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1. Isolation and identification of novel coffee diterpenoids

The green coffee beans of *Coffea arabica* L. cultivated in Yunnan province were harvested in December 2018. The material was authenticated by Ming-Hua Qiu, Kunming Institute of Botany, Chinese Academy of Sciences. Green coffee beans were roasted to a moderate degree according to the color value by a professional barista. A voucher specimen (18120603) has been deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

The 2.76 kg of PE (petroleum ether) extract was isolated with PE/EtOAc system to obtain ten fractions (Fr.A-Fr.J). Further, Fr. J (100.2 g) was divided into eight fractions (Fr. J-1–Fr. J-8) by silica gel column chromatography by PE/EtOAc (1:0-0:1, v/v) system. Fr. J-5 was then purified by silica gel column chromatography (PE/EtOAc 5:3) to obtain compound **1** (>20 mg). The Fr.H was divided into Fr.H1-Fr.H5 by silica gel column chromatography. Fr.H3 was purified via HPLC (ZORBAX, RX-C8, 5 μ m, 9.4 \times 250 mm, CNCH₃: H₂O= 70:30) to obtain compounds **2** (3.1 mg, t_R =30.5 min) and **3** (3.4 mg, t_R =28.2 min). Fr.H4 was separated by HPLC (ZORBAX, RX-C8, 9.4 \times 250 mm, 5 μ m, CNCH₃: H₂O= 80:20) to afford **4** (5.0 mg, t_R =22.3 min).

Dehydrocaffarolide B (1). white powder, UV (MeOH) λ_{max} (log ϵ): 195.0 (3.91); HRESIMS m/z 353.1733 [M + Na]⁺ (calcd for C₂₀H₂₆O₄Na⁺, 353.1723); ¹H and ¹³C NMR spectroscopic data were shown in Table S1.

Caffarolide L (2). colorless oil, [α]_D²¹ -50.4 (c 0.11, MeOH); UV (MeOH) λ_{max} (log

ϵ): 203.5 (3.94); HRESIMS m/z 601.4435 $[M + H]^+$ (calcd for $C_{37}H_{61}O_6^+$, 601.4463);

1H and ^{13}C NMR spectroscopic data were shown in Table S1.

Mascarolide I (3). colorless oil, $[\alpha]^{22}_D$ -30.48 (c 0.21, MeOH); UV (MeOH) λ_{max} (log ϵ): 195.5 (3.97); HRESIMS m/z 607.3963 $[M + Na]^+$ (calcd for $C_{36}H_{56}O_6Na^+$, 607.3969); 1H and ^{13}C NMR spectroscopic data were shown in Table S1.

Toscarolide I (4). colorless oil, $[\alpha]^{22}_D$ -56.5 (c 0.26, MeOH); UV (MeOH) λ_{max} (log ϵ): 196.0 (4.07), 239.5 (3.91); HRESIMS m/z 583.4014 $[M - H]^-$ (calcd for $C_{36}H_{55}O_6^-$, 583.4004); 1H and ^{13}C NMR spectroscopic data were shown in Table S1.

2.Spectra data of compounds

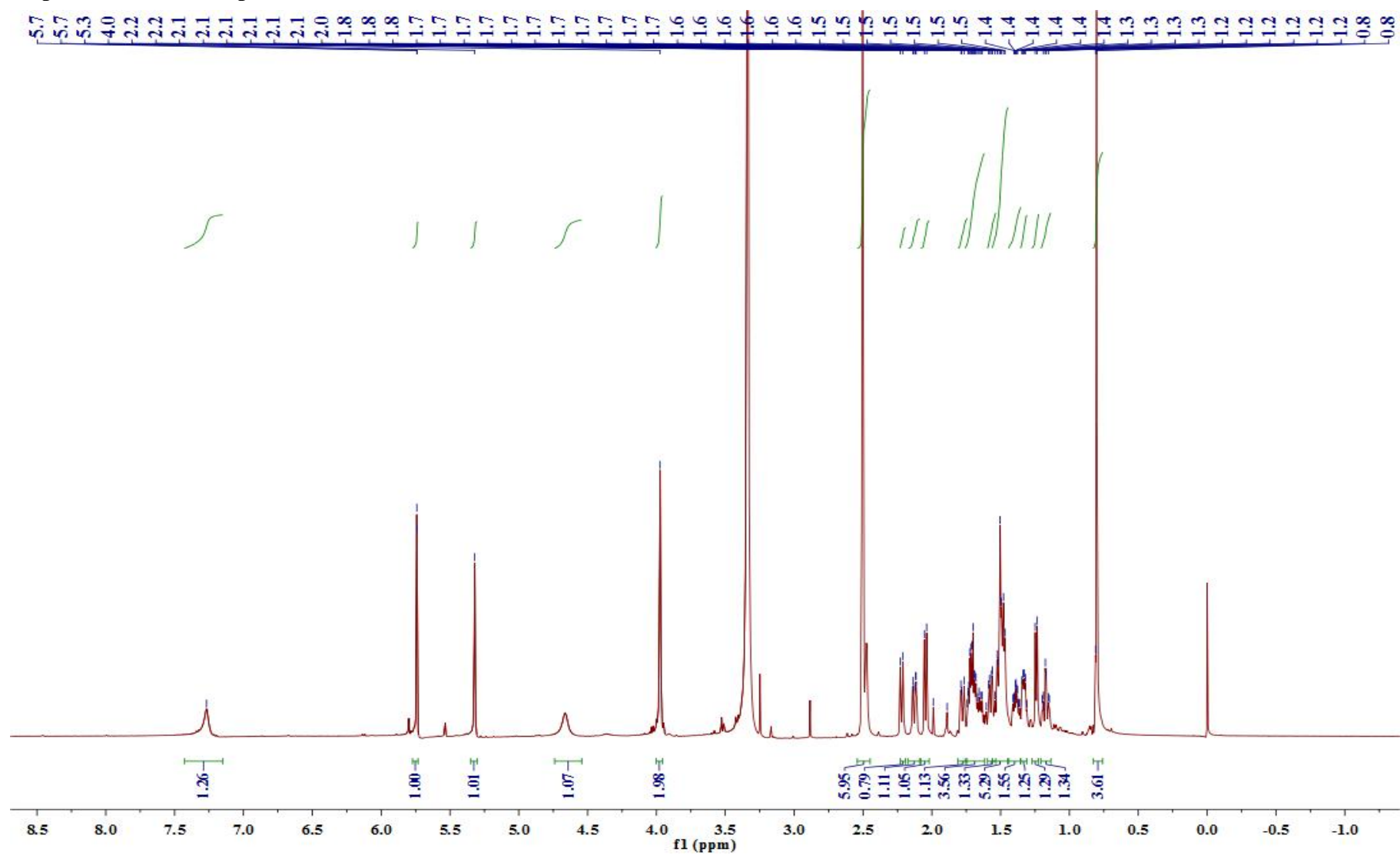


Figure S1 ^1H NMR of 1 (DMSO- d_6)

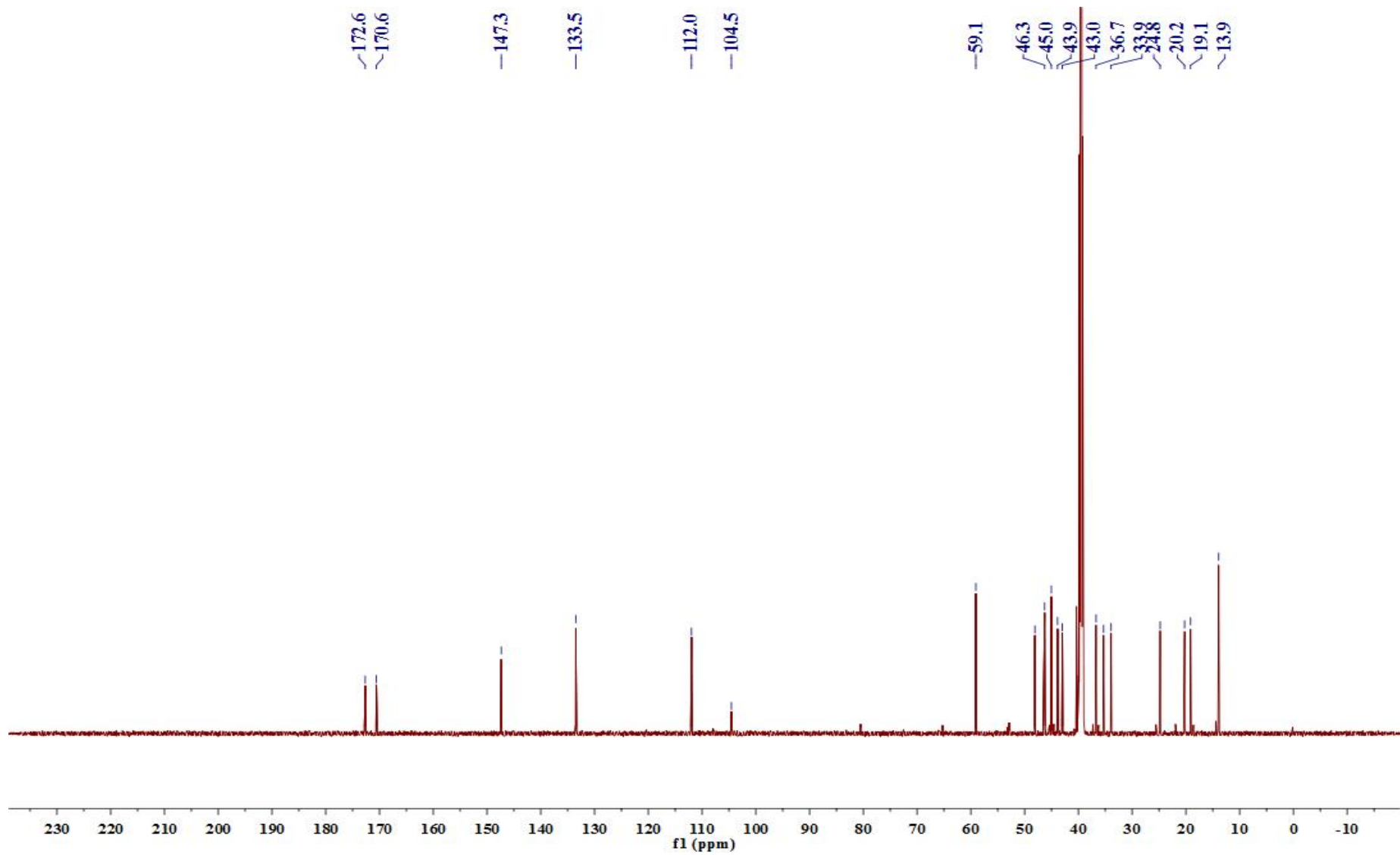


Figure S2 ¹³C NMR spectra of 1 (DMSO-D₆)

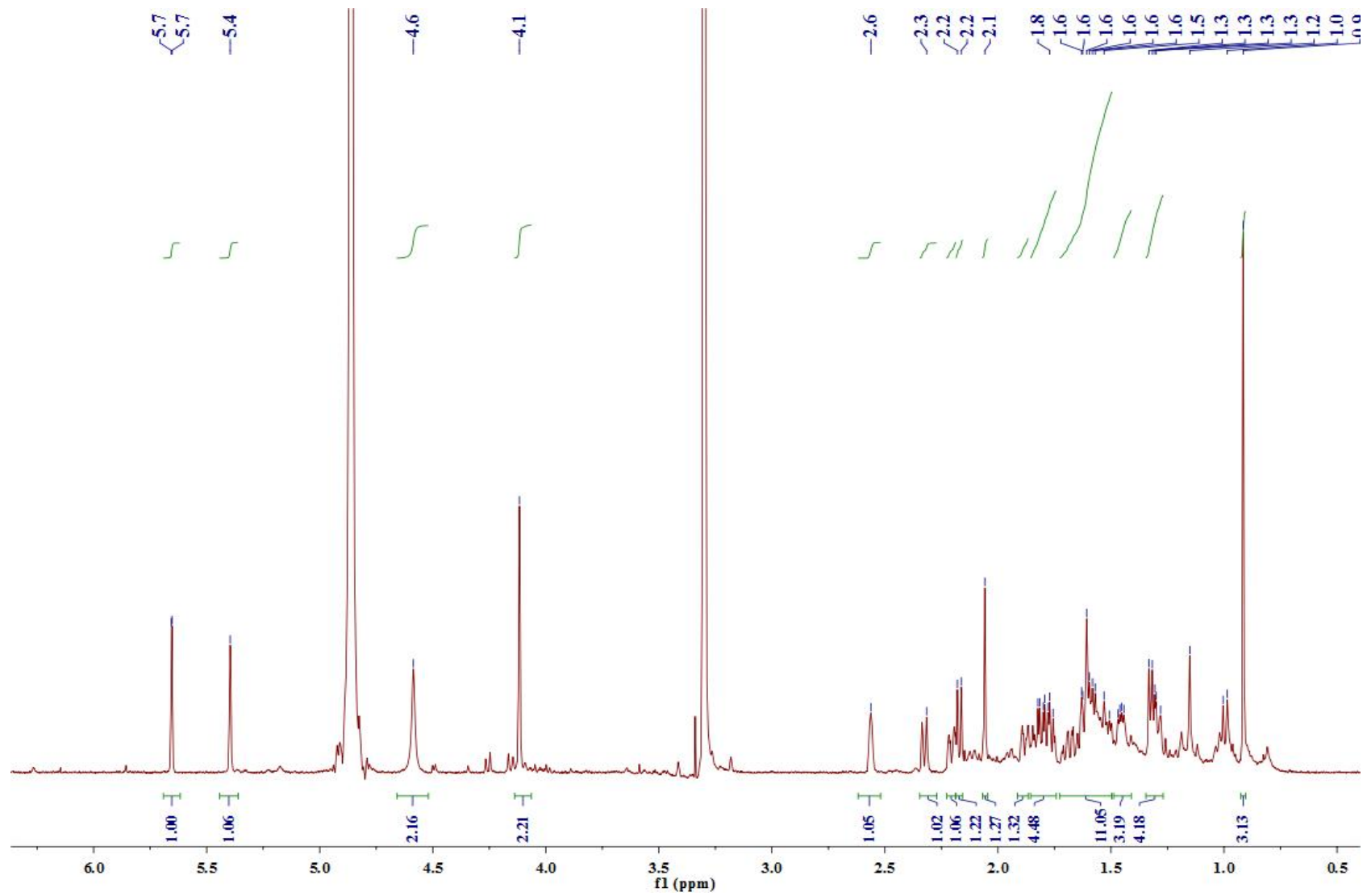


Figure S3 ^1H NMR of **1** (CD_3OD)

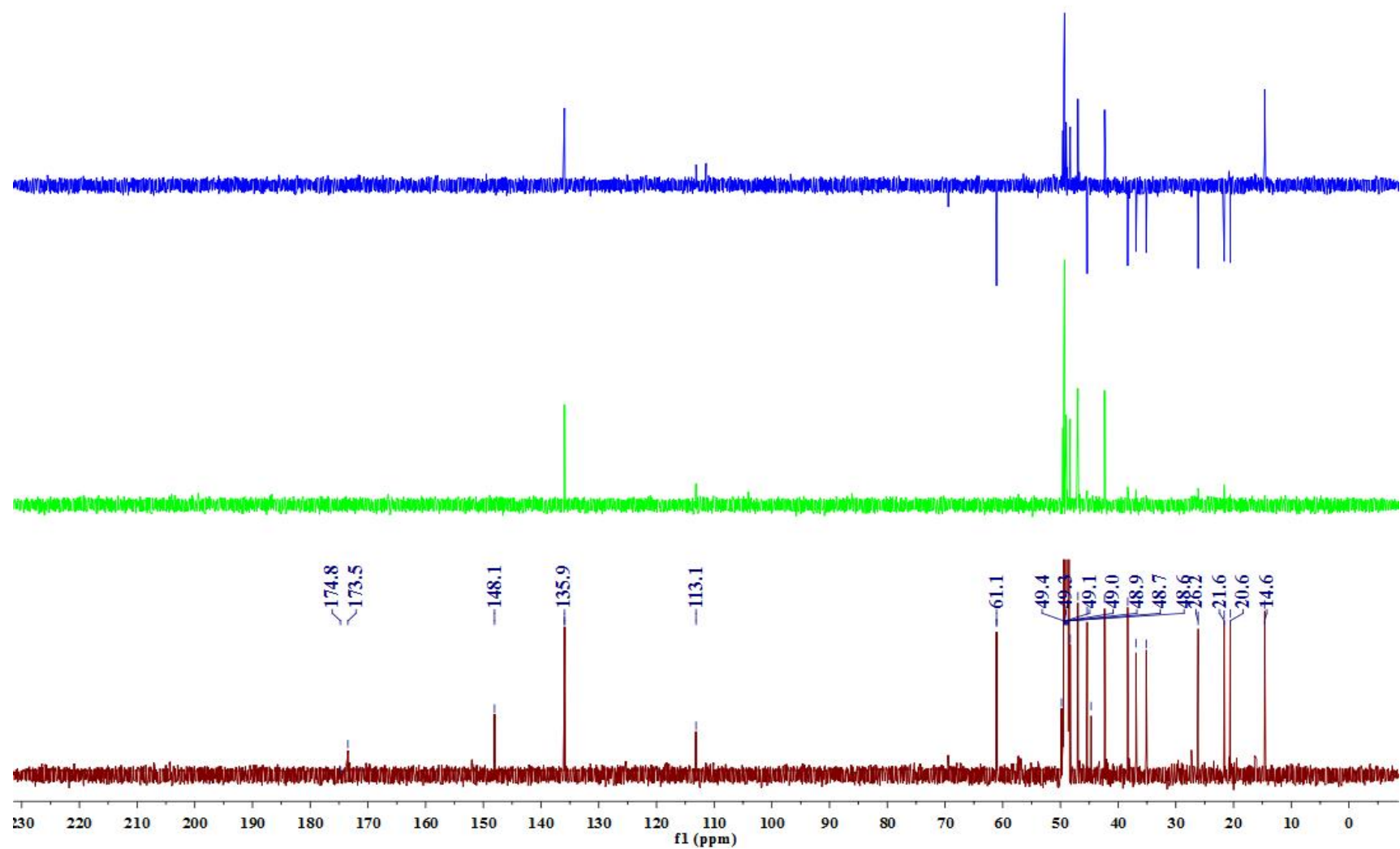


Figure S4 ^{13}C NMR spectra of **1** (CD_3OD)

