

Supporting Information

Iridium-Catalyzed Regio- and Enantioselective Allylic Esterification of Secondary Allylic Alcohols with Carboxylic Acids

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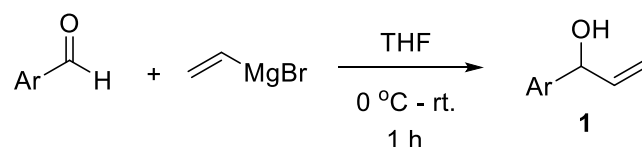
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General information

All reactions were carried out using an oven-dried tube with magnetic stirring under an argon atmosphere unless otherwise noted. Anhydrous solvents were dried prior to use. Reagents were purchased from Energy Chemical and used without further purification. For column chromatography, 200-300 mesh silica gel was used. Thin layer chromatography (TLC) was performed on Silicycle 250 μ m silica gel 60Å plates. Visualization was accomplished with UV light (254 nm), Iodine, or Potassium Permanganate.

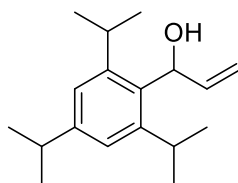
¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300 MHz (300 MHz for ¹H; 282 MHz for ¹⁹F; 75 MHz for ¹³C) or 400 MHz (400 MHz for ¹H; 376 MHz for ¹⁹F; 100 MHz for ¹³C) spectrometers at ambient temperature. The chemical shifts (δ) are given in parts per million relative to CDCl₃ (7.26 ppm for ¹H) or TMS (0 ppm for ¹H) and CDCl₃ (77.16 ppm for ¹³C). Coupling constants (*J*) are reported in Hz, and multiplicity is described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, or combinations thereof. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI).

General procedure for synthesis of allylic alcohols



To a round bottomed flask was charged with corresponding aldehydes (2 mmol, 1 equiv) in THF (10 mL), and cooled to 0 °C. Vinylmagnesium bromide (3 mmol, 1.5 equiv) was added slowly to the solution. The reaction then was stirred and warm to room temperature for 1 hour. After the raw aldehyde was disappeared, the solution was quenched with NH₄Cl (sat. aqueous). The aqueous layer was extracted three times with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated to give the corresponding allyl alcohols **1**. The characterization data of new compounds are shown as follows:

(±) **1-(2,4,6-triisopropylphenyl)prop-2-en-1-ol (1k)**



1k

Chemical Formula: C₁₈H₂₈O

Exact Mass: 260.2140

Molecular Weight: 260.4210

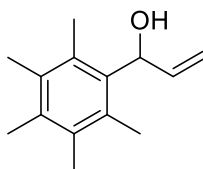
The title compound was prepared from 2,4,6-triisopropylphenyl aldehyde (521 mg, 2 mmol) and vinylmagnesium bromide (3 mmol, 1.5 equiv) via general procedure, silica gel column chromatography (EtOAc/PE = 1:10), as a white solid (458 mg, 88% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.02 (s, 2H), 6.26 (ddd, *J* = 17.3, 10.7, 3.8 Hz, 1H), 5.85 (s, 1H), 5.20-5.02 (m, 2H), 3.49-3.35 (m, 2H), 2.94-2.80 (m, 1H), 1.93 (brs, 1H, -OH), δ 1.25 (d, *J* = 6.9 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 1.21 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 148.4, 147.8, 141.1, 133.7, 122.2, 114.3, 69.9, 34.3, 29.6, 24.9, 24.3, 24.11, 24.07.

HRMS (EI) calculated for C₁₈H₂₈O [M]: 260.2140, found: 260.2136.

(±) **1-(2,3,4,5,6-pentamethylphenyl)prop-2-en-1-ol (II)**



11

Chemical Formula: C₁₄H₂₀O

Exact Mass: 204.1514

Molecular Weight: 204.3130

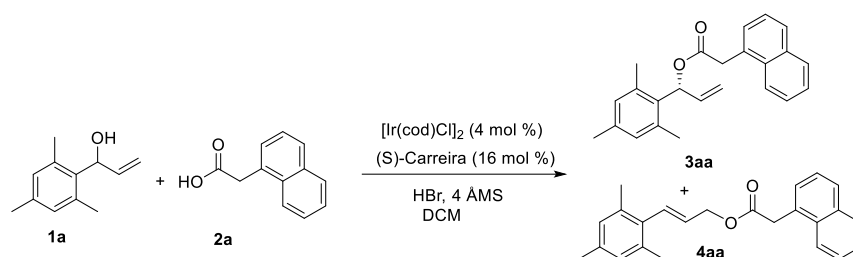
The **11** was prepared from 2,3,4,5,6-pentamethylphenyl aldehyde (521 mg, 2 mmol, 1eq.) and vinylmagnesium bromide (3 mmol, 1.5 eq.) via general procedure, silica gel column chromatography (EtOAc/PE = 1:10), white solid (368 mg, 85% yield).

¹H NMR (300 MHz, CDCl₃) δ 6.30-6.18 (m, 1H), 5.86 (s, 1H), 5.29-5.08 (m, 2H), 2.34 (s, 6H), 2.27 (s, 3H), 2.24 (s, 6H), 1.98 (s, 1H, -OH).

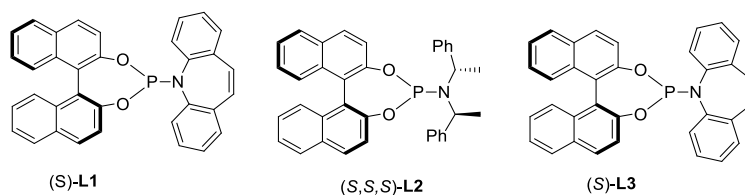
¹³C NMR (75 MHz, CDCl₃) δ 139.9, 136.0, 134.8, 133.5, 132.5, 114.4, 72.2, 17.4, 16.8.

HRMS (EI) calculated for C₁₄H₂₀O [M]: 204.1514, found: 204.1508.

Table S1. Optimization of the reaction conditions^a

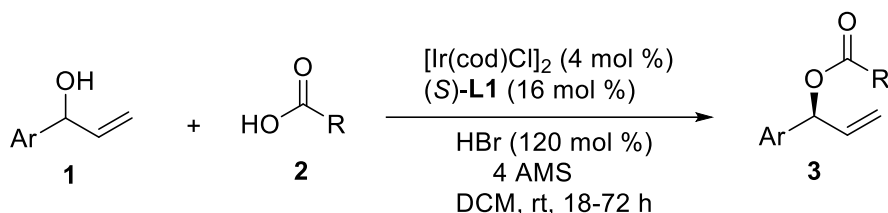


entry	solvent	Additive	Conversion ^b	3aa (%) ^c	4aa (%) ^c	ee (%) ^d
1	CH ₂ Cl ₂	Zn(OTf) ₂	-	0	23	-
2	CH ₂ Cl ₂	TFA	45	31	-	53
3	CH ₂ Cl ₂	(PhO) ₂ PO ₂ H	trace	-	-	-
4	CH ₂ Cl ₂	PhCO ₂ H	-	-	-	-
5	CH ₂ Cl ₂	TsOH.H ₂ O	N.D.	23	34	-
6	CH ₂ Cl ₂	HF (48-55 wt.% in H ₂ O)	N.D.	31	-	91
7	CH ₂ Cl ₂	HCl (36-38 wt.% in H ₂ O)	N.D.	39	-	96
8	CH ₂ Cl ₂	HBr (40 wt.% in H ₂ O)	64	58	8	95
9	CH ₂ Cl ₂	HI (40 wt.% in H ₂ O)	68	55	N.D.	90
10	CH ₂ Cl ₂	HF ₄ (48 wt.% in H ₂ O)	N.D.	43	N.D.	88
11	CH ₂ Cl ₂	H ₂ SO ₄ (concentrated)	-	-	-	-
12	CH ₂ Cl ₂	KHF ₂	74	60	N.D.	89
13	toluene	HBr (40 wt.% in H ₂ O)	N.D.	8	-	N.D.
14	CHCl ₃	HBr (40 wt.% in H ₂ O)	N.D.	33	-	90
15	THF	HBr (40 wt.% in H ₂ O)	N.D.	trace	-	-
16	DCE	HBr (40 wt.% in H ₂ O)	60	50	N.D.	96
17 ^e	CH ₂ Cl ₂	HBr (40 wt.% in H ₂ O)	71	61	-	96
18 ^{e,f}	CH ₂ Cl ₂	HBr (40 wt.% in H ₂ O)	78	68	-	96
19 ^{e,g}	CH ₂ Cl ₂	HBr (40 wt.% in H ₂ O)	86	76	-	97
20 ^{e,h}	CH ₂ Cl ₂	HBr (40 wt.% in H ₂ O)	90	78	N.D.	94
21 ⁱ	CH ₂ Cl ₂	HBr (40 wt.% in H ₂ O)	-	trace	-	N.D.
22 ^j	CH ₂ Cl ₂	HBr (40 wt.% in H ₂ O)	-	trace	-	N.D.



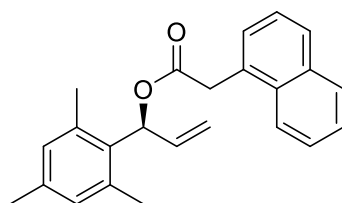
^a General conditions: **1a** (0.2 mmol), **2a** (0.1 mmol), [Ir(cod)Cl]₂ (4 mol %), **L1** (16 mol%), additive (100 mol%) and 4AMS (40 mg) in solvent (1 mL) at room temperature for 48 h. ^b Determined by the recovered yield of **2a**. ^cYield of isolated product. ^d Determined by chiral HPLC analysis. ^e 1.2 equivalent of HBr was used. ^f **1a** (0.25 mmol). ^g **1a** (0.3 mmol). ^h **1a** (0.4 mmol). ⁱ **L2** (16 mol%) instead of **L1**. ^j **L3** (16 mol %) instead of **L1**. N.D. = not determined.

General procedure for synthesis of **3aa-3na**



To a tube was charged with [Ir(cod) Cl]₂ (2.6 mg, 4 μmol, 4 mol %) and (*S*)-**L1** (8.0 mg, 16 μmol, 16 mol %). The tube backfilled with argon gas. The tube was added freshly distilled CH₂Cl₂ (1.0 mL), and stirred at rt. for 10 min. The allylic alcohols **1** (0.3 mmol, 3.0 equiv), carboxylic acids **2** (0.1 mmol, 1.0 equiv.), 4AMS (40 mg) and HBr (40wt.% in water; 24 mg, 0.12 mmol, 120 mol%) were added. The tube was sealed and stirred at rt. for 18 -72 h. Later, the solution was quenched with aq. NaHCO₃ (5 mL) and extracted with CH₂Cl₂ (3* 5mL). The organic layer was dried over Na₂SO₄ and concentrated by rotary evaporation. The crude product was purified by preparative TLC (eluent: EtOAc/PE) to afford the desired products (**3aa-3na**).

(*1S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-1-naphthaleneacetate (**3aa**)



Chemical Formula: C₂₄H₂₄O₂
Exact Mass: 344.1776
Molecular Weight: 344.4540

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3aa** (26.2 mg, 76% yield, 97% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.00-7.89 (m, 1H), 7.89-7.81 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.53-7.34 (m, 4H), 6.77 (s, 2H), 6.73-6.65 (m, 1H), 5.94 (ddd, *J* = 17.2, 10.6, 4.2 Hz, 1H), 5.06 (d, *J* = 10.6 Hz, 1H), 4.91 (d, *J* = 17.2 Hz, 1H), 4.10 (s, 2H), 2.23 (s, 3H), 2.22 (s, 6H).

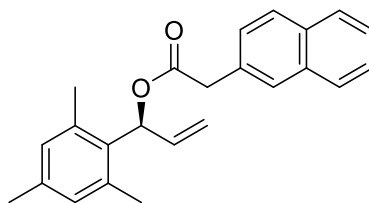
¹³C NMR (126 MHz, CDCl₃) δ 169.6, 136.5, 136.1, 134.1, 132.7, 131.1, 130.4, 129.5, 128.6, 127.6, 127.0, 125.3, 124.7, 124.4, 122.7, 114.9, 72.3, 38.3, 19.8, 19.2.

HRMS (ESI) *m/z* calculated for C₂₄H₂₄NaO₂ [M+Na]⁺: 367.1669, found: 367.1662.

Optical Rotation: [α]_D³¹ = -66.1 (*c* = 0.3, CHCl₃, 97% ee).

HPLC: Daicel Chiralpak OD-H column (hexane/*i*PrOH = 99:1, flow rate: 1.0 mL/min, λ = 254 nm, *t*_R(major) = 9.88 min, *t*_R (minor) = 9.14 min. ee = 97%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-2-naphthaleneacetate (3ab)



3ab

Chemical Formula: C₂₄H₂₄O₂

Exact Mass: 344.1776

Molecular Weight: 344.4540

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2b** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ab** (26.5 mg, 77% yield, 98% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.87-7.73 (m, 3H), 7.68 (s, 1H), 7.49-7.40 (m, 2H), 7.38 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.80 (s, 2H), 6.72 (dt, *J* = 4.1, 2.0 Hz, 1H), 6.02 (ddd, *J* = 17.2, 10.6, 4.3 Hz, 1H), 5.12 (ddd, *J* = 10.6, 1.8, 1.3 Hz, 1H), 5.06-4.88 (m, 1H), 3.84 (d, *J* = 15.3 Hz, 1H), 3.79 (d, *J* = 15.3 Hz, 1H), 2.31 (s, 6H), 2.24 (s, 3H).

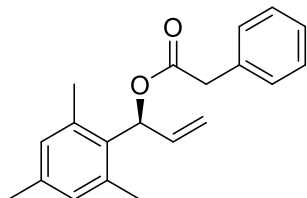
¹³C NMR (100 MHz, CDCl₃) δ 170.7, 137.7, 137.3, 135.3, 133.6, 132.6, 131.6, 131.5, 129.9, 128.3, 128.2, 127.8, 127.7, 127.6, 126.2, 125.9, 116.2, 73.6, 41.7, 21.0, 20.6.

HRMS (ESI) *m/z* calculated for C₂₄H₂₄NaO₂ [M+Na]⁺: 367.1669, found: 367.1662.

Optical Rotation: [α]_D³¹ = -16.9 (*c* = 0.1, CHCl₃, 98% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/iPrOH = 90:10), flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{major}) = 5.57$ min, $t_R(\text{minor}) = 4.89$ min. e.e. = 98%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-1-benzeneacetate (3ac)



3ac

Chemical Formula: C₂₀H₂₂O₂

Exact Mass: 294.1620

Molecular Weight: 294.3940

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2c** (15.1 mg, 0.1 mmol, 1 eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ac** (19.2 mg, 65% yield, 96% ee) as colorless oil.

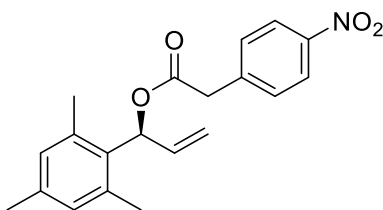
¹H NMR (500 MHz, CDCl₃) δ 7.37-7.19 (m, 5H), 6.80 (s, 2H), 6.69 (dt, $J = 4.1, 2.0$ Hz, 1H), 6.01 (ddd, $J = 17.2, 10.6, 4.3$ Hz, 1H), 5.15-5.12 (m, 1H), 5.06-4.92 (m, 1H), 3.68 (d, $J = 15.3$ Hz, 1H), 3.63 (d, $J = 15.3$ Hz, 1H), 2.31 (s, 6H), 2.24 (s, 3H). **¹³C NMR** (126 MHz, CDCl₃) δ 170.8, 137.7, 137.3, 135.3, 134.0, 131.6, 129.9, 129.5, 128.7, 127.2, 116.1, 73.4, 41.6, 21.0, 20.5.

HRMS (ESI) m/z calculated for C₂₀H₂₂NaO₂ [M+Na]⁺: 317.1512, found: 317.1509.

Optical Rotation: $[\alpha]_D^{31} = -28.1$ ($c = 0.2$, CHCl₃).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column (hexane/iPrOH = 99:1), flow rate: 1.0 mL/min, $\lambda = 234$ nm, $t_R(\text{major}) = 6.91$ min, $t_R(\text{minor}) = 4.87$ min. ee = 94%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-1-(4-nitro)-benzeneacetate (3ad)



3ad

Chemical Formula: C₂₀H₂₁NO₄

Exact Mass: 339.1471

Molecular Weight: 339.3910

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2d** (18.1 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:5) furnished **3ad** (27.1 mg, 80% yield, 94% ee) as yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 2H), 6.71 (dt, *J* = 4.2, 2.0 Hz, 1H), 6.03 (ddd, *J* = 17.1, 10.6, 4.4 Hz, 1H), 5.19-5.11 (m, 1H), 5.07-5.00 (m, 1H), 3.80 (d, *J* = 15.6 Hz, 1H), 3.74 (d, *J* = 15.6 Hz, 1H), 2.31 (s, 6H), 2.25 (s, 3H).

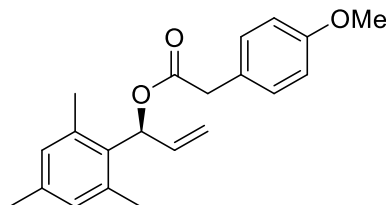
¹³C NMR (75 MHz, CDCl₃) δ 169.4, 147.3, 141.4, 138.0, 137.2, 135.0, 131.2, 130.5, 130.0, 123.9, 116.7, 74.1, 41.2, 21.0, 20.5.

HRMS (ESI) calculated for C₂₀H₂₁NNaO₄ [M+Na]⁺: 362.1363, found: 362.11366.

Optical Rotation: [α]_D³¹ = -23.0 (*c* = 0.2, CHCl₃).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IE column (hexane/*i*PrOH = 90:10), flow rate: 1.0 mL/min, λ = 225 nm, t_R(major) = 10.05 min, t_R(minor) = 9.40 min. ee = 94%.

(*1S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-1-(4-methoxy)-benzeneacetate (3ae**)**



3ae

Chemical Formula: C₂₁H₂₄O₃

Exact Mass: 324.1725

Molecular Weight: 324.4200

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2e** (18.1 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:5) furnished **3ae** (22.0 mg, 68% yield, 98% ee) as yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 7.19-7.05 (m, 2H), 6.88-6.78 (m, 4H), 6.68 (dt, *J* = 4.2, 2.0 Hz, 1H), 6.01 (ddd, *J* = 17.3, 10.6, 4.3 Hz, 1H), 5.13 (ddd, *J* = 10.6, 1.9, 1.3 Hz, 1H), 5.07-4.93 (m, 1H), 3.78 (s, 3H), 3.62 (d, *J* = 15.5 Hz, 1H), 3.56 (d, *J* = 15.5 Hz, 1H), 2.32 (s, 6H), 2.24 (s, 3H).

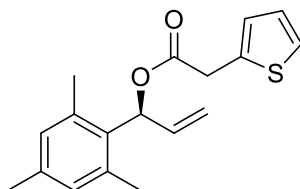
¹³C NMR (100 MHz, CDCl₃) δ 171.1, 158.8, 137.7, 137.2, 135.3, 131.6, 130.5, 129.9, 126.1, 116.1, 114.1, 73.4, 55.4, 40.6, 21.0, 20.5.

HRMS (ESI) calculated for C₂₁H₂₄NaO₃ [M+Na]⁺: 347.1618, found: 347.1619.

Optical Rotation: [α]_D³¹ = -33.1 (*c* = 0.1, CHCl₃, 98% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/iPrOH = 90:10), flow rate: 1.0 mL/min, $\lambda = 225$ nm, $t_R(\text{major}) = 5.75$ min, $t_R(\text{minor}) = 5.06$ min. ee = 98%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-2-thiopheneacetate (3af)



3af

Chemical Formula: $C_{18}H_{20}O_2S$

Exact Mass: 300.1184

Molecular Weight: 300.4160

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2f** (14.1 mg, 0.1 mmol, 1 eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3af** (22.2 mg, 74% yield, 97% ee) as yellow oil.

¹H NMR (400 MHz, $CDCl_3$) δ 7.19 (dd, $J = 5.1, 1.2$ Hz, 1H), 6.97-6.91 (m, 2H), 6.82 (s, 2H), 6.72 (dt, $J = 4.2, 2.0$ Hz, 1H), 6.04 (ddd, $J = 17.2, 10.6, 4.3$ Hz, 1H), 5.23-5.13 (m, 1H), 5.10-4.98 (m, 1H), 3.90 (d, $J = 16.6$ Hz, 1H), 3.83 (d, $J = 16.6$ Hz, 1H), 2.34 (s, 6H), 2.24 (s, 3H).

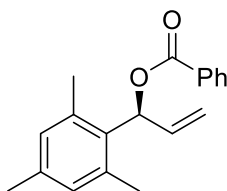
¹³C NMR (75 MHz, $CDCl_3$) δ 169.6, 137.8, 137.3, 135.2, 135.0, 131.4, 129.9, 127.1, 126.9, 125.2, 116.4, 73.8, 35.6, 21.0, 20.6.

HRMS (ESI) m/z calculated for $C_{18}H_{20}NaO_2S$ $[M+Na]^+$: 323.1076, found: 323.1078.

Optical Rotation: $[\alpha]_D^{31} = -55.0$ ($c = 0.1$, $CHCl_3$, 97% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column (hexane/iPrOH = 99:1), flow rate: 1.0 mL/min, $\lambda = 224$ nm, $t_R(\text{major}) = 6.54$ min, $t_R(\text{minor}) = 5.01$ min. ee = 97%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-benzoate (3ag)



3ag

Chemical Formula: $C_{19}H_{20}O_2$

Exact Mass: 280.1463

Molecular Weight: 280.3670

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2g** (12.0 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ag** (21.2 mg, 76% yield, 99% ee) as colorless oil. The ¹H NMR and ¹³C NMR were consistent with the reported literature.^[1]

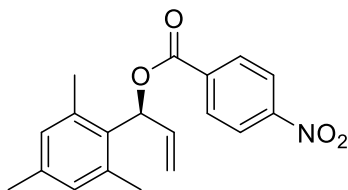
¹H NMR (400 MHz, CDCl₃) δ 8.12-7.86 (m, 2H), 7.59-7.48 (m, 1H), 7.42 (dd, *J* = 10.6, 4.7 Hz, 2H), 6.94 (dt, *J* = 4.2, 2.1 Hz, 1H), 6.84 (s, 2H), 6.19 (ddd, *J* = 17.2, 10.6, 4.2 Hz, 1H), 5.25-5.17 (m, 2H), 2.48 (s, 6H), 2.24 (s, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 165.7, 137.7, 137.2, 135.6, 133.1, 131.8, 130.4, 129.9, 129.8, 128.5, 116.3, 73.6, 21.0, 20.8.

Optical Rotation: [α]_D³¹ = -8.0 (*c* = 0.2, CHCl₃, 99% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak ID column (hexane/iPrOH = 90:10), flow rate: 1.0 mL/min, λ = 225 nm, *t*_R(major) = 3.99 min, *t*_R(minor) = 5.10 min. ee = 99%.

(*1S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-(4-nitro)-benzoate (3ah)



3ah

Chemical Formula: C₁₉H₁₉NO₄

Exact Mass: 325.1314

Molecular Weight: 325.3640

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2h** (16.6 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:4) furnished **3ah** (21.1 mg, 65% yield, 93% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.30-8.22 (m, 4H), 7.04-6.92 (m, 1H), 6.87 (s, 2H), 6.21 (ddd, *J* = 17.2, 10.6, 4.3 Hz, 1H), 5.29 (d, *J* = 10.6 Hz, 1H), 5.20 (d, *J* = 17.2 Hz, 1H), 2.48 (s, 6H), 2.26 (s, 3H).

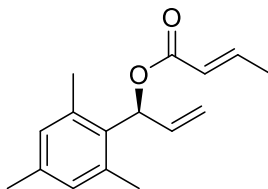
¹³C NMR (75 MHz, CDCl₃) δ 163.9, 150.6, 138.2, 137.2, 135.8, 135.0, 131.1, 130.9, 130.1, 123.7, 117.1, 74.8, 21.0, 20.7.

HRMS (ESI) calculated for C₁₉H₁₉NNaO₄ [M+Na]⁺: 348.1206, found: 348.1200.

Optical Rotation: [α]_D³¹ = -2.1 (*c* = 0.1, CHCl₃, 93% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak OJ column (hexane/iPrOH = 97:3), flow rate: 1.0 mL/min, $\lambda = 234$ nm, $t_R(\text{major}) = 6.13$ min, $t_R(\text{minor}) = 5.60$ min. 93% ee.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-(2*E*)-2-butenolate (3ai)



3ai

Chemical Formula: C₁₆H₂₀O₂

Exact Mass: 244.1463

Molecular Weight: 244.3340

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2i** (8.6 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ai** (19.3 mg, 79% yield, 99% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.10-6.91 (m, 1H), 6.82 (s, 2H), 6.74 (dt, $J = 4.1, 2.0$ Hz, 1H), 6.09 (ddd, $J = 17.2, 10.6, 4.3$ Hz, 1H), 5.88 (dd, $J = 15.5, 1.7$ Hz, 1H), 5.24-5.12 (m, 1H), 5.13-5.02 (m, 1H), 2.40 (s, 6H), 2.24 (s, 3H), 1.87 (dd, $J = 6.9, 1.6$ Hz, 3H).

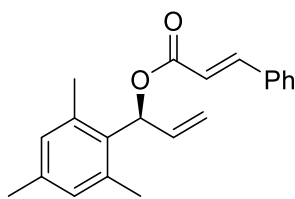
¹³C NMR (100 MHz, CDCl₃) δ 165.7, 145.0, 137.6, 137.2, 135.6, 131.9, 129.9, 122.8, 116.0, 72.74, 21.0, 20.7, 18.2.

HRMS (ESI) calculated for C₁₆H₂₀NaO₂ [M+Na]⁺: 267.1356, found: 267.1360.

Optical Rotation: $[\alpha]_D^{31} = -21.0$ ($c = 0.2$, CHCl₃, 99% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak OJ-H column (hexane/iPrOH = 99:1), flow rate: 0.6 mL/min, $\lambda = 225$ nm, $t_R(\text{major}) = 10.13$ min, $t_R(\text{minor}) = 8.83$ min. ee = 99%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-(2*E*)-3-phenyl-2-acrylate (3aj)



3aj

Chemical Formula: C₂₁H₂₂O₂

Exact Mass: 306.1620

Molecular Weight: 306.4050

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2j** (14.8 mg, 0.1 mmol, 1 eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3aj** (21.8 mg, 71% yield, 98% ee) as colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.69 (d, *J* = 16.0 Hz, 1H), 7.52-7.41 (m, 2H), 7.38-7.36 (m, 3H), 6.89-6.70 (m, 3H), 6.47 (dd, *J* = 16.0, 0.5 Hz, 1H), 6.20-6.09 (m, 1H), 5.29-5.01 (m, 2H), 2.44 (s, 6H), 2.25 (s, 3H).

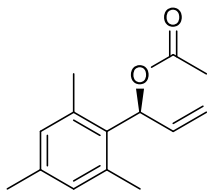
¹³C NMR (75 MHz, CDCl₃) δ 166.2, 145.2, 137.7, 137.2, 135.6, 134.5, 131.9, 130.4, 129.9, 129.0, 128.2, 118.2, 116.3, 73.2, 21.0, 20.7.

HRMS (ESI) *m/z* calculated for C₂₁H₂₂NaO₂ [M+Na]⁺: 329.1512, found: 329.1507.

Optical Rotation: [α]_D³¹ = -15.0 (*c* = 0.1, CHCl₃, 98% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IE column (hexane/*i*PrOH = 90:10, flow rate: 1.0 mL/min, λ = 234 nm, *t*_R(major) = 5.33 min, *t*_R(minor) = 5.79 min. ee = 98%.

(1S)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-acetate(3ak)



3ak

Chemical Formula: C₁₄H₁₈O₂

Exact Mass: 218.1307

Molecular Weight: 218.2960

The title compound was prepared from **1a** (106.0 mg, 0.6 mmol, 3 eq.) and **2k** (12.0 mg, 0.2 mmol, 1 eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:15) furnished **3ak** (33.1 mg, 76% yield, 99% ee) as colorless oil. The NMR data is consistent with the reported literature.^[1]

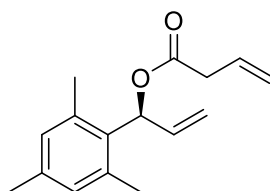
¹H NMR (300 MHz, CDCl₃) δ 6.83 (s, 2H), 6.69 (dt, *J* = 4.2, 2.0 Hz, 1H), 6.06 (ddd, *J* = 17.2, 10.6, 4.4 Hz, 1H), 5.17 (ddd, *J* = 10.6, 2.0, 1.2 Hz, 1H), 5.08 (ddd, *J* = 17.2, 1.9, 1.2 Hz, 1H), 2.38 (s, 6H), 2.25 (s, 3H), 2.08 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 170.2, 137.7, 137.2, 135.5, 131.8, 129.9, 116.2, 73.0, 21.2, 21.0, 20.6.

Optical Rotation: [α]_D³¹ = -16.0 (*c* = 0.4, CHCl₃, 99% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak ID column (hexane/*i*PrOH = 99:1), flow rate: 0.8 mL/min, λ = 224 nm, *t*_R(major) = 5.94 min, *t*_R (minor) = 7.73 min. ee = 99%.

(*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-4-butenolate (3aI)



3aI

Chemical Formula: C₁₆H₂₀O₂

Exact Mass: 244.1463

Molecular Weight: 244.3340

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2I** (8.6 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:15) furnished **3aI** (17.6 mg, 72% yield, 96% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.83 (s, 2H), 6.71 (dt, *J* = 4.2, 2.0 Hz, 1H), 6.06 (ddd, *J* = 17.3, 10.6, 4.4 Hz, 1H), 5.98-5.84 (m, 1H), 5.21-4.94 (m, 4H), 3.24-3.00 (m, 2H), 2.38 (s, 6H), 2.25 (s, 3H).

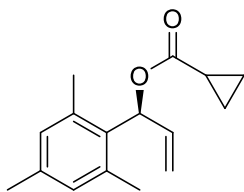
¹³C NMR (100 MHz, CDCl₃) δ 170.7, 137.8, 137.2, 135.4, 131.7, 130.3, 129.9, 118.8, 116.2, 73.26, 39.4, 21.0, 20.6.

HRMS (ESI) calculated for C₁₆H₂₄NO₂ [M+NH₄]⁺: 262.1802, found: 262.1795.

Optical Rotation: [α]_D³¹ = -27.1 (*c* = 0.1, CHCl₃, 96% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak ID column (hexane/*i*PrOH = 99:1), flow rate: 1.0 mL/min, λ = 224 nm, *t*_R(major) = 4.24 min, *t*_R (minor) = 4.99 min. ee = 96%.

(*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-2-cyclopropanecarboxylate (3aM)



3am

Chemical Formula: C₁₆H₂₀O₂

Exact Mass: 244.1463

Molecular Weight: 244.3340

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2m** (8.6 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3am** (19.7 mg, 81% yield, >99% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 6.83 (s, 2H), 6.69 (dt, *J* = 4.1, 2.0 Hz, 1H), 6.07 (ddd, *J* = 17.2, 10.6, 4.3 Hz, 1H), 5.24-5.14 (m, 1H), 5.14-4.95 (m, 1H), 2.39 (s, 6H), 2.25 (s, 3H), 1.65 (ddd, *J* = 16.0, 10.3, 6.2 Hz, 1H), 1.09-0.92 (m, 2H), 0.89-0.78 (m, 2H).

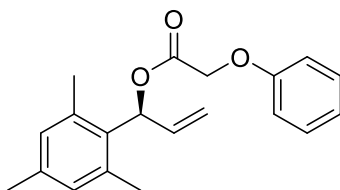
¹³C NMR (100 MHz, CDCl₃) δ 174.1, 137.6, 137.2, 135.6, 131.9, 129.9, 116.0, 73.0, 21.0, 20.6, 13.1, 8.6, 8.6.

HRMS (ESI) calculated for C₁₆H₂₀NaO₂ [M+Na]⁺: 267.1356, found: 267.1360.

Optical Rotation: [α]_D³¹ = -18.0 (*c* = 0.15, CHCl₃, >99% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak ID column (hexane/*i*PrOH = 99:1), flow rate: 1.0 mL/min, λ = 224 nm, *t*_R(major) = 4.09 min, *t*_R (minor) = 5.50 min. ee > 99%.

(1S)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-2-phenoxyacetate (3an)



3an

Chemical Formula: C₂₀H₂₂O₃

Exact Mass: 310.1569

Molecular Weight: 310.3930

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2n** (15.2 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:8) furnished **3an** (23.7 mg, 76% yield, 95% ee) as colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 7.35-7.17 (m, 1H), 7.04-6.74 (m, 3H), 6.15-5.88 (m, 1H), 5.28-5.03

(m, 1H), 4.73-4.47 (m, 1H), 2.35 (s, 3H), 2.25 (s, 1H).

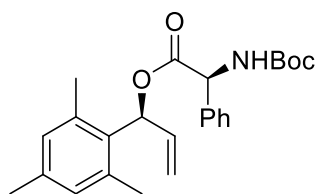
^{13}C NMR (75 MHz, CDCl_3) δ 168.3, 157.9, 138.0, 137.3, 134.9, 131.2, 129.9, 129.7, 121.8, 116.8, 114.7, 74.1, 65.4, 21.0, 20.6.

HRMS (ESI) calculated for $\text{C}_{20}\text{H}_{22}\text{NaO}_3$ $[\text{M}+\text{Na}]^+$: 333.1461, found: 333.1458.

Optical Rotation: $[\alpha]_{\text{D}}^{31} = -39.4$ ($c = 0.2$, CHCl_3 , 95% ee).

HPLC: Daicel Chiralpak IC column (hexane/*i*PrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 225$ nm, t_{R} (major) = 5.37 min, t_{R} (minor) = 4.99 min. ee = 95%.

(*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-2-L-(*tert*-butoxycarbonylamino)-2-benzeneacetate (3ao**)**



3ao

Chemical Formula: $\text{C}_{25}\text{H}_{31}\text{NO}_4$

Exact Mass: 409.2253

Molecular Weight: 409.5260

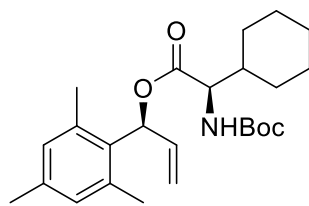
The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2o** (25.1 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:4) furnished **3ao** (26.1 mg, 64% yield) as colorless oil. Dr = 10:1, determined by crude ^1H NMR. The major isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.09 (m, 5H), 6.69 (s, 2H), 6.66-6.57 (m, 1H), 6.04 (ddd, $J = 17.2, 10.6, 4.3$ Hz, 1H), 5.49 (d, $J = 7.5$ Hz, 1H, -NHBoc), 5.38 (d, $J = 7.5$ Hz, 1H), 5.21-5.12 (m, 1H), 5.10-4.96 (m, 1H), 2.20 (s, 3H), 2.06 (s, 6H), 1.41 (s, 9H).

^{13}C NMR (75 MHz, CDCl_3) δ 170.2, 154.9, 137.5, 137.1, 134.8, 130.7, 129.6, 128.8, 128.3, 127.4, 127.1, 116.5, 80.1, 74.82, 57.7, 28.3, 20.9, 20.0.

HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{31}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$: 432.2145, found: 432.2145.

Optical Rotation: $[\alpha]_{\text{D}}^{31} = -72.1$ ($c = 0.2$, CHCl_3).

(*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-2-L-(*tert*-butoxycarbonylamino)-2-cyclohexyl acetate (3ap**)**



3ap

Chemical Formula: C₂₅H₃₇NO₄

Exact Mass: 415.2723

Molecular Weight: 415.5740

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2p** (25.7 mg, 0.1 mmol, 1 eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:4) furnished **3ap** (22.0 mg, 53% yield) as yellow oil. Dr > 19:1, determined by crude ¹H NMR.

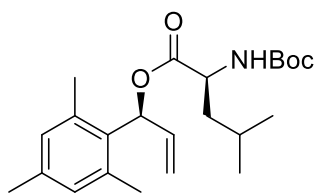
¹H NMR (400 MHz, CDCl₃) δ 6.81 (s, 2H), 6.72-6.61 (m, 1H), 6.09 (ddd, *J* = 17.2, 10.7, 4.2 Hz, 1H), 5.20 (d, *J* = 10.7 Hz, 1H), 5.13-5.05 (m, 1H), 4.98 (d, *J* = 9.3 Hz, 1H), 4.32 (dd, *J* = 9.4, 4.7 Hz, 1H), 2.39 (s, 6H), 2.24 (s, 3H), 1.85-1.58 (m, 4H), 1.43 (s, 9H), 1.26-0.99 (m, 6H), 0.92-0.84 (m, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 171.8, 155.8, 137.8, 137.2, 135.3, 131.4, 129.8, 116.5, 79.8, 74.12, 58.32, 41.0, 29.6, 28.4, 27.4, 26.2, 25.97, 25.96, 21.0, 20.6.

HRMS (ESI) calculated for C₂₅H₃₇NNaO₄ [M+Na]⁺: 438.2615, found: 438.2613.

Optical Rotation: [α]_D³¹ = -176.2 (*c* = 0.3, CHCl₃).

(1S)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-2-L-(tert-butoxycarbonylamino)-4-methylvalerate(3aq)



3aq

Chemical Formula: C₂₃H₃₅NO₄

Exact Mass: 389.2566

Molecular Weight: 389.5360

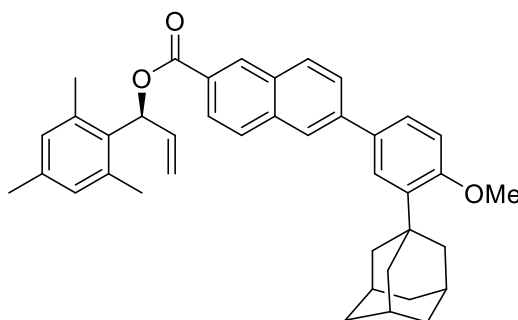
The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2q** (23.0 mg, 0.1 mmol, 1 eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:5) furnished **3aq** (19.4 mg, 50% yield) as yellow oil. Dr > 19:1, determined by crude ¹H NMR.

¹H NMR (400 MHz, CDCl₃) δ 6.82 (s, 1H), 6.72 (s, 1H), 6.07 (ddd, *J* = 17.3, 10.6, 4.2 Hz, 1H), 5.19 (d, *J* = 10.6 Hz, 1H), 5.09 (d, *J* = 17.3 Hz, 1H), 4.87 (d, *J* = 8.9 Hz, 1H), 4.39 (td, *J* = 9.3, 4.5 Hz, 1H), 2.38 (s, 3H), 2.25 (s, 2H), 1.70 – 1.48 (m, 1H), 1.43 (s, 4H), 0.91 (d, *J* = 6.4 Hz, 2H), 0.86 (d, *J* = 6.5 Hz, 2H). **¹³C NMR** (75 MHz, CDCl₃) δ 172.8, 155.5, 137.8, 137.2, 135.3, 131.3, 129.9, 116.5, 79.9, 73.9, 52.3, 41.8, 28.4, 24.8, 23.1, 21.9, 21.0, 20.6.

HRMS (ESI) calculated for C₂₃H₃₅NNaO₄ [M+Na]⁺: 412.2458, found: 412.2454.

Optical Rotation: [α]_D³¹ = -107.1 (*c* = 0.2, CHCl₃).

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-adapalene ester(3ar)



3ar

Chemical Formula: C₄₀H₄₂O₃

Exact Mass: 570.3134

Molecular Weight: 570.7730

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2r** (41.1 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:5) furnished **3ar** (30.8 mg, 54% yield, 99% ee) as yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 1H), 8.09 (dd, *J* = 8.6, 1.5 Hz, 1H), 8.02-7.95 (m, 2H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.79 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.54 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.99 (d, *J* = 8.5 Hz, 2H), 6.87 (s, 2H), 6.26 (ddd, *J* = 17.2, 10.6, 4.2 Hz, 1H), 5.33-5.06 (m, 2H), 3.90 (s, 3H), 2.53 (s, 6H), 2.26 (s, 3H), 2.18 (s, 6H), 2.10 (s, 3H), 1.80 (s, 6H).

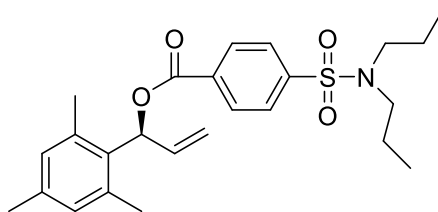
¹³C NMR (100 MHz, CDCl₃) δ 166.0, 159.0, 141.5, 139.1, 137.8, 137.3, 136.1, 135.7, 132.7, 131.9, 131.4, 131.1, 130.0, 129.9, 128.4, 127.2, 126.6, 126.1, 125.9, 125.8, 124.9, 116.4, 112.2, 73.7, 55.3, 40.7, 37.34, 37.26, 29.8, 29.2, 21.0, 20.8.

HRMS (ESI) *m/z* calculated for C₄₀H₄₂NaO₃ [M+Na]⁺: 593.3026, found: 593.3008.

Optical Rotation: [α]_D³¹ = -101.8 (*c* = 0.1, CHCl₃, 99% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak ID column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{major}) = 5.67$ min, $t_R(\text{minor}) = 7.21$ min. ee = 99%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-4-(*N,N*-dipropylsulfonamido) Benzoate (3as)



3as

Chemical Formula: $C_{25}H_{33}NO_4S$

Exact Mass: 443.2130

Molecular Weight: 443.6020

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2s** (28.5 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:5) furnished **3as** (32.8 mg, 74% yield, 86% ee) as yellow oil.

¹H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, $J = 7.5$ Hz, 2H), 7.87 (d, $J = 7.6$ Hz, 2H), 6.96 (dd, $J = 3.7, 1.5$ Hz, 1H), 6.86 (s, 2H), 6.21-6.17 (m, 1H), 5.30-5.25 (m, 1H), 5.24-5.15 (m, 1H), 3.17-3.03 (m, 4H), 2.48 (s, 6H), 2.25 (s, 3H), 1.68-1.47 (m, 4H), 0.86 (td, $J = 7.3, 0.7$ Hz, 6H).

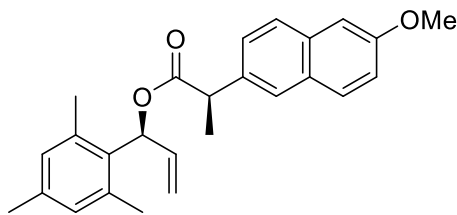
¹³C NMR (75 MHz, $CDCl_3$) δ 164.4, 144.4, 138.0, 137.2, 135.2, 133.7, 131.3, 130.4, 130.0, 127.1, 116.8, 74.3, 50.0, 22.0, 21.0, 20.7, 11.3.

HRMS (ESI) m/z calculated for $C_{25}H_{33}NNaO_4S$ $[M+Na]^+$: 466.2023, found: 466.2019.

Optical Rotation: $[\alpha]_D^{31} = -48.0$ ($c = 0.3$, $CHCl_3$, 86% ee).

HPLC: Daicel Chiralpak OD-H column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_R(\text{major}) = 5.46$ min, $t_R(\text{minor}) = 6.76$ min. ee = 86%.

(1*S*)-1-(2,4,6-Trimethylphenyl)-prop-2-en-1-yl-(2*R*)-2-(5-methoxy-2-naphthyl)-propionate (3at)



3at

Chemical Formula: C₂₆H₂₈O₃

Exact Mass: 388.2038

Molecular Weight: 388.5070

The title compound was prepared from **1a** (53.0 mg, 0.3 mmol, 3 eq.) and **2at** (23.0 mg, 0.1 mmol, 1eq.) via general procedure. Purified by preparative TLC (eluent: EtOAc/PE = 1:5) furnished **3at** (26.8 mg, 69% yield) as yellow oil. Dr > 19:1, determined by crude ¹H NMR.

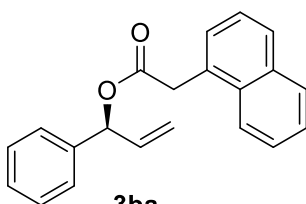
¹H NMR (300 MHz, CDCl₃) δ 7.62 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 1H), 7.45-7.44 (m, 1H), 7.27 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.13-7.07 (m, 2H), 6.70-6.62 (m, 3H), 6.03 (ddd, *J* = 17.3, 10.6, 4.4 Hz, 1H), 5.16-4.98 (m, 2H), 3.96-3.79 (m, 1H), 3.89 (s, 3H), 2.20 (s, 3H), 2.16 (s, 6H), 1.56 (d, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 173.7, 157.6, 137.4, 137.2, 135.7, 135.4, 133.7, 131.5, 129.7, 129.4, 129.0, 127.2, 126.4, 126.0, 118.9, 116.1, 105.6, 73.6, 55.3, 45.8, 20.9, 20.3, 18.8.

HRMS (ESI) *m/z* calculated for C₂₆H₂₈NaO₃ [M+Na]⁺: 411.1931, found: 411.1926.

Optical Rotation: [α]_D³¹ = -158.0 (*c* = 0.1, CHCl₃).

(1S)-1-Phenylprop-2-en-1-yl 1-naphthaleneacetate (3ba)



3ba

Chemical Formula: C₂₁H₁₈O₂

Exact Mass: 302.1307

Molecular Weight: 302.3730

The title compound was prepared from **1b** (40.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ba** (10.9 mg, 36% yield, 96% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 8.01-7.90 (m, 1H), 7.89-7.82 (m, 1H), 7.79 (dd, *J* = 6.9, 2.3 Hz, 1H), 7.53-7.38 (m, 4H), 7.32-7.17 (m, 5H), 6.26 (d, *J* = 5.8 Hz, 1H), 5.93 (ddd, *J* = 17.2, 10.3, 5.9 Hz, 1H), 5.16 (dd, *J* = 9.7, 6.3 Hz, 2H), 4.13 (s, 2H).

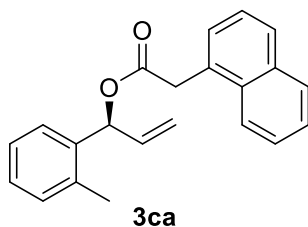
¹³C NMR (75 MHz, CDCl₃) δ 170.6, 138.8, 136.1, 133.9, 132.2, 130.6, 128.8, 128.6, 128.2, 128.1, 127.2, 126.4, 125.9, 125.6, 124.0, 117.1, 76.7, 39.5.

HRMS (ESI) *m/z* calculated for C₂₁H₂₂NO₂ [M+NH₄]⁺: 320.1645, found: 320.1641.

Optical Rotation: [α]_D³¹ = -15.0 (*c* = 0.3, CHCl₃, 96% ee).

HPLC: Daicel Chiralpak OD-H column (hexane/*i*PrOH = 98:2, flow rate: 1.0 mL/min, λ = 224 nm, *t*_R(major) = 12.11 min, *t*_R (minor) = 9.83 min. ee = 96%.

(*S*)-1-(2-Methylphenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ca)



Chemical Formula: C₂₂H₂₀O₂

Exact Mass: 316.1463

Molecular Weight: 316.4000

The title compound was prepared from **1c** (45.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ca** (16.2 mg, 51% yield, 84% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.99-7.89 (m, 1H), 7.89-7.82 (m, 1H), 7.81-7.75 (m, 1H), 7.50-7.43 (m, 2H), 7.42-7.35 (m, 2H), 7.20-7.04 (m, 4H), 6.43 (d, *J* = 5.6 Hz, 1H), 5.90 (ddd, *J* = 17.1, 10.5, 5.6 Hz, 1H), 5.13 (dt, *J* = 10.5, 1.2 Hz, 1H), 5.07 (dt, *J* = 17.2, 1.3 Hz, 1H), 4.12 (s, 2H), 2.27 (s, 3H).

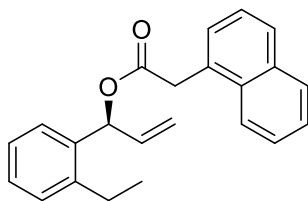
¹³C NMR (100 MHz, CDCl₃) δ 170.6, 136.9, 135.8, 135.5, 133.9, 132.2, 130.6, 128.8, 128.20, 128.16, 128.07, 126.9, 126.4, 126.2, 125.9, 125.6, 124.0, 117.1, 74.1, 39.5, 19.2.

HRMS (ESI) calculated for C₂₂H₂₄NO₂ [M+NH₄]⁺: 334.1802, found: 334.1797.

Optical Rotation: [α]_D³¹ = -47.6 (*c* = 0.3, CHCl₃, 84% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/*i*PrOH = 98:2), flow rate: 1.0 mL/min, λ = 234 nm, *t*_R(major) = 7.38 min, *t*_R (minor) = 6.32 min. ee = 84%.

(1*S*)-1-(2-Ethylphenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3da)



3da

Chemical Formula: C₂₃H₂₂O₂

Exact Mass: 330.1620

Molecular Weight: 330.4270

The title compound was prepared from **1d** (47.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3da** (21.0 mg, 63% yield, 94% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.97-7.89 (m, 1H), 7.88-7.77 (m, 2H), 7.50-7.36 (m, 4H), 7.25-7.07 (m, 4H), 6.51 (d, *J* = 5.4 Hz, 1H), 5.93 (ddd, *J* = 17.1, 10.5, 5.4 Hz, 1H), 5.15-5.04 (m, 2H), 4.22-3.99 (m, 2H), 2.77-2.52 (m, 2H), 1.17 (t, *J* = 7.6 Hz, 3H).

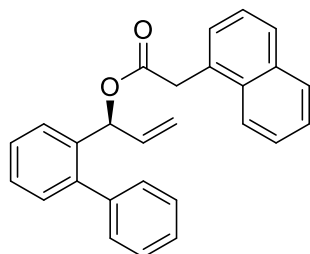
¹³C NMR (100 MHz, CDCl₃) δ 170.6, 141.8, 136.3, 136.3, 133.9, 132.2, 130.6, 128.79, 128.75, 128.32, 128.19, 128.16, 127.32, 126.4, 126.2, 125.9, 125.6, 124.0, 116.9, 73.4, 39.5, 25.5, 15.4.

HRMS (ESI) calculated for C₂₃H₂₆NO₂ [M+NH₄]⁺: 348.1958, found: 348.1954.

Optical Rotation: [α]_D³¹ = -81.0 (*c* = 0.1, CHCl₃, 94% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/*i*PrOH = 95:5), flow rate: 1.0 mL/min, λ = 225 nm, *t*_R(major) = 5.32 min, *t*_R (minor) = 4.86 min. ee = 94%.

(1*S*)-1-(2-biphenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ea)



3ea

Chemical Formula: C₂₇H₂₂O₂

Exact Mass: 378.1620

Molecular Weight: 378.4710

The title compound was prepared from **1e** (63.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ea** (26.7 mg, 71% yield, >99% ee) as colorless oil.

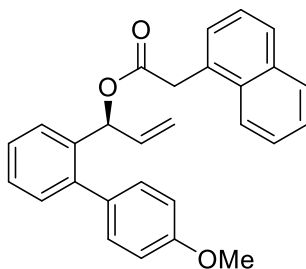
¹H NMR (400 MHz, CDCl₃) δ 8.01-7.94 (m, 1H), 7.93-7.86 (m, 1H), 7.83 (d, *J* = 7.9 Hz, 1H), 7.57-7.49 (m, 2H), 7.48-7.19 (m, 11H), 6.34 (d, *J* = 5.5 Hz, 1H), 5.88 (ddd, *J* = 16.2, 10.5, 5.4 Hz, 1H), 5.09 (d, *J* = 10.5 Hz, 1H), 4.91 (d, *J* = 17.2 Hz, 1H), 4.11 (d, *J* = 1.4 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 141.5, 140.5, 136.5, 136.4, 133.9, 132.2, 130.6, 130.1, 129.3, 128.8, 128.3, 128.2, 127.9, 127.7, 127.4, 126.9, 126.4, 125.9, 125.6, 124.0, 116.9, 74.1, 39.4.

HRMS (ESI) calculated for C₂₇H₂₆NO₂ [M+NH₄]⁺: 396.1958, found: 396.1957.

Optical Rotation: [α]_D³¹ = -12.0 (*c* = 0.5, CHCl₃, 99% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/iPrOH = 95:5), flow rate: 1.0 mL/min, λ = 225 nm, *t*_R(major) = 5.63 min, *t*_R (minor) = 5.05 min. ee = 99%.

(1*S*)-1-(2-(*p*-Methoxy)-biphenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3fa)



3fa

Chemical Formula: C₂₈H₂₄O₃

Exact Mass: 408.1725

Molecular Weight: 408.4970

The title compound was prepared from **1f** (72.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3fa** (29.0 mg, 71% yield, 99% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.94-7.91 (m, 1H), 7.89-7.82 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.52-7.35 (m, 4H), 7.31-7.14 (m, 6H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.30 (d, *J* = 5.4 Hz, 1H), 5.85 (ddd, *J* = 16.9, 10.5, 5.5 Hz, 1H), 5.05 (d, *J* = 10.5 Hz, 1H), 4.88 (d, *J* = 17.2 Hz, 1H), 4.09 (d, *J* = 15.5 Hz, 1H), 4.04 (d, *J* = 15.5 Hz, 1H), 3.79 (s, 3H).

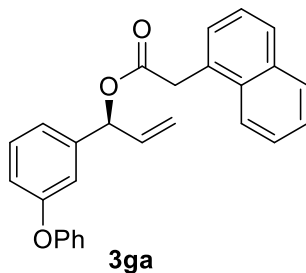
¹³C NMR (101 MHz, CDCl₃) δ 170.2, 158.9, 141.2, 136.6, 136.4, 133.9, 132.8, 132.2, 130.6, 130.4, 130.3, 128.8, 128.2, 127.9, 127.5, 127.0, 126.4, 125.9, 125.6, 124.1, 116.9, 113.7, 74.2, 55.4, 39.5.

HRMS (ESI) calculated for $C_{28}H_{24}NaO_3$ $[M+Na]^+$: 431.1618, found: 431.1616.

Optical Rotation: $[\alpha]_D^{31} = -5.9$ ($c = 0.3$, $CHCl_3$, 99% ee).

HPLC: Daicel Chiralpak OD-H column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 224$ nm, $t_R(\text{major}) = 9.80$ min, $t_R(\text{minor}) = 9.00$ min. ee = 99%.

(1S)-1-(3-phenoxy-phenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ga)



Chemical Formula: $C_{27}H_{22}O_3$

Exact Mass: 394.1569

Molecular Weight: 394.4700

The title compound was prepared from **1g** (68.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ga** (21.3 mg, 54% yield, 96% ee) as colorless oil.

1H NMR (400 MHz, $CDCl_3$) δ 8.00-7.90 (m, 1H), 7.87-7.82 (m, 1H), 7.80-7.76 (m, 1H), 7.50-7.43 (m, 2H), 7.43-7.37 (m, 2H), 7.35-7.29 (m, 2H), 7.25-7.19 (m, 1H), 7.11 (t, $J = 7.4$ Hz, 1H), 6.98-6.91 (m, 4H), 6.90-6.85 (m, 1H), 6.22 (d, $J = 5.9$ Hz, 1H), 5.89 (ddd, $J = 17.3, 10.2, 5.9$ Hz, 1H), 5.20-5.07 (m, 2H), 4.12 (s, 2H).

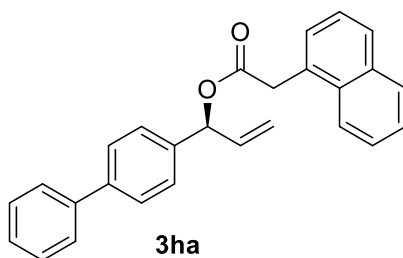
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 157.4, 157.1, 140.9, 135.8, 133.9, 132.2, 130.5, 129.9, 128.8, 128.3, 128.1, 126.5, 125.9, 125.6, 123.9, 123.5, 121.9, 118.9, 118.4, 117.6, 117.4, 76.3, 39.5.

HRMS (ESI) calculated for $C_{27}H_{26}NO_3$ $[M+NH_4]^+$: 412.1907, found: 412.1906.

Optical Rotation: $[\alpha]_D^{31} = -58.4$ ($c = 0.2$, $CHCl_3$, 96% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/iPrOH = 98:2), flow rate: 1.0 mL/min, $\lambda = 234$ nm, $t_R(\text{major}) = 12.50$ min, $t_R(\text{minor}) = 8.63$ min. ee = 96%.

(1S)-1-(4-biphenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ha)



Chemical Formula: C₂₇H₂₂O₂

Exact Mass: 378.1620

Molecular Weight: 378.4710

The title compound was prepared from **1h** (63.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1 eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ha** (24.1 mg, 64% yield, 87% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.99-7.91 (m, 1H), 7.90-7.83 (m, 1H), 7.82-7.76 (m, 1H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.51-7.39 (m, 8H), 7.34 (t, *J* = 7.3 Hz, 1H), 7.27 (d, *J* = 8.2 Hz, 2H), 6.30 (d, *J* = 5.8 Hz, 1H), 6.10-5.84 (m, 1H), 5.32-5.04 (m, 2H), 4.14 (s, 2H).

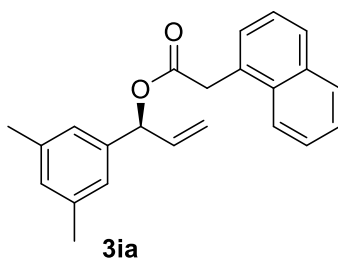
¹³C NMR (101 MHz, CDCl₃) δ 170.6, 141.2, 140.8, 137.8, 136.0, 133.9, 132.2, 130.6, 128.9, 128.8, 128.22, 128.16, 127.6, 127.5, 127.4, 127.2, 126.4, 125.9, 125.6, 124.0, 117.2, 76.5, 39.6.

HRMS (ESI) calculated for C₂₇H₂₂NaO₂ [M+Na]⁺: 401.1512, found: 401.1505.

Optical Rotation: [α]_D³¹ = -33.0 (*c* = 0.2, CHCl₃, 87% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak AD-H column (hexane/iPrOH = 99:1), flow rate: 1.0 mL/min, λ = 234 nm, *t*_R(major) = 20.30 min, *t*_R (minor) = 14.53 min. ee = 87%.

(1S)-1-(3,5-dimethyl-phenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ia)



Chemical Formula: C₂₃H₂₂O₂

Exact Mass: 330.1620

Molecular Weight: 330.4270

The title compound was prepared from **1i** (49.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:8) furnished **3ia** (16.6 mg, 50% yield, 92% ee) as colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 8.10-7.92 (m, 1H), 7.90-7.73 (m, 2H), 7.59-7.31 (m, 4H), 6.87 (s, 1H), 6.76 (s, 2H), 6.18 (d, *J* = 6.0 Hz, 1H), 5.90 (ddd, *J* = 17.1, 10.4, 6.0 Hz, 1H), 5.20-5.11 (m, 2H), 4.12 (s, 2H), 2.21 (s, 6H).

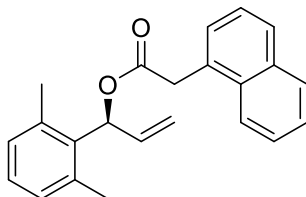
¹³C NMR (75 MHz, CDCl₃) δ 170.6, 138.8, 138.1, 136.3, 133.9, 132.2, 130.7, 129.8, 128.8, 128.2, 126.4, 125.9, 125.6, 124.7, 124.1, 116.8, 76.80, 39.6, 21.3.

HRMS (ESI) calculated for C₂₃H₂₆NO₂ [M+NH₄]⁺: 348.1958, found: 348.1954.

Optical Rotation: [α]_D³¹ = -33.1 (*c* = 0.2, CHCl₃, 92% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/iPrOH = 90:10), flow rate: 1.0 mL/min, λ = 254 nm, *t*_R(major) = 8.57 min, *t*_R(minor) = 5.49 min. ee = 92%.

(1*S*)-1-(2,6-dimethyl-phenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ja)



3ja

Chemical Formula: C₂₃H₂₂O₂

Exact Mass: 330.1620

Molecular Weight: 330.4270

The title compound was prepared from **1j** (49.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ja** (24.7 mg, 75% yield, 97% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.92-1.89 (m, 1H), 7.87-7.82 (m, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.51-7.33 (m, 4H), 7.08-7.03 (m, 1H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.73 (dt, *J* = 4.2, 2.1 Hz, 1H), 5.95 (ddd, *J* = 17.3, 10.6, 4.2 Hz, 1H), 5.07 (ddd, *J* = 10.7, 2.0, 1.2 Hz, 1H), 4.92 (ddd, *J* = 17.3, 1.9, 1.2 Hz, 1H), 4.10 (s, 3H), 2.25 (s, 6H).

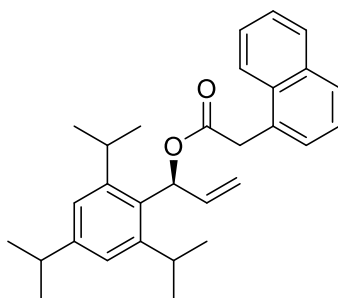
¹³C NMR (100 MHz, CDCl₃) δ 170.8, 137.3, 135.0, 134.4, 133.9, 132.2, 130.6, 129.0, 128.8, 128.18, 128.16, 128.09, 126.4, 125.9, 125.5, 123.8, 116.3, 73.6, 39.5, 20.5.

