

Supporting Information

Gold-Catalyzed Intermolecular [4+1] Spiroannulation by Aromatic C(sp²)-H Functionalization and Dearomatization of Phenol Derivatives

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Table of Contents

1. General Information	2
2. Optimization of conditions	3
3. Synthesis of diazo compound 1	6
4. Synthesis of compound 3 and 6	9
5. Transformations of products	27
6. Reference	29
7. X-ray Crystal data for 3aa, 3aa' and 3aq.	29
8. NMR Spectra of new compounds	29

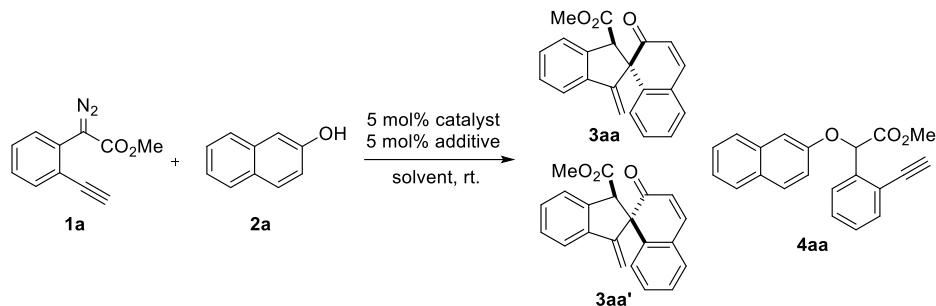
1. General Information

Unless otherwise noted, all air- and moisture-sensitive manipulations were carried out with standard Schlenk techniques under nitrogen or in a glove box under nitrogen. All reactions were carried out under a nitrogen atmosphere; materials obtained from commercial suppliers were used directly without further purification. Solvents were distilled following standard procedures before use. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 300-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. The substrates **1** were synthesized according to the reported methods.^[1] All reagents and solvents were used as received from commercial sources without further purification.

Trichloromethane (CHCl_3), dichloromethane, dichloroethane and ethyl acetate were freshly distilled from CaH_2 ; tetrahydrofuran (THF), toluene and ether were dried with sodium benzophenone and distilled before use.

^1H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 500 MHz in chloroform-d₃. Chemical shifts (in ppm) were referenced to tetramethylsilane (0 ppm) in CDCl_3 as an internal standard. ^{13}C -NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 (77.00 ppm). The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration).

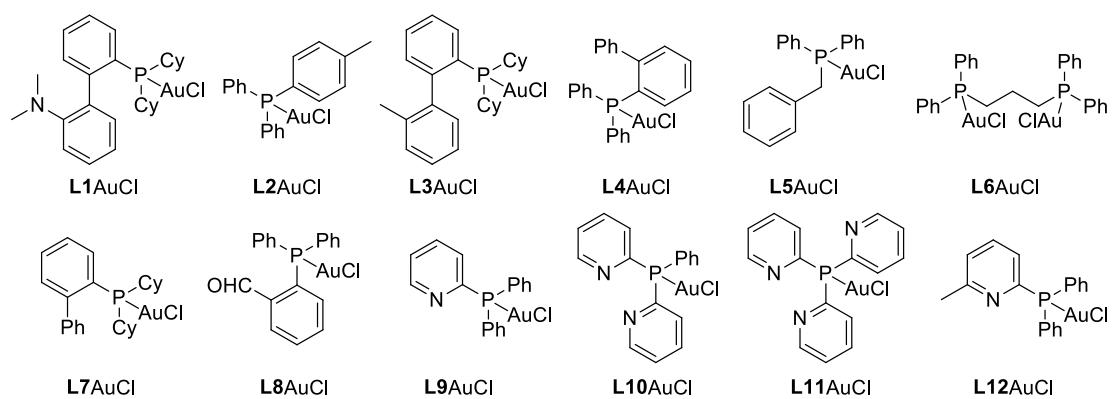
2. Optimization of conditions



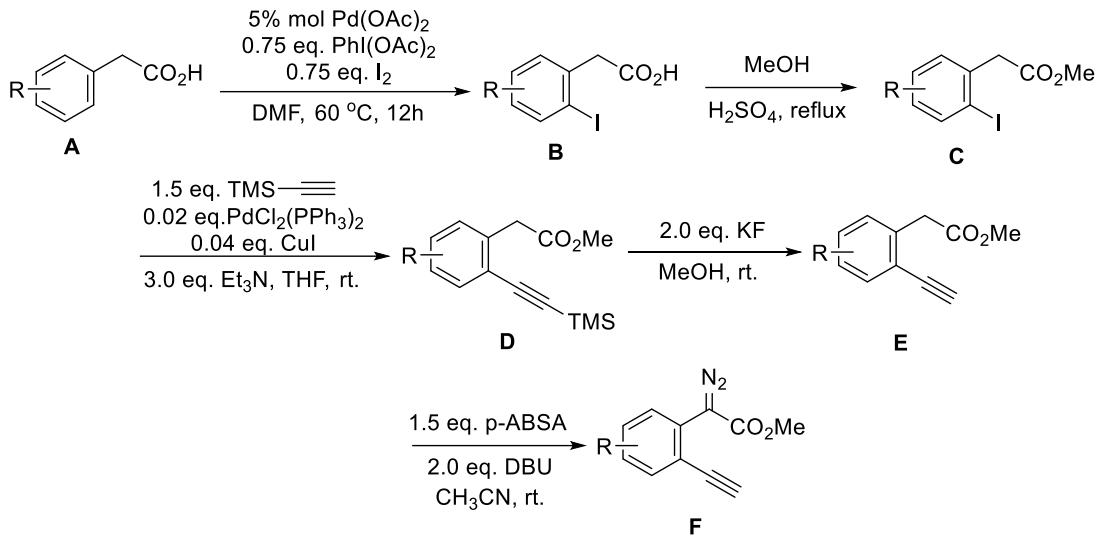
Entry	Catalyst	Additive	Solvent	3aa/3aa'/4aa ^[a]
1	Ph ₃ PAuCl	AgNTf ₂	CH ₂ Cl ₂	Messy
2	(2,4- ^t Bu ₂ C ₆ H ₃ O) ₃ PAuCl	AgNTf ₂	CH ₂ Cl ₂	Messy
3	JohnPhosAuCl	AgNTf ₂	CH ₂ Cl ₂	51/24/6
4	XPhosAuCl	AgNTf ₂	CH ₂ Cl ₂	Trace
5	IPrAuCl	AgNTf ₂	CH ₂ Cl ₂	Trace
6	PicAuCl ₂	AgNTf ₂	CH ₂ Cl ₂	Trace
7	SPhosAuCl	AgNTf ₂	CH ₂ Cl ₂	36/19/20
8	DavaPhosAuCl	AgNTf ₂	CH ₂ Cl ₂	20/11/19
9	^t BuDavaPhosAuCl	AgNTf ₂	CH ₂ Cl ₂	Messy
10	^t Bu ₃ PAuCl	AgNTf ₂	CH ₂ Cl ₂	59/16/5
11	Cy ₃ PAuCl	AgNTf ₂	CH ₂ Cl ₂	54/19/6
12	Ph ₂ MePAuCl	AgNTf ₂	CH ₂ Cl ₂	56/16/8
13	L1AuCl	AgNTf ₂	CH ₂ Cl ₂	Trace
14	L2AuCl	AgNTf ₂	CH ₂ Cl ₂	15/45/5
15	L3AuCl	AgNTf ₂	CH ₂ Cl ₂	48/24/6
16	L3AuCl	-	CH ₂ Cl ₂	NR
17	L3AuCl	AgOTf	CH ₂ Cl ₂	8/49/3
18	L3AuCl	AgSbF ₆	CH ₂ Cl ₂	9/47/4
19	L3AuCl	AgOMs	CH ₂ Cl ₂	Trace
20	L3AuCl	AgBF ₄	CH ₂ Cl ₂	Trace
21	L4AuCl	AgNTf ₂	CH ₂ Cl ₂	39/17/13
22	L5AuCl	AgNTf ₂	CH ₂ Cl ₂	Trace
23	L6AuCl	AgNTf ₂	CH ₂ Cl ₂	32/8/12
24	L7AuCl	AgNTf ₂	CH ₂ Cl ₂	46/24/9
25	L8AuCl	AgNTf ₂	CH ₂ Cl ₂	59/12/5
26	L9AuCl	AgNTf ₂	CH ₂ Cl ₂	77/17/2 (66/15/0)
27	L9AuCl	AgBF ₄	CH ₂ Cl ₂	36/18/9
28	L9AuCl	NaBAR _F	CH ₂ Cl ₂	85/11/2 (75/9/0)
29	L10AuCl	NaBAR _F	CH ₂ Cl ₂	79/11/3

30	L11AuCl	NaBAR _F	CH ₂ Cl ₂	55/16/3
31	L12AuCl	NaBAR _F	CH ₂ Cl ₂	80/17/2 (70/14/0)
32	L9AuCl	NaBAR _F	1,2-dichlorethane	61/10/0
33	L9AuCl	NaBAR _F	THF	NR
34	L9AuCl	NaBAR _F	Toluene	45/14/3
35	L9AuCl	NaBAR _F	Et ₂ O	Messy
36	L9AuCl	NaBAR _F	1,4-dioxane	Trace
37	L9AuCl	NaBAR _F	CH ₃ CN	Trace
38	L9AuCl	NaBAR _F	DMF	Trace
39	L9AuCl	NaBAR _F	PhCl	54/13/5
40	L9AuCl	NaBAR _F	CHCl ₃	59/10/6
41	L9AuCl	NaBAR _F	CCl ₄	Messy
42	L9AuCl	NaBAR _F	CH ₂ Br ₂	(66/8/3)
43	L9AuCl	NaBAR _F	PhCF ₃	55/14/5
44 ^[b]	L9AuCl	NaBAR _F	CH ₂ Cl ₂	72/14/2 (65/10/0)
45 ^[c]	L9AuCl	NaBAR _F	CH ₂ Cl ₂	80/12/2 (67/11/0)
46	CuCl	-	CH ₂ Cl ₂	Messy
47	Cu(CH ₃ CN) ₄ BF ₄	-	CH ₂ Cl ₂	25/15/8
48	Cu(OTf) ₂	-	CH ₂ Cl ₂	Messy
49	(C ₆ F ₅) ₃ B	-	CH ₂ Cl ₂	Trace
50	AgOTf	-	CH ₂ Cl ₂	Trace
51	In(OTf) ₃	-	CH ₂ Cl ₂	Trace

Reaction Conditions: **1a** (0.4 mmol), **2a** (0.6 mmol), catalyst (5 mol%), solvent (5 mL), r.t, 6 hours. The dr ratio was determined by ¹H NMR of the crude reaction mixture. ^[a] Determined by ¹H NMR analysis, CH₂Br₂ as internal standard. The number in parenthesis is isolated yield. ^[b]1.0 equiv. 2,6-dibromopyridine was added, isolated yield. ^[c]1.0 equiv. benzoic acid was added, isolated yield.



3. Synthesis of diazo compound 1



In a 250 mL bottom reaction flask, phenylacetic acid **A**, Pd(OAc)₂ (5 mol%), PhI(OAc)₂ (0.75 equiv.), I₂ (0.75 equiv.) were dissolved in 80 mL anhydrous DMF under air. Wrapped by aluminum foil to keep the system in the dark. The reaction mixture was then stirred at 60 °C for 12 h. After cooled to room temperature, the mixture was concentrated under vacuum and the residue was either subjected to column chromatography using hexanes : ethyl acetate : acetic acid / 2:1:0.05 to get the acids or converted to methyl esters as follows to get the compound **B**.

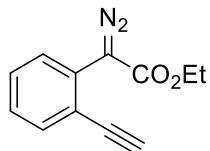
Then a 100 mL round bottom flask was taken, followed by the addition of the substituted *o*-iodophenylacetic acid **B**, anhydrous methanol solution, concentrated sulfuric acid, and reflux at 90 °C for 6 hours. The solution was cooled, reduced pressure remove the solvent, quenched with water and extracted with ethyl acetate three times, combined organic layers were dried over Na₂SO₄, filtrated and concentrated under reduced pressure. The residue was purified via flash chromatography to afford methyl *o*-iodophenylacetate **C**.

To a stirred solution of 2-iodophenylacetic acid methyl ester in THF was added CuI, Pd(PPh₃)₂Cl₂, and trimethylamine, trimethylsilylacetylene was slow dropped. This mixture was stirred at room temperature for 12h, then the reaction was quenched

by addition of water, followed by extraction with EtOAc. The organic phase was washed with sat. aq. NaCl, dried over Na₂SO₄ and concentrated under reduced pressure to yield crude product that was purified via silica gel chromatography to get the **D**. To remove the TMS-group the (2-ethynyl-phenyl)-acetic acid methyl ester was dissolved in 50 mL anhydrous methanol. Potassium fluoride was added to this mixture and stirred for 1 h at room temperature. Then the mixture was washed with water, NaHCO₃ solution and NaCl solution, dried over Na₂SO₄ and concentrated under reduced pressure to yield crude product that was purified via silica gel chromatography.

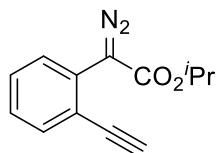
Finally, compound **E** was dissolved in anhydrous acetonitrile and *p*-ABSA, DBU was added, Stir overnight in the dark at room temperature, the reaction was quenched by addition of water, followed by extraction with Et₂O. The organic phase was washed with sat. aq. NaCl, dried over Na₂SO₄ and concentrated under reduced pressure to yield crude product that was purified via silica gel chromatography to get the diazo compound **1**.

1) Ethyl 2-diazo-2-(2-ethynylphenyl)acetate (1b)



¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.42-7.38 (m, 1H), 7.29-7.21 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 3.48 (s, 1H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.6, 133.4, 133.0, 129.1, 127.7, 127.4, 120.1, 84.3, 80.8, 61.2, 14.5; HRMS (ESI) m/z calculated for C₁₂H₁₀N₂NaO₂ [M+Na]⁺ = 237.0634, found 237.0635;

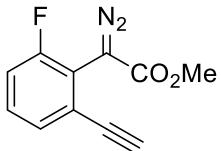
2) Isopropyl 2-diazo-2-(2-ethynylphenyl)acetate (1c)



¹H NMR (500 MHz, CDCl₃) δ 7.61 (d, *J* = 8.0 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.40 (dd, *J* = 11.2, 4.3 Hz, 1H), 7.25 (t, *J* = 7.6 Hz, 1H), 5.18 (hept, *J* = 6.2 Hz, 1H), 3.48

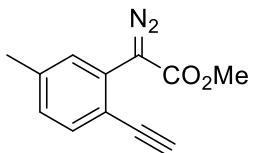
(s, 1H), 1.31 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.1, 133.4, 129.9, 129.1, 127.8, 127.3, 120.0, 84.3, 80.8, 68.8, 22.0; HRMS (ESI) m/z calculated for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{NaO}_2$ [M+Na] $^+$ = 251.0791, found 251.0784;

3) Methyl 2-diazo-2-(2-ethynyl-6-fluorophenyl)acetate (1d)



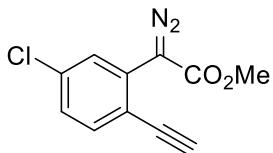
^1H NMR (500 MHz, CDCl_3) δ 7.39-7.30 (m, 2H), 7.20-7.11 (m, 1H), 3.83 (s, 3H), 3.43 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 161.2, 159.2, 130.5, 130.4, 128.9 (d, $J = 3.5$ Hz), 124.6 (d, $J = 3.2$ Hz), 116.8 (d, $J = 22.1$ Hz), 116.1 (d, $J = 16.4$ Hz), 83.8, 79.9 (d, $J = 4.3$ Hz), 52.3; HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_7\text{FN}_2\text{NaO}_2$ [M+Na] $^+$ = 241.0384, found 241.0379;

4) Methyl 2-diazo-2-(2-ethynyl-5-methylphenyl)acetate (1f)



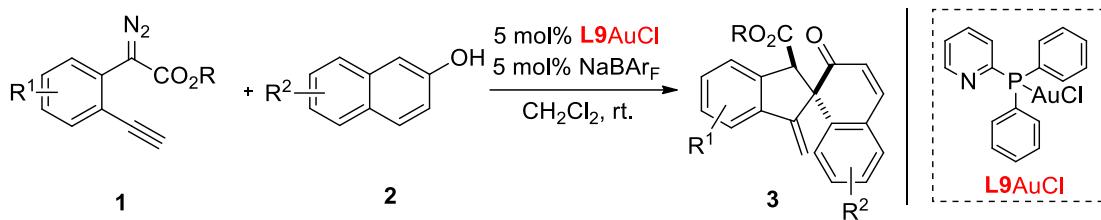
^1H NMR (500 MHz, CDCl_3) δ 7.46-7.38 (m, 1H), 7.08 (d, $J = 7.9$ Hz, 1H), 3.85 (s, 3H), 3.43 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.1, 139.5, 133.3, 130.5, 128.6, 127.2, 117.3, 83.6, 80.9, 52.1, 21.5; HRMS (ESI) m/z calculated for $\text{C}_{12}\text{H}_{10}\text{N}_2\text{NaO}_2$ [M+Na] $^+$ = 237.0634, found 237.0635;

5) Methyl 2-(5-chloro-2-ethynylphenyl)-2-diazoacetate (1g)



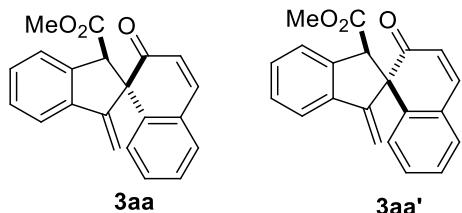
^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 1.9$ Hz, 1H), 7.45 (d, $J = 8.4$ Hz, 1H), 7.23 (dd, $J = 8.4, 2.1$ Hz, 1H), 3.86 (s, 3H), 3.52 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 165.5, 135.3, 134.5, 129.6, 129.2, 127.6, 118.1, 85.4, 79.8, 52.3. HRMS (ESI) m/z calculated for $\text{C}_{11}\text{H}_{17}\text{ClN}_2\text{NaO}_2$ [M+Na] $^+$ = 257.0088, found 257.0089;

4. Synthesis of compound 3 and 6



In a dried glass tube, a mixture of **L9AuCl** (0.02 mmol), additive (5 mol%) in solvent (3 mL) was stirred at room temperature for 15 mins. Subsequently, naphthalenol **2** (0.6 mmol) was added to the reaction mixture at room temperature. Then a solution of diazo compounds **1** (0.4 mmol) in solvent (1 mL) was introduced into the reaction mixture by a syringe in 20 mins. Then the resulting mixture was continually stirred at room temperature for 6-12 hours and **1** was consumed completely determined by TLC analysis. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 10:1 to 5:1 or PE/EA = 20:1 to 10:1) to afford the desired product.

1) Methyl 3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (**3aa**)

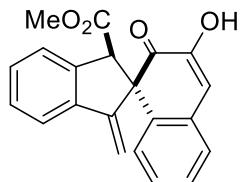


3aa, *cis*-isomer, 94.9 mg, 75% yield (isolated yield of single isomer), yellow solid, m.p. = 172-174 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.51 (d, *J* = 9.9 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 1H), 7.44-7.39 (m, 2H), 7.38 (dd, *J* = 7.4, 1.9 Hz, 1H), 7.35 (dt, *J* = 12.6, 4.5 Hz, 2H), 7.22 (d, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 9.9 Hz, 1H), 5.39 (s, 1H), 4.82 (s, 1H), 4.50 (s, 1H), 3.60 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.7, 171.0, 150.6, 145.1, 144.6, 141.4, 137.7, 130.4, 130.2, 129.5, 129.3, 128.1, 127.5, 127.4, 126.2, 123.9, 121.5, 105.6, 65.5, 60.5, 51.9; HRMS (ESI) m/z calculated

for $C_{21}H_{16}NaO_3 [M+Na]^+$ = 339.0992, found 339.0995;

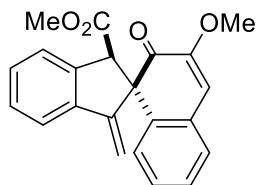
3aa', *trans*-isomer, 11.4 mg, 9% yield (isolated yield of single isomer), light yellow solid, m.p. = 208~210 °C ; 1H NMR (500 MHz, $CDCl_3$) δ 7.75-7.68 (m, 1H), 7.59 (d, J = 9.9 Hz, 1H), 7.50 (d, J = 7.7 Hz, 1H), 7.44 (dd, J = 10.8, 4.1 Hz, 1H), 7.39-7.31 (m, 2H), 7.23 (td, J = 7.5, 1.1 Hz, 1H), 7.12 (td, J = 7.7, 1.3 Hz, 1H), 6.84 (d, J = 7.9 Hz, 1H), 6.41 (d, J = 9.9 Hz, 1H), 5.40 (d, J = 0.8 Hz, 1H), 5.23 (s, 1H), 4.86 (d, J = 0.7 Hz, 1H), 3.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.6, 170.6, 154.0, 146.6, 144.2, 140.7, 139.1, 130.2, 129.7, 129.6, 128.3, 128.0, 127.4, 126.8, 125.5, 125.3, 121.3, 104.6, 64.5, 59.2, 51.4; HRMS (ESI) m/z calculated for $C_{21}H_{16}NaO_3 [M+Na]^+$ = 339.0992, found 339.0984

2) *cis*-Methyl 3'-hydroxy-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ab)



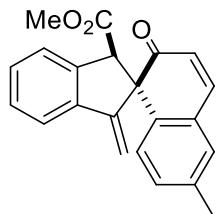
71.1 mg, 68% yield (isolated yield of single isomer), dr = 7.5:1, yellow oil; 1H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.7 Hz, 1H), 7.49 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7.4 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 7.30 (d, J = 4.3 Hz, 2H), 7.24 (dd, J = 7.6, 4.5 Hz, 1H), 7.13 (d, J = 7.7 Hz, 1H), 6.88 (s, 1H), 6.23 (s, 1H), 5.40 (s, 1H), 4.90 (s, 1H), 4.53 (s, 1H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 170.4, 150.8, 144.3, 140.8, 140.4, 138.0, 131.2, 129.5, 128.3, 128.2, 127.8, 127.7, 127.3, 126.2, 121.6, 117.2, 106.2, 64.3, 61.5, 52.1; HRMS (ESI) m/z calculated for $C_{21}H_{16}NaO_4 [M+Na]^+$ = 355.0941, found 355.0934;

3) *cis*-Methyl 3'-methoxy-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ac)



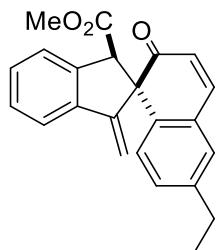
71.3 mg, 63% yield (isolated yield of single isomer), dr = 4.3:1, yellow oil, ¹H NMR (500 MHz, CDCl₃) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.35-7.27 (m, 3H), 7.25-7.21 (m, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.61 (s, 1H), 5.39 (s, 1H), 4.86 (s, 1H), 4.56 (s, 1H), 3.80 (s, 3H), 3.62 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 192.4, 170.8, 150.2, 148.6, 141.3, 140.5, 137.5, 131.0, 129.3, 128.1, 127.9, 127.7, 127.6, 126.9, 126.1, 121.6, 115.3, 105.9, 66.6, 60.5, 55.5, 52.0; HRMS (ESI) m/z calculated for C₂₂H₁₈NaO₄ [M+Na]⁺ = 369.1097, found 369.1093;

4) *cis*-Methyl 6'-methyl-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ad)



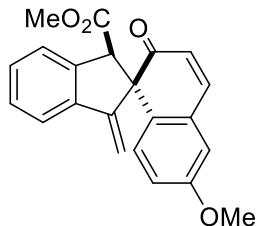
89.0 mg, 74% yield (isolated yield of single isomer), dr = 7.7:1, yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.92 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 9.7 Hz, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.26-7.21 (m, 2H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.14 (d, *J* = 9.9 Hz, 1H), 5.42 (s, 1H), 4.84 (s, 1H), 4.55 (s, 1H), 3.63 (s, 3H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.8, 171.0, 150.6, 145.3, 141.5, 141.4, 137.6, 137.1, 131.2, 130.0, 129.9, 129.2, 128.0, 127.2, 126.1, 123.8, 121.4, 105.4, 65.2, 60.3, 51.8, 20.8; HRMS (ESI) m/z calculated for C₂₂H₁₈NaO₃ [M+Na]⁺ = 353.1148, found 353.1146;

5) *cis*-Methyl 6'-ethyl-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ae)



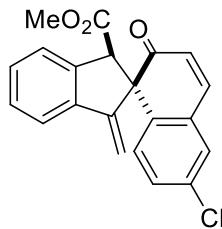
107.2 mg, 71% yield (isolated yield of single isomer), dr = 7:1; yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 8.2 Hz, 2H), 7.41 (td, J = 7.6, 1.0 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.24-7.18 (m, 2H), 7.16-7.08 (m, 1H), 6.11 (d, J = 9.9 Hz, 1H), 5.38 (s, 1H), 4.80 (s, 1H), 4.51 (s, 1H), 3.60 (s, 3H), 2.70 (q, J = 7.6 Hz, 2H), 1.29 (t, J = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 198.1, 171.1, 150.8, 145.5, 143.4, 141.8, 141.5, 137.8, 130.1, 130.1, 129.3, 128.9, 128.1, 127.4, 126.2, 123.8, 121.5, 105.5, 65.3, 60.5, 51.9, 28.2, 15.2; HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{20}\text{NaO}_3$ [M+Na] $^+$ = 367.1305, found 367.1306;

6) *cis*-Methyl 6'-methoxy-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3af)



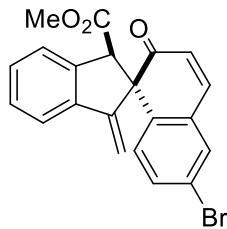
80.1 mg, 58% yield (isolated yield of single isomer), dr = 7.8:1, light yellow solid; m.p. = 215-217 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.86 (d, J = 7.7 Hz, 1H), 7.45 (t, J = 8.4 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.33 (t, J = 7.5 Hz, 1H), 7.13 (d, J = 8.5 Hz, 1H), 6.99-6.87 (m, 2H), 6.13 (d, J = 9.9 Hz, 1H), 5.38 (s, 1H), 4.77 (s, 1H), 4.51 (s, 1H), 3.86 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.9, 171.1, 158.6, 150.8, 145.0, 141.4, 137.8, 136.4, 131.2, 129.3, 128.6, 128.1, 126.2, 124.4, 121.5, 116.3, 114.1, 105.5, 65.1, 60.5, 55.4, 51.9; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{NaO}_4$ [M+Na] $^+$ = 369.1097, found 369.1090;

7) *cis*-Methyl 6'-chloro-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ag)



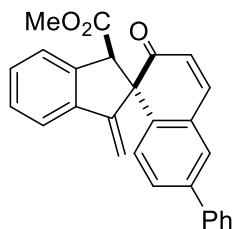
75.2 mg, 54% yield (isolated yield of single isomer), dr = 5.1:1, light yellow solid, m.p. = 196-198 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, J = 7.7 Hz, 1H), 7.48-7.42 (m, 2H), 7.42-7.39 (m, 2H), 7.34 (dd, J = 11.2, 4.6 Hz, 2H), 7.16 (d, J = 8.4 Hz, 1H), 6.16 (d, J = 9.9 Hz, 1H), 5.40 (s, 1H), 4.76 (s, 1H), 4.50 (s, 1H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 196.9, 170.7, 150.2, 143.5, 142.7, 141.2, 137.4, 133.3, 131.8, 130.1, 129.5, 129.0, 129.0, 128.3, 126.2, 125.1, 121.6, 105.8, 65.2, 60.5, 52.0; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{15}\text{ClNaO}_3$ $[\text{M}+\text{Na}]^+$ = 373.0602, found 373.0609;

8) *cis*-Methyl 6'-bromo-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ah)



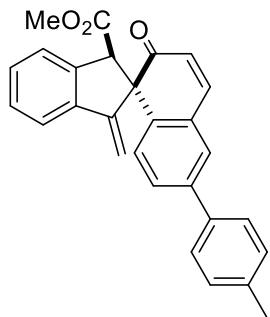
98.1 mg, 59% yield (isolated yield of single isomer), dr = 5.4:1, yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.72 (d, J = 7.7 Hz, 1H), 7.54 (d, J = 10.0 Hz, 1H), 7.51 (d, J = 7.4 Hz, 2H), 7.47 (t, J = 7.4 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.25 (dd, J = 8.4, 1.5 Hz, 1H), 6.74 (d, J = 8.4 Hz, 1H), 6.48 (d, J = 9.9 Hz, 1H), 5.42 (s, 1H), 5.25 (s, 1H), 4.87 (s, 1H), 3.30 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.8, 170.4, 153.6, 144.9, 142.8, 140.4, 138.8, 132.8, 132.2, 130.0, 129.7, 128.4, 127.1, 126.8, 126.5, 121.3, 121.1, 104.9, 64.3, 59.0, 51.6; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{15}\text{BrNaO}_3$ $[\text{M}+\text{Na}]^+$ = 417.0097, found 417.0102;

9) *cis*-Methyl 3-methylene-2'-oxo-6'-phenyl-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ai)



94.2 mg, 53% yield (isolated yield of single isomer), dr = 5.4:1, yellow solid, m.p. = 222-224 °C; ¹H NMR (500 MHz, CDCl_3) δ 7.89 (d, J = 7.7 Hz, 1H), 7.61 (dd, J = 13.1, 5.7 Hz, 4H), 7.57 (d, J = 9.9 Hz, 1H), 7.50-7.32 (m, 6H), 7.28 (d, J = 8.2 Hz, 1H), 6.17 (d, J = 9.9 Hz, 1H), 5.42 (s, 1H), 4.86 (s, 1H), 4.57 (s, 1H), 3.62 (s, 3H); ¹³C NMR (125 MHz, CDCl_3) δ 197.6, 171.0, 150.6, 145.1, 143.3, 141.4, 140.4, 139.7, 137.7, 130.6, 129.3, 129.0, 128.9, 128.2, 128.0, 127.9, 127.8, 127.0, 126.2, 124.3, 121.5, 105.8, 65.3, 60.5, 52.0; HRMS (ESI) m/z calculated for $\text{C}_{27}\text{H}_{20}\text{NaO}_3$ [M+Na]⁺ = 415.1305, found 415.1297;

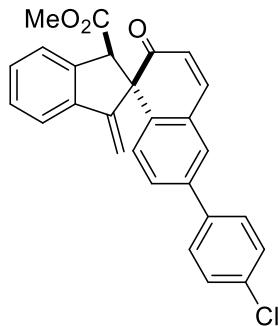
10) *cis*-Methyl 3-methylene-2'-oxo-6'-(p-tolyl)-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3aj)



94.7 mg, 49% yield (isolated yield of single isomer), dr = 5.2:1, light yellow solid, m.p. = 216-218 °C; ¹H NMR (500 MHz, CDCl_3) δ 7.89 (d, J = 7.7 Hz, 1H), 7.60-7.57 (m, 2H), 7.56 (d, J = 10.0 Hz, 1H), 7.52 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 7.7 Hz, 1H), 7.42 (d, J = 7.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H), 7.27-7.23 (m, 2H), 6.16 (d, J = 9.9 Hz, 1H), 5.41 (s, 1H), 4.85 (s, 1H), 4.57 (s, 1H), 3.61 (s, 3H), 2.41 (s, 3H); ¹³C NMR (125 MHz, CDCl_3) δ 197.7, 171.0, 150.6, 145.2, 143.0, 141.4, 140.4, 137.7, 137.6, 136.8, 130.5, 129.6, 129.3, 128.8, 128.2, 127.9, 127.8, 126.8, 126.2, 124.2, 121.5,

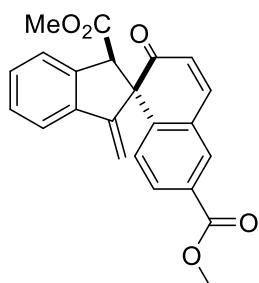
105.7, 65.3, 60.5, 51.9, 21.1; HRMS (ESI) m/z calculated for C₂₈H₂₂NaO₃ [M+Na]⁺ = 429.1461, found 429.1464;

11) *cis*-Methyl 6'-(4-chlorophenyl)-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro [indene-2,1'-naphthalene]-1-carboxylate (3ak)



96.4 mg, 48% yield (isolated yield of single isomer), dr = 5:1, white solid, m.p. = 230-232 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.58-7.56 (m, 3H), 7.55 (d, *J* = 2.8 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.46-7.40 (m, 3H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 5.42 (s, 1H), 4.85 (s, 1H), 4.56 (s, 1H), 3.62 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.5, 171.0, 150.5, 144.8, 143.7, 141.3, 139.2, 138.2, 137.6, 133.9, 130.8, 129.4, 129.1, 128.8, 128.2, 128.1, 127.8, 126.2, 124.5, 121.6, 105.8, 65.3, 60.6, 52.0; HRMS (ESI) m/z calculated for C₂₇H₁₉ClNaO₃ [M+Na]⁺ = 449.0915, found 449.0903;

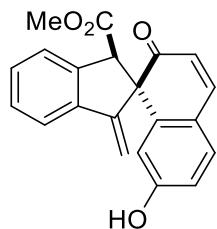
12) *cis*-Dimethyl 3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1,6'-dicarboxylate (3al)



71.8 mg, 41% yield (isolated yield of single isomer), dr = 5:1, white solid, 157-158 °C; ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, *J* = 1.7 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.56 (d, *J* = 9.9 Hz, 1H), 7.49-7.40 (m, 2H), 7.38-7.29 (m,

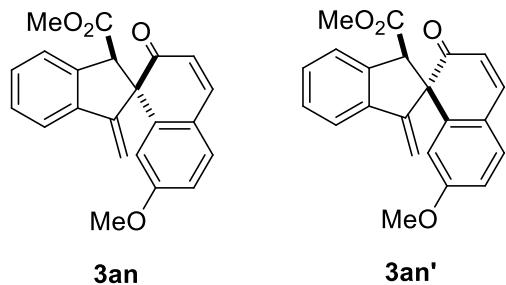
2H), 6.19 (d, J = 9.9 Hz, 1H), 5.40 (d, J = 0.8 Hz, 1H), 4.84 (s, 1H), 4.48 (d, J = 0.6 Hz, 1H), 3.96 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 196.8, 170.7, 166.1, 150.1, 149.3, 144.1, 141.2, 137.4, 131.1, 130.5, 130.5, 129.6, 129.5, 128.3, 127.8, 126.2, 124.8, 121.6, 105.9, 65.7, 60.5, 52.4, 52.0; HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{18}\text{NaO}_5$ [M+Na] $^+$ = 397.1046, found 397.1045;

13) *cis*-Methyl 7'-hydroxy-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3am)



62.8 mg (0.3 mmol scale), 55% yield (isolated yield of single isomer), dr = 6:1, yellow oil liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.81 (d, J = 7.8 Hz, 1H), 7.41 (dd, J = 8.7, 4.3 Hz, 2H), 7.37 (dd, J = 10.8, 4.2 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 8.3 Hz, 1H), 6.70 (d, J = 8.3 Hz, 1H), 6.60 (d, J = 2.3 Hz, 1H), 6.42 (s, 1H), 5.92 (d, J = 9.8 Hz, 1H), 5.34 (s, 1H), 4.71 (s, 1H), 4.50 (s, 1H), 3.54 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 198.7, 171.3, 158.5, 150.4, 146.9, 146.1, 141.3, 137.6, 131.4, 129.3, 128.1, 126.2, 123.0, 121.5, 120.6, 114.8, 105.7, 65.7, 60.5, 51.9; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{16}\text{NaO}_4$ [M+Na] $^+$ = 355.0941, found 355.0937;

14) Methyl 7'-methoxy-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3an and 3an')

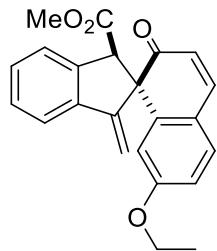


3an, major, 68.5 mg, 49% yield (isolated yield of single isomer), dr = 3.5:1, light

yellow oil liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.88 (d, $J = 7.7$ Hz, 1H), 7.46 (dd, $J = 8.7, 5.6$ Hz, 2H), 7.42 (t, $J = 7.5$ Hz, 1H), 7.33 (dd, $J = 8.0, 5.6$ Hz, 2H), 6.87 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.73 (d, $J = 2.3$ Hz, 1H), 5.99 (d, $J = 9.8$ Hz, 1H), 5.39 (s, 1H), 4.76 (s, 1H), 4.54 (s, 1H), 3.78 (s, 3H), 3.60 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.7, 171.0, 161.5, 150.7, 146.7, 145.1, 141.4, 137.6, 131.1, 129.3, 128.1, 126.2, 123.6, 121.5, 121.3, 113.7, 112.5, 105.6, 65.7, 60.6, 55.4, 51.9; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{NaO}_4[\text{M}+\text{Na}]^+ = 369.1097$, found 369.1087;

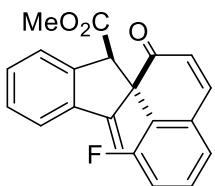
3an', minor, 19.5 mg, 14% yield, light yellow oil, ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 7.7$ Hz, 1H), 7.51-7.40 (m, 3H), 7.38-7.31 (m, 2H), 6.88 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.74 (d, $J = 2.4$ Hz, 1H), 6.00 (d, $J = 9.8$ Hz, 1H), 5.40 (s, 1H), 4.77 (s, 1H), 4.55 (s, 1H), 3.80 (s, 3H), 3.61 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.7, 171.0, 161.5, 150.7, 146.8, 145.1, 141.4, 137.7, 131.1, 129.3, 128.1, 126.2, 123.6, 121.5, 121.3, 113.7, 112.6, 105.6, 65.7, 60.6, 55.5, 51.9, 29.7. HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{NaO}_4[\text{M}+\text{Na}]^+ = 369.1097$, found 369.1099;

15) *cis*-Methyl 7'-ethoxy-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ao)



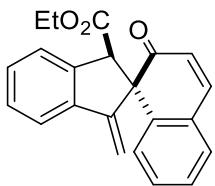
61.6 mg, 31% yield (isolated yield of single isomer), dr = 2.6:1, yellow oil liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, $J = 7.7$ Hz, 1H), 7.45 (dd, $J = 8.7, 5.2$ Hz, 2H), 7.41 (t, $J = 7.5$ Hz, 1H), 7.35-7.30 (m, 2H), 6.85 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.73 (d, $J = 2.3$ Hz, 1H), 5.99 (d, $J = 9.8$ Hz, 1H), 5.39 (s, 1H), 4.76 (s, 1H), 4.54 (s, 1H), 4.02-3.96 (m, 2H), 3.60 (s, 3H), 1.36 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.7, 171.0, 160.9, 150.8, 146.8, 145.1, 141.4, 137.6, 131.1, 129.2, 128.1, 126.2, 123.4, 121.4, 121.1, 114.3, 112.7, 105.5, 65.6, 63.7, 60.6, 51.8, 14.6; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{16}\text{NaO}_3[\text{M}+\text{Na}]^+ = 383.1254$, found 383.1244;

16) *cis*-Methyl 8'-fluoro-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ap)



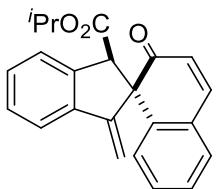
50.3 mg, 30% yield (isolated yield of single isomer), dr = 4:1, yellow solid, m.p. = 182-184 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.85 (d, J = 7.7 Hz, 1H), 7.50 (dd, J = 12.9, 4.6 Hz, 2H), 7.44-7.30 (m, 3H), 7.23 (d, J = 7.4 Hz, 1H), 7.09 (dd, J = 10.8, 8.6 Hz, 1H), 6.17 (d, J = 9.9 Hz, 1H), 5.38 (s, 1H), 5.00 (d, J = 1.7 Hz, 1H), 4.51 (s, 1H), 3.61 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 196.8, 171.3, 160.1 (d, J = 249.2 Hz), 149.8, 144.1 (d, J = 3.6 Hz), 141.4, 138.3, 132.5 (d, J = 4.3 Hz), 130.5 (d, J = 10.4 Hz), 129.3 (d, J = 9.4 Hz), 129.2, 127.8, 126.3, 125.5 (d, J = 2.8 Hz), 125.0, 121.4, 118.0 (d, J = 23.0 Hz), 103.8, 61.5 (d, J = 2.3 Hz), 59.3 (d, J = 6.8 Hz), 51.9; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{15}\text{FNaO}_3$ [M+Na] $^+$ = 357.0897, found 357.0903;

17) *cis*-Ethyl 3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ba)



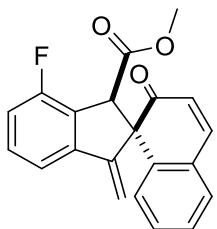
83.3 mg, 63% yield (isolated yield of single isomer), dr = 5.8:1, yellow solid, m.p. = 163-165 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, J = 7.7 Hz, 1H), 7.48 (dd, J = 17.8, 8.8 Hz, 2H), 7.45-7.30 (m, 5H), 7.23 (d, J = 7.5 Hz, 1H), 6.13 (d, J = 9.9 Hz, 1H), 5.38 (s, 1H), 4.79 (s, 1H), 4.49 (s, 1H), 4.16-3.96 (m, 2H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.6, 170.4, 150.7, 145.0, 144.7, 141.6, 137.7, 130.3, 130.2, 129.4, 129.3, 128.1, 127.5, 127.4, 126.2, 124.1, 121.5, 105.5, 65.5, 60.9, 60.5, 13.8; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{NaO}_3$ [M+Na] $^+$ = 355.1148, found 355.1153;

18) *cis*-Isopropyl 3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ca)



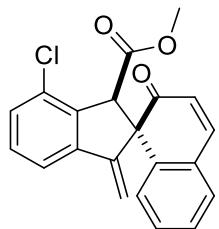
82.8 mg, 60% yield (isolated yield of single isomer), dr = 5.5:1, light yellow solid, m.p. = 122-123 °C, ¹H NMR (500 MHz, CDCl₃) δ 7.90 (d, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 17.4, 8.8 Hz, 2H), 7.43-7.29 (m, 5H), 7.22 (d, *J* = 7.4 Hz, 1H), 6.12 (d, *J* = 9.9 Hz, 1H), 5.37 (s, 1H), 5.01-4.87 (m, 1H), 4.76 (s, 1H), 4.48 (s, 1H), 1.09 (d, *J* = 6.2 Hz, 3H), 1.06 (d, *J* = 6.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.4, 169.9, 150.79, 144.9, 144.8, 141.9, 137.7, 130.3, 130.3, 129.3, 129.3, 128.0, 127.5, 127.3, 126.1, 124.2, 121.5, 105.4, 68.7, 65.5, 60.6, 21.6, 21.3; HRMS (ESI) m/z calculated for C₂₃H₂₀NaO₃ [M+Na]⁺ = 367.1305, found 367.1305;

19) *cis*-Methyl 4-fluoro-1-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-3-carboxylate (3da)



