Supporting Information

A Concise Bioinspired Semisynthesis of Rumphellaones A – C and their C-8 Epimers from β-Caryophyllene

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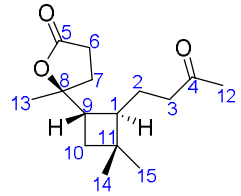
CONTENTS

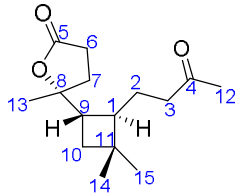
Table S1. Comparison of specific rotation data $[\alpha]_D^T$ (*c*, $CHCl_3$)

Entry	Compd	[α]	T	*c*	Reference
1	**1** isolated	+257	25	0.014	*Tetrahedron Lett.* **2010**, *51* (46), 6025
2	**1** synthesized	+79.5	30	1.03	this work
3		+75.8	30	1.11	*Tetrahedron Lett.* **2012**, *53* (6), 705
4		+83.4	19	0.45	*Tetrahedron* **2012**, *68* (24), 4581
5		+65.6	25	1.11	*Org. Lett.* **2016**, *18* (7), 1614
6		+43.4	25	0.35	*Chem. Sci.* **2019**, *10* (8), 2315
7	**2** isolated	+18	25	0.25	*Molecules* **2014**, *19* (8), 12320
8	**2** synthesized	+180	20	0.54	this work
9	**3** isolated	-8	25	0.18	*Molecules* **2014**, *19* (8), 12320
10	**3** synthesized	+67	20	0.78	this work
11	**8**	+42	25	0.41	this work
12		+38.5	25	0.41	*Chem. Sci.* **2019**, *10* (8), 2315
13	**9**	+140	20	0.85	this work
14	**10**	+64	20	0.73	this work

Table S2. NMR spectra of rumphellaone A (**1**) and 8-*epi*-rumphellaone A (**8**)



Rumphellaone A (**1**)

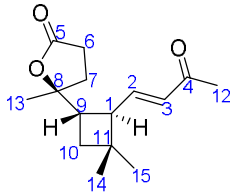


8-*epi*-Rumphellaone A (**8**)

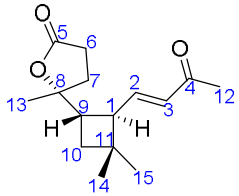
Position	δ_H, (*J* in Hz)	δ_C, type	^1H-^1H NOESY	HMBC	Position	δ_H, (*J* in Hz)	δ_C, type	^1H-^1H NOESY	HMBC
1	1.93-1.85, m*	44.6, CH	H-2, -3, -15	H-3, -14, -15	**1**	1.81-1.72, m	44.0, CH	H-2, -3, -9, -13, -15	H-2, -3, -14, -15
2	1.69 – 1.60, m	25.2, CH_2	H-1, -3, -13, -14	H-3	**2**	1.68-1.56, m*	24.9, CH_2	H-1, -3, -9, -14	H-3
3	2.35, t (7.7)	42.1, CH_2	H-1, -2, -12, -14	H-12	**3**	2.38, dd (8.5, 6.6)	41.8, CH_2	H-1, -2, -12, -14, -15	H-2, -12
4	-	208.7, C	-	H-3, -12	**4**	-	208.8, C	-	H-2, -3, -12
5	-	177.1, C	-	H-6	**5**	-	177.2, C	-	H-6, -7α, -7β
6	2.67-2.47, m	29.3, CH_2	H-7α, -7β		**6**	2.59, td (8.8, 1.7)	29.2, CH_2	H-7α, -7β, -13	
7α	2.01-1.95, m*	30.8, CH_2	H-6, -7β	H-13	**7α**	2.07-2.03, m*	31.5, CH_2	H-6, -7β, -9	H-6, -13
7β	1.87-1.78, m*		H-6, -7α, -13		**7β**	1.89, ddd (12.9, 8.8, 7.2)		H-6, -7α, -13	
8	-	87.3, C	-	H-7α, -7β, -10α, -10β, -13	**8**	-	87.3, C	-	H-1, -6, -7α, -10β, -13
9	2.10 – 2.00, m*	44.4, CH	H-10α, -10β, -14	H-1, -7α, -10α, -10β, -13	**9**	2.05-1.97, m*	44.5, CH	H-1, -2, -7α, -10α, -10β, -13, -14	H-10β, -13
10α	1.56, ddd (10.7, 8.6, 0.8)	33.7, CH_2	H-9, -10β, -14	H-14, -15	**10α**	1.68-1.56, m*	34.4, CH_2	H-9, -10β, -14	H-1, -9, -15
10β	1.41, t, (10.3)		H-9, -10α, -15		**10β**	1.50, t (10.4)		H-9, -10α, -13, -15	
11	-	33.1, C	-	H-10α, -10β	**11**	-	33.3, C	-	H-10α
12	2.11, s	30.1, CH_3	H-3		**12**	2.12, s	30.1, CH_3	H-3	
13	1.30, s	25.0, CH_3	H-2, -7β		**13**	1.28, s	23.9, CH_3	H-1, -6, -7β, -9, -10β	H-7α, -7β
14	1.02, s	22.6, CH_3	H-2, -3, -9, -10α	H-10α, -10β, -15	**14**	1.02, s	22.5, CH_3	H-2, -3, -9, -10α	H-10α, -10β, -15
15	1.05, s	31.1, CH_3	H-1, -10β	H-14	**15**	1.04, s	31.0, CH_3	H-1, -3, -10β	H-14

* Proton signal partly overlaps with other proton signal

Table S3. NMR spectra of rumphellaone B (**2**) and 8-*epi*-rumphellaone B (**9**)



Rumphellaone B (**2**)

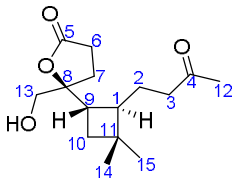


epi-(C8)-Rumphellaone B (**9**)

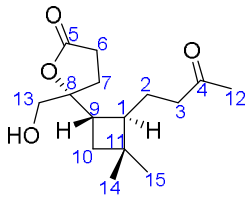
Position	δ_H, (*J* in Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC	Position	δ_H, (*J* in Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC
1	2.77, ddt (9.5, 8.5, 1.0)	48.1, CH	H-2, -3, -9, -10, -13, -15	H-3, -9, -10, -14, -15	**1**	2.56, dd (10.0, 8.8)*	47.4, CH	H-3, -9, -15	H-3, -10, -14, -15
2	6.76, dd (16.0, 8.5)	147.3, CH	H-1, -2, -9, -12, -14	H-1, -9, -12, -10	**2**	6.75, dd (15.9, 8.5)	147.1, CH	H-3, -12, -14	H-1, -9, -12, -10
3	6.07, dd (15.9, 1.1)	131.5, CH	H-1, -3, -9, -12, -13	H-1, -12	**3**	6.03, dt (15.9, 1.0)	131.4, CH	H-1, -2, -9, -12	H-1, -12
4	-	198.3, C	-	H-2, -3, -12	**4**	-	198.0, C	-	H-2, -3, -12
5	-	176.8, C	-	H-6α, -6β, -7	**5**	-	176.8, C	-	H-6α, -6β, -7
6α	2.63, ddd (18.1, 10.1, 8.9)	29.3, CH_2	H-6β, -7	H-13	**6α**	2.65-2.51, m*	29.1, CH_2	H-6β, -7	
6β	2.50, ddd (18.1, 9.8, 5.1)		H-6α, -7		**6β**	2.50-2.37, m*		H-6α, -7	
7	2.01-1.84, m	31.1, CH_2	H-6α, -6β, -9, -13	H-6α, -6β, -13	**7**	1.98-1.80, m	30.9, CH_2	H-6α, -6β, -13	H-13
8	-	86.7, C	-	H-1, -6α, -6β, -7, -10, -13	**8**	-	86.5, C	-	H-1, -6α, -6β, -7, -10, -13
9	2.40, td (9.8, 8.5)	43.1, CH	H-1, -2, -3, -7, -10, -13, -14	H-1, -2, -7, -13	**9**	2.39, q (9.5)*	42.9, CH	H-1, -3, -10, -13, -14	H-2, -7, -13
10	1.70-1.58, m	33.2, CH_2	H-1, -9, -14, -15	H-9, -14, -15	**10**	1.80-1.67, m	34.1, CH_2	H-9, -14, -15	H-9, -14, -15
11	-	36.1, C	-	H-1, -14, -15	**11**	-	36.5, C	-	H-1, -10, -14, -15
12	2.24, s	27.5, CH_3	H-2, -3		**12**	2.22, s	27.5, CH_3	H-2, -3	H-3
13	1.25, s	24.7, CH_3	H-1, -3, -7, -9	H-7	**13**	1.25, s	24.2, CH_3	H-7, -9	H-7
14	1.03, s	23.9, CH_3	H-2, -9, -10	H-10, -15	**14**	1.01, s	23.9, CH_3	H-2, -9, -10	H-1, -10, -15
15	1.09, s	29.8, CH_3	H-1, -10	H-1, -14	**15**	1.07, s	29.7, CH_3	H-1, -10	H-1, -10, -14

* Proton signal partly overlaps with other proton signal

Table S4. NMR spectra of rumphellaone C (**3**) and 8-*epi*-rumphellaone C (**10**)



Rumphellaone C (**3**)

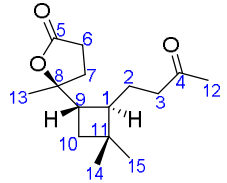


epi-(C8)-Rumphellaone C (**10**)

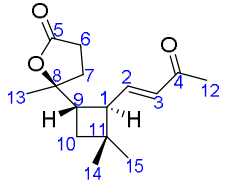
Position	δ_H, (*J* in Hz)	δ_C, type	^1H-^1H NOESY	HMBC	Position	δ_H, (*J* in Hz)	δ_C, type	^1H-^1H NOESY	HMBC
1	1.98-1.87, m*	44.1, CH	H-2, -3, -10β, -15	H-2, -3, -10α, -14, -15	**1**	1.79, td (9.4, 6.8)	43.9, CH	H-2, -9, -10, -15	H-2, -3, -10, -9, -15
2	1.64 – 1.58, m*	25.0, CH_2	H-1, -3, -14	H-3, -9	**2**	1.70-1.60, m	25.1, CH_2	H-1, -3, -7β, -9, -14	H-3, -9
3	2.35, t (7.4)	41.9, CH_2	H-1, -2, -12, -14, -15	H-2	**3**	2.44-2.30, m*	41.8, CH_2	H-2, -12, -14, -15	H-2,-12
4	-	208.8, C	-	H-2, -3, -12	**4**	-	208.5, C	-	H-2, -3, -12
5	-	177.9, C	-	H-6α, -6β, -7α, -7β	**5**	-	178.0, C	-	H-6, -7α, -7β
6α	2.71, ddd (18.7, 10.9, 7.9)	29.9, CH_2	H-6β, -7α, -7β		**6**	2.75-2.53, m	29.8, CH_2	H-7α, -7β	H-7β
6β	2.54, ddd (18.2, 10.9, 5.1)		H-6α, -7α, -7β						
7α	2.21, ddd (13.0, 10.9, 5.1)	25.7, CH_2	H-6α, -6β, -7β, -13β	H-6α, -13α, -13β	**7α**	2.30-2.22, m	26.1, CH_2	H-6, -7β	H-6, -13α, 9
7β	1.98-1.87, m*		H-6α, -6β, -7α, -10α		**7β**	1.98, ddd (13.1, 10.7, 7.2)		H-2, -6, -7α	
8	-	89.7, C	-	H-7β, -10α, -13α	**8**	-	89.3, C	-	H-1, -6, -7α, -7β, -10, -13α
9	2.17-2.06, m*	40.3, CH	H-10α, -10β, -13α, -13β, -14	H-10β, -13α, -13β	**9**	2.07, q (9.3)	40.7, CH	H-1, -2, -10, -13α, -13β, -14	H-4, -7, -10, -13α
10α	1.60-1.53, m*	33.1, CH_2	H-7β, -9, -10β, -13α, -13β, -14	H-9	**10**	1.57, d (9.3)	34.2, CH_2	H-1, -9, -13α, -13β, -14, -15	H-2, -9, -15
10β	1.43, t (10.3)		H-1, -9, -10α,-15						
11	-	33.6, C	-	H-2, -14, -15	**11**	-	34.1, C	-	H-2, -15
12	2.12, s*	30.1, CH_3	H-3		**12**	2.11, s	30.2, CH_3	H-3	
13α	3.73, d (11.8)	66.7, CH_2	H-9, -10α, -13β	H-7α, -7β, -9	**13α**	3.67, d (12.0)	66.3, CH_2	H-9, -10, -13β	H-7α, -7β, -9
13β	3.43, d, (11.8)		H-7α, -9, -10α,-13α		**13β**	3.42, d (12.0)		H-9, -10, -13α	
14	1.03, s	22.6, CH_3	H-2, -3, -9, -10α	H-1, -10α, -10β, -15	**14**	1.02, s	22.5	H-2, -3, -9, -10	H-10, -15
15	1.06, s	31.0, CH_3	H-1, -3, -10β	H-10β, -14	**15**	1.05, s	31.2, CH_3	H-1, -3, -10	H-14

* Proton signal partly overlaps with other proton signal

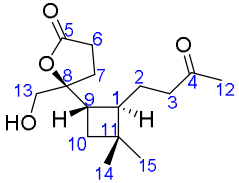
Table S5. Comparison of NMR data of isolated and synthesised rumphellaones A – C



Rumphellaone A (**1**)



Rumphellaone B (**2**)



Rumphellaone C (**3**)

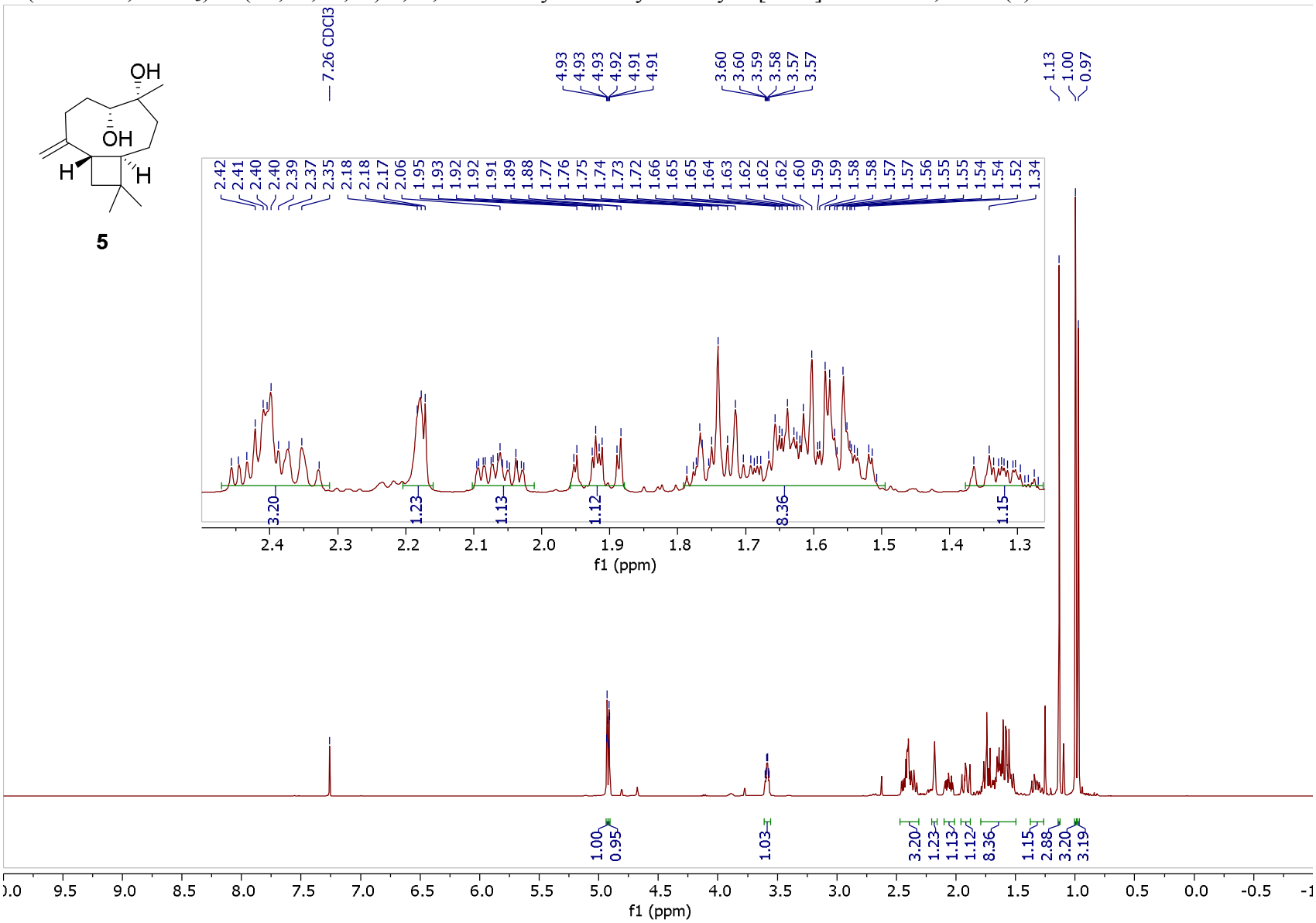
Position	this work	isolated[a]	this work	isolated[a]	Position	this work	isolated[b]	this work	isolated[b]	Position	this work	isolated[b]	this work	isolated[b]
	δ_H, type	δ_H, type	δ_C	δ_C		δ_H, type	δ_H, type	δ_C	δ_C		δ_H, type	δ_H, type	δ_C	δ_C
1	1.93-1.85, m[c]	1.91, ddd	44.6	44.5	**1**	2.77, ddt	2.78, dd	48.1	48.0	**1**	1.98-1.87, m[c]	1.90, m	44.1	44.0
2	1.69-1.60, m	1.67, m	25.2	25.1	**2**	6.76, dd	6.77, dd	147.3	147.1	**2**	1.64-1.58, m[c]	1.62, m	25.0	24.9
3	2.35, t	2.37, t	42.1	42.0	**3**	6.07, dd	6.09, d	131.5	131.4	**3**	2.35, t	2.36, t	41.9	41.8
4	-	-	208.7	208.6	**4**	-	-	198.3	198.1	**4**	-	-	208.8	208.6
5	-	-	177.1	177.0	**5**	-	-	176.8	176.7	**5**	-	-	177.9	177.6
6α	2.67-2.47, m	2.63, ddd	29.3	29.2	**6α**	2.63, ddd	2.68-2.51, m	29.3	29.1	**6α**	2.71, ddd	2.71, ddd	29.9	29.7
6β		2.54, ddd			**6β**	2.50, ddd				**6β**	2.54, ddd	2.54, ddd		
7α	2.01-1.95, m[c]	2.01, m	30.8	30.6	**7**	2.01-1.84, m	2.02-1.85, m	31.1	30.9	**7α**	2.21, ddd	2.20, ddd	25.7	25.6
7β	1.87-1.78, m[c]	1.84, m								**7β**	1.98-1.87, m[c]	1.94, ddd		
8	-	-	87.3	87.2	**8**	-	-	86.7	86.6	**8**	-	-	89.7	89.5
9	2.10-2.00, m[c]	2.06, ddd	44.4	44.3	**9**	2.40, td	2.39, m	43.1	43.0	**9**	2.17-2.06, m[c]	2.12, ddd	40.3	40.2
10α	1.56, ddd	1.57, dd	33.7	33.6	**10**	1.70-1.58, m	1.70-1.51, m	33.2	33.1	**10α**	1.60-1.53, m[c]	1.57, dd	33.1	33.0
10β	1.41, t	1.42, dd								**10β**	1.43, t	1.43, dd		
11	-	-	33.1	33.0	**11**	-	-	36.1	36.0	**11**	-	-	33.6	33.5
12	2.11, s	2.13, s	30.1	29.9	**12**	2.24, s	2.25, s	27.5	27.4	**12**	2.12, s[c]	2.12, s	30.1	30.0
13	1.30, s	1.31, s	25.0	24.9	**13**	1.25, s	1.25, s	24.7	24.6	**13α**	3.73, d	3.73, d	66.7	66.6
										13β	3.43, d	3.43, d		
14	1.02, s	1.03, s	22.6	22.5	**14**	1.03, s	1.04, s	23.9	23.8	**14**	1.03, s	1.03, s	22.6	22.5
15	1.05, s	1.07, s	31.1	30.9	**15**	1.09, s	1.10, s	29.8	29.6	**15**	1.06, s	1.07, s	31.0	30.8

[a] *Tetrahedron Lett.* **2010**, *51*, 6025; [b] *Molecules* **2014**, *19*, 12320; [c] Proton signal partly overlaps with other proton signal

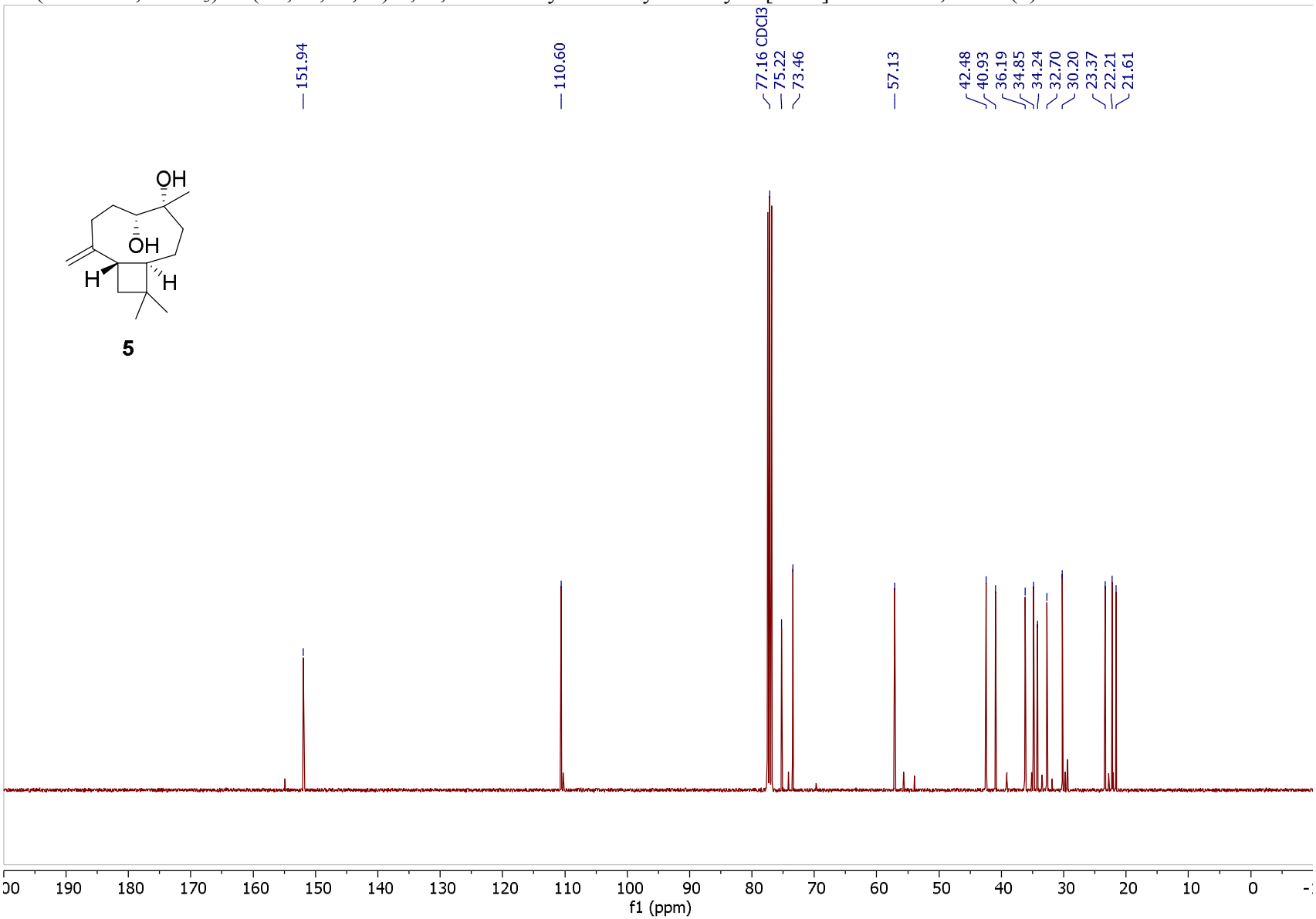
NMR spectra of isolated compounds

S1. NMR spectra of compound **5**

^{1}H NMR (400 MHz, $CDCl_3$) of (1*R*,4*R*,5*R*,9*S*)-4,11,11-trimethyl-8-methylenebicyclo[7.2.0]undecane-4,5-diol (**5**)

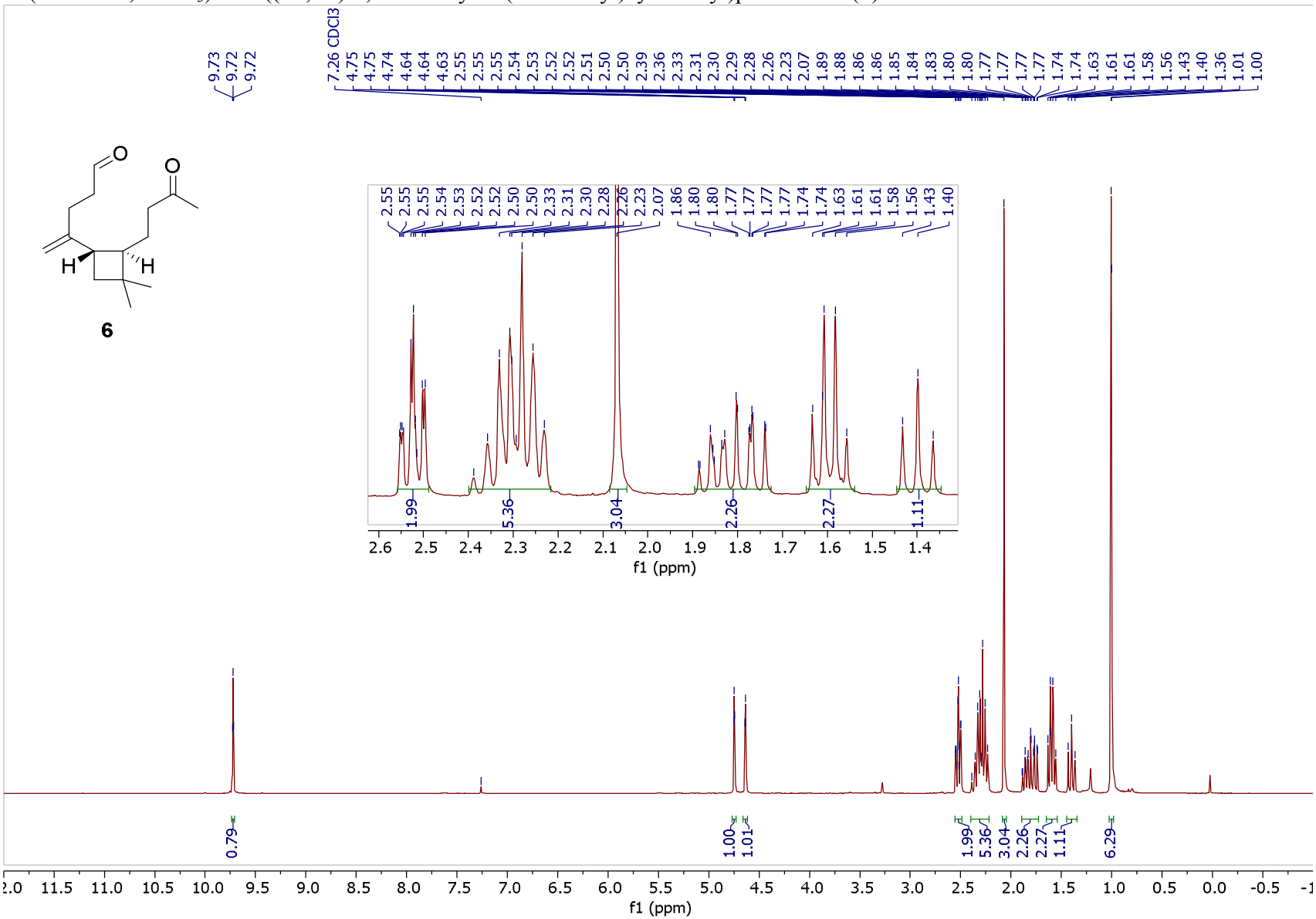


^{13}C NMR (101 MHz, $CDCl_3$) of (1*R*,4*R*,5*R*,9*S*)-4,11,11-trimethyl-8-methylenebicyclo[7.2.0]undecane-4,5-diol (**5**)

