

Supplementary Information

Enantioselective Total Syntheses of Six Natural and Two Proposed Meroterpenoids from *Psoralea Corylifolia*

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1. General Information

All moisture- or oxygen-sensitive reactions were carried out under an argon atmosphere in oven flasks. The solvents were purified by distillation over the drying agents indicated and were transferred under argon: toluene, THF and Et₂O from Na; MeOH from Mg and I₂; CH₂Cl₂, Et₃N and DMF from CaH₂. All reactions were monitored by thin-layer chromatography (TLC) on silica gel GF₂₅₄ plates using UV light as visualizing agent (if applicable), and a solution of phosphomolybdic acid (50 g/L) in EtOH followed by heating as developing agents. The products were purified by flash column chromatography on silica gel (200-300 meshes) from the Qingdao Marine Chemical Company (China).

¹H NMR and **¹³C NMR** spectra were recorded in CDCl₃, (CD₃)₂CO or CD₃OD solution on a Bruker AM 400 MHz instrument or 600 MHz NMR instrument. Chemical shifts were denoted in ppm (δ), and calibrated by using residual undeuterated solvent (CDCl₃ (7.26 ppm), (CD₃)₂CO (2.05 ppm), CD₃OD (3.31 ppm) or tetramethylsilane (0.00 ppm)) as internal reference for **¹H NMR** and the deuterated solvent (CDCl₃ (77.00 ppm), (CD₃)₂CO (29.84 ppm), CD₃OD (49.00 ppm) or tetramethylsilane (0.00 ppm)) as internal standard for **¹³C NMR**. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad, dd = double doublet, td = triple doublet, dt = double triplet, m = multiplet.

The high-resolution mass spectral analysis (**HRMS**) data were measured on Thermo Fisher Orbitrap Elite Mass Spectrometer or a LCT Premier XE (Waters) mass spectrometer (Waters, Milford, MA, U.S.) by means of the ESI technique.

Electron ionization mass spectra (**EI-MS**) were measured on a Shimadzu GCMSQP2010SE spectrometer by direct inlet at 70 eV and the corresponding signals were given in m/z with relative intensity (%) in brackets.

Melting points (m.p.) were measured on a Kolfer melting point apparatus without calibration (Beijing Tech Instrument Co., LTD).

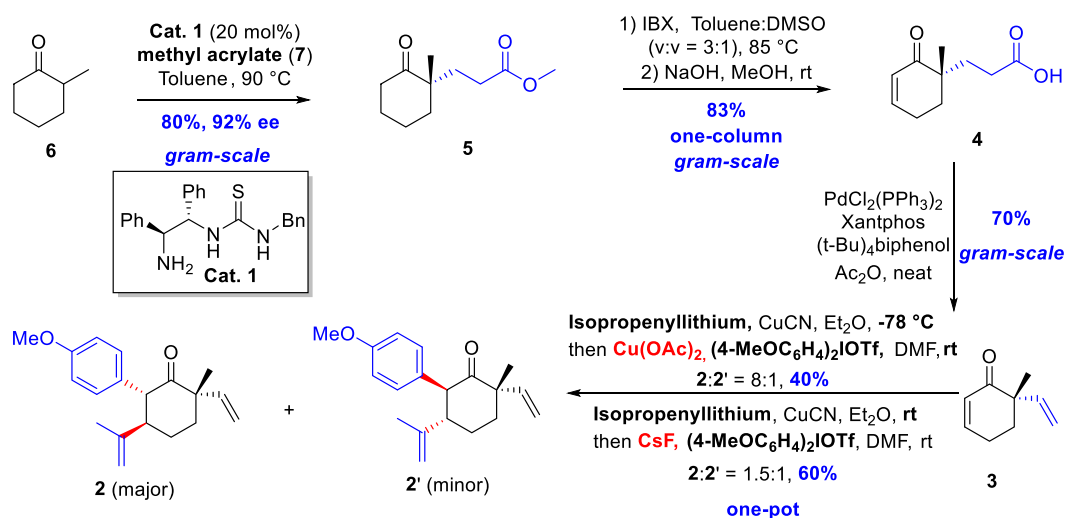
The **IR** spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer.

The **X-ray** single-crystal determination was performed on an Agilent Super Nova single crystal X-ray diffractometer.

Optical rotations were detected on RUDOLPH A21202-J APTV/GW.

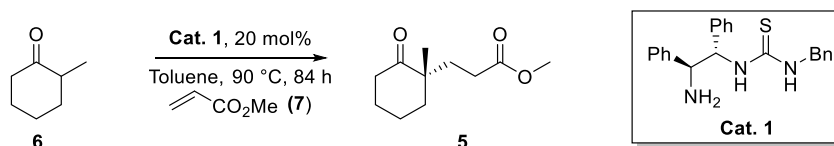
The **enantiomeric excesses** (ee) value of the products was determined by Ultra Performance Convergence Chromatography (UPC²) equipped with Waters 2998 Photodiode Array Detector instruments.

2. Synthesis of precursors 2 and 2'

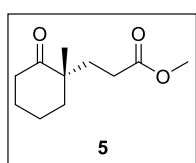


Scheme S1 Synthesis of precursors **2** and **2'**.

2.1 Synthesis of compound δ -keto ester **5**



Compound δ -keto ester **5** was prepared according to the literature by a modified procedure¹. To a solution of **Cat. 1** (6.0 mmol, 20.0 mol %) in toluene (20.0 mL) were added the 2-methylcyclohexanone (**6**) (3.64 mL, 30.0 mmol) and methyl acrylate (**7**) (5.40 mL, 60.0 mmol, 2.0 equiv.) at room temperature, and the resulting mixture was stirred at 90 °C. After 84 h, the residue was purified by chromatography on silica gel, eluting with 10-60% Et₂O/pentane to give the Michael product δ -keto ester **5** as a colorless oil (4.75 g, 80% yield, 92% ee. R_f = 0.4 (10% Et₂O in pentane)).

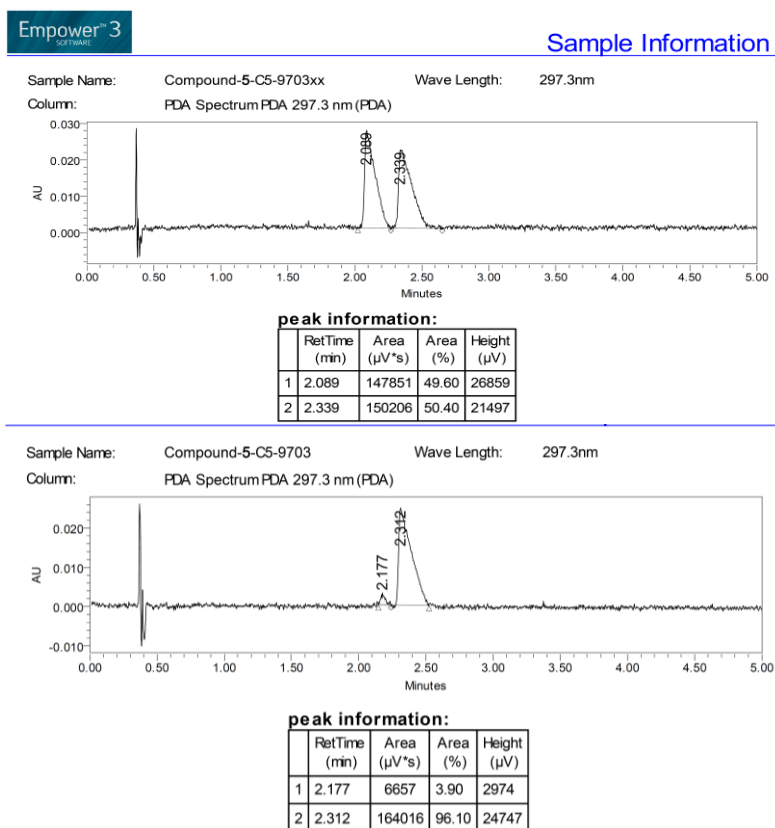


Compound 5: Colorless oil; $[\alpha]_D^{25} = -32.0$ (c = 3.0 in EtOH).

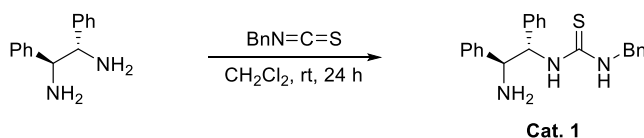
¹H NMR (400 MHz, CDCl₃) δ : 3.59 (s, 3H), 2.34-2.29 (m, 2H), 2.27-2.21 (m, 1H), 2.13-2.05 (m, 1H), 2.01-1.93 (m, 1H), 1.80-1.65 (m, 6H), 1.56-1.51 (m, 1H), 1.00 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ : 214.8,

173.7, 51.3, 47.6, 38.9, 38.4, 32.2, 28.7, 27.1, 22.1, 20.7. **HRMS** (ESI) m/z found 221.1449, calculated for C₁₁H₁₆O₃Na [M+Na]⁺ 221.1448. **MS** (EI) m/z (%): 198 (9), 154 (36), 96 (52), 83 (54), 69 (62), 112 (98), 55 (100). **IR** (KBr plate) ν_{max} : 2937, 2866, 1739, 1705, 1437, 1377, 1306, 1257, 1172, 1123, 1097 cm⁻¹. **Enantiomeric excess** was determined by **UPC²** (CHIRALPAK[®] IC-3 column, CO₂/Methanol = 97/3, flow rate: 2 mL/min, 40 °C, $\lambda = 297.3$

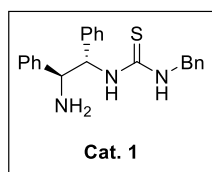
nm), 92% ee, $t_R = 2.177$ min (minor), 2.312 min (major).



2.2.1 Synthesis of chiral thiourea catalyst 1 (Cat. 1)



Catalyst **1** (**Cat. 1**) were synthesized according to the literature procedures.² An isothiocyanate (2.12 g, 10.0 mmol) was dropped to a solution of an ethylenediamine (1.33 mL, 10.0 mmol) in CH_2Cl_2 (20.0 mL), and the mixture was stirred at room temperature for 24 h. When the starting material disappears (monitored by TLC), the solvent was removed under reduced pressure, the residue was purified by column chromatography to afford the thiourea catalysts **1** (**Cat. 1**) as white solid (2.89 g, 80% yield. $R_f = 0.4$ (10% MeOH in DCM)).



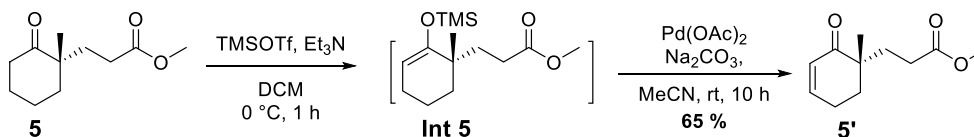
Catalyst 1 (**Cat. 1**): White solid; $[\alpha]_D^{26} = -71.8$ ($c = 1.0$ in $CHCl_3$), $[\text{lit}^2, [\alpha]_D^{24} = -74.3$ ($c = 1.0$ in $CHCl_3$); **m.p.**: 66-68 °C.

1H NMR (600 MHz, $CDCl_3$) δ : 7.43 (brs, 1H), 7.29-7.22 (m, 11H), 7.13 (brs, 4H), 6.50 (brs, 1H), 5.11 (brs, 1H), 4.60 (brs, 1H), 4.52-4.94 (m, 1H), 4.29 (brs, 1H), 1.57 (brs, 2H); **^{13}C NMR** (150 MHz, $CDCl_3$) δ : 181.8, 141.7, 139.6, 137.1, 128.8, 128.7, 128.6, 127.7, 127.6, 127.4, 126.6, 63.9, 60.2, 48.4. **MS** (EI) m/z (%):

361 (0.1), 327 (4), 256 (15), 194 (3), 165 (7), 106 (100), 91 (31), 79 (12). IR (KBr plate) ν_{max} : 3268, 3061, 3029, 2964, 1538, 1495, 1453, 1347, 1287, 1262, 1076, 1028, 799, 757, 699 cm^{-1} .

2.2 Synthesis of compound 4

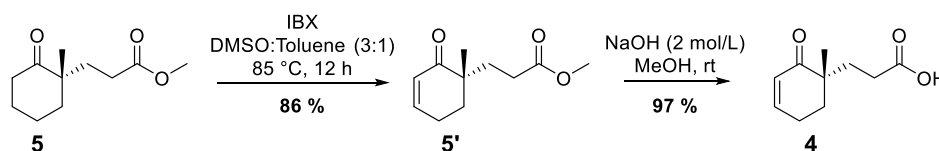
Method I:



To a stirred solution of δ -keto ester **5** (39.6 mg, 0.2 mmol) in dichloromethane (2 mL) was added freshly distilled Et₃N (41.7 μL , 0.3 mmol) and TMSOTf (36.3 μL , 0.2 mmol) at 0 °C and was stirred at the same temperature for 1 h. The reaction was quenched by addition of saturated aqueous NaHCO₃ and the aqueous phase was extracted with diethyl ether (3 \times 20 mL). The combined organic extracts were washed with brine, dried over anhydrous Na₂SO₄, and concentrated to give **Int 5** as a yellow oil.

To a stirred solution of the crude product **Int 5** in anhydrous CH₃CN (2 mL) was added Na₂CO₃ (63.6 mg, 0.6 mmol) and Pd(OAc)₂ (48.5 mg, 0.2 mmol). The resulting mixture was stirred at the room temperature for 10 hours, treated with Et₃N (0.31 mL, 2.40 mmol) and then concentrated. The residue was purified by column chromatography to afford **5'** as a yellow oil (25.5 mg, 65%). R_f = 0.4 (silica gel, petroleum ether: ethyl acetate = 5:1).

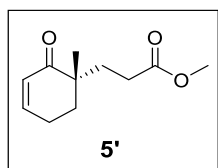
Method II:



To a stirred solution of **5** (6.6 g, 31.0 mmol) in DMSO:toluene (3:1/v:v) was added IBX (26.1 g, 93.3 mmol), and the mixture was stirred at 85 °C.³ After the starting material disappears (monitored by TLC), aqueous saturated NaHCO₃ (300 mL) and diethyl ether (300 mL) were added to the reaction mixture at room temperature, which was filtered through a Celite pad. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 \times 100 mL). The combined organic phase was washed with brine, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure to give a residue **5'** as a yellow oil. The crude product **5'** was used for next step without purification.

To a solution of the crude product **5'** (5.22 g, 26.6 mmol) in MeOH (11.0 mL) was added aqueous 2.0 mol/L NaOH (26.6 mL, 53.2 mmol, 2.0 equiv.). The reaction mixture was

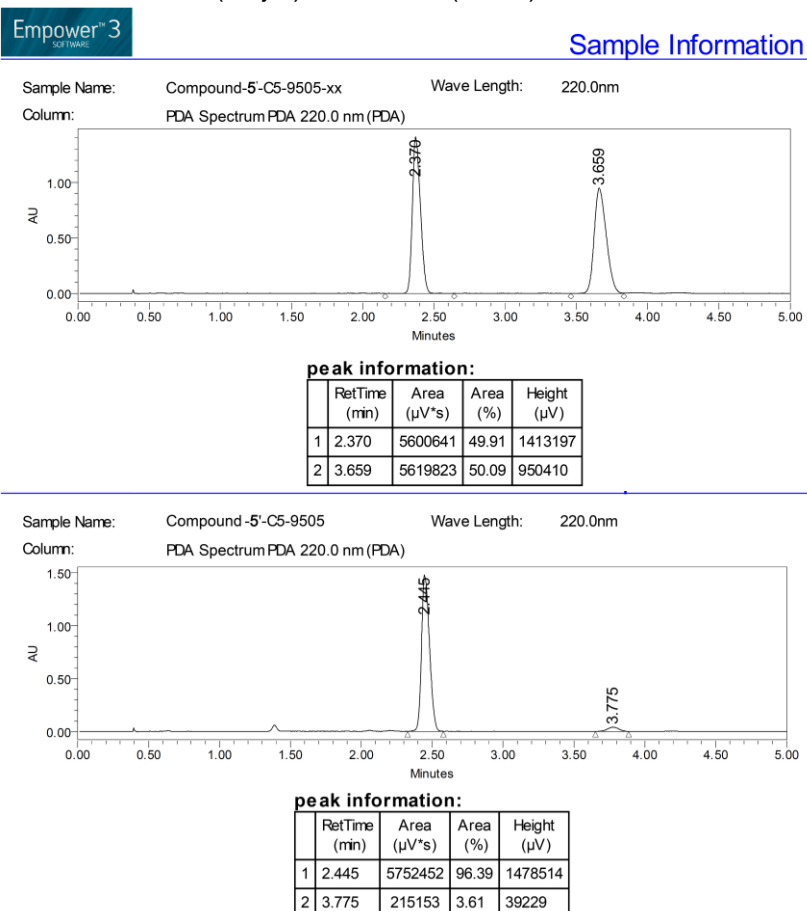
stirred at room temperature. When the starting material disappears (monitored by TLC), MeOH was evaporated under reduced pressure. The aqueous layer was washed with Et₂O (1×100 mL), the pH value of the aqueous layer was adjusted to pH = 4 using HCl (1.0 mol/L) before being extracted with ethyl acetate (3×100 mL). The combined extracts were washed with brine, dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The crude product was purified by flash column chromatography to afford carboxylic acid **4** as a yellow oil (4.68 g, 83% yield from **5**, two steps.). R_f = 0.2 (25% ethyl acetate-petroleum ether).

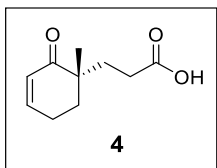


Compound 5': Light yellow oil; $[\alpha]_D^{25} = 2.1$ (c = 0.5 in MeOH).

¹H NMR (400 MHz, CDCl₃) δ: 6.89 (dt, *J* = 10.0, 4.0 Hz, 1H), 5.91 (dt, *J* = 10.0, 2.0 Hz, 1H), 3.66 (s, 3H), 2.45-2.34 (m, 2H), 2.31-2.21 (m, 2H), 1.95-1.77 (m, 4H), 1.10 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ:

202.9, 173.7, 148.4, 128.1, 51.3, 43.6, 33.3, 31.0, 28.8, 22.8, 21.4. **HRMS** (ESI) *m/z* found 219.0990, calculated for C₁₁H₁₆O₃Na [M+Na]⁺ 219.0992. **MS** (EI) *m/z* (%): 196 (75), 191 (60), 180 (37), 165(40), 137 (92), 105 (70), 106 (54). **IR** (KBr plate) ν_{\max} : 2953, 2931, 2873, 1738, 1674, 1436, 1382, 1200, 1174 cm⁻¹. **Enantiomeric excess** was determined by **UPC²** (CHIRALPAK[®] IC-3 column, CO₂/Methanol = 95/5, flow rate: 2 mL/min, 40 °C, λ = 220.0 nm), 92% ee, t_R = 2.445 min (major), 3.775 min (minor).





Compound 4: Yellow oil; $[\alpha]_D^{25} = -0.9$ (c = 0.5 in MeOH).

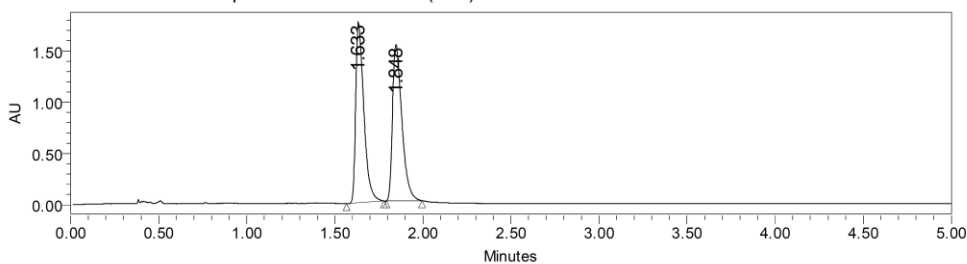
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 11.18 (brs, 1H), 6.87 (dt, $J = 10.0, 4.0$ Hz, 1H), 5.91 (dt, $J = 10.4, 1.6$ Hz, 1H), 2.40-2.26 (m, 4H), 1.92-1.76 (m, 4H), 1.09 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ : 203.4, 179.6,

148.8, 128.4, 43.8, 33.6, 31.1, 29.1, 23.0, 21.6. **HRMS** (ESI) m/z found 205.0835, calculated for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 205.0832. **MS** (EI) m/z (%): 182 (53), 164 (23), 148(75), 138 (42), 110 (100), 101 (58). **IR** (KBr plate) ν_{max} : 3433, 2961, 2928, 2872, 1710, 1672, 1454, 1389, 1284, 1225, 1077 cm^{-1} . **Enantiomeric excess** was determined by **UPC²** (CHIRALPAK[®] IC-3 column, $\text{CO}_2/\text{Methanol} = 90/10$, flow rate: 2 mL/min, 40 °C, $\lambda = 210.0$ nm), 94% ee, $t_R = 1.637$ min (major), 1.871 min (minor).

Empower[®] 3
SOFTWARE

Sample Information

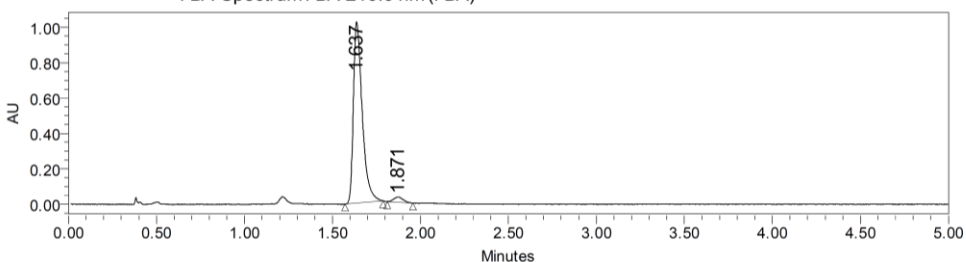
Sample Name: Compound-4-C5-9010xx Wave Length: 210.0nm
Column: PDA Spectrum PDA 210.0 nm (PDA)



peak information:

	RetTime (min)	Area ($\mu\text{V}\cdot\text{s}$)	Area (%)	Height (μV)
1	1.633	5653674	50.09	1767231
2	1.848	5633489	49.91	1528376

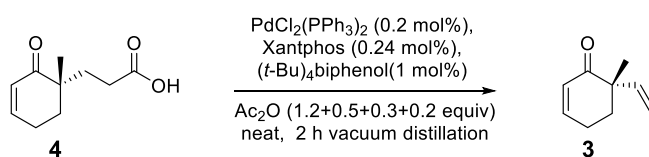
Sample Name: Compound-4-C5-9010 Wave Length: 210.0nm
Column: PDA Spectrum PDA 210.0 nm (PDA)



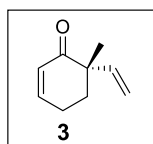
peak information:

	RetTime (min)	Area ($\mu\text{V}\cdot\text{s}$)	Area (%)	Height (μV)
1	1.637	3569507	97.05	1025589
2	1.871	108487	2.95	29459

2.3 Synthesis of compound 3



Compound **3** was synthesized following the literature procedure.⁴ A flame-dried 25.0 mL round-bottom flask, PdCl₂(PPh₃)₂ (15.4 mg, 0.022 mmol, 2% equiv.), Xantphos (15.0 mg, 0.026 mmol, 2.4% equiv.), (*t*-Bu)₄biphenol (45.2 mg, 0.11 mmol, 0.01 equiv.) and carboxylic acid **4** (2.0 g, 11.0 mmol, 1.0 equiv.) were added under the argon atmosphere. The flask was equipped with a distillation head and a 10 mL round-bottom receiving flask. The system was evacuated and backfilled with argon three times, and the first portion of acetic anhydride (6.0 mmol, 1.2 equiv.) was added *via* syringe through the septum that seals the top of the distillation head. The flask was immersed in a pre-heated 60 °C oil bath and rapidly heated to 130 °C. When the oil bath temperature reached 120 °C, switched to vacuum to allow distillation of resultant acetic acid and trace product into a receiving flask, which was cooled to -78 °C. When the oil bath temperature reached 130 °C. The system a vacuum was drawn and the mixture was stirred for approximate 30 min at 130 °C. The system was backfilled with argon atmosphere, and the second portion of acetic anhydride (2.5 mmol, 0.5 equiv.) was added *via* syringe. The system was then gradually resubjected to a vacuum. Acetic anhydride was added as follows (0.3, 0.2 equiv.) in the same manner every 30 min. The reaction was stopped about 2 h and allowed to cool to the room temperature under the argon atmosphere. The distillate was added to a saturated aqueous solution of NaHCO₃, stirred for 30 min, and the biphasic mixture and residual dark red reaction mixtures were extracted with CH₂Cl₂ (3×20 mL). The combined extracts were washed with brine, dried over Na₂SO₄. The solvents were evaporated and the residue was purified by flash column chromatography on silica gel to afford vinyl ketone **3** (1.05 g, 70% yield) as a colorless oil. (*R*_f = 0.5, 16% Et₂O in pentane).

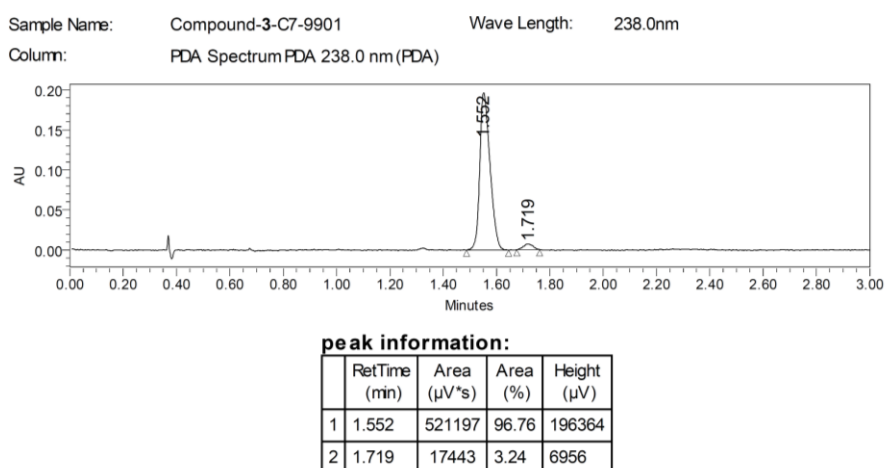
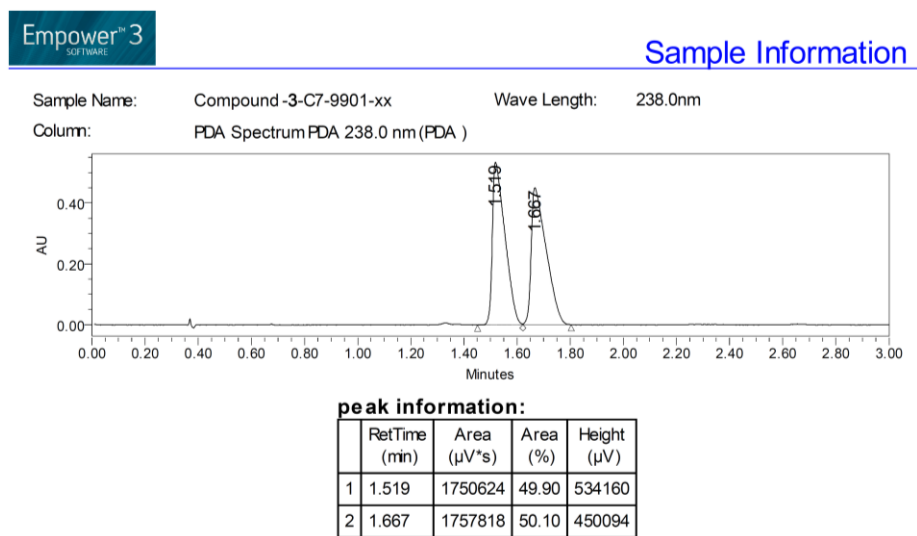


Compound 3: Colorless oil; $[\alpha]_D^{26} = -71.8$ (*c* = 1.0 in CHCl₃).

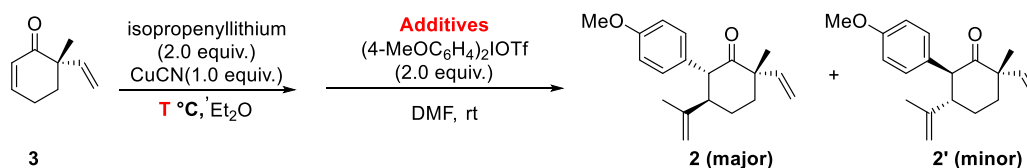
¹H NMR (400 MHz, CDCl₃) δ : 6.93-6.88 (m, 1H), 5.97 (dt, *J* = 10.0, 2.0 Hz, 1H), 5.93 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.05 (dd, *J* = 10.8, 0.4 Hz, 1H), 5.00 (dd, *J* = 17.6, 0.4 Hz, 1H), 2.44-2.31 (m, 2H), 2.03-1.97 (m, 1H), 1.93-1.86

(m, 1H), 1.20 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ : 201.4, 149.1, 140.3, 128.5, 114.0, 47.9, 34.5, 23.3, 22.6. **HRMS** (ESI) *m/z* found 137.0962, calculated for C₁₁H₁₇O₃ [M+H]⁺ 137.0961. **MS** (EI) *m/z* (%): 136 (72), 128 (39), 120 (34), 107 (60). **IR** (KBr plate) ν_{max} : 2958, 2925, 2854, 1730, 1515, 1469, 1337, 1289, 1068, 749 cm⁻¹. **Enantiomeric excess**

was determined by **UPC²** (CHIRALPAK[®] IG-3 column, CO₂/Methanol = 99/1, flow rate: 2 mL/min, 40 °C, λ = 238.0 nm), 94% ee, t_R = 1.552 min (major), 1.719 min (minor).



2.4 Synthesis of precursors 2 and 2'



Method I:

According to the literature⁵, to a stirred suspension of CuCN (89.6 mg, 1.0 mmol, 1.0 equiv.) in Et₂O (15 mL) was slowly added via syringe a solution of isopropenyllithium (5.0 mL, 0.4 M in Et₂O, 2.0 equiv.) at -78 °C under an argon atmosphere. The mixture was stirred for approximate 30 min at -78 °C until a homogeneous solution was observed, and enone **3** (136.0 mg, 1.0 mmol) was then added at **-78 °C**. After the starting material disappeared, the reaction mixture was allowed to warm to -20 °C, diluted with dry DMF (10.0 mL),

Cu(OAc)₂ (181.6 mg, 1.0 mmol, 1.0 equiv.) and the diaryliodonium triflate (4-MeOC₆H₄)₂IOTf (1.024 g, 2.0 mmol, 2.0 equiv.) was sequentially added. The reaction mixture was stirred for 12 h at -20 °C, and quenched with a saturated aqueous solution of NH₄Cl. The mixture was extracted with ethyl acetate (3×30 mL) and the combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered, and concentrated under vacuum. The resultant crude products (dr~8:1) were purified by flash column chromatography to give the desired product **2** (101.0 mg, 35.6% yield) and its isomer **2'** (12.5 mg, 4.4% yield). (R_f = 0.50 and 0.51, respectively, 10% ethyl acetate-petroleum ether).

Method II:

According to the literature⁵, to a stirred suspension of CuCN (89.6 mg, 1.0 mmol, 1.0 equiv.) in Et₂O (15.0 mL) was slowly added *via* syringe a solution of isopropenyllithium (5.0 mL, 0.4 M in Et₂O, 2.0 equiv.) at -78 °C under an argon atmosphere. The mixture was stirred for approximate 30 min at -78 °C until a homogeneous solution was observed. After the reaction mixture was allowed to warm to room temperature, and enone **3** (136.0 mg, 1.0 mmol) was then added at room temperature. After the starting material disappeared, **CsF** (608.0 mg, 4.0 mmol, 4.0 equiv.) was added and the reaction mixture was stirred for 10 minutes. Subsequently, diaryliodonium triflate (4-MeOC₆H₄)₂IOTf (1.024 g, 2.0 mmol, 2.0 equiv.) in anhydrous DMF (6.5 mL) was added *via* syringe. The reaction mixture was stirred for 24 h at room temperature, and quenched with a saturated aqueous solution of NH₄Cl. The mixture was extracted with ethyl acetate (3×30 mL) and the combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered, and concentrated under vacuum. The resultant crude products (dr = 1.5:1) were purified by flash column chromatography to give the product **2** (102.0 mg, 35.9% yield) and its isomer **2'** (68.4 mg, 24.1% yield). (R_f = 0.50 and 0.51, respectively, 10% ethyl acetate-petroleum ether).

(4-MeOC₆H₄)₂IOTf were prepared according to the reported procedures.⁶

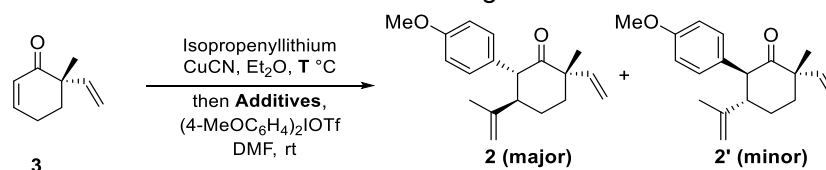
Isopropenyllithium was prepared according to the following manner⁷: To a precooled (-78 °C) solution of 2-bromopropene (281.7 μL, 3.2 mmol) in dry Et₂O (2.8 mL) was added dropwise *tert*-butyllithium (4.92 mL, 1.3 M in pentane, 6.4 mmol). The resulting solution was stirred at -78 °C for 30 min, and then used immediately.

2.4.1 The Optimization of the Cu-mediated one-pot Michael addition/arylation reaction

Unless otherwise noted, the reaction was performed according to the Method I and Method II, and the details were listed in Table S1-S4

2.4.1.1 The screening of additives

Table S1. The screening of additives^a

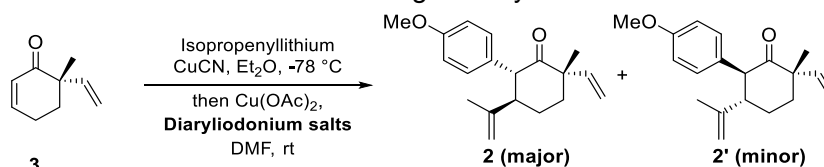


Entry	Temp.	Additives (equiv.)	dr (2:2')	Yield ^b
1	-78 °C	CuCl (1.0)	--	25%
2	-78 °C	CuI (1.0)	--	20%
3	-78 °C	CuOAc (1.0)	--	32%
4	-78 °C	Cu(OTf) ₂ (1.0)	--	34%
5	-78 °C	Cu(OAc)₂ (1.0)	8:1	40%
6	-78 °C	Cu(OAc) ₂ (1.0)	8:1	32%
7	rt	Cu(OAc) ₂ (1.0)	1.4:1	35%
8	40 °C	Cu(OAc) ₂ (1.0)	1.7:1	20%
9	-78 °C to rt	LiHMDS (2.0)	4:1	44%
10	-78 °C to rt	LiCA (2.0)	2:1	38%
11	-78 °C to rt	Cs ₂ CO ₃ (2.0)	1.8:1	25%
12	-78 °C to rt	CsOH·H ₂ O (2.0)	1.7:1	20%
13	-78 °C to rt	NaH (2.0)	--	ND
14	-78 °C to rt	DBU (2.0)	--	trace
15	-78 °C to rt	Na ₂ CO ₃ (2.0)	--	trace
16	-78 °C to rt	DMAP (2.0)	--	NR
17	-78 °C to rt	DIPEA (2.0)	--	NR
18	-78 °C to rt	HMPA (5.0), Cu(OAc) ₂ (1.0)	--	21%
19	-78 °C to rt	TMEDA (5.0), Cu(OAc) ₂ (1.0)	--	25%
20	-78 °C to rt	CsF (2.0)	3:1	50%
21	rt	CsF (2.0)	1.51:1	50%
22	rt	CsF (3.0)	1.51:1	53%
23	rt	CsF (4.0)	1.49:1	60.0%
24	rt	CsF (5.0)	1.49:1	59.6%

^aReaction was performed using isopropenyllithium (0.2 mmol) and CuCN (0.1 mmol) in 1.5 mL Et₂O at -78 °C and stirred for 30 min; then enone **3** (0.1 mmol) was added to the reaction mixture. After the starting material (**3**) disappeared, additives and (4-MeOC₆H₄)₂lOTf (0.2 mmol) in DMF was added to the reaction mixture at the note temperature. ^bIsolated yield; rt = Room temperature; DMF = *N,N*-dimethylformamide; LiCA = Lithium cyclohexylisopropylamide; HMPA = Hexamethylphosphoramide; DMAP = 4-dimethylaminopyridine; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene; DIPEA = *N,N*-diisopropylethylamine; TMEDA = *N,N,N',N'*-tetramethylethylenediamine.

2.4.1.2 The screening of diaryliodonium salts

Table S2. The screening of diaryliodonium salts^a

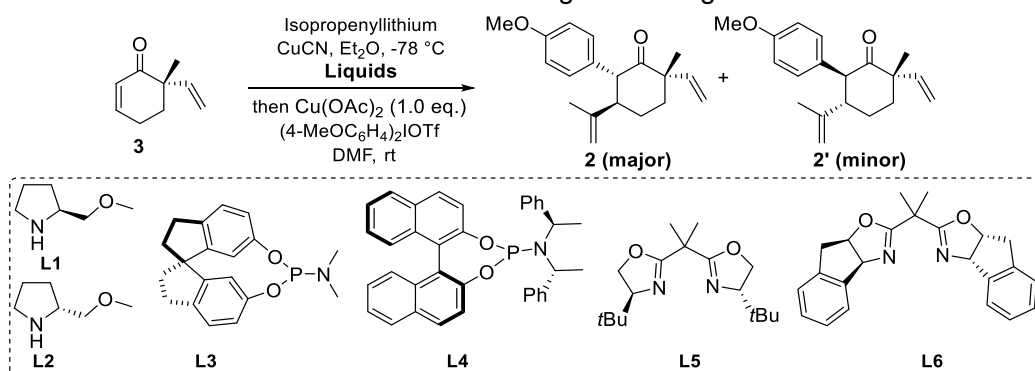


Entry	Diaryliodonium salts	dr (2:2')	Yield ^b
1	(4-MeOC₆H₄)₂IOTf	8:1	40%
2	(4-MeOC ₆ H ₄) ₂ IBF ₄	4.8:1	27%
3	(4-MeOC ₆ H ₄) ₂ IOTs	8:1	10%
4	(4-MeOC ₆ H ₄) ₂ IBF ₆	8:1	30%

^aReaction was performed using isopropenyllithium (0.2 mmol) and CuCN (0.1 mmol) in 1.5 mL Et₂O at -78 °C and stirred for 30 min, then enone **3** (0.1 mmol) was added to the reaction mixture, after the starting material (**3**) disappeared. Then Cu(OAc)₂ (0.1 mmol) and diaryliodonium salts (0.2 mmol) in DMF was added to the reaction mixture at rt. ^bIsolated yield; rt = Room temperature; DMF = *N,N*-Dimethylformamide.

2.4.1.3 The screening of chiral ligands

Table S3. The screening of chiral ligands^a

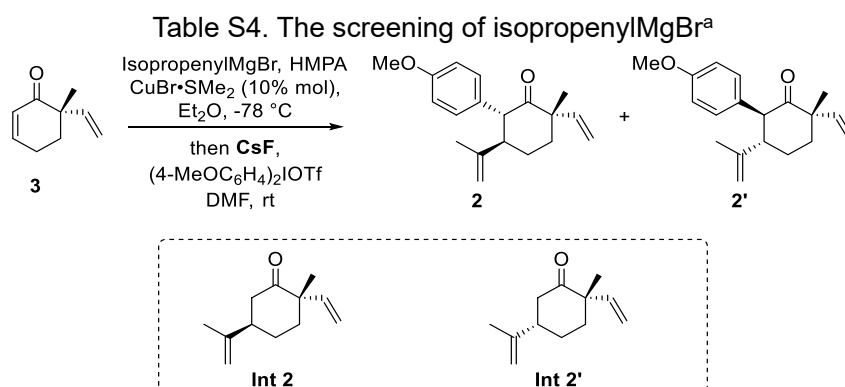


Entry	Liquids	Additives (equiv.)	dr (2:2')	Yield ^b
1	L1	Cu(OAc) ₂ (1.0)	2.9:1	11.7%
2	L2	Cu(OAc) ₂ (1.0)	3:1	10.5%
3	L3	Cu(OAc) ₂ (1.0)	--	trace
4	L4	Cu(OAc) ₂ (1.0)	--	trace
5	L5	Cu(OAc) ₂ (1.0)	--	trace
6	L6	Cu(OAc) ₂ (1.0)	--	trace
7	L1	CsF (4.0)	4.5:1	31.7%
8	L2	CsF (4.0)	3:1	28.7%
9	L3	CsF (4.0)	--	trace
10	L4	CsF (4.0)	--	trace
11	L5	CsF (4.0)	--	trace
12	L6	CsF (4.0)	--	trace

^aReaction was performed using isopropenyllithium (0.2 mmol) and CuCN (0.1 mmol) in 1.5 mL Et₂O at -78 °C and stirred for 30 min; then chiral ligand (**L**) was added to the reaction mixture and stirred for 1 h; enone **3** (0.1 mmol) was added. After the starting material (**3**) disappeared, Cu(OAc)₂ (0.1 mmol) and (4-MeOC₆H₄)₂IOTf (0.2 mmol) in DMF was added to the reaction mixture; ^bIsolated yield; rt = Room temperature; DMF = *N,N*-Dimethylformamide.

2.4.1.4 The screening of organmetallic reagents

1) IsopropenylMgBr:



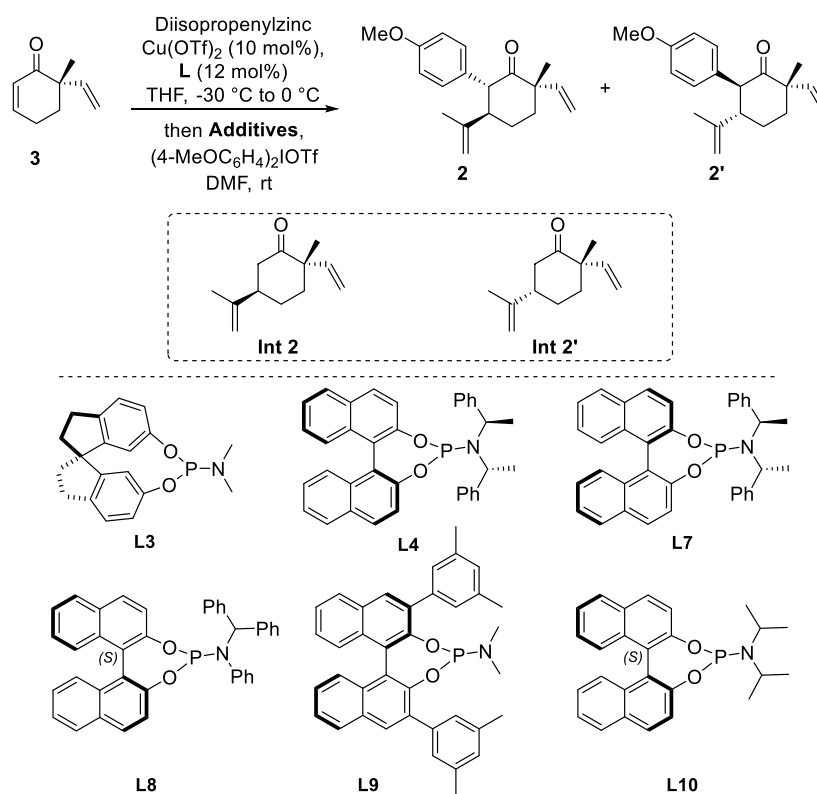
Entry	Solvent	Additives (equiv.)	dr (2:2')	Yield ^b
1	Et ₂ O	Cu(OAc) ₂ (1.0)	--	ND
3	Et ₂ O	HMPA (5.0), Cu(OAc) ₂ (1.0)	--	ND
2	Et ₂ O	TMEDA (5.0), Cu(OAc) ₂ (1.0)	--	ND
4	Et ₂ O	LiHMDS (2.0)	4:1	10%
5	THF	LiHMDS (2.0)	--	trace
6	2-MeTHF	LiHMDS (2.0)	--	trace
7	MTBE	LiHMDS (2.0)	--	trace
8	THF	CsF (4.0)	--	trace
9	THF	HMPA (5.0), LiHMDS (2.0)	--	trace

^aReaction was performed using isopropenylmagnesium bromide (0.12 mmol) and CuBr·SMe₂ in 1.5 mL solvent at the note temperature and stirred for 30 min; then enone **3** (0.1 mmol) was added to the reaction mixture. After the starting material (**3**) disappeared, additives and (4-MeOC₆H₄)₂IOTf (0.2 mmol) in DMF were added to the reaction mixture; ^bIsolated yield; ND = No detected; TMEDA = *N,N,N',N'*-tetramethylethylenediamine; HMPA = Hexamethylphosphoramide; rt = Room temperature; IsopropenylMgBr = Isopropenylmagnesium bromide; HMPA = Hexamethylphosphoramide; LiHMDS = Lithium bis(trimethylsilyl)amide; MTBE = *tert*-Butyl methyl ether; DMF = *N,N*-Dimethylformamide; THF = Tetrahydrofuran; 2-MeTHF = 2-Methyltetrahydrofuran.

To a stirred suspension of CuBr·SMe₂ (2.05 mg, 0.01 mmol, 0.1 equiv.) and HMPA (174.0 μL, 0.5 mmol, 5.0 equiv.) in Et₂O (1.0 mL) was slowly added *via* syringe a solution of isopropenylmagnesium bromide (0.4 mL, 0.5 M in THF, 2.0 equiv.) at -78 °C under an argon atmosphere. The mixture was stirred for approximate 30 min at -78 °C until a homogeneous solution was observed. Enone **3** (13.6 mg, 1.0 mmol) was then added at -78 °C. After the starting material disappeared, **CsF** (60.8 mg, 0.4 mmol, 4.0 equiv.) was

added and the reaction was stirred for 10 minutes. Subsequently, diaryliodonium triflate (4-MeOC₆H₄)₂IOTf (102.4 mg, 0.2 mmol, 2.0 equiv.) in anhydrous DMF (1.5 mL) was added *via* syringe. The reaction mixture was stirred for 24 h at room temperature, and quenched with a saturated aqueous solution of NH₄Cl. The mixture was extracted with diethyl ether (3x30 mL) and the combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered, and concentrated under vacuum. The resultant crude products (dr = 4:1) were purified by flash column chromatography on silica gel, eluting with 0.5-1% Et₂O/pentane to only afford the Michael addition product **Int 2** (11.9 mg, 67.0% yield) and its isomer **Int 2'** (3.2 mg, 18.0% yield). (R_f = 0.50 and 0.51, respectively, 20% Et₂O/pentane).

2) Diisopropenylzinc:



Cu(OTf)₂ (4.0 mg, 0.01 mmol, 0.1 equiv.) and chiral ligands (0.01 mmol, 0.12 equiv.) were suspended in dry THF (1.0 mL) and stirred at room temperature for 30 min before cooling to -30 °C, diisopropenylzinc (0.61 mL, 0.33 mol/L in THF, 2.0 equiv.) was added dropwise. The mixture was stirred for approximate 30 min at -30 °C, and enone **3** (13.6 mg, 0.1 mmol) was then added. The mixture was slowly warmed up to room temperature and stirred for 12 h. **CsF** (60.8 mg, 0.4 mmol, 4.0 equiv.) was added and the reaction was stirred for 10 minutes, then diaryliodonium triflate (4-MeOC₆H₄)₂IOTf (102.4 mg, 0.2 mmol, 0.2 equiv.) in anhydrous DMF (1.5 mL) was added *via* syringe. The reaction mixture was stirred for 24 h

at room temperature, and quenched with a saturated aqueous solution of NH_4Cl . The mixture was extracted with diethyl ether (3×30 mL) and the combined organic layers were washed with water and brine, dried over Na_2SO_4 , filtered, and concentrated under vacuum. The resultant crude products (dr~1.4:1) were purified by flash column chromatography on silica gel, eluting with 0.5-1.0% Et_2O /pentane to only afford the Michael addition product **Int 2** (6.4 mg, 36.0% yield) and its isomer **Int 2'** (4.6 mg, 25.7% yield), and without the isolation of expected products **2** and **2'**,

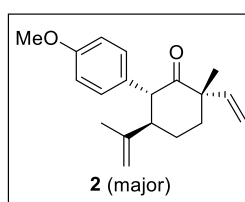
Preparation of diisopropenylzinc reagent⁸

Preparation of isopropenylMgBr·LiCl

In an oven-dried 10 mL flask, Mg turnings (97.2 mg, 4.0 mmol), I_2 (5 mg, 0.02 mmol) and LiCl (84.8 mg, 2.0 mmol) were weighed. The system was evacuated and backfilled with argon three times. THF (2.0 mL) was added at room temperature and stirred for 5 minutes. The mixture was then cooled to 0 °C and 2-bromopropene (0.18 mL, 2.0 mmol) was added dropwise. The mixture was removed from the ice bath and allowed to stir for 1 h at room temperature.

Preparation of diisopropenylzinc

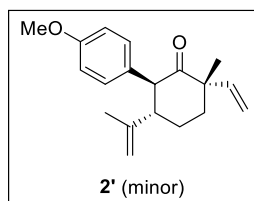
In an oven-dried flask, ZnCl_2 (1.0 mL, 1.0 mol/L in THF, 1.0 equiv., 1.0 mmol) was added under the argon atmosphere. Then, isopropenylMgBr·LiCl (2.0 mL, 2.0 equiv., 2.0 mmol) was added dropwise *via* syringe. A dense-grey solution was formed and used without further titration ($c = 0.33$ mol/L).



Precursor 2: Yellow oil; $[\alpha]_D^{25} = 82.3$ ($c = 0.5$ in MeOH).

¹H NMR (400 MHz, CDCl_3) δ : 6.93 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 6.23 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.10 (d, $J = 10.8$ Hz, 1H), 5.04 (d, $J = 17.6$ Hz, 1H), 4.60 (brs, 2H), 3.84 (d, $J = 12.4$ Hz, 1H), 3.77 (s, 3H), 2.74 (td, $J = 12.4, 3.6$ Hz, 1H), 2.19-2.08 (m, 1H),

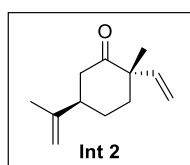
2.03-1.84 (m, 3H), 1.59 (s, 3H), 1.44 (s, 3H); **¹³C NMR** (100 MHz, CDCl_3) δ : 212.1, 158.2, 145.8, 142.9, 130.3, 129.0, 113.4, 112.8, 112.3, 56.0, 55.1, 53.1, 50.5, 36.7, 27.3, 23.0, 18.8. **HRMS** (ESI) m/z found 285.1846, calculated for $\text{C}_{18}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$ 285.1849. **MS** (EI) m/z (%): 284 (33), 257 (30), 236 (25), 186 (28), 160 (36), 121(100), 107 (30). **IR** (KBr plate) ν_{max} : 2935, 2868, 2836, 1707, 1643, 1612, 1514, 1461, 1249, 1179, 1038, 914, 894, 817, 783 cm^{-1} .



Precursor 2': Yellow oil; $[\alpha]_D^{24} = -125.6$ ($c = 0.5$ in MeOH).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ : 6.93 (d, $J = 8.4$ Hz, 2H), 6.82 (d, $J = 8.6$ Hz, 2H), 6.06 (dd, $J = 17.4, 10.2$ Hz, 1H), 5.26 (d, $J = 10.8$ Hz, 1H), 5.07 (d, $J = 18.0$ Hz, 1H), 4.59 (brs, 1H), 4.57 (brs, 1H), 3.90 (d, $J = 12.6$ Hz, 1H), 3.78 (s, 3H), 2.74 (t, $J = 13.2$ Hz, 1H),

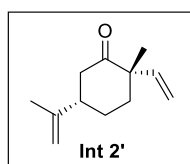
2.17-2.08 (m, 2H), 1.81-1.75 (m, 2H), 1.55 (s, 3H), 1.17 (s, 3H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ : 211.2, 158.2, 145.8, 142.8, 130.3, 129.0, 116.0, 113.4, 112.6, 56.8, 55.1, 53.9, 52.2, 39.0, 28.2, 24.8, 18.6. **HRMS** (ESI) m/z found 285.1847, calculated for $\text{C}_{18}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$ 285.1849. **MS** (EI) m/z (%): 284 (30), 173 (24), 159 (19), 135 (21), 121 (100), 91 (12). **IR** (KBr plate) ν_{max} : 2933, 2867, 1709, 1615, 1514, 1458, 1249, 1179, 1067, 966, 892, 817, 750 cm^{-1} .



Int 2: Colorless oil; $[\alpha]_D^{18} = 19.2$ ($c = 1.0$ in CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ : 6.07 (dd, $J = 18.0, 10.8$ Hz, 1H), 5.12 (d, $J = 11.4$ Hz, 1H), 5.02 (d, $J = 18.0$ Hz, 1H), 4.80 (brs, 1H), 4.71 (brs, 1H), 2.56-2.52 (m, 1H), 2.48-2.44 (m, 2H), 1.91-1.86 (m, 1H), 1.82-1.75 (m,

3H), 1.73 (s, 3H), 1.23 (s, 3H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ : 213.4, 147.1, 142.7, 113.4, 110.6, 50.7, 44.9, 43.0, 36.0, 25.5, 22.9, 21.0. **HRMS** (ESI) m/z found 285.1848, calculated for $\text{C}_{18}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$ 285.1849. **MS** (EI) m/z (%): 178 (59), 121 (78), 111 (84), 107 (63), 105 (100).

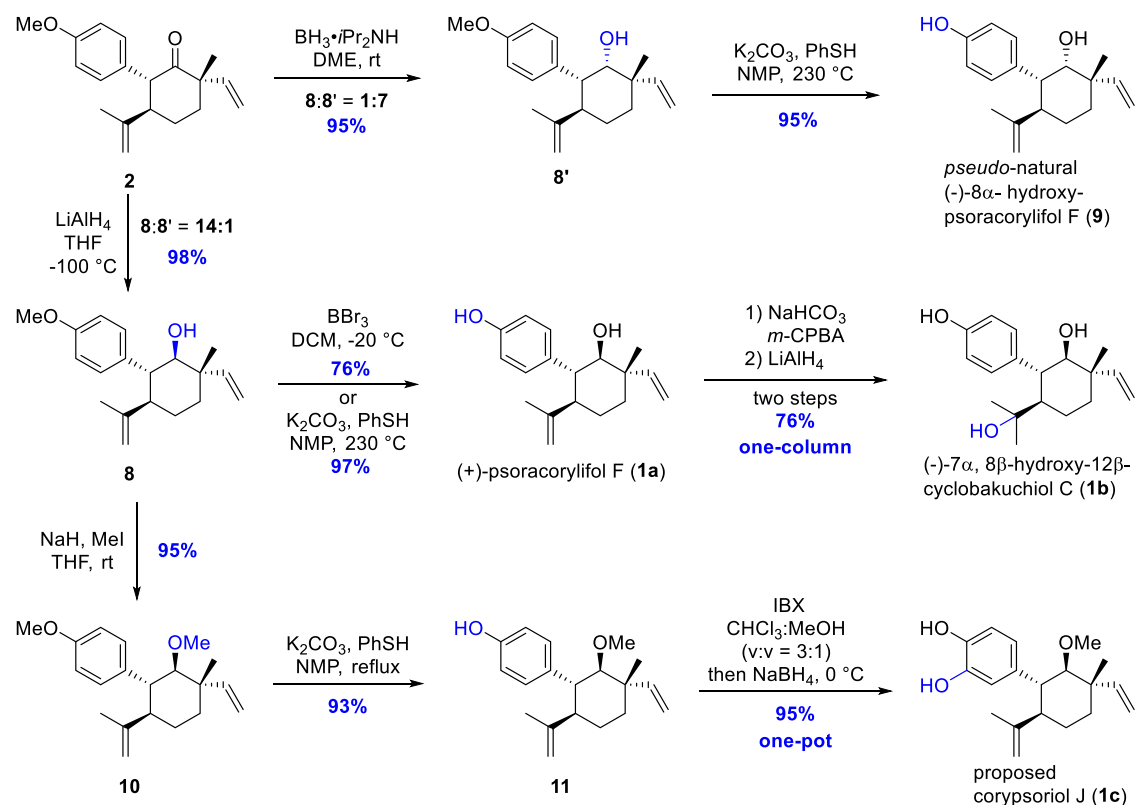


Int 2': Colorless oil; $[\alpha]_D^{18} = 96.9$ ($c = 1.0$ in CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ : 5.91 (dd, $J = 17.4, 10.2$ Hz, 1H), 5.15 (d, $J = 10.8$ Hz, 1H), 5.00 (d, $J = 18.0$ Hz, 1H), 4.75 (brs, 1H), 4.71 (brs, 1H), 2.55 (t, $J = 13.8$ Hz, 1H), 2.36-2.31 (m, 2H), 2.06 (dt, $J = 13.8, 3.6$

Hz, 1H), 1.78-1.74 (m, 2H), 1.72 (s, 3H), 1.62-1.57 (m, 1H), 1.14 (s, 3H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ : 212.6, 147.5, 142.3, 115.6, 109.7, 51.6, 46.7, 44.1, 38.8, 27.1, 24.0, 20.4. **HRMS** (ESI) m/z found 285.1849, calculated for $\text{C}_{18}\text{H}_{25}\text{O}_2$ $[\text{M}+\text{H}]^+$ 285.1849. **MS** (EI) m/z (%): 178 (1), 121 (9), 111 (6), 107 (5), 105 (100).

3. Collective total syntheses of 7 α -aryl-12 β -alkyl type meroterpenoids



Scheme S2 Collective total syntheses of 7 α -aryl-12 β -alkyl type meroterpenoids.

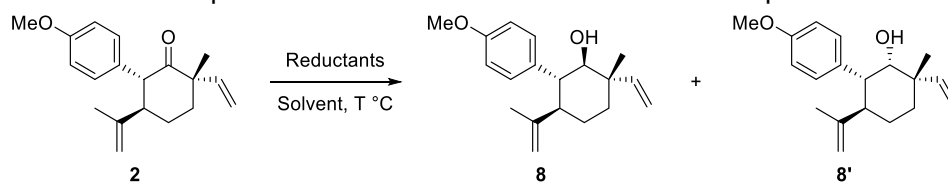
3.1 Synthesis of natural (+)-psoracorylifol F (**1a**)

3.1.1 Synthesis of compounds **8** and **8'**

Method:

To a solution of the precursor **2** (5.0 mg, 0.018 mmol) in solvents (1.0 mL) was added reductants (0.09 mmol, 5.0 equiv.) under an argon atmosphere at the noted temperature, respectively. When the reaction completed (monitored by TLC), the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl , and extracted with CH_2Cl_2 (3 \times 20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 , and filtered. The filtrate was concentrated under reduced pressure, and the dr value was measured by ^1H NMR (entries 1-6, Table S5).

