Supporting Information

Asymmetric Organocatalytic Allylic Alkylation of Reissert Compounds: A Facile Access to Chiral 1, 1-Disubstituted 1, 2-Dihydroisoquinolines

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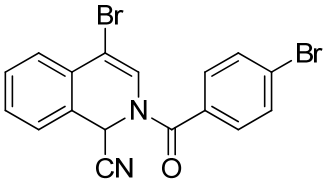
I. General Information

All reactions were carried out under inert atmospheric condition unless otherwise noted, and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC) visualizing with ultraviolet light (UV), $KMnO_4$, *p*-anisaldehyde stain, and phosphomolybdic acid (PMA) stain; column chromatography purifications were carried out using silica gel. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a 300 or 500 MHz spectrometer in $CDCl_3$, and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on 75 or 125 MHz spectrometer in $CDCl_3$ unless otherwise noted. Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26 ppm). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane (TMS) and are referenced to the carbon resonances of the solvent residual peak ($CDCl_3$ = δ 77.16 ppm). NMR data are presented as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant in Hertz (Hz), integration. Infrared (IR) spectra were recorded on a spectrometer. Mass spectra were recorded on the Bruker MicrOTOF Q II. Melting points were measured on a melting point apparatus and were uncorrected. The enantiomeric excesses of products were determined by chiral phase HPLC analysis.

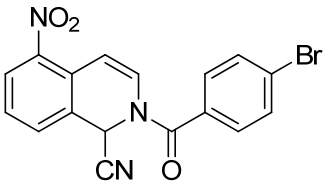
II. Preparation of Substrates

Morita-Baylis-Hillman Carbonates were prepared according to the literature procedure.[1] Reissert compounds were prepared by the literature procedure.[2, 3]



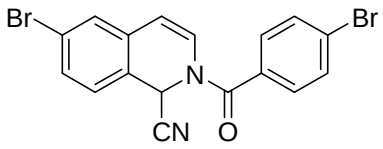
1j

Mp: 204.0-206.0 ℃. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.67-7.61 (m, 3H), 7.55-7.41 (m, 4H), 7.36-7.34 (m, 1H), 6.94 (brs, 1H), 6.52 (brs, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.88, 132.28, 130.84, 130.71, 130.31, 129.99, 129.66, 127.47, 126.59, 126.28, 126.02, 124.59, 115.79, 45.06. IR (KBr): 3090, 3038, 2954, 1658, 1622, 1585, 1321, 838, 853, 758. HRMS (ESI):. for calcd $C_{17}H_{11}Br_2N_2O$ ($[M+H]^+$): 416.9233, found 416.9232.



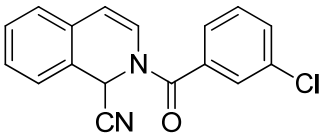
1k

Mp: 202.0-204.0 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.68-7.64 (m, 3H), 7.53-7.48 (m, 3H), 6.90 (d, *J* = 8.1 Hz, 1H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.61 (s, 1H).^{13}C NMR (125 MHz, $CDCl_3$) δ 167.59, 145.02, 132.30, 131.86, 131.01, 129.97, 129.94, 128.53, 127.79, 126.99, 126.79, 125.32, 115.28, 105.21, 44.94. IR (KBr): 3102, 3080, 2937, 1676, 1625, 1587, 1523, 1329, 844, 743, 695. HRMS (ESI):. for calcd $C_{17}H_{11}BrN_3O$ ($[M+H]^+$): 383.9978, found 383.9974.



1l

Mp: 204-206 ℃. ^{1}H NMR (300MHz, $CDCl_3$) δ 7.65-7.61 (m, 2H), 7.49-7.45 (m, 3H), 7.39 (d, *J* = 1.9 Hz, 1H), 7.23 (d, *J* = 8.1 Hz, 1H), 6.64 (d, *J* = 7.5 Hz, 1H), 6.48 (s, 1H), 6.03 (d, *J* = 7.8 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.75, 132.14, 132.01, 131.40, 130.84, 130.64, 128.70, 128.21, 127.20, 126.96, 124.39, 123.10, 115.74, 109.25, 44.66. IR (KBr): 3067, 3030, 2923, 1675, 1635, 1587, 1430, 833, 749, 696. HRMS (ESI):. for calcd $C_{17}H_{11}Br_2N_2O$ ($[M+H]^+$): 416.9233, found 416.9231.

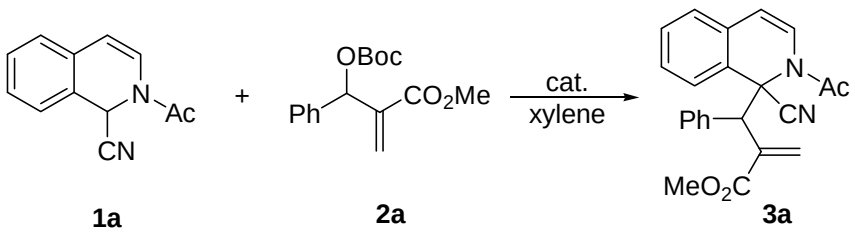


1i

Mp: 193-195 ℃. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60-7.59 (m, 1H), 7.55-7.50 (m, 2H), 7.48-7.35 (m, 4H), 7.24 (d, *J* = 7.2 Hz, 1H), 6.60-6.55 (m, 2H), 6.11 (d, *J* = 7.7 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.45, 135.07, 134.00, 132.32, 130.52, 130.27, 130.22, 129.44, 128.86, 127.49, 126.96, 126.14, 125.67, 124.52, 116.35, 110.91, 45.07. IR (KBr): 3058, 3030, 2963, 1662, 1630, 1568, 1455, 884, 782, 690. HRMS (ESI):. for calcd $C_{17}H_{12}ClN_2O$ ($[M+H]^+$): 295.0633, found 295.0634.

III. Reaction Condition Screening

Table 1 Effect of Solvent [a]



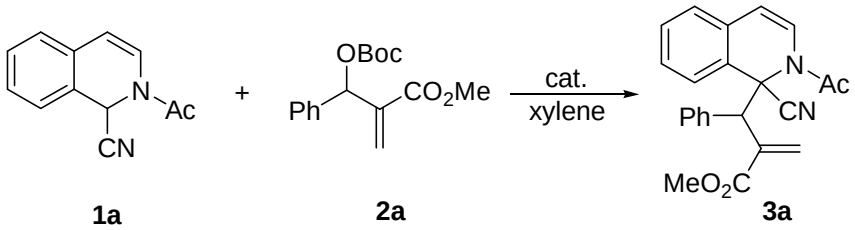
1a **2a** **3a**

entry	cat.	solvent	yield(%)[b]	dr[c]	ee(%)[c]

1	Quinine	$CHCl_3$	42	5.5:1	13
2	Quinine	CH_3CN	45	41:1	21
3	Quinine	DCE	42	14:1	-15
4	Quinine	DCM	80	13:1	-10
5	Quinine	toluene	50	20:1	-54
6	Quinine	EA	32	22:1	-6
7	Quinine	1,4-dioxane	64	29:1	-25
8	Quinine	THF	80	40:1	-6
9	Quinine	xylene	80	38:1	-74
10	Quinine	$PhCF_3$	69	24:1	-58
11	Quinidine	*o*-xylene	67	18:1	80
12	Quinidine	*m*-xylene	62	17:1	82
13	Quinidine	*p*-xylene	66	20:1	85
14	Quinidine	benzene	74	18:1	78
15	Quinidine	mesitylene	38	18:1	76
16	Quinidine	xylene	77	25/1	85

[a] Reactions were carried out using **1a** (0.1 mmol), **2a** (1.5 equiv), catalyst (10 mol%) in xylene (0.2 mL) at 30 ℃ for 72 h. [b] Isolated yields. [c] Determined by chiral HPLC analysis.

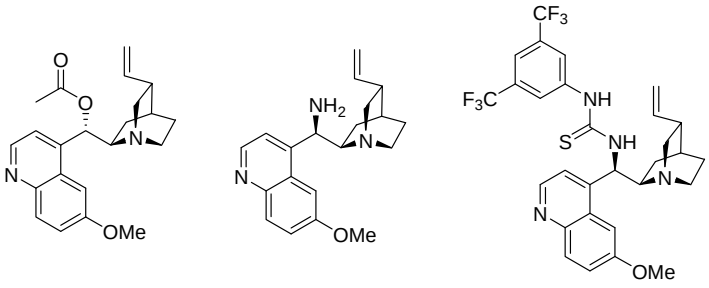
Table 2 Catalyst optimization study [a]



1a **2a** **3a**

entry	cat.	yield (%)[b]	dr[c]	ee (%)[c]
1	$(DHQ)_2PHAL$	23	7:1	3
2	$(DHQD)_2PHAL$	18	2:1	18
3	$(DHQ)_2AQN$	30	10:1	-27
4	$(DHQD)_2AQN$	46	2:1	71
5	cinchonine	21	26:1	65
6	cinchonidine	46	22:1	-40
7	quinine	80	38:1	-74
8	quinidine	77	25:1	85
9	hydroquinidine	49	9:1	81
10	β-ICPD	44	9:1	-9
11	β-IQD	96	6:1	-16
12	AcO-QD	3	3/1	35
13	amine-eQD	-	-	nr
14	thiourea-eQD	-	-	nr

[a] Reactions were performed with **1a** (0.1 mmol), **2a** (1.5 equiv) and catalyst (10 mol %) in xylene (0.2 mL) at 30℃ for 72 hours. [b] Isolated yields. [c] Determined by chiral HPLC analysis. $(DHQ)_2PHAL$: Hydroquinine 1,4-phthalazinediyl diether; $(DHQD)_2PHAL$: hydroquinidine 1,4-phthalazinediyl diether; $(DHQ)_2AQN$: hydroquinine anthraquinone-1,4-diyl diether; $(DHQD)_2AQN$: hydroquinidine anthraquinone-1,4-diyl diether; β-ICPD: β-isocupreidine; β-IQD: β-isoquinidine.



AcO-QD **amine-eQD** **thiourea-eQD**

Table 3 Screening of additives [a]

entry	cat.	additive	yield(%)[b]	dr[c]	ee(%)[c]
1	Quinidine	Ti(*i*-OPr)$_4$	50	10:1	73
2	Quinidine	CuI	55	22:1	84
3	Quinidine	$MgSO_4$	65	22:1	85
4	Quinidine	$MgBr_2$	15	19:1	84
5	quinidine	$FeCl_3$	-[d]	-	-
6	quinidine	$FeCl_2$	28	14:1	84
7[e]	quinine	4ÅMS	15	-	-72

[a] Reactions were carried out using **1a** (0.1 mmol), **2a** (1.5 equiv), catalyst (10 mol%) and additive (10 mol%) xylene (0.2 mL) at 30℃ for 72 hours. [b] Isolated yields. [c] Determined by chiral HPLC analysis. [d] No desired product was detected. [e] 4ÅMS (30 mg) was added and the reaction was carried out in xylene (1.0 mL).

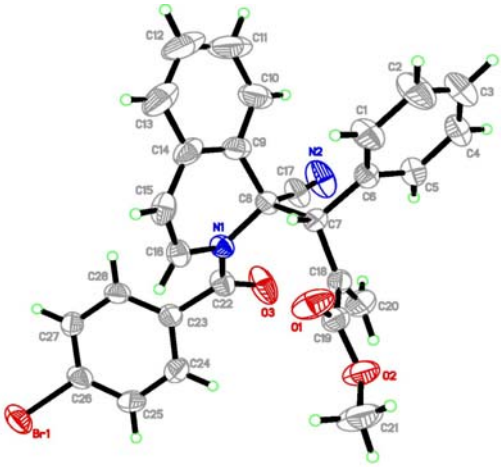
Reference

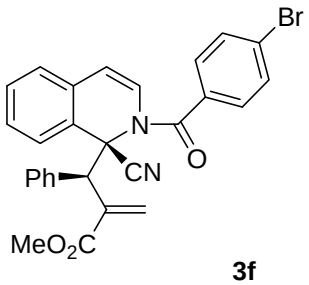
1. J. Feng, X. Lu, A. Kong and X. Han, *Tetrahedron,* 2007, **63**, 6035.

2. A. W. Bridge, M. B. Hursthouse, C. W. Lehmann, D. J. Lythgoe and C. G. Newtona, *J. Chem. Soc. Perkin Trans.,* 1993, **1**, 1839.

3. F. D. Popp, L. E. Katz, C. W. Klinowski and J. M. Wefer, *J. Org. Chem.,* 1968, **33**, 4447

IV. Crystal data and structure refinement for enantiopure 3f





3f

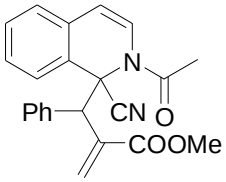
I

dentification code **3f**

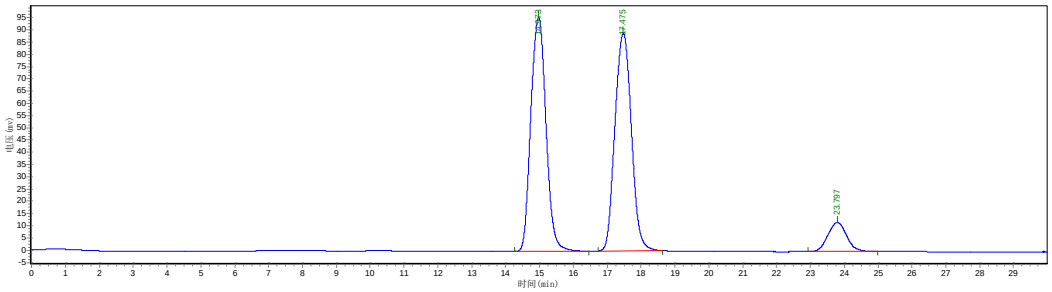
Empirical formula	$C_{28}H_{21}BrN_2O_3$
Formula weight	513.38
Temperature	293(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 9.098(3) A alpha = 90 deg. b = 15.524(6) A beta = 90 deg. c = 17.674(6) A gamma = 90 deg.
Volume	2496.2(15) A^3
Z, Calculated density	4, 1.366 Mg/m^3
Absorption coefficient	1.678 mm^-1
F(000)	1048
Crystal size	0.34 x 0.31 x 0.25 mm
Theta range for data collection	3.21 to 27.48 deg.
Limiting indices	-11<=h<=11, -20<=k<=19, -22<=l<=22

Reflections collected / unique	22577 / 5671 [R(int) = 0.0440]
Completeness to theta = 27.48	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6830 and 0.5976
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5671 / 0 / 308
Goodness-of-fit on F^2	1.006
Final R indices [I>2sigma(I)]	R1 = 0.0415, wR2 = 0.0942
R indices (all data)	R1 = 0.0799, wR2 = 0.1073
Absolute structure parameter	-0.002(9)
Largest diff. peak and hole	0.344 and -0.424 e.A^-3

V. HPLC Spectra

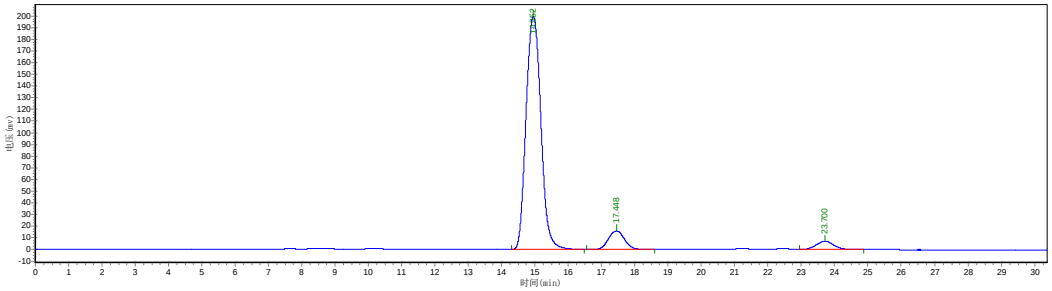


3a



Result Table

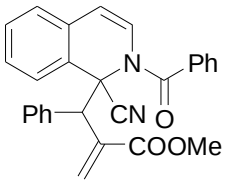
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	14.973	95567.359	2977062.000	46.3265
2	17.475	88871.125	2992779.000	46.5711
3	23.797	11953.398	456421.281	7.1024
total		196391.883	6426262.281	100.000



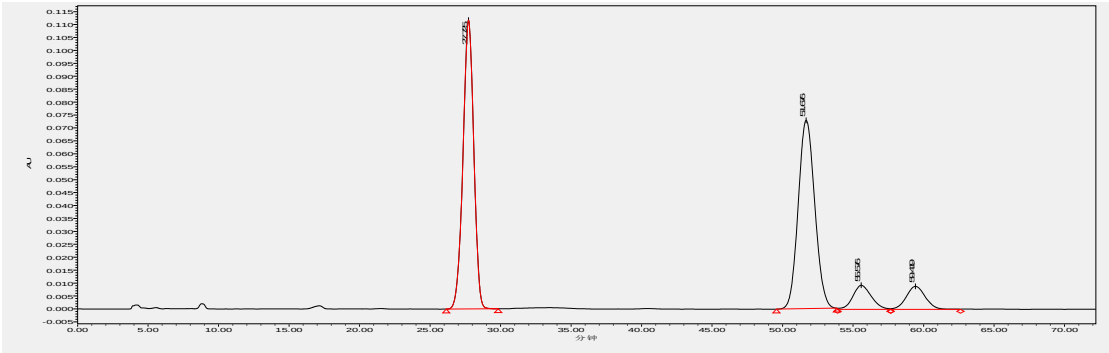
Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	14.952	199473.047	6159053.500	88.6807
2	17.448	15699.683	526684.625	7.5834
3	23.700	6996.474	25946.000	3.7359
total		222169.204	6945204.125	100.000

84 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 15.0 min (major) and t_R = 17.5 min (minor), minor diastereomer: t_R = 23.8 min).

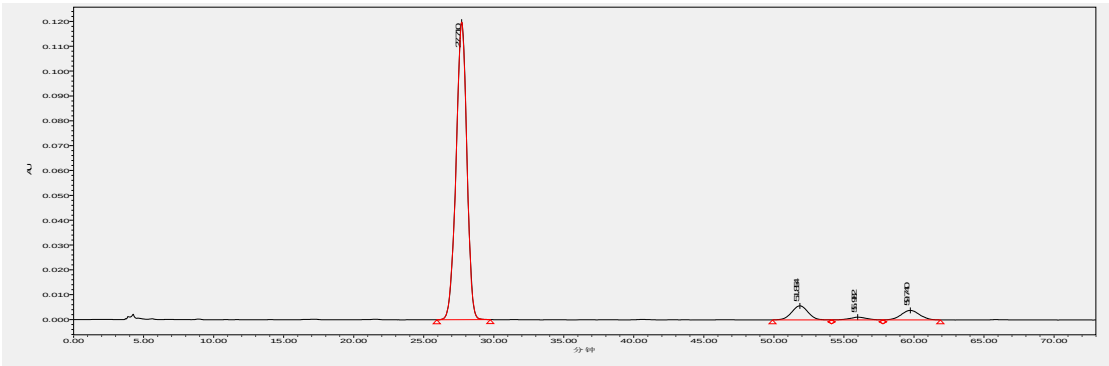


3b



Result Table

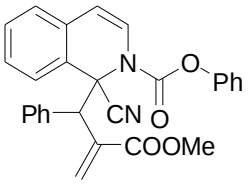
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	27.725	111739	5957811	43.87
2	51.676	72860	5939115	43.73
3	55.576	9316	843466	6.21
4	59.419	8883	839791	6.18
total		202798	13580183	99.99



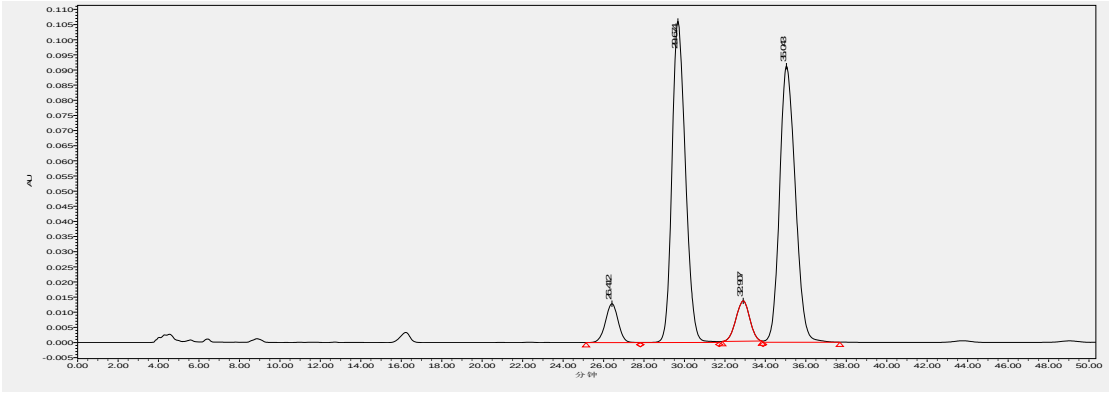
Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	27.710	119777	6408716	87.80
2	51.854	5636	455000	6.23
3	55.982	1080	88588	1.21
4	59.740	3805	346731	4.75
total		130298	7299035	99.99

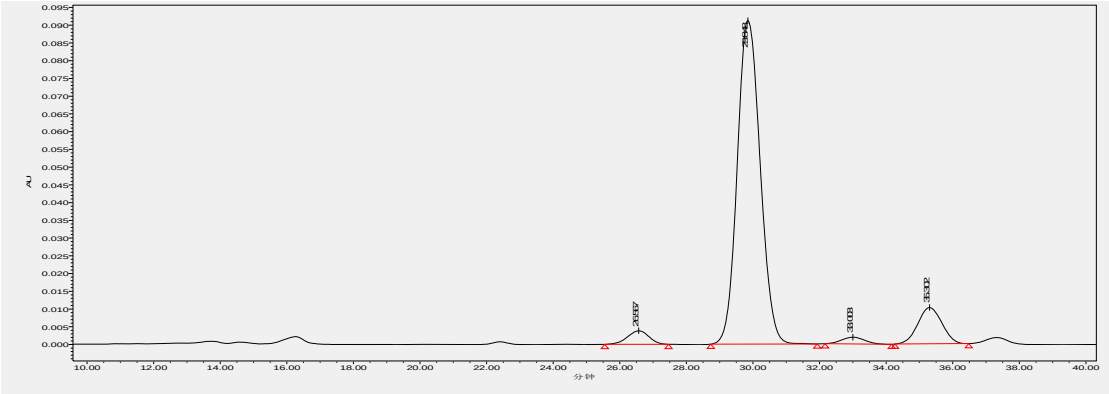
87 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 95/5, flow rate 0.8 ml/min, λ= 254 nm, major diastereomer: t_R = 27.7 min (major) and t_R = 51.7 min (minor), minor diastereomer: t_R = 55.6 min (minor), and t_R = 59.4 min (major).



3c

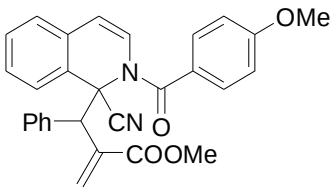


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	26.412	12812	560548	5.08
2	29.674	106028	4919828	44.56
3	32.907	13321	629386	5.70
4	35.043	91194	4932190	44.66
total		223355	11041952	100.00

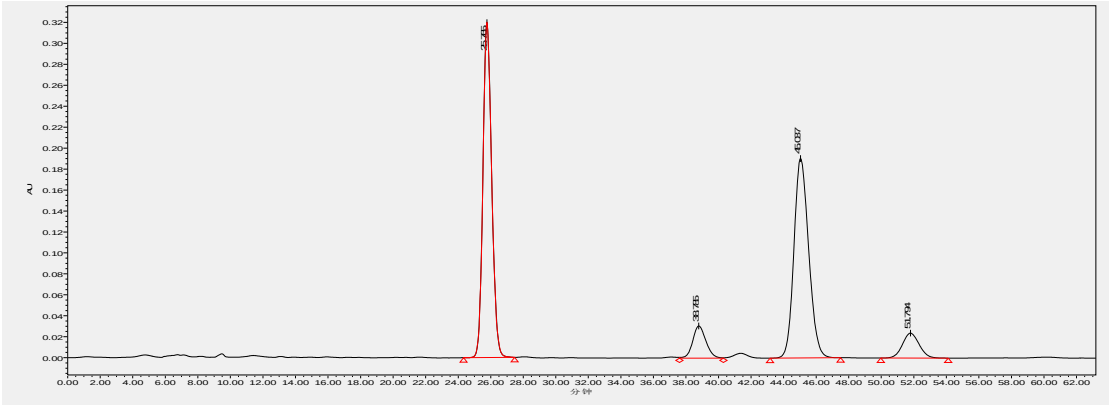


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	26.567	3825	170332	3.31
2	29.848	91174	4371372	84.93
3	33.003	1910	91536	1.78
4	35.302	10229	513725	9.98
total		107138	5146965	100.00

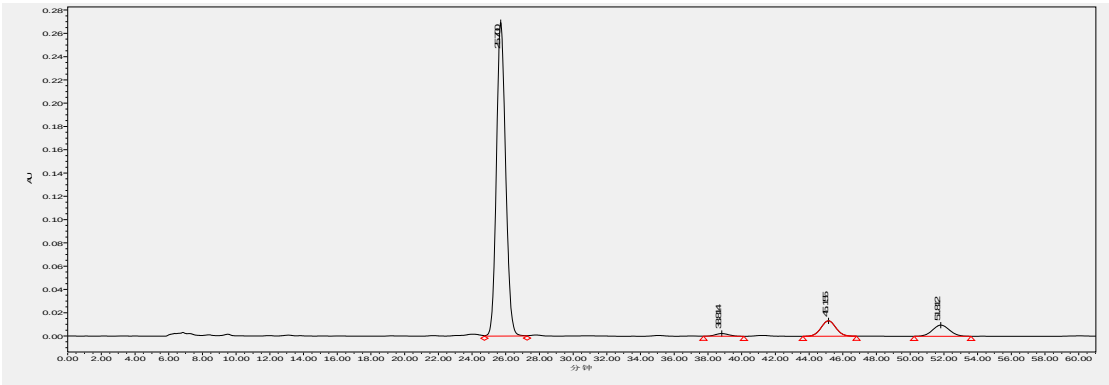
79 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 95/5, flow rate 0.8 ml/min, λ= 254 nm, major diastereomer: t_R = 29.7 min (major) and t_R = 35.0 min (minor), minor diastereomer: t_R = 26.4 min (major), and t_R = 32.9 min (minor).



3d

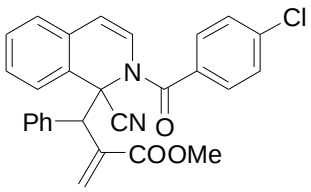


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	25.765	319719	11990607	43.74
2	38.785	30679	1715342	6.26
3	45.037	190315	12008030	43.81
4	51.794	23807	1697316	6.19
total		564520	27411295	100.00

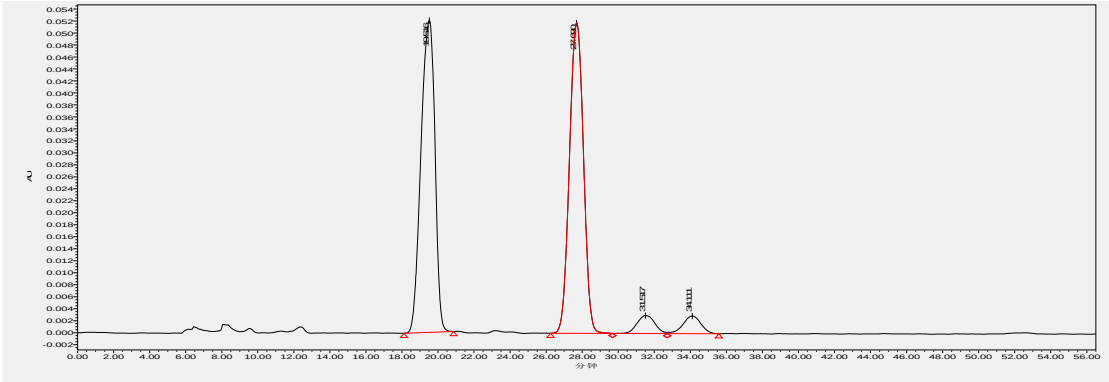


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	25.700	269283	10219815	86.37
2	38.814	2329	128043	1.08
3	45.155	13241	812240	6.86
4	51.812	9573	672365	5.68
total		294426	11832463	99.99

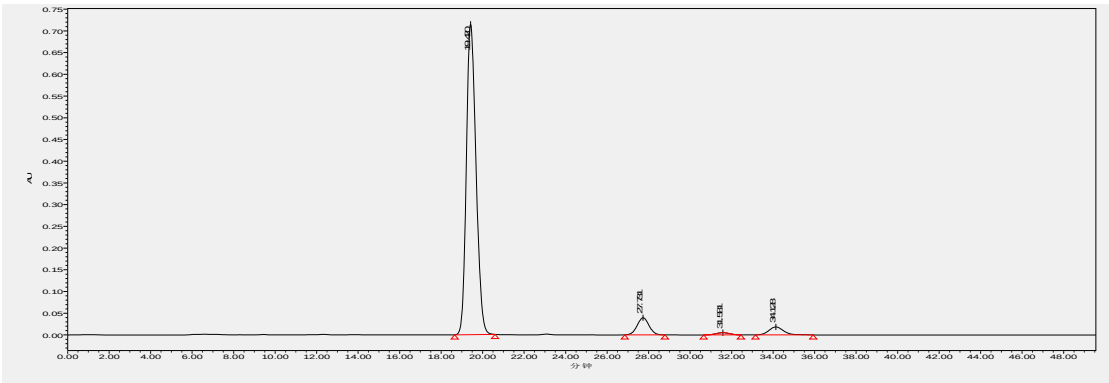
85 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min,λ= 254 nm, major diastereomer: t_R = 25.8 min (major) and t_R = 38.8 min (minor), minor diastereomer: t_R = 45.0 min (minor), and t_R = 51.8 min (major).



