

Supplementary Materials

Penigrisacids A–D, Four New Sesquiterpenes from the Deep-Sea-Derived *Penicillium griseofulvum*

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Table S1. Energy analysis for 2*S*,3*R*,6*S*,7*R*-**1**, (6*S*,7*R*,10*S*,11*S*)-**2**, and (2*R*,3*R*,6*S*,7*S*,10*R*)-**3**.

Compounds	conformers	Gibbs free energy (298.15 K)		
		G (Hartree)	ΔE (kcal/mol)	Population (%)
1	C1	-885.814127	0	100
2	C1	-887.0162631	0	59.96
	C2	-887.0152285	0.001035	20.02
	C3	-887.0152282	0.001035	20.02
3	C1	-962.2614876	0	52.37
	C2	-962.2613983	0.00008937	47.63

Table S2. Calculated ECD data for 2S,3R,6S,7R-**1 (1a)** and (6S,7R,10S,11S)-**2 (2a)**

State	Excitation energies (ev)				Rotatory strength ^a			
	1-C1	2-C1	2-C2	2-C3	1-C1	2-C1	2-C2	2-C3
1	5.3386	4.8494	4.8272	4.8275	5.9147	12.8201	-6.5465	-6.4019
2	5.6098	5.0891	5.0568	5.0574	1.5175	-39.5845	-7.6845	-7.7548
3	5.6571	5.4380	5.4254	5.4254	1.4859	24.4594	-2.1097	-2.1647
4	5.9040	5.7025	5.7052	5.7059	-26.2110	2.3496	1.8929	1.9463
5	6.0490	5.8931	5.8368	5.8367	-19.7277	16.4094	5.2373	5.2511
6	6.1331	6.0712	6.0482	6.0486	86.8292	-20.3495	-18.0219	-18.1252
7	6.1920	6.1616	6.1704	6.1707	-2.5575	-9.4667	-7.3380	-7.1236
8	6.2694	6.2215	6.1878	6.1883	5.3327	-4.6239	-0.6867	-0.7401
9	6.3591	6.3439	6.3660	6.3666	-3.5681	-2.7571	-3.6331	-3.6922
10	6.5186	6.4326	6.4180	6.4180	-13.3508	24.5131	20.3259	20.4596
11	6.5400	6.5040	6.5172	6.5183	-6.1392	-0.8312	0.4324	0.4102
12	6.6821	6.6334	6.6006	6.6007	-3.6383	29.6529	20.4106	20.3614
13	6.6953	6.6602	6.6420	6.6419	3.6735	-7.6371	-4.7818	-4.9282
14	6.7627	6.7227	6.7220	6.7223	-0.6138	-40.5224	-13.0492	-13.0714
15	6.7899	6.7369	6.7459	6.7463	-0.2693	22.7328	-1.8263	-2.0245
16	6.8946	6.7896	6.7941	6.7944	-4.9629	2.3344	0.2456	0.3429
17	6.9521	6.8813	6.8291	6.8295	-11.3712	-13.2261	-15.5354	-15.4001
18	6.9882	6.8967	6.8945	6.8947	7.8980	1.0085	6.3925	6.3062
19	7.0152	6.9080	6.9061	6.9061	2.7649	5.6400	-8.4112	-8.3278
20	7.0436	6.9896	6.9745	6.9746	-6.1447	4.1590	-6.0588	-5.8168
21	7.1016	7.0294	7.0454	7.0455	4.3433	-29.5758	44.2191	44.2126
22	7.1203	7.1363	7.1145	7.1144	-0.7839	-4.4138	-3.8099	-3.8801
23	7.1817	7.1959	7.1828	7.1829	7.0059	5.1211	5.9225	5.8723
24	7.2850	7.2038	7.1948	7.1948	11.4784	22.6396	0.6583	0.8543
25	7.3096	7.2167	7.2080	7.2082	-6.3801	3.1666	26.1300	25.9073
26	7.3168	7.2373	7.2280	7.2280	2.3336	0.5304	-5.2686	-5.2962
27	7.3593	7.3057	7.3086	7.3086	-0.4547	-12.4655	-8.8393	-8.6322
28	7.3708	7.3223	7.3278	7.3279	-10.0520	1.7436	-38.9753	-39.6880
29	7.4080	7.3693	7.3410	7.3412	-9.1630	-5.6420	4.3430	4.6839
30	7.4528	7.4067	7.3889	7.3891	2.6219	12.0279	-3.1905	-3.0816

