Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supplementary information for:

Convergent Biomimetic Semisynthesis of Disesquiterpenoid Rumphellolide J

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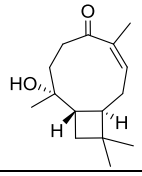
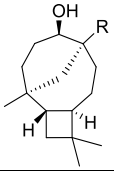
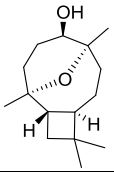
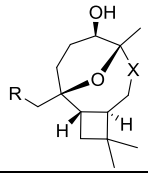
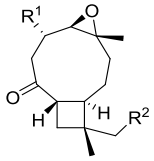
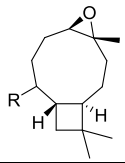
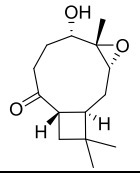
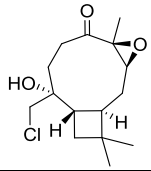
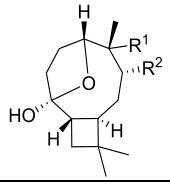
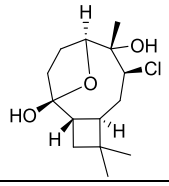
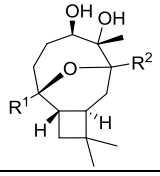
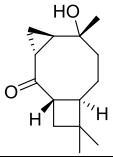
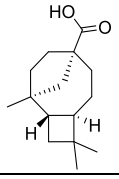
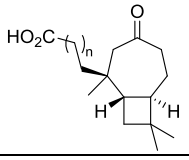
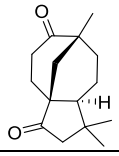
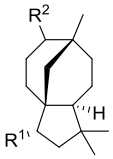
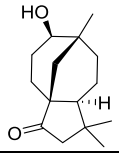
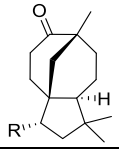
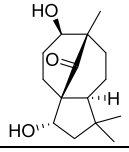
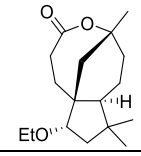
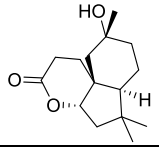
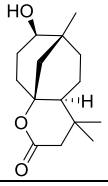
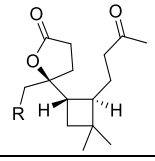
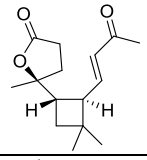
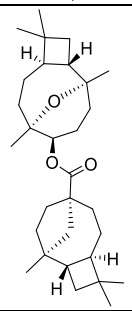
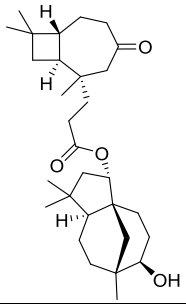
Table S1. β-Caryophyllene-derived terpenoids isolated from *Rumphella antipathies* (relative configuration is depicted)

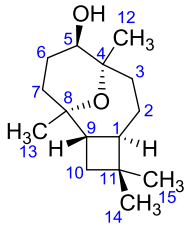
Entry	Structure	Name	Biological activity	Reference
1		Rumphellol A	Anti-inflammatory[*,†]	*Int. J. Mol. Sci.* **2014**, *15* (9), 15679
2		Rumphellol B (R = OEt)	Anti-inflammatory[*,†]	*Int. J. Mol. Sci.* **2014**, *15* (9), 15679
3		(8*R*,9*R*)-Isocaryolane-8,9-diol (R = OH)	Anti-inflammatory[†]	*Nat. Prod. Commun.* **2015**, *10* (6), 835
4		4β,8β-Epoxycaryophyllan-5-ol	Inflammatory[‡]	*Nat. Prod. Commun.* **2015**, *10* (6), 835
5		Rumphellolide I (R = H; X = CO)	Anti-inflammatory[†]	*Chem. Lett.* **2009**, *38* (3), 282
6		Rumphellolide H (R = OH; X = CH_2)	Anti-inflammatory[†]	*Heterocycles* **2009**, *78* (6), 1563
7		Kobusone (R^1 = R^2 = H)	-	*Biochem. Syst. Ecol.* **2007**, *35* (7), 470
8		Rumphellolide D (R^1 = OH, R^2 = H)	Antibacterial[§]	*Chem. Pharm. Bull.* **2007**, *55* (9), 1296
9		Rumphellolide E (R^1 = H, R^2 = OH)	Antibacterial[§]	*Chem. Pharm. Bull.* **2007**, *55* (9), 1296
10		Rumphellolide A (R = β-CO_2H)	Antibacterial[§]	*Chem. Pharm. Bull.* **2007**, *55* (9), 1296
11		Rumphellolide B (R = α-CO_2H)	Antibacterial[§]	*Chem. Pharm. Bull.* **2007**, *55* (9), 1296
12		Rumphellolide C	Antibacterial[§]	*Chem. Pharm. Bull.* **2007**, *55* (9), 1296
13		Rumphellatin D	Anti-inflammatory[†]	*Chem. Lett.* **2008**, *37* (12), 1244
14		Rumphellatin A (R^1 = Cl, R^2 = H)	Antibacterial[§]	*Tetrahedron Lett.* **2007**, *48* (23), 3987
15		Rumphellatin C (R^1 = OH, R^2 = Cl)	-	*Bull. Chem. Soc. Jpn.* **2007**, *80* (12), 2395

16		Rumphellatin B	Antibacterial[¶]	*Bull. Chem. Soc. Jpn.* **2007**, *80* (12), 2395
17		Rumphellolide G (R^1 = H, R^2 = β–H)	-	*Chem. Lett.* **2007**, *36* (11), 1322
18		Rumphellolide K (R^1 = CH_3, R^2 = α–H)	Anti-inflammatory[*,†]	*Heterocycles* **2020**, *100* (9), 1473
19		Rumphellolide F	Antibacterial[§,¶]	*Chem. Pharm. Bull.* **2007**, *55* (9), 1296
20		Rumphellaoic acid A	Anti-inflammatory[†]	*Mar. Drugs* **2014**, *12* (12), 5856
21		Antipacid A (n = 1)	-	*Mar. Drugs* **2020**, *18* (11), 554
22		Antipacid B (n = 0)	Anti-inflammatory[*,†]	*Mar. Drugs* **2020**, *18* (11), 554
23		Clovane-2,9-dione	Anti-inflammatory[*,†]	*Tetrahedron* **2013**, *69* (13), 2740
24		Clovane-2β,9α-diol (R^1 = OH, R^2 = α-OH)	-	*Mar. Drugs* **2020**, *18* (11), 554
25		Clovane-2β,9β-diol (R^1 = OH, R^2 = β-OH)	-	*Nat. Prod. Commun.* **2013**, *8* (8), 1037
26		2β-Acetoxyclovan-9α-ol (R^1 = OAc, R^2= α-OH)	Anti-inflammatory[*,†]	*Nat. Prod. Commun.* **2013**, *8* (8), 1037
27		9α-Acetoxyclovan-2β-ol (R^1 = OH, R^2 = α-OAc)	Anti-inflammatory[†]	*Nat. Prod. Commun.* **2013**, *8* (8), 1037
28		9α-Hydroxyclovan-2-one	-	*Bull. Chem. Soc. Jpn.* **2011**, *84* (1), 119
29		Rumphellclovane D (R = OEt)	Anti-inflammatory[*,†]	*Tetrahedron* **2013**, *69* (13), 2740
30		2β-Hydroxyclovan-9-one (R = OH)	Anti-inflammatory[†]	*Tetrahedron Lett.* **2010**, *51* (20), 2734
31		Rumphellclovane E	Anti-inflammatory[*,†]	*Tetrahedron* **2013**, *69* (13), 2740

32		Rumphellclovane C	Anti-inflammatory*,†	*Tetrahedron* **2013**, *69* (13), 2740
33		Rumphellclovane A	Anti-inflammatory†	*Tetrahedron Lett.* **2010**, *51* (20), 2734
34		Rumphellclovane B	Anti-inflammatory*	*Bull. Chem. Soc. Jpn.* **2011**, *84* (1), 119
35		Rumphellaone A (R = H)	Anticancer#	*Tetrahedron Lett.* **2010**, *51* (46), 6025
36		Rumphellaone C (R = OH)	Anti-inflammatory*,†	*Molecules* **2014**, *19* (8), 12320
37		Rumphellaone B	-	*Molecules* **2014**, *19* (8), 12320
38		Rumphellolide J	-	*Nat. Prod. Commun.* **2017**, *12* (12), 1835
39		Rumphellolide L	Anti-inflammatory†	*Mar. Drugs* **2020**, *18* (11), 554

* inhibits the generation of superoxide anions; † inhibits the release of elastase by human neutrophils; ‡ enhances the generation of superoxide anions; § tested on gram-negative bacteria; ¶ tested on gram-positive bacteria; # cytotoxicity towards CCRF-CEM (human T-cell acute lymphoblastic leukemia) tumor cells

Table S2. NMR spectra of 4β,8β-epoxycaryophyllan-5-ol ((−)-**6**)

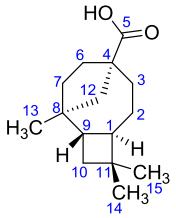


Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	2.07, ddd (12.0, 10.4, 5.9)	42.6, CH	H-2β, -3β, -13, -10β, -15	H-2α, -2β, -9, -10α, -10β, -14, -15,
2α	1.48 – 1.40, m*	18.6, CH_2	H-2β, -9, -14	H-1, -3α, -3β, -9
2β	1.69 – 1.62, m		H-1, -2α, -12	
3α	1.32 – 1.27, m	29.3, CH_2	H-3β	H-2α, -2β, -12
3β	1.86, dd (14.0, 4.6)		H-1, -3α	
4	–	76.8, C†	–	H-2α, -2β, -3α, -3β, -5, -6α, -6β, -12
5	3.45, dd (11.5, 4.9)	75.6, CH	H-6α, -6β, -7, -12	H-3α, -3β, -6α, -6β, -7, -12
6α	2.00 – 1.89, m	25.5, CH_2	H-5, -6β, -7, -9	H-5, -7
6β	1.78 – 1.70, m		H-5, -6α, -7	
7	1.62 – 1.53, m	36.3, CH_2	H-5, -6α, -6β, -13	H-6α, -6β, -9, -13
8	–	72.9, C	–	H-1, -6β, -7, -9, -10α, -10β, -13
9	2.51, ddd (12.0, 9.9, 8.0)	36.4, CH	H-2α, -6α, -10α, -14	H-1, -7, -13
10α	1.34, d (9.8)	35.3, CH_2	H-9, -14	H-1, -9, -14, -15
10β	1.42, t (9.9)*		H-1, -15	
11	–	34.5, C	–	H-1, -9, -14, -15, -10
12	1.18, s	27.2, CH_3	H-2β, -5	H-3α, -3β, -5
13	1.03, s	26.2, CH_3	H-1, -7	H-7, -9
14	0.99, s	21.4, CH_3	H-2α, -9, -10α	H-1, -10, -15
15	1.00, s	30.6, CH_3	H-1, -10β	H-1, -10, -14

* Proton signal partly overlaps with other proton signal

† Carbon signal partly overlaps with $CDCl_3$ signal

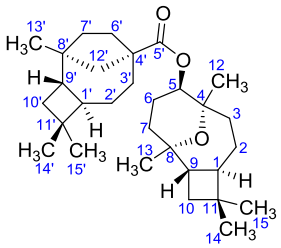
Table S3. NMR spectra of rumphellaoic acid A ((+)-**5**)



Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	1.58 – 1.50, m*	49.1, CH	H-3, -12, -15	H-3, -9, -10, -14, -15
2	1.69 – 1.62, m* 1.38 – 1.30, m*	26.0, CH_2	H-3	H-1, -3, -9
3	1.77, dd (12.8, 5.4) 1.70 – 1.61, m*	34.4, CH_2	H-1, -2	H-1, -2, -6, -12
4	–	52.9, C	–	H-2, -3, -6, -7, -12
5	–	185.8, C	–	H-3, -6, -12
6	2.14, dd (8.6, 7.6) 1.72 – 1.65, m*	29.6, CH_2	H-7	H-3, -7, -12
7	1.54 – 1.48, m* 1.46 – 1.39, m	45.6, CH_2	H-6	H-6, -12, -13
8	–	42.0, C	–	H-6, -7, -10, -12, -13
9	1.59 – 1.56, m*	46.1, CH	H-10	H-2, -7, -10, -12, -13
10	1.59 – 1.54, m* 1.37 – 1.31, m*	37.3, CH_2	H-9, -13, -14, -15	H-1, -9, -14, -15
11	–	33.6, C	–	H-1, -2, -9, -10, -14, -15
12	1.93, dd (12.8, 2.9) 1.63 – 1.60, m*	49.1, CH_2	H-1	H-3, -6, -7, -13
13	0.93, s	22.2, CH_3	H-10	H-9, -12
14	0.98, s	20.5, CH_3	H-10	H-1, -10, -15
15	0.98, s	30.6, CH_3	H-10, -1	H-1, -10, -14

* Proton signal partly overlaps with other proton signal

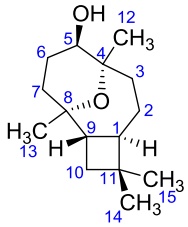
Table S4. NMR spectra of rumphellolide J ((–)-**7**)



Position	δ_H, (*J*, Hz)	δ_C, type	^{1}H-^{1}H NOESY	HMBC (C→H)
1	2.09 – 2.03, m*	42.6, CH	H-2, -10, -13, -15	H-3, -9, -10, -14, -15
2	1.70 – 1.60, m*; 1.47 – 1.40, m*	18.7, CH_2	H-1, -3	H-1, -3, -9
3	2.01 – 1.96, m*; 1.34 – 1.27, m*	30.56, CH_2	H-2	H-1, -5, -12
4	–	75.6, C	–	H-2, -5, -6, -12
5	4.58, dd (11.4, 5.1)	76.6, CH	H-6, -12, -3’	H-3, -6, -7, -12
6	1.96 – 1.89, m*; 1.85 – 1.77, m	21.8, CH_2	H-5, -7	H-7
7	1.72 – 1.65, m* 1.67 – 1.61, m*	35.7, CH_2	H-6	H-6, -9, -13
8	–	73.2, C	–	H-1, -6, -7, -9, -10, -13
9	2.55, ddd (12.0, 9.9, 8.0)	36.4, CH	H-6, -10, -14	H-1, -7, -10, -13
10	1.45 – 1.40, m*; 1.38 – 1.32, m*	35.3, CH_2	H-1, -9, -14, -15	H-9, -14, -15
11	–	34.5, C	–	H-9, -10, -14, -15
12	1.08, s	27.4, CH_3	H-5, -6’	H-3, -5
13	1.04, s	26.0, CH_3	H-1, -7	H-9
14	1.01, s	21.5, CH_3	H-9, -10	H-1, -10, -15
15	1.01, s	30.64, CH_3	H-1, -10	H-1, -10, -14
1’	1.52 – 1.48, m	49.1, CH	H-12’, -15’	H-9’, -10’, -14’, -15’
2’	1.64 – 1.57, m*; 1.34 – 1.28, m*	26.1, CH_2	H-3’, -14’	H-3’
3’	1.72 – 1.53, m*	34.6, CH_2	H-2’, -6’, 5	H-12’
4’	–	53.2, C	–	H-3’, -6’, -7’
5’	–	178.7, C	–	H-5, -3’, -6’, -12’
6’	2.13, ddd (13.8, 8.2, 1.2) 1.67 – 1.57, m*	29.3, CH_2	H-12, -3’, -7’	H-3’, -7’, -12’
7’	1.57 – 1.54, m*; 1.47 – 1.45, m*	45.6, CH_2	H-6’	H-6’, -9’, -12’, -13’
8’	–	41.9, C	–	H-6’, -12’, -13’
9’	1.60 – 1.54, m*	46.1, CH	H-10’, -14’	H-1’, -10’, -12’, -13’
10’	1.59 – 1.53, m*; 1.32 – 1.29, m*	37.4, CH_2	H-9’, -13’, -14’, -15’	H-14’, -15’
11’	–	33.6, C	–	H-14’, -15’
12’	1.92 – 1.87, m*; 1.46 – 1.41, m*	49.4, CH_2	H-1’	H-6’, -7’, -13’
13’	0.91, s	22.3, CH_3	H-10’	
14’	0.98, s	20.5, CH_3	H-9’, -10’, -2’	H-10’, -15’
15’	0.98, s	30.64, CH_3	H-1’, -10’	H-10’, -14’

* Proton signal partly overlaps with other proton signal

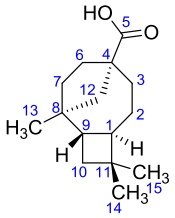
Table S5. Comparison of NMR data of isolated and synthesized 4β,8β-epoxycaryophyllan-5-ol



Position	this work	isolated‡	this work	isolated‡
	δ_H, type	δ_H, type	δ_C, type	δ_C, type
1	2.07, ddd	2.08, ddd	42.6, CH	42.4, CH
2α	1.48 – 1.40, m*	1.46, m	18.6, CH_2	18.5, CH_2
2β	1.69 – 1.62, m	1.66, m		
3α	1.32 – 1.27, m	1.30, m	29.3, CH_2	29.1, CH_2
3β	1.86, dd	1.88, ddd		
4	–	–	76.8, C†	77.2, C
5	3.45, dd	3.45, dd	75.6, CH	75.4, CH
6α	2.00 – 1.89, m	1.96, m	25.5, CH_2	25.3, CH_2
6β	1.78 – 1.70, m	1.74, m		
7	1.62 – 1.53, m	1.60, m	36.3, CH_2	36.1, CH_2
8	–	–	72.9, C	72.7, C
9	2.51, ddd	2.52, dd	36.4, CH	36.2, CH
10α	1.34, d	1.34, d	35.3, CH_2	35.1, CH_2
10β	1.42, t*	1.43, dd		
11	–	–	34.5, C	34.4, C
12	1.18, s	1.19, s	27.2, CH_3	27.1, CH_3
13	1.03, s	1.03, s	26.2, CH_3	26.0, CH_3
14	0.99, s	0.99, s	21.4, CH_3	21.3, CH_3
15	1.00, s	1.00, s	30.6, CH_3	30.5, CH_3

* Proton signal partly overlaps with other proton signal.
† Carbon signal partly overlaps with $CDCl_3$ signal.
‡ from *Rumphella antipathies*, *Nat. Prod. Commun.* **2015**, *10* (6), 835–838

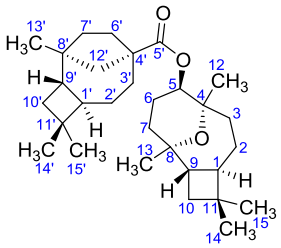
Table S6. Comparison of NMR data of isolated and synthesized rumphellaoic acid A



Position	this work	isolated†	isolated‡	this work	isolated†	isolated‡
	δ_H, type	δ_H, type	δ_H, type	δ_C, type	δ_C, type	δ_C, type
1	1.58 – 1.50, m*	1.55, m	1.55, m	49.1, CH	48.9, CH	48.9, CH
2	1.69 – 1.62, m* 1.38 – 1.30, m*	1.64, m 1.32, m	1.66, m 1.36, m	26.0, CH_2	25.8, CH_2	25.8, CH_2
3	1.77, dd 1.70 – 1.61, m*	1.78, dd 1.61, m	1.80, dd 1.66, m	34.4, CH_2	34.2, CH_2	34.3, CH_2
4	–	–	–	52.9, C	52.6, C	52.6, C
5	–	–	–	185.8, C	184.2, C§	184.5, C§
6	2.14, dd 1.72 – 1.65, m*	2.14, dd 1.68, m	2.17, dd 1.70, m	29.6, CH_2	29.4, CH_2	29.5, CH_2
7	1.54 – 1.48, m* 1.46 – 1.39, m	1.68, m 1.44, m	1.55, m 1.46, m	45.6, CH_2	45.4, CH_2	45.4, CH_2
8	–	–	–	42.0, C	41.9, C	41.9, C
9	1.59 – 1.56, m*	1.58, m	1.62, m	46.1, CH	46.0, CH	46.0, CH
10	1.59 – 1.54, m* 1.37 – 1.31, m*	1.56, m 1.35, m	1.58, m 1.36, m	37.3, CH_2	37.2, CH_2	37.2, CH_2
11	–	–	–	33.6, C	33.5, C	33.5, C
12	1.93, dd 1.63 – 1.60, m*	1.94, dd 1.59, d	1.95, dd 1.62, m	49.1, CH_2	48.9, CH_2	48.9, CH_2
13	0.93, s	0.93, s	0.95, s	22.2, CH_3	22.0, CH_3	22.0, CH_3
14	0.98, s	0.98, s	1.01, s	20.5, CH_3	20.3, CH_3	20.3, CH_3
15	0.98, s	0.98, s	1.01, s	30.6, CH_3	30.5, CH_3	30.5, CH_3

* Proton signal partly overlaps with other proton signal.
† from *Rumphella antipathies*, *Mar. Drugs* **2014**, *12* (12), 5856–5863
‡ from *Psidium guajava*, *Nat. Prod. Res.* **2016**, *30* (8), 898–903
§ Signal assigned by 2D NMR spectra

Table S7. Comparison of NMR data of isolated and synthesized rumphellolide J



Position	this work	isolated†	this work	isolated†
	δ_H, type	δ_H, type	δ_C, type	δ_C, type
1	2.09 – 2.03, m*	2.07, ddd	42.6, CH	42.5, CH
2	1.70 – 1.60, m* 1.47 – 1.40, m*	1.47, m 1.41, m	18.7, CH_2	18.5, CH_2
3	2.01 – 1.96, m* 1.34 – 1.27, m*	1.98, ddd 1.29, m	30.56, CH_2	30.4, CH_2
4	–	–	75.6, C	75.4, C
5	4.58, dd	4.58, dd	76.6, CH	76.7, CH
6	1.96 – 1.89, m* 1.85 – 1.77, m	1.84, m 1.81, m	21.8, CH_2	21.6, CH_2
7	1.72 – 1.65, m* 1.67 – 1.61, m*	1.70, m 1.54, m	35.7, CH_2	35.5, CH_2
8	–	–	73.2, C	73.1, C
9	2.55, ddd	2.55, ddd	36.4, CH	36.2, CH
10	1.45 – 1.40, m* 1.38 – 1.32, m*	1.44, m 1.32, m	35.3, CH_2	35.1, CH_2
11	–	–	34.5, C	34.4, C
12	1.08, s	1.08, s	27.4, CH_3	27.2, CH_3
13	1.04, s	1.04, s	26.0, CH_3	25.9, CH_3
14	1.01, s	1.01, s	21.5, CH_3	21.3, CH_3
15	1.01, s	1.01, s	30.64, CH_3	30.5, CH_3
1’	1.52 – 1.48, m	1.53, m	49.1, CH	49.0, CH
2’	1.64 – 1.57, m* 1.34 – 1.28, m*	1.59, m 1.33, m	26.1, CH_2	25.9, CH_2
3’	1.72 – 1.53, m*	1.67, m 1.58, m	34.6, CH_2	34.5, CH_2
4’	–	–	53.2, C	53.0, C
5’	–	–	178.7, C	178.5, C
6’	2.13, ddd 1.67 – 1.57, m*	2.13, dd 1.61, m	29.3, CH_2	29.1, CH_2
7’	1.57 – 1.54, m* 1.47 – 1.45, m*	1.48, m 1.42, m	45.6, CH_2	45.5, CH_2
8’	–	–	41.9, C	41.7, C
9’	1.60 – 1.54, m*	1.56, m	46.1, CH	46.0, CH
10’	1.59 – 1.53, m* 1.32 – 1.29, m*	1.57, m 1.30, m	37.4, CH_2	37.2, CH_2

11'	–	–	33.6, C	33.5, C
12'	1.92 – 1.87, m* 1.46 – 1.41, m*	1.89, dd 1.44, d	49.4, CH_2	49.2, CH_2‡
13'	0.91, s	0.91, s	22.3, CH_3	22.1, CH_3
14'	0.98, s	0.98, s	20.5, CH_3	20.3, CH_3
15'	0.98, s	0.98, s	30.64, CH_3	30.5, CH_3

* Proton signal partly overlaps with other proton signal.
† from *Rumphella antipathies*, *Nat. Prod. Commun.* **2017**, *12* (12), 1835–1837
‡ In the publication, authors assign the shift for C-12' as 39.2 ppm, however in the supplementary material no relevant signal was found in this region. The signal at 49.2 ppm in the authors' ^{13}C NMR spectrum is absent in the table of chemical shifts presented in their paper. We conclude a typo must have occurred, therefore 49.2 ppm is the correct chemical shift for C-12'.