3e

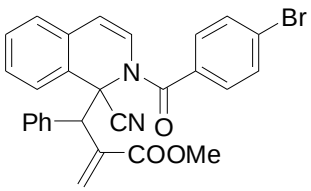


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	19.516	52021	2808284	46.57
2	27.690	51770	2808712	46.57
3	31.517	3015	207732	3.44
4	34.111	2944	205829	3.41
total		109750	6030557	99.99

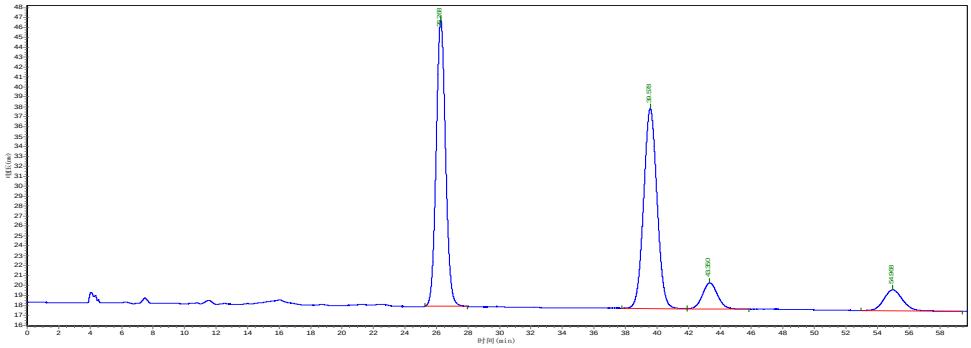


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	19.420	714915	23017025	89.48
2	27.731	39424	1560776	6.07
3	31.581	5194	238108	0.93
4	34.128	18349	905866	3.52
total		777882	25721775	100.00

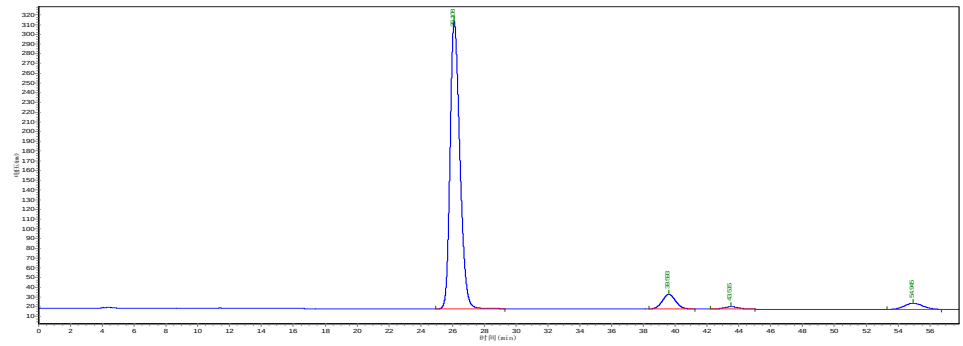
87 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 19.5 min (major) and t_R = 27.7 min (minor), minor diastereomer: t_R = 31.5 min (minor), and t_R = 34.1 min (major).



3f

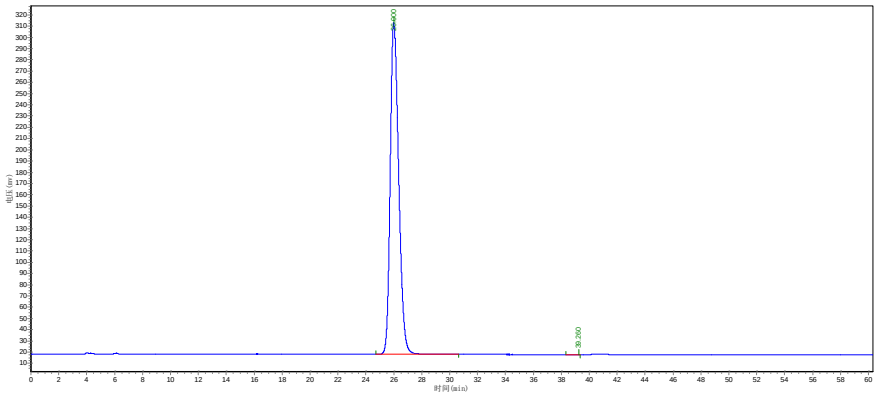


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	26.268	28837.811	1196065.000	43.8036
2	39.578	20141.268	1186904.000	43.4681
3	43.350	2620.233	173596.375	6.3576
4	54.968	2108.310	173954.063	6.3707
total		53707.621	2730519.438	100.0000



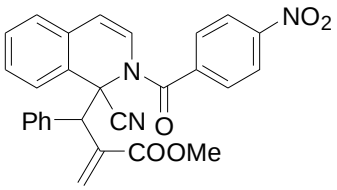
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	26.108	295674.000	12583588.000	89.3220
2	39.593	14854.839	862765.000	6.1242
3	43.515	2392.794	153525.672	1.0898
4	54.945	6122.271	488010.156	3.4640
total		319043.904	14087888.828	100.0000

87% ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane/i-PrOH = 90/10, flow rate 0.8 ml/min, λ= 254 nm, major diastereomer: t_R = 26.3 min (major) and t_R = 39.6 min (minor), minor diastereomer: t_R = 43.4 min (minor), and t_R = 55.0 min (major).

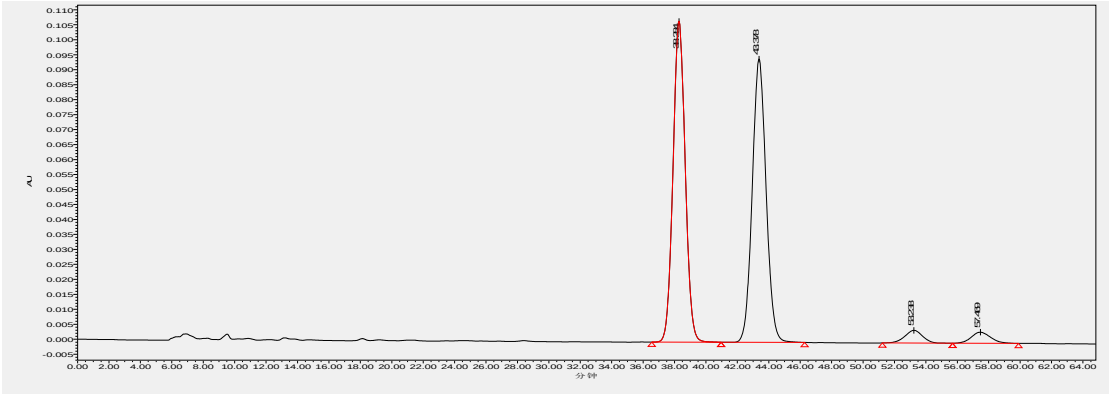


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	26.000	295143.875	12409329.000	99.9923
2	32.260	33.741	952.662	0.0077
total		295177.616	12410281.662	100.0000

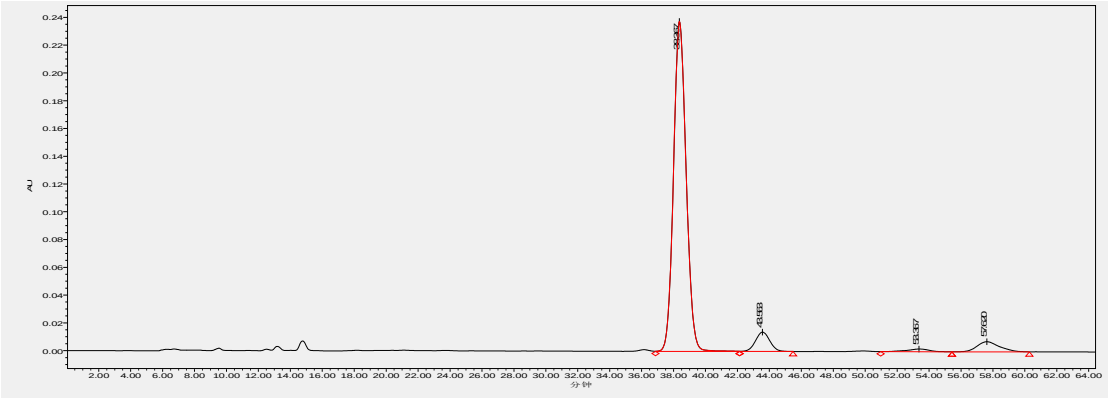
After a single recrystallization, **3f** can be obtained with excellent optical purity (>99 % ee, 53 % yield).



3g

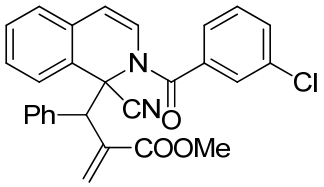


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	38.284	107103	5798784	47.33
2	43.378	94599	5799616	47.34
3	53.238	4250	333494	2.72
4	57.469	3702	319639	2.61
total		209654	12251533	100.00

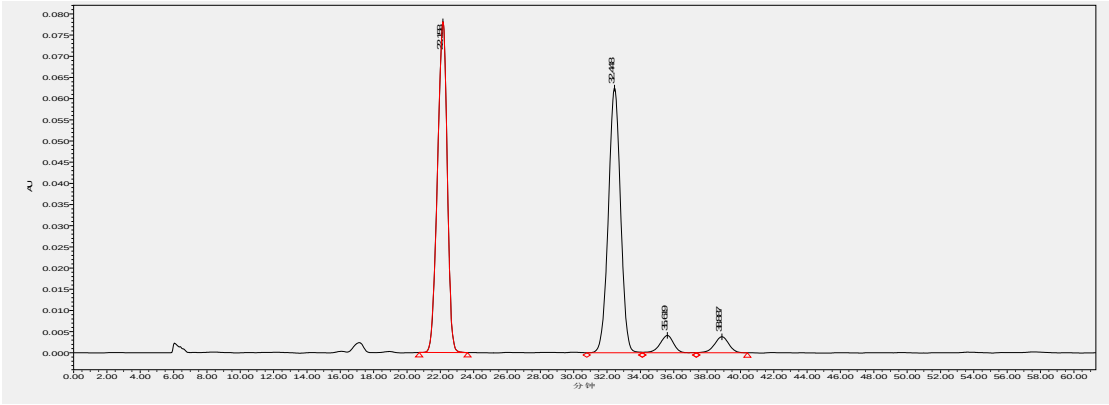


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	38.367	237588	13068706	88.07
2	43.563	13922	868551	5.85
3	53.367	1956	192642	1.30
4	57.620	7263	708869	4.78
total		260729	14838768	100.00

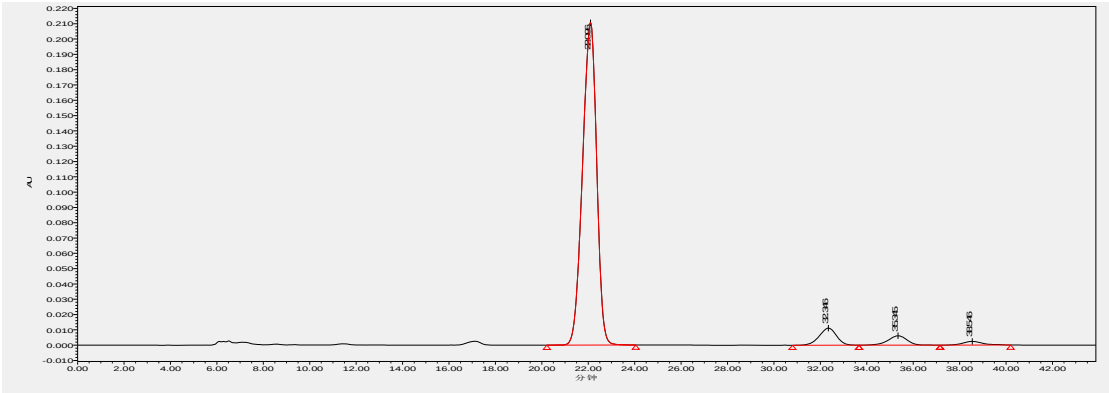
88 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 38.3 min (major) and t_R = 43.4 min (minor), minor diastereomer: t_R = 53.3 min (minor), and t_R = 57.5 min (major).



3i

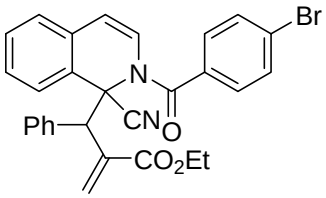


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	22.158	78091	3167540	46.55
2	32.448	62491	3176843	46.69
3	35.619	4104	233418	3.43
4	38.887	3778	226903	3.33
total		148464	6804704	100.00



Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	22.096	210666	8942950	89.31
2	32.346	11170	577734	5.77
3	35.345	6121	348961	3.49
4	38.546	2392	143466	1.43
total		230349	10013111	100.00

88 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 22.2 min (major) and t_R = 32.4 min (minor), minor diastereomer: t_R = 35.6 min (major), and t_R = 38.9 min (minor)



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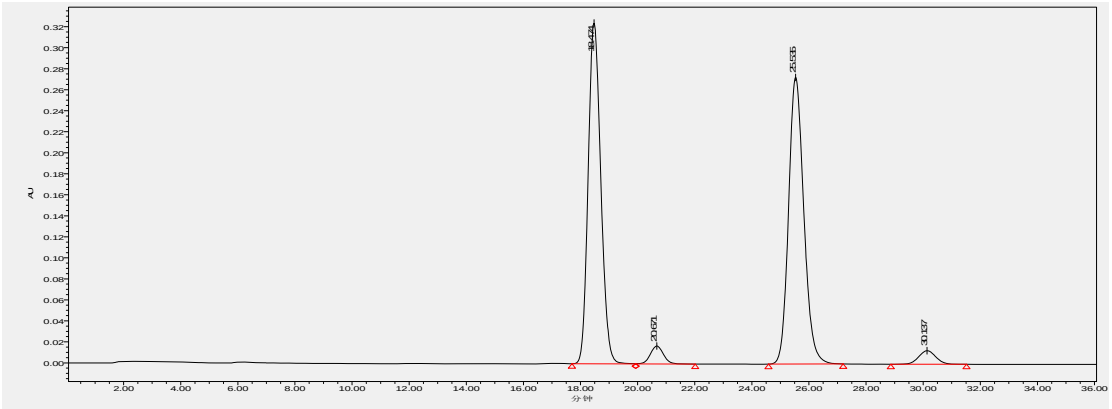
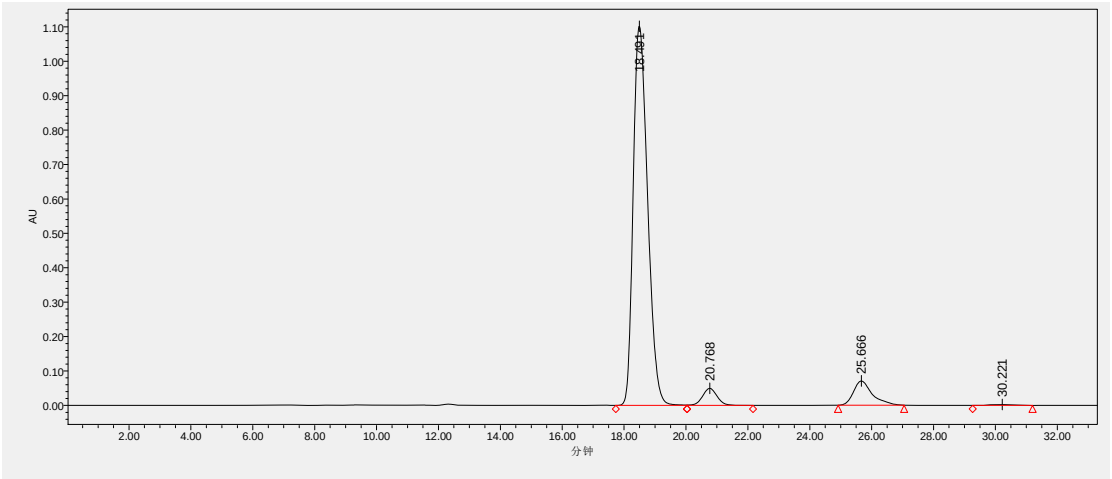
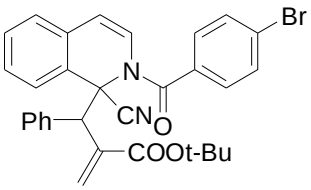


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	18.474	324572	9955151	47.10
2	20.671	17105	540971	2.56
3	25.535	272889	10099614	47.79
4	30.137	12918	537973	2.55
total		627484	21133709	100.00

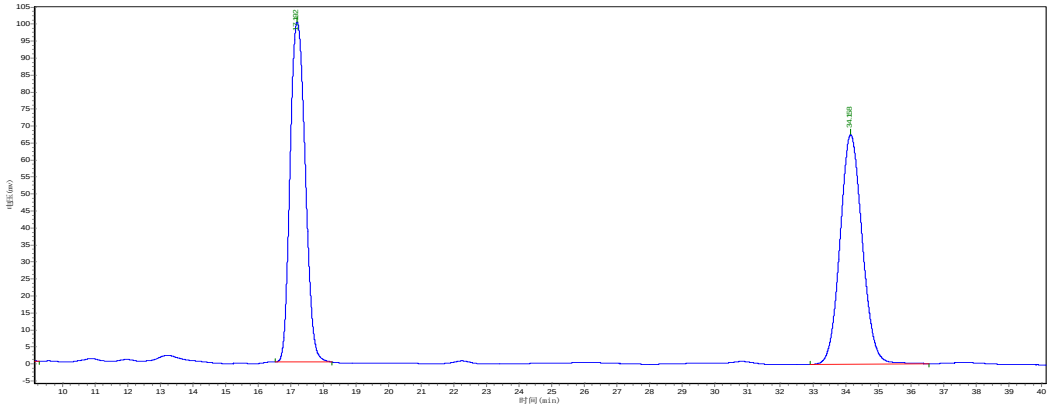


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	18.491	1102585	35584094	88.32
2	20.768	49581	1632829	4.05
3	25.666	70478	2963021	7.35
4	30.221	2729	111782	0.28
total		1225373	40291726	100.00

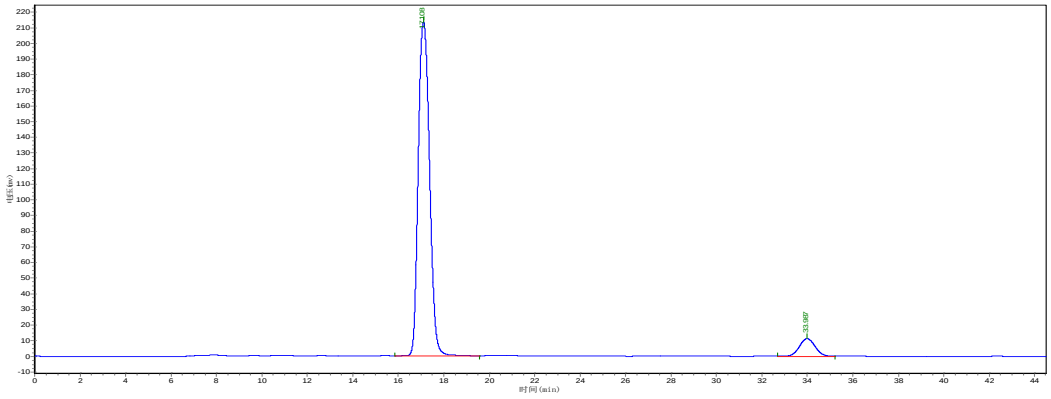
85 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 18.5 min (major) and t_R = 25.5 min (minor), minor diastereomer: t_R = 20.7 min (major), and t_R = 30.1 min (minor)



3k

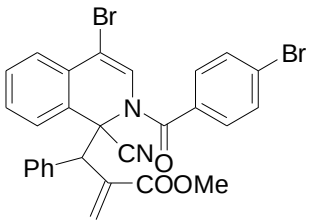


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	17.192	100034.727	3229034.250	50.3043
2	34.158	67542.117	3189963.750	49.6957
total		167576.844	6418998.000	100.0000

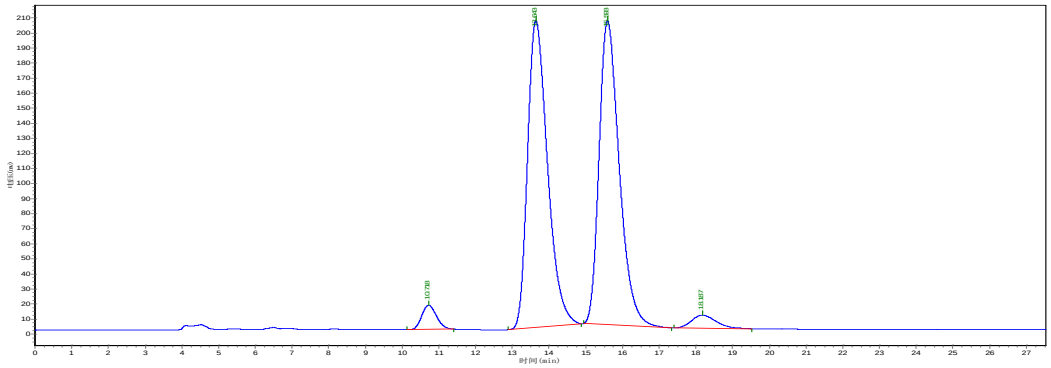


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	17.108	213652.469	7411426.000	92.8846
2	33.987	11468.972	567753.688	7.1154
total		225121.440	7979179.688	100.0000

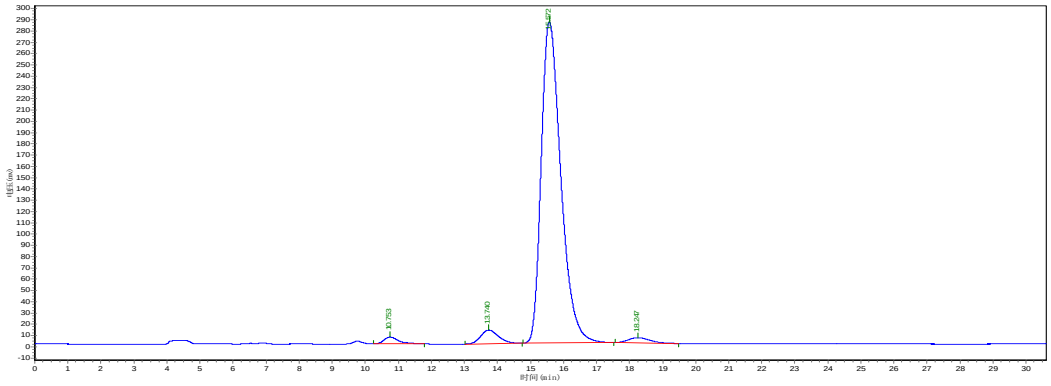
86 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 17.2 min (major) and t_R = 34.2 min (minor).



3l

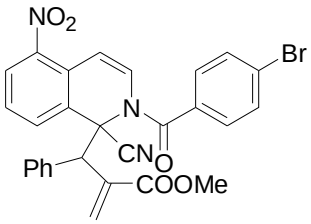


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	10.718	16067.002	449428.125	2.7653
2	13.643	203688.828	7700952.000	47.3826
3	15.593	201844.141	7700133.000	47.3776
4	18.187	8652.739	402188.594	2.4746
total		430252.710	16252701.719	100.0000

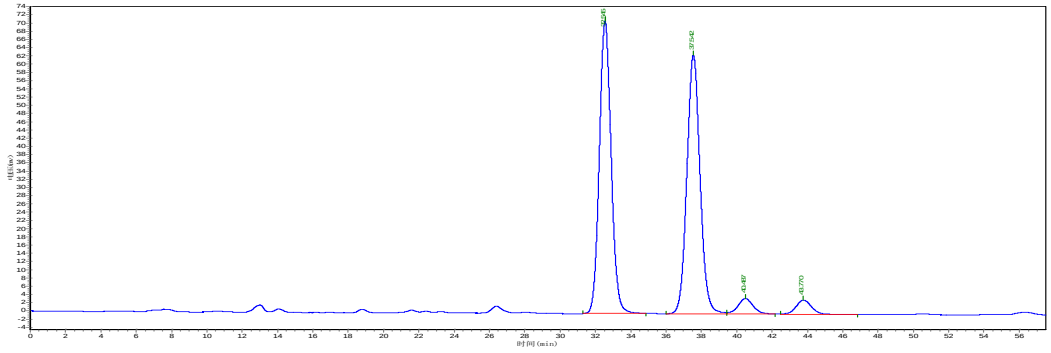


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	10.753	6158.054	188024.406	1.4906
2	13.740	12172.722	454083.594	3.5999
3	15.572	284966.250	11767909.000	93.2941
4	18.247	4576.417	203759.281	1.6154
total		307873.433	12613776.281	100.0000

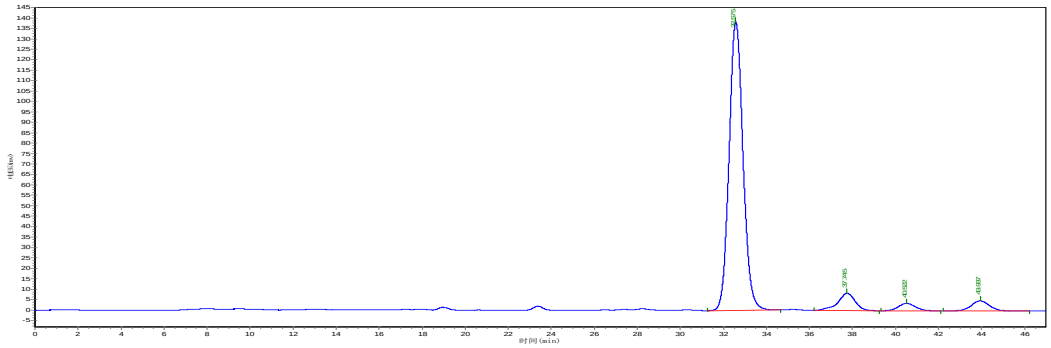
93 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.8 ml/min, λ= 254 nm, major diastereomer: t_R = 13.6 min (minor) and t_R = 15.6 min (major), minor diastereomer: t_R = 10.7 min (major), and t_R = 18.2 min (minor)



3m

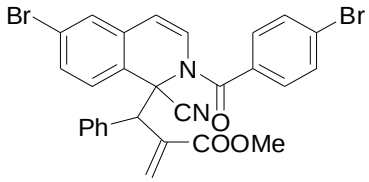


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	32.545	71137.234	3308556.250	47.1413
2	37.542	62930.648	3272337.750	46.6253
3	40.487	3770.478	224174.281	3.1941
4	43.770	3470.470	213309.203	3.0393
total		141308.831	7018377.484	100.0000



Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	32.575	138242.344	6238146.000	86.9208
2	37.745	8279.750	462704.219	6.4472
3	40.522	3521.198	192302.703	2.6795
4	43.937	4817.027	283660.500	3.9525
total		154860.319	7176813.422	100.0000

86 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min,λ= 254 nm, major diastereomer: t_R = 32.5 min (major) and t_R = 37.5 min (minor), minor diastereomer: t_R = 40.5 min (minor), and t_R = 43.8 min (major).



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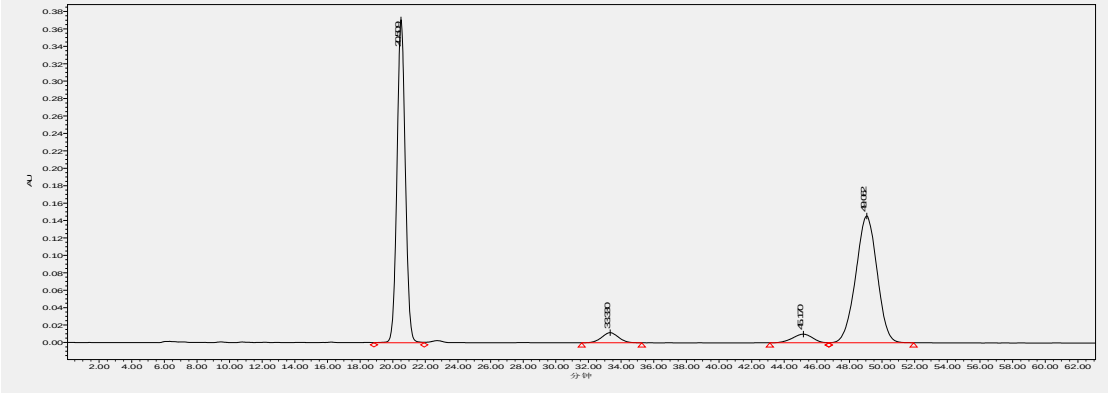
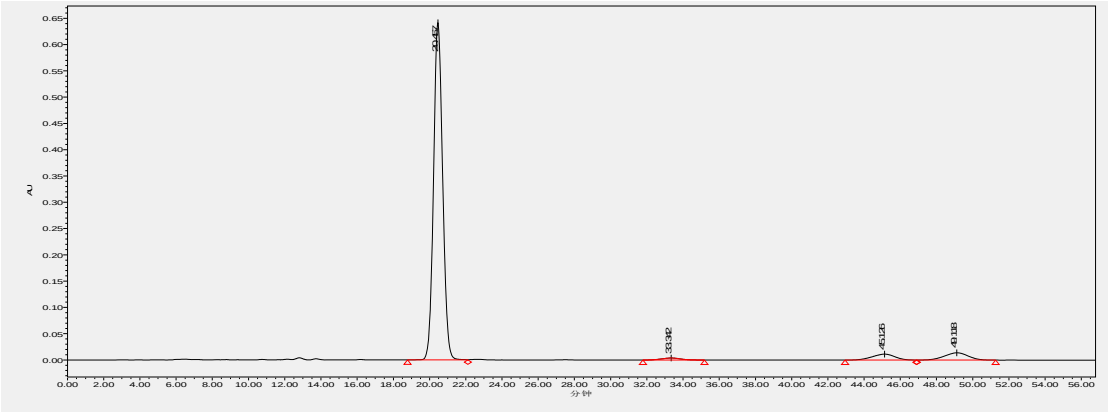
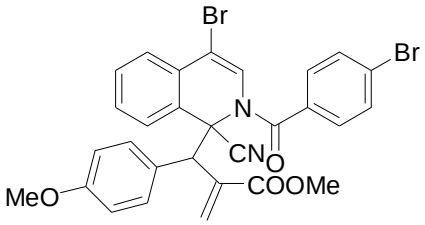


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	20.509	370811	13133654	46.88
2	33.330	11607	830141	2.96
3	45.170	9908	841395	3.00
4	49.062	145516	13208497	47.15
total		537842	28013687	99.99



Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	20.457	641654	22350146	89.84
2	33.342	3873	283870	1.14
3	45.126	11334	984207	3.96
4	49.118	13845	1258558	5.06
total		670706	24876781	100.00

89 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 80/20, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 20.5 min (major) and t_R = 49.1 min (minor), minor diastereomer: t_R = 33.3 min (minor), and t_R = 45.2 min (major).



