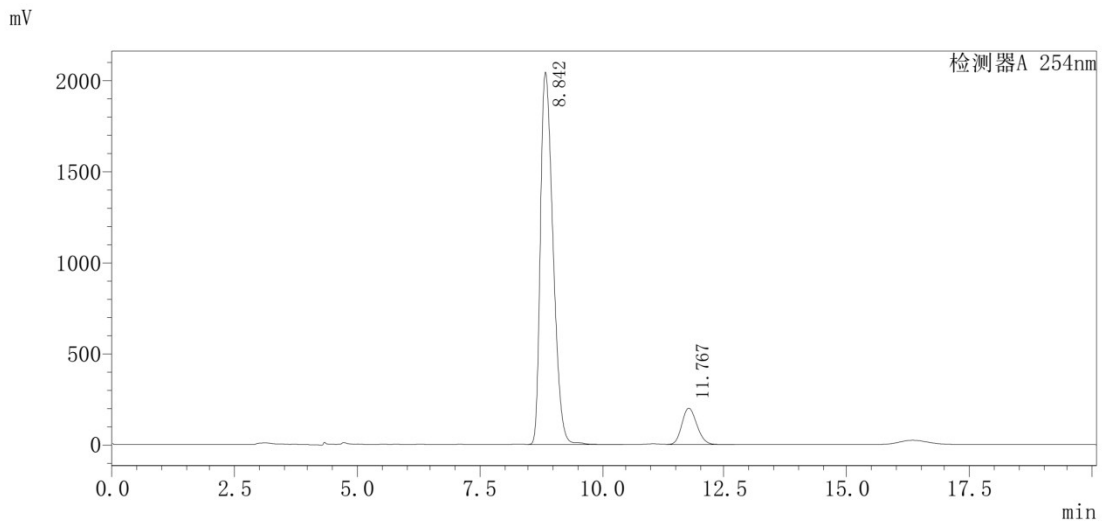
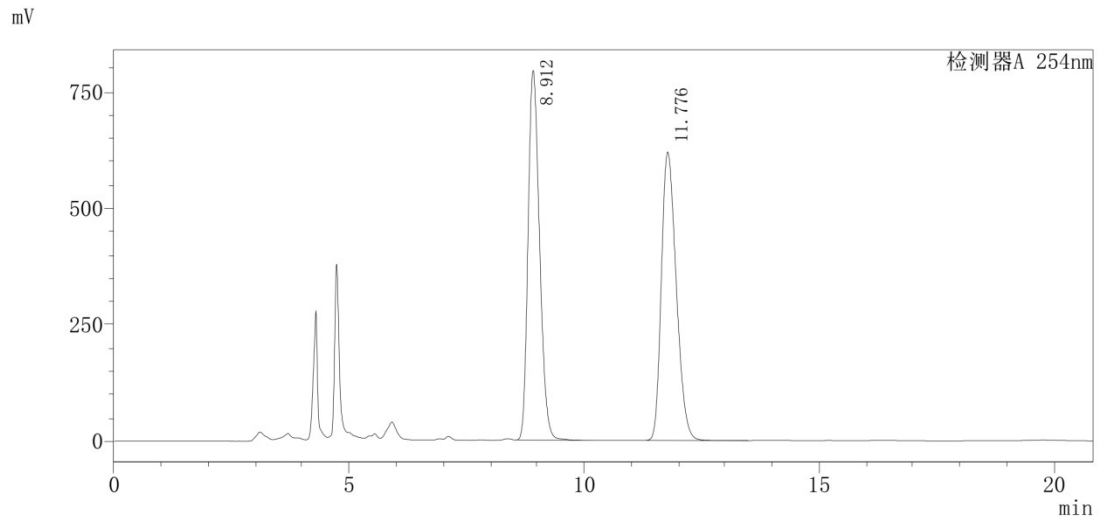
Peak#	Ret Time	Area	Height	Area%
1	11.862	28904141	927189	94.575
2	14.499	1657989	54061	5.425

(11) 3j



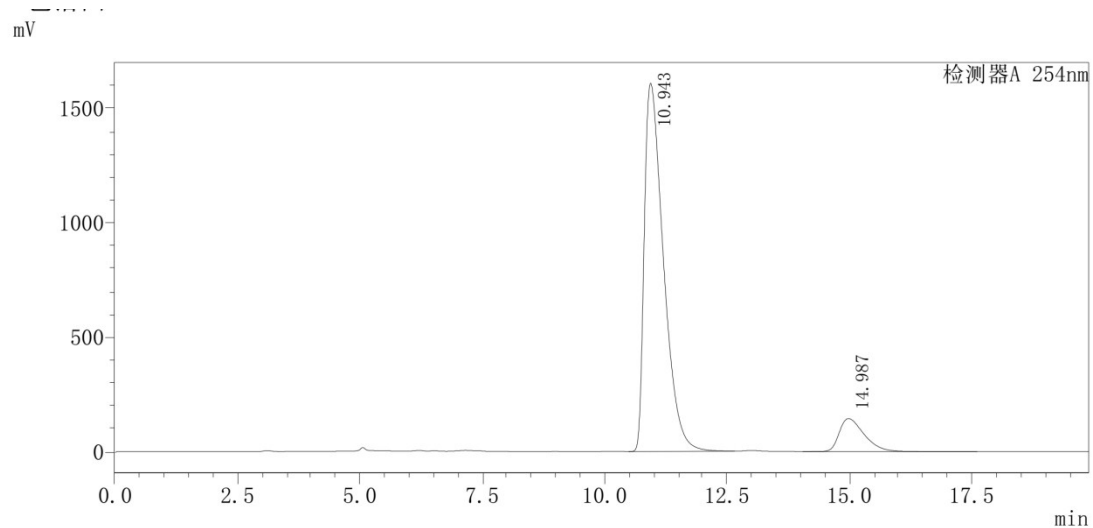
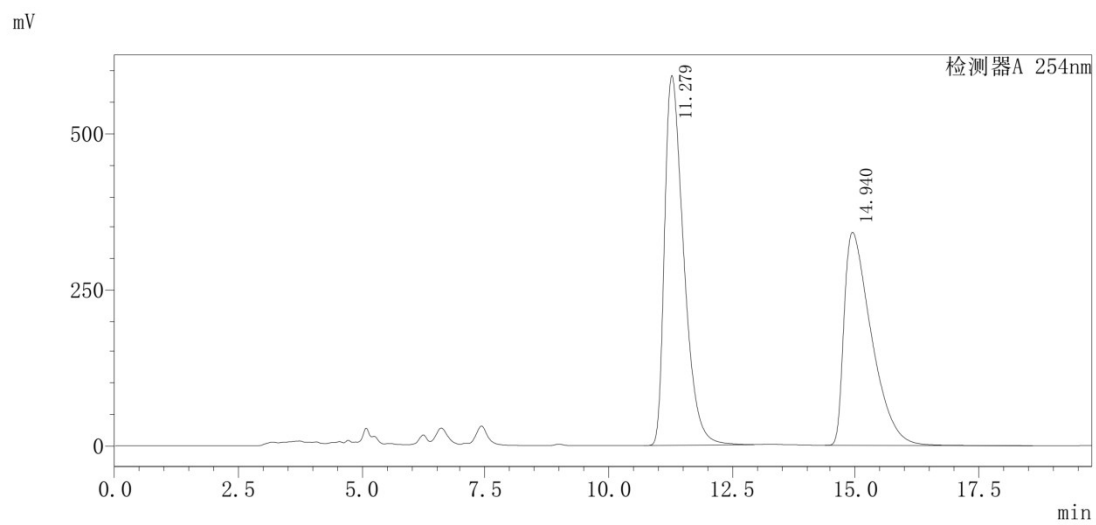
Peak#	Ret Time	Area	Height	Area%
1	12.241	41347734	1352742	94.123
2	15.454	2581562	74395	5.877

(12) 3k



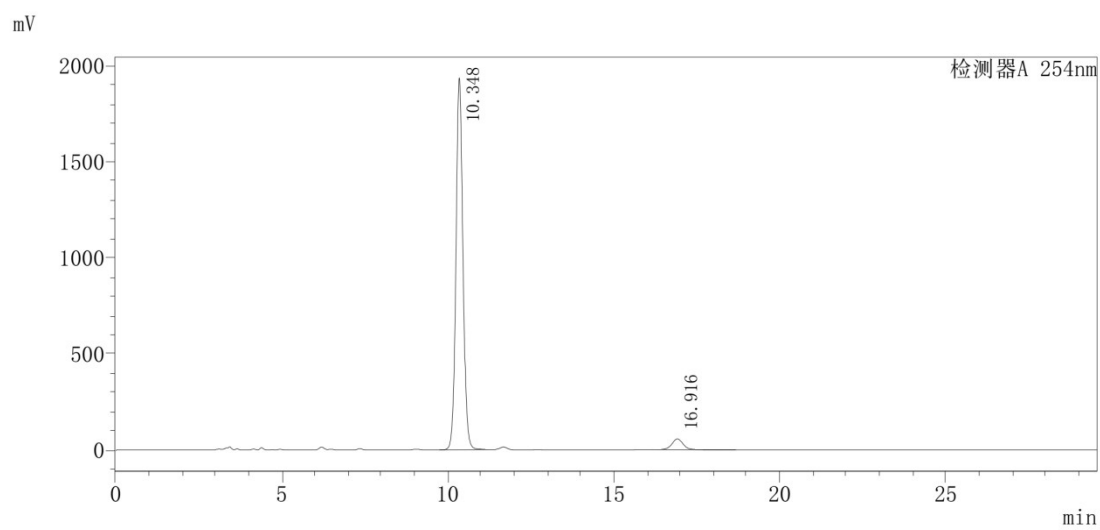
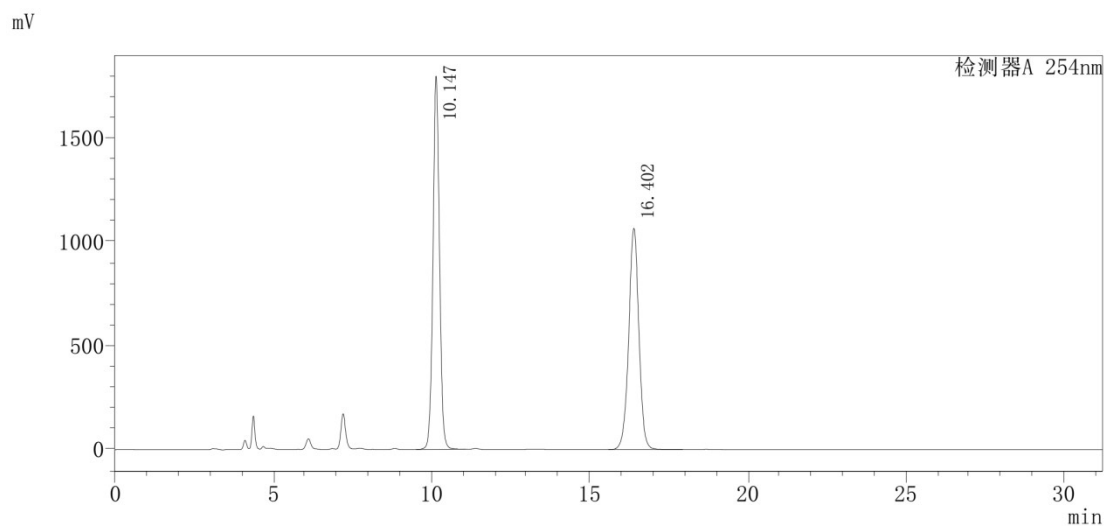
Peak#	Ret Time	Area	Height	Area%
1	8.842	36759662	2050060	89.691
2	11.767	4224974	200087	10.309

(13) 31



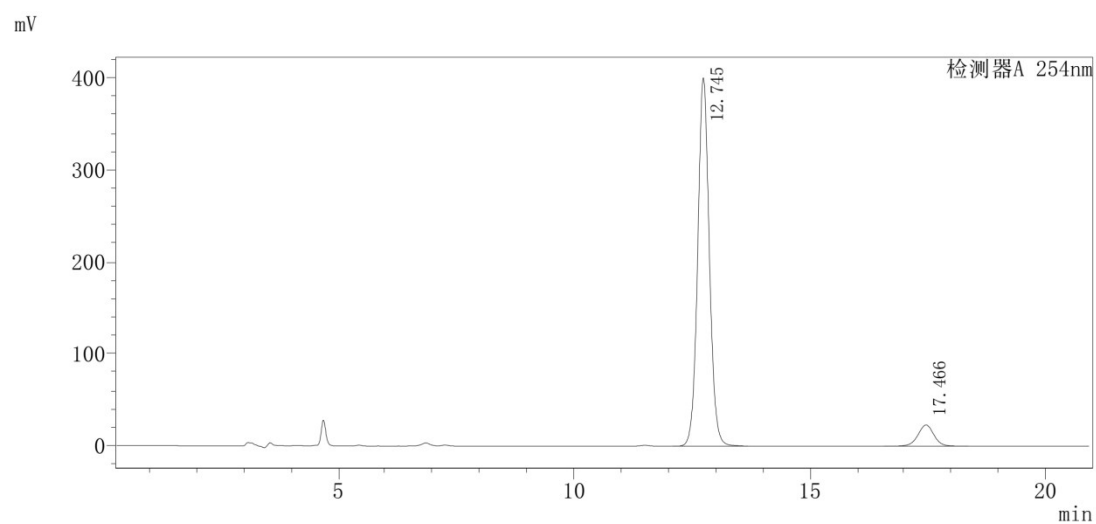
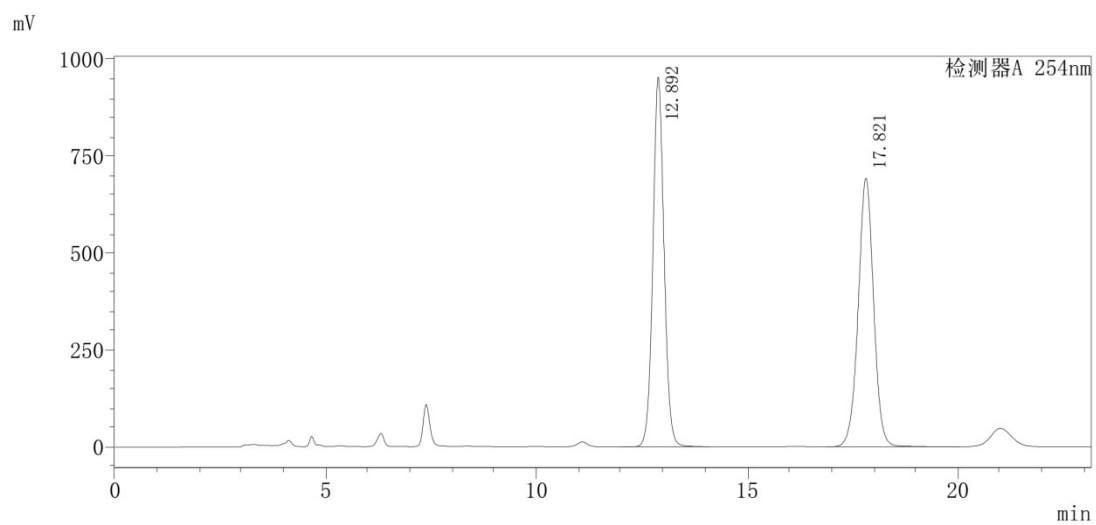
Peak#	Ret Time	Area	Height	Area%
1	10.943	43853461	1609351	89.528
2	14.987	5129686	144380	10.472

(14) 3m



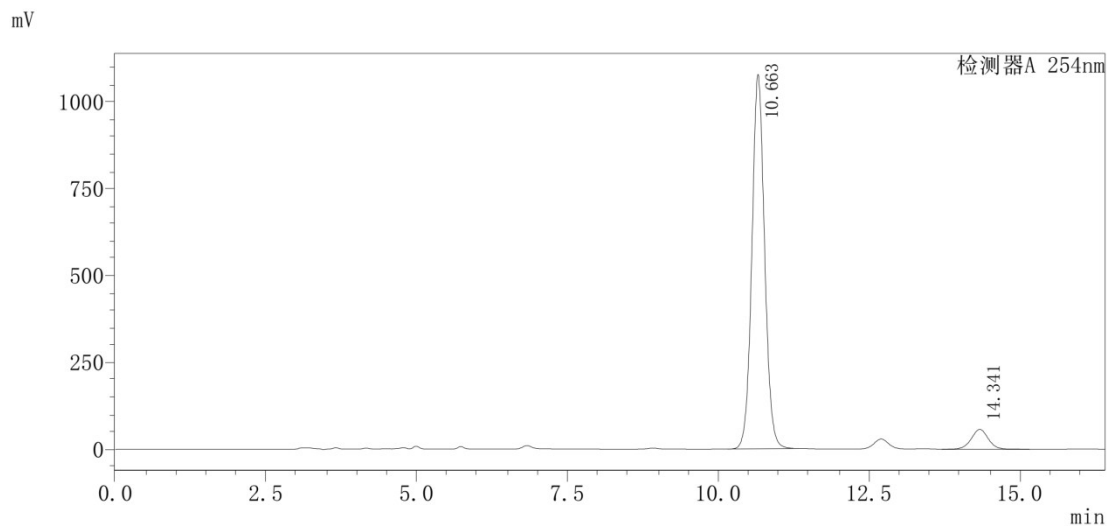
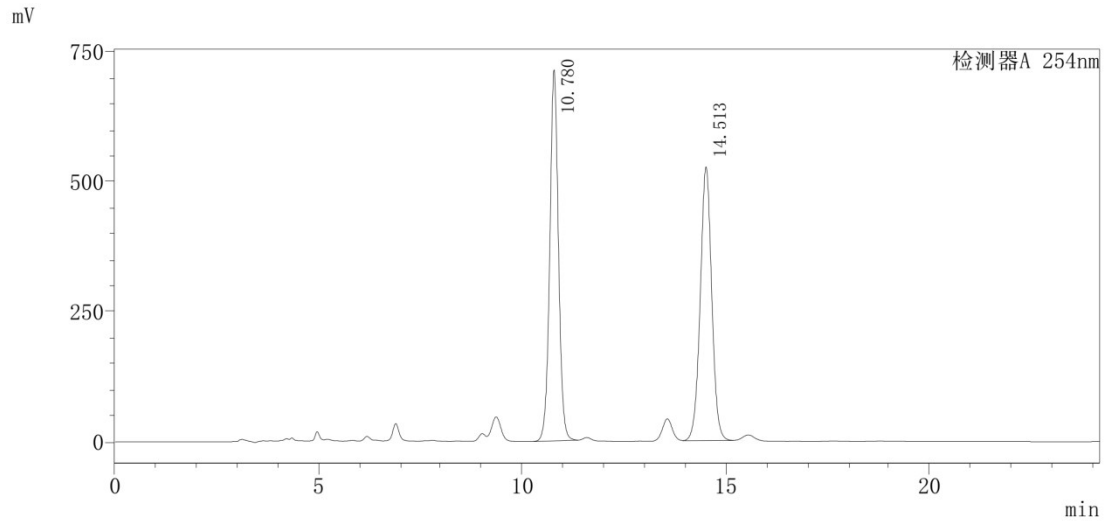
Peak#	Ret Time	Area	Height	Area%
1	10.348	28426366	1935021	95.460
2	16.916	1351896	56743	4.540

(15) 3n



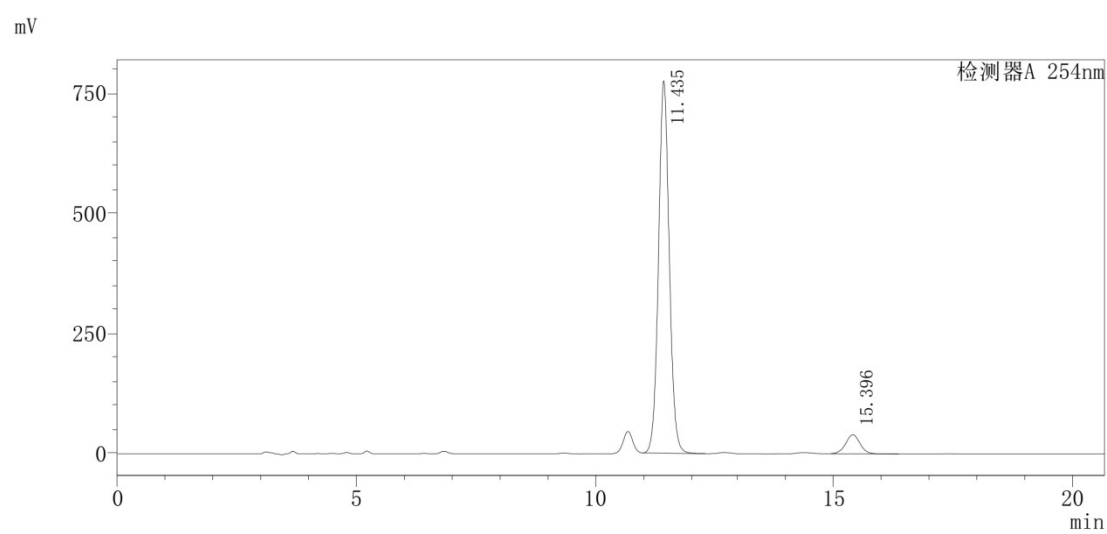
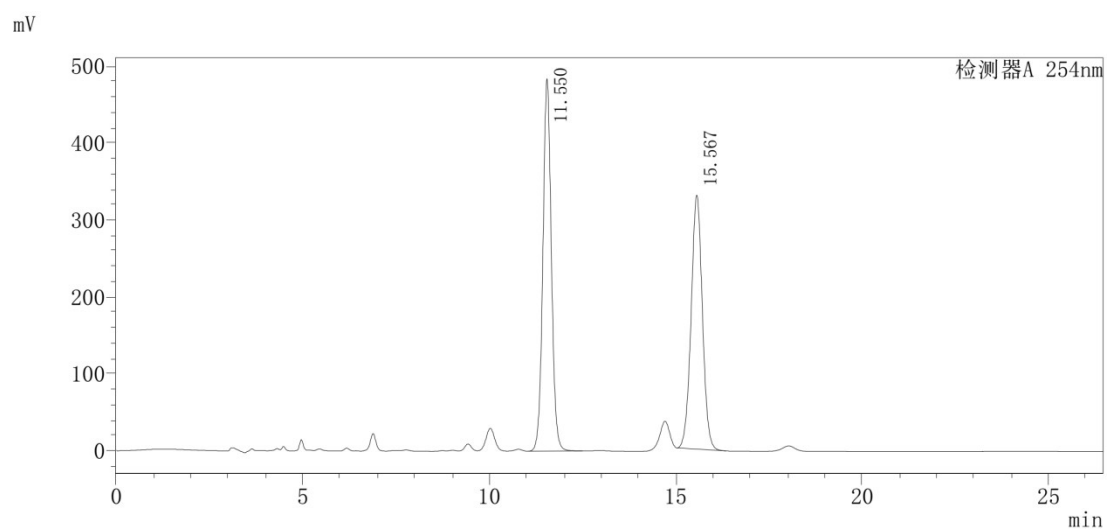
Peak#	Ret Time	Area	Height	Area%
1	12.745	6877187	400786	92.674
2	17.466	543689	23048	7.326

(16) 3o



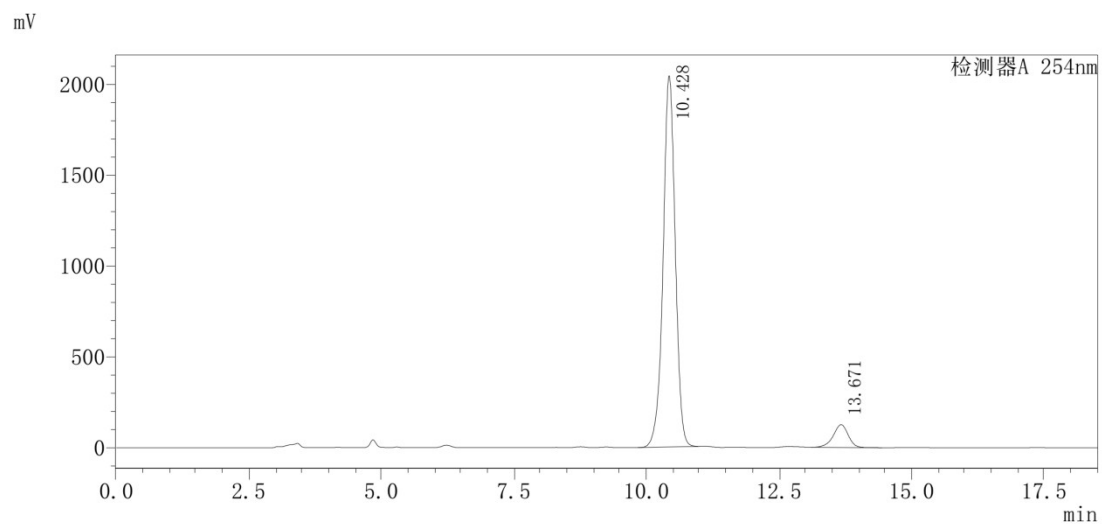
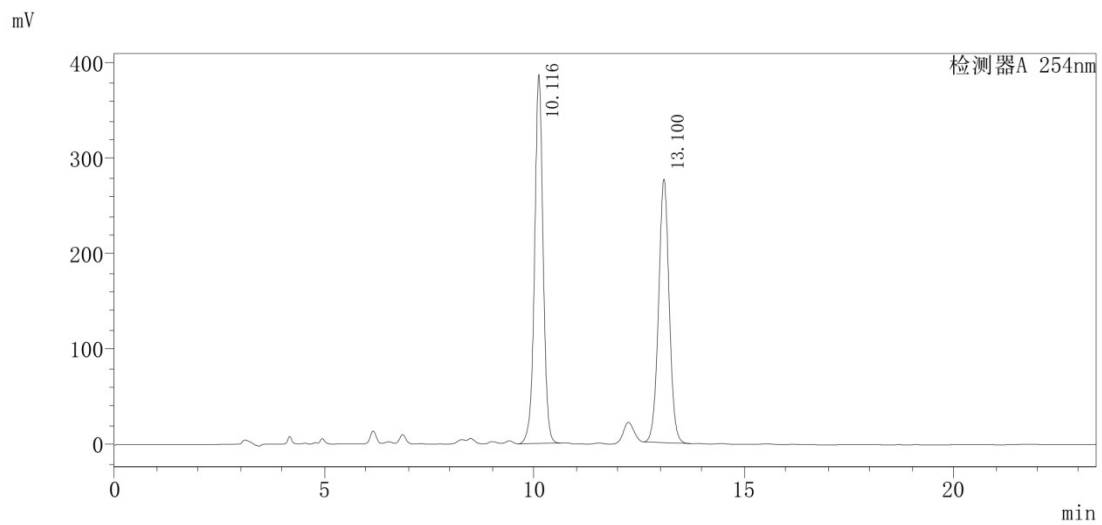
Peak#	Ret Time	Area	Height	Area%
1	10.663	15889075	1078063	93.421
2	14.341	1119045	57035	6.579