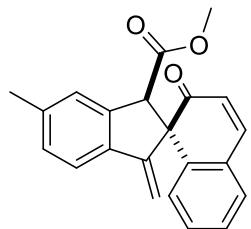
83.0 mg, 59% yield (isolated yield of single isomer), dr = 7:1, light yellow solid, m.p. = 173-175 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.54 (d, *J* = 9.9 Hz, 1H), 7.42-7.29 (m, 5H), 7.09 (dd, *J* = 11.5, 5.9 Hz, 2H), 6.18 (d, *J* = 9.9 Hz, 1H), 5.49 (s, 1H), 4.77 (s, 1H), 4.64 (s, 1H), 3.60 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 198.3, 169.4, 160.6, 158.6, 152.5 (d, *J* = 2.4 Hz), 145.8, 142.4 (d, *J* = 5.1 Hz), 130.8, 130.7 (d, *J* = 7.5 Hz), 129.5, 129.0, 127.7, 127.3 (d, *J* = 16.6 Hz), 127.2, 124.5, 117.0 (d, *J* = 3.6 Hz), 116.2, 116.0, 107.4, 64.8, 60.6 (d, *J* = 2.4 Hz), 52.1; HRMS (ESI) m/z calculated for C₂₁H₁₅FNaO₃ [M+Na]⁺ = 357.0898, found 357.0897;

20) *cis*-Methyl 4-chloro-1-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-3-carboxylate (3ea)



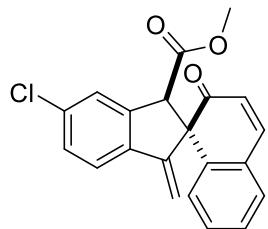
82.8 mg, 58% yield (isolated yield of single isomer), dr = 7:1, yellow oil liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.55 (d, $J = 9.9$ Hz, 1H), 7.47 (d, $J = 7.5$ Hz, 1H), 7.40-7.27 (m, 5H), 6.23 (d, $J = 9.9$ Hz, 1H), 5.57 (s, 1H), 4.74 (s, 1H), 4.58 (s, 1H), 3.63 (s, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ 199.1, 169.2, 153.6, 146.3, 145.8, 142.5, 138.7, 132.6, 130.8, 130.2, 129.8, 129.5, 128.4, 127.8, 126.7, 125.2, 119.6, 108.0, 64.2, 63.4, 52.2; HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{15}\text{ClNaO}_3$ [M+Na] $^+$ = 373.0595, found 373.0602;

21) *cis*-Methyl 5-methyl-1-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-3-carboxylate (3fa)



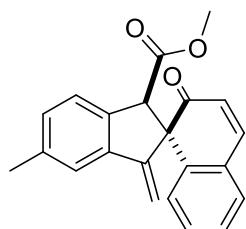
92.5 mg, 74% yield (isolated yield of single isomer), dr = 8:1, yellow solid, m.p. = 220-222 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.69 (s, 1H), 7.49 (d, $J = 9.9$ Hz, 1H), 7.40-7.31 (m, 4H), 7.20 (d, $J = 7.5$ Hz, 1H), 7.15 (d, $J = 7.8$ Hz, 1H), 6.12 (d, $J = 9.9$ Hz, 1H), 5.31 (s, 1H), 4.78 (s, 1H), 4.44 (s, 1H), 3.59 (s, 3H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.7, 171.1, 150.4, 145.1, 144.7, 141.5, 139.5, 135.1, 130.3, 130.2, 129.4, 129.2, 127.4, 127.4, 126.7, 124.0, 121.3, 104.5, 65.7, 60.3, 51.8, 21.7; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{18}\text{NaO}_3$ [M+Na] $^+$ = 353.1154, found 353.1148;

22) *cis*-Methyl 5-chloro-1-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-3-carboxylate (3ga)



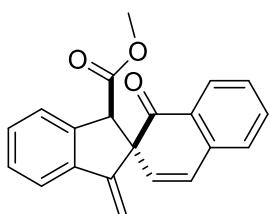
73.4 mg, 53% yield (isolated yield of single isomer), dr = 4.5:1, light yellow solid, m.p. = 197-198 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.88 (s, 1H), 7.51 (d, *J* = 9.9 Hz, 1H), 7.44-7.34 (m, 4H), 7.30 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.11 (d, *J* = 9.9 Hz, 1H), 5.36 (s, 1H), 4.79 (s, 1H), 4.51 (s, 1H), 3.61 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.4, 170.4, 149.3, 145.3, 143.9, 143.0, 136.2, 135.2, 130.5, 130.2, 129.6, 128.5, 127.6, 127.4, 126.5, 123.7, 122.4, 106.3, 65.6, 59.9, 52.1; HRMS (ESI) m/z calculated for C₂₁H₁₅ClNaO₃ [M+Na]⁺ = 373.0595, found 373.0602;

23) *cis*-Methyl 5-methyl-3-methylene-2'-oxo-1,3-dihydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (3ha)

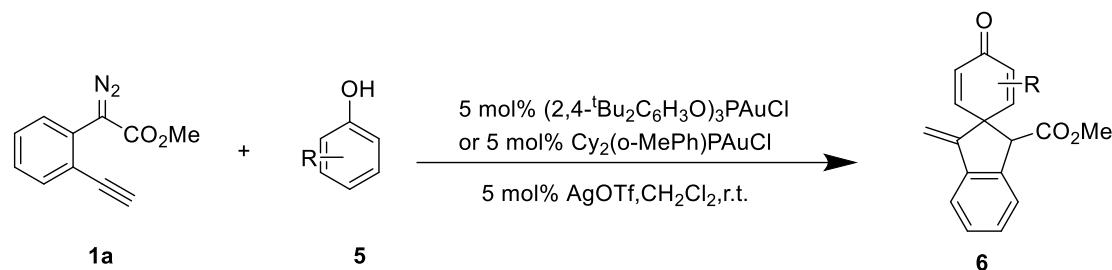


73.2 mg, 69% yield (isolated yield of single isomer), dr = 7.2:1, yellow oil liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.74 (d, *J* = 7.9 Hz, 1H), 7.49 (d, *J* = 9.9 Hz, 1H), 7.42-7.30 (m, 3H), 7.27 (s, 1H), 7.22 (dd, *J* = 17.6, 7.9 Hz, 2H), 6.12 (d, *J* = 9.9 Hz, 1H), 5.36 (s, 1H), 4.77 (s, 1H), 4.47 (s, 1H), 3.59 (s, 3H), 2.38 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 197.7, 171.1, 150.7, 145.1, 144.7, 138.7, 137.9, 137.7, 130.4, 130.3, 130.1, 129.4, 127.5, 127.4, 125.9, 124.0, 121.8, 105.2, 65.7, 60.4, 51.8, 21.3; HRMS (ESI) m/z calculated for C₂₂H₁₈NaO₃ [M+Na]⁺ = 353.1148, found 353.1142;

24) *cis*-Methyl 3-methylene-1'-oxo-1,3-dihydro-1'H-spiro[indene-2,2'-naphthalene]-1-carboxylate (3aq)

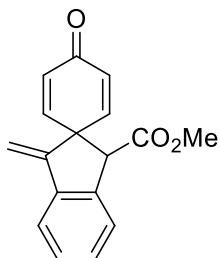


59.2 mg, 50% yield (isolated yield of single isomer), dr = 6:1, yellow liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, *J* = 7.6 Hz, 1H), 7.87 (d, *J* = 7.7 Hz, 1H), 7.57 (td, *J* = 7.5, 1.1 Hz, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.29 (t, *J* = 7.7 Hz, 2H), 6.84 (d, *J* = 9.7 Hz, 1H), 6.27 (d, *J* = 9.7 Hz, 1H), 5.42 (s, 1H), 4.96 (s, 1H), 4.35 (s, 1H), 3.61 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 196.5, 171.1, 145.3, 141.5, 137.9, 137.8, 136.6, 134.3, 129.2, 128.2, 127.9, 127.8, 127.2, 126.1, 125.9, 121.9, 105.6, 64.2, 58.2, 51.9. HRMS (ESI) m/z calculated for C₂₁H₁₆NaO₃ [M+Na]⁺ = 339.0993, found 339.0992;



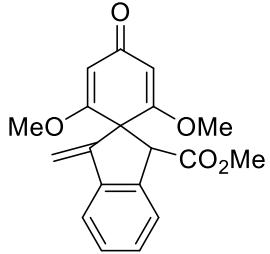
In a dried glass tube, a mixture of LAuCl (0.015 mmol), additive (5 mol%) in solvent (4 mL) was stirred at room temperature for 15 mins. Subsequently, phenol (0.45 mmol) was added to the reaction mixture at room temperature. Then a solution of diazo compounds (0.3 mmol) in solvent (1 mL) was introduced into the reaction mixture by a syringe in 15 mins. Then the resulting mixture was continually stirred at room temperature for 6 hours and diazo compound was consumed completely determined by TLC analysis. The mixture was concentrated under reduced pressure and the residue was purified by column chromatography on silica gel (PE/EA = 10:1 to 5:1 or PE/EA = 20:1 to 10:1) to afford the desired product.

25) Methyl 3'-methylene-4-oxo-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-2,5-diene-1'-carboxylate (6a)



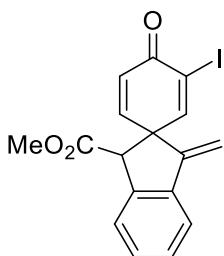
50.1 mg, 45% yield, yellow solid, m.p. = 131-132 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.60-7.52 (m, 1H), 7.47-7.33 (m, 3H), 6.93 (dd, J = 10.0, 3.0 Hz, 1H), 6.79 (dd, J = 10.1, 3.0 Hz, 1H), 6.52-6.40 (m, 1H), 6.30-6.16 (m, 1H), 5.58 (d, J = 0.6 Hz, 1H), 5.19-4.92 (m, 1H), 4.34 (s, 1H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.8, 170.3, 150.6, 148.3, 147.7, 139.4, 138.8, 129.8, 129.4, 128.7, 128.4, 126.7, 121.9, 107.3, 57.3, 55.8, 52.3; HRMS (ESI) m/z calculated for $\text{C}_{17}\text{H}_{14}\text{NaO}_3$ [M+Na] $^+$ = 289.0835, found 289.0827;

26) Methyl 3,5-dimethoxy-3'-methylene-4-oxo-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-2,5-diene-1'-carboxylate (6b)



57.2 mg, 57% yield, colorless solid, m.p. = 178-180 °C, ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, J = 7.7 Hz, 1H), 7.44 (d, J = 7.7 Hz, 1H), 7.34 (t, J = 7.4 Hz, 1H), 7.28 (d, J = 7.5 Hz, 1H), 5.48 (s, 1H), 5.47 (s, 1H), 5.17 (d, J = 1.7 Hz, 1H), 5.09 (s, 1H), 5.06 (s, 1H), 3.87 (s, 3H), 3.67 (s, 3H), 3.48 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 197.2, 175.8, 172.4, 170.7, 150.7, 141.4, 138.1, 129.1, 127.7, 126.5, 120.7, 103.9, 93.9, 91.1, 65.2, 56.3, 56.2, 55.9, 51.7; HRMS (ESI) m/z calculated for $\text{C}_{19}\text{H}_{18}\text{NaO}_5$ [M+Na] $^+$ = 349.1040, found 349.1046;

27) Methyl 2-iodine-3'-methylene-4-oxo-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-2,5-diene-1'-carboxylate (6c and 6c')

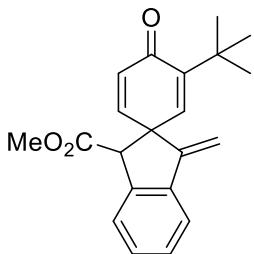


dr = 2:1

Major: 44.9 mg, 38% yield, yellow liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.65 (d, *J* = 2.7 Hz, 1H), 7.57 – 7.55 (m, 1H), 7.44 – 7.39 (m, 3H), 6.88 (dd, *J* = 9.9, 2.7 Hz, 1H), 6.36 (d, *J* = 9.9 Hz, 1H), 5.61 (d, *J* = 0.9 Hz, 1H), 5.03 (d, *J* = 0.8 Hz, 1H), 4.36 (s, 1H), 3.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 179.4, 170.0, 158.4, 148.6, 146.5, 139.1, 138.4, 129.9, 128.9, 126.6, 125.5, 122.0, 107.8, 104.5, 59.5, 56.7, 52.5; HRMS (ESI) m/z calculated for C₁₇H₁₃INaO₃ [M+Na]⁺ = 414.9807, found 414.9800;

Minor: 22.5 mg, 19% yield, yellow liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.57 – 7.56 (m, 1H), 7.54 (d, *J* = 2.6 Hz, 1H), 7.45 – 7.39 (m, 3H), 6.99 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.54 (d, *J* = 9.8 Hz, 1H), 5.61 (s, 1H), 5.04 (s, 1H), 4.36 (s, 1H), 3.71 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 179.5, 169.8, 156.2, 150.7, 146.3, 139.0, 138.3, 130.0, 128.9, 126.7, 126.5, 122.0, 107.9, 103.5, 59.8, 57.0, 52.6; HRMS (ESI) m/z calculated for C₁₇H₁₃INaO₃ [M+Na]⁺ = 414.9807, found 414.9793;

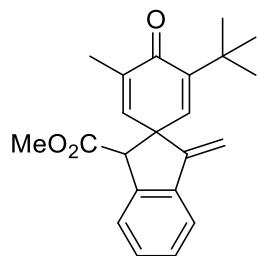
28) Methyl 2-tert-butyl-3'-methylene-4-oxo-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-2,5-diene-1'-carboxylate (6d)



64.1 mg, 66% yield, dr = 1.4:1, yellow liquid; ¹H NMR (500 MHz, CDCl₃) δ 1H NMR (500 MHz, CDCl₃) δ 7.68-7.55 (m, 1 H), 7.43-7.37 (m, 3H), [6.81 (dd, *J* = 9.8,

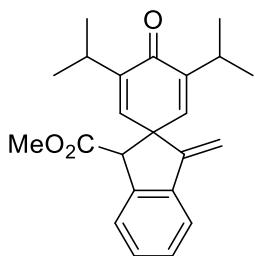
2.8 Hz, 0.6H), 6.70 (d, J = 2.8 Hz, 0.4H)], [6.64 (dd, J = 9.8, 2.8 Hz, 0.4H), 6.52 (d, J = 2.8 Hz, 0.6H)], [6.35 (d, J = 9.7 Hz, 0.6H), 6.15 (d, J = 9.8 Hz, 0.4H)], 5.53 (d, J = 4.9 Hz, 1H), 4.93 (d, J = 6.5 Hz, 1H), 4.31 (s, 1H), 3.64 (d, J = 1.6 Hz, 3H), [1.29 (s, 3.8H), 1.17 (s, 5.3H)]; ^{13}C NMR (125 MHz, CDCl_3) δ [186.0, 185.9], 170.4, [148.6, 148.5], [148.2, 146.6], [145.7, 145.4], [144.1, 141.7], [139.6, 139.5], [139.1, 138.9], [131.1, 130.1], [129.7, 129.6], 128.5, [126.8, 126.7], 121.8, [106.7, 106.6], [57.6, 57.3], [56.0, 55.6], [52.0, 51.9], [34.6, 34.5], [29.1, 29.0]. HRMS (ESI) m/z calculated for $\text{C}_{21}\text{H}_{22}\text{NaO}_3$ [$\text{M}+\text{Na}]^+$ = 345.1467, found 345.1460;

29) Methyl 2-tert-butyl-6-methyl-3'-methylene-4-oxo-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-2,5-diene-1'-carboxylate (6e)



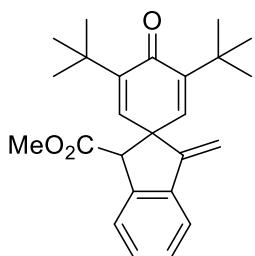
70.3 mg, 70% yield, dr = 1.4:1, yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.56 (dd, J = 7.9, 4.4 Hz, 1H), 7.43-7.35 (m, 3H), [6.69 (d, J = 3.0 Hz, 0.4H), 6.62 (dd, J = 2.7, 1.3 Hz, 0.6H)], [6.51 (d, J = 3.0 Hz, 0.6H), 6.46 (dd, J = 2.7, 1.3 Hz, 0.4H)], 5.50 (d, J = 4.9 Hz, 1H), 4.91 (d, J = 2.3 Hz, 1H), 4.28 (d, J = 1.8 Hz, 1H), [3.63 (s, 1.7H), 3.60 (s, 1.3H)], [1.97 (d, J = 1.2 Hz, 1.7H), 1.83 (d, J = 1.2 Hz, 1.3H)], [1.29 (s, 3.7H), 1.17 (s, 5.2H)]; ^{13}C NMR (125 MHz, CDCl_3) δ [186.5, 186.4], [170.7, 170.6], [149.1, 149.0], [146.2, 145.0], [144.1, 144.0], [141.4, 141.1], [139.8, 139.6], [139.2, 139.1], [136.6, 136.0], [129.5, 129.4], [128.5, 128.4], [126.8, 126.7], [121.8, 121.7], [106.3, 106.1], [57.5, 57.4], [55.5, 55.1], [51.9, 51.8], [34.6, 34.5], [29.2, 29.1], [16.4, 16.3]; HRMS (ESI) m/z calculated for $\text{C}_{22}\text{H}_{24}\text{NaO}_3$ [$\text{M}+\text{Na}]^+$ = 359.1623, found 359.1609;

30) Methyl 2,6-diisopropyl-3'-methylene-4-oxo-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-2,5-diene-1'-carboxylate (6f)



66.8 mg (0.5 mmol scale), 41% yield, yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.58-7.56 (m, 1H), 7.43-7.37 (m, 3H), 6.59 (d, J = 2.4 Hz, 1H), 6.41 (dd, J = 2.8, 0.6 Hz, 1H), 5.49 (s, 1H), 4.87 (s, 1H), 4.30 (s, 1H), 3.60 (s, 3H), 3.11 (hept, J = 6.8 Hz, 1H), 3.01 ((hept, J = 6.8 Hz, 1H), 1.12 (d, J = 6.9 Hz, 6H), 0.97 (dd, J = 6.9, 4.7 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.0, 170.5, 149.1, 145.5, 144.6, 142.3, 139.7, 139.6, 139.2, 129.5, 128.4, 126.7, 121.8, 106.2, 57.5, 54.9, 51.8, 26.4, 26.2, 22.1, 22.0, 21.7, 21.6; HRMS (ESI) m/z calculated for $\text{C}_{23}\text{H}_{26}\text{NaO}_3$ [M+Na] $^+$ = 373.1780, found 373.1768;

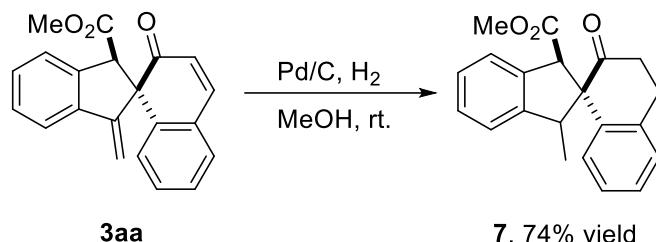
31) Methyl 2,6-di-tert-butyl-3'-methylenec-4-oxo-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-2,5-diene-1'-carboxylate (6g)



33.3 mg, 30% yield, yellow oil; ^1H NMR (500 MHz, CDCl_3) δ 7.56 (dd, J = 5.7, 2.9 Hz, 1H), 7.43 – 7.35 (m, 3H), 6.61 (d, J = 2.9 Hz, 1H), 6.39 (d, J = 2.9 Hz, 1H), 5.49 (s, 1H), 4.88 (s, 1H), 4.27 (s, 1H), 3.61 (s, 3H), 1.29 (s, 9H), 1.16 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 186.4, 170.6, 149.7, 147.8, 146.6, 141.9, 139.7, 139.3, 139.2, 129.5, 128.4, 126.8, 121.8, 106.1, 57.7, 55.0, 51.8, 34.9, 34.8, 29.5, 29.4; HRMS (ESI) m/z calculated for $\text{C}_{25}\text{H}_{30}\text{NaO}_3$ [M+Na] $^+$ = 401.2093, found 401.2086.

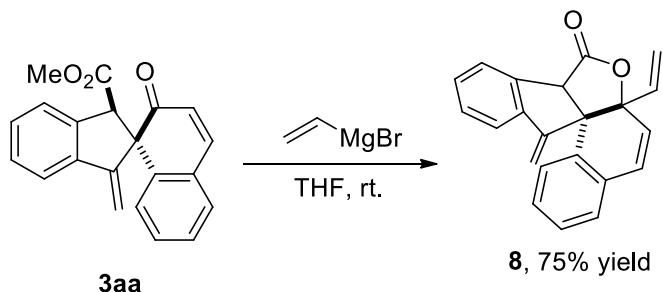
5. Transformations of products

1) Methyl 3-methyl-2'-oxo-1,3,3',4'-tetrahydro-2'H-spiro[indene-2,1'-naphthalene]-1-carboxylate (7)



In a dried Schlenk tube, Pd/C (16.0 mg, palladium on activated carbon, 10% Pd basis, 0.1 equiv.) was added to a solution of **3aa** (63.3 mg, 0.2 mmol) in MeOH (3.0 mL). The reaction mixture was stirred under H₂ atmosphere (1 atm) at rt for 12 h. After the reaction was complete (monitored by TLC), the crude reaction mixture was filtered with celite and washed with EtOAc. The solvent was removed under reduced pressure. Then the residue was purified by silica gel column chromatography (PE/EA = 10:1) to afford the desired product **7** (47.4 mg, 74% yield) as a colorless liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.69 (d, *J* = 7.1 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.34-7.20 (m, 5H), 7.07 (d, *J* = 6.9 Hz, 1H), 4.53 (s, 1H), 3.80 (q, *J* = 7.1 Hz, 1H), 3.65 (s, 3H), 3.43-3.26 (m, 1H), 3.11 (ddd, *J* = 15.7, 6.2, 3.9 Hz, 1H), 2.81-2.57 (m, 2H), 1.26 (d, *J* = 7.2 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 210.5, 171.7, 143.2, 140.9, 138.6, 137.7, 128.3, 127.5, 127.3, 126.9, 126.7, 126.7, 124.0, 122.3, 64.8, 62.3, 52.9, 51.9, 41.2, 29.2, 14.0; HRMS (ESI) m/z calculated for C₂₁H₂₀NaO₃ [M+Na]⁺ = 343.1298, found 343.1305.

2) 13-methylene-6a-vinyl-8a,13-dihydro-6aH,8H-indeno[2,1-c]naphtho[2,1-b]furan-8-one (8)

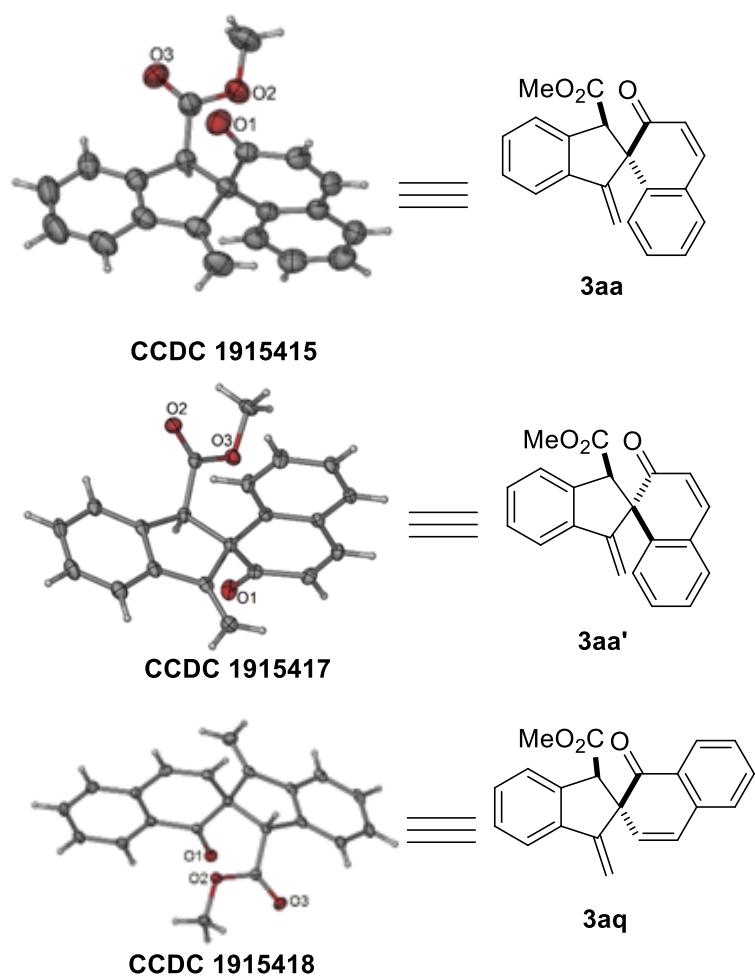


To a solution of **3aa** (63.3 mg, 0.2 mmol) in THF (2 mL) was added vinyl magnesium bromide (0.6 mmol, 3.0 equiv) slowly, and the reaction was then stirred at room temperature. After the reaction was complete (monitored by TLC), the reaction was quenched with saturated aqueous NaHCO₃, and extracted with ethyl acetate. The organic layers were combined and dried over Na₂SO₄, filtered and concentrated by rotary evaporation. Then the residue was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 20/1) to afford product **8** as a yellow oil, 46.9 mg, 75% yield; ¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J* = 7.5 Hz, 1H), 7.35 (dd, *J* = 14.3, 7.3 Hz, 2H), 7.27 (dd, *J* = 13.8, 6.3 Hz, 1H), 7.21 (d, *J* = 4.3 Hz, 2H), 7.02 (s, 1H), 6.68 (d, *J* = 7.4 Hz, 1H), 6.63 (d, *J* = 9.7 Hz, 1H), 6.42 (d, *J* = 9.7 Hz, 1H), 6.16 (s, 1H), 5.90 (dd, *J* = 17.0, 10.7 Hz, 1H), 5.50 (d, *J* = 17.0 Hz, 1H), 5.39 (s, 1H), 5.15 (d, *J* = 10.7 Hz, 1H), 4.19 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 175.4, 149.4, 140.7, 139.1, 138.6, 137.7, 132.5, 129.6, 129.6, 128.8, 128.5, 128.4, 127.8, 127.6, 125.0, 123.0, 121.6, 116.3, 107.8, 87.2, 63.5, 53.4; RMS (ESI) m/z calculated for C₂₂H₁₆NaO₂ [M+Na]⁺ = 335.1045, found 335.1043;

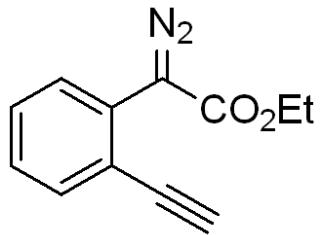
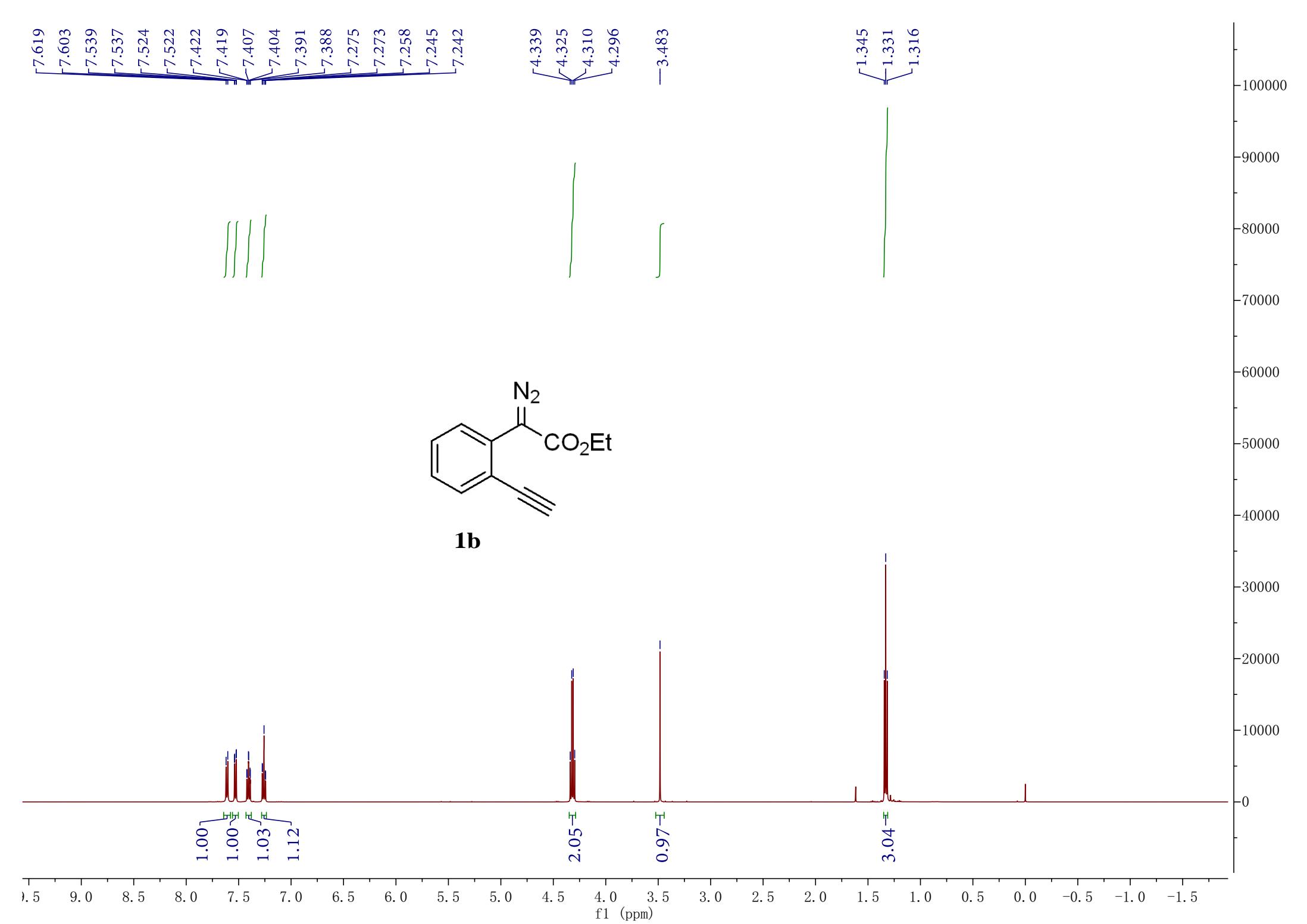
6. Reference

[1] (a) T. Mei, D. Wang, J. Yu, *Org. Lett.* **2010**, *12*, 3140-3143; (b) P. Wessig, C. Glombitza, G. Müller, J. Teubner, *J. Org. Chem.* **2004**, *69*, 7582-7591; (c) F. J. Reboreda, M. Treus, J. C. Estévez, L. Castedo, R. J. Estévez, *Synlett*, **2003**, *11*, 1603-1606; (d) C. Peng, J. Cheng, J. Wang, *Adv. Synth. Catal.* **2008**, *350*, 2359-2364.

7. X-ray Crystal data for 3aa, 3aa' and 3aq.



8. NMR Spectra of new compounds



1b

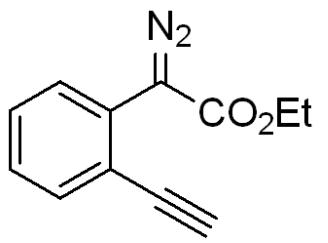
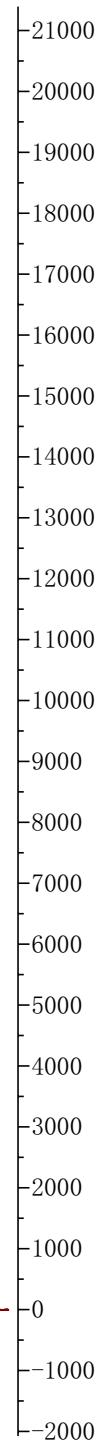
—165.570

133.437
129.984
129.108
127.663
127.380
120.113

84.329
80.778
77.254
77.000
76.746

—61.152

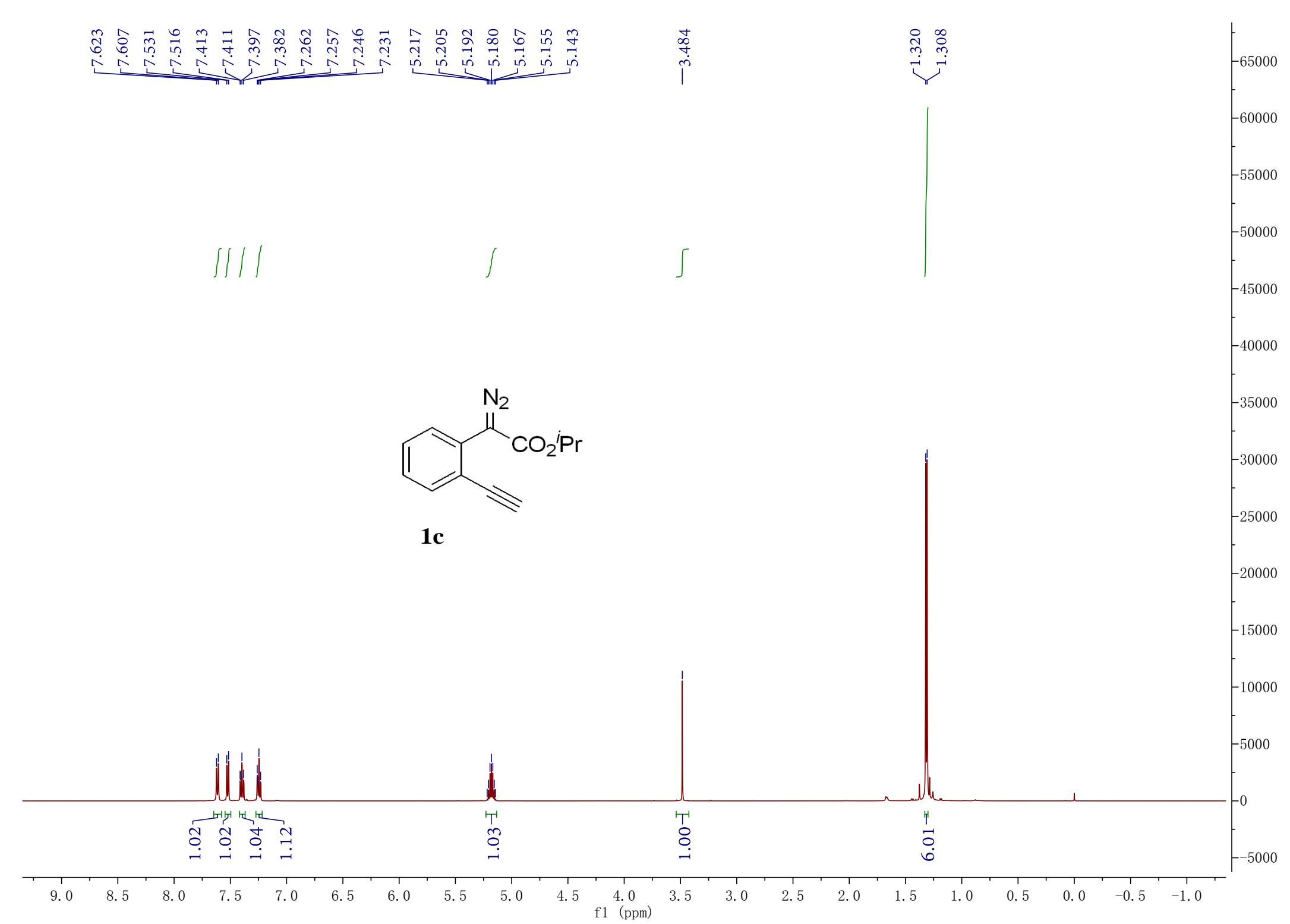
—14.454



1b

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

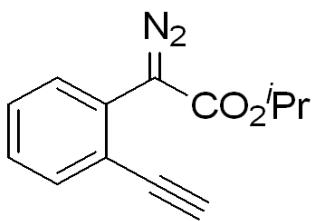


—165.121

133.430
129.910
129.046
127.790
127.257
120.008

84.331
80.815
77.255
77.000
76.746
68.837

—22.015

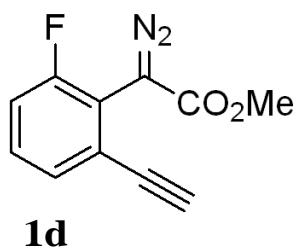
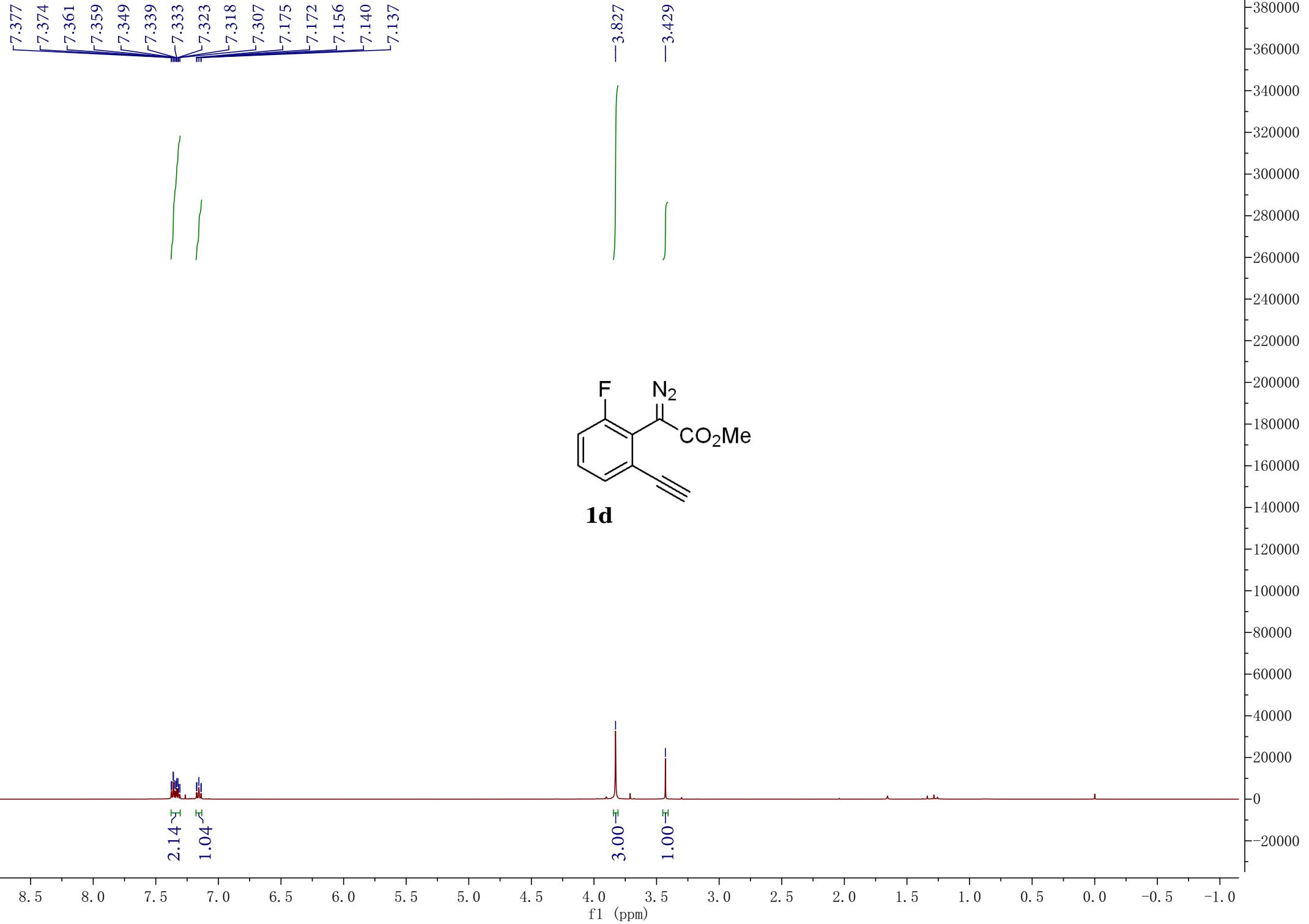


1c

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

45000
40000
35000
30000
25000
20000
15000
10000
5000
0



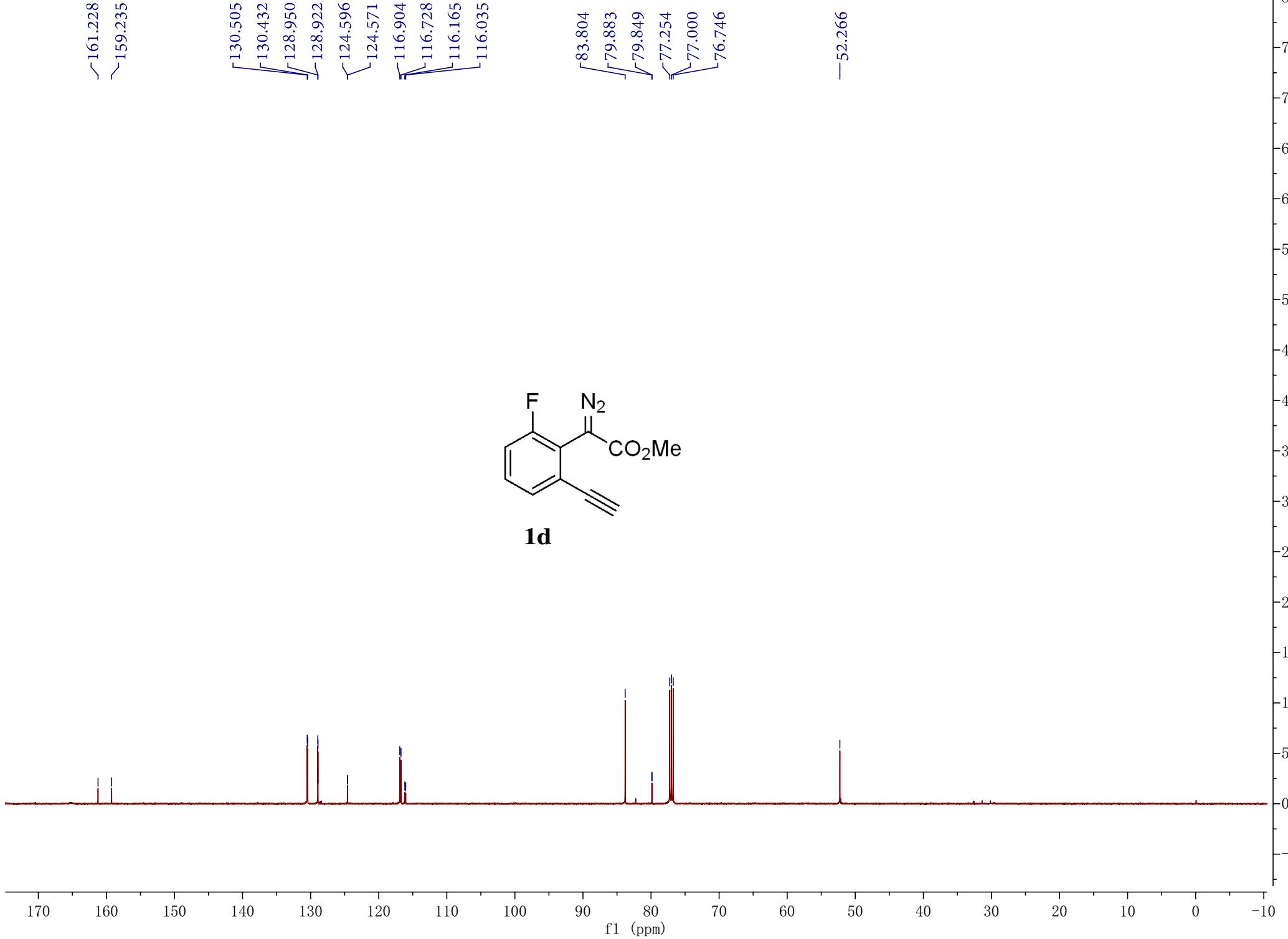
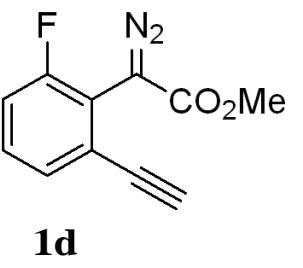
~161.228
~159.235

