

Divergent Synthesis of Fused Tricyclic Compounds via a Tandem Reaction from Alkynyl-cyclohexadienones and Diazoesters

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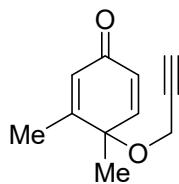
General Information

All of the reactions were carried out in flame-dried tubes. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. ¹H NMR were recorded on Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and ¹³C NMR were recorded on Bruker 75 MHz, 100 MHz or 125MHz spectrometer in CDCl₃ or CD₃CN or DMSO-*d*₆. HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus.

All of the diazo compounds were known and prepared according to the literature procedures.¹ Sodium phenolate, sodium benzenethiolate and sodium 4-methylbenzenethiolate were commercial available. Sodium 4-methylphenolate,² sodium 4-methoxyphenolate,³ sodium 4-fluorophenolate,⁴ sodium 4-bromophenolate⁵ and sodium benzeneselenolate⁶ were known compounds and prepared according to the literature procedures.

Preparation of substrates

The alkynes were prepared according to the literature procedure.⁷ The unreported alkynes were showing as below:

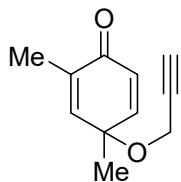


3,4-dimethyl-4-(prop-2-nyloxy)cyclohexa-2,5-dienone (1b):

To a solution of 3,4-dimethylphenol (1.22 g) in propargyl alcohol (10 mL) was added PhI(OAc)₂ (3.8 g) in three portions under argon atmosphere at 0 °C. The mixture was then allowed to room temperature for 12 h. The reaction was quenched with sat. NaHCO₃ and extracted with ethyl acetate; the organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:10) to give

title product (0.77 g, yield: 44%) as yellow oil.

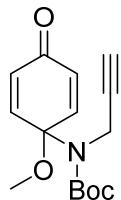
¹H NMR (300 MHz, CDCl₃) δ 6.79 (d, *J* = 10.1 Hz, 1H), 6.25 (dd, *J* = 10.1, 2.0 Hz, 1H), 6.19-6.10 (m, 1H), 3.80 (qd, *J* = 15.1, 2.5 Hz, 2H), 2.44 (t, *J* = 2.5 Hz, 1H), 1.99 (d, *J* = 1.4 Hz, 3H), 1.42 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 185.25, 159.51, 151.01, 130.27, 129.35, 79.60, 75.06, 74.87, 53.29, 25.54, 18.03. HRMS (ESI) calcd. for C₁₁H₁₃O₂ [M+H]⁺: 177.0910, found: 177.0913.



2,4-dimethyl-4-(prop-2-ynyloxy)cyclohexa-2,5-dienone (1c):

To a solution of 2,4-dimethylphenol (1.22 g) in propargyl alcohol (10 mL) was added PhI(OAc)₂ (3.8 g) in three portions under argon atmosphere at 0 °C. The mixture was then allowed to room temperature for 12 h. The reaction was quenched with sat. NaHCO₃ and extracted with ethyl acetate; the organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:10) to give title product (0.62 g, yield: 35%) as yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 6.80 (dd, *J* = 10.0, 3.1 Hz, 1H), 6.62-6.56 (m, 1H), 6.31 (d, *J* = 10.0 Hz, 1H), 3.97 (d, *J* = 2.4 Hz, 2H), 2.48 (t, *J* = 2.4 Hz, 1H), 1.92 (d, *J* = 1.4 Hz, 3H), 1.46 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 185.73, 150.38, 145.92, 137.22, 130.42, 80.51, 74.71, 73.59, 53.42, 26.42, 15.75. HRMS (ESI) calcd. for C₁₁H₁₃O₂ [M+H]⁺: 177.0910, found: 177.0913.



tert-butyl 1-methoxy-4-oxocyclohexa-2,5-dienyl(prop-2-ynyl)carbamate (1d):

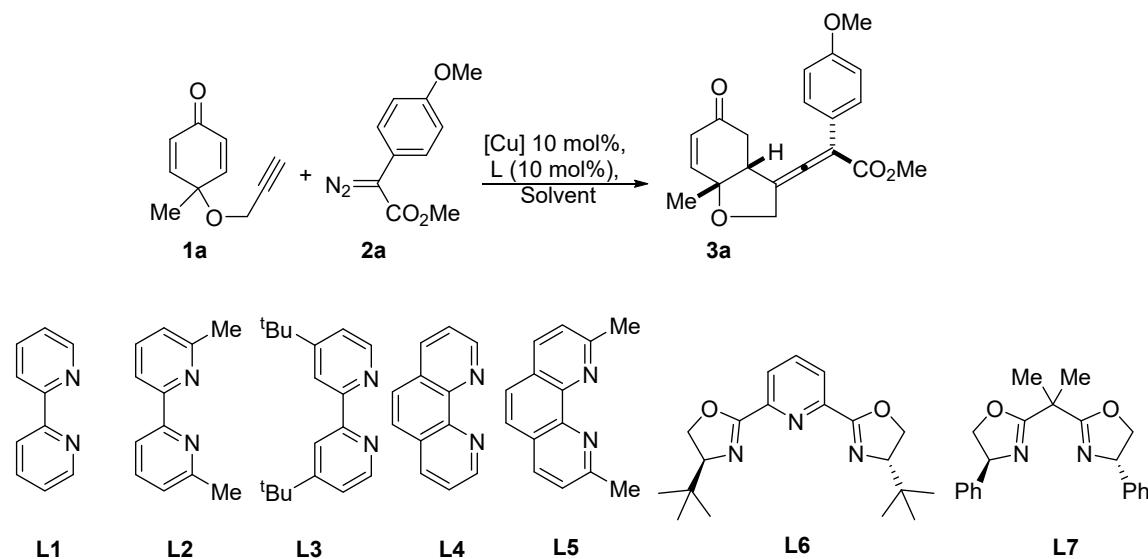
To a solution of tert-butyl (4-hydroxyphenyl)(prop-2-yn-1-yl)carbamate (2 g) in

MeOH (20 mL) was added PhI(OAc)₂ (3.1 g) in three portions under argon atmosphere at 0 °C. The mixture was then allowed to room temperature for 5 h. The reaction was quenched with sat. NaHCO₃ and extracted with ethyl acetate; the organic layers were washed with brine, dried over Na₂SO₄, filtered and concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20-1:10) to give title product (1 g, yield: 46%) as red oil.

¹H NMR (300 MHz, CDCl₃) δ 6.82 (d, *J* = 10.2 Hz, 2H), 6.31 (d, *J* = 10.2 Hz, 2H), 4.27 (d, *J* = 2.4 Hz, 2H), 3.27 (s, 3H), 2.22 (t, *J* = 2.4 Hz, 1H), 1.42 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 185.34, 153.24, 145.04, 129.49, 82.40, 82.24, 81.30, 70.71, 51.24, 32.03, 28.16. HRMS (ESI) calcd. for C₁₅H₂₀NO₄ [M+H]⁺: 278.1387, found: 278.1384.

Optimization of the reaction conditions

1. Optimization of the reaction conditions for allenoates^{a, b, c}

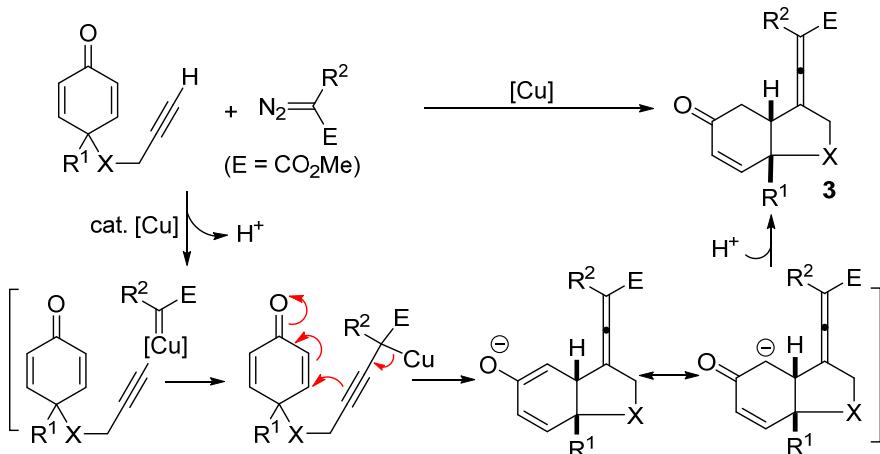


Entry	Catalyst	L	Solvent	Dr ^b	Yield (%) ^c
1	CuCl	-	MeCN	4:1	73
2	CuBr	-	MeCN	2.6:1	10
3	CuI	-	MeCN	4:1	87
4	CuOTf•1/2(C ₆ H ₆)	-	MeCN	-	<5
5	Cu(OAc) ₂	-	MeCN	-	<5
6	CuBr ₂	-	MeCN	-	<5

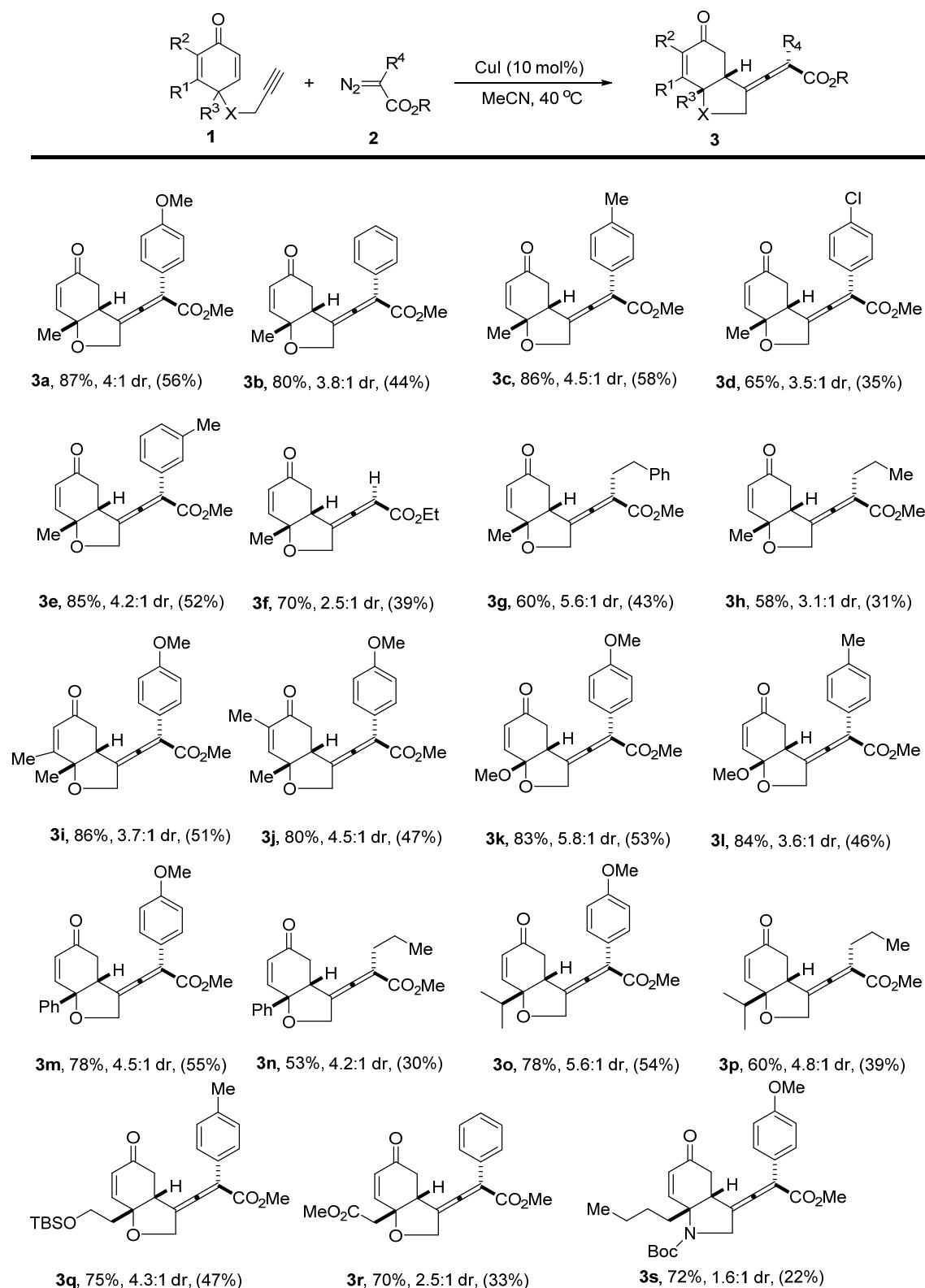
7	$\text{Cu}(\text{OTf})_2$	-	MeCN	-	<5
8	$\text{Cu}(\text{acac})_2$	-	MeCN	-	<5
9	$\text{Cu}(\text{MeCN})_4\text{PF}_6$	-	MeCN	2.5:1	15
10	CuI	L1	MeCN	3.8:1	86
11	CuI	L2	MeCN	-	<5
12	CuI	L3	MeCN	4.1:1	64
13	CuI	L4	MeCN	4.3:1	65
14	CuI	L5	MeCN	4.5:1	50
15	CuI	L6	MeCN	-	0
16	CuI	L7	MeCN	-	0
17	CuI	-	CH_2Cl_2	3.4:1	40
18	CuI	-	DCE	-	<5
19	CuI	-	Toluene	-	<5
20	CuI	-	dioxane	1.5:1	25

^aAll reactions were performed with **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (10 mol%), L (10 mol%) in solvent (5 mL) at 40 °C for 5 h. ^bDetermined by ¹H NMR analysis. ^cIsolated yields of two isomers.

2. Proposed reaction mechanism of allenolate formation

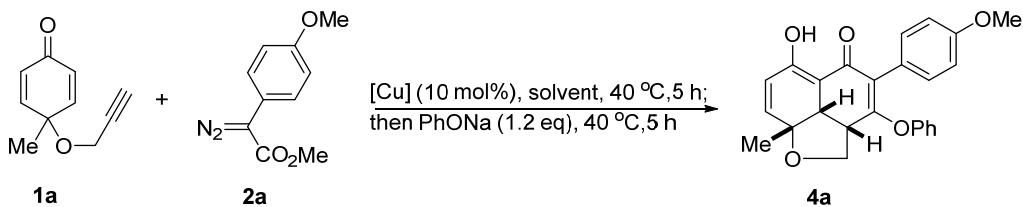


3. Substrate scope for allenoates 3^{a,b}



^aAll reactions were performed with **1** (0.5 mmol), **2** (0.6 mmol), CuI (10 mol%) in MeCN (5 mL) at 40 °C for 5-16 h. ^bCombined yields of two isomers, dr values were determined by ¹H NMR analysis; isolated yields of the major isomers were in brackets.

4. Optimization of the reaction conditions for tricyclic compounds^{a, b, c}

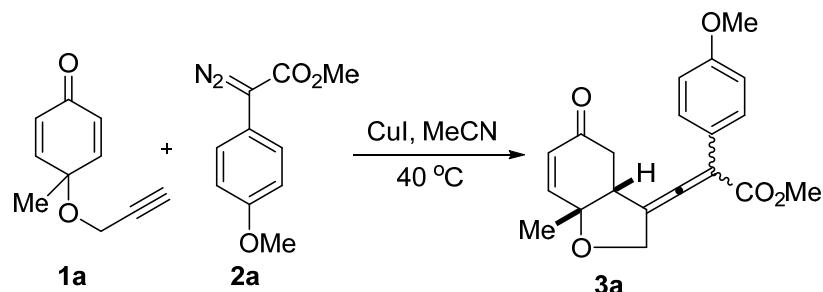


Entry	Catalyst	Solvent	Dr ^b	Yield (%) ^c
1	CuCl	MeCN	>20:1	67
2	CuBr	MeCN	-	<5
3	CuI	MeCN	>20:1	85
4	CuOTf•1/2(C ₆ H ₆)	MeCN	-	<5
5	Cu(OAc) ₂	MeCN	-	<5
6	CuBr ₂	MeCN	-	<5
7	Cu(OTf) ₂	MeCN	-	<5
8	Cu(acac) ₂	MeCN	-	<5
9	Cu(MeCN) ₄ PF ₆	MeCN	>20:1	20
10	CuI	CH ₂ Cl ₂	>20:1	35
11	CuI	DCE	-	<5
12	CuI	toluene	-	<5
13	CuI	dioxane	>20:1	20

^aAll reactions were performed with **1a** (0.5 mmol), **2a** (0.6 mmol), catalyst (10 mol%) in solvent (5 mL) at 40 °C for 5 h, followed by addition of PhONa (0.6 mmol). ^bDetermined by NMR analysis of crude products. ^cIsolated yields of **4a**

Initial studies for Scheme 2

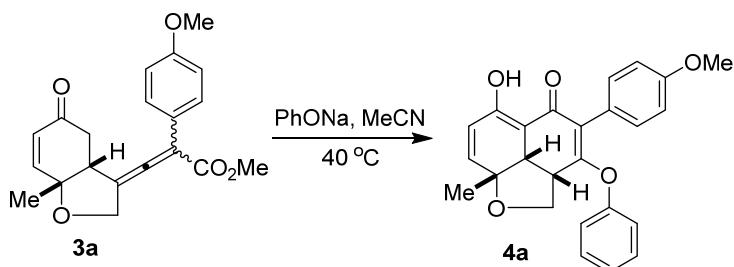
1. Scheme 2A for 3a



To a Schlenk tube was added CuI (9.5 mg, 0.05 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then **1a** (81 mg, 0.5 mmol) and **2a** (123mg, 0.6 mmol) in anhydrous MeCN (2 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 5 h. The reaction mixture was cooled and concentrated, the residue

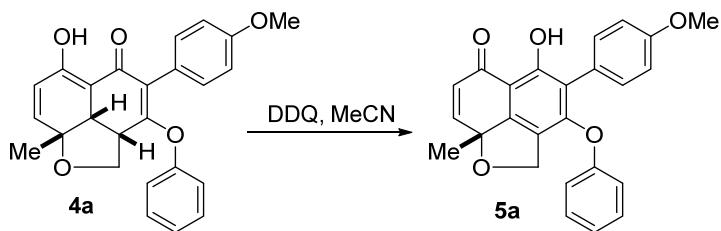
was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:10-1:4) to give **3a** (148 mg, yield: 87%; 4:1 dr) as a white solid. Mp: 152-154 °C. The major isomer of **3a** was obtained by recrystallization. ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.21 (m, 2H), 6.92-6.80 (m, 2H), 6.58 (dd, *J* = 10.3, 1.9 Hz, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 4.68 (dd, *J* = 12.6, 0.7 Hz, 1H), 4.40 (dd, *J* = 12.6, 2.0 Hz, 1H), 3.80 (d, *J* = 0.7 Hz, 6H), 3.42-3.33 (m, 1H), 2.81 (dd, *J* = 17.4, 1.8 Hz, 1H), 2.70 (dd, *J* = 17.4, 5.2 Hz, 1H), 1.58 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 200.91, 195.97, 166.86, 159.50, 150.87, 130.14, 129.48, 124.09, 113.79, 110.08, 108.21, 80.62, 67.07, 55.28, 52.47, 48.07, 37.00, 23.01. HRMS (ESI) calcd. for C₂₀H₂₁O₅ [M+H]⁺: 341.1384, found: 341.1388.

2. Scheme 2B for **4a** from **3a**



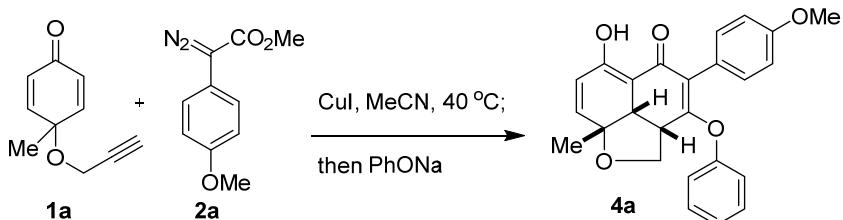
To a Schlenk tube was added **3a** (124 mg, 0.36 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then PhONa (51 mg, 0.44 mmol) was added; the reaction mixture was stirred at 40 °C for 5 h. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:10-1:5) to give **4a** (139 mg, yield: 95%) as a yellow solid. Mp: 135-137 °C. ¹H NMR (300 MHz, CDCl₃) δ 14.86 (s, 1H), 7.42-7.24 (m, 4H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.31 (d, *J* = 9.9 Hz, 1H), 6.17 (d, *J* = 9.9 Hz, 1H), 3.91-3.82 (m, 1H), 3.79 (s, 3H), 3.78-3.69 (m, 1H), 3.47-3.33 (m, 2H), 1.30 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.35, 168.60, 163.64, 158.99, 154.01, 141.60, 131.44, 130.01, 125.91, 125.23, 123.34, 123.29, 120.01, 113.50, 97.46, 78.49, 71.42, 55.23, 44.02, 42.18, 27.30. HRMS (ESI) calcd. for C₂₅H₂₂NaO₅ [M+Na]⁺: 425.1359, found: 425.1355.

3. Scheme 2C for **5a** from **4a**



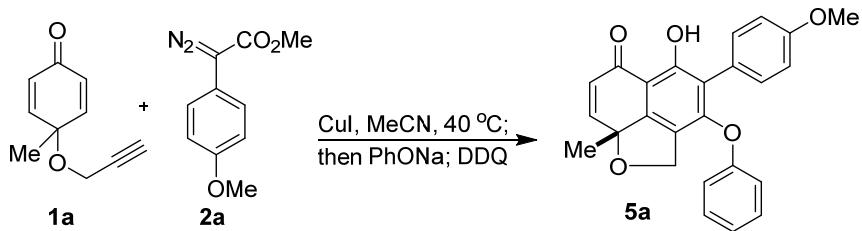
To a tube was added **4a** (60 mg, 0.15 mmol) and anhydrous MeCN (3 mL), then DDQ (51 mg, 0.225 mmol) was added in one portion. The mixture was stirred at room temperature for 1 h. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give **5a** (54 mg, yield: 90%). Mp: 158-160 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.57 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.35-7.27 (m, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.18 (d, *J* = 10.0 Hz, 1H), 4.43 (d, *J* = 12.3 Hz, 1H), 4.32 (d, *J* = 12.3 Hz, 1H), 3.82 (s, 3H), 1.50 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.60, 159.21, 158.97, 156.50, 154.77, 152.74, 150.35, 131.70, 129.90, 128.67, 124.29, 123.82, 120.27, 118.99, 118.75, 113.60, 108.24, 81.33, 69.95, 55.20, 27.57. HRMS (ESI) calcd. for C₂₅H₂₁O₅ [M+H]⁺: 401.1384, found: 401.1388.

4. Scheme 2D for **4a** (one-pot)



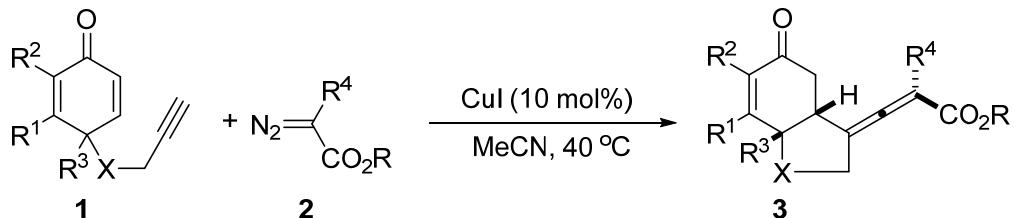
To a Schlenk tube was added CuI (9.5 mg, 0.05 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then **1a** (81 mg, 0.5 mmol) and **2a** (123mg, 0.6 mmol) in anhydrous MeCN (2 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 5 h; then PhONa (70 mg, 0.6 mmol) was added, the mixture was stirred for further 5 h at 40 °C. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give **4a** (171 mg, yield: 85%).

5. Scheme 2E for **5a** (one-pot)

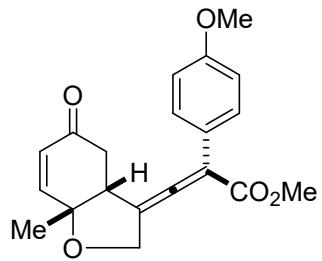


To a Schlenk tube was added CuI (9.5 mg, 0.05 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then **1a** (81 mg, 0.5 mmol) and **2a** (123mg, 0.6 mmol) in anhydrous MeCN (2 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 5 h; PhONa (70 mg, 0.6 mmol) was added and the mixture was stirred for further 5 h at 40 °C; DDQ (170 mg, 0.75 mmol) was added at room temperature and stirred for 1 h. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give **5a** (150 mg, yield: 75%).

General procedure for allenotes **3**



To a schlenk tube was added CuI (0.05 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then **1** (0.5 mmol) and **2** (0.6 mmol) in anhydrous MeCN (2 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 5-16 h. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5 or CH₂Cl₂: Petroleum ether = 1:5-3:1) to give **3**.

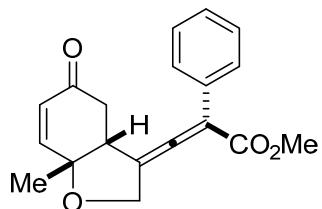


methyl 2-(4-methoxyphenyl)-3-7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)acrylate (3a):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a white solid (148 mg, combined yield: 87%; 4:1 dr).

Mp: 152-154°C. The major isomer was isolated (96 mg, yield: 56%).

¹H NMR (300 MHz, CDCl₃) δ 7.31-7.21 (m, 2H), 6.92-6.80 (m, 2H), 6.58 (dd, *J* = 10.3, 1.9 Hz, 1H), 6.02 (d, *J* = 10.3 Hz, 1H), 4.68 (dd, *J* = 12.6, 0.7 Hz, 1H), 4.40 (dd, *J* = 12.6, 2.0 Hz, 1H), 3.80 (d, *J* = 0.7 Hz, 6H), 3.42-3.33 (m, 1H), 2.81 (dd, *J* = 17.4, 1.8 Hz, 1H), 2.70 (dd, *J* = 17.4, 5.2 Hz, 1H), 1.58 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 200.91, 195.97, 166.86, 159.50, 150.87, 130.14, 129.48, 124.09, 113.79, 110.08, 108.21, 80.62, 67.07, 55.28, 52.47, 48.07, 37.00, 23.01. HRMS (ESI) calcd. for C₂₀H₂₁O₅ [M+H]⁺: 341.1384, found: 341.1388.

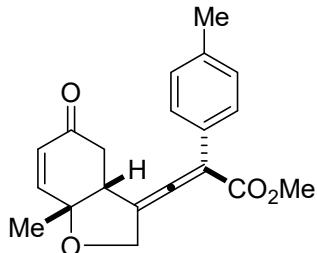


methyl 3-(7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-phenylacrylate (3b):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (124 mg, combined yield: 80%; 3.8:1 dr). The major isomer was isolated (69 mg, yield: 44%).

¹H NMR (300 MHz, CDCl₃) δ 7.37-7.23 (m, 5H), 6.57 (dd, *J* = 10.3, 1.9 Hz, 1H), 6.00 (dd, *J* = 10.3, 0.8 Hz, 1H), 4.70 (dd, *J* = 12.6, 0.9 Hz, 1H), 4.42 (dd, *J* = 12.6, 2.0 Hz, 1H), 3.81 (s, 3H), 3.46-3.35 (m, 1H), 2.85-2.75 (m, 1H), 2.70 (dd, *J* = 17.4, 5.1

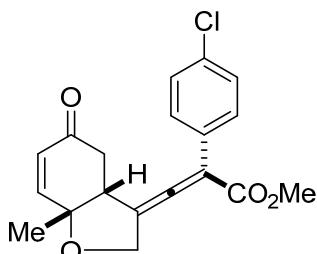
Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 201.38, 195.74, 166.57, 150.74, 132.01, 130.15, 128.33, 128.24, 128.16, 110.24, 108.65, 80.68, 67.03, 52.51, 48.16, 36.91, 22.98. HRMS (ESI) calcd. for $\text{C}_{19}\text{H}_{19}\text{O}_4$ [$\text{M}+\text{H}]^+$: 311.1278, found: 311.1282.



methyl 3-(7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-p-tolylacrylate (3c):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (139 mg, combined yield: 86%; 4.5:1 dr). The major isomer was isolated (94 mg, yield: 58%).

^1H NMR (400 MHz, CDCl_3) δ 7.22 (d, $J = 8.2$ Hz, 2H), 7.13 (d, $J = 8.2$ Hz, 2H), 6.57 (dd, $J = 10.3, 1.8$ Hz, 1H), 6.01 (d, $J = 10.3$ Hz, 1H), 4.69 (d, $J = 12.6$ Hz, 1H), 4.41 (dd, $J = 12.6, 1.9$ Hz, 1H), 3.80 (s, 3H), 3.39 (d, $J = 2.2$ Hz, 1H), 2.80 (dd, $J = 17.4, 1.7$ Hz, 1H), 2.70 (dd, $J = 17.4, 5.3$ Hz, 1H), 2.33 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 201.03, 195.64, 166.68, 150.68, 138.02, 130.13, 129.05, 128.98, 128.08, 110.11, 108.63, 80.61, 67.02, 52.37, 48.13, 36.91, 23.03, 21.16. HRMS (ESI) calcd. for $\text{C}_{20}\text{H}_{21}\text{O}_4$ [$\text{M}+\text{H}]^+$: 325.1434, found: 325.1431.

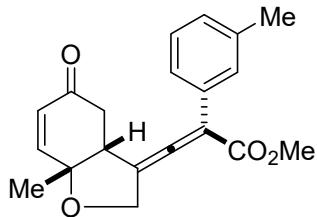


methyl 2-(4-chlorophenyl)-3-(7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)acrylate (3d):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the

title compound was isolated as yellow sticky oil (112 mg, combined yield: 65%; 3.5:1 dr). The major isomer was isolated (60 mg, yield: 35%).

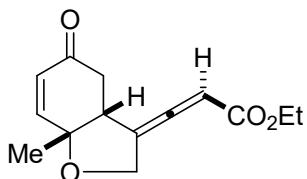
¹H NMR (400 MHz, CDCl₃) δ 7.43 (d, *J* = 8.6 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.58 (dd, *J* = 10.3, 1.8 Hz, 1H), 6.06 (d, *J* = 10.3 Hz, 1H), 4.70 (d, *J* = 12.7 Hz, 1H), 4.46 (dd, *J* = 12.7, 1.9 Hz, 1H), 3.70 (s, 3H), 3.33 (s, 1H), 2.79-2.71 (m, 1H), 2.66 (dd, *J* = 17.5, 5.2 Hz, 1H), 1.58 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 201.49, 195.13, 165.65, 150.34, 134.05, 130.64, 130.16, 129.75, 128.55, 110.61, 107.24, 80.73, 66.75, 52.16, 48.01, 36.17, 22.98. HRMS (ESI) calcd. for C₁₉H₁₈ClO₄ [M+H]⁺: 345.0888, found: 345.0891.



methyl 3-(7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-m-tolylacrylate (3e):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (138 mg, combined yield: 85%; 4.2:1 dr). The major isomer was isolated (85 mg, yield: 52%).

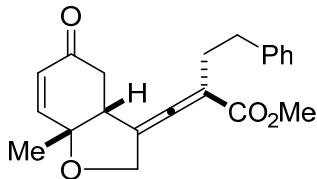
¹H NMR (400 MHz, CDCl₃) δ 7.27-7.04 (m, 4H), 6.57 (d, *J* = 10.3 Hz, 1H), 6.01 (d, *J* = 10.3 Hz, 1H), 4.69 (d, *J* = 12.6 Hz, 1H), 4.41 (d, *J* = 12.6 Hz, 1H), 3.80 (s, 3H), 3.39 (s, 1H), 2.82 (d, *J* = 17.5 Hz, 1H), 2.71 (dd, *J* = 17.5, 5.2 Hz, 1H), 2.35 (s, 3H), 1.58 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 201.32, 195.72, 166.67, 150.81, 138.12, 131.83, 130.18, 128.96, 128.89, 128.20, 125.26, 110.07, 108.73, 80.65, 67.05, 52.48, 48.06, 36.95, 23.00, 21.26. HRMS (ESI) calcd. for C₂₀H₂₁O₄ [M+H]⁺: 325.1434, found: 325.1431.



ethyl 3-(7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)acrylate (3f):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless oil (87 mg, combined yield: 70%; 2.5:1 dr). The major isomer was isolated (48 mg, yield: 39%).

¹H NMR (500 MHz, CDCl₃) δ 6.55 (dd, *J* = 10.3, 1.9 Hz, 1H), 6.03 (d, *J* = 10.3 Hz, 1H), 5.71 (dd, *J* = 9.0, 4.0 Hz, 1H), 4.62 (dd, *J* = 12.6, 3.2 Hz, 1H), 4.42 (ddd, *J* = 12.6, 4.1, 2.0 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.23 (s, 1H), 2.71 (dd, *J* = 17.6, 2.0 Hz, 1H), 2.63 (dd, *J* = 17.6, 5.2 Hz, 1H), 1.56 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 202.20, 194.94, 165.11, 150.18, 130.17, 109.13, 93.78, 80.63, 66.60, 61.12, 47.68, 35.94, 23.00, 13.99. HRMS (ESI) calcd. for C₁₄H₁₇O₄ [M+H]⁺: 249.1121, found: 249.1125.

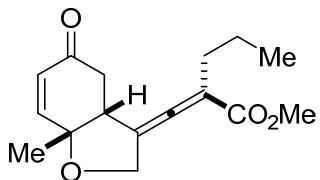


methyl 2-(7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)methylene-4-phenylbutanoate (3g):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (101 mg, combined yield: 60%; 5.6:1 dr). The major isomer was isolated (73 mg, yield: 43%).

¹H NMR (400 MHz, CDCl₃) δ 7.28-7.22 (m, 2H), 7.18-7.10 (m, 3H), 6.50 (dd, *J* = 10.3, 1.7 Hz, 1H), 6.01 (d, *J* = 10.3 Hz, 1H), 4.42 (d, *J* = 12.6 Hz, 1H), 3.85 (dd, *J* = 12.6, 1.7 Hz, 1H), 3.73 (s, 3H), 3.24 (s, 1H), 2.69-2.56 (m, 5H), 2.47-2.37 (m, 1H), 1.53 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 200.19, 196.39, 167.44, 150.90, 141.00, 129.88, 128.59, 128.29, 125.88, 109.10, 105.49, 80.43, 66.67, 52.25, 47.64, 36.89,

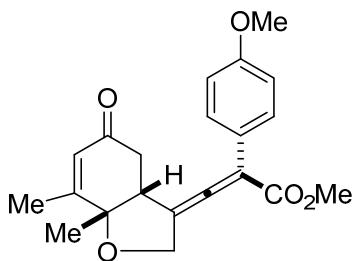
33.96, 30.56, 22.92. HRMS (ESI) calcd. for $C_{21}H_{23}O_4$ $[M+H]^+$: 339.1591, found: 339.1595.



methyl 2-(7a-methyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)methylene)pentanoate (3h):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (80 mg, combined yield: 58%; 3.1:1 dr). The major isomer was isolated (42 mg, yield: 31%).

1H NMR (400 MHz, $CDCl_3$) δ 6.55 (dd, $J = 10.3, 1.8$ Hz, 1H), 6.01 (d, $J = 10.3$ Hz, 1H), 4.62 (d, $J = 12.4$ Hz, 1H), 4.30 (dd, $J = 12.4, 1.8$ Hz, 1H), 3.72 (s, 3H), 3.28 (s, 1H), 2.66 (d, $J = 4.6$ Hz, 2H), 2.24-2.05 (m, 2H), 1.55 (s, 3H), 1.35-1.24 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.84, 196.25, 167.63, 150.89, 129.90, 108.65, 106.55, 80.50, 66.92, 52.19, 47.48, 36.74, 31.17, 22.99, 21.26, 13.67. HRMS (ESI) calcd. for $C_{16}H_{21}O_4$ $[M+H]^+$: 277.1434, found: 277.1438.

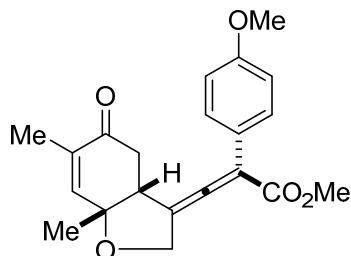


methyl 3-(7,7a-dimethyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-(4-methoxyphenyl)acrylate (3i):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (152 mg, combined yield: 86%; 3.7:1 dr). The major isomer was isolated (90 mg, yield: 51%).

1H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, 8.8 Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 5.93 (s, 1H), 4.65 (d, $J = 12.8$ Hz, 1H), 4.24 (dd, $J = 12.7, 1.9$ Hz, 1H), 3.80 (s, 3H), 3.79 (s,

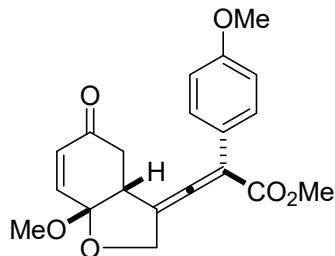
3H), 3.37 (d, J = 4.6 Hz, 1H), 2.80 (dd, J = 17.6, 1.5 Hz, 1H), 2.70 (dd, J = 17.6, 5.4 Hz, 1H), 1.97 (d, J = 1.0 Hz, 3H), 1.59 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 200.74, 195.51, 166.91, 161.09, 159.47, 129.50, 128.75, 124.17, 113.79, 110.08, 108.28, 82.61, 66.62, 55.28, 52.45, 49.00, 36.71, 22.12, 17.72. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{23}\text{O}_5$ [$\text{M}+\text{H}]^+$: 355.1540, found: 355.1543.



methyl 3-(6,7a-dimethyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-(4-methoxyphenyl)acrylate (3j):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a white solid (142 mg, combined yield: 80%; 4.5:1 dr). Mp: 81–83 °C. The major isomer was isolated (84 mg, yield: 47%).

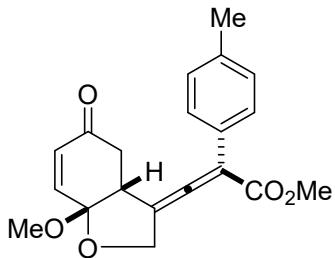
^1H NMR (400 MHz, CDCl_3) δ 7.25 (d, J = 8.7 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 6.34 (s, 1H), 4.67 (d, J = 12.6 Hz, 1H), 4.39 (d, J = 12.6 Hz, 1H), 3.80 (s, 6H), 3.34 (s, 1H), 2.81 (dd, J = 17.4, 2.0 Hz, 1H), 2.68 (dd, J = 17.4, 5.2 Hz, 1H), 1.75 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 201.00, 196.20, 166.85, 159.45, 146.05, 136.59, 129.71, 129.46, 124.29, 113.77, 110.38, 81.09, 66.90, 55.30, 52.43, 48.44, 36.95, 23.23, 15.93. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{23}\text{O}_5$ [$\text{M}+\text{H}]^+$: 355.1540, found: 355.1543.



methyl 3-(7a-methoxy-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-(4-methoxyphenyl)acrylate (3k):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as yellow sticky oil (148 mg, combined yield: 83%; 5.8:1 dr). The major isomer was isolated (94 mg, yield: 53%).

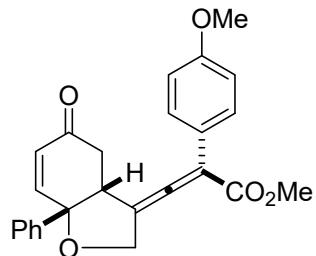
¹H NMR (400 MHz, CD₃CN) δ 7.37-7.30 (m, 2H), 6.93-6.83 (m, 3H), 6.02 (d, *J* = 10.4 Hz, 1H), 4.76-4.62 (m, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 3.58 (t, *J* = 7.4 Hz, 1H), 3.42 (s, 3H), 2.68-2.55 (m, 2H); ¹³C NMR (125 MHz, CD₃CN) δ 200.61, 196.08, 166.36, 159.57, 141.25, 130.03, 129.59, 124.58, 113.70, 108.59, 107.13, 103.54, 66.92, 54.98, 52.03, 49.20, 46.61, 39.22. HRMS (ESI) calcd. for C₂₀H₂₁O₆ [M+H]⁺: 357.1333, found: 357.1330.



methyl 3-(7a-methoxy-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-p-tolylacrylate (3l):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (143 mg, combined yield: 84%; 3.6:1 dr). The major isomer was isolated (78 mg, yield: 46%).

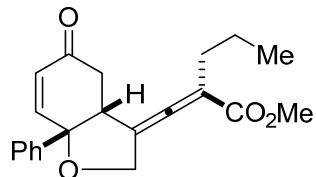
¹H NMR (400 MHz, CDCl₃) δ 7.27 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 10.5 Hz, 1H), 6.10 (d, *J* = 10.5 Hz, 1H), 4.79-4.64 (m, 2H), 3.81 (s, 3H), 3.61 (t, *J* = 7.1 Hz, 1H), 3.48 (s, 3H), 2.77-2.63 (m, 2H), 2.34 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 201.20, 196.13, 166.36, 140.97, 138.18, 130.58, 129.16, 129.04, 128.10, 108.21, 107.99, 103.48, 67.29, 52.46, 49.87, 46.67, 39.54, 21.16. HRMS (ESI) calcd. for C₂₀H₂₁O₅ [M+H]⁺: 341.1384, found: 341.1388.



methyl 2-(4-methoxyphenyl)-3-(5-oxo-7a-phenyl-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)acrylate (3m):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (157 mg, combined yield: 78%; 4.5:1 dr). The major isomer was isolated (110 mg, yield: 55%).

¹H NMR (400 MHz, CDCl₃) δ 7.58-7.51 (m, 2H), 7.46-7.37 (m, 3H), 7.29 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.70 (dd, *J* = 10.3, 1.9 Hz, 1H), 6.29 (d, *J* = 10.3 Hz, 1H), 4.94 (d, *J* = 12.5 Hz, 1H), 4.61 (dd, *J* = 12.5, 1.9 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.53 (s, 1H), 2.78-2.68 (m, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 200.54, 196.24, 165.28, 159.56, 148.37, 138.86, 131.53, 129.51, 128.91, 128.69, 125.38, 124.04, 113.84, 110.06, 84.20, 67.27, 55.30, 52.50, 50.17, 36.37. HRMS (ESI) calcd. for C₂₅H₂₃O₅ [M+H]⁺: 403.1540, found: 403.1544.

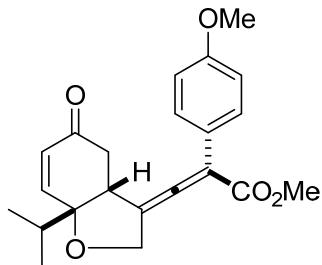


methyl 2-((5-oxo-7a-phenyl-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)methylene)pentanoate (3n):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (90 mg, combined yield: 53%; 4.2:1 dr). The major isomer was isolated (50 mg, yield: 30%).

¹H NMR (400 MHz, CDCl₃) δ 7.52 (d, *J* = 7.2 Hz, 2H), 7.45-7.33 (m, 3H), 6.66 (d, *J* = 10.3 Hz, 1H), 6.29 (d, *J* = 10.3 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 4.57 (d, *J* = 12.3 Hz, 1H), 3.65 (s, 3H), 3.35 (s, 1H), 2.63 (d, *J* = 3.6 Hz, 2H), 2.23 (t, *J* = 7.4 Hz, 2H), 1.48-1.39 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 199.72,

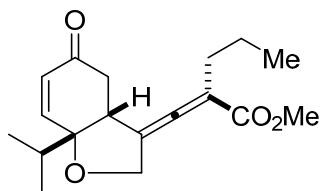
195.74, 167.13, 147.88, 139.10, 131.45, 128.86, 128.58, 125.36, 108.67, 106.34, 84.07, 67.05, 51.87, 49.53, 35.58, 30.39, 21.20, 13.55. HRMS (ESI) calcd. for C₂₁H₂₃O₄ [M+H]⁺: 339.1591, found: 339.1595.



methyl 3-(7a-isopropyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-(4-methoxyphenyl)acrylate (3o):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (144 mg, combined yield: 78%; 5.6:1 dr). The major isomer was isolated (100 mg, yield: 54%).

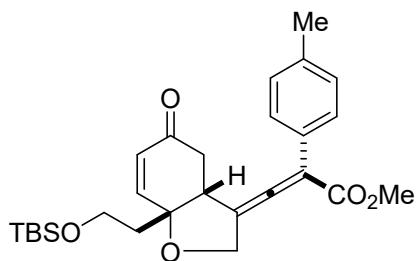
¹H NMR (300 MHz, CDCl₃) δ 7.30-7.23 (m, 2H), 6.89-6.81 (m, 2H), 6.62 (dd, *J* = 10.5, 1.9 Hz, 1H), 6.15 (d, *J* = 10.5 Hz, 1H), 4.65 (dd, *J* = 12.5, 0.9 Hz, 1H), 4.40 (dd, *J* = 12.5, 2.0 Hz, 1H), 3.80 (d, *J* = 2.3 Hz, 6H), 3.52 (s, 1H), 2.79-2.68 (m, 2H), 2.22-2.08 (m, 1H), 1.14-1.06 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 200.86, 196.42, 166.89, 159.49, 149.33, 131.63, 129.39, 124.12, 113.81, 111.42, 108.36, 84.97, 66.64, 55.28, 52.47, 44.01, 38.34, 35.39, 17.89, 17.18. HRMS (ESI) calcd. for C₂₂H₂₅O₅ [M+H]⁺: 369.1697, found: 369.1693.



methyl 2-(7a-isopropyl-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)methylenepentanoate (3p):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (91 mg, combined yield: 60%; 4.8:1 dr). The major isomer was isolated (59 mg, yield: 39%).

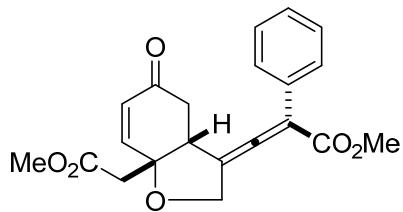
¹H NMR (400 MHz, CDCl₃) δ 6.57 (dd, *J* = 10.5, 1.7 Hz, 1H), 6.14 (d, *J* = 10.5 Hz, 1H), 4.53 (d, *J* = 12.3 Hz, 1H), 4.34 (dd, *J* = 12.3, 1.8 Hz, 1H), 3.62 (s, 3H), 3.33 (s, 1H), 2.64 (d, *J* = 3.8 Hz, 2H), 2.22 (t, *J* = 7.4 Hz, 2H), 2.16-2.06 (m, 1H), 1.50-1.38 (m, 2H), 1.12-1.04 (m, 6H), 0.91 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 200.03, 196.03, 167.24, 148.98, 131.53, 109.88, 106.21, 84.84, 66.40, 51.85, 43.13, 37.43, 35.29, 30.39, 21.24, 17.87, 17.14, 13.60. HRMS (ESI) calcd. for C₁₈H₂₅O₄ [M+H]⁺: 305.1747, found: 305.1751.



methyl 3-(7a-(2-(tert-butyldimethylsilyloxy)ethyl)-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-p-tolylacrylate (3q):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (176 mg, combined yield: 75%; 4.3:1 dr). The major isomer was isolated (110 mg, yield: 47%).

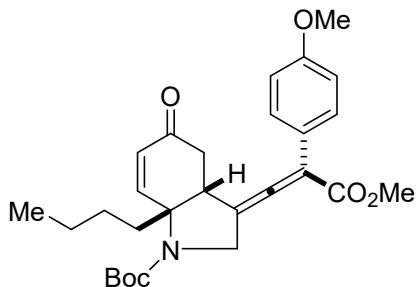
¹H NMR (300 MHz, CD₃CN) δ 7.29 (d, *J* = 8.2 Hz, 2H), 7.10 (d, *J* = 8.2 Hz, 2H), 6.54 (dd, *J* = 10.4, 1.9 Hz, 1H), 5.92 (dd, *J* = 10.4, 1.0 Hz, 1H), 4.59 (dd, *J* = 12.7, 1.1 Hz, 1H), 4.28 (dd, *J* = 12.7, 2.0 Hz, 1H), 3.89-3.71 (m, 2H), 3.60-3.55 (m, 1H), 3.55 (s, 3H), 2.73 (dd, *J* = 17.5, 5.2 Hz, 1H), 2.49 (dd, *J* = 17.5, 2.3 Hz, 1H), 2.26 (s, 3H), 2.05-1.92 (m, 2H), 0.82 (s, 9H), -0.00 (s, 6H); ¹³C NMR (75 MHz, CD₃CN) δ 200.55, 195.37, 165.76, 149.64, 137.68, 129.49, 129.27, 128.54, 128.27, 128.00, 110.36, 81.71, 65.89, 57.94, 51.07, 45.54, 38.67, 35.54, 24.88, 19.85, 17.43, -6.58. HRMS (ESI) calcd. for C₂₇H₃₇O₅Si [M+H]⁺: 469.2405, found: 469.2408.



methyl 3-(7a-(2-methoxy-2-oxoethyl)-5-oxo-4,5-dihydrobenzofuran-3(2H,3aH,7aH)-ylidene)-2-phenylacrylate (3r):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (129 mg, combined yield: 70%; 2.5:1 dr). The major isomer was isolated (60 mg, yield: 33%).

^1H NMR (400 MHz, CD_3CN) δ 7.35-7.26 (m, 5H), 6.74 (dd, $J = 10.4, 1.8$ Hz, 1H), 5.97 (d, $J = 10.4$ Hz, 1H), 4.62 (d, $J = 12.8$ Hz, 1H), 4.43 (dd, $J = 12.8, 1.8$ Hz, 1H), 3.76 (s, 3H), 3.73 (s, 1H), 3.67 (s, 3H), 2.98-2.78 (m, 3H), 2.61 (t, $J = 17.4$ Hz, 1H); ^{13}C NMR (75 MHz, CD_3CN) δ 200.50, 195.28, 169.23, 165.92, 148.00, 132.22, 130.01, 128.62, 127.90, 127.80, 127.62, 109.94, 80.09, 66.18, 51.69, 51.15, 45.85, 40.30, 35.77. HRMS (ESI) calcd. for $\text{C}_{21}\text{H}_{21}\text{O}_6$ [$\text{M}+\text{H}]^+$: 369.1333, found: 369.1337.



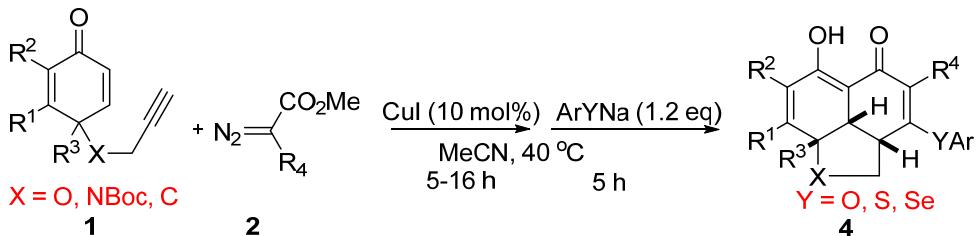
tert-butyl 7a-butyl-3-(3-methoxy-2-(4-methoxyphenyl)-3-oxoprop-1-enylidene)-5-oxo-3,3a,4,5-tetrahydro-2H-indole-1(7aH)-carboxylate (3s):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as colorless sticky oil (173 mg, combined yield: 72%; 1.6:1 dr). The major isomer was isolated (53 mg, yield: 22%).

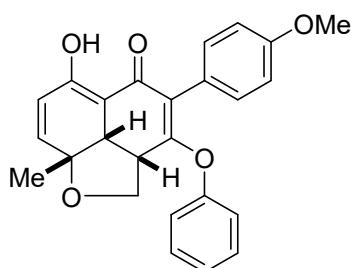
^1H NMR (400 MHz, CD_3CN) δ 7.41 (d, $J = 8.8$ Hz, 2H), 6.91 (d, $J = 8.8$ Hz, 3H), 5.86 (d, $J = 10.3$ Hz, 1H), 4.23 (d, $J = 14.5$ Hz, 1H), 4.13 (d, $J = 14.5$ Hz, 1H), 3.79 (s, 3H), 3.67-3.56 (m, 4H), 2.69 (dd, $J = 17.5, 5.6$ Hz, 1H), 2.47 (dd, $J = 17.5, 2.1$ Hz, 1H), 1.80-1.70 (m, 1H), 1.48 (s, 9H), 1.43-1.30 (m, 5H), 0.94 (t, $J = 6.6$ Hz, 3H); ^{13}C

NMR (125 MHz, CD₃CN) δ 202.56, 195.30, 166.01, 159.66, 153.36, 148.38, 129.74, 126.85, 124.49, 113.73, 107.26, 99.99, 64.41, 55.00, 54.73, 51.44, 48.64, 35.48, 29.33, 27.62, 25.27, 22.52, 17.75, 13.41. HRMS (ESI) calcd. for C₂₈H₃₆NO₆ [M+H]⁺: 482.2537, found: 482.2541.

General procedure for Scheme 3



To a 25 mL schlenk tube was added CuI (0.05 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then **1** (0.5 mmol) and **2** (0.6 mmol) in anhydrous MeCN (2 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 5-16 h; ArONa, ArSNa or PhSeNa (0.6 mmol) was added, the reaction mixture was stirred for further 5 h at 40 °C. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give **4**.

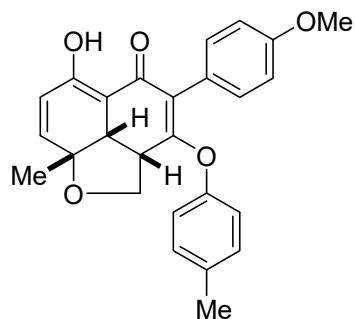


6-hydroxy-4-(4-methoxyphenyl)-8a-methyl-3-phenoxy-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4a):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (171 mg, yield: 85%). Mp: 135-137 °C.

¹H NMR (300 MHz, CDCl₃) δ 14.86 (s, 1H), 7.42-7.24 (m, 4H), 7.19 (t, *J* = 7.4 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 2H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.31 (d, *J* = 9.9 Hz, 1H), 6.17 (d, *J* = 9.9 Hz, 1H), 3.91-3.82 (m, 1H), 3.79 (s, 3H), 3.78-3.69 (m, 1H), 3.47-3.33 (m,

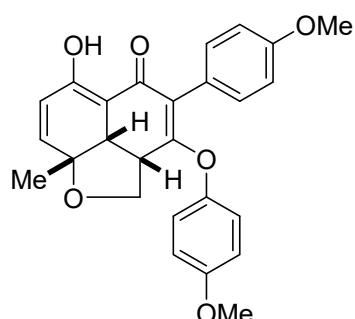
2H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.35, 168.60, 163.64, 158.99, 154.01, 141.60, 131.44, 130.01, 125.91, 125.23, 123.34, 123.29, 120.01, 113.50, 97.46, 78.49, 71.42, 55.23, 44.02, 42.18, 27.30. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{22}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 425.1359, found: 425.1355.



6-hydroxy-4-(4-methoxyphenyl)-8a-methyl-3-(p-tolyloxy)-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4b):

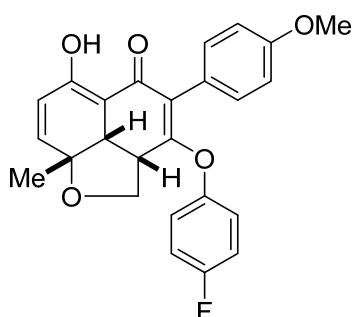
The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (183 mg, yield: 88%). Mp: 178-180 °C.

^1H NMR (400 MHz, CDCl_3) δ 14.86 (s, 1H), 7.28 (d, $J = 8.6$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 6.91 (d, $J = 8.6$ Hz, 2H), 6.86 (d, $J = 8.1$ Hz, 2H), 6.30 (d, $J = 9.9$ Hz, 1H), 6.17 (d, $J = 9.9$ Hz, 1H), 3.87-3.78 (m, 4H), 3.76-3.67 (m, 1H), 3.44-3.32 (m, 2H), 2.34 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.48, 168.34, 164.16, 158.94, 151.60, 141.45, 135.14, 131.46, 130.47, 125.93, 123.44, 122.66, 120.07, 113.50, 97.44, 78.45, 71.44, 55.23, 44.06, 42.02, 27.32, 20.83. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 439.1516, found: 439.1513.



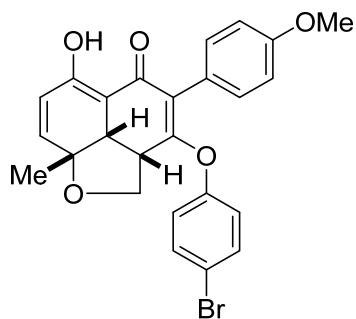
6-hydroxy-3-(4-methoxyphenoxy)-4-(4-methoxyphenyl)-8a-methyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4c):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (182 mg, yield: 84%). Mp: 157-159 °C. ^1H NMR (300 MHz, CDCl_3) δ 14.86 (s, 1H), 7.32-7.27 (m, 2H), 6.96-6.83 (m, 6H), 6.30 (d, J = 9.9 Hz, 1H), 6.17 (d, J = 9.9 Hz, 1H), 3.85-3.74 (m, 7H), 3.74-3.65 (m, 1H), 3.43-3.31 (m, 2H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.57, 168.13, 164.66, 158.92, 157.11, 147.15, 141.33, 131.49, 125.94, 123.49, 122.01, 121.54, 114.91, 113.52, 97.36, 78.46, 71.32, 55.67, 55.23, 44.07, 41.93, 27.29. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{24}\text{NaO}_6$ [$\text{M}+\text{Na}$] $^+$: 455.1465, found: 455.1462.



3-(4-fluorophenoxy)-6-hydroxy-4-(4-methoxyphenyl)-8a-methyl-2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4d):

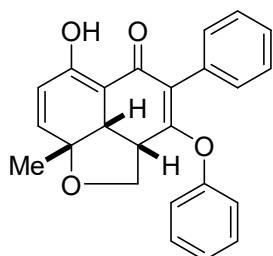
The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (162 mg, yield: 77%). Mp: 157-159 °C. ^1H NMR (400 MHz, CDCl_3) δ 14.80 (s, 1H), 7.28-7.20 (m, 2H), 7.07-6.98 (m, 2H), 6.96-6.87 (m, 4H), 6.32 (d, J = 9.9 Hz, 1H), 6.17 (d, J = 9.9 Hz, 1H), 3.88 (t, J = 7.6 Hz, 1H), 3.79 (s, 3H), 3.77-3.72 (m, 1H), 3.43-3.33 (m, 2H), 1.31 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.23, 168.66, 163.56, 161.36, 159.05, 158.12, 149.91 (d, J = 2.8 Hz), 141.60, 131.43, 125.91, 123.17 (d, J = 6.3 Hz), 121.39 (d, J = 8.5 Hz), 116.66 (d, J = 23.6 Hz), 113.53, 97.33, 78.54, 71.23, 55.23, 44.00, 42.15, 27.29. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{22}\text{FO}_5$ [$\text{M}+\text{H}$] $^+$: 421.1446, found: 421.1443.



3-(4-bromophenoxy)-6-hydroxy-4-(4-methoxyphenyl)-8a-methyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4e):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (187 mg, yield: 78%). Mp: 195-197 °C.

^1H NMR (400 MHz, CDCl_3) δ 14.79 (s, 1H), 7.43 (d, $J = 8.8$ Hz, 2H), 7.22 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.82 (d, $J = 8.8$ Hz, 2H), 6.33 (d, $J = 9.9$ Hz, 1H), 6.18 (d, $J = 9.9$ Hz, 1H), 3.95 (t, $J = 7.7$ Hz, 1H), 3.82-3.74 (m, 4H), 3.44-3.32 (m, 2H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 186.98, 169.03, 162.72, 159.12, 153.29, 141.81, 132.96, 131.36, 125.89, 124.18, 122.92, 121.27, 117.76, 113.53, 97.39, 78.57, 71.28, 55.24, 43.97, 42.27, 27.34. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{22}\text{BrO}_5$ $[\text{M}+\text{H}]^+$: 481.0645, found: 481.0642.

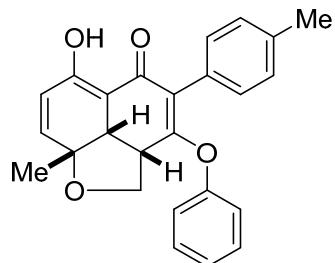


6-hydroxy-8a-methyl-3-phenoxy-4-phenyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4f):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (134 mg, yield: 72%). Mp: 142-144 °C.

^1H NMR (300 MHz, CDCl_3) δ 14.80 (s, 1H), 7.41-7.27 (m, 7H), 7.23-7.12 (m, 1H), 7.03-6.92 (m, 2H), 6.32 (d, $J = 9.8$ Hz, 1H), 6.18 (d, $J = 9.8$ Hz, 1H), 3.87 (t, $J = 7.7$ Hz, 1H), 3.77 (t, $J = 7.7$ Hz, 1H), 3.47-3.32 (m, 2H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.18, 168.55, 164.08, 153.92, 141.59, 131.28, 130.26, 130.01, 127.97,

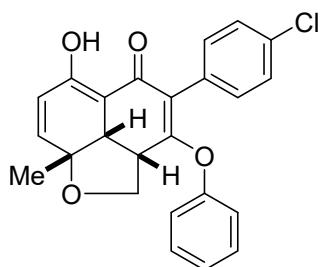
127.71, 125.90, 125.32, 123.65, 120.12, 97.37, 78.52, 71.40, 44.08, 42.13, 27.30.
 HRMS (ESI) calcd. for $C_{24}H_{20}NaO_4 [M+Na]^+$: 395.1254, found: 395.1250.



6-hydroxy-8a-methyl-3-phenoxy-4-p-tolyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4g):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (158 mg, yield: 82%). Mp: 128-130 °C.

1H NMR (300 MHz, $CDCl_3$) δ 14.85 (s, 1H), 7.41-7.31 (m, 2H), 7.25-7.15 (m, 5H), 7.02-6.93 (m, 2H), 6.31 (d, J = 9.9 Hz, 1H), 6.17 (d, J = 9.9 Hz, 1H), 3.85 (t, J = 7.7 Hz, 1H), 3.80-3.71 (m, 1H), 3.47-3.30 (m, 2H), 2.33 (s, 3H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 187.20, 171.23, 168.64, 163.78, 153.97, 141.58, 137.48, 130.05, 130.00, 128.77, 128.20, 125.94, 125.28, 120.14, 97.40, 78.49, 71.42, 44.09, 42.10, 27.31, 21.34. HRMS (ESI) calcd. for $C_{25}H_{23}O_4 [M+H]^+$: 387.1591, found: 387.1594.

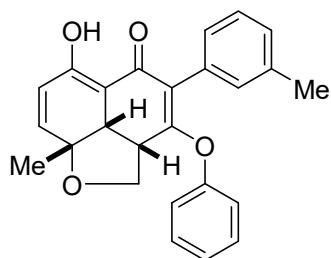


4-(4-chlorophenyl)-6-hydroxy-8a-methyl-3-phenoxy-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4h):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (112 mg, yield: 55%). Mp: 120-122 °C.

1H NMR (300 MHz, $CDCl_3$) δ 14.72 (s, 1H), 7.43-7.16 (m, 7H), 7.00-6.92 (m, 2H), 6.32 (d, J = 9.9 Hz, 1H), 6.18 (d, J = 9.9 Hz, 1H), 3.91-3.81 (m, 1H), 3.79-3.70 (m,

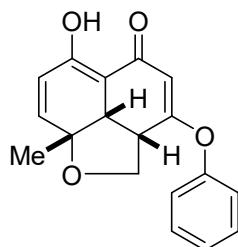
1H), 3.46-3.34 (m, 2H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 186.93, 168.49, 164.50, 153.71, 141.67, 133.59, 131.74, 130.12, 129.70, 128.19, 125.80, 125.55, 122.38, 120.09, 97.27, 78.53, 71.30, 44.00, 42.05, 27.25. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{19}\text{ClNaO}_4$ $[\text{M}+\text{Na}]^+$: 429.0864, found: 429.0861.



6-hydroxy-8a-methyl-3-phenoxy-4-m-tolyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4i):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (155 mg, yield: 80%). Mp: 130-132 °C.

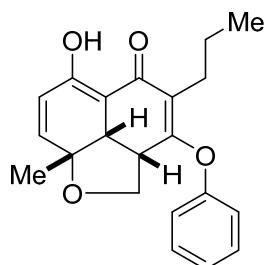
^1H NMR (300 MHz, CDCl_3) δ 14.80 (s, 1H), 7.40-7.32 (m, 2H), 7.29-7.15 (m, 2H), 7.15-7.06 (m, 3H), 7.01-6.92 (m, 2H), 3.91-3.80 (m, 1H), 3.80-3.70 (m, 1H), 3.46-3.32 (m, 2H), 2.34 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.28, 168.50, 164.05, 153.97, 141.55, 137.49, 131.21, 130.85, 129.97, 128.58, 127.90, 127.23, 125.91, 125.30, 123.78, 120.19, 97.36, 78.51, 71.41, 44.10, 42.14, 27.30, 21.56. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{23}\text{O}_4$ $[\text{M}+\text{H}]^+$: 387.1591, found: 387.1594.



6-hydroxy-8a-methyl-3-phenoxy-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4j):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (93 mg, yield: 63%). Mp: 162-165 °C.

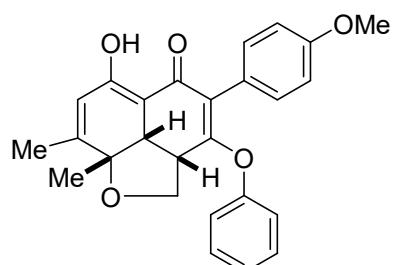
¹H NMR (400 MHz, CDCl₃) δ 14.27 (s, 1H), 7.42 (t, J = 7.7 Hz, 2H), 7.32-7.23 (m, 1H), 7.04 (d, J = 7.8 Hz, 2H), 6.32 (d, J = 9.9 Hz, 1H), 6.16 (d, J = 9.9 Hz, 1H), 5.11 (s, 1H), 4.45 (t, J = 7.9 Hz, 1H), 3.84-3.73 (m, 1H), 3.67-3.57 (m, 1H), 3.42 (d, J = 7.0 Hz, 1H), 1.45 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 188.42, 173.43, 166.66, 152.60, 140.99, 130.19, 126.46, 125.77, 121.30, 103.41, 96.94, 79.04, 70.48, 44.11, 43.60, 27.25. HRMS (ESI) calcd. for C₁₈H₁₇O₄ [M+H]⁺: 297.1121, found: 297.1124.



6-hydroxy-8a-methyl-3-phenoxy-4-propyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4k):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (73 mg, yield: 43%). Mp: 90-92 °C.

¹H NMR (300 MHz, CDCl₃) δ 14.80 (s, 1H), 7.40 (t, J = 7.9 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 6.98 (d, J = 7.9 Hz, 2H), 6.26 (d, J = 9.9 Hz, 1H), 6.14 (d, J = 9.9 Hz, 1H), 3.82-3.71 (m, 1H), 3.62-3.50 (m, 1H), 3.33-3.18 (m, 2H), 2.55-2.31 (m, 2H), 1.55-1.41 (m, 2H), 1.25 (s, 3H), 0.95 (t, J = 7.4 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 188.13, 167.74, 163.63, 154.27, 141.25, 130.07, 125.83, 125.00, 119.68, 97.43, 78.34, 71.20, 44.09, 41.64, 27.31, 24.44, 22.10, 14.20. HRMS (ESI) calcd. for C₂₁H₂₂NaO₄ [M+Na]⁺: 361.1410, found: 361.1414.

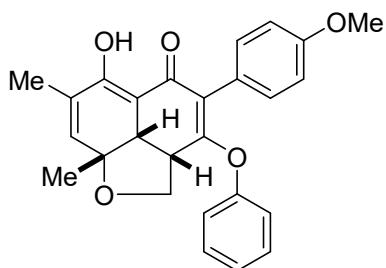


6-hydroxy-4-(4-methoxyphenyl)-8,8a-dimethyl-3-phenoxy-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one:

o[1,8-*bc*]furan-5(8a*H*)-one (**4l**):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (170 mg, yield: 82%). Mp: 165-167 °C.

¹H NMR (400 MHz, CDCl₃) δ 14.93 (s, 1H), 7.38-7.26 (m, 4H), 7.17 (t, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.98 (s, 1H), 3.90-3.81 (m, 1H), 3.79 (s, 3H), 3.77-3.67 (m, 1H), 3.47-3.35 (m, 2H), 2.01 (s, 3H), 1.28 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 185.94, 169.97, 162.79, 158.95, 154.22, 151.84, 131.42, 129.96, 125.01, 123.40, 123.37, 122.75, 119.80, 113.47, 96.29, 81.15, 71.26, 55.22, 44.65, 42.26, 25.64, 19.89. HRMS (ESI) calcd. for C₂₆H₂₄NaO₅ [M+Na]⁺: 439.1516, found: 439.1513.

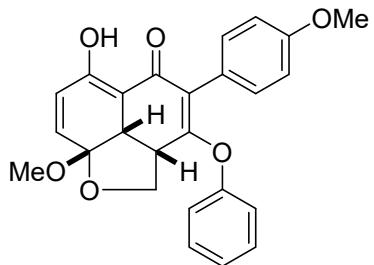


6-hydroxy-4-(4-methoxyphenyl)-7,8a-dimethyl-3-phenoxy-2,2a-dihydro-3H-naphth

o[1,8-*bc*]furan-5(8a*H*)-one (**4m**):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (156 mg, yield: 75%). Mp: 146-148 °C.

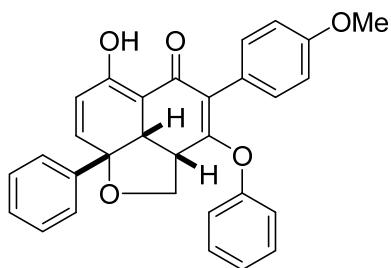
¹H NMR (300 MHz, CDCl₃) δ 15.56 (s, 1H), 7.39-7.26 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.00-6.84 (m, 4H), 6.10 (d, *J* = 1.3 Hz, 1H), 3.89-3.81 (m, 1H), 3.79 (s, 3H), 3.78-3.69 (m, 1H), 3.40-3.32 (m, 2H), 1.97 (d, *J* = 1.5 Hz, 3H), 1.27 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 186.10, 171.76, 163.28, 158.97, 154.02, 137.83, 134.05, 131.43, 129.99, 125.17, 123.43, 122.85, 120.02, 113.51, 97.32, 78.75, 71.20, 55.22, 44.15, 42.15, 27.31, 15.97. HRMS (ESI) calcd. for C₂₆H₂₄NaO₅ [M+Na]⁺: 439.1516, found: 439.1513.



6-hydroxy-8a-methoxy-4-(4-methoxyphenyl)-3-phenoxy-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4n):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (167 mg, yield: 80%). Mp: 152-154 °C.

¹H NMR (300 MHz, CDCl₃) δ 14.80 (s, 1H), 7.41-7.2 (m, 5H), 7.00-6.86 (m, 4H), 6.58 (d, *J* = 10.2 Hz, 1H), 6.23 (d, *J* = 10.2 Hz, 1H), 3.94-3.81 (m, 2H), 3.79 (s, 3H), 3.60-3.44 (m, 2H), 3.25 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 186.78, 168.39, 164.40, 159.00, 153.92, 134.12, 131.45, 130.05, 127.31, 125.29, 123.25, 120.22, 113.51, 104.99, 97.80, 72.25, 55.23, 49.19, 44.74, 39.83. HRMS (ESI) calcd. for C₂₅H₂₃O₆ [M+H]⁺: 419.1489, found: 419.1485.

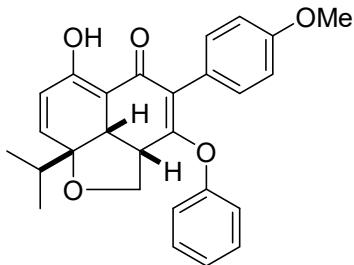


6-hydroxy-4-(4-methoxyphenyl)-3-phenoxy-8a-phenyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4o):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (169 mg, yield: 73%). Mp: 184-186 °C.

¹H NMR (300 MHz, CDCl₃) δ 14.85 (s, 1H), 7.36-7.20 (m, 9H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.92-6.81 (m, 4H), 6.32 (s, 2H), 4.02-3.86 (m, 2H), 3.84-3.72 (m, 4H), 3.13-2.98 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 187.49, 168.06, 164.04, 158.99, 153.80, 144.80, 140.58, 131.41, 129.83, 128.37, 127.60, 126.35, 125.20, 125.15, 123.37, 123.27, 119.92, 113.50, 97.26, 83.10, 72.12, 55.22, 46.15, 41.36. HRMS (ESI) calcd.

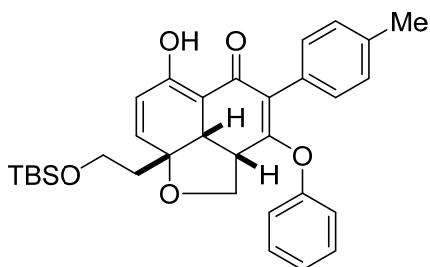
for $C_{30}H_{24}NaO_5 [M+Na]^+$: 487.1516, found: 487.1513.



6-hydroxy-8a-isopropyl-4-(4-methoxyphenyl)-3-phenoxy-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4p):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (155 mg, yield: 72%). Mp: 140-142 °C.

¹H NMR (300 MHz, CDCl₃) δ 14.76 (s, 1H), 7.43-7.24 (m, 4H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.01-6.82 (m, 4H), 6.37 (d, *J* = 10.1 Hz, 1H), 6.24 (d, *J* = 10.1 Hz, 1H), 3.79 (s, 3H), 3.78-3.67 (m, 2H), 3.59 (d, *J* = 6.9 Hz, 1H), 3.37-3.24 (m, 1H), 1.74-1.62 (m, 1H), 0.97 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.79, 167.98, 163.57, 158.97, 154.12, 137.78, 131.42, 129.97, 126.80, 125.10, 123.67, 123.33, 119.87, 113.49, 97.35, 83.98, 70.49, 55.22, 42.38, 40.47, 35.54, 19.68, 16.42. HRMS (ESI) calcd. for C₂₇H₂₇O₅ [M+H]⁺: 431.1853, found: 431.1857.

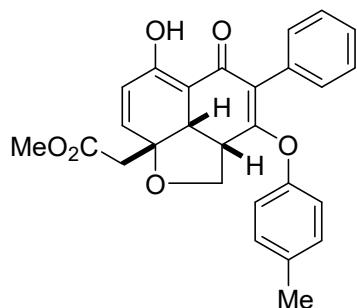


8a-(2-(tert-butyldimethylsilyloxy)ethyl)-6-hydroxy-3-(phenoxy)-4-p-tolyl-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4q):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (185 mg, yield: 70%). Mp: 66-68 °C.

¹H NMR (300 MHz, CDCl₃) δ 14.78 (s, 1H), 7.40-7.29 (m, 2H), 7.25-7.14 (m, 5H), 6.96 (dd, *J* = 8.5, 1.0 Hz, 2H), 6.39 (d, *J* = 9.9 Hz, 1H), 6.21 (d, *J* = 9.9 Hz, 1H),

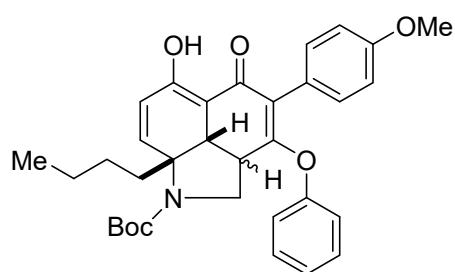
3.82-3.73 (m, 2H), 3.73-3.57 (m, 3H), 3.42-3.31 (m, 1H), 2.33 (s, 3H), 1.76 (t, J = 6.2 Hz, 2H), 0.88 (s, 9H), 0.02 (d, J = 0.8 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.47, 168.00, 163.92, 153.99, 140.39, 137.45, 130.06, 129.99, 128.77, 128.27, 126.55, 125.25, 123.80, 120.12, 97.37, 80.40, 70.68, 59.21, 42.03, 41.91, 25.89, 21.35, 18.19, -5.43. HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{39}\text{O}_5\text{Si} [\text{M}+\text{H}]^+$: 531.2561, found: 531.2565.



Methyl 2-(6-hydroxy-5-oxo-4-phenyl-3-(p-tolyloxy)-2a,3,5,8a-tetrahydro-2H-naphtho[1,8-bc]fur an-8a-yl)acetate (4r):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (144 mg, yield: 65%). Mp: 127-129 °C.

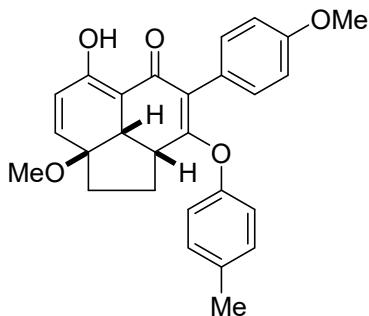
^1H NMR (300 MHz, CDCl_3) δ 14.76 (s, 1H), 7.42-7.27 (m, 5H), 7.15 (d, J = 8.4 Hz, 2H), 6.86 (d, J = 8.4 Hz, 2H), 6.49 (d, J = 9.9 Hz, 1H), 6.24 (d, J = 9.9 Hz, 1H), 3.87-3.76 (m, 2H), 3.76-3.68 (m, 1H), 3.65 (s, 3H), 3.42-3.29 (m, 1H), 2.63 (d, J = 14.3 Hz, 1H), 2.50 (d, J = 14.3 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.53, 169.82, 167.54, 164.10, 151.46, 138.52, 135.29, 131.29, 130.52, 130.25, 127.98, 127.71, 126.82, 123.43, 120.08, 97.07, 79.15, 71.28, 52.07, 44.29, 42.07, 41.68, 20.83. HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{25}\text{O}_6 [\text{M}+\text{H}]^+$: 445.1646, found: 445.1649.



tert-butyl 8a-butyl-6-hydroxy-4-(4-methoxyphenyl)-5-oxo-3-phenoxy-2,2a-dihydrobenzo[cd]indole-1(3H,5H,8aH)-carboxylate (4s):

The reaction was carried out according to the general procedure in 0.5 mmol scale to give a mixture of diastereo isomers (1.2:1 dr), the title compound was isolated as a yellow solid (168 mg, yield: 62%). Mp: 133-135 °C.

¹H NMR (400 MHz, CDCl₃) δ 15.34 (s, 1H), 15.31 (s, 0.8H), 7.39-7.27 (m, 5H), 7.26-7.12 (m, 4H), 7.02-6.95 (m, 3H), 6.94-6.80 (m, 5.2H), 6.53 (d, *J* = 10.0 Hz, 0.8H), 6.13 (dd, *J* = 10.0, 2.9 Hz, 1.8H), 3.79 (s, 5.3H), 3.64-3.13 (m, 7.4H), 2.24-2.12 (m, 1H), 2.02-1.89 (m, 0.8H), 1.44 (s, 7.2H), 1.40 (s, 9H), 1.36-1.01 (m, 9H), 0.91-0.81 (m, 5.4H); ¹³C NMR (75 MHz, CDCl₃) δ 186.91, 186.54, 171.43, 170.51, 164.29, 163.76, 159.01, 154.37, 153.97, 152.77, 152.47, 143.54, 142.96, 131.40, 131.37, 130.06, 129.90, 129.64, 125.16, 124.81, 124.68, 124.58, 123.90, 123.20, 123.17, 119.90, 119.46, 115.30, 113.51, 113.48, 97.02, 96.78, 80.62, 80.00, 63.30, 62.56, 55.22, 51.87, 51.60, 41.92, 40.66, 38.17, 37.38, 36.99, 35.97, 29.09, 28.83, 28.58, 28.49, 23.10, 23.05, 14.07, 13.95. HRMS (ESI) calcd. for C₃₃H₃₈NO₆ [M+H]⁺: 544.2694, found: 544.2697.

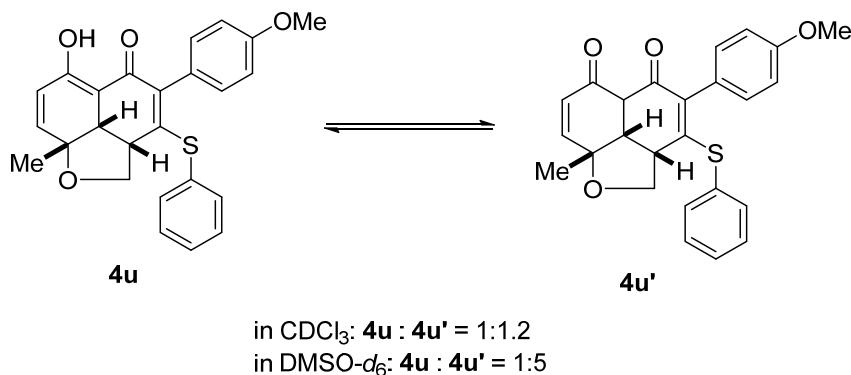


6-hydroxy-8a-methoxy-4-(4-methoxyphenyl)-3-(p-tolyloxy)-1,2,2a,8a-tetrahydroace naphthylen-5(3H)-one (4t):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (69 mg, yield: 32%). Mp: 156-158 °C.

¹H NMR (400 MHz, CDCl₃) δ 15.22 (s, 1H), 7.33-7.28 (m, 2H), 7.11 (d, *J* = 8.2 Hz, 2H), 6.90 (t, *J* = 8.8 Hz, 4H), 6.55 (d, *J* = 10.1 Hz, 1H), 6.07 (d, *J* = 10.1 Hz, 1H), 3.79 (s, 3H), 3.59 (d, *J* = 7.5 Hz, 1H), 3.19 (s, 3H), 3.13-3.04 (m, 1H), 2.33 (s, 3H), 2.02-1.84 (m, 3H), 1.78-1.66 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 187.16, 169.59, 169.33, 158.73, 151.75, 144.50, 134.74, 131.56, 130.22, 129.37, 126.10, 123.99,

120.55, 113.44, 98.50, 88.09, 55.21, 52.26, 40.42, 39.21, 38.23, 29.86, 20.82. HRMS (ESI) calcd. for $C_{27}H_{27}O_5$ [M+H]⁺: 431.1853, found: 431.1856.



6-hydroxy-4-(4-methoxyphenyl)-8a-methyl-3-(phenylthio)-2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4u):

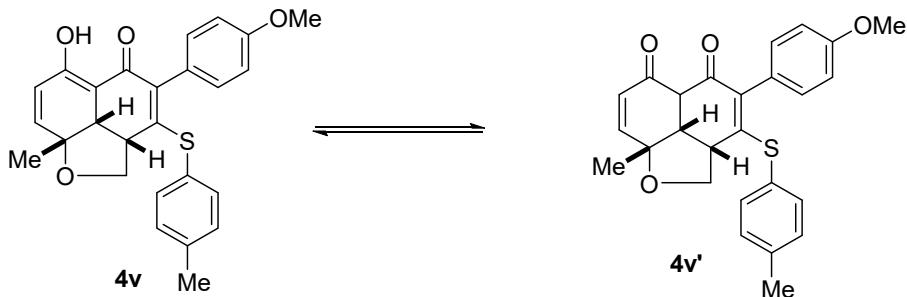
The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a white solid (163 mg, yield: 78%). Mp: 140-142 °C.

The ratio of enol form with keto form was 1:1.2 in $CDCl_3$ and 1:5 in $DMSO-d_6$.

¹H NMR (300 MHz, $CDCl_3$) δ 13.45 (s, 1H), 7.33-7.17 (m, 11H), 7.05-6.95 (m, 2.4H), 6.88 (d, $J = 8.7$ Hz, 2H), 6.81 (s, 4.4H), 6.67 (dd, $J = 10.2, 1.7$ Hz, 1.2H), 6.41 (d, $J = 10.1$ Hz, 1H), 6.15 (dd, $J = 10.2, 5.9$ Hz, 2.2H), 4.78-4.65 (m, 2.2H), 4.58-4.42 (m, 2.2H), 4.14 (s, 1H), 3.95 (d, $J = 2.2$ Hz, 1.2H), 3.79 (s, 6.6H), 3.67 (d, $J = 5.1$ Hz, 1.2H), 3.47-3.37 (m, 1.2H), 3.31 (s, 1H), 1.62 (s, 3.6H), 1.42 (s, 3H); ¹³C NMR (75 MHz, $CDCl_3$) δ 202.48, 195.56, 191.90, 167.90, 159.09, 158.95, 151.24, 149.15, 144.65, 140.98, 132.44, 131.72, 131.27, 130.81, 130.21, 129.43, 129.24, 128.49, 128.18, 127.93, 127.67, 126.58, 125.79, 124.54, 123.81, 114.41, 114.01, 101.70, 79.06, 77.27, 69.21, 65.68, 58.33, 55.33, 55.22, 55.16, 54.21, 49.28, 45.57, 27.64, 23.54.