^a R(velocity) 10**-40 erg-esu-cm

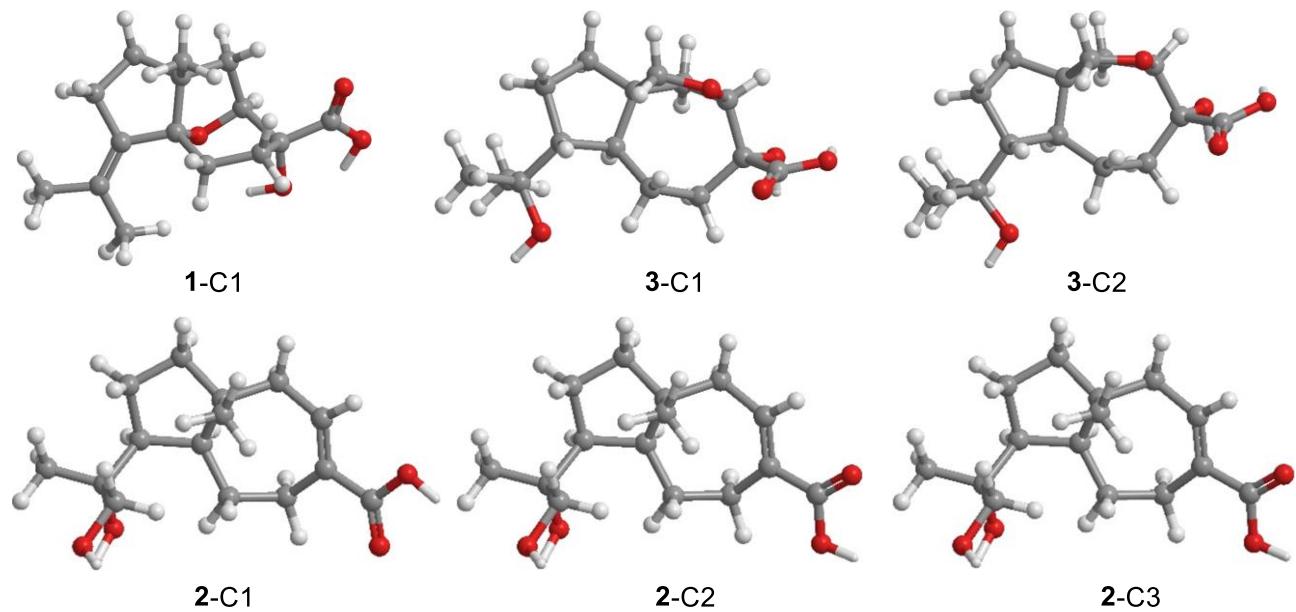
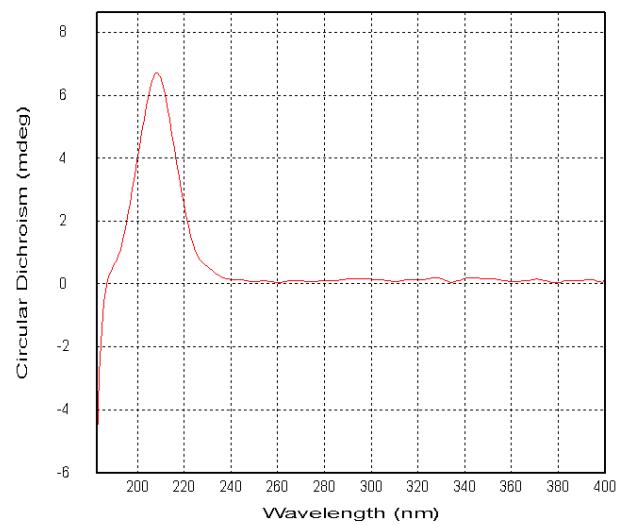
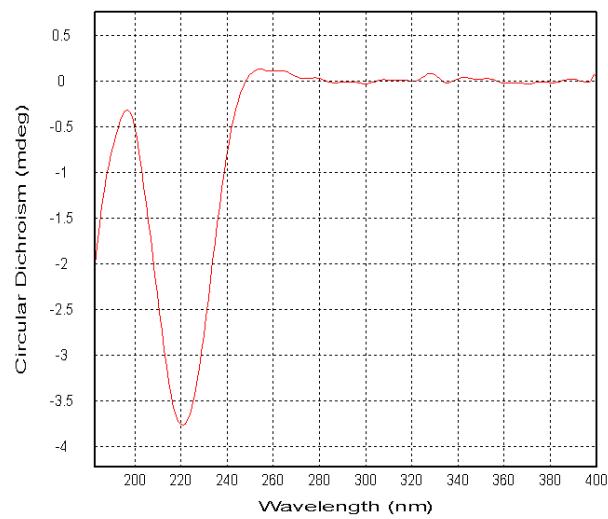


