Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Total Synthesis of (±)-Villosin C and (±)-Teuvincenone B

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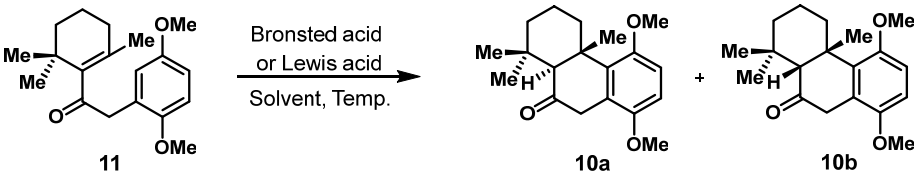
1. General Experimental

Solvents and reagents were purchased from Energy Chemical, Leyan, Bide and Sinopharm Chemical. All reactions were stirred magnetically. All moisture and oxygen sensitive reactions were performed in flame-dried glassware under a slight argon overpressure. Sensitive solutions, solvents and reagents were transferred via cannula or syringe. DCM, DMF, diethyl ether, and toluene were purified by STEEMA solvent purification system. Other solvents, starting materials, and reagents are commercially available and used directly as received, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) and NMR of the crude mixture. Evaporations were conducted under reduced pressure at temperatures less than 40 ℃. Further dryings of the residues were accomplished using a high vacuum pump. Flash column chromatography was performed with silica gel from SiliaFlash (230-400 mesh). NMR spectra were recorded on Bruker Avance III 400, Avance III 500, and Avance III 600 instruments. Chemical shifts are given in ppm and calibrated using the residual undeuterated solvent peaks (Chloroform-*d* ^{1}H, δ = 7.26 ppm, ^{13}C, δ = 77.16 ppm; DMSO-d_6 ^{1}H, δ = 2.50 ppm, ^{13}C, δ = 39.52 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant *J*, integration. High-resolution mass spectra were recorded on Agilent 1290/6545 UHPLC-QTOF/MS. Melting points were recorded on a SGWX-4A melting point apparatus (Shanghai instrument physical optics instrument Co., LTD.).

2. Optimization Details

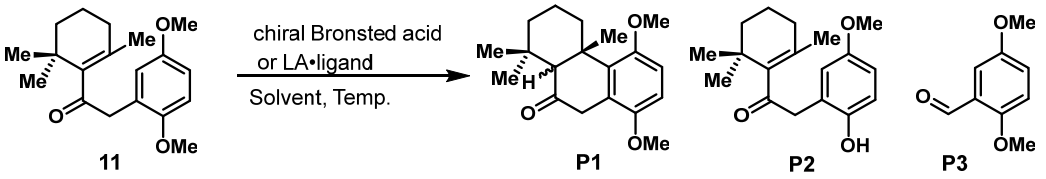
Table S1: Screening of racemic reaction conditions[1]



Entry	Bronsted acid or Lewis acid	Solvent	Temp. (°C)	Yield (%)[a]	Conversion (%)[a]	d.r.[a]
1	TfOH	as solvent	r.t.[b]	0	> 95	-
2	MsOH	as solvent	r.t.	42	> 95	2.5:1
3	H_3PO_4	as solvent	150	n.r.[c]	< 5	-
4	TFA	as solvent	85	n.r.	< 5	-
5	*p*-TsOH	DCE	85	n.r.	< 5	-
6	CSA	DCE	85	n.r.	< 5	-
7	Tf_2NH	DCE	85	n.r.	< 5	-
8[d]	H_2SO_4	DCM	r.t.	60	> 95	1:1
9[e]	MsOH	DCE	85	45	> 95	1:2
10	$AlCl_3$	DCE	60	23	93	5:1
11	$Sc(OTf)_3$	DCE	60	44	> 95	4.3:1
12[f]	TfOH	DCE	r.t.	68	> 95	2.9:1
13[f]	TfOH	DCE	0	78	> 95	2.6:1

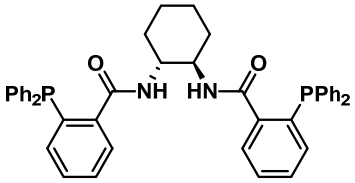
Reaction conditions: **11** (0.1 mmol), Lewis acid or Bronsted acid (0.1 mmol, 1 equiv), Solvent (2 mL), Ar. [a] Determined by ^1H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b] Room temperature. [c] No reaction. [d] H_2SO_4 (0.4 mmol, 4 equiv), [e] MsOH (0.3 mmol, 3 equiv), [f] TfOH (0.3 mmol, 3 equiv).

Table S2: Screening of asymmetric reaction conditions

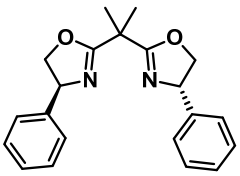


Entry	Chiral Bronsted acid or Lewis acid	Ligand	Solvent	Temp. (°C)	Yield (**P1**/**P2**/**P3**, %)[a]	Conversion (%)[a]
1	$CuBr_2$	**L1**	toluene	120	-	< 5
2	$Sc(OTf)_3$	**L1**	toluene	120	-	< 5
3	$Cu(OTf)_2$	**L1**	toluene	120	-	< 5
4	$CuBr_2$	**L2**	toluene	120	n.d.[b]/14/n.d.	40
5	$Sc(OTf)_3$	**L2**	toluene	120	n.d./n.d./n.d.	> 95
6	$Cu(OTf)_2$	**L2**	toluene	120	-	< 5
7	$CuBr_2$	**L3**	toluene	120	-	< 5
8	$Sc(OTf)_3$	**L3**	toluene	120	-	< 5
9	$Cu(OTf)_2$	**L3**	toluene	120	n.d./n.d./n.d.	78
10	$CuBr_2$	**L4**	toluene	120	-	< 5
11	$Sc(OTf)_3$	**L4**	toluene	120	-	< 5
12	$Cu(OTf)_2$	**L4**	toluene	100	n.d./60/n.d.	> 95
13	Al^+	**L5**	toluene	120	n.d./24/n.d.	36
14	**C1**	-	toluene	120	-	< 5
15	**C2**	-	toluene	120	-	< 5
16	**C3**	-	toluene	120	n.d./15/n.d.	80
17	**C4**	-	toluene	120	-	< 5
18	**C5**	-	toluene	120	-	< 5
19	**C6**	-	toluene	120	n.d./50/n.d.	90
20[c]	**C7**	-	toluene	130	-	< 5
21[c]	**C7**	-	EtOAc	80	-	< 5
22[c]	**C7**	-	DCM	r.t.[d]	n.d./n.d./83	> 95
23[c]	**C7**	-	DCE	60	n.d./n.d./80	> 95

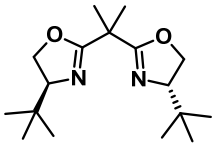
Reaction conditions: **11** (0.05 or 0.01 mmol), chiral Bronsted acid (1 equiv) or LA·ligand (1 equiv), Solvent (0.5 or 0.1 mL), Ar. [a]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]Not detected. [c]**11** (0.01 mmol), Solvent (0.2 mL), **C7** (0.1 equiv). [d]Room temperature.



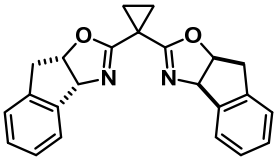
L1



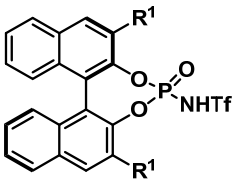
L2



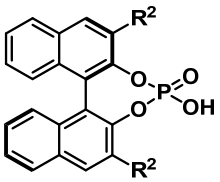
L3



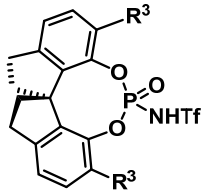
L4



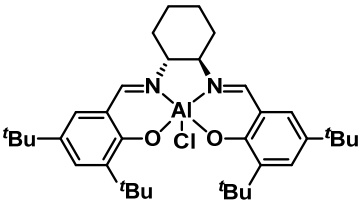
C1: R^1 = 1-naphthyl
C2: R^1 = 4-(NO_2)-phenyl
C3: R^1 = Ph



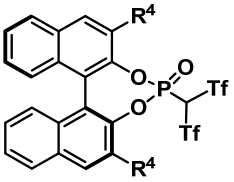
C4: R^2 = 4-(NO_2)-phenyl
C5: R^2 = 2,3,4,5,6-pentafluoro-phenyl



C6: R^3 = 9-anthryl

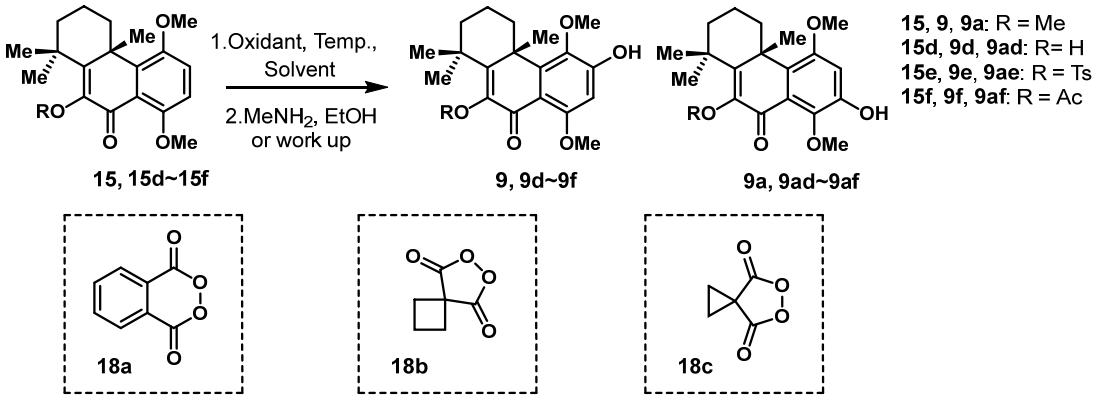


L5



C7: R^4 = 3,5-(CF_3)$_2$-phenyl

Table S3: Screening of substrates, oxidants and solvents[2]



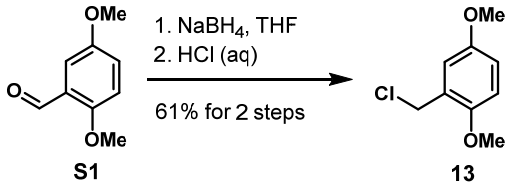
Entry	R	Oxidant	Solvent	Temp. (°C)	Yield of **9** (%)[a]	**9** : **9a**[a]
1[b]	Me	**18a**	HFIP	r.t.[c]	28[d]	1 : 1.6[d]
2	Me	**18a**	TFE	r.t.	8	1 : 3.5
3	Me	**18c**	HFIP	r.t.	19	1 : 2.1
4	Me	**18c**	TFE	r.t.	31	1 : 1.3
5[e]	Me	**18c**	TFE	-20	37[d]	1 : 1.2[d]
6	Me	**18b**	HFIP	r.t.	-	1 : 2.6
7	Me	**18b**	TFE	r.t.	-	1 : 1.6
8	H	**18c**	TFE	-20	30[d]	1.3 : 1[d]
9	H	**18c**	HFIP	r.t. to 40	25	1 : 1
10	H	**18a**	HFIP	r.t. to 40	10	1 : 3.7
11	Ts	**18c**	TFE	r.t.	33[d]	1 : 1[d]
12	Ts	**18c**	HFIP	r.t. to 40	22	1 : 2
13	Ts	**18a**	TFE	r.t. to 40	15	1 : 1
14	Ts	**18a**	HFIP	r.t. to 40	22	1.3 : 1
15[f]	Ac	**18c**	TFE	r.t.	22	1 : 1.6
16[f]	Ac	**18c**	HFIP	r.t.	20	1 : 1.9
17	Ac	**18a**	TFE	r.t.	28[d]	1 : 1.2[d]
18	Ac	**18a**	HFIP	r.t.	20	1 : 1.6

Reaction conditions: **15** (0.05 mmol), **18a** (1.5 equiv) or **18b** (2.5 equiv) or **18c** [2.5 equiv (entries 1-7) or 2.0 equiv (entries 8-19)], solvent [0.5 mL (entries 1-7) or 0.1 mL (entries 8-19)], Ar. [a]Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard. [b]**15** (0.1 mmol), **18c** (1.5 equiv), solvent (1 mL). [c]Room temperature. [d]Isolated yield. [e]**15** (1.0 mmol), **18c** (2.0 equiv), solvent (5 mL), under argon atmosphere. [f]Ac was deprotected in step 2.

3. Experimental Procedures and Characterization Data

Synthesis of Compound 13[3]

2-(chloromethyl)-1,4-dimethoxybenzene



2,5-dimethoxybenzaldehyde **S1** (20 g, 120 mmol) was dissolved in THF (120 mL) and cooled to 0 ℃. $NaBH_4$ (1.8 g, 48 mmol) was added in 3 portions, and the solution was warmed up to room temperature and stirred overnight. The reaction was quenched with HCl (1.5 M) and extracted with EtOAc for 3 times. The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was poured into a separating funnel. Concentrated HCl (30 mL) was added and the resulting mixture was shaken vigorously for about 7 minutes. Aqueous $NaHCO_3$ was added and the mixture was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Purified by trituration with hexane and diethyl ether afforded compound **13** (13.68 g, 61%).

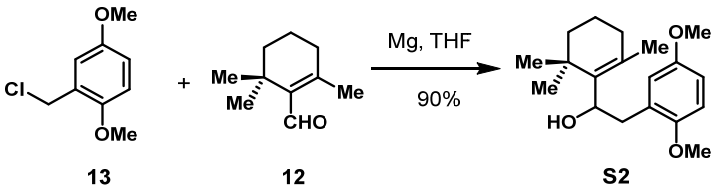
Physical State: white solid.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.94 (d, *J* = 2.5 Hz, 1H), 6.82 – 6.85 (m, 2H), 4.63 (s, 2H), 3.84 (s, 3H), 3.78 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 153.6, 151.7, 126.8, 116.3, 114.8, 112.2, 56.4, 55.9, 41.6.

Synthesis of Compound S2

2-(2,5-dimethoxyphenyl)-1-(2,6,6-trimethylcyclohex-1-en-1-yl)ethan-1-ol



To a suspension of magnesium turnings (2.53 g, 106 mmol) in THF (10 mL) at room temperature was added 1,2-dibromoethane (0.1 mL) under argon. Then, the mixture was heated to reflux by a heat gun until the observation of gas evolution. After cooling to room temperature, a solution of benzyl chloride **13** (12 g, 66 mmol) in THF (70 mL) was added in a dropwise

manner over 30 min. After addition, the mixture was stirred at 30 ℃ for additional 30 min. The Grignard reagent was then added to a solution of enal **12** (5.0 g, 33 mmol) in THF (10 mL) at 0 ℃ under argon. After addition, the reaction was warmed to room temperature and the consumption of enal was monitored by TLC (typically within 30 min). The reaction was quenched by addition of saturated aqueous NH_4Cl and extracted with EtOAc for 3 times. The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 – 5:1) afforded compound **S2** (9.0 g, 90%).

Physical State: colorless solid.

Melting Point: 71 – 73 ℃.

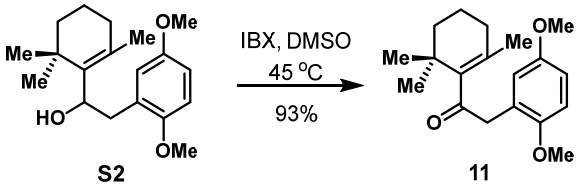
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.84 – 6.78 (m, 2H), 6.74 (dd, *J* = 8.7, 3.1 Hz, 1H), 4.49 (dd, *J* = 10.4, 3.1 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.13 (dd, *J* = 13.8, 10.4 Hz, 1H), 2.89 (dd, *J* = 13.9, 3.0 Hz, 1H), 2.00 – 1.96 (m, 2H), 1.96 (s, 3H) 1.64 – 1.52 (m, 2H), 1.50 – 1.36 (m, 2H), 1.09 (s, 3H), 1.03 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 153.7, 152.0, 139.6, 131.5, 129.6, 118.0, 111.7, 111.5, 71.1, 56.0, 55.8, 40.2, 38.6, 34.9, 34.3, 28.5, 28.2, 21.3, 19.5.

HRMS (ESI-TOF): calculated for $C_{19}H_{28}NaO_3^+$ ([M+Na]$^+$) m/z: 327.1931; Found 327.1937.

Synthesis of Compound 11

2-(2,5-dimethoxyphenyl)-1-(2,6,6-trimethylcyclohex-1-en-1-yl)ethan-1-one



To a solution of allylic alcohol **S2** (3.04 g, 10.0 mmol) in DMSO (20 mL) was added IBX (3.64 g, 13.0 mmol, 1.3 equiv) at 45 ℃. After consumption of the starting material as indicated by TLC, the reaction was cooled to room temperature and diluted with water. The mixture was then extracted with EtOAc and the organic layer was washed with brine and $NaHCO_3$ (aq.) successively. After drying with anhydrous Na_2SO_4, the mixture was concentrated under reduced pressure, and purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 – 5:1) to afford compound **11** (2.82 g, 93%).

Physical State: white solid.

Melting Point: 61 – 67 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.84 – 6.75 (m, 2H), 6.69 (d, *J* = 2.9 Hz, 1H), 3.85 (s, 2H), 3.76 (s, 3H), 3.75 (s, 3H), 2.01 – 1.96 (m, 2H), 1.72 – 1.65 (m, 5H), 1.50 – 1.45 (m, 2H), 1.13 (s, 6H).

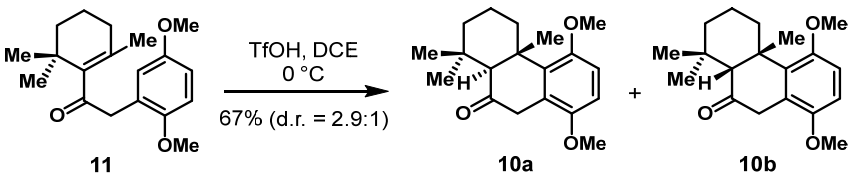
^{13}C NMR (101 MHz, Chloroform-*d*): δ 207.6, 153.5, 152.2, 143.1, 129.5, 124.3, 117.8, 112.5, 111.5, 56.0, 55.8, 47.5, 39.2, 33.5, 31.40, 28.8, 20.9, 19.0.

HRMS (ESI-TOF): calculated for $C_{19}H_{27}O_3^+$ ([M+H]$^+$) m/z: 303.1955; Found 303.1955.

Synthesis of Compound 10a and 10b

(±)-(4bS,8aS)-1,4-dimethoxy-4b,8,8-trimethyl-4b,6,7,8,8a,10-hexahydrophenanthren-9(5H)-one (Compound 10a)

(±)-(4bS,8aR)-1,4-dimethoxy-4b,8,8-trimethyl-4b,6,7,8,8a,10-hexahydrophenanthren-9(5H)-one (Compound 10b)



To a solution of enone **11** (3.0 g, 10.0 mmol) in DCE (150 mL) was added TfOH (2.6 mL, 30 mmol) at 0 ℃ under argon. After stirring for 4 h, the starting material was completely consumed as indicated by TLC. The reaction was diluted with water and extracted with EtOAc. The combined organic layers were washed with $NaHCO_3$ (aq.) and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1) to afford compound **10a** (1.52 g, 50%) and compound **10b** (500 mg, 17%).

Compound 10a:

Physical State: white solid.

Melting Point: 138 – 142 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.75 (d, *J* = 8.9 Hz, 1H), 6.67 (d, *J* = 8.9 Hz, 1H), 3.76 (s, 6H), 3.61 (d, *J* = 20.5 Hz, 1H), 3.26 – 3.18 (m, 2H), 2.66 (s, 1H), 1.73 (qt, *J* = 14.1, 3.6 Hz, 1H), 1.55 (dt, *J* = 14.2, 3.6 Hz, 1H), 1.43 (td, *J* = 13.6, 4.0 Hz, 1H), 1.37 (s, 3H), 1.35 (d, *J* = 14.2 Hz, 1H), 1.26 (s, 3H), 1.13 (td, *J* = 13.6, 3.7 Hz, 1H), 1.01 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 210.8, 152.0, 151.1, 137.7, 123.7, 110.8, 107.7, 63.3, 55.9, 55.7, 45.7, 42.5, 37.2, 33.0, 32.9, 22.2, 20.9, 19.4.

HRMS (ESI-TOF): calculated for $C_{19}H_{27}O_3^+$ ([M+H]$^+$) m/z: 303.1955; Found 303.1953.

Compound 10b:

Physical State: white solid.

Melting Point: 105 – 107 ℃.

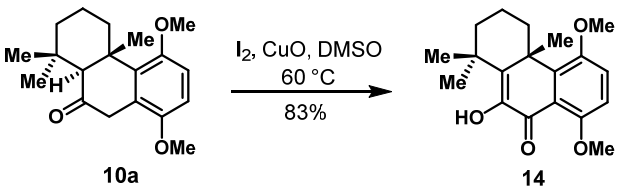
^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.79 (d, *J* = 8.9 Hz, 1H), 6.70 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H), 3.76 (s, 3H), 3.69 (d, *J* = 23.7 Hz, 1H), 3.39 – 3.34 (m, 1H), 3.27 (d, *J* = 23.7 Hz, 1H), 1.96 (s, 1H), 1.55 – 1.43 (m, 2H), 1.36 – 1.24 (m, 2H), 1.09 (s, 3H), 1.02 (td, *J* = 13.1, 3.1 Hz, 1H), 0.91 (s, 3H), 0.45 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 212.7, 152.0, 150.9, 131.1, 125.3, 111.4, 108.3, 69.0, 56.3, 55.8, 42.5, 41.2, 39.0, 38.7, 34.2, 32.3, 31.6, 23.1, 20.5.

HRMS (ESI-TOF): calculated for $C_{19}H_{27}O_3^+$ ([M+H]$^+$) m/z: 303.1955; Found 303.1953.

Synthesis of Compound 14[4]

10-hydroxy-5,8-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one



A mixture of ketone **10a** (1.68 g, 5.6 mmol), I_2 (1.55 g, 6.1 mmol) and CuO (220 mg, 2.8 mmol) in DMSO (11 mL) was stirred at 60 ℃ under argon for 2 h and then at room temperature for another 1 h. The reaction was quenched with water and $Na_2S_2O_3$ (aq.). The resulting mixture was extracted with EtOAc. Then, the organic layer was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 20:1 – 3:1) to afford compound **14** (1.46 g, 83%).

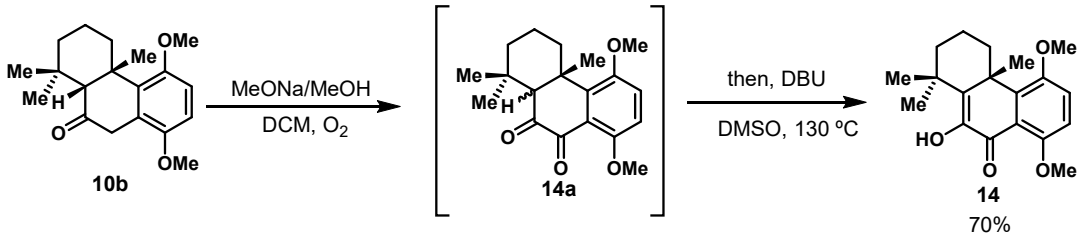
Physical State: yellow solid.

Melting Point: 96 – 98 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.40 (s, 1H), 7.09 (d, *J* = 9.1 Hz, 1H), 6.88 (d, *J* = 9.1 Hz, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 2.97 – 2.89 (m, 1H), 1.98 (td, *J* = 12.7, 5.2 Hz, 1H), 1.82 (m, 1H), 1.64 (s, 3H), 1.61 – 1.57 (m, 2H), 1.45 (s, 6H), 1.41 (dt, *J* = 13.5, 4.8 Hz, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 179.9, 154.6, 150.8, 144.7, 143.3, 141.3, 117.9, 117.6, 110.4, 56.7, 56.0, 41.6, 36.6, 36.5, 31.3, 28.1, 28.1, 27.4, 18.6.

HRMS (ESI-TOF): calculated for $C_{19}H_{25}O_4^+$ ([M+H]$^+$) m/z: 317.1747; Found 317.1744.



To a solution of ketone **10b** (703 mg, 2.3 mmol) in MeOH (10 mL) were added MeONa (30% in MeOH, 1.02 g, 2.5 equiv) and DCM (3 mL) under an atmosphere of O_2. After stirring at room temperature for 3 – 4 h, the starting material was converted to **14** and **14a** as indicated by TLC. The reaction was quenched with water and the resulting mixture was extracted with EtOAc for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was redissolved in DMSO (10 mL) and DBU (0.46 mL, 3.1 mmol) was added. After heated at 130 ℃ until the consumption of **14a** as indicated by TLC analysis, the reaction was cooled to room temperature and diluted with water. The mixture was extracted with EtOAc, and the organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography on silica gel to afford compound **14** (518 mg, 70%).

Compound 14a:

Physical State: yellow solid.

Melting Point: 146 – 150 ℃.

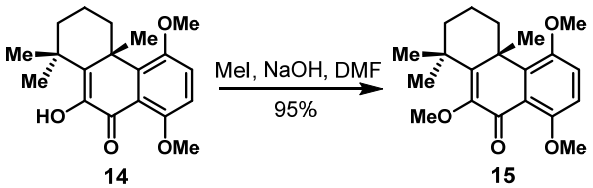
^{1}H NMR (600 MHz, Chloroform-*d*): 7.17 (d, *J* = 9.1 Hz, 1H), 6.90 (d, *J* = 9.1 Hz, 1H), 3.86 (s, 3H), 3.82 (s, 3H), 3.43 – 3.37 (m, 1H), 2.37 (s, 1H), 1.61 – 1.54 (m, 1H), 1.41 – 1.32 (m, 1H), 1.41 – 1.32 (m, 2H), 1.26 (s, 3H), 1.05 (td, *J* = 13.7, 2.9 Hz, 1H), 0.99 (s, 3H), 0.45 (s, 3H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 198.2, 180.6, 156.6, 151.0, 138.0, 125.3, 120.8, 111.7, 68.6, 56.7, 56.6, 42.3, 40.2, 39.2, 36.1, 35.3, 31.9, 24.8, 20.3.

HRMS (ESI-TOF): calculated for $C_{19}H_{25}O_4^+$ ($[M+H]^+$) m/z: 317.1747; Found 317.1747.

Synthesis of Compound 15

5,8,10-trimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one



To a solution of enol **14** (1.57 g, 5.0 mmol) and NaOH (600 mg, 15 mmol) in DMF (43 mL) was added MeI (0.9 mL, 15 mmol). After stirring at room temperature overnight, the reaction was diluted with water. The resulting mixture was then extracted with Et_2O for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography on silica gel to afford compound **15** (1.56 g, 95%).

Physical State: white solid.

Melting Point: 114 – 115 ℃.

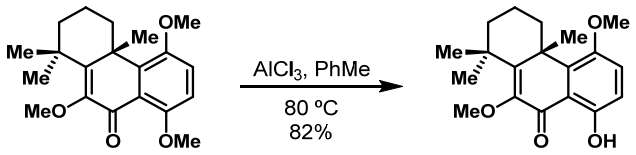
^{1}H NMR (600 MHz, Chloroform-*d*): δ 7.02 (d, *J* = 9.0 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H), 2.98 – 2.90 (m, 1H), 1.94 (td, *J* = 12.7, 5.2 Hz, 1H), 1.84 – 1.75 (m, 1H), 1.62 – 1.58 (m, 5H), 1.41 (s, 3H), 1.40 (s, 3H), 1.39 – 1.34 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 181.0, 154.1, 153.9, 150.6, 149.8, 142.8, 121.7, 116.5, 110.9, 59.0, 56.9, 56.0, 42.2, 37.4, 37.0, 31.5, 29.6, 29.1, 28.1, 18.5.

HRMS (ESI-TOF): calculated for $C_{20}H_{27}O_4^+$ ($[M+H]^+$) m/z: 331.1904; Found 331.1901.

Synthesis of Compound S3

8-hydroxy-5,10-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one



15 **S3**

A mixture of compound **15** (107 mg, 0.32 mmol) and $AlCl_3$ (45 mg, 0.34 mmol) in toluene (3.2 mL) was stirred at 80 ℃ for 2 – 3 h before cooled to room temperature and quenched with water. The resulting mixture was then extracted with EtOAc for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography on silica gel to afford compound **S3** (84 mg, 82%).

Physical State: yellow oil.

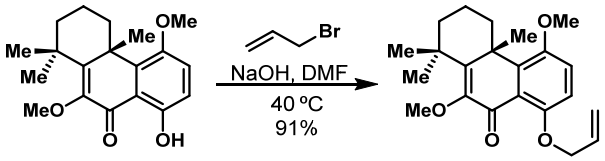
^{1}H NMR (600 MHz, Chloroform-*d*): δ 12.76 (s, 1H), 7.10 (d, *J* = 9.0 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.04 – 2.94 (m, 1H), 2.03 (td, *J* = 13.1, 6.1 Hz, 1H), 1.90 – 1.79 (m, 1H), 1.65 – 1.60 (m, 5H), 1.43 (s, 3H), 1.43 (s, 3H), 1.42 – 1.38 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 186.6, 161.7, 156.2, 148.8, 148.1, 140.8, 120.5, 115.1, 114.8, 59.9, 56.4, 43.0, 37.6, 36.9, 30.2, 29.4, 29.1, 27.5, 17.9.

HRMS (ESI-TOF): calculated for $C_{19}H_{25}O_4^+$ ($[M+H]^+$) m/z: 317.1747; Found 317.1751.

Synthesis of Compound 16

8-(allyloxy)-5,10-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one



S3 **16**

To a solution of compound **S3** (189 mg, 0.6 mmol) and NaOH (75 mg, 1.88 mmol) in DMF (2.4 mL) was added allyl bromide (0.16 mL, 1.85 mmol). After stirring at 40 ℃ overnight, the reaction was cooled to room temperature and diluted with water. The resulting mixture was then extracted with Et_2O for 3 times. After removal of the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel to afford compound **16** (192 mg, 91%).

Physical State: pale yellow solid.

Melting Point: 102 – 105 ℃.

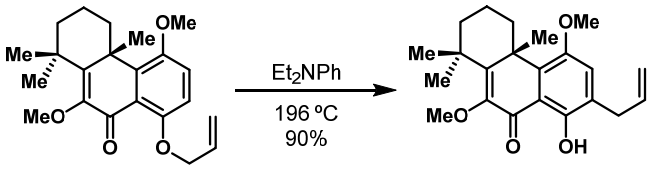
^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.98 (d, *J* = 8.8 Hz, 1H), 6.86 (d, *J* = 9.0 Hz, 1H), 6.17 – 6.03 (m, 1H), 5.54 (d, *J* = 17.3 Hz, 1H), 5.27 (d, *J* = 10.6 Hz, 1H), 4.60 (qd, *J* = 13.3, 5.1, 2H), 3.83 (s, 3H), 3.78 (s, 3H), 3.01 – 2.87 (m, 1H), 1.94 (td, *J* = 12.9, 5.5 Hz, 1H), 1.86 – 1.74 (m, 1H), 1.65 – 1.57 (m, 5H), 1.44 – 1.33 (m, 7H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.8, 154.1, 152.6, 150.9, 149.8, 142.6, 133.8, 122.4, 117.3, 116.2, 113.5, 71.1, 58.9, 55.9, 42.2, 37.3, 37.0, 31.4, 29.6.

HRMS (ESI-TOF): calculated for $C_{22}H_{29}O_4^+$ ($[M+H]^+$) m/z: 357.2066; Found 357.2065.

Synthesis of Compound S4

7-allyl-8-hydroxy-5,10-dimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one



16 **S4**

Compound **16** (183 mg, 0.5 mmol) was dissolved in 5 mL $PhNEt_2$, and stirred at 196 ℃ under argon. After 7 h, the reaction was cooled to room temperature. Water and 6 M HCl were added successively. The resulting mixture was extracted with EtOAc, and the organic layer was dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography on silica gel to afford compound **S4** (165 mg, 90%).

Physical State: pale yellow oil.

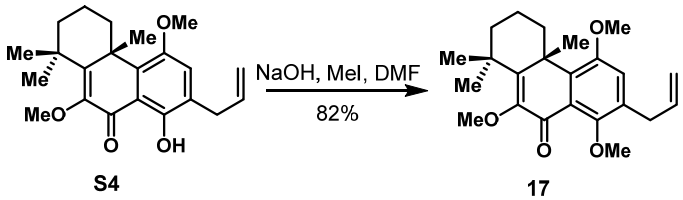
^{1}H NMR (600 MHz, Chloroform-*d*): δ 13.07 (s, 1H), 6.99 (s, 1H), 6.02 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.16 – 5.06 (m, 2H), 3.83 (s, 3H), 3.82 (s, 3H), 3.49 – 3.35 (m, 2H), 3.03 – 2.92 (m, 1H), 2.02 (td, *J* = 13.0, 5.9 Hz, 1H), 1.86 – 1.82 (m, 1H), 1.65 – 1.59 (m, 5H), 1.42 (s, 6H), 1.41 – 1.37 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 186.8, 161.5, 153.9, 148.3, 148.2, 138.7, 136.4, 126.1, 121.1, 116.2, 114.4, 59.9, 56.4, 42.7, 37.5, 37.0, 33.5, 30.3, 29.4, 29.1, 27.7, 17.9.

HRMS (ESI-TOF): calculated for $C_{22}H_{29}O_4^+$ ([M+H]$^+$) m/z: 357.2066; Found 357.2063.

Synthesis of Compound 17

7-allyl-5,8,10-trimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one



S4 **17**

To a solution of enol **S4** (56 mg, 0.16 mmol) and NaOH (20 mg, 0.5 mmol) in DMF (0.64 mL) was added MeI (0.03 mL, 0.18 mmol). After stirring at room temperature overnight, additional NaOH (9 mg) and MeI (0.03 mL) was added. After consumption of the starting material as indicated by TLC, the reaction was diluted with water. The resulting mixture was then extracted with Et_2O for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography on silica gel to afford compound **17** (48 mg, 82%).

Physical State: orange solid.

Melting Point: 81– 83 ℃.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.90 (s, 1H), 5.97 (ddt, *J* = 16.8, 10.1, 6.7 Hz, 1H), 5.20 – 5.04 (m, 2H), 3.84 (s, 3H), 3.78 (s, 3H), 3.78 (s, 3H), 3.45 (qdt, *J* = 15.4, 6.6, 1.6 Hz, 2H), 2.99 – 2.83 (m, 1H), 1.95 (td, *J* = 12.8, 5.4 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.65 – 1.54 (m, 5H), 1.42 (s, 3H), 1.41 (s, 3H), 1.39 – 1.34 (m, 1H).