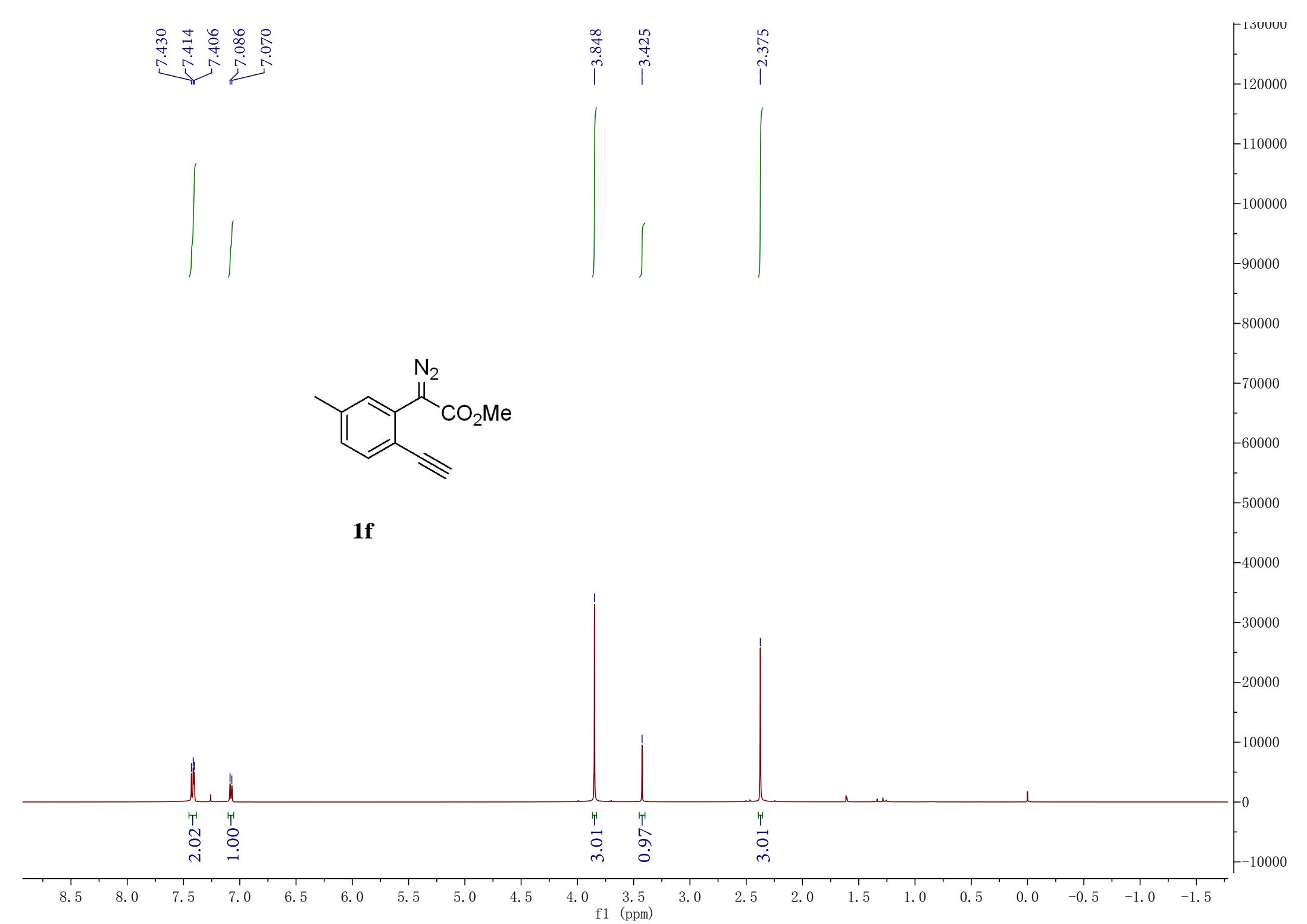
130.505
130.432
128.950
128.922
124.596
124.571
116.904
116.728
116.165
116.035

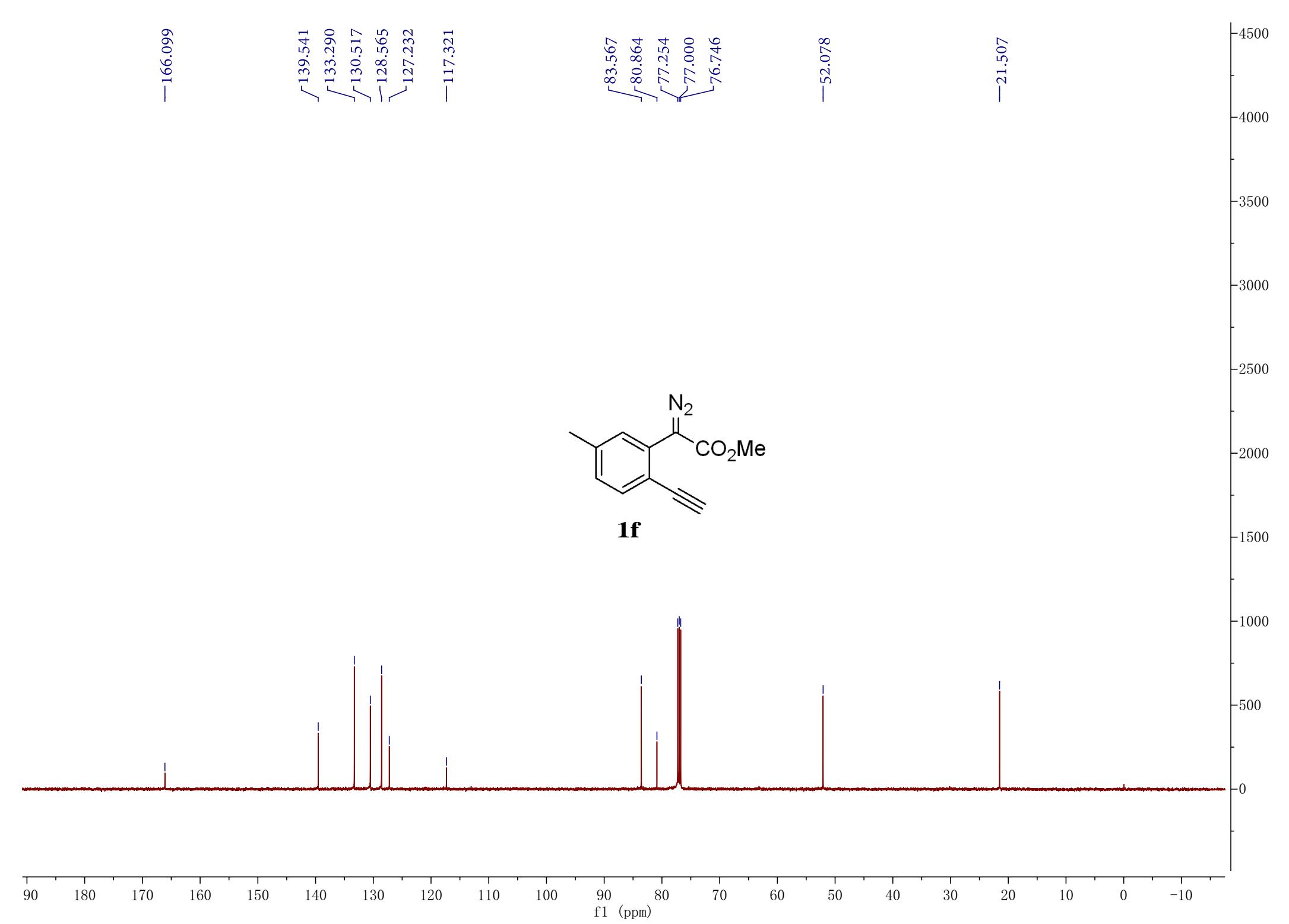
83.804
79.883
79.849
77.254
77.000
76.746

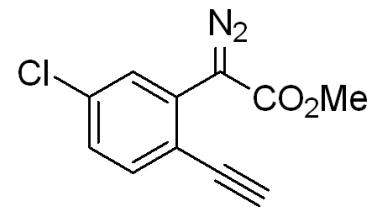
-52.266

δ_{UVV}
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

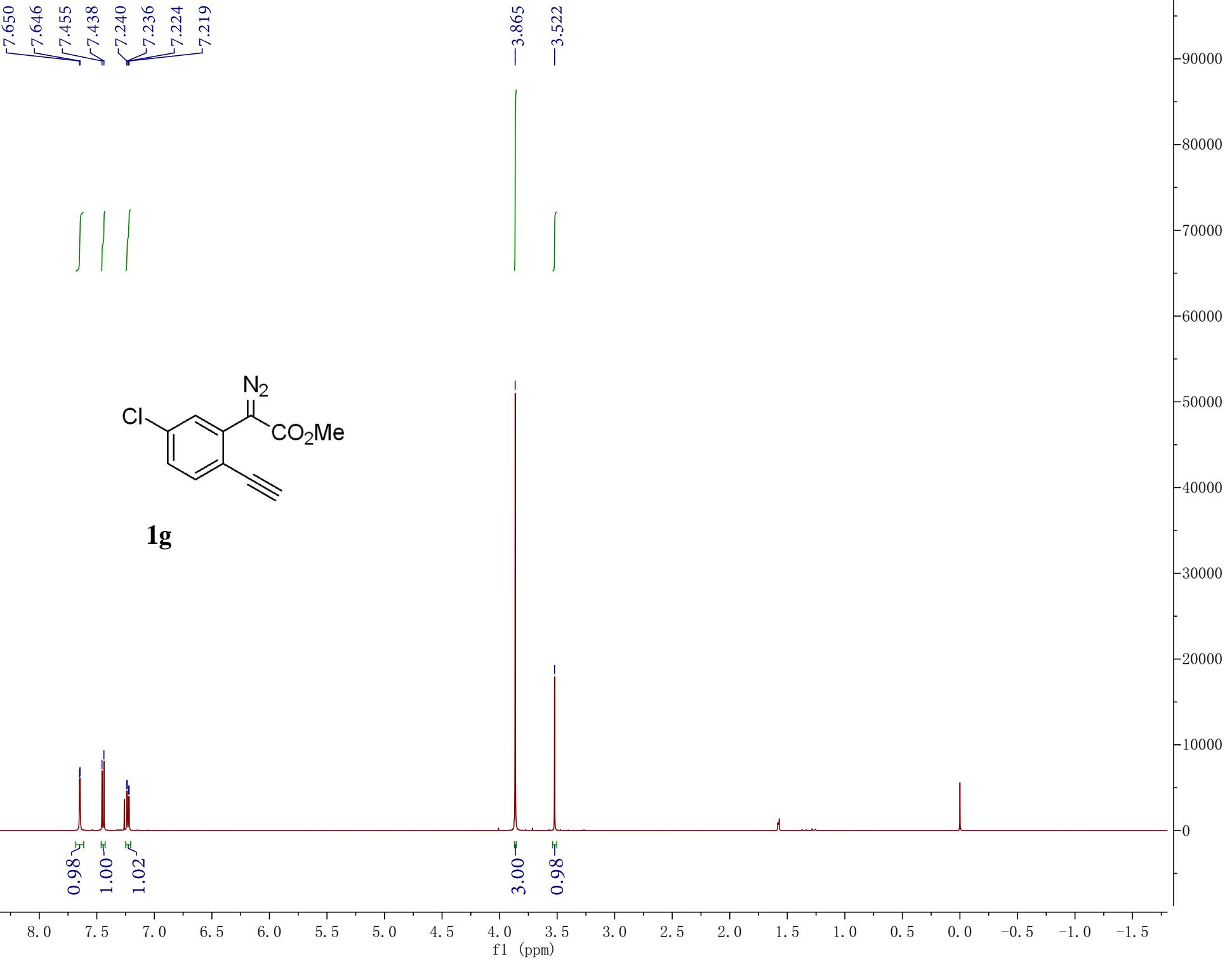








1g

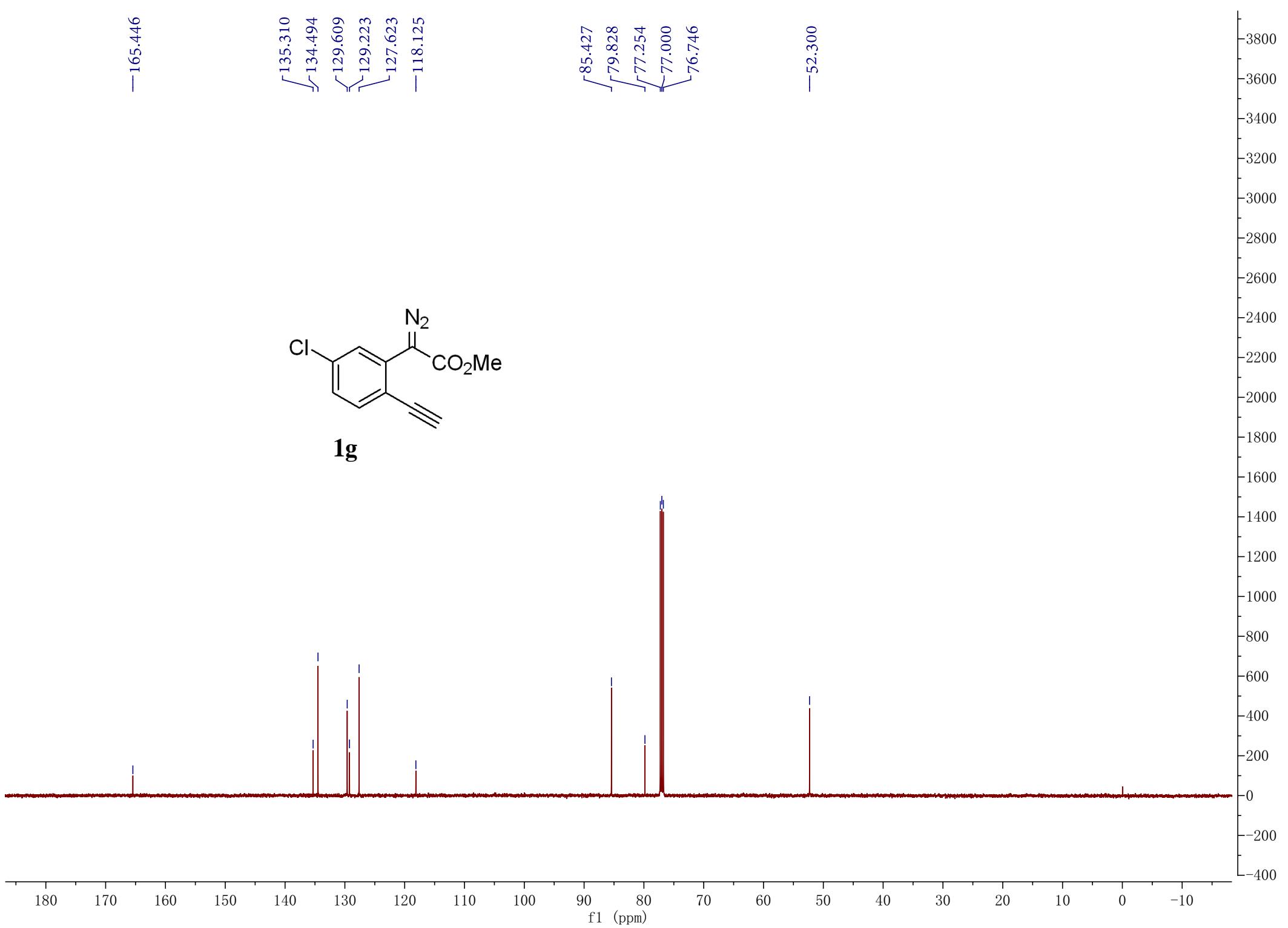
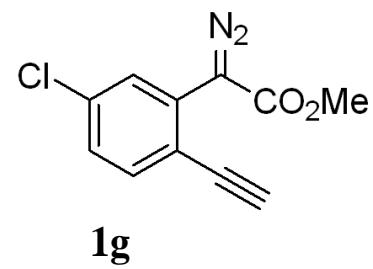


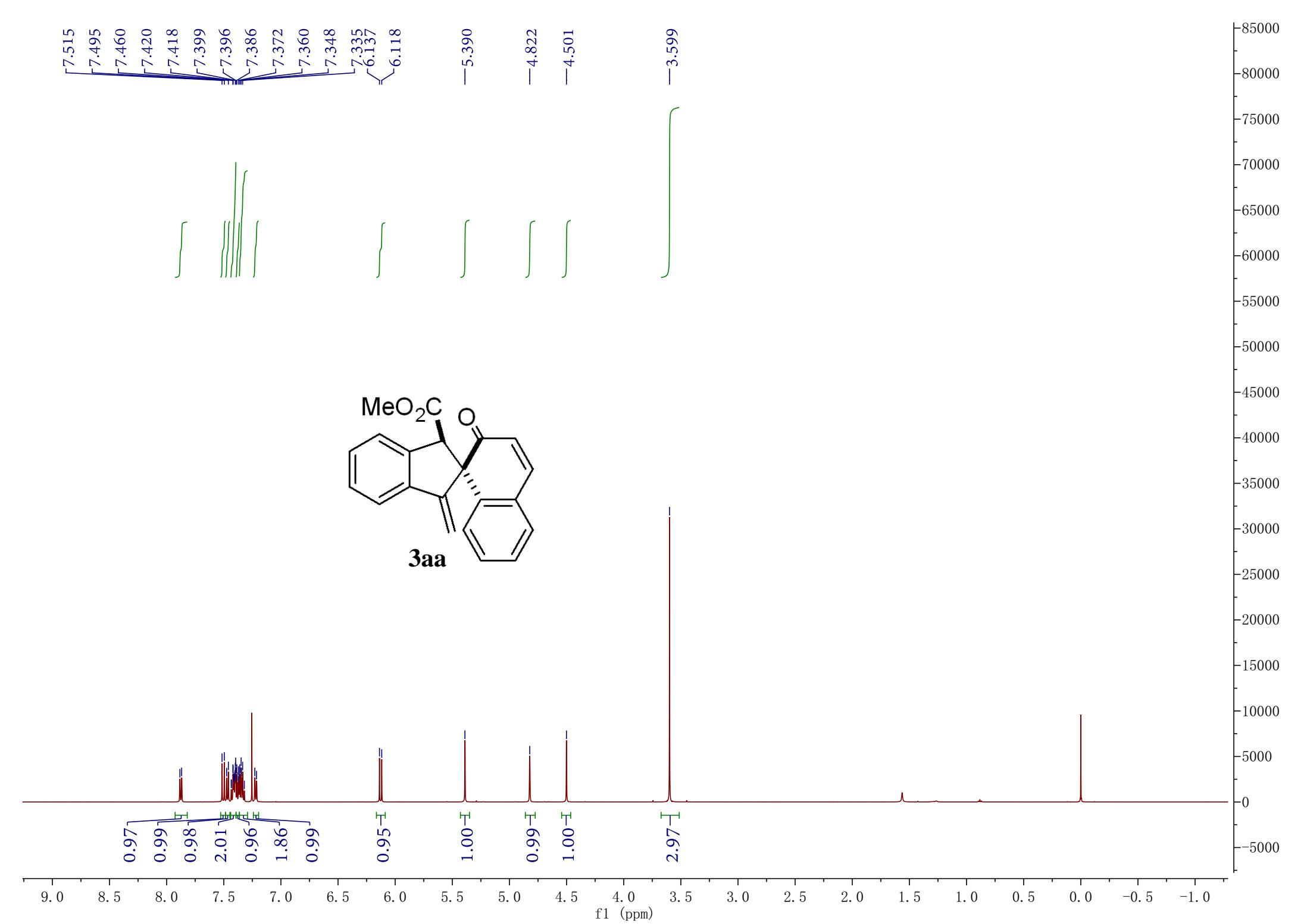
—165.446

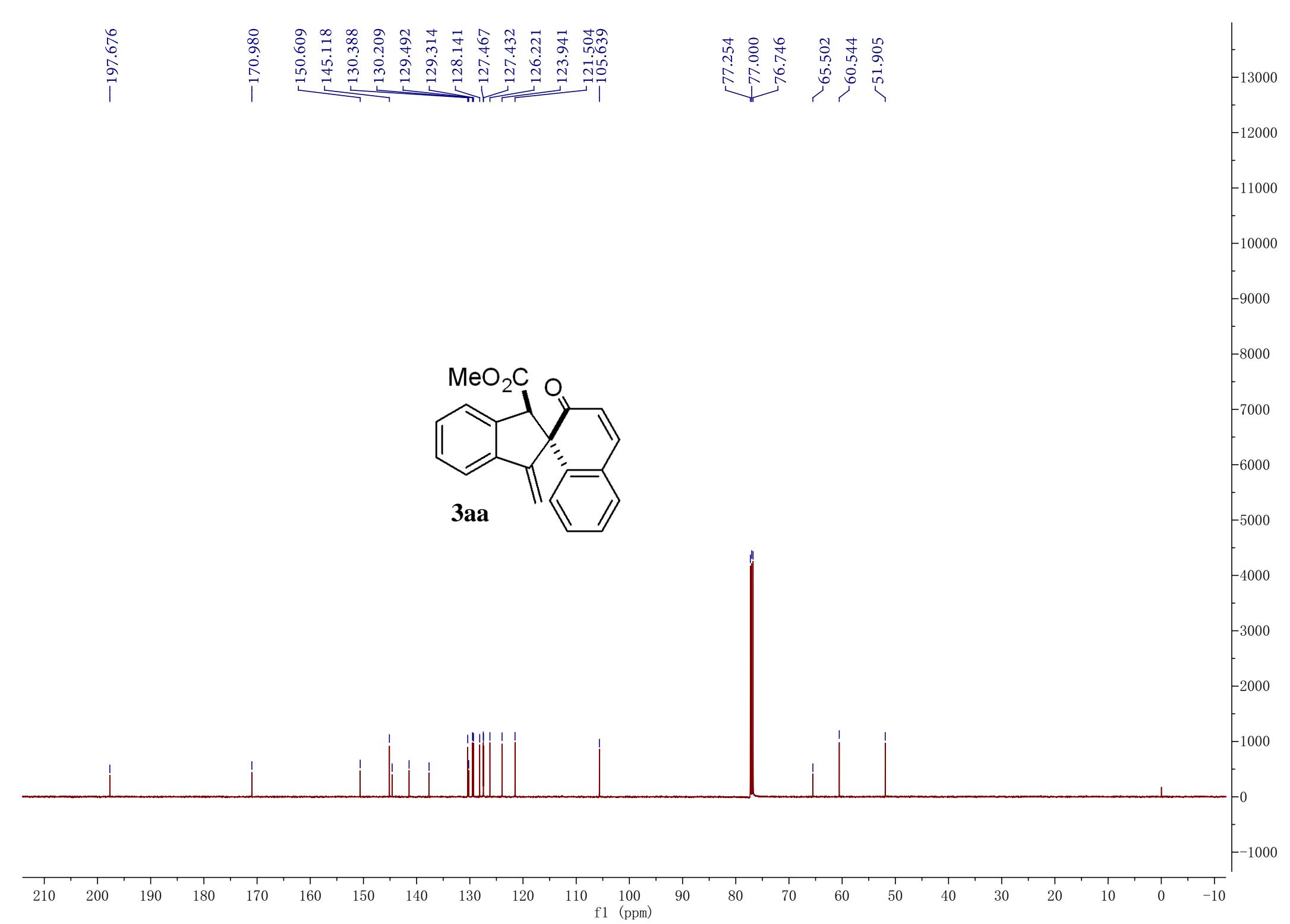
135.310
134.494
129.609
129.223
127.623
—118.125

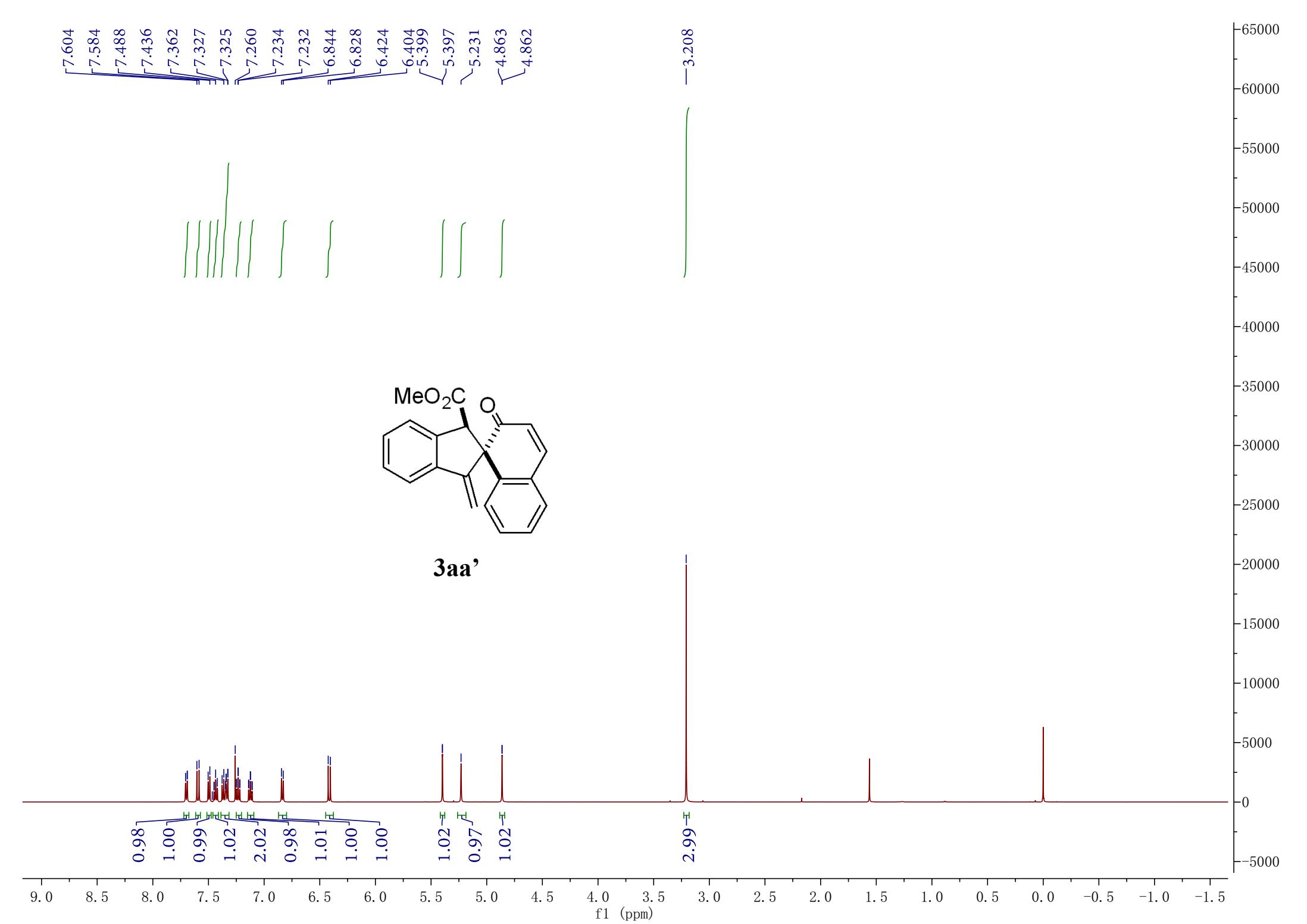
85.427
79.828
77.254
77.000
76.746

—52.300









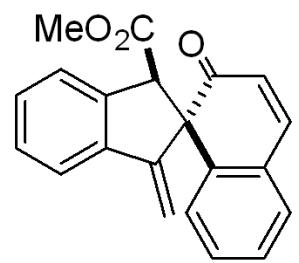
—200.554

—170.588

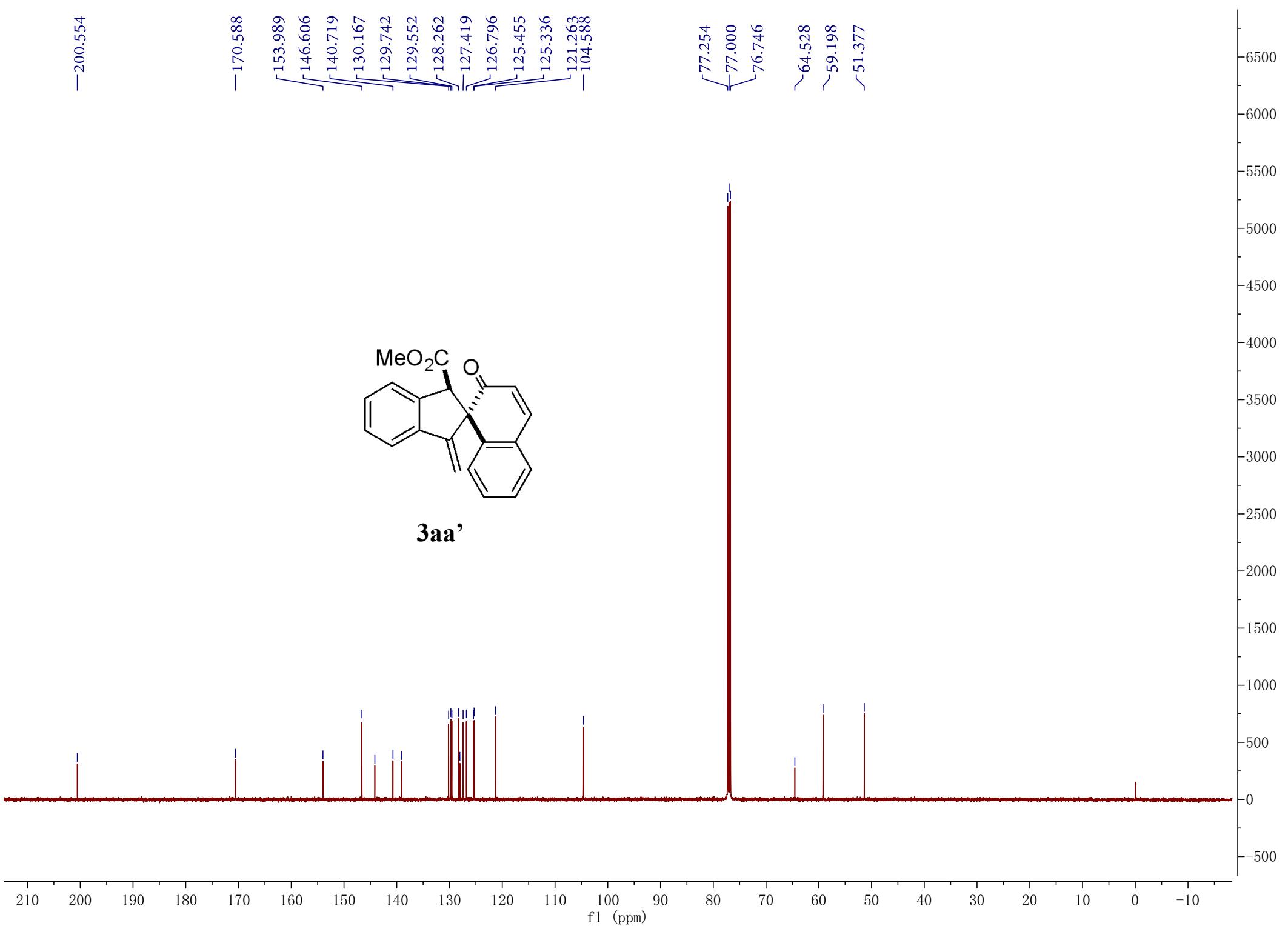
153.989
146.606
140.719
130.167
129.742
129.552
128.262
127.419
126.796
125.455
125.336
121.263
—104.588

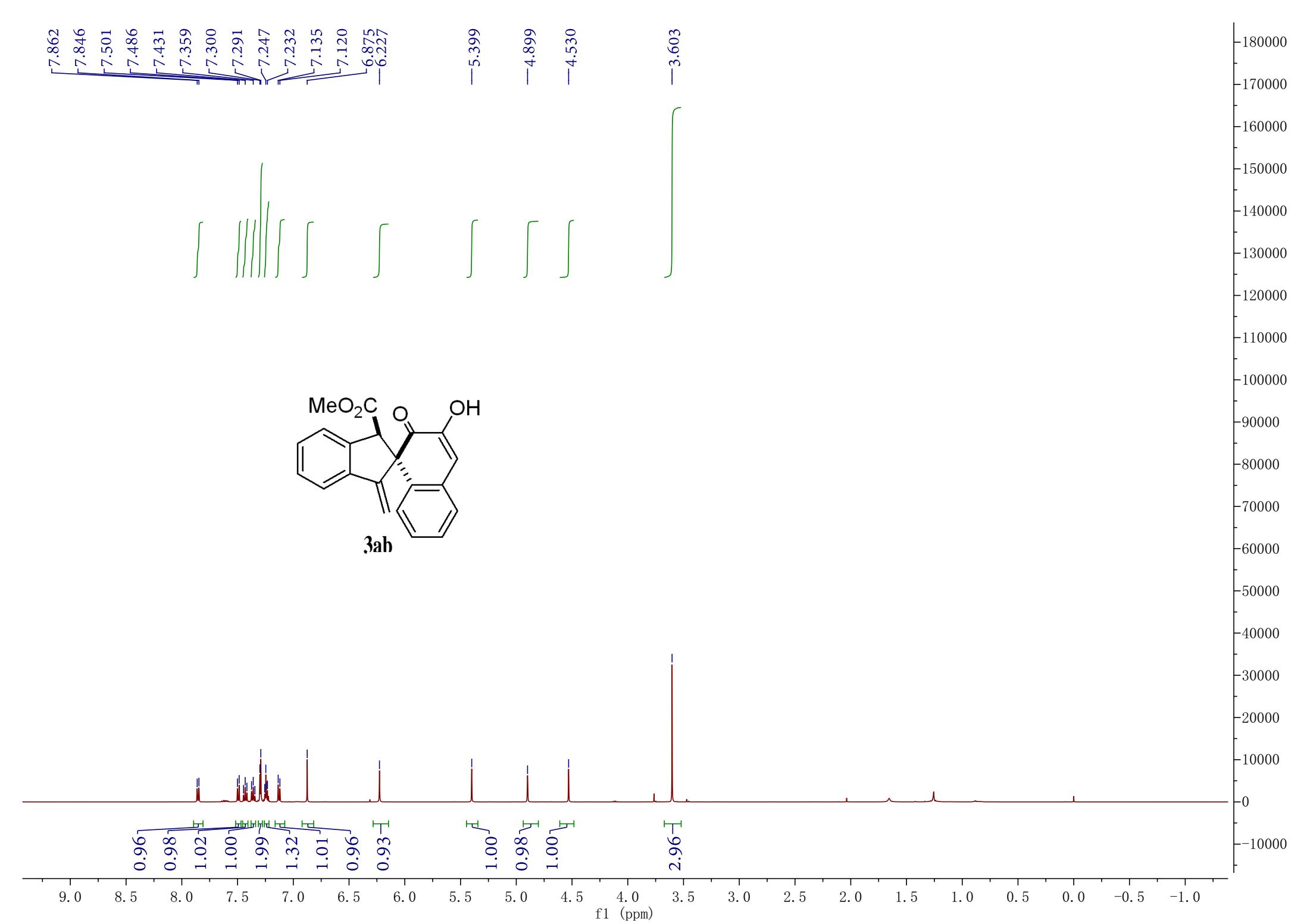
77.254
77.000
76.746

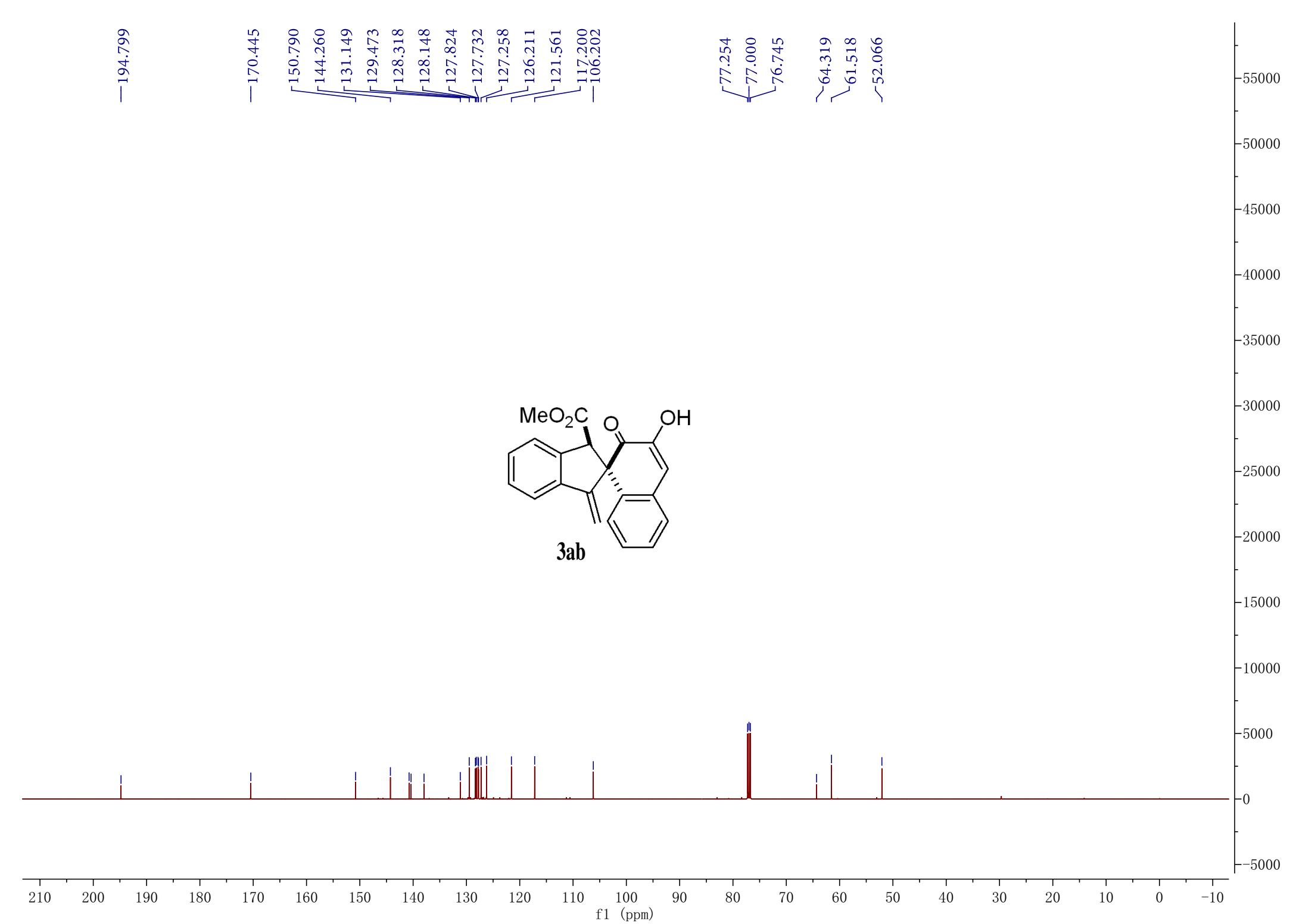
~64.528
~59.198
~51.377

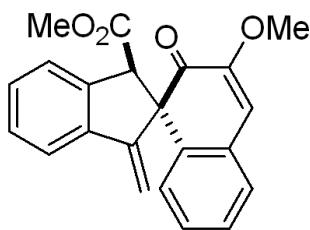
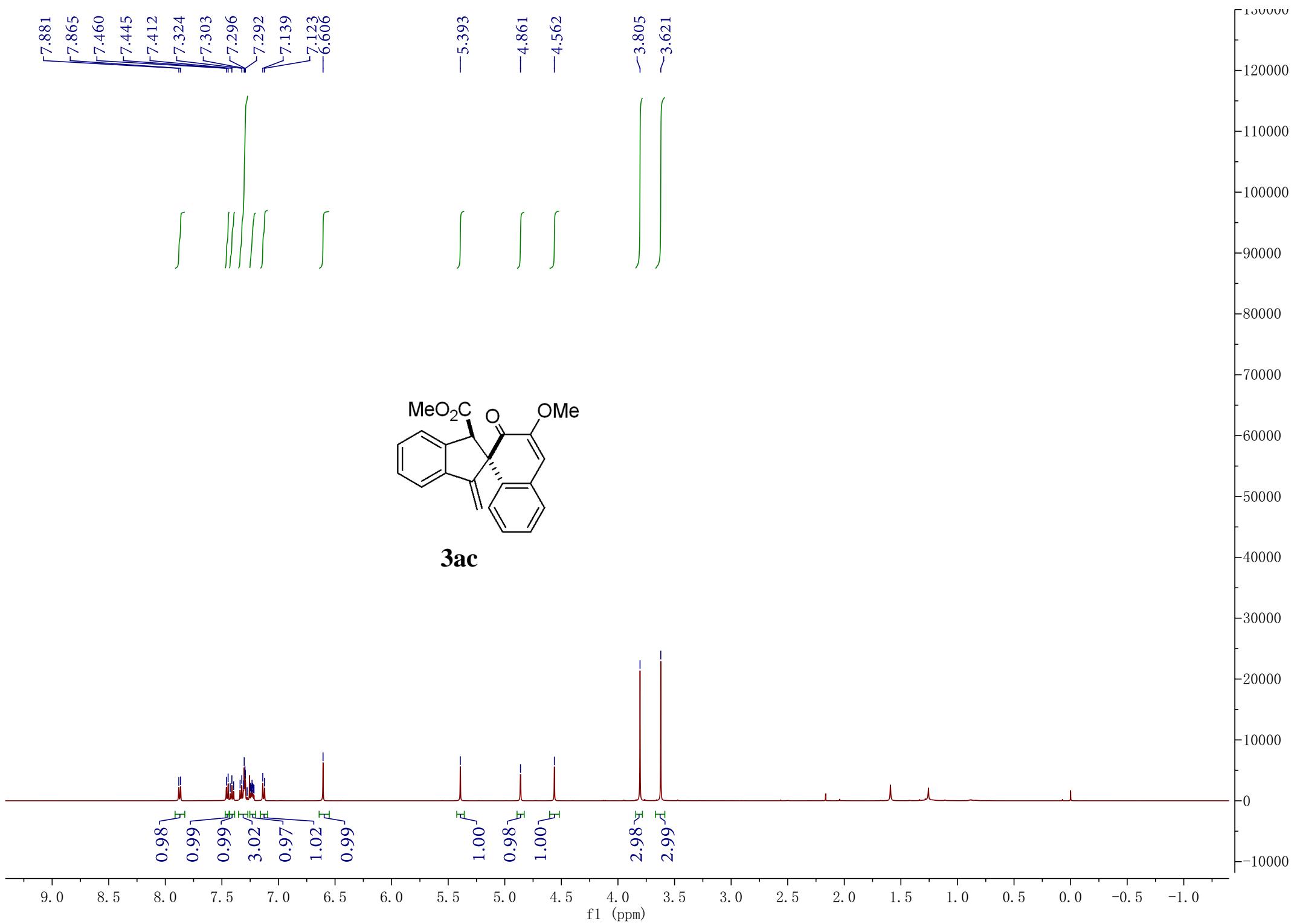


3aa'