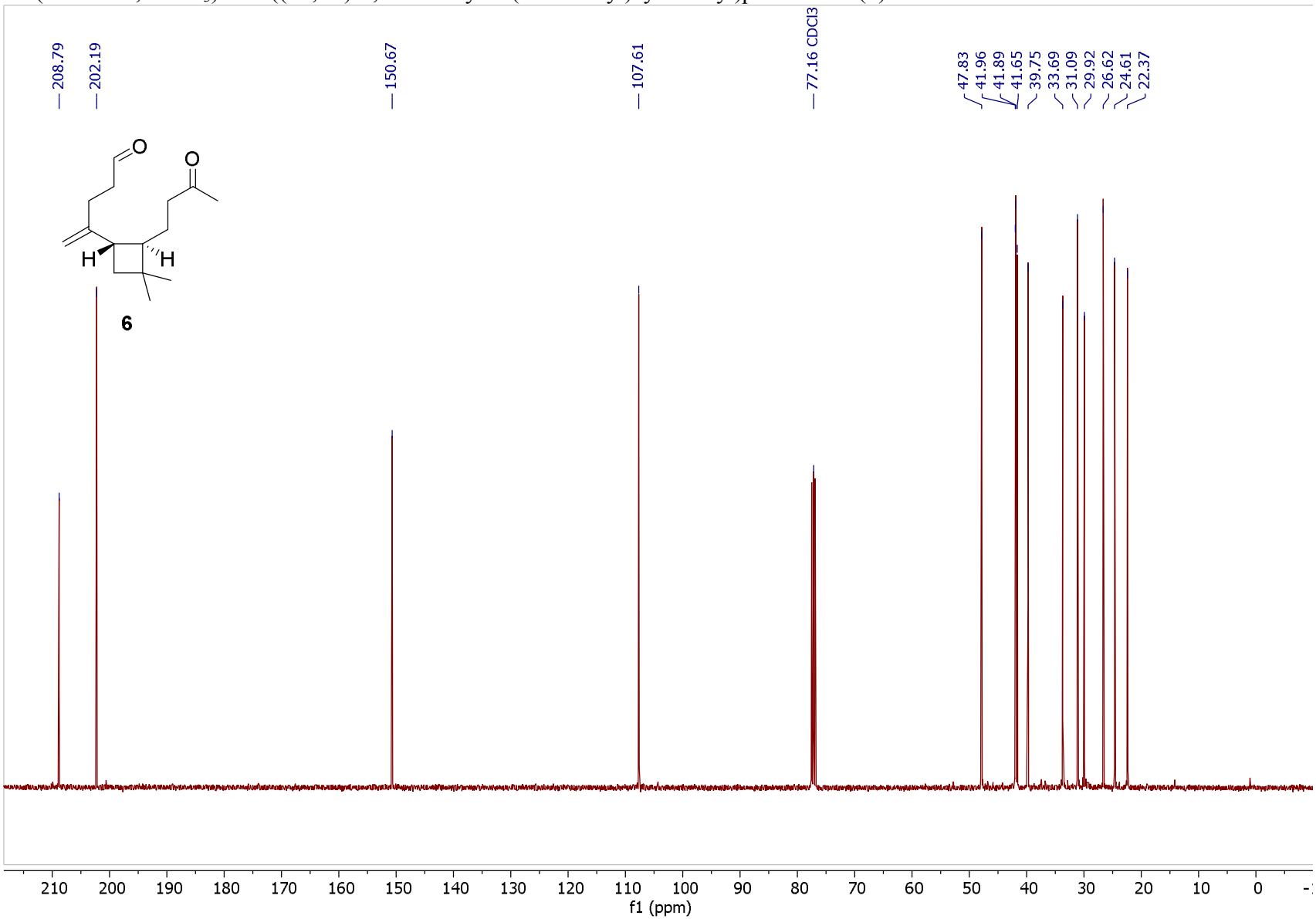


S2. NMR spectra of compound **6**

^{1}H NMR (400 MHz, $CDCl_3$) of 4-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)pent-4-enal (**6**)

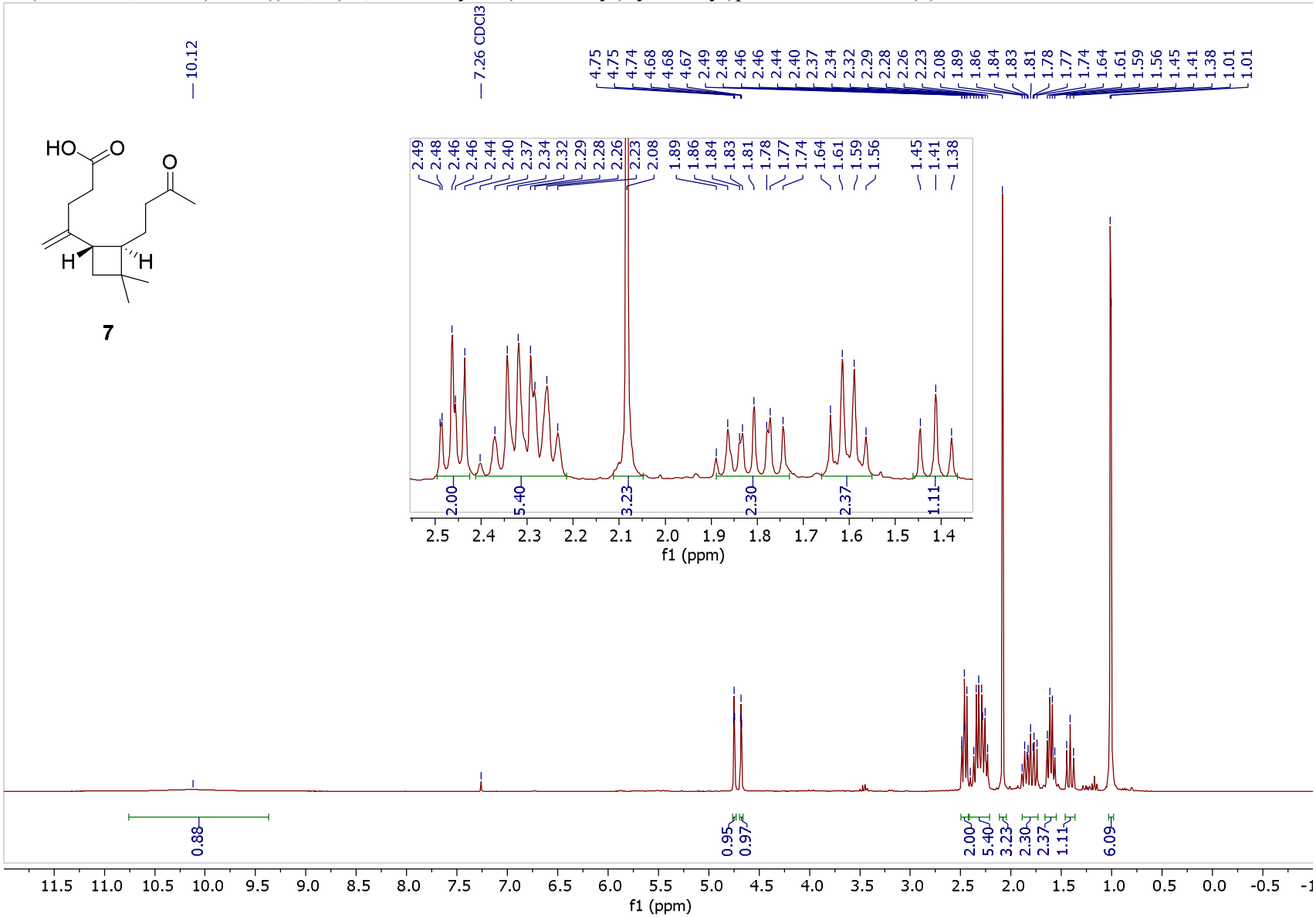


^{13}C NMR (101 MHz, $CDCl_3$) of 4-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)pent-4-enal (**6**)

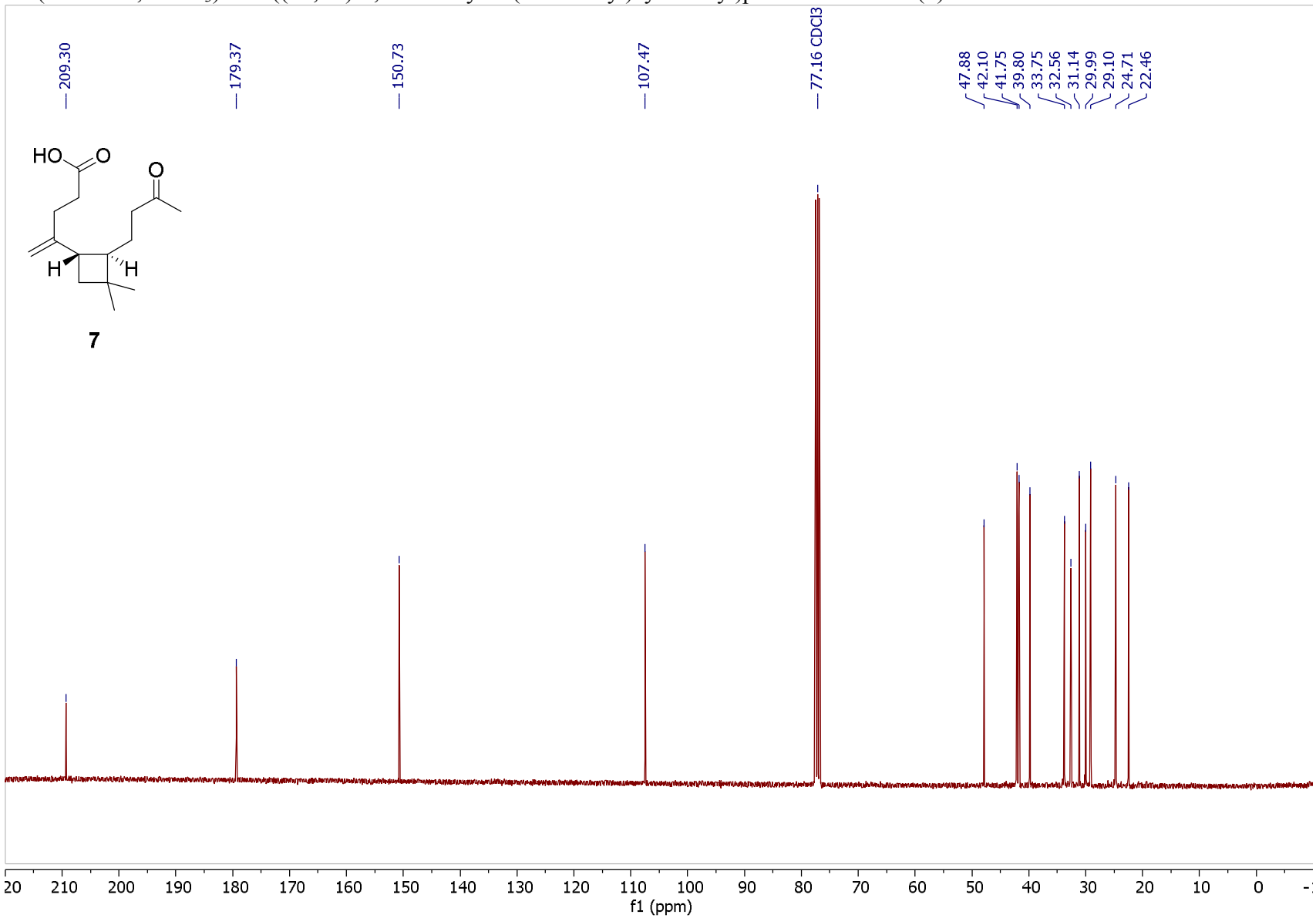


S3. NMR spectra of compound **7**

^{1}H NMR (300 MHz, $CDCl_3$) of 4-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)pent-4-enoic acid (**7**)

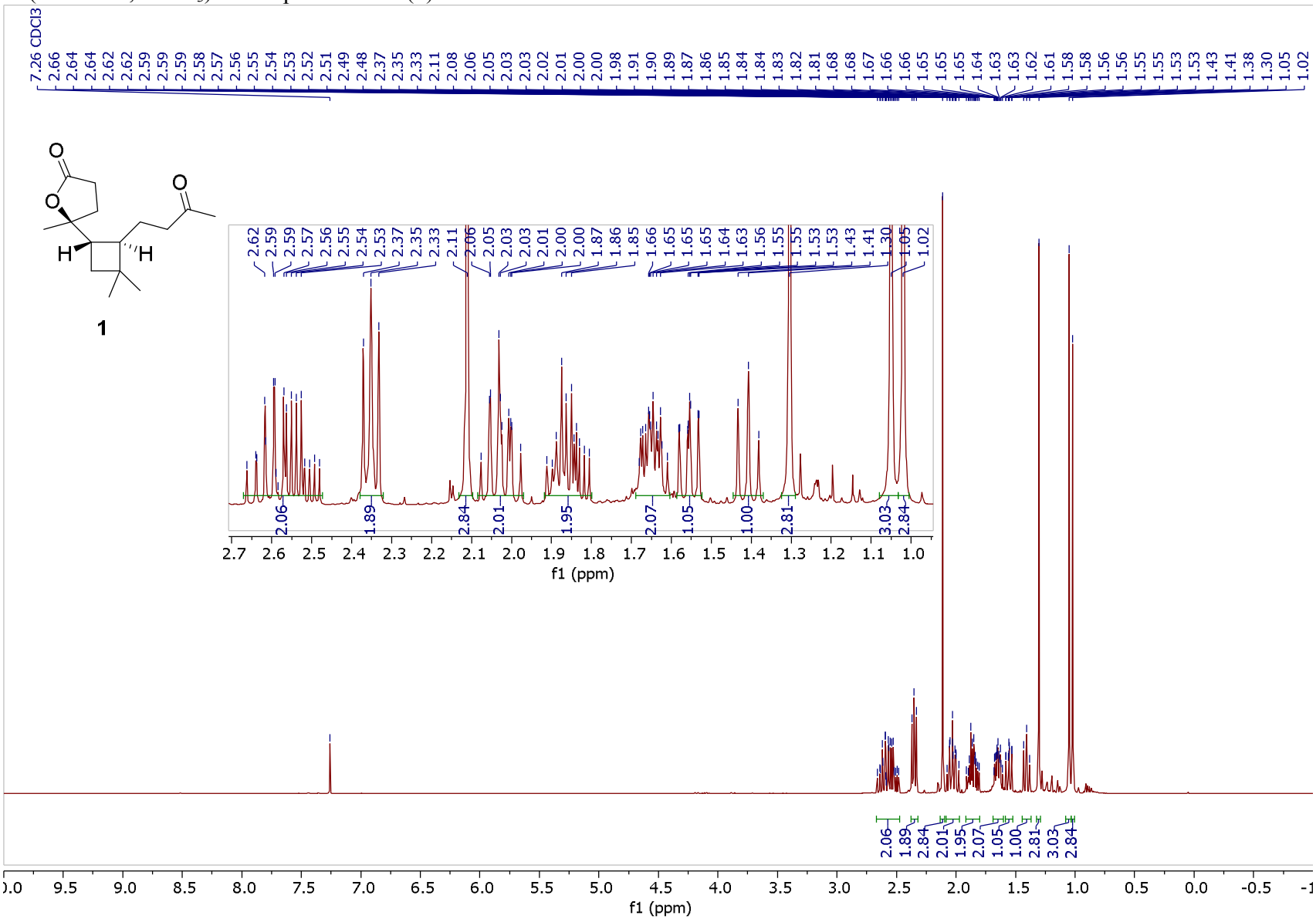


^{13}C NMR (101 MHz, $CDCl_3$) of 4-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)pent-4-enoic acid (**7**)

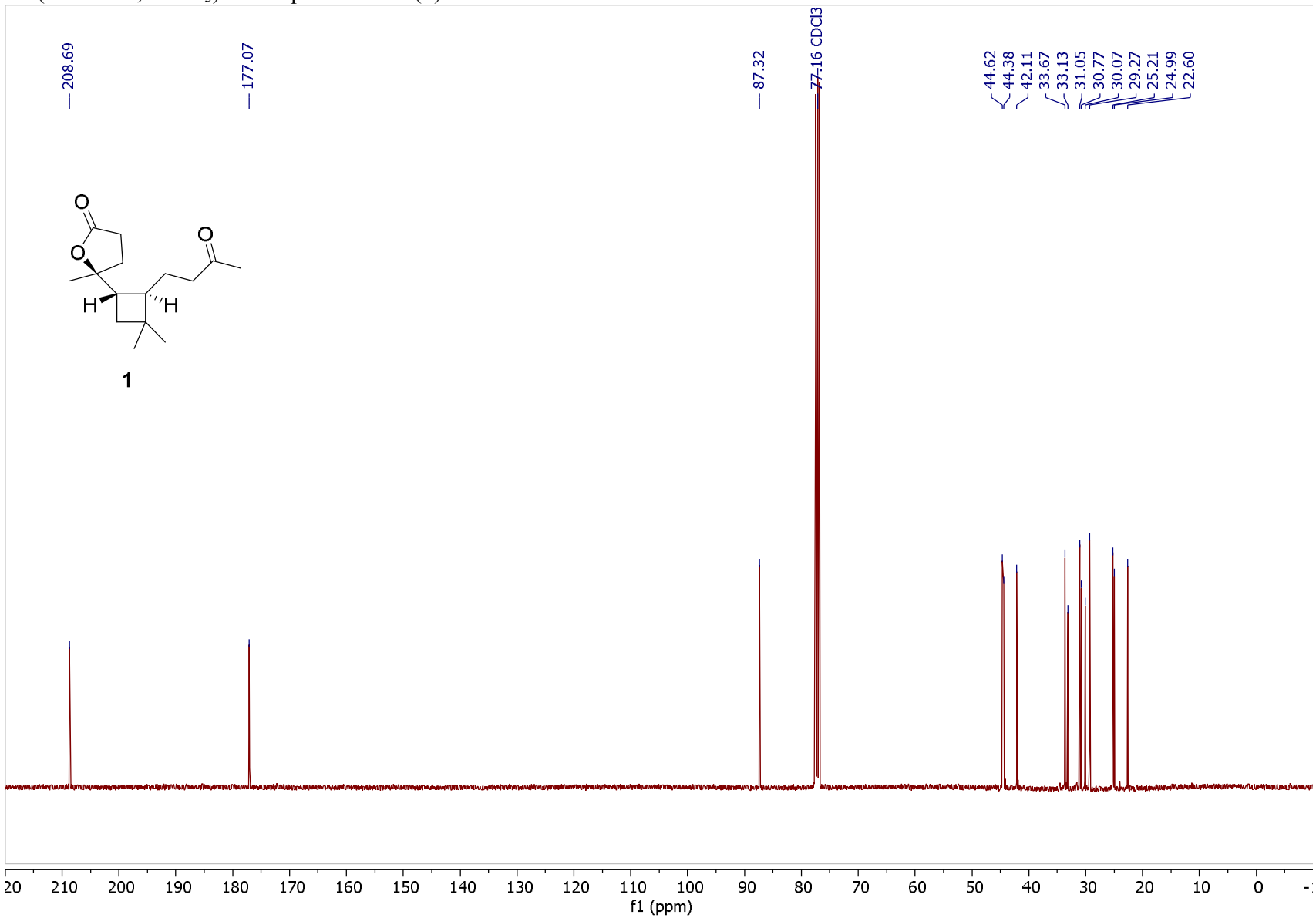


S4. NMR spectra of rumphellaone A (**1**)

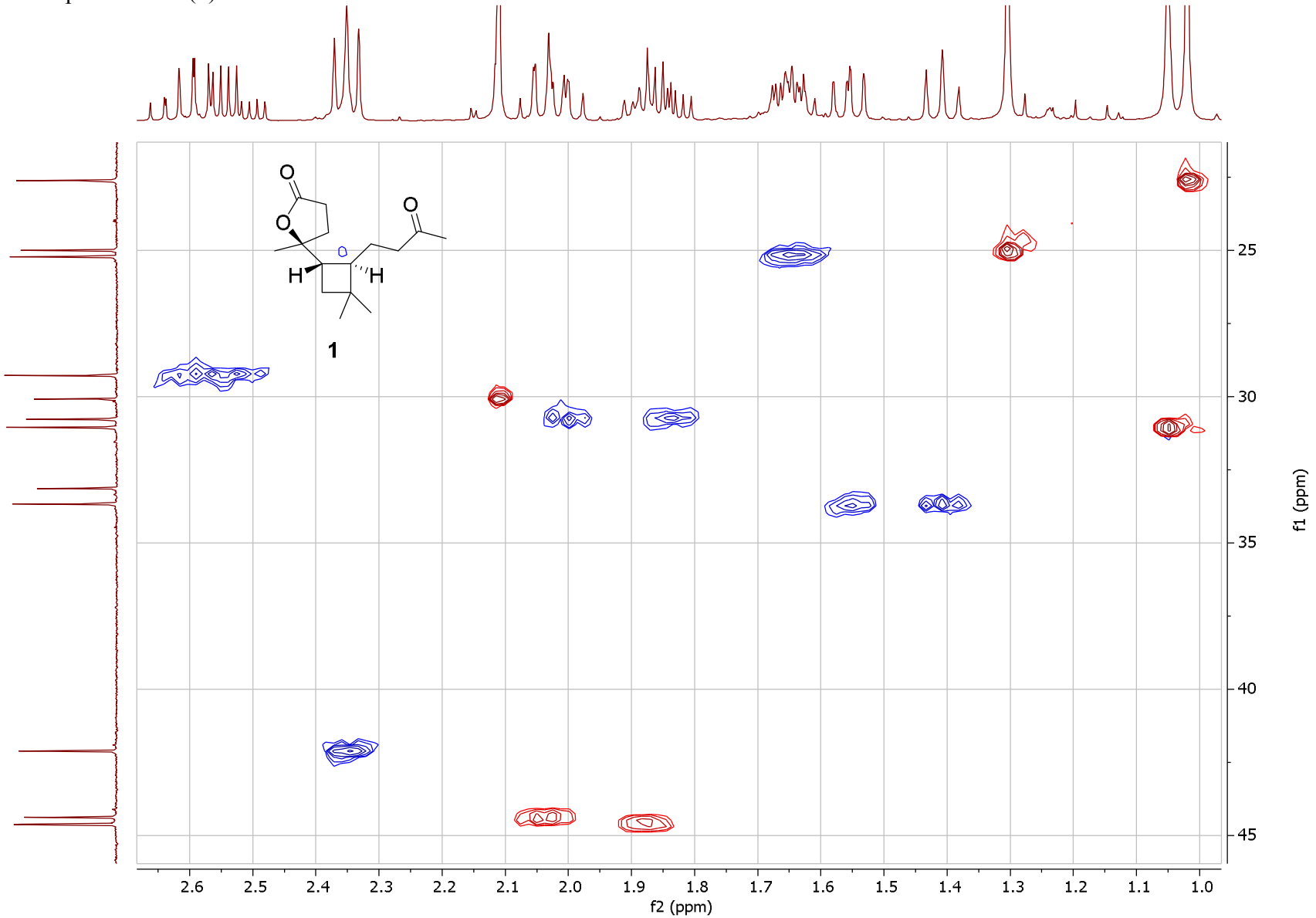
^{1}H NMR (400 MHz, $CDCl_3$) of rumphellaone A (**1**)



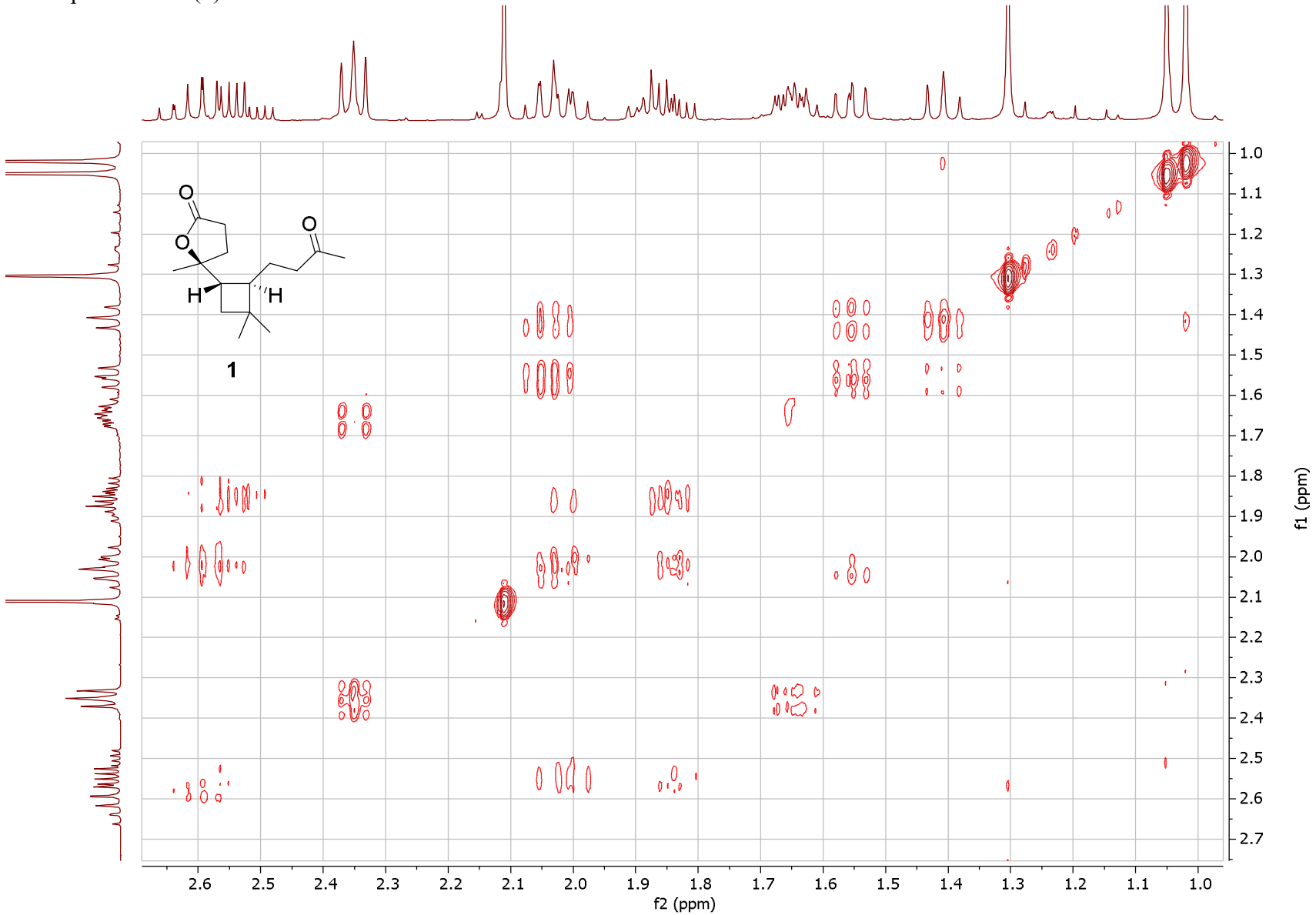
^{13}C NMR (101 MHz, $CDCl_3$) of rumphellaone A (**1**)



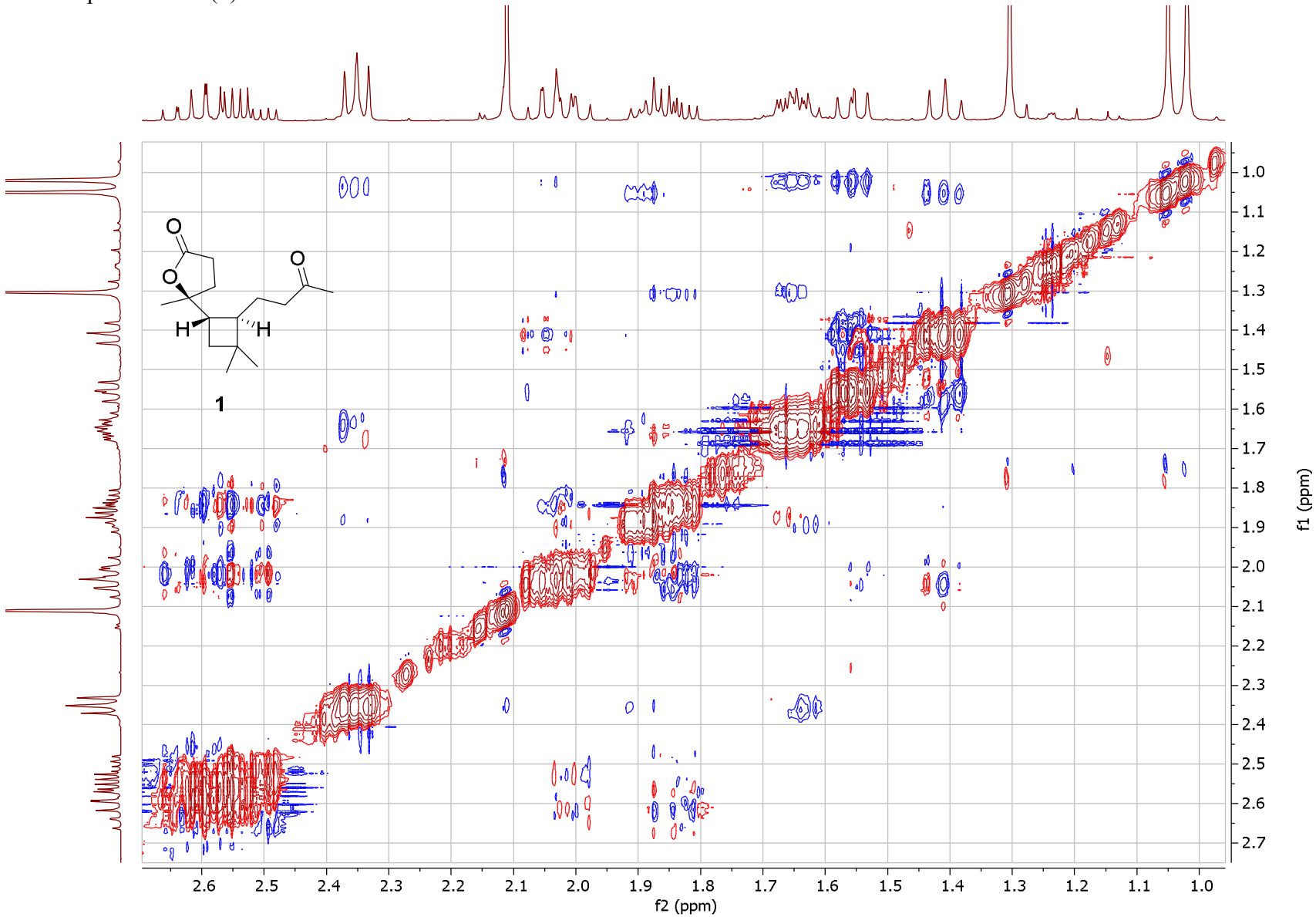
HSQC of rumphellaone A (**1**)