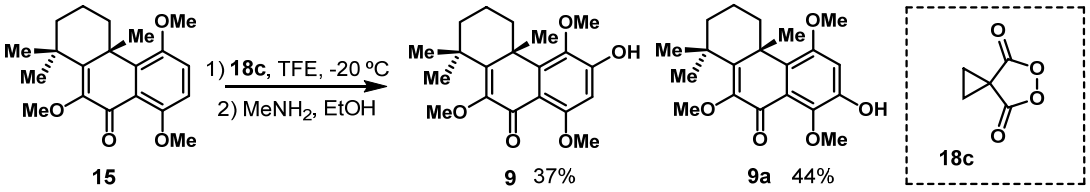
^{13}C NMR (101 MHz, Chloroform-*d*): δ 181.0, 155.1, 152.5, 151.2, 149.9, 140.5, 137.0, 132.8, 124.9, 117.3, 116.4, 62.2, 58.9, 55.8, 42.1, 37.3, 37.0, 33.8, 31.4, 29.5, 29.1, 28.2, 18.4.

HRMS (ESI-TOF): calculated for $C_{23}H_{31}O_4^+$ ([M+H]$^+$) m/z: 371.2217; Found 371.2225.

Synthesis of Compound 9 and 9a

6-hydroxy-5,8,10-trimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one (Compound 9)

7-hydroxy-5,8,10-trimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one (Compound 9a)



A mixture of compound **15** (330 mg, 1 mmol) and malonoyl peroxide **18c** (257 mg, 2 mmol) in TFE (5 mL) was stirred at -20 ℃ under argon for 12 h. Solvent was removed under reduced pressure and the residue was dissolved in EtOAc. $Na_2S_2O_5$ (aq.) was added and the resulting mixture was stirred at room temperature for 1 h. The mixture was then extracted with EtOAc, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was dissolved in EtOH, and excess $MeNH_2$ in EtOH was added. After stirring at room temperature for 2 h, solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 3:1 – 1:1) to afford compound **9** (129 mg, 37%) and compound **9a** (153 mg, 44%).

Compound 9:

Physical State: brown solid.

Melting Point: 250 ℃.

^{1}H NMR (400 MHz, DMSO-*d*$_6$): δ 10.33 (s, 1H), 6.55 (s, 1H), 3.76 (s, 3H), 3.69 (s, 3H), 3.60 (s, 3H), 2.89 – 2.78 (m, 1H), 1.90 (td, *J* = 12.6, 4.8 Hz, 1H), 1.76 (dt, *J* = 13.9, 4.5 Hz, 1H), 1.63 – 1.50 (m, 5H), 1.37 – 1.29 (m, 7H).

^{13}C NMR (151 MHz, DMSO-*d*$_6$): δ 178.1, 156.2, 155.2, 150.5, 149.0, 146.8, 138.3, 112.0, 100.0, 59.6, 58.2, 55.7, 41.5, 36.7, 36.0, 32.2, 29.8, 29.2, 28.9, 18.0.

HRMS (ESI-TOF): calculated for $C_{20}H_{26}NaO_5^+$ ([M+Na]$^+$) m/z: 369.1672; Found 369.1669.

Compound 9a:

Physical State: yellow solid.

Melting Point: 148 – 150 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.78 (s, 1H), 6.05 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.79 (s, 3H), 2.95 – 2.88 (m, 1H), 1.97 (td, *J* = 12.5, 5.0 Hz, 1H), 1.84 – 1.76 (m, 1H), 1.63 – 1.57 (m, 5H), 1.42 (s, 3H), 1.41 (s, 3H), 1.40 – 1.35 (m, 1H).

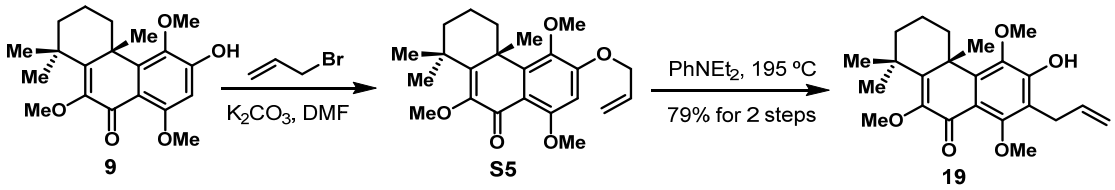
^{13}C NMR (151 MHz, Chloroform-*d*): δ 180.8, 157.0, 153.4, 149.6, 148.4, 139.0, 133.7, 124.1, 104.1, 62.2, 59.2, 55.8, 42.1, 37.2, 37.1, 31.2, 29.4, 29.2, 28.2, 18.3.

HRMS (ESI-TOF): calculated for $C_{20}H_{27}O_5^+$ ([M+H]$^+$) m/z: 347.1853; Found 347.1854.

Synthesis of Compound S5 and 19

6-(allyloxy)-5,8,10-trimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one (Compund S5)

7-allyl-6-hydroxy-5,8,10-trimethoxy-1,1,4a-trimethyl-2,3,4,4a-tetrahydrophenanthren-9(1H)-one (Compound 19)



To a solution of phenol **9** (41 mg, 0.12 mmol) and K_2CO_3 (35 mg, 0.25 mmol) in DMF (2 mL) was added allyl bromide (0.02 mL, 0.23 mmol). After stirring at room temperature overnight, the reaction was diluted with water. The resulting mixture was then extracted with EtOAc for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, concentrated, and purified by flash column chromatography on silica gel to afford compound **S5**. Compound **S5** was dissolved in $PhNEt_2$ (2 mL) and stirred at 195 ℃ under argon for 8 h. After cooling to room temperature, the reaction was diluted with water. 6 M HCl was added and the resulting mixture was extracted with EtOAc. The organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash column chromatography on silica gel to afford compound **19** (36 mg, 79%).

Compound S5:

Physical State: colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.52 (s, 1H), 6.09 (ddt, *J* = 17.4, 10.5, 5.3 Hz, 1H), 5.46 (dq, *J* = 17.3, 1.6 Hz, 1H), 5.34 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.64 (dt, *J* = 5.0, 1.5 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.78 (s, 3H), 2.91 (ddd, *J* = 13.3, 8.8, 7.3 Hz, 1H), 1.94 (td, *J* = 13.0, 4.9 Hz, 1H), 1.82 (ddq, *J* = 13.6, 8.9, 4.2 Hz, 1H), 1.74 – 1.63 (m, 2H), 1.62 (s, 3H), 1.41 (s, 3H), 1.39 (s, 3H), 1.38 – 1.33 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.2, 157.0, 155.8, 152.8, 149.8, 147.6, 140.4, 132.7, 118.4, 114.3, 97.9, 69.7, 60.8, 59.1, 56.8, 42.5, 37.5, 36.9, 33.0, 29.9, 29.6, 29.2, 18.6.

HRMS (ESI-TOF): calculated for $C_{23}H_{31}O_5^+$ ([M+H]$^+$) m/z: 387.2166; Found 387.2169.

Compound 19:

Physical State: white solid.

Melting Point: 134 – 138 ℃.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 6.00 (ddd, *J* = 16.5, 10.3, 5.5 Hz, 1H), 5.80 (s, 1H), 5.15 – 5.05 (m, 2H), 3.84 (s, 3H), 3.80 (s, 3H), 3.76 (s, 3H), 3.50 (d, *J* = 6.1 Hz, 2H), 2.88 (dt, *J* = 14.5, 7.7 Hz, 1H), 1.91 (td, *J* = 12.7, 4.8 Hz, 1H), 1.83 (ddq, *J* = 13.6, 9.6, 5.1 Hz, 1H), 1.74 (dt, *J* = 13.8, 7.1 Hz, 1H), 1.66 (dt, *J* = 12.8, 6.1 Hz, 1H), 1.62 (s, 3H), 1.41 (s, 3H), 1.40 (s, 3H), 1.39 – 1.36 (m, 1H).

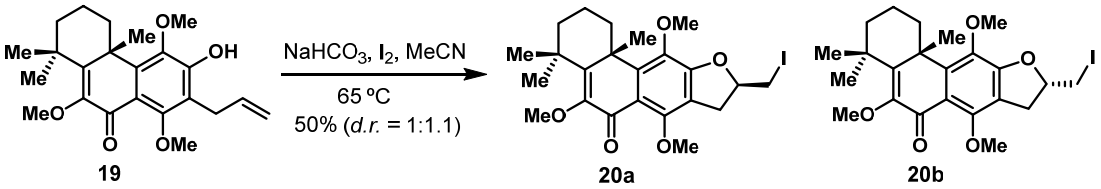
^{13}C NMR (151 MHz, Chloroform-*d*): δ 180.0, 155.6, 152.9, 152.6, 150.1, 145.2, 141.2, 136.3, 120.4, 117.9, 116.0, 62.5, 61.2, 58.9, 42.3, 37.8, 36.7, 33.0, 31.0, 29.8, 29.1, 28.2, 18.4.

HRMS (ESI-TOF): calculated for $C_{23}H_{31}O_5^+$ ([M+H]$^+$) m/z: 387.2166; Found 387.2165.

Synthesis of Compound 20a and 20b

(±)-(9R,11bR)-9-(iodomethyl)-5,7,11-trimethoxy-4,4,11b-trimethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one (Compound 20a)

(±)-(9S,11bR)-9-(iodomethyl)-5,7,11-trimethoxy-4,4,11b-trimethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one (Compound 20b)



A mixture of compound **19** (10 mg, 0.026 mmol), I_2 (13 mg, 0.05 mmol), $NaHCO_3$ (3.4 mg, 0.04 mmol) in MeCN (0.5 mL) was stirred at 65 °C under argon. After consumption of the starting material as indicated by TLC, the reaction was cooled to room temperature, diluted with water. The mixture was extracted with EtOAc and the organic layer was washed with $Na_2S_2O_3$ (aq.) and dried over anhydrous Na_2SO_4. After removal of the solvent under reduced pressure, purification by flash column chromatography on silica gel afforded **20a** (3.2 mg, 24%) and **20b** (3.4 mg, 26%).

Compound 20a:

Physical State: white solid.

Melting Point: 112 °C.

^{1}H NMR (600 MHz, Chloroform-*d*): δ 5.04 – 4.93 (m, 1H), 3.91 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 3.50 – 3.36 (m, 3H), 3.14 – 3.09 (m, 1H), 2.93 – 2.83 (m, 1H), 1.96 (t, *J* = 13.5 Hz, 1H), 1.86 – 1.77 (m, 1H), 1.66 – 1.59 (m, 5H), 1.41 (s, 3H), 1.40 (s, 3H), 1.38 – 1.34 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 180.1, 155.4, 153.8, 152.6, 149.6, 147.2, 137.6, 119.7, 118.6, 83.4, 61.0, 59.8, 59.1, 42.8, 37.3, 36.9, 33.6, 32.3, 29.5, 29.4, 29.2, 18.4, 8.5.

HRMS (ESI-TOF): calculated for $C_{23}H_{30}IO_5^+$ ([M+H]$^+$) m/z: 513.1132; Found 513.1142.

Compound 20b:

Physical State: white solid.

Melting Point: 123 – 126 ℃.

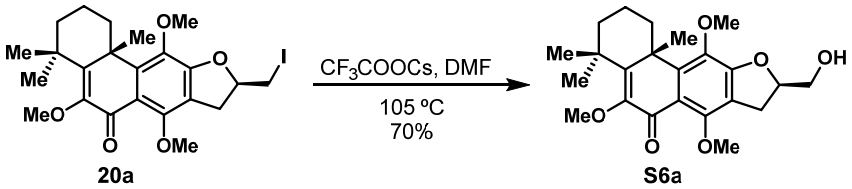
^{1}H NMR (600 MHz, Chloroform-*d*): δ 4.99 – 4.90 (m, 1H), 3.92 (s, 3H), 3.86 (s, 3H), 3.77 (s, 3H), 3.52 – 3.42 (m, 3H), 3.05 (dd, *J* = 16.1, 5.2 Hz, 1H), 2.93 – 2.79 (m, 1H), 1.99 – 1.91 (m, 1H), 1.86 – 1.79 (m, 1H), 1.72 (td, *J* = 9.9, 4.4 Hz, 1H), 1.64 – 1.60 (m, 4H), 1.43 (s, 3H), 1.41 – 1.35 (m, 4H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 180.1, 155.6, 153.8, 152.6, 149.8, 147.4, 137.5, 119.8, 118.4, 83.2, 61.0, 59.8, 59.0, 42.8, 37.4, 37.0, 33.8, 32.6, 29.9, 29.5, 29.2, 18.7, 8.9.

HRMS (ESI-TOF): calculated for $C_{23}H_{30}IO_5^+$ ([M+H]$^+$) m/z: 513.1132; Found 513.1140.

Synthesis of Compound S6a

(±)-(9R,11bR)-9-(hydroxymethyl)-5,7,11-trimethoxy-4,4,11b-trimethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one



20a S6a

A mixture of iodide **20a** (12.4 mg, 0.02 mmol) and CF_3COOCs (47 mg, 0.19 mmol) in DMF (1.6 mL) was stirred at 105 ℃ under argon. After 6 h, the starting material was consumed as indicated by TLC and water (0.04 mL) was added at 105 ℃ and stirring for 5 min. After cooling to room temperature, the reaction was diluted with brine and extracted with Et_2O for 3 times. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give compound **S6a** (6.8 mg, 70%).

Physical State: white solid.

Melting Point: 89 – 92 ℃.

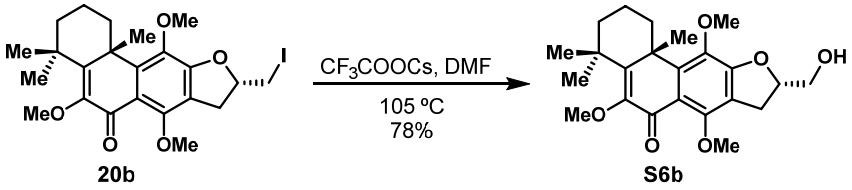
^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.04 (dtd, *J* = 9.8, 6.6, 3.5 Hz, 1H), 3.91 – 3.82 (m, 7H), 3.80 – 3.75 (m, 4H), 3.29 (dd, *J* = 15.8, 9.5 Hz, 1H), 3.10 (dd, *J* = 15.9, 7.0 Hz, 1H), 2.86 (ddd, *J* = 12.7, 8.9, 7.0 Hz, 1H), 1.94 (td, *J* = 13.1, 4.9 Hz, 1H), 1.86 – 1.76 (m, 1H), 1.74 – 1.58 (m, 5H), 1.42 (s, 3H), 1.39 – 1.34 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.1, 155.9, 153.8, 152.7, 149.7, 147.2, 137.6, 120.5, 118.2, 85.3, 64.8, 60.9, 59.6, 59.1, 42.8, 37.4, 36.9, 32.5, 29.8, 29.5, 29.1, 28.9, 18.6.

HRMS (ESI-TOF): calculated for $C_{23}H_{31}O_6^+$ ([M+H]$^+$) m/z: 403.2215; Found 403.2214.

Synthesis of Compound S6b

(±)-(9S,11bR)-9-(hydroxymethyl)-5,7,11-trimethoxy-4,4,11b-trimethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one



A mixture of iodide **20b** (6.7 mg, 0.01 mmol) and CF_3COOCs (27.8 mg, 0.11 mmol) in DMF (0.8 mL) was stirred at 105 °C under argon. After 6 h, the starting material was consumed as indicated by TLC. After cooling to room temperature, the reaction was quenched with brine and the mixture was extracted with Et_2O for 3 times. The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to give compound **S6b** (4.1 mg, 78%).

Physical State: colorless oil.

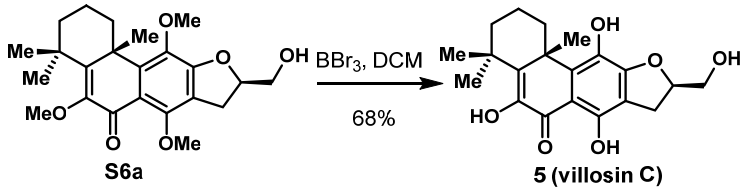
^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.03 (dddd, *J* = 9.3, 7.5, 5.7, 3.3 Hz, 1H), 3.93 – 3.98 (m, 4H), 3.84 (s, 3H), 3.80 – 3.75 (m, 4H), 3.33 (dd, *J* = 15.8, 9.4 Hz, 1H), 3.08 (dd, *J* = 15.8, 7.4 Hz, 1H), 2.93 – 2.83 (m, 1H), 1.94 (td, *J* = 13.1, 5.3 Hz, 2H), 1.86 – 1.76 (m, 1H), 1.70 – 1.54 (m, 5H), 1.40 (s, 3H), 1.40 – 1.33 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 180.2, 155.9, 153.7, 152.7, 149.6, 147.2, 137.6, 120.6, 118.2, 85.3, 64.8, 60.9, 59.6, 59.1, 42.7, 37.3, 36.9, 32.3, 29.5, 29.5, 29.2, 28.9, 18.4.

HRMS (ESI-TOF): calculated for $C_{23}H_{31}O_6^+$ ($[M+H]^+$) m/z: 403.2215; Found 403.2212.

Synethesis of Compound 5 (villosin C)

(±)-(9R,11bR)-5,7,11-trihydroxy-9-(hydroxymethyl)-4,4,11b-trimethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one



To a solution of compound **S6a** (13.7 mg, 0.03 mmol) in DCM (0.4 mL) was added BBr_3 (0.15 mmol, dissolved in 0.15 mL DCM) at room temperature under argon. After consumption of the starting material as indicated by TLC, the reaction was quenched with water. The resulting

mixture was then extracted with EtOAc for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford villosin C (**5**, 8.4 mg, 68%).

Physical State: yellow solid.

Melting Point: 72 – 76 °C.

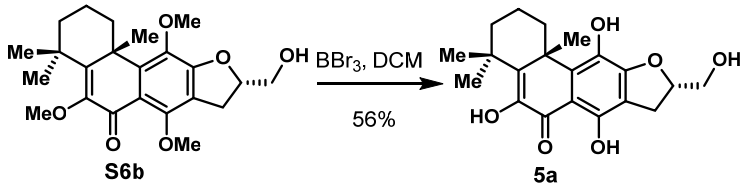
^{1}H NMR (600 MHz, Chloroform-*d*): δ 12.58 (s, 1H), 6.92 (s, 1H), 5.13 (dtd, *J* = 9.8, 6.9, 3.1 Hz, 1H), 4.98 (s, 1H), 3.92 (dd, *J* = 12.2, 3.2 Hz, 1H), 3.83 (dd, *J* = 12.2, 6.6 Hz, 1H), 3.32 (dd, *J* = 15.4, 9.5 Hz, 1H), 3.10 – 3.04 (m, 2H), 2.01 (td, *J* = 13.3, 5.4 Hz, 2H), 1.90 – 1.83 (m, 1H), 1.69 – 1.64 (m, 5H), 1.45 (s, 3H), 1.43 (s, 3H), 1.42 – 1.40 (m, 1H).

^{13}C NMR (126 MHz, Chloroform-*d*): δ 183.0, 154.4, 153.4, 144.4, 141.7, 140.1, 130.8, 110.5, 107.2, 86.6, 64.9, 42.0, 36.7, 36.4, 29.9, 28.9, 28.1, 27.5, 27.2, 17.8.

HRMS (ESI-TOF): calculated for $C_{20}H_{25}O_6^+$ ($[M+H]^+$) m/z: 361.1646; Found 361.1647.

Synethesis of Compound 5a

(±)-(9S,11bR)-5,7,11-trihydroxy-9-(hydroxymethyl)-4,4,11b-trimethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one



To a solution of compound **S6b** (7.2 mg, 0.02 mmol) in DCM (0.5 mL) was added BBr_3 (0.18 mmol, dissolved in 0.18 mL DCM, 9.0 equiv) at 0 °C under argon. After 2 – 3 h, the reaction was warmed up to room temperature. After consumption of the starting material as indicated by TLC, the reaction was quenched with water. The resulting mixture was then extracted with EtOAc for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford to 16-*epi*-villosin C (**5a**, 3.6 mg, 56%).

Physical State: yellow soild.

Melting Point: 45 – 50 °C.

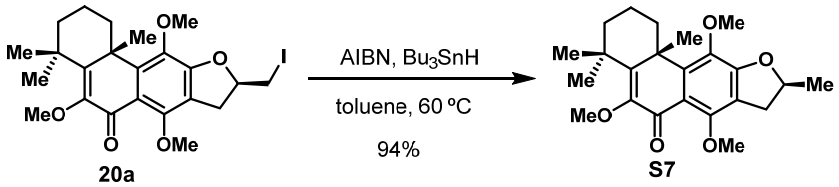
^{1}H NMR (400 MHz, Chloroform-*d*): δ 12.59 (s, 1H), 6.92 (s, 1H), 5.12 (dtd, *J* = 10.0, 7.0, 3.1 Hz, 1H), 4.99 (s, 1H), 3.91 (dd, *J* = 12.2, 3.1 Hz, 1H), 3.82 (dd, *J* = 12.2, 6.8 Hz, 1H), 3.32 (dd, *J* = 15.5, 9.5 Hz, 1H), 3.11 – 3.00 (m, 2H), 2.01 (td, *J* = 12.9, 5.8 Hz, 1H), 1.91 – 1.80 (m, 1H), 1.71 – 1.64 (m, 5H), 1.44 (s, 3H), 1.43 (s, 3H), 1.42 – 1.39 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*): δ 183.1, 154.4, 153.4, 144.5, 141.7, 140.2, 130.8, 110.6, 107.3, 86.6, 65.0, 42.0, 36.7, 36.4, 29.9, 28.9, 28.1, 27.4, 27.2, 17.8.

HRMS (ESI-TOF): calculated for $C_{20}H_{23}O_6^-$ ([M-H]$^-$) m/z: 359.1495; Found 359.1496.

Synethesis of Compound S7

(±)-(9S,11bR)-5,7,11-trimethoxy-4,4,9,11b-tetramethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one



20a S7

To a solution of compound **20a** (5.8 mg, 0.01 mmol) and AIBN (2 mg, 0.01 mmol) in toluene (0.6 mL) was added Bu_3SnH (9 μL, 0.03 mmol). After stirring at 60 °C overnight, the reaction was quenched with water. The resulting mixture was then extracted with EtOAc for 3 times. The combined organic phases were washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel to afford compound **S7** (4.1 mg, 94%)

Physical State: colorless oil.

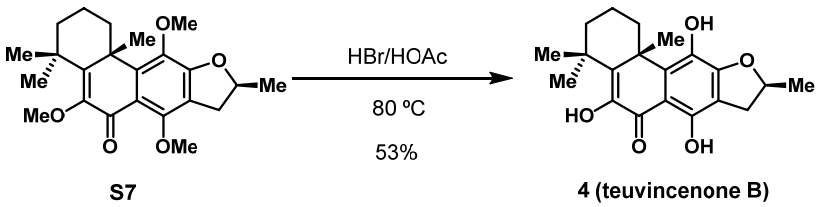
^{1}H NMR (600 MHz, Chloroform-*d*): δ 5.09 – 5.02 (m, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.77 (s, 3H), 3.37 (dd, *J* = 15.5, 8.9 Hz, 1H), 2.92 – 2.86 (m, 2H), 1.95 (td, *J* = 13.0, 5.0 Hz, 1H), 1.85 – 1.78 (m, 1H), 1.70 – 1.61 (m, 5H), 1.50 (d, *J* = 6.4 Hz, 3H), 1.42 (s, 3H), 1.39 (s, 3H), 1.39 – 1.35 (m, 1H).

^{13}C NMR (151 MHz, Chloroform-*d*): δ 180.2, 156.2, 153.6, 152.8, 149.7, 147.0, 137.6, 120.8, 117.9, 81.8, 60.9, 59.5, 59.1, 42.7, 37.4, 36.9, 34.5, 32.4, 29.6, 29.5, 29.2, 22.1, 18.5.

HRMS (ESI-TOF): calculated for $C_{23}H_{31}O_5^+$ ([M+H]$^+$) m/z: 387.2166; Found 387.2165.

Synethesis of Compound 4 (teuvincenone B)

(9S,11bR)-5,7,11-trihydroxy-4,4,9,11b-tetramethyl-1,3,4,8,9,11b-hexahydrophenanthro[3,2-b]furan-6(2H)-one



S7 4 (teuvincenone B)

Compound **S7** (3.4 mg, 0.009 mmol) was dissolved in HBr (33% in HOAc, 0.3 mL) and stirred at 80 ℃. After 3 h, more HBr (33% in HOAc, 0.25 mL) was added, and the reaction was stirred for another 3 h before cooling to room temperature and quenched with aqueous $NaHCO_3$. The resulting mixture was extracted with EtOAc for 3 times. The organic layers were combined, washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by chromatography on silica gel to afford teuvincenone (**4**, 1.6 mg, 53%).

Physical State: yellow solid.

Melting Point: 189 – 192 ℃.

^{1}H NMR (500 MHz, Chloroform-*d*): δ 12.59 (s, 1H), 6.94 (s, 1H), 5.19 – 5.08 (m, 1H), 4.71 (s, 1H), 3.40 (dd, *J* = 15.3, 9.0 Hz, 1H), 3.09 – 3.01 (m, 1H), 2.88 (dd, *J* = 15.3, 7.4 Hz, 1H), 2.01 (td, *J* = 13.2, 6.2 Hz, 1H), 1.91 – 1.82 (m, 1H), 1.69 – 1.63 (m, 5H), 1.53 (d, *J* = 6.3 Hz, 3H), 1.45 (s, 3H), 1.43 (s, 3H), 1.42 – 1.39 (m, 1H).

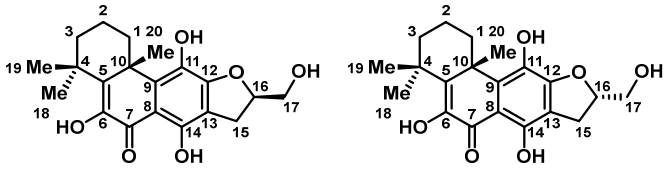
^{13}C NMR (126 MHz, Chloroform-*d*): δ 183.0, 154.8, 153.6, 144.0, 141.6, 139.6, 130.8, 110.8, 106.8, 83.4, 41.9, 36.6, 36.4, 34.5, 29.9, 28.1, 27.5, 27.2, 22.1, 17.8.

HRMS (ESI-TOF): calculated for $C_{20}H_{25}O_5^+$ ($[M+H]^+$) m/z: 345.1697; Found 345.1697.

4. Spectral Data Comparison of Natural Products with Synthetic Products

4.1 villosin C

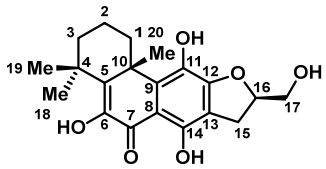
Table S4 ^{1}H NMR spectroscopic data of villosin C and compound 5a in $CDCl_3$ (δ in ppm, *J* in Hz)[5]



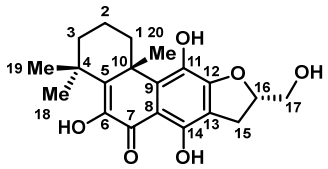
villosin C (5) 5a

No.	**5** (isolated)	**5** (synthetic)		**5a** (synthetic)	
	δ_H (500 MHz)	δ_H (600MHz)	$\Delta\delta_H$	δ_H (400 MHz)	$\Delta\delta_H$
1α	1.65, m	1.69 – 1.64, m	-	1.71 – 1.64, m	-
1β	3.07, m	3.10 – 3.04, m	-	3.11 – 3.00, m	-
2α	1.65, m	1.69 – 1.64, m	-	1.71 – 1.64, m	-
2β	1.87, m	1.90 – 1.83, m	-	1.91 – 1.80, m	-
3α	1.41, m	1.42 – 1.40, m	-	1.42 – 1.39, m	-
3β	2.01, td (13.0, 6.1)	2.01, td (13.3, 5.4)	0.00	2.01, td (12.9, 5.8)	0.00
15α	3.31, dd (15.5, 9.5)	3.32, dd (15.4, 9.5)	0.01	3.32, dd (15.5, 9.5)	0.01
15	3.03, m	3.10 – 3.04, m	-	3.11 – 3.00, m	-
16α	5.12, m	5.13, dtd (9.8, 6.9, 3.1)	0.01	5.12, dtd (10.0, 7.0, 3.1)	0.00
17a	3.82, dd (12.2, 6.7)	3.83, dd (12.2, 6.6)	0.01	3.82, dd (12.2, 6.8)	0.00
17b	3.91, dd (12.2, 2.9)	3.92, dd (12.2, 3.2)	0.01	3.91, dd (12.2, 3.1)	0.00
18	1.43, s	1.43, s	0.00	1.43, s	0.00
19	1.45, s	1.45, s	0.00	1.44, s	-0.01
20	1.66, s	1.69 – 1.64, m	-	1.71 – 1.64, m	-
6-OH	6.92, s	6.92, s	0.00	6.92, s	0.00
11-OH	5.12, s	4.98, s	-0.14	4.99, s	-0.13
14-OH	12.58, s	12.58, s	0.00	12.59, s	0.01

Table S5 ^{13}C NMR spectroscopic data of villosin C and compound 5a in $CDCl_3$ (δ in ppm)[5]



villosin C (5)

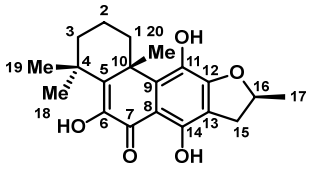


5a

No.	**5** (isolated)	**5** (synthetic)		**5a** (synthetic)	
	δ_C (125 MHz)	δ_C (126 MHz)	$\Delta\delta_C$	δ_C (101 MHz)	$\Delta\delta_C$
1	29.8	29.9	0.1	29.9	0.1
2	17.7	17.8	0.1	17.8	0.1
3	36.3	36.4	0.1	36.4	0.1
4	36.5	36.7	0.2	36.7	0.2
5	144.4	144.4	0.0	144.5	0.1
6	141.5	141.7	0.2	141.7	0.2
7	182.9	183.0	0.1	183.1	0.2
8	107.2	107.2	0.0	107.3	0.1
9	140.1	140.1	0.0	140.2	0.1
10	41.9	42.0	0.1	42.0	0.1
11	130.7	130.8	0.1	130.8	0.1
12	153.3	153.4	0.1	153.4	0.1
13	110.4	110.5	0.1	110.6	0.2
14	154.3	154.4	0.1	154.4	0.1
15	28.8	28.9	0.1	28.9	0.1
16	86.4	86.6	0.2	86.6	0.2
17	64.8	64.9	0.1	65.0	0.2
18	27.9	28.1	0.2	28.1	0.2
19	27.1	27.2	0.1	27.2	0.1
20	27.3	27.5	0.2	27.4	0.1

4.2 teuvincenone B

Table S6 ^{1}H NMR spectroscopic data of teuvincenone B in $CDCl_3$ (δ in ppm, *J* in Hz)[6]

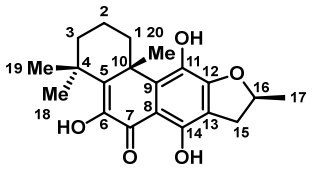


teuvincenone B (4)

No.	**4** (isolated)	**4** (synthetic)	
	δ_H (300 MHz)	δ_H (500MHz)	$\Delta\delta_H$
1α	[a]	1.69 – 1.63, m	-
1β	3.06, m	3.09 – 3.01, m	-
2α	[a]	1.69 – 1.63, m	-
2β	[a]	1.91 – 1.82, m	-
3α	[a]	1.42 – 1.39, m	-
3β	[a]	2.01, td (13.2, 6.2)	-
15α	3.40, dd (15.2, 9.1)	3.40, dd (15.3, 9.0)	0.00
15	2.88, dd (15.2, 7.3)	2.88, dd (15.3, 7.4)	0.00
16α	5.14, ddq (9.0, 7.3, 6.3)	5.19 – 5.08, m	-
17	1.53, d	1.53, d (6.3)	0.00
18	1.45, s	1.45, s	0.00
19	1.43, s	1.43, s	0.00
20	1.66, s	1.69 – 1.63, m	-
6-OH	6.94, s	6.94, s	0.00
11-OH	4.73, s	4.71, s	-0.02
14-OH	12.60, s	12.59, s	-0.01

[a] overlapped signal.

Table S7 ^{13}C NMR spectroscopic data of Teuvincenone B $CDCl_3$ (δ in ppm)[7-9]



teuvincenone B (4)

No.	**4** (isolated)[7]	**4** (isolated)[8]	**4** (isolated)[9]	**4** (synthetic)	
	δ_C (50 MHz)	δ_C (125 MHz)	δ_C (100 MHz)	δ_C (126 MHz)	$\Delta\delta_C$[9]
1	27.9	29.7	30.0	29.9	-0.1
2	17.6	17.7	17.9	17.8	-0.1
3	36.3	36.1	36.5	36.4	-0.1
4	36.5	27.5	36.7	36.6	-0.1
5	141.5	144.2	141.7	141.6	-0.1
6	143.9	143.5	144.1	144.0	-0.1
7	182.8	182.5	183.0	183.0	0.0
8	107.5	107.7	106.9	106.8	-0.1
9	139.5	141.2	139.7	139.6	-0.1
10	41.8	41.8	42.0	41.9	-0.1
11	130.7	130.7	130.9	130.8	-0.1
12	153.4	156.5	153.6	153.6	0.0
13	110.6	111.1	110.8	110.8	0.0
14	154.6	153.3	154.8	154.8	0.0
15	34.3	33.9	34.6	34.5	-0.1
16	83.2	81.7	83.4	83.4	0.0
17	22.0	21.5	22.2	22.1	-0.1
18	27.9	27.9	27.6[a]	27.5	-0.1
19	22.0	27.3	27.3[a]	27.2	-0.1
20	27.1	27.3	28.2[a]	28.1	-0.1

[a]The original reported chemical shifts in ref 9 for C-18, C-19 and C-20 were 28.2, 22.2 and 27.3 ppm, which were revised to 27.6, 27.3 and 28.2 ppm as told by Linzhen Li (first author of ref 9) though email communication.