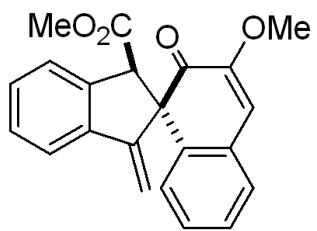
3ac

— 192.363

— 170.811

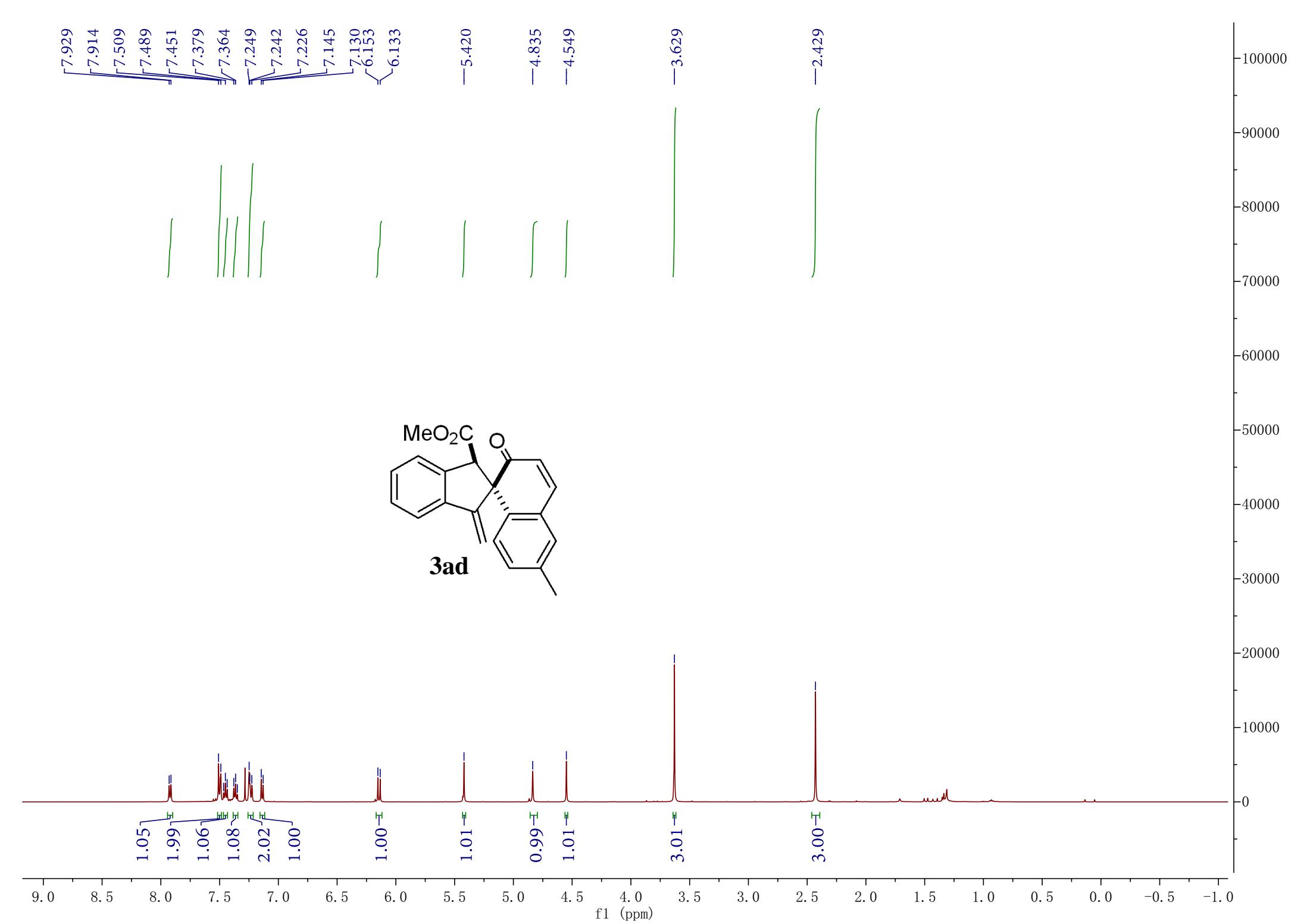
150.210
148.587
141.246
130.969
129.295
128.061
127.915
127.718
127.565
126.915
126.133
121.578
115.299
105.886

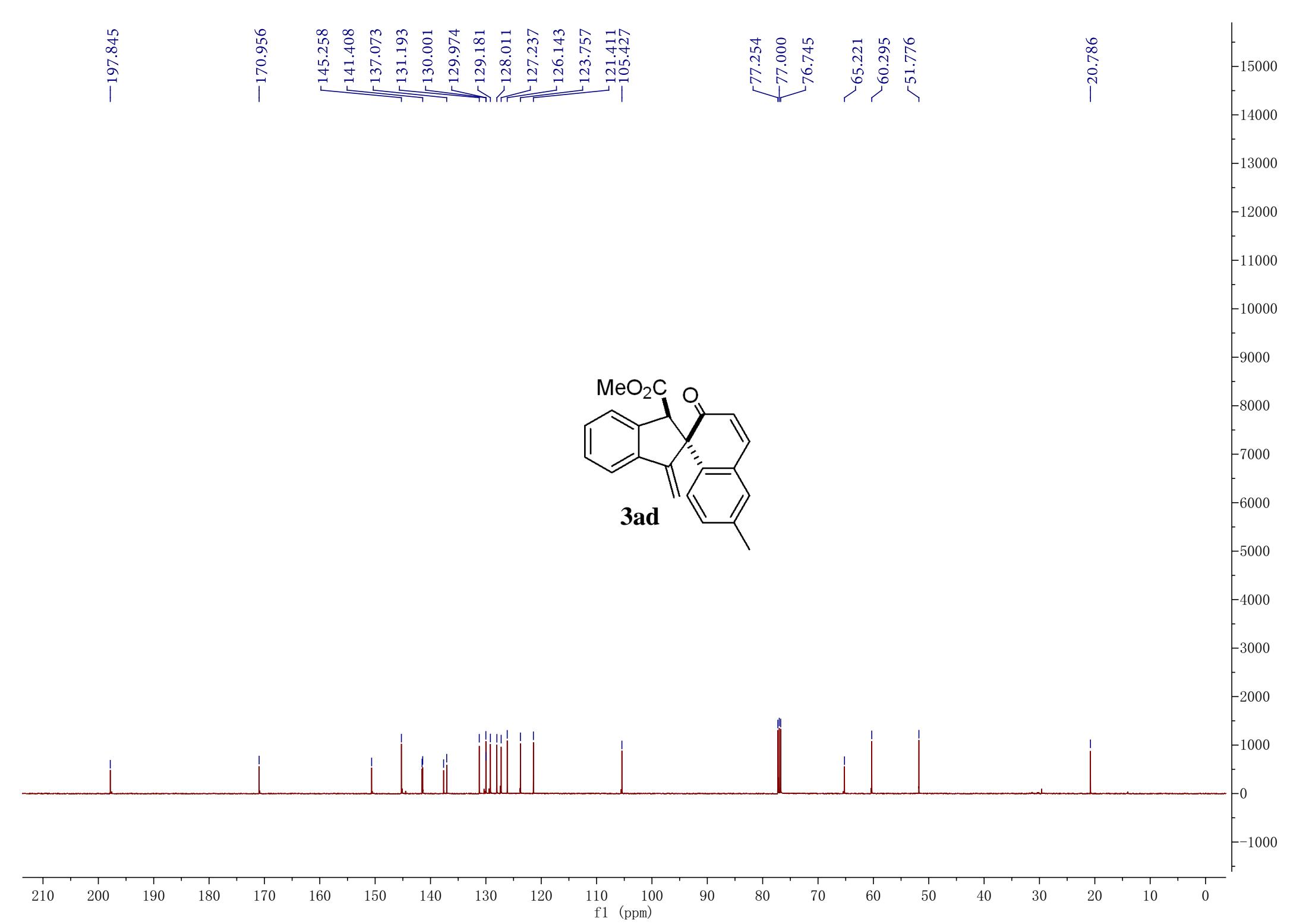
77.255
77.000
76.746
~66.641
~60.512
~55.514
~52.016

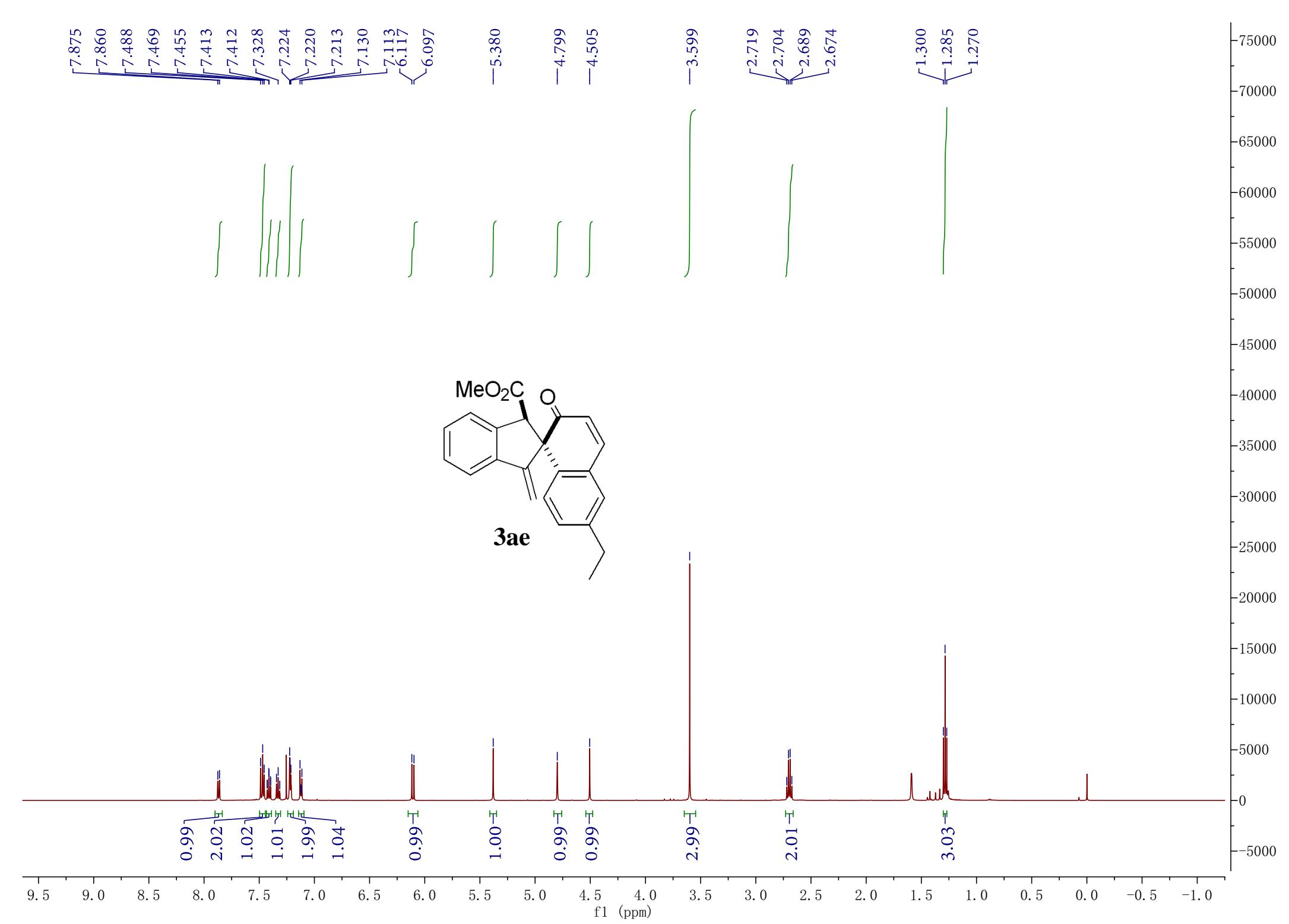


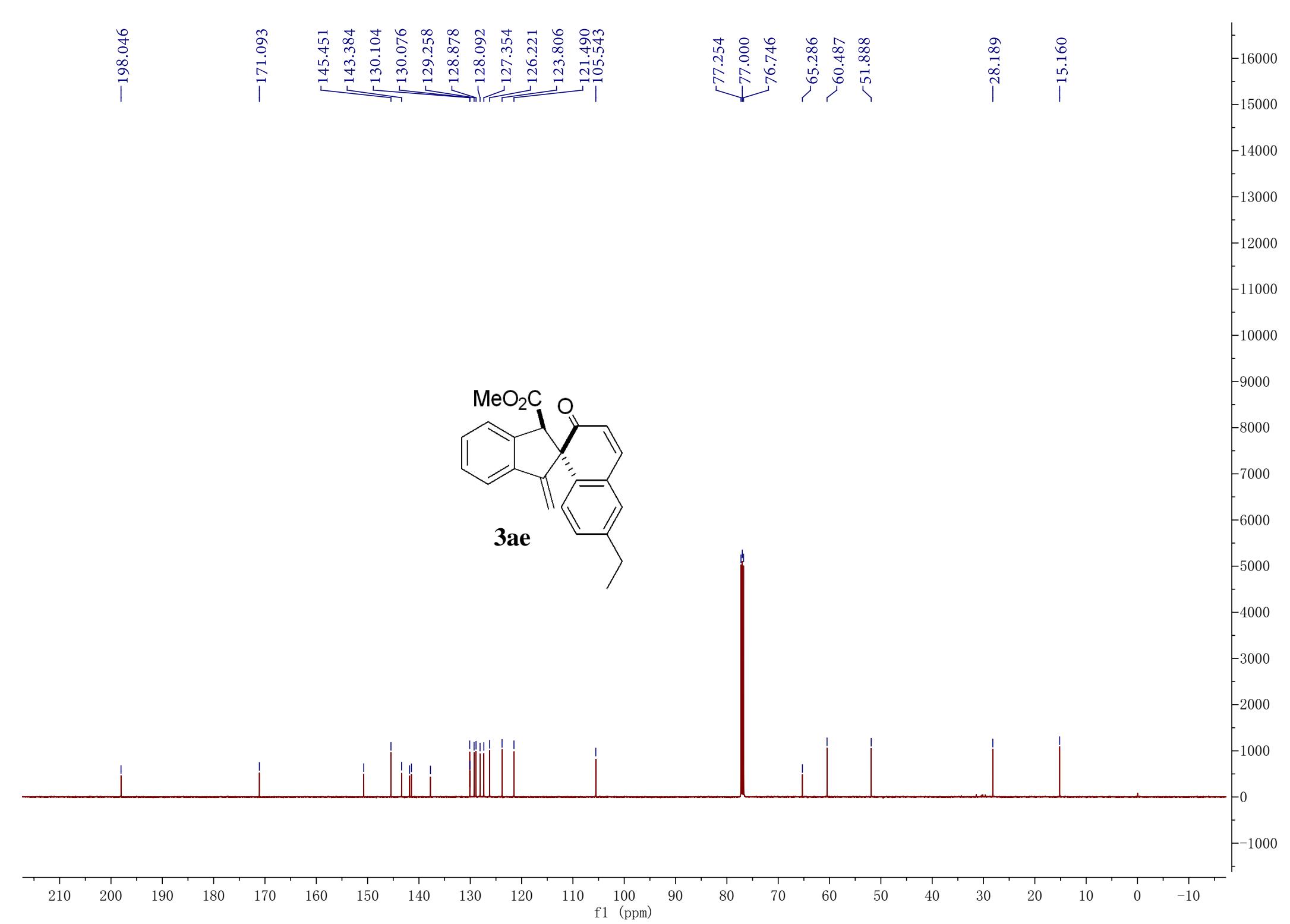
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

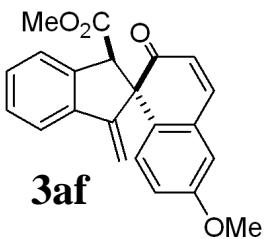
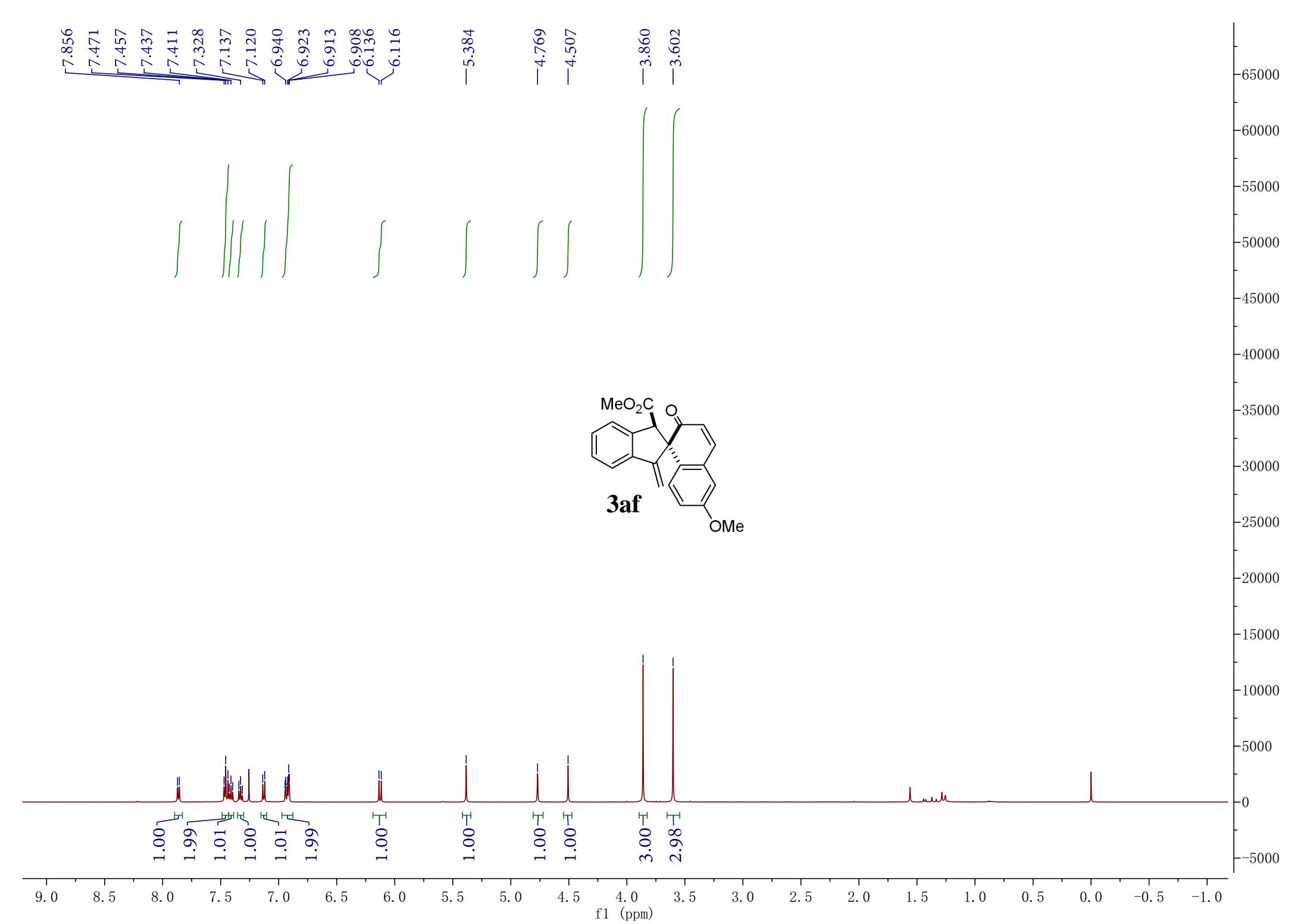
f1 (ppm)







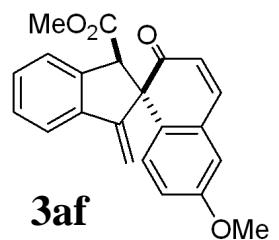




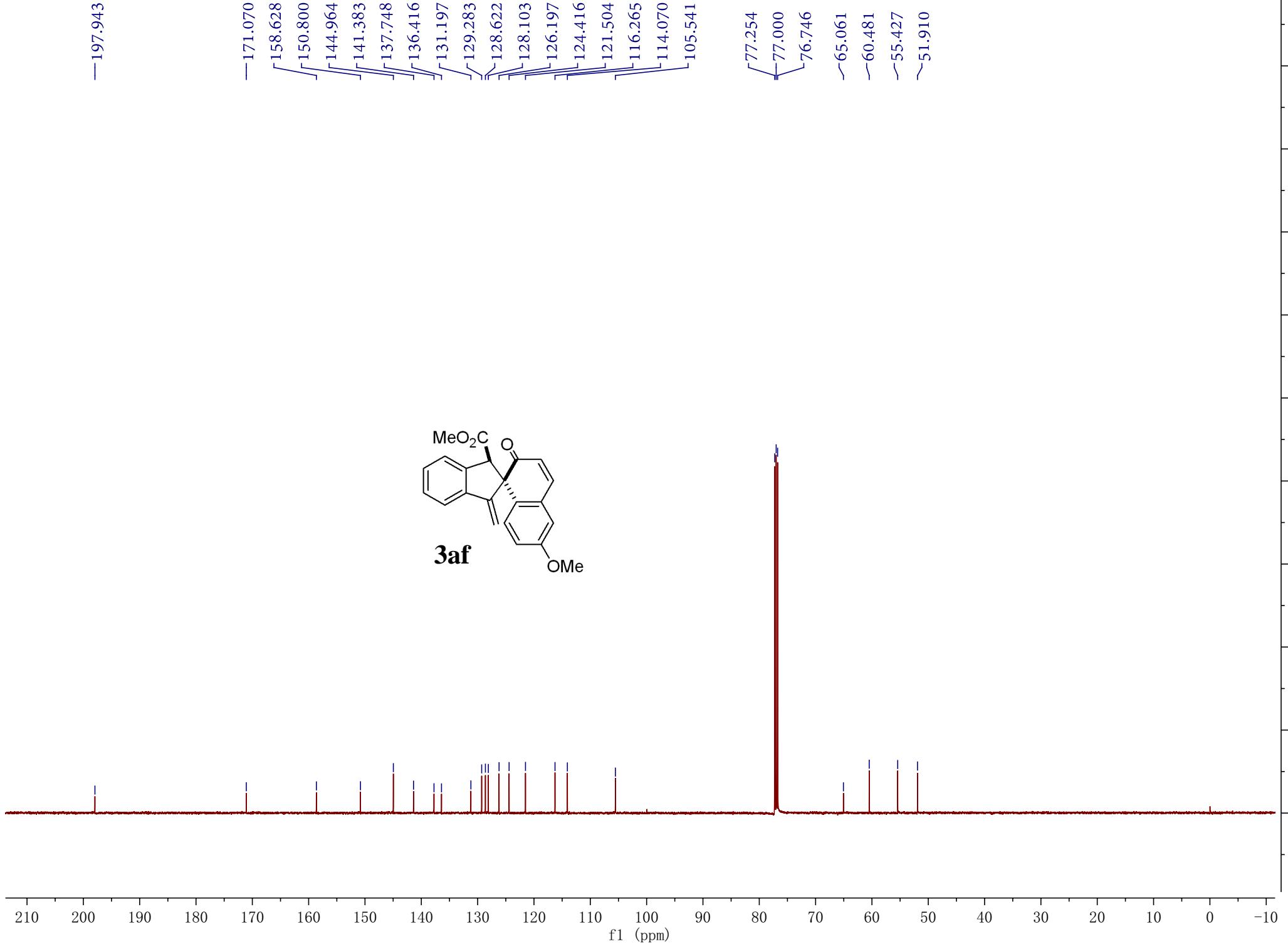
—197.943

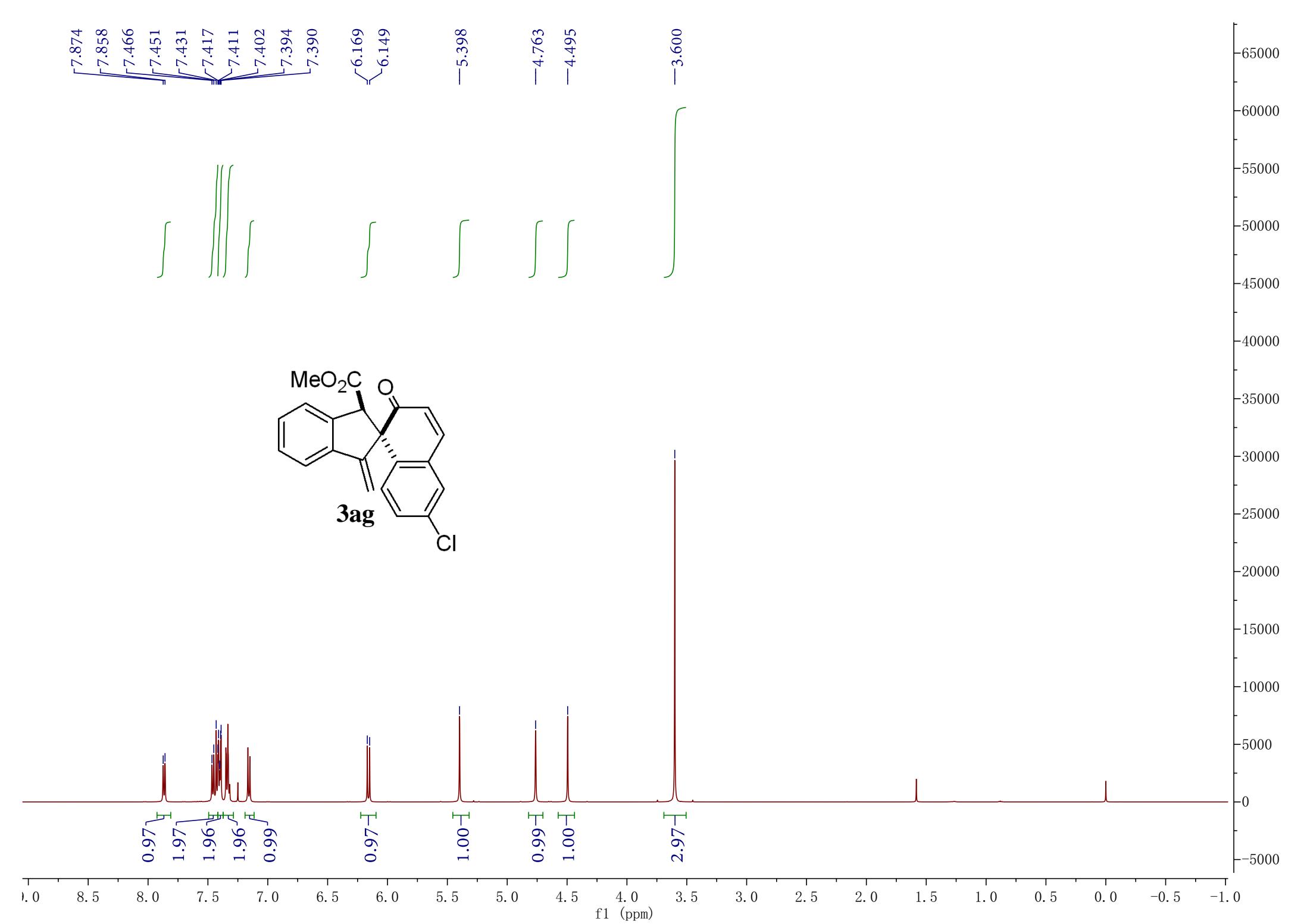
—171.070
—158.628
—150.800
—144.964
—141.383
—137.748
—136.416
—131.197
—129.283
—128.622
—128.103
—126.197
—124.416
—121.504
—116.265
—114.070
—105.541

9000
8000
7000
6000
5000
4000
3000
2000
1000
0



3af



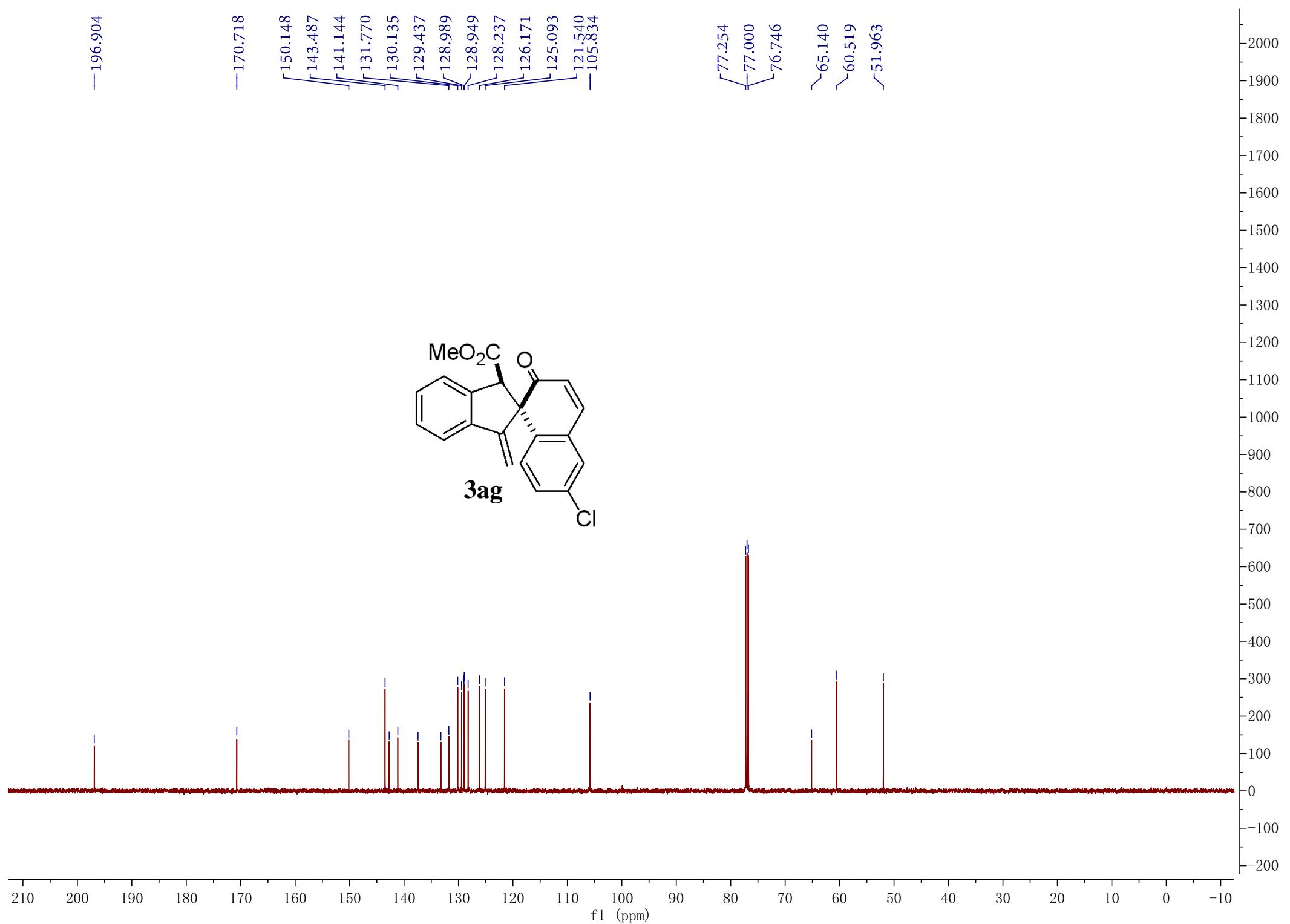
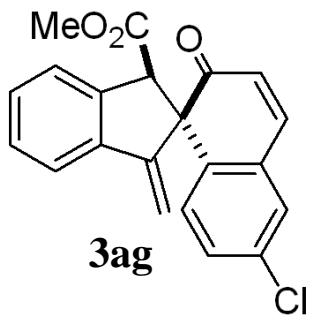


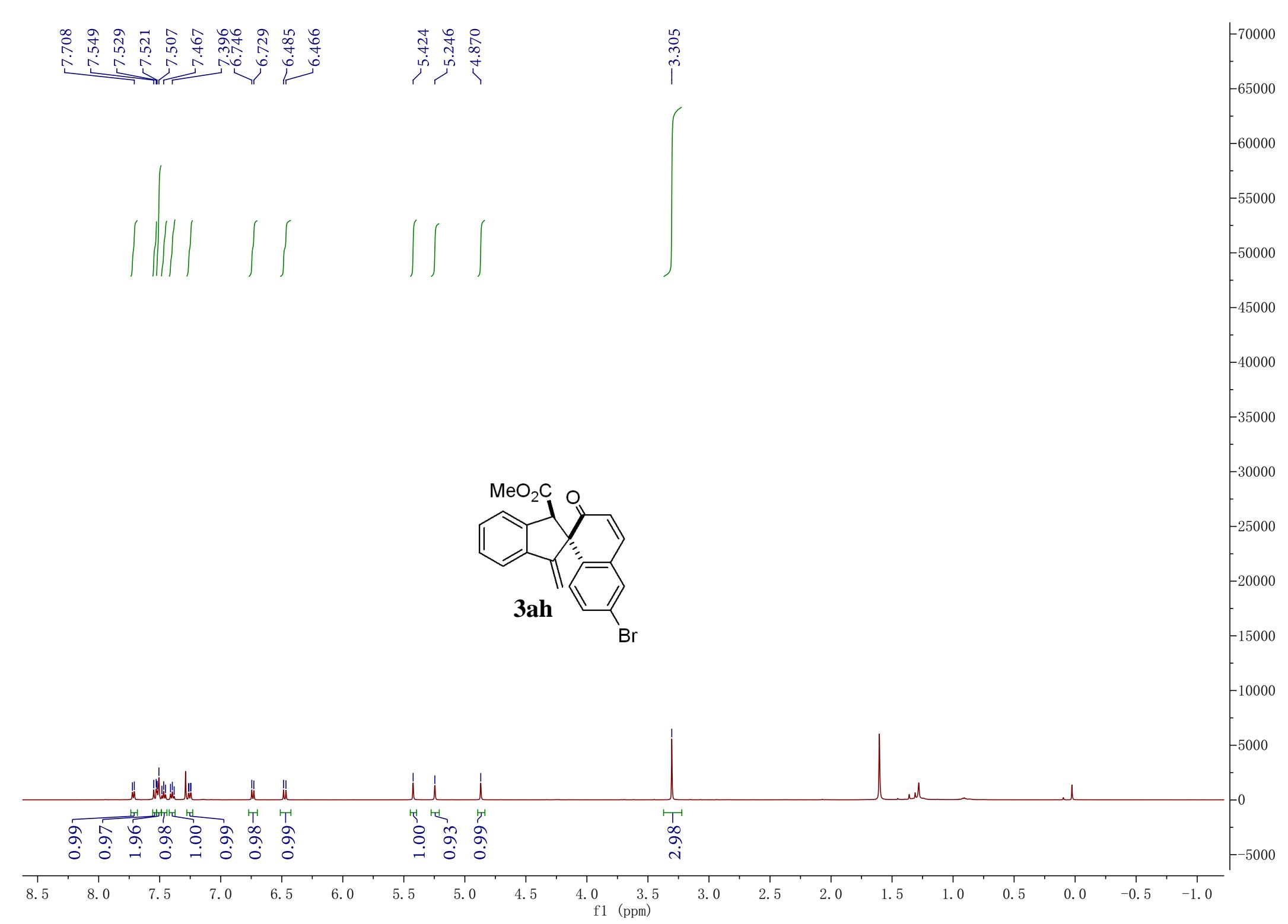
—196.904

—170.718

150.148
143.487
141.144
131.770
130.135
129.437
128.989
128.949
128.237
126.171
125.093
121.540
105.834

77.254
77.000
76.746
65.140
60.519
51.963





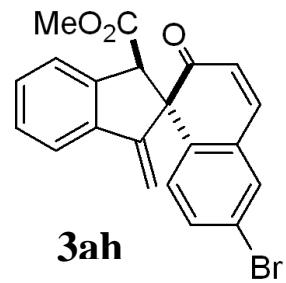
—199.751

—170.364

144.887
140.397
132.774
132.162
130.013
129.739
128.437
127.067
126.813
126.493
121.329
—104.846

77.254
77.000
76.746

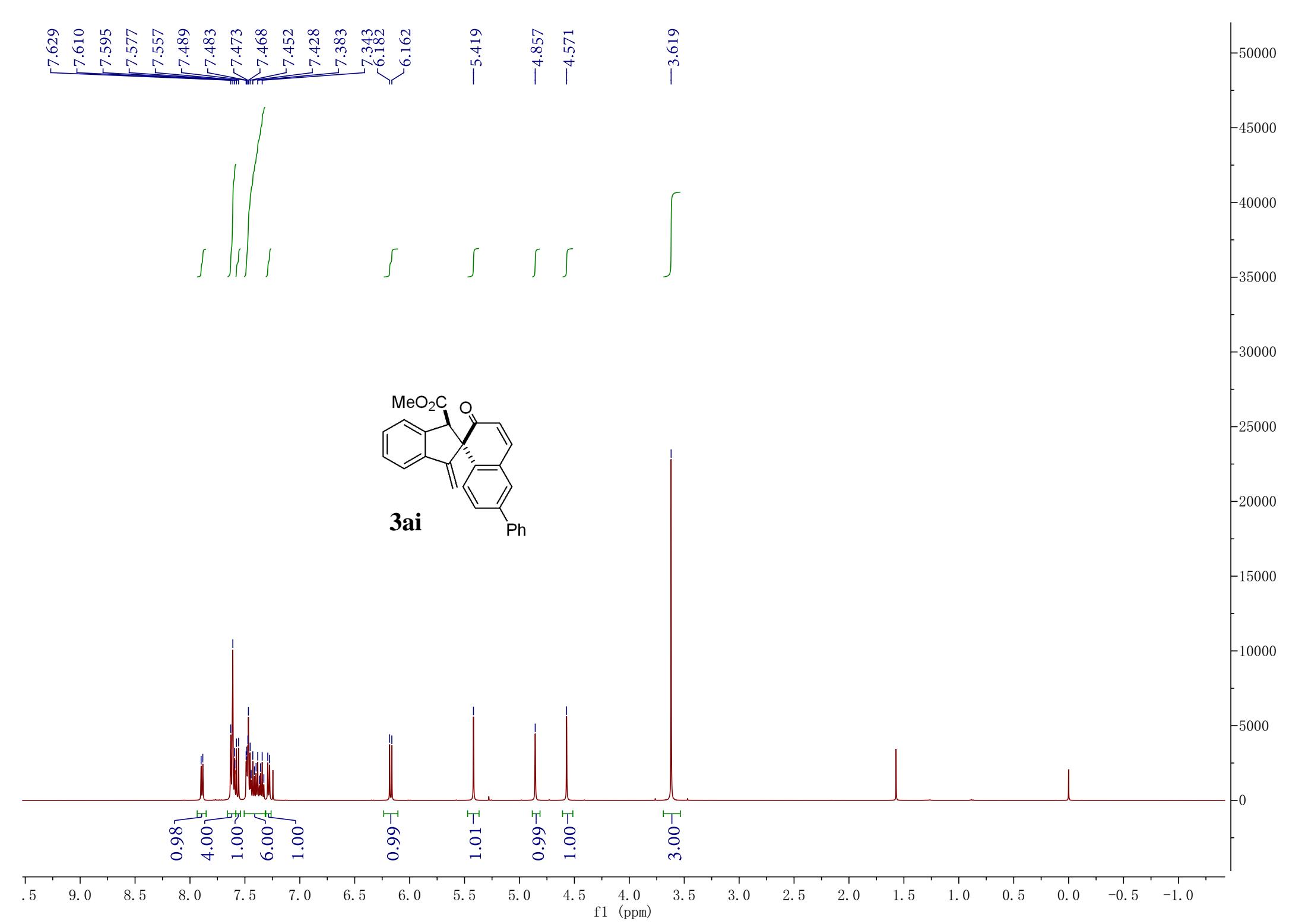
~64.264
~58.972
~51.612

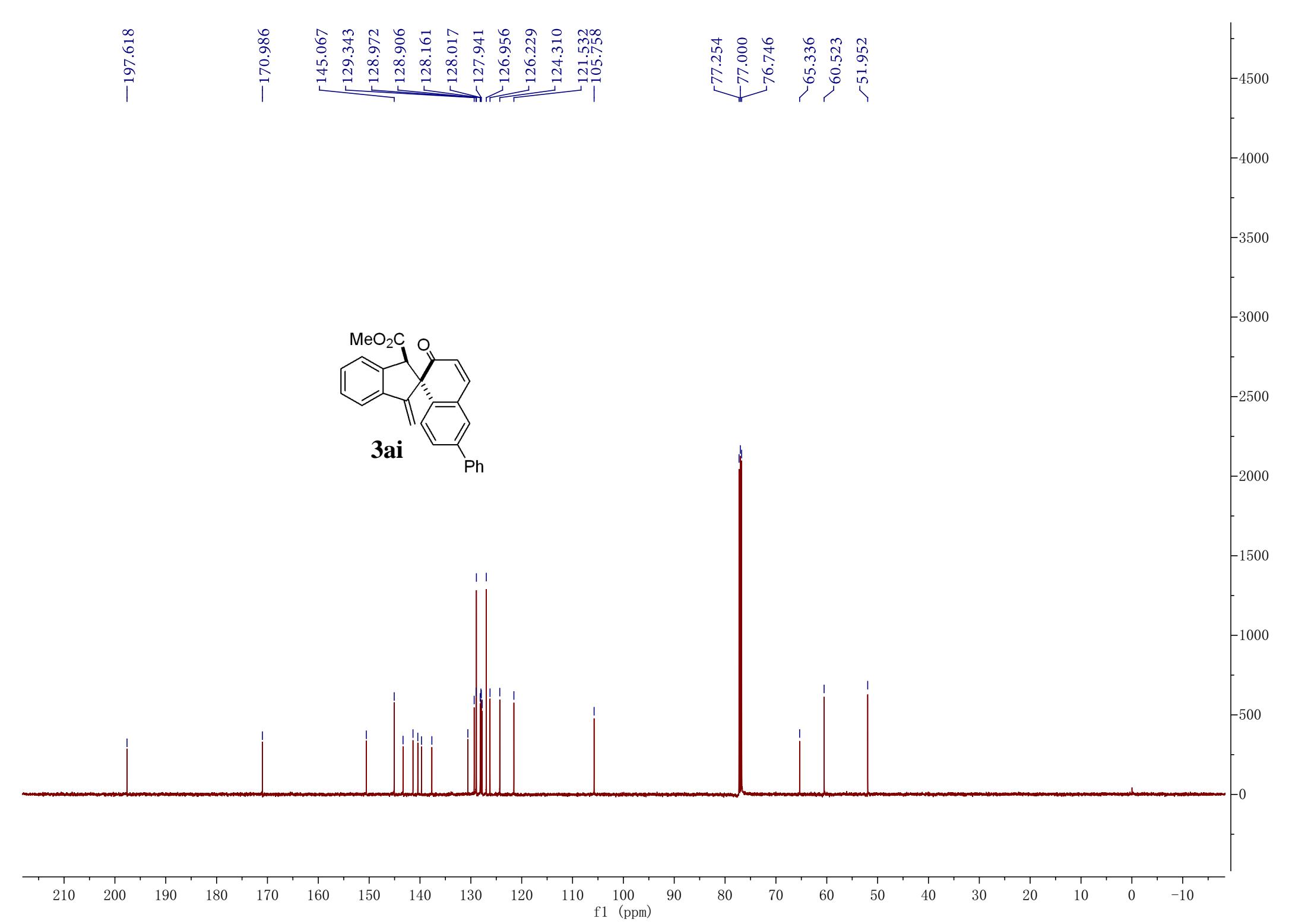


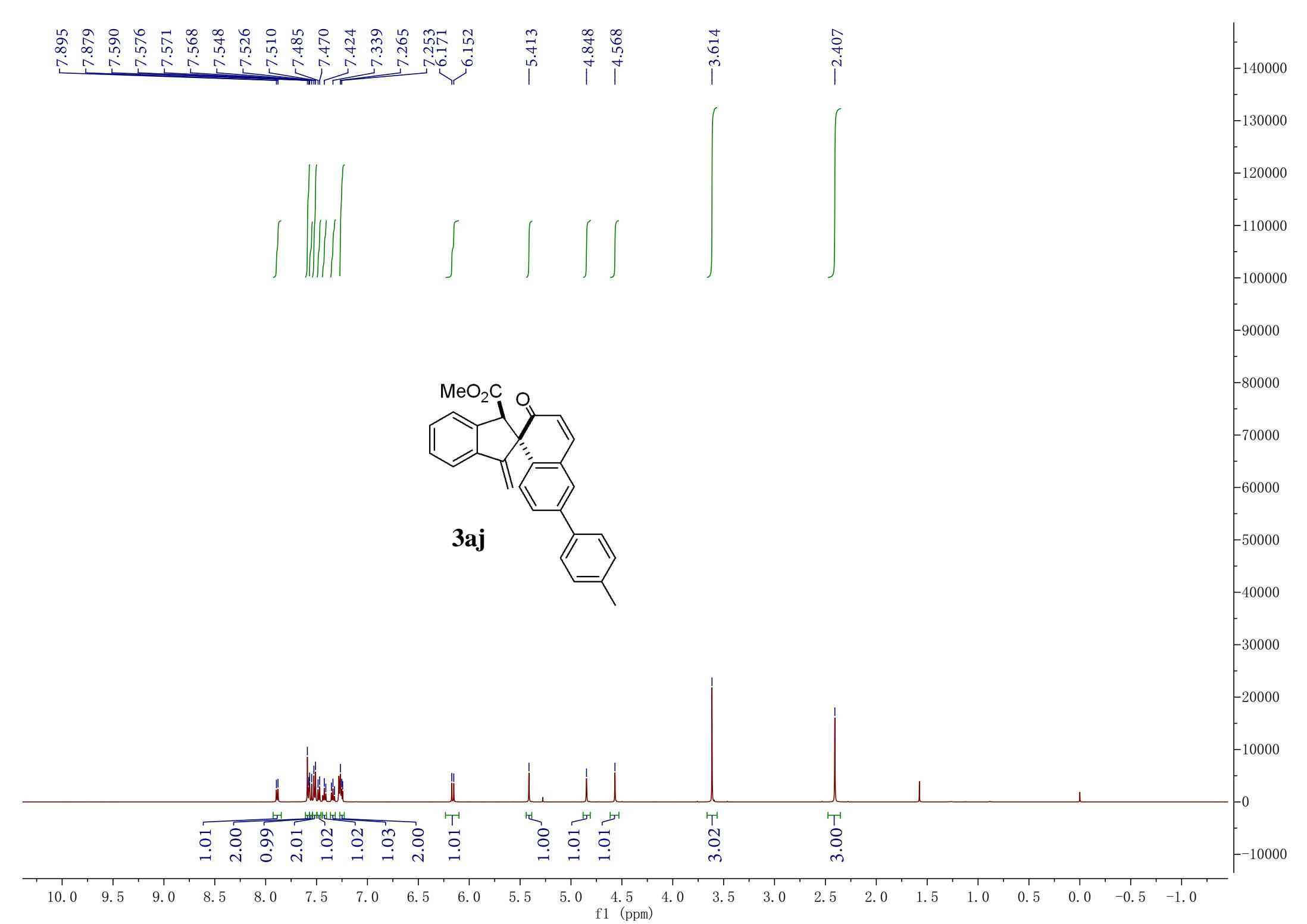
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500