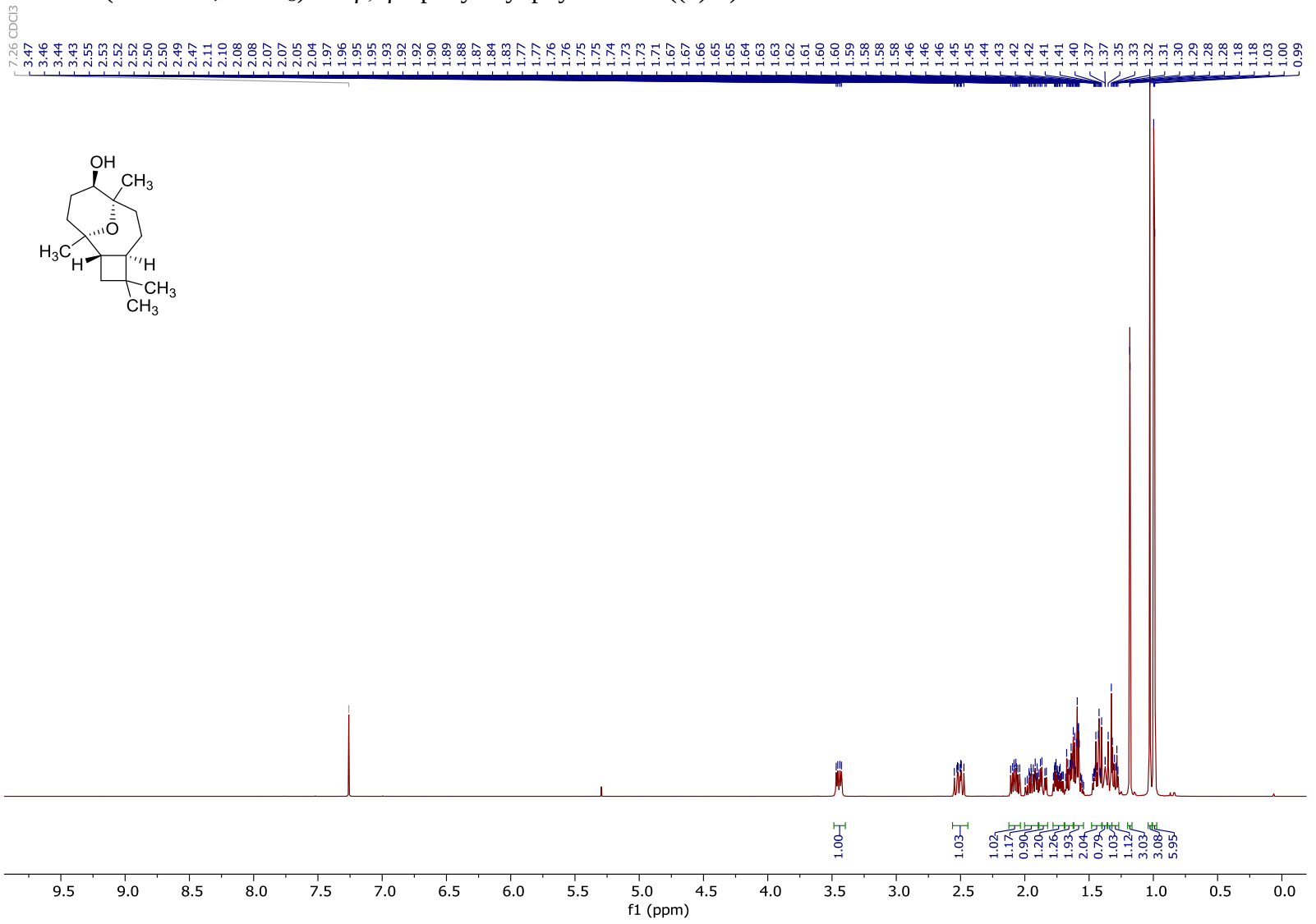
Table S8. Comparison of specific rotation values (all measurements done in $CHCl_3$)

Entry	**Compound**	**[α]**	**T**	***c***	**Reference**
1	**4β,8β-Epoxycaryophyllan-5-ol** isolated	**–**70	26	0.03	*Nat. Prod. Commun.* **2015**, *10* (6), 835
2	**4β,8β-Epoxycaryophyllan-5-ol** synthetic	–26.0	Not specified	2.17	*J. Chem. Soc. Perkin Trans. 1* **1996**, *20*, 2507
3		–65.3	20	1.03	*this work*
4	**Rumphellaoic acid A (guavacid A)** isolated	–32	23	0.07	*Mar. Drugs* **2014**, *12* (12), 5856
5		–11.8	Not specified	0.06	*Nat. Prod. Res.* **2016**, *30* (8), 898
6	**Rumphellaoic acid A (guavacid A)** synthetic	+25.5	20	1.04	*this work*
7	**Rumphellolide J** isolated	**–**51	25	0.3	*Nat. Prod. Commun.* **2017**, *12* (12), 1835
8	**Rumphellolide J** synthetic	–44.0	20	1.01	*this work*

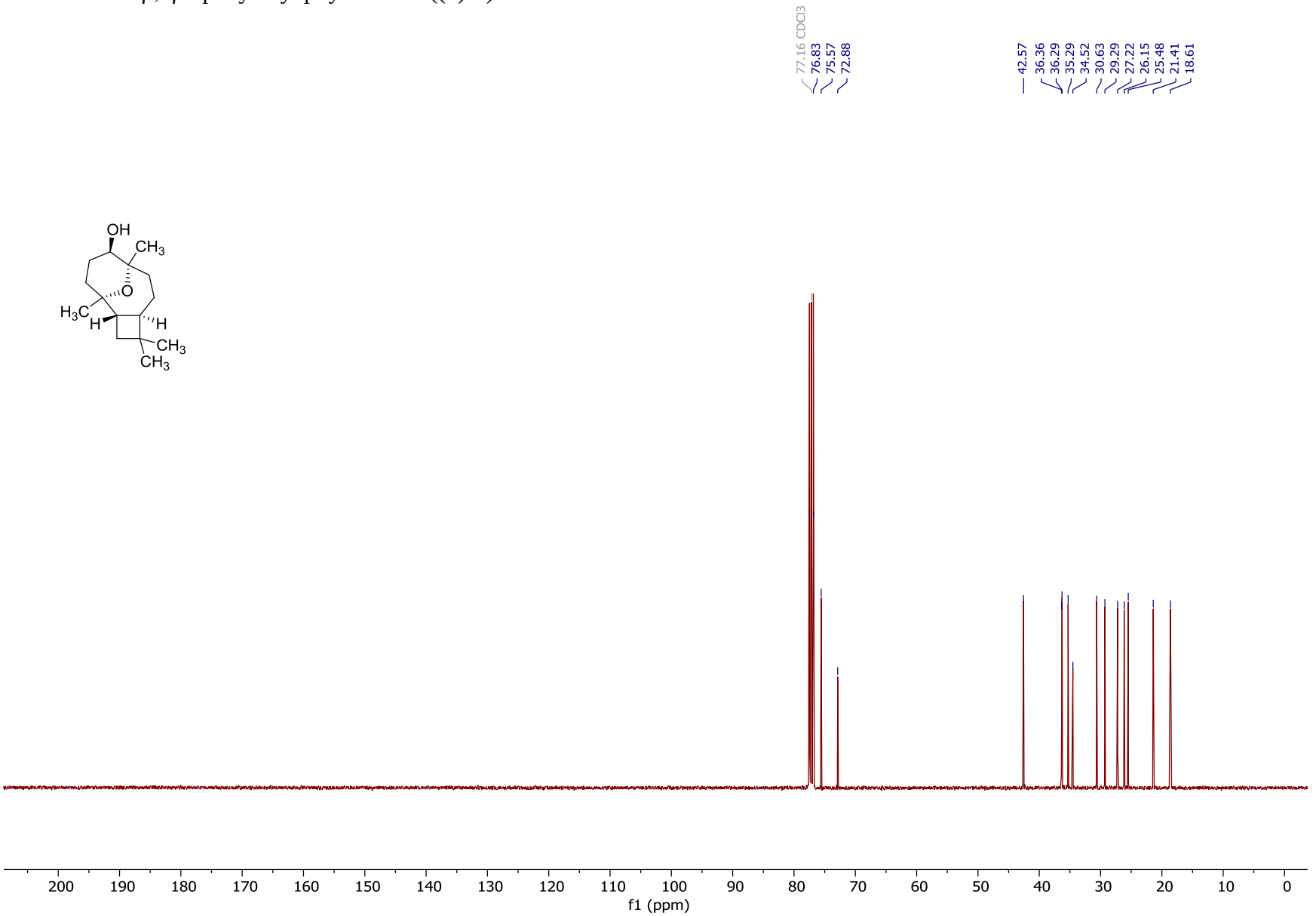
NMR spectra of compounds

S1. NMR of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)

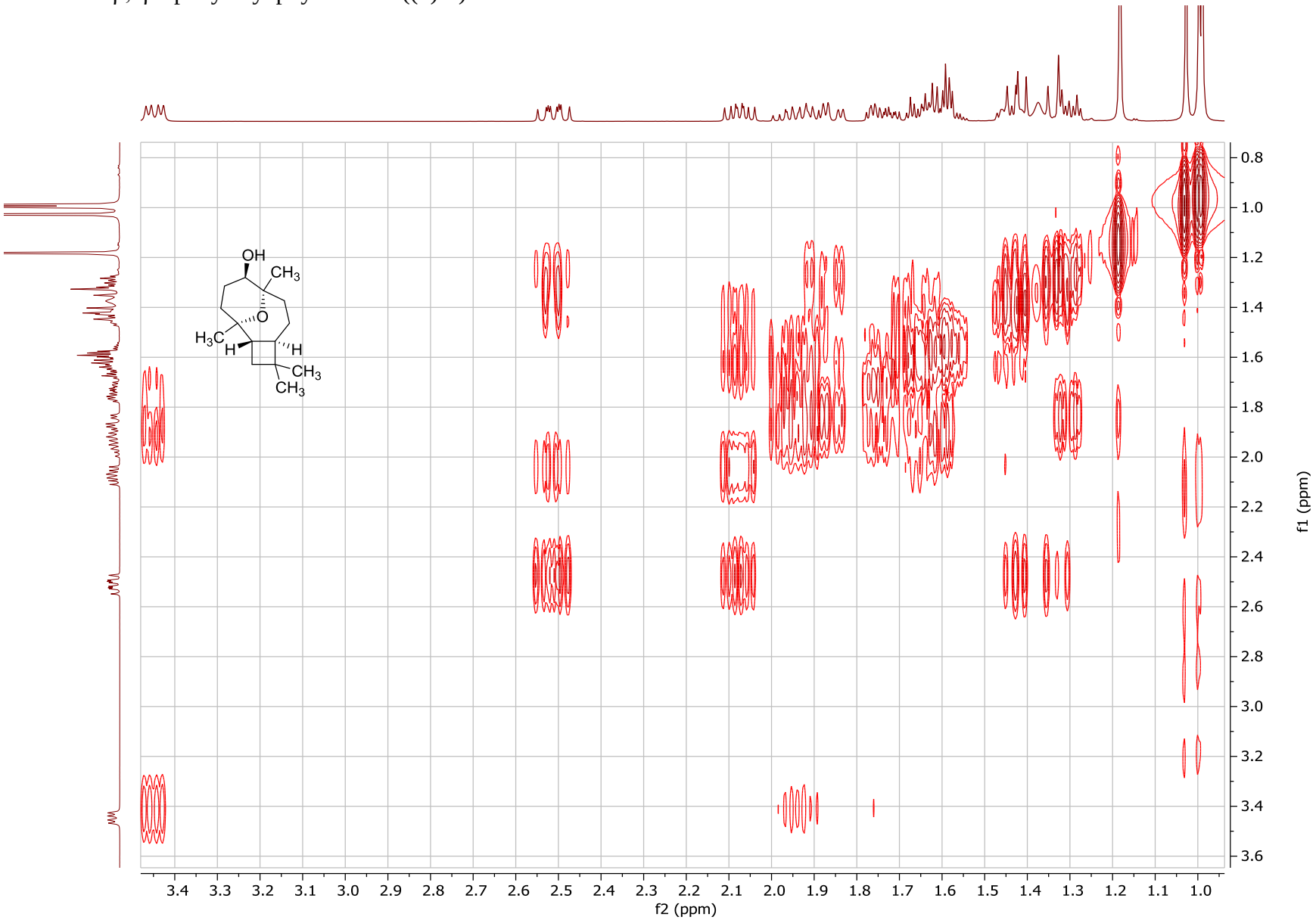
^{1}H NMR (400 MHz, $CDCl_3$) of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)



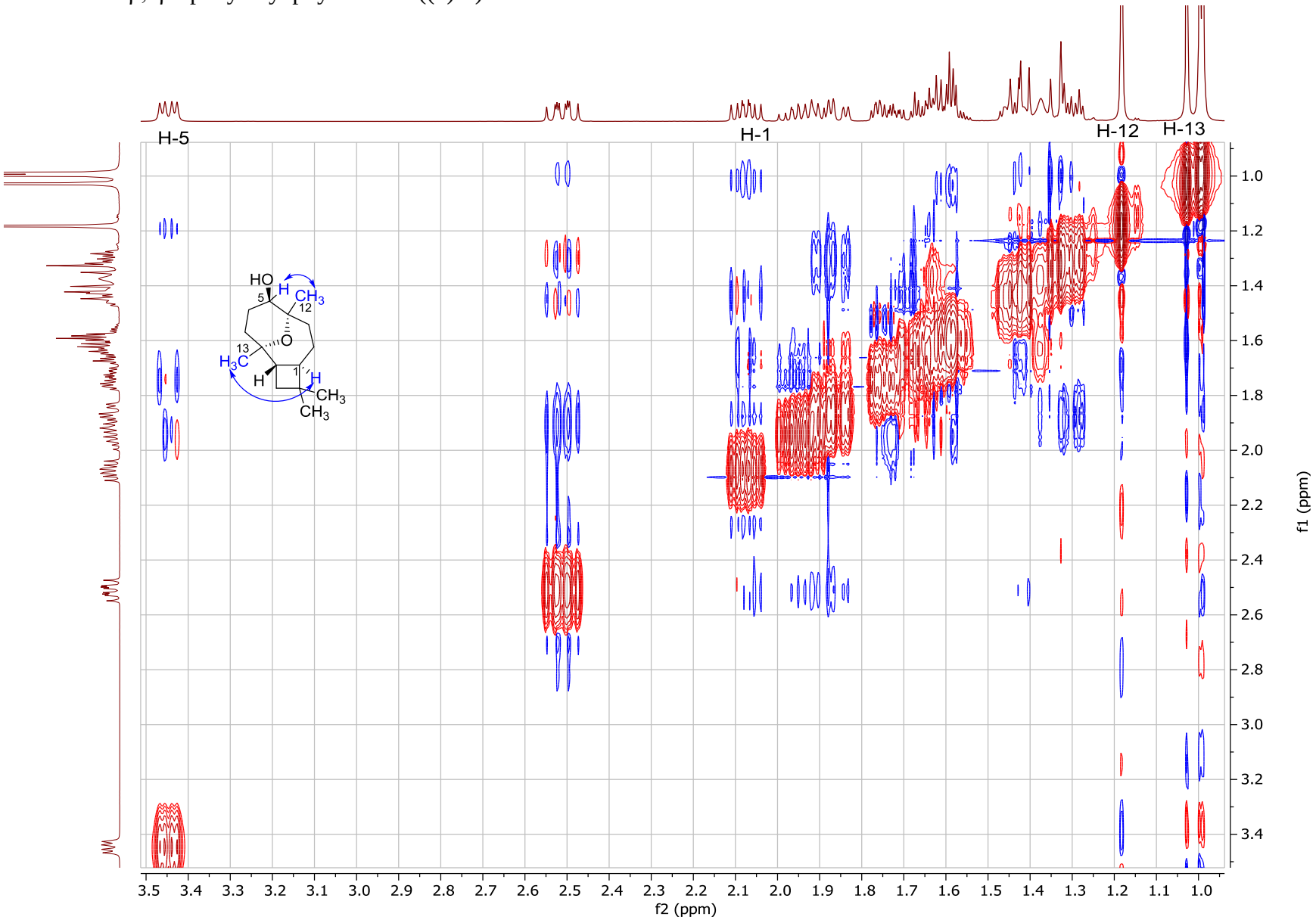
^{13}C NMR of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)



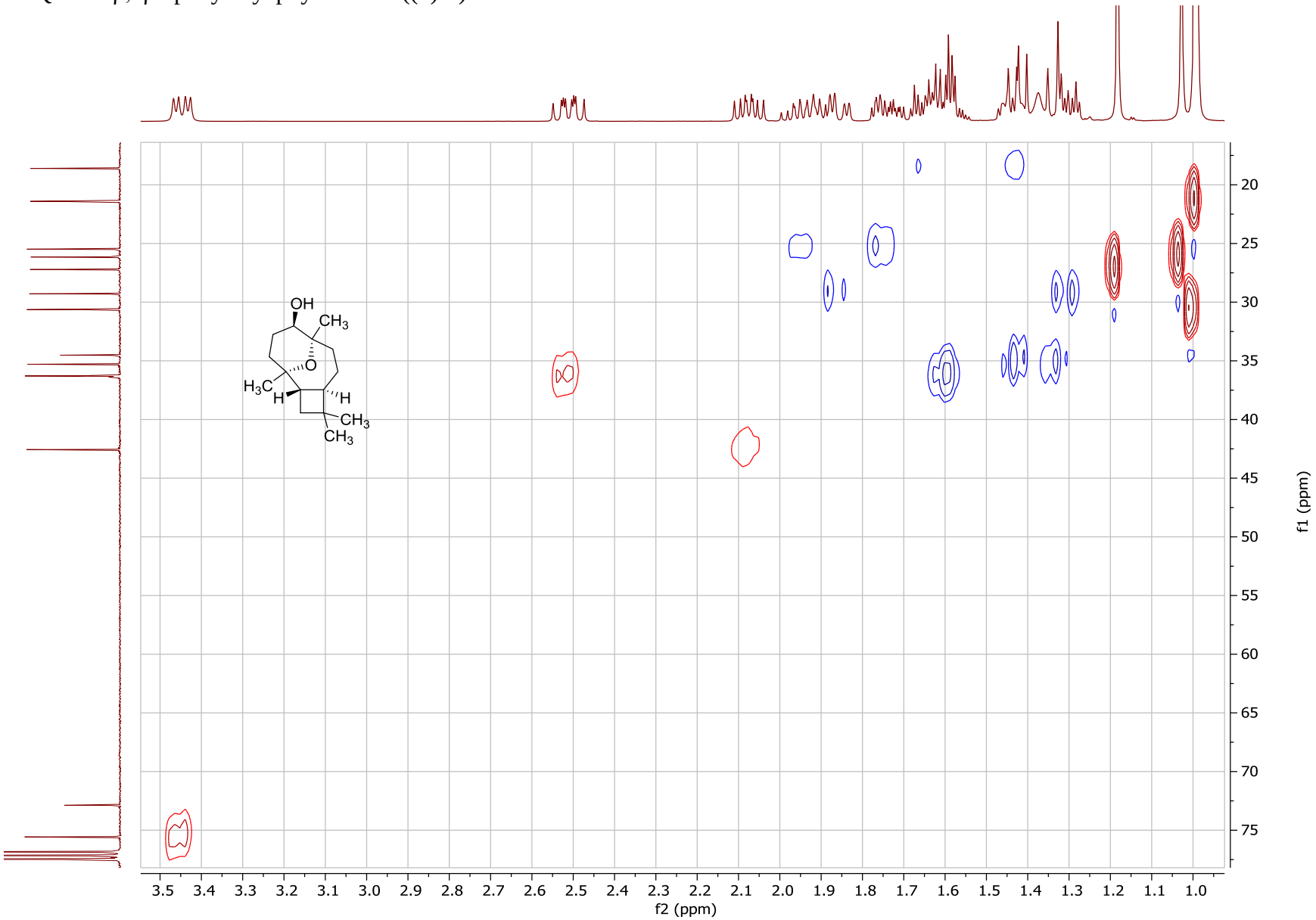
COSY of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)



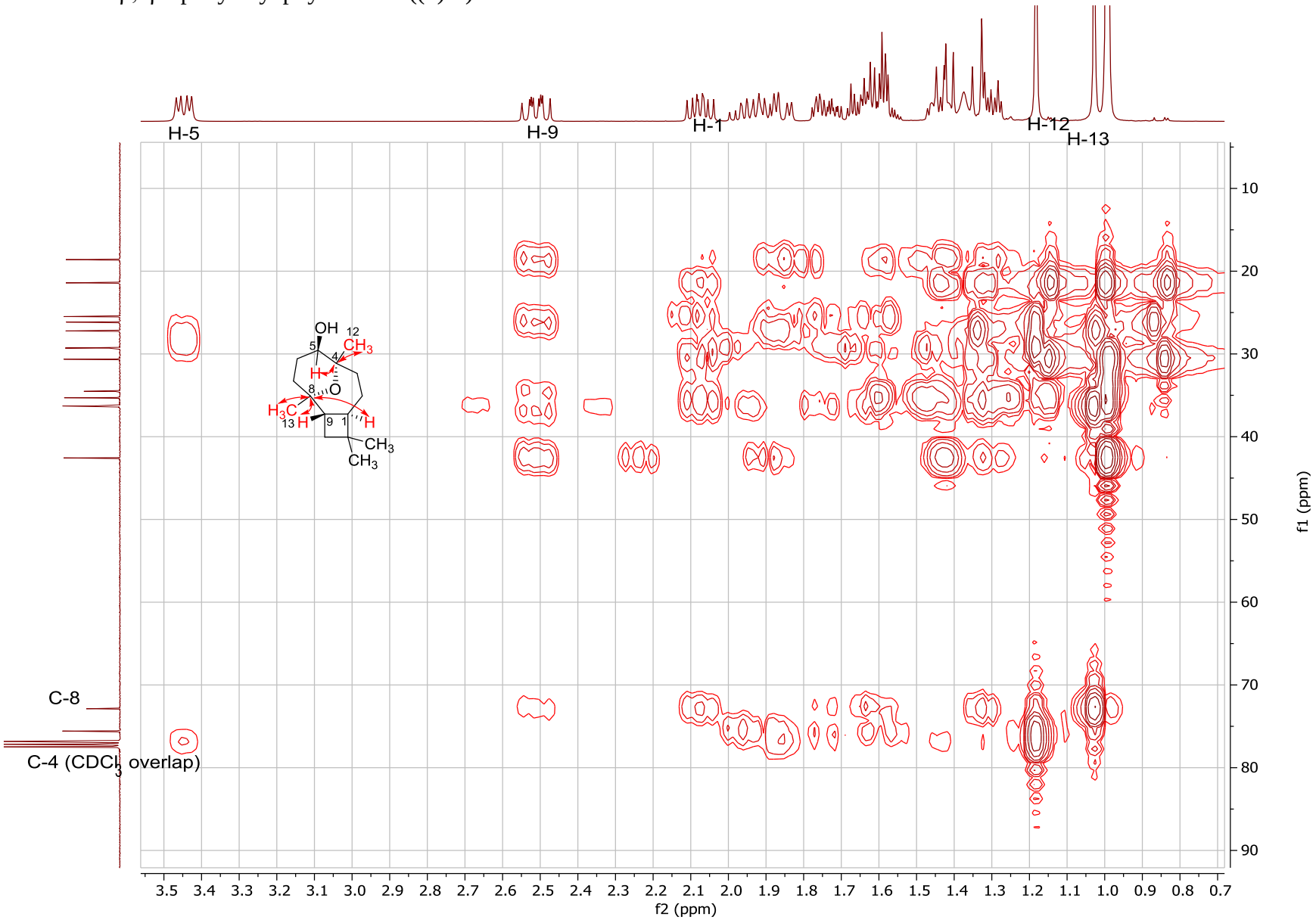
NOESY of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)