(17) 3p



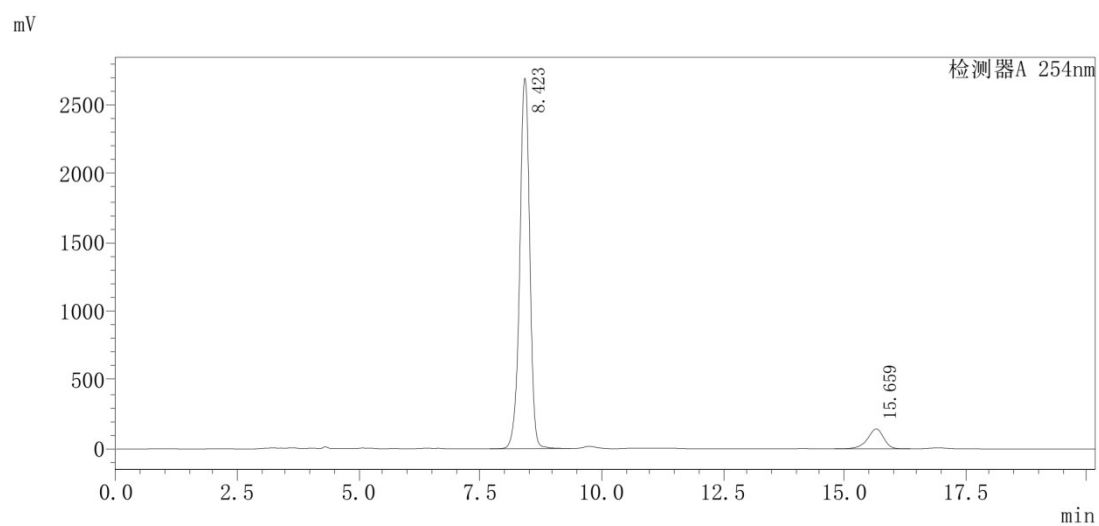
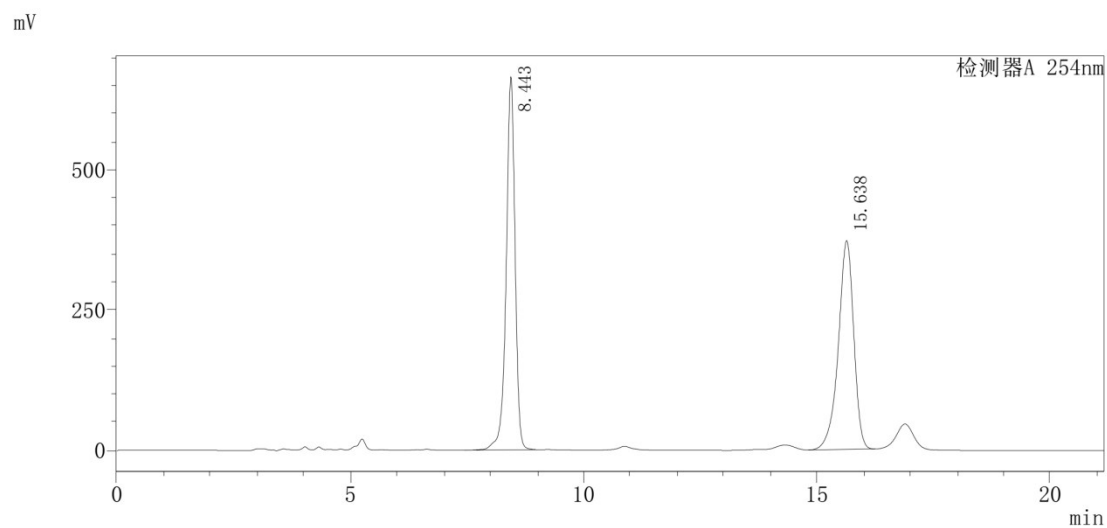
Peak#	Ret Time	Area	Height	Area%
1	11.435	12131499	774194	93.594
2	15.396	830306	39638	6.406

(18) 3q



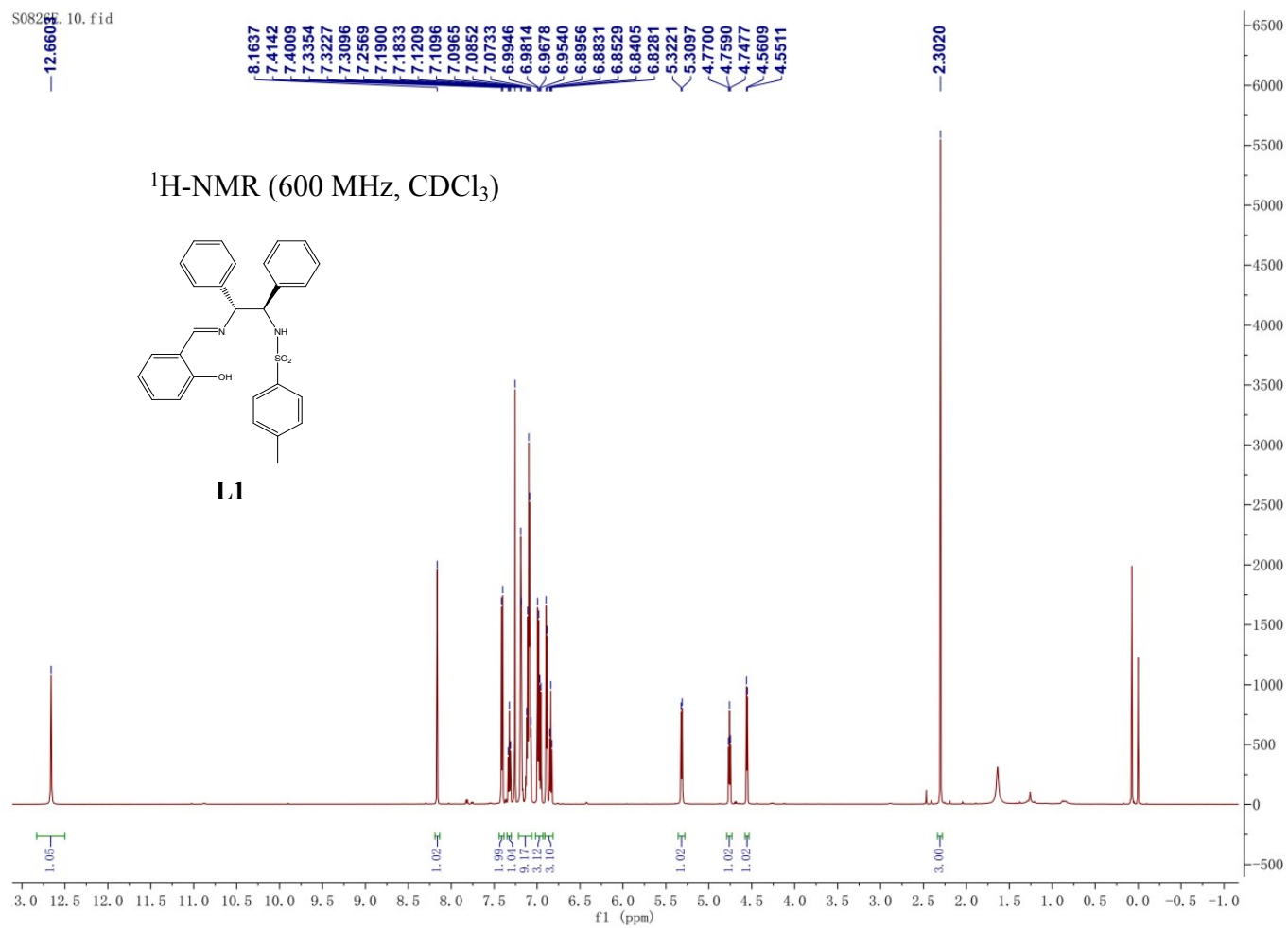
Peak#	Ret Time	Area	Height	Area%
1	10.428	32505028	2041564	92.929
2	13.671	2473402	125519	7.071

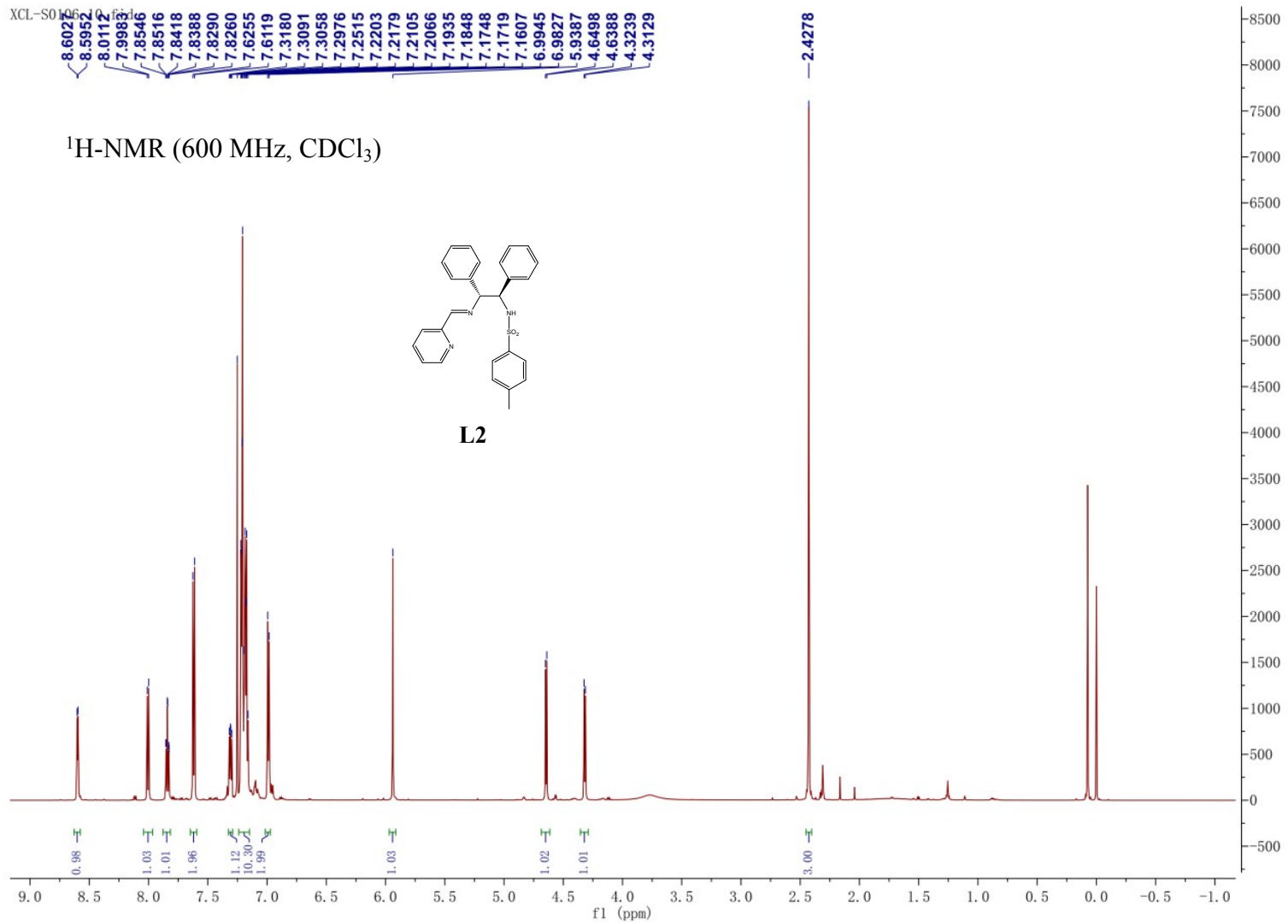
(19) 3r



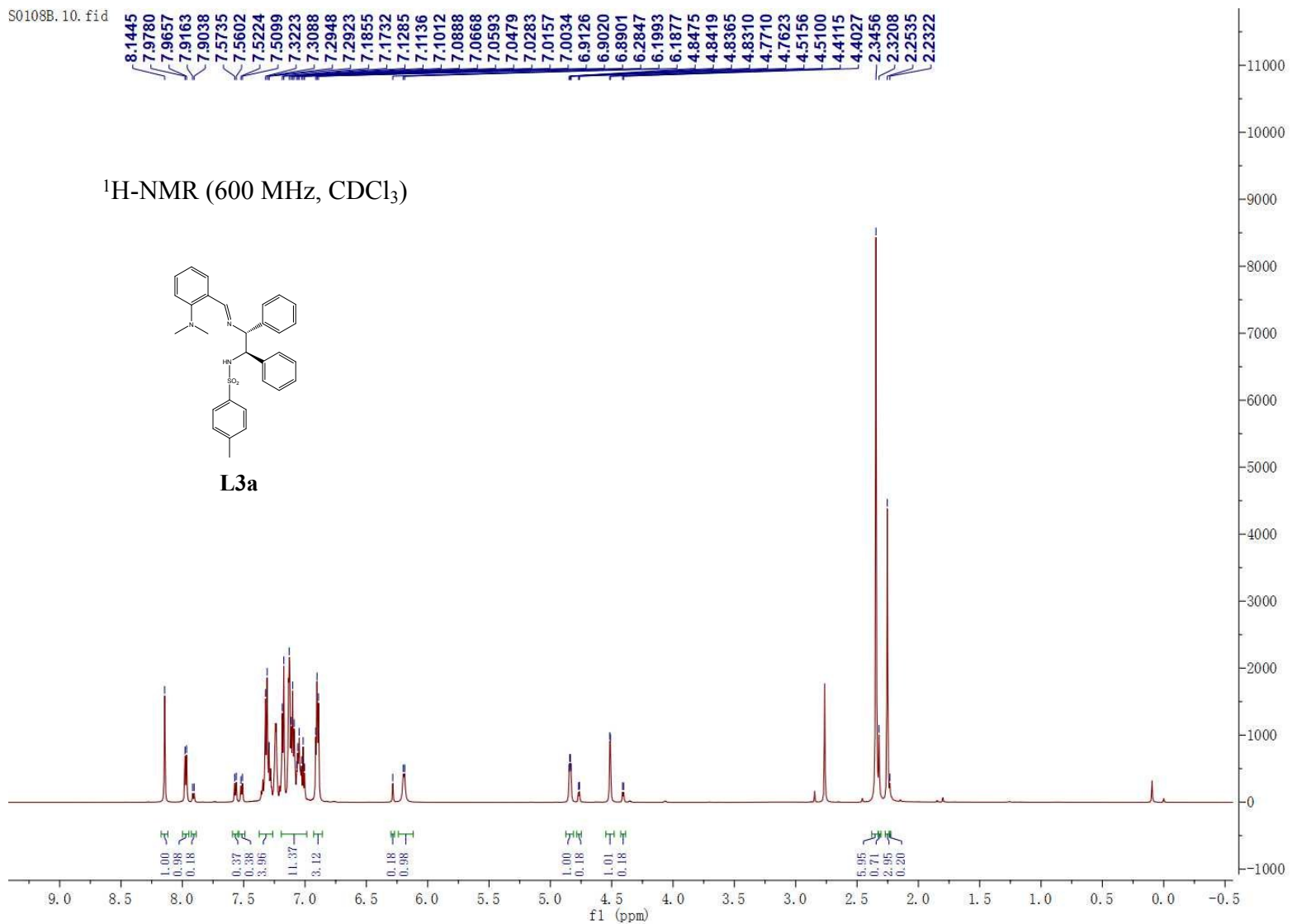
Peak#	Ret Time	Area	Height	Area%
1	8.423	38703431	2692387	91.990
2	15.659	3370236	144656	8.010

4. Copies of NMR spectra



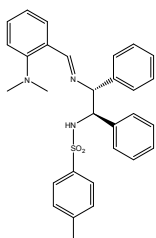


S0108B.10.fid

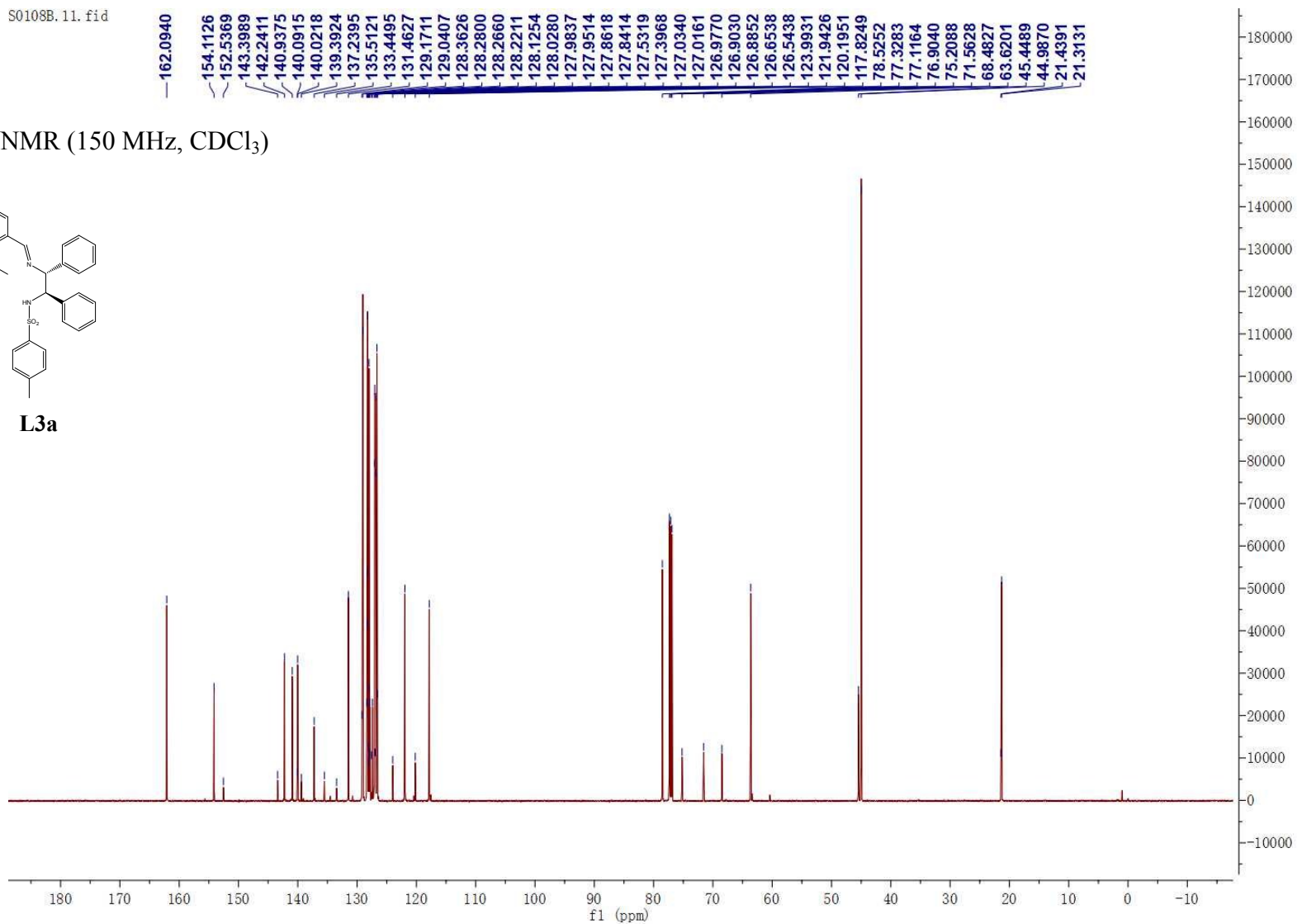


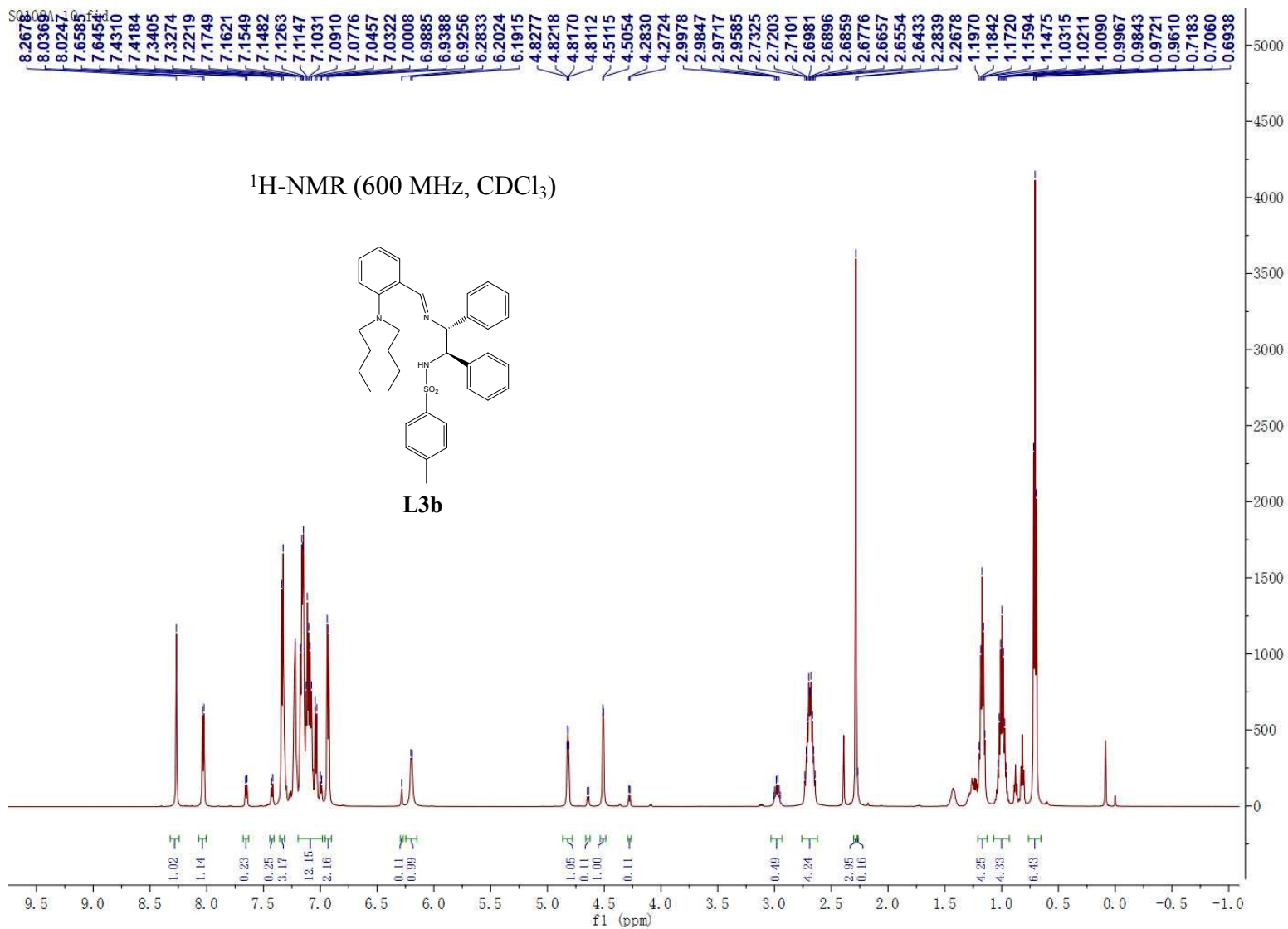
S0108B.11.fid

^{13}C -NMR (150 MHz, CDCl_3)