HRMS (ESI) calculated for C₂₃H₂₆NO₂ [M+NH₄]⁺: 348.1958, found: 348.1955.

Optical Rotation: $[\alpha]_D^{31} = -73.2$ ($c = 0.2$, CHCl_3 , 97% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IA column (hexane/*i*PrOH = 98:2), flow rate: 1.0 mL/min, $\lambda = 225$ nm, $t_R(\text{major}) = 5.66$ min, $t_R(\text{minor}) = 5.19$ min. ee = 97%.

(*IS*)-1-(2,4,6-Triisopropyl-phenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ka)



3ka

Chemical Formula: $\text{C}_{30}\text{H}_{36}\text{O}_2$

Exact Mass: 428.2715

Molecular Weight: 428.6160

The title compound was prepared from **1k** (78.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ka** (30.4 mg, 71% yield, 97% ee) as colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.03-7.90 (m, 1H), 7.89-7.83 (m, 1H), 7.83-7.73 (m, 1H), 7.56-7.35 (m, 4H), 7.06-6.96 (m, 3H), 6.03 (ddd, $J = 17.3, 10.7, 3.7$ Hz, 1H), 5.16-4.92 (m, 1H), 4.83 (d, $J = 17.3$ Hz, 1H), 4.12 (d, $J = 15.6$ Hz, 1H), 4.06 (d, $J = 15.6$ Hz, 1H), 3.46-3.22 (m, 2H), 2.87 (dt, $J = 13.8, 6.9$ Hz, 1H), 1.25 (d, $J = 6.9$ Hz, 6H), 1.17 (d, $J = 6.8$ Hz, 12H).

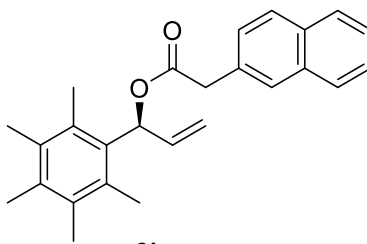
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 171.1, 148.9, 137.8, 134.0, 132.2, 130.6, 129.6, 128.8, 128.3, 128.2, 126.4, 125.9, 125.6, 123.9, 116.2, 72.1, 39.7, 34.3, 29.8, 25.2, 24.1, 23.9.

HRMS (ESI) calculated for $\text{C}_{30}\text{H}_{36}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 451.2608, found: 451.2598.

Optical Rotation: $[\alpha]_D^{31} = -78.1$ ($c = 0.25$, CHCl_3 , 97% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak OD-H column (hexane/*i*PrOH = 99:1), flow rate: 1.0 mL/min, $\lambda = 224$ nm, $t_R(\text{major}) = 5.98$ min, $t_R(\text{minor}) = 5.09$ min. ee = 97%.

(*IS*)-1-(2,3,4,5,6-Pentamethyl-phenyl)-prop-2-en-1-yl-1-naphthaleneacetate (3la)



3la

Chemical Formula: C₂₆H₂₈O₂

Exact Mass: 372.2089

Molecular Weight: 372.5080

The title compound was prepared from **11** (61.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1 eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:8) furnished **3la** (21.5 mg, 58% yield, 94% ee) as colorless oil.

¹H NMR (300 MHz, CDCl₃) δ 8.03-7.69 (m, 3H), 7.55-7.29 (m, 4H), 6.89 (dt, *J* = 4.2, 2.2 Hz, 1H), 5.99 (ddd, *J* = 17.3, 10.6, 4.1 Hz, 1H), 5.05 (ddd, *J* = 10.6, 2.2, 1.3 Hz, 1H), 4.90 (ddd, *J* = 17.3, 2.1, 1.3 Hz, 1H), 4.07 (s, 2H), 2.21 (s, 3H), 2.15 (s, 6H), 2.14 (s, 6H).

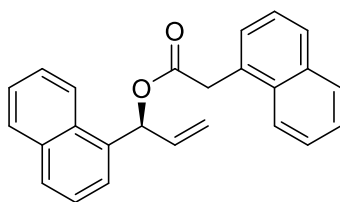
¹³C NMR (75 MHz, CDCl₃) δ 170.9, 136.3, 135.2, 133.9, 133.2, 132.9, 132.3, 132.2, 130.8, 128.8, 128.2, 128.1, 126.3, 125.8, 125.5, 123.9, 116.1, 74.4, 39.6, 17.3, 17.2, 16.8.

HRMS (ESI) calculated for C₂₆H₂₈NaO₂ [M+Na]⁺: 395.1982, found: 395.1975.

Optical Rotation: [α]_D³¹ = -44.2 (*c* = 0.1, CHCl₃, 94% ee).

HPLC: Daicel Chiralpak ID column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, λ = 224 nm, *t*_R(major) = 6.63 min, *t*_R(minor) = 5.79 min. ee = 94%.

(1S)-1-(1-naphthyl)-prop-2-en-1-yl-1-naphthaleneacetate (3ma)



3ma

Chemical Formula: C₂₅H₂₀O₂

Exact Mass: 352.1463

Molecular Weight: 352.4330

The title compound was prepared from **1m** (55.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1 eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3ma** (24.3 mg, 69% yield, 95% ee) as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.93 (dd, *J* = 17.4, 8.4 Hz, 2H), 7.87-7.72 (m, 4H), 7.49-7.30 (m,

8H), 6.96 (d, $J = 5.2$ Hz, 1H), 6.09 (ddd, $J = 17.1, 10.6, 5.3$ Hz, 1H), 5.19-5.12 (m, 2H), 4.14 (s, 2H).

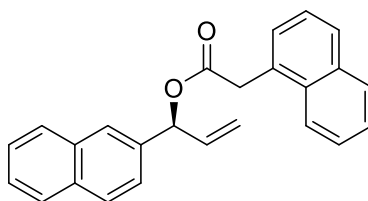
$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.7, 135.8, 134.4, 134.0, 133.9, 132.2, 130.7, 130.5, 129.1, 128.85, 128.78, 128.22, 126.42, 126.33, 125.89, 125.82, 125.60, 125.56, 125.30, 123.98, 117.4, 74.5, 39.5.

HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{20}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 375.1356, found: 375.1355.

Optical Rotation: $[\alpha]_{\text{D}}^{31} = -73.1$ ($c = 0.1$, CHCl_3 , 87% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/*i*PrOH = 90:10), flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{R}}(\text{major}) = 8.97$ min, $t_{\text{R}}(\text{minor}) = 6.82$ min. ee = 87%.

(*S*)-1-(2-naphthyl)-prop-2-en-1-yl-1-naphthaleneacetate (3na**)**



3na

Chemical Formula: $\text{C}_{25}\text{H}_{20}\text{O}_2$

Exact Mass: 352.1463

Molecular Weight: 352.4330

The title compound was prepared from **1n** (55.0 mg, 0.3 mmol, 3 eq.) and **2a** (18.6 mg, 0.1 mmol, 1eq.) via general procedure. Preparative TLC (eluent: EtOAc/PE = 1:10) furnished **3na** (24.2 mg, 69% yield, 95% ee) as colorless oil.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 (d, $J = 8.1$ Hz, 1H), 7.88-7.84 (m, 1H), 7.82-7.70 (m, 3H), 7.69-7.64 (m, 1H), 7.60 (s, 1H), 7.51-7.38 (m, 6H), 7.29 (dd, $J = 8.5, 1.6$ Hz, 1H), 6.42 (d, $J = 5.8$ Hz, 1H), 6.06-5.89 (m, 1H), 5.23-5.16 (m, 2H), 4.15 (s, 2H).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ 170.6, 136.12, 136.07, 133.9, 133.19, 133.15, 132.2, 130.6, 128.8, 128.4, 128.23, 128.19, 127.74, 126.5, 126.3, 126.1, 125.9, 125.6, 124.9, 124.0, 117.4, 76.8, 39.6.

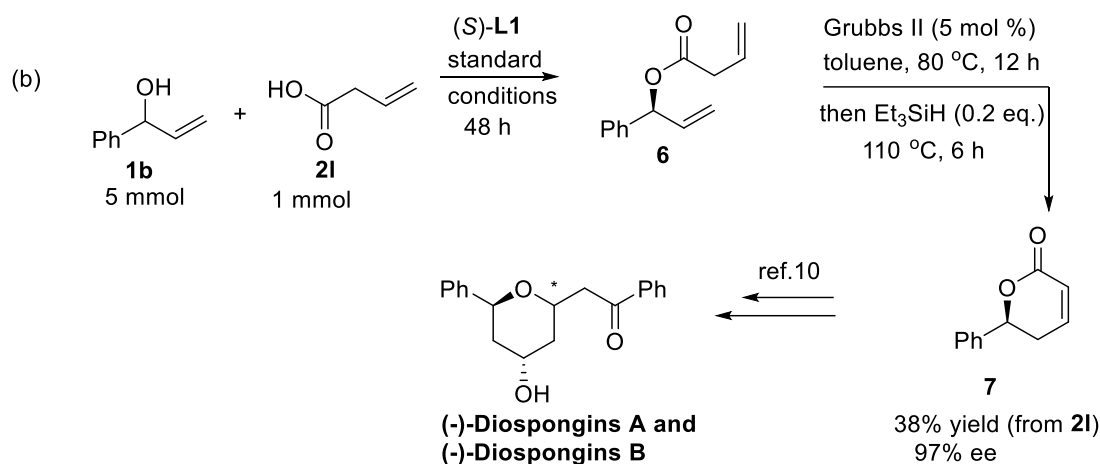
HRMS (ESI) calculated for $\text{C}_{25}\text{H}_{20}\text{NaO}_2$ $[\text{M}+\text{Na}]^+$: 375.1356, found: 375.1355.

Optical Rotation: $[\alpha]_{\text{D}}^{31} = -45.0$ ($c = 0.2$, CHCl_3 , 95% ee).

HPLC: The enantiomeric excess was determined by HPLC analysis on a Daicel Chiralpak IC column (hexane/*i*PrOH = 90:10), flow rate: 1.0 mL/min, $\lambda = 254$ nm, $t_{\text{R}}(\text{major}) = 9.72$ min, $t_{\text{R}}(\text{minor}) = 6.55$ min. ee = 95%.

Further applications:

The synthesis of compound 7



A flame dried round bottom flask was cooled to rt. and charged with $[\text{Ir}(\text{cod})\text{Cl}]_2$ (26 mg, 40 μmol , 4 mol %) and **(S)-L1** (80.0 mg, 160 μmol , 16 mol %). The flask backfilled with argon gas three times. To the flask was added distilled CH_2Cl_2 (10.0 mL), and stirred at rt. for 10 min. The allylic alcohols **1b** (670.0 mg, 5 mmol, 5.0 equiv), carboxylic acids **2I** (86 mg, 1 mmol, 1.0 equiv), 4AMS (400 mg) and HBr (40wt.% in water; 240 mg, 1.2 mmol, 120 mol%) were added. The flask was sealed and stirred at rt. for 48 h. Later, the solution was quenched with aq. NaHCO_3 (50 mL) and extracted with CH_2Cl_2 (3* 50mL). The organic layer was dried over Na_2SO_4 and concentrated by rotary evaporation. The crude product was fast purified by preparative TLC (eluent: EtOAc/PE = 1:10) to afford the ester **6**.

Follow the reported method: The ester **6** was all dissolved in toluene (5.0 mL) which was preheated to 80 °C, the Grubbs II (5 mol %) was added. After the substrate was fully consumed (monited by TLC, approx. 12 h), the Et_3SiH (17 μL , 0.1 mmol, 0.2 eq.) was added, and the solution was heated to 110 °C for 6 h. the solvent were evaporated, and the residue was purified by chromatography on silica (eluent: hexane:EA = 3:1) to give lactone **7** (66.2 mg, 38% over yield from **2I**) as a powder. The ^1NMR is consistant with those reported literatures.^{[3][4]}

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.60-7.26 (m, 5H), 6.97 (ddd, $J = 9.6, 5.1, 3.3$ Hz, 1H), 6.21-5.91 (m, 1H), 5.45 (dd, $J = 10.2, 5.7$ Hz, 1H), 2.77-2.43 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 164.2, 145.0, 138.6, 128.8, 128.7, 126.2, 121.8, 79.4, 31.82.

Optical Rotation: $[\alpha]_{\text{D}}^{31} = -227.0$ (c = 0.2 in CHCl_3 , 97% ee); and the Ref. ^[4]: $[\alpha]_{\text{D}}^{26} = -210$ (c = 0.755, CHCl_3 , 92% ee)

HPLC: Daicel Chiralpak OD-H column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 225$ nm, $t_{\text{R}}(\text{major}) = 17.28$ min, $t_{\text{R}}(\text{minor}) = 20.82$ min. ee = 97%.

Reference

[1] A. Serra-Muns, A. Guérinot, S. Reymond, J. Cossy, *Chem. Commun.*, 2010, **46**, 4178.

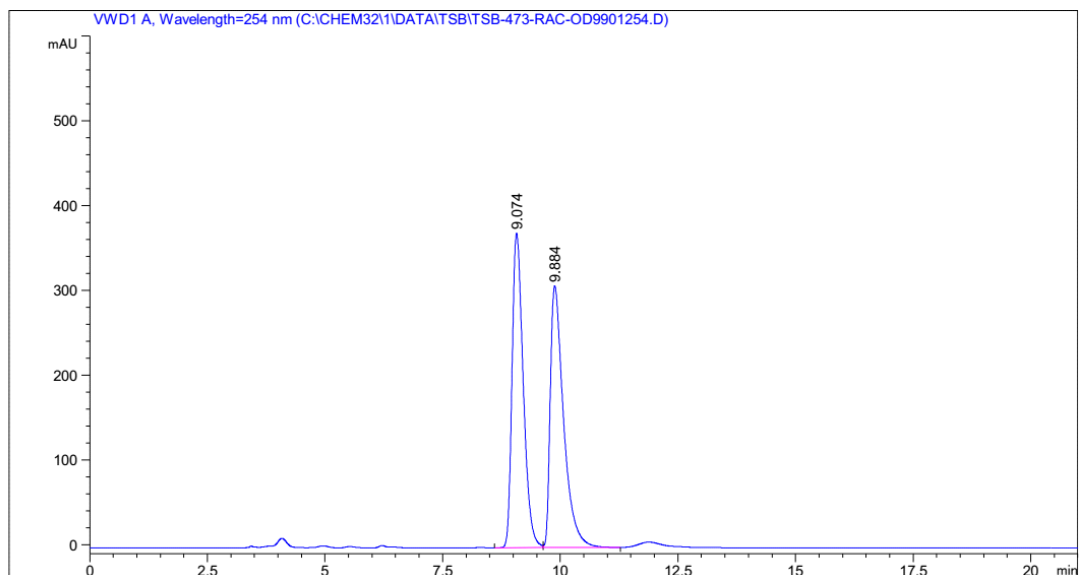
[2] B. Schmidt, O. Kunz, *Synlett* 2012, **23**, 851.

[3] H.-J. Zhang, L. Yin, *J. Am. Chem. Soc.* 2018, **140**, 12270.

[4] A. Padarti, H. Han, *Org. Lett.* 2018, **20**, 1448

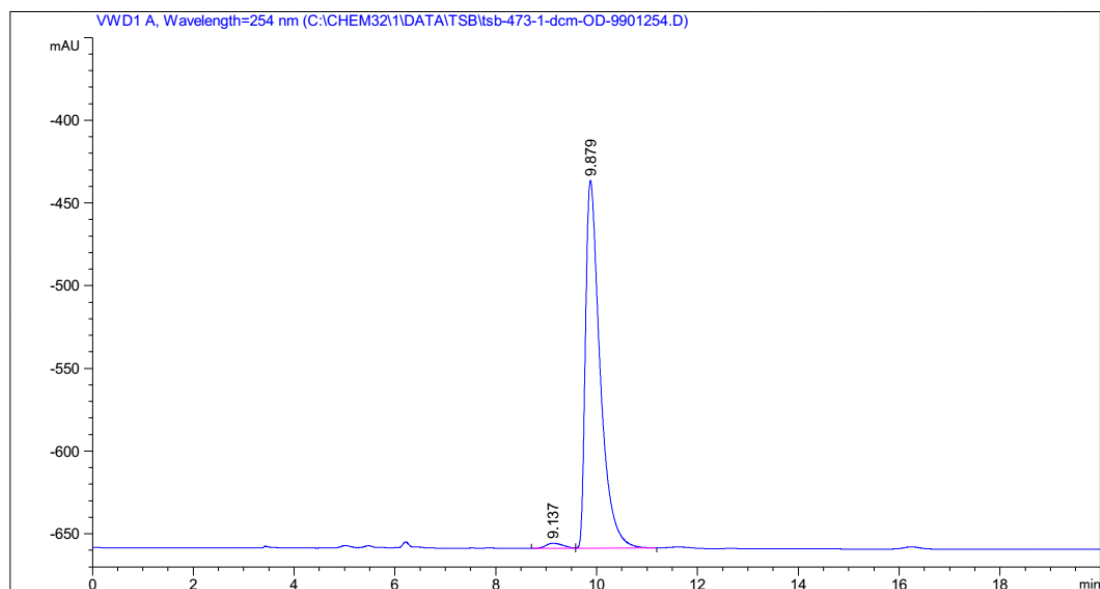
HPLC Chromatograms

Racemic sample 3aa: HPLC (Daicel Chiralpak OD-H column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



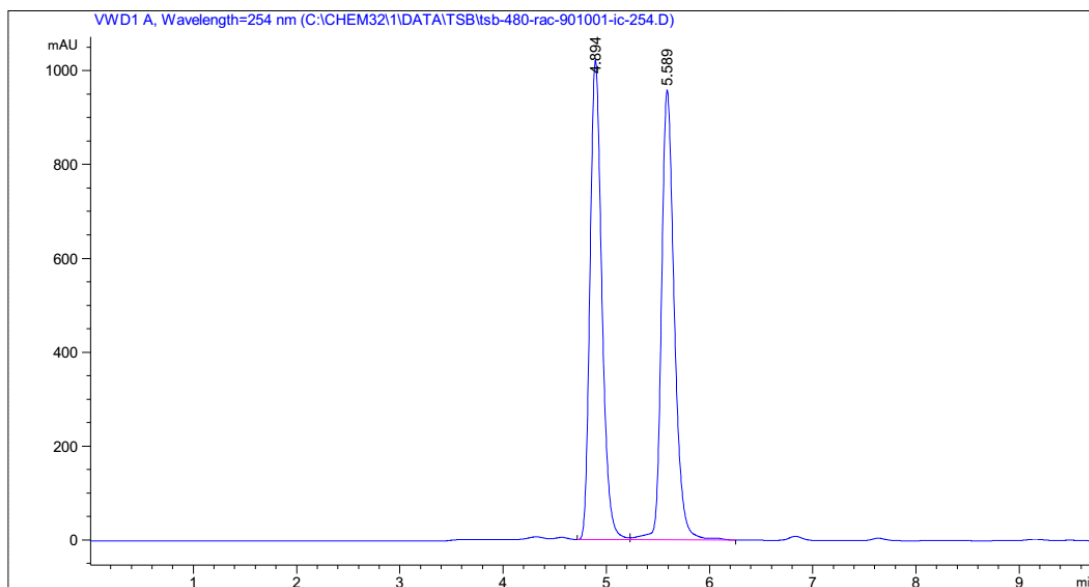
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	9.074	BV	0.2532	6109.49170	370.83450	50.1618
2	9.884	VB	0.2955	6070.07568	308.62259	49.8382

Enantioenriched sample 3aa:



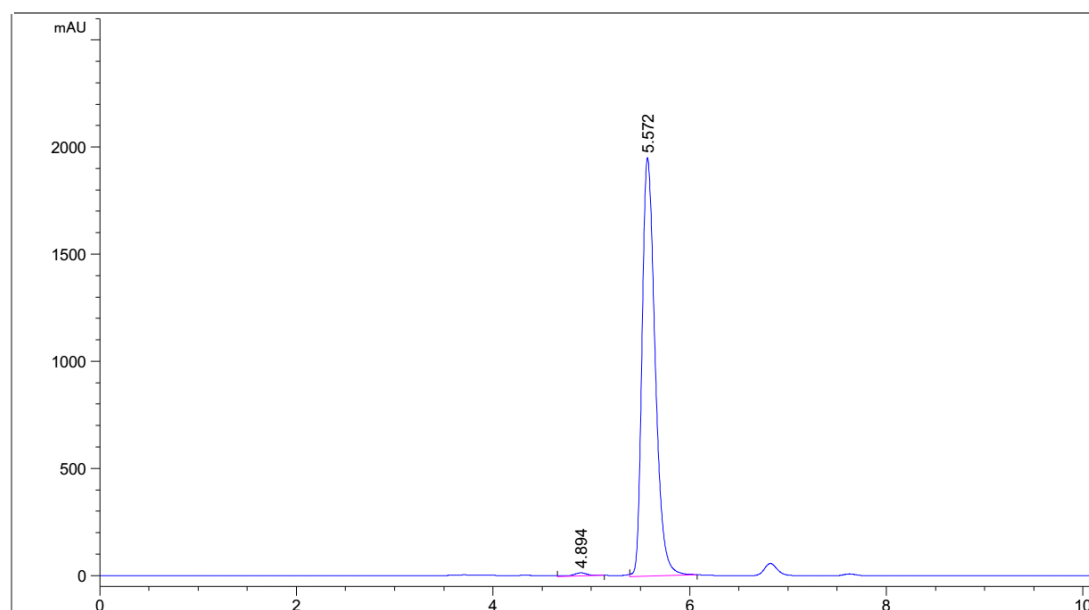
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	9.137	BV	0.3725	71.31754	3.07603	1.5683
2	9.879	VB	0.3020	4476.00195	222.23903	98.4317

Racemic sample 3ab: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



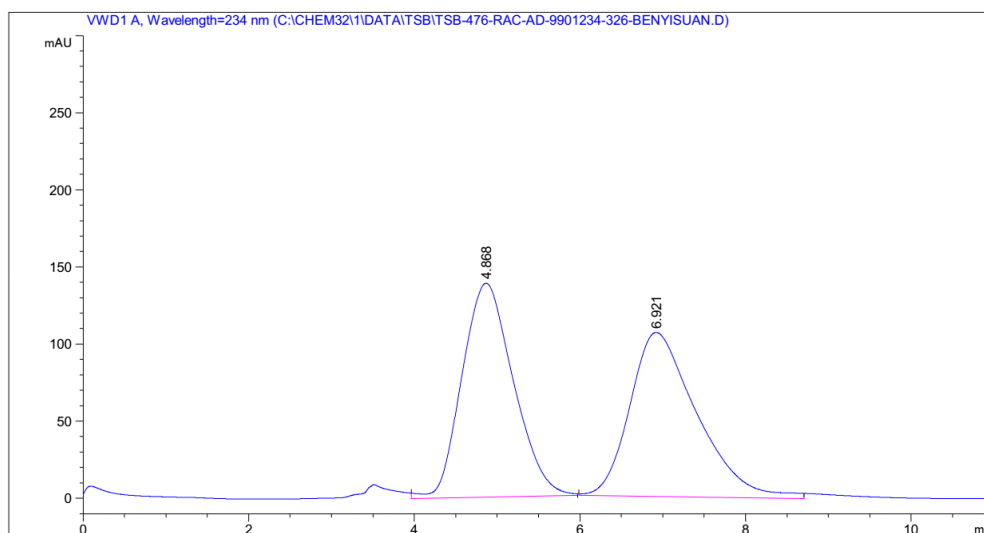
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.894	BV	0.1229	8131.83154	1020.89941	49.4851
2	5.589	VV R	0.1317	8301.06641	958.75323	50.5149

Enantioenriched sample 3ab:



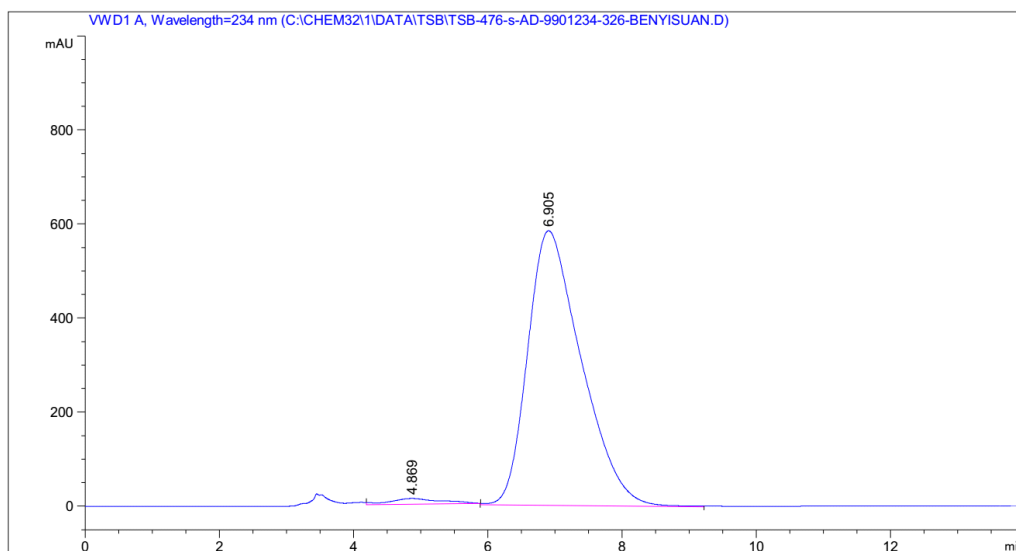
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	6.969	MM	0.1974	162.44135	13.71311	0.9298
2	7.838	MM	0.2937	1.73083e4	982.17554	99.0702

Racemic sample 3ac: HPLC (Daicel Chiralpak AD-H column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda = 234$ nm)



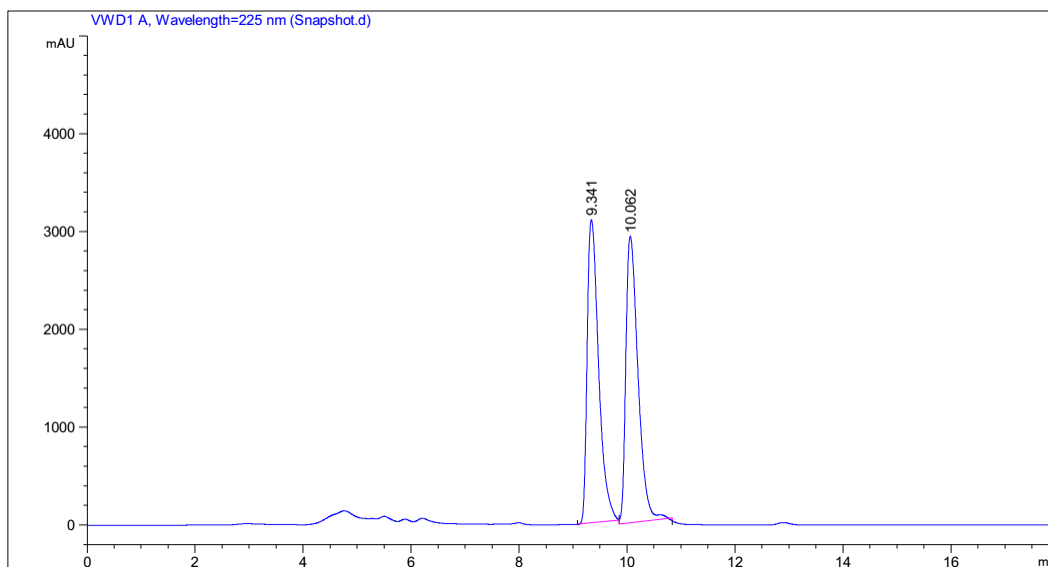
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.868	MM	0.7178	5971.49365	138.65198	50.0457
2	6.921	MM	0.9345	5960.58789	106.30811	49.9543

Enantioenriched sample 3ac:



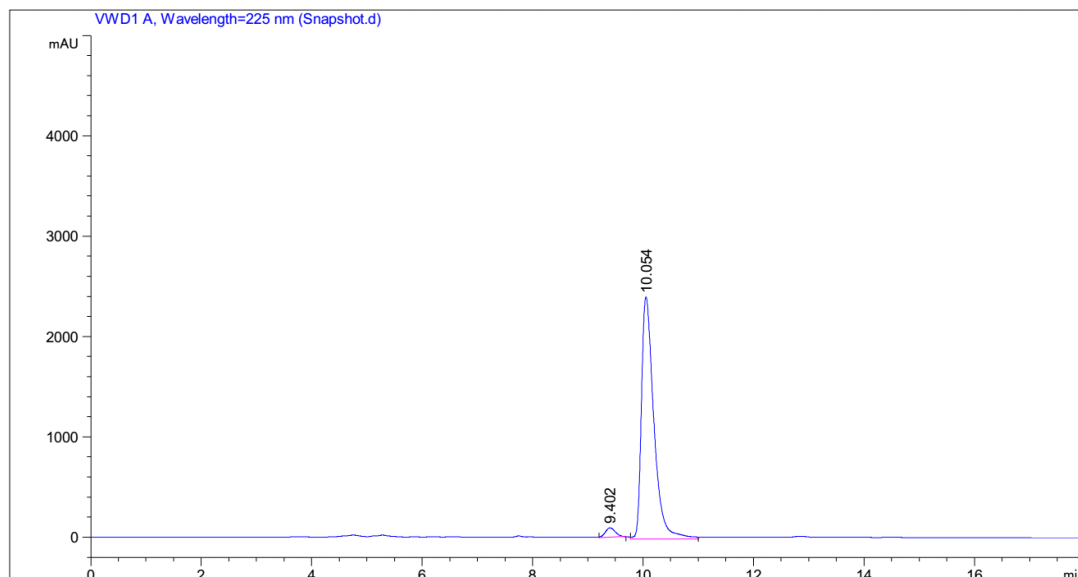
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.869	MM	0.8707	622.35193	11.91269	1.8828
2	6.905	MM	0.9257	3.24324e4	583.90521	98.1172

Racemic sample 3ad: HPLC (Daicel Chiralpak IE column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 225$ nm)



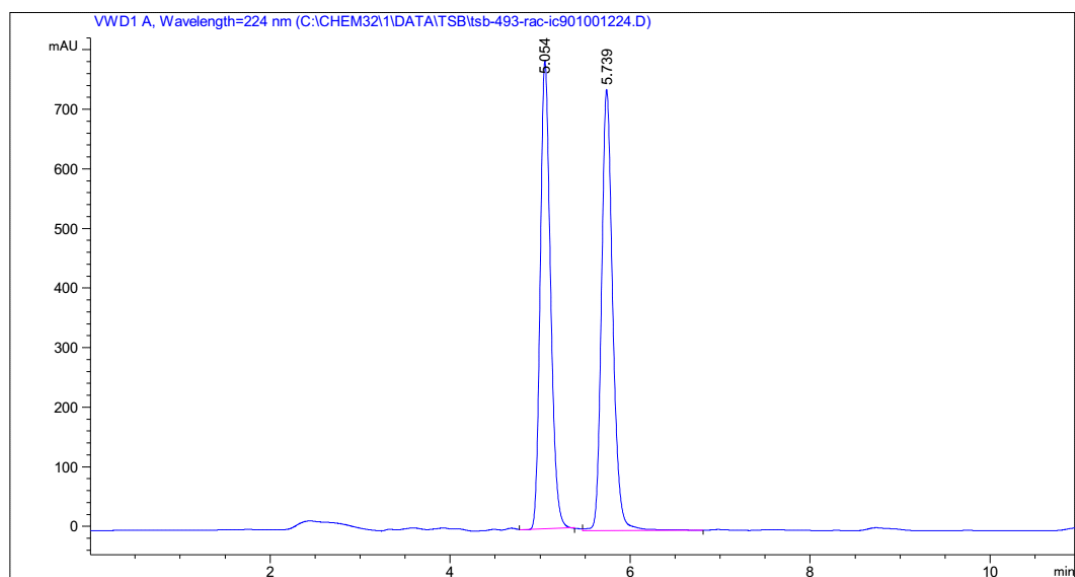
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	9.341	MM	0.2454	4.56275e4	3098.51001	49.8984
2	10.062	MM	0.2607	4.58134e4	2928.42969	50.1016

Enantioenriched sample 3ad:



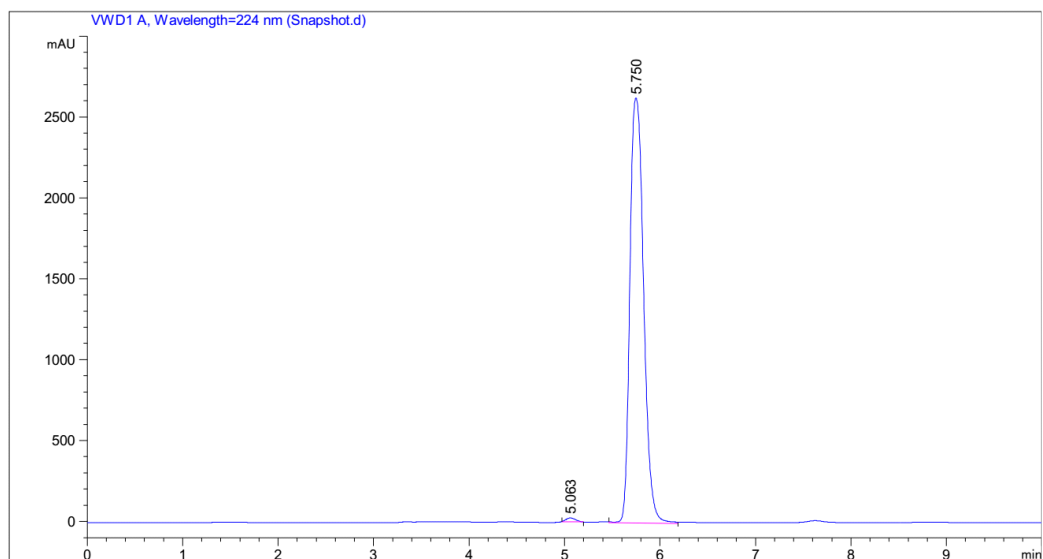
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	9.402	MM	0.2058	1140.75317	92.36864	2.9442
2	10.054	MM	0.2599	3.76055e4	2411.67773	97.0558

Racemic sample 3ae: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 224$ nm)



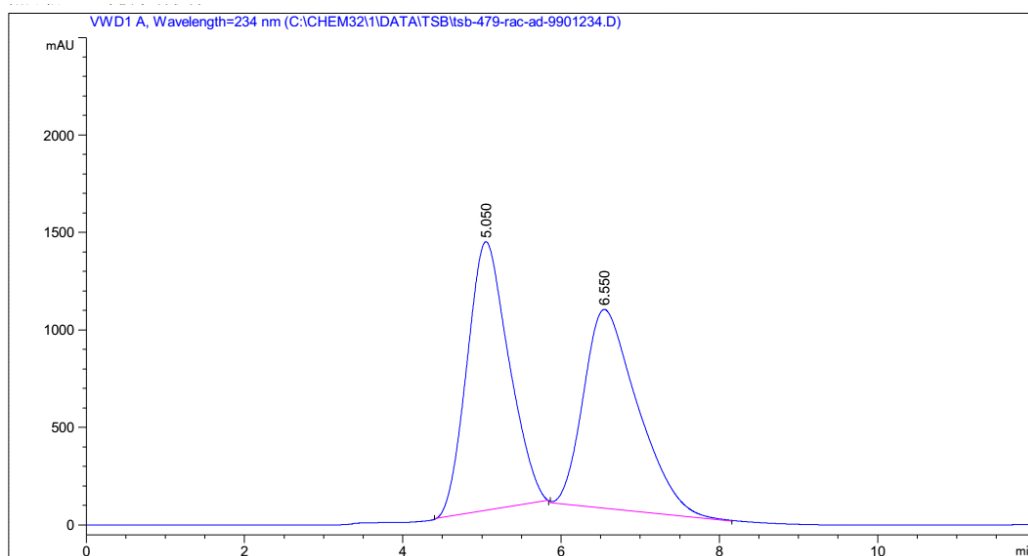
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.054	MM	0.1317	6202.67139	785.11359	49.1314
2	5.739	VB	0.1322	6421.99072	740.40649	50.8686

Enantioenriched sample 3ae:



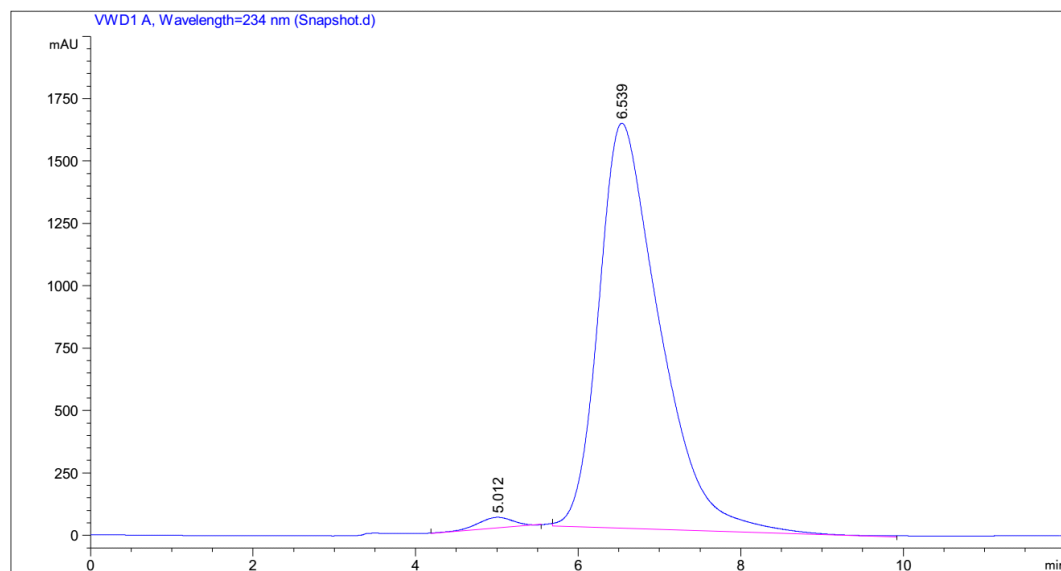
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.063	MM	0.1181	175.21301	24.72530	0.6632
2	5.750	MM	0.1664	2.62442e4	2628.57544	99.3368

Racemic sample 3af: HPLC (Daicel Chiralpak AD-H column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda = 234$ nm)



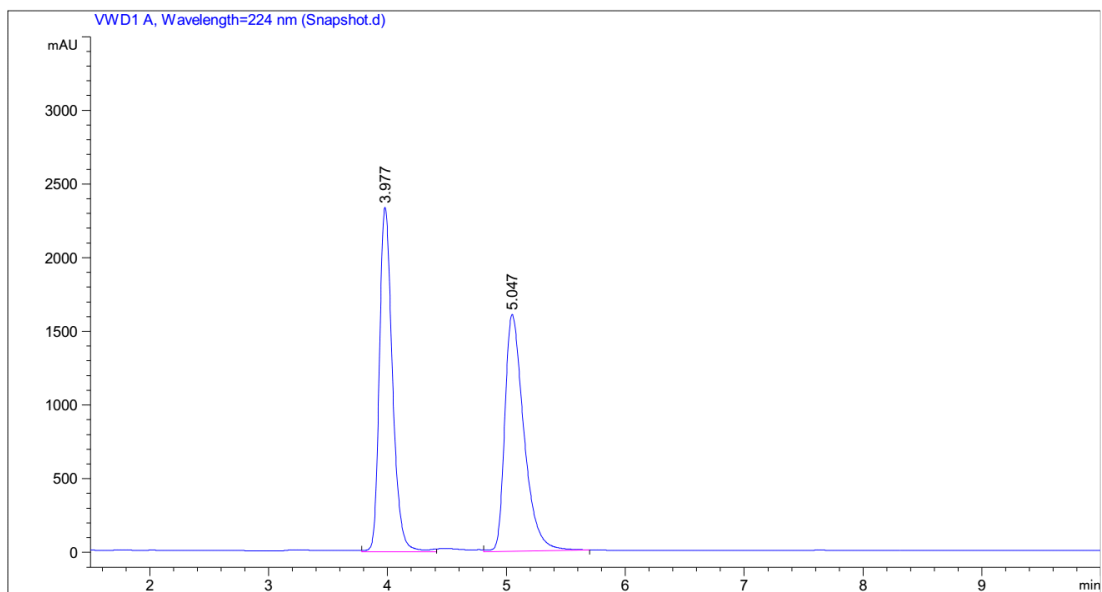
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.050	MM	0.6093	5.03443e4	1377.06030	50.9537
2	6.550	MM	0.7931	4.84597e4	1018.35785	49.0463

Enantioenriched sample 3af:



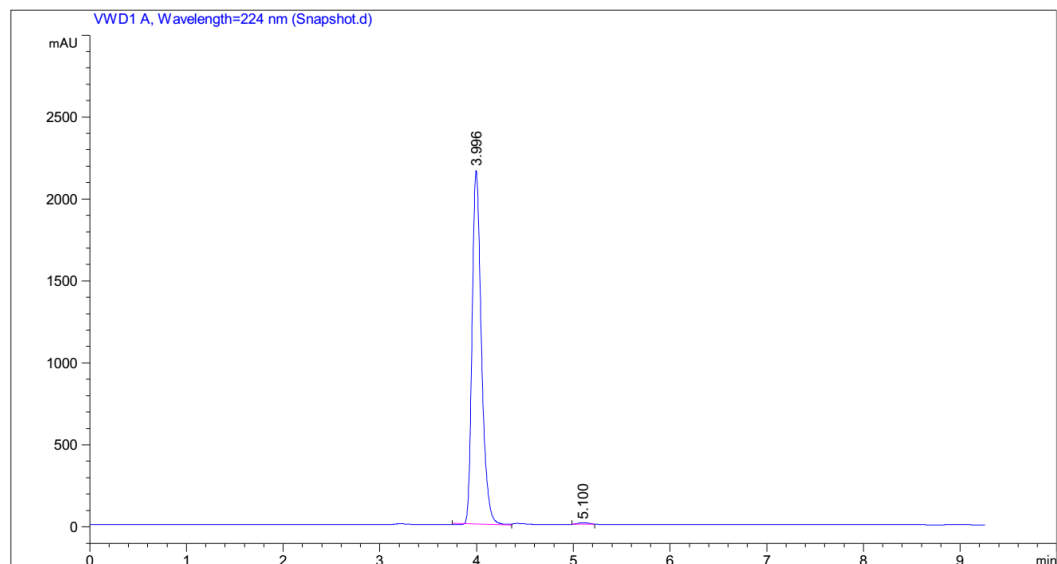
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.012	MM	0.4958	1265.40015	42.53933	1.4733
2	6.539	MM	0.8687	8.46250e4	1623.57764	98.5267

Racemic sample 3ag: HPLC (Daicel Chiralpak AD-H column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda = 224$ nm)



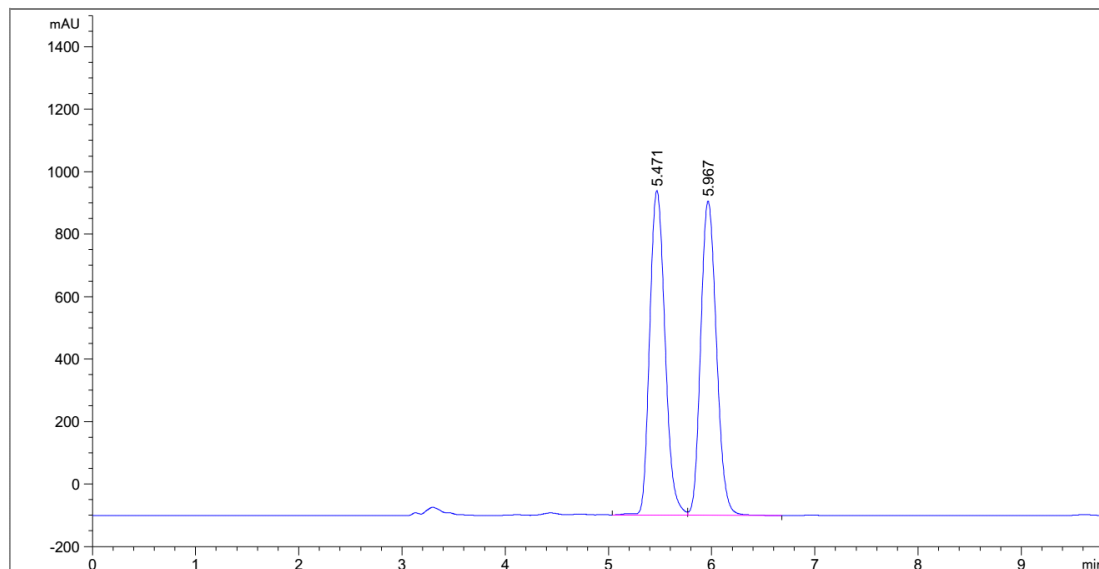
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	3.977	MM	0.1270	1.78005e4	2336.25439	49.7994
2	5.047	MM	0.1861	1.79440e4	1606.99146	50.2006

Enantioenriched sample 3ag:



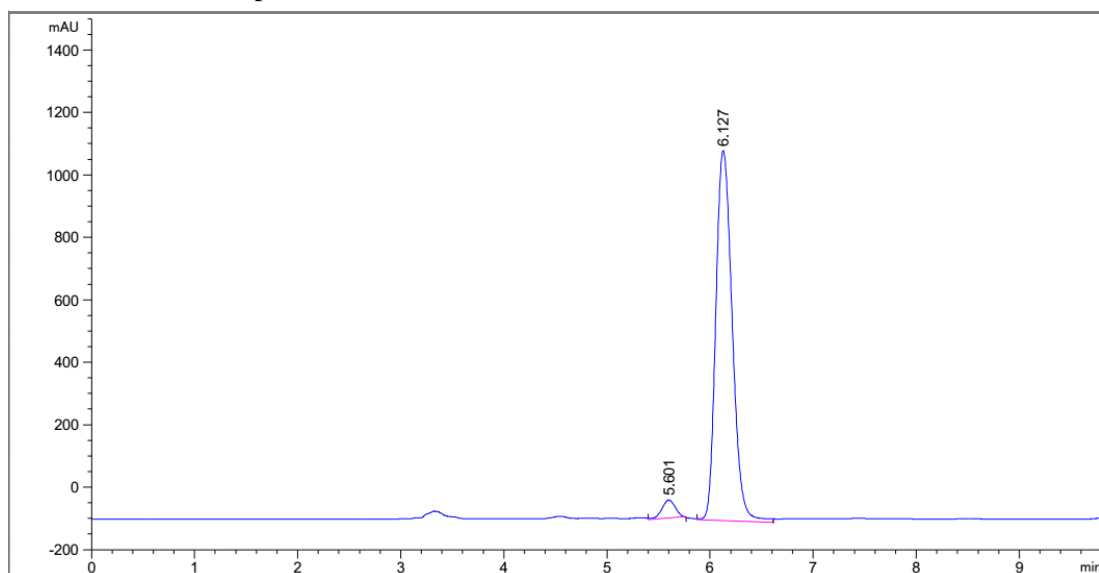
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	3.996	MM	0.1116	1.44544e4	2158.07788	99.5263
2	5.100	MM	0.1220	68.79845	9.39519	0.4737

Racemic sample 3ah: HPLC (Daicel Chiralpak OJ column (hexane/iPrOH = 98:2, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



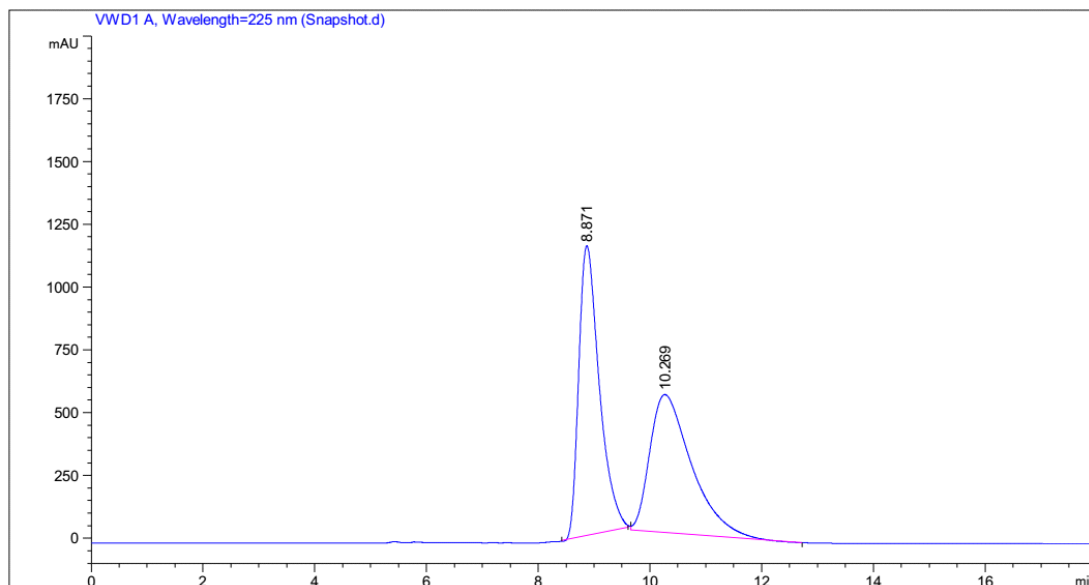
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.471	VV R	0.1618	1.07038e4	1038.93140	50.0642
2	5.967	VB	0.1678	1.06763e4	1006.32996	49.9358

Enantioenriched sample 3ah:



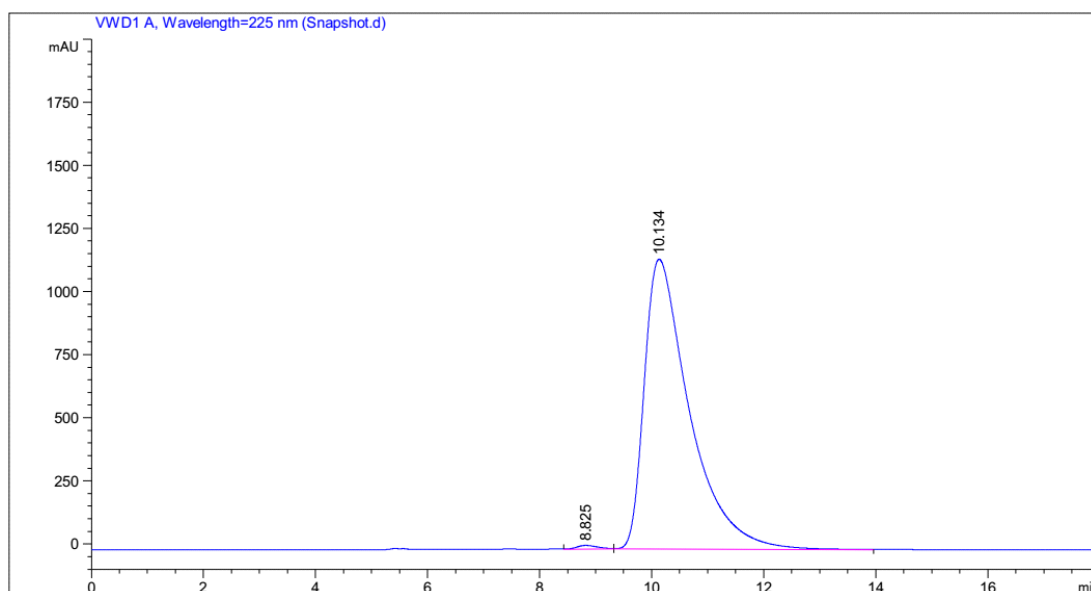
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.601	MM	0.1511	518.56927	57.20169	3.8238
2	6.127	MM	0.1835	1.30430e4	1184.41650	96.1762

Racemic sample 3ai: HPLC (Daicel Chiralpak OJ-H column (hexane/iPrOH = 99:1, flow rate: 0.6 mL/min, $\lambda = 225$ nm)



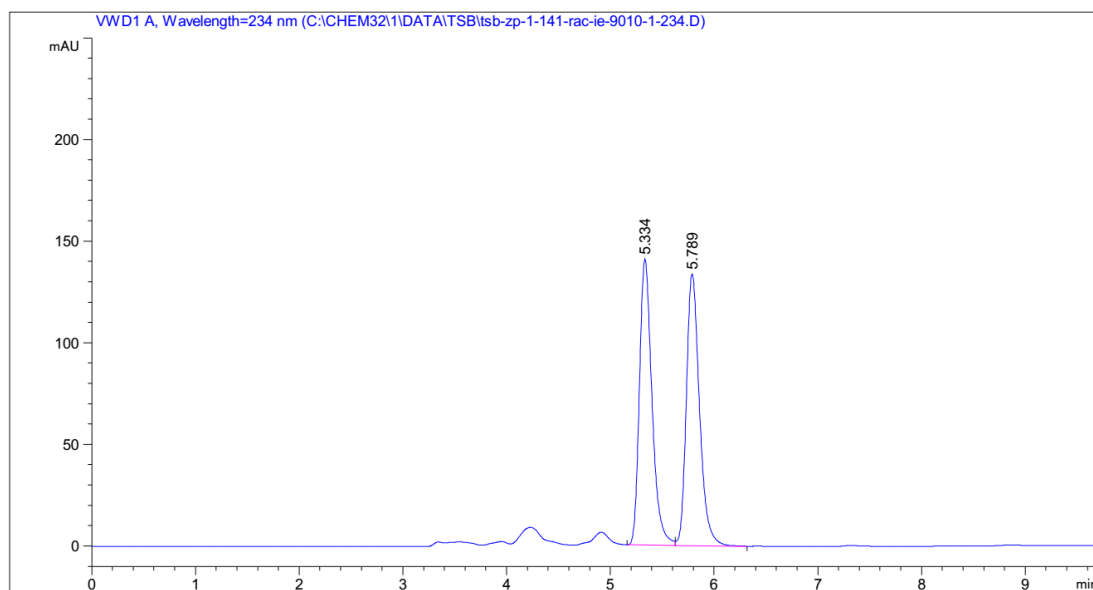
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	8.871	MM	0.4249	2.94068e4	1153.56030	50.7388
2	10.269	MM	0.8666	2.85504e4	549.06744	49.2612

Enantioenriched sample 3ai:



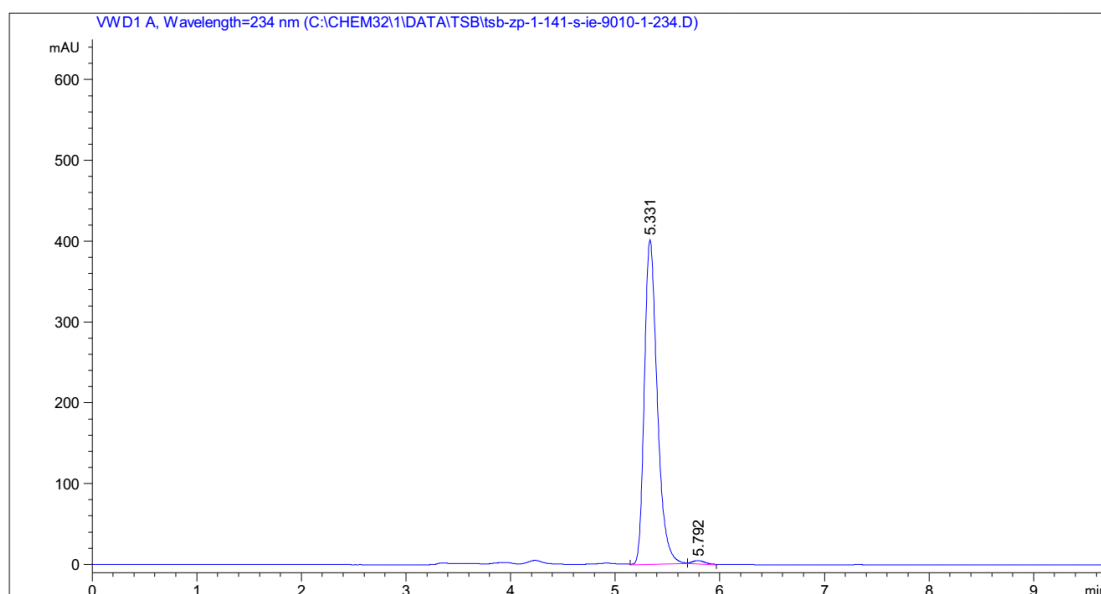
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	8.825	MM	0.4544	423.24597	15.52276	0.6531
2	10.134	MM	0.9342	6.43796e4	1148.54407	99.3469

Racemic sample 3aj: HPLC (Daicel Chiralpak IE column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 234$ nm)



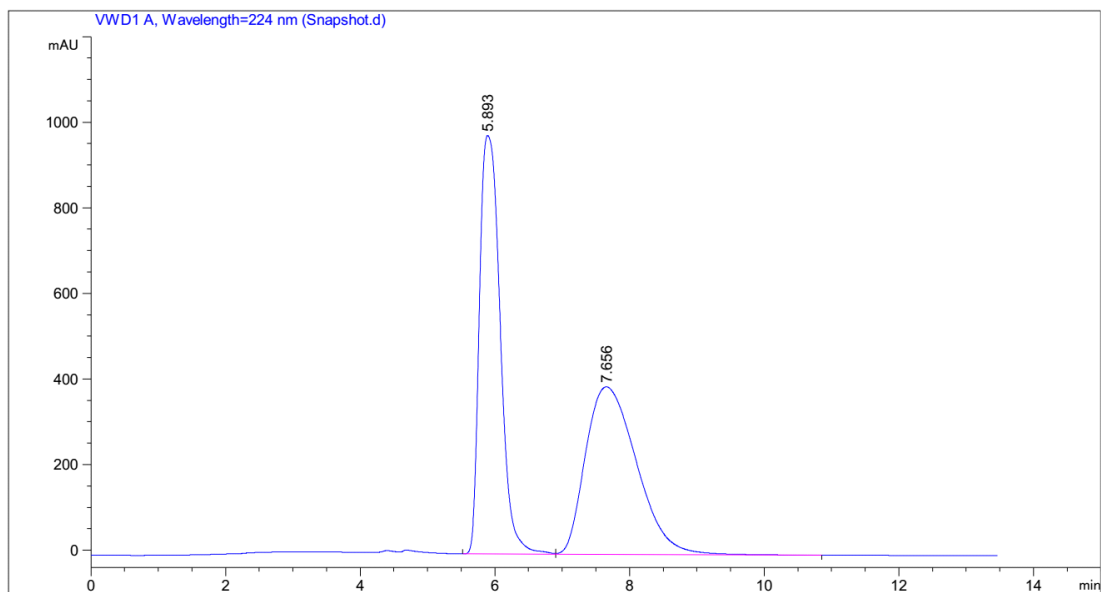
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.334	BV	0.1289	1180.73389	140.64307	50.1562
2	5.789	VB	0.1343	1173.38123	133.78452	49.8438

Enantioenriched sample 3aj:



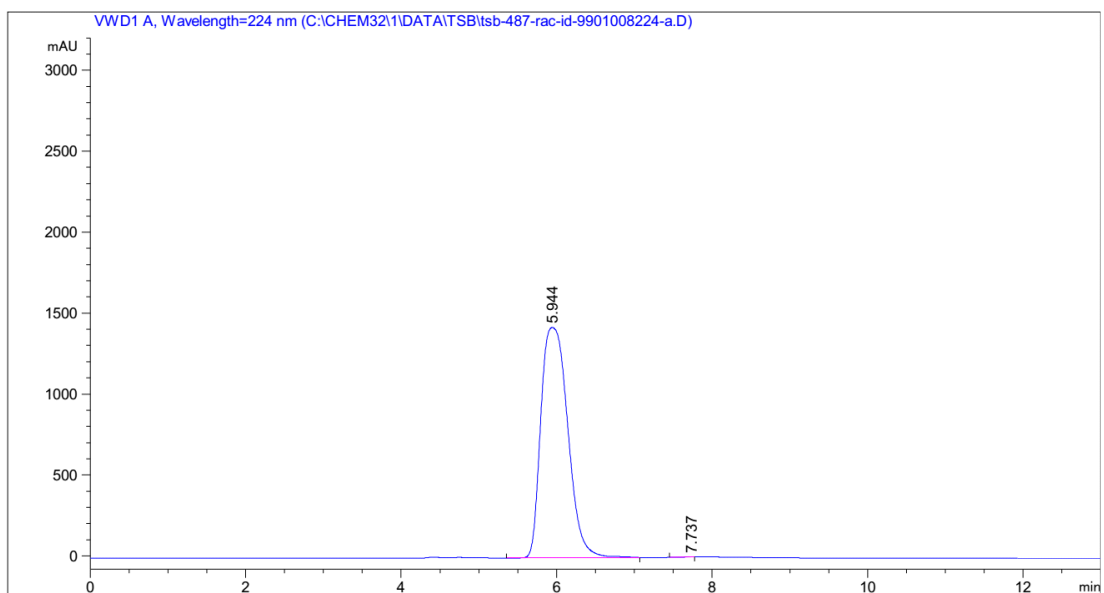
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.331	MM	0.1423	3427.90723	401.62619	98.9801
2	5.792	MM	0.1440	35.32218	4.08705	1.0199