¹H NMR (300 MHz, $DMSO-d_6$) δ 8.32 (s, 0.3H), 7.46-7.13 (m, 4.4H), 7.07-6.49 (m, 7.8H), 6.17 (d, $J = 10.2$ Hz, 1.2H), 4.75-4.45 (m, 1.4H), 4.30 (d, $J = 14.9$ Hz, 1H), 4.10-3.90 (m, 1.4H), 3.73 (s, 5.6H), 1.58 (s, 3H), 1.41 (s, 0.6H); ¹³C NMR (75 MHz, $DMSO-d_6$) δ 203.18, 194.40, 193.28, 168.69, 159.26, 158.84, 152.46, 151.17, 149.06, 143.15, 132.76, 132.42, 130.79, 130.57, 130.35, 130.17, 129.81, 129.52, 129.00,

128.17, 127.85, 125.96, 123.93, 121.88, 114.98, 114.22, 101.73, 79.74, 79.64, 77.37, 68.91, 65.42, 58.19, 55.59, 55.48, 54.80, 48.59, 45.45, 27.49, 23.16. HRMS (ESI) calcd. for C₂₅H₂₃O₄S [M+H]⁺: 419.1312, found: 419.1315.



in CDCl₃: **4v** : **4v'** = 1:1.1
in DMSO-d₆: **4v** : **4v'** = 1:5

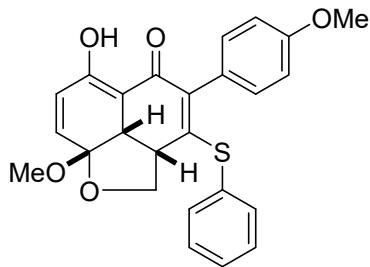
6-hydroxy-4-(4-methoxyphenyl)-8a-methyl-3-(p-tolylthio)-2,2a,2a1,8a-tetrahydro-5H-naphtho[1,8-bc]furan-5-one (4v):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a white solid (173 mg, yield: 80%). Mp: 171-173 °C. The ratio of enol form with keto form was 1:1.1 in CDCl₃ and 1:5 in DMSO-d₆.

¹H NMR (300 MHz, CDCl₃) δ 13.43 (s, 1H), 7.29 (s, 1.1H), 7.17-7.01 (m, 6.3H), 6.94-6.85 (m, 4.4H), 6.85-6.76 (m, 4.4H), 6.67 (dd, *J* = 10.3, 1.8 Hz, 1.1H), 6.40 (d, *J* = 10.3 Hz, 1H), 6.14 (dd, *J* = 10.3, 4.9 Hz, 2.1H), 4.76-4.65 (m, 2.1H), 4.58-4.48 (m, 1.1H), 4.45 (dd, *J* = 13.3, 1.5 Hz, 1H), 4.11 (s, 1H), 3.94-3.87 (m, 1.1H), 3.79 (s, 6.3H), 3.65 (d, *J* = 5.1 Hz, 1.1H), 3.45-3.36 (m, 1.1H), 3.29 (s, 1H), 2.33 (s, 3.3H), 2.32 (s, 3H), 1.62 (s, 3.3H), 1.41 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 202.65, 195.77, 191.86, 167.68, 159.05, 158.92, 151.20, 147.60, 143.54, 140.94, 138.30, 138.06, 132.30, 131.54, 130.22, 130.19, 130.00, 128.50, 128.47, 128.27, 128.13, 127.36, 127.18, 125.86, 124.50, 114.38, 113.97, 101.79, 78.98, 77.20, 69.20, 65.61, 58.35, 55.32, 55.21, 54.85, 53.99, 49.23, 45.53, 27.64, 23.54, 21.18, 21.16.

¹H NMR (300 MHz, DMSO-d₆) δ 8.32 (s, 0.2H), 7.25-7.08 (m, 3.2H), 6.96-6.75 (m, 7.4H), 6.56 (d, *J* = 10.3 Hz, 0.2H), 6.14 (d, *J* = 10.3 Hz, 1.2H), 4.65 (d, *J* = 15.0 Hz, 1H), 4.50 (s, 0.4H), 4.31 (d, *J* = 15.0 Hz, 1H), 4.02 (d, *J* = 4.8 Hz, 1H), 3.91 (s, 0.2H), 3.73 (s, 3.6H), 3.71-3.68 (m, 2.2H), 2.28 (s, 3.6H), 1.57 (s, 3H), 1.39 (s, 0.6H); ¹³C

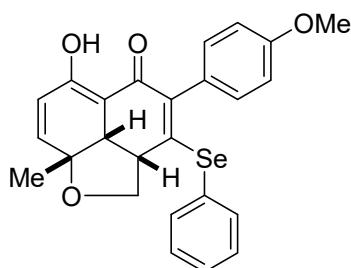
NMR (75 MHz, DMSO-*d*₆) δ 203.28, 193.19, 158.82, 152.40, 147.92, 137.72, 131.04, 130.77, 130.45, 129.57, 128.55, 128.12, 124.56, 114.20, 79.66, 68.89, 58.20, 55.48, 54.56, 48.54, 23.17, 21.07. HRMS (ESI) calcd. for C₂₆H₂₅O₄S [M+H]⁺: 433.1468, found: 433.1471.



6-hydroxy-8a-methoxy-4-(4-methoxyphenyl)-3-(phenylthio)-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4w):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a brown solid (156 mg, yield: 72%). Mp: 58-60 °C.

¹H NMR (300 MHz, CDCl₃) δ 13.30 (s, 1H), 7.36-7.18 (m, 7H), 6.87 (d, *J* = 8.7 Hz, 2H), 6.64 (d, *J* = 10.3 Hz, 1H), 6.22 (d, *J* = 10.3 Hz, 1H), 4.70 (dd, *J* = 12.6, 1.7 Hz, 1H), 4.50 (dd, *J* = 12.6, 1.7 Hz, 1H), 4.14 (s, 1H), 3.78 (s, 3H), 3.52 (s, 1H), 3.41 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 195.68, 166.68, 159.14, 146.76, 133.08, 132.34, 131.00, 129.44, 128.54, 127.77, 126.32, 125.64, 124.71, 114.45, 102.81, 102.33, 66.87, 55.45, 55.32, 48.99, 47.37. HRMS (ESI) calcd. for C₂₅H₂₃O₅S [M+H]⁺: 435.1261, found: 435.1261.

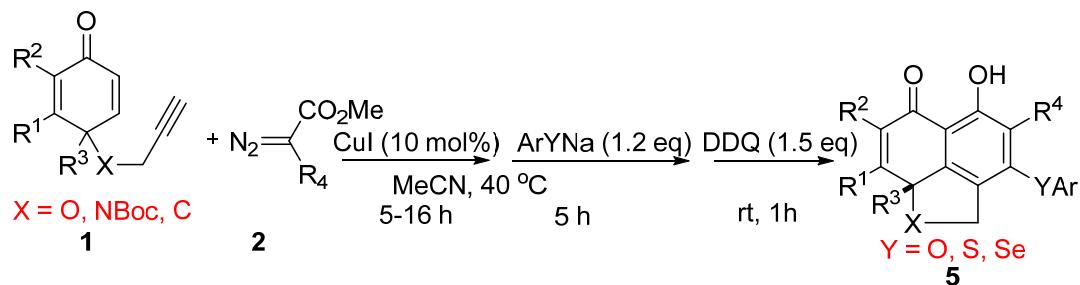


6-hydroxy-4-(4-methoxyphenyl)-8a-methyl-3-(phenylselanyl)-2,2a-dihydro-3H-naphtho[1,8-bc]furan-5(8aH)-one (4x):

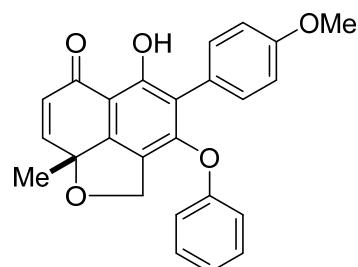
The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as yellow oil (102 mg, yield: 44%).

¹H NMR (400 MHz, CDCl₃) δ 14.73 (s, 1H), 7.65 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.22 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.25 (d, *J* = 9.9 Hz, 1H), 6.12 (d, *J* = 9.9 Hz, 1H), 3.85 (s, 3H), 3.69 (t, *J* = 7.7 Hz, 1H), 3.57-3.50 (m, 1H), 3.43-3.32 (m, 1H), 3.27 (d, *J* = 6.8 Hz, 1H), 1.12 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 181.18, 170.98, 159.65, 155.14, 142.07, 137.21, 135.41, 130.90, 129.97, 129.65, 127.43, 126.87, 126.18, 114.01, 97.81, 78.70, 71.46, 55.25, 44.32, 44.20, 26.96. HRMS (ESI) calcd. for C₂₅H₂₃O₄Se [M+H]⁺: 467.0756, found: 467.0759.

General procedure for Scheme 4



To a 25 mL schlenk tube was added CuI (0.05 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then **1** (0.5 mmol) and **2** (0.6 mmol) in anhydrous MeCN (2 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 5-16 h; ArONa, ArSNa or PhSeNa (0.6 mmol) was added, the mixture was stirred for further 5 h at 40 °C; DDQ (0.75 mmol) was added at room temperature and stirred for 1 h. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give **5**.

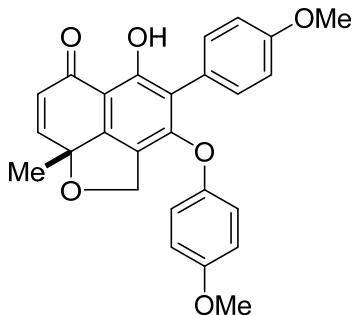


5-hydroxy-4-(4-methoxyphenyl)-8a-methyl-3-phenoxy-2,8a-dihydro-6H-naphtho[1,

8-bcfuran-6-one (5a):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (150 mg, yield: 75%). Mp: 158-160 °C.

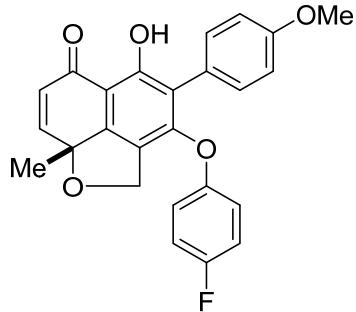
¹H NMR (400 MHz, CDCl₃) δ 10.57 (s, 1H), 7.38 (d, *J* = 8.7 Hz, 2H), 7.35-7.27 (m, 3H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 8.7 Hz, 2H), 6.18 (d, *J* = 10.0 Hz, 1H), 4.43 (d, *J* = 12.3 Hz, 1H), 4.32 (d, *J* = 12.3 Hz, 1H), 3.82 (s, 3H), 1.50 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.60, 159.21, 158.97, 156.50, 154.77, 152.74, 150.35, 131.70, 129.90, 128.67, 124.29, 123.82, 120.27, 118.99, 118.75, 113.60, 108.24, 81.33, 69.95, 55.20, 27.57. HRMS (ESI) calcd. for C₂₅H₂₁O₅ [M+H]⁺: 401.1384, found: 401.1388.



5-hydroxy-3-(4-methoxyphenoxy)-4-(4-methoxyphenyl)-8a-methyl-2,8a-dihydro-6H-naphtho[1,8-bcfuran-6-one (5b):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (168 mg, yield: 78%). Mp: 192-194 °C.

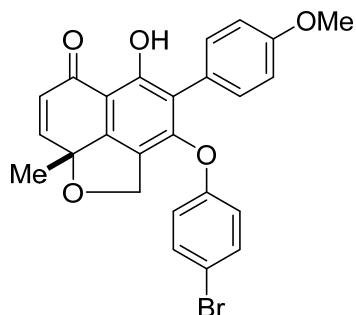
¹H NMR (400 MHz, CDCl₃) δ 10.58 (s, 1H), 7.40 (d, *J* = 9 Hz, 2H), 7.29 (d, *J* = 10.0 Hz, 1H), 6.97 (dd, *J* = 8.7, 2.8 Hz, 4H), 6.85 (d, *J* = 9.0 Hz, 2H), 6.17 (d, *J* = 10.0 Hz, 1H), 4.37 (d, *J* = 12.3 Hz, 1H), 4.26 (d, *J* = 12.3 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.48 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 187.53, 159.21, 158.96, 156.49, 155.85, 152.87, 150.22, 150.05, 131.75, 128.65, 124.02, 120.66, 119.46, 117.81, 114.82, 113.61, 107.84, 81.22, 70.04, 55.67, 55.20, 27.60. HRMS (ESI) calcd. for C₂₆H₂₃O₆ [M+H]⁺: 431.1489, found: 431.1492.



3-(4-fluorophenoxy)-5-hydroxy-4-(4-methoxyphenyl)-8a-methyl-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5c):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (142 mg, yield: 68%). Mp: 209-211 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.56 (s, 1H), 7.36 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 10.0 Hz, 1H), 7.05-6.89 (m, 6H), 6.18 (d, *J* = 10.0 Hz, 1H), 4.46 (d, *J* = 12.2 Hz, 1H), 4.35 (d, *J* = 12.2 Hz, 1H), 3.82 (s, 3H), 1.50 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.57, 160.77, 159.13 (d, *J* = 16.5 Hz), 157.54, 154.83, 152.86, 152.47 (d, *J* = 2.6 Hz), 150.35, 131.66, 128.65, 123.69, 120.36 (d, *J* = 8.3 Hz), 120.18, 118.42, 116.49 (d, *J* = 23.5 Hz), 113.63, 108.32, 81.35, 69.90, 55.21, 27.58. HRMS (ESI) calcd. for C₂₅H₂₀FO₅ [M+H]⁺: 419.1289, found: 419.1285.

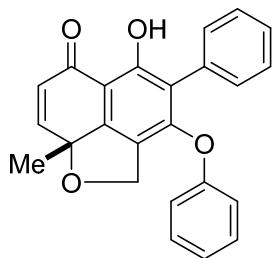


3-(4-bromophenoxy)-5-hydroxy-4-(4-methoxyphenyl)-8a-methyl-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5d):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (168 mg, yield: 70%). Mp: 230-231 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.55 (s, 1H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 3H), 6.93 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 6.19 (d, *J* = 10.0 Hz, 1H), 4.55 (d, *J* = 12.2 Hz, 1H), 4.43 (d, *J* = 12.2 Hz, 1H), 3.81 (s, 3H), 1.52 (s, 3H); ¹³C

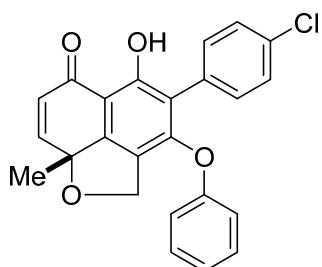
NMR (75 MHz, CDCl₃) δ 187.60, 159.24, 159.06, 155.69, 153.85, 152.78, 150.46, 132.84, 131.59, 128.66, 123.49, 120.81, 120.15, 119.13, 116.63, 113.64, 108.69, 81.45, 69.92, 55.21, 27.59. HRMS (ESI) calcd. for C₂₅H₂₀BrO₅ [M+H]⁺: 479.0489, found: 479.0493.



5-hydroxy-8a-methyl-3-phenoxy-4-phenyl-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5e):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (126 mg, yield: 68%). Mp: 139-141 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.56 (s, 1H), 7.49-7.38 (m, 4H), 7.37-7.26 (m, 4H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.19 (d, *J* = 10.0 Hz, 1H), 4.43 (d, *J* = 12.3 Hz, 1H), 4.32 (d, *J* = 12.3 Hz, 1H), 1.51 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.57, 159.13, 156.45, 154.74, 153.10, 150.36, 131.81, 130.57, 129.90, 128.66, 128.06, 127.67, 124.35, 120.55, 119.06, 118.67, 108.23, 81.34, 69.95, 27.57. HRMS (ESI) calcd. for C₂₄H₁₉O₄ [M+H]⁺: 371.1278, found: 371.1282.

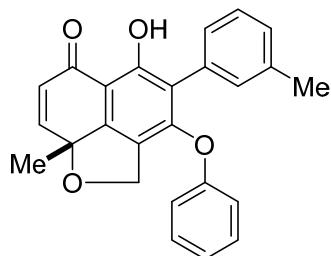


4-(4-chlorophenyl)-5-hydroxy-8a-methyl-3-phenoxy-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5f):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (101 mg, yield: 50%). Mp: 189-191 °C.

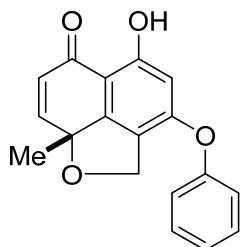
¹H NMR (400 MHz, CDCl₃) δ 10.58 (s, 1H), 7.43-7.28 (m, 7H), 7.15 (t, *J* = 7.4 Hz,

1H), 7.00 (d, J = 7.9 Hz, 2H), 6.19 (d, J = 10.0 Hz, 1H), 4.42 (d, J = 12.3 Hz, 1H), 4.31 (d, J = 12.3 Hz, 1H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.53, 158.99, 156.24, 154.60, 153.45, 150.43, 133.58, 132.01, 130.23, 129.99, 128.59, 128.32, 124.54, 119.24, 118.98, 118.65, 108.25, 81.32, 69.90, 27.53. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{18}\text{ClO}_4$ $[\text{M}+\text{H}]^+$: 405.0888, found: 405.0884.



5-hydroxy-8a-methyl-3-phenoxy-4-(m-tolyl)-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5g):

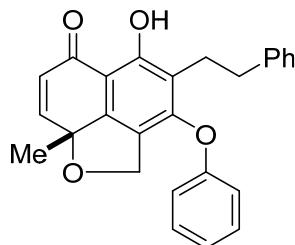
The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (133 mg, yield: 69%). Mp: 147-149 °C. ^1H NMR (400 MHz, CDCl_3) δ 10.54 (s, 1H), 7.36-7.27 (m, 4H), 7.25-7.20 (m, 2H), 7.15 (d, J = 7.9 Hz, 2H), 7.01 (d, J = 7.9 Hz, 2H), 6.18 (d, J = 10.0 Hz, 1H), 4.41 (d, J = 12.3 Hz, 1H), 4.31 (d, J = 12.3 Hz, 1H), 2.37 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.55, 159.15, 156.50, 154.86, 152.98, 150.32, 137.58, 131.69, 131.17, 129.86, 128.67, 128.54, 127.97, 127.52, 124.34, 120.69, 119.17, 118.59, 108.17, 81.32, 69.95, 27.56, 21.56. HRMS (ESI) calcd. for $\text{C}_{25}\text{H}_{21}\text{O}_4$ $[\text{M}+\text{H}]^+$: 385.1434, found: 385.1437.



5-hydroxy-8a-methyl-3-phenoxy-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5h):

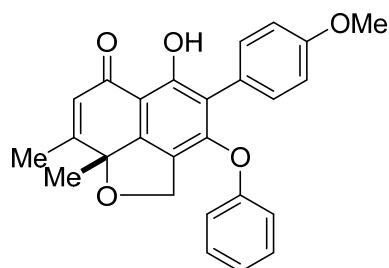
The reaction was carried out according to the general procedure in 0.5 mmol scale, the

title compound was isolated as a yellow solid (85 mg, yield: 58%). Mp: 112-114 °C.
¹H NMR (400 MHz, CDCl₃) δ 10.12 (s, 1H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.33-7.21 (m, 2H), 7.10 (d, *J* = 7.7 Hz, 2H), 6.25 (s, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 4.92 (d, *J* = 12.1 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 1.53 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.10, 161.91, 158.93, 154.67, 154.53, 150.21, 130.16, 128.64, 125.47, 120.60, 117.83, 107.59, 103.15, 81.71, 69.78, 27.58. HRMS (ESI) calcd. for C₁₈H₁₅O₄ [M+H]⁺: 295.0965, found: 295.0969.



5-hydroxy-8a-methyl-4-phenethyl-3-phenoxy-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5i):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (92 mg, yield: 46%). Mp: 104-106 °C.
¹H NMR (400 MHz, CDCl₃) δ 10.48 (s, 1H), 7.35 (t, *J* = 7.9 Hz, 2H), 7.29-7.14 (m, 7H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.15 (d, *J* = 10.0 Hz, 1H), 4.36 (d, *J* = 12.2 Hz, 1H), 4.24 (d, *J* = 12.2 Hz, 1H), 3.04 (dd, *J* = 9.9, 6.1 Hz, 2H), 2.89 (dd, *J* = 9.9, 6.1 Hz, 2H), 1.45 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.62, 159.68, 156.42, 155.47, 151.67, 150.31, 142.16, 129.96, 128.66, 128.57, 128.28, 125.84, 124.36, 119.45, 118.93, 118.14, 107.96, 81.23, 69.87, 35.24, 27.54, 25.39. HRMS (ESI) calcd. for C₂₆H₂₃O₄ [M+H]⁺: 399.1591, found: 399.1595.

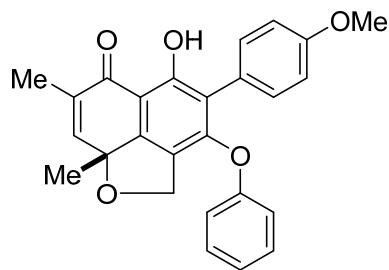


5-hydroxy-4-(4-methoxyphenyl)-8,8a-dimethyl-3-phenoxy-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one:

o[1,8-bc]furan-6-one (5j):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (155 mg, yield: 75%). Mp: 162-164 °C.

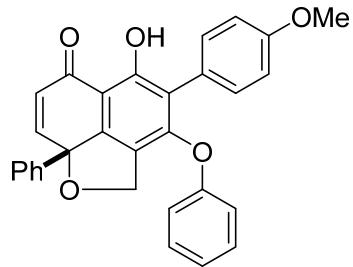
¹H NMR (400 MHz, CDCl₃) δ 10.66 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.31 (t, *J* = 7.9 Hz, 2H), 7.12 (t, *J* = 7.4 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 5.96 (d, *J* = 1.4 Hz, 1H), 4.43 (d, *J* = 12.3 Hz, 1H), 4.32 (d, *J* = 12.3 Hz, 1H), 3.81 (s, 3H), 2.16 (d, *J* = 1.2 Hz, 3H), 1.51 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.92, 164.11, 158.98, 158.92, 156.51, 154.08, 153.14, 131.69, 129.86, 125.24, 124.15, 123.95, 120.18, 118.91, 118.25, 113.57, 108.27, 83.36, 69.82, 55.20, 27.31, 17.39. HRMS (ESI) calcd. for C₂₆H₂₃O₅ [M+H]⁺: 415.1540, found: 415.1544.



5-hydroxy-4-(4-methoxyphenyl)-7,8a-dimethyl-3-phenoxy-2,8a-dihydro-6H-naphthalen-6-one (5k):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (145 mg, yield: 70%). Mp: 68-70 °C.

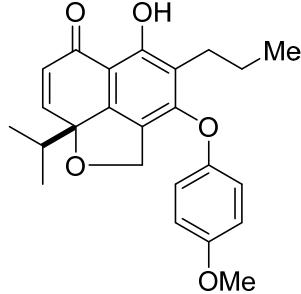
¹H NMR (400 MHz, CDCl₃) δ 10.72 (s, 1H), 7.42-7.28 (m, 4H), 7.17-7.06 (m, 2H), 6.97 (dd, *J* = 22.4, 8.3 Hz, 4H), 4.41 (d, *J* = 12.2 Hz, 1H), 4.30 (d, *J* = 12.2 Hz, 1H), 3.82 (s, 3H), 1.98 (d, *J* = 0.9 Hz, 3H), 1.47 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 188.21, 159.12, 158.93, 156.55, 154.55, 153.19, 145.49, 135.35, 131.69, 129.87, 124.21, 123.97, 120.13, 118.96, 118.69, 113.59, 108.02, 80.78, 69.65, 55.20, 27.42, 16.18. HRMS (ESI) calcd. for C₂₆H₂₃O₅ [M+H]⁺: 415.1540, found: 415.1544.



5-hydroxy-4-(4-methoxyphenyl)-3-phenoxy-8a-phenyl-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5l):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (155 mg, yield: 67%). Mp: 80-82 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.66 (s, 1H), 7.43-7.19 (m, 10H), 7.08 (t, *J* = 7.4 Hz, 1H), 6.93 (dd, *J* = 15.9, 8.3 Hz, 4H), 6.15 (d, *J* = 9.9 Hz, 1H), 4.30 (d, *J* = 12.0 Hz, 1H), 4.22 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 188.38, 159.00, 158.91, 156.24, 154.91, 150.46, 149.44, 138.90, 131.73, 129.86, 128.86, 128.23, 127.85, 125.77, 124.30, 123.77, 120.55, 119.97, 118.99, 113.61, 109.28, 84.32, 70.21, 55.21. HRMS (ESI) calcd. for C₃₀H₂₃O₅ [M+H]⁺: 463.1540, found: 463.1544.

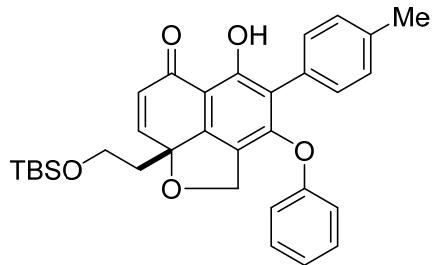


5-hydroxy-8a-isopropyl-3-(4-methoxyphenoxy)-4-propyl-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5m):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (89 mg, yield: 45%). Mp: 75-77 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.38 (s, 1H), 7.08 (d, *J* = 10.2 Hz, 1H), 6.98 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 6.26 (d, *J* = 10.2 Hz, 1H), 4.30 (d, *J* = 12.2 Hz, 1H), 4.21 (d, *J* = 12.2 Hz, 1H), 3.82 (s, 3H), 2.81-2.61 (m, 2H), 2.02-1.92 (m, 1H), 1.68-1.57 (m, 2H), 0.99 (dd, *J* = 9.5, 7.2 Hz, 6H), 0.73 (d, *J* = 6.8 Hz, 3H); ¹³C NMR

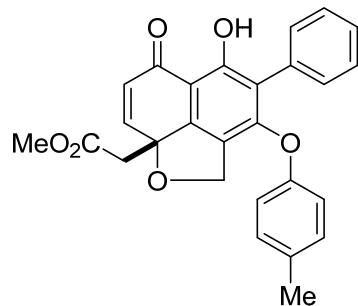
(75 MHz, CDCl₃) δ 187.84, 159.08, 156.39, 156.34, 150.24, 150.19, 146.61, 130.89, 120.50, 119.54, 117.93, 114.81, 108.96, 87.10, 70.42, 55.67, 37.03, 25.04, 22.47, 18.02, 17.28, 14.26. HRMS (ESI) calcd. for C₂₄H₂₇O₅ [M+H]⁺: 395.1853, found: 395.1857.



8a-(2-((tert-butyldimethylsilyl)oxy)ethyl)-5-hydroxy-3-phenoxy-4-(p-tolyl)-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5n):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as sticky yellow oil (159 mg, yield: 60%).

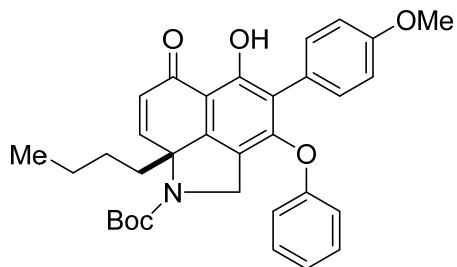
¹H NMR (400 MHz, CDCl₃) δ 10.54 (s, 1H), 7.39-7.27 (m, 5H), 7.22 (d, J = 7.9 Hz, 2H), 7.13 (t, J = 7.4 Hz, 1H), 7.00 (d, J = 7.7 Hz, 2H), 6.19 (d, J = 10.1 Hz, 1H), 4.39-4.30 (m, 2H), 3.82-3.66 (m, 2H), 2.36 (s, 3H), 2.09-2.00 (m, 1H), 1.93-1.83 (m, 1H), 0.86 (s, 9H), 0.02 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 187.68, 159.01, 156.61, 154.62, 152.51, 149.85, 137.38, 130.37, 129.87, 128.88, 128.74, 128.63, 124.25, 120.56, 119.03, 118.76, 108.71, 83.05, 70.22, 59.01, 44.15, 25.86, 21.39, 18.19, -5.39, -5.44. HRMS (ESI) calcd. for C₃₂H₃₇O₅Si [M+H]⁺: 529.2405, found: 529.2408.



methyl 2-(5-hydroxy-6-oxo-4-phenyl-3-(p-tolyl)oxy)-2H-naphtho[1,8-bc]furan-8a(6H)-yl acetate (5o):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the

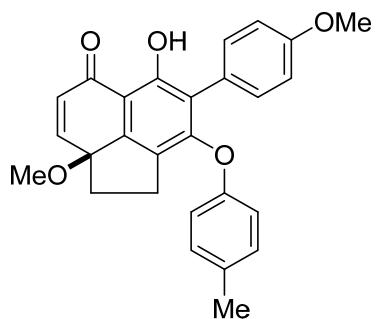
title compound was isolated as a yellow solid (135 mg, yield: 61%). Mp: 178-180 °C.
¹H NMR (400 MHz, CDCl₃) δ 10.52 (s, 1H), 7.55 (d, *J* = 10.1 Hz, 1H), 7.49-7.38 (m, 4H), 7.34 (t, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 6.25 (d, *J* = 10.1 Hz, 1H), 4.36 (dd, *J* = 29.2, 12.5 Hz, 2H), 3.68 (s, 3H), 2.93 (d, *J* = 14.6 Hz, 1H), 2.61 (d, *J* = 14.6 Hz, 1H), 2.33 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 187.18, 169.19, 159.09, 155.32, 154.09, 150.61, 148.20, 134.36, 131.71, 130.56, 130.39, 129.58, 128.07, 127.73, 120.72, 119.22, 118.55, 108.28, 81.23, 70.72, 52.15, 45.72, 20.79. HRMS (ESI) calcd. for C₂₇H₂₃O₆ [M+H]⁺: 443.1489, found: 443.1493.



tert-butyl 8a-butyl-5-hydroxy-4-(4-methoxyphenyl)-6-oxo-3-phenoxy-6,8a-dihydrobenzo[cd]indole-1(2H)-carboxylate (5p):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as yellow oil (146 mg, yield: 54%).

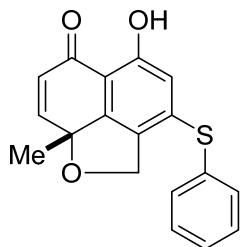
¹H NMR (400 MHz, CDCl₃) δ 10.96 (s, 1H), 7.97 (dd, *J* = 127.5, 10.1 Hz, 1H), 7.43-7.20 (m, 4H), 7.07 (t, *J* = 7.2 Hz, 1H), 6.92 (d, *J* = 7.9 Hz, 4H), 6.24 (d, *J* = 10.1 Hz, 1H), 4.29-4.11 (m, 1H), 3.99-3.86 (m, 1H), 3.80 (s, 3H), 2.37-2.19 (m, 1H), 1.57-1.34 (m, 10H), 1.25-1.16 (m, 2H), 1.13-0.99 (m, 2H), 0.84 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 188.17, 187.86, 159.56, 159.40, 159.01, 156.98, 156.88, 153.90, 153.69, 153.64, 150.46, 149.46, 149.35, 131.57, 129.88, 129.69, 128.52, 128.30, 123.72, 123.59, 123.54, 123.46, 121.82, 121.54, 117.77, 117.56, 113.56, 110.14, 109.90, 81.16, 80.38, 67.64, 67.18, 55.19, 52.38, 51.87, 44.44, 42.19, 28.56, 28.36, 26.65, 26.55, 22.51, 22.44, 14.07. HRMS (ESI) calcd. for C₃₃H₃₆NO₆ [M+H]⁺: 542.2537, found: 542.2533.



6-hydroxy-2a-methoxy-7-(4-methoxyphenyl)-8-(p-tolyloxy)-2,2a-dihydroacenaphthylene-5(1H)-one (5q):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (64 mg, yield: 30%). Mp: 143-145 °C.

^1H NMR (400 MHz, CDCl_3) δ 11.00 (s, 1H), 7.35 (d, $J = 8.7$ Hz, 2H), 7.06 (d, $J = 8.3$ Hz, 2H), 6.91 (d, $J = 8.7$ Hz, 2H), 6.88 (d, $J = 10.0$ Hz, 1H), 6.79 (d, $J = 8.3$ Hz, 2H), 6.48 (d, $J = 10.0$ Hz, 1H), 3.80 (s, 3H), 2.96 (s, 3H), 2.76-2.66 (m, 1H), 2.43-2.32 (m, 2H), 2.30 (s, 3H), 2.11-2.01 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 188.49, 158.89, 158.32, 155.98, 155.17, 146.93, 144.06, 132.65, 132.37, 131.54, 130.13, 127.15, 124.04, 122.77, 117.18, 113.50, 112.06, 79.29, 55.18, 51.21, 39.56, 29.19, 20.66. HRMS (ESI) calcd. for $\text{C}_{27}\text{H}_{25}\text{O}_5$ [$\text{M}+\text{H}]^+$: 429.1697, found: 429.1693.

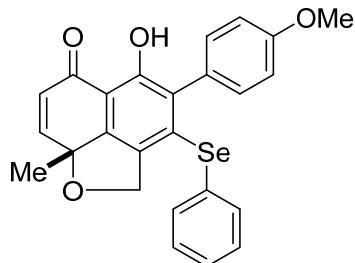


(5-hydroxy-8a-methyl-3-(phenylthio)-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5r):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as yellow oil (95 mg, yield: 61%).

^1H NMR (400 MHz, CDCl_3) δ 9.97 (s, 1H), 7.57-7.48 (m, 2H), 7.46-7.38 (m, 3H), 7.30 (d, $J = 10.0$ Hz, 1H), 6.41 (s, 1H), 6.13 (d, $J = 10.0$ Hz, 1H), 4.86 (d, $J = 12.2$ Hz, 1H), 4.79 (d, $J = 12.2$ Hz, 1H), 1.51 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.64, 159.63, 151.91, 150.52, 142.94, 134.38, 130.22, 129.87, 129.50, 128.53, 127.20,

113.35, 109.86, 81.58, 70.54, 27.63. HRMS (ESI) calcd. for $C_{18}H_{15}O_3S$ $[M+H]^+$: 311.0736, found: 311.0739.

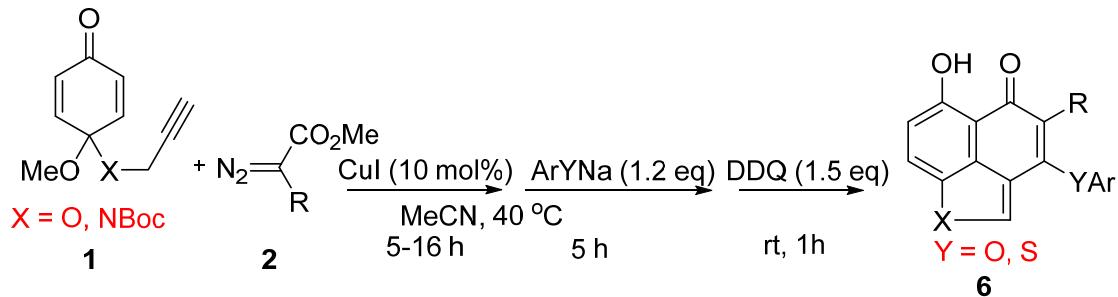


5-hydroxy-4-(4-methoxyphenyl)-8a-methyl-3-(phenylselanyl)-2,8a-dihydro-6H-naphtho[1,8-bc]furan-6-one (5s):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as yellow oil (58 mg, yield: 25%).

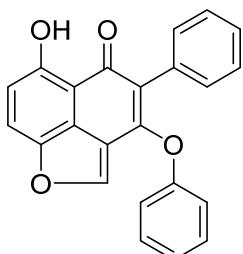
1H NMR (400 MHz, $CDCl_3$) δ 10.39 (s, 1H), 7.54-7.44 (m, 2H), 7.40-7.22 (m, 5H), 7.22-6.92 (m, 3H), 6.16 (d, J = 10.0 Hz, 1H), 4.37 (d, J = 12.6 Hz, 1H), 4.10 (d, J = 12.6 Hz, 1H), 3.86 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.33, 159.46, 156.30, 150.79, 150.21, 139.44, 134.57, 131.52, 130.30, 129.77, 129.38, 128.81, 128.62, 128.49, 128.09, 114.11, 110.53, 81.19, 71.68, 55.26, 27.45. HRMS (ESI) calcd. for $C_{25}H_{21}O_4Se$ $[M+H]^+$: 465.0600, found: 465.0604.

General procedure for Scheme 5



To a 25 mL schlenk tube was added CuI (0.05 mmol) and anhydrous MeCN (3 mL) under argon atmosphere, then **1** (0.5 mmol) and **2** (0.6 mmol) in anhydrous MeCN (2 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 5-16 h; ArONa or ArSNa (0.6 mmol) was added, the mixture was stirred for further 5 h at 40 °C; DDQ (0.75 mmol) was added at room temperature and stirred for 1 h. The reaction

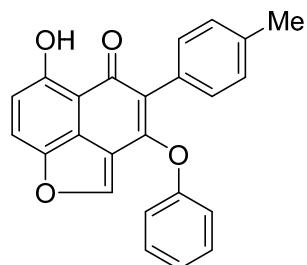
mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give **6**.



6-hydroxy-3-phenoxy-4-phenyl-5H-naphtho[1,8-bc]furan-5-one (6a):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (106 mg, yield: 60%). Mp: 169-171 °C.

¹H NMR (300 MHz, CDCl₃) δ 10.90 (s, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.52-7.29 (m, 8H), 7.24-7.19 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 1H), 6.69 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 187.00, 158.54, 156.68, 155.86, 146.89, 145.54, 132.02, 130.66, 130.10, 128.07, 127.86, 126.34, 126.02, 125.95, 120.66, 118.42, 114.78, 110.83, 109.54. HRMS (ESI) calcd. for C₂₃H₁₅O₄ [M+H]⁺: 355.0965, found: 355.0969.

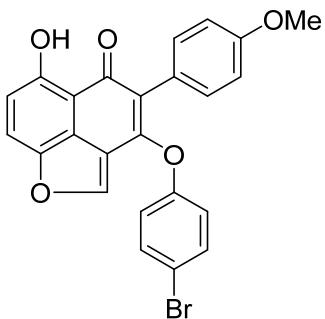


6-hydroxy-3-phenoxy-4-(p-tolyl)-5H-naphtho[1,8-bc]furan-5-one (6b):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (120 mg, yield: 65%). Mp: 192-194 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.92 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.46-7.34 (m, 4H), 7.33-7.26 (m, 3H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.68 (s, 1H), 2.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 187.14, 158.54, 156.44, 155.95, 146.71, 145.54, 137.62, 130.48, 130.06, 128.93, 128.86, 126.45, 126.03, 125.85, 120.65, 118.33, 114.74, 110.92, 109.57, 21.40. HRMS (ESI) calcd. for C₂₄H₁₇O₄

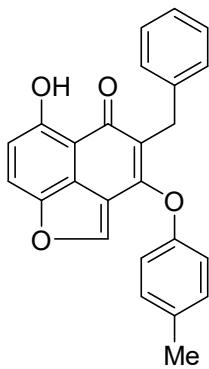
$[M+H]^+$: 369.1121, found: 369.1125.



3-(4-bromophenoxy)-6-hydroxy-4-(4-methoxyphenyl)-5H-naphtho[1,8-bc]furan-5-one (6c):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (164 mg, yield: 71%). Mp: 226-228 °C.

^1H NMR (300 MHz, CDCl_3) δ 10.84 (s, 1H), 7.62 (d, $J = 8.8$ Hz, 1H), 7.54-7.47 (m, 2H), 7.43-7.35 (m, 2H), 7.10-6.95 (m, 6H), 3.84 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 187.21, 159.31, 158.64, 155.14, 155.02, 146.29, 145.68, 133.05, 131.76, 127.33, 125.94, 123.62, 121.63, 118.66, 118.25, 114.93, 113.65, 110.98, 109.61, 55.27. HRMS (ESI) calcd. for $\text{C}_{24}\text{H}_{16}\text{BrO}_5$ $[M+H]^+$: 463.0176, found: 463.0173.

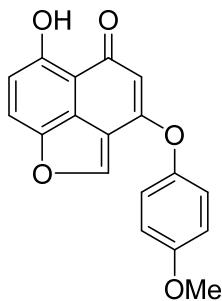


4-benzyl-6-hydroxy-3-(p-tolyloxy)-5H-naphtho[1,8-bc]furan-5-one (6d):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (94 mg, yield: 49%). Mp: 118-119 °C.

^1H NMR (300 MHz, CDCl_3) δ 10.88 (s, 1H), 7.51 (d, $J = 8.8$ Hz, 1H), 7.48-7.43 (m, 2H), 7.30-7.13 (m, 5H), 7.06 (d, $J = 8.5$ Hz, 2H), 6.94 (d, $J = 8.8$ Hz, 1H), 6.56 (s, 1H), 4.15 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 187.25, 158.17, 157.70,

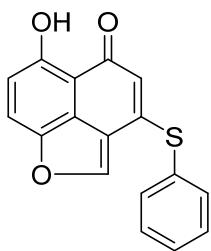
153.45, 146.29, 145.39, 140.64, 136.02, 130.61, 128.94, 128.30, 125.92, 124.80, 120.71, 118.02, 114.46, 110.55, 109.35, 28.90, 20.98. HRMS (ESI) calcd. for C₂₅H₁₉O₄ [M+H]⁺: 383.1278, found: 383.1275.



6-hydroxy-3-(4-methoxyphenoxy)-5H-naphtho[1,8-bc]furan-5-one (6e):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (86 mg, yield: 56%). Mp: 152-154 °C.

¹H NMR (300 MHz, CDCl₃) δ 10.48 (s, 1H), 7.91 (s, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.13 (d, *J* = 9.0 Hz, 2H), 7.04-6.90 (m, 3H), 5.81 (s, 1H), 3.85 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 188.83, 163.51, 157.81, 146.55, 146.14, 146.04, 127.05, 122.24, 118.40, 115.21, 114.57, 112.18, 109.55, 108.86, 55.73. HRMS (ESI) calcd. for C₁₈H₁₃O₅ [M+H]⁺: 309.0757, found: 309.0760.

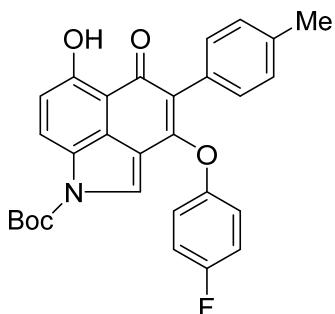


6-hydroxy-3-(phenylthio)-5H-naphtho[1,8-bc]furan-5-one (6f):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (77 mg, yield: 52%). Mp: 134-136 °C.

¹H NMR (400 MHz, CDCl₃) δ 10.37 (s, 1H), 7.86 (s, 1H), 7.69-7.57 (m, 3H), 7.56-7.43 (m, 3H), 6.95 (d, *J* = 8.7 Hz, 1H), 6.12 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 185.34, 162.74, 158.27, 149.17, 146.22, 145.91, 135.56, 130.52, 130.19, 127.77, 123.52, 118.64, 115.43, 114.48, 110.21. HRMS (ESI) calcd. for C₁₇H₁₁O₃S [M+H]⁺:

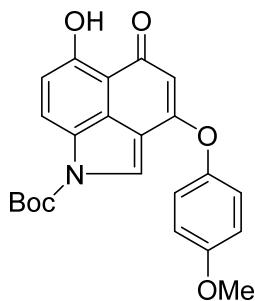
295.0423, found: 2295.0427.



tert-butyl 3-(4-fluorophenoxy)-6-hydroxy-5-oxo-4-(p-tolyl)benzo[cd]indole-1(5H)-carboxylate (6g):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (153 mg, yield: 63%). Mp: 152-154 °C.

¹H NMR (300 MHz, CDCl₃) δ 11.58 (s, 1H), 8.04 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.26-7.20 (m, 2H), 7.15-6.98 (m, 5H), 6.92 (s, 1H), 2.38 (s, 3H), 1.64 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 187.59, 161.30, 159.47, 158.06, 156.96, 152.44, 148.82, 137.54, 130.41, 128.97, 128.83, 127.74, 127.35, 126.76, 125.23, 122.94, 121.12 (d, *J* = 8.4 Hz), 116.49 (d, *J* = 23.5 Hz), 114.99, 109.24 (d, *J* = 22.8 Hz), 85.88, 27.98, 21.40. HRMS (ESI) calcd. for C₂₉H₂₅FNO₅ [M+H]⁺: 486.1711, found: 486.1715.

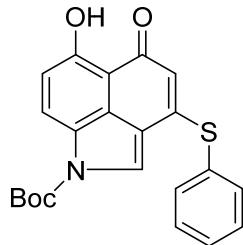


tert-butyl 6-hydroxy-3-(4-methoxyphenoxy)-5-oxobenzo[cd]indole-1(5H)-carboxylate (6h):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (114 mg, yield: 56%). Mp: 72-74 °C.

¹H NMR (300 MHz, CDCl₃) δ 11.16 (s, 1H), 8.05 (d, *J* = 9.2 Hz, 2H), 7.16-7.03 (m, 2H), 7.00-6.92 (m, 3H), 5.75 (s, 1H), 3.85 (s, 3H), 1.71 (s, 9H); ¹³C NMR (75 MHz,

CDCl_3) δ 189.31, 164.81, 158.63, 157.65, 149.10, 146.47, 128.17, 126.70, 125.86, 122.82, 122.29, 115.16, 114.63, 110.33, 109.17, 107.55, 85.72, 55.71, 28.09. HRMS (ESI) calcd. for $\text{C}_{23}\text{H}_{22}\text{NO}_6$ [$\text{M}+\text{H}]^+$: 408.1442, found: 408.1446.



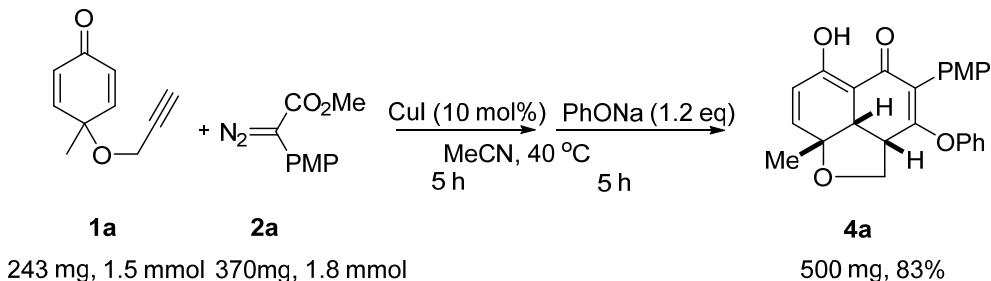
tert-butyl 6-hydroxy-5-oxo-3-(phenylthio)benzo[cd]indole-1(5H)-carboxylate (6i):

The reaction was carried out according to the general procedure in 0.5 mmol scale, the title compound was isolated as a yellow solid (88 mg, yield: 45%). Mp: 272-274 °C.

^1H NMR (300 MHz, CDCl_3) δ 11.09 (s, 1H), 8.11-7.91 (m, 2H), 7.69-7.56 (m, 2H), 7.55-7.41 (m, 3H), 6.96 (d, $J = 8.8$ Hz, 1H), 6.06 (s, 1H), 1.71 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.95, 159.15, 150.39, 149.06, 135.62, 130.30, 130.09, 128.67, 127.82, 126.71, 125.66, 123.07, 122.20, 114.60, 113.81, 109.93, 85.76, 28.11. HRMS (ESI) calcd. for $\text{C}_{22}\text{H}_{20}\text{NO}_4\text{S}$ [$\text{M}+\text{H}]^+$: 394.1108, found: 394.1104.

Large scale reaction for preparation of 4a, 5a and 6a

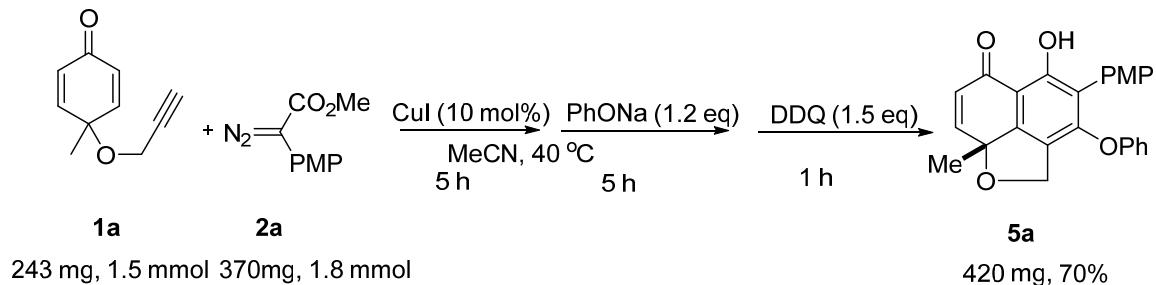
1. Large scale reaction for preparation of 4a



To a schlenk tube was added CuI (28.5 mg, 0.15 mmol) and anhydrous MeCN (9 mL) under argon atmosphere, then **1a** (243 mg, 1.5 mmol) and **2a** (370 mg, 1.8 mmol) in anhydrous MeCN (6 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 12 h; PhONa (209 mg, 1.8 mmol) was added, the reaction mixture was stirred for further 5 h at 40 °C. The reaction mixture was concentrated, the residue

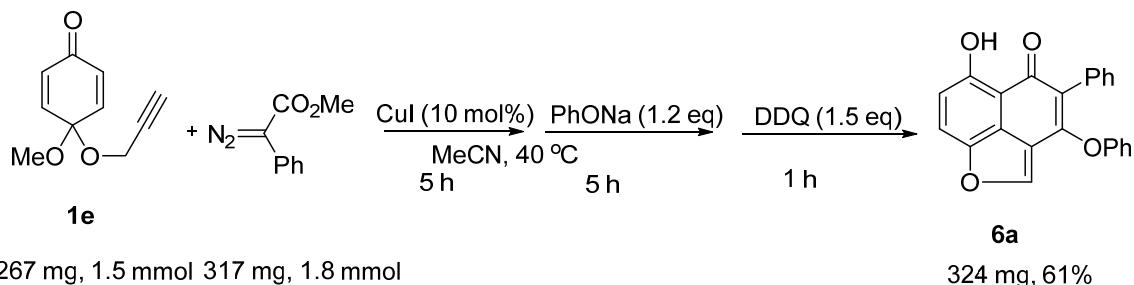
was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:5) to give **4a** (500 mg, 83%).

2. Large scale reaction for preparation of **5a**



To a schlenk tube was added CuI (28.5 mg, 0.15 mmol) and anhydrous MeCN (9 mL) under argon atmosphere, then **1a** (243 mg, 1.5 mmol) and **2a** (370 mg, 1.8 mmol) in anhydrous MeCN (6 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 12 h; PhONa (209 mg, 1.8 mmol) was added, the reaction mixture was stirred for further 5 h at 40 °C. DDQ (510 mg, 2.25 mmol) was added at room temperature and stirred for 1 h. The reaction mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:15-1:5) to give **5a** (420 mg, 70%).

3. Large scale reaction for preparation of **6a**

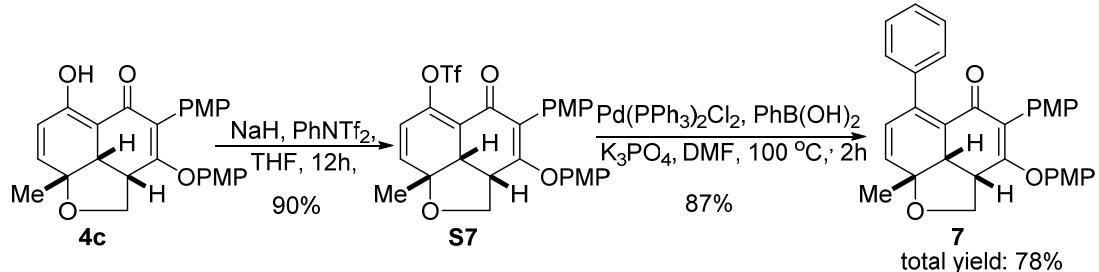


To a schlenk tube was added CuI (28.5 mg, 0.15 mmol) and anhydrous MeCN (9 mL) under argon atmosphere, then **1e** (267 mg, 1.5 mmol) and methyl 2-diazo-2-phenylacetate (317 mg, 1.8 mmol) in anhydrous MeCN (6 mL) was added in one portion and the reaction mixture was stirred at 40 °C for 16 h; PhONa (209 mg, 1.8 mmol) was added, the reaction mixture was stirred for further 5 h at 40 °C. DDQ (510 mg, 2.25 mmol) was added at room temperature and stirred for 1 h. The reaction

mixture was concentrated, the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether = 1:20-1:7) to give **6a** (324 mg, 61%).

Synthetic applications for Scheme 6

1. Scheme 6 for preparation of 7

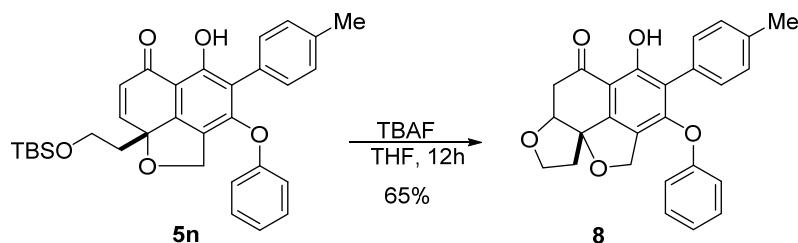


Step (1): To a schlenk tube was added **4c** (43 mg) and THF (3mL), then 60% NaH (7 mg) was added in a portion at 0 °C under argon atmosphere. After stirring for 0.5 h at 0 °C, PhNTf₂ (50 mg) was added, the reaction mixture was stirred at RT for 12 h. The reaction was quenched with H₂O (5 mL) and extracted with EtOAc (15 mL), the organic layer was dried over Na₂SO₄ and filtered, the filtrate was concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:5) to give **S7** as a yellow solid (51 mg, yield: 90%). Mp: 136-138 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.23-7.17 (m, 2H), 6.93-6.80 (m, 6H), 6.11 (dd, *J* = 10.0, 1.1 Hz, 1H), 6.01 (d, *J* = 10.0 Hz, 1H), 3.86 (t, *J* = 6.8 Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 3.70-3.54 (m, 3H), 1.34 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 184.32, 165.98, 159.01, 157.11, 147.17, 143.65, 136.96, 131.57, 125.26, 122.93, 121.77, 121.76, 121.27, 119.80, 116.28, 114.96, 113.50, 69.82, 55.68, 55.19, 46.67, 42.87, 29.72, 27.94. HRMS (ESI) calcd. for C₂₇H₂₄F₃O₈S [M+H]⁺: 565.1138, found: 565.1135.

Step (2): To a schlenk tube was added Pd(PPh₃)₂Cl₂ (1.9 mg), **S7** (30 mg), PhB(OH)₂ (9.7 mg), K₃PO₄ (34 mg) and anhydrous DMF (3 mL), the mixture was degassed and refilled with argon for four times, then the mixture was heated to 100 °C for 2 h. The reaction mixture was cooled, diluted with H₂O (5 mL) and extracted with Et₂O (5 mL*2); the combined organic layers was washed with brine (5 mL*3), dried over

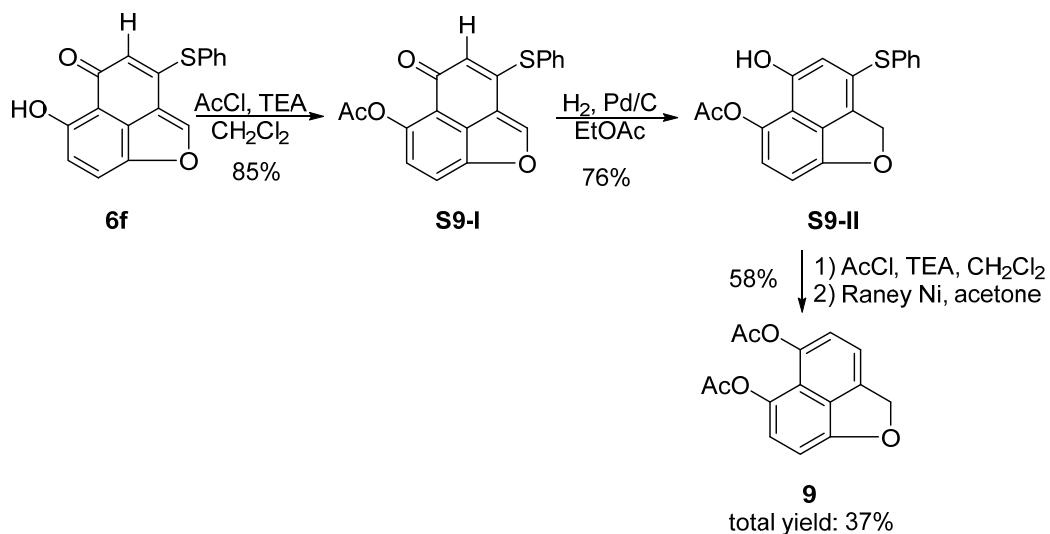
Na_2SO_4 , filtered and concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:10-1:5) to give **7** as a white solid (22.7 mg, yield: 87%). Mp: 188-190 °C. ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.22 (m, 3H), 7.22-7.08 (m, 4H), 6.95 (d, J = 9.0 Hz, 2H), 6.86 (d, J = 9.0 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 6.20 (d, J = 9.6 Hz, 1H), 5.96 (d, J = 9.6 Hz, 1H), 3.89 (s, 1H), 3.80 (s, 3H), 3.74 (s, 3H), 3.71-3.65 (m, 2H), 3.42 (d, J = 5.5 Hz, 1H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 188.64, 164.90, 158.72, 156.90, 147.56, 140.64, 140.08, 131.43, 131.39, 130.06, 128.22, 127.45, 127.29, 126.21, 125.77, 123.90, 121.22, 114.93, 113.32, 77.39, 69.71, 55.68, 55.16, 46.69, 43.50, 28.30. HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{29}\text{O}_5$ [$\text{M}+\text{H}]^+$: 493.2010, found: 493.2014.

2. Scheme 6 for preparation of **8**



To a solution of **5n** (30 mg) in THF (3 mL) was added 1M solution of TBAF in THF (0.56 mL) at 0 °C under argon atmosphere. The resulting solution was stirred at room temperature for 12 h. The reaction was quenched with 0.5N HCl (5 mL), extracted with EtOAc (10 mL); the organic layer was dried over Na_2SO_4 , filtered, concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:5) to give **8** (15 mg, yield: 65%) as a white solid. Mp: 131-133 °C. ^1H NMR (400 MHz, CDCl_3) δ 11.19 (s, 1H), 7.38-7.28 (m, 4H), 7.22 (d, J = 7.9 Hz, 2H), 7.15 (t, J = 7.4 Hz, 1H), 7.01 (d, J = 7.9 Hz, 2H), 4.54 (t, J = 8.0 Hz, 1H), 4.33 (dd, J = 29.1, 12.3 Hz, 2H), 4.27-4.10 (m, 2H), 3.09 (dd, J = 18.9, 7.4 Hz, 1H), 2.56 (dd, J = 18.9, 8.6 Hz, 1H), 2.42 (dd, J = 13.2, 5.1 Hz, 1H), 2.37 (s, 3H), 2.17 (dt, J = 13.2, 10.0 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 198.93, 159.70, 156.20, 155.79, 147.05, 137.51, 130.29, 129.88, 128.88, 128.48, 124.48, 121.08, 120.17, 119.18, 109.22, 89.78, 80.77, 70.21, 67.67, 43.72, 35.44, 21.35. HRMS (ESI) calcd. for $\text{C}_{26}\text{H}_{23}\text{O}_5$ [$\text{M}+\text{H}]^+$: 415.1540, found: 415.1543.

3. Scheme 6 for preparation of 9



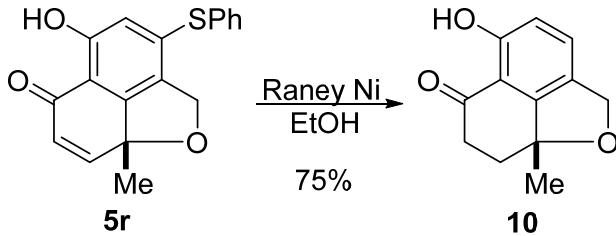
Step (1): To a solution of **6f** (50 mg) and TEA (52 mg) in CH₂Cl₂ (5 mL) was AcCl (20 mg) at 0 °C. The mixture was stirred at RT for 1 h. The reaction solution was diluted with CH₂Cl₂ (10 mL) and washed with 0.5 M HCl (5 mL*2); the organic layer was dried and concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:10-1:5) to give **S9-I** (49 mg, yield: 85%) as a white solid. Mp: 172-174 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.88 (s, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 2H), 7.53-7.43 (m, 3H), 7.14 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 1H), 2.42 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 180.65, 169.59, 150.30, 146.40, 146.26, 146.05, 135.42, 130.35, 130.10, 129.89, 127.72, 125.81, 121.12, 117.68, 116.68, 116.00, 21.07. HRMS (ESI) calcd. for C₁₉H₁₃O₄S [M+H]⁺: 337.0529, found: 337.0525.

Step (2): To a solution of **S9-I** (50 mg) in EtOAc (5 mL) was added 10% Pd/C (15 mg). The resulting mixture was stirred under a H₂ balloon at 40 °C for 12 h. The mixture was filtered through a pad of celite and the filtrate was concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:5) to give **S9-II** (38 mg, yield: 76%) as a yellow solid. Mp: 109-111 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.19 (m, 5H), 7.00 (d, *J* = 7.9 Hz, 1H), 6.72 (s, 1H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.41 (s, 2H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 170.16, 159.39, 150.17, 137.02, 134.07, 131.95, 131.82, 130.61,

129.35, 127.33, 123.55, 121.02, 116.24, 114.91, 101.17, 77.29, 21.27. HRMS (ESI) calcd. for $C_{19}H_{15}O_4S$ [M+H]⁺: 339.0686, found: 339.0690.

Step (3): To a solution of **S9-II** (30 mg) and TEA (27 mg) in CH_2Cl_2 (3 mL) was AcCl (10.4 mg) at 0 °C, the mixture was stirred at RT for 1 h. The reaction solution was diluted with CH_2Cl_2 (10 mL), washed with 0.5 M HCl (5 mL*2) and sat. $NaHCO_3$ (5 mL); the organic layer was dried and concentrated to give the crude product which was used directly without purification. The crude product was dissolved in Acetone (5 mL) and Raney Ni (300 mg) was added, the mixture was stirred at RT for 3 h. The mixture was filtered through a pad of celite and the filtrate was concentrated; the residue was purified by column chromatography (silica gel, eluted with CH_2Cl_2 : Petroleum ether=1:1) to give **9** (14 mg, two steps yield: 58%) as a white solid. Mp: 146-148 °C. 1H NMR (300 MHz, $CDCl_3$) δ 7.22-7.12 (m, 2H), 7.02 (d, J = 7.9 Hz, 1H), 6.65 (d, J = 7.9 Hz, 1H), 5.77 (d, J = 1.0 Hz, 2H), 2.39 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.05, 169.50, 159.87, 142.58, 137.04, 135.71, 131.54, 123.22, 122.66, 119.21, 116.03, 100.88, 77.48, 21.09, 21.06. HRMS (ESI) calcd. for $C_{15}H_{13}O_5$ [M+H]⁺: 273.0757, found: 273.0761.

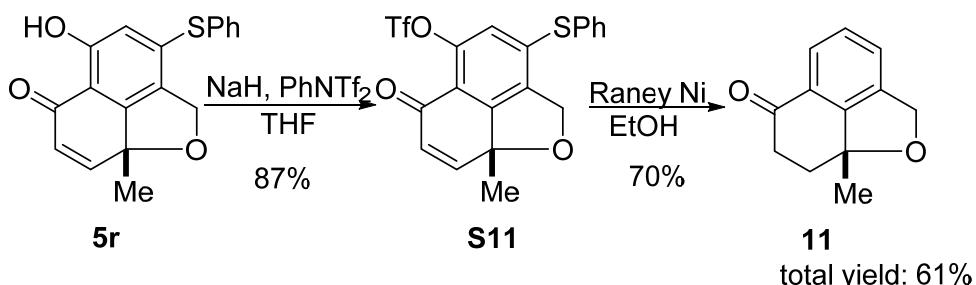
4. Scheme 6 for preparation of **10**



To a solution of **5r** (20 mg) in EtOH (3 mL) was added Raney Ni (200 mg), the mixture was stirred at room temperature for 5 h. The mixture was filtered through a pad of celite; the filtrate was concentrated and the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:10-1:5) to give **10** (9.8 mg, yield: 75%) as a white solid. Mp: 103-105 °C. 1H NMR (400 MHz, $CDCl_3$) δ 10.53 (s, 1H), 7.33 (d, J = 8.3 Hz, 1H), 6.82 (d, J = 8.3 Hz, 1H), 5.19 (d, J = 11.8 Hz, 1H), 4.90 (d, J = 11.8 Hz, 1H), 2.82-2.69 (m, 2H), 2.38-2.23 (m, 2H), 1.53 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 202.02, 159.19, 151.89, 130.15, 128.55, 116.32,

112.45, 81.61, 71.45, 36.07, 35.86, 22.38. HRMS (ESI) calcd. for $C_{12}H_{13}O_3$ $[M+H]^+$: 205.0859, found: 205.0856.

5. Scheme 6 for preparation of 11

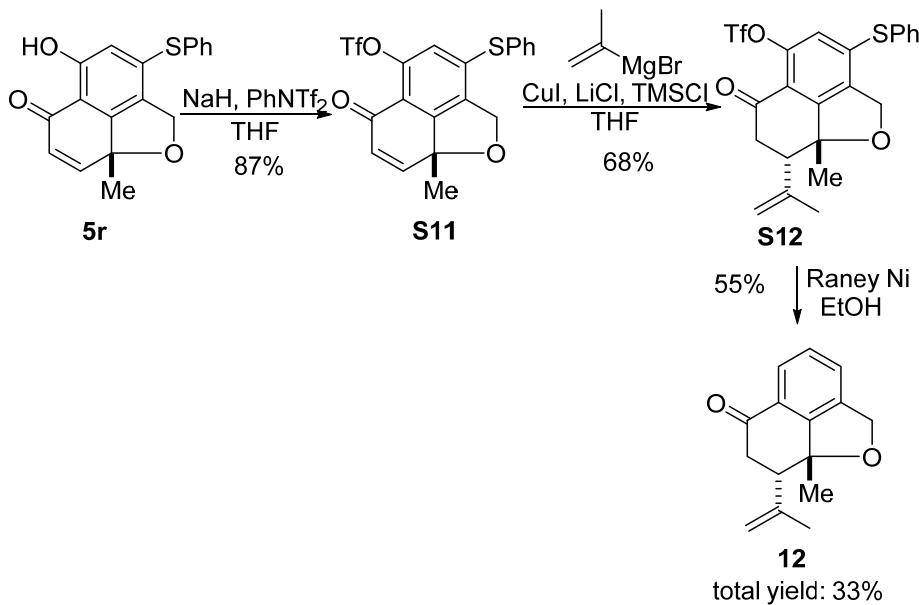


Step (1): To a flask was added **5r** (200 mg) and THF (10 mL), then 60% NaH (31 mg) was added in a portion at 0 °C under argon atmosphere. After stirring for 0.5 h at 0 °C, PhNTf₂ (276 mg) was added in three portions, the reaction mixture was stirred at RT for 6 h. The reaction was quenched with H₂O (15 mL) and extracted with EtOAc (25 mL), the organic layer was dried over Na₂SO₄ and filtered, the filtrate was concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20-1:10) to give **S11** as a white solid (248 mg, yield: 87%). Mp: 114-115 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.44 (m, 5H), 7.29 (d, *J* = 10.0 Hz, 1H), 6.64 (s, 1H), 6.18 (d, *J* = 10.0 Hz, 1H), 4.91 (q, *J* = 13.4 Hz, 2H), 1.56 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 180.75, 153.28, 148.25, 146.09, 141.53, 135.74, 134.52, 130.19, 130.17, 129.56, 129.15, 120.27, 119.48, 117.08, 116.93, 81.40, 70.14, 27.87. HRMS (ESI) calcd. for $C_{19}H_{14}F_3O_5S_2$ $[M+H]^+$: 443.0229, found: 443.0226.

Step (2): To a solution of **S11** (30 mg) in EtOH (4 mL) was added Raney Ni (240 mg), the mixture was stirred at room temperature for 5 h. The mixture was filtered through a pad of celite; the filtrate was concentrated and the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:15-1:8) to **11** (8.9 mg, yield: 70%) as a white solid. Mp: 99-101 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.68 (d, *J* = 7.4 Hz, 1H), 7.44 (d, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.4 Hz, 1H), 5.28 (d, *J* = 12.7 Hz, 1H), 5.00 (d, *J* = 12.7 Hz, 1H), 2.79-2.67 (m, 2H), 2.43-2.34 (m, 1H), 2.31-2.18 (m, 1H), 1.55 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.78, 151.64, 139.01, 128.63,

127.34, 126.65, 123.70, 81.71, 71.24, 36.00, 35.89, 22.40. HRMS (ESI) calcd. for C₁₂H₁₃O₂ [M+H]⁺: 189.0910, found: 189.0914.

6. Scheme 6 for preparation of 12



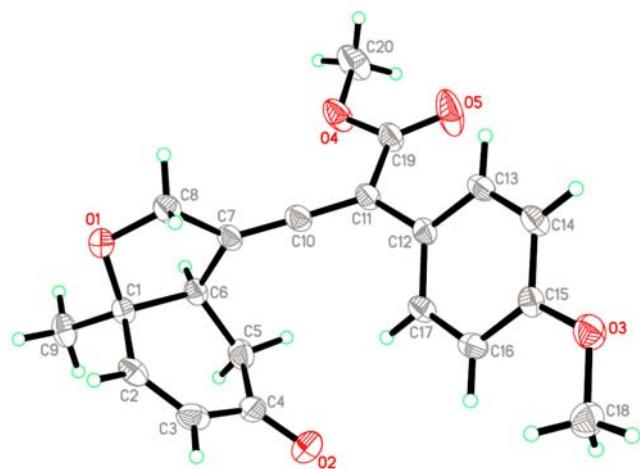
Step (1): To a flask was added **5r** (200 mg) and THF (10 mL), then 60% NaH (31 mg) was added in a portion at 0 °C under argon atmosphere. After stirring for 0.5 h at 0 °C, PhNTf₂ (276 mg) was added in three portions, the reaction mixture was stirred at RT for 6 h. The reaction was quenched with H₂O (15 mL) and extracted with EtOAc (25 mL), the organic layer was dried over Na₂SO₄ and filtered, the filtrate was concentrated; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20-1:10) to give **S11** as a white solid (248 mg, yield: 87%).

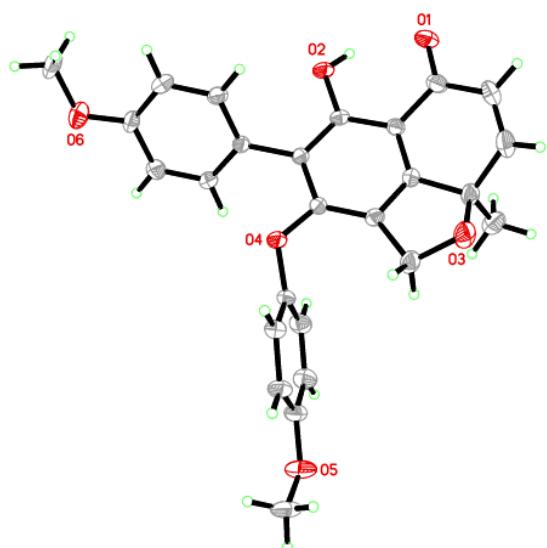
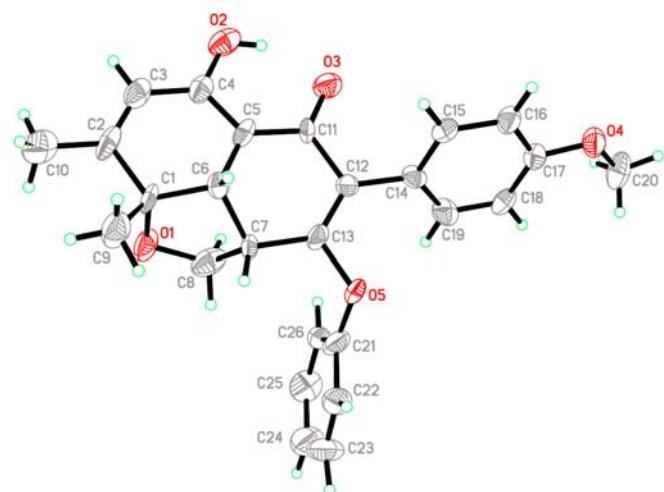
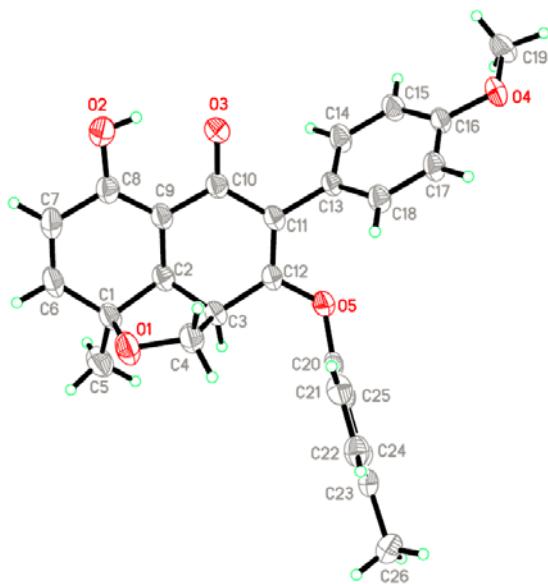
Step (2): To a flask was added **S11** (210 mg), CuI (180 mg), LiCl (80 mg), TMSCl (1.2 mL) and anhydrous THF (10 mL) under argon atmosphere at -10 °C, then 0.5 M isopropenylmagnesium bromide in THF (10 mL) was added dropwise over 20 min. The mixture was stirred at -10 °C for 1 h and 1 h at RT. The reaction was quenched with MeOH/H₂O (3 ml/ 1.5 mL) at 0 °C, then stirred at RT for 1 h and extracted with EtOAc (20 mL*2); the combined organic layers were dried over Na₂SO₄ and concentrated; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:50-1:15) to give **S12** (156 mg, yield: 68%).

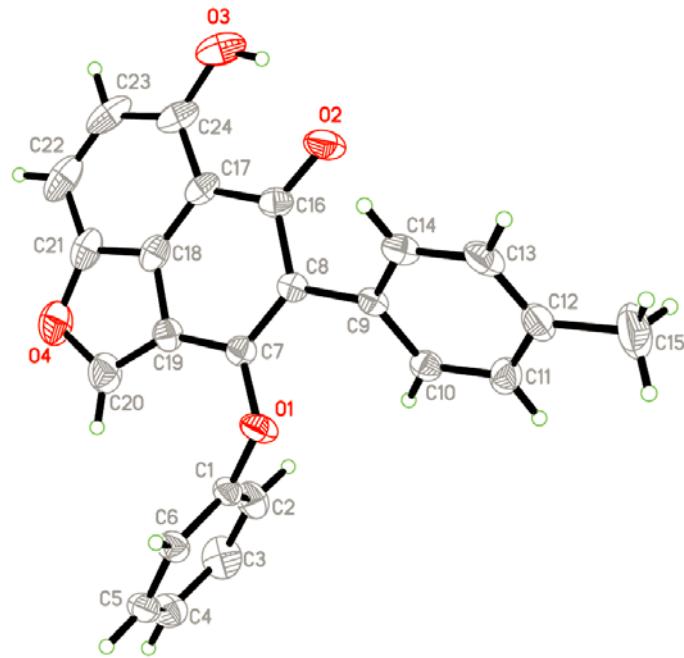
Step (3): To a solution of **S12** (100 mg) in EtOH (10 mL) was added Raney Ni (1.2 g) in three portions within 15 min, then stirred at room temperature for 0.5 h. The mixture was filtered through a pad of celite; the filtrate was concentrated and the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20-1:10) to give **12** (26 mg, yield: 55%) as a white solid. Mp: 77-79 °C. ^1H NMR (300 MHz, CDCl_3) δ 7.70 (d, J = 7.4 Hz, 1H), 7.48-7.42 (m, 1H), 7.38 (t, J = 7.4 Hz, 1H), 5.25 (d, J = 12.8 Hz, 1H), 4.99 (d, J = 12.8 Hz, 1H), 4.71-4.63 (m, 1H), 4.38 (s, 1H), 3.21 (d, J = 6.3 Hz, 1H), 3.00 (dd, J = 19.1, 6.3 Hz, 1H), 2.73 (dd, J = 19.1, 1.4 Hz, 1H), 1.64 (s, 3H), 1.46 (d, J = 0.4 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.37, 149.48, 145.54, 139.10, 128.69, 127.98, 126.81, 123.31, 113.47, 84.01, 71.32, 51.93, 42.11, 26.21, 23.36. HRMS (ESI) calcd. for $\text{C}_{15}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 229.1223, found: 229.1220.