5. HPLC Chromatographs

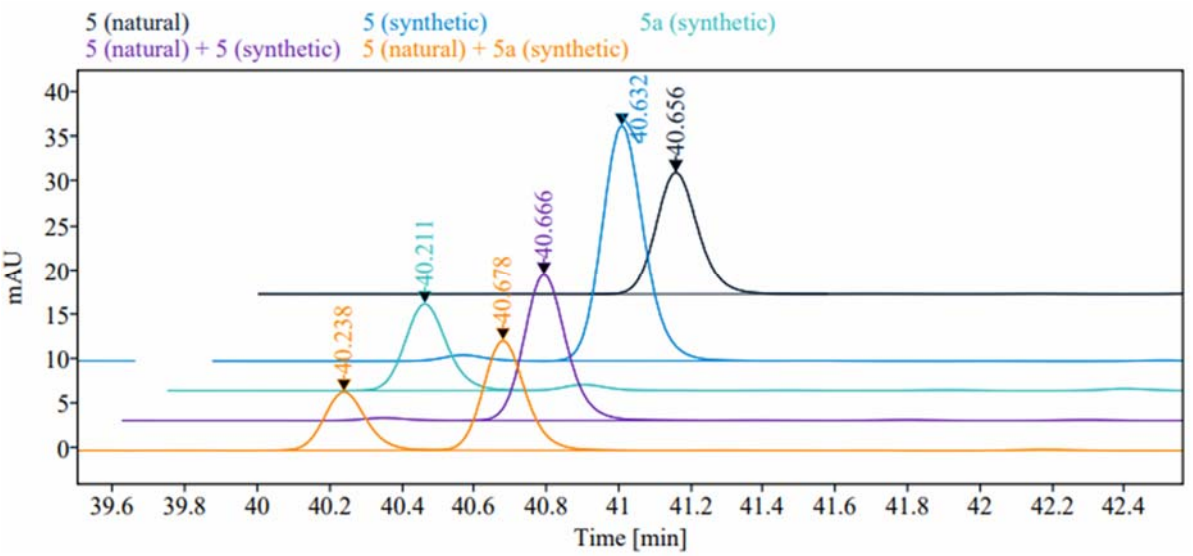


Figure S1 HPLC trace comparison

The identification of compound **5** and compound **5a** was determined by HPLC analysis on an Agilent 1260 LC/MS instrument, employing an InfinityLab Poroshell 120 column (EC-C18 2.7μm, 1000 bar, 3.0*150 mm). Experimental conditions: 5% – 70% MeCN in H_2O, v = 0.8 mL/min, λ = 254 nm.

6. X-Ray Crystallographic Data for Compound 20b

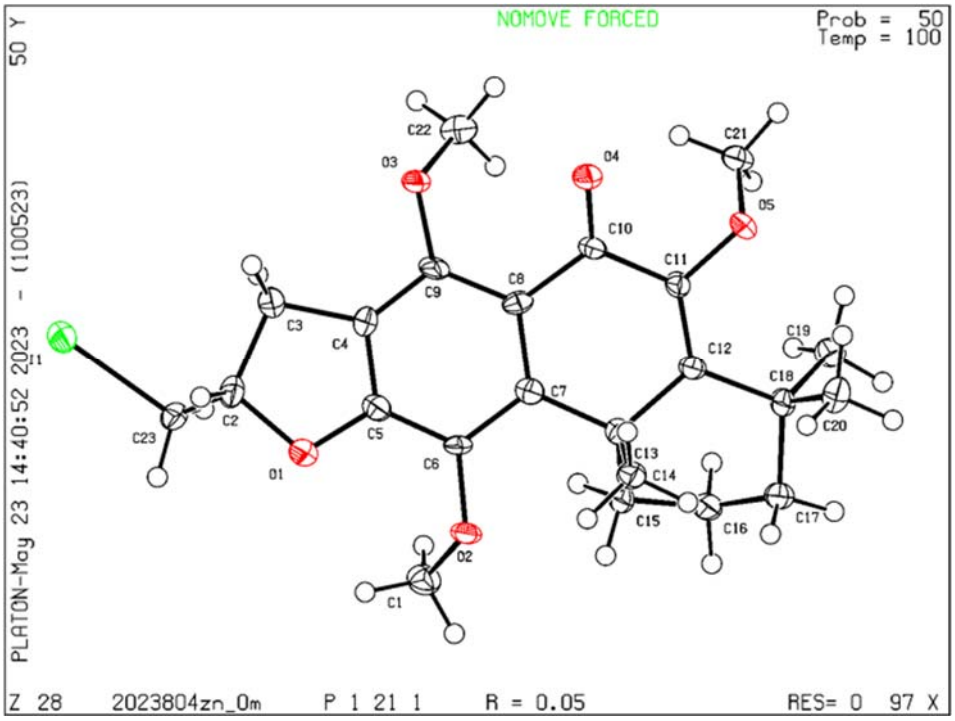


Figure S2 X-Ray Crystallographic Structure for Compound 20b

Table S8 Crystal data and structure refinement for 20b

Identification code	2023804zn_0m
Empirical formula	$C_{23}H_{29}IO_5$
Formula weight	512.36
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.1561(4)
b/Å	17.3244(10)
c/Å	10.0988(6)
α/°	90
β/°	102.522(2)
γ/°	90
Volume/Å^3	1051.42(11)
Z	2
ρ_{calc}g/cm^3	1.618
μ/mm^{-1}	12.232
F(000)	520.0
Crystal size/mm^3	0.12 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.97 to 148.918
Index ranges	-7 ⩽ h ⩽ 7, -21 ⩽ k ⩽ 21, -12 ⩽ l ⩽ 12

Reflections collected	11659
Independent reflections	4067 [R_{int} = 0.0889, R_{sigma} = 0.0936]
Data/restraints/parameters	4067/1/268
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0456, wR_2 = 0.1112
Final R indexes [all data]	R_1 = 0.0475, wR_2 = 0.1138
Largest diff. peak/hole / e Å^{-3}	1.13/-1.48
Flack parameter	0.086(8)

Table S9 Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2023804zn_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
I1	-2312.1(6)	2697.2(4)	-275.2(4)	25.47(17)
O3	4693(10)	3639(3)	4774(6)	23.1(12)
O2	6766(9)	5340(3)	530(6)	20.0(11)
C9	5345(14)	4076(4)	3779(9)	19.9(16)
O1	3553(10)	4134(3)	191(6)	26.1(12)
C4	4304(13)	3914(4)	2476(9)	22.3(16)
C5	4781(13)	4333(4)	1418(8)	20.2(16)
O4	8714(9)	4258(3)	6253(6)	22.5(12)
C14	11042(13)	5547(5)	2626(9)	22.1(16)
C6	6292(12)	4950(4)	1630(8)	18.2(15)
C18	11345(14)	6742(4)	5052(9)	21.8(16)
C23	-171(13)	3675(4)	-359(9)	22.7(16)
C19	10702(15)	7199(5)	6219(9)	26.5(17)
C17	10981(14)	7288(4)	3823(9)	24.8(17)
O5	10713(9)	5601(3)	7018(6)	21.3(11)
C22	4111(15)	4023(5)	5912(10)	27.8(18)
C15	7853(13)	6534(4)	2435(8)	21.1(15)
C16	8555(15)	7299(4)	3134(9)	24.6(17)
C3	2451(15)	3356(5)	1922(9)	28.5(18)
C7	7370(12)	5132(4)	2969(8)	18.6(15)
C2	2135(12)	3478(5)	377(9)	24.0(18)

Table S9 Fractional Atomic Coordinates (× 10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 2023804zn_0m. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C8	6971(13)	4668(4)	4042(9)	18.2(15)
C12	9936(13)	6007(4)	4709(8)	18.2(15)
C11	9648(12)	5508(4)	5676(8)	17.6(14)
C20	13854(14)	6519(5)	5506(11)	28.7(19)
C1	4896(14)	5687(5)	-368(9)	26.5(17)
C13	9004(12)	5812(4)	3207(8)	18.2(15)
C21	9231(14)	5652(5)	7940(9)	25.0(16)
C10	8437(13)	4761(4)	5395(8)	17.8(15)

Table S10 Anisotropic Displacement Parameters (Å^2×10^3) for 2023804zn_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I1	26.2(2)	28.8(2)	21.1(3)	-3.3(3)	4.46(18)	-3.9(3)
O3	36(3)	18(2)	14(3)	3(2)	4(2)	-6(2)
O2	24(3)	24(3)	13(3)	5(2)	5(2)	0(2)
C9	25(4)	18(4)	14(4)	8(3)	-1(3)	4(3)
O1	36(3)	25(3)	17(3)	0(2)	4(2)	-8(2)
C4	26(4)	18(3)	22(4)	-2(3)	3(3)	-7(3)
C5	28(4)	15(3)	16(4)	0(3)	3(3)	2(3)
O4	29(3)	19(3)	18(3)	4(2)	3(2)	-2(2)
C14	27(4)	23(4)	19(4)	-3(3)	10(3)	-4(3)
C6	24(4)	17(3)	13(4)	6(3)	4(3)	-1(3)
C18	31(4)	15(3)	18(4)	-2(3)	2(3)	-5(3)
C23	30(4)	18(3)	21(4)	-1(3)	7(3)	-7(3)
C19	38(4)	23(4)	21(4)	-5(3)	11(4)	-5(3)
C17	37(4)	20(4)	18(4)	0(3)	6(3)	-5(3)
O5	26(3)	24(3)	12(3)	-2(2)	2(2)	-3(2)

Table S10 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 2023804zn_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C22	33(4)	27(4)	26(5)	5(4)	11(4)	1(3)
C15	31(4)	13(3)	18(4)	-2(3)	2(3)	-3(3)
C16	42(5)	12(4)	18(4)	1(3)	3(4)	-2(3)
C3	36(4)	25(4)	21(4)	1(3)	-2(4)	-10(3)
C7	23(3)	16(3)	17(4)	0(3)	5(3)	3(3)
C2	26(4)	21(4)	25(5)	-5(3)	5(4)	-8(3)
C8	21(4)	14(3)	20(4)	7(3)	5(3)	3(3)
C12	23(4)	17(3)	14(4)	1(3)	4(3)	0(3)
C11	19(3)	15(3)	16(4)	2(3)	-1(3)	0(3)
C20	27(4)	25(4)	33(5)	-4(4)	5(4)	-7(3)
C1	32(4)	23(4)	23(4)	4(3)	2(4)	3(3)
C13	21(3)	16(3)	17(4)	0(3)	3(3)	2(3)
C21	33(4)	25(4)	16(4)	3(3)	4(3)	-2(3)
C10	22(3)	19(4)	12(4)	2(3)	4(3)	1(3)

Table S11 Bond Lengths for 2023804zn_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C23	2.159(7)	C18	C17	1.538(11)
O3	C9	1.385(10)	C18	C12	1.538(10)
O3	C22	1.439(11)	C18	C20	1.562(12)
O2	C6	1.384(9)	C23	C2	1.492(11)
O2	C1	1.434(10)	C17	C16	1.505(12)
C9	C4	1.362(11)	O5	C11	1.381(9)
C9	C8	1.417(11)	O5	C21	1.441(10)
O1	C5	1.349(10)	C15	C16	1.520(10)
O1	C2	1.470(10)	C15	C13	1.561(10)
C4	C5	1.376(12)	C3	C2	1.545(12)
C4	C3	1.507(11)	C7	C8	1.414(11)

Table S11 Bond Lengths for 2023804zn_0m.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C5	C6	1.402(10)	C7	C13	1.533(10)
O4	C10	1.214(10)	C8	C10	1.473(13)
C14	C13	1.565(10)	C12	C11	1.344(11)
C6	C7	1.406(11)	C12	C13	1.538(11)
C18	C19	1.540(11)	C11	C10	1.490(10)

Table S12 Bond Angles for 2023804zn_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O3	C22	119.2(6)	C4	C3	C2	101.9(7)
C6	O2	C1	115.6(6)	C6	C7	C8	119.0(7)
O3	C9	C8	124.3(8)	C6	C7	C13	118.7(7)
C4	C9	O3	116.0(7)	C8	C7	C13	122.2(7)
C4	C9	C8	119.7(8)	O1	C2	C23	106.6(7)
C5	O1	C2	108.1(6)	O1	C2	C3	106.7(6)
C9	C4	C5	120.4(7)	C23	C2	C3	115.6(7)
C9	C4	C3	130.6(8)	C9	C8	C10	121.2(7)
C5	C4	C3	108.8(7)	C7	C8	C9	120.1(8)
O1	C5	C4	114.0(7)	C7	C8	C10	118.4(7)
O1	C5	C6	123.8(7)	C18	C12	C13	118.4(6)
C4	C5	C6	122.0(8)	C11	C12	C18	121.7(7)
O2	C6	C5	119.8(7)	C11	C12	C13	119.7(7)
O2	C6	C7	121.7(7)	O5	C11	C10	113.6(6)
C5	C6	C7	118.5(7)	C12	C11	O5	121.9(7)
C19	C18	C20	107.7(8)	C12	C11	C10	124.0(7)
C17	C18	C19	106.5(6)	C15	C13	C14	111.2(6)
C17	C18	C20	110.5(7)	C7	C13	C14	105.5(6)
C12	C18	C19	111.8(7)	C7	C13	C15	109.0(6)
C12	C18	C17	110.6(7)	C7	C13	C12	114.5(6)
C12	C18	C20	109.5(6)	C12	C13	C14	106.1(6)

Table S12 Bond Angles for 2023804zn_0m.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C23	I1	108.9(5)	C12	C13	C15	110.4(6)
C16	C17	C18	109.7(7)	O4	C10	C8	123.1(7)
C11	O5	C21	114.1(6)	O4	C10	C11	120.0(7)
C16	C15	C13	114.5(7)	C8	C10	C11	116.9(6)
C17	C16	C15	111.0(7)				

Table S13 Torsion Angles for 2023804zn_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
I1	C23	C2	O1	175.3(5)	C19	C18	C12	C13	136.0(7)
I1	C23	C2	C3	-66.4(8)	C17	C18	C12	C11	-167.7(7)
O3	C9	C4	C5	177.9(7)	C17	C18	C12	C13	17.4(10)
O3	C9	C4	C3	3.4(13)	O5	C11	C10	O4	-10.7(10)
O3	C9	C8	C7	-173.9(7)	O5	C11	C10	C8	170.6(7)
O3	C9	C8	C10	12.6(12)	C22	O3	C9	C4	-130.2(8)
O2	C6	C7	C8	-174.1(6)	C22	O3	C9	C8	49.2(11)
O2	C6	C7	C13	3.7(11)	C16	C15	C13	C14	-97.4(8)
C9	C4	C5	O1	-177.1(7)	C16	C15	C13	C7	146.6(7)
C9	C4	C5	C6	-1.7(12)	C16	C15	C13	C12	20.0(9)
C9	C4	C3	C2	-179.8(9)	C3	C4	C5	O1	-1.5(10)
C9	C8	C10	O4	17.2(13)	C3	C4	C5	C6	173.8(7)
C9	C8	C10	C11	-164.1(7)	C7	C8	C10	O4	-156.4(7)
O1	C5	C6	O2	-7.0(12)	C7	C8	C10	C11	22.3(11)
O1	C5	C6	C7	176.0(7)	C2	O1	C5	C4	-3.3(9)
C4	C9	C8	C7	5.5(12)	C2	O1	C5	C6	-178.5(7)
C4	C9	C8	C10	-167.9(8)	C8	C9	C4	C5	-1.6(12)
C4	C5	C6	O2	178.1(7)	C8	C9	C4	C3	-176.1(8)
C4	C5	C6	C7	1.1(11)	C8	C7	C13	C14	108.9(8)
C4	C3	C2	O1	-7.0(8)	C8	C7	C13	C15	-131.5(7)

Table S13 Torsion Angles for 2023804zn_0m.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C4	C3	C2	C23	-125.3(8)	C8	C7	C13	C12	-7.3(10)
C5	O1	C2	C23	130.6(7)	C12	C18	C17	C16	40.8(9)
C5	O1	C2	C3	6.5(9)	C12	C11	C10	O4	161.3(7)
C5	C4	C3	C2	5.3(9)	C12	C11	C10	C8	-17.5(12)
C5	C6	C7	C8	2.8(11)	C11	C12	C13	C14	-103.1(8)
C5	C6	C7	C13	-179.4(6)	C11	C12	C13	C15	136.3(7)
C6	C7	C8	C9	-6.1(11)	C11	C12	C13	C7	12.9(10)
C6	C7	C8	C10	167.6(7)	C20	C18	C17	C16	162.3(7)
C6	C7	C13	C14	-68.8(8)	C20	C18	C12	C11	70.3(10)
C6	C7	C13	C15	50.7(9)	C20	C18	C12	C13	-104.6(8)
C6	C7	C13	C12	174.9(6)	C1	O2	C6	C5	58.7(9)
C18	C17	C16	C15	-69.7(9)	C1	O2	C6	C7	-124.4(8)
C18	C12	C11	O5	-4.2(11)	C13	C15	C16	C17	36.1(10)
C18	C12	C11	C10	-175.5(7)	C13	C7	C8	C9	176.1(7)
C18	C12	C13	C14	71.9(8)	C13	C7	C8	C10	-10.2(11)
C18	C12	C13	C15	-48.7(9)	C13	C12	C11	O5	170.6(6)
C18	C12	C13	C7	-172.1(6)	C13	C12	C11	C10	-0.7(11)
C19	C18	C17	C16	-80.9(8)	C21	O5	C11	C12	122.4(8)
C19	C18	C12	C11	-49.1(10)	C21	O5	C11	C10	-65.4(8)

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2023804zn_0m.

Atom	*x*	*y*	*z*	U(eq)
H14A	10548.91	5434.07	1656.48	33
H14B	11694.47	5081.04	3103.92	33
H14C	12159.25	5958.5	2754.46	33
H23A	-179.42	3803.65	-1314.81	27
H23B	-714.68	4129.67	67.62	27
H19A	11422.93	7705.92	6294.75	40

Table S14 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 2023804zn_0m.

Atom	*x*	*y*	*z*	U(eq)
H19B	11191	6914.97	7070.96	40
H19C	9083.47	7265.53	6033.05	40
H17A	11472.87	7815.99	4125.56	30
H17B	11876.71	7111.75	3176.23	30
H22A	4178.77	4583.52	5790.16	42
H22B	5158.93	3873.14	6747.88	42
H22C	2599.14	3875.72	5972.83	42
H15A	8187.1	6545.88	1519.55	25
H15B	6221.88	6477.74	2318.83	25
H16A	8279.17	7720.39	2456.47	30
H16B	7650.46	7401.58	3814.93	30
H3A	1079.94	3485.84	2237.66	34
H3B	2888	2818.14	2183.46	34
H2	2644.39	3005.51	-37.6	29
H20A	14758.14	6988.88	5672.2	43
H20B	14299.11	6215.45	4789.23	43
H20C	14080.27	6212.16	6339.61	43
H1A	4220.94	5312.84	-1063.52	40
H1B	5393.77	6139.88	-802.85	40
H1C	3796.74	5846.02	149.62	40
H21A	8119.86	5238.65	7739.81	38
H21B	8478.94	6153.56	7833.52	38
H21C	10085.28	5597.13	8874.24	38

Reference

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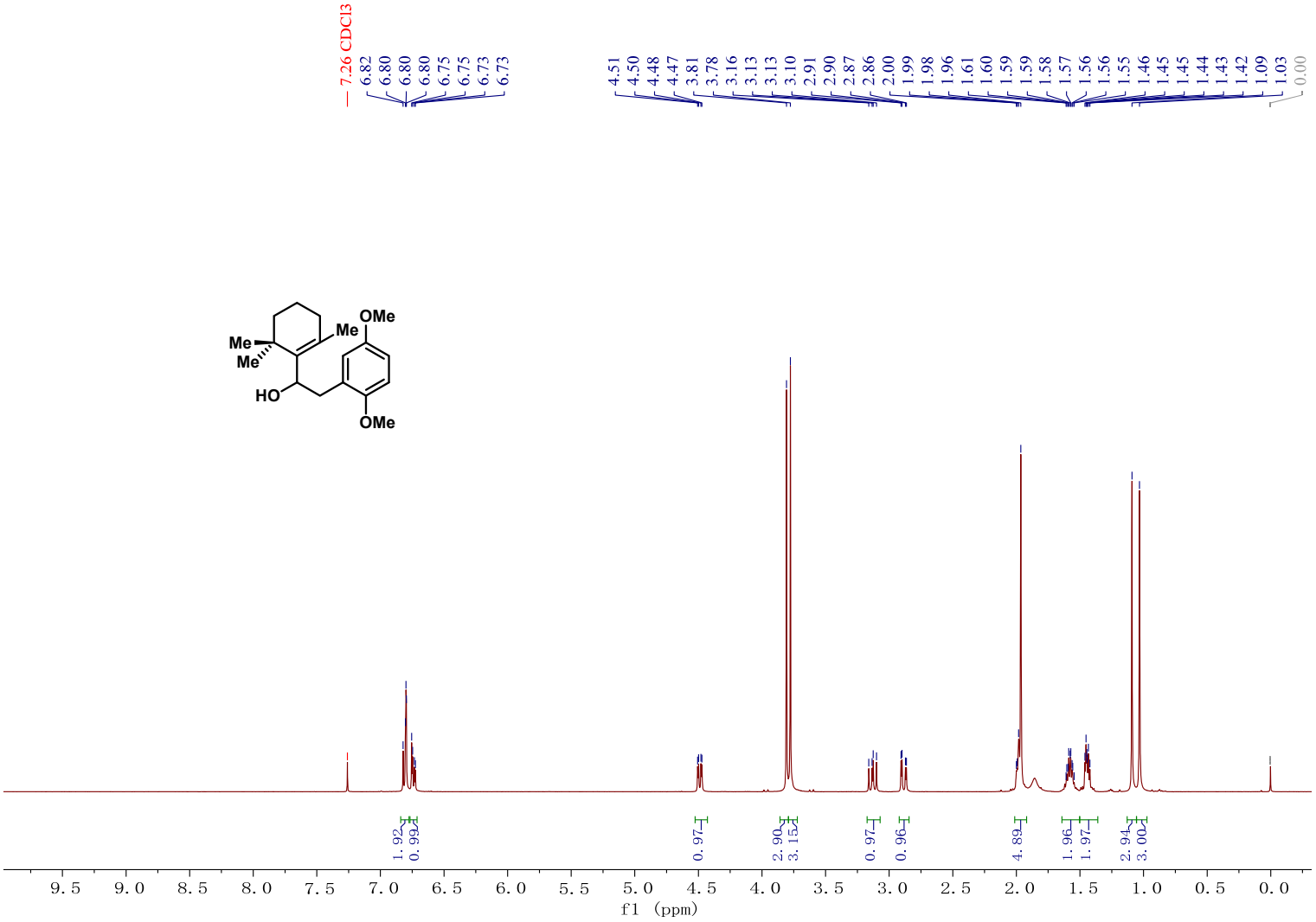
NMR Spectra

Compound S2 ^{1}H NMR



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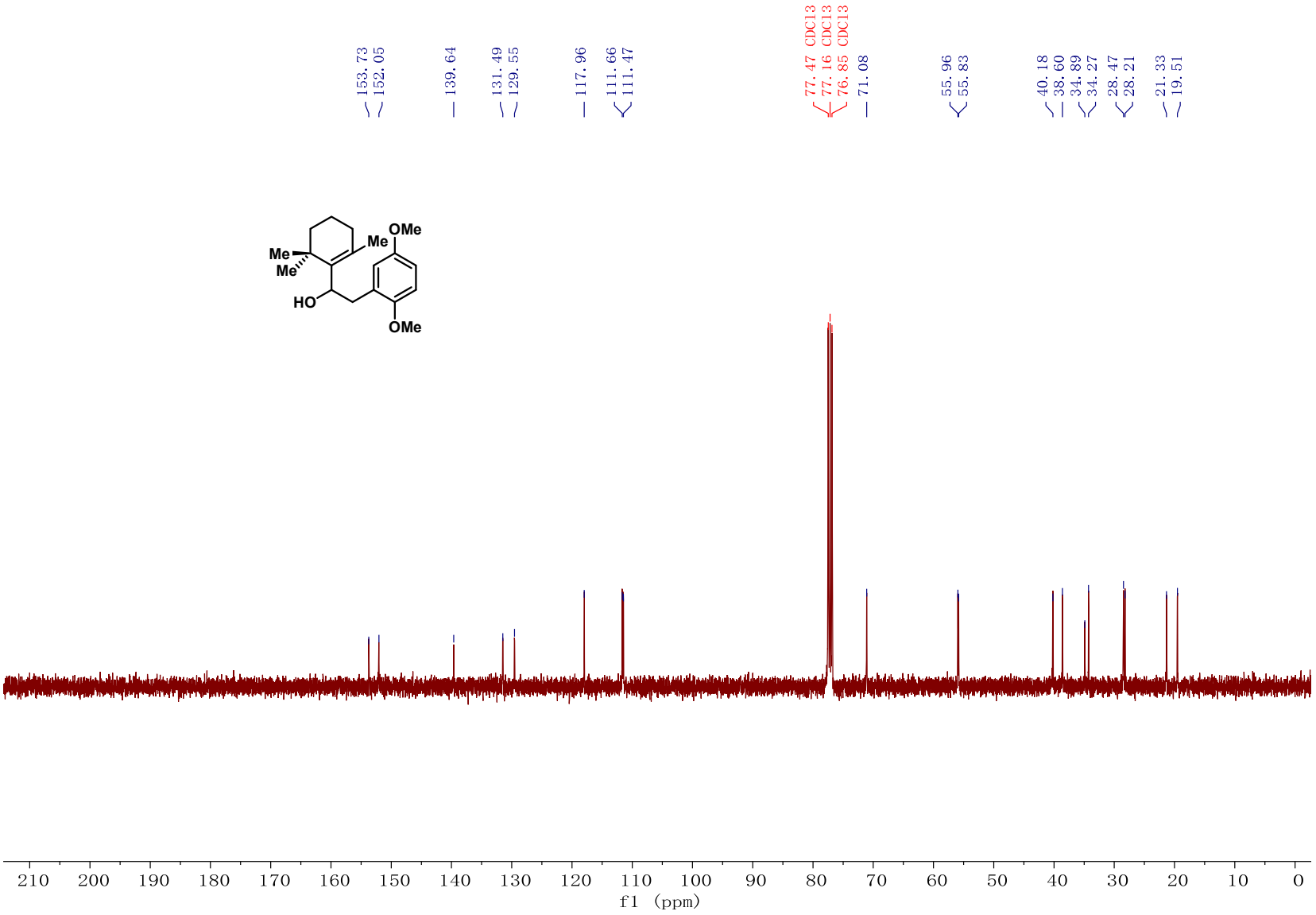

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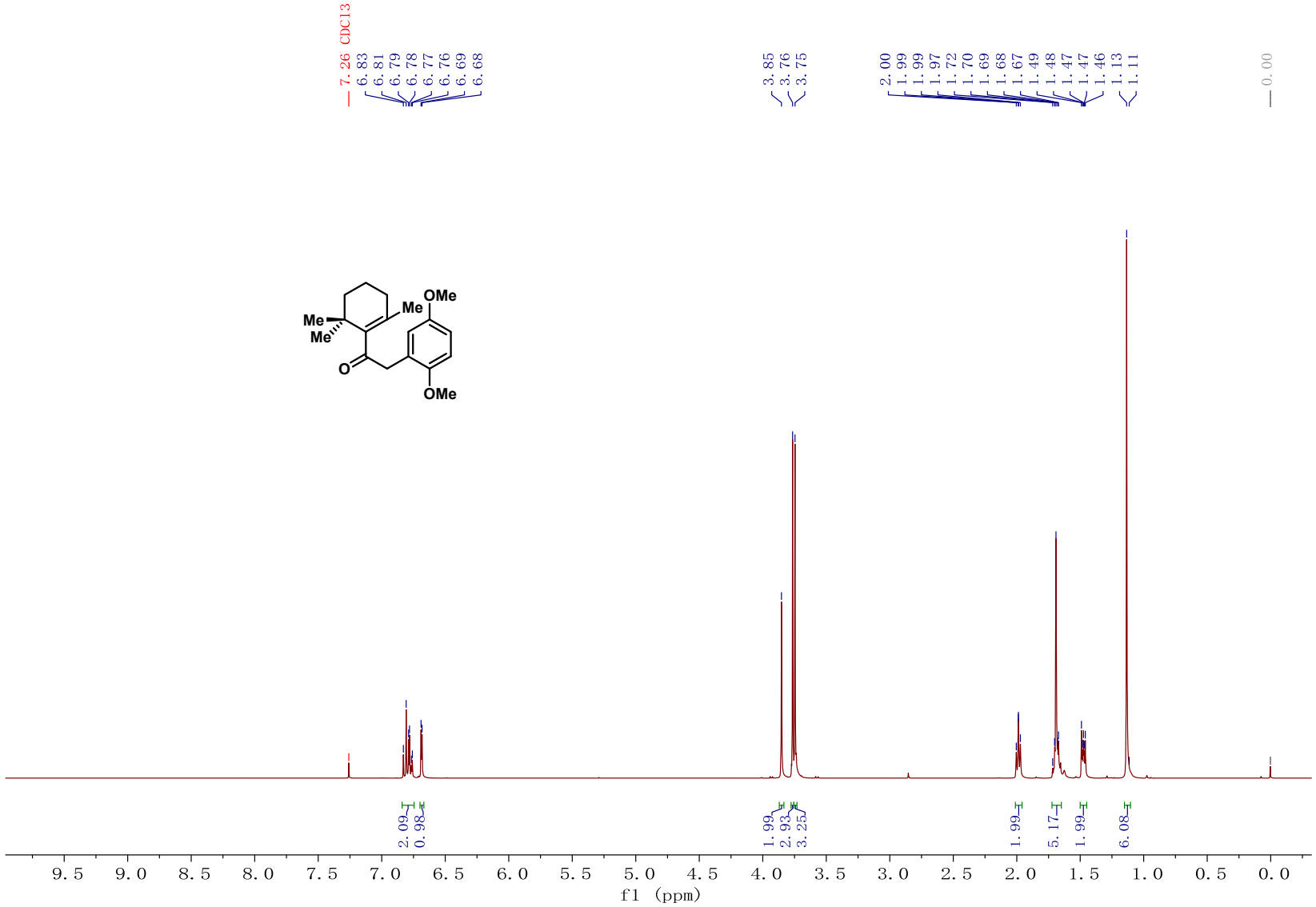

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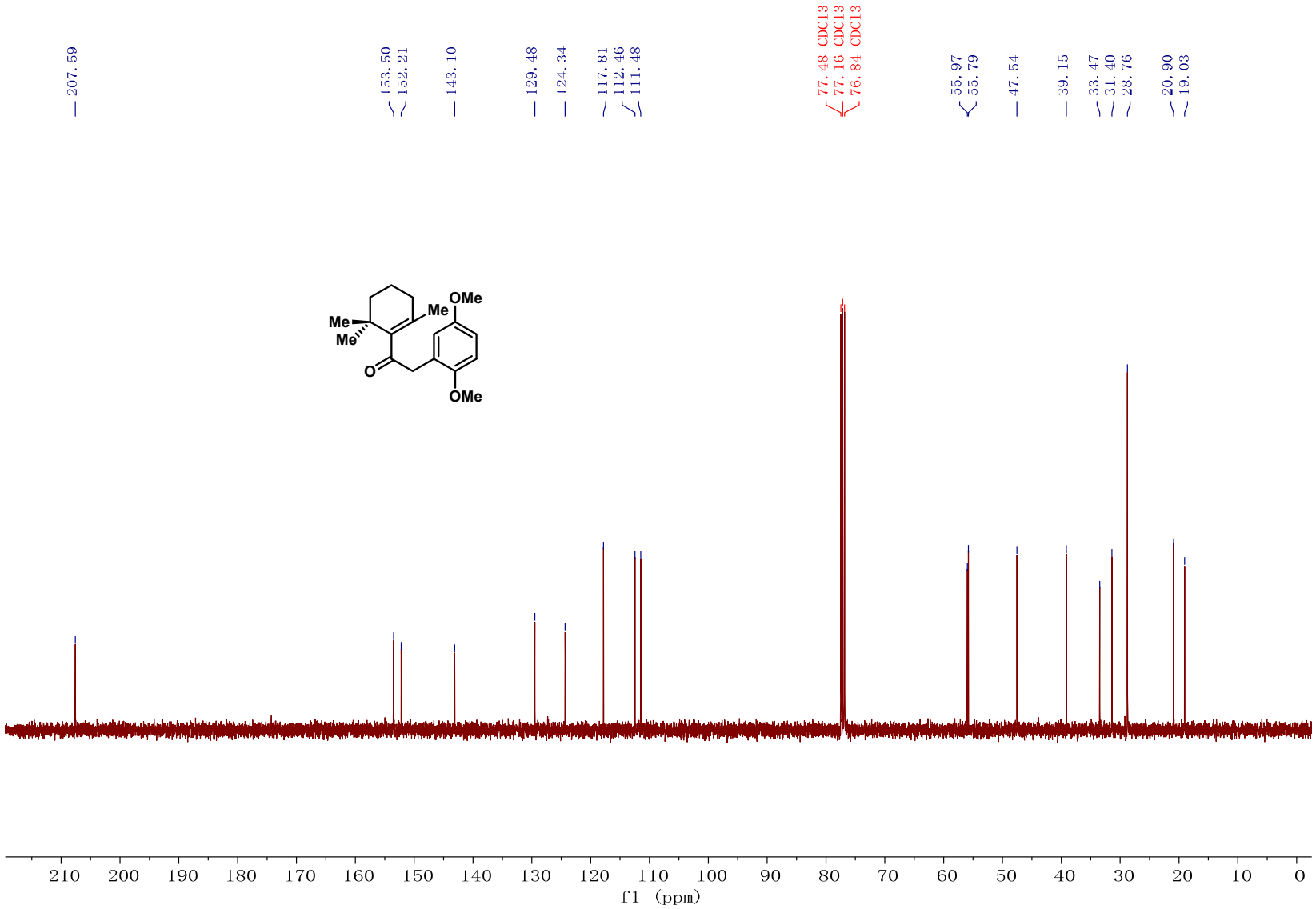