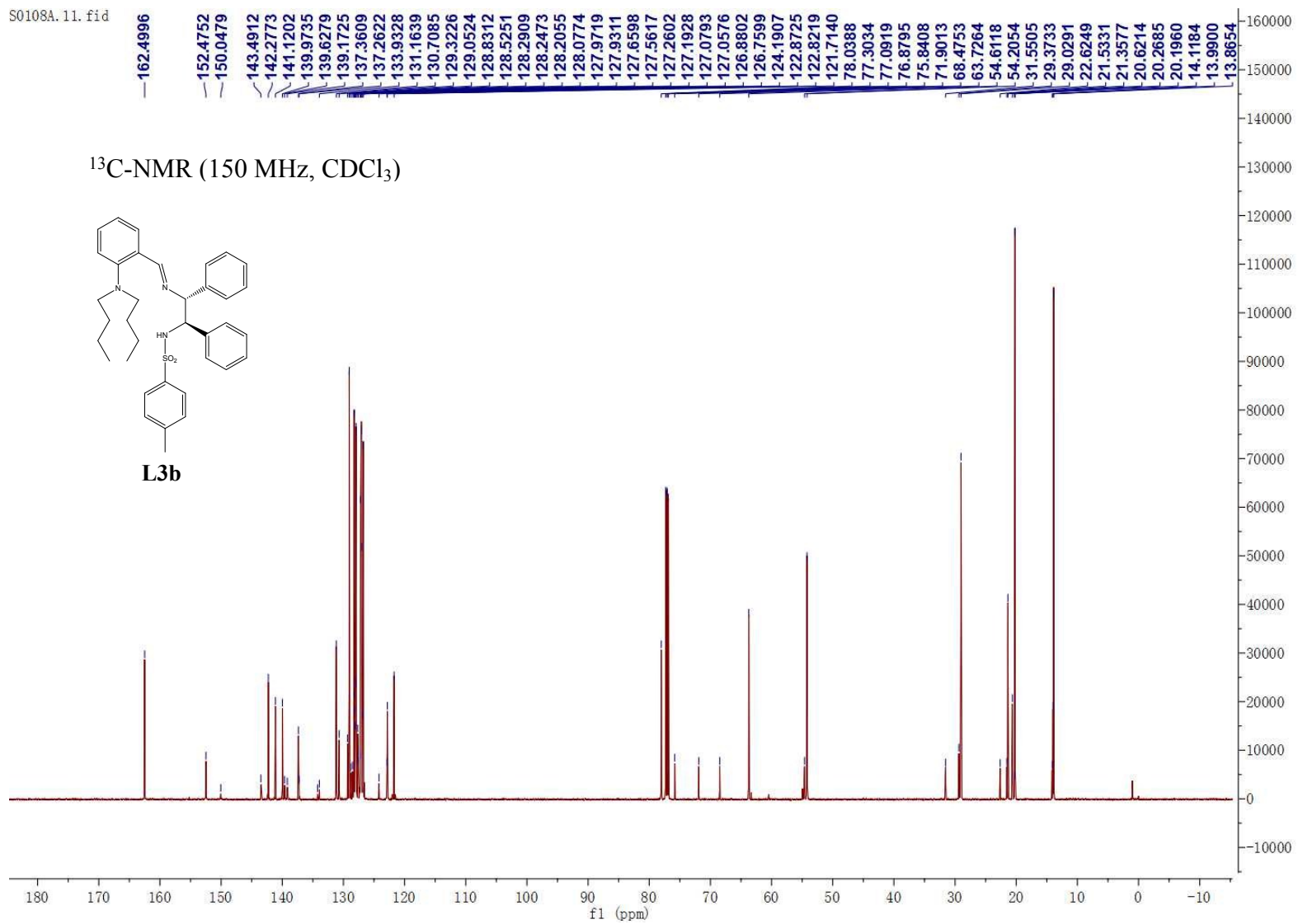


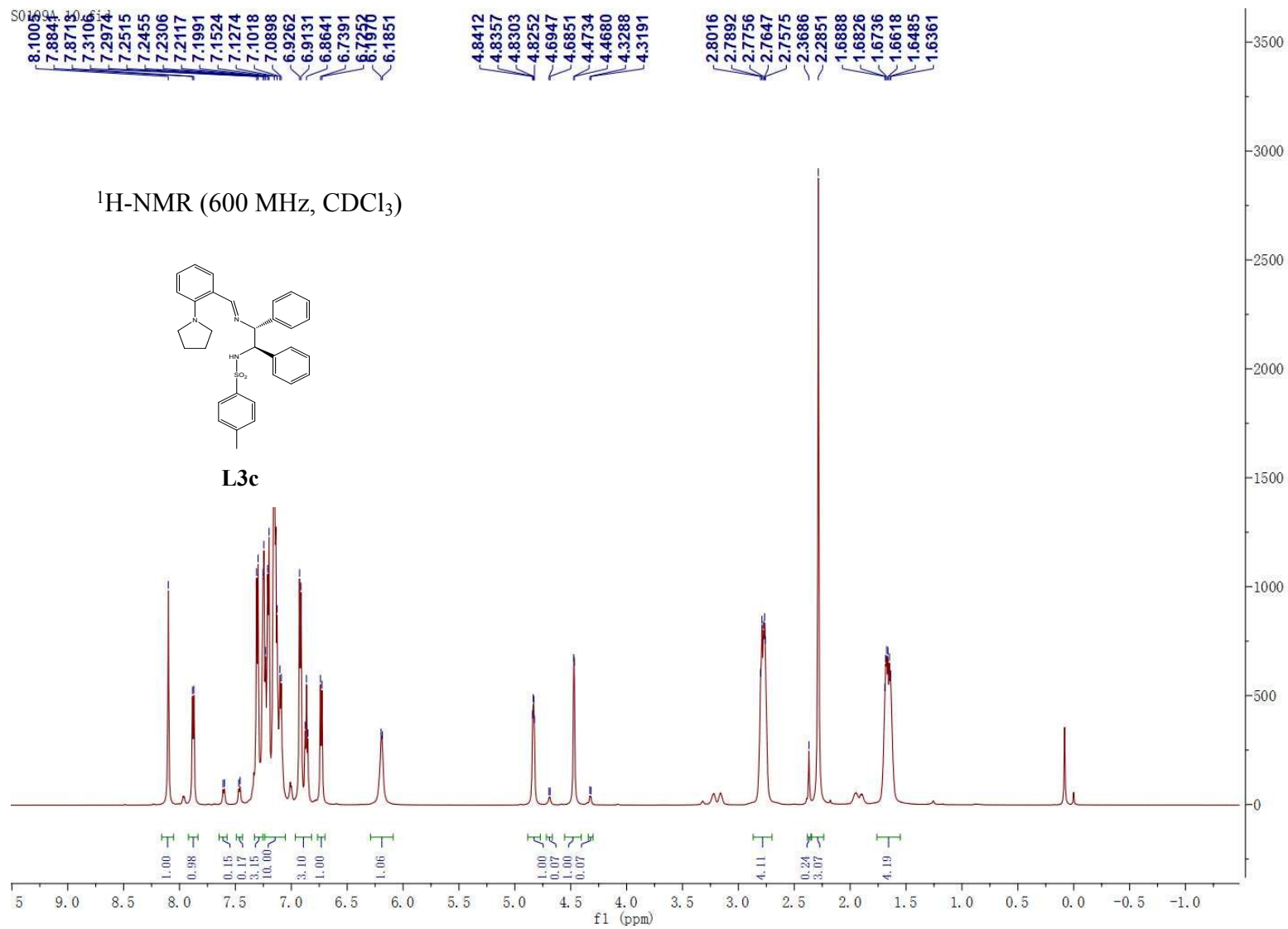
L3a





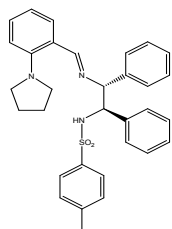
S0108A.11. fid



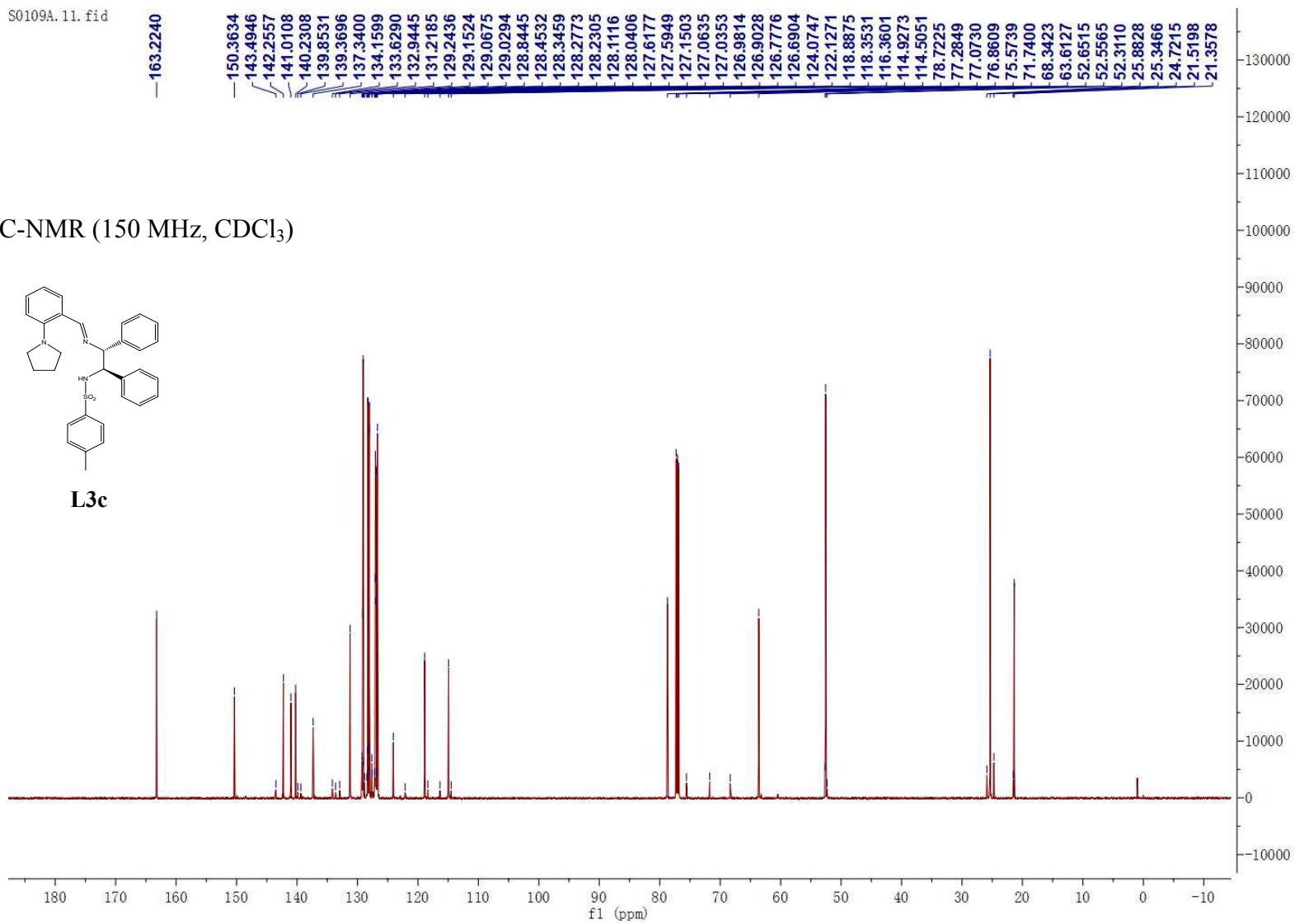


S0109A.11.fid

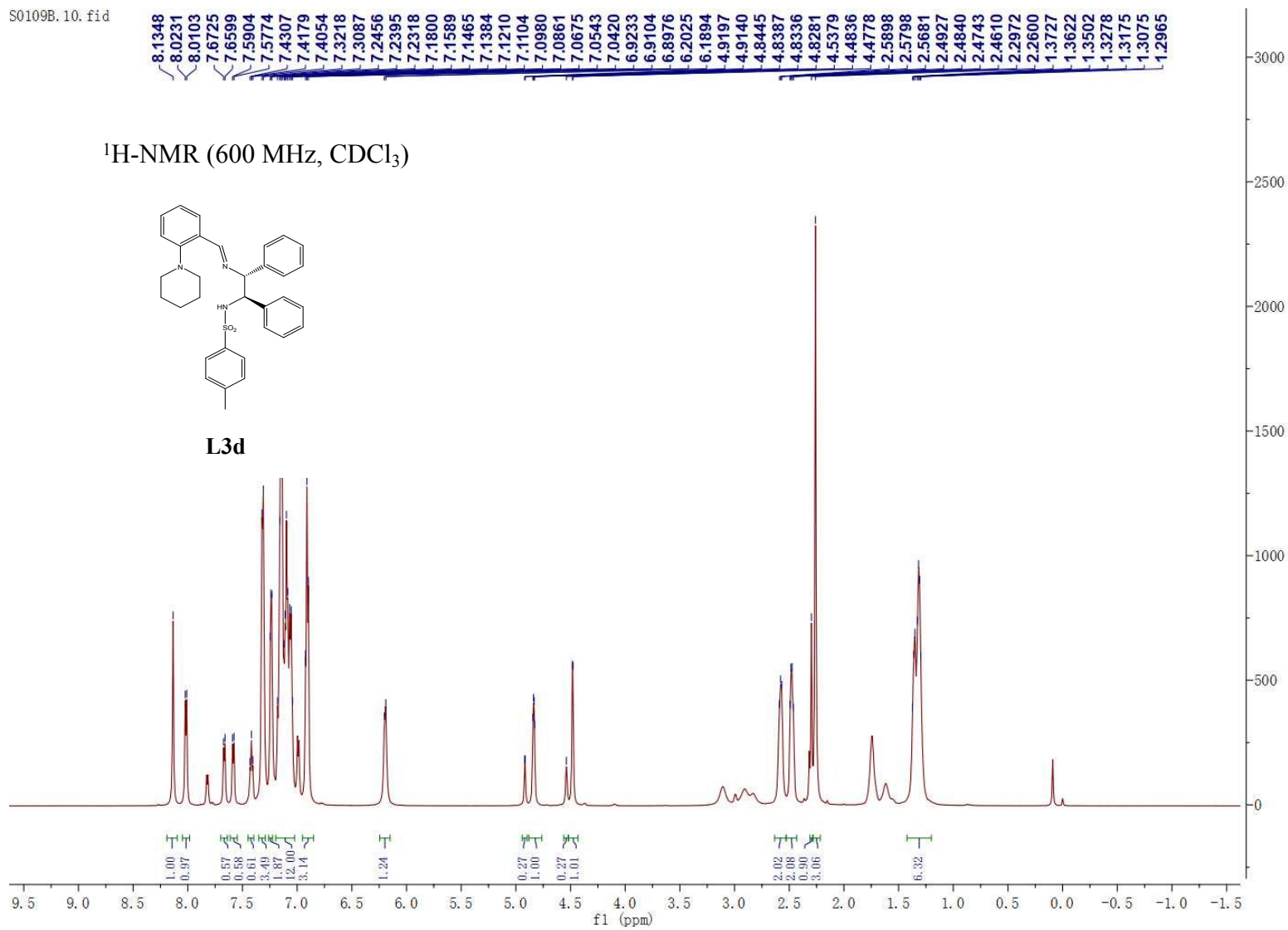
^{13}C -NMR (150 MHz, CDCl_3)



L3c

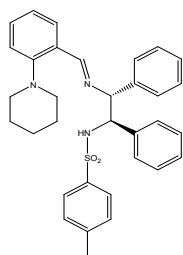


S0109B.10. f1d

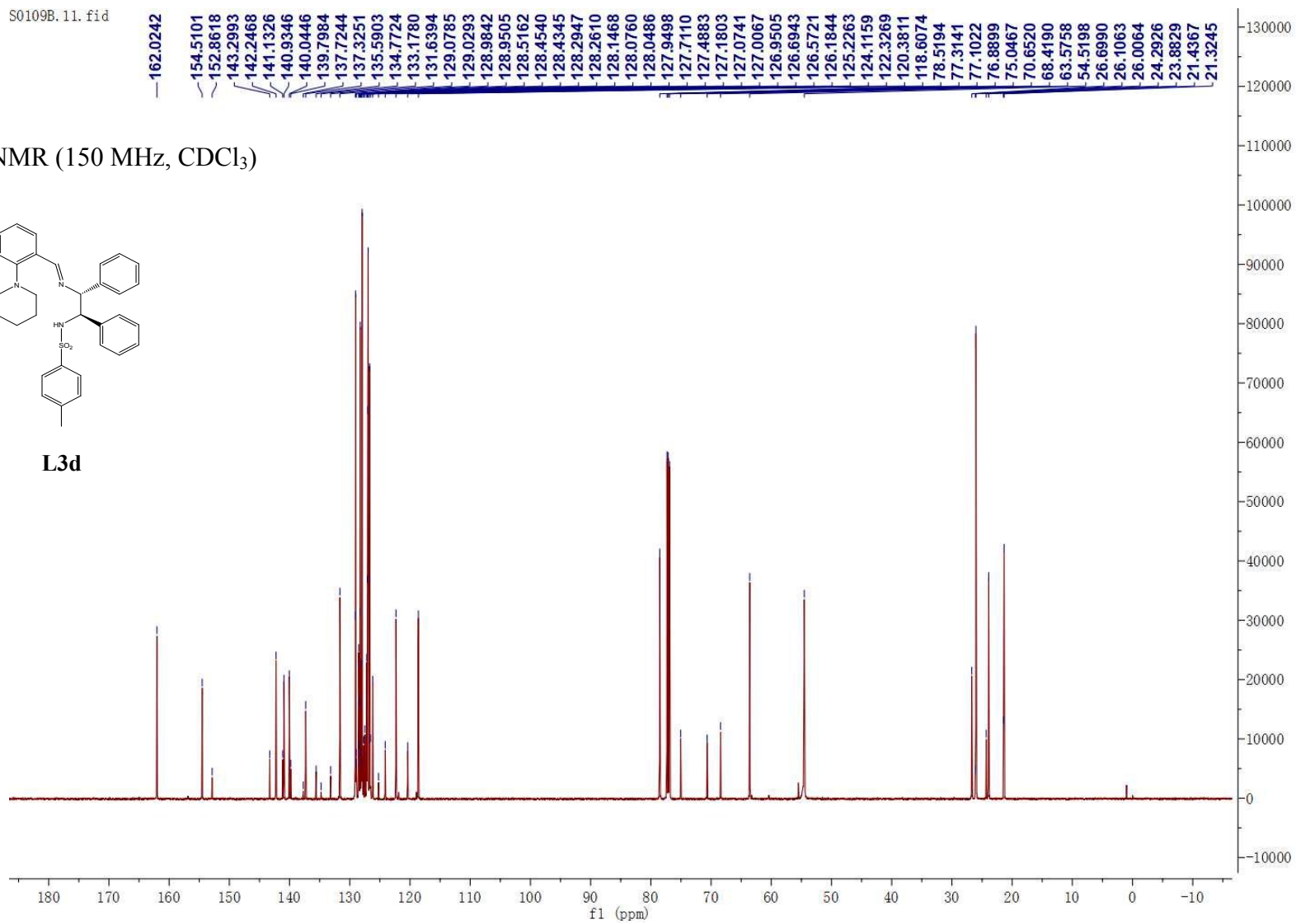


S0109B.11.fid

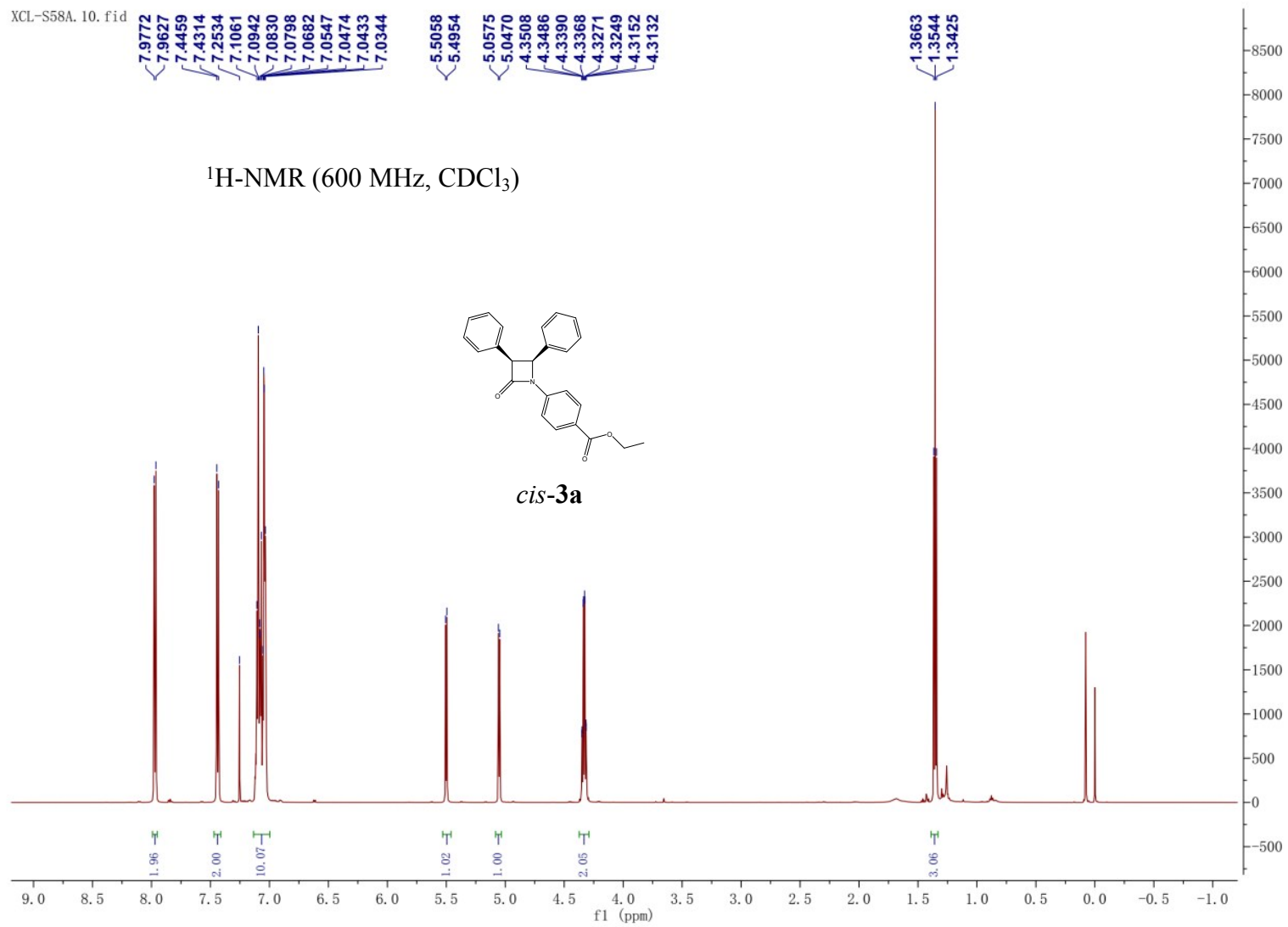
^{13}C -NMR (150 MHz, CDCl_3)