X-ray structure of **3a**, **4b**, **4l**, **5b** and **6b**

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1447631, **3a**), (CCDC 1448896, **4b**), (CCDC 1447629, **4l**), (CCDC 1479469, **5b**) and (CCDC 1514211, **6b**). The data can be obtained free of charge via the internet at www.ccdc.cam.ac.uk/conts/retrieving







References:

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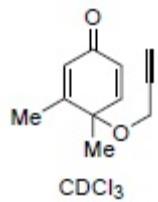
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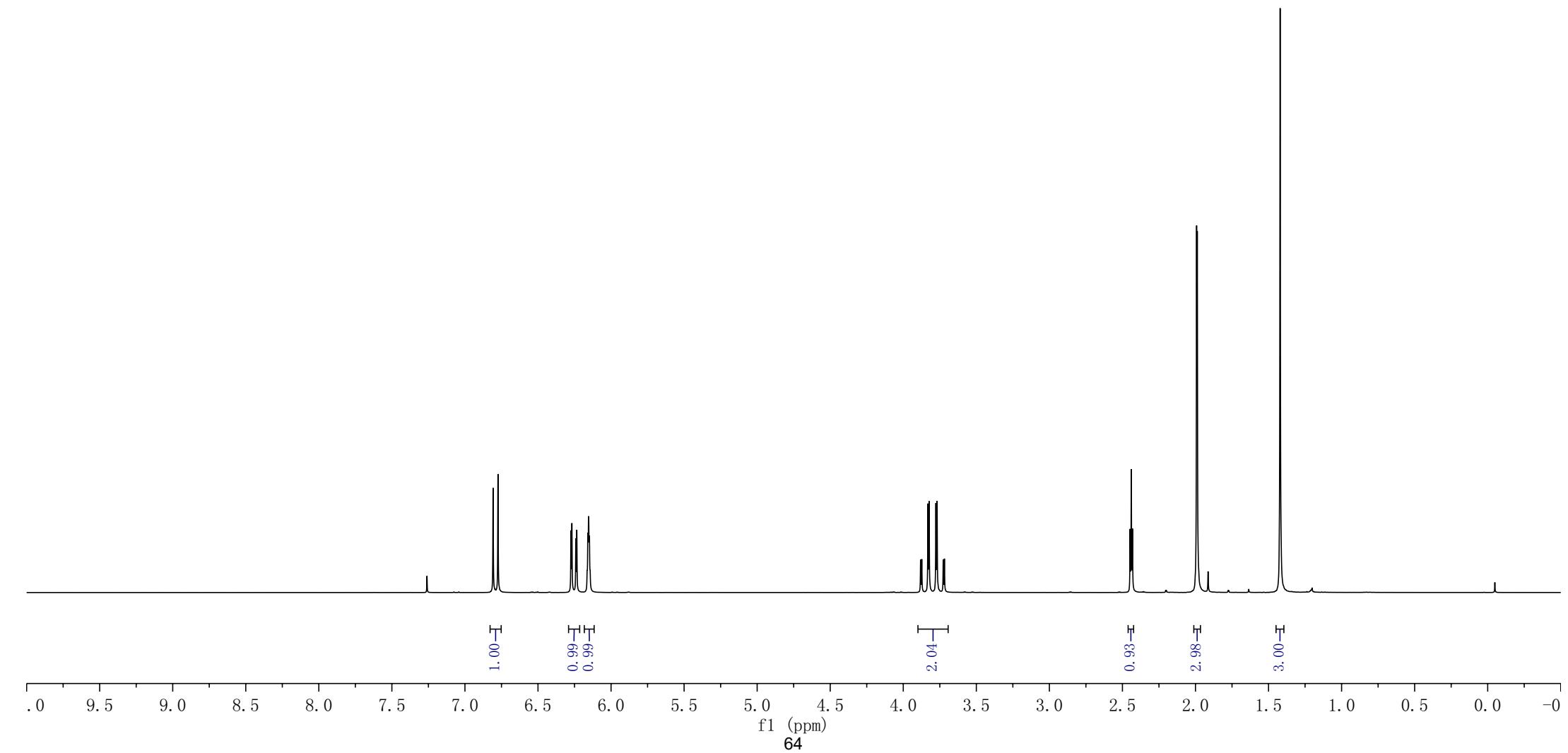
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—1.42



1b



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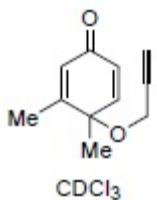
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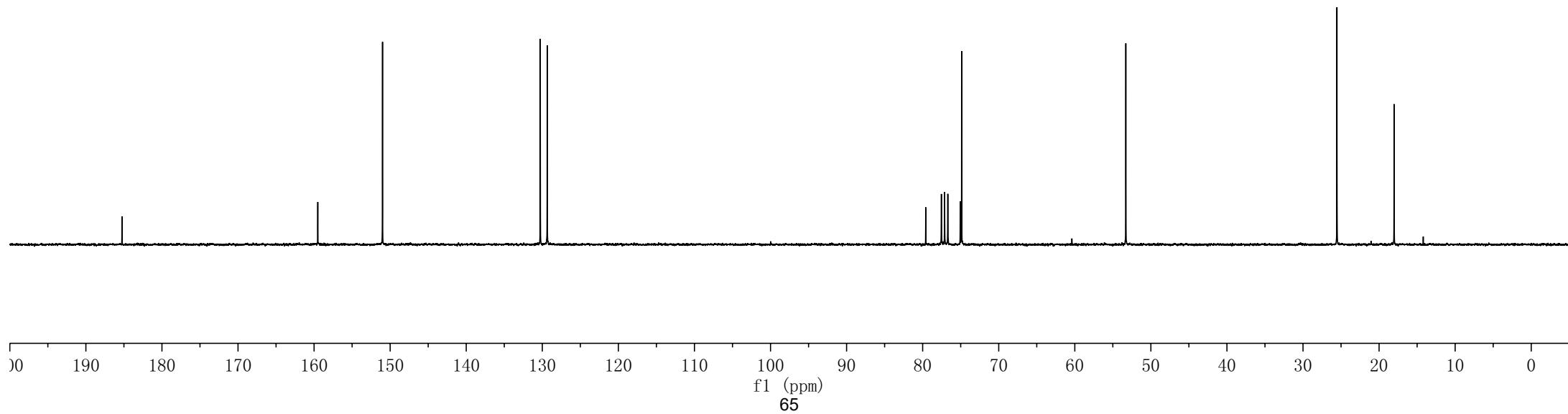
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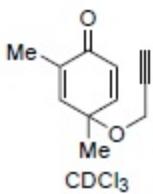
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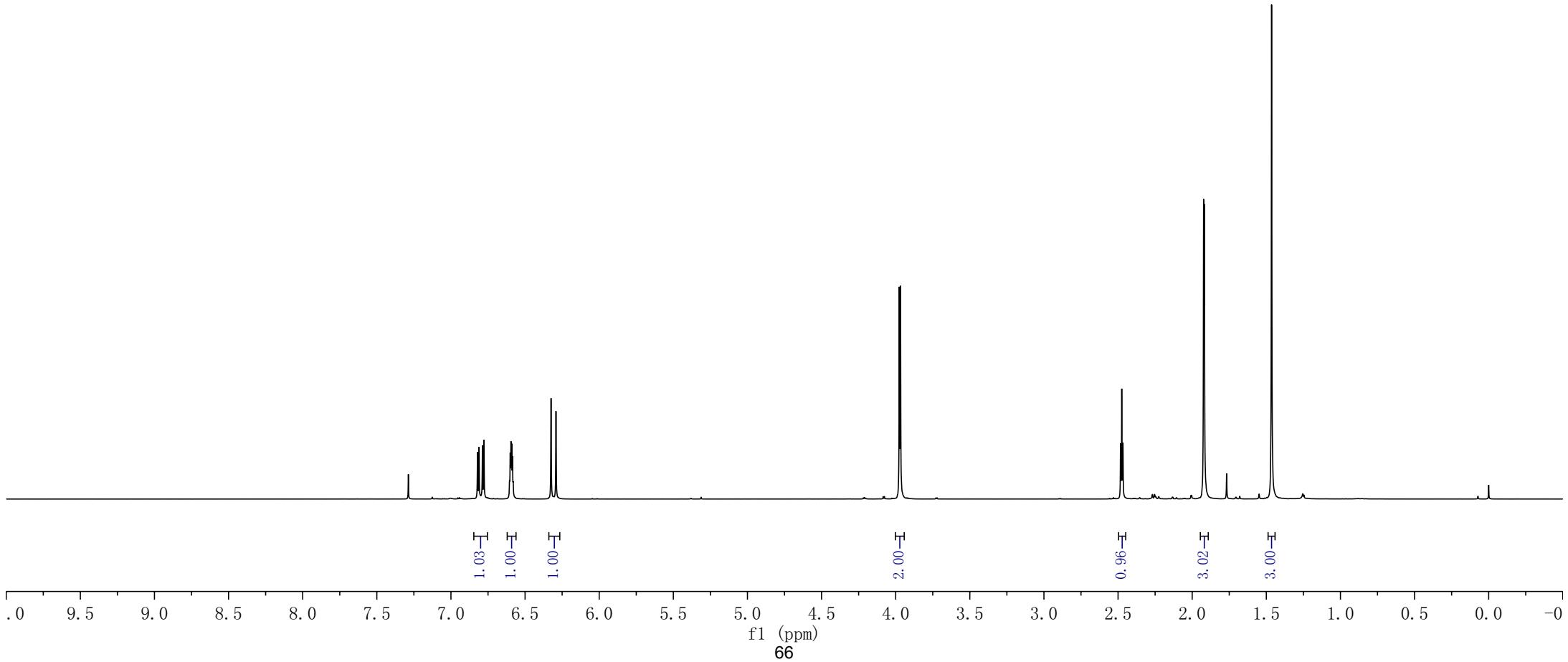
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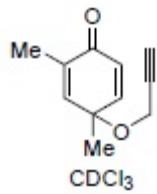
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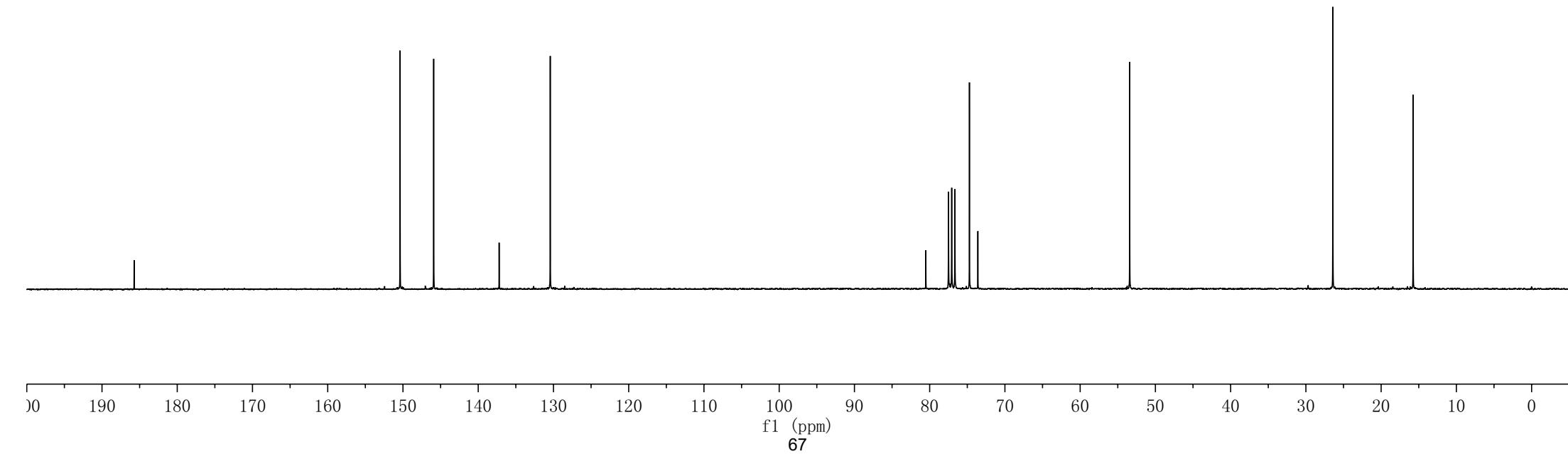
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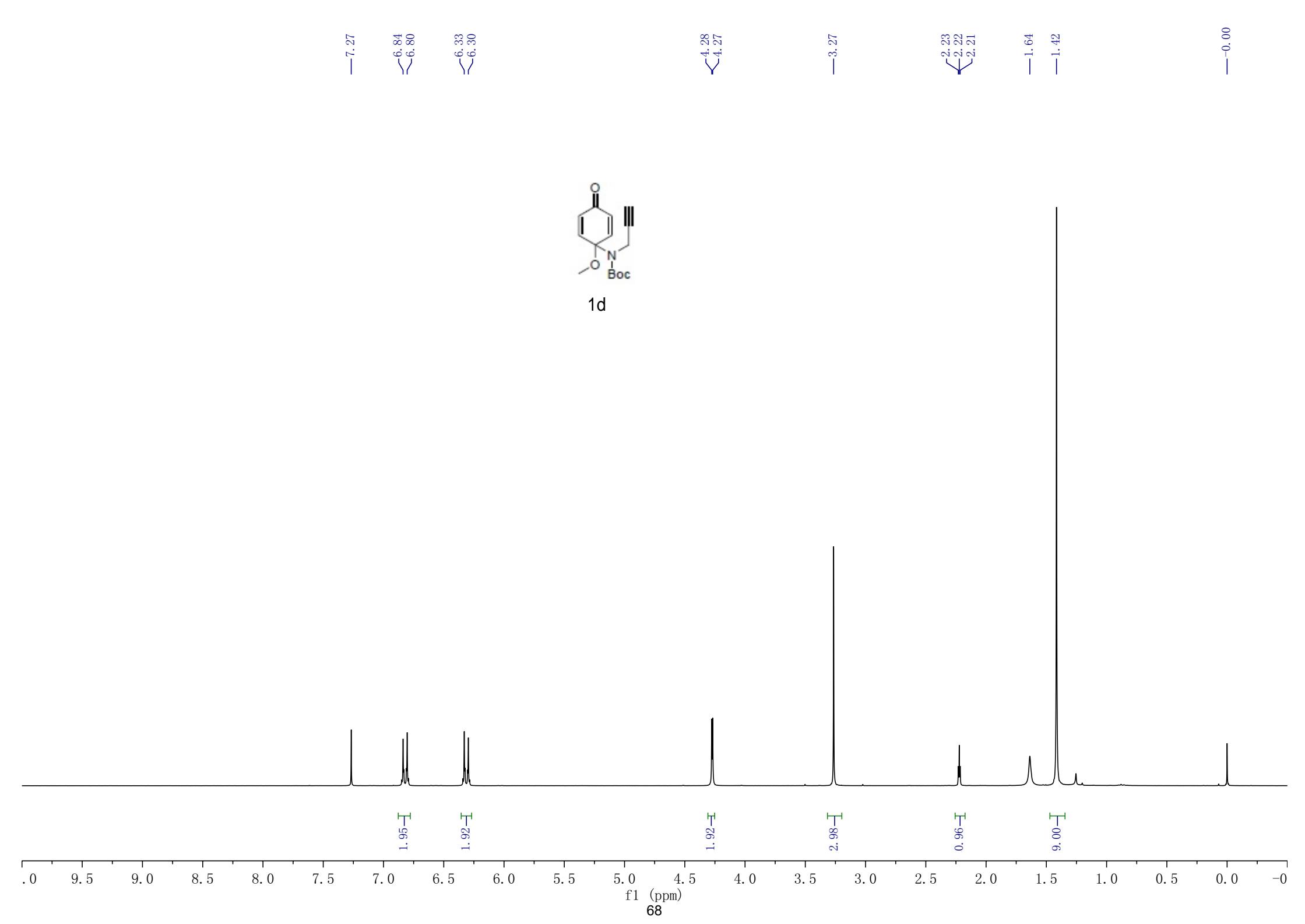
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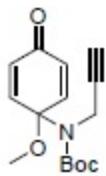
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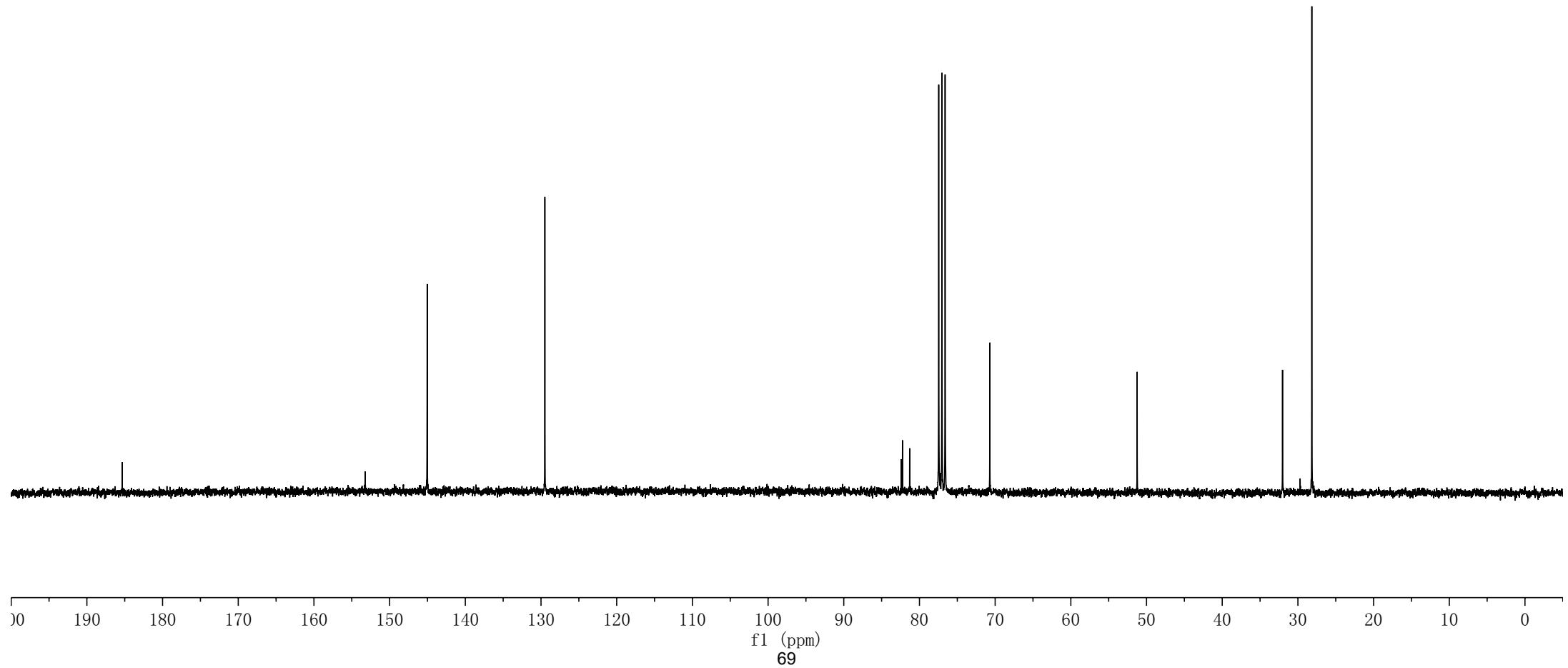
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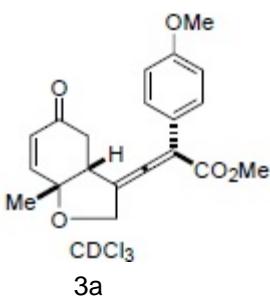
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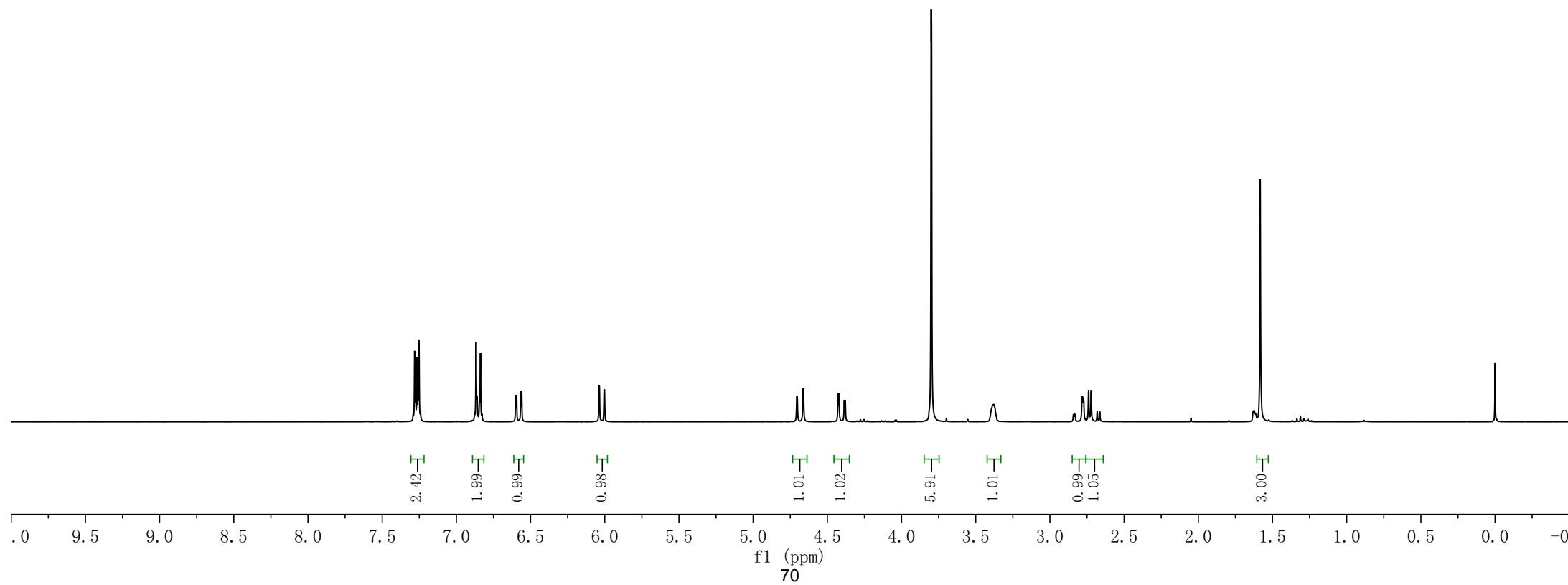
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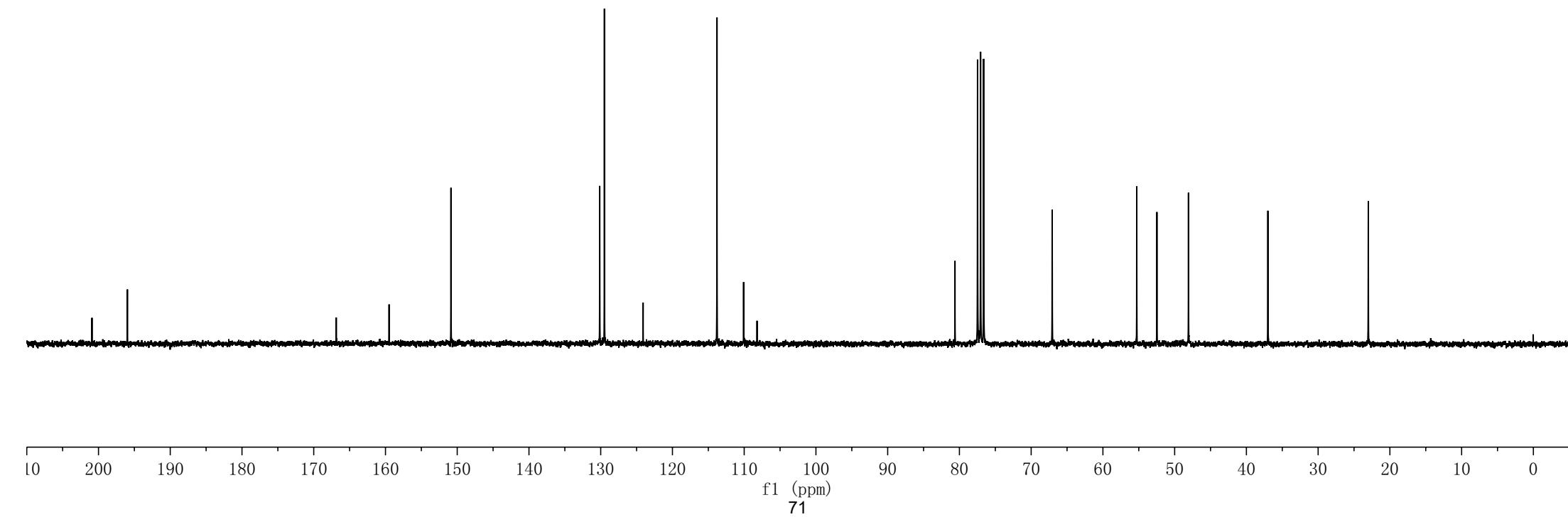
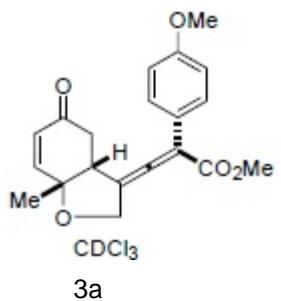
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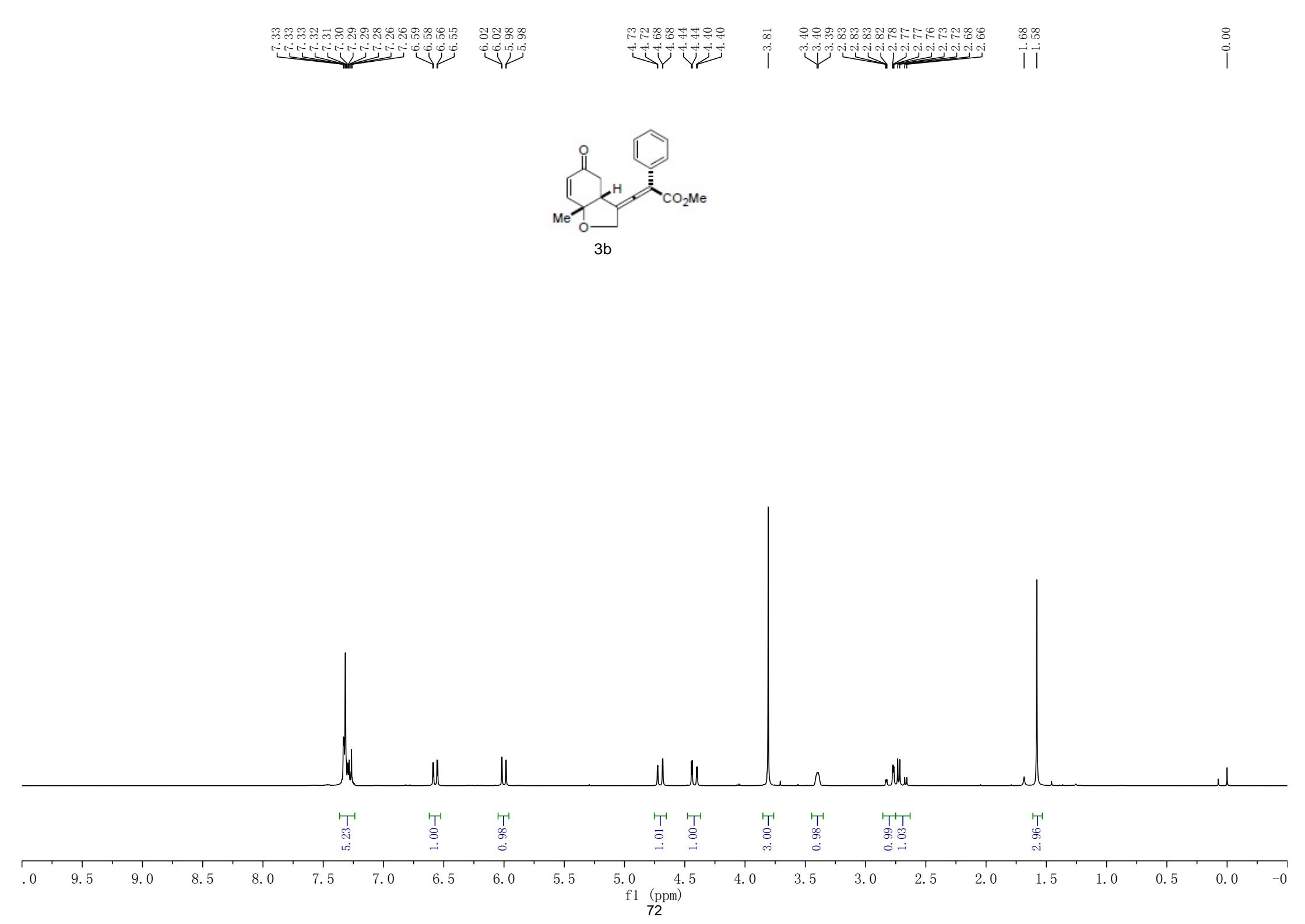
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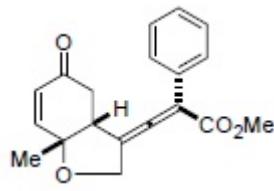
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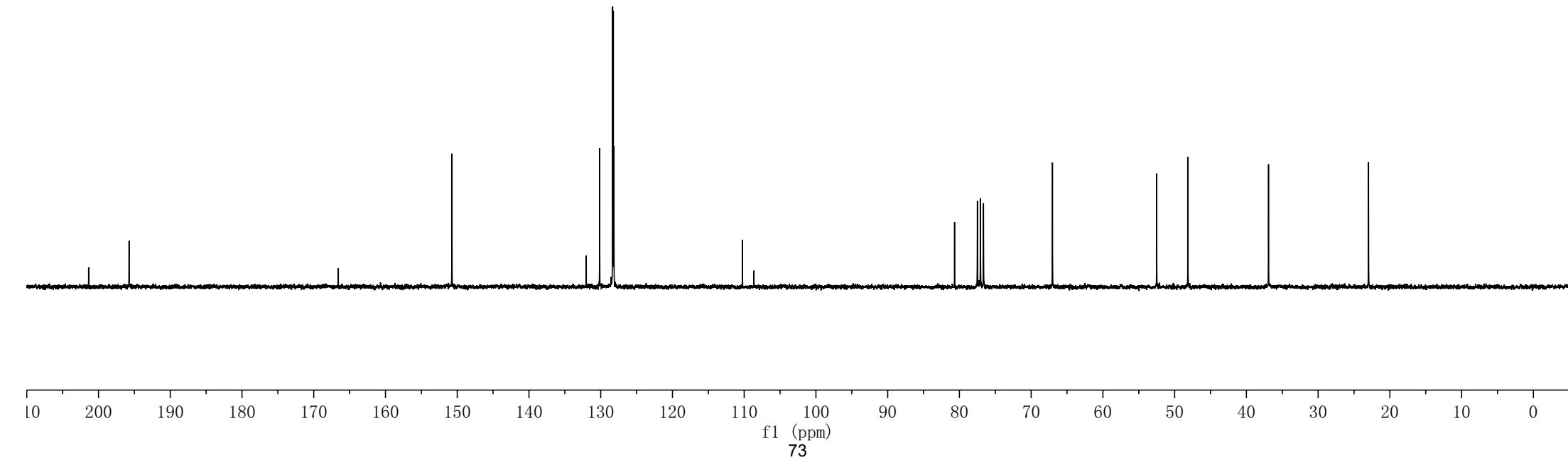
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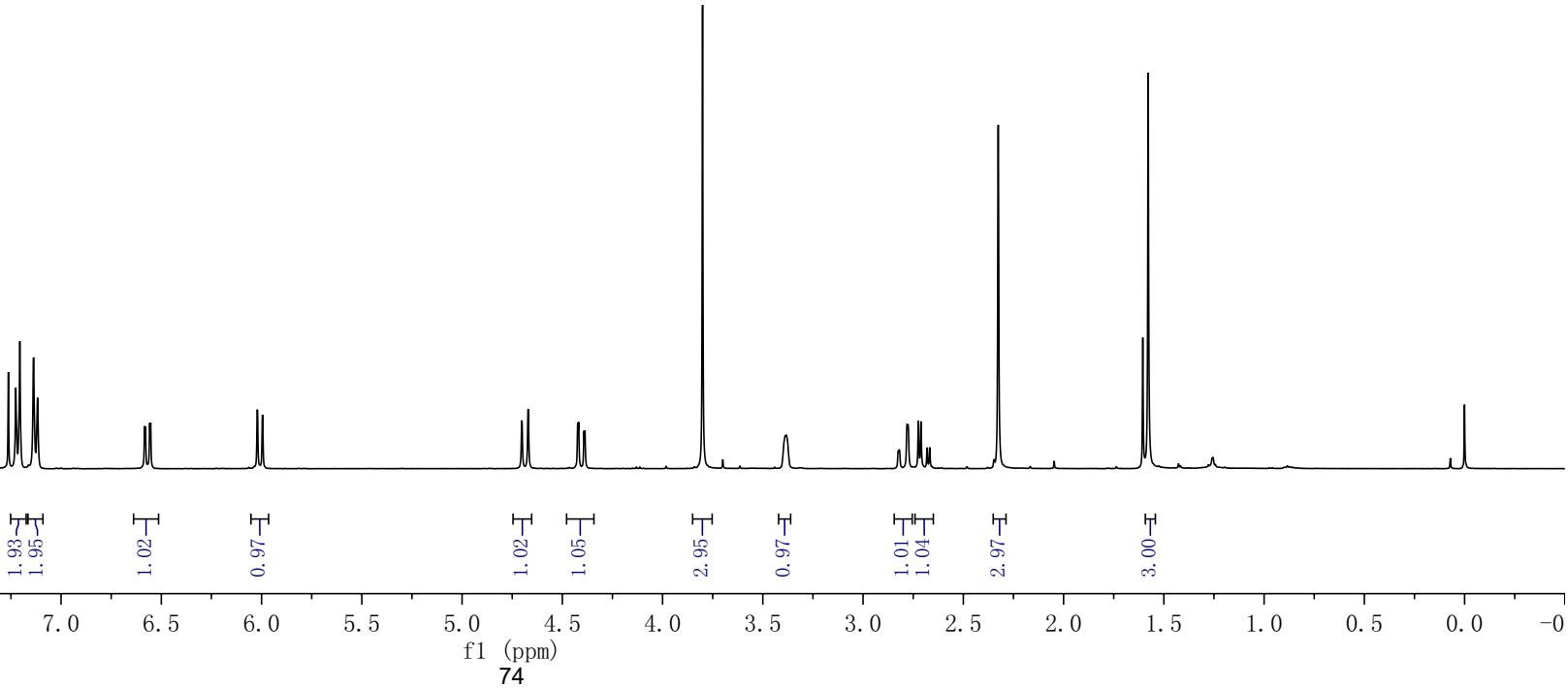
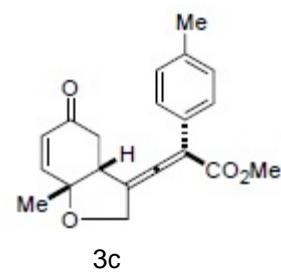
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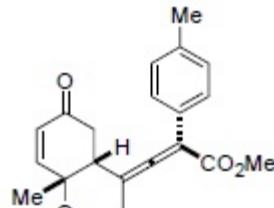
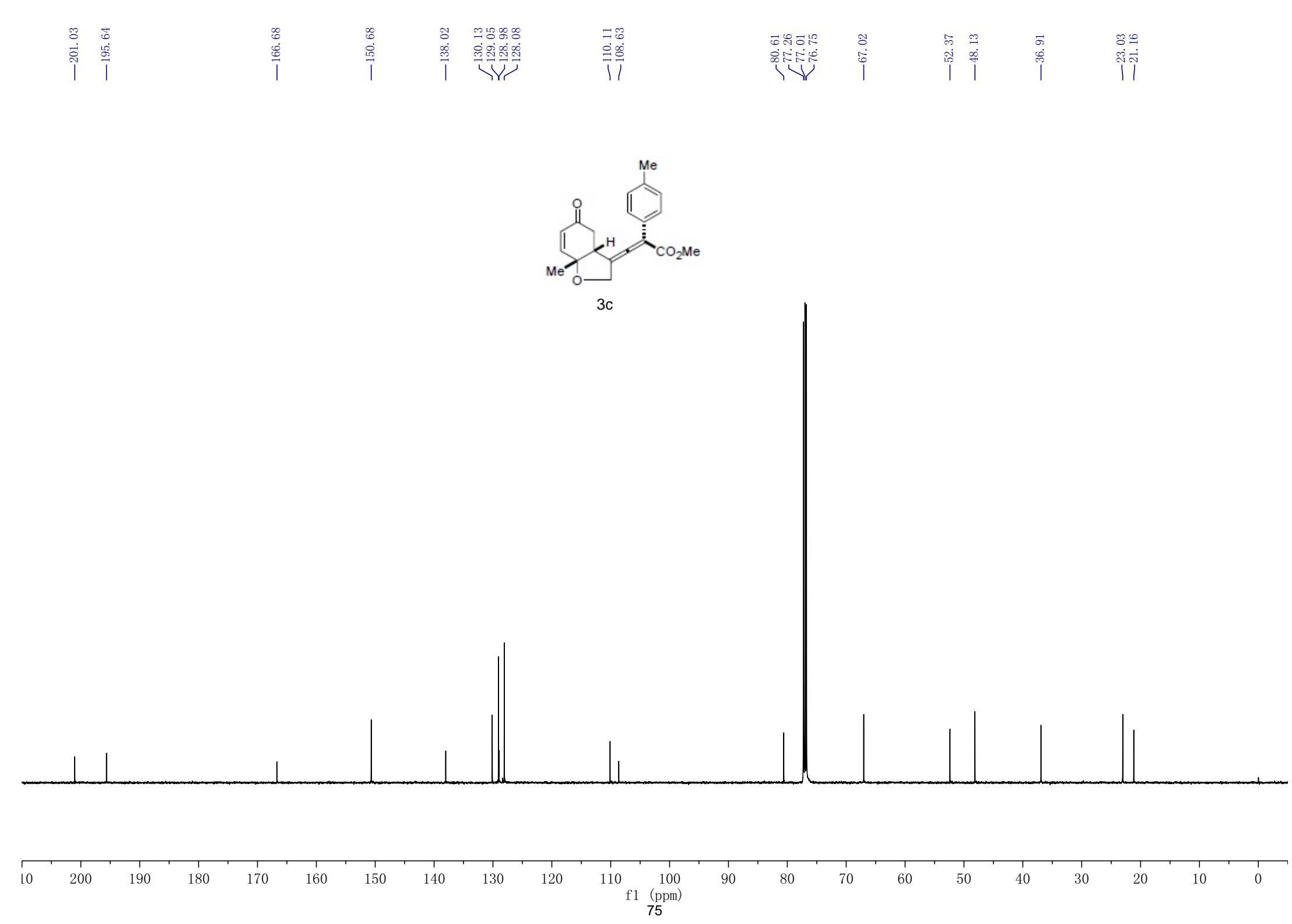
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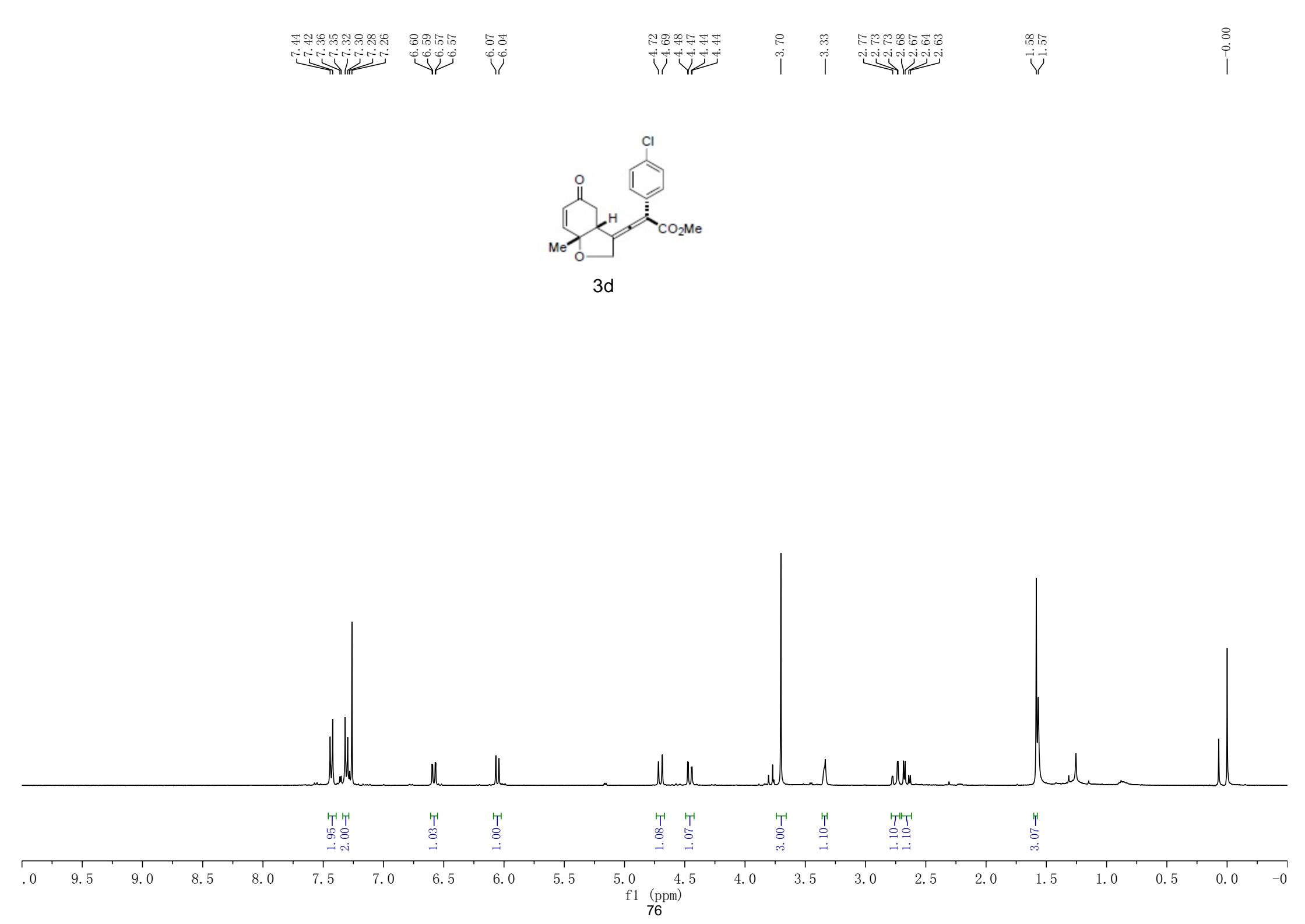
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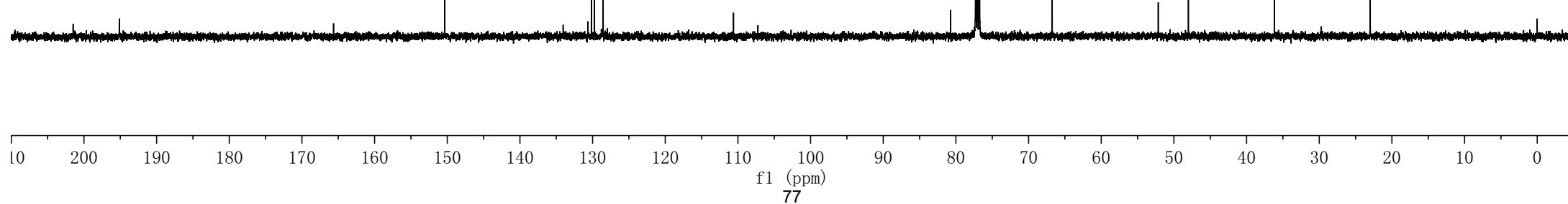
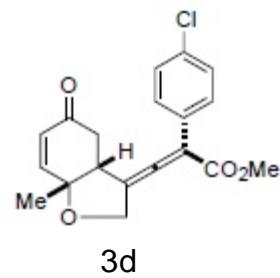
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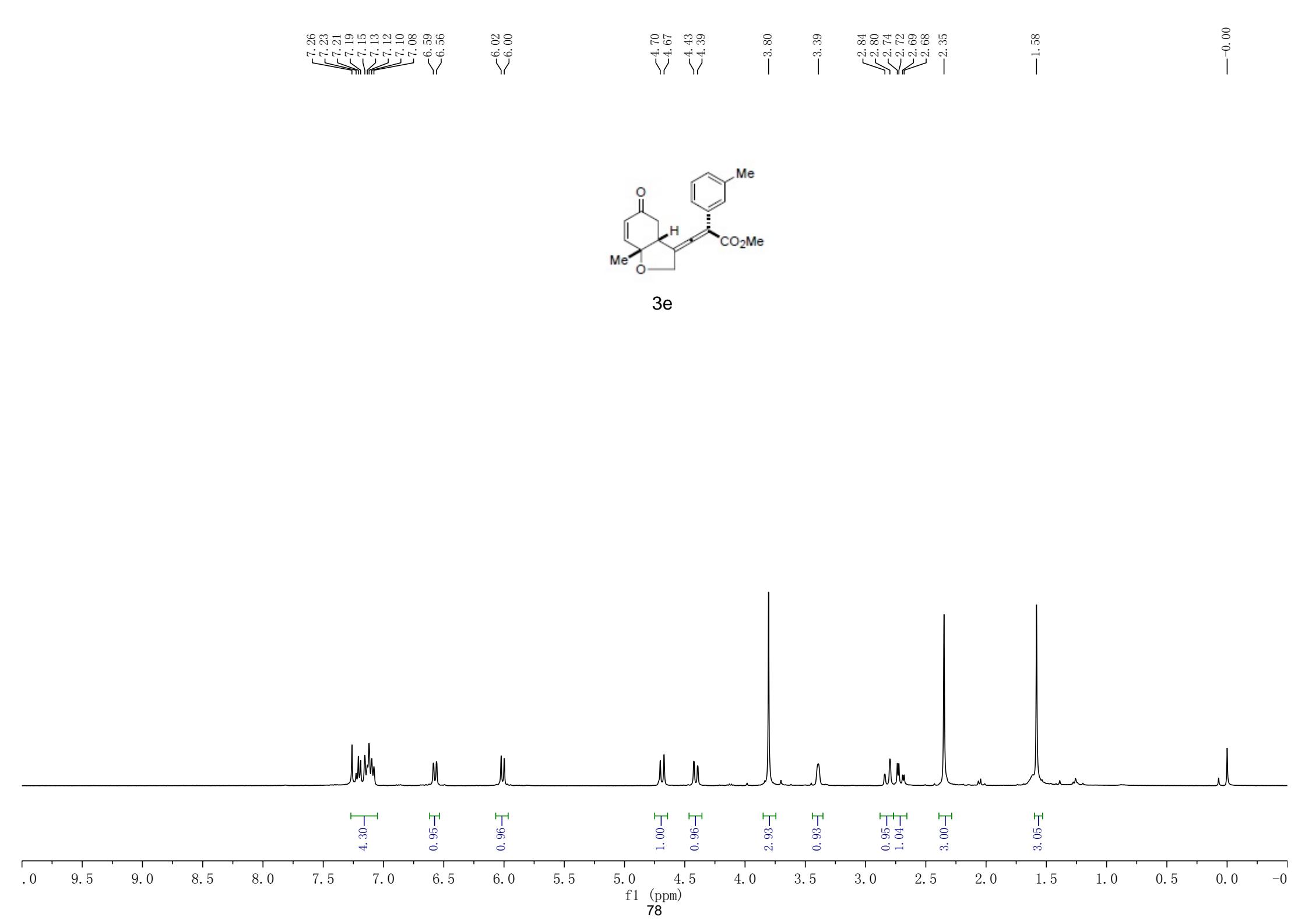
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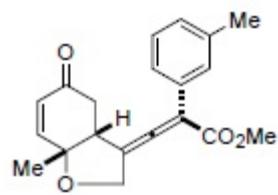
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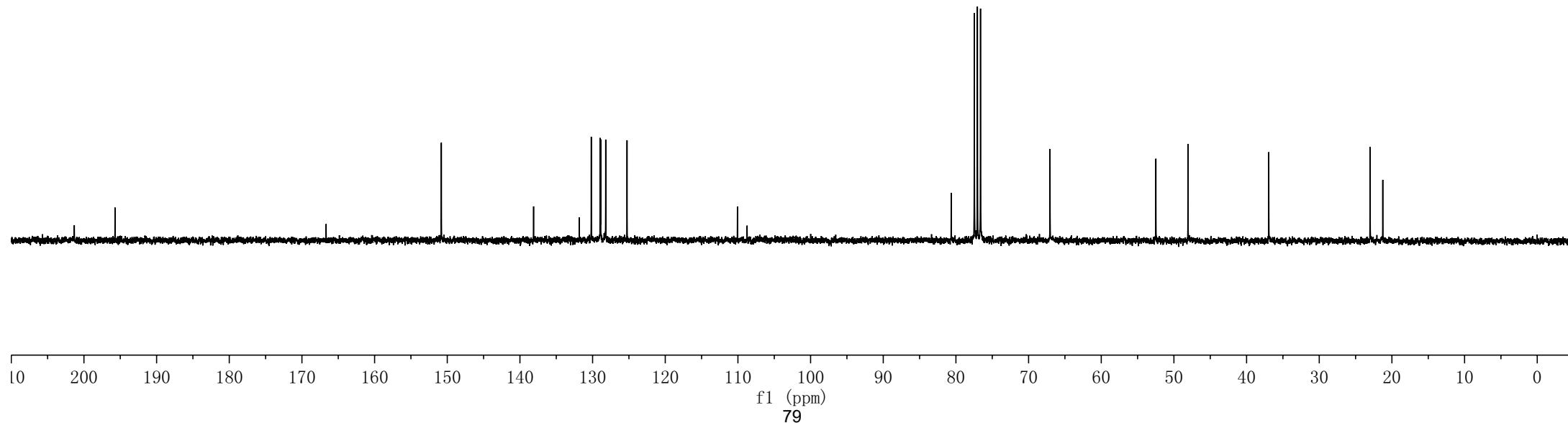
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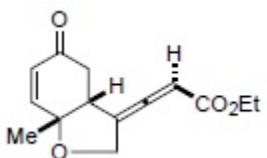


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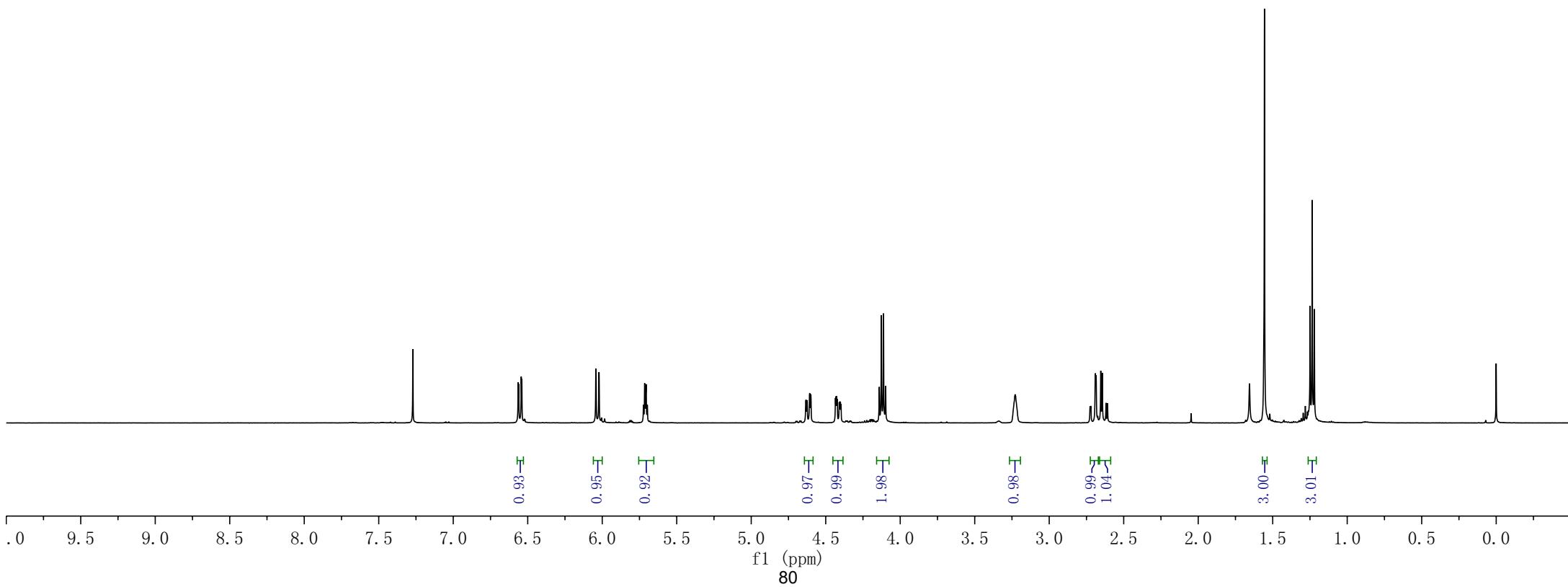
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— 6.02
— 6.04
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— 6.56



3f



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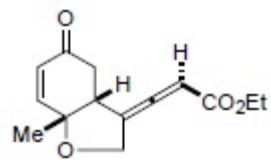
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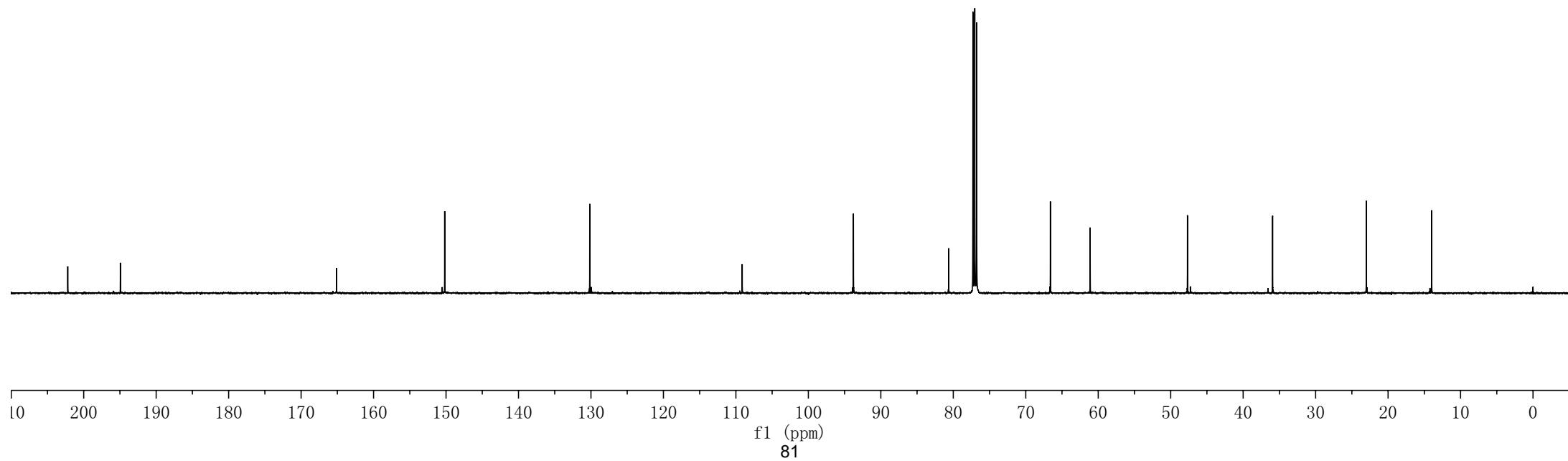
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—23.00

—13.99



3f

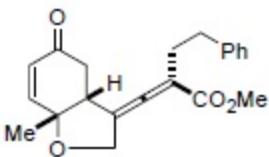


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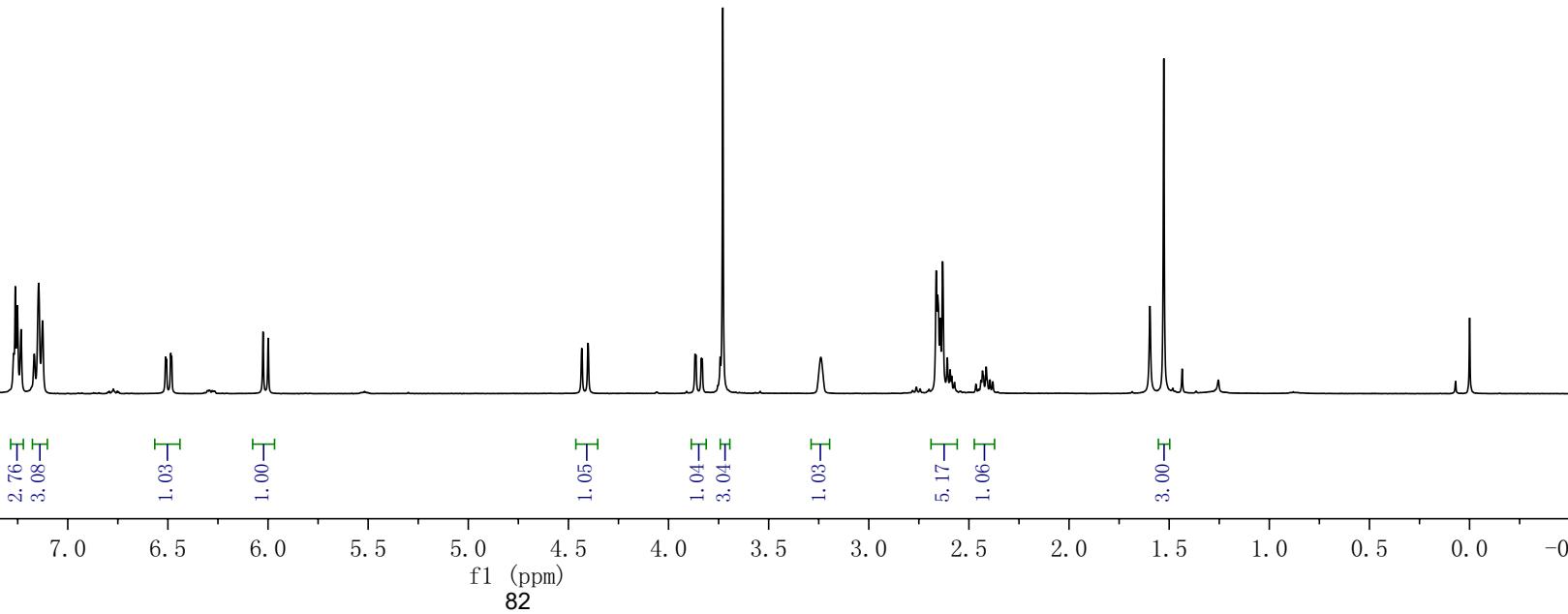
—1.60
—1.53
—1.44

—3.24
—2.66
—2.64
—2.63
—2.61
—2.59
—2.57
—2.46
—2.44
—2.43
—2.41
—2.39
—2.38

—4.43
—4.40



3g



0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0

82

—200.19
—196.39

—167.44

—150.90

—141.00

~129.88
~128.59
~128.29
~125.88

—109.10

—105.49

~80.43
~77.46
~77.04
~76.62

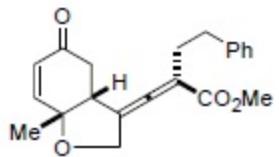
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—52.25

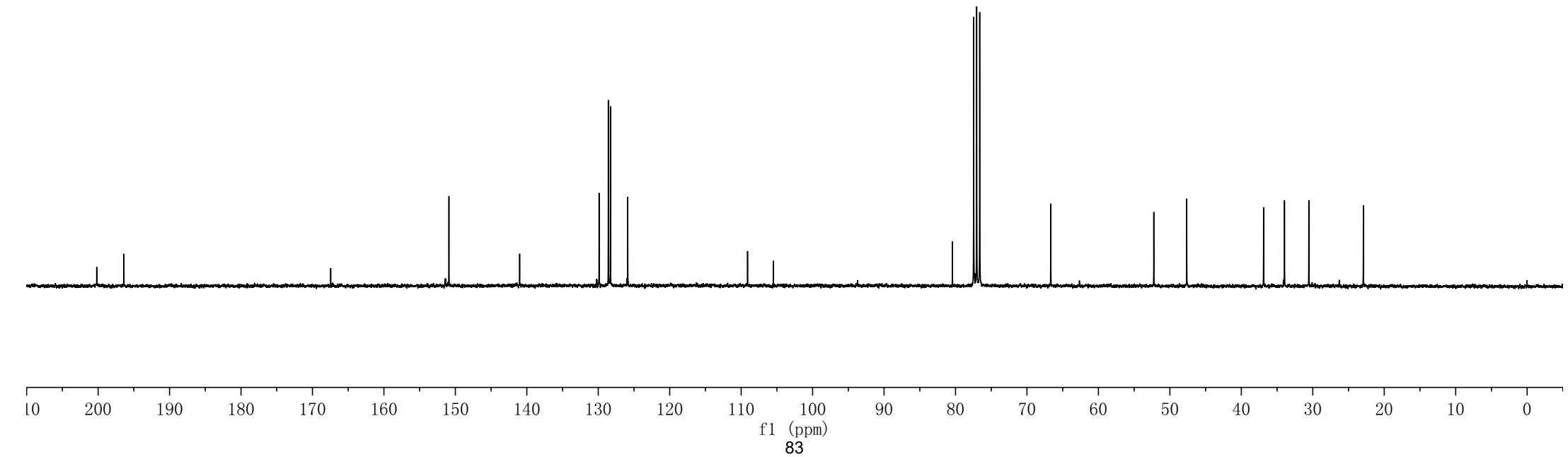
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~36.89
~33.96
~30.56

—22.92



3g



— 0.00

< 0.87
< 0.85

— 3.28

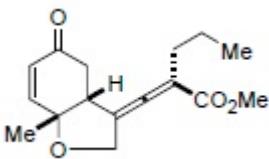
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< 2.66

— 3.72

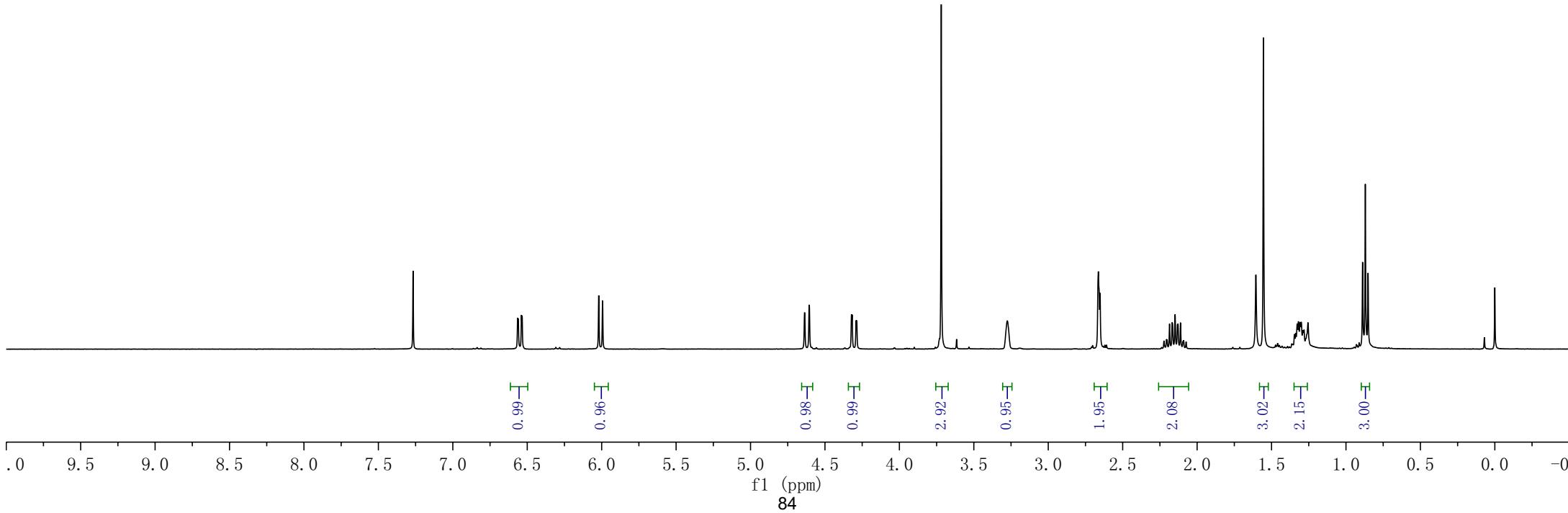
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< 4.29
< 4.32
< 4.32
< 4.64

< 5.99
< 6.02
< 6.53
< 6.54
< 6.56

— 7.27



3h



—199.84
—196.25

—167.63

—150.89

—129.90

—108.65
—106.55

—80.50
—77.46
—77.03
—76.61

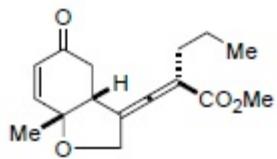
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—52.19
—47.48

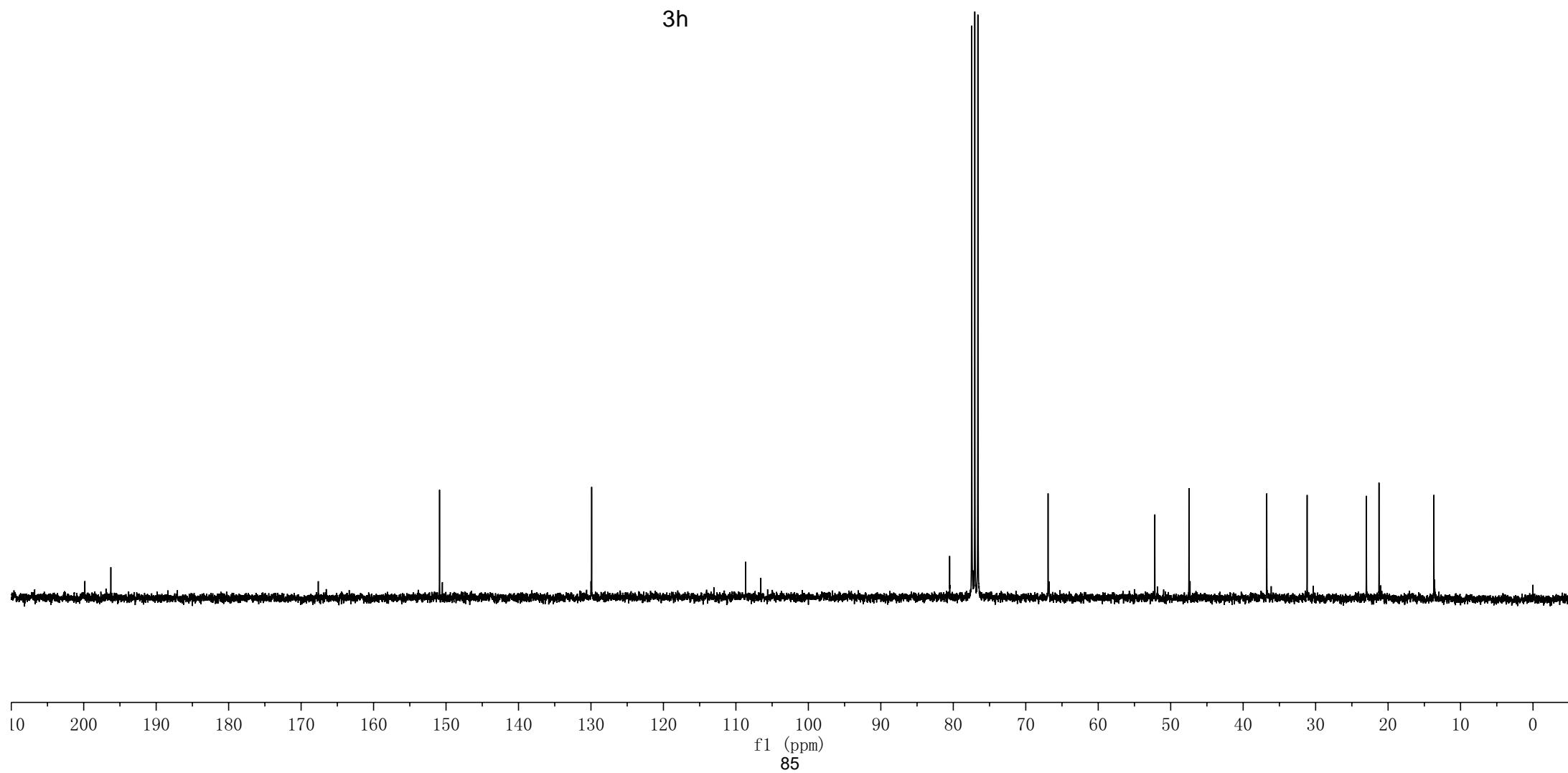
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—31.17

—22.99
—21.26

—13.67



3h



—0.00

—1.62
—1.59

—1.98
—1.97

—2.67
—2.69
—2.72
—2.73
—2.78
—2.78
—2.82
—2.83

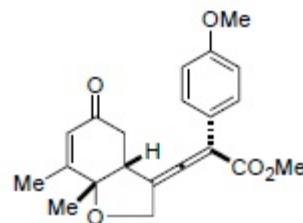
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—3.37

—3.79
—3.80

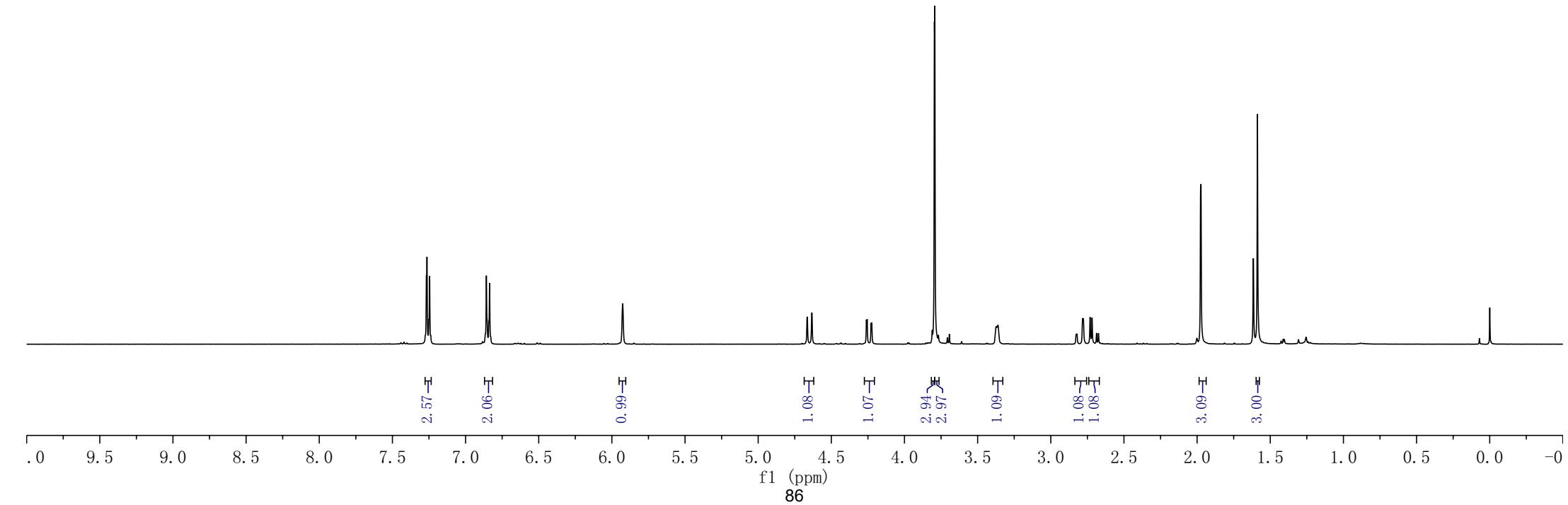
—4.22
—4.23
—4.26
—4.63
—4.66

—5.93

—6.84
—6.86
—7.25
—7.26
—7.27



3i



—200.74

—195.51

—166.91

—161.09

—159.47

~129.50

~128.75

—124.17

~113.79

~110.08

~108.28

—82.61

~77.46

~77.04

~76.62

—66.62

~55.28

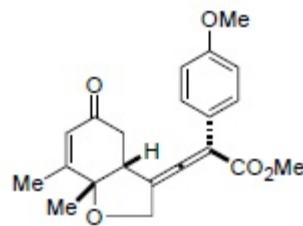
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~49.00

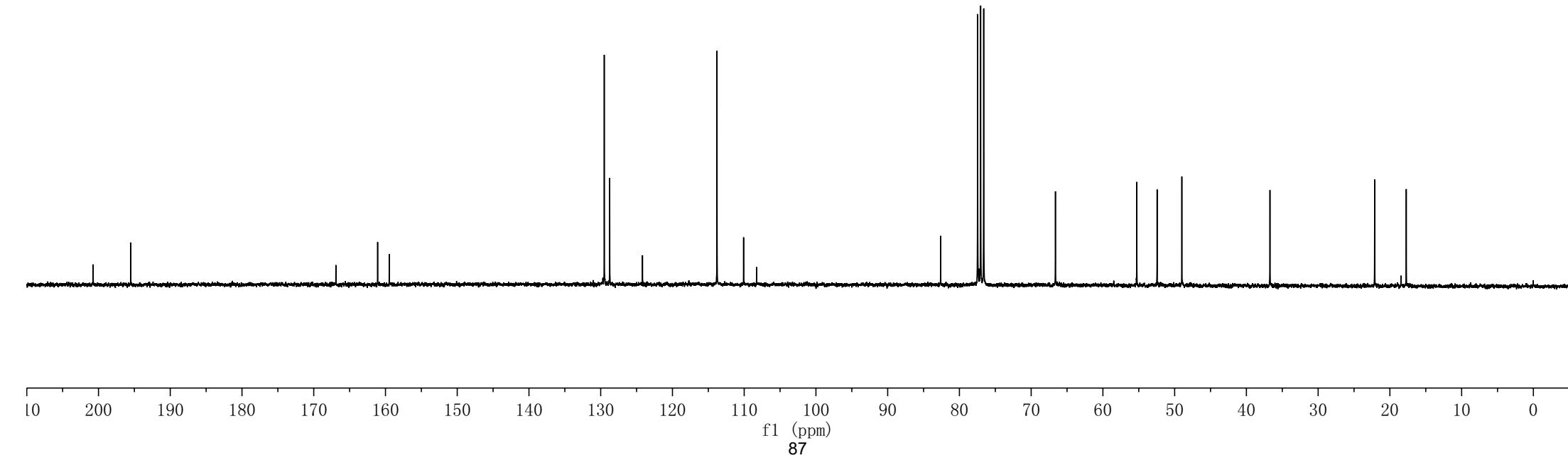
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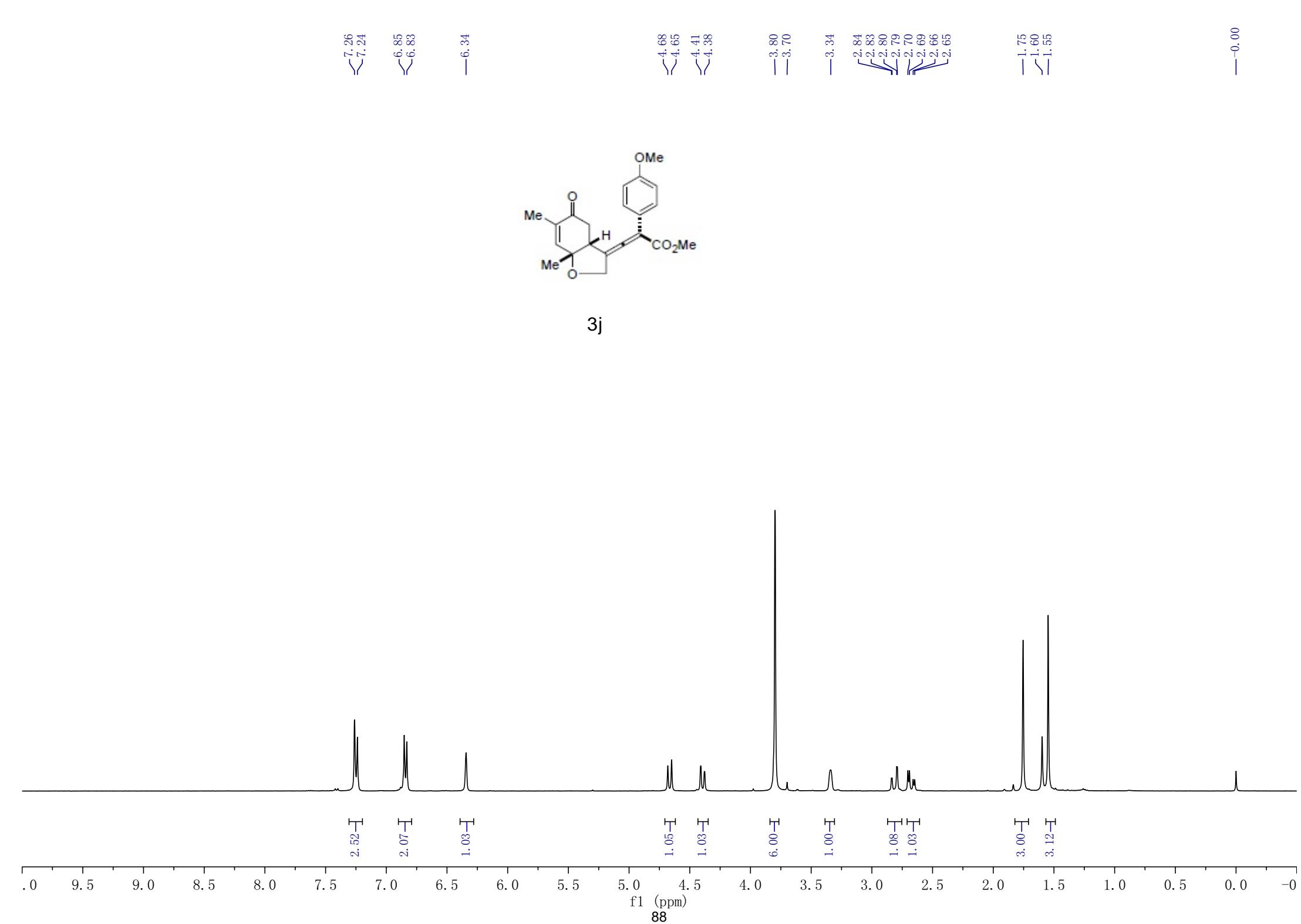
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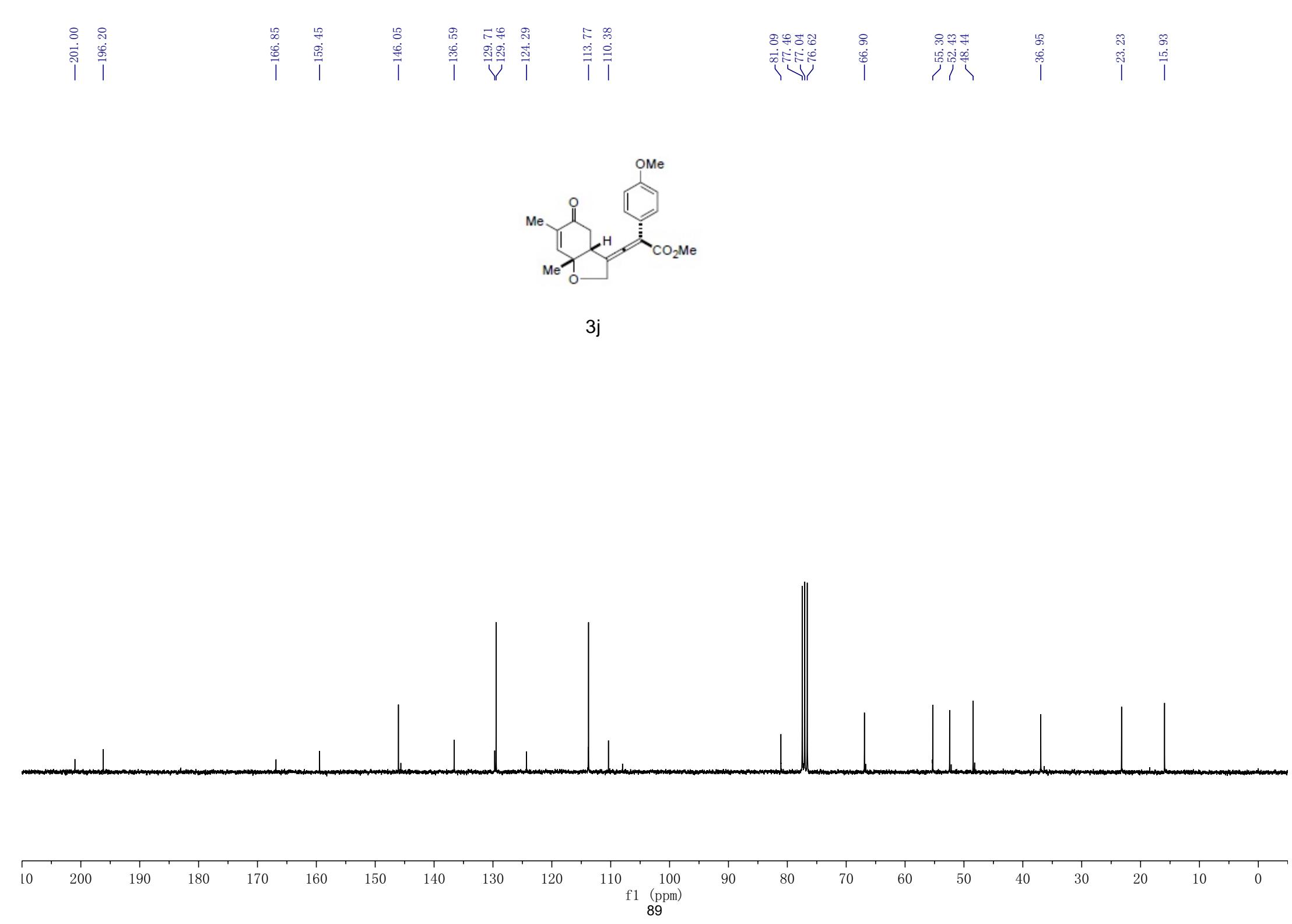
—17.72



3i





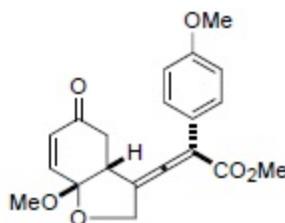


7.35
7.33
7.33
6.91
6.90
6.88
6.88
6.87

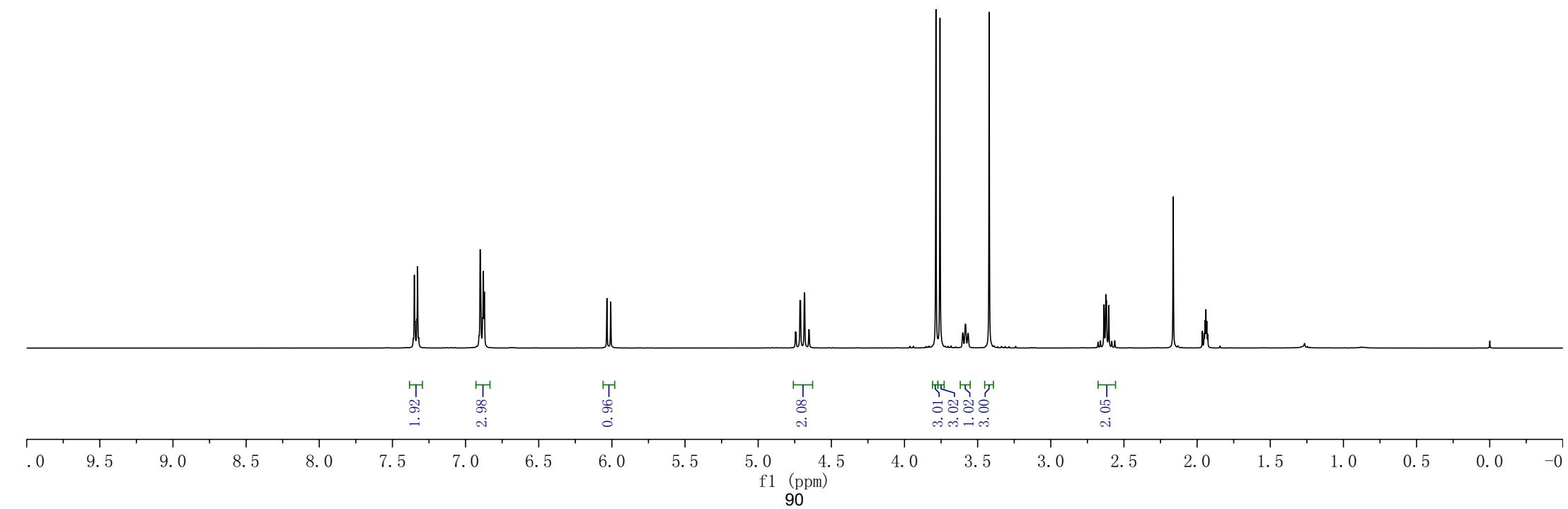
6.03
6.01

4.74
4.74
4.71
4.71
4.68
4.65

3.79
3.76
3.60
3.58
3.57
3.42



3k



—200.61
—196.08

—166.36

—159.57

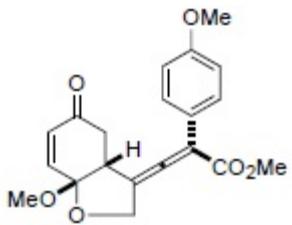
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—130.03
—129.59
—124.58
—117.33
—113.70
—108.59
—107.13
—103.54

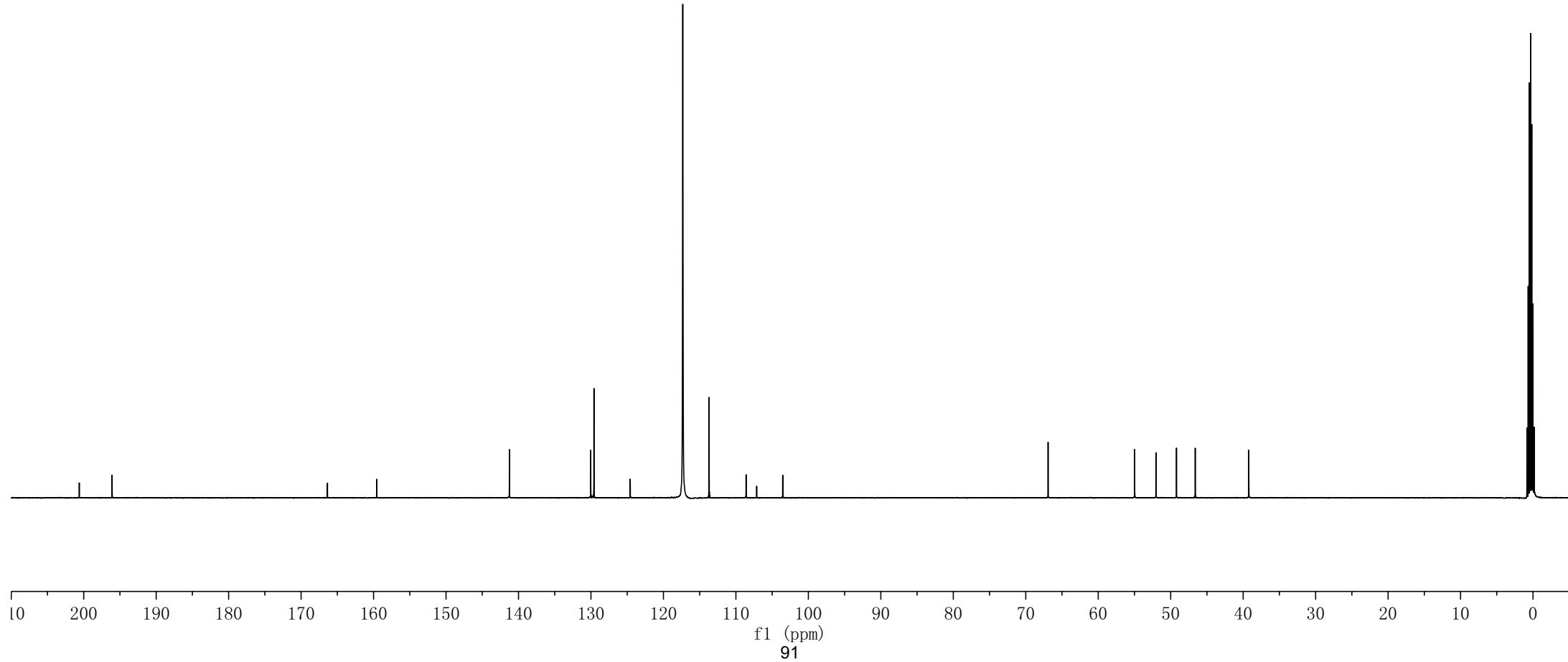
—66.92
—54.98
—52.03
—49.20
—46.61

—39.22

0.83
0.67
0.50
0.34
0.28
0.17
0.13
0.01
—0.16



3k



—0.00

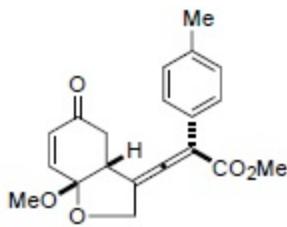
-1.54

—

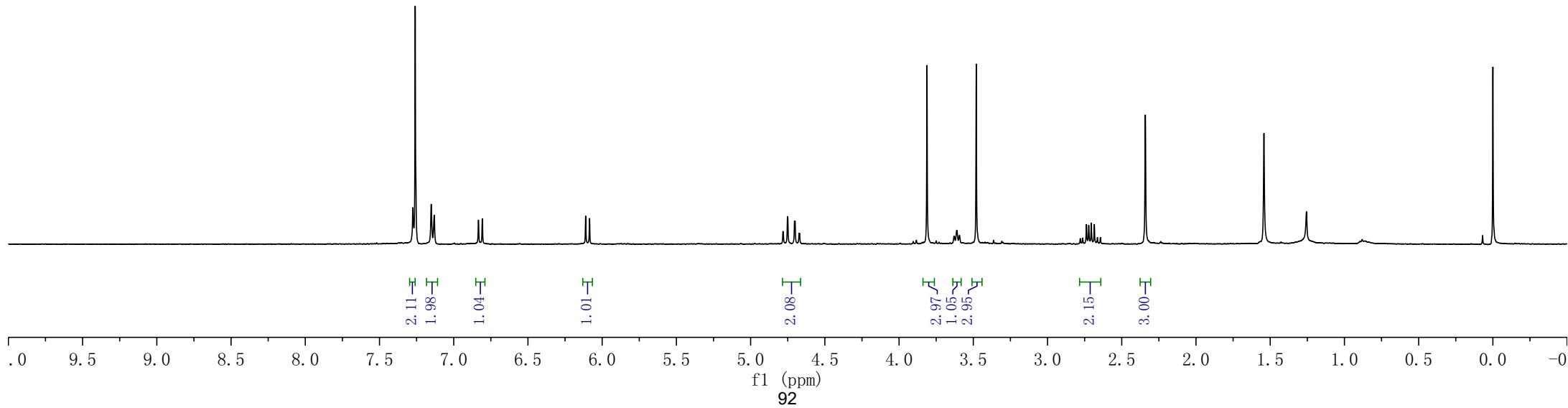
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4.70
4.70
4.67

3.81
3.63
3.61
3.59
3.48

2.78
2.76
2.74
2.72
2.70
2.68
2.66
2.64
2.34



3l



—201.20

—196.13

—166.36

—140.97
—138.18
—130.58
—129.16
—129.04
—128.10

—108.21
—107.99
—103.48

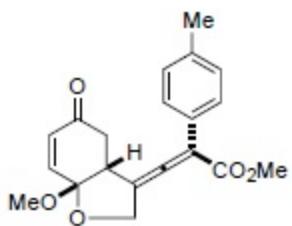
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—76.99
—76.74

—67.29

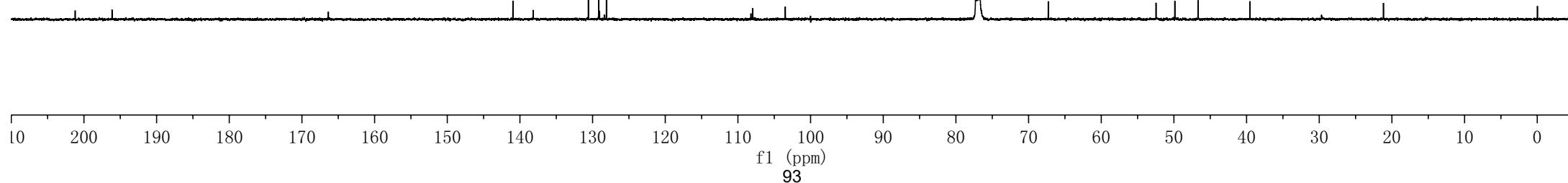
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—46.67

—39.54

—21.16



3l



—0.00

—1.26

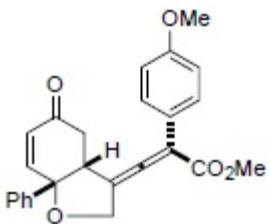
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2.75
2.75
2.74
2.73