Table S5. Optimization of the reduction conditions of the precursor **2**

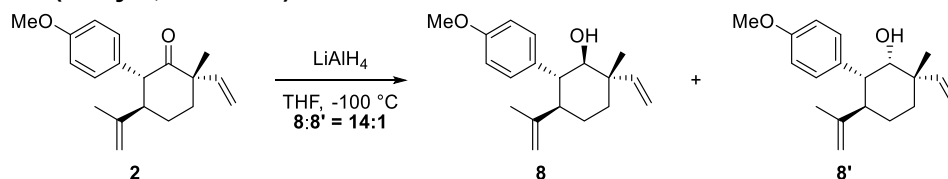


Entry	reductors	Solvents	Temp.	dr (8:8')	yield ^b
1	LiAlH₄	THF	-100 °C	14:1	98%
2	LiAlH ₄	Et ₂ O	-100 °C	4:1	98%
3	BH ₃ ·Me ₂ NH	DME	rt	1:4.6	96%
4	BH ₃ ·Me ₂ NH	DME	-60 °C	1:4	95%
5	BH ₃ · <i>i</i> Pr ₂ NH	DME	-60 °C	1:3	90%
5	BH₃·<i>i</i>Pr₂NH	DME	rt	1:7	95%
6	BH ₃ · <i>i</i> Pr ₂ NH	DME	90 °C	1:7	56%

^aThe reactions were performed using the precursor **2** (0.018 mmol), reductants (5.0 equiv.) in 1.0 mL THF;

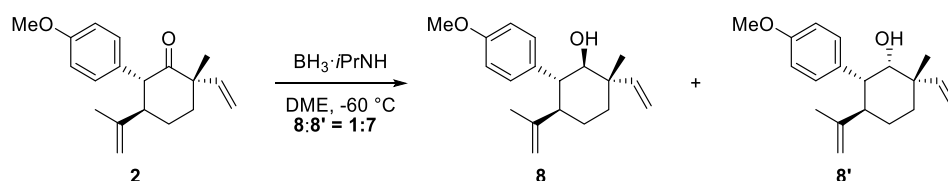
^bIsolated yield; rt = Room temperature; THF = Tetrahydrofuran; DME = 1,2-dimethoxyethane.

Method I (entry 1, Table S6):



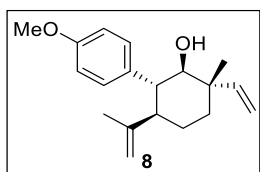
To a solution of the precursor **2** (5.0 mg, 0.018 mmol) in THF (1.0 mL) was added LiAlH₄ (3.4 mg, 0.09 mmol) under an argon atmosphere at -100 °C, and the mixture was stirred for 2 h. When the reaction completed (monitored by TLC), the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl, and extracted with CH₂Cl₂ (3×20 mL). The combined organic phase was washed with brine, dried over Na₂SO₄, and filtered. The filtrate was concentrated under reduced pressure. The resulting crude product **8** and **8'** (dr = 14:1) was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate (50:1)) to give the desired product **8** (4.6 mg, 91% yield) as a white solid and its isomer **8'** (0.35 mg, 7% yield).

Method II (entry 5, Table S6):



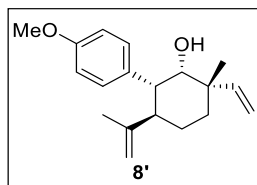
To a solution of the precursor **2** (5.0 mg, 0.018 mmol) in DME (1.0 mL) was added BH₃·*i*Pr₂NH (10.3 mg, 0.09 mmol) under an argon atmosphere at -60 °C, and the mixture

was stirred for 24h. When the reaction completed (monitored by TLC), the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl , and extracted with CH_2Cl_2 (3×20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 , and filtered. The filtrate was concentrated under reduced pressure. The resulting crude product **8** and **8'** (dr = 1:7) was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate (50:1)) to give the desired product **8'** (4.2 mg, 83% yield) as a white solid and its isomer **8** (0.6 mg, 12% yield).



Compound 8: Colorless needle; $[\alpha]_D^{25} = 3.9$ ($c = 0.5$ in MeOH); **m.p.:** 105-107 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.12 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 5.92 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.11 (dd, $J = 17.6, 1.2$ Hz, 1H), 5.07 (dd, $J = 10.8, 0.8$ Hz, 1H), 4.53 (brs, 2H), 4.78 (s, 3H), 3.45 (d, $J = 10.4$ Hz, 1H), 2.68 (t, $J = 11.6$ Hz, 1H), 2.37 (td, $J = 11.6, 3.6$ Hz, 1H), 1.79-1.64 (m, 1H), 1.63-1.56 (m, 3H), 1.54 (s, 3H), 1.18 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ : 158.2, 147.9, 147.0, 133.0, 129.3, 113.8, 112.1, 111.7, 78.9, 55.1, 50.9, 49.0, 41.7, 36.2, 27.3, 19.5, 15.2. **HRMS** (ESI) m/z found 309.1826, calculated for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 309.1825. **MS** (EI) m/z (%): 286 (87), 253 (5), 204 (8), 150 (100), 137 (22), 121(91). **IR** (KBr plate) ν_{max} : 3506, 3069, 2975, 2928, 2903, 2852, 1720, 1611, 1512, 1298, 810 cm^{-1} .

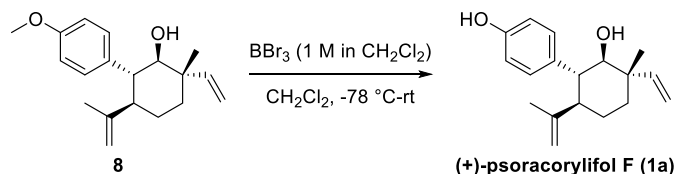


Compound 8': White solid; $[\alpha]_D^{25} = 35.6$ ($c = 0.5$ in MeOH); **m.p.:** 82-83 °C.

$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.15 (d, $J = 8.4$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 2H), 5.88 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.11 (dd, $J = 4.4, 0.8$ Hz, 1H), 5.08 (dd, $J = 11.2, 1.2$ Hz, 1H), 4.70 (brs, 1H), 4.63 (brs, 1H), 3.77 (s, 3H), 3.39 (brs, 1H), 3.00 (dd, $J = 12.4, 2.0$ Hz, 1H), 2.94-2.90 (m, 1H), 2.05-1.99 (m, 1H), 1.73-1.71 (m, 2H), 1.56 (s, 3H), 1.40 (dt, $J = 13.2, 2.8$ Hz, 1H), 1.20 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ : 158.0, 147.9, 147.0, 134.1, 129.8, 113.4, 112.8, 111.9, 77.5, 55.1, 45.4, 42.0, 41.4, 28.5, 28.0, 22.4, 19.2. **HRMS** (ESI) m/z found 309.1827, calculated for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 309.1825. **MS** (EI) m/z (%): 286 (23), 150 (71), 137 (16), 121 (100), 68 (13), 55 (10). **IR** (KBr plate) ν_{max} : 3461, 3075, 2927, 2858, 1643, 1611, 1583, 1511, 1456, 1248, 1178, 1038, 912, 887, 821 cm^{-1} .

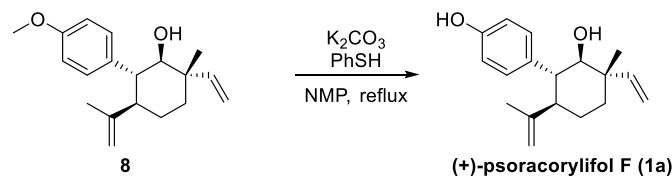
3.1.2 Synthesis of natural (+)-psoracorylifol F (1a)

Method I:

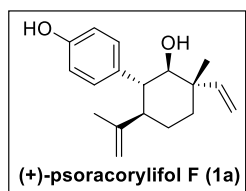


To a stirred solution of alcohol **8** (28.4 mg, 0.1 mmol) in dry CH_2Cl_2 (2.0 mL) at -78°C was added BBr_3 (0.6 mL, 0.6 mmol, 1 M in CH_2Cl_2 , 6.0 equiv.). After stirred for at -40°C for 12 h, and gradually warmed to room temperature for 16 h, after which reaction was quenched by careful addition of H_2O (1.0 mL) at 0°C . The pH of the aqueous layer was adjusted to pH 8 using sat. NaHCO_3 before being extracted CH_2Cl_2 (3x20 mL). The combined organic layer was washed with brine, dried with Na_2SO_4 , and concentrated in vacuum. The crude product was purified by preparative thin layer chromatography (petroleum ether/ethyl acetate) to afford (+)-psoracorylifol F (**1a**) (20.7 mg, 76% yield) as a white solid.

Method II:



To a suspension solution of alcohol **8** (19.4 mg, 0.067 mmol) and K_2CO_3 (3.7 mg, 0.027 mmol) in NMP (1.0 mL) was added PhSH (27.3 μL , 0.27 mmol). The mixture was stirred under reflux for 12 h, and then cooled to room temperature and quenched with H_2O . The resulting mixture was extracted with ethyl acetate (3x20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 , and concentrated. The crude product was purified by chromatography on silica gel (petroleum ether/ethyl acetate) to give (+)-psoracorylifol F (**1a**) (17.7 mg, 97% yield) as a white solid.



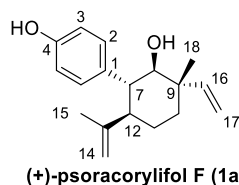
(+)-psoracorylifol F (1a): White solid; $[\alpha]_D^{25} = +6.7$ ($c = 0.1$ in MeOH); m.p.: $157\text{-}159^\circ\text{C}$.

$^1\text{H NMR}$ (600 MHz, methanol- d_4) δ : 6.91 (d, $J = 8.4$ Hz, 2H), 6.57 (d, $J = 8.4$ Hz, 2H), 5.88 (dd, $J = 18.0, 10.8$ Hz, 1H), 4.94 (dd, $J = 17.4, 1.2$ Hz, 1H), 4.87 (dd, $J = 10.8, 1.8$ Hz, 1H), 4.40 (brs, 1H),

4.37 (brs, 1H), 3.37 (d, $J = 10.8$ Hz, 1H), 2.54 (t, $J = 10.8$ Hz, 1H), 2.23 (td, $J = 12.0, 3.6$ Hz, 1H), 1.69-1.60 (m, 1H), 1.56-1.51 (m, 1H), 1.48-1.45 (m, 1H), 1.44-1.40 (m, 1H), 1.41 (s, 3H), 1.04 (s, 3H); **$^{13}\text{C NMR}$** (150 MHz, methanol- d_4) δ : 156.8, 150.1, 149.1, 134.7, 131.0,

116.1, 112.3, 111.9, 80.6, 53.4, 51.0, 43.3, 37.6, 28.9, 20.1, 16.6. **HRMS** (ESI) *m/z* found 295.1669, calculated for C₁₈H₂₄O₂Na [M+Na]⁺ 295.1669. **MS** (EI) *m/z* (%): 272 (89), 245 (56), 220 (60), 187 (43), 121 (63), 113 (69), 100 (55). **IR** (KBr plate) ν_{max} : 3344, 2969, 2924, 2866, 1643, 1615, 1600, 1514, 1245, 1081, 822 cm⁻¹.

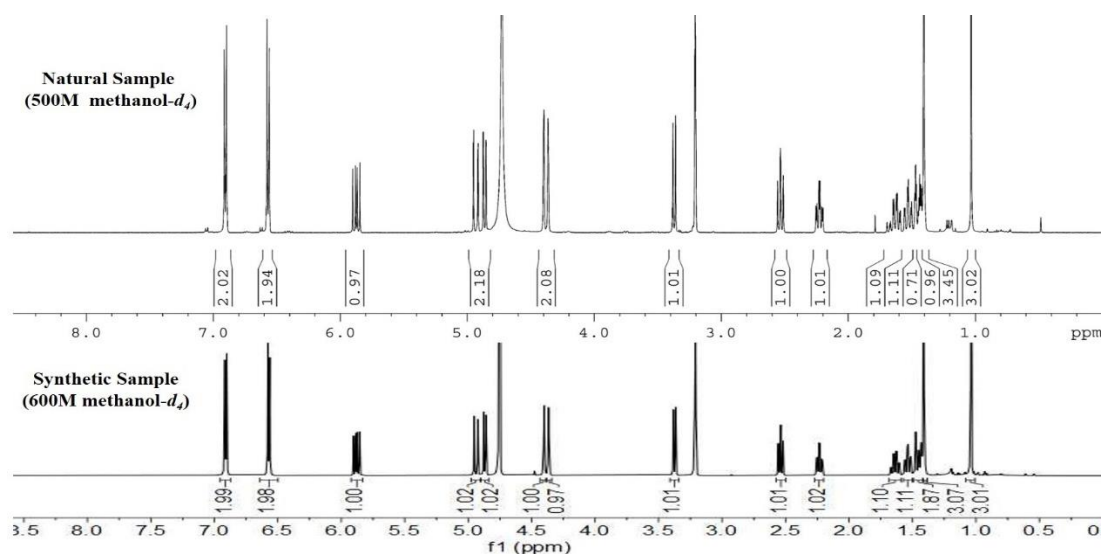
Comparison of ¹H NMR data for synthetic and natural (+)-psoracorylifol F



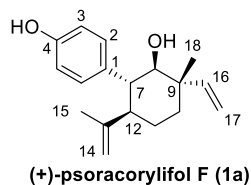
Position	Natural psoracorylifol F ^{a,9}	Synthetic psoracorylifol F ^b	$\Delta\delta$ (ppm)
1	-	-	-
2,5	6.90, d ($J = 8.5$ Hz)	6.91, d ($J = 8.4$ Hz)	-0.01
3,6	6.58, d ($J = 8.5$ Hz)	6.57, d ($J = 8.4$ Hz)	0.01
4	-	-	-
7	2.54, t ($J = 11.0$ Hz)	2.54, t ($J = 10.8$ Hz)	0.00
8	3.37, d ($J = 10.5$ Hz)	3.37, d ($J = 10.8$ Hz)	0.00
9	-	-	-
10	1.44, m	1.44-1.40, m (1.42, m)	0.02
	1.64, m	1.69-1.59, m (1.64, m)	0.00
11	1.48, m	1.48-1.45, m (1.47, m)	0.01
	1.54, o ^c	1.56-1.51, m (1.54, m)	0.00
12	2.24, m	2.23, td ($J = 12.0, 3.6$ Hz)	0.01
13	-	-	-
14	4.36, s	4.37, brs	-0.01
	4.40, s	4.40, brs	0.00
15	1.41, s	1.41, s	0.00
16	5.87, dd ($J = 17.5, 11.0$ Hz)	5.88, dd ($J = 18.0, 10.8$ Hz)	-0.01
17	4.86, dd ($J = 11.0, 1.5$ Hz)	4.87, dd ($J = 10.8, 1.8$ Hz)	-0.01
	4.94, dd ($J = 18.0, 1.5$ Hz)	4.94, dd ($J = 17.4, 1.2$ Hz)	0.00
18	1.04, s	1.04, s	0.00

^a NMR data measured at 500 MHz in methanol-*d*₄; ^b NMR data measured at 600 MHz in methanol-*d*₄; ^c "o" means overlapped.

Comparison of ^1H NMR spectra of (+)-psoracorylifol F



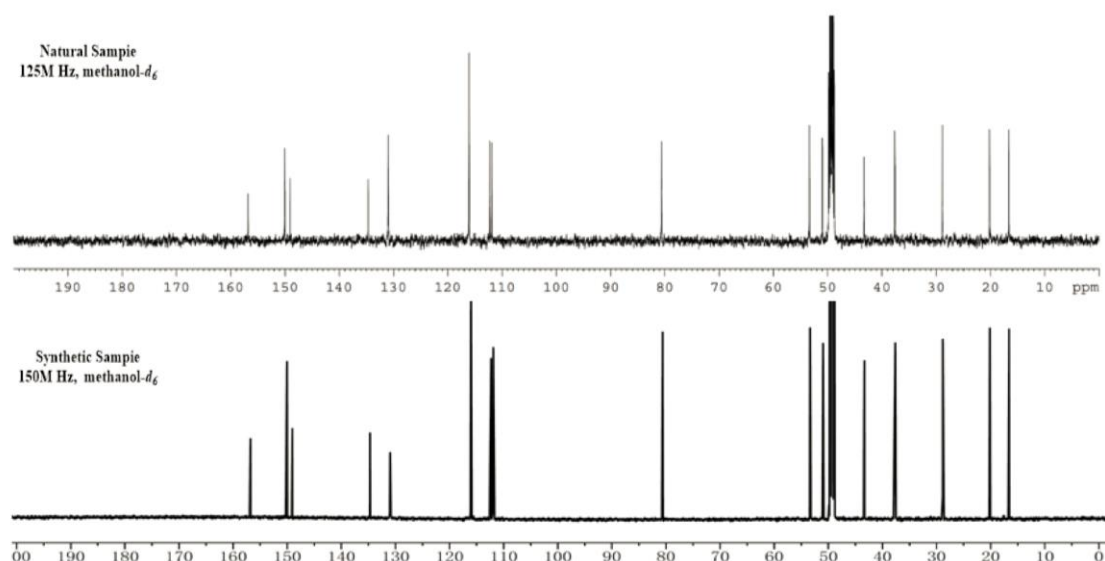
Comparison of ^{13}C NMR data for synthetic and natural (+)-psoracorylifol F



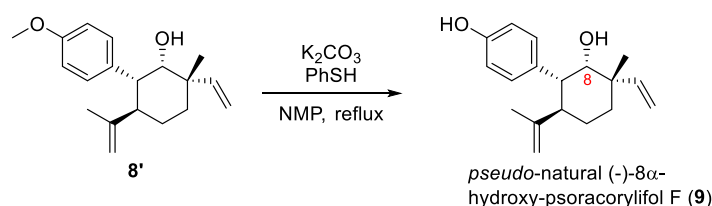
Position	Natural psoracorylifol F ^{a,9}	Synthetic psoracorylifol F ^b	$\Delta\delta$ (ppm)
1	134.9	134.7	0.2
2	131.0	131.0	0.0
3	116.1	116.1	0.0
4	156.8	156.8	0.0
5	116.1	116.1	0.0
6	131.0	131.0	0.0
7	51.0	51.0	0.0
8	80.6	80.6	0.0
9	43.3	43.3	0.0
10	37.6	37.6	0.0
11	28.9	28.9	0.0
12	53.4	53.4	0.0
13	149.1	149.1	0.0
14	112.3	112.3	0.0
15	20.2	20.1	0.1
16	150.0	150.1	-0.1
17	111.9	111.9	0.0
18	16.6	16.6	0.0

^a NMR data measured at 125 MHz in methanol- d_4 ; ^b NMR data measured at 150 MHz in methanol- d_4 .

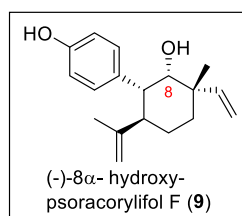
Comparison of ^{13}C NMR spectra of (+)-psoracorylifol F



3.2 Synthesis of *pseudo*-natural (-)-8 α -hydroxy-psoracorylifol F (9)



To a suspension solution of alcohol **8'** (10.0 mg, 0.035 mmol) and K_2CO_3 (1.9 mg, 0.014 mmol) in NMP (1.0 mL) was added PhSH (17.9 μL , 0.175 mmol). The mixture was stirred under reflux for 12 h, then cooled to room temperature and quenched with H_2O . The resulting mixture was extracted with ethyl acetate (3 \times 20 mL). The combined extracts were washed with brine, dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 20:1-10:1) on silica gel to give *pseudo*-natural (-)-8 α -hydroxy-psoracorylifol F (**9**) (9.0 mg, 95% yield) as a white solid.



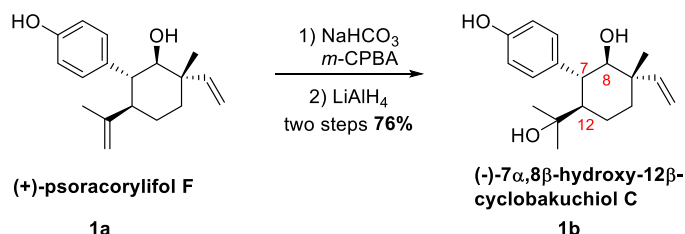
***Pseudo*-natural (-)-8 α -hydroxy-psoracorylifol F (9):** White solid. $[\alpha]_D^{21} = -40.7$ ($c = 1.0$ in MeOH). **m.p.:** 114-116 $^\circ\text{C}$.

^1H NMR (600 MHz, CDCl_3) δ : 7.09 (d, $J = 8.4$ Hz, 2H), 6.74 (d, $J = 8.4$ Hz, 2H), 5.88 (dd, $J = 18.0, 11.4$ Hz, 1H), 5.10 (d, $J = 10.8$ Hz, 1H), 5.08 (d, $J = 16.8$ Hz, 1H), 4.68 (s, 1H), 4.61 (brs, 2H), 3.38 (s, 1H),

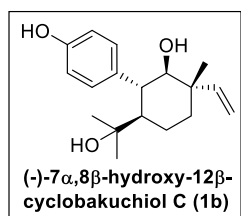
2.98 (dd, $J = 12.6, 1.8$ Hz, 1H), 2.90-2.86 (m, 1H), 2.05-1.99 (m, 1H), 1.72-1.68 (m, 2H), 1.54 (s, 3H), 1.40 (dt, $J = 13.2, 3.0$ Hz, 1H), 1.19 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ : 153.9, 147.9, 147.0, 134.4, 130.0, 115.0, 112.9, 111.9, 77.5, 45.4, 42.0, 41.4, 28.5, 28.0,

22.4, 19.2. **HRMS** (ESI) m/z found 295.1671, calculated for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 295.1669. **MS** (EI) m/z (%): 272 (17), 136 (87), 123 (21), 107 (100), 68 (17), 55 (11). **IR** (KBr plate) ν_{max} : 3394, 3076, 2963, 2922, 2861, 1641, 1613, 1514, 1451, 1374, 1224, 1174, 963, 912, 888, 821 cm^{-1} .

3.3 Synthesis of natural (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (1b)



To an ice-cold suspension solution of NaHCO_3 (21.0 mg, 0.25 mmol) and $m\text{-CPBA}$ (13.4 mg, 80%, 0.06 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of (+)-psoracorylifol F (**1a**, 14.8 mg, 0.05 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C. The mixture was stirred at 5 °C for 4 h and the reaction was quenched by addition of Me_2S (5.3 μL , 0.07 mmol) and saturated NaHCO_3 with vigorous stirring. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 \times 20 mL). The combined extracts were washed with brine, dried over Na_2SO_4 , and concentrated to give a residue, which was directly used for the next step. To an ice-cold solution of above oxirane in THF (2.0 mL) was added LiAlH_4 (9.5 mg, 0.25 mmol) slowly at 0 °C. The resulting mixture was stirred for 3 h under reflux, then cooled to room temperature and quenched with H_2O . The resulting mixture was extracted with ethyl acetate (3 \times 20 mL). The combined extracts were washed with saturated NaHCO_3 and brine, dried over Na_2SO_4 , and concentrated. The residual oil was purified by column chromatographed on silica gel (petroleum ether/ethyl acetate) to give (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (**1b**) (11.0 mg, 76% yield for 2 steps from natural (+)-psoracorylifol F (**1a**)).

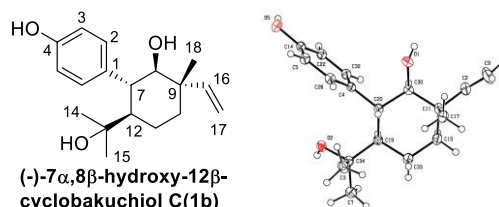


(-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (1b): Colorless needles; $[\alpha]_D^{25} = -22.0$ ($c = 0.1$ in MeOH), $[\text{lit}^{10}]$, $[\alpha]_D^{25} = -27.2$ ($c = 0.1$ in MeOH). **m.p.**: 104-106 °C.

$^1\text{H NMR}$ (600 MHz, acetone- d_6) δ : 8.13 (s, 1H), 7.09 (d, $J = 7.8$ Hz, 2H), 6.73 (d, $J = 8.4$ Hz, 2H), 5.97 (dd, $J = 17.4, 10.8$ Hz, 1H), 4.96 (dd, $J = 17.4, 1.8$ Hz, 1H), 4.86 (dd, $J = 10.8, 1.2$ Hz, 1H), 3.40 (dd, $J = 9.6, 4.2$ Hz, 1H), 2.55 (t, $J = 11.4$ Hz, 1H), 2.44 (d, $J = 4.2$ Hz, 1H), 2.21 (s, 1H), 1.90-1.87 (m, 1H), 1.82 (td, $J = 11.4, 4.2$ Hz, 1H), 1.53-1.51 (m, 2H), 1.44-1.36 (m, 1H), 1.04 (s, 3H), 0.96 (s, 3H), 0.79 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, acetone- d_6) δ : 156.8, 149.9, 135.1, 131.1, 116.1, 110.9, 80.4,

73.2, 52.9, 49.4, 42.0, 36.0, 27.6, 23.5, 16.2. **HRMS** (ESI) m/z found 313.1774, calculated for $C_{18}H_{26}O_3Na$ $[M+Na]^+$ 313.1774. **MS** (EI) m/z (%): 290 (6), 214 (23), 161 (32), 133 (100), 107 (83), 59 (56). **IR** (KBr plate) ν_{max} : 3530, 2920, 2851, 1614, 1514, 1461, 1376, 1229, 1172, 960, 897, 827, 784 cm^{-1} .

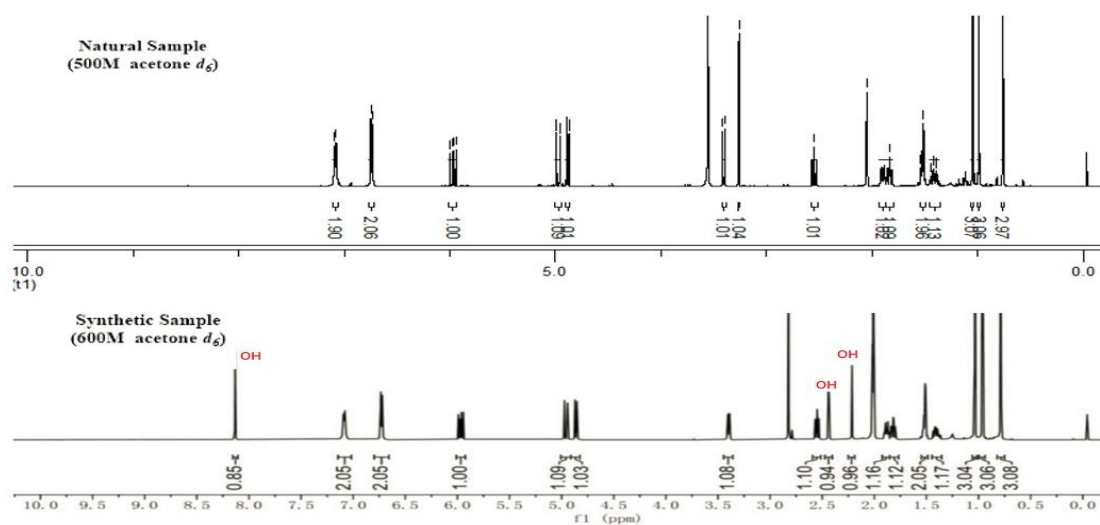
Comparison of 1H NMR data of synthetic and natural (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (1b)



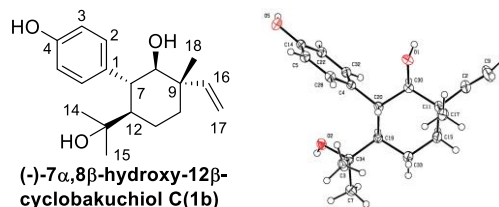
Position	Natural	Synthetic	$\Delta\delta$ (ppm)
	7 α ,8 β -hydroxy-12 β -cyclobakuchiol C ^{a,10}	7 α ,8 β -hydroxy-12 β -cyclobakuchiol C ^b	
1	-	-	-
2,6	7.09, d ($J = 8.0$ Hz)	7.09, d ($J = 7.8$ Hz)	0.00
3,5	6.74, d ($J = 8.5$ Hz)	6.73, d ($J = 8.4$ Hz)	0.01
4	-	-	-
7	2.55, t ($J = 11.0$ Hz)	2.55, t ($J = 11.4$ Hz)	0.00
8	3.41, d ($J = 10.0$ Hz)	3.40, dd ($J = 9.6, 4.2$ Hz)	0.01
9	-	-	-
10 _{ax}	1.53, m	1.53-1.51, m (1.52, m)	0.01
10 _{eq}	1.53, m	1.53-1.51, m (1.52, m)	0.01
11 _{ax}	1.90, m	1.90-1.87, m (1.89, m)	0.01
11 _{eq}	1.40, m	1.44-1.36, m (1.40, m)	0.00
12	1.83, m	1.82, td ($J = 11.4, 4.2$ Hz)	0.01
13	-	-	-
14	0.99, s	0.96 (s)	0.03
15	0.76, s	0.79 (s)	-0.03
16	5.97, dd ($J = 17.5, 10.5$ Hz)	5.97, dd ($J = 17.4, 10.8$ Hz)	0.00
17 _{ax}	4.97, dd ($J = 17.5, 1.5$ Hz)	4.96, dd ($J = 17.4, 1.8$ Hz)	0.01
17 _{eq}	4.88, dd ($J = 11.0, 1.5$ Hz)	4.86, dd ($J = 10.8, 1.2$ Hz)	0.02
18	1.05, s	1.04 (s)	0.01

^a NMR data measured at 500 MHz in acetone- d_6 ; ^b NMR data measured at 600 MHz in acetone- d_6 .

Comparison of ^1H NMR spectra of (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (1b)



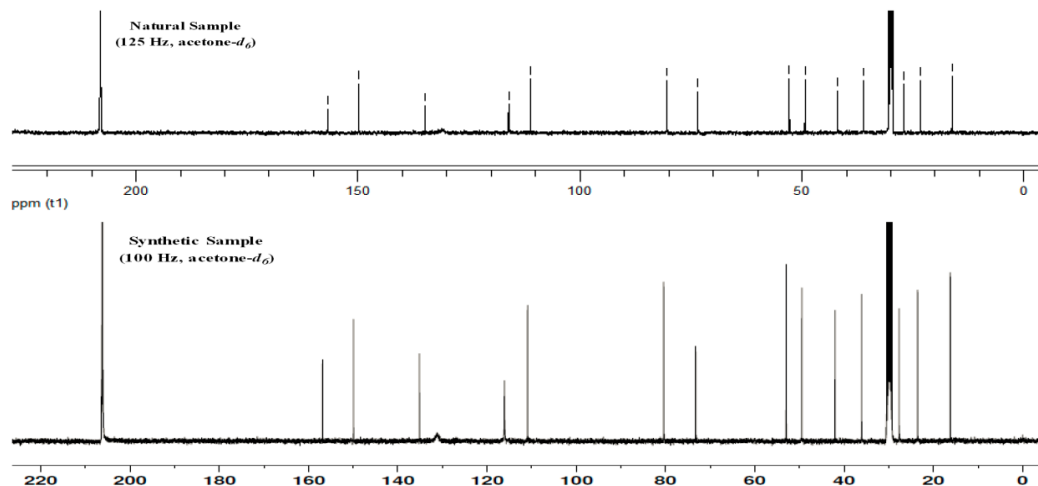
Comparison of ^{13}C NMR data for synthetic and natural (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (1b)



Position	Natural 7 α ,8 β -hydroxy-12 β -cyclobakuchiol C ^{a,10}	Synthetic 7 α ,8 β -hydroxy-12 β -cyclobakuchiol C ^b	$\Delta\delta$ (ppm)
1	134.8	135.1	-0.3
2,6	131.1	131.1	0.0
3,5	116.0	116.1	-0.1
4	156.8	156.8	0.0
7	49.3	49.4	-0.1
8	80.4	80.4	0.0
9	42.0	42.0	0.0
10	36.1	36.0	0.1
11	23.3	23.5	-0.2
12	52.8	52.9	-0.1
13	73.4	73.2	0.2
14	27.0	27.6	-0.6
15	29.6	29.2	0.4
16	149.8	149.9	-0.1
17	111.0	110.9	0.1
18	16.2	16.2	0.0

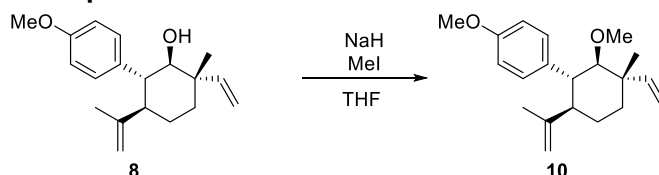
^a NMR data measured at 125 MHz in acetone- d_6 ; ^b NMR data measured at 100 MHz in acetone- d_6 .

Comparison of ^{13}C NMR spectra of (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (**1b**)

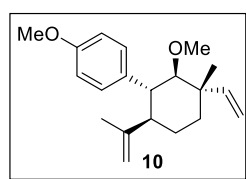


3.4 Synthesis of the proposed corypsorior J (**1c**)

3.4.1 Synthesis of compound **10**



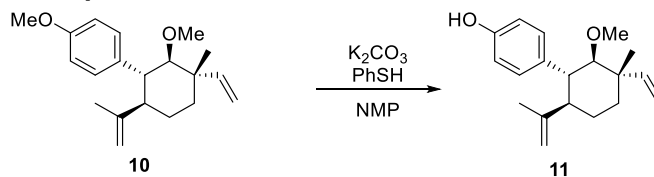
To a suspension solution of alcohol **8** (70.0 mg, 0.24 mmol) and NaH (38.4 mg, 60%, 0.96 mmol) in THF (5.0 mL) was added MeI (60.0 μL , 0.96 mmol). The mixture was stirred at room temperature for 20 h, and quenched with H_2O . The resulting mixture was extracted with ethyl acetate (3 \times 20 mL). The combined extracts were washed with brine, dried over Na_2SO_4 , and filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 100:1) on silica gel to give methylether **10** (68.4 mg, 95% yield) as a colorless oil.



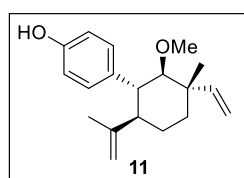
Compound 10: Colorless oil; $[\alpha]_D^{23} = 22.7$ ($c = 0.5$ in MeOH).

^1H NMR (600 MHz, CDCl_3) δ : 7.12 (d, $J = 8.4$ Hz, 2H), 6.79 (d, $J = 8.4$ Hz, 2H), 5.97 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.04 (dd, $J = 17.4, 1.2$ Hz, 1H), 4.98 (dd, $J = 10.8, 1.2$ Hz, 1H), 4.55 (brs, 1H), 4.53 (brs, 1H), 3.77 (s, 3H), 2.89 (d, $J = 10.2$ Hz, 1H), 2.70 (t, $J = 10.8$ Hz, 1H), 2.70 (s, 3H), 2.38 (td, $J = 11.4, 3.6$ Hz, 1H), 1.69-1.55 (m, 4H), 1.53 (s, 3H), 1.13 (s, 3H); **^{13}C NMR** (150 MHz, CDCl_3) δ : 157.8, 148.3, 147.1, 134.2, 129.5, 113.2, 111.7, 111.0, 90.8, 61.2, 55.0, 50.8, 48.5, 42.2, 35.9, 27.2, 19.3, 16.4. **HRMS** (ESI) m/z found 323.1981, calculated for $\text{C}_{20}\text{H}_{28}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 323.1982. **MS** (EI) m/z (%): 300 (65), 255 (20), 179 (42), 164 (100), 121 (46). **IR** (KBr plate) ν_{max} : 3076, 3033, 2970, 2929, 2864, 2830, 1645, 1613, 1512, 1455, 1269, 1247, 1176, 1126, 1038, 911, 888, 818 cm^{-1} .

3.4.2 Synthesis of compound 11



To a suspension solution of methylether **10** (42.0 mg, 0.14 mmol) and K_2CO_3 (8.1 mg, 0.06 mmol) in NMP (2.0 mL) was added PhSH (58.0 μ L, 0.56 mmol). The mixture was stirred under reflux for 14 h. The reaction was quenched by addition of HCl (1.0 mol/L) and extracted with ethyl acetate (3 \times 10 mL). The combined extracts were washed with brine, dried (Na_2SO_4), and concentrated. The crude product was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give phenol **11** (37.2 mg, 93% yield).

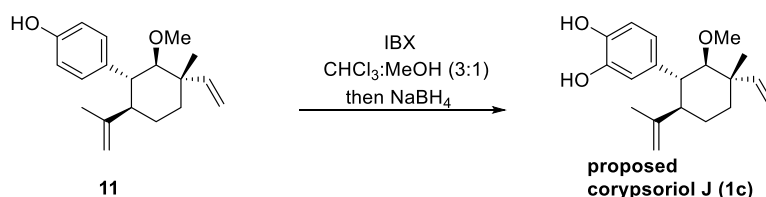


Compound 11: White solid; $[\alpha]_D^{25} = 20.0$ ($c = 0.5$ in MeOH); **m.p.:** 94.2-95.3 $^{\circ}C$.

1H NMR (400 MHz, $CDCl_3$) δ : 7.07 (d, $J = 8.4$ Hz, 2H), 6.72 (d, $J = 8.8$ Hz, 2H), 5.96 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.04 (dd, $J = 17.6,$

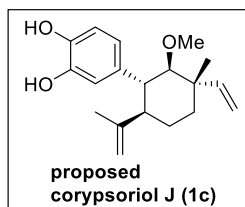
1.2 Hz, 1H), 4.99 (dd, $J = 10.8, 1.2$ Hz, 1H), 4.95 (s, 1H), 4.54 (brs, 1H), 4.53 (brs, 1H), 2.91 (d, $J = 10.4$ Hz, 1H), 2.73 (s, 3H), 2.75-2.67 (m, 1H), 2.37 (td, $J = 11.6, 3.2$ Hz, 1H), 1.71-1.56 (m, 4H), 1.53 (s, 3H), 1.13 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ : 153.8, 148.2, 147.0, 134.3, 129.7, 114.8, 111.7, 111.2, 90.9, 61.2, 50.9, 48.5, 42.3, 36.0, 27.2, 19.3, 16.4. **HRMS** (ESI) m/z found 309.1823, calculated for $C_{19}H_{26}O_2Na$ $[M+Na]^+$ 309.1825. **MS** (EI) m/z (%): 286 (12), 241 (13), 186 (11), 150 (100), 135 (23), 107 (64). **IR** (KBr plate) ν_{max} : 3077, 2973, 2931, 2867, 1644, 1614, 1515, 1449, 1413, 1375, 1225, 1103, 913, 890, 827 cm^{-1} .

3.4.3 Synthesis of the proposed corypsoriol J (1c)



To a solution of phenol **11** (17.0 mg, 0.06 mmol) in $CHCl_3/MeOH$ (3:1 v/v, 1.2 mL) was added IBX (20.2 mg, 0.07 mmol) at 0 $^{\circ}C$ under an argon atmosphere. A yellow-to-orange color was observed and the mixture was stirred for 2 h, then $NaBH_4$ (20.5 mg, 0.54 mmol) was added at 0 $^{\circ}C$ under vigorous stirring for 30 min.¹¹ The reaction was quenched by addition of HCl (1.0 mol/L) and extracted with ethyl acetate (3 \times 10 mL). The combined extracts were washed with brine, dried over Na_2SO_4 , and filtered. The filtrate was

concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel using ethyl acetate-petroleum ether (1:1) to give the proposed corypsoriol J (**1c**) (17.2 mg, 95% yield).



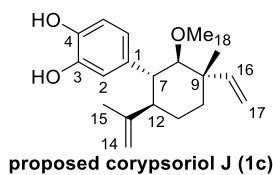
Proposed corypsoriol J (1c**):** White solid; $[\alpha]_D^{25} = 13.3$ ($c = 0.1$ in MeOH); $[\text{lit}^{12}, [\alpha]_D^{25} = 30.0$ ($c = 0.1$ in MeOH)]. **m.p.:** 160-163 °C.

¹H NMR (600 MHz, methanol-*d*₄) δ : 6.65 (brs, 1H), 6.64 (brs, 1H), 6.54 (d, $J = 7.2$ Hz, 1H), 5.98 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.04 (dd, $J = 17.6, 1.2$ Hz, 1H), 4.97 (dd, $J = 10.8, 1.2$ Hz, 1H), 4.55 (d, $J =$

1.2 Hz, 1H), 4.50 (d, $J = 1.2$ Hz, 1H), 3.00 (d, $J = 10.4$ Hz, 1H), 2.77 (s, 3H), 2.58 (t, $J = 10.8$ Hz, 1H), 2.38 (td, $J = 12.0, 3.6$ Hz, 1H), 1.71-1.64 (m, 2H), 1.53 (s, 3H), 1.52-1.49 (m, 2H), 1.11 (s, 3H); **¹³C NMR** (150 MHz, methanol-*d*₄) δ : 149.7, 148.5, 145.7, 144.4, 135.0, 121.4, 115.8, 115.8, 112.3, 111.7, 92.2, 61.7, 52.4, 50.1, 43.4, 37.3, 28.4, 19.7, 16.7.

HRMS (ESI) m/z found 325.1772, calculated for C₁₉H₂₆O₃Na [M+Na]⁺ 325.1774. **MS** (EI) m/z (%): 302 (22), 271 (50), 257 (11), 202 (13), 198 (63), 166 (100), 123 (39). **IR** (KBr plate) ν_{max} : 3339, 2972, 2929, 2856, 1642, 1565, 1520, 1444, 1375, 1281, 1194, 1105, 912, 886, 751 cm⁻¹.

Comparison of ^1H NMR data for synthetic and natural corypsoriorol J (1c)

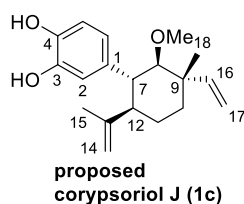


Position	Natural corypsoriorol J ^{a,12}	Synthetic corypsoriorol J ^b	$\Delta\delta$ (ppm)
1	-	-	-
2	6.61 (d, $J = 2.0$ Hz)	6.64, brs	-0.03
3	-	-	-
4	-	-	-
5	6.61 (d, $J = 8.0$ Hz)	6.64, brs	-0.03
6	6.50 (dd, $J = 8.0, 2.0$ Hz)	6.54, d ($J = 7.2$ Hz)	-0.04
7	2.03 (t, $J = 9.4$ Hz)	2.58, t ($J = 10.8$ Hz)	-0.55
8	3.75 (d, $J = 9.4$ Hz)	3.00, d ($J = 10.4$ Hz)	0.75
9	-	-	-
10 α	1.70, m	1.65, m	0.05
10 β	1.52, m	1.52, m	0
11 α	1.92, m	1.70, m	0.22
11 β	1.37, o ^c	1.49, m	-0.12
12	2.30 (td, $J = 9.7, 4.1$ Hz)	2.38, td ($J = 12.0, 3.6$ Hz)	-0.08
14	4.14, brs	4.55, d ($J = 1.2$ Hz)	-0.41
	4.08, brs	4.50, d ($J = 1.2$ Hz)	-0.42
15	1.36, s	1.53, s	-0.17
16	6.15 (dd, $J = 18.0, 10.5$ Hz)	5.98, dd ($J = 17.6, 10.9$ Hz)	0.17
17a	5.04 (dd, $J = 10.5, 1.7$ Hz)	4.97, dd ($J = 10.8, 1.2$ Hz)	0.07
17b	5.07 (dd, $J = 18.0, 1.7$ Hz)	5.04, dd ($J = 17.6, 1.2$ Hz)	0.03
18	1.28, s	1.11, s	-0.17
8-OCH ₃	3.00, s	2.77, s	0.23

^a NMR data measured at 500 MHz in methanol- d_4 ; ^b NMR data measured at 600 MHz in methanol- d_4 ; ^c

"o" means overlapped.

Comparison of ^{13}H NMR data for synthetic and natural corypsoriol J (**1c**)

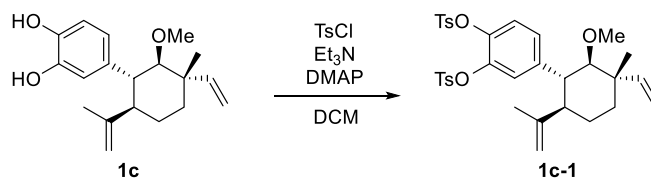


Position	Natural corypsoriol J ^{a,12}	Synthetic corypsoriol J ^b	$\Delta\delta$ (ppm)
1	134.0	135.0	-0.1
2	115.7	115.8	-0.1
3	146.1	143.0	3.1
4	146.1	143.0	3.1
5	116.7	115.8	0.9
6	121.5	121.4	-1.4
7	59.4	50.1	9.3
8	88.2	92.2	-4
9	50.1	43.4	6.7
10	41.1	37.3	4.1
11	31.7	28.4	3.3
12	51.3	52.4	-1.1
13	149.2	148.5	0.7
14	110.4	112.3	-1.9
15	19.8	19.7	0.1
16	145.5	149.7	-4.2
17	111.9	111.7	0.2
18	28.4	16.7	11.7
8-OCH ₃	55.8	61.7	-5.9

^a NMR data measured at 125 MHz in methanol- d_4 ; ^b NMR data measured at 150 MHz in methanol- d_4 .

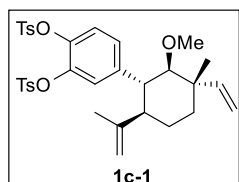
3.5 Synthesis of proposed corypsoriol J's derivatives

3.5.1 Synthesis of compound **1c-1**



To a suspension solution of the proposed corypsoriol J (**1c**, 13.3 mg, 0.044 mmol), Et₃N (12.2 μ L, 0.088 mmol) and DMAP (0.5 mg, 0.0044 mmol) in DCM (5.0 mL) was added TsCl

(16.4 mg, 0.099 mmol) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 2 h, and quenched with H₂O. The resulting mixture was extracted with ethyl acetate (3x20 mL). The combined extracts were washed with brine, dried over Na₂SO₄, and filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 50:1) on silica gel to give compound **1c-1** (25.2 mg, 94% yield) as a white foamy solid.

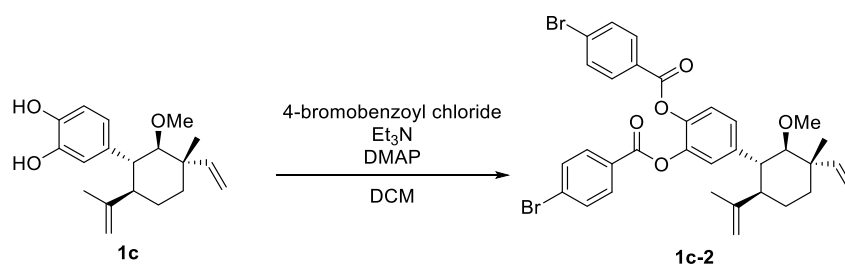


Compound 1c-1: White foamy solid; $[\alpha]_D^{20} = -1.3$ (c = 0.5 in CHCl₃).

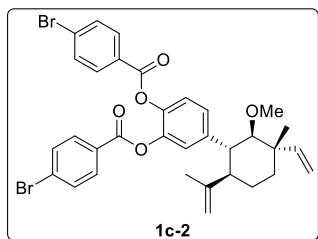
¹H NMR (600 MHz, CDCl₃) δ : 7.58 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.14 (brs, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.03 (dd, *J* = 8.4, 1.8 Hz, 1H),

5.93 (dd, *J* = 18.0, 10.8 Hz, 1H), 5.05 (dd, *J* = 17.4, 1.2 Hz, 1H), 5.01 (dd, *J* = 10.8, 1.2 Hz, 1H), 4.54 (brs, 1H), 4.52 (brs, 1H), 2.89 (d, *J* = 10.2 Hz, 1H), 2.72 (s, 3H), 2.70 (t, *J* = 10.2 Hz, 1H), 2.44 (s, 3H), 2.41 (s, 3H), 2.29 (td, *J* = 11.4, 3.6 Hz, 1H), 1.68-1.61 (m, 1H), 1.60-1.52 (m, 3H), 1.51 (s, 3H), 1.11 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ : 147.7, 146.0, 145.53, 145.50, 143.3, 140.7, 139.1, 132.0, 131.7, 129.6, 129.5, 128.62, 128.57, 123.4, 112.3, 111.6, 90.3, 61.2, 50.9, 49.1, 42.2, 35.7, 26.7, 21.74, 21.70, 19.3, 16.2. **HRMS** (ESI) *m/z* found 633.1963, calculated for C₁₈H₂₄O₂Na [M+Na]⁺ 633.1961. **MS** (EI) *m/z* (%): 610 (10), 565 (7), 423 (13), 355 (10), 319 (66), 155 (76), 135 (28), 91 (100).

3.5.2 Synthesis of compound 1c-2



To a suspension solution of the proposed corypsoriol J (**1c**, 20.0 mg, 0.066 mmol), Et₃N (18.0 μ L, 0.13 mmol) and DMAP (0.8 mg, 0.007 mmol) in DCM (5.0 mL) was added 4-bromobenzoyl chloride (28.6 mg, 0.13 mmol) at 0 °C under an argon atmosphere. The mixture was stirred at room temperature for 2 h, and quenched with H₂O. The resulting mixture was extracted with ethyl acetate (3x20 mL). The combined extracts were washed with brine, dried over Na₂SO₄, and filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 50:1) on silica gel to give compound **1c-2** (41.0 mg, 93% yield) as a white foamy solid.

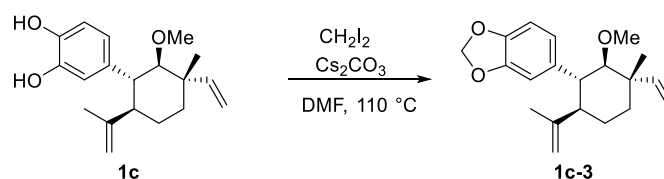


Compound 1c-2: White foamy solid; $[\alpha]_D^{20} = 14.5$ ($c = 0.5$ in CHCl_3).

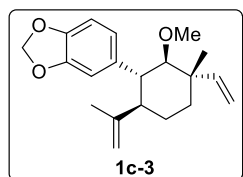
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ : 7.90 (d, $J = 8.4$ Hz, 2H), 7.88 (d, $J = 8.4$ Hz, 2H), 7.54 (d, $J = 4.8$ Hz, 2H), 7.53 (d, $J = 4.8$ Hz, 2H), 7.27 (d, $J = 7.8$ Hz, 1H), 7.25 (d, $J = 1.8$ Hz, 1H),

7.19 (dd, $J = 8.4, 1.8$ Hz, 1H), 5.97 (dd, $J = 18.0, 10.8$ Hz, 1H), 5.05 (dd, $J = 17.4, 1.2$ Hz, 1H), 5.00 (dd, $J = 10.8, 1.2$ Hz, 1H), 4.63 (brs, 1H), 4.61 (brs, 1H), 2.96 (d, $J = 10.2$ Hz, 1H), 2.85 (s, 3H), 2.83 (t, $J = 10.8$ Hz, 1H), 2.42 (td, $J = 12.0, 3.6$ Hz, 1H), 1.73-1.67 (m, 1H), 1.64-1.54 (m, 3H), 1.58 (s, 3H), 1.15 (s, 3H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ : 163.5, 147.9, 146.2, 141.7, 140.3, 131.9, 131.47, 131.45, 129.0, 127.8, 122.5, 122.4, 111.4, 90.6, 61.4, 50.6, 49.1, 42.3, 35.8, 27.1, 19.5, 16.4. **HRMS** (ESI) m/z found 691.0484, calculated for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 691.0488. **MS** (EI) m/z (%): 668 (2), 532 (8), 183 (100), 179 (20), 157 (12), 147 (9), 104 (8), 93 (6), 68 (6).

3.5.3 Synthesis of compound 1c-3



To a suspension solution of the proposed corypsoriol J (**1c**, 12.0 mg, 0.04 mmol) and Cs_2CO_3 (19.6 mg, 0.06 mmol) in DMF (2.0 mL) was added CH_2I_2 (4.8 μL , 0.06 mmol) at room temperature. The mixture was stirred at 110 $^\circ\text{C}$ for 20 h, and quenched with H_2O at room temperature. The resulting mixture was extracted with ethyl acetate (3 \times 20 mL). The combined extracts were washed with brine, dried over Na_2SO_4 , and filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 20:1) on silica gel to give compound **1c-3** (8.2 mg, 65% yield) as a colorless oil.



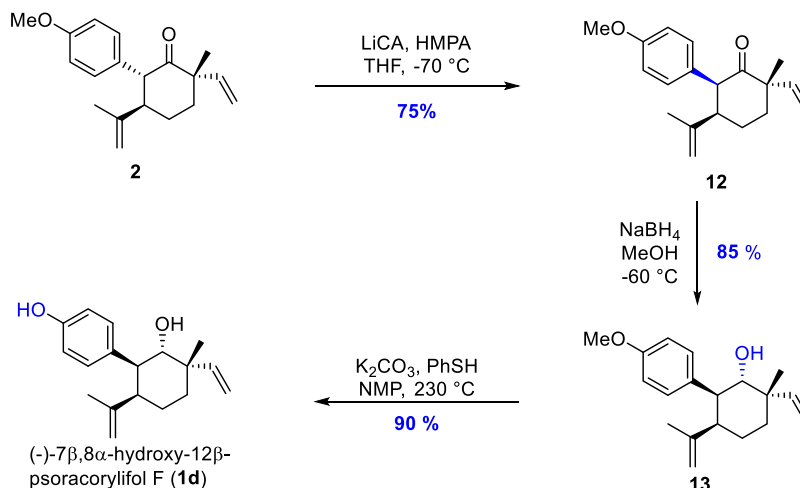
Compound 1c-3: Colorless oil; $[\alpha]_D^{20} = 0.8$ ($c = 0.5$ in CHCl_3).

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ : 6.72 (brs, 1H), 6.71 (d, $J = 8.4$ Hz, 1H), 6.66 (d, $J = 7.8$ Hz, 1H), 5.96 (dd, $J = 18.0, 10.8$ Hz, 1H), 5.91 (s, 2H), 5.04 (d, $J = 17.4$ Hz, 1H), 4.97 (d, $J = 10.8$ Hz, 1H), 4.55 (brs, 2H), 2.89 (d, $J = 10.2$ Hz, 1H), 2.78 (s, 3H), 2.68 (t, $J = 11.4$ Hz, 1H), 2.33 (td, $J = 12.0, 3.6$ Hz, 1H), 1.69-1.59 (m, 2H), 1.57-1.52 (m, 2H), 1.55 (s, 3H), 1.12 (s, 3H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ : 148.2, 147.2, 146.9, 145.6, 136.2, 122.1, 111.8, 111.2, 108.7, 107.7, 100.7,

90.7, 61.3, 51.0, 49.2, 42.3, 35.9, 27.2, 19.3, 16.4. **HRMS** (ESI) m/z found 337.1772,

calculated for C₁₈H₂₄O₂Na [M+Na]⁺ 337.1774. **MS** (EI) m/z (%): 314 (34), 178 (90), 149 (69), 135 (49), 105 (41), 84 (100), 57 (77).

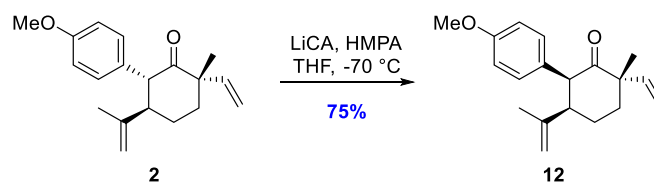
4. Total synthesis of 7β-aryl-12β-alkyl type meroterpenoid



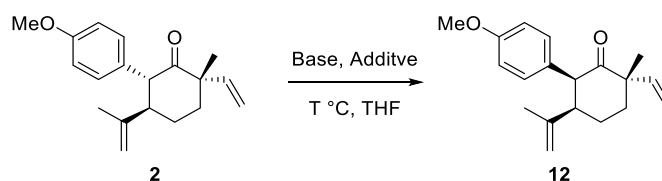
Scheme S3 Total synthesis of (-)-7β,8α-hydroxy-12β-psoracorylifol F.

4.1 Synthesis of natural (-)-7β,8α-hydroxy-12β-psoracorylifol F (1d)

4.1.1 Synthesis of compound 12

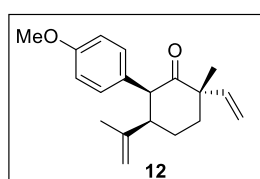


Under an argon atmosphere, to a solution of the precursor **2** (5.0 mg, 0.018 mmol) in THF (1.0 mL) was added lithium isopropylcyclohexylamide (LiCA, 0.5 mL, 0.09 mmol, 5.0 equiv.) and hexamethylphosphoramide (HMPA, 31.1 μL, 0.18 mmol, 10.0 equiv.) at -70 °C and the resulting mixture was stirred for 2 h at the same temperature. The reaction mixture was added silica gel (400 mg) and stirred for 30 min. The crude reaction mixture was filtrated through celite and washed with ethyl acetate, then concentrated under vacuum. The crude product was purified by flash column chromatography to give the desired *cis*-product **12** (3.75 mg, 75% yield) as a colorless oil along with the starting material **2** (0.5 mg, 10% yield). The yield based on the recover starting material is 83% yield.

Table S6 Optimization of the enolization/protonation conditions^a

Entry	Base (equiv.)	Additive	Temp.	Yield ^c	Remark
1 ^b	KOH (2.0)	--	rt to 70 °C	NR	Quenched by aq. NH ₄ Cl
2 ^b	NaOH (2.0)	--	rt to 70 °C	NR	Quenched by aq. NH ₄ Cl
3	LDA (2.0)	--	-78 °C to rt	NR	Quenched by aq. NH ₄ Cl
4	NaH (2.0)	--	0 °C to 20 °C	29%	Quenched by cold aq. NH ₄ Cl
5	NaH (5.0)	--	0 °C to 20 °C	30%	Quenched by cold aq. NH ₄ Cl
6	NaH (5.0)	--	100 °C	33%	Quenched by cold aq. NH ₄ Cl
7	LiHMDS (2.0)	--	-78 °C to 20 °C	30%	Quenched by cold aq. NH ₄ Cl
8	LiHMDS (4.0)	--	-78 °C to 20 °C	50%	Quenched by cold aq. NH ₄ Cl
9	LiCA (5.0)	--	-70 to 0 °C	NR	Quenched by aq. NH ₄ Cl
10	LTMP (5.0)	--	-70 to 0 °C	ND	Quenched by silica gel in 0 °C
11	LiCA (5.0)	HMPA	-70 °C	40%	Quenched by aq. NH ₄ Cl in -70 °C
12	LiCA (5.0)	HMPA	-70 °C	71%	Quenched by silica gel in -40 °C
13	LiCA (5.0)	HMPA	-70 °C	75%	Quenched by silica gel in -70 °C
14	LiCA (5.0)	HMPA	-70 °C	59%	Quenched by silica gel in -110 °C
15	LTMP (5.0)	HMPA	-70 °C	25%	Quenched by silica gel in -70 °C
16	<i>t</i> -BuLi (5.0)	HMPA	-70 °C	26%	Quenched by silica gel in -70 °C
17	<i>t</i> -BuLi (5.0)	HMPA	-70 °C	45%	Quenched by silica gel in -110 °C

^aThe reactions were performed using precursor **2** (0.018 mmol), base (5.0 equiv.), additive (10.0 equiv.) in 1.0 mL THF; ^b MeOH as solvent; ^c Isolated yield; rt = Room temperature; THF = Tetrahydrofuran; HMPA = Hexamethylphosphoramide; LDA = Lithium diisopropylamide; LiHMDS = Lithium bis(trimethylsilyl)amide; LiCA = lithium cyclohexylisopropylamide; LTMP = 2,2,6,6-tetramethylpiperidyl-lithium; NR = No reaction; ND = No detected.



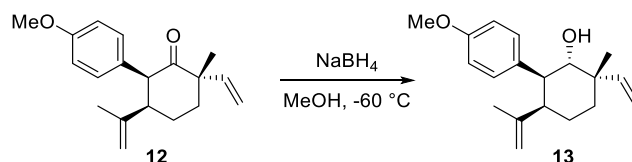
Compound 12: Colorless oil; $[\alpha]_D^{23} = -78.8$ ($c = 0.5$ in MeOH).

¹H NMR (600 MHz, CDCl₃) δ : 7.19 (d, $J = 8.4$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 6.03 (dd, $J = 18.0, 10.8$ Hz, 1H), 5.19 (d, $J = 10.2$ Hz, 1H), 5.13 (d, $J = 18.0$ Hz, 1H), 4.96, (brs, 1H), 4.60, (brs, 1H),

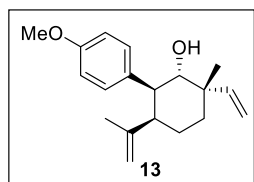
4.15 (d, $J = 5.4$ Hz, 1H), 3.78 (s, 3H), 3.08 (dd, $J = 9.0, 4.8$ Hz, 1H), 2.43-2.18 (m, 1H), 2.92-1.93 (m, 2H), 1.91-1.87 (m, 1H), 1.70 (s, 3H), 1.18 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃)

δ : 211.9, 158.0, 143.9, 143.5, 130.7, 129.1, 115.1, 114.3, 113.0, 55.2, 54.8, 52.2, 49.2, 34.9, 26.1, 24.9, 24.0. **HRMS** (ESI) m/z found 307.1668, calculated for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 307.1669. **MS** (EI) m/z (%): 284 (13), 216 (16), 173 (26), 160 (46), 134 (24), 121 (100). **IR** (KBr plate) ν_{max} : 3447, 2955, 2926, 2853, 1696, 1609, 1512, 1416, 1375, 1296, 1253, 1184, 1035, 1008, 918, 892, 829 cm^{-1} .