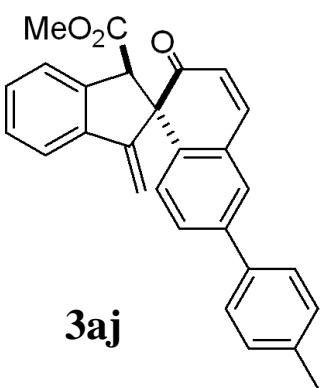
—197.695

—171.007

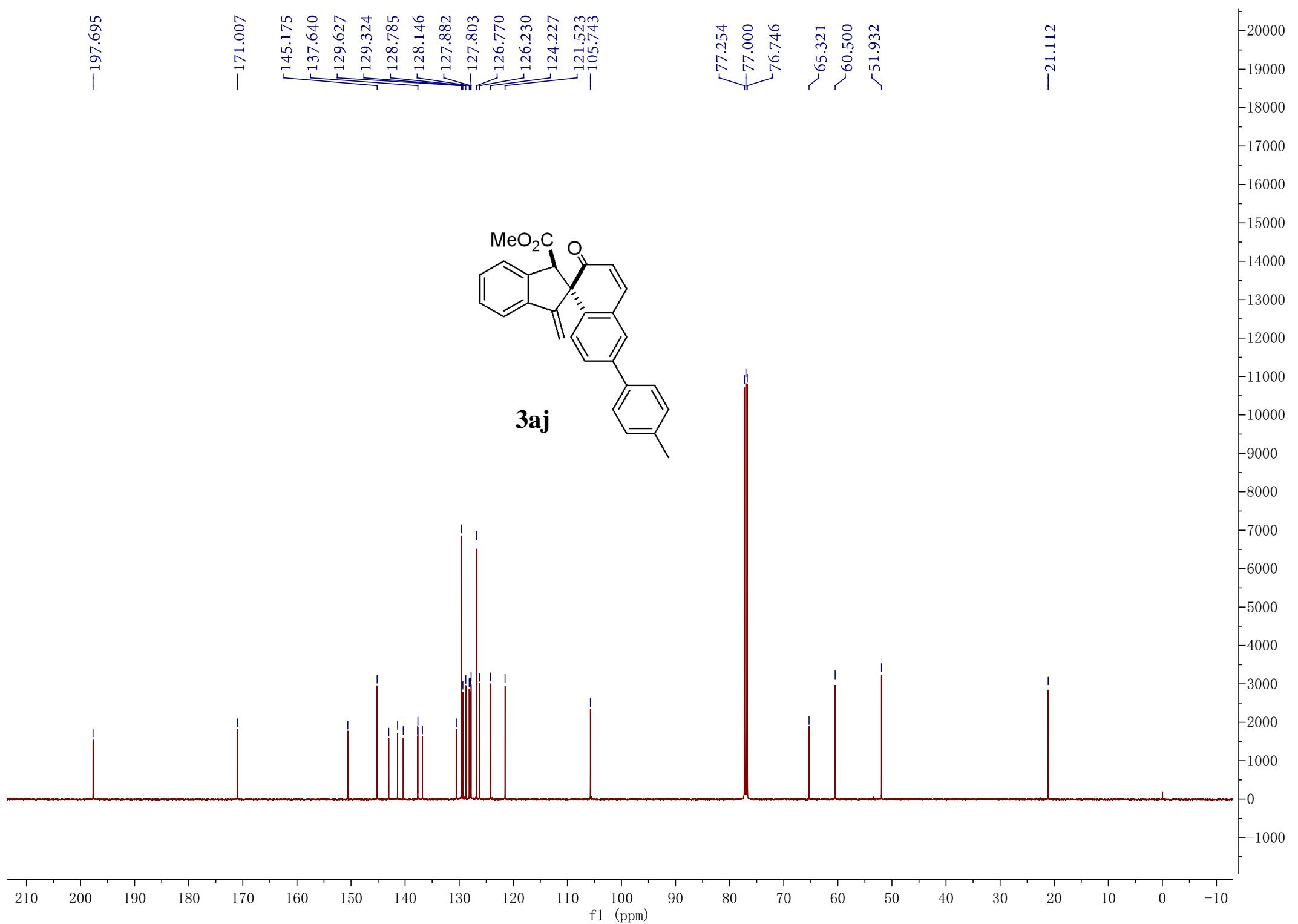
145.175
137.640
129.627
129.324
128.785
128.146
127.882
127.803
126.770
126.230
124.227
121.523
105.743

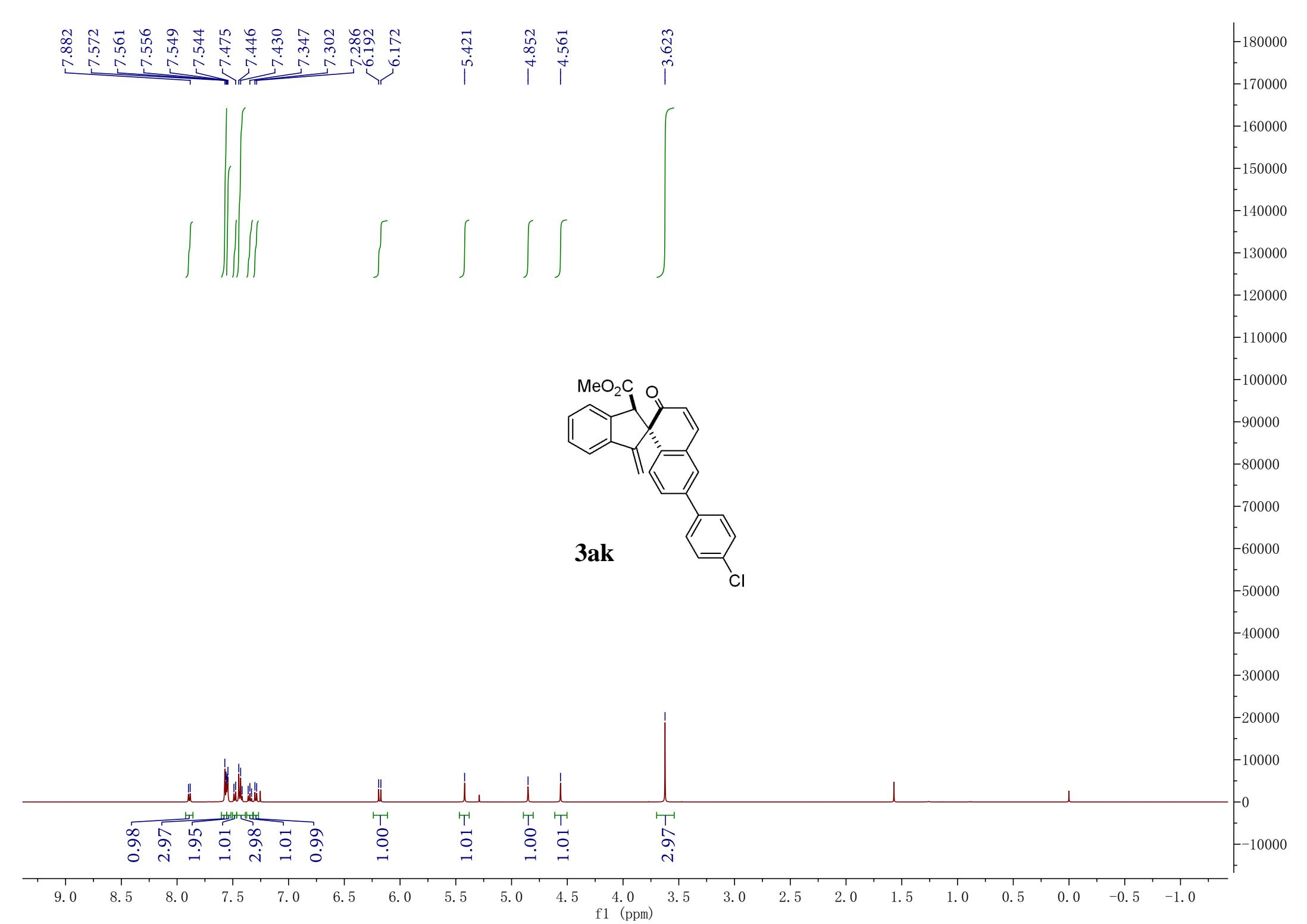
77.254
77.000
76.746
~65.321
~60.500
~51.932

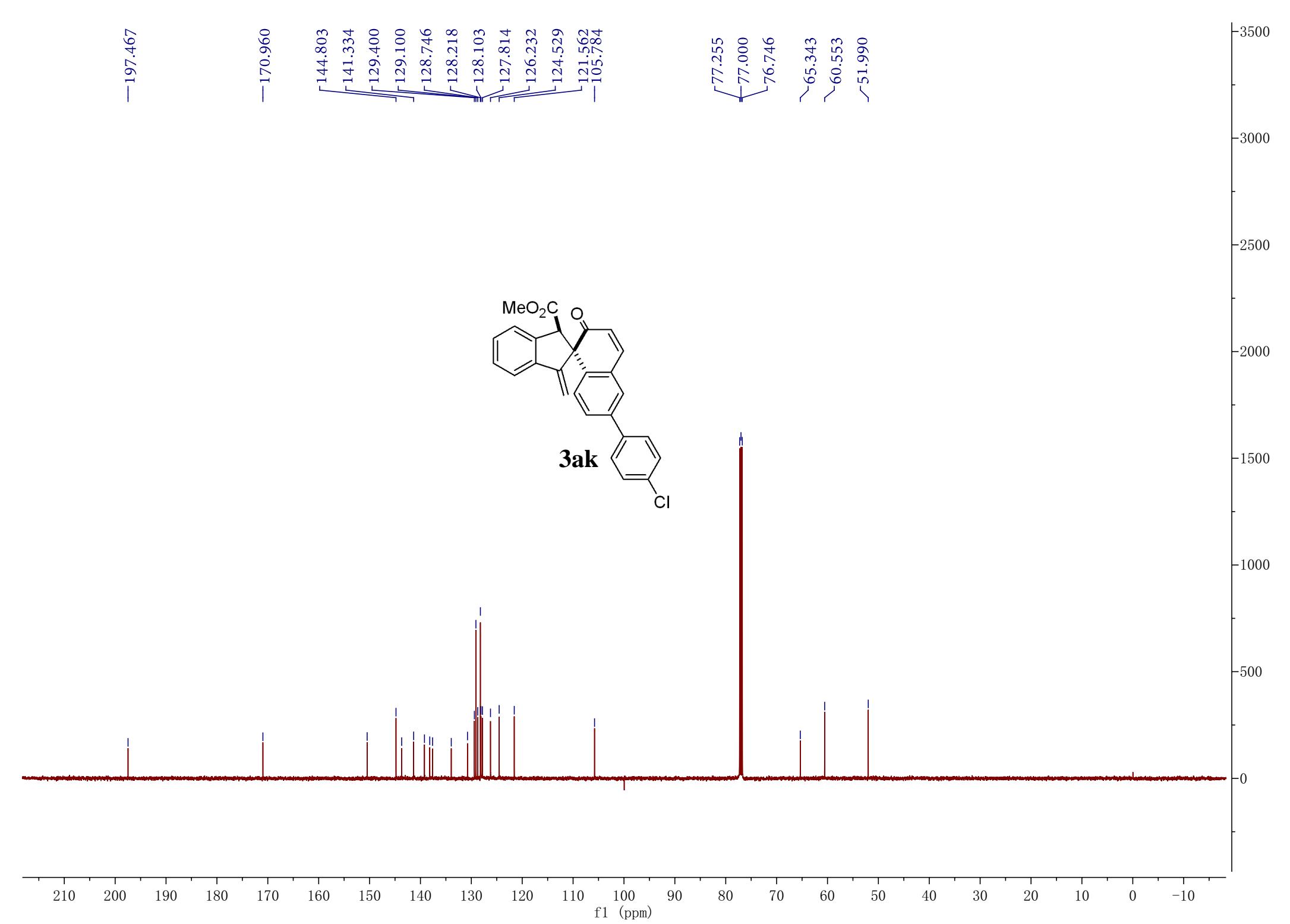
—21.112

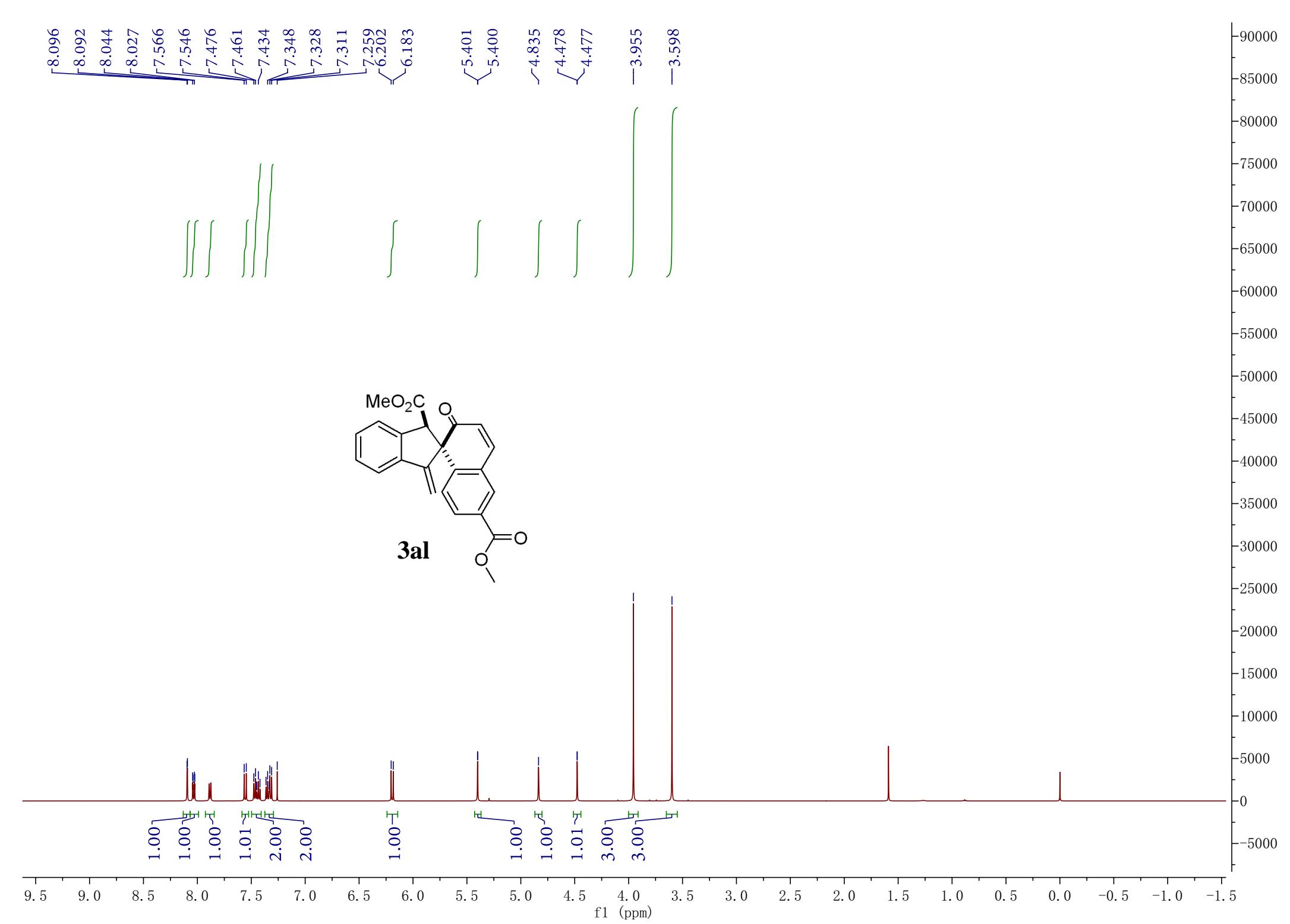


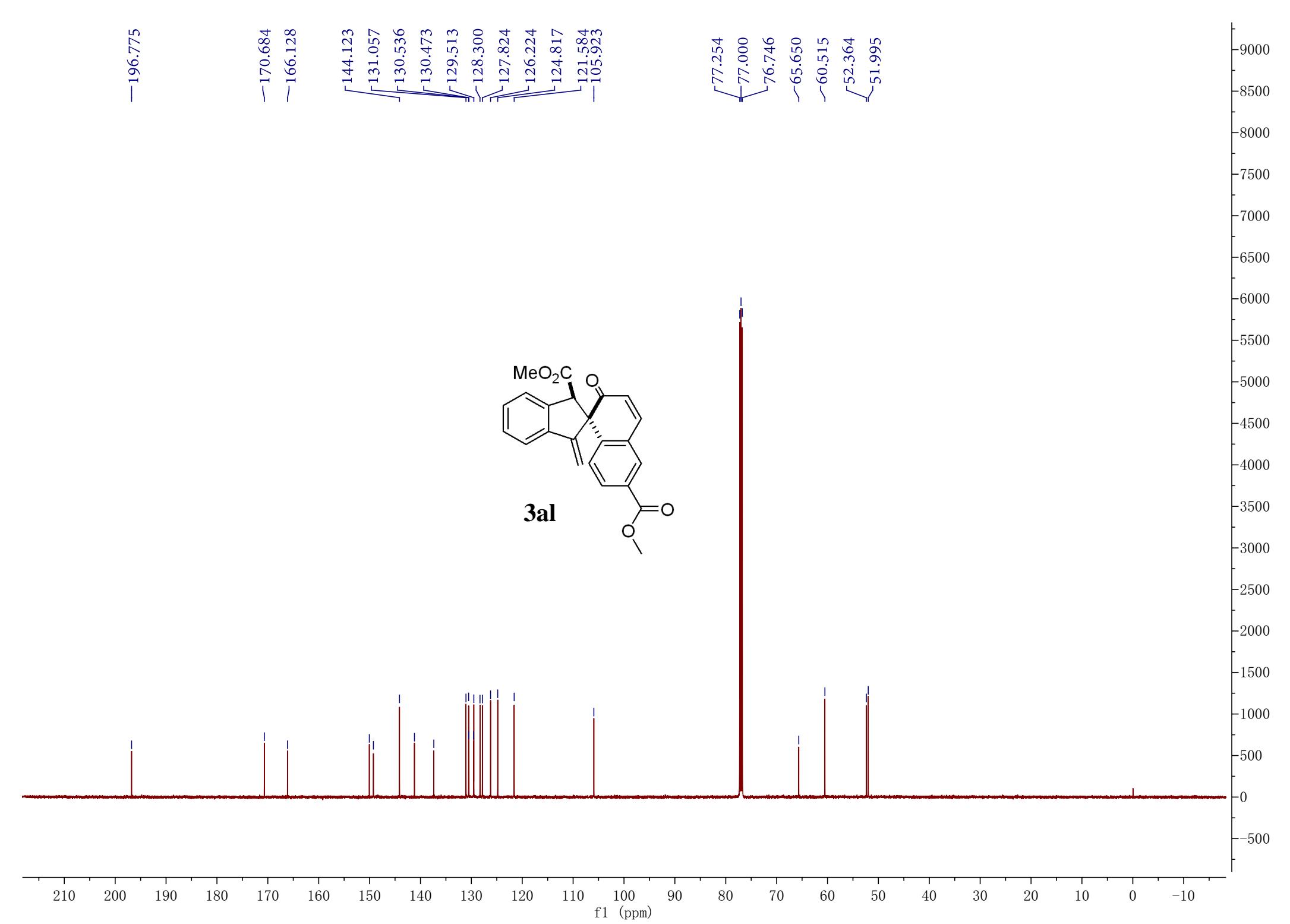
3aj

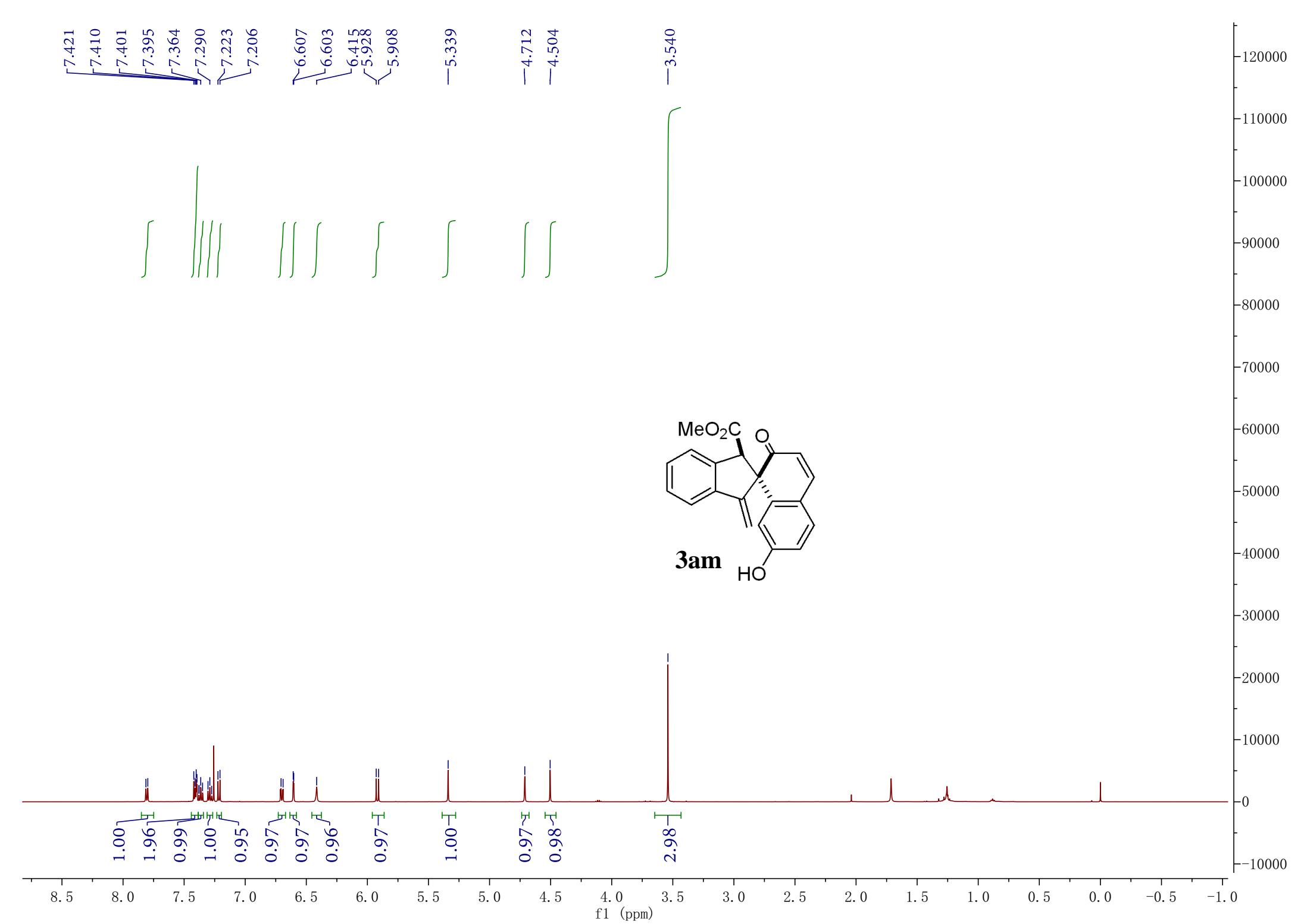








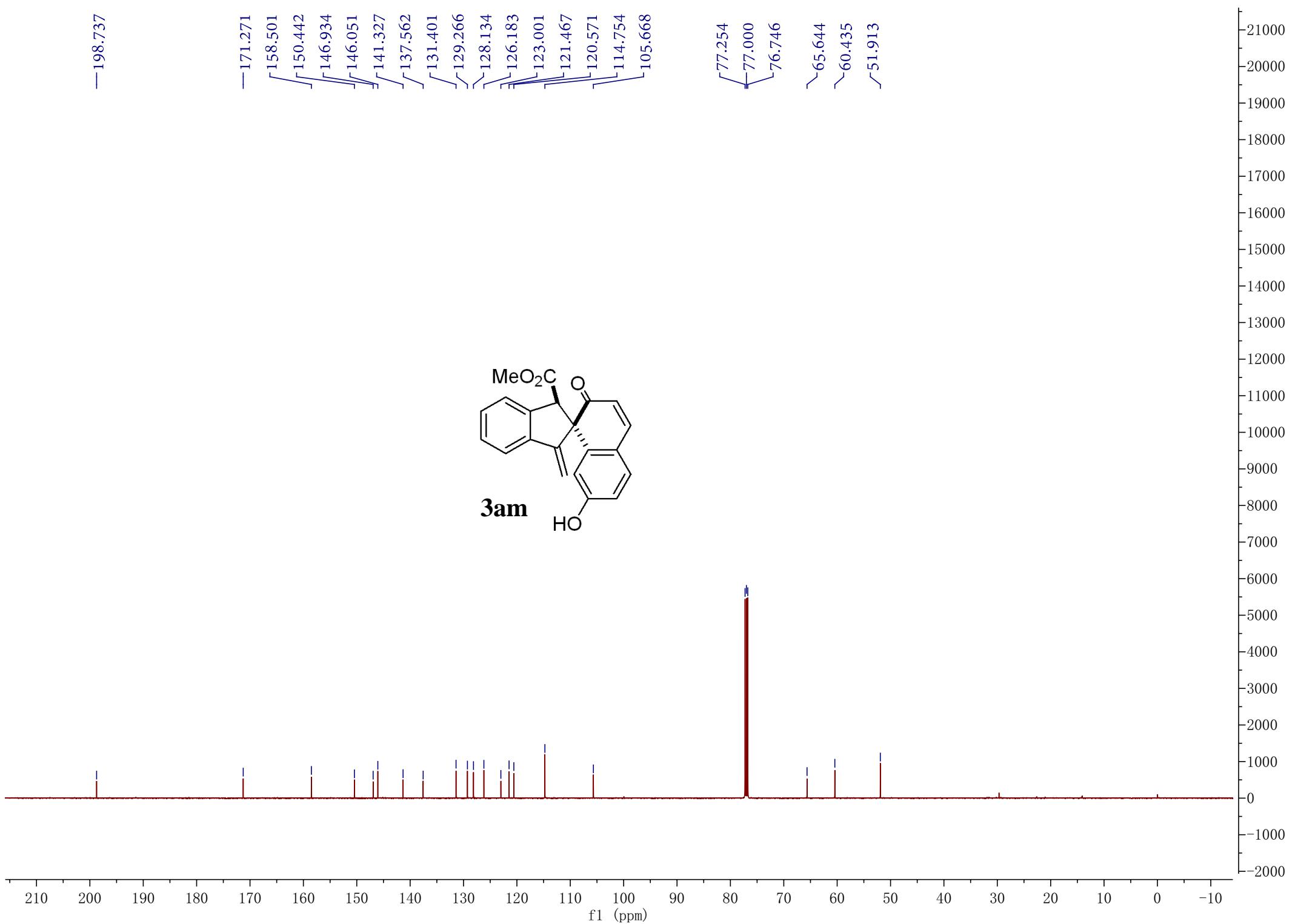
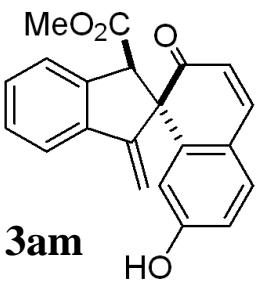


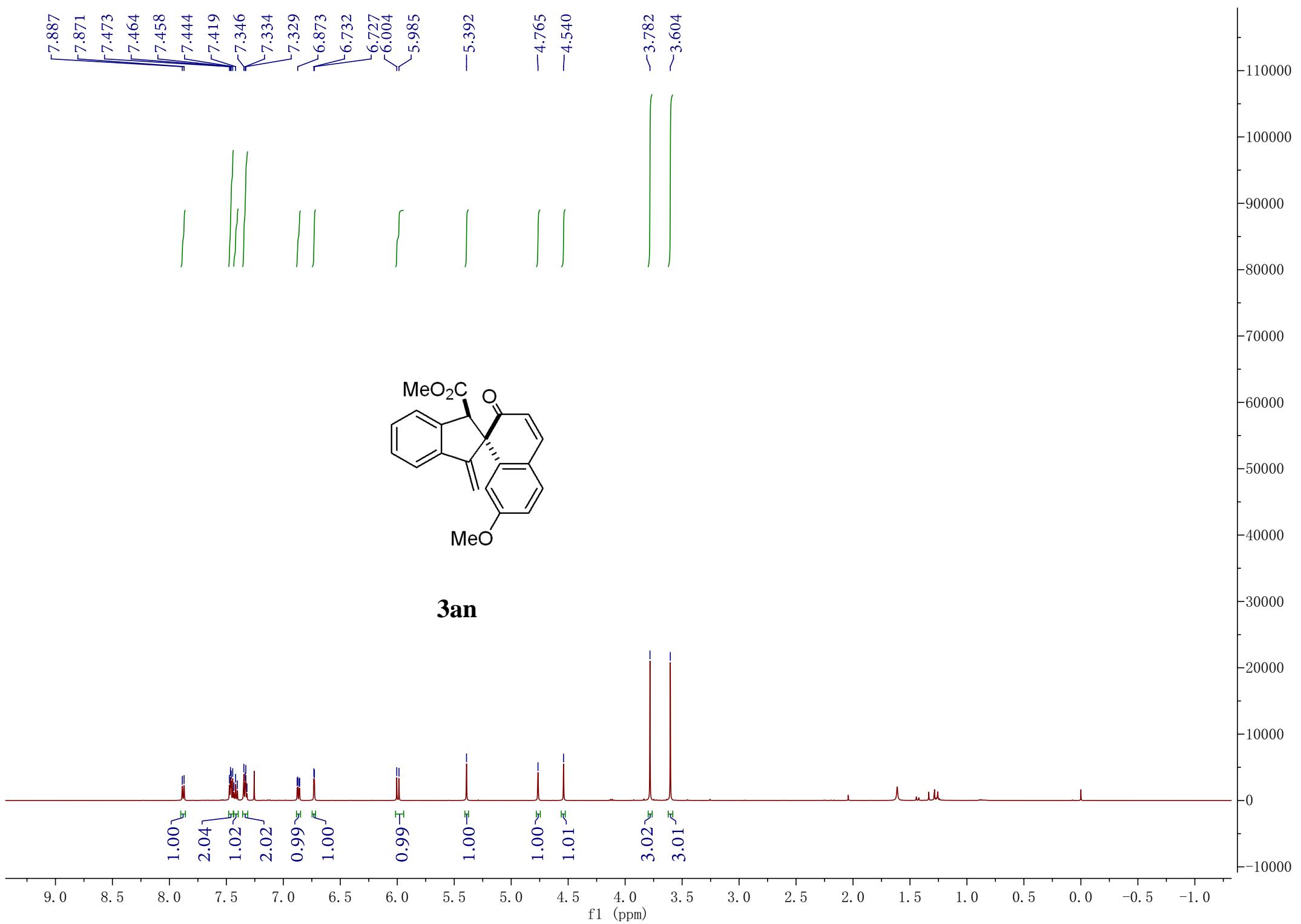


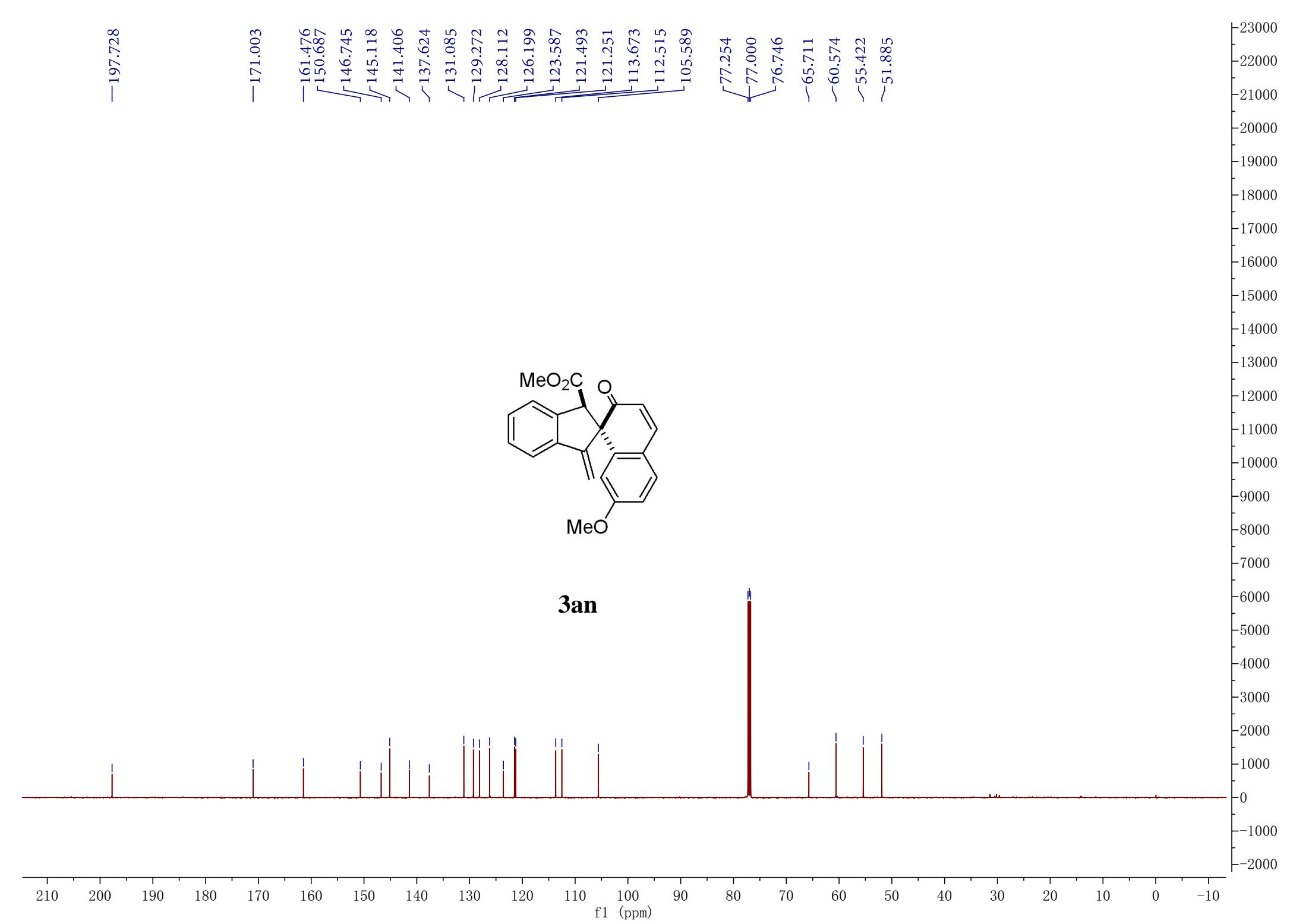
—198.737

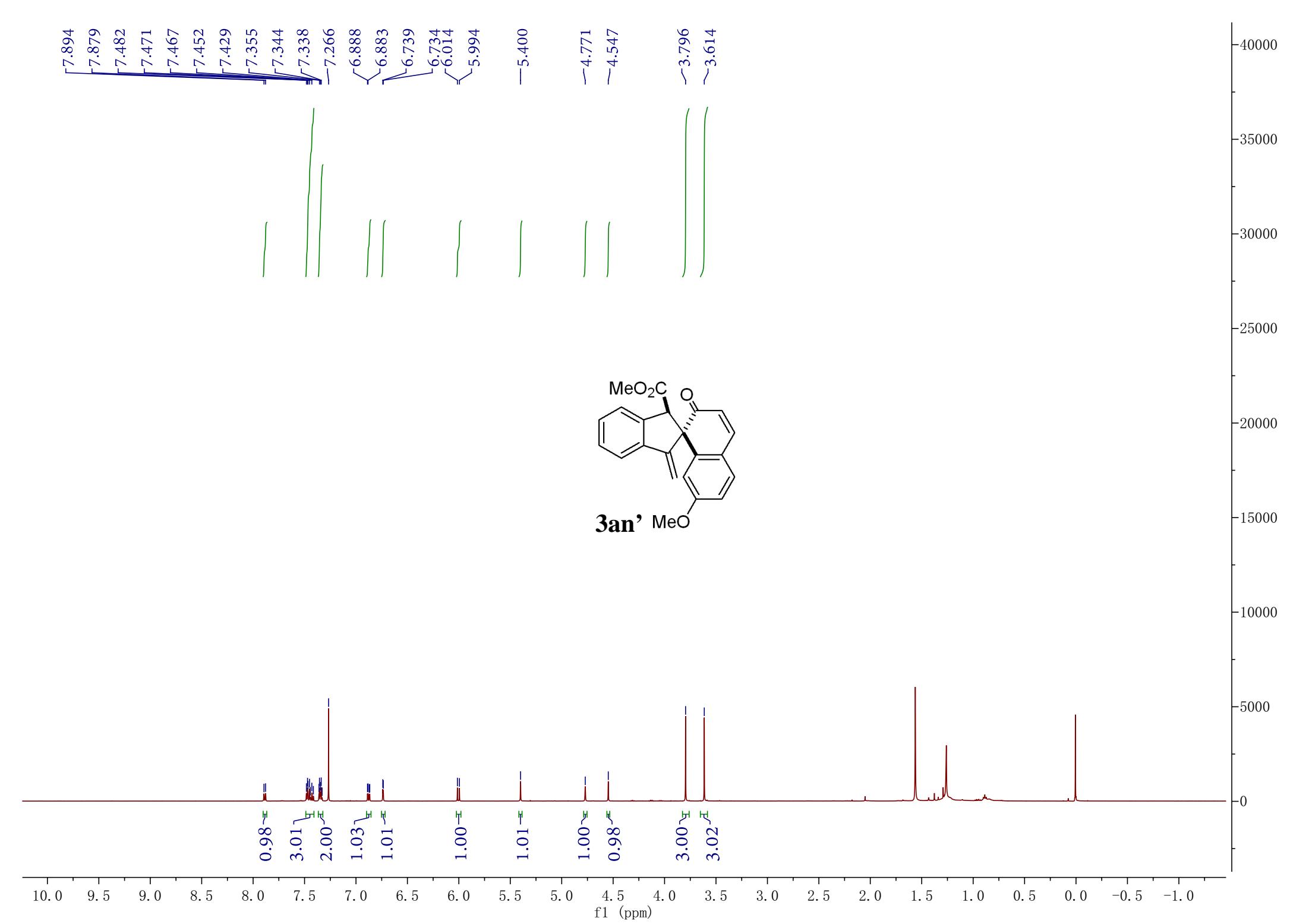
—171.271
—158.501
—150.442
—146.934
—146.051
—141.327
—137.562
—131.401
—129.266
—128.134
—126.183
—123.001
—121.467
—120.571
—114.754
—105.668