HSQC of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)

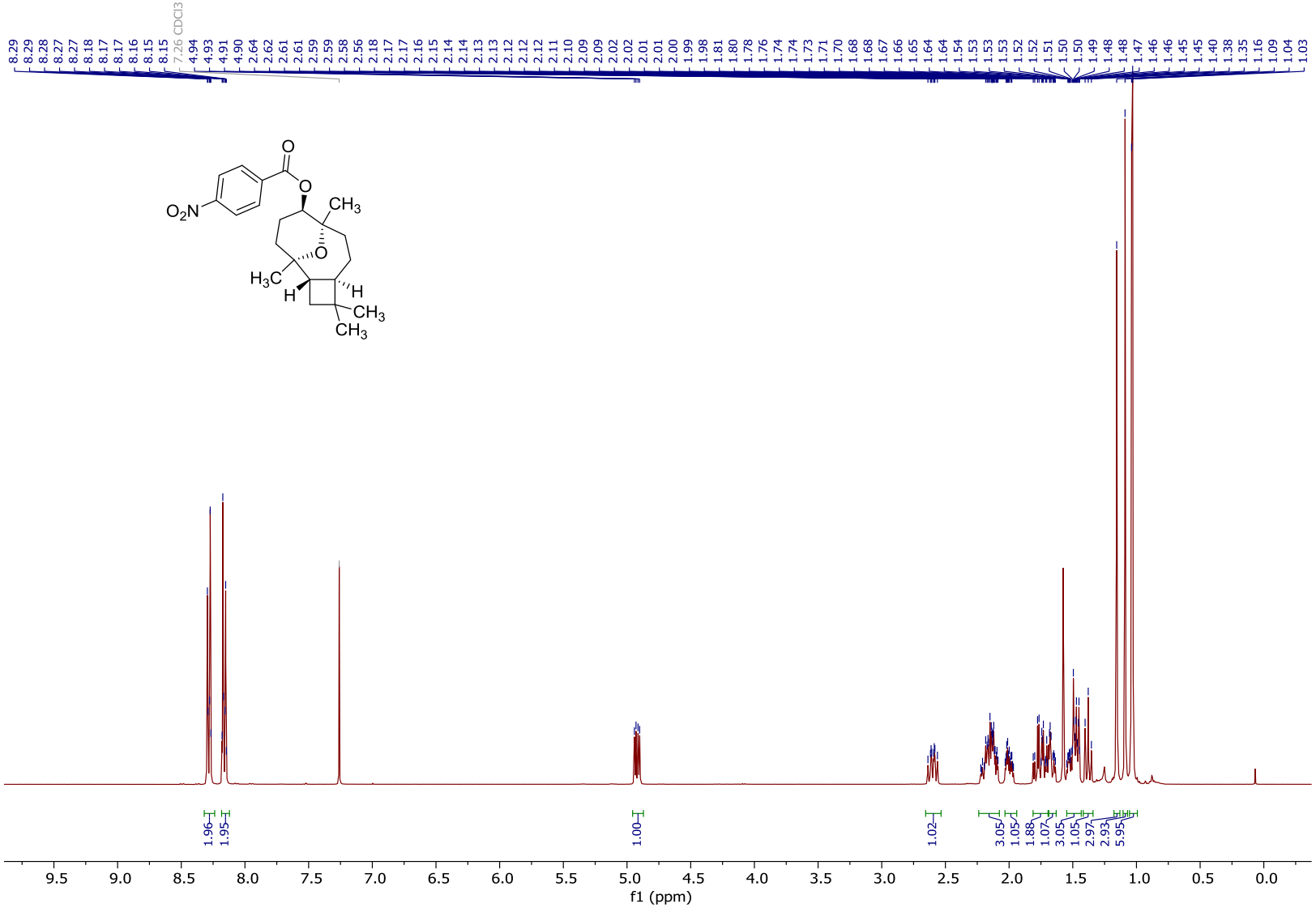


HMBC of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)

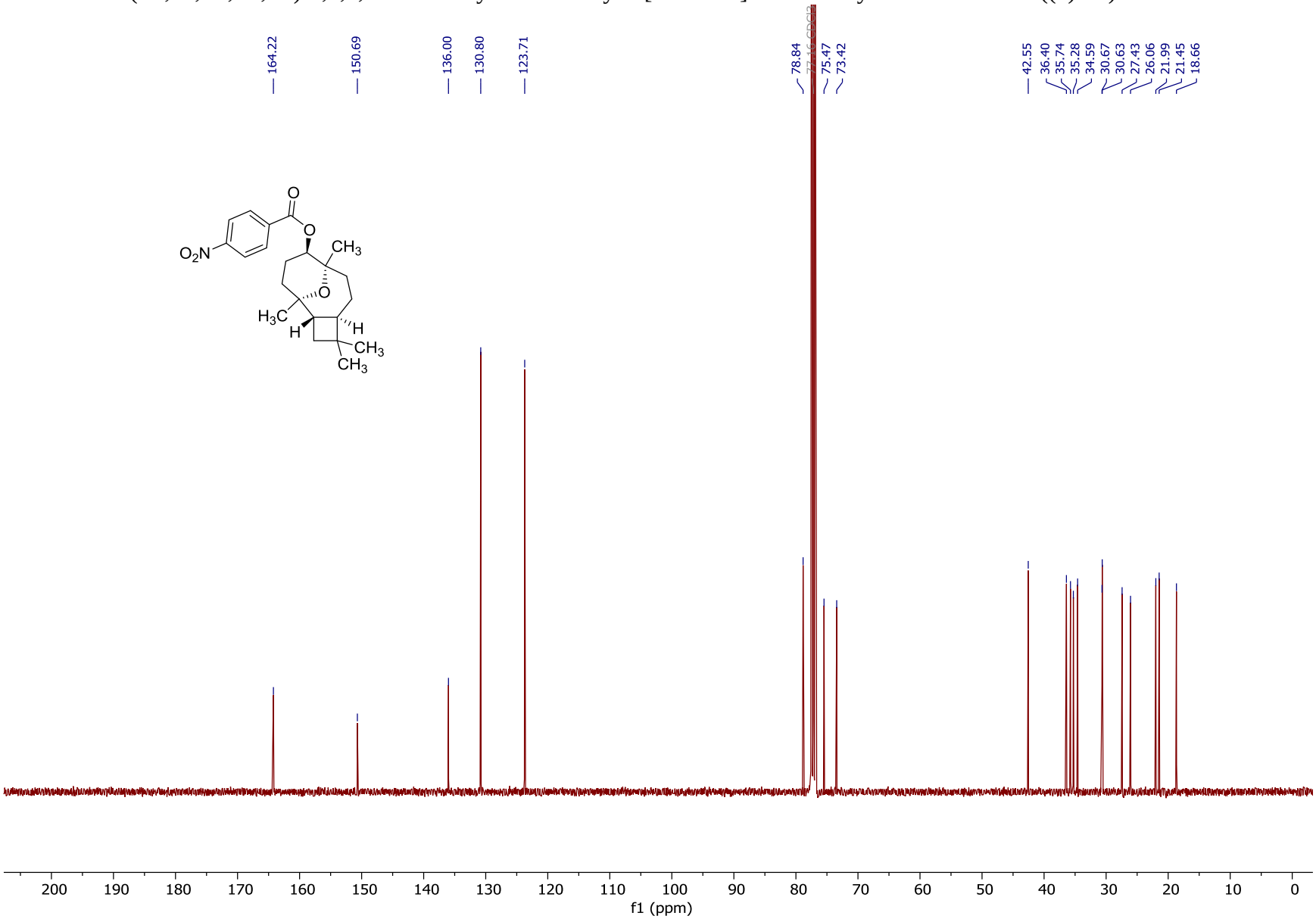


S2. NMR of compound (–)-**12**

^{1}H NMR of (1*R*,2*S*,5*R*,8*R*,9*R*)-1,4,4,8-tetramethyl-12-oxatricyclo[6.3.1.0^{2,5}]dodecan-9-yl 4-nitrobenzoate ((–)-**12**)

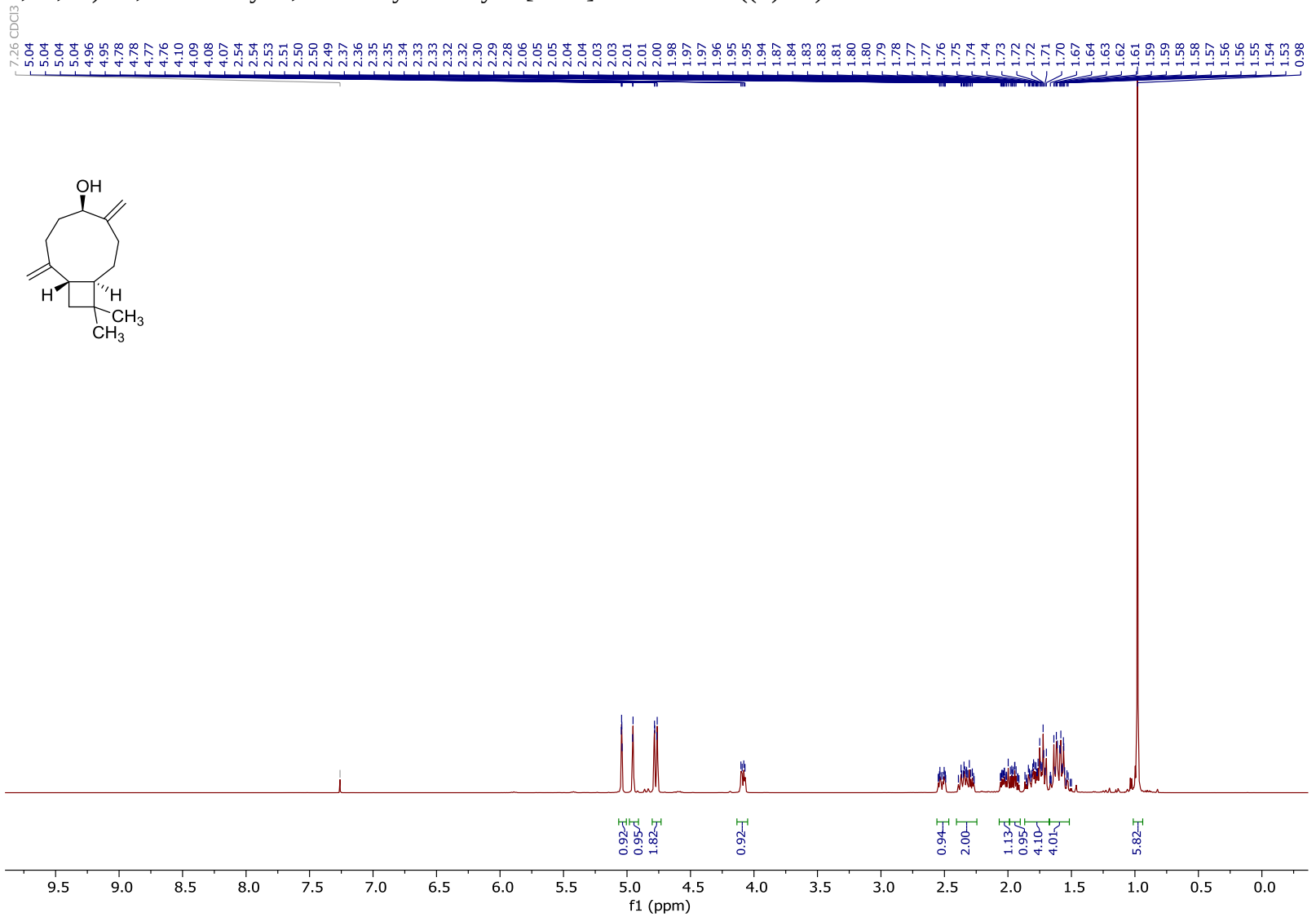


^{13}C NMR of (1*R*,2*S*,5*R*,8*R*,9*R*)-1,4,4,8-tetramethyl-12-oxatricyclo[6.3.1.0^{2,5}]dodecan-9-yl 4-nitrobenzoate ((–)-**12**)

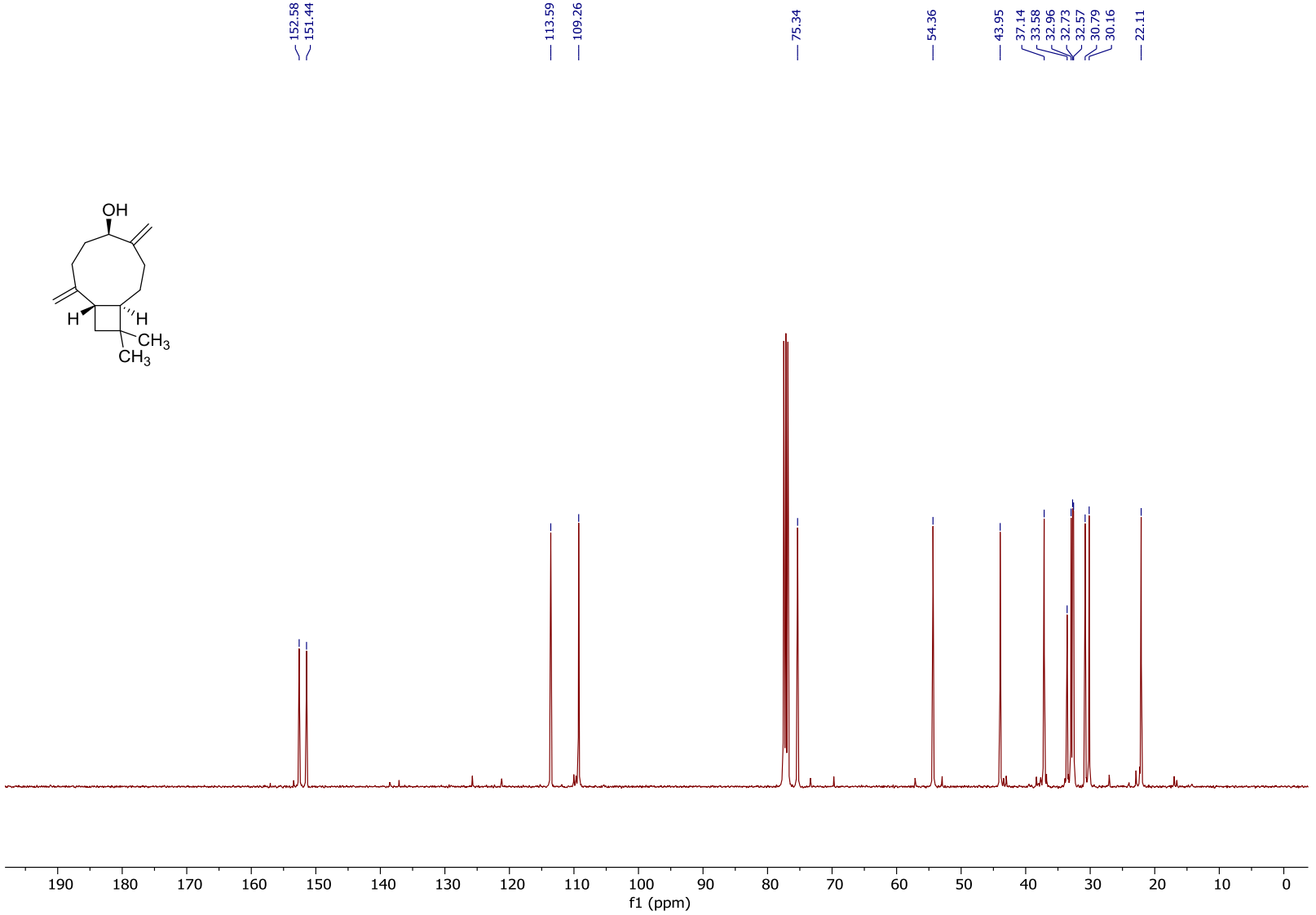


S3. NMR of compound (+)-**13**

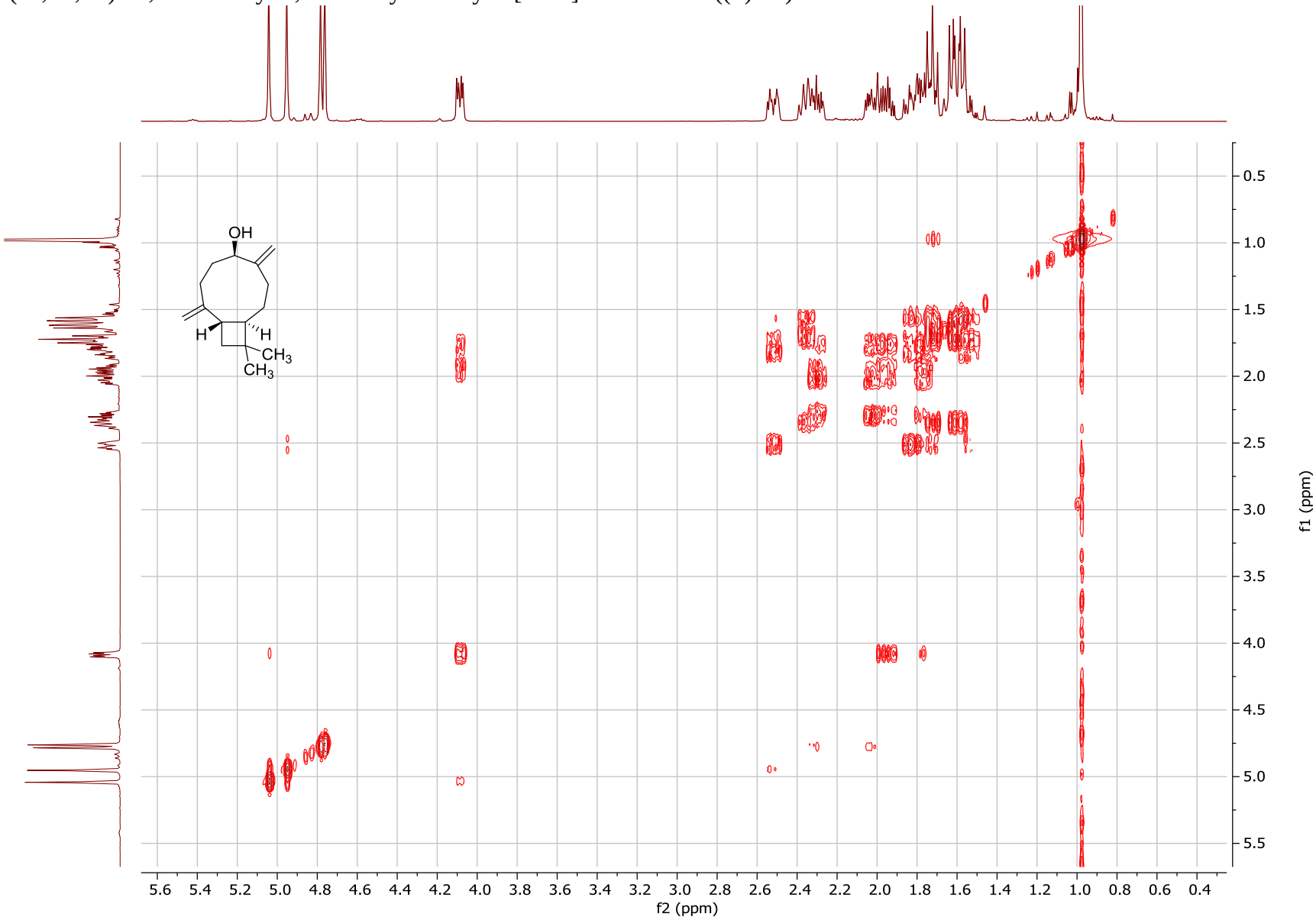
^{1}H NMR of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol ((+)-**13**)



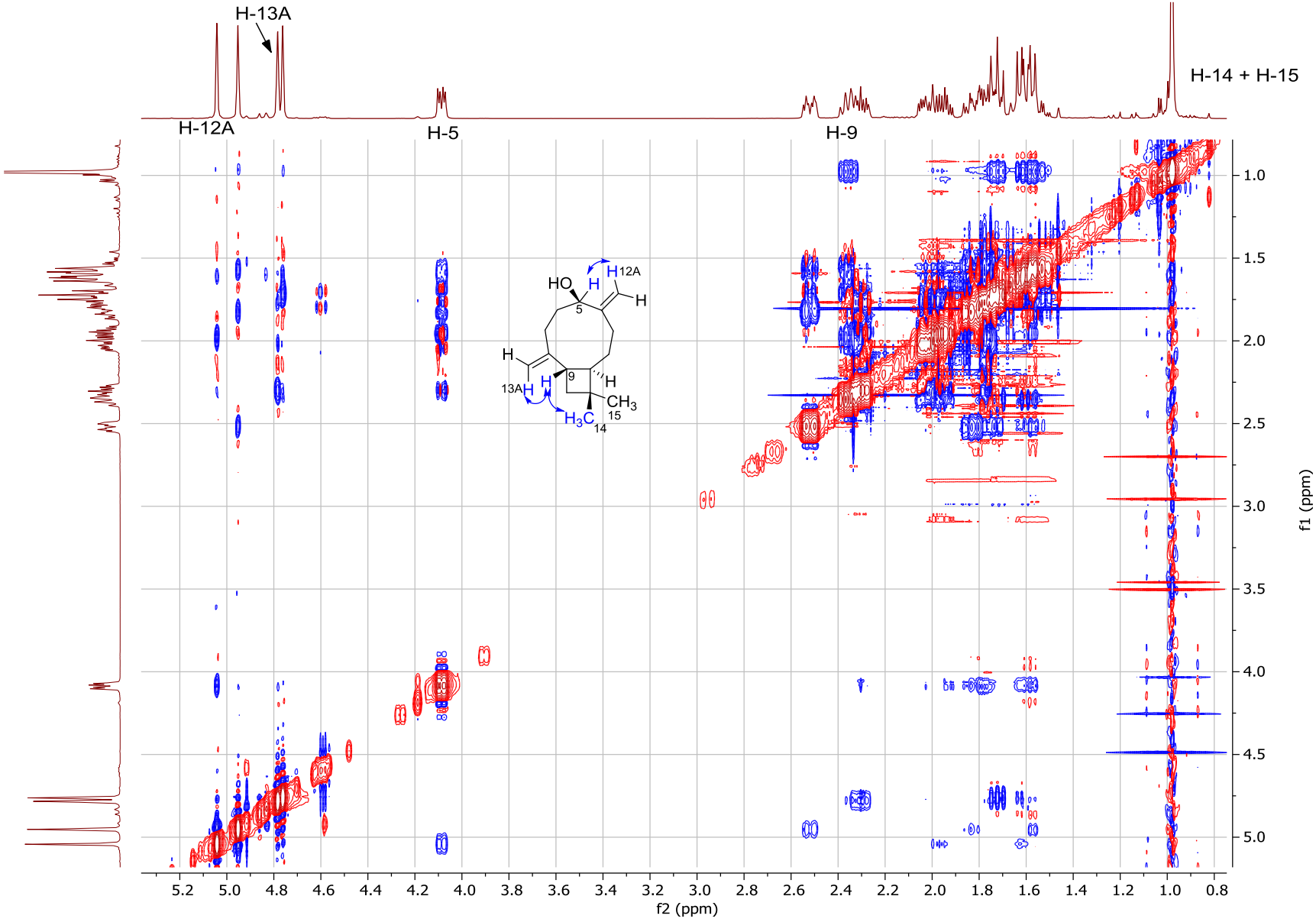
^{13}C NMR of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol ((+)-**13**)