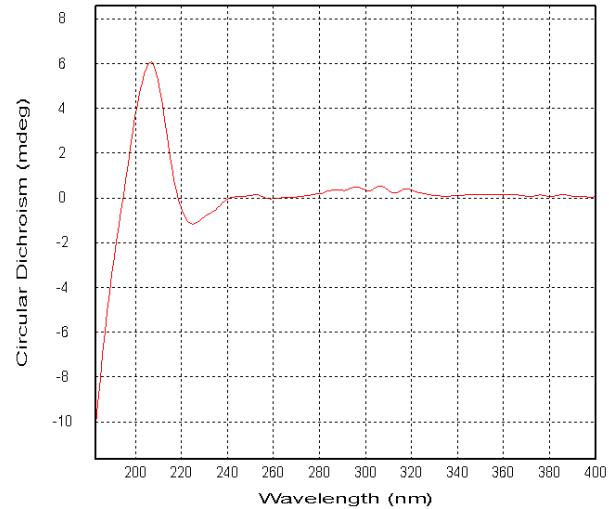
Figure S1. B3LYP-SCRF (PCM, ACN)/6-31G(d) optimized lowest energy conformers for 2*S*,3*R*,6*S*,7*R*-**1** (**1a**), (6*S*,7*R*,10*S*,11*S*)-**2**, and (2*R*,3*R*,6*S*,7*S*,10*R*)-**3**.