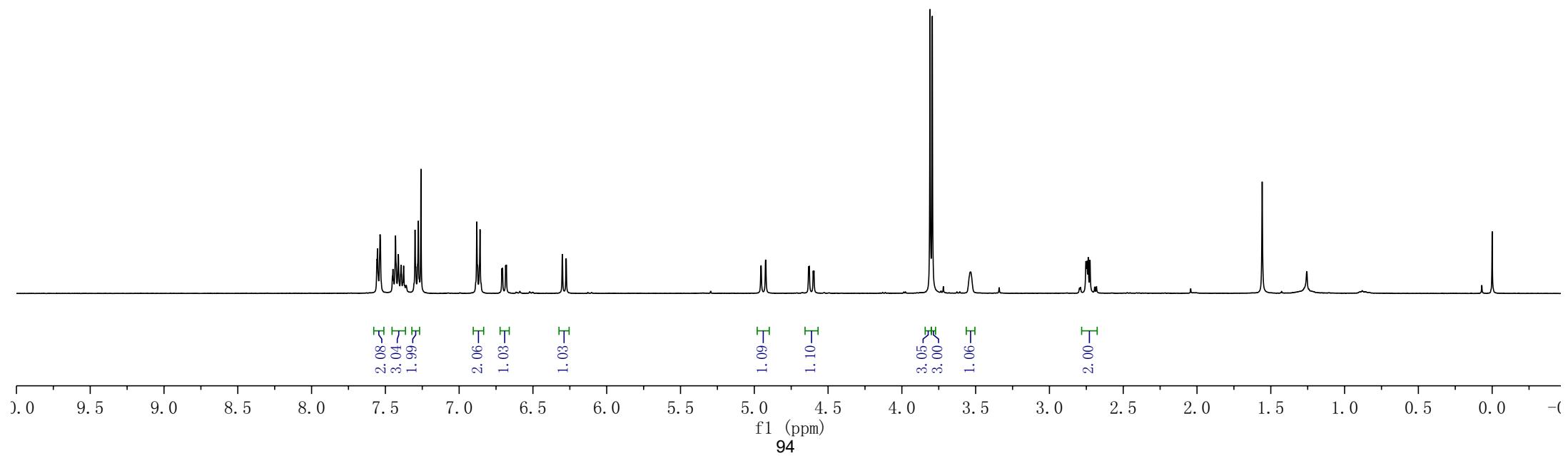
3.81
3.79
3.53

4.95
4.92
4.63
4.63
4.60
4.60

7.56
7.55
7.54
7.45
7.43
7.41
7.39
7.38
7.30
7.28
7.26
6.88
6.86
6.71
6.71
6.68
6.68
6.30
6.27



3m



—200.54

—196.24

—165.28

—159.56

—148.37

—138.86

131.53
129.51
128.91
128.69
125.38
124.04

—113.84
—110.06

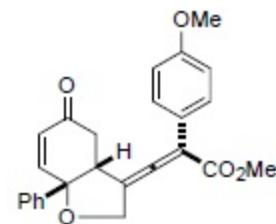
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77.46
77.04
76.61

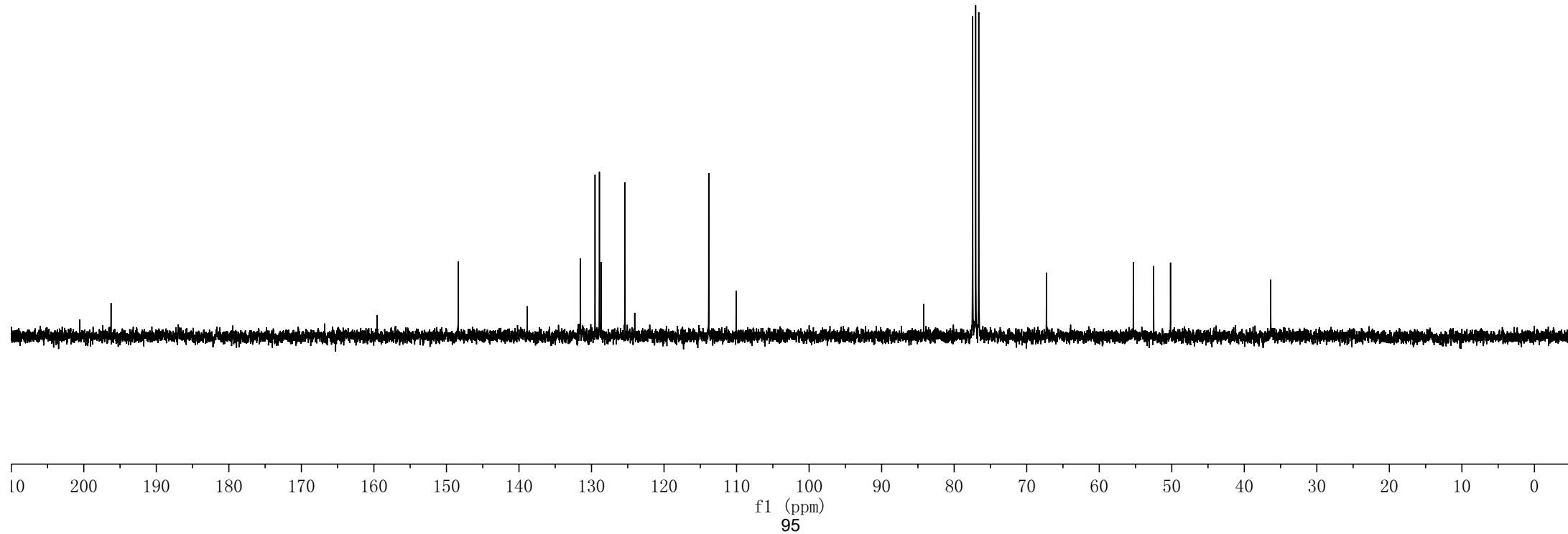
—67.27

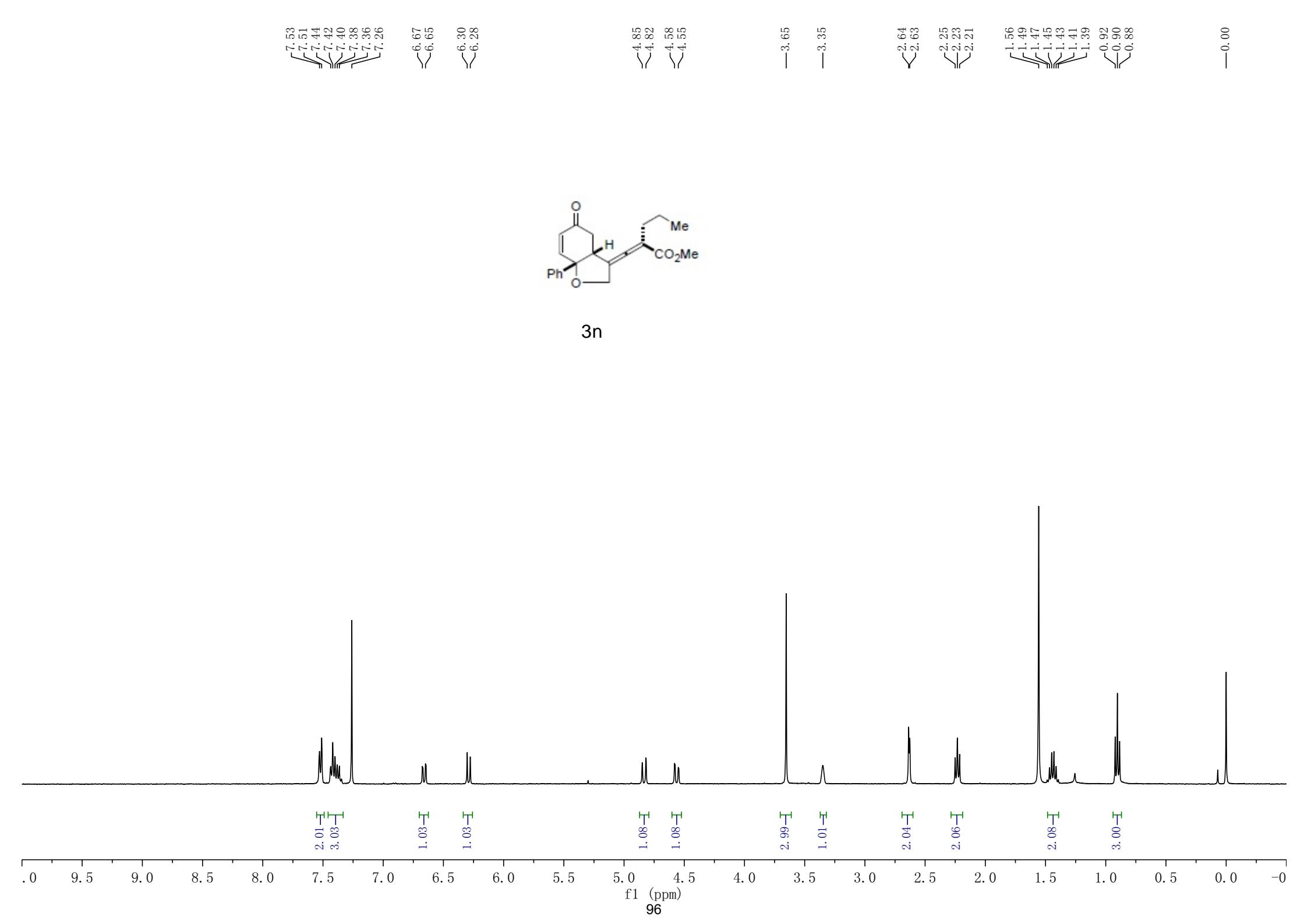
—55.30
—52.50
—50.17

—36.37



3m





—199.72
—195.74

—167.13

—147.88

—139.10

—131.45
—128.86
—128.58
—125.36

—108.67
—106.34

—84.07

—77.27
—77.02
—76.77

—67.05

—51.87

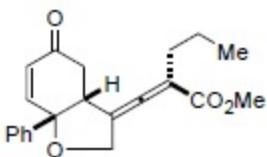
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—35.58

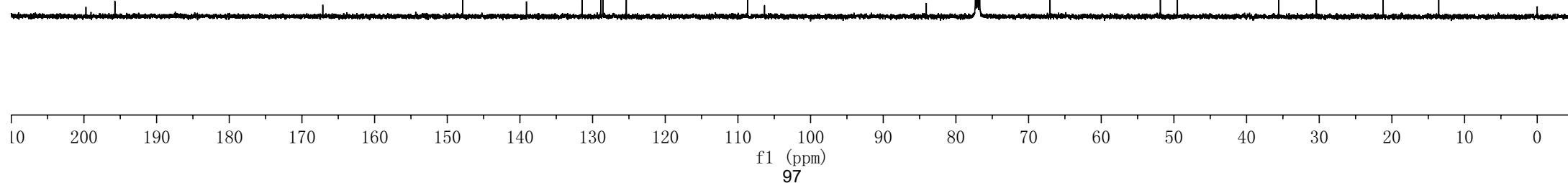
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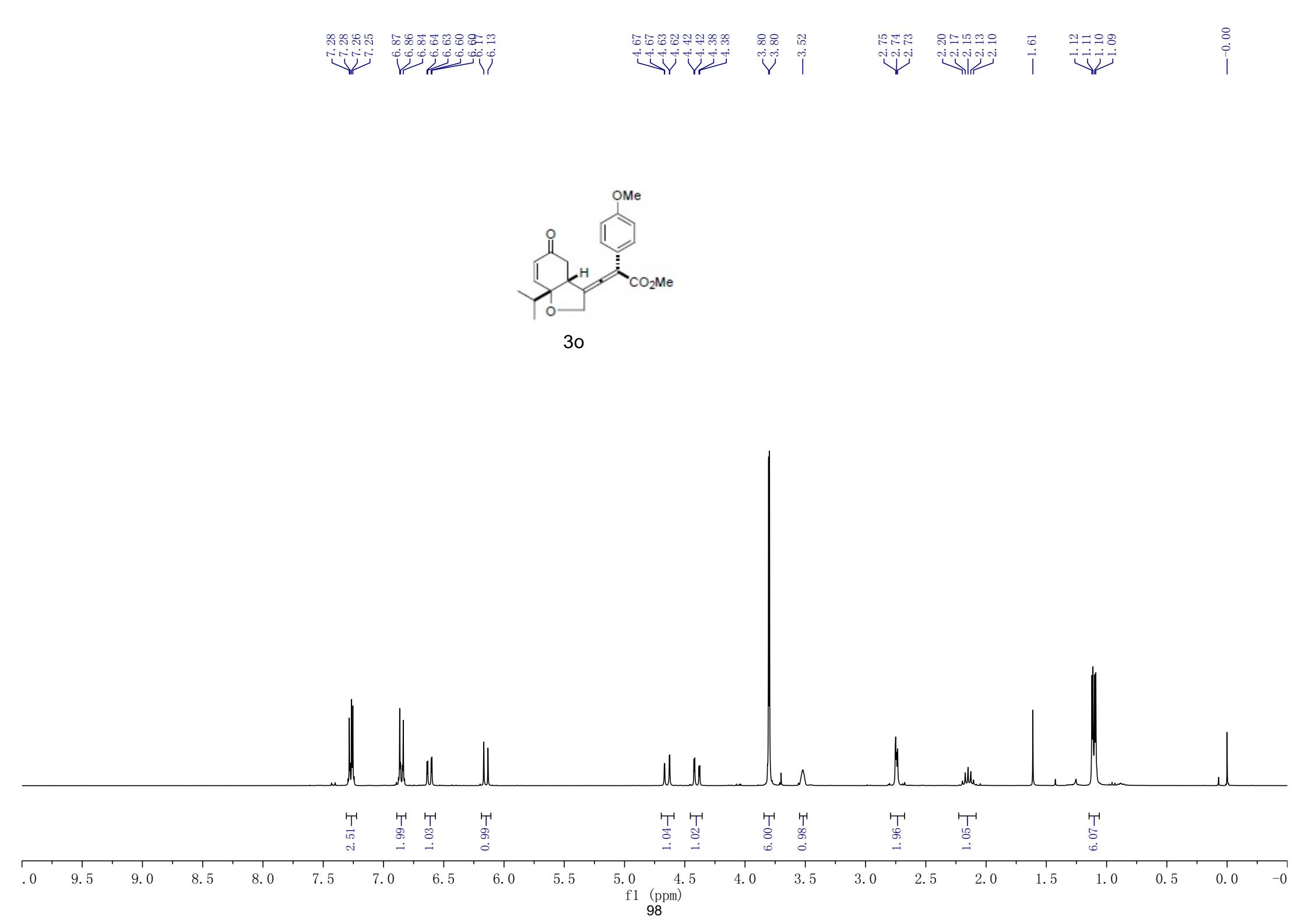
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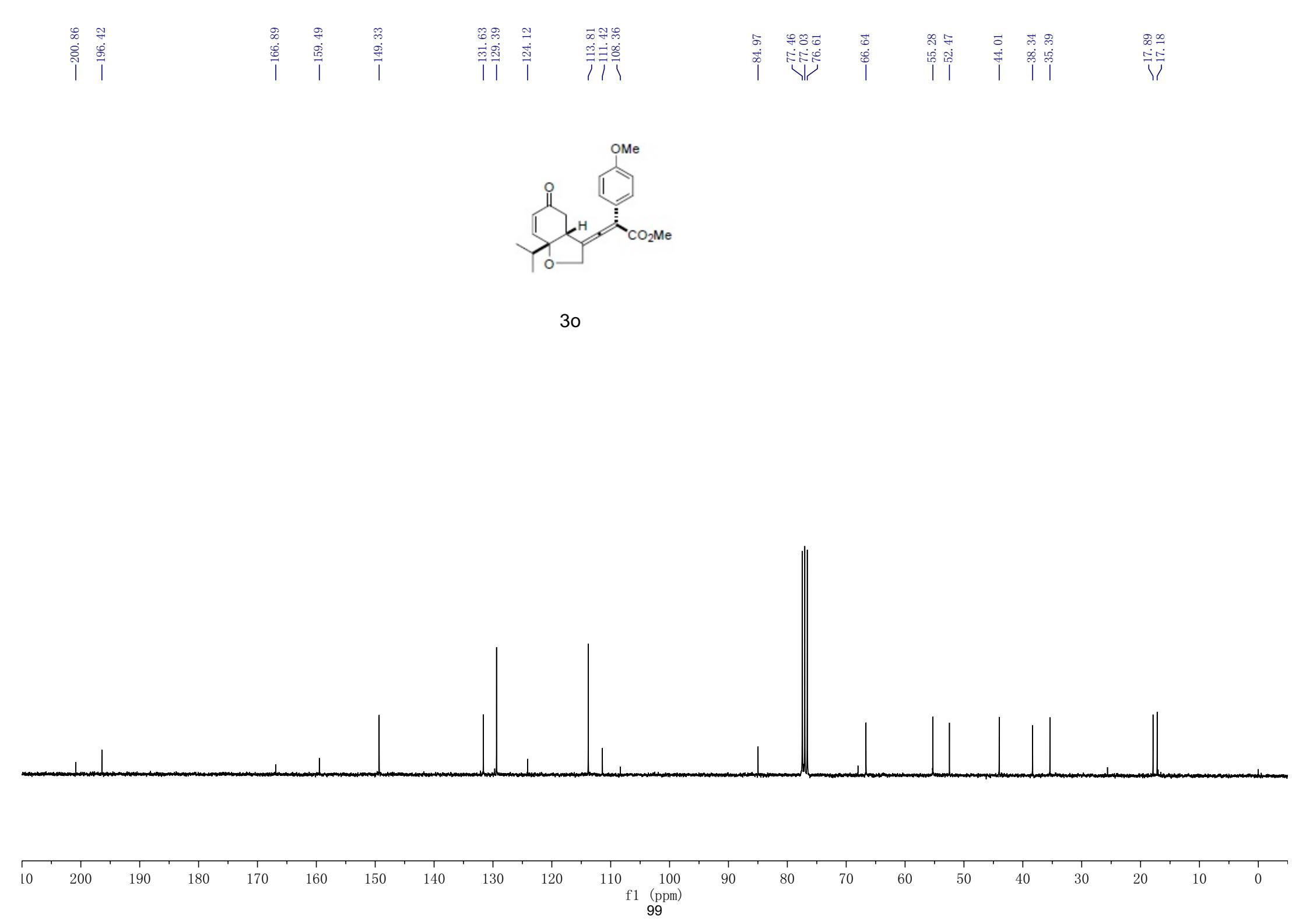
—13.55



3n







—0.00

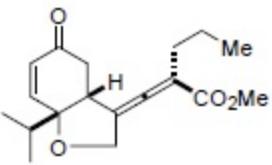
—7.27

6.59
6.59
6.56
6.56
6.15
6.13

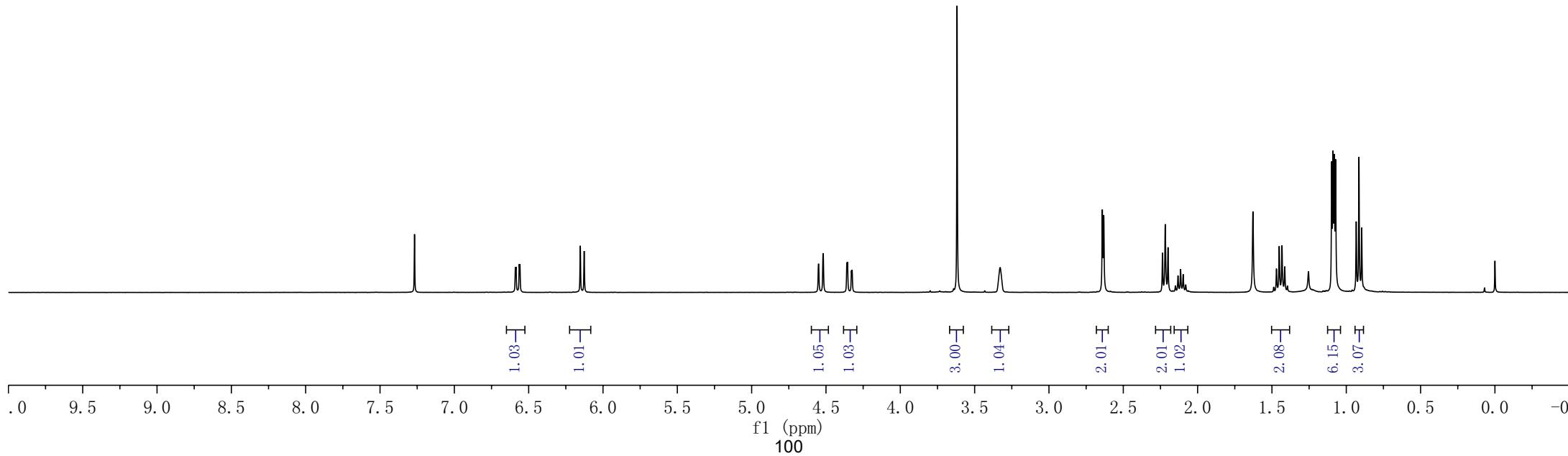
4.55
4.52
4.36
4.36
4.33
4.32

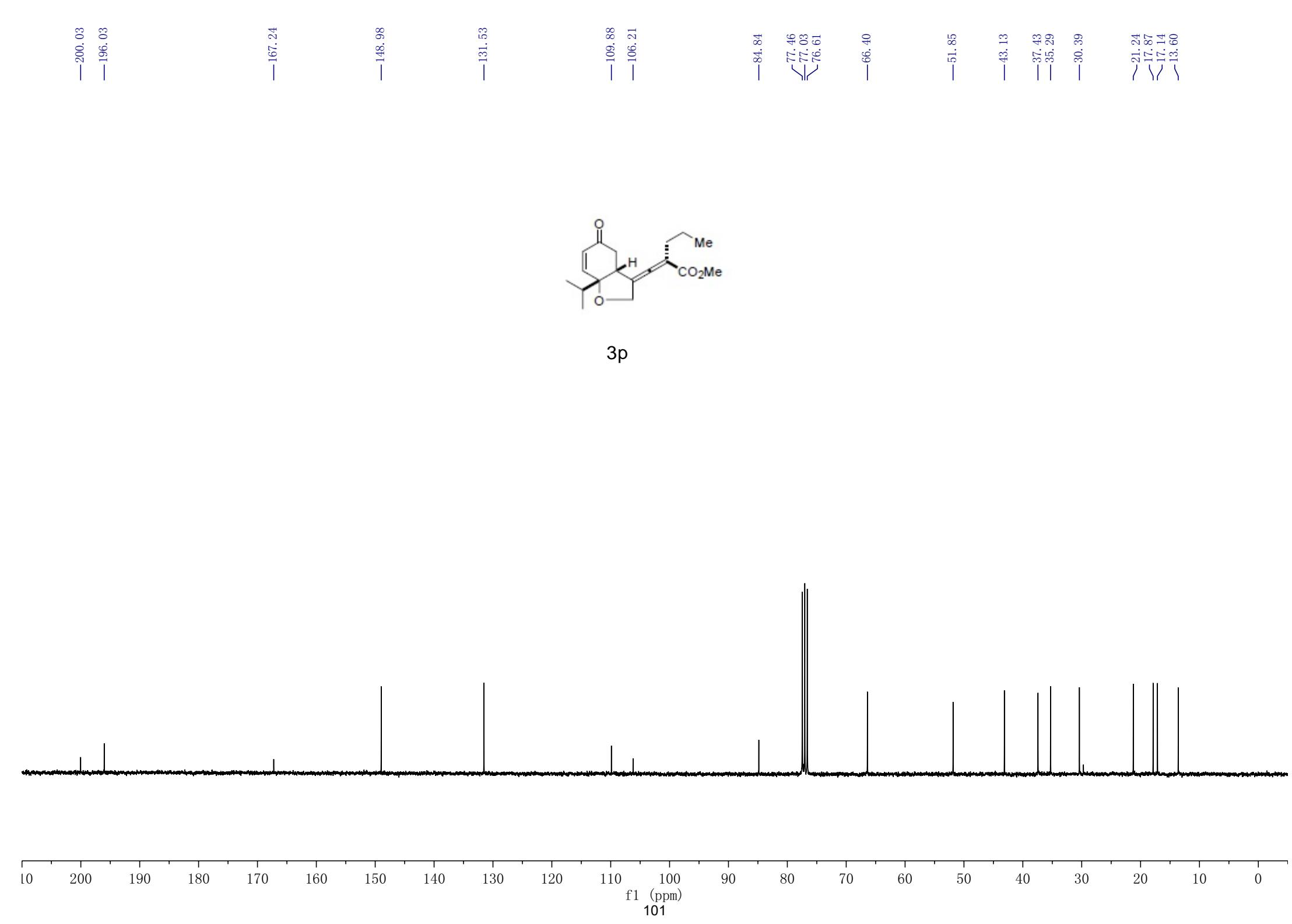
—3.62
—3.33

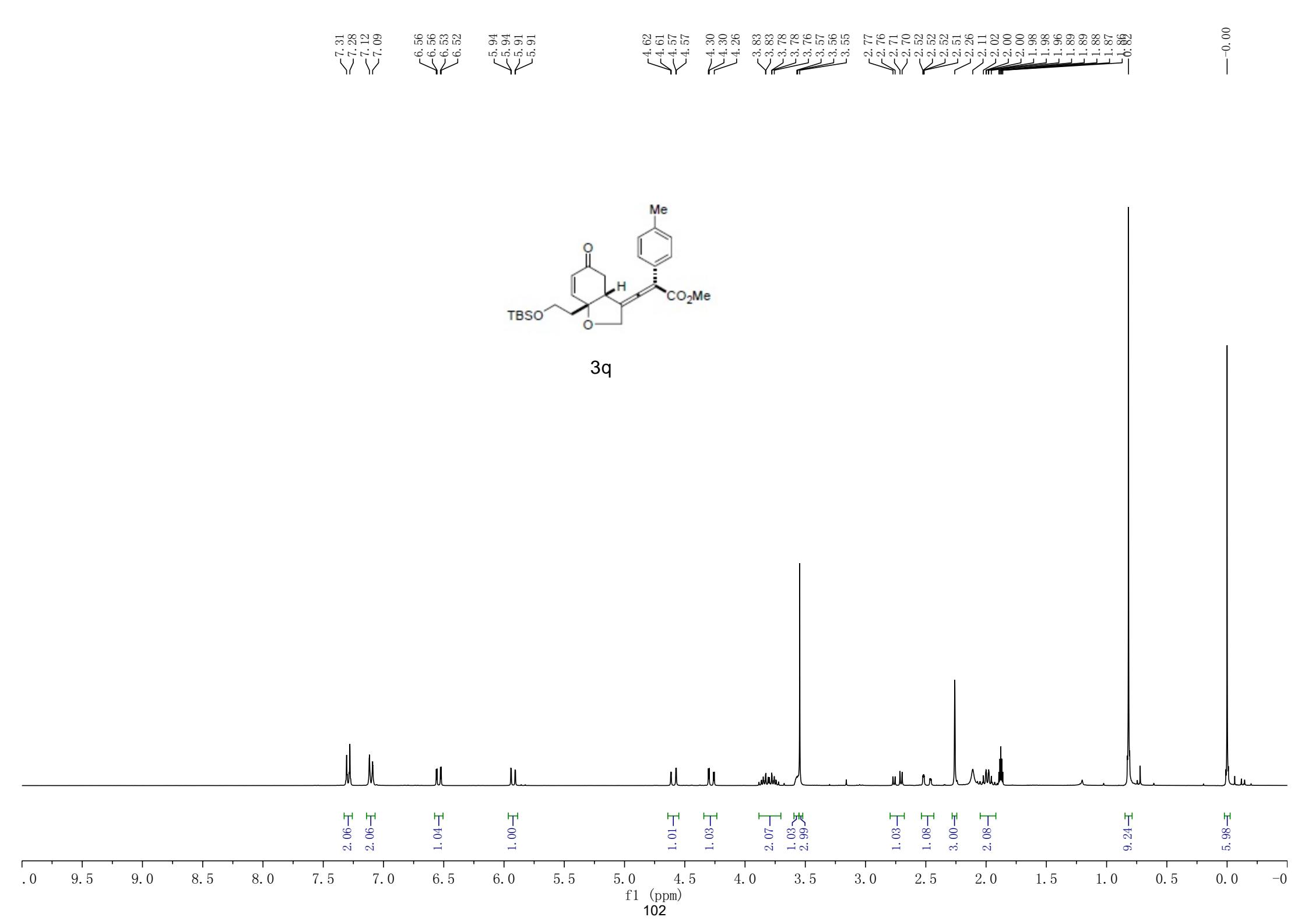
2.64
2.63
2.24
2.22
2.20
2.13
2.11
2.09
1.63
1.47
1.45
1.43
1.41
1.25
1.10
1.09
1.08
1.07
0.93
0.91
0.90

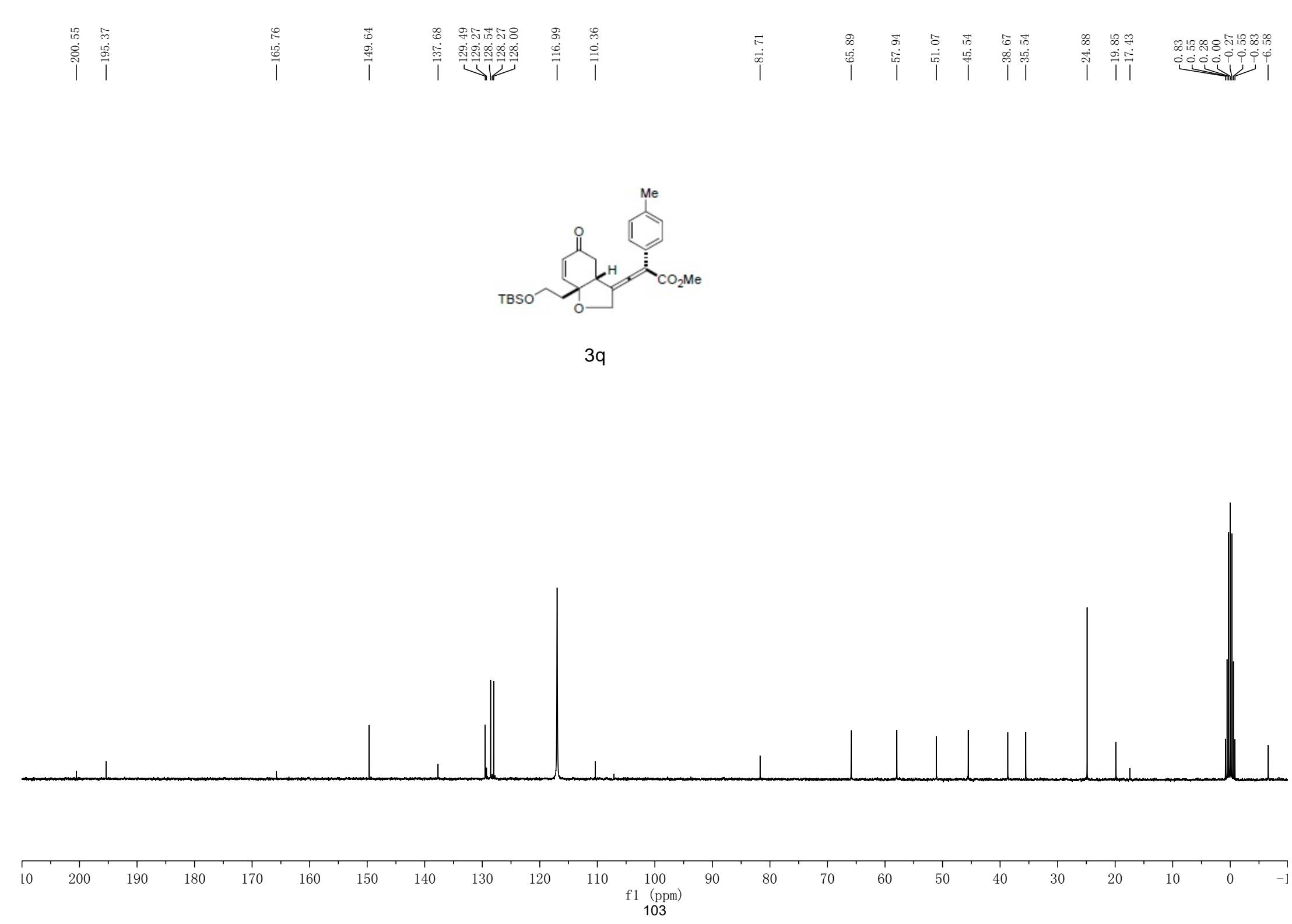


3p

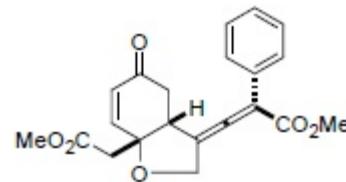
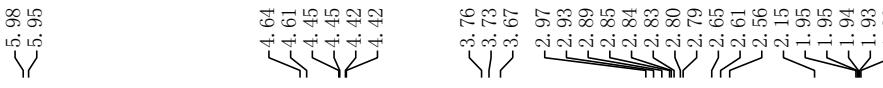




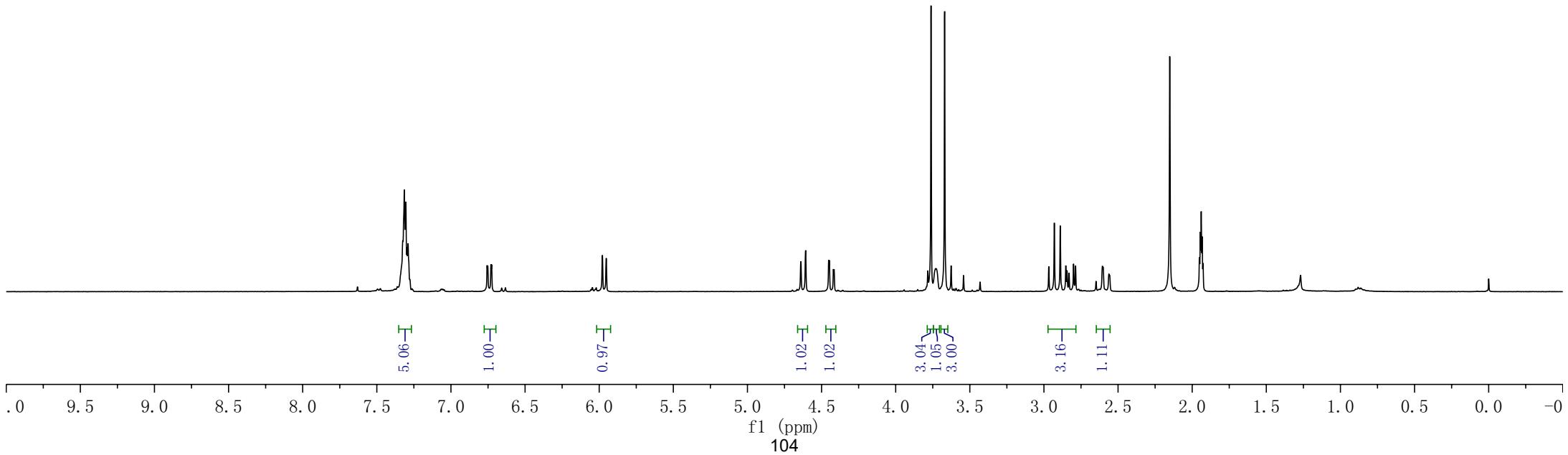


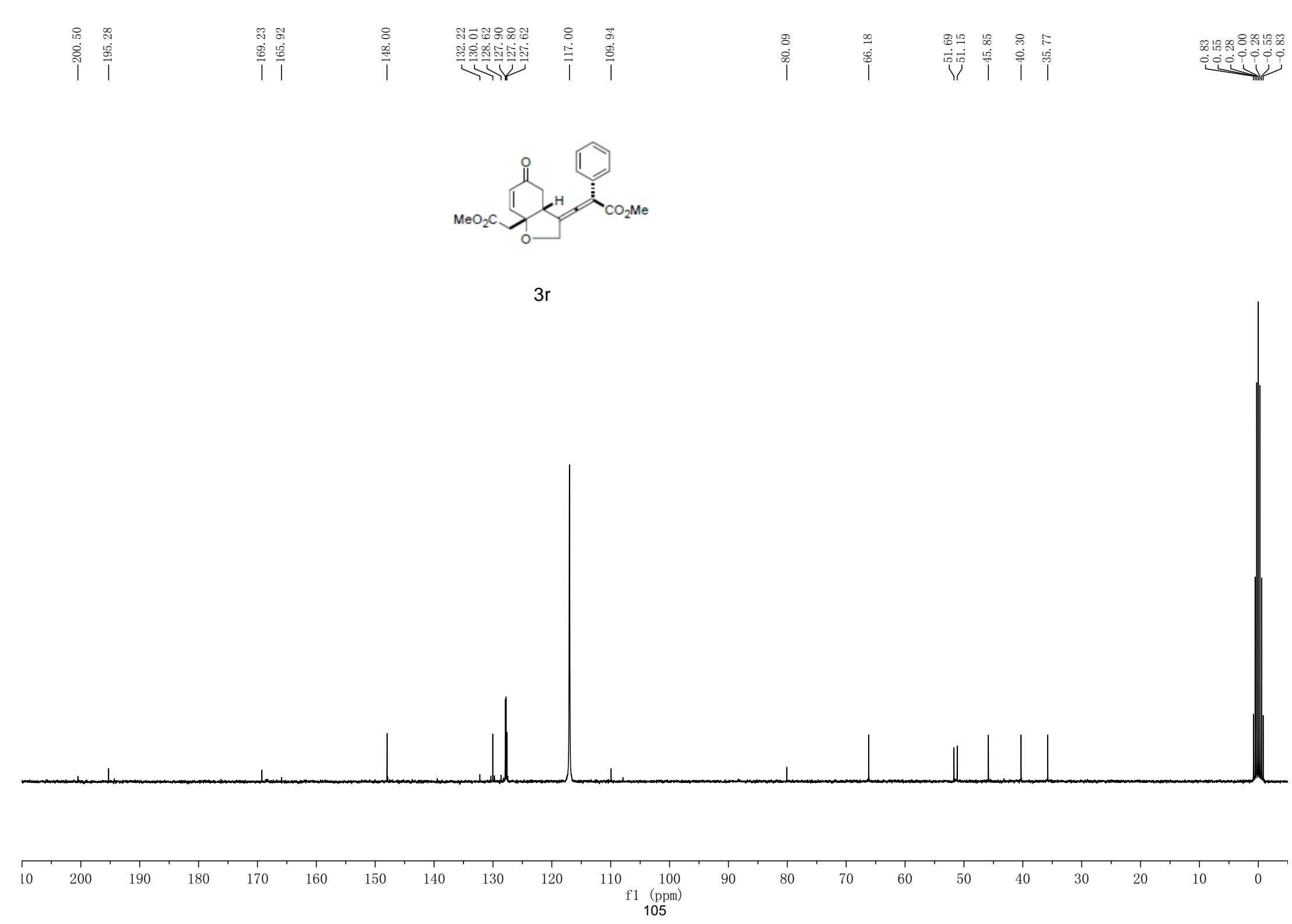


—0.00



3r





—0.00

0.94

0.92

0.95

1.43

1.48

1.76

1.93

1.94

2.16

2.45

2.45

2.49

2.50

2.66

2.68

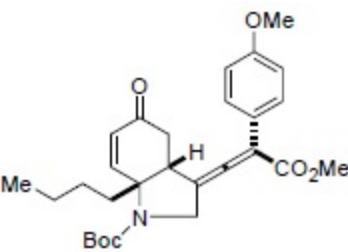
2.71

2.72

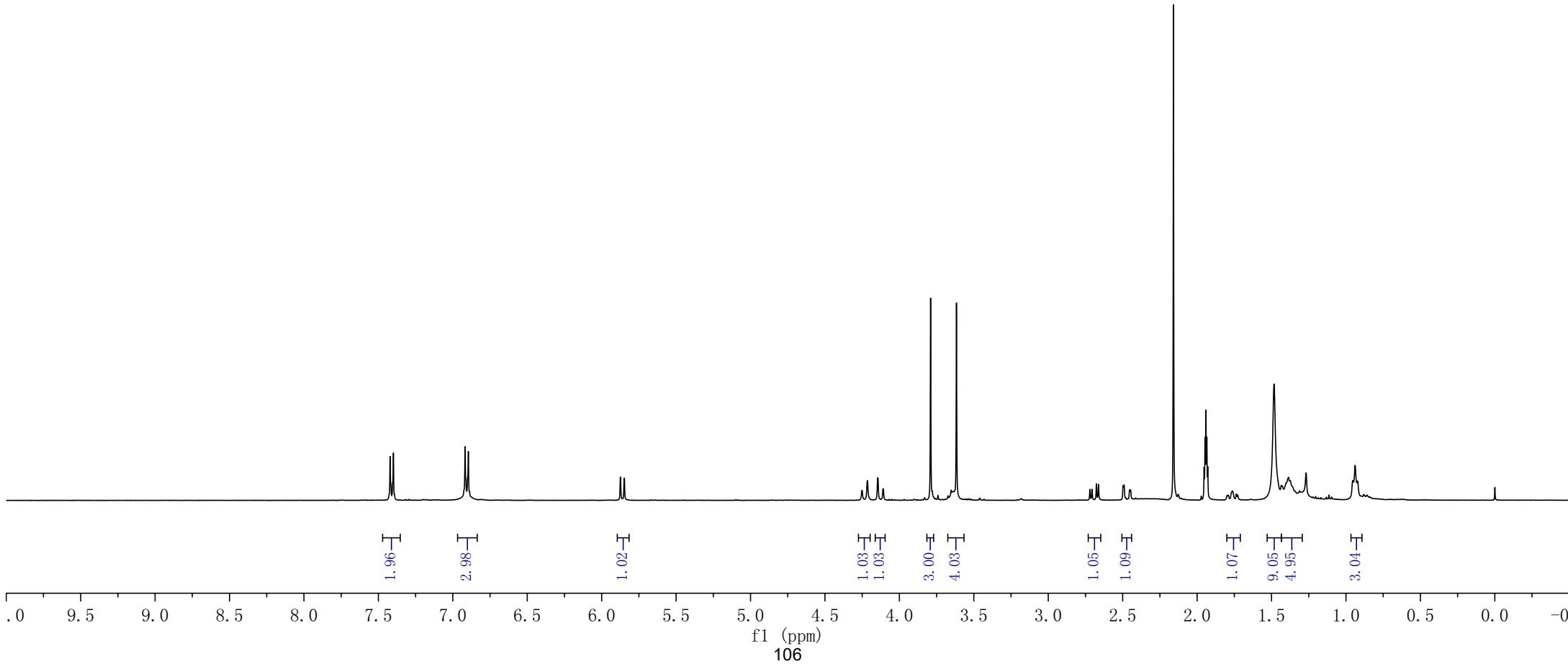
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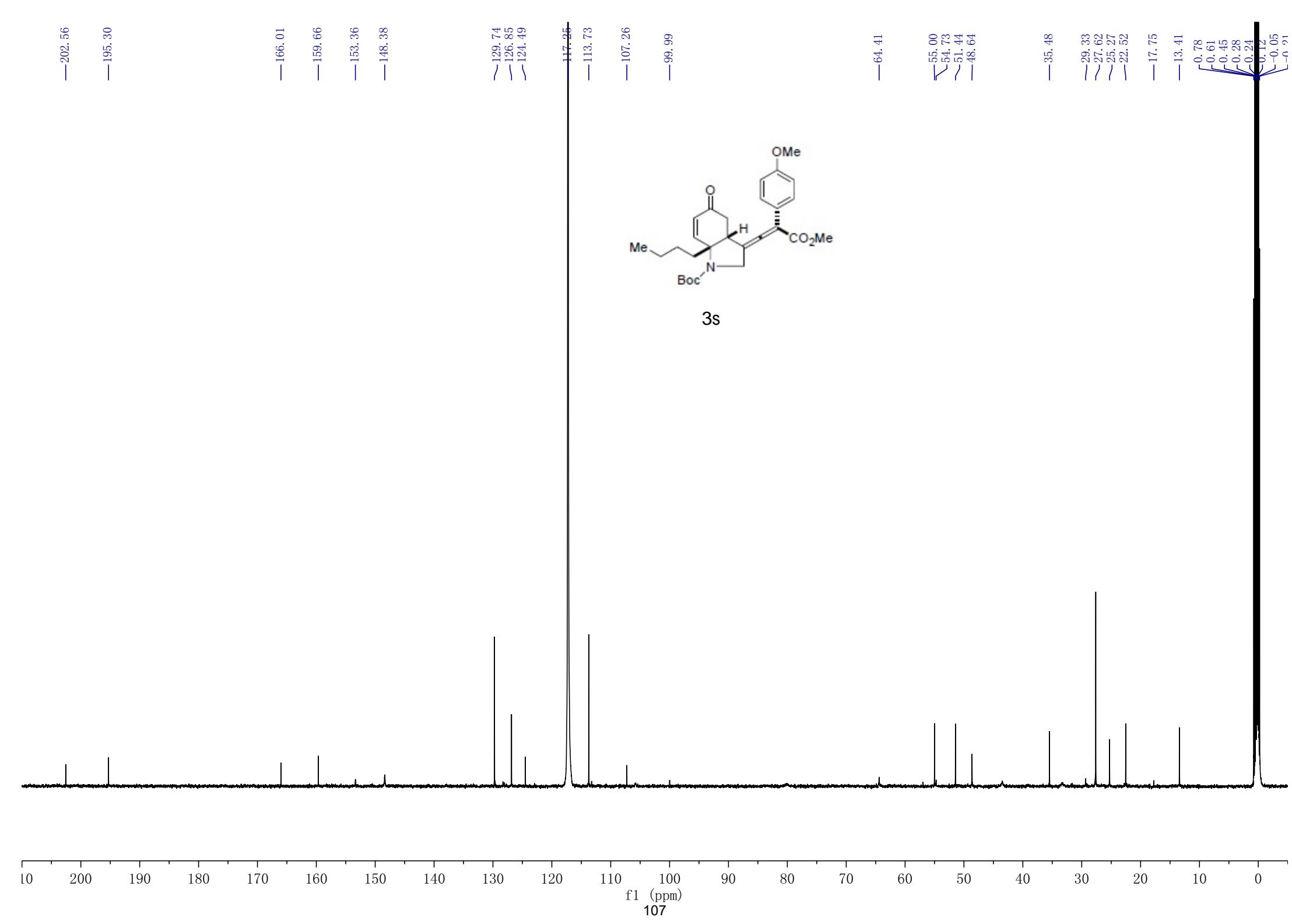
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3.79



3s

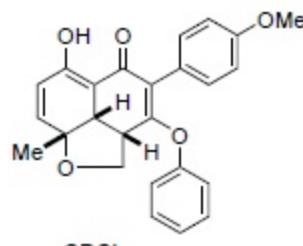




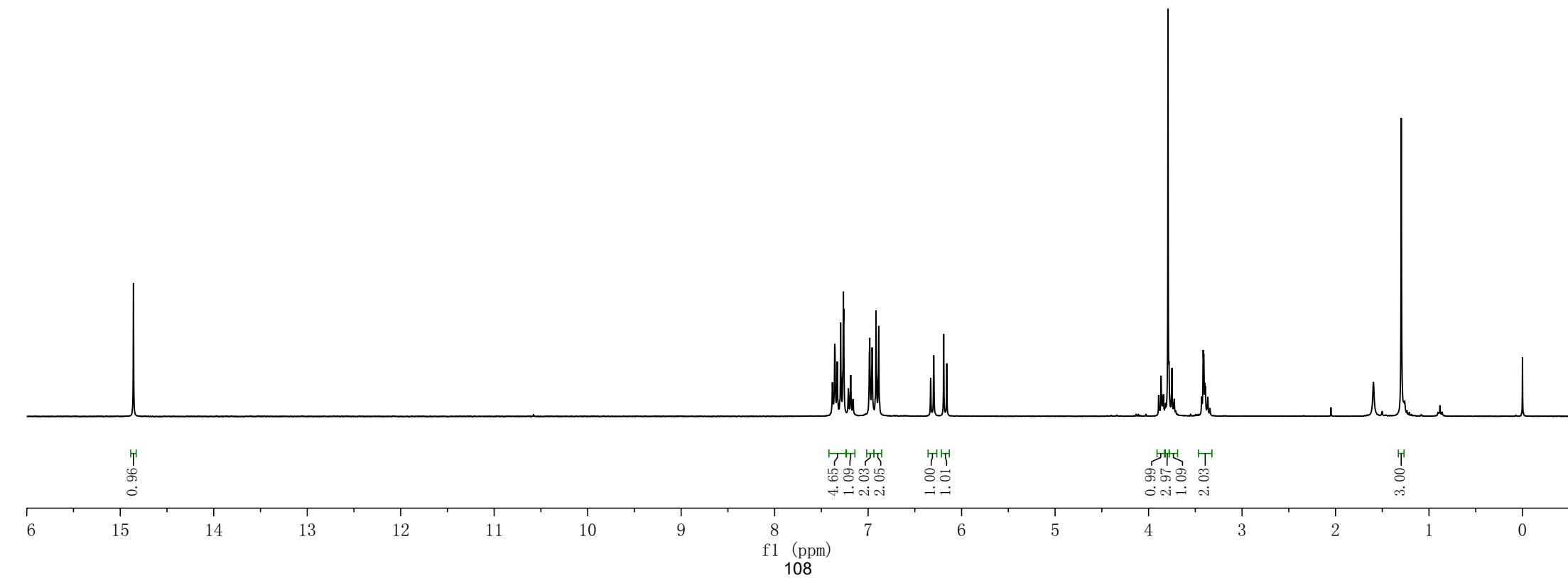
-14.86

7.38
7.36
7.33
7.29
7.26
7.26
7.21
7.19
7.16
6.98
6.96
6.92
6.89
6.33
6.30
6.19
6.16
3.89
3.87
3.85
3.84
3.82
3.79
3.78
3.75
3.72
3.43
3.40
3.39
3.37
3.34
3.30
1.30
-1.26

-0.00



4a



— 187.35

∫ 168.60
~ 163.64
~ 158.99
∫ 154.01

— 141.60

∫ 131.44
∫ 130.01
∫ 125.91
∫ 125.23
∫ 123.34
∫ 123.29
∫ 120.01
— 113.50

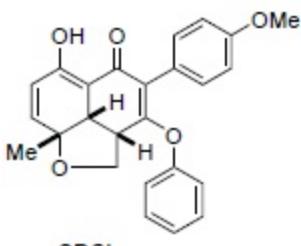
— 97.46

∫ 78.49
∫ 77.48
∫ 77.06
∫ 76.63
∫ 71.42

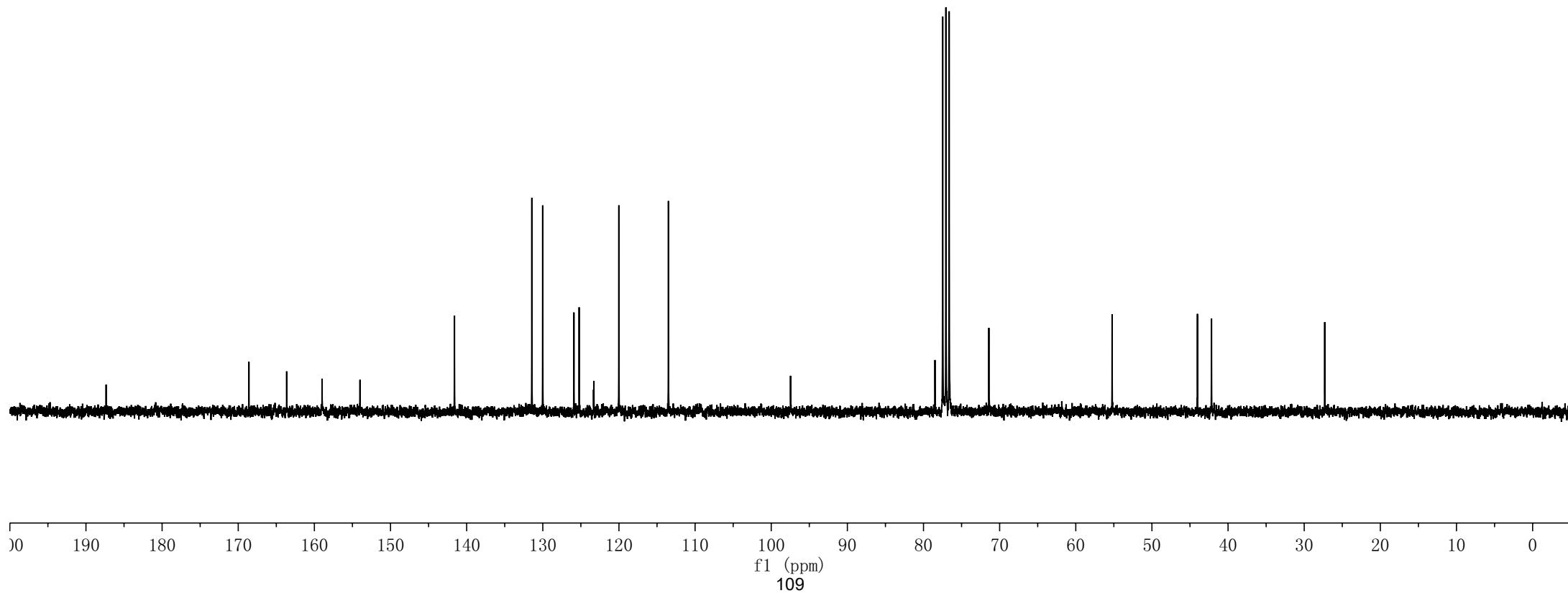
— 55.23

~ 44.02
~ 42.18

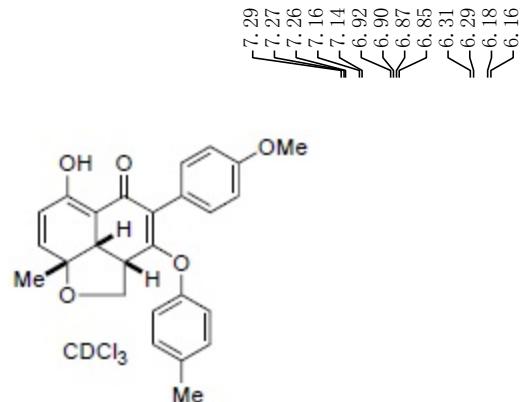
— 27.30



4a



—14.86



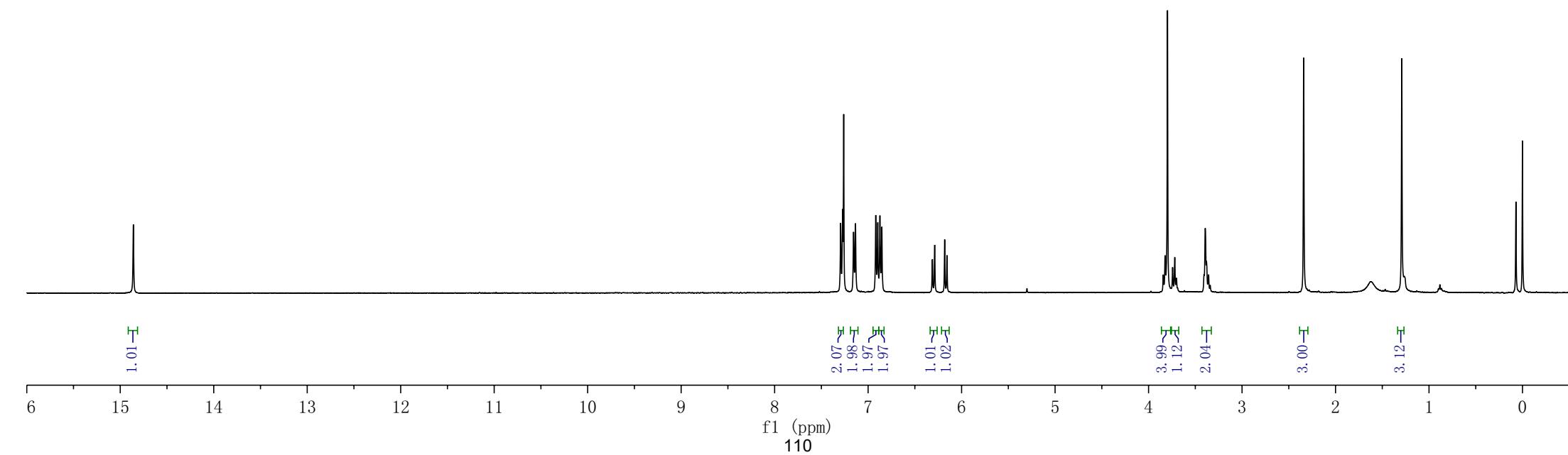
4b

—3.84
—3.82
—3.80
—3.74
—3.72
—3.70
—3.41
—3.39
—3.38
—3.36
—3.34

—2.34

—1.62
—1.29

—0.00

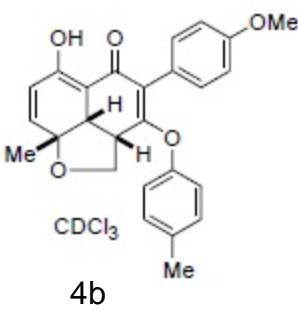


— 187.48

~ 168.34
~ 164.16
✓ 158.94

— 151.60

— 141.45
✓ 135.14
✓ 131.46
— 130.47
✓ 125.93
✓ 123.44
✓ 122.66
~ 120.07
— 113.50



— 97.44

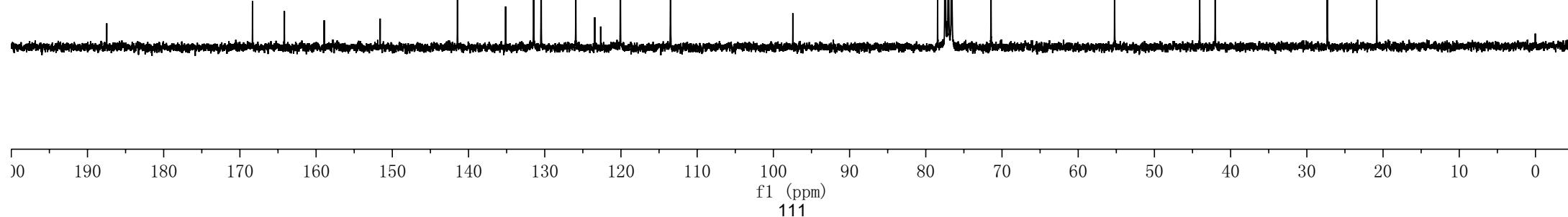
✓ 78.45
✓ 77.47
✓ 77.04
✓ 76.62
✓ 71.44

— 55.23

~ 44.06
~ 42.02

— 27.32

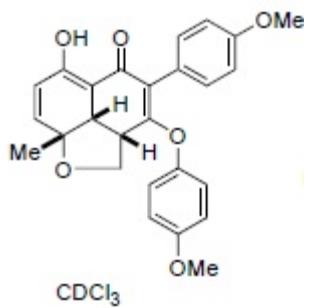
— 20.83



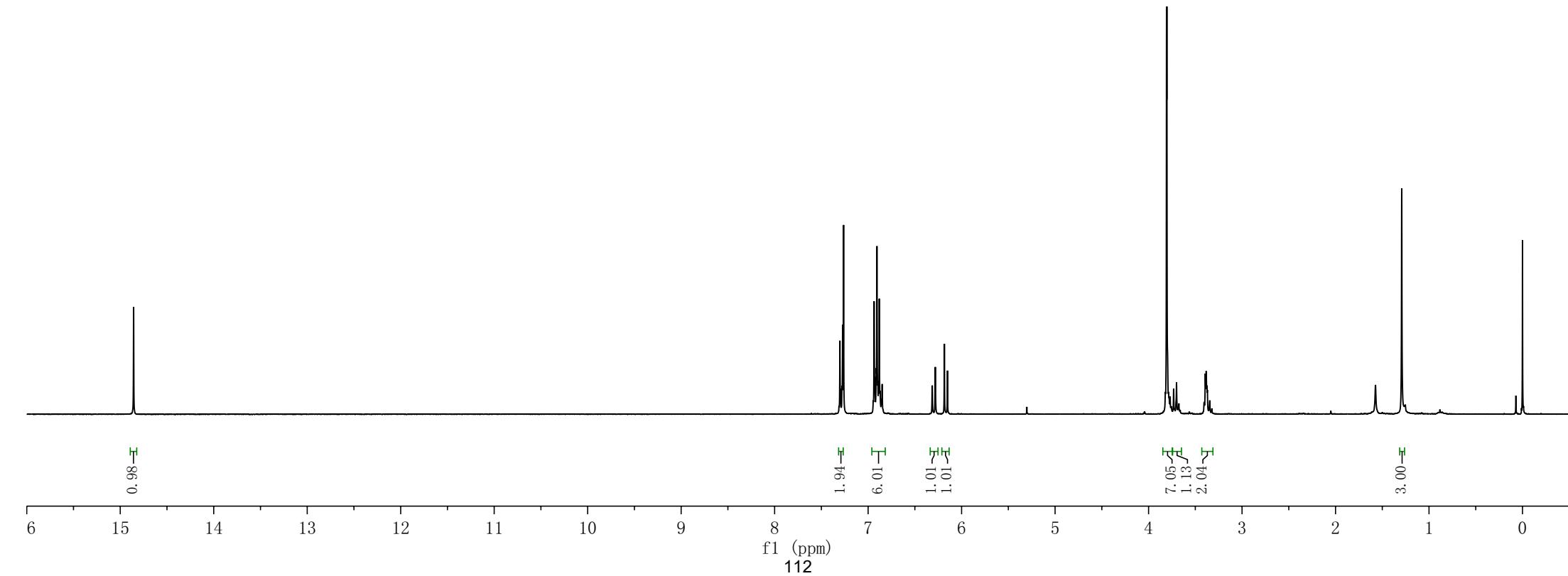
-14.86

7.31
7.30
7.30
7.28
7.27
7.26
6.95
6.94
6.93
6.91
6.91
6.90
6.89
6.88
6.87
6.86
6.85
6.31
6.28
6.18
6.15

-0.00



4c



—187.57

~168.13
~164.66
~158.92
~157.11

—147.15

—141.33

~131.49
~125.94
~123.49
~122.01
~121.54
~114.91
~113.52

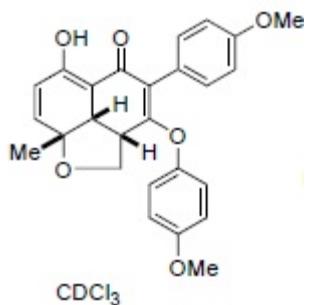
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~78.46
~77.47
~77.04
~76.62
~71.32

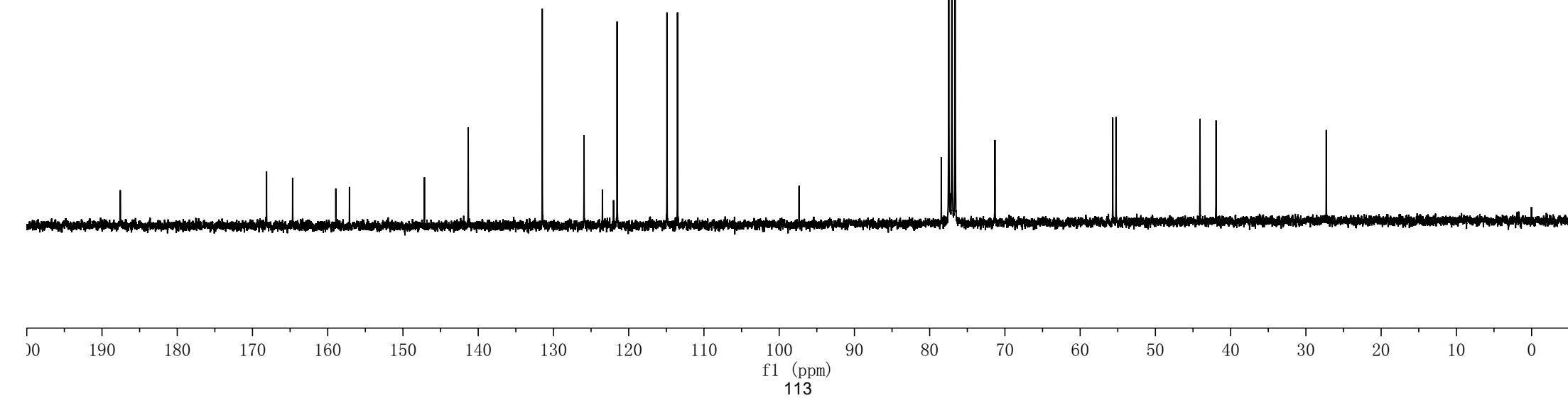
~55.67
~55.23

~44.07
~41.93

—27.29



4c

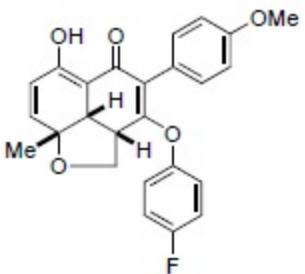


—14.80

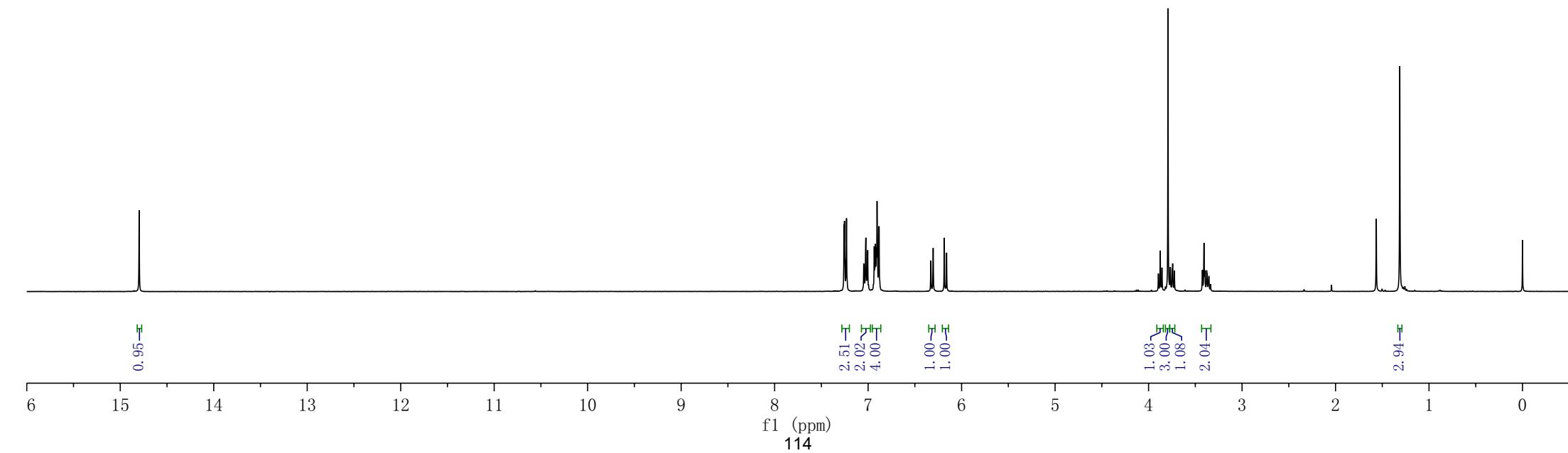
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3.79
3.77
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3.74
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3.42
3.41
3.40
3.38
3.37
3.36
3.35
3.34

—1.56
—1.31

—0.00



4d



— 187.23

— 168.66

— 163.56

— 161.36

— 159.05

— 158.12

< 149.93

< 149.89

— 141.60

— 131.43

— 125.91

— 123.21

— 123.13

— 121.45

— 121.34

— 116.82

— 116.51

— 113.53

— 97.33

— 78.54

— 77.47

— 77.05

— 76.62

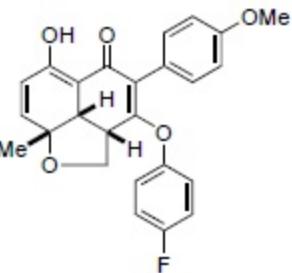
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— 55.23

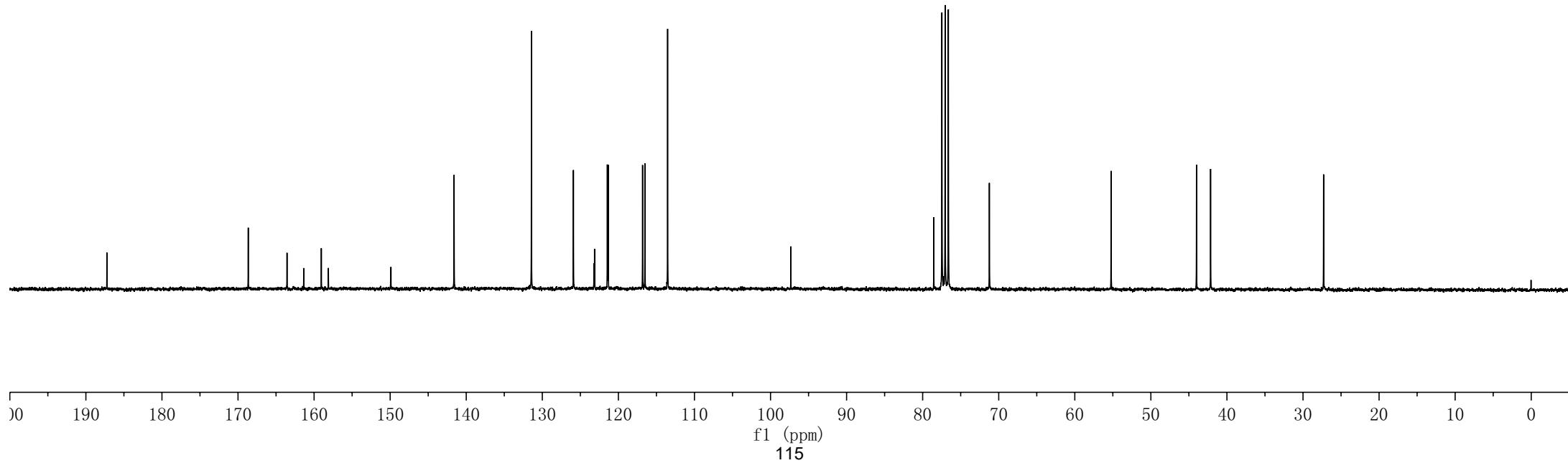
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— 42.15

— 27.29



4d



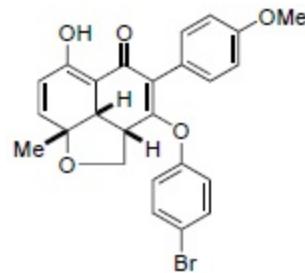
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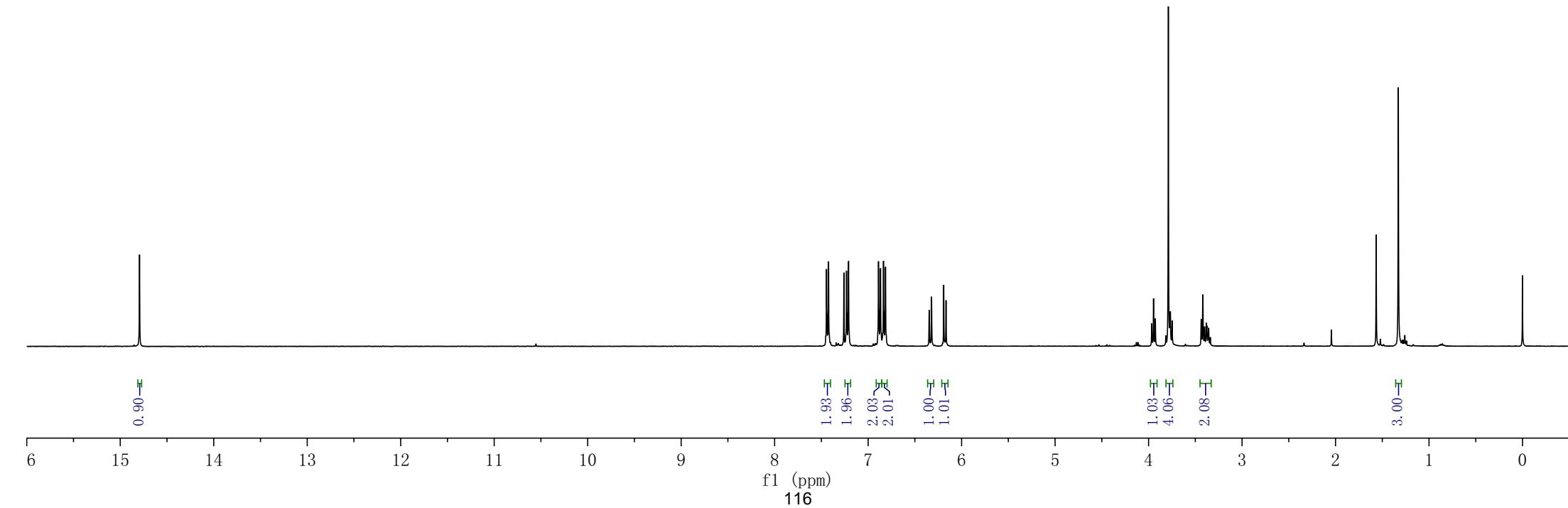
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3.36
3.36
3.34

—1.57
—1.33

—0.00



4e



—186.98

—169.03

—162.72

—159.12

—153.29

—141.81

—132.96

—131.36

—125.89

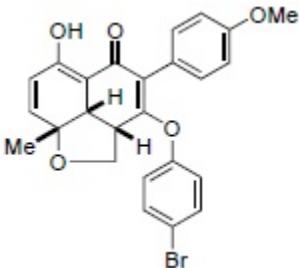
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—122.92

—121.27

—117.76

—113.53



4e

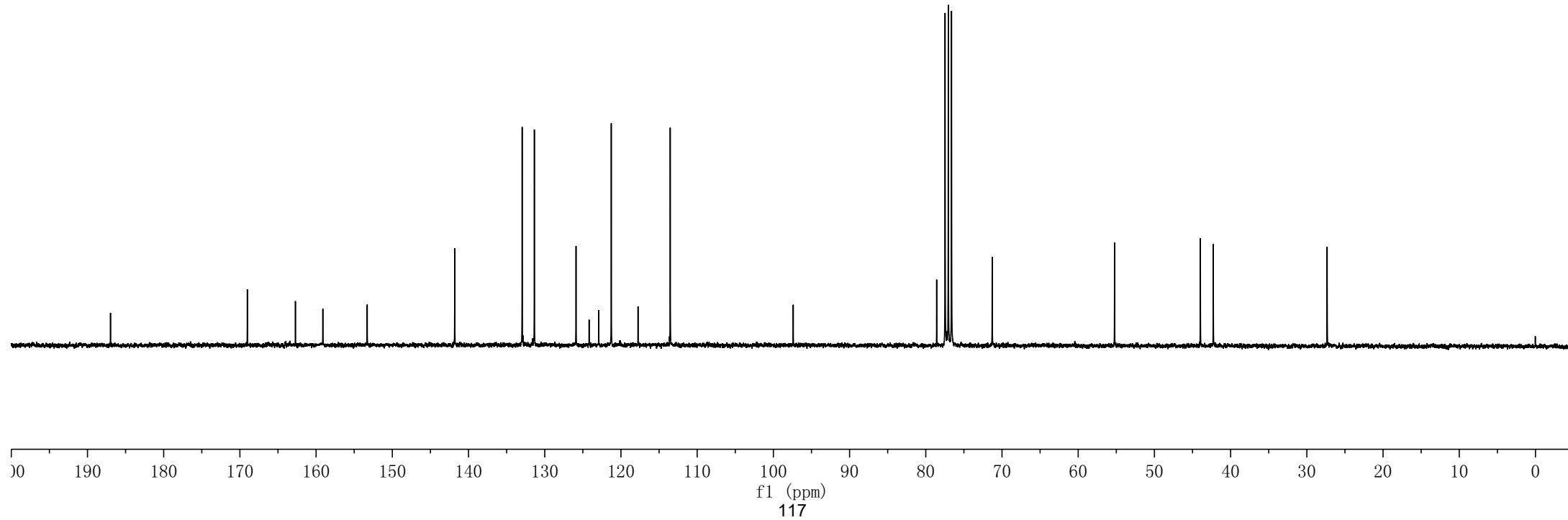
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—43.97

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—27.34



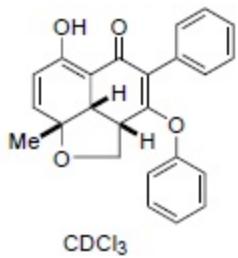
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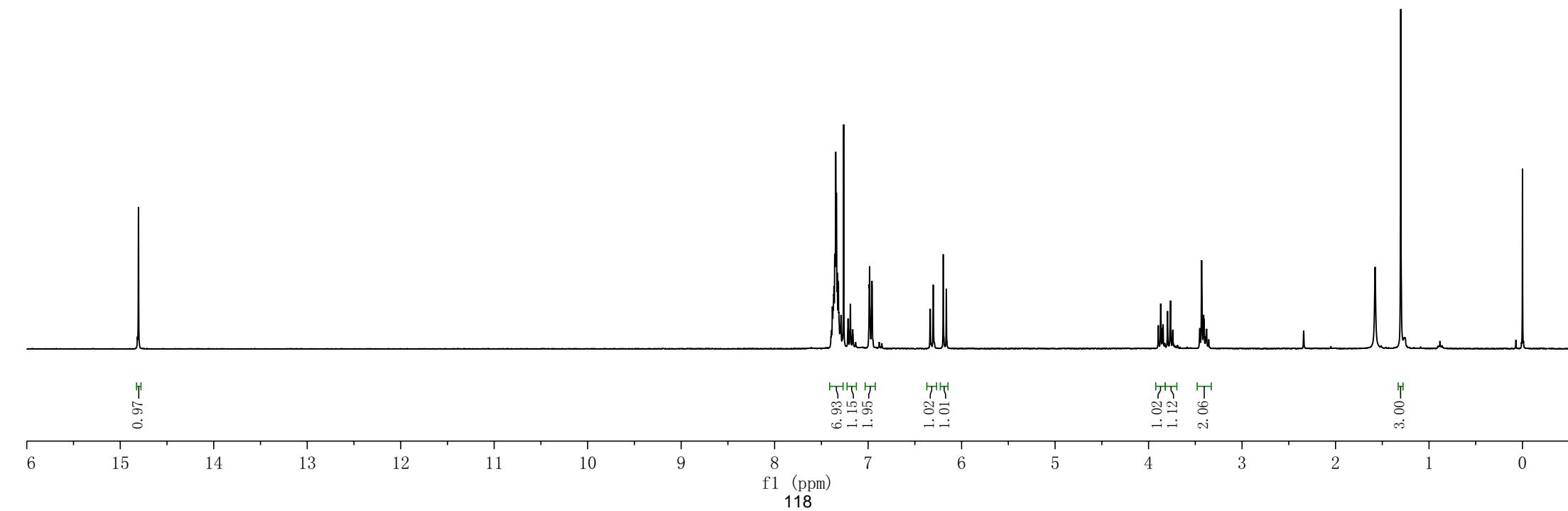
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-1.30

-0.00



4f



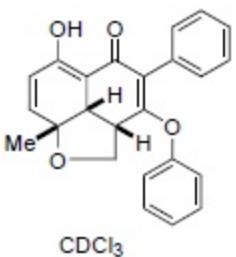
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123.65
120.12



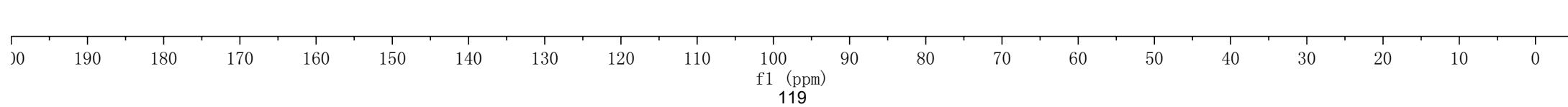
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—44.08
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—27.30



—14.85

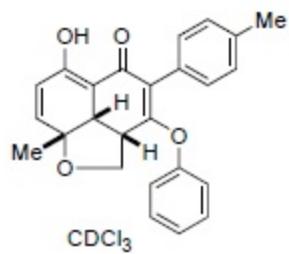
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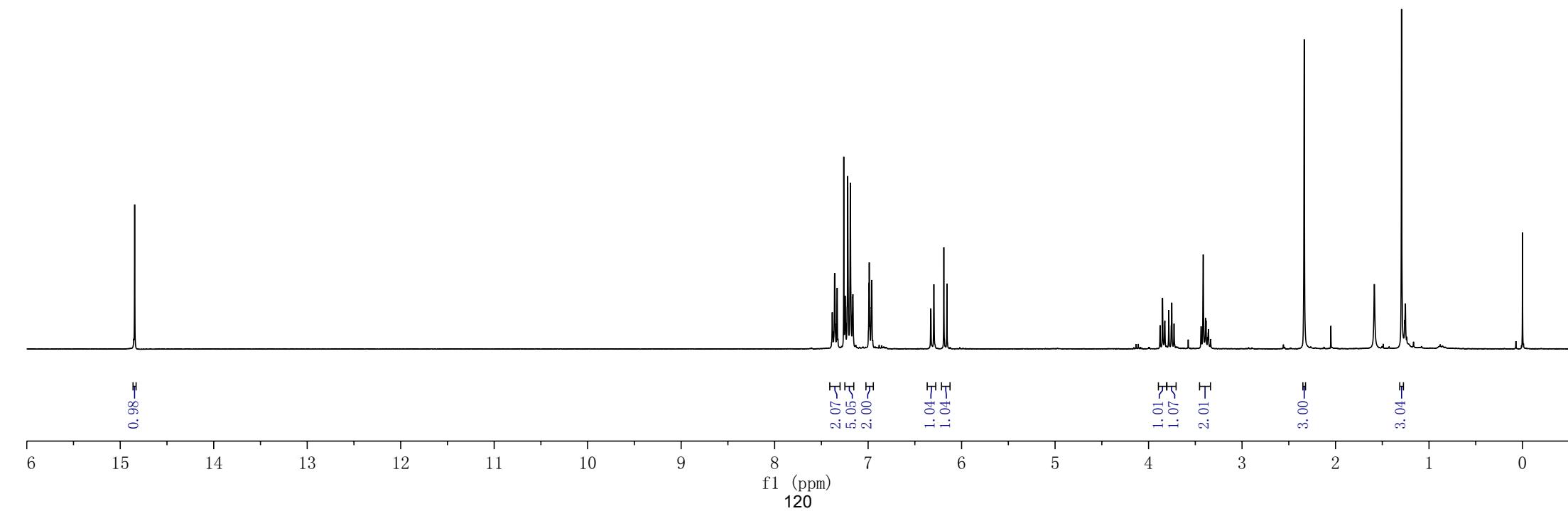
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—0.00



4g



— 187.20

— 171.23

— 168.64

— 163.78

— 153.97

— 141.58

— 137.48

✓ 130.05

✓ 130.00

✓ 128.77

✓ 128.20

✓ 125.94

✓ 125.28

— 120.14

— 97.40

✓ 78.49

✓ 77.47

✓ 77.05

✓ 76.63

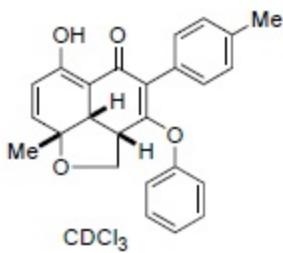
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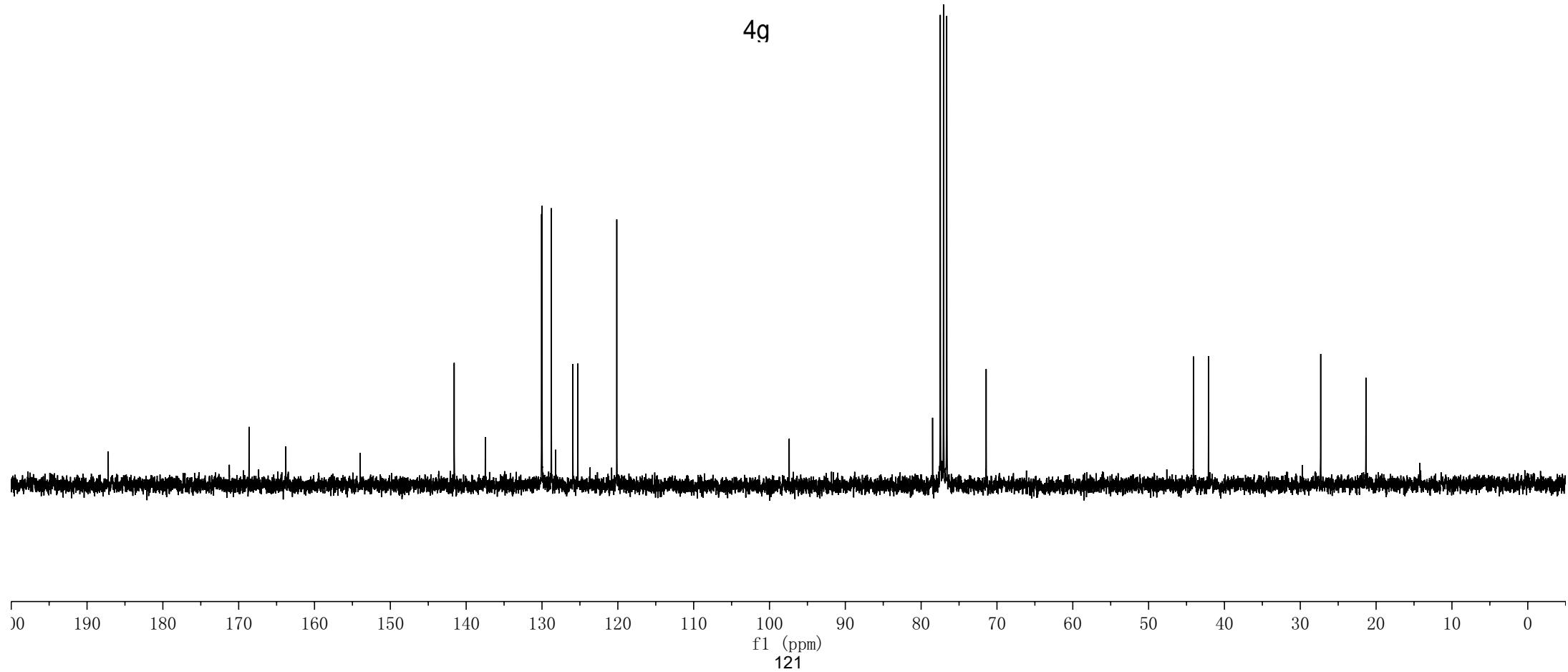
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— 27.31