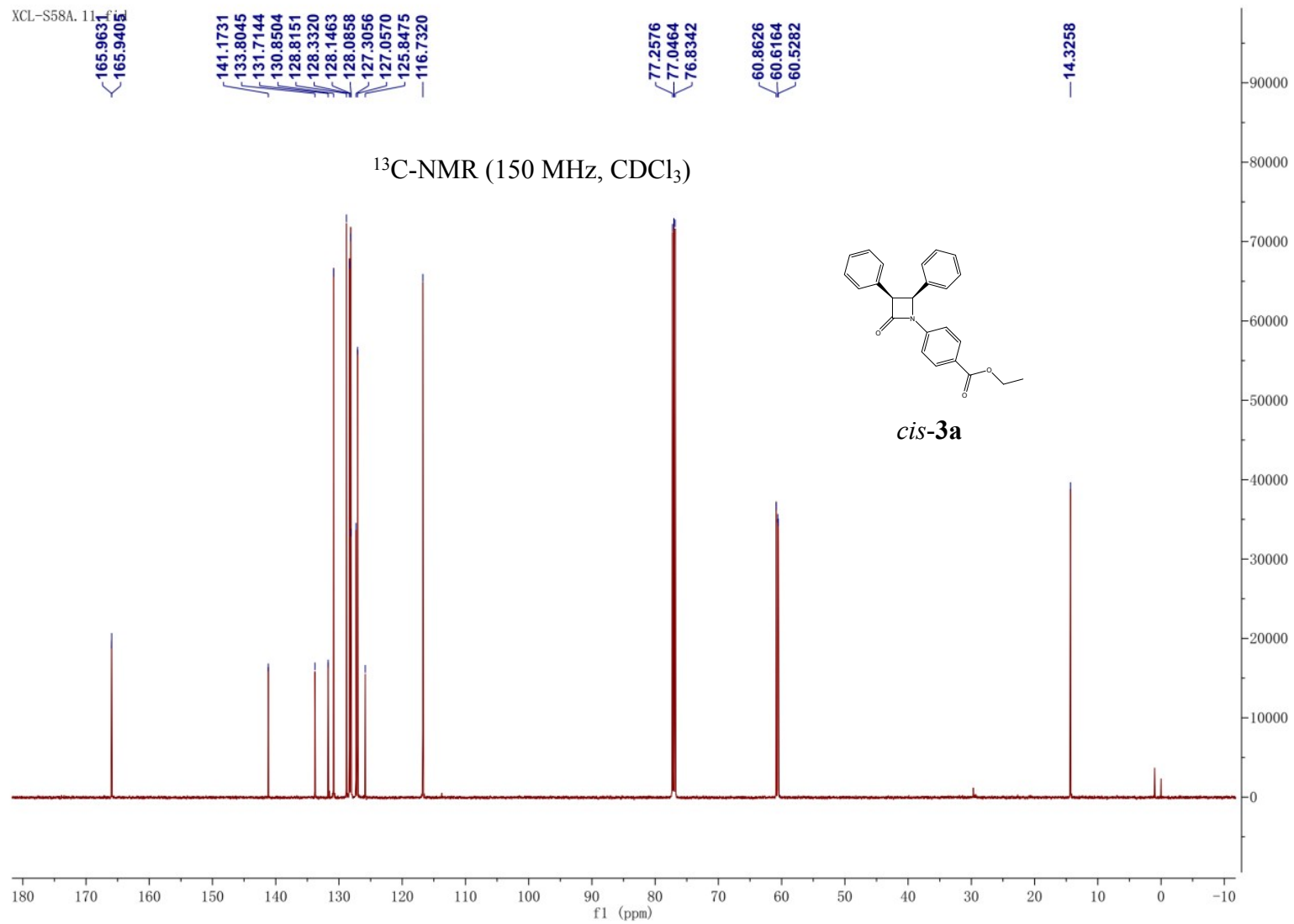
L3d



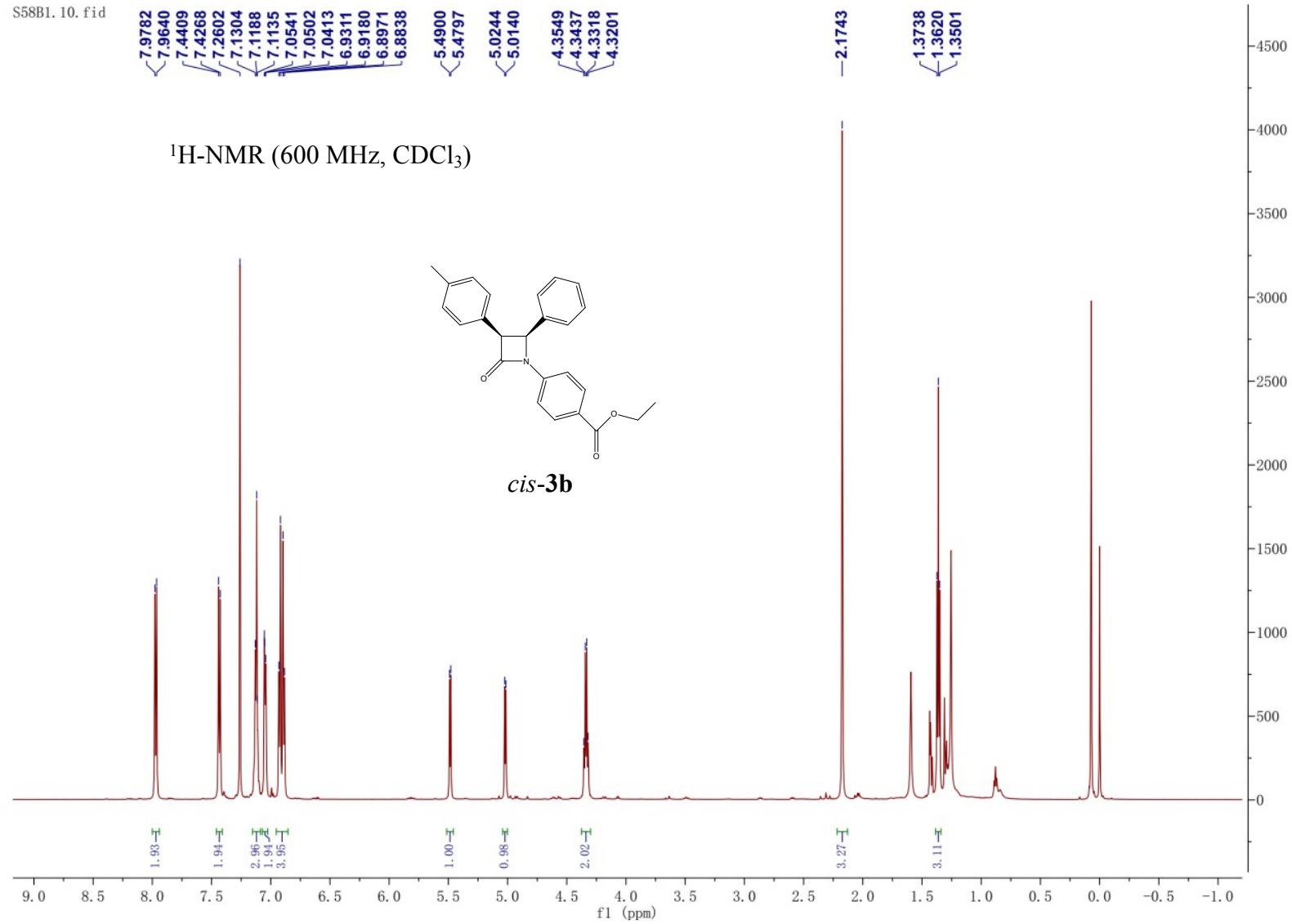
XCL-S58A. 10. fid



XCL-S58A.11

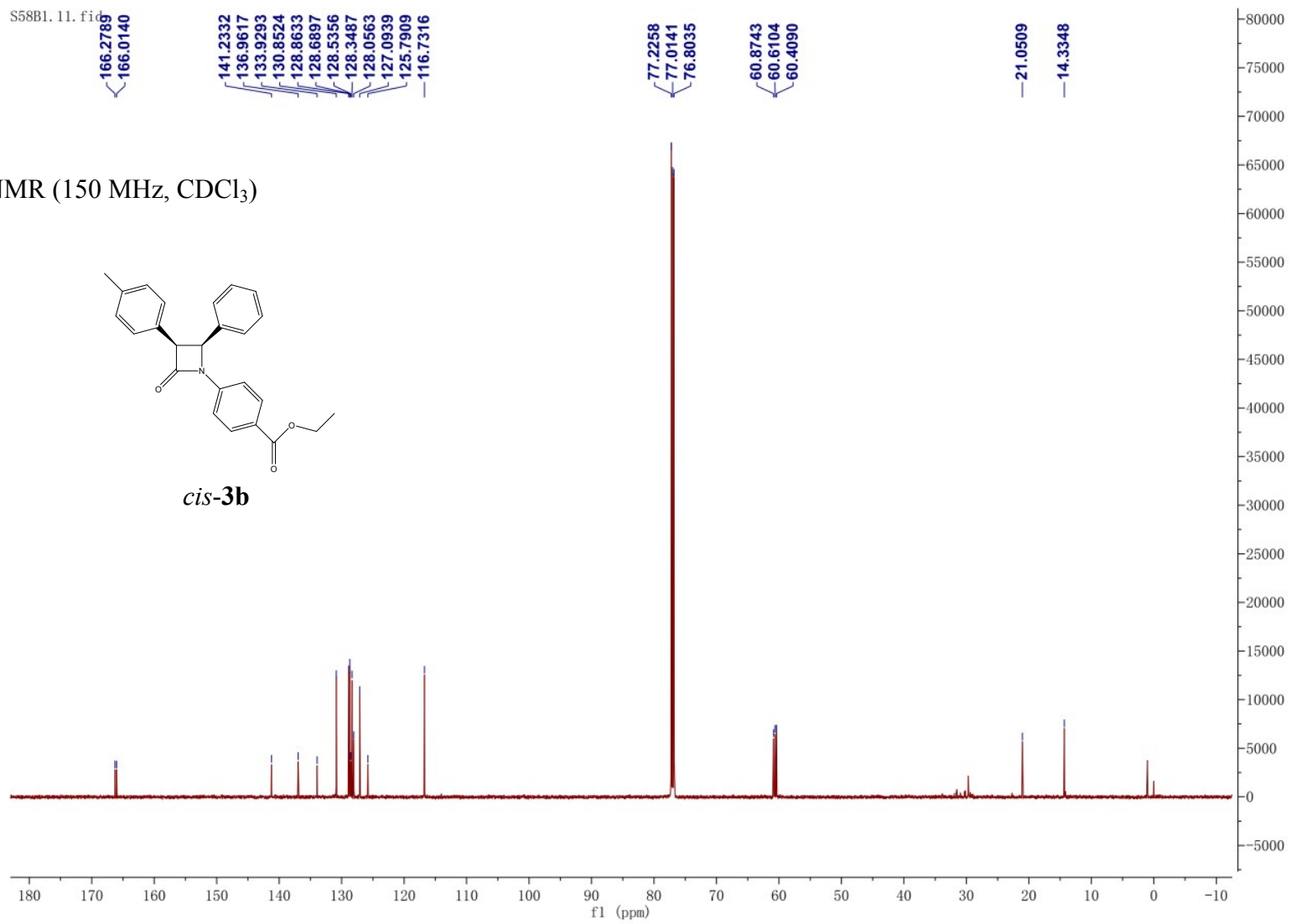
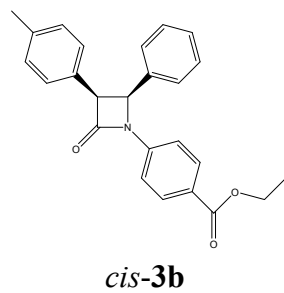


S58B1.10.fid

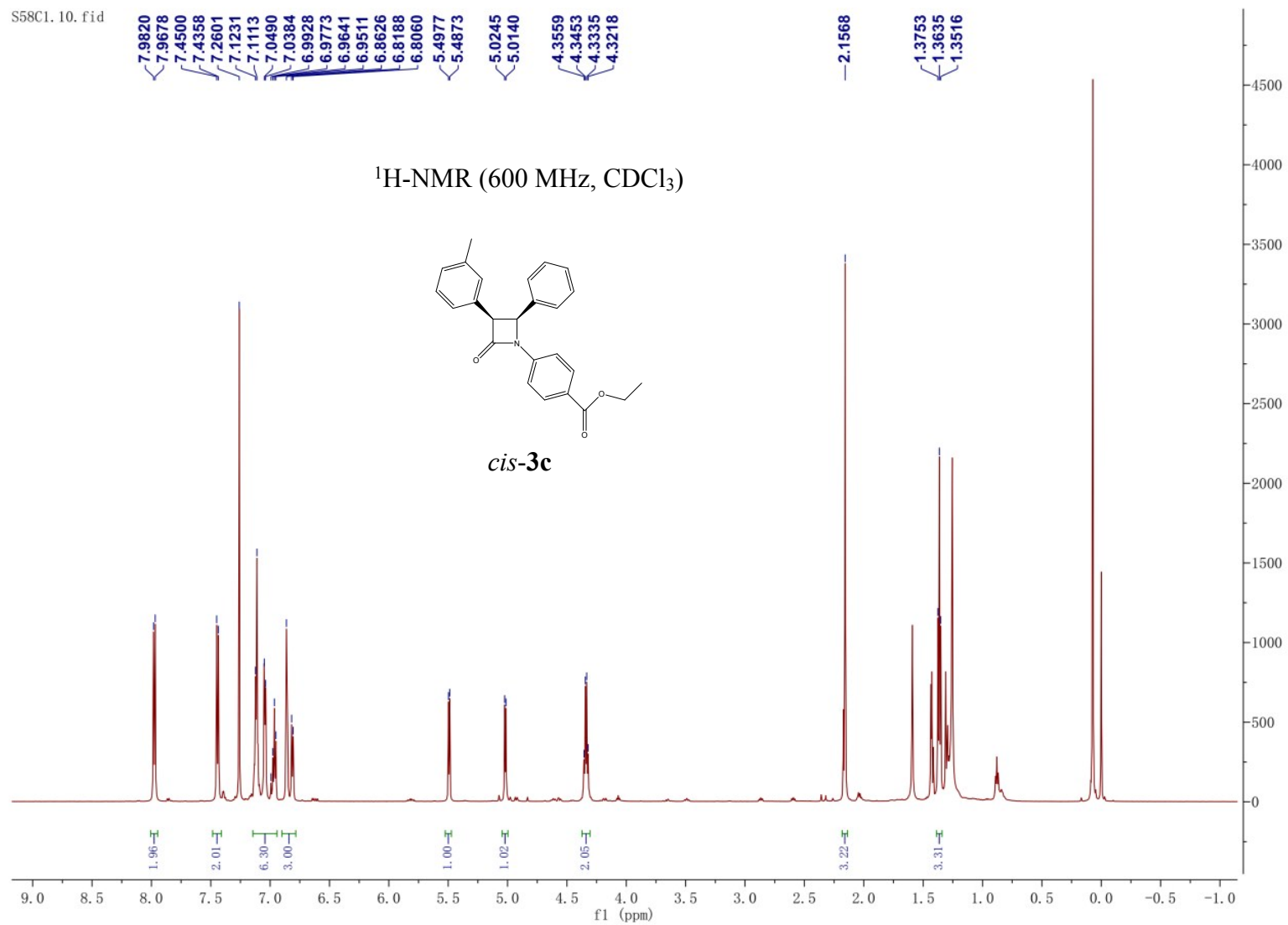


S58B1.11.fid

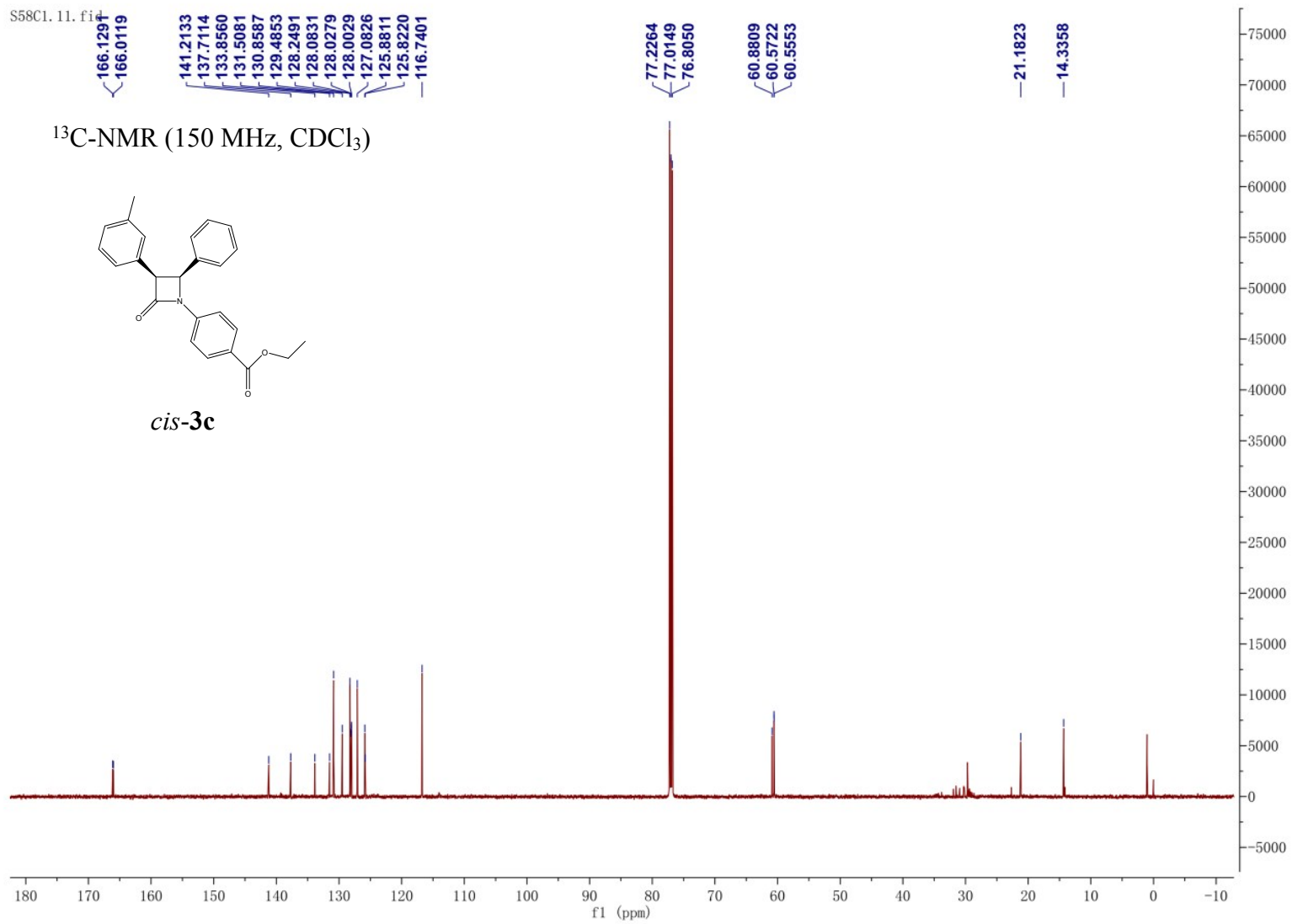
$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)



S58Cl. 10. fid



S58Cl. 11. fi

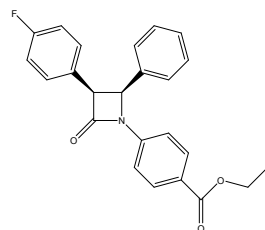


S99Cl.10.fid

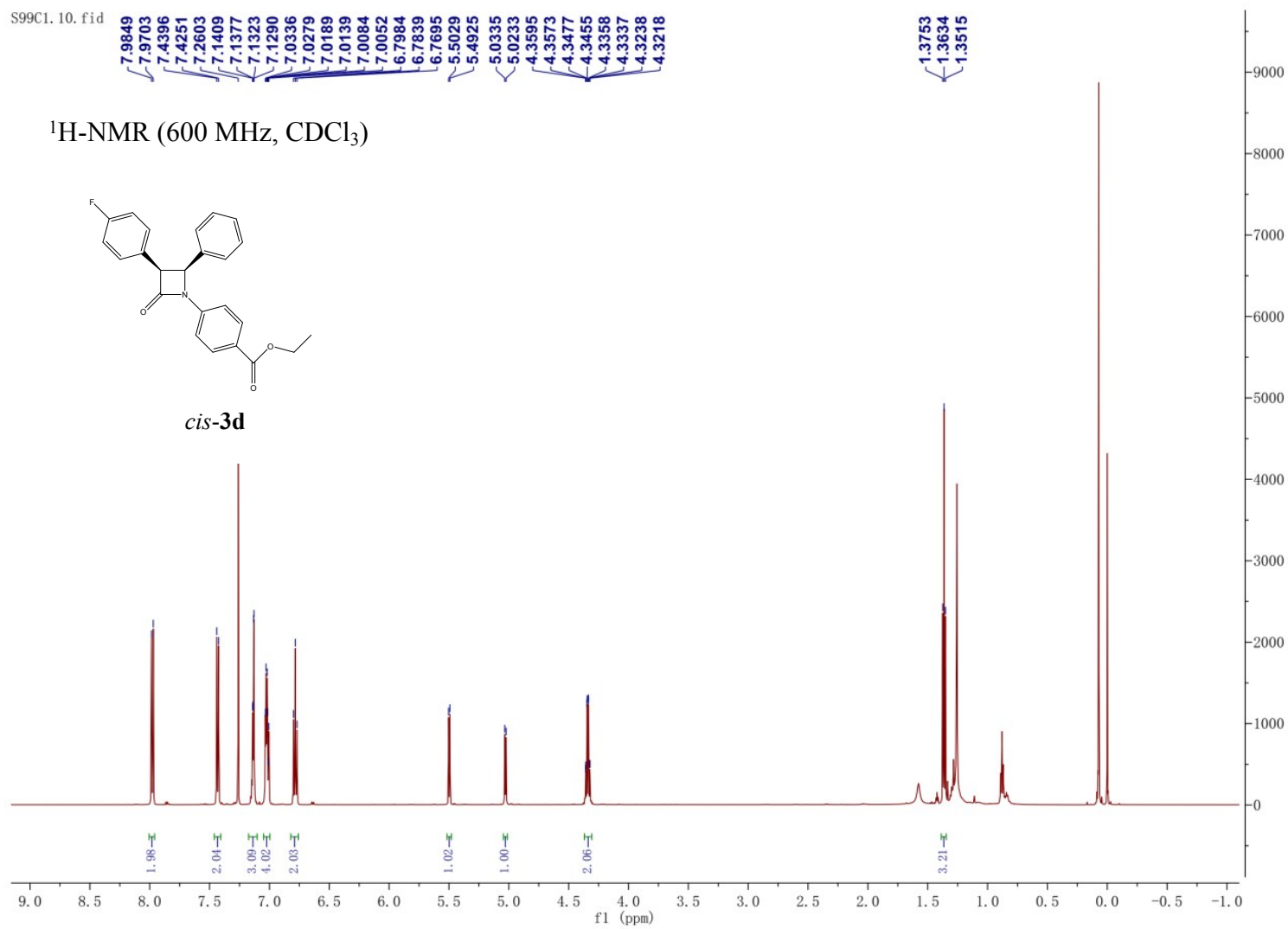
7.9849
7.9703
7.4396
7.4251
7.2603
7.1409
7.1377
7.1323
7.1290
7.0336
7.0279
7.0189
7.0139
7.0084
7.0052
6.7984
6.7839
6.7695
5.5029
5.4925
5.0335
5.0233
4.3595
4.3573
4.3477
4.3455
4.3358
4.3337
4.3238
4.3218

1.3753
1.3634
1.3515

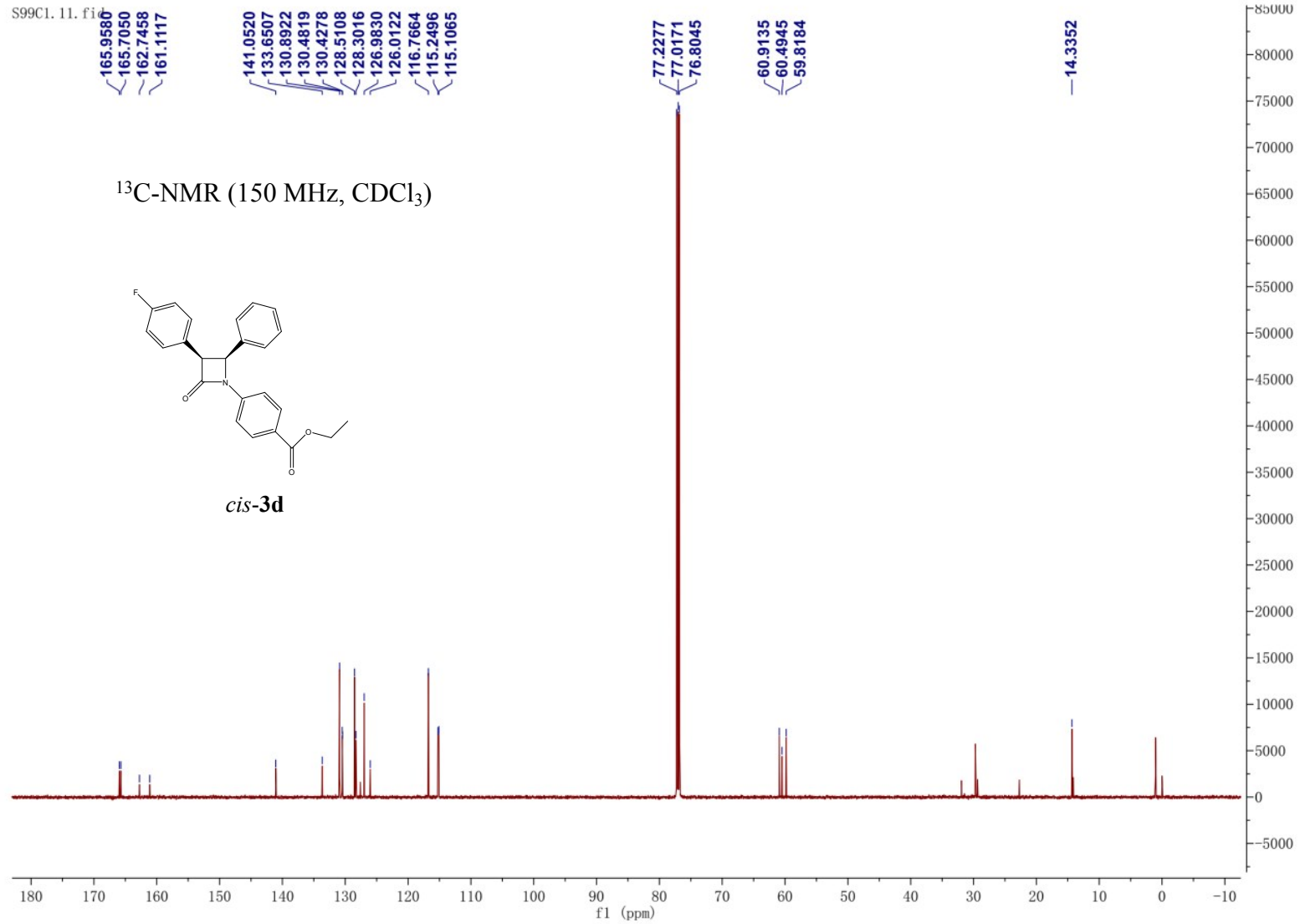
$^1\text{H-NMR}$ (600 MHz, CDCl_3)