3



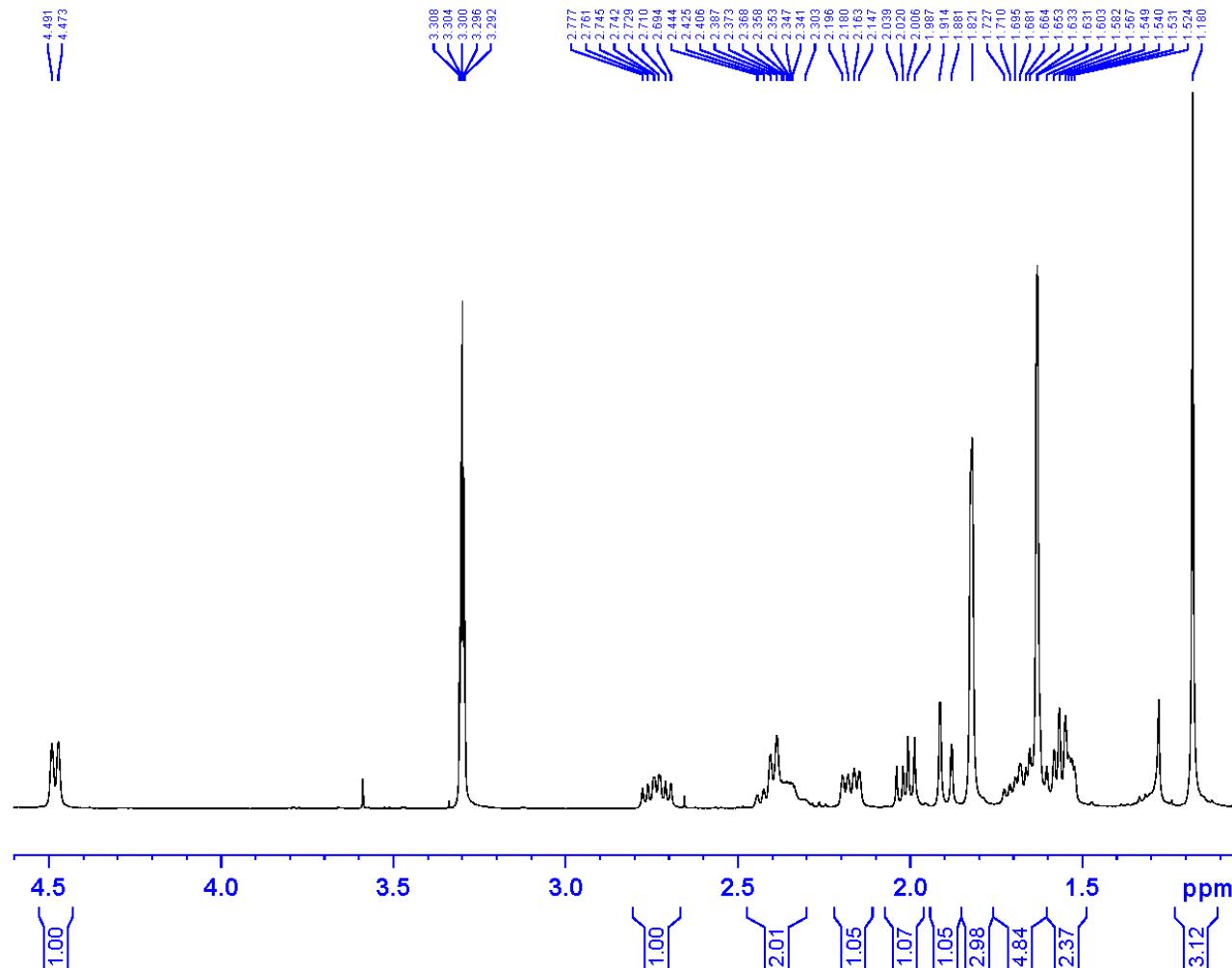
4



5

Figure S2. The CD spectra of compounds **3–5** in ACN.

xin3-14 H



Current Data Parameters
NAME xin3-14
EXPNO 1
PROCNO 1

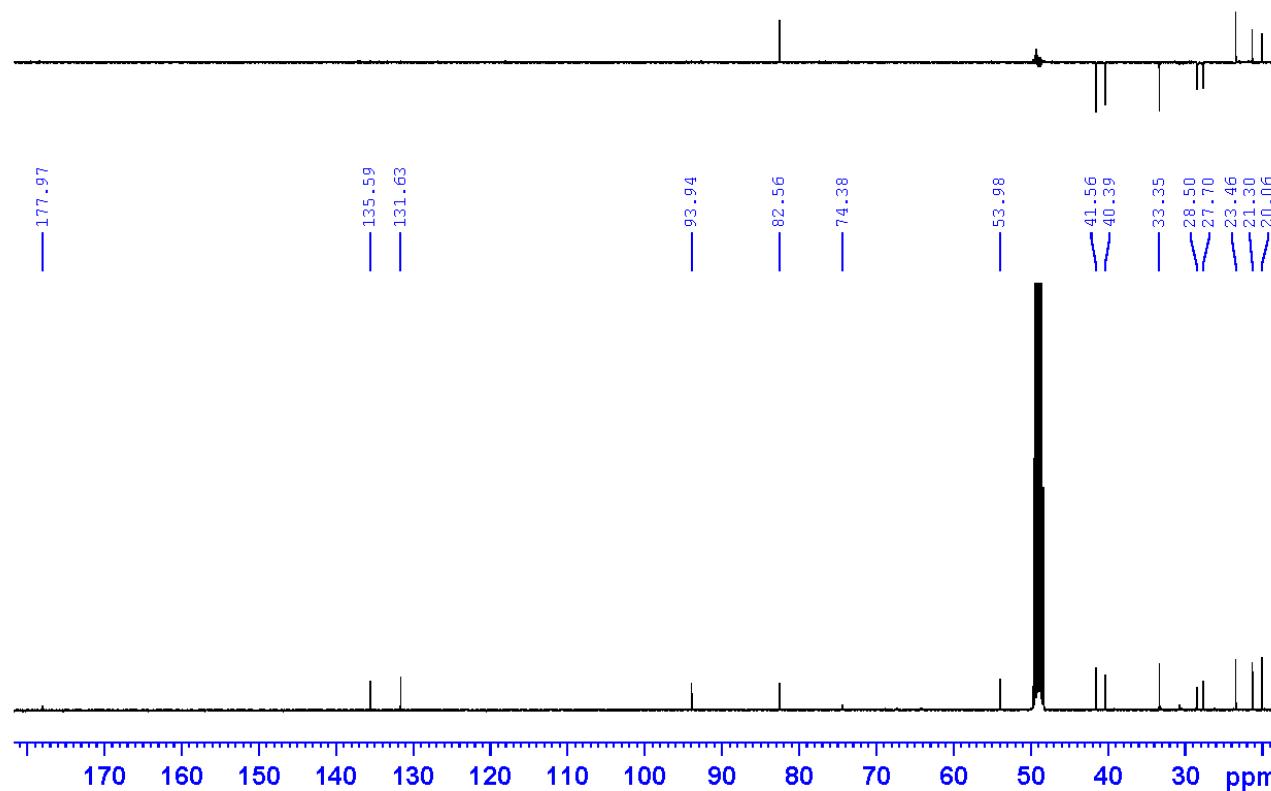
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PULPROG zg30
TD 65536
SOLVENT MeOD
NS 18
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 295.9 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.09 usec
PL1 -1.00 dB
PL1W 12.14314651 W
SF01 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300068 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S3. ^1H NMR spectrum of **1** in CD_3OD .