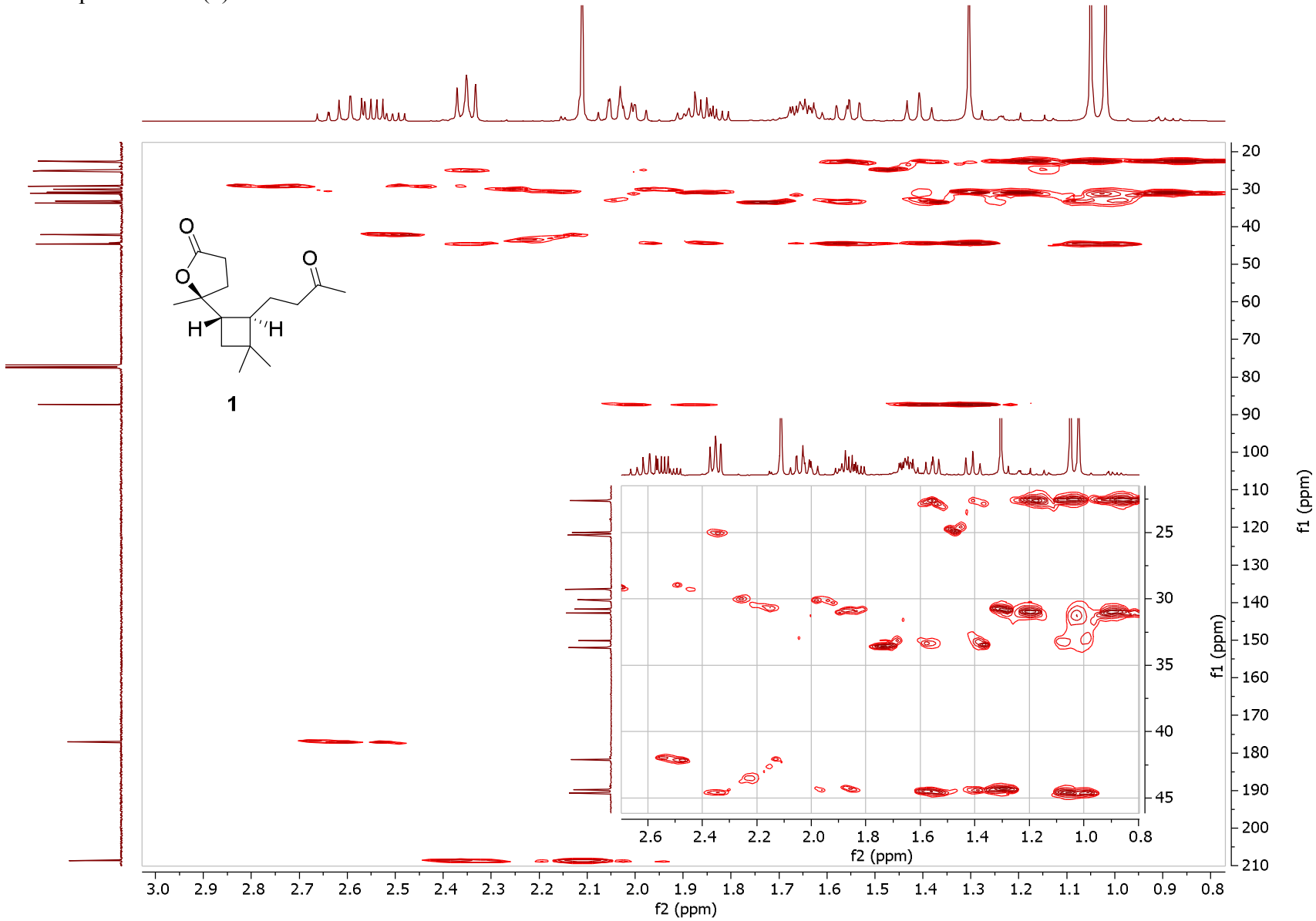
COSY of rumphellaone A (**1**)



NOESY of rumphellaone A (**1**)

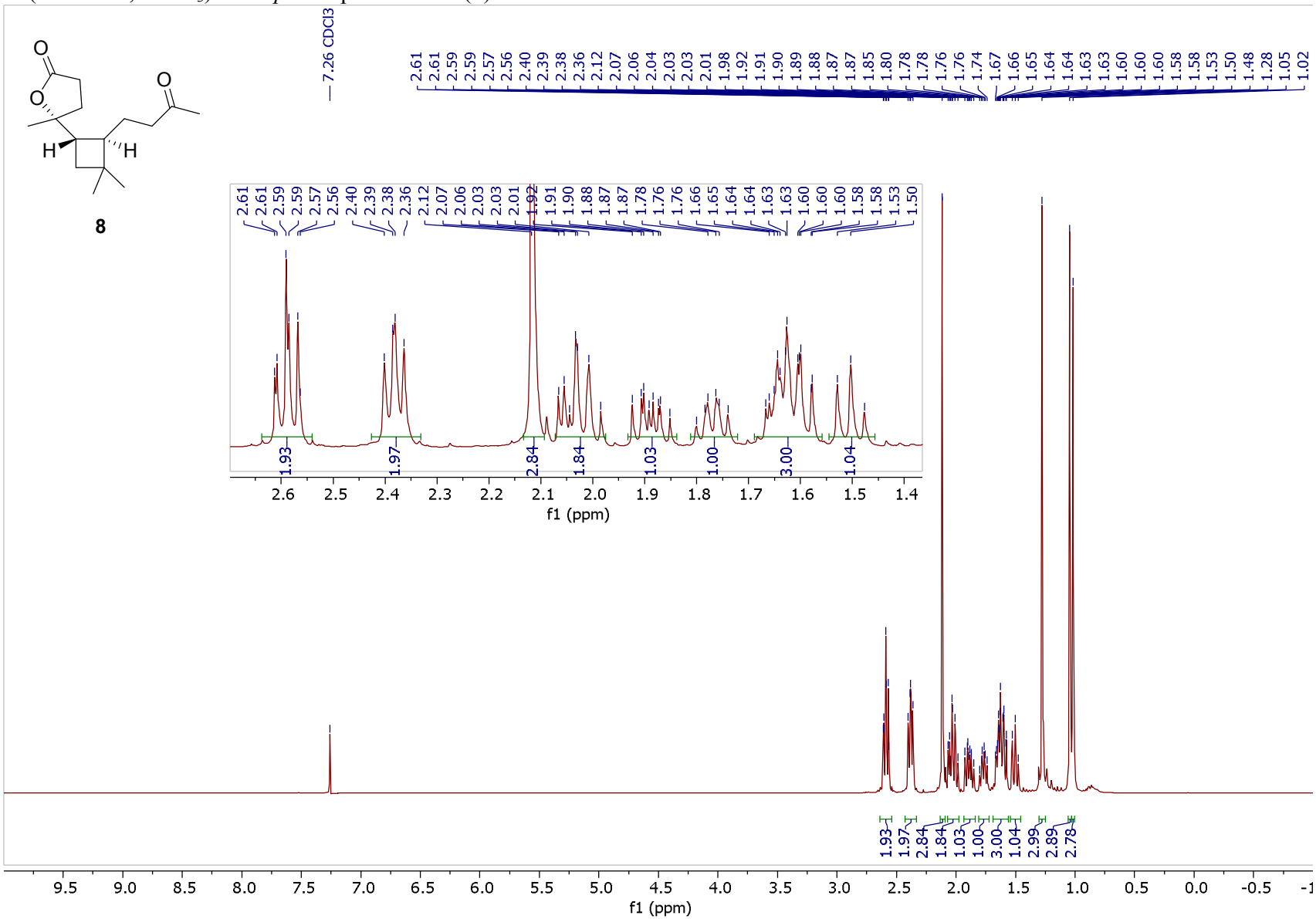


HMBC of rumphellaone A (**1**)

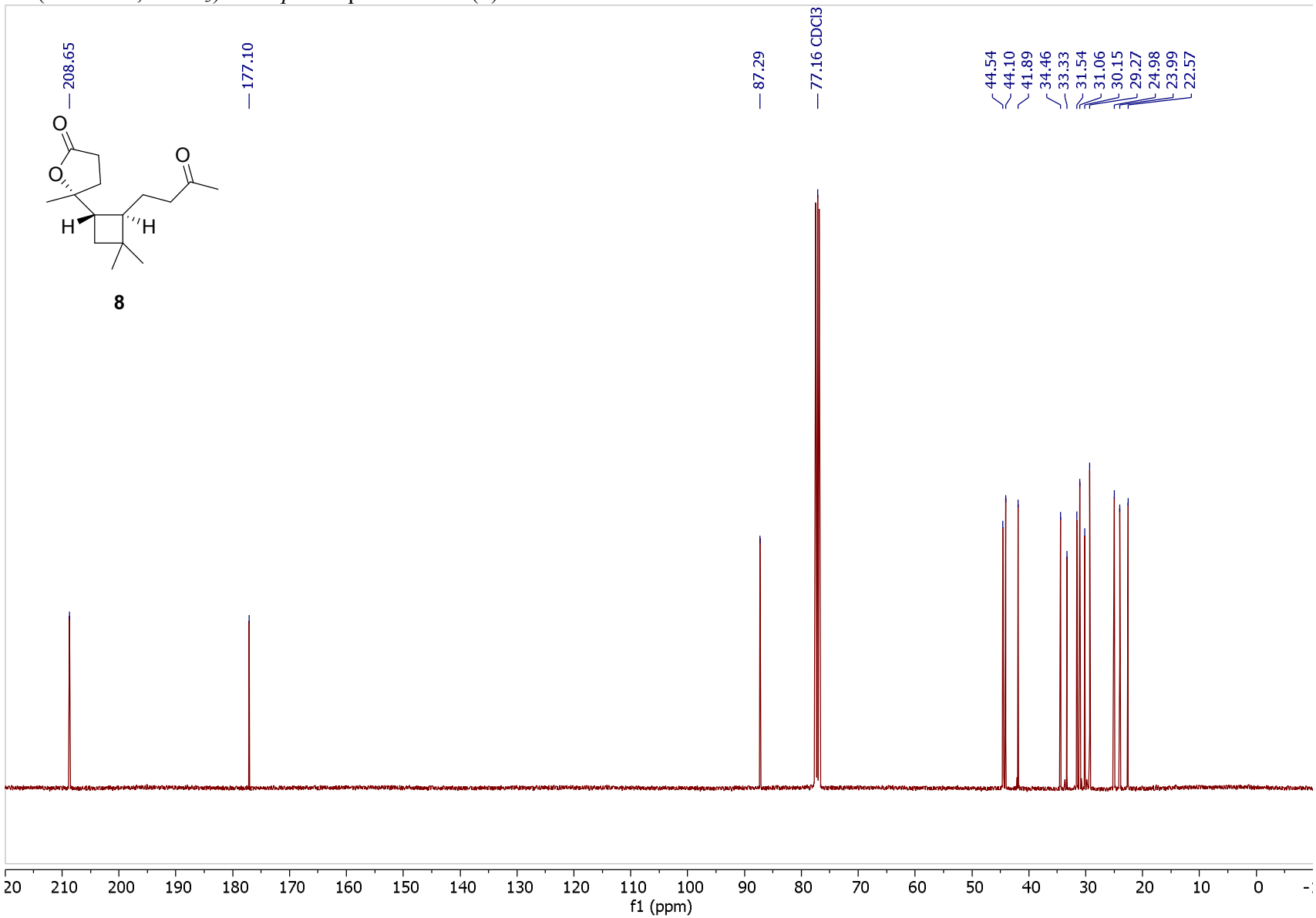


S5. NMR spectra of 8-*epi*-rumphellaone A (**8**)

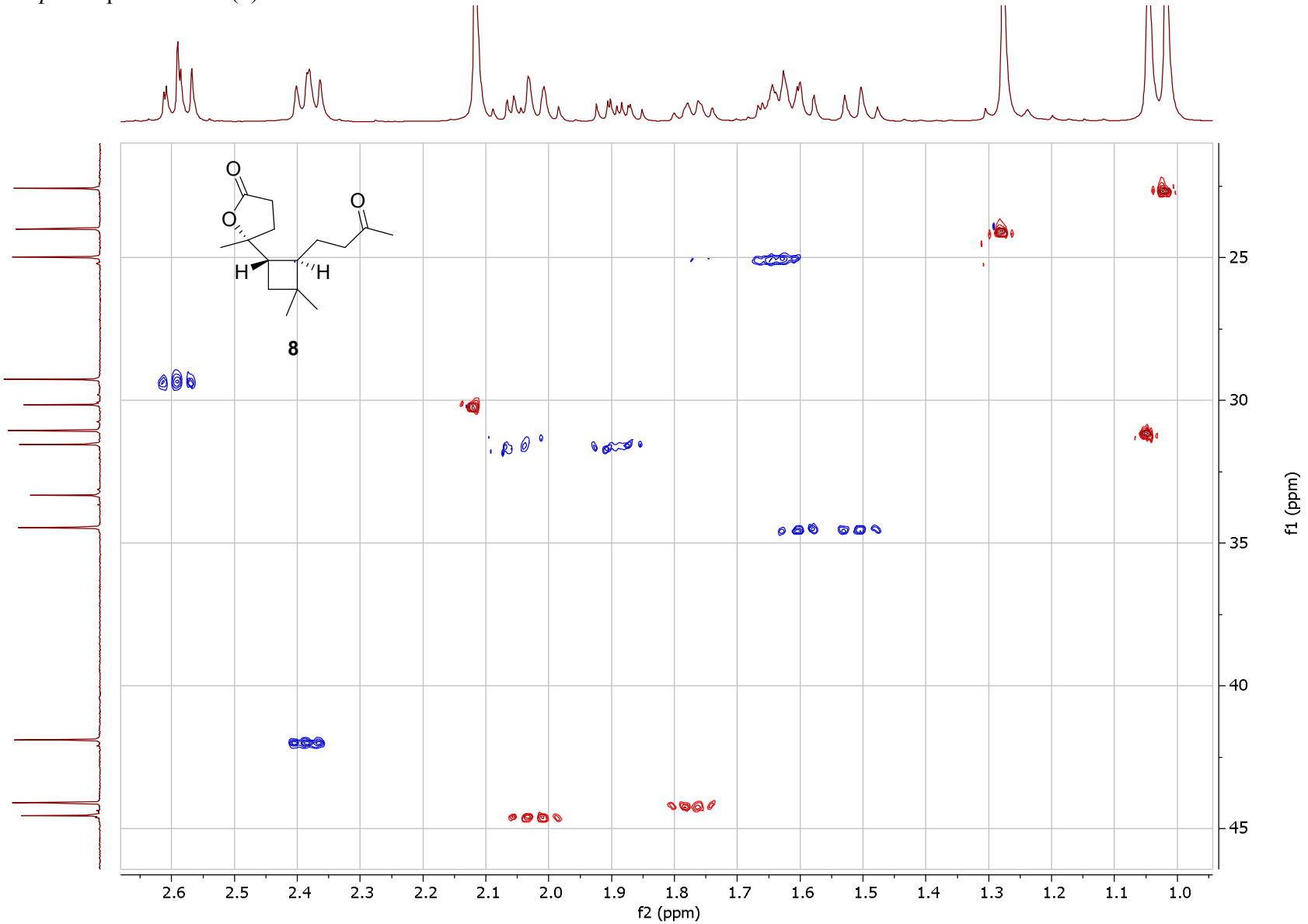
^{1}H NMR (400 MHz, $CDCl_3$) of 8-*epi*-rumphellaone A (**8**)



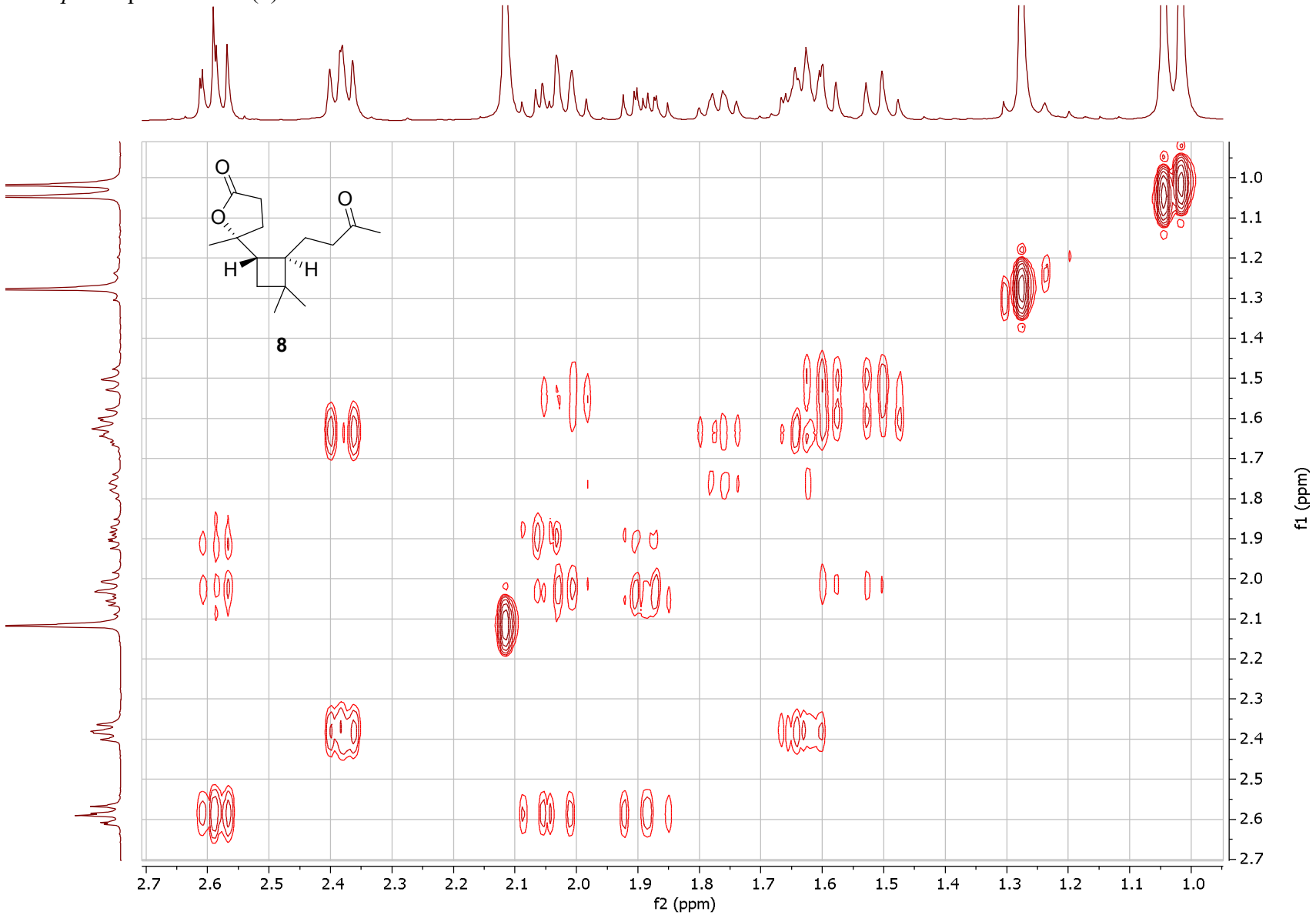
^{13}C NMR (101 MHz, $CDCl_3$) of 8-*epi*-rumphellaone A (**8**)



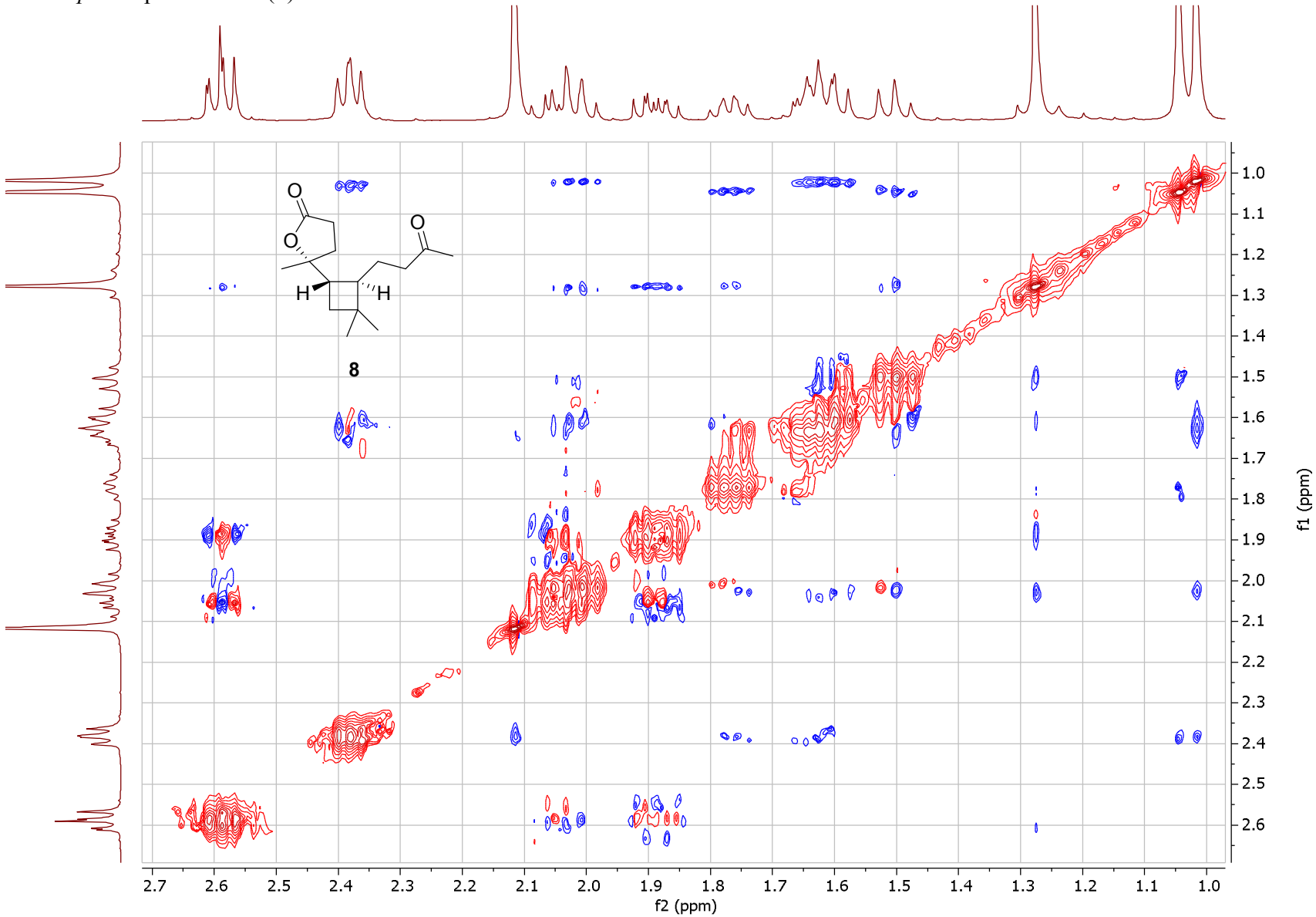
HSQC of 8-*epi*-rumphellaone A (**8**)



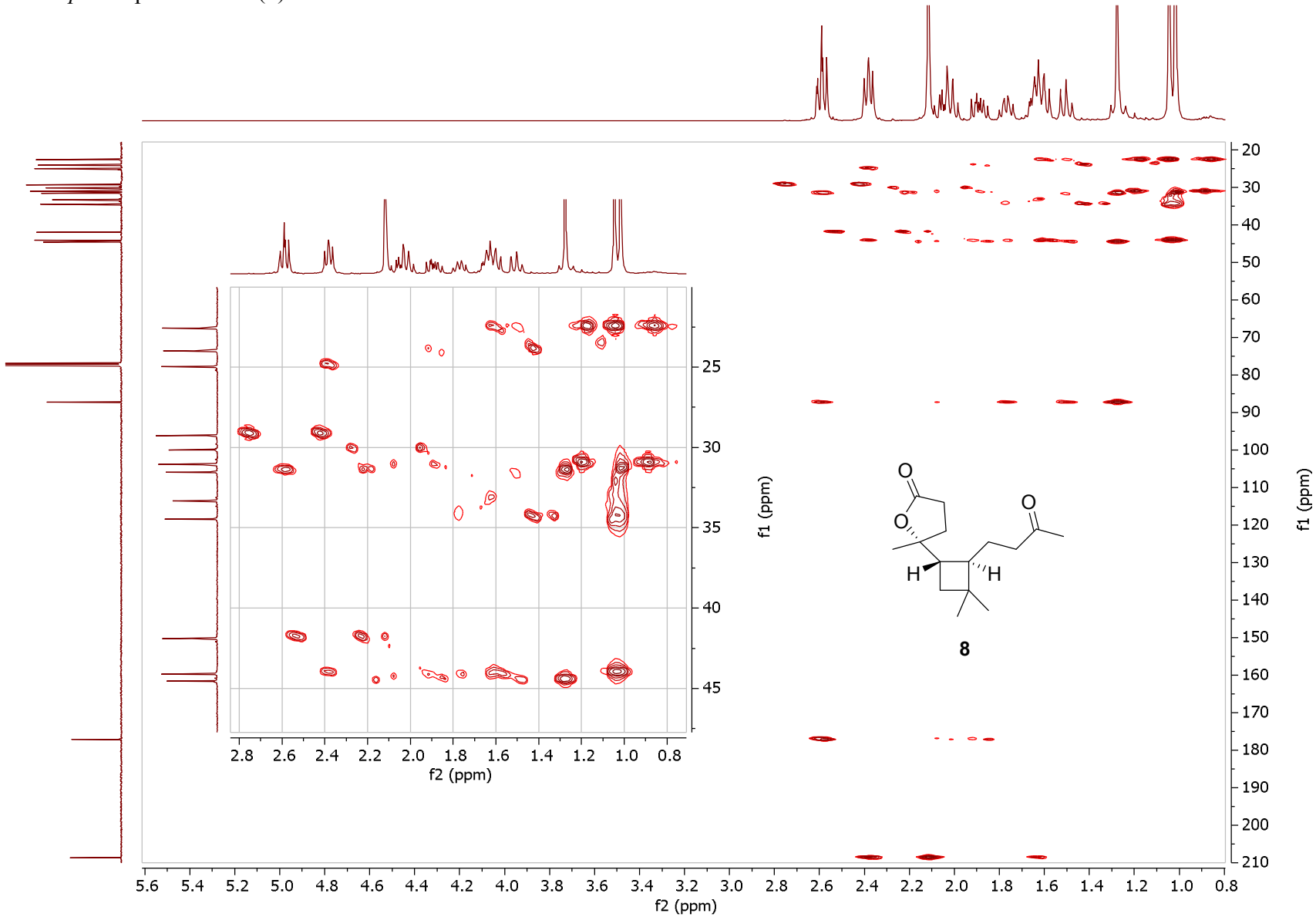
COSY of 8-*epi*-rumphellaone A (**8**)



NOESY of 8-*epi*-rumphellaone A (**8**)

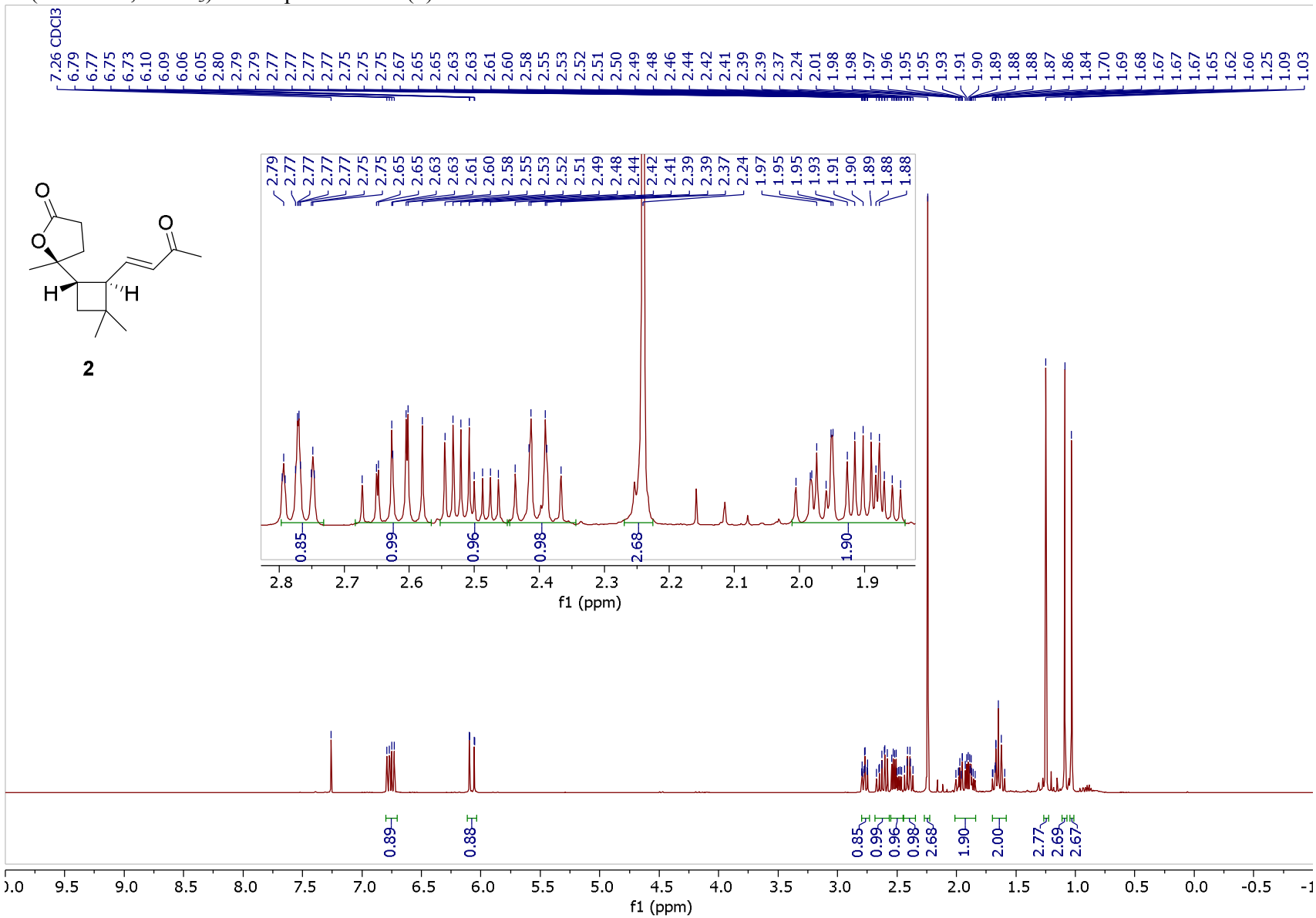


HMBC of 8-*epi*-rumphellaone A (**8**)