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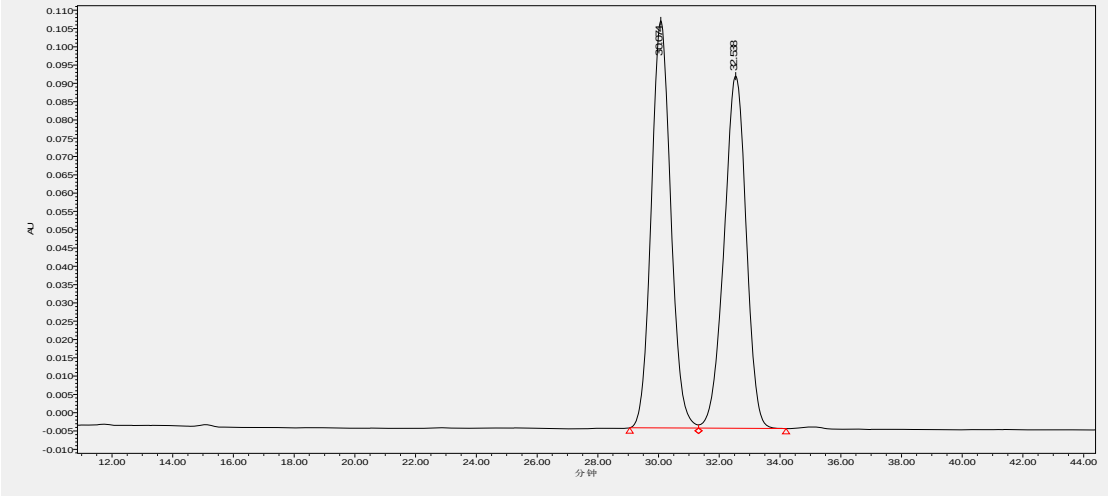
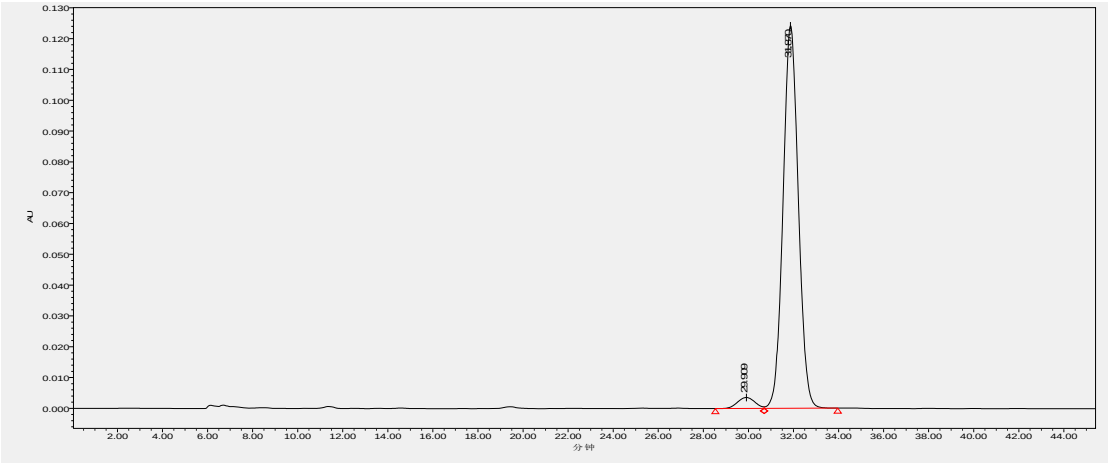
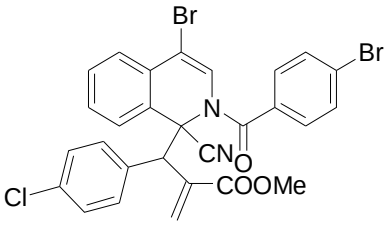


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	30.074	111258	4980800	50.51
2	32.538	96264	4879507	49.48
total		207522	9860307	99.99



Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	29.909	3560	191446	3.17
2	31.870	124179	5855306	96.83
total		127739	6046752	100.00

94 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 30.1 min (minor) and t_R = 32.5 min (major).



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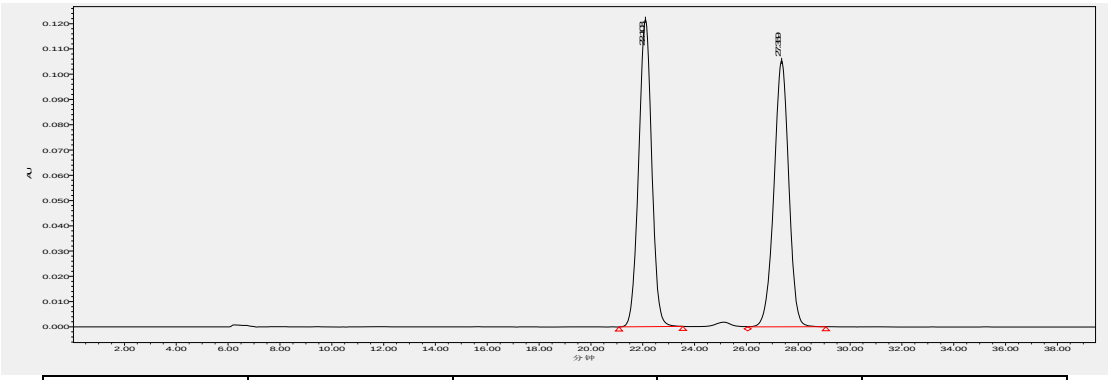
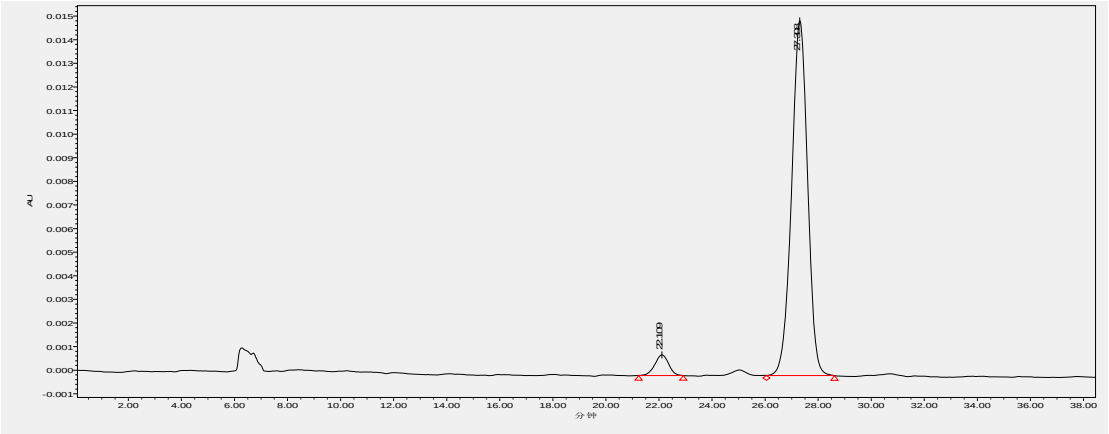
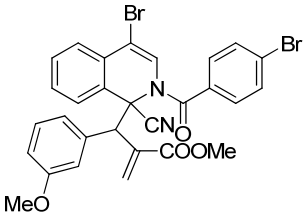


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	22.103	121538	4257802	50.40
2	27.359	105297	4189457	49.60
total		226835	8447259	100.00

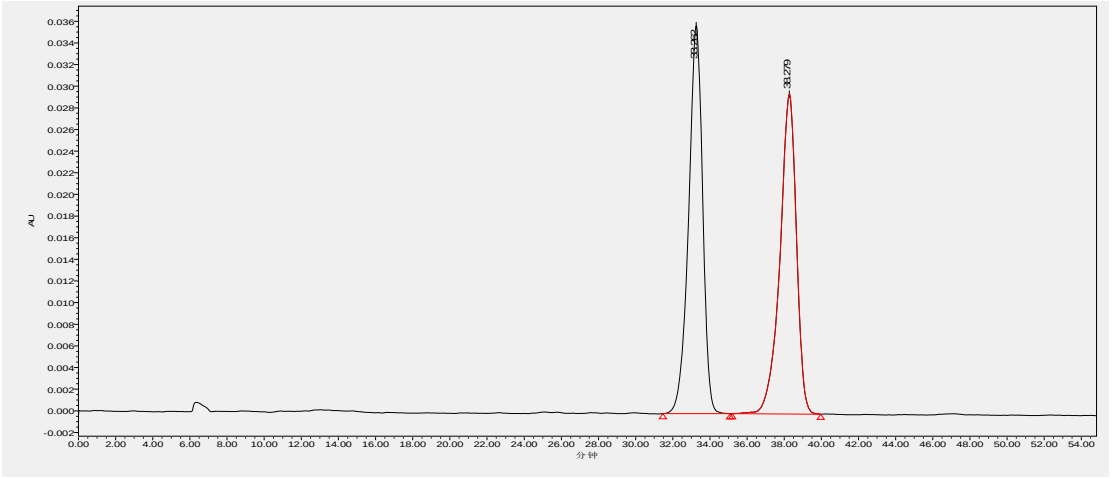


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	22.109	872	31513	4.77
2	27.308	15033	629724	95.23
total		15905	661237	100.00

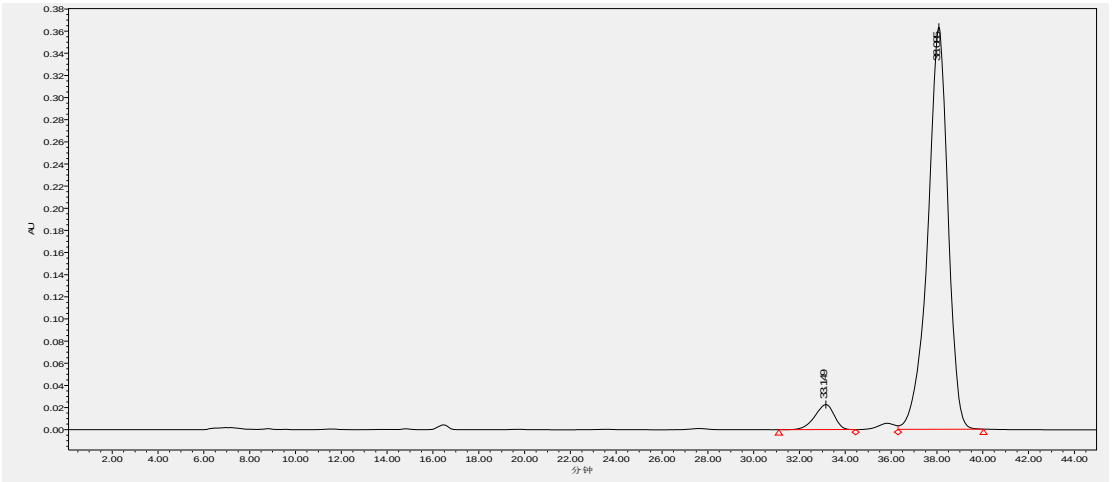
90 % ee. The ee of the product was determined by HPLC using an AD-H column (n-Hexane/i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 22.1 min (minor) and t_R = 27.4 min (major).



3q

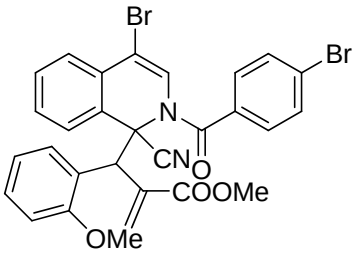


Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	33.262	35876	1888716	50.74
2	38.279	29562	1833478	49.26
total		65438	3722194	100.00



Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	33.149	22638	1332046	5.65
2	38.085	363183	22235438	94.35
total		385821	23567484	100.00

89 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 33.3 min (minor) and t_R = 38.3 min (major).



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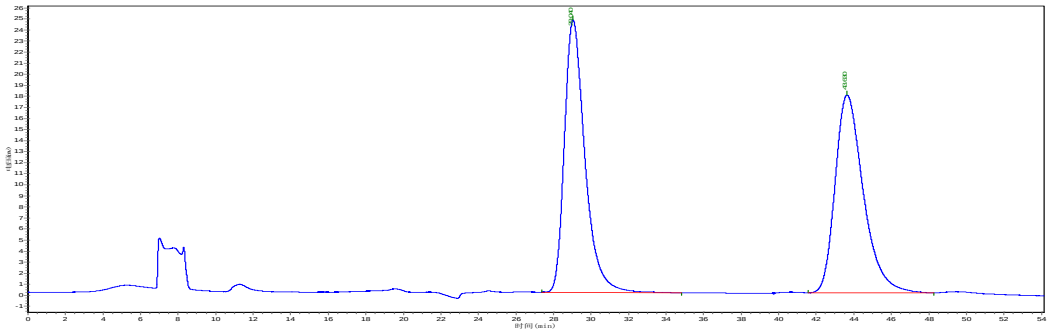
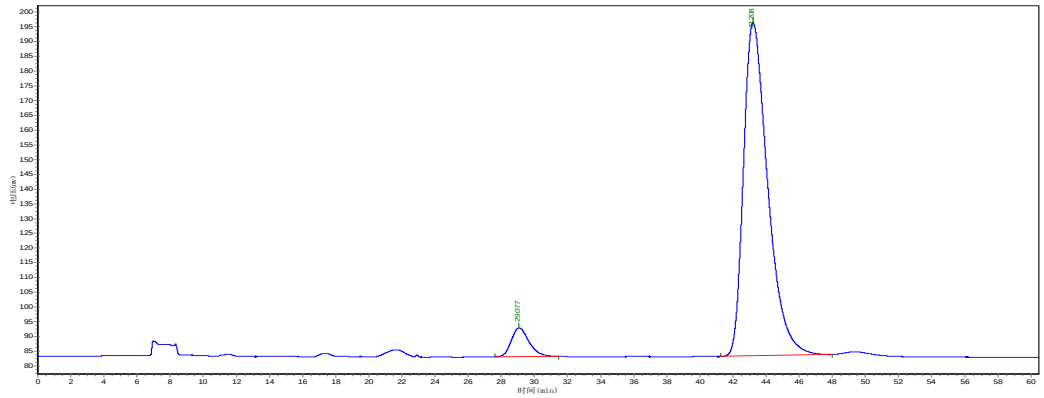


Result Table

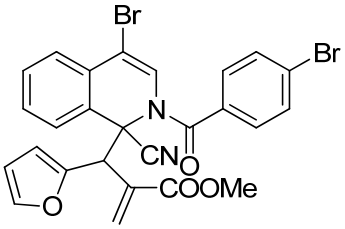
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	29.040	24630.375	1870532.250	50.0166
2	43.630	17885.387	1869287.125	49.9834
total		42515.762	3739819.375	100.000



Result Table

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	29.077	9715.331	718772.250	5.8864
2	43.208	112865.484	11491898.000	94.1136
tota		122580.815	12210670.250	100.000

88 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 29.0 min (minor) and t_R = 43.6 min (major).



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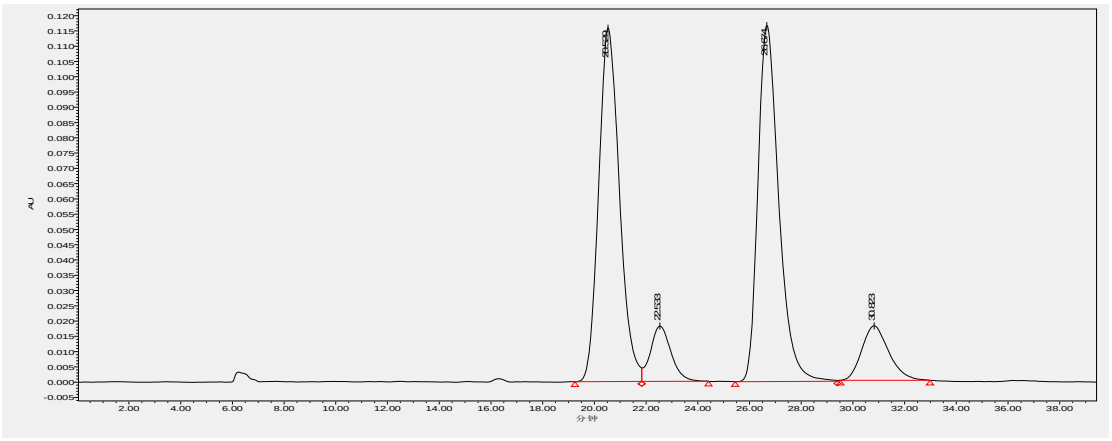
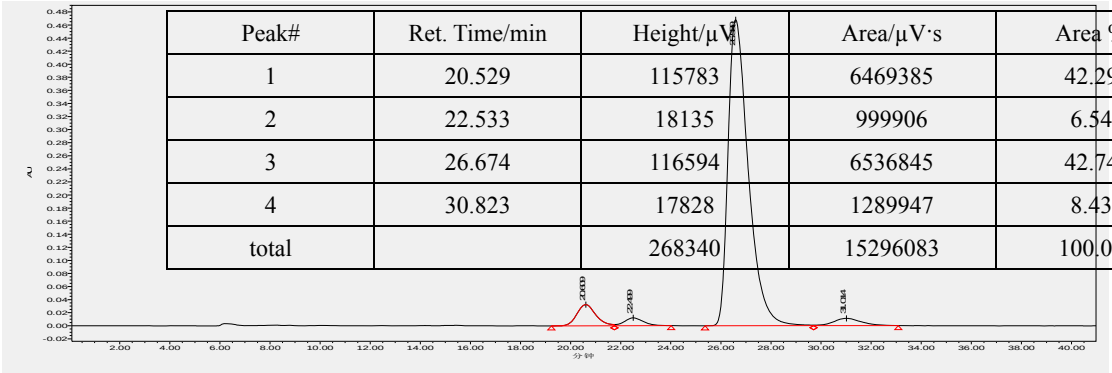
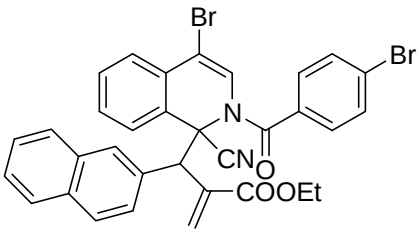




Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	20.529	115783	6469385	42.29
2	22.533	18135	999906	6.54
3	26.674	116594	6536845	42.74
4	30.823	17828	1289947	8.43
total		268340	15296083	100.00

88 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 20.5 min (minor) and t_R = 26.7 min (major), minor diastereomer: t_R = 22.5 min (minor), and t_R = 30.8 min (major).

Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	20.609	32518	1700267	5.75
2	22.499	12067	631840	2.14
3	26.589	468131	26349066	89.18
4	31.014	11077	865595	2.93
total		523793	29546768	100.00



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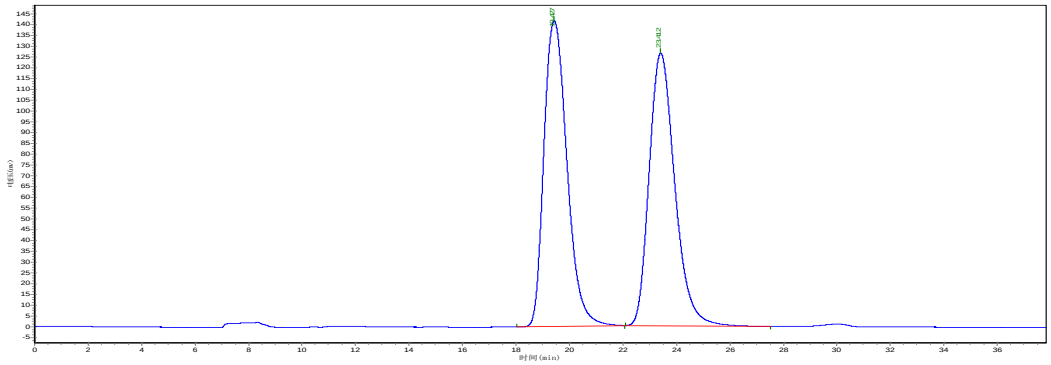
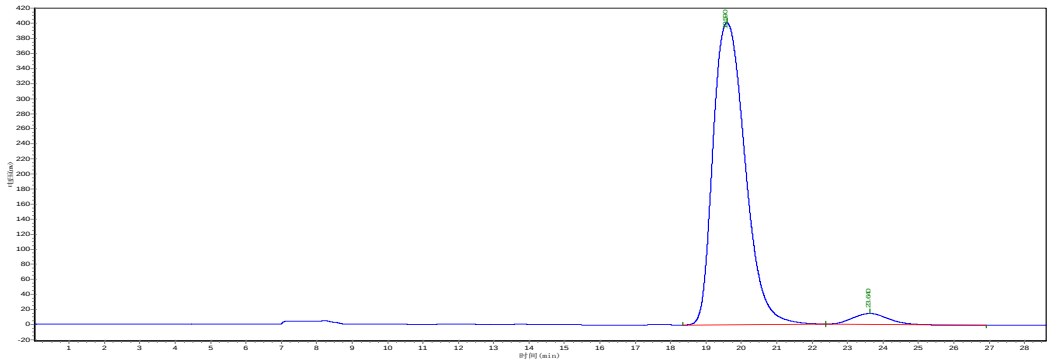


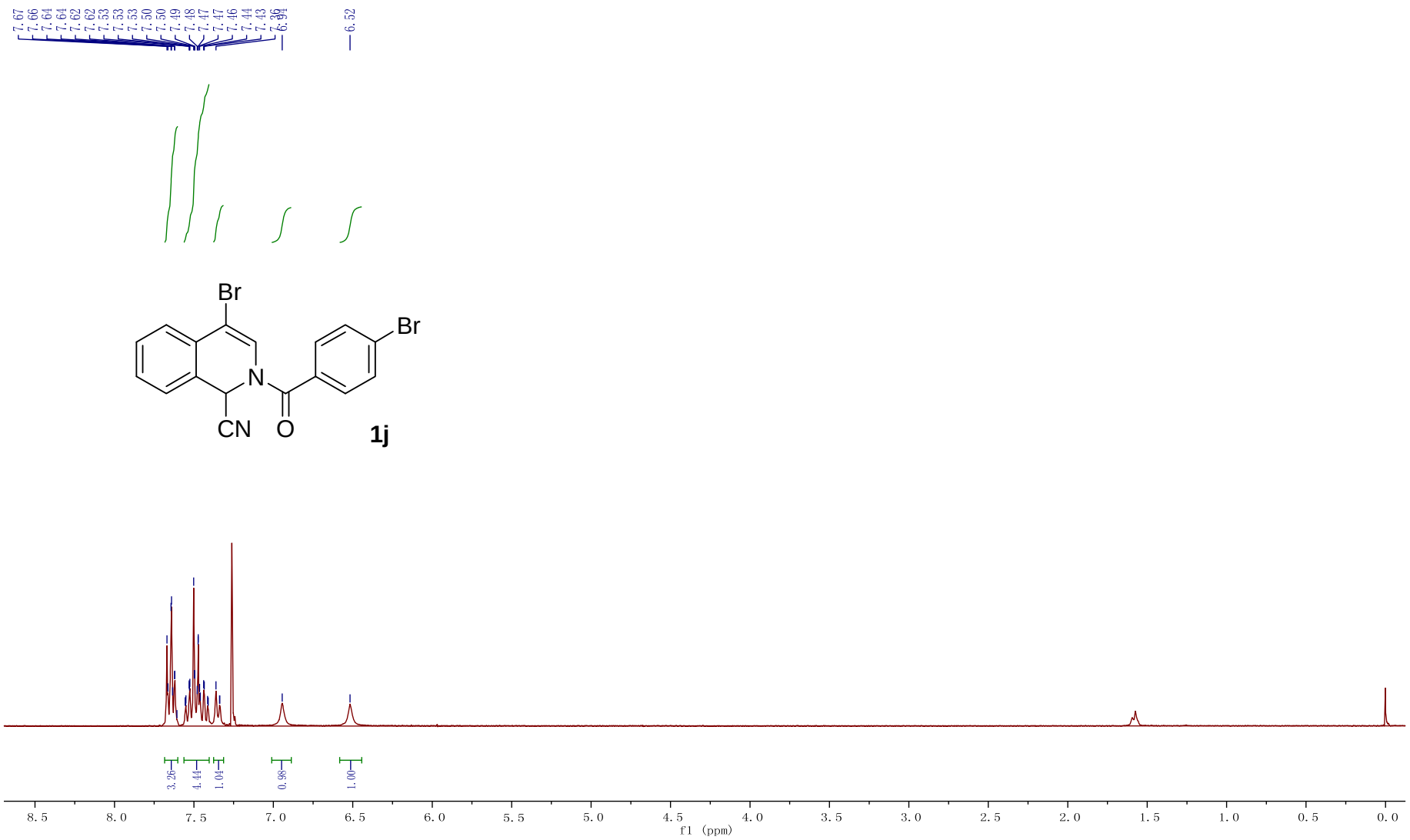
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	19.427	141436.719	8466582.000	50.2023
2	23.412	126207.898	8398342.000	49.7977
tota		267644.617	16864924.000	100.0000