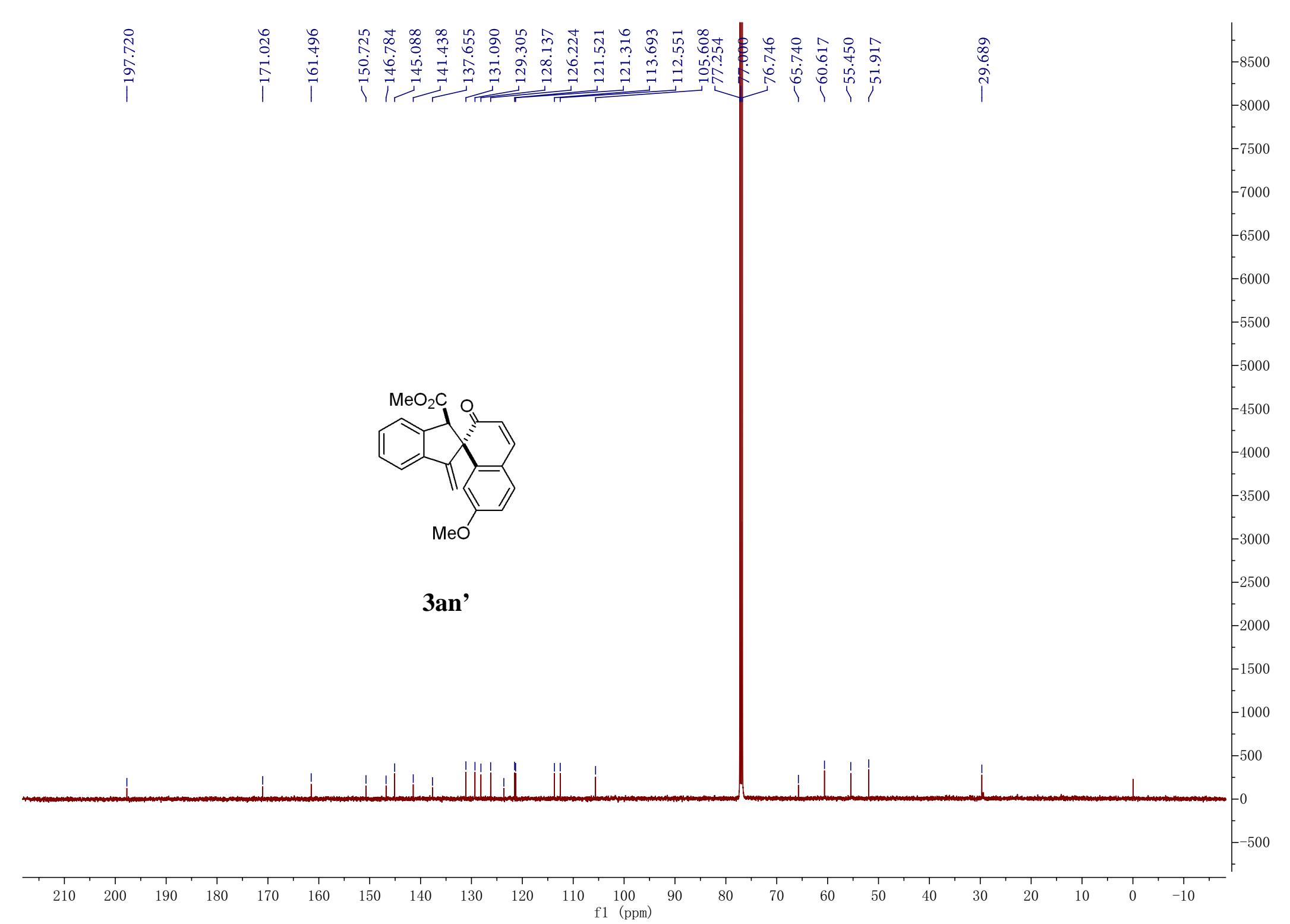
—77.254
—77.000
—76.746
—65.644
—60.435
—51.913

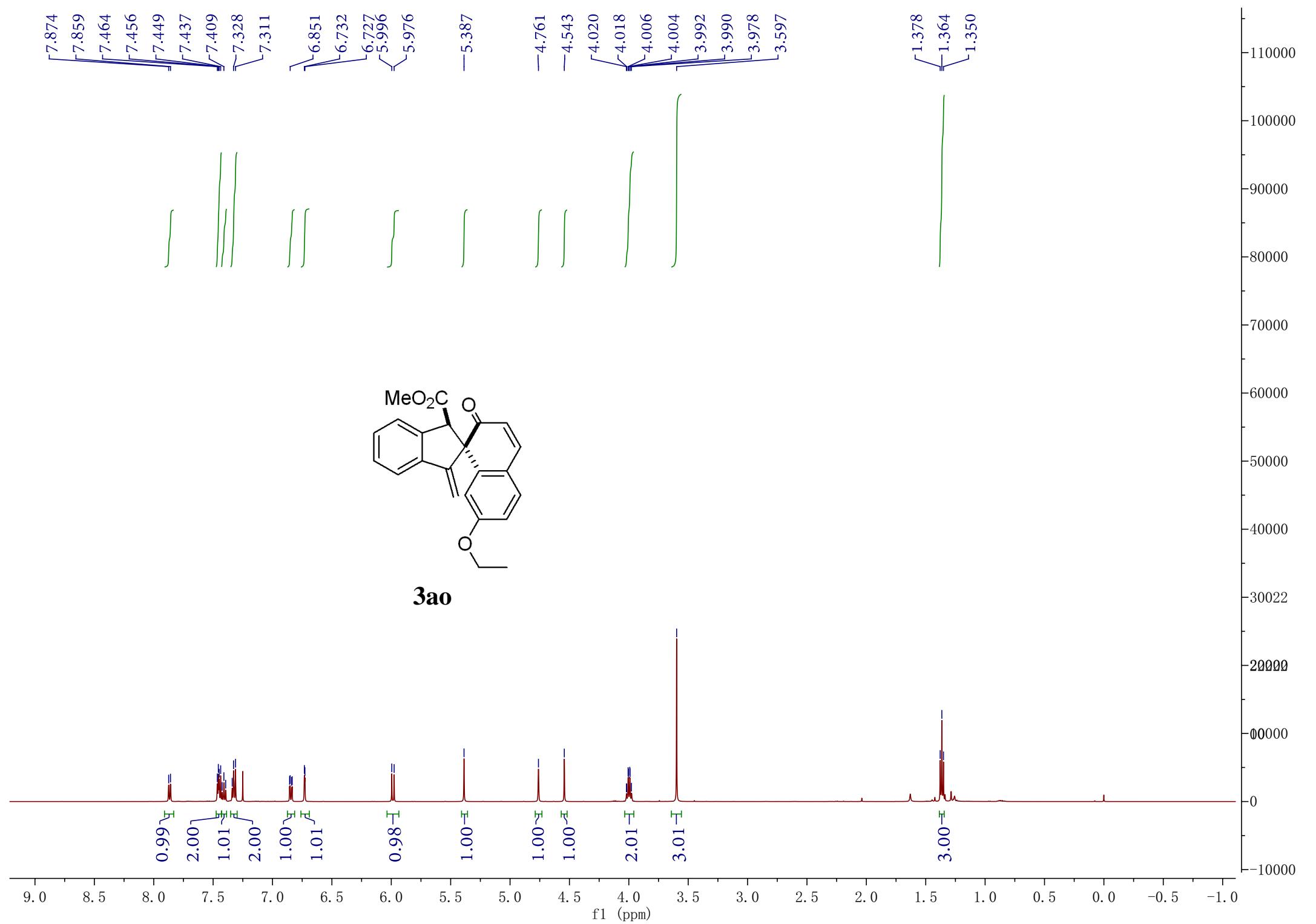


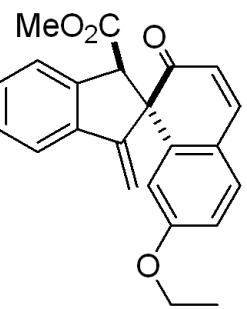
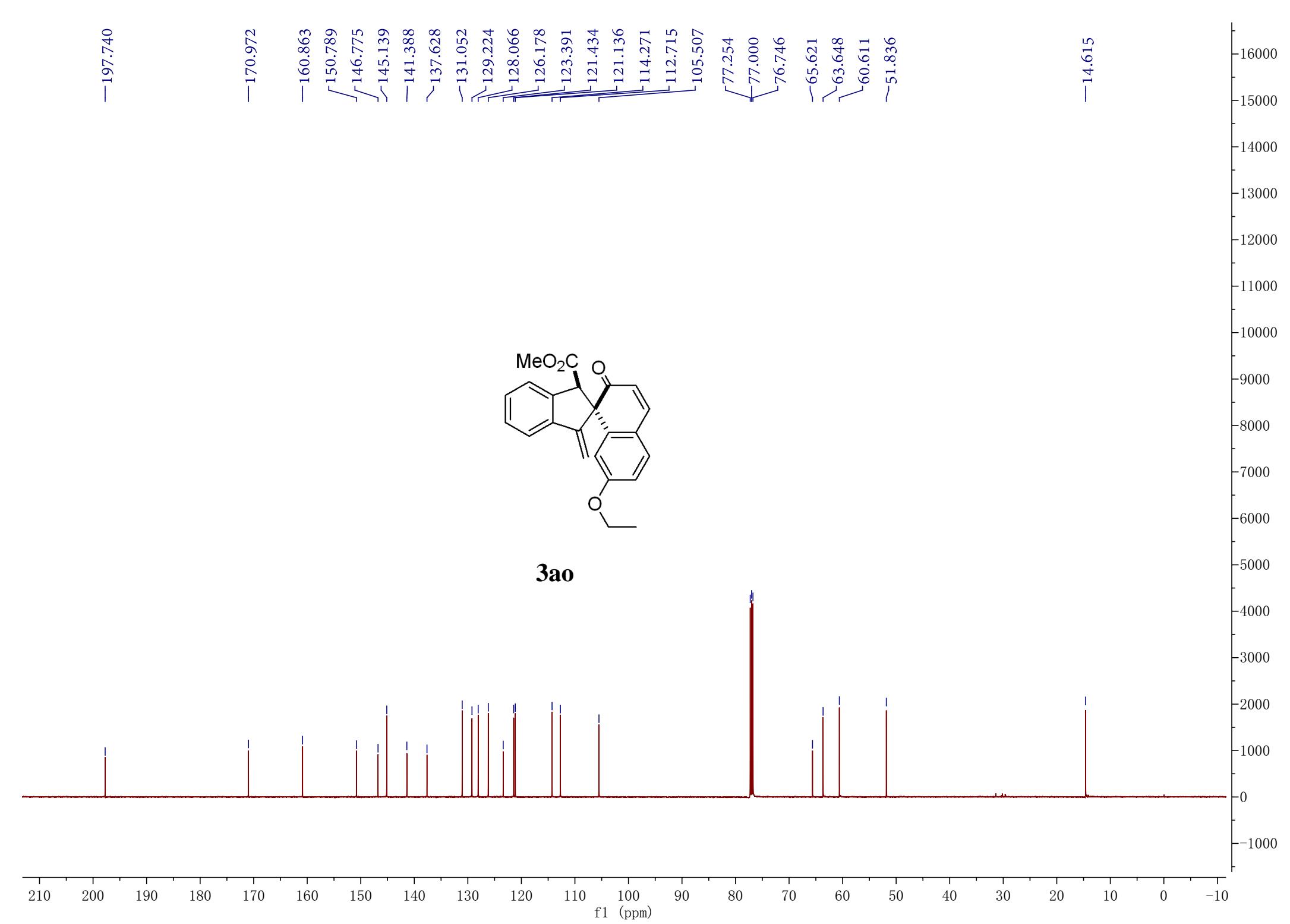




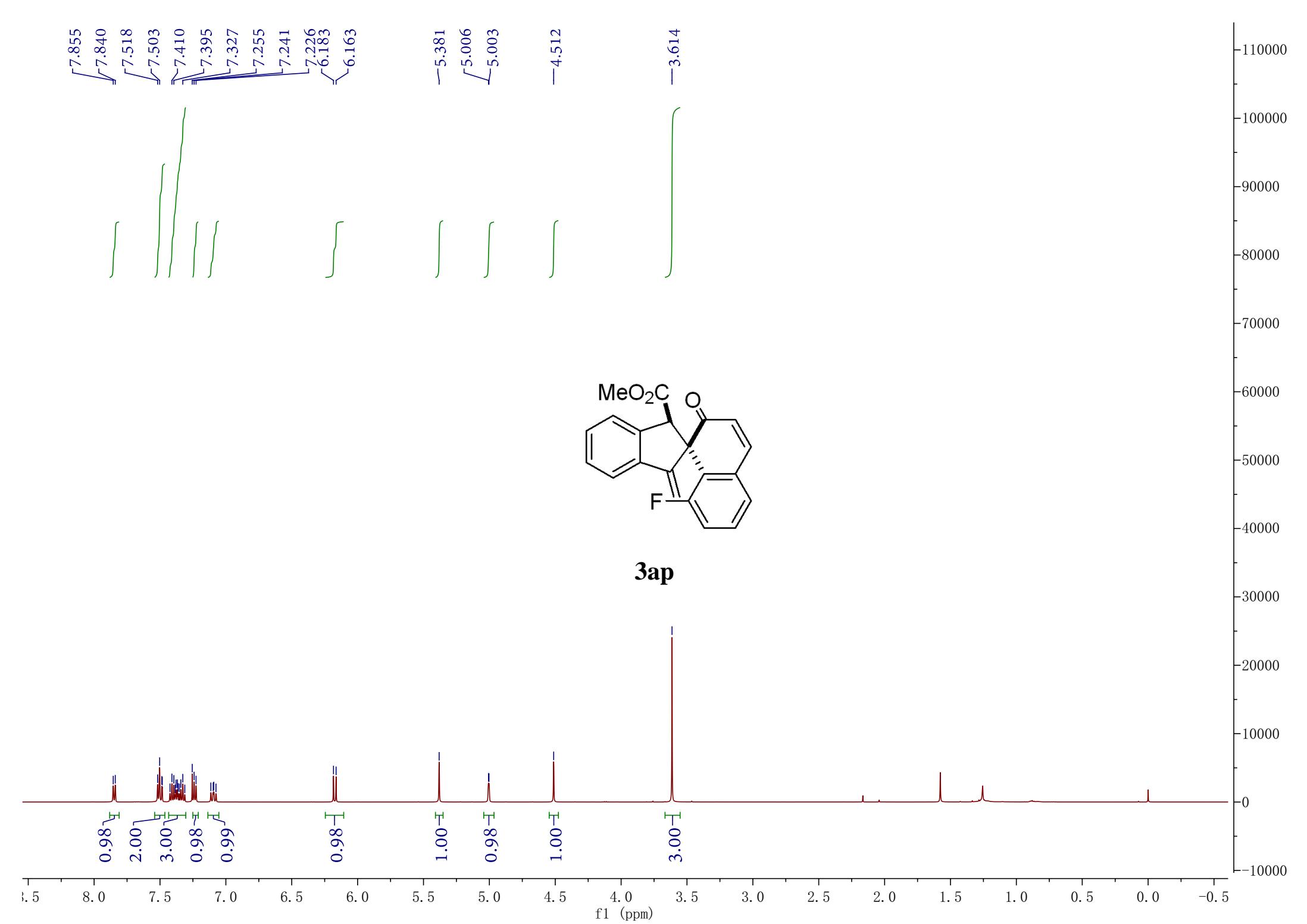








3ao

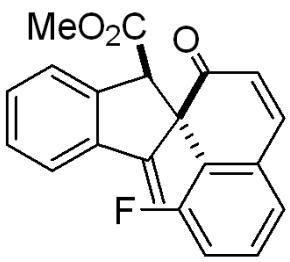


— 196.803

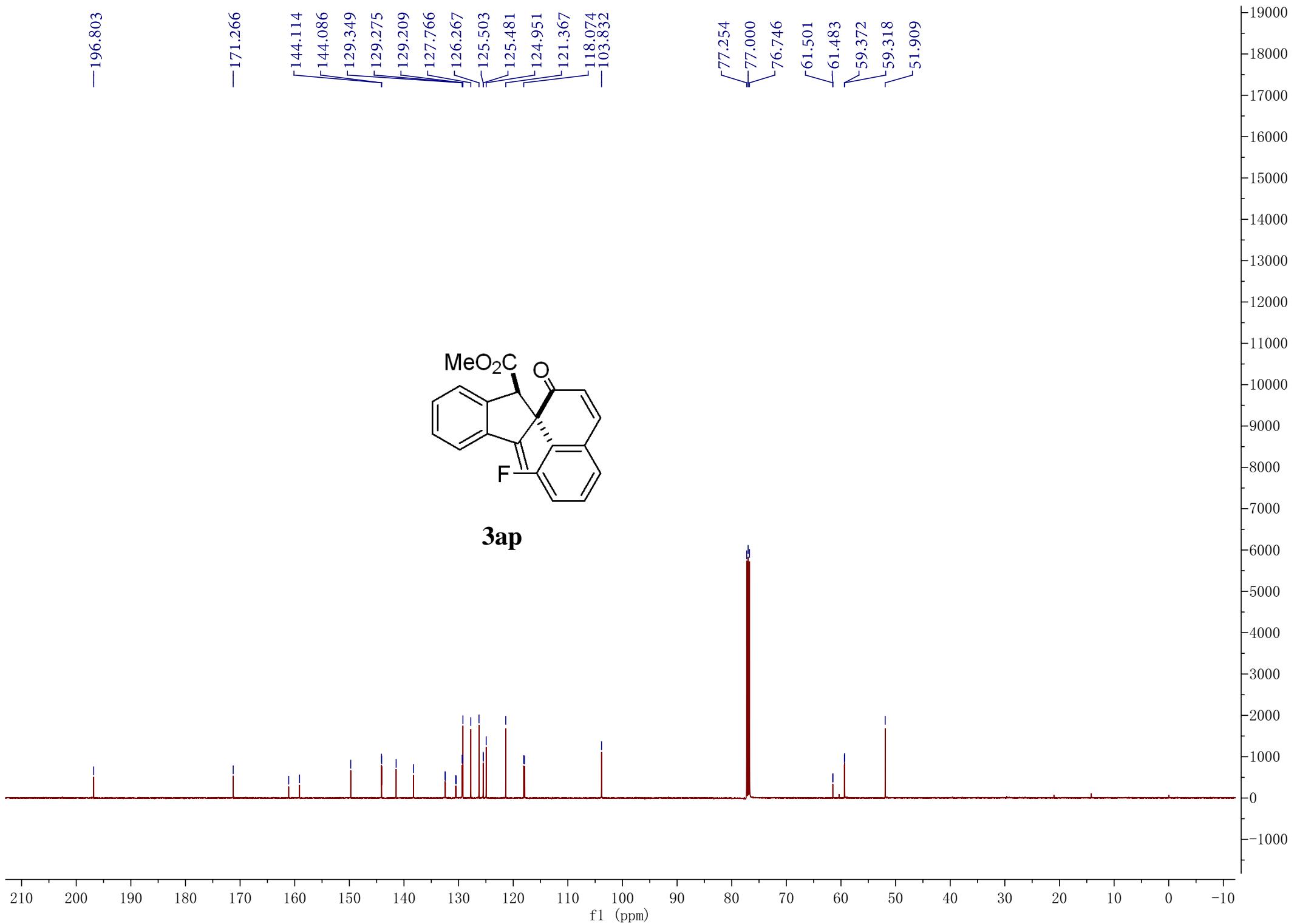
— 171.266

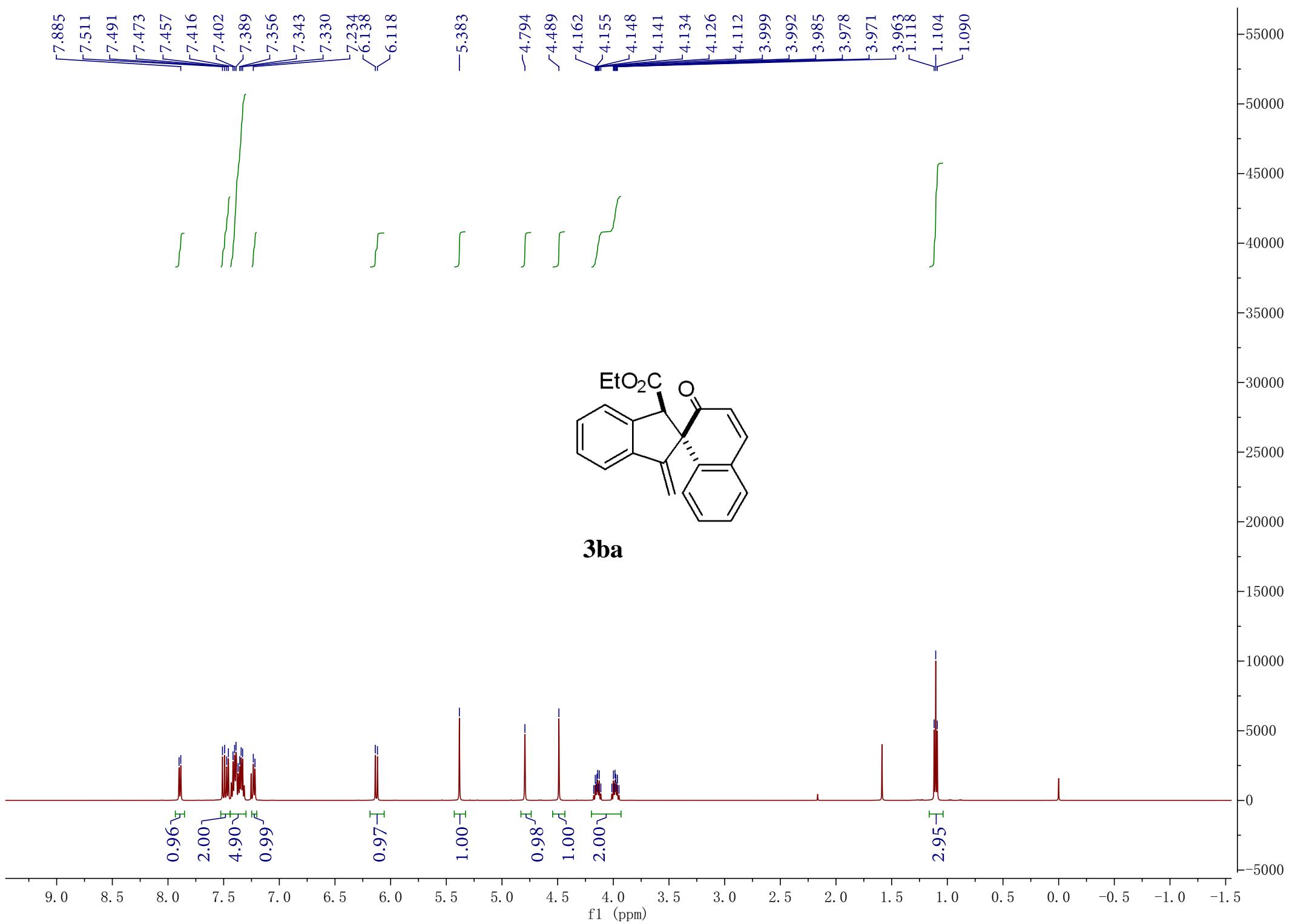
144.114
144.086
129.349
129.275
129.209
127.766
126.267
125.503
125.481
124.951
121.367
118.074
— 103.832

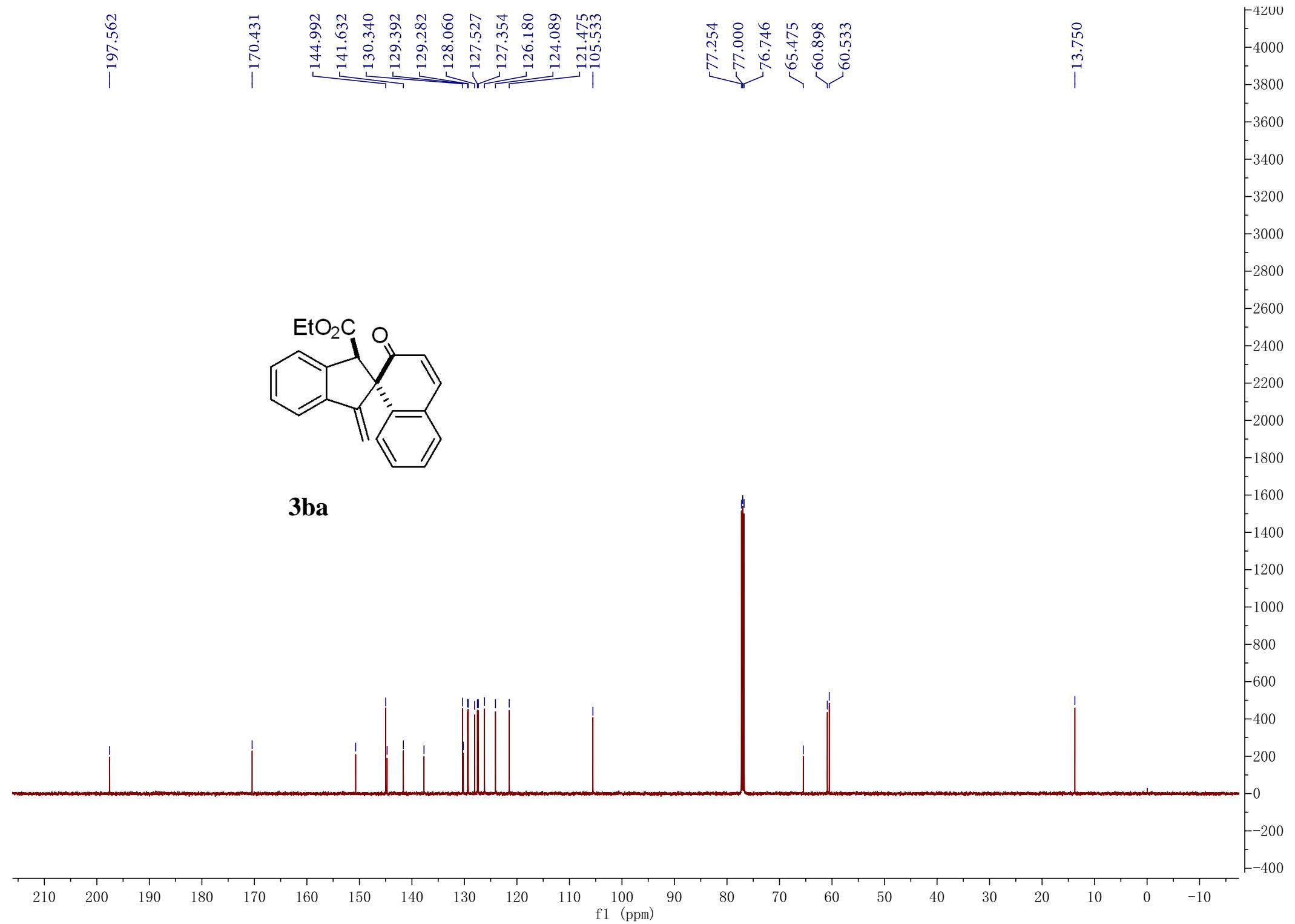
77.254
77.000
76.746
61.501
61.483
59.372
59.318
51.909



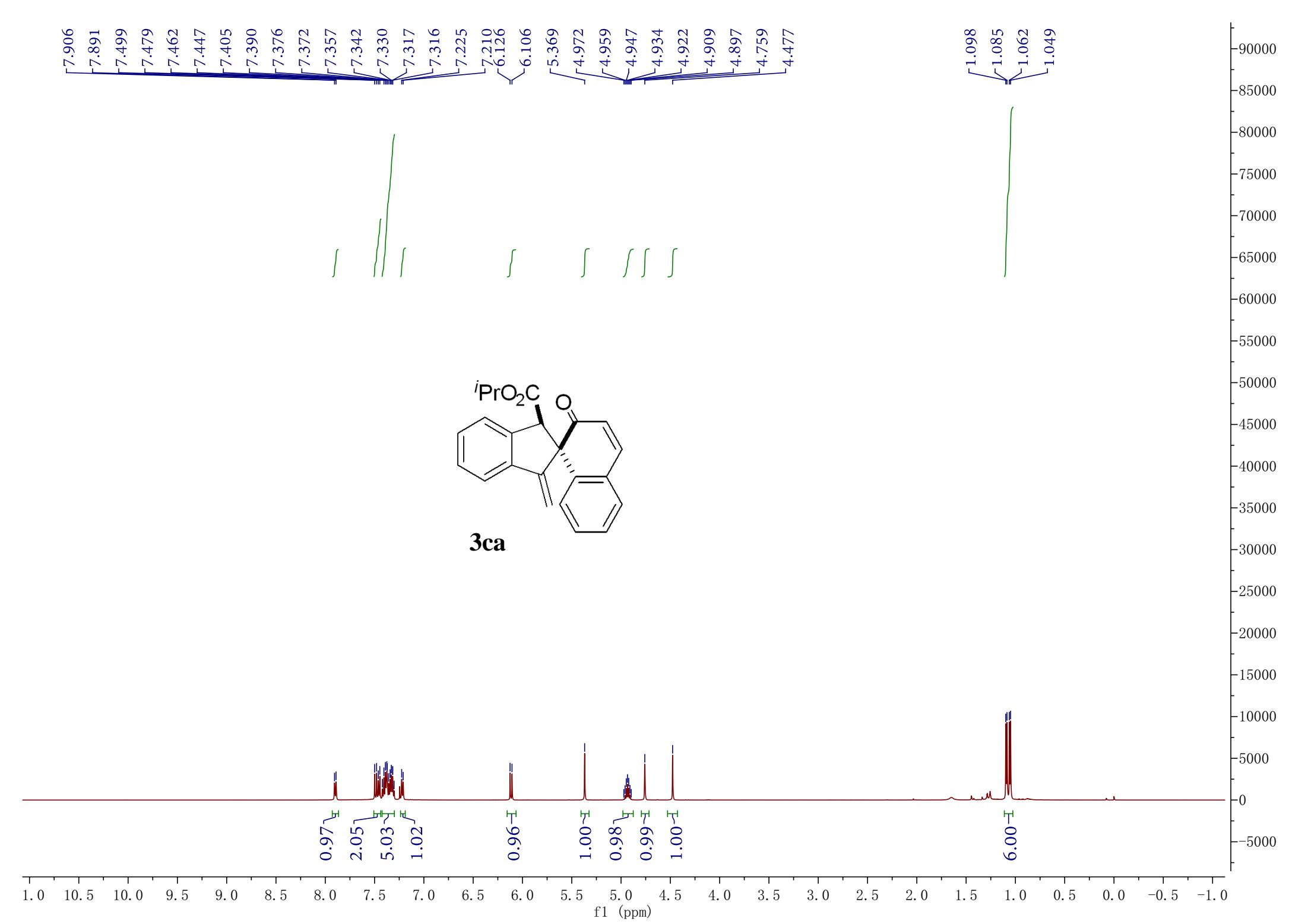
3ap







3ba



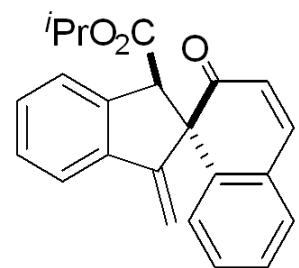
—197.386

—169.872

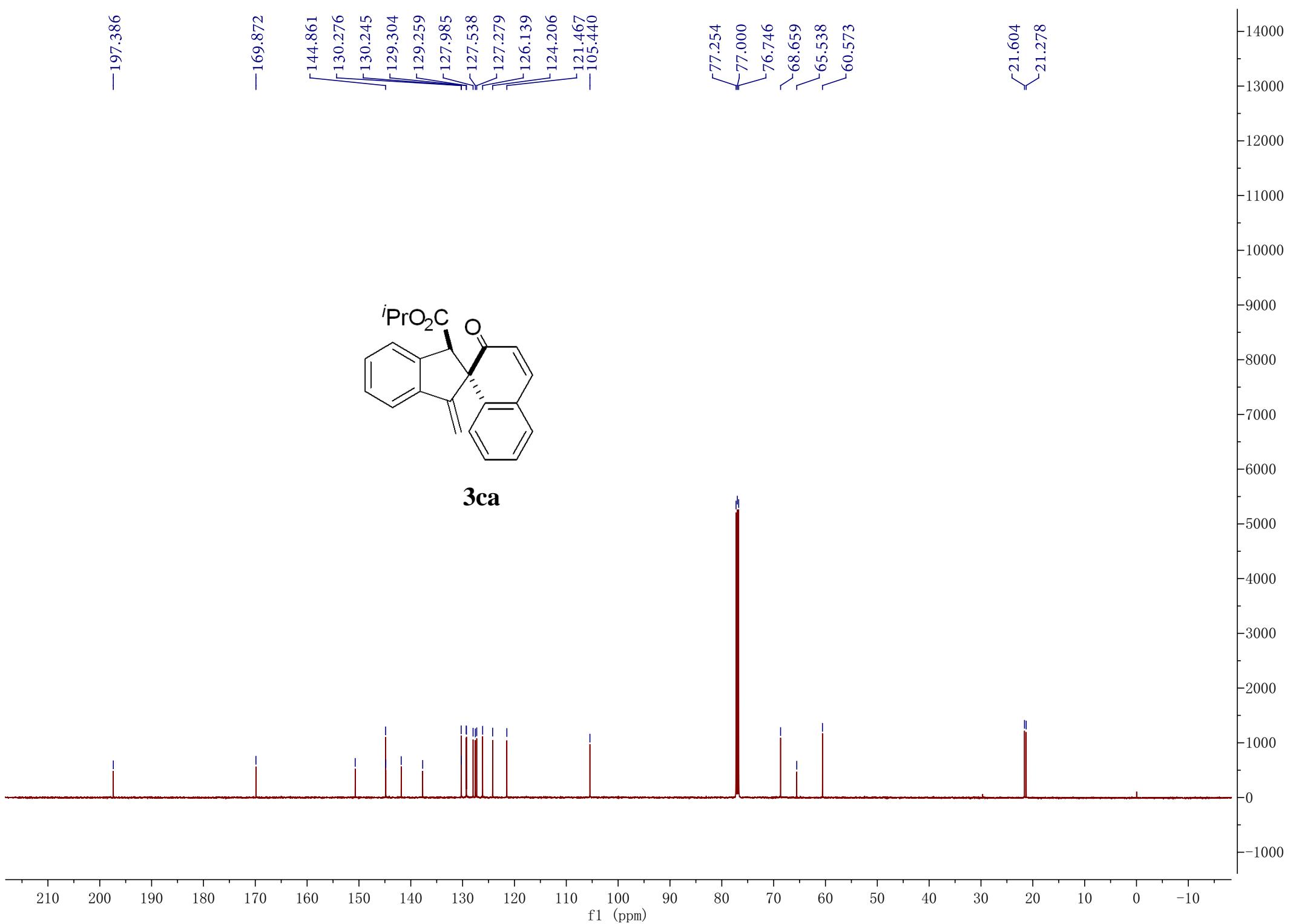
144.861
130.276
130.245
129.304
129.259
127.985
127.538
127.279
126.139
124.206
121.467
—105.440

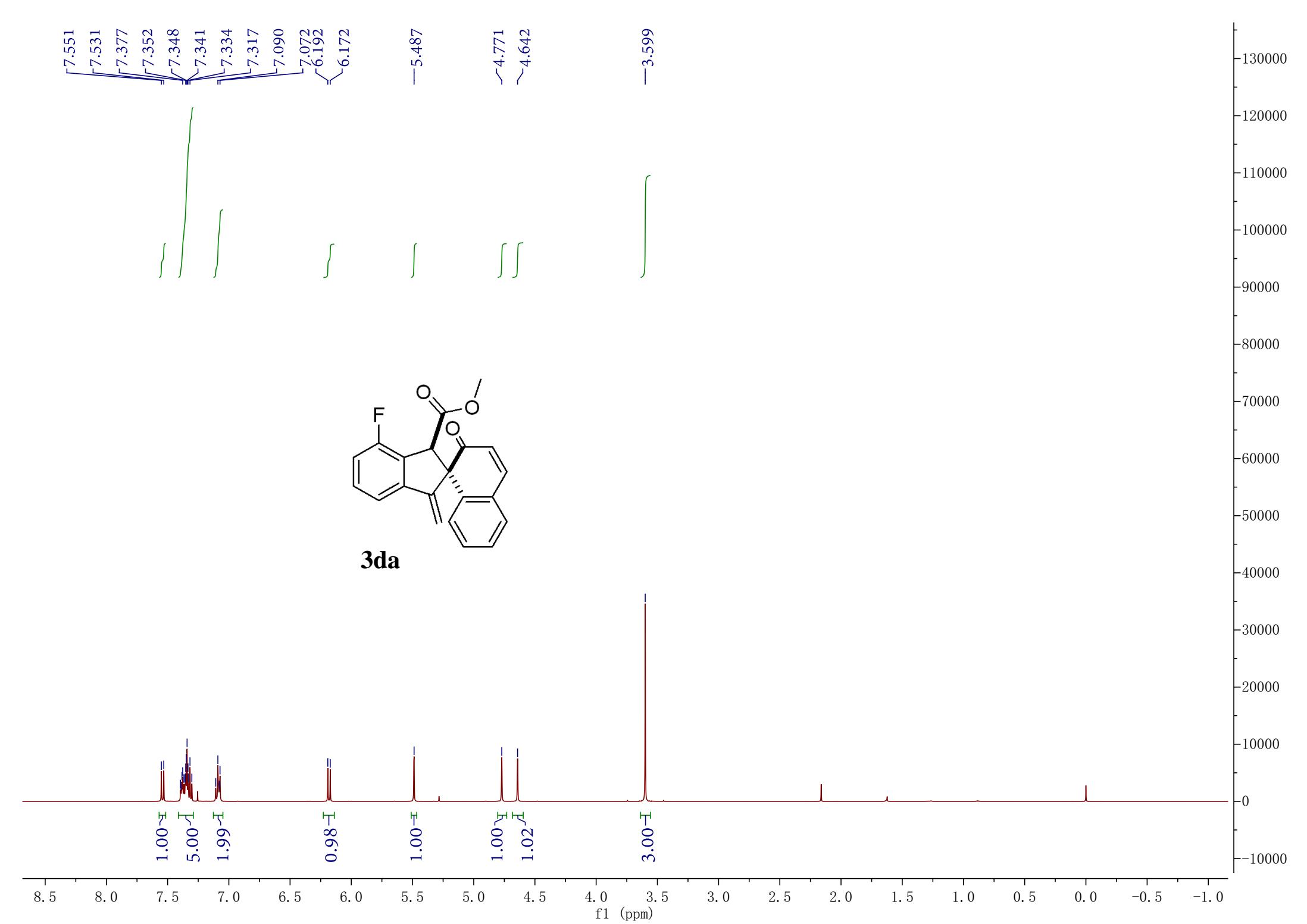
77.254
77.000
76.746
68.659
65.538
60.573

21.604
21.278



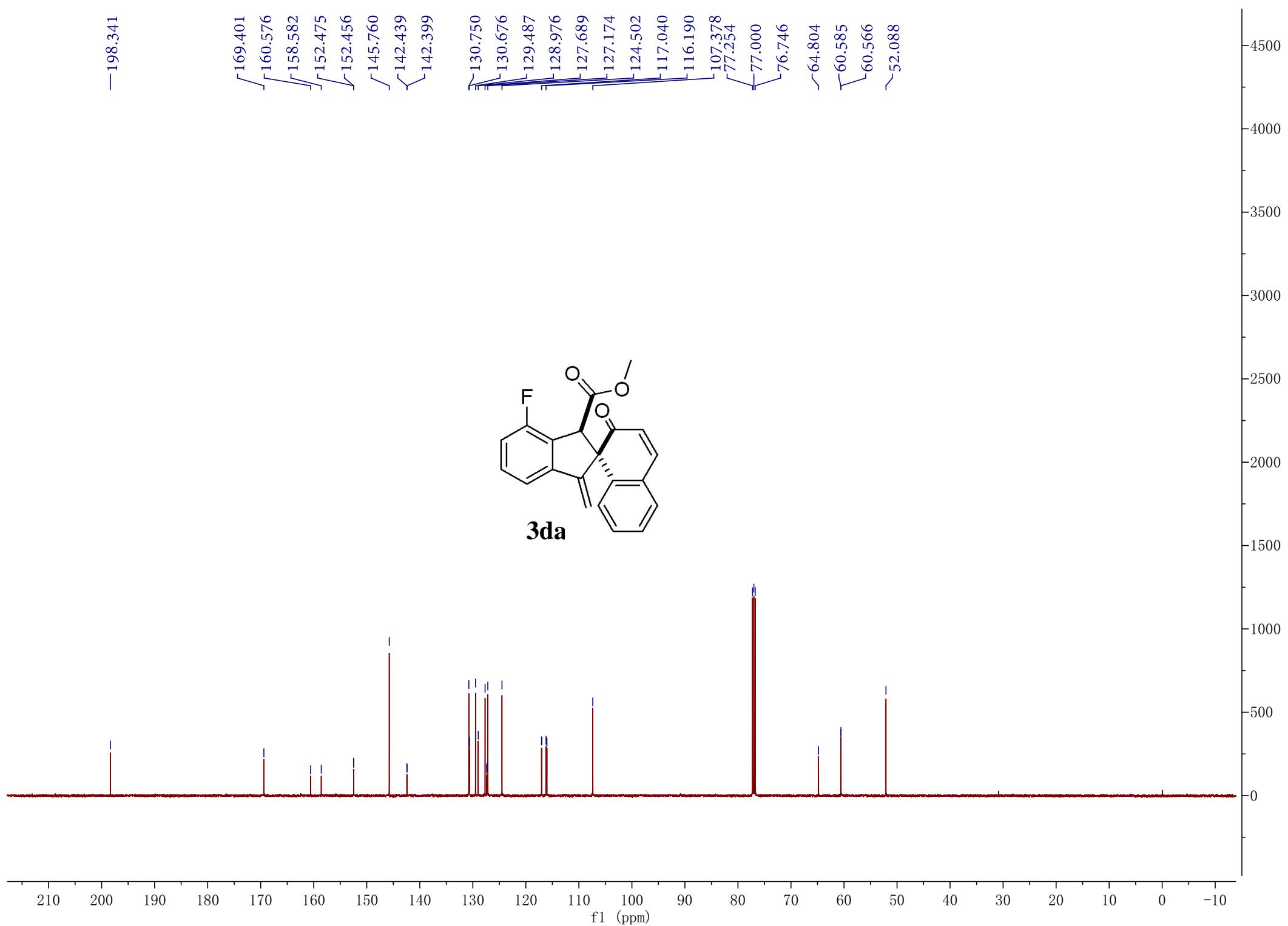
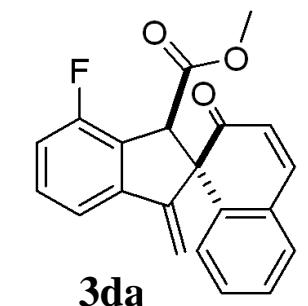
3ca