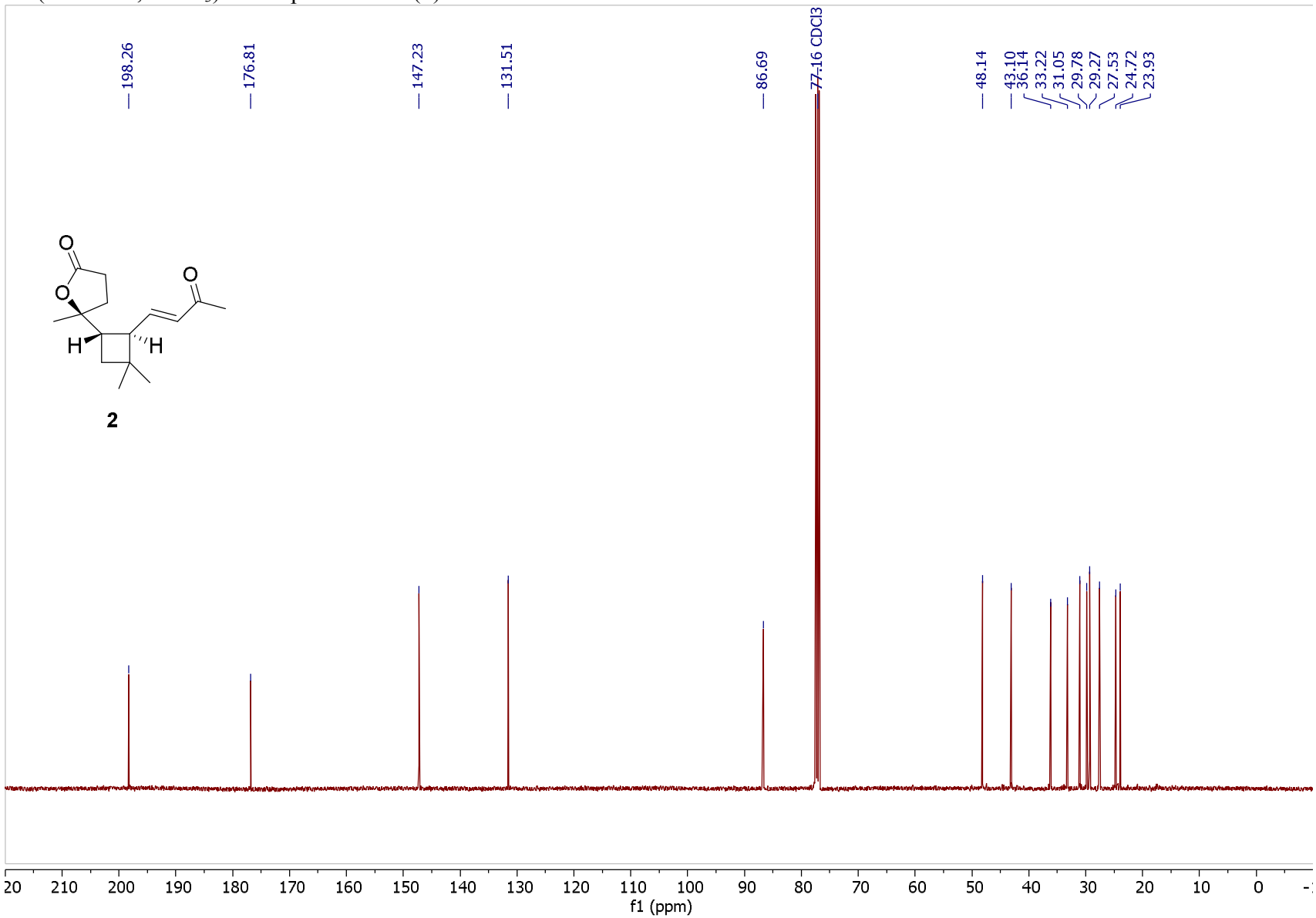


S6. NMR spectra of rumphellaone B (**2**)

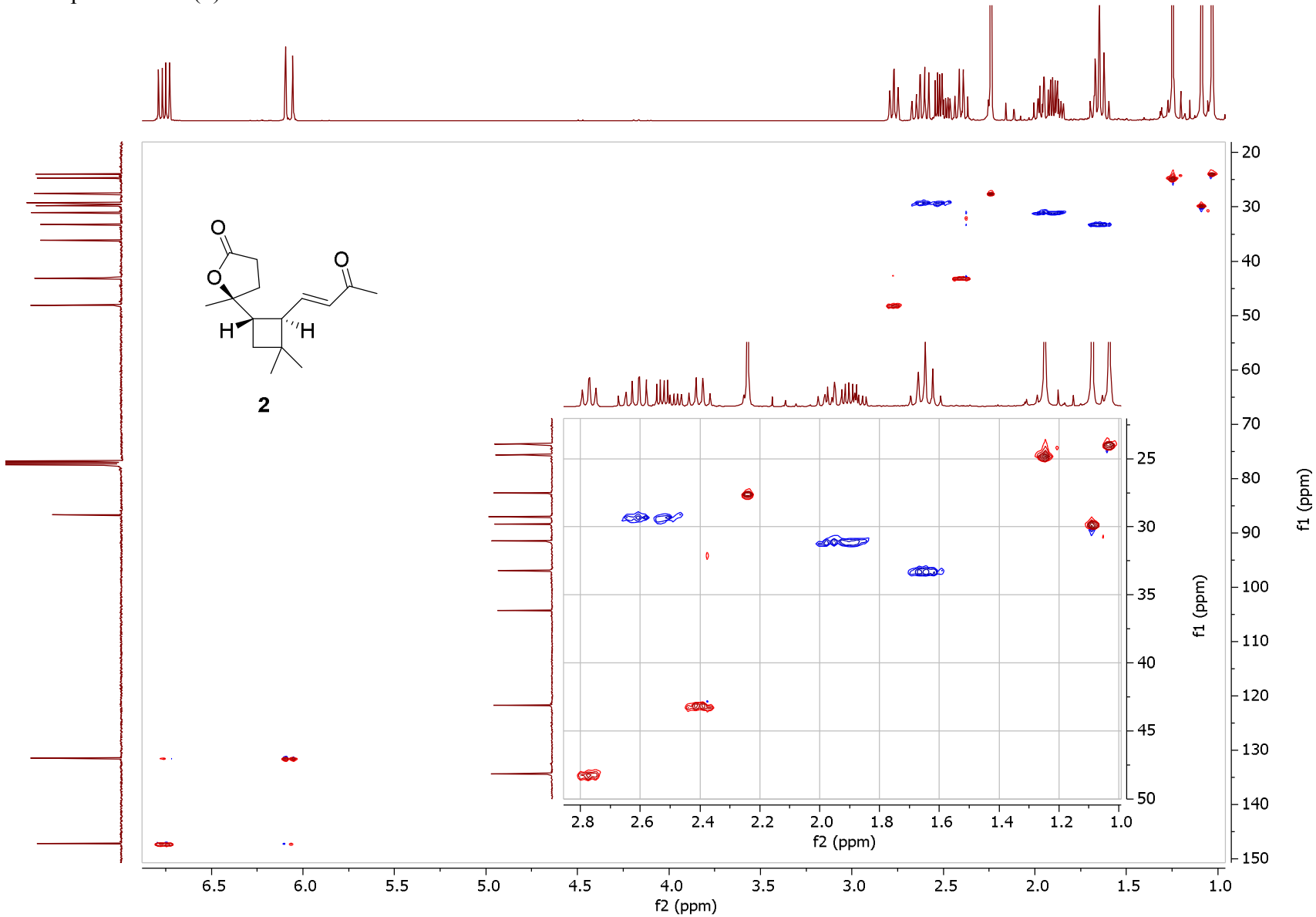
^{1}H NMR (400 MHz, $CDCl_3$) of rumphellaone B (**2**)



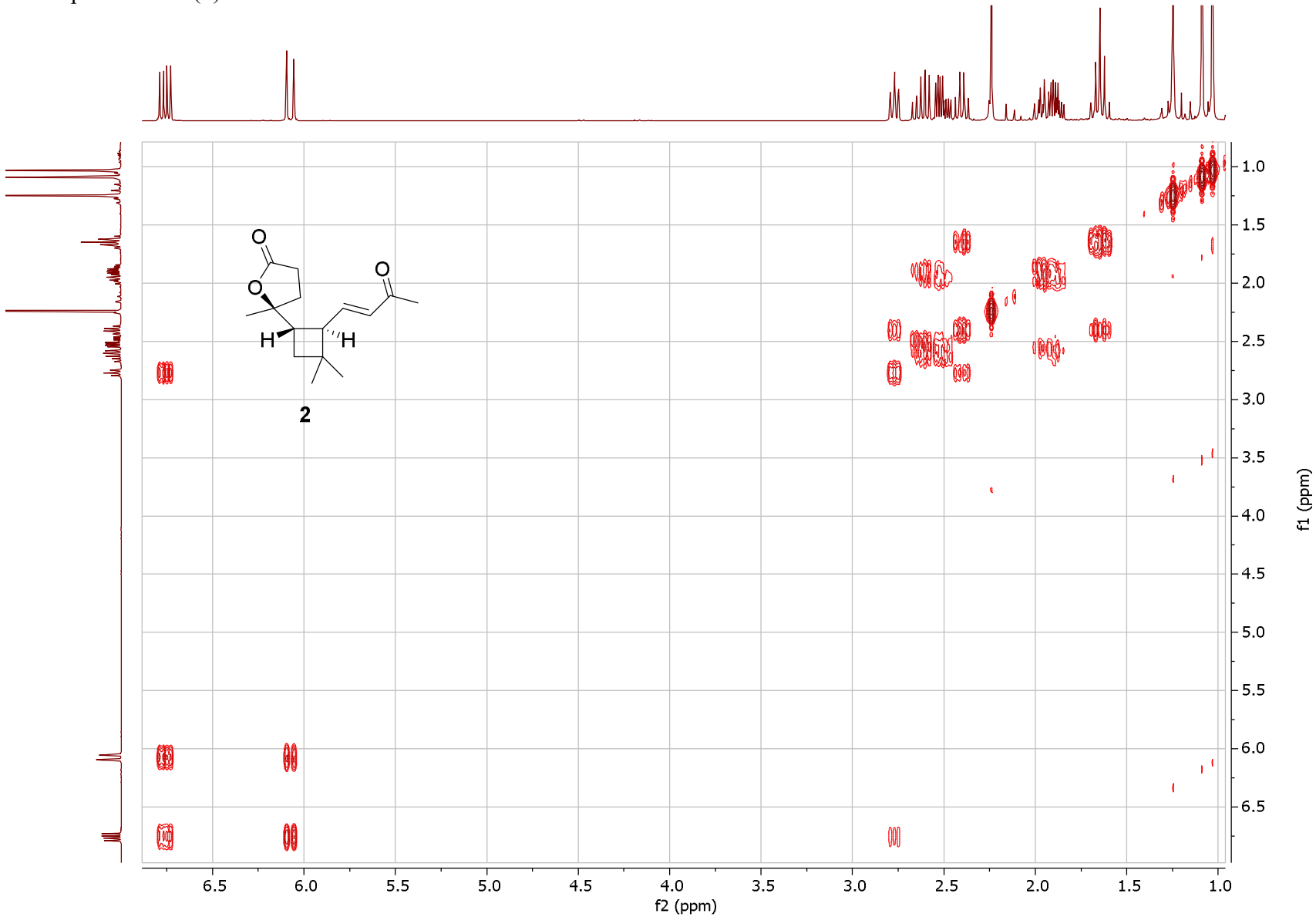
^{13}C NMR (101 MHz, $CDCl_3$) of rumphellaone B (**2**)



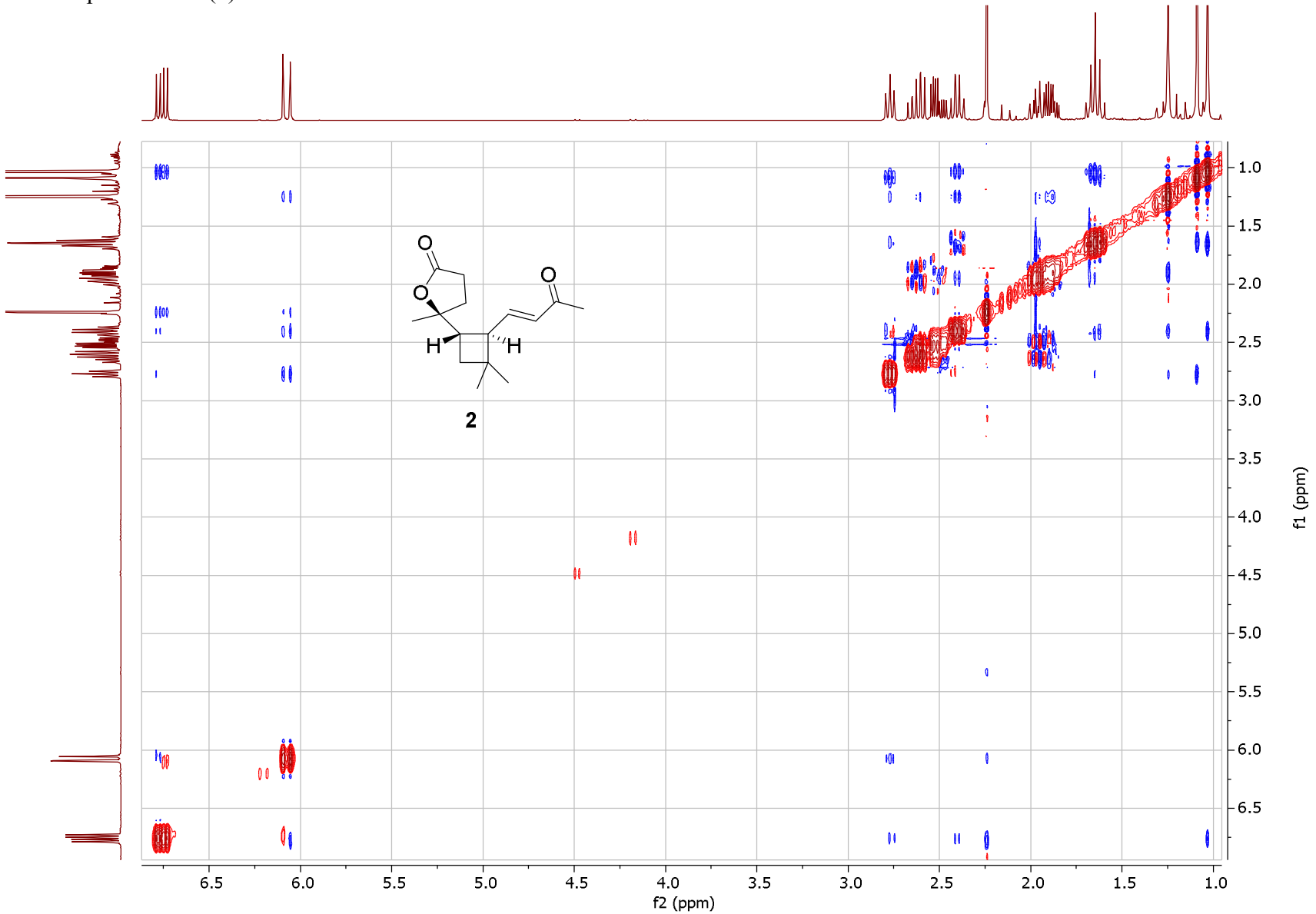
HSQC of rumphellaone B (**2**)



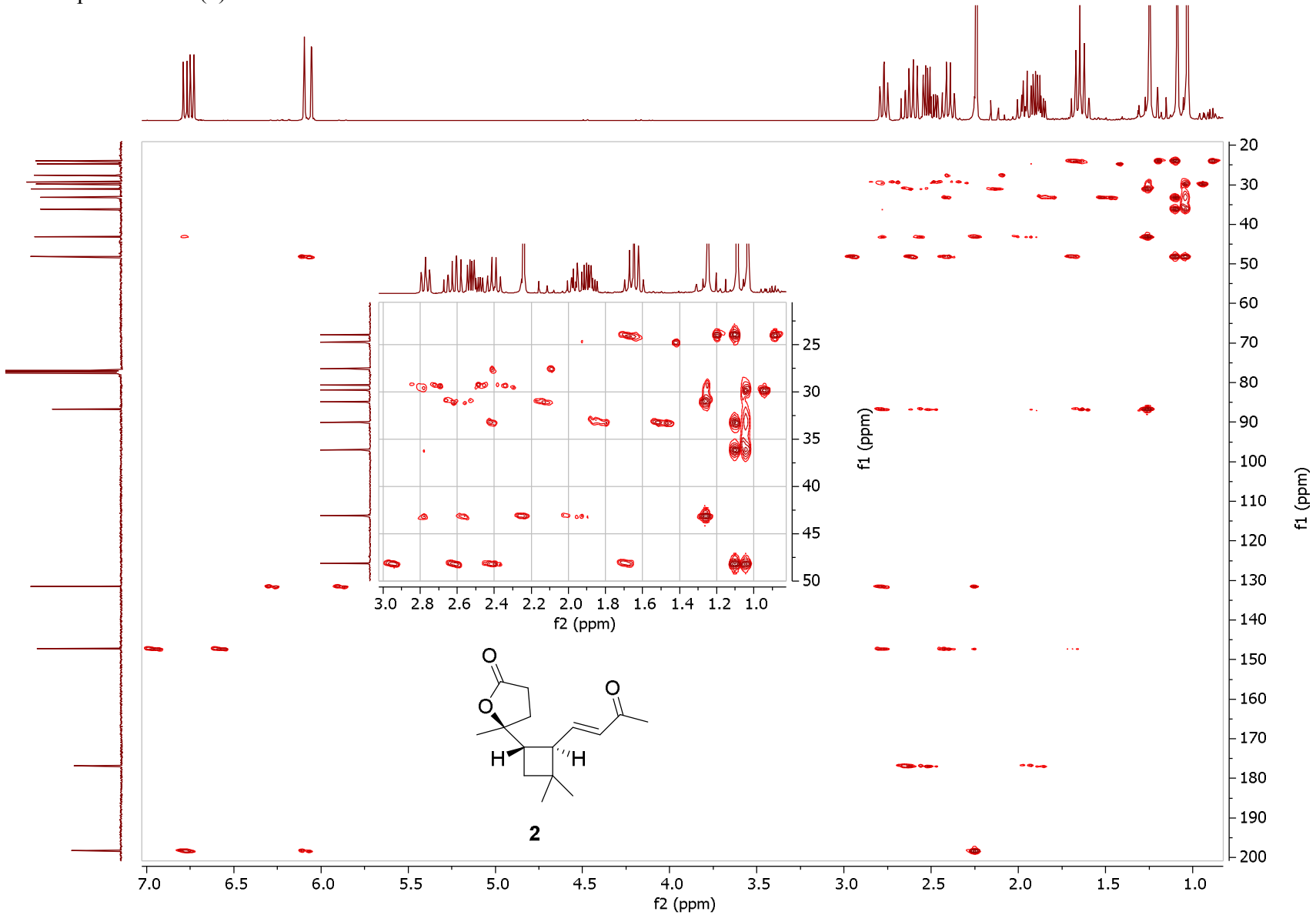
COSY of rumphellaone B (**2**)



NOESY of rumphellaone B (**2**)

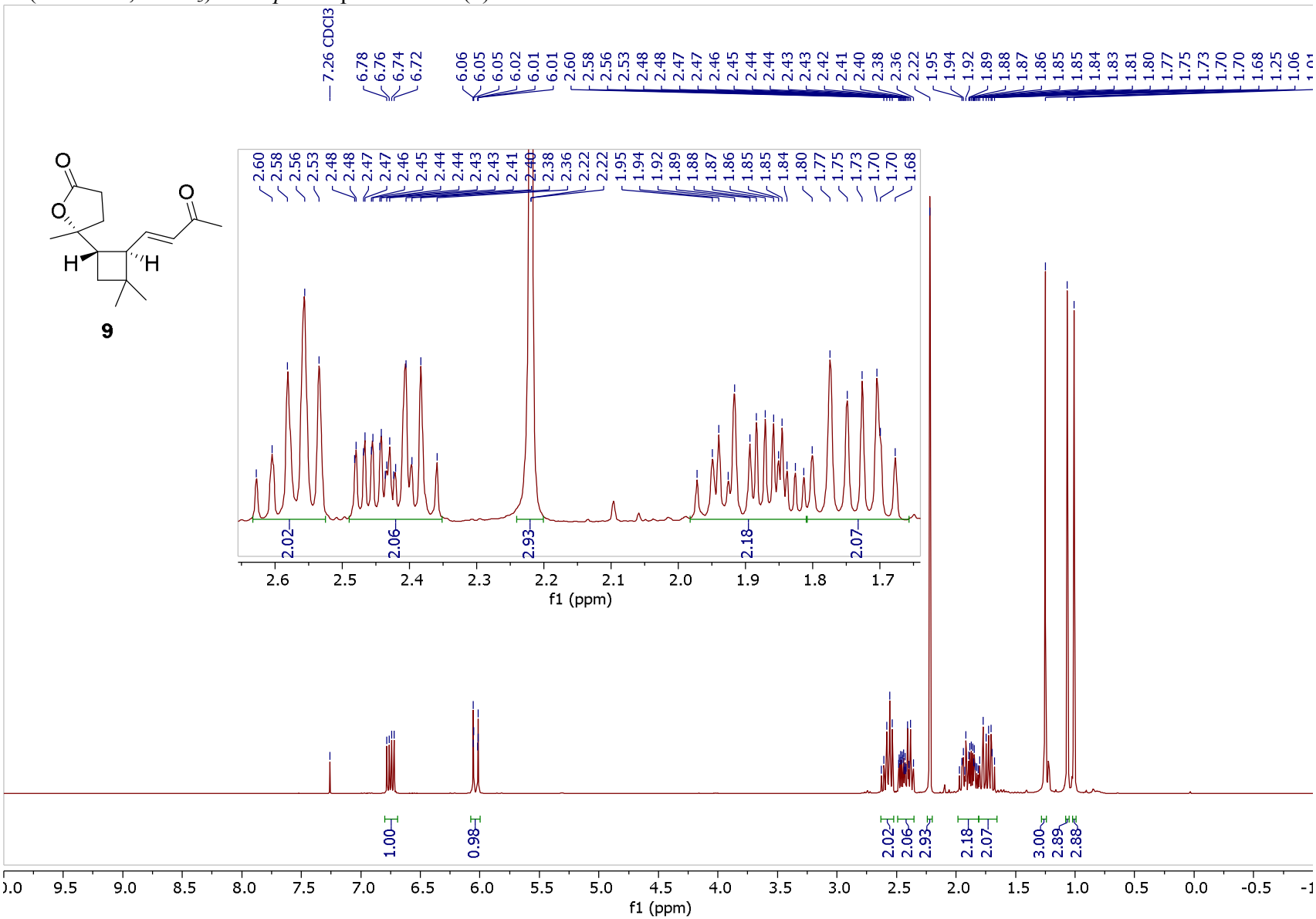


HMBC of rumphellaone B (**2**)

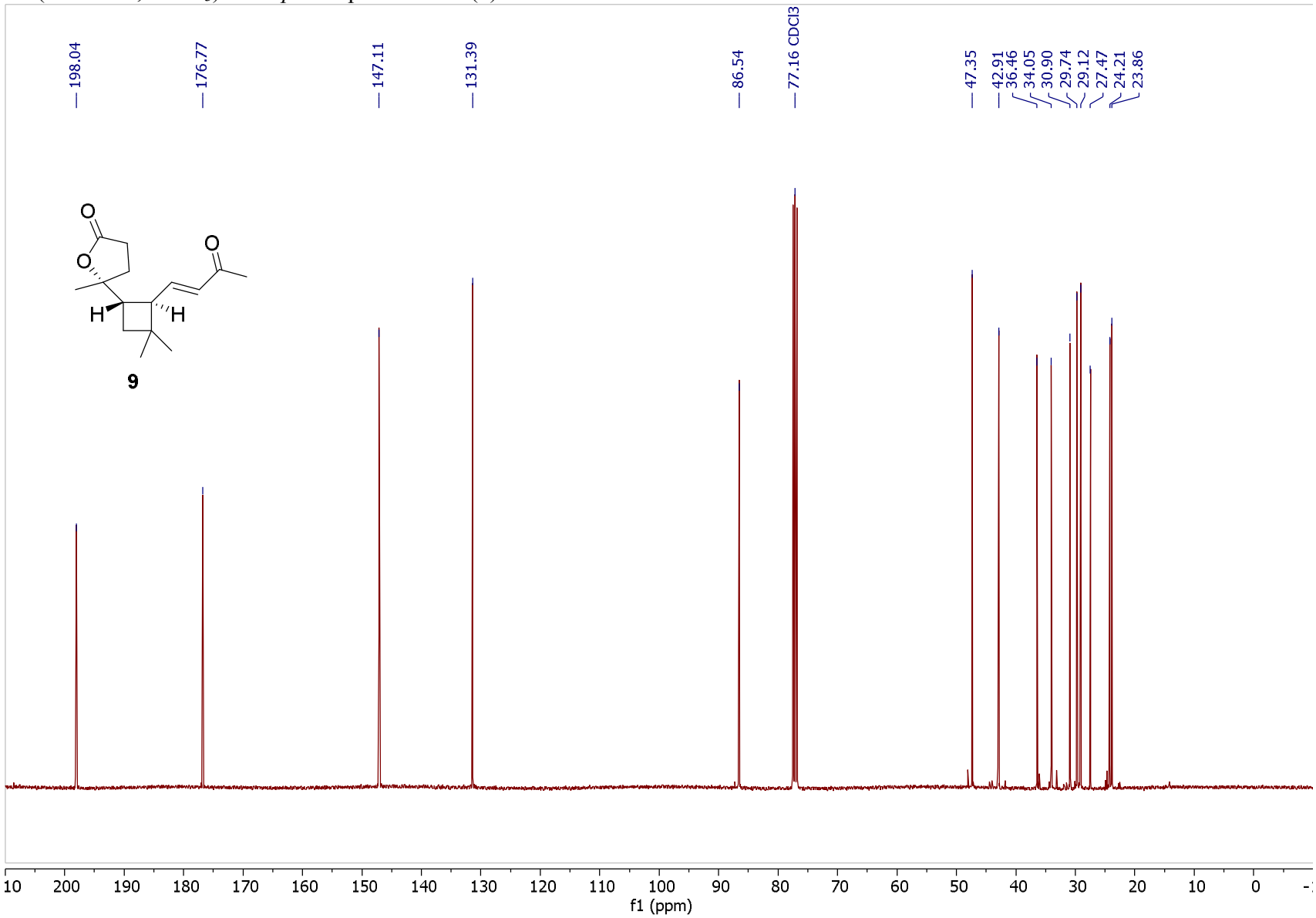


S7. NMR spectra of 8-*epi*-rumphellaone B (**9**)