Racemic sample 3ak: HPLC (Daicel Chiralpak ID column (hexane/iPrOH = 99:1, flow rate: 0.8 mL/min, $\lambda = 224$ nm)



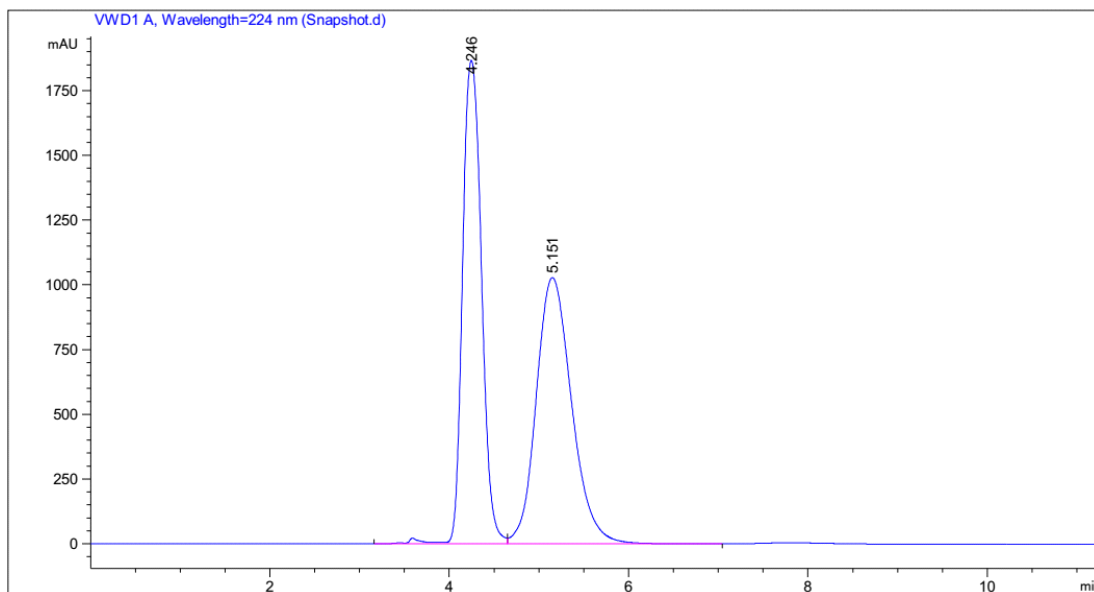
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.893	BV	0.3386	2.08470e4	978.18805	50.2211
2	7.656	VB	0.8474	2.06634e4	391.74585	49.7789

Enantioenriched sample 3ak:



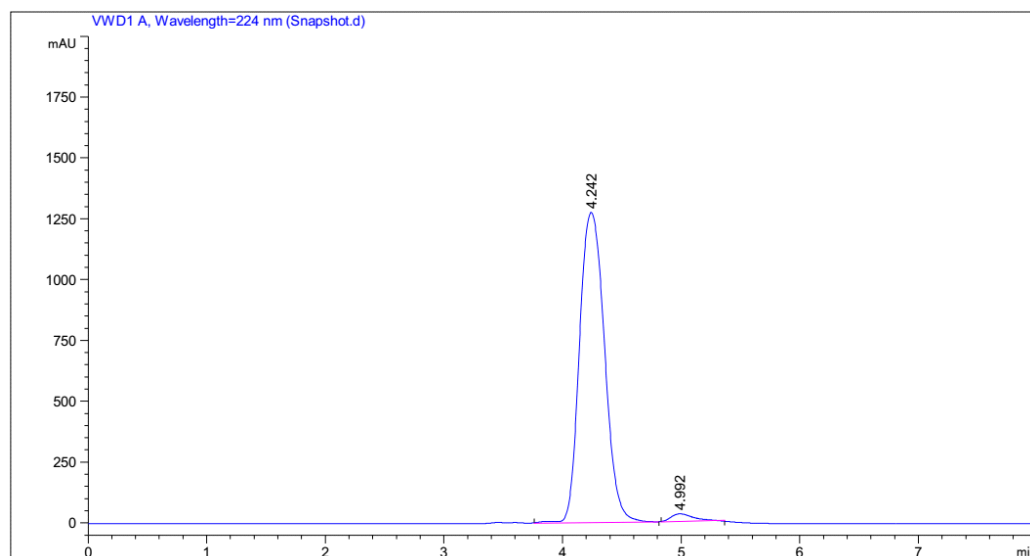
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.944	MM	0.4016	3.42694e4	1422.09314	99.9893
2	7.737	MM	0.1402	3.65587	4.34561e-1	0.0107

Racemic sample 3a1: HPLC (Daicel Chiralpak ID column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda=224$ nm)



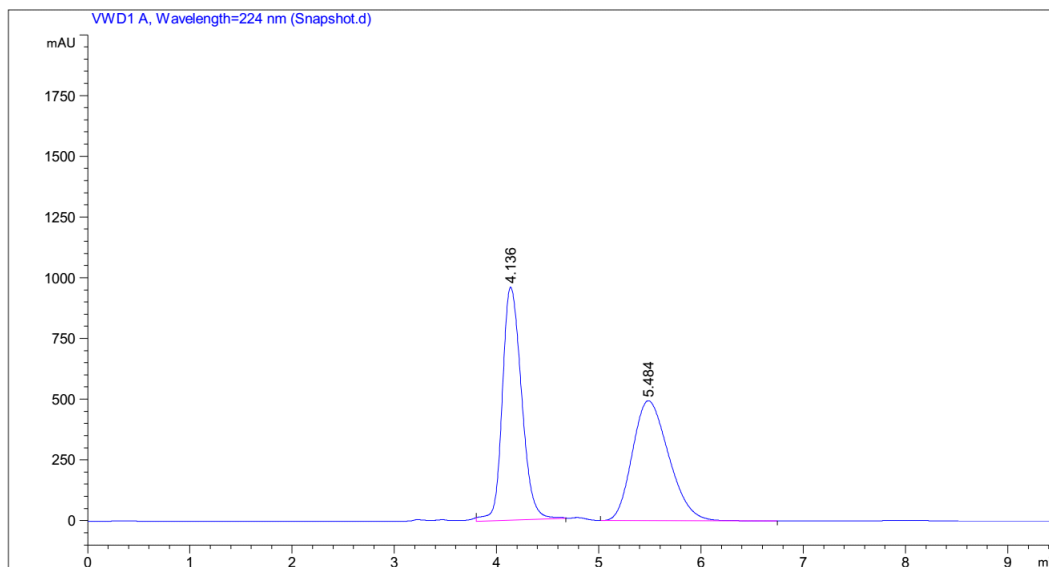
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.246	VV R	0.2340	2.74709e4	1866.99036	49.3064
2	5.151	VB	0.4284	2.82438e4	1028.41479	50.6936

Enantioenriched sample 3a1:



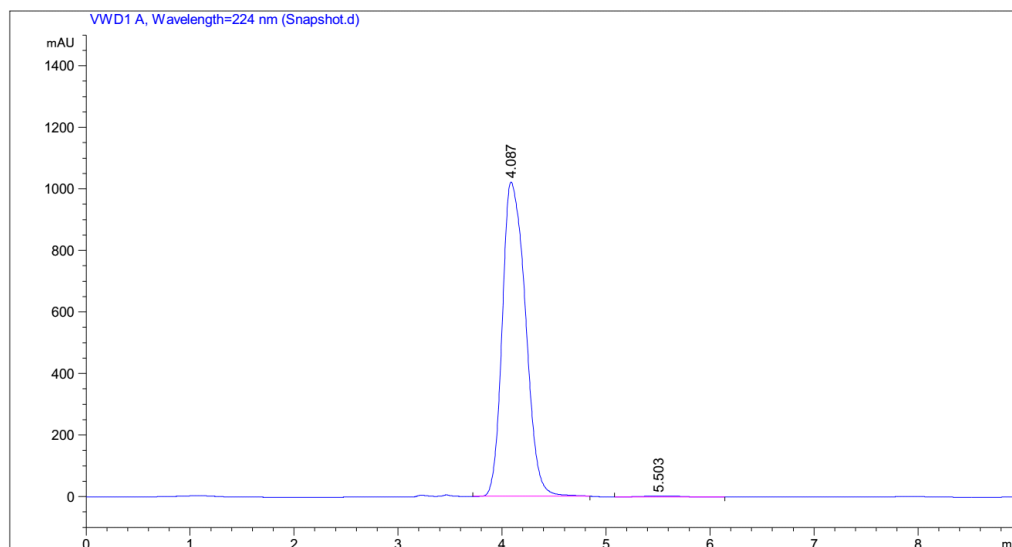
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.242	MM	0.2440	1.86533e4	1274.01868	97.9006
2	4.992	MM	0.2153	400.01483	30.96504	2.0994

Racemic sample 3am: HPLC (Daicel Chiralpak ID column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda = 224$ nm)



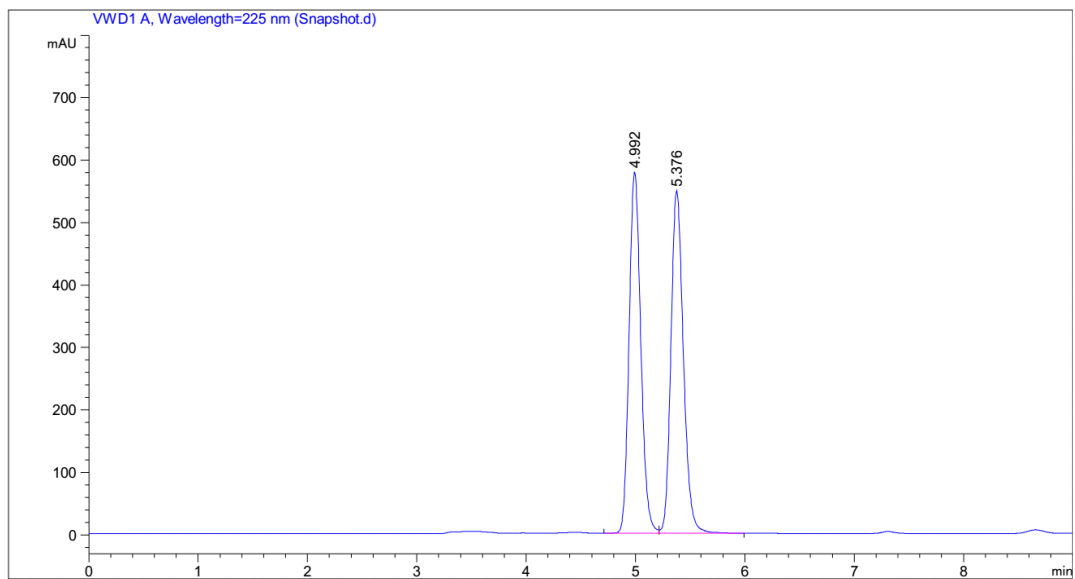
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.136	MM	0.2173	1.25038e4	959.01917	50.6343
2	5.484	BB	0.3850	1.21906e4	493.87051	49.3657

Enantioenriched sample 3am:



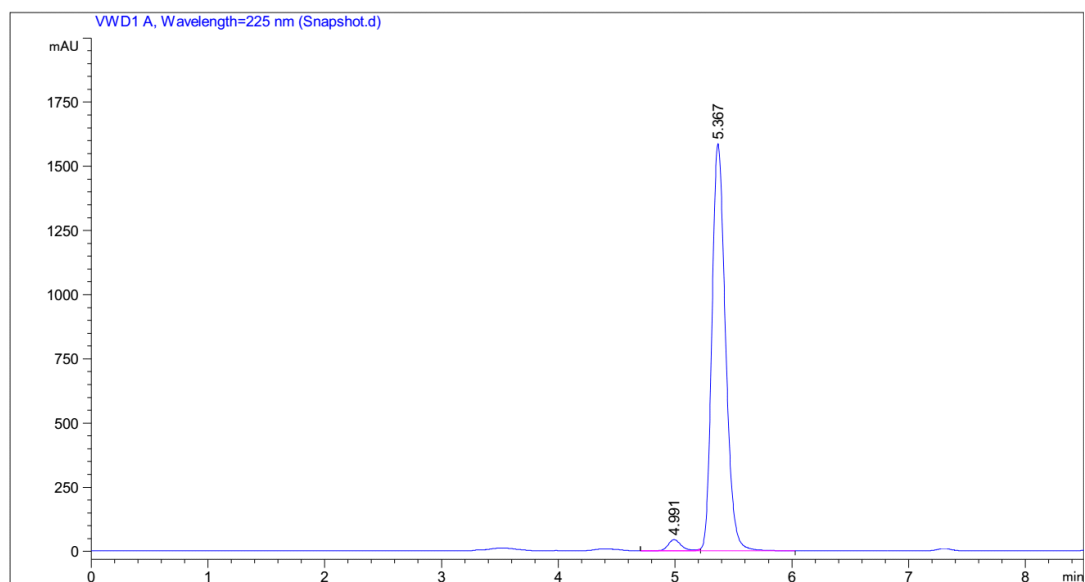
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.087	MM	0.2574	1.57722e4	1021.36707	99.4488
2	5.503	BB	0.4091	87.41776	3.01687	0.5512

Racemic sample 3an: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 225$ nm)



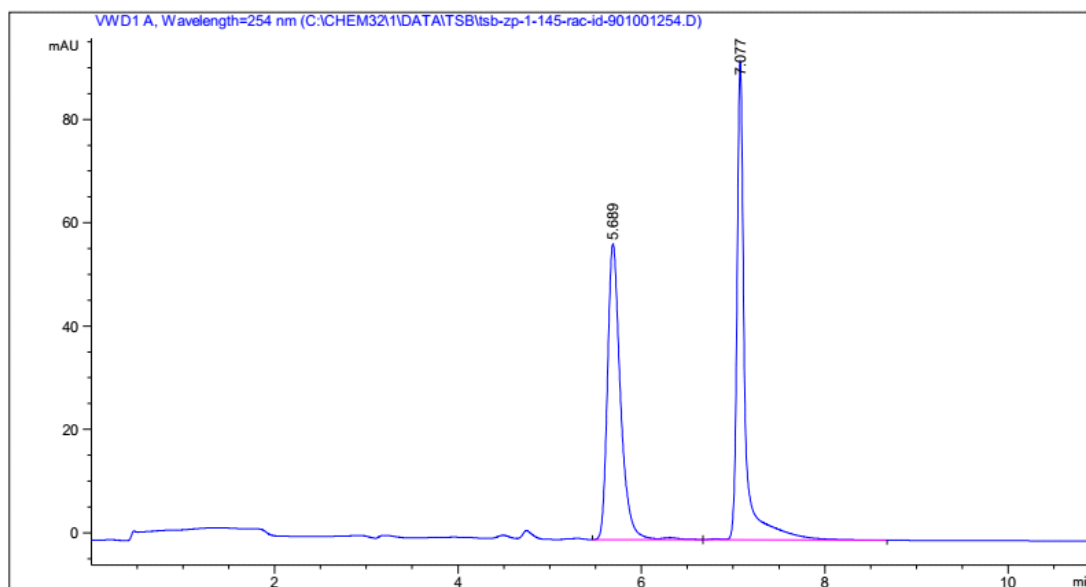
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.992	BV	0.1146	4295.67236	578.68378	49.6933
2	5.376	VB	0.1214	4348.70361	548.85614	50.3067

Enantioenriched sample 3an:



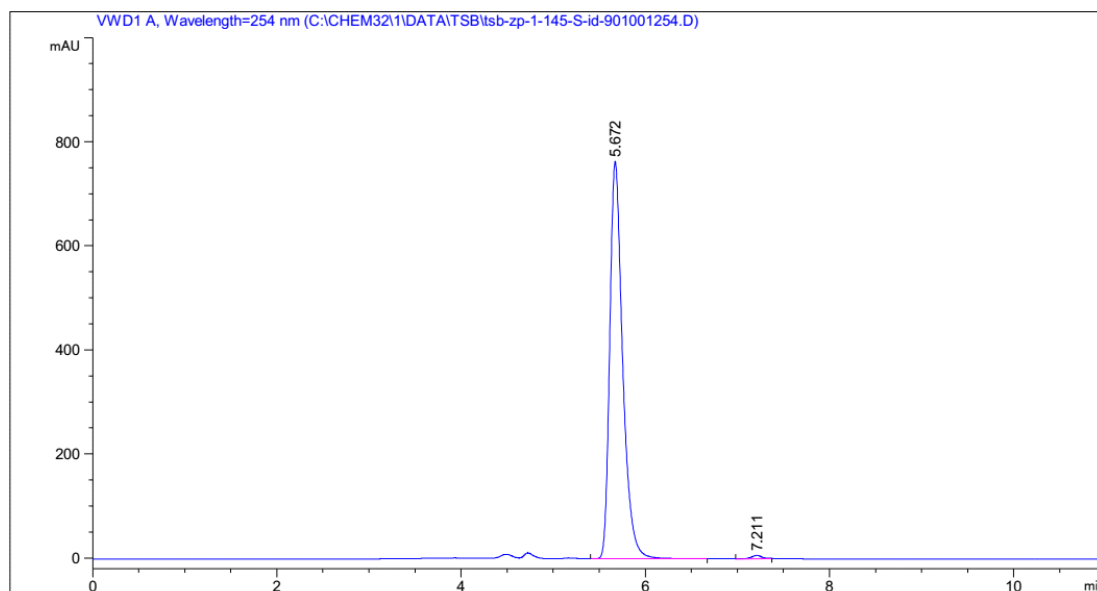
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.991	BV E	0.1193	338.81140	43.30105	2.5733
2	5.367	VB R	0.1264	1.28274e4	1585.02124	97.4267

Racemic sample 3ar: HPLC (Daicel Chiralpak ID column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



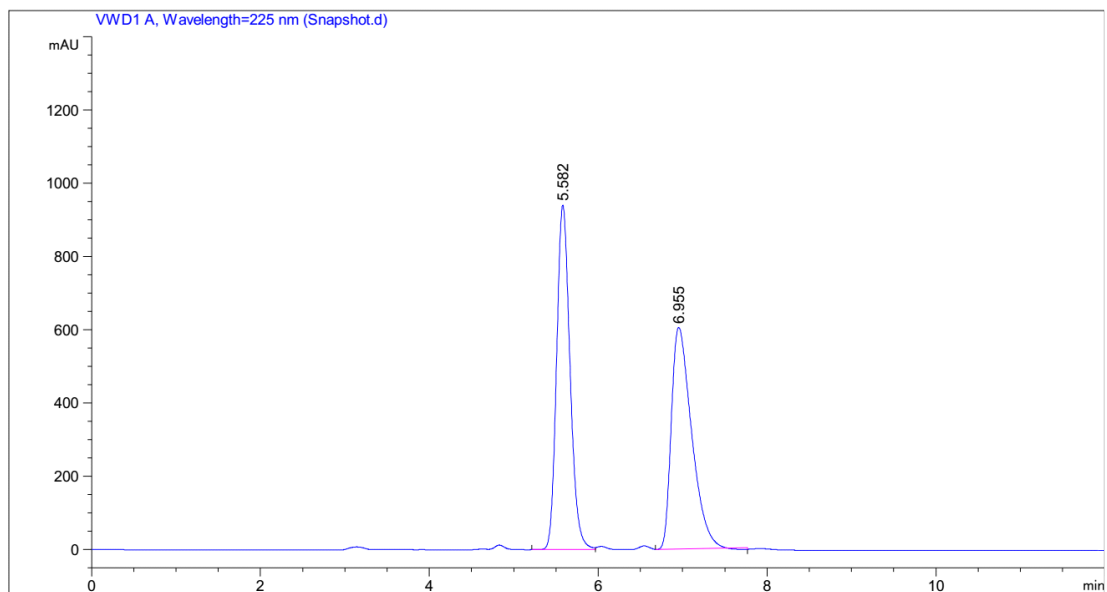
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.689	BV R	0.1475	561.51886	57.22531	50.1884
2	7.077	VB R	0.0893	557.30286	92.48210	49.8116

Enantioenriched sample 3ar



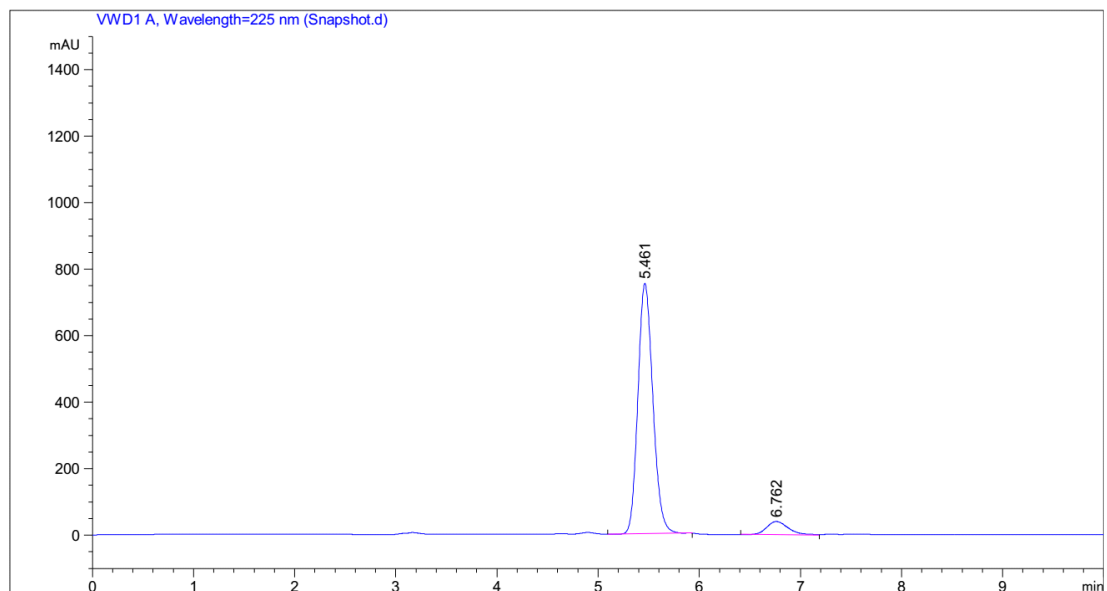
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.672	BB	0.1460	7394.72070	763.27765	99.3220
2	7.211	MM	0.1282	50.48053	6.56200	0.6780

Racemic sample 3as: HPLC (Daicel Chiralpak OD-H column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



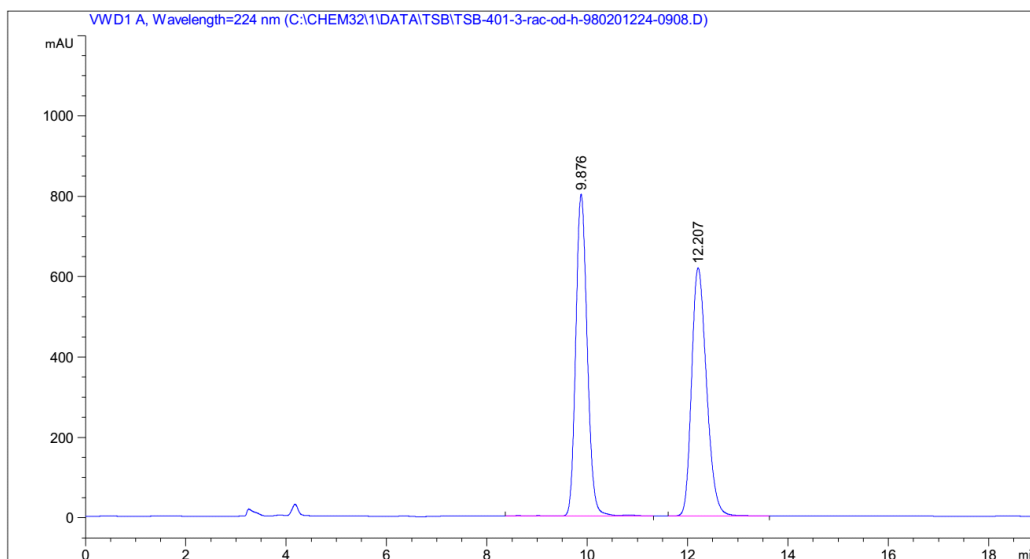
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.582	MM	0.1838	1.03719e4	940.61340	50.6554
2	6.955	MM	0.2782	1.01035e4	605.36255	49.3446

Enantioenriched sample 3as



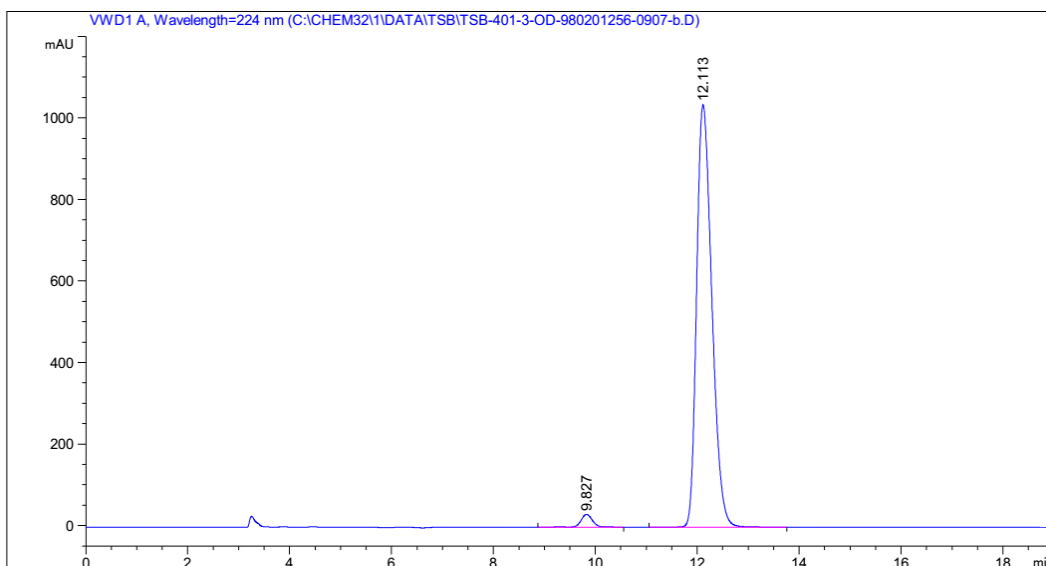
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.461	MM	0.1711	7730.61133	752.93494	93.0446
2	6.762	MM	0.2444	577.89392	39.40478	6.9554

Racemic sample 3ba: HPLC (Daicel Chiralpak OD-H column (hexane/iPrOH = 98:2, flow rate: 1.0 mL/min, $\lambda = 224$ nm)



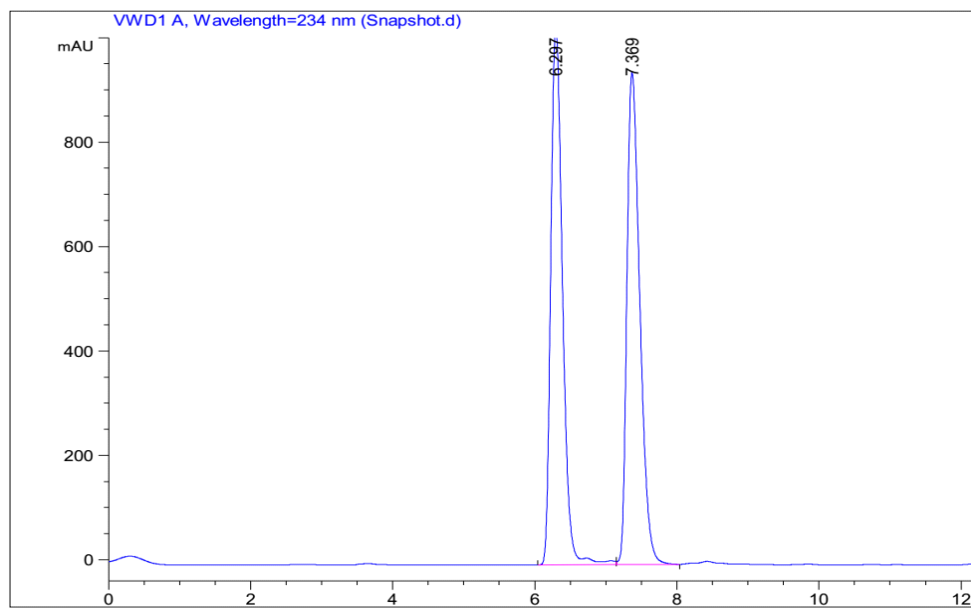
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	9.876	VV R	0.2468	1.27329e4	800.64240	49.9718
2	12.207	BB	0.3197	1.27472e4	617.86584	50.0282

Enantioenriched sample 3ba



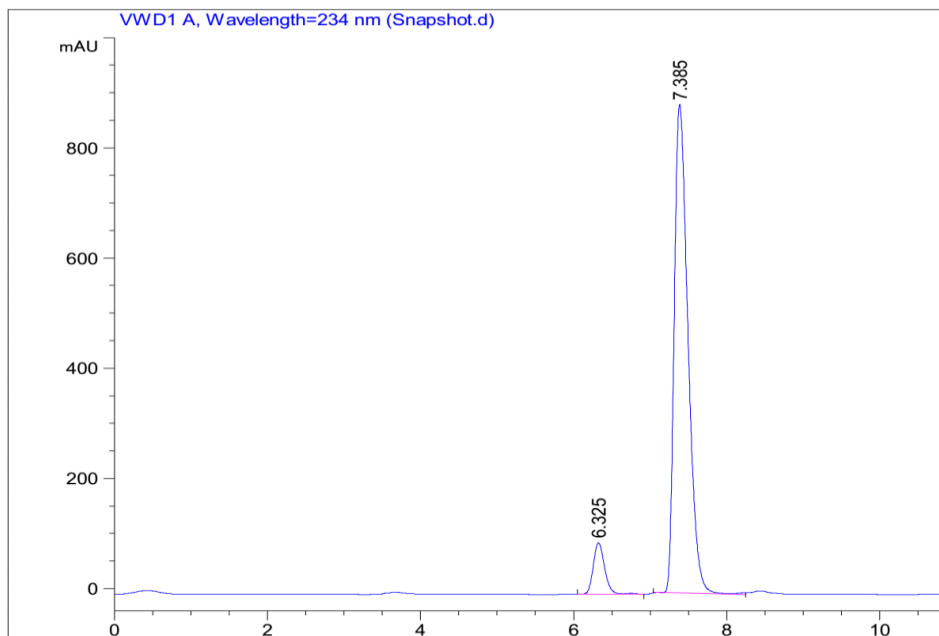
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	9.827	VB R	0.2419	491.14609	31.32950	2.2336
2	12.113	BB	0.3241	2.14981e4	1036.11121	97.7664

Racemic sample 3ca: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 98:2, flow rate: 1.0 mL/min, λ = 234 nm)



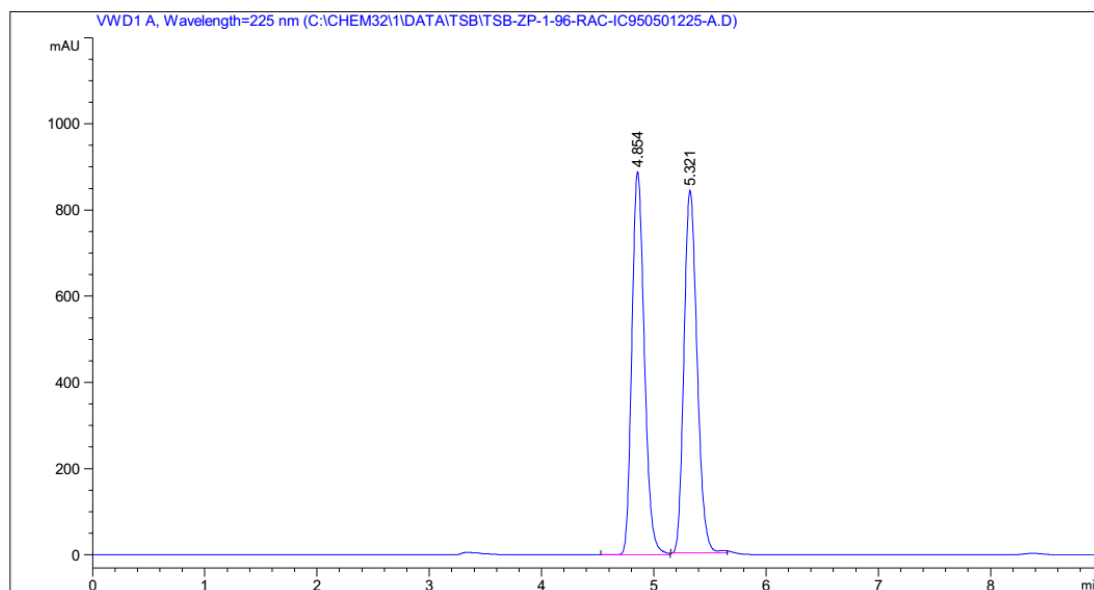
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	6.297	BV R	0.1760	1.18454e4	1033.76001	49.8816
2	7.369	VB	0.1953	1.19017e4	942.43555	50.1184

Enantioenriched sample 3ca



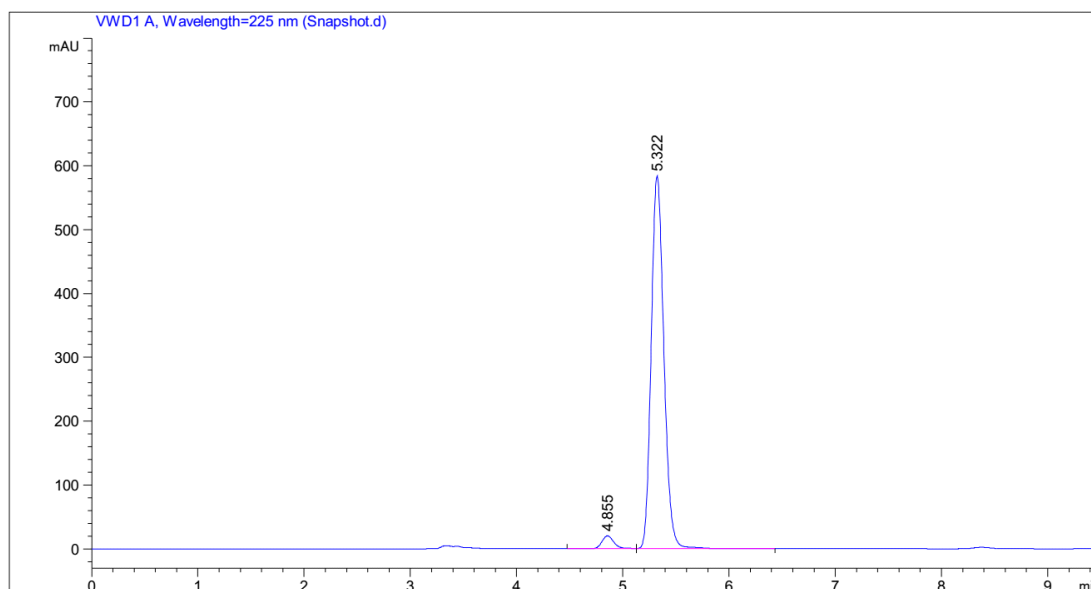
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	6.325	BV R	0.1593	963.19940	93.42186	8.0360
2	7.385	MM	0.2073	1.10229e4	886.03912	91.9640

Racemic sample 3da: HPLC: Daicel Chiralpak IC column (hexane/iPrOH = 95:5, flow rate: 1.0 mL/min, $\lambda = 225$ nm)



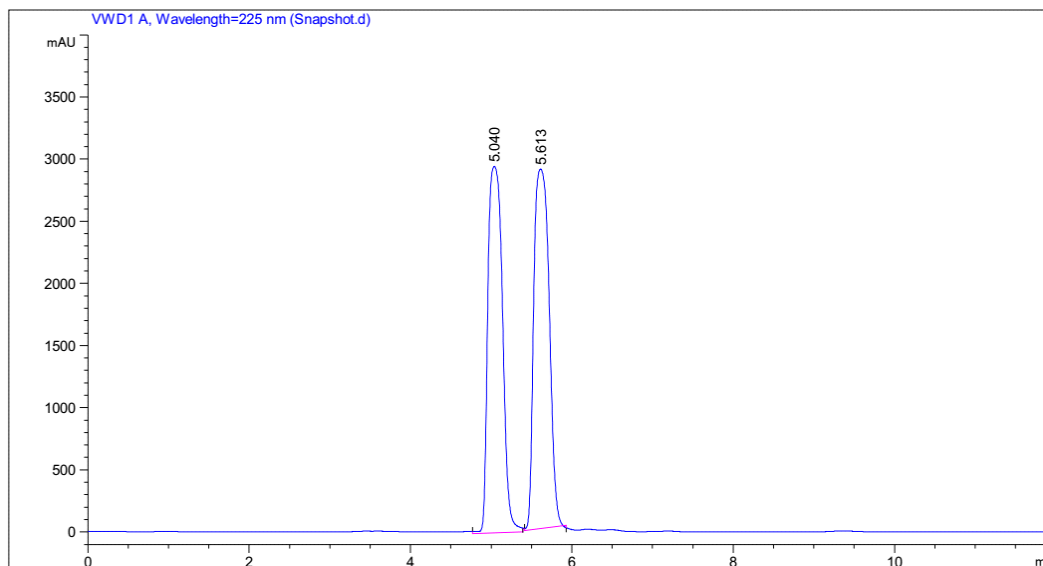
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.854	BV	0.1210	6854.69629	888.57056	50.0634
2	5.321	MM	0.1354	6837.32422	841.69513	49.9366

Enantioenriched sample 3da



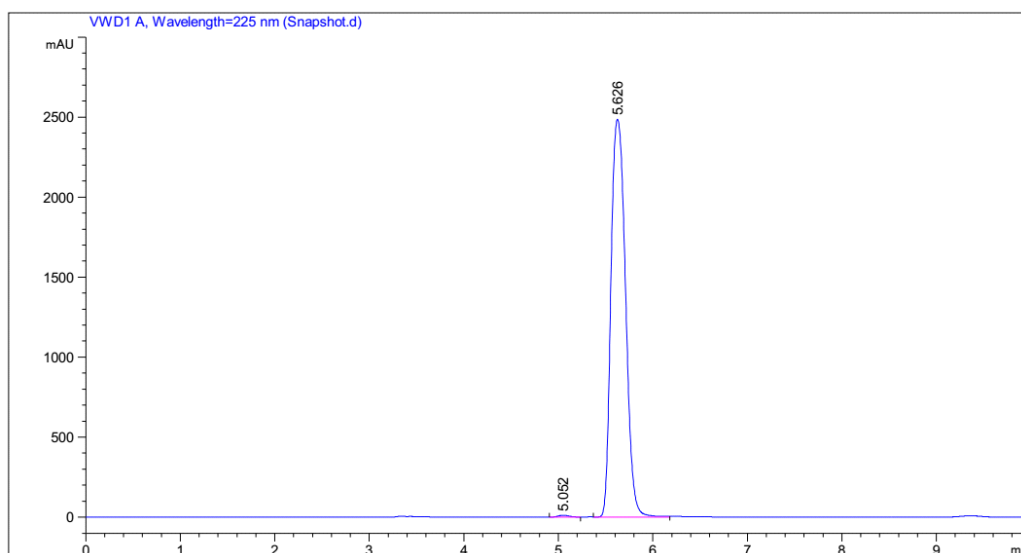
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	4.855	BV	0.1226	159.18486	20.06286	3.1925
2	5.322	VB	0.1285	4827.01416	583.80560	96.8075

Racemic sample 3ea: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 95:5, flow rate: 1.0 mL/min, $\lambda = 225$ nm)



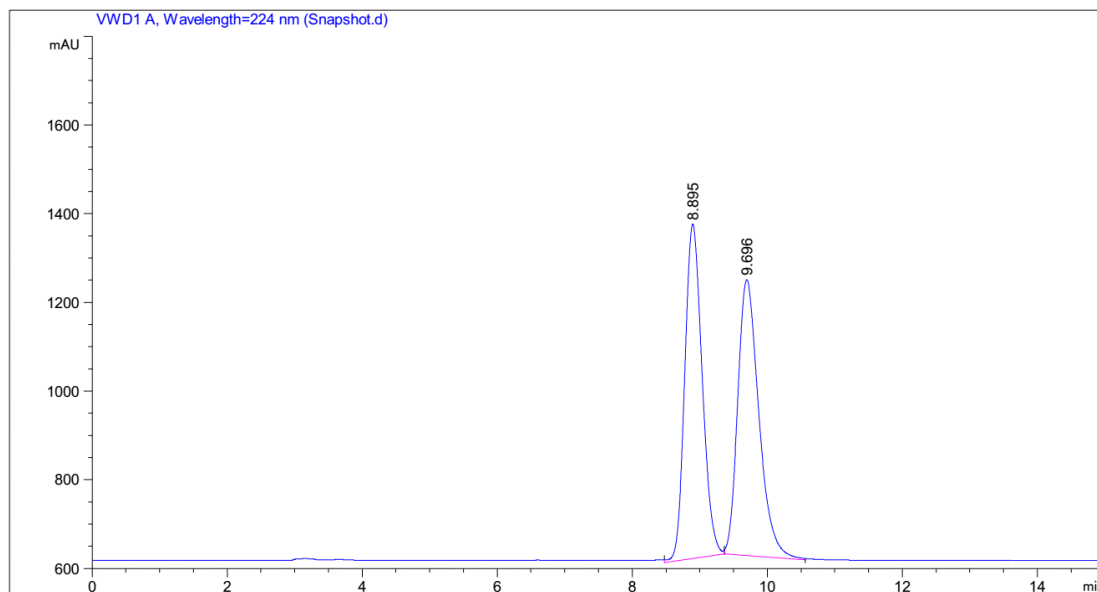
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.040	MM	0.2099	3.71554e4	2950.33813	49.3615
2	5.613	MM	0.2197	3.81166e4	2891.91699	50.6385

Enantioenriched sample 3ea



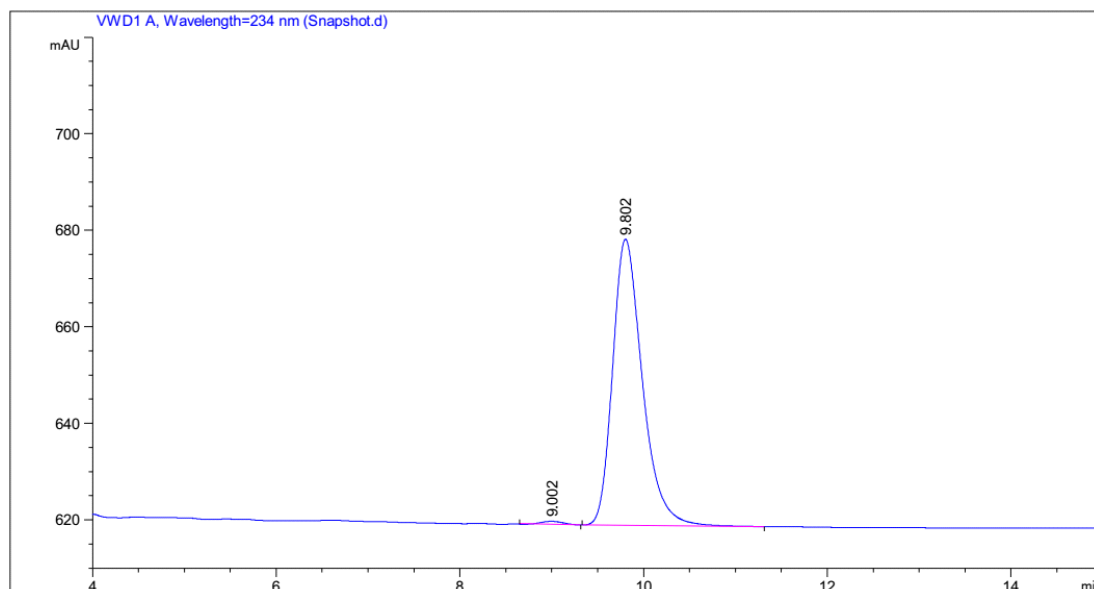
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.052	BB	0.1186	88.17324	11.60594	0.3307
2	5.626	MM	0.1782	2.65728e4	2484.87842	99.6693

Racemic sample 3fa: HPLC (Daicel Chiralpak OD-H column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 224$ nm)



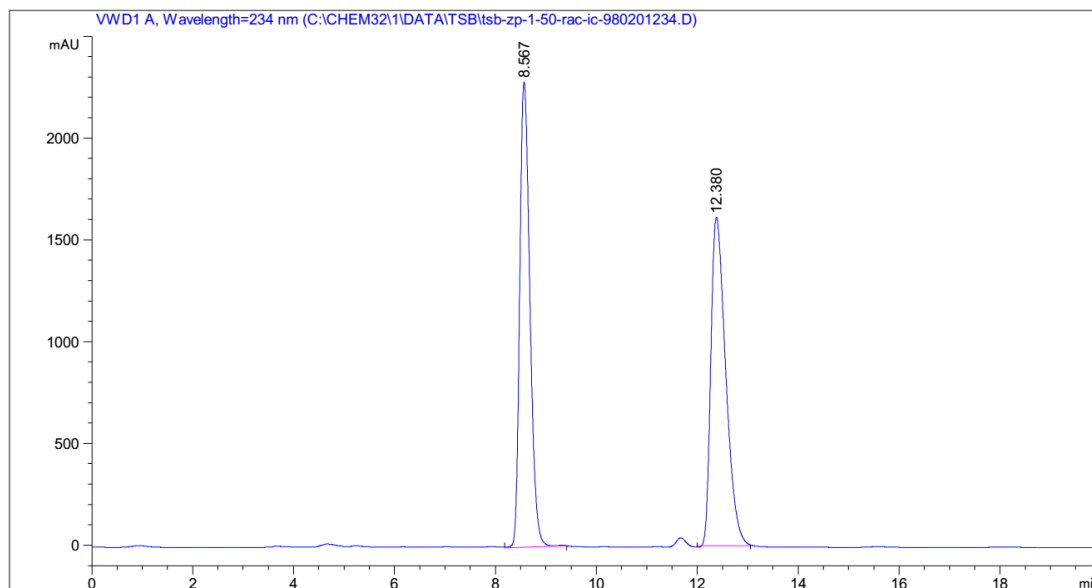
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	8.895	MM	0.2979	1.34789e4	754.03918	49.9575
2	9.696	MM	0.3617	1.35019e4	622.11243	50.0425

Enantioenriched sample 3fa



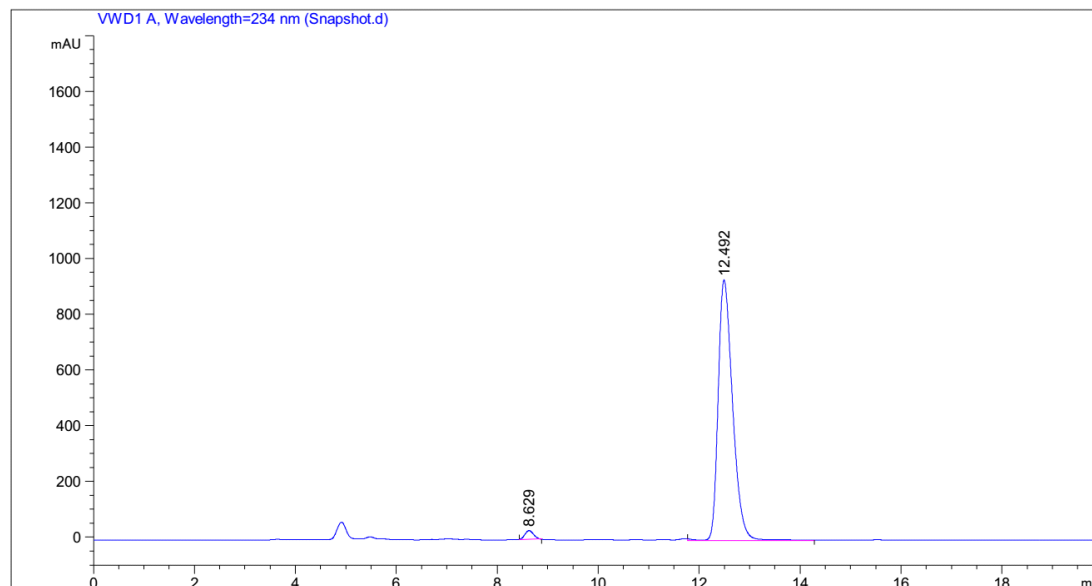
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	9.002	MM	0.2655	10.05481	6.31110e-1	0.7479
2	9.802	BB	0.3425	1334.33582	59.30146	99.2521

Racemic sample 3ga: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 98:2, flow rate: 1.0 mL/min, $\lambda = 234$ nm)



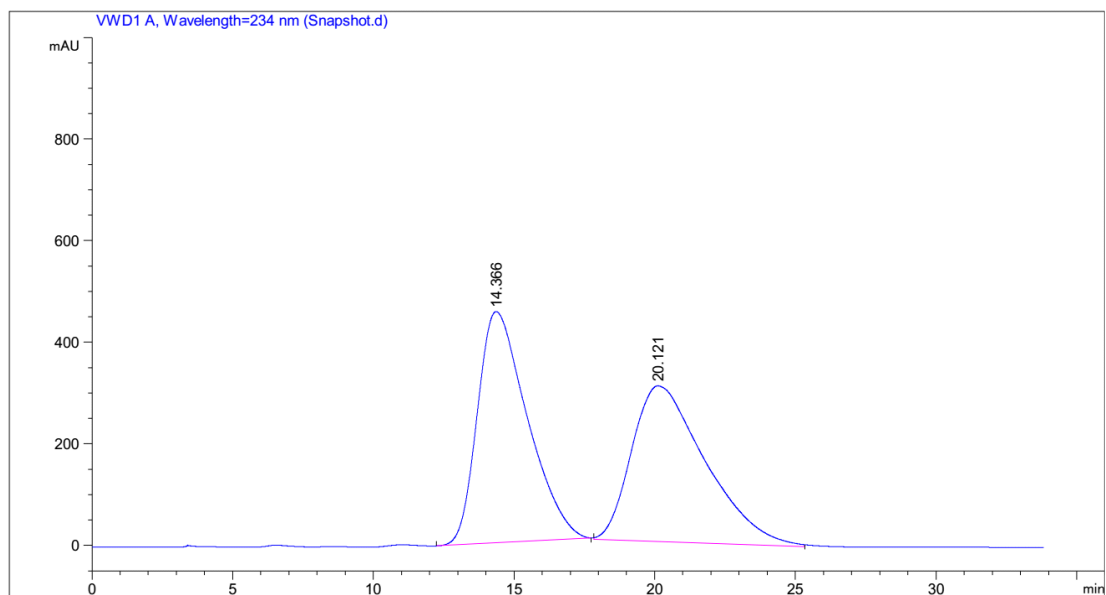
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	8.567	MM	0.2330	3.19526e4	2285.52490	49.2605
2	12.380	MM	0.3401	3.29119e4	1612.87048	50.7395

Enantioenriched sample 3ga



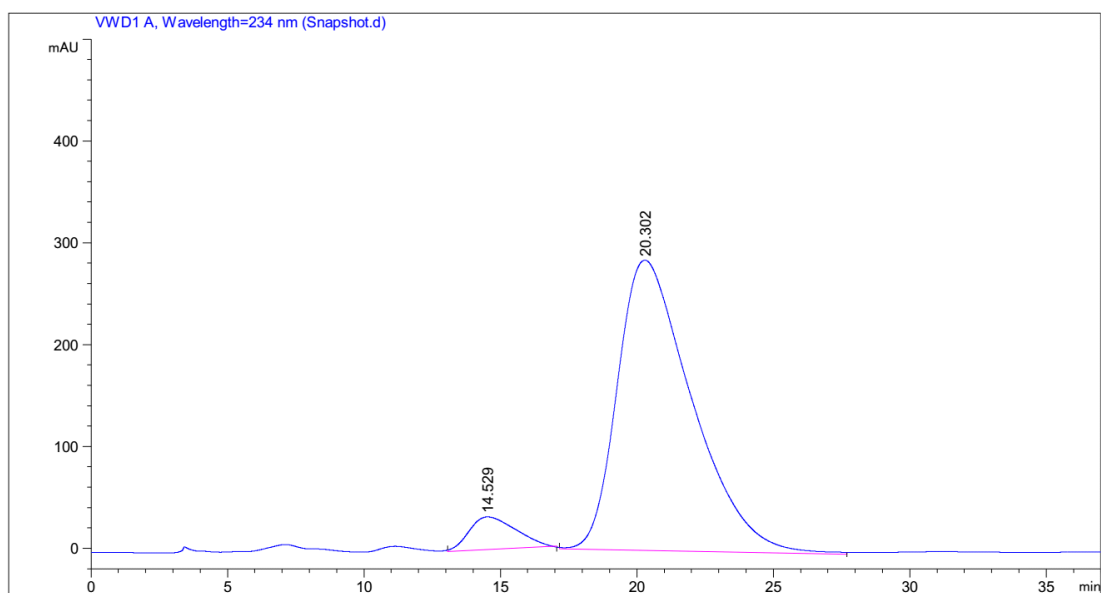
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	8.629	MM	0.1947	362.27817	31.00468	1.9074
2	12.492	MM	0.3323	1.86313e4	934.50745	98.0926

Racemic sample 3ha: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 234$ nm)



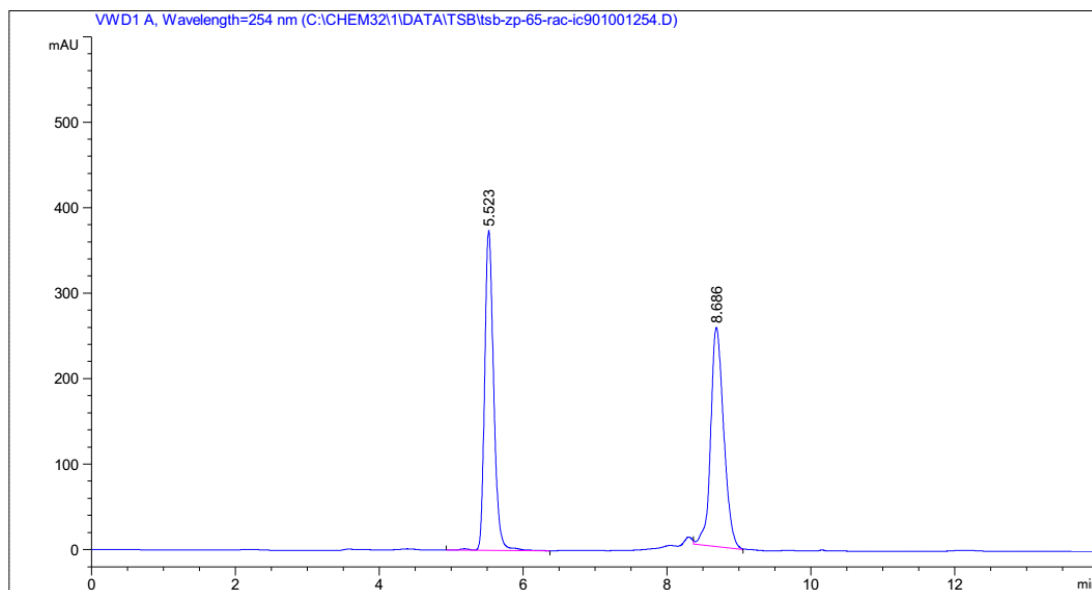
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	14.366	BB	1.7663	5.60237e4	455.37814	50.1534
2	20.121	MM	3.0289	5.56809e4	306.38831	49.8466

Enantioenriched sample 3ha



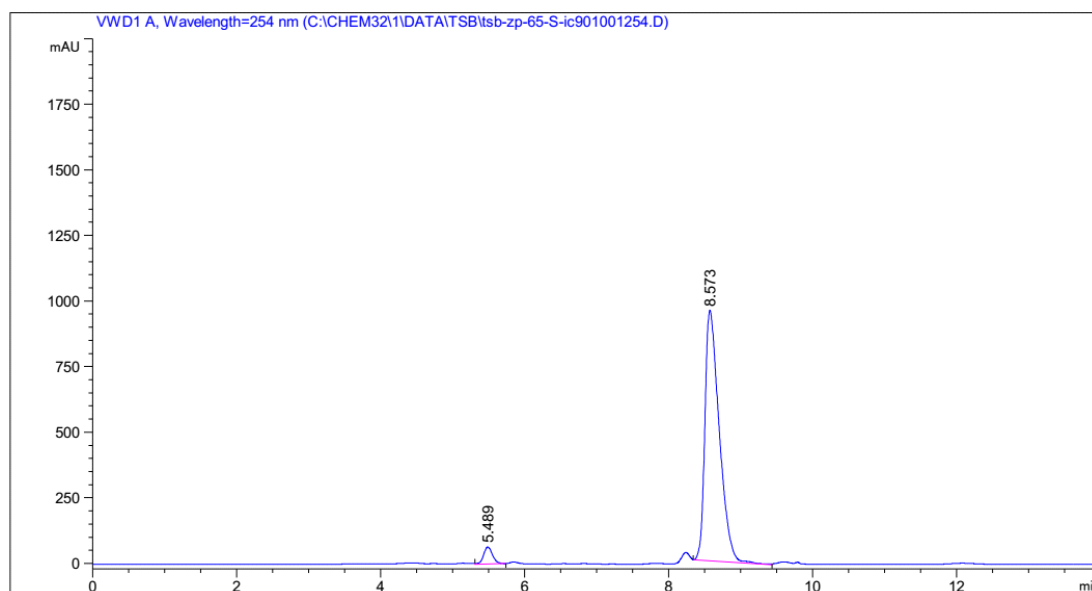
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	14.529	MM	1.9680	3784.65601	32.05178	6.5237
2	20.302	MM	3.1714	5.42296e4	284.98914	93.4763

Racemic sample 3ia: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



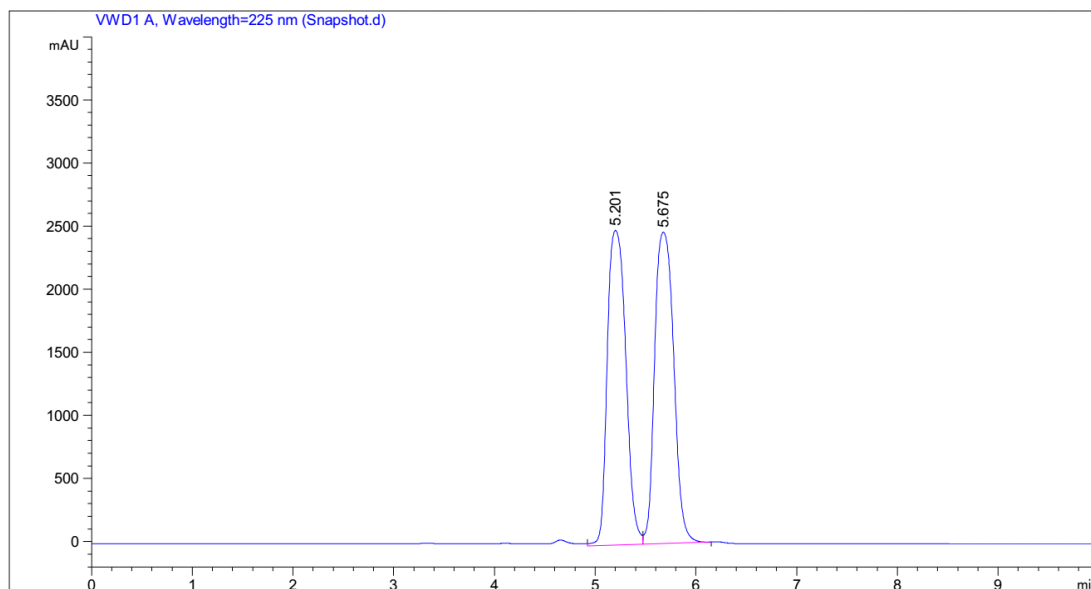
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.523	VB R	0.1331	3258.14771	374.06778	50.1689
2	8.686	MM	0.2102	3236.21045	256.54895	49.8311

Enantioenriched sample 3ia



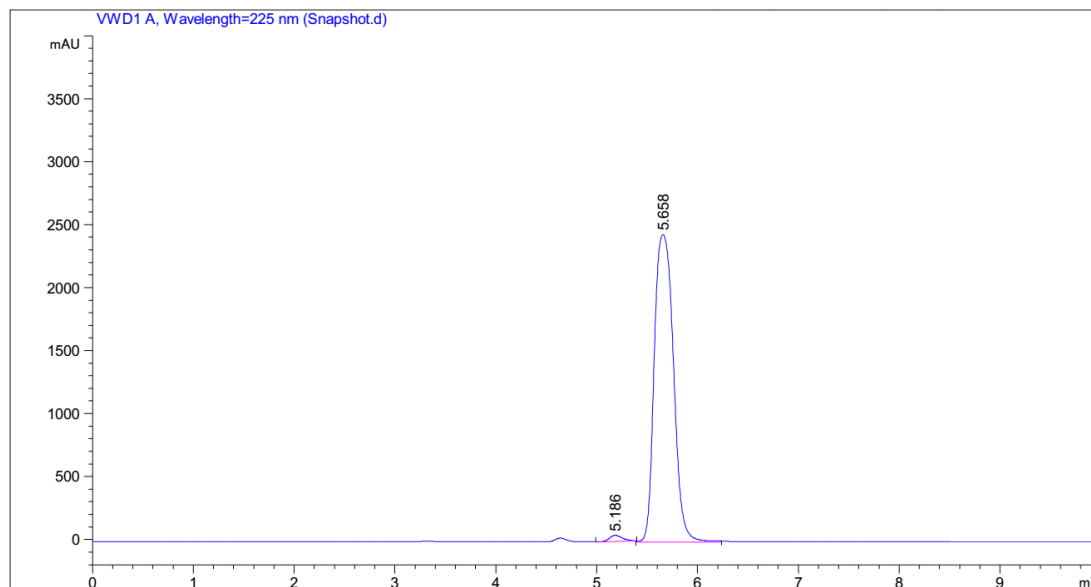
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.489	MM	0.1427	553.73529	64.67613	4.0299
2	8.573	MM	0.2302	1.31868e4	954.93646	95.9701