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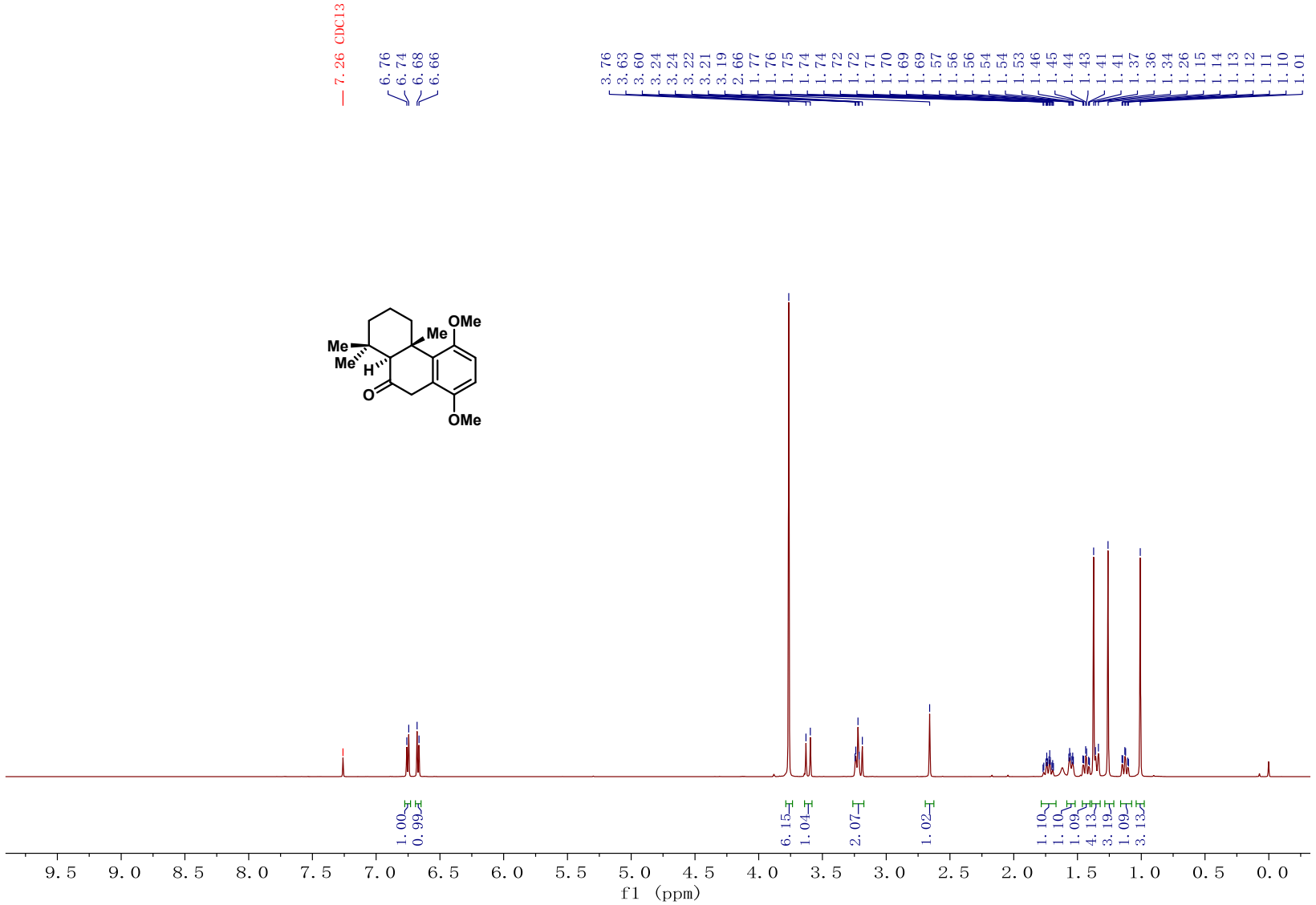

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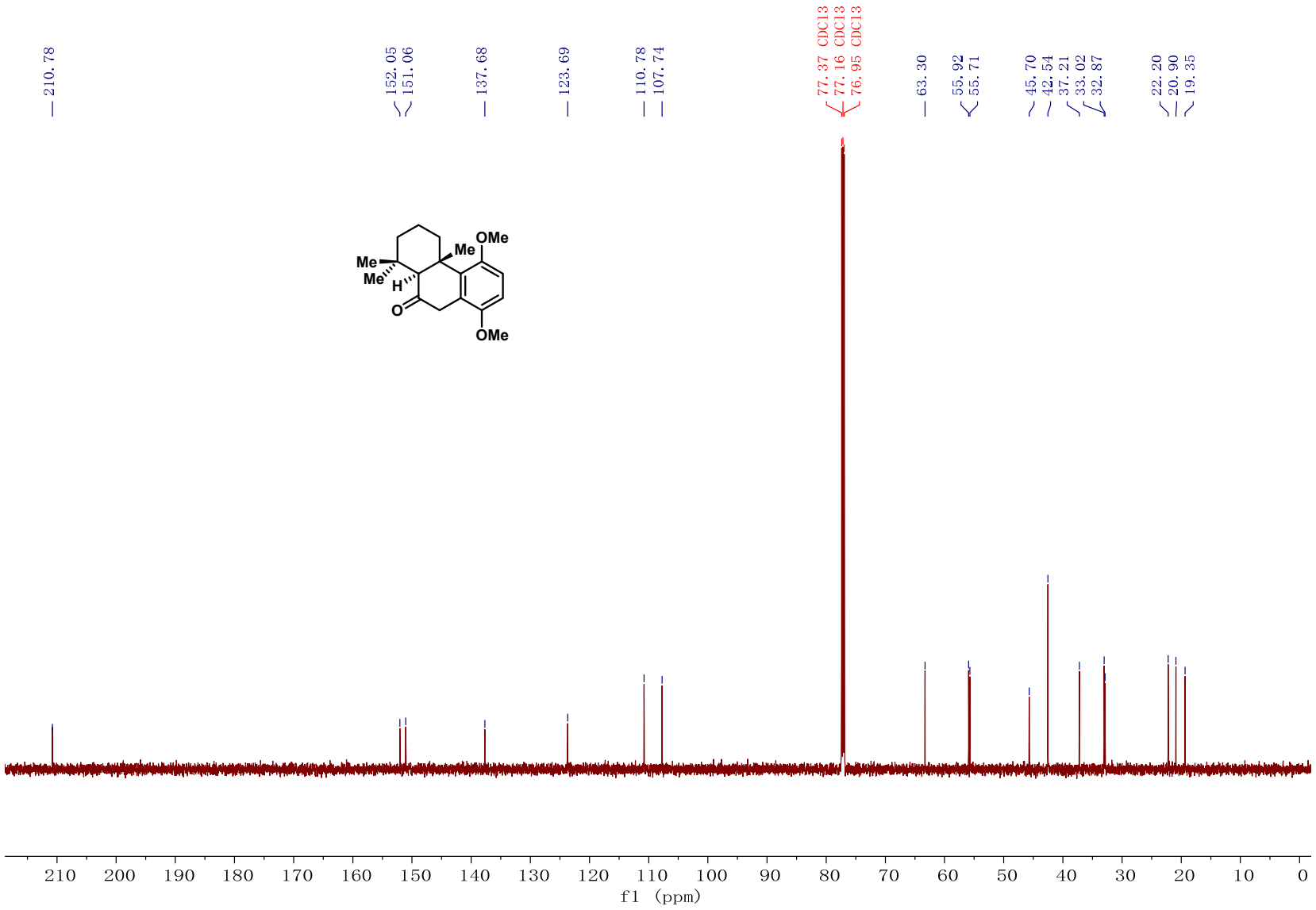

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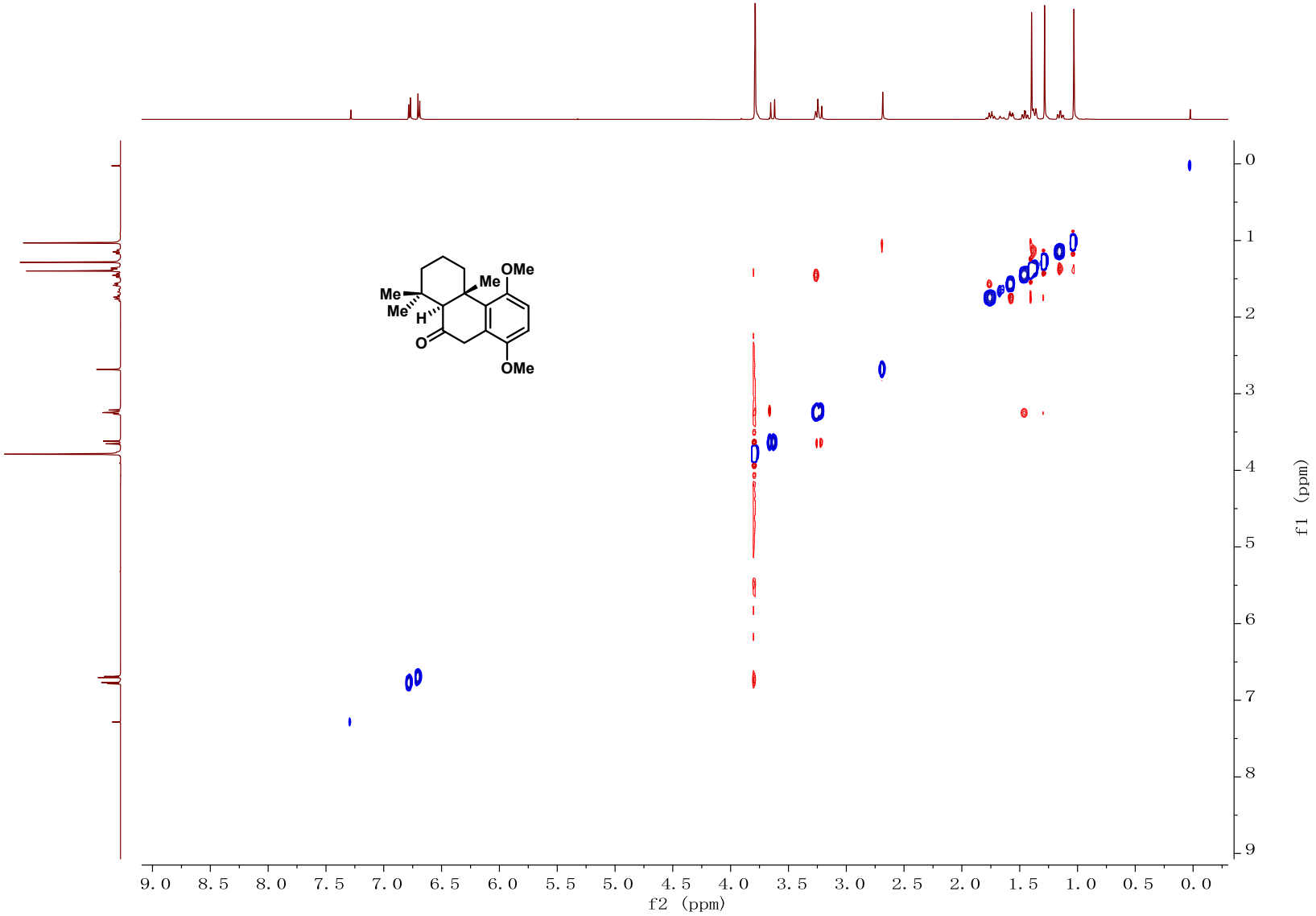

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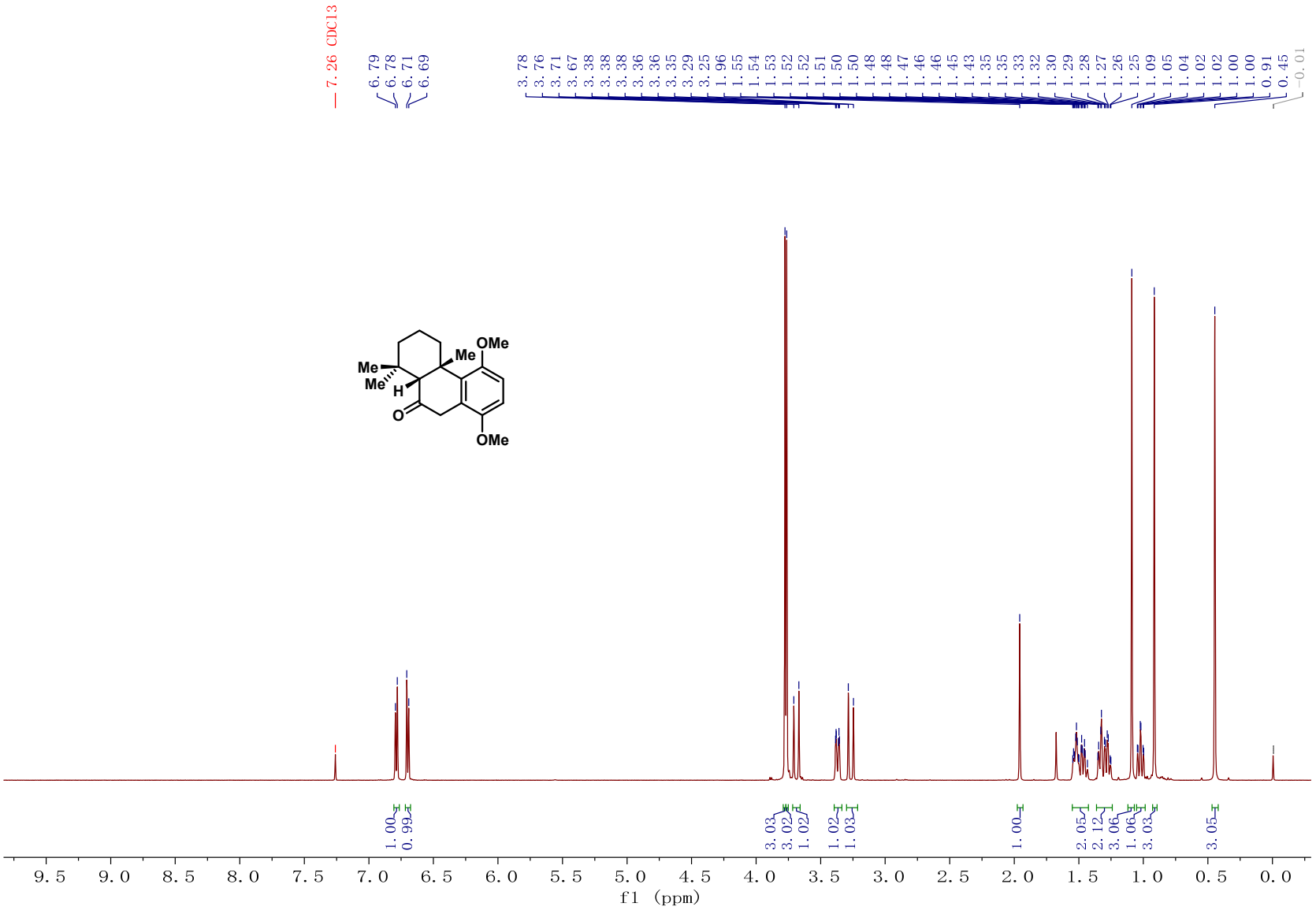

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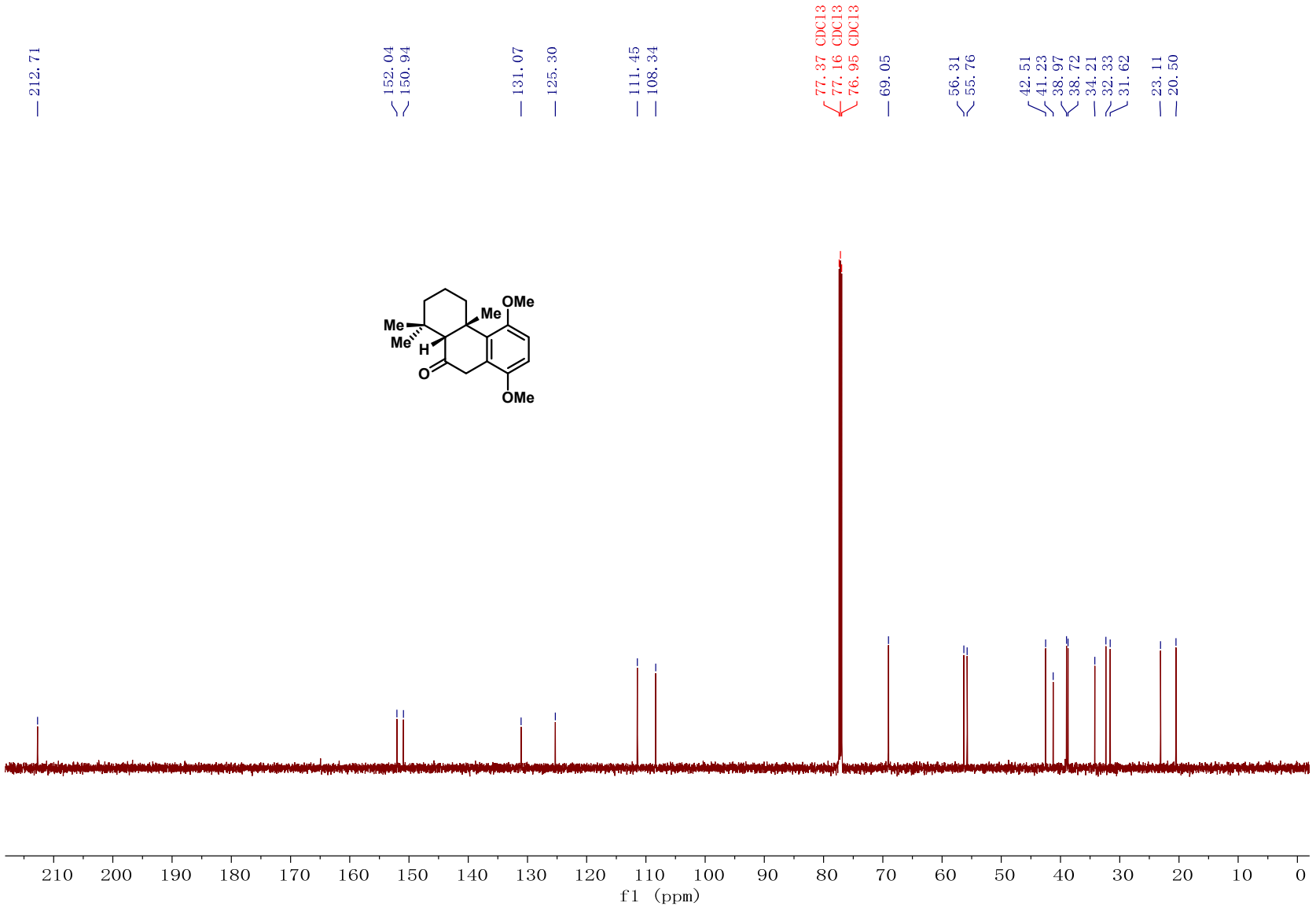

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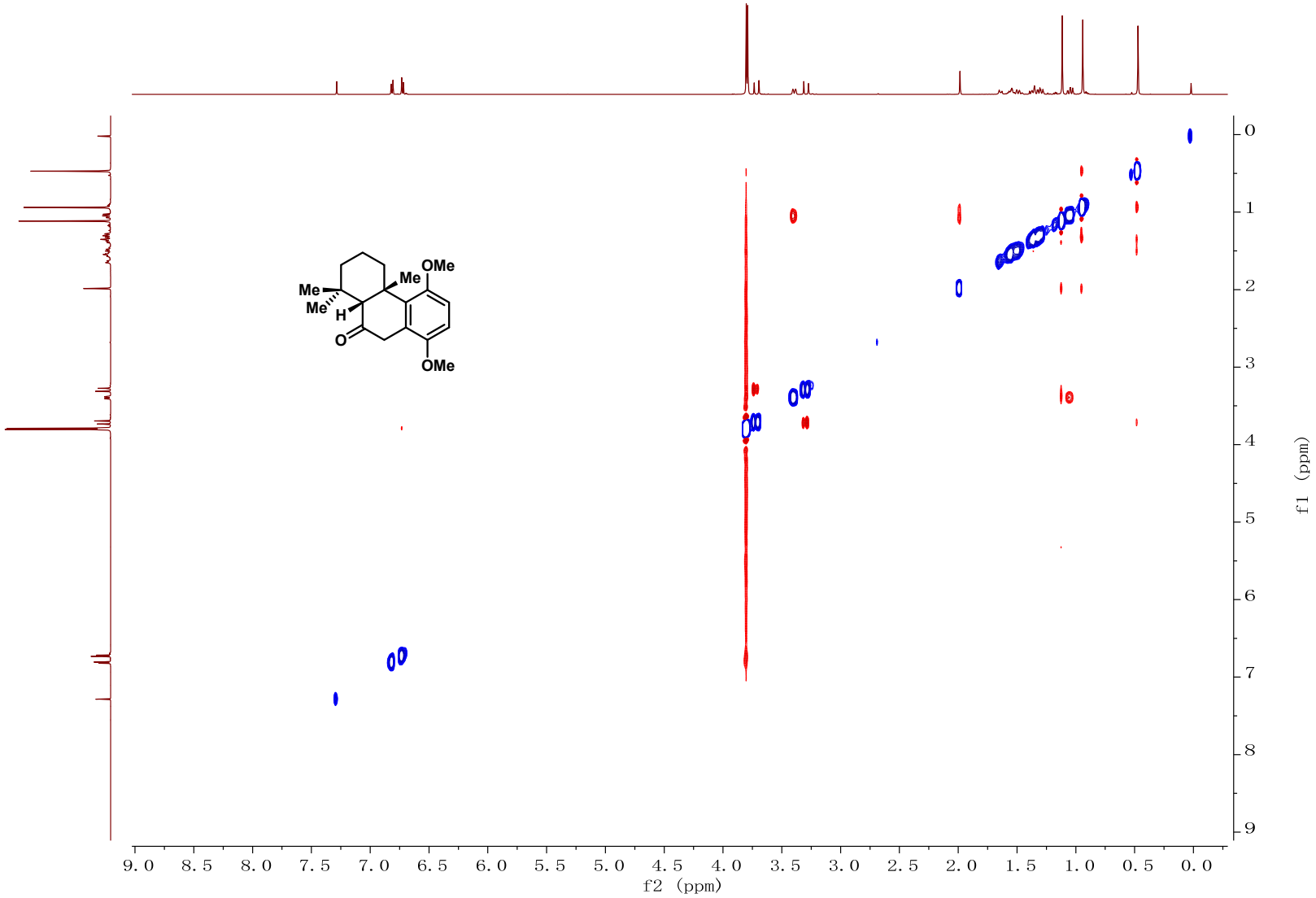

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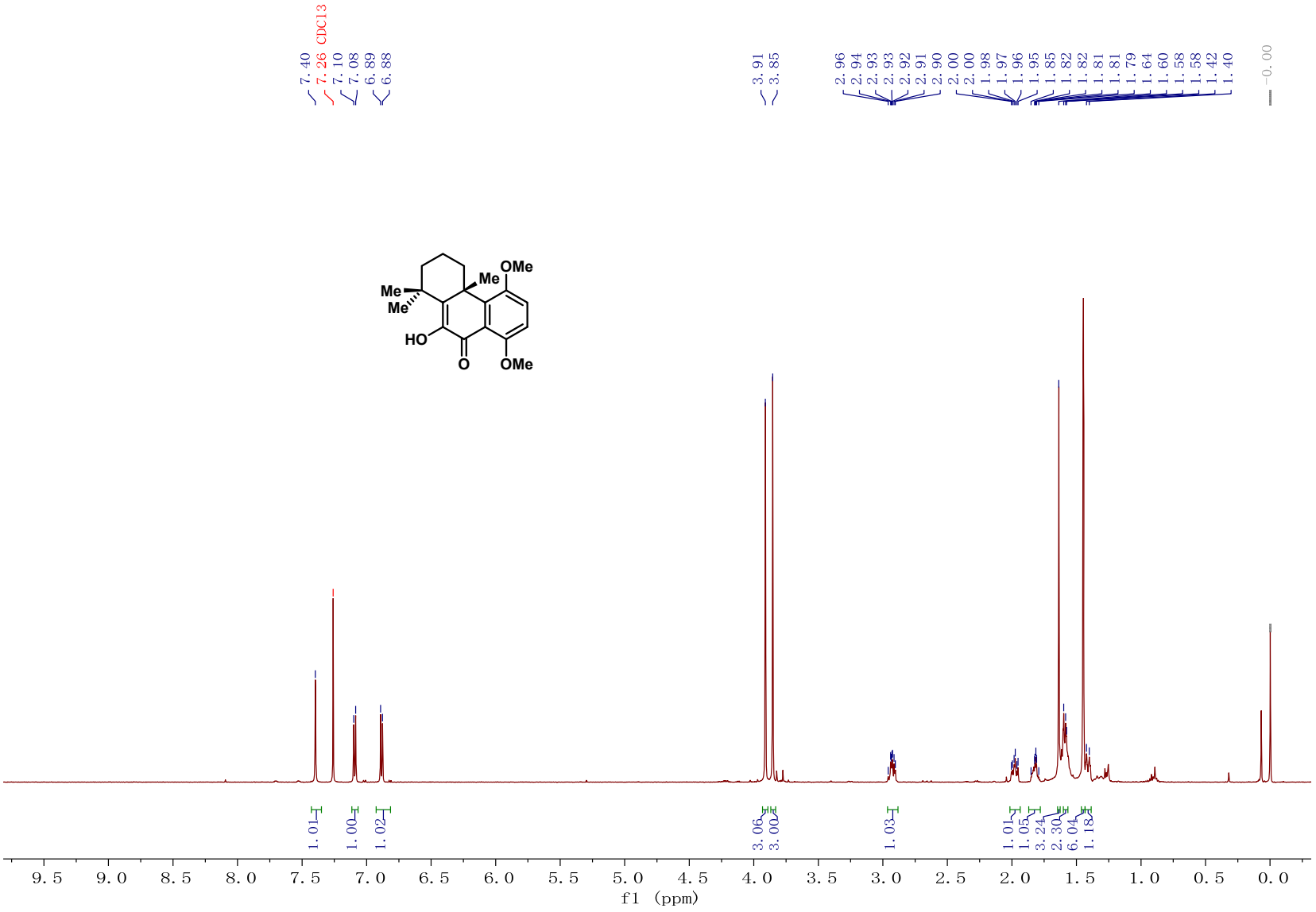

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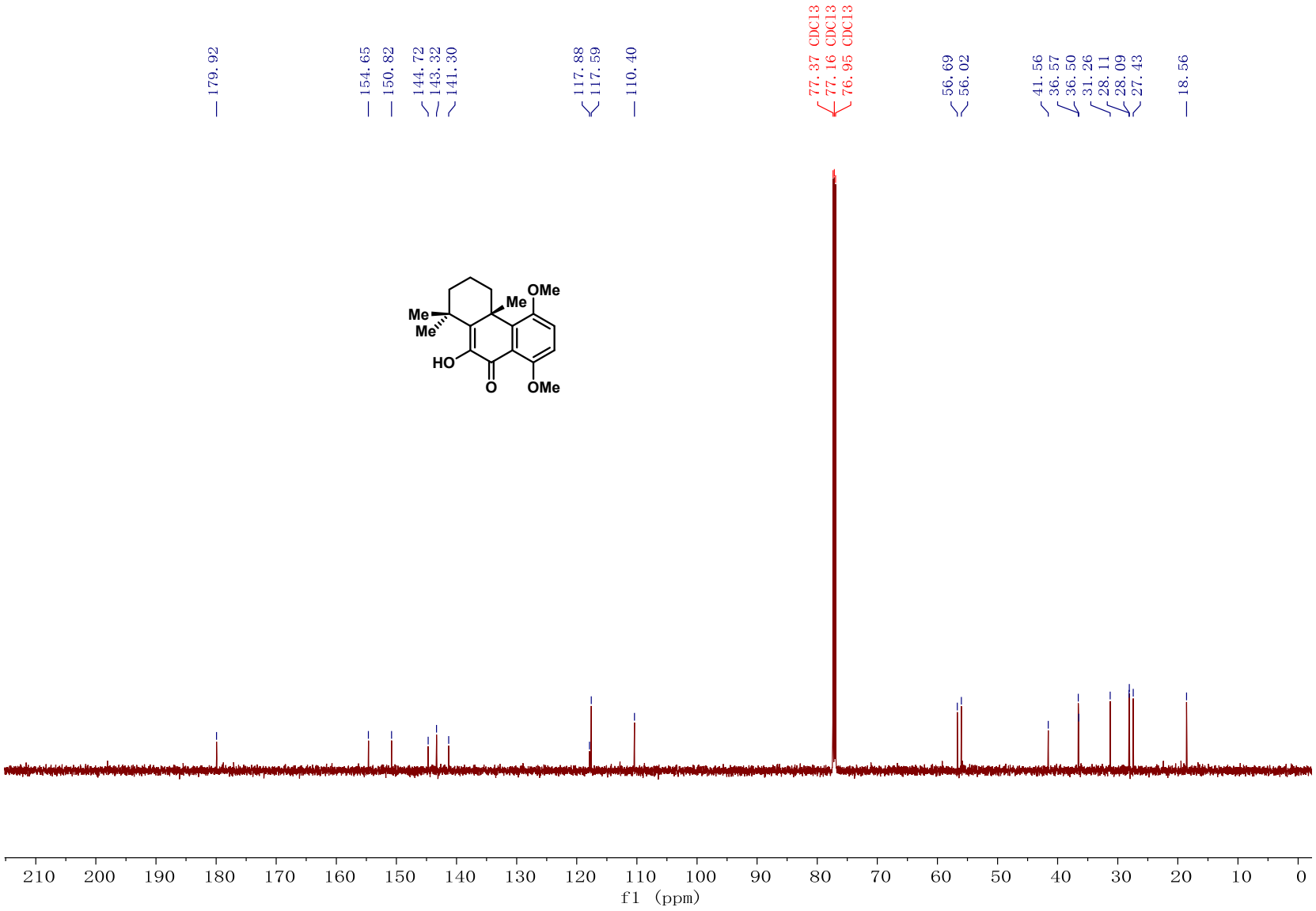

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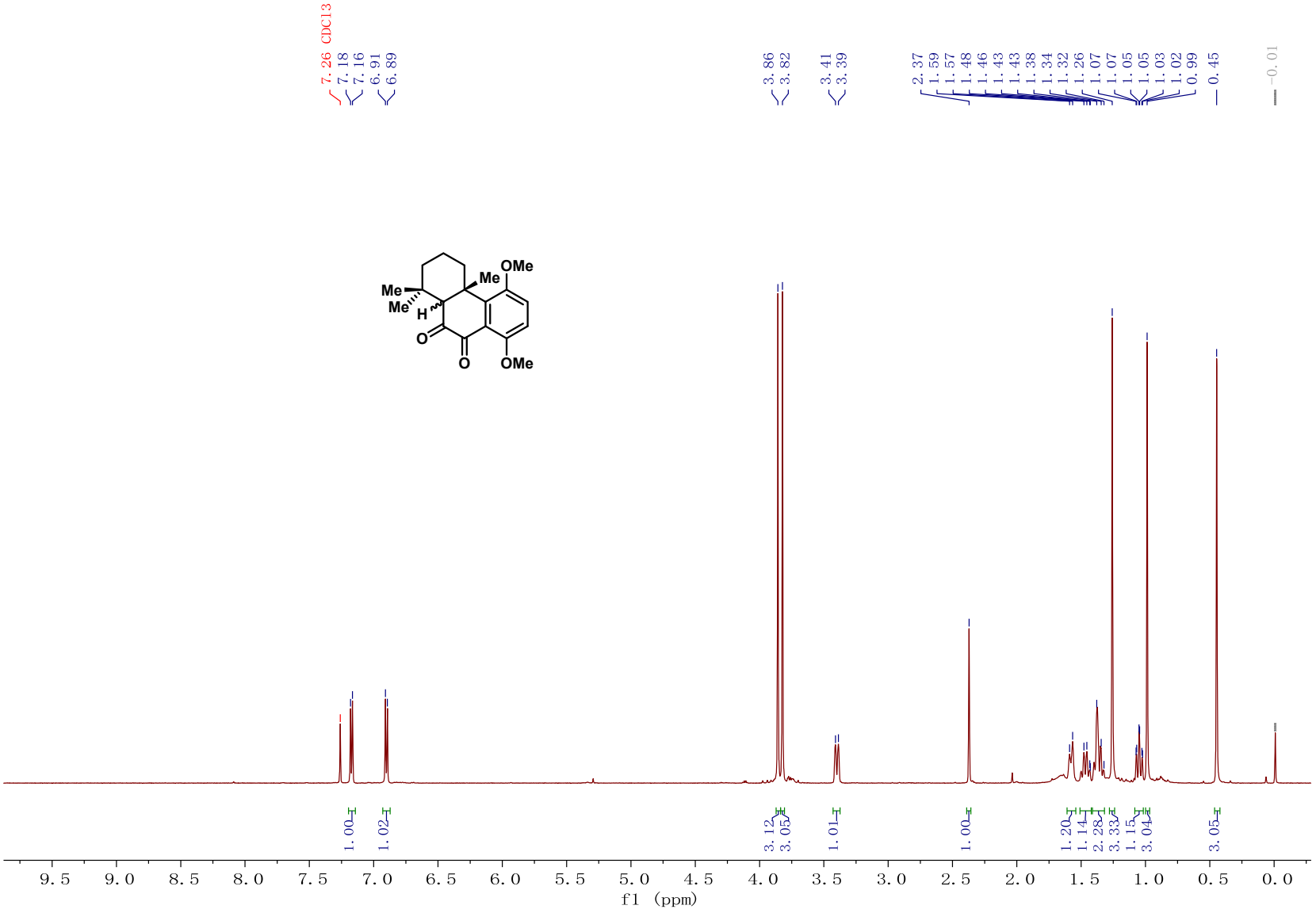