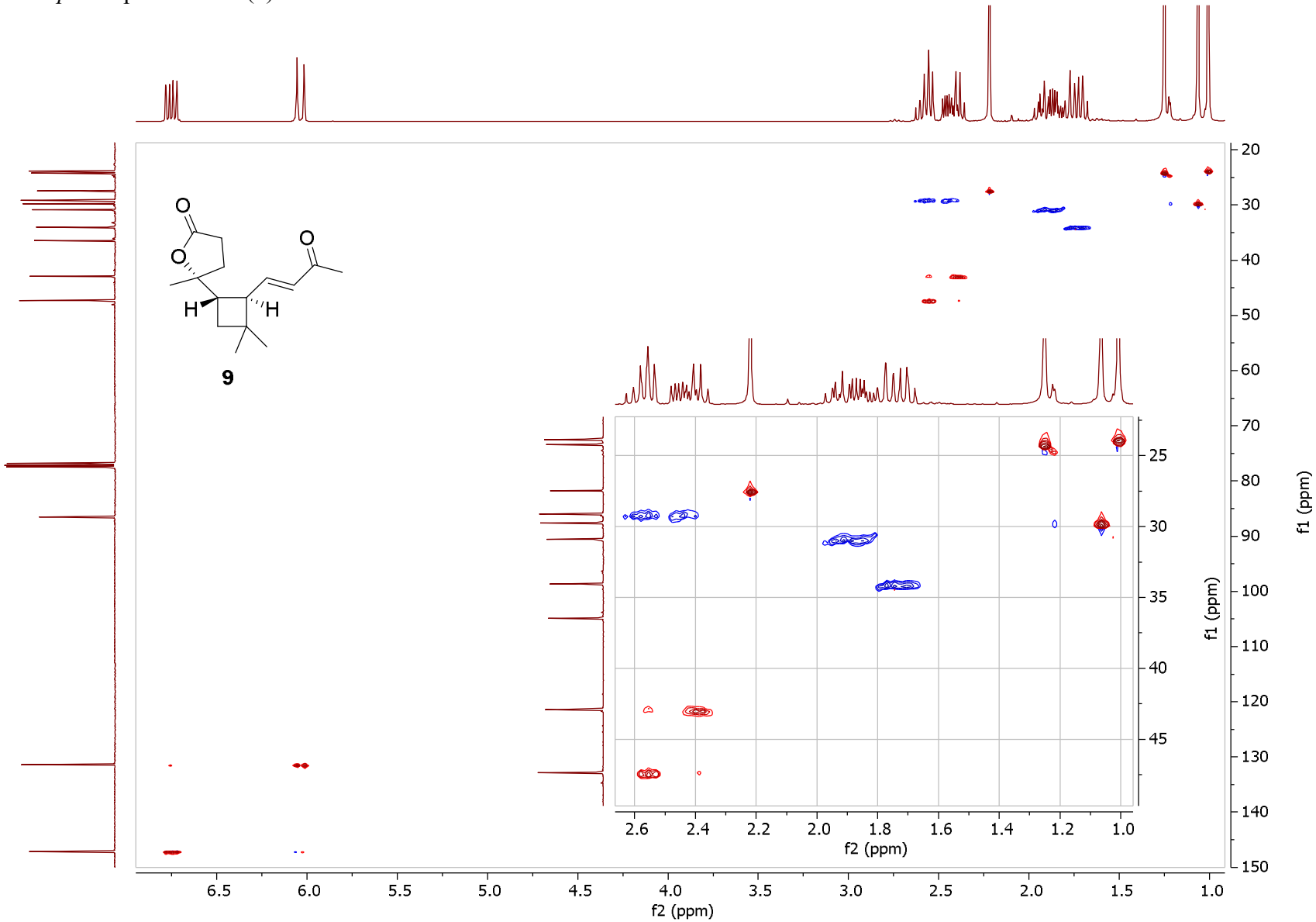
^{1}H NMR (400 MHz, $CDCl_3$) of 8-*epi*-rumphellaone B (**9**)



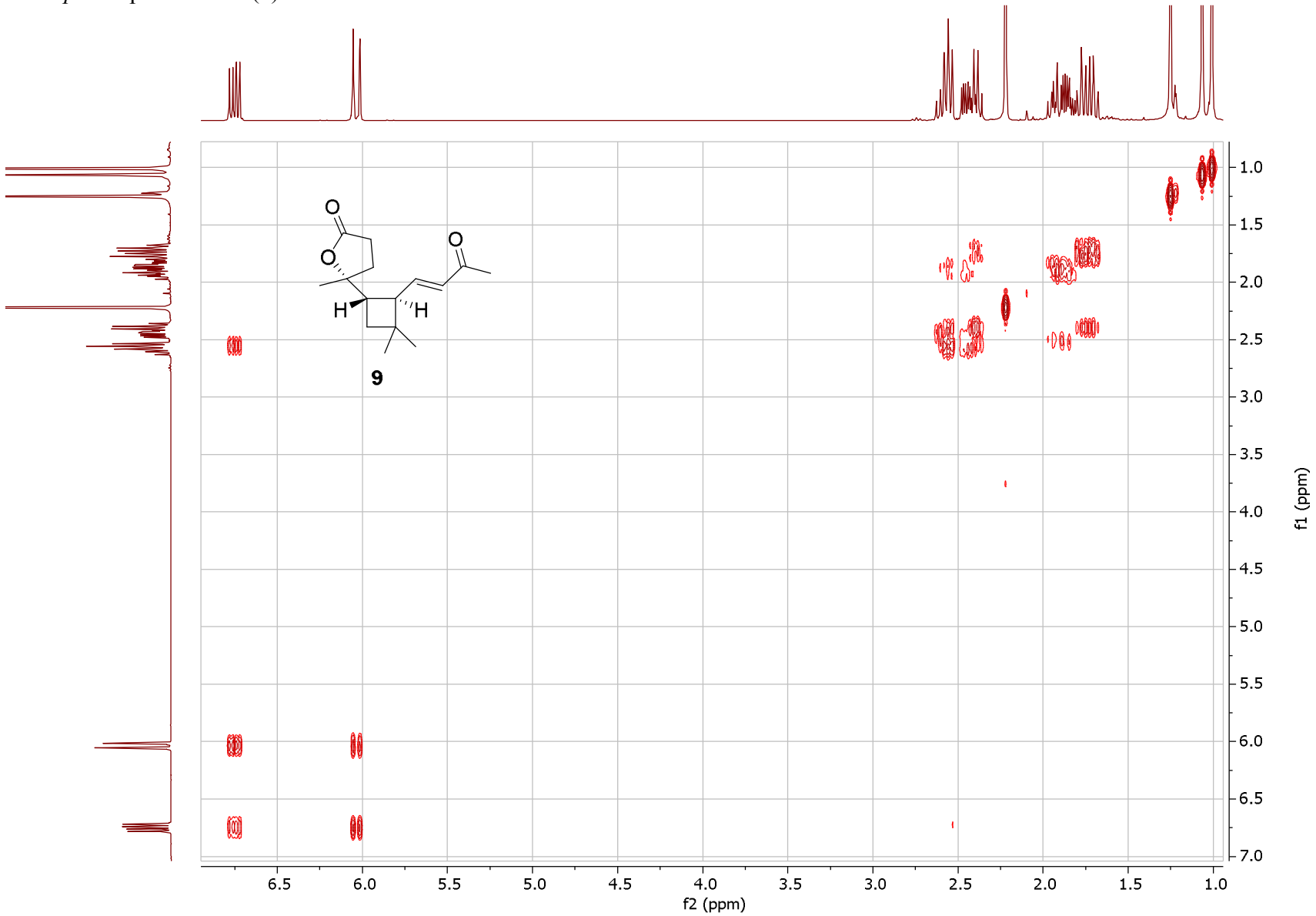
^{13}C NMR (101 MHz, $CDCl_3$) of 8-*epi*-rumphellaone B (**9**)



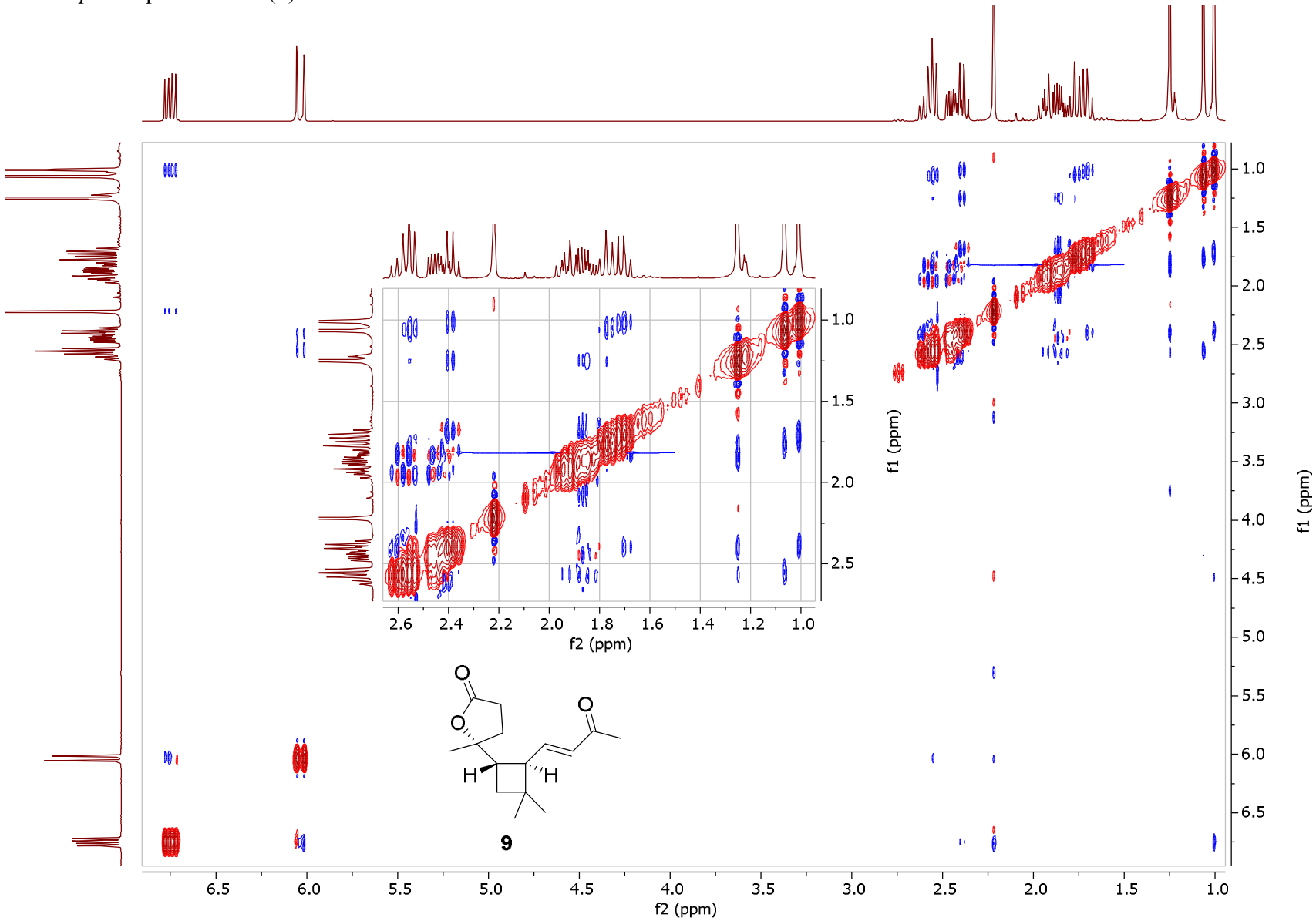
HSQC of 8-*epi*-rumphellaone B (**9**)



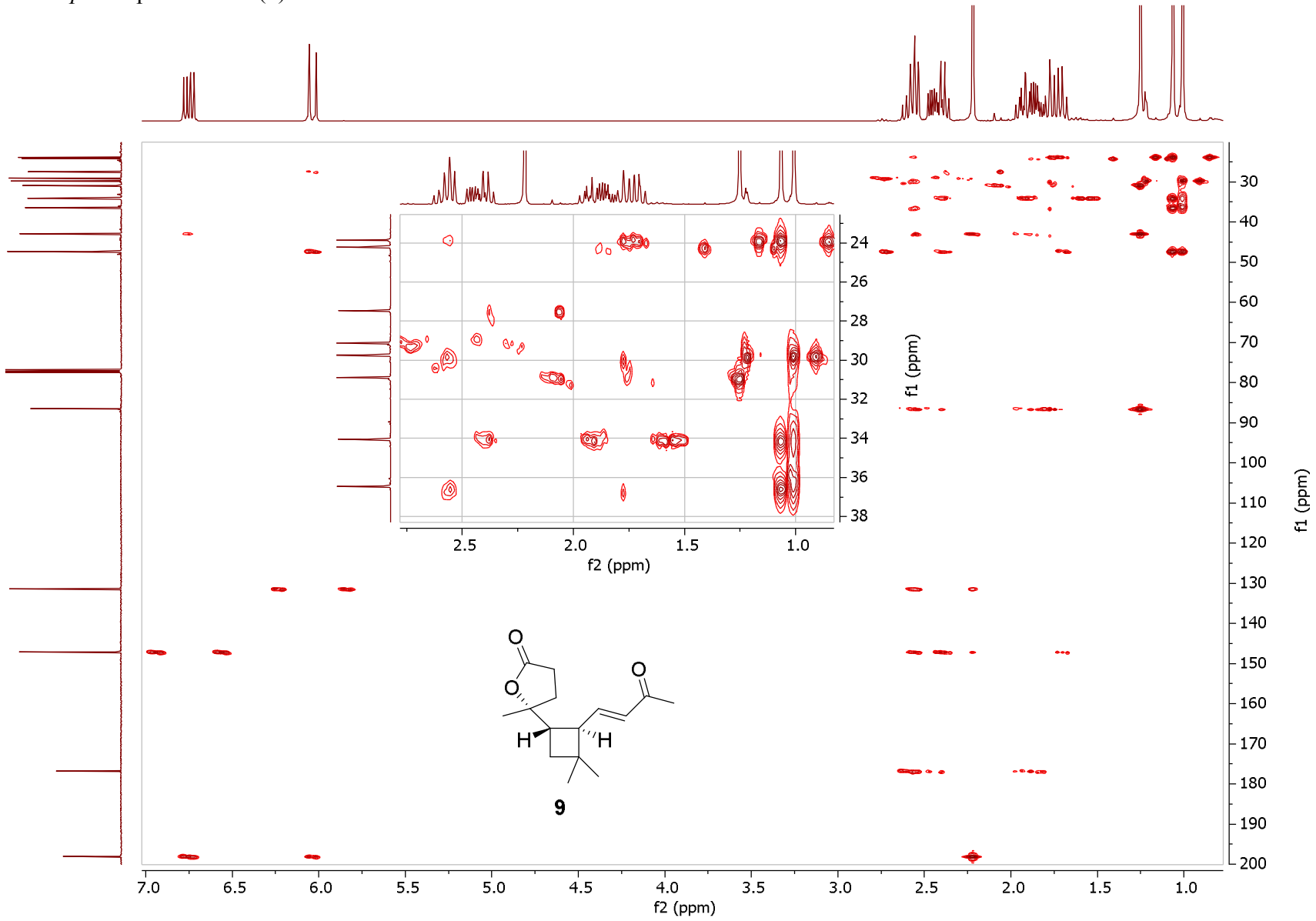
COSY of 8-*epi*-rumphellaone B (**9**)



NOESY of 8-*epi*-rumphellaone B (**9**)

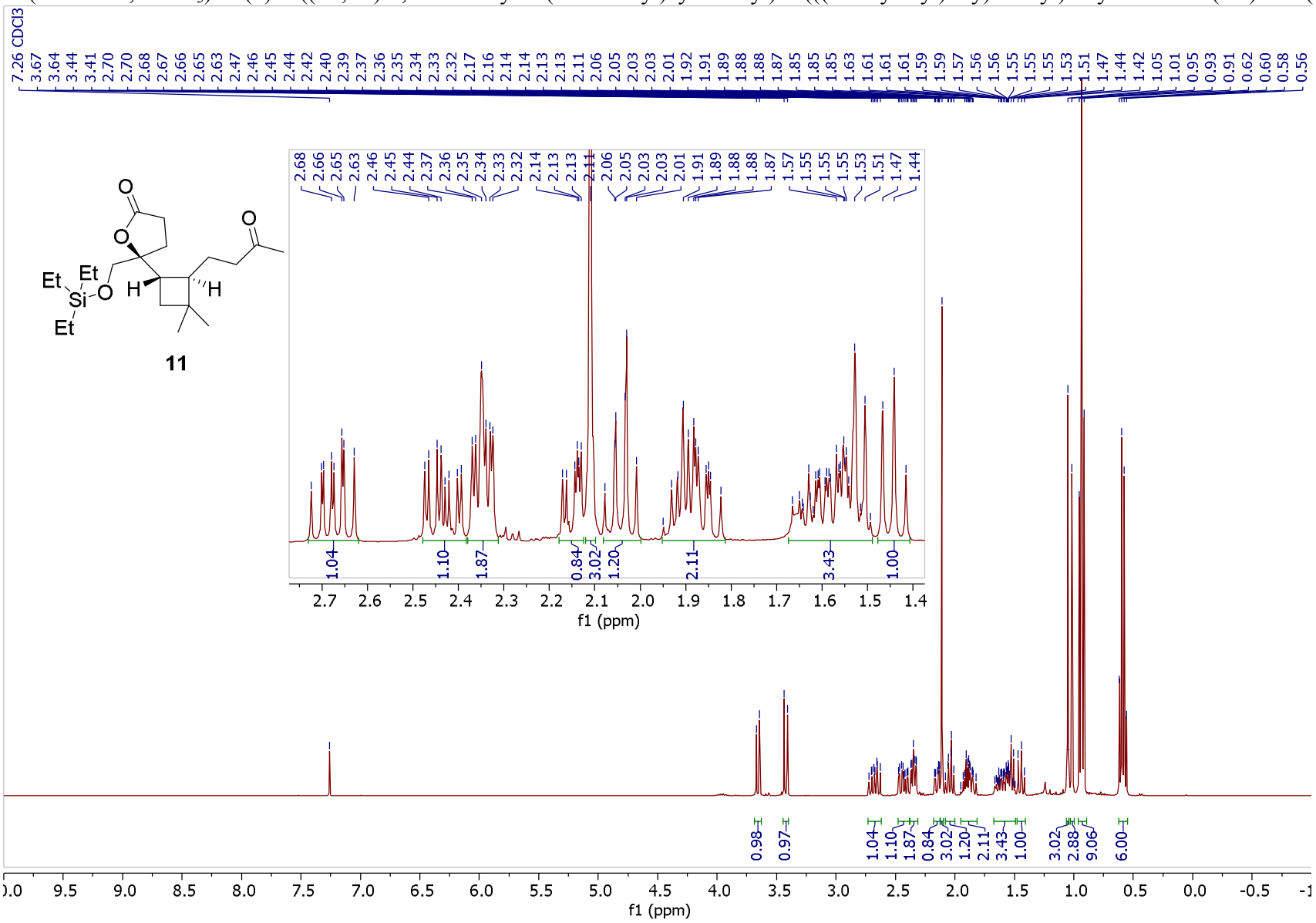


HMBC of 8-*epi*-rumphellaone B (**9**)

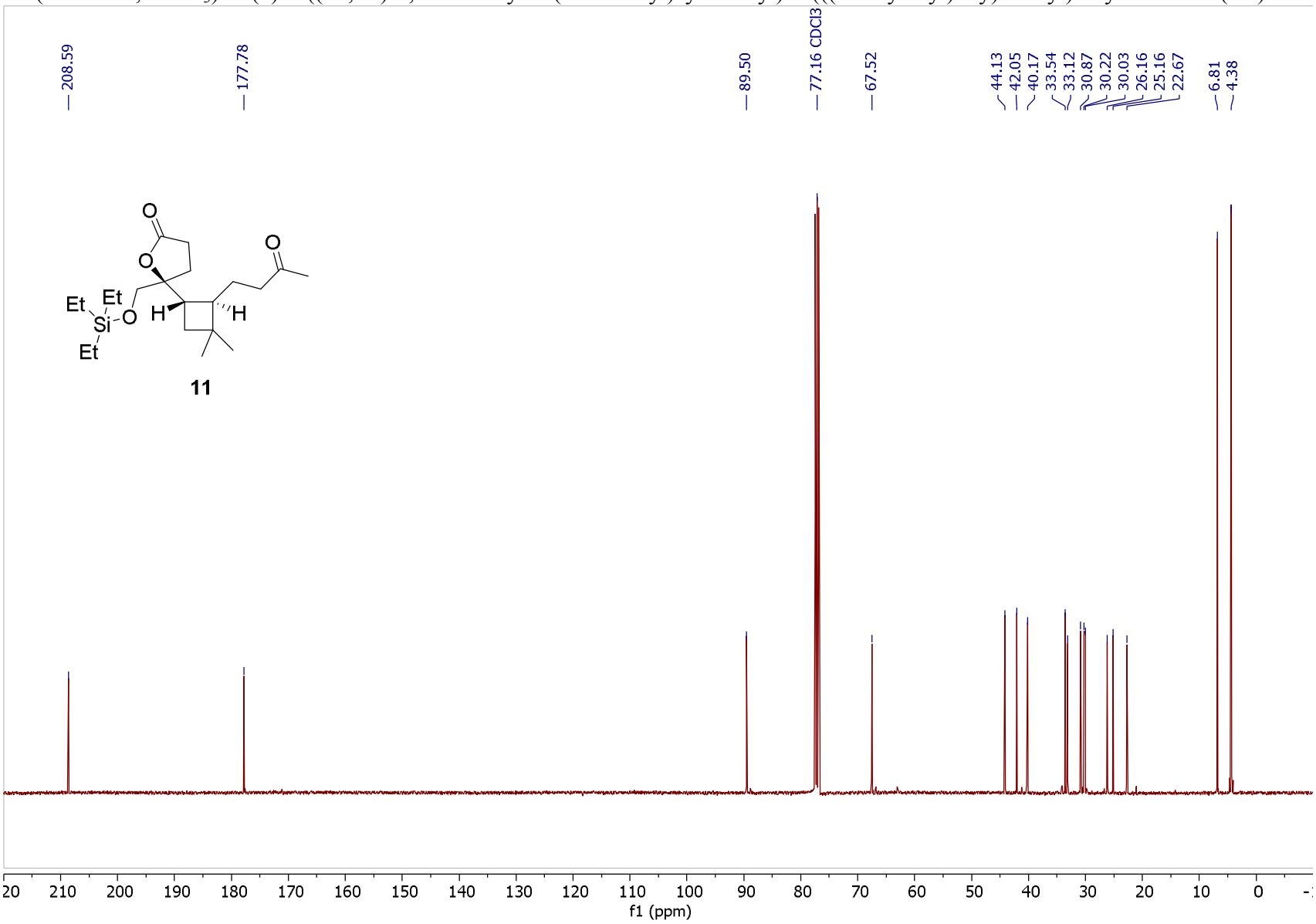


S8. NMR spectra of compound **11**

^{1}H NMR (400 MHz, $CDCl_3$) of (*S*)-5-((1*S*,2*R*)-3,3-Dimethyl-2-(3-oxobutyl)cyclobutyl)-5-(((triethylsilyl)oxy)methyl)dihydrofuran-2(3*H*)-one (**11**)

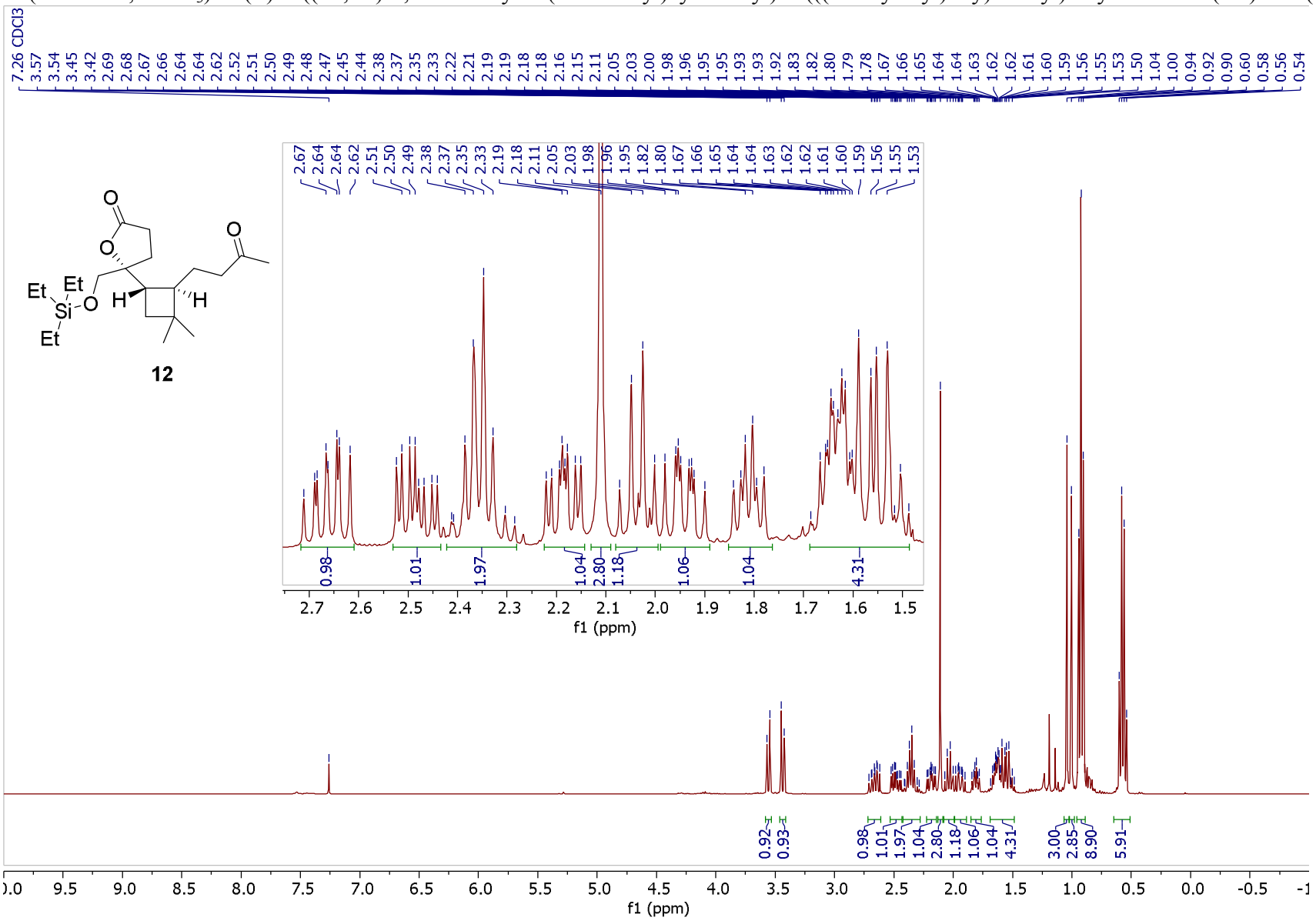


^{13}C NMR (101 MHz, $CDCl_3$) of (*S*)-5-((1*S*,2*R*)-3,3-Dimethyl-2-(3-oxobutyl)cyclobutyl)-5-(((triethylsilyl)oxy)methyl)dihydrofuran-2(3*H*)-one (**11**)

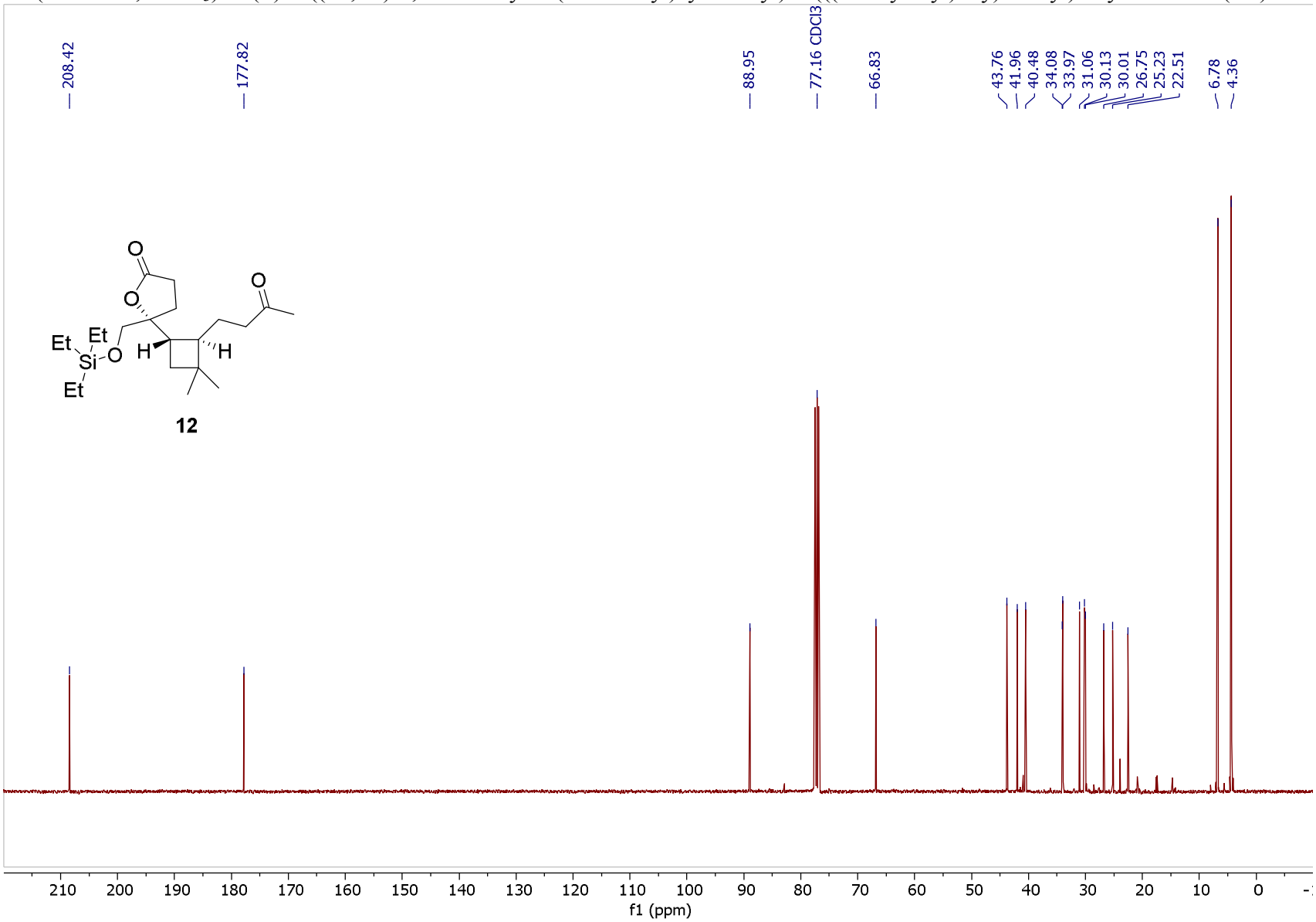


S9. NMR spectra of compound **12**

^{1}H NMR (400 MHz, $CDCl_3$) of (*R*)-5-((1*S*,2*R*)-3,3-Dimethyl-2-(3-oxobutyl)cyclobutyl)-5-(((triethylsilyl)oxy)methyl)dihydrofuran-2(3*H*)-one (**12**)