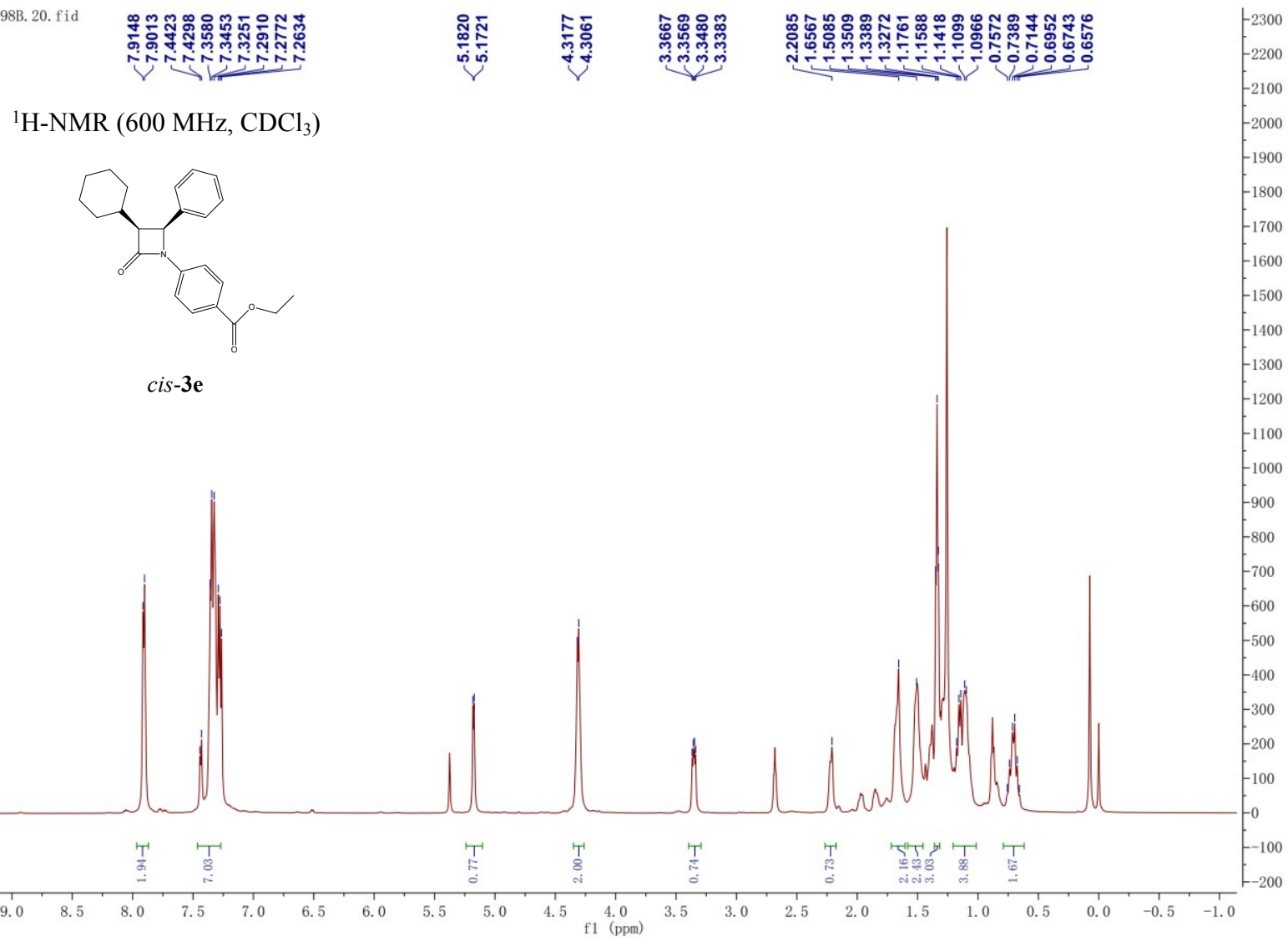
cis-3d



S99Cl. 11. fi



S98B. 20. fid



S98B. 21. f1.d

167.7457
166.0452

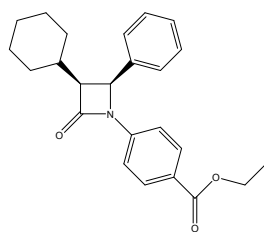
141.1070
137.1754
134.5536
130.7902
130.7540
129.0249
128.6582
128.5779
125.3386
124.9068
116.5801
115.9150

77.2514
77.0397
76.8278

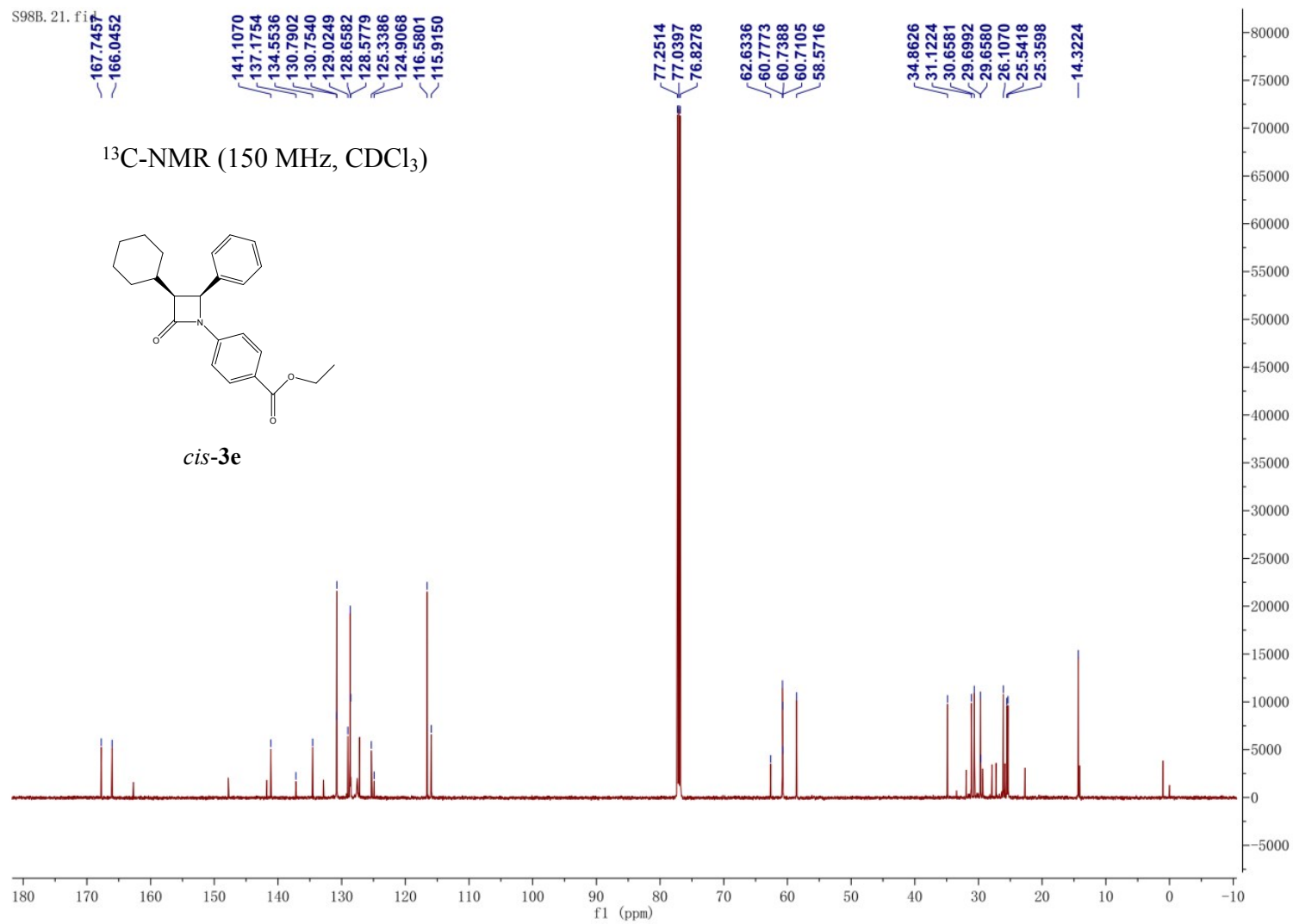
62.6336
60.7773
60.7388
60.7105
58.5716

34.8626
31.1224
30.6581
29.6992
29.6580
26.1070
25.5418
25.3598
14.3224

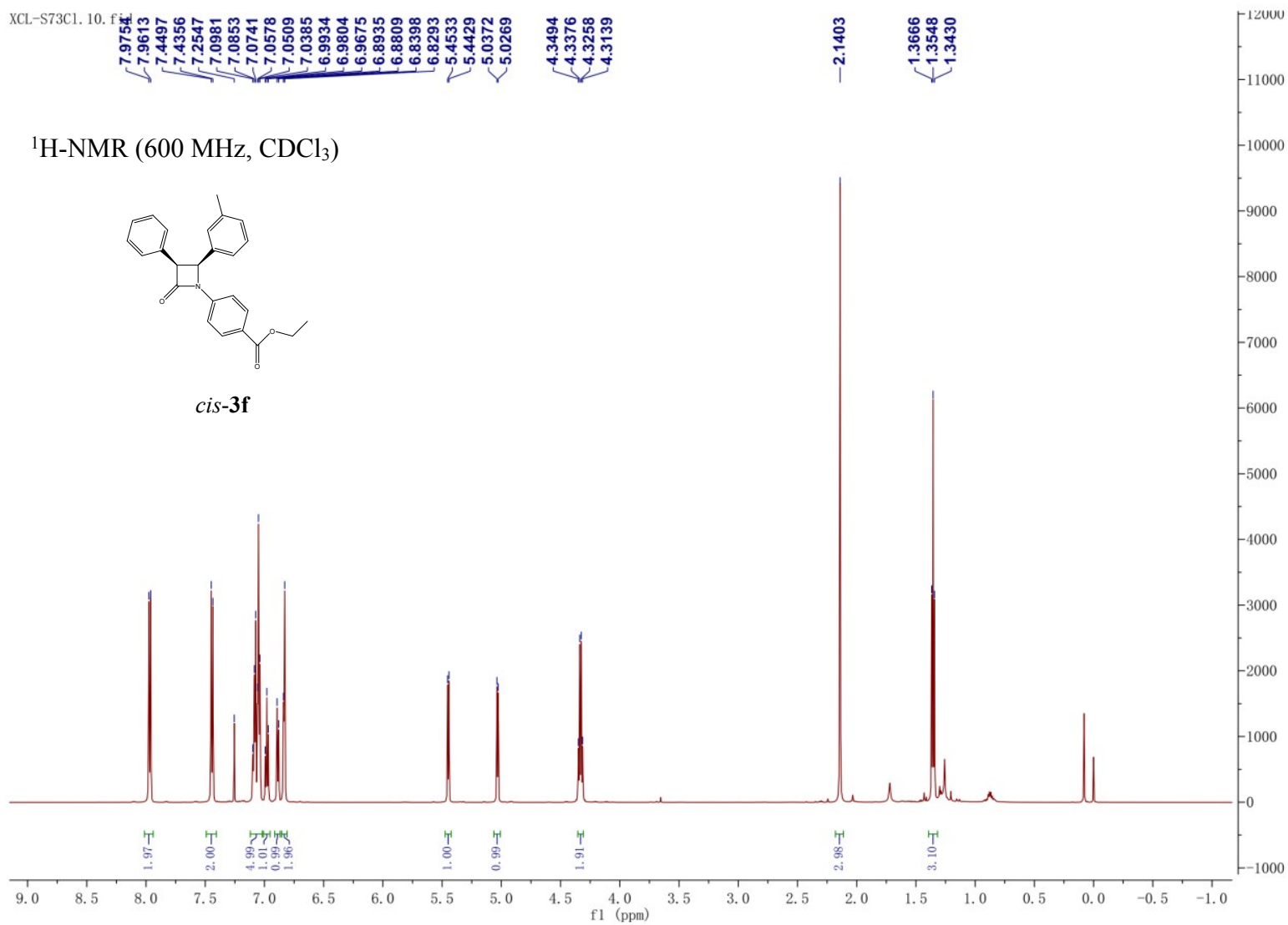
$^{13}\text{C-NMR}$ (150 MHz, CDCl_3)

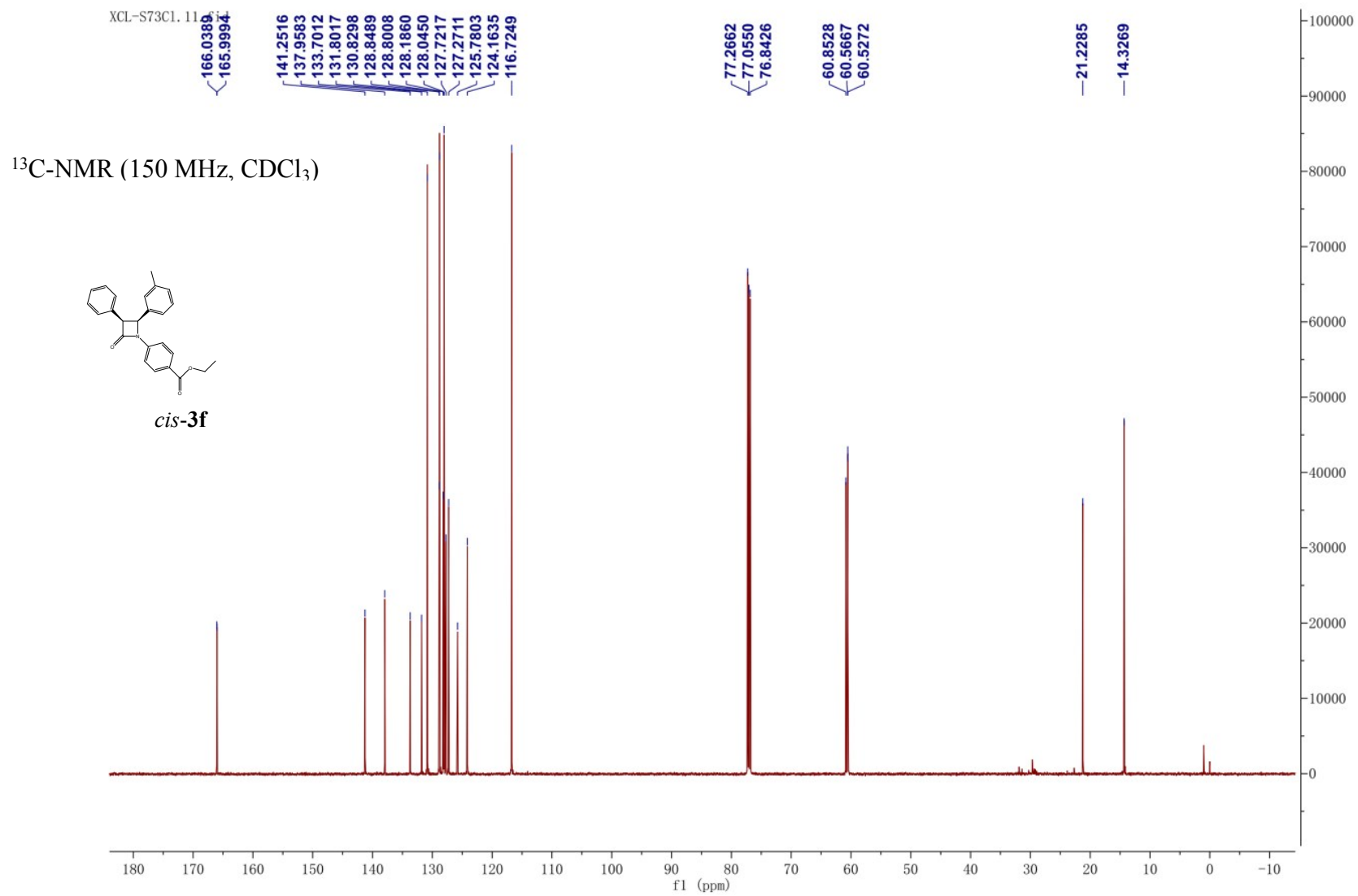


cis-3e



XCL-S73Cl. 10. f1

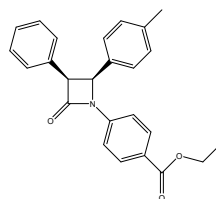




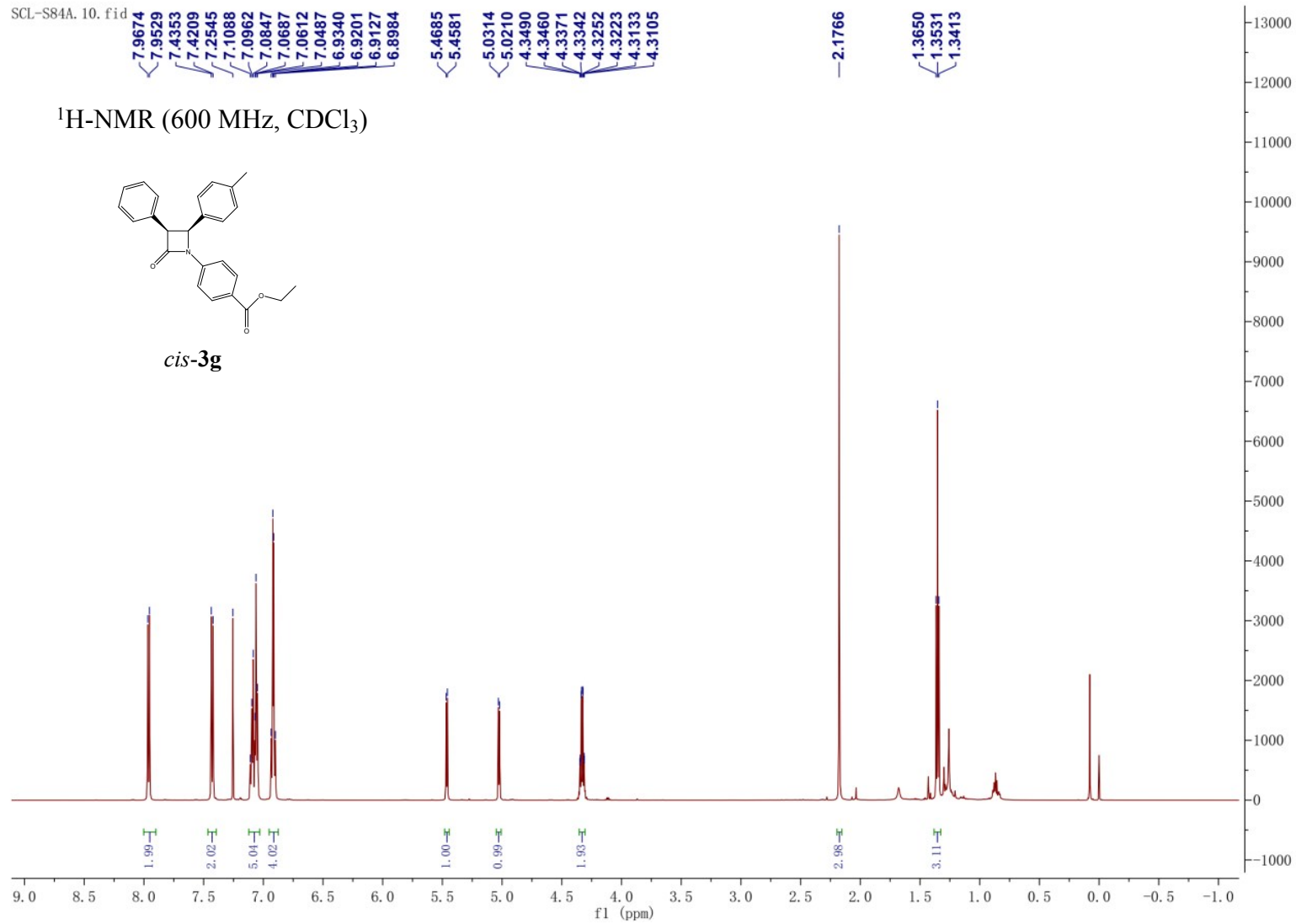
SCL-S84A. 10. fid

7.9674
7.9529
7.4353
7.4209
7.2545
7.1088
7.0962
7.0847
7.0687
7.0612
7.0487
6.9340
6.9201
6.9127
6.8984
5.4685
5.4581
5.0314
5.0210
4.3490
4.3460
4.3371
4.3342
4.3252
4.3223
4.3133
4.3105

$^1\text{H-NMR}$ (600 MHz, CDCl_3)

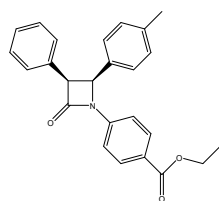


cis-3g

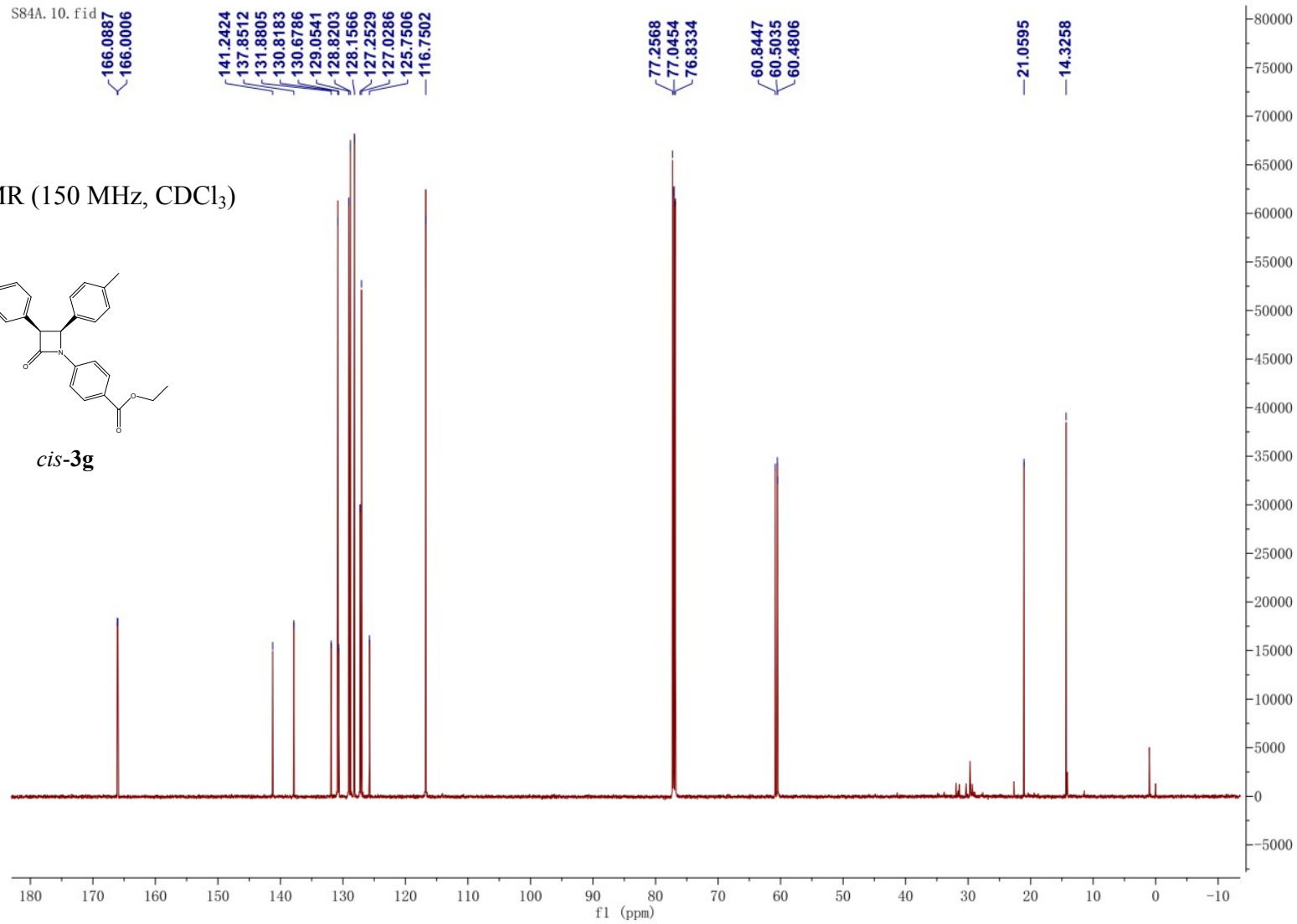


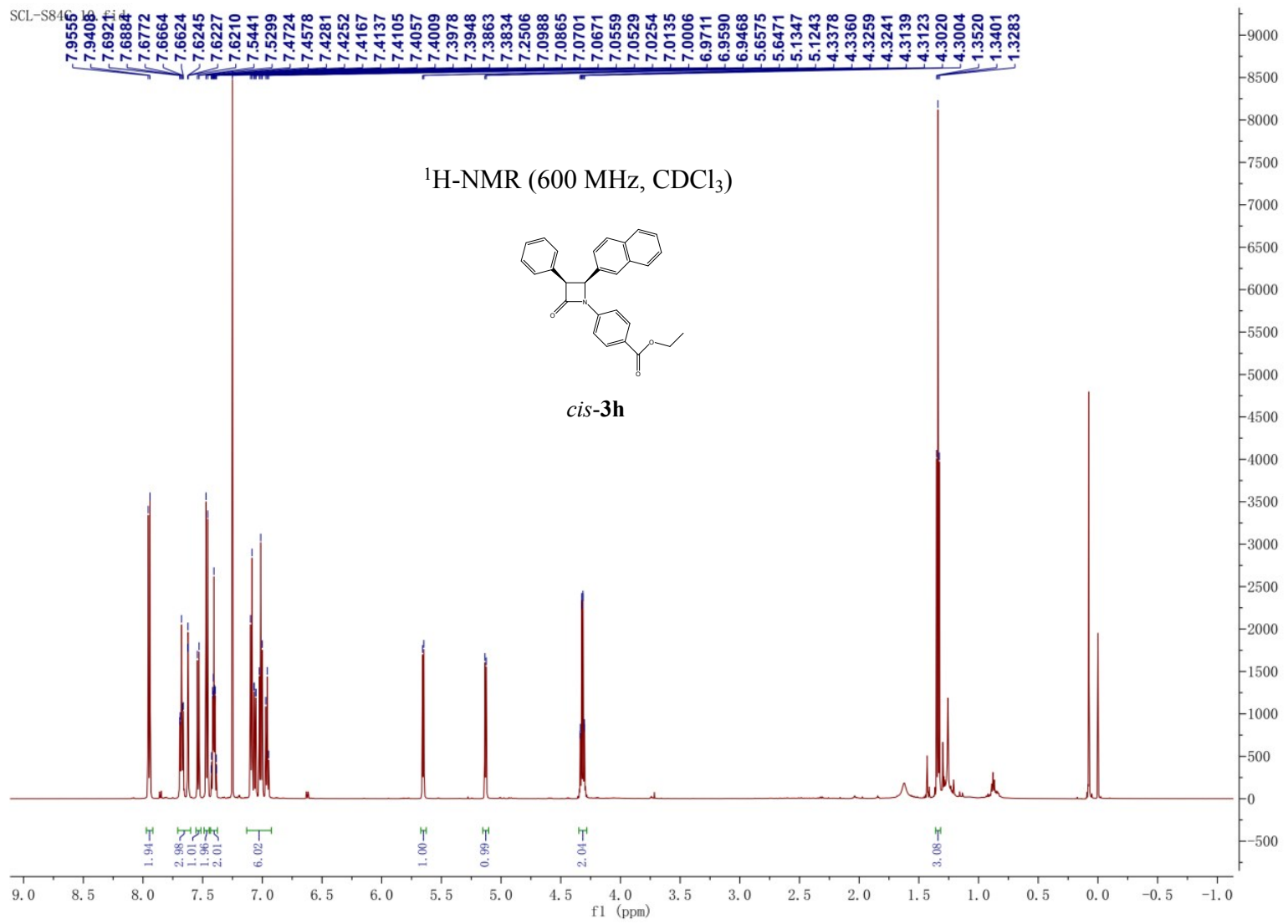
S84A. 10. fid

^{13}C -NMR (150 MHz, CDCl_3)