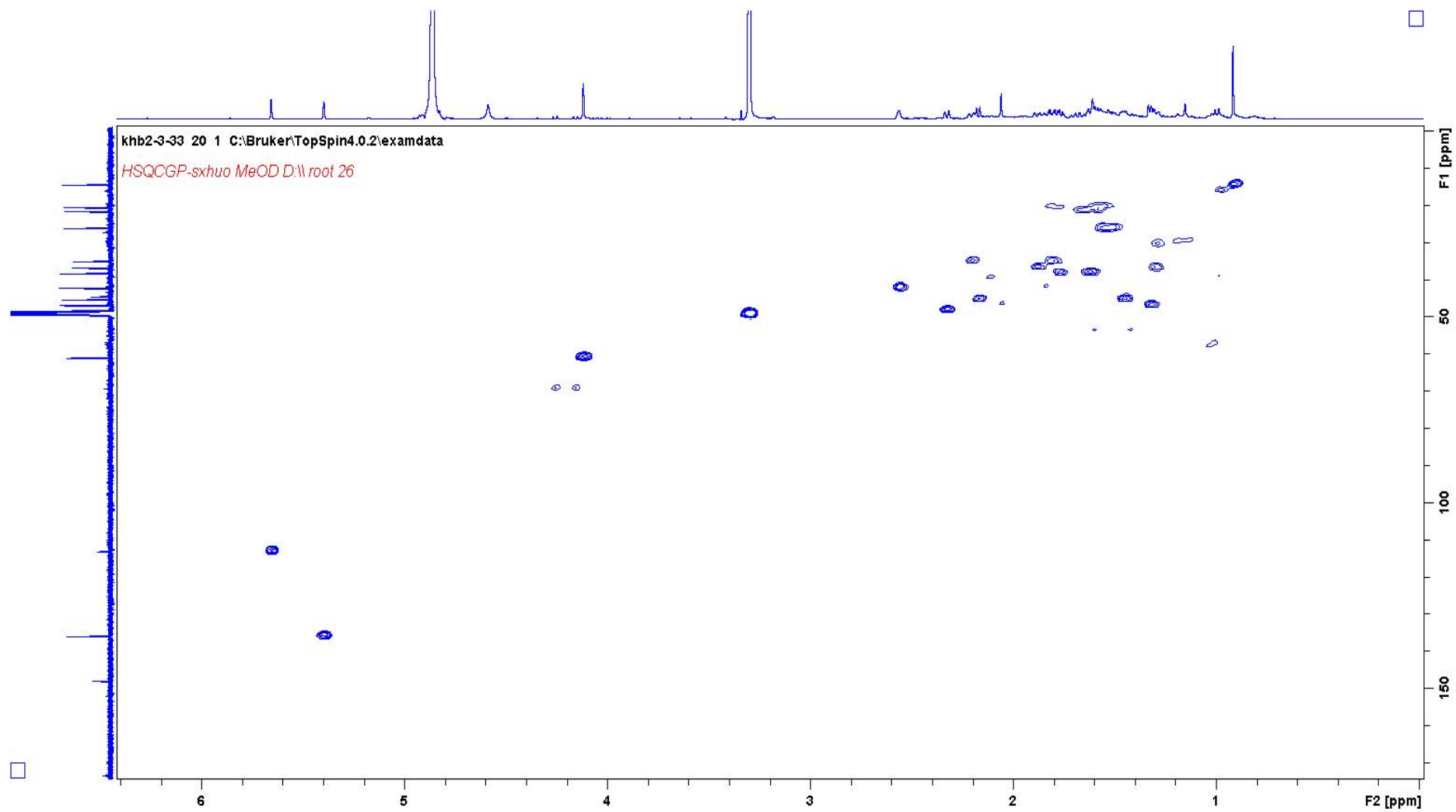


Figure S5 HSQC spectra of **1** (CD₃OD)

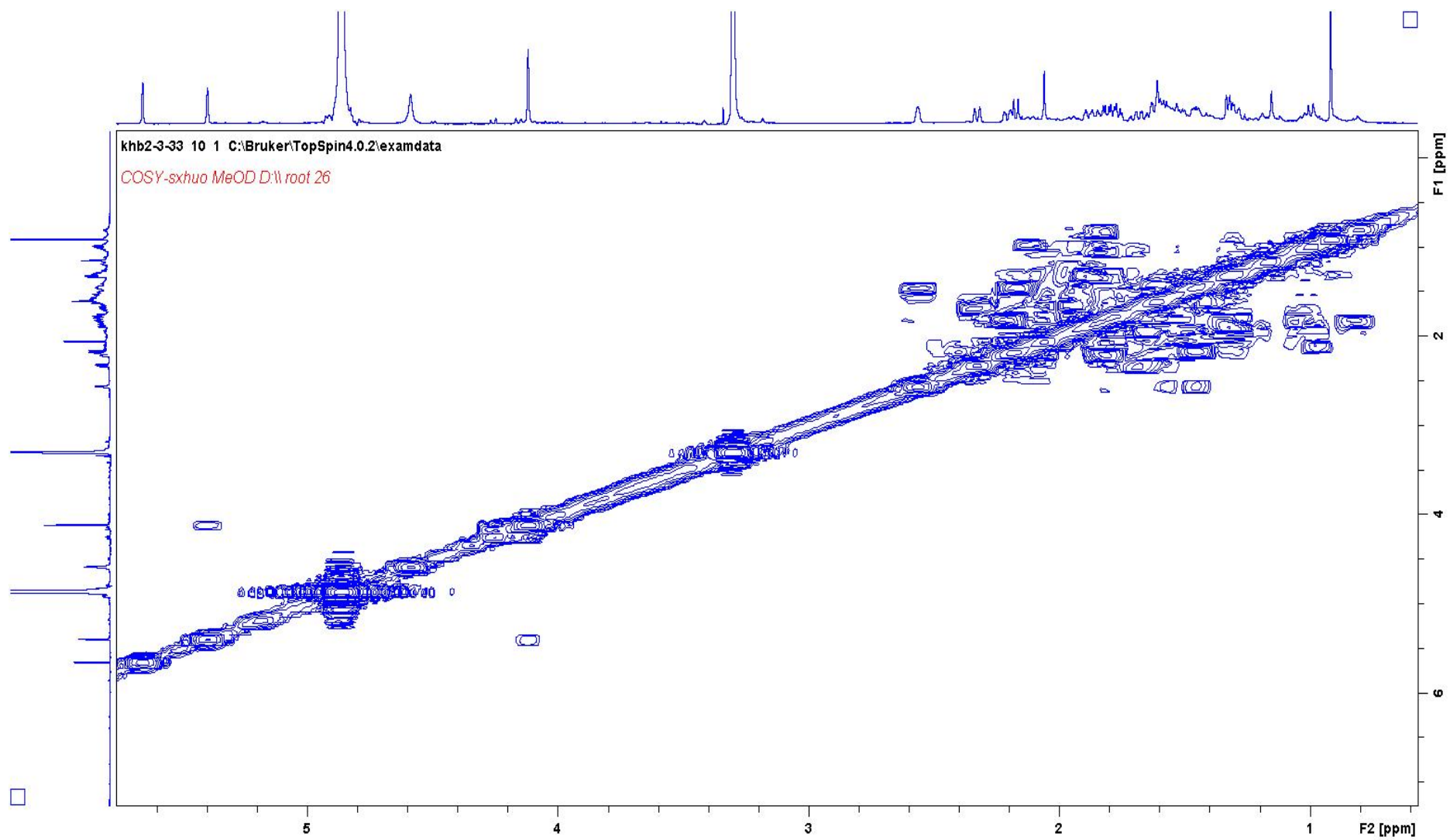


Figure S6 ^1H ^1H COSY spectra of **1** (CD_3OD)

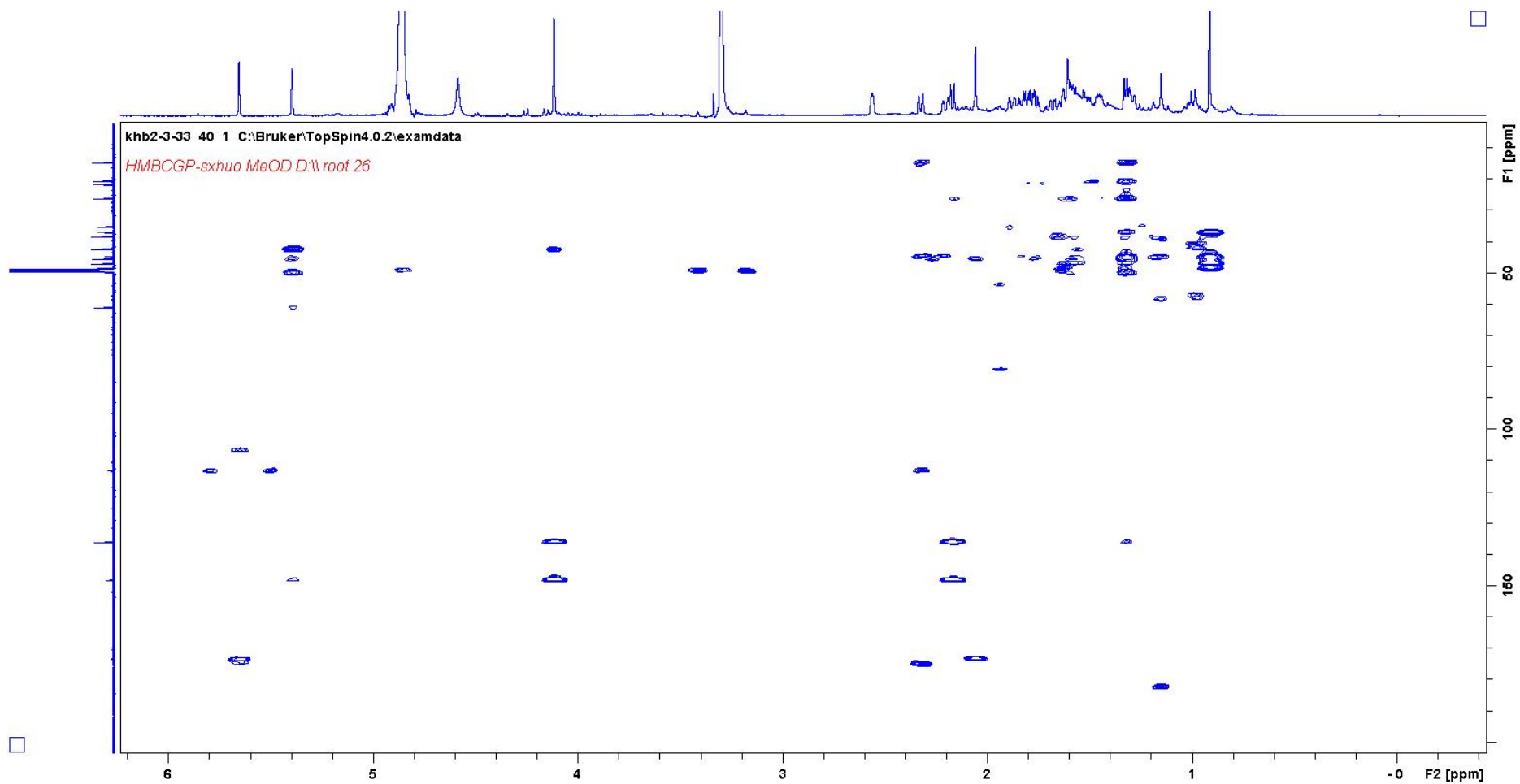


Figure S7 HMBC spectra of **1** (CD₃OD)

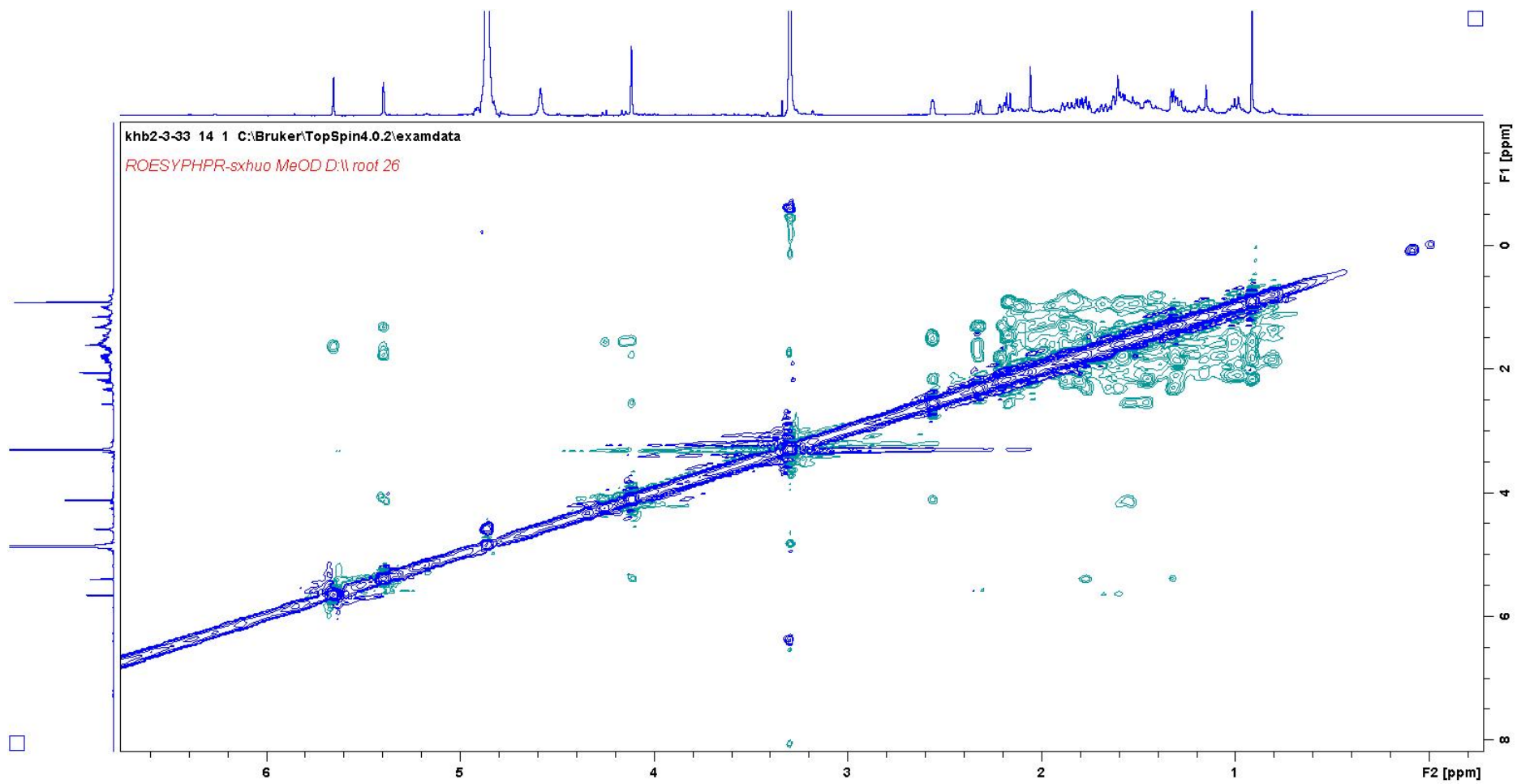


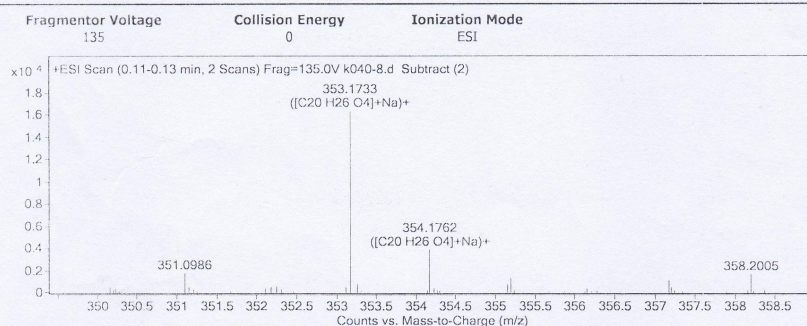
Figure S8 ROESY spectra of **1** (CD₃OD)