xin3-14 C



Current Data Parameters
NAME xin3-14
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180331
Time 19.57
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 10240
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.1 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 ¹³C
P1 12.37 usec
PL1 1.00 dB
PL1W 28.13319778 W
SFO1 100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG[2] waltz16
NUC2 ^{1H}
PCPD2 80.00 usec
PL2 -1.00 dB
PL12 14.72 dB
PL13 14.50 dB
PL2W 12.14314651 W
PL12W 0.32533529 W
PL13W 0.34224036 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6126270 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S4. ¹³C NMR spectrum of **1** in CD_3OD .

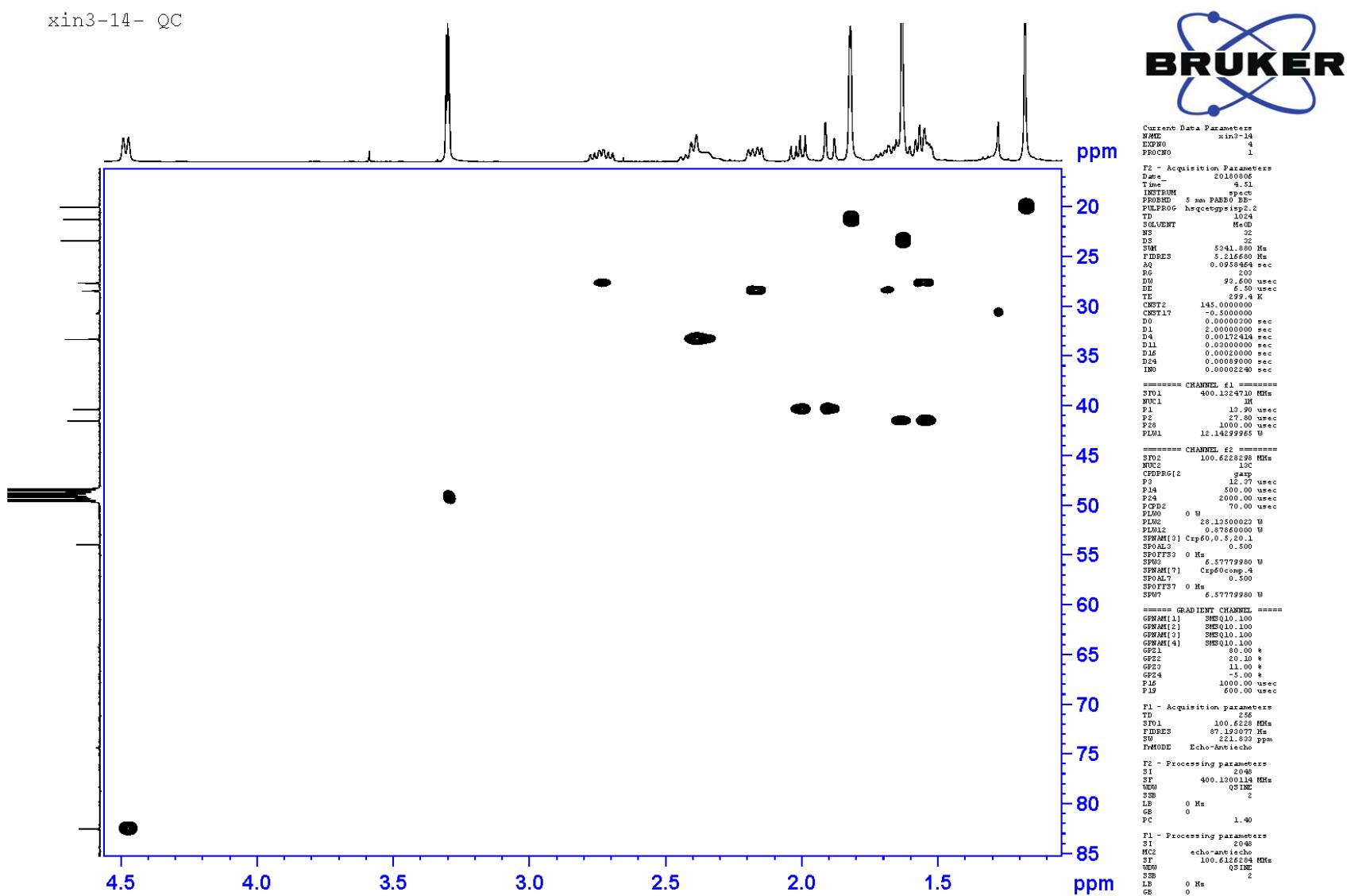


Figure S5. HSQC spectrum of **1** in CD_3OD .