— 21.34



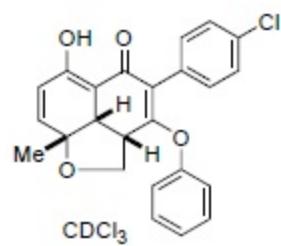
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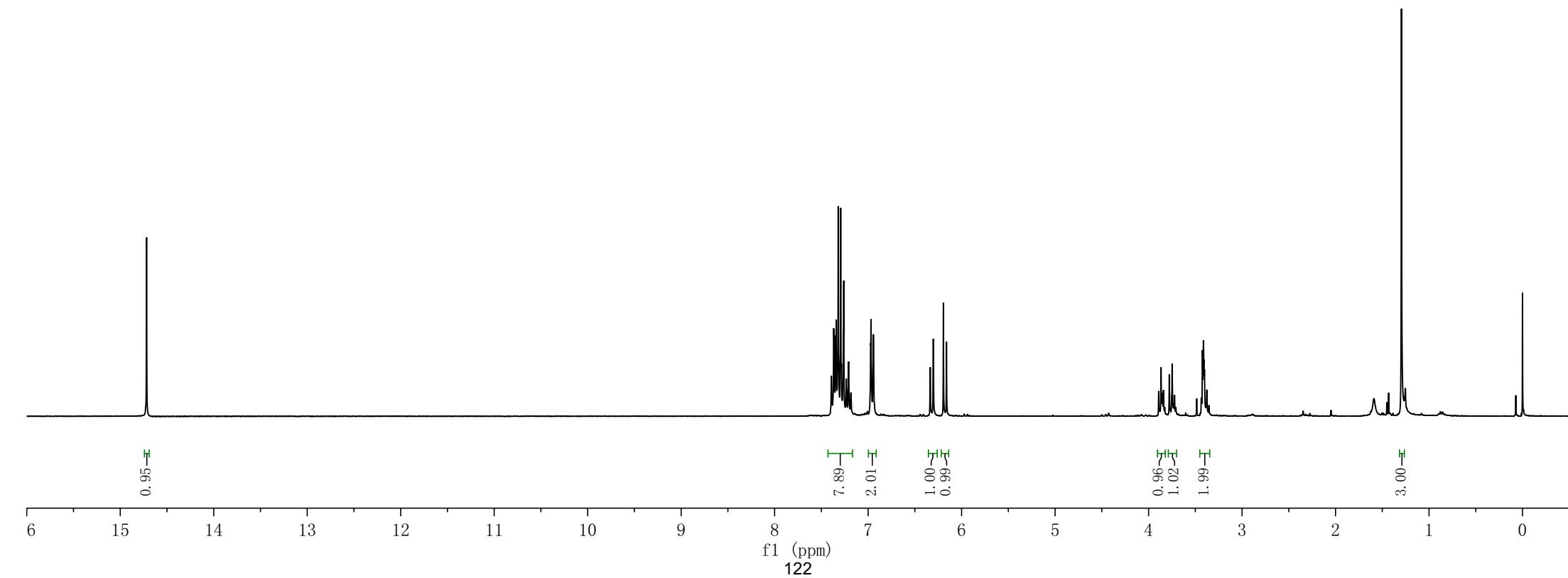
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3.78
3.75
3.73
3.72
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3.35
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-0.00



4h



—186.93

—168.49

—164.50

—153.71

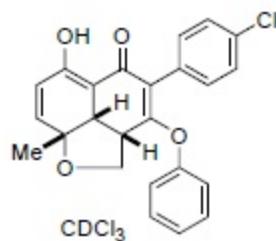
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125.55
122.38
120.09

—97.27

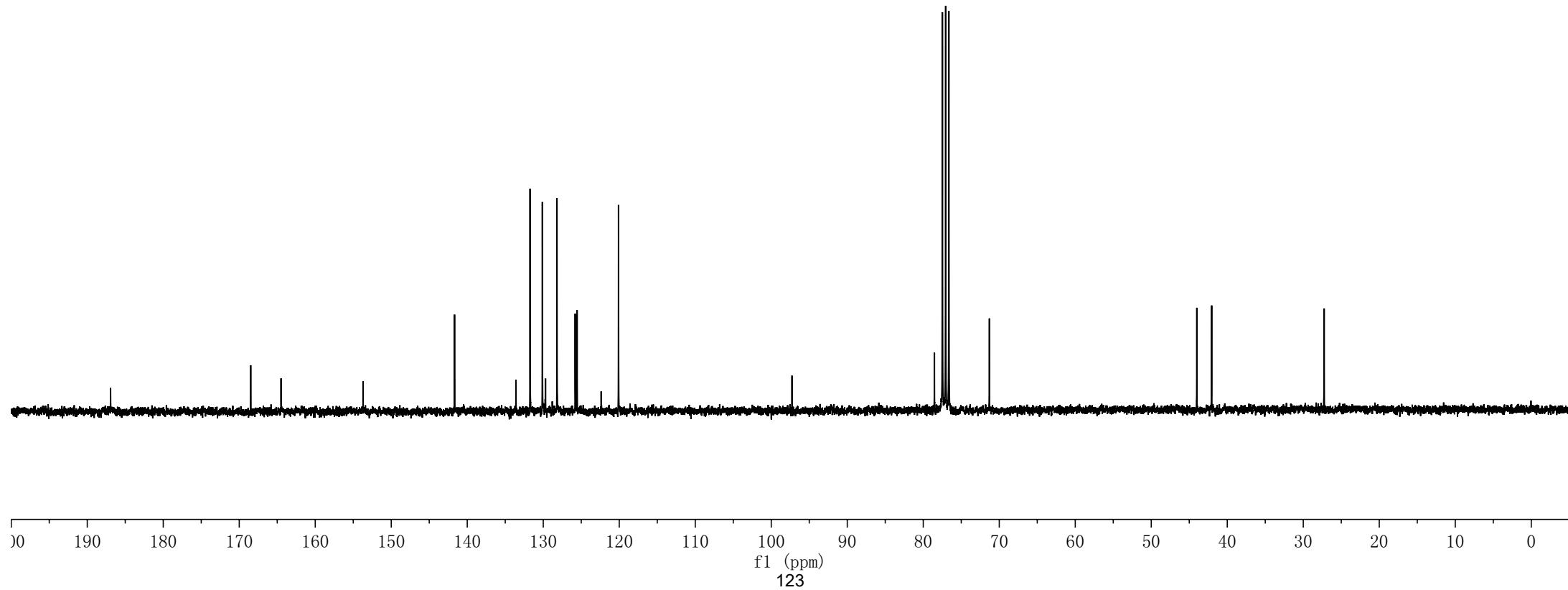
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—27.25



4h



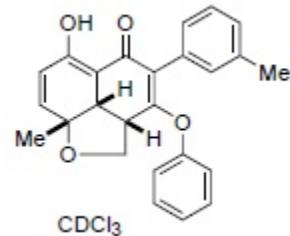
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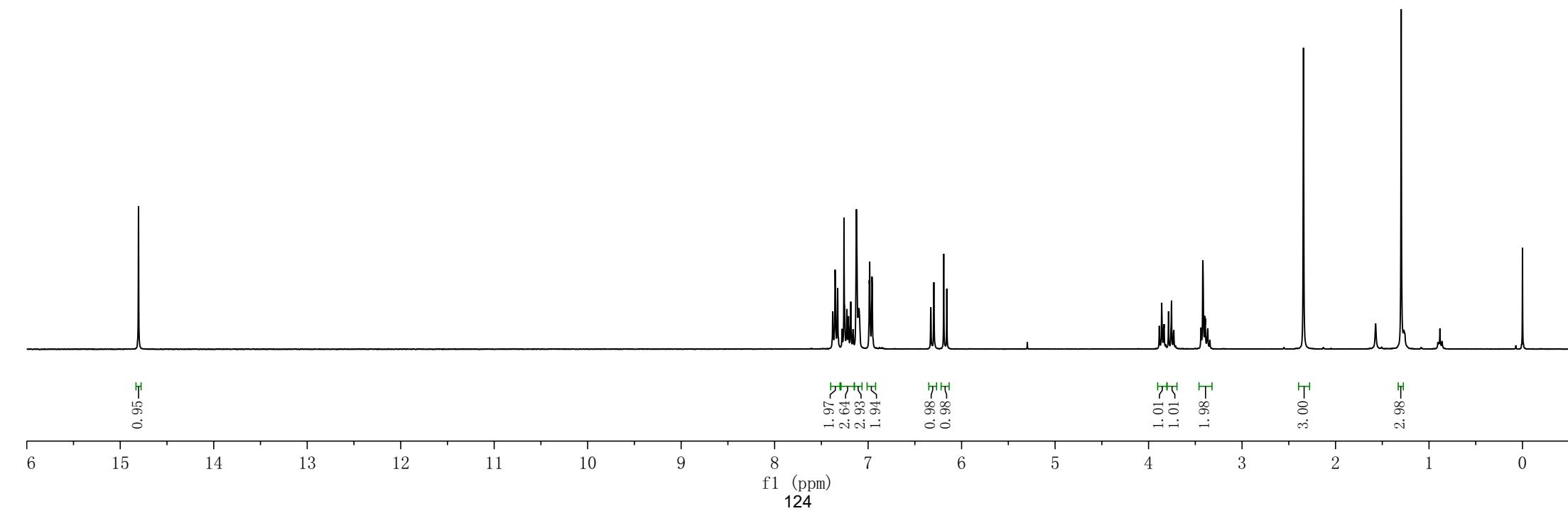
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-1.57
-1.30

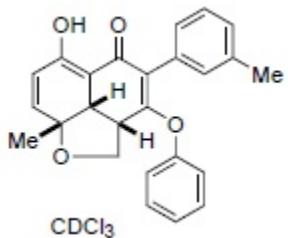
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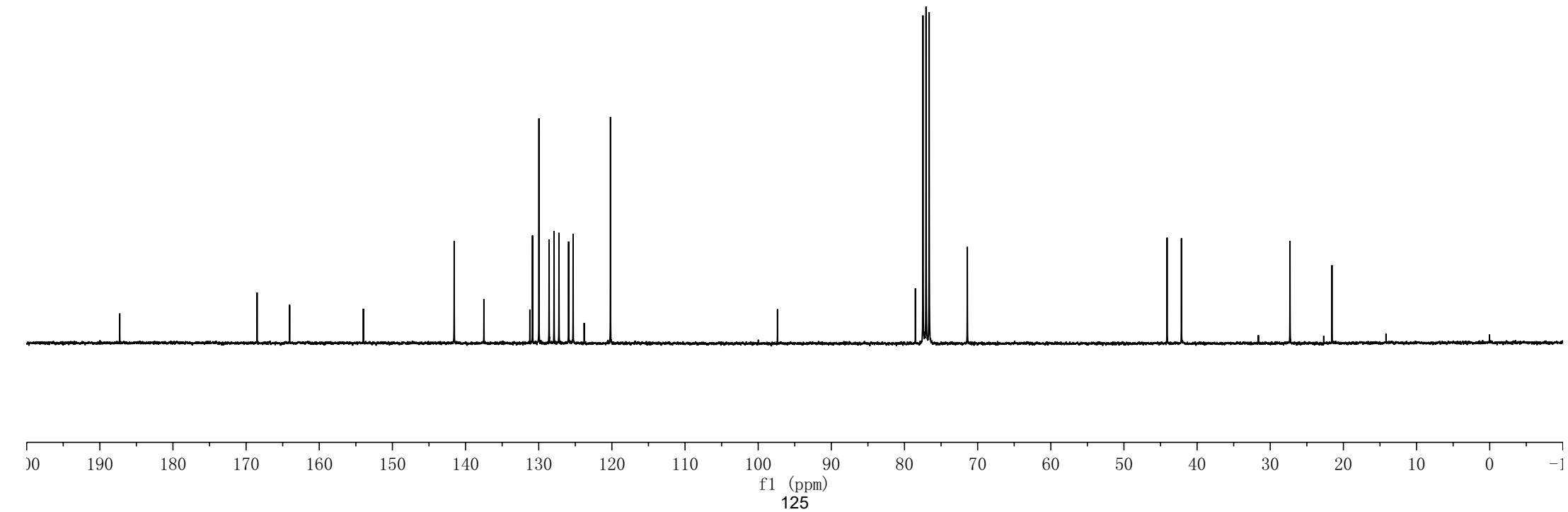
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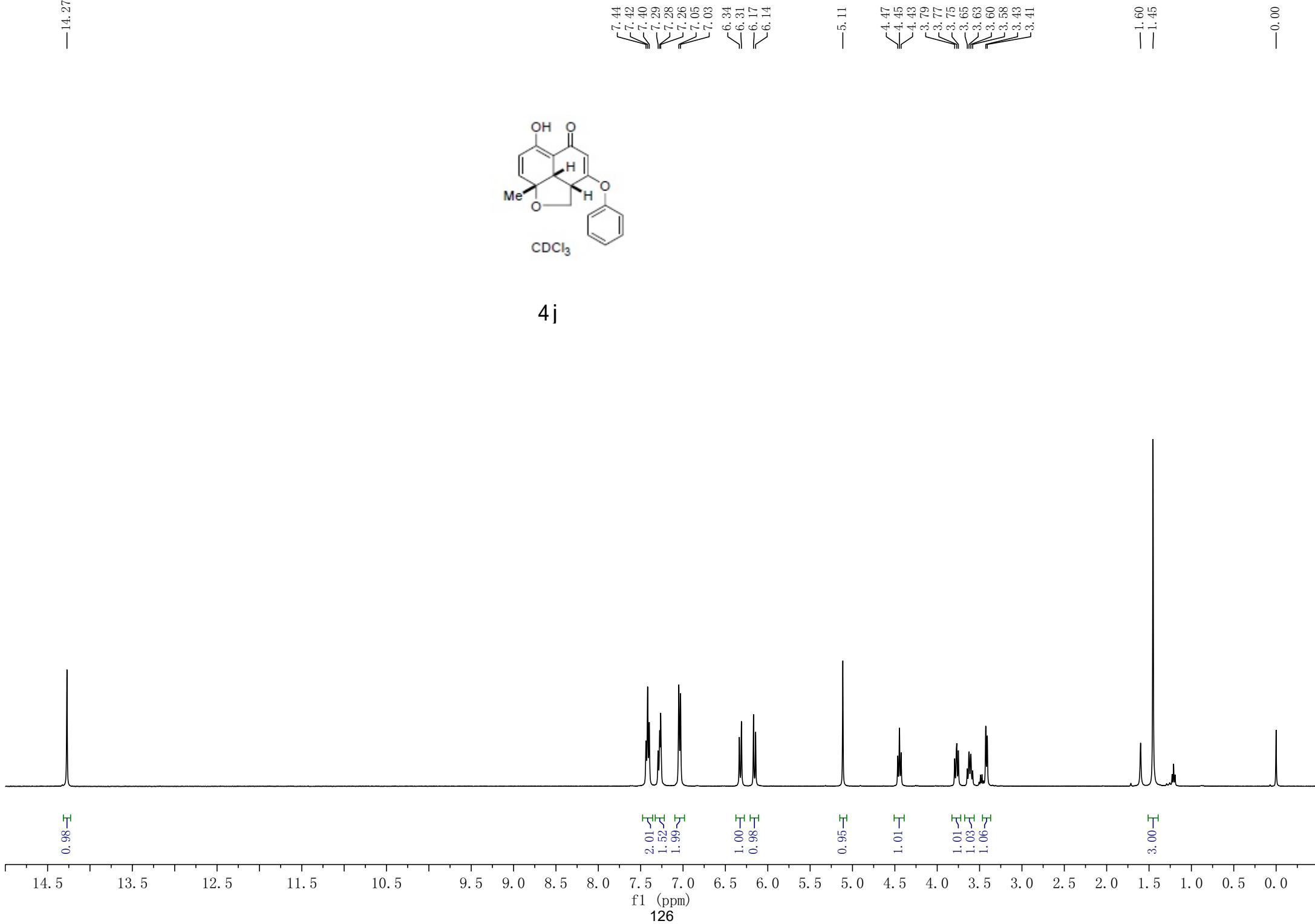


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—168.50
—164.05
—153.97
—141.55
—137.49
—131.21
—130.85
—129.97
—128.58
—127.90
—127.23
—125.91
—125.30
—123.78
—120.19
—97.36
—78.51
—77.47
—77.05
—76.63
—71.41
—44.10
—42.14
—27.30
—21.56



4i





—188.42

—173.43

—166.66

—152.60

—140.99

~130.19
~126.46
~125.77
~121.30

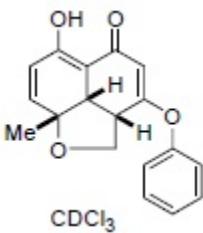
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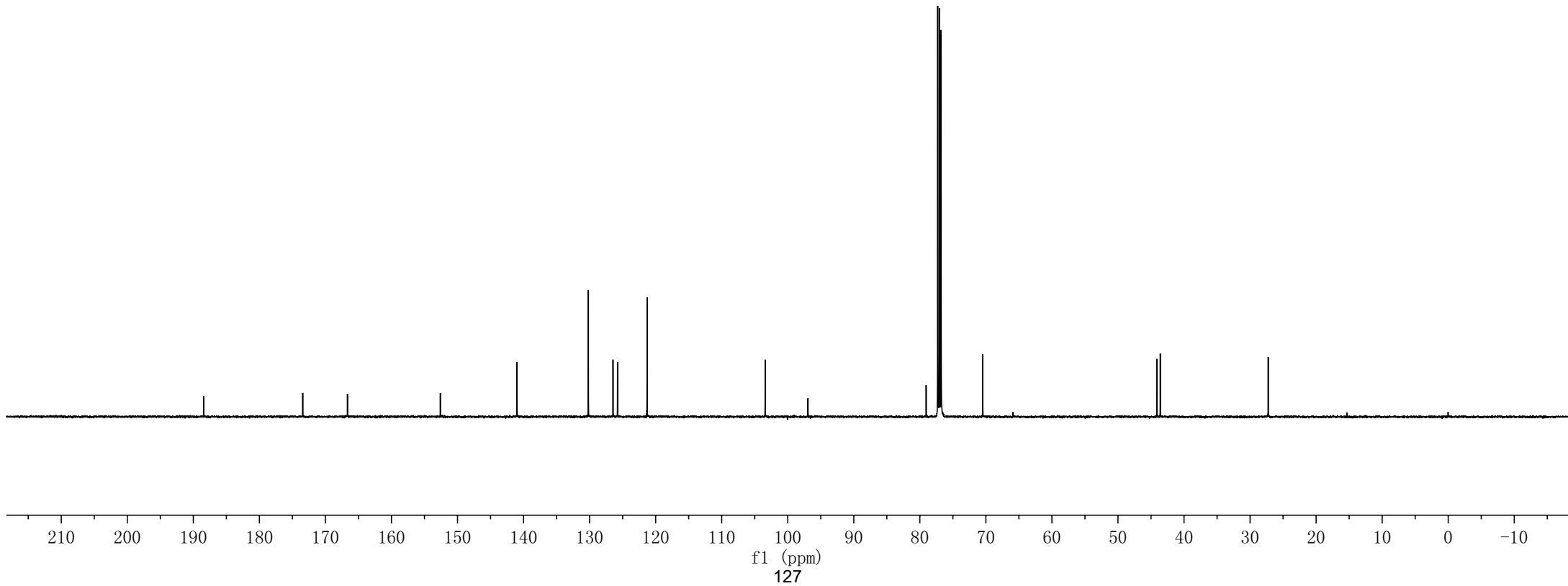
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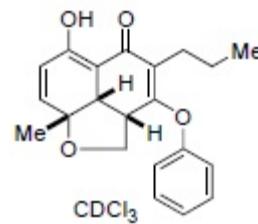


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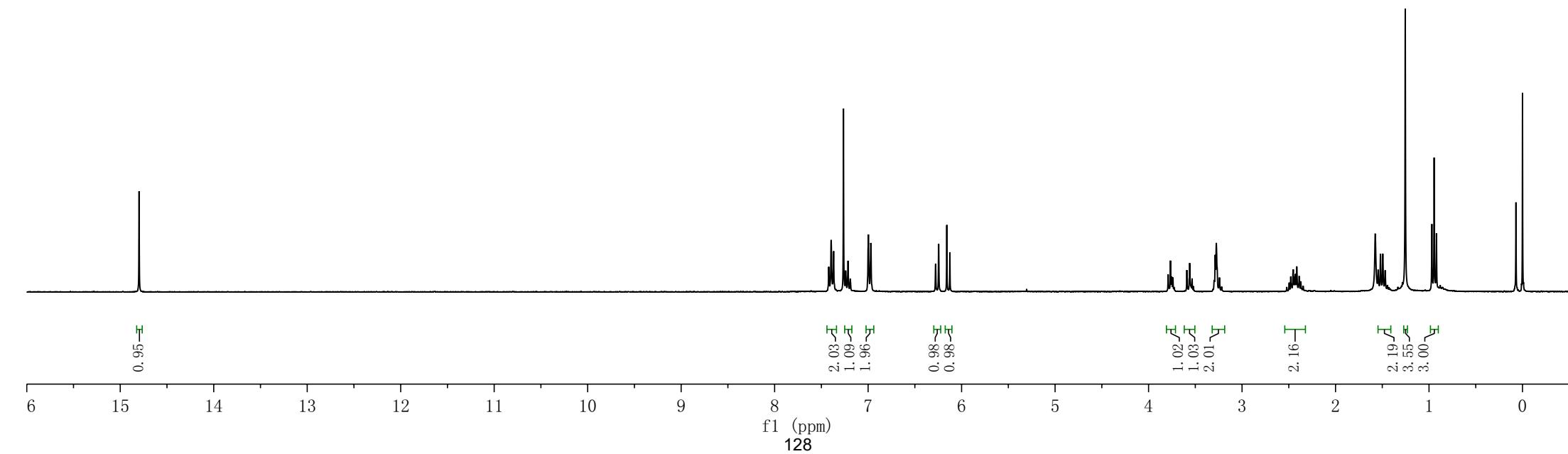


-14.80

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6.13
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3.77
3.75
3.74
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3.30
3.29
3.28
3.24
2.45
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1.49
1.25
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0.95
-0.92
-0.00



4k



—188.13

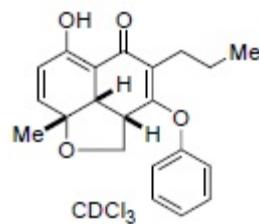
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~119.68



4k

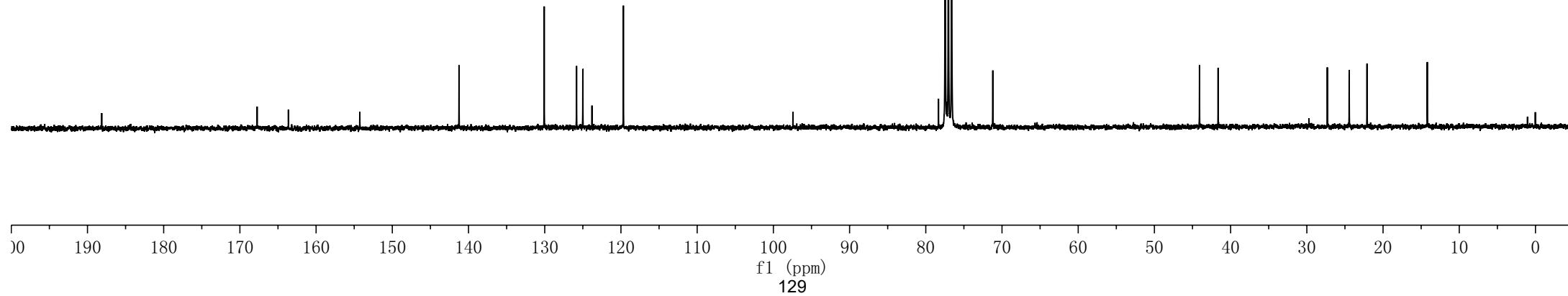
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71.20

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—41.64

—27.31
—24.44
—22.10

—14.20



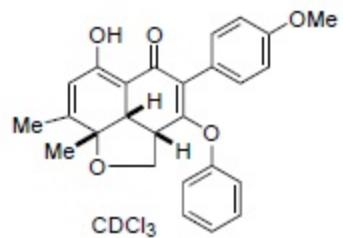
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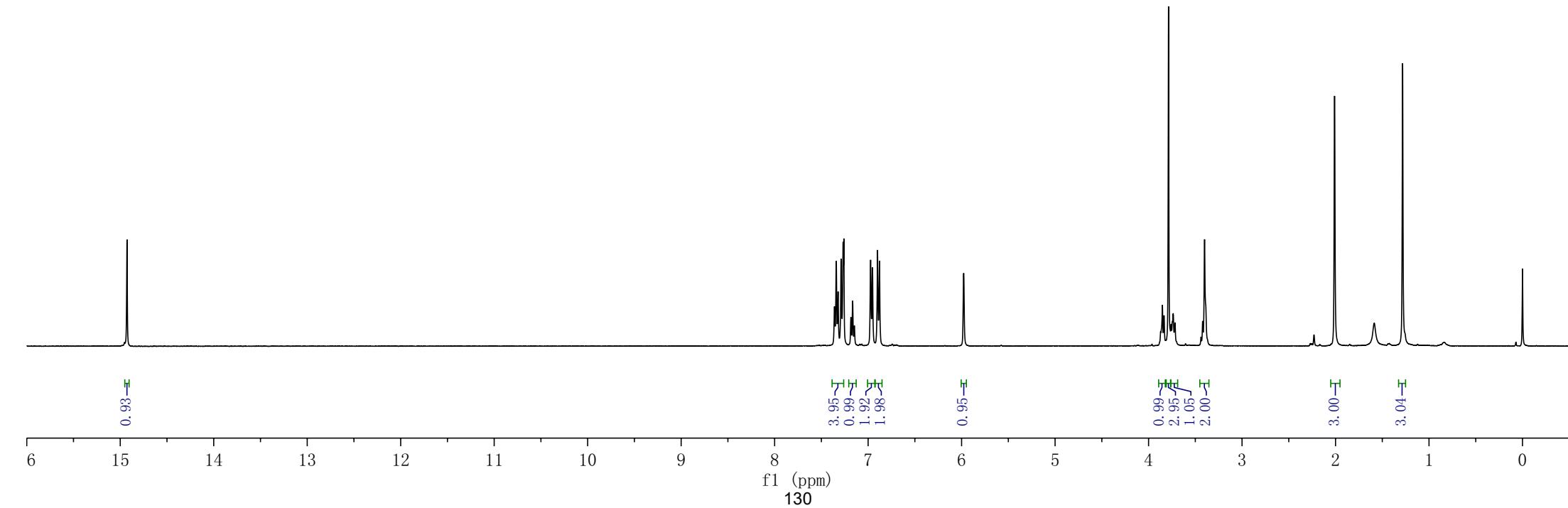
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—1.59
—1.28

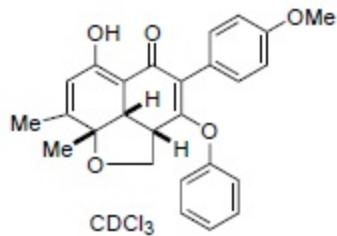
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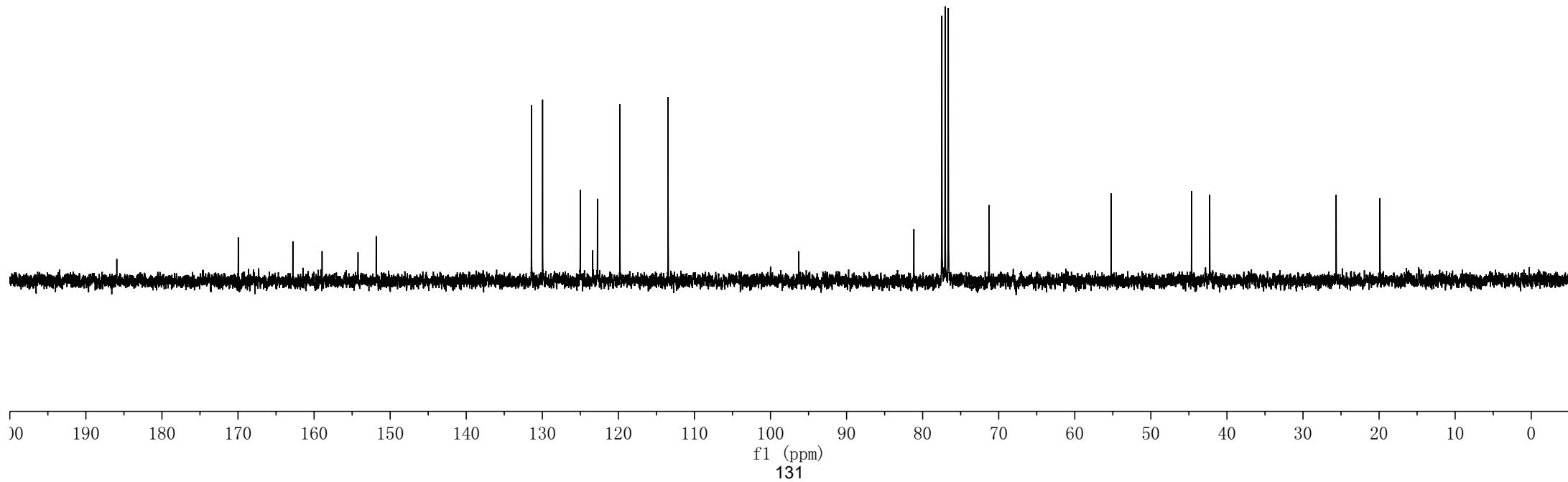
4l



—185.94
—169.97
—162.79
—158.95
—154.22
—151.84
—131.42
—129.96
✓125.01
✓123.40
✓123.37
✓122.75
✓119.80
—113.47
—96.29
✓81.15
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✓76.63
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—55.22
—44.65
—42.26
—25.64
—19.89



4l

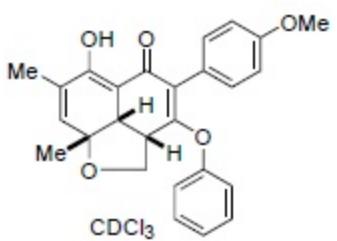


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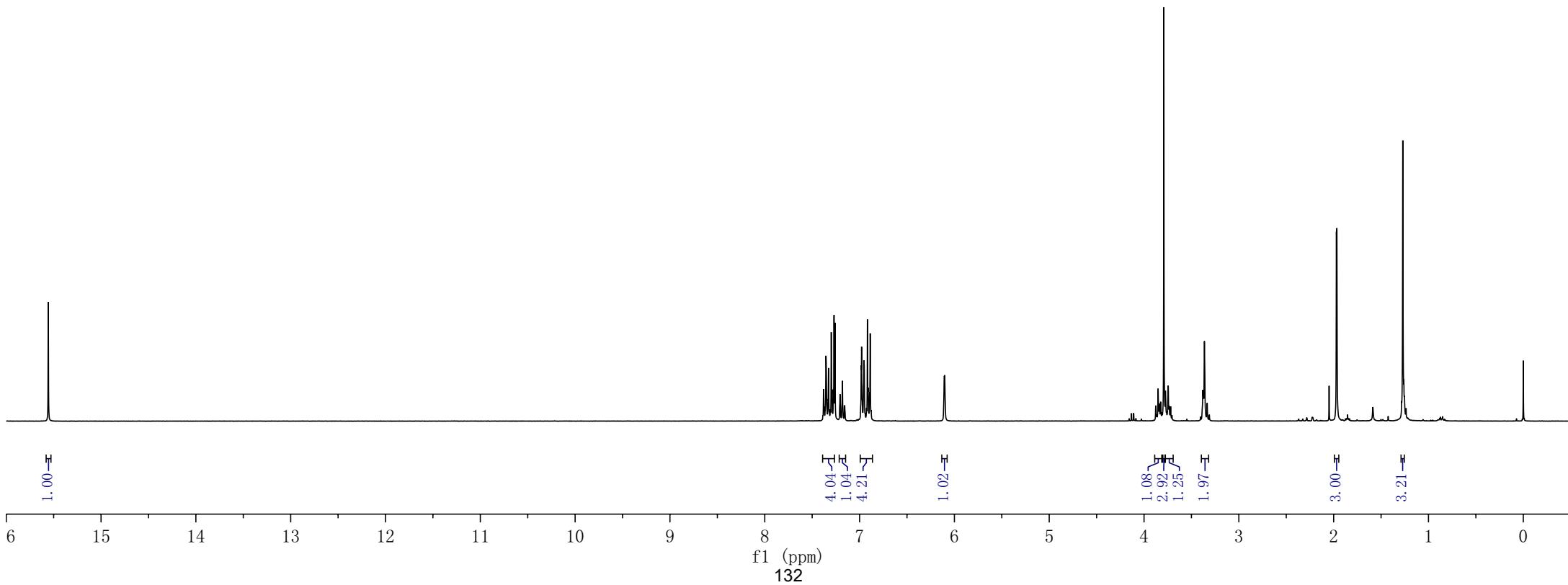
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7.18
7.16
6.98
6.98
6.95
6.93
6.92
6.91
6.89
6.89
6.88
6.11
6.10

—1.27

—0.00



4m



—186.10

—171.76

—163.28

—158.97

—154.02

~137.83
~134.05
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~129.99

~125.17
~123.43
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—113.51

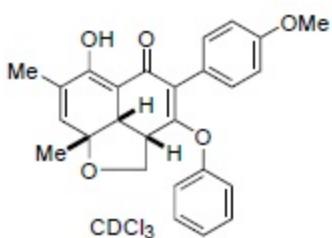
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—55.22

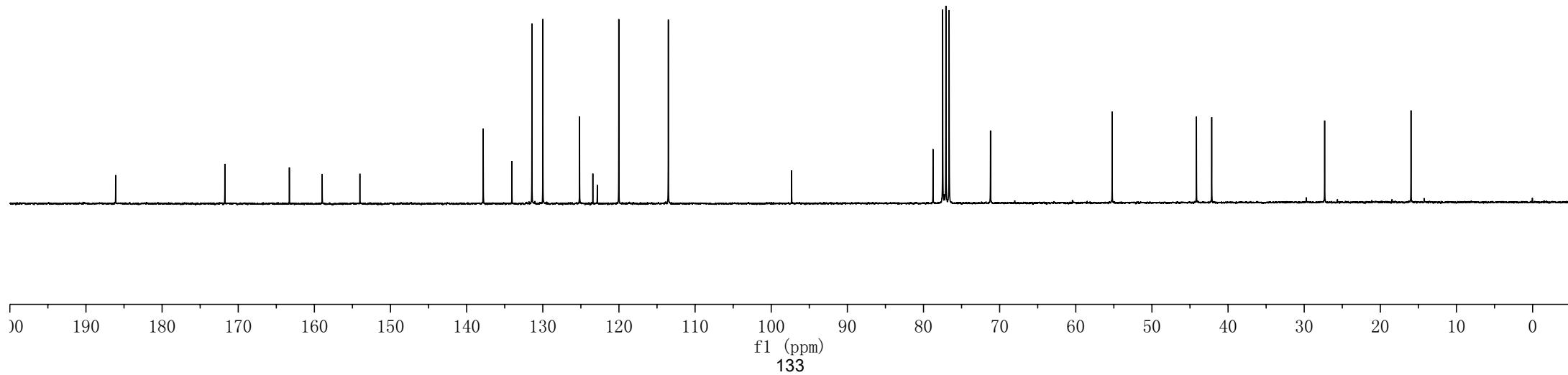
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—27.31

—15.97



4m

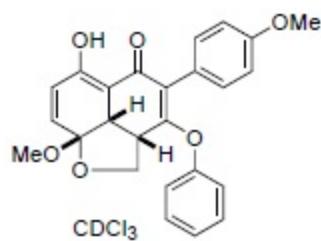


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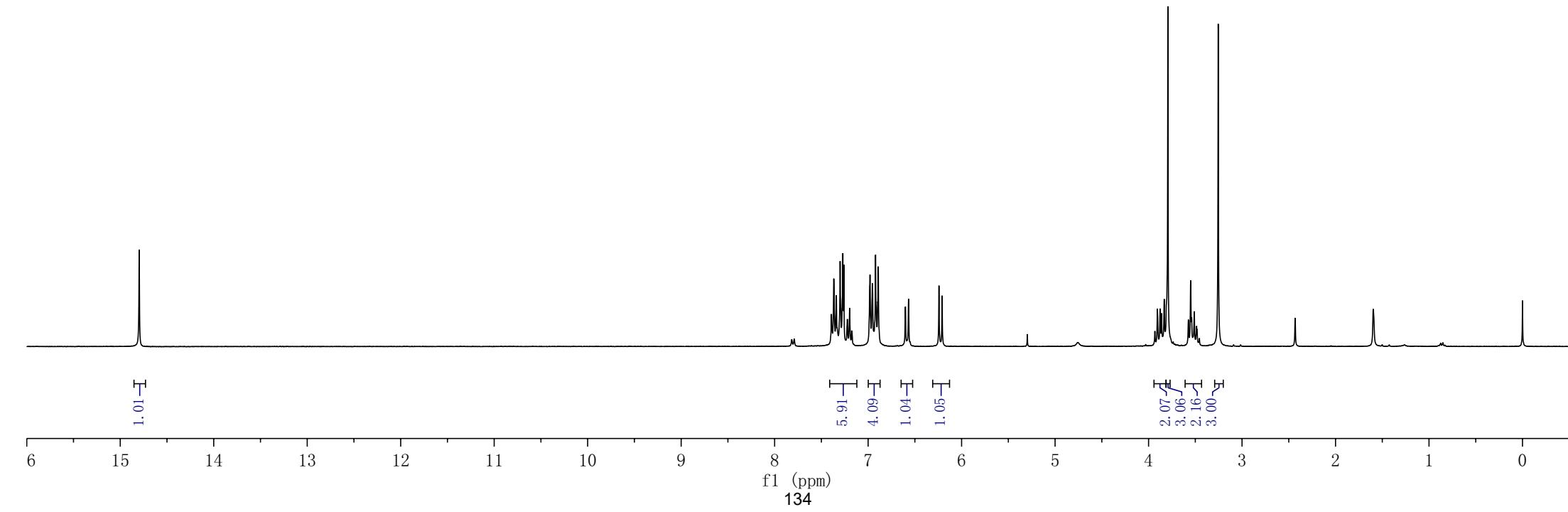
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—0.00

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6.95
6.94
6.92
6.90
6.89
6.80
6.60
6.57
6.24
6.21



4n



—186.78

—168.39

—164.40

—159.00

—153.92

~134.12
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—125.29
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~120.22

—113.51

—104.99

—97.80

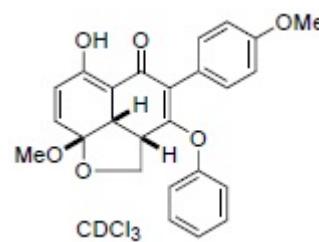
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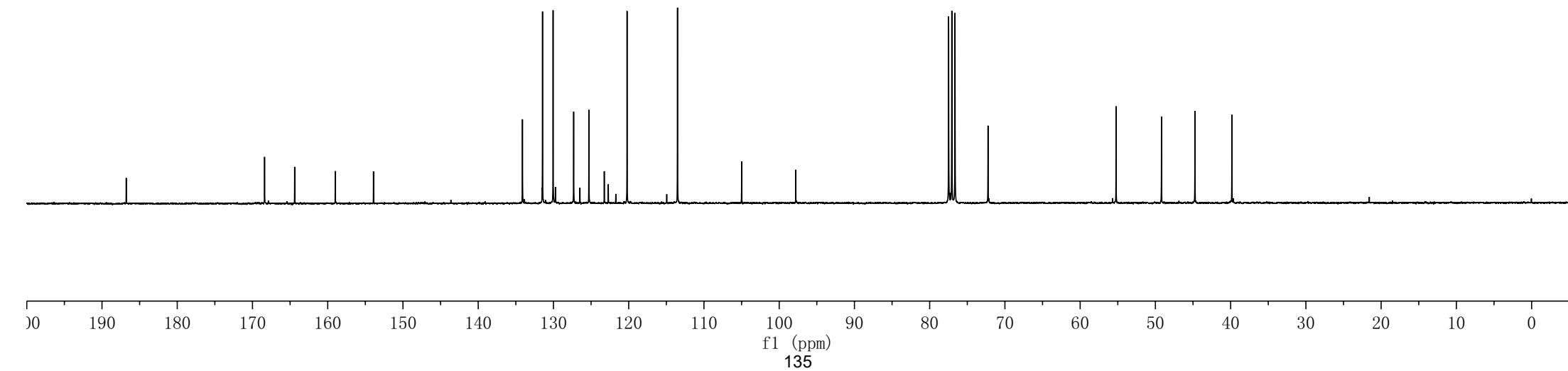
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4n

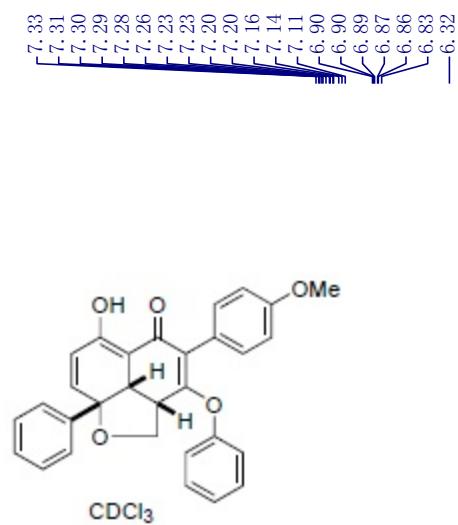


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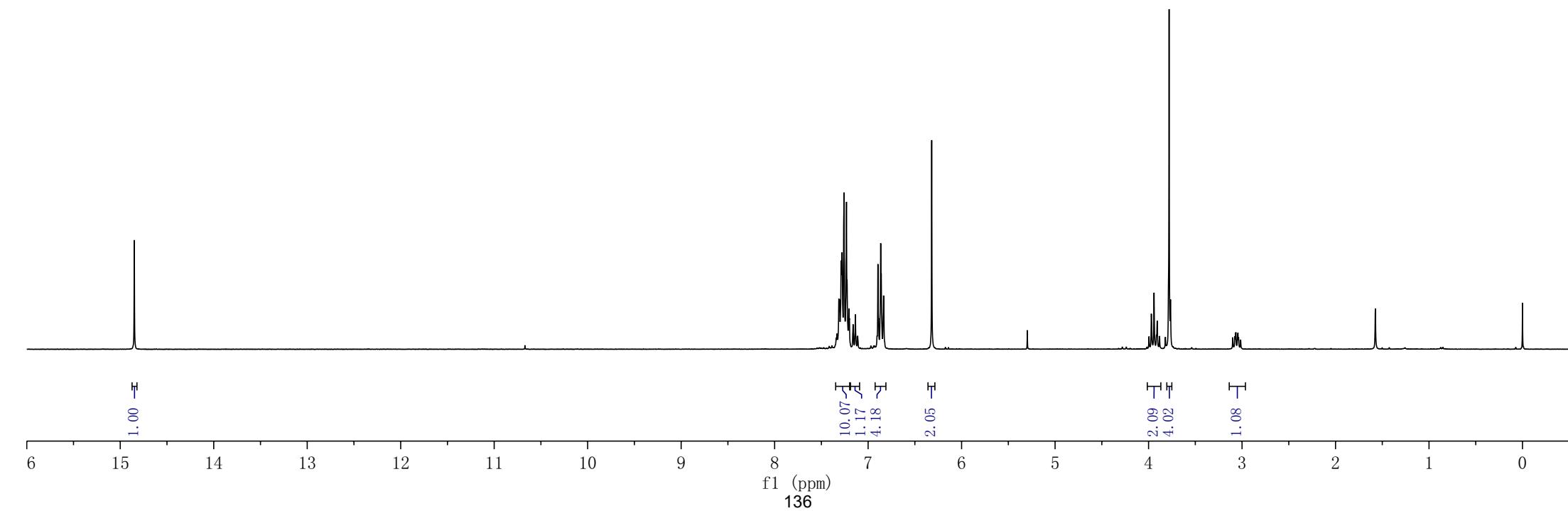
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3.05
3.04
3.04
3.02

—1.57

—0.00



4o



—187.49

—168.06

—164.04

—158.99

—153.80

—144.80

—140.58

131.41
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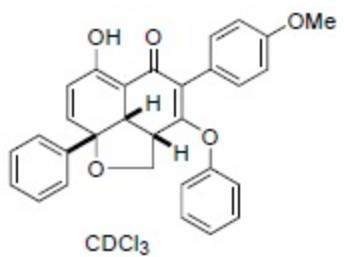
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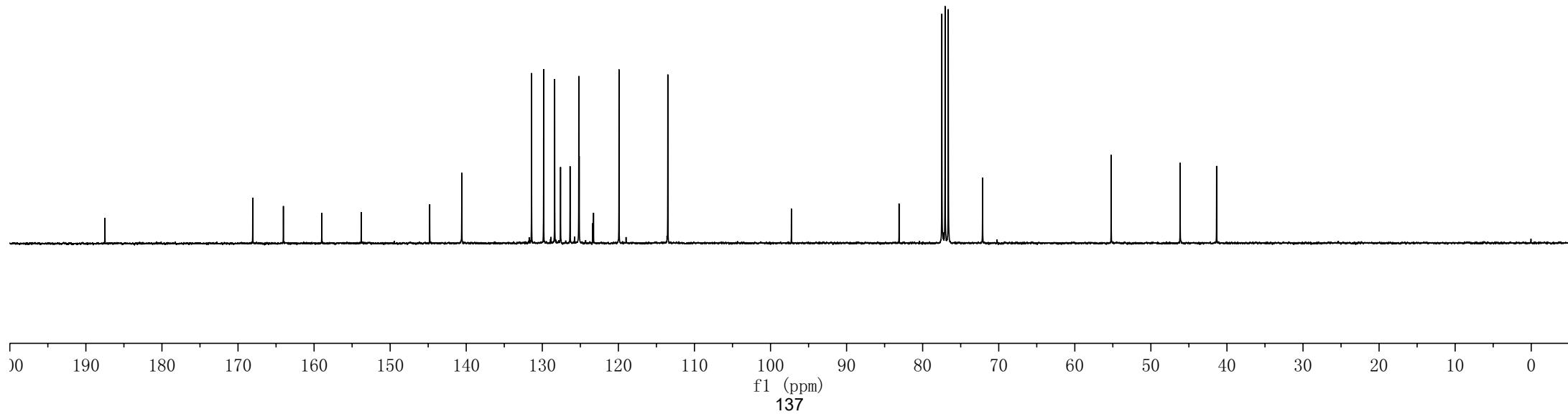
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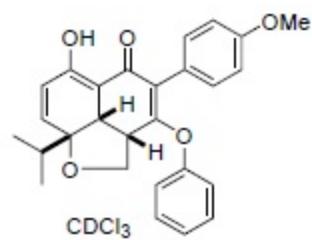
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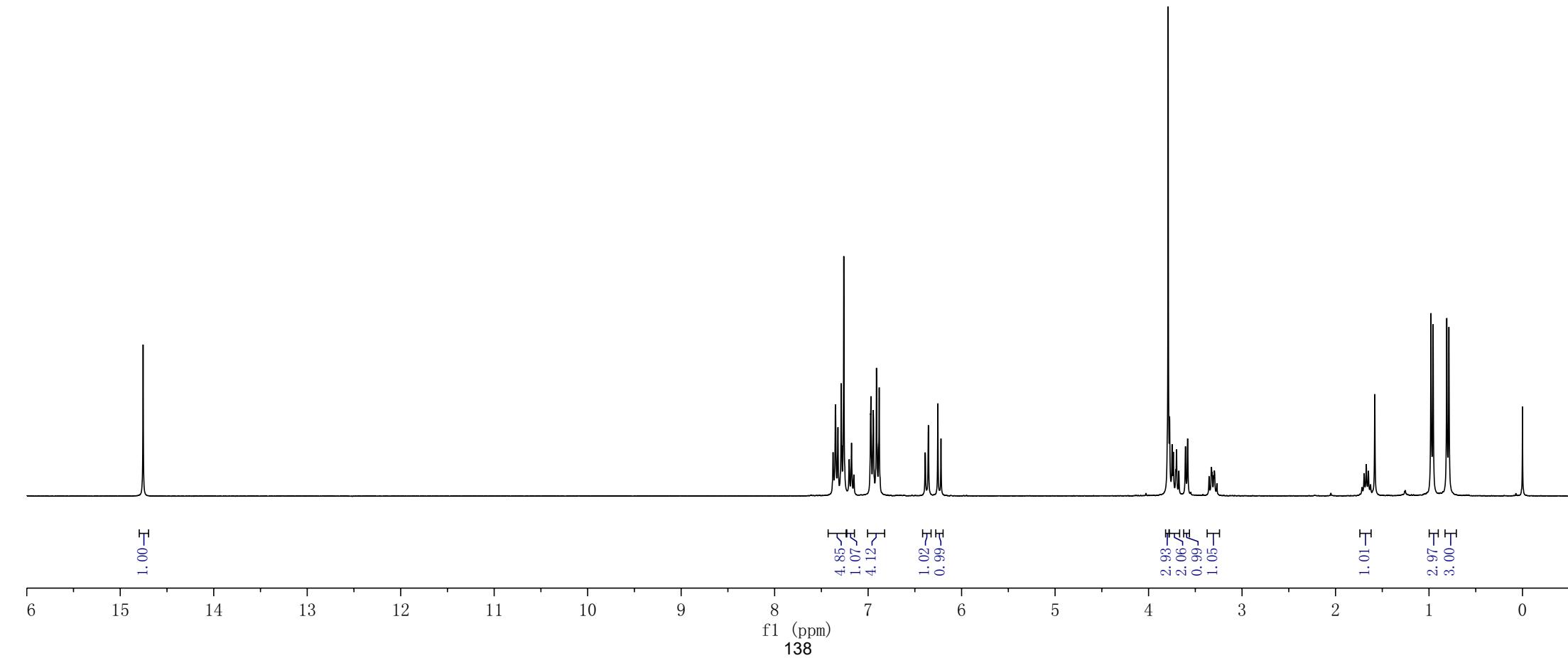
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1.72
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0.96
0.81
0.79

—0.00



4p



—187.79

—167.98

—163.57

—158.97

—154.12

—137.78

—131.42

—129.97

—126.80

—125.10

—123.67

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—83.98

—77.47

—77.05

—76.63

—70.49

—55.22

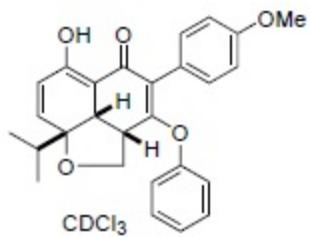
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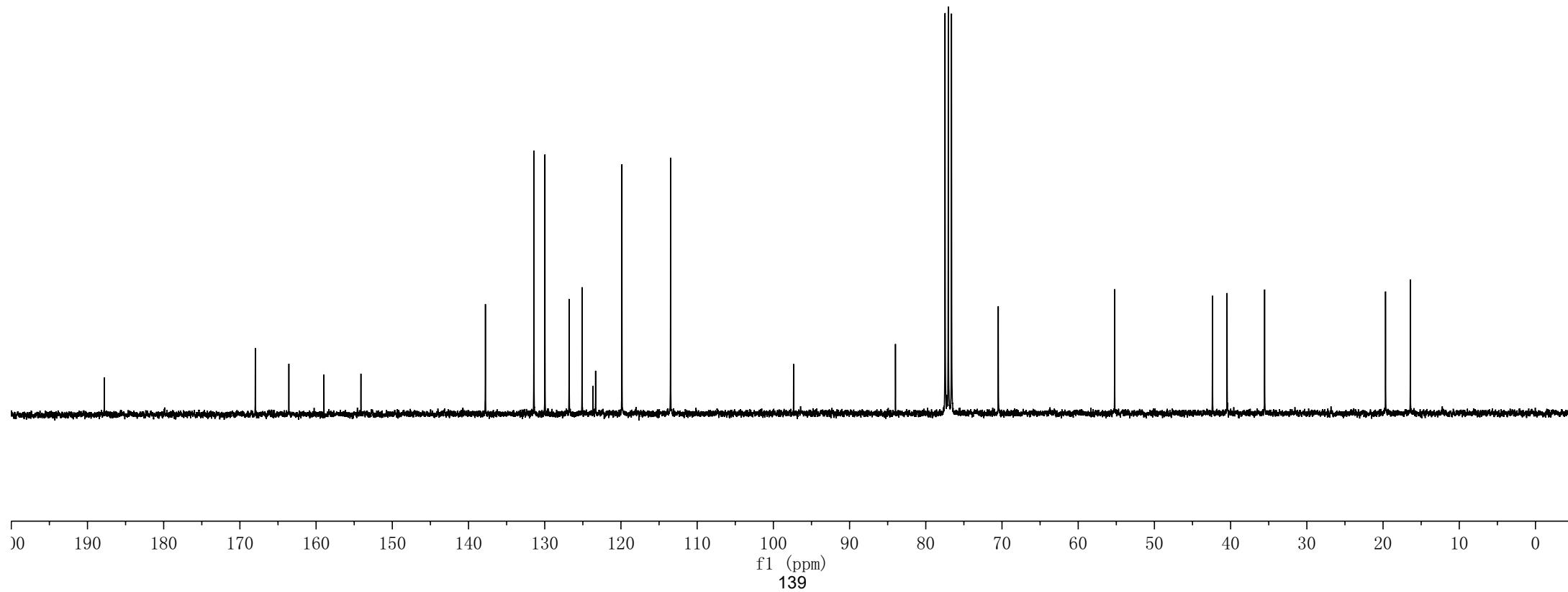
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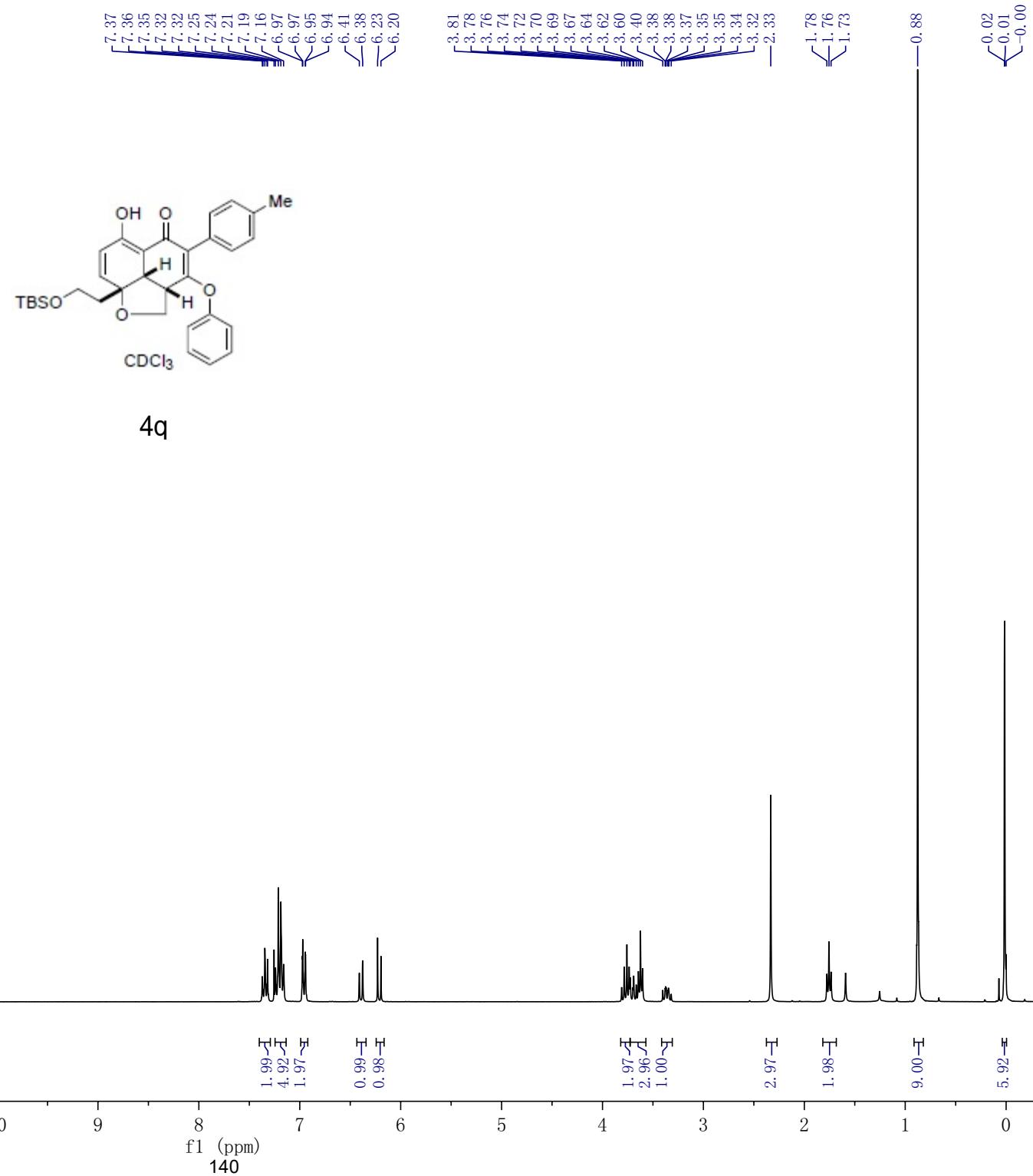
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4p



— 14.78



—187.47

—168.00

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—153.99

—140.39

—137.45

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128.77

128.27

126.55

125.25

123.80

120.12

—97.37

80.40

77.49

77.06

76.64

—70.68

—59.21

—42.03

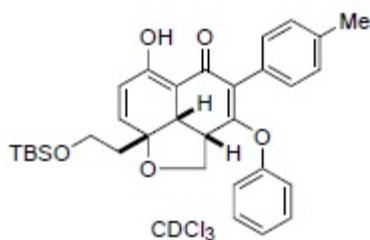
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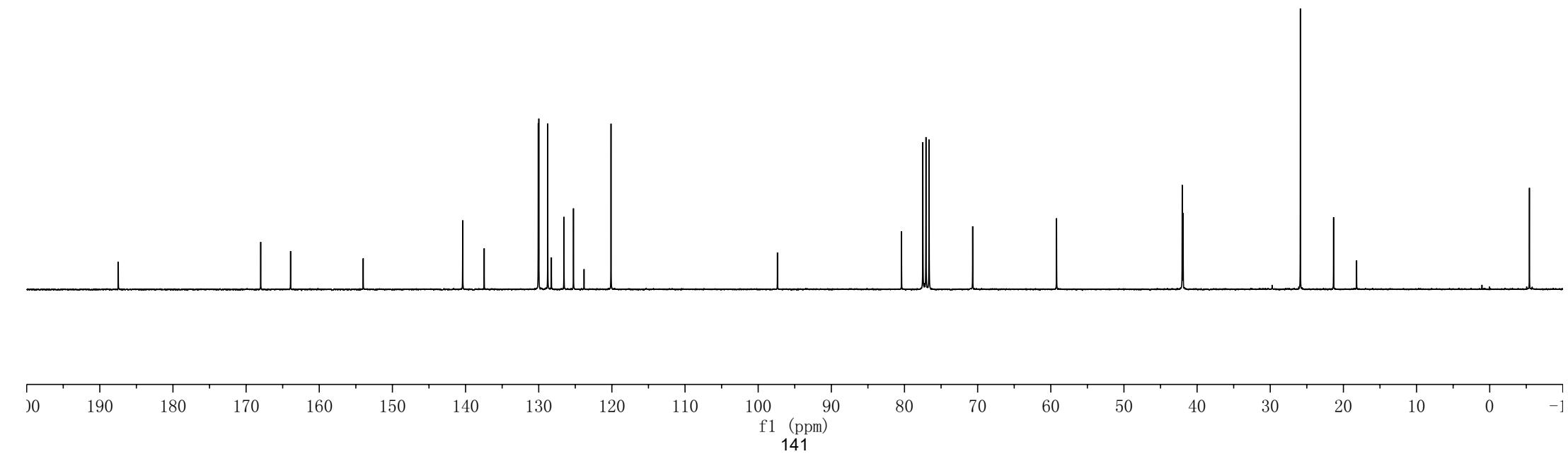
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—18.19

—5.43

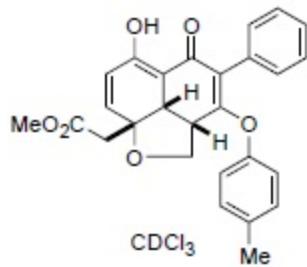


4q

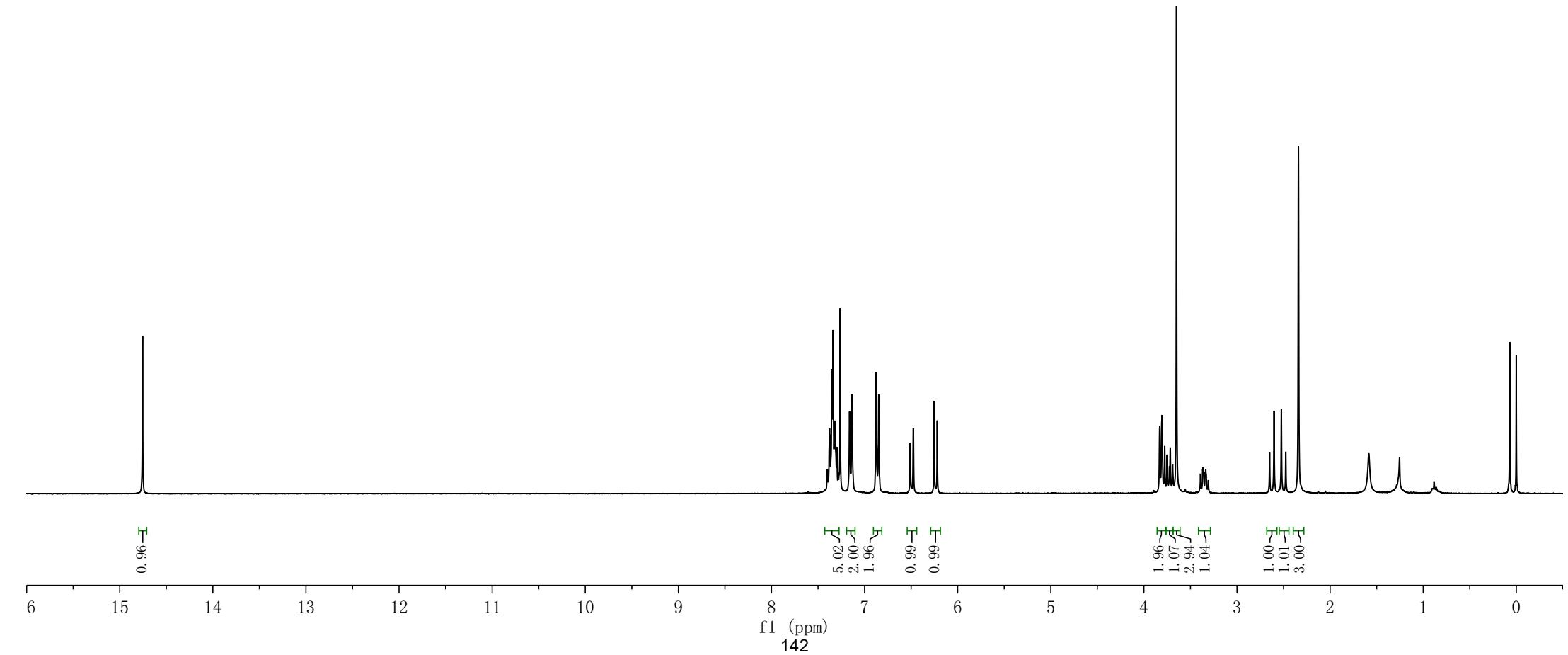


-14.76

7.40
7.38
7.37
7.35
7.34
7.32
7.32
7.30
7.28
7.27
7.26
7.16
7.13
6.88
6.85
6.51
6.48
6.25
6.22
3.83
3.80
3.78
3.75
3.72
3.72
3.69
3.65
2.65
2.60
2.52
2.48
2.34
-1.58
-0.07
~0.00



4r

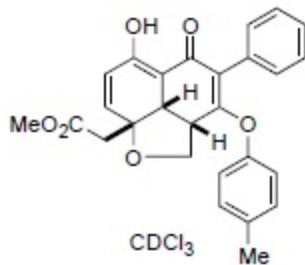


— 187.53

— 169.82
~ 167.54
— 164.10

— 151.46

138.52
135.29
131.29
130.52
130.25
127.98
127.71
126.82
123.43
120.08

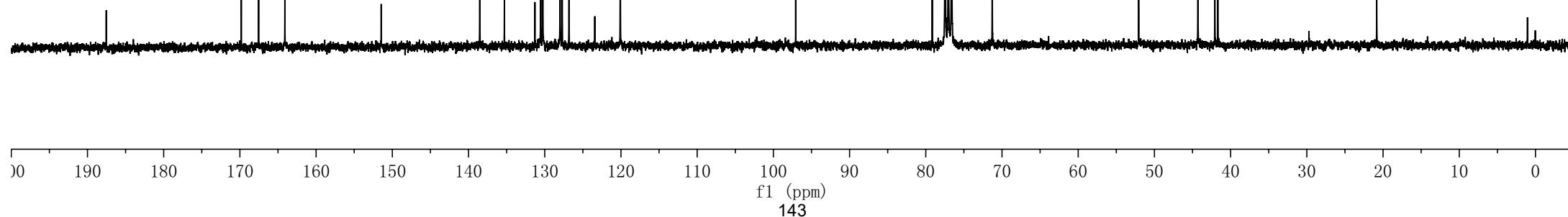


4r

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77.05
76.62
71.28

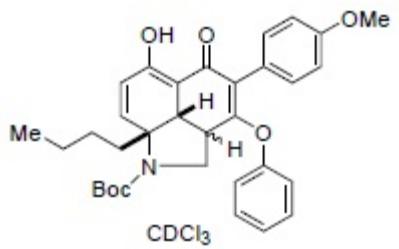
— 52.07
~ 44.29
~ 42.07
~ 41.68

— 20.83

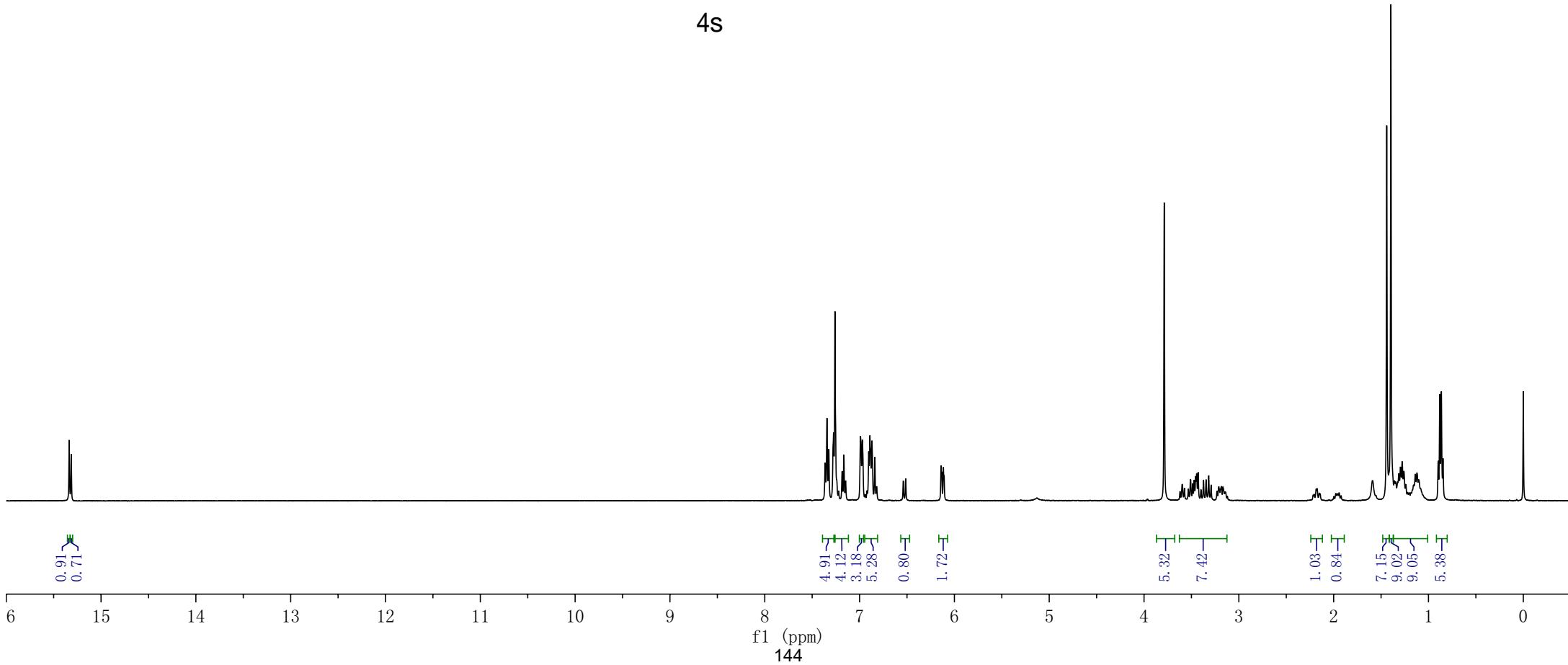


<15.34
<15.31

7.36
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7.22
7.18
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7.15
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6.97
6.94
6.92
6.90
6.89
6.87
6.84
6.82
6.54
6.51
6.14
6.13
6.12
6.11
3.79
3.60
3.57
3.53
3.51
3.49
3.47
3.45
3.44
3.43
3.40
3.37
3.35
3.32
3.29
3.21
3.18
3.17
2.18
2.17
2.15
1.98
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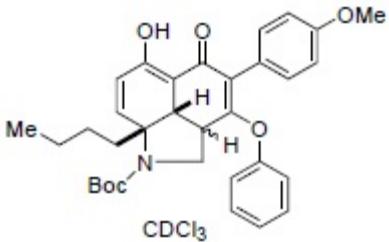


4s

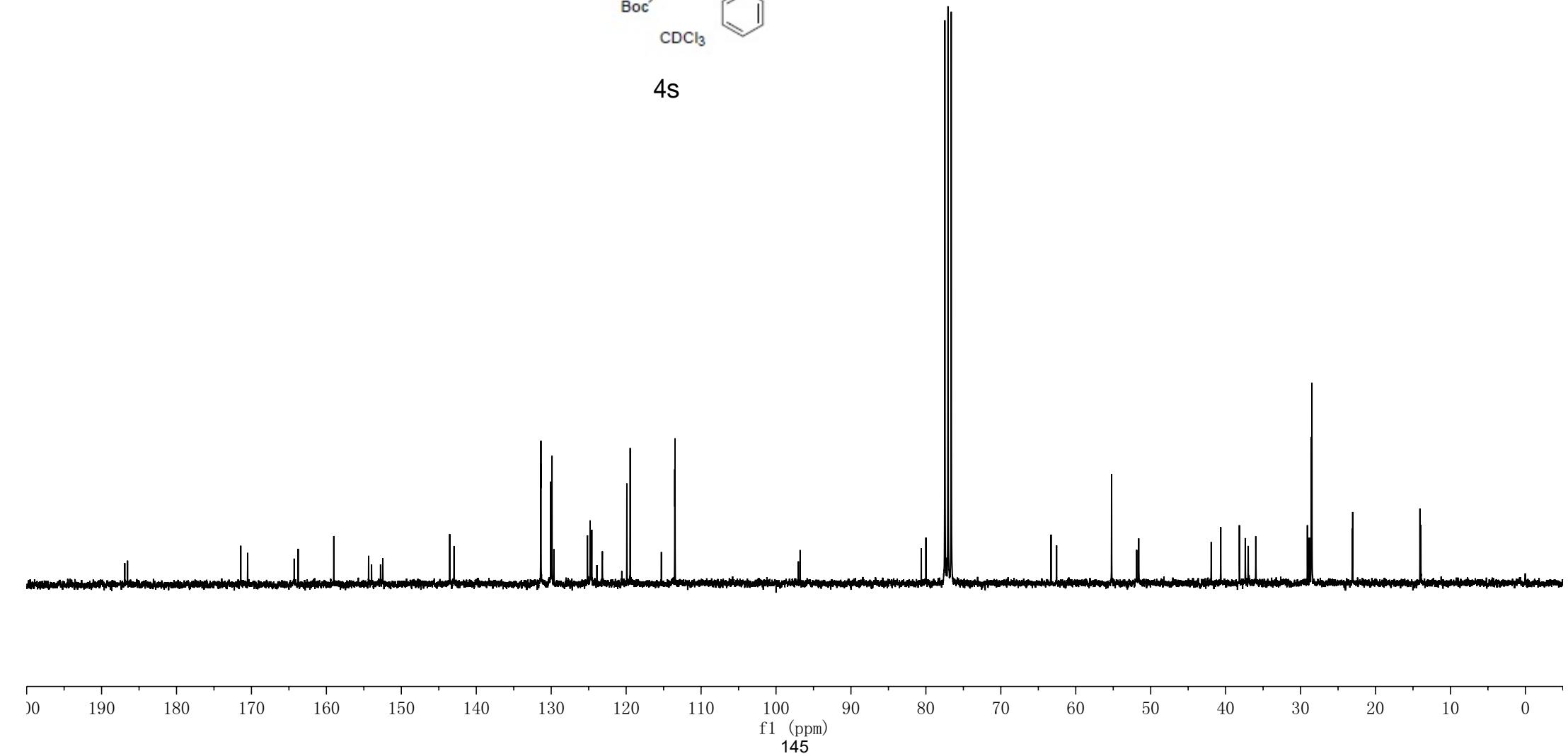


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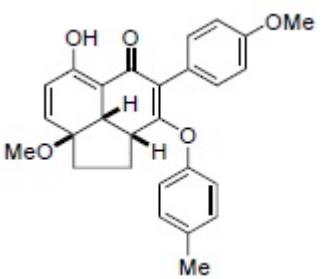
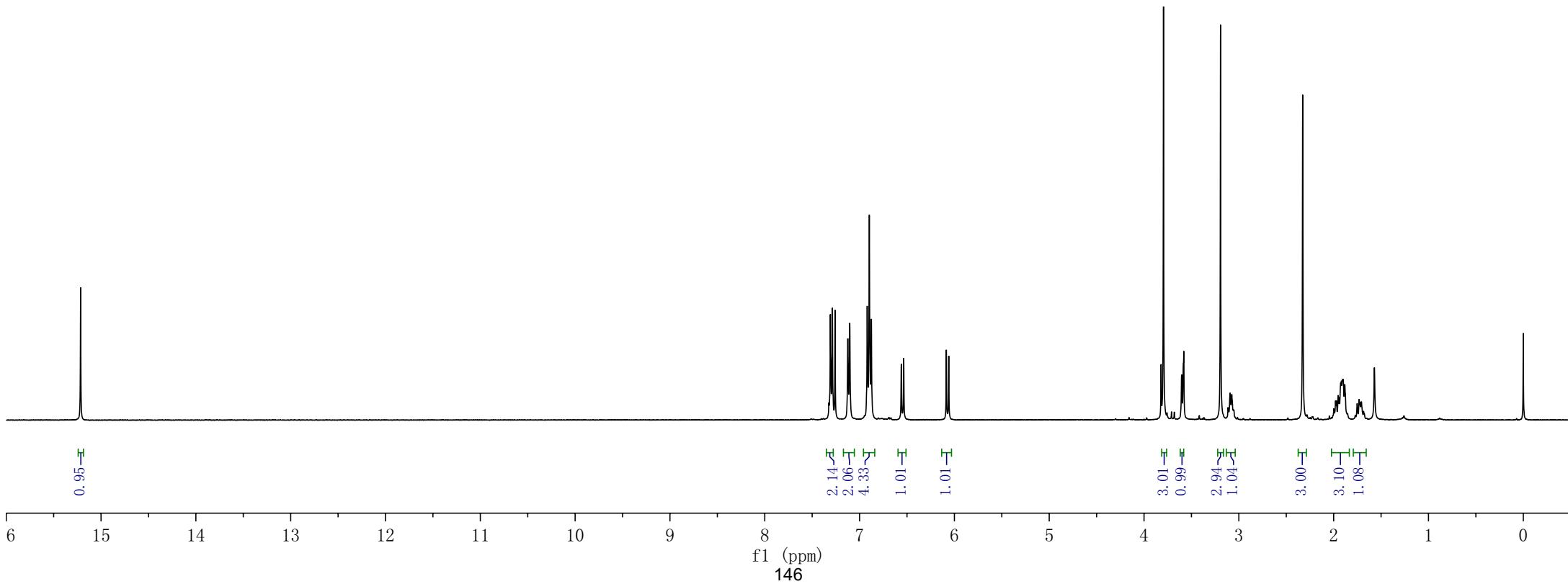
131.40
 131.37
 130.06
 129.90
 129.64
 125.16
 124.81
 124.68
 124.58
 119.90
 119.46
 113.51
 113.48
 97.02
 96.78



4s



7.32
7.31
7.29
7.26
7.12
7.10
6.92
6.90
6.88
6.56
6.53
6.08
3.79
3.60
3.58
3.19
3.11
3.09
2.95
2.05
2.00
1.98
1.97
1.95
1.94
1.93
1.92
1.91
1.88
1.77
1.75
1.57
0.00

**4t**

—187.16

~169.59
~169.33

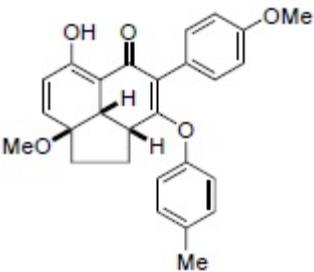
—158.73

—151.75

—144.50

~134.74
~131.56
~130.22
~129.37
~126.10
~123.99
~120.55

—113.44



4t

—98.50
—88.09

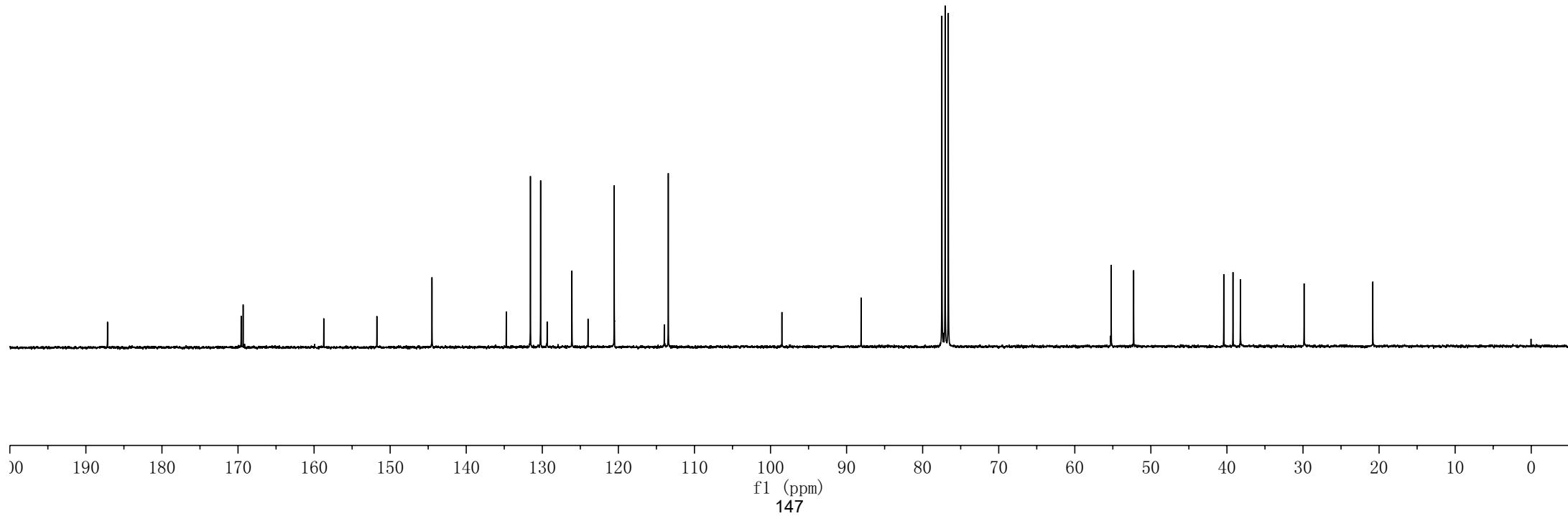
~77.47
~77.05
~76.63

—55.21
—52.26

~40.42
~39.21
~38.23

—29.86

—20.82

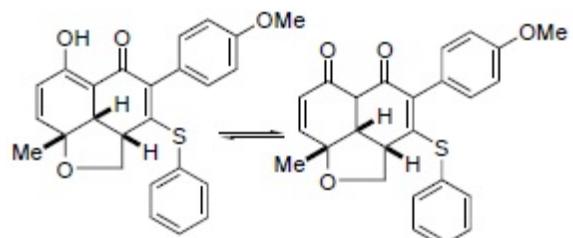


-13.45

7.29
7.26
7.25
7.22
7.22
7.20
7.01
7.00
6.99
6.98
6.90
6.87
6.81
6.69
6.69
6.66
6.65
6.43
6.39
6.18
6.16
6.14
6.12

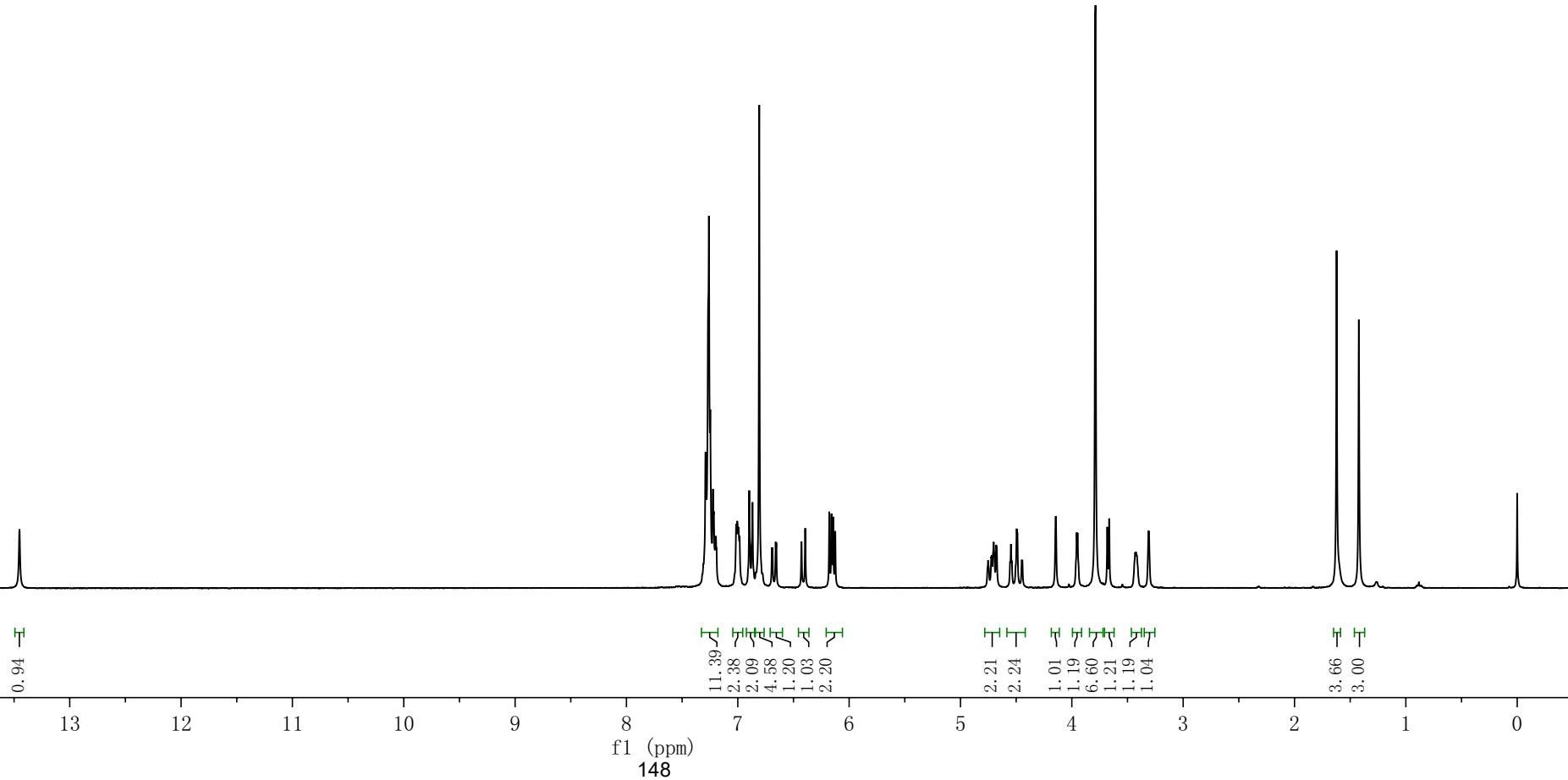
4.70
4.68
4.67
4.55
4.49
4.49
4.49
4.14
3.96
3.95
3.79
3.68
3.66
3.43
3.42
3.31
3.21
-1.82
-1.42