Qualitative Analysis Report

Data Filename	k040-8.d	Sample Name	k040-8
Sample Type	Sample	Position	P1-E1
Instrument Name	Instrument 1	User Name	
Acq Method	s.m	Acquired Time	2/26/2019 11:12:24 AM
IRM Calibration Status	Success	DA Method	Default.m
Comment			

Sample Group	Info.
Acquisition SW	6200 series TOF/6500 series
Version	Q-TOF B.05.01 (B5125.2)

User Spectra



Peak List

m/z	z	Abund	Formula	Ion
301.1411	1	17658.48		
324.2173		8970.08		
353.1733	1	16308.25	C20 H26 O4	(M+Na)+
369.1463	1	15424.41		
383.1831	1	34097.79		
399.1585	1	9521.54		
417.225	1	27159.88		
747.4084	1	11477.39		
775.2786	1	12557.65		
811.4592	1	8894.99		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	120
O	0	30

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C20 H26 O4	330.1831	353.1723	353.1733	-1.00	-2.83	8.0000

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Figure S9 HRMS spectra of 1

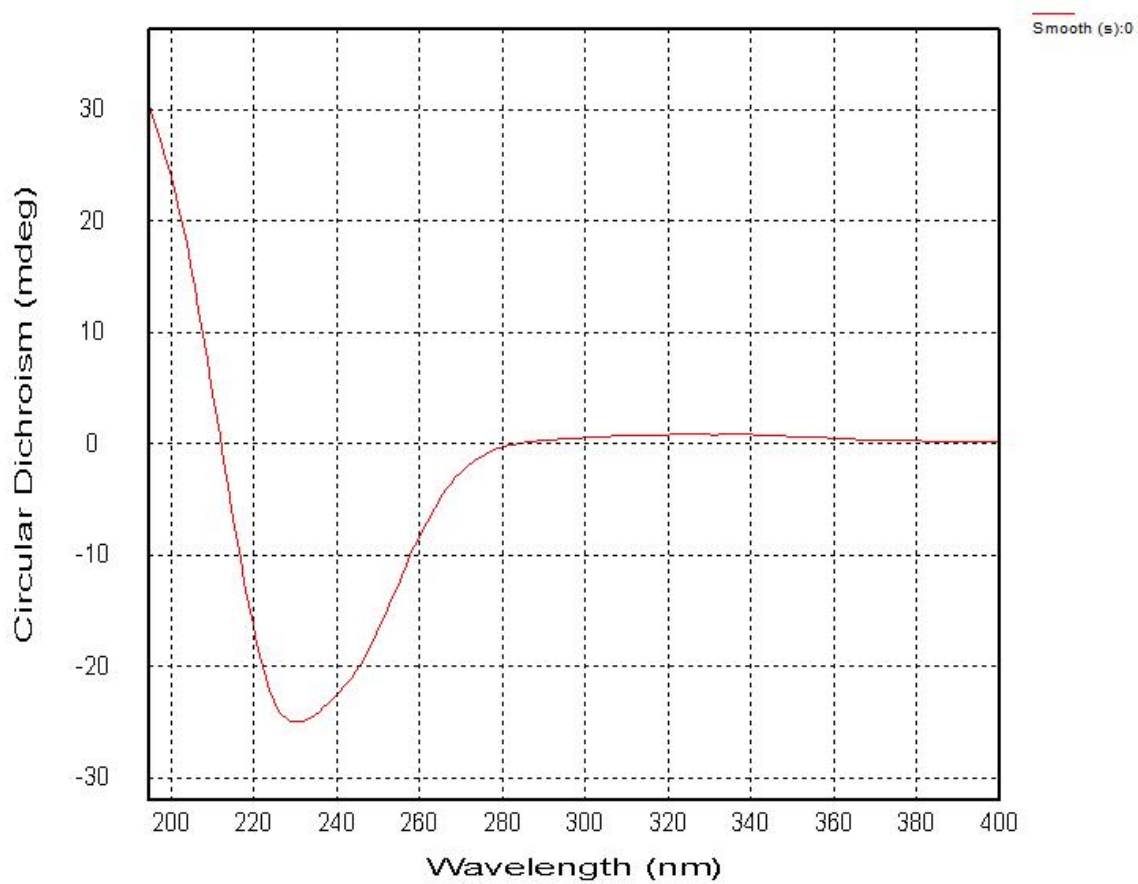


Figure S10 The Circular Dichroism spectrum of **1**

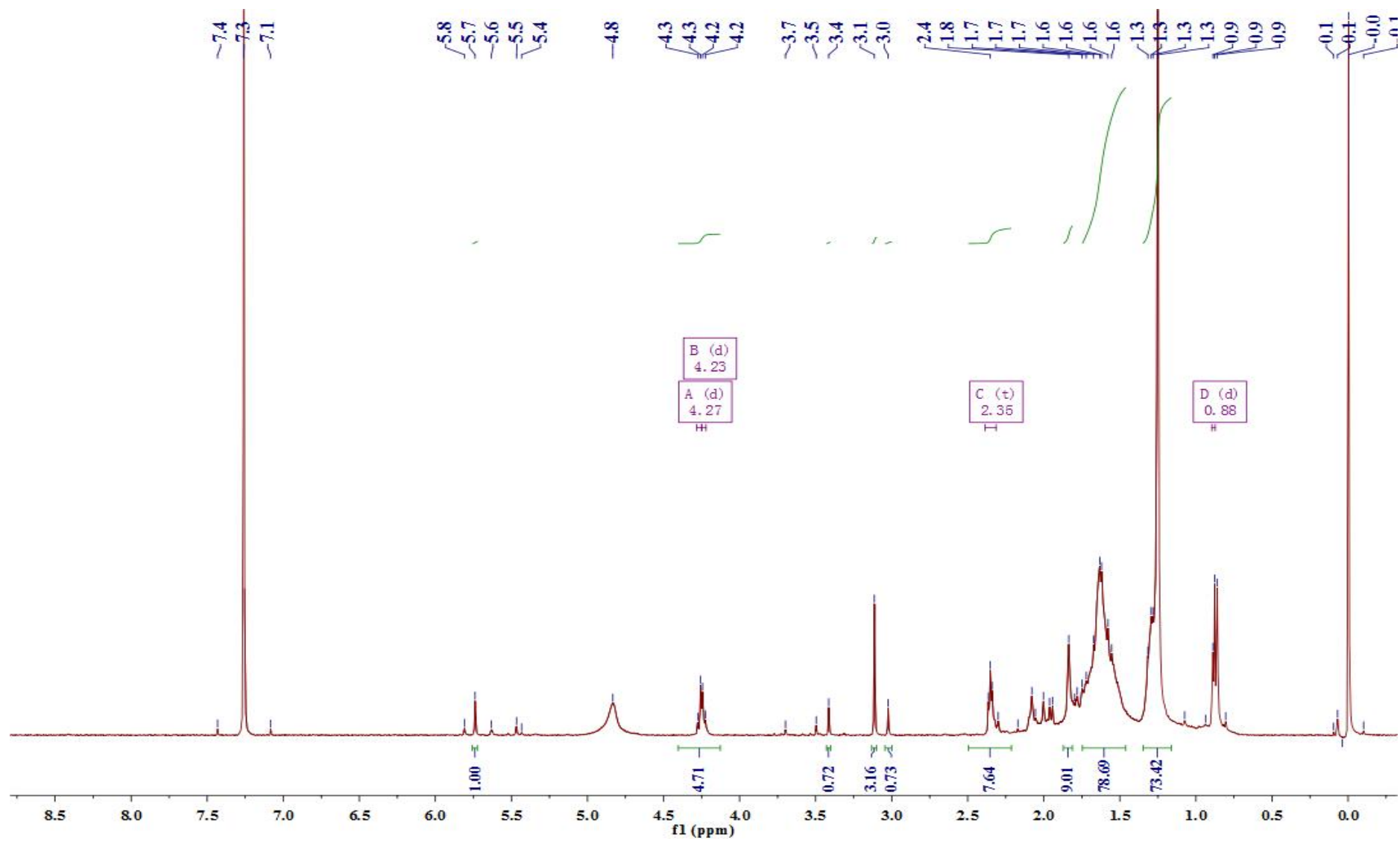


Figure S11 ^1H NMR of **2** (CD_3Cl)

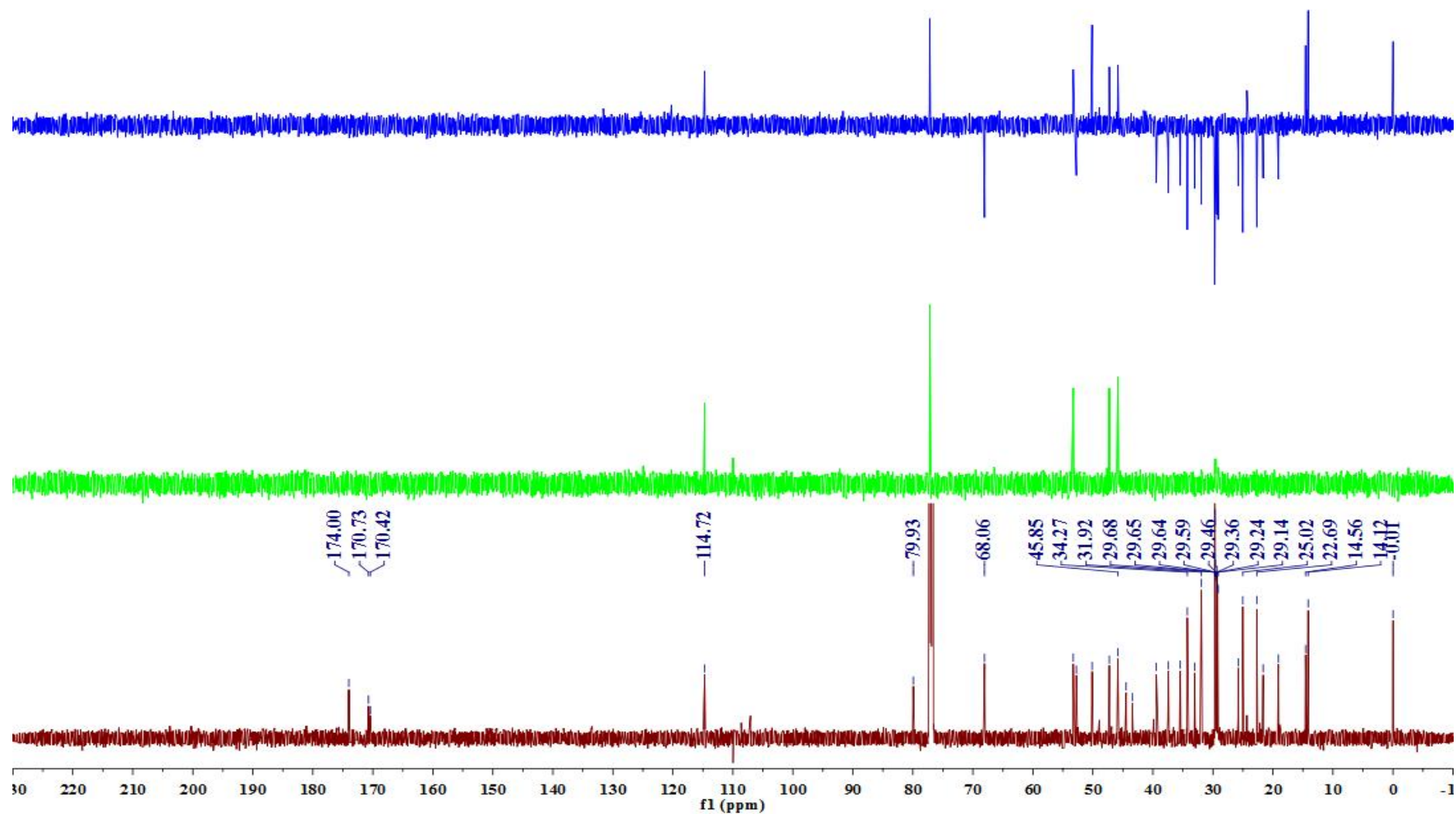


Figure S12 ^{13}C NMR spectra of **2** (CD_3Cl)

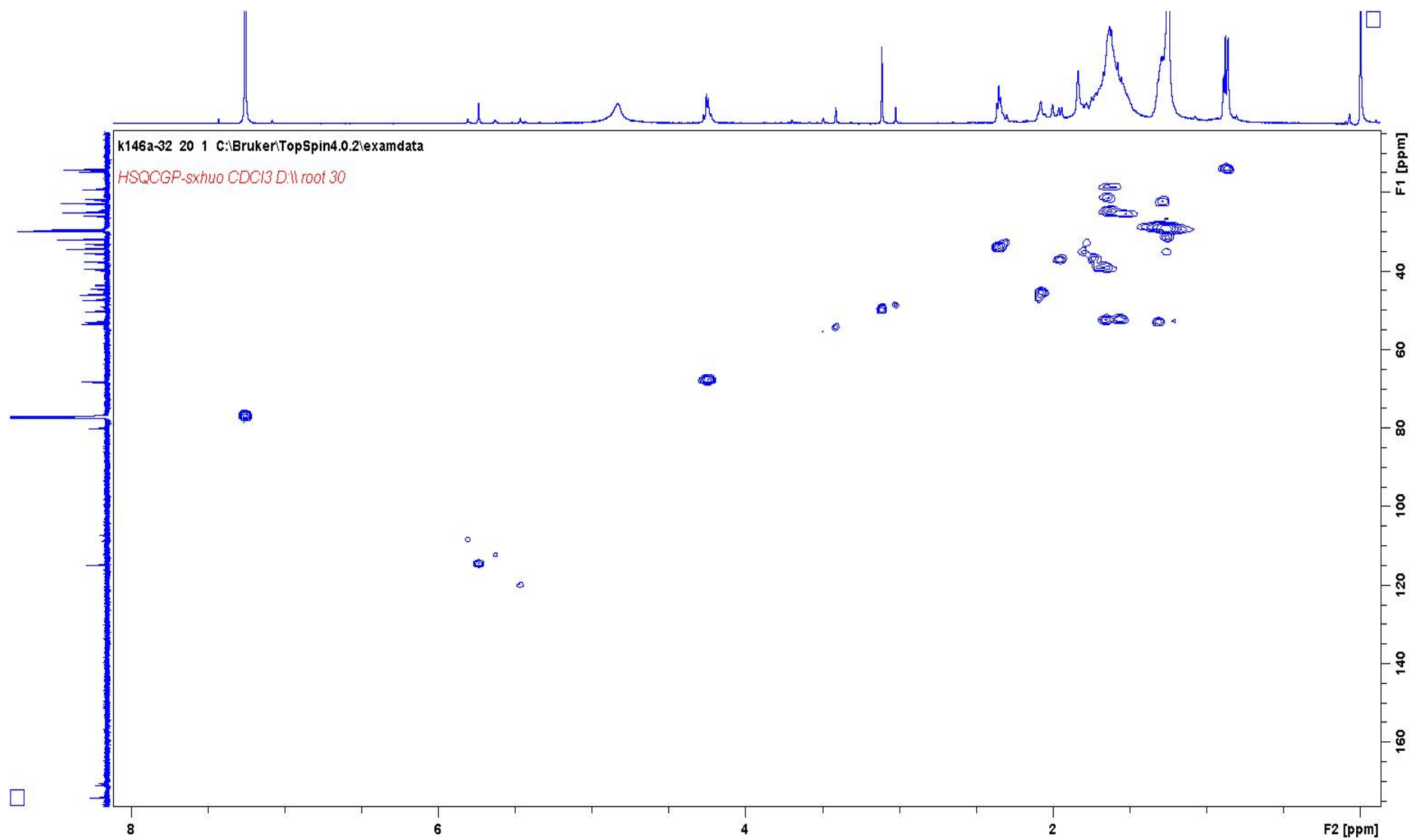


Figure S13 HSQC spectra of **2** (CD₃Cl)