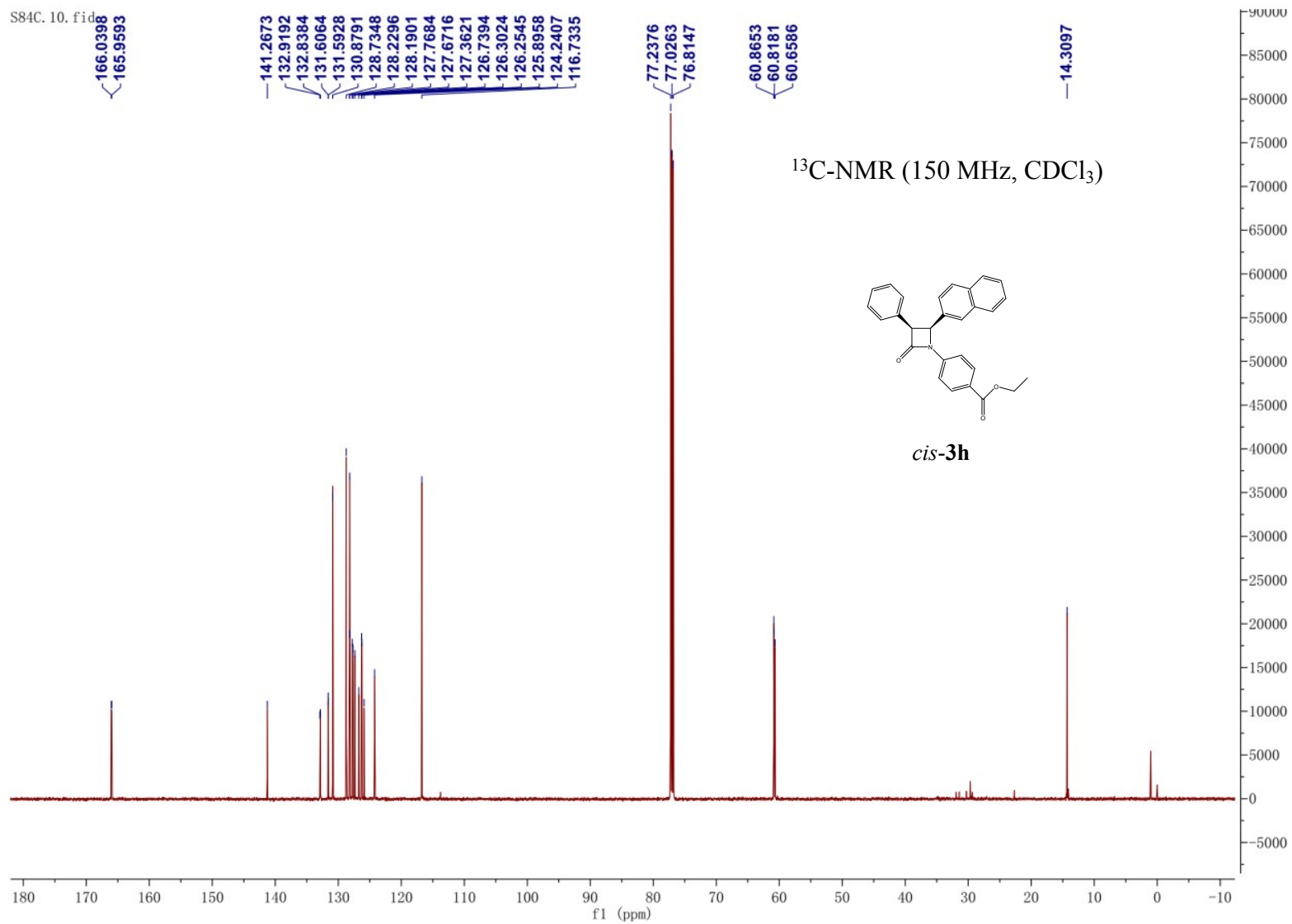


cis-**3g**



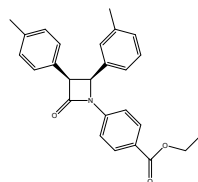


S84C.10.fid

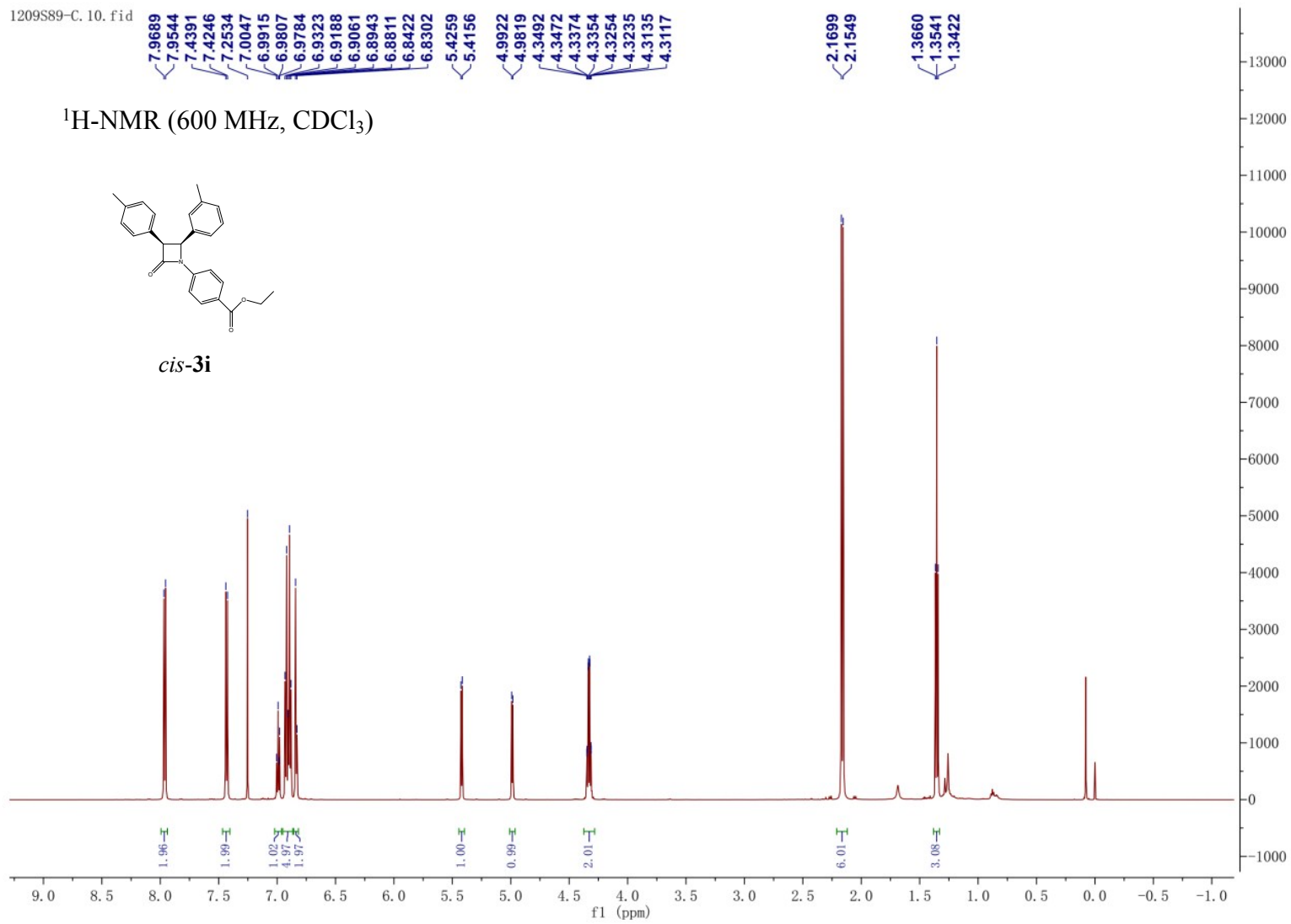


1209S89-C. 10. fid

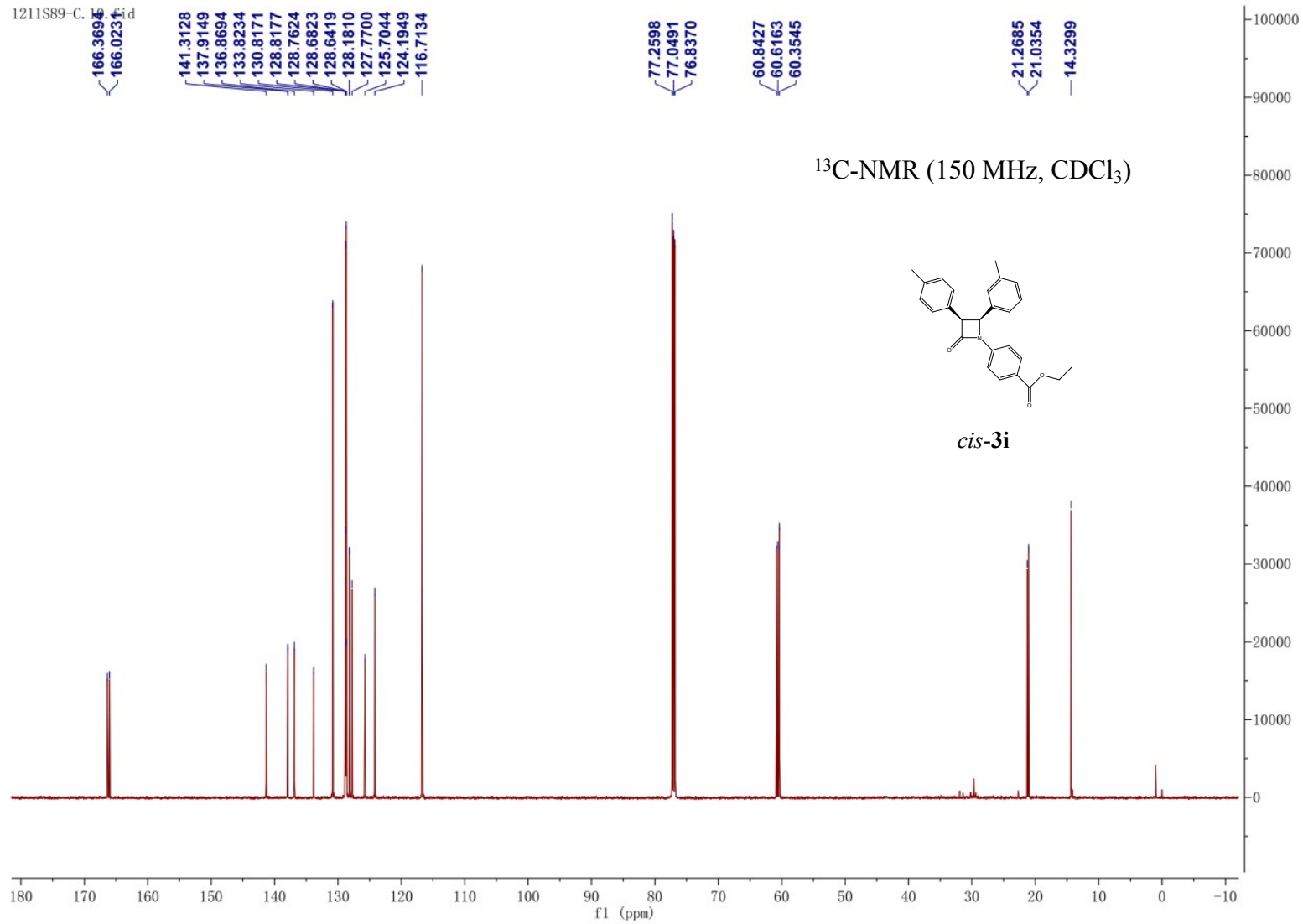
¹H-NMR (600 MHz, CDCl₃)