-0.00



CDCl₃

4u + 4u'



—202.48

—195.56

—191.90

—167.90

<159.09
<158.95

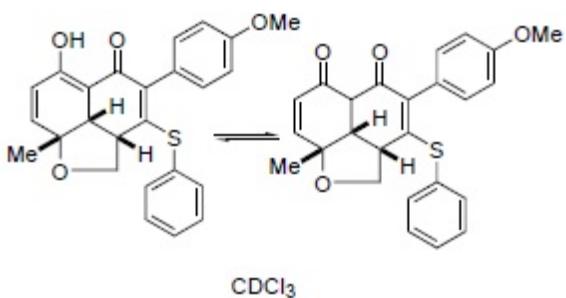
~151.24
~149.15
—144.65
—140.98

131.72
130.81
130.21
129.43
129.24
128.49
124.41
114.01

—101.70

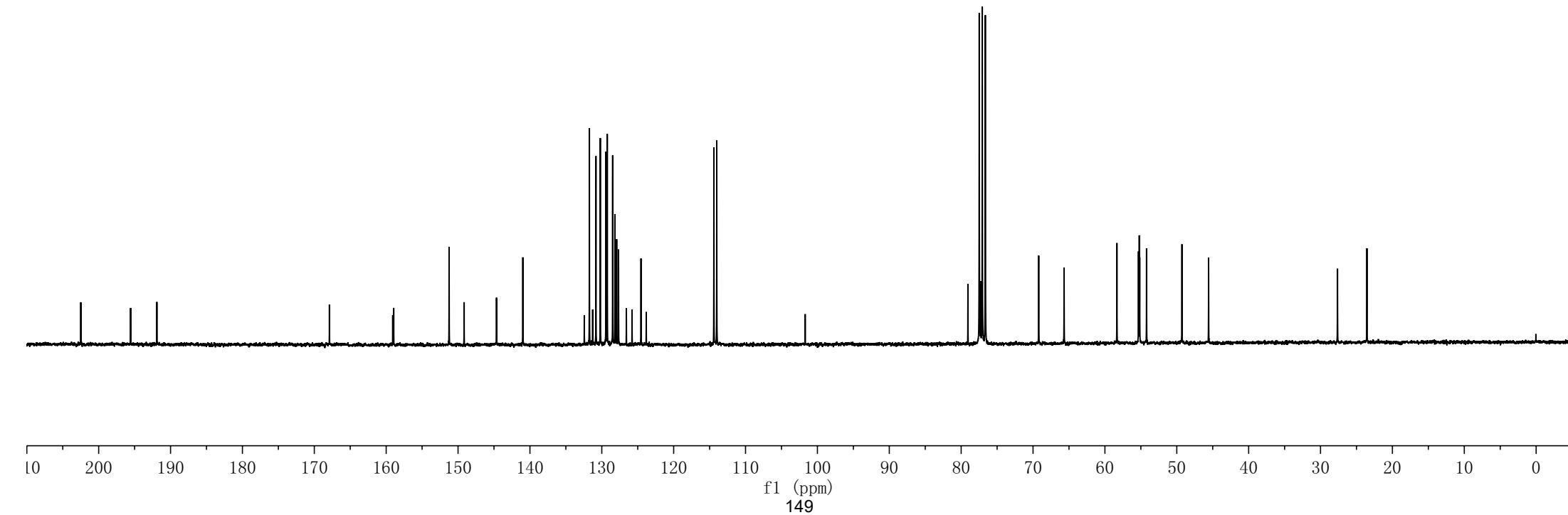
79.06
77.48
77.27
77.06
76.64
—69.21
—65.68
58.33
55.33
55.22
55.16
54.21
49.28
45.57

—27.64
—23.54



CDCl₃

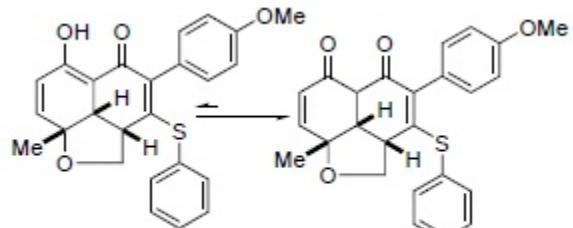
4u + 4u'



7.29
 7.24
 7.22
 7.19
 6.99
 6.97
 6.92
 6.84
 6.81
 6.78
 6.59
 6.55
 6.18
 6.15

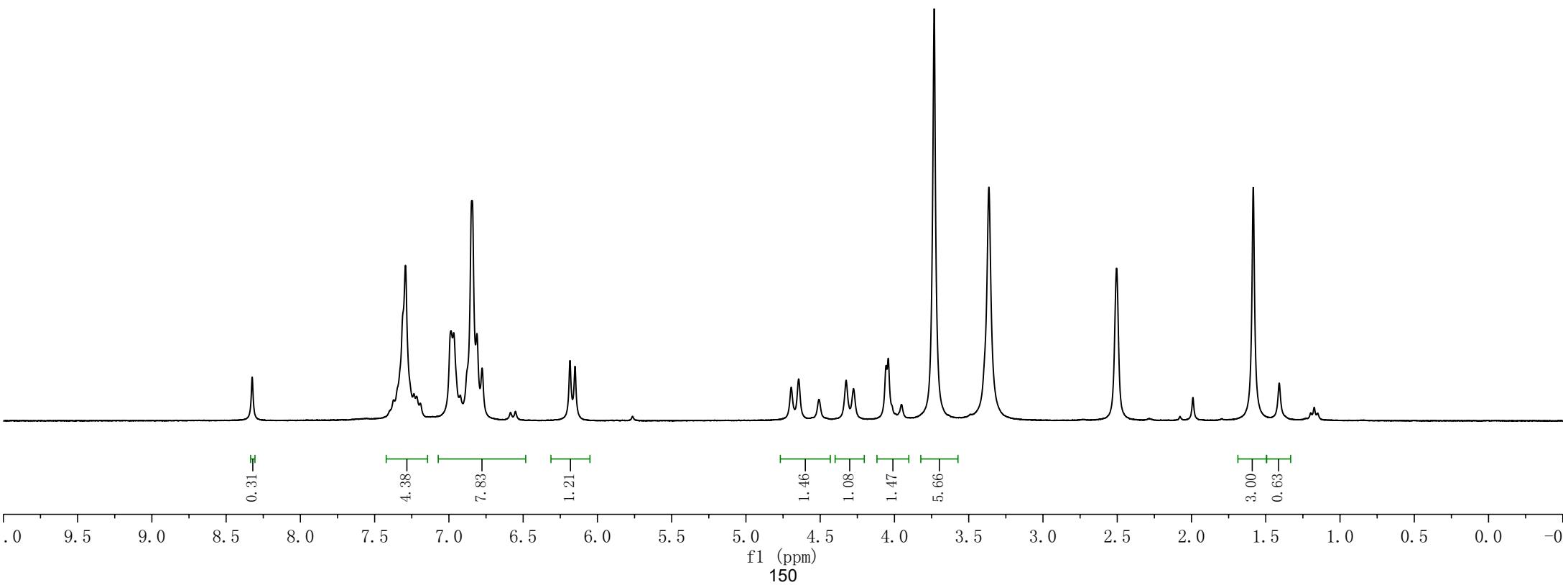
4.69
 4.65
 4.51
 4.33
 4.28
 4.06
 4.04
 3.95
 3.73

-3.36
 -2.50
 -1.58
 -1.41



DMSO-*d*₆

4u + 4u'



—203.18

~194.40
~193.28

-168.69

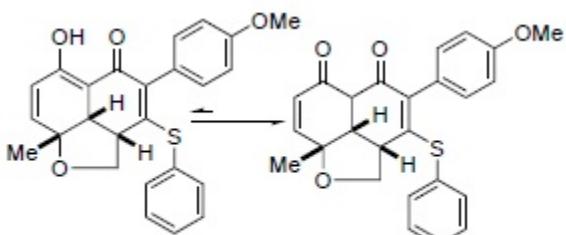
159.26
 158.84
 - 152.46
 151.17
 149.06
 - 143.15

130.79
130.35
129.81
129.52
128.17
127.85
123.93
114.22

-101.73

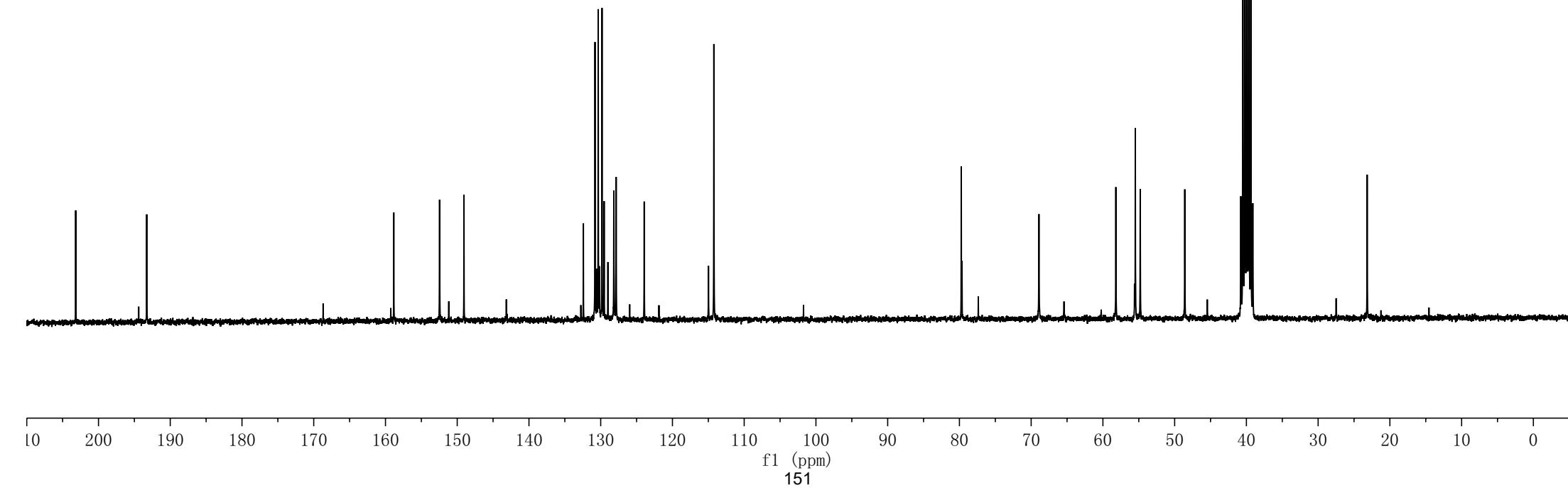
79.74
79.64
77.37

-68.91
-65.42

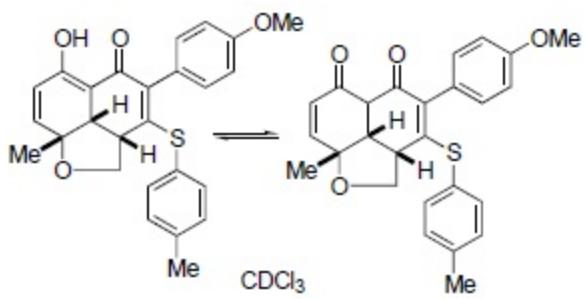


DMSO-*d*₆

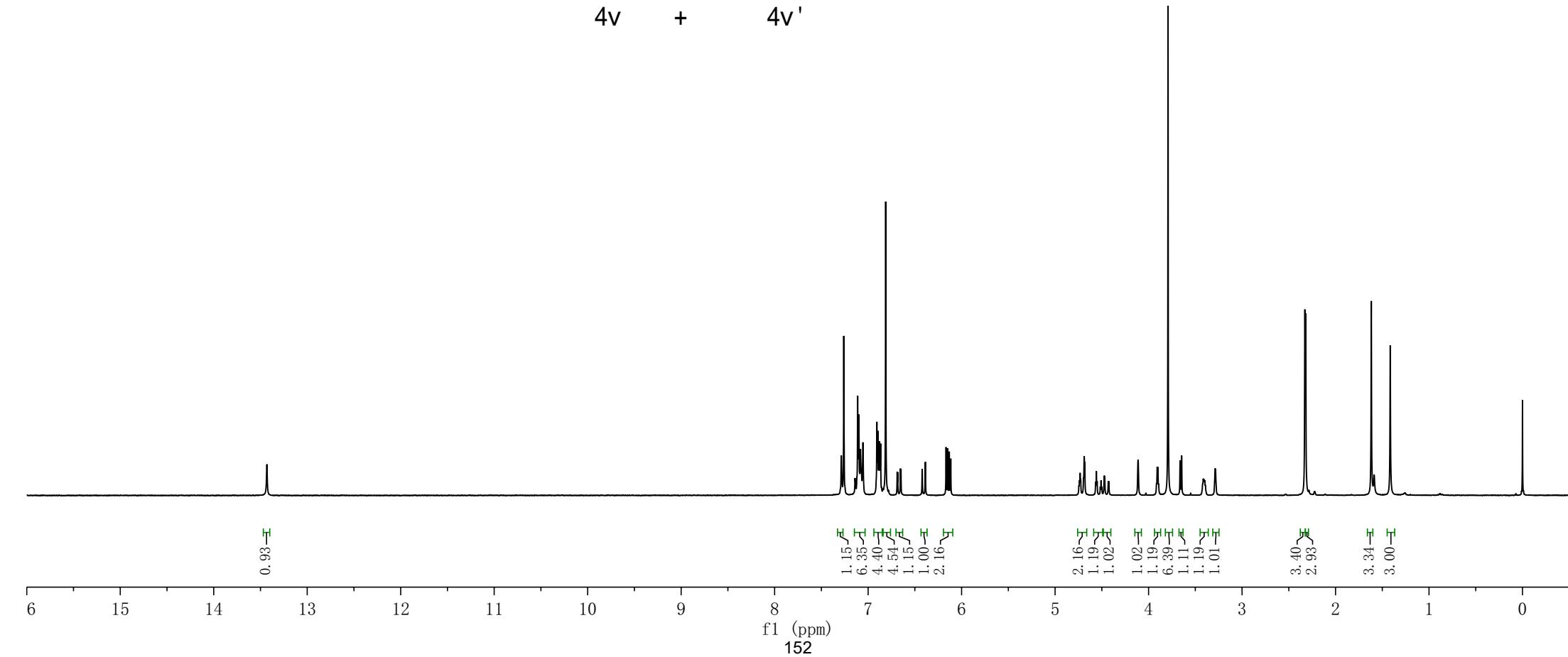
$$4u + 4u'$$



—13.43



4v + 4v'



—202.65

—195.77

—191.86

—167.68

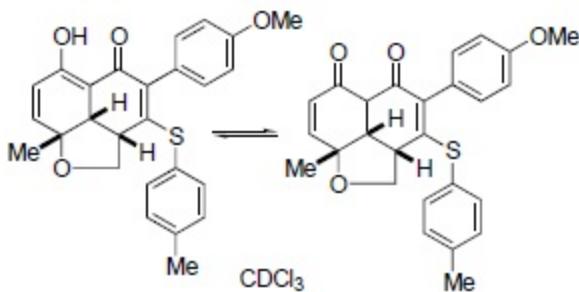
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<158.92

—151.20
—143.54
✓140.94
✓132.30
✓131.54
✓130.22
✓130.19
✓130.00
✓128.50
✓128.27
✓128.13
✓124.58
<113.97

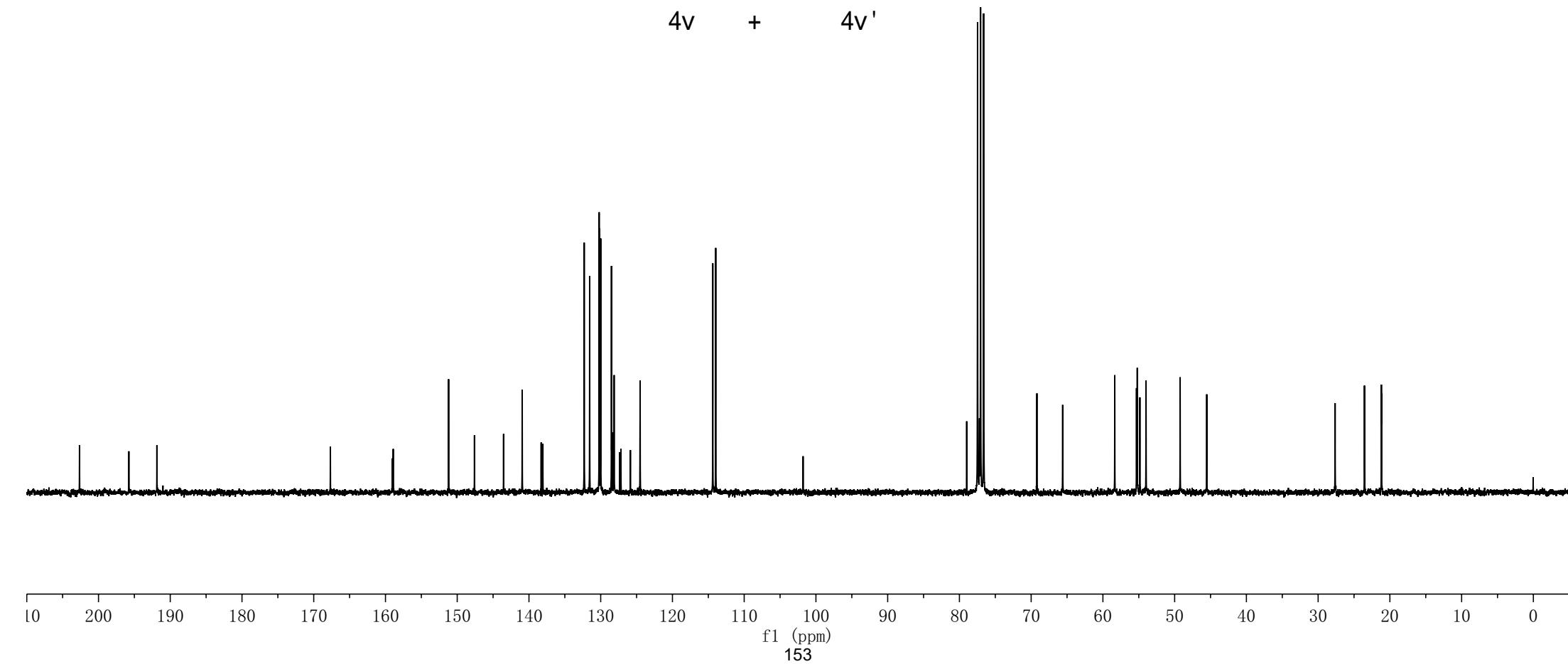
—101.79

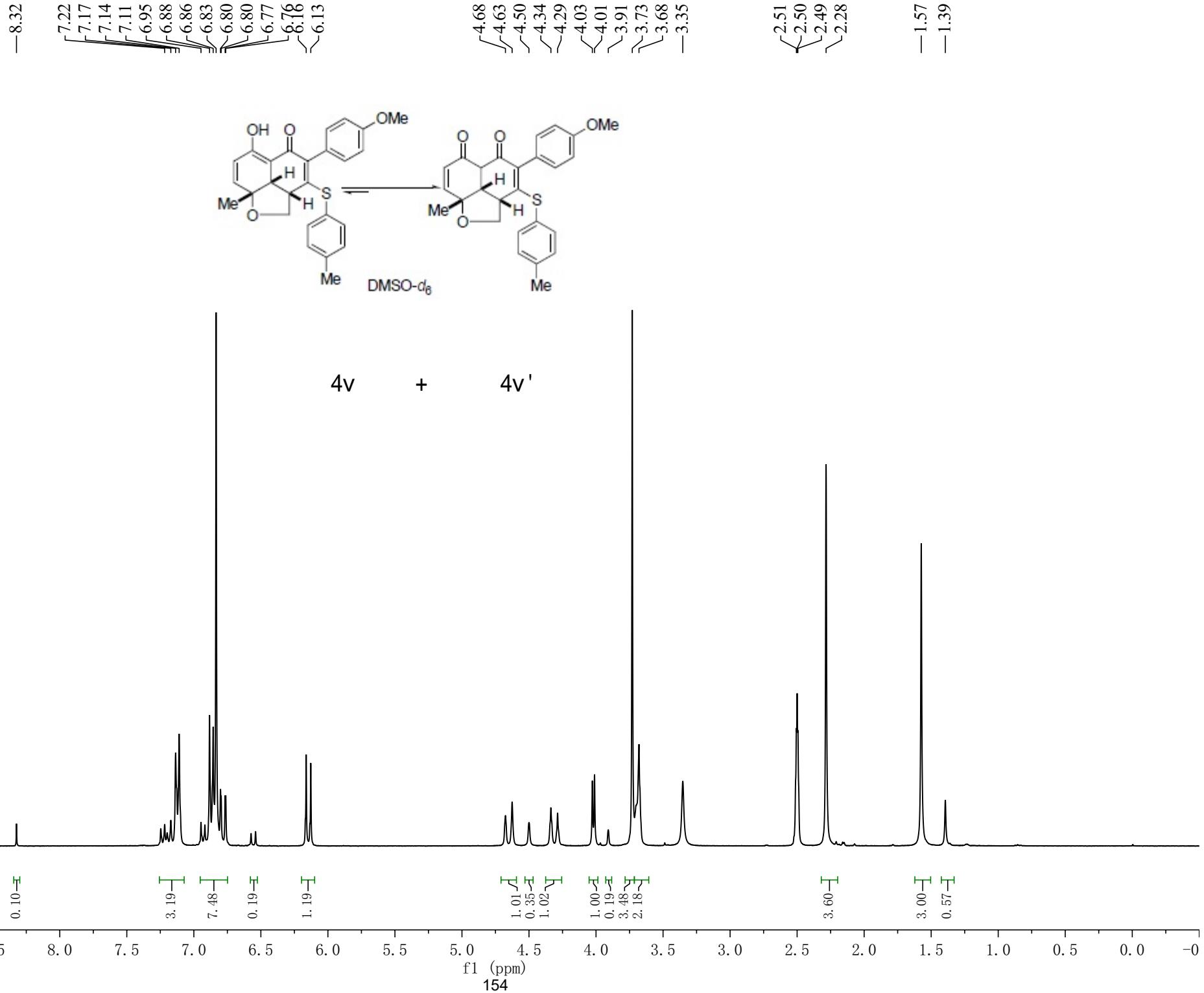
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✓77.47
✓77.20
✓77.05
✓76.63
—69.20
—65.61
✓58.35
✓55.32
✓55.21
✓54.85
✓53.99
✓49.23
✓45.53

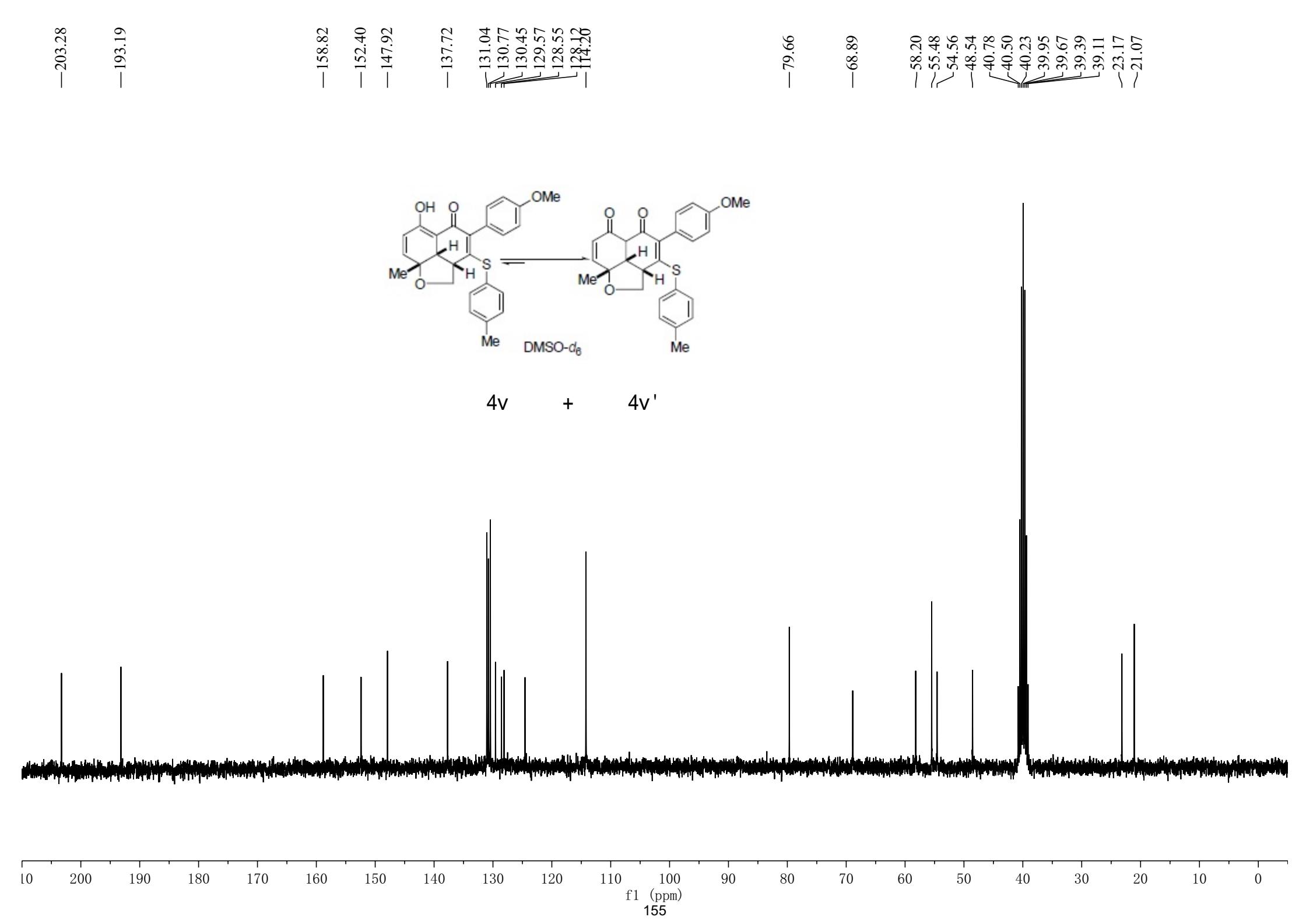
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✓23.54
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4v + 4v'

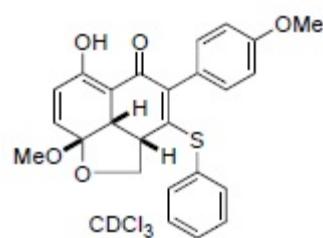
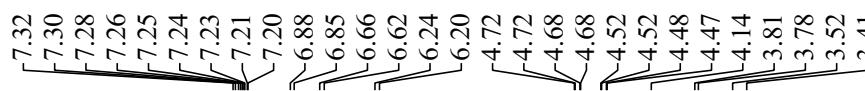




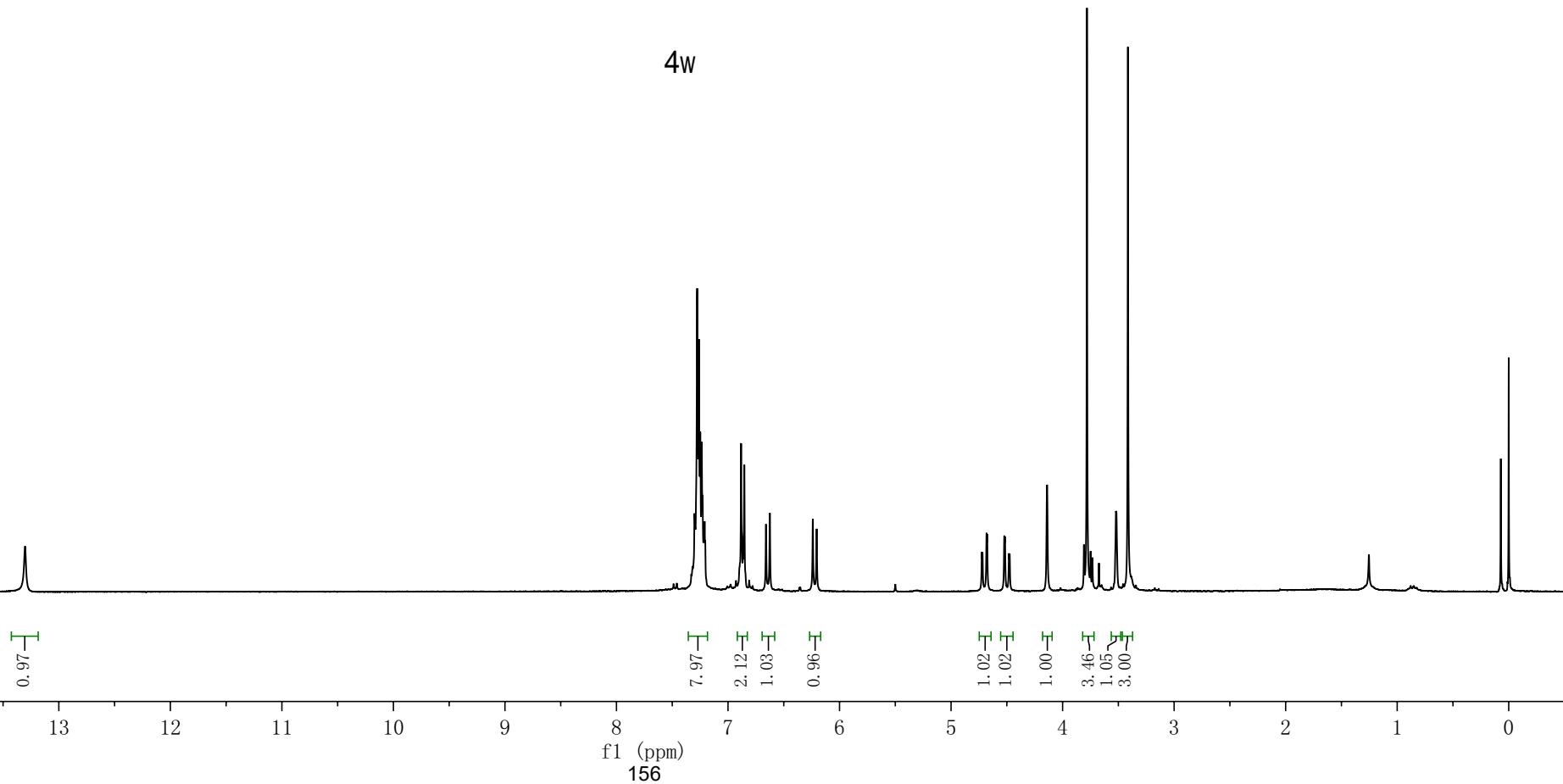


-0.00

-13.30



4w



— 195.68

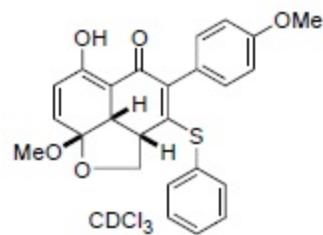
— 166.68

— 159.14

— 146.76

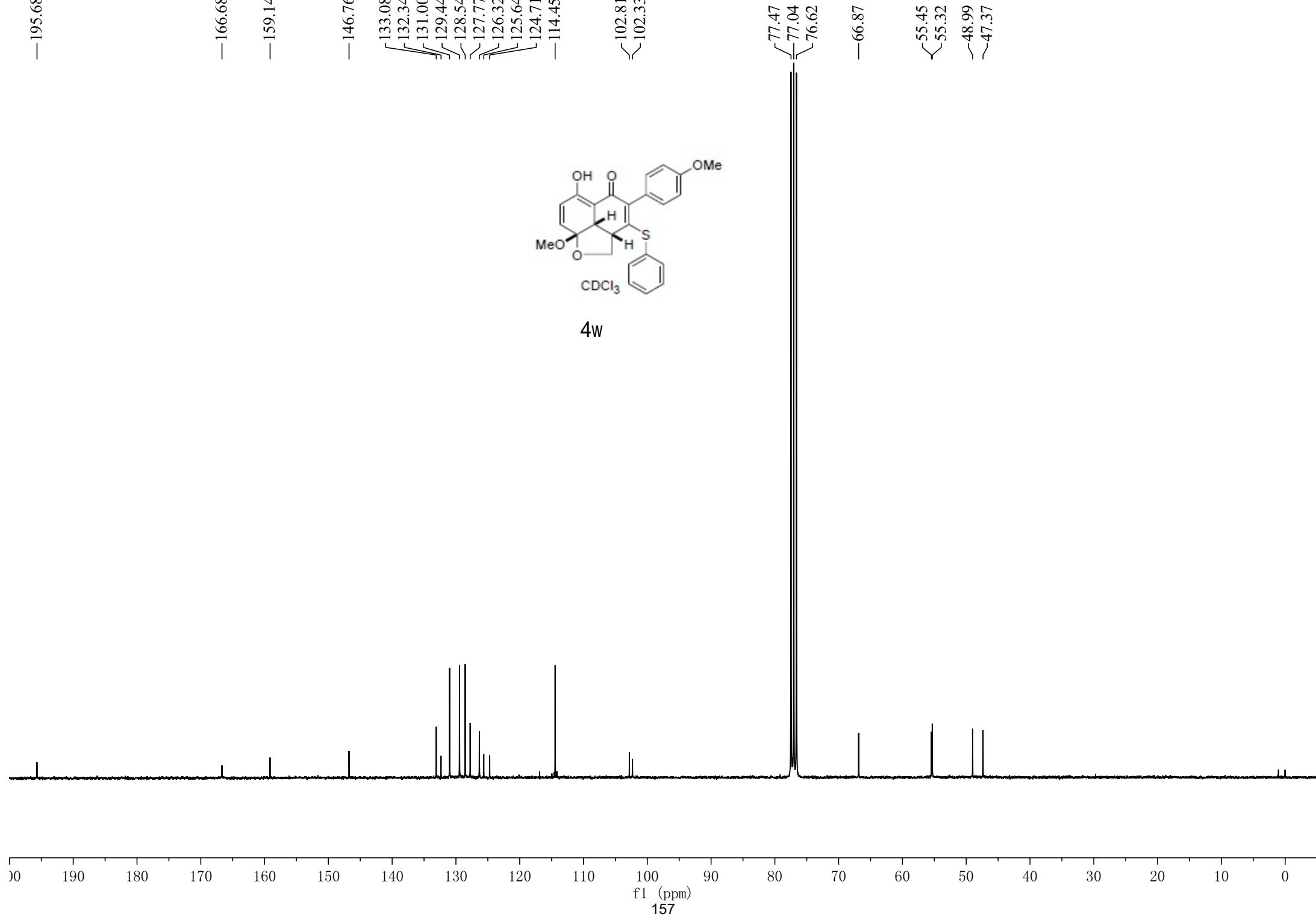
133.08
132.34
131.00
129.44
128.54
127.77
126.32
125.64
124.71
— 114.45

102.81
102.33



4W

77.47
77.04
76.62
— 66.87
55.45
55.32
— 48.99
— 47.37



—14.73

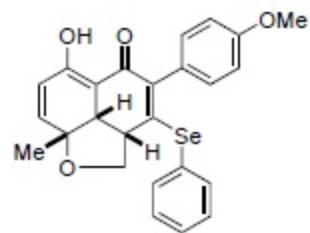
7.66
7.65
7.49
7.47
7.46
7.41
7.39
7.37
7.26
7.23
7.21
7.01
6.98
6.26
6.23
6.14
6.11

3.85
3.70
3.69
3.67
3.56
3.54
3.52
3.41
3.39
3.37
3.37
3.35
3.28
3.26

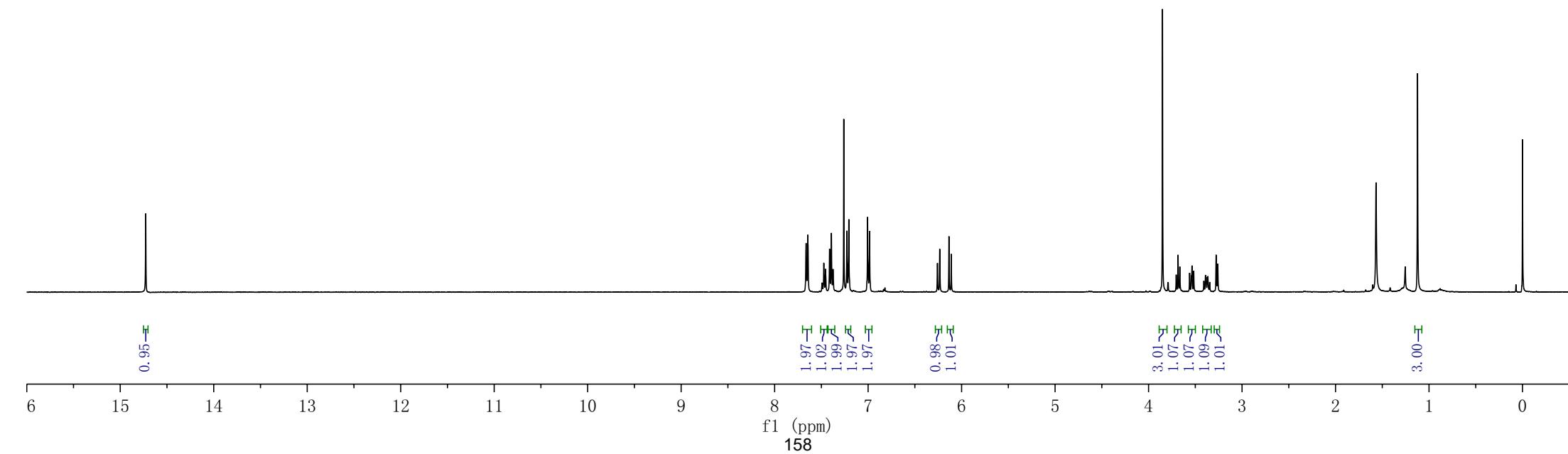
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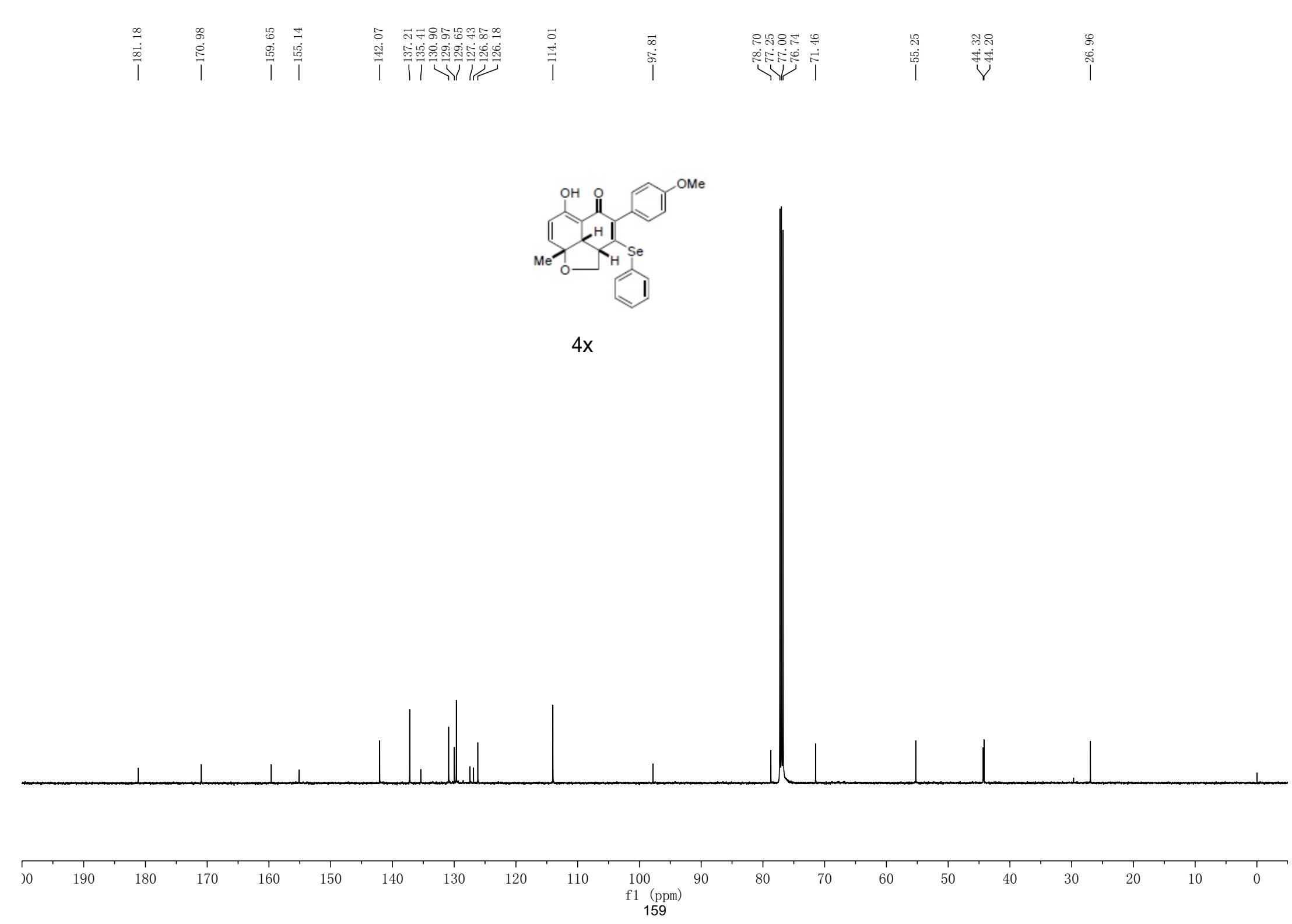
—1.12

—0.00

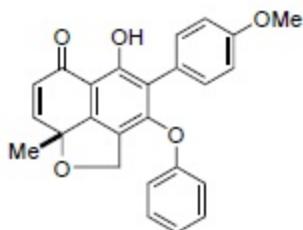


4x

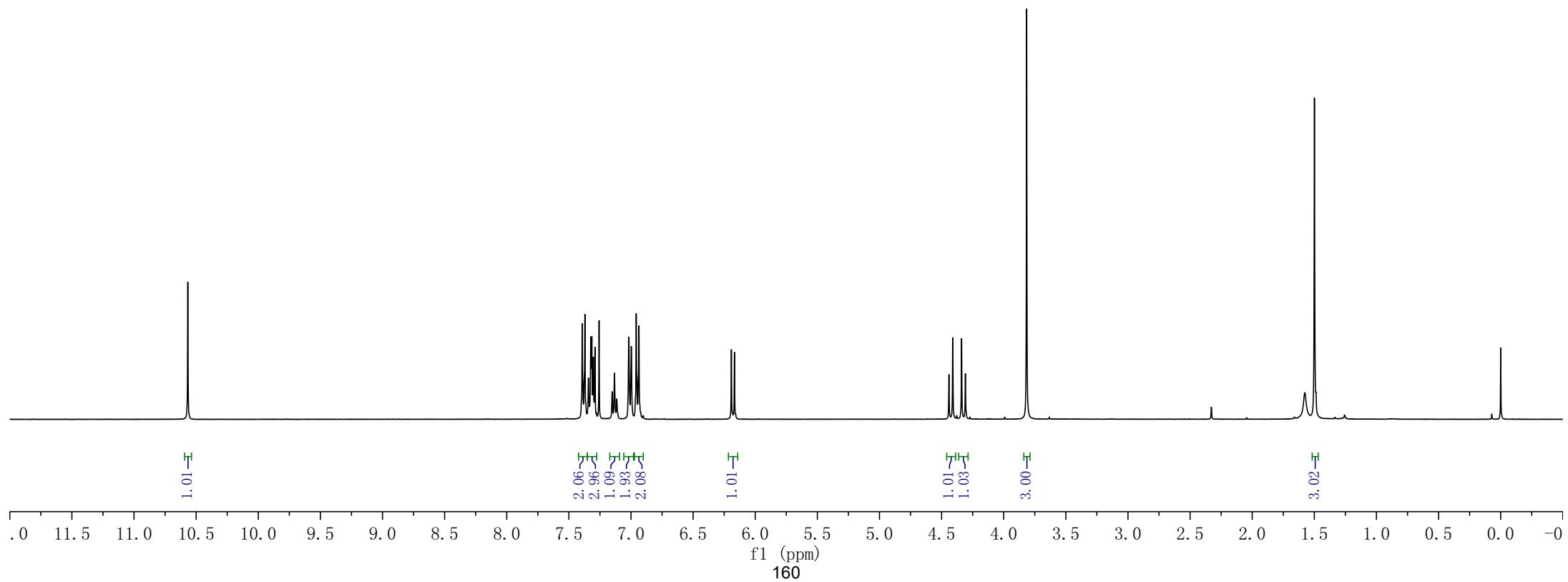




—10.57
7.39
7.37
7.34
7.32
7.31
7.30
7.29
7.26
7.15
7.13
7.11
7.02
7.00
6.96
6.94
6.19
6.17
4.44
4.41
4.34
4.31
—3.82
—1.58
—1.50
—0.00



5a



—187.60

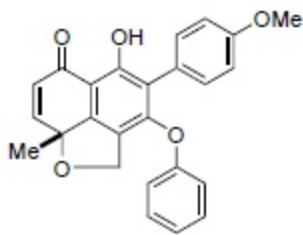
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~158.97
~156.50
~154.77
~152.74
~150.35

~131.70
~129.90
~128.67
~124.29
~123.82
~120.27
~118.99
~118.75
~113.60
~108.24

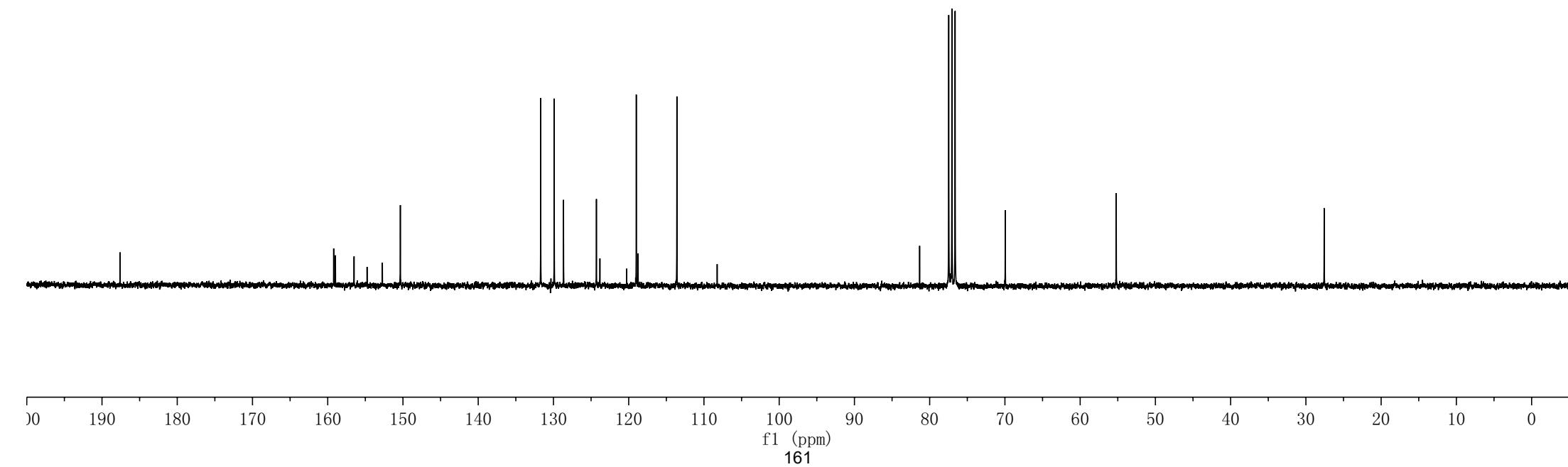
~81.33
~77.47
~77.04
~76.62
~69.95

~55.20

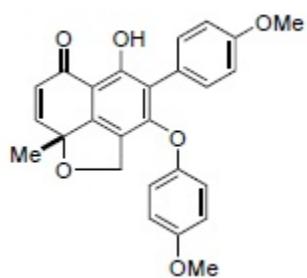
—27.57



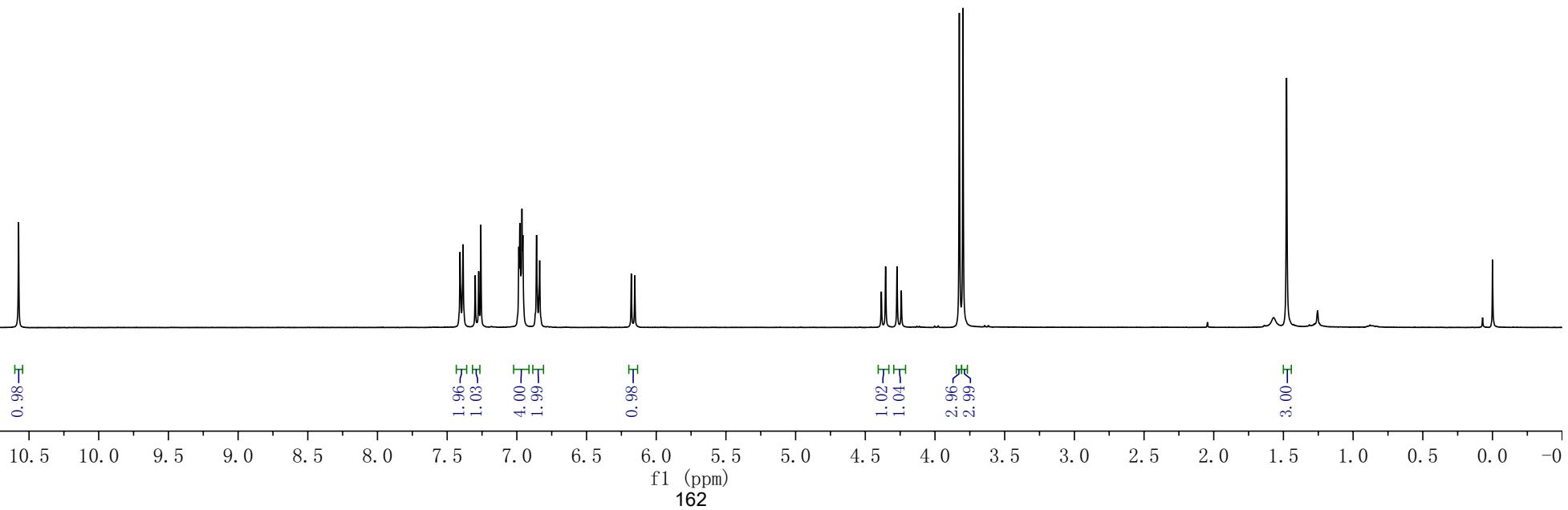
5a



—10.58
—
—7.41
—7.39
—7.30
—7.27
—7.26
—6.99
—6.98
—6.96
—6.96
—6.86
—6.84
—6.18
—6.15
—
—1.57
—1.48
—
—0.00



5b



—187.53

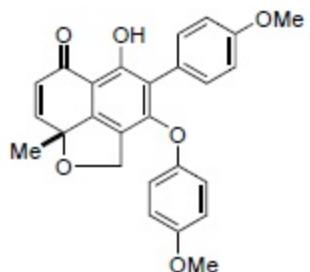
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~158.96
~156.49
~155.85
~152.87
~150.22
~150.05

—131.75
—128.65
—124.02
~120.66
~119.46
—117.81
~114.82
~113.61
—107.84

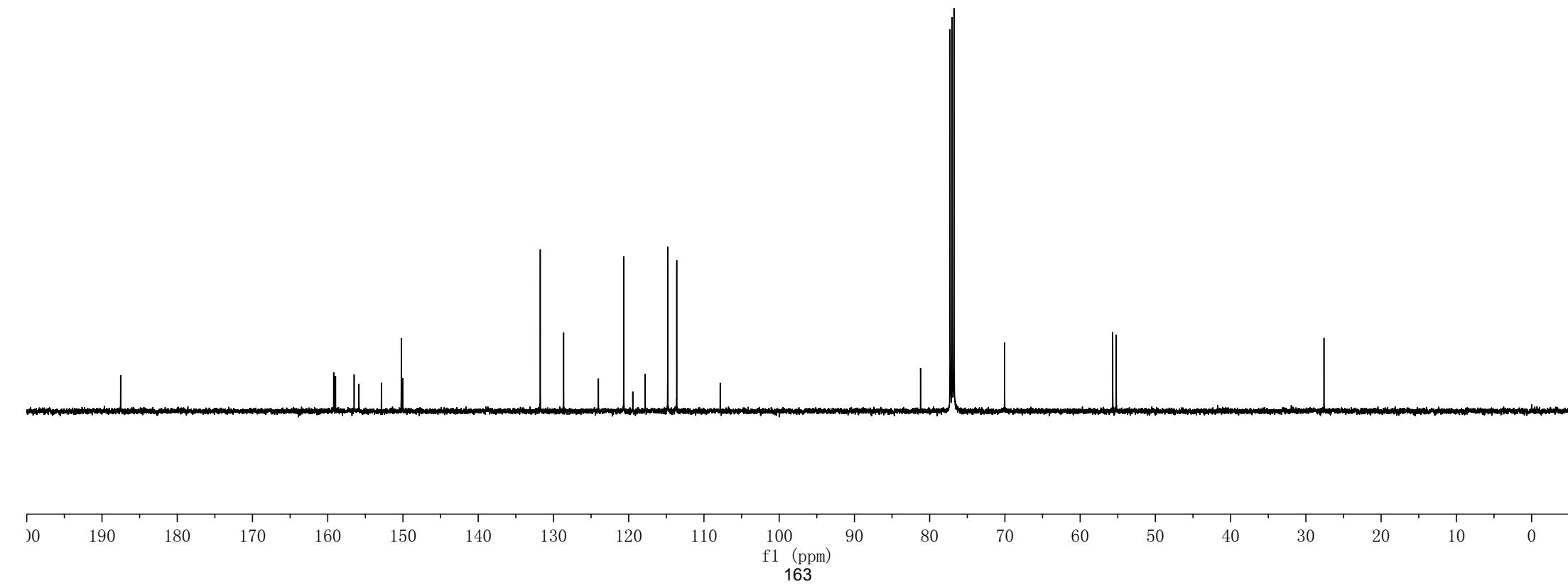
~81.22
~77.29
~77.03
~76.78
—70.04

~55.67
~55.20

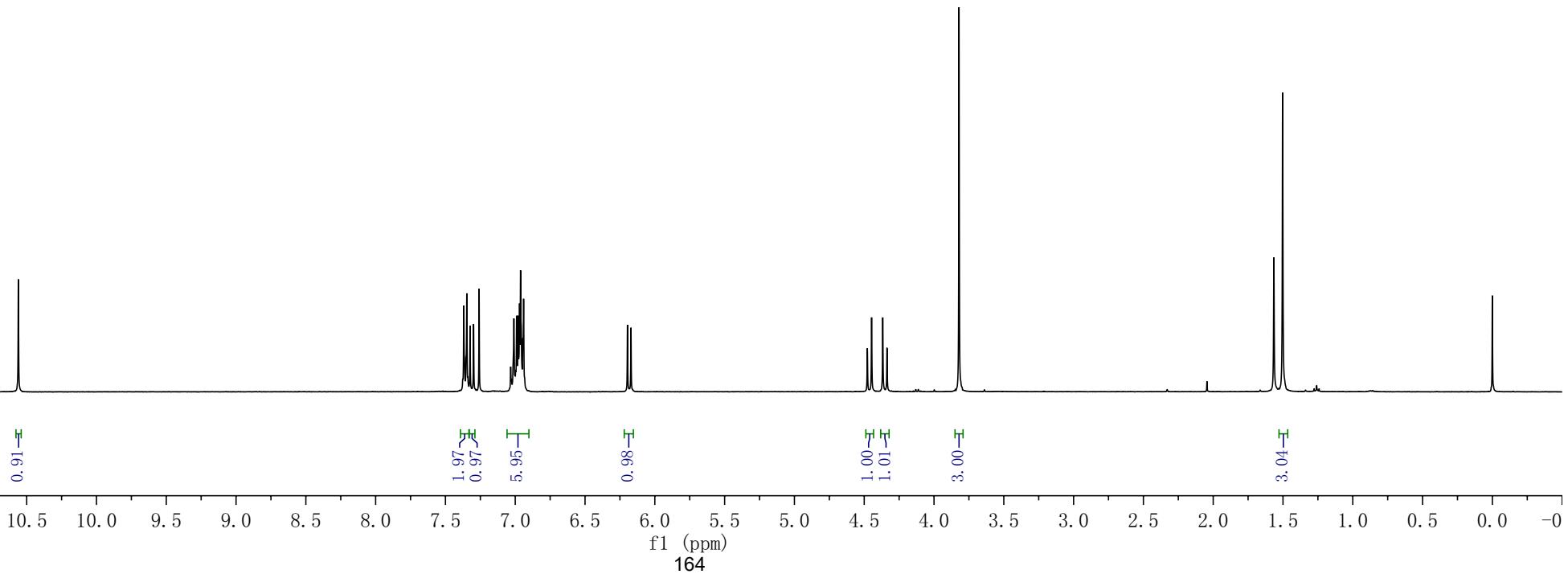
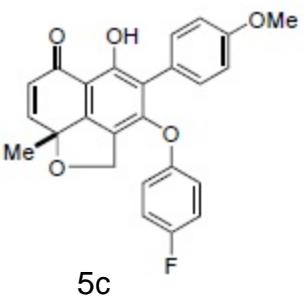
—27.60



5b



—10.56 —
7.37
7.35
7.32
7.30
7.26
7.03
7.03
7.01
7.00
6.99
6.98
6.97
6.96
6.95
6.94
6.20
6.17
—3.82 —
—1.57
—1.50
—0.00 —



—187.57

160.77
159.24
159.02
157.54
154.83
152.86
152.48
152.45
150.35

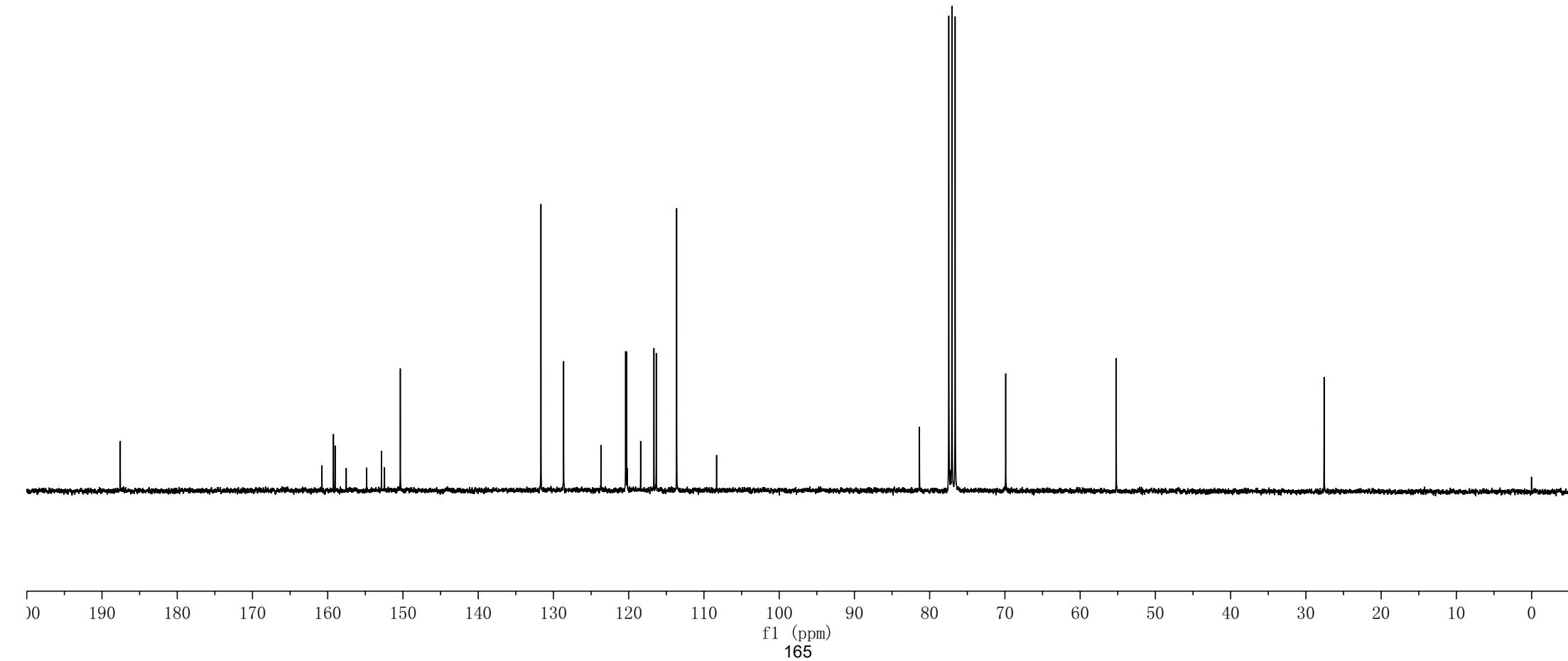
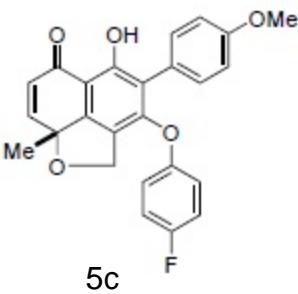
—131.66
—128.65
—123.69
—120.41
—120.30
—120.18
—118.42
—116.65
—116.34
—113.63
—108.32

~81.35
~77.46
~77.04
~76.61

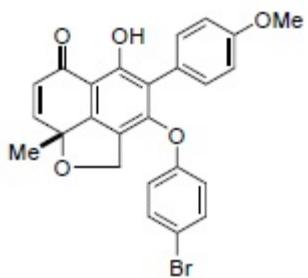
—69.90

—55.21

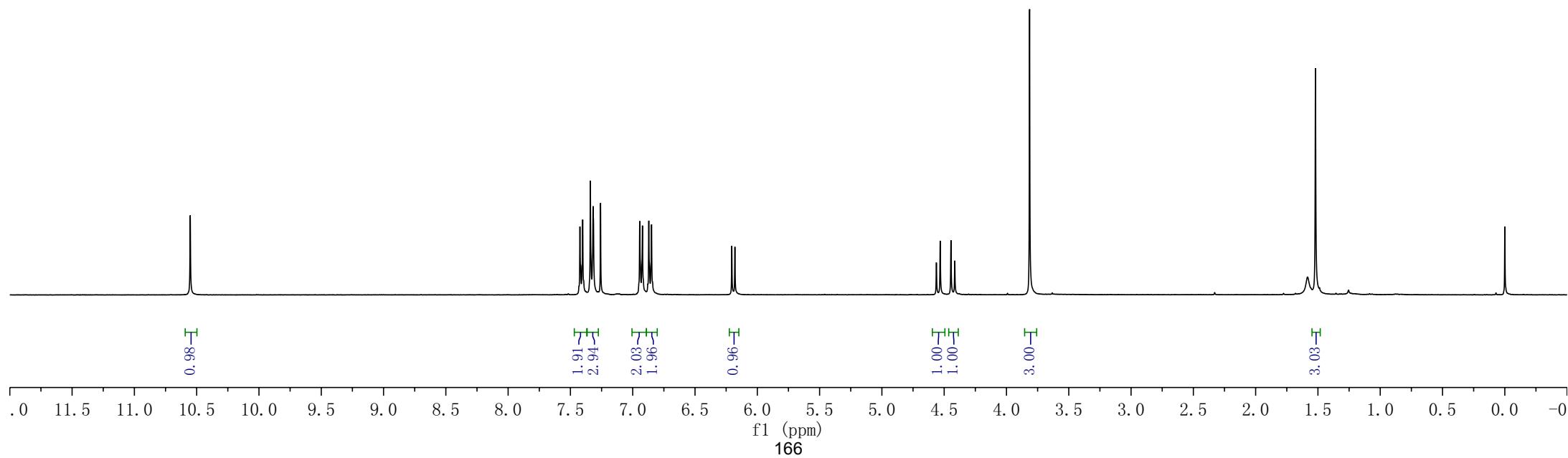
—27.58



—10.55
—
—7.42
—7.40
—7.34
—7.32
—7.26
—6.94
—6.92
—6.87
—6.85
—6.20
—6.18
—
—4.56
—4.53
—4.45
—4.42
—
—3.81
—
—1.58
—1.52
—
—0.00



5d



— 187.60

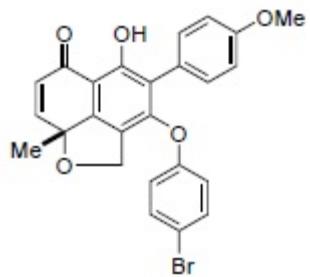
159.24
159.06
155.69
153.85
152.78
150.46

$$\begin{array}{r} -132.84 \\ \sim -131.59 \\ -128.66 \\ \hline -123.49 \\ \sim -120.81 \\ \sim -120.15 \\ \sim -119.13 \\ \sim -116.63 \\ \sim -113.64 \\ \hline -108.69 \end{array}$$

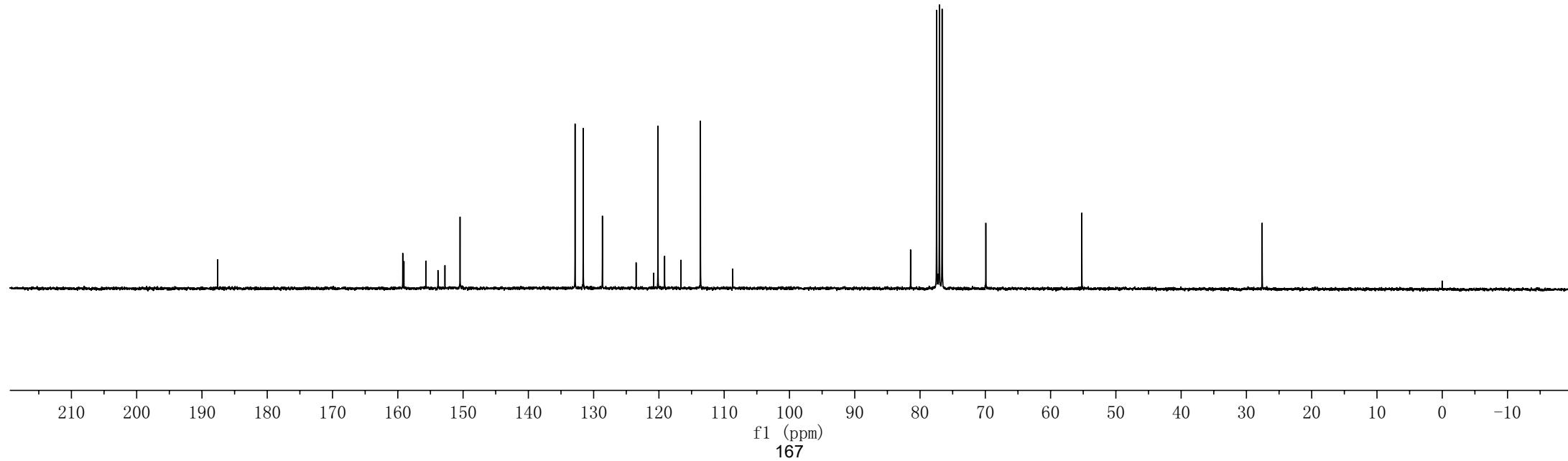
$$\begin{array}{r} 81.45 \\ - 77.46 \\ \hline 37.04 \\ - 76.62 \\ \hline = 69.92 \end{array}$$

۳۱

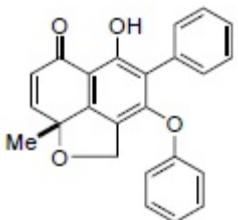
C 1



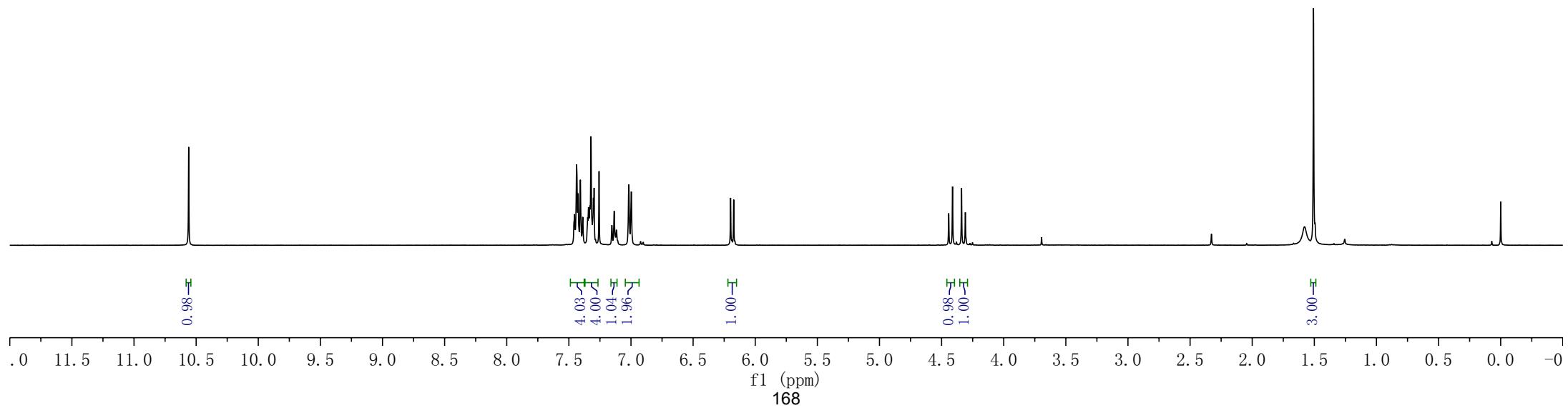
5d



—10.56 —
7.46
7.43
7.41
7.39
7.35
7.34
7.33
7.32
7.30
7.26
7.15
7.14
7.12
7.02
7.00
6.20
6.17
—1.58
—1.51
—0.00



5e



—187.57

—159.13
—156.45
—154.74
—153.10
—150.36

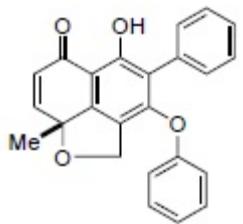
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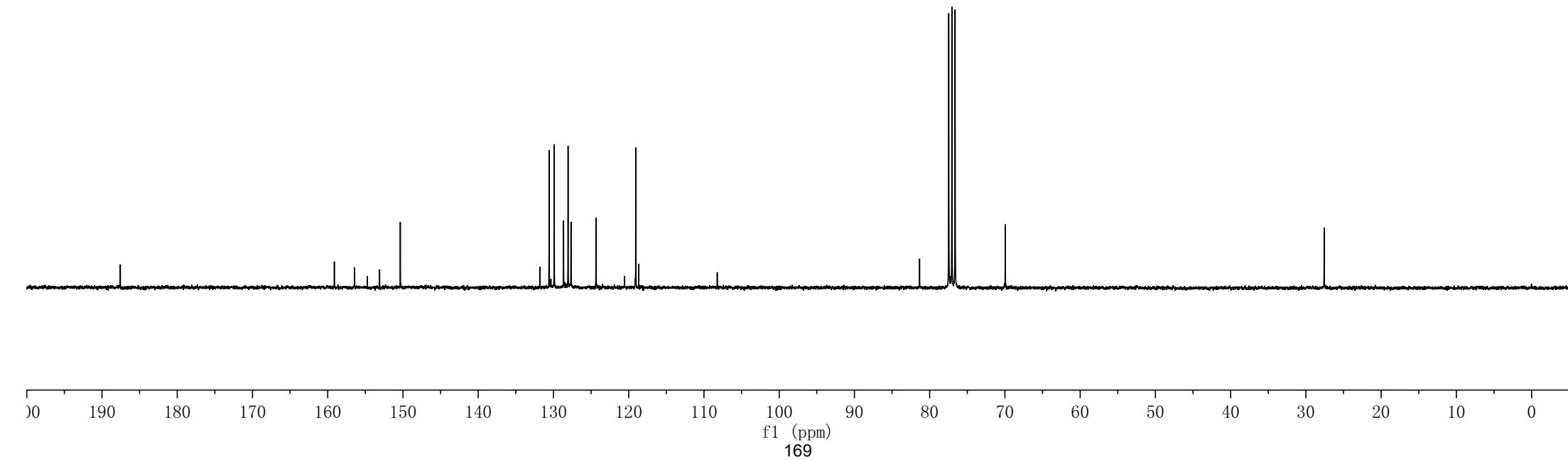
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—69.95

—27.57



5e



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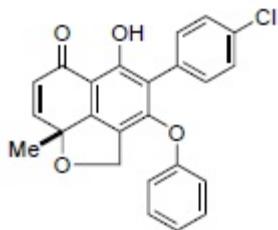
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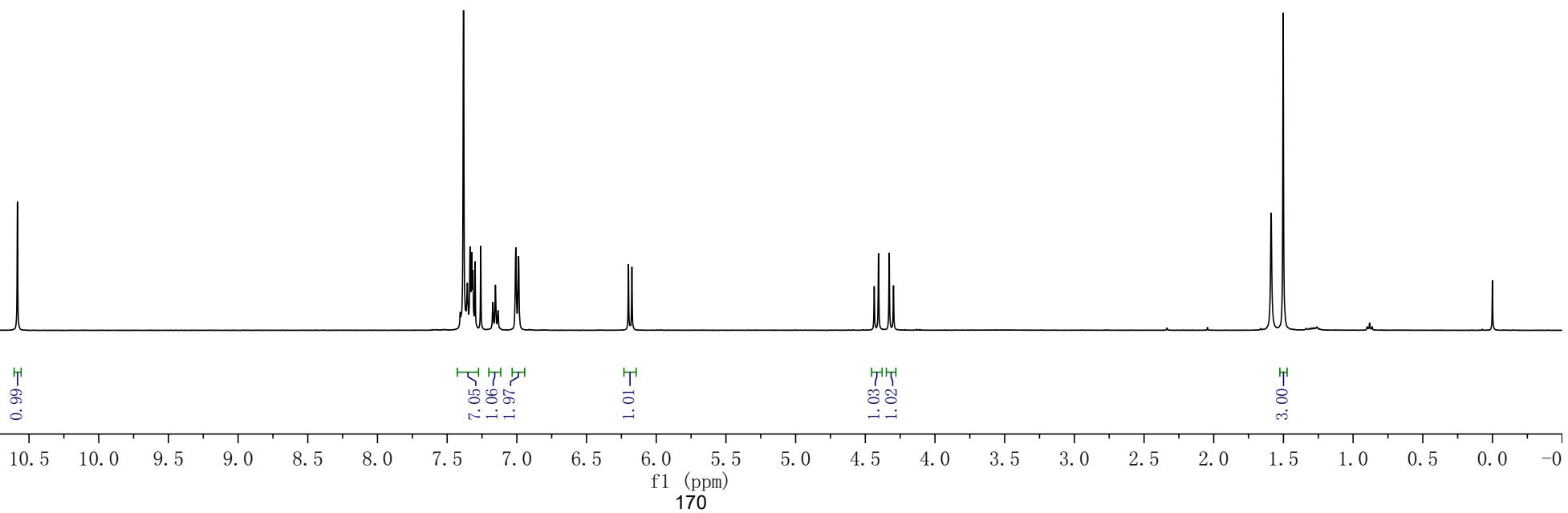
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5f



—187.53

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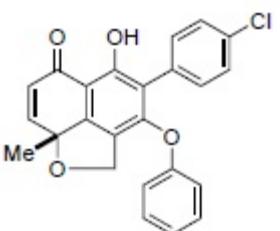
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✓118.65

—108.25

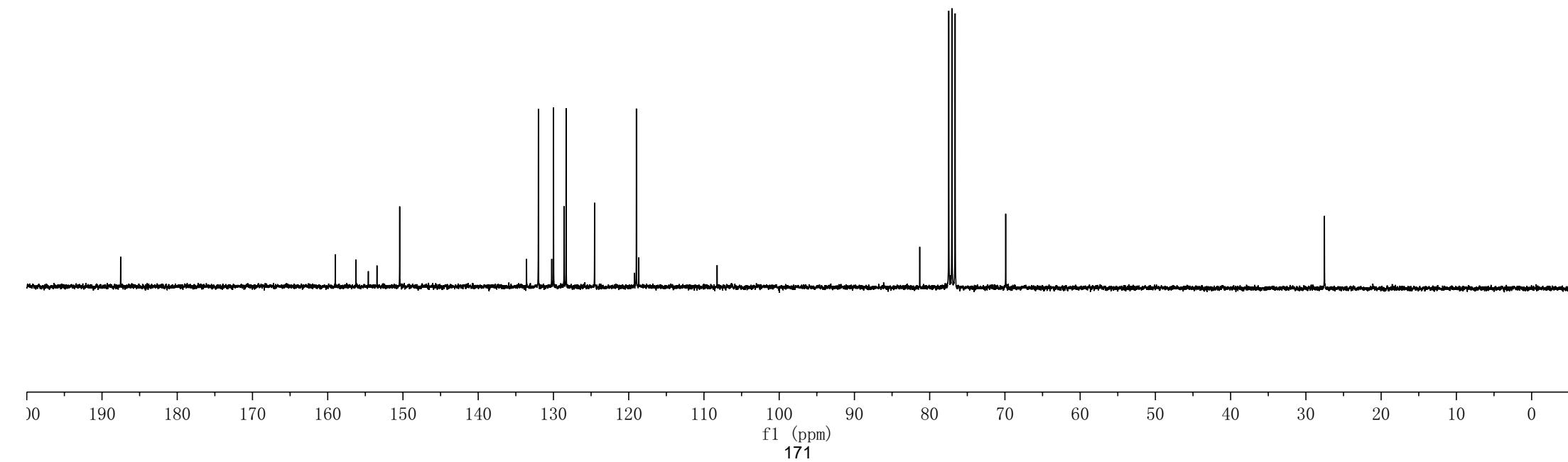
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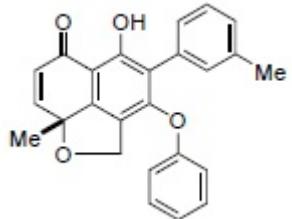
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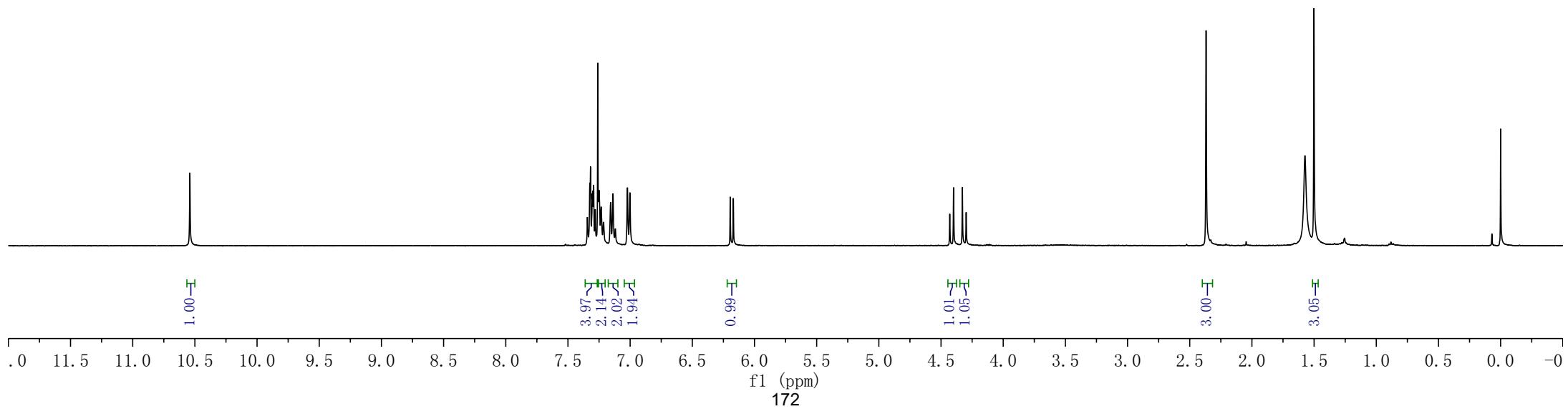
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7.16
7.14
7.12
7.02
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6.17
—4.43
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4.33
4.30
—2.37
—1.57
—1.50
—0.00



5g



—187.55

—159.15
—156.50
—154.86
—152.98
—150.32

—137.58
—131.69
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—128.67
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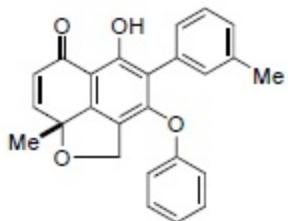
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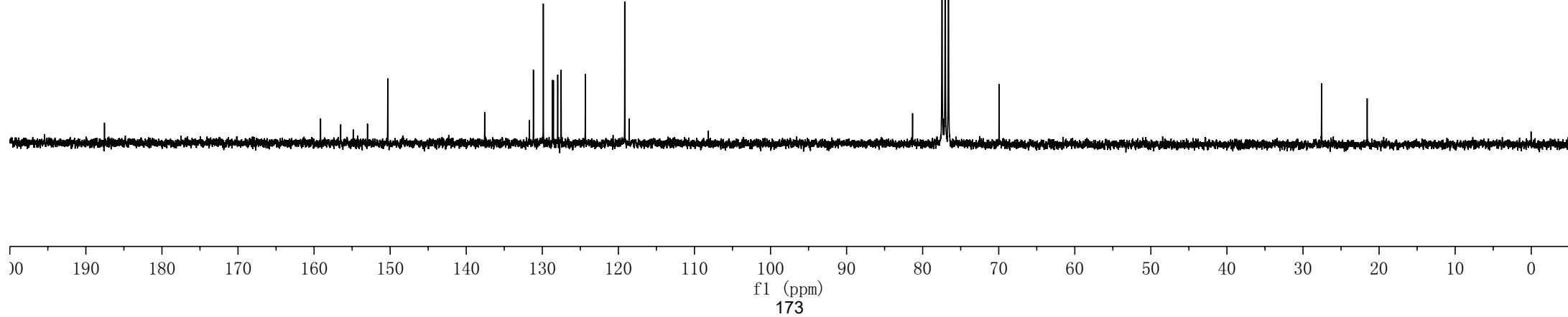
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—21.56



5g



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7.09

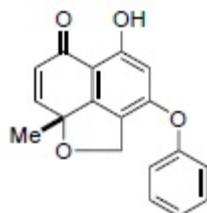
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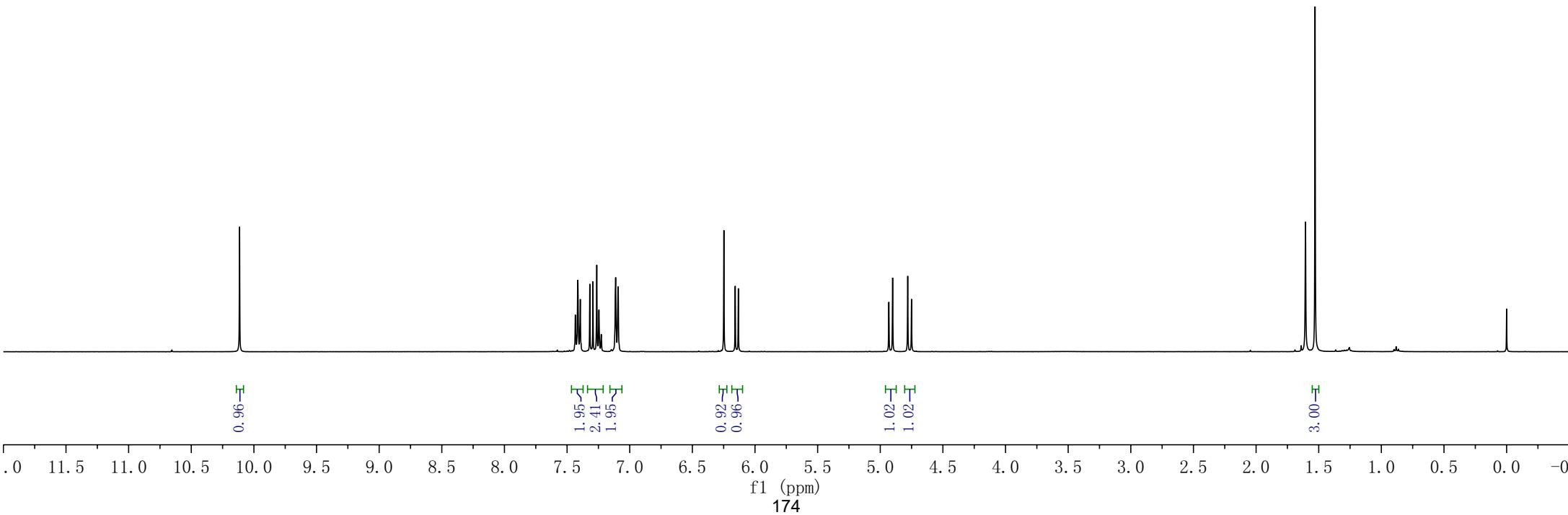
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5h