Racemic sample 3ja: HPLC (Daicel Chiralpak IA column (hexane/iPrOH = 98:2, flow rate: 1.0 mL/min, $\lambda = 225$ nm)



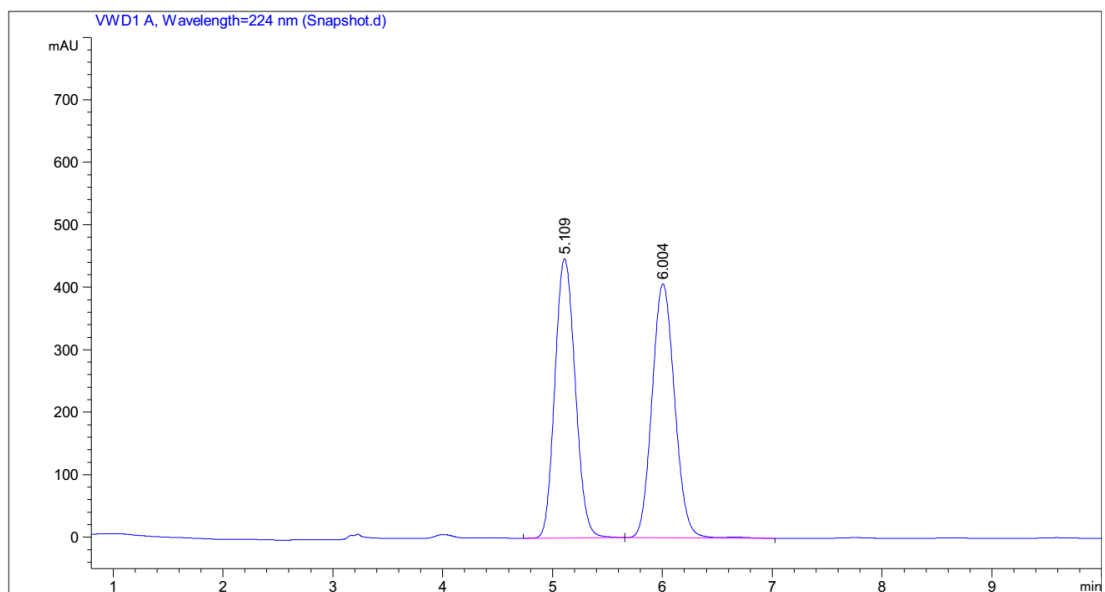
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.201	MF	0.2125	3.17912e4	2493.34839	49.5392
2	5.675	FM	0.2187	3.23827e4	2467.29688	50.4608

Enantioenriched sample 3ja



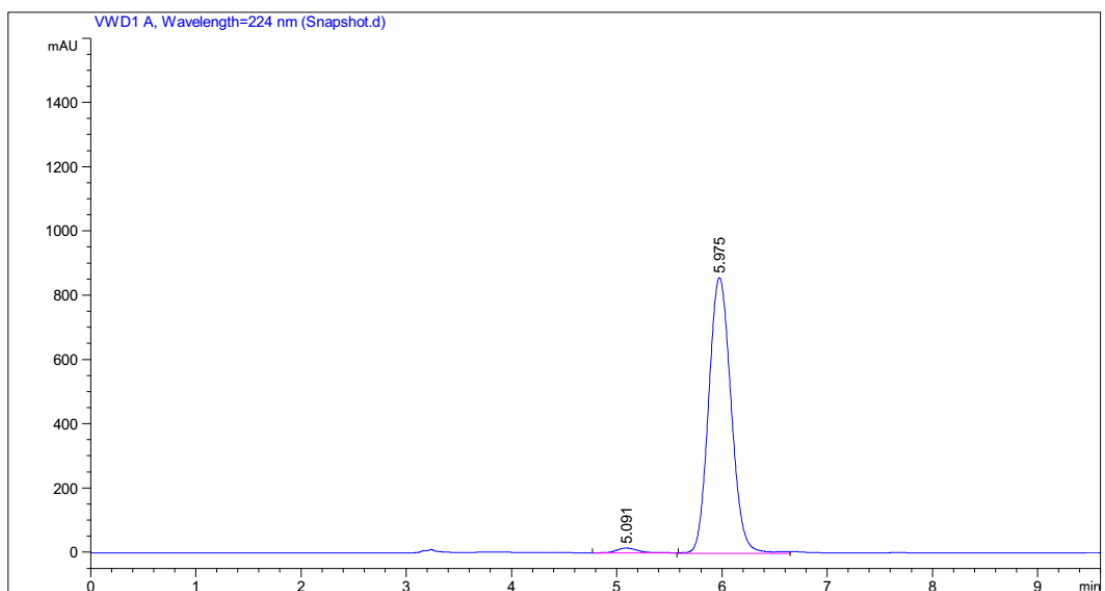
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.186	MM	0.1471	427.08121	48.38269	1.3069
2	5.658	MM	0.2201	3.22510e4	2442.00464	98.6931

Racemic sample 3ka: HPLC (Daicel Chiralpak OD-H column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda=224$ nm)



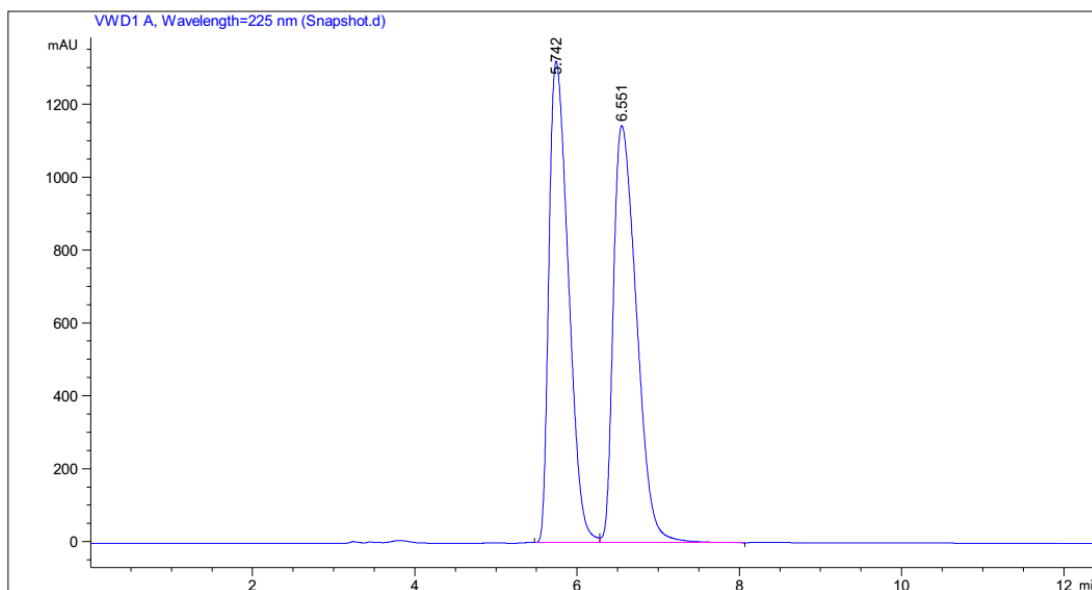
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.109	BB	0.2026	5731.81152	446.95035	49.6701
2	6.004	BV R	0.2239	5807.95166	406.15750	50.3299

Enantioenriched sample 3ka



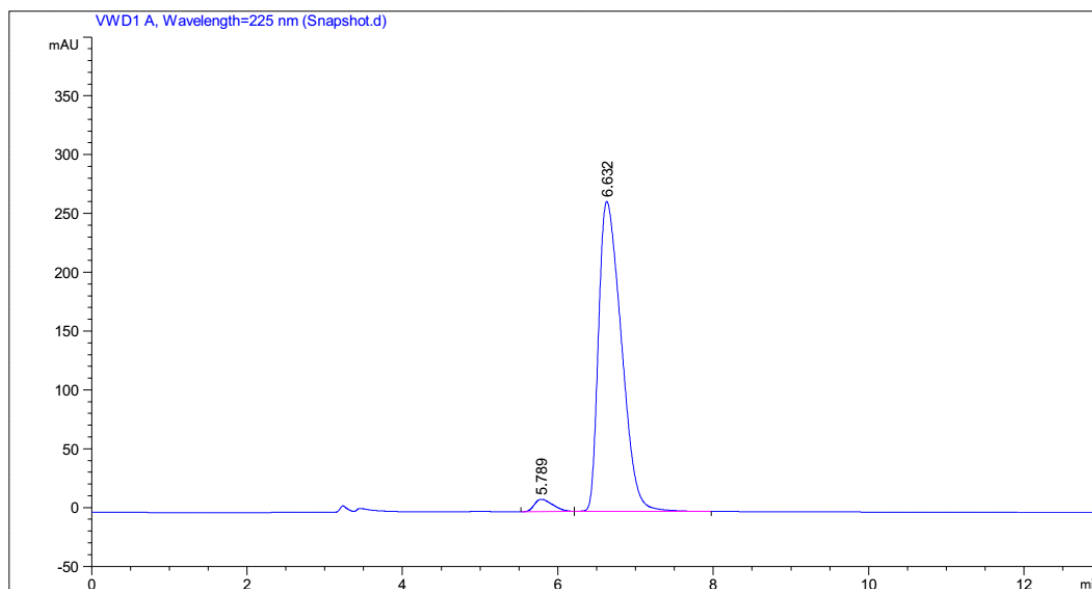
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.091	BV	0.2120	197.38728	14.57574	1.5340
2	5.975	MM	0.2462	1.26698e4	857.74286	98.4660

Racemic sample 3la: HPLC (Daicel Chiralpak ID column (hexane/iPrOH = 99:1, flow rate: 1.0 mL/min, $\lambda=225$ nm)



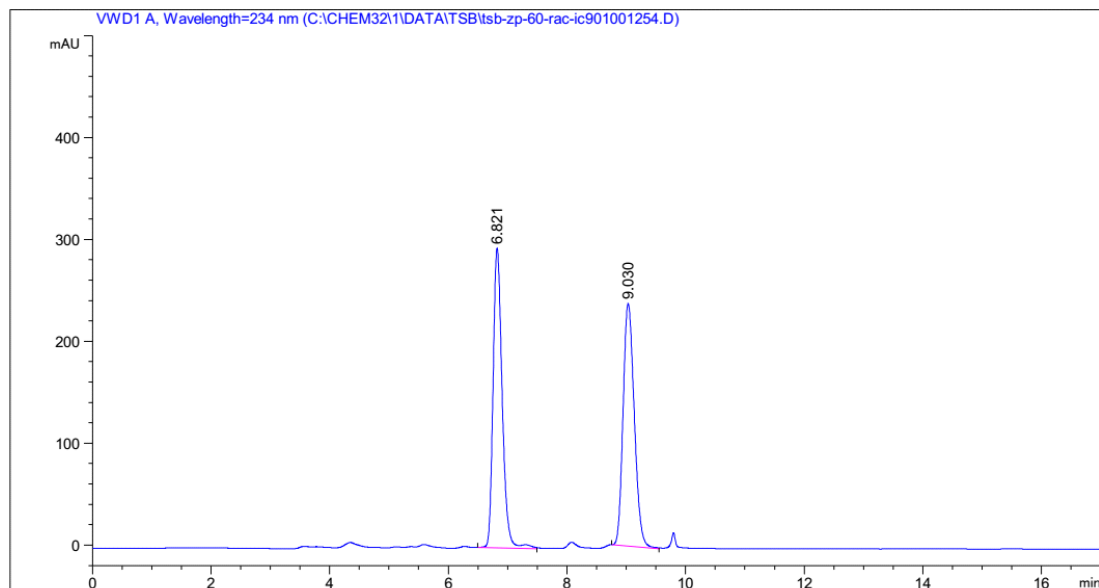
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.742	BV	0.2655	2.18991e4	1320.29614	49.1397
2	6.551	VB	0.3191	2.26659e4	1144.37134	50.8603

Enantioenriched sample 3la



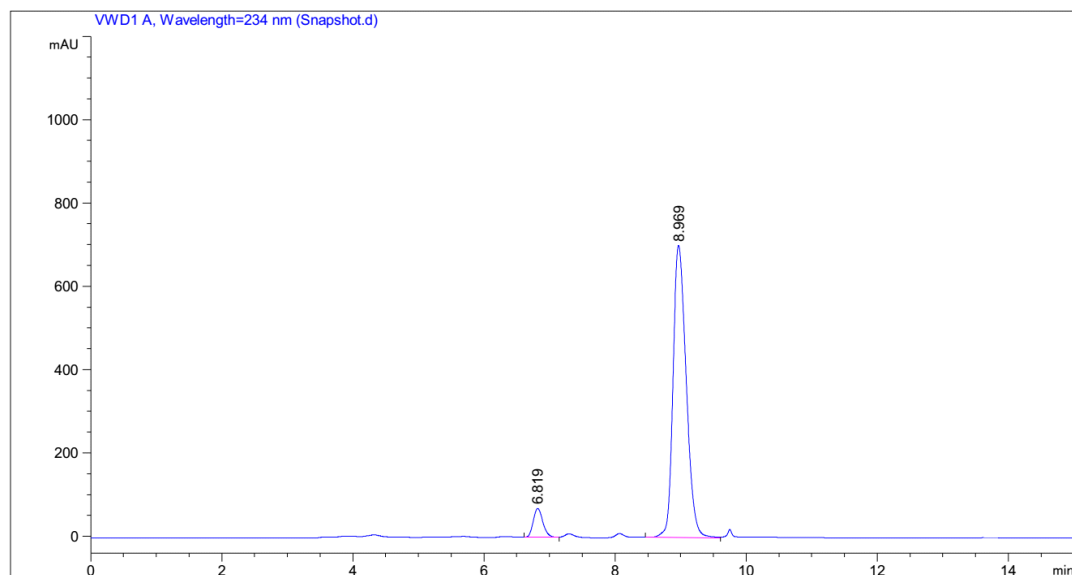
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	5.789	BB	0.2508	166.12143	10.42877	3.0165
2	6.632	BB	0.3296	5340.97705	263.35590	96.9835

Racemic sample 3ma: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



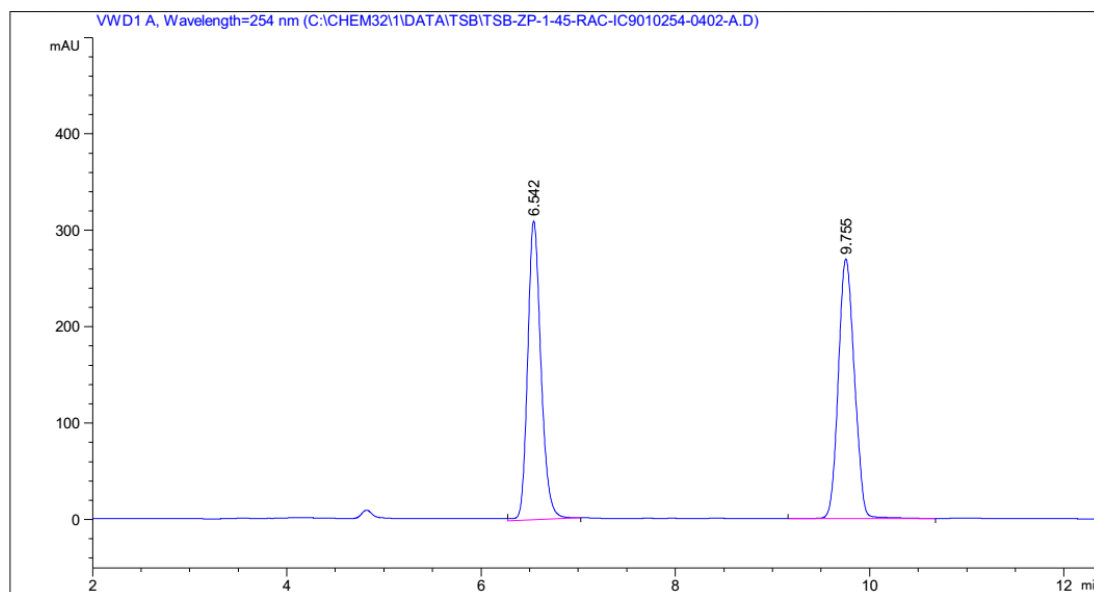
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	6.821	MM	0.1776	3132.41113	293.98260	50.1178
2	9.030	MM	0.2183	3117.68823	238.07489	49.8822

Enantioenriched sample 3ma



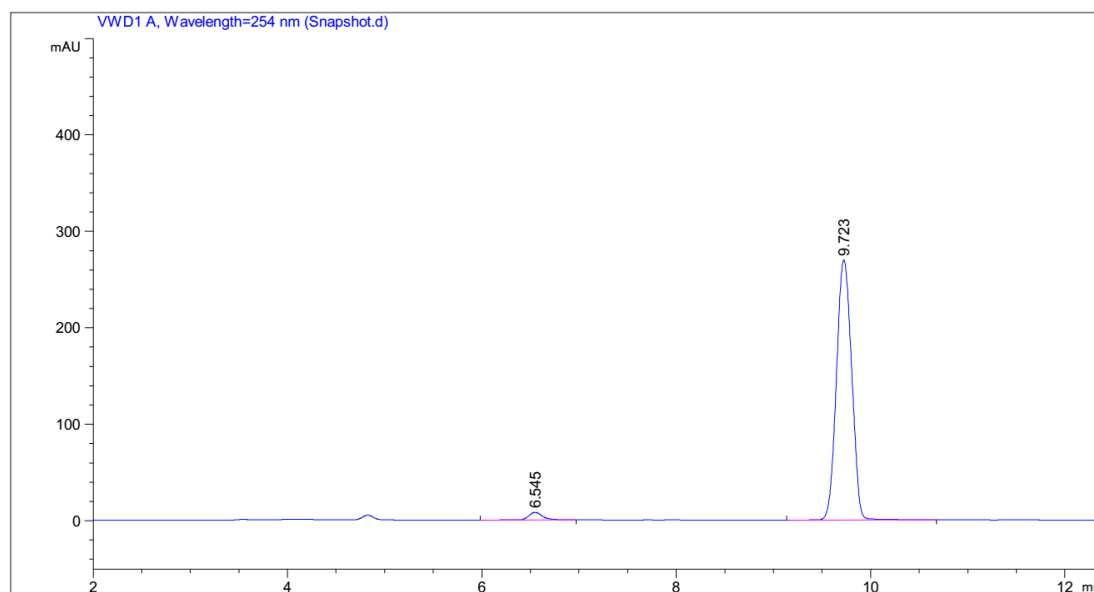
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	6.819	MM	0.1654	679.97943	68.50309	6.5137
2	8.969	MM	0.2322	9759.23730	700.63928	93.4863

Racemic sample 3na: HPLC (Daicel Chiralpak IC column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 254$ nm)



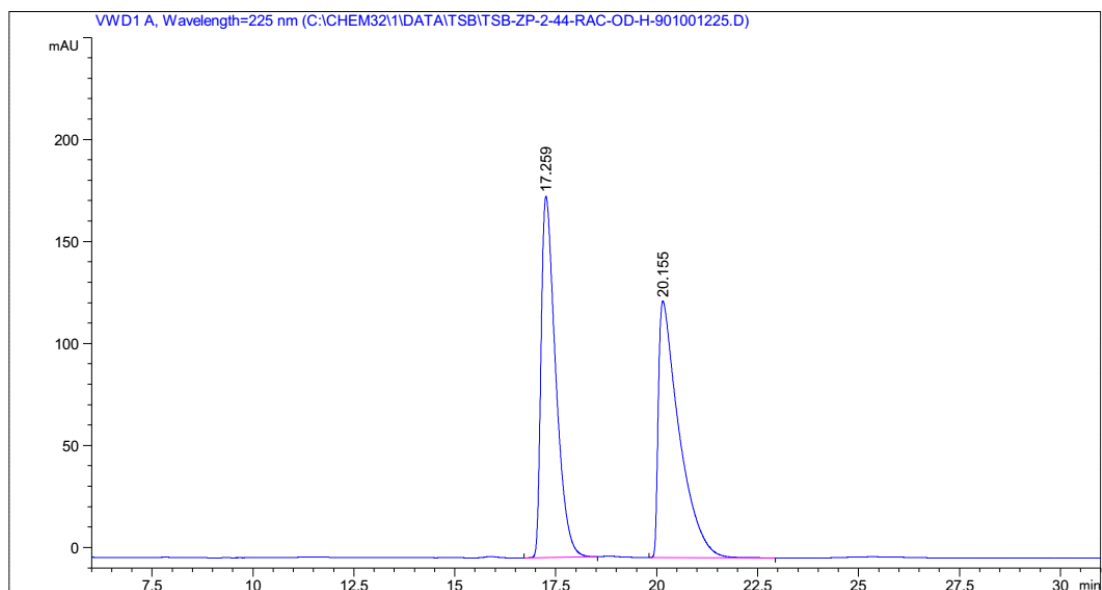
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	6.542	MM	0.1583	2945.53979	310.12479	48.7028
2	9.755	BB	0.1773	3102.45313	269.44174	51.2972

Enantioenriched sample 3na



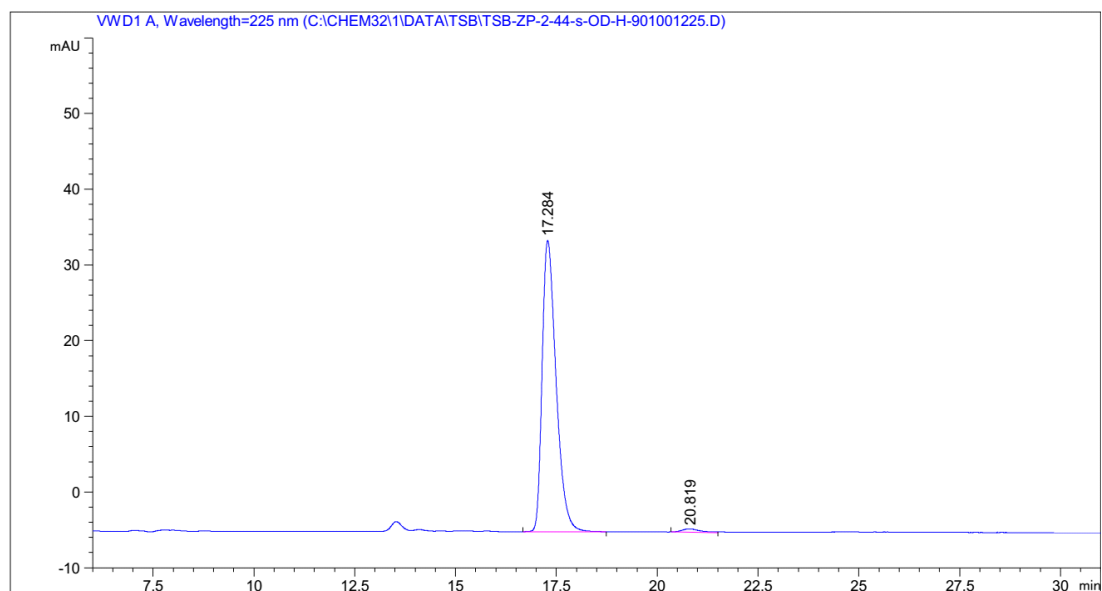
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	6.545	VB R	0.1564	81.20518	7.86732	2.6897
2	9.723	BB	0.1721	2937.91357	269.58154	97.3103

Racemic sample 7: HPLC (Daicel Chiralpak OD column (hexane/iPrOH = 90:10, flow rate: 1.0 mL/min, $\lambda = 224$ nm)

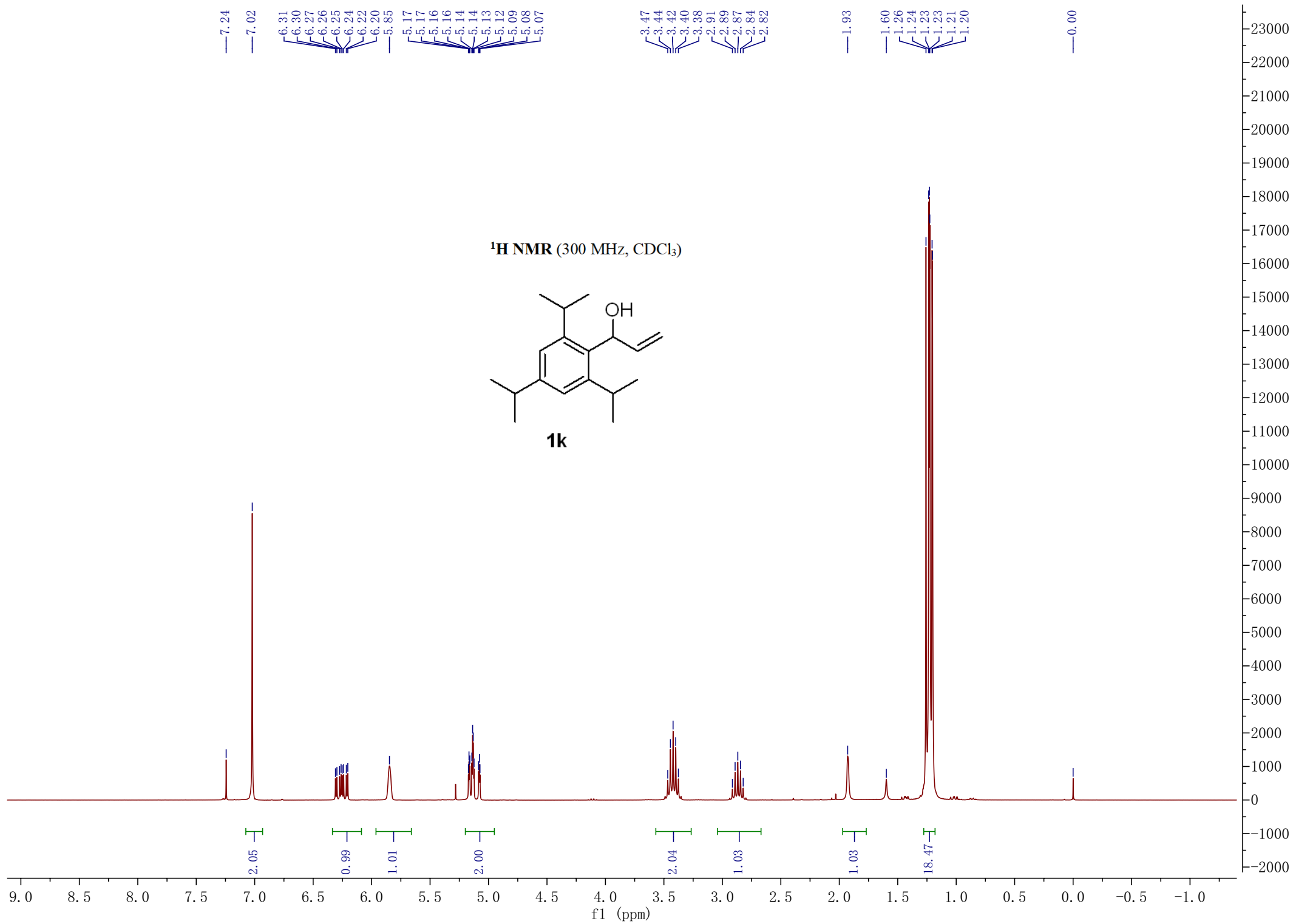


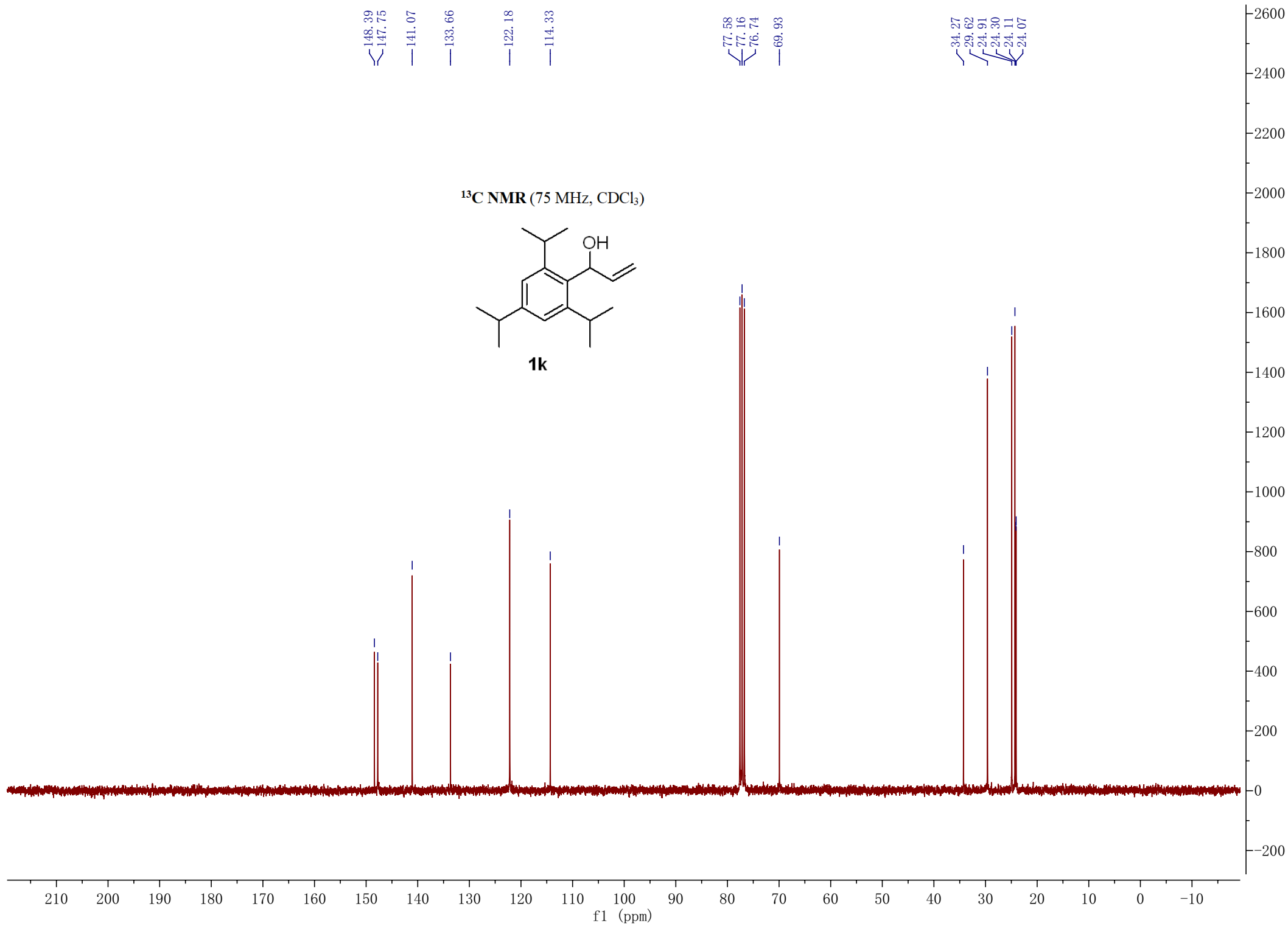
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	22.643	BV	0.5558	7019.26758	189.19167	49.8638
2	24.060	VB	0.7345	7057.61279	133.76520	50.1362

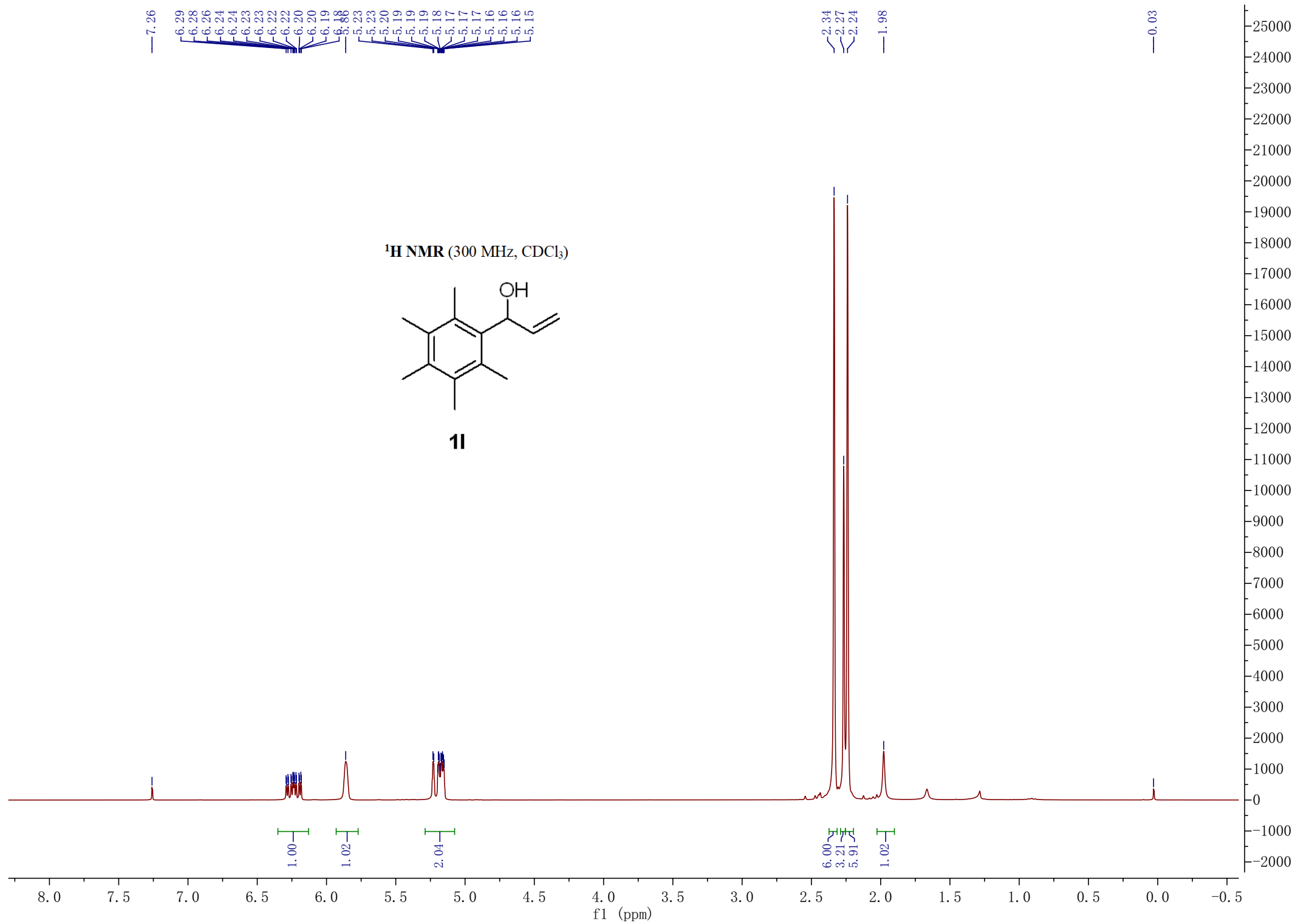
Enantioenriched sample 7



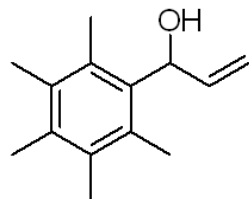
Peak Name	RT [min]	Type	width [min]	Area [mAU*s]	Height [mAu]	Area ratio %
1	22.675	BB	0.5514	4986.94482	134.87524	98.2886
2	25.206	BB	0.5374	86.83026	2.46252	1.7114







¹³C NMR (75 MHz, CDCl₃)



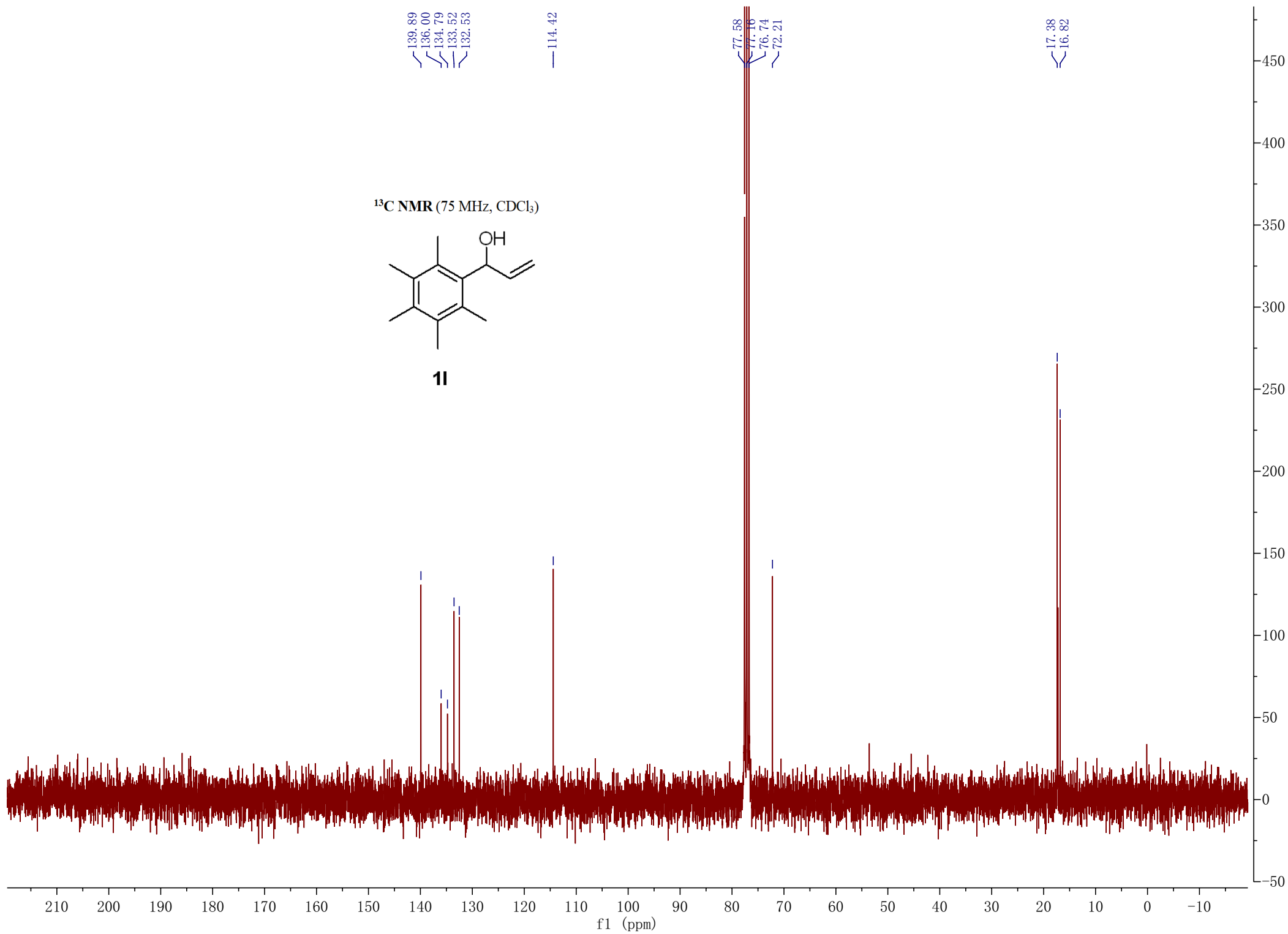
11

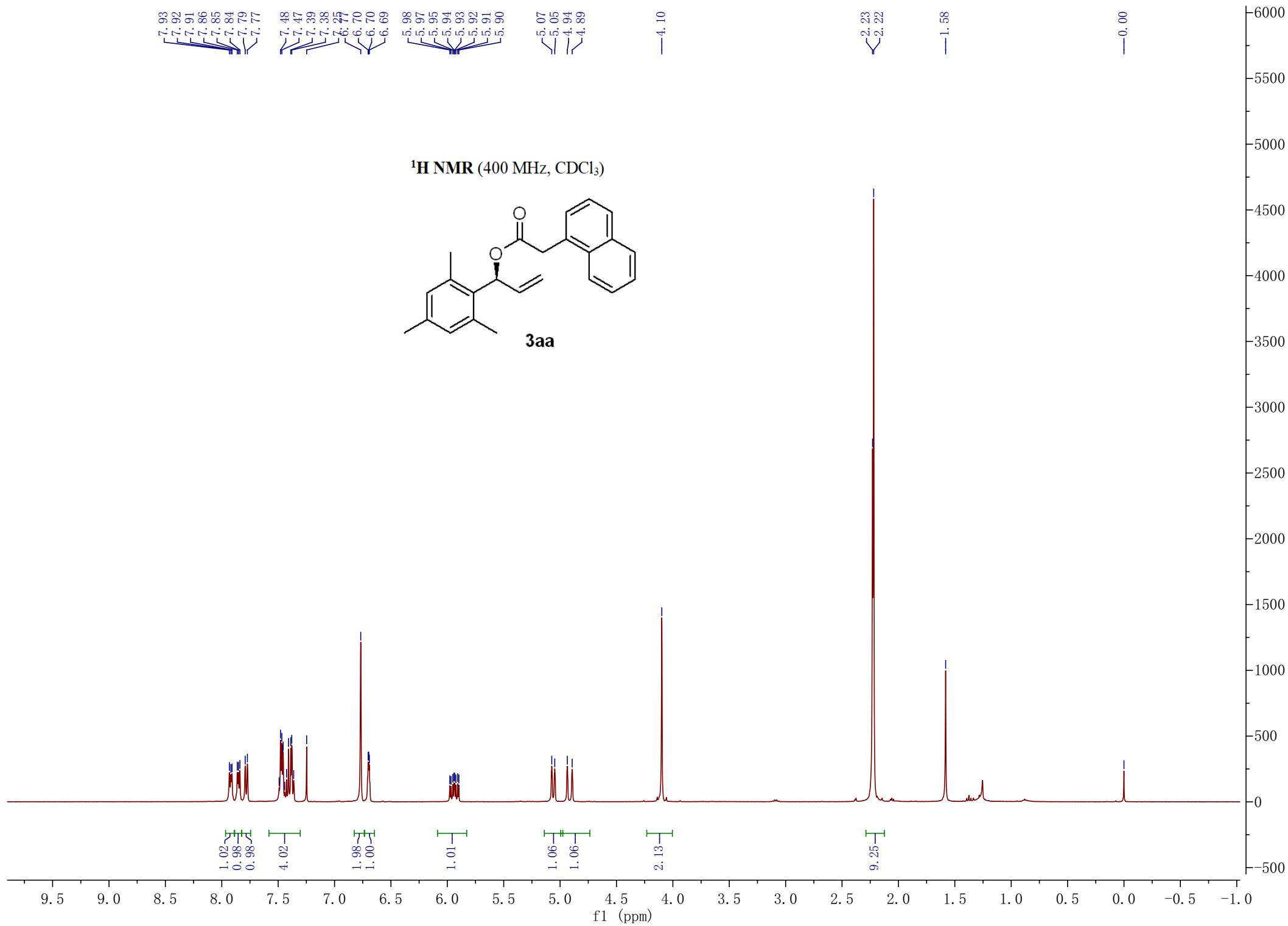
139.89
136.00
134.79
133.52
132.53

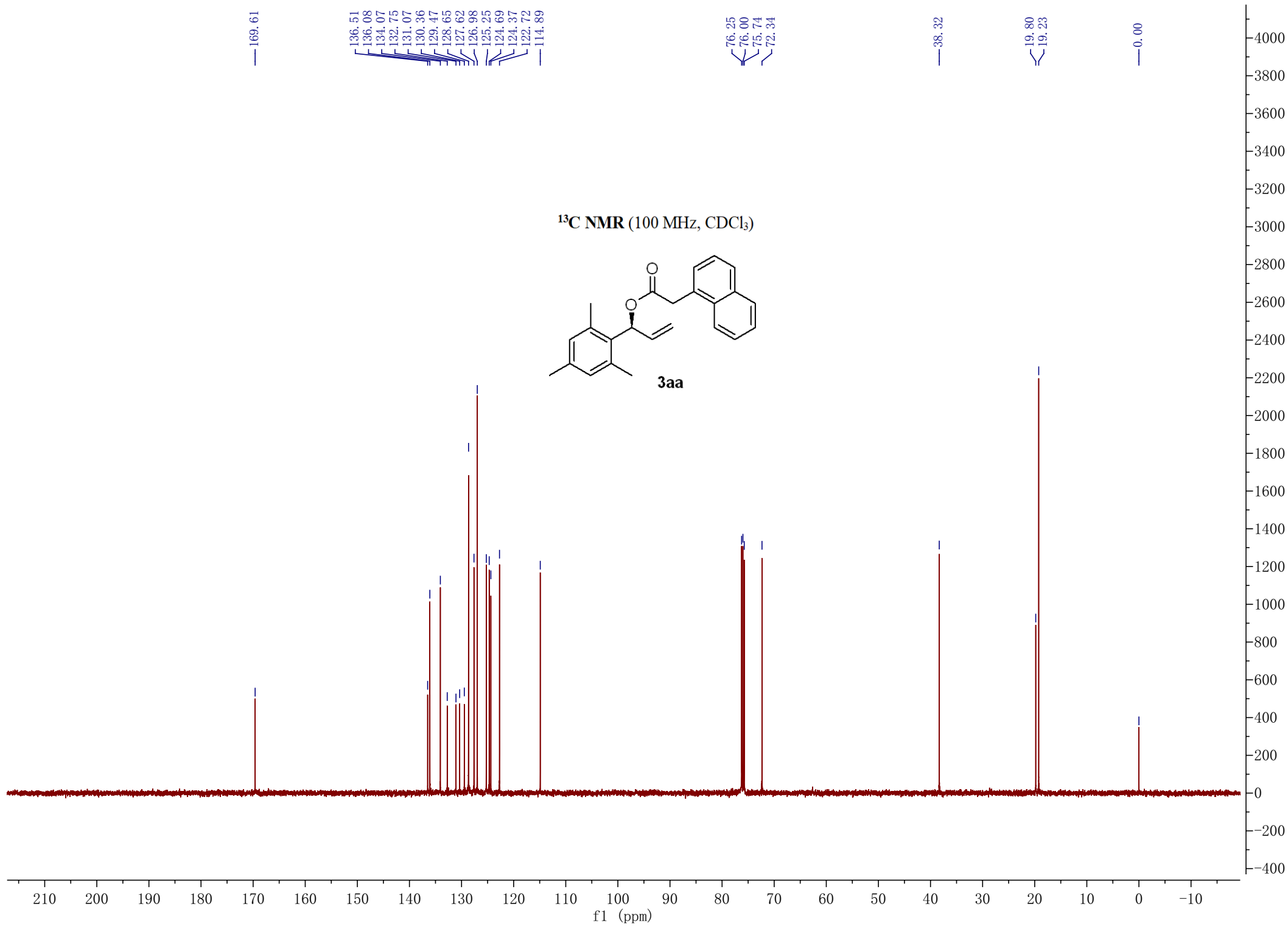
114.42

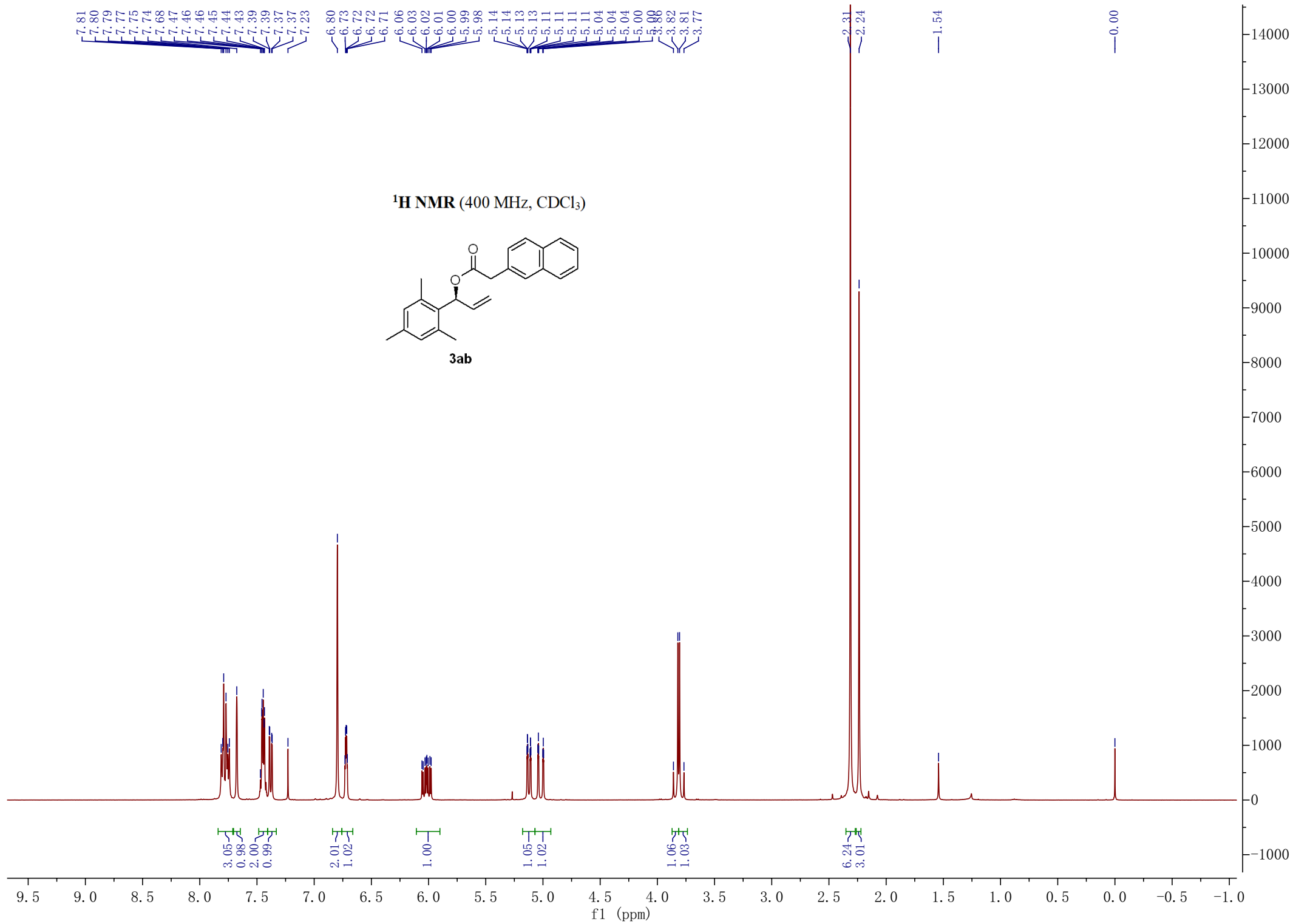
77.58
77.10
76.74
72.21

17.38
16.82

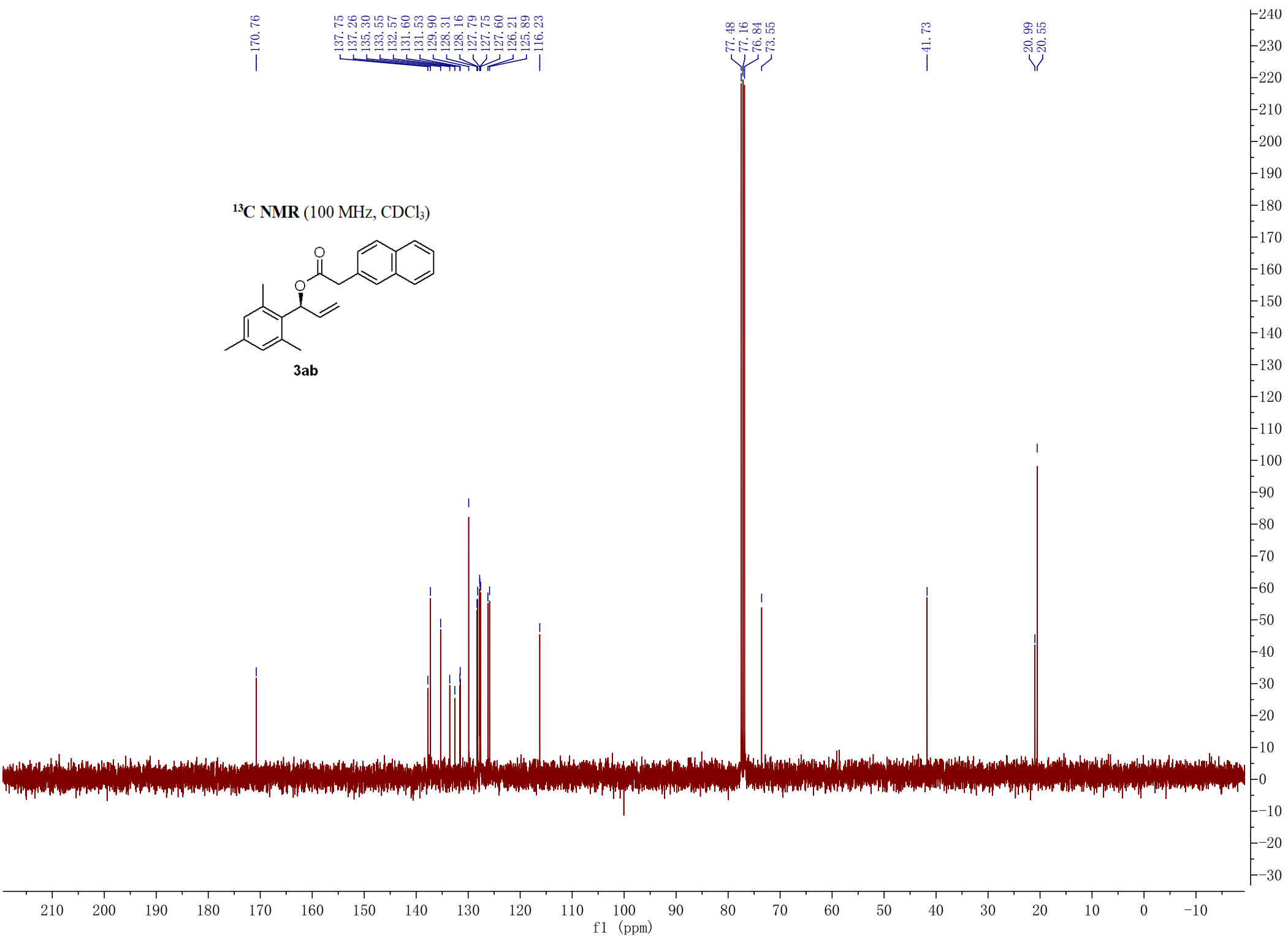
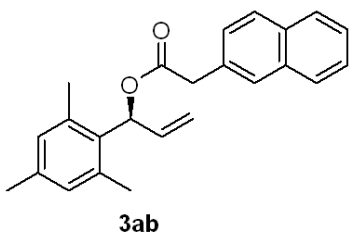