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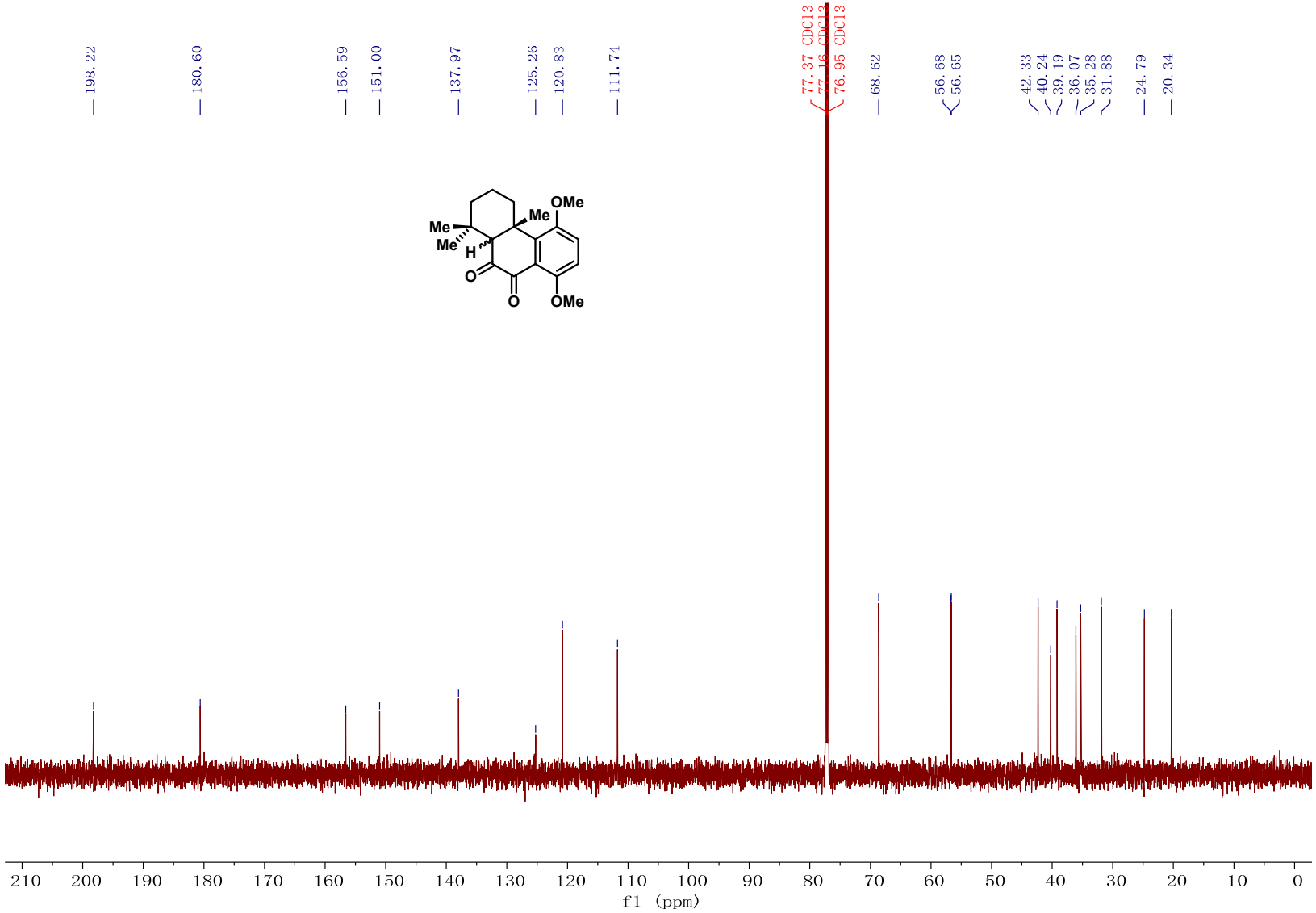

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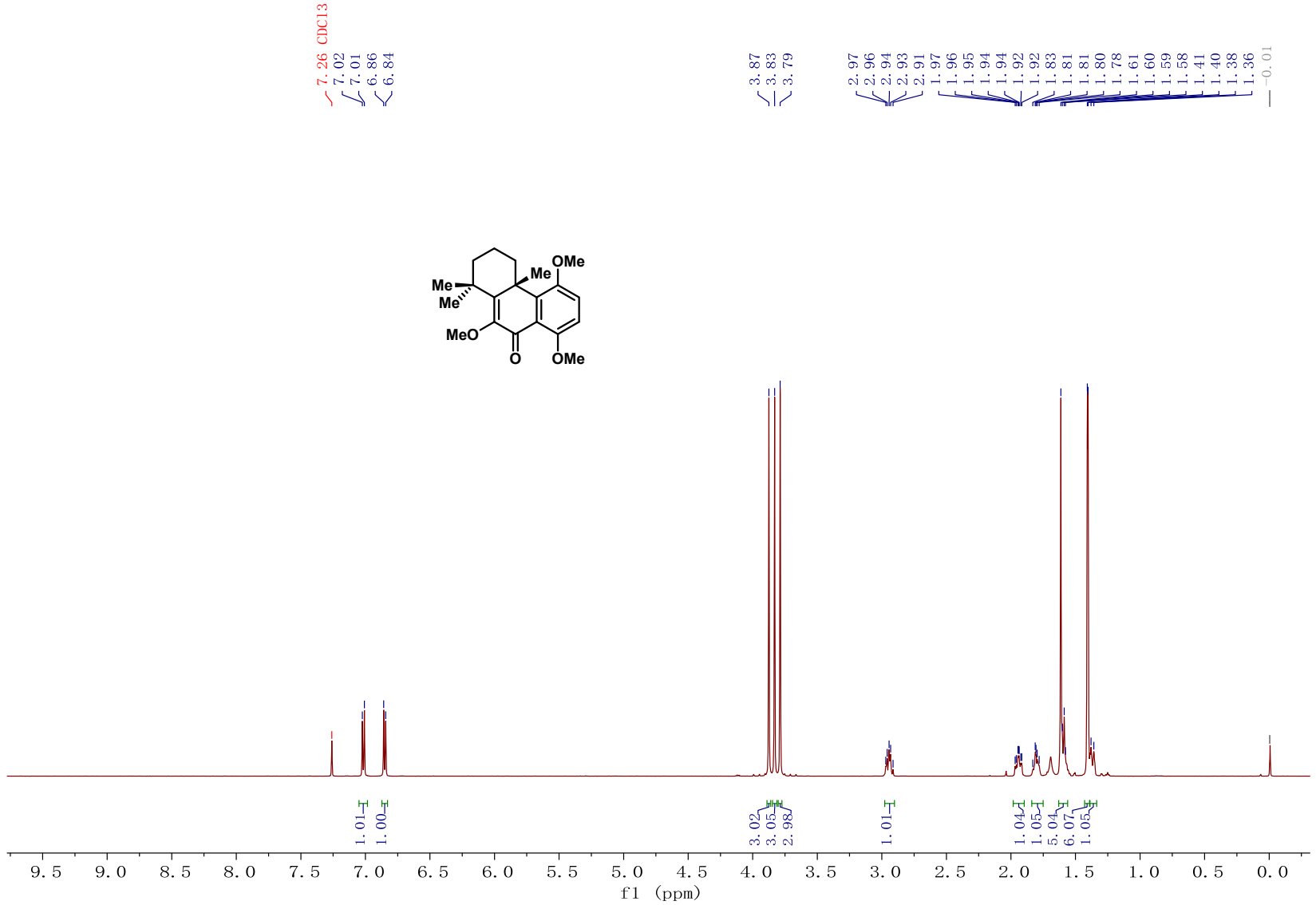

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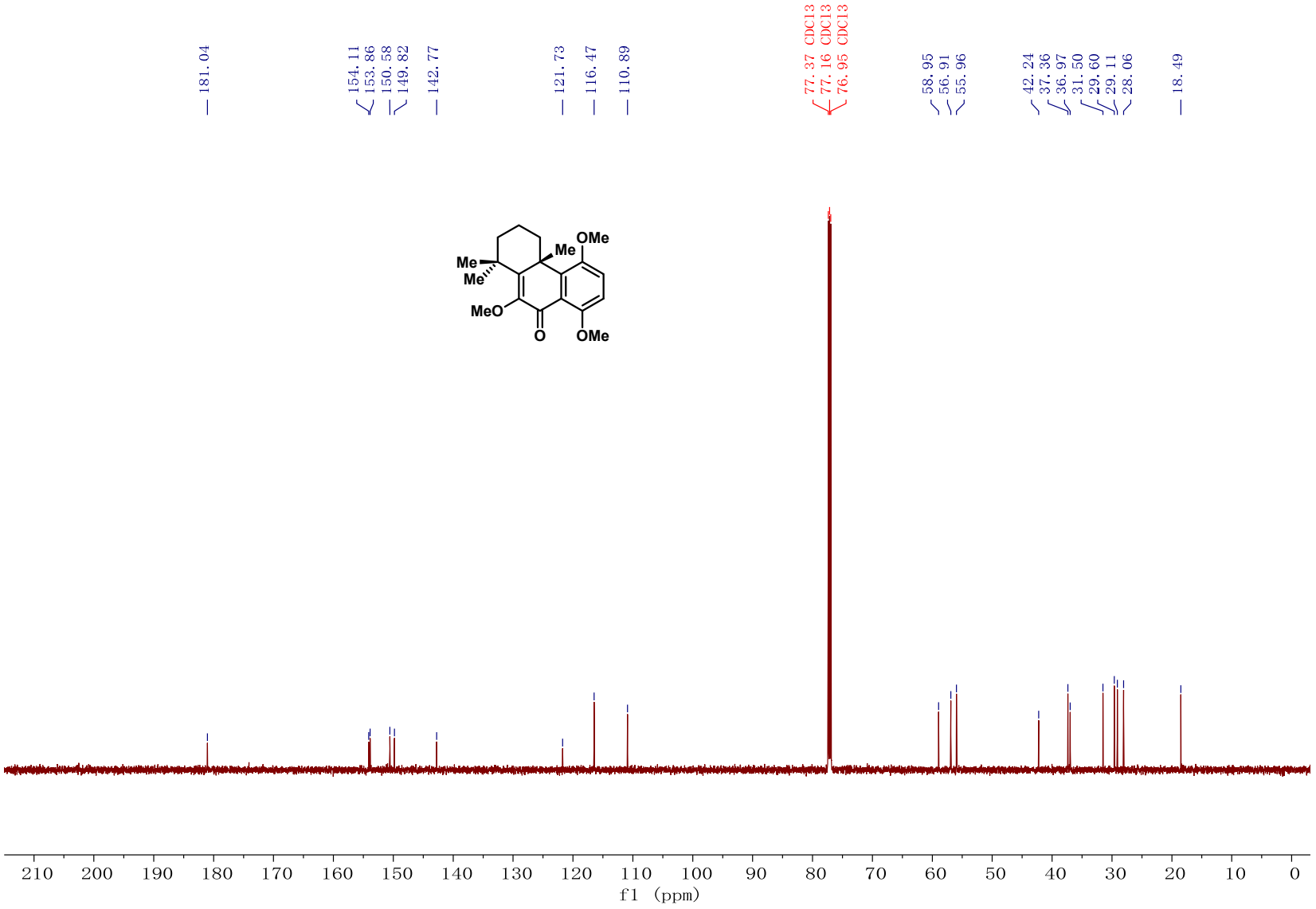

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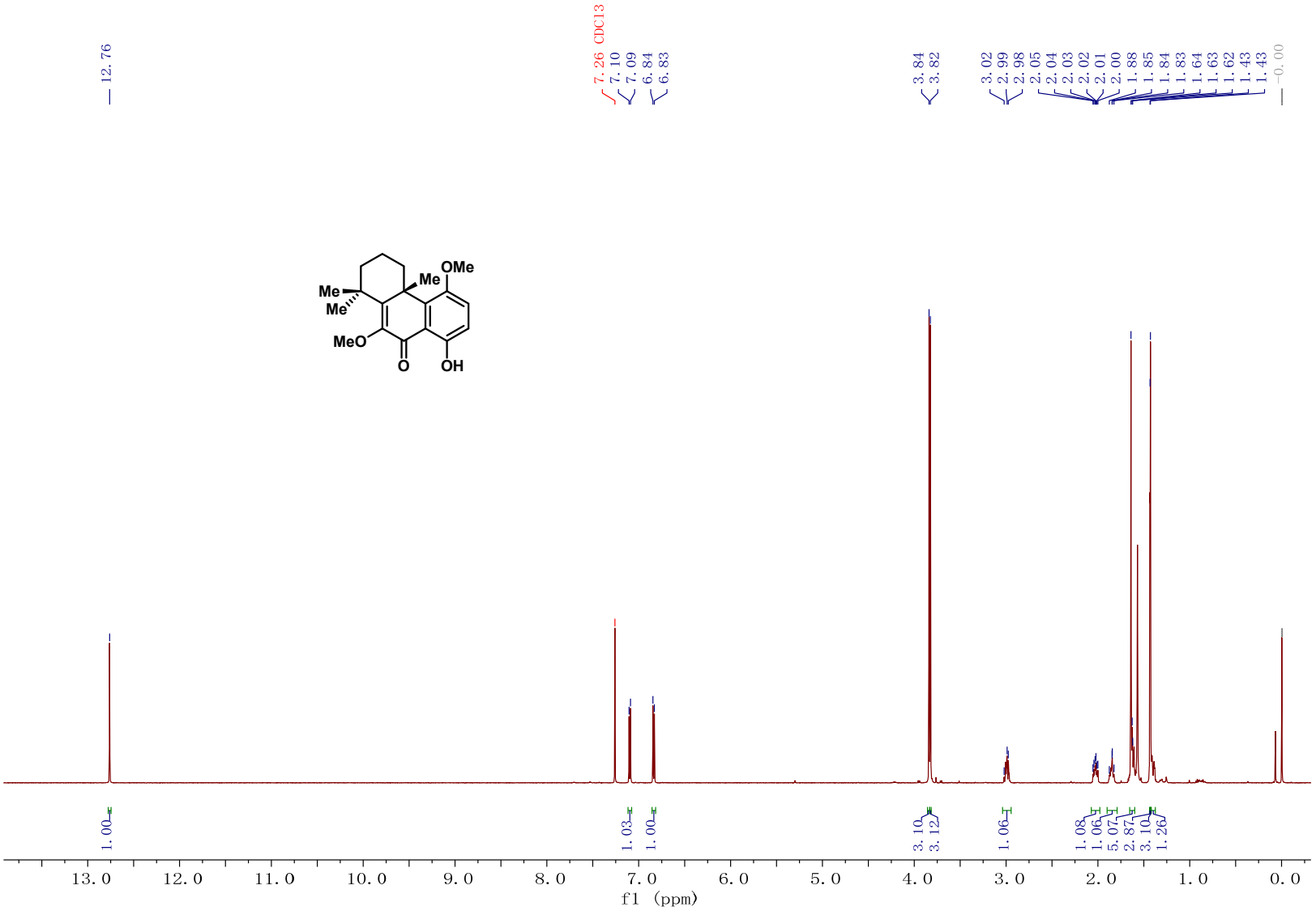

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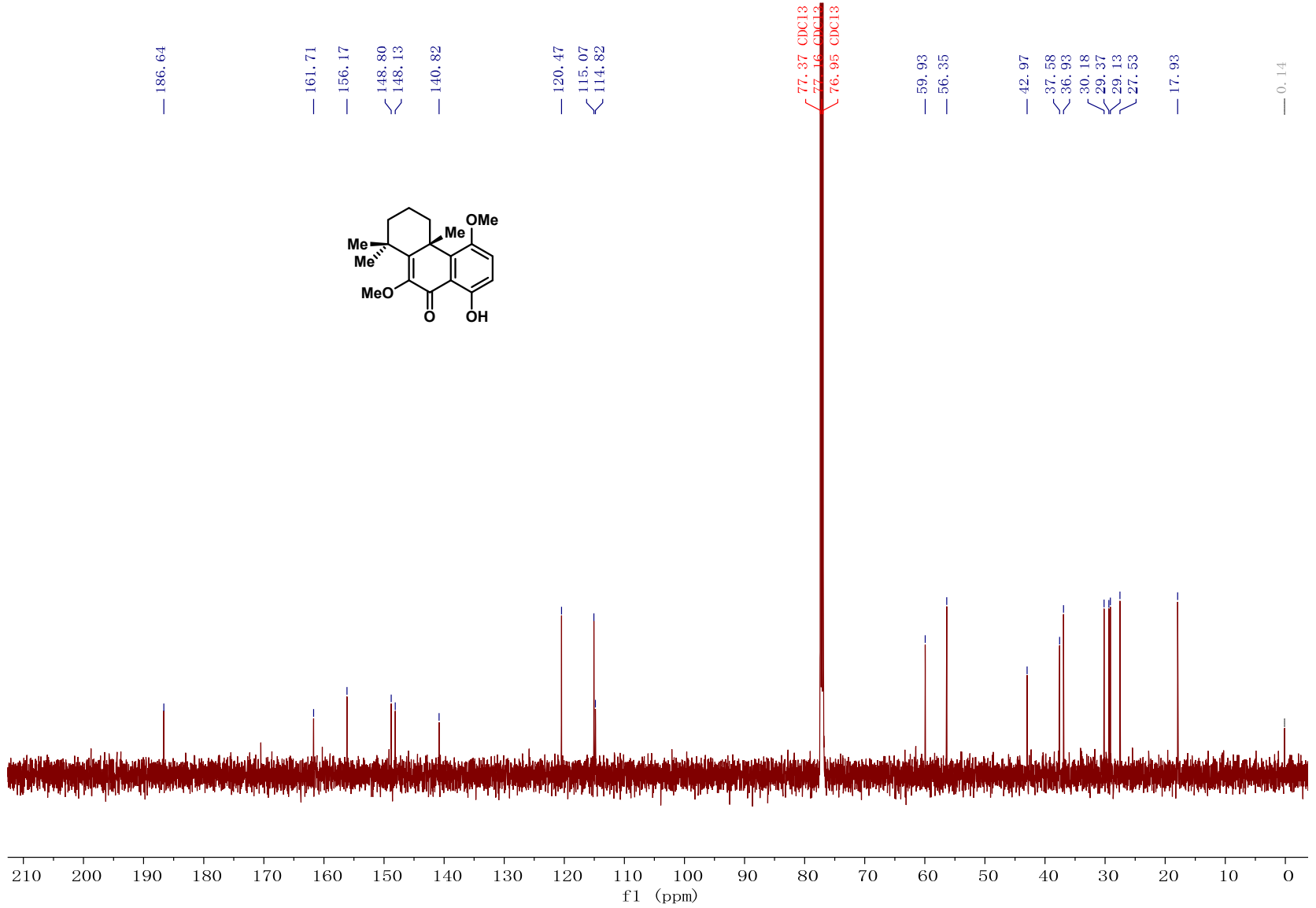

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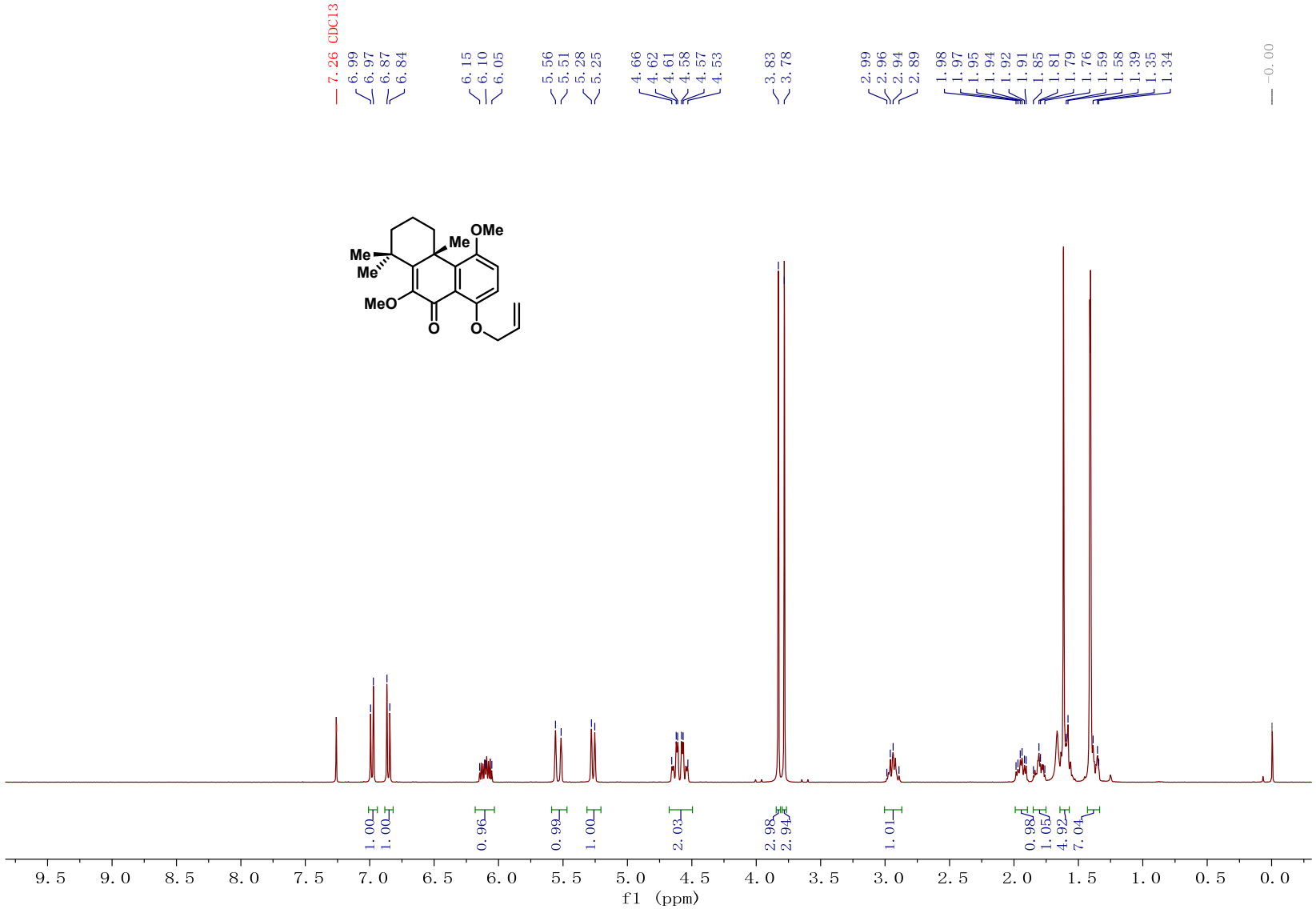

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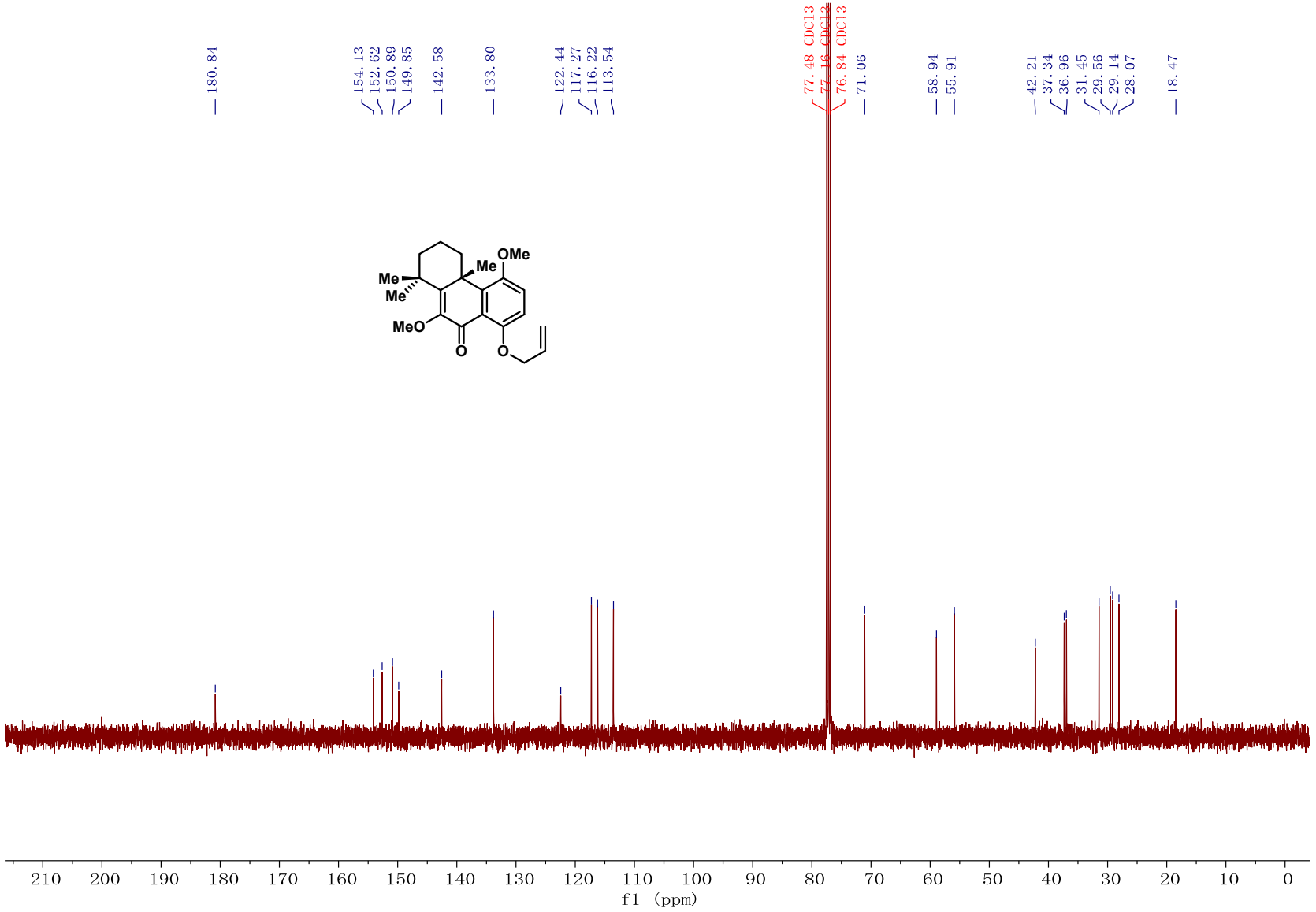
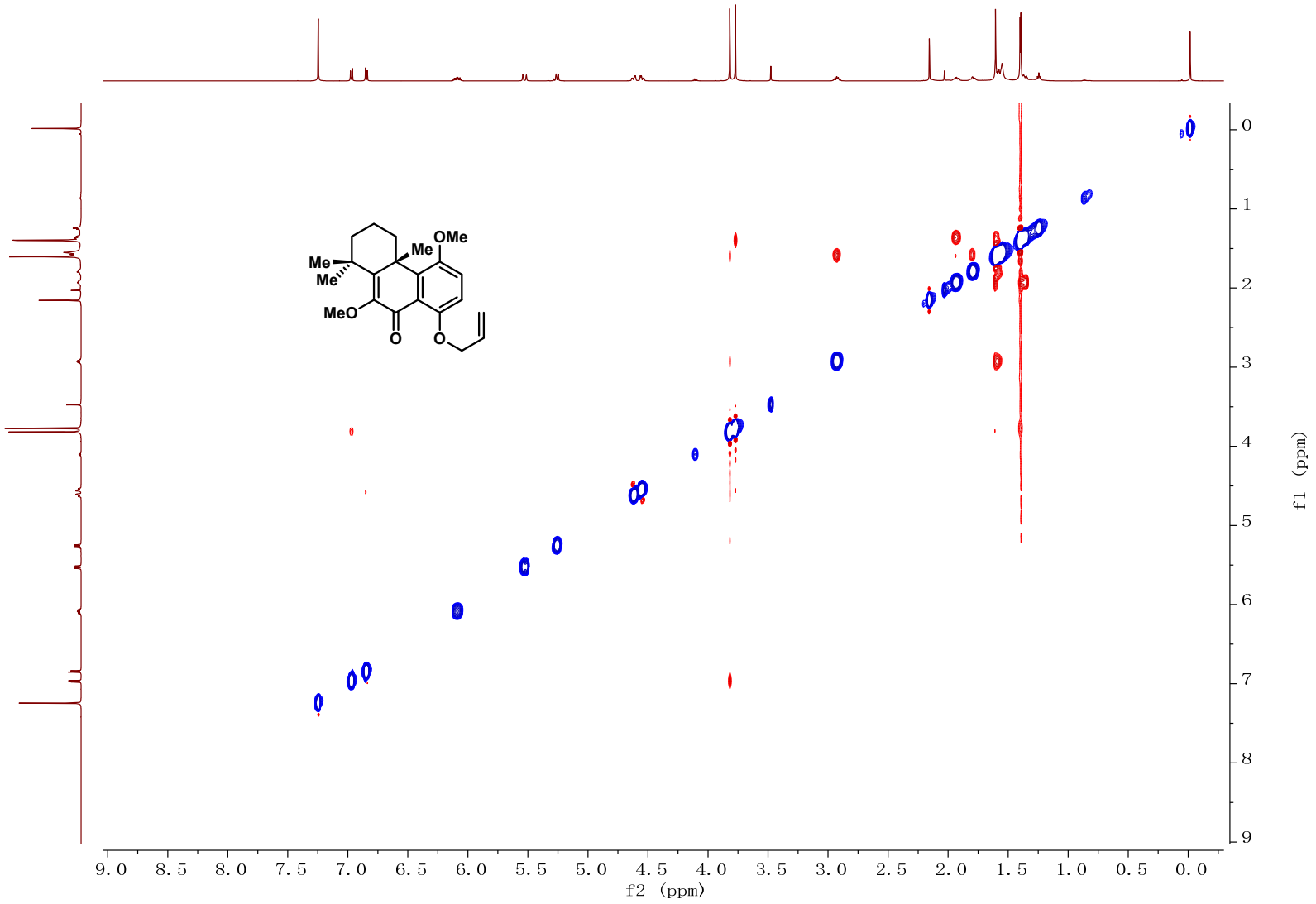


Compound 16 ^{1}H-^{1}H NOSEY NMR



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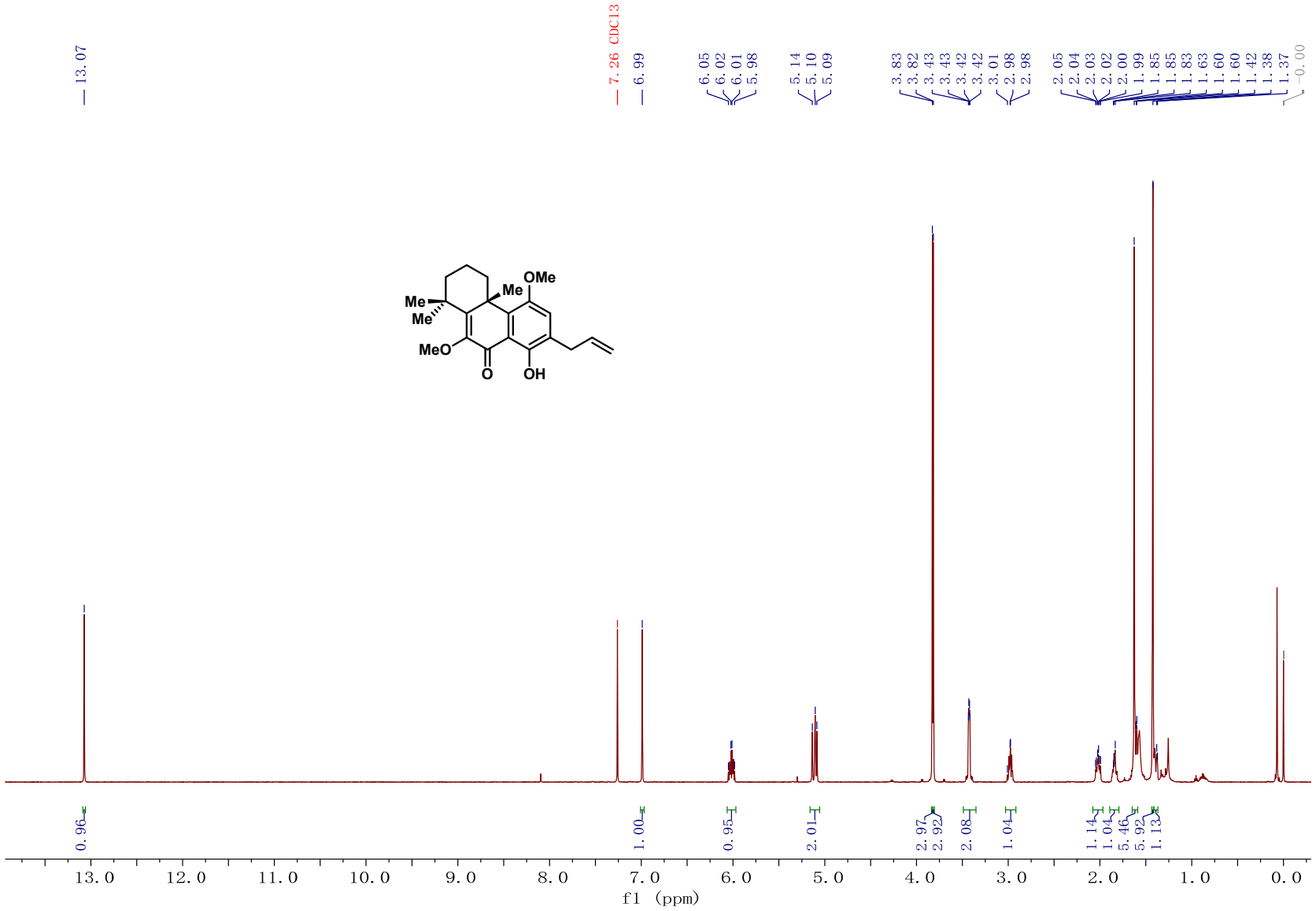

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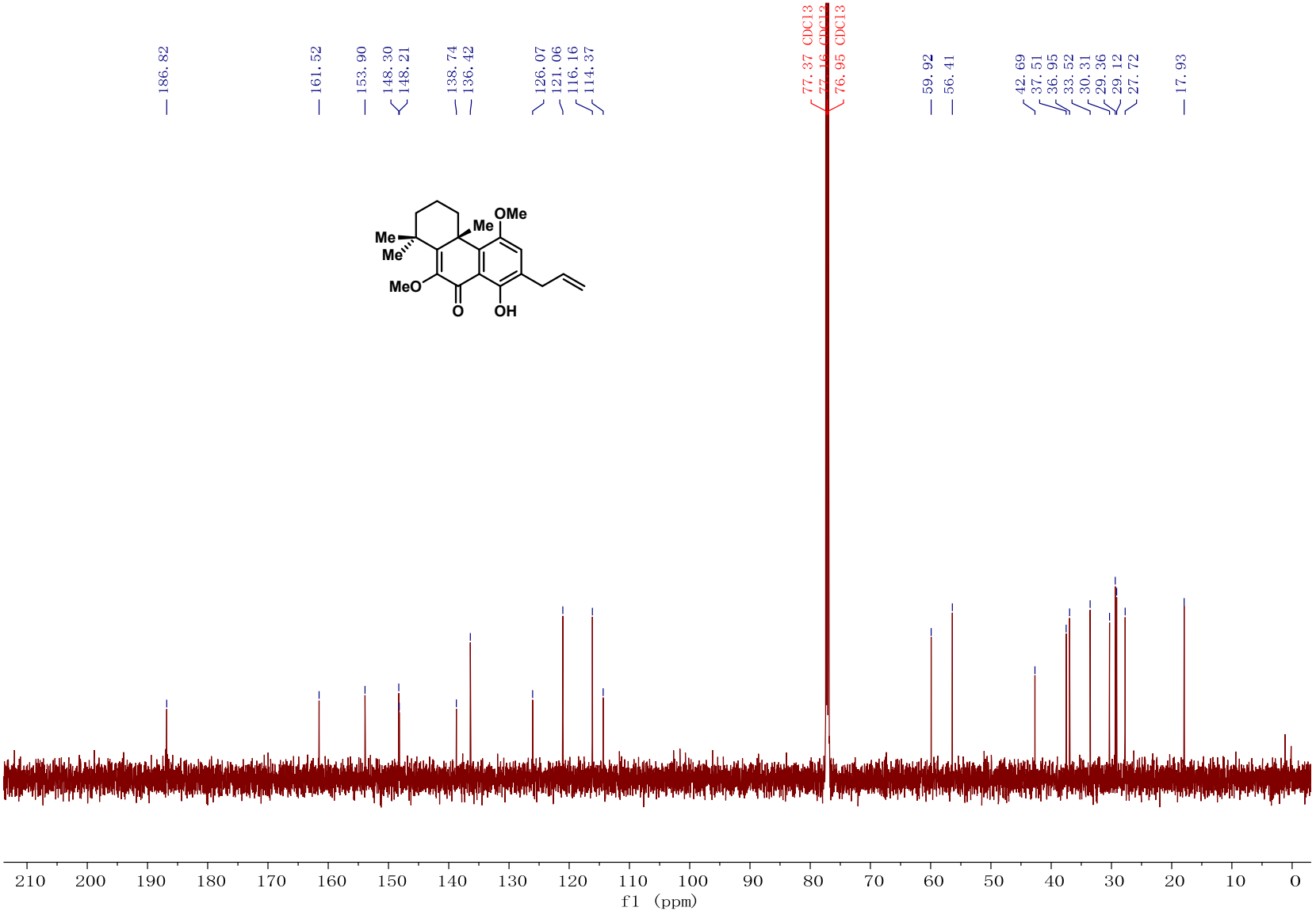