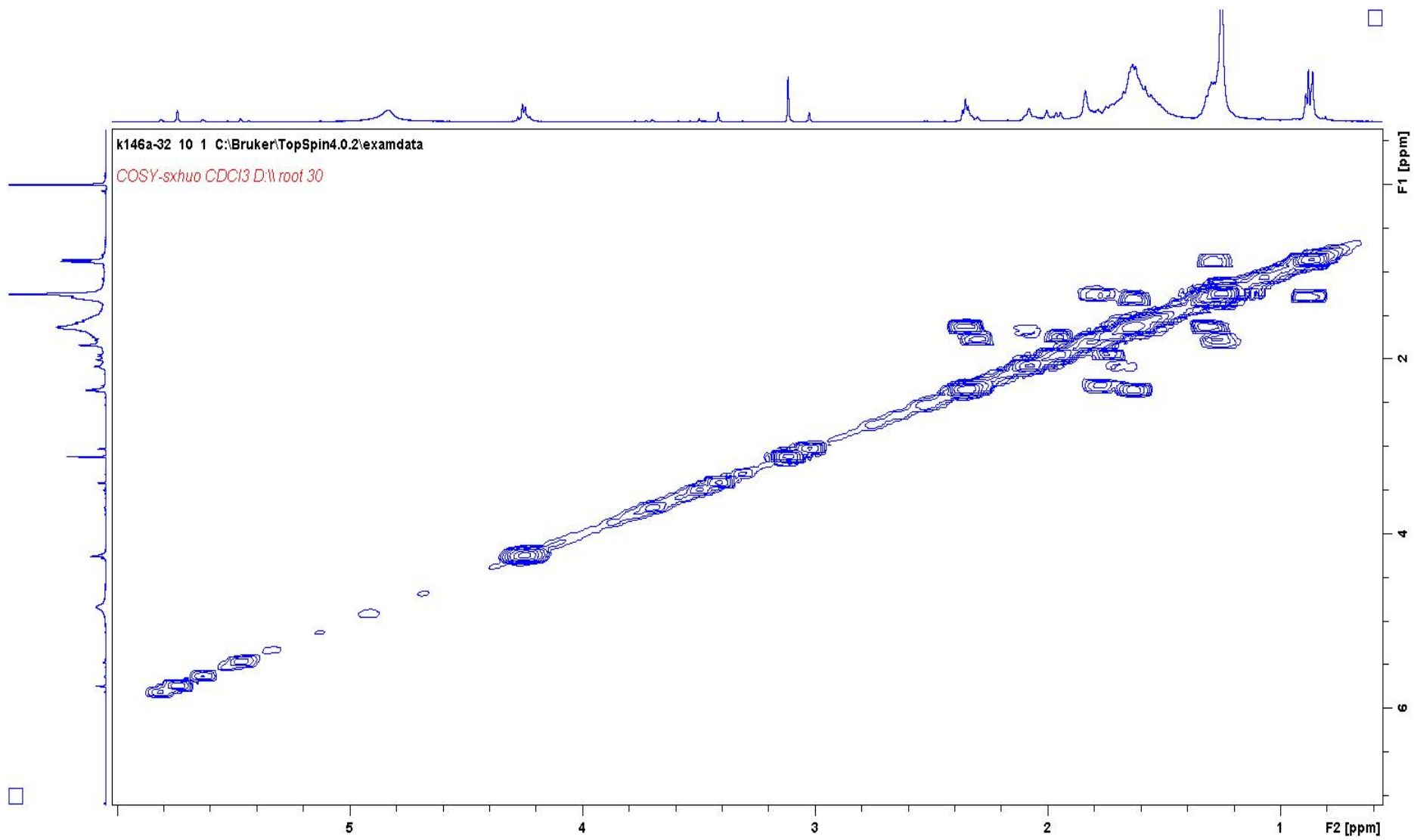


Figure S14 ^1H ^1H COSY spectra of **2**

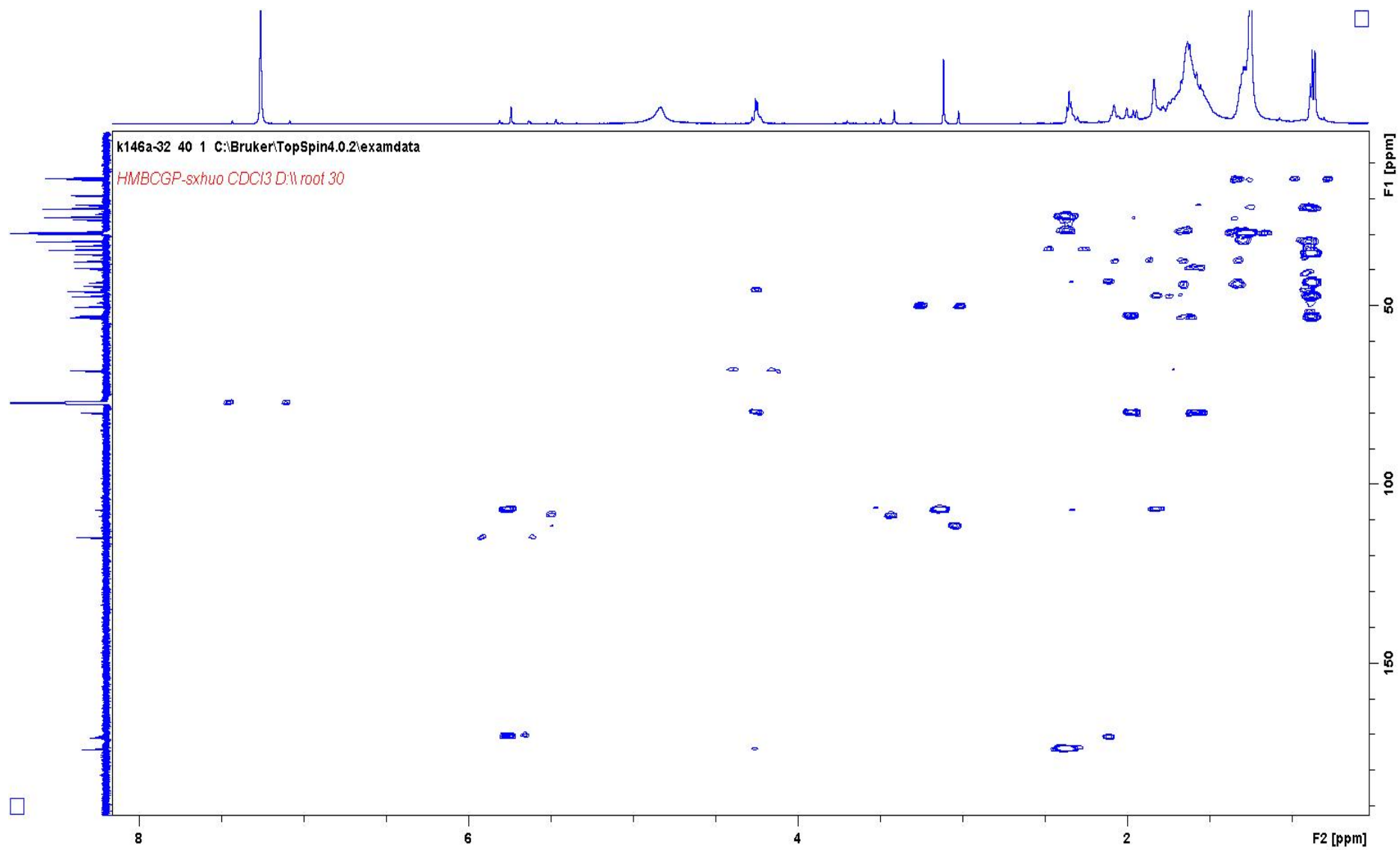


Figure S15 HMBC spectra of **2** (CD₃Cl)

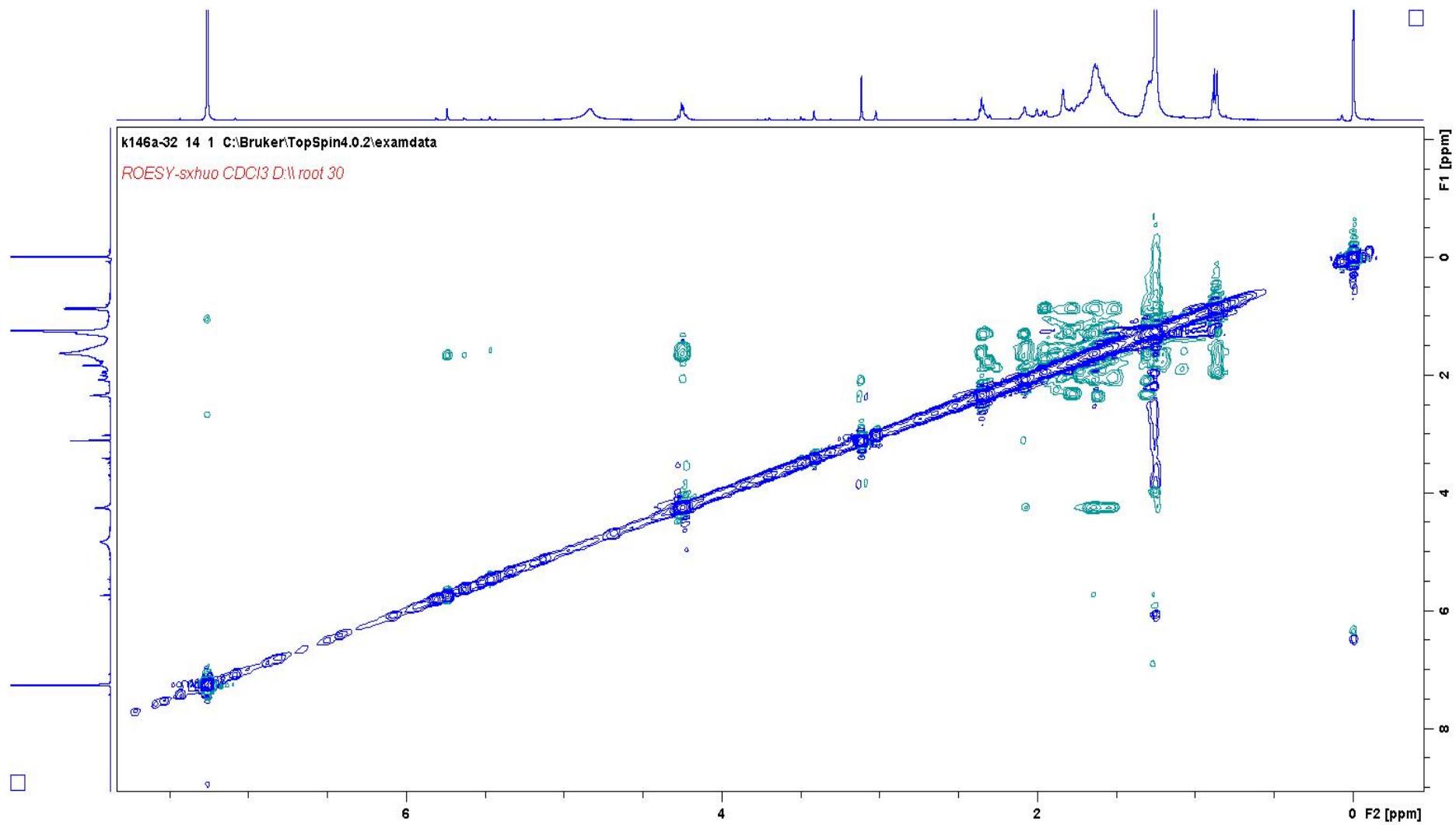


Figure S16 ROESY spectra of **2** (CD₃Cl)

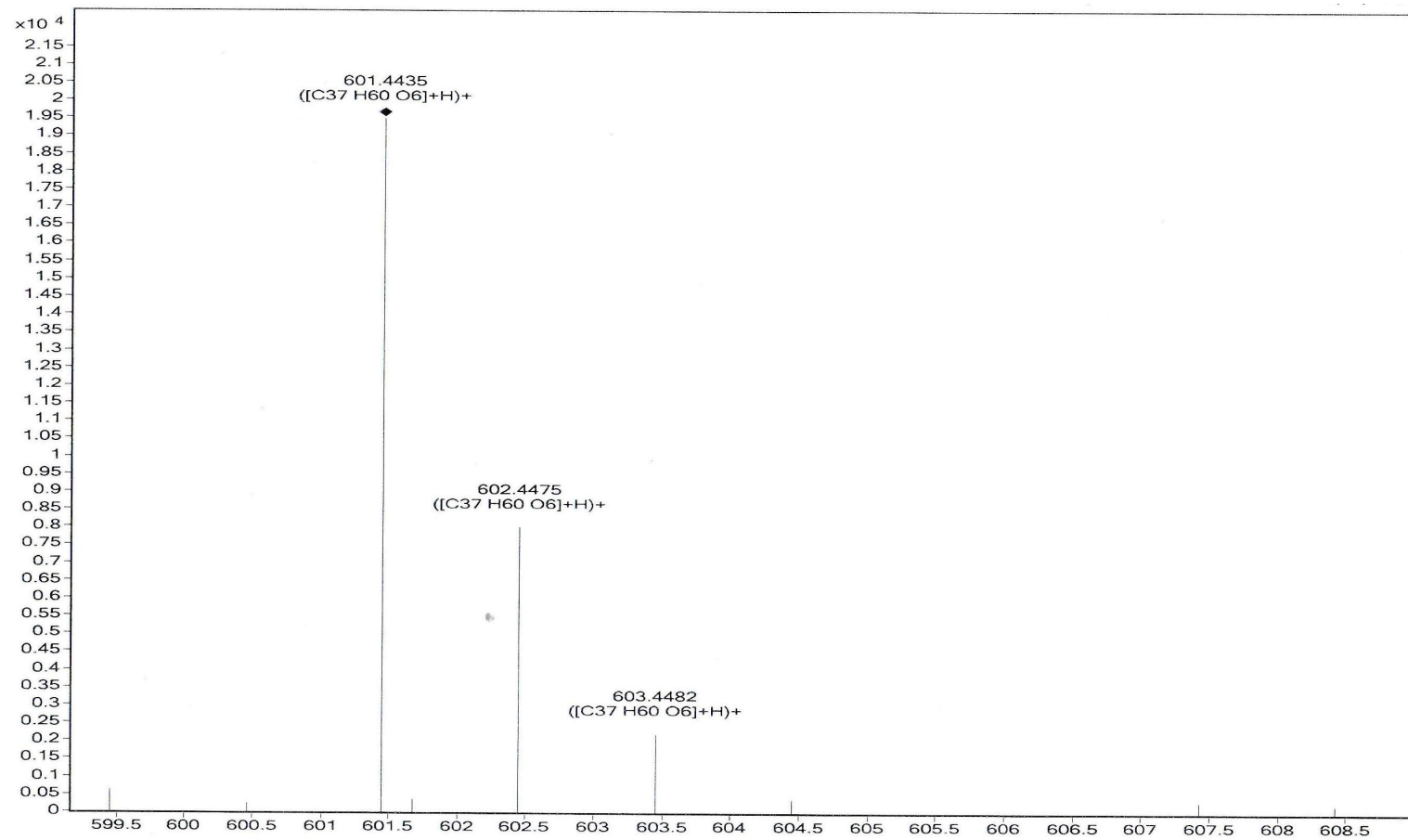


Figure S17 HRMS spectra of **2**

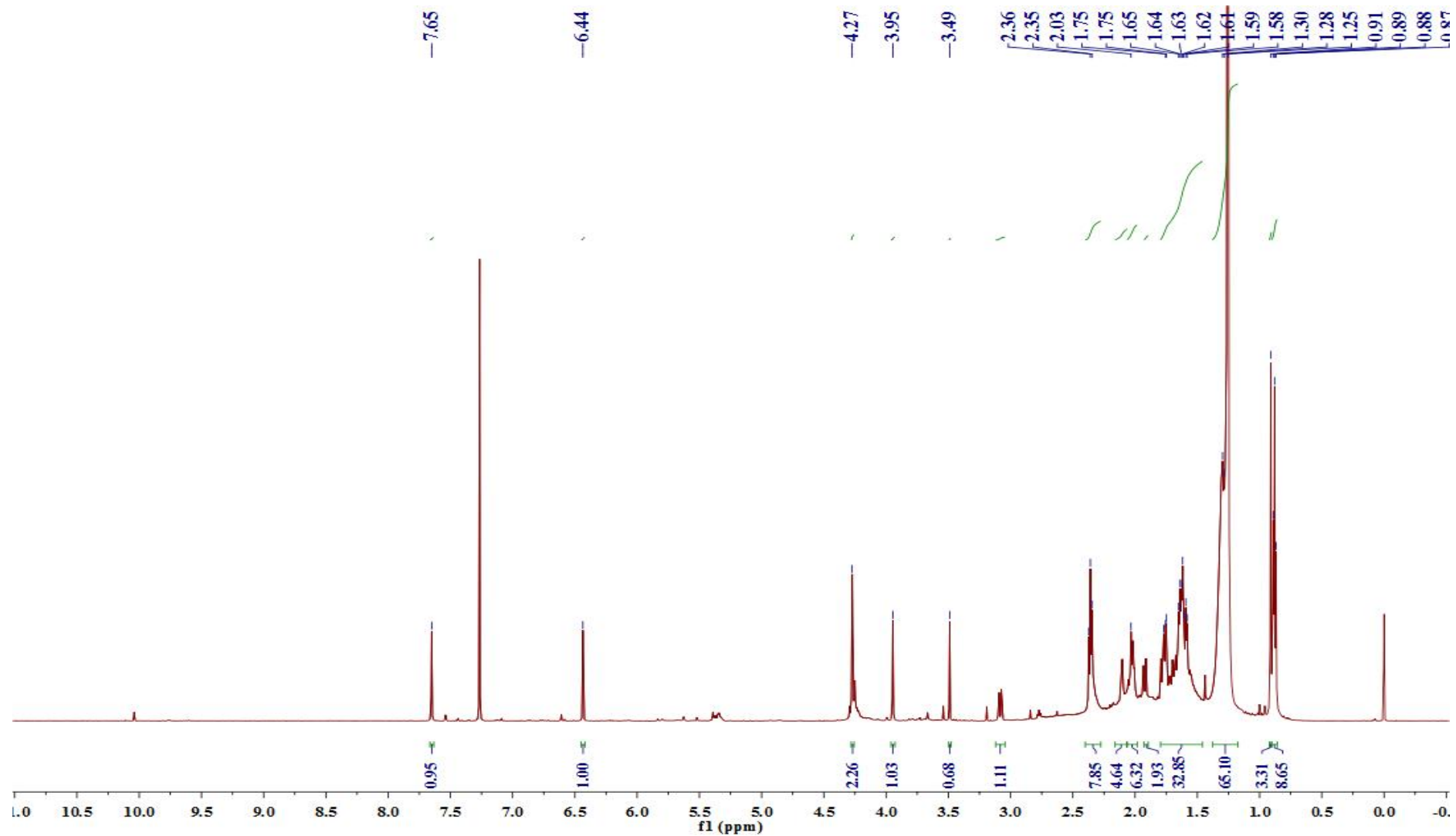


Figure S18 ¹H NMR spectra of **3** (CD₃Cl)