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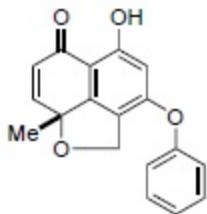
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Λ154.53
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Λ125.47
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—117.83

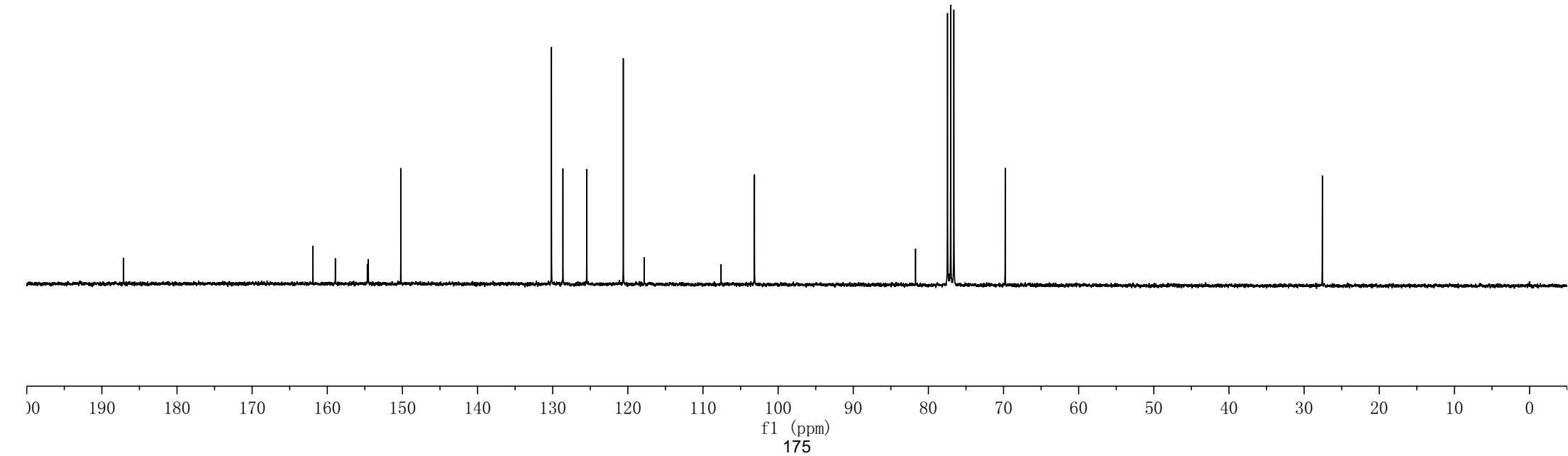
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—27.58



5h



—10.48

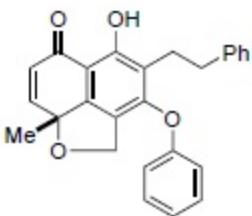
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7.15
6.96
6.94
6.16
6.14

4.38
4.35
4.25
4.22

3.07
3.05
3.04
3.03
2.91
2.89
2.89
2.87

1.59
1.58
1.45

—0.00



5i

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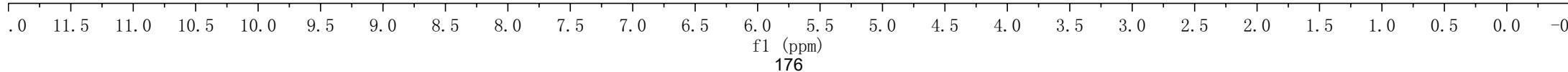
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—142.16

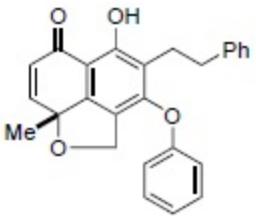
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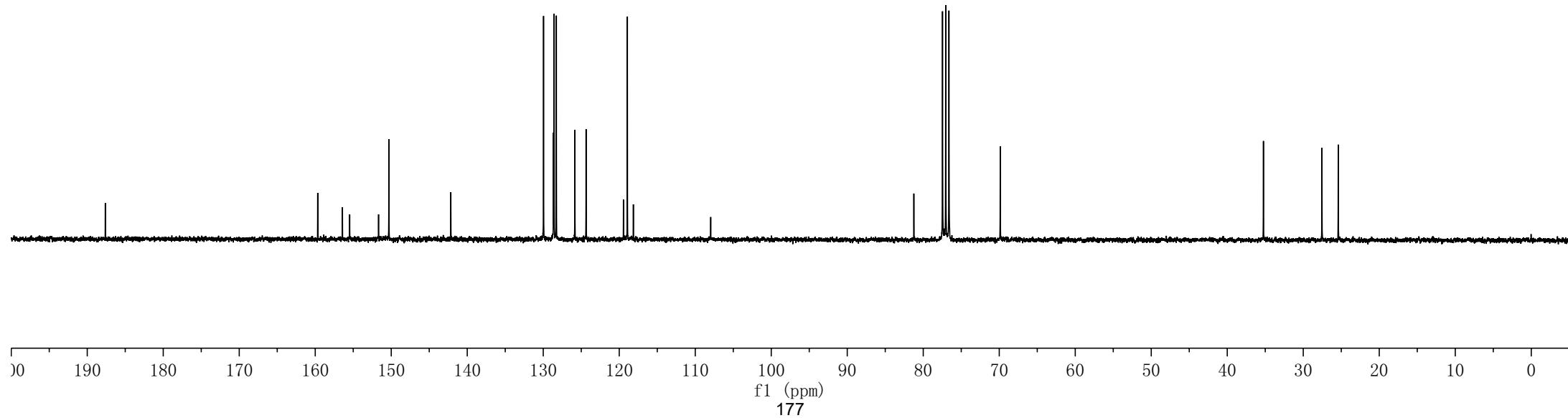
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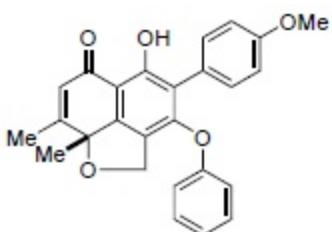


5i



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7.10
7.00
6.98
6.95
6.93
5.96
5.96
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5j

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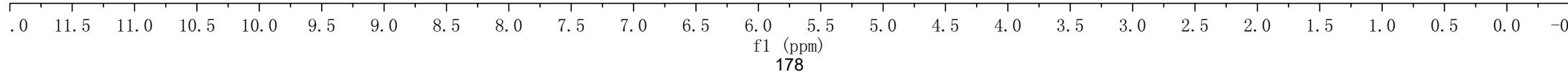
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3.04



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—158.92
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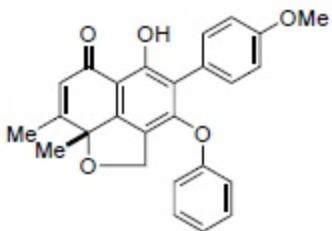
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—69.82

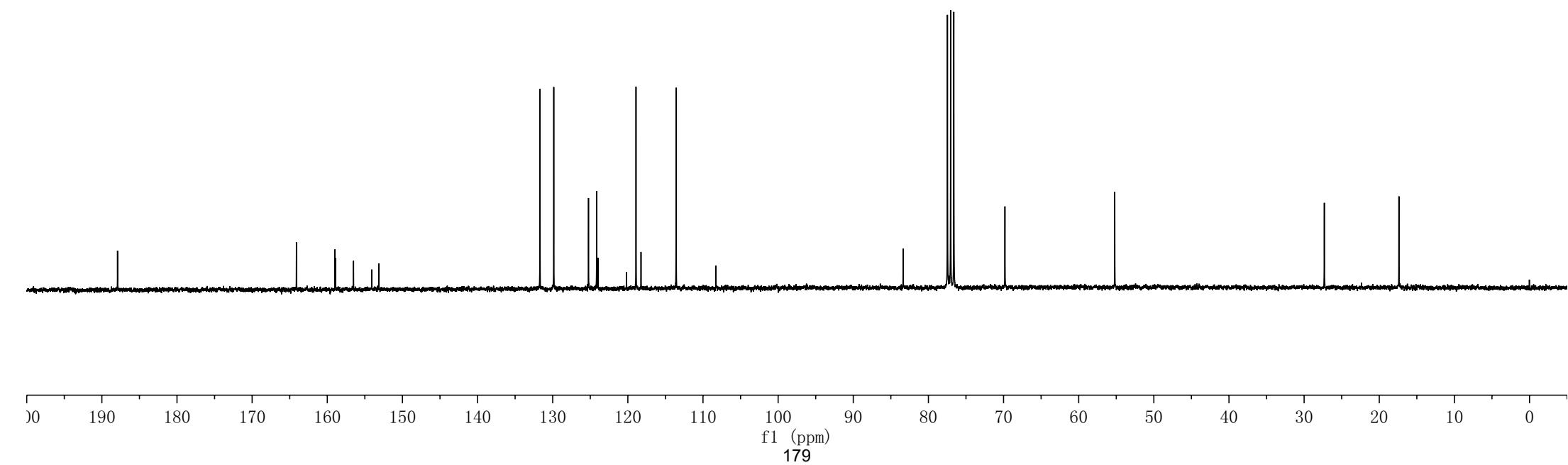
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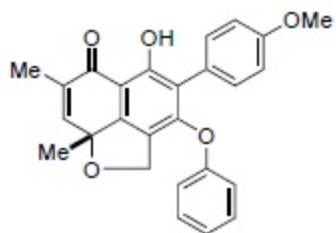
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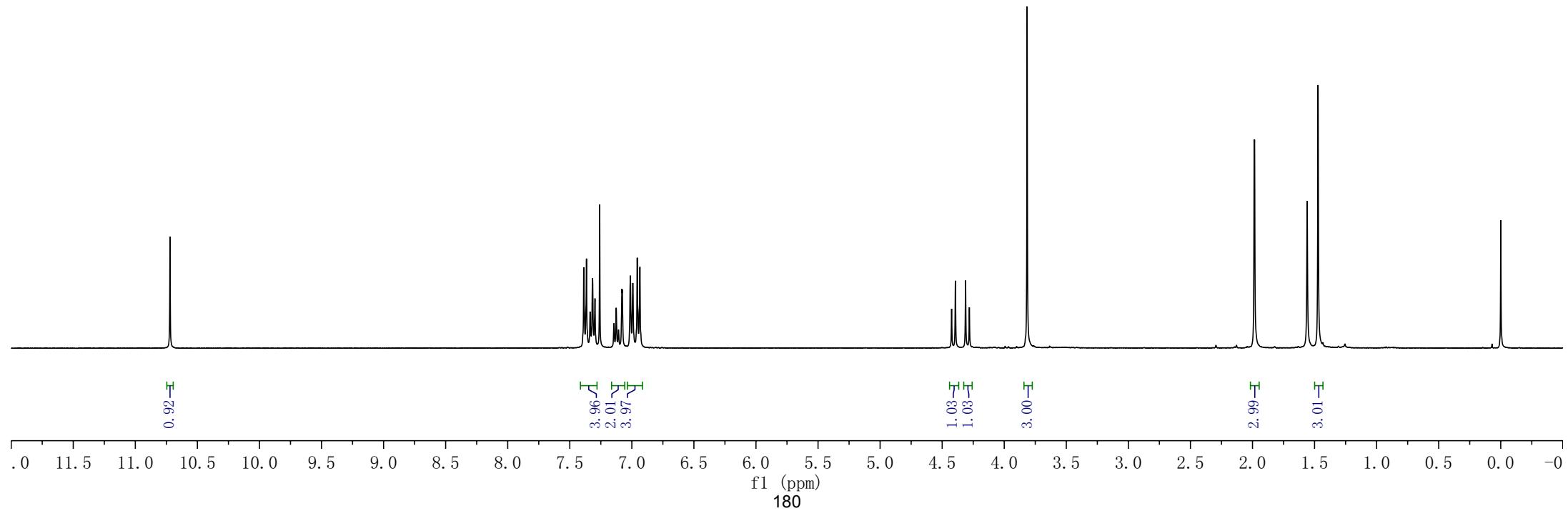
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7.08
7.08
7.01
6.99
6.96
6.93
4.42
4.39
4.31
4.28
—3.82
1.99
1.98
—1.56
—1.47
—0.00



5k



—188.21

159. 12
158. 93
156. 55
154. 55
153. 19

— 145.49

~135.35
 ~131.69
 ~129.87
 ↙124.21
 ↙123.97
 ↙120.13
 ↙118.96
 ↙118.69
 —113.59
 —108.02

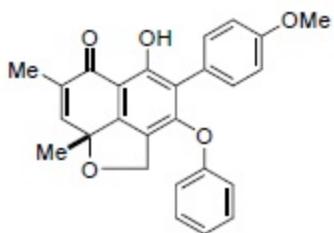
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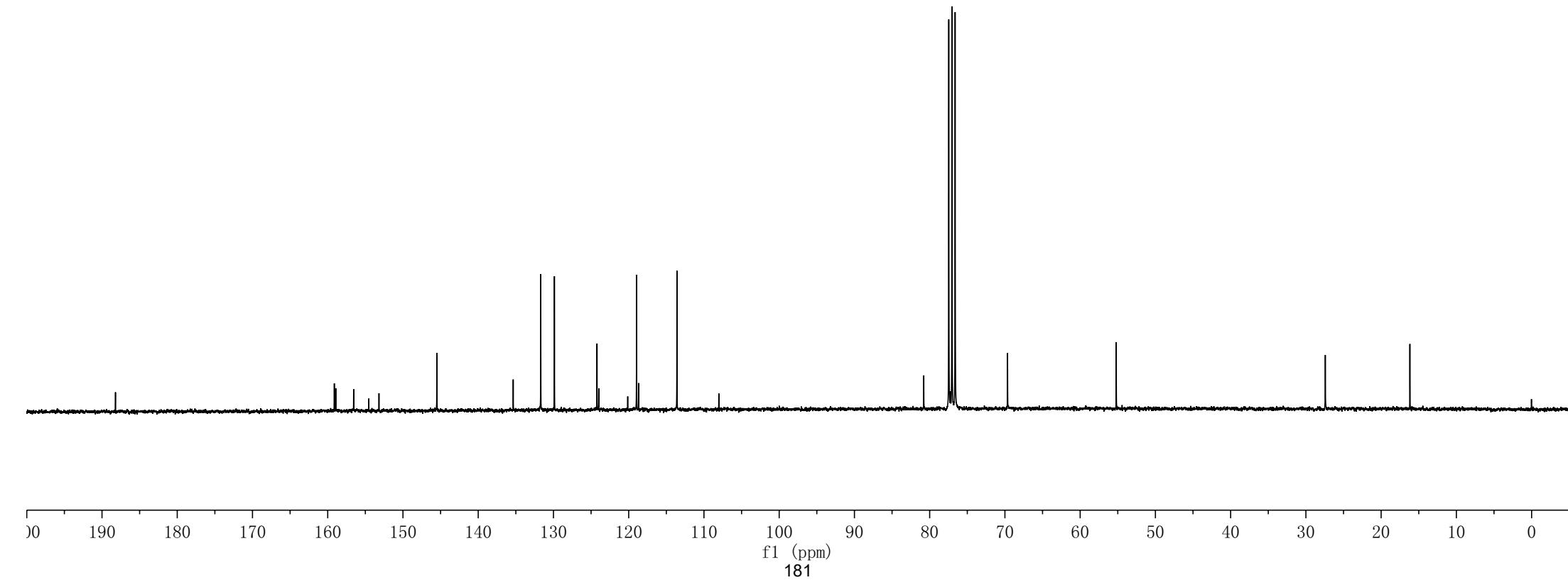
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25 10

18



5k

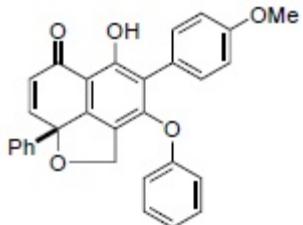


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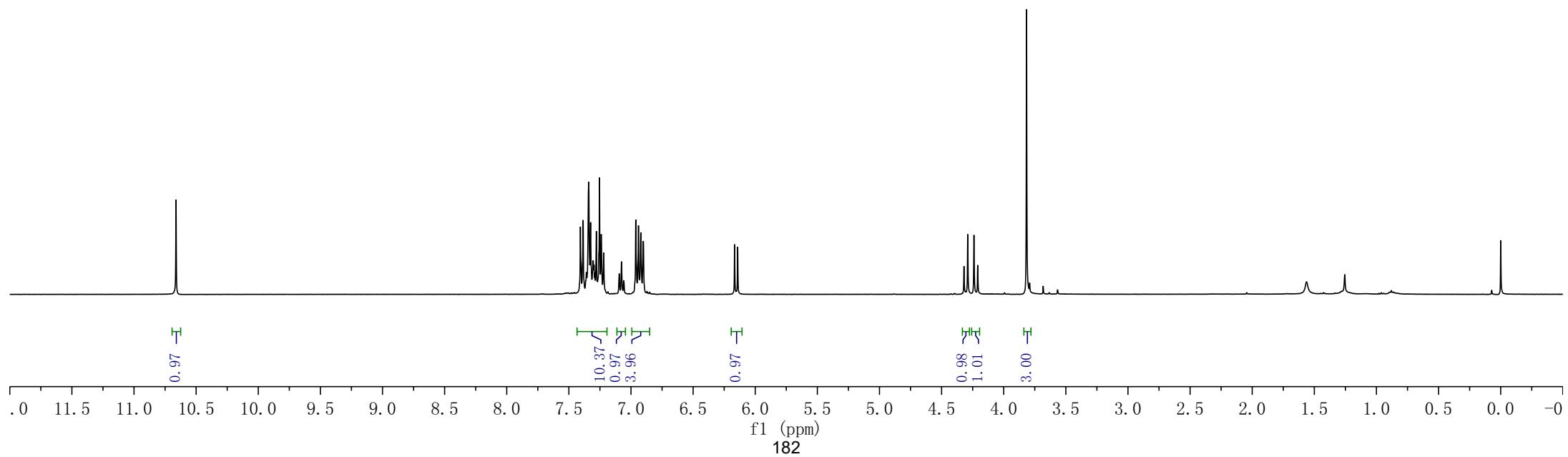
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7.06
6.96
6.94
6.92
6.90
6.17
6.14

4.32
4.29
4.24
4.21

3.82



5l



—188.38

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—>156.24
—>154.91
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—>149.44

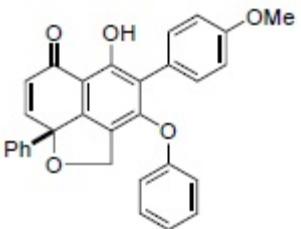
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—128.86
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—113.61
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—84.32

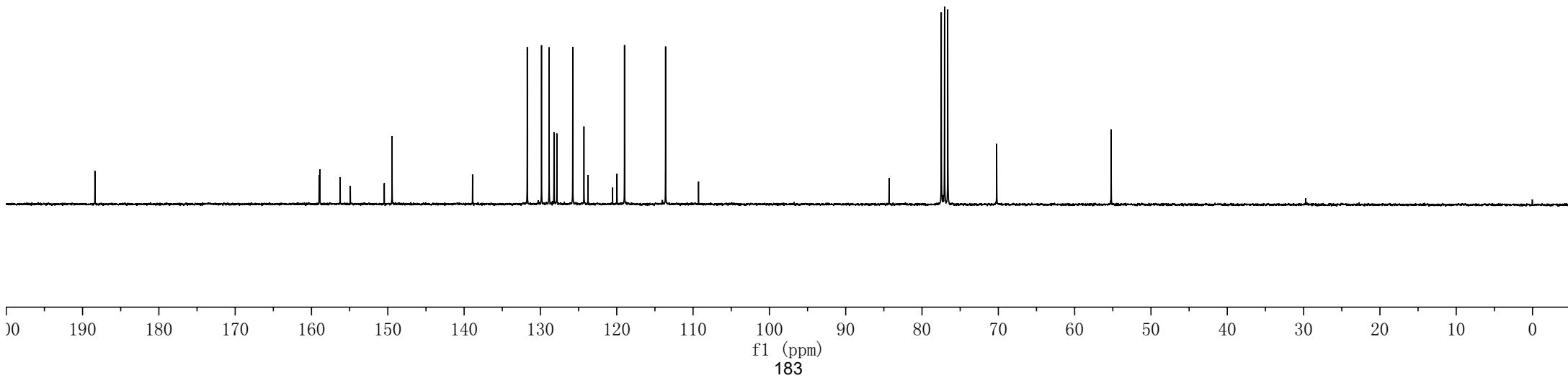
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—77.05
—76.63

—70.21

—55.21



5l



-10.38

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6.25

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4.23
4.20

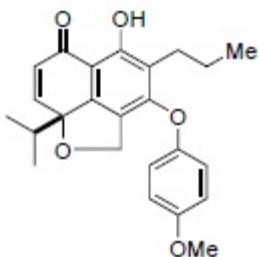
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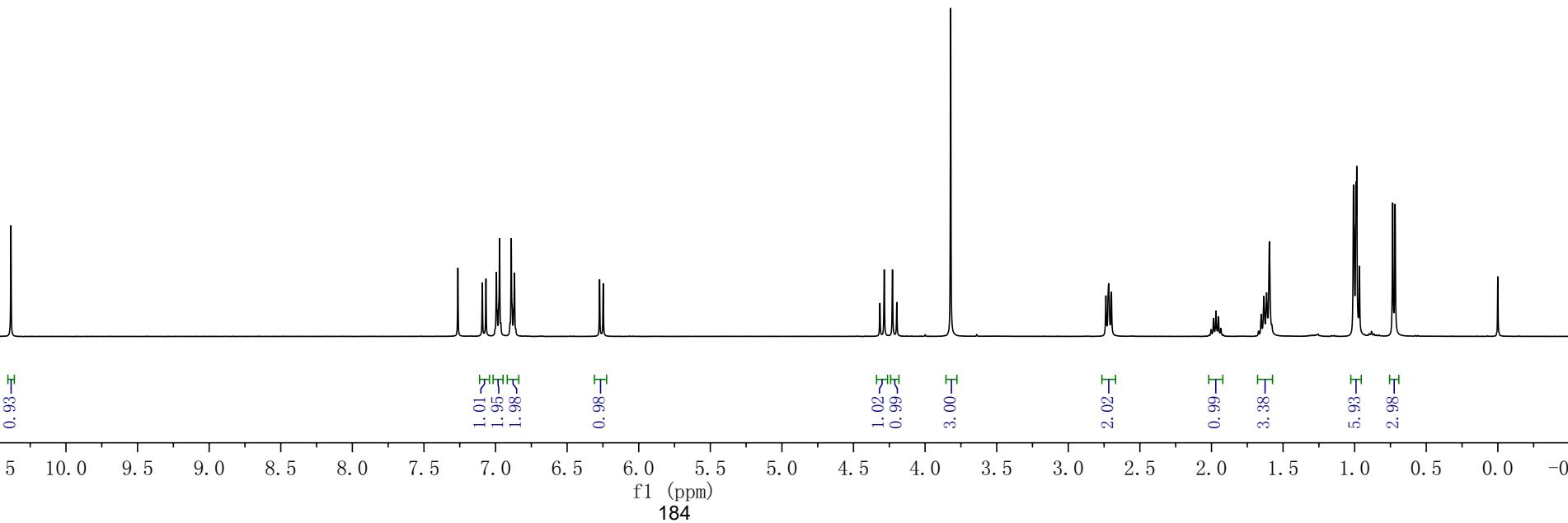
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-0.00



5m



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~156.34

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—130.89

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~119.54
~117.93
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—108.96

—87.10

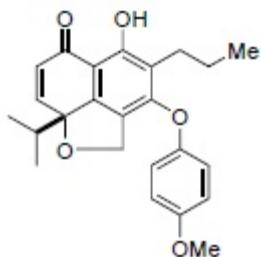
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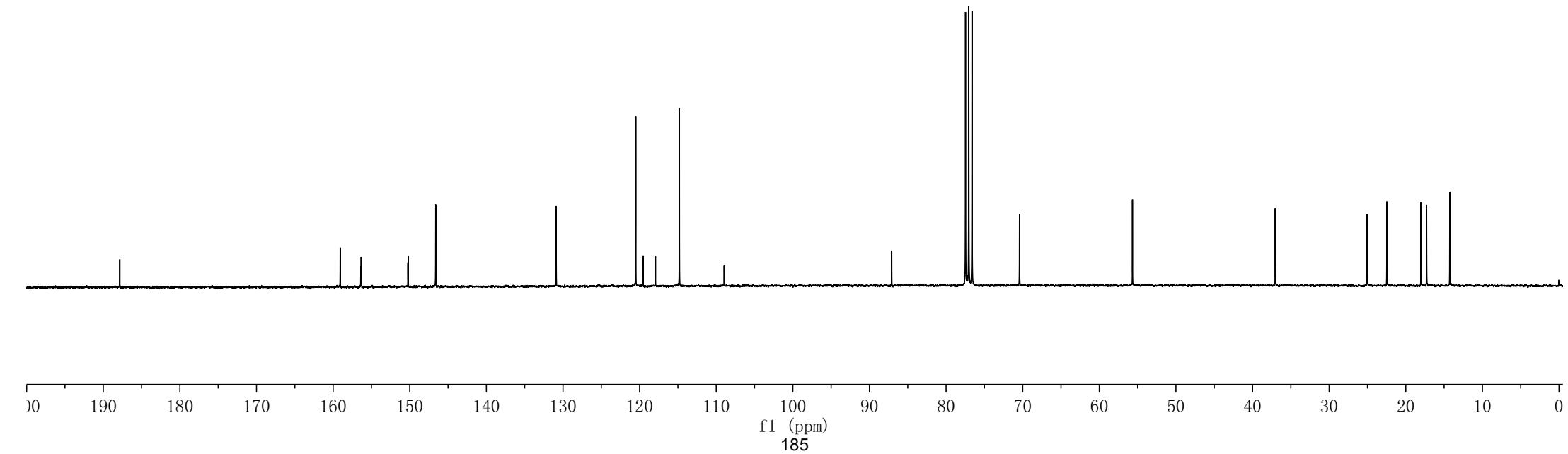
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5m



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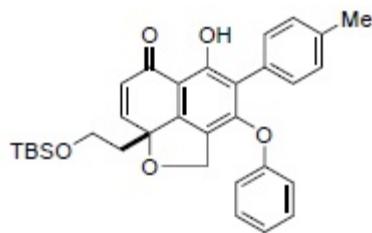
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7.01
6.99
6.20
6.18

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4.33
4.31
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3.78
3.78
3.76
3.74
3.73
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3.68

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2.05
2.04
2.03
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5n

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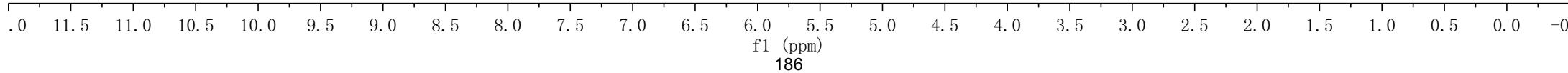
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9.00

6.00



—187.68

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—137.38
—130.37
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—108.71

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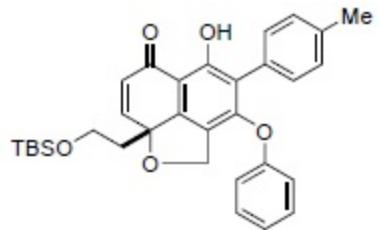
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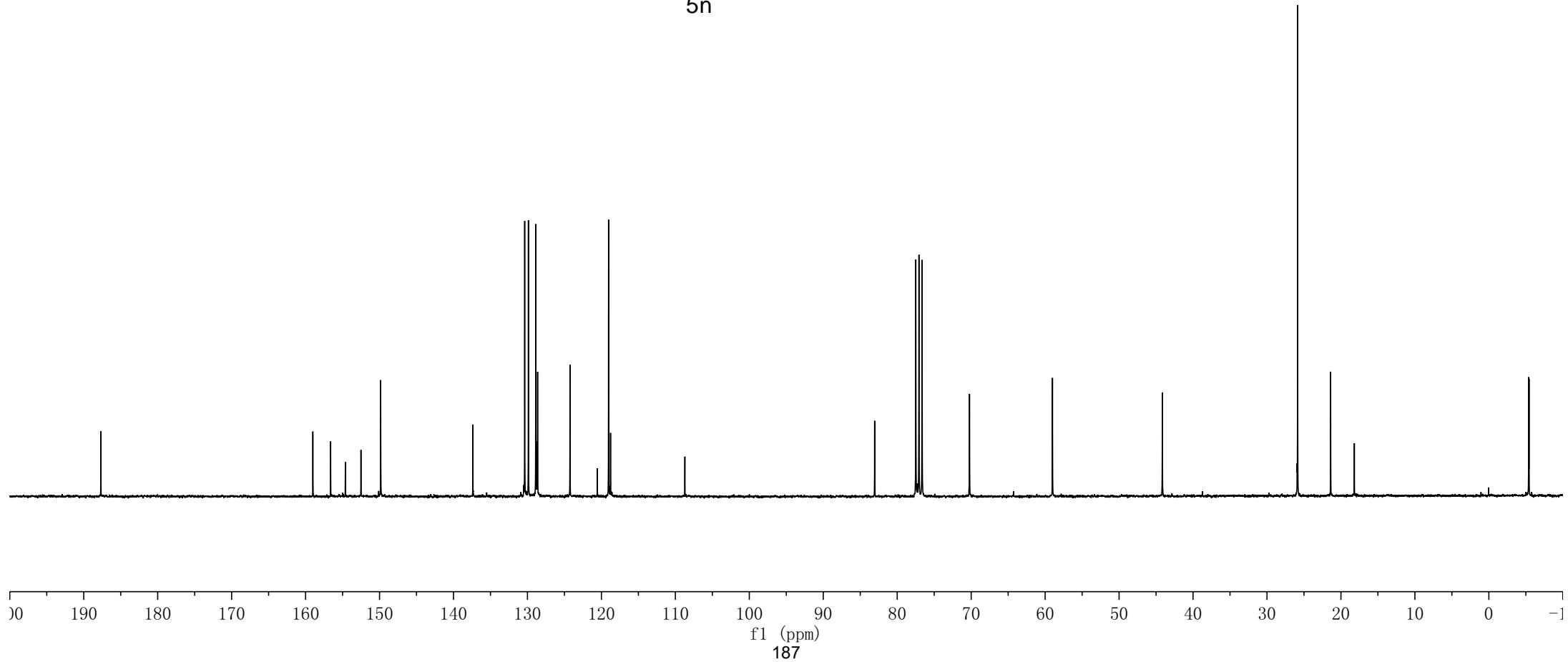
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—5.44



5n



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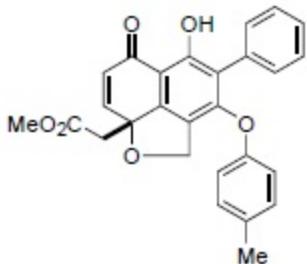
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—0.00



5o

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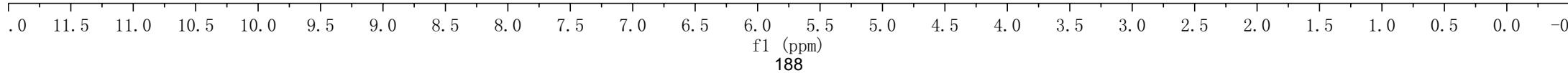
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0.98

2.08

2.96

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1.04
3.00



—187.18

—169.19

~159.09
~155.32
~154.09
~150.61
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—108.28

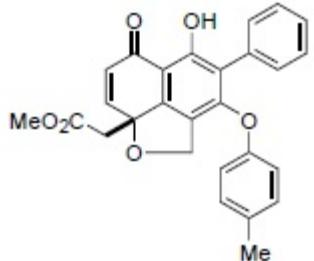
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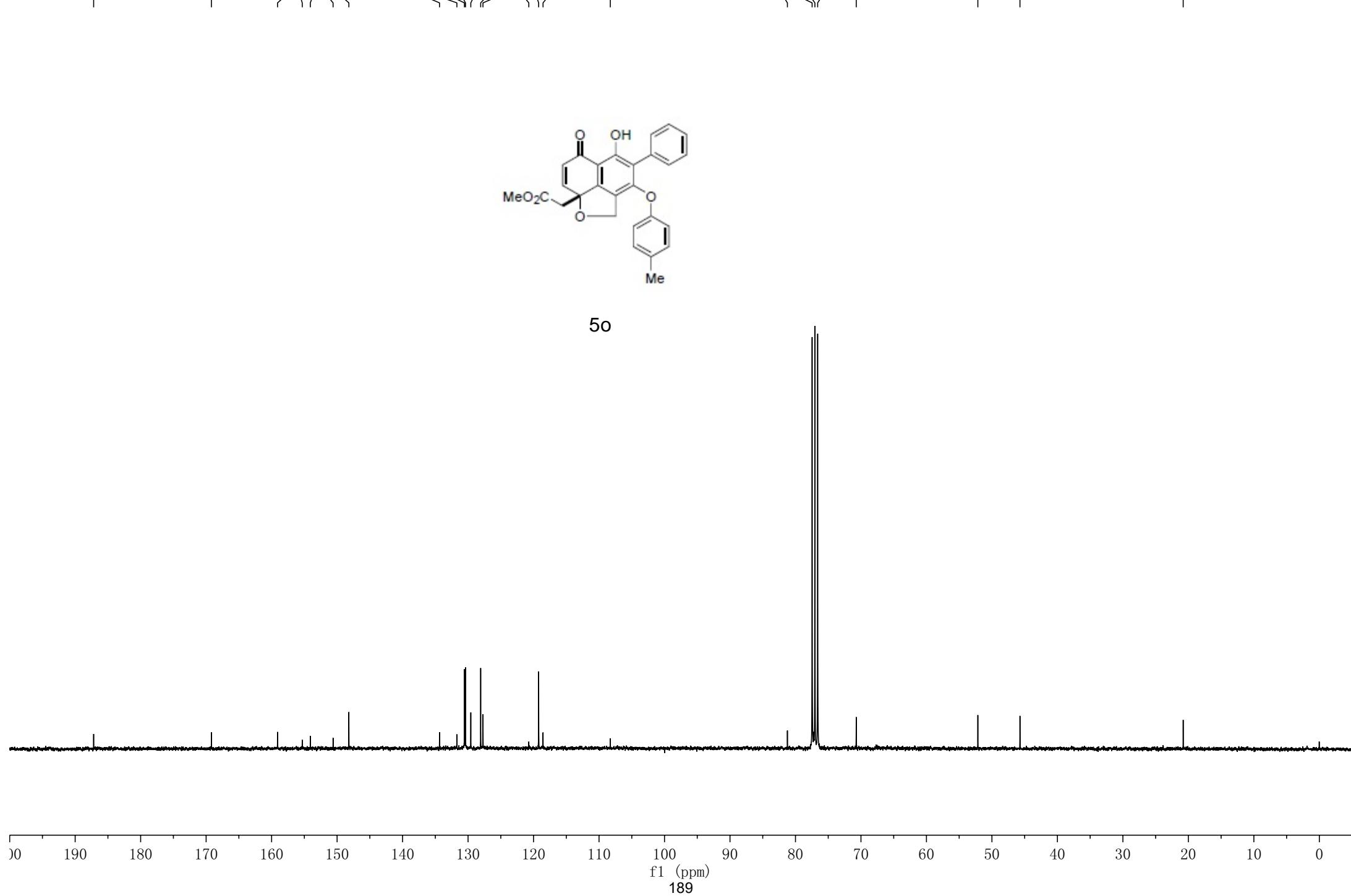
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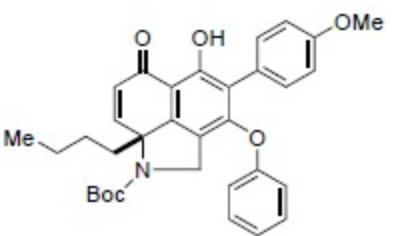


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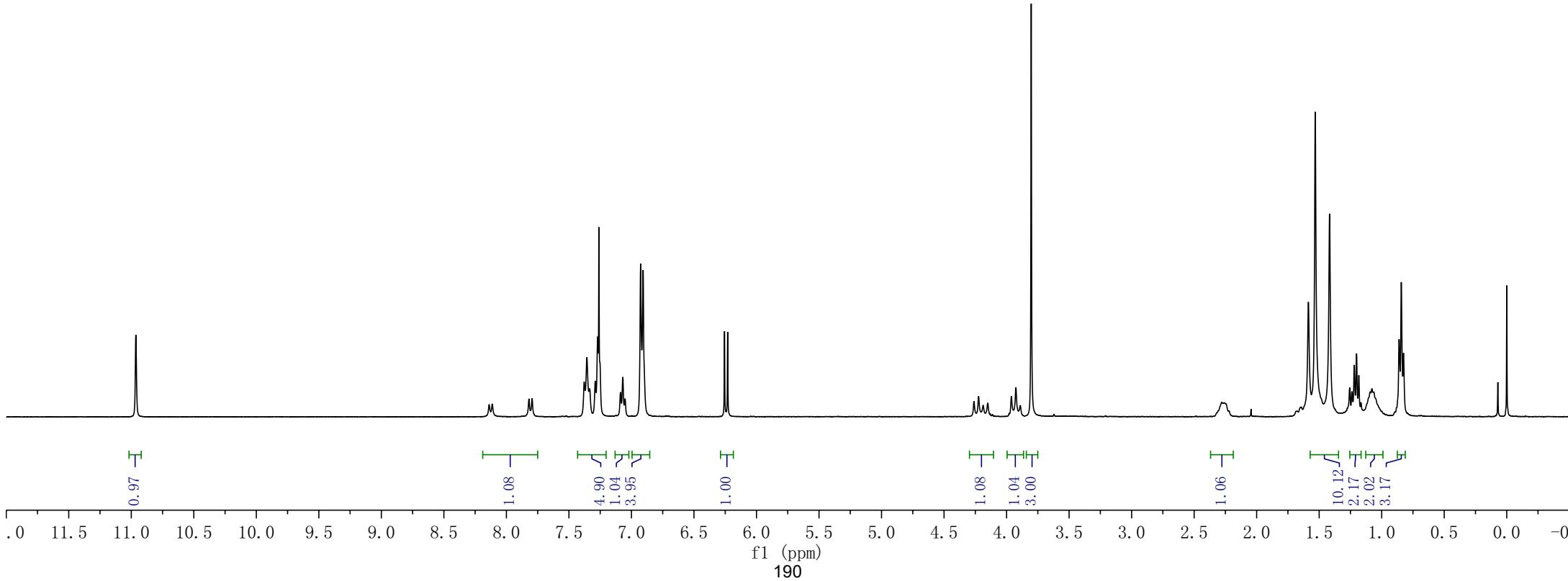
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1.08
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0.00



5p



188.17
187.86

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149.46
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131.57
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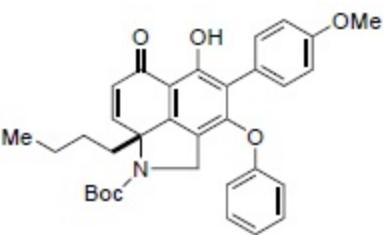
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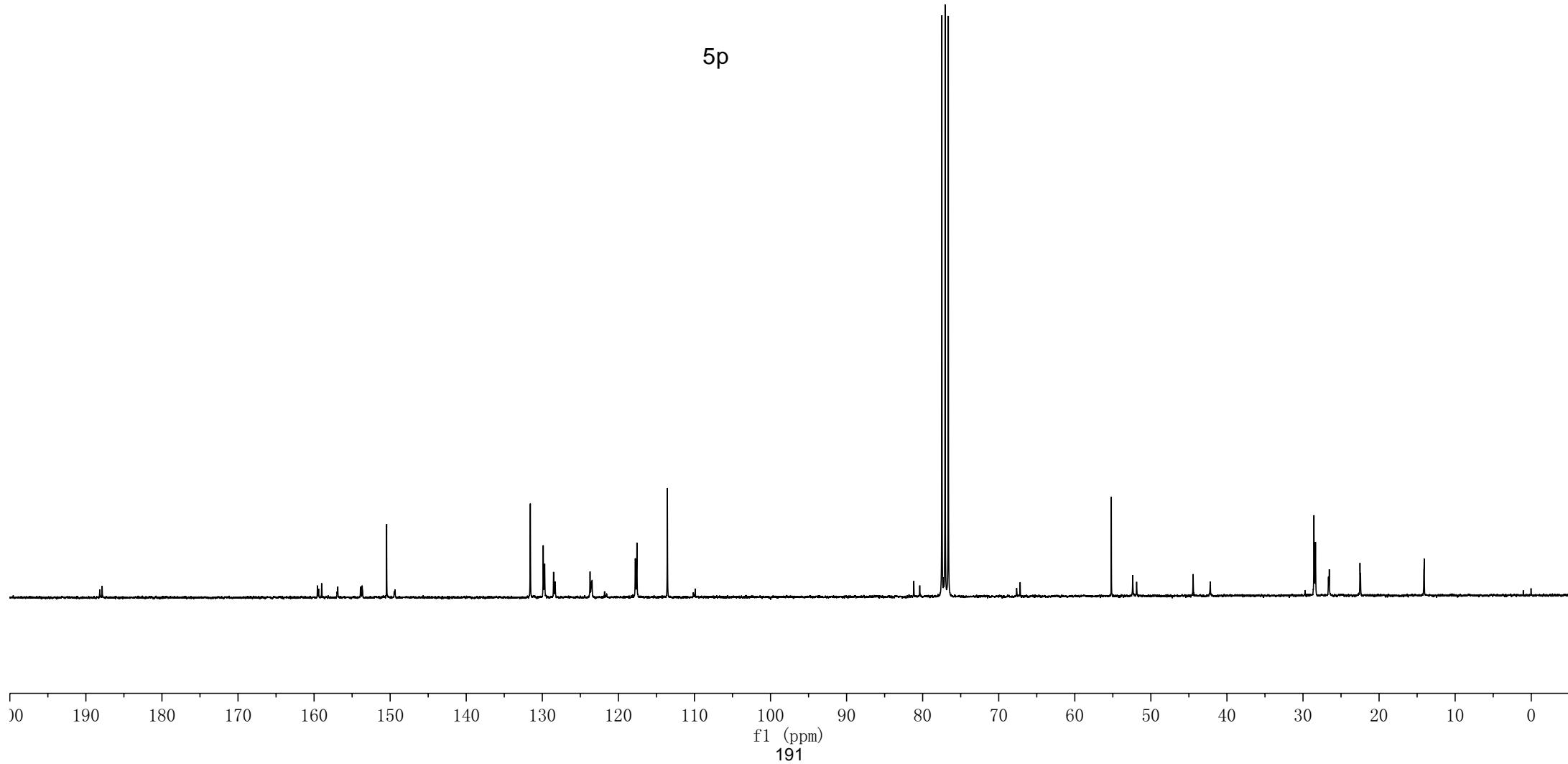
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5p

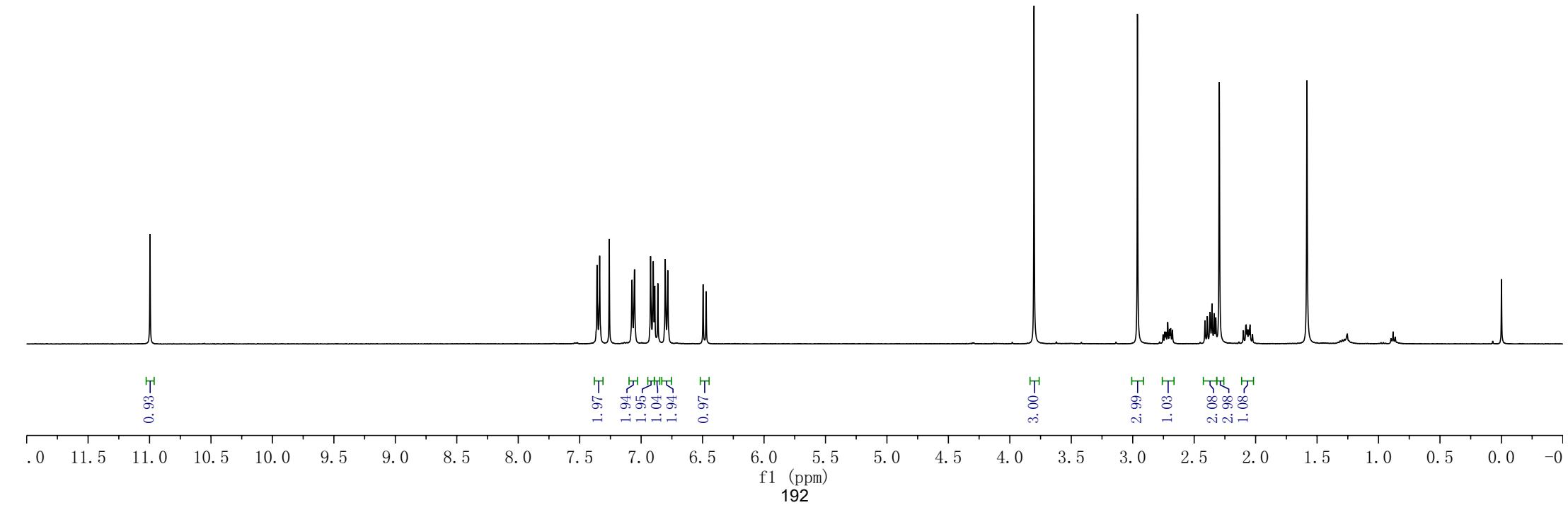


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5q

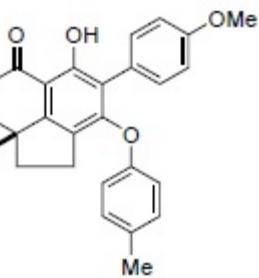


—188.49

—158.89
—158.32
—155.98
—155.17

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—144.06

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5q

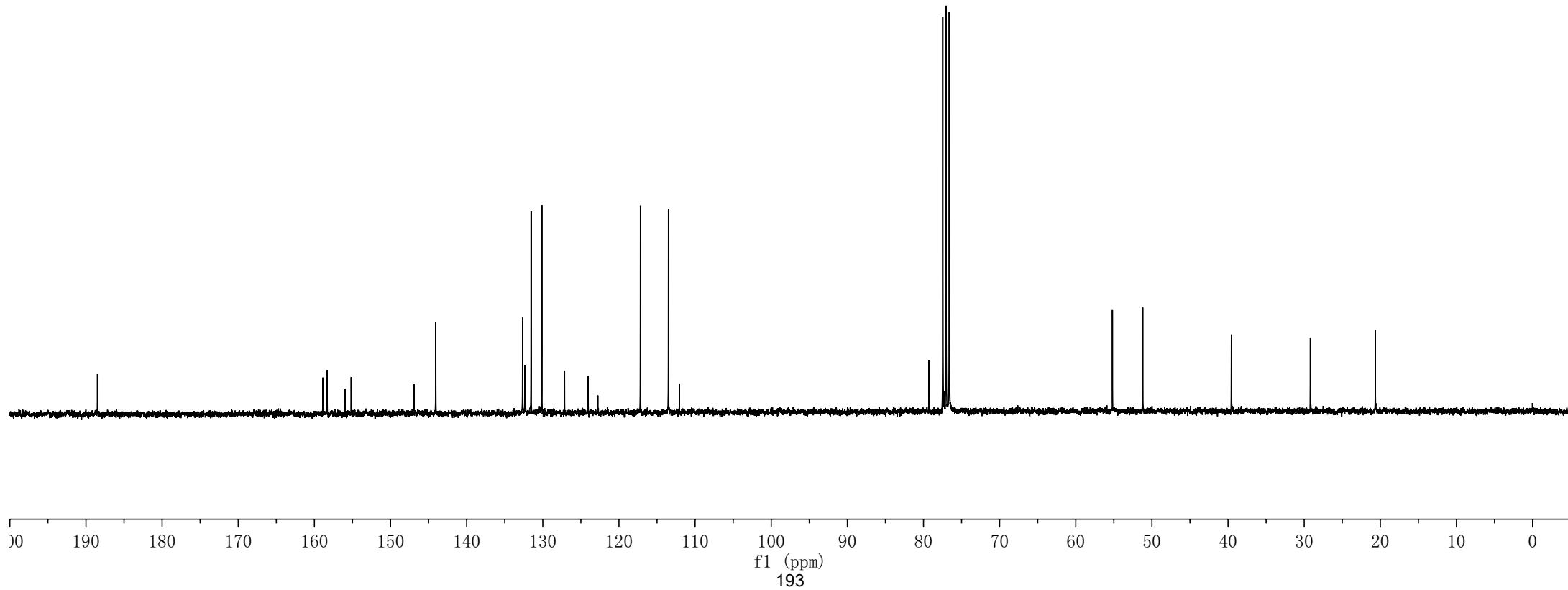
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—1.62

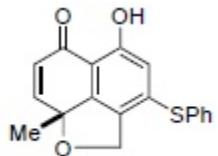
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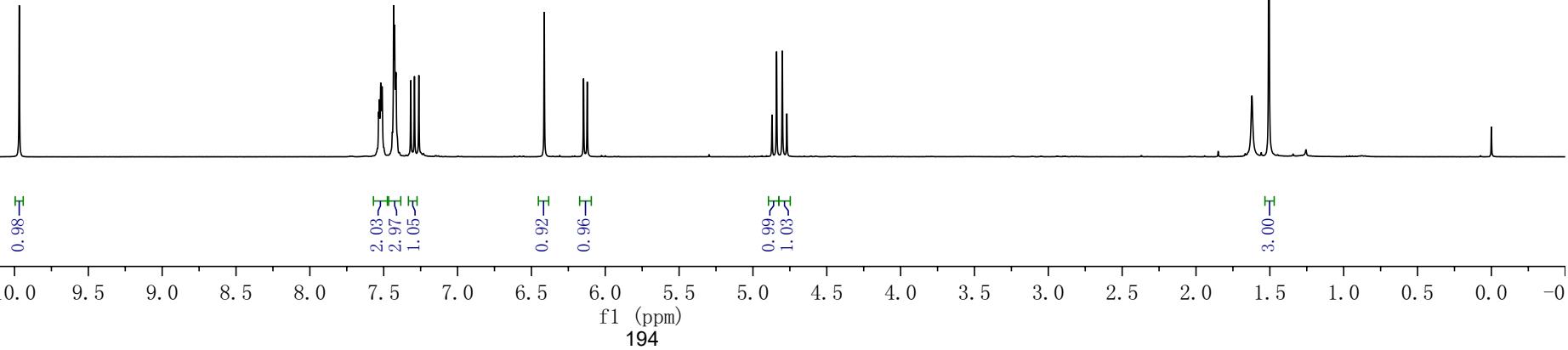
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4.84
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6.15
6.12

—6.41



5r



—187.64

—159.63

—151.91

—150.52

—142.94

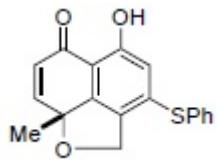
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—113.35
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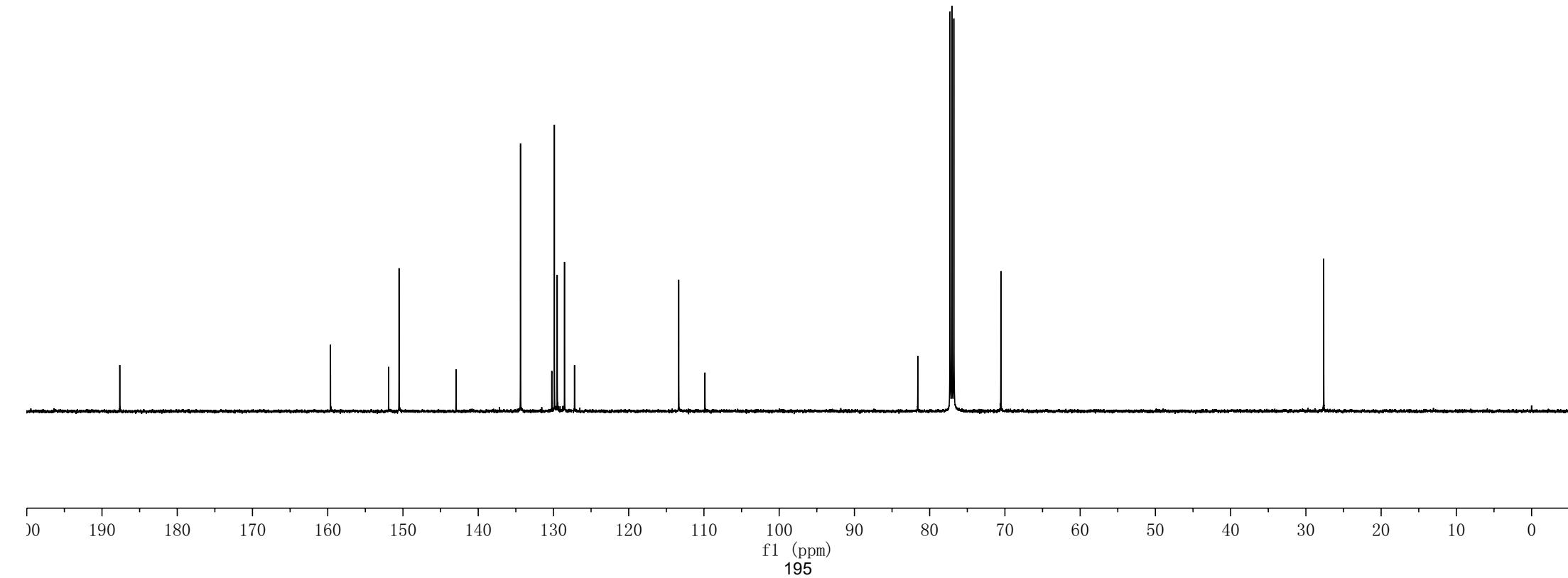
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—76.79

—70.54

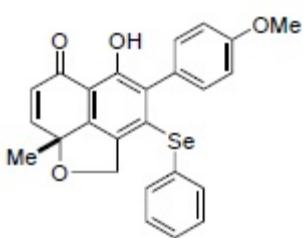
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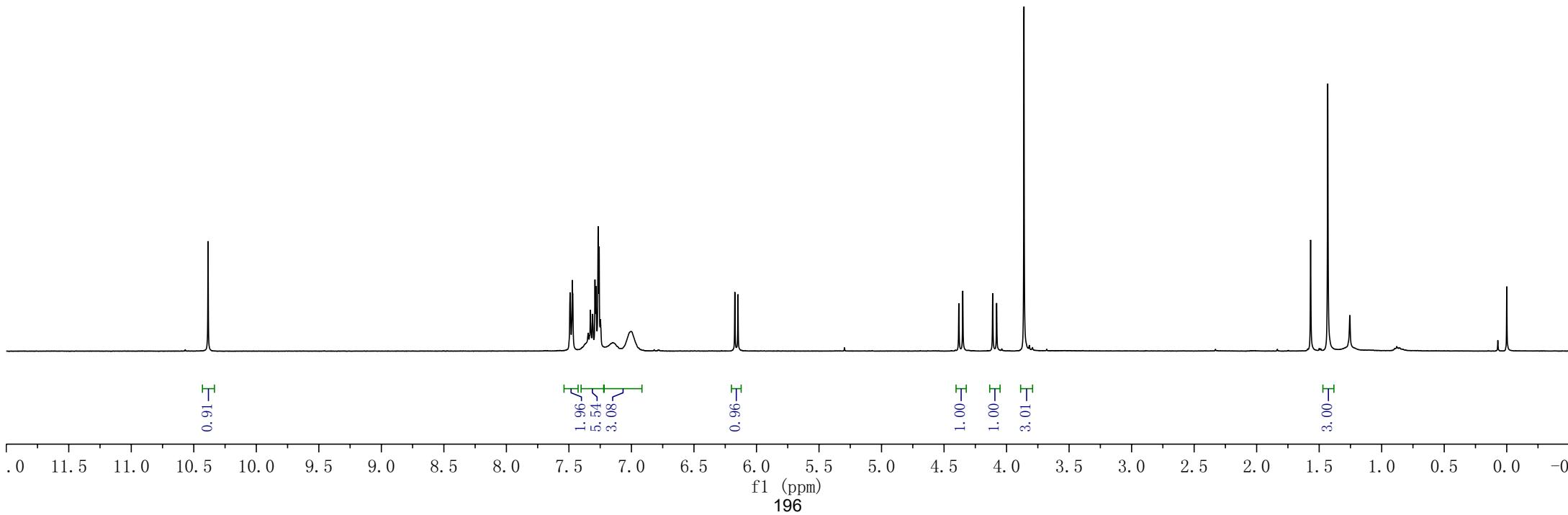
5r



—10.39
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7.27
7.26
7.25
7.18
7.16
7.15
7.11
7.02
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—4.35
—4.11
—4.08
—3.86
—1.57
—1.43
—0.00



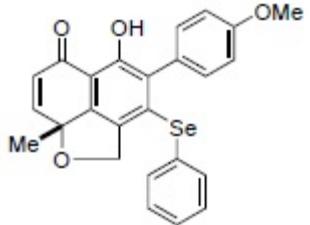
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—188.33

—159.46
—156.30
~150.79
~150.21

—139.44
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/128.62
/128.49
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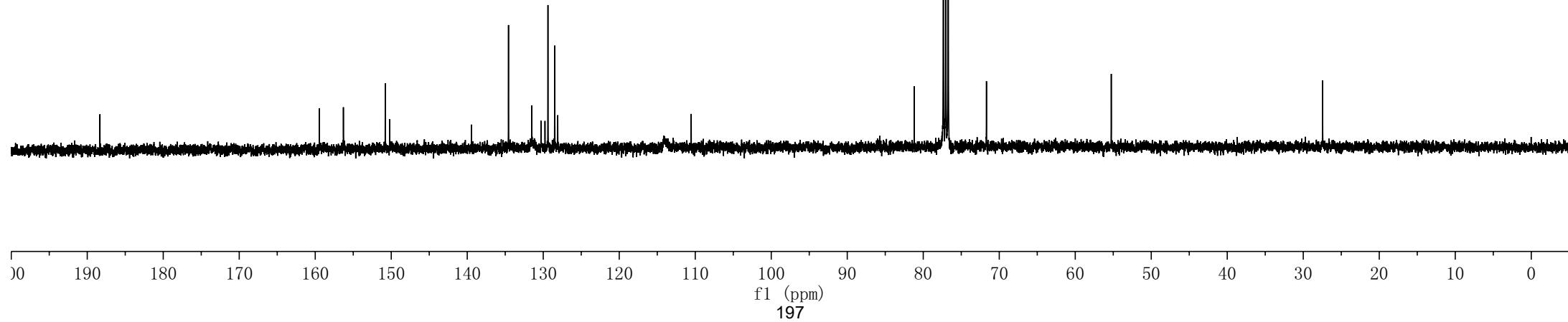


5s

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—55.26

—27.45



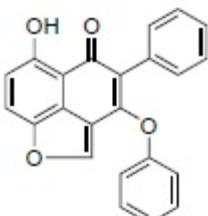
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6.69

—1.58

—1.25

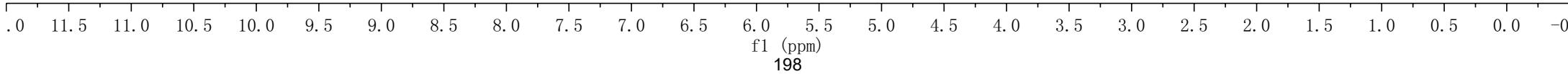
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6a

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1.00
0.99



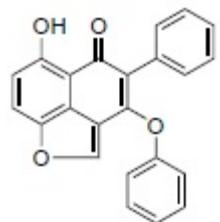
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— 158.54
— 156.68
— 155.86

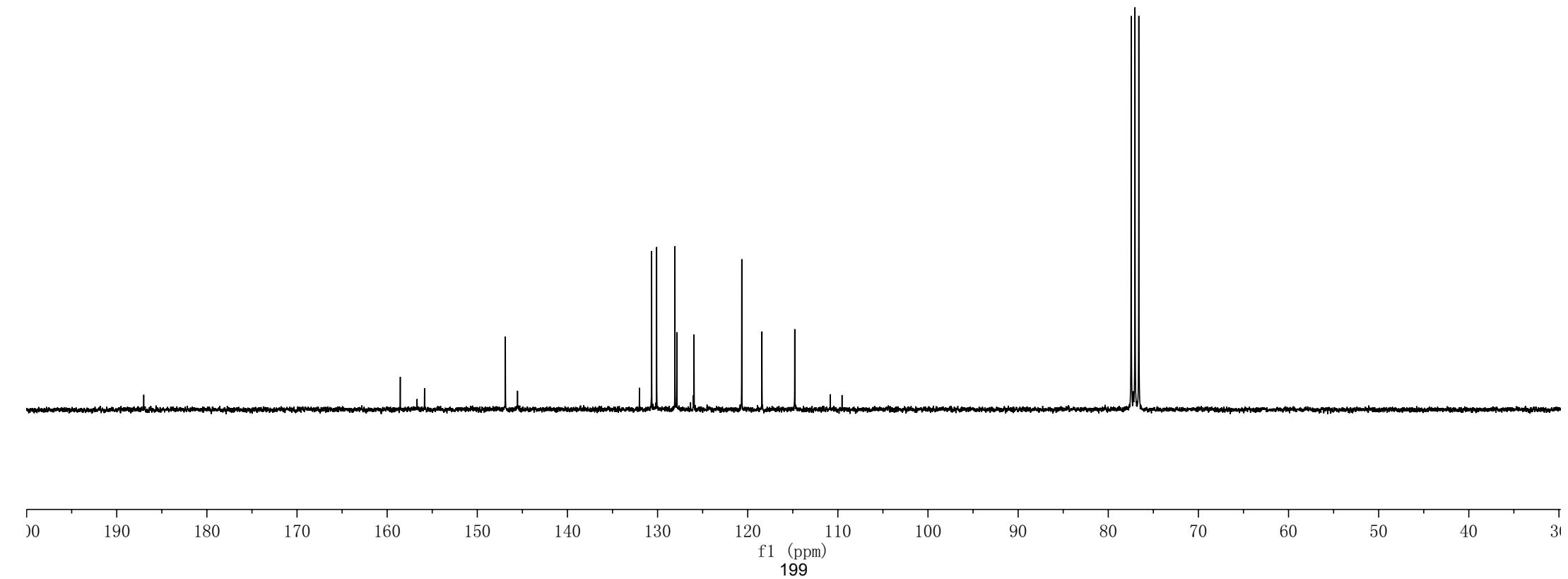
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— 145.54

132.02
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126.34
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— 118.42
— 114.78
— 110.83
— 109.54

— 77.46
— 77.03
— 76.61



6a



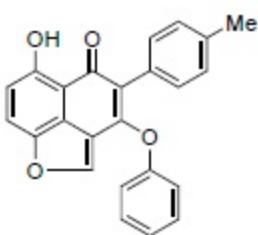
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7.20
7.01
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6.68

—2.40

—1.56

—0.00



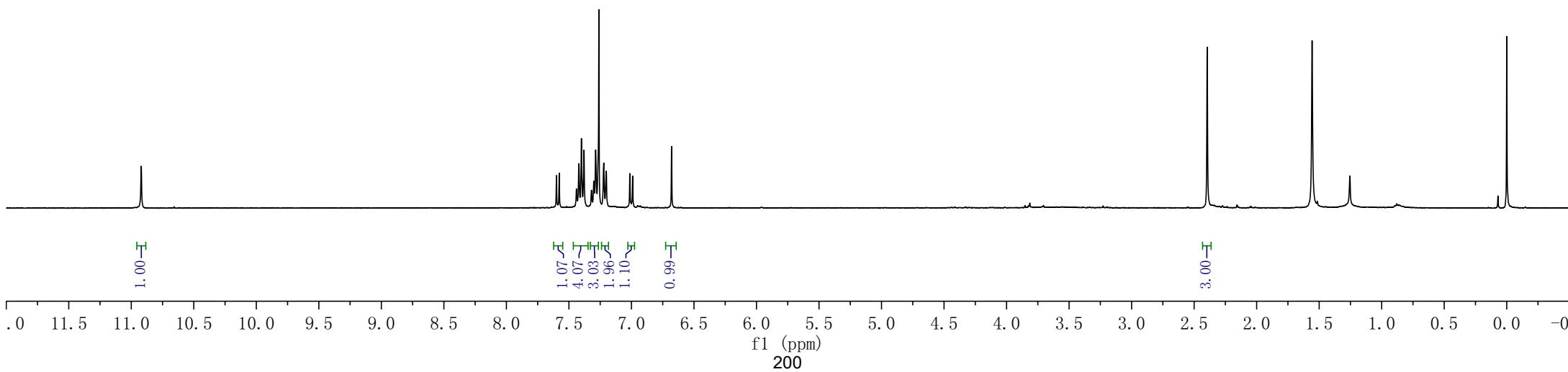
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3.00



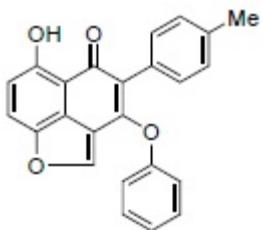
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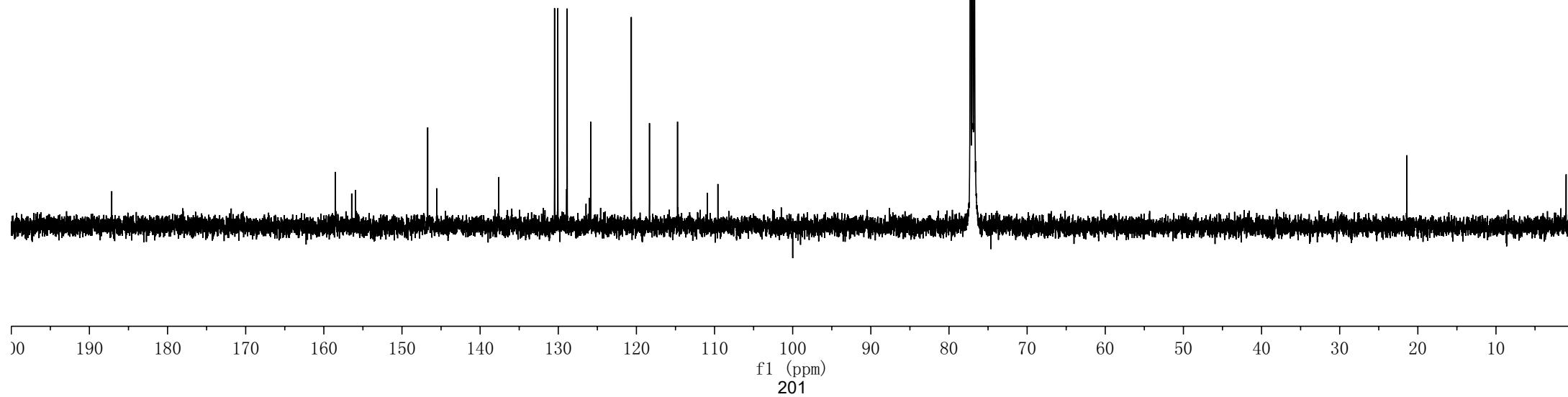
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~126.45
~126.03
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~110.92
~109.57



6b

77.27
77.09
76.76

—21.40



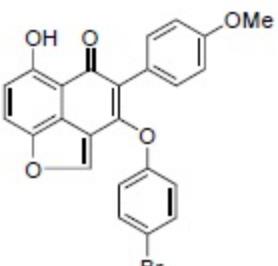
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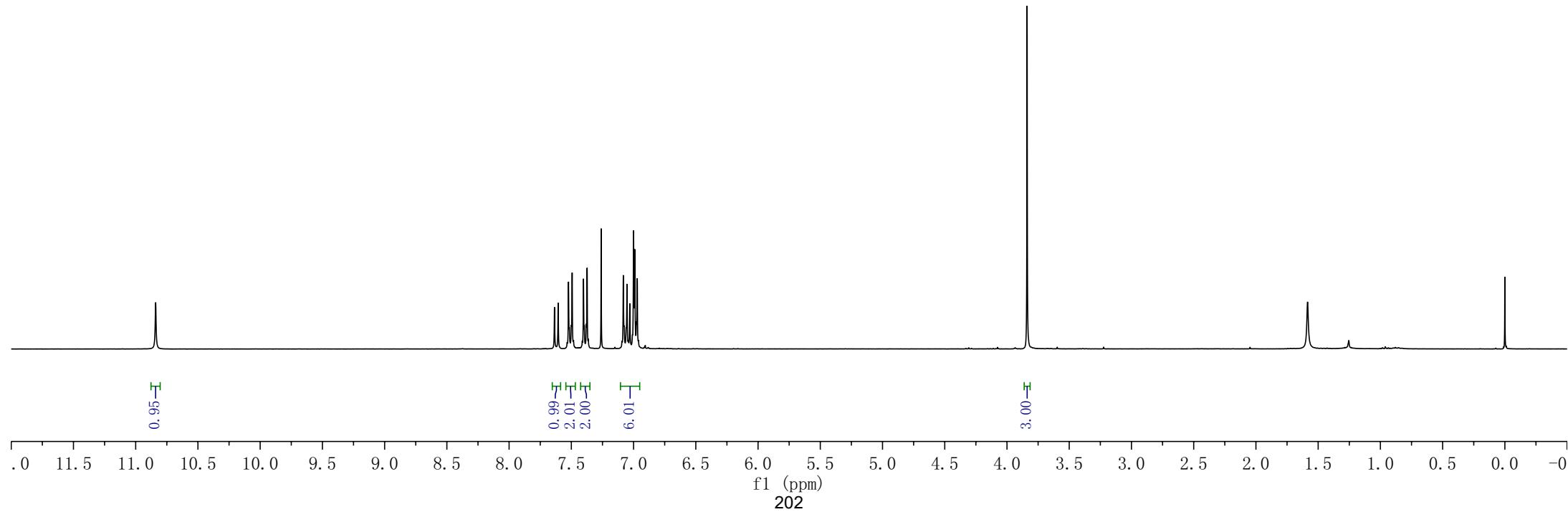
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—0.00



6c



— 187.21

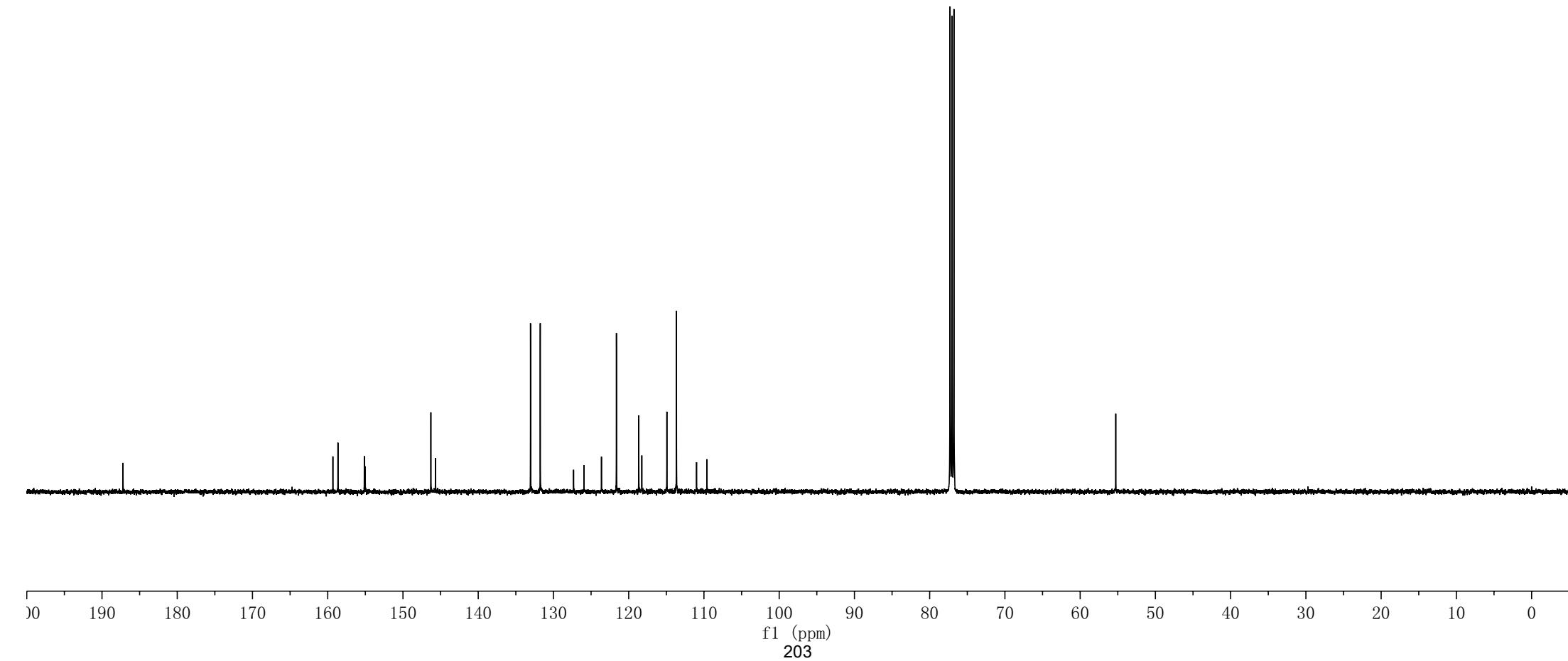
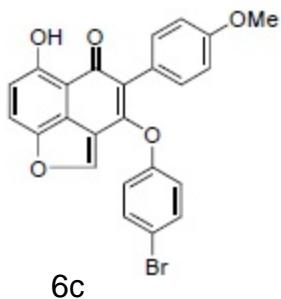
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~ 158.64
~ 155.14
~ 155.02

~ 146.29
~ 145.68

~ 133.05
~ 131.76
~ 127.33
~ 125.94
~ 123.62
~ 121.63
~ 118.66
~ 118.25
~ 114.93
~ 113.65
~ 110.98
~ 109.61

77.29
77.03
76.78

— 55.27



—10.88

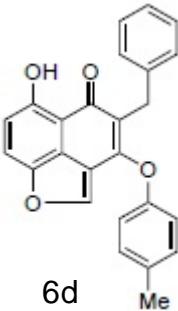
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7.07
7.04
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6.93
—6.56

—4.15

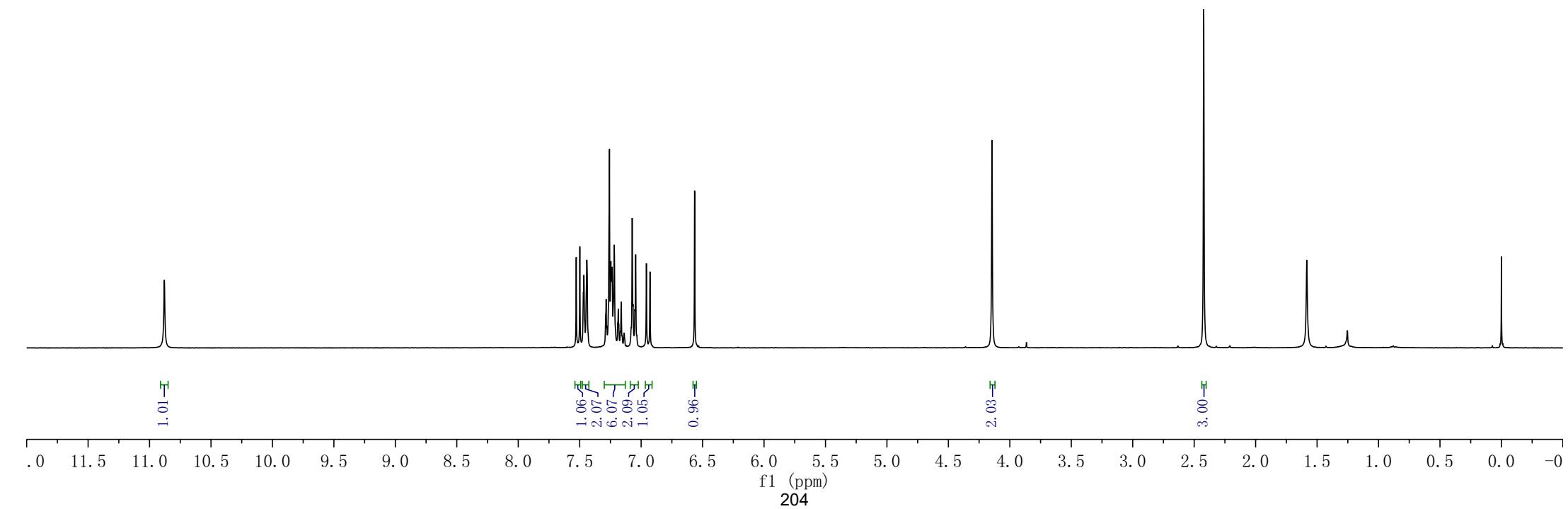
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—1.58

—0.00



6d



— 187.25

— 158.17

— 157.70

— 153.45

— 146.29

— 145.39

— 140.64

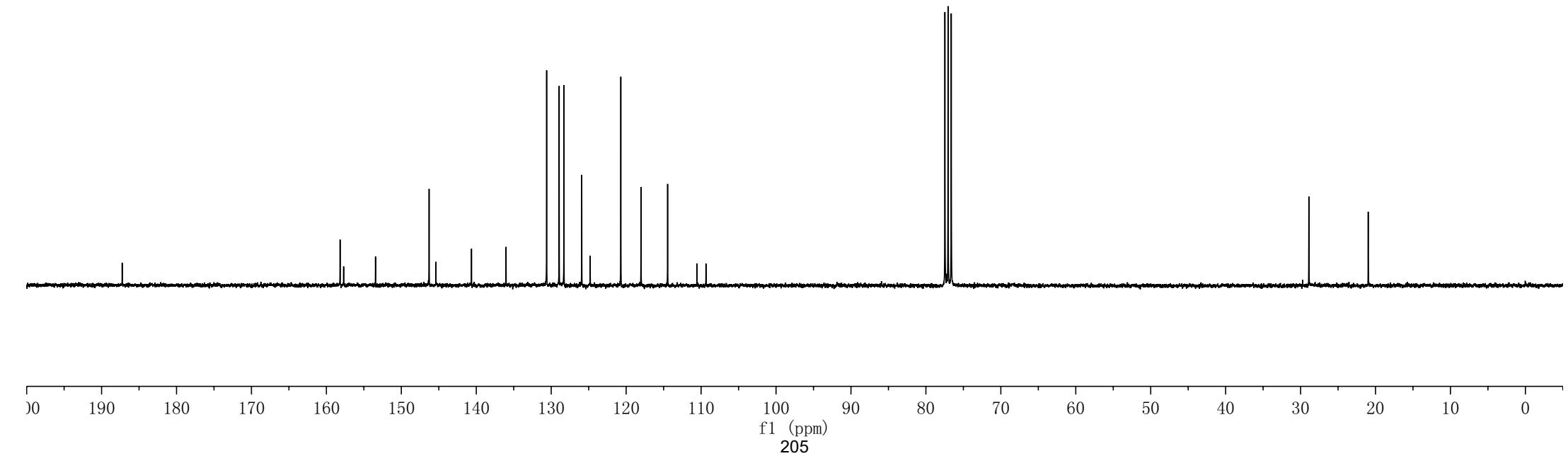
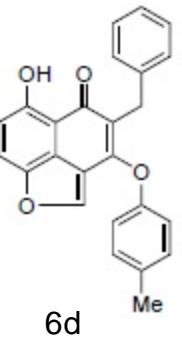
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— 130.61
— 128.94
— 128.30
— 125.92
— 124.80
— 120.71
— 118.02
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— 110.55
— 109.35

— 77.46
— 77.04
— 76.62

— 28.90

— 20.98



—10.48

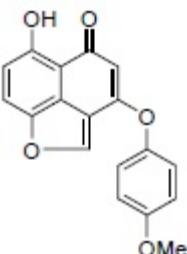
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—7.61
—7.59
—7.27
—7.14
—7.11
—6.98
—6.97
—6.95
—6.94

—5.81

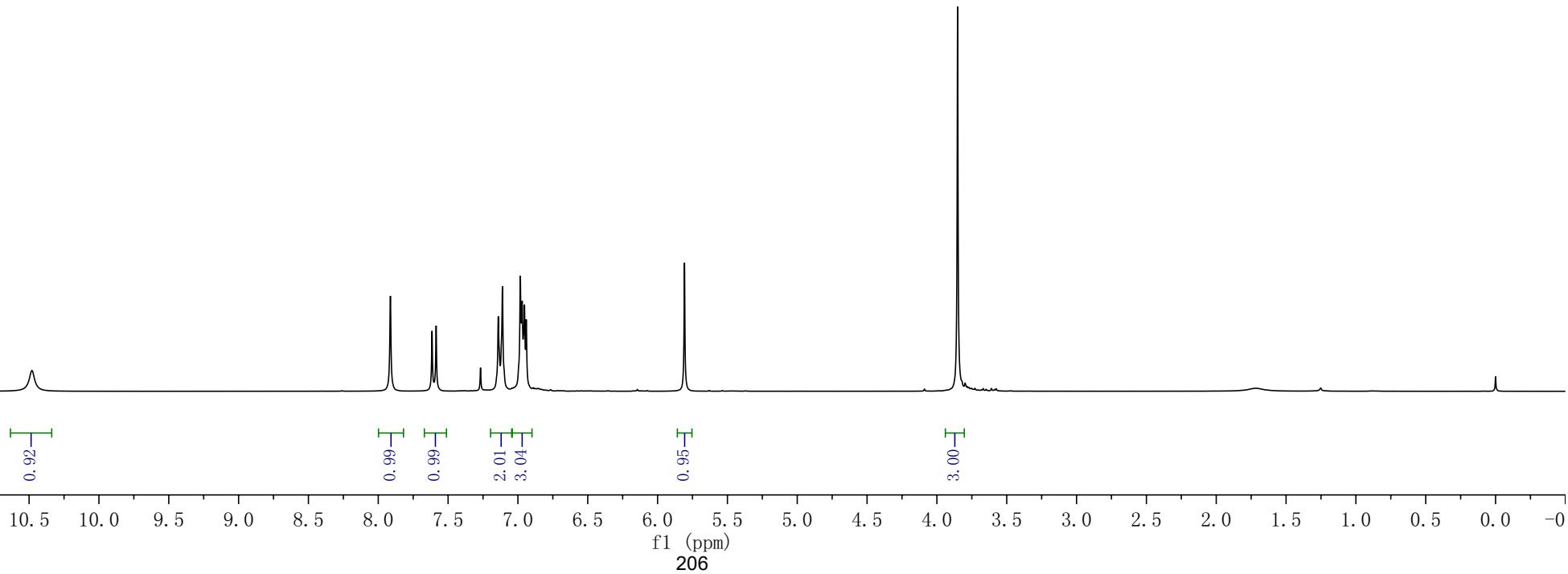
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—1.71

—0.00



6e



—188.83

—163.51
—157.81

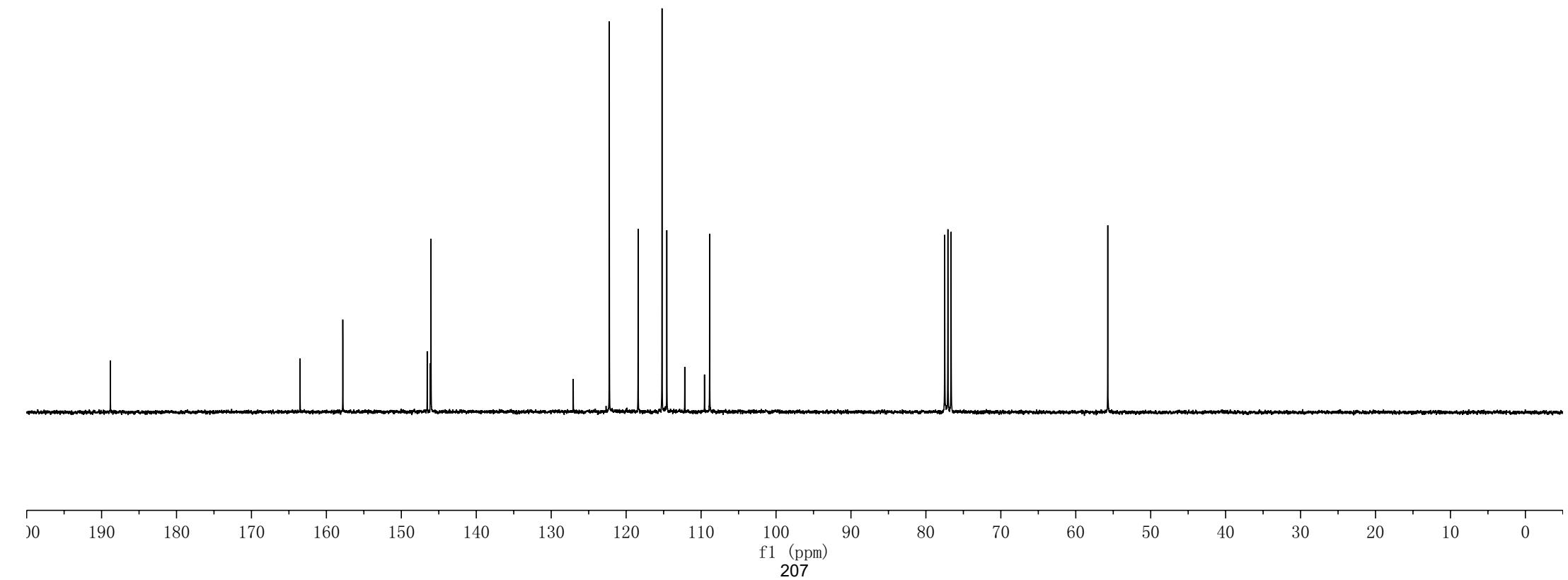
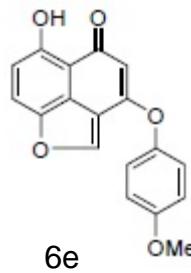
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146.14
146.04