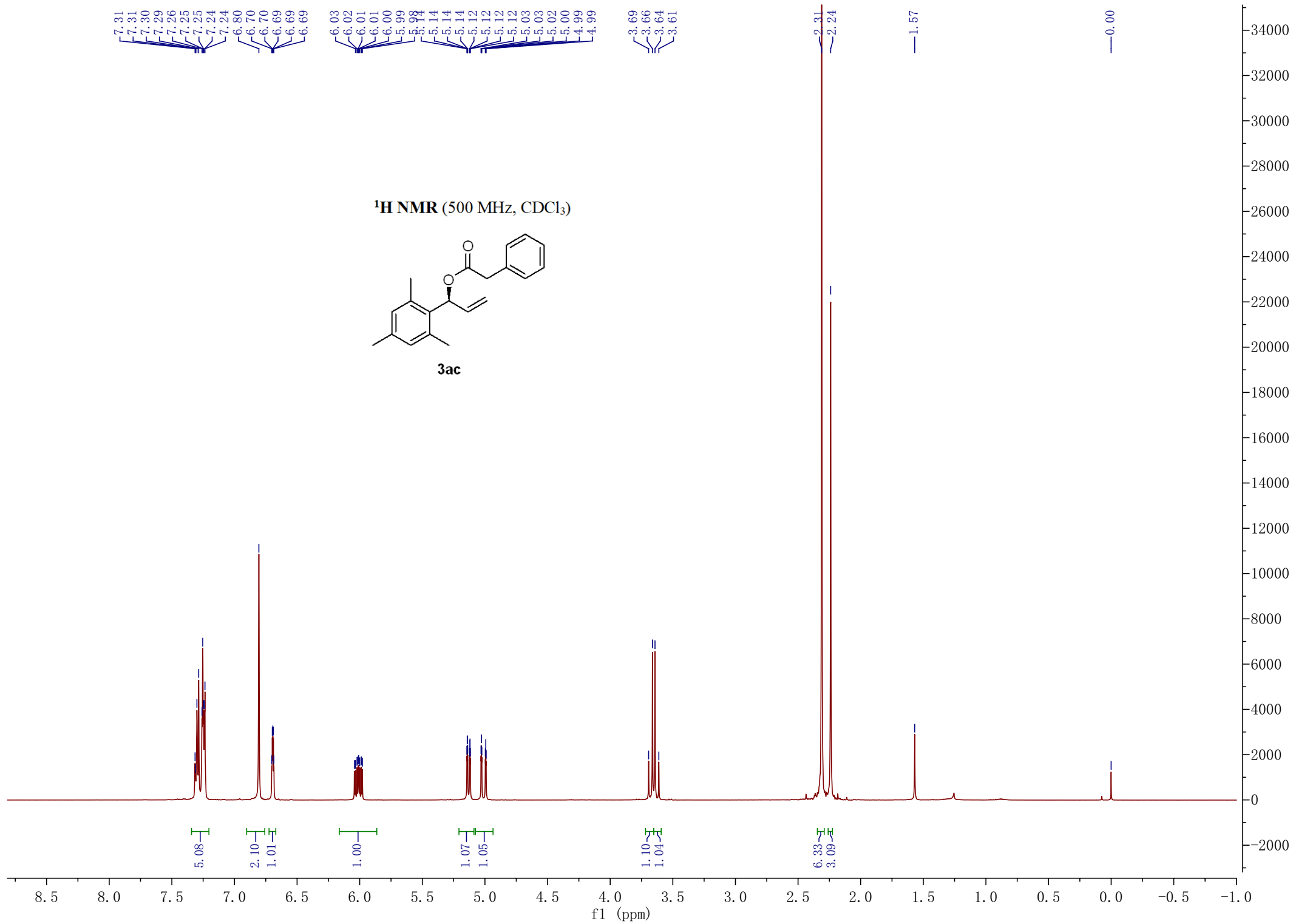


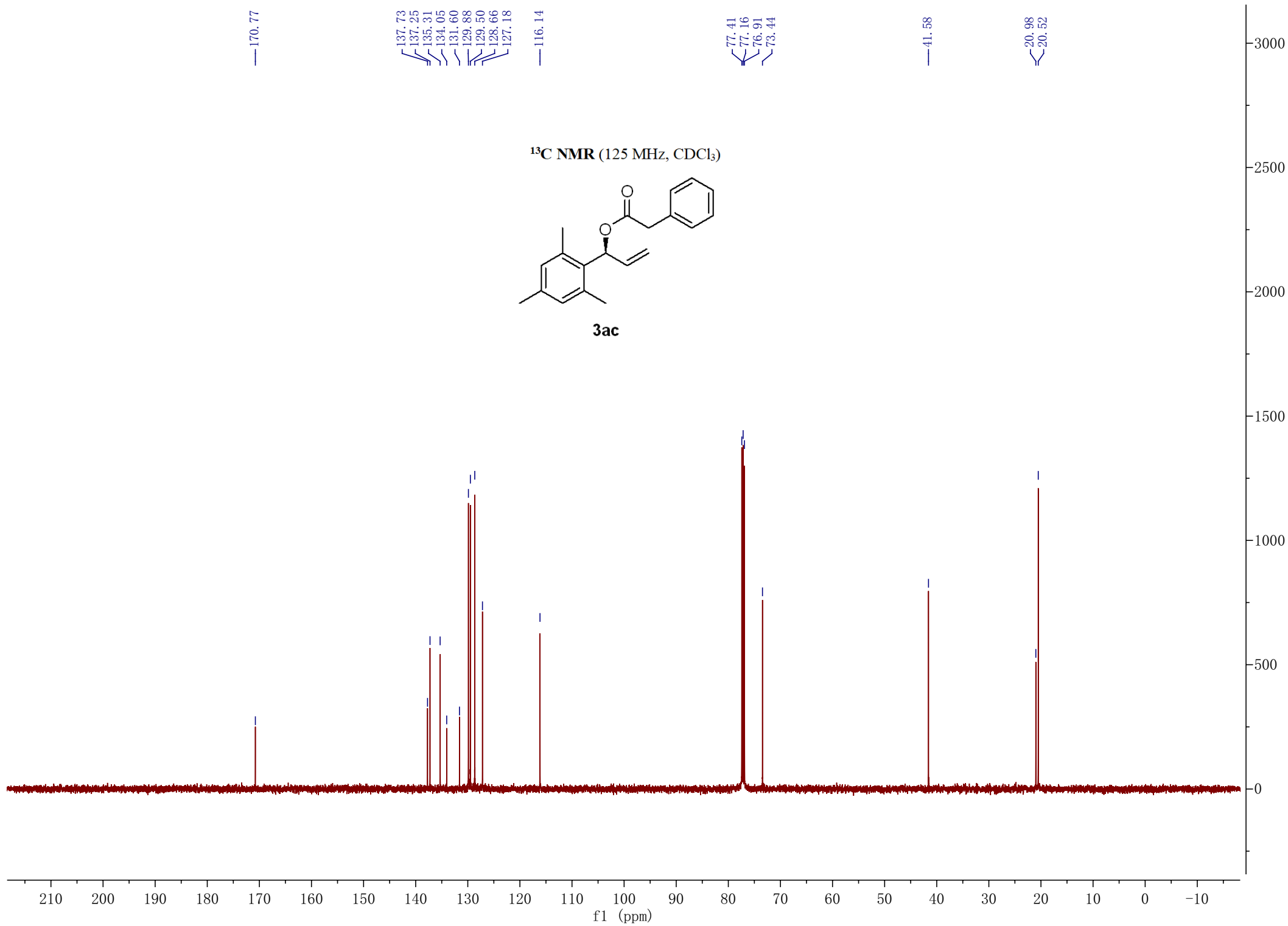


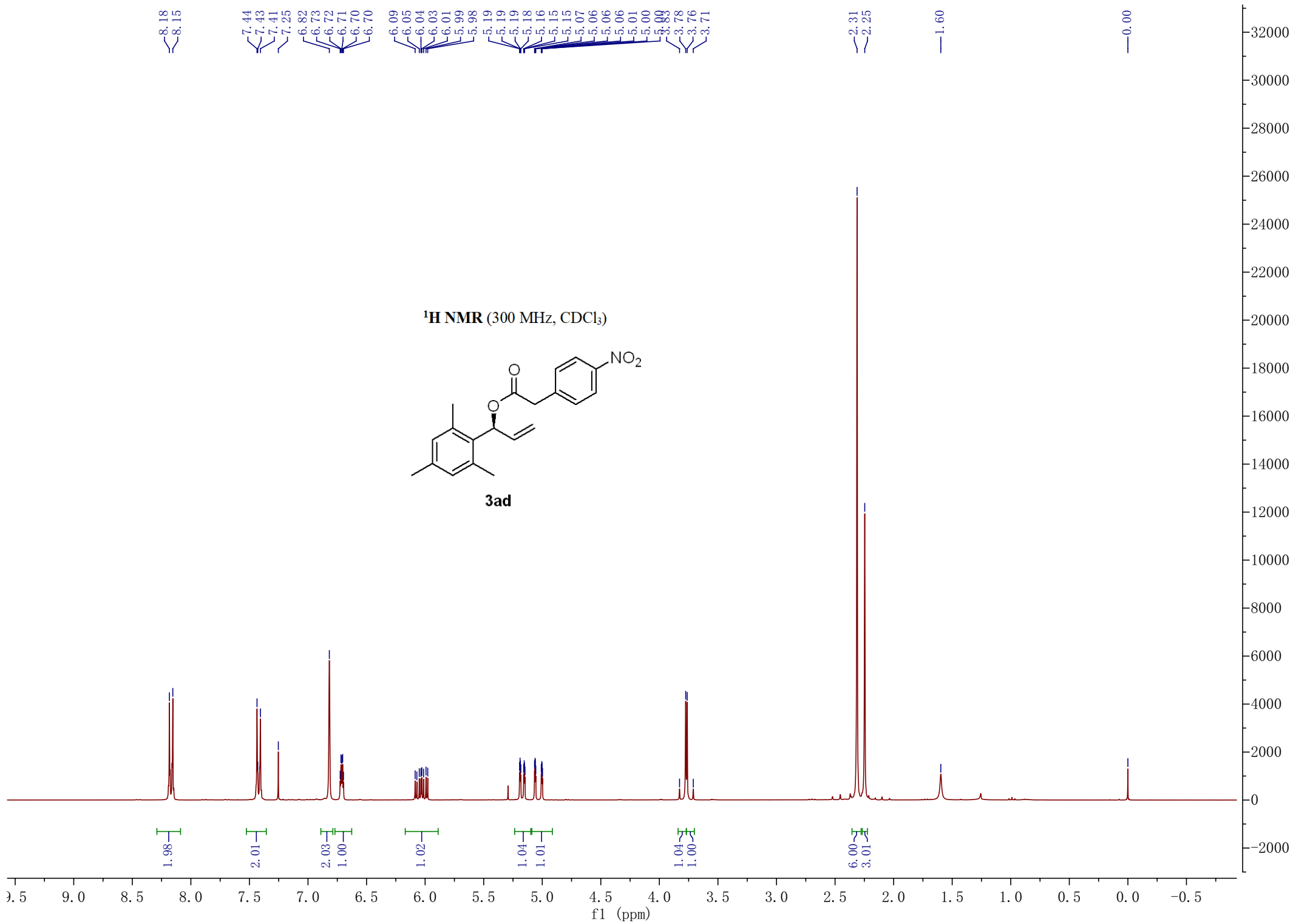


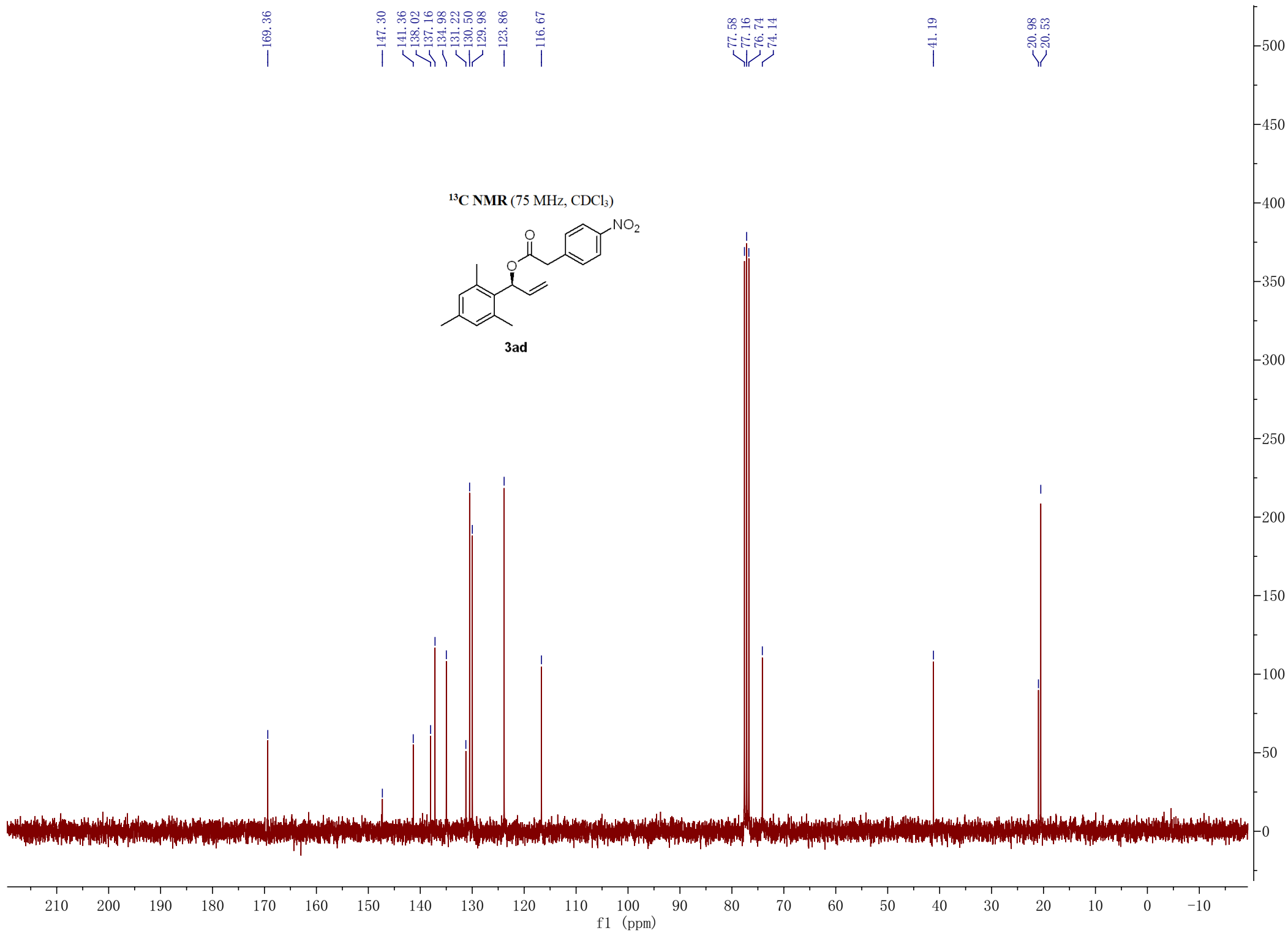
¹³C NMR (100 MHz, CDCl₃)





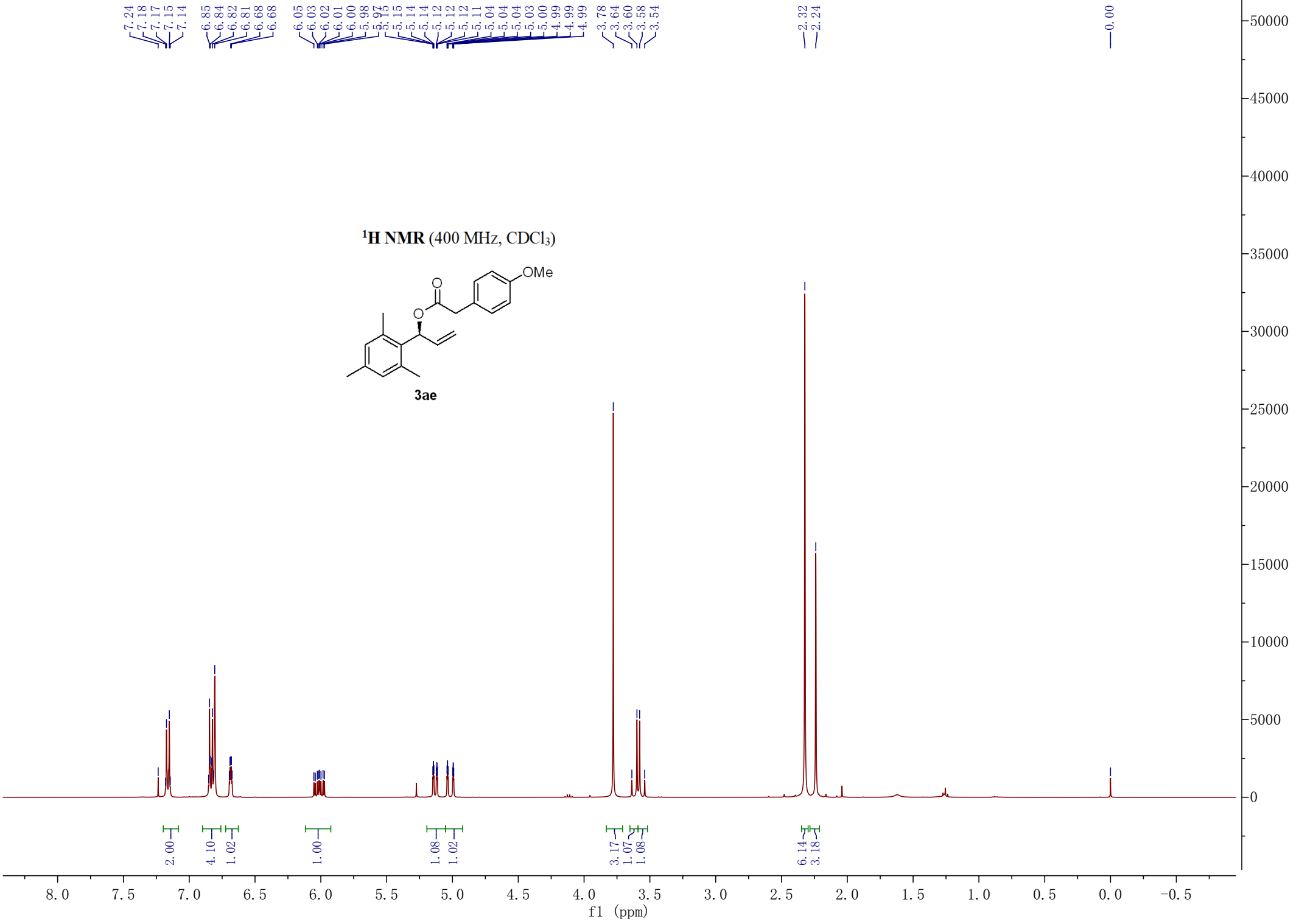
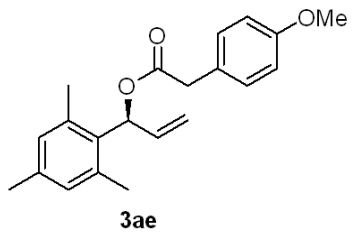


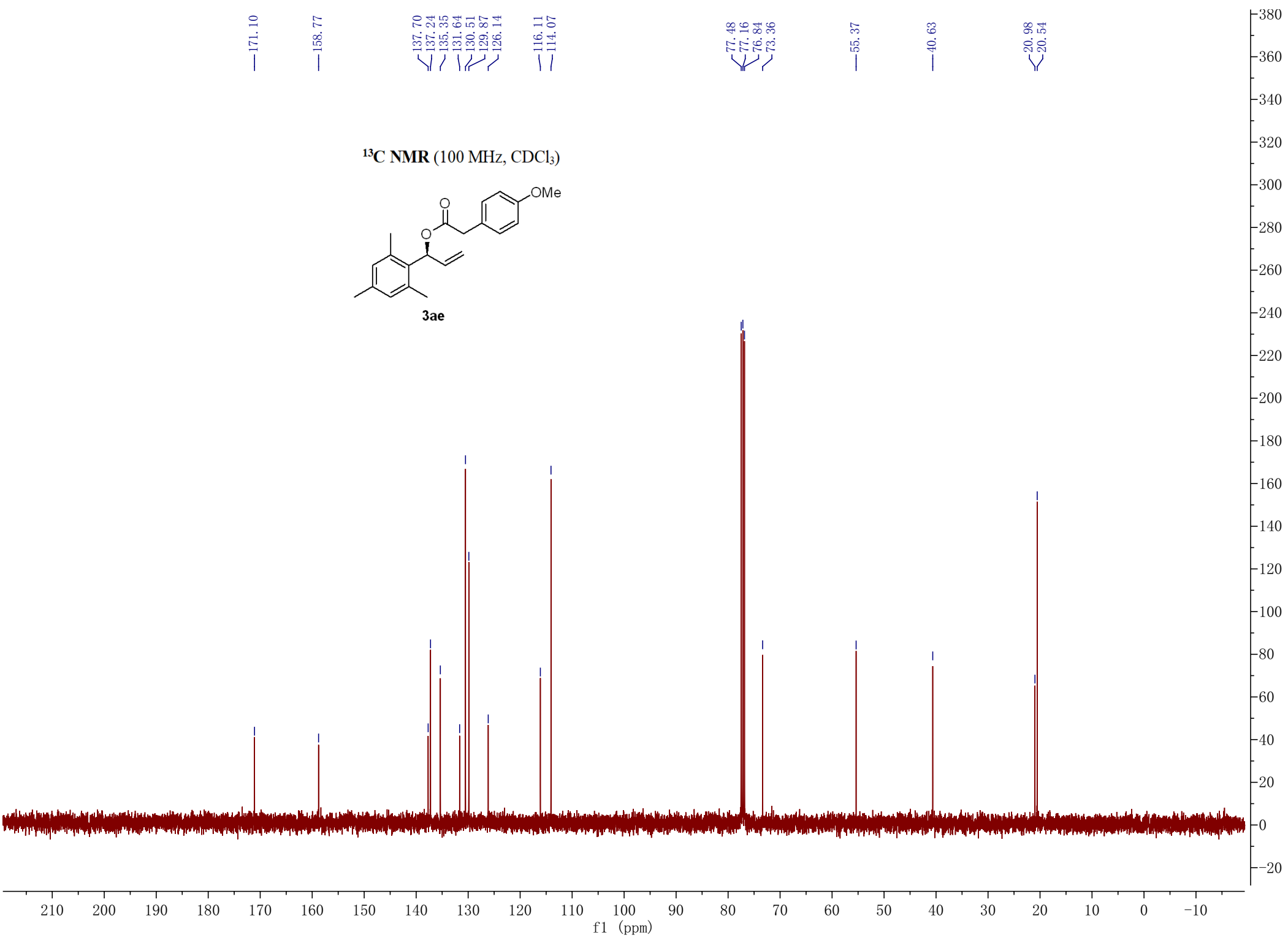
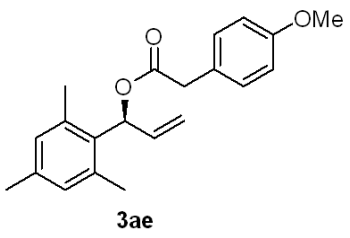


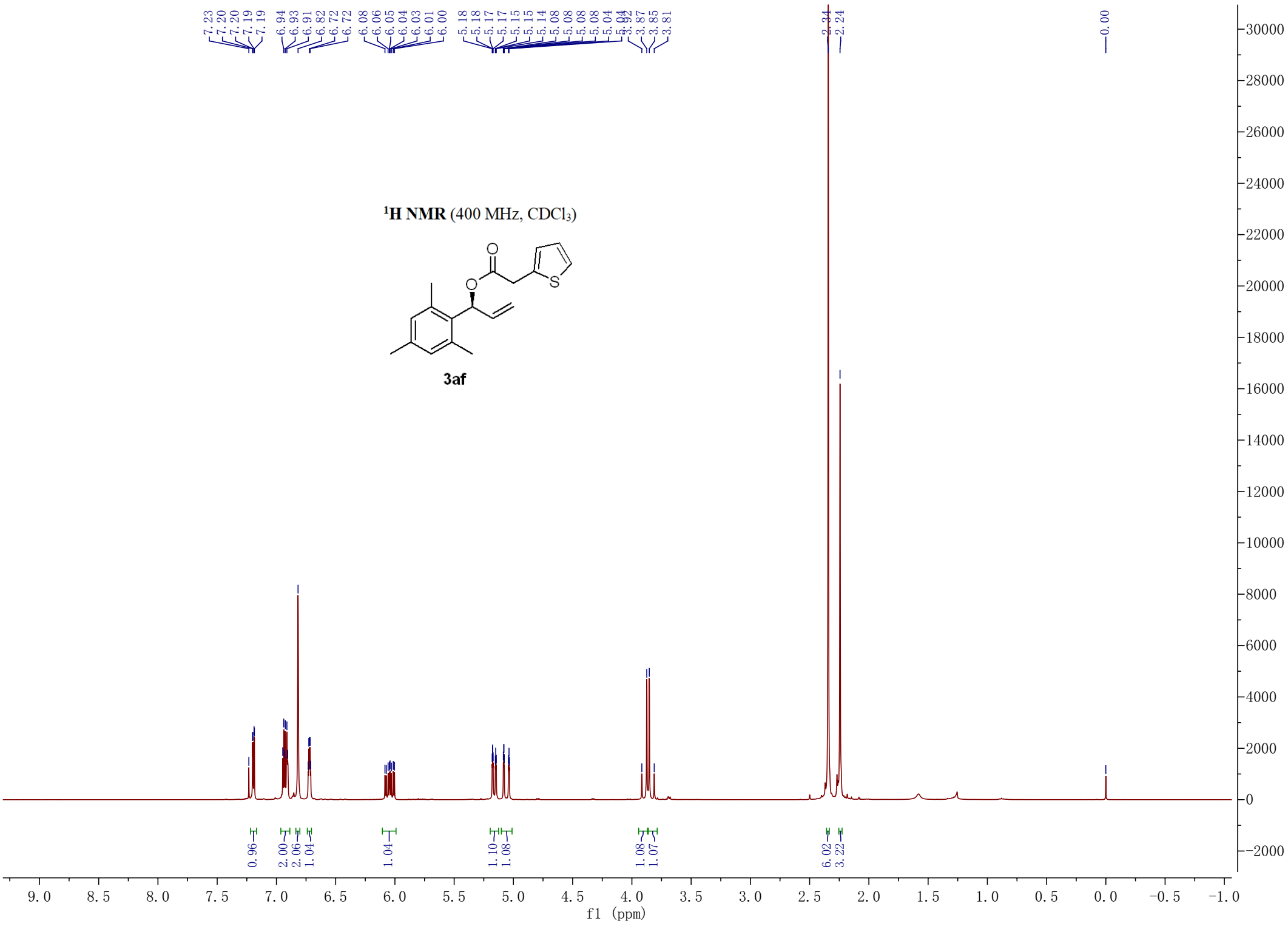


7.24
7.18
7.17
7.15
7.14
6.85
6.84
6.82
6.81
6.68
6.68
6.05
6.03
6.02
6.01
6.00
5.98
5.97
5.15
5.14
5.14
5.12
5.12
5.12
5.11
5.04
5.04
5.03
5.00
4.99
4.99
4.99
3.78
3.64
3.60
3.58
3.54
2.32
2.24
0.00

¹H NMR (400 MHz, CDCl₃)







169.64

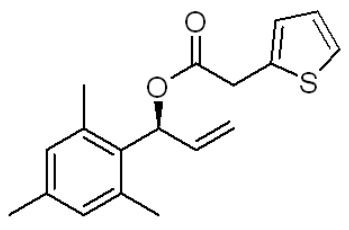
137.82
137.28
135.18
135.03
131.44
129.91
127.07
126.92
125.15
116.36

77.58
77.16
76.74
73.82

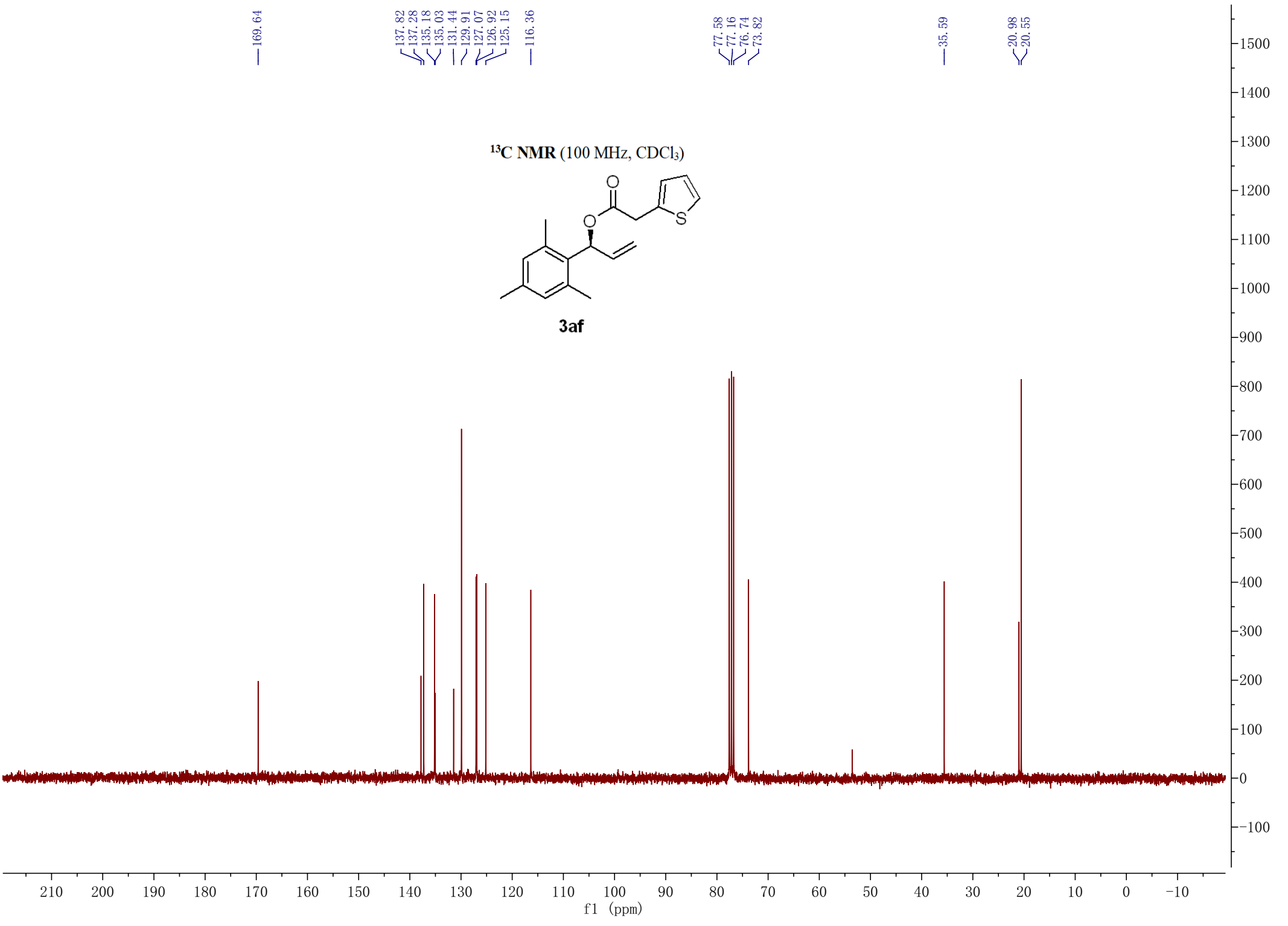
35.59

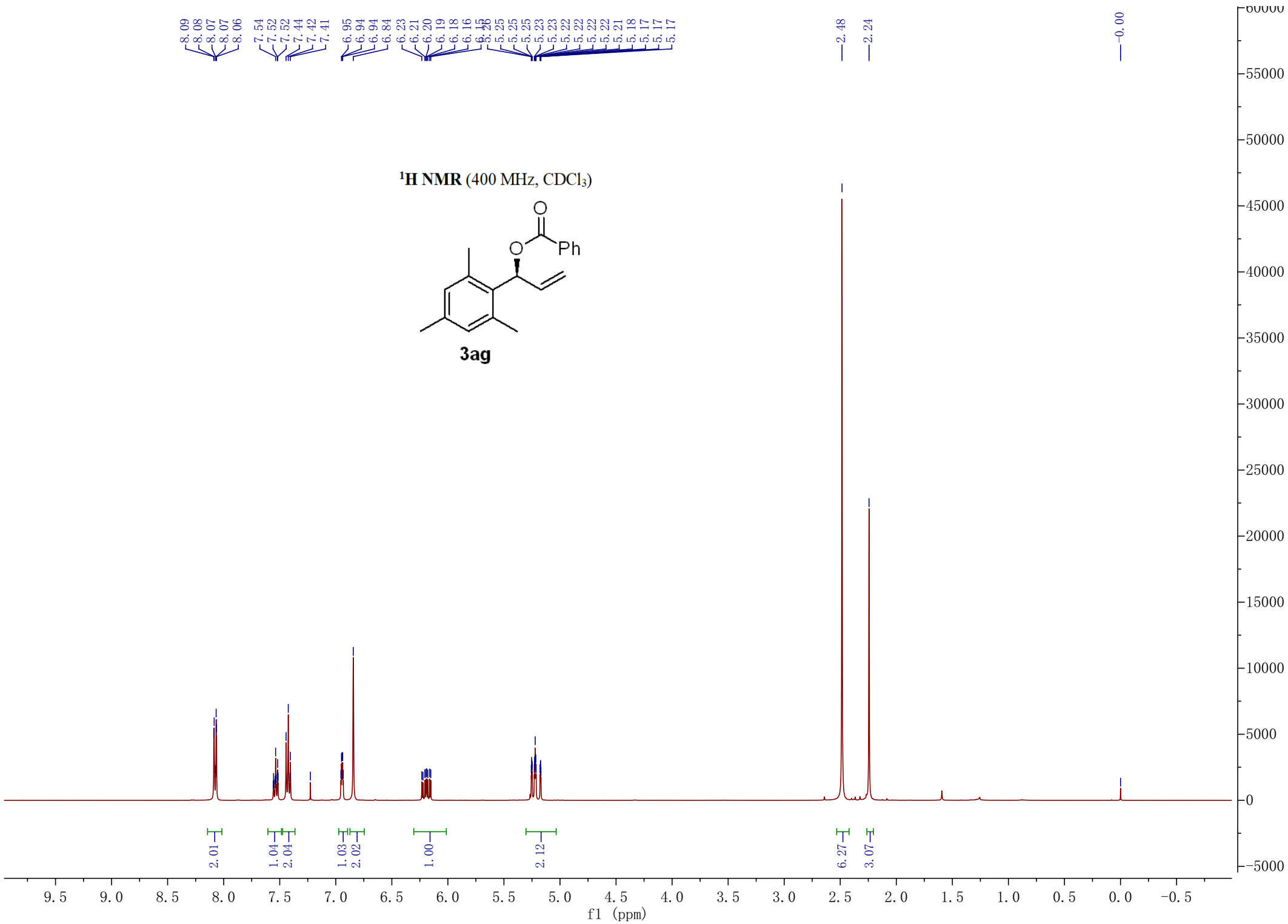
20.98
20.55

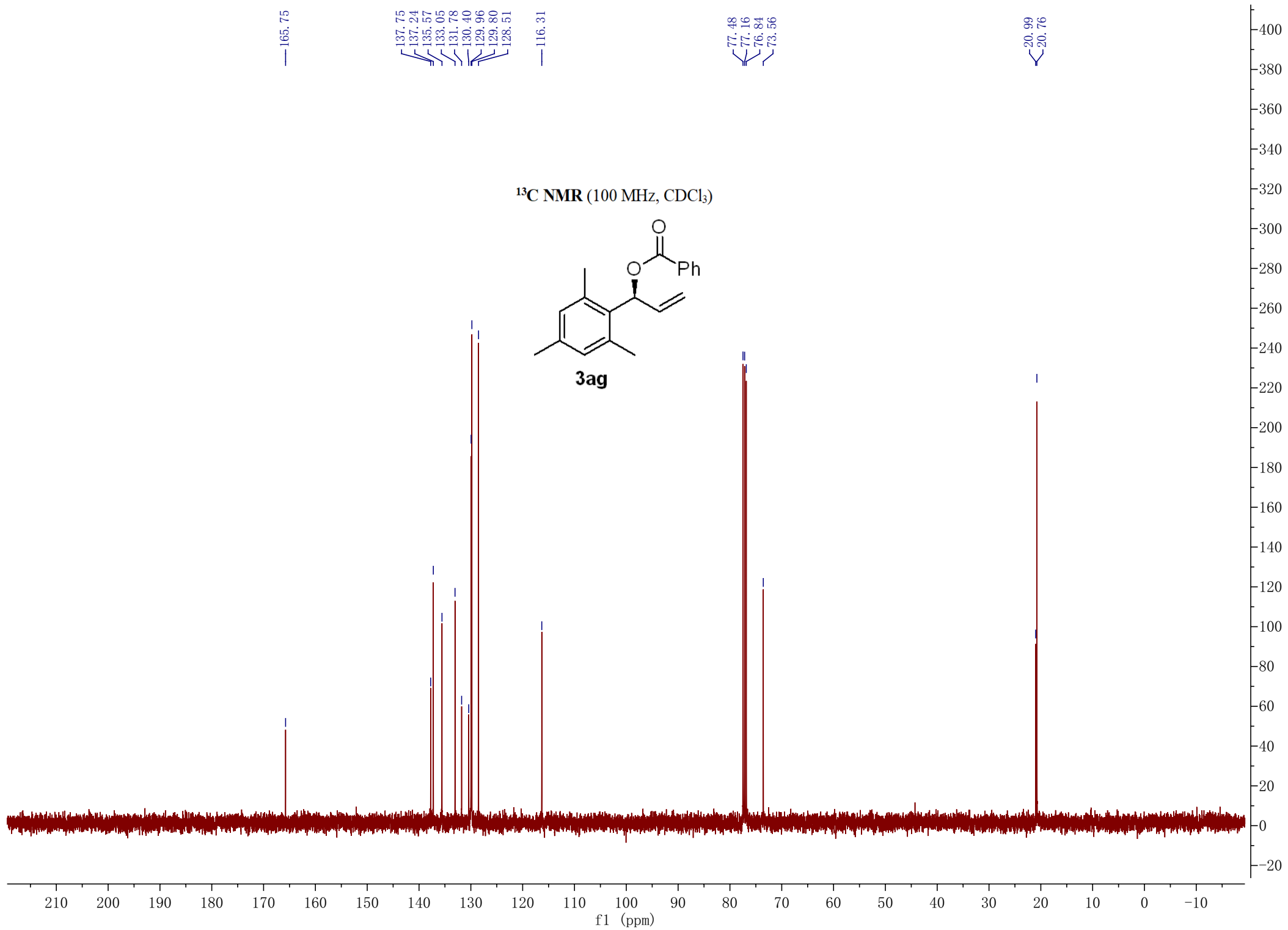
¹³C NMR (100 MHz, CDCl₃)