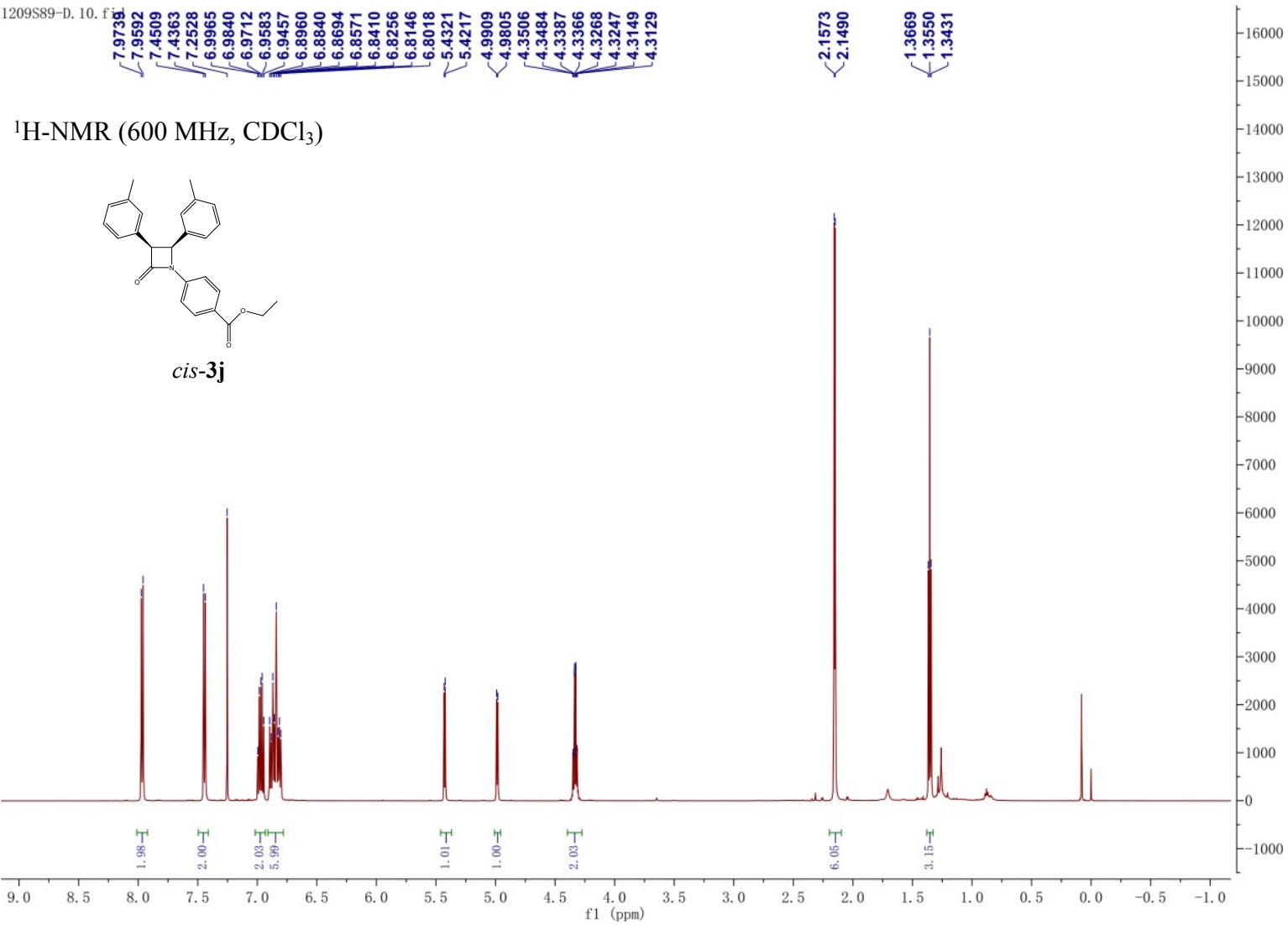
cis-3i

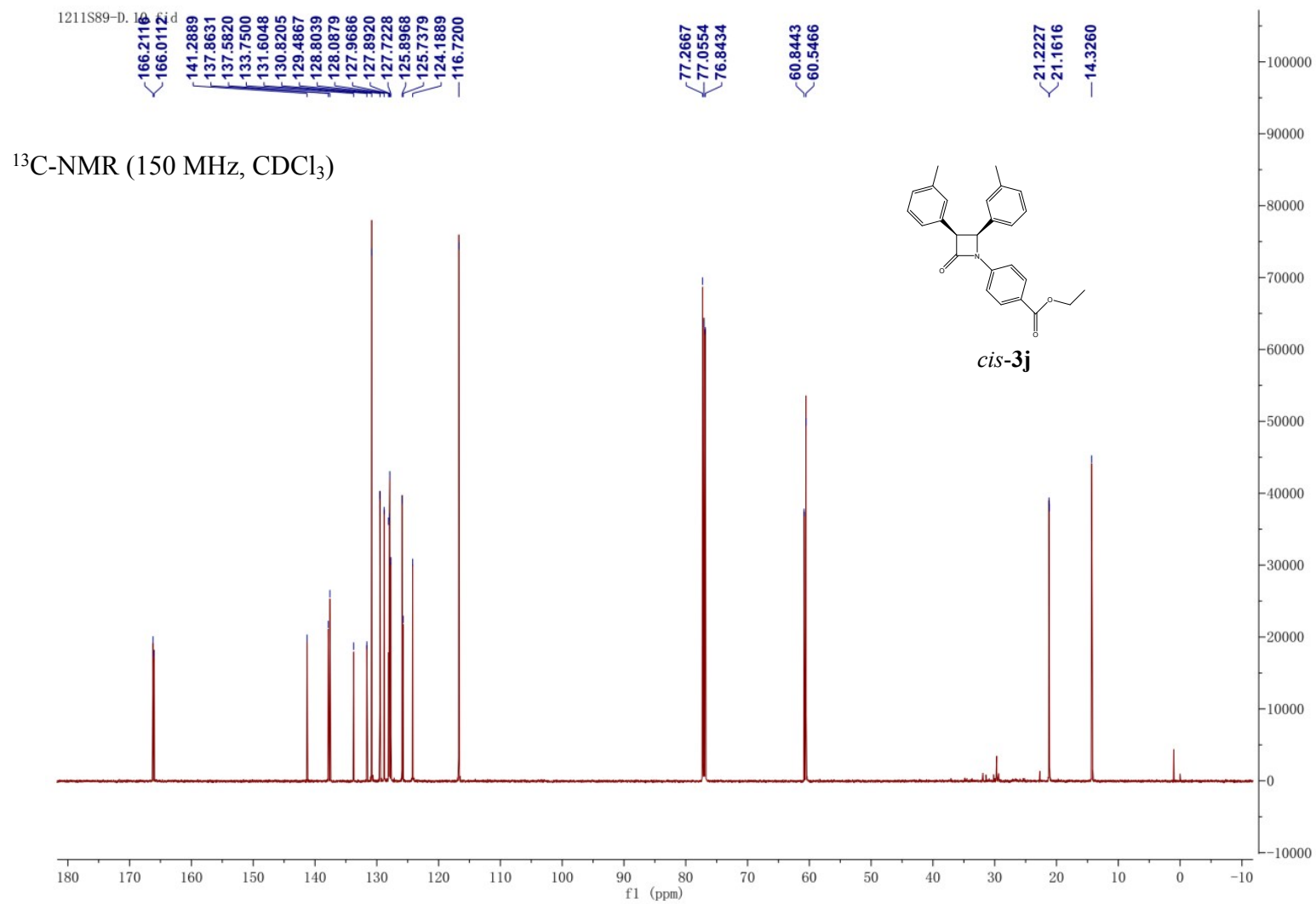


1211S89-C...
166.3694
166.0231

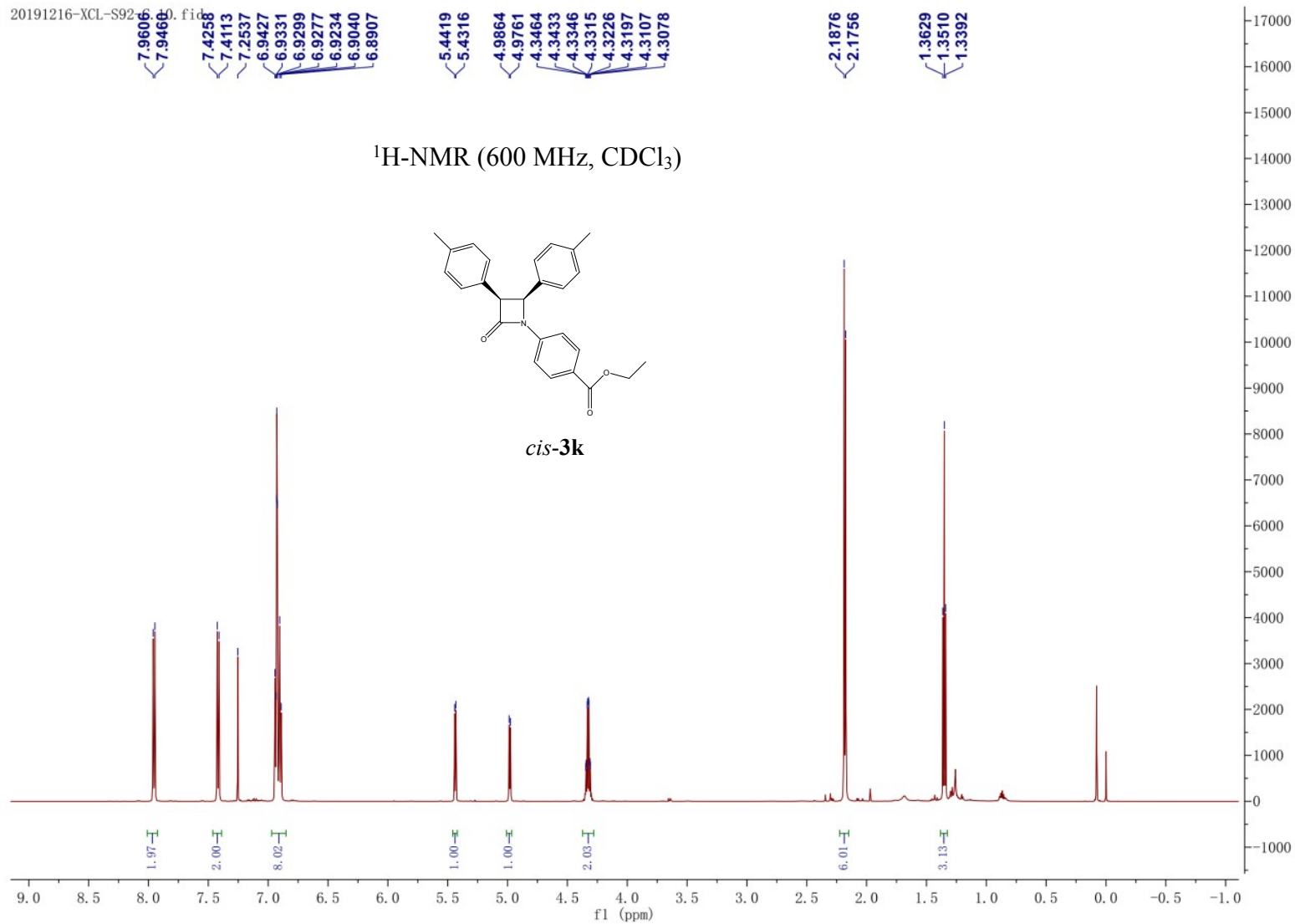


1209S89-D. 10. f1

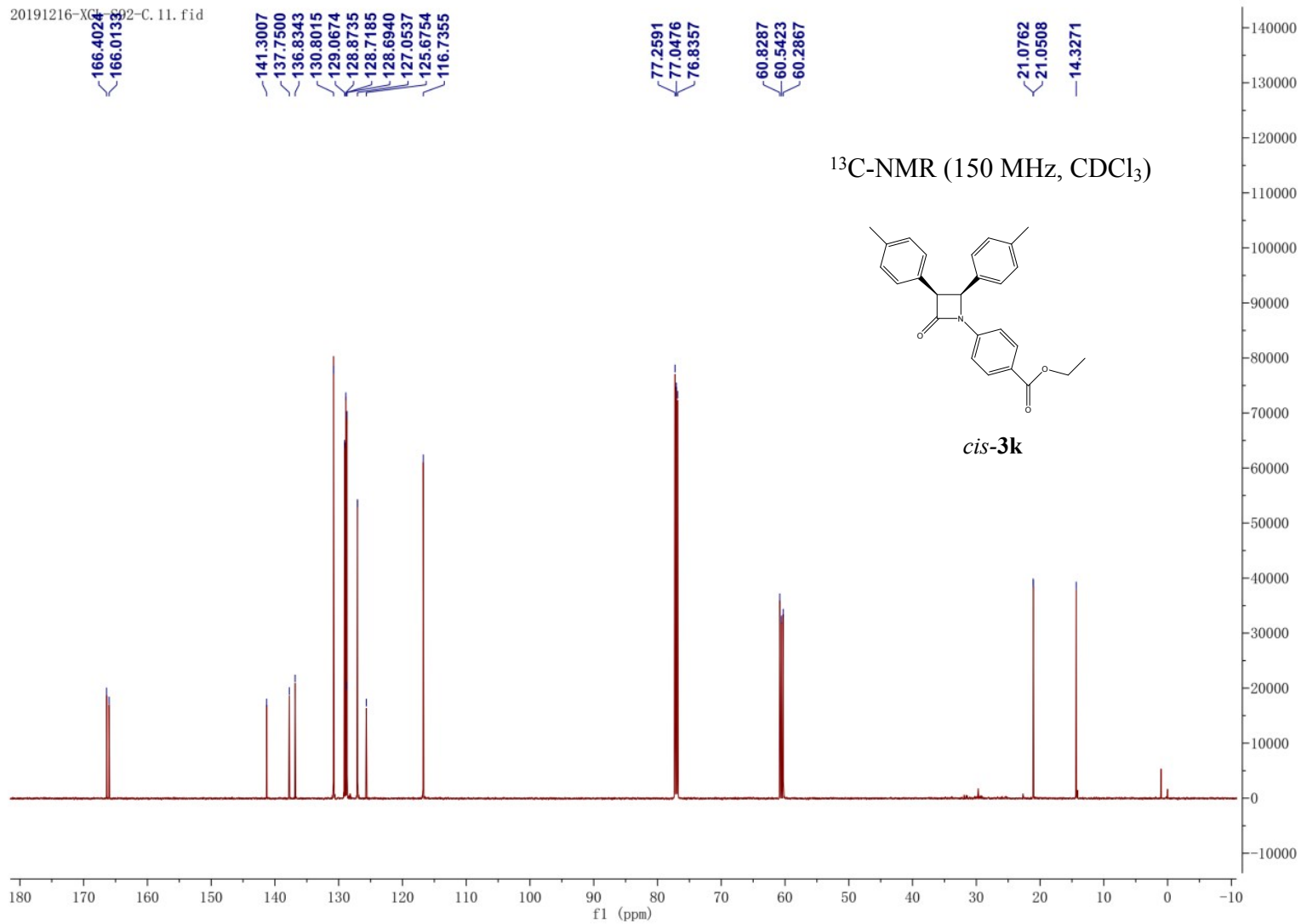




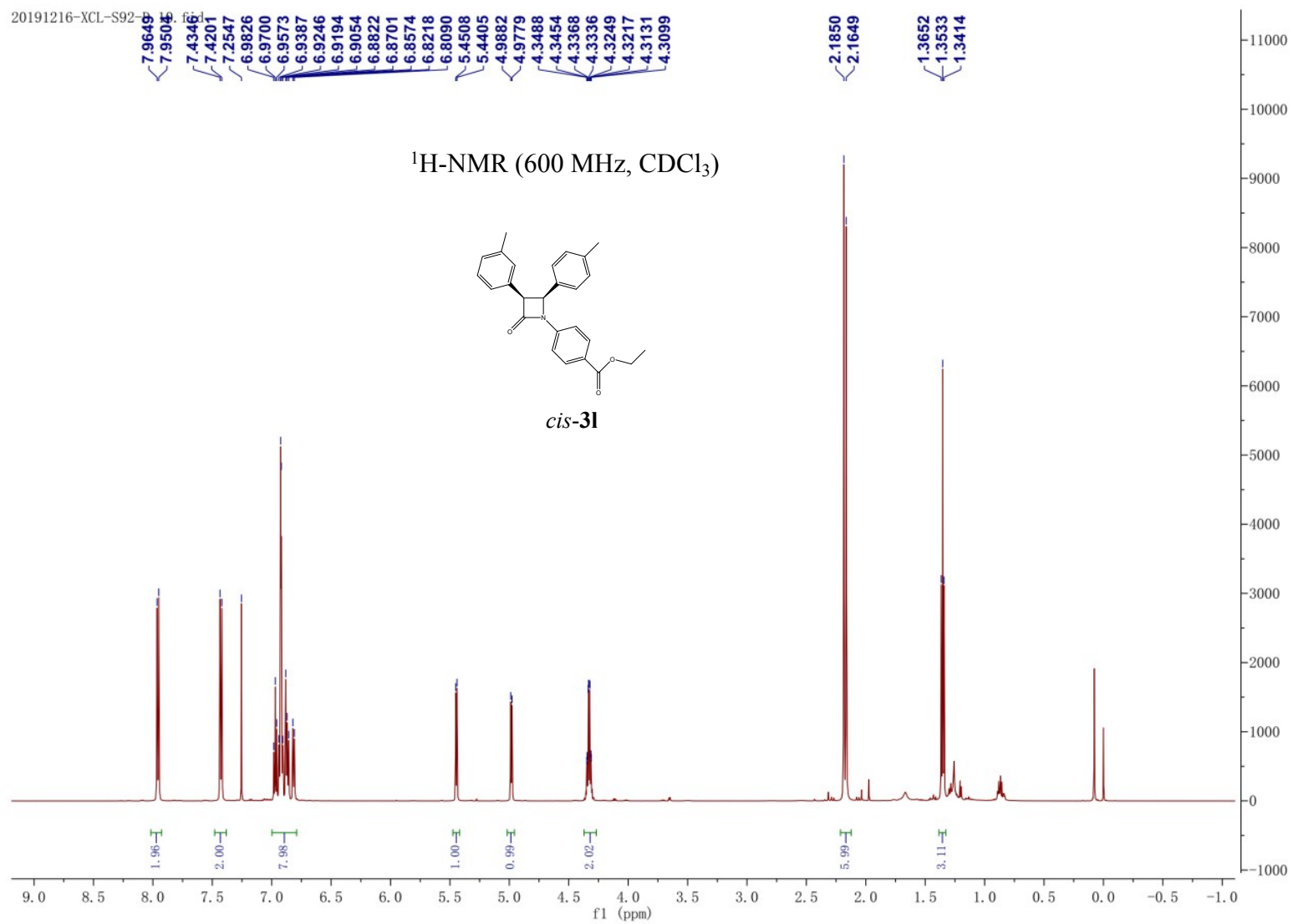
20191216-XCL-S92-0.fid



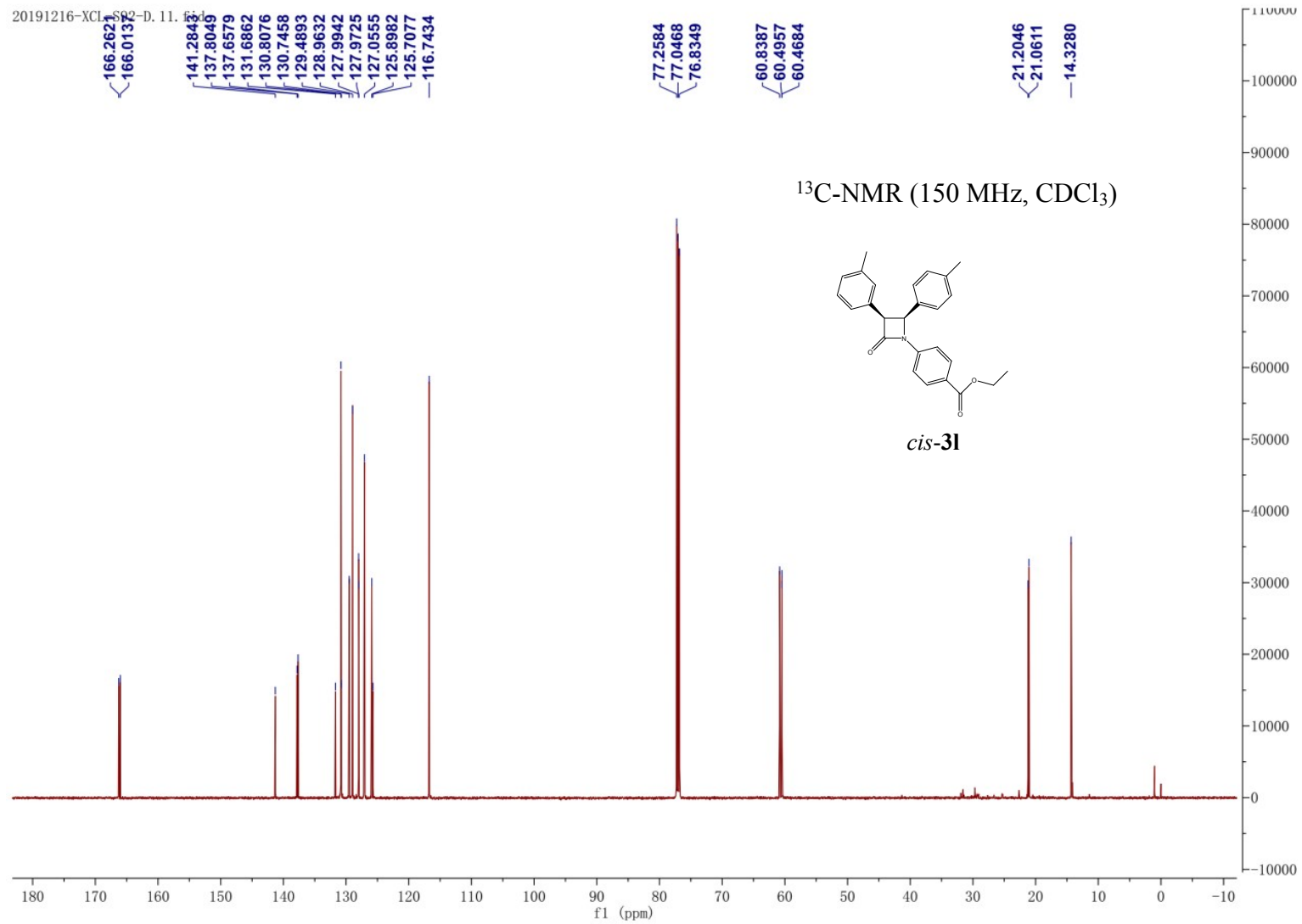
20191216-XE-002-C. 11. fid

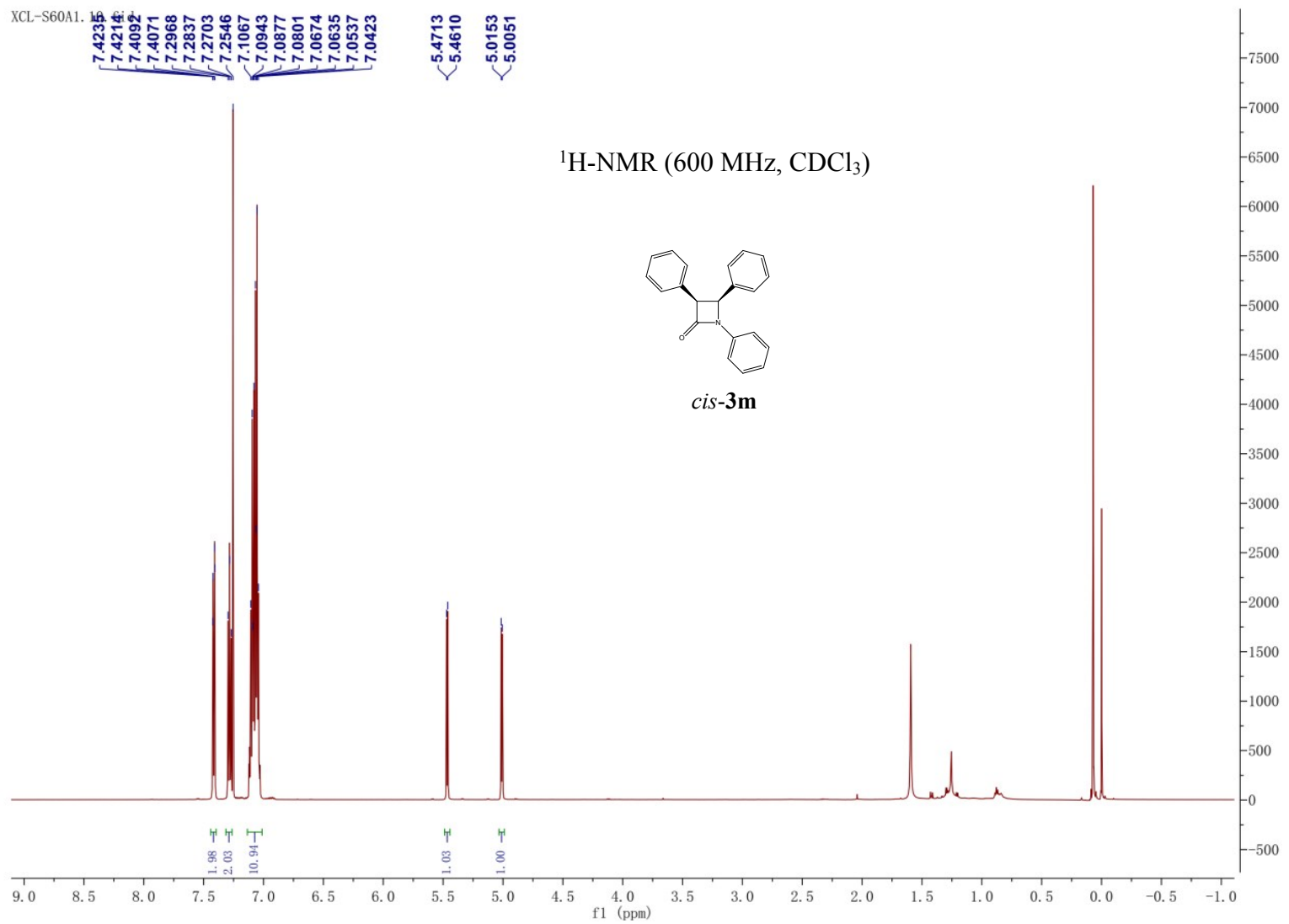


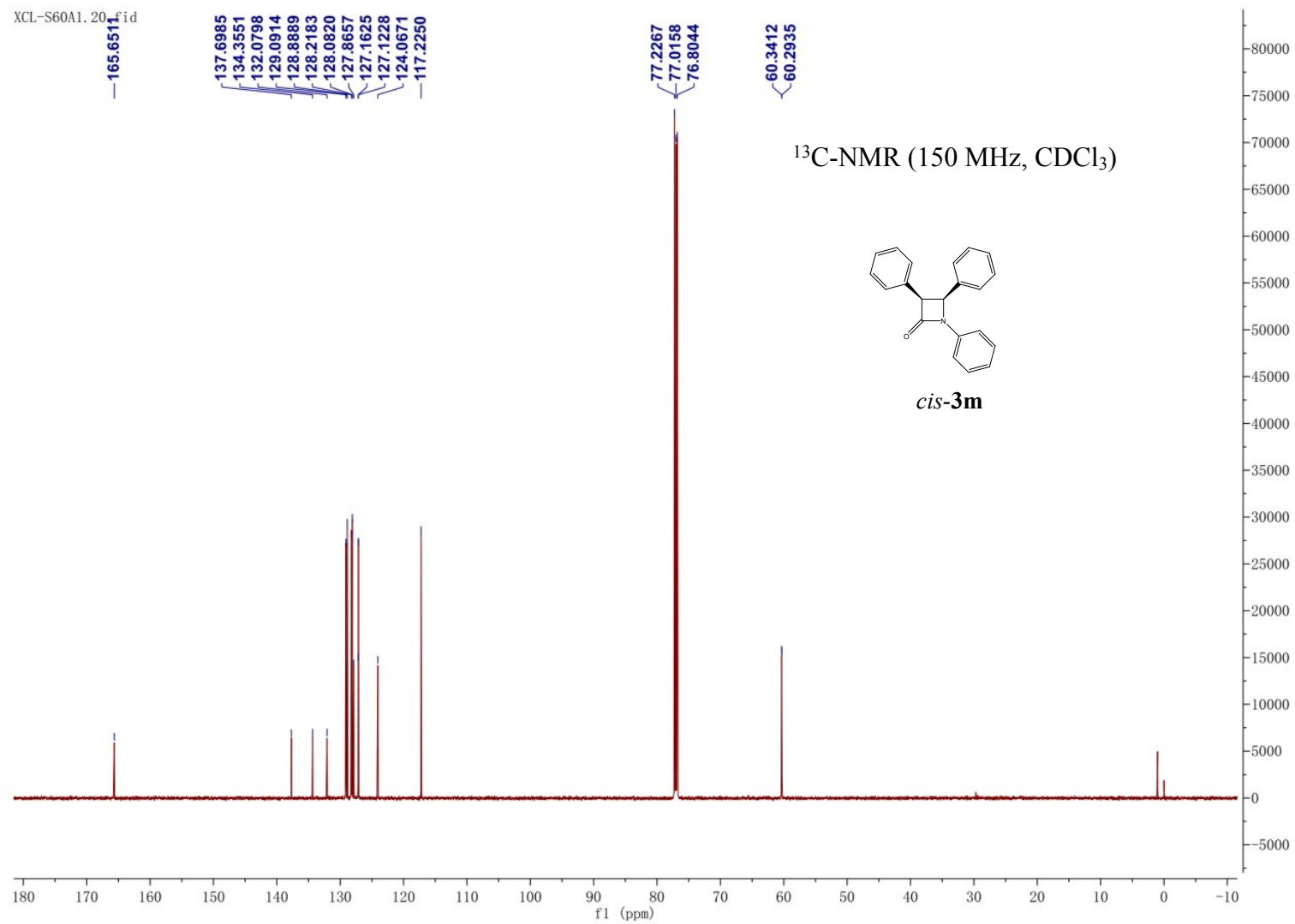
20191216-XCL-S92-1



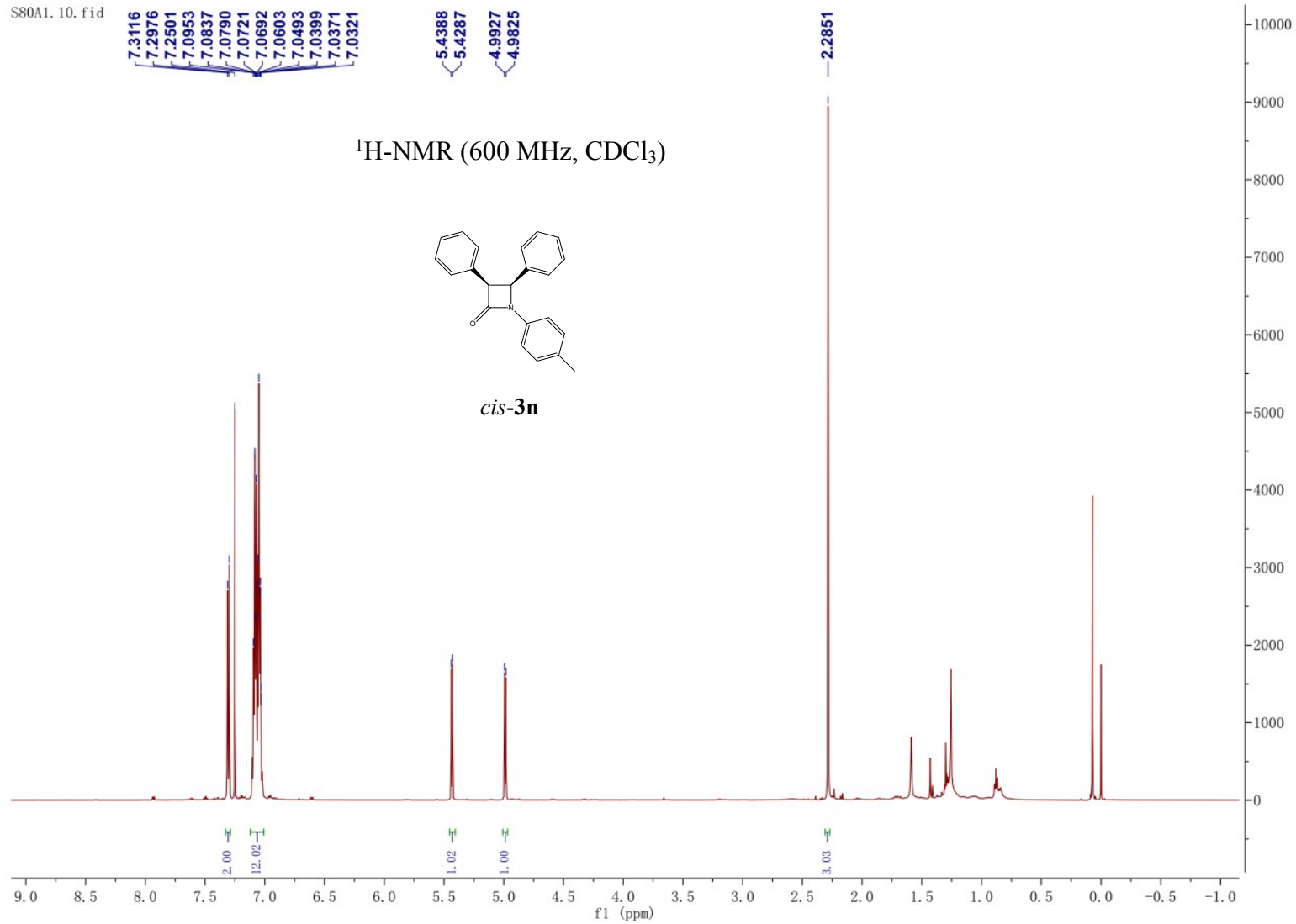
20191216-XCL-892-D. 11.