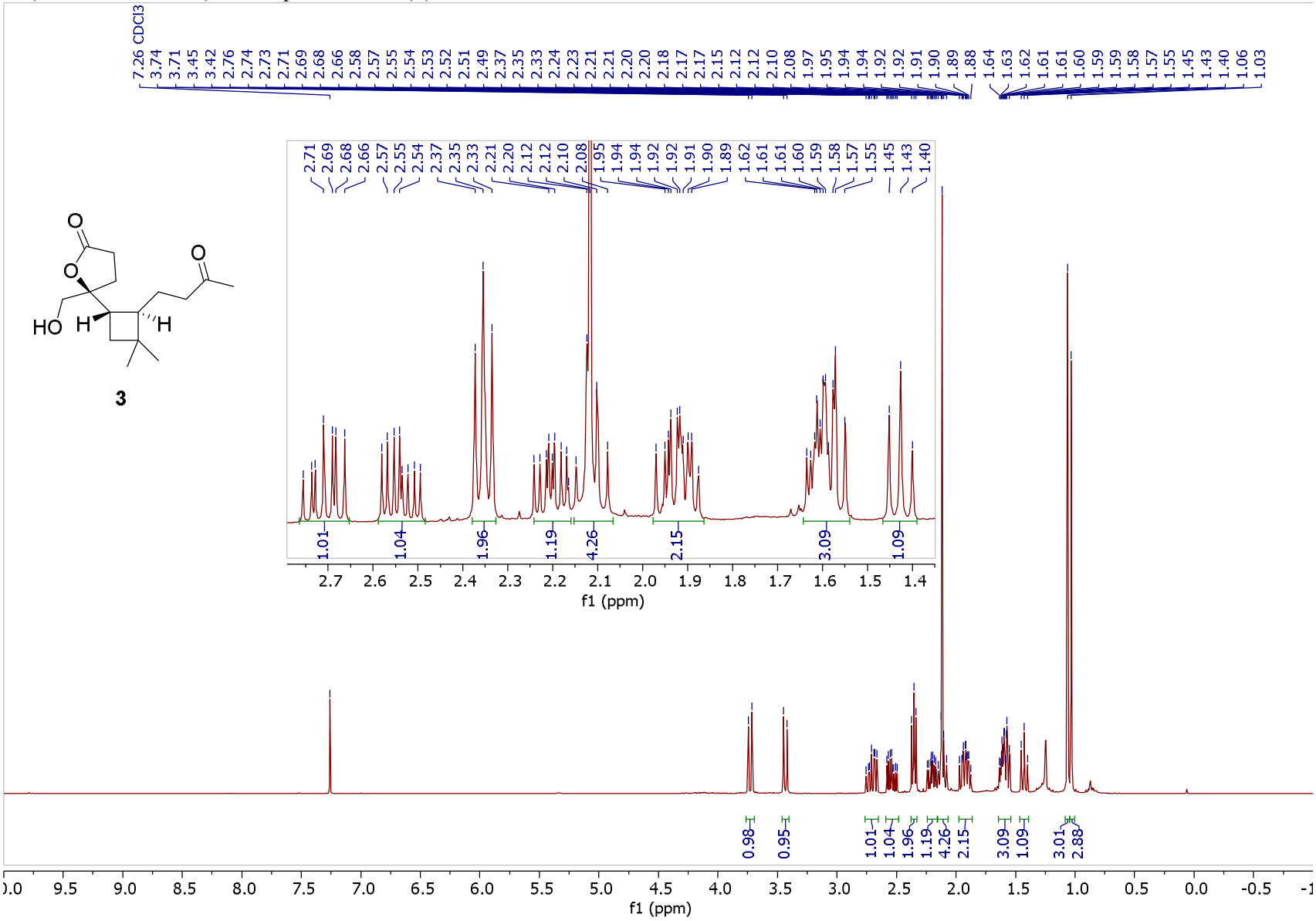


^{13}C NMR (400 MHz, $CDCl_3$) of (*R*)-5-((1*S*,2*R*)-3,3-Dimethyl-2-(3-oxobutyl)cyclobutyl)-5-(((triethylsilyl)oxy)methyl)dihydrofuran-2(3*H*)-one (**12**)

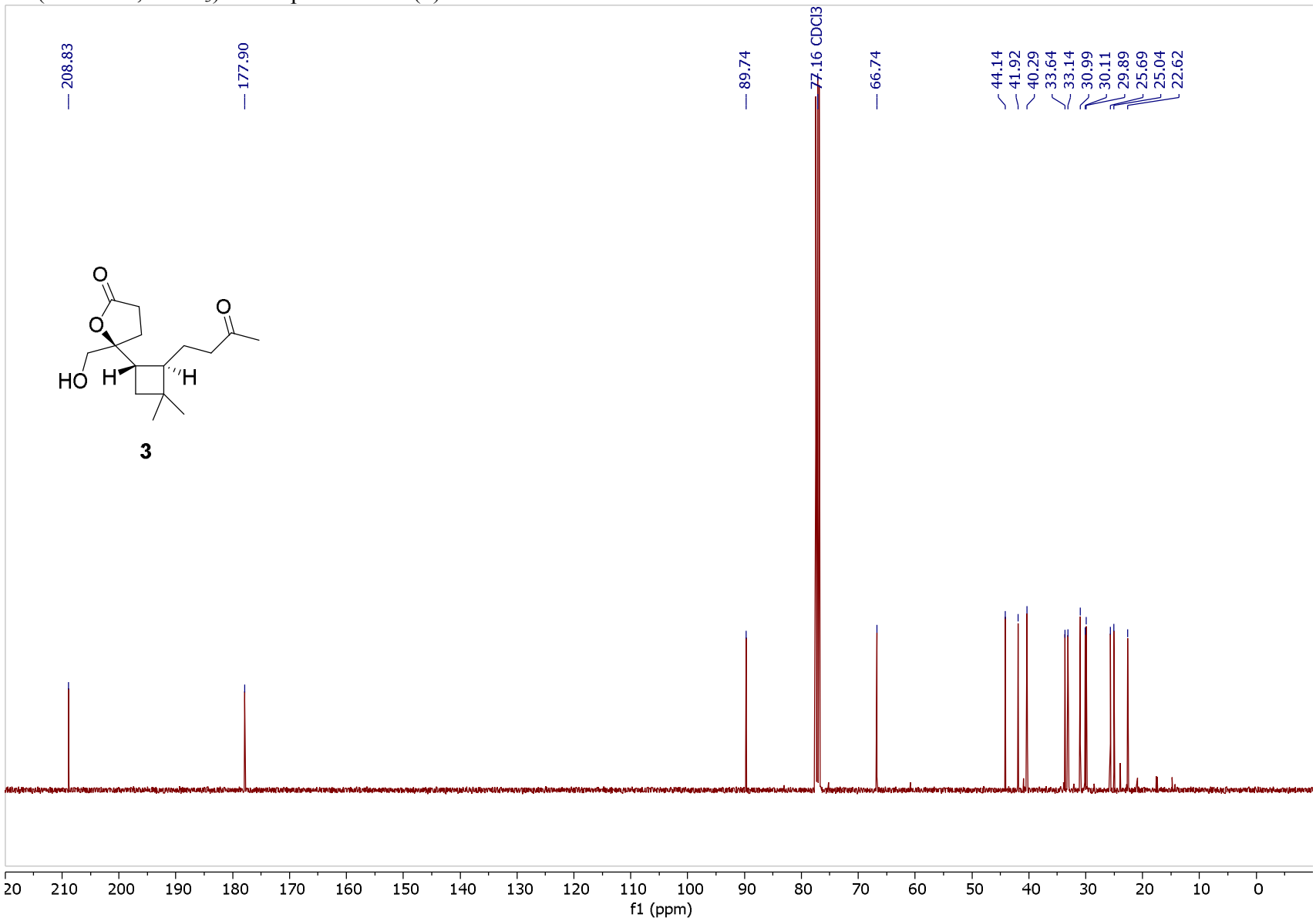


S10. NMR spectra of rumphellaone C (**3**)

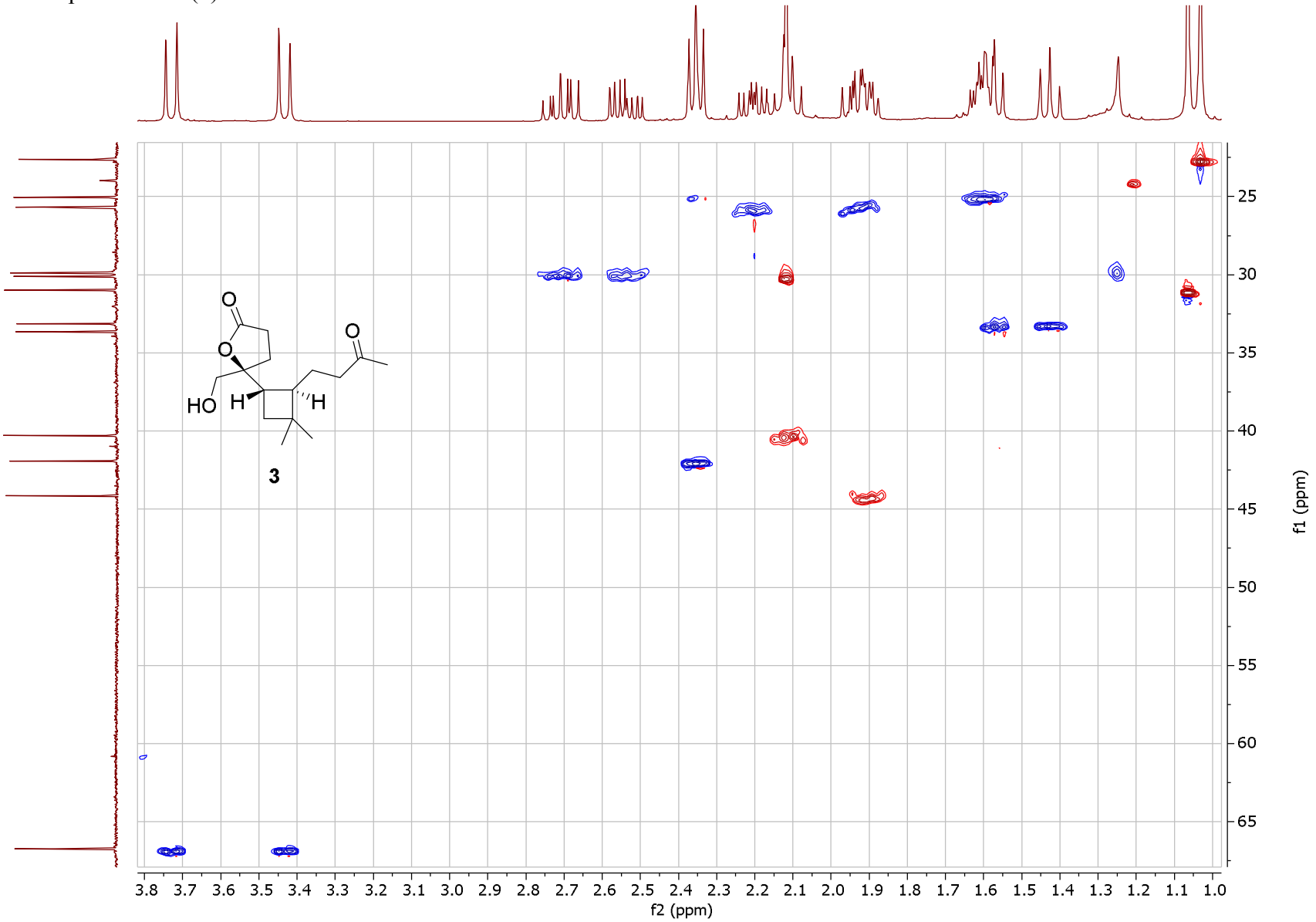
^{1}H NMR (400 MHz, $CDCl_3$) of rumphellaone C (**3**)



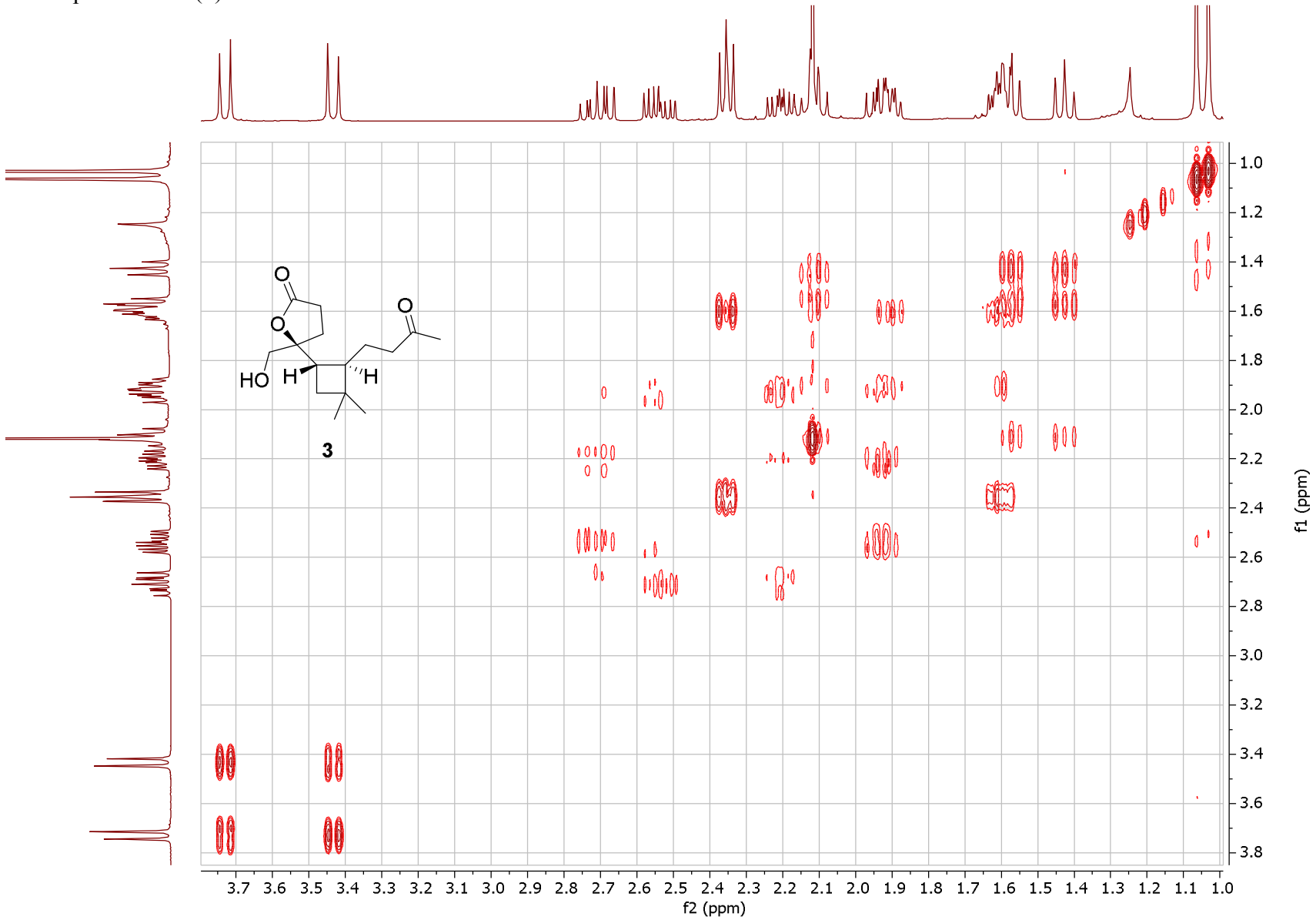
^{13}C NMR (400 MHz, $CDCl_3$) of rumphellaone C (**3**)



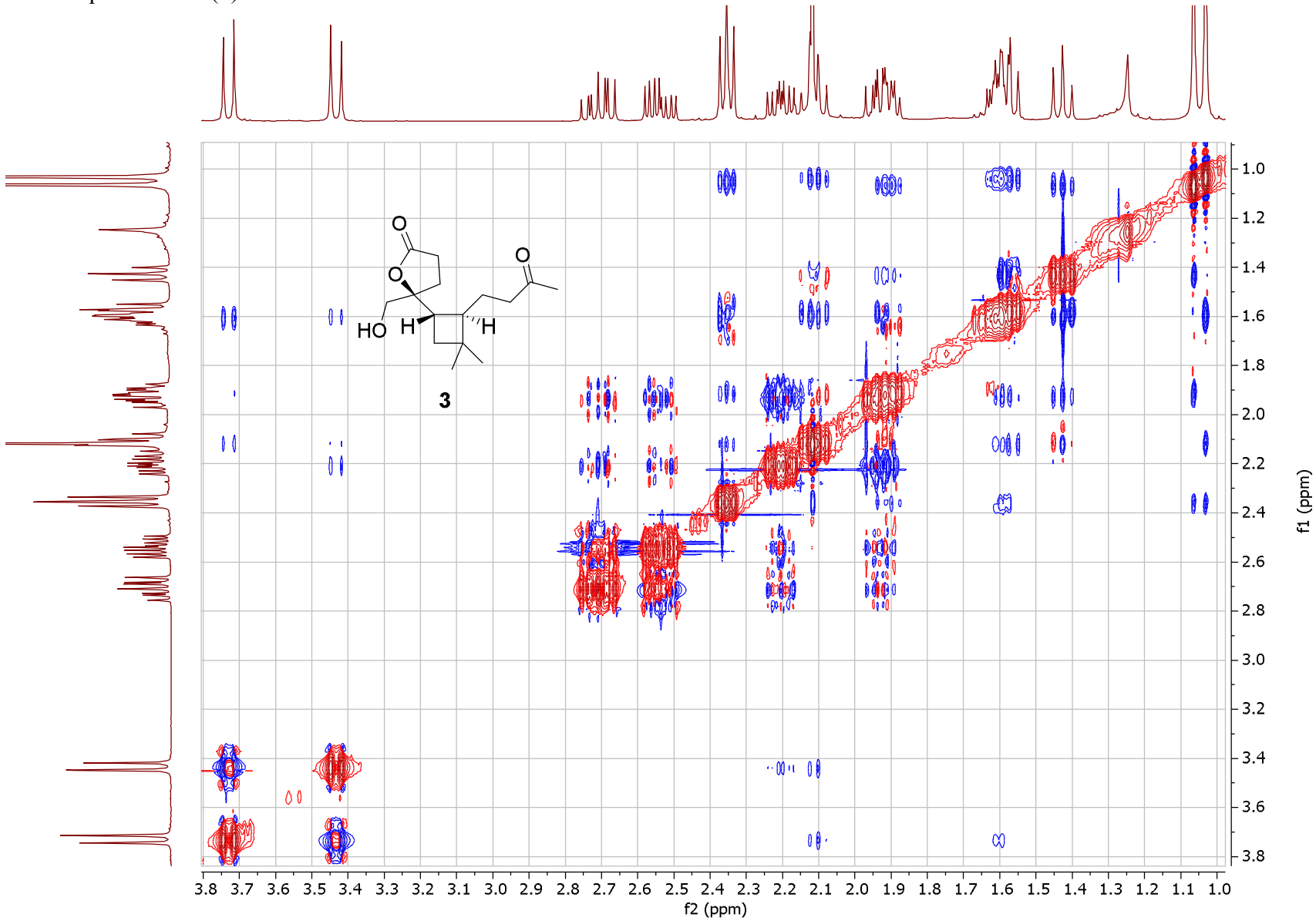
HSQC of rumphellaone C (**3**)



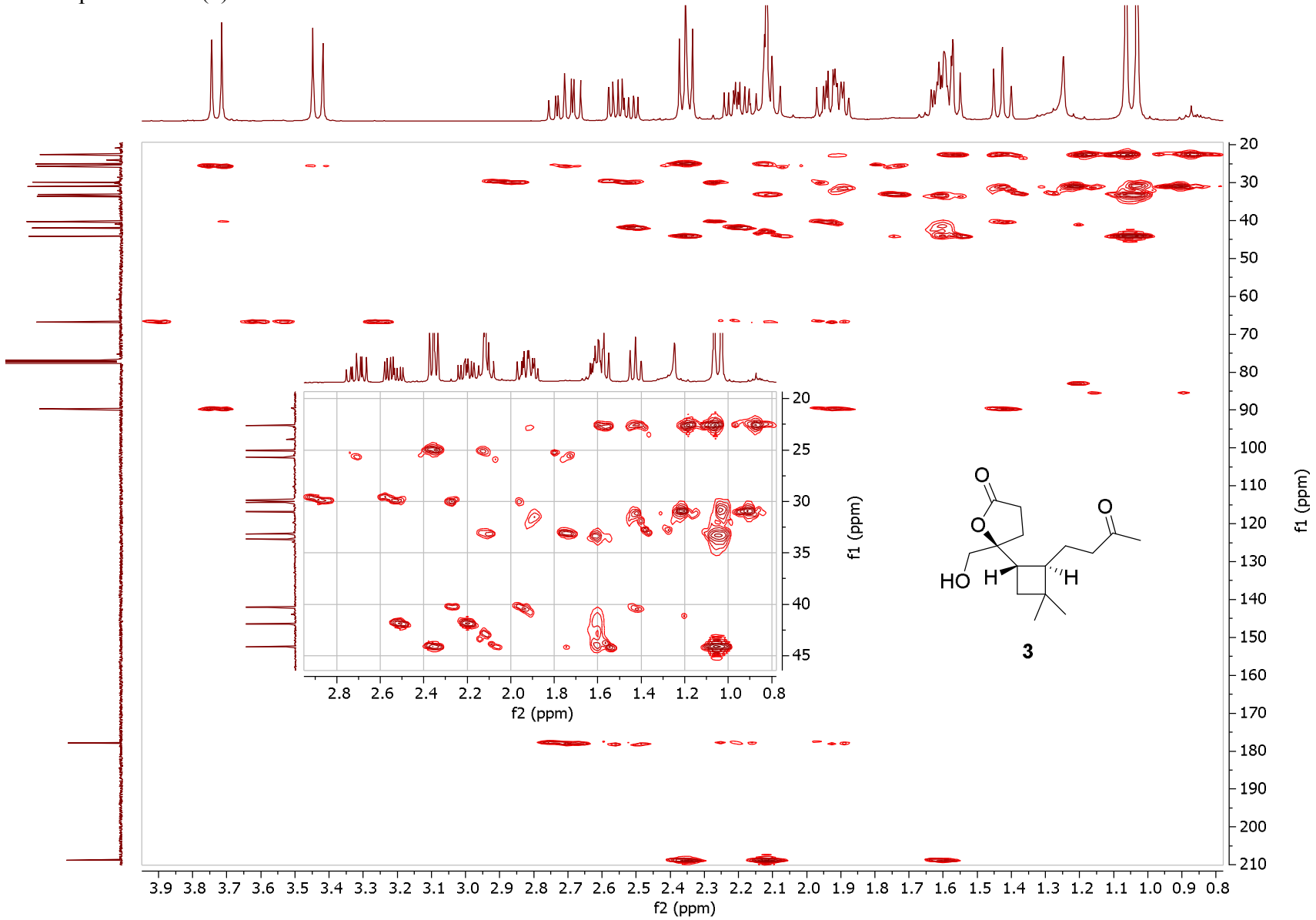
COSY of rumphellaone C (**3**)



NOESY of rumphellaone C (**3**)

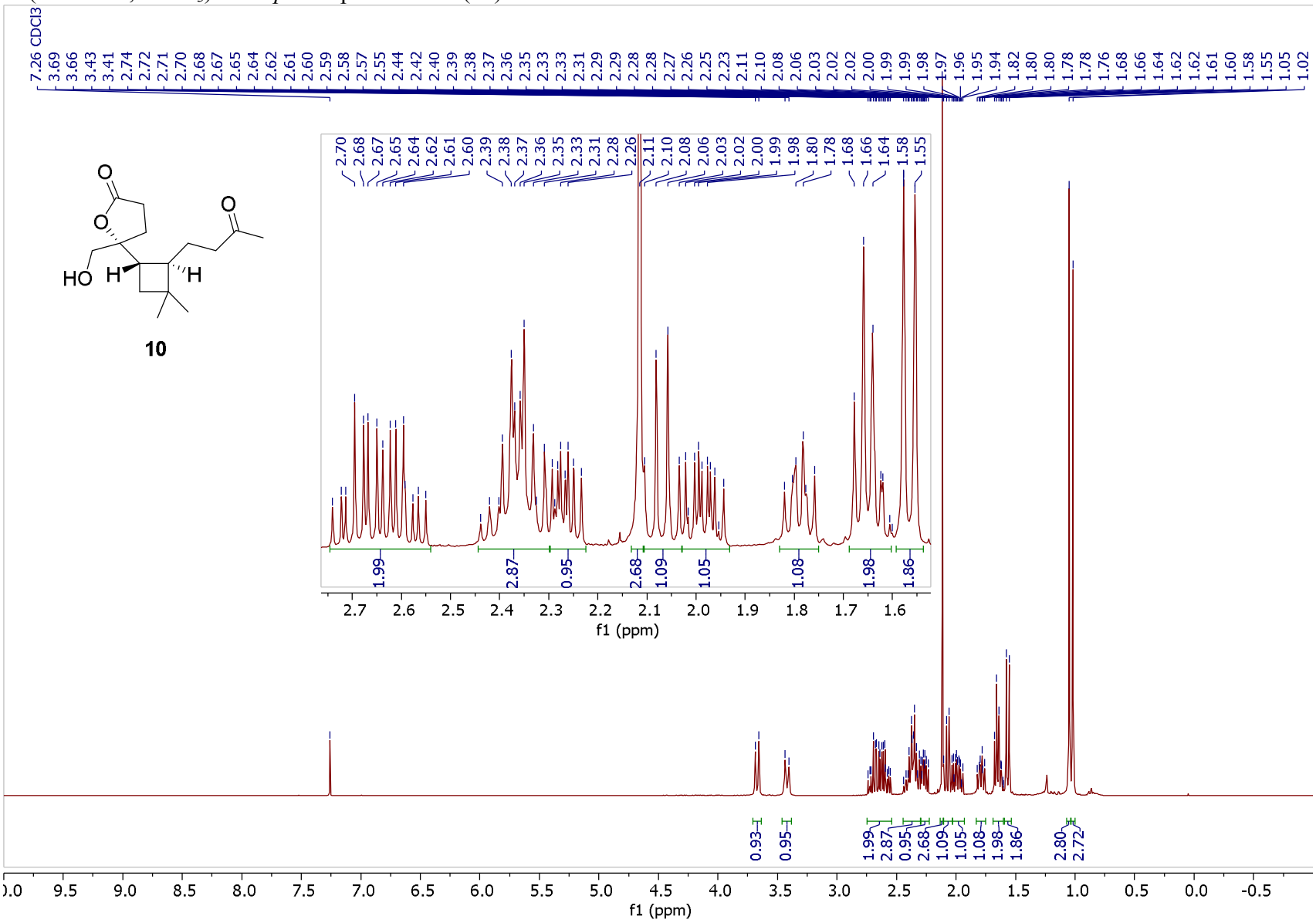


HMBC of rumphellaone C (**3**)