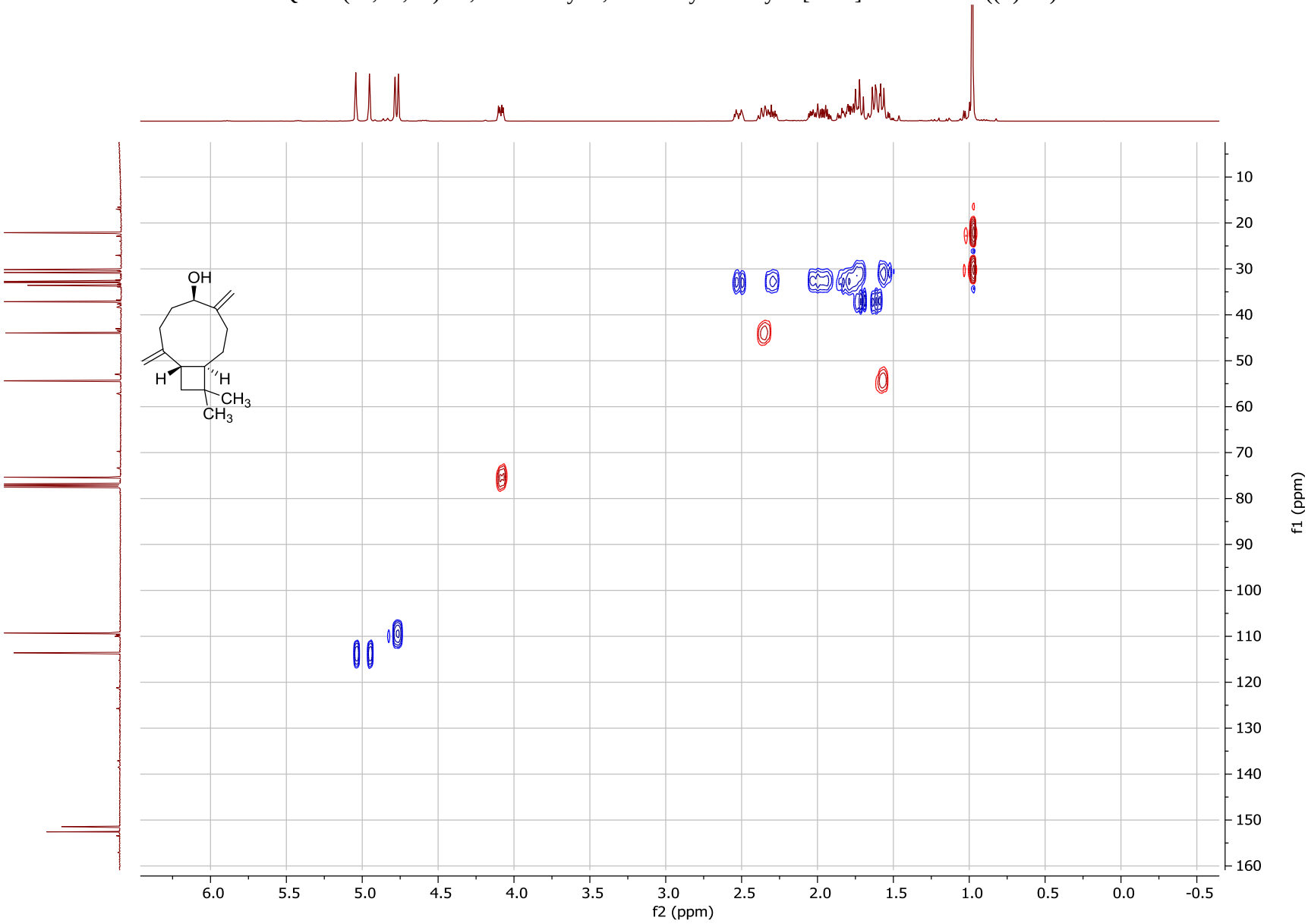
COSY of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol ((+)-**13**)



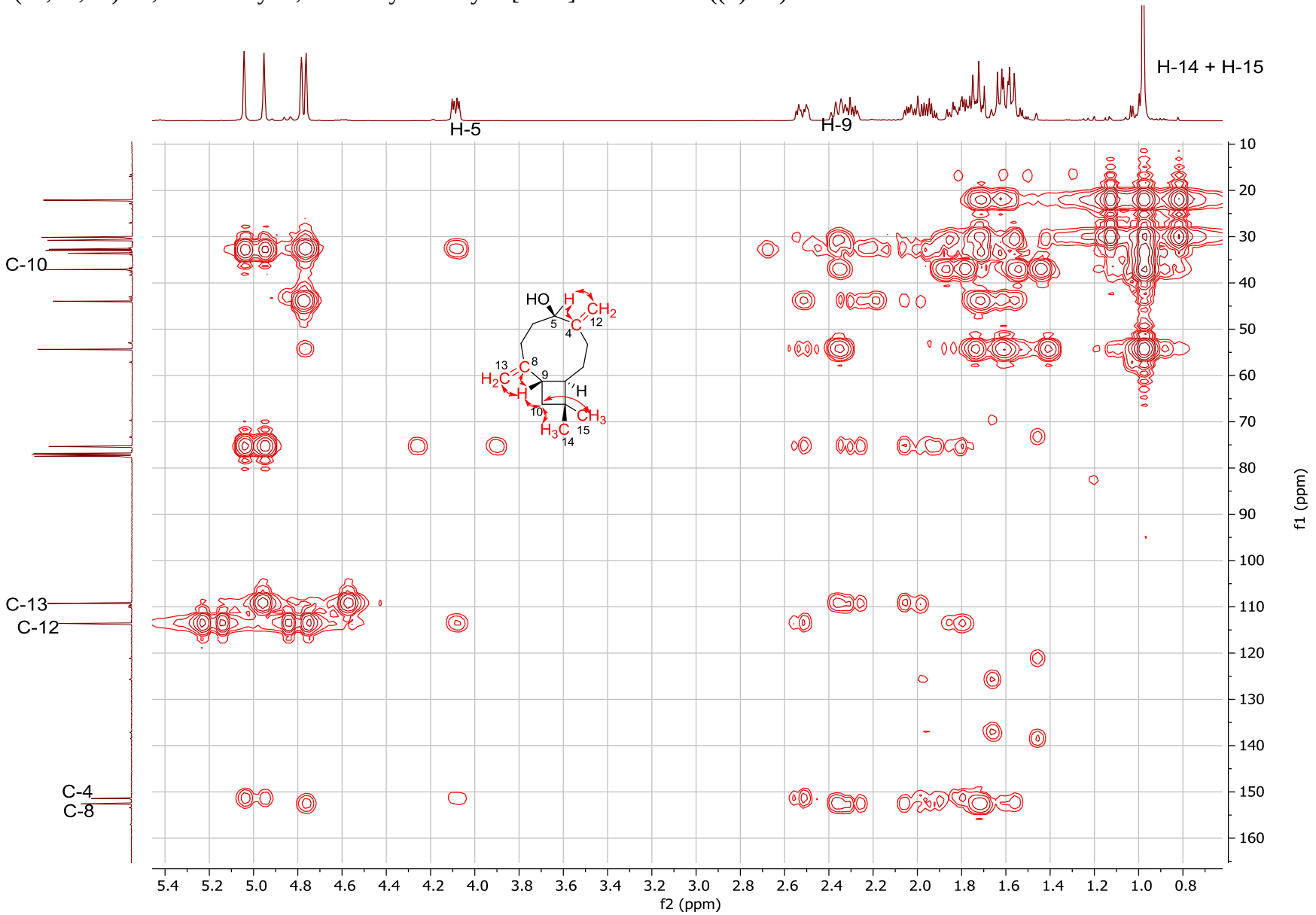
NOESY of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol ((+)-**13**)



HSQC of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol ((+)-**13**)

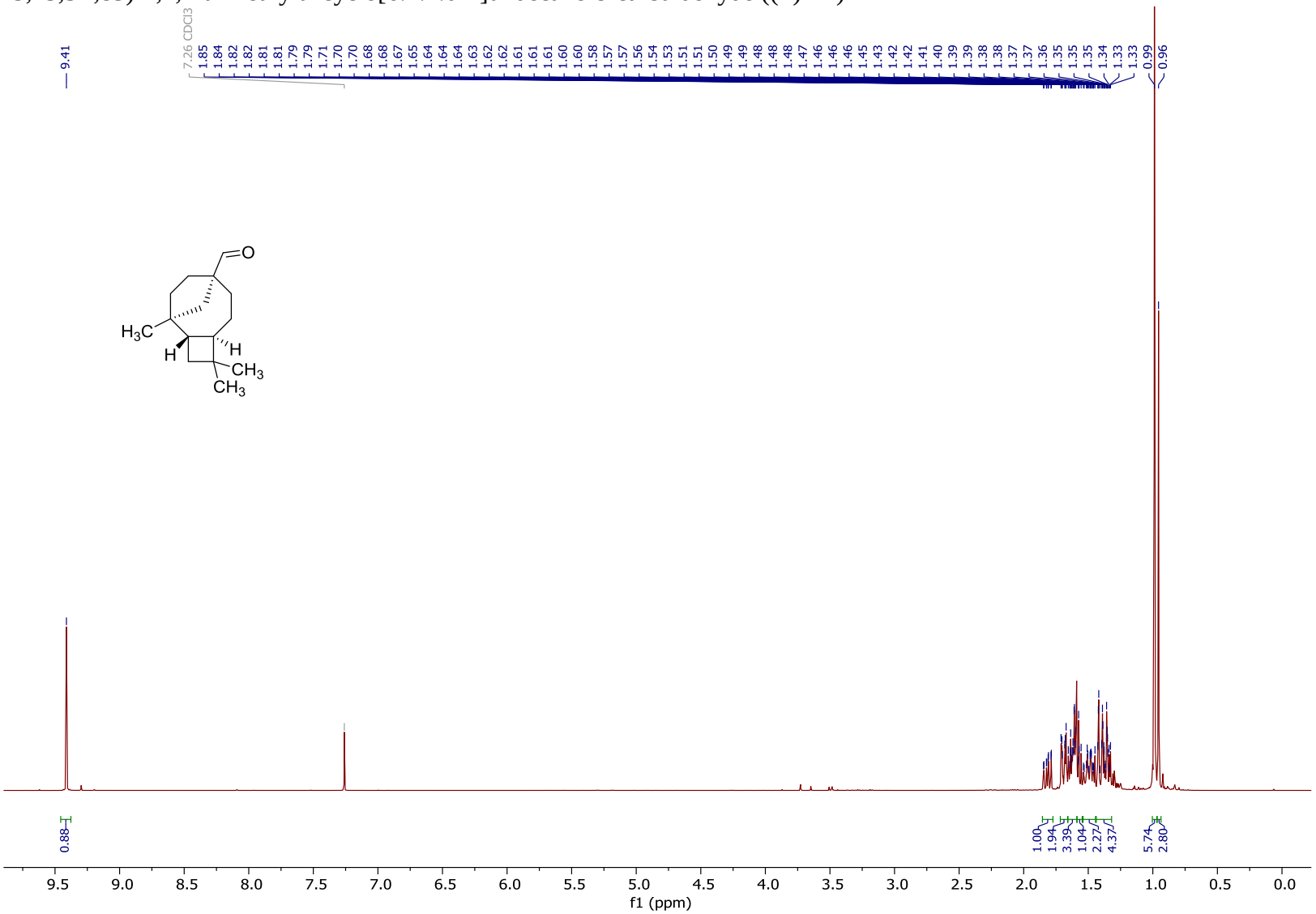


HMBC of (1*S*,5*R*,9*R*)-10,10-dimethyl-2,6-dimethylenebicyclo[7.2.0]undecan-5-ol ((+)-**13**)

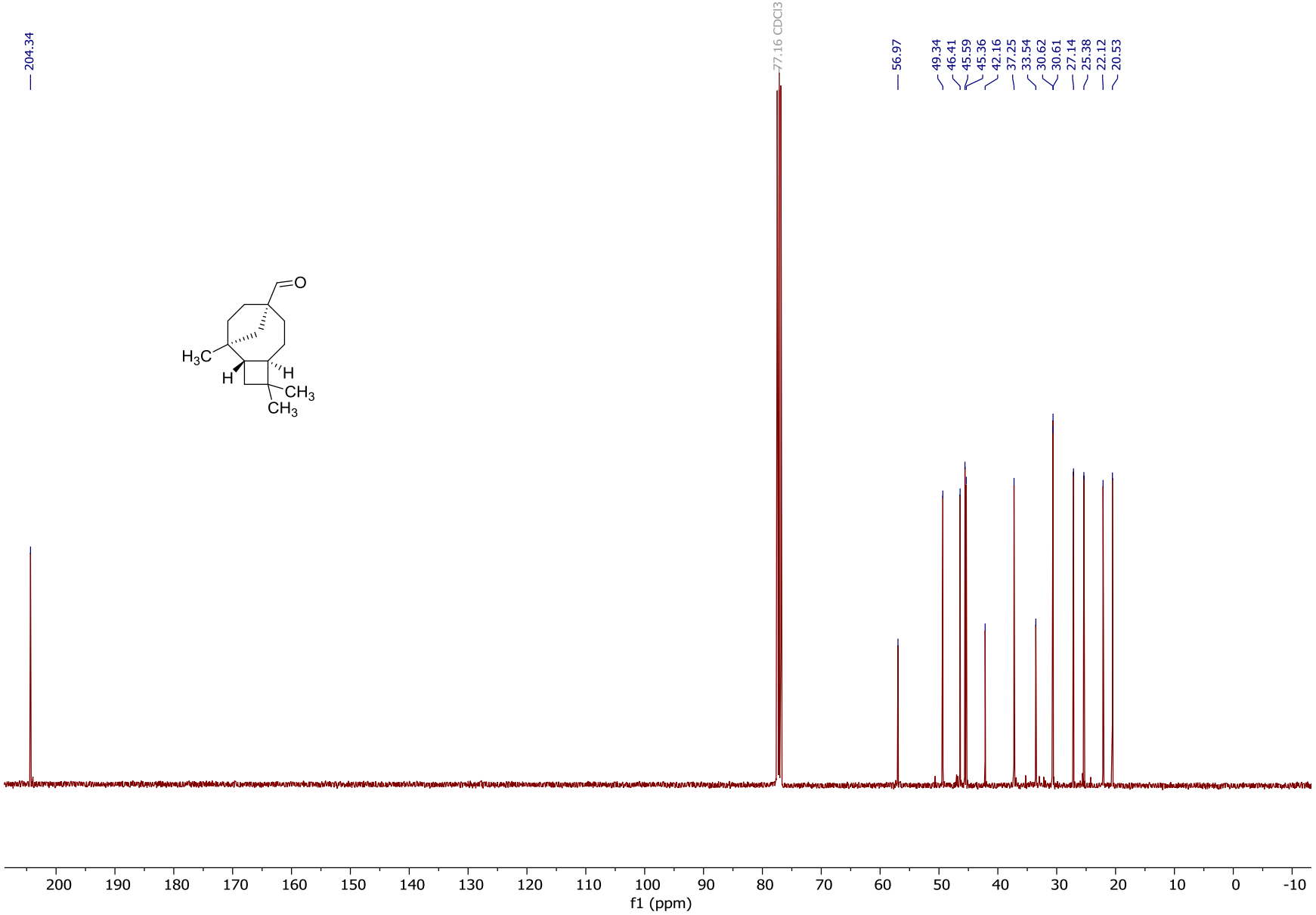


S4. NMR of compound (+)-**14**

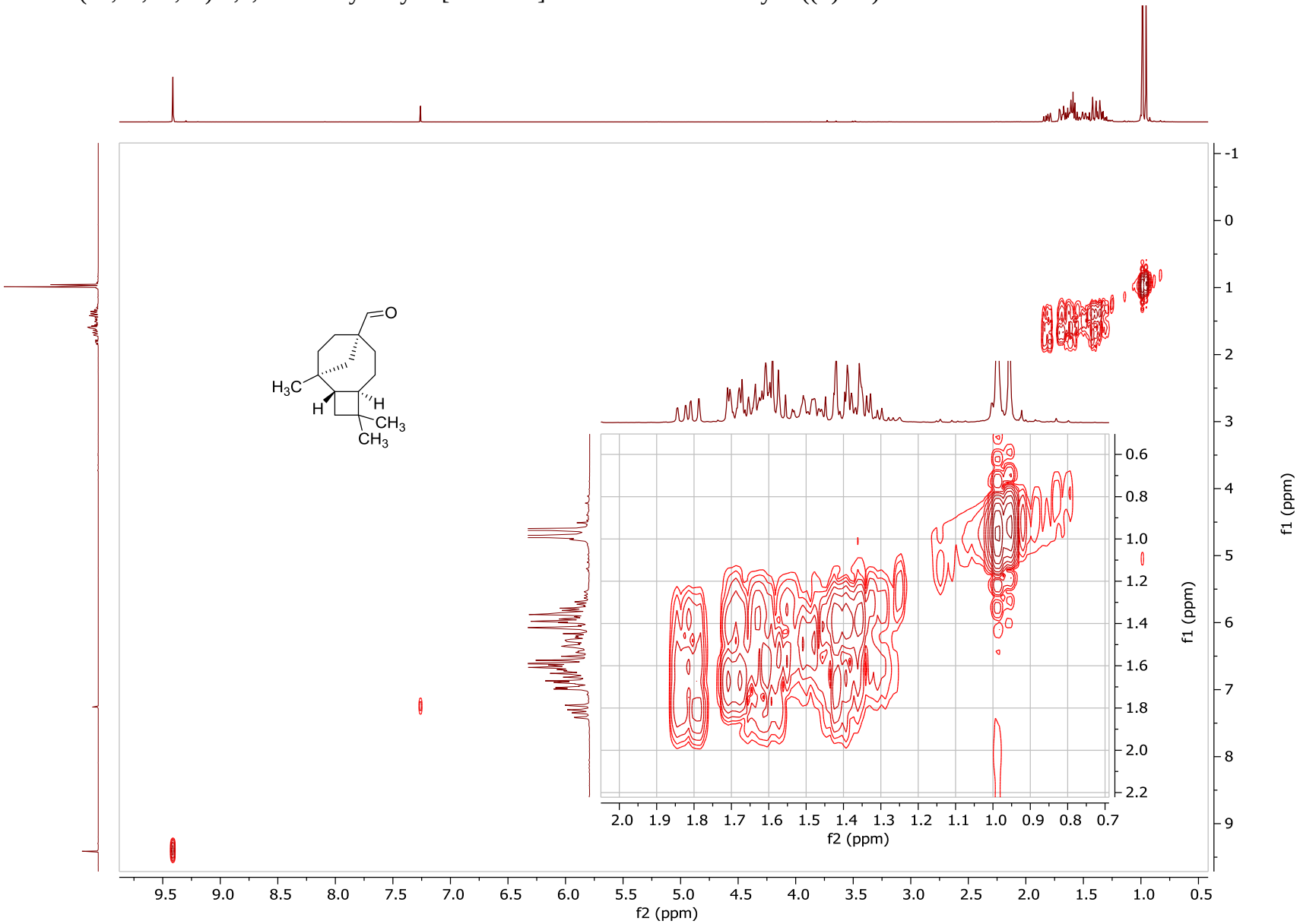
^{1}H NMR of (1*S*,2*S*,5*R*,8*S*)-1,4,4-trimethyltricyclo[6.2.1.0^{2,5}]undecane-8-carbaldehyde ((+)-**14**)



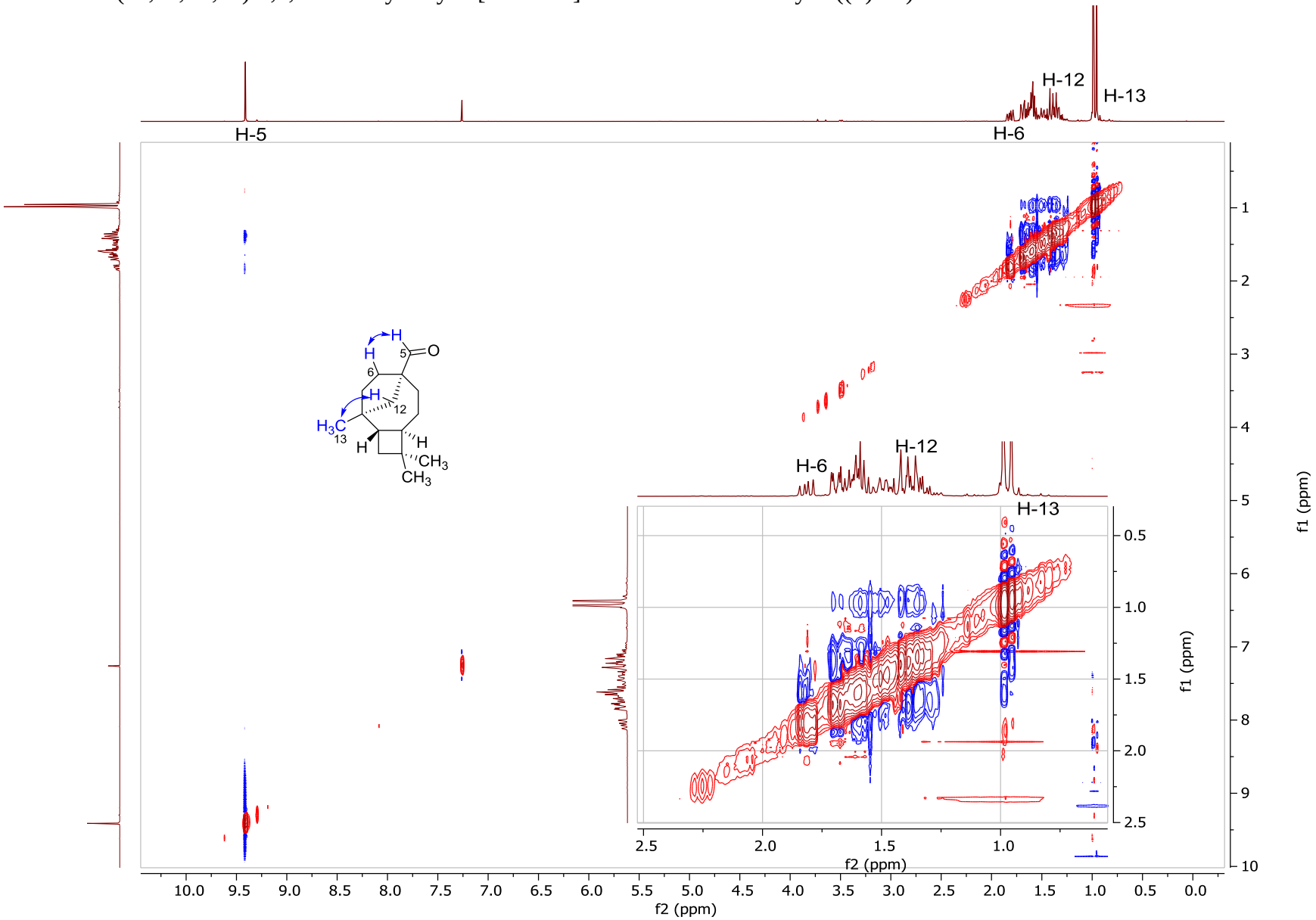
^{13}C NMR of (1*S*,2*S*,5*R*,8*S*)-1,4,4-trimethyltricyclo[6.2.1.0^{2,5}]undecane-8-carbaldehyde ((+)-**14**)