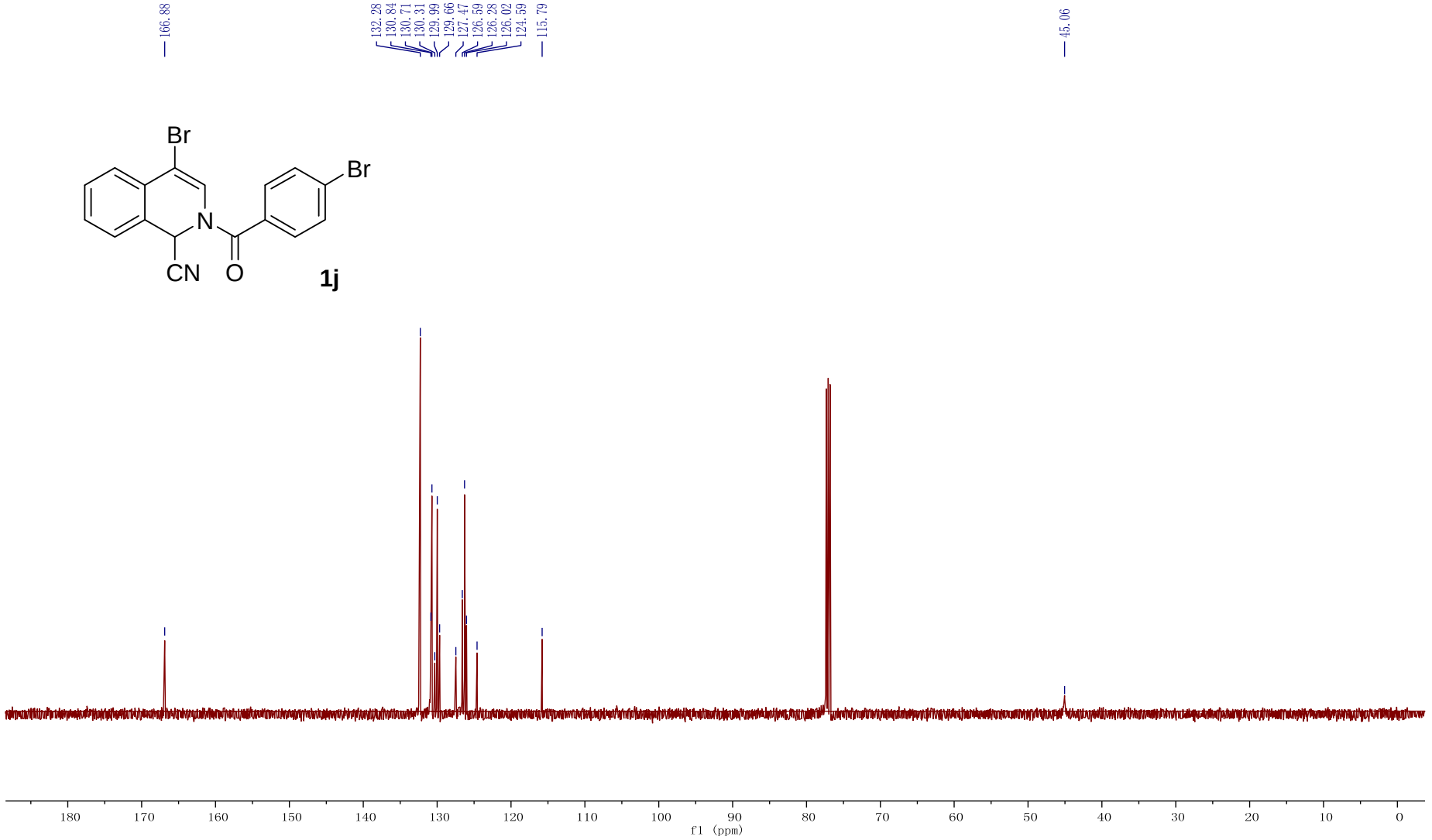


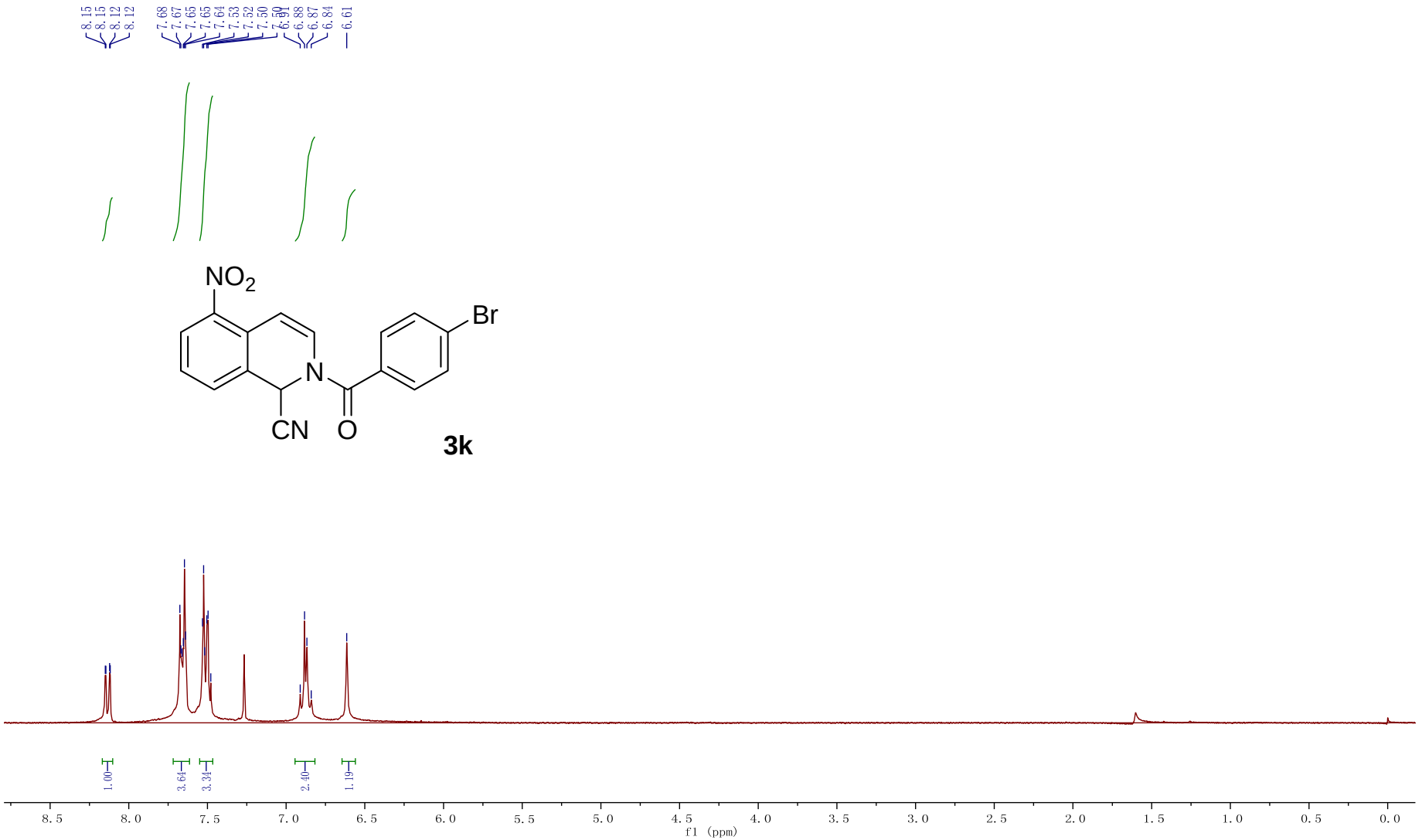
Peak#	Ret. Time/min	Height/μV	Area/μV·s	Area %
1	19.590	401231.406	25197620.000	96.2104
2	23.641	14479.261	992490.000	3.7896
tota		415710.667	26190110.000	100.0000

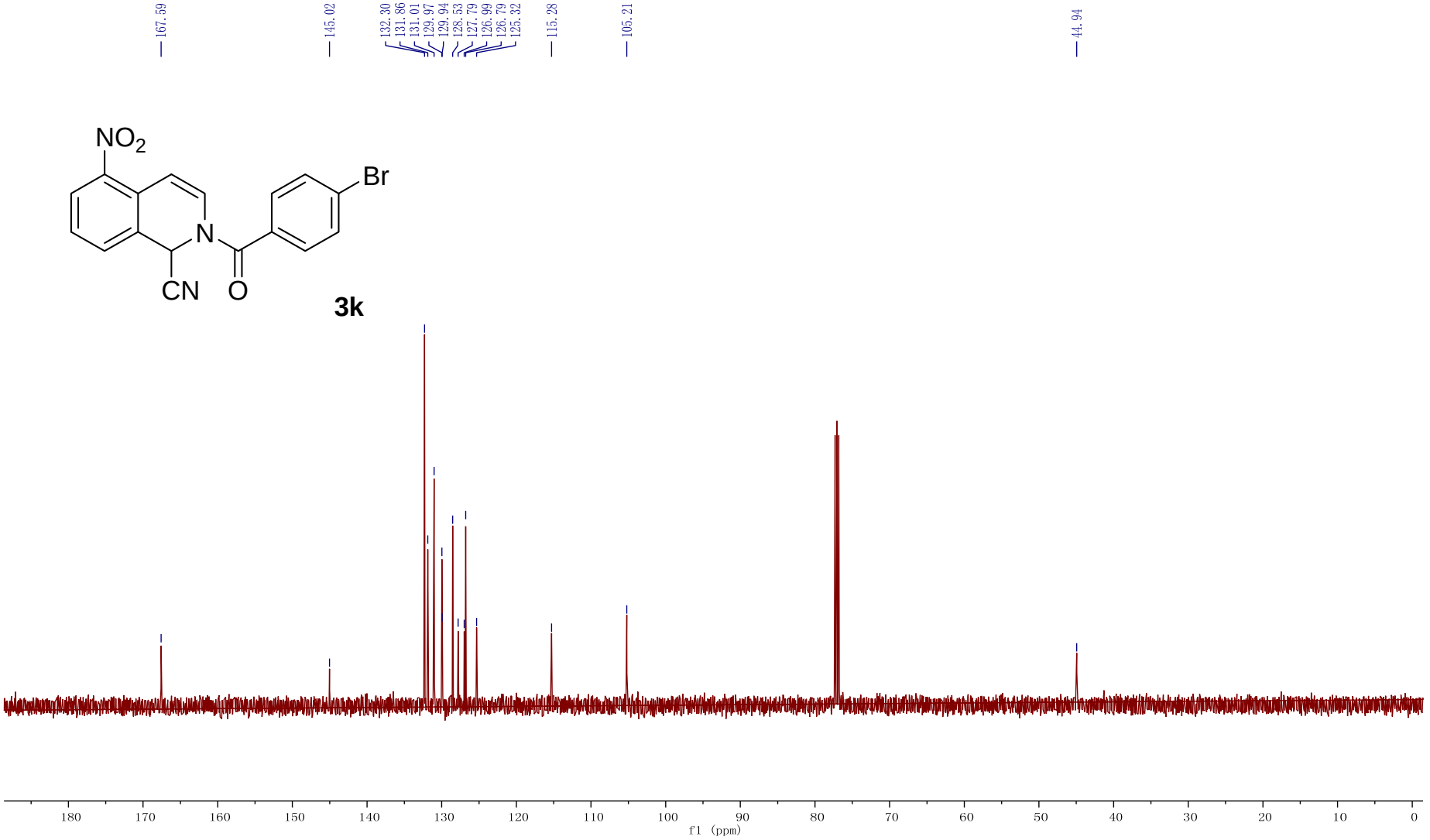
92 % ee. The ee of the product was determined by HPLC using an OD-H column (n-Hexane / i-PrOH = 90/10, flow rate 0.5 ml/min, λ= 254 nm, major diastereomer: t_R = 19.4 min (major) and t_R = 23.4 min (minor).

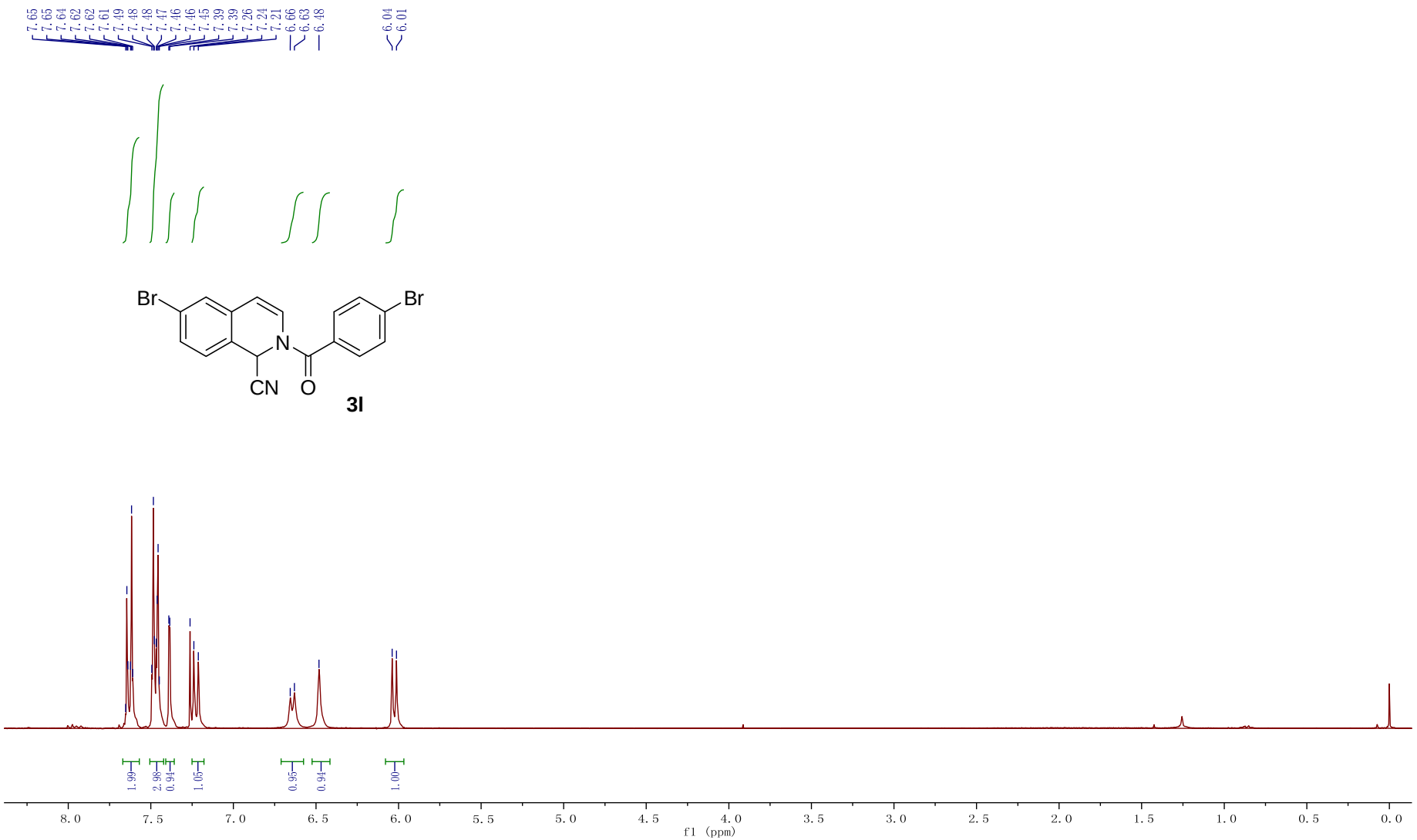
NMR Spectra

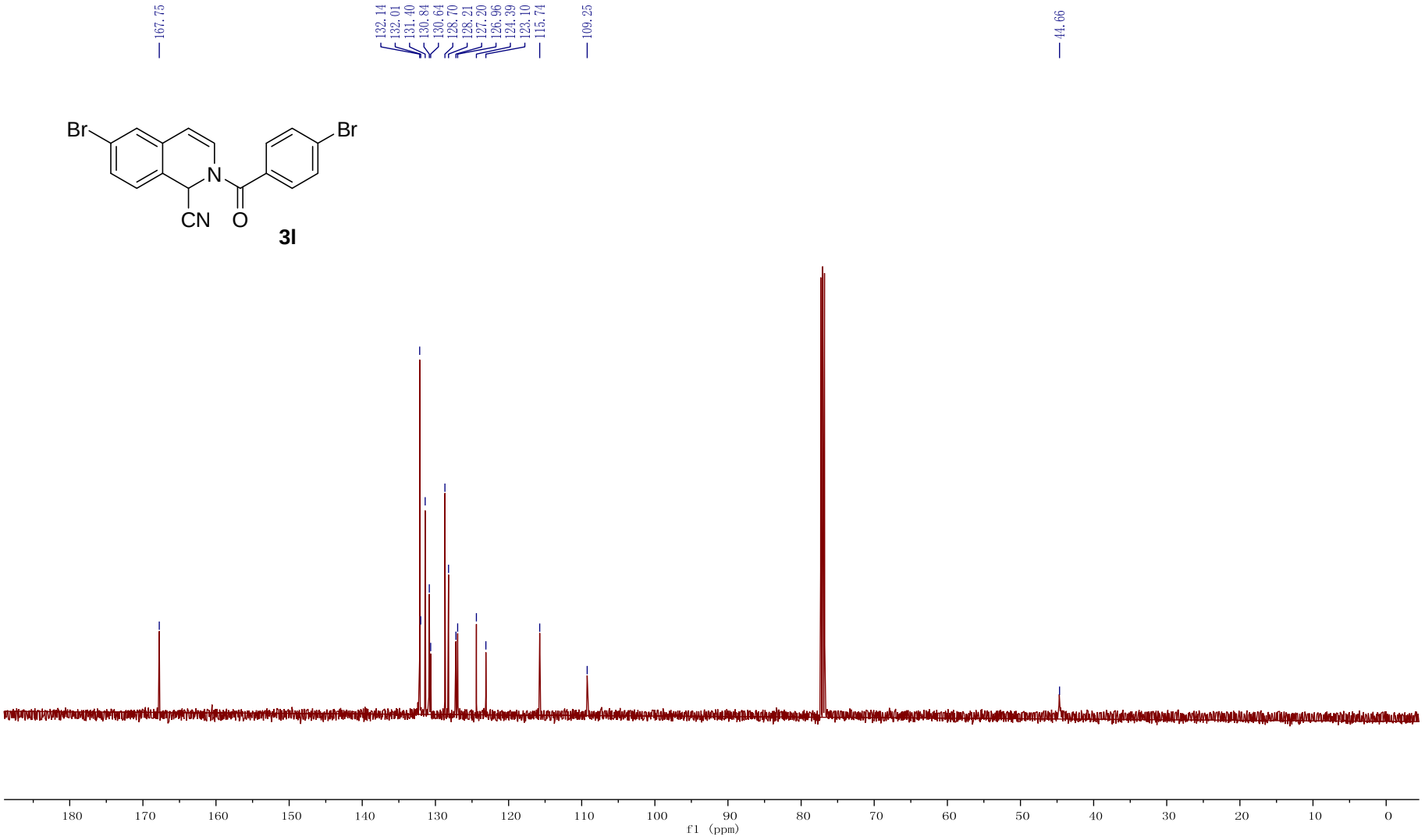


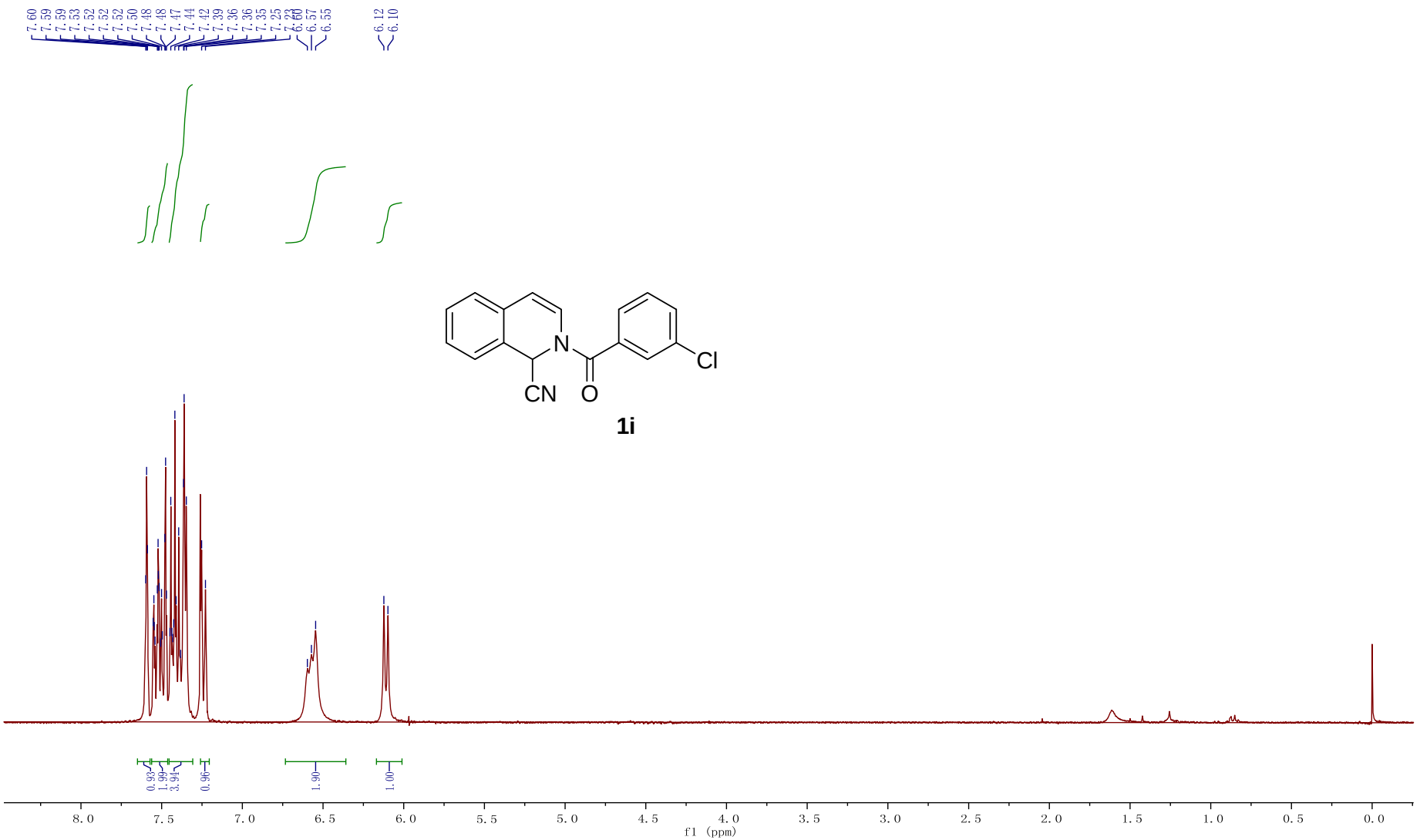












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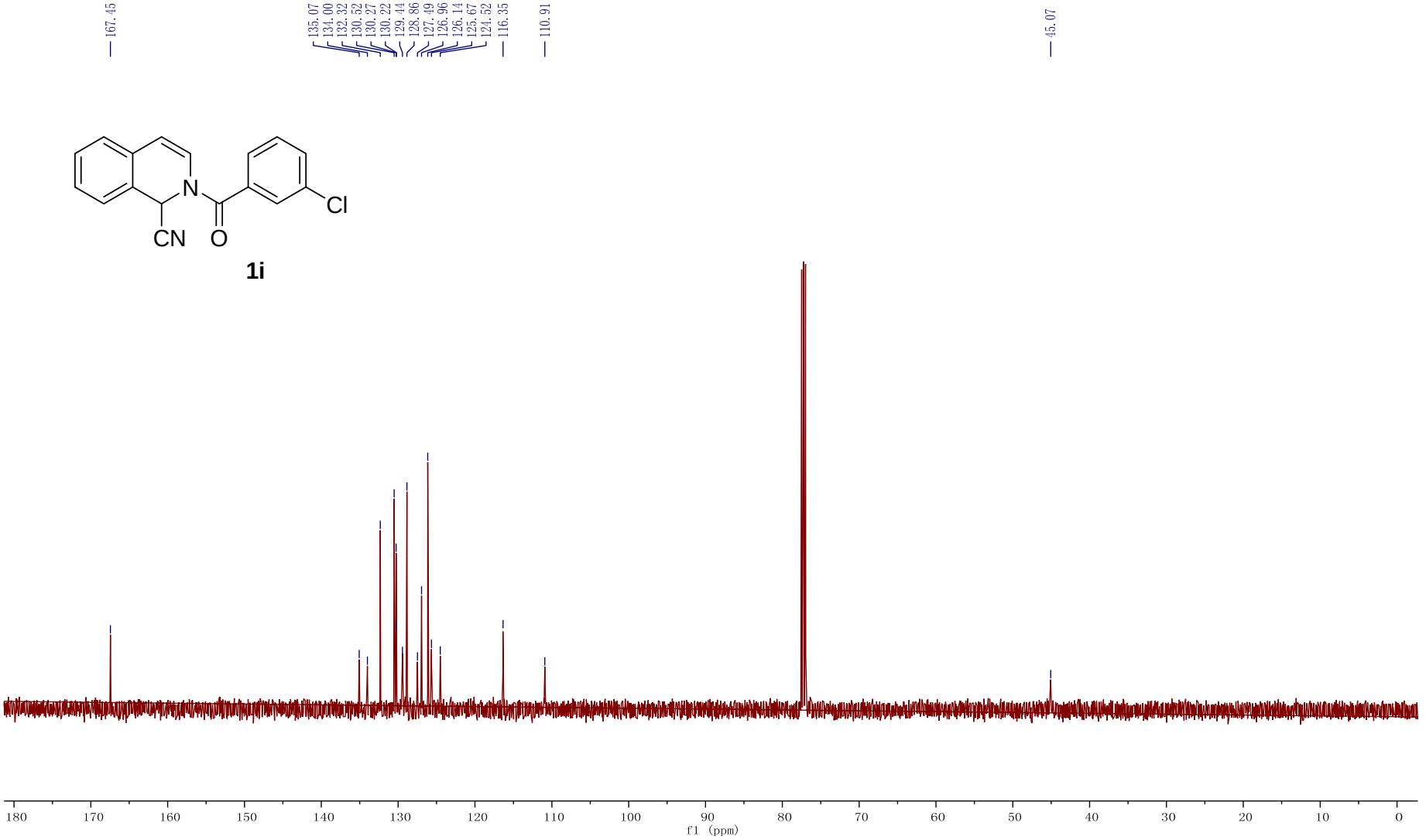

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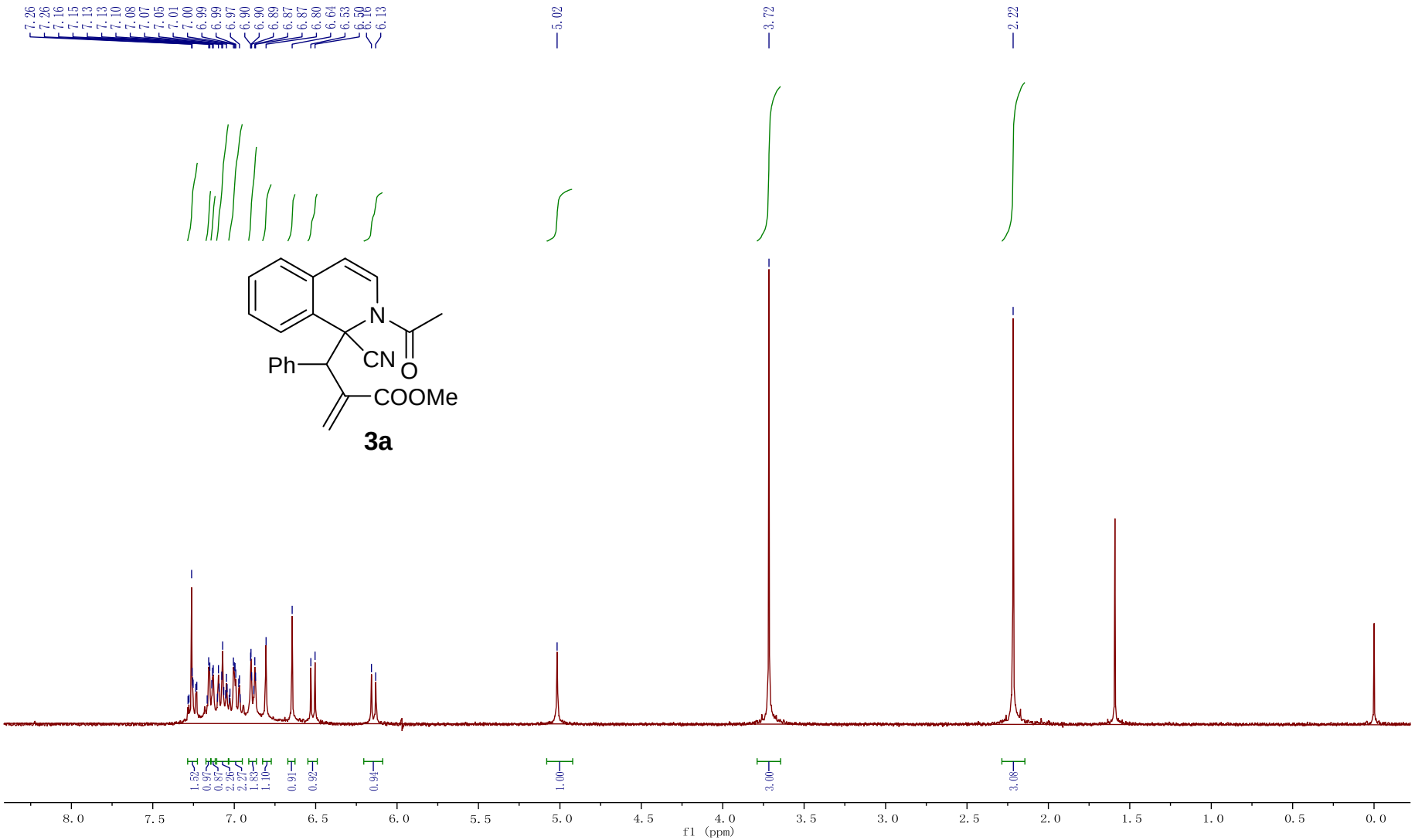

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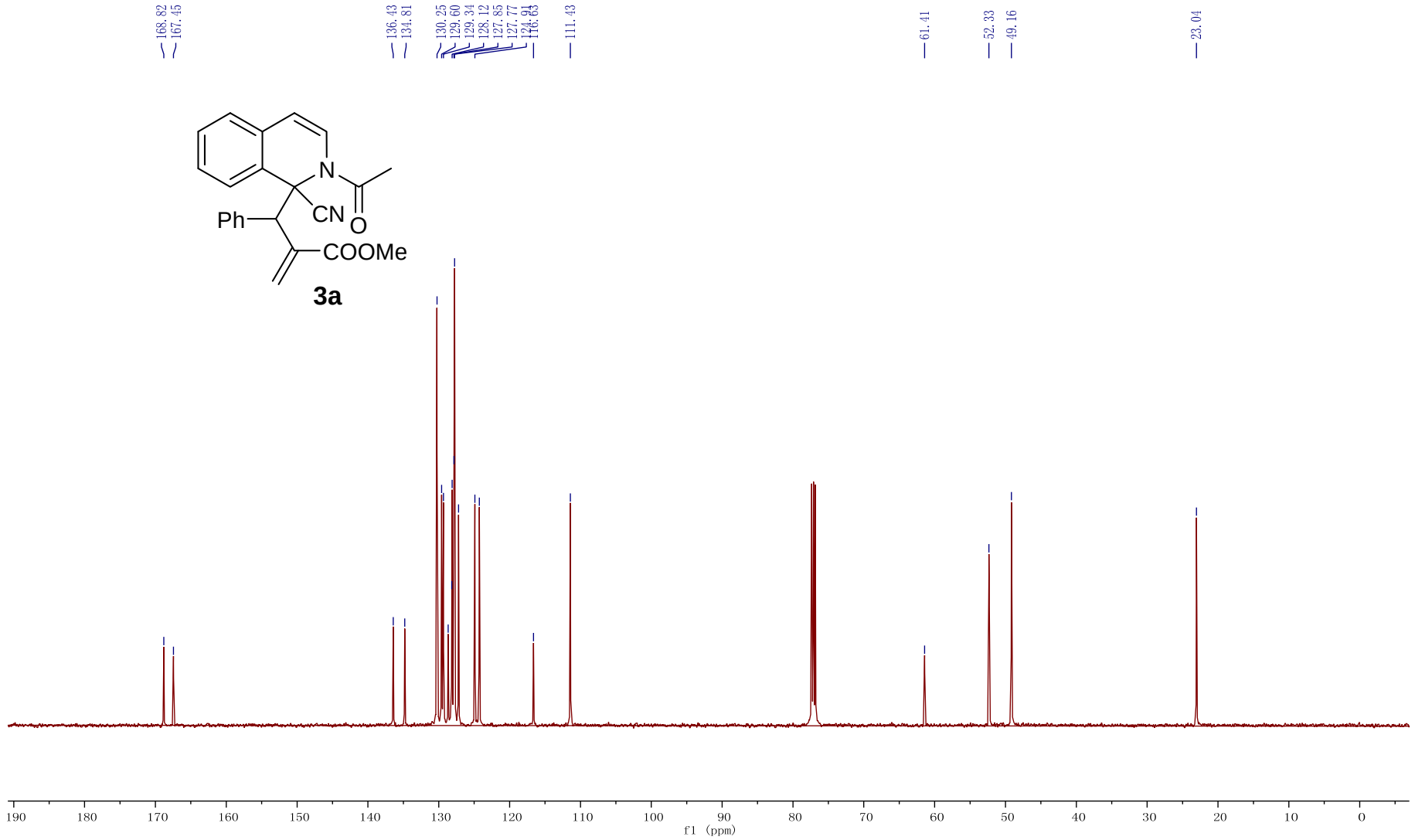