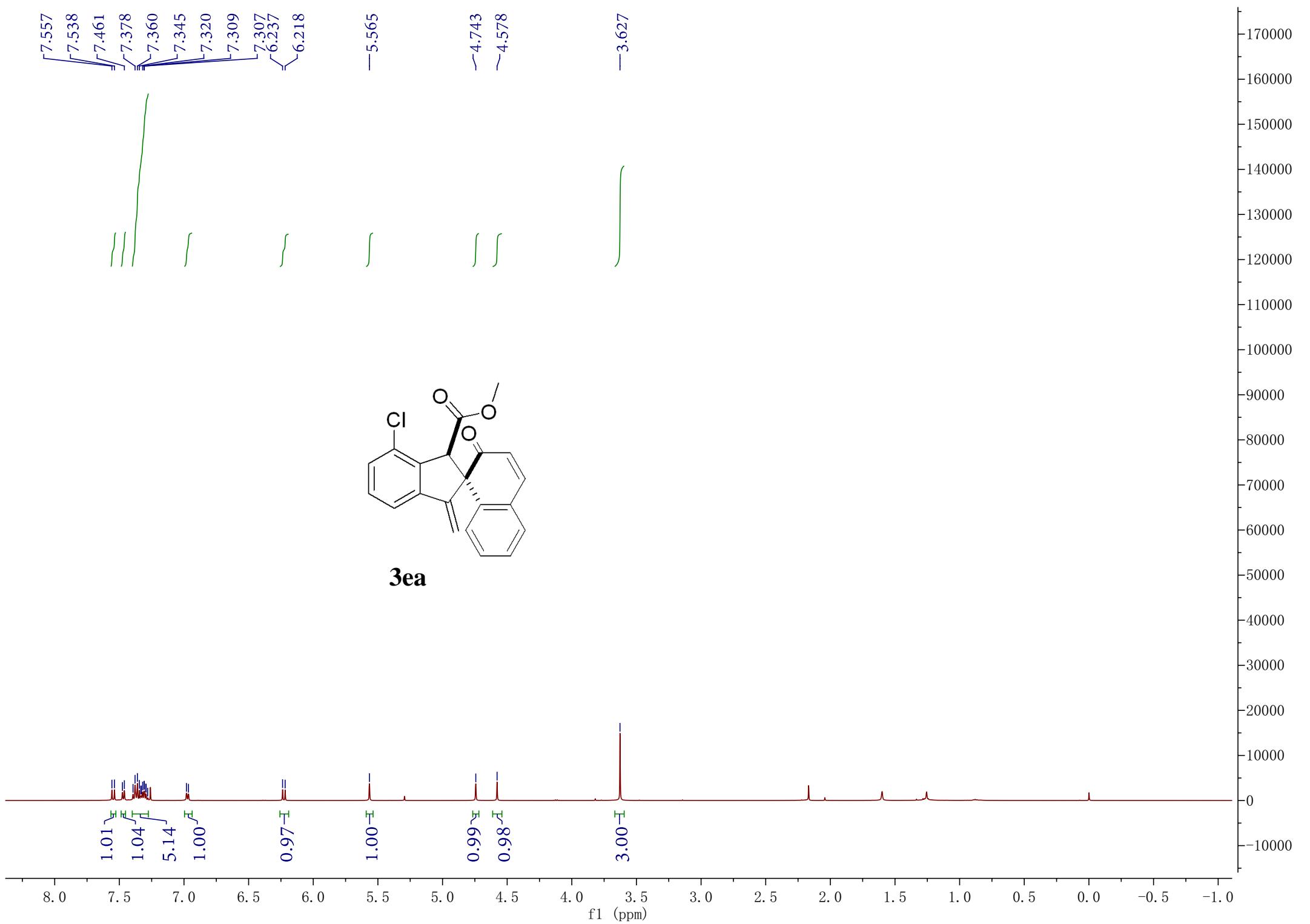


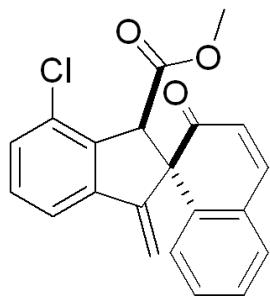
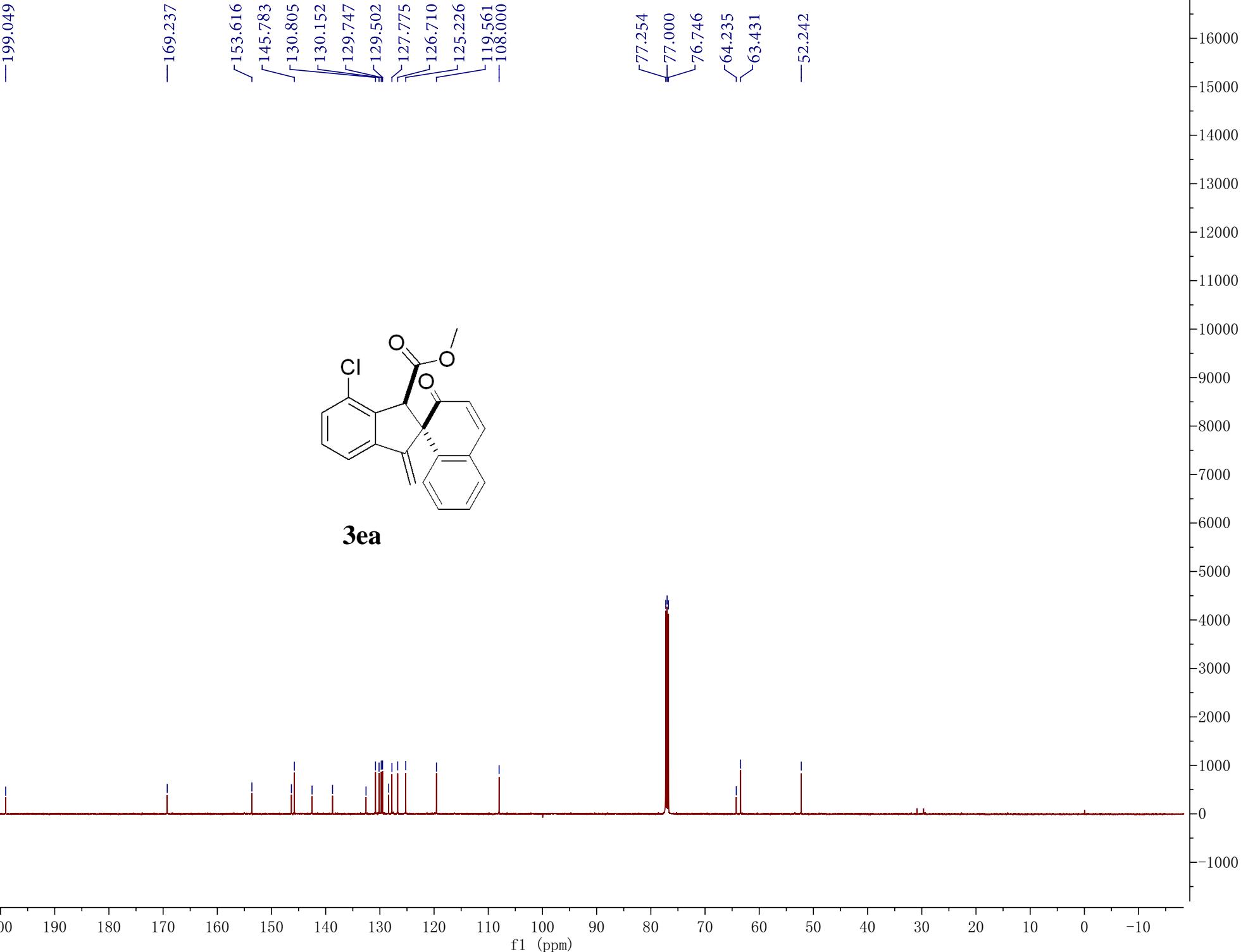


—198.341

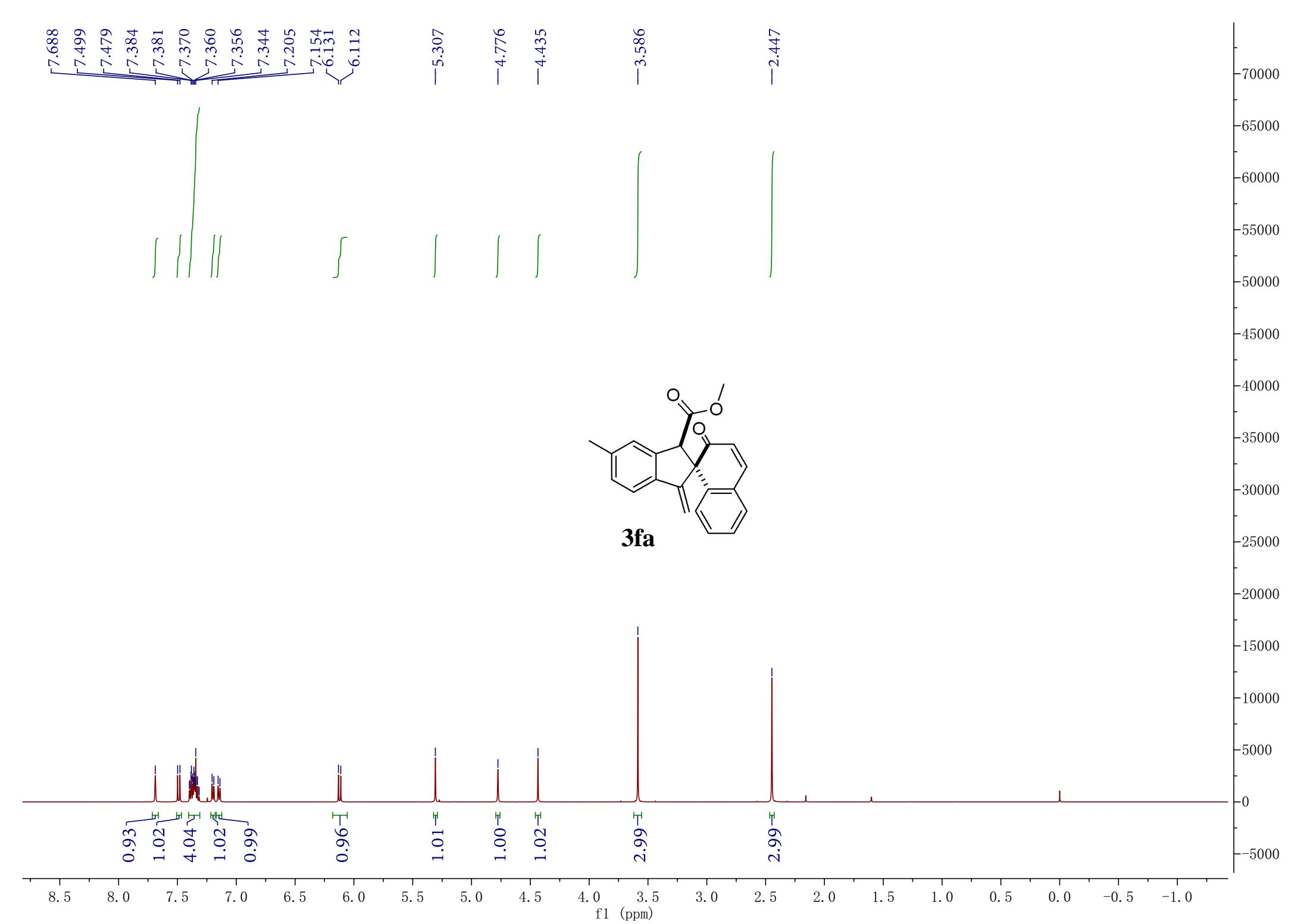
169.401
160.576
158.582
152.475
152.456
145.760
142.439
142.399

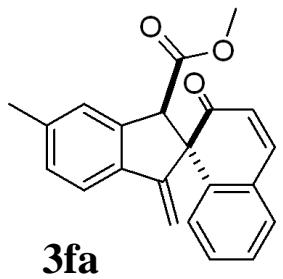
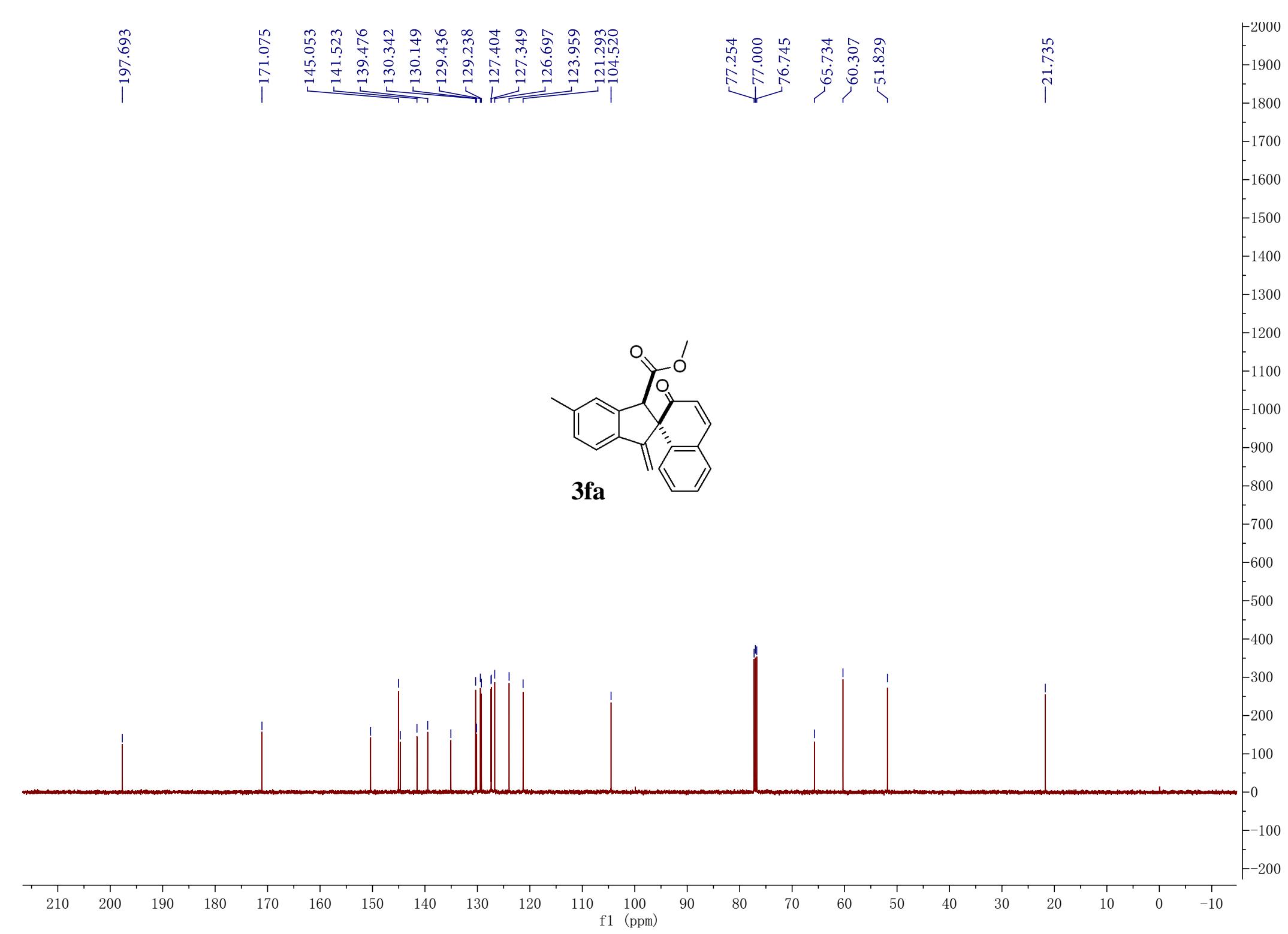


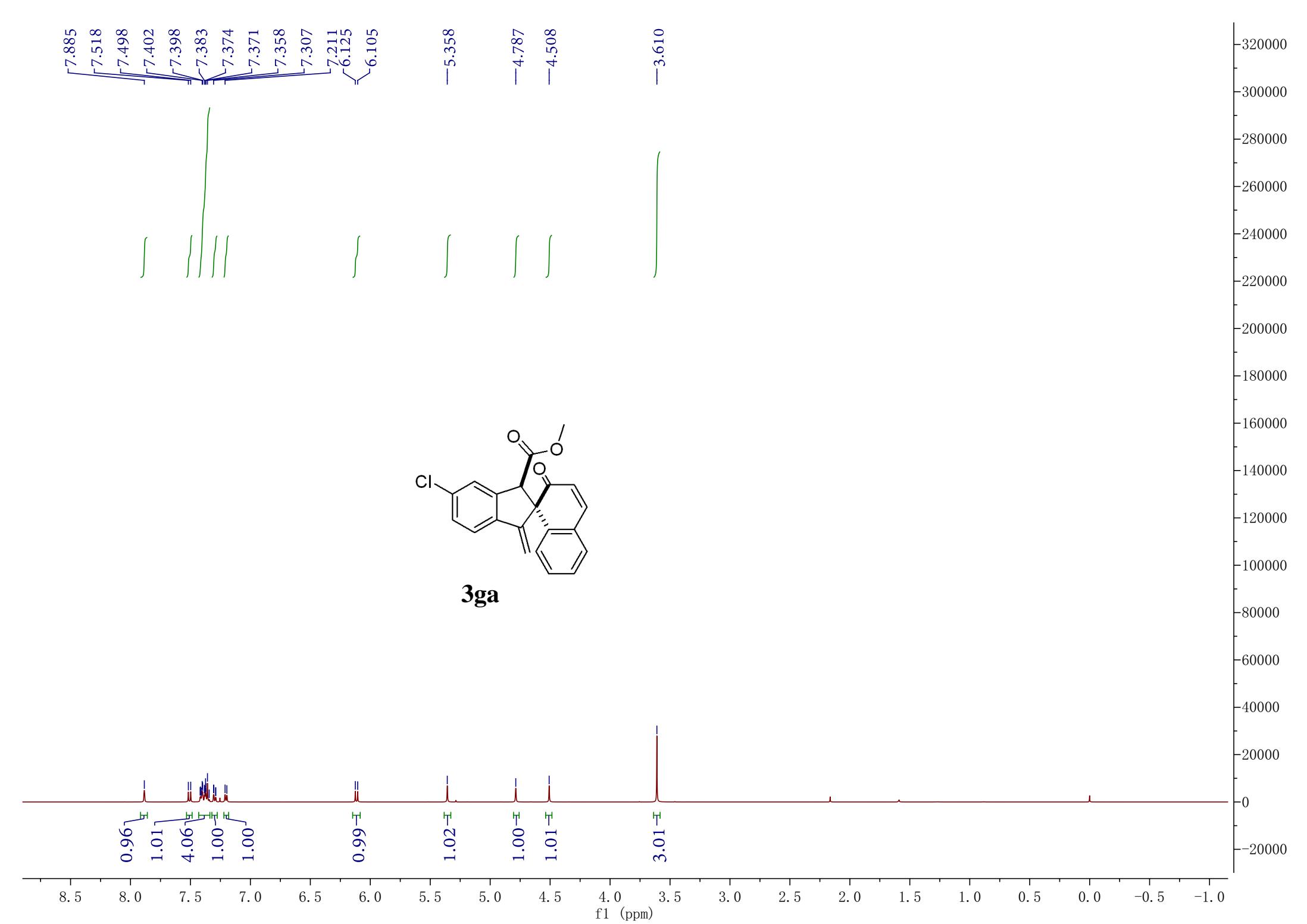




3ea





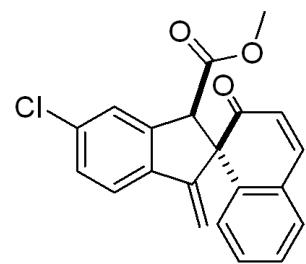


— 197.405

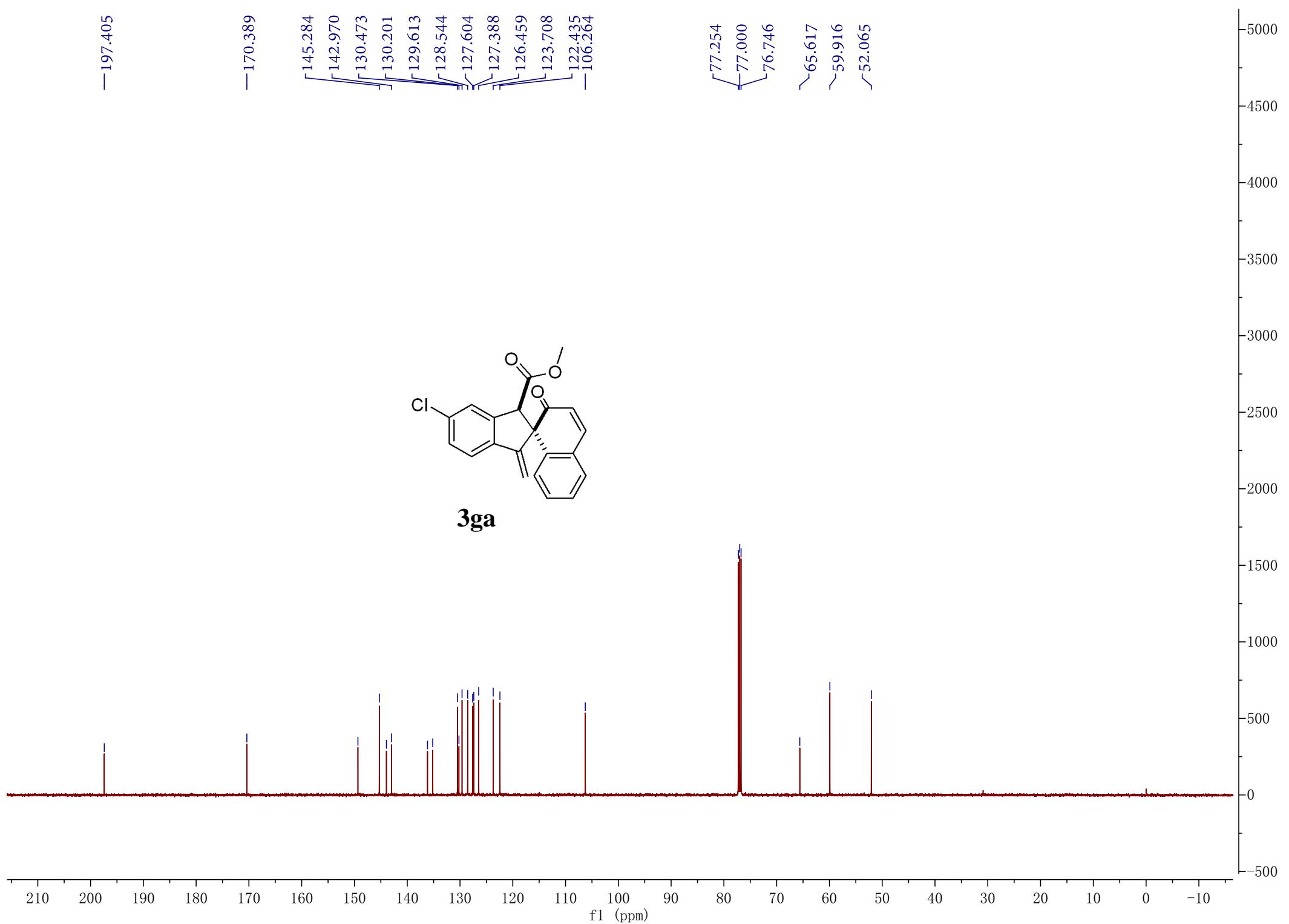
— 170.389

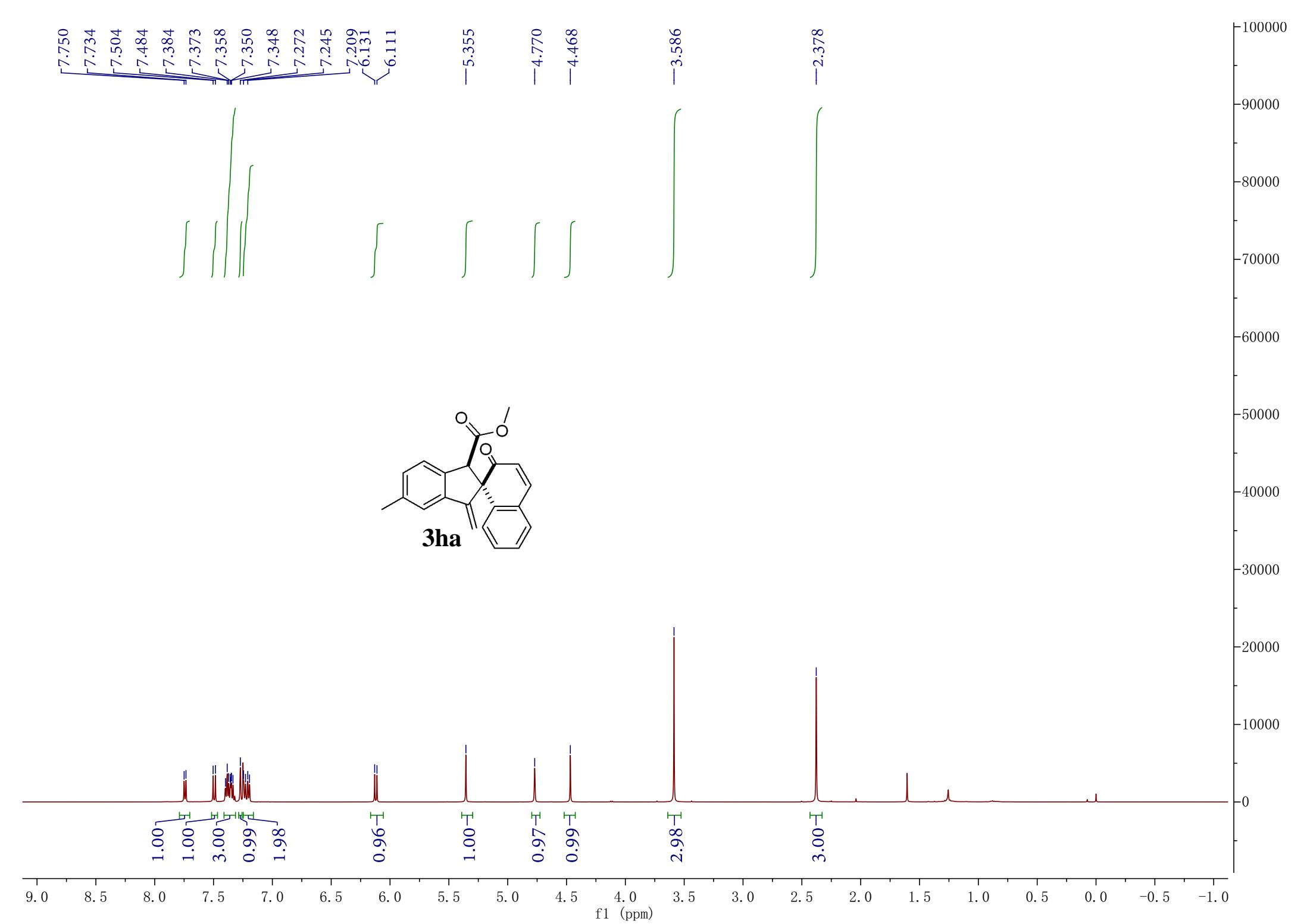
145.284
142.970
130.473
130.201
129.613
128.544
127.604
127.388
126.459
123.708
122.435
— 106.264

77.254
77.000
76.746
~65.617
~59.916
~52.065



3ga





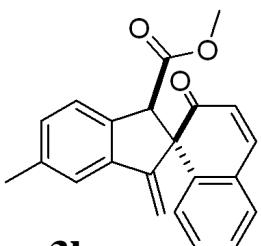
—197.741

—171.085

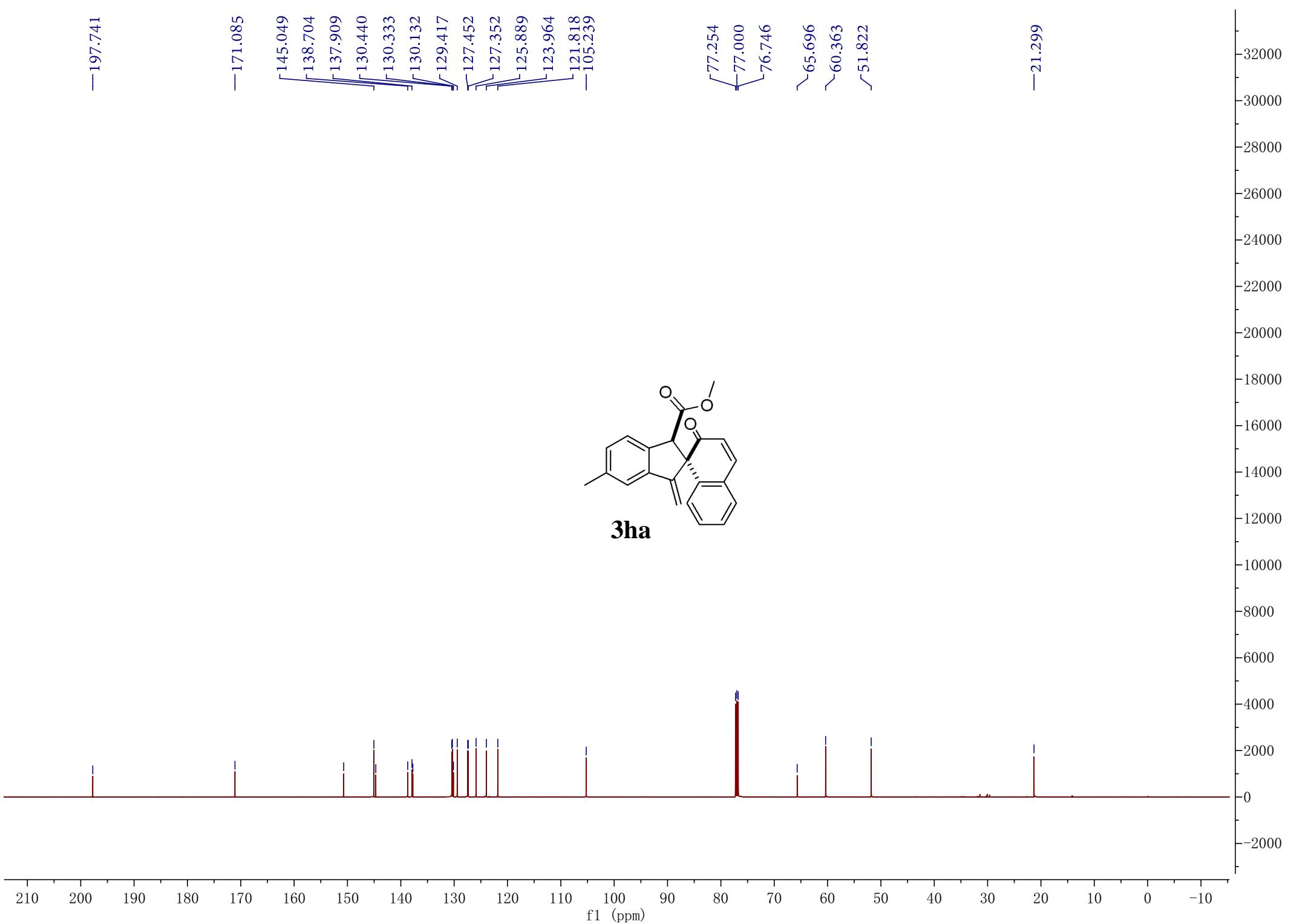
145.049
138.704
137.909
130.440
130.333
130.132
129.417
127.452
127.352
125.889
123.964
121.818
105.239

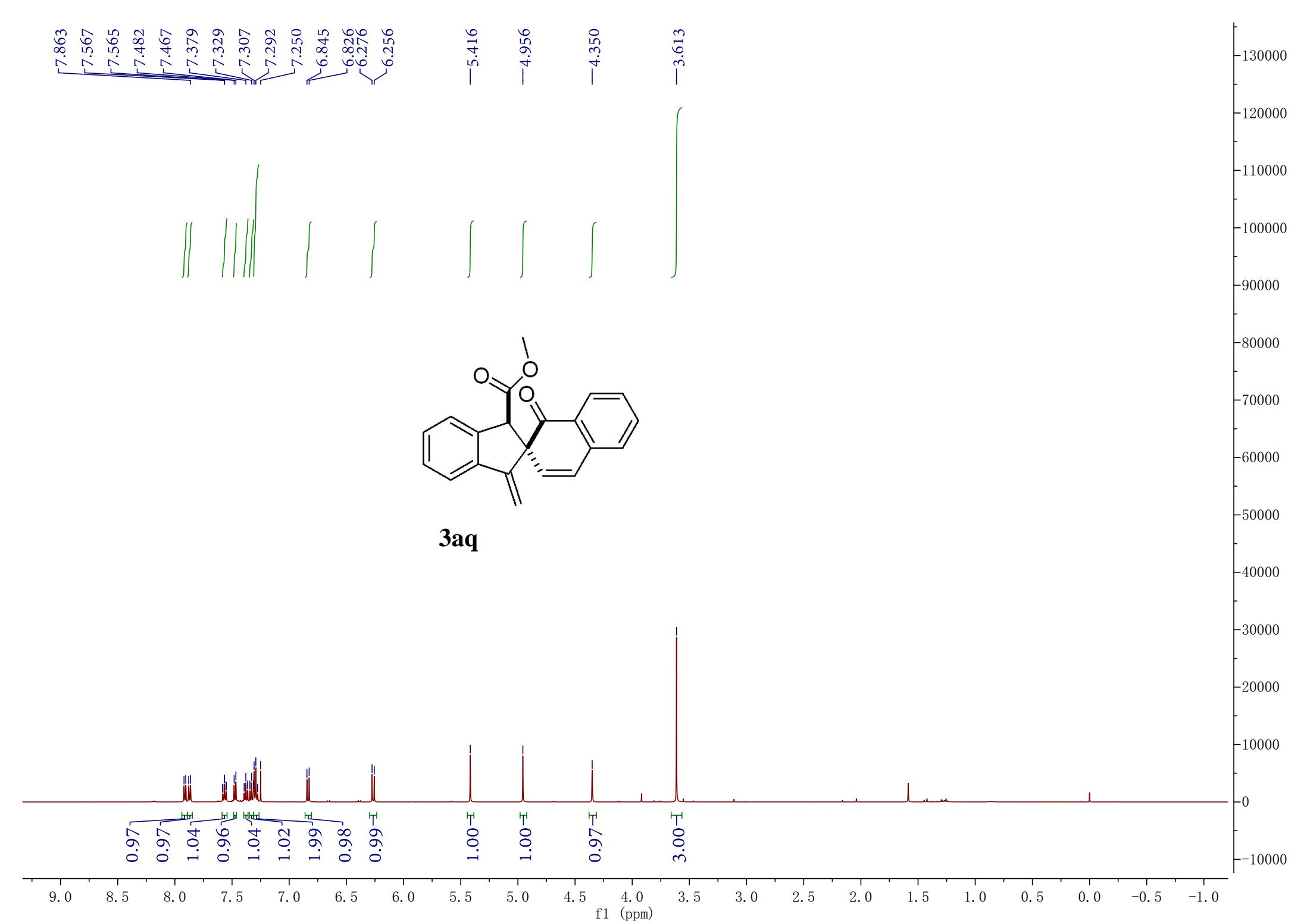
77.254
77.000
76.746
65.696
60.363
51.822