—127.05

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112.18
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108.86

77.49
77.06
76.64

—55.73



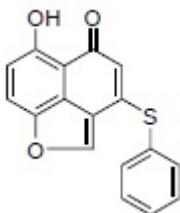
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6.94

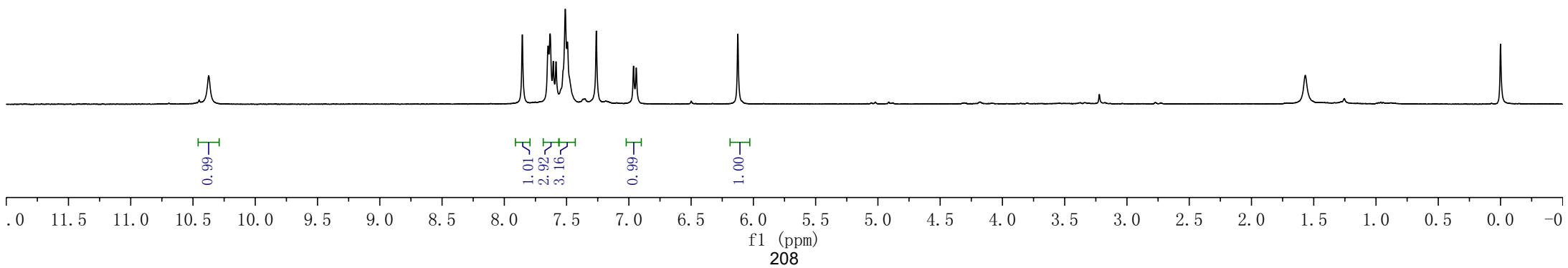
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—1.57

—0.00



6f



—185.34

—162.74

—158.27

~149.17

~146.22

~145.91

—135.56

~130.52

~130.19

~127.77

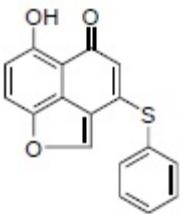
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—118.64

~115.43

~114.48

—110.21

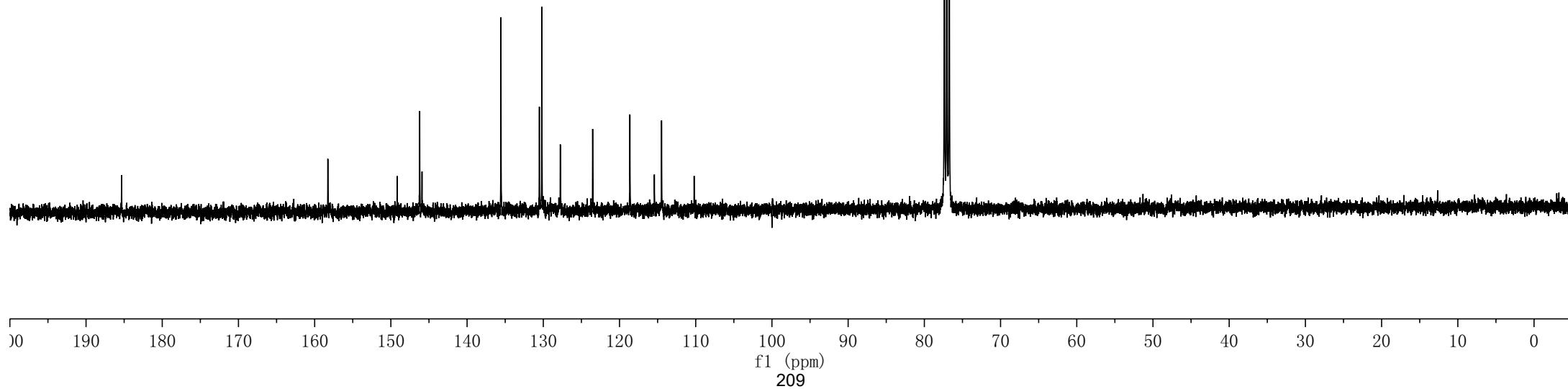


6f

77.38

77.06

76.74



—11.58

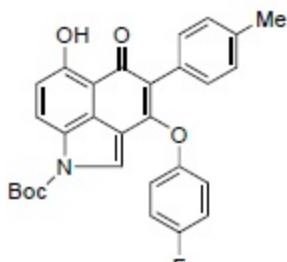
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—1.64

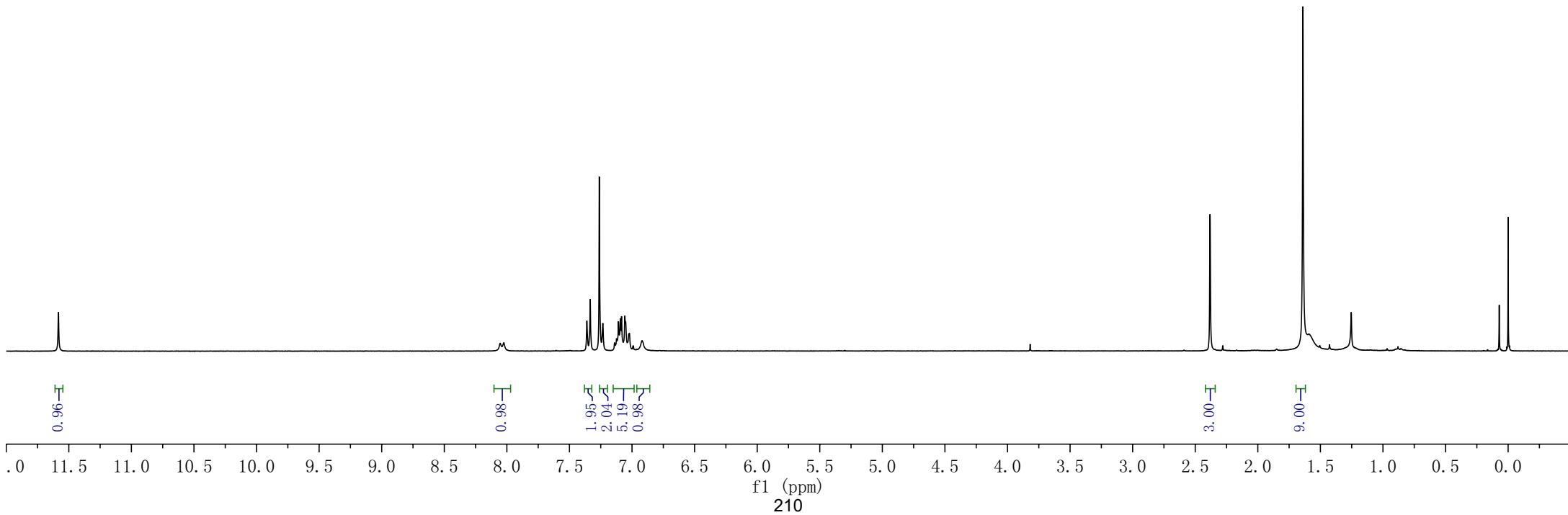
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—0.00

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7.23
7.14
7.12
7.11
7.09
7.08
7.06
7.05
7.03
7.02
6.99
6.92



6g



—187.59

—161.30
—159.47
—158.06
—156.96
—152.44
—148.82

—137.54

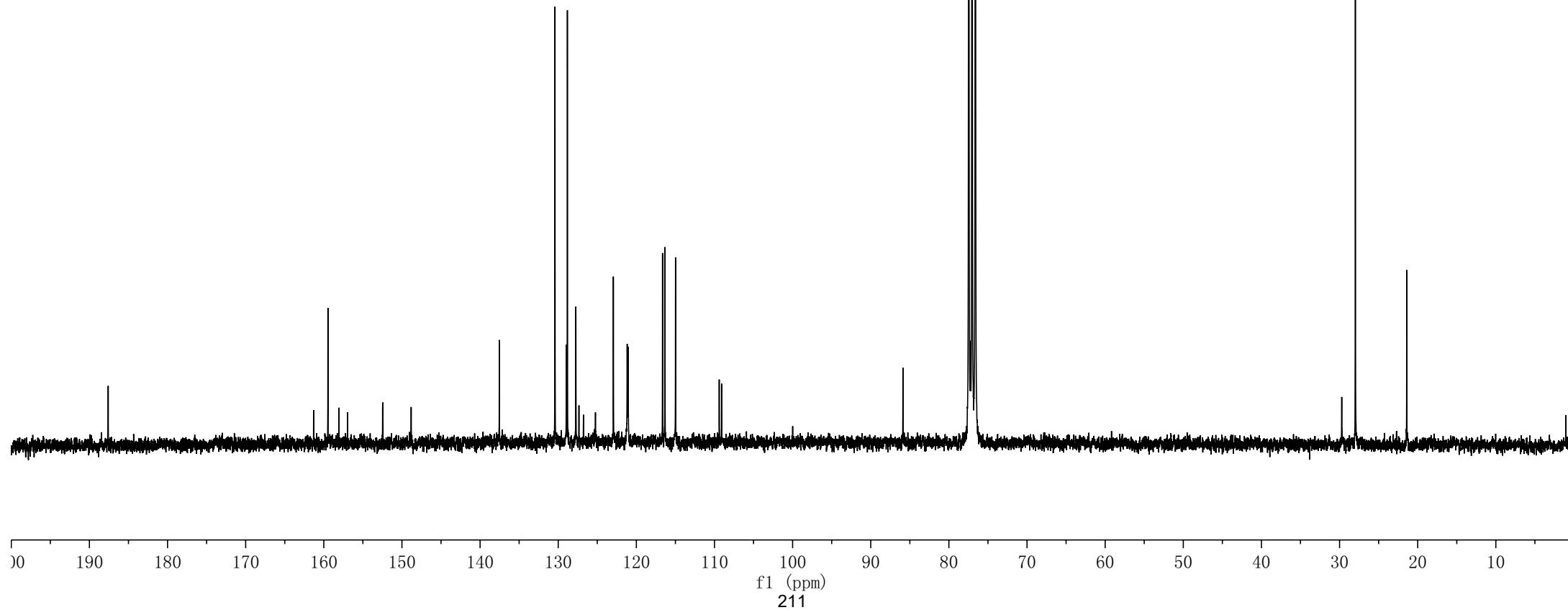
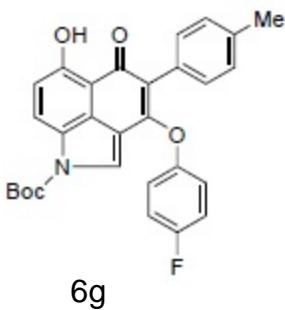
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—128.97
—128.83
—127.74
—127.35
—122.94
—121.17
—120.06
—116.34
—114.99
—109.39
—109.09

—85.88

—77.46
—77.68
—76.61
—76.61

—27.98

—21.40



—11.16

~8.06
~8.03

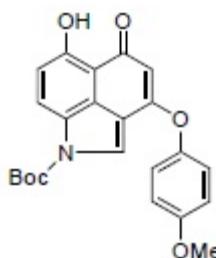
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7.04
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6.96

5.75

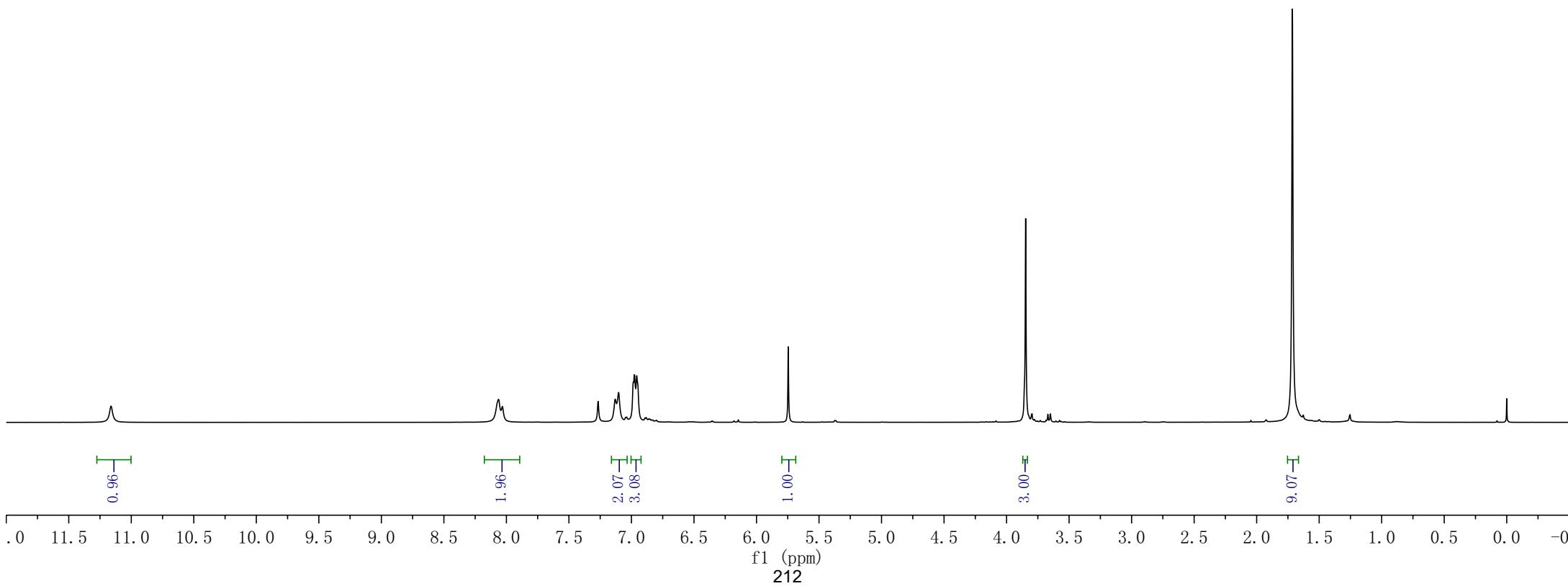
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—0.00



6h



—189.31

—164.81

~158.63

~157.65

—149.10

—146.47

~128.17
~126.70
~125.86
~122.82
~122.29

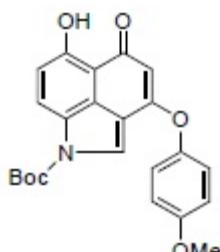
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—85.72

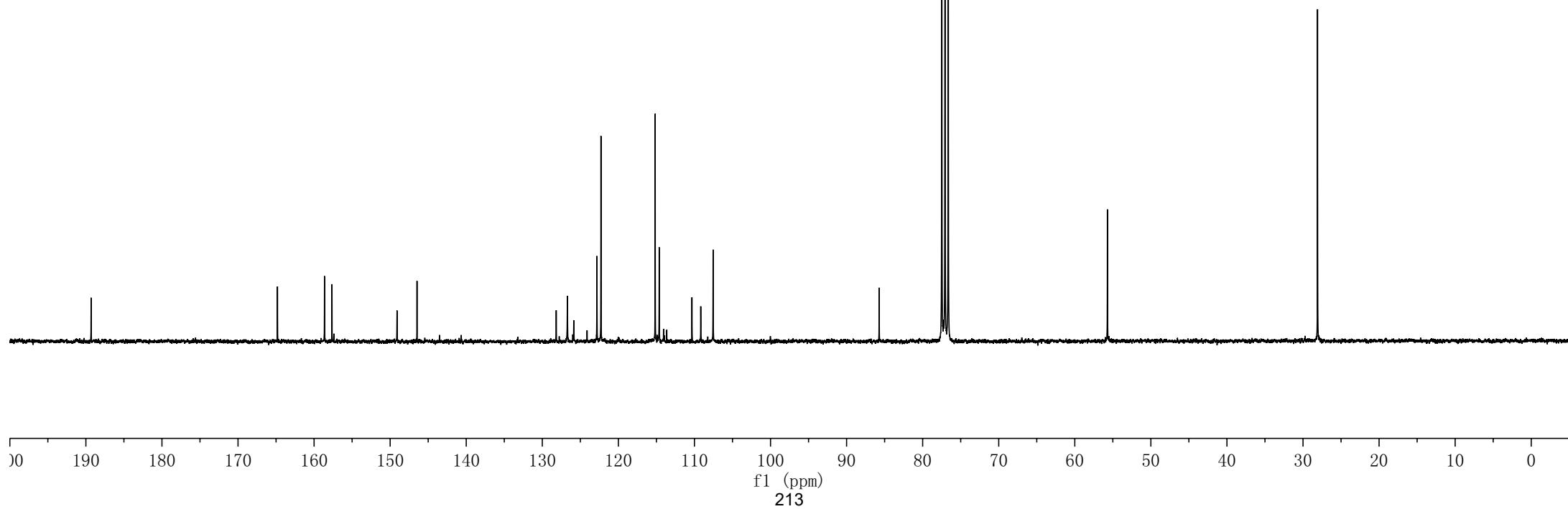
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77.06
76.64

—55.71

—28.09



6h



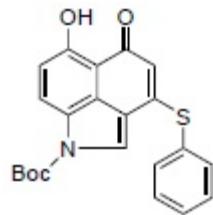
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8.01
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6.95

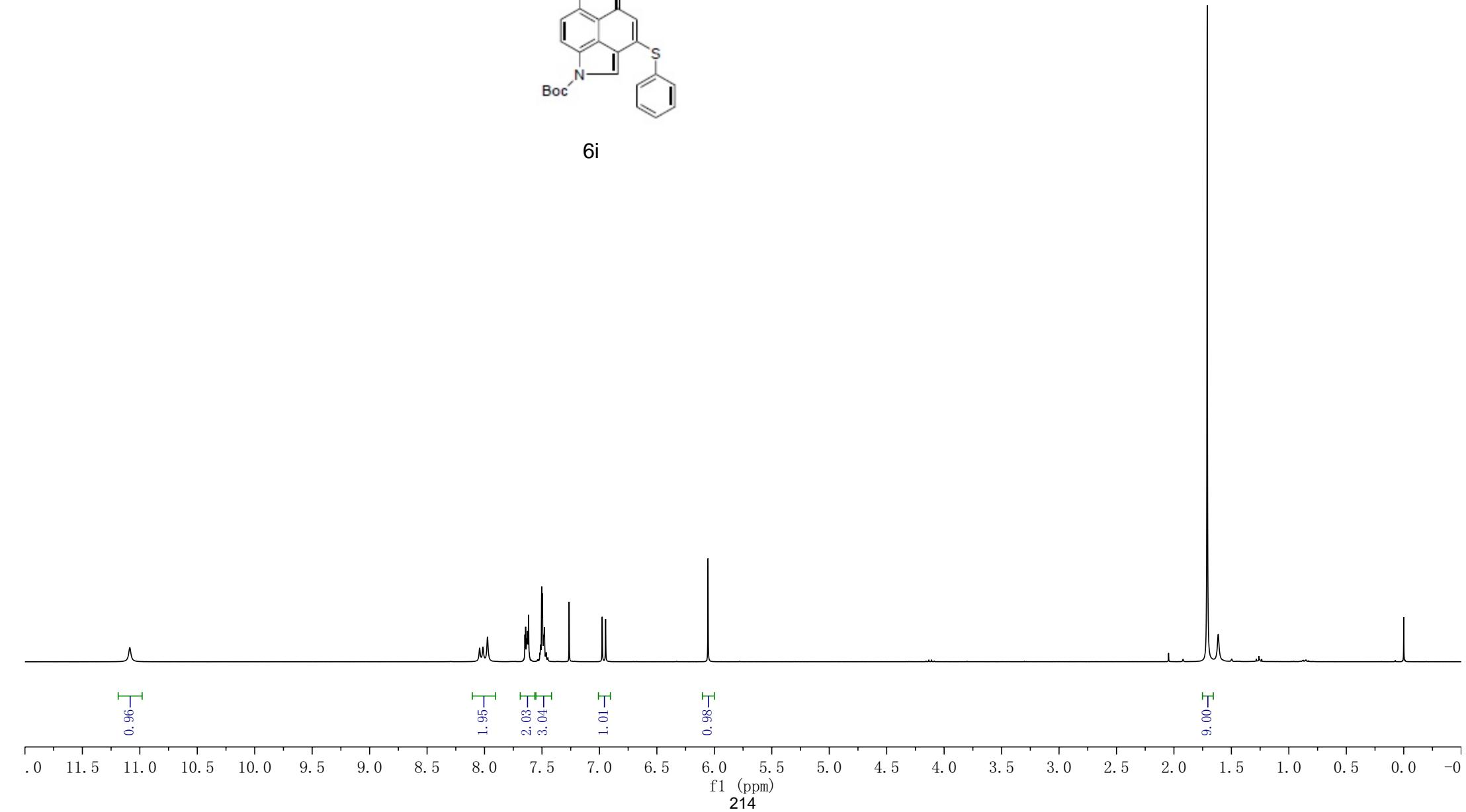
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—1.71
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6i



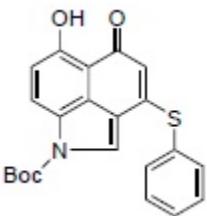
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— 159.15

— 150.39

— 149.06

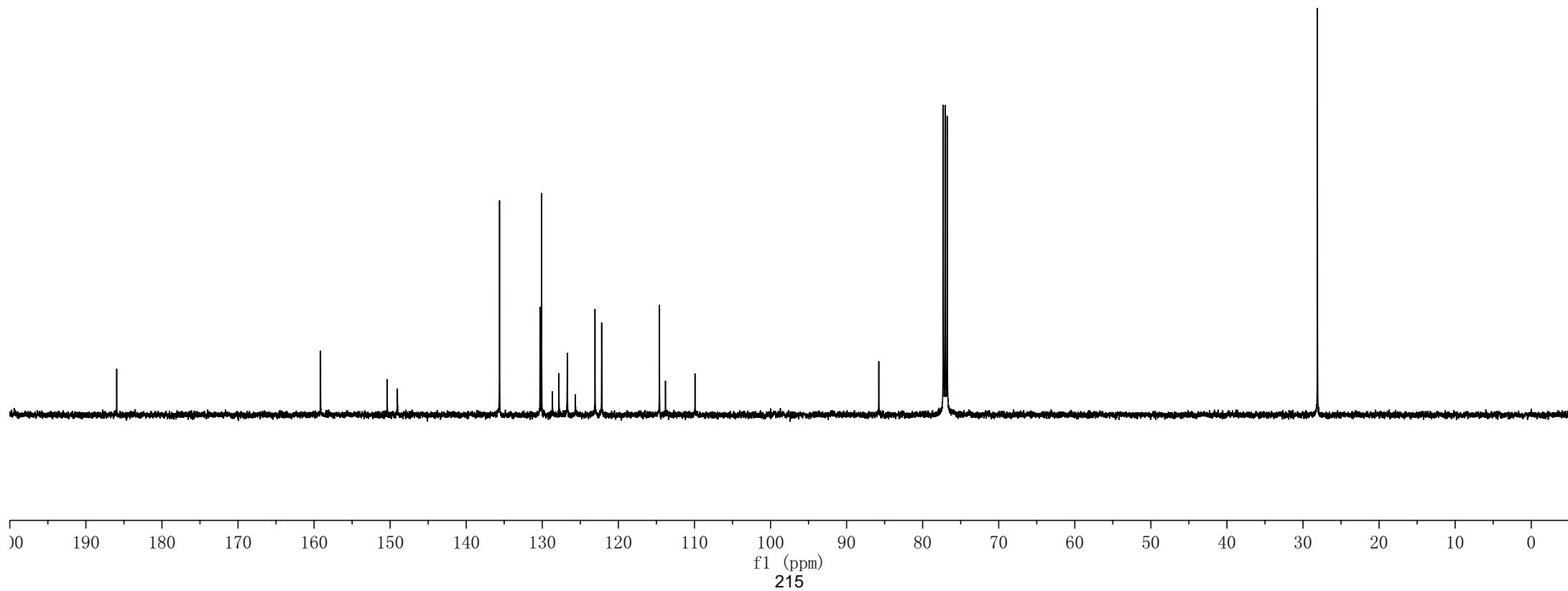
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— 130.30
— 130.09
— 128.67
— 127.82
— 126.71
— 125.66
— 123.07
— 122.20



6i

— 85.76
— 77.29
— 77.03
— 76.78

— 28.11

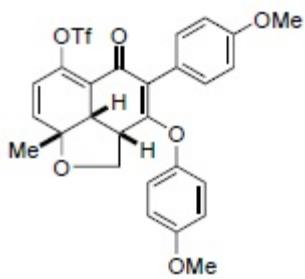


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 ~ -0.00

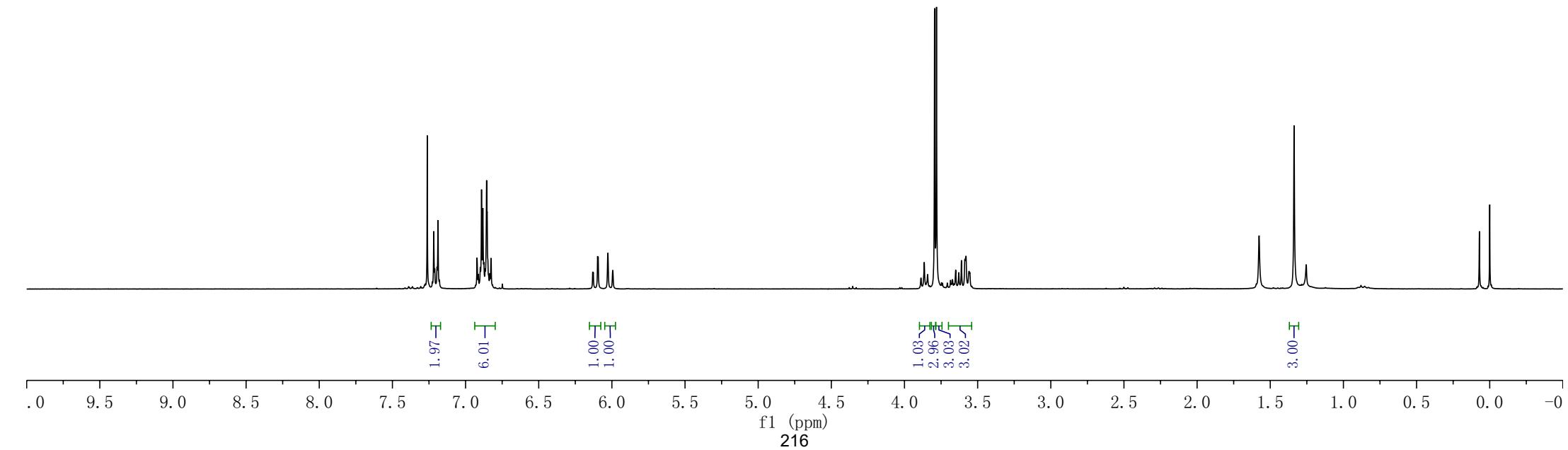
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 3.59
 3.58
 3.56
 3.55

7.26
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 7.20
 7.19
 6.92
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 6.88
 6.86
 6.85
 6.83
 6.13
 6.10
 6.09
 6.03
 5.99



S7



—184.32

—165.98

—159.01

—157.11

—147.17

—143.65

—136.96

—131.57

✓125.26
✓122.93
✓121.77
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✓114.96
✓113.50

✓77.46
✓77.04
✓76.62

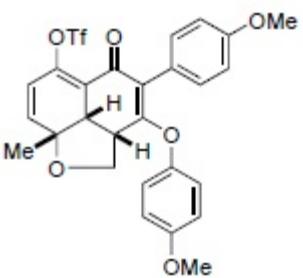
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✓55.68
✓55.19

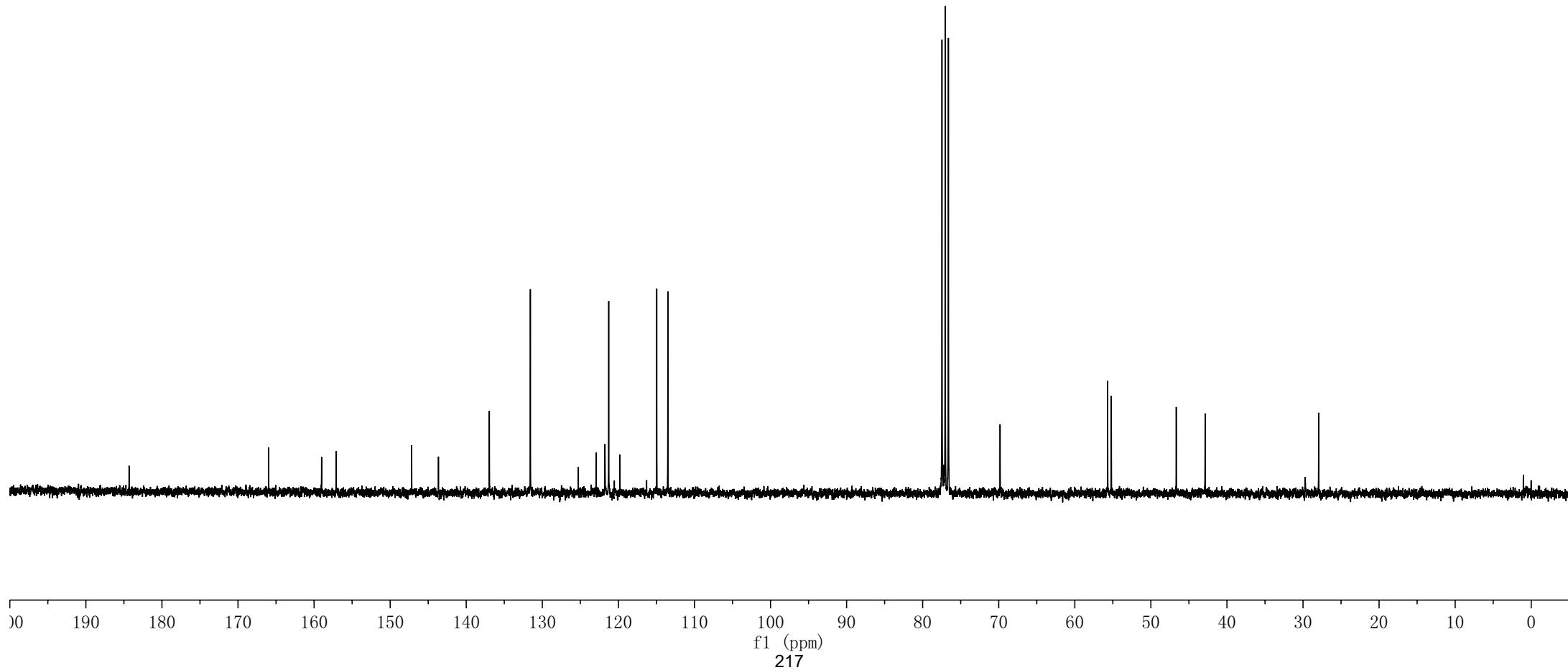
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—29.72

—27.94



S7



— 0.00

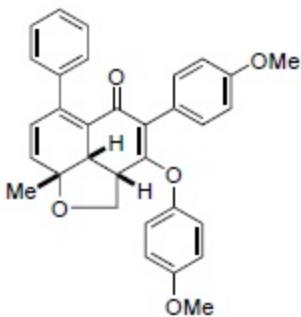
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— 1.36

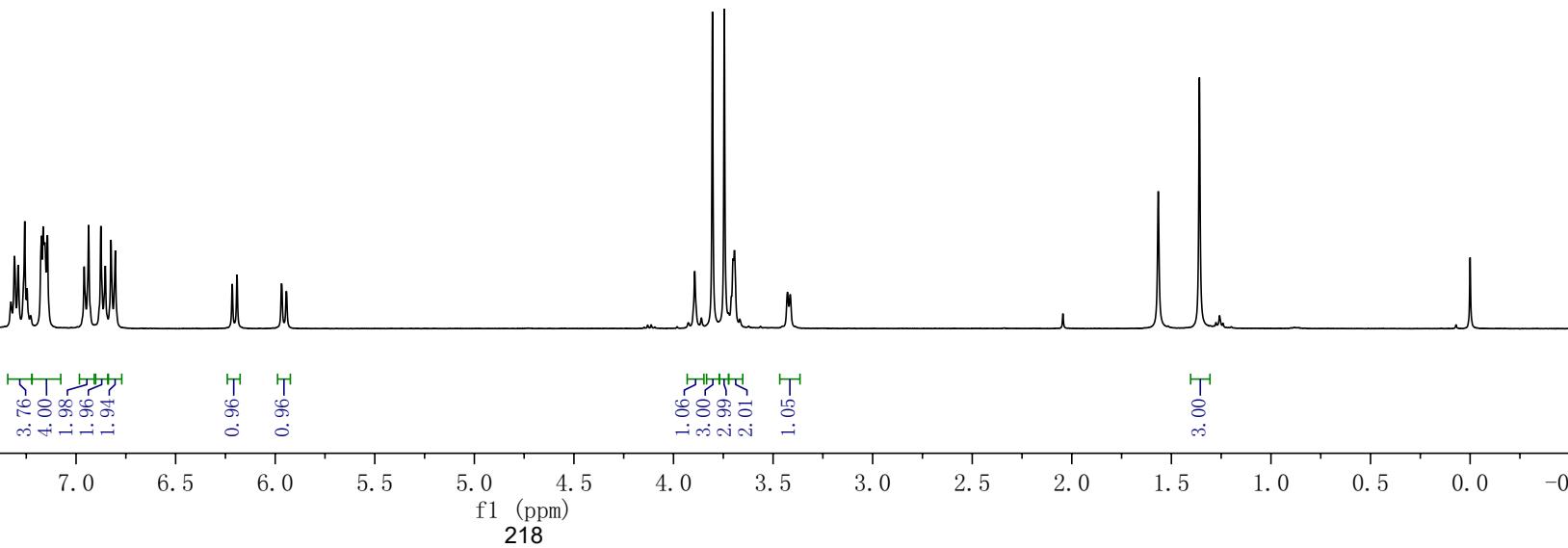
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6.85
6.82
6.80
6.22
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5.97
5.94

3.89
3.80
3.74
3.70
3.69
3.43
3.41



7



—188.64

—164.90

—158.72

—156.90

—147.56

~140.64

~140.08

131.43

131.39

130.06

128.22

127.45

127.29

126.21

125.77

123.90

121.22

~114.93

~113.32

77.47

77.39

77.04

76.62

~69.71

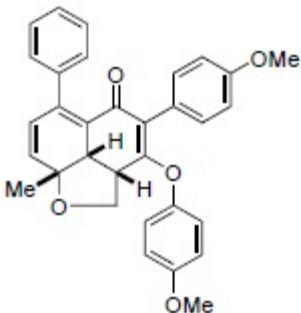
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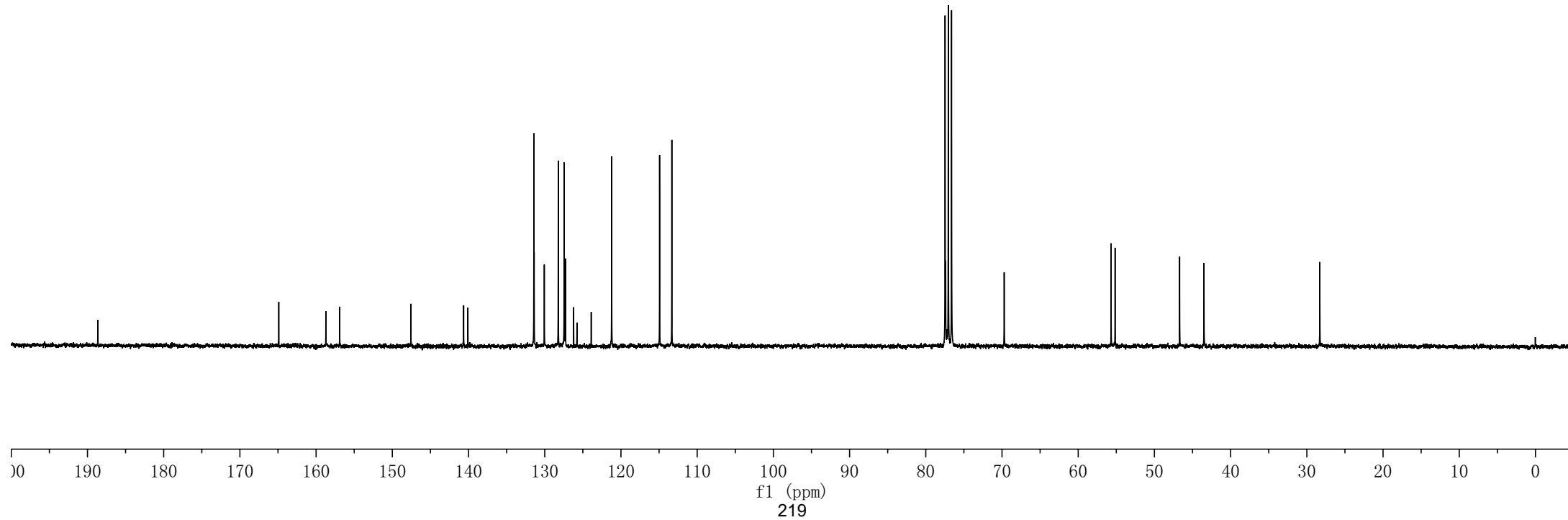
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—28.30



7

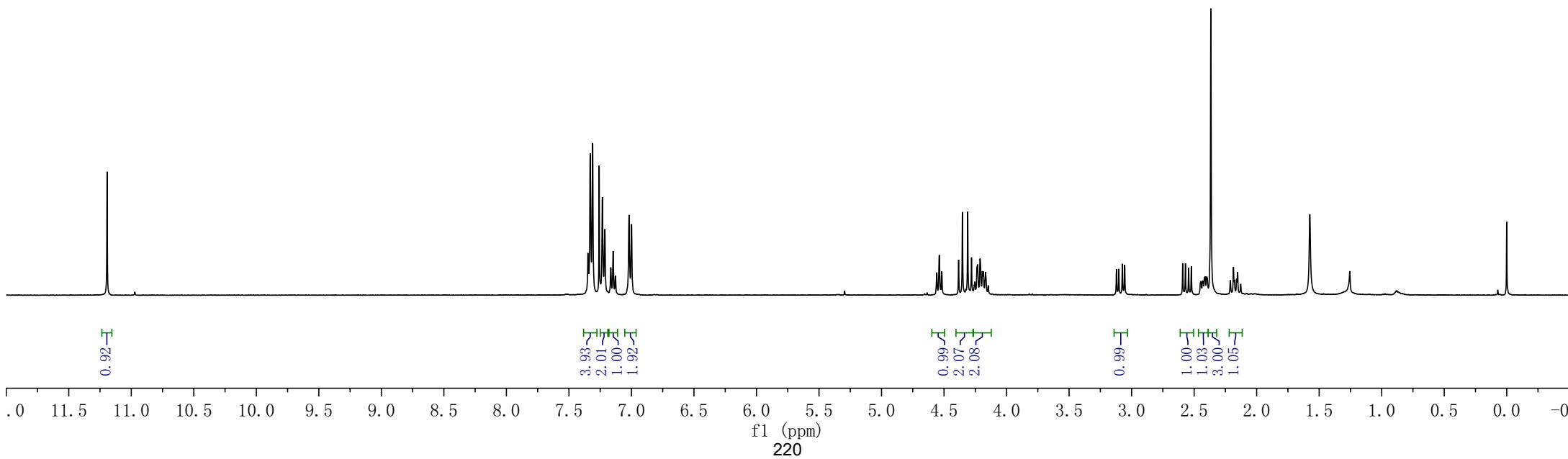


—11.19

—0.00



8



—198.93

—159.70
—156.20
—155.79

—147.05

—137.51

—130.29
—129.88
—128.88
—128.48
—124.48
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—120.17
—119.18

—109.22

—89.78

—80.77
—77.28
—77.02
—76.77

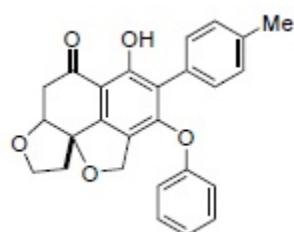
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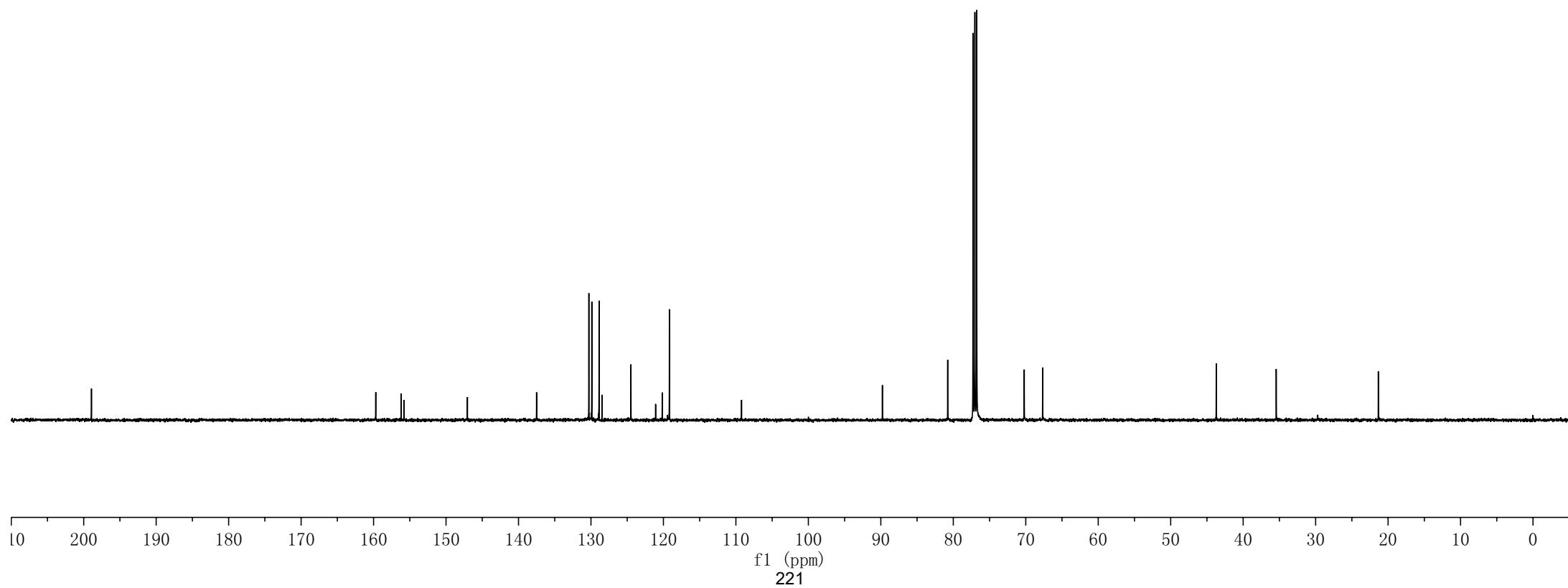
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—21.35



8



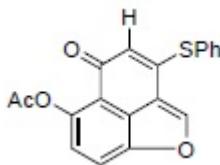
7.88
7.68
7.66
7.62
7.60
7.48
7.46
7.26
7.15
7.13

— 6.01

— 2.42

— 1.57

— 0.00

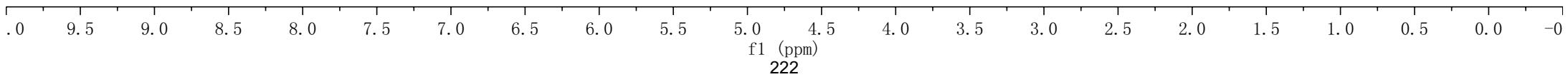


S9-I

0.97
1.07
1.94
3.09
1.04

0.96

3.00



— 180.65

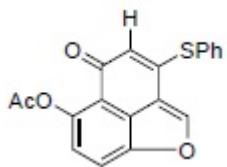
— 169.59

— 150.30
— 146.40
— 146.26
— 146.05

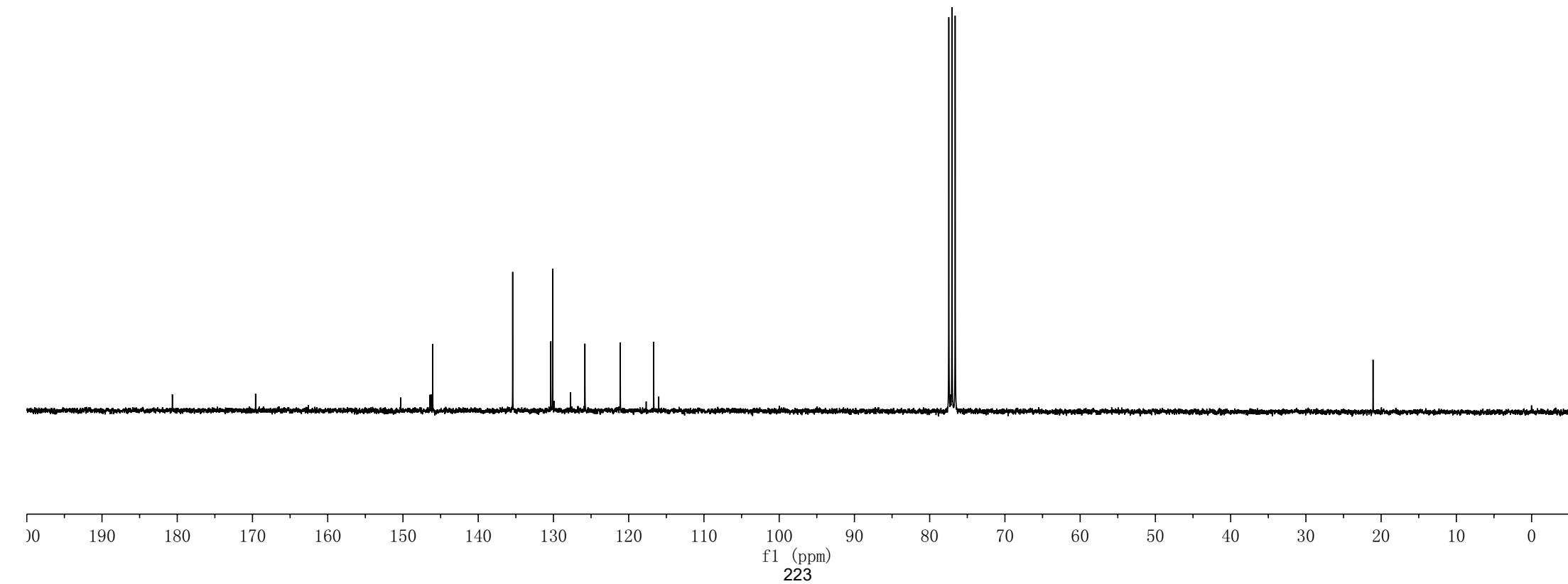
— 135.42
— 130.35
— 130.10
— 129.89
— 127.72
— 125.81
— 121.12
— 117.68
— 116.68
— 116.00

— 77.46
— 77.03
— 76.61

— 21.07



S9-I



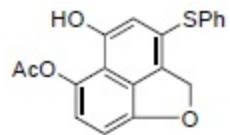
—0.00

—1.25

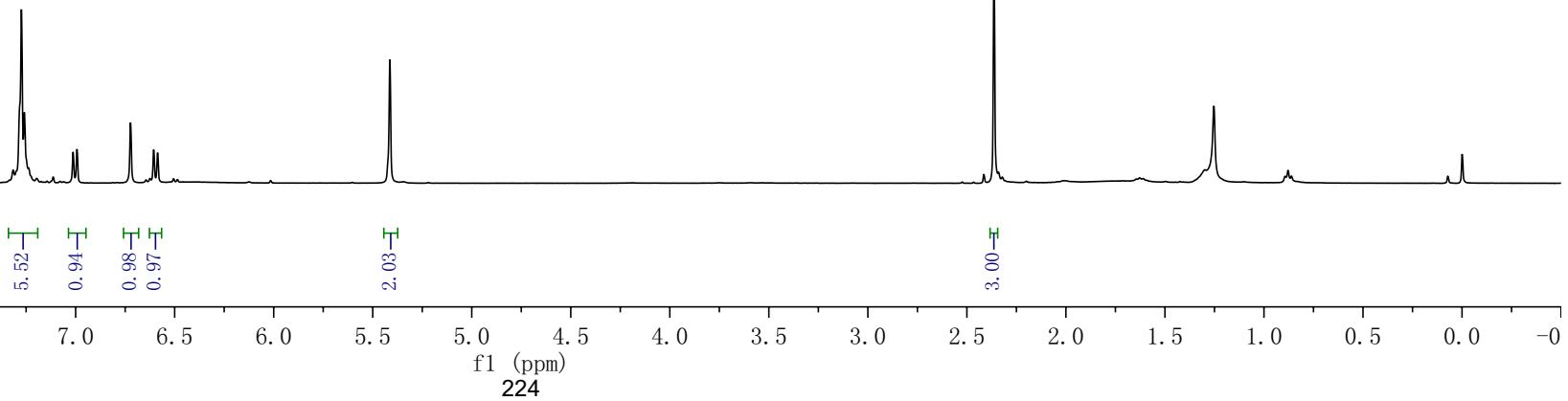
—2.36

—5.41

7.32
7.27
7.26
7.20
7.01
6.99
6.72
6.61
6.59



S9-II



—170.16

—159.39

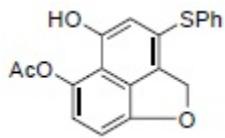
—150.17

—137.02
—134.07
—131.95
—131.82
—130.61
—129.35
—127.33
—123.55
—121.02
—116.24
—114.91

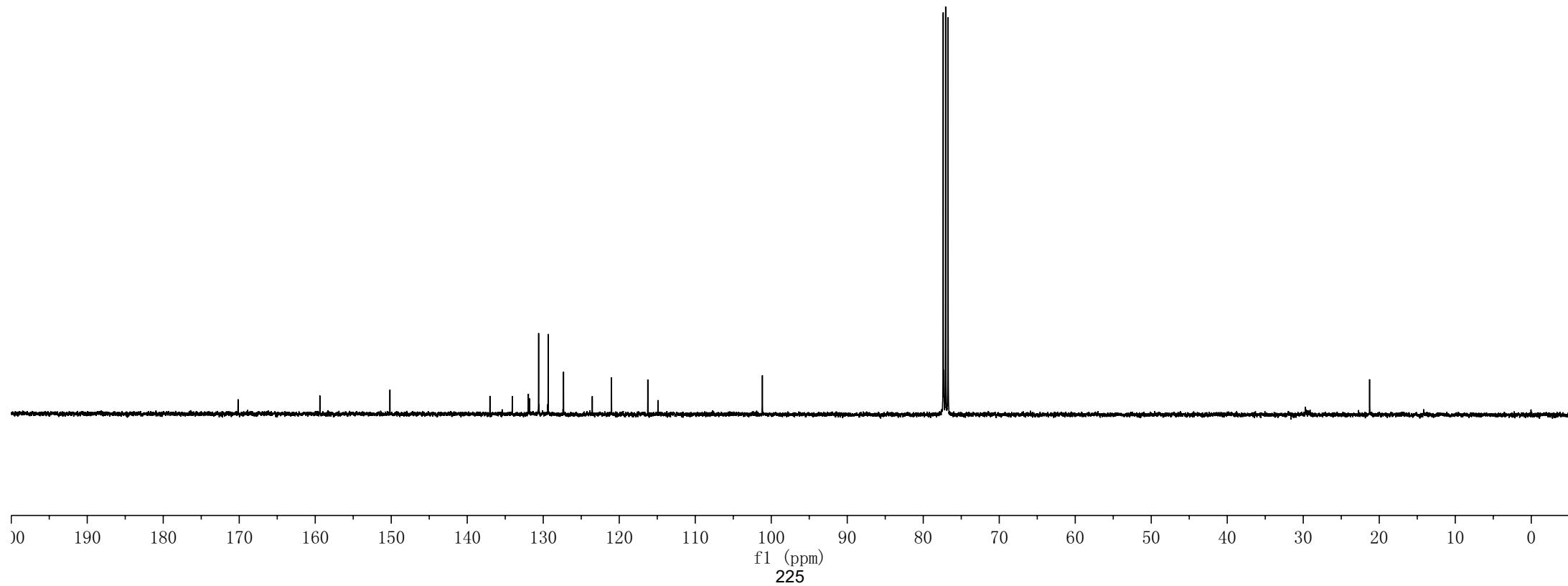
—101.17

77.37
77.29
77.05
76.74

—21.27



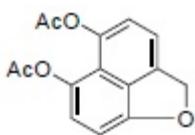
S9-II



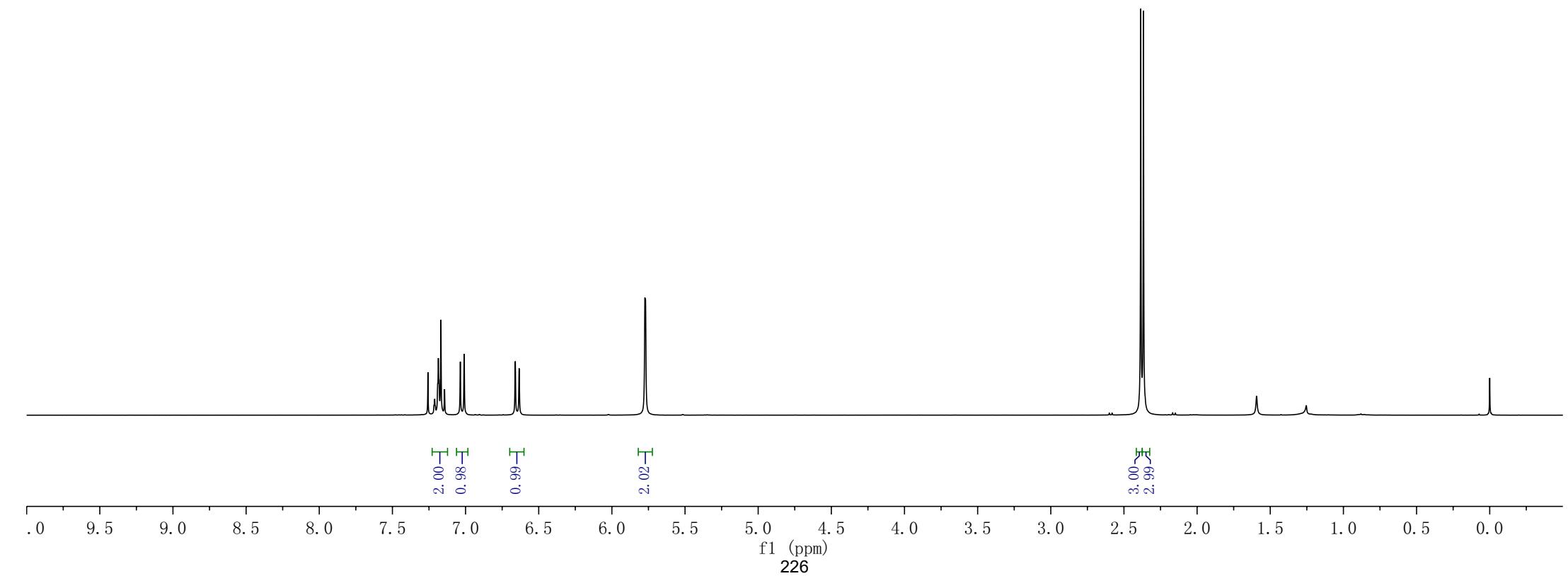
—0.00

—1.59

—2.39
—2.37



9



\sim 170.05
 \sim 169.50

—159.87

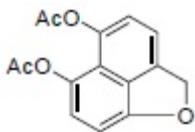
—142.58
—137.04
 \sim 135.71
—131.54

\sim 123.22
 \sim 122.66
 \sim 119.21
 \sim 116.03

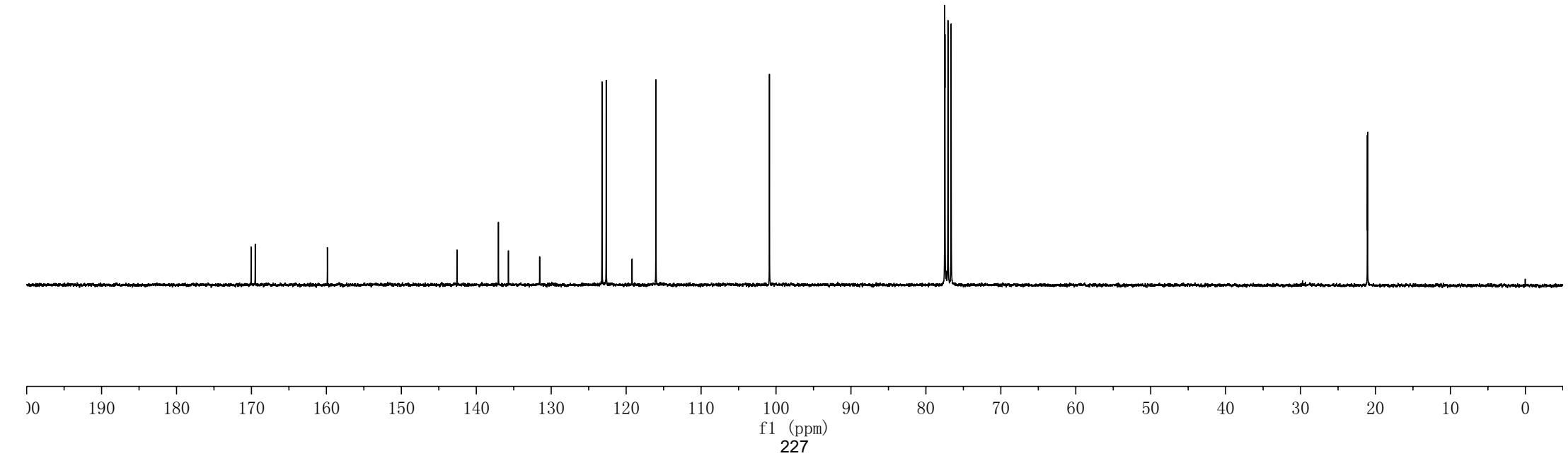
—100.88

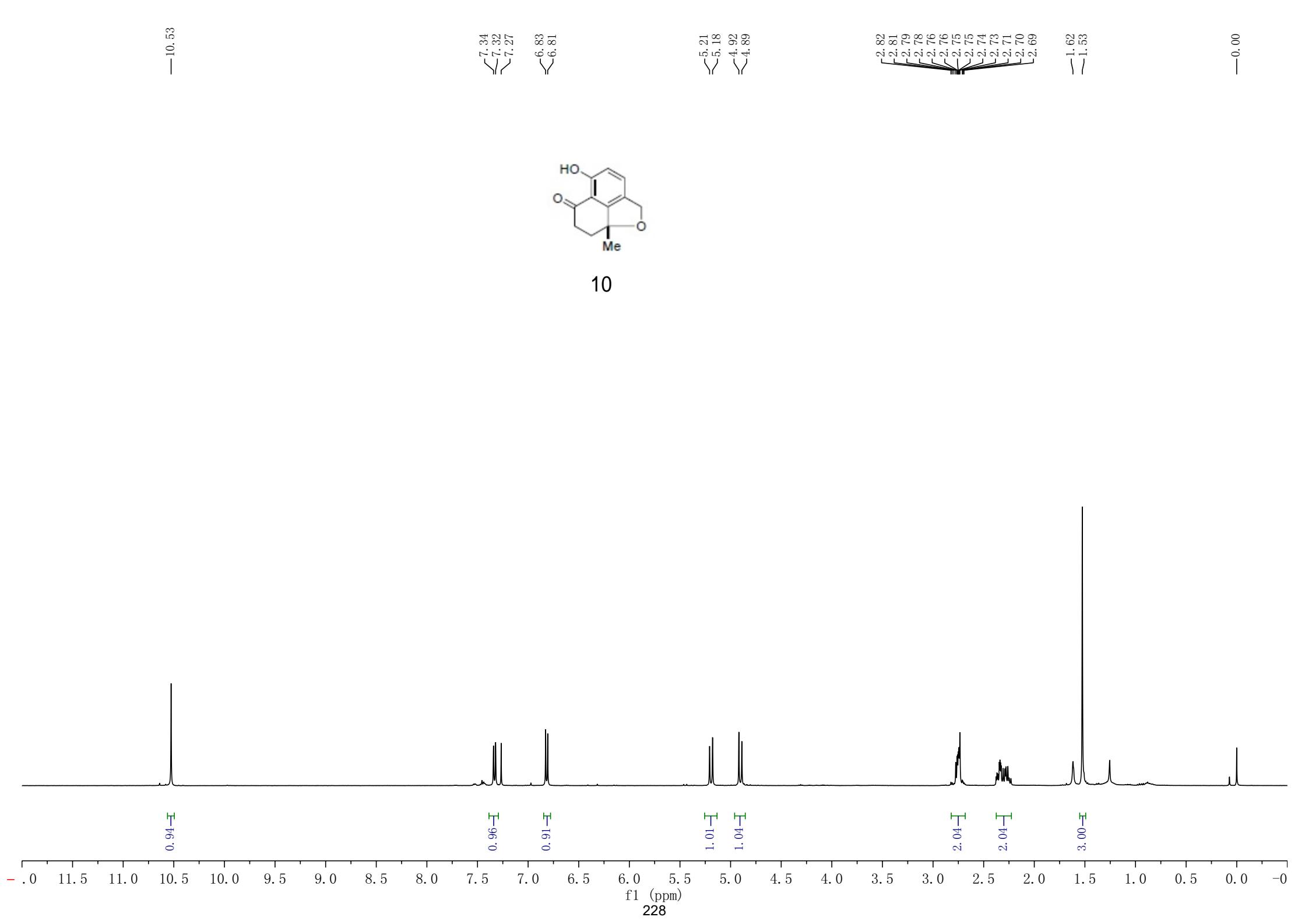
77.48
77.45
77.06
76.64

\sim 21.09
 \sim 21.06



9





—202.02

—159.19

—151.89

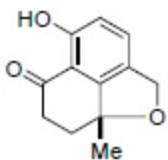
—130.15
—128.55

—116.32
—112.45

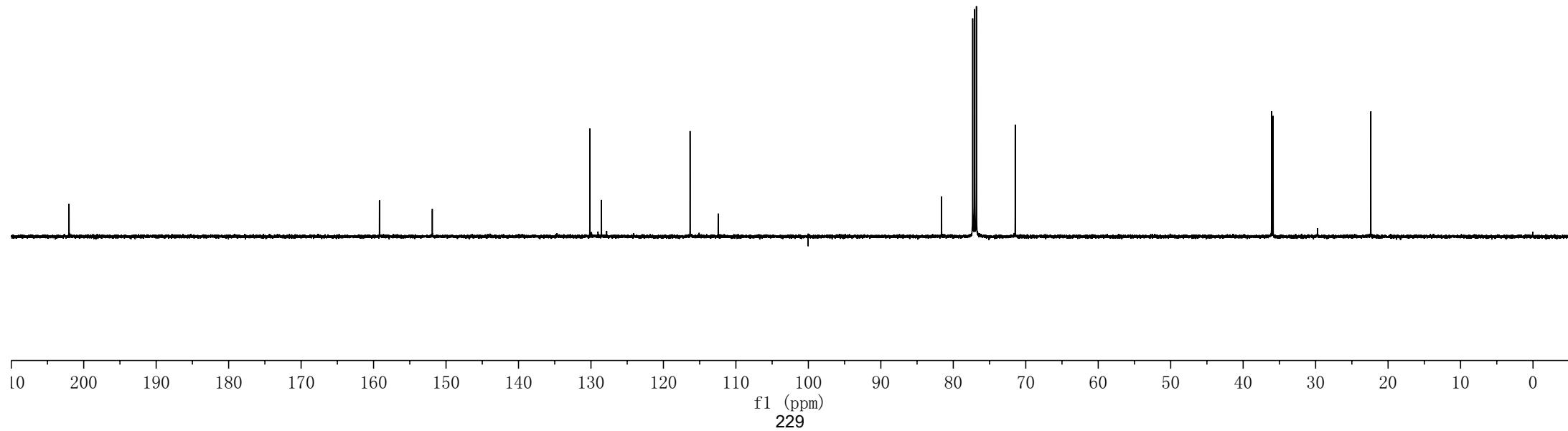
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—36.07
—35.86

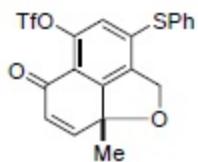
—22.38



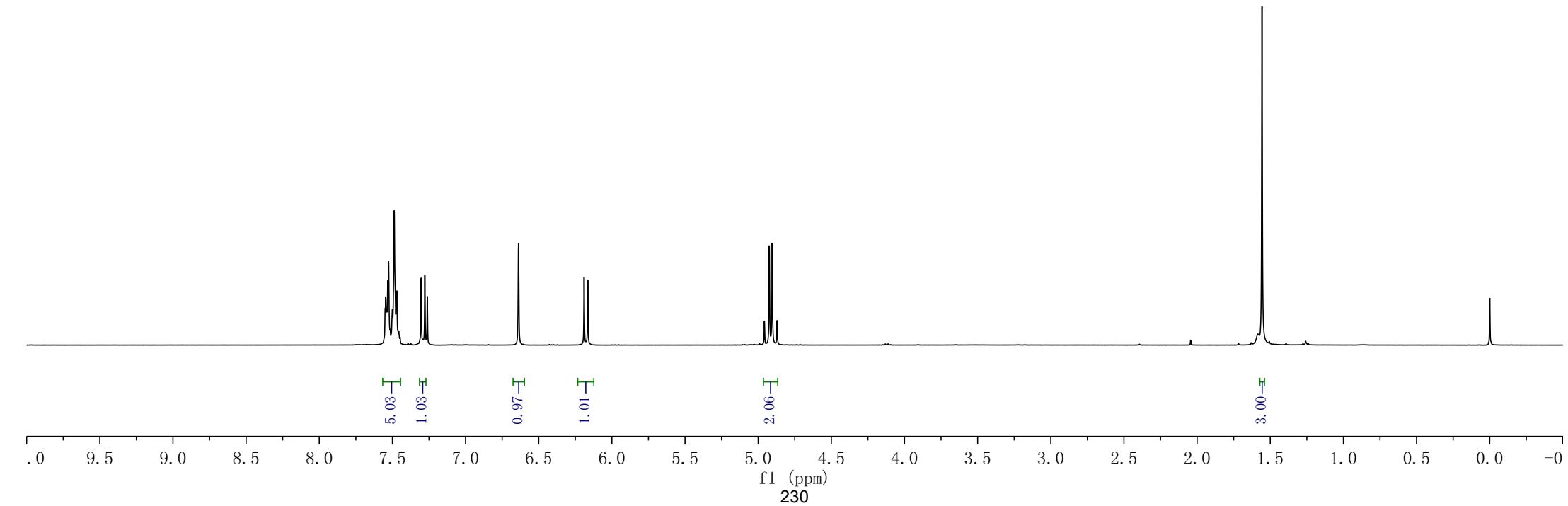
10



7.55
7.55
7.53
7.53
7.52
7.50
7.49
7.47
7.46
7.30
7.28
7.26
6.64
6.19
6.16
4.96
4.92
4.90
4.87
1.58
1.56
—0.00



S11



—180.75

—153.28

—148.25

—146.09

—141.53

~135.74

~134.52

130.19

~130.17

129.56

~129.15

~120.27

119.48

~117.08

116.93

~81.40

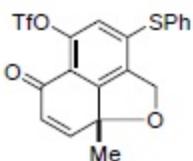
~77.36

~77.04

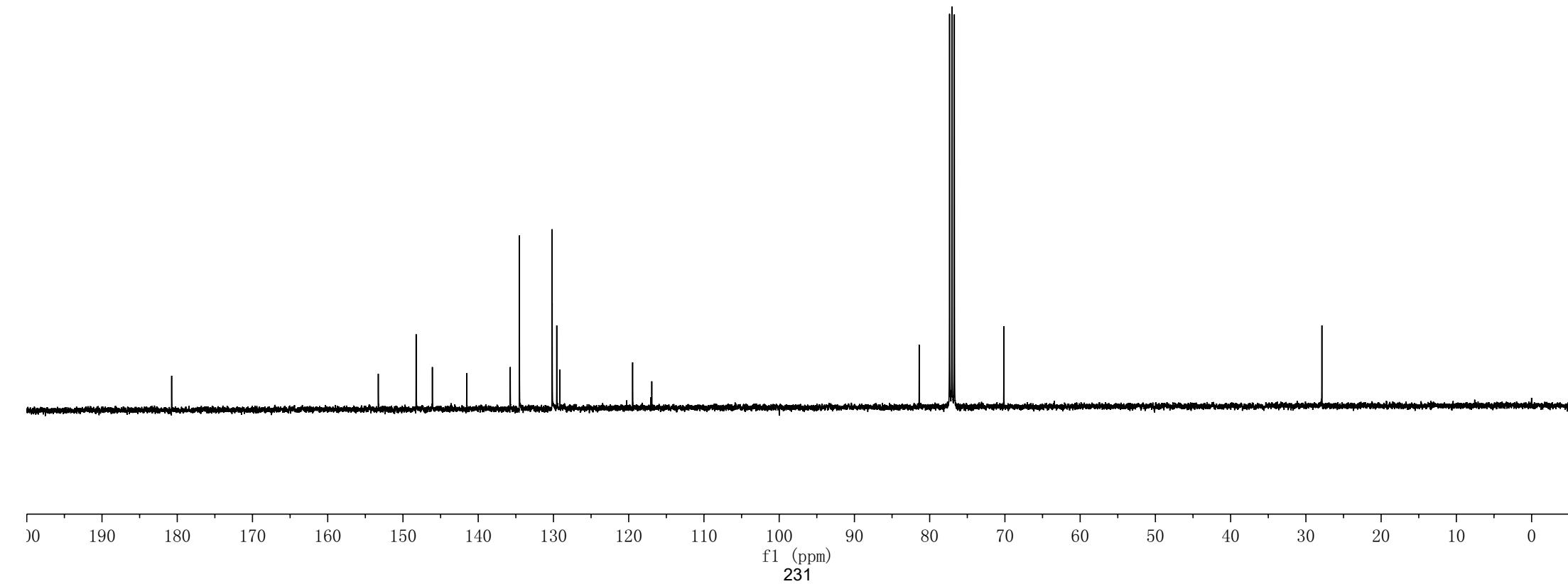
~76.72

—70.14

—27.87



S11

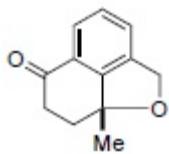


— 0.00

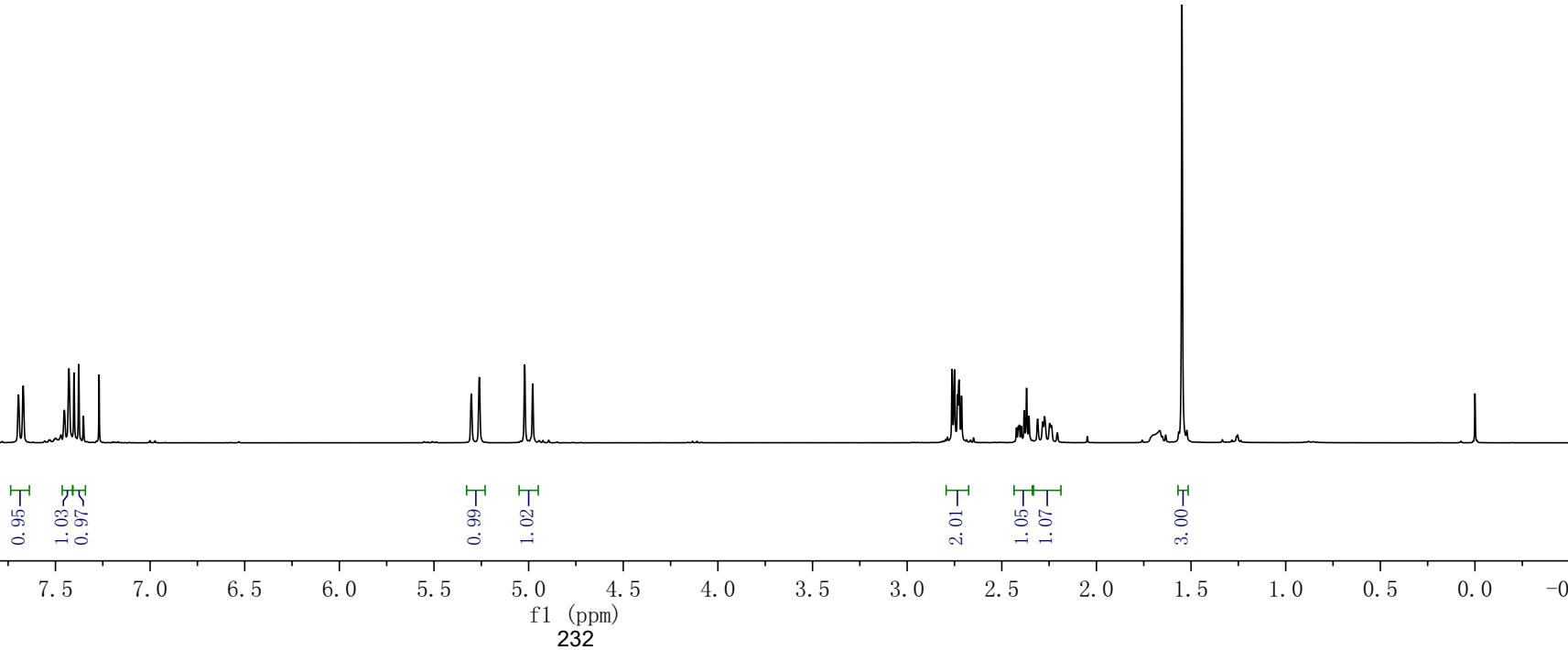
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<7.67
<7.45
7.43
7.40
<7.38
<7.35
<7.27

<5.30
<5.26
<5.02
<4.98

2.76
2.75
2.73
2.73
2.71
2.38
2.37
2.36
2.31
2.28
2.27
2.165
1.67
1.56
1.55
<1.52



11



—196.78

—151.64

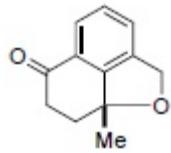
—139.01

~128.63
~127.34
~126.65
~123.70

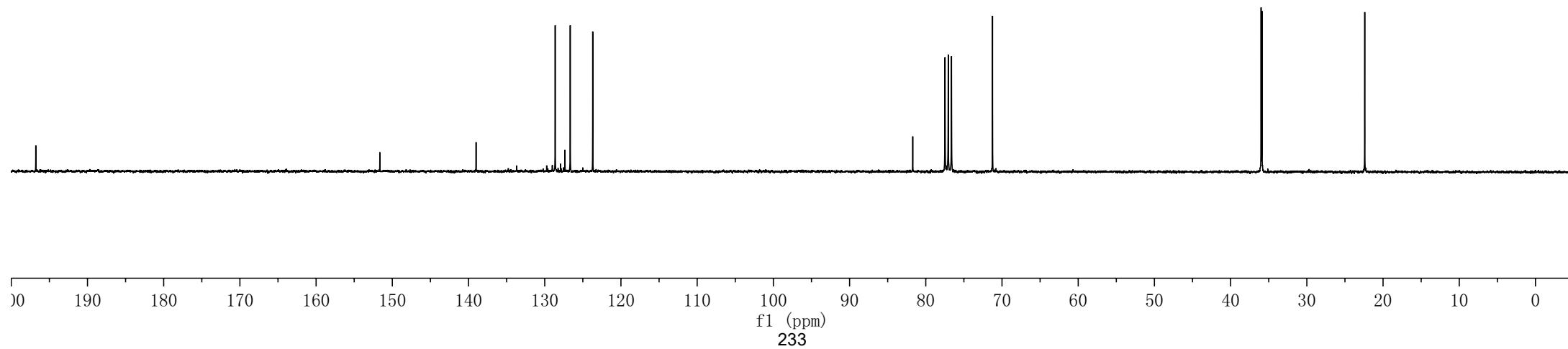
—81.71
~77.48
~77.05
~76.63
—71.24

~36.00
~35.89

—22.40



11



7.55
7.54
7.53
7.53
7.51
7.50
7.49
7.48
7.47
7.46
7.45
7.26

—6.52

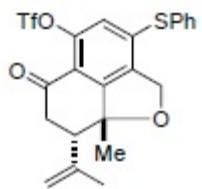
4.99
4.96
4.91
4.88
4.74

—4.42

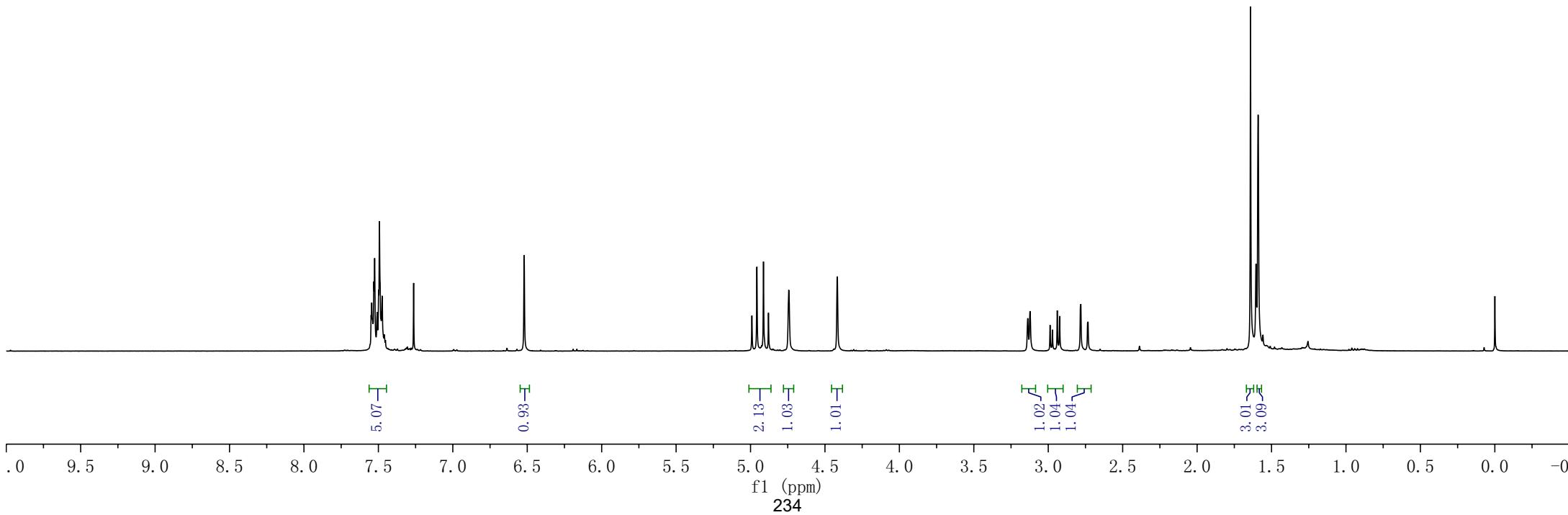
3.14
3.12
2.99
2.97
2.94
2.92
2.78
2.78
2.74
2.73

1.64
1.60
1.59

—0.00



S12



—192.32

—151.70

~145.75

~144.97

~142.48

~135.45

~134.78

~130.28

~130.19

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~119.85

~119.24

~117.42

~113.93

—85.00

77.29

77.03

76.78

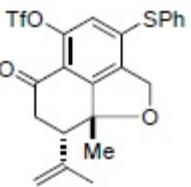
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—50.86

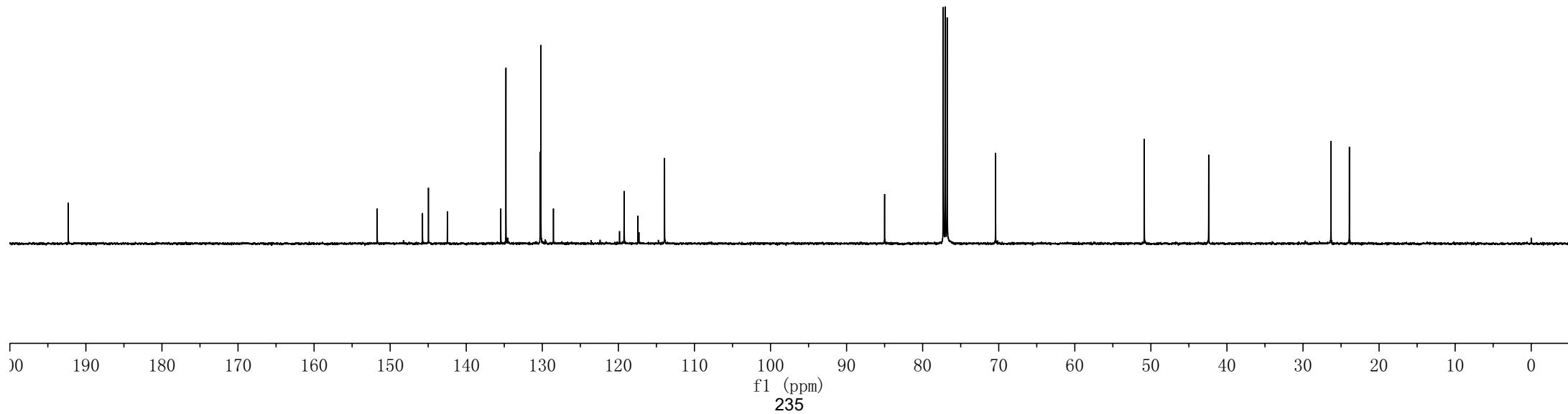
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—26.32

—23.90



S12



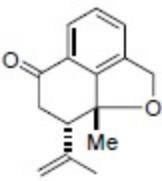
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—0.00

—0.00

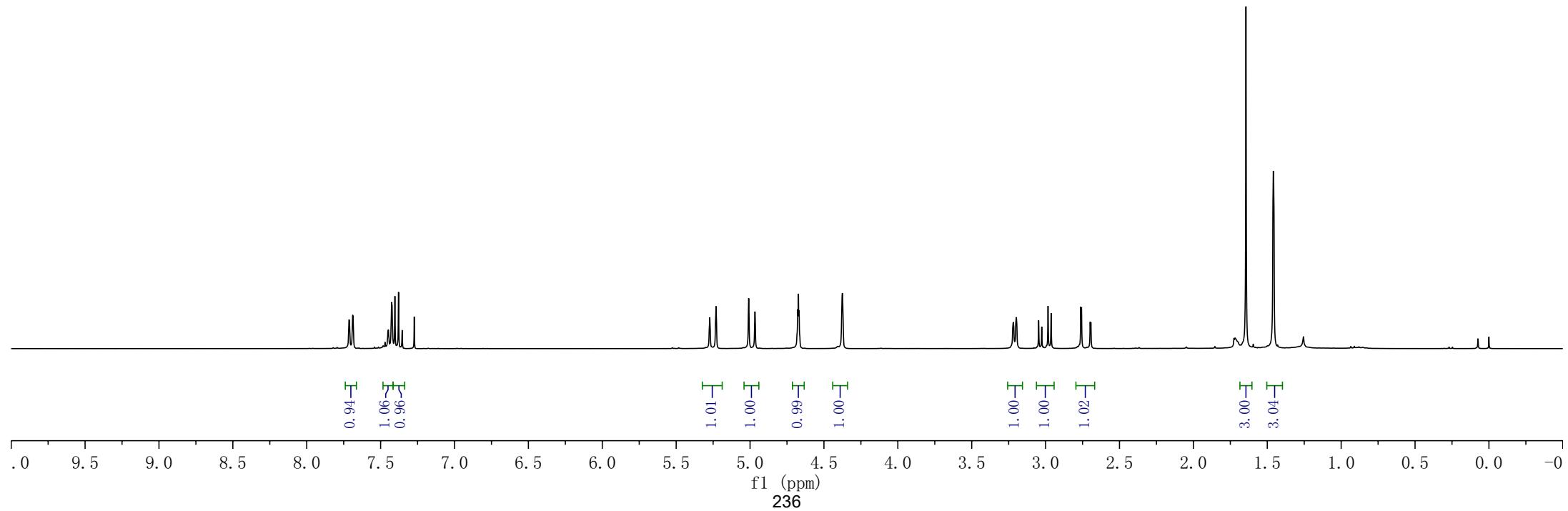
—1.72
—1.64
—1.46
—1.46

—5.27
—5.23
—5.01
—4.97
—4.68
—4.67
—4.67
—4.38

—7.71
—7.69
—7.47
—7.45
—7.43
—7.42
—7.40
—7.38
—7.35
—7.27



12



—196.37

—149.48

—145.54

—139.10

—128.69
—127.98
—126.81
—123.31

—113.47

—84.01

—77.36
—77.04
—76.73

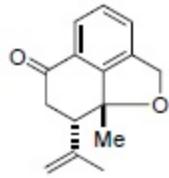
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—51.93

—42.11

—26.21

—23.36



12