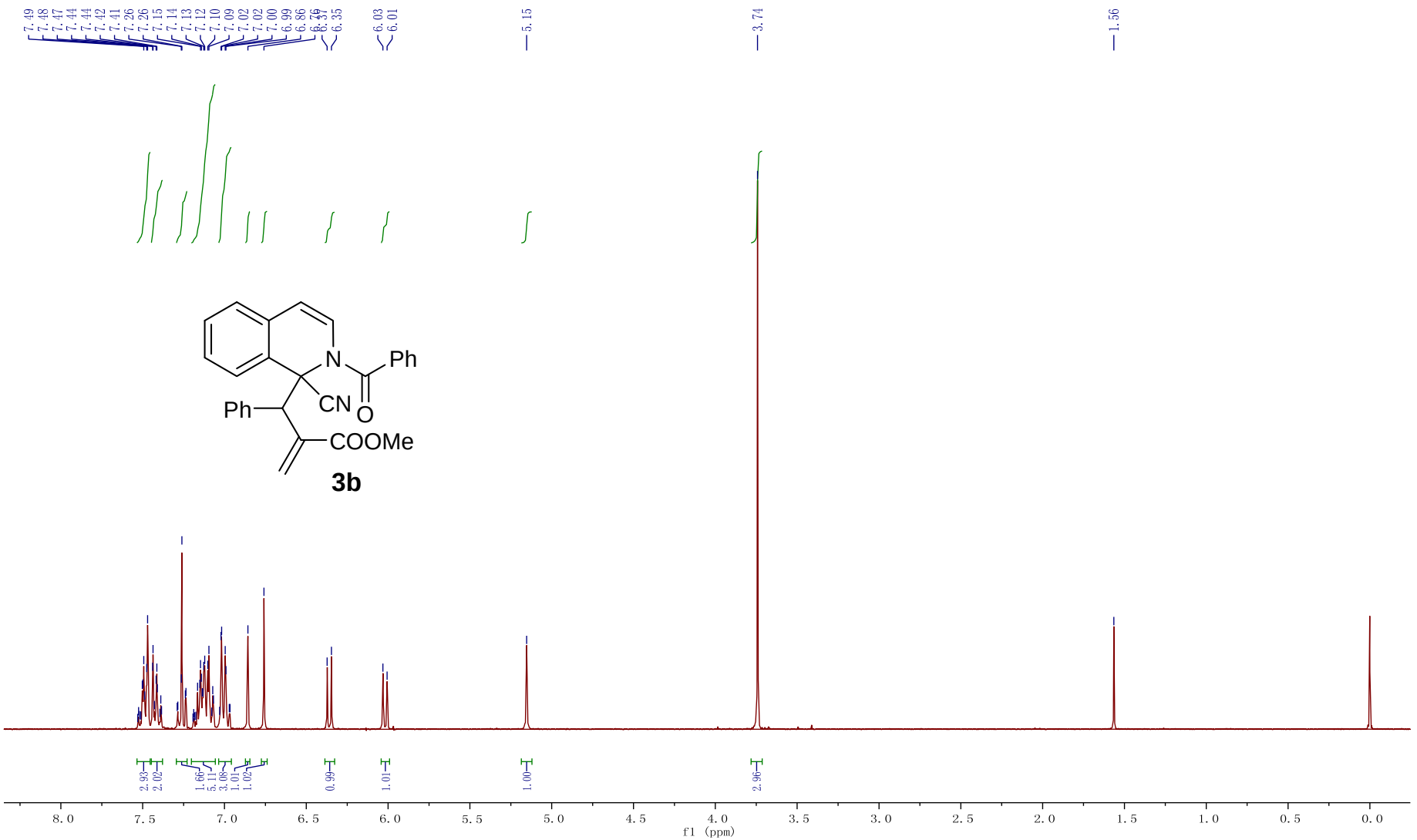

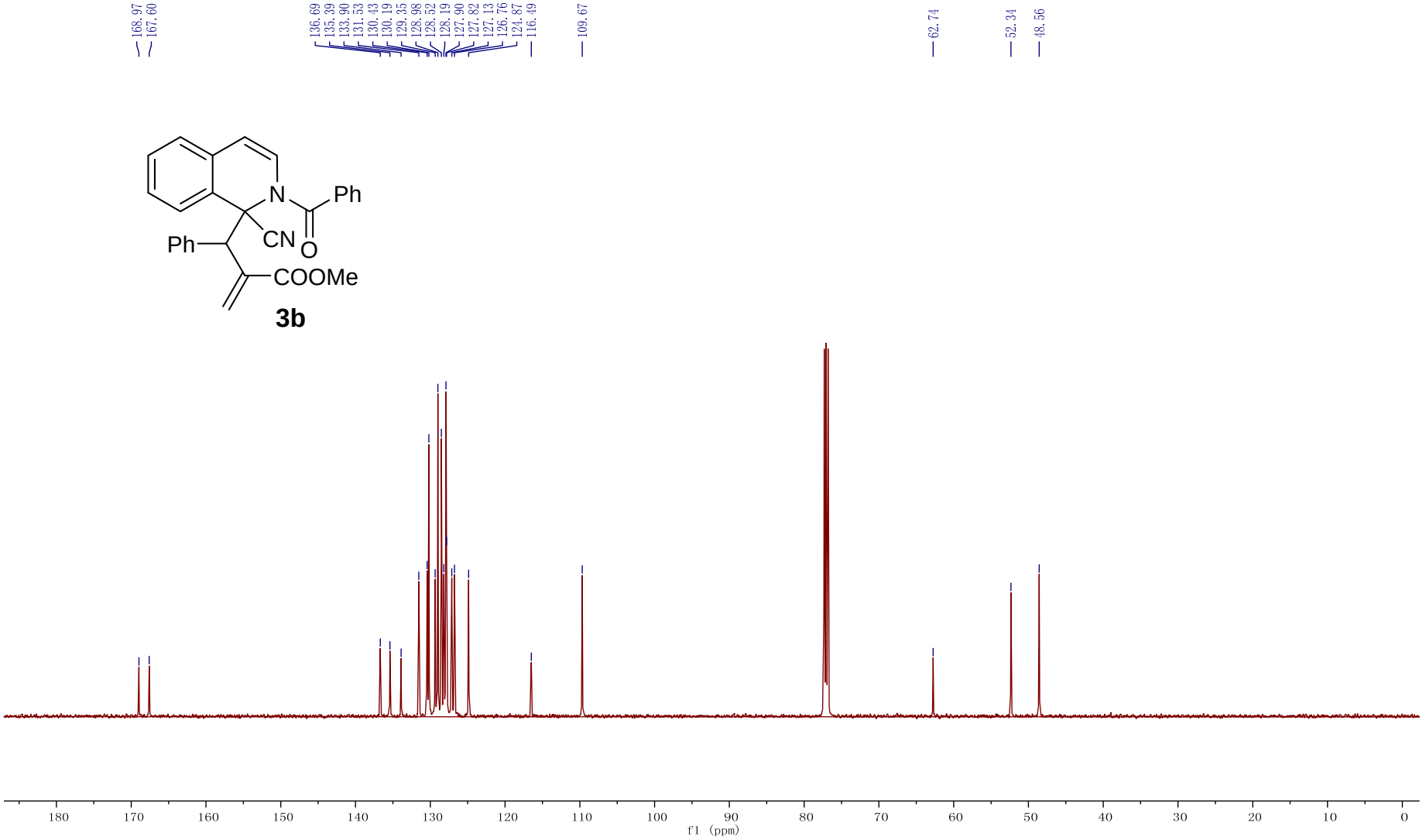

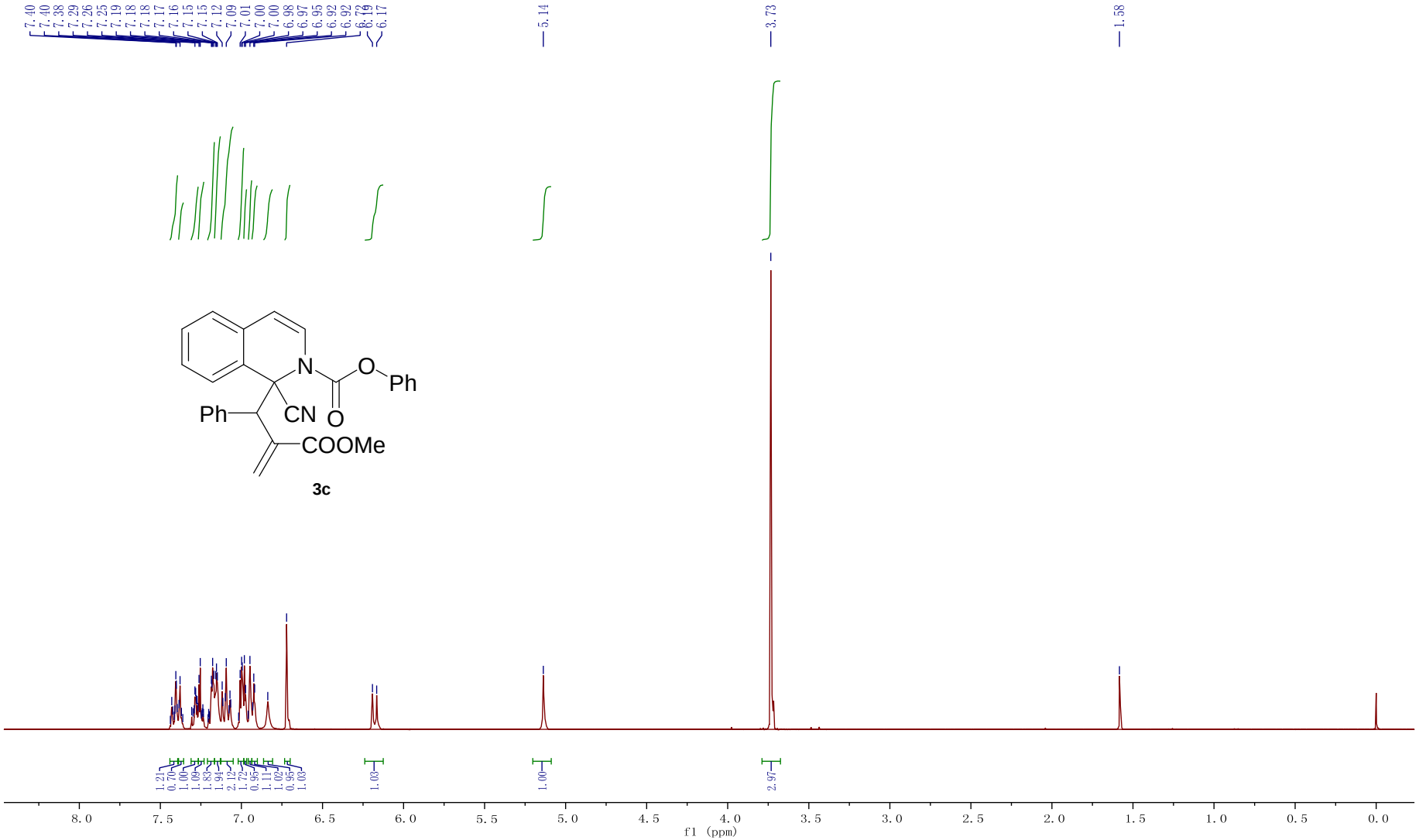

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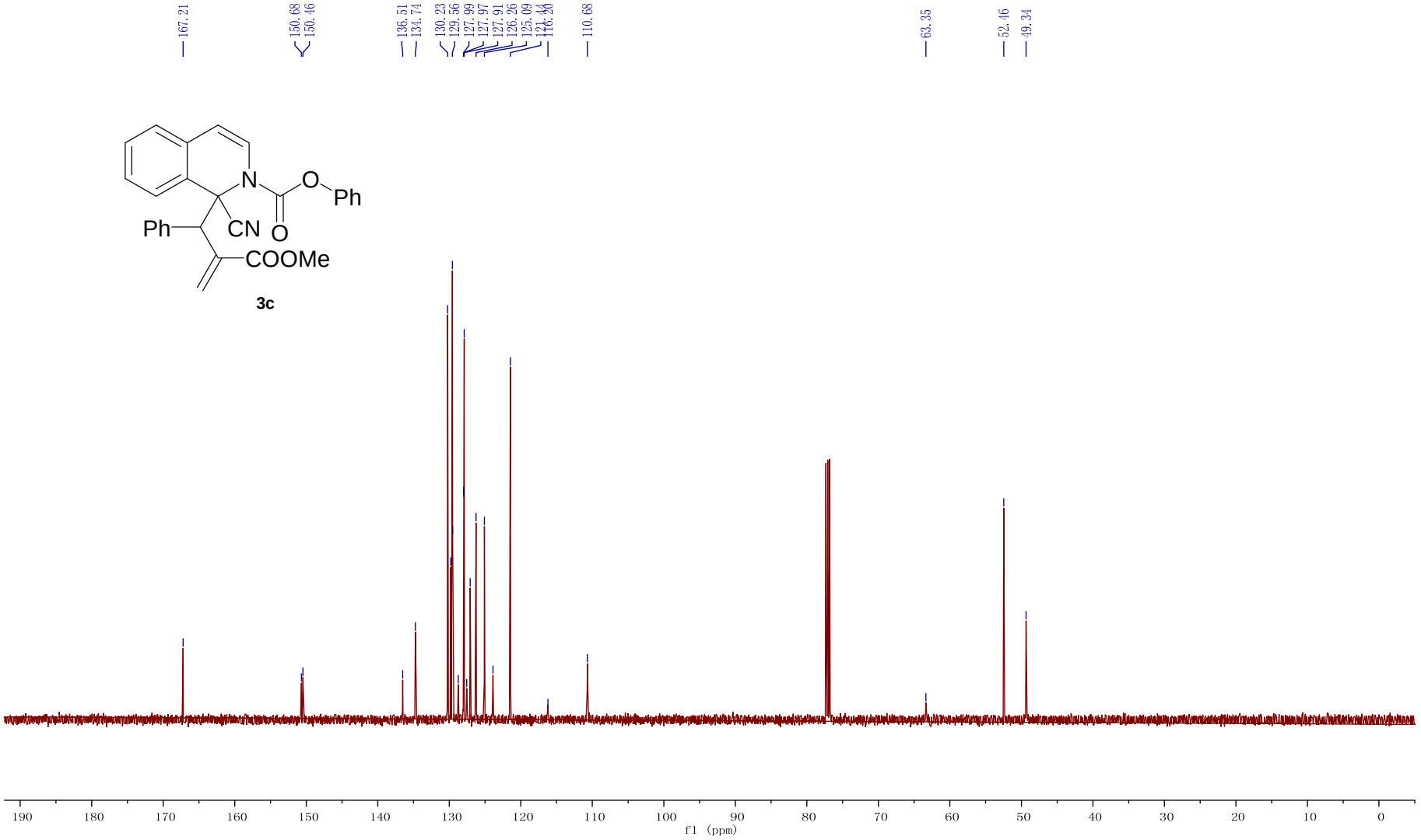