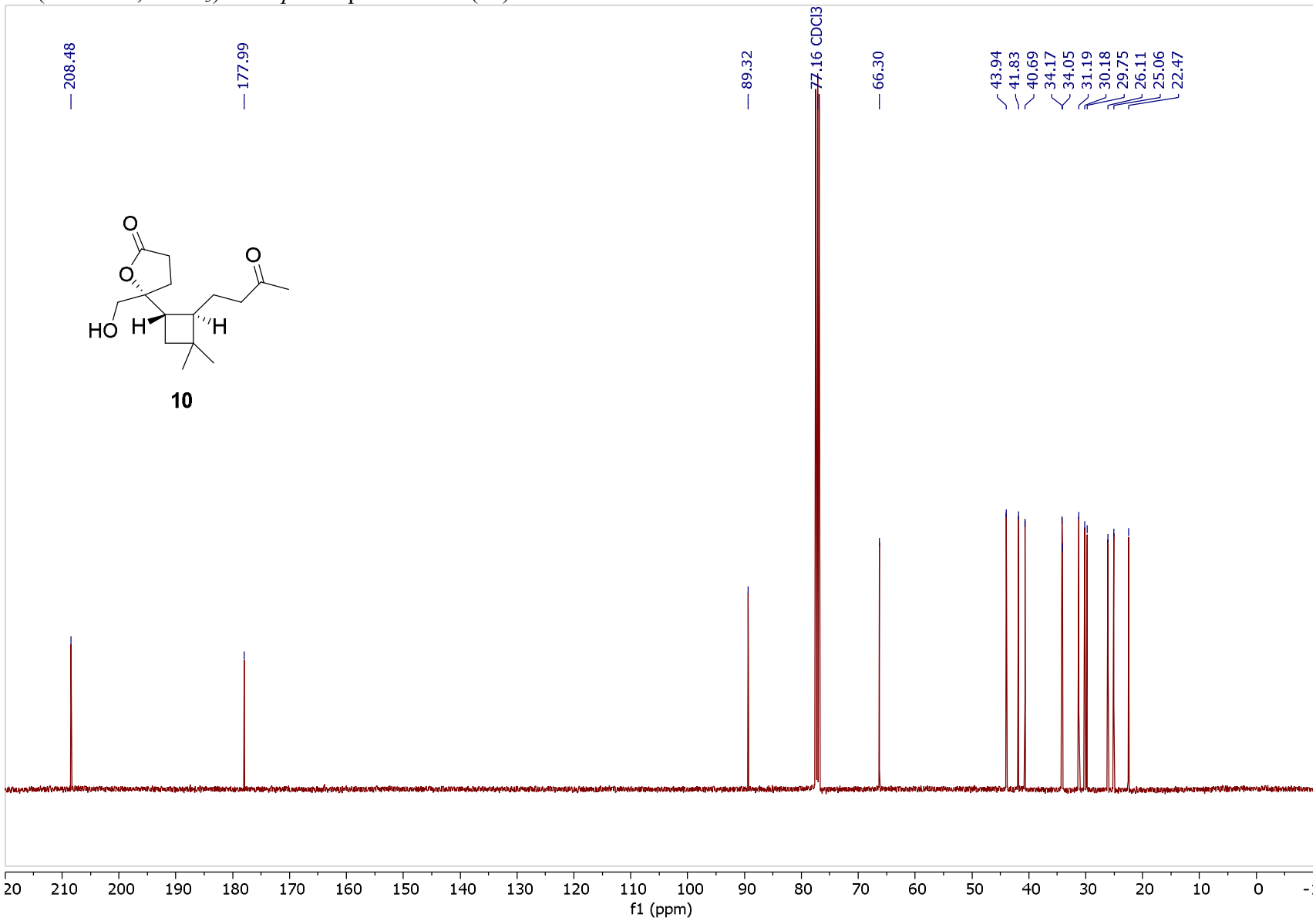


S11. NMR spectra of 8-*epi*-rumphellaone C (**10**)

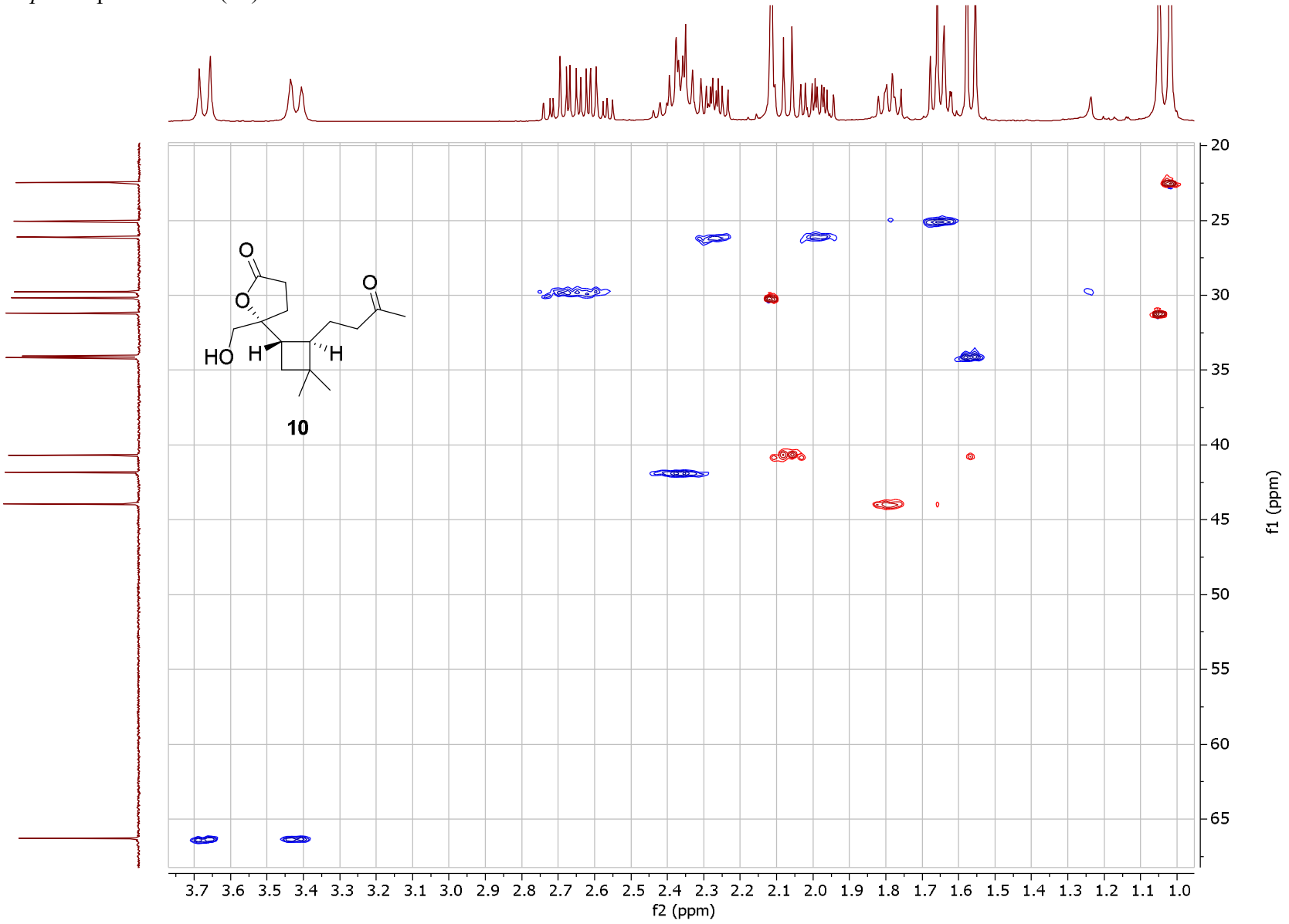
^{1}H NMR (400 MHz, $CDCl_3$) of 8-*epi*-rumphellaone C (**10**)



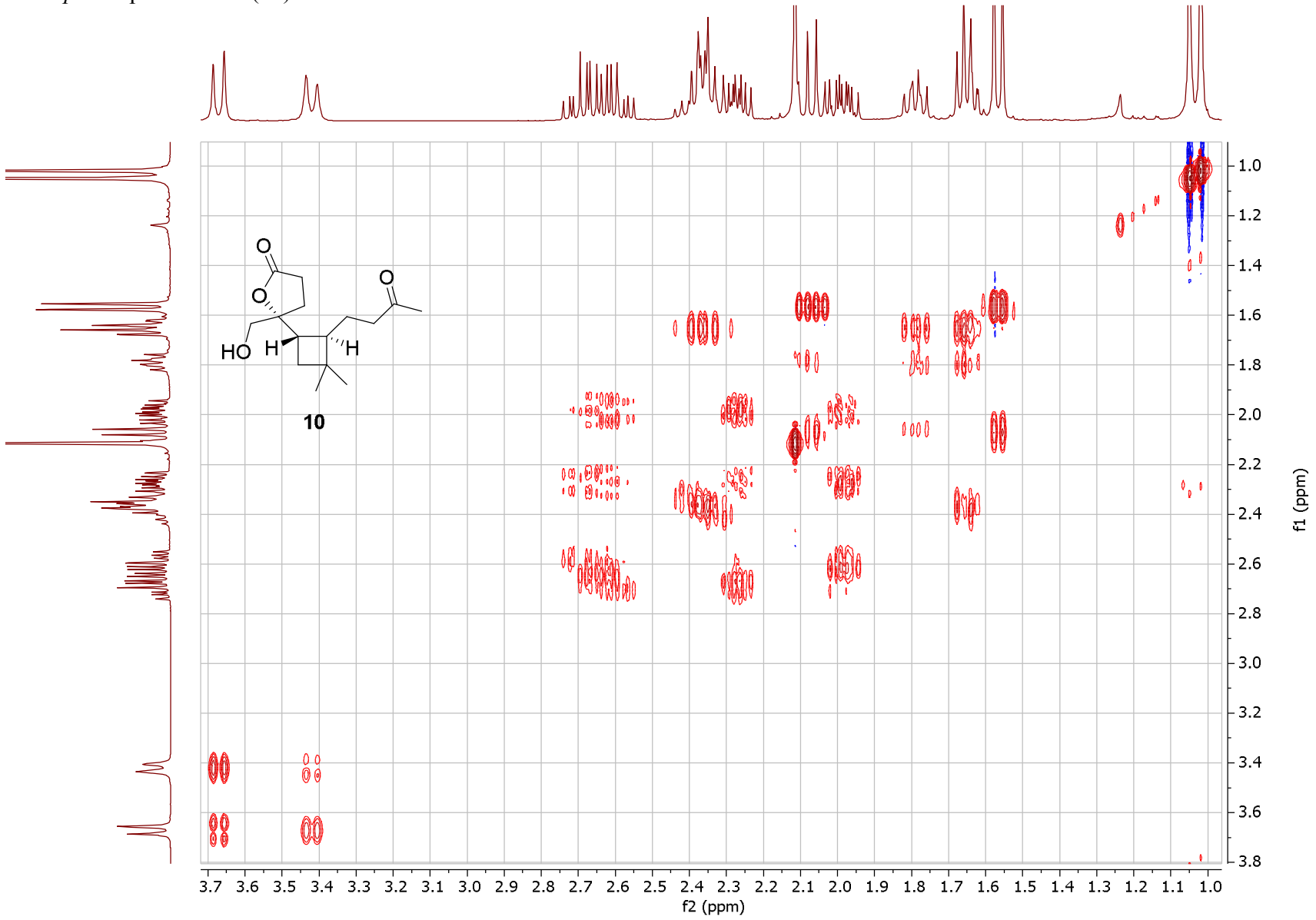
^{13}C NMR (101 MHz, $CDCl_3$) of 8-*epi*-rumphellaone C (**10**)



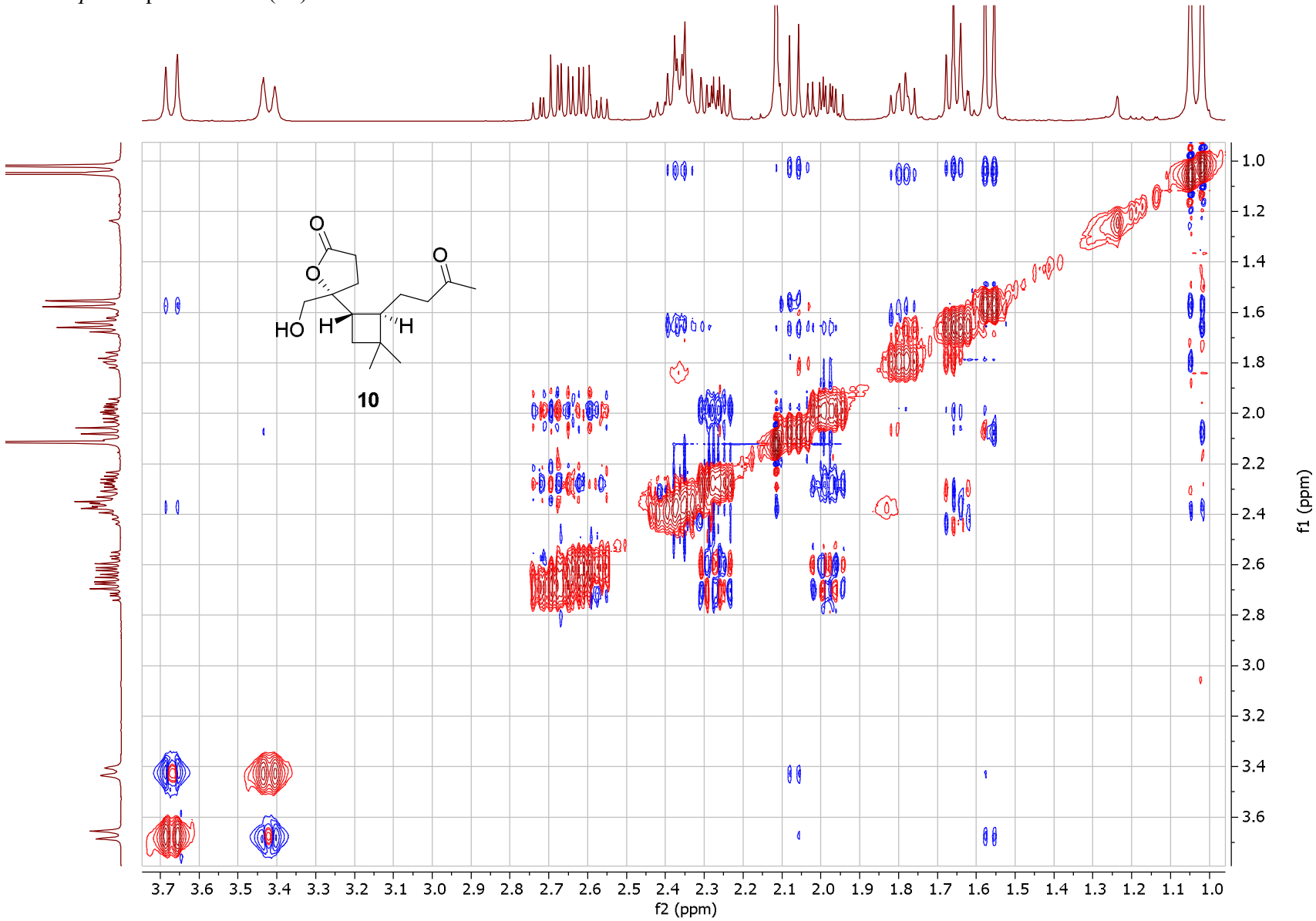
HSQC of 8-*epi*-rumphellaone C (**10**)



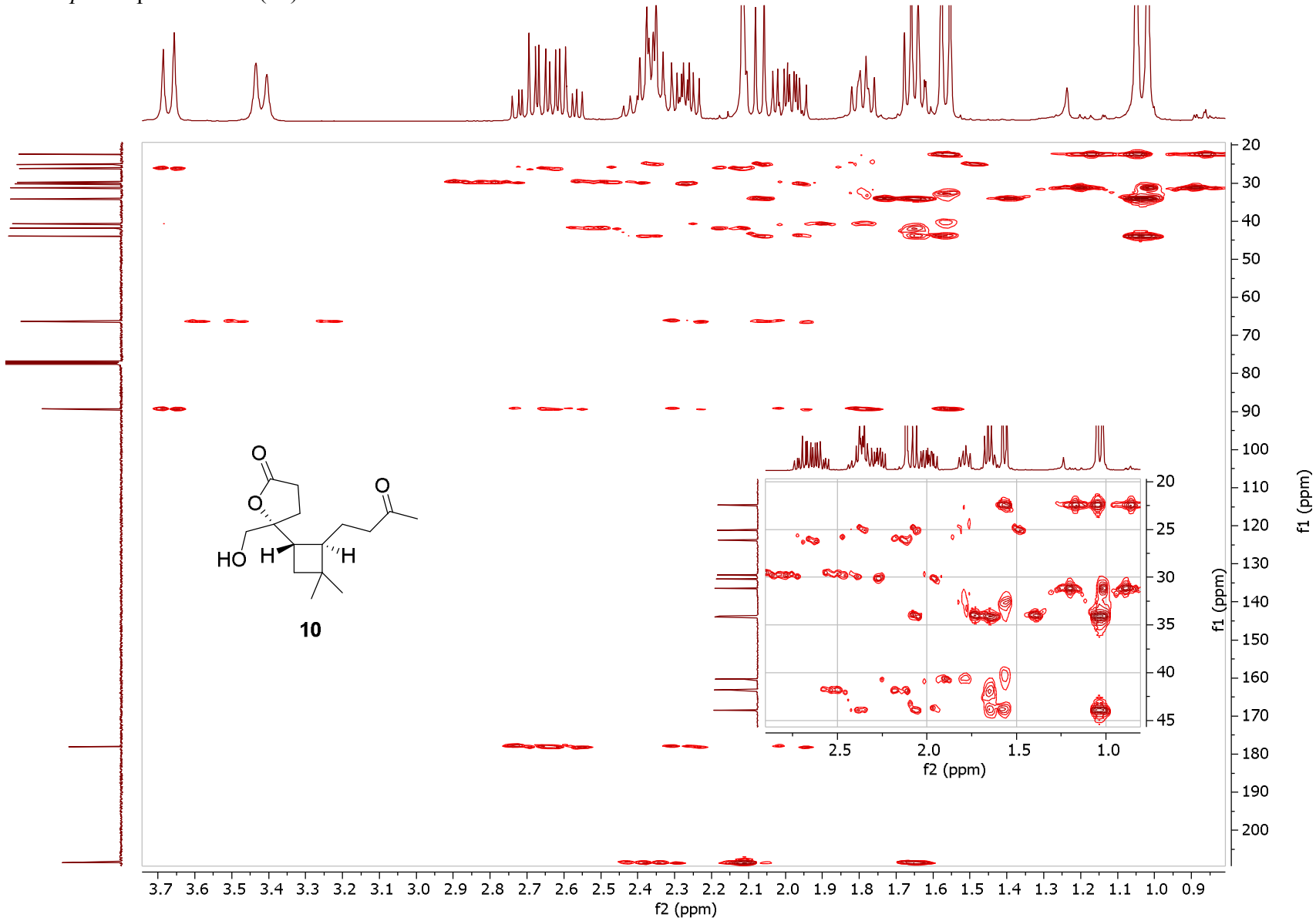
COSY of 8-*epi*-rumphellaone C (**10**)



NOESY of 8-*epi*-rumphellaone C (**10**)

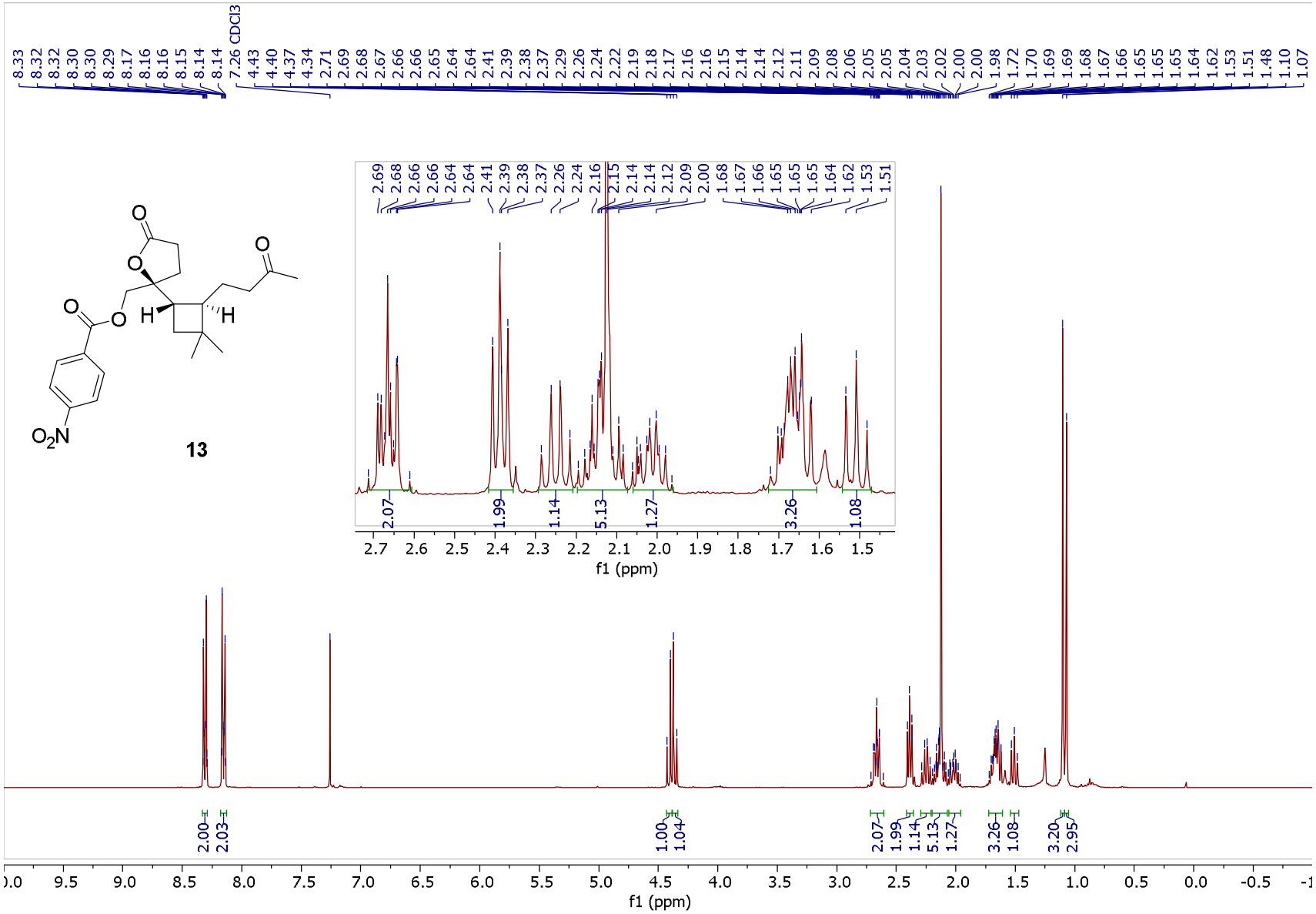


HMBC of 8-*epi*-rumphellaone C (**10**)

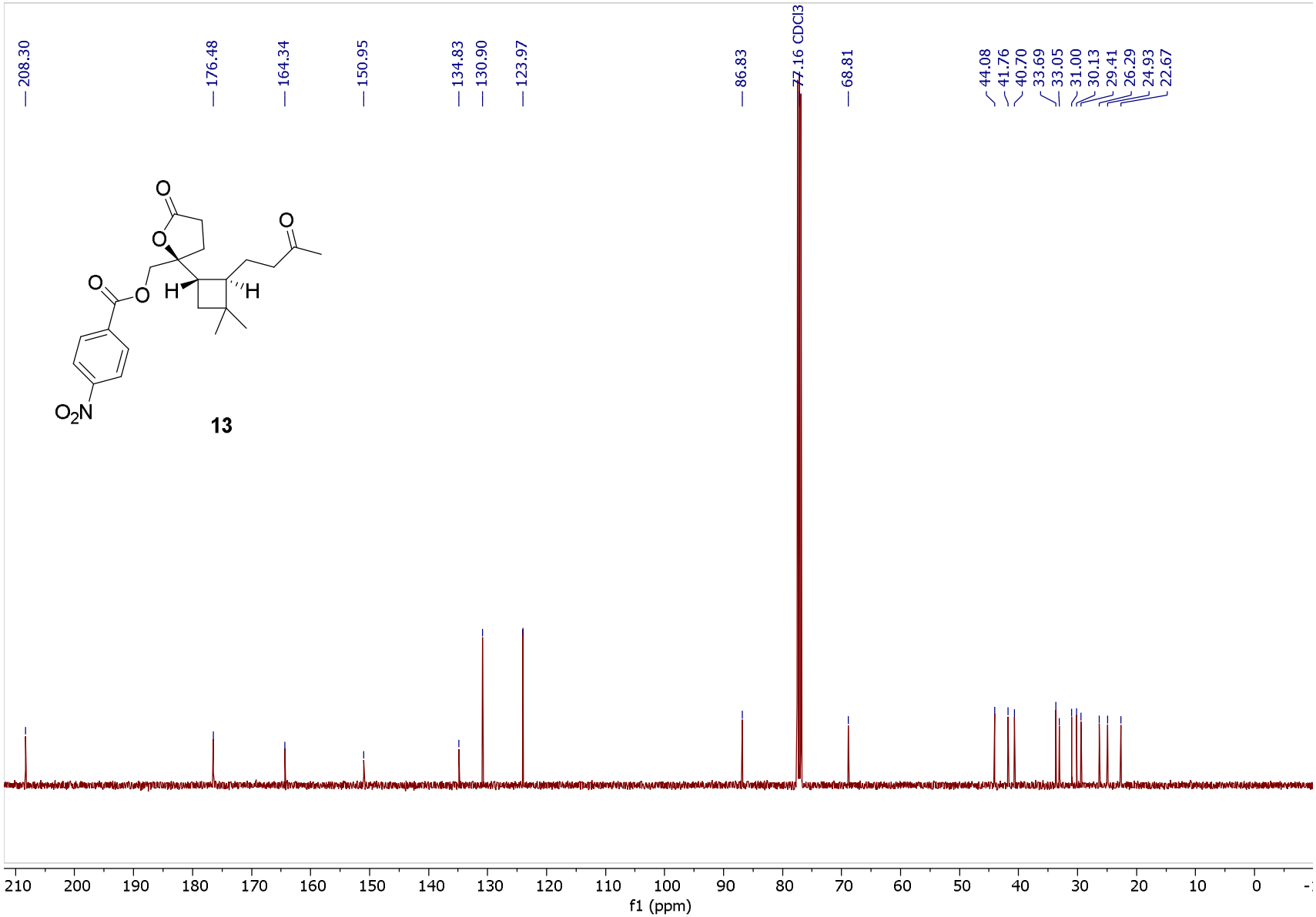


S12. NMR spectra of compound **13**

^{1}H NMR (400 MHz, $CDCl_3$) of ((*S*)-2-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)-5-oxotetrahydrofuran-2-yl)methyl 4-nitrobenzoate (**13**)

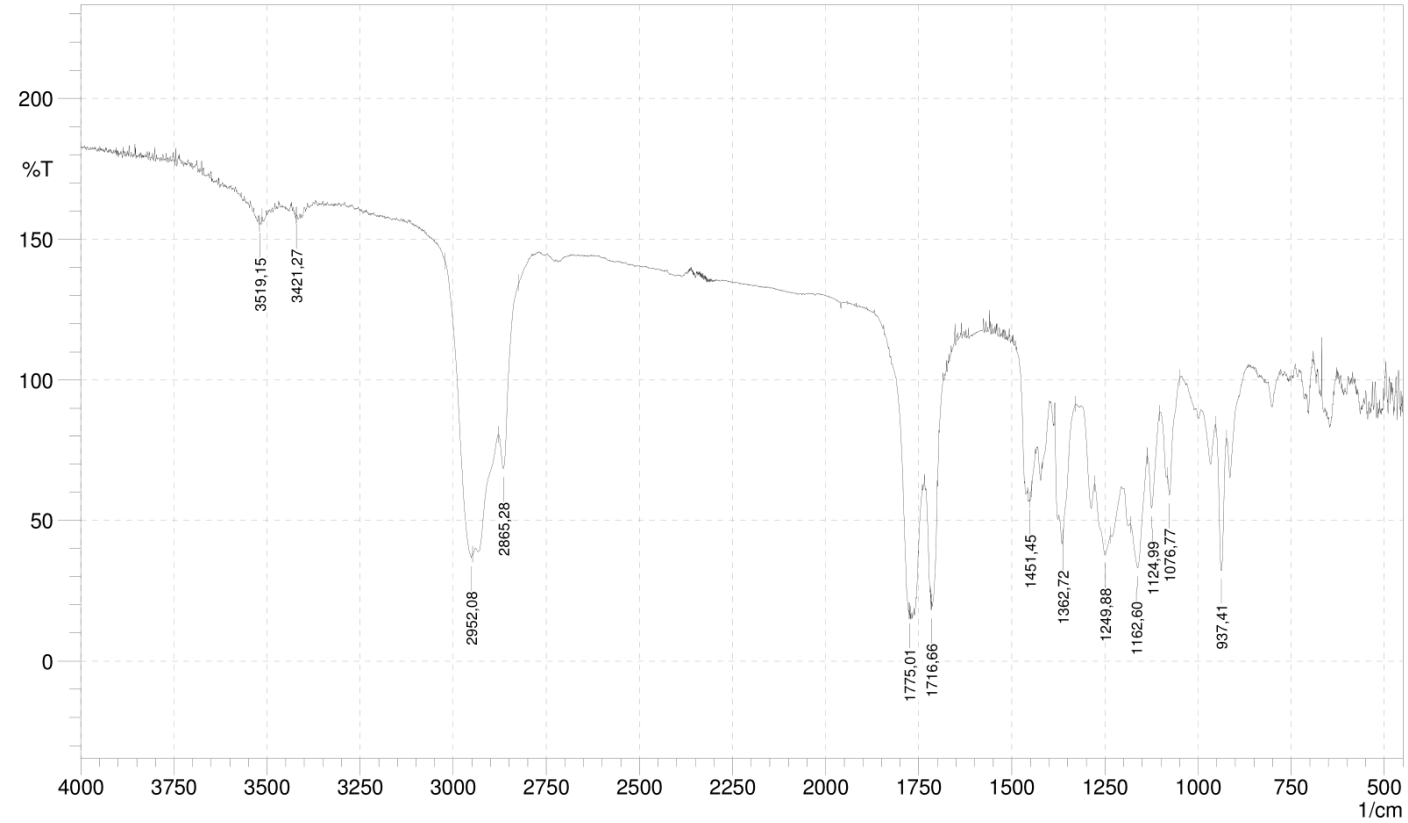


^{13}C NMR (101 MHz, $CDCl_3$) of ((*S*)-2-((1*S*,2*R*)-3,3-dimethyl-2-(3-oxobutyl)cyclobutyl)-5-oxotetrahydrofuran-2-yl)methyl 4-nitrobenzoate (**13**)