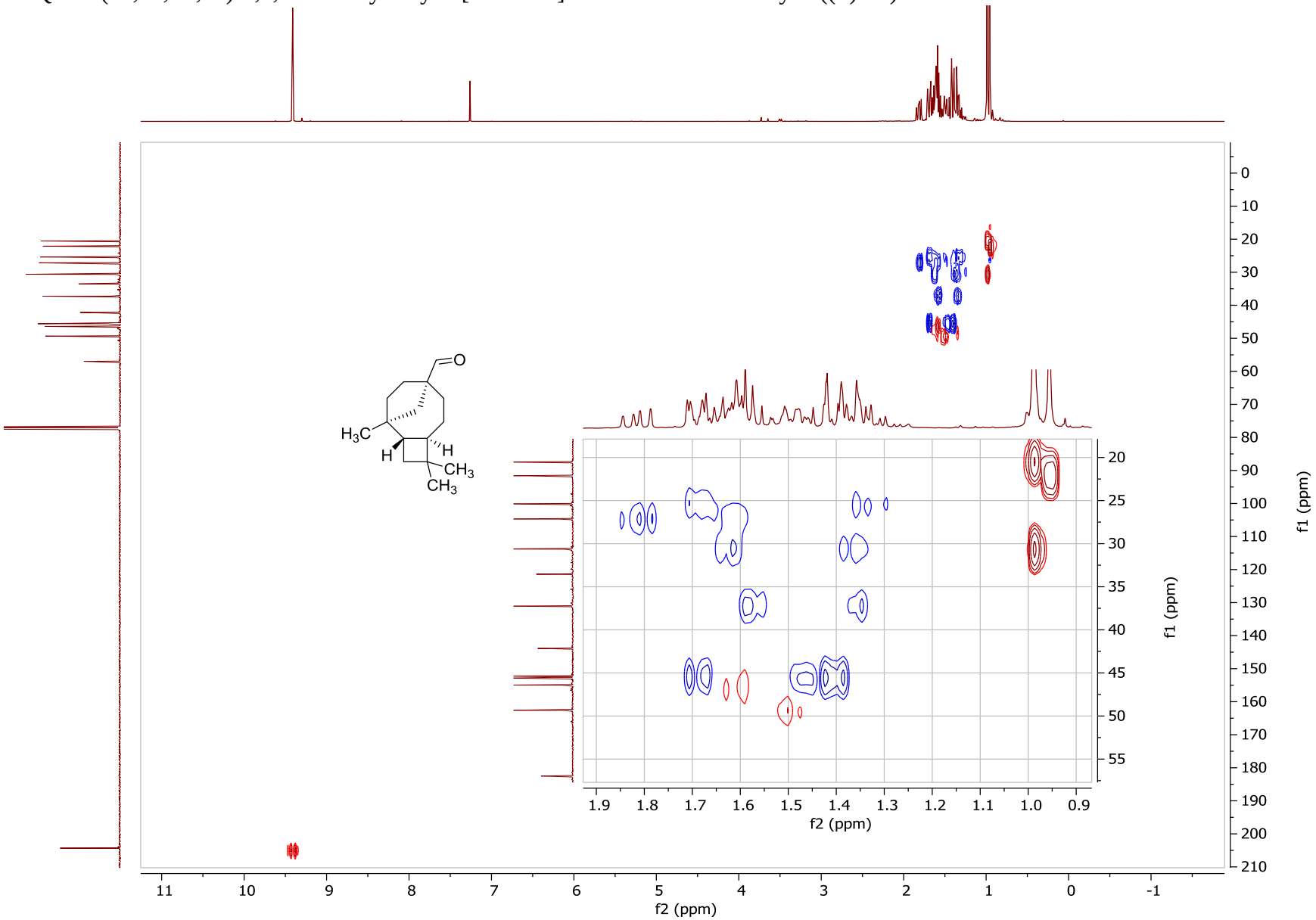
COSY of (1*S*,2*S*,5*R*,8*S*)-1,4,4-trimethyltricyclo[6.2.1.$0^{2,5}$]undecane-8-carbaldehyde ((+)-**14**)



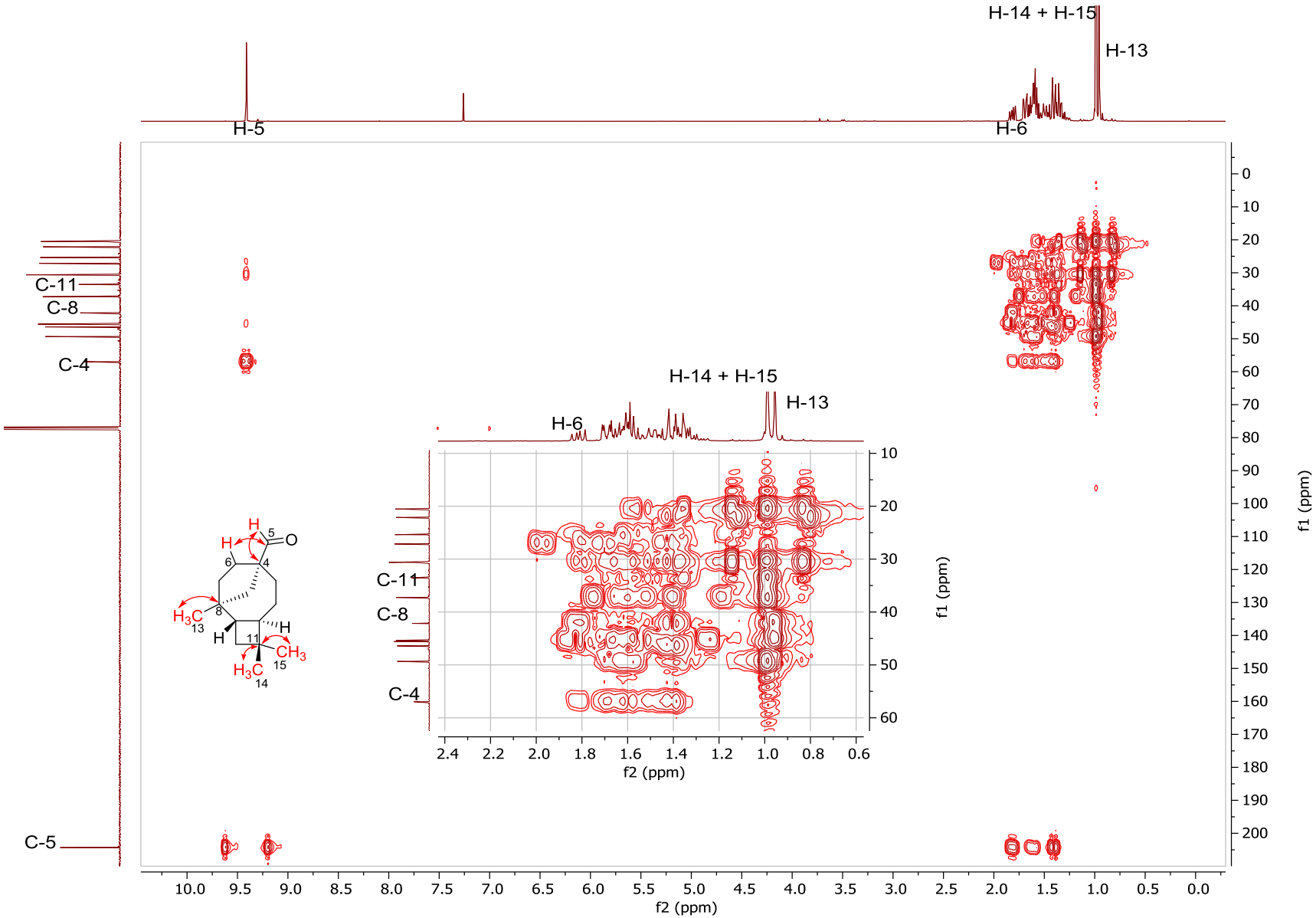
NOESY of (1*S*,2*S*,5*R*,8*S*)-1,4,4-trimethyltricyclo[6.2.1.0^{2,5}]undecane-8-carbaldehyde ((+)-**14**)



HSQC of (1*S*,2*S*,5*R*,8*S*)-1,4,4-trimethyltricyclo[6.2.1.0^{2,5}]undecane-8-carbaldehyde ((+)-**14**)

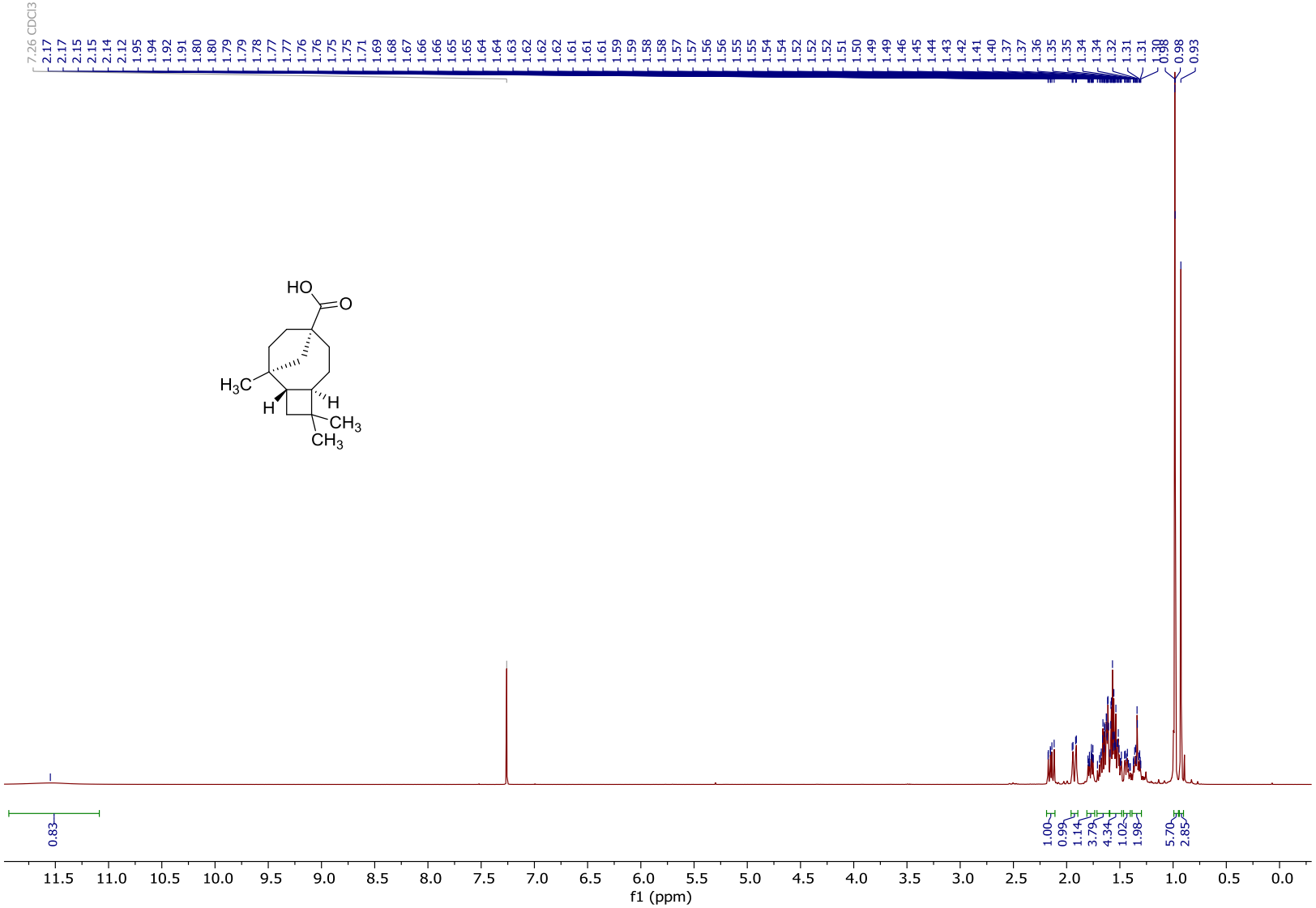


HMBC of (1*S*,2*S*,5*R*,8*S*)-1,4,4-trimethyltricyclo[6.2.1.0^{2,5}]undecane-8-carbaldehyde ((+)-**14**)

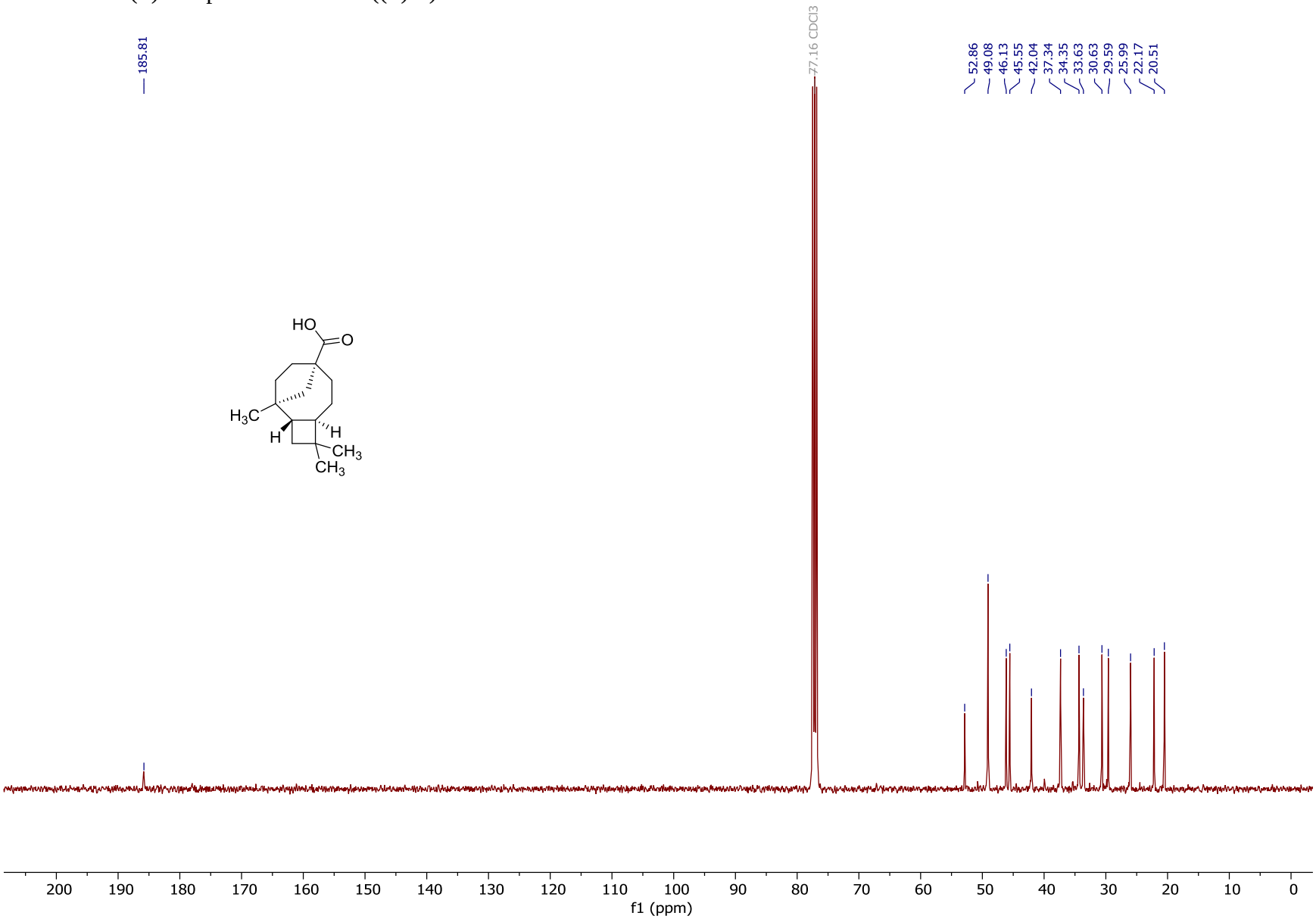


S5. NMR of (+)-rumphellaoic acid A ((+)-**5**)

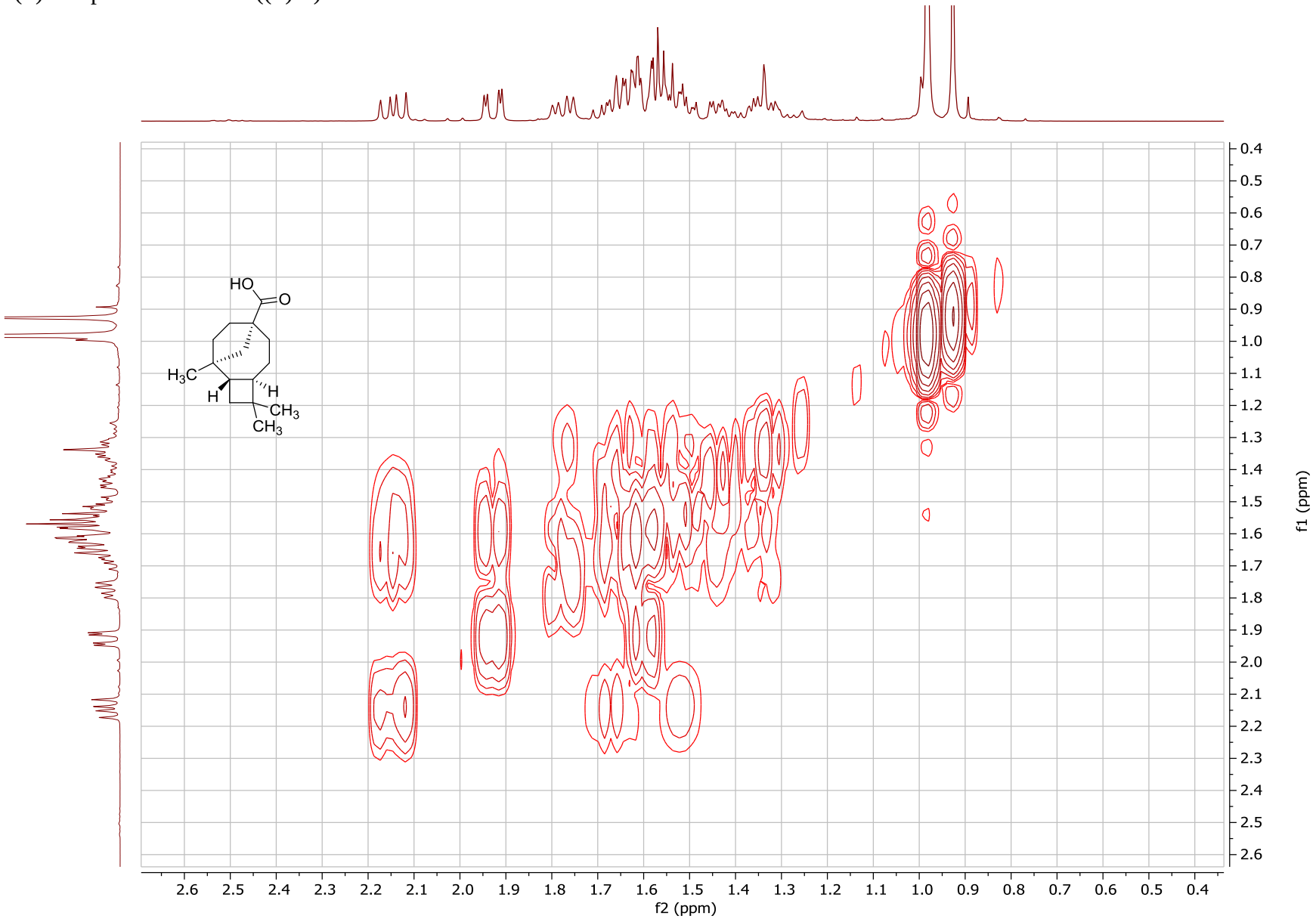
^{1}H NMR of (+)-rumphellaoic acid A ((+)-**5**)



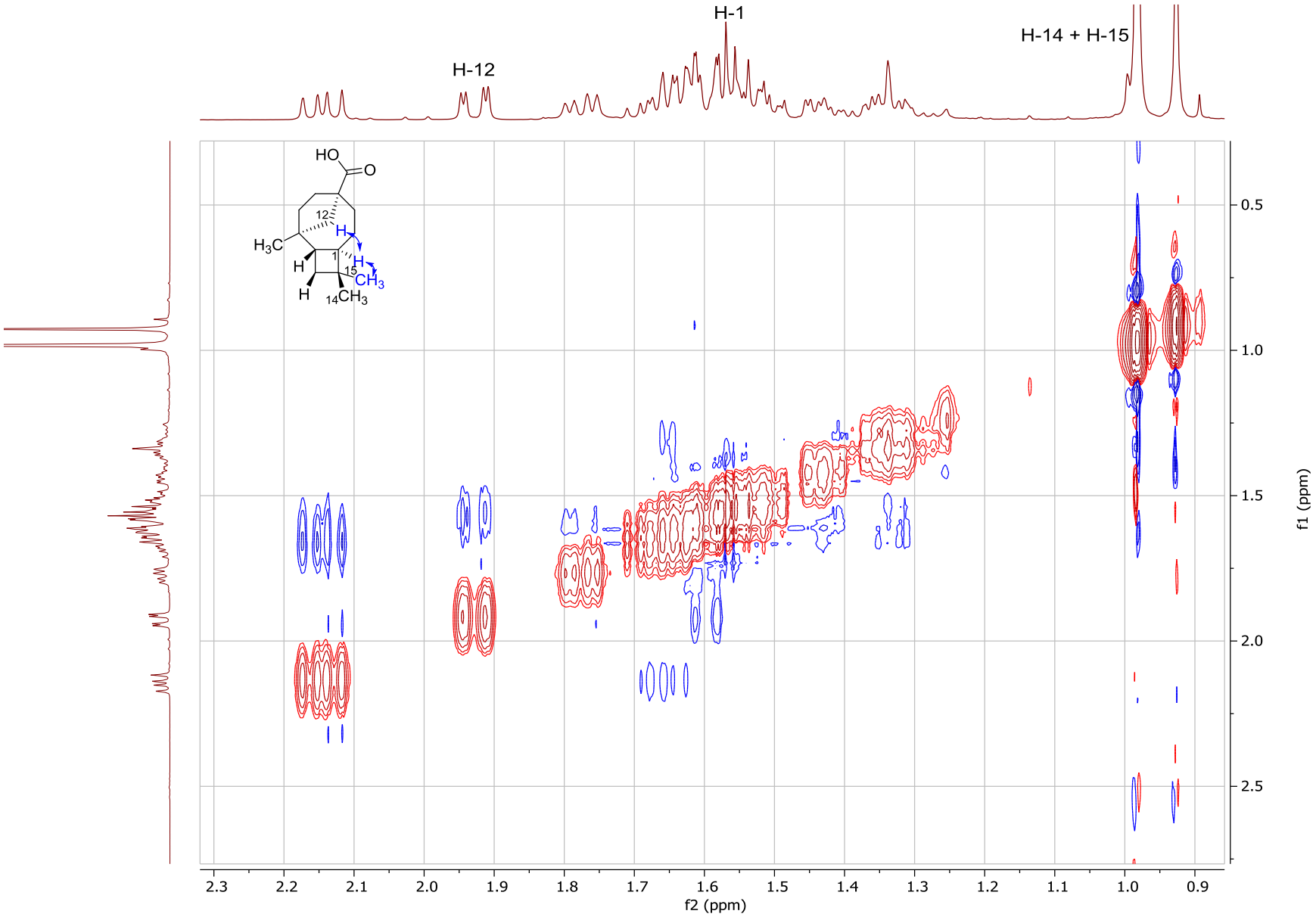
^{13}C NMR of (+)-rumphellaoic acid A ((+)-**5**)