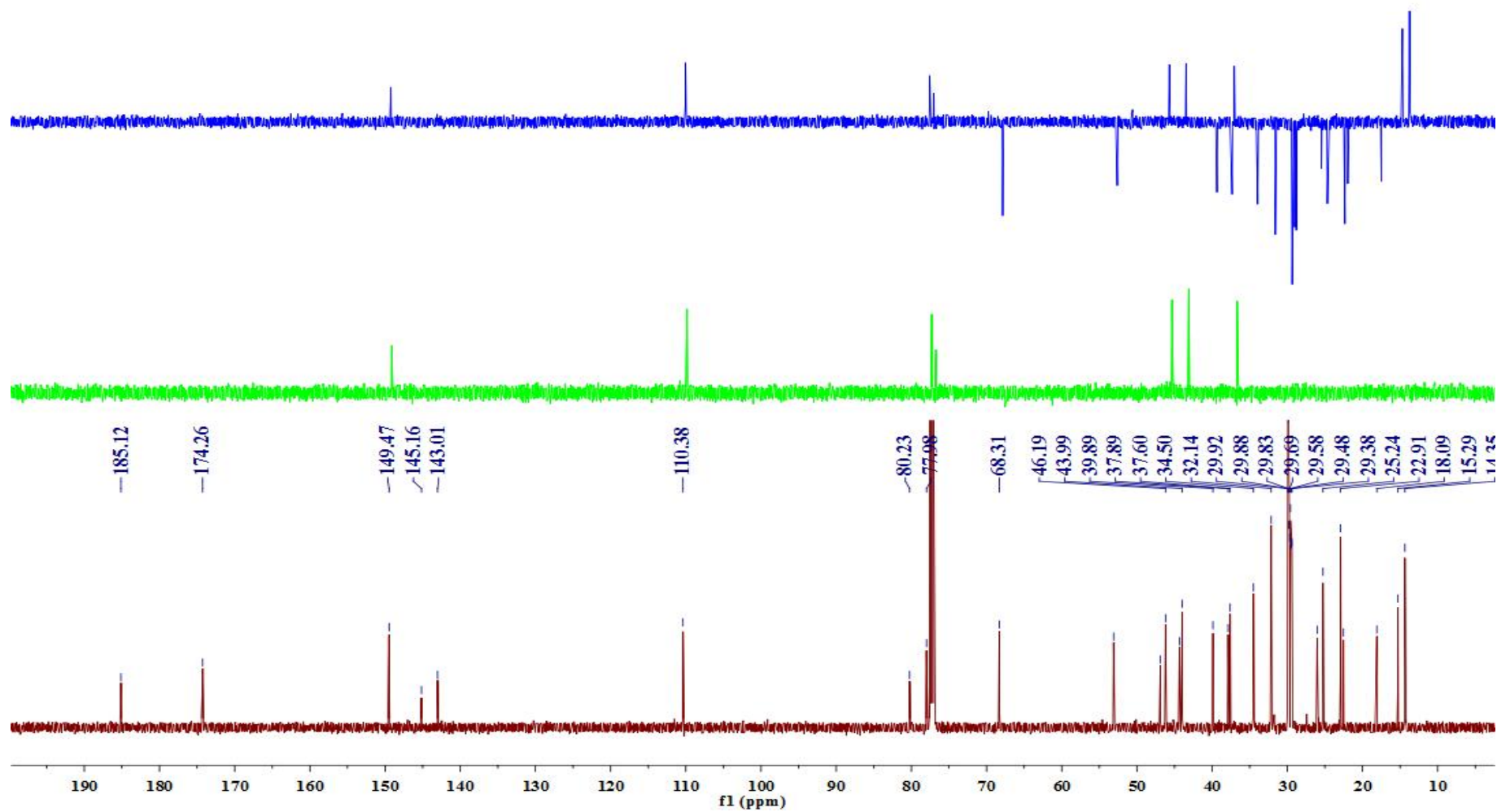


Figure S19 ^{13}C NMR spectra of **3** (CD_3Cl)

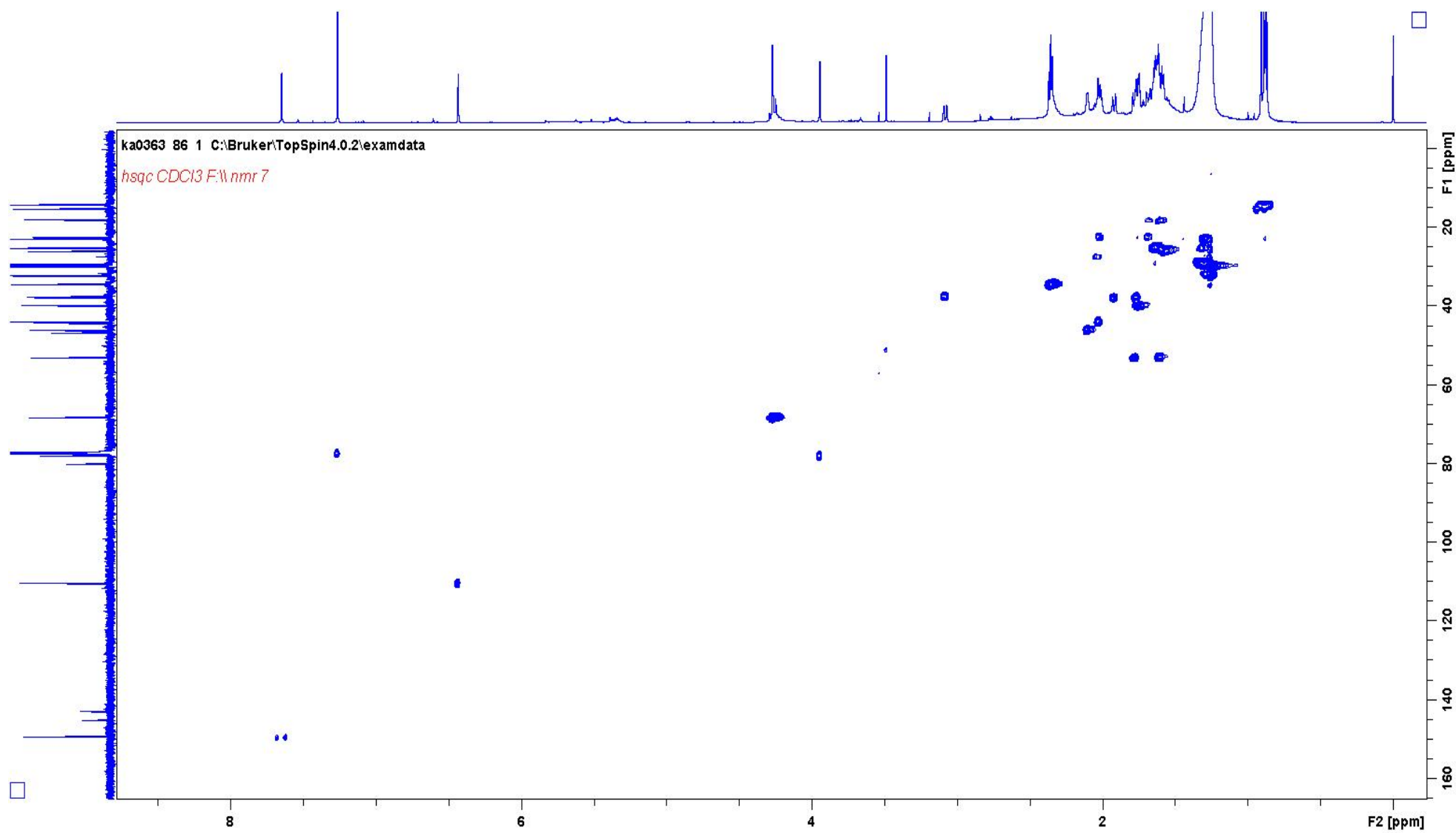


Figure S20 HSQC spectra of **3** (CD₃Cl)

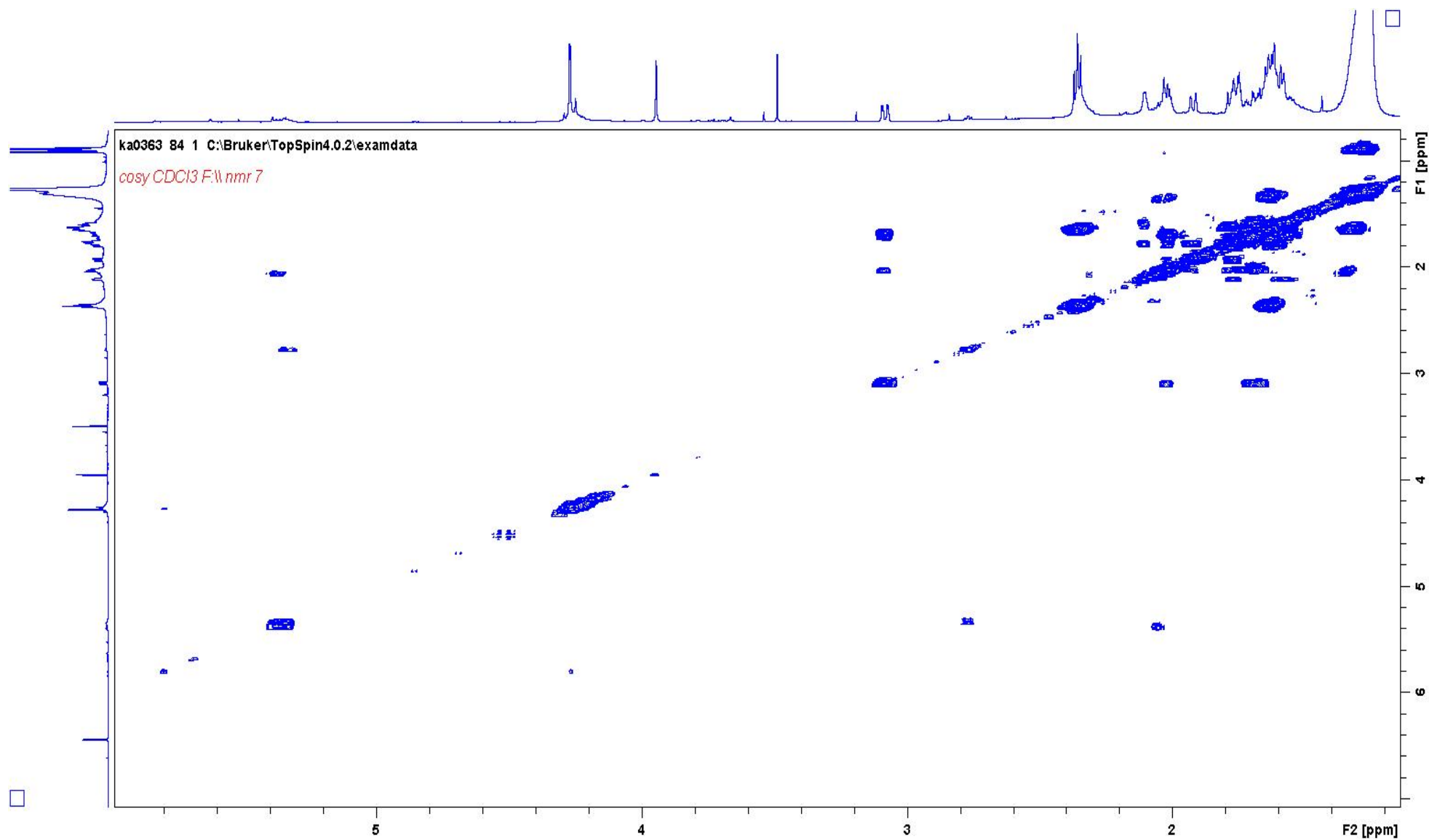


Figure S21 ^1H ^1H COSY spectra of **3** (CD_3Cl)

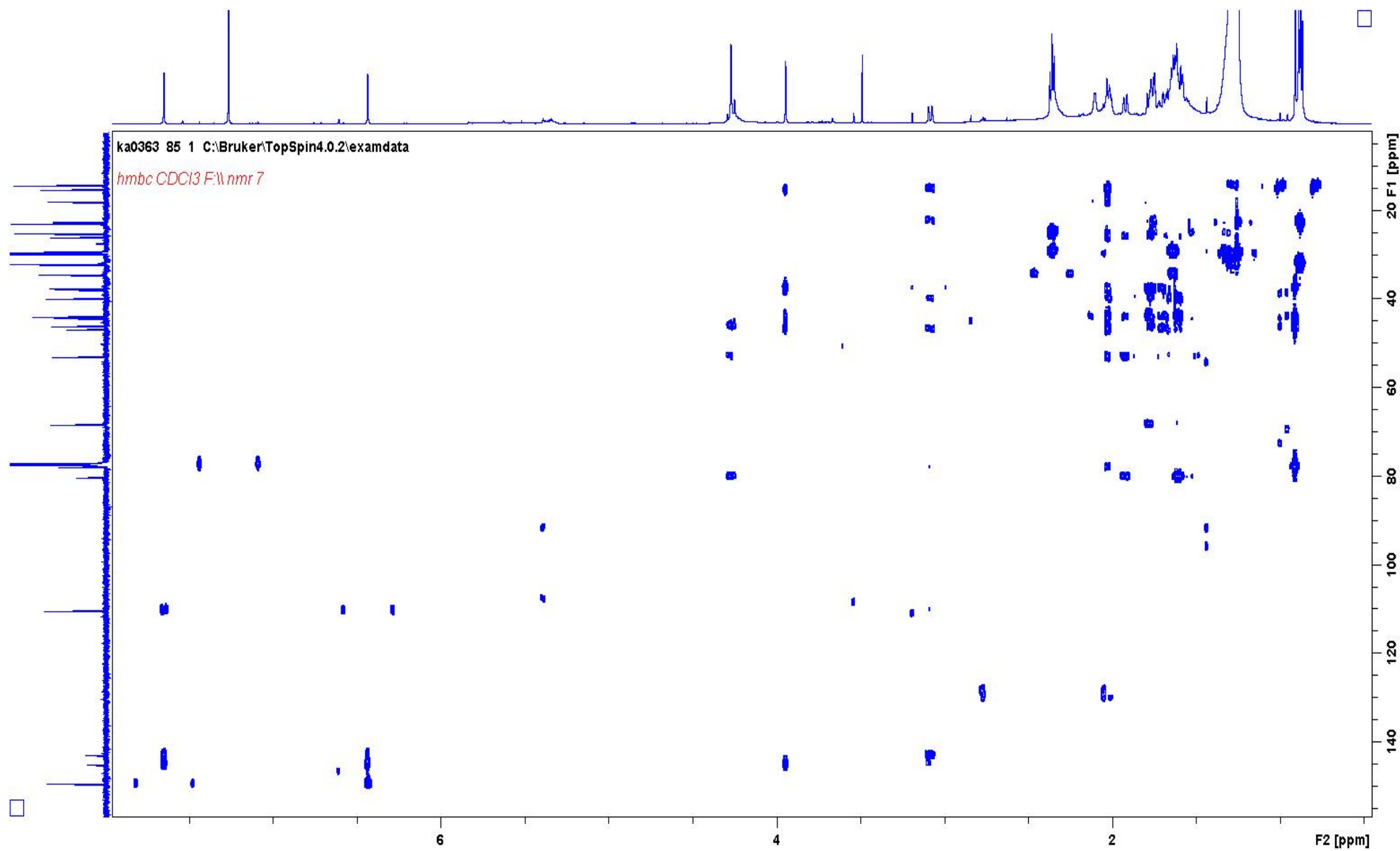


Figure S22 HMBC spectra of **3** (CD₃Cl)