xin3-14-cosy

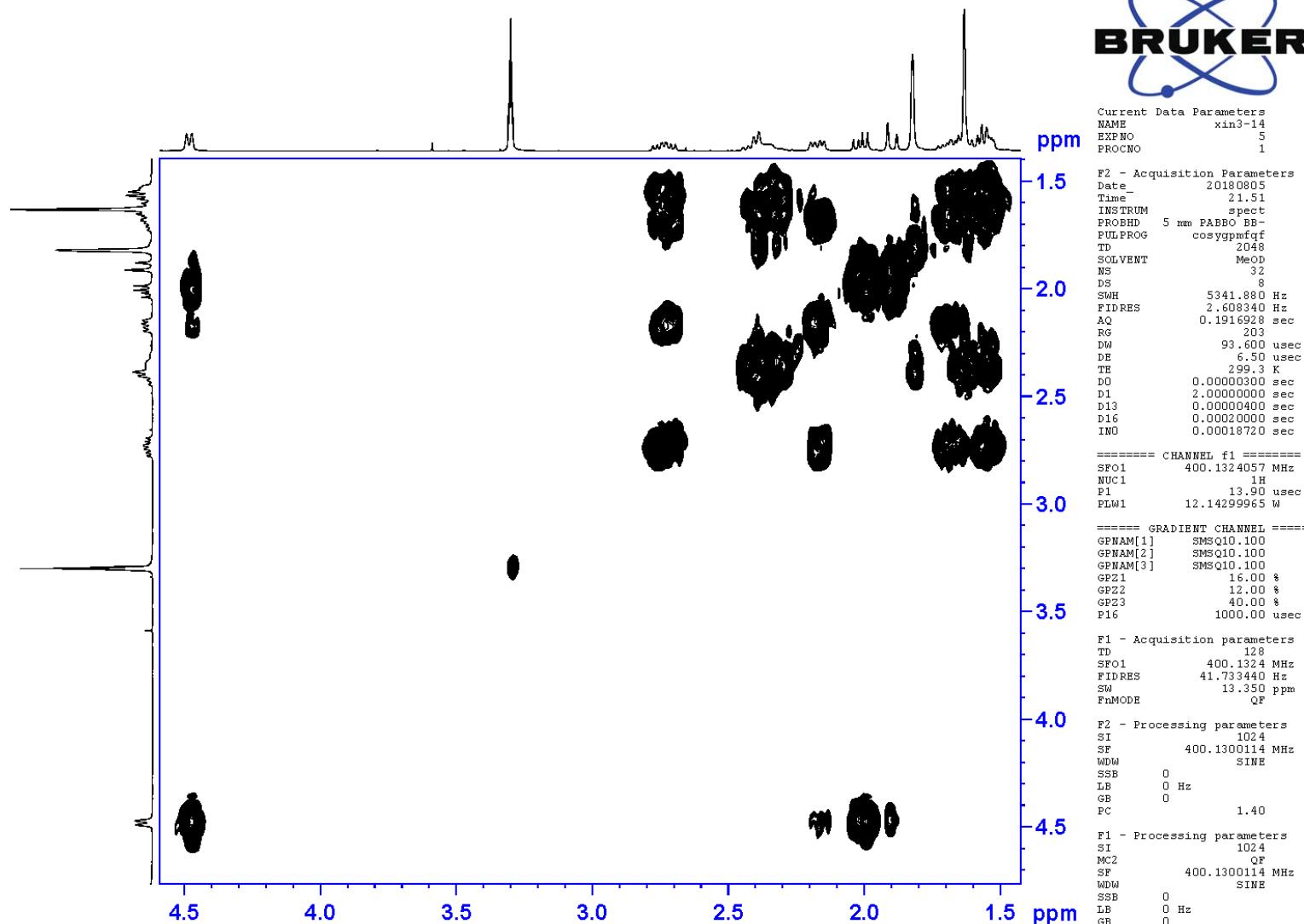


Figure S6. COSY NMR spectrum of **1** in CD₃OD.

xin3-14-bc



Current Data Parameters
NAME xin3-14
EXPNO 6
PROCNO 1

F2 - Acquisition Parameters
Date 20180806
Time 0.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG habcgndqf
TD 4096
SOLVENT MeOD
NS 64
DS 16
SWH 5330.490 Hz
FIDRES 1.301389 Hz
AQ 0.384204 sec
RG 93.800 usec
DM 93.800 usec
DE 6.50 usec
TE 299.2 K
CNUST13 8.0000000
D0 0.00000300 sec
D1 1.50000000 sec
D6 0.06250000 sec
D16 0.00020000 sec
INO 0.00002240 sec