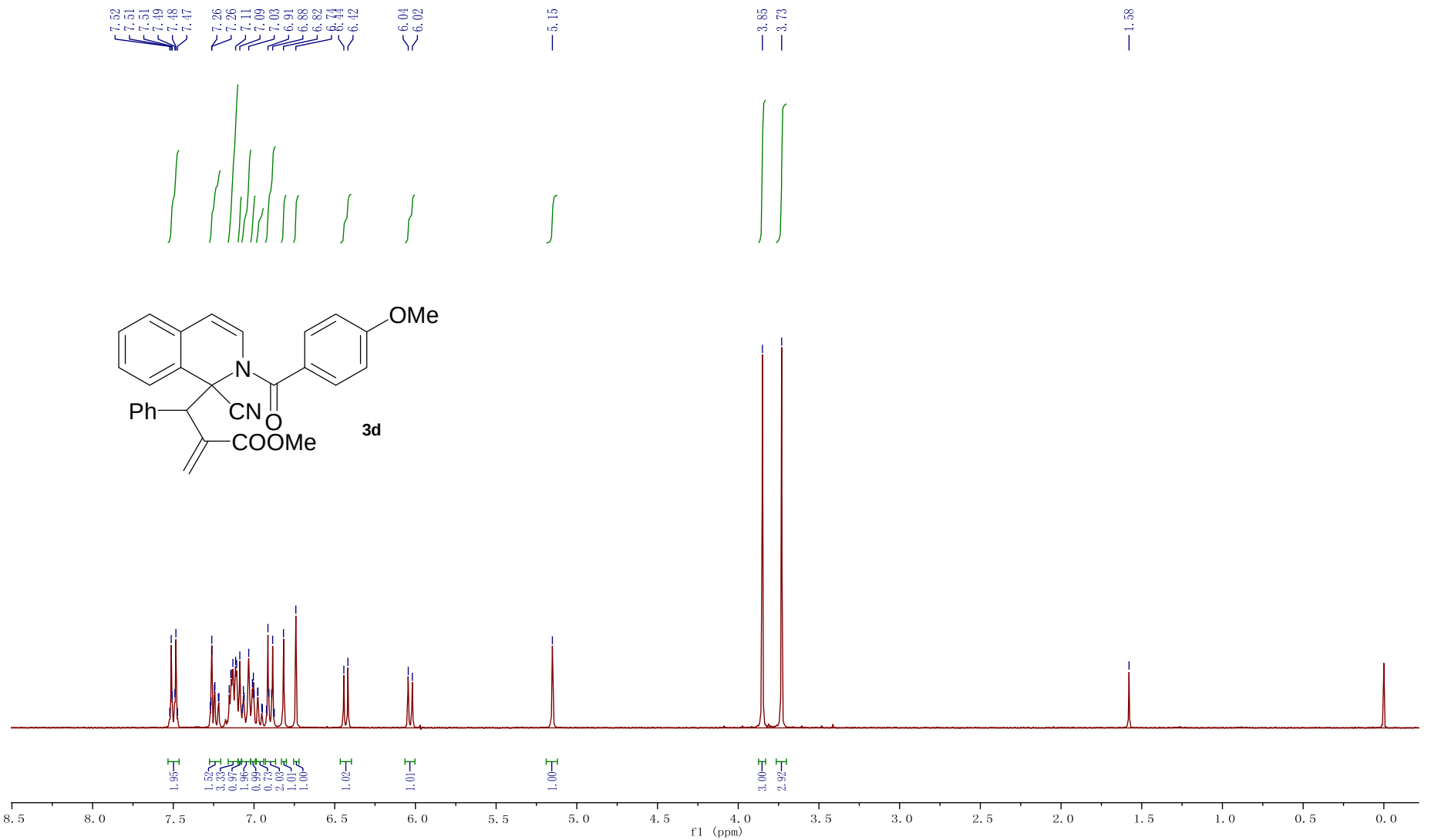

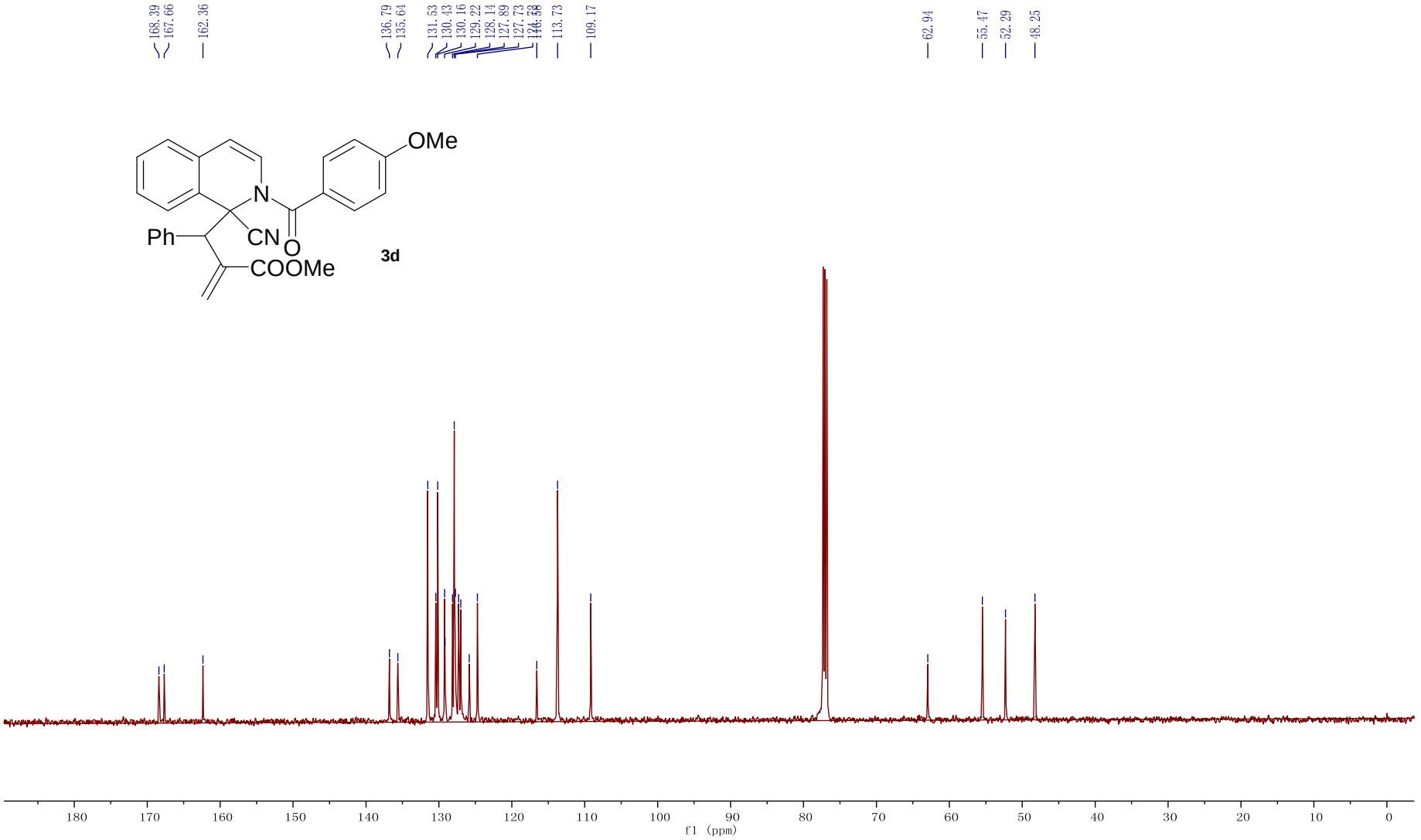

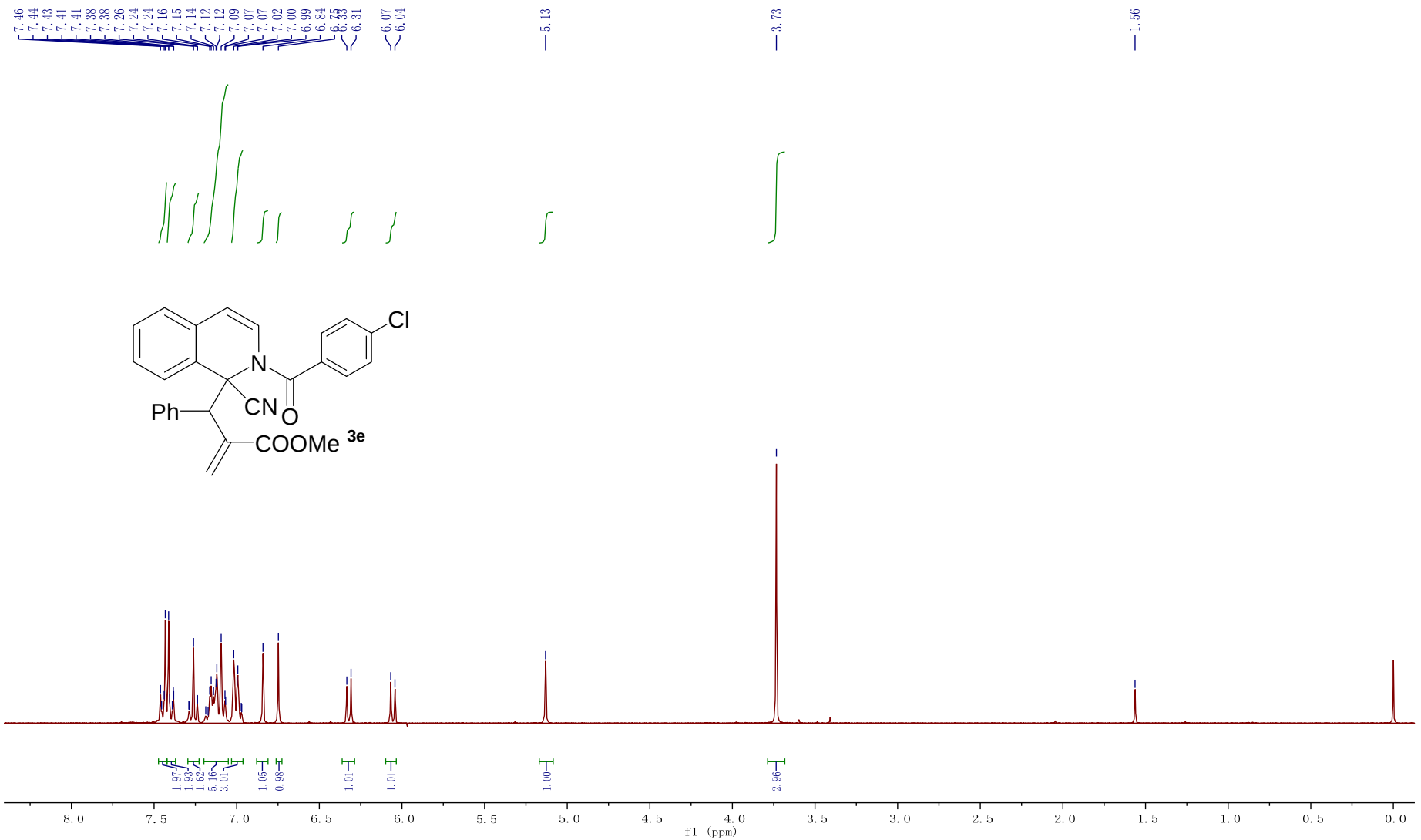

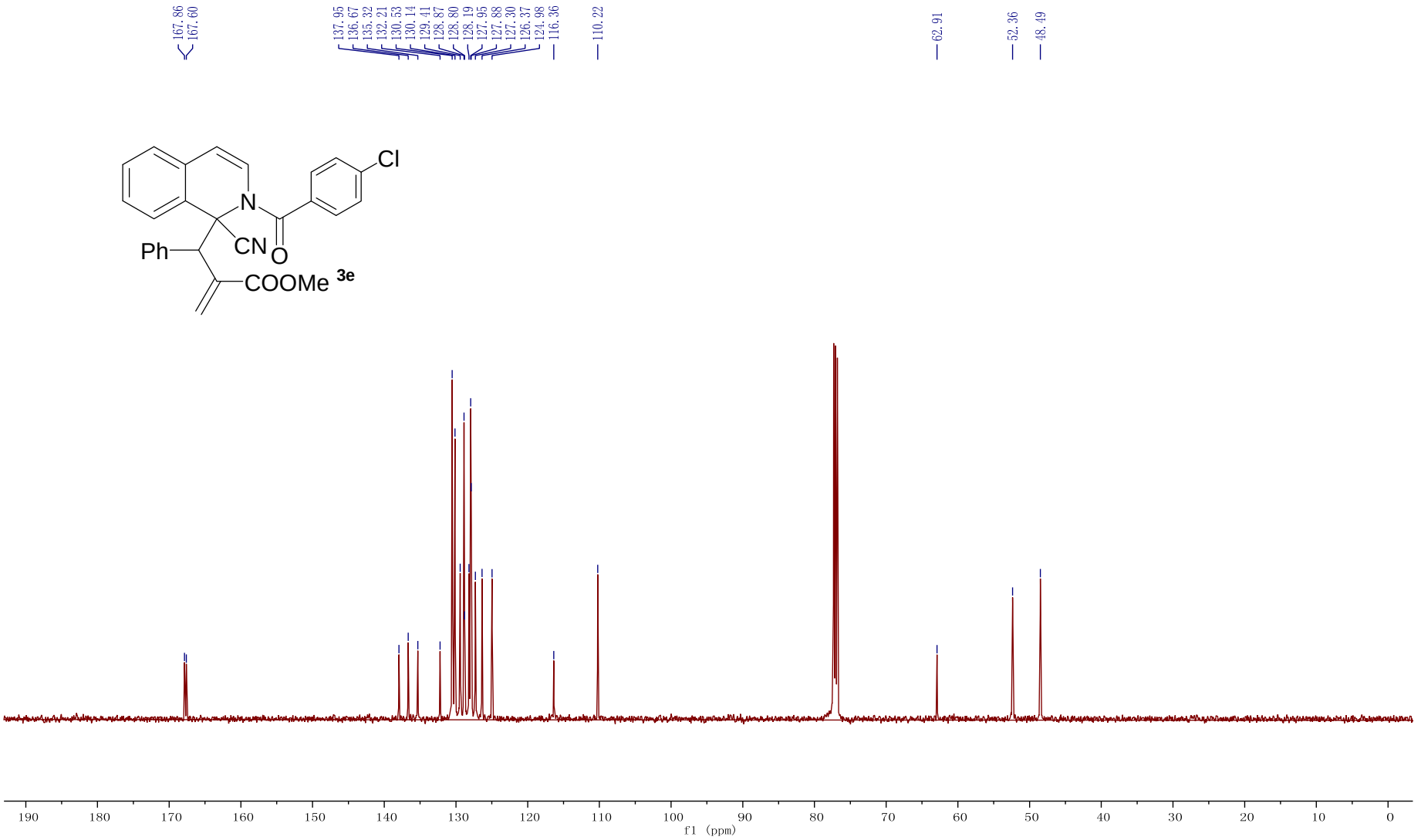

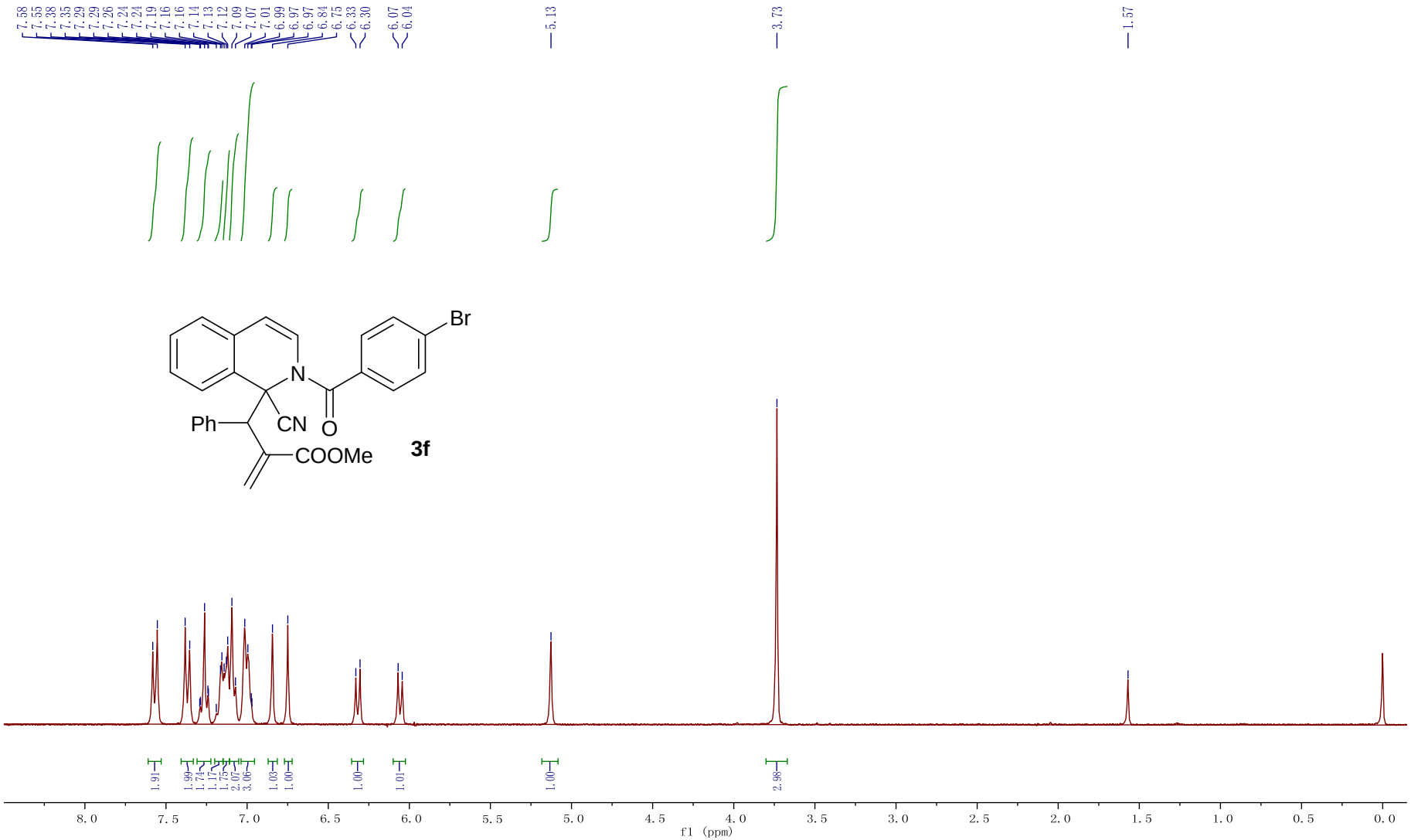

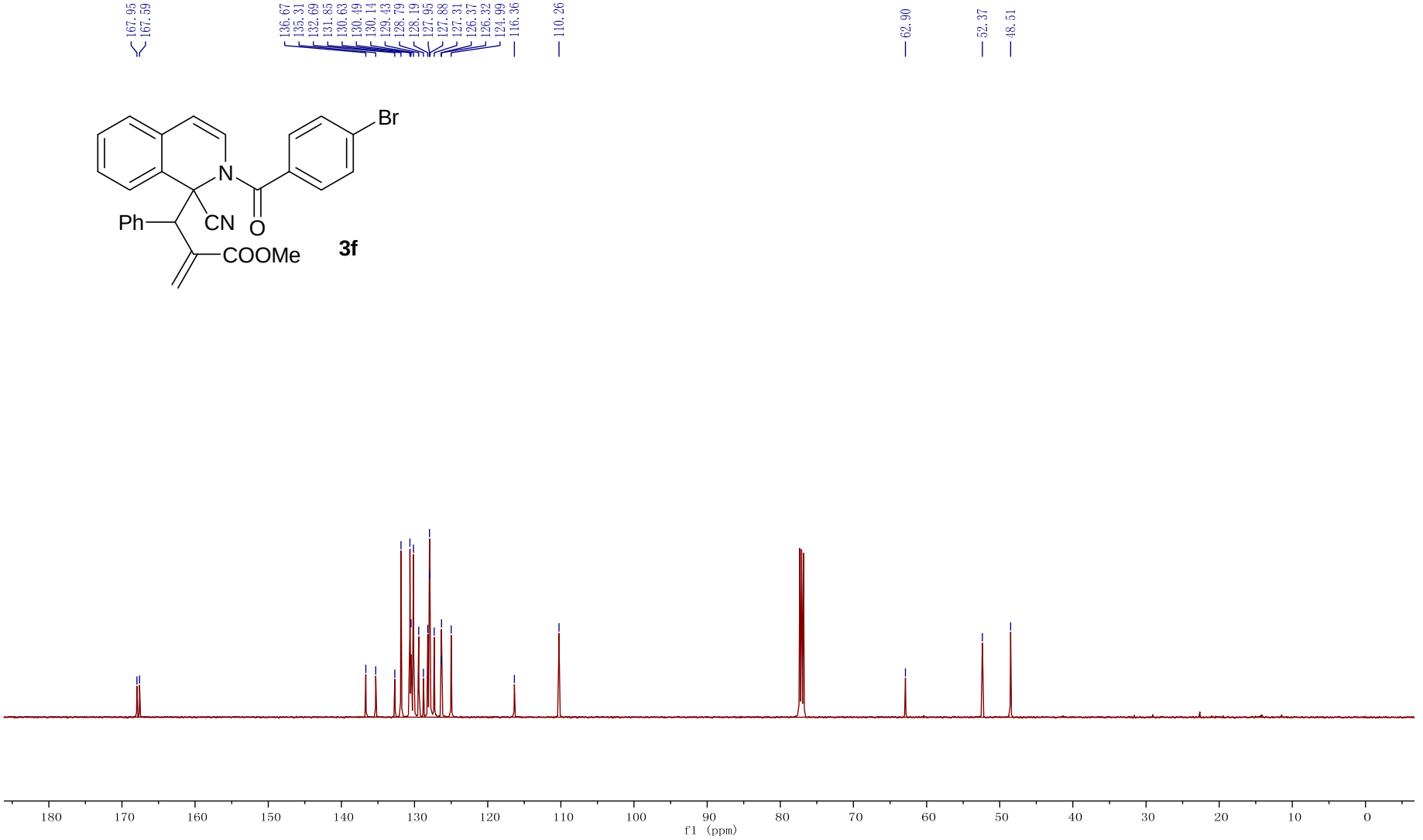

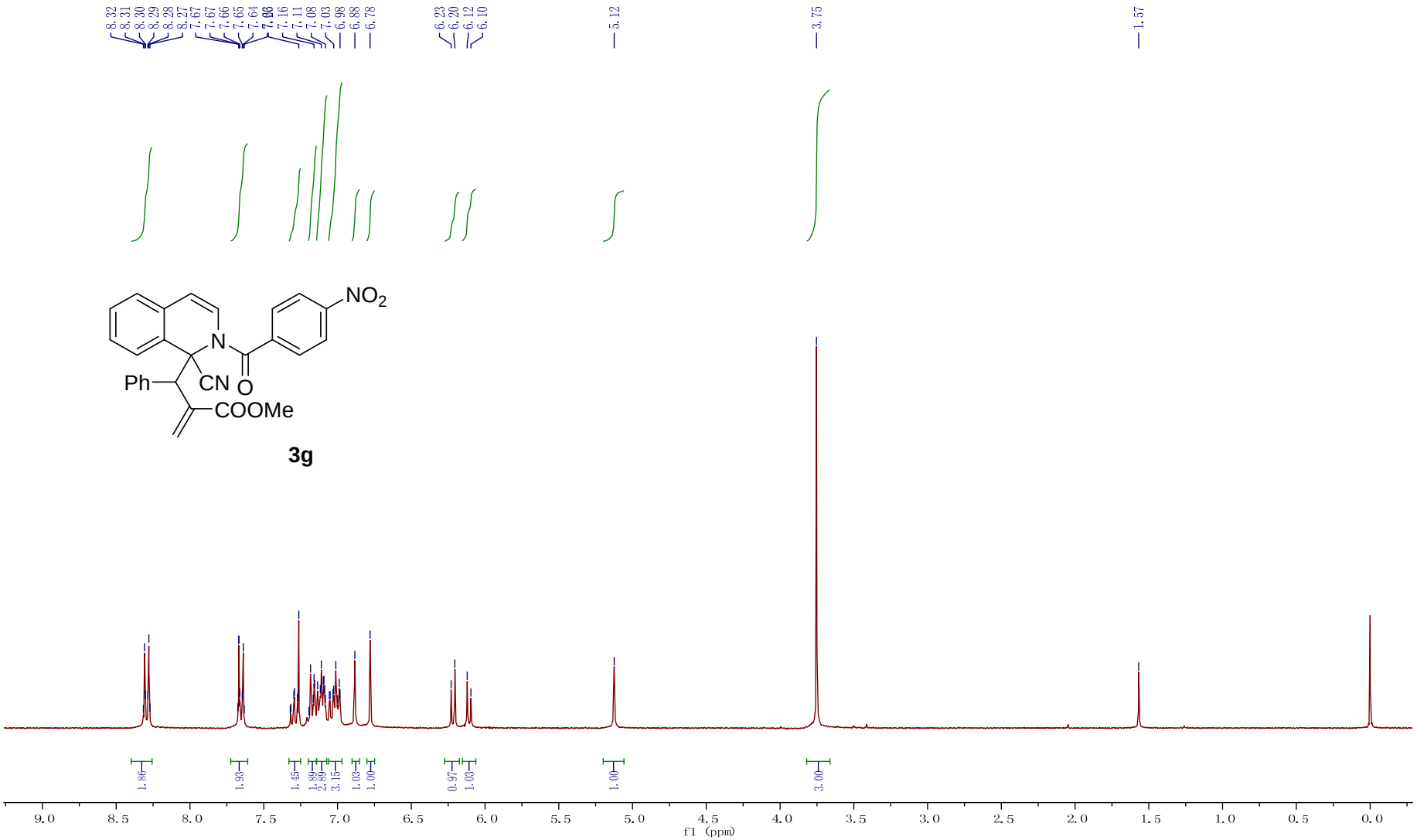

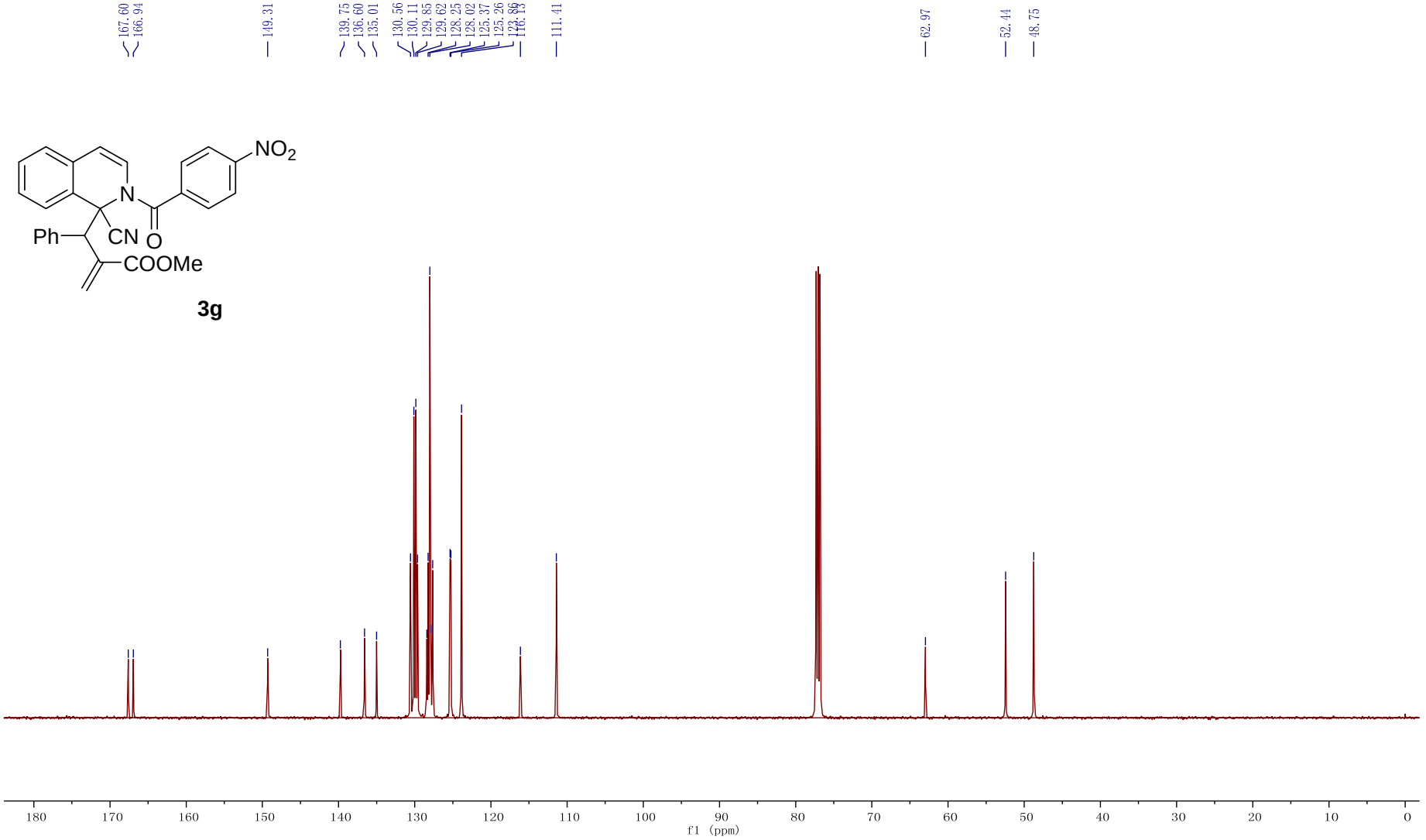

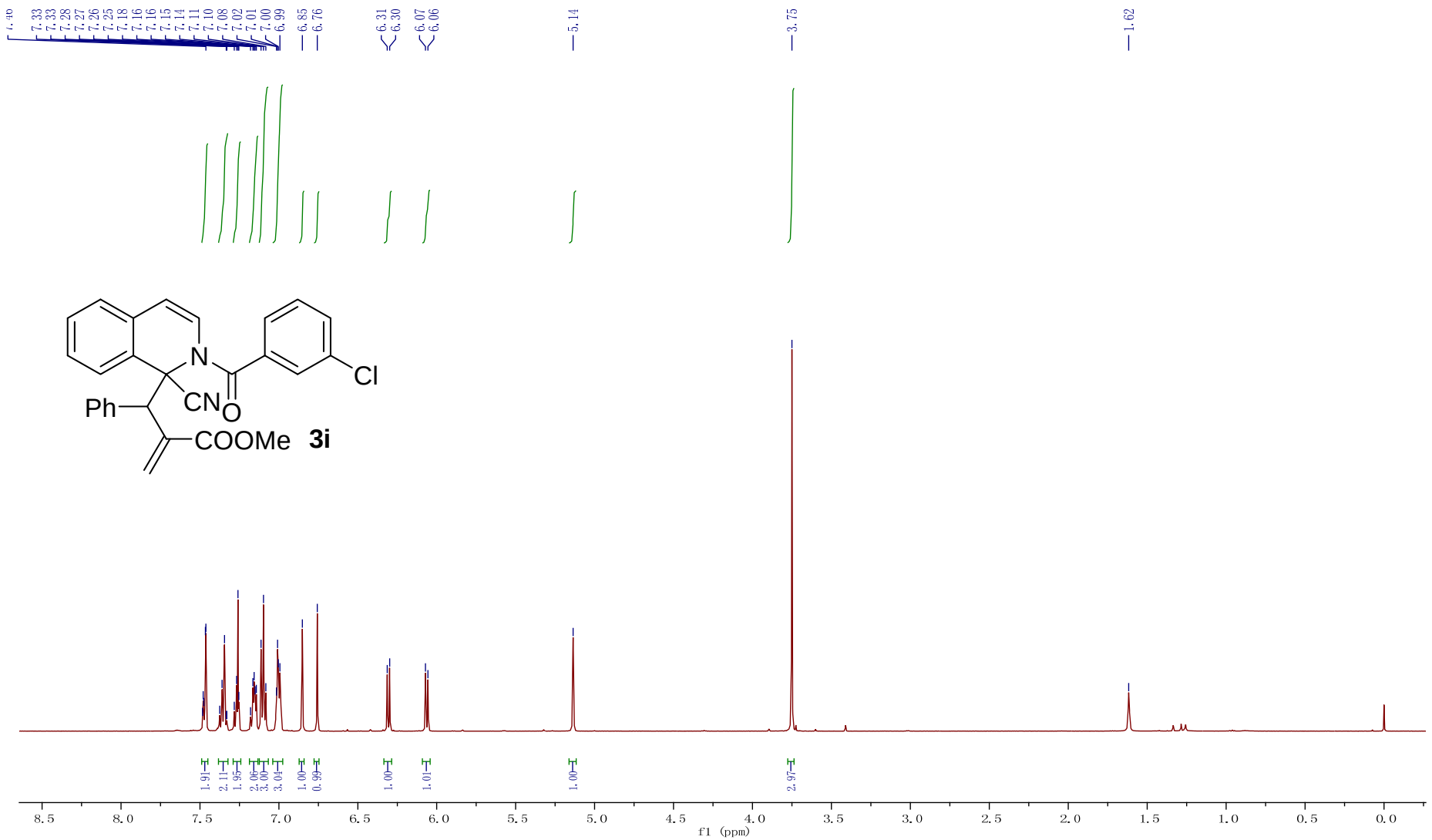

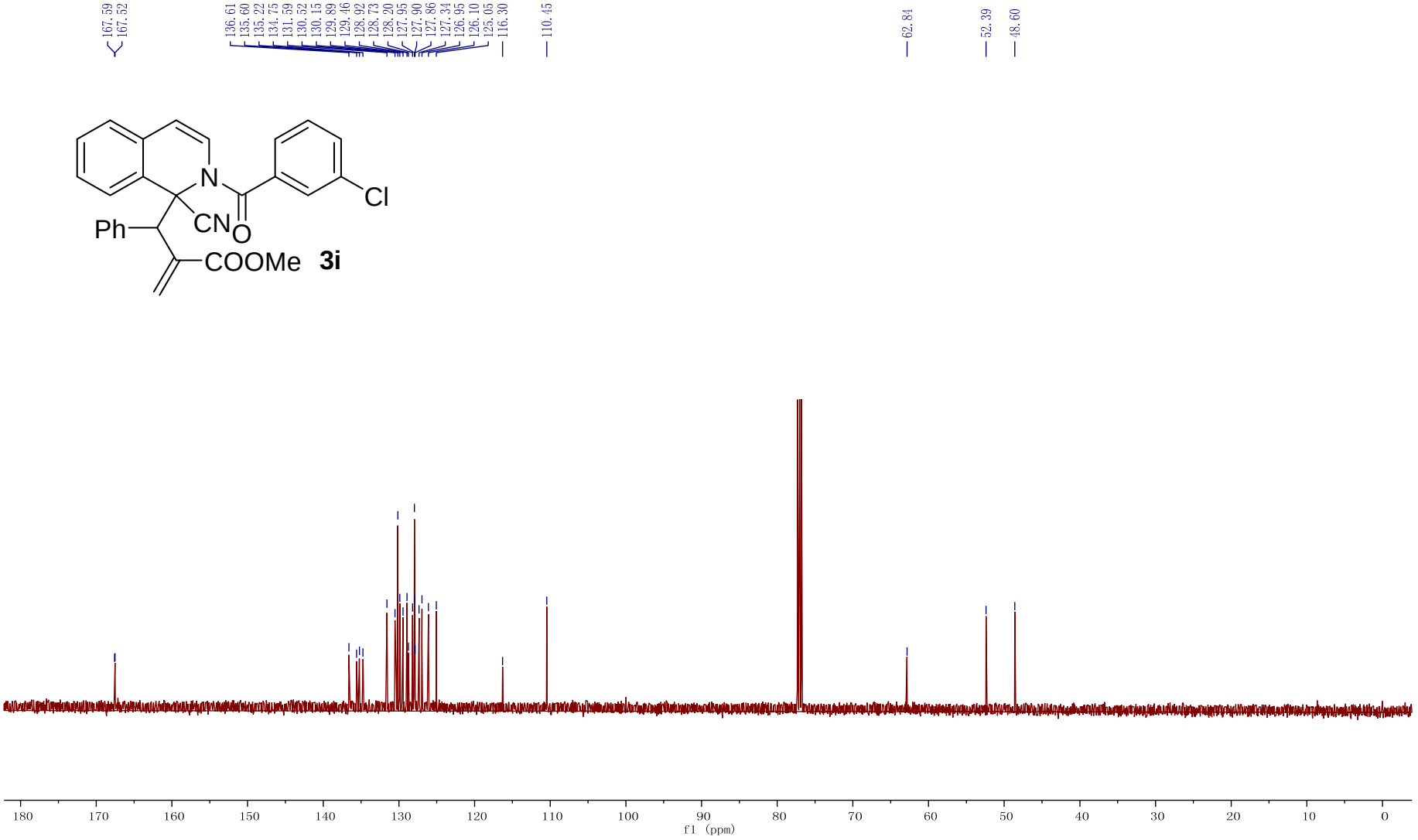

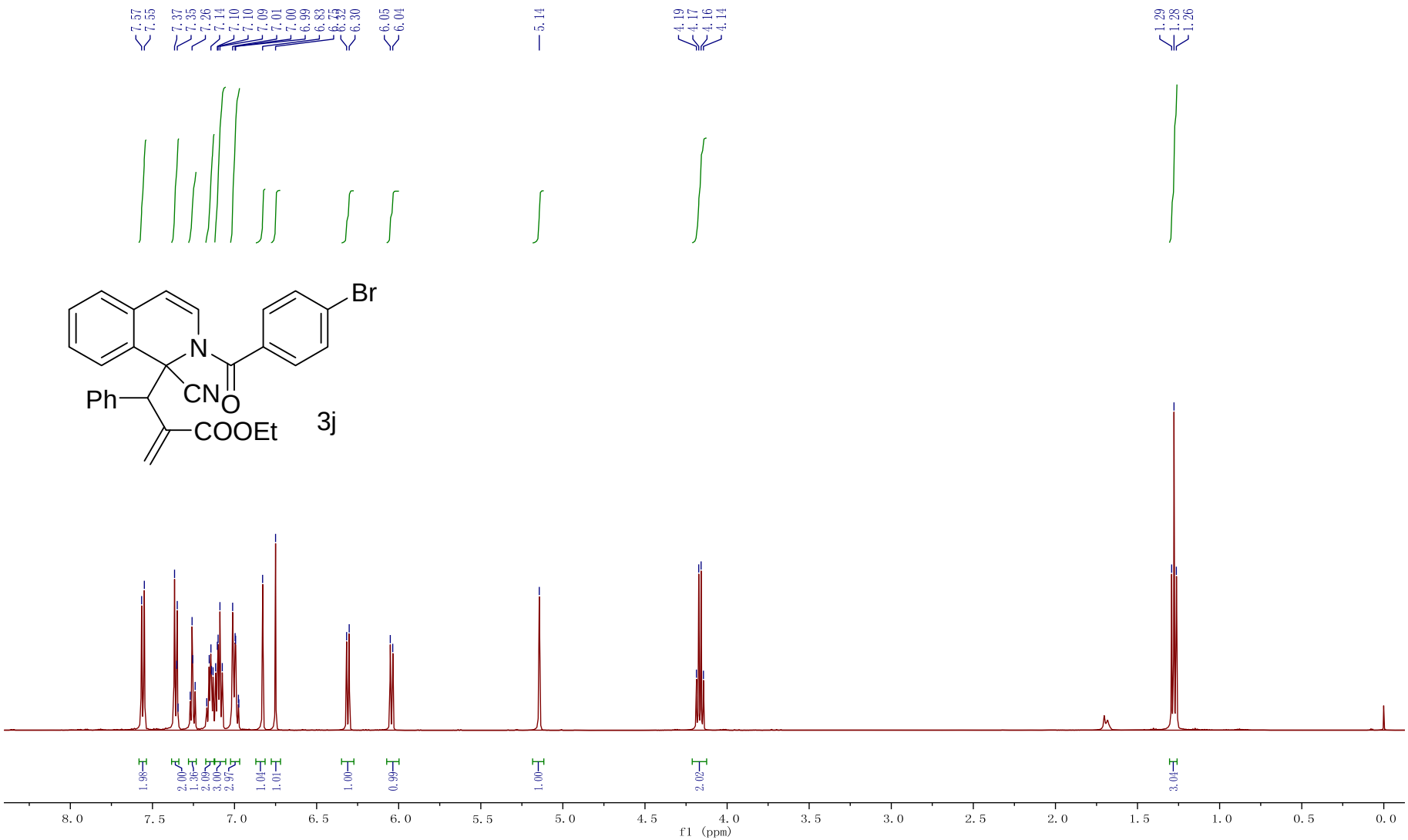