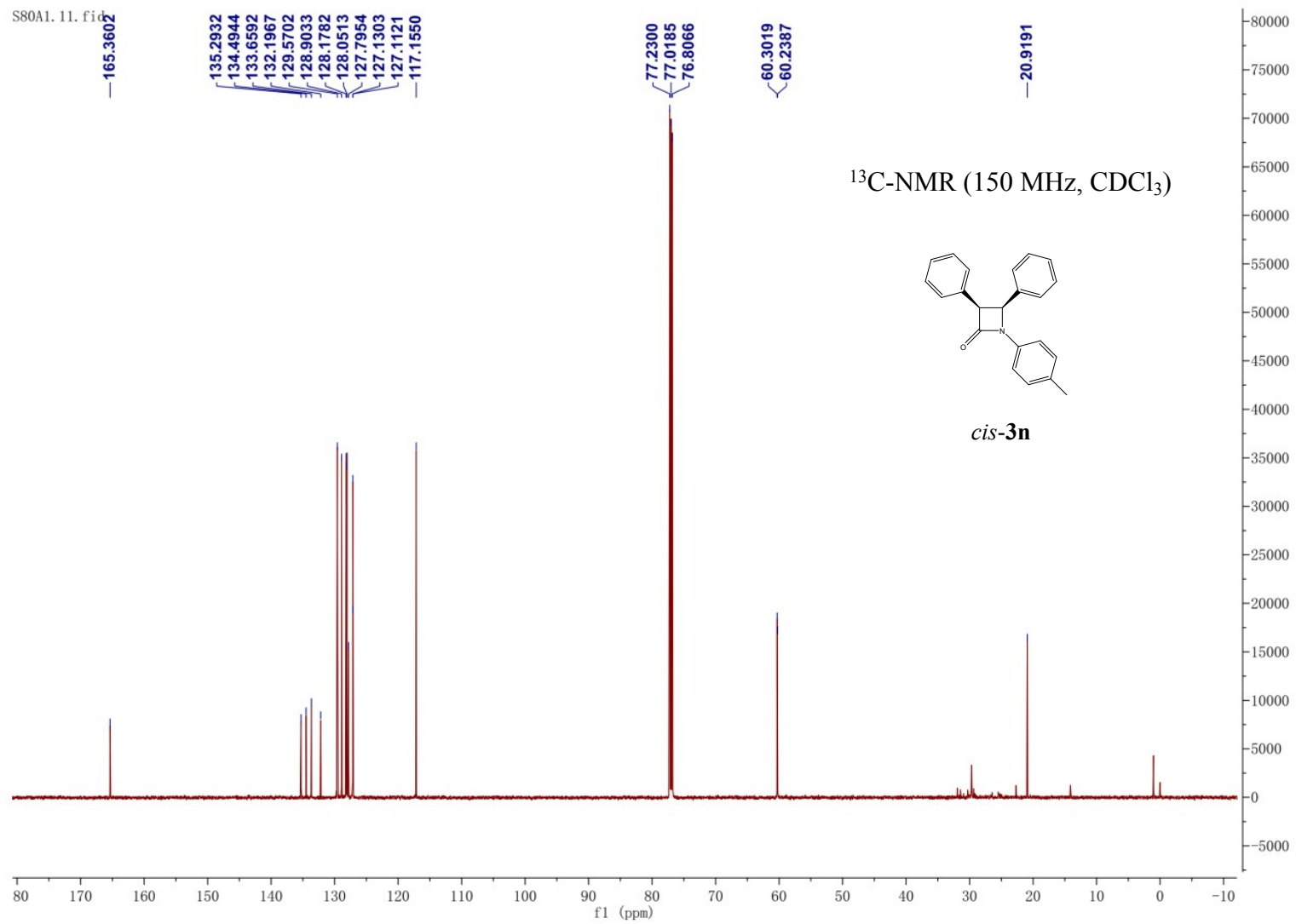




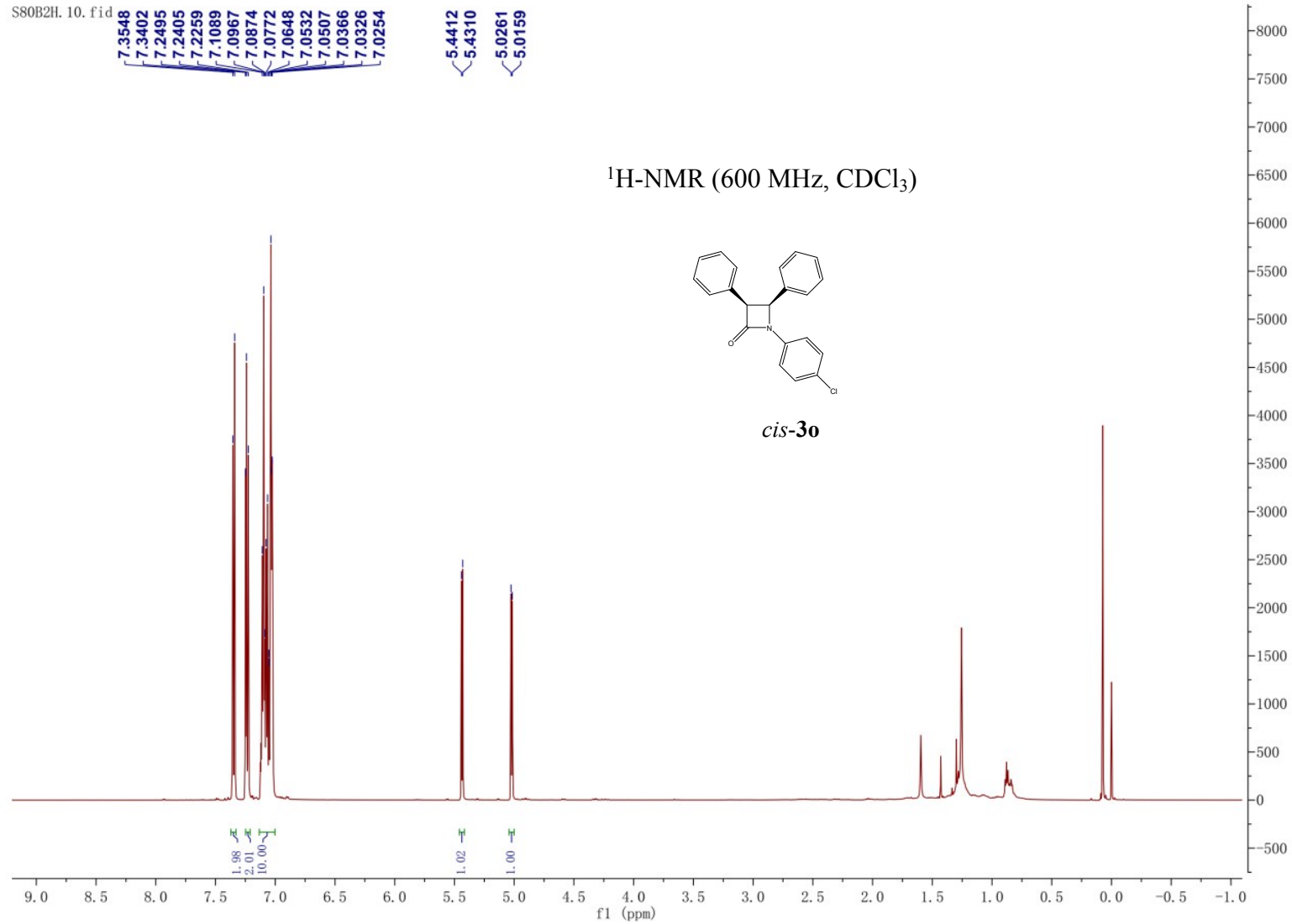


S80A1.10.fid

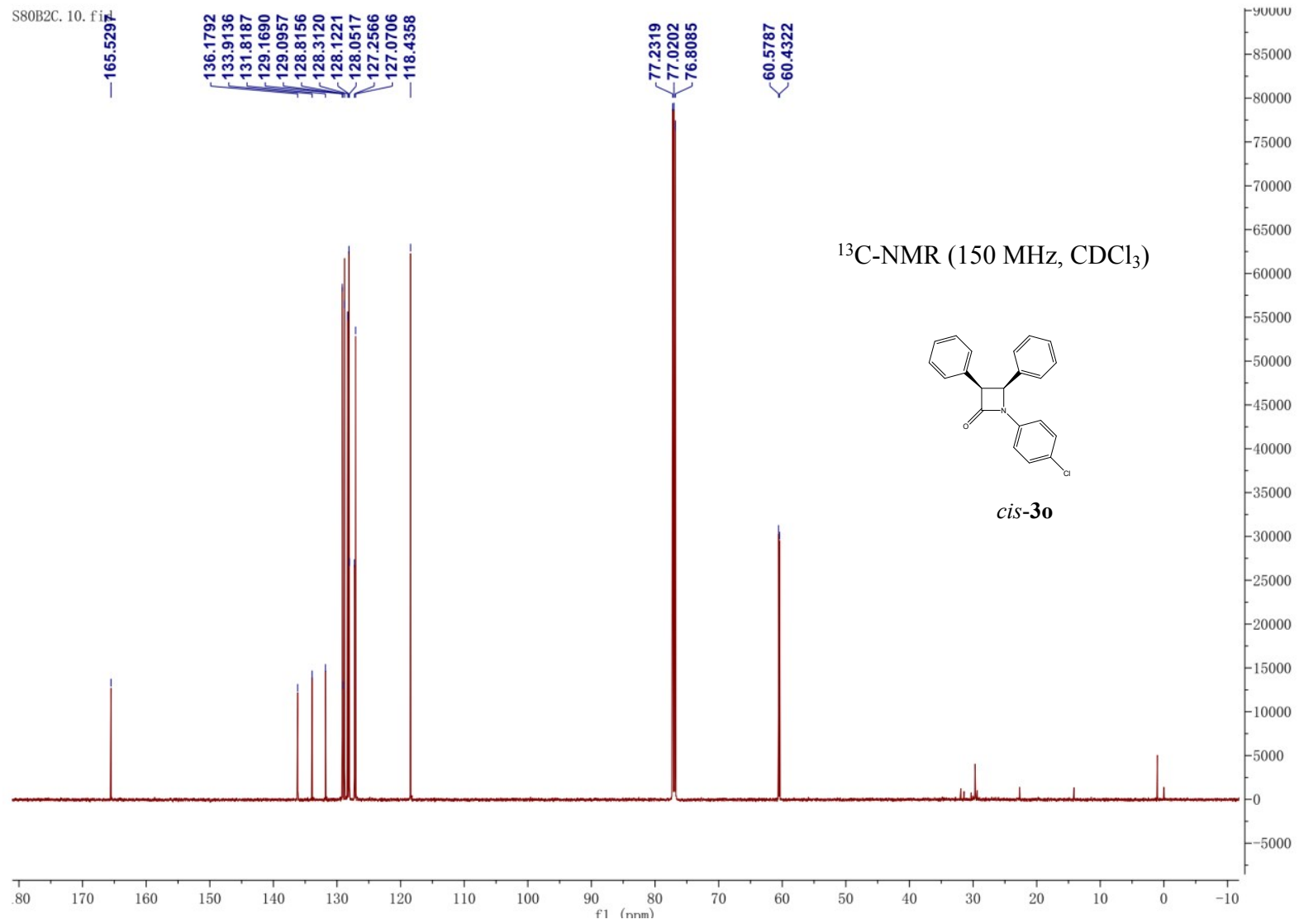


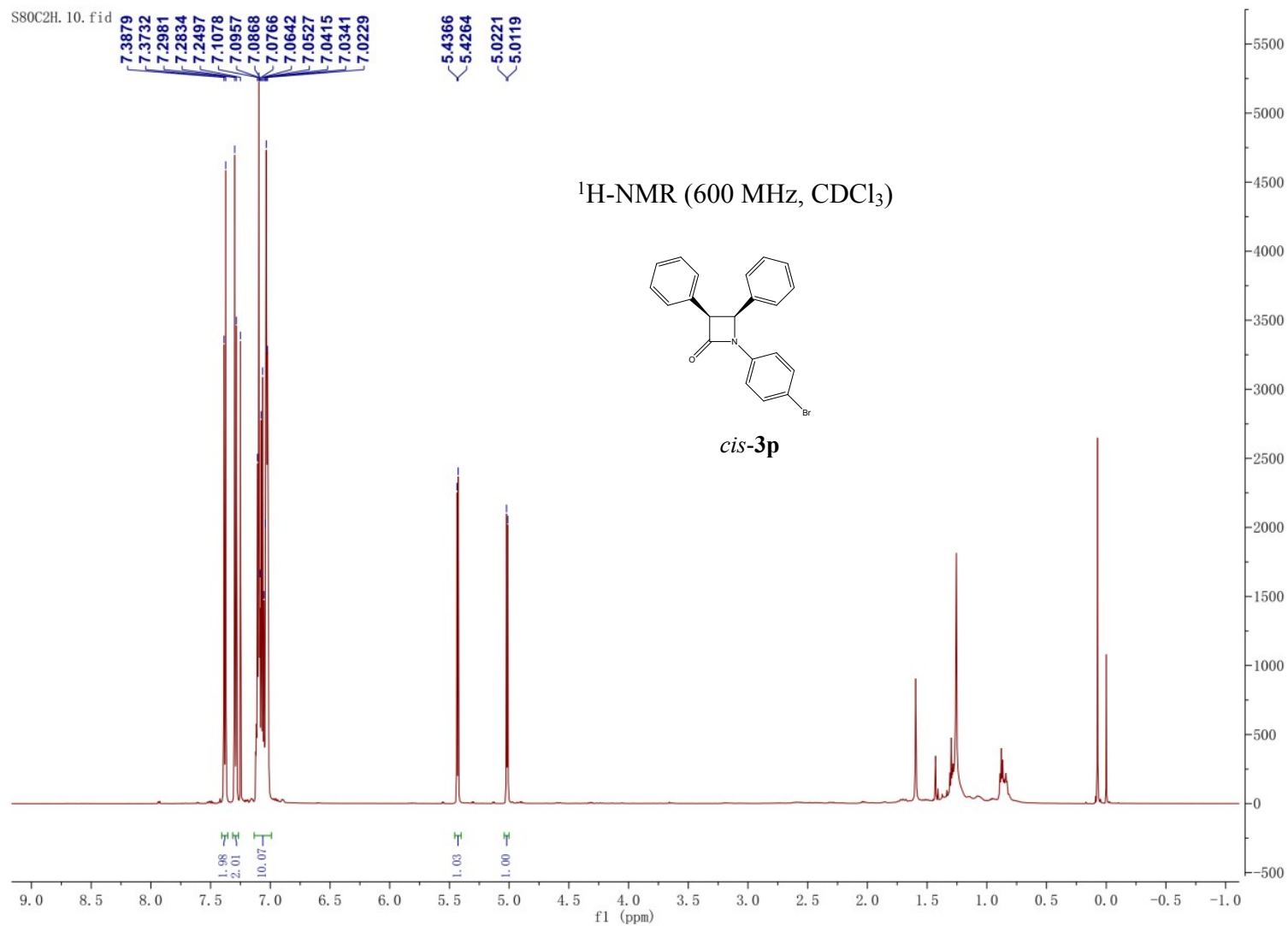


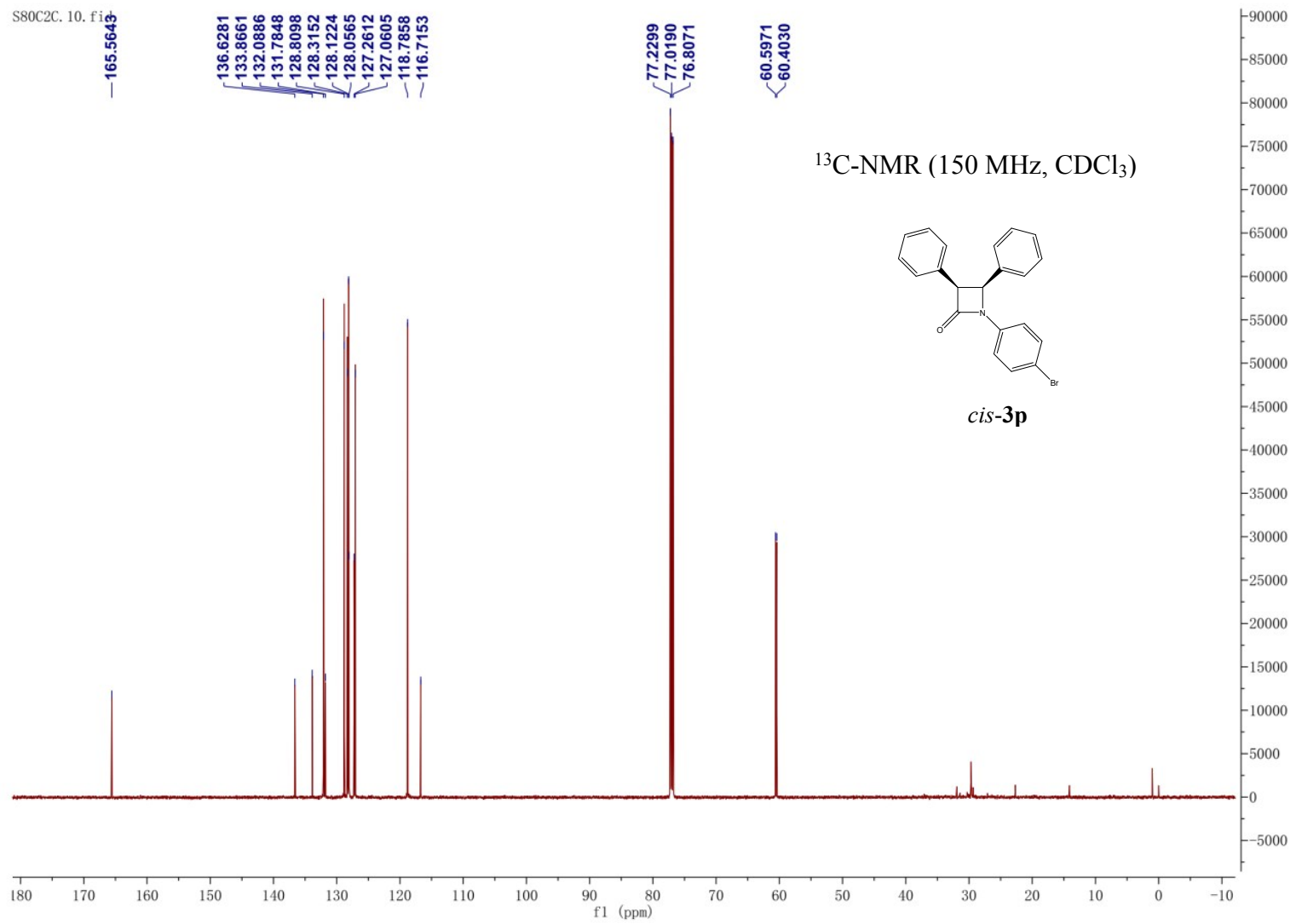
S80B2H. 10. fid

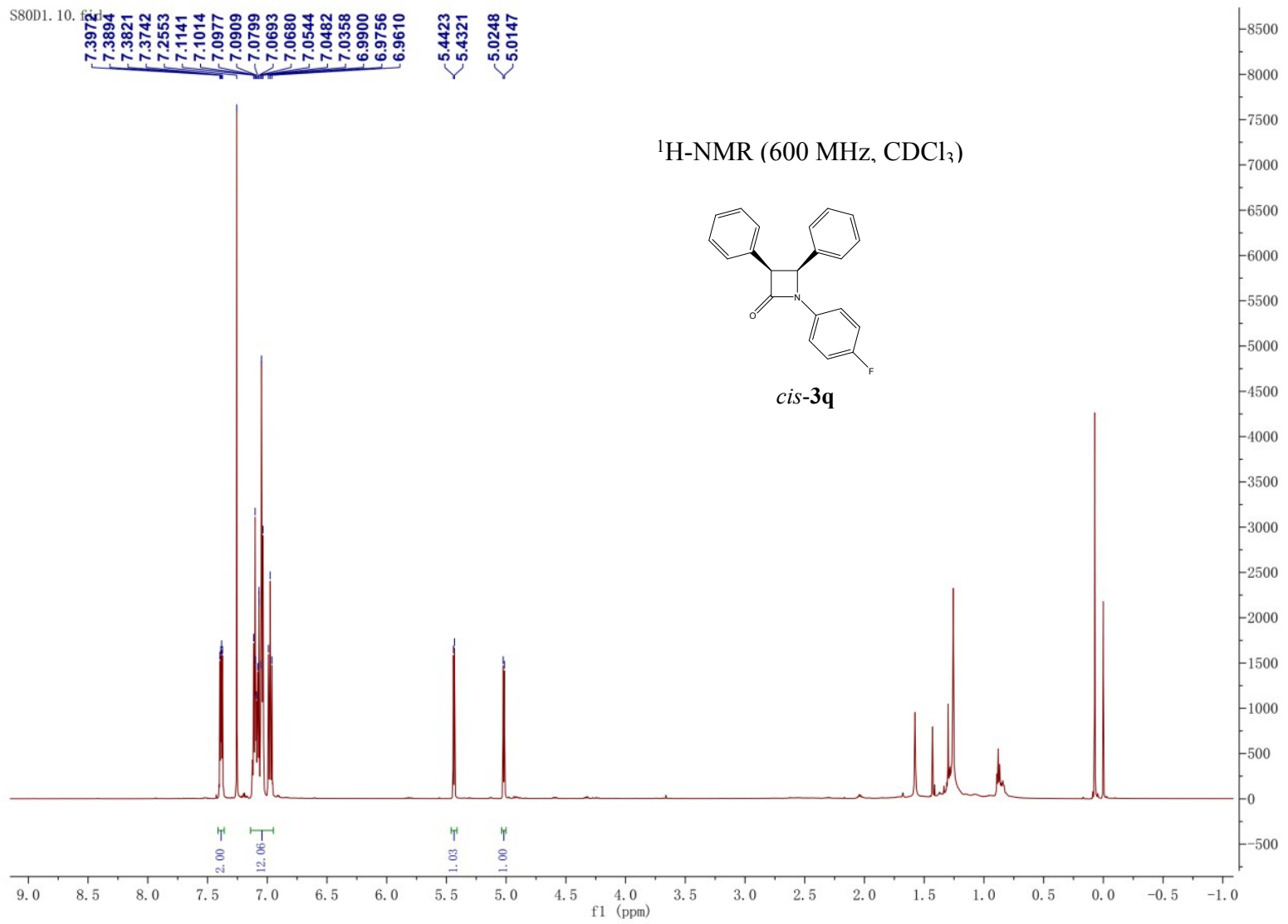


S80B2C. 10. f1









S80D1. 11. fid

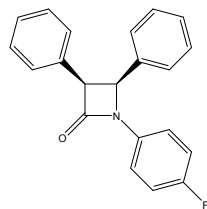
165.3356
159.9091
158.2947

134.0888
133.9685
133.9506
131.9454
128.8368
128.2935
128.1135
128.0180
127.2212
127.1176
118.6584
118.6069
115.9547
115.8044

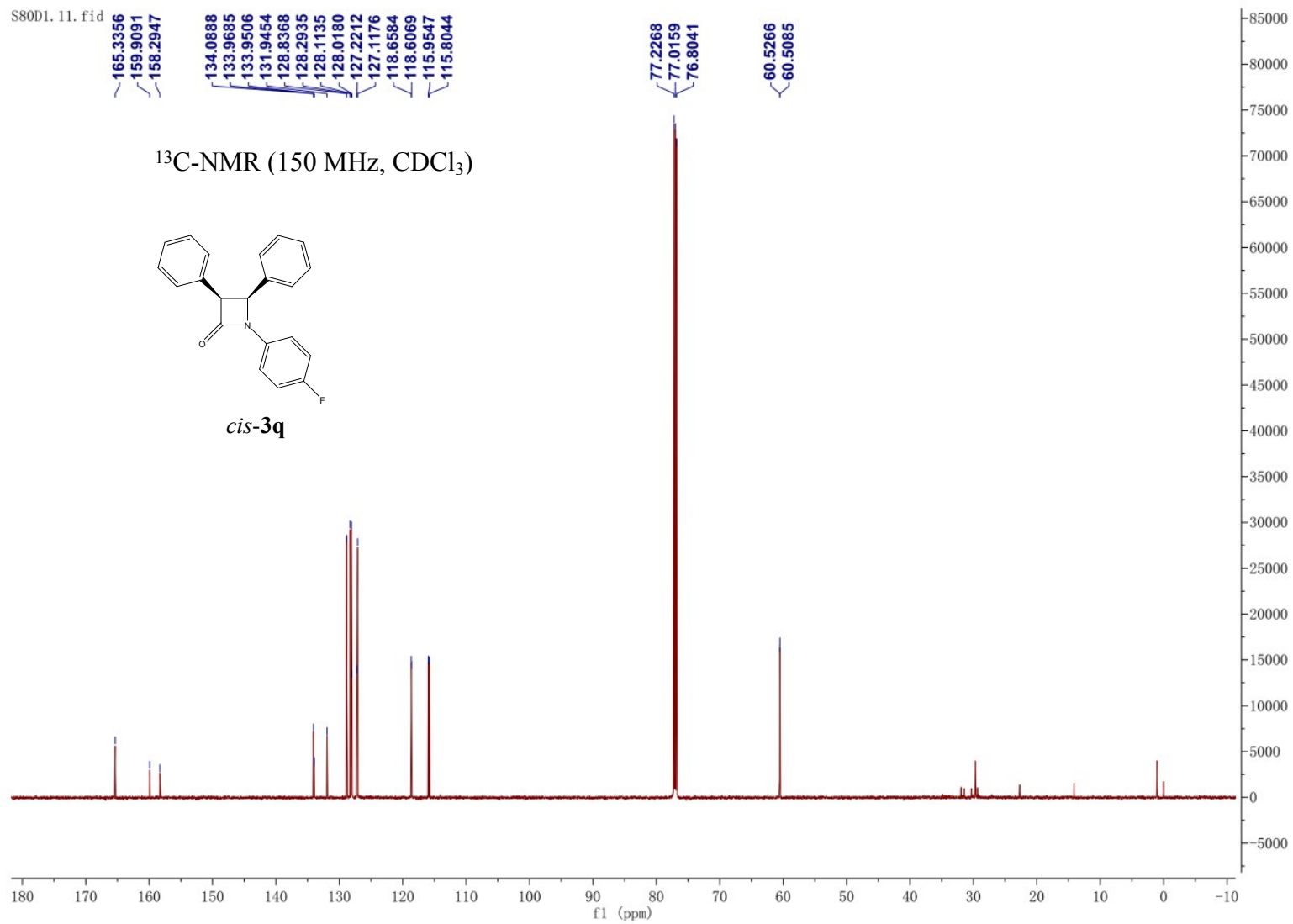
77.2268
77.0159
76.8041

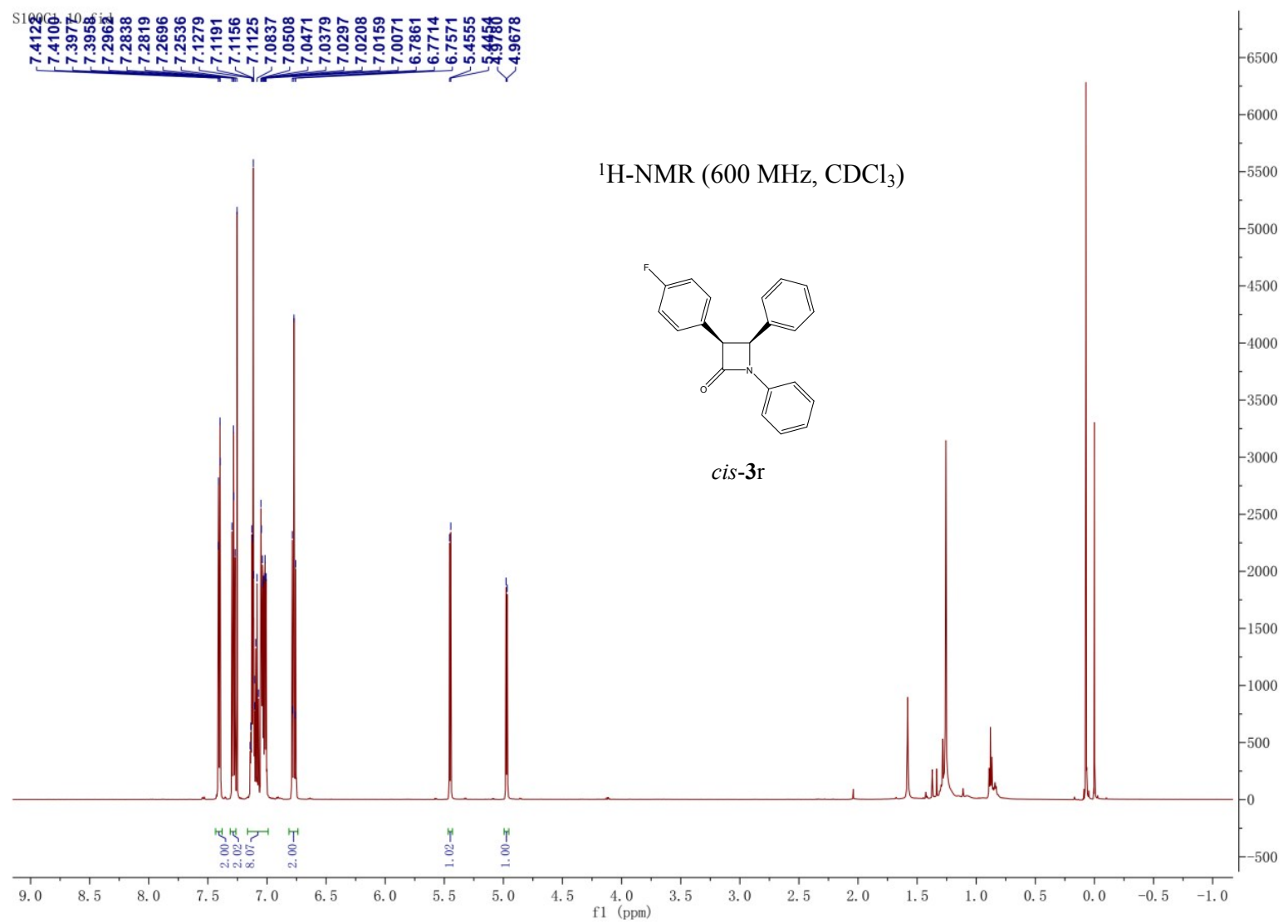
60.5266
60.5085

^{13}C -NMR (150 MHz, CDCl_3)



cis-3q





S100C1. 11. fi