===== CHANNEL f1 =====
SF01 400.1324057 MHz
NUC1 1H
P1 13.90 usec
P2 27.80 usec
PLW1 12.14299965 W

===== CHANNEL f2 =====
SF02 100.6228143 MHz
NUC2 13C
P3 12.37 usec
PLW2 28.13500023 W

===== GRADIENT CHANNEL =====
GPNAME[1] SMSQ10.100
GPNAME[2] SMSQ10.100
GPNAME[3] SMSQ10.100
GPZ1 50.00 %
GPZ2 30.00 %
GPZ3 40.10 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 128
SF01 100.6228 MHz
FIDRES 174.386154 Hz
SW 221.633 ppm
PwMode QF

F2 - Processing parameters
SI 1024
SF 400.13000114 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0
PC 1.40

F1 - Processing parameters
SI 1024
MC2 0F
SF 100.6126284 MHz
WDW SINE
SSB 0
LB 0 Hz
GB 0

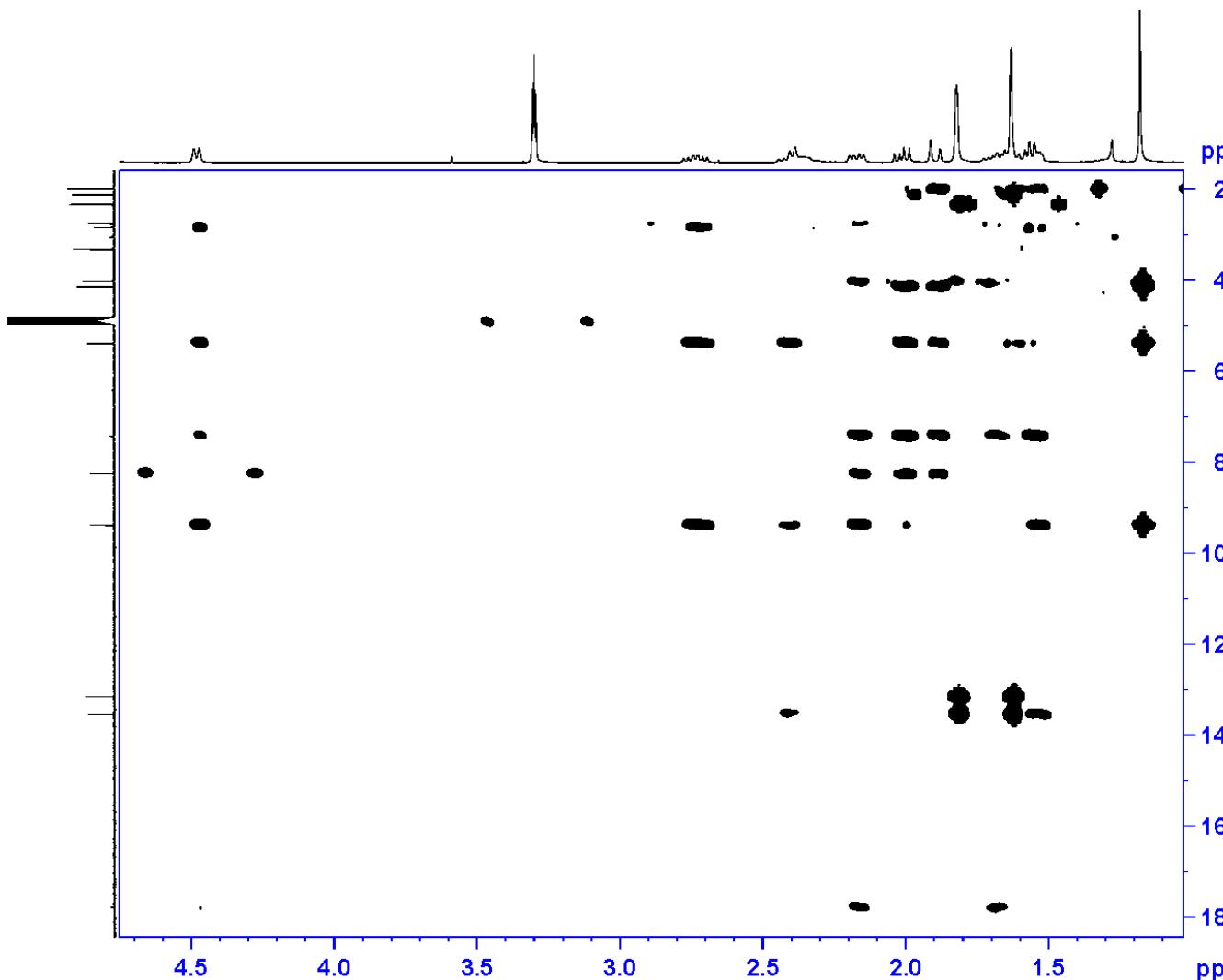


Figure S7. HMBC NMR spectrum of **1** in CD₃OD.