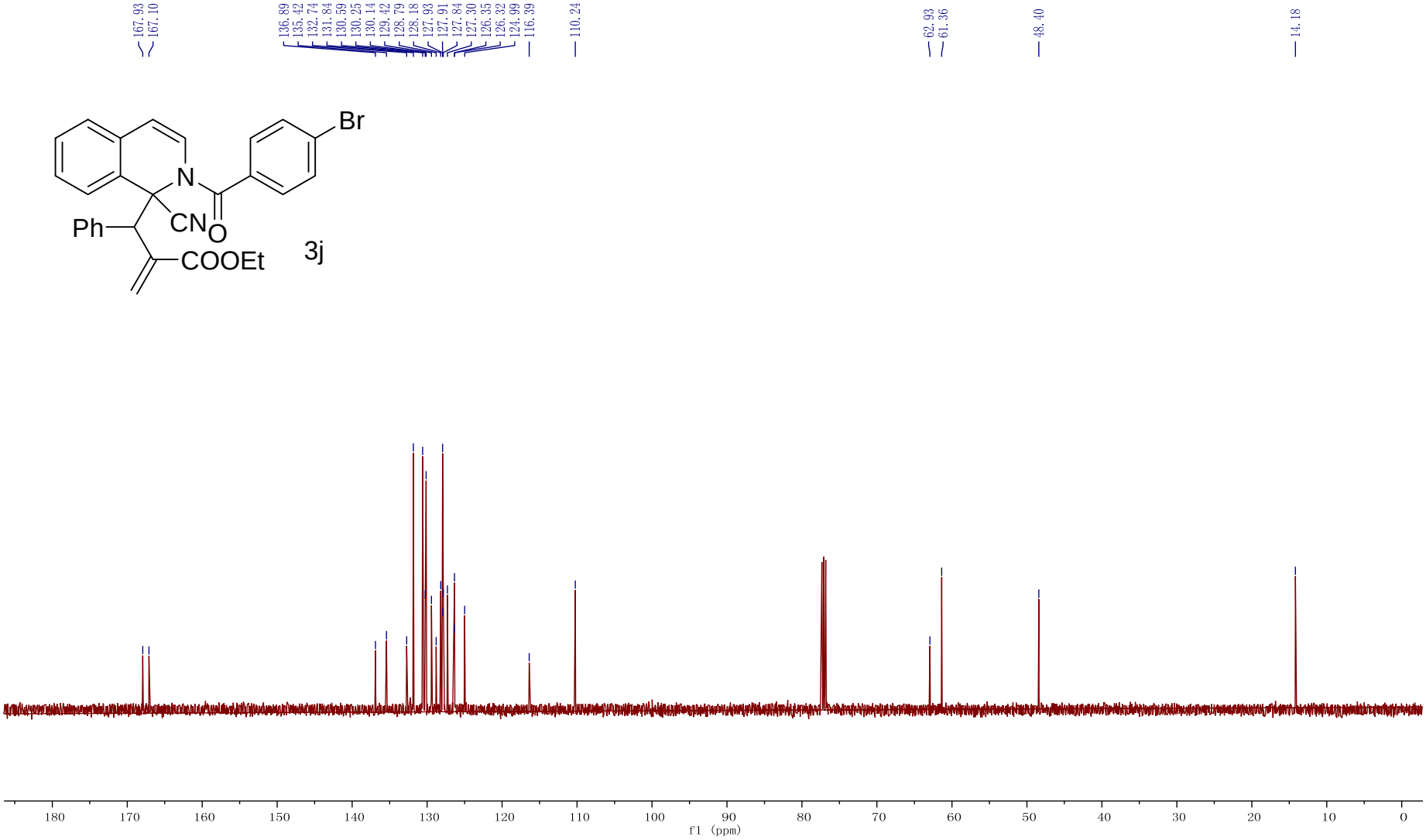

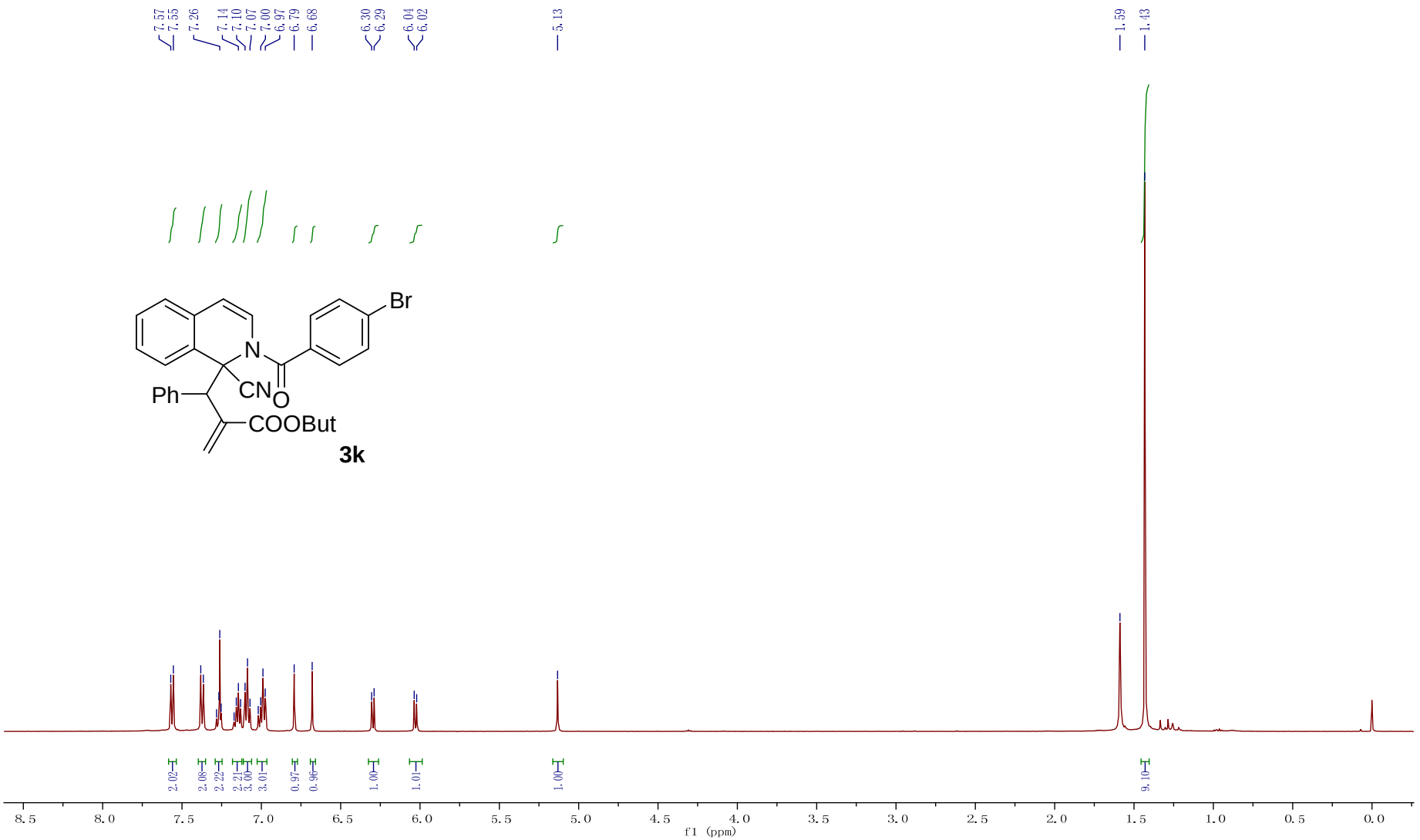

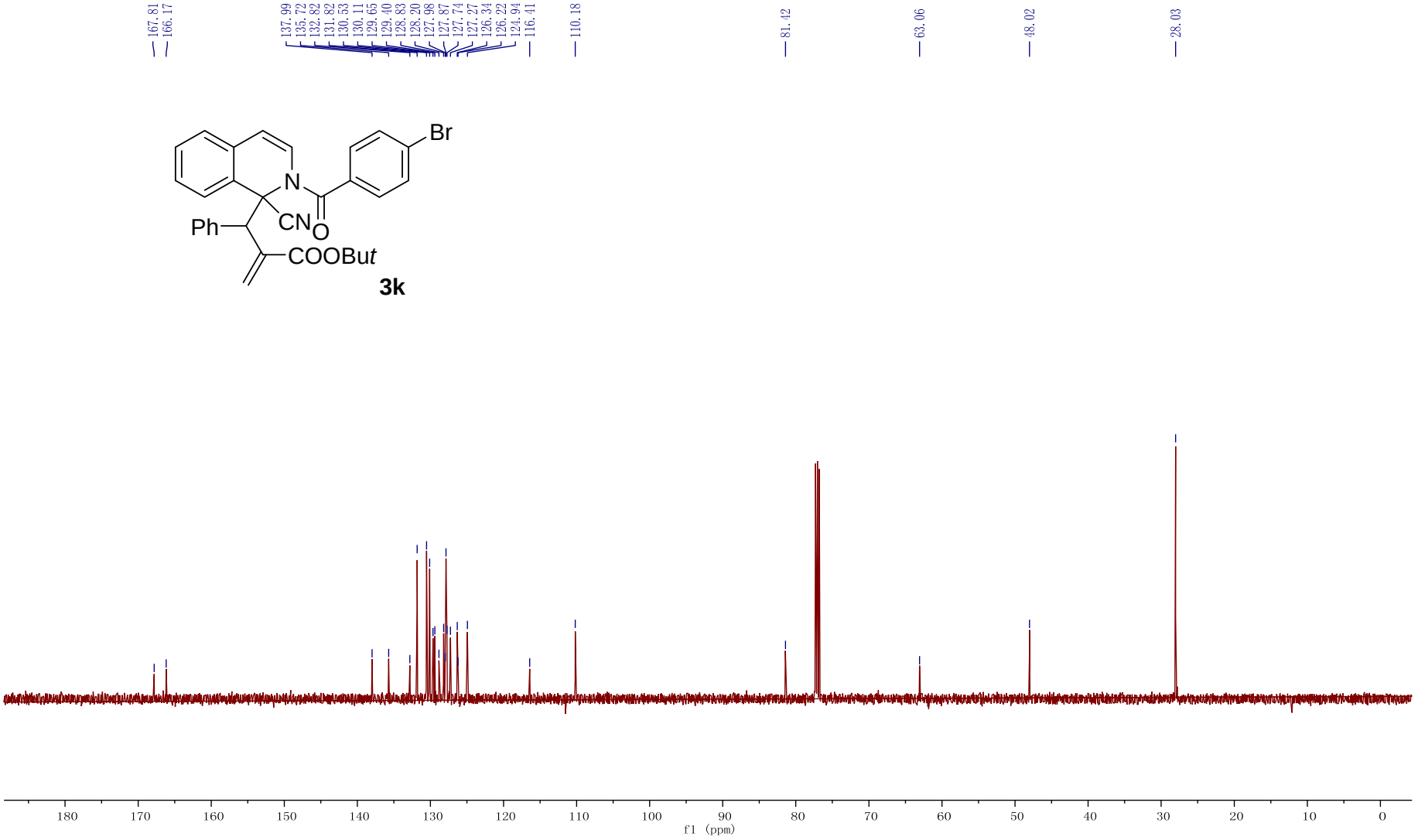

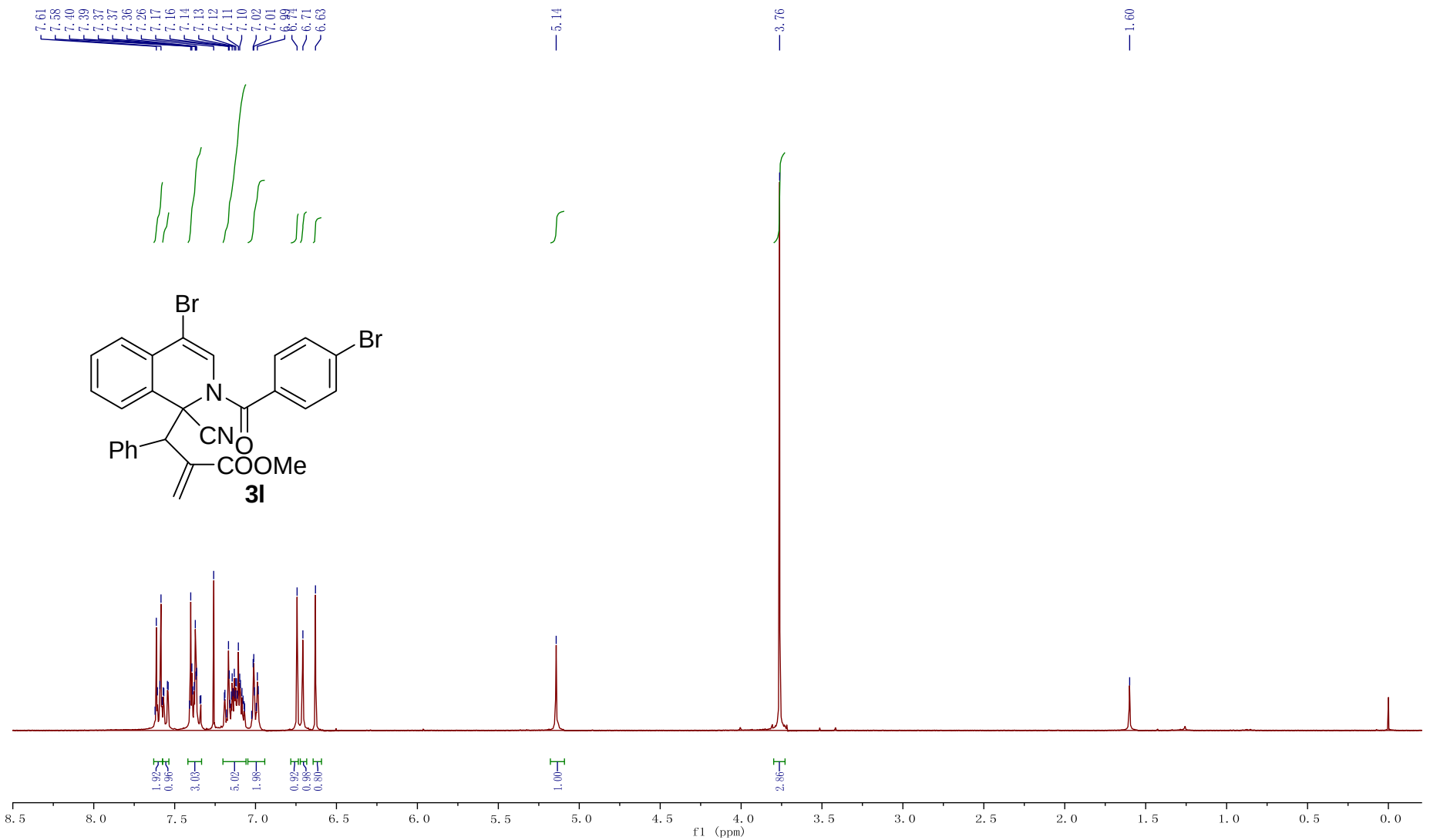

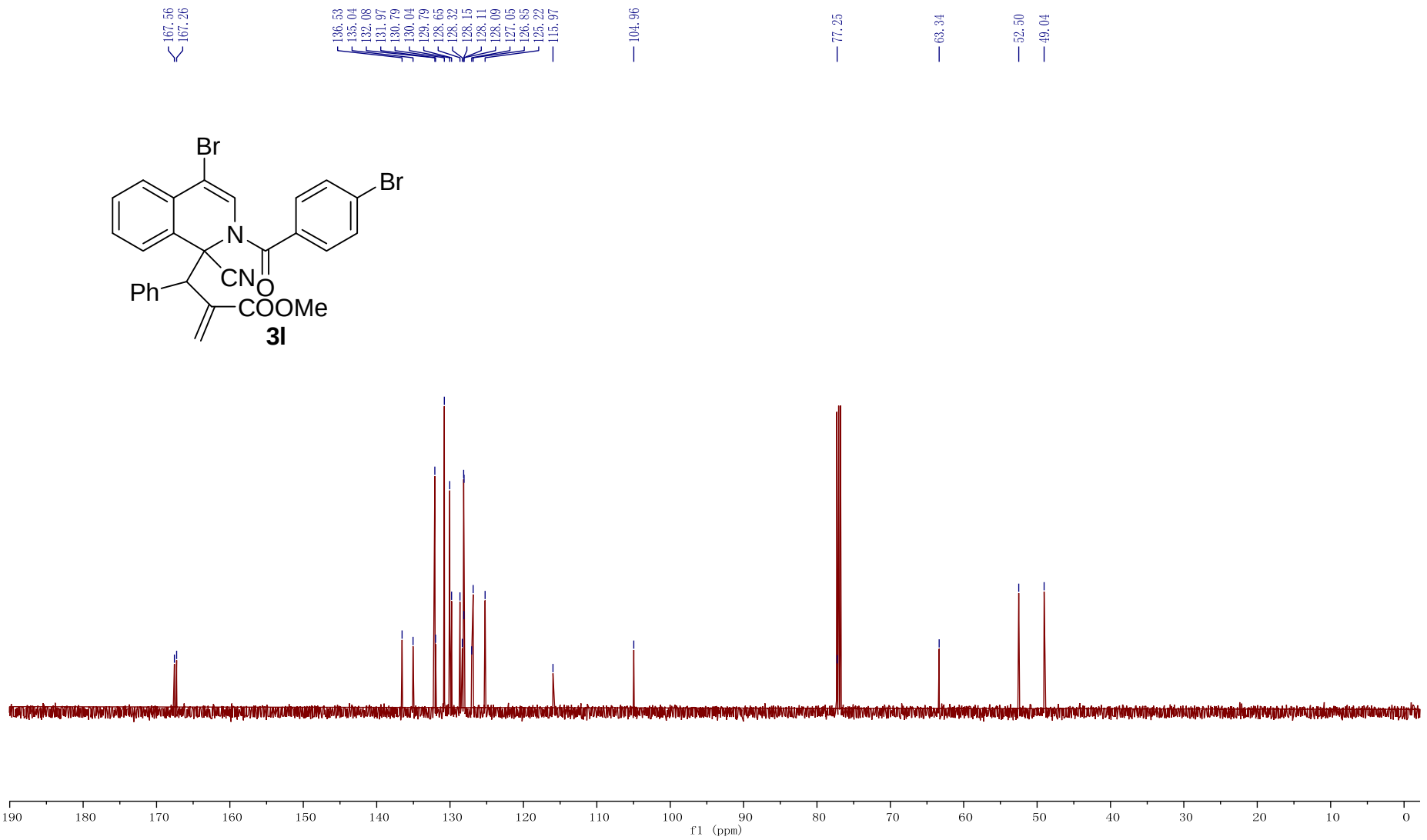

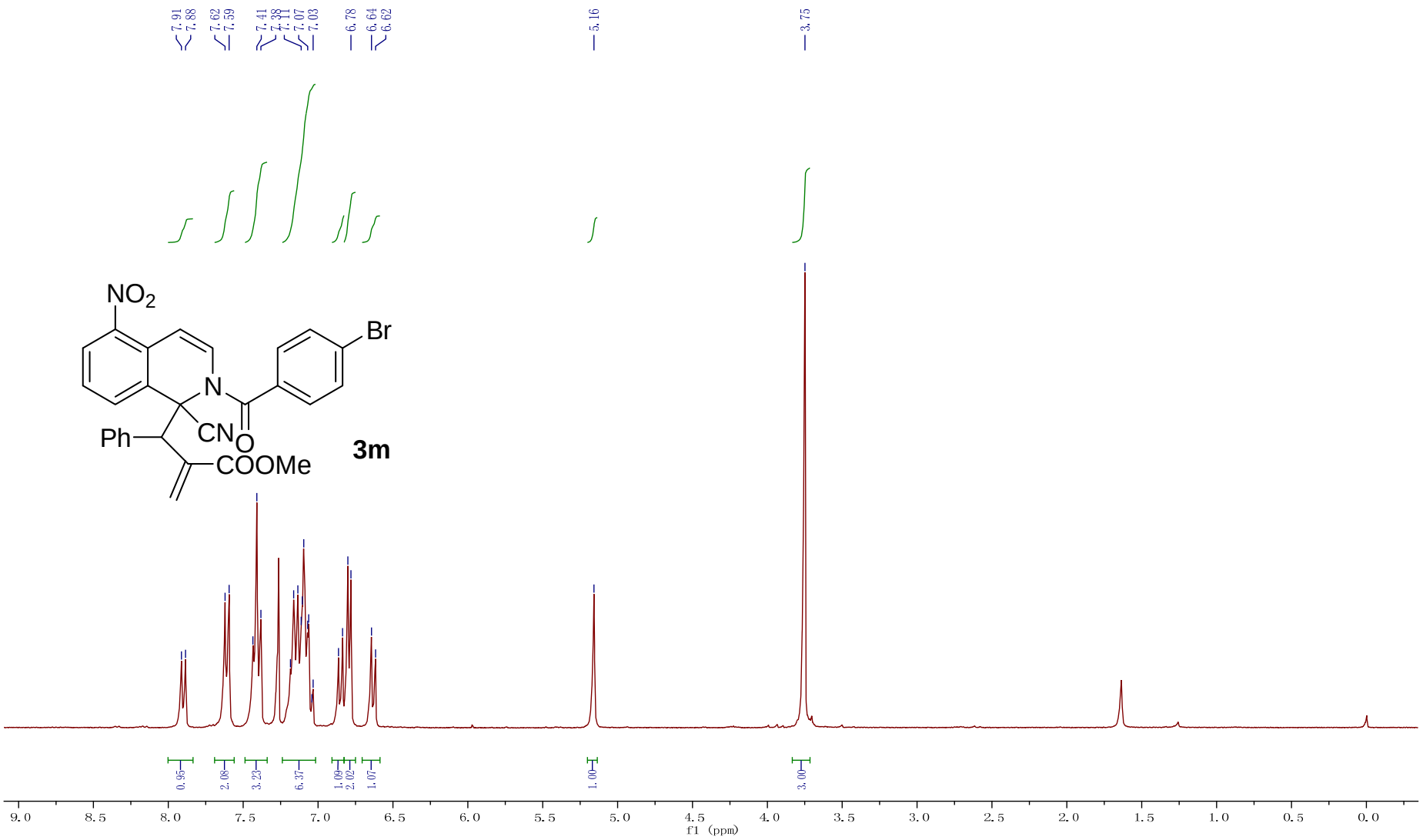

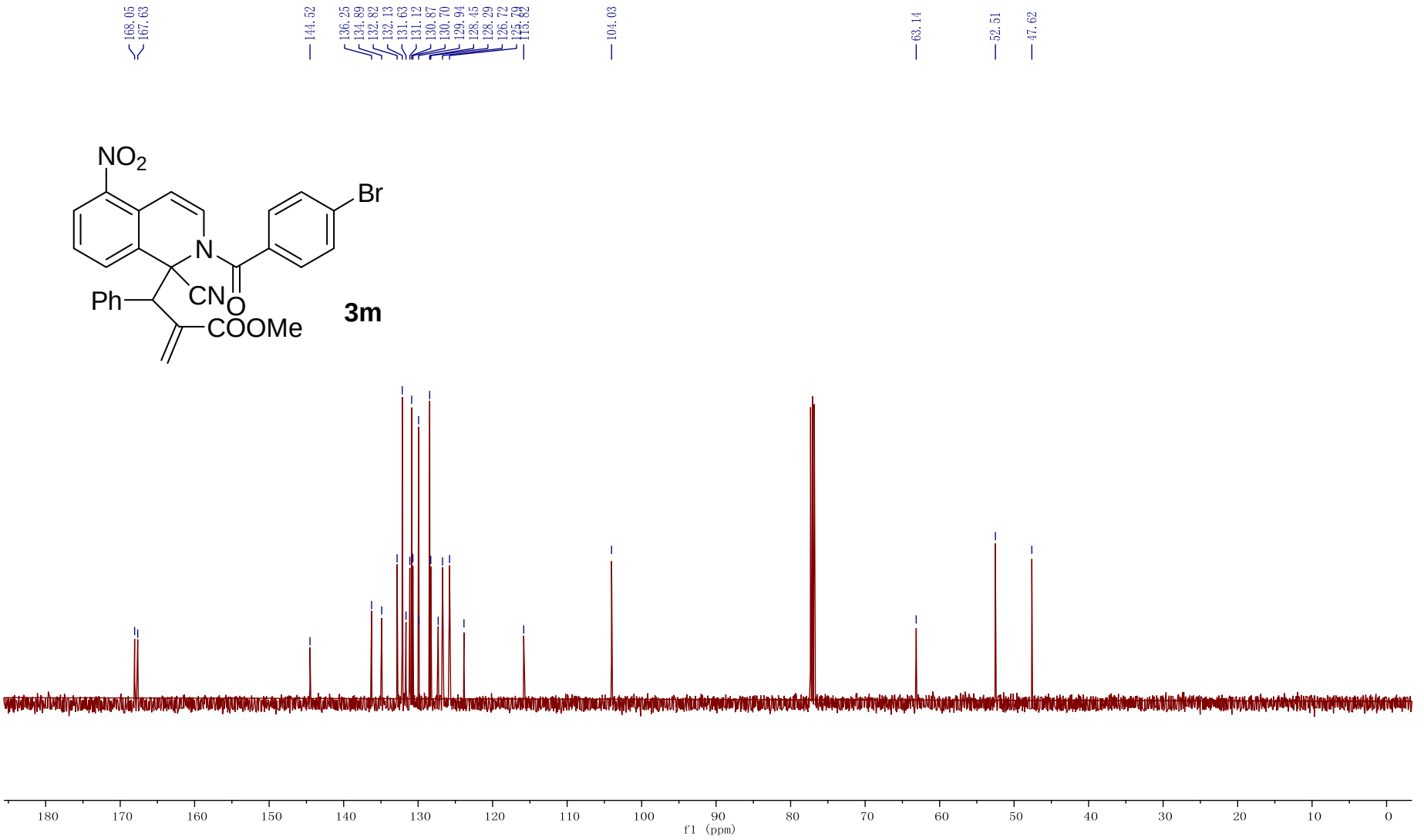

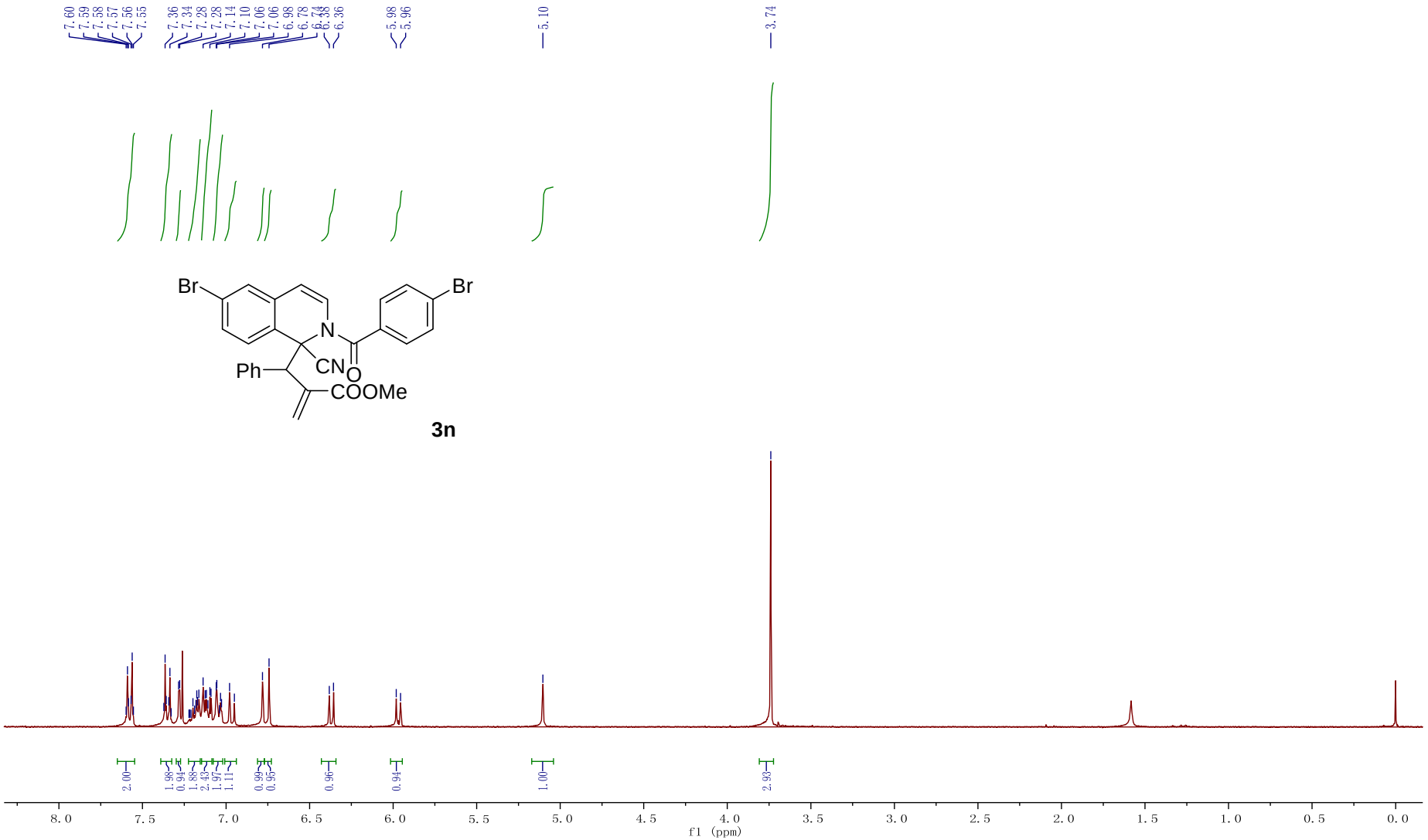

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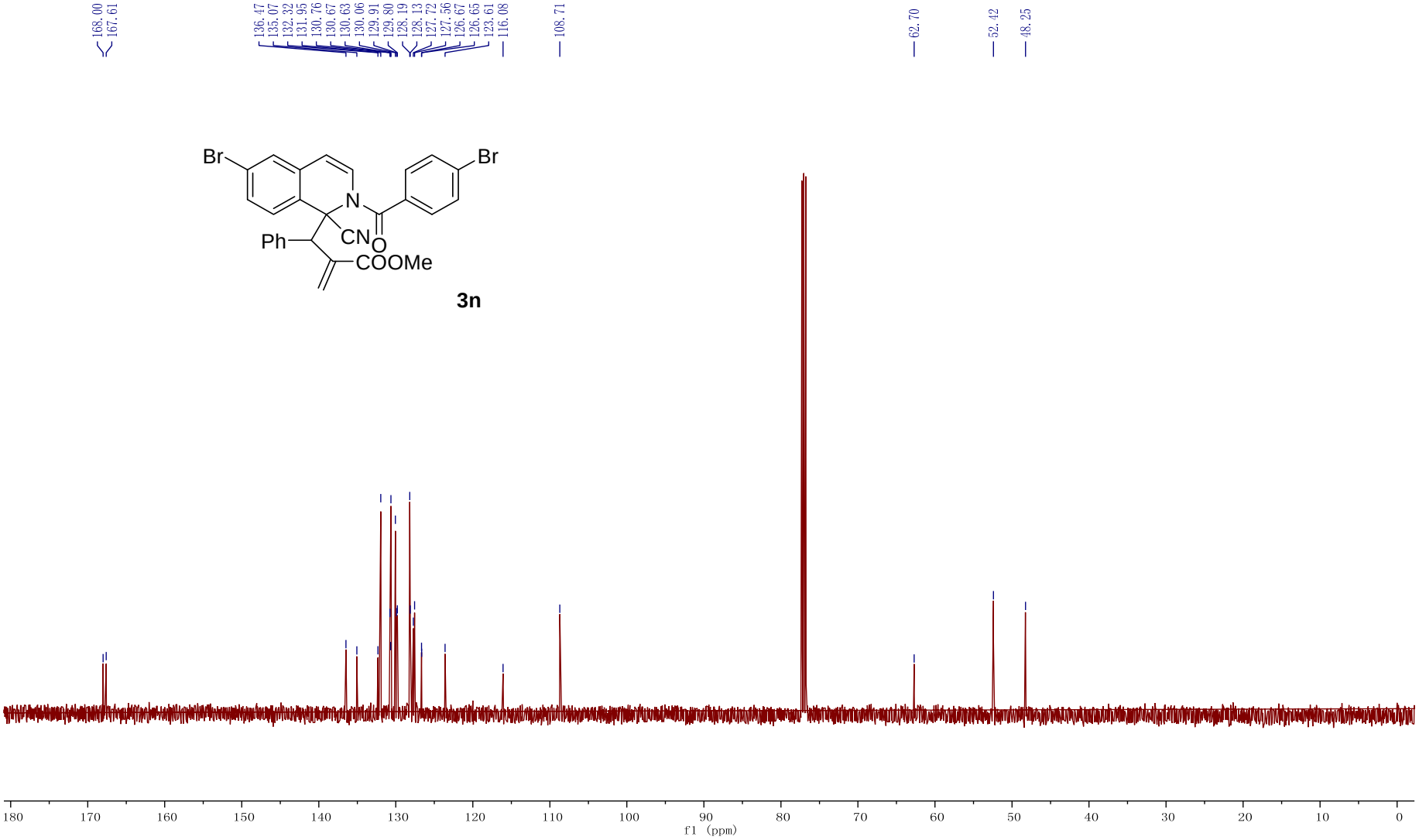