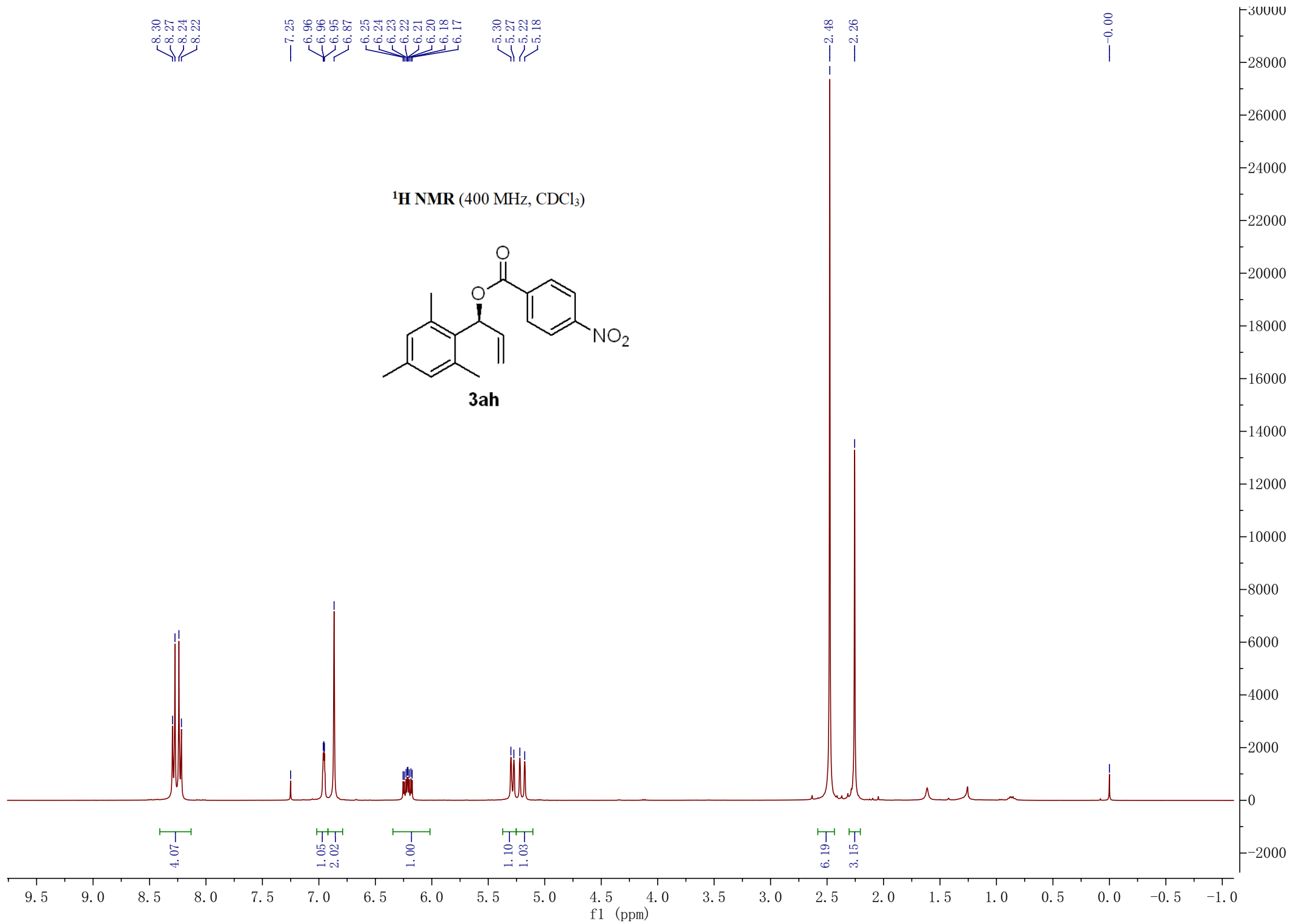


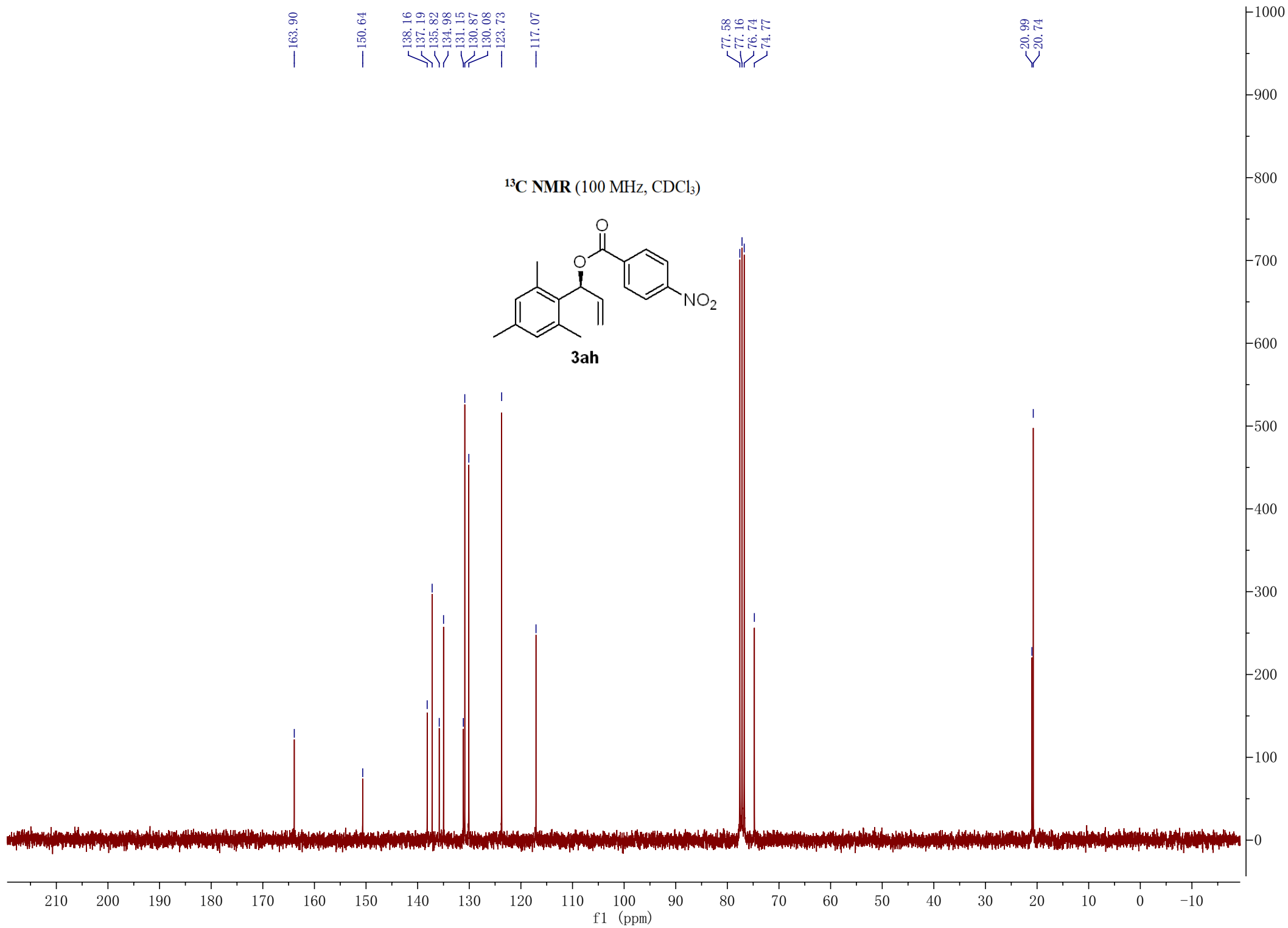
3af

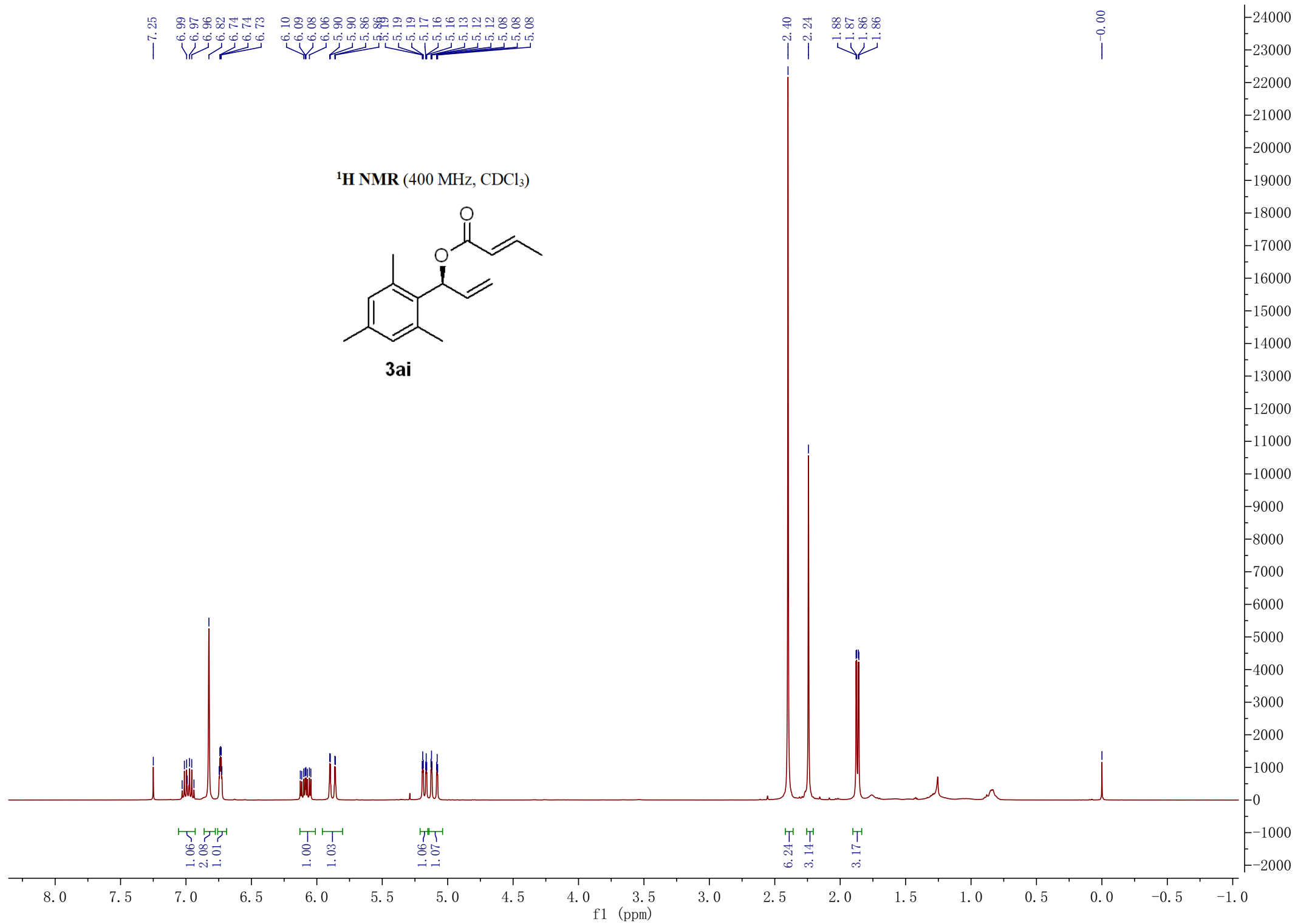


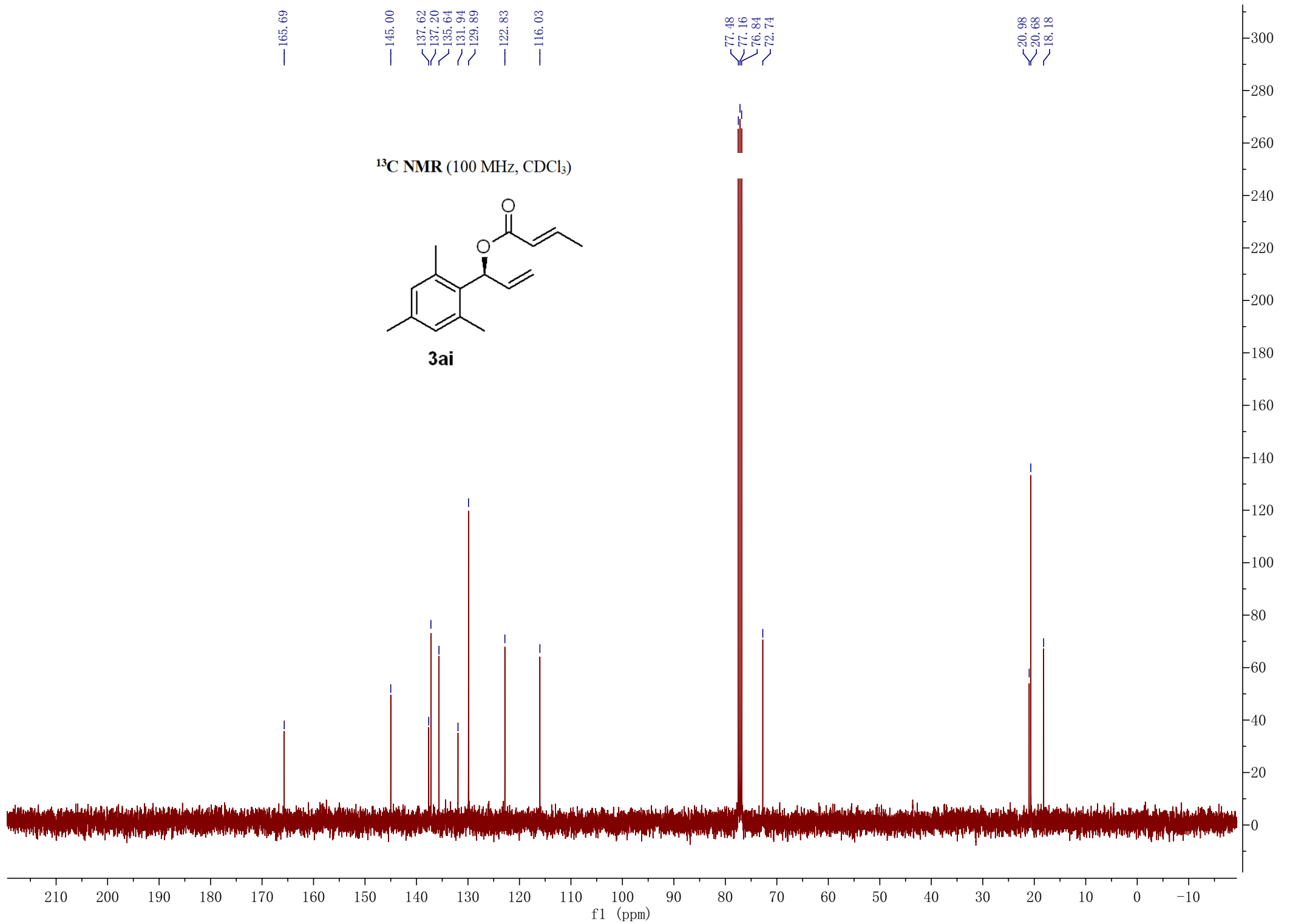


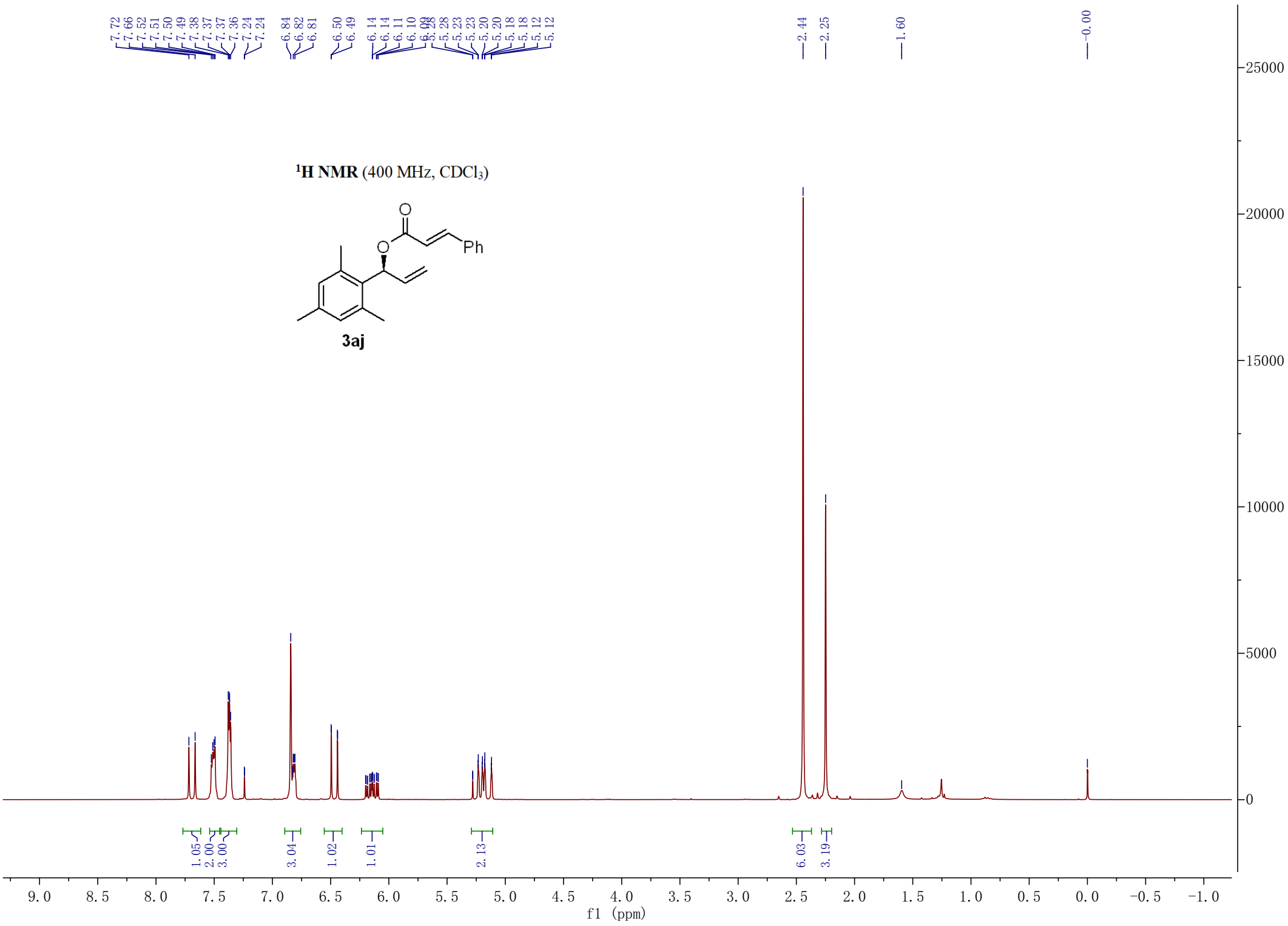


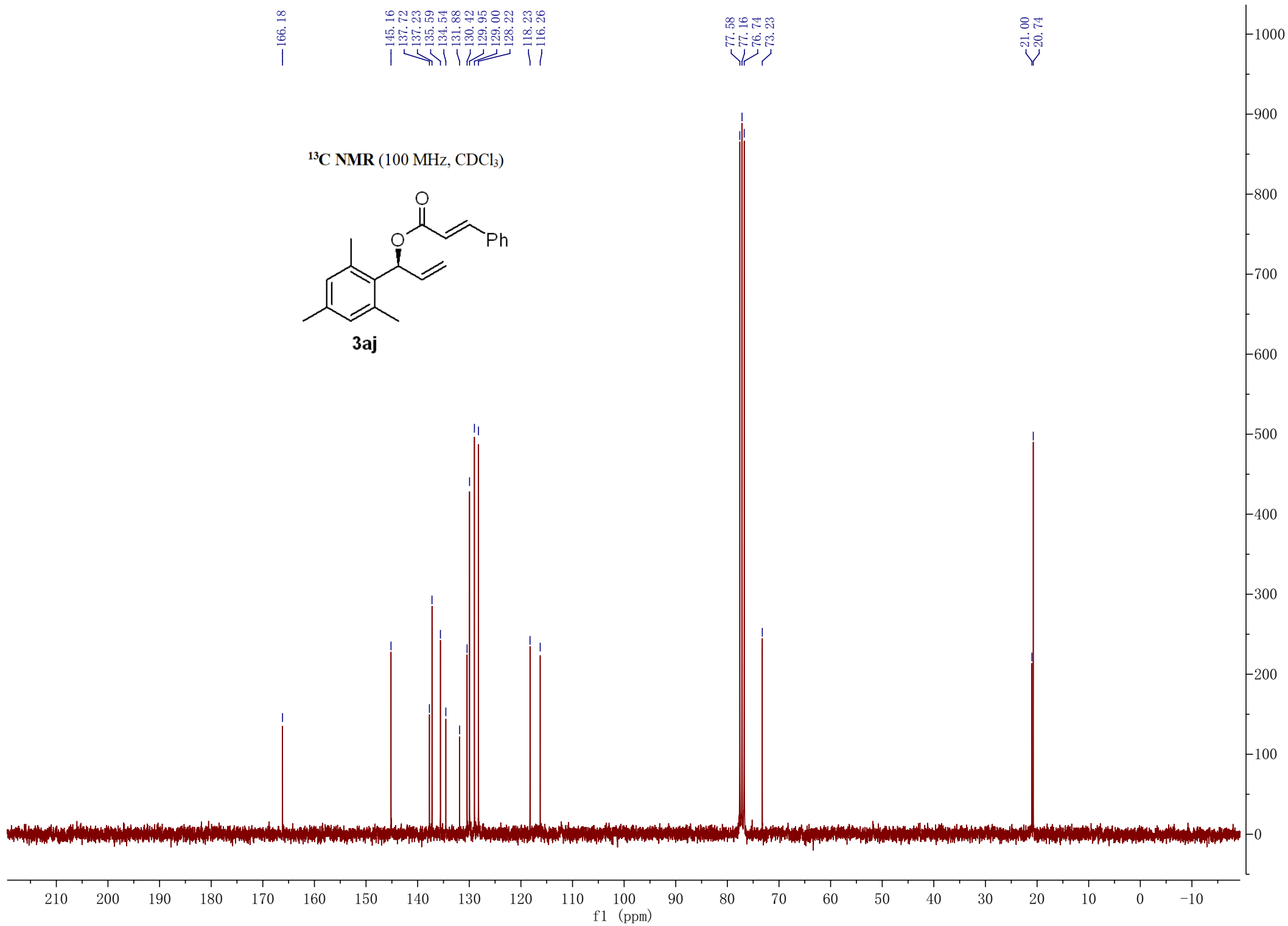


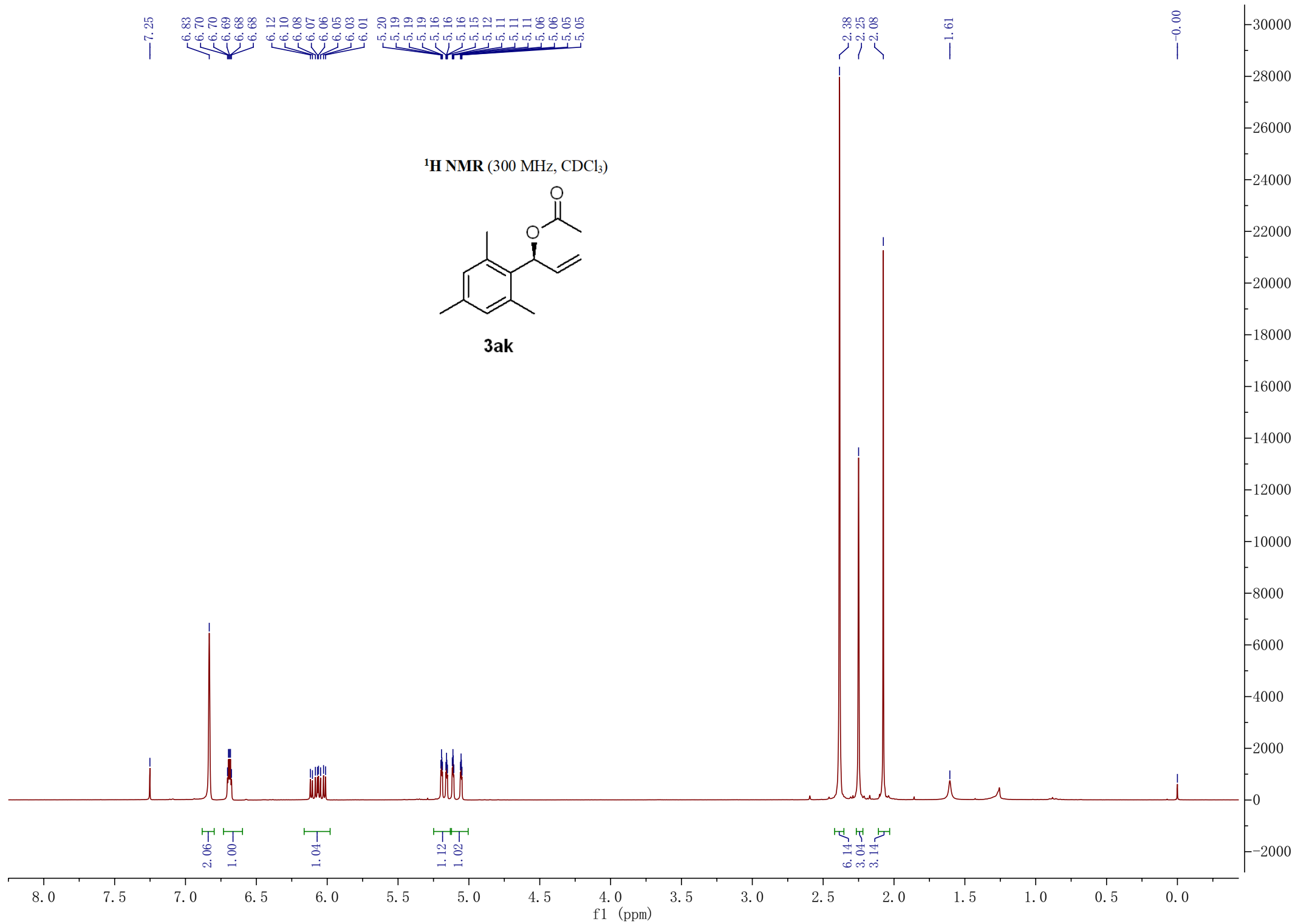












170.24

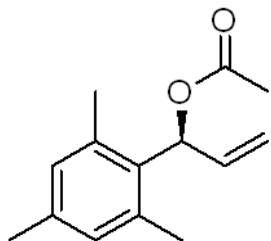
137.74
137.24
135.52
131.83
129.91

116.16

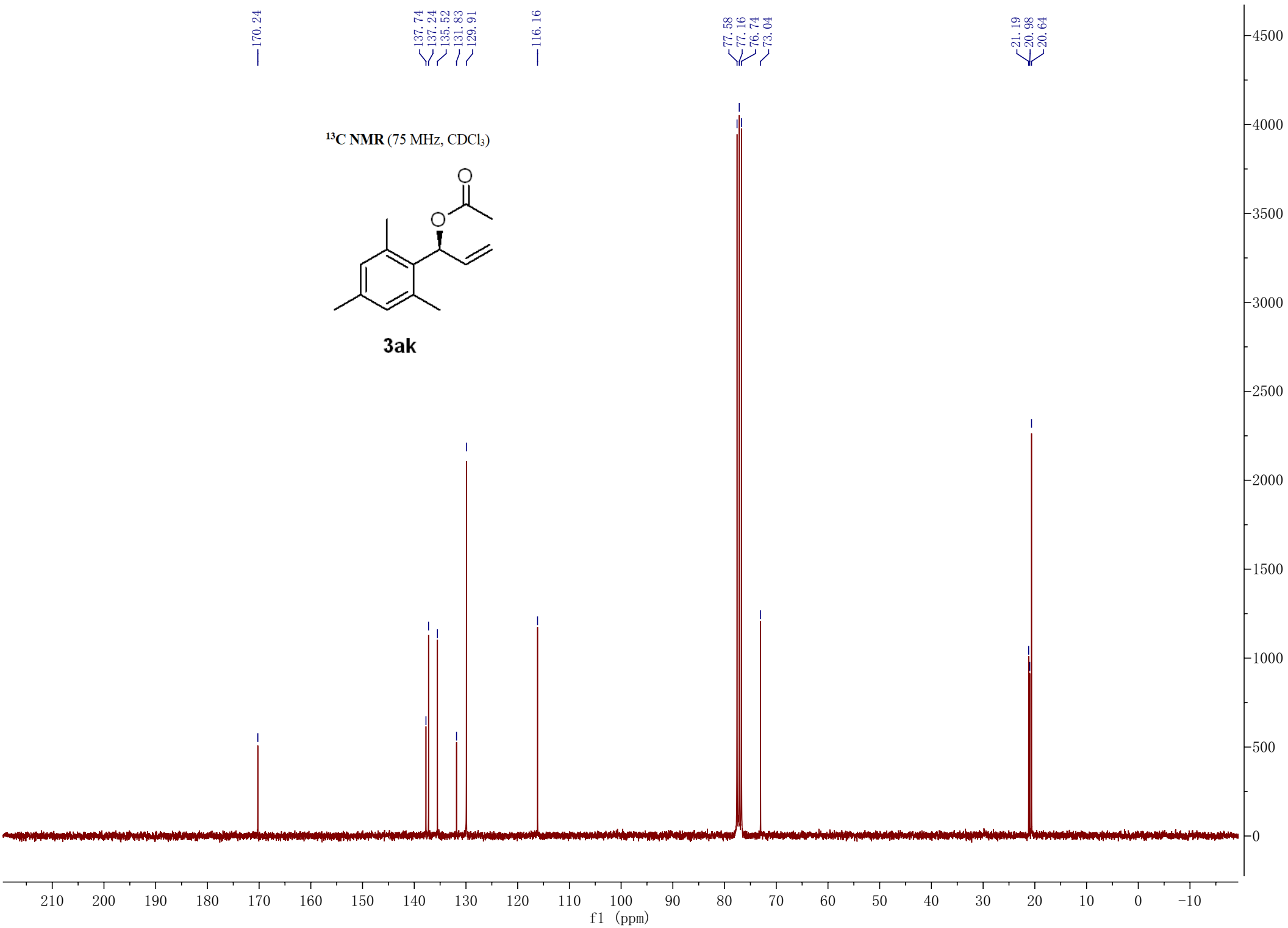
77.58
77.16
76.74
73.04

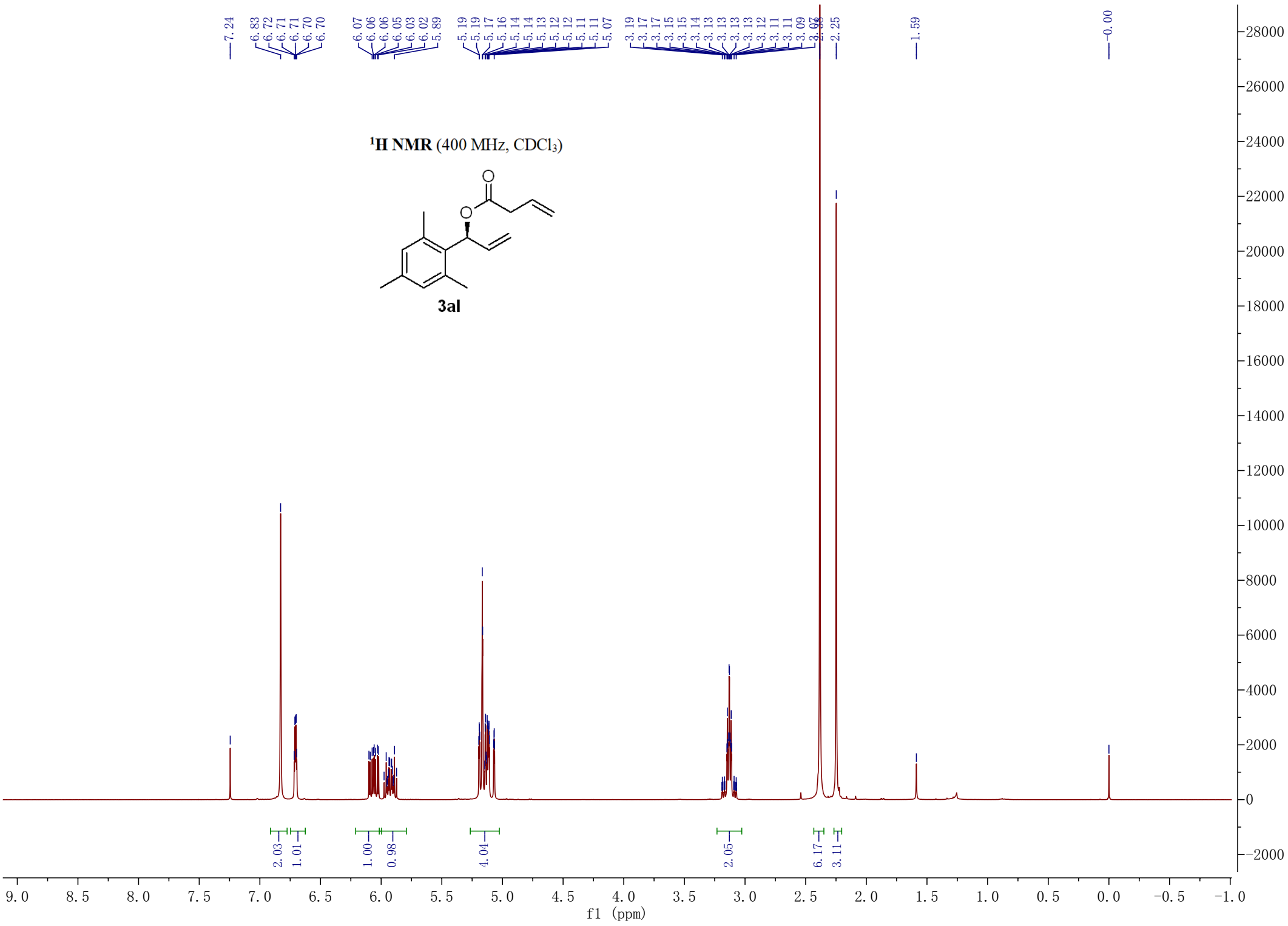
21.19
20.98
20.64

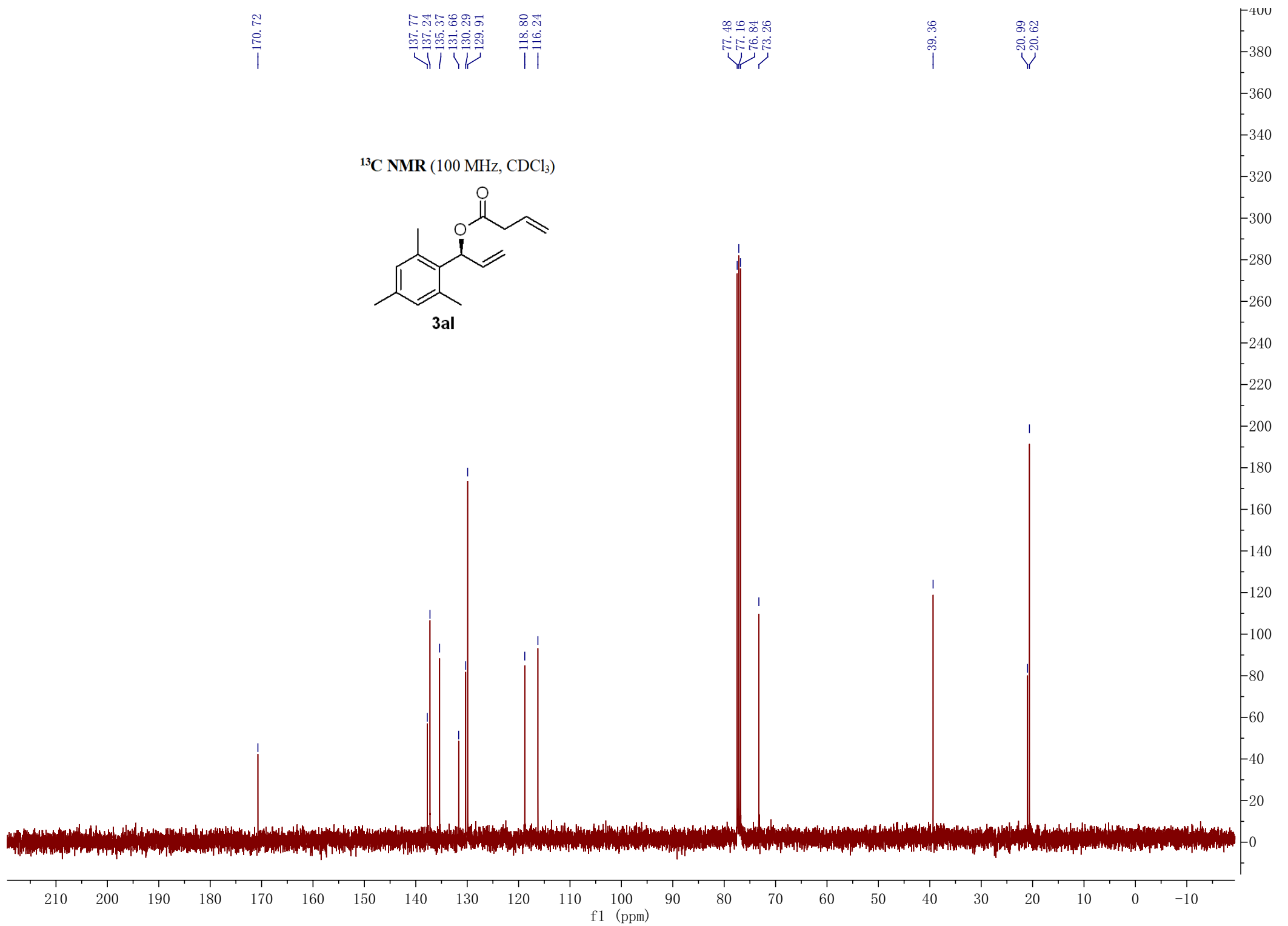
¹³C NMR (75 MHz, CDCl₃)

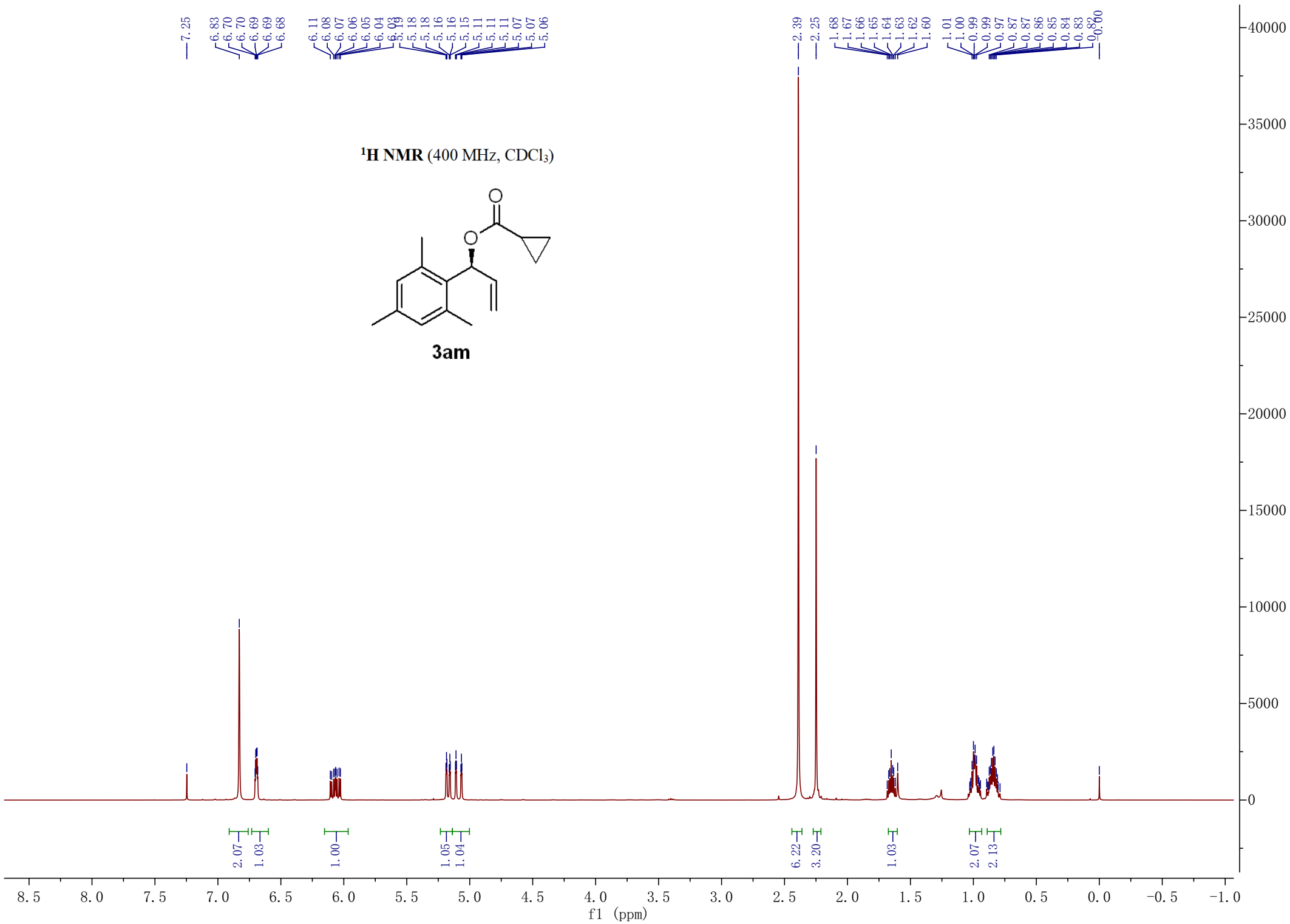


3ak









— 174.12

137.63
137.18
135.62
131.88
129.90

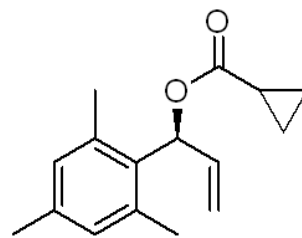
— 116.05

77.48
77.16
76.84
72.96

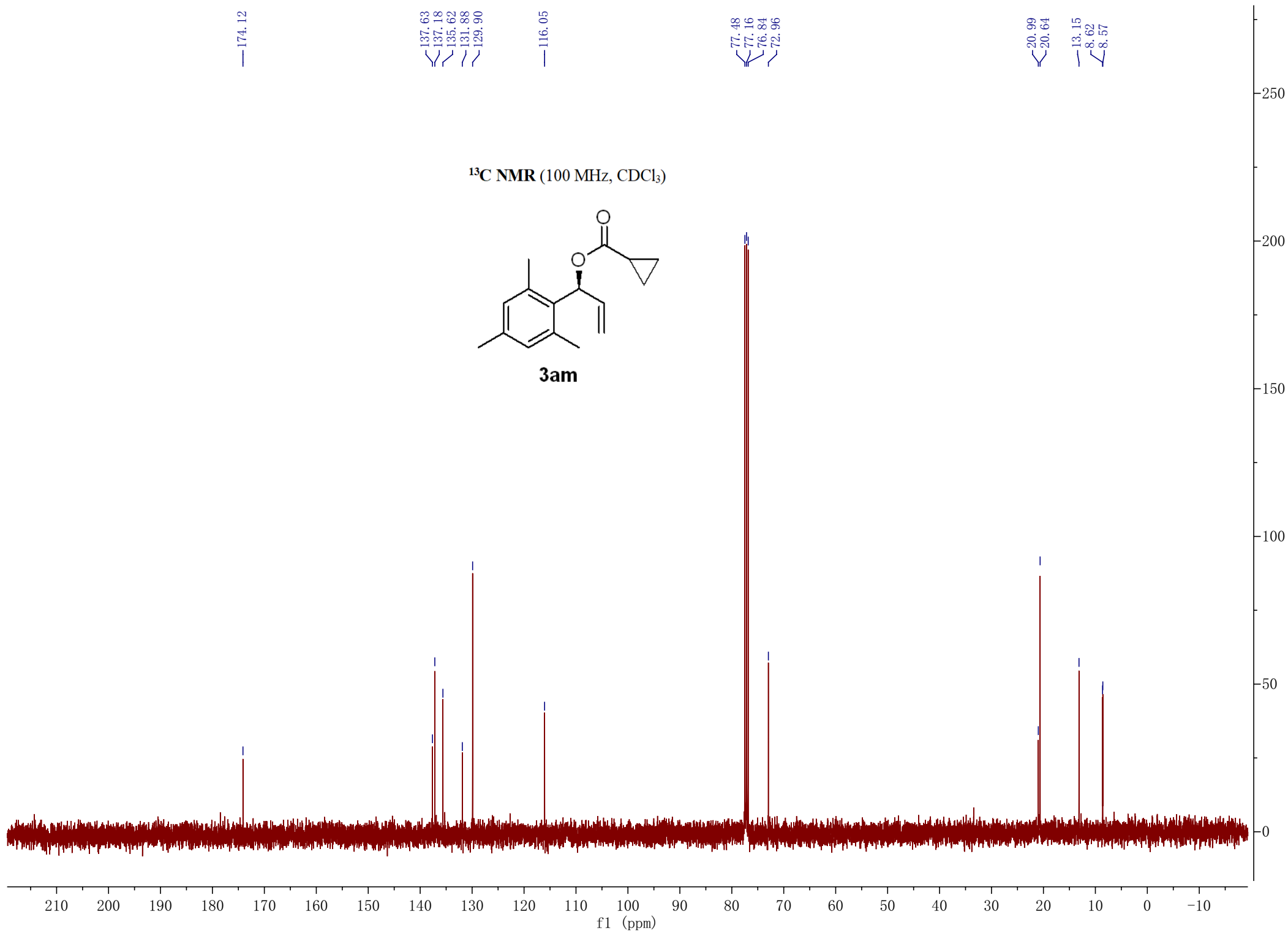
20.99
20.64

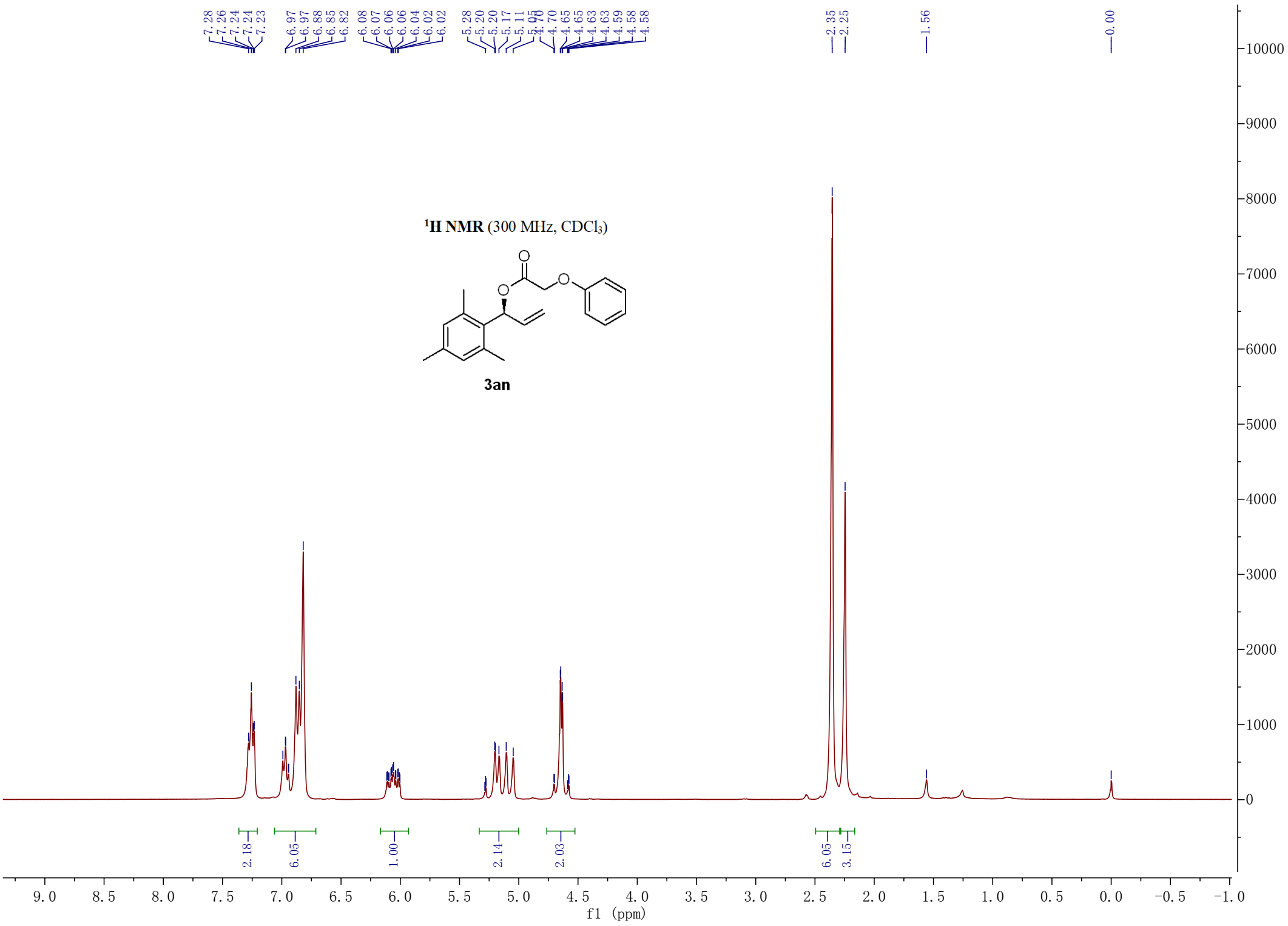
13.15
8.62
8.57

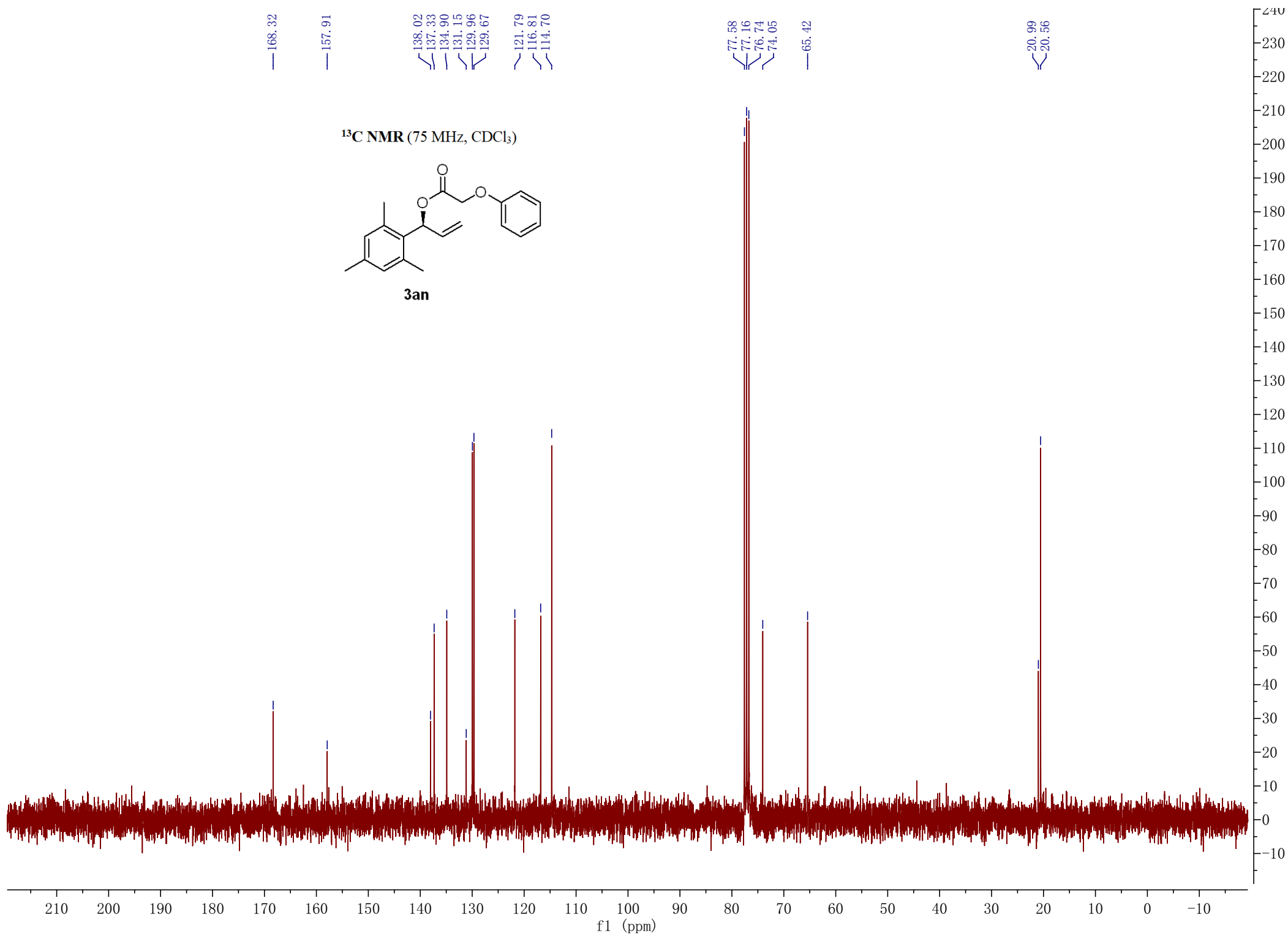
¹³C NMR (100 MHz, CDCl₃)

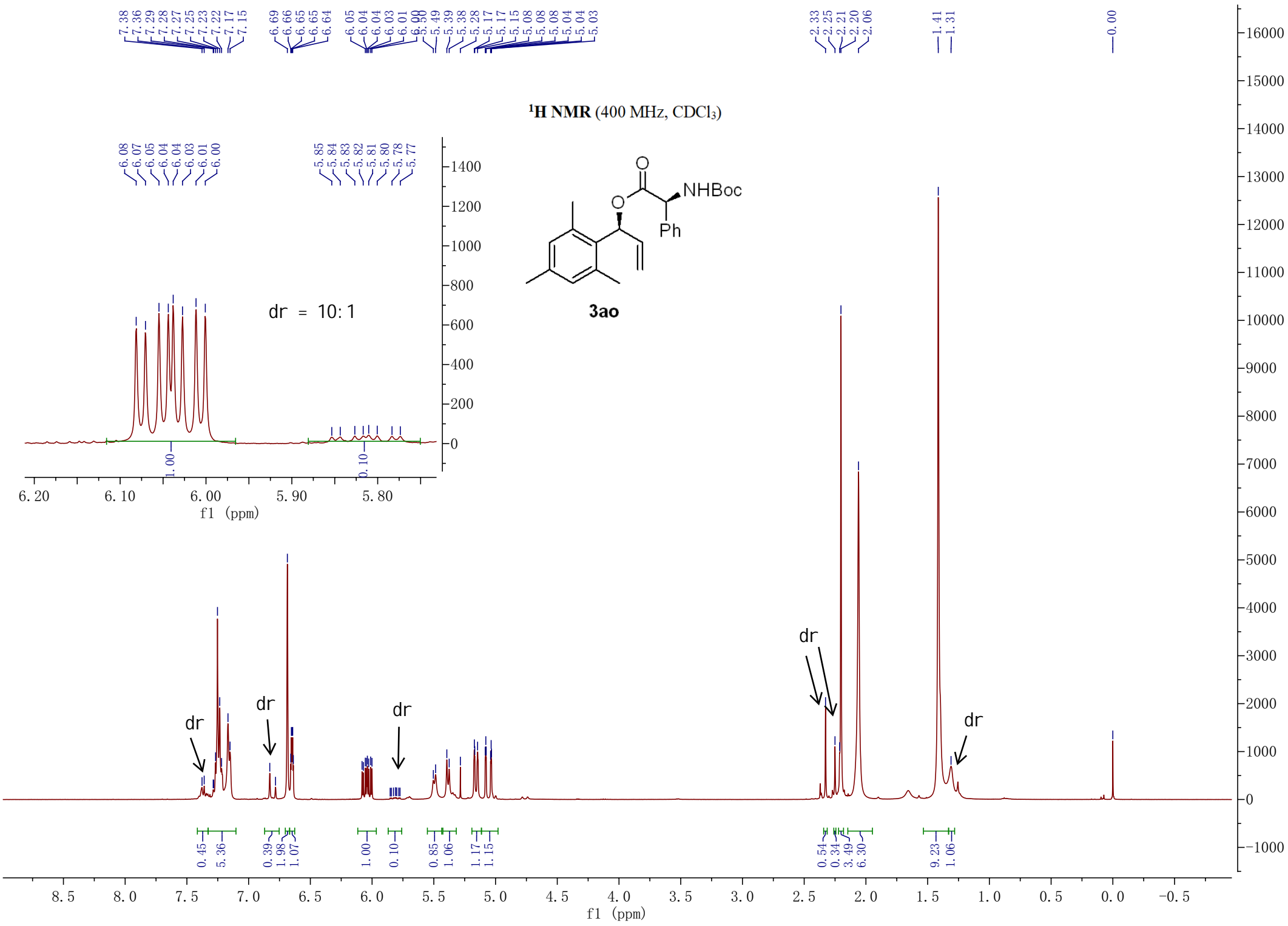


3am

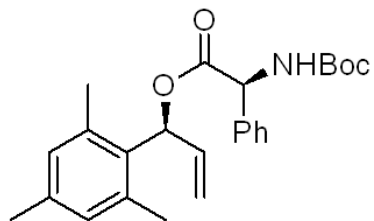






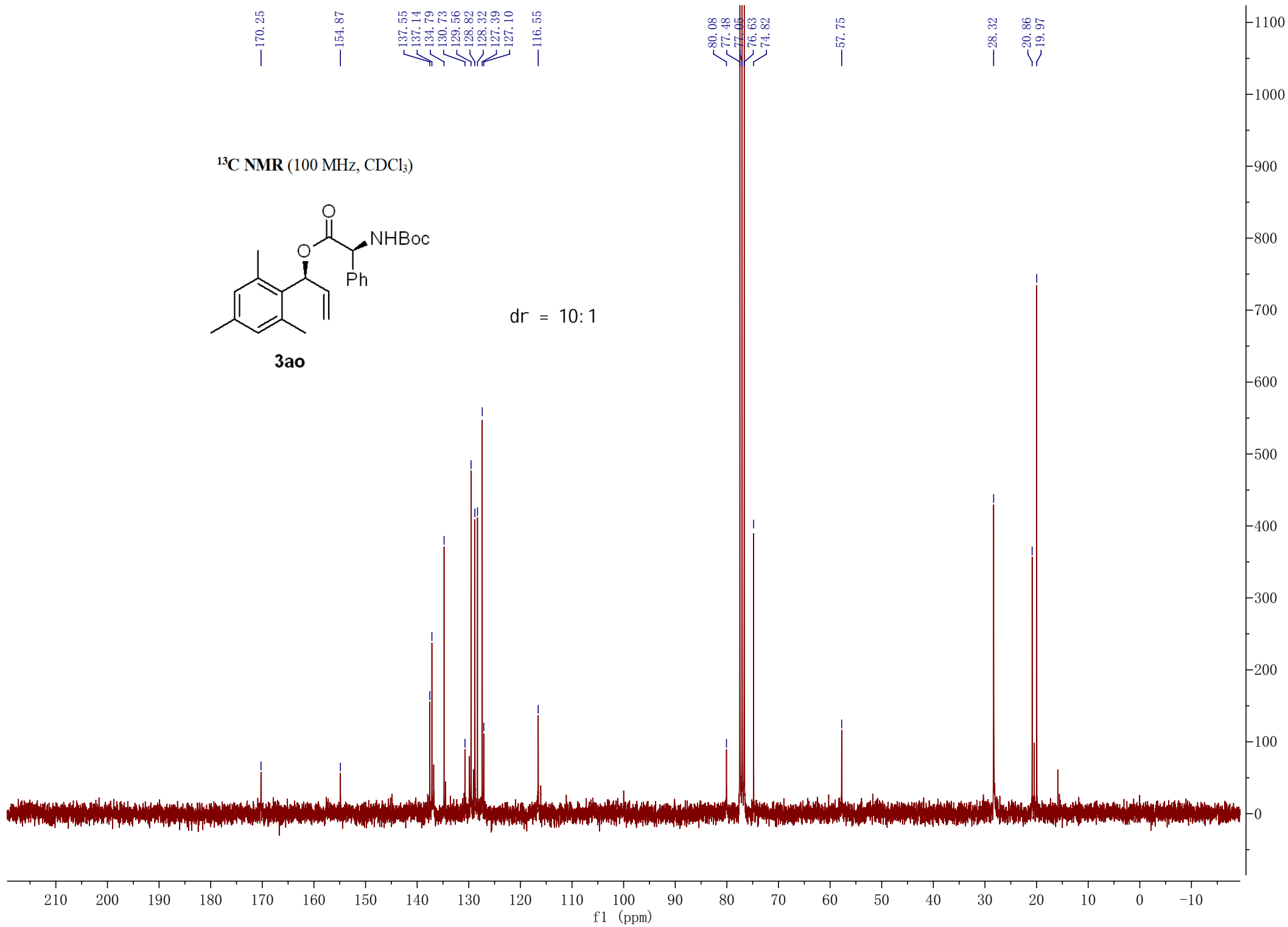


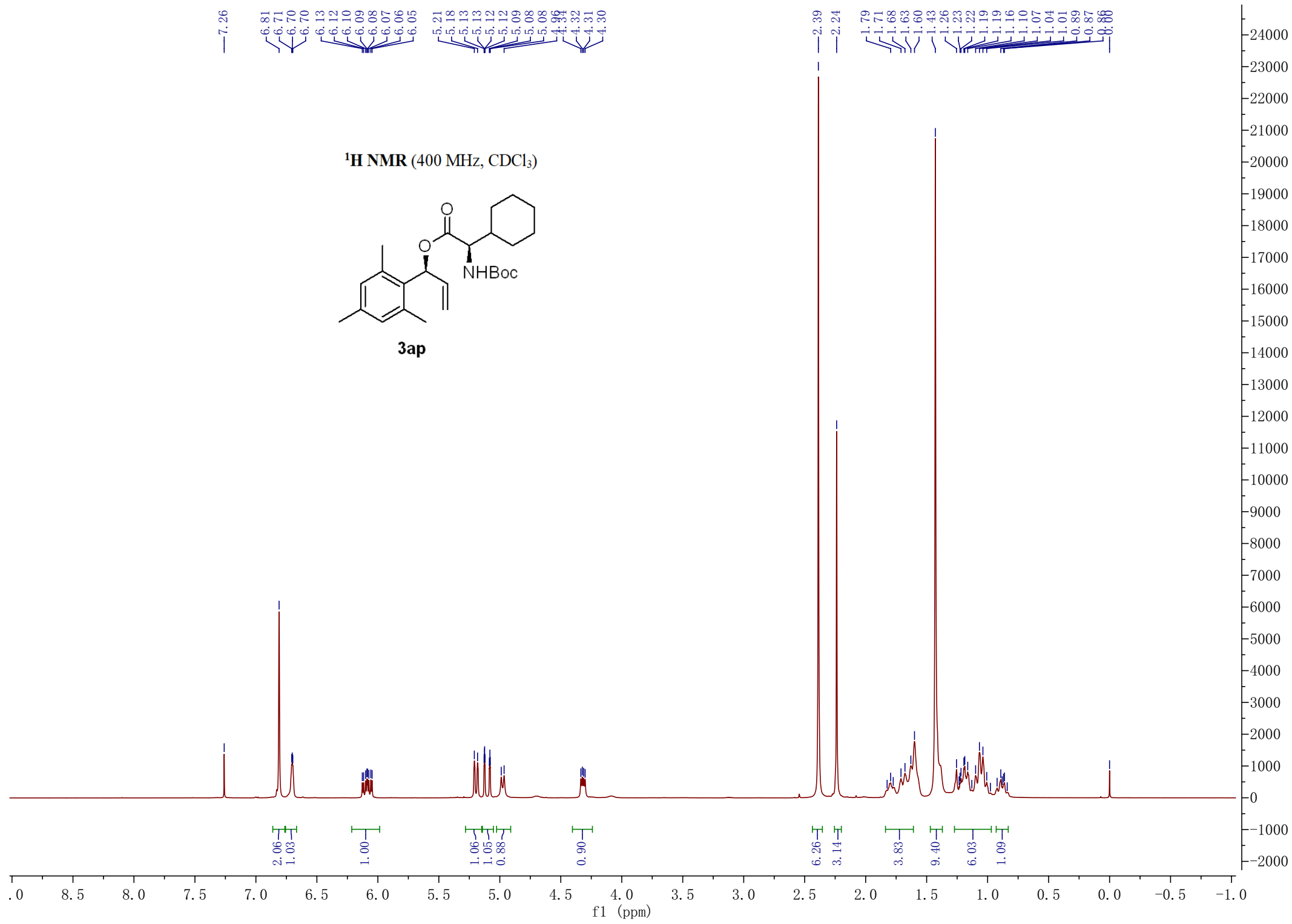
¹³C NMR (100 MHz, CDCl₃)

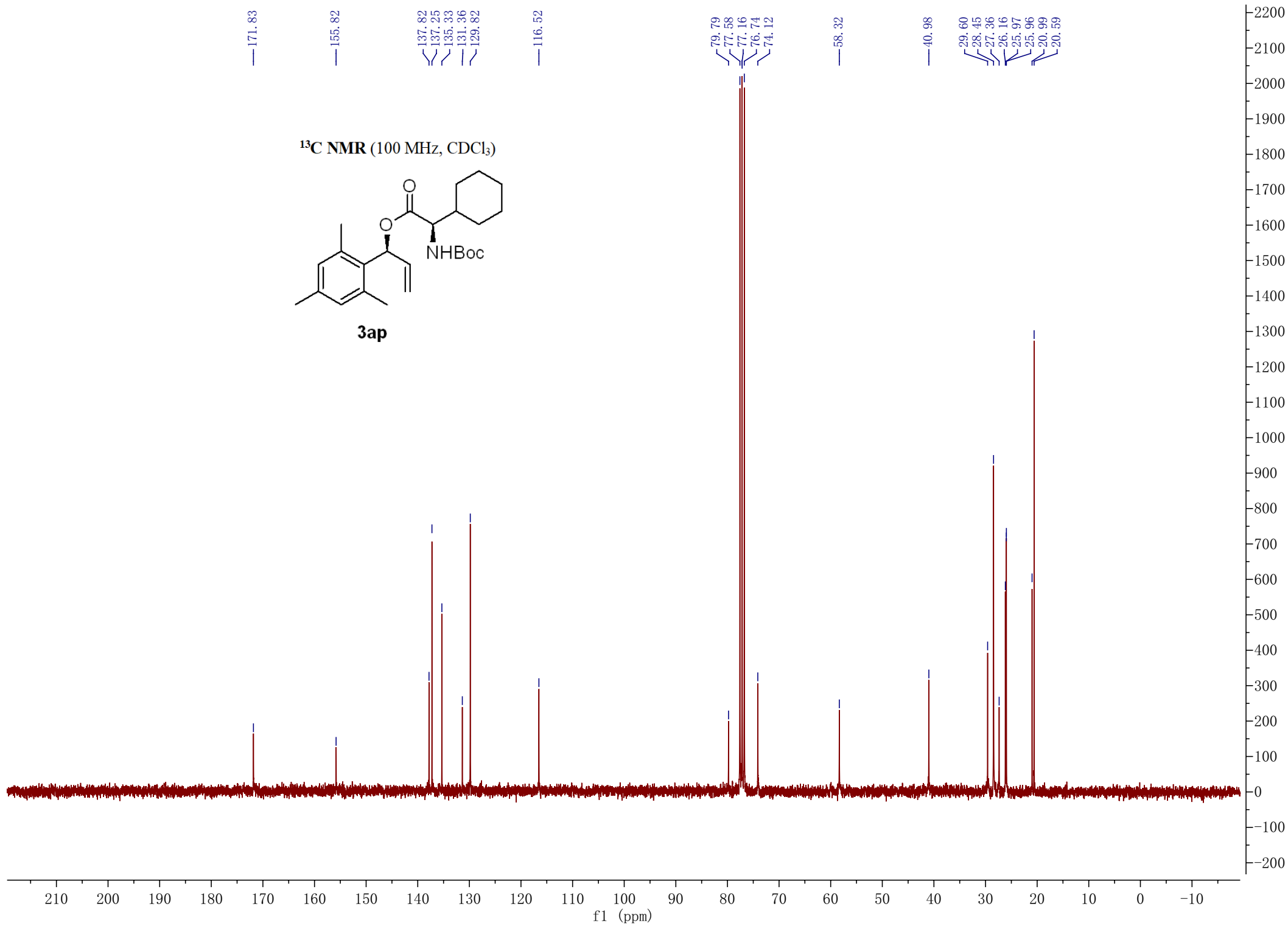


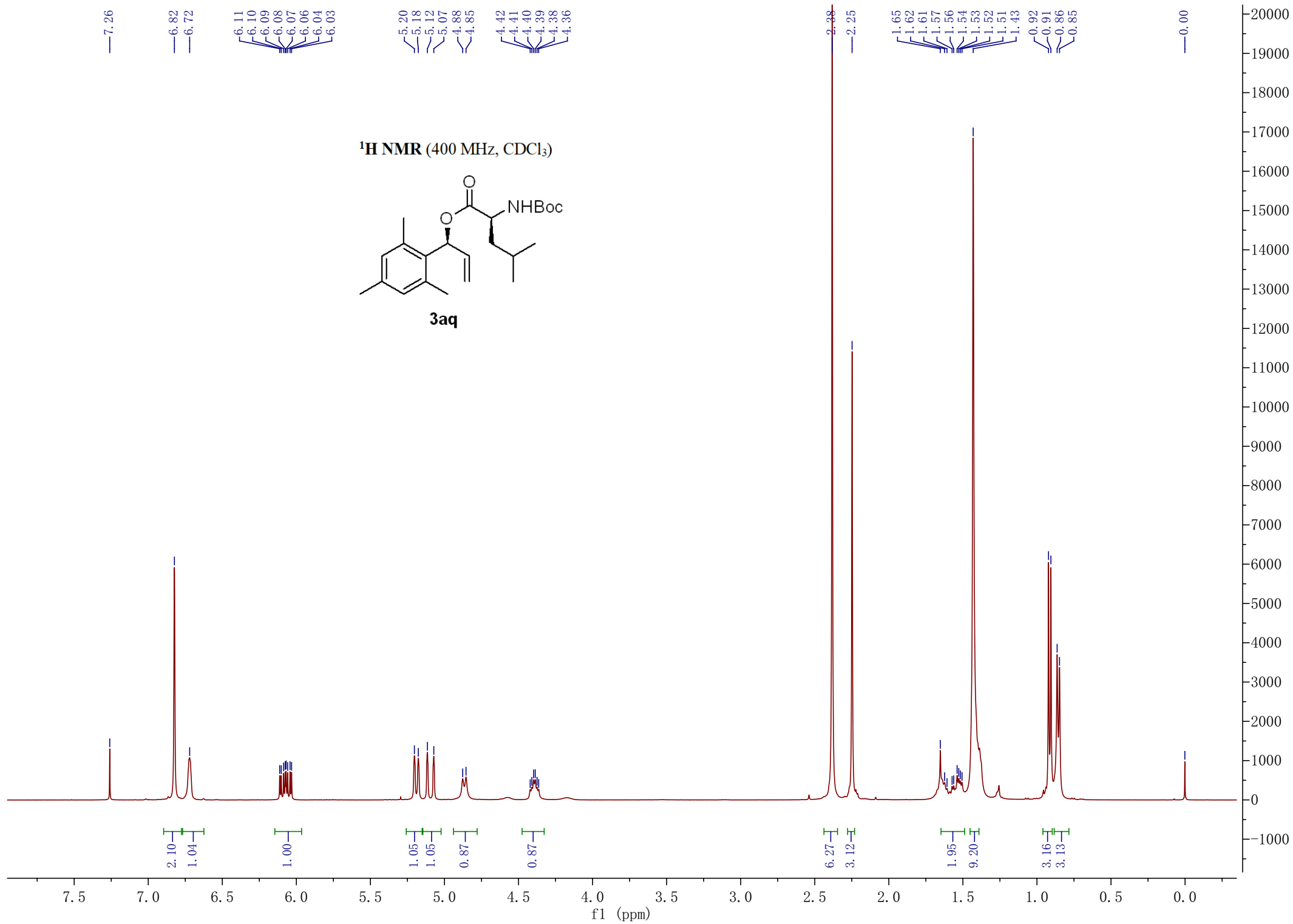
3ao

dr = 10:1









172.78

155.52

137.81

137.24

135.28

131.34

129.90

116.46

79.88

77.58

77.16

76.74

73.92

52.29

41.85

28.44

24.85

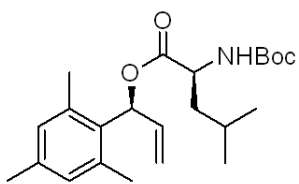
23.10

21.87

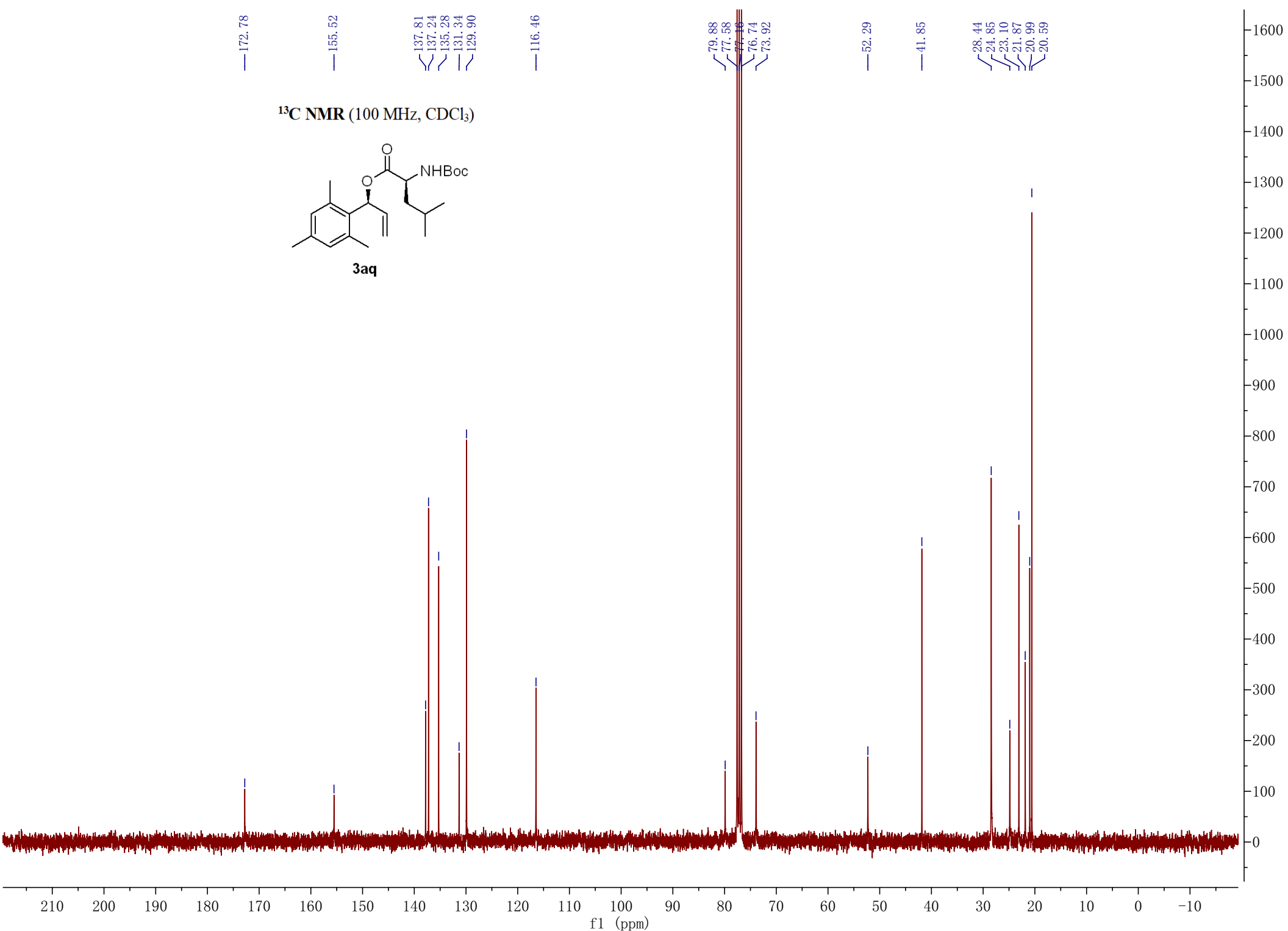
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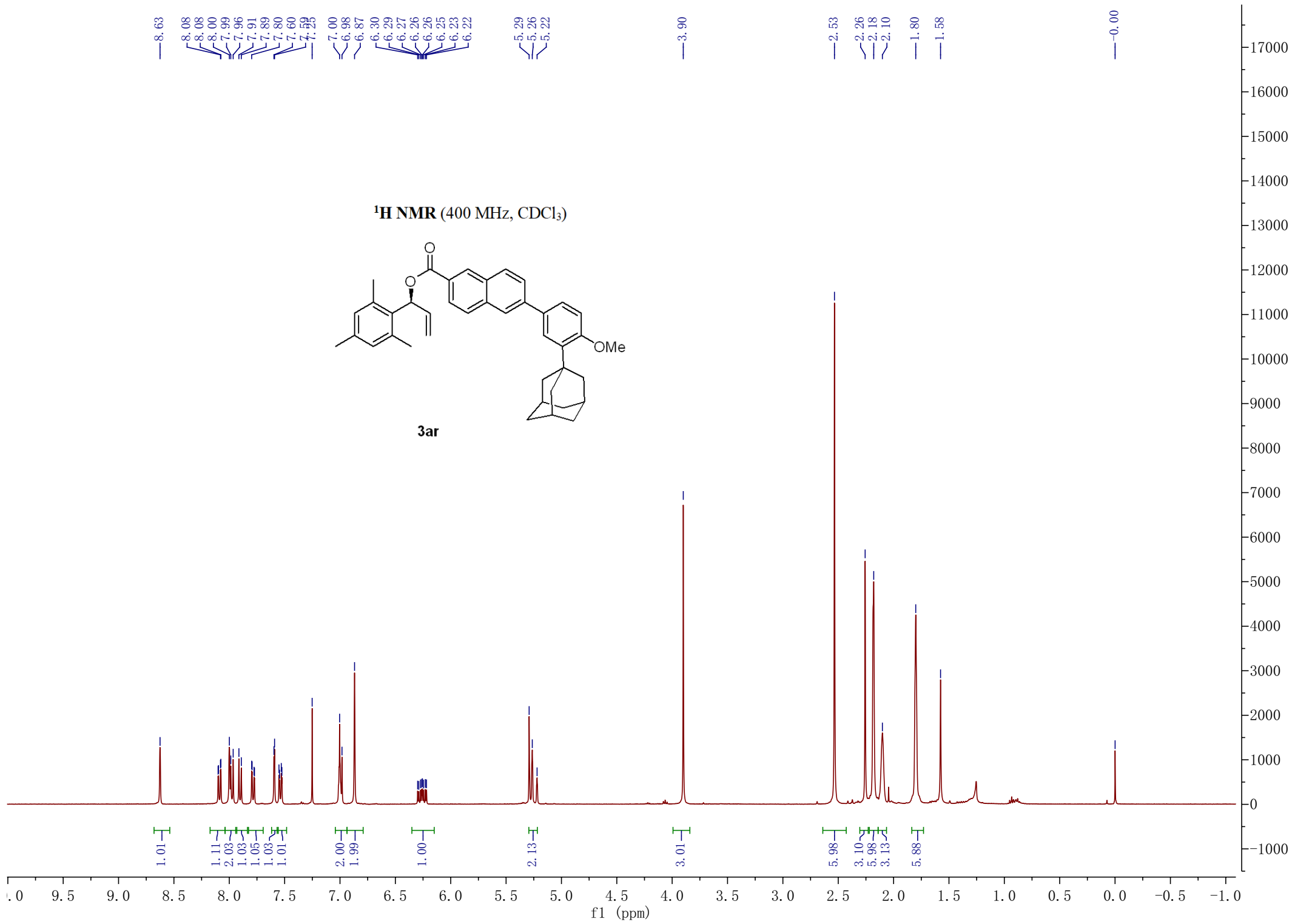
20.59

¹³C NMR (100 MHz, CDCl₃)

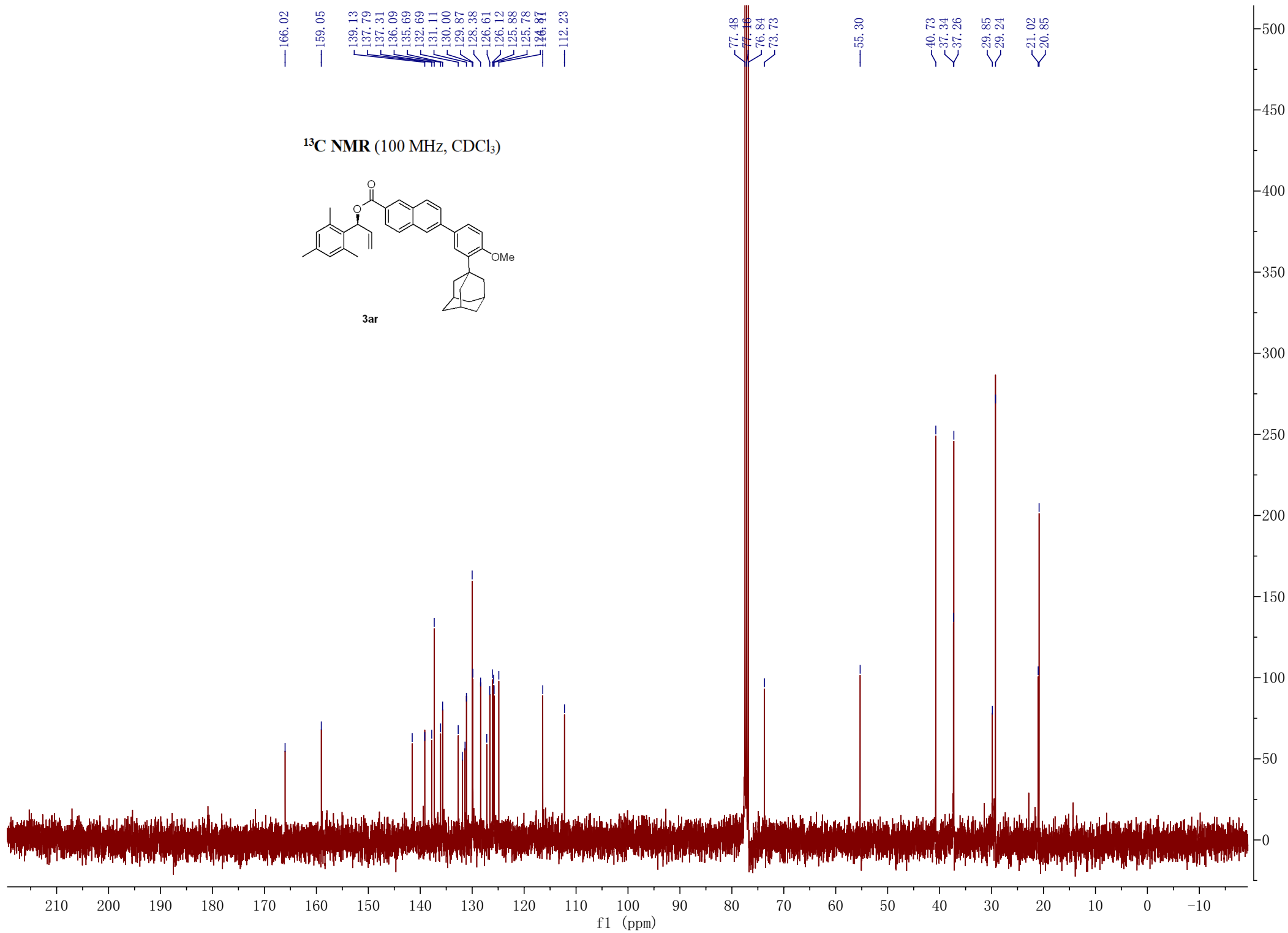
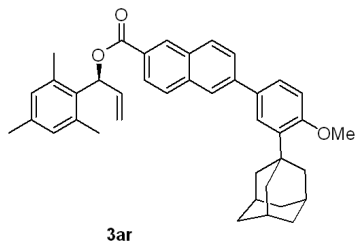


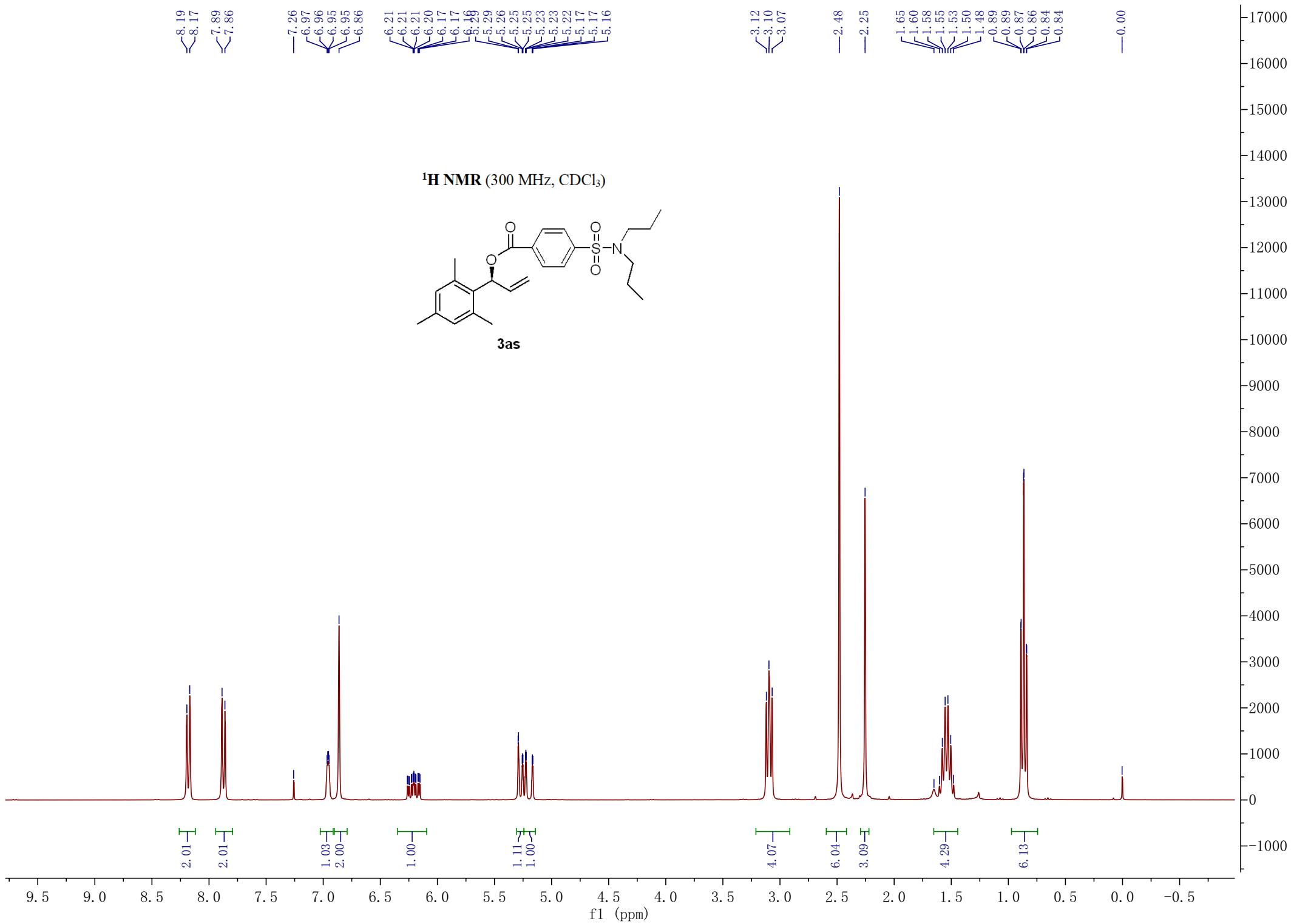
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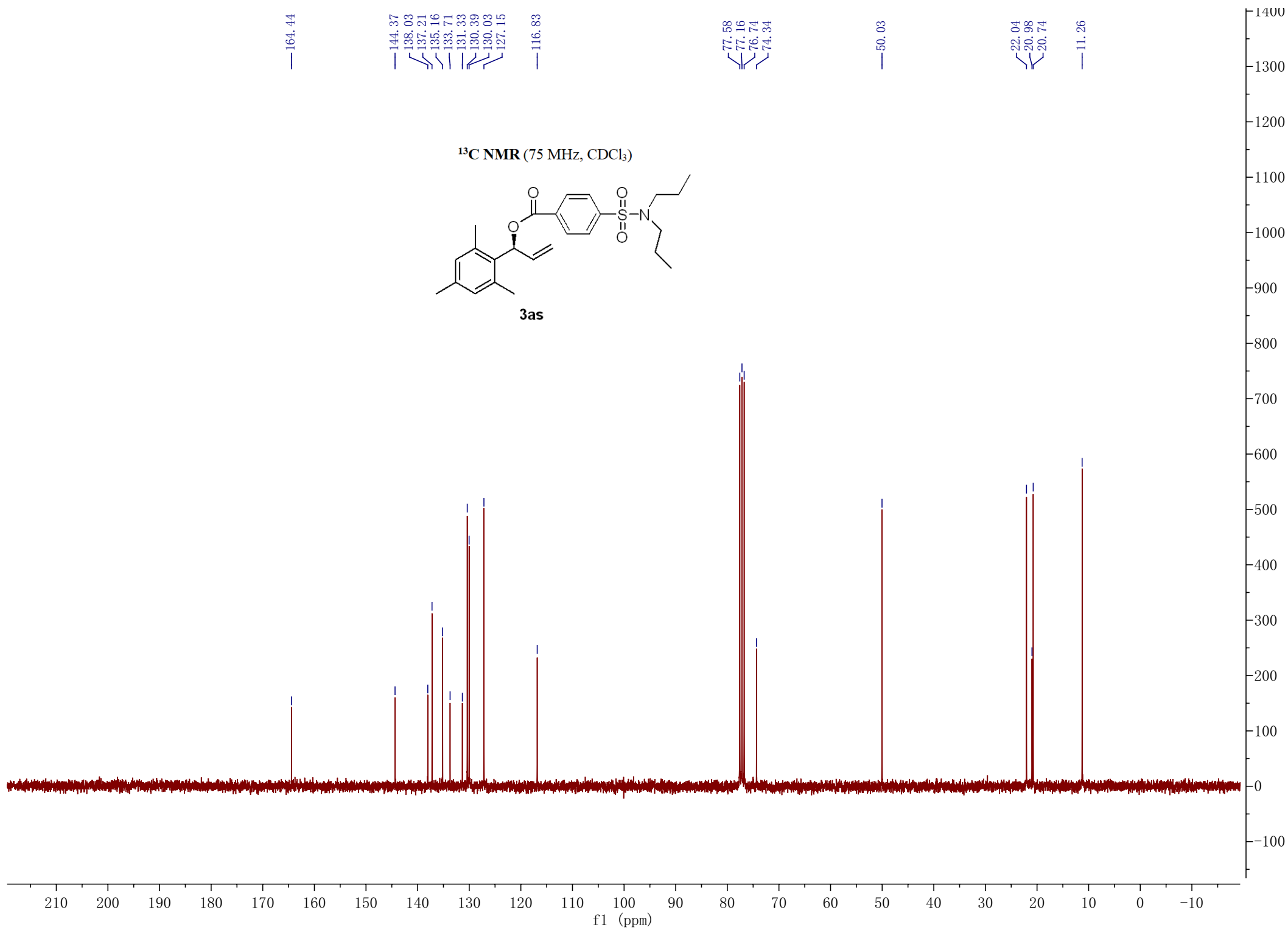