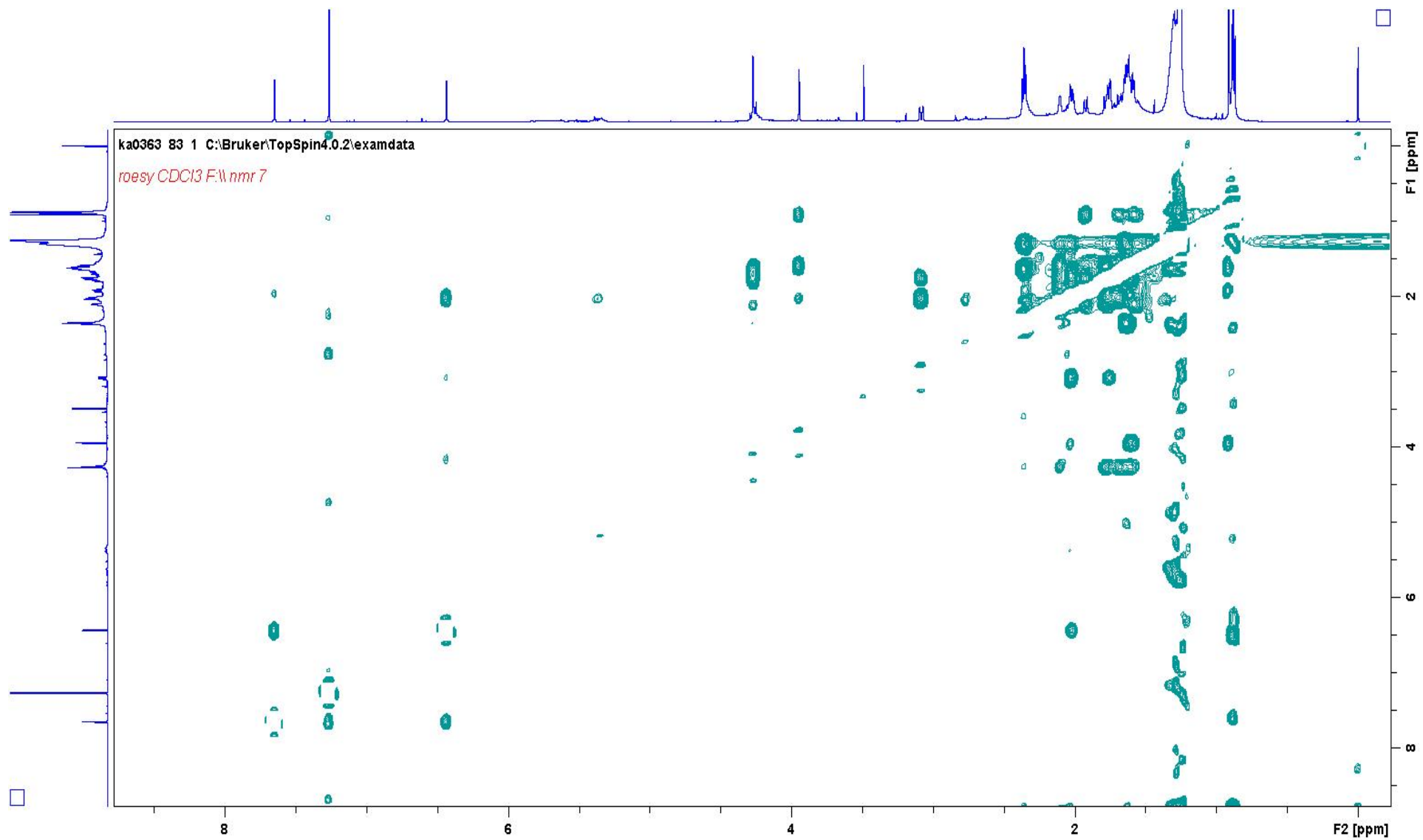


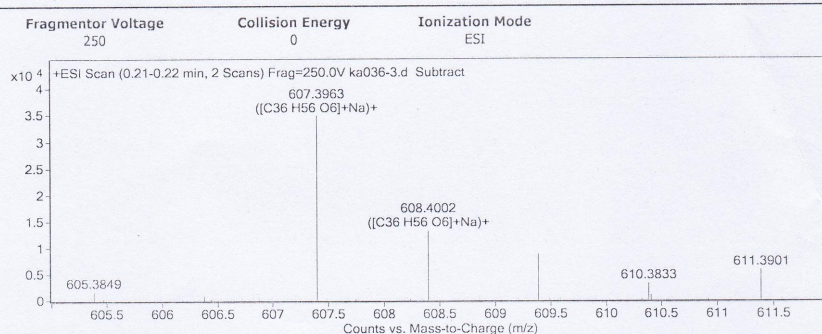
Figure S23 ROESY spectra of **3** (CD₃Cl)

Qualitative Analysis Report

Data Filename	ka036-3.d	Sample Name	ka036-3
Sample Type	Sample	Position	P1-B7
Instrument Name	Instrument 1	User Name	
Acq Method	s.m	Acquired Time	9/3/2020 11:01:38 AM
IRM Calibration Status	Success	DA Method	Default.m
Comment			

Sample Group	Info.
Acquisition SW	6200 series TOF/6500 series
Version	Q-TOF B.05.01 (B5125.2)

User Spectra



Peak List

m/z	z	Abund	Formula	Ion
119.0854		10434.42		
256.2631	1	23151.21		
274.2735	1	16545.89		
318.2999	1	21165.05		
362.326	1	11794.89		
437.1933	1	72975.1		
438.1967	1	18030.93		
607.3963	1	34877.97	C36 H56 O6	(M+Na)+
608.4002	1	13255.16	C36 H56 O6	(M+Na)+
639.3863	1	19304.59		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	60
O	0	10
N	0	10

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C36 H56 O6	584.4077	607.3969	607.3963	0.60	0.99	9.0000

--- End Of Report ---

Figure S24 HRMS spectra of 3

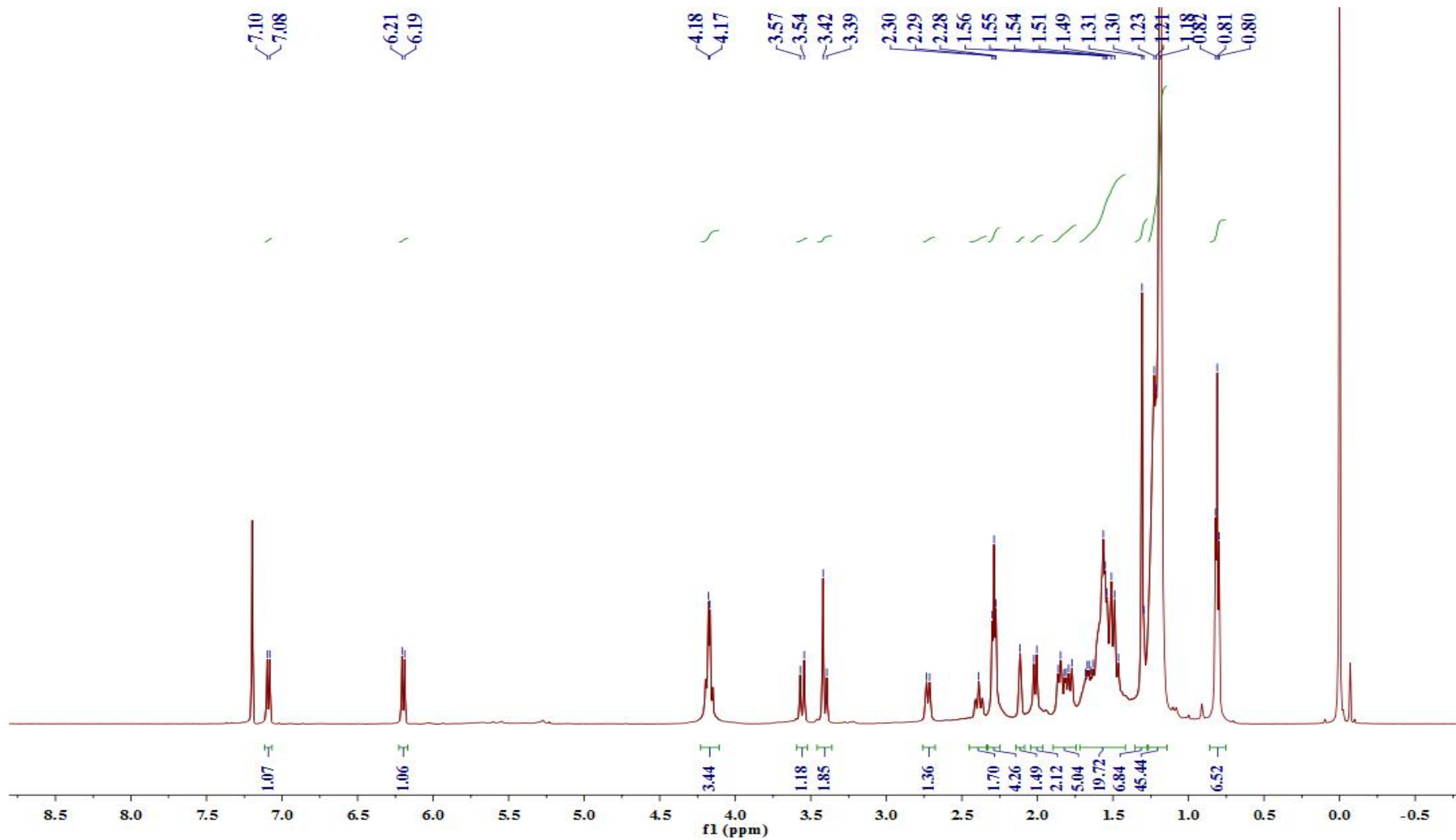


Figure S25 ^1H NMR of **4** (CD_3Cl)

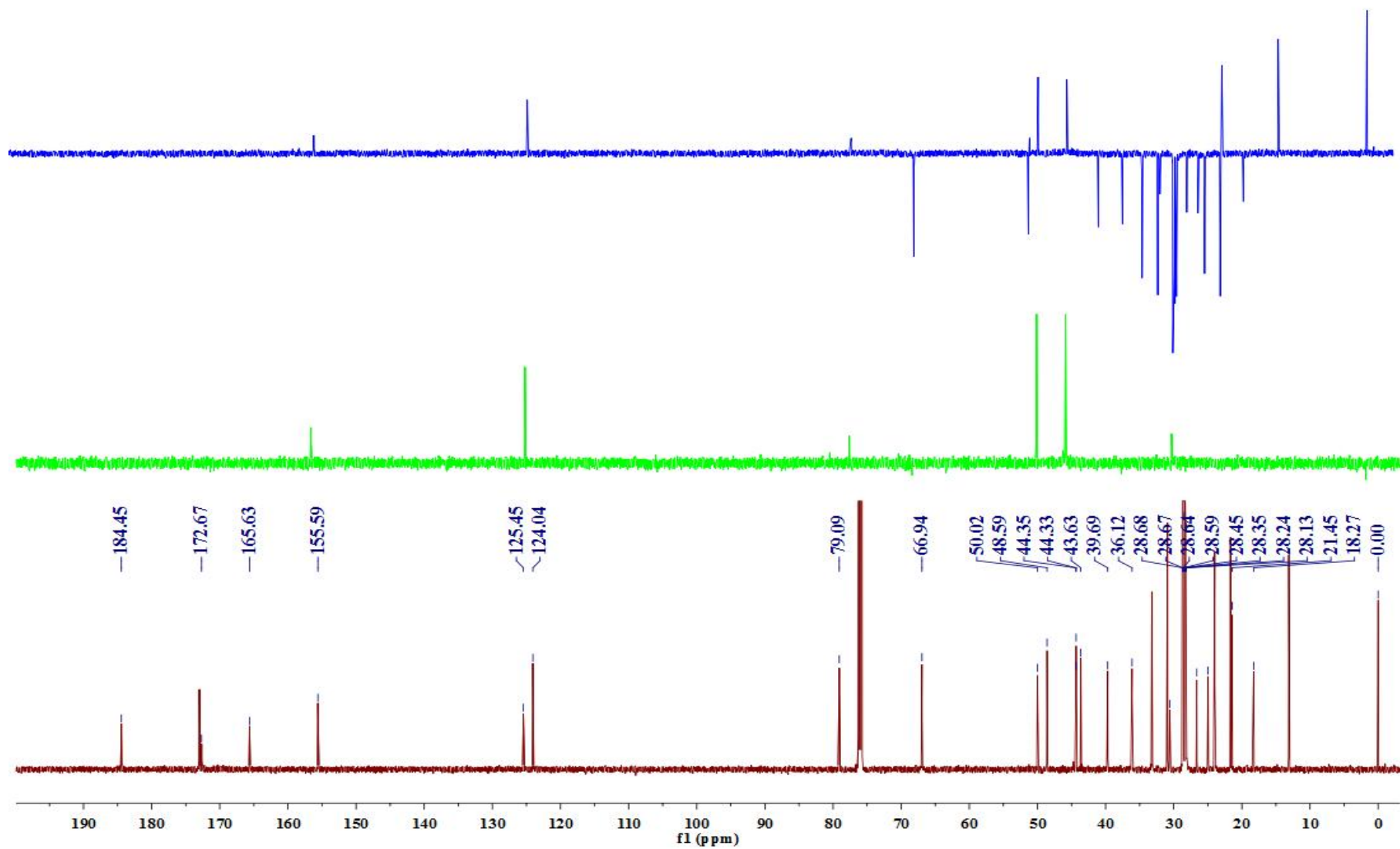


Figure S26 ^{13}C NMR spectra of 4 (CD_3Cl)

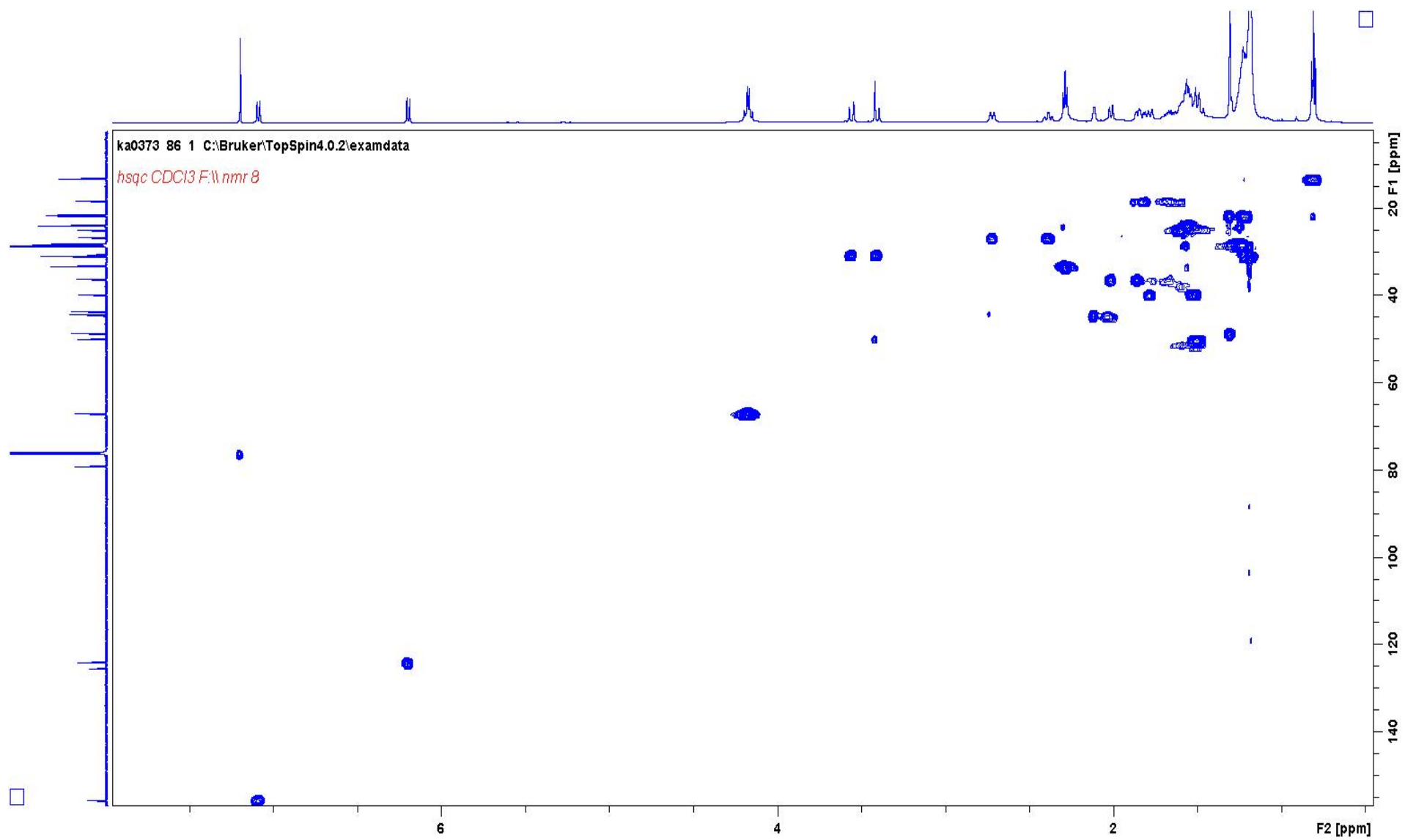


Figure S27 HSQC spectra of **4** (CD₃Cl)