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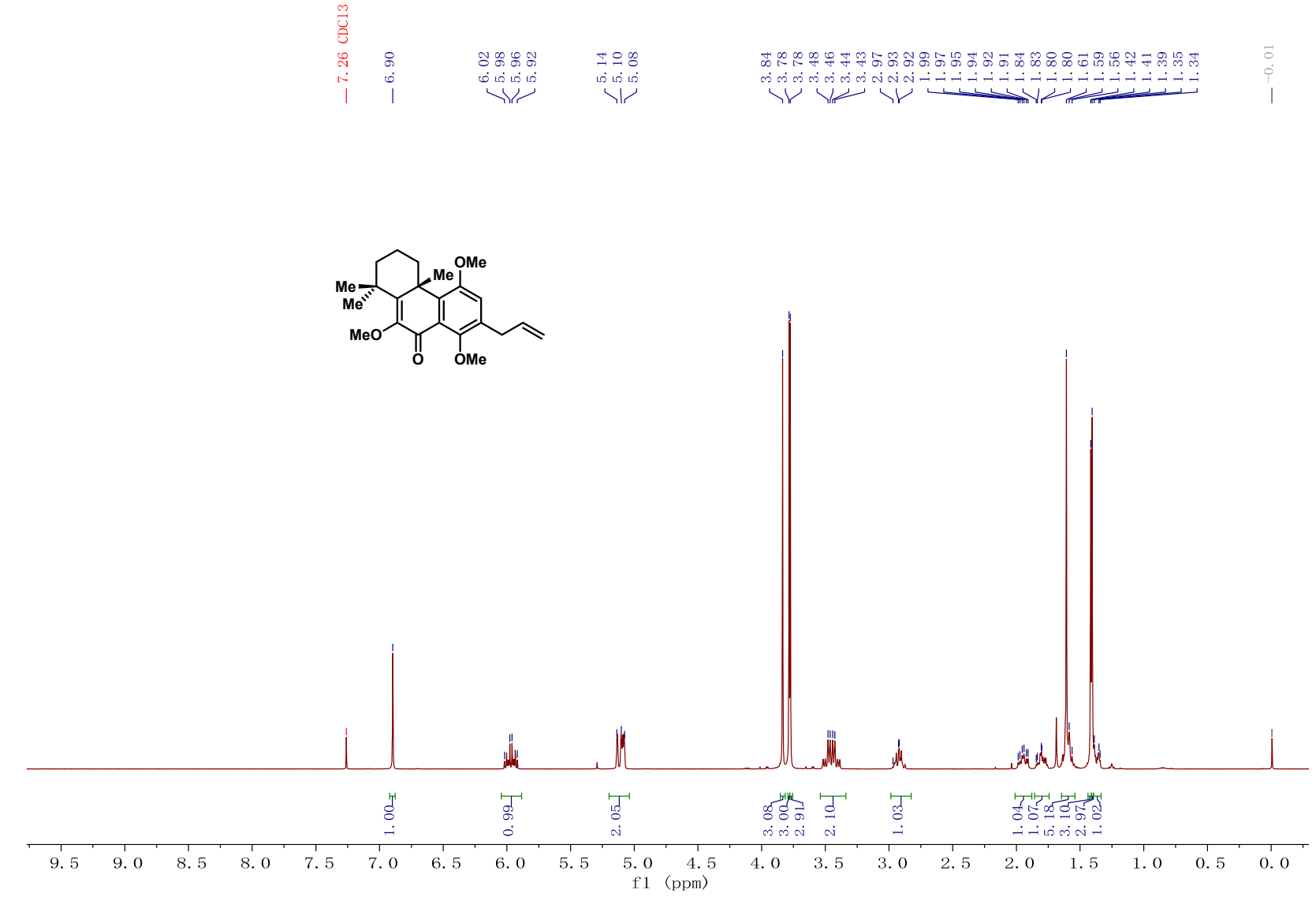

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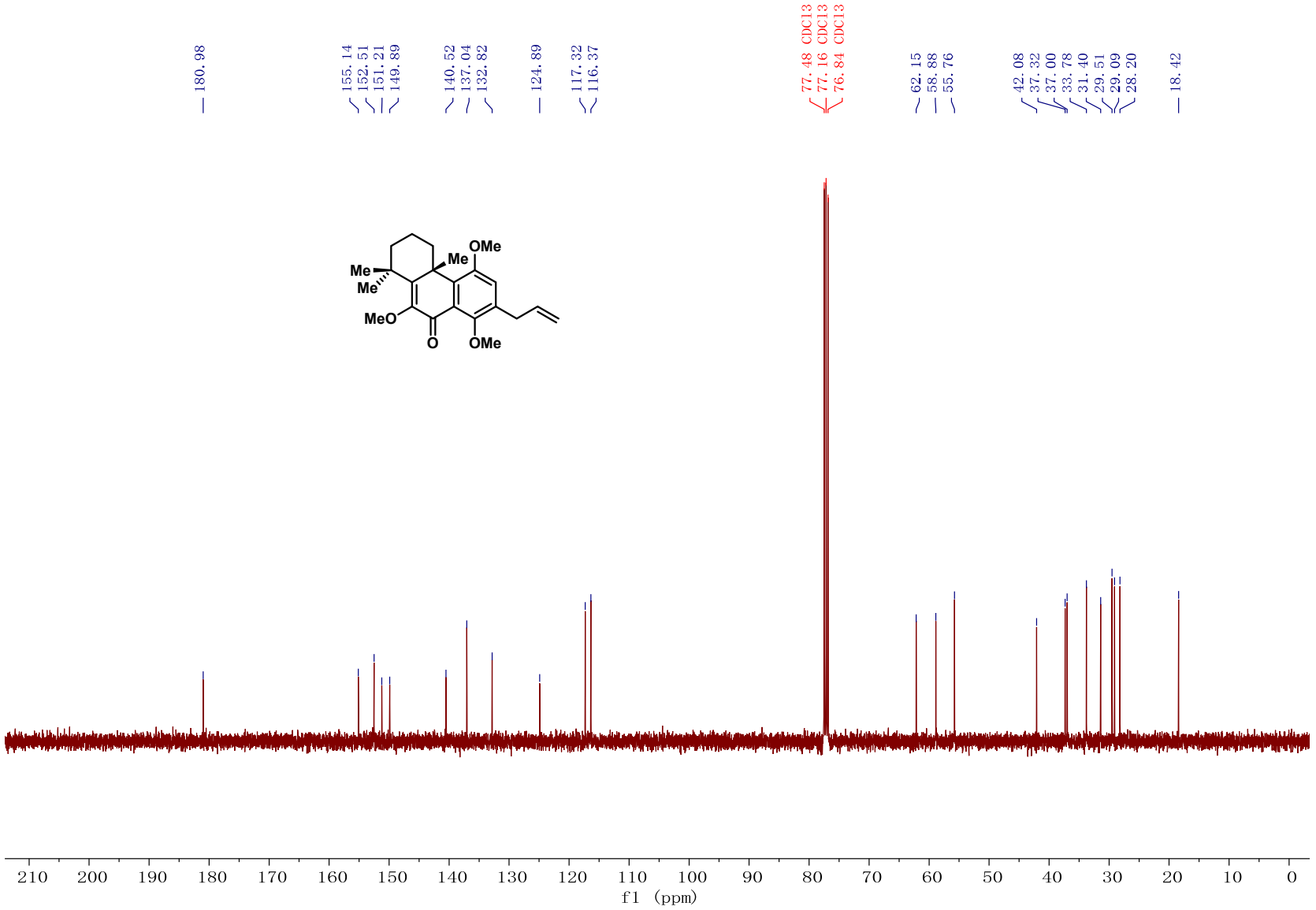

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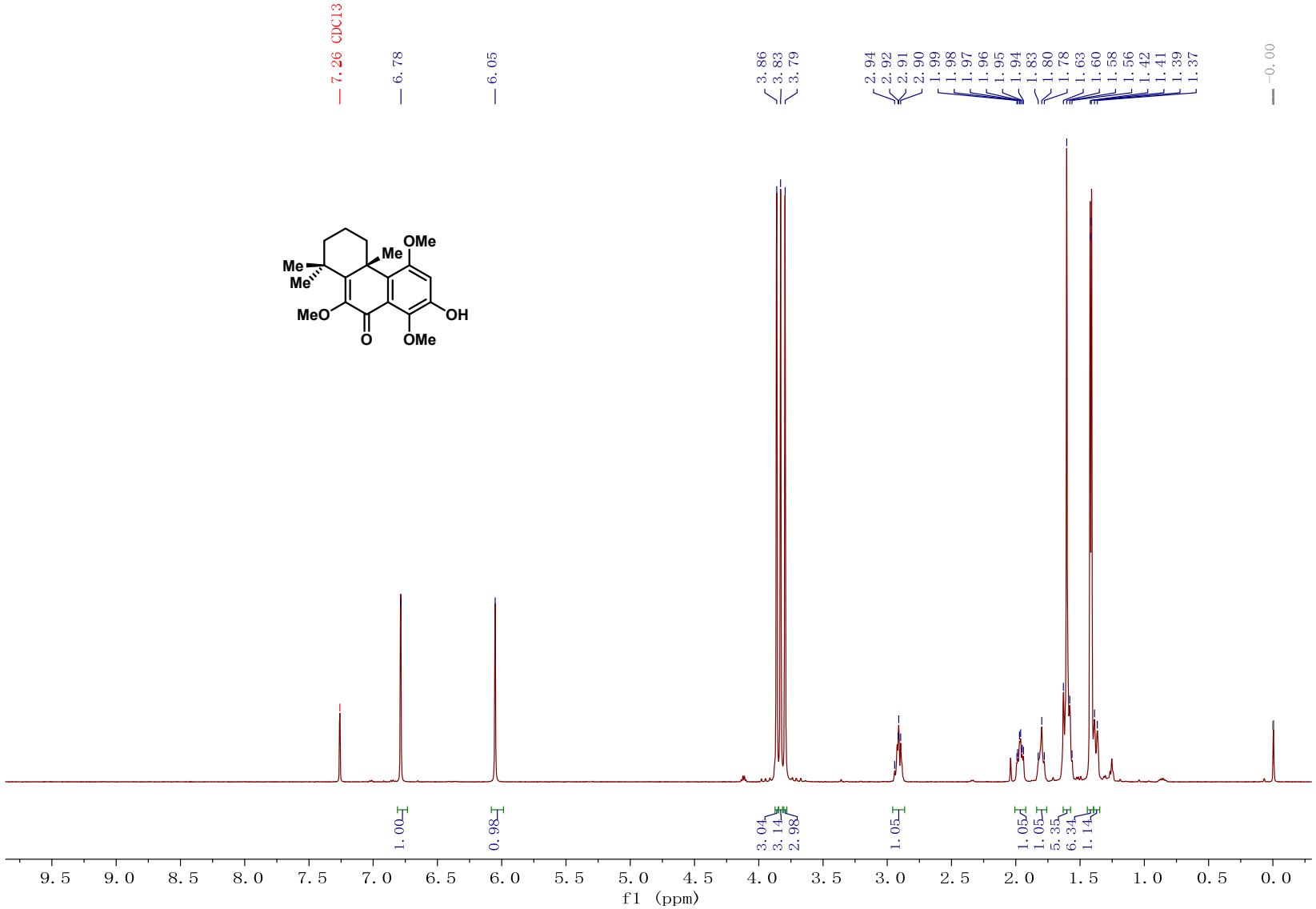

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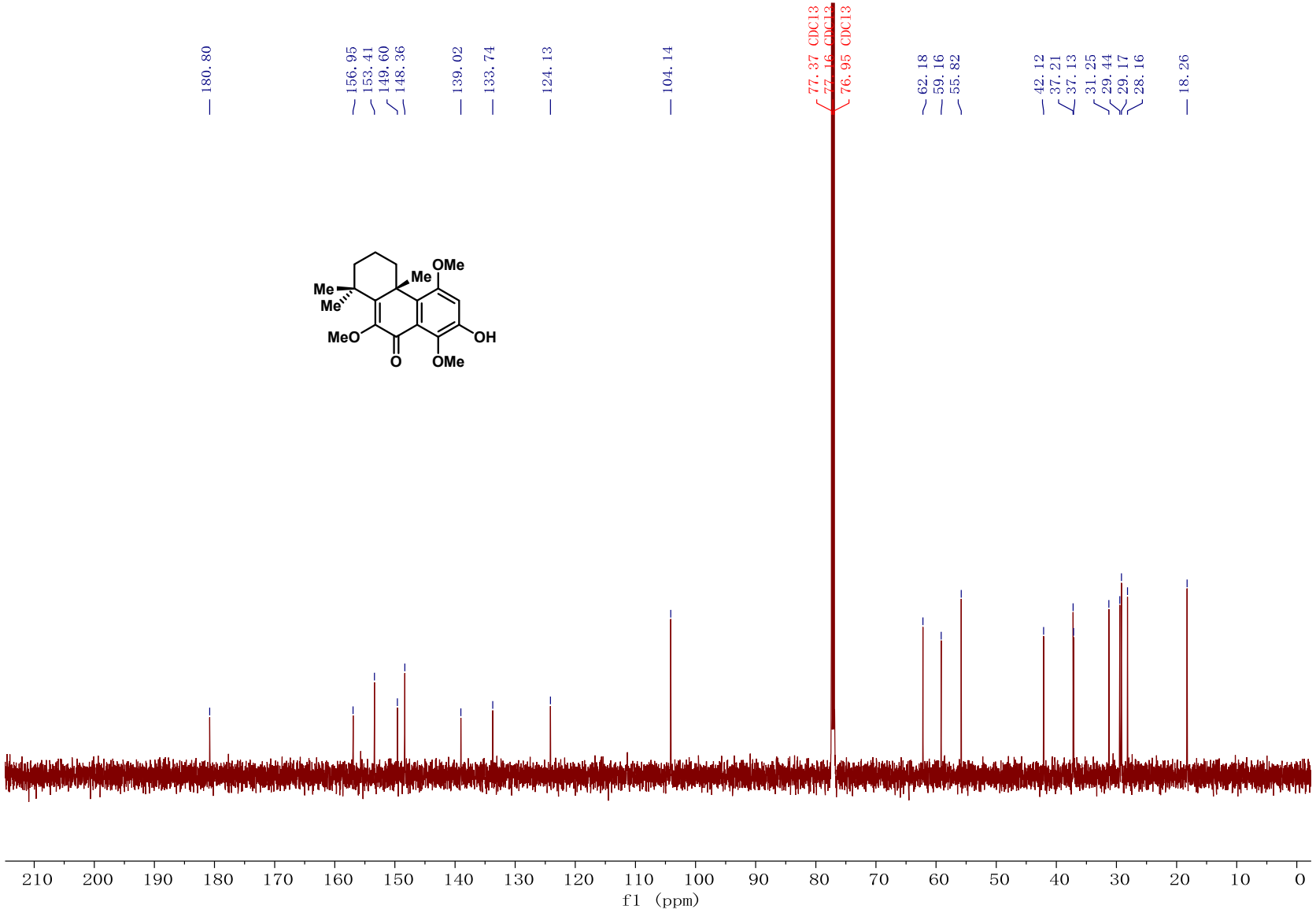
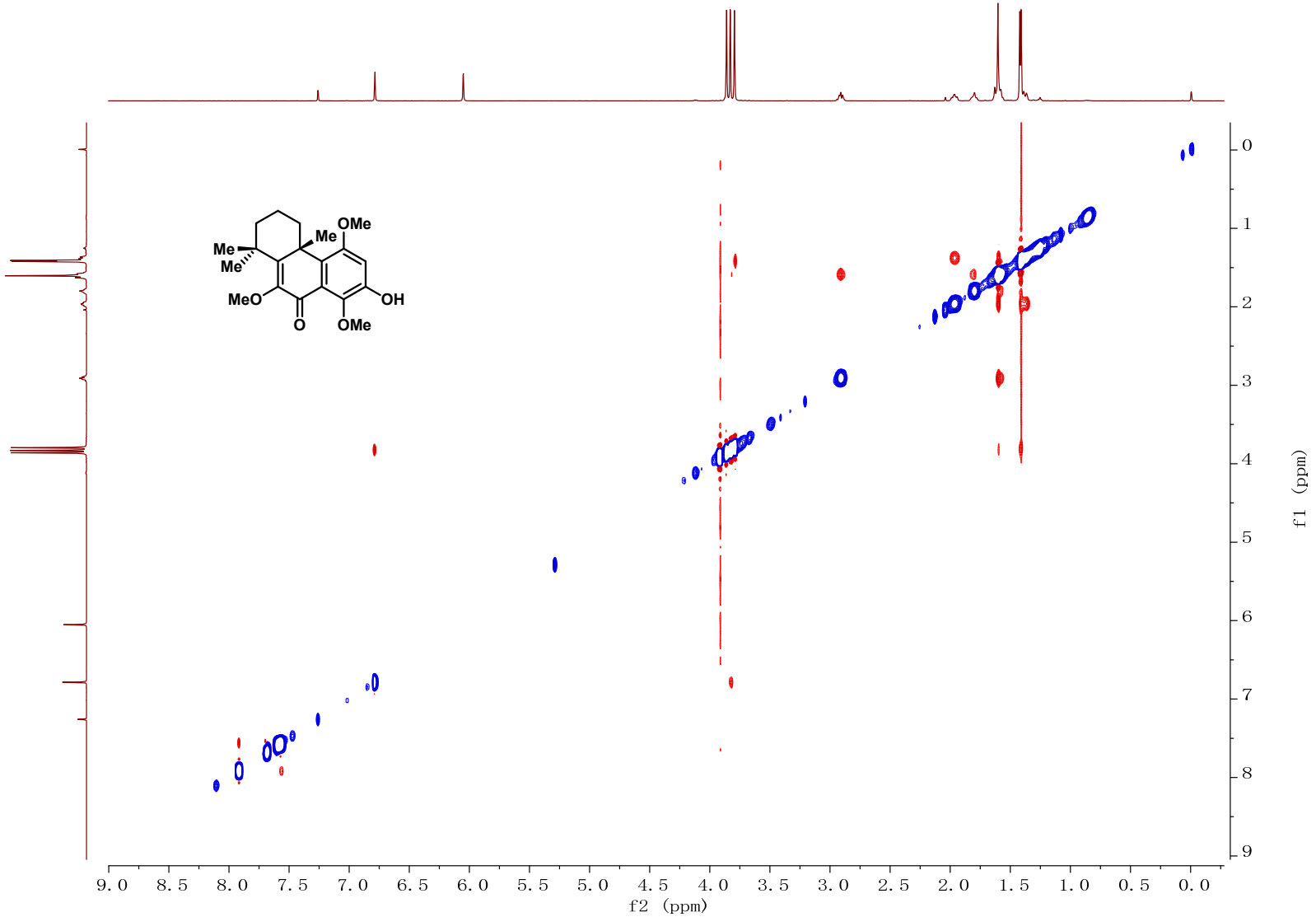


Compound 9a ^{1}H-^{1}H NOSEY NMR



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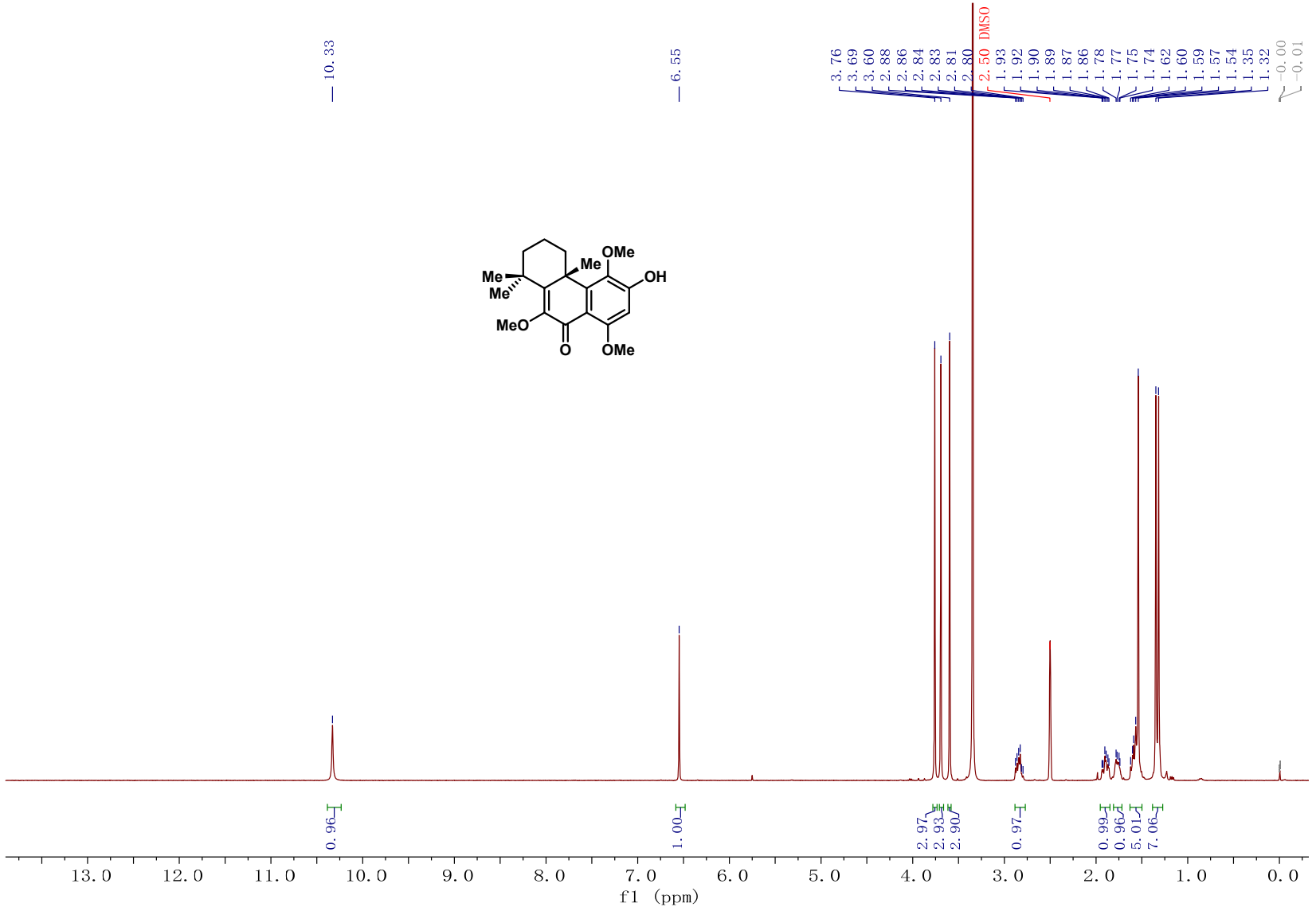

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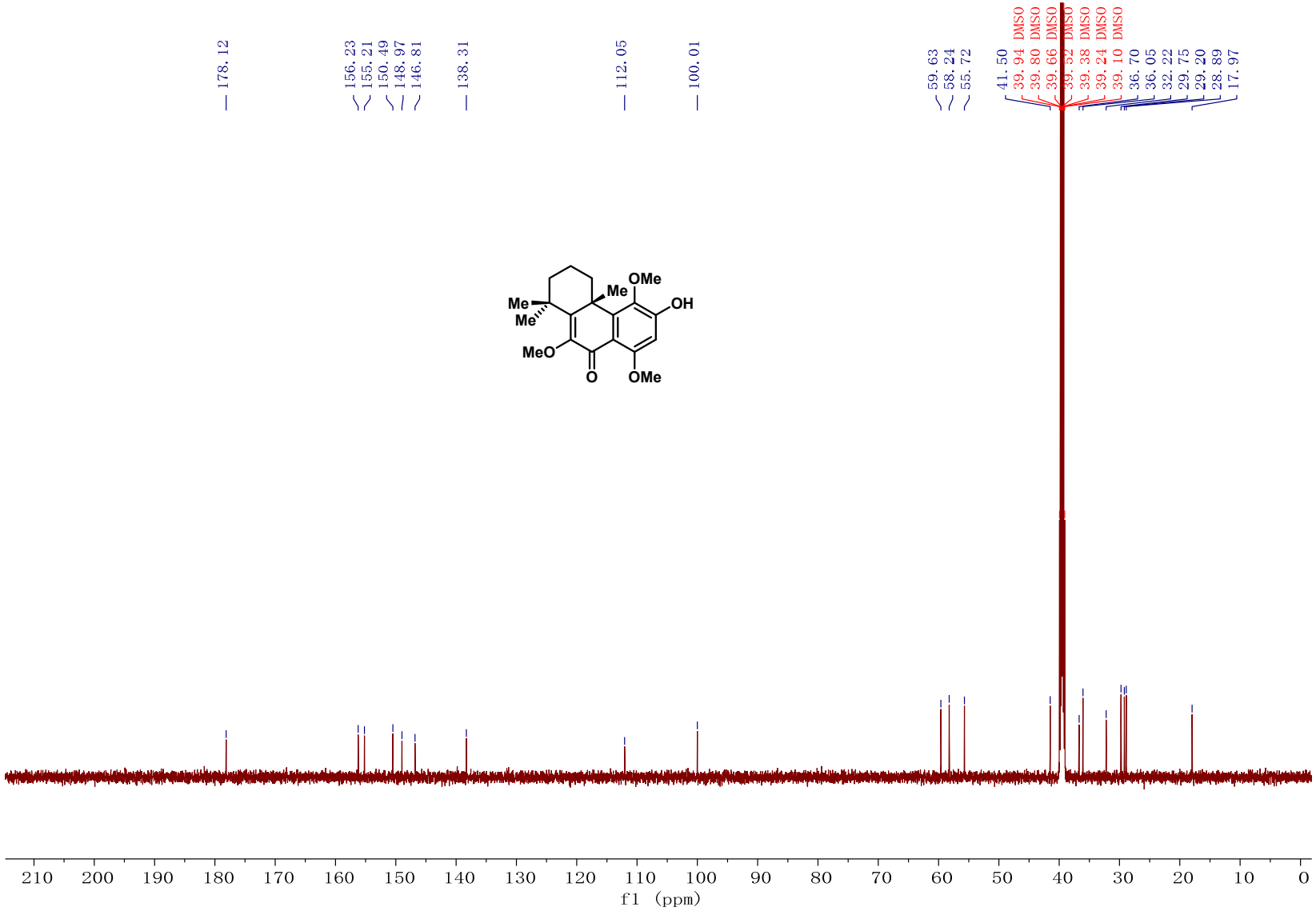

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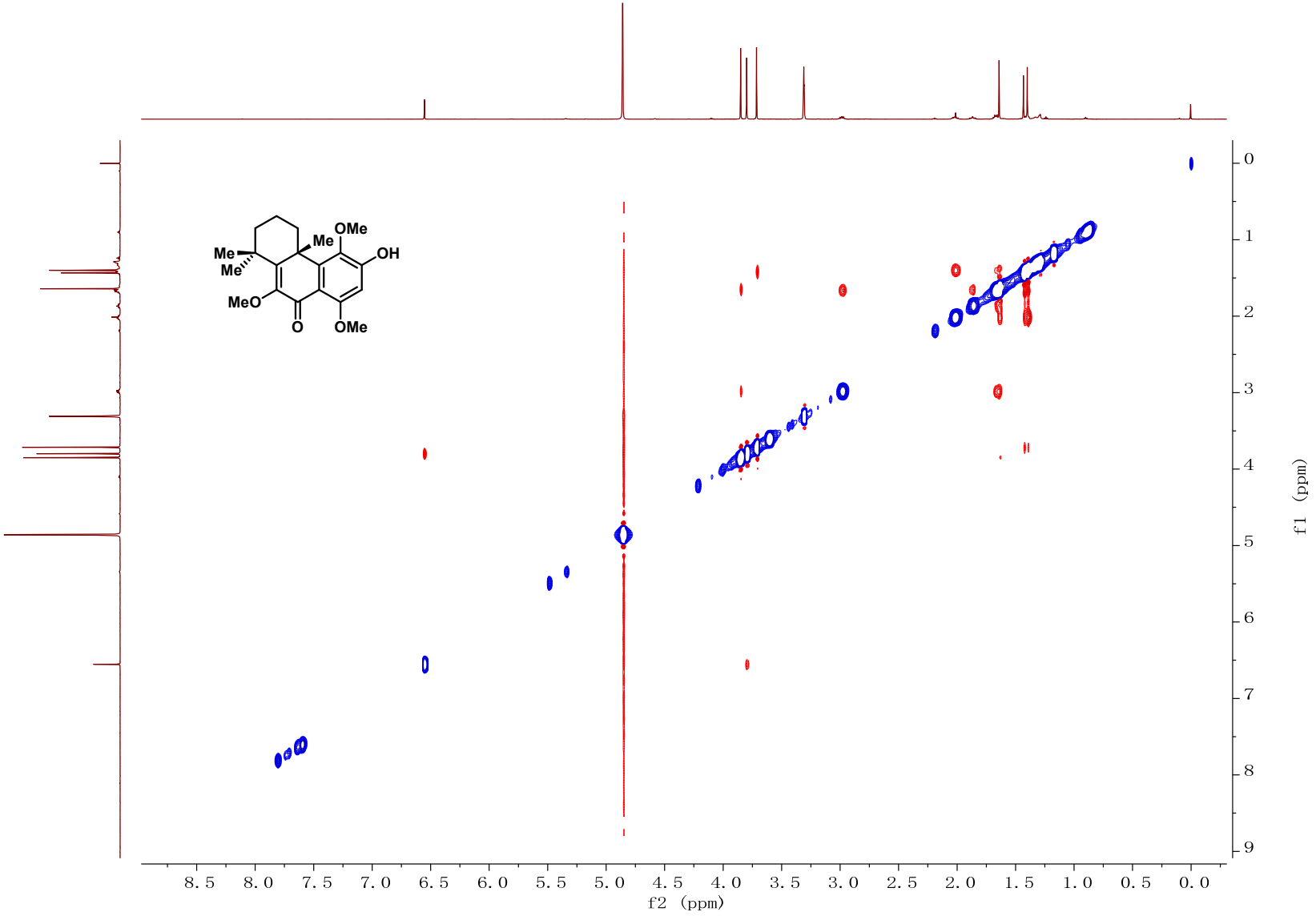

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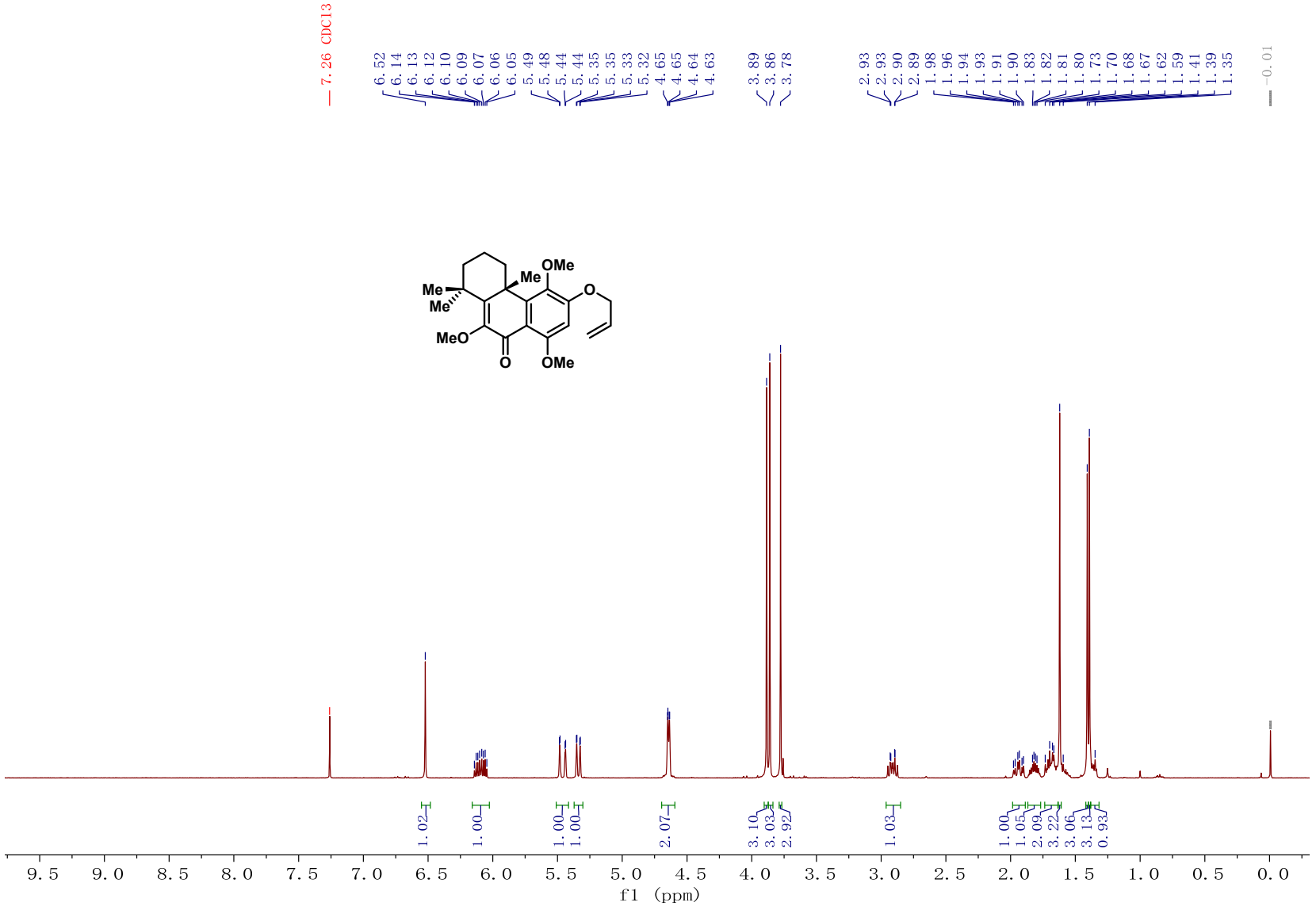