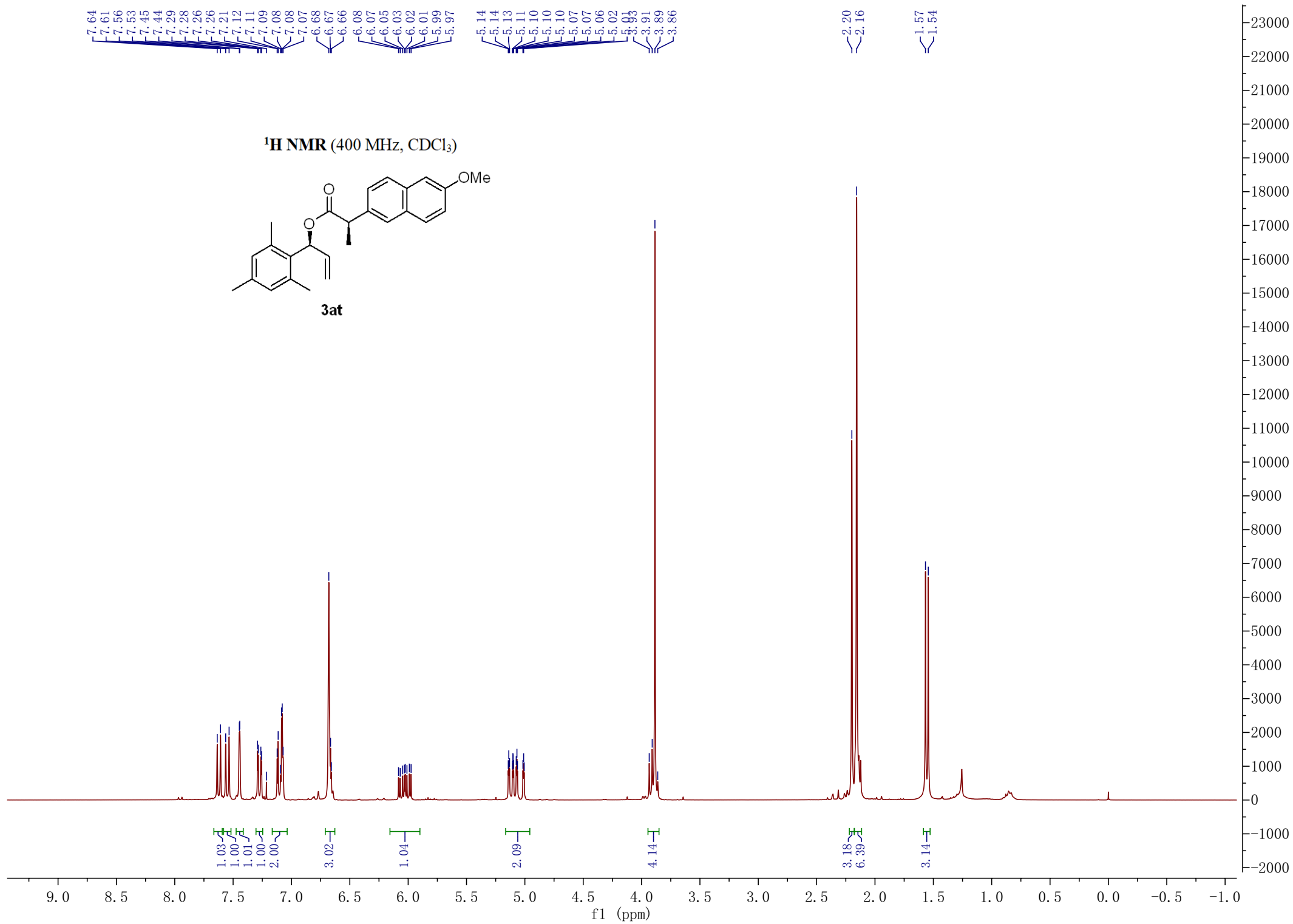


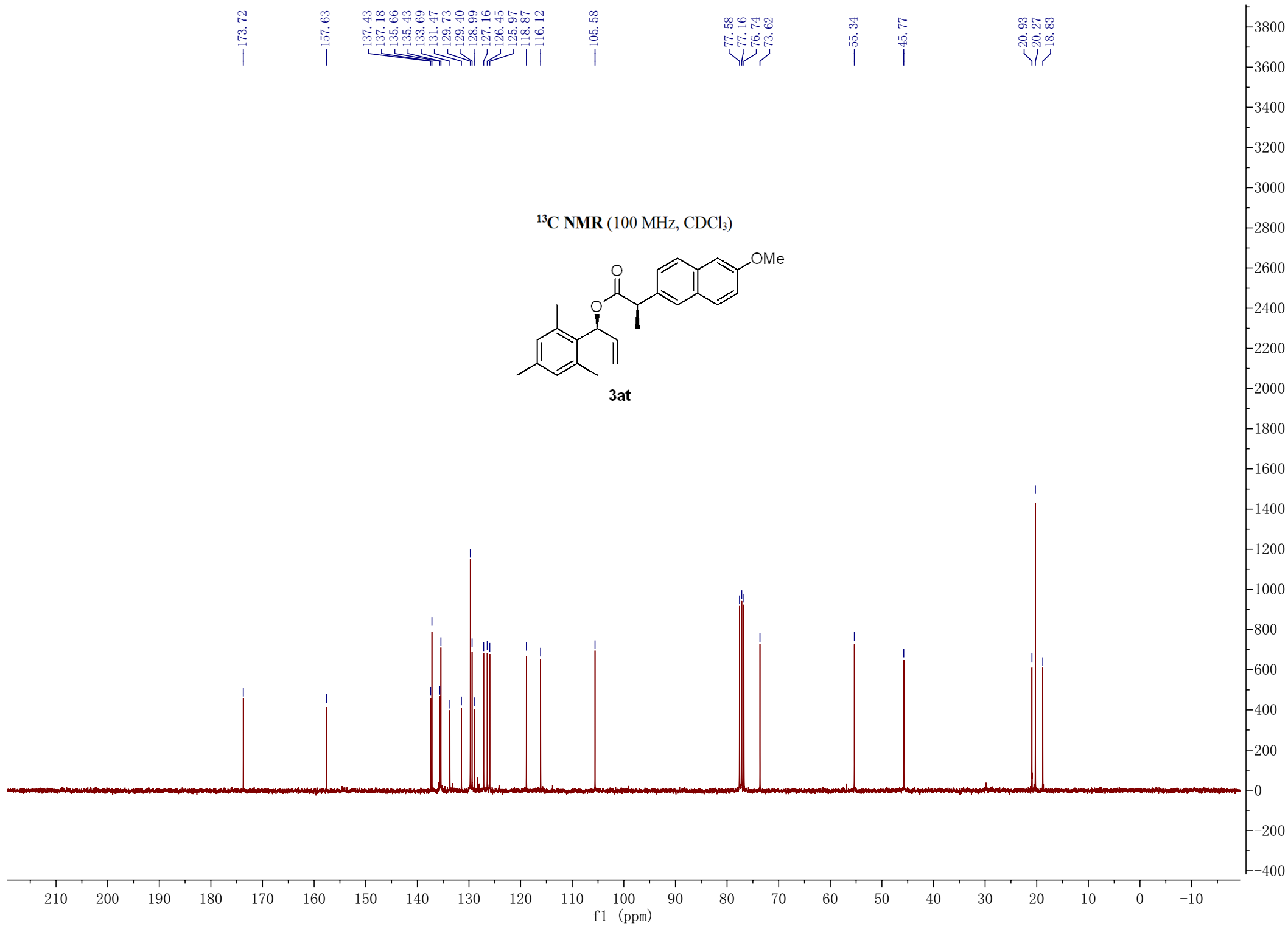
¹³C NMR (100 MHz, CDCl₃)

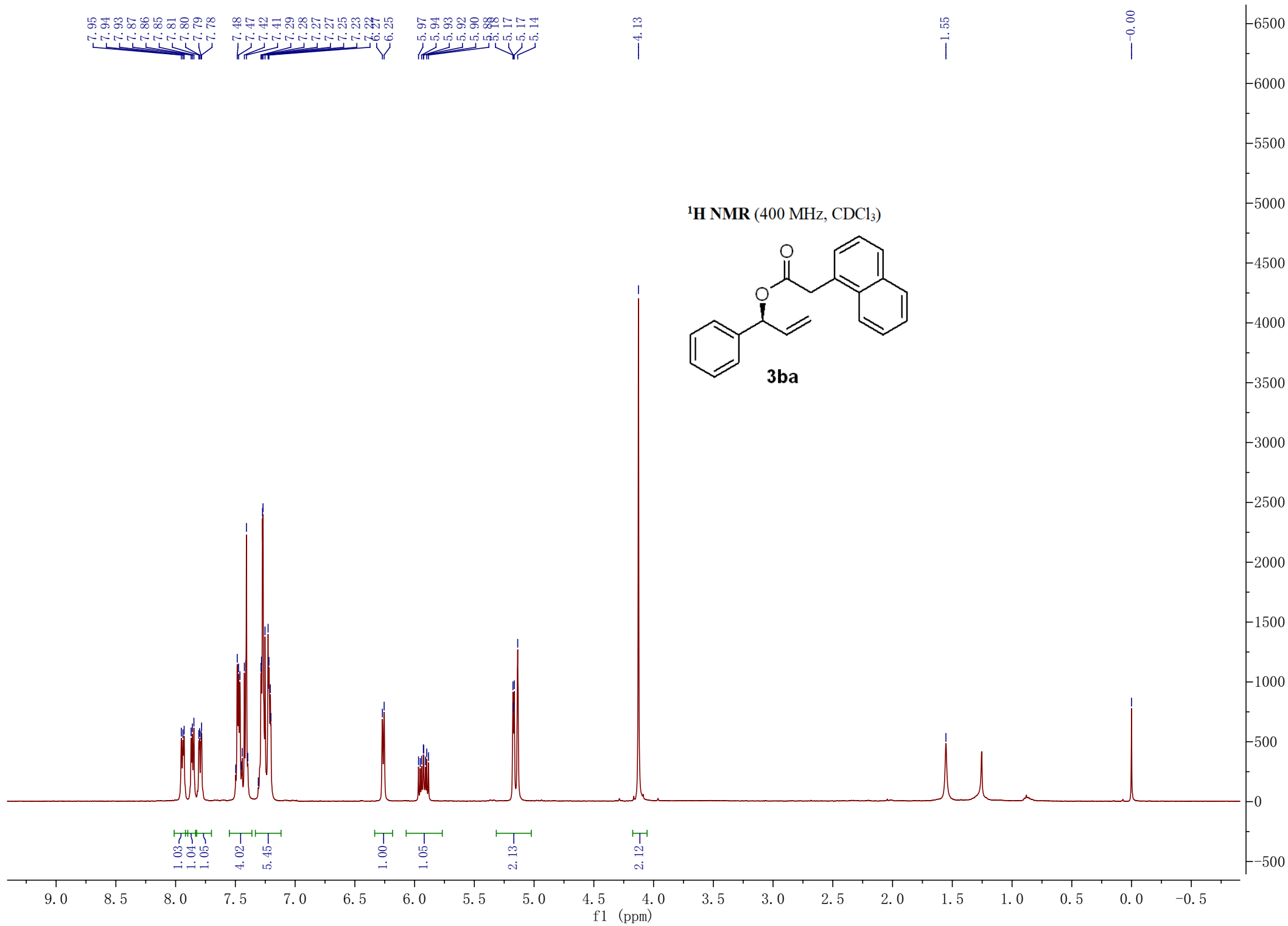




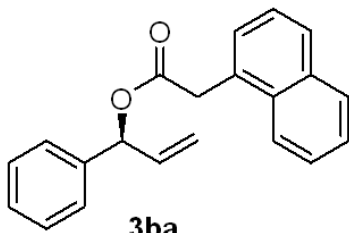








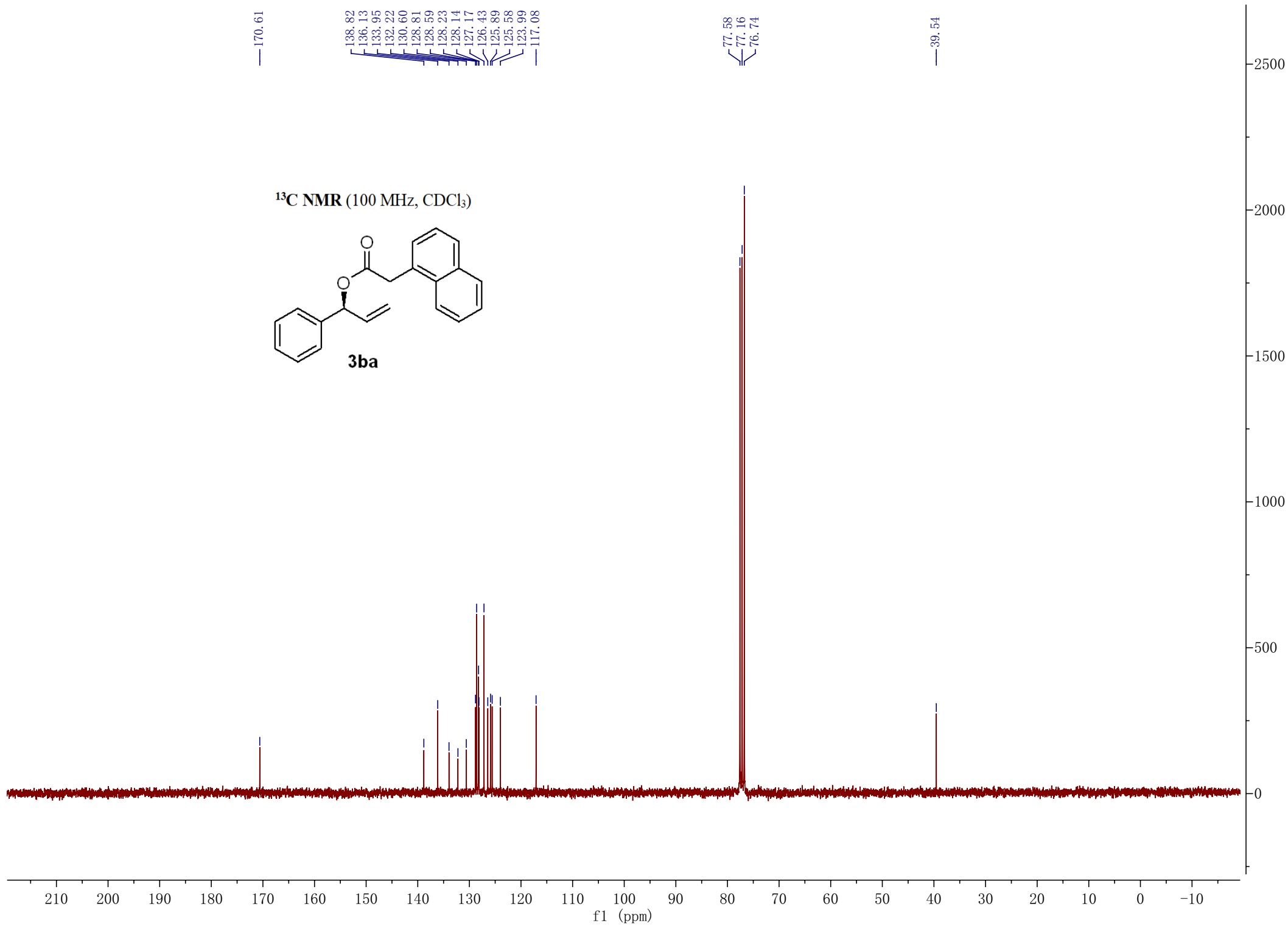
¹³C NMR (100 MHz, CDCl₃)

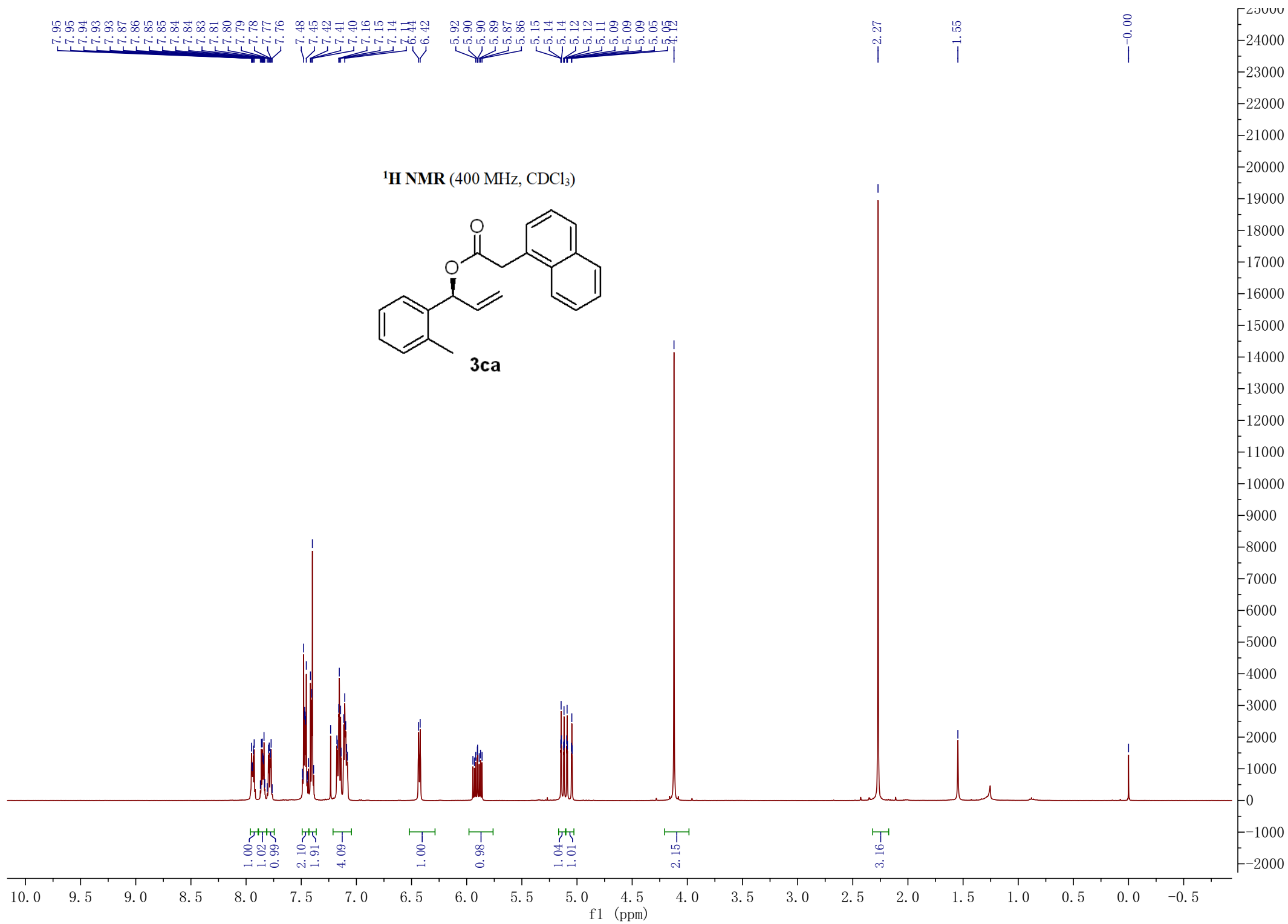


170.61
138.82
136.13
133.95
132.22
130.60
128.81
128.59
128.23
128.14
127.17
126.43
125.89
125.58
123.99
117.08

77.58
77.16
76.74

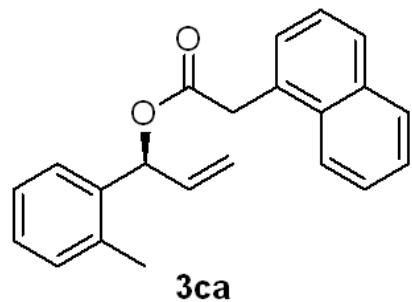
39.54





170.60
136.94
135.78
135.55
133.92
132.20
130.57
128.79
128.20
128.16
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126.88
126.43
126.21
125.89
125.57
123.98
117.06

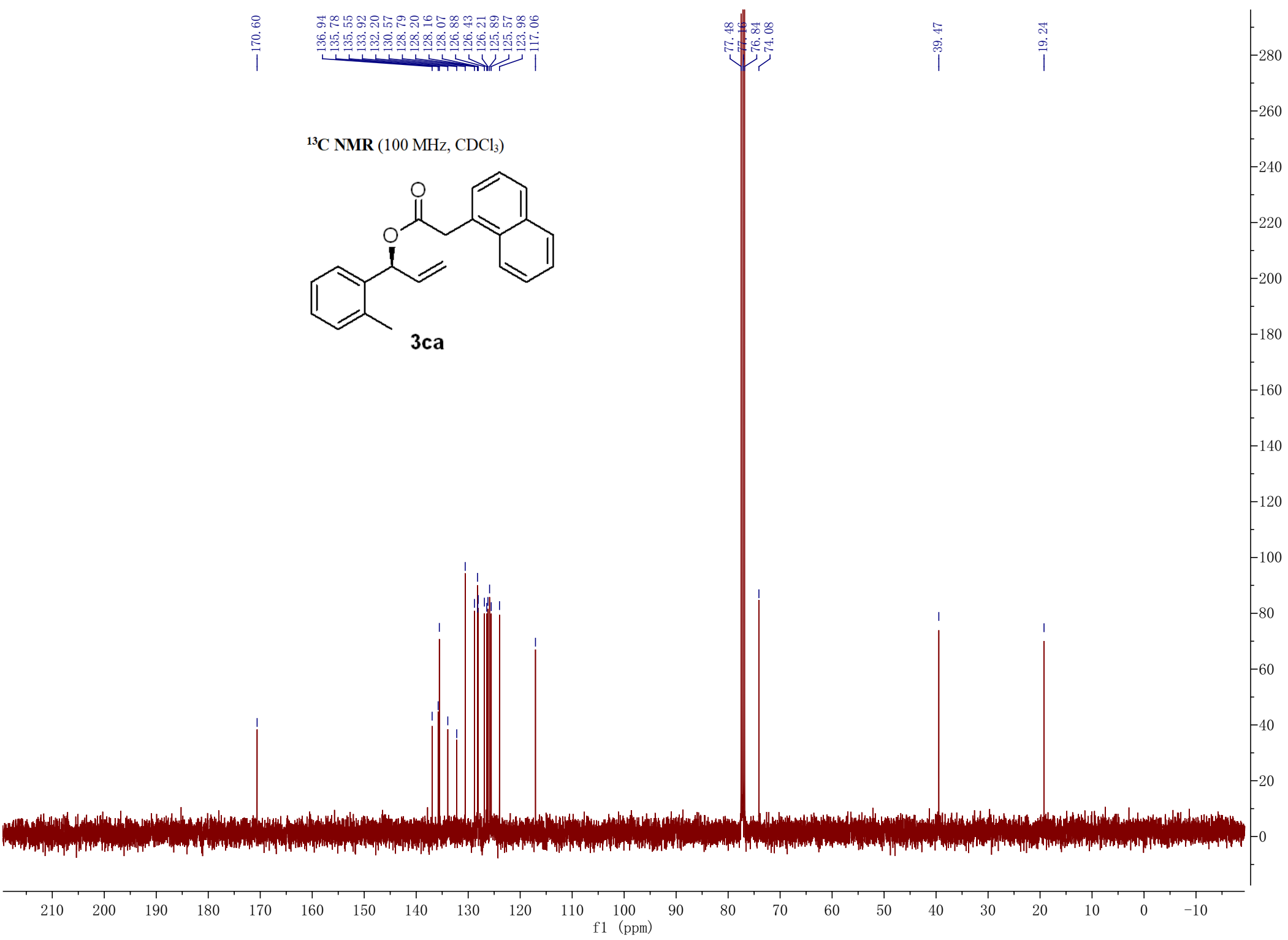
¹³C NMR (100 MHz, CDCl₃)

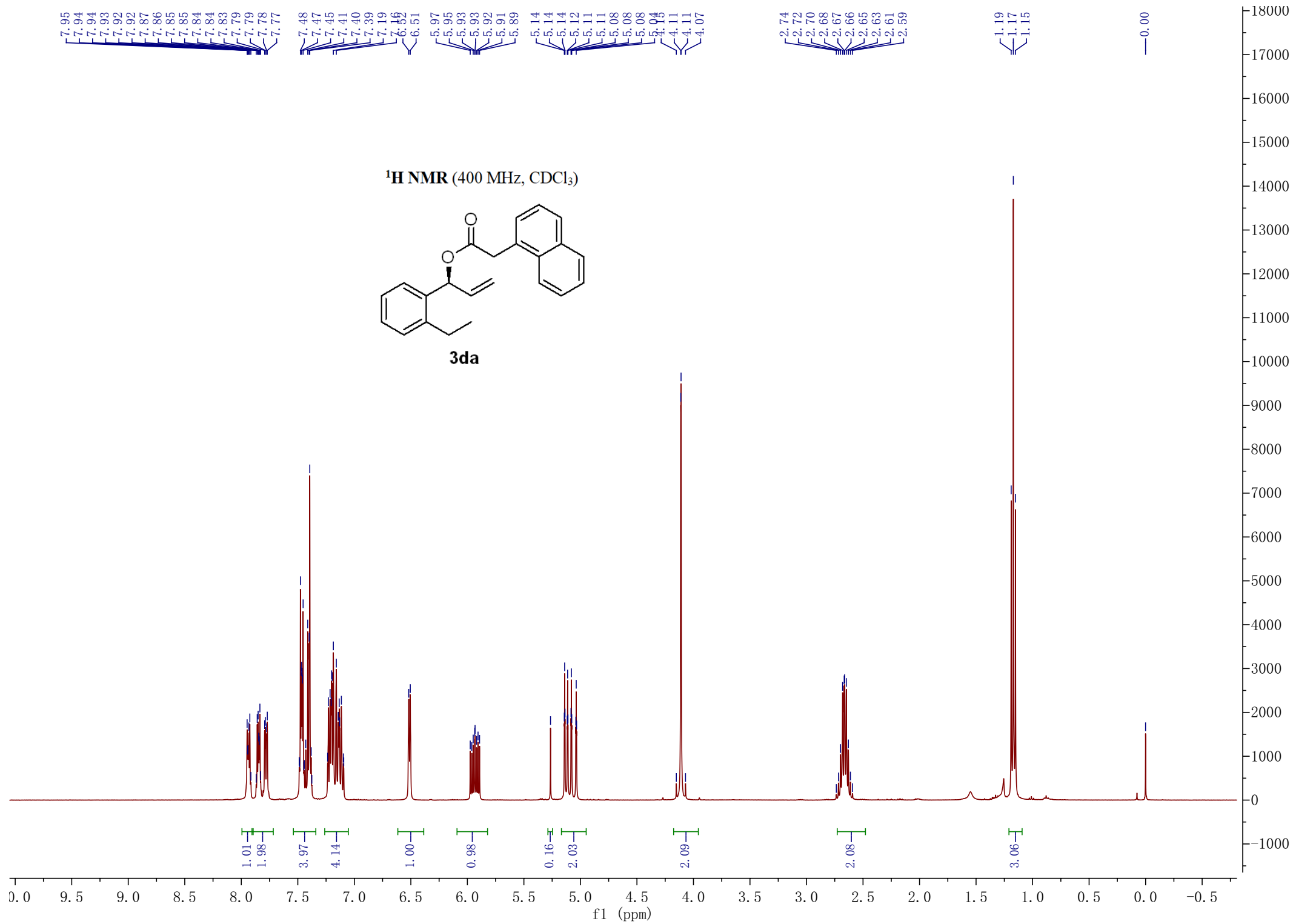


77.48
77.16
76.84
74.08

39.47

19.24





170.62

141.81

128.79

128.75

128.32

128.19

128.16

127.32

126.18

116.99

77.48

77.16

76.84

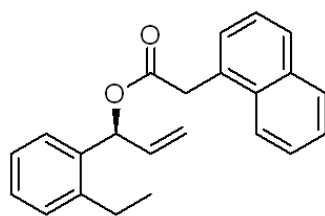
73.41

39.49

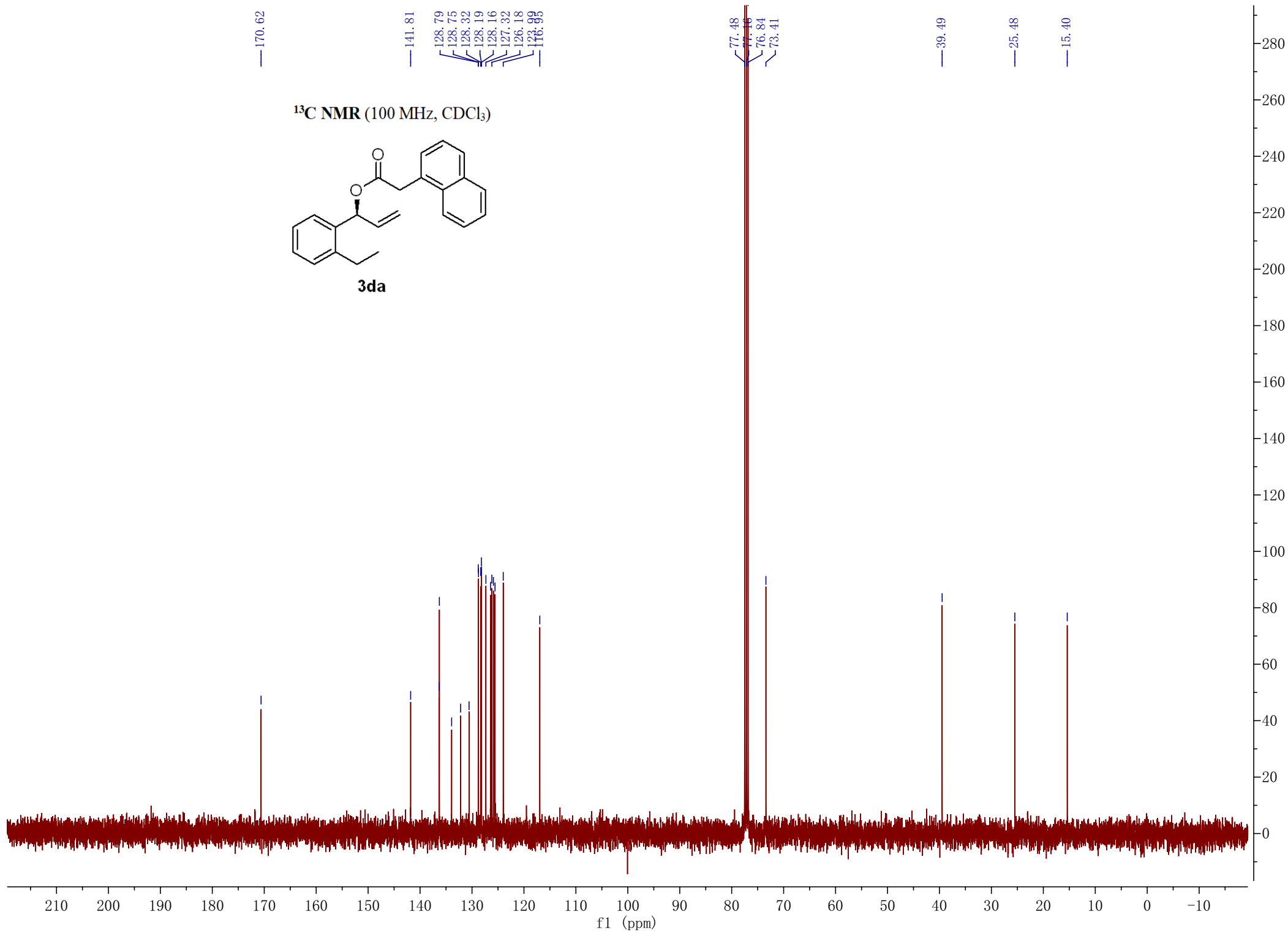
25.48

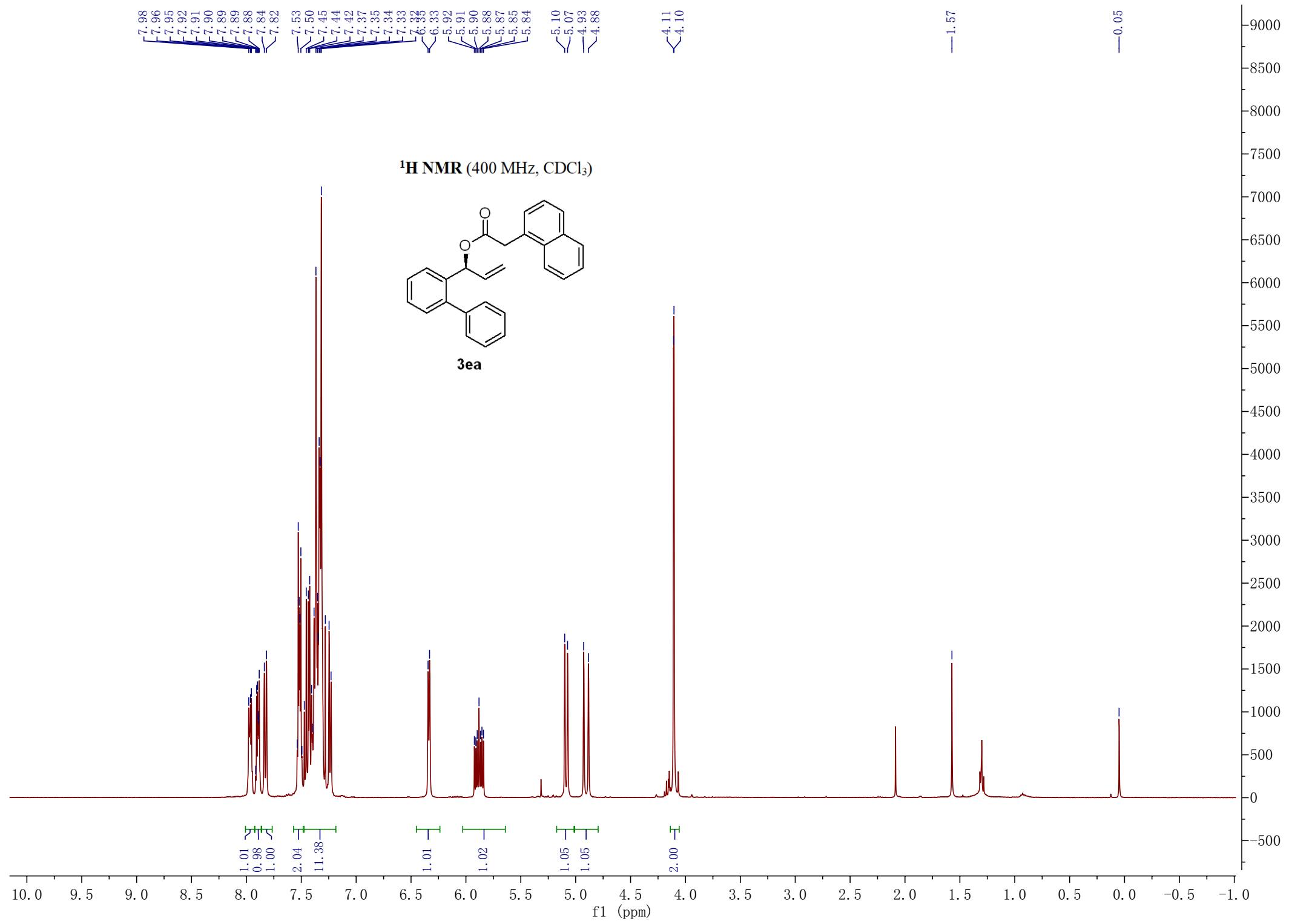
15.40

¹³C NMR (100 MHz, CDCl₃)

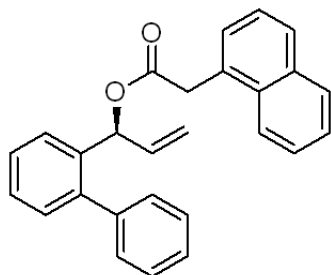


3da





¹³C NMR (100 MHz, CDCl₃)

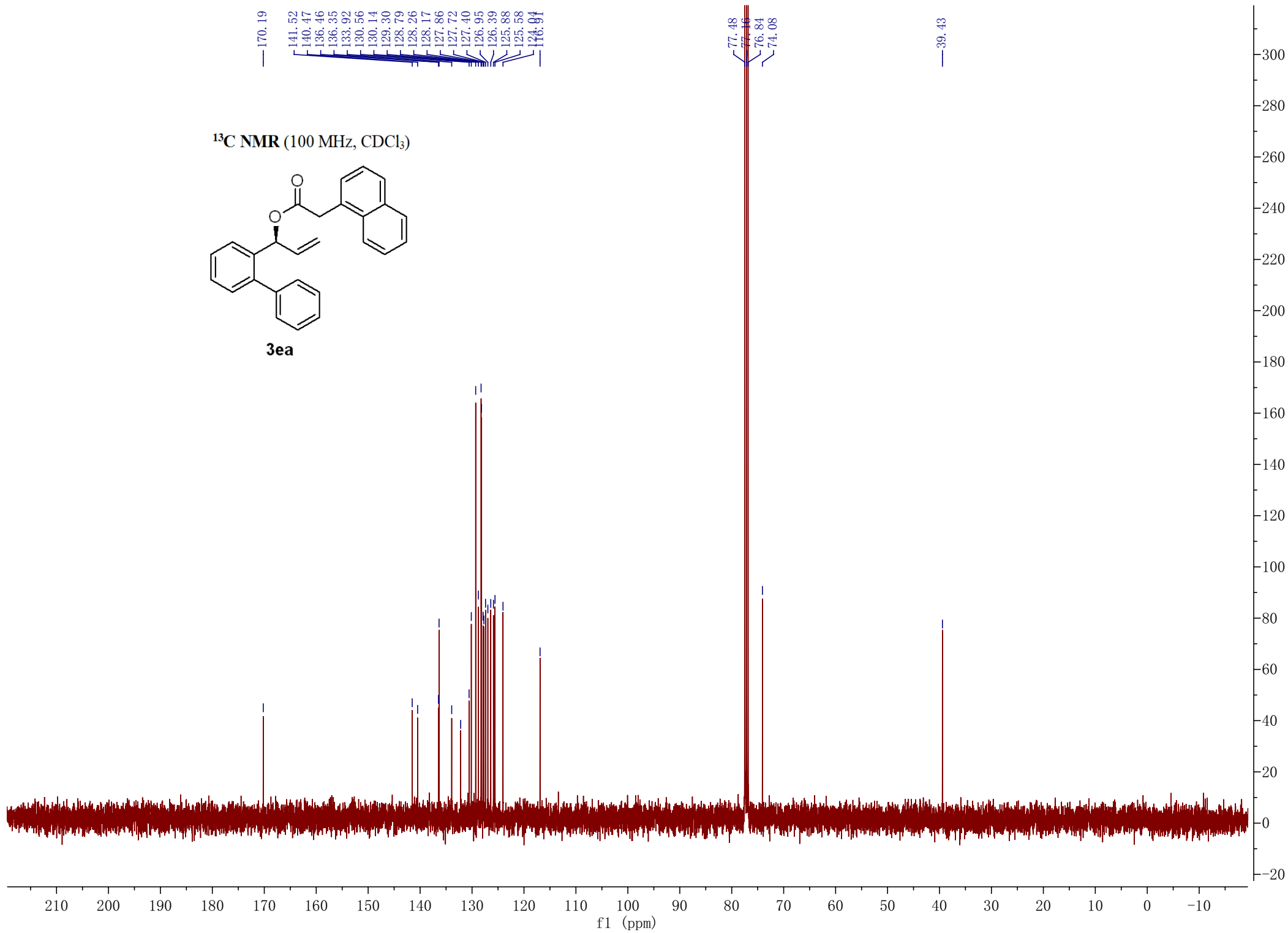


3ea

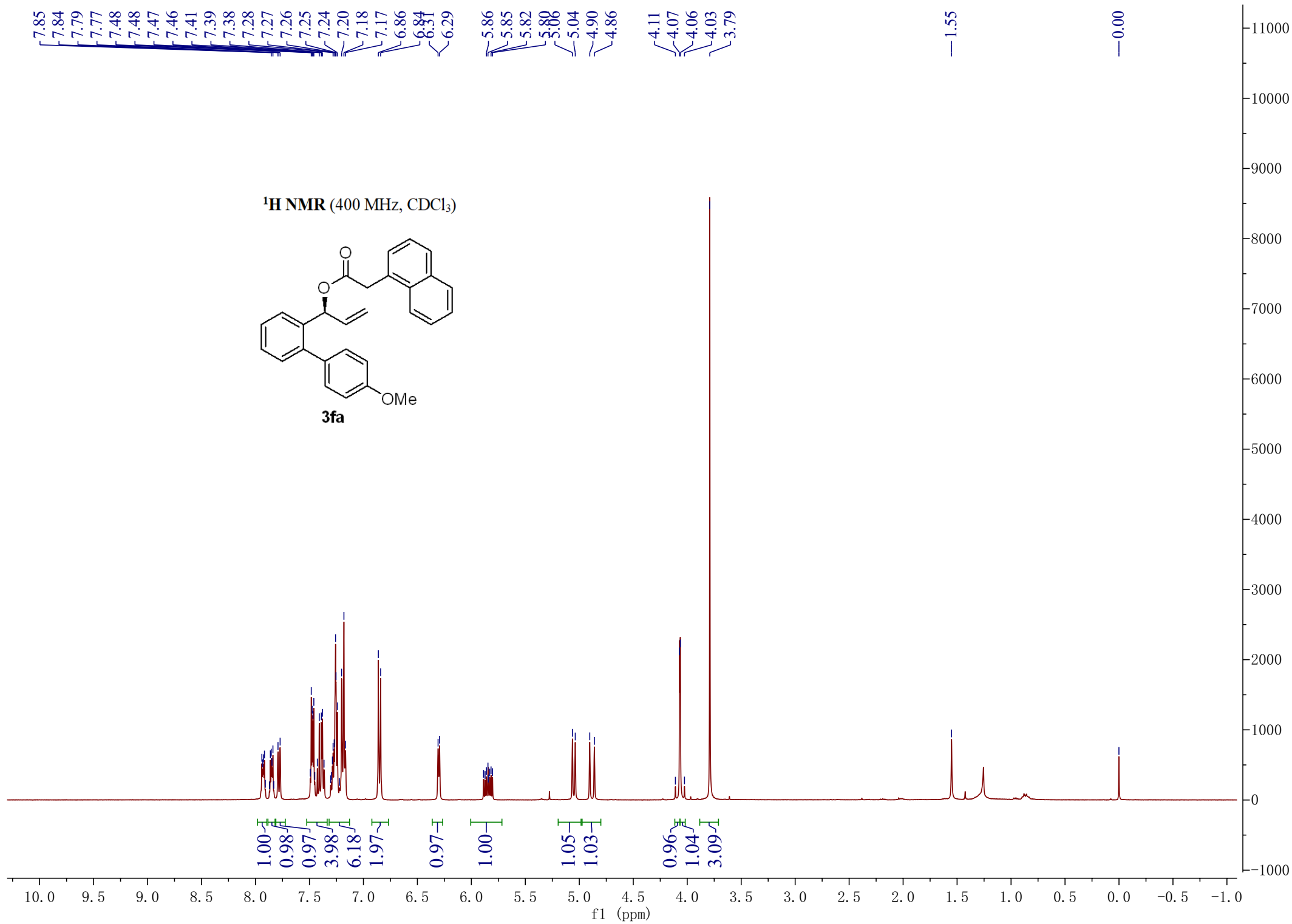
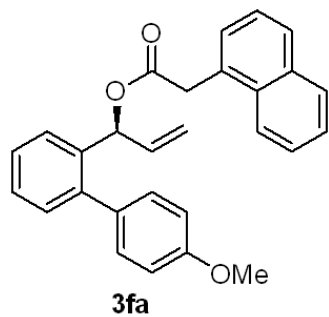
170.19
141.52
140.47
136.46
136.35
133.92
130.56
130.14
129.30
128.79
128.26
128.17
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125.88
125.58
124.94

77.48
77.16
76.84
74.08

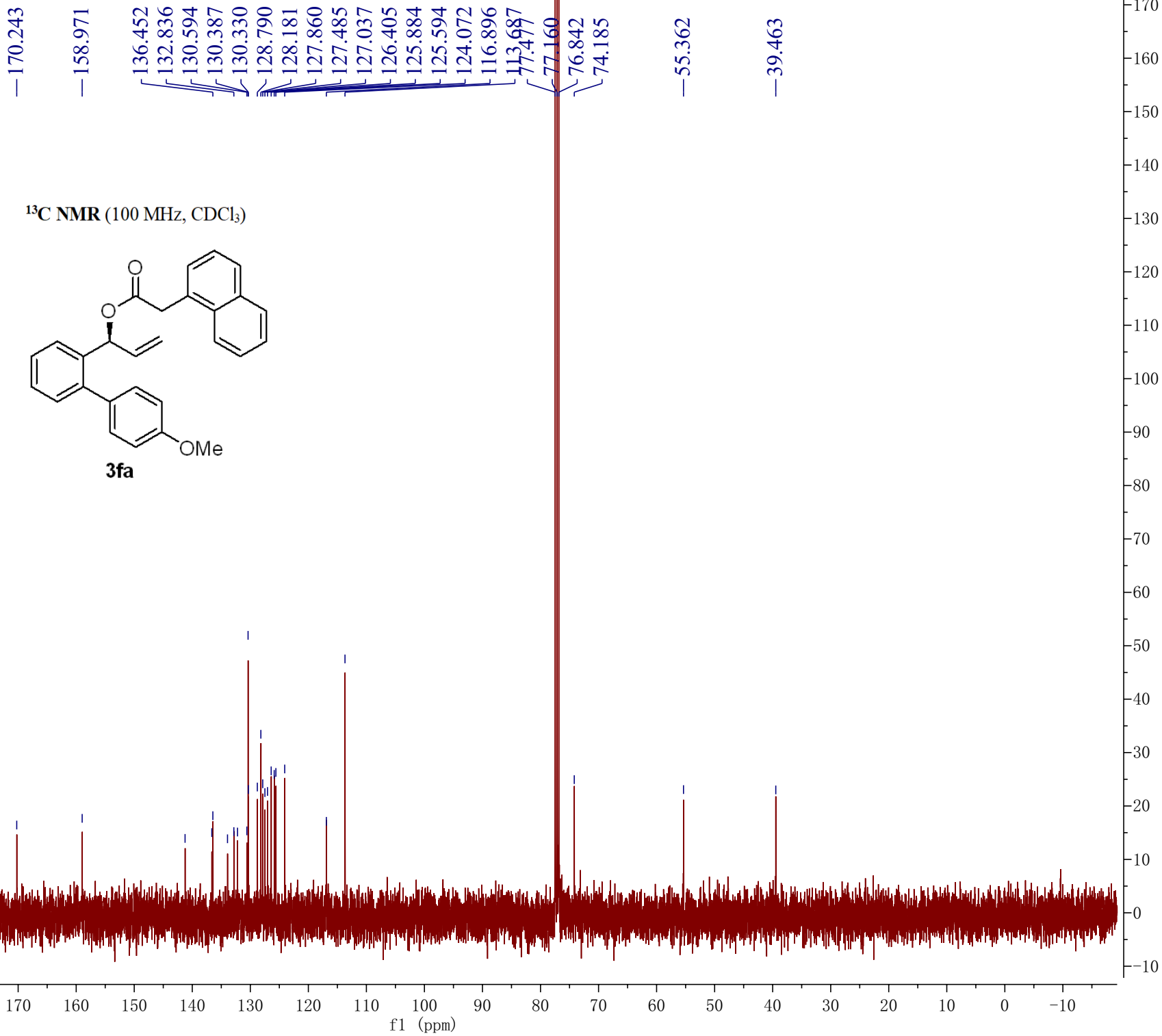
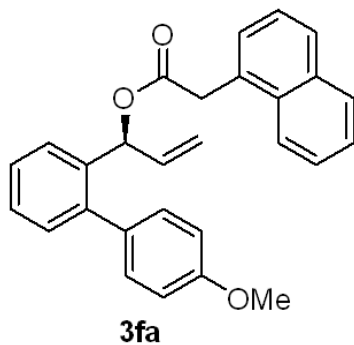
39.43



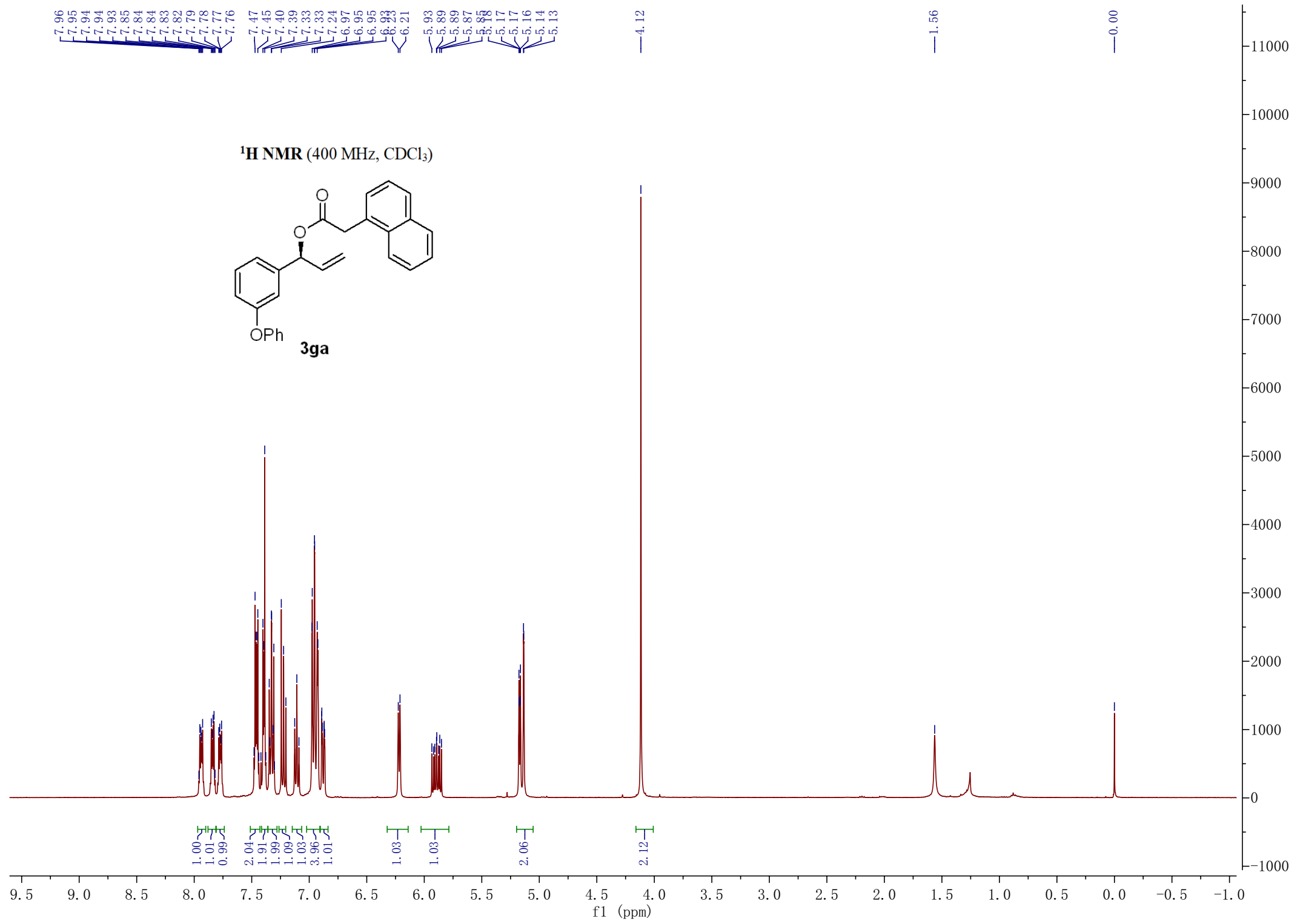
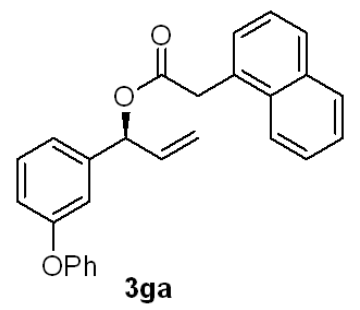
¹H NMR (400 MHz, CDCl₃)



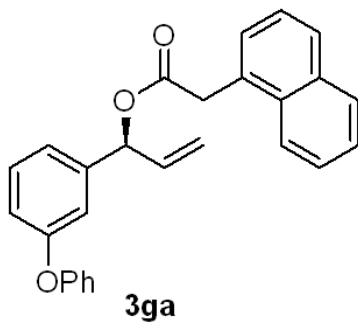
¹³C NMR (100 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)



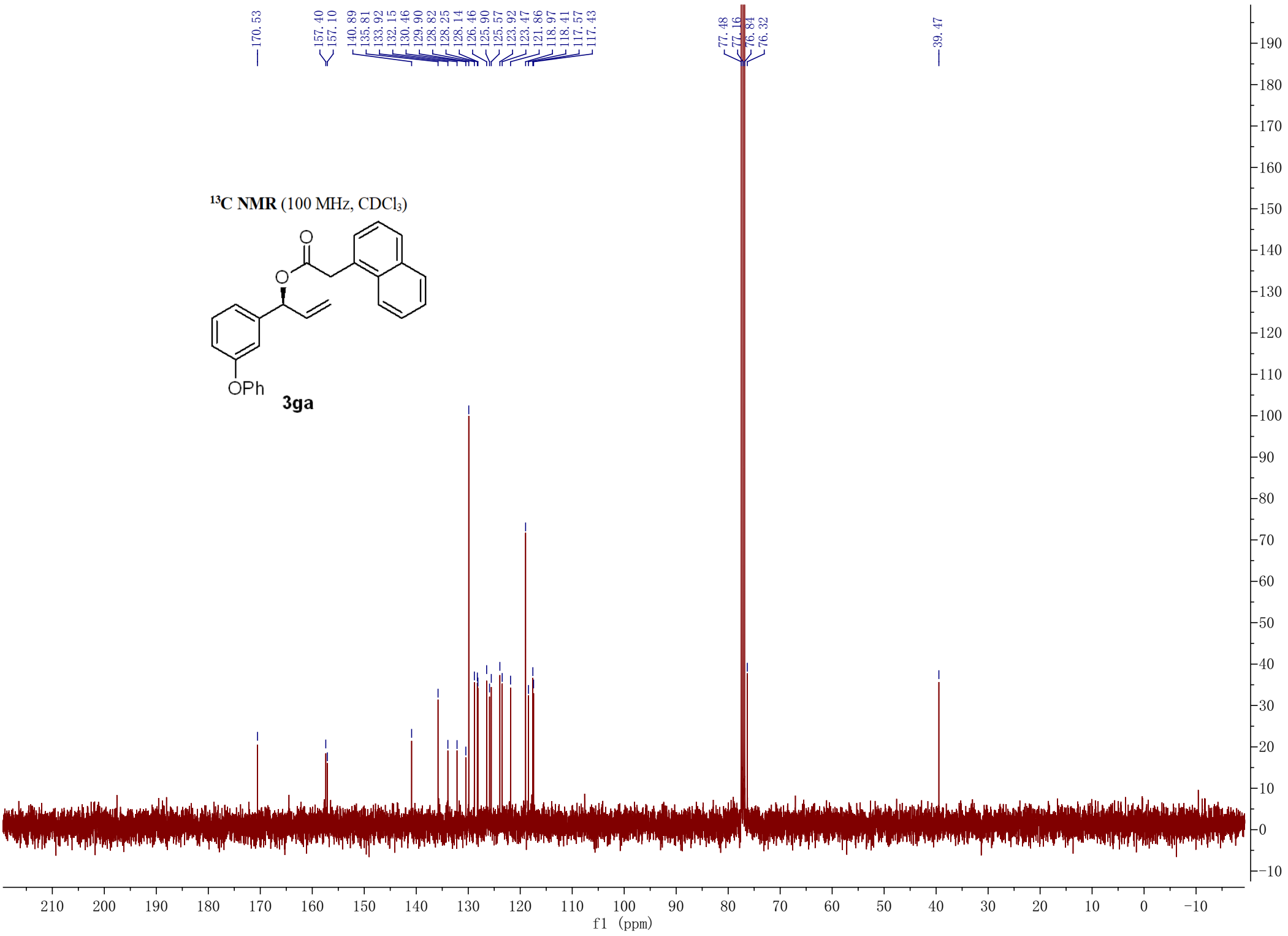
¹³C NMR (100 MHz, CDCl₃)