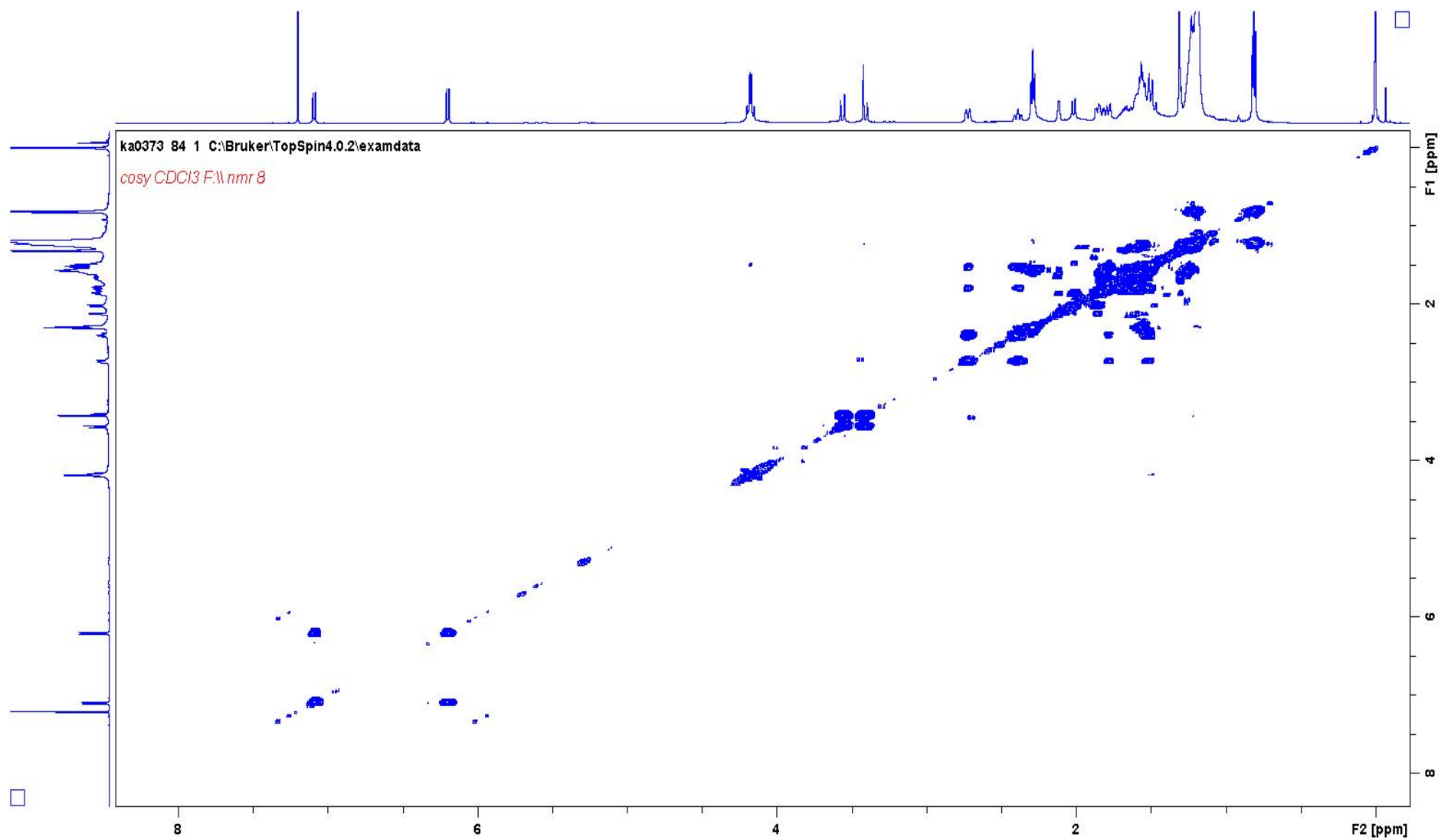


Figure S28 ^1H ^1H COSY spectra of **4** (CD_3Cl)

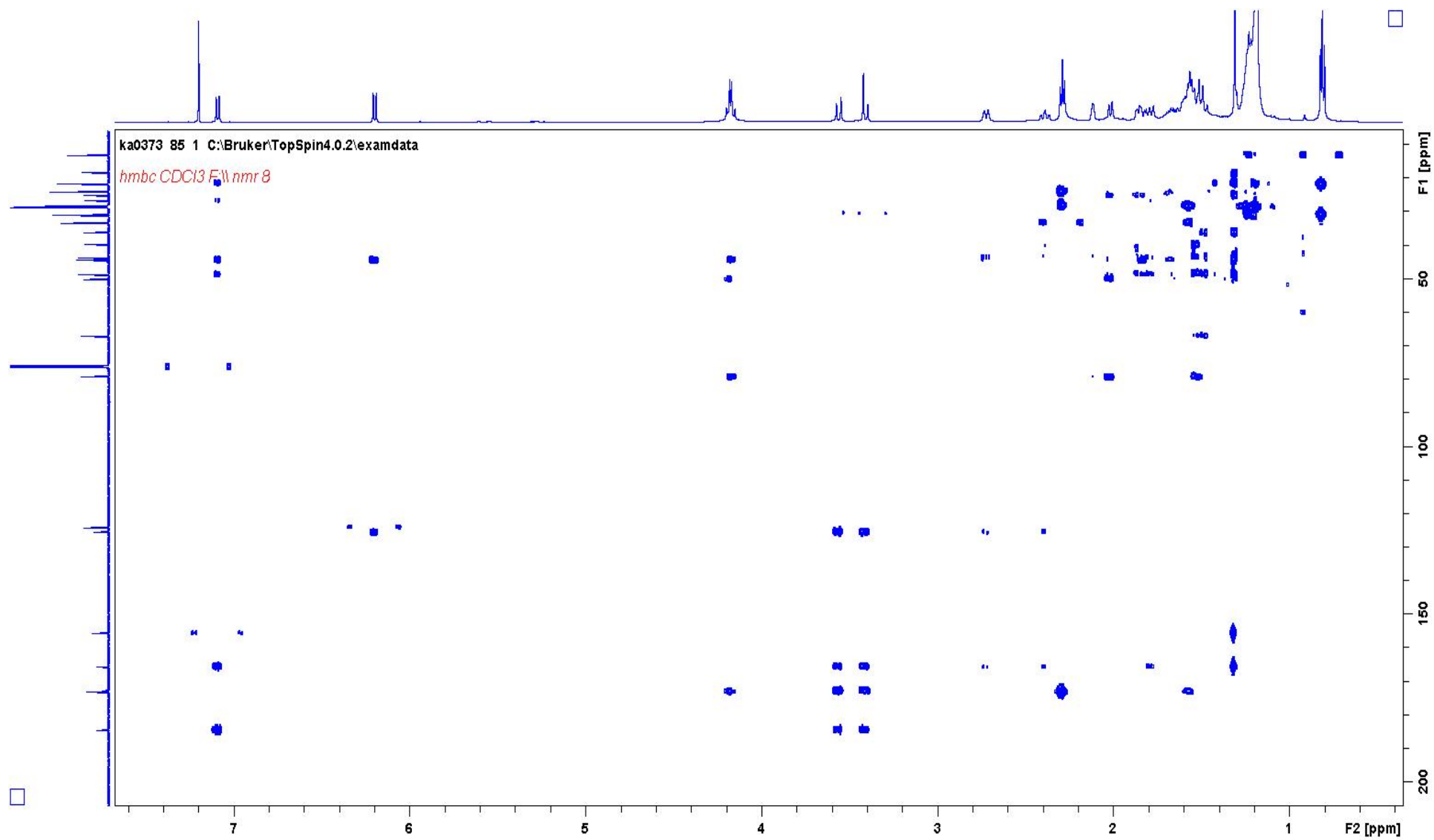


Figure S29 HMBC spectra of **4** (CD₃Cl)

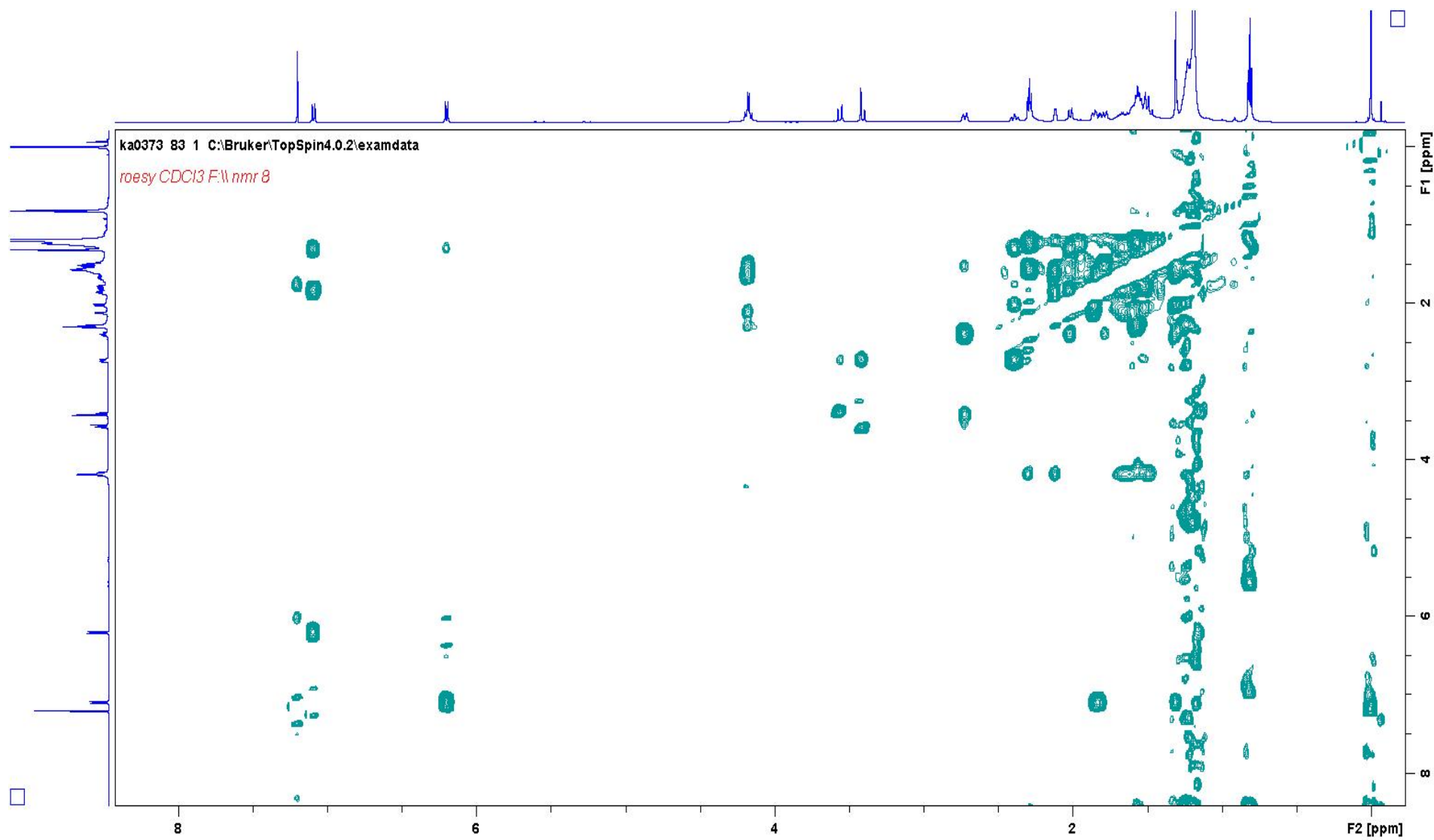


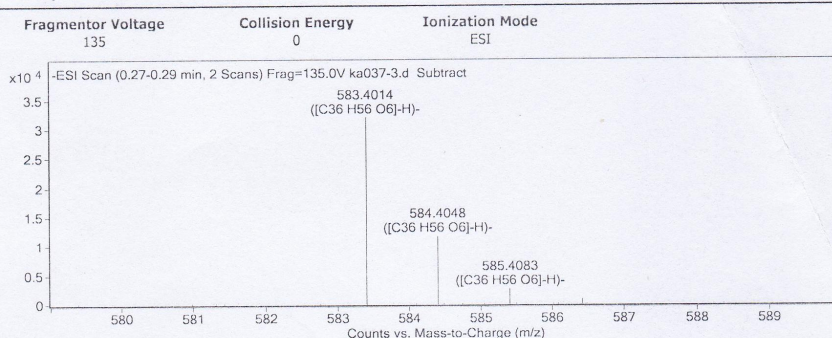
Figure S30 ROESY spectra of **4** (CD₃Cl)

Qualitative Analysis Report

Data Filename	ka037-3.d	Sample Name	ka037-3
Sample Type	Sample	Position	P1-B8
Instrument Name	Instrument 1	User Name	
Acq Method	s-.m	Acquired Time	9/3/2020 11:12:31 AM
IRM Calibration Status	Success	DA Method	Default.m
Comment			

Sample Group	Info.
Acquisition SW	6200 series TOF/6500 series
Version	Q-TOF B.05.01 (B5125.2)

User Spectra



Peak List

m/z	z	Abund	Formula	Ion
112.9855	1	29270.06		
154.9734	1	4791.04		
583.4014	1	31995.64	C36 H56 O6	(M-H)-
584.4048	1	11780.78	C36 H56 O6	(M-H)-
651.3882	1	5125.93		
734.0079	1	7707.34		
982.9912	1	26440.8		
983.9935	1	6442.5		
1033.9881	1	70640.19		
1034.9913	1	16001.08		

Formula Calculator Element Limits

Element	Min	Max
C	3	60
H	0	60
O	0	10
N	0	10

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C36 H56 O6	584.4077	583.4004	583.4014	-1.00	-1.71	9.0000

--- End Of Report ---

Figure S31 HRMS spectra of 4

Table S1 ¹H NMR, ¹³C NMR and DEPT data of compounds 1–4^a

NO.	1 ^c		2 ^b		3 ^b		4 ^b	
1	1.30, m	36.9 (t)	1.26, m	35.4 (t)	3.94, s	78.0 (d)	7.09, d,	155.6 (d)
	1.88, m		1.77, m				10.1	
2	1.65, m	38.3 (t)	1.78, m	33.1 (t)	--	185.1 (s)	6.20, d,	124.0 (d)
	1.75, m		1.82, m				10.1	
3	--	107.3	--	107.0 (s)	--	145.1 (s)	--	184.0 (s)
		(s)						
4	--	173.5	--	170.4 (s)	--	143.0 (s)	--	125.4 (s)
		(s)						
5	2.33, m	48.5 (d)	1.30, m	53.3 (d)	3.09, m	37.6 (d)	--	165.6 (s)
6	1.57, m	21.6 (t)	1.62, m	21.6 (t)	1.68, m	22.5 (t)	2.72, d,	26.6 (t)
	1.64 m		1.64, m		2.02, m		12.8	
							2.39, t,	
							12.8	
7	1.81, m	35.2 (t)	1.63, m	39.4 (t)	1.68, m	39.9 (t)	1.52, m	39.7 (t)
	2.20, m		1.71, m		1.76, m		1.78, m	
8	--	49.8 (s)	--	44.5 (s)	--	44.3 (s)	--	43.6 (s)
9	1.32, m	47.0 (d)	2.07, m	47.3 (d)	2.02, m	43.9 (d)	1.30, m	48.6 (d)
10	--	44.9 (s)	--	43.5 (s)	--	46.9 (s)	--	44.6 (s)
11	1.58, m	20.6 (t)	1.61, 2H,	19.1 (t)	1.59, m	18.2 (t)	1.67, m	18.2 (t)
	1.63, m		m		1.65, m		1.82, m	
12	1.50, m	26.2 (t)	1.58, m	25.8 (t)	1.58, m	26.0 (t)	1.55, m	25.0 (t)
	1.53, m		1.63, m		1.62, m		1.57, m	
13	2.56,	42.4 (d)	2.07, m	45.9 (d)	2.10, m	46.2 (d)	2.02, m	44.3 (d)
	br.d							
14	1.44, m	45.4 (t)	1.73, m	37.4 (t)	1.76, m	37.9 (t)	1.86, m	36.1 (t)
	2.18, m		1.95, m		1.92, m		2.02, m	
15	5.4, s	135.9	1.65, m	52.9 (t)	1.60, m	53.0 (t)	1.49, m	50.0 (t)
		(d)	1.64, m		1.78, m		1.50, m	
16	--	148.1	--	79.9 (s)	--	80.2 (s)	--	79.1 (s)
		(s)						
17	4.12, s	61.1 (t)	4.23, d,	68.1 (t)	4.27,	68.3 (t)	4.15, d,	66.9 (t)
	4.12, s		11.2		2H, s		11.3	
			4.27, d,				4.19, d,	
			11.2				11.3	
18	5.7, s	113.2	5.70, s	114.7 (d)	6.44,	110.4 (d)	3.41, d,	30.9 (t)
		(d)			brs		15.2	
							3.56, d,	
							15.2	
19	--	175.1	--	170.7 (s)	7.65,	149.5 (d)	--	173.1 (s)
		(s)			brs			
20	0.91,	14.6 (q)	0.90, s	14.6 (q)	0.91, s	15.3 (q)	1.31, s	21.5 (q)
	3H, s							
21	--	--	3.11, 3H, s	50.1 (q)	--	--	--	--
1'			--	174.0 (s)	--	174.3 (s)	--	172.7 (s)

2'	2.35, t, 7.3	34.3 (t)	2.36, t, 7.5	34.5 (t)	2.29, t, 7.2	33.2 (t)
3'	1.62, 2H, m	25.0 (t)	1.62, m	25.2 (t)	1.57, m	24.0 (t)
4'-1 3'	1.21-1.33, m	29.1-29. 7 (t)	1.25-1. 30, m	29.4-29.9 (t)	1.18-1.27, m	28.1-28.7 (t)
14'	1.21-1.33, m	32.0 (t)	1.25-1. 30, m	32.1 (t)	1.18-1.27, m	30.9 (t)
15'	1.21-1.33, m	22.7 (t)	1.25-1. 30, m	22.9 (t)	1.18-1.27, m	21.7 (t)
16'	0.90, t, 6.7	14.1 (q)	0.89, t, 6.8	14.3 (q)	0.81, t, 6.7	13.1 (q)

^a δ in parts per million, *J* in Hz, and obtained at 600/150MHz. NMR solvent was ^bCDCl₃, ^cCD₃OD

3. Calculated NMR for compound 1

Theoretical calculations of compound **1** was performed using Gaussian 16¹. Conformation searches of **1** were performed employing the CREST computer code (version 2.10.2) using the default iMTD-GC procedure. The conformers were optimized further by the DFT method at the B3LYP/6-31G(d) level using the Gaussian 16 program. NMR calculation of **1** was calculated with the GIAO method³ at mPW1PW91/6-31+G (d, p) in methanol. The shielding constants (including ¹³C and ¹H) obtained were directly performed statistical analyses with experimental chemical shifts by using DP4⁺ ³probability.