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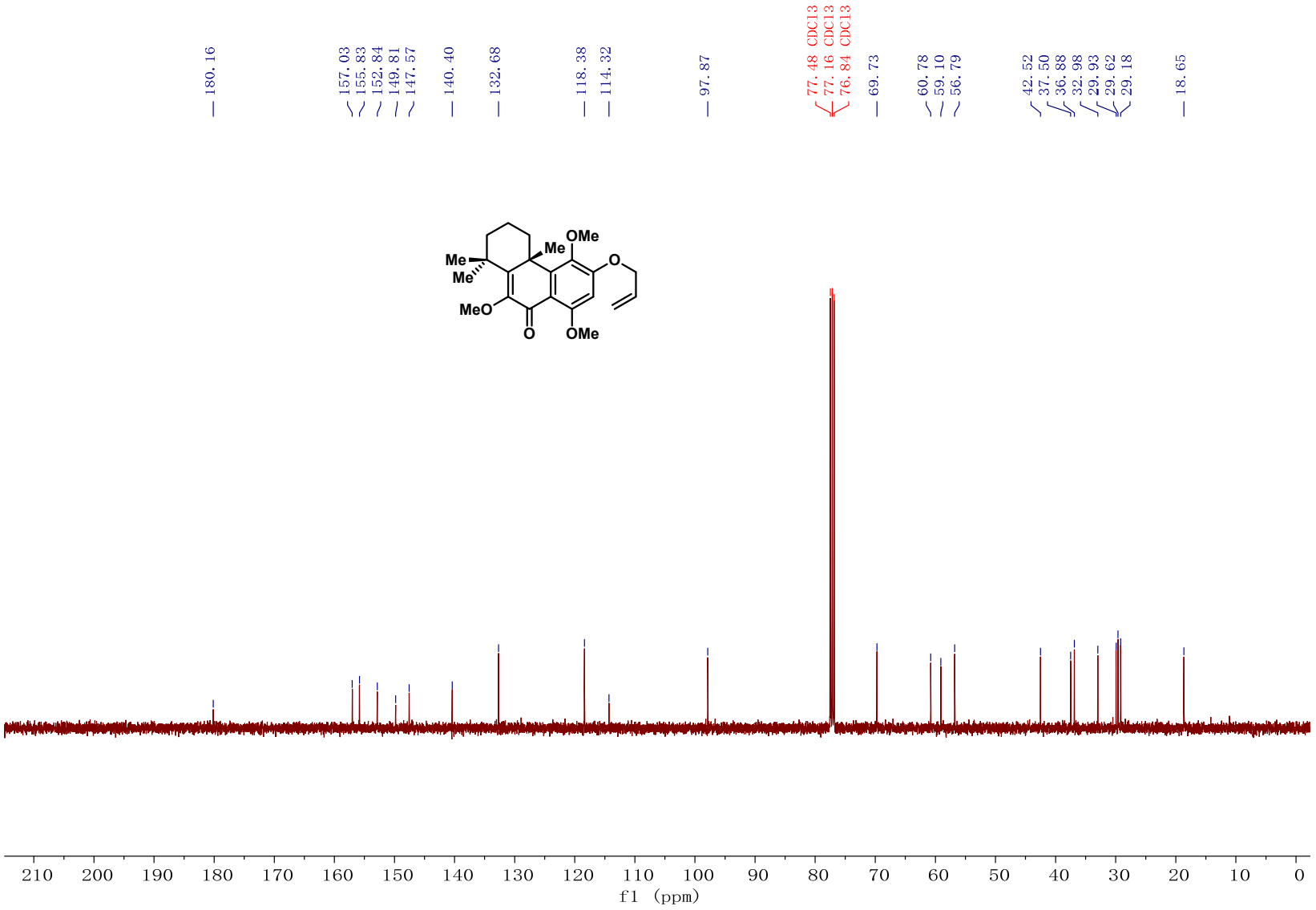

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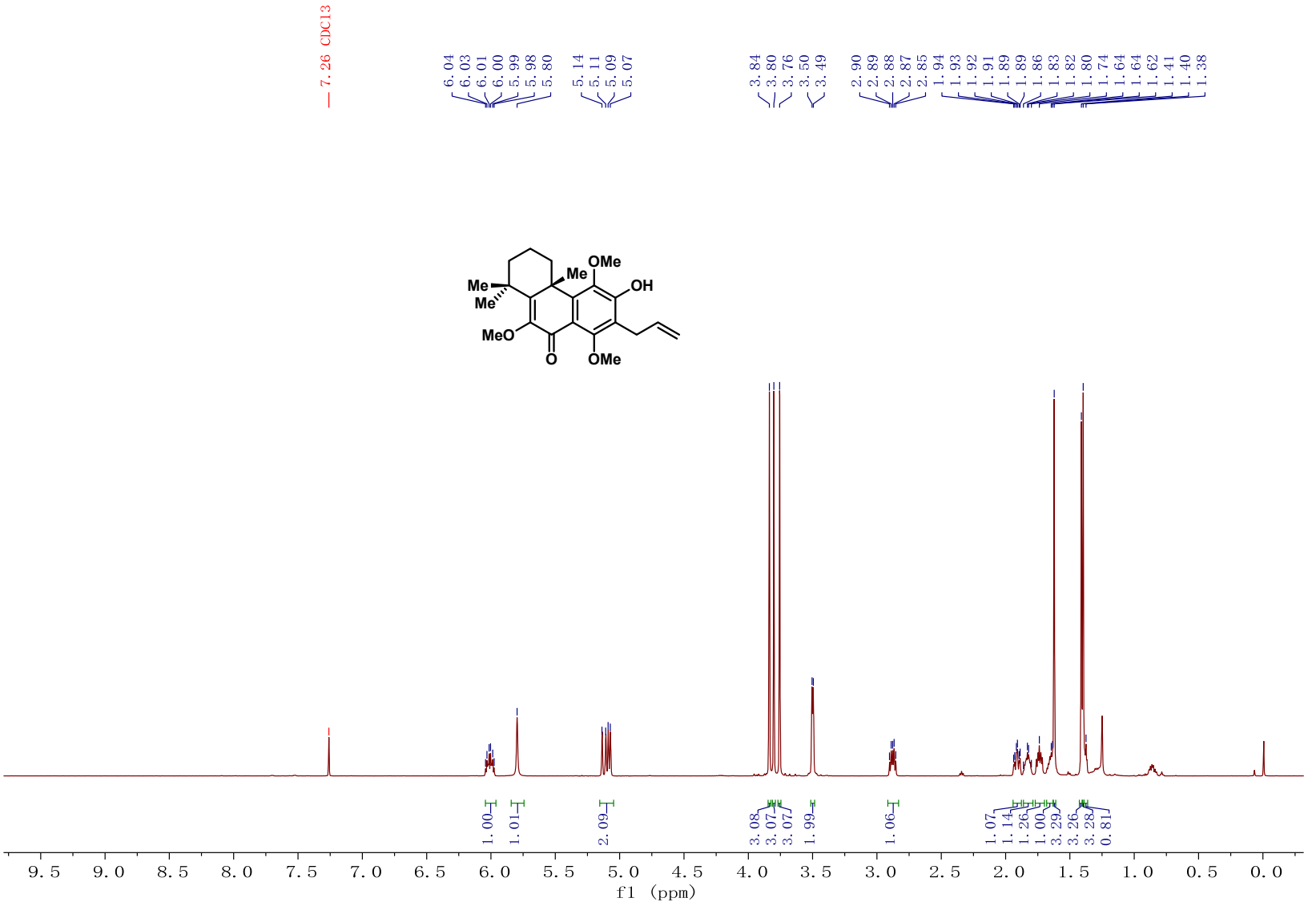

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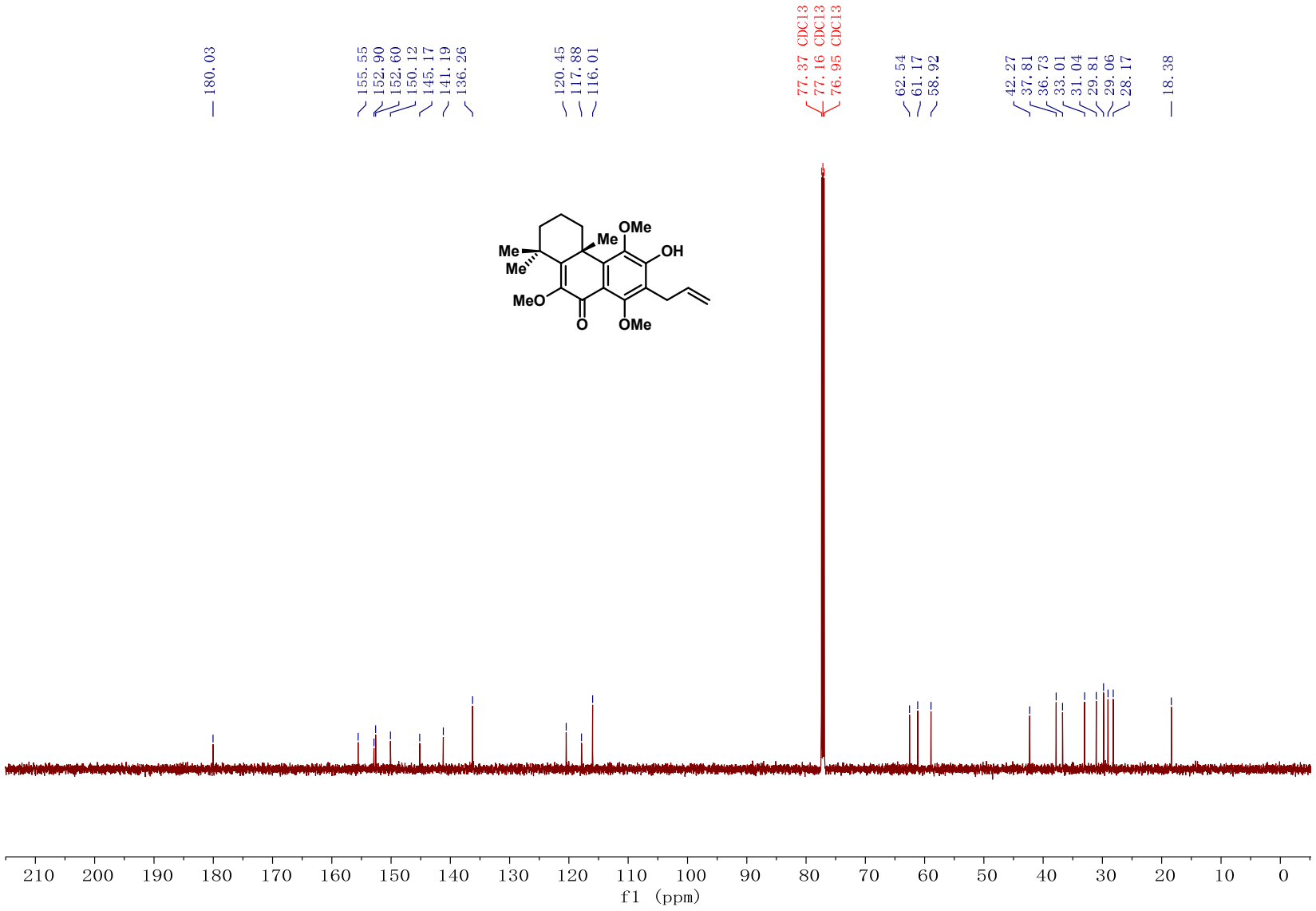

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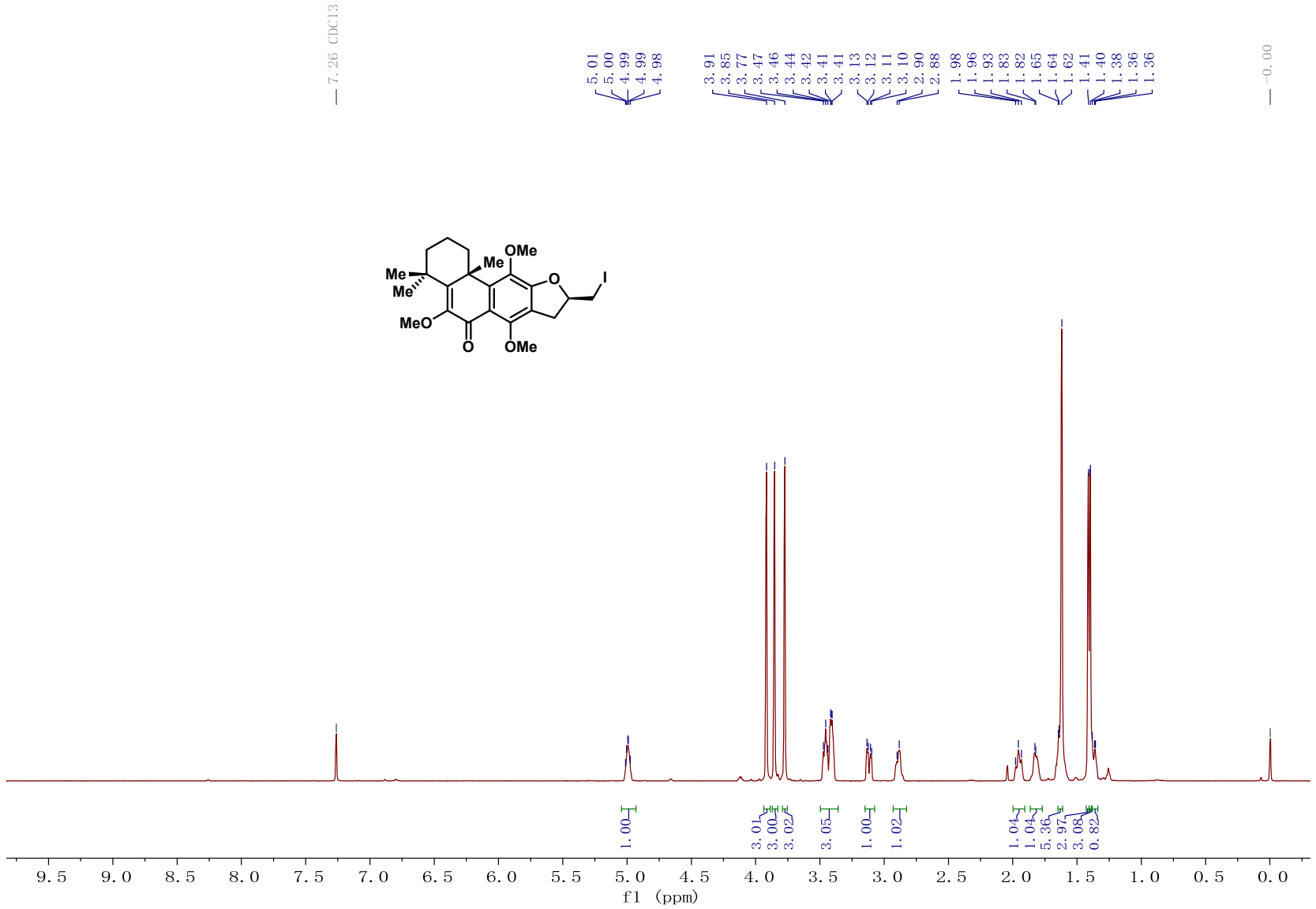

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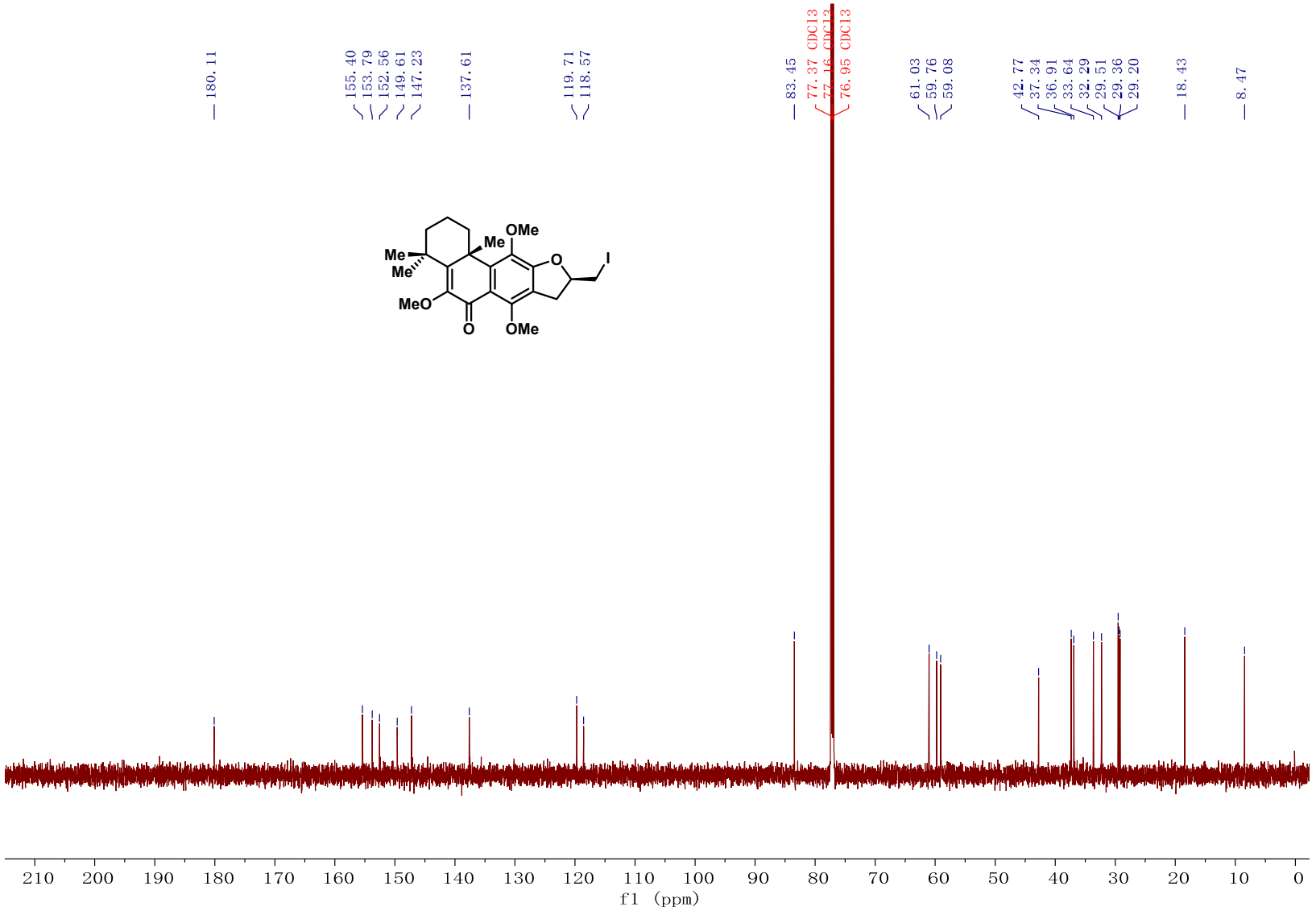

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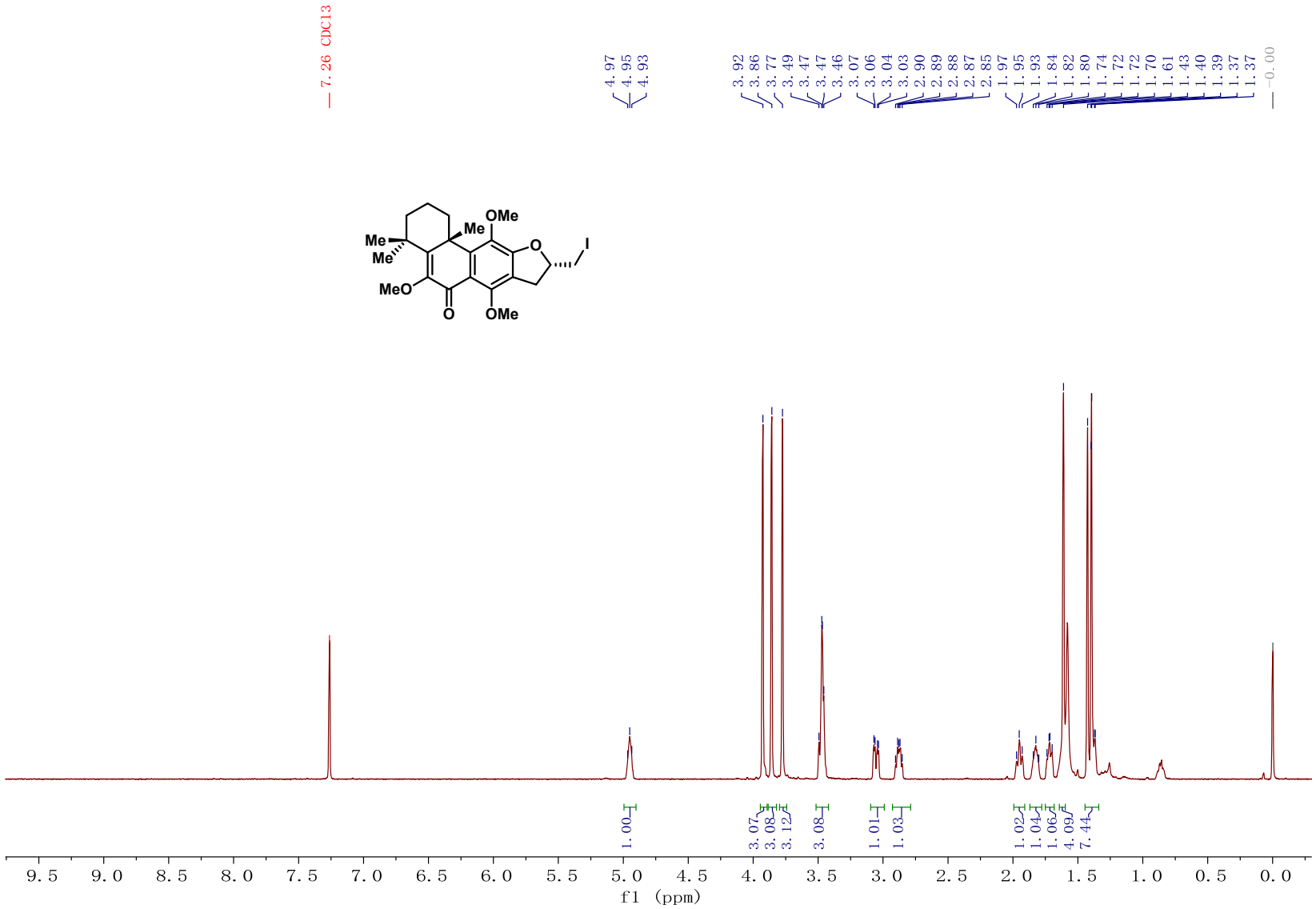

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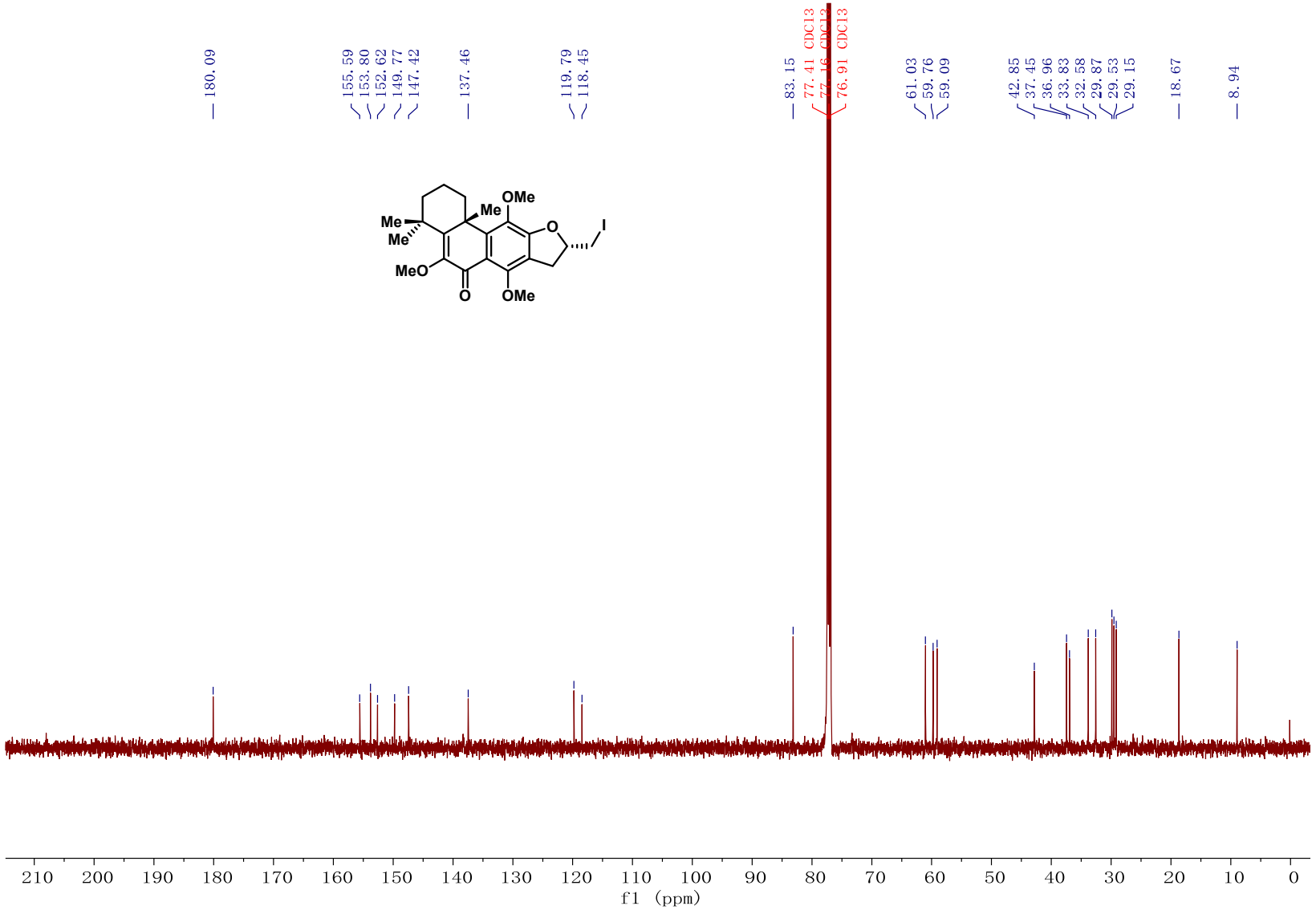

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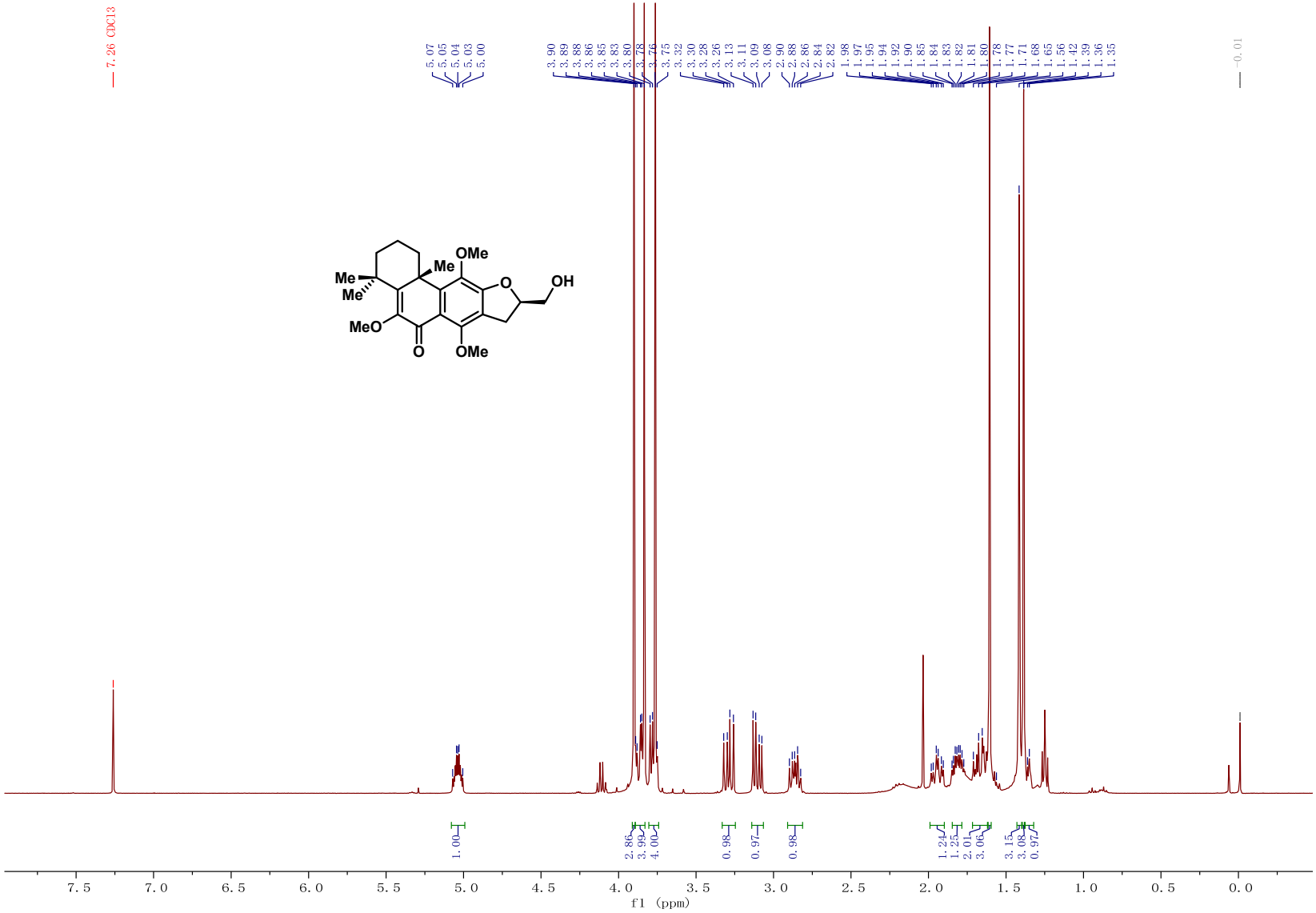

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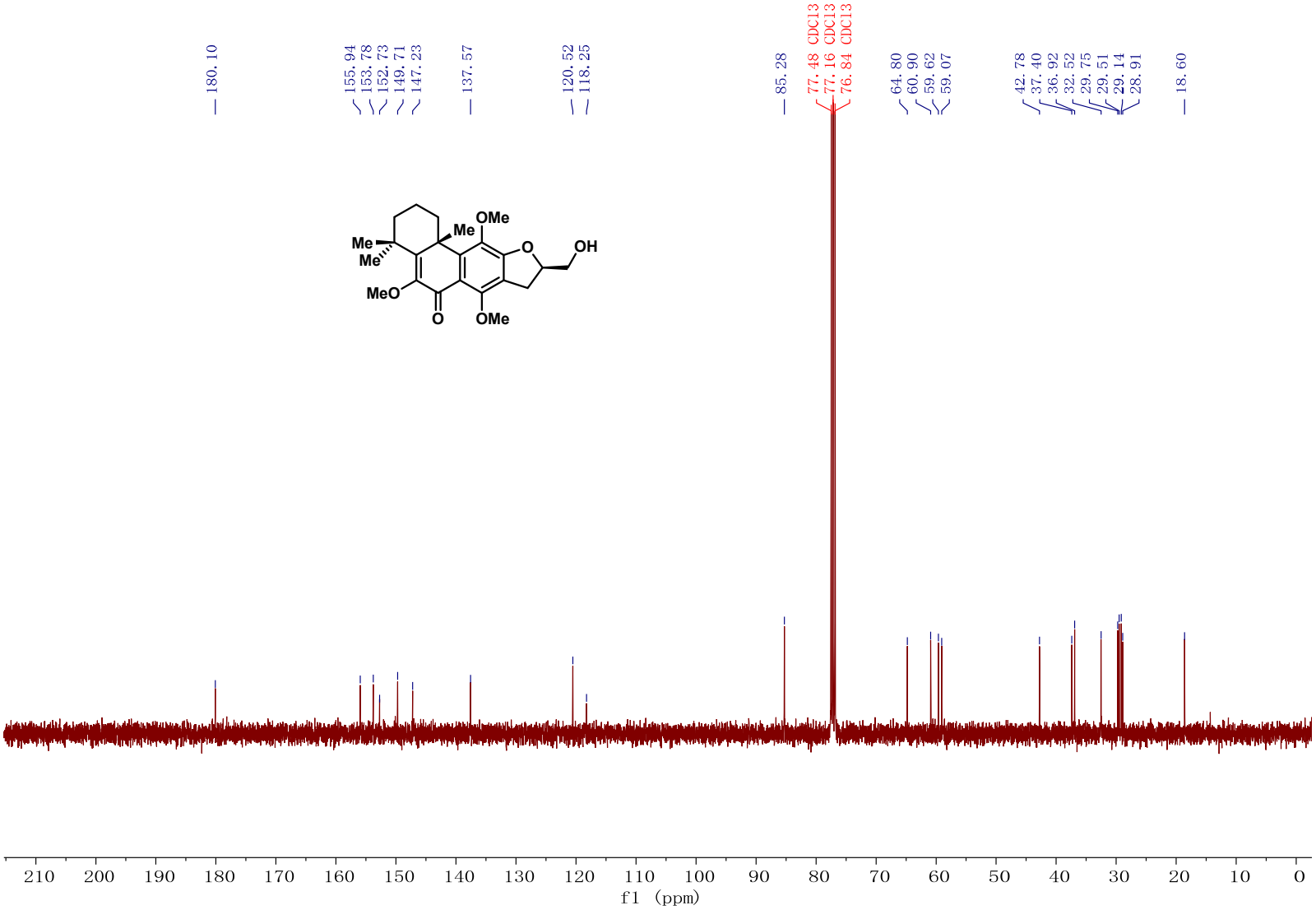