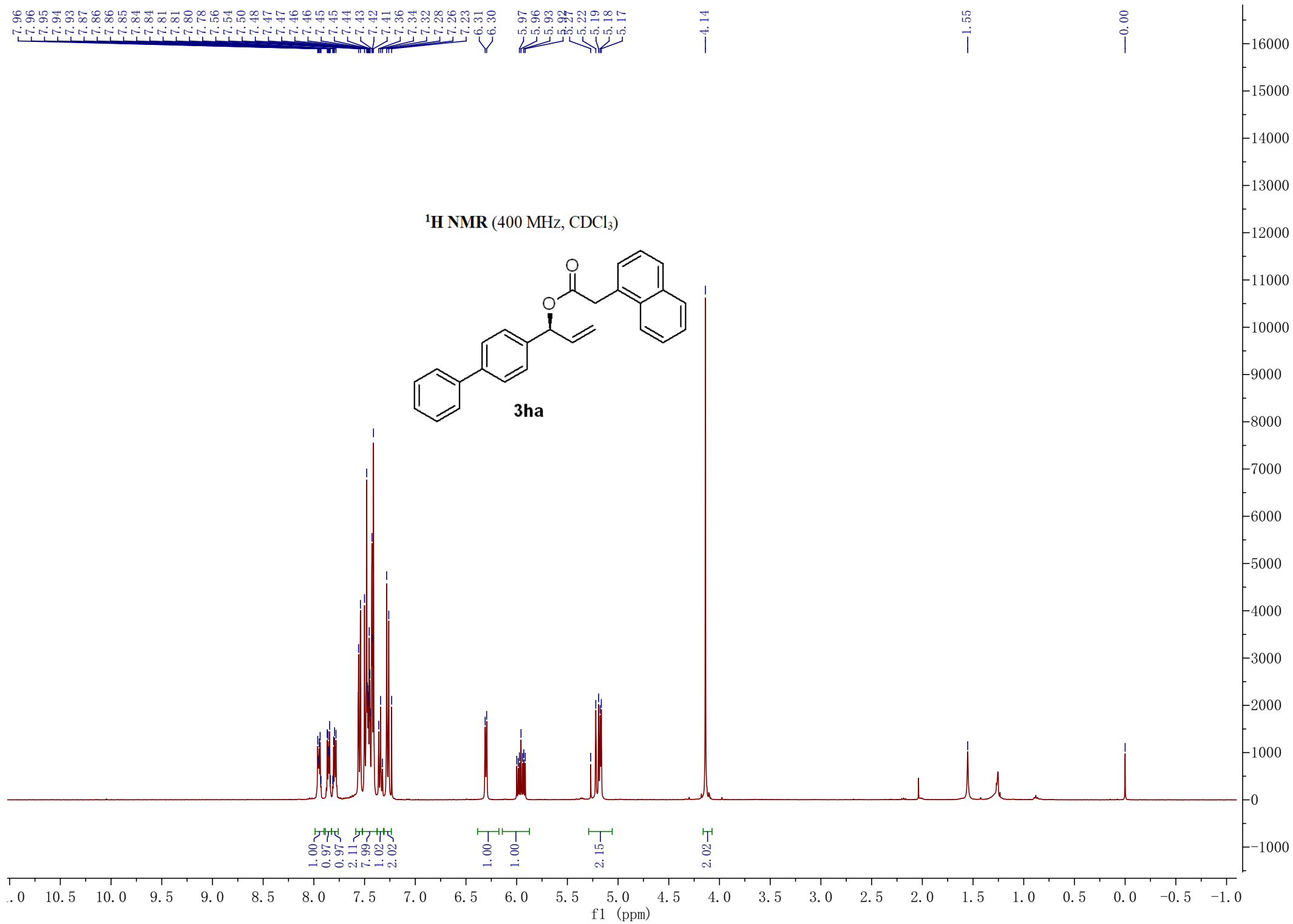


170.53
157.40
157.10
140.89
135.81
133.92
132.15
130.46
129.90
128.82
128.25
128.14
126.46
125.90
125.57
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117.57
117.43

77.48
77.16
76.84
76.32

39.47



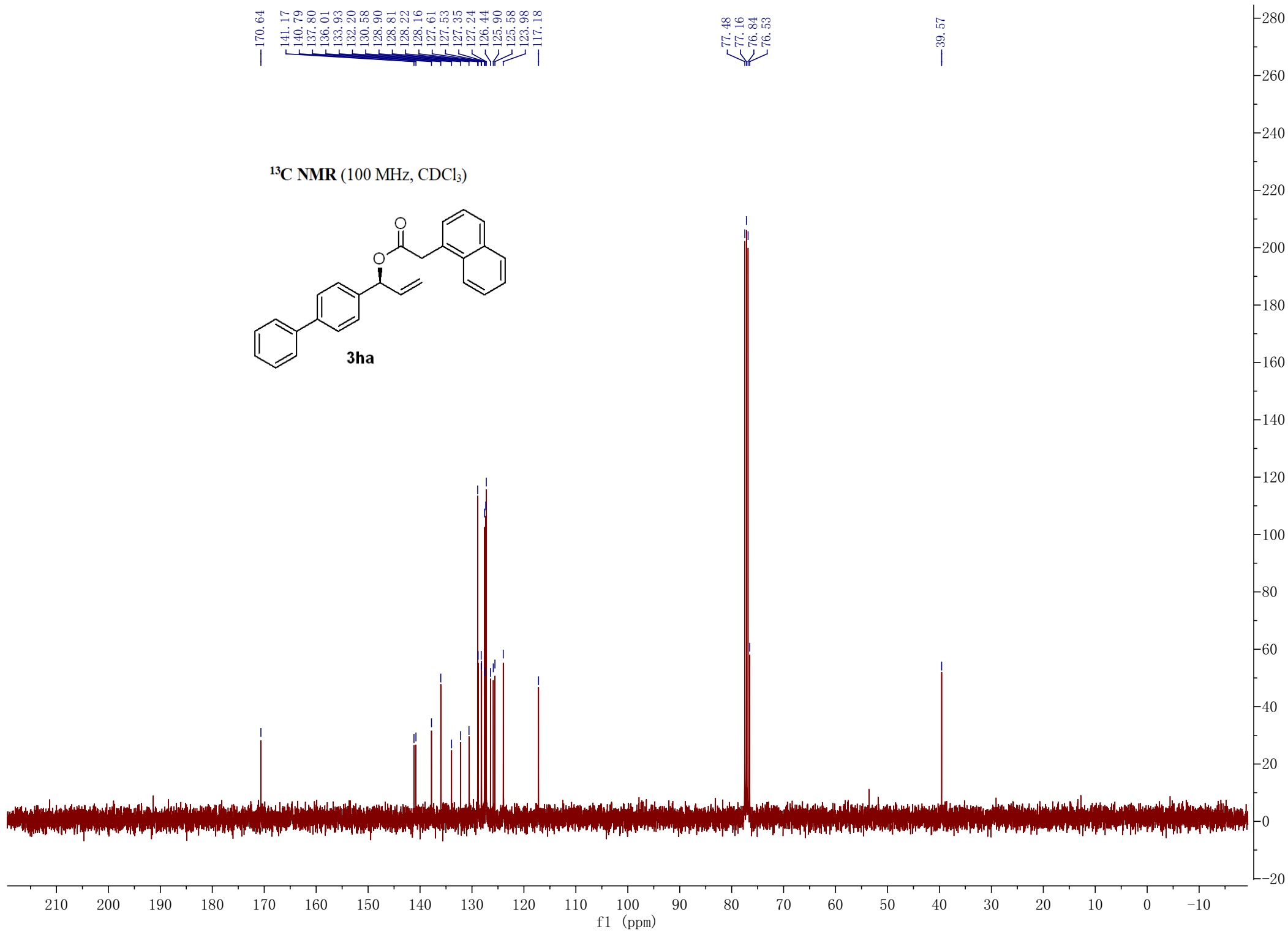
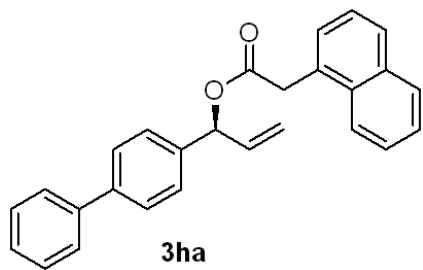


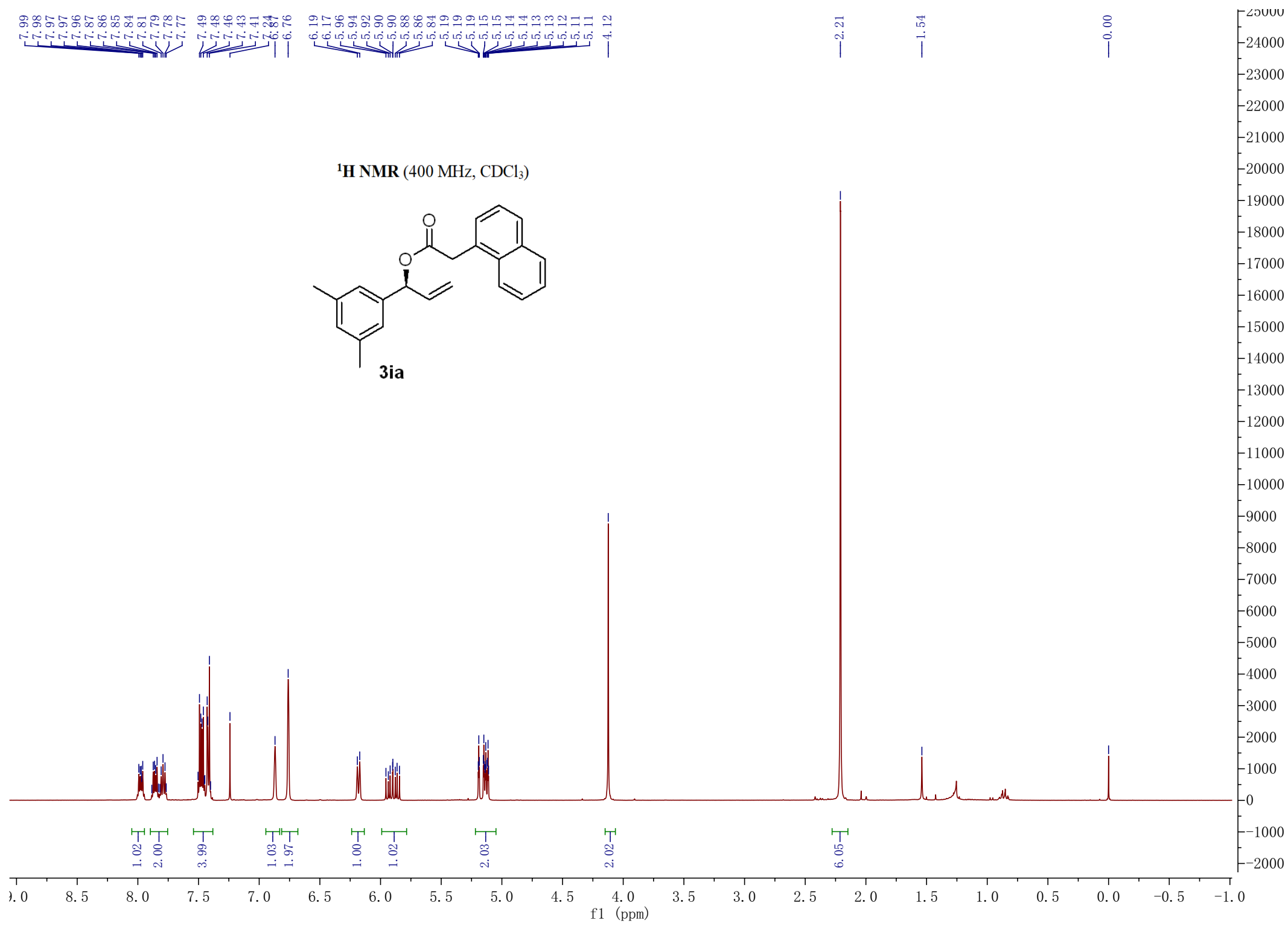
170.64
141.17
140.79
137.80
136.01
133.93
132.20
130.58
128.90
128.81
128.22
128.16
127.61
127.53
127.35
127.24
126.44
125.90
125.58
123.98
117.18

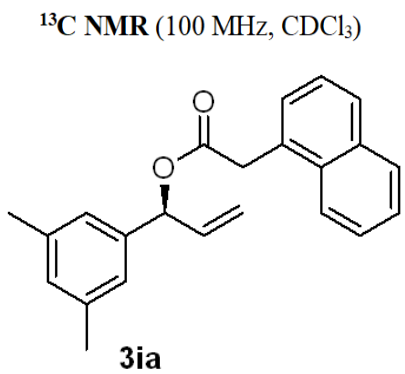
77.48
77.16
76.84
76.53

39.57

¹³C NMR (100 MHz, CDCl₃)





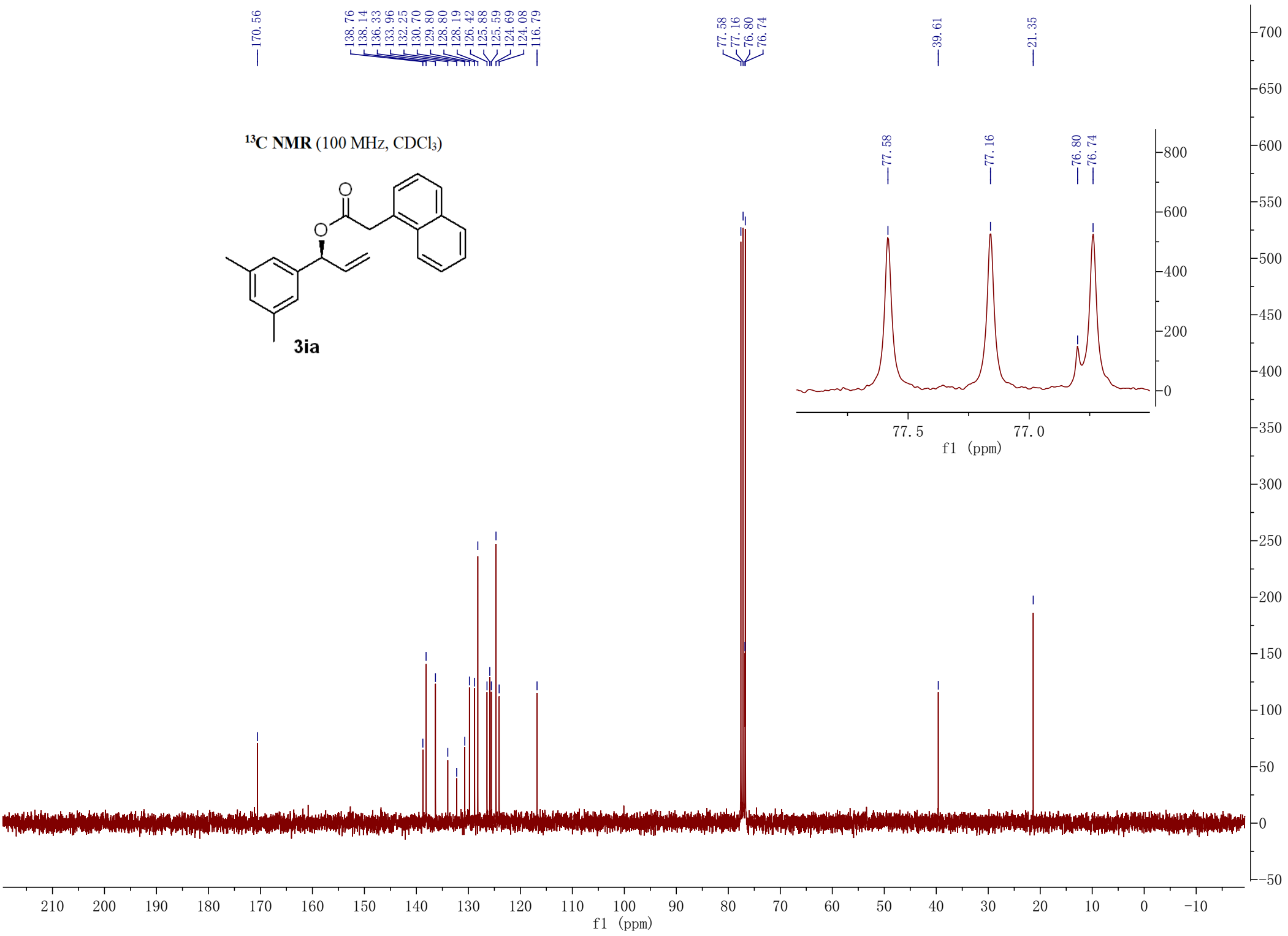


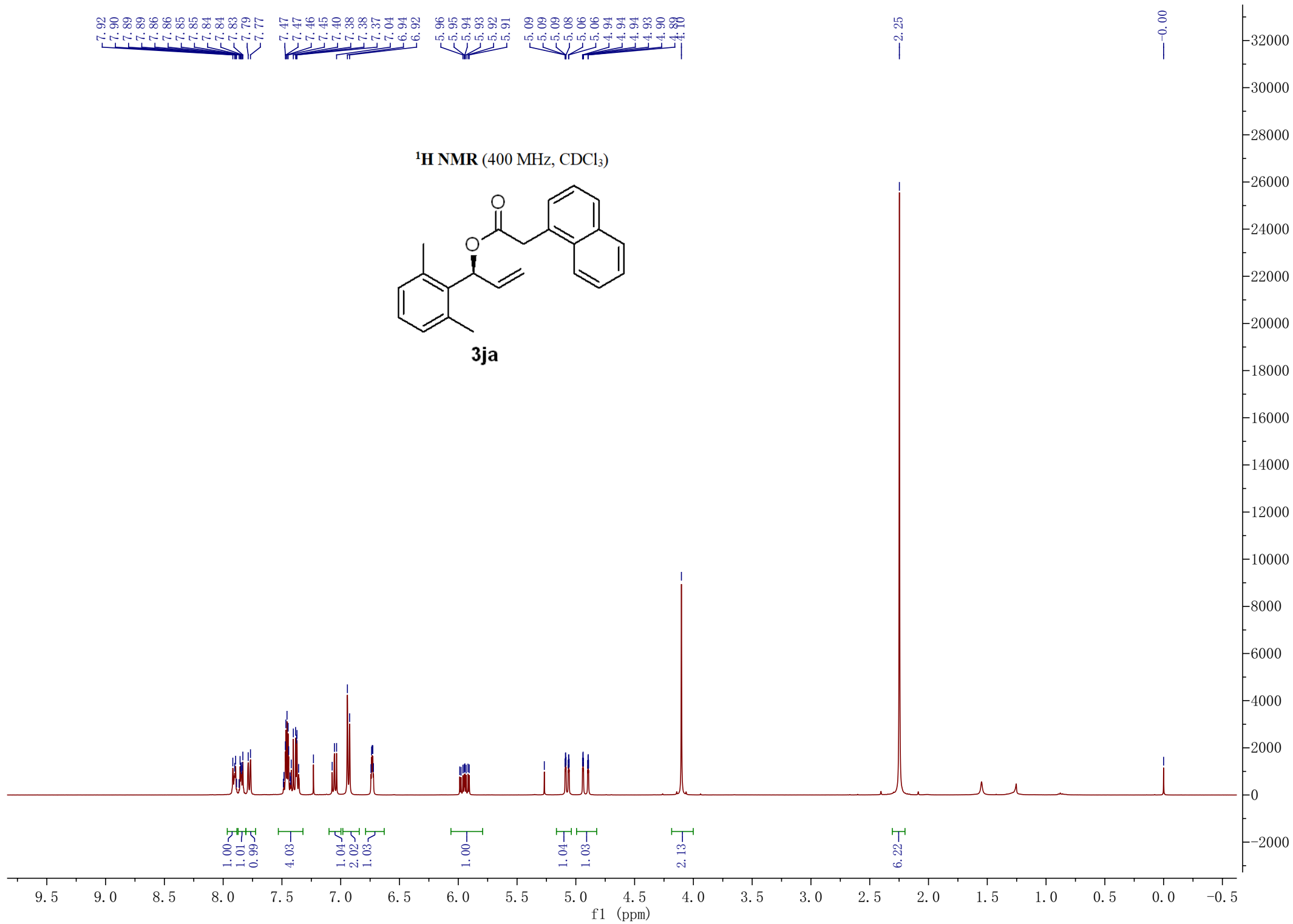
170.56
138.76
138.14
136.33
133.96
132.25
130.70
129.80
128.80
128.19
126.42
125.88
125.59
124.69
124.08
116.79

77.58
77.16
76.80
76.74

39.61

21.35





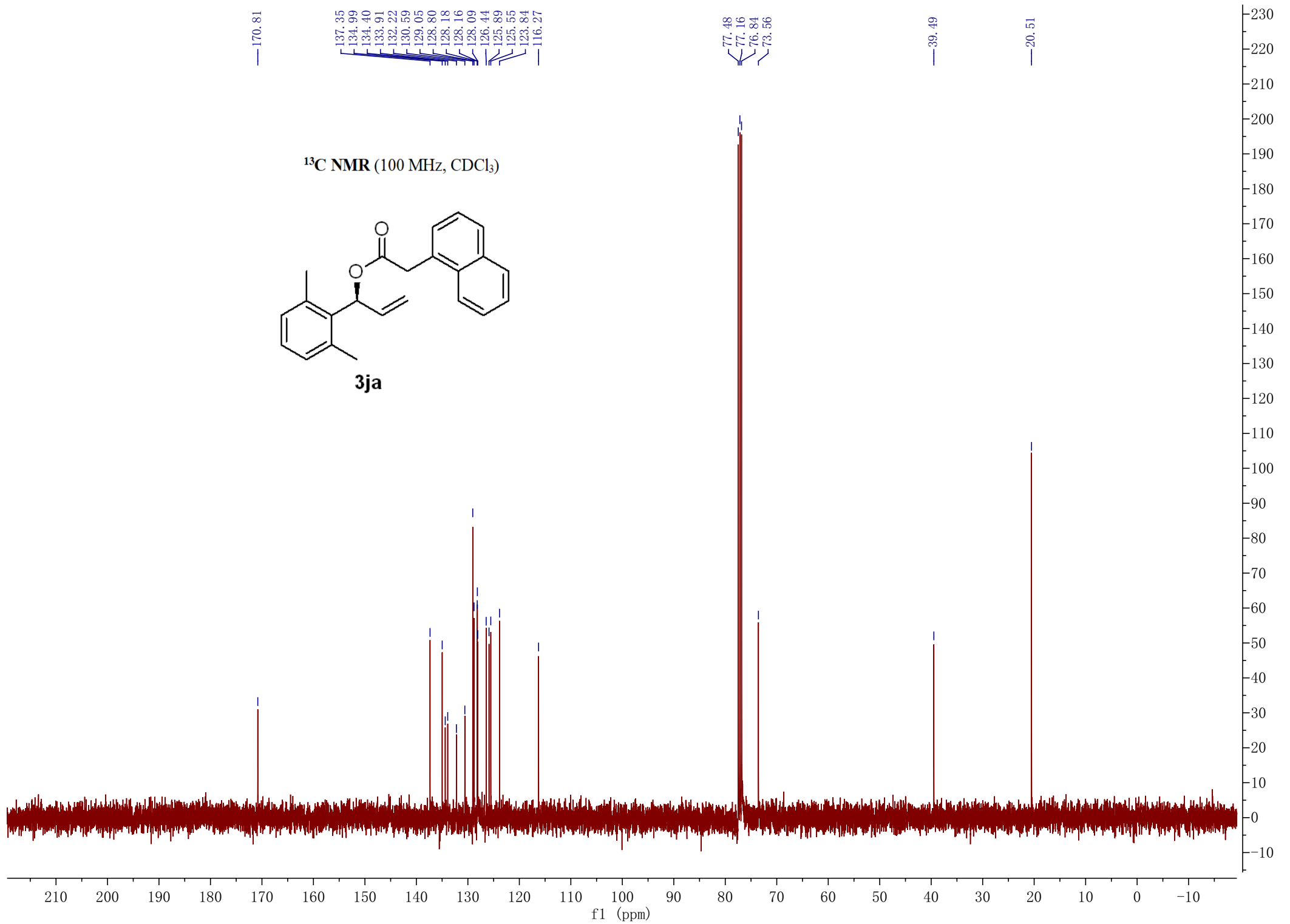
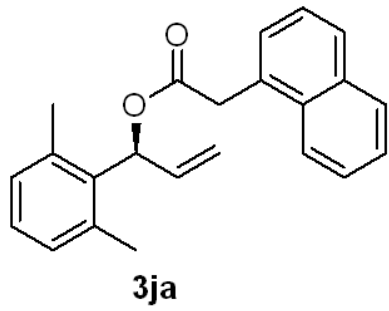
170.81
137.35
134.99
134.40
133.91
132.22
130.59
129.05
128.80
128.18
128.16
128.09
126.44
125.89
125.55
123.84
116.27

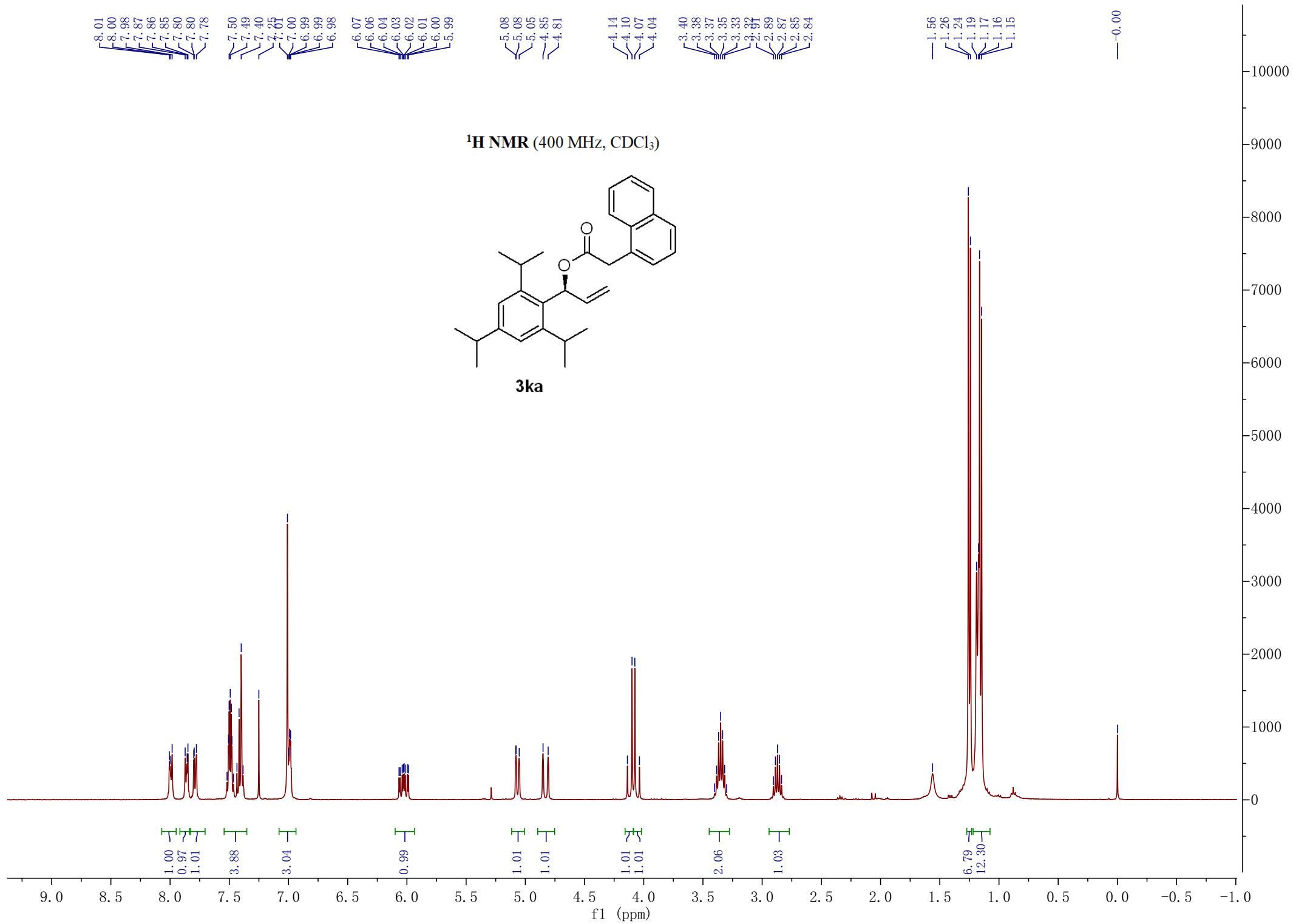
77.48
77.16
76.84
73.56

39.49

20.51

¹³C NMR (100 MHz, CDCl₃)





171.10

148.91

137.83

133.99

130.65

129.58

128.85

128.29

128.22

126.43

125.89

125.61

118.96

77.48

77.16

76.84

72.12

39.71

34.27

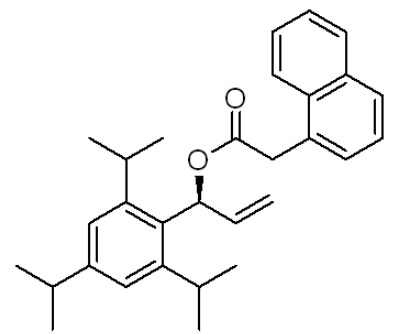
29.80

25.19

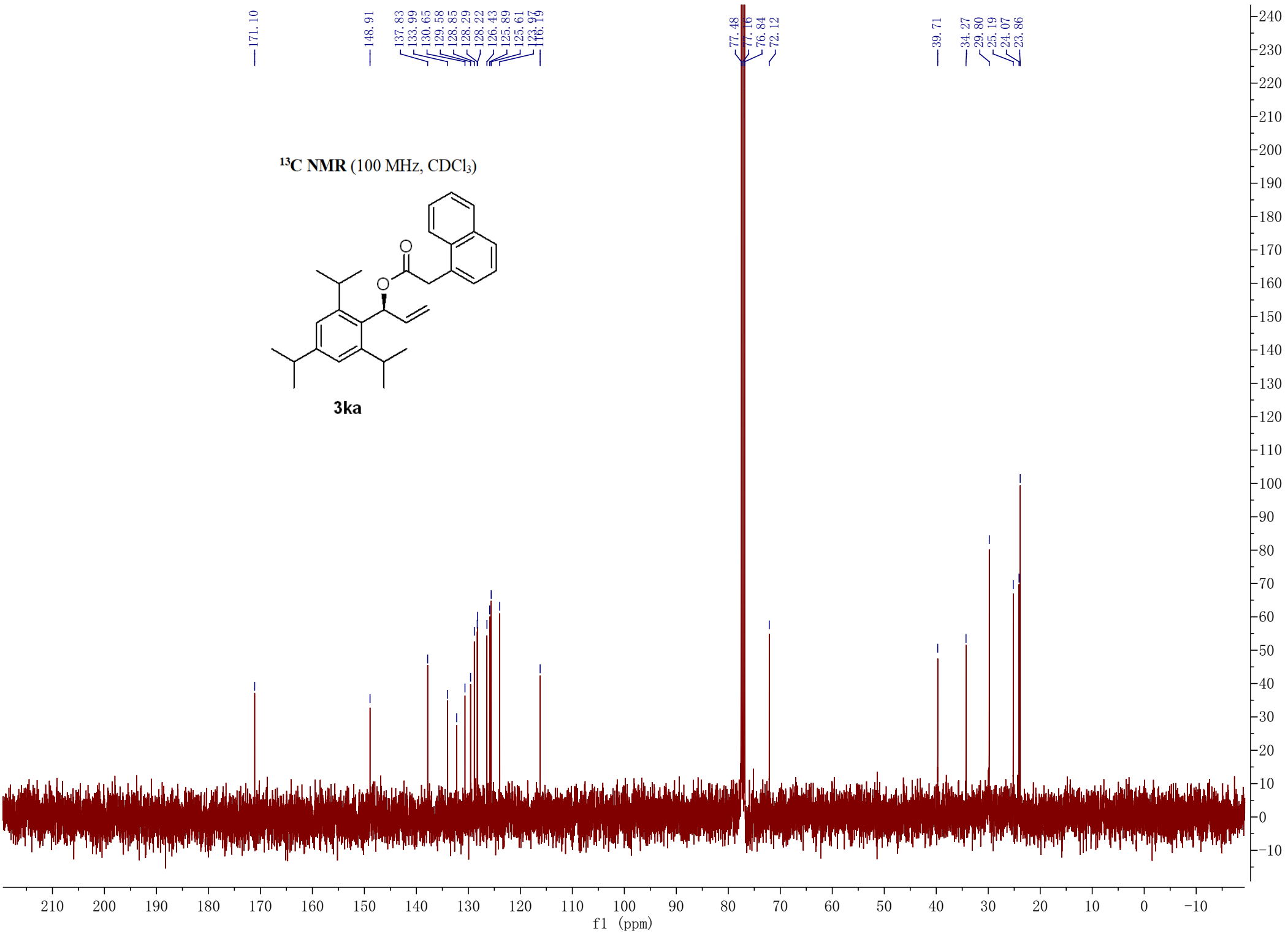
24.07

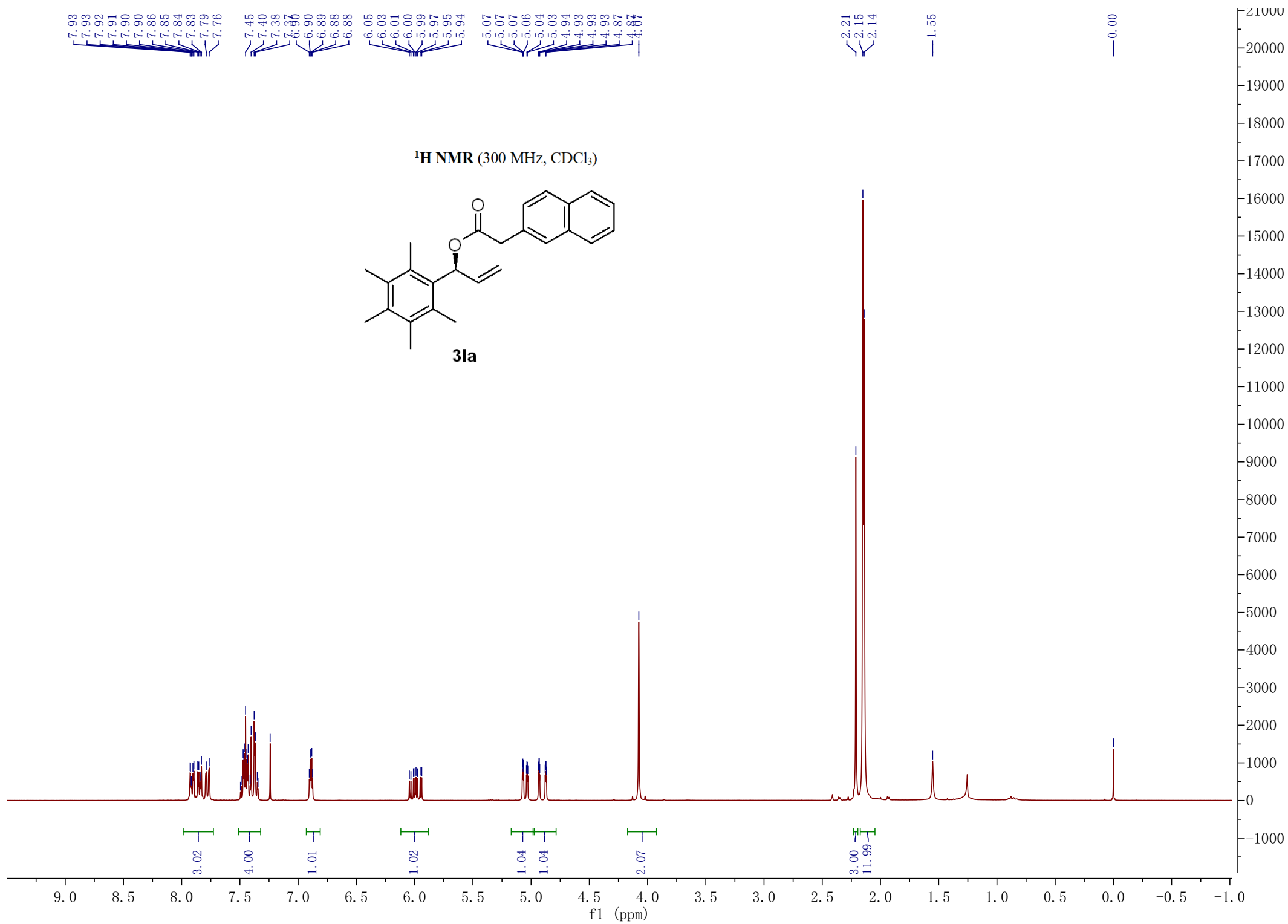
23.86

¹³C NMR (100 MHz, CDCl₃)



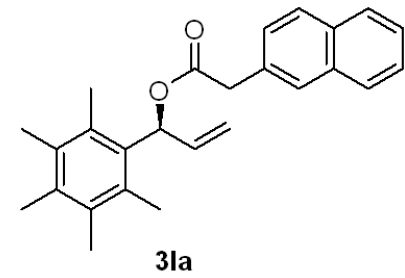
3ka



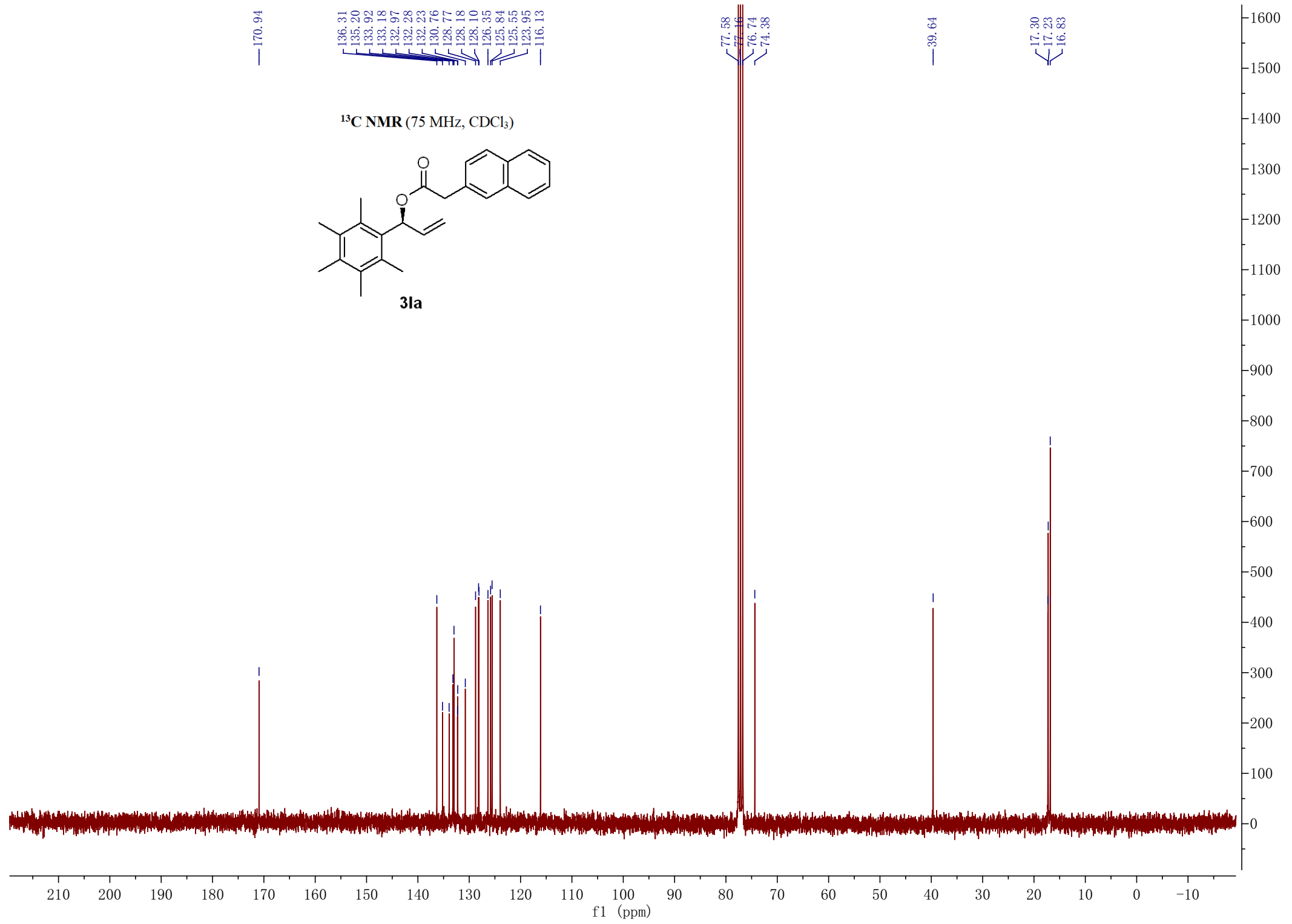


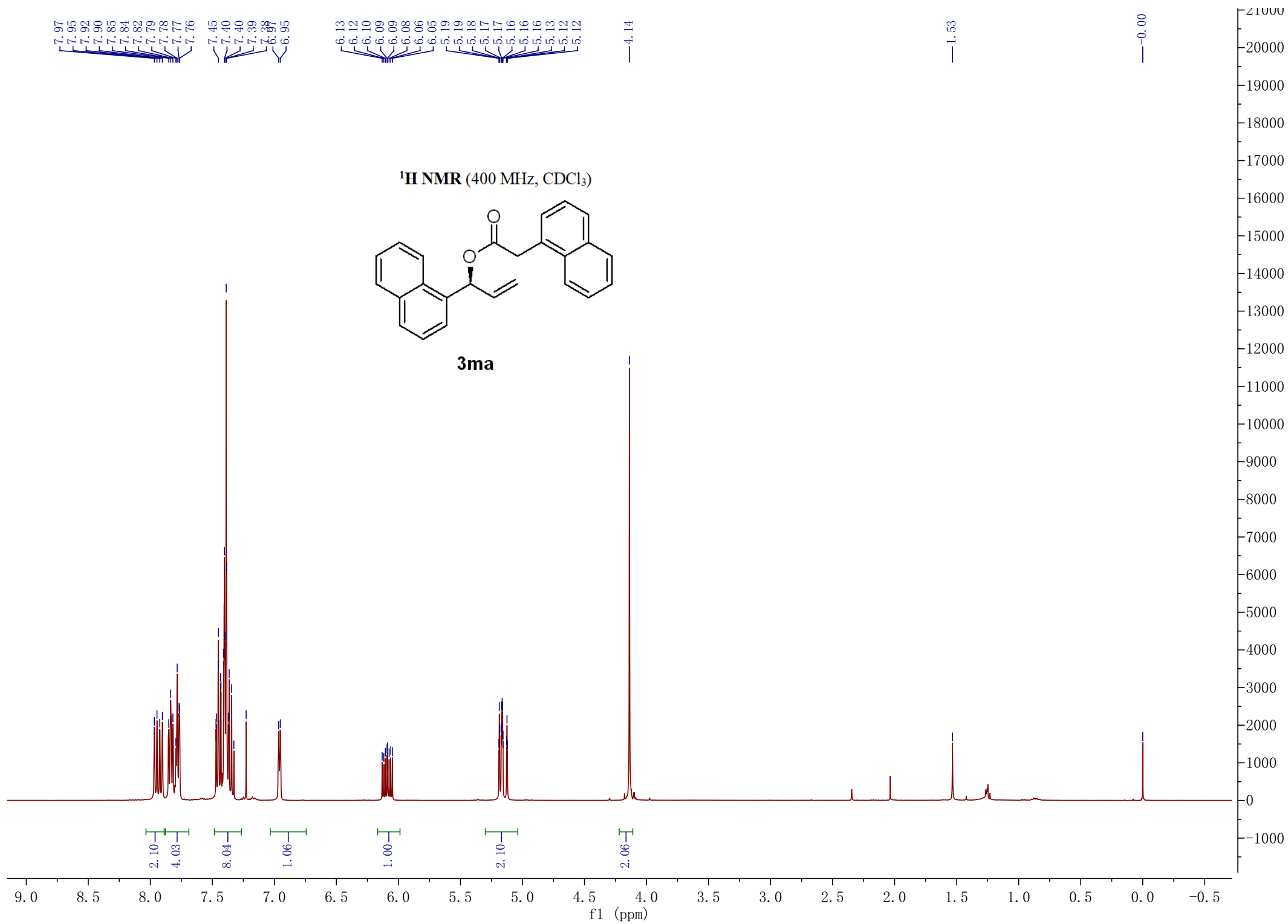
170.94
136.31
135.20
133.92
133.18
132.97
132.28
132.23
130.76
128.77
128.18
128.10
126.35
125.84
125.55
123.95
116.13

¹³C NMR (75 MHz, CDCl₃)

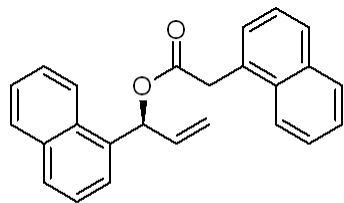


77.58
77.16
76.74
74.38
39.64
17.30
17.23
16.83





¹³C NMR (100 MHz, CDCl₃)

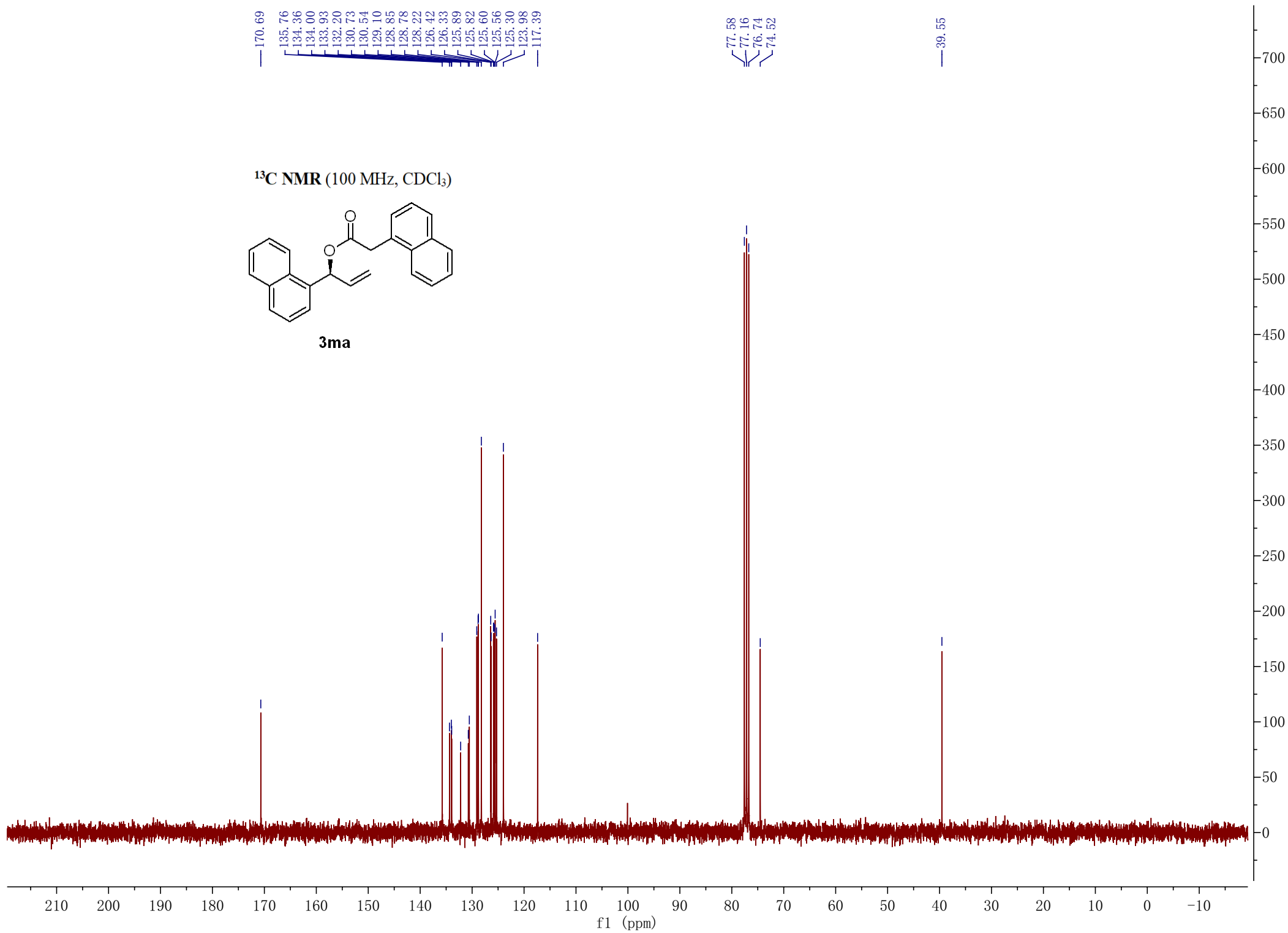


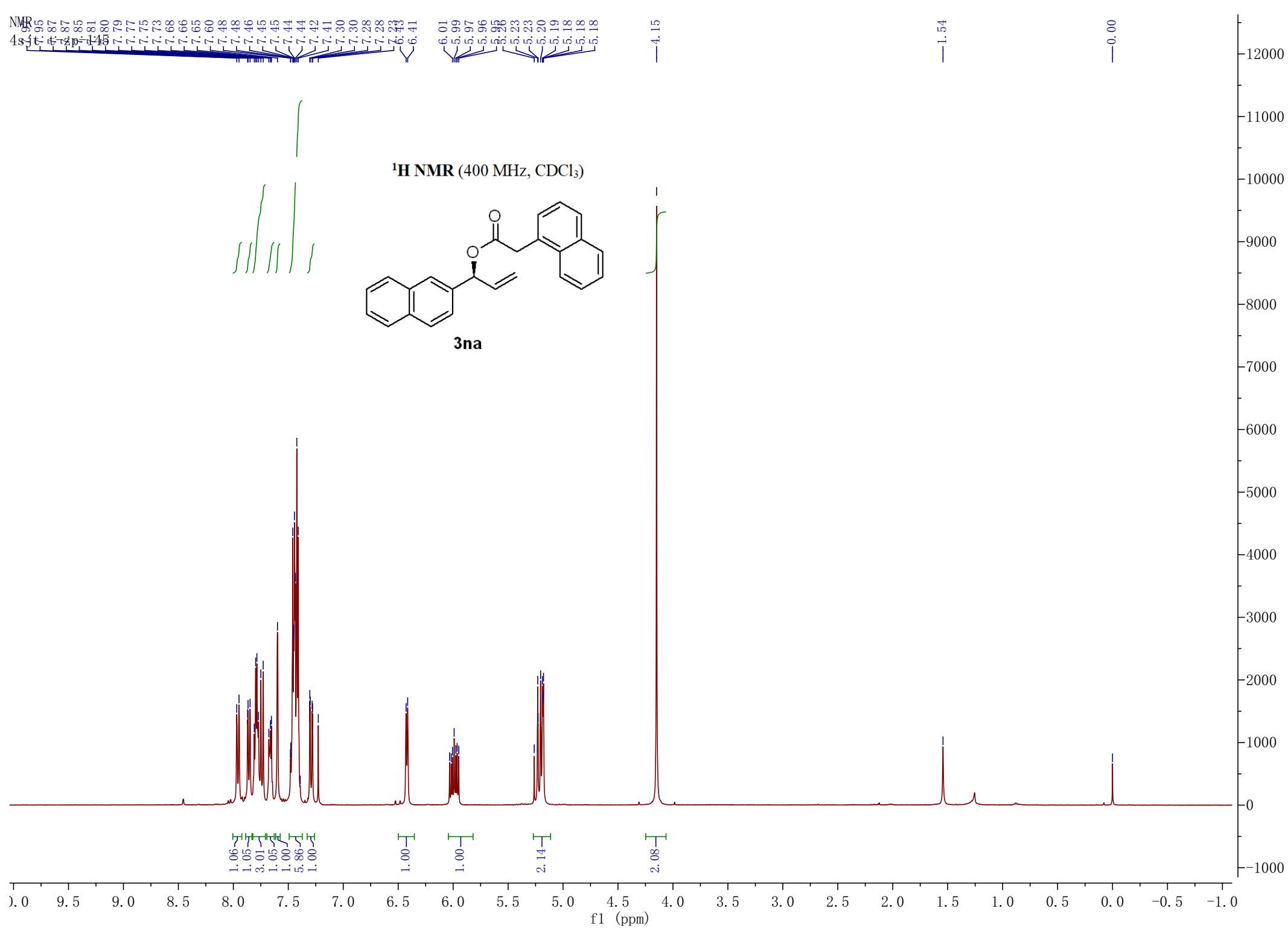
3ma

170.69
135.76
134.36
134.00
133.93
132.20
130.73
130.54
129.10
128.85
128.78
128.22
126.42
126.33
125.89
125.82
125.60
125.56
125.30
123.98
117.39

77.58
77.16
76.74
74.52

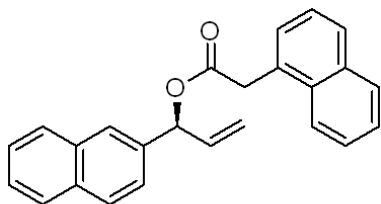
39.55





170.60
136.12
136.07
133.94
133.19
133.15
132.21
130.60
128.81
128.36
128.23
128.19
127.74
126.46
126.30
126.13
125.91
125.60
124.86
123.99
117.35

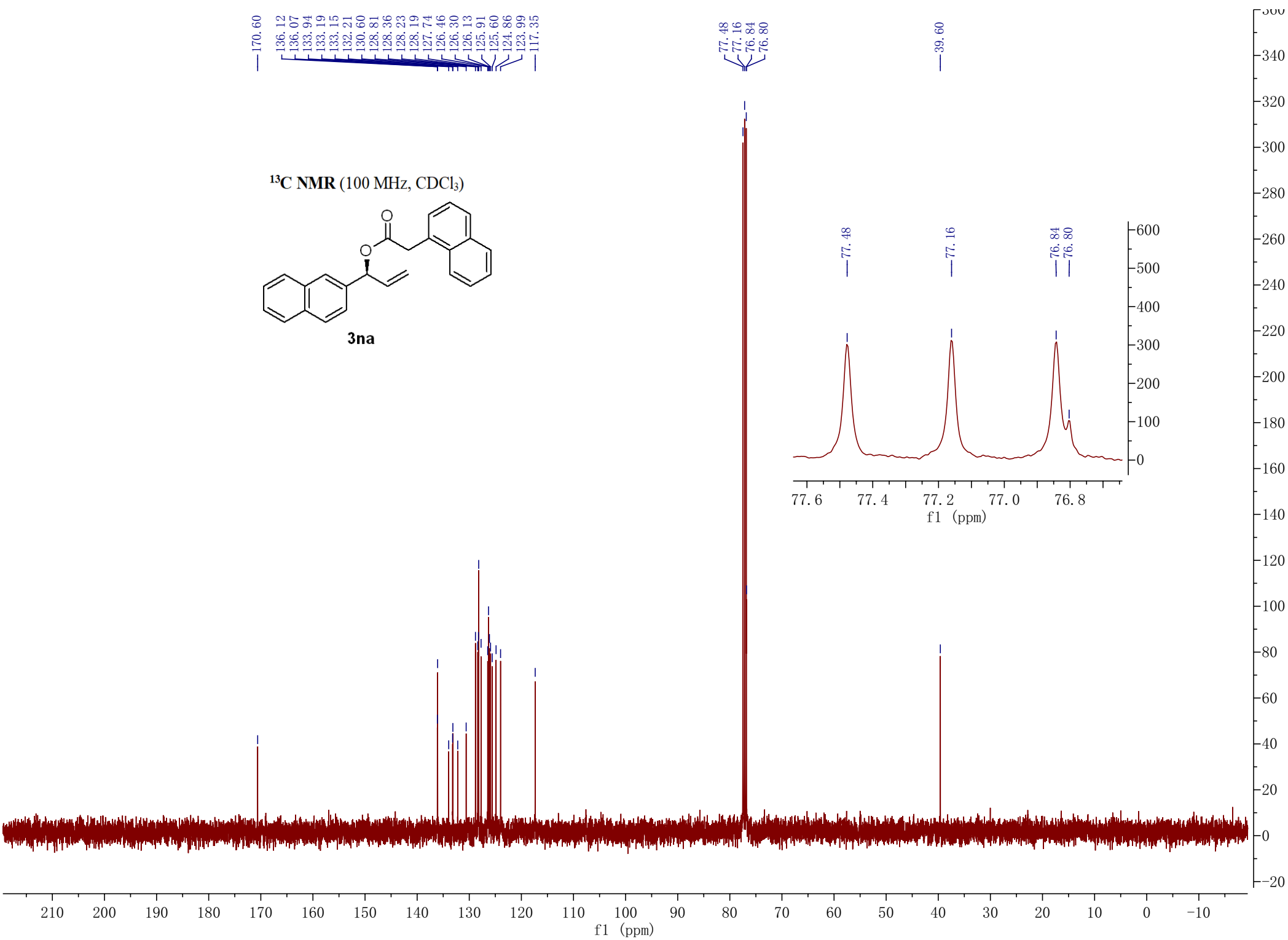
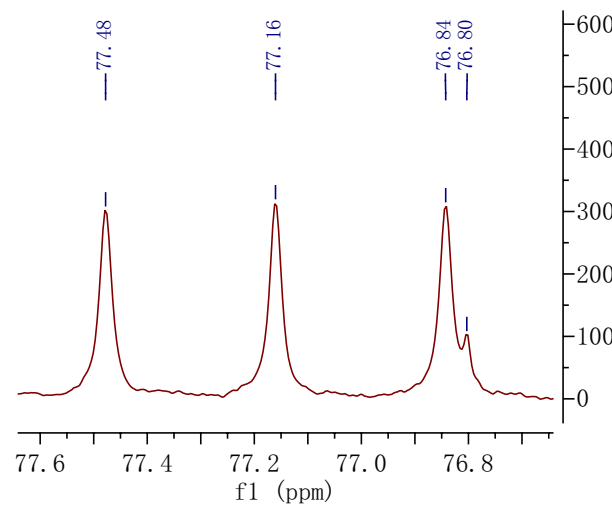
¹³C NMR (100 MHz, CDCl₃)

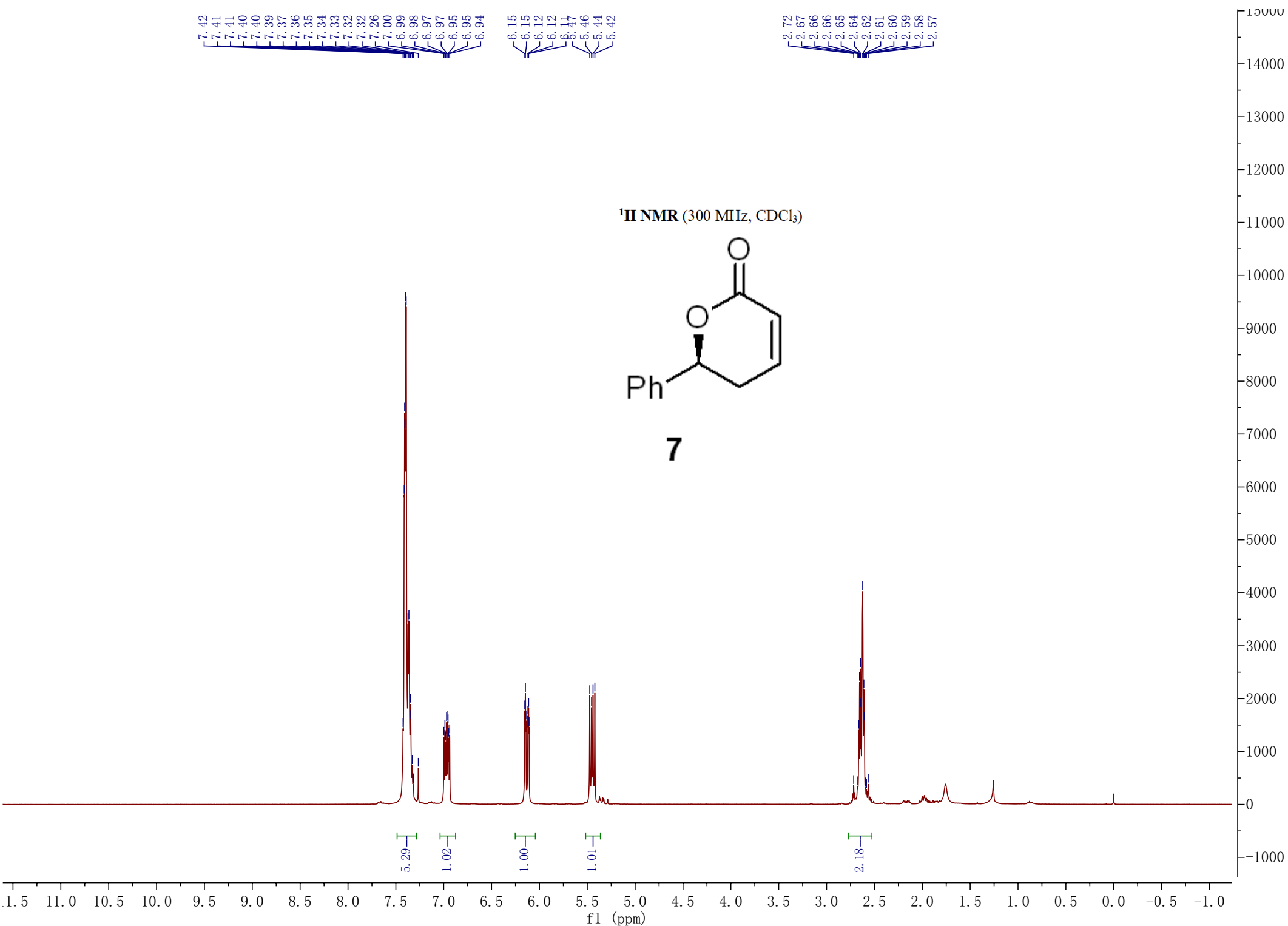


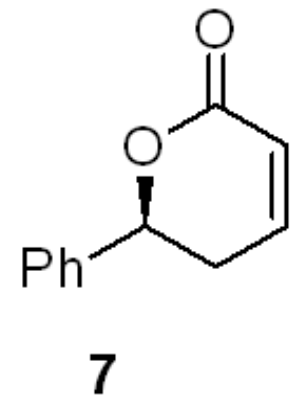
3na

77.48
77.16
76.84
76.80

39.60







¹³C NMR (75 MHz, CDCl₃)

- 164.23
- 145.02
- 138.57
- 128.80
- 128.76
- 126.17
- 121.85

- 79.38
- 77.48
- 77.16
- 76.84

- 31.82