xin3-14-NOESY

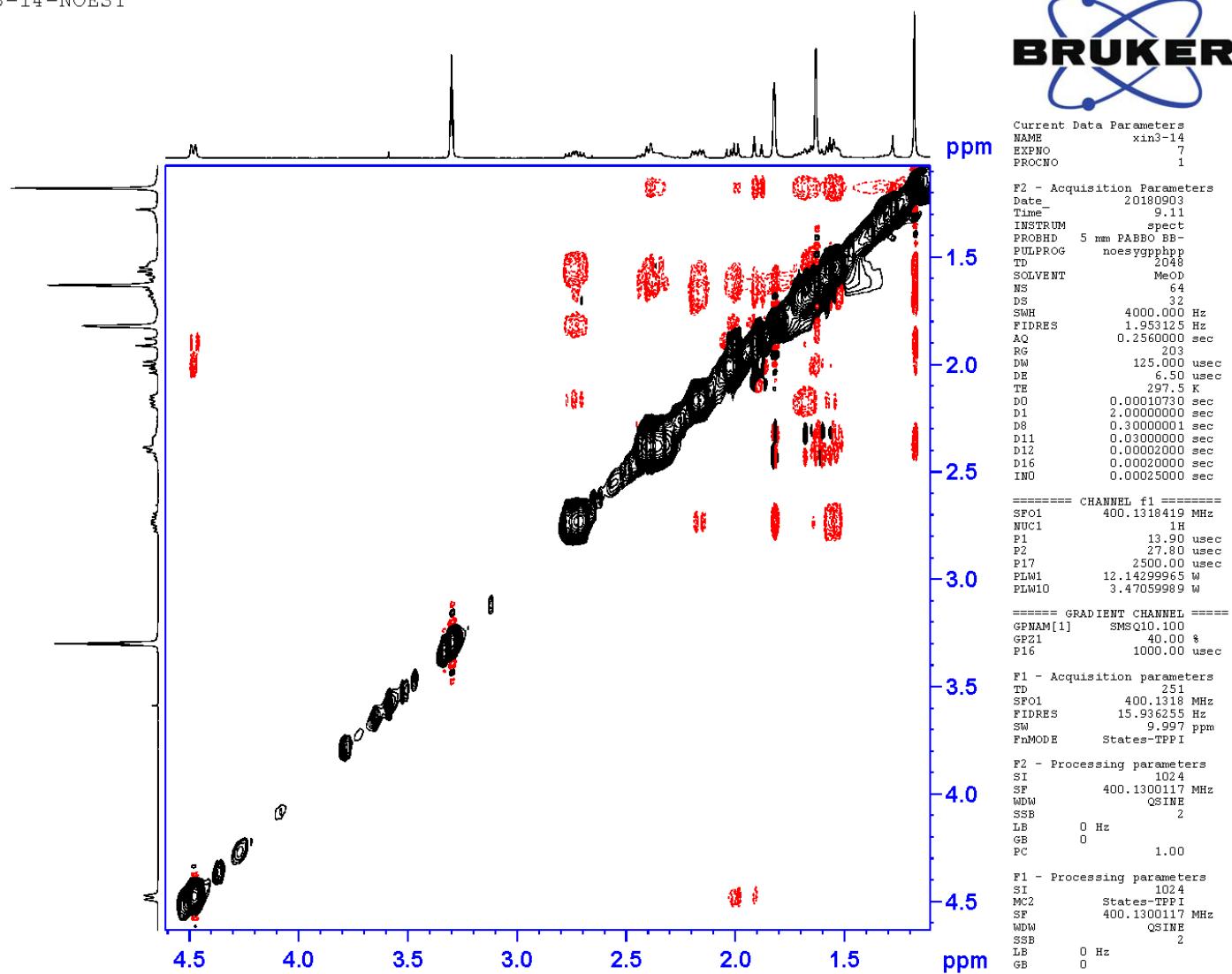


Figure S8. NOESY NMR spectrum of **1** in CD₃OD.