Reference

- (1) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.
- (2) Grimblat, N.; Zanardi, M. M.; Sarotti, A. M. *J. Org. Chem.* 2015, 80, 12526.
- (3) Srebro-Hooper, M.; Autschbach, J. *Annu. Rev. Phys. Chem.* 2017, 68, 399.

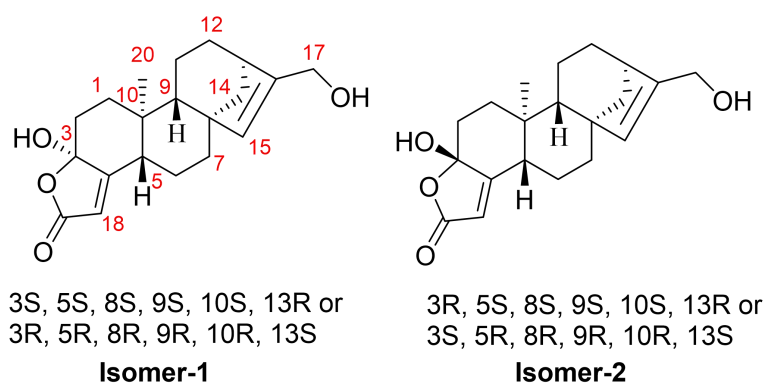


Figure S32 Possible diastereoisomers of **1**

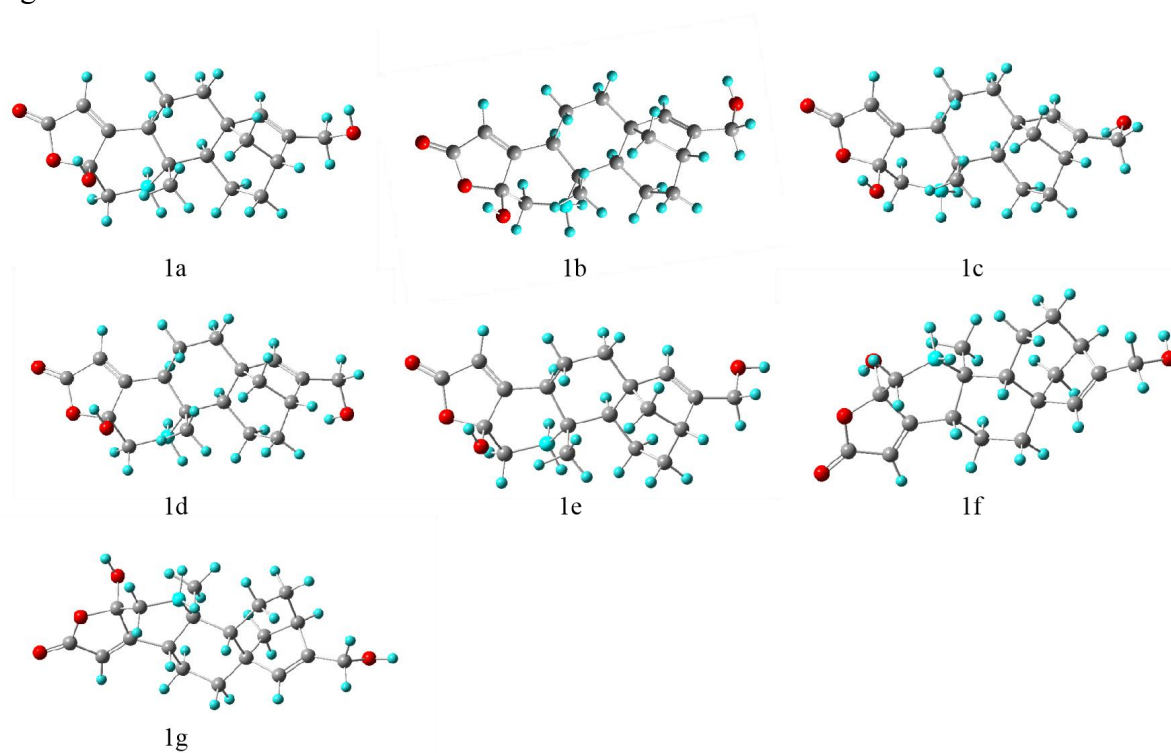


Figure S33 Conformers of isomer-1

Table S2 Boltzmann distributions of the optimized isomer-1

Conformations	Δ (kcal/mol)	%
1a	0	31.79%
1b	0.2	22.68%
1c	0.44	15.12%
1d	0.66	10.42%
1e	0.69	9.91%
1f	0.91	6.83%
1g	1.35	3.25%

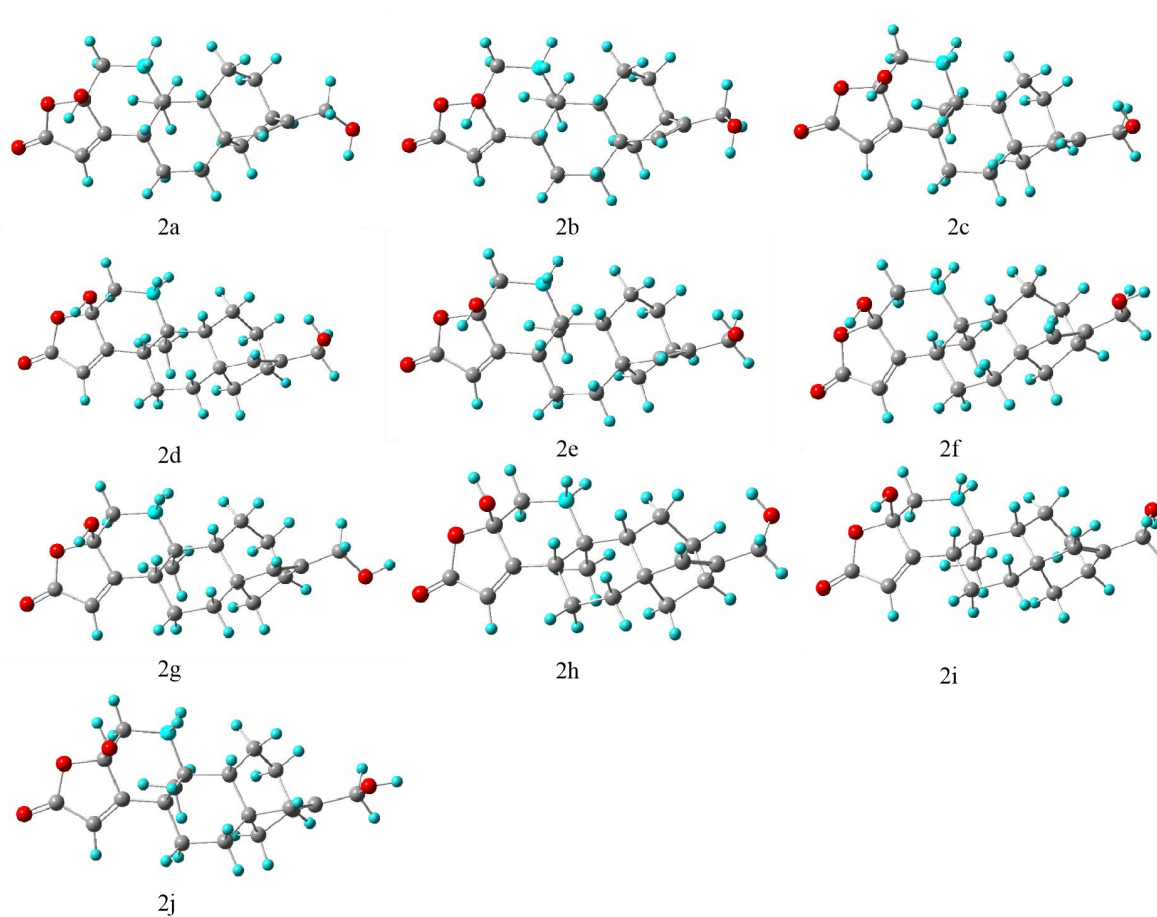


Figure S34 Conformers of isomer-2

Table S3 Boltzmann distributions of the optimized isomer-2

Conformations	Δ (kcal/mol)	%
2a	0	28.29%
2b	0.33	16.20%
2c	0.57	10.80%
2d	0.59	10.44%
2e	0.61	10.10%
2f	0.73	8.24%
2g	0.91	6.08%
2h	1.19	3.79%
2i	1.29	3.20%
2j	1.36	2.84%

Table S4 Calculated shielding tensors and chemical shifts of isomers

Nuclie	Exptl. data	Isomer-1			Isomer-2		
		σ_{iso}	unscaled	scaled	σ_{iso}	unscaled	scaled
C-1	36.9	160.21	36.09	38.19	160.33	35.96	38.28
C-2	38.3	164.69	31.60	39.56	159.07	37.22	39.64
C-3	107.3	91.64	104.65	107.02	92.28	104.02	106.47
C-4	173.5	18.38	177.92	171.75	21.60	174.70	170.59
C-5	48.5	145.50	50.80	49.53	146.99	49.31	49.52
C-6	21.6	170.63	25.66	23.23	173.16	23.13	23.46
C-7	35.2	156.10	40.20	36.53	157.59	38.71	36.64
C-8	49.8	144.45	51.84	50.80	144.64	51.66	50.78
C-9	47.0	147.53	48.77	48.07	148.73	47.56	48.07
C-10	44.9	155.42	40.87	46.01	148.23	48.07	46.03
C-11	20.6	173.62	22.68	22.26	172.90	23.40	22.50
C-12	26.2	168.21	28.09	27.73	168.39	27.90	27.92
C-13	42.4	151.80	44.50	43.57	151.93	44.36	43.61
C-14	45.4	149.37	46.92	46.50	149.38	46.91	46.52
C-15	135.9	62.20	134.09	134.98	61.96	134.34	134.17
C-16	148.1	47.54	148.76	146.91	47.83	148.47	145.99
C-17	61.1	133.12	63.17	61.85	133.11	63.19	61.72
C-18	113.2	83.05	113.24	112.79	85.35	110.94	112.19
C-19	175.1	28.28	168.01	173.31	28.87	167.42	172.14
C-20	14.6	177.12	19.17	16.39	180.62	15.68	16.68
H-1	1.3	29.59	1.86	1.34	29.82	1.3	1.14
H-1	1.88	30.06	1.40	1.90	30.25	1.88	1.74
H-2	1.65	29.51	1.95	1.68	29.72	1.65	1.50
H-2	1.75	29.70	1.75	1.78	29.74	1.75	1.61
H-5	2.33	29.21	2.24	2.34	29.14	2.33	2.21
H-6	1.57	29.62	1.83	1.60	29.87	1.57	1.42
H-6	1.64	29.74	1.72	1.67	30.01	1.64	1.49
H-7	1.81	29.82	1.64	1.84	29.84	1.81	1.67
H-7	2.20	30.04	1.42	2.22	30.04	2.20	2.07
H-9	1.32	30.64	0.82	1.36	30.36	1.32	1.16
H-11	1.58	29.89	1.57	1.61	29.78	1.58	1.43
H-11	1.63	30.09	1.36	1.66	30.07	1.63	1.48
H-12	1.50	29.98	1.48	1.53	30.09	1.50	1.35
H-12	1.53	30.01	1.44	1.56	30.12	1.53	1.38
H-13	2.56	28.91	2.55	2.57	29.32	2.56	2.44
H-14	1.44	29.24	2.21	1.47	29.64	1.44	1.28
H-14	2.18	30.37	1.09	2.20	30.06	2.18	2.05
H-15	5.4	25.79	5.67	5.34	25.76	5.4	5.38

H-17	4.12	27.21	4.25	4.09	27.22	4.12	4.06
H-17	4.12	27.36	4.10	4.09	27.35	4.12	4.06
H-19	5.7	25.65	5.81	5.63	25.87	5.7	5.69
H-20	0.91	29.27	2.19	0.96	30.23	0.91	0.74
H-20	0.91	30.13	1.32	0.96	30.87	0.91	0.74
H-20	0.91	30.77	0.68	0.96	30.99	0.91	0.74

Table S5 Detailed DP4+ probability of 1(calculated at mPW1PW91/6-311G (d) level

	A	B	C	D	E	F	G	H
1	Functional		Solvent?		Basis Set		Type of Data	
2	mPW1PW91		PCM		6-311G(d,p)		Shielding Tensors	
3								
4			Isomer 1	Isomer 2	Isomer 3	Isomer 4	Isomer 5	Isomer 6
5	sDP4+ (H data)		0.00%	100.00%	-	-	-	-
6	sDP4+ (C data)		0.00%	100.00%	-	-	-	-
7	sDP4+ (all data)		0.00%	100.00%	-	-	-	-
8	uDP4+ (H data)		0.00%	100.00%	-	-	-	-
9	uDP4+ (C data)		98.55%	1.45%	-	-	-	-
10	uDP4+ (all data)		0.01%	99.99%	-	-	-	-
11	DP4+ (H data)		0.00%	100.00%	-	-	-	-
12	DP4+ (C data)		0.02%	99.98%	-	-	-	-
13	DP4+ (all data)		0.00%	100.00%	-	-	-	-

4. Antibodies used for western blotting

Table S6 Antibodies used for western blotting.

Antigen	Catalogue	Maker	MW, kDa	Dilution
PPAR γ	2435	Cell signalling, Danvers, MA, UK	~53-57	1:2000
C/EBP β	3087	Cell signalling, Danvers, MA, UK	~35-38	1:1000
C/EBP α	2295	Cell signalling, Danvers, MA, UK	~42	1:1000
FABP4	2120	Cell signalling, Danvers, MA, UK	~15	1:2000
FAS	3180	Cell signalling, Danvers, MA, UK	~273	1:1000
SCD1	2794	Cell signalling, Danvers, MA, UK	~37	1:1000
CDK2	18048	Cell signalling, Danvers, MA, UK	~33	1:1000
CDK4	12790	Cell signalling, Danvers, MA, UK	~30	1:1000
Cyclin D1	ET1601-31	HuaBio	~34	1:1000
E2F-1	3742	Cell signalling, Danvers, MA, UK	~70	1:1000
p21	64016	Cell signalling, Danvers, MA, UK	~21	1:1000
p27	3698	Cell signalling, Danvers, MA, UK	~27	1:1000
P-GSK-3 β (Ser9)	5558	Cell signalling, Danvers, MA, UK	~46	1:1000
GSK-3 β	12456	Cell signalling, Danvers, MA, UK	~46	1:1000
P-Akt (Ser473)	4060	Cell signalling, Danvers, MA, UK	~60	1:1000
Akt	4691	Cell signalling, Danvers, MA, UK	~60	1:1000
P-mTOR (Ser2448)	5536	Cell signalling, Danvers, MA, UK	~289	1:1000
mTOR	2983	Cell signalling, Danvers, MA, UK	~289	1:1000
β -actin	4970	Cell signalling, Danvers, MA, UK	~45	1:1000