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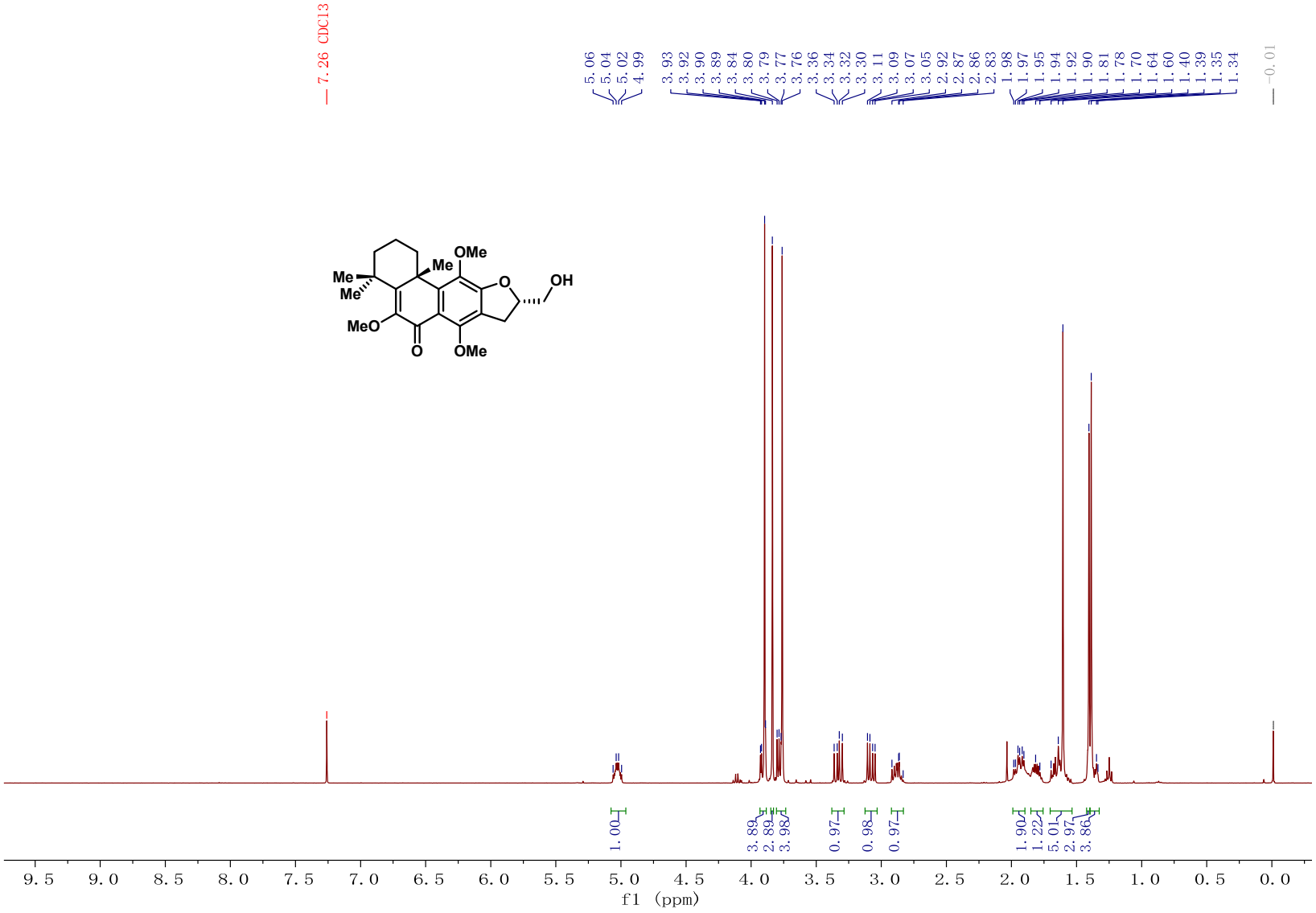

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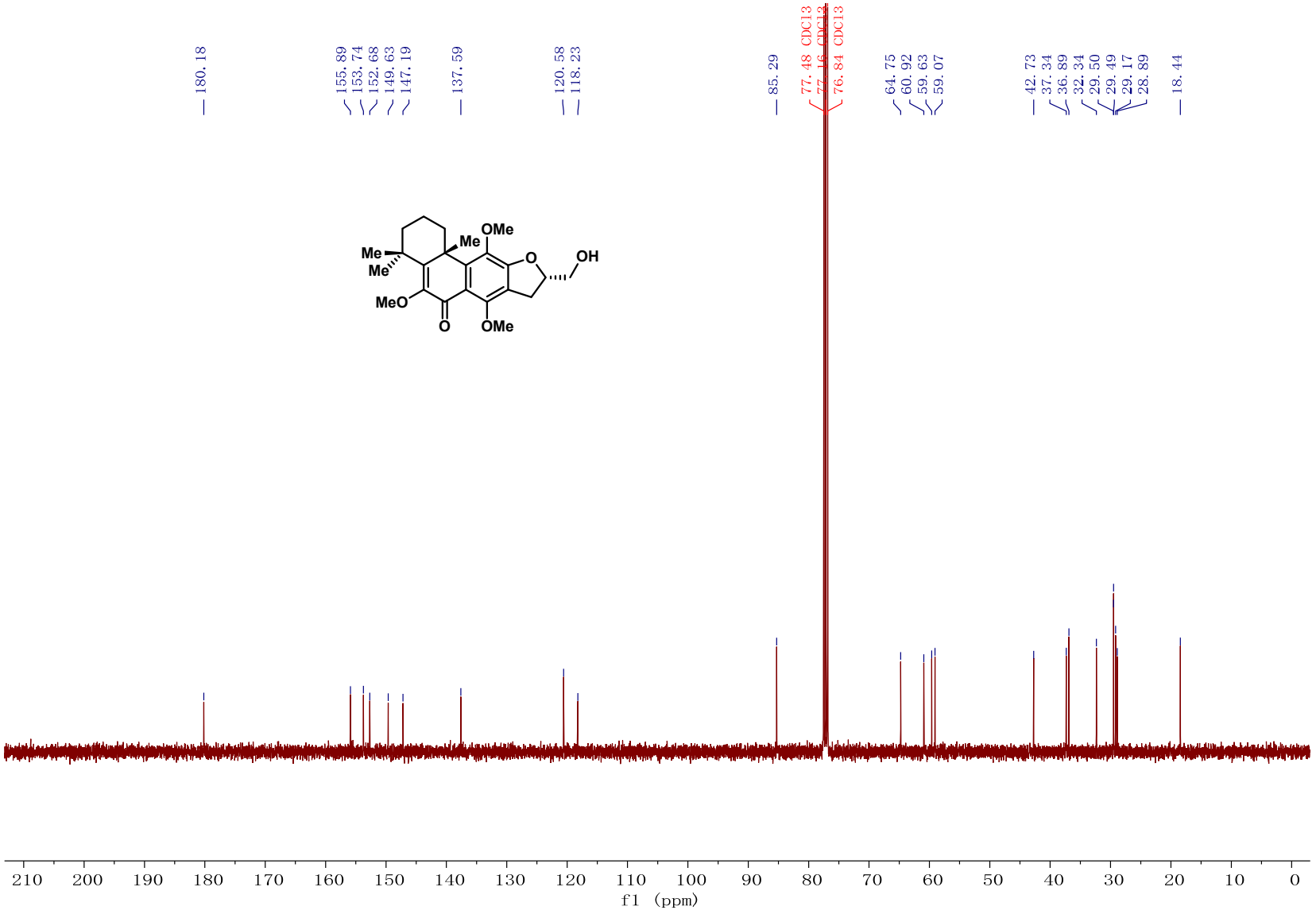

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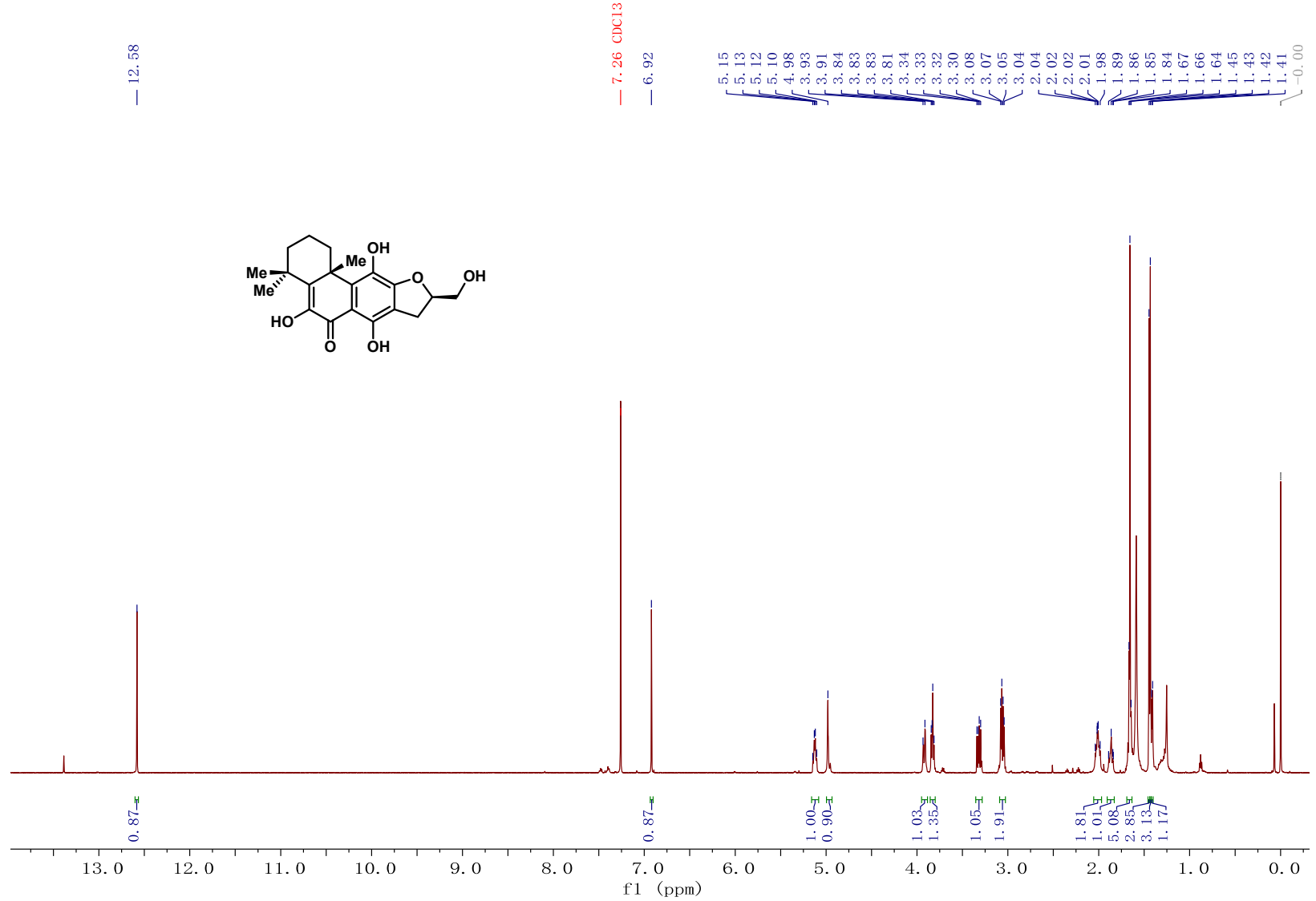

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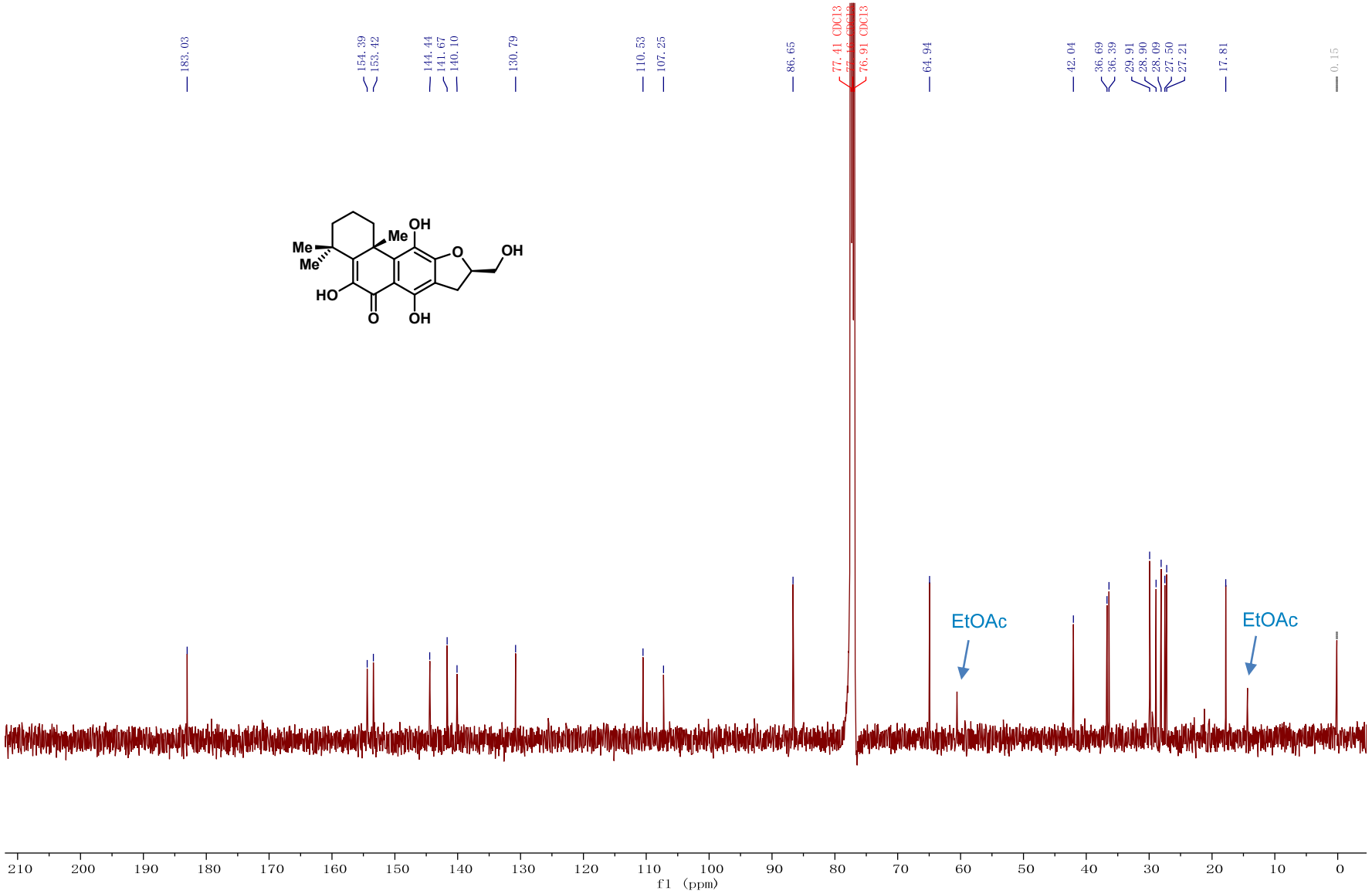

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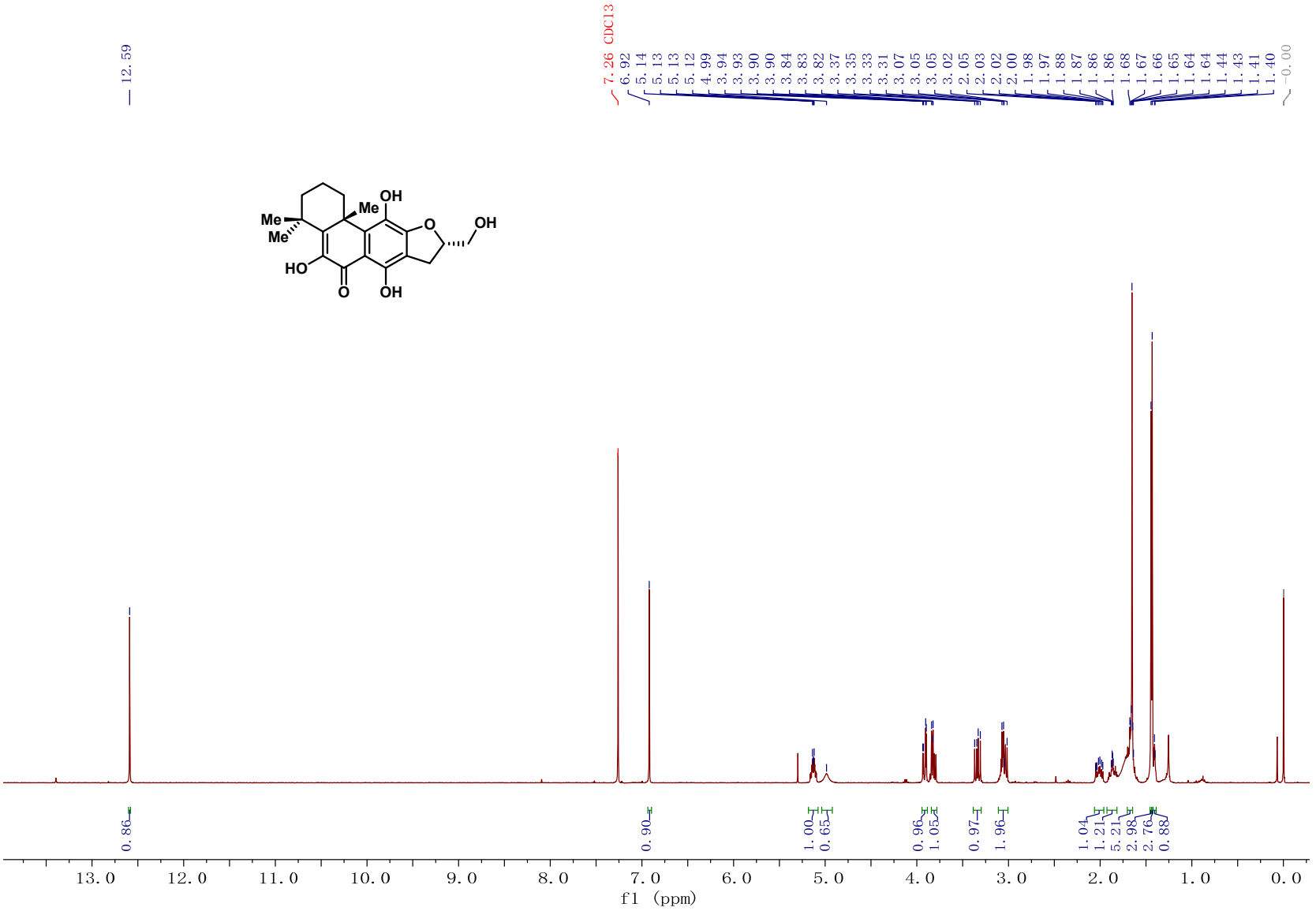

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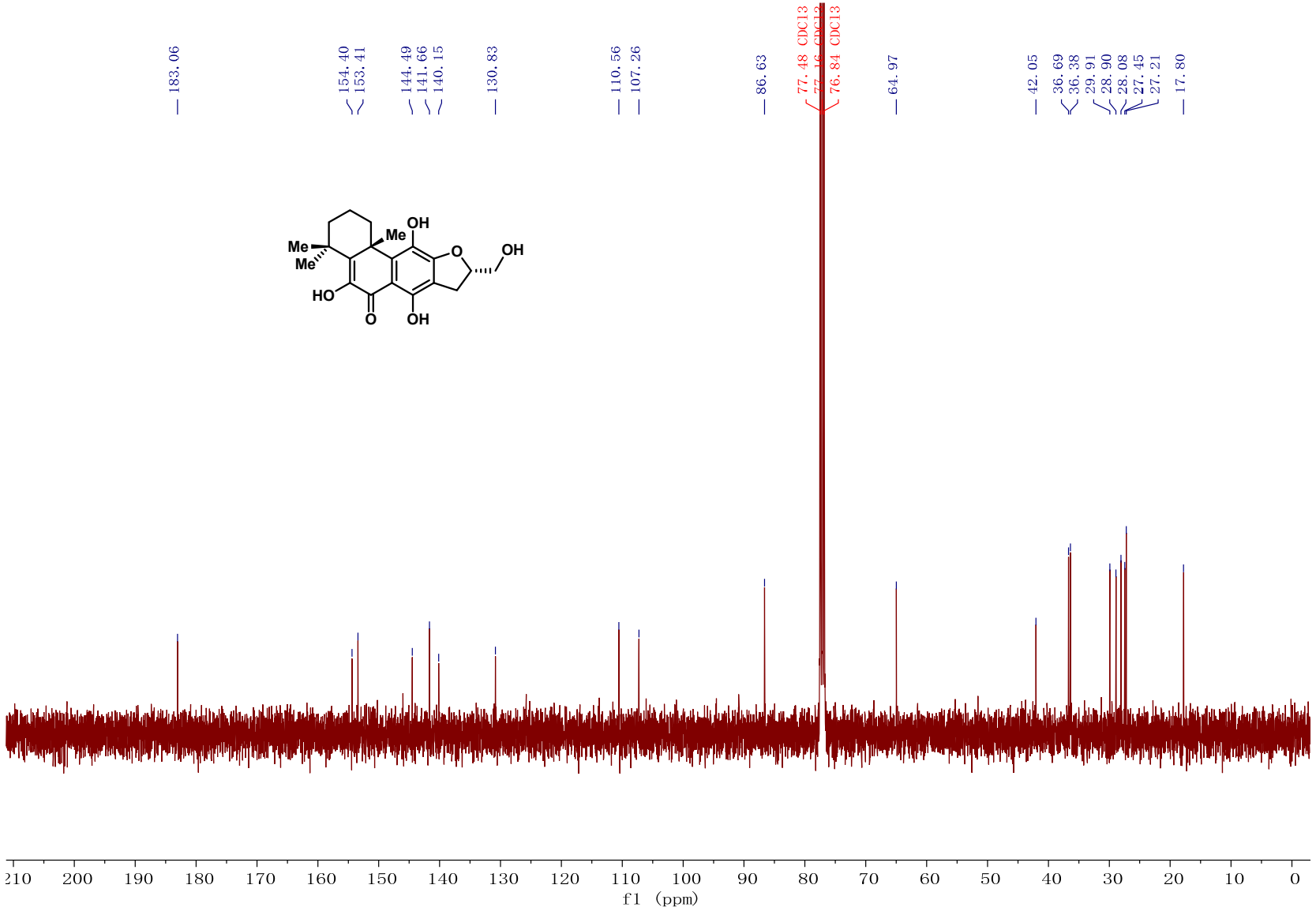

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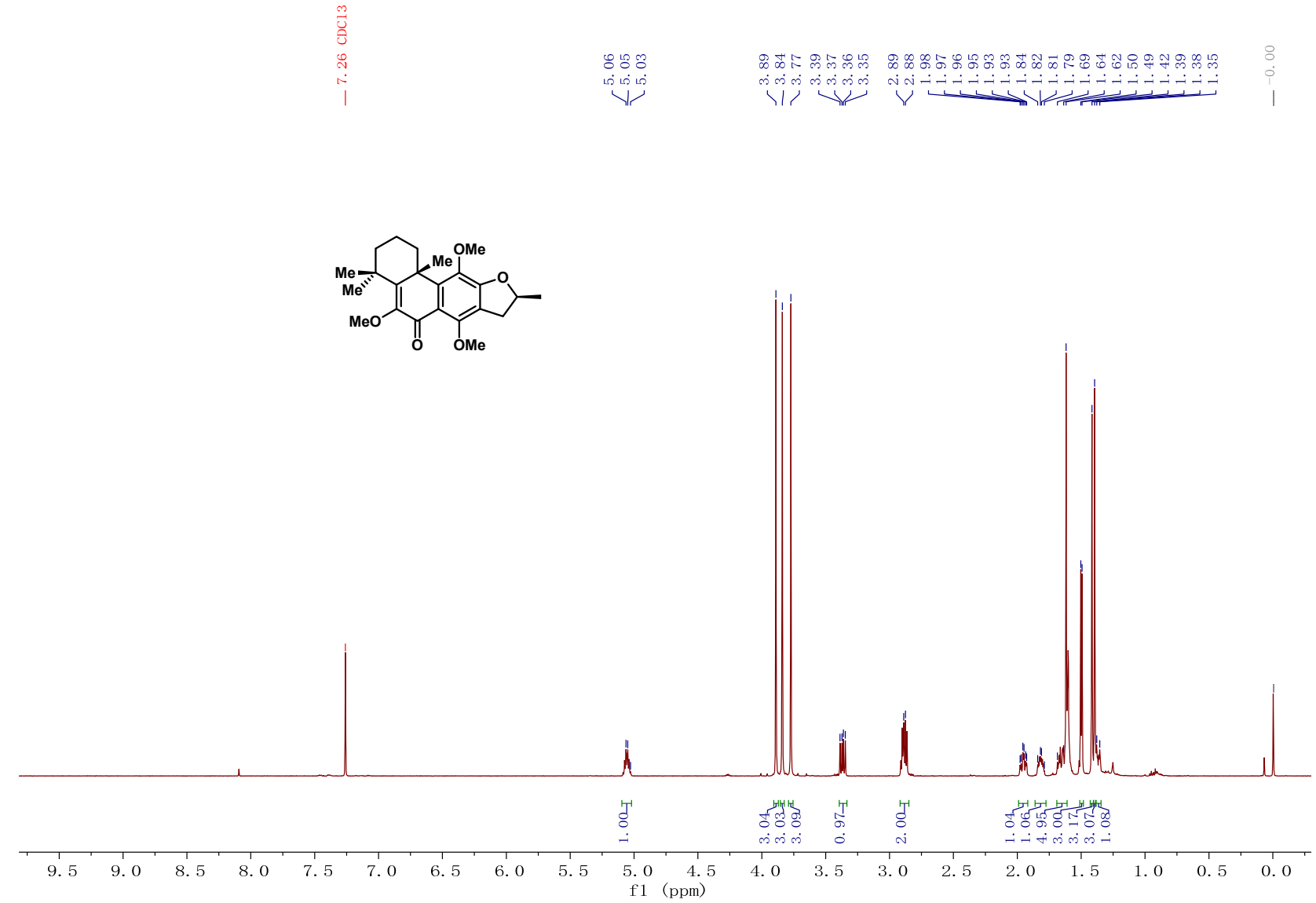

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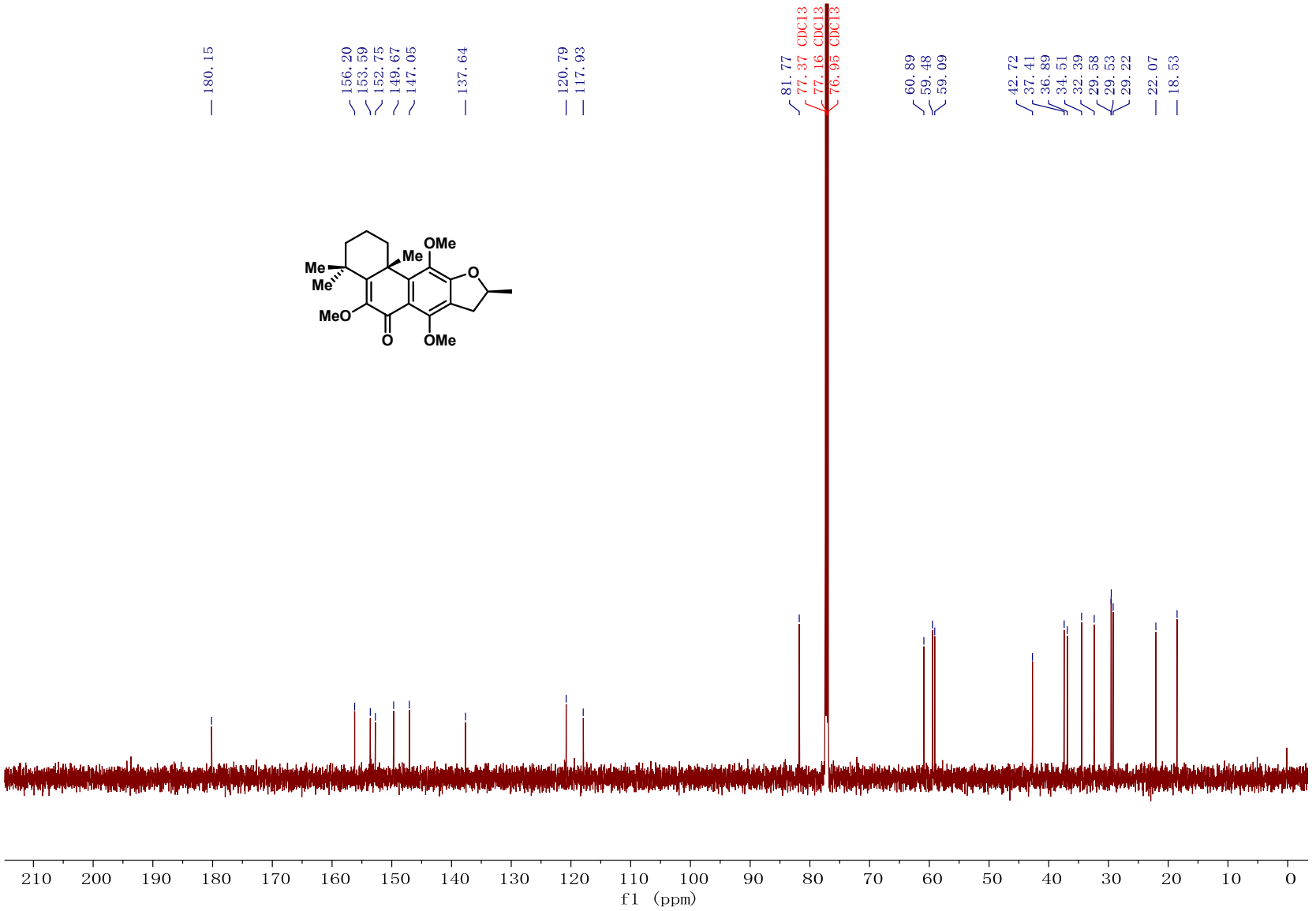
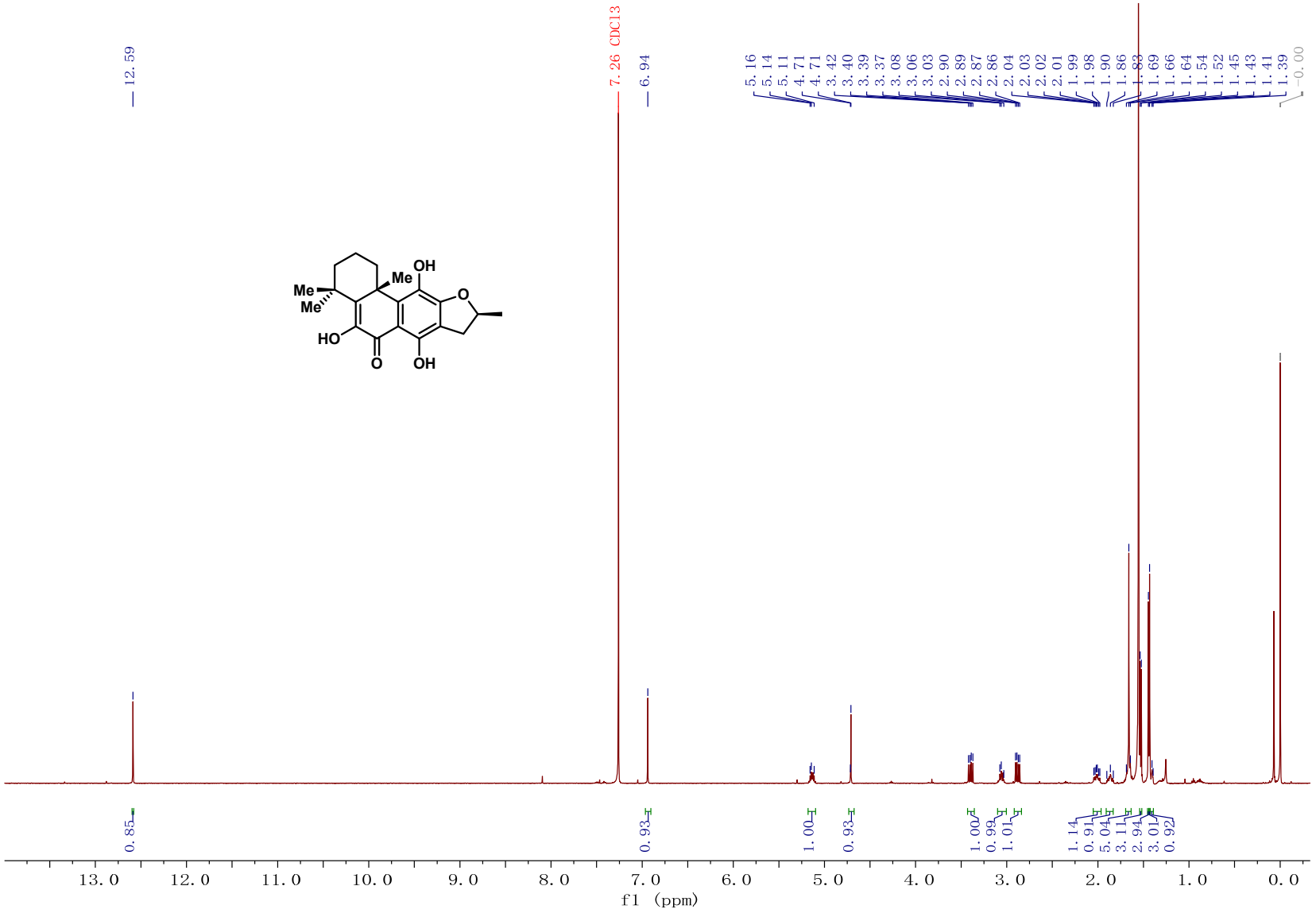


Compound 4 ^{1}H NMR



Compound 4 ^{13}C NMR