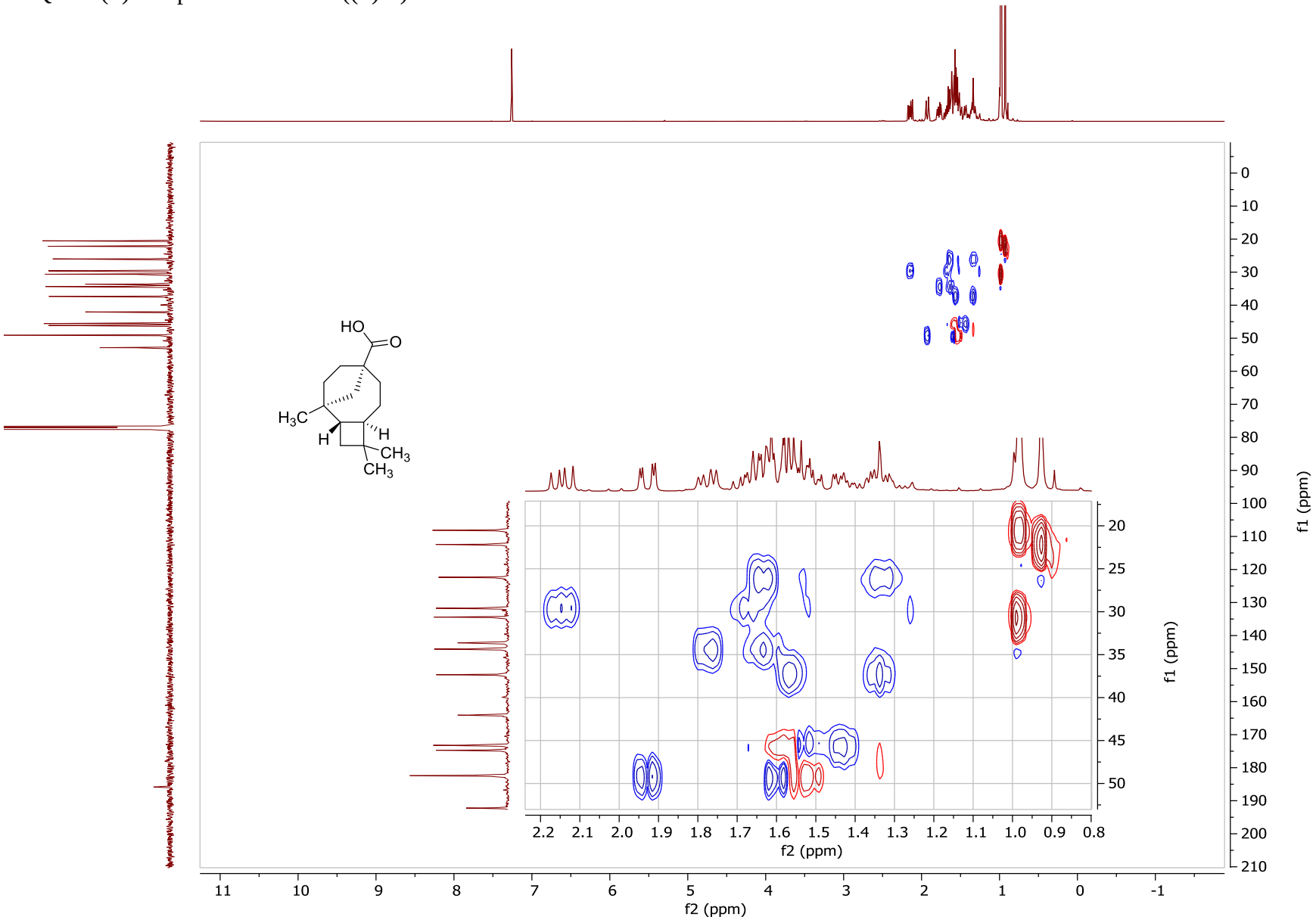
COSY of (+)-rumphellaoic acid A ((+)-**5**)



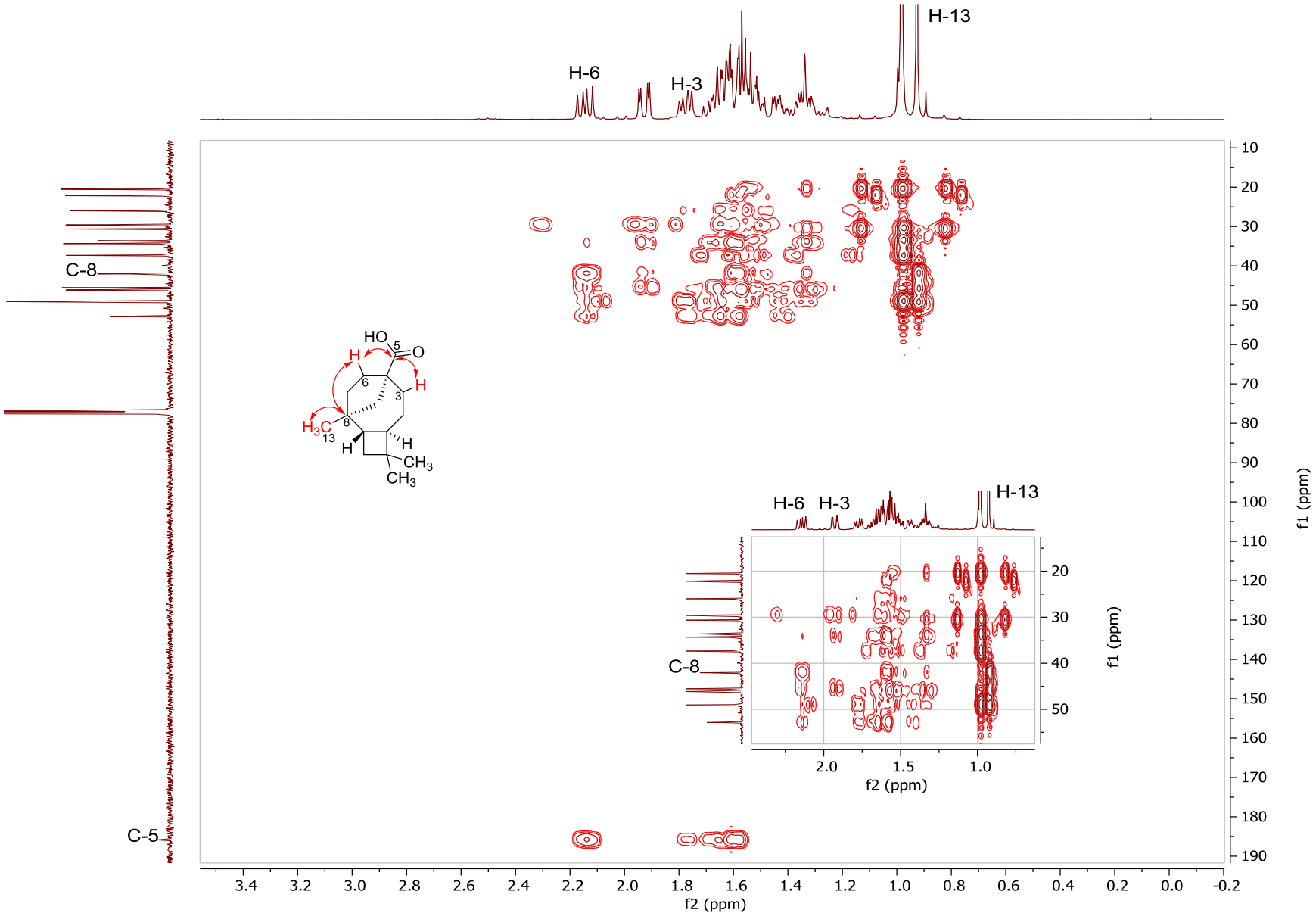
NOESY of (+)-rumphellaoic acid A ((+)-**5**)



HSQC of (+)-rumphellaoic acid A ((+)-**5**)

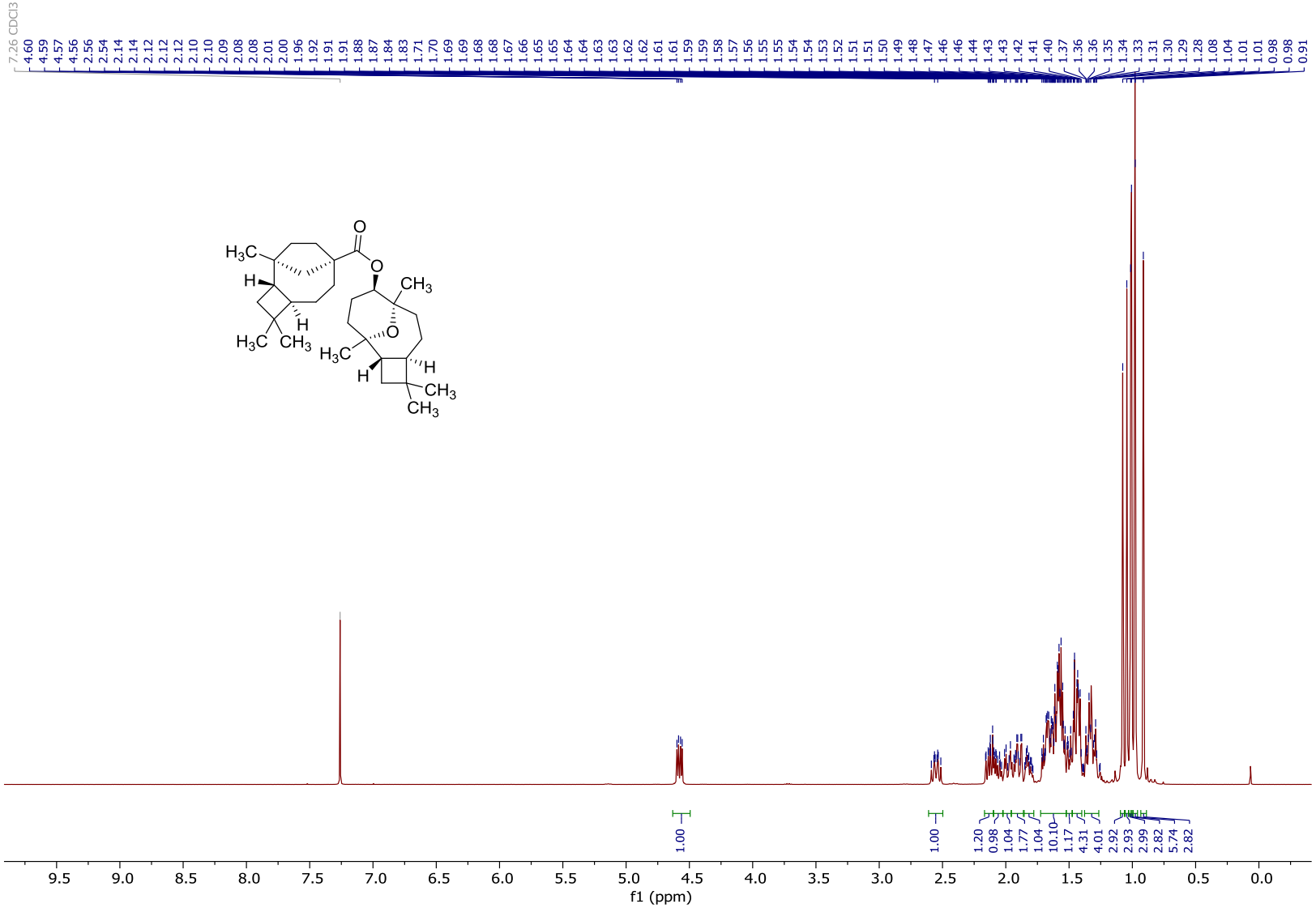


HMBC of (+)-rumphellaoic acid A ((+)-**5**)

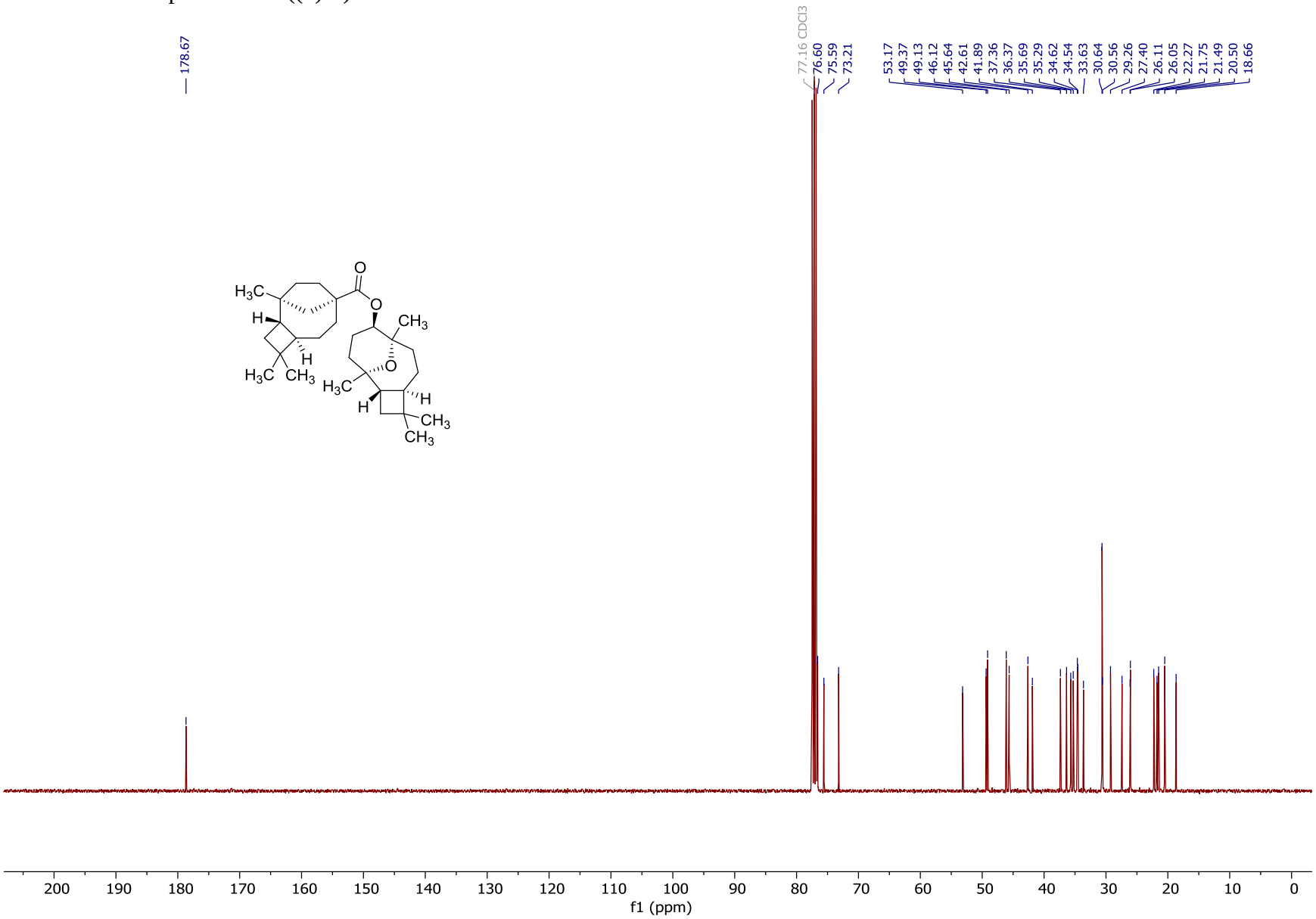


S6. NMR of rumphellolide J ((–)-**7**)

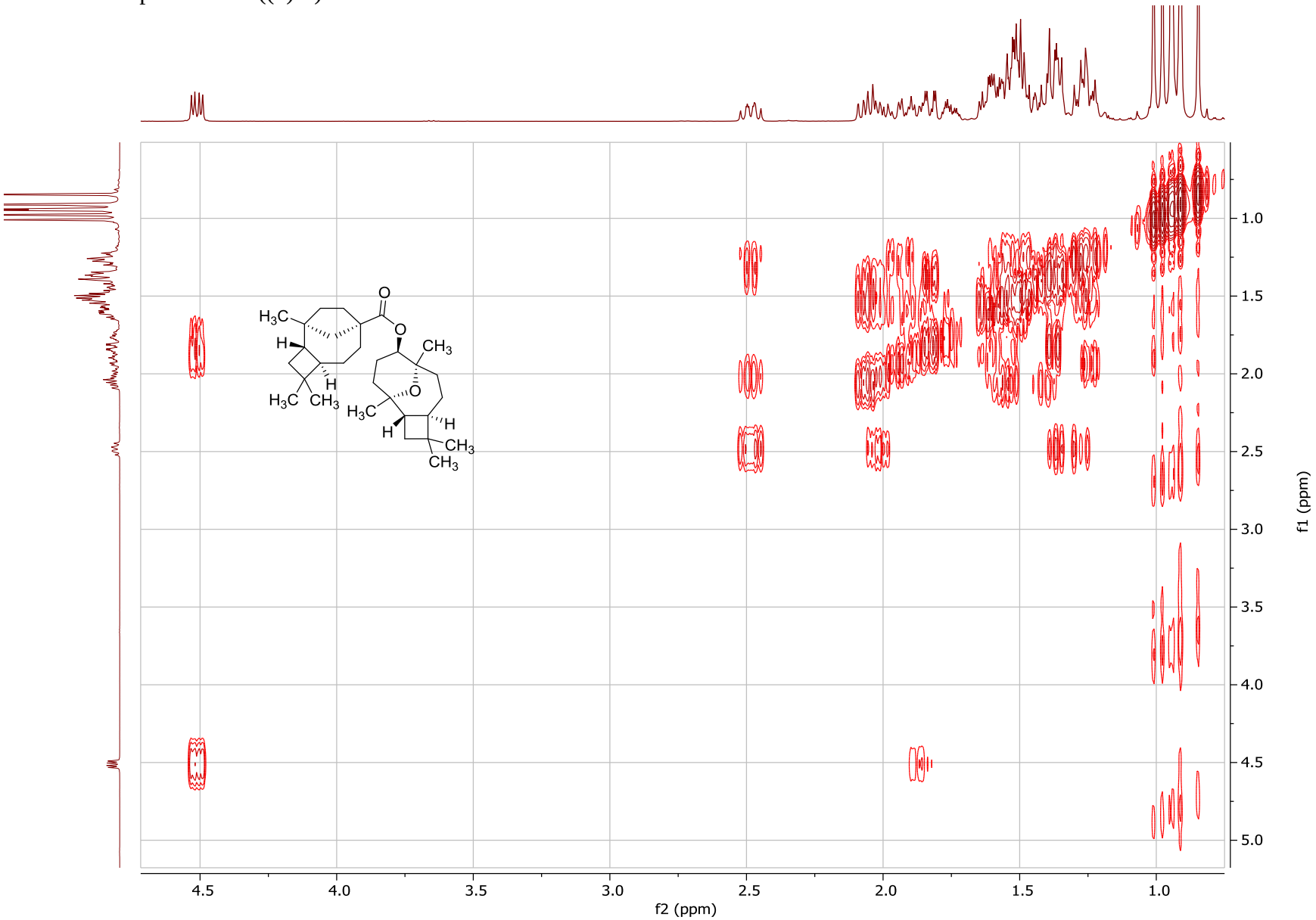
^{1}H NMR of rumphellolide J ((–)-**7**)



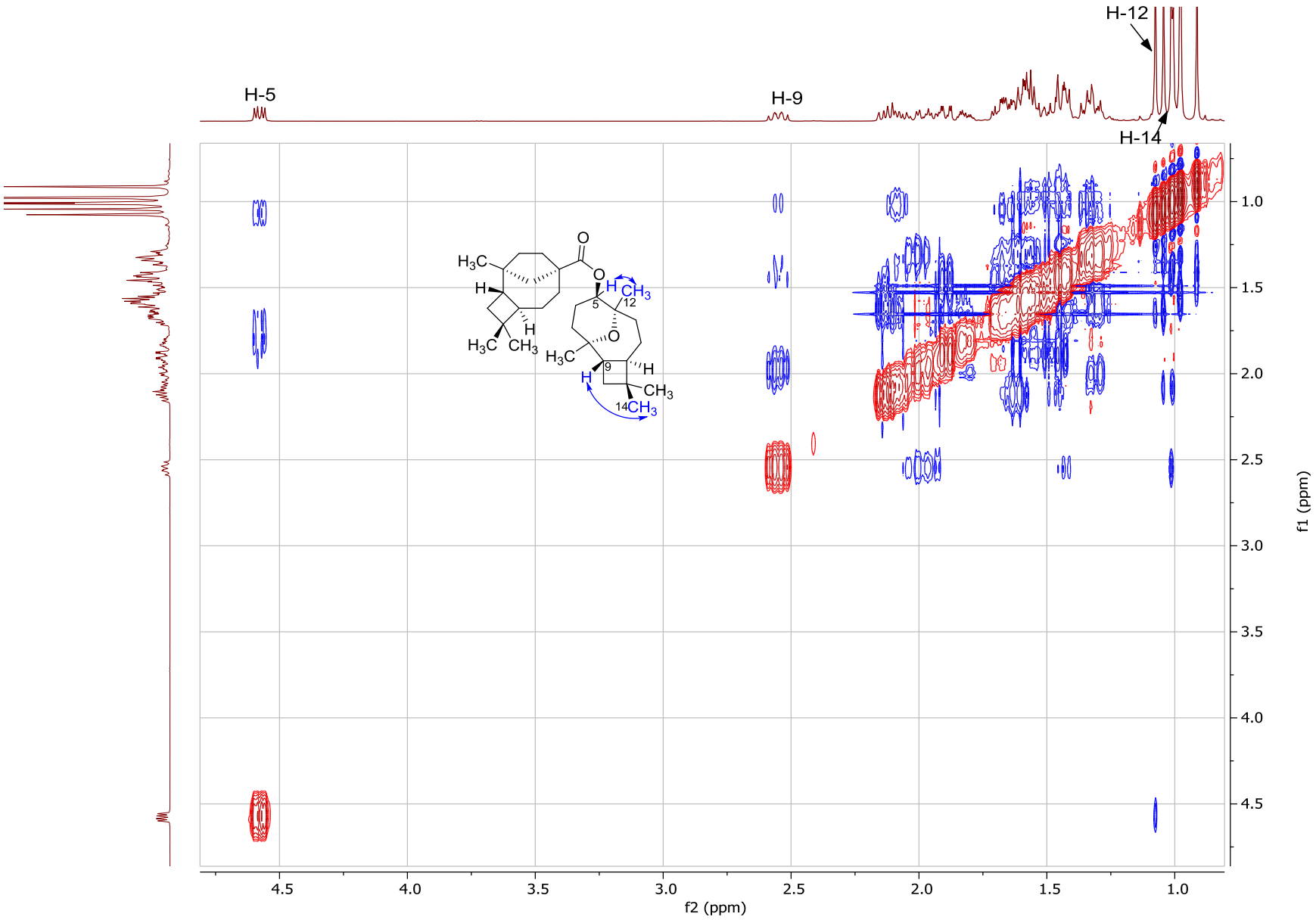
^{13}C NMR of rumphellolide J ((–)-**7**)