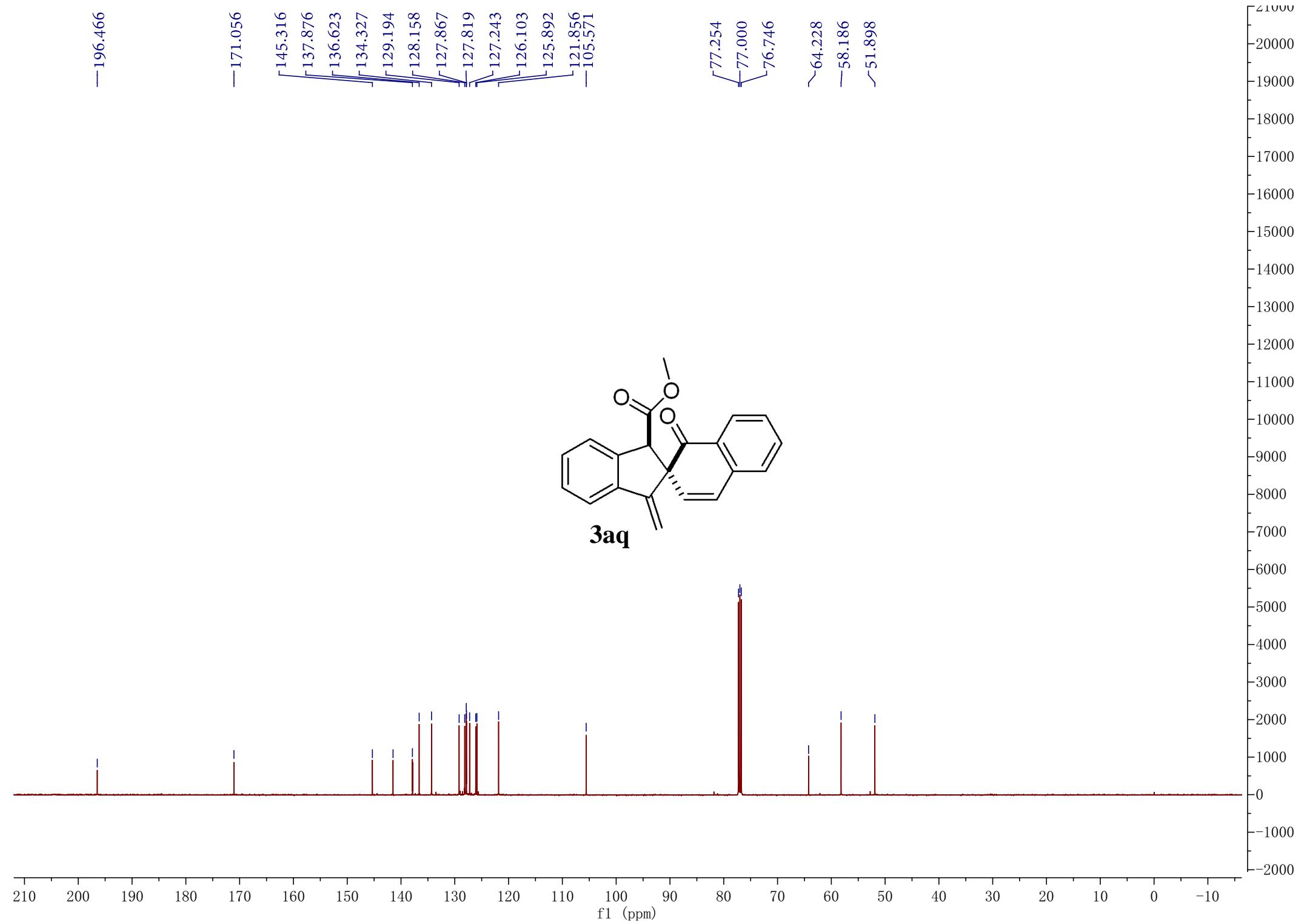
—21.299

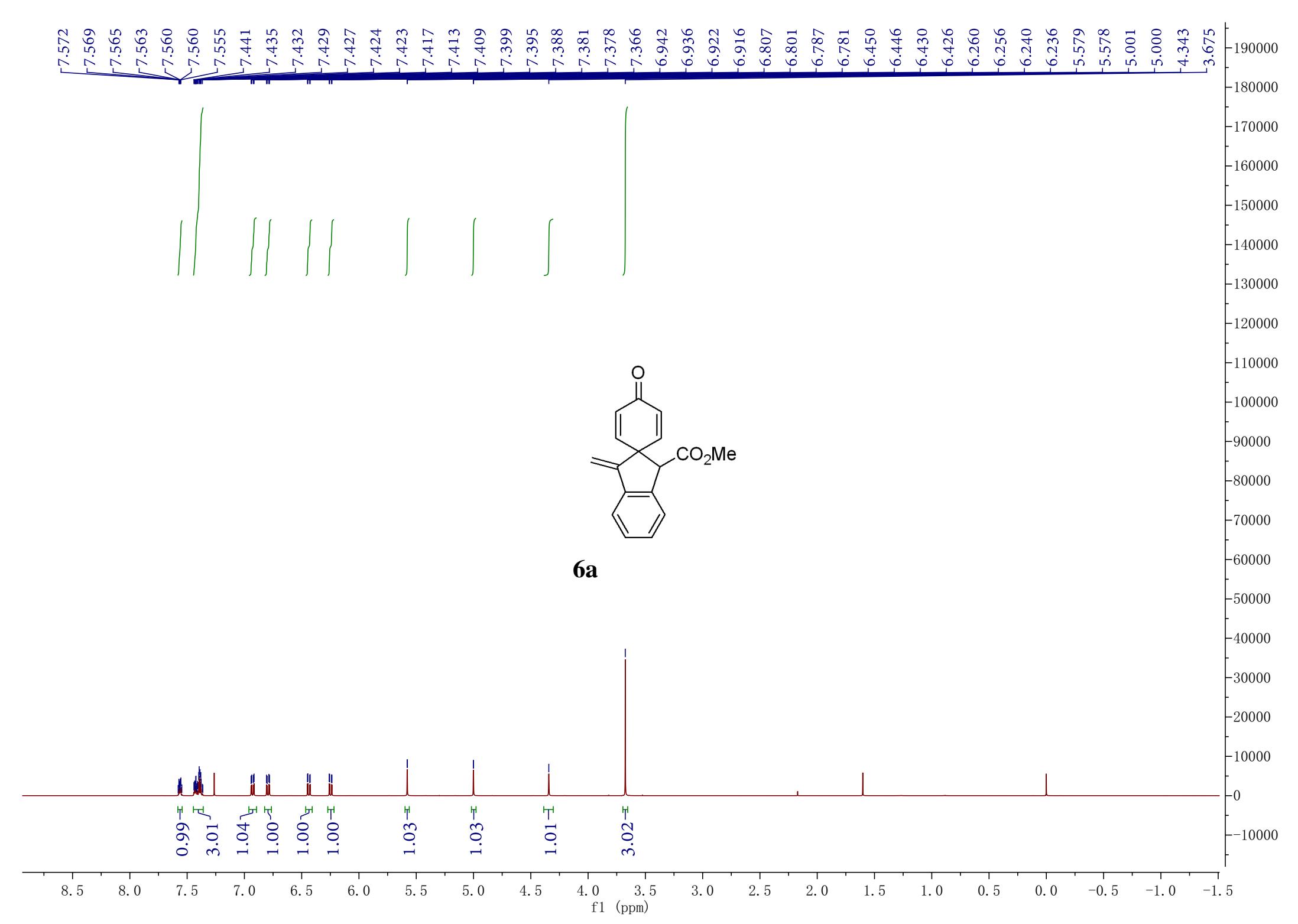


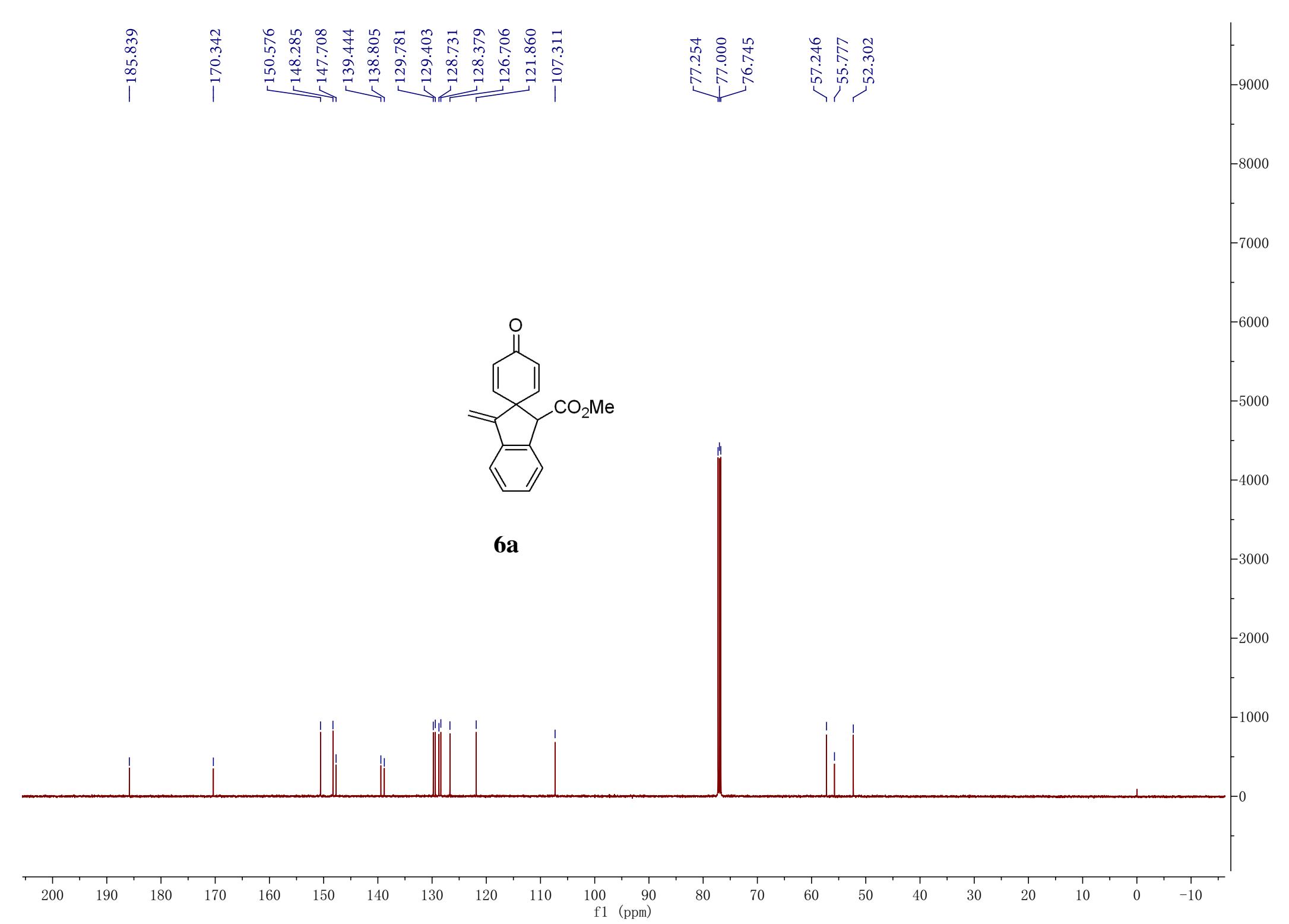
3ha

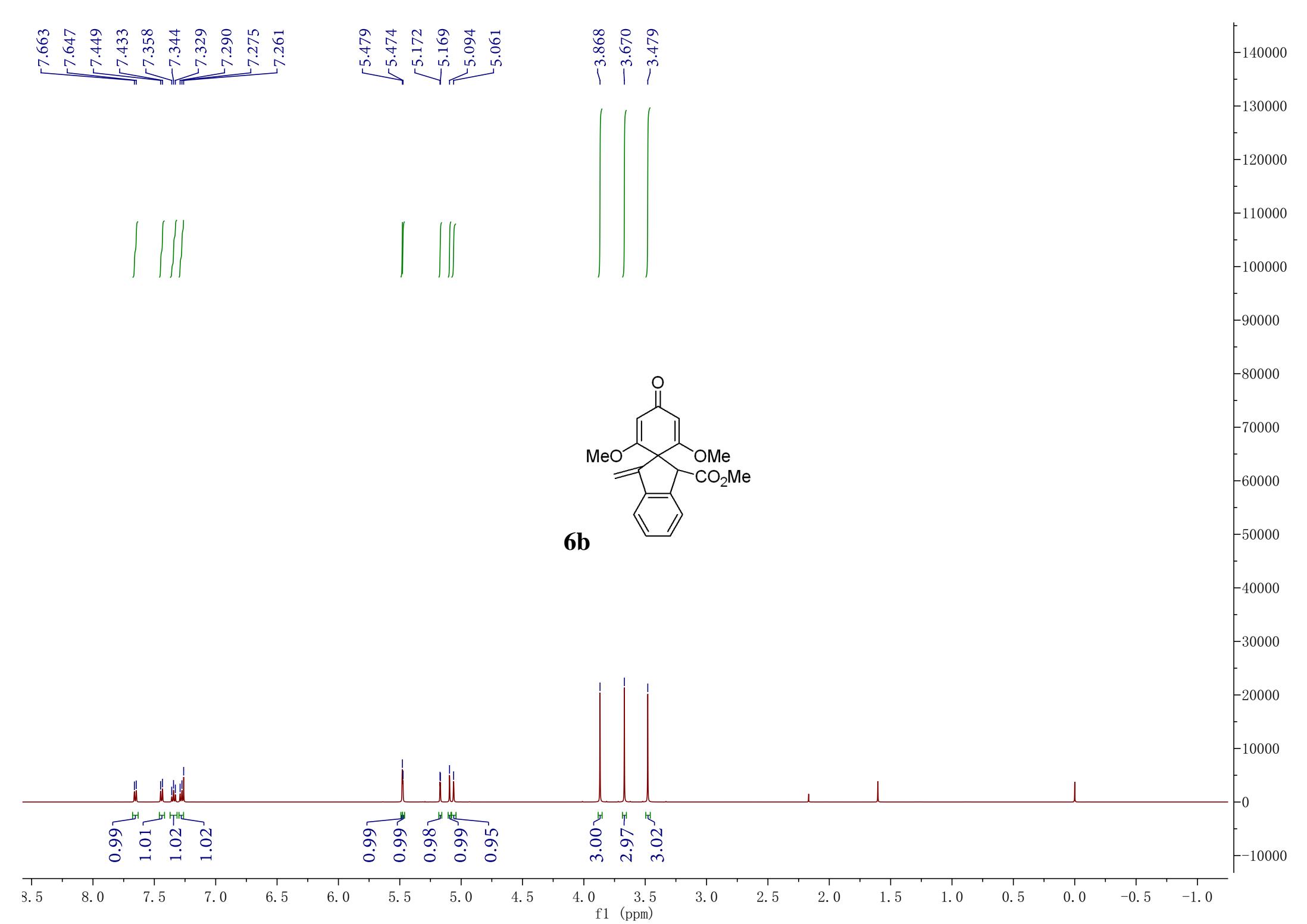


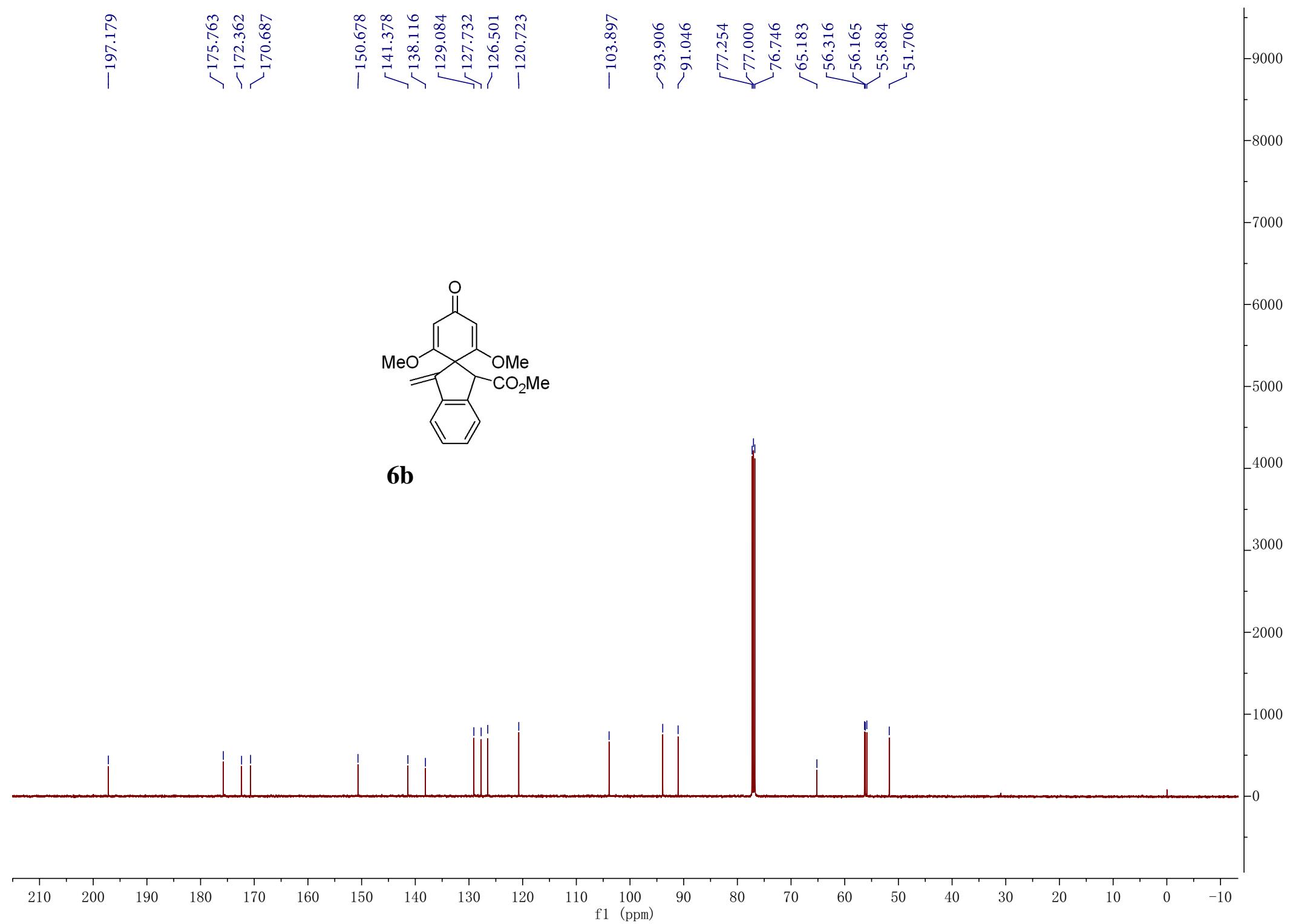


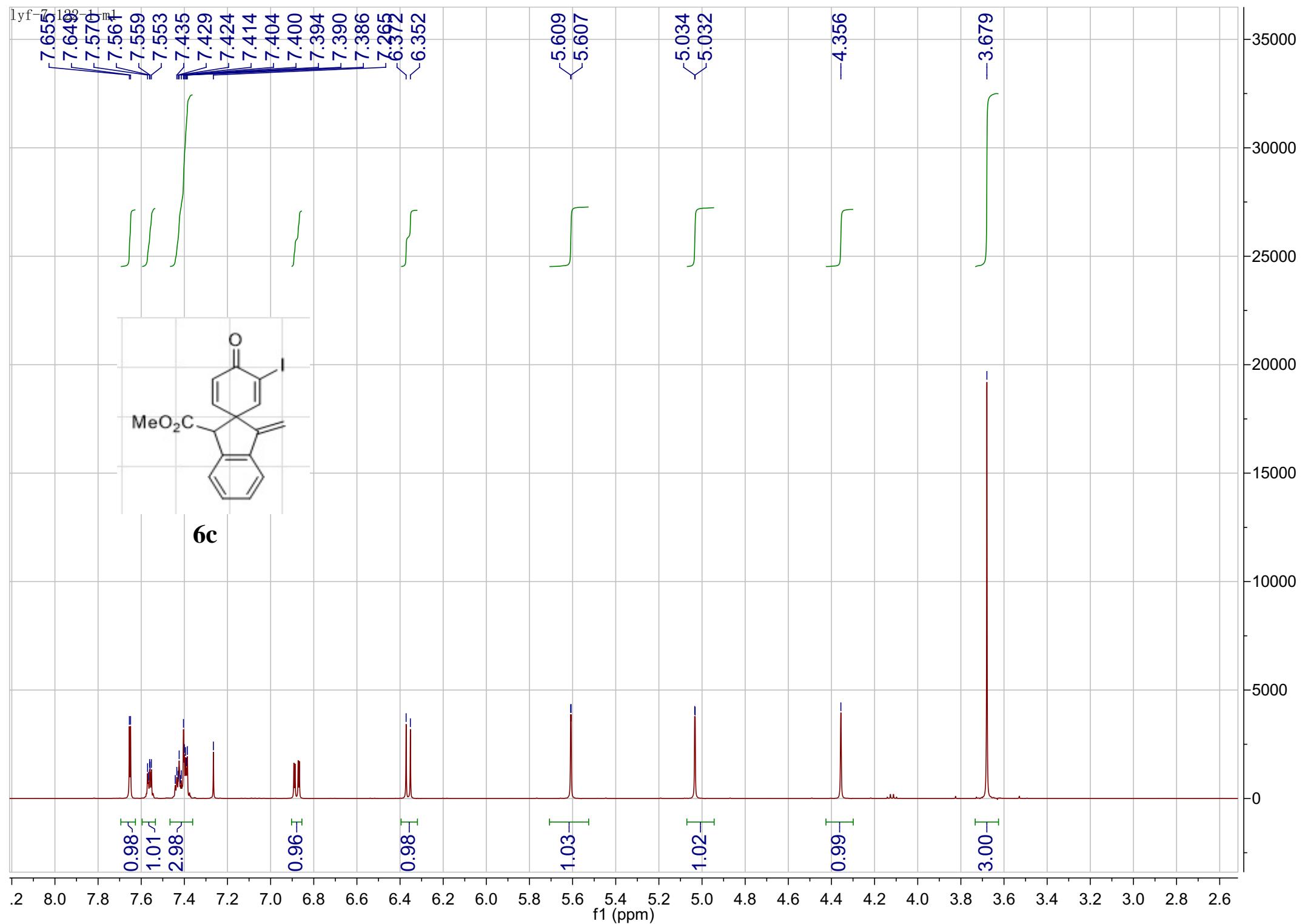


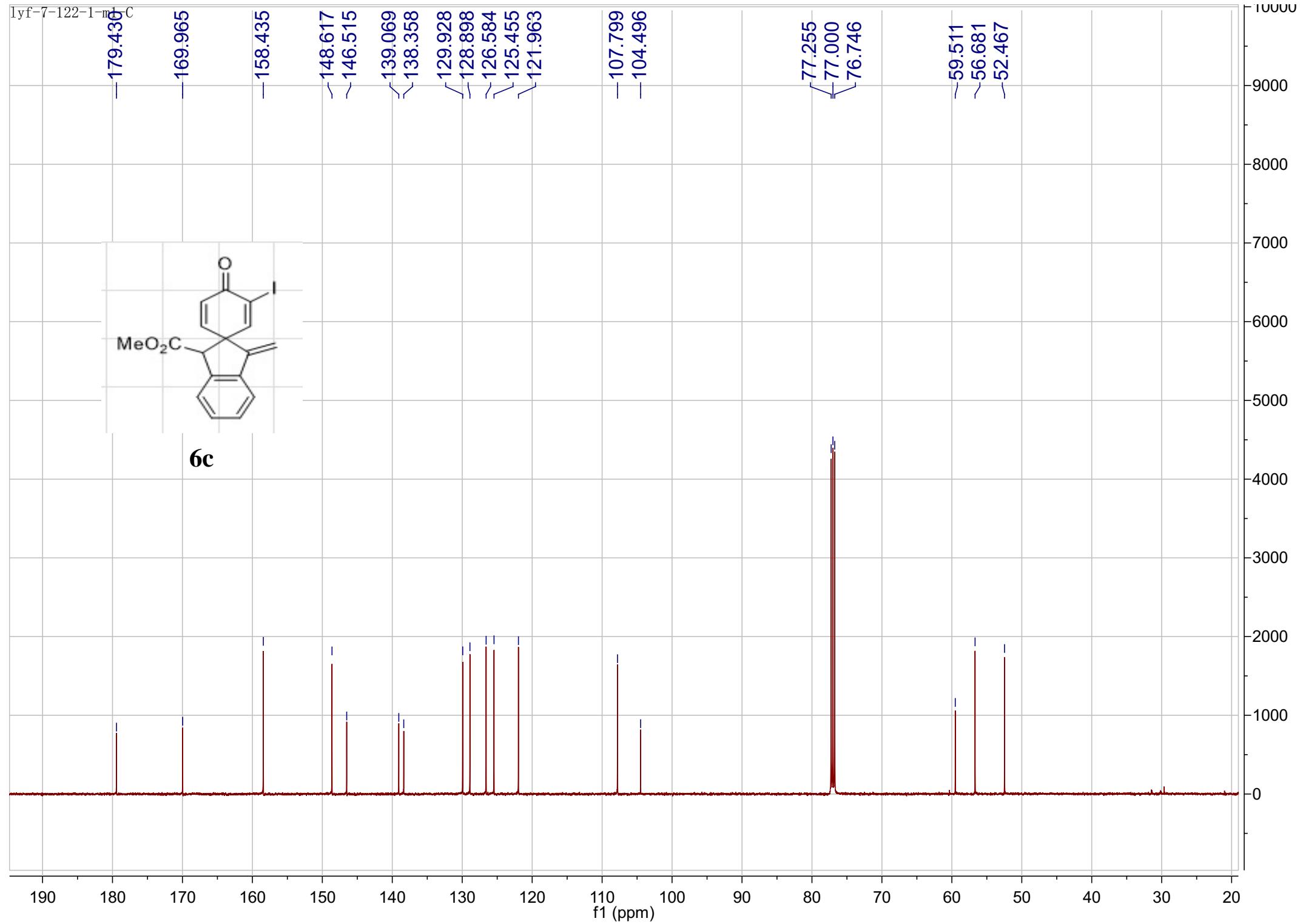


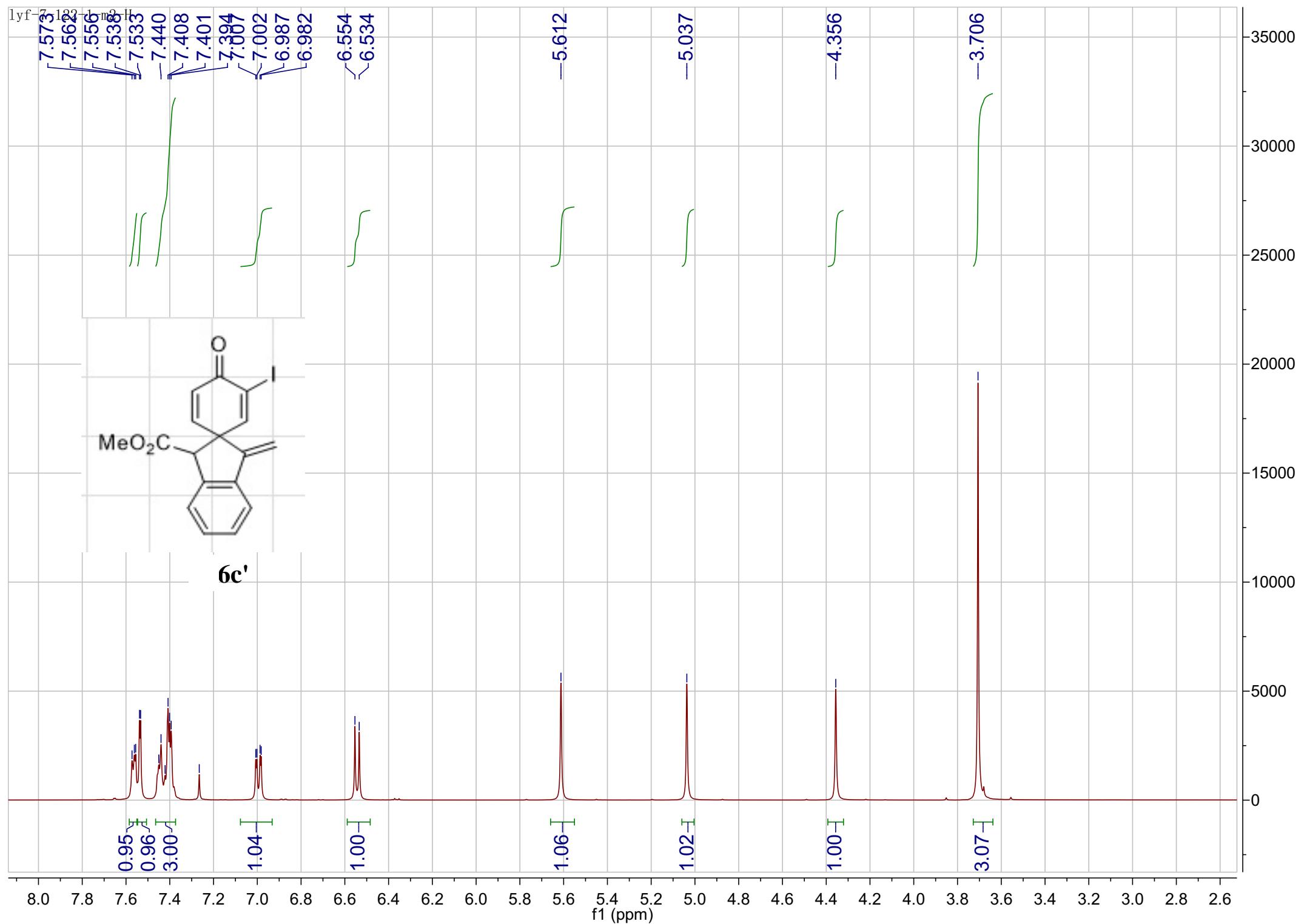




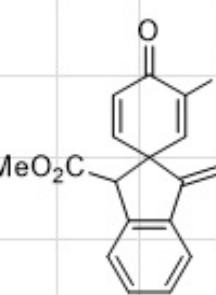








1yf-7-122-1m2-C

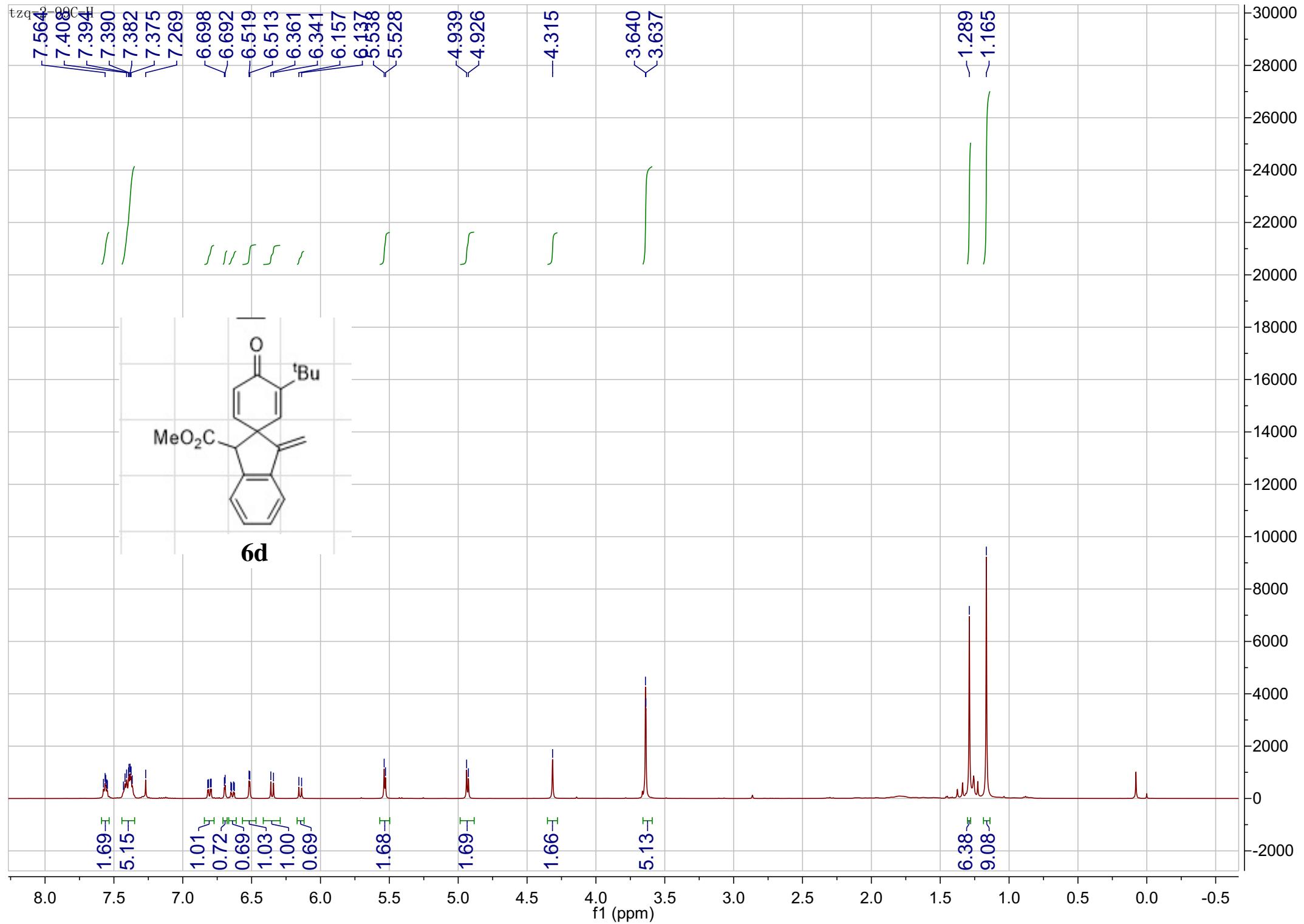
-179.452
-169.844\ 156.235
\ 150.688
/\ 146.317\ 138.967
\ 138.344
/\ 129.934
\ 128.881
/\ 126.720
\ 126.492
\ 121.958-107.904
-103.526\ 77.254
\ 77.000
\ 76.746\ 59.785
\ 56.958
\ 52.624**6c'**

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -500

f1 (ppm)

CCW

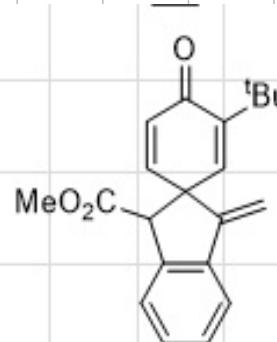
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500



tzq-2+99C-C

185.965
185.916

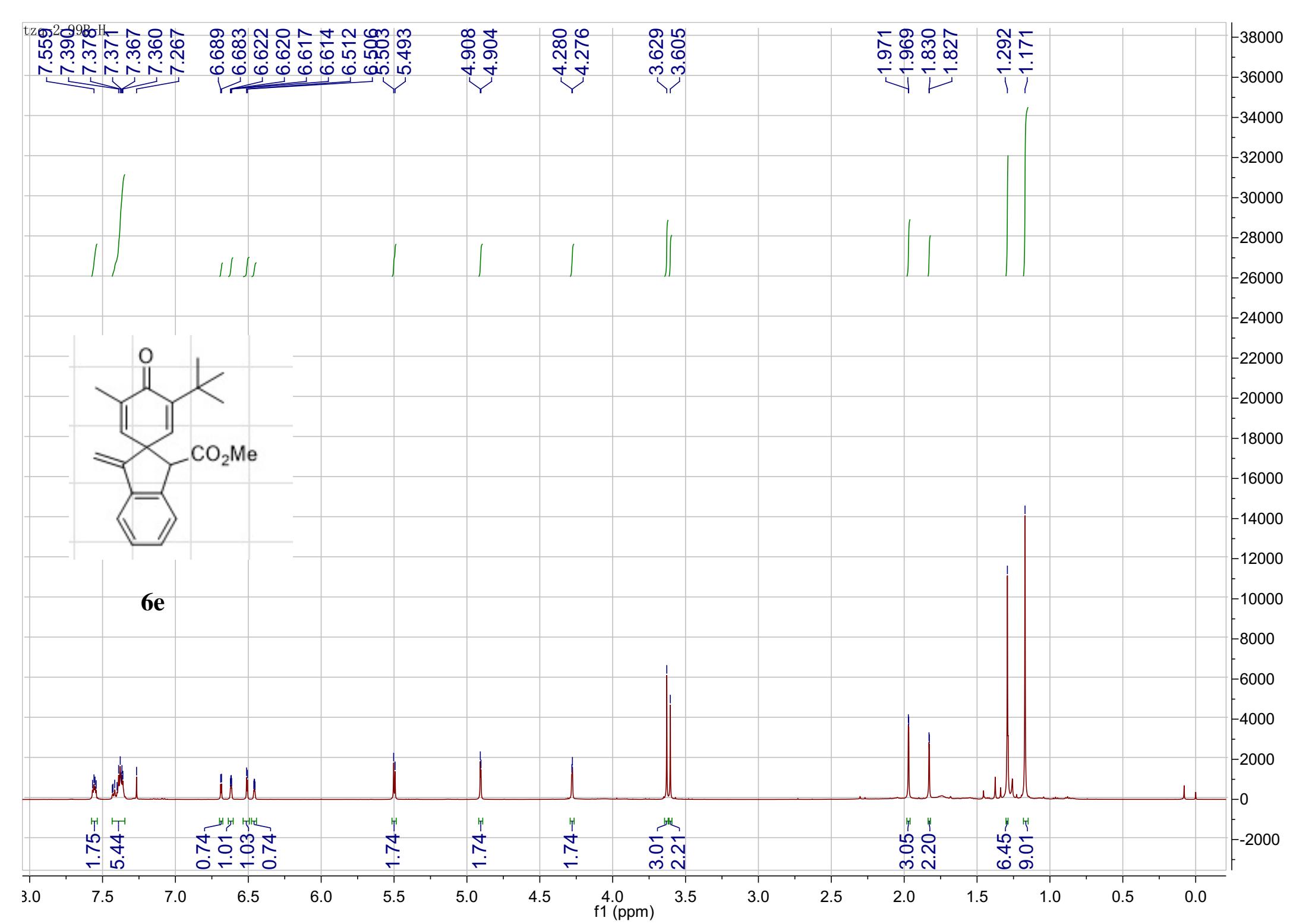
-170.445

148.173
145.703
-145.406
144.068
-141.588
131.115
130.095
-129.621
129.601
128.541
126.815
126.659
121.765
106.742
106.61777.254
77.000
76.74657.557
57.279
55.976
55.589
52.044
51.96734.589
34.528
29.089
28.998**6d**

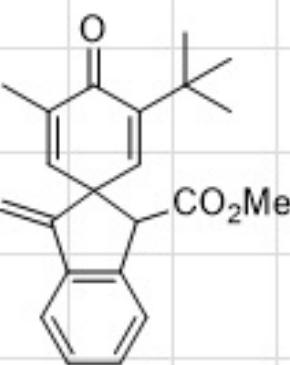
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200



tzq-2-99B-C

**6e**186.404
186.390170.643
170.566144.084
143.927
141.431
141.131
129.514
129.480
128.457
128.444
126.736
126.695
121.758
106.323
106.09777.255
77.000
76.74657.484
57.471
55.495
55.064
51.928
51.87134.624
34.566
29.244
29.165

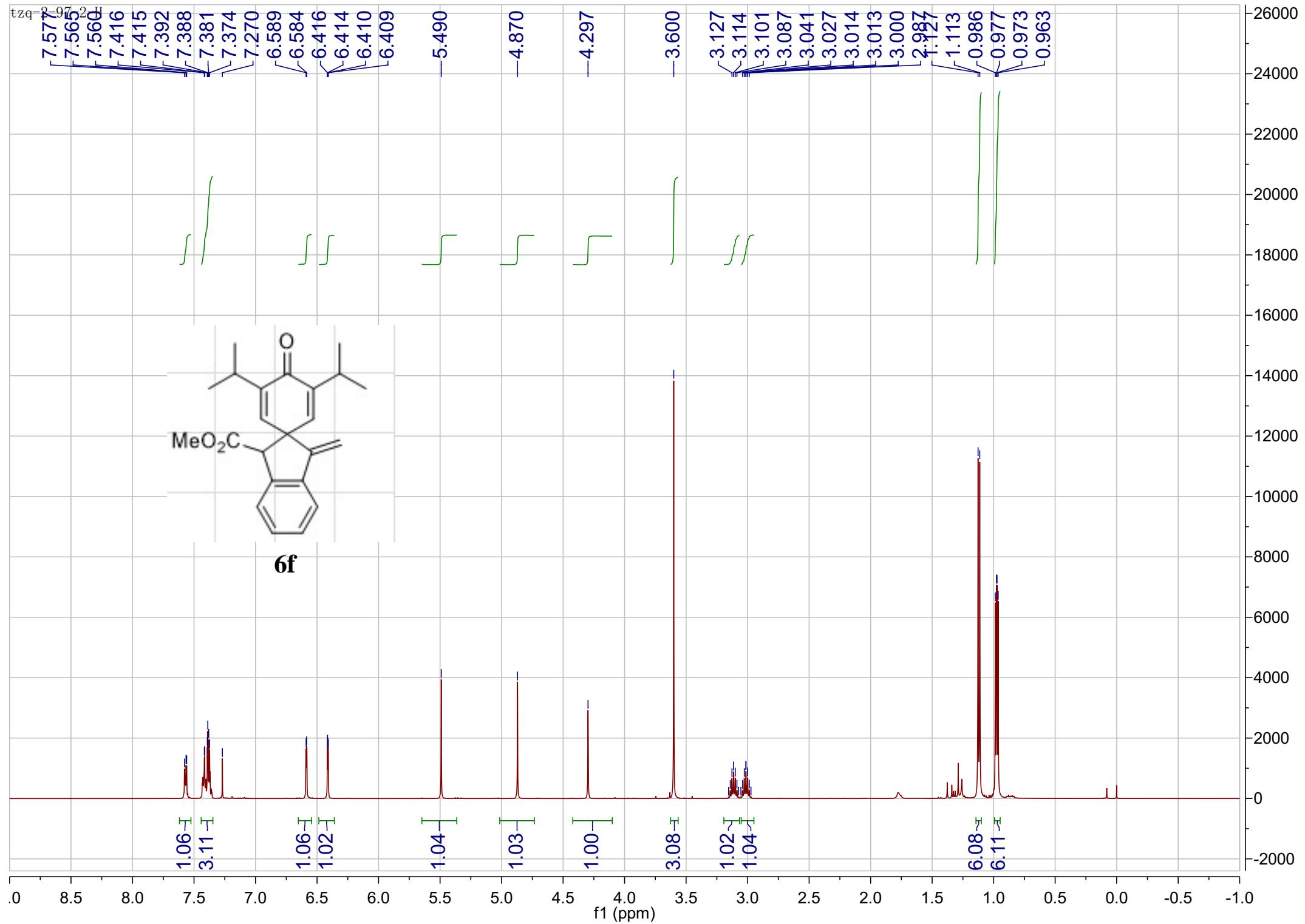
16.358

16.251

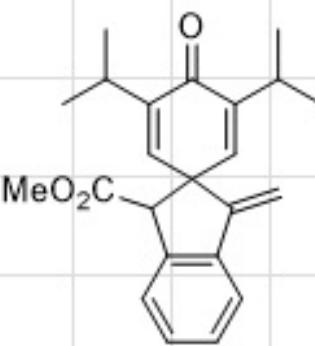
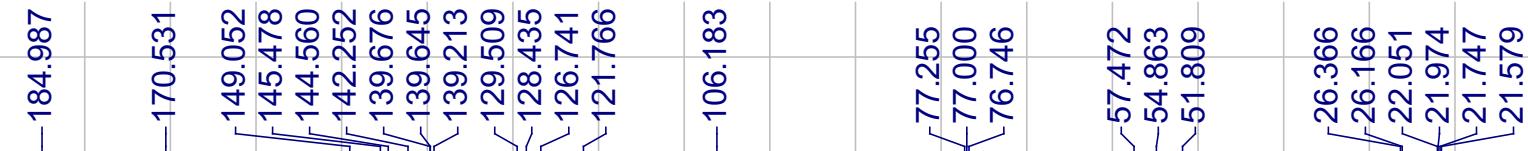
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

4000
3500
3000
2500
2000
1500
1000
500
0

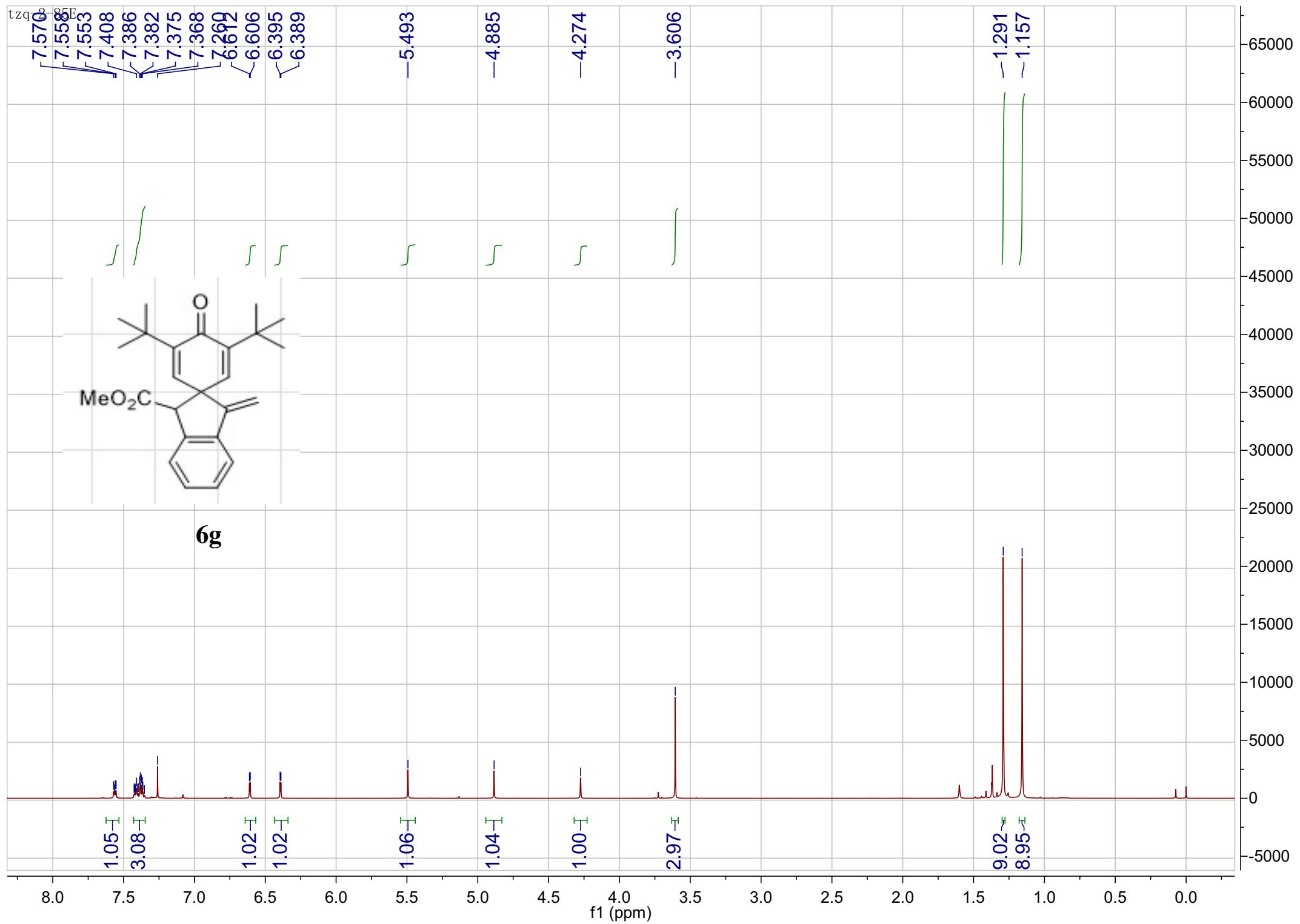


tzq-2+97-2-C

**6f**

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)



tzq-2+85E-C

-186.409

-170.599

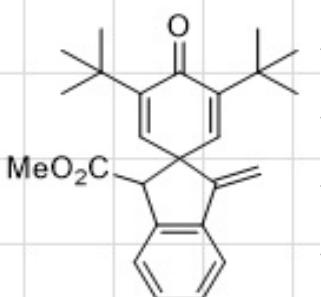
149.682
147.781
146.635
141.929
139.693
139.297
139.289
129.536
128.433
126.833
121.754

-106.110

77.254
77.000
76.746

57.715
54.970
51.795

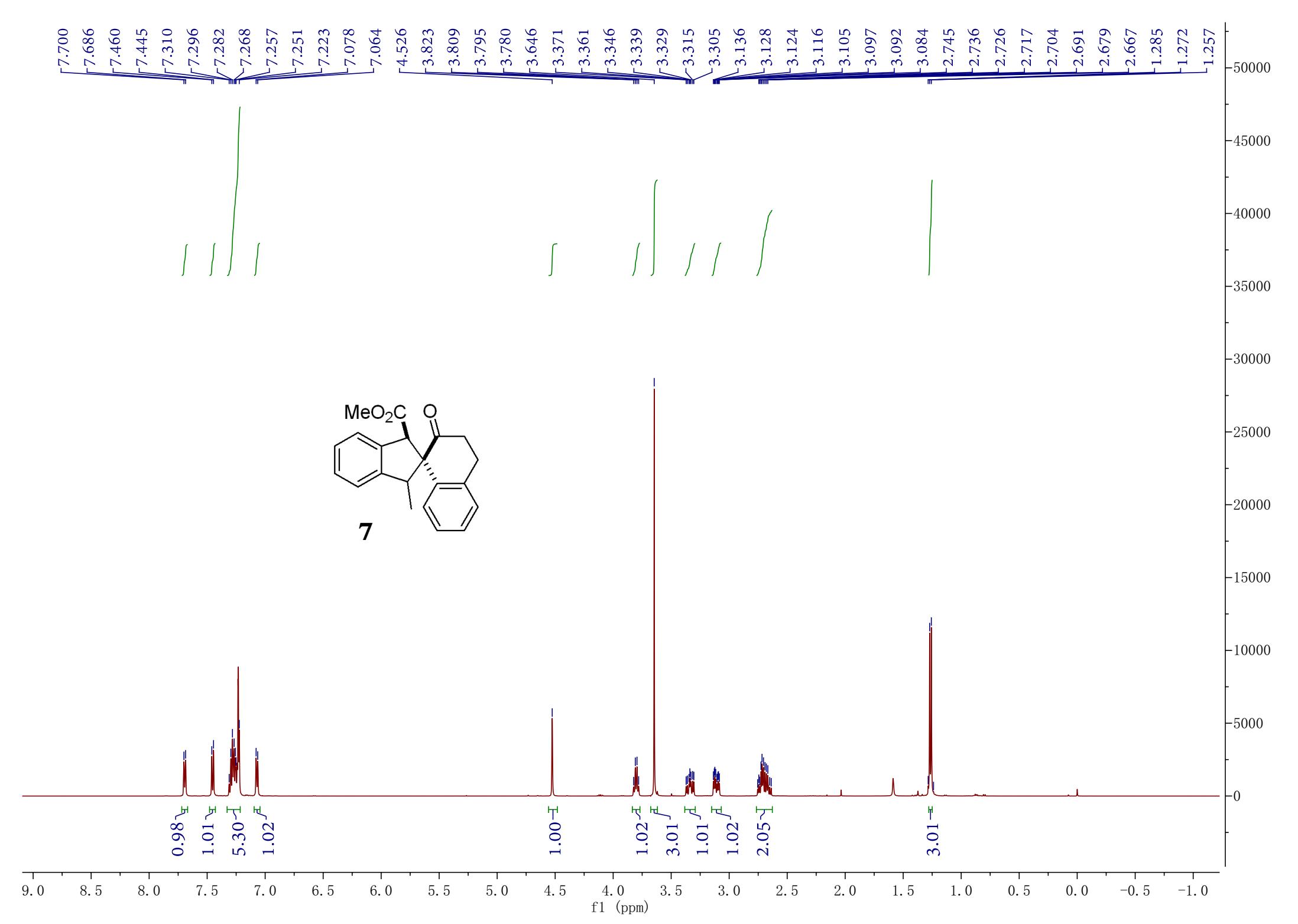
34.854
34.772
29.483
29.395

**6g**

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000



—210.513

—171.744

143.216
140.921
138.624
137.680
128.321
127.464
127.309
126.852
126.726
126.693
123.975
122.326

77.255
77.000
76.746
64.798
62.304
52.898
51.915

—41.232

—29.146

—13.964