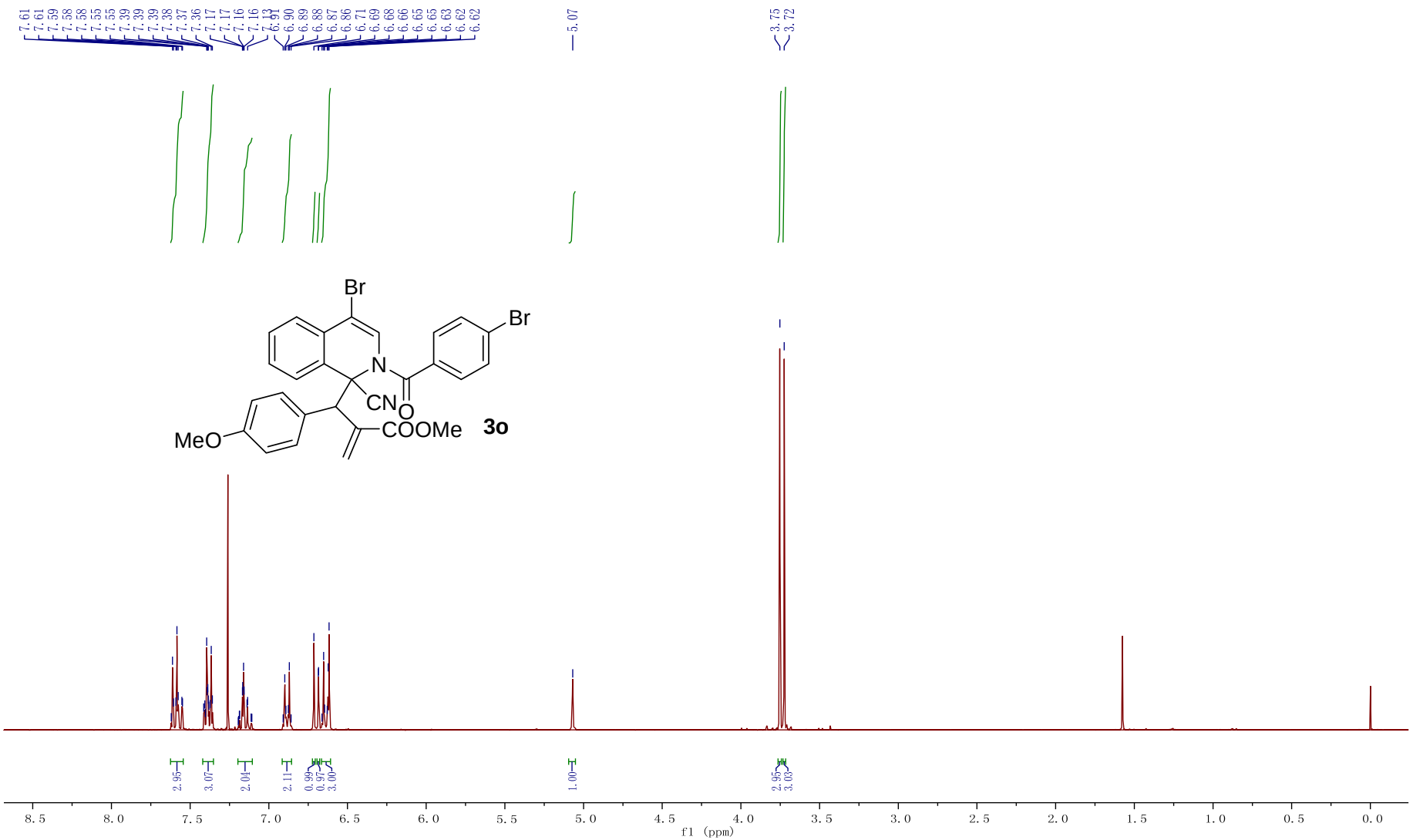

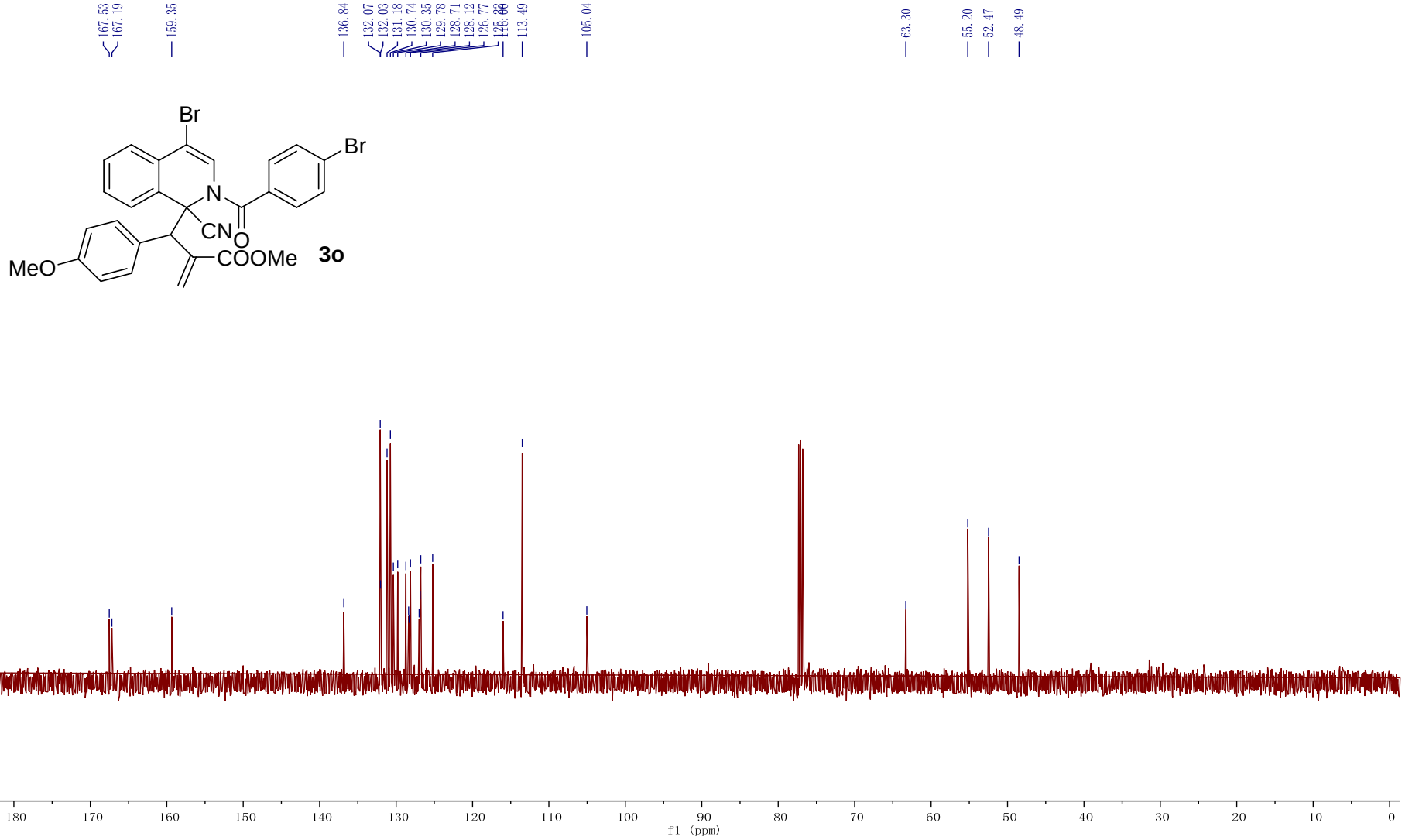

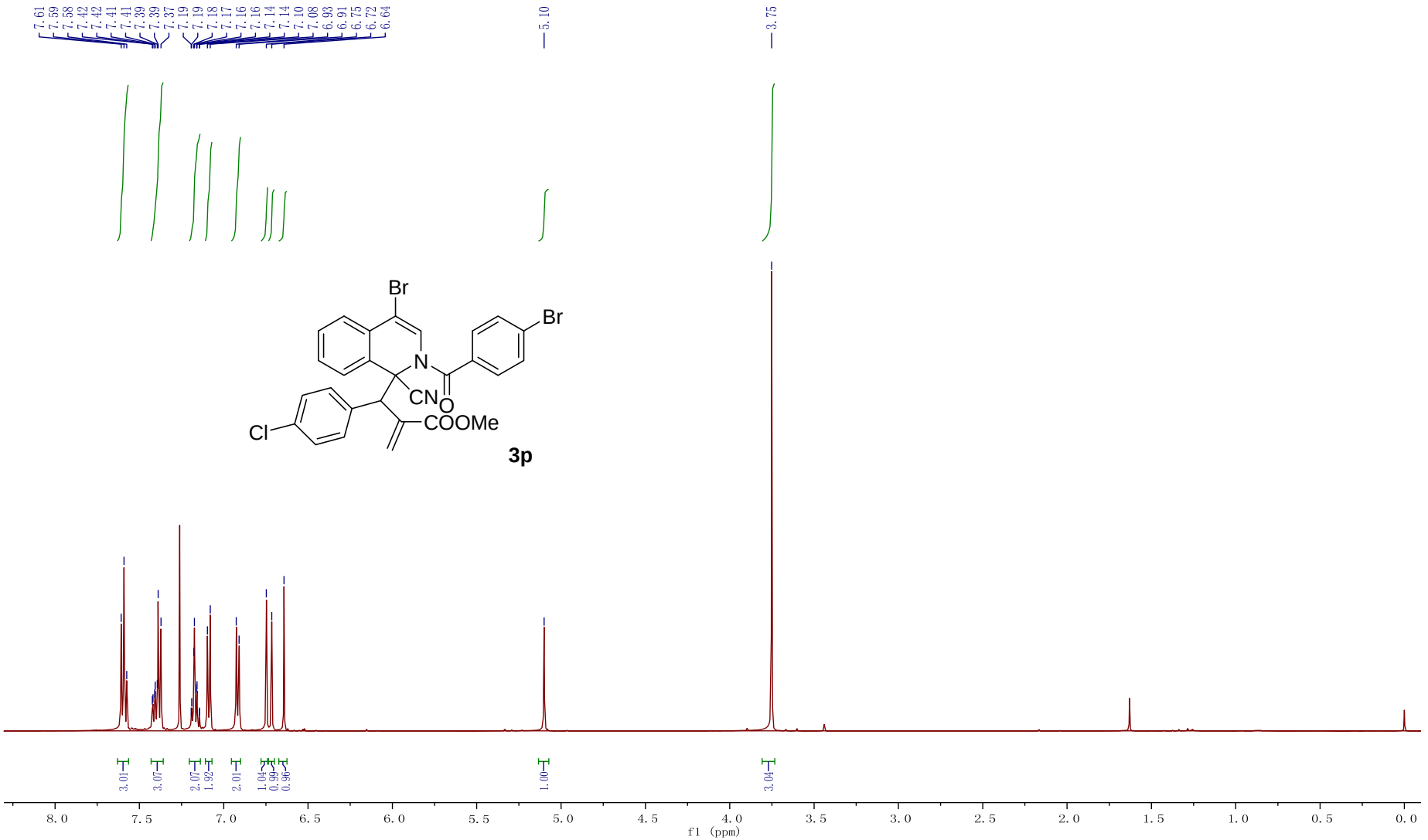

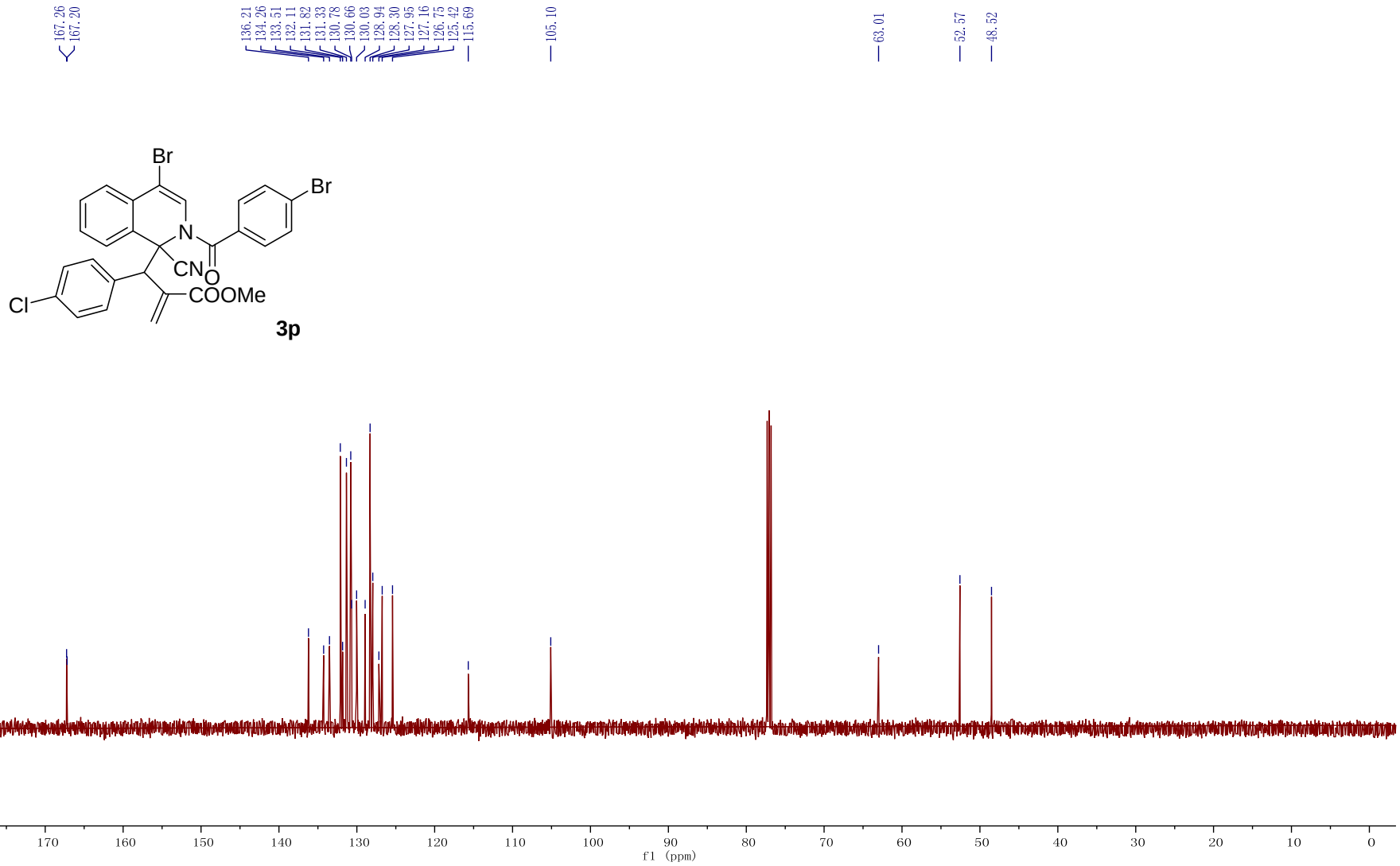

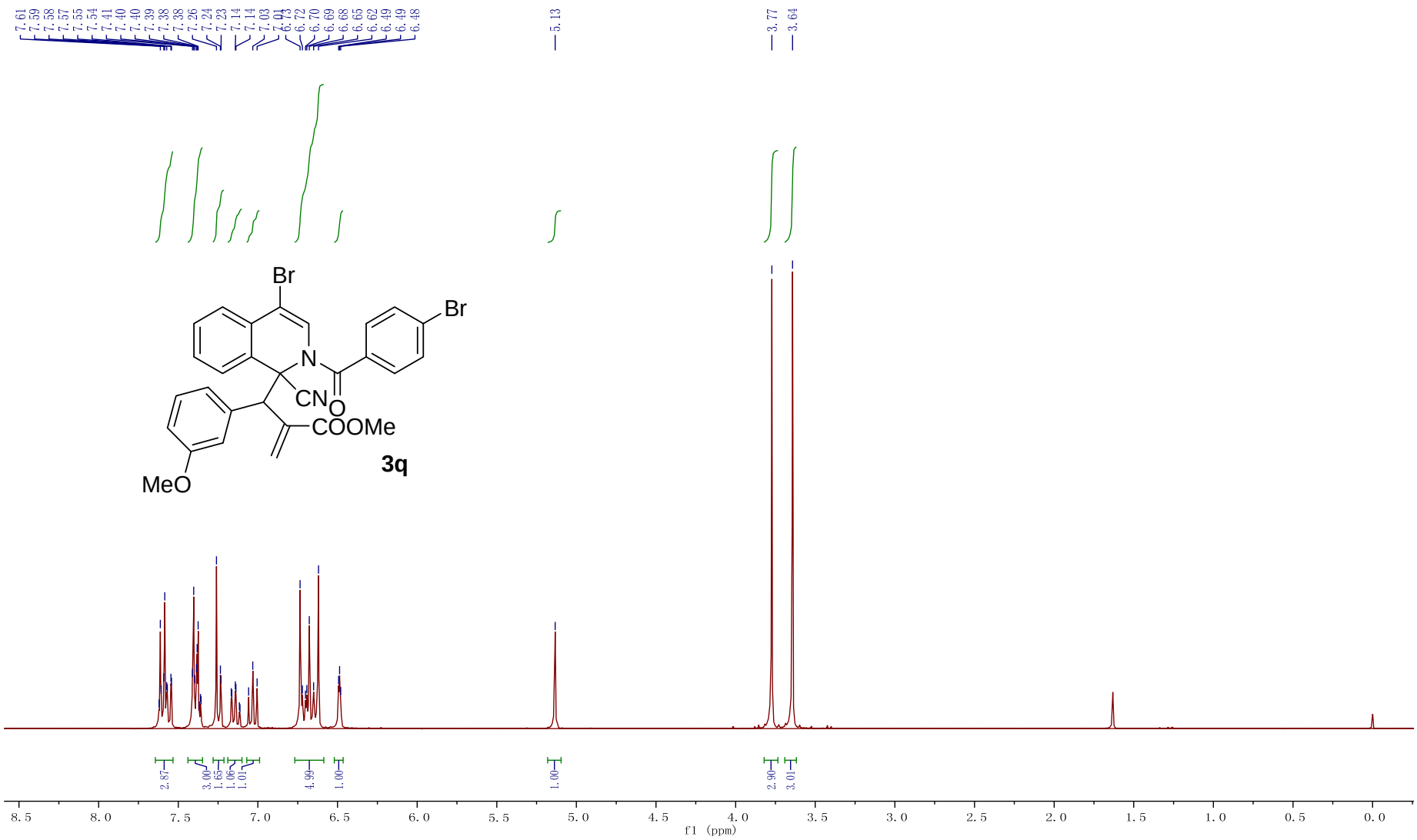

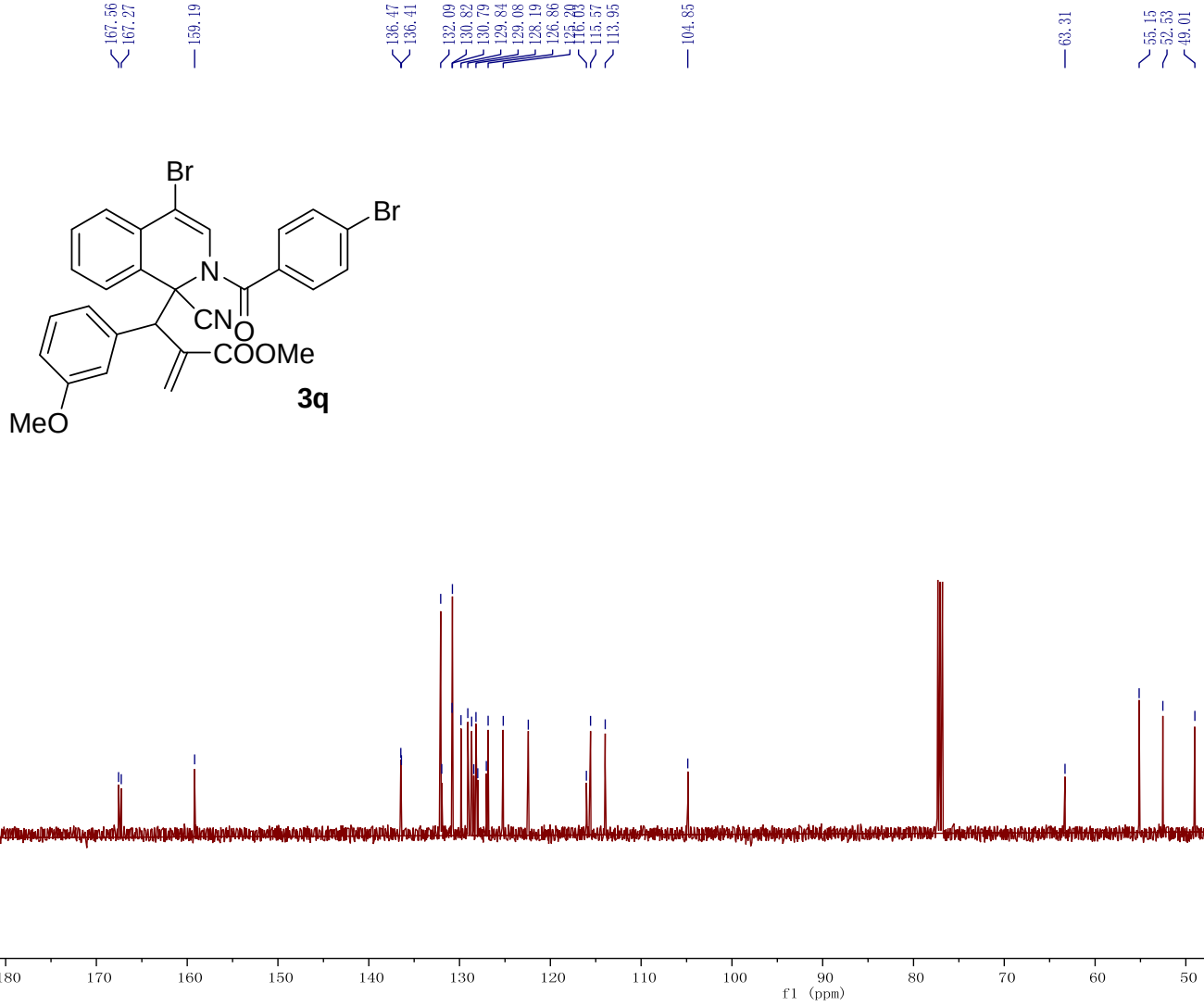

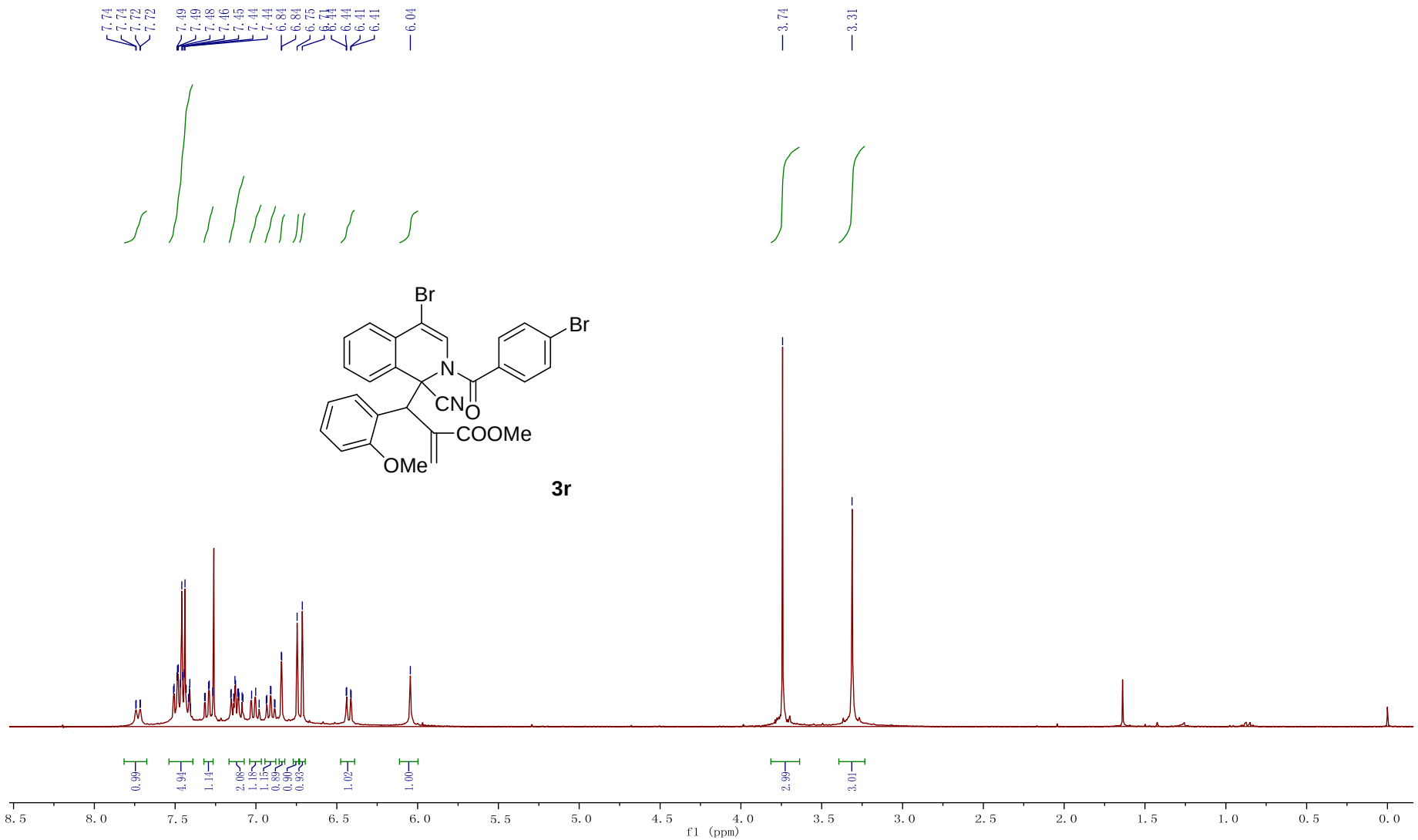

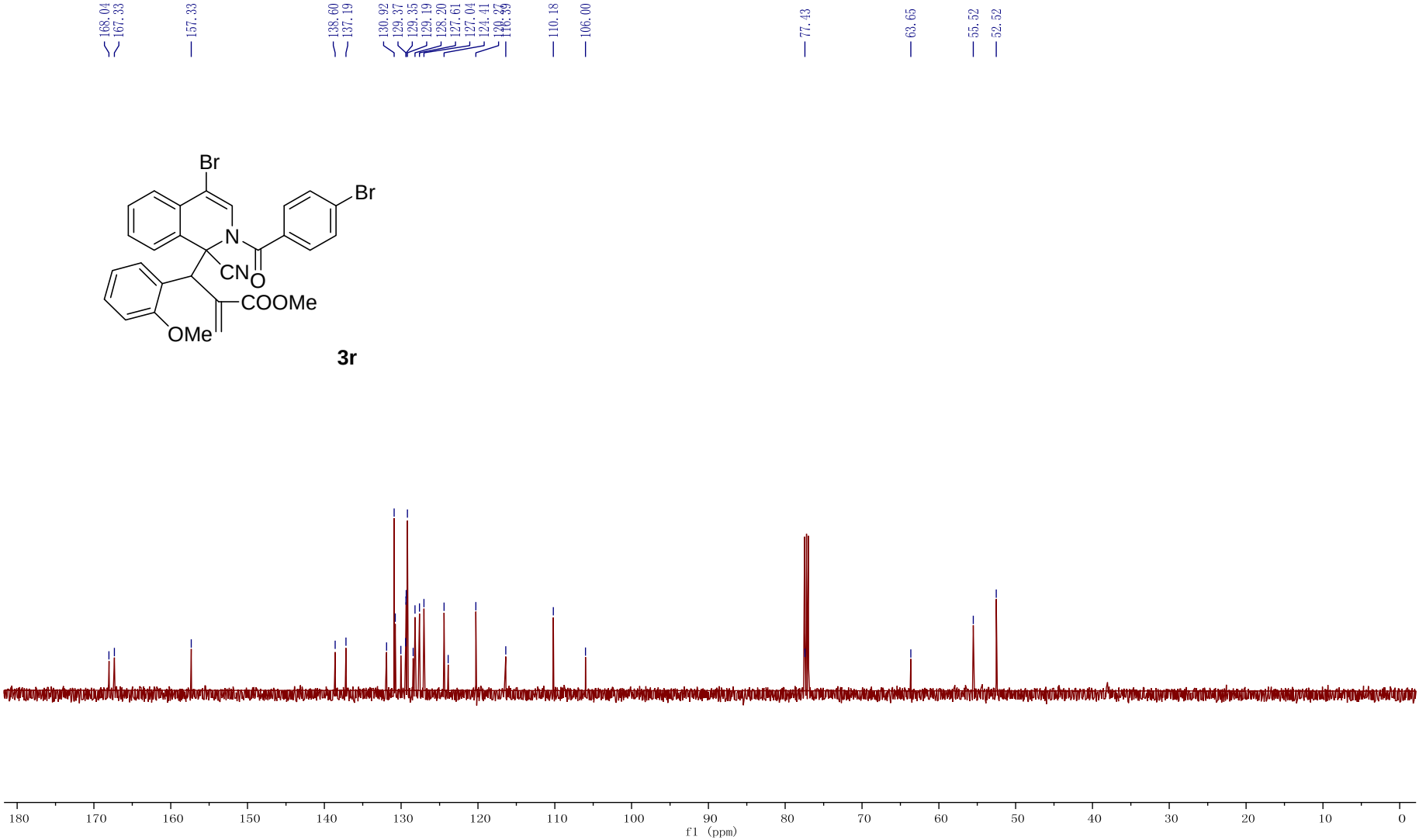

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