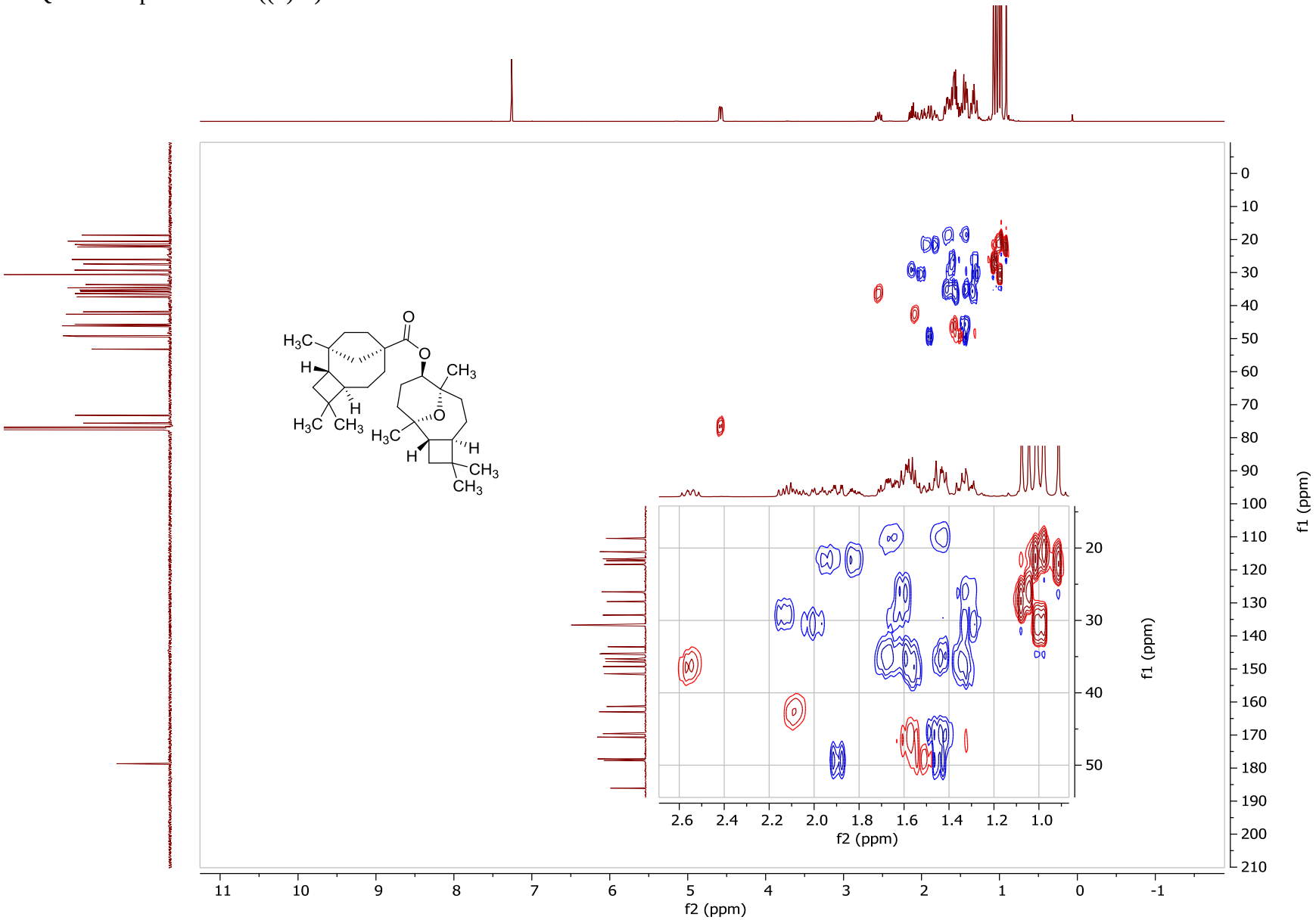
COSY of rumphellolide J ((–)-**7**)



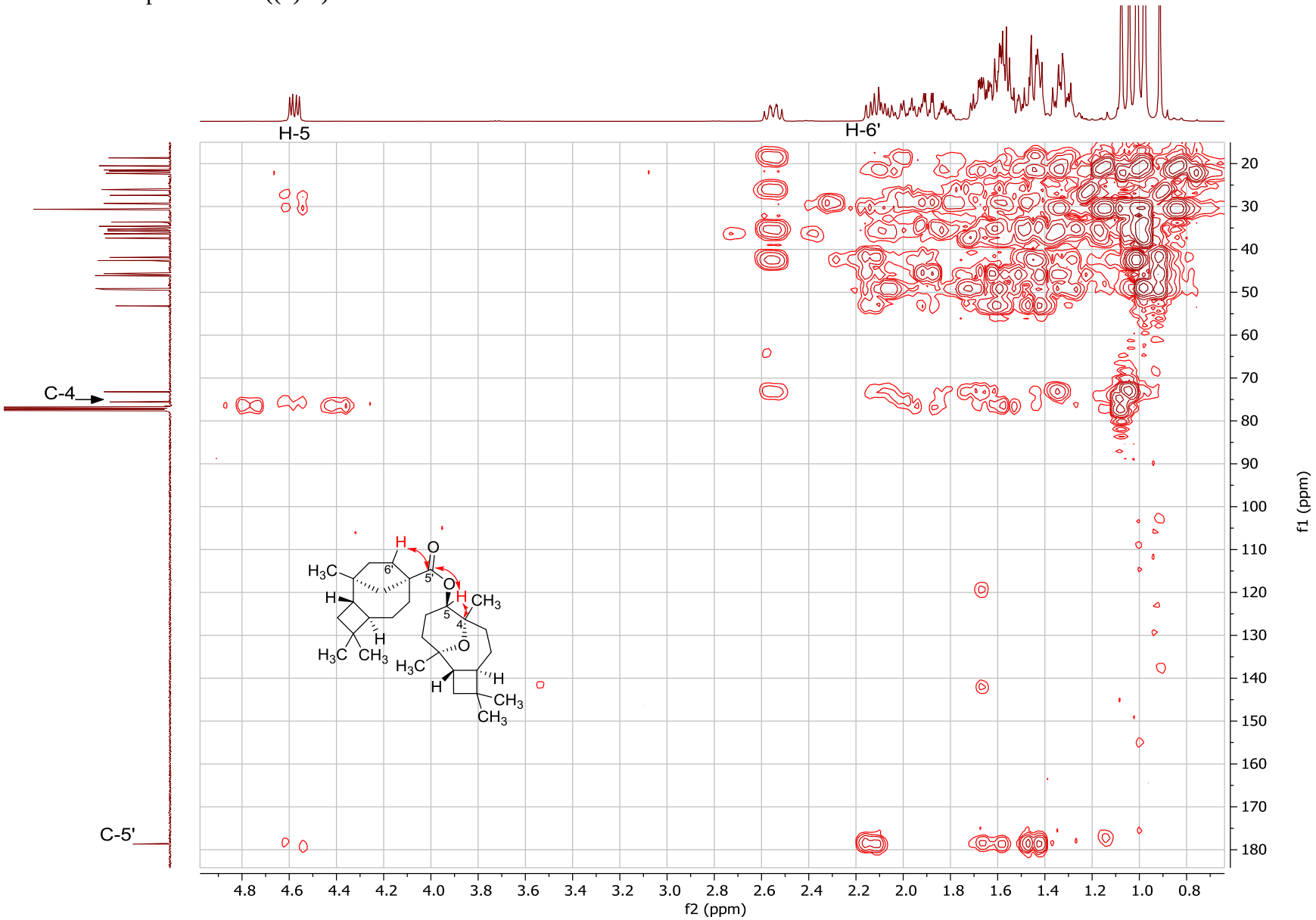
NOESY of rumphellolide J ((–)-**7**)



HSQC of rumphellolide J ((–)-**7**)

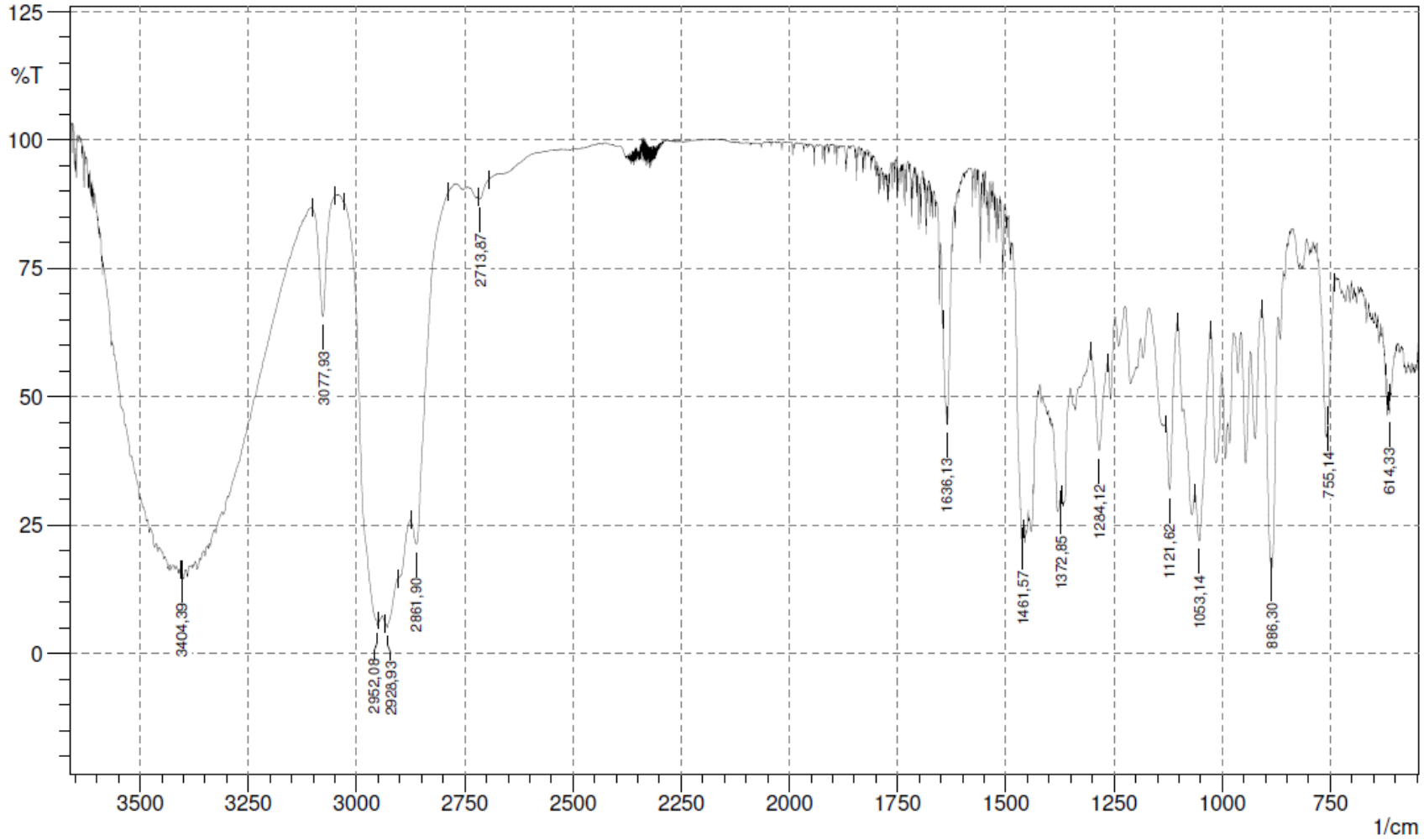


HMBC of rumphellolide J ((–)-**7**)

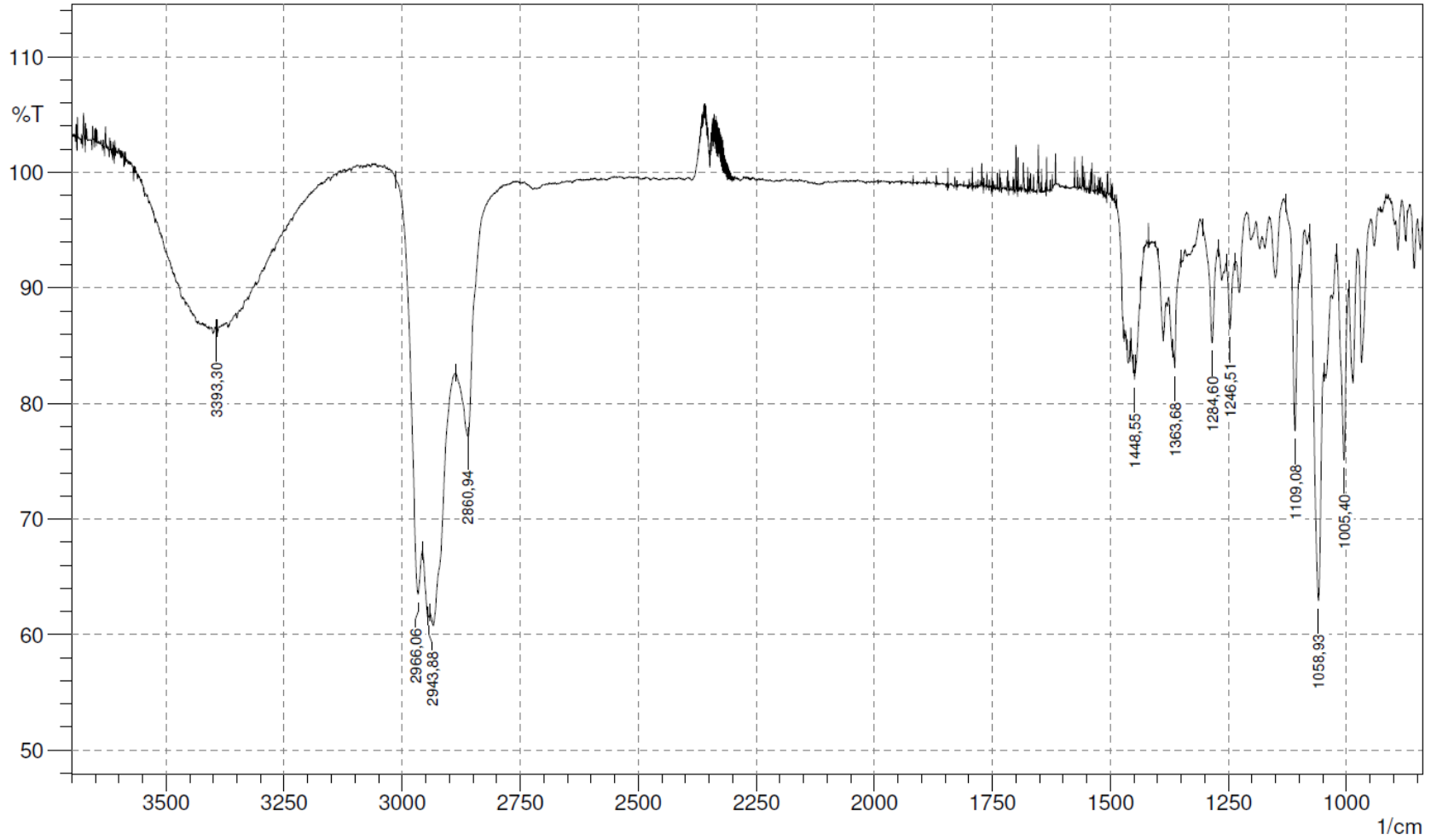


IR spectra

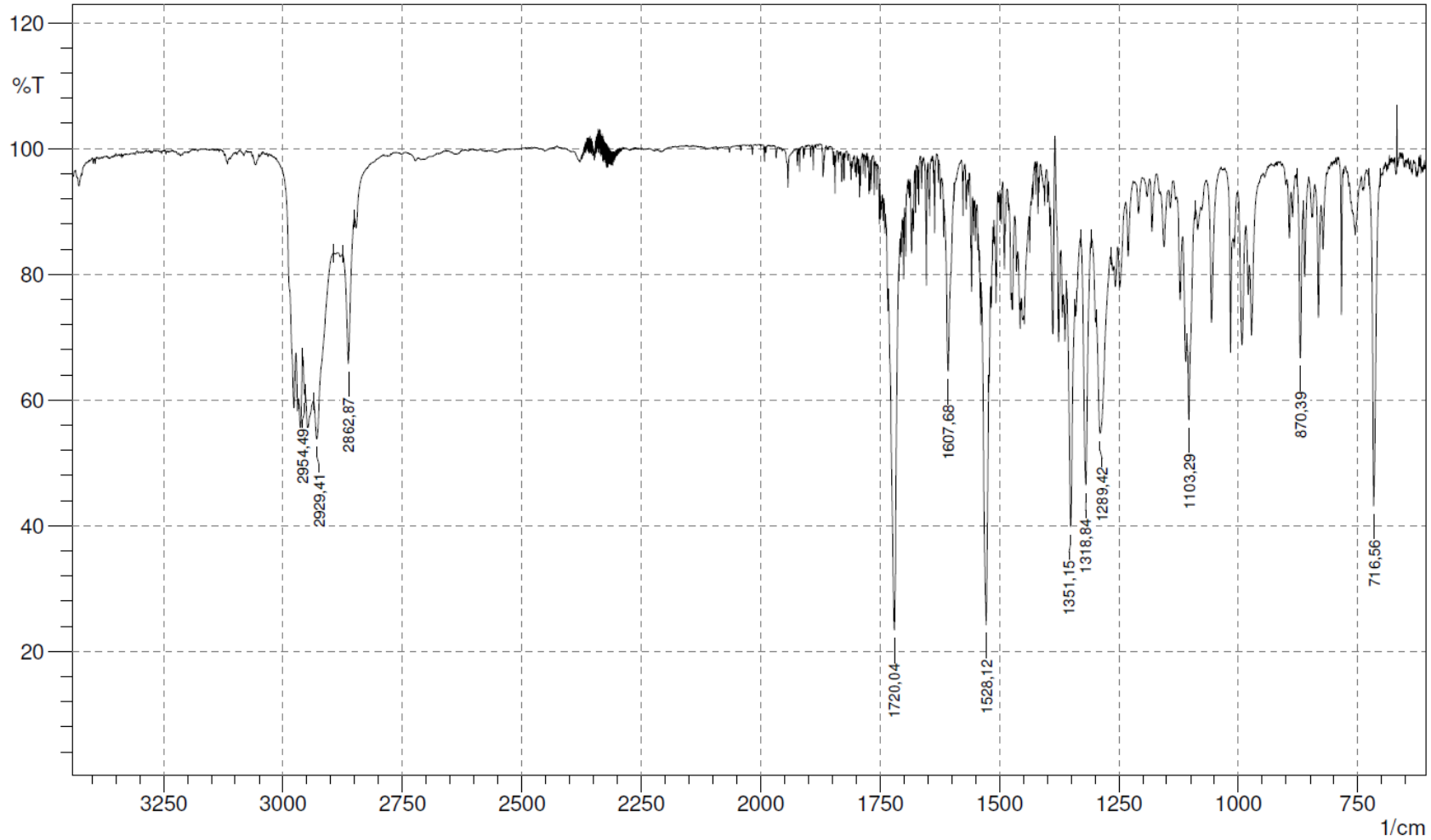
IR (thin film) of compound (–)-**11**



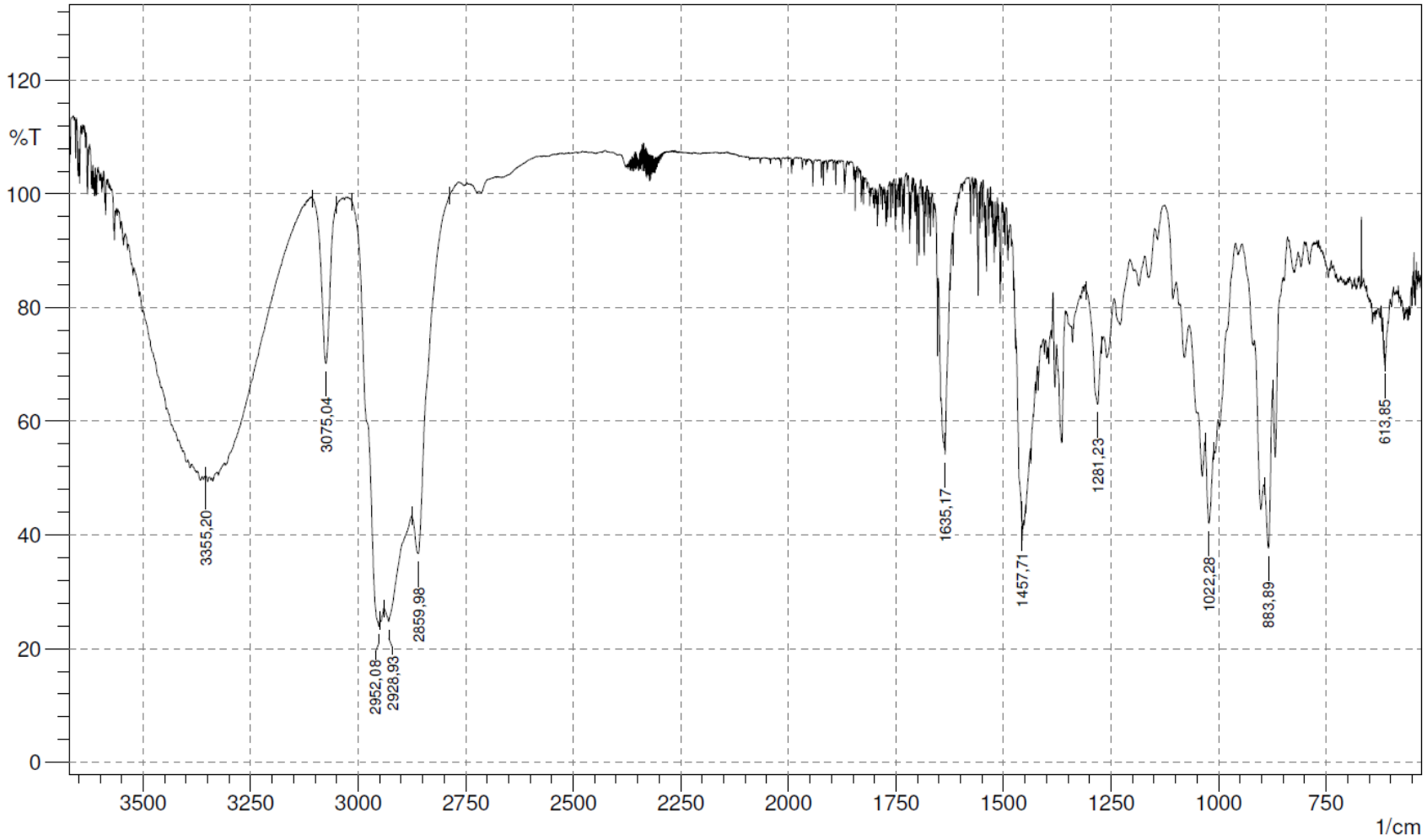
IR (thin film) of 4β,8β-epoxycaryophyllan-5-ol ((–)-**6**)