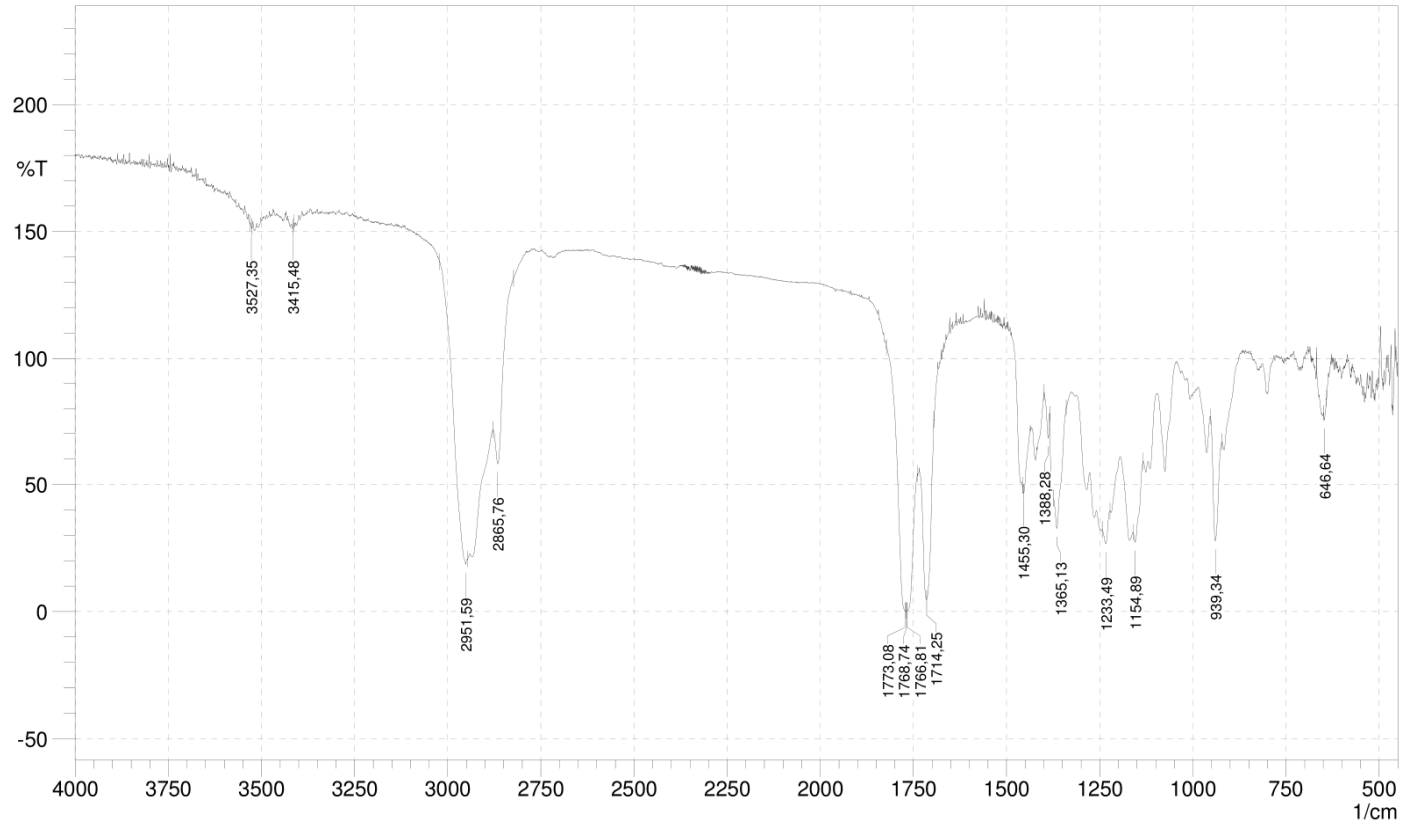


IR spectra of rumphellaones A – C and their C-8 epimers

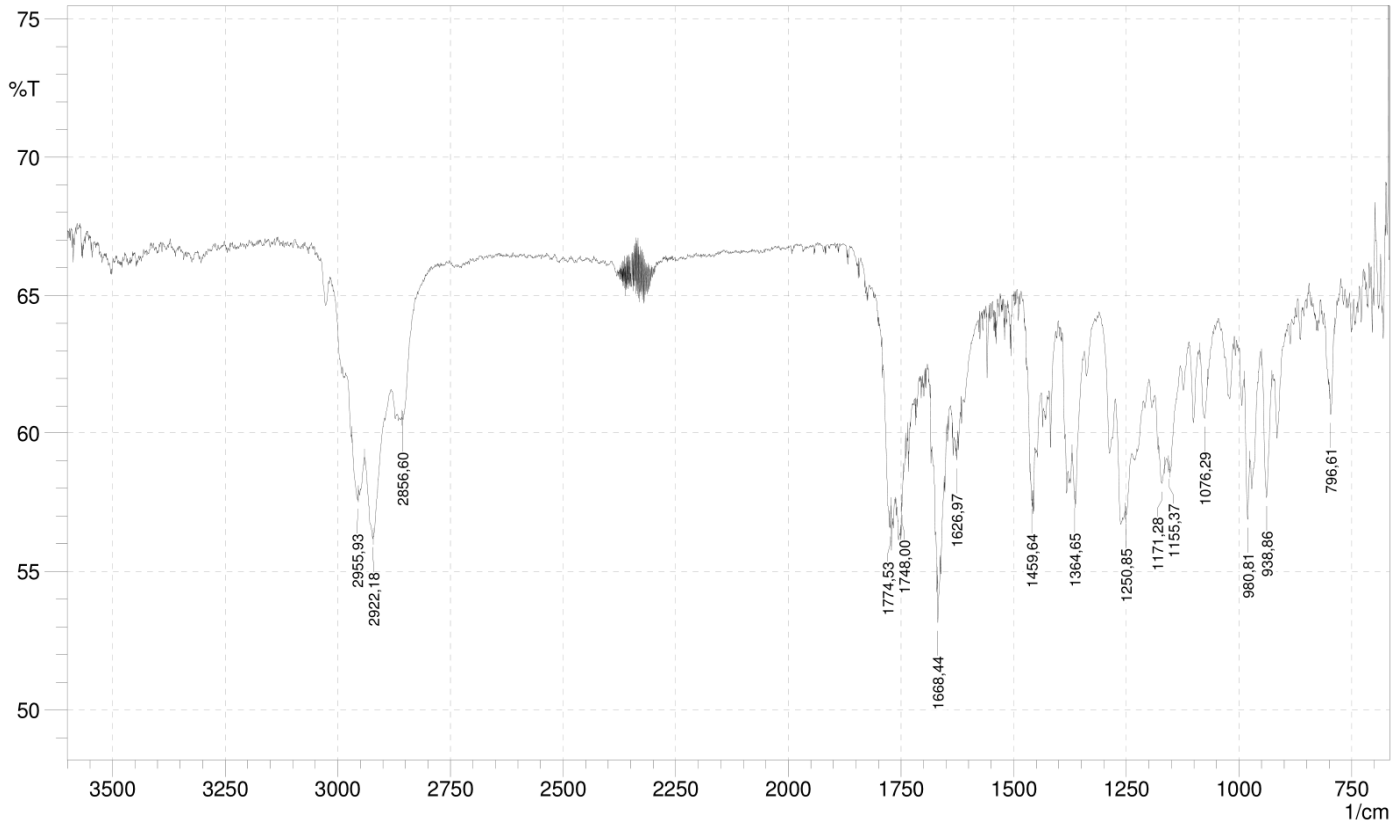
IR (thin film) of rumphellaone A (**1**)



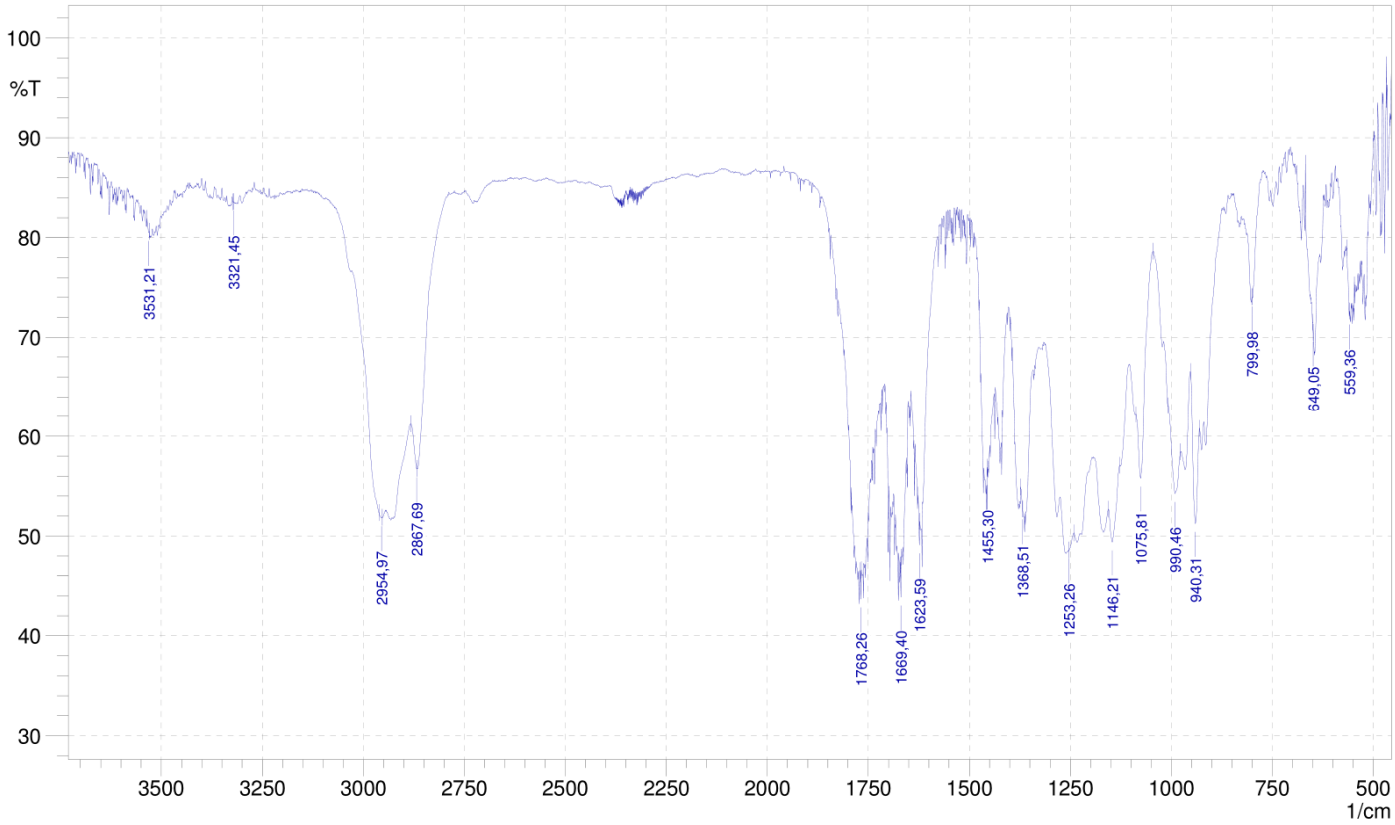
IR (thin film) of 8-*epi*-rumphellaone A (**8**)



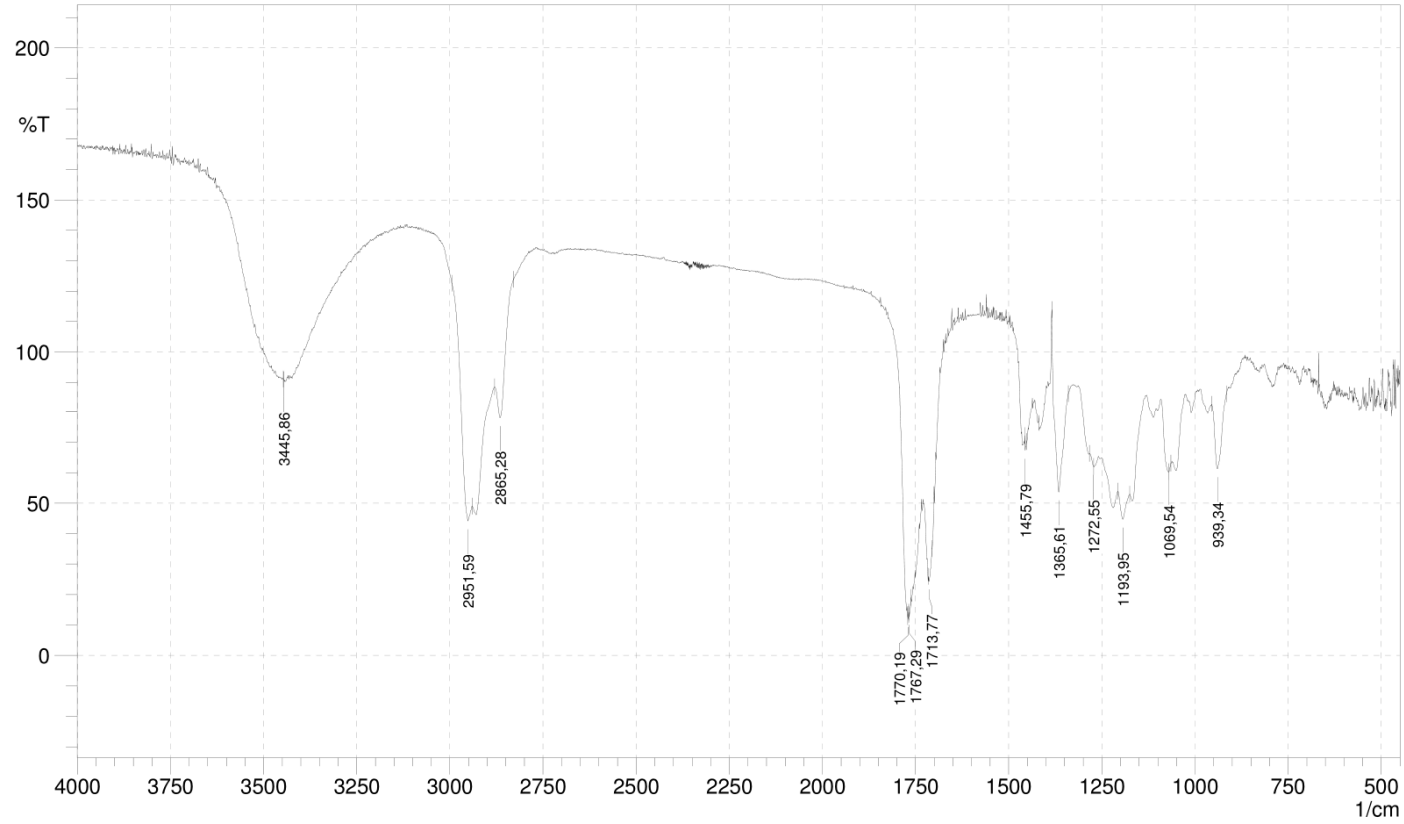
IR (thin film) of rumphellaone B (**2**)



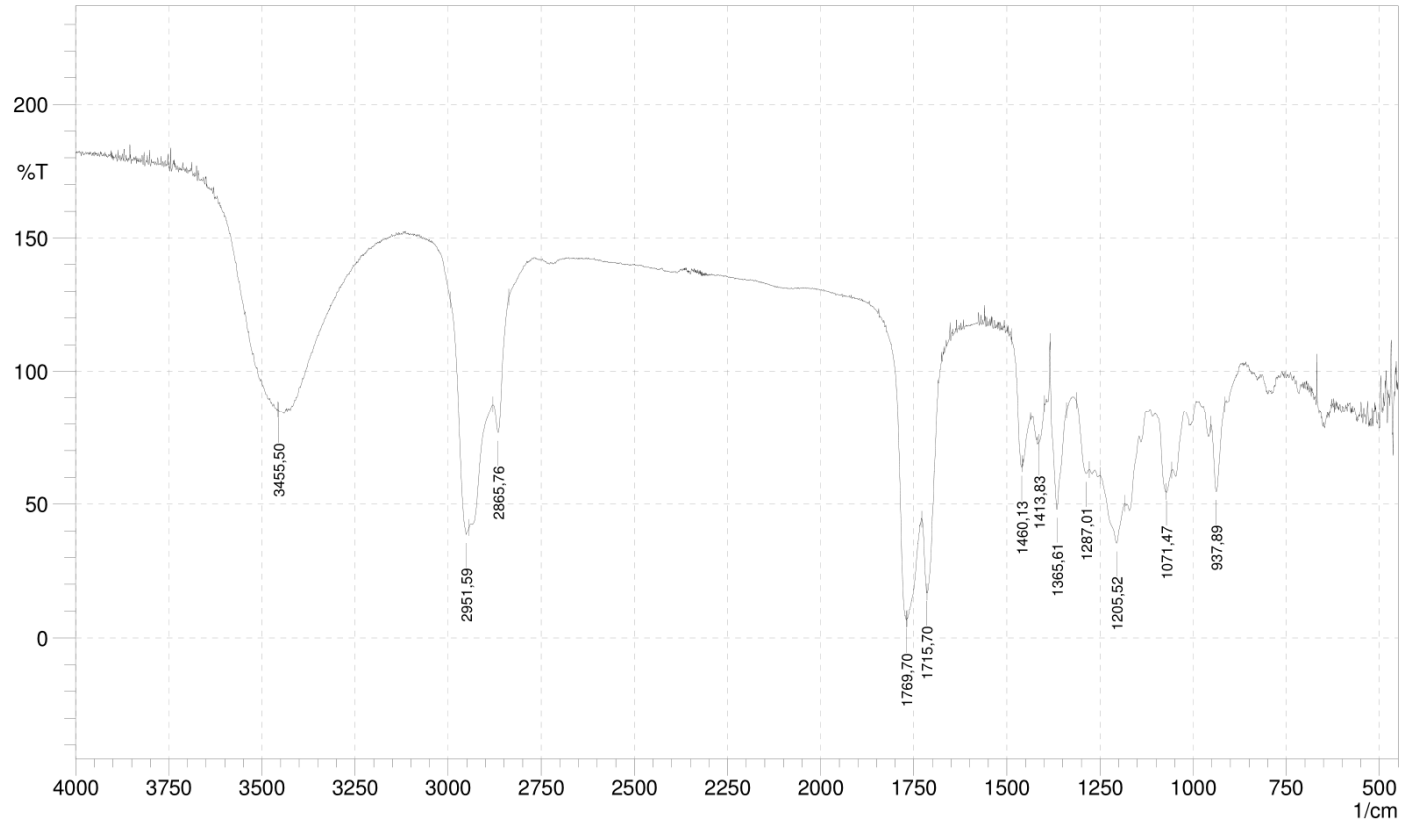
IR (thin film) of 8-*epi*-rumphellaone B (**9**)



IR (thin film) of rumphellaone C (**3**)



IR (thin film) of 8-*epi*-rumphellaone C (**10**)



X-Ray crystallographic supplementary data for rumphellaone B (2)

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).

Compound 2

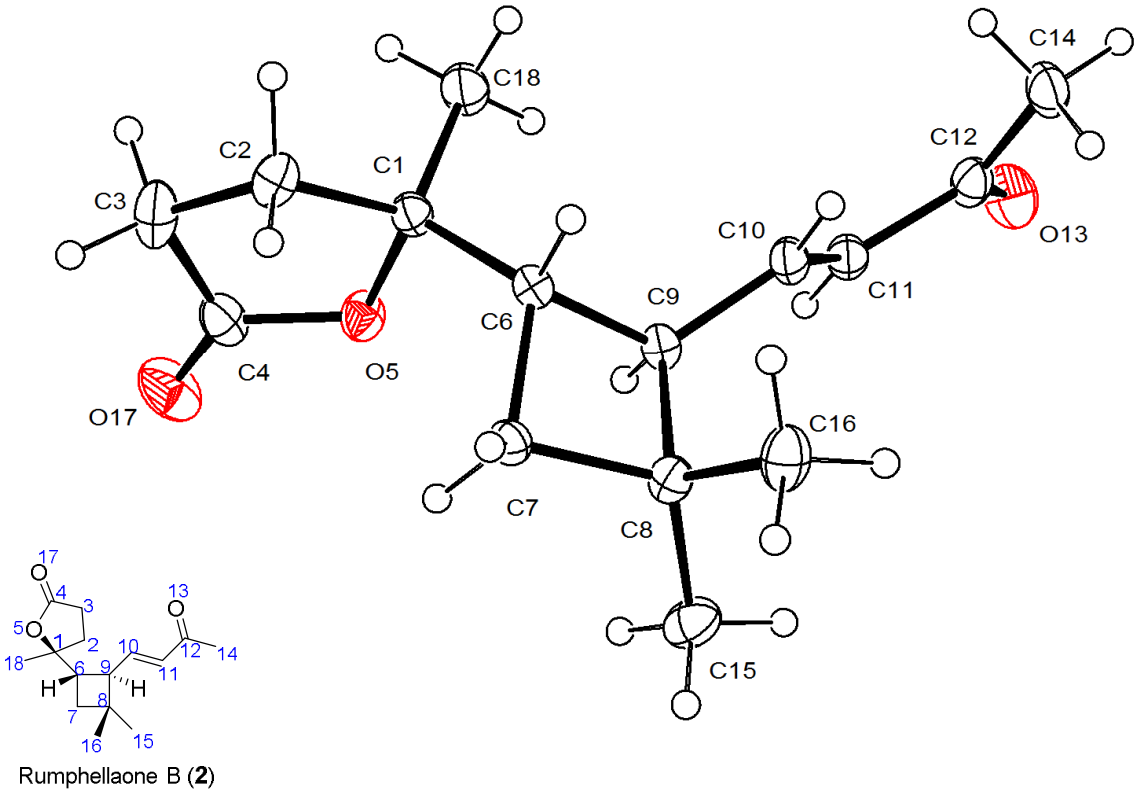


Fig S1. The asymmetric unit of the compound **2** drawn with displacement ellipsoids at the 50% probability level.

Crystal data

$C_{15}H_{22}O_3$	D_x = 1.160 Mg m^{-3}
M_r = 250.32	Cu $K\alpha$ radiation, λ = 1.54184 Å
Orthorhombic, $P2_12_12_1$	Cell parameters from 11165 reflections
a = 5.8085 (3) Å	θ = 2.6–77.5°
b = 7.3835 (4) Å	μ = 0.64 mm^{-1}
c = 33.4086 (17) Å	T = 150 K
V = 1432.81 (13) Å^3	Plate, colourless
Z = 4	0.20 × 0.08 × 0.06 mm
F(000) = 544	

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	2914 reflections with $I > 2\sigma(I)$
Radiation source: micro-focus sealed X-ray tube	R_{int} = 0.025
ω scans	θ_{max} = 77.6°, θ_{min} = 2.7°
Absorption correction: multi-scan *CrysAlis PRO* 1.171.40.71a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	h = -7→7
T_{min} = 0.858, T_{max} = 1.000	k = -8→9
13362 measured reflections	l = -40→42
2978 independent reflections	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.2237P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.031	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.083	$\Delta\rho_{max}$ = 0.22 e Å^{-3}
S = 1.07	$\Delta\rho_{min}$ = -0.17 e Å^{-3}
2978 reflections	Extinction correction: *SHELXL2017*/1 (Sheldrick 2017), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
168 parameters	Extinction coefficient: 0.0028 (7)
0 restraints	Absolute structure: Flack x determined using 1157 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Hydrogen site location: inferred from neighbouring sites	Absolute structure parameter: 0.01 (7)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Document origin: *publCIF* [Westrip, S. P. (2010). *J. Apply. Cryst.*, **43**, 920-925].

X-Ray crystallographic supplementary data for compound 13

Computing details

Data collection: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); cell refinement: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); data reduction: *CrysAlis PRO* 1.171.40.35a (Rigaku OD, 2018); program(s) used to solve structure: SHELXT 2014/4 (Sheldrick, 2014); program(s) used to refine structure: *SHELXL2017*/1 (Sheldrick, 2017).

Compound 13

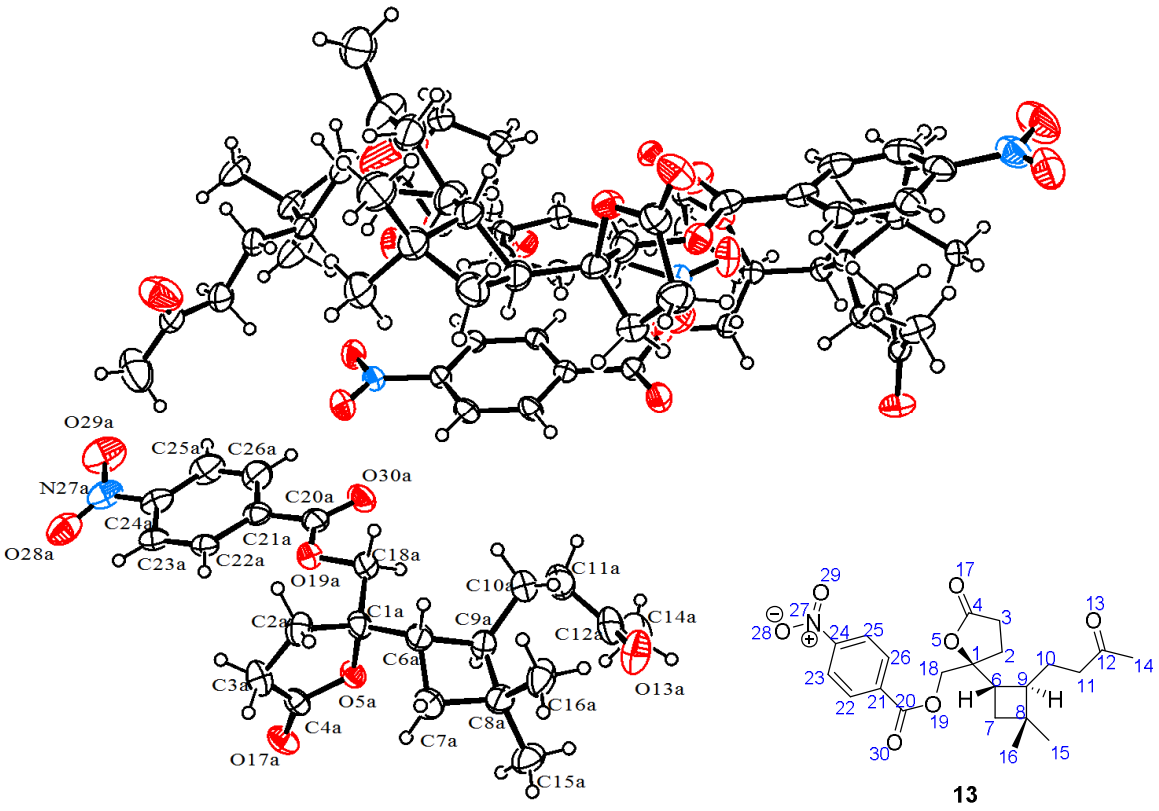


Fig S2. The asymmetric unit containing four independent molecules (A, B, C and D) of the compound **13** drawn with displacement ellipsoids at the 50% probability level. For clarity only atoms of the the molecule A are labeled.

ADDSYM procedure of PLATON (Spek, A. L. (2015). Acta Cryst. C71, 9–18) computer program was used to confirm the correctness of the space group $P2_1$ with four molecules in the asymmetric unit. All four molecules are one and the same diastereomer. The molecules differ in their conformation. The largest scatter has the C9-C10-C11-C12 torsion angle (-69.31°, 176.61°, 175.06° and -176.34° for A, B, C, and D molecules, respectively). Adjacent A and D molecules, as well as B and C, due to π-π interactions of nitrophenyl fragments arrange pairs. Nitrophenyl fragments of adjacent molecules are not completely parallel but form dihedral angles of 10.13° between A and D molecules and 12.99° for B and C molecules. The shortest intermolecular distances are 3.450Å for A and D molecules and 3.439 Å for B and C pair.

Crystal data

$C_{22}H_{27}NO_7$	$F(000) = 1776$
$M_r = 417.44$	$D_x = 1.275$ Mg m^{-3}
Monoclinic, $P2_1$	Cu $K\alpha$ radiation, $\lambda = 1.54184$ Å
$a = 18.7540$ (2) Å	Cell parameters from 30997 reflections
$b = 9.0751$ (1) Å	$\theta = 3.3$–$75.9°$
$c = 26.1928$ (3) Å	$\mu = 0.79$ mm^{-1}
$\beta = 102.750$ (1)°	$T = 160$ K
$V = 4347.95$ (8) Å^3	Block, colourless
$Z = 8$	0.22 × 0.08 × 0.06 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer	13218 reflections with $I > 2\sigma(I)$
Radiation source: micro-focus sealed X-ray tube	$R_{int} = 0.026$
ω scans	$\theta_{max} = 78.2°$, $\theta_{min} = 2.6°$
Absorption correction: multi-scan *CrysAlis PRO* 1.171.40.74a (Rigaku Oxford Diffraction, 2020) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.	$h = -22 \rightarrow 23$
$T_{min} = 0.737$, $T_{max} = 1.000$	$k = -11 \rightarrow 10$
42816 measured reflections	$l = -33 \rightarrow 32$
14036 independent reflections	

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.1007P)^2 + 2.7967P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.177$	$(\Delta/\sigma)_{max} = 0.003$
$S = 1.03$	$\Delta\rangle_{max} = 0.67$ e Å^{-3}
14036 reflections	$\Delta\rangle_{min} = -0.55$ e Å^{-3}
1090 parameters	Absolute structure: Flack x determined using 4207 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
1 restraint	Absolute structure parameter: 0.03 (6)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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