4.1.2 Synthesis of compound 13



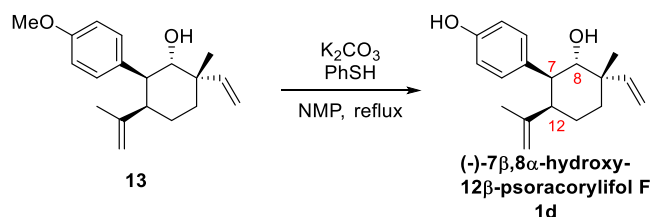
To a solution of compound **12** (25.0 mg, 0.09 mmol) in methanol (2.0 mL) was added $NaBH_4$ (34.2 mg, 0.9 mmol) at $-60\text{ }^\circ\text{C}$ under an argon atmosphere. The mixture was stirred for 1 h. When the reaction completed (monitored by TLC), 10.0 mL of water were added and then stirred for another 1 h. The methanol of mixture was removed under the reduce pressure, and the resulting aqueous layer was extracted with ethyl acetate (3 \times 20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 , and filtered. The filtrate was concentrated under reduced pressure, and the resulting crude product (dr > 20:1) was purified by column chromatography on silica gel using petroleum ether-ethyl acetate (5:1) to afford compound **13** (21.9 mg, 85% yield).



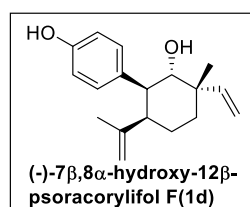
Compound 13: Colorless oil; $[\alpha]_D^{21} = -62.7$ ($c = 1.0$ in MeOH).

1H NMR (400 MHz, $CDCl_3$) δ : 7.67 (d, $J = 8.8$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 5.85 (dd, $J = 17.6, 10.8$ Hz, 1H), 5.04 (dd, $J = 10.8, 0.8$ Hz, 1H), 4.99 (dd, $J = 17.6, 0.8$ Hz, 1H), 4.93 (brs, 1H), 4.92 (brs, 1H), 3.79 (s, 3H), 3.66 (s, 1H), 2.88 (brs, 1H), 2.55 (dd, $J = 12.4, 3.2$ Hz, 1H), 2.26-2.15 (m, 1H), 2.09-2.03 (m, 1H), 1.75 (s, 3H), 1.70-1.66 (m, 2H), 0.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ : 158.5, 148.2, 146.1, 132.8, 130.3, 113.8, 112.33, 112.25, 83.4, 77.6, 55.0, 53.8, 42.4, 36.1, 25.4, 25.0, 15.5. **HRMS** (ESI) m/z found 309.1824, calculated for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 309.1825. **MS** (EI) m/z (%): 286 (1), 189 (10), 166 (33), 135 (100), 108 (15), 77 (11), 55 (7). **IR** (KBr plate) ν_{max} : 3478, 2959, 2925, 2855, 1611, 1514, 1460, 1414, 1255, 1184, 1086, 1035, 901, 827, 803 cm^{-1} .

4.1.3 Synthesis of natural (-)-7 β ,8 α -hydroxy-12 β -psoracorylifol F (**1d**)



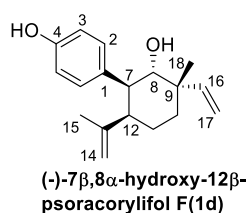
To a suspension solution of compound **13** (7.0 mg, 0.025 mmol) and K₂CO₃ (1.4 mg, 0.01 mmol) in NMP (1.0 mL) was added PhSH (12.6 μ L, 0.12 mmol). The mixture was stirred under reflux for 14 h. The reaction was quenched by addition of HCl (1.0 mol/L) and extracted with ethyl acetate (3 \times 10 mL). The combined extracts were washed with brine, dried (Na₂SO₄), and concentrated. The resulting crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 10:1-2:1) to give (-)-7 β ,8 α -hydroxy-12 β -psoracorylifol F (**1d**) (6.3 mg, 93% yield).



(-)-7 β ,8 α -hydroxy-12 β -psoracorylifol F (1d**):** White solid; $[\alpha]_D^{25} = -32.0$ ($c = 0.1$ in MeOH), $[\text{lit}^{10}, [\alpha]_D^{25} = -15.1$ ($c = 0.1$ in MeOH)]. **m.p.:** 164-167 °C.

¹H NMR (600 MHz, acetone-*d*₆) δ : 8.02 (s, 1H), 7.02 (d, $J = 8.4$ Hz, 2H), 6.70 (d, $J = 8.4$ Hz, 2H), 6.33 (dd, $J = 18.0, 11.4$ Hz, 1H), 5.18 (dd, $J = 5.4, 1.2$ Hz, 1H), 5.15 (dd, $J = 12.0, 1.2$ Hz, 1H), 4.49 (brs, 1H), 4.42 (brs, 1H), 3.43 (dd, $J = 10.2, 4.8$ Hz, 1H), 2.94 (s, 1H), 2.78 (s, 1H), 2.73 (d, $J = 4.2$ Hz, 1H), 2.55 (t, $J = 11.4$ Hz, 1H), 2.44 (td, $J = 12.0, 4.2$ Hz, 1H), 1.94-1.92 (m, 1H), 1.78-1.75 (m, 1H), 1.55-1.53 (m, 1H), 1.46 (s, 3H), 1.43-1.41 (m, 1H), 1.13 (s, 3H); **¹³C NMR** (150 MHz, acetone-*d*₆) δ : 156.6, 148.7, 142.8, 133.7, 130.6, 115.8, 113.9, 111.8, 81.6, 52.4, 51.7, 43.1, 36.9, 29.7, 29.6, 19.8. **HRMS** (ESI) m/z found 295.1671, calculated for C₁₈H₂₄O₂Na [M+Na]⁺ 295.1669. **MS** (EI) m/z (%): 272 (22), 136 (100), 123 (18), 107 (94), 81 (13), 68 (18). **IR** (KBr plate) ν_{max} : 3444, 2923, 2852, 1514, 1461, 1376, 1229, 1015, 914, 819, 720 cm⁻¹.

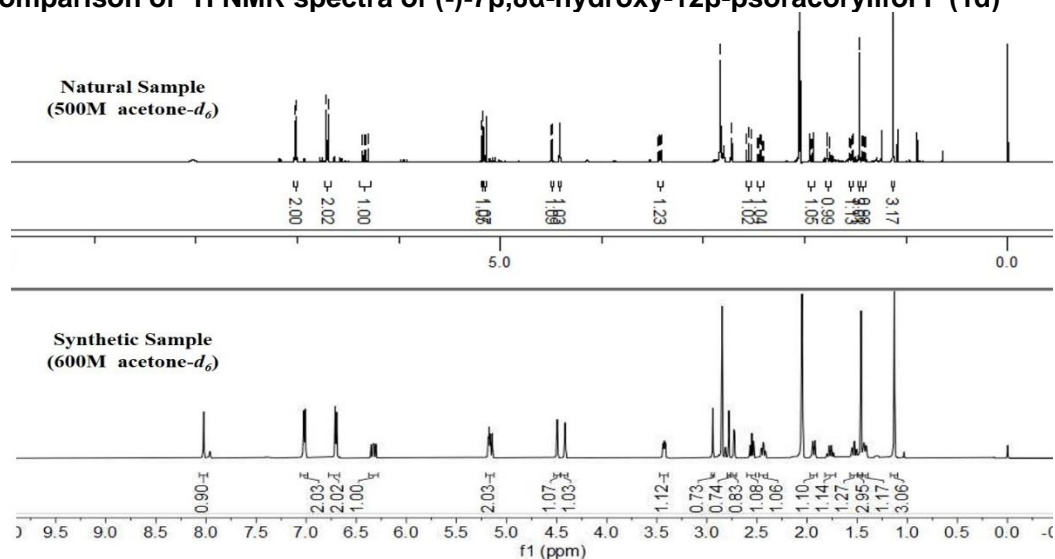
Comparison of ^1H NMR data of synthetic and natural (-)-7 β ,8 α -hydroxy-12 β -psoracorylifol F (1d)



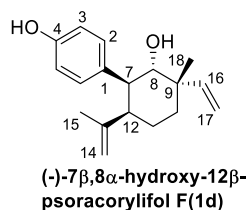
Position	Natural 7 β ,8 α -hydroxy-12 β -psoracorylifol F ^{a,10}	Synthetic 7 β ,8 α -hydroxy-12 β -psoracorylifol F ^b	$\Delta\delta$ (ppm)
1	-	-	-
2,6	7.02, d (J = 8.5 Hz)	7.02, d (J = 8.4 Hz)	0.00
3,5	6.70, d (J = 8.5 Hz)	6.70, d (J = 8.4 Hz)	0.00
4	-	-	-
7	2.55, t (J = 11.5 Hz)	2.55, t (J = 11.4 Hz)	0.00
8	3.43, d (J = 10.0 Hz)	3.43, dd (J = 10.2, 4.8 Hz)	0.00
9	-	-	-
10 _{ax}	1.93, m	1.95-1.92, m (1.93, m)	0.00
10 _{eq}	1.54, m	1.55-1.53, m (1.54, m)	0.00
11 _{ax}	1.76, m	1.78-1.75, m (1.77, m)	-0.01
11 _{eq}	1.41, m	1.43-1.41, m (1.42, m)	-0.01
12	2.44, td (J = 12.0, 4.0 Hz)	2.44, td (J = 12.0, 4.2 Hz)	0.00
13	-	-	-
14 _{ax}	4.49, brs	4.49 (brs)	0.00
14 _{eq}	4.41, brs	4.42 (brs)	-0.01
15	1.46, s	1.46 (s)	0.00
16	6.33, dd (J = 16.0, 11.0 Hz)	6.33, dd (J = 18.0, 11.4 Hz)	0.00
17 _{ax}	5.18, dd (J = 4.0, 1.4 Hz)	5.18, dd (J = 5.4, 1.2 Hz)	0.00
17 _{eq}	5.15, dd (J = 10.5, 1.5 Hz)	5.15, dd (J = 12.0, 1.2 Hz)	0.00
18	1.13, s	1.13 (s)	0.00

^a NMR data measured at 500 MHz in acetone- d_6 ; ^b NMR data measured at 600 MHz in acetone- d_6 .

Comparison of ^1H NMR spectra of (-)-7 β ,8 α -hydroxy-12 β -psoracorylifol F (1d)



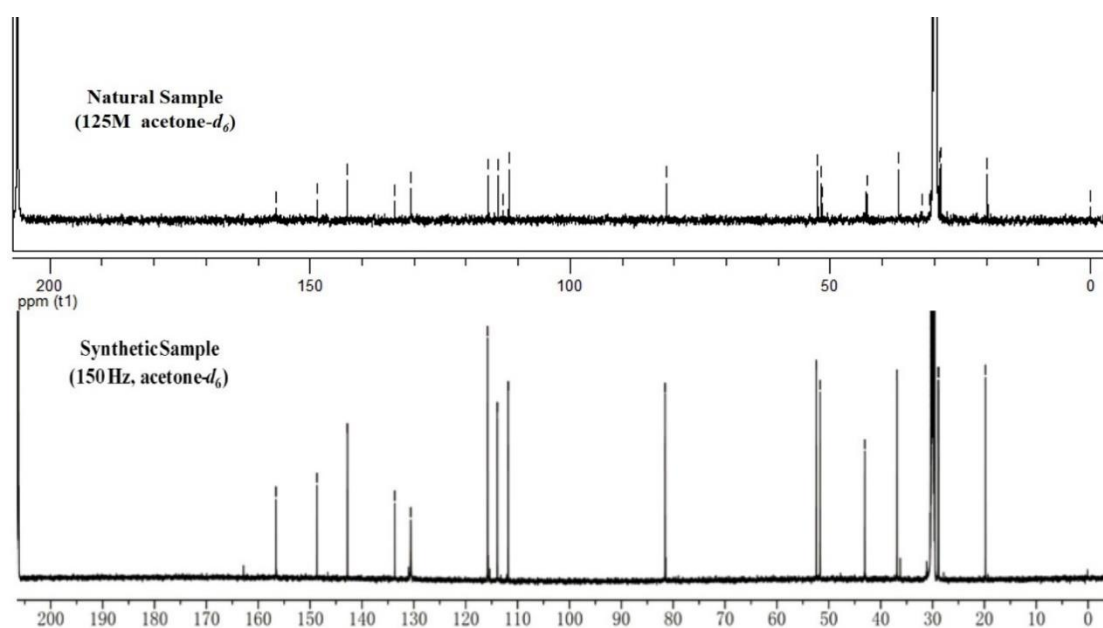
Comparison of ^{13}C NMR data of synthetic and natural (-)-7 β ,8 α -hydroxy-12 β -psoracorylifol F (1d)



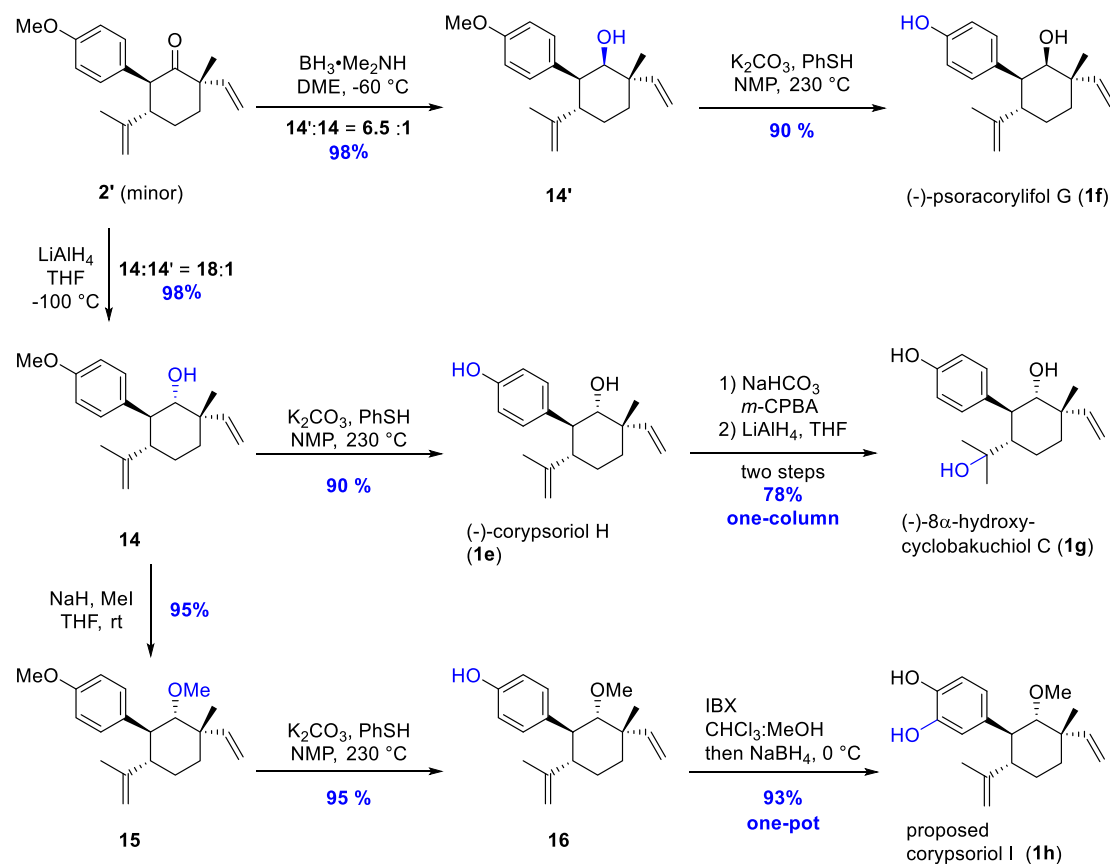
Position	Natural 7 β ,8 α -hydroxy-12 β -psoracorylifol F ^{a,10}	Synthetic 7 β ,8 α -hydroxy-12 β -psoracorylifol F ^b	$\Delta\delta$ (ppm)
1	133.7	133.7	0.0
2,6	130.6	130.6	0.0
3,5	115.8	115.8	0.0
4	156.5	156.6	-0.1
7	51.7	51.7	0.0
8	81.6	81.6	0.0
9	43.0	43.1	-0.1
10	36.9	36.9	0.0
11	28.8	28.8	0.0
12	52.4	52.4	0.0
13	148.7	148.7	0.0
14	111.8	111.9	-0.1
15	19.8	19.8	0.0
16	142.8	142.8	0.0
17	113.9	113.9	0.0
18	28.9	28.9	0.0

^a NMR data measured at 125 MHz in acetone- d_6 ; ^b NMR data measured at 150 MHz in acetone- d_6 .

Comparison of ^{13}C NMR spectra of (-)-7 β ,8 α -hydroxy-12 β -psoracorylifol F (1d)



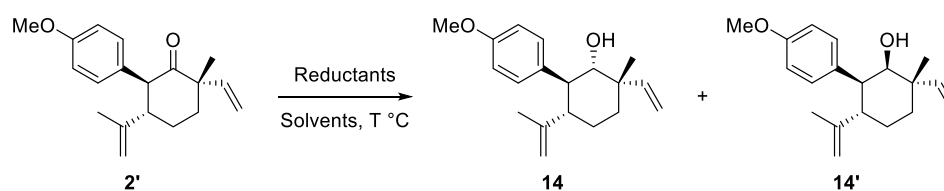
5. Collective total syntheses of 7 β -aryl-12 α -alkyl type meroterpenoids



Scheme S4 Collective total syntheses of 7 β -aryl-12 α -alkyl type meroterpenoids.

5.1 Synthesis of natural (-)-corypsoriol H (**1e**)

5.1.1 Synthesis of compounds **14** and **14'**



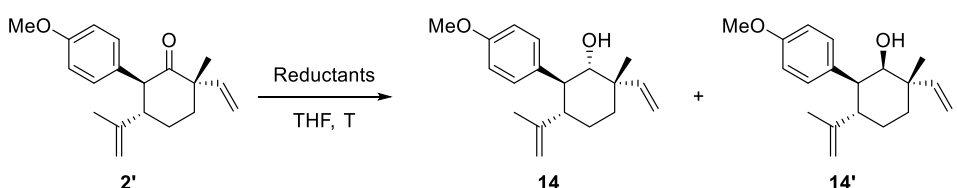
Method:

To a solution of the precursor **2'** (5.0 mg, 0.018 mmol) in THF (1.0 mL) was added reductants (0.09 mmol, 5.0 equiv.) under an argon atmosphere at the noted temperature, respectively, and the mixture was stirred. When the reaction completed (monitored by TLC), the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl , and was extracted with CH_2Cl_2 (3 \times 20 mL). The combined organic phase was washed with brine, dried over Na_2SO_4 , and filtered. The filtrate was concentrated under reduced pressure, and the dr value was measured by ^1H NMR (entries 1-24, Table S7 and entries 1-11, Table S8).

5.1.2 The optimization of the reduction of precursor 2'

5.1.2.1 The screening of reductants

Table S7. The screening of reductants^a



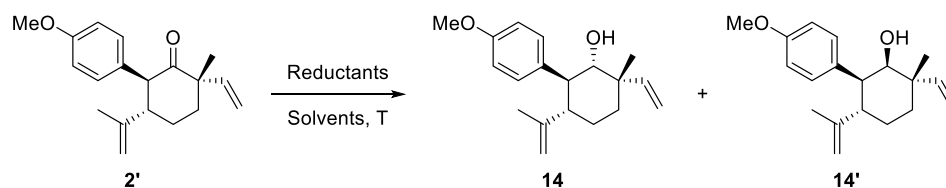
Entry	Reductants	Solvents	Temp.	dr (14:14')	Yield ^b
1	BH ₃	THF	rt	--	Decompose
2	BH ₃ ·Me ₂ S	THF	-70 °C	1:1	38%
3	BH ₃ ·Me ₂ S	THF	80 °C	--	ND
4	BH₃·Me₂NH	THF	-70 °C	1:4	97%
5	BH ₃ ·Me ₂ NH	THF	80 °C	1:3.6	92%
6	BH ₃ ·Pyr	THF	rt	1.5:1	38%
7	NaBH ₄	THF	-70 °C	2.7:1	92%
8	NaBH ₄	THF	80 °C	2:1	95%
9	LiBH ₄	THF	rt	3:1	94%
10	ZnBH ₄	THF	rt	1.5:1	95%
11	9-BBN	THF	-70 °C to rt	--	NR
12	9-BBN	THF	80 °C	--	ND
13	Red-Al	THF	-70 °C to rt	1:1	50%
14	Red-Al	THF	80 °C	1.4:1	85%
15	DIBAL-H	THF	-70 °C to rt	--	NR
16	DIBAL-H	THF	80 °C	1:2	90%
17	Al(O ⁱ Pr) ₃	THF	rt	--	NR
18	LiAlH₄	THF	-70 °C	12.5:1	96%
19	LiAlH ₄	THF	80 °C	7.9:1	95%
20	<i>L</i> -Selectride	THF	-70 °C to rt	--	NR
21	<i>L</i> -Selectride	THF	80 °C	1:3	trace
22	<i>K</i> -Selectride	THF	-70 °C to rt	--	NR
23	<i>K</i> -Selectride	THF	80 °C	--	ND
24	(<i>R</i>)-CBS, BH ₃	THF	-40 °C	--	ND

^aThe reactions were performed using precursor **2'** (0.018 mmol), reductants (5.0 equiv.) in 1.0 mL THF;

^bIsolated yield. NR = No reaction; ND = No detected; 9-BBN = 9-Borabicyclo[3.3.1]nonane; Red-Al = Sodium bis(2-methoxyethoxy)aluminiumhydride; DIBAL-H = Diisobutylaluminium hydride; *L*-Selectride = Lithium triisobutylhydroborate; *K*-Selectride = Potassium *tri*-*sec*-butylborohydride;

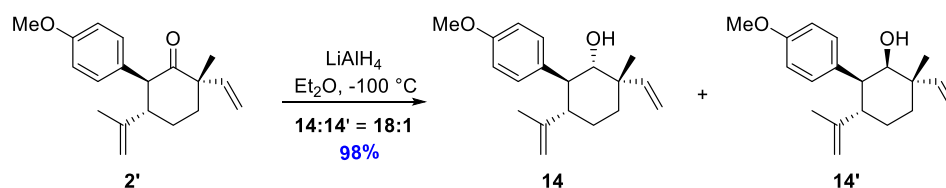
5.1.2.2 The screening of solvents and temperature

Table S8. The screening of solvents and temperature^a



Entry	Reductants	Solvents	Temp.	dr (14 : 14')	Yield ^b
1	BH ₃ ·Me ₂ NH	Et ₂ O	rt	1:4	93%
2	BH ₃ ·Me ₂ NH	1,4-dioxane	rt	1:5	90%
3	BH ₃ ·Me ₂ NH	DME	rt	1:6.6	97%
4	BH ₃ ·Me ₂ NH	MTBE	rt	1:4	95%
5	BH ₃ ·Me ₂ NH	Toluene	rt	1:4.5	92%
6	BH ₃ ·Me ₂ NH	DCM	rt	1:5	90%
7	BH ₃ · <i>i</i> Pr ₂ NH	DME	rt	1:6	90%
8	BH ₃ ·Me ₂ NH	DME	90 °C	1:4	95%
9	BH₃·Me₂NH	DME	-60 °C	1:6.5	98%
10	LiAlH₄	THF	-100 °C	18:1	98%
11	LiAlH₄	Et₂O	-100 °C	18:1	98%

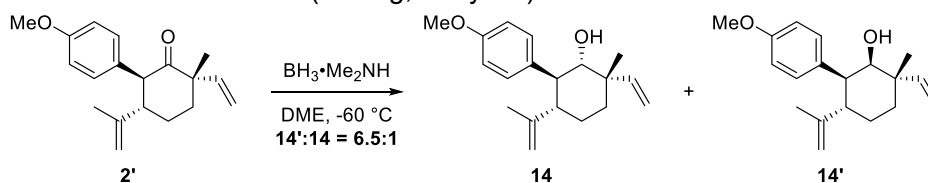
^aThe reactions were performed using the precursor **2'** (0.018 mmol), Reductants (5.0 equiv.) in 1.0 mL solvent; ^bIsolated yield; rt = Room temperature; THF = Tetrahydrofuran; MTBE = *tert*-Butyl methyl ether, DCM = Dichloromethane; DME = 1,2-dimethoxyethane.



Method I (entry 10, Table S8):

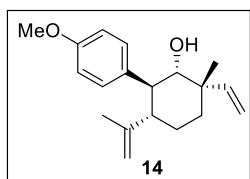
To a solution of the precursor **2'** (5.0 mg, 0.018 mmol) in THF (1.0 mL) was added LiAlH₄ (3.4 mg, 0.09 mmol) under an argon atmosphere at -100 °C, and the mixture was stirred for 1 h. When the reaction completed (monitored by TLC), the reaction mixture was quenched with a saturated aqueous solution of NH₄Cl, and was extracted with CH₂Cl₂ (3×20 mL). The combined organic phase was washed with brine, dried over Na₂SO₄, and filtered. The filtrate was concentrated under reduced pressure, and the resulting crude product **14** and **14'** (dr = 18:1) was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate (50:1)) to give the desired product **14** (4.7 mg, 94% yield) as

a white solid and its isomer **14'** (0.2 mg, 4% yield).



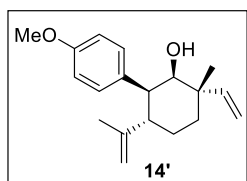
Method II (entry 9, Table S8):

To a solution of the precursor **2'** (5.0 mg, 0.018 mmol) in DME (1.0 mL) was added $\text{BH}_3 \cdot \text{Me}_2\text{NH}$ (5.3 mg, 0.09 mmol) under an argon atmosphere at $-60\text{ }^\circ\text{C}$, and the mixture was stirred for 48 h. When the reaction completed (monitored by TLC), the reaction mixture was quenched with a saturated aqueous solution of NH_4Cl , and was extracted with CH_2Cl_2 ($3 \times 20\text{ mL}$). The combined organic phase was washed with brine, dried over Na_2SO_4 , and filtered. The filtrate was concentrated under reduced pressure, and the resulting crude product **14'** and **14** (dr = 6.5:1) was purified by flash column chromatography (silica gel, petroleum ether/ethyl acetate (50:1)) to give the desired product **14'** (4.25 mg, 85% yield) as a white solid and its isomer **14** (0.65 mg, 13% yield).



Compound 14: Colorless needles; $[\alpha]_D^{25} = -32.0$ ($c = 0.5$ in MeOH);
m.p.: 59-62 $^\circ\text{C}$.

$^1\text{H NMR}$ (600 MHz, CDCl_3) δ : 7.09 (d, $J = 7.2$ Hz, 2H), 6.83 (d, $J = 8.4$ Hz, 2H), 6.30 (dd, $J = 18.0, 10.8$ Hz, 1H), 5.26 (dd, $J = 11.4, 1.2$ Hz, 1H), 5.19 (dd, $J = 17.4, 1.2$ Hz, 1H), 4.51 (brs, 1H), 4.50 (brs, 1H), 3.78 (s, 3H), 3.40 (d, $J = 10.8$ Hz, 1H), 2.60 (t, $J = 11.4$ Hz, 1H), 2.39 (td, $J = 12.0, 3.6$ Hz, 1H), 1.92-1.88 (m, 1H), 1.81-1.74 (m, 1H), 1.55-1.48 (m, 2H), 1.49 (s, 3H), 1.18 (s, 3H); **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ : 158.2, 147.1, 140.6, 132.7, 129.4, 114.5, 113.9, 111.6, 81.2, 55.1, 51.2, 50.5, 41.7, 36.6, 27.7, 27.4, 19.4. **HRMS** (ESI) m/z found 309.1826, calculated for $\text{C}_{18}\text{H}_{24}\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$ 309.1825. **MS** (EI) m/z (%): 286 (26), 150 (65), 121 (100), 91 (12), 81 (10), 68 (15), 57 (14). **IR** (KBr plate) ν_{max} : 3532, 2928, 2892, 2851, 1637, 1611, 1511, 1446, 1243, 1182, 1012, 918, 892, 829, 812, 568 cm^{-1} .

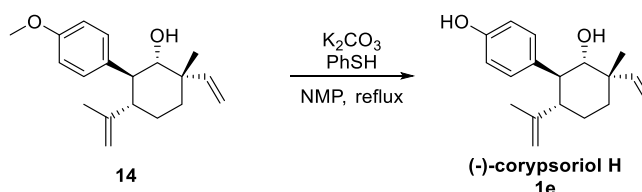


Compound 14': Colorless needles; $[\alpha]_D^{25} = -5.6$ ($c = 0.5$ in MeOH);
m.p.: 86-88 $^\circ\text{C}$.

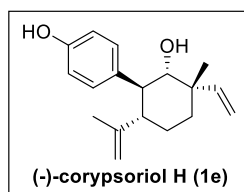
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ : 7.11 (d, $J = 8.8$ Hz, 2H), 6.83 (d, $J = 8.8$ Hz, 2H), 5.95 (dd, $J = 17.6, 11.2$ Hz, 1H), 5.20 (dd, $J = 10.8, 0.8$ Hz, 1H), 5.15 (dd, $J = 18.0, 1.2$ Hz, 1H), 4.67 (brs, 1H), 4.60 (brs, 1H), 3.78 (s, 3H), 3.46 (brs, 1H), 2.97 (dd, $J = 12.0, 1.6$ Hz, 1H), 2.86 (td, $J = 11.6, 3.6$ Hz, 1H), 1.86-1.78 (m, 1H), 1.74-1.66 (m, 1H), 1.64-1.56 (m, 2H), 1.49 (s, 3H), 1.07 (s, 3H); **$^{13}\text{C NMR}$** (100 MHz, CDCl_3)

δ : 158.0, 148.1, 144.9, 134.5, 129.5, 113.7, 113.2, 111.8, 78.7, 55.1, 46.5, 41.6, 41.4, 30.5, 28.5, 27.0, 19.1. **HRMS** (ESI) m/z found 309.1824, calculated for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 309.1825. **MS** (EI) m/z (%): 286 (19), 150 (62), 137 (18), 121 (100), 68 (12), 55 (7). **IR** (KBr plate) ν_{max} : 3569, 2929, 2861, 2835, 1610, 1511, 1457, 1245, 1177, 1037, 913, 886, 840, 819 cm^{-1} .

5.1.2 Synthesis of natural (-)-corypsoriol H (1e)



To a suspension solution of alcohol **14** (28.6 mg, 0.1 mmol) and K_2CO_3 (5.5 mg, 0.04 mmol) in NMP (1.0 mL) was added PhSH (52.0 μ L, 0.5 mmol). The mixture was stirred under reflux for 14 h, cooled to room temperature, and quenched with H_2O . The resulting mixture was extracted with ethyl acetate (3 \times 20 mL). The combined extracts were washed with brine, dried over Na_2SO_4 , and concentrated. The crude residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give (-)-corypsoriol H (**1e**) (24.5 mg, 90% yield) as a colorless solid.

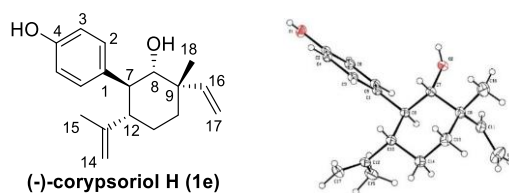


(-)-corypsoriol H (1e): Colorless needles; $[\alpha]_D^{25} = -32.0$ ($c = 0.1$ in MeOH), $[lit^{12}, [\alpha]_D^{25} = -120$ ($c = 0.1$ in MeOH)]. **m.p.**: 151-153 $^{\circ}C$.

1H NMR (600 MHz, methanol- d_4) δ : 7.01 (d, $J = 8.4$ Hz, 2H), 6.69 (d, $J = 9.0$ Hz, 2H), 6.30 (dd, $J = 17.4, 10.8$ Hz, 1H), 5.24 (d, $J = 12.0$ Hz, 1H), 5.18 (d, $J = 18.0$ Hz, 1H), 4.49 (brs, 1H), 4.46 (brs, 1H),

3.43 (d, $J = 10.2$ Hz, 1H), 2.58 (t, $J = 10.8$ Hz, 1H), 2.39 (td, $J = 12.6, 4.2$ Hz, 1H), 1.93 (dt, $J = 13.8, 3.0$ Hz, 1H), 1.84-1.77 (m, 1H), 1.55 (td, $J = 13.8, 4.2$ Hz, 1H), 1.48 (s, 3H), 1.46-1.43 (m, 1H), 1.15 (s, 3H); **^{13}C NMR** (150 MHz, methanol- d_4) δ : 156.7, 149.0, 142.5, 134.5, 130.8, 116.0, 114.8, 112.2, 82.4, 53.6, 51.9, 43.6, 37.9, 29.1, 28.7, 20.0. **HRMS** (ESI) m/z found 295.1670, calculated for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 295.1669. **MS** (EI) m/z (%): 272 (22), 149 (39), 136 (100), 107 (98), 84 (90), 55 (50). **IR** (KBr plate) ν_{max} : 3433, 3243, 2960, 2927, 1644, 1614, 1513, 1449, 1370, 1231, 1037, 915, 887, 818, 733 cm^{-1} .

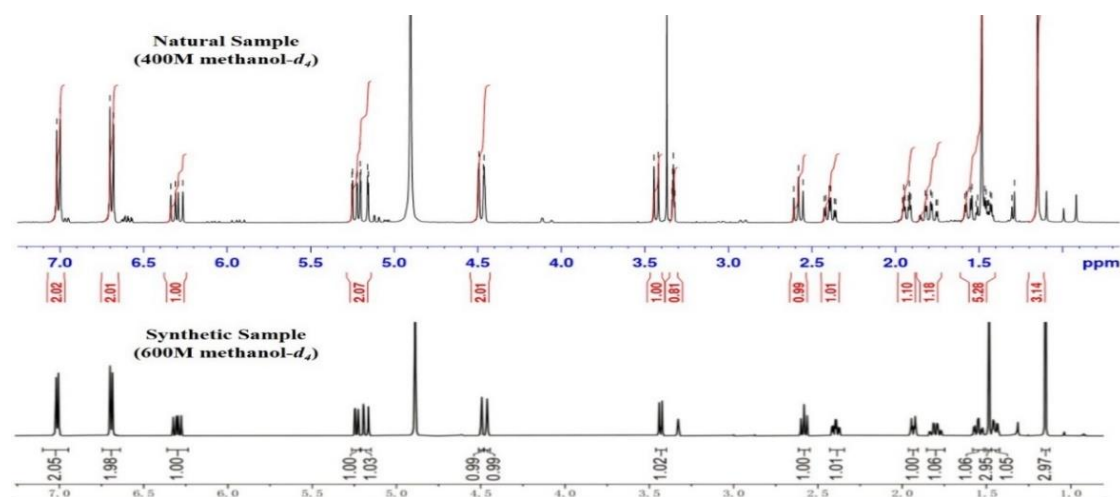
Comparison of ¹H NMR data for synthetic and natural (-)-corypsoriol H (1e)



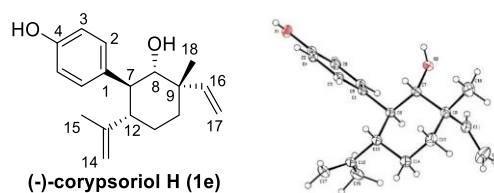
Position	Natural corypsoriol H ^{a,12}	Synthetic corypsoriol H ^b	Δδ (ppm)
1	-	-	-
2,6	7.01, d (<i>J</i> = 8.5 Hz)	7.01, d (<i>J</i> = 8.4 Hz)	0.00
3,5	6.68, d (<i>J</i> = 8.5 Hz)	6.69, d (<i>J</i> = 8.4 Hz)	-0.01
4	-	-	-
7	2.58, t (<i>J</i> = 10.6 Hz)	2.58, t (<i>J</i> = 10.8 Hz)	0.00
8	3.43, d (<i>J</i> = 10.6 Hz)	3.43, d (<i>J</i> = 10.2 Hz)	0.00
9	-	-	-
10	1.55, td (<i>J</i> = 13.5, 3.4 Hz)	1.55, td (13.8, 4.2 Hz)	0.00
	1.94, dt (<i>J</i> = 13.5, 3.4 Hz)	1.93, dt (13.8, 3.0 Hz)	0.01
11	1.80, m	1.84-1.77, m (1.81, m)	-0.01
	1.44, m	1.47-1.43, m (1.45, m)	-0.01
12	2.39, td (<i>J</i> = 12.0, 3.8 Hz)	2.39, td (<i>J</i> = 12.6, 4.2 Hz)	0.00
13	-	-	-
14	4.50, brs	4.49, brs	0.01
	4.46, brs	4.46, brs	0.00
15	1.49, s	1.48, s	0.01
16	6.30, dd (<i>J</i> = 17.9, 11.0 Hz)	6.30, dd (<i>J</i> = 17.4, 10.8 Hz)	0.00
17	5.24, d (<i>J</i> = 11.0 Hz)	5.24, d (<i>J</i> = 12.0 Hz)	0.00
	5.18, d (<i>J</i> = 17.9 Hz)	5.18, d (<i>J</i> = 18.0 Hz)	0.00
18	1.15, s	1.15, s	0.00

^a NMR data measured at 400 MHz in methanol-*d*₄; ^b NMR data measured at 600 MHz in methanol-*d*₄.

Comparison of ¹H NMR data for synthetic and natural (-)-corypsoriol H (1e)



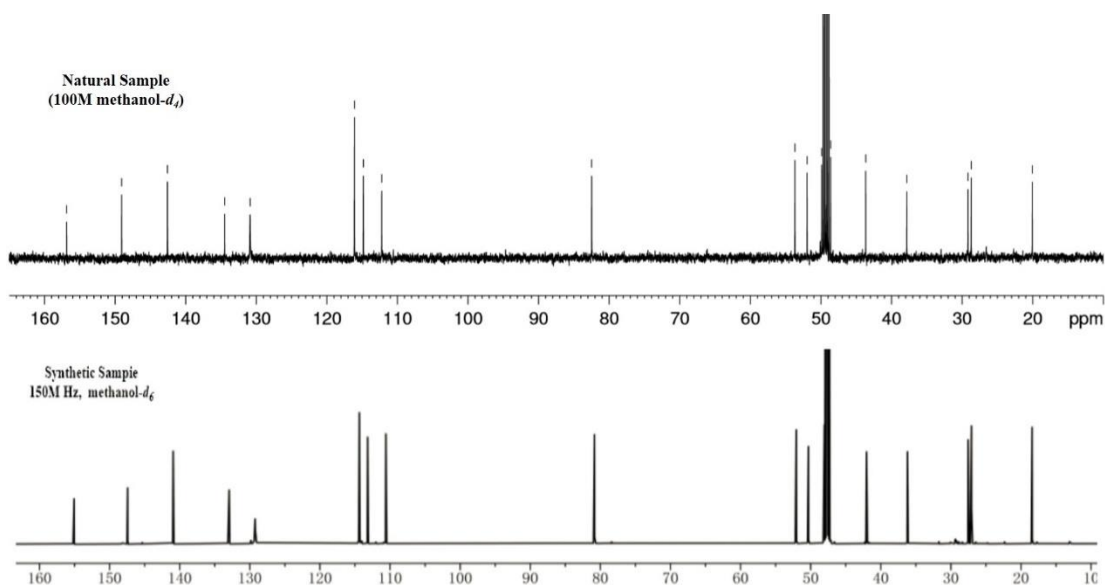
Comparison of ^{13}C NMR data for synthetic and natural (-)-corypsoriol H (1e)



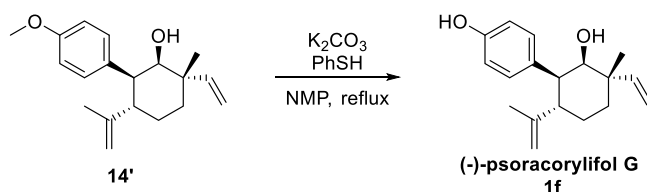
Position	Natural corypsoriol H ^{a,12}	Synthetic corypsoriol H ^b	$\Delta\delta$ (ppm)
1	134.5	134.5	0.0
2	130.9	130.8	0.1
3	116.1	116.0	0.1
4	156.9	156.7	0.2
5	116.1	116.0	0.1
6	130.9	130.8	0.1
7	53.7	53.6	0.1
8	82.5	82.4	0.1
9	43.7	43.6	0.1
10	37.9	37.9	0.0
11	28.7	28.7	0.0
12	52.0	51.9	0.1
13	149.0	149.0	0.0
14	112.2	112.2	0.0
15	20.0	20.0	0.0
16	142.6	142.5	0.1
17	114.8	114.8	0.0
18	29.2	29.1	0.1

^a NMR data measured at 100 MHz in methanol- d_4 ; ^b NMR data measured at 150 MHz in methanol- d_4 .

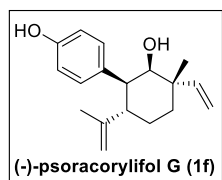
Comparison of ^{13}C NMR data for synthetic and natural (-)-corypsoriol H (1e)



5.2. Synthesis of natural (-)-psoracorylifol G (1f)



To a suspension solution of alcohol **14'** (19.4 mg, 0.068 mmol) and K_2CO_3 (3.8 mg, 0.027 mmol) in NMP (1.0 mL) was added PhSH (35.0 μ L, 0.34 mmol). The mixture was stirred under reflux for 14 h, cooled to room temperature, and quenched with H_2O . The resulting mixture was extracted with ethyl acetate (3x20 mL). The combined extracts were washed with brine, dried over Na_2SO_4 , and concentrated. The crude residue was purified by flash column chromatography on silica gel (hexane/ ethyl acetate) to furnish (-)-psoracorylifol G (**1f**) (16.6 mg, 90% yield).

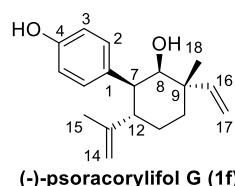


(-)-psoracorylifol G (1f): Colorless needles; $[\alpha]_D^{25} = -4.7$ ($c = 0.1$ in MeOH), [lit¹³, $[\alpha]_D^{25} = -20.0$ ($c = 0.1$ in MeOH)]. **m.p.**: 129-131 °C.

¹H NMR (600 MHz, $CDCl_3$) δ : 7.05 (d, $J = 7.8$ Hz, 2H), 6.74 (d, $J = 7.2$ Hz, 2H), 5.94 (dd, $J = 18.0, 11.4$ Hz, 1H), 5.20 (d, $J = 10.8$ Hz, 1H),

5.15 (d, $J = 18.0$ Hz, 1H), 5.07 (brs, 1H), 4.66 (brs, 1H), 4.59 (brs, 1H), 3.47 (brs, 1H), 2.95 (d, $J = 12.6$ Hz, 1H), 2.83 (td, $J = 10.8$ Hz, 1H), 1.80 (t, $J = 13.2$ Hz, 1H), 1.70-1.56 (m, 4H), 1.48 (s, 3H), 1.07 (s, 3H); **¹³C NMR** (150 MHz, $CDCl_3$) δ : 154.0, 148.0, 144.9, 134.5, 129.7, 115.2, 113.3, 111.9, 78.8, 46.4, 41.6, 41.4, 30.5, 28.5, 27.1, 19.0. **HRMS** (ESI) m/z found 295.1670, calculated for $C_{18}H_{24}O_2Na$ $[M+Na]^+$ 295.1669. **MS** (EI) m/z (%): 272 (21), 136 (90), 123 (21), 107 (100), 81 (13), 68 (18), 55 (12). **IR** (KBr plate) ν_{max} : 3393, 2963, 2929, 2863, 1642, 1613, 1514, 1452, 1373, 1230, 1173, 1018, 914, 888, 818 cm^{-1} .

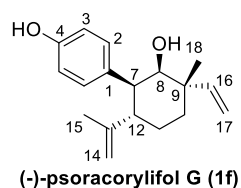
Comparison of ¹H NMR data of synthetic and natural (-)-psoracorylifol G (1f)



Position	Natural psoracorylifol G ^{a,13}	Synthetic psoracorylifol G ^b	Δδ (ppm)
2	7.06, d (<i>J</i> = 8.5 Hz)	7.05, d (<i>J</i> = 7.8 Hz)	0.01
3	6.75, d (<i>J</i> = 8.5 Hz)	6.74, d (<i>J</i> = 7.2 Hz)	0.01
5	6.75, d (<i>J</i> = 8.5 Hz)	6.74, d (<i>J</i> = 7.2 Hz)	0.01
6	7.06, d (<i>J</i> = 8.5 Hz)	7.05, d (<i>J</i> = 7.8 Hz)	0.01
7	2.95, dd (<i>J</i> = 12.0, 1.9 Hz)	2.95, dd (<i>J</i> = 12.6 Hz)	0.00
8	3.47, d (<i>J</i> = 1.9 Hz)	3.47, brs	0.00
10	1.81, m	1.80, t, (<i>J</i> = 13.2 Hz)	0.01
	1.60, m	1.62-1.56, m (1.57, m)	0.03
11	1.69, td (<i>J</i> = 12.0, 4.0 Hz)	1.71-1.64, m (1.68, m)	0.01
	1.59, m	1.62-1.56, m (1.57, m)	0.02
12	2.84, td (<i>J</i> = 12.0, 4.0 Hz)	2.83, td (<i>J</i> = 10.8, 4.2 Hz)	0.01
14	4.66, brs	4.66, brs	-0.01
	4.59, brs	4.59, brs	0.00
15	1.48, s	1.48, s	0.00
16	5.95, dd (<i>J</i> = 17.7, 11.1 Hz)	5.94, dd (<i>J</i> = 18.0, 11.4 Hz)	0.01
17	5.19, dd (<i>J</i> = 11.1, 1.0 Hz)	5.20, d (<i>J</i> = 10.8 Hz)	0.01
	5.15, dd (<i>J</i> = 17.7, 1.0 Hz)	5.15, d (<i>J</i> = 18.0 Hz)	0.00
18	1.07, s	1.07, s	0.00
8-OH	4.78, brs		

^a NMR data measured at 400 MHz in CDCl₃; ^b NMR data measured at 600 MHz in CDCl₃.

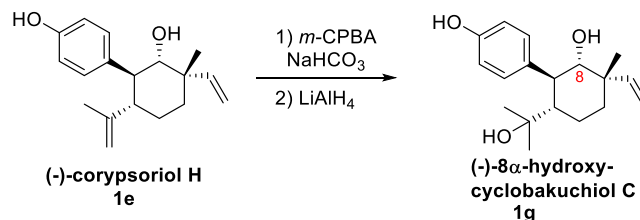
Comparison of ^{13}C NMR data of synthetic and natural (-)-psoracorylifol G (1f)



Position	Natural psoracorylifol G ^{a,13}	Synthetic psoracorylifol G ^b	$\Delta\delta$ (ppm)
1	134.7	134.5	0.2
2	129.8	129.7	0.1
3	115.2	115.2	0.0
4	153.9	154.0	-0.1
5	115.2	115.2	0.0
6	129.8	129.7	0.1
7	46.5	46.4	0.1
8	78.7	78.8	-0.1
9	41.4	41.4	0.0
10	30.5	30.5	0.0
11	28.5	28.5	0.0
12	41.7	41.6	0.1
13	148.0	148.0	0.0
14	111.8	111.9	-0.1
15	19.0	19.0	0.0
16	144.9	144.9	0.0
17	113.3	113.3	0.0
18	27.0	27.1	-0.1

^a NMR data measured at 100 MHz in CDCl_3 ; ^b NMR data measured at 150 MHz in CDCl_3 .

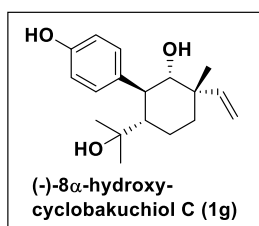
5.3 Synthesis of natural (-)-8 α -hydroxy-cyclobakuchiol C (1g)



To an ice-cold suspension of NaHCO_3 (21.0 mg, 0.25 mmol) and *m*-CPBA (16.1 mg, 80%, 0.75 mmol) in CH_2Cl_2 (1.0 mL) was added a solution of (-)-corypsoriol H (**1e**, 13.6 mg, 0.05 mmol) in CH_2Cl_2 (1.0 mL) at 0 °C. The mixture was stirred at 5 °C for about 4 h. When the

starting material disappeared, the reaction was quenched by addition of Me₂S (5.3 μL, 0.07 mmol) and saturated NaHCO₃ with vigorous stirring. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3×20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated to give a residue, which was used for the next step.

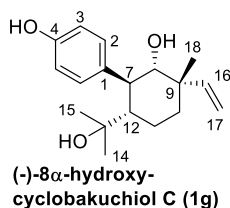
To an ice-cold solution of above oxirane in THF (2.0 mL) was added slowly LiAlH₄ (9.5 mg, 0.25 mmol) at 0 °C. The resulting mixture was stirred for 3 h under reflux. After reaction completion, the mixture was cooled to room temperature, quenched by addition of aqueous HCl (1.0 mol/L), and then extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with saturated NaHCO₃ and brine, dried over Na₂SO₄, and concentrated. The residual oil was purified by flash column chromatography on silica gel (hexane/ethyl acetate) to give (-)-8α-hydroxy-cyclobakuchiol C (**1g**) (11.3 mg, 78% yield from natural (-)-corypsoriol H (**1e**)).



(-)-8α-hydroxy-cyclobakuchiol C (1g**):** Colorless needles; $[\alpha]_D^{25} = -33.4$ (c = 0.1 in MeOH), [lit¹⁰, $[\alpha]_D^{25} = -18.5$ (c = 0.1 in MeOH)].
m.p.: 123-125 °C.

¹H NMR (600 MHz, acetone-*d*₆) δ: 8.16 (s, 1H), 7.08 (brs, 2H), 6.74 (d, *J* = 7.8 Hz, 2H), 6.23 (dd *J* = 17.4, 10.8 Hz, 1H), 5.11 (dd, *J* = 10.8, 1.2 Hz, 1H), 5.09 (dd, *J* = 10.2, 1.8 Hz, 1H), 3.38 (dd, *J* = 10.2, 4.2 Hz, 1H), 2.48 (s, 1H), 2.46 (t, *J* = 10.8 Hz, 1H), 2.12 (s, 1H), 1.88-1.83 (m, 2H), 1.79-1.76 (m, 1H), 1.46-1.38 (m, 2H), 1.07 (s, 3H), 0.93 (s, 3H), 0.75 (s, 3H); **¹³C NMR** (150 MHz, acetone-*d*₆) δ: 156.8, 142.5, 134.7, 130.9, 116.1, 113.7, 82.1, 73.2, 53.3, 50.5, 42.4, 36.5, 29.3, 28.6, 27.5, 24.0. **HRMS** (ESI) *m/z* found 313.1775, calculated for C₁₈H₂₆O₃Na [M+Na]⁺ 313.1774. **MS** (EI) *m/z* (%): 290 (5), 272 (6), 214 (38), 161 (32), 133 (82), 107 (100), 59 (55). **IR** (KBr plate) ν_{\max} : 3546, 2956, 2930, 2868, 1616, 1543, 1513, 1455, 1383, 1256, 1227, 1172, 1010, 928, 907, 827 cm⁻¹.

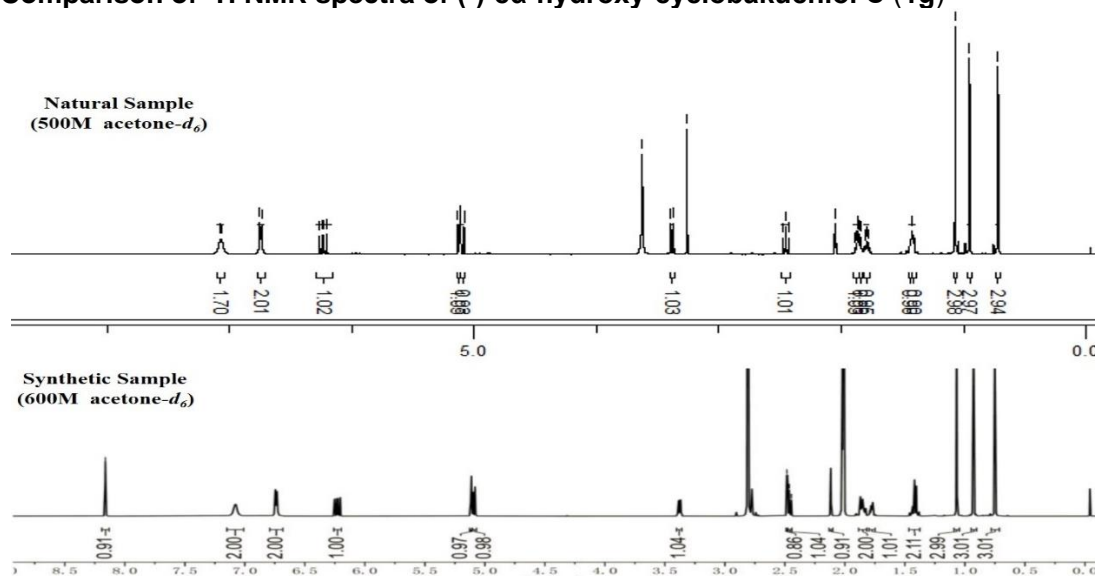
Comparison of ¹H NMR data of synthetic and natural (-)-8 α -hydroxy-cyclobakuchiol C (1g)



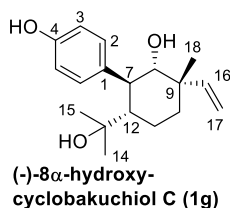
Position	Natural 8 α -hydroxy-cyclobakuchiol C ^{a,10}	Synthetic 8 α -hydroxy-cyclobakuchiol C ^b	$\Delta\delta$ (ppm)
1	-	-	-
2,6	7.07, d ($J = 5.5$ Hz)	7.08, d ($J = 6.6$ Hz)	-0.01
3,5	6.74, d ($J = 8.5$ Hz)	6.74, d ($J = 7.8$ Hz)	0.00
4	-	-	-
7	2.45, t ($J = 11.0$ Hz)	2.46, t ($J = 10.8$ Hz)	-0.01
8	3.38, d ($J = 10.0$ Hz)	3.38, dd ($J = 10.2, 4.2$ Hz)	0.00
9	-	-	-
10	1.89, m	1.88-1.83, m (1.86, m)	0.03
	1.43, m	1.46-1.38, m (1.42, m)	0.01
11	1.79, m	1.79-1.76, m (1.78, m)	0.01
	1.42, m	1.46-1.38, m (1.42, m)	0.00
12	1.89, m	1.85-1.83, m (1.84, m)	0.05
13	-	-	-
14	0.95, s	0.93, s	0.02
15	0.72, s	0.75, s	-0.03
16	6.23, dd ($J = 17.5, 11.5$ Hz)	6.23, dd ($J = 17.4, 10.8$ Hz)	0.00
17	5.13, dd ($J = 17.5, 1.5$ Hz)	5.11, dd ($J = 10.8, 1.2$ Hz)	0.02
	5.10, dd ($J = 11.5, 1.5$ Hz)	5.09, dd ($J = 10.2, 1.8$ Hz)	0.01
18	1.07, s	1.07, s	0.00

^a NMR data measured at 500 MHz in acetone- d_6 ; ^b NMR data measured at 600 MHz in acetone- d_6 .

Comparison of ¹H NMR spectra of (-)-8 α -hydroxy-cyclobakuchiol C (1g)



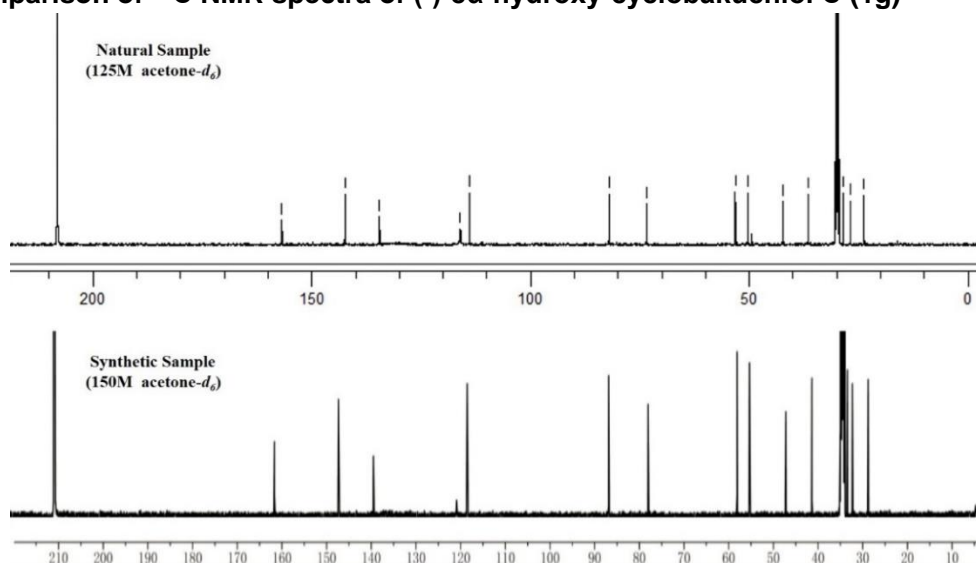
Comparison of ^{13}C NMR data of synthetic and natural (-)-8 α -hydroxy-cyclobakuchiol C (1g)



Position	Natural 8 α -hydroxy-cyclobakuchiol C ^{a,10}	Synthetic 8 α -hydroxy-cyclobakuchiol C ^b	$\Delta\delta$ (ppm)
1	134.5	134.7	-0.2
2	130.3	130.5	-0.2
3	116.1	116.1	0.0
4	156.8	156.8	0.0
5	116.1	116.1	0.0
6	130.3	130.9	-0.6
7	50.4	50.5	-0.1
8	82.1	82.1	0.0
9	42.4	42.4	0.0
10	36.6	36.5	0.1
11	23.8	24.0	-0.2
12	53.2	53.3	-0.1
13	73.5	73.2	0.3
14	26.9	27.5	-0.6
15	29.4	29.3	0.1
16	142.4	142.5	-0.1
17	114.0	113.7	0.3
18	28.6	28.6	0.0

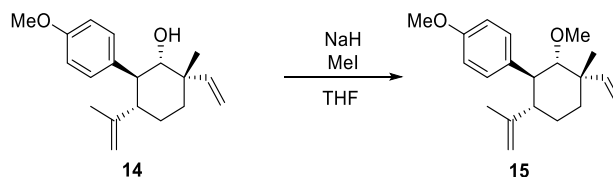
^a NMR data measured at 125 MHz in acetone- d_6 ; ^b NMR data measured at 150 MHz in acetone- d_6 .

Comparison of ^{13}C NMR spectra of (-)-8 α -hydroxy-cyclobakuchiol C (1g)

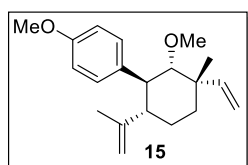


5.4. Synthesis of the proposed corypsoriol I (1h)

5.4.1 Synthesis of compound 15



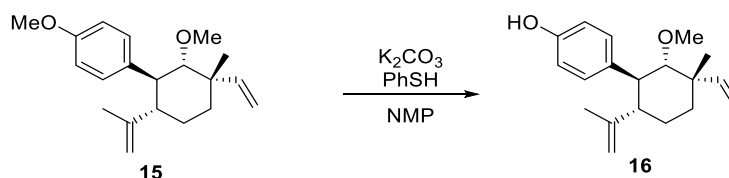
To a suspension solution of alcohol **14** (70.0 mg, 0.25 mmol) and NaH (39.2 mg, 60%, 0.98 mmol) in THF (2.0 mL) was added MeI (61.0 μ L, 0.98 mmol). The mixture was stirred at room temperature for 20 h, and quenched with H₂O. The resulting mixture was extracted with ethyl acetate (3 \times 20 mL). The combined organic phase was washed with brine, dried over Na₂SO₄, and filtered, and concentrated in vacuo. The crude residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10:1) on silica gel to give methylether **15** (71.3 mg, 95% yield) as a colorless oil.



Compound 15: Colorless oil; $[\alpha]_D^{25} = -61.4$ ($c = 0.5$ in MeOH).

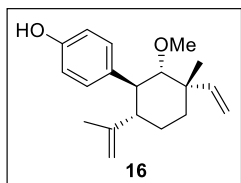
¹H NMR (400 MHz, CDCl₃) δ : 7.11 (d, $J = 8.4$ Hz, 2H), 6.80 (d, $J = 8.8$ Hz, 2H), 6.23 (dd, $J = 18.0, 11.2$ Hz, 1H), 5.21 (dd, $J = 11.2, 1.6$ Hz, 1H), 5.13 (dd, $J = 18.0, 1.6$ Hz, 1H), 4.54 (brs, 1H), 4.51 (brs, 1H), 3.78 (s, 3H), 2.83 (d, $J = 10.4$ Hz, 1H), 2.74 (s, 3H), 2.64 (t, $J = 11.6$ Hz, 1H), 2.45 (td, $J = 12.0, 3.6$ Hz, 1H), 1.91-1.87(m, 1H), 1.77-1.65 (m, 1H), 1.52-1.43 (m, 2H), 1.49 (s, 3H), 1.13 (s, 3H); **¹³C NMR** (100 MHz, CDCl₃) δ : 157.7, 147.2, 141.4, 134.1, 129.8, 113.8, 113.1, 111.7, 92.7, 61.4, 55.0, 51.0, 49.4, 43.1, 36.7, 27.8, 27.6, 19.2. **HRMS** (ESI) m/z found 323.1981, calculated for C₂₀H₂₈O₂Na [M+Na]⁺ 323.1982. **MS** (EI) m/z (%): 300 (21), 164 (100), 149 (31), 121 (80), 68 (22), 55 (24). **IR** (KBr plate) ν_{\max} : 3402, 3074, 2970, 2929, 2862, 2830, 1644, 1612, 1512, 1456, 1247, 1178, 1106, 1039, 912, 886, 818 cm⁻¹.

5.4.2 Synthesis of phenol 16



To a suspension solution of methylether **15** (42.0 mg, 0.14 mmol) and K₂CO₃ (7.7 mg, 0.056 mmol) in NMP (2.0 mL) was added PhSH (44.0 μ L, 0.42 mmol). The mixture was stirred under reflux for 14 h. The reaction was quenched by addition of HCl (1.0 mol/L) and extracted with ethyl acetate (3 \times 20 mL). The combined organic layers were washed with brine, dried (Na₂SO₄), and concentrated. The resulting crude product was purified by flash

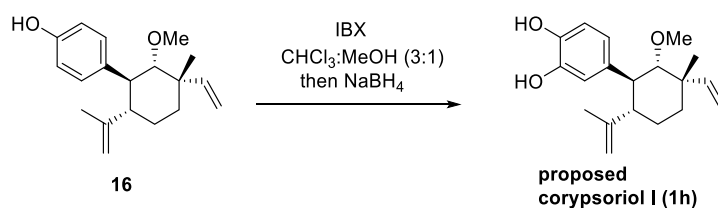
column chromatography on silica gel (hexane/ethyl acetate) to furnish phenol **16** (38.0 mg, 95% yield).



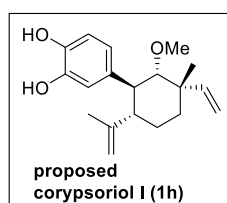
Compound 16: White solid; $[\alpha]_D^{21} = -56.7$ ($c = 0.1$ in MeOH); **m.p.:** 164.2-165.3 °C.

¹H NMR (400 MHz, CDCl₃) δ : 7.06 (d, $J = 8.0$ Hz, 2H), 6.72 (d, $J = 8.8$ Hz, 2H), 6.22 (dd, $J = 18.0, 11.2$ Hz, 1H), 5.20 (dd, $J = 11.2, 0.8$ Hz, 1H), 5.12 (dd, $J = 18.0, 1.2$ Hz, 1H), 4.82 (s, 1H), 4.54 (brs, 1H), 4.51 (brs, 1H), 2.84 (d, $J = 10.4$ Hz, 1H), 2.77 (s, 3H), 2.64 (t, $J = 11.6$ Hz, 1H), 2.43 (td, $J = 12.0, 4.0$ Hz, 1H), 1.90-1.85 (m, 1H), 1.77-1.65 (m, 1H), 1.51-1.43 (m, 2H), 1.49 (s, 3H), 1.13 (s, 3H); **¹³C NMR** (150 MHz, CDCl₃) δ : 153.7, 147.2, 141.3, 134.3, 130.0, 114.8, 113.9, 111.7, 92.8, 61.4, 51.1, 49.4, 43.1, 36.8, 27.8, 27.6, 19.2. **HRMS** (ESI) m/z found 309.1822, calculated for C₁₉H₂₆O₂Na [M+Na]⁺ 309.1825; **MS** (EI) m/z (%): 286 (9), 242 (6), 203 (6), 150 (100), 107 (56), 84 (40), 57 (37). **IR** (KBr plate) ν_{\max} : 3421, 3079, 2960, 2925, 2853, 1712, 1616, 1516, 1454, 1374, 1223, 1101, 1016, 910, 886, 800 cm⁻¹.

5.4.3 Synthesis of the proposed corypsorior I (1h)



To a solution of phenol **16** (18.0 mg, 0.06 mmol) in CHCl₃/MeOH (1.2 mL) (3:1 v/v) was added IBX (20.0 mg, 0.07 mmol) at 0 °C under an argon atmosphere. A yellow-to-orange color developed and the mixture was stirred for 2 h, then NaBH₄ (21.0 mg, 0.54 mmol) was added at 0 °C under vigorous stirring until the color disappeared (usually within 30 min).¹¹ The reaction was quenched by addition of HCl (1.0 mol/L) and extracted with ethyl acetate (3x20 mL). The combined extracts were washed with brine, dried over Na₂SO₄, and filtered. The filtrate was concentrated under reduced pressure, and the residue was subjected to column chromatography on silica gel using ethyl acetate-petroleum ether (1:1) to give the proposed corypsorior I (**1h**) (16.9 mg, 93% yield).

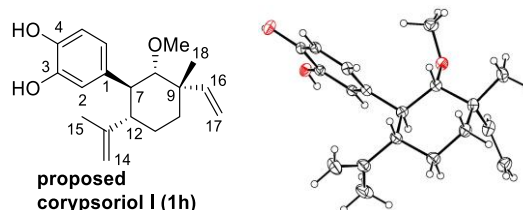


Proposed corypsorior I (1h): White solid; $[\alpha]_D^{25} = -50.0$ ($c = 0.1$ in MeOH), $[\text{lit}^{12}, [\alpha]_D^{25} = -60.0$ ($c = 0.1$ in MeOH)]. **m.p.:** 175-177 °C.

¹H NMR (600 MHz, methanol-*d*₄) δ : 6.65 (d, $J = 8.4$ Hz, 2H), 6.53 (brs, 1H), 6.19 (dd, $J = 18.0, 11.4$ Hz, 1H), 5.17 (dd, $J = 10.8, 1.2$ Hz, 1H), 5.12 (dd, $J = 18.0, 1.2$ Hz, 1H), 4.52 (brs, 1H), 4.48 (brs, 1H), 2.95 (d, $J = 10.2$ Hz, 1H), 2.82 (s, 3H), 2.51 (t, $J = 11.4$ Hz, 1H), 2.44 (td, $J = 12.0, 4.2$ Hz, 1H),

1.89 (dt, $J = 13.8, 3.0$ Hz, 1H), 1.75-1.68 (m, 1H), 1.54-1.49 (m, 1H), 1.48 (s, 3H), 1.43-1.39 (m, 1H), 1.11 (s, 3H); $^{13}\text{C NMR}$ (150 MHz, methanol- d_4) δ : 148.6, 145.7, 144.4, 142.9, 135.0, 115.8, 114.2, 112.2, 94.0, 61.8, 52.6, 51.2, 44.3, 37.5, 28.9, 28.6, 19.6. **HRMS** (ESI) m/z found 325.1773, calculated for $\text{C}_{19}\text{H}_{26}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$ 325.1774. **MS** (EI) m/z (%): 302 (19), 257 (9), 202 (10), 166 (100), 123 (37), 68 (18), 55 (17). **IR** (KBr plate) ν_{max} : 3368, 2931, 2864, 2829, 1641, 1605, 1518, 1443, 1375, 1278, 1190, 1104, 911, 888, 810 cm^{-1} .

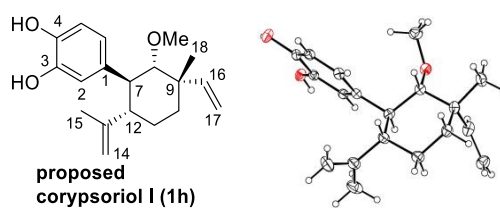
Comparison of $^1\text{H NMR}$ data of synthetic and natural corypsorior I (1h)



Position	Natural corypsorior I ^{a,12}	Synthetic corypsorior I ^b	$\Delta\delta$ (ppm)
1	-	-	-
2	6.64 (d, $J = 2.0$ Hz)	6.64 (d, $J = 8.4$ Hz)	0.00
3	-	-	-
4	-	-	-
5	6.62 (d, $J = 8.0$ Hz)	6.64 (d, $J = 8.4$ Hz)	-0.02
6	6.52 (dd, $J = 8.0, 2.0$ Hz)	6.53 (d, $J = 7.2$ Hz)	-0.01
7	2.12 (t, $J = 9.2$ Hz)	2.51 (t, $J = 11.4$ Hz)	-0.39
8	3.84 (d, $J = 9.6$ Hz)	2.95 (d, $J = 10.4$ Hz)	0.99
9	-	-	-
10 $_{\alpha}$	1.34, m	1.89 (dt, $J = 13.8, 3.0$ Hz)	-0.55
10 $_{\beta}$	1.77, m	1.54-1.49, m (1.52, m)	0.25
11 $_{\alpha}$	1.92, m	1.75-1.68, m (1.72, m)	-0.20
11 $_{\beta}$	1.34, o ^c	1.43-1.39, m (1.41, m)	-0.07
12	2.36 (td, $J = 9.7, 4.1$)	2.44 (td, $J = 12.0, 4.2$ Hz)	-0.08
13	-	-	-
14	4.14, brs	4.52, brs	-0.38
	4.09, brs	4.48, brs	-0.39
15	1.37, s	1.48, s	-0.11
16	6.16 (dd, $J = 17.8, 10.8$ Hz)	6.19 (dd, $J = 18.0, 11.4$ Hz)	-0.03
17 $_{\alpha}$	4.79 (dd, $J = 10.8, 1.2$ Hz)	5.12 (dd, $J = 10.8, 1.2$ Hz)	-0.33
17 $_{\beta}$	4.90 (dd, $J = 17.7, 1.2$ Hz)	5.17 (dd, $J = 18.0, 1.2$ Hz)	-0.27
18	1.14, s	1.11, s	0.03
8-OCH ₃	3.02, s	2.82, s	0.20

^a NMR data measured at 400 MHz in methanol- d_4 ; ^b NMR data measured at 600 MHz in methanol- d_4 ; ^c "o" means overlapped.

Comparison of ^{13}C NMR data of synthetic and natural (-)-corypsorior I (1h)



Position	Natural corypsorior I ^{a,12}	Synthetic corypsorior I ^b	$\Delta\delta$ (ppm)
1	134.0	135.0	-1.0
2	115.8	115.8	0.0
3	146.2	145.7	0.5
4	146.1	144.4	1.7
5	116.6	115.8	0.8
6	121.4	115.8	
7	58.2	51.2	7.0
8	87.8	94.0	-6.2
9	49.6	44.3	5.3
10	41.3	28.9	-12.4
11	31.5	37.5	-6.0
12	50.2	52.6	-2.4
13	149.4	148.6	0.8
14	110.3	112.2	-1.9
15	20.0	19.6	-0.4
16	151.6	142.9	8.7
17	109.1	114.2	-5.1
18	20.4	28.6	-8.2
8-OCH ₃	55.9	61.8	-5.9

^a NMR data measured at 100 MHz in methanol-*d*₄; ^b NMR data measured at 150 MHz in methanol-*d*₄.

6. X-Ray crystallography Data

6.1 X-Ray crystallography of compound **8**

The crystal of compound **8** for X-ray diffraction study was obtained through the dissolving of compound in ethyl acetate and petroleum ether, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

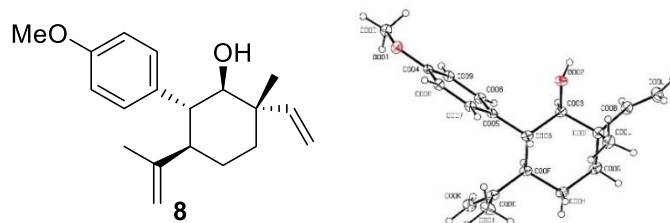


Figure S1. X-Ray coordinate of compound **8** (CCDC 2226753). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	Compound 8
Empirical formula	C ₁₉ H ₂₆ O ₂
Formula weight	286.40
Temperature/K	149.95(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.55997(12)
b/Å	14.3262(3)
c/Å	17.4645(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1641.30(6)
Z	4
ρ _{calc} /cm ³	1.159
μ/mm ⁻¹	0.569
F(000)	624.0
Crystal size/mm ³	0.13 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.982 to 154.694
Index ranges	-7 ≤ h ≤ 3, -17 ≤ k ≤ 18, -21 ≤ l ≤ 21
Reflections collected	5454
Independent reflections	2925 [R _{int} = 0.0741, R _{sigma} = 0.0814]
Data/restraints/parameters	2925/0/194
Goodness-of-fit on F ²	1.043
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0541, wR ₂ = 0.1472
Final R indexes [all data]	R ₁ = 0.0580, wR ₂ = 0.1513
Largest diff. peak/hole / e Å ⁻³	0.33/-0.32
Flack parameter	0.04(18)

6.2 X-Ray crystallography of natural (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (1b)

The crystal of natural (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (**1b**) for X-ray diffraction study was obtained through the dissolving of compound in ethyl acetate and petroleum ether, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

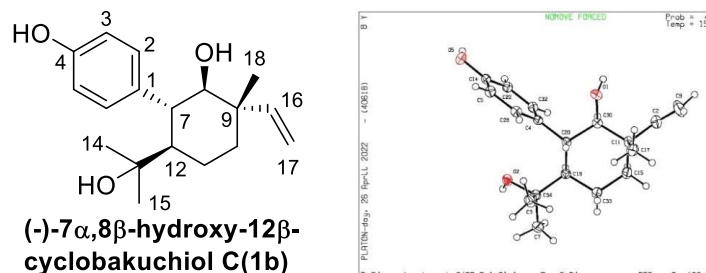


Figure S1. X-Ray coordinate of natural (-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (**1b**) (CCDC 2226760). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	(-)-7 α ,8 β -hydroxy-12 β -cyclobakuchiol C (1b)
Empirical formula	C ₃₇ H ₅₆ O ₇
Formula weight	612.81
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	15.3362(3)
b/Å	6.95130(12)
c/Å	16.3195(3)
α /°	90
β /°	101.0819(18)
γ /°	90
Volume/Å ³	1707.32(5)
Z	2
ρ calg/cm ³	1.192
μ /mm ⁻¹	0.643
F(000)	668.0
Crystal size/mm ³	0.14 × 0.13 × 0.12
Radiation	Cu K α (λ = 1.54184)
2 θ range for data collection/°	5.518 to 154.338
Index ranges	-19 ≤ h ≤ 19, -7 ≤ k ≤ 8, -20 ≤ l ≤ 20
Reflections collected	16825
Independent reflections	6125 [R _{int} = 0.0500, R _{sigma} = 0.0468]
Data/restraints/parameters	6125/1/445
Goodness-of-fit on F ²	1.060
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0401, wR ₂ = 0.1058
Final R indexes [all data]	R ₁ = 0.0421, wR ₂ = 0.1075
Largest diff. peak/hole / e Å ⁻³	0.22/-0.23
Flack parameter	0.22(13)

6.3 X-Ray crystallography of compound 11

The crystal of compound **11** for X-ray diffraction study was obtained through the dissolving of compound in petroleum ether and ethyl acetate, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

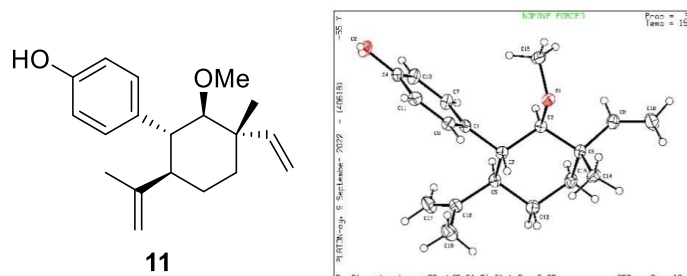


Figure S1. X-Ray coordinate of compound **11** (CCDC 2226754). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	Compound 11
Empirical formula	C ₁₉ H ₂₆ O ₂
Formula weight	286.40
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.1934(2)
b/Å	13.5942(4)
c/Å	20.6761(6)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1740.81(9)
Z	4
ρ _{calc} /cm ³	1.093
μ/mm ⁻¹	0.536
F(000)	624.0
Crystal size/mm ³	0.11 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.784 to 155.622
Index ranges	-5 ≤ h ≤ 7, -16 ≤ k ≤ 16, -24 ≤ l ≤ 26
Reflections collected	8246
Independent reflections	3406 [R _{int} = 0.0619, R _{sigma} = 0.0610]
Data/restraints/parameters	3406/0/194
Goodness-of-fit on F ²	1.103
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0519, wR ₂ = 0.1406
Final R indexes [all data]	R ₁ = 0.0615, wR ₂ = 0.1477
Largest diff. peak/hole / e Å ⁻³	0.26/-0.23
Flack parameter	-0.1(2)

6.4 X-Ray crystallography of compound **14**

The crystal of compound **14** for X-ray diffraction study was obtained through the dissolving of compound in petroleum ether and ethyl acetate, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

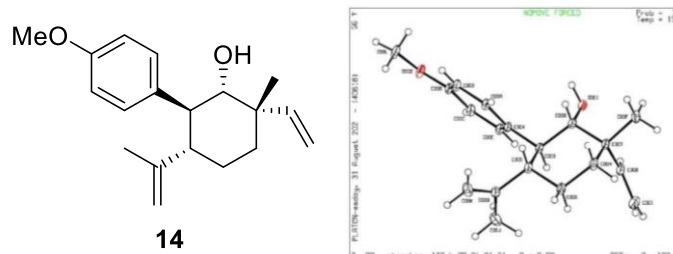


Figure S1. X-Ray coordinate of compound **14** (CCDC 2226756). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	Compound 14
Empirical formula	C ₁₉ H ₂₆ O ₂
Formula weight	286.40
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.02770(10)
b/Å	10.7851(2)
c/Å	25.2404(4)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	1640.86(5)
Z	4
ρ _{calc} /cm ³	1.159
μ/mm ⁻¹	0.569
F(000)	624.0
Crystal size/mm ³	0.16 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	7.004 to 154.842
Index ranges	-4 ≤ h ≤ 7, -13 ≤ k ≤ 13, -31 ≤ l ≤ 26
Reflections collected	8138
Independent reflections	3260 [R _{int} = 0.0874, R _{sigma} = 0.0730]
Data/restraints/parameters	3260/0/194
Goodness-of-fit on F ²	1.068
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0792, wR ₂ = 0.1914
Final R indexes [all data]	R ₁ = 0.0814, wR ₂ = 0.1933
Largest diff. peak/hole / e Å ⁻³	0.45/-0.52
Flack parameter	-0.1(2)

6.5 X-Ray crystallography of compound 14'

The crystal of compound **14'** for X-ray diffraction study was obtained through the dissolving of compound in petroleum ether and ethyl acetate, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

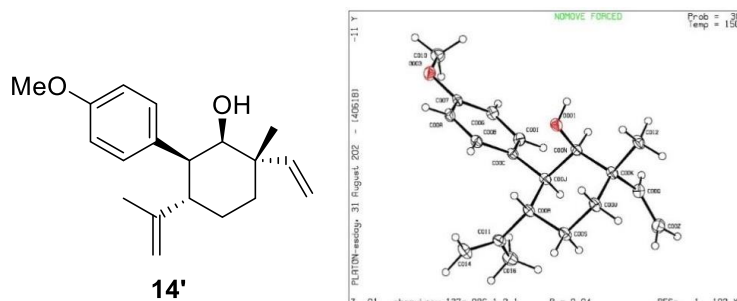


Figure S1. X-Ray coordinate of compound **14'** (CCDC 2226759). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	compound 14'
Empirical formula	C ₃₈ H ₅₂ O ₄
Formula weight	572.79
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2
a/Å	25.3714(5)
b/Å	6.05801(10)
c/Å	23.3168(5)
α/°	90
β/°	112.787(2)
γ/°	90
Volume/Å ³	3304.08(12)
Z	4
ρ _{calc} /cm ³	1.151
μ/mm ⁻¹	0.565
F(000)	1248.0
Crystal size/mm ³	0.25 × 0.16 × 0.15
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	4.11 to 154.916
Index ranges	-31 ≤ h ≤ 31, -6 ≤ k ≤ 7, -26 ≤ l ≤ 29
Reflections collected	19488
Independent reflections	6149 [R _{int} = 0.0678, R _{sigma} = 0.0565]
Data/restraints/parameters	6149/2/393
Goodness-of-fit on F ²	1.069
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0446, wR ₂ = 0.1146
Final R indexes [all data]	R ₁ = 0.0474, wR ₂ = 0.1169
Largest diff. peak/hole / e Å ⁻³	0.18/-0.25
Flack parameter	0.03(18)

6.6 X-Ray crystallography of natural (-)-corypsoriol H (1e)

The crystal of (-)-corypsoriol H (**1e**) for X-ray diffraction study was obtained through the dissolving of compound in MeOH, CH₂Cl₂ and petroleum ether, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

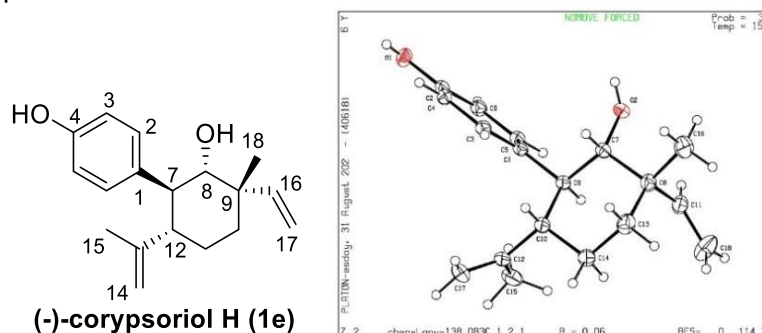


Figure S1. X-Ray coordinate of (-)-corypsoriol H (**1e**) (CCDC 2226749). Displacement ellipsoids are scaled to the 30% probability level.

Identification code	(-)-corypsoriol H (1e)
Empirical formula	C ₁₈ H ₂₅ O ₂
Formula weight	281.38
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2
a/Å	17.9138(6)
b/Å	6.1604(2)
c/Å	15.2956(6)
α/°	90
β/°	106.418(4)
γ/°	90
Volume/Å ³	1619.14(10)
Z	4
ρ _{calc} /cm ³	1.154
μ/mm ⁻¹	0.592
F(000)	612.0
Crystal size/mm ³	0.3 × 0.26 × 0.24
Radiation	Cu Kα (λ = 1.54184)
2θ range for data collection/°	6.024 to 154.302
Index ranges	-22 ≤ h ≤ 22, -7 ≤ k ≤ 7, -18 ≤ l ≤ 19
Reflections collected	7068
Independent reflections	2909 [R _{int} = 0.0811, R _{sigma} = 0.0806]
Data/restraints/parameters	2909/1/193
Goodness-of-fit on F ²	1.041
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0562, wR ₂ = 0.1412
Final R indexes [all data]	R ₁ = 0.0626, wR ₂ = 0.1477
Largest diff. peak/hole / e Å ⁻³	0.31/-0.27
Flack parameter	0.0(2)

6.7 X-Ray crystallography of proposed corypsoriol I (1h)

The crystal of proposed (-)-corypsoriol I (**1h**) for X-ray diffraction study was obtained through the dissolving of compound in CHCl_3 , ethyl acetate and petroleum ether, followed by slow evaporation of the solvent at room temperature. X-ray data collections were performed in an Agilent Super Nova.

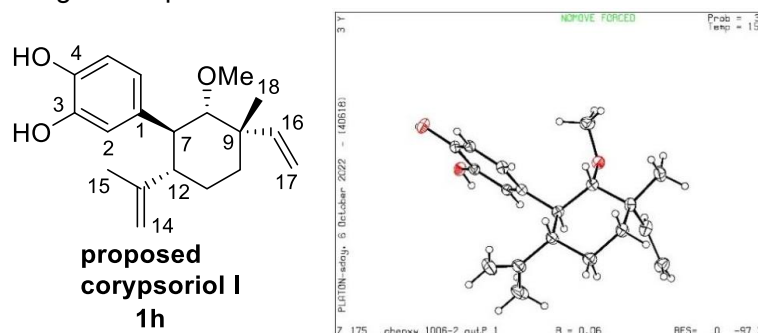


Figure S1. X-Ray coordinate of proposed corypsoriol I (**1h**) (CCDC 2226751).

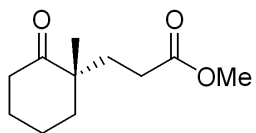
Displacement ellipsoids are scaled to the 30% probability level.

Identification code	Proposed corypsoriol I (1h)
Empirical formula	$\text{C}_{76}\text{H}_{104}\text{O}_{12}$
Formula weight	1209.59
Temperature/K	149.99(10)
Crystal system	triclinic
Space group	P1
a/Å	9.51230(10)
b/Å	11.7533(2)
c/Å	16.8232(2)
$\alpha/^\circ$	109.4870(10)
$\beta/^\circ$	90.4410(10)
$\gamma/^\circ$	100.6710(10)
Volume/Å ³	1737.54(4)
Z	1
$\rho_{\text{calc}}/\text{cm}^3$	1.156
μ/mm^{-1}	0.607
F(000)	656.0
Crystal size/mm ³	0.16 × 0.13 × 0.12
Radiation	Cu K α ($\lambda = 1.54184$)
2 θ range for data collection/ $^\circ$	5.588 to 153.732
Index ranges	-11 ≤ h ≤ 10, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20
Reflections collected	59003
Independent reflections	12367 [R _{int} = 0.0890, R _{sigma} = 0.0529]
Data/restraints/parameters	12367/3/859
Goodness-of-fit on F ²	1.025
Final R indexes [$ I \geq 2\sigma(I)$]	R ₁ = 0.0558, wR ₂ = 0.1411
Final R indexes [all data]	R ₁ = 0.0592, wR ₂ = 0.1439
Largest diff. peak/hole / e Å ⁻³	0.48/-0.20
Flack parameter	0.15(12)

7. References

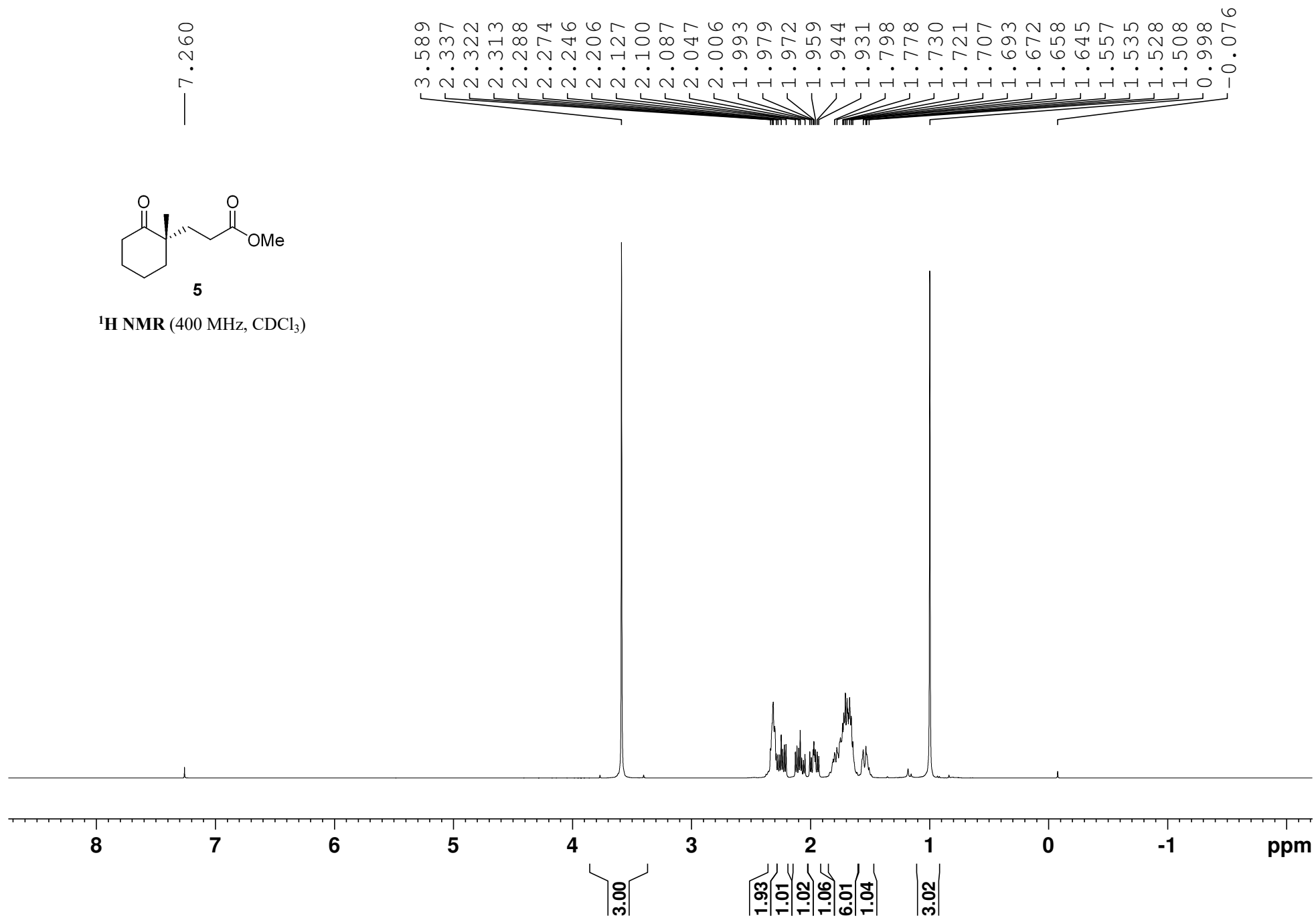
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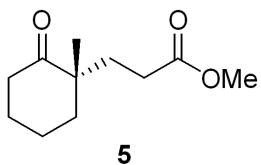
8. Copies of ^1H and ^{13}C NMR spectra UPC² data of products



5

¹H NMR (400 MHz, CDCl₃)





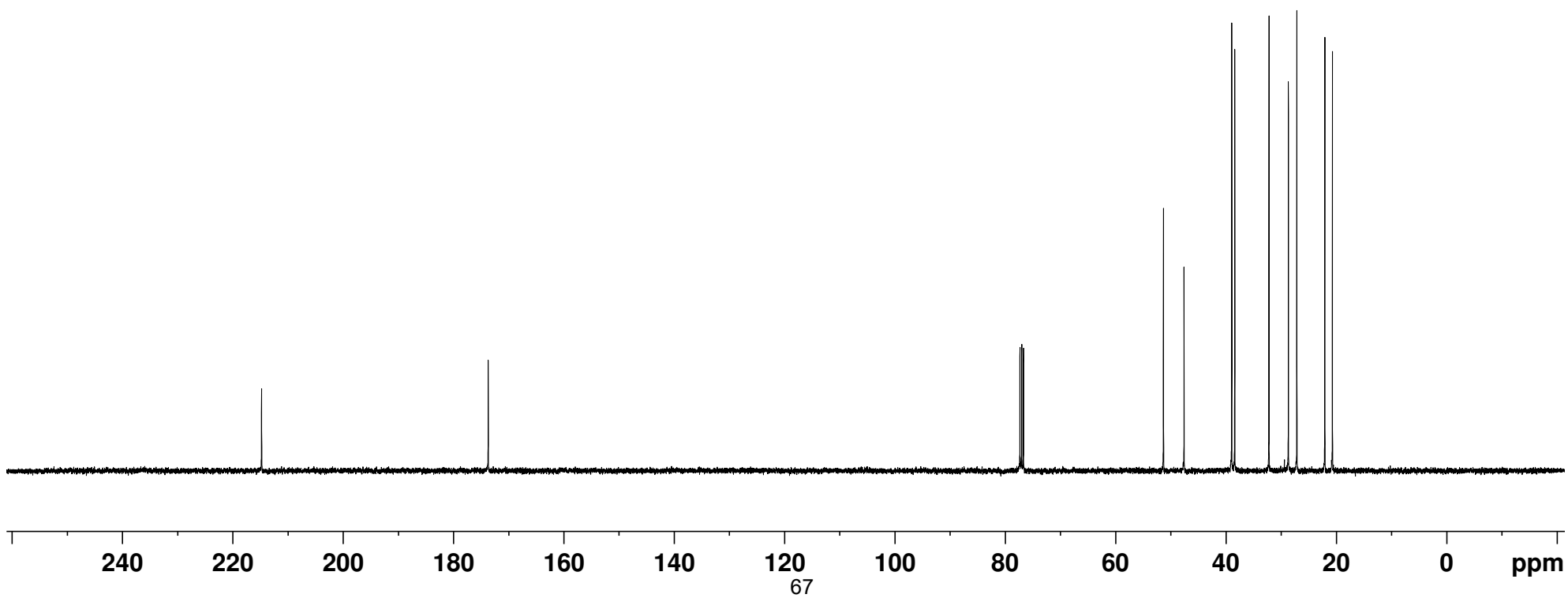
¹³C NMR (100 MHz, CDCl₃)

— 214.76

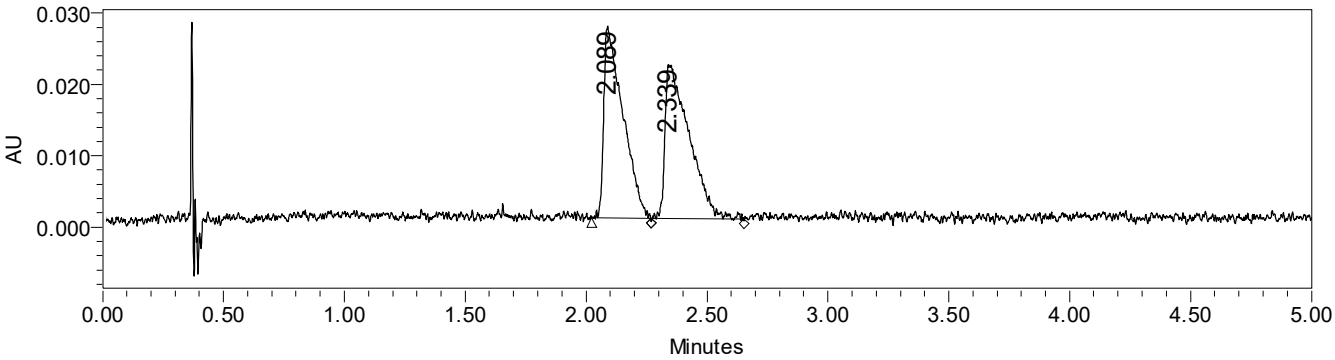
— 173.69

77.32
77.00
76.68

51.31
47.58
38.94
38.39
32.19
28.67
27.13
22.06
20.69



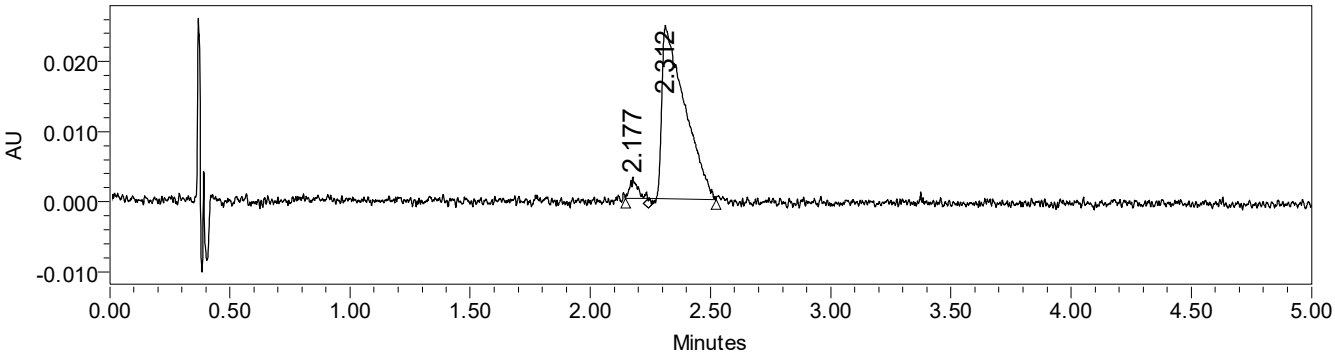
Sample Name: Compound-5-C5-9703xx Wave Length: 297.3nm
 Column: PDA Spectrum PDA 297.3 nm (PDA)



peak information:

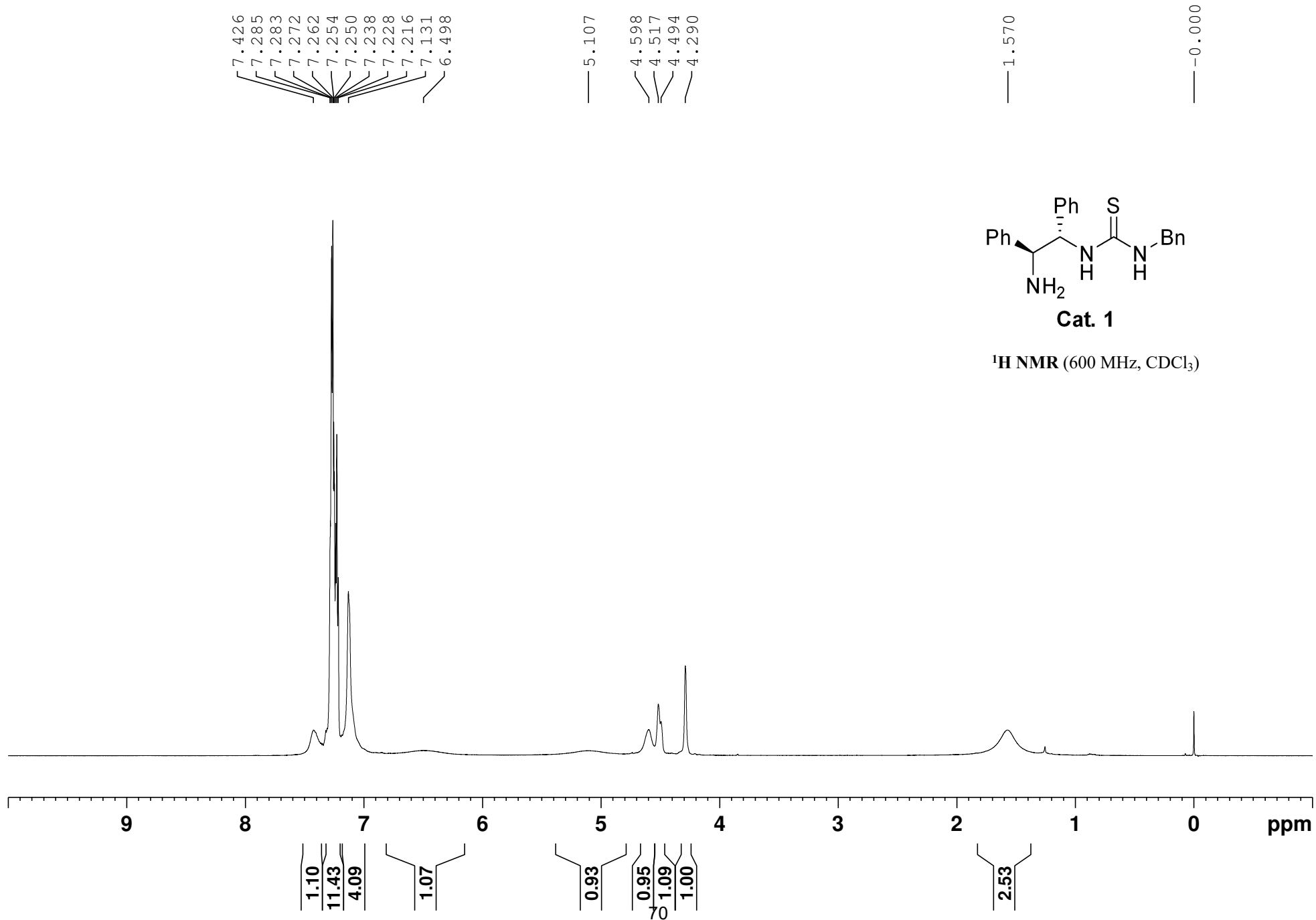
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.089	147851	49.60	26859
2	2.339	150206	50.40	21497

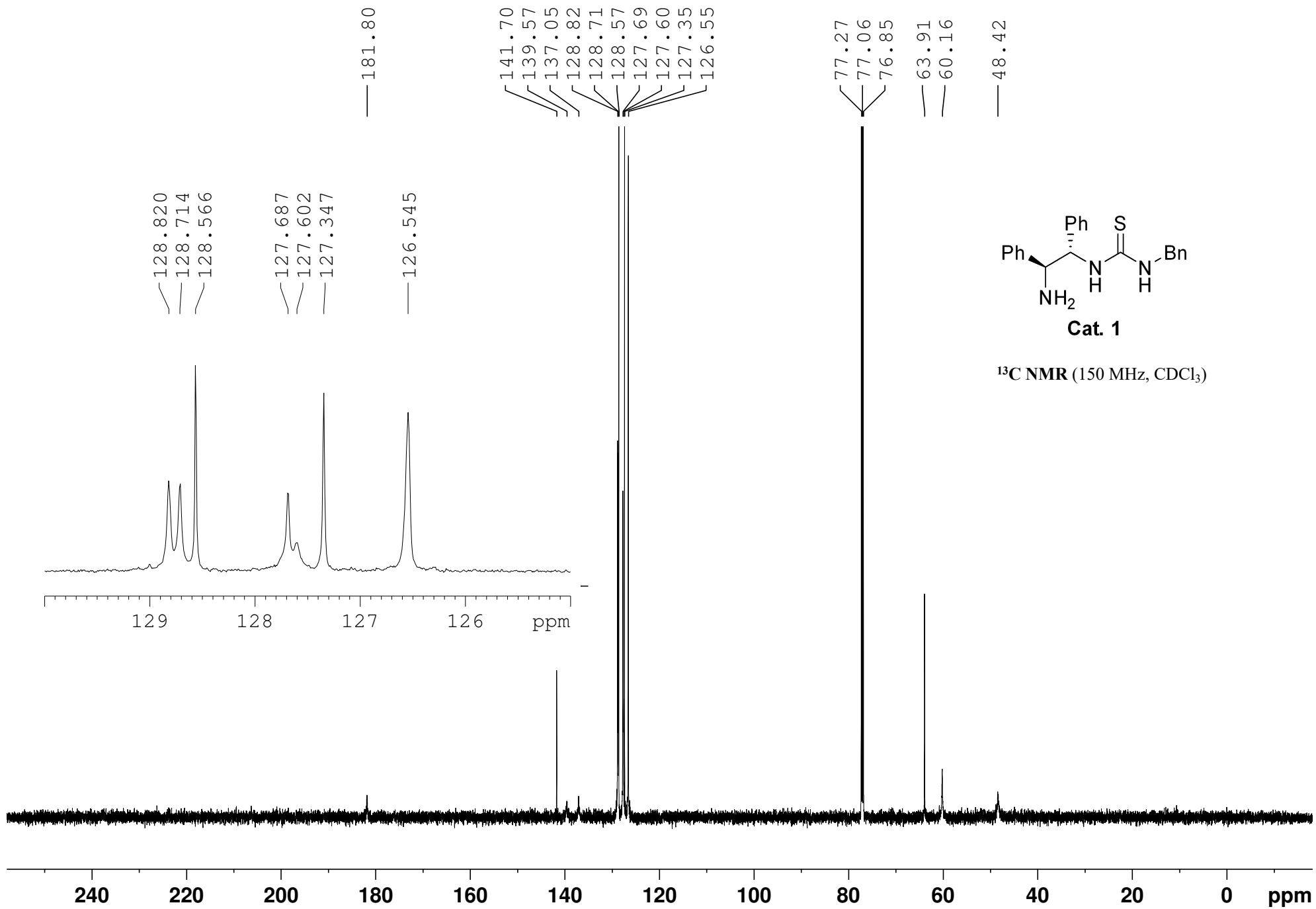
Sample Name: Compound-5-C5-9703 Wave Length: 297.3nm
 Column: PDA Spectrum PDA 297.3 nm (PDA)

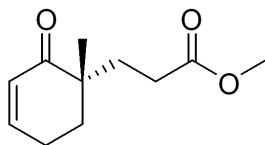


peak information:

	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.177	6657	3.90	2974
2	2.312	164016	96.10	24747

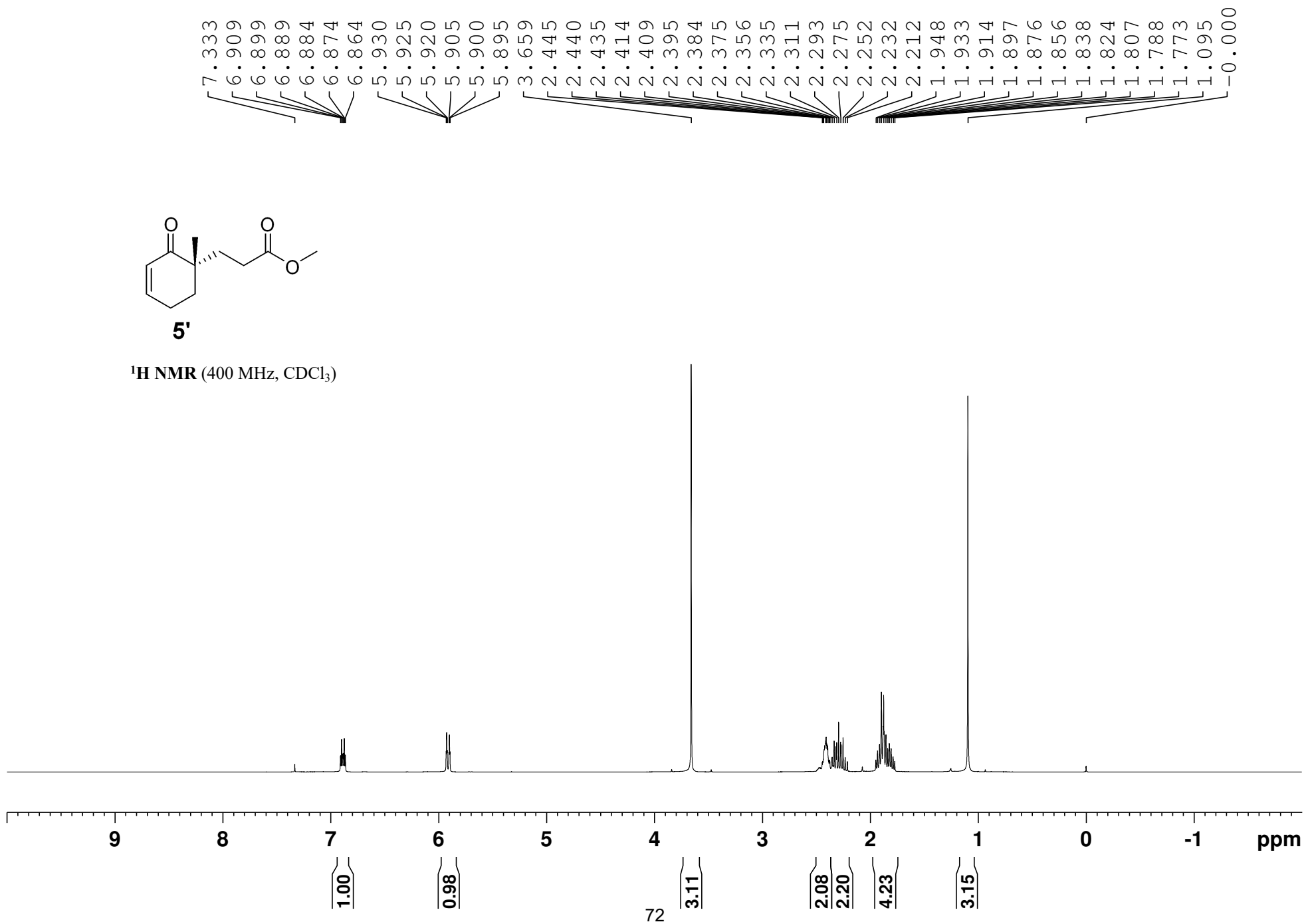


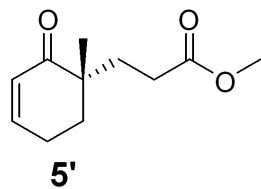




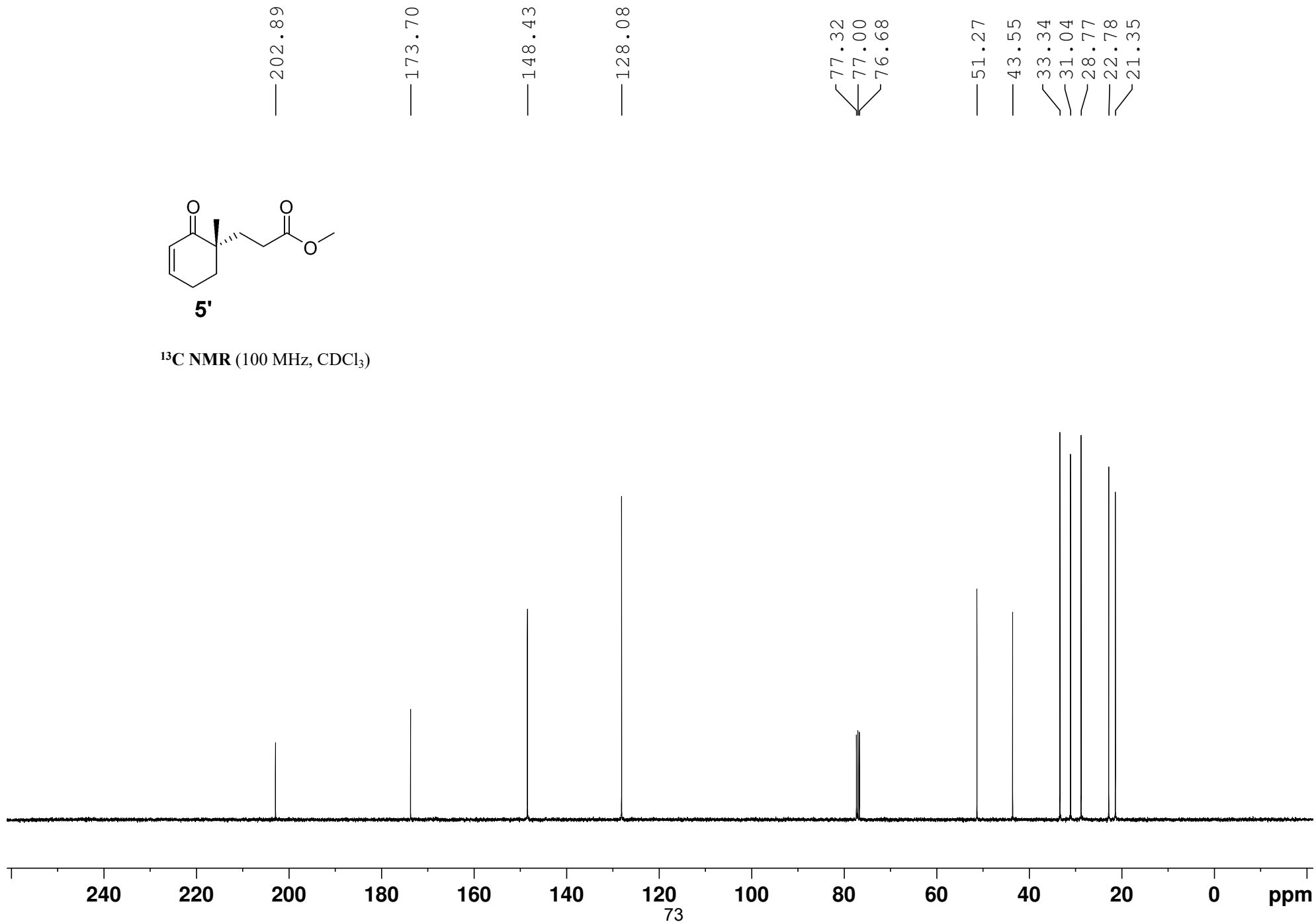
5'

¹H NMR (400 MHz, CDCl₃)

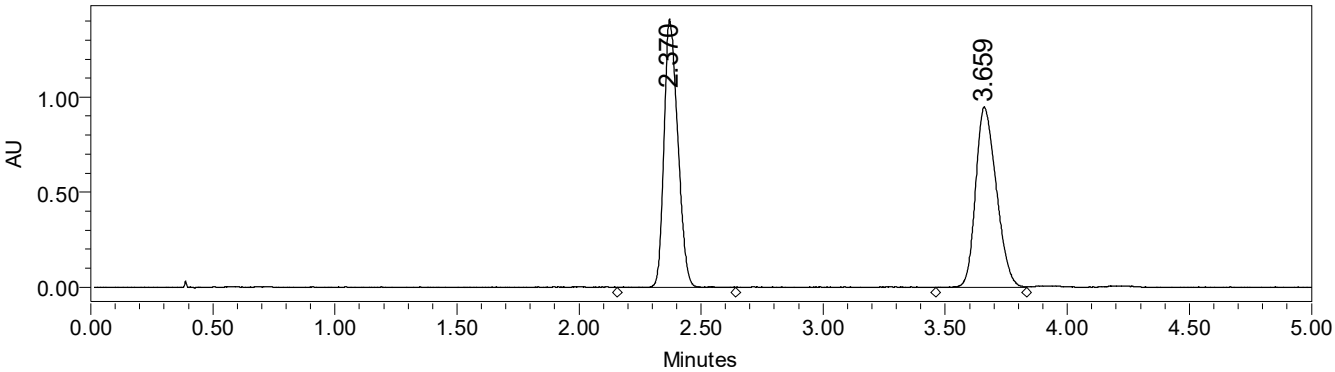




¹³C NMR (100 MHz, CDCl₃)



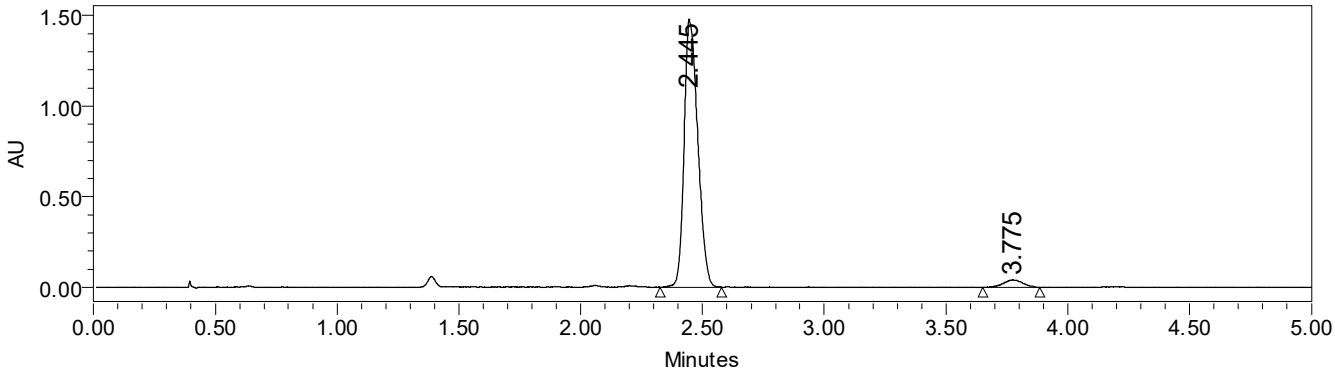
Sample Name: Compound-5'-C5-9505-xx Wave Length: 220.0nm
 Column: PDA Spectrum PDA 220.0 nm (PDA)



peak information:

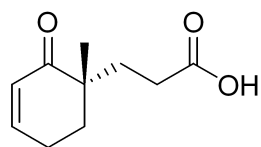
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.370	5600641	49.91	1413197
2	3.659	5619823	50.09	950410

Sample Name: Compound -5'-C5-9505 Wave Length: 220.0nm
 Column: PDA Spectrum PDA 220.0 nm (PDA)



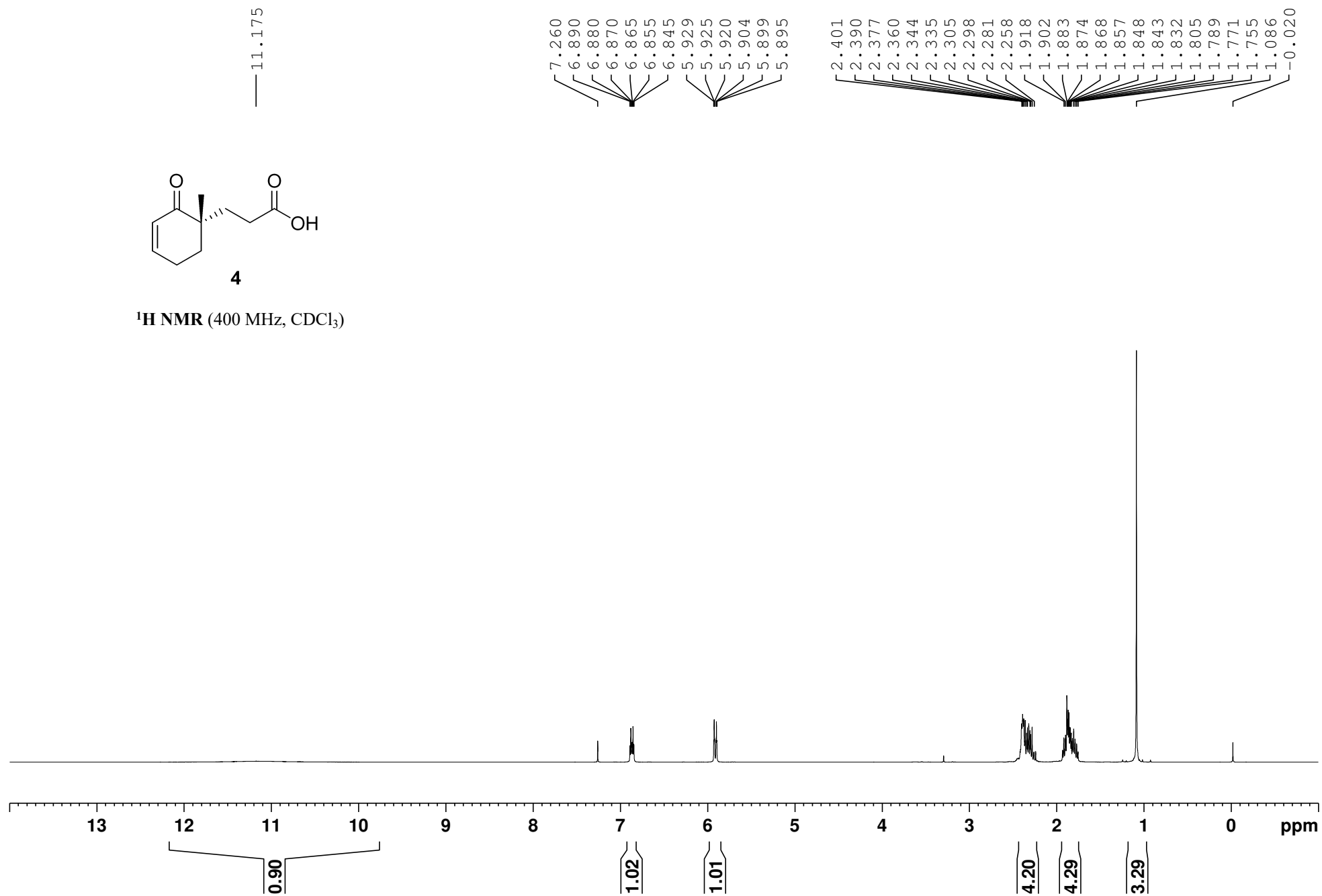
peak information:

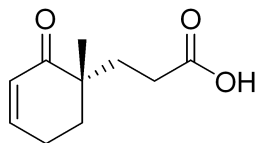
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	2.445	5752452	96.39	1478514
2	3.775	215153	3.61	39229



4

¹H NMR (400 MHz, CDCl₃)





4

^{13}C NMR (100 MHz, CDCl_3)

— 203.40

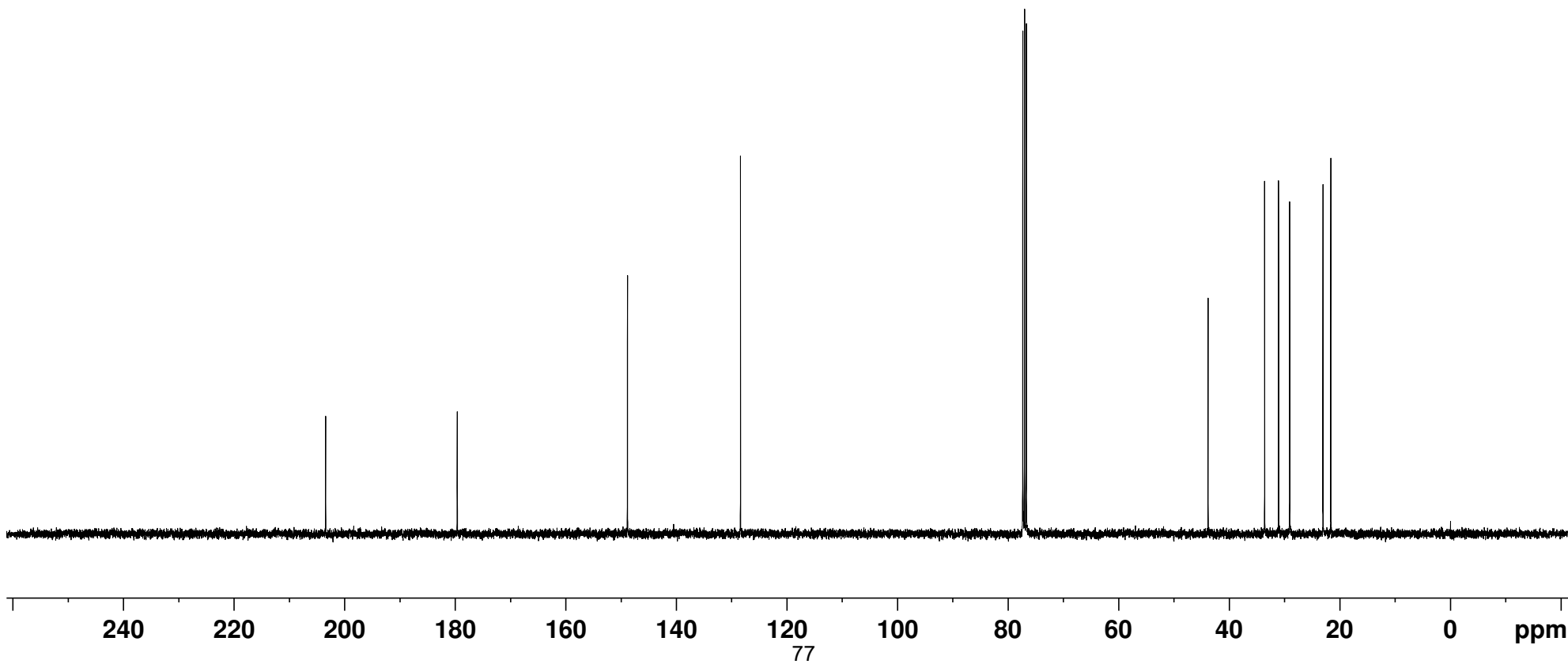
— 179.60

— 148.81

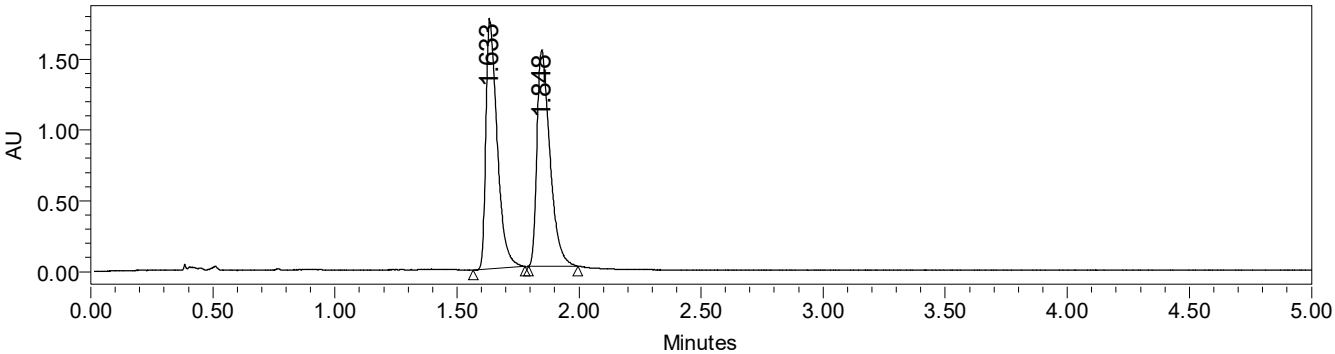
— 128.37

77.31
77.00
76.68

43.80
33.58
31.05
29.05
23.03
21.61



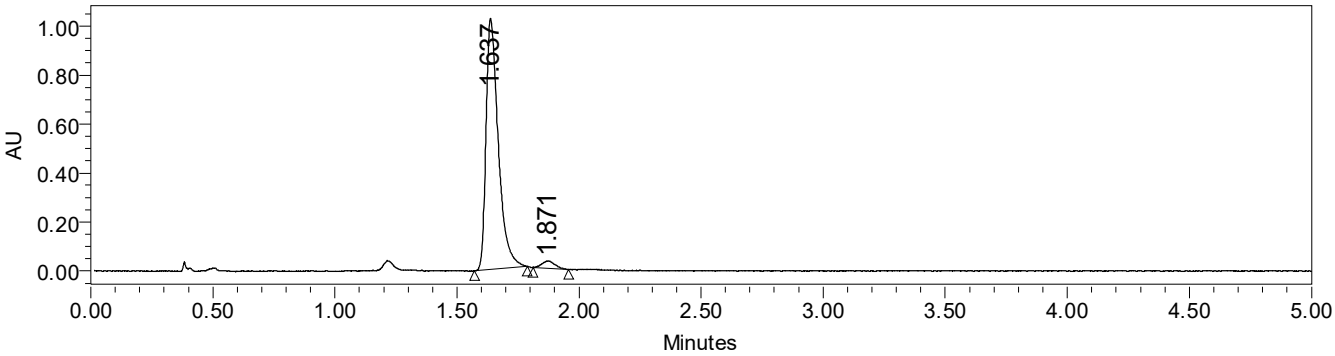
Sample Name: Compound-4-C5-9010xx Wave Length: 210.0nm
 Column: PDA Spectrum PDA 210.0 nm (PDA)



peak information:

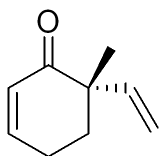
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.633	5653674	50.09	1767231
2	1.848	5633489	49.91	1528376

Sample Name: Compound-4-C5-9010 Wave Length: 210.0nm
 Column: PDA Spectrum PDA 210.0 nm (PDA)



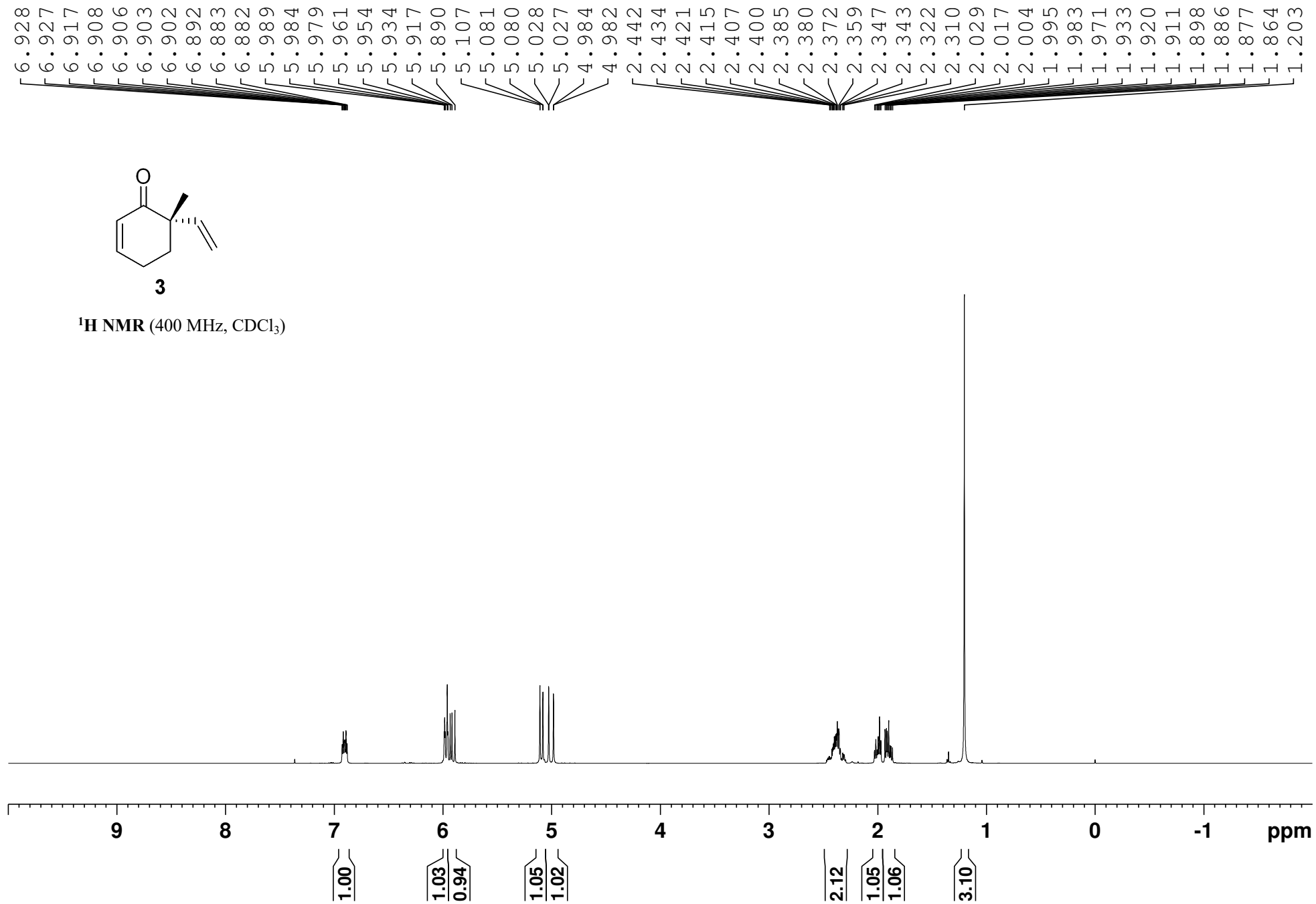
peak information:

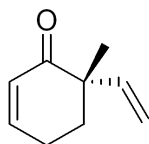
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.637	3569507	97.05	1025589
2	1.871	108487	2.95	29459



3

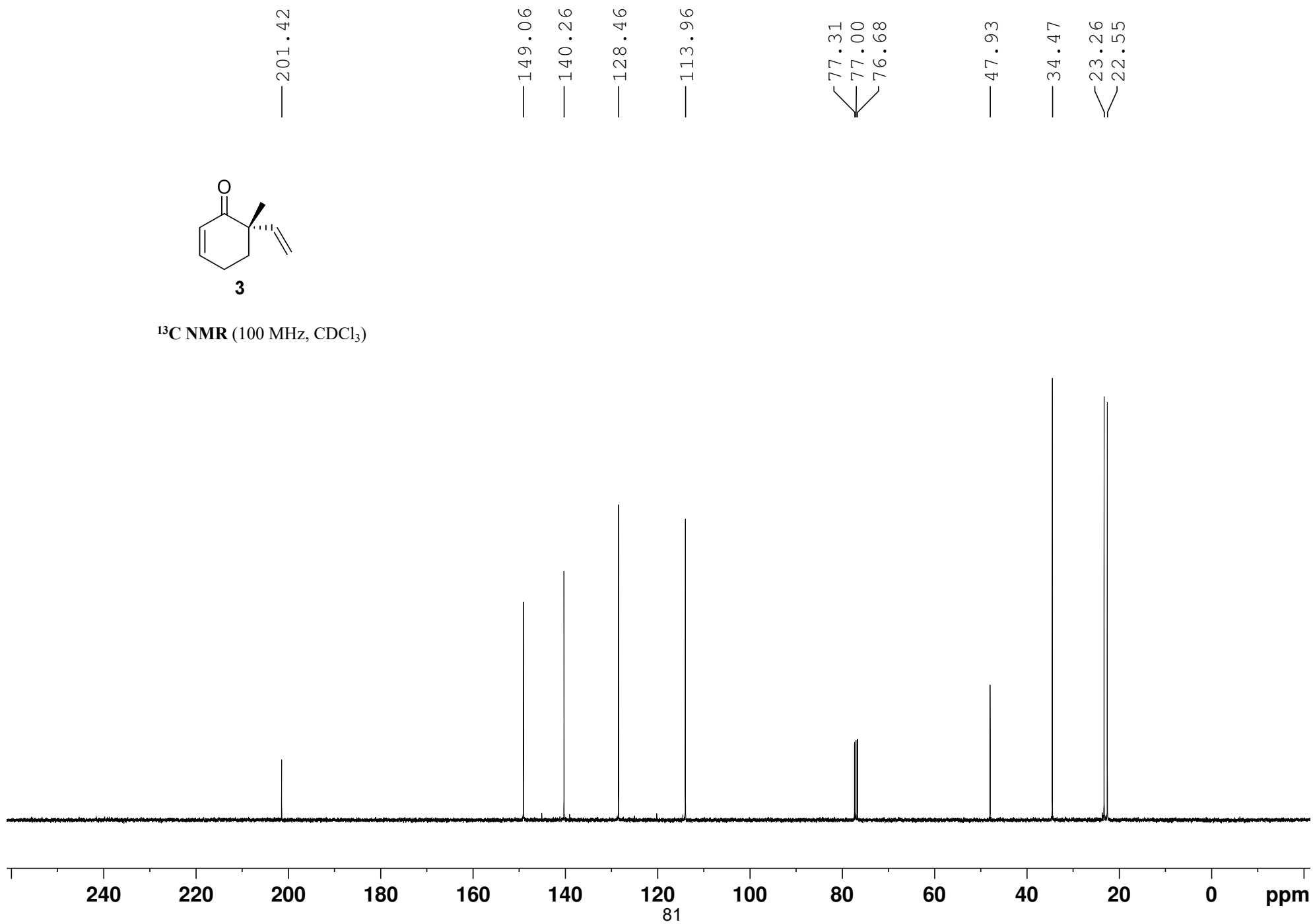
¹H NMR (400 MHz, CDCl₃)



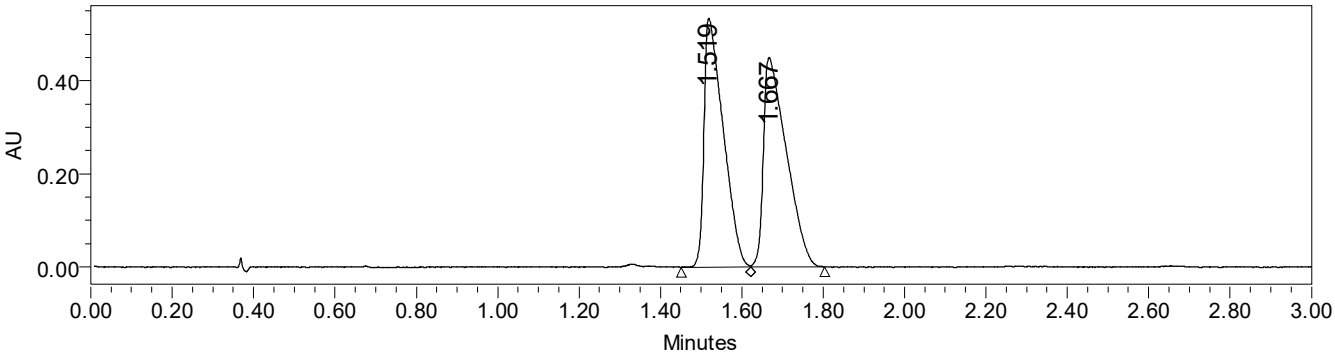


3

^{13}C NMR (100 MHz, CDCl_3)



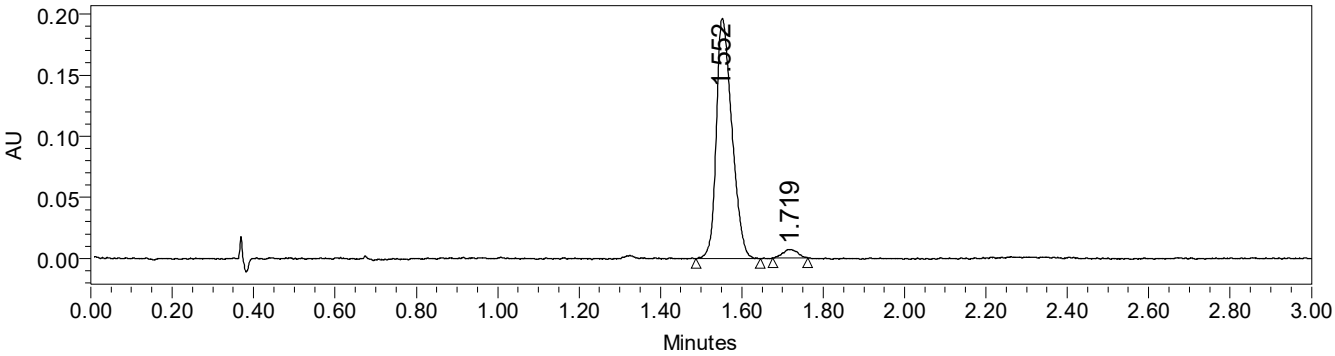
Sample Name: Compound -3-C7-9901-xx Wave Length: 238.0nm
 Column: PDA Spectrum PDA 238.0 nm (PDA)



peak information:

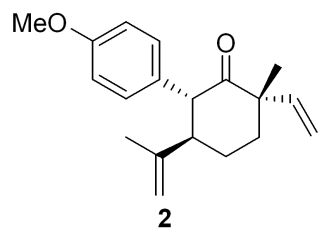
	RetTime (min)	Area (μV*s)	Area (%)	Height (μV)
1	1.519	1750624	49.90	534160
2	1.667	1757818	50.10	450094

Sample Name: Compound-3-C7-9901 Wave Length: 238.0nm
 Column: PDA Spectrum PDA 238.0 nm (PDA)

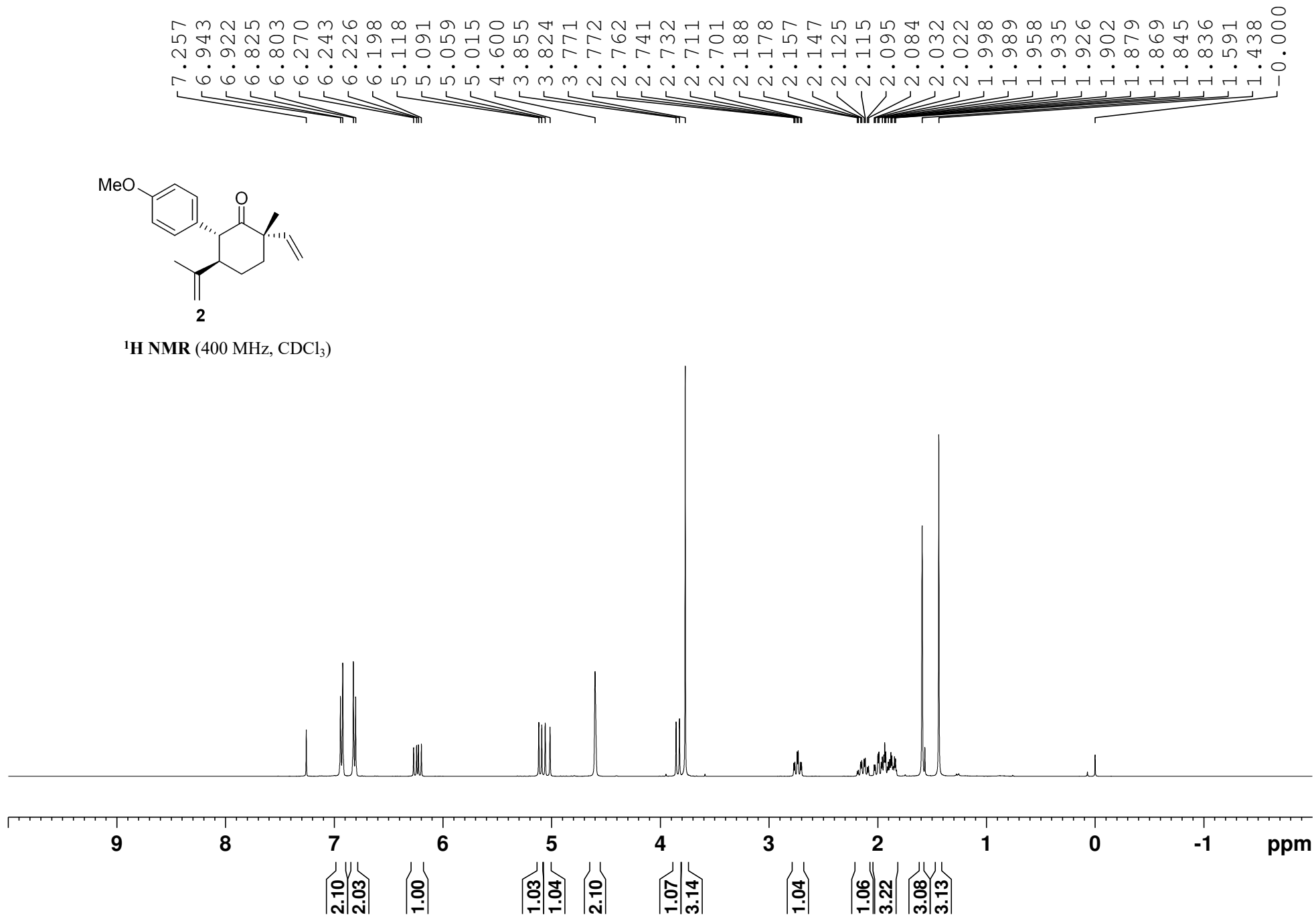


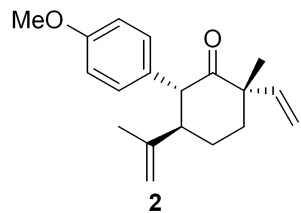
peak information:

	RetTime (min)	Area (µV*s)	Area (%)	Height (µV)
1	1.552	521197	96.76	196364
2	1.719	17443	3.24	6956



¹H NMR (400 MHz, CDCl₃)





^{13}C NMR (100 MHz, CDCl_3)

— 212.08

— 158.20

— 145.77

— 142.94

— 130.33

— 129.04

— 113.42

— 112.75

— 112.25

— 77.36

— 77.04

— 76.73

— 55.98

— 55.11

— 53.13

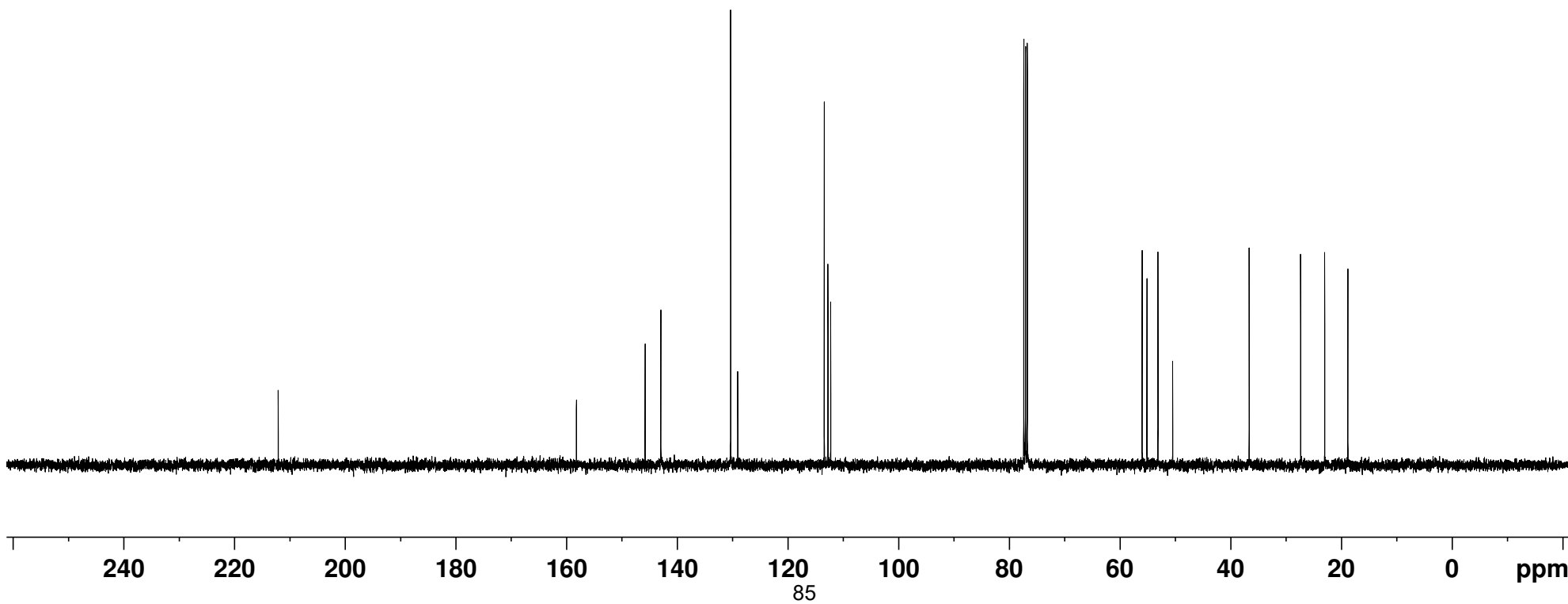
— 50.46

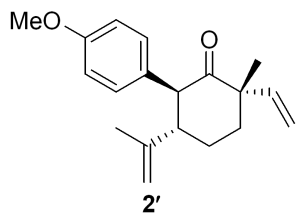
— 36.65

— 27.34

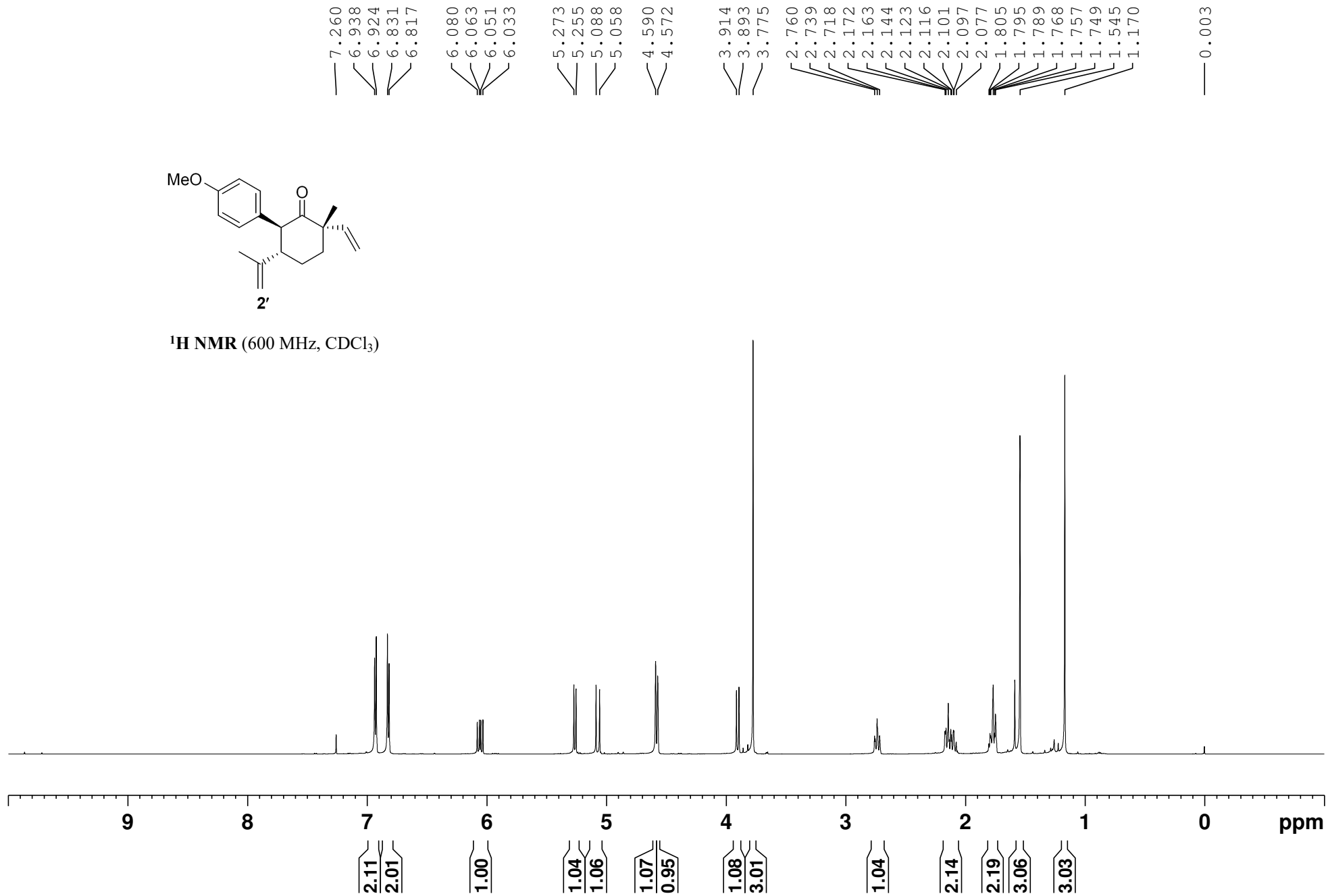
— 22.99

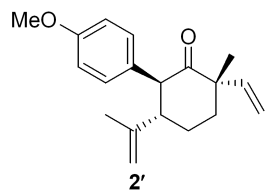
— 18.81



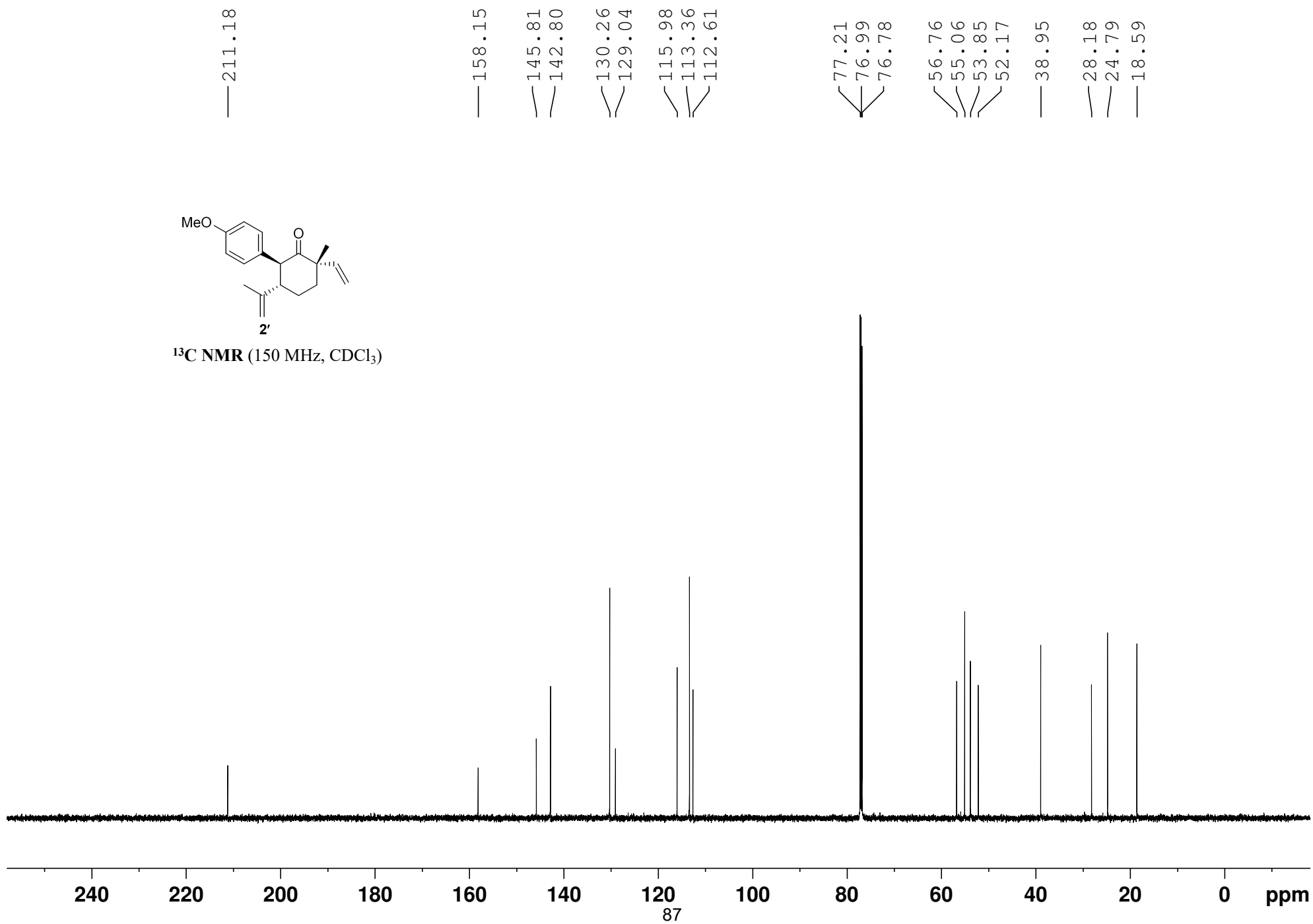


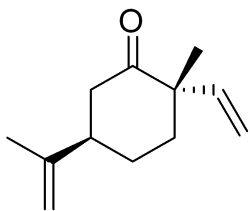
¹H NMR (600 MHz, CDCl₃)





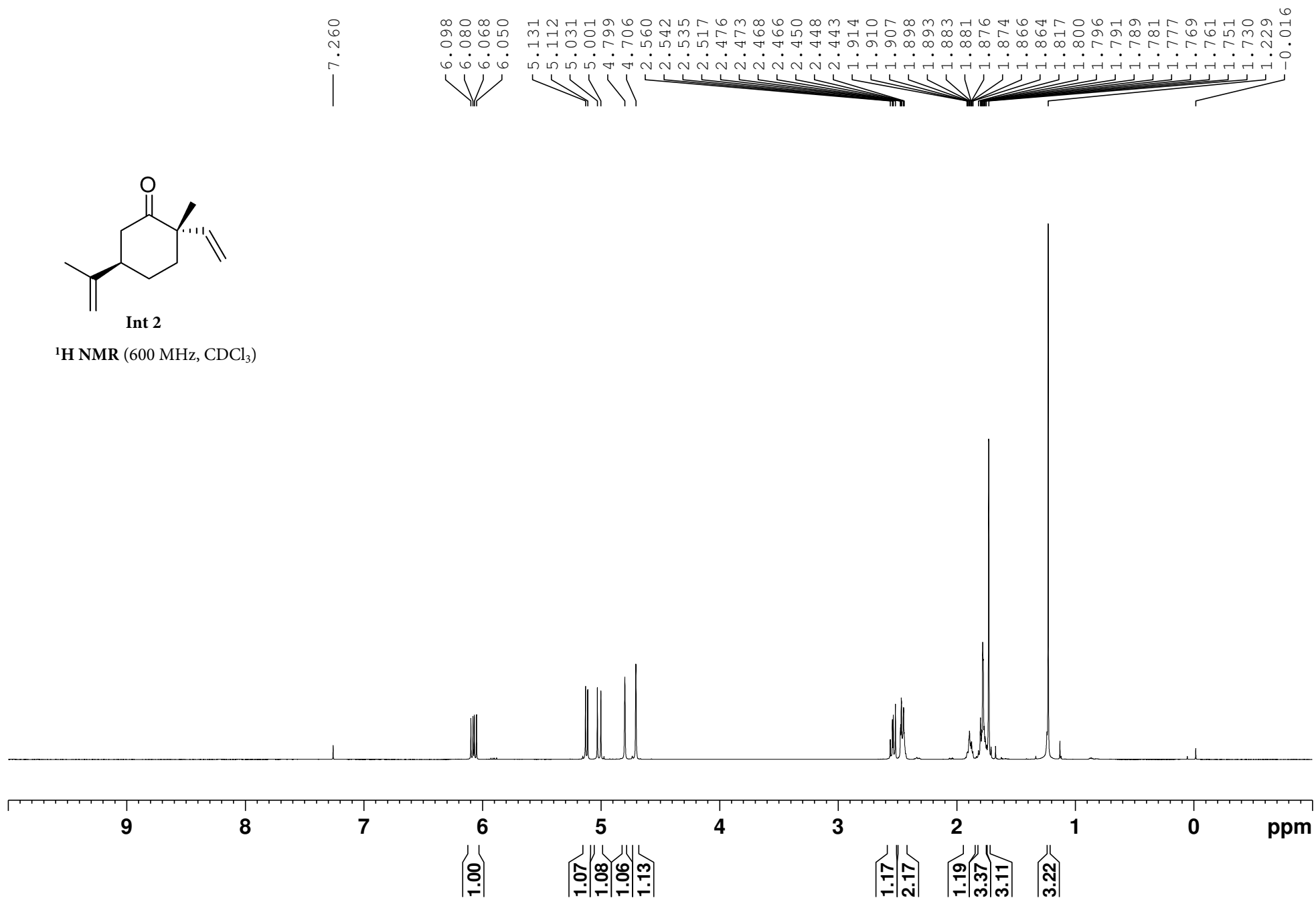
¹³C NMR (150 MHz, CDCl₃)

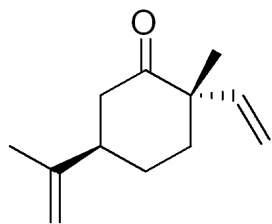




Int 2

¹H NMR (600 MHz, CDCl₃)





Int 2

^{13}C NMR (150 MHz, CDCl_3)

— 213.37

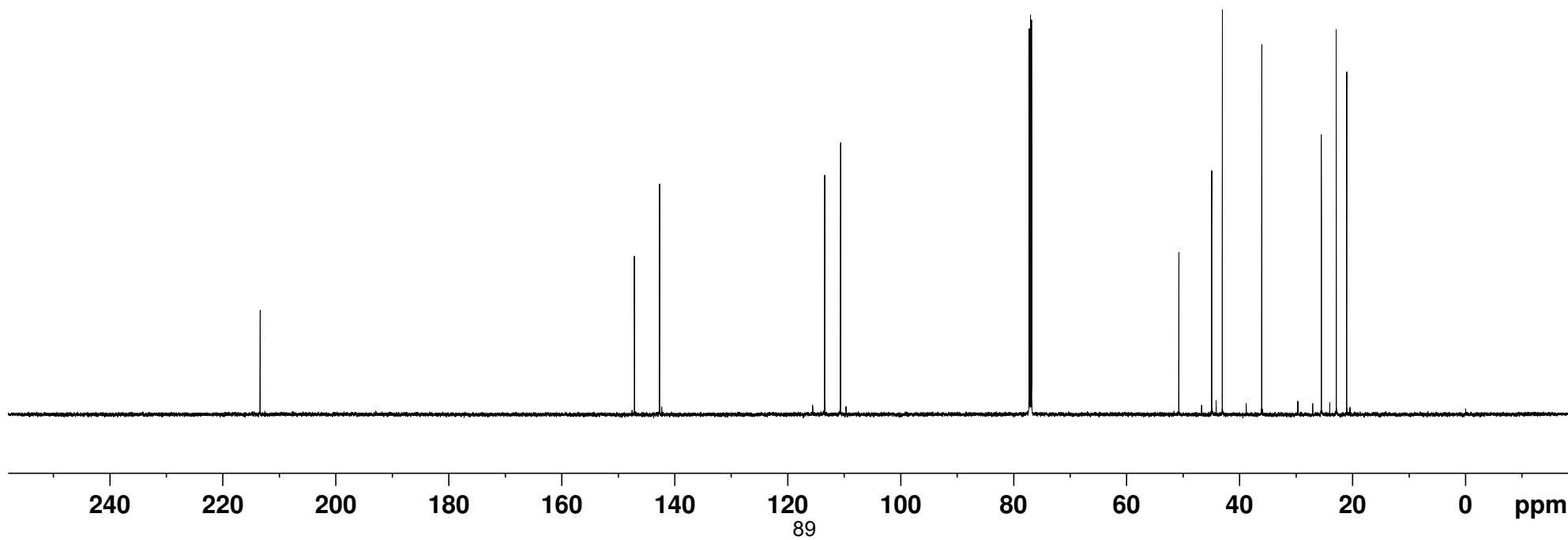
— 147.10
— 142.65

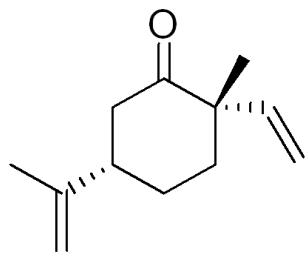
— 113.42
— 110.62

— 77.21
— 77.00
— 76.78

— 50.71
— 44.91
— 43.03
— 36.04

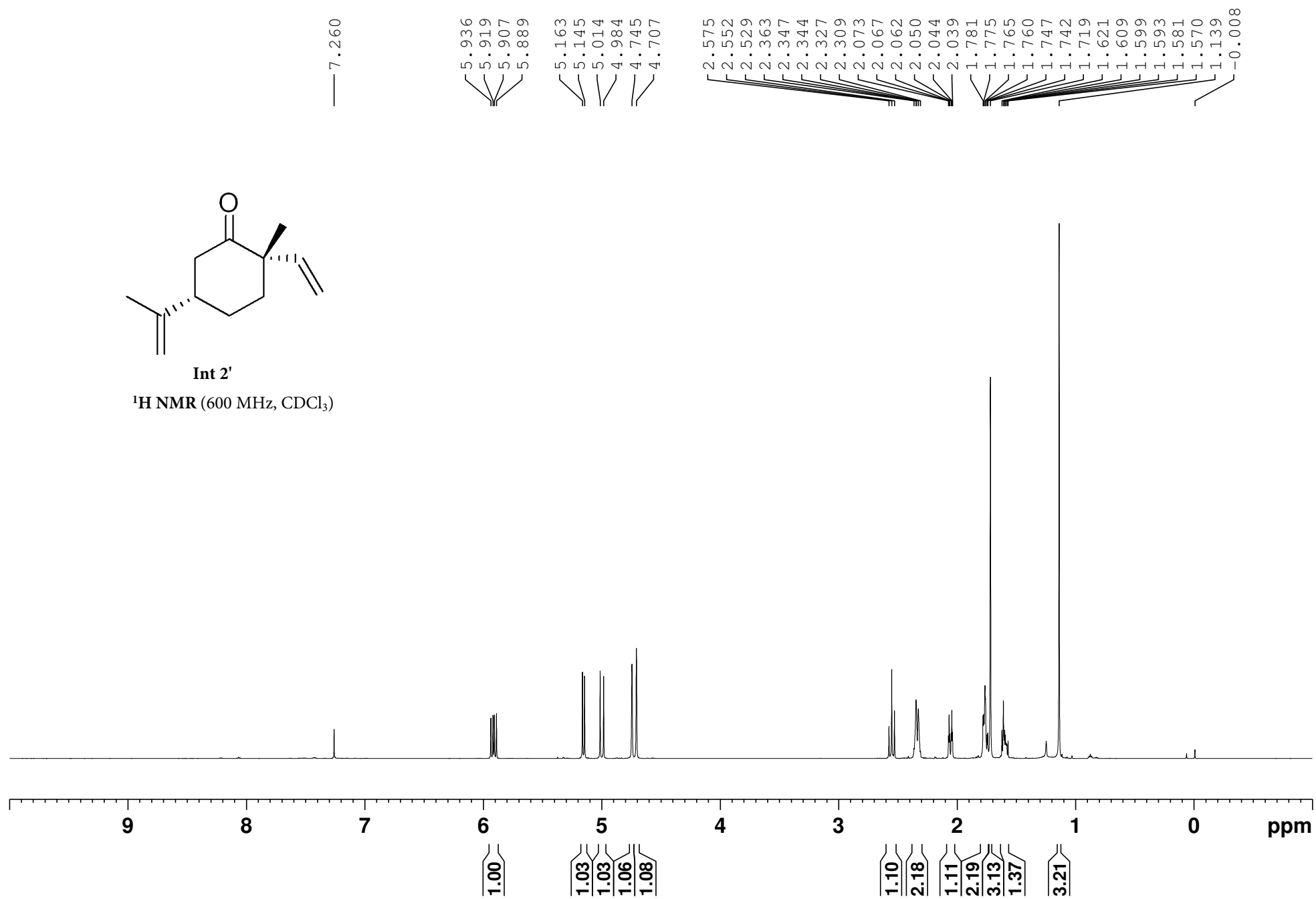
— 25.49
— 22.85
— 21.00

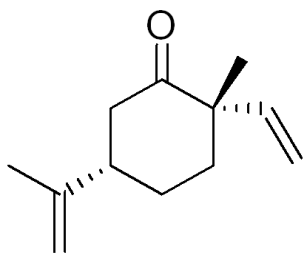




Int 2'

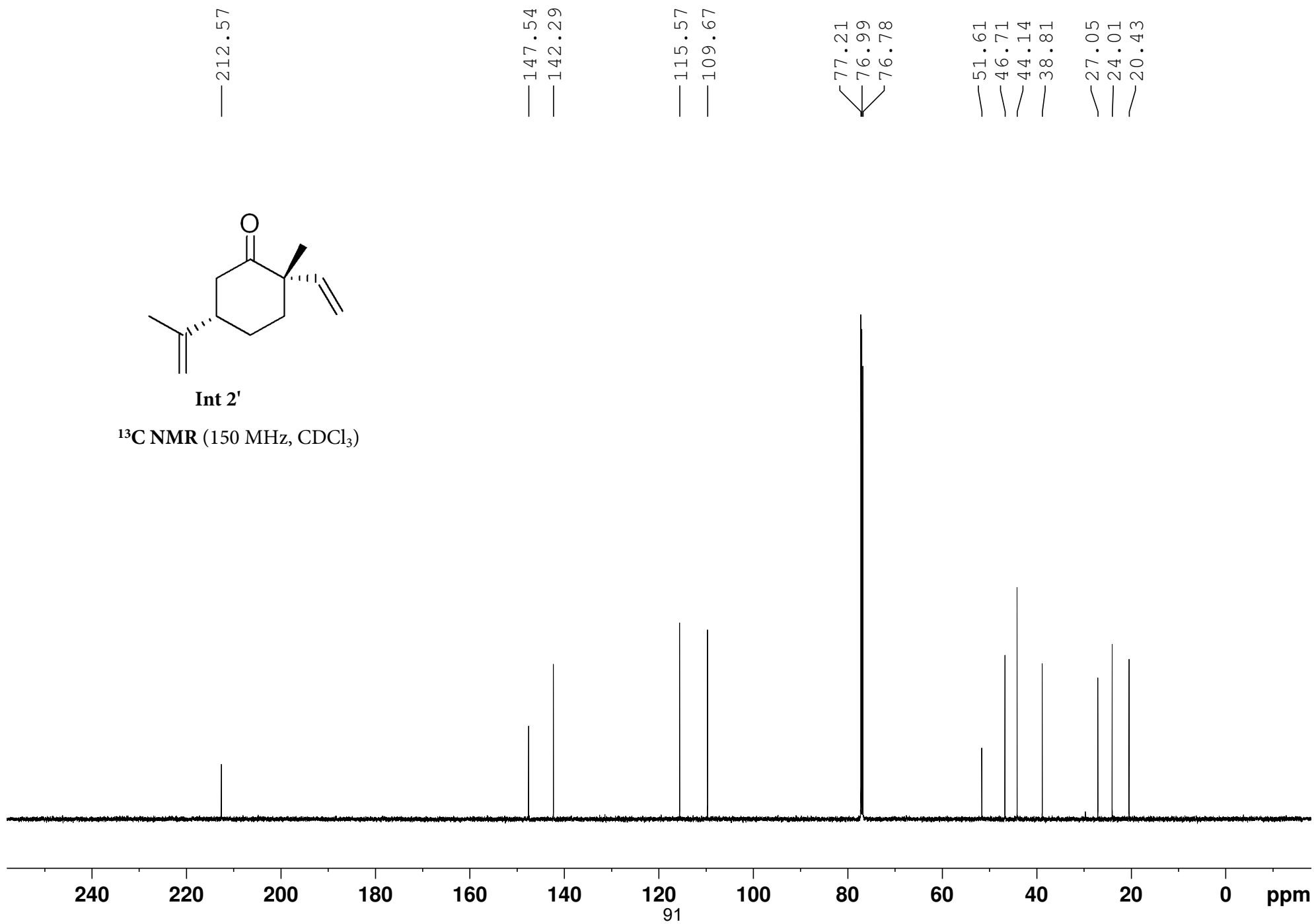
¹H NMR (600 MHz, CDCl₃)



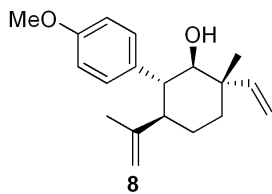


Int 2'

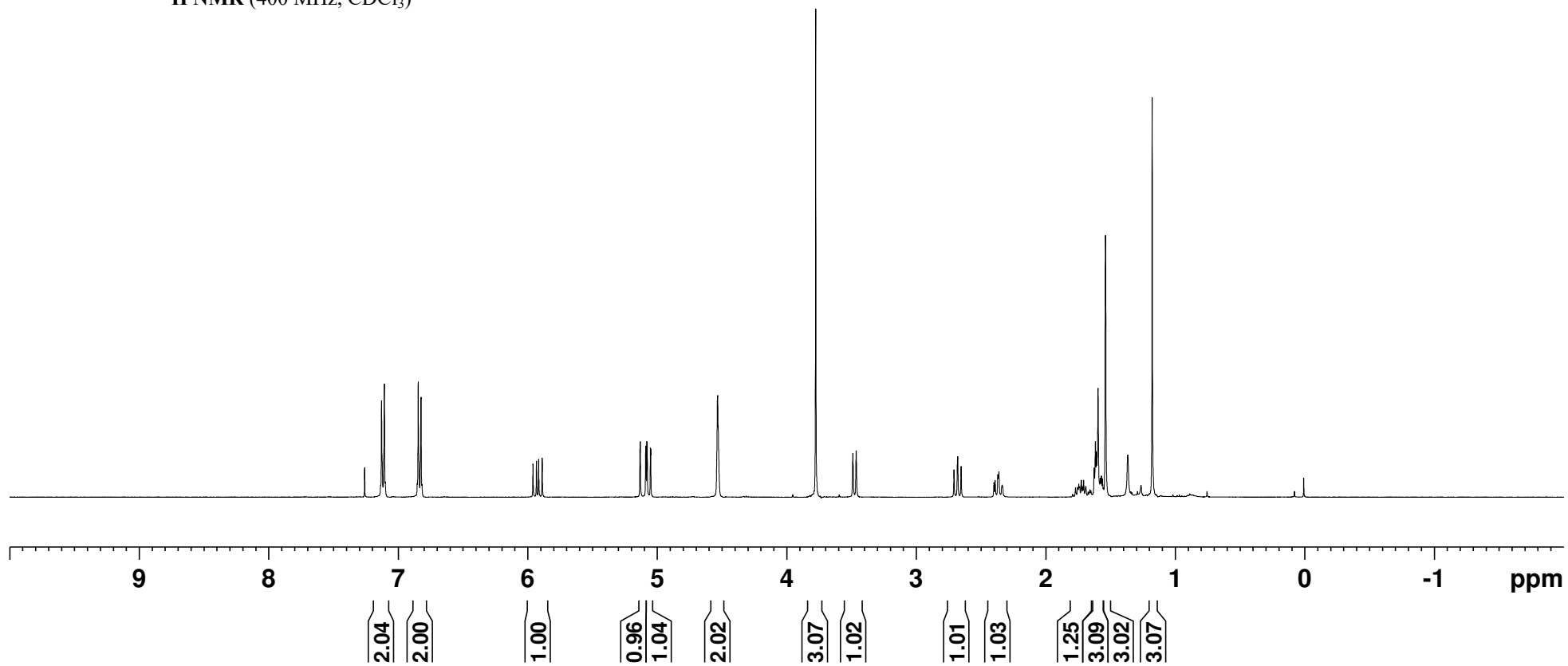
¹³C NMR (150 MHz, CDCl₃)

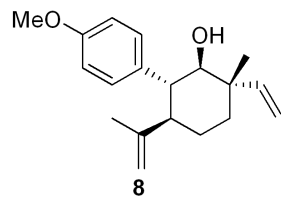


7.260
7.129
7.108
6.846
6.825
5.960
5.933
5.916
5.889
5.134
5.131
5.090
5.087
5.080
5.078
5.053
5.051
4.533
4.529
3.777
3.490
3.464
2.709
2.680
2.654
2.400
2.391
2.371
2.362
2.337
1.793
1.746
1.726
1.708
1.690
1.665
1.659
1.651
1.641
1.626
1.617
1.609
1.596
1.579
1.570
1.562
1.539
1.178

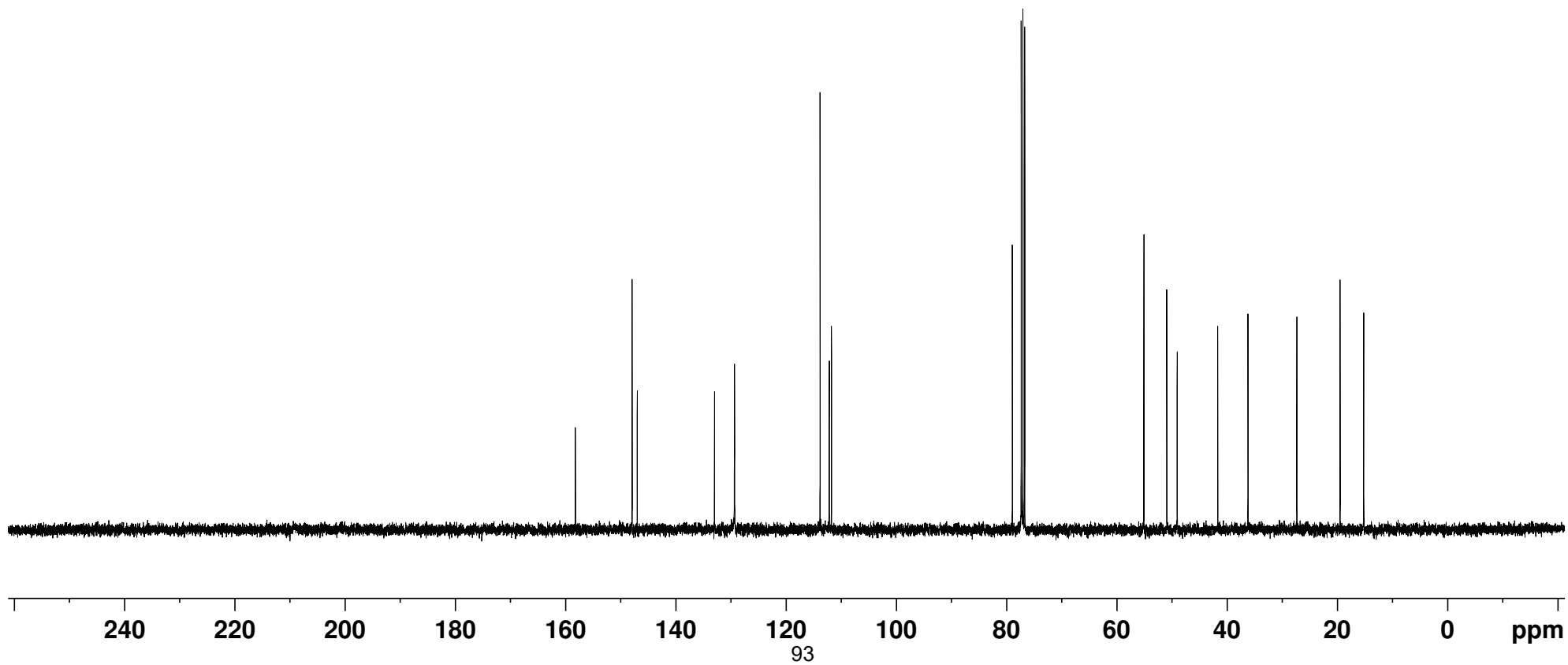


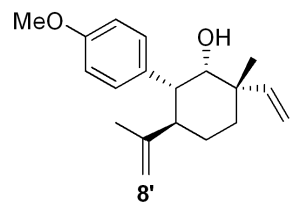
¹H NMR (400 MHz, CDCl₃)



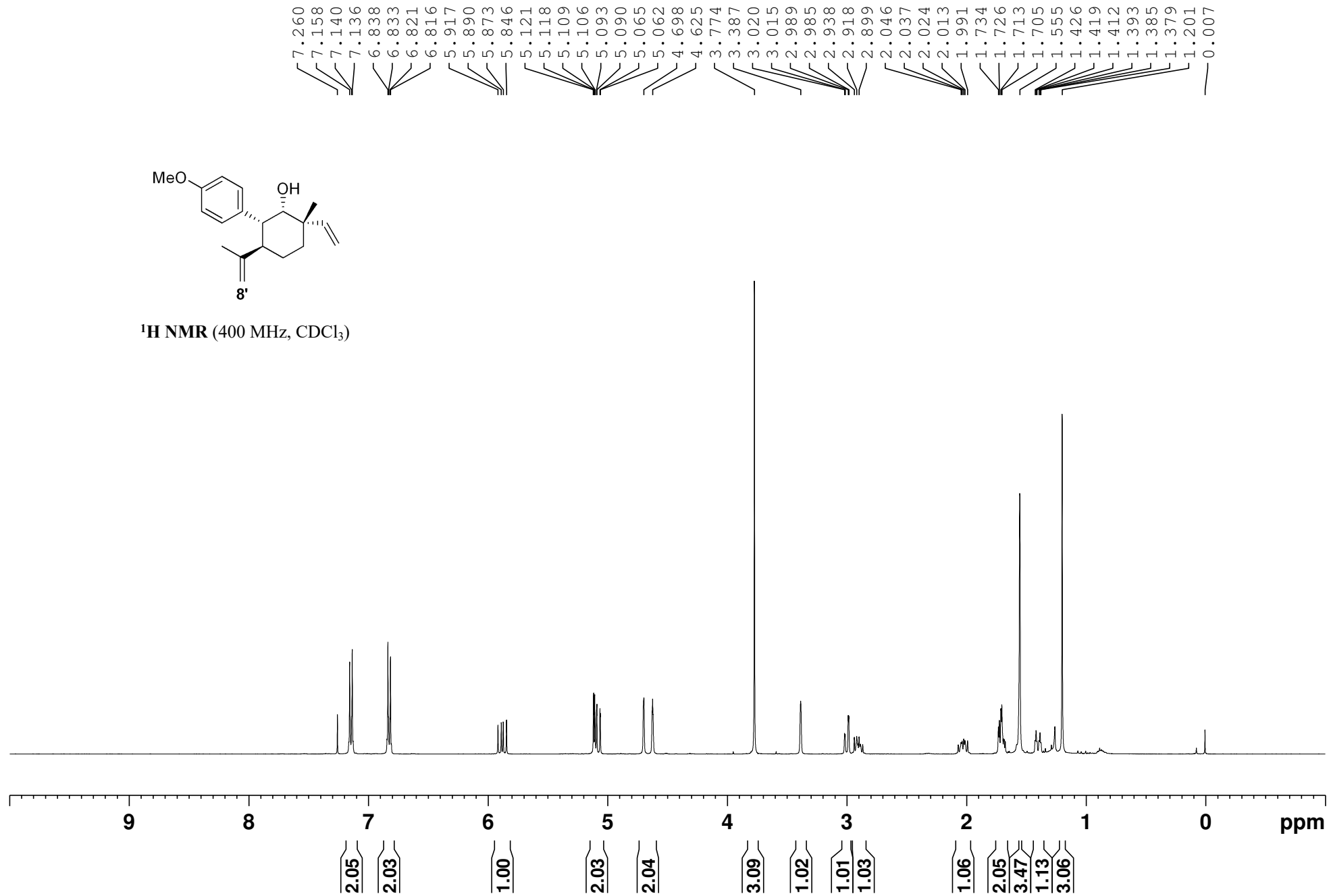


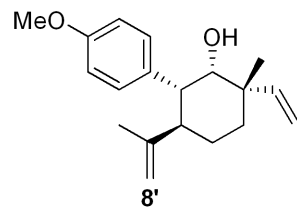
^{13}C NMR (100 MHz, CDCl_3)





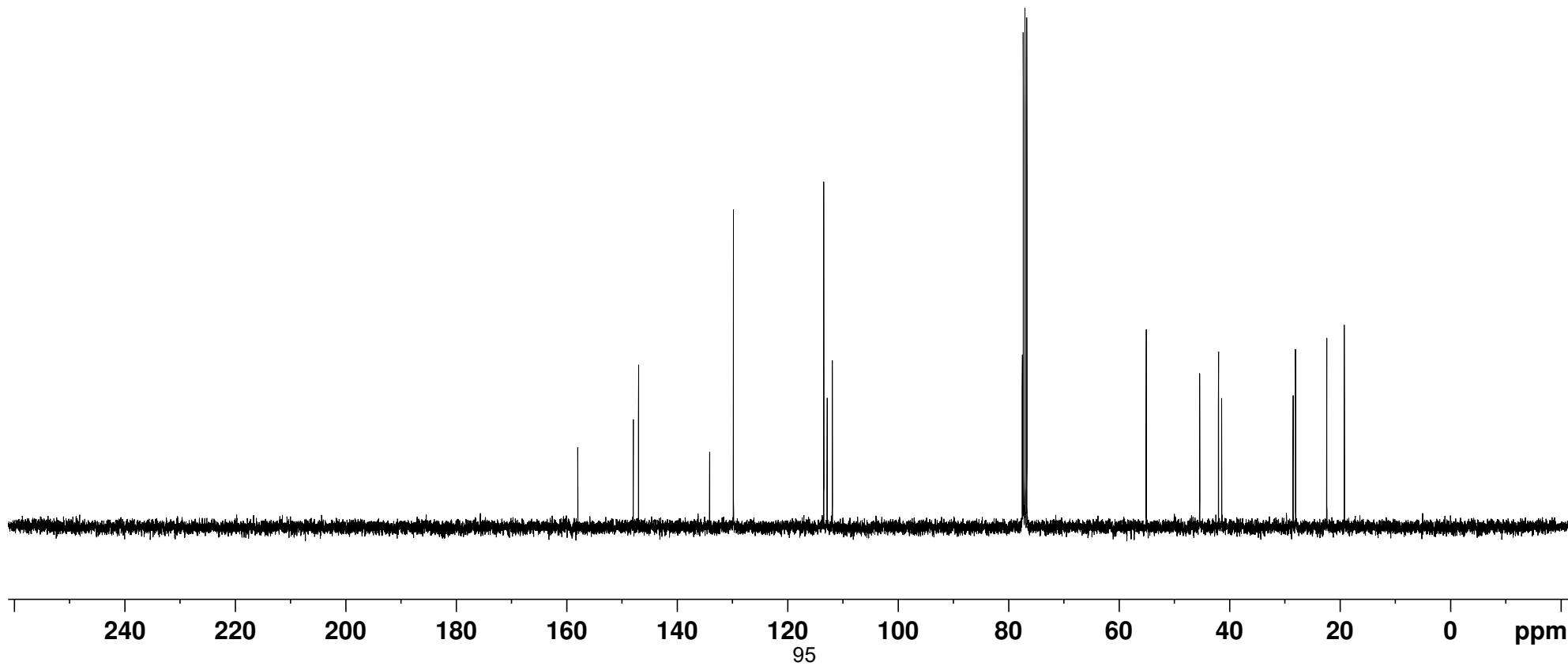
¹H NMR (400 MHz, CDCl₃)

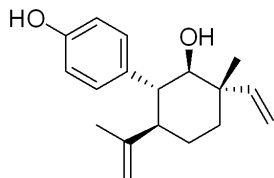




¹³C NMR (100 MHz, CDCl₃)

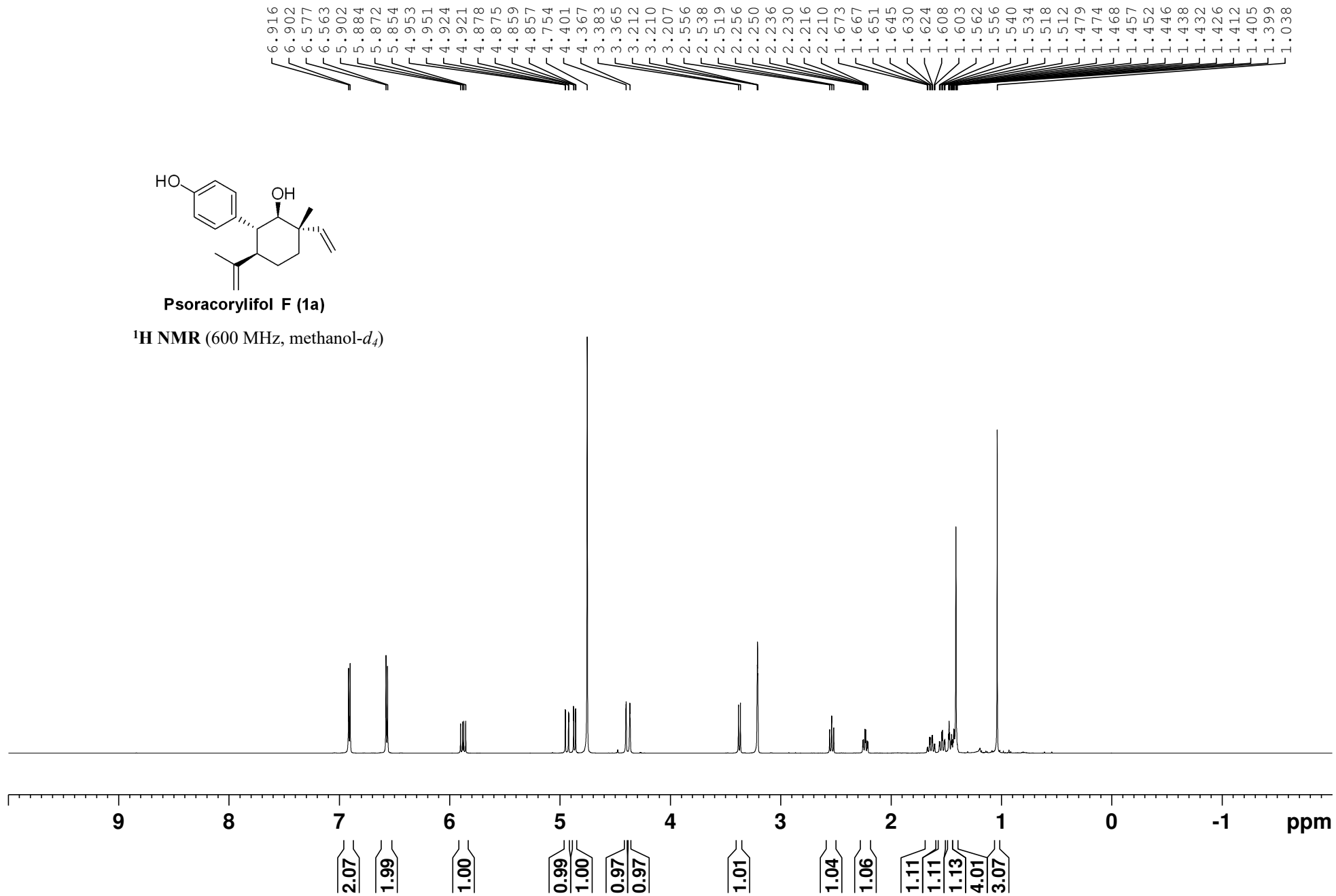
— 157.96
〈 147.91
 146.98
— 134.10
— 129.79
 113.44
 112.82
 111.89
 77.49
 77.31
 76.99
 76.68
— 55.07
〈 45.39
 41.97
 41.40
 28.47
 28.02
— 22.37
 19.18

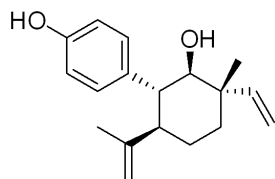




Psoracorylifol F (1a)

¹H NMR (600 MHz, methanol-d₄)

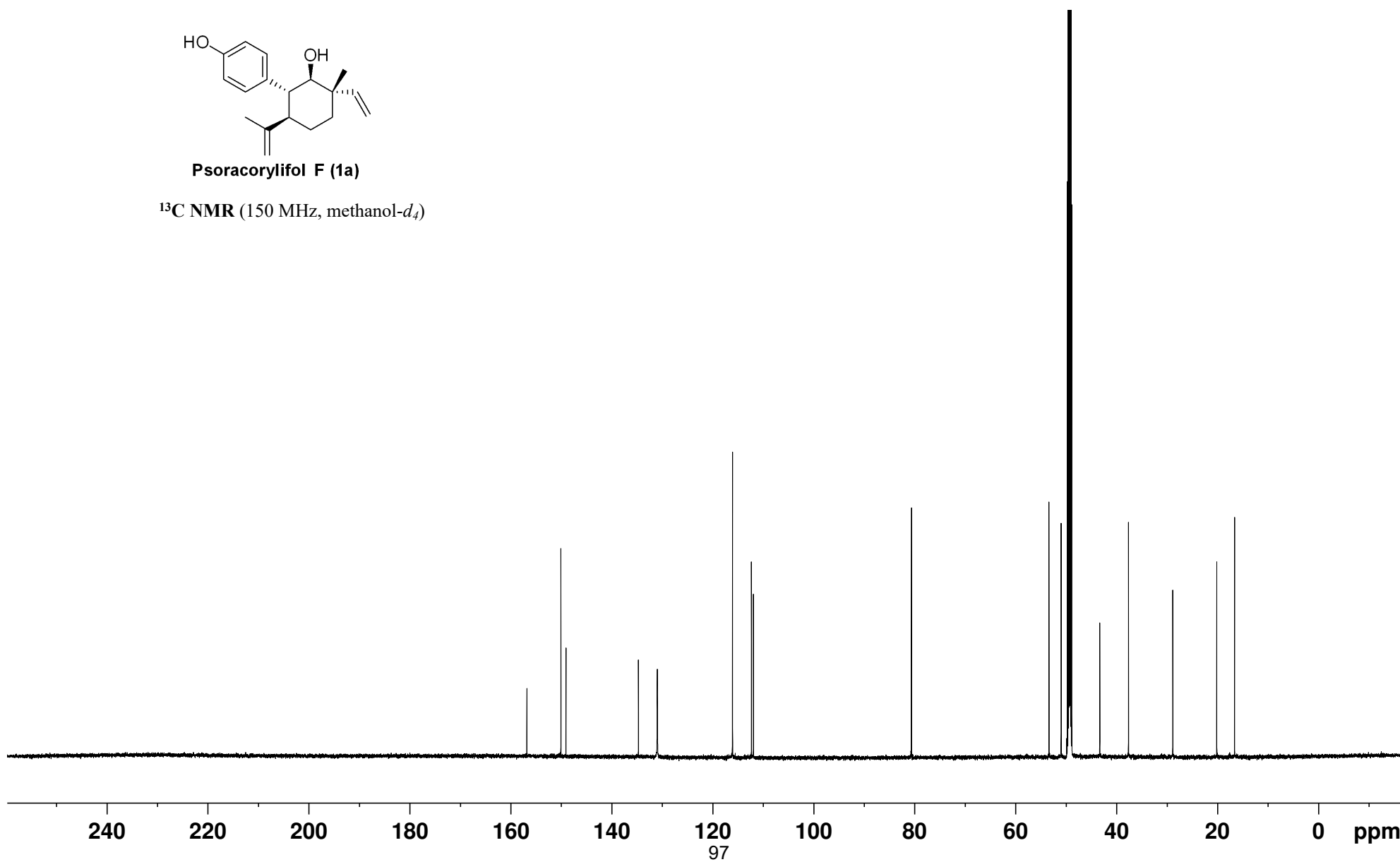


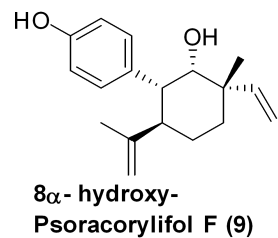


Psoracorylifol F (1a)

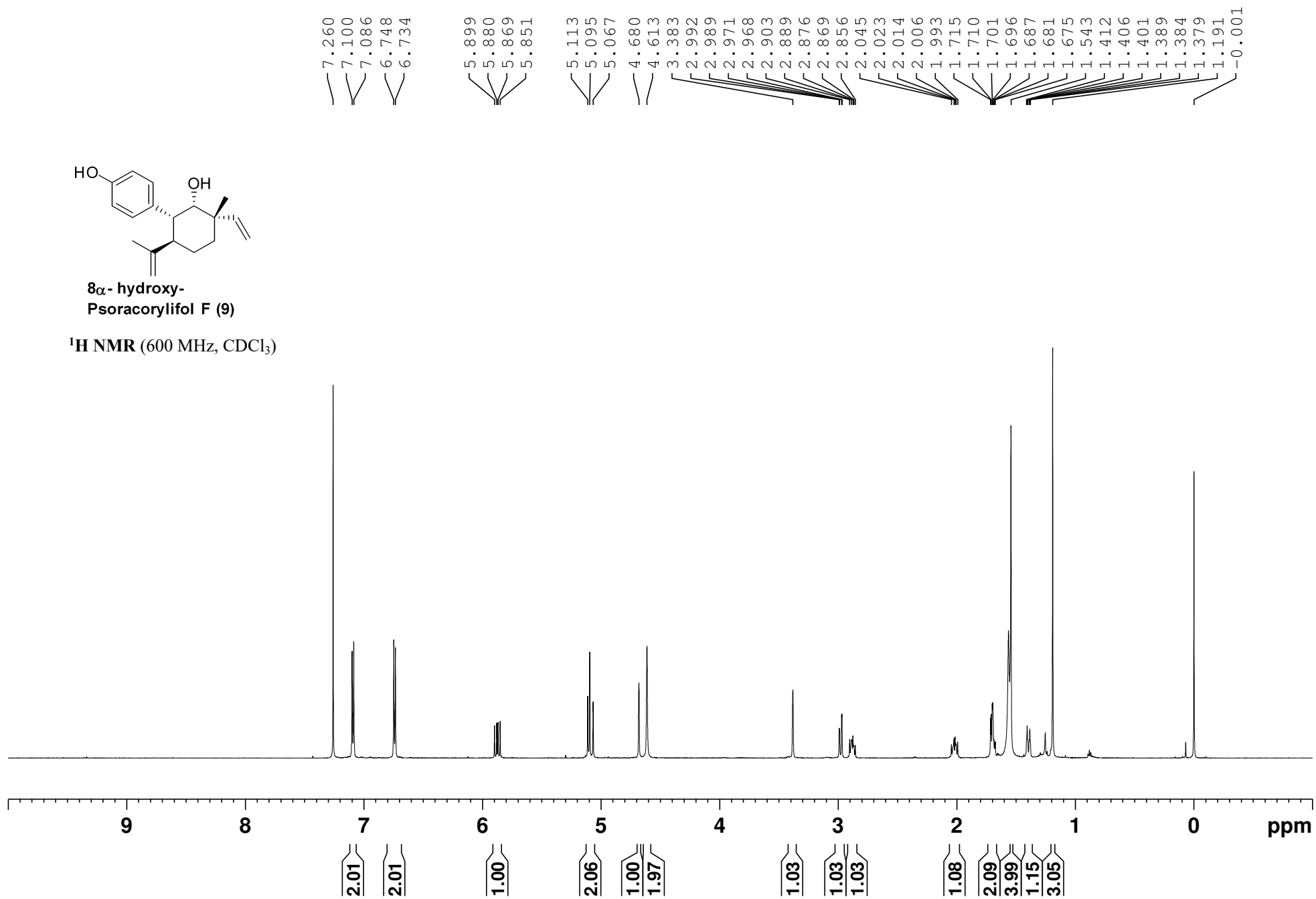
^{13}C NMR (150 MHz, methanol- d_4)

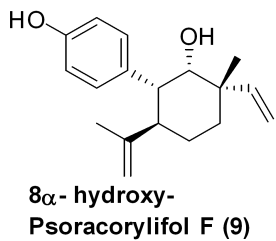
- 156.79
- 150.05
- 149.05
- 134.69
- 130.95
- 116.05
- 112.31
- 111.91
- 80.61
- 53.37
- 50.97
- 49.72
- 49.57
- 49.43
- 49.29
- 49.15
- 49.01
- 48.86
- 43.32
- 37.62
- 28.85
- 20.14
- 16.61



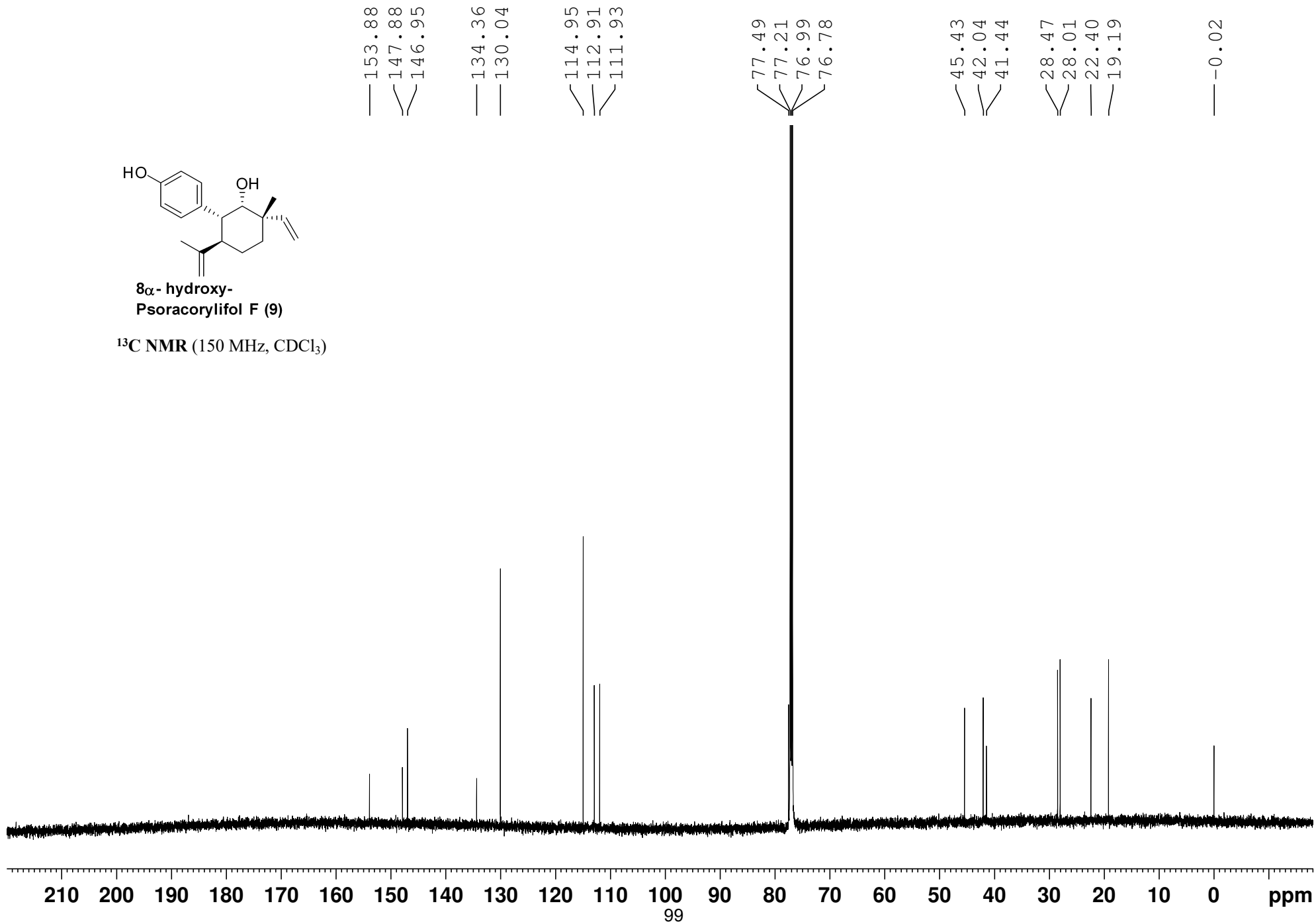


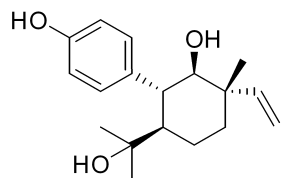
$^1\text{H NMR}$ (600 MHz, CDCl_3)





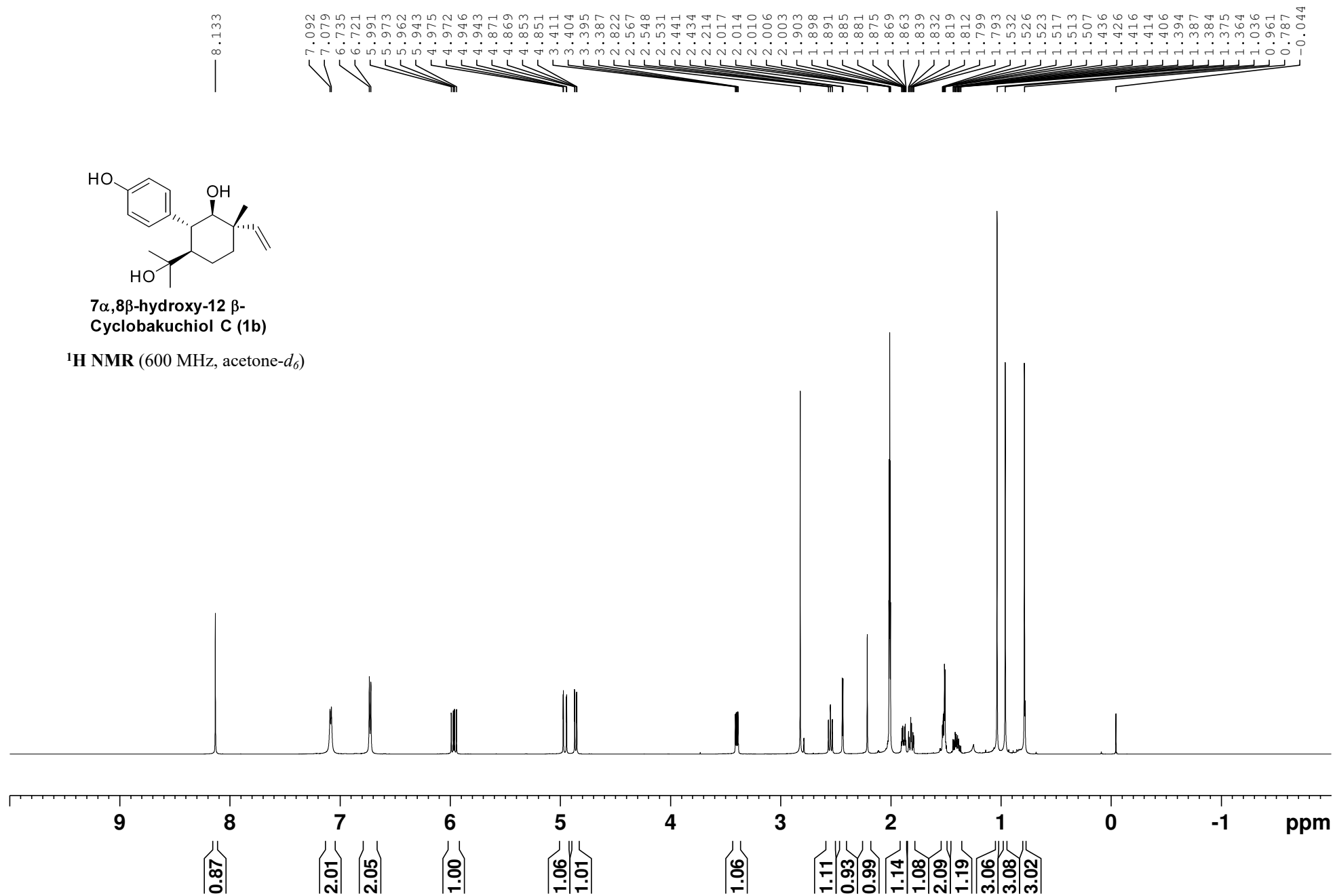
^{13}C NMR (150 MHz, CDCl_3)

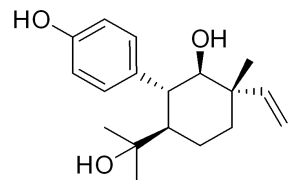




7 α ,8 β -hydroxy-12 β -Cyclobakuchiol C (1b)

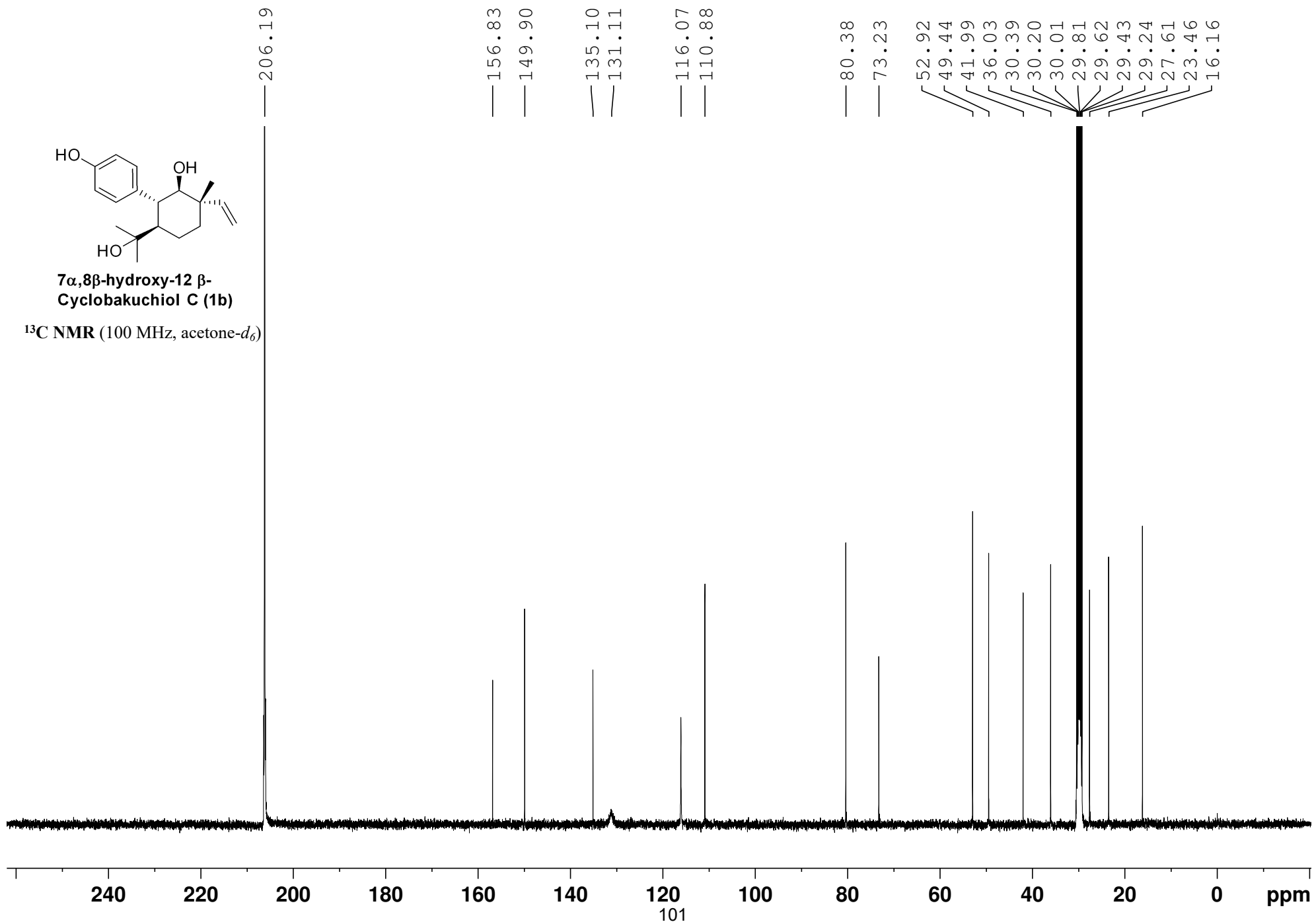
¹H NMR (600 MHz, acetone-*d*₆)

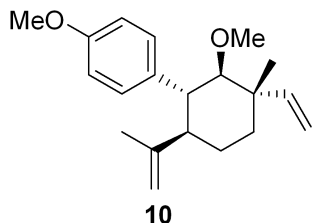




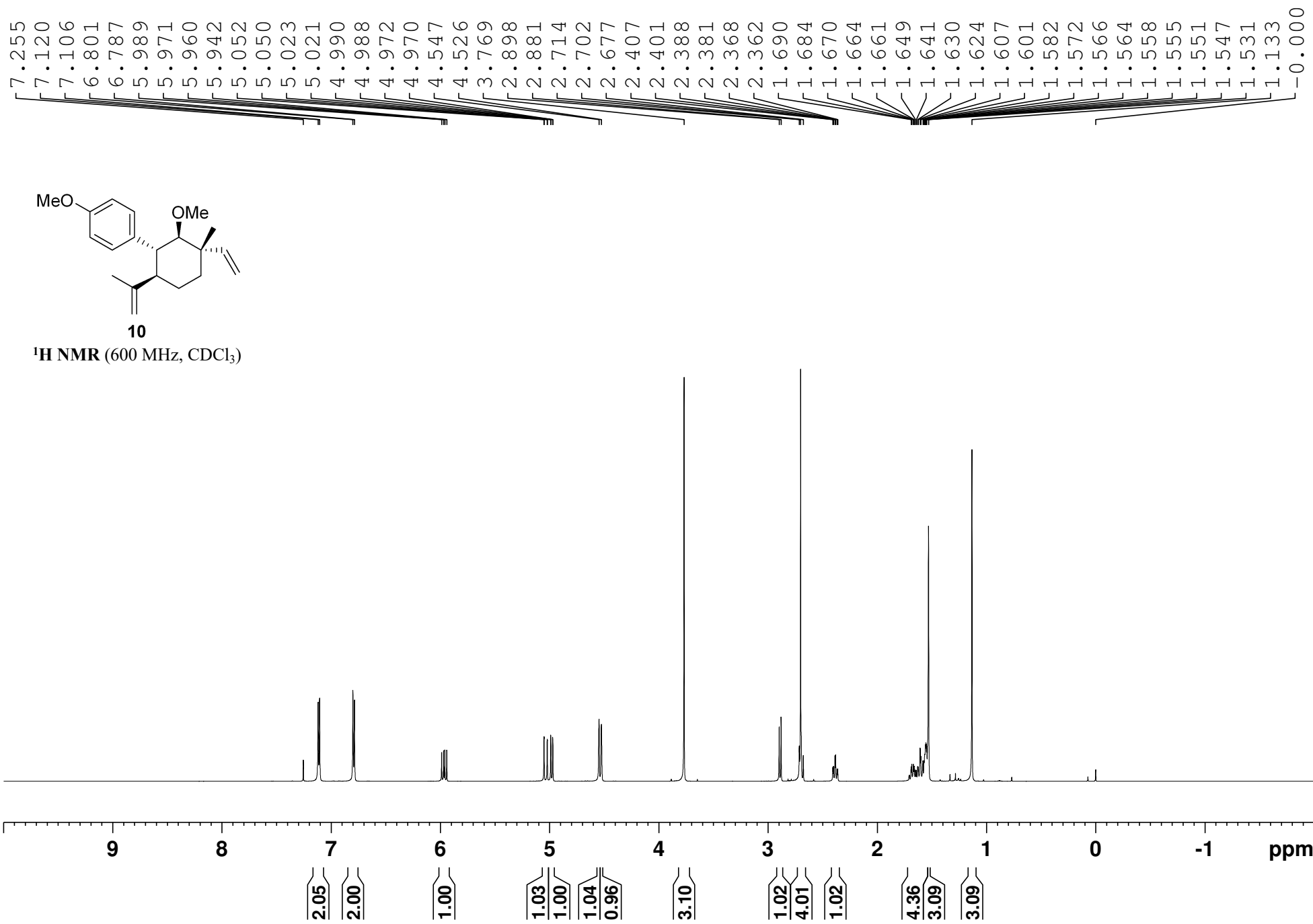
**7 α ,8 β -hydroxy-12 β -
Cyclobakuchiol C (1b)**

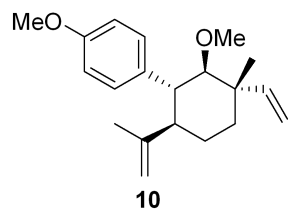
^{13}C NMR (100 MHz, acetone- d_6)





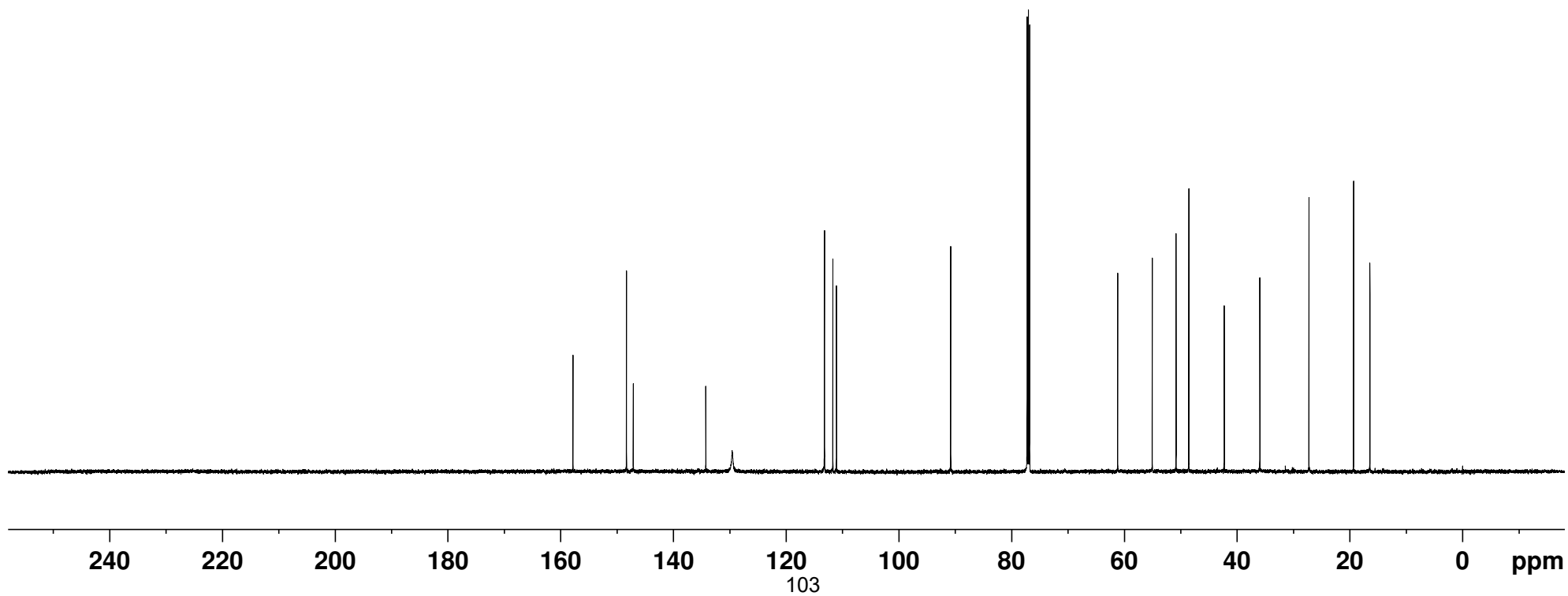
¹H NMR (600 MHz, CDCl₃)

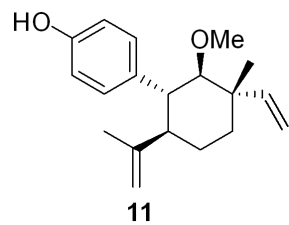




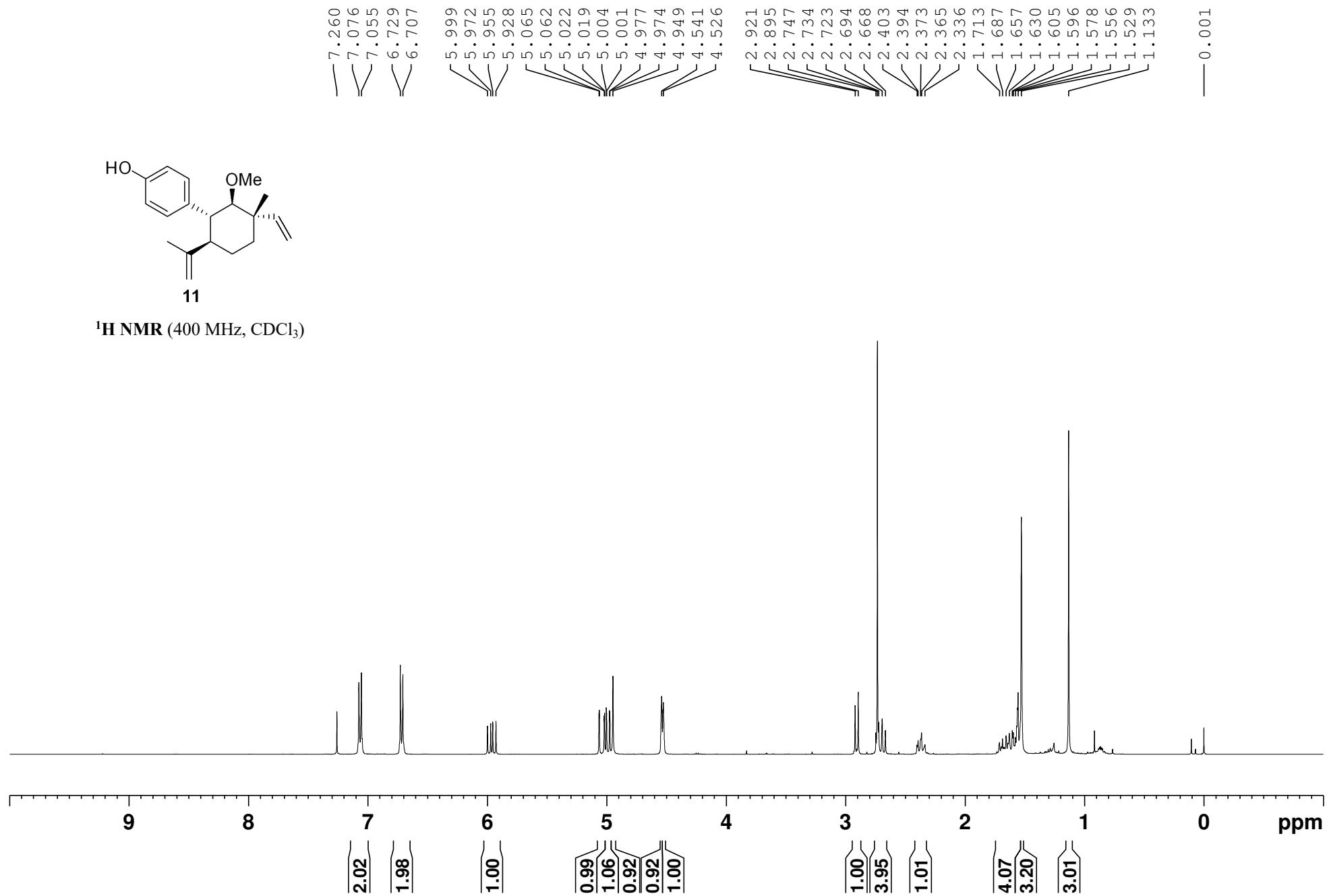
¹³C NMR (150 MHz, CDCl₃)

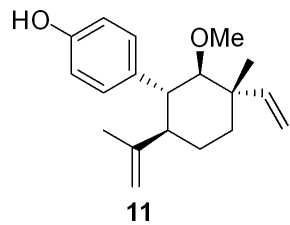
- 157.78
- 148.29
- 147.08
- 134.23
- 129.54
- 113.17
- 111.69
- 111.04
- 90.77
- 77.21
- 77.00
- 76.78
- 61.16
- 55.02
- 50.80
- 48.53
- 42.24
- 35.93
- 27.23
- 19.31
- 16.41





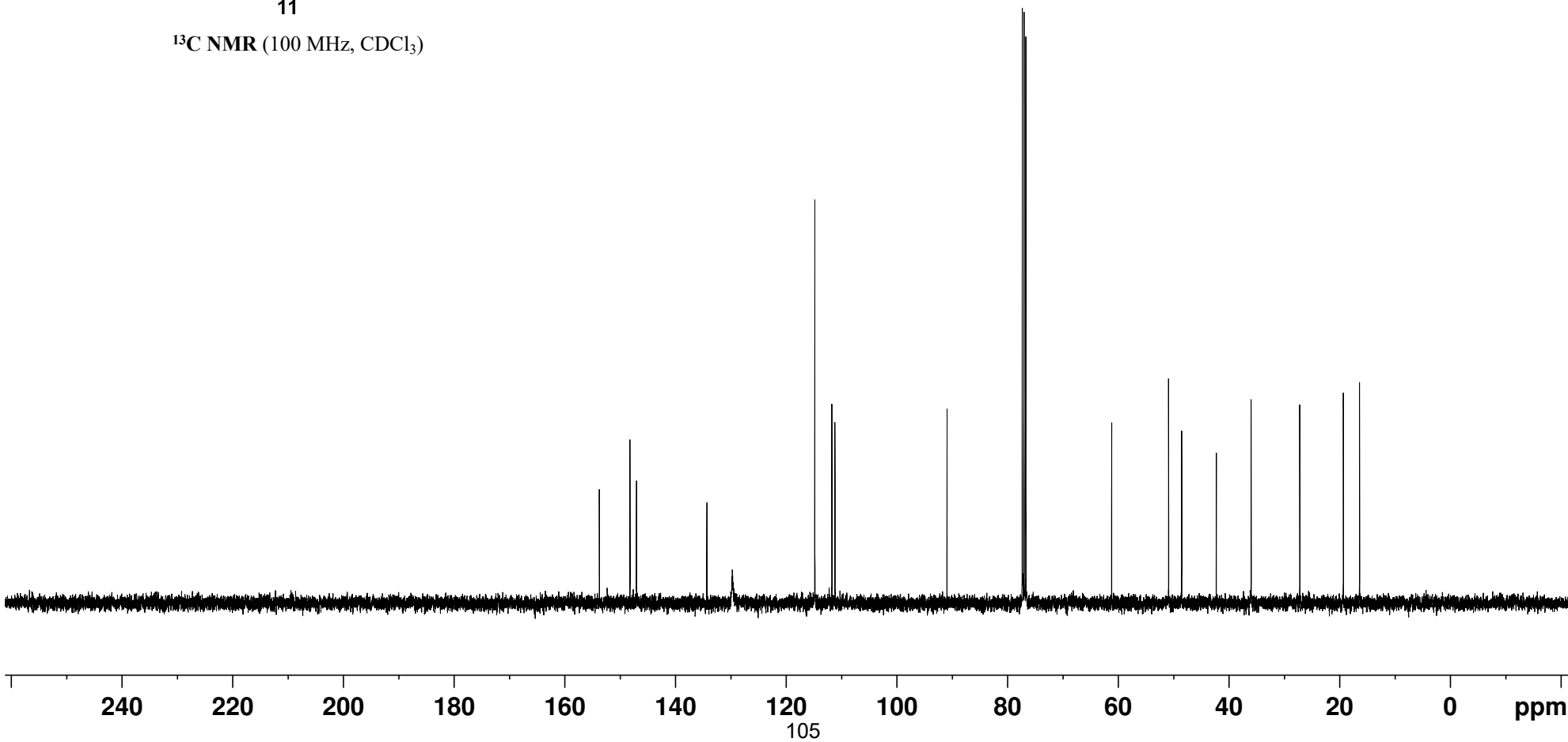
¹H NMR (400 MHz, CDCl₃)



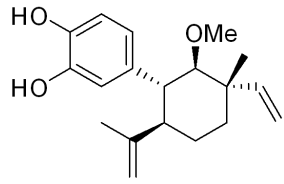


¹³C NMR (100 MHz, CDCl₃)

- 153.75
- 148.21
- 147.03
- 134.31
- 129.72
- 114.81
- 111.73
- 111.16
- 90.92
- 77.31
- 77.00
- 76.68
- 61.18
- 50.89
- 48.52
- 42.26
- 35.98
- 27.18
- 19.32
- 16.38

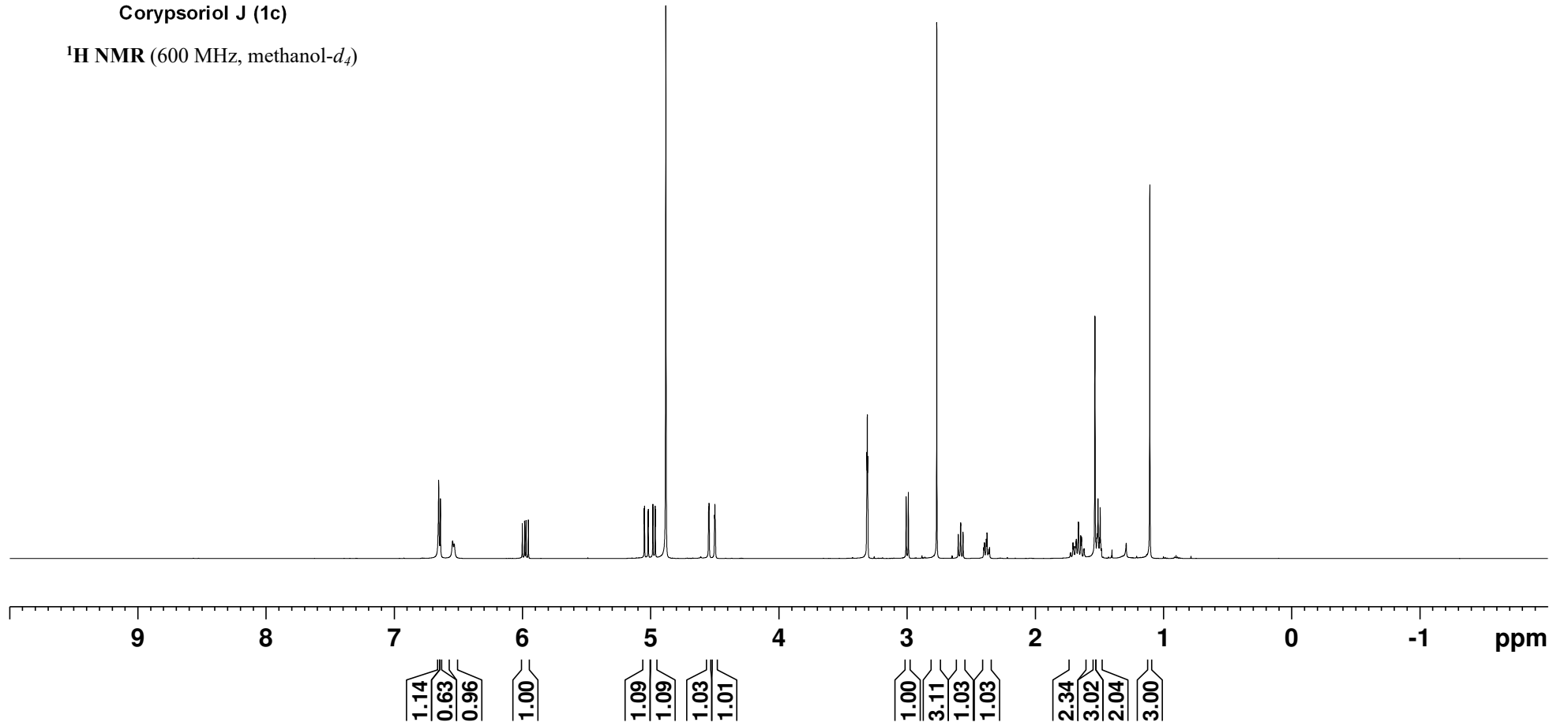


6.654
6.640
6.545
6.533
6.001
5.983
5.972
5.954
5.050
5.048
5.020
5.018
4.983
4.981
4.965
4.963
4.882
4.547
4.545
4.501
4.499
3.315
3.313
3.310
3.307
3.305
3.007
2.990
2.768
2.601
2.581
2.564
2.402
2.396
2.382
2.376
2.357
1.706
1.699
1.683
1.680
1.667
1.663
1.645
1.639
1.534
1.519
1.516
1.510
1.505
1.499
1.493
1.106



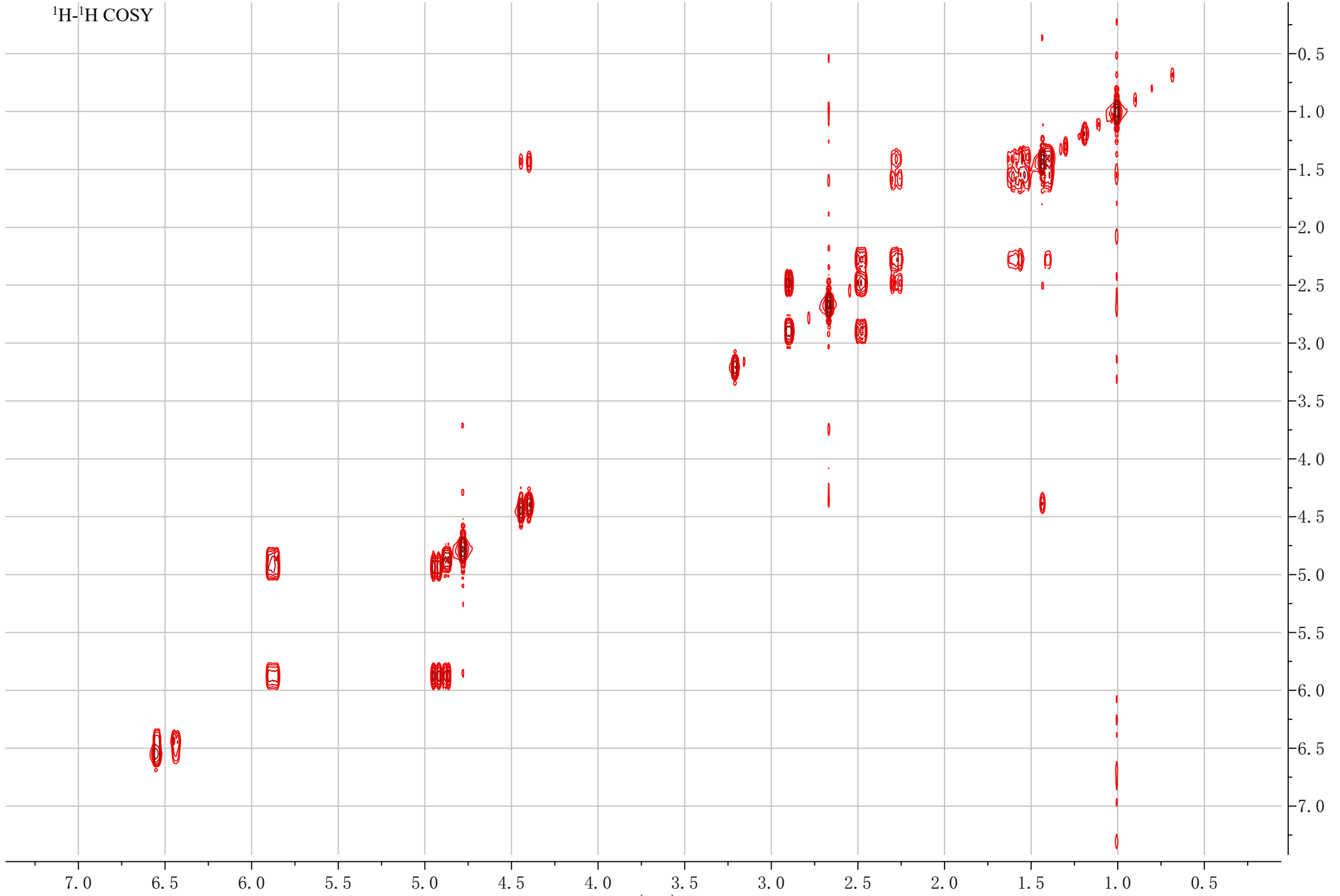
proposed
Corypsoriol J (1c)

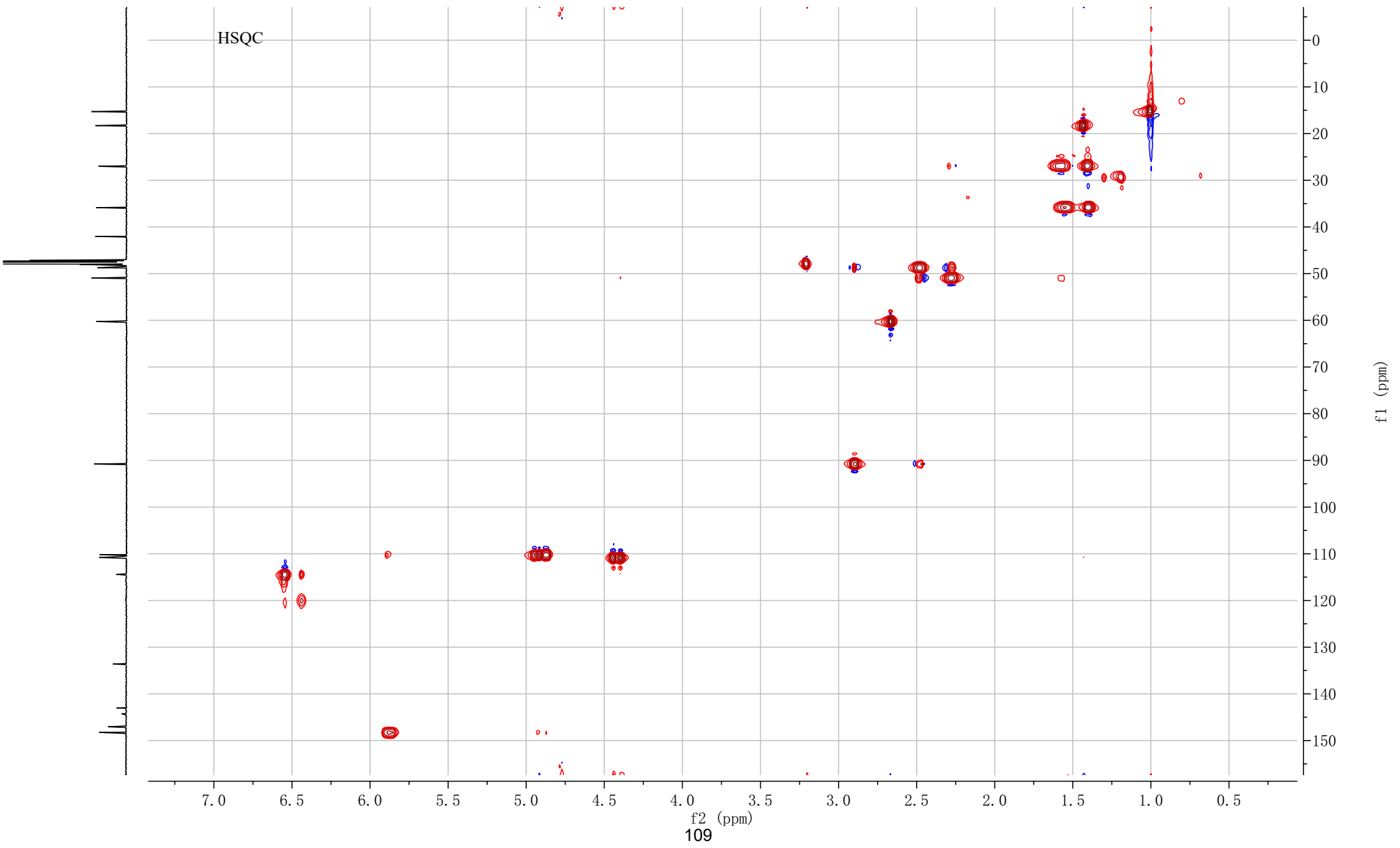
¹H NMR (600 MHz, methanol-*d*₄)

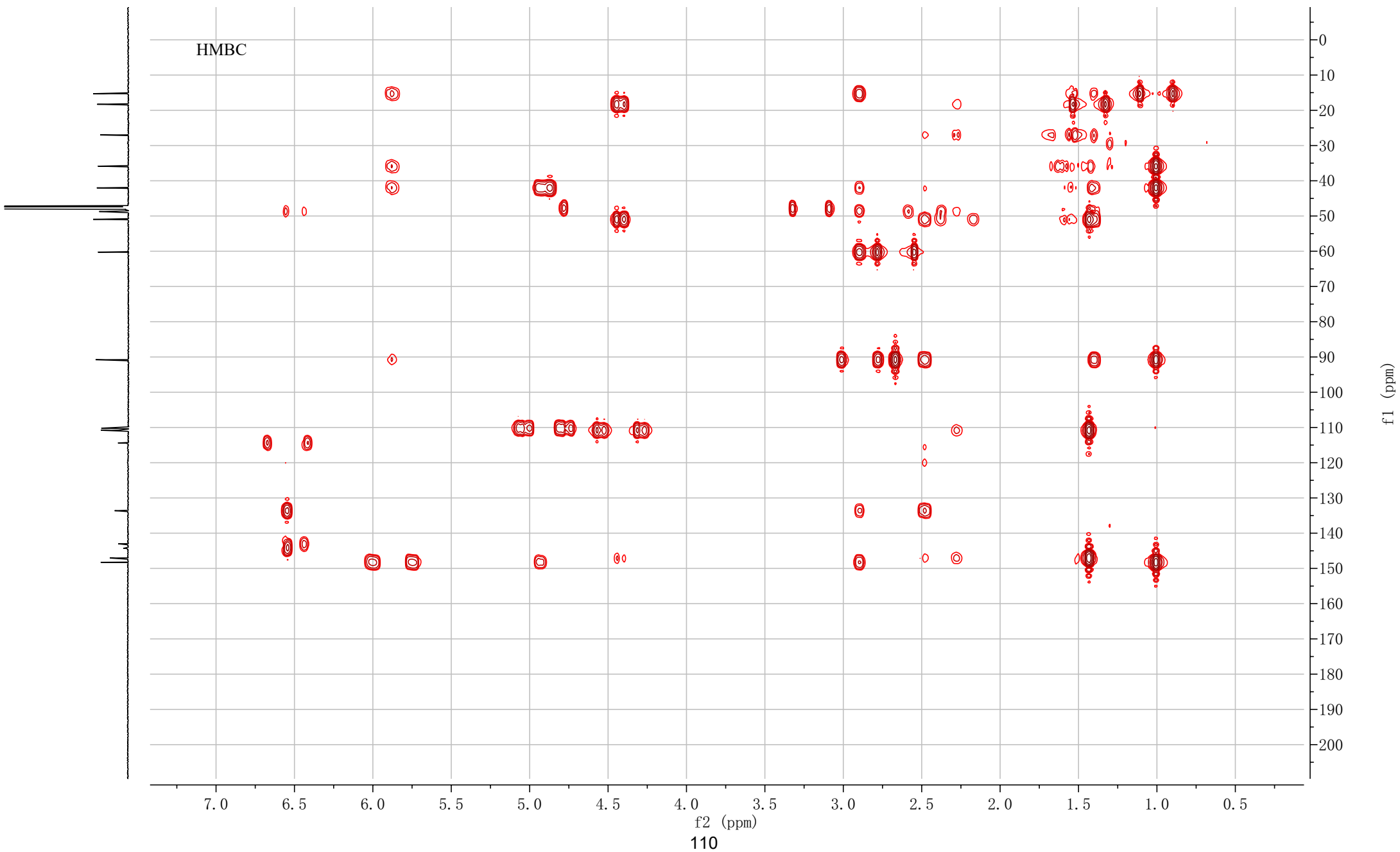


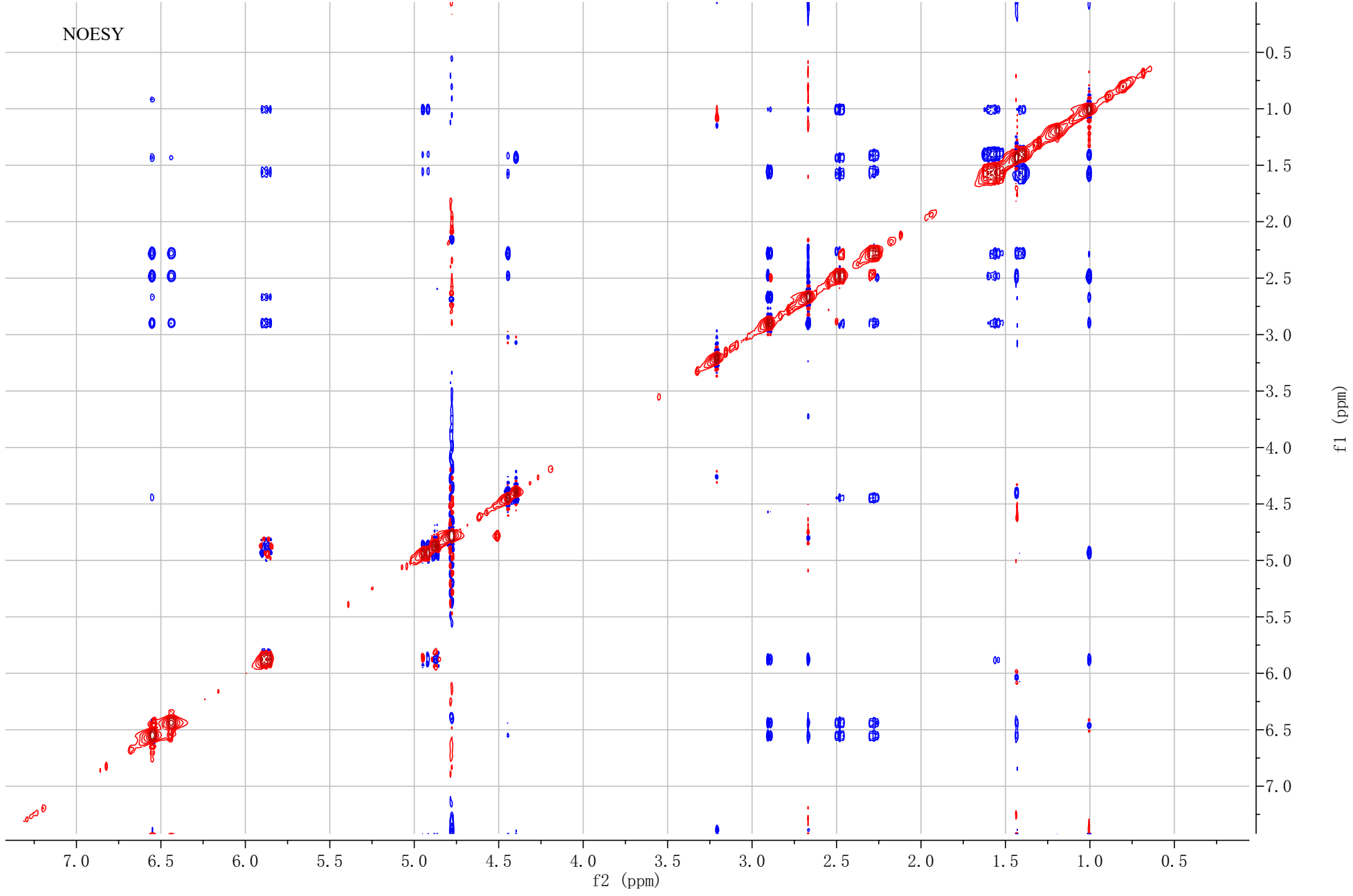
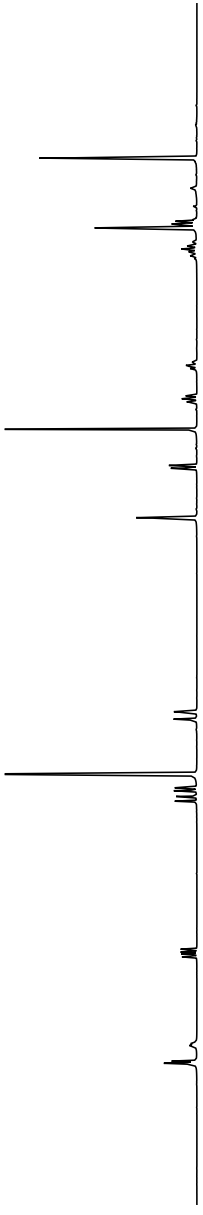


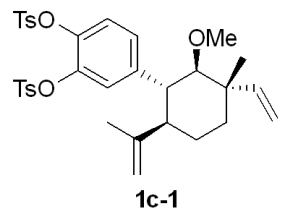
^1H - ^1H COSY



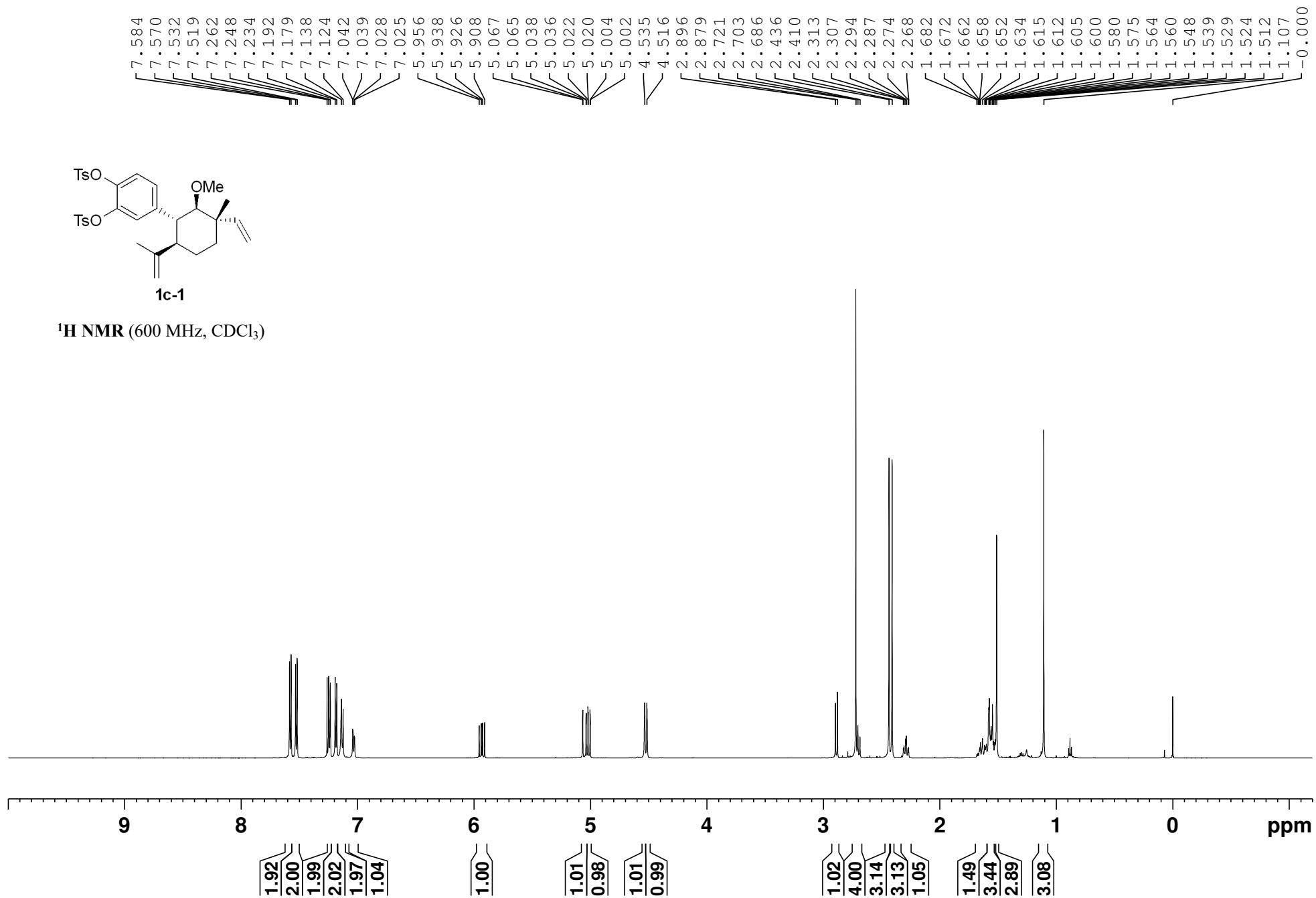




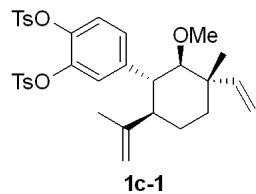
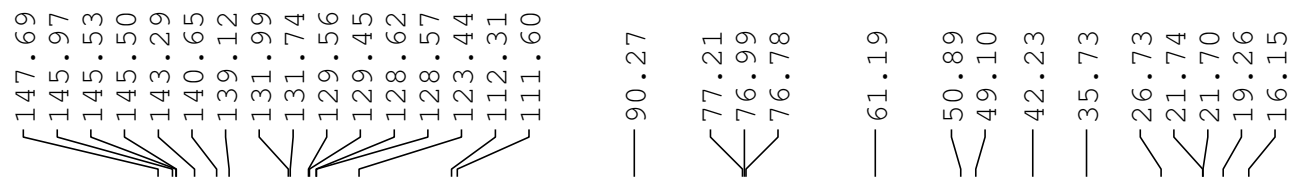




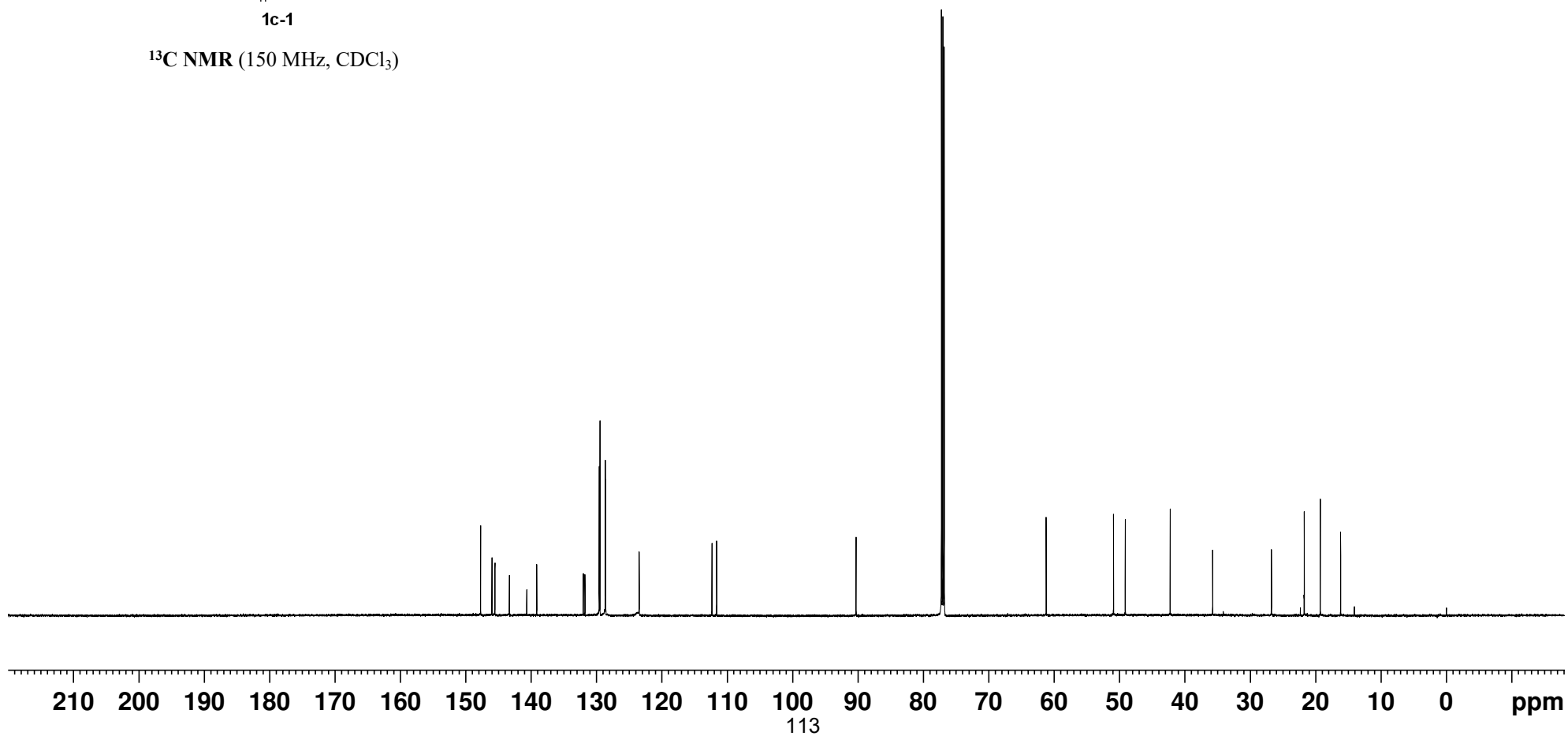
¹H NMR (600 MHz, CDCl₃)

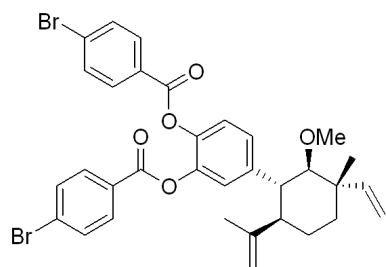


¹³C NMR (150 MHz, CDCl₃)



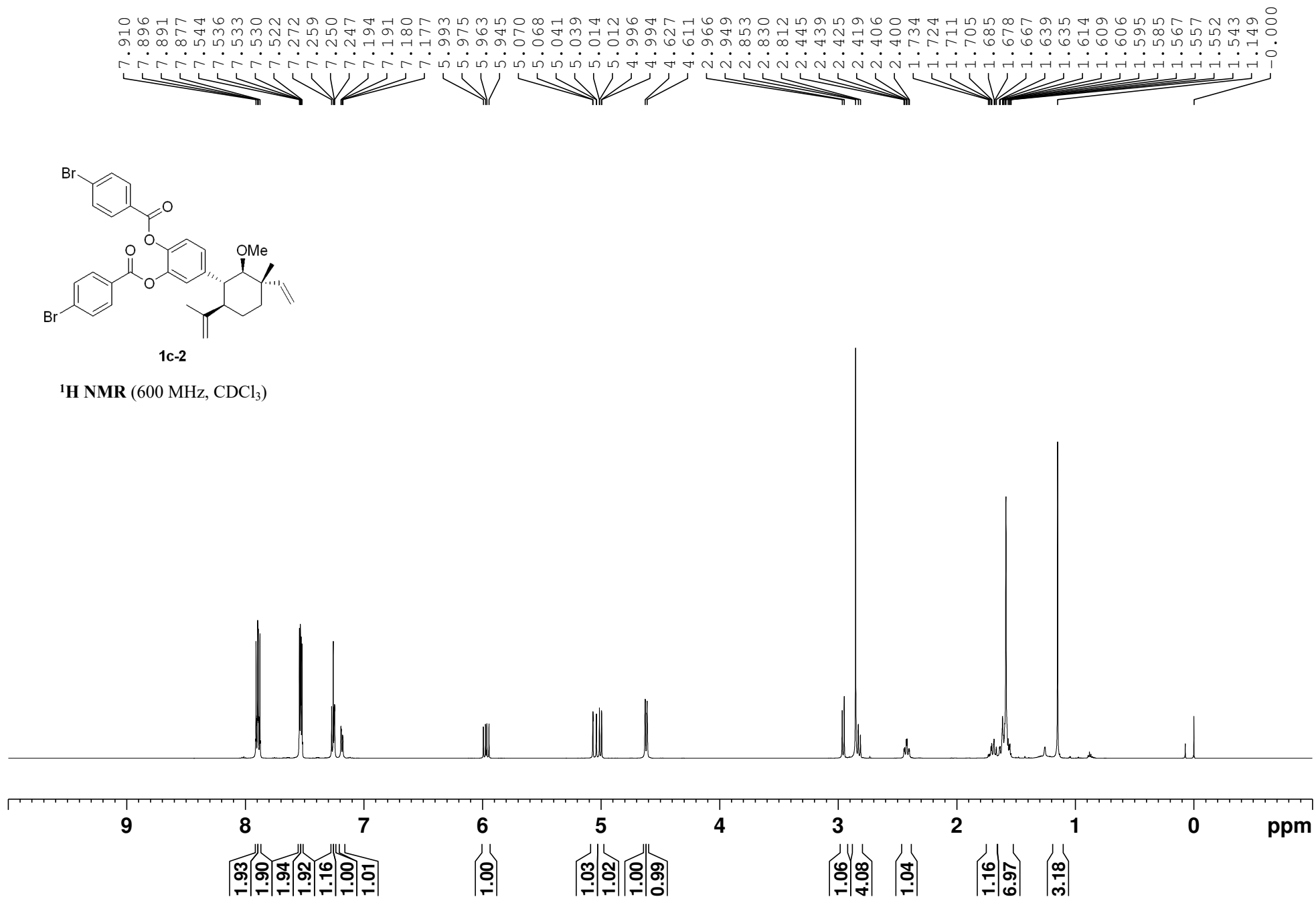
¹³C NMR (150 MHz, CDCl₃)





1c-2

¹H NMR (600 MHz, CDCl₃)



^{13}C NMR (150 MHz, CDCl_3)

163.48
147.91
146.23
141.70
140.26
131.93
131.47
131.45
128.97
127.76
122.47
112.42
111.39

90.60

77.21
77.00
76.79

61.44

50.58
49.13

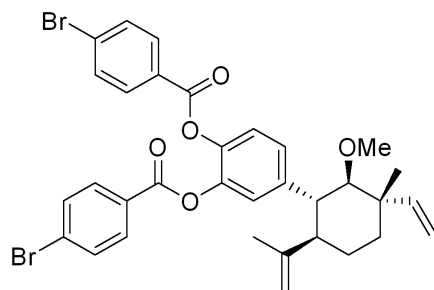
42.28

35.82

27.09

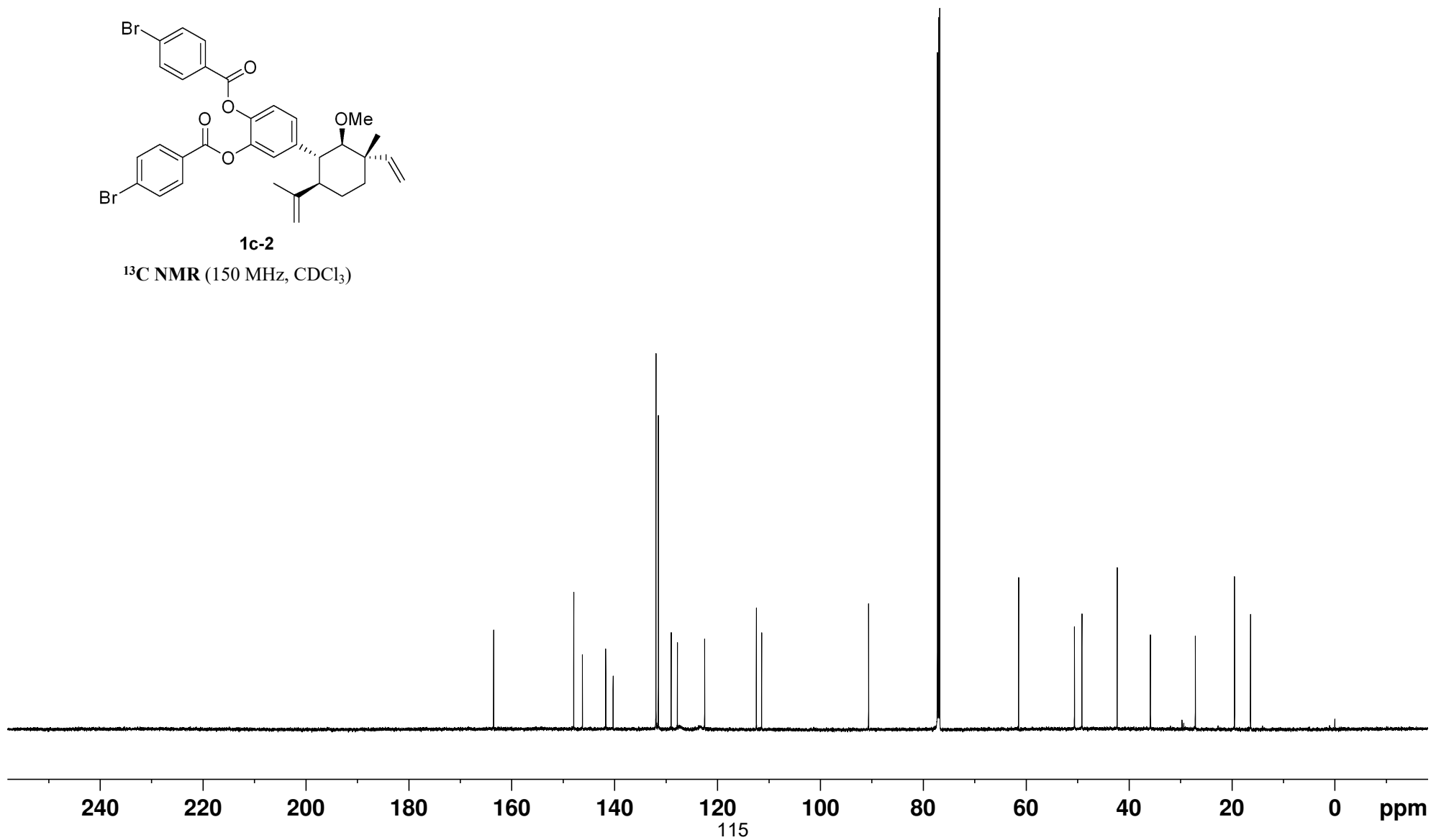
19.49

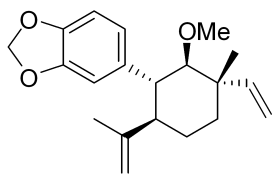
16.36



1c-2

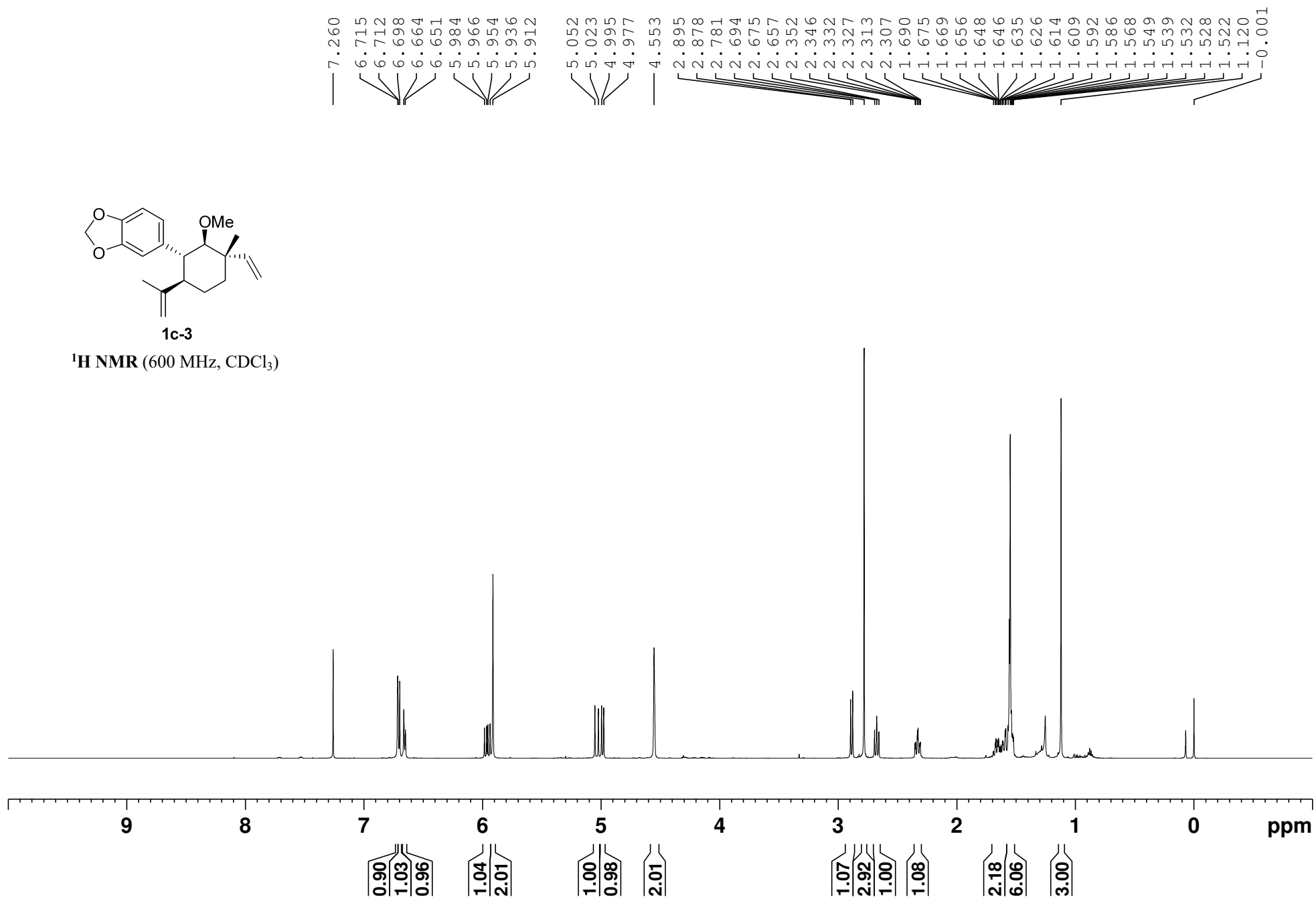
^{13}C NMR (150 MHz, CDCl_3)

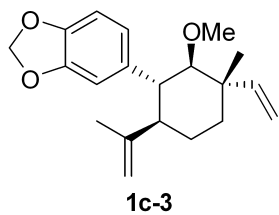




1c-3

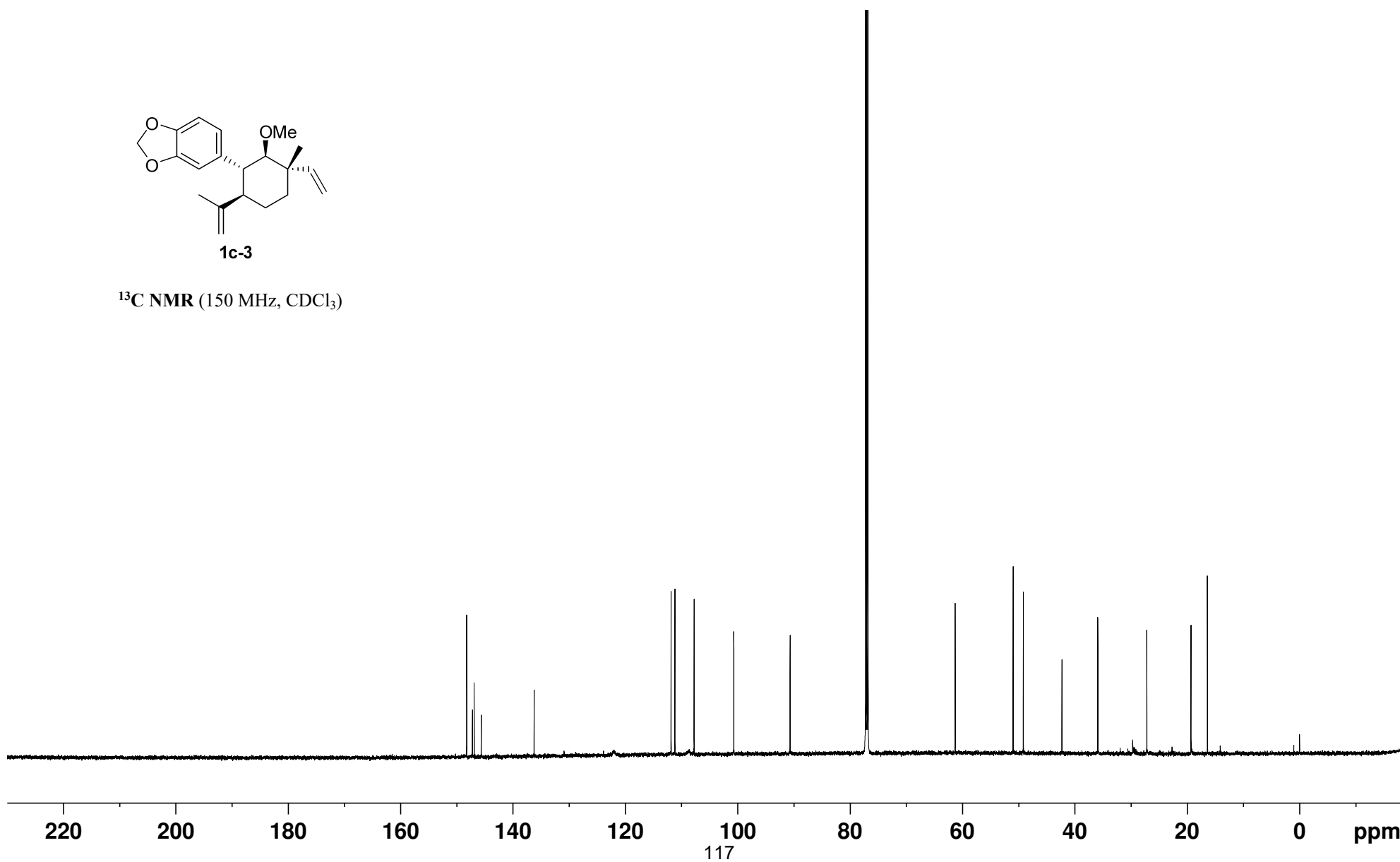
¹H NMR (600 MHz, CDCl₃)

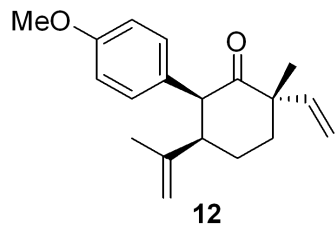




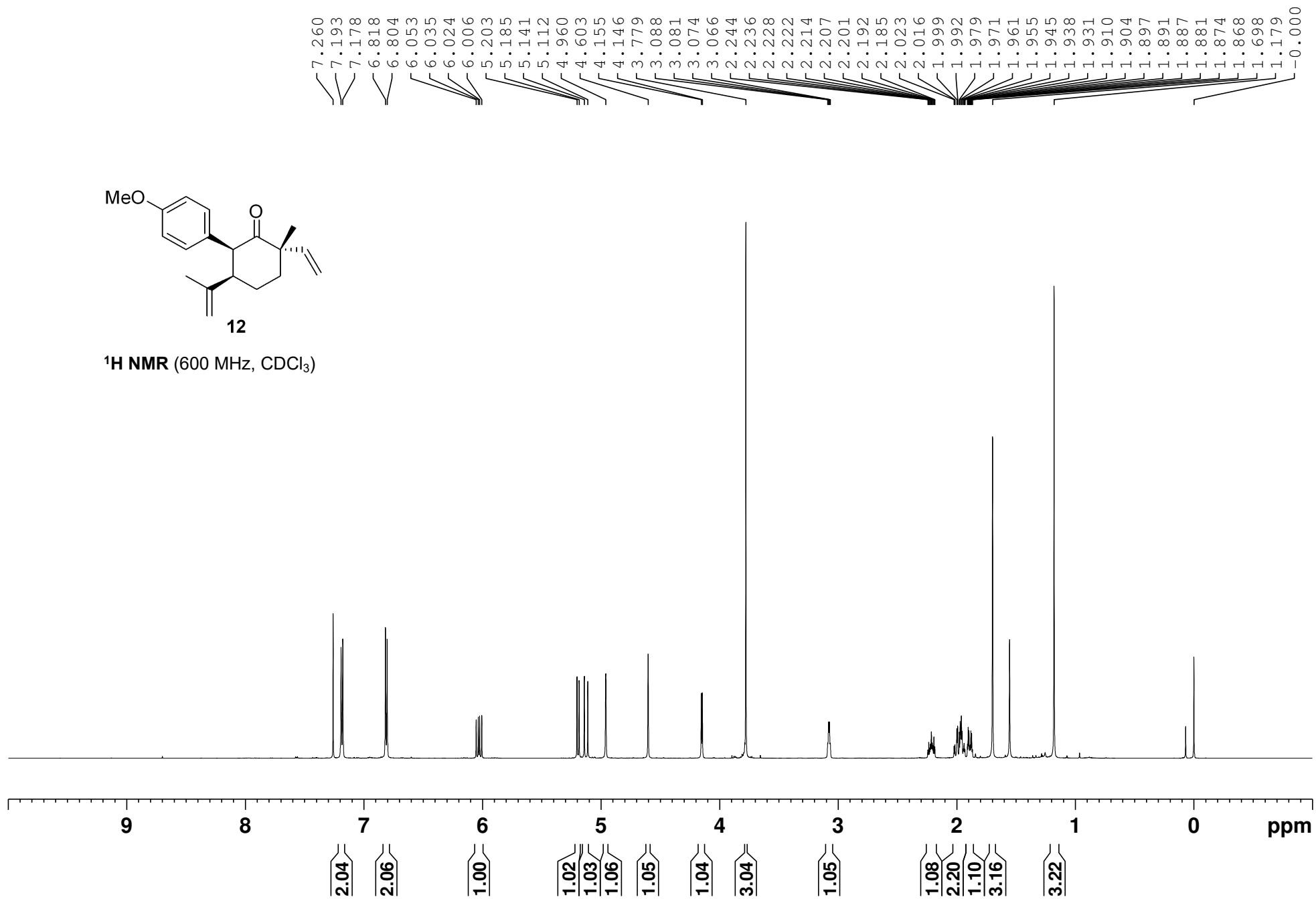
¹³C NMR (150 MHz, CDCl₃)

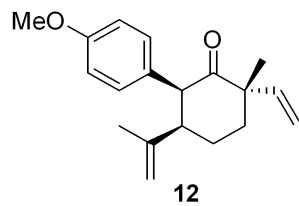
148.22
147.20
146.89
145.62
136.21
122.13
111.83
111.15
108.72
107.74
100.67
90.66
77.21
77.00
76.78
61.27
50.97
49.15
42.28
35.89
27.17
19.30
16.38



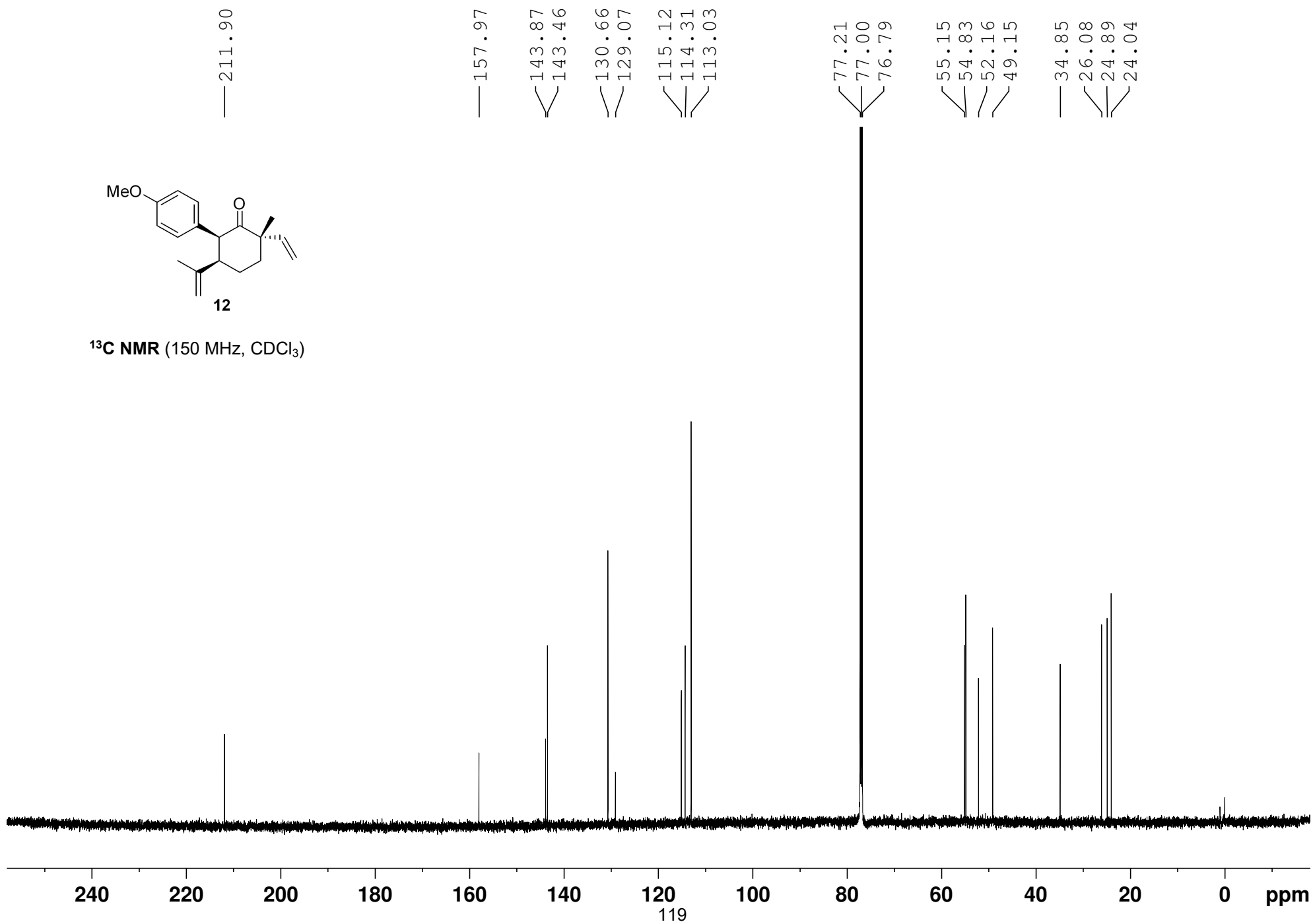


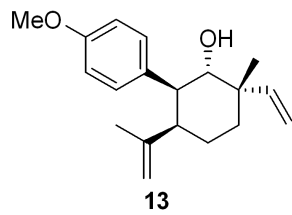
¹H NMR (600 MHz, CDCl₃)



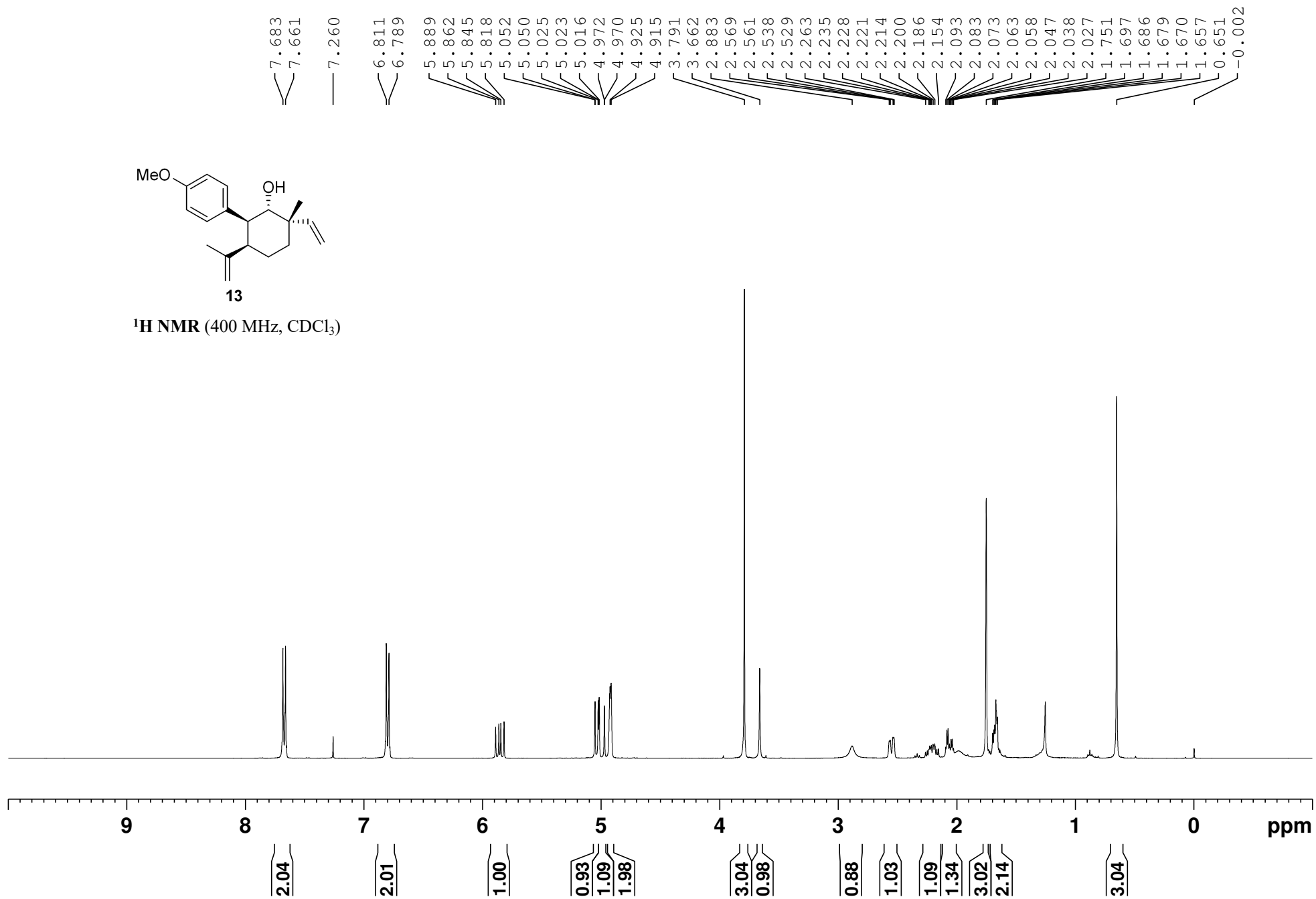


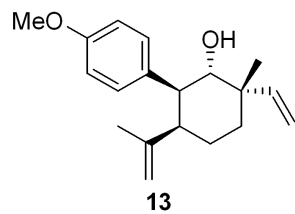
¹³C NMR (150 MHz, CDCl₃)





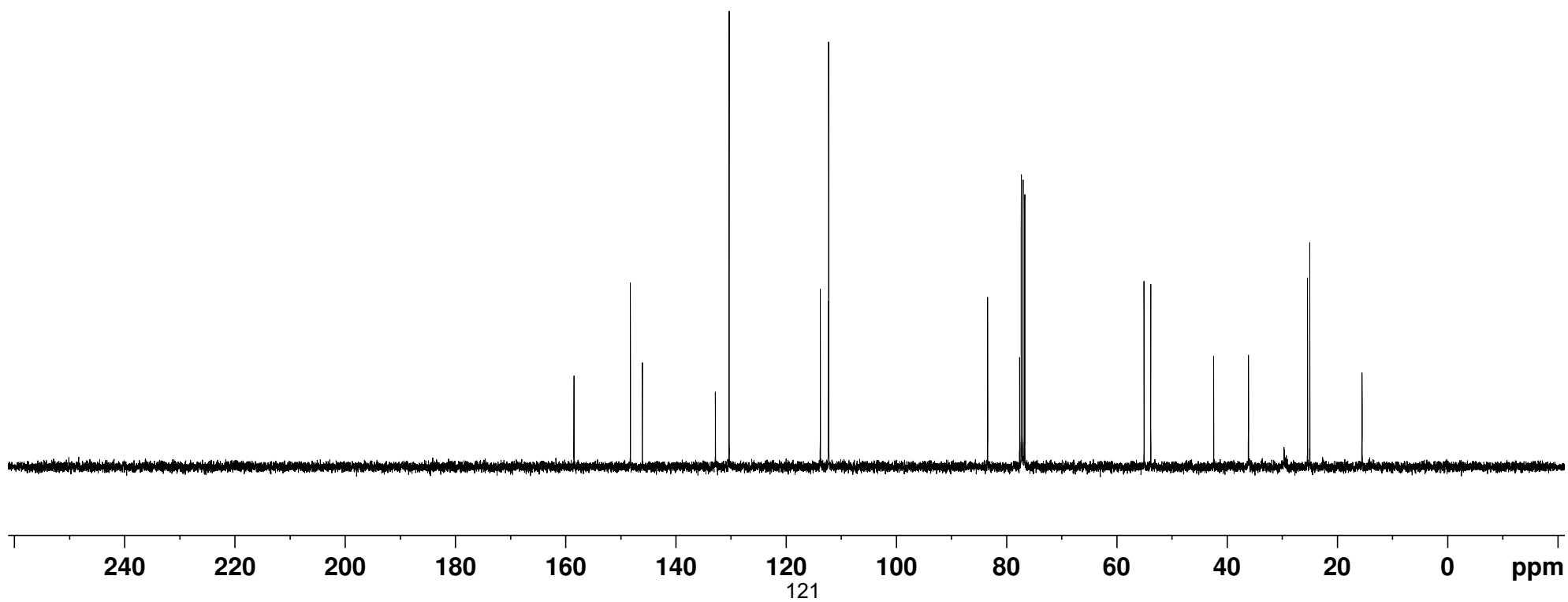
¹H NMR (400 MHz, CDCl₃)

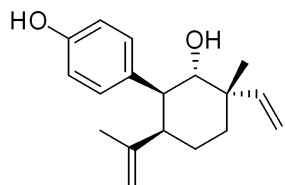




¹³C NMR (100 MHz, CDCl₃)

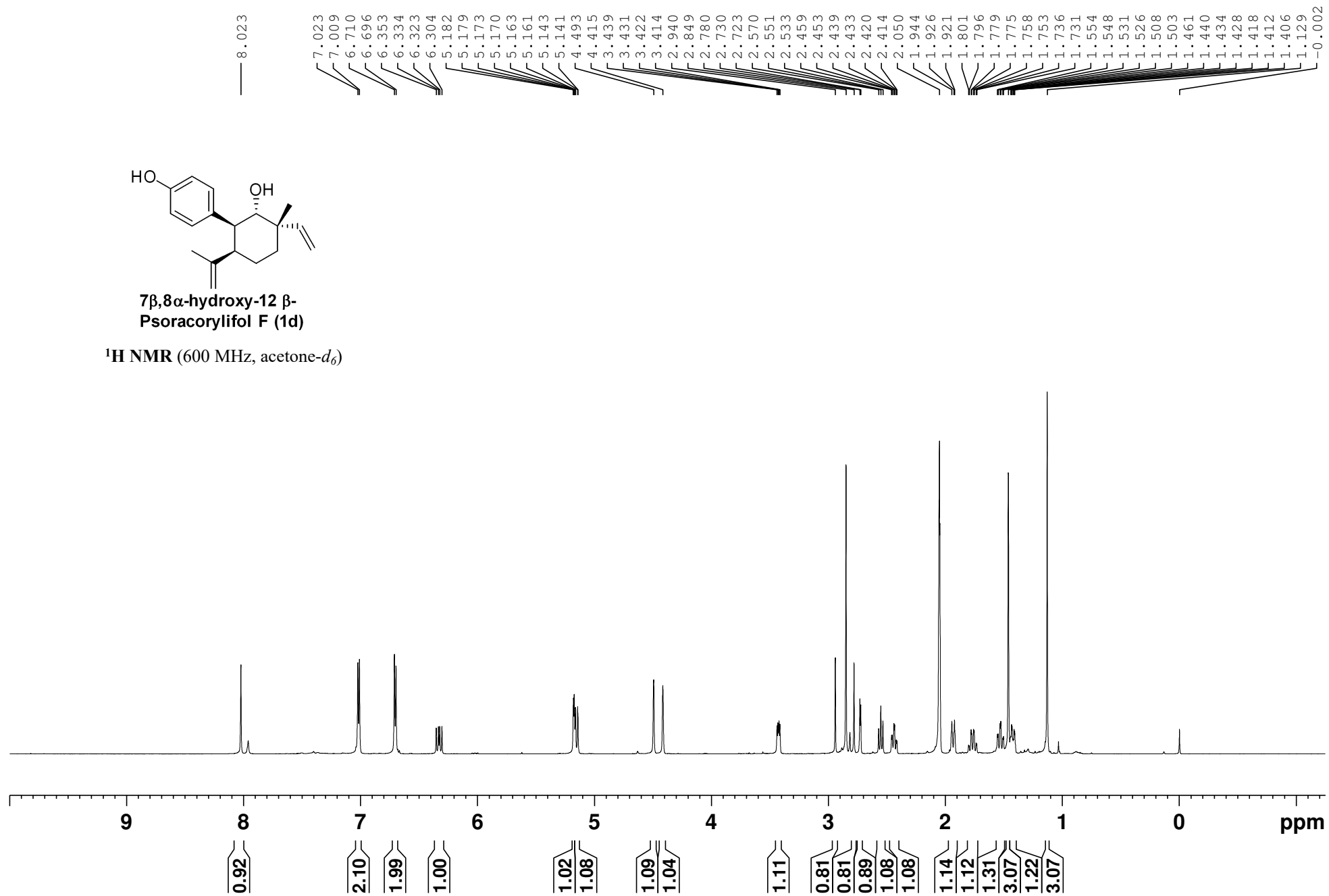
— 158.46
— 148.22
— 146.05
— 132.82
— 130.32
— 113.78
— 112.33
— 112.25
— 83.43
— 77.61
— 77.32
— 77.00
— 76.68
— 55.04
— 53.82
— 42.41
— 36.10
— 25.38
— 24.98
— 15.49

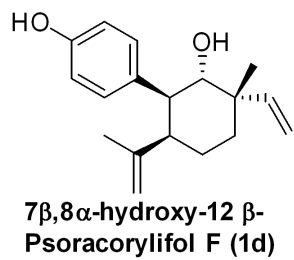




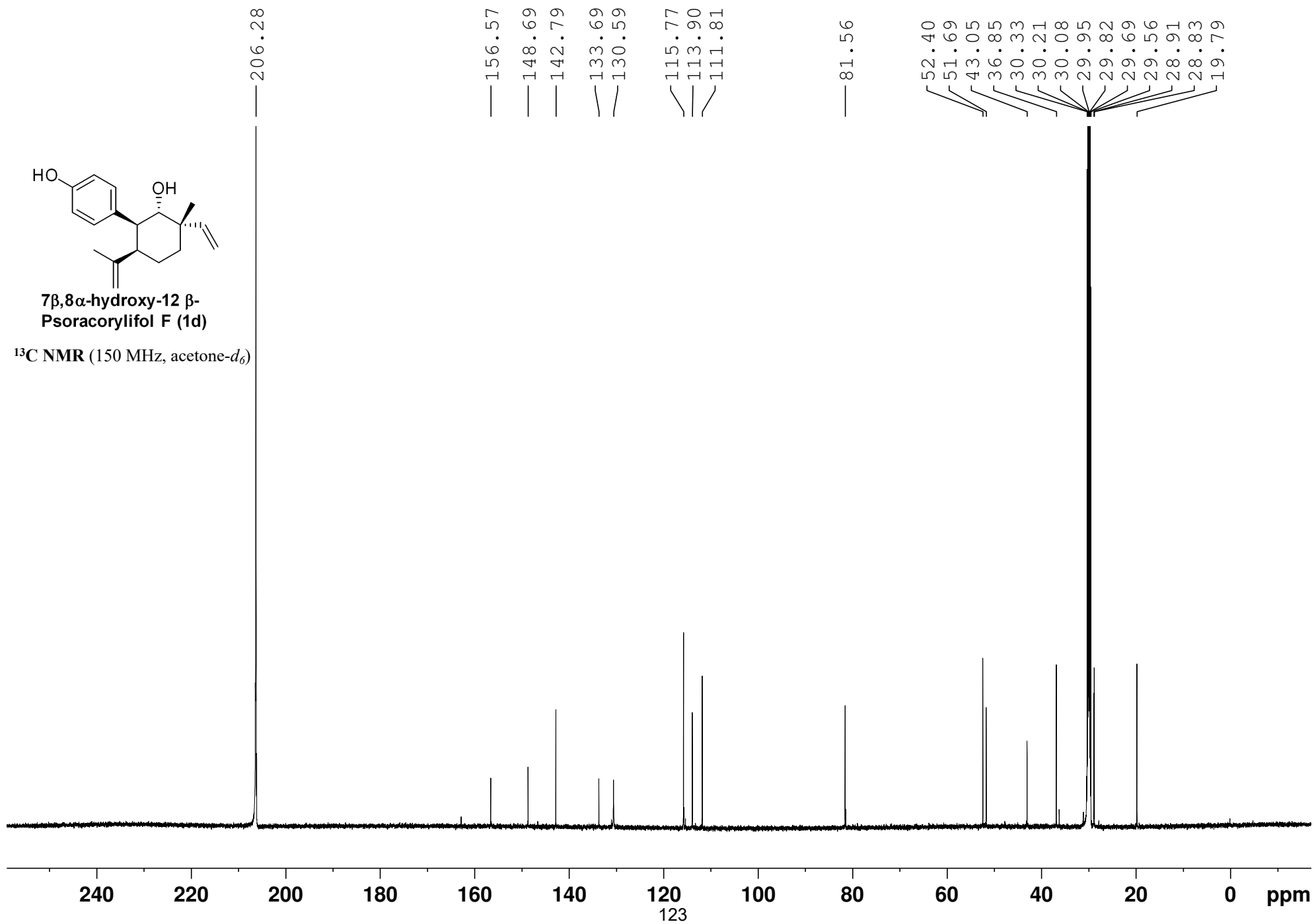
7 β ,8 α -hydroxy-12 β -
Psoracorylifol F (1d)

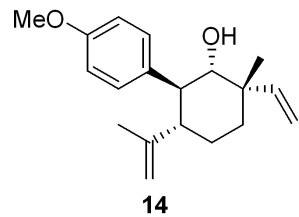
^1H NMR (600 MHz, acetone- d_6)



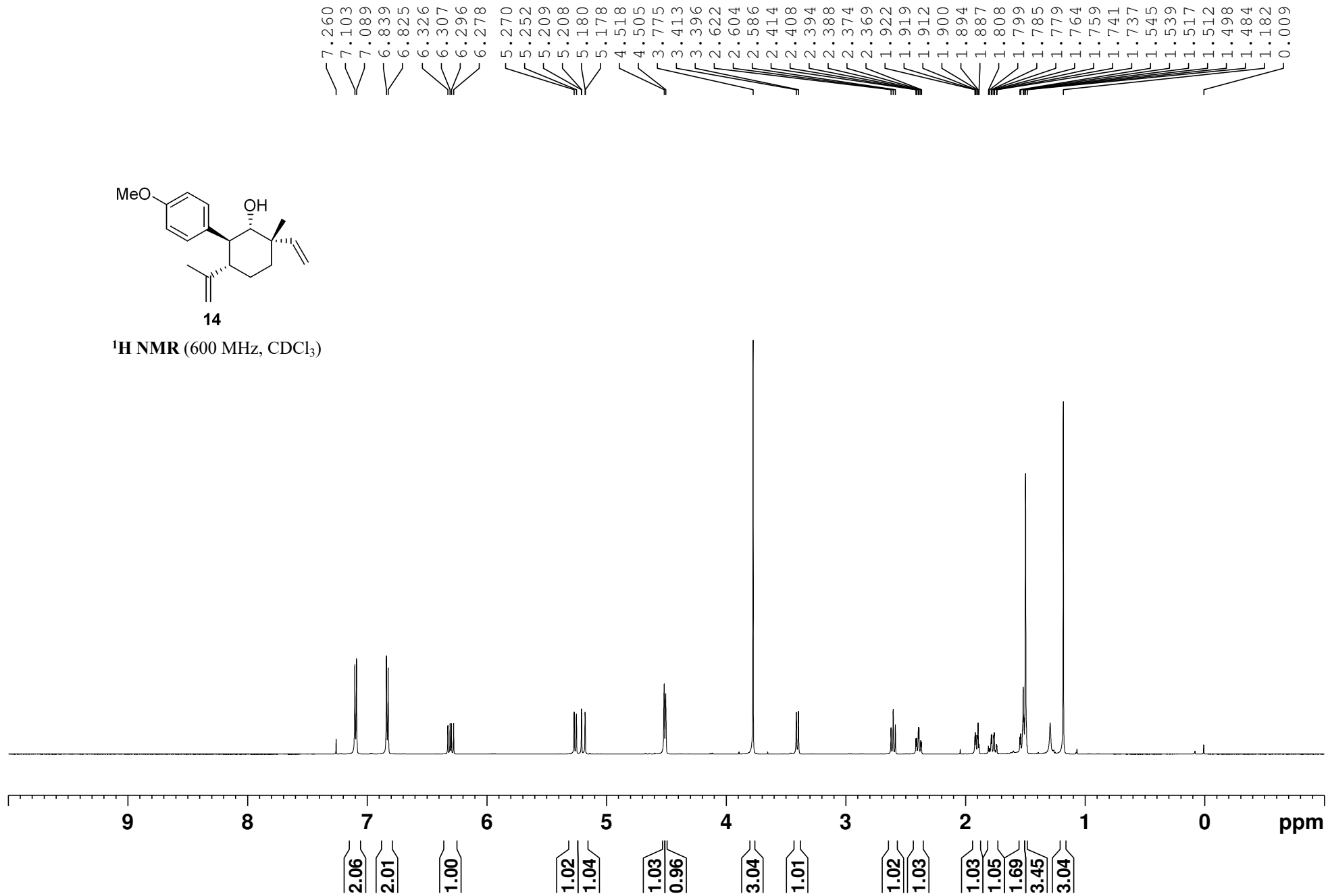


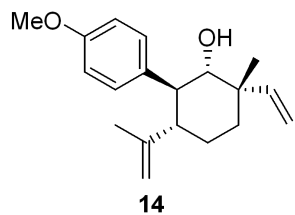
^{13}C NMR (150 MHz, acetone- d_6)





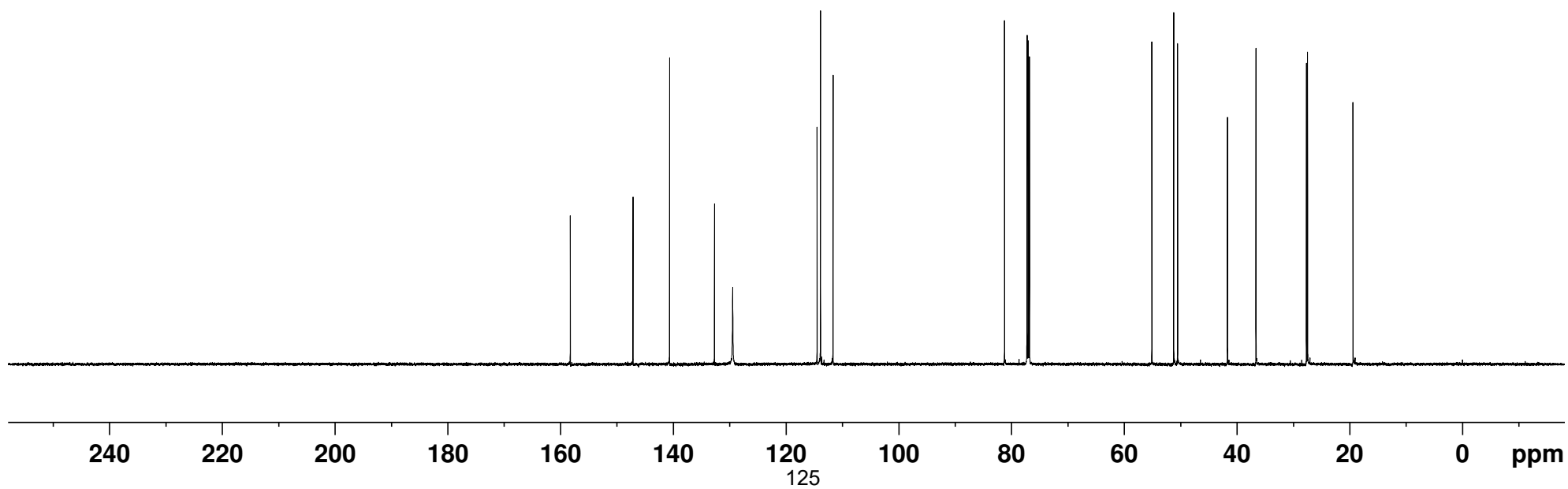
¹H NMR (600 MHz, CDCl₃)

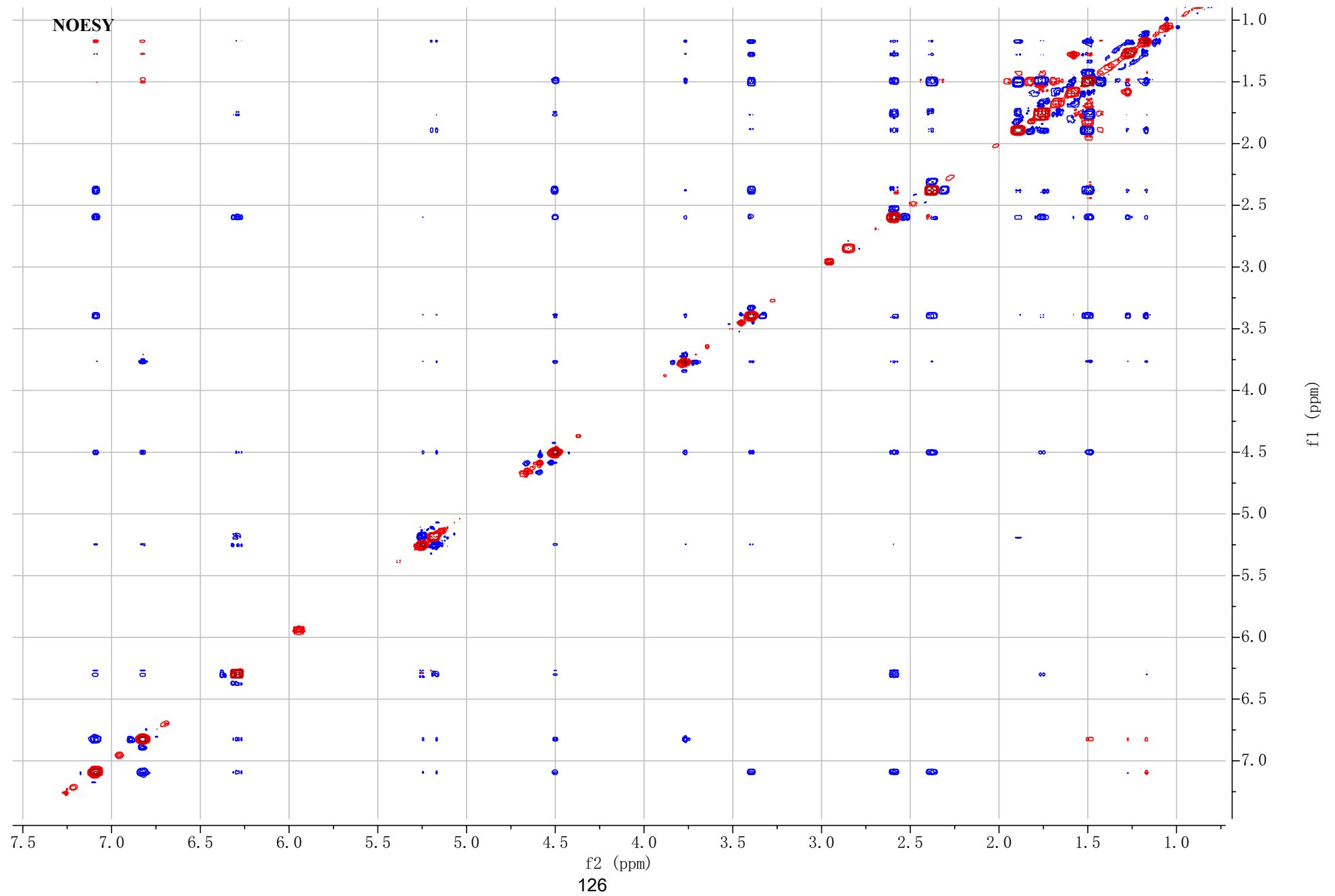
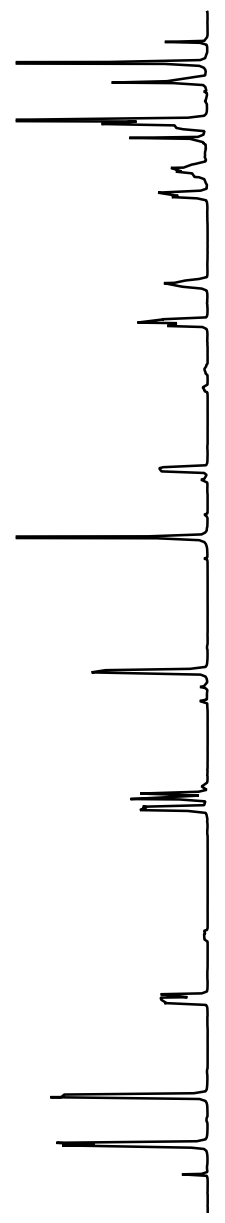
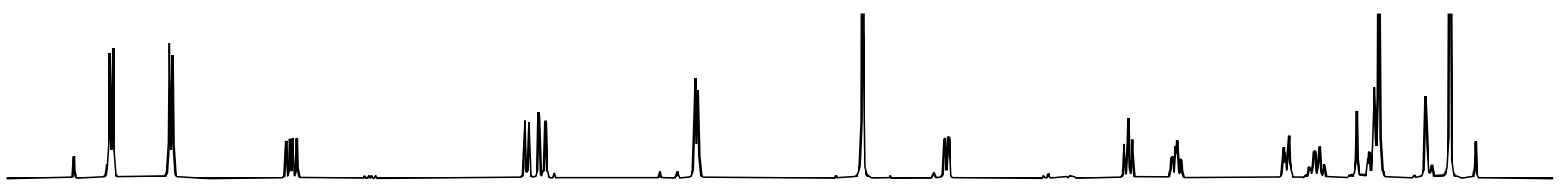


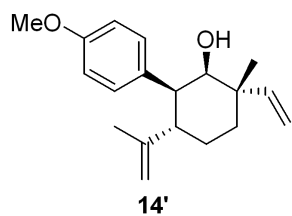


¹³C NMR (150 MHz, CDCl₃)

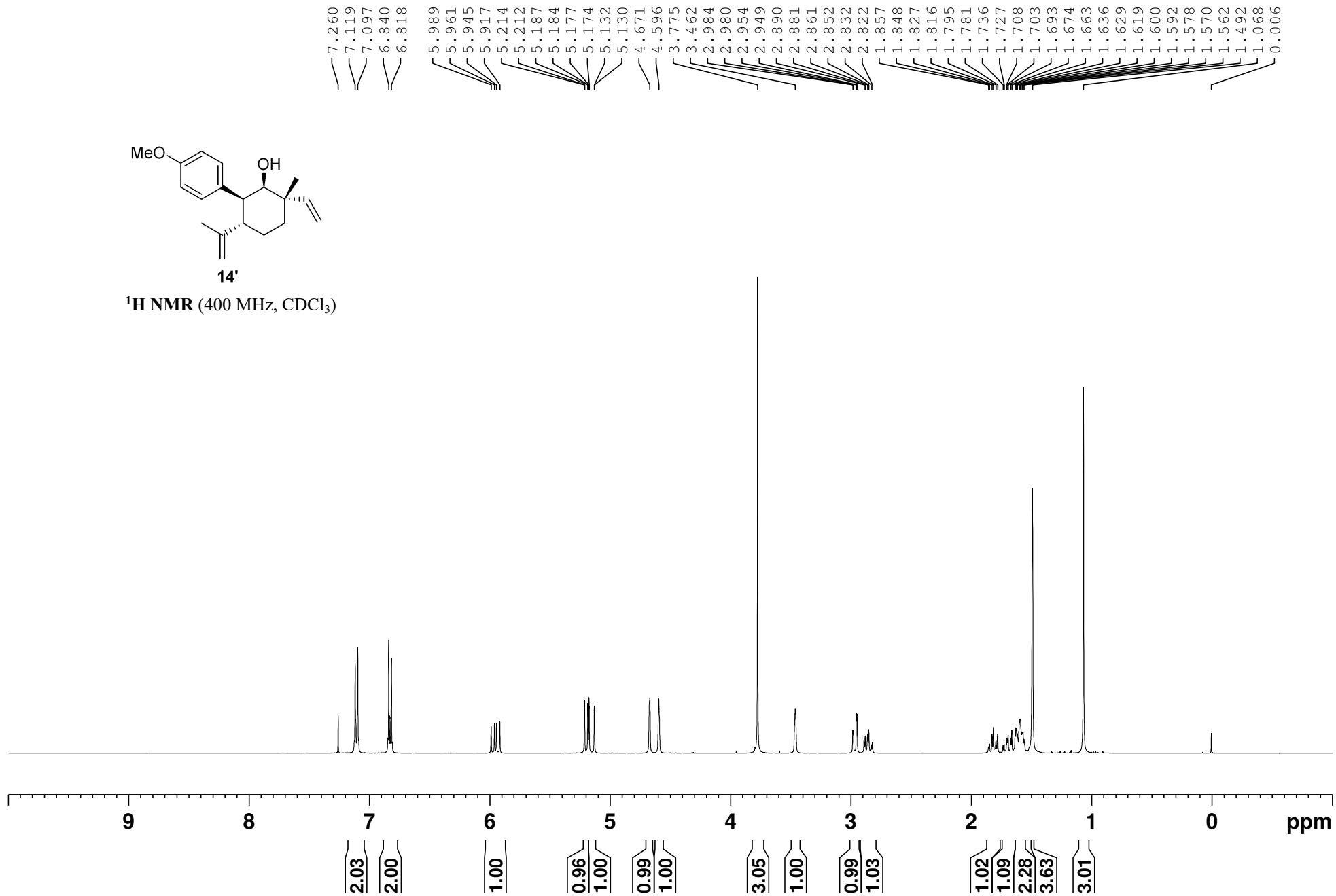
— 158.24
— 147.11
— 140.63
— 132.67
— 129.44
— 114.46
— 113.86
— 111.64
— 81.21
— 77.22
— 77.00
— 76.79
— 55.08
— 51.20
— 50.51
— 41.66
— 36.60
— 27.66
— 27.45
— 19.40

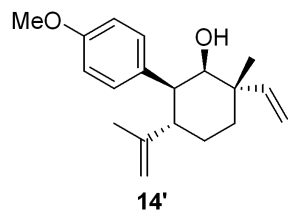




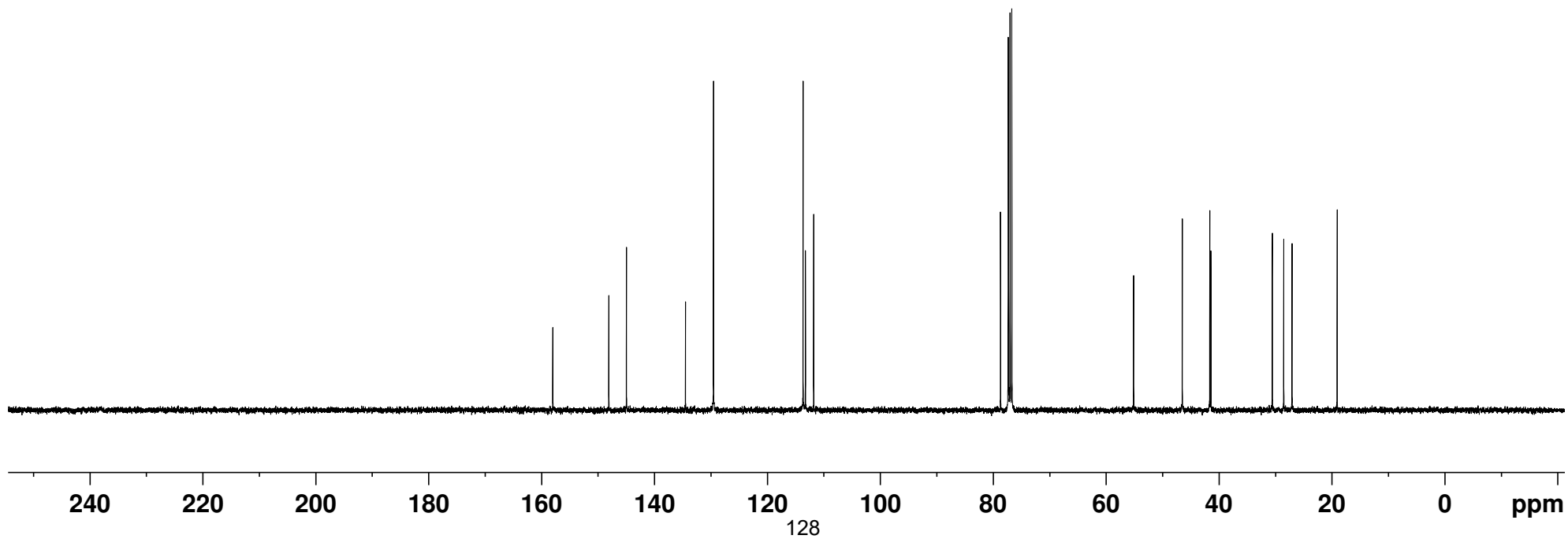


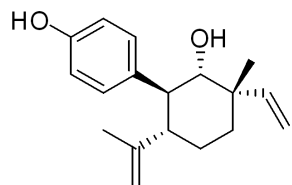
¹H NMR (400 MHz, CDCl₃)





¹³C NMR (100 MHz, CDCl₃)



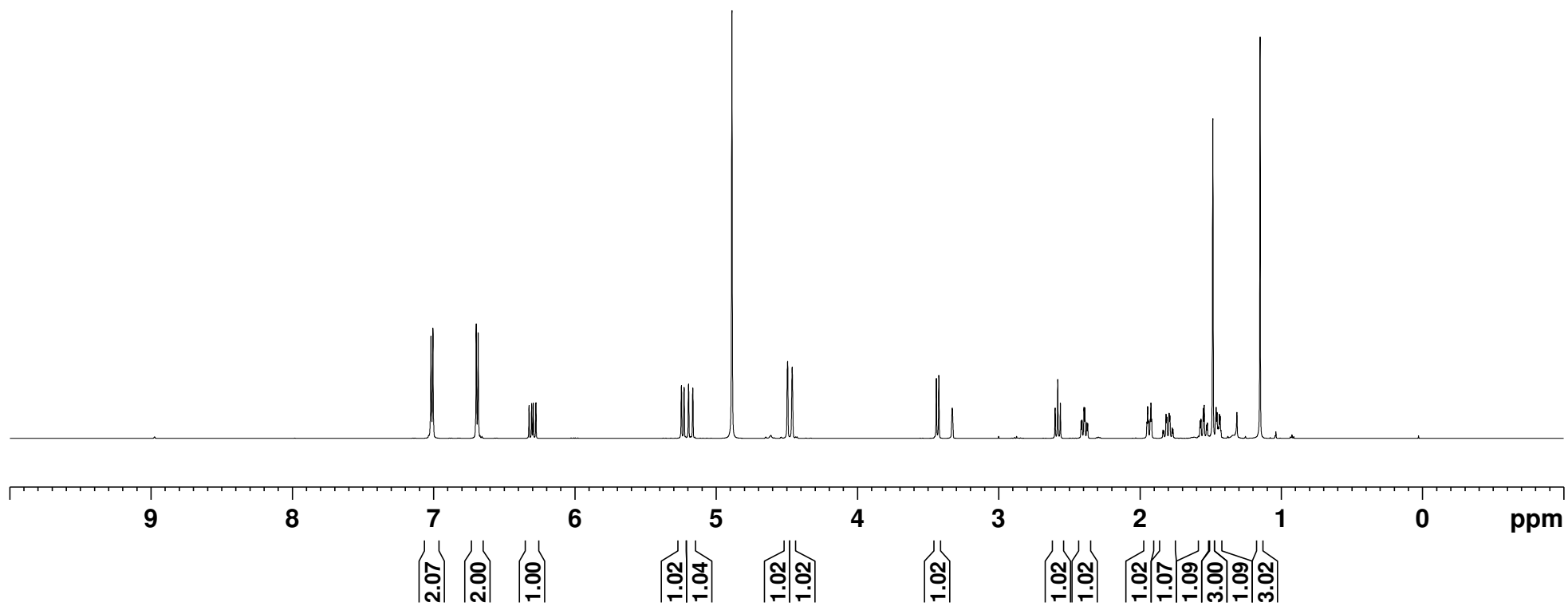


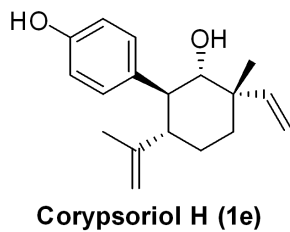
Corypsoriol H (1e)

¹H NMR (600 MHz, methanol-d₄)

7.019
7.005
6.698
6.685
6.324
6.306
6.295
6.276

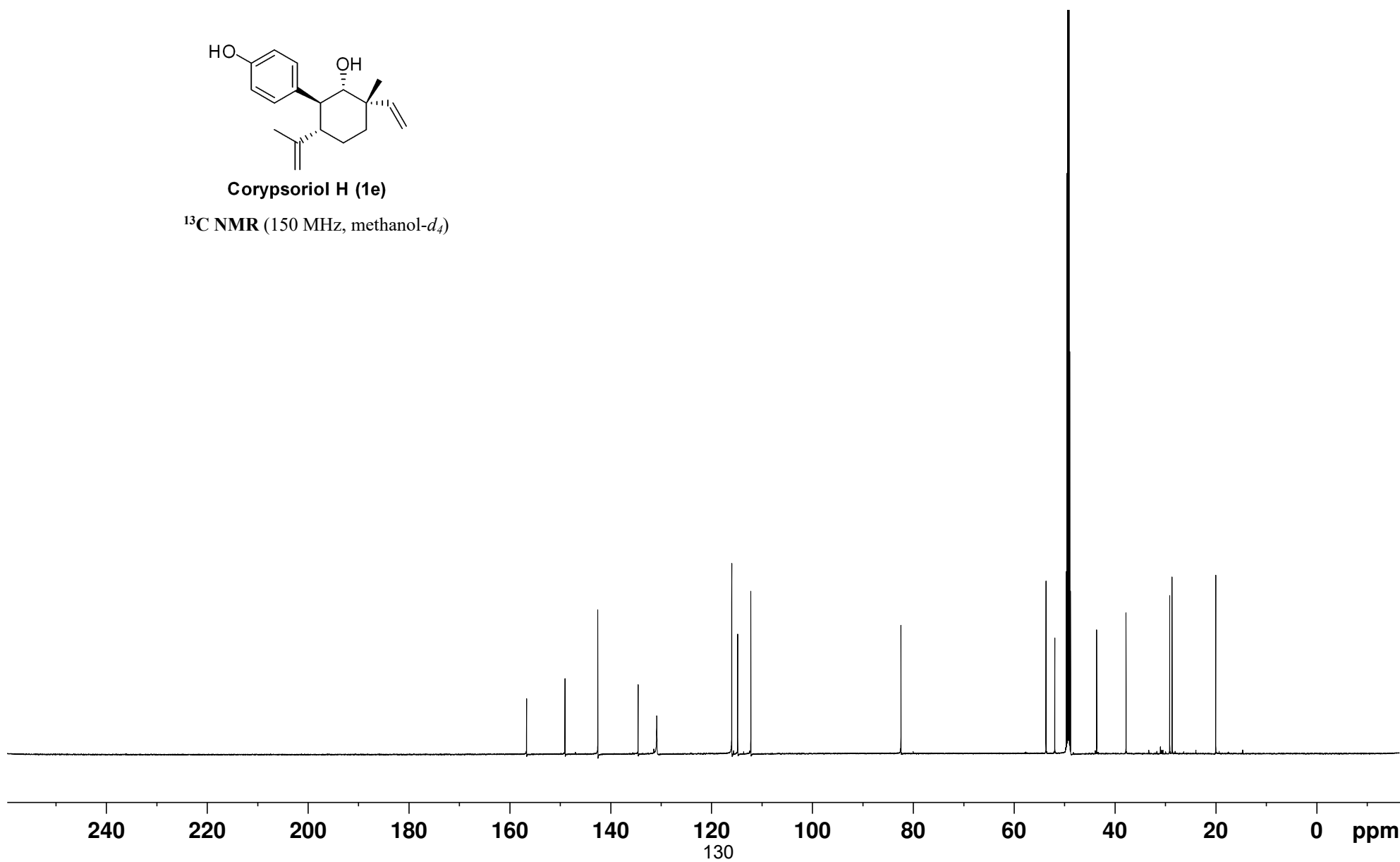
5.246
5.227
5.195
5.165
4.888
4.494
4.462
3.441
3.424
3.329
2.600
2.582
2.563
2.416
2.410
2.396
2.390
2.377
2.370
1.951
1.945
1.940
1.928
1.923
1.918
1.837
1.832
1.815
1.810
1.794
1.788
1.772
1.766
1.574
1.568
1.552
1.546
1.529
1.523
1.484
1.461
1.455
1.449
1.444
1.438
1.432
1.427
1.150
0.028

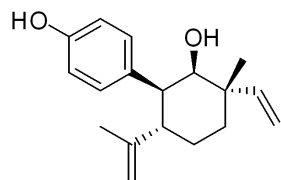




¹³C NMR (150 MHz, methanol-*d*₄)

- 156.65
- 149.01
- 142.52
- 134.54
- 130.84
- 115.97
- 114.78
- 112.18
- 82.42
- 53.64
- 51.91
- 49.64
- 49.50
- 49.35
- 49.21
- 49.07
- 48.93
- 48.79
- 43.62
- 37.78
- 29.12
- 28.65
- 20.00

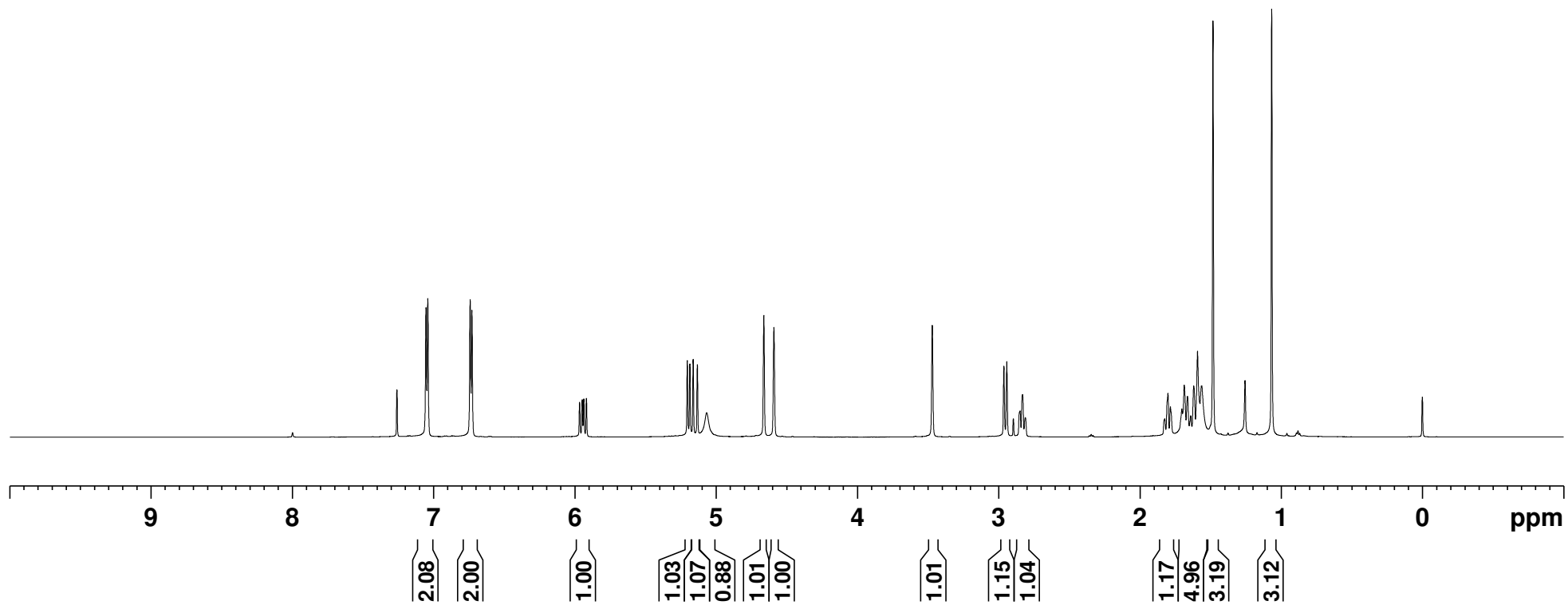


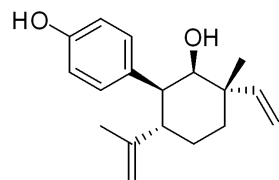


Psoracorylifol G (1f)

¹H NMR (600 MHz, CDCl₃)

7.260
7.054
7.041
6.741
6.729
5.967
5.948
5.937
5.918
5.204
5.186
5.163
5.133
5.067
4.662
4.591
3.470
2.963
2.942
2.849
2.831
2.812
1.824
1.802
1.784
1.704
1.686
1.663
1.640
1.620
1.592
1.577
1.565
1.562
1.483
1.068
0.001

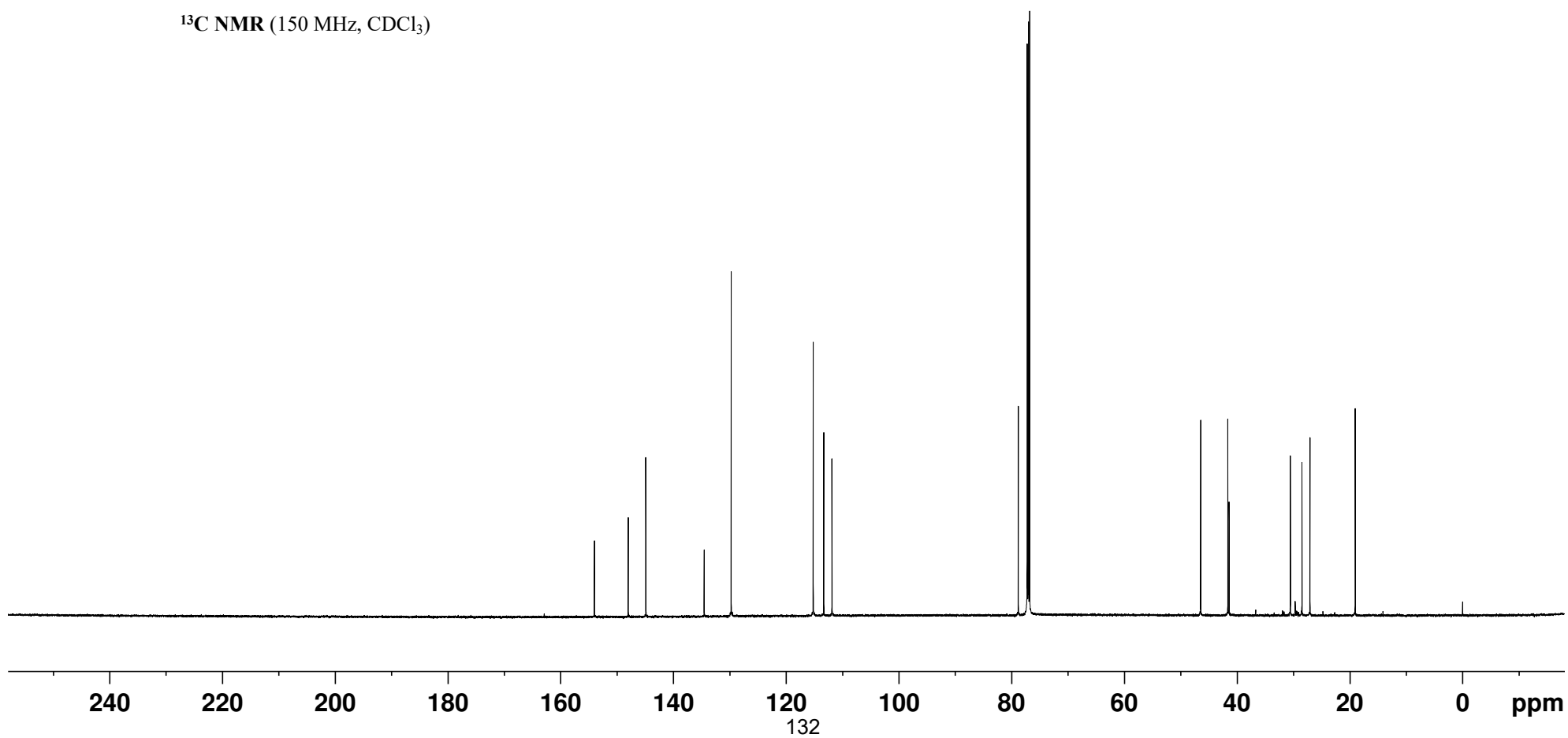


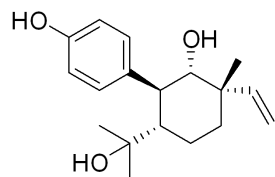


Psoracorylifol G (1f)

^{13}C NMR (150 MHz, CDCl_3)

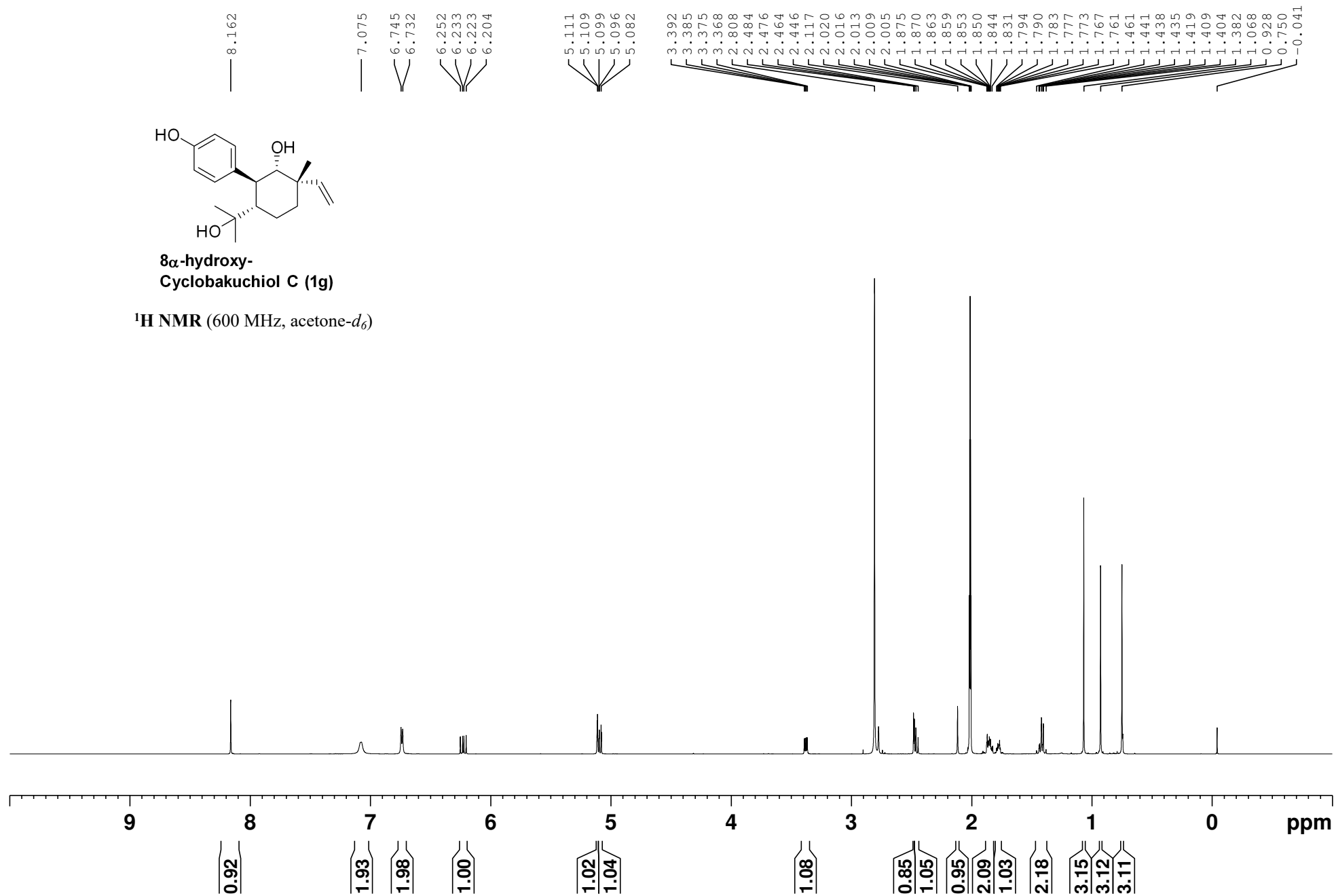
154.00
147.99
144.88
134.53
129.74
115.18
113.30
111.85
78.80
77.21
77.00
76.79
46.44
41.63
41.39
30.53
28.47
27.05
19.03

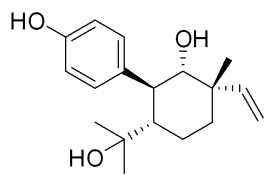




**8 α -hydroxy-
Cyclobakuchiol C (1g)**

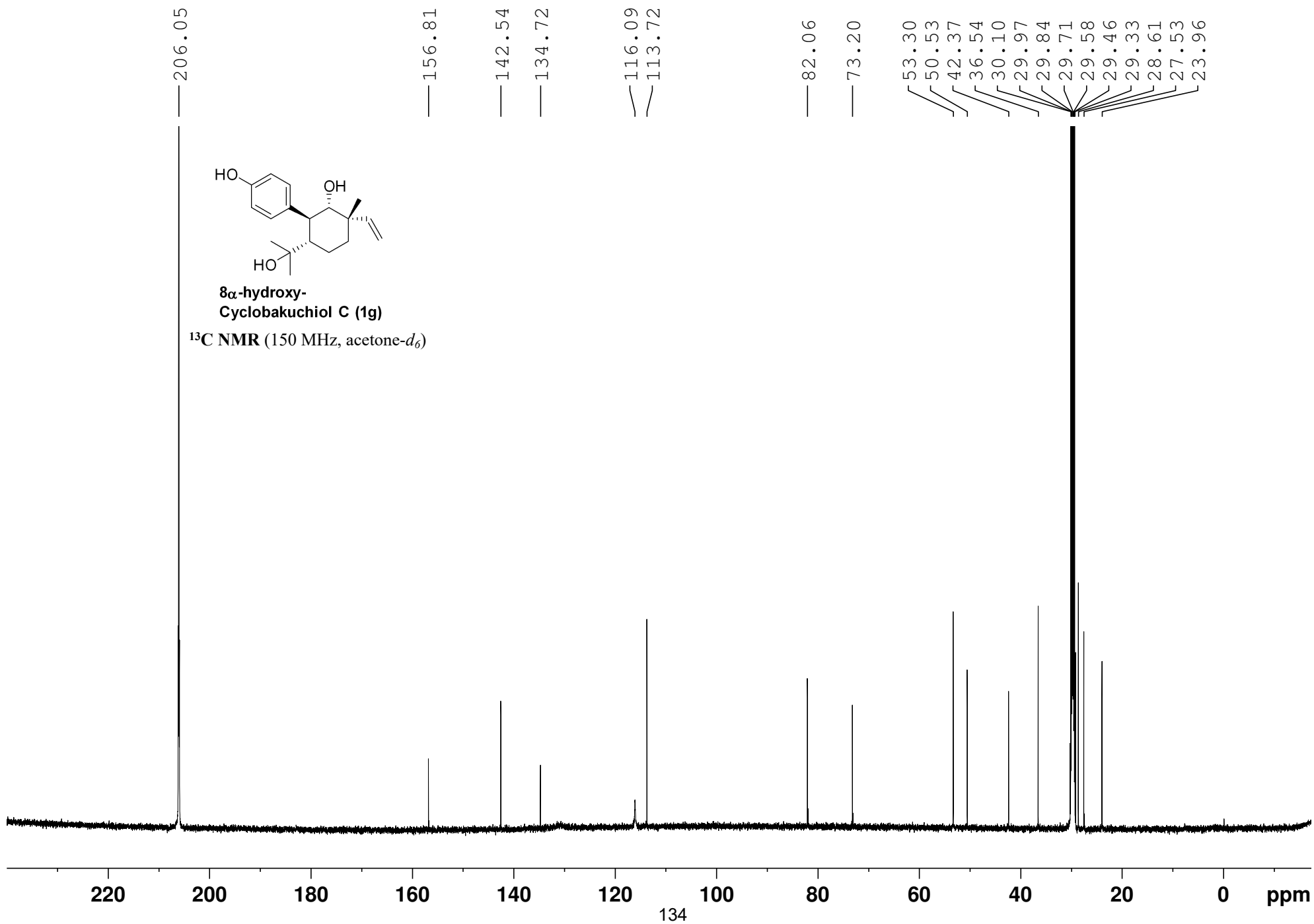
^1H NMR (600 MHz, acetone- d_6)

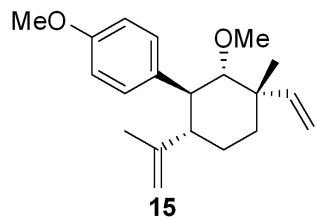




**8 α -hydroxy-
Cyclobakuchiol C (1g)**

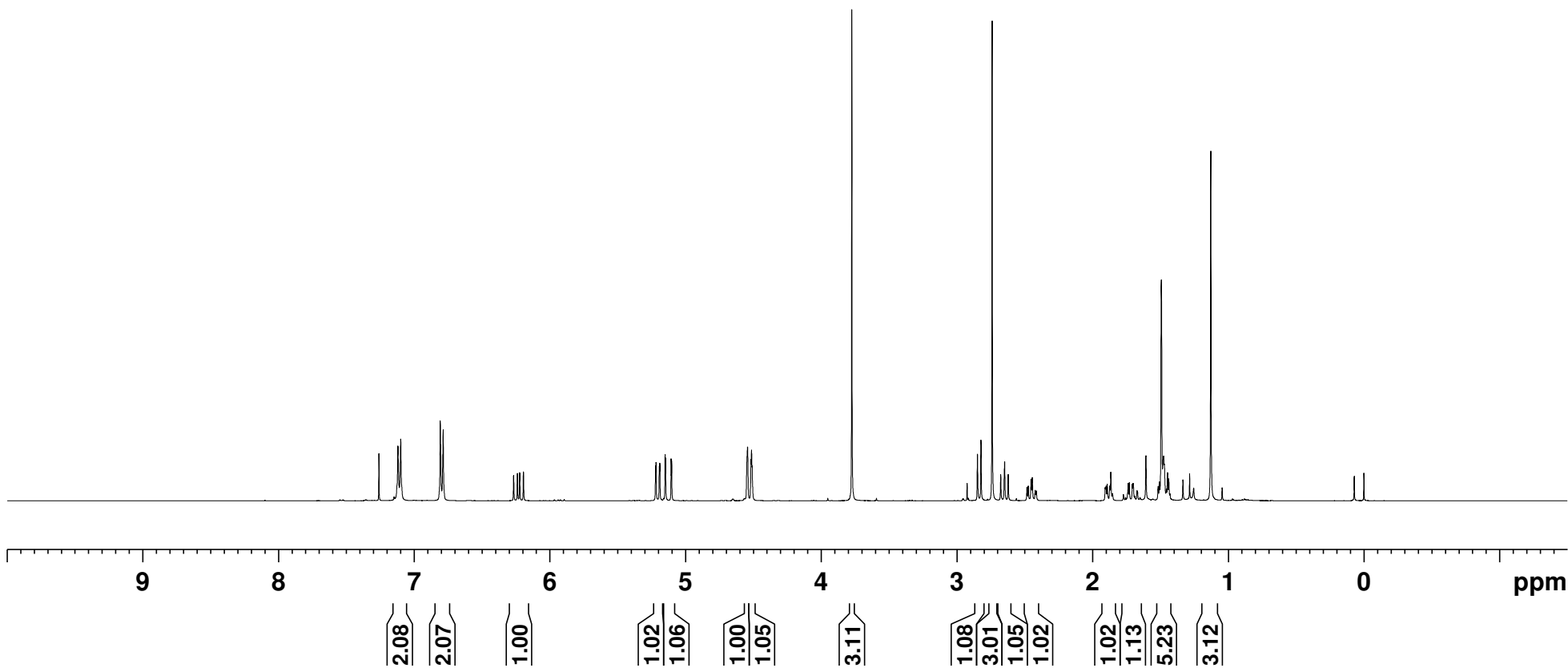
^{13}C NMR (150 MHz, acetone- d_6)

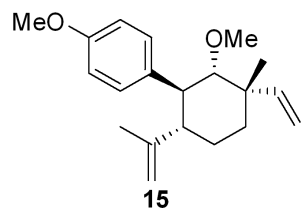




¹H NMR (400 MHz, CDCl₃)

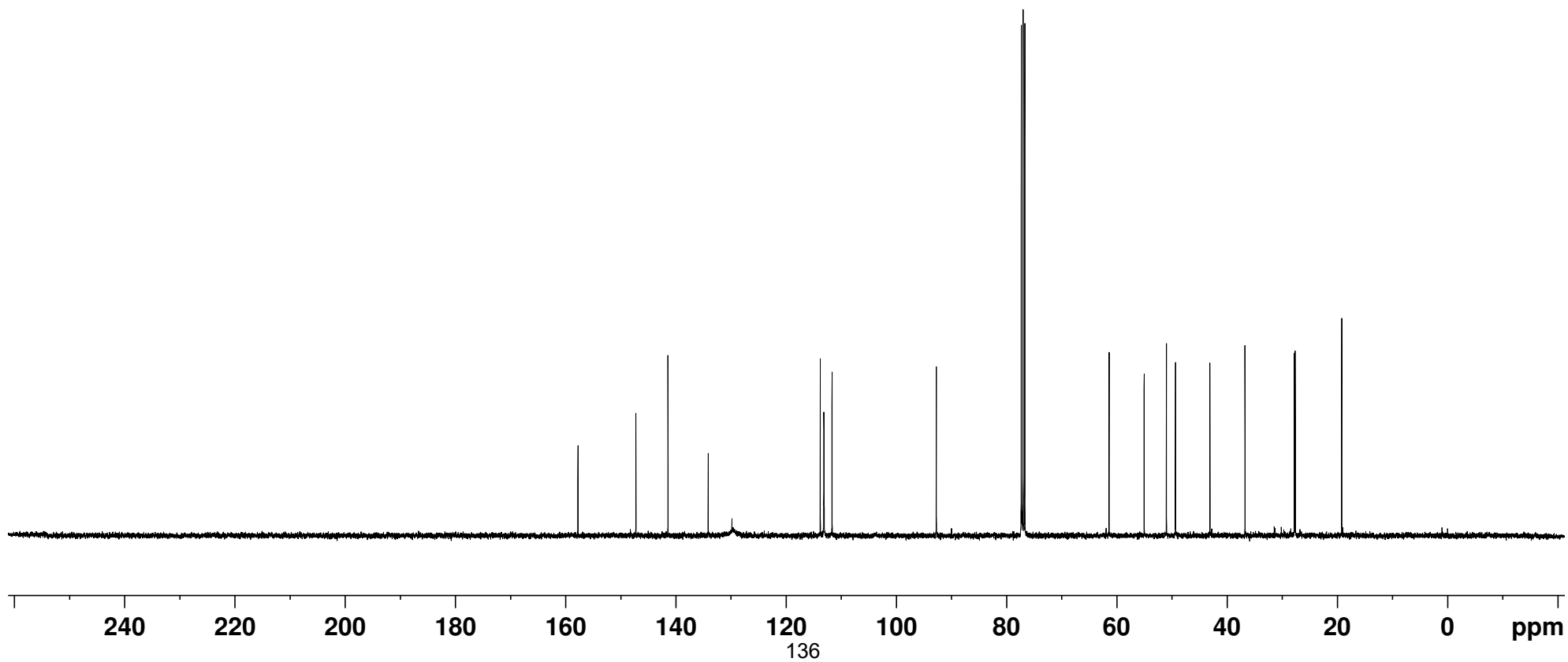
7.260
7.120
7.099
6.808
6.786
6.267
6.239
6.222
6.195
5.221
5.217
5.193
5.190
5.151
5.147
5.106
5.102
4.543
4.514
3.775
2.848
2.822
2.740
2.677
2.648
2.622
2.483
2.474
2.453
2.444
2.423
2.414
1.907
1.900
1.892
1.873
1.866
1.773
1.757
1.738
1.729
1.707
1.699
1.689
1.672
1.668
1.651
1.517
1.507
1.493
1.476
1.471
1.460
1.456
1.447
1.439
1.429
1.129
0.000

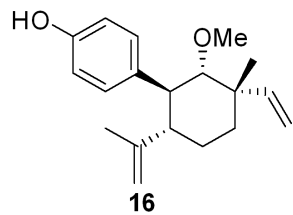




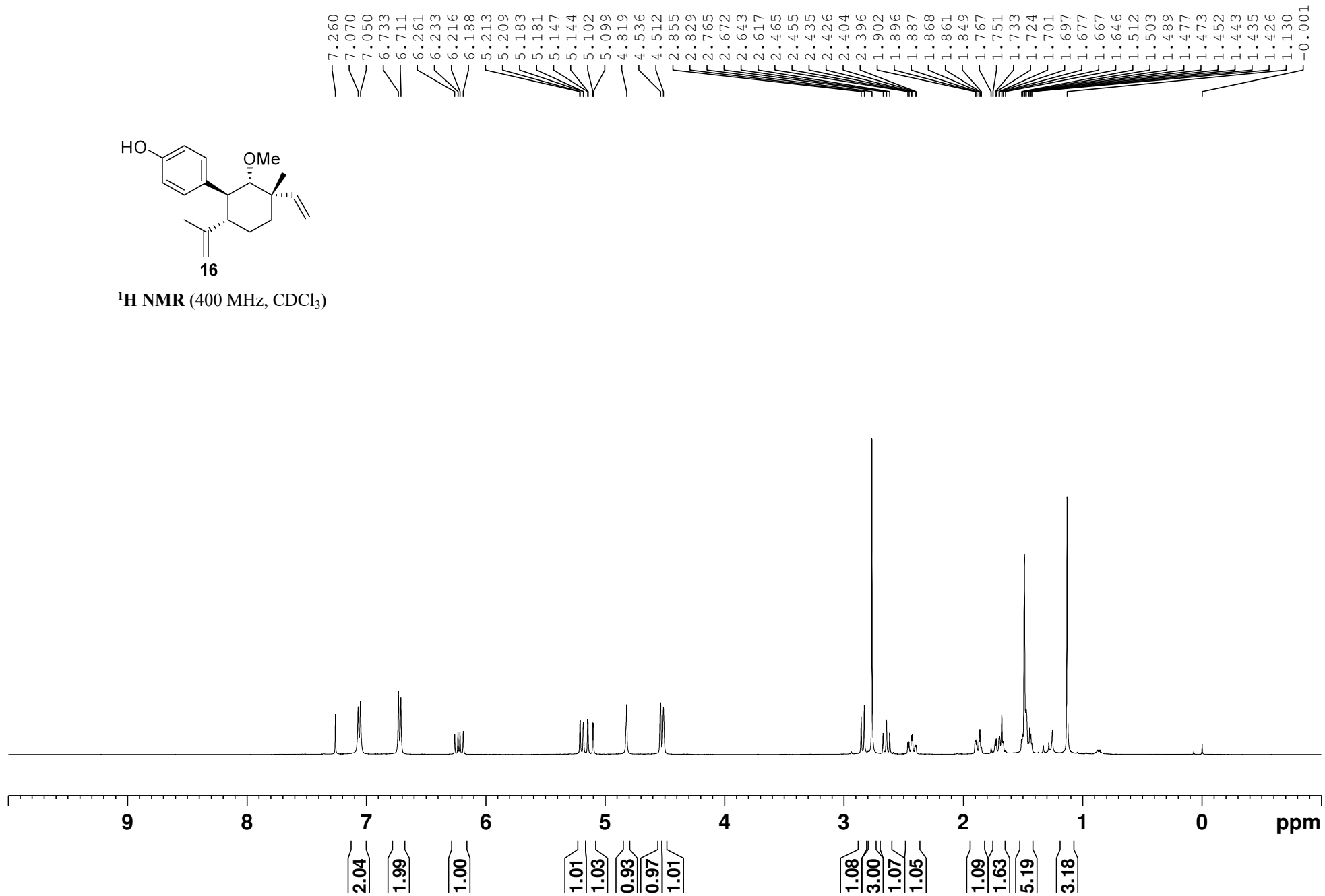
¹³C NMR (100 MHz, CDCl₃)

- 157.74
- 147.22
- 141.41
- 134.11
- 129.80
- 113.78
- 113.12
- 111.65
- 92.73
- 77.31
- 77.00
- 76.68
- 61.39
- 55.03
- 50.99
- 49.35
- 43.10
- 36.73
- 27.78
- 27.62
- 19.18

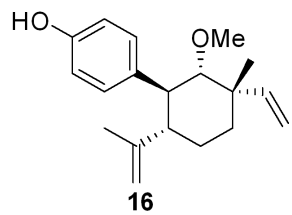




¹H NMR (400 MHz, CDCl₃)

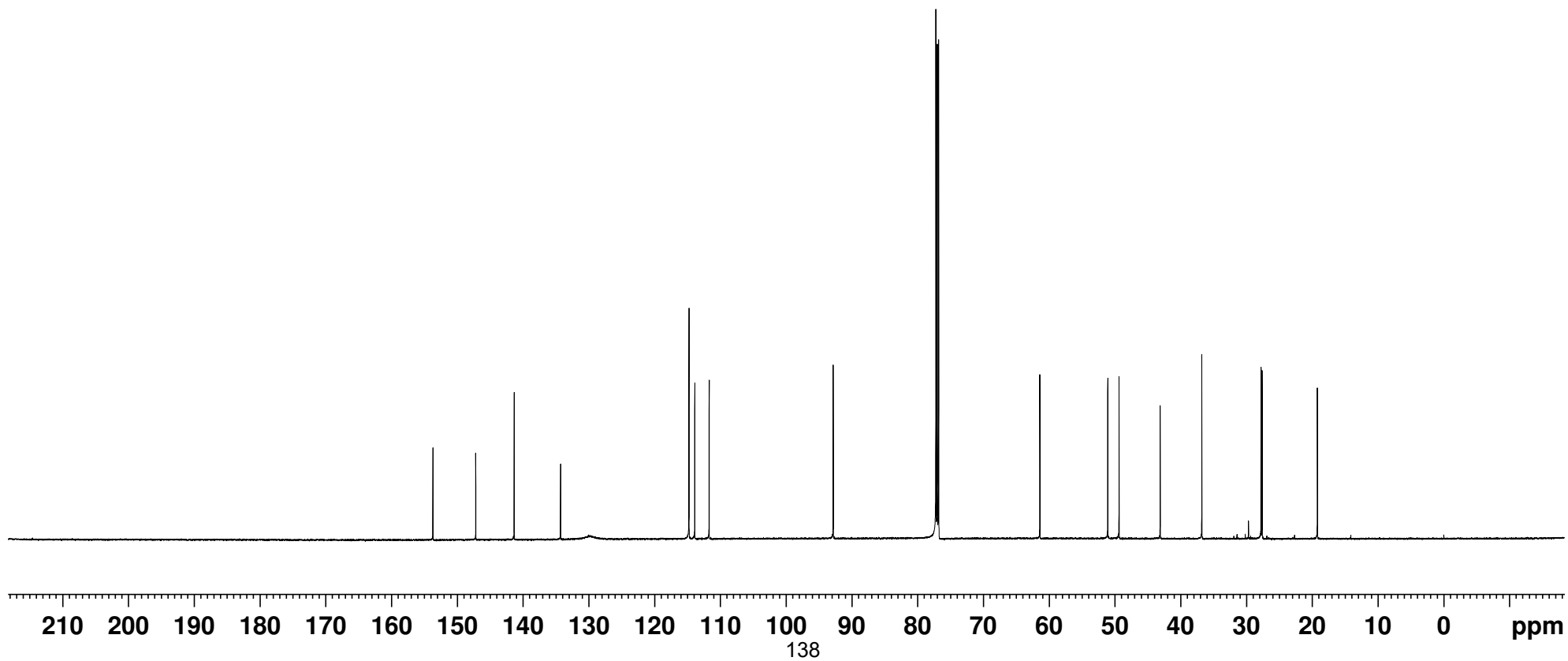


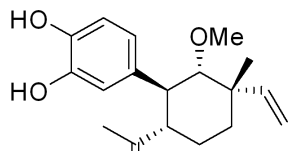
7.260
7.070
7.050
6.733
6.711
6.261
6.233
6.216
6.188
5.213
5.209
5.183
5.181
5.147
5.144
5.102
5.099
4.819
4.536
4.512
2.855
2.829
2.765
2.672
2.643
2.617
2.465
2.455
2.435
2.426
2.404
2.396
1.902
1.896
1.887
1.868
1.861
1.849
1.767
1.751
1.733
1.724
1.701
1.697
1.677
1.667
1.646
1.512
1.503
1.489
1.477
1.473
1.452
1.443
1.435
1.426
1.130
-0.001



¹³C NMR (150 MHz, CDCl₃)

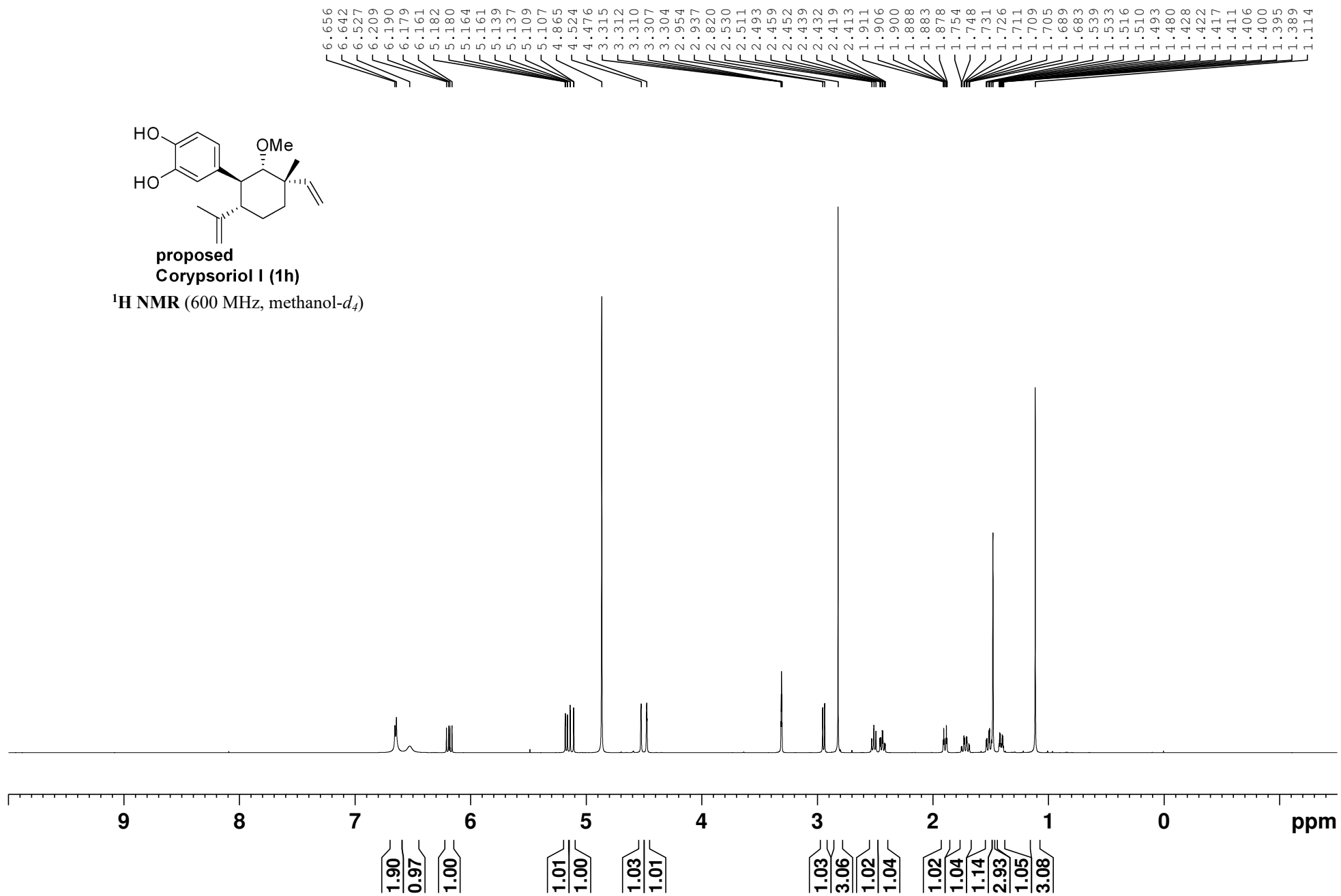
- 153.68
- 147.17
- 141.32
- 134.26
- 130.00
- 114.75
- 113.86
- 111.68
- 92.81
- 77.21
- 76.99
- 76.78
- 61.39
- 51.06
- 49.35
- 43.10
- 36.77
- 27.77
- 27.59
- 19.19

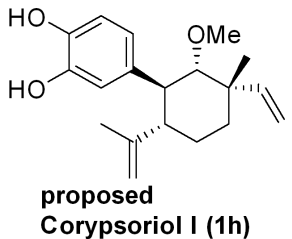




**proposed
Corypsoriol I (1h)**

¹H NMR (600 MHz, methanol-*d*₄)





¹³C NMR (150 MHz, methanol-*d*₄)

- 148.55
- 145.68
- 144.39
- 142.87
- 134.97
- 115.80
- 114.16
- 112.15
- 93.96
- 61.80
- 52.55
- 51.16
- 49.42
- 49.27
- 49.13
- 48.99
- 48.85
- 48.71
- 48.57
- 44.29
- 37.48
- 28.86
- 28.59
- 19.57