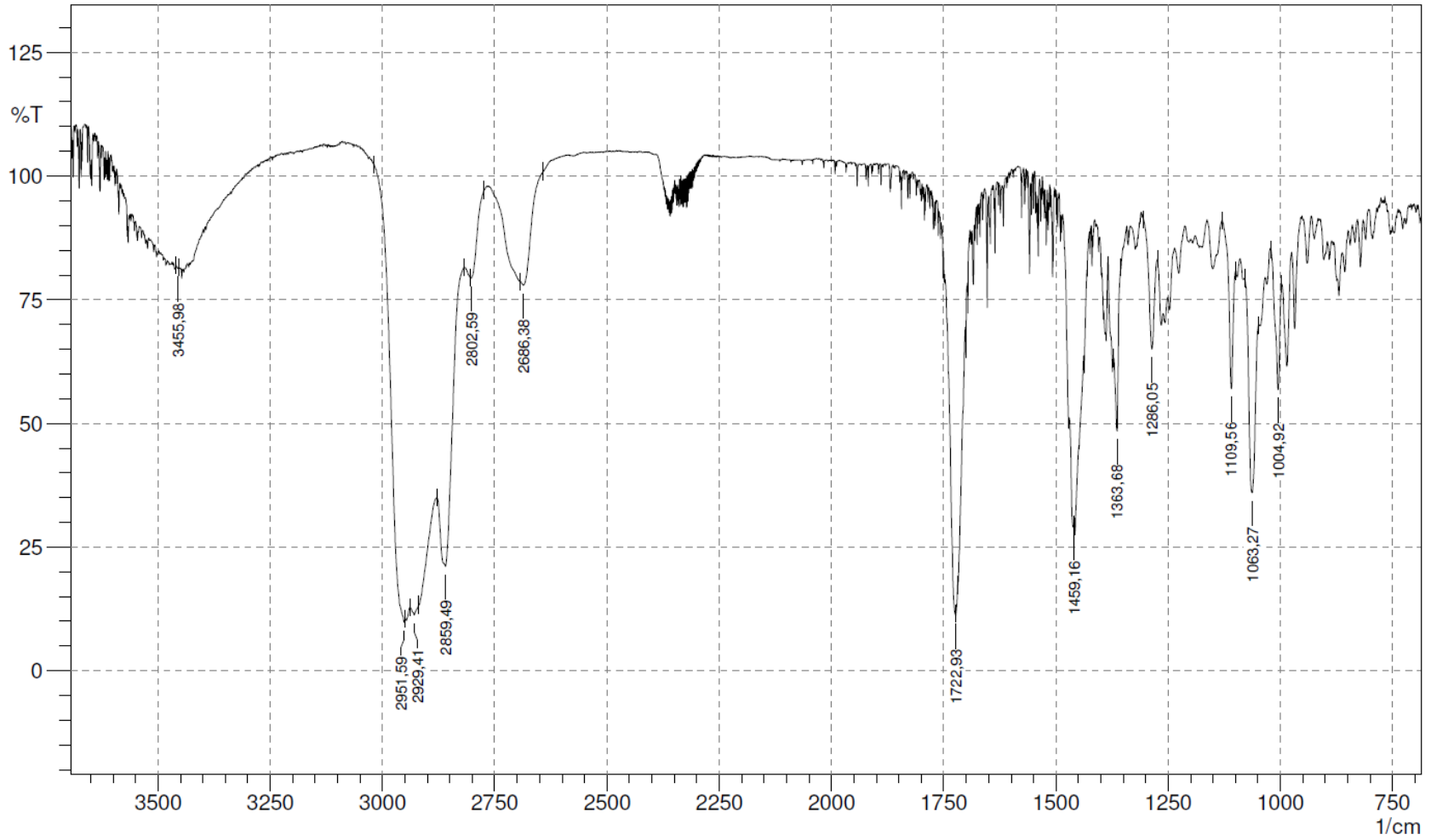
IR (thin film) of compound (–)-**12**



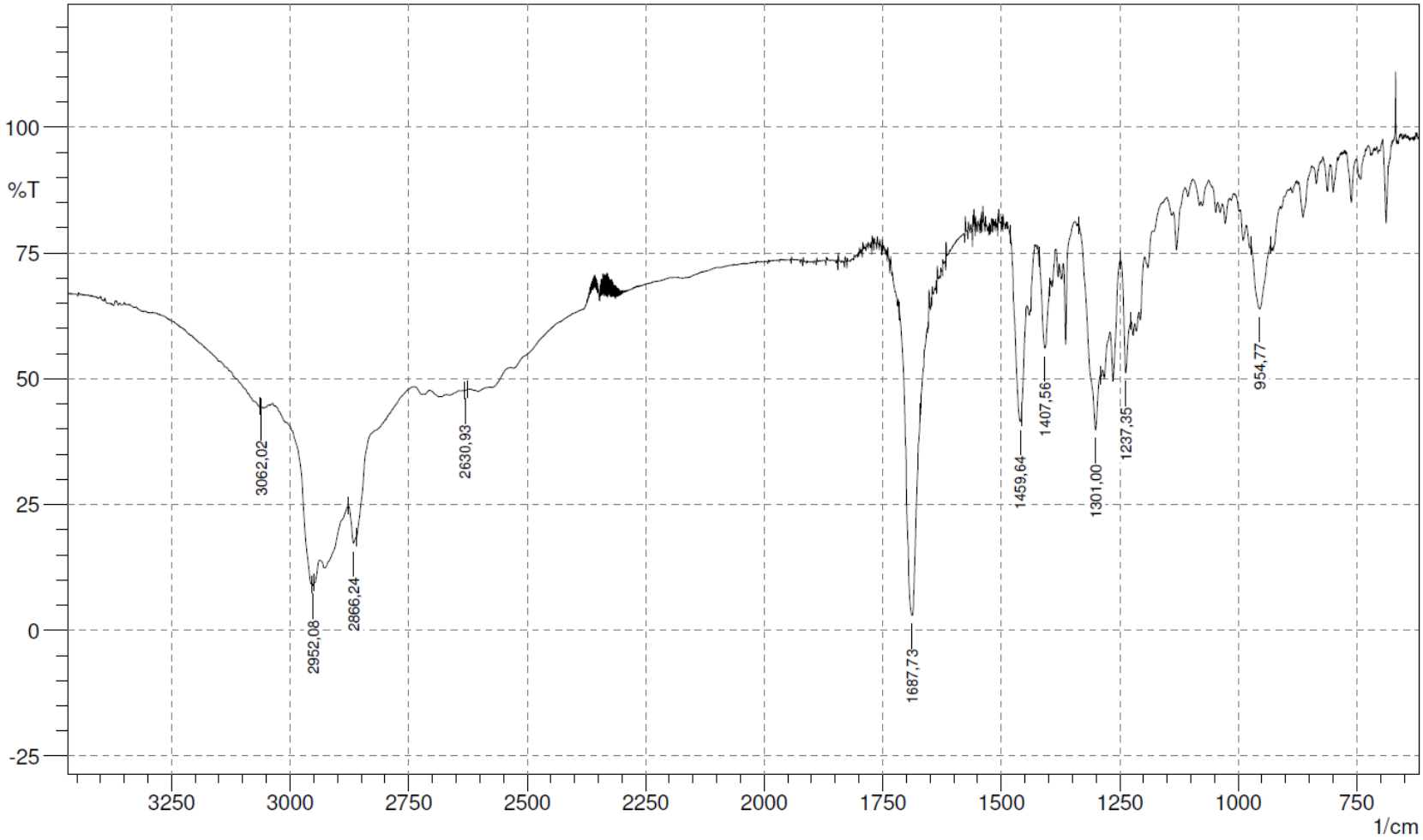
IR (thin film) of compound (+)-**13**



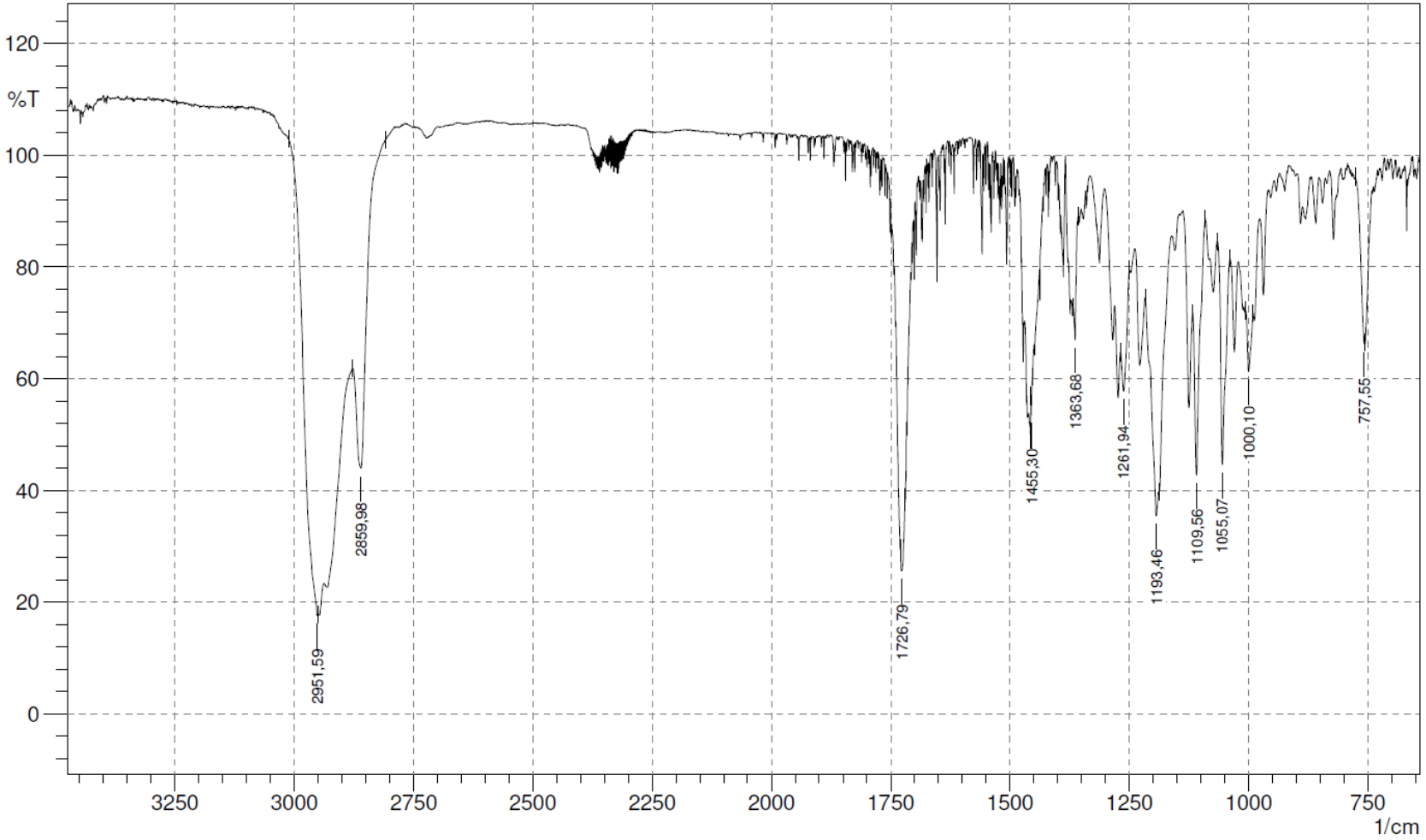
IR (thin film) of compound (+)-**14**



IR (thin film) of (+)-rumphellaoic acid A ((+)-**5**)



IR (thin film) of rumphellolide J ((–)-**7**)



X-Ray crystallographic supplementary data for compound (–)-12

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 (–)-12

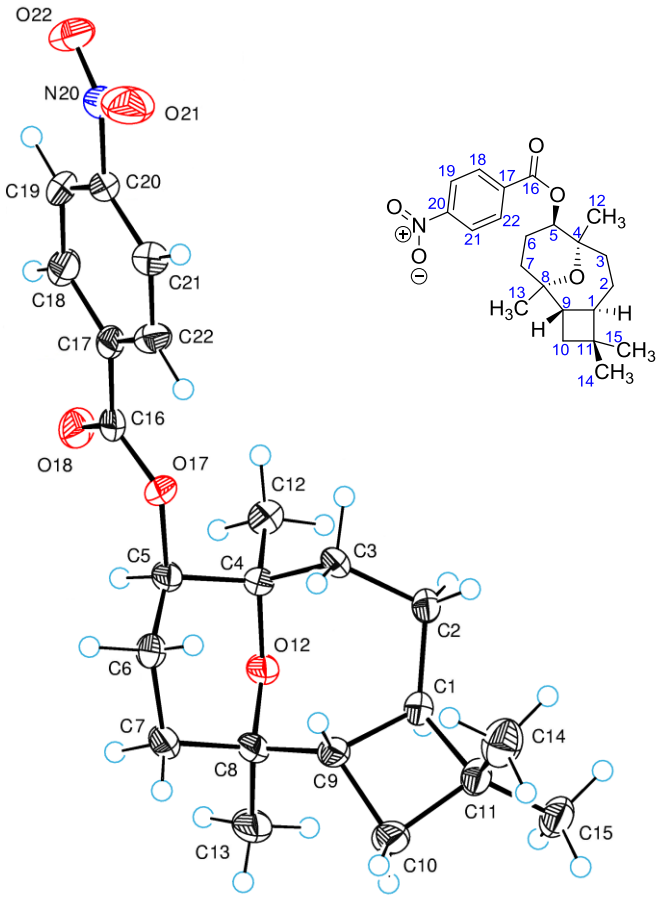


Fig S1. The asymmetric unit of the compound (–)-**12** drawn with displacement ellipsoids at the 50% probability level

Crystal data and structure refinement

Empirical formula	$C_{22}H_{29}NO_5$
Formula weight	387.46
Temperature/K	150.0(1)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.9706(8)
b/Å	8.0539(8)
c/Å	42.817(5)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2058.9(4)
Z	4
ρ_{calc}g/cm^3	1.250
μ/mm^{-1}	0.717
F(000)	832.0
Crystal size/mm^3	0.22 × 0.04 × 0.01
Radiation	CuKα (λ = 1.54184)
2Θ min. for data collection/°	8.3
2Θ max. for data collection/°	156.0
Index ranges	$-7 \leq h \leq 7$, $-10 \leq k \leq 5$, $-53 \leq l \leq 52$
Reflections collected	10856
Independent reflections	4065 [R_{int} = 0.0853, R_{sigma} = 0.0756]
Data/restraints/parameters	4065/0/257
Goodness-of-fit on F^2	1.051
Final *R* indexes [$I > 2\sigma(I)$]	R_1 = 0.0789, wR_2 = 0.1769
Final *R* indexes [all data]	R_1 = 0.0980, wR_2 = 0.1965
Largest diff. peak/hole / e Å^{-3}	0.30/-0.38
Flack′s *x* parameter	0.03(4)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2127464 and is available free of charge.

X-Ray crystallographic supplementary data for (+)-rumphellaoic acid A ((+)-5)

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).

(+)-Rumphellaoic acid A ((+)-5)

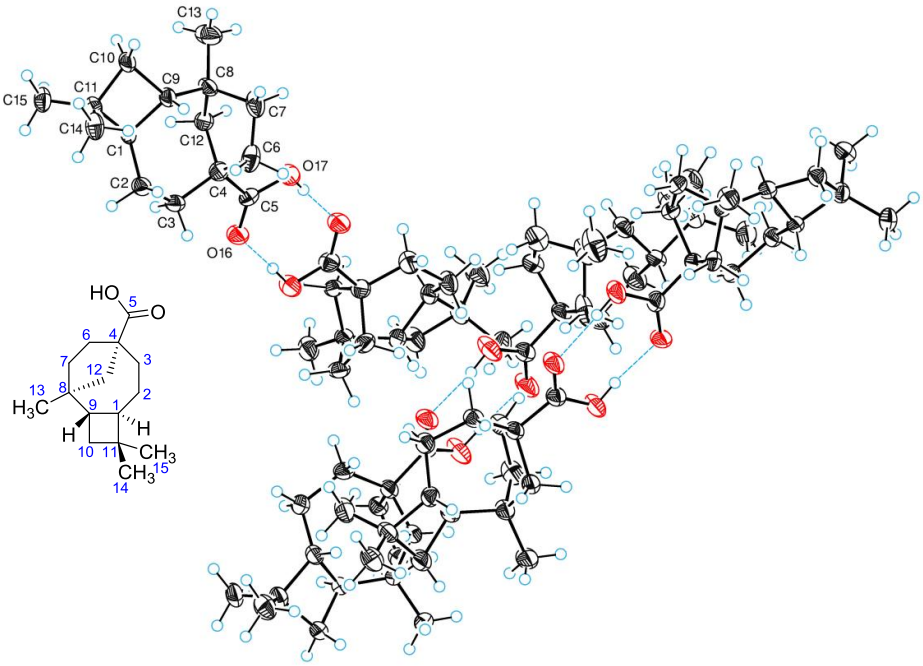


Fig S2. The asymmetric unit of the compound (+)-**5** drawn with displacement ellipsoids at the 50% probability level. The unit consists of 6 independent molecules (forming 3 hydrogen-bonded dimers), all of them being one and the same stereoisomer

Crystal data and structure refinement

Empirical formula	$C_{90}H_{144}O_{12}$
Formula weight	1418.14
Temperature/K	150.0(1)
Crystal system	triclinic
Space group	*P*1
a/Å	9.17564(16)
b/Å	15.1486(3)
c/Å	16.0961(4)
α/°	102.879(2)
β/°	100.4135(17)
γ/°	102.0461(16)
Volume/Å^3	2071.53(8)
Z	1
ρ_{calc}g/cm^3	1.1367
μ/mm^{-1}	0.571
F(000)	782.3
Crystal size/mm^3	0.21 × 0.02 × 0.01
Radiation	Cu Kα (λ = 1.54184)
2Θ min. for data collection/°	5.8
2Θ max. for data collection/°	155.0
Index ranges	$-11 \leq h \leq 10$, $-19 \leq k \leq 19$, $-20 \leq l \leq 20$
Reflections collected	37044
Independent reflections	11863 [R_{int} = 0.0562, R_{sigma} = 0.0503]
Data/restraints/parameters	11863/3/961
Goodness-of-fit on F^2	1.058
Final *R* indexes [$I > 2\sigma(I)$]	R_1 = 0.0680, wR_2 = 0.1745
Final *R* indexes [all data]	R_1 = 0.0738, wR_2 = 0.1787
Largest diff. peak/hole / e Å^{-3}	0.62/-0.21
Flack′s *x* parameter	0.1(2)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2127465 and is available free of charge.

X-Ray crystallographic supplementary data for rumphellolide J ((–)-7)

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).

(–)-Rumphellolide J ((–)-7)

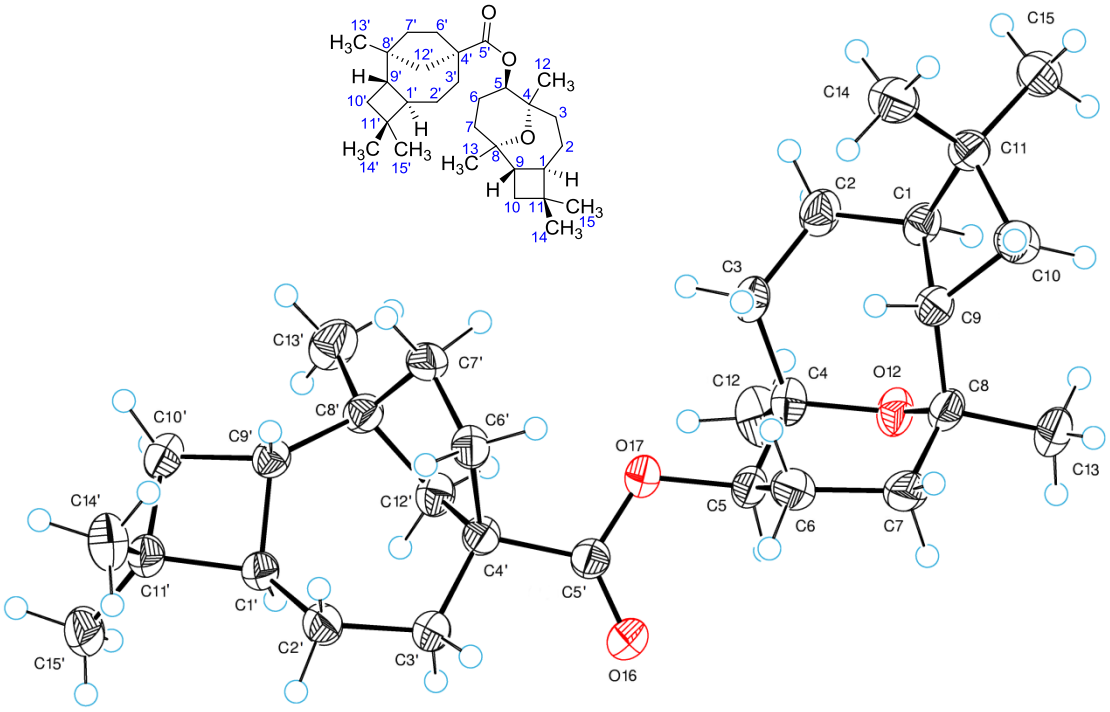


Fig S3. The asymmetric unit of the compound (–)-**7** drawn with displacement ellipsoids at the 50% probability level

Crystal data and structure refinement

Empirical formula	$C_{30}H_{48}O_3$
Formula weight	456.714
Temperature/K	150.0(1)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.14005(15)
b/Å	15.6385(2)
c/Å	10.95867(19)
α/°	90
β/°	99.0409(17)
γ/°	90
Volume/Å^3	1377.69(4)
Z	2
ρ_{calc}g/cm^3	1.101
μ/mm^{-1}	0.529
F(000)	504
Crystal size/mm^3	0.017 × 0.08 × 0.02
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ min. for data collection/°	8.0
2Θ max. for data collection/°	155.0
Index ranges	$-10 \leq h \leq 10$, $-15 \leq k \leq 19$, $-13 \leq l \leq 13$
Reflections collected	14302
Independent reflections	4645[R_{int} = 0.0280, R_{sigma} = 0.0270]
Data/restraints/parameters	4645/1/305
Goodness-of-fit on F^2	1.049
Final *R* indexes [$I > 2\sigma(I)$]	R_1 = 0.0319, wR_2 = 0.0829
Final *R* indexes [all data]	R_1 = 0.0331, wR_2 = 0.0836
Largest diff. peak/hole / e Å^{-3}	0.14/-0.12
Flack′s *x* parameter	0.13(14)

Crystallographic data have been deposited at the Cambridge Crystallographic Data Center with the deposition number 2127466 and is available free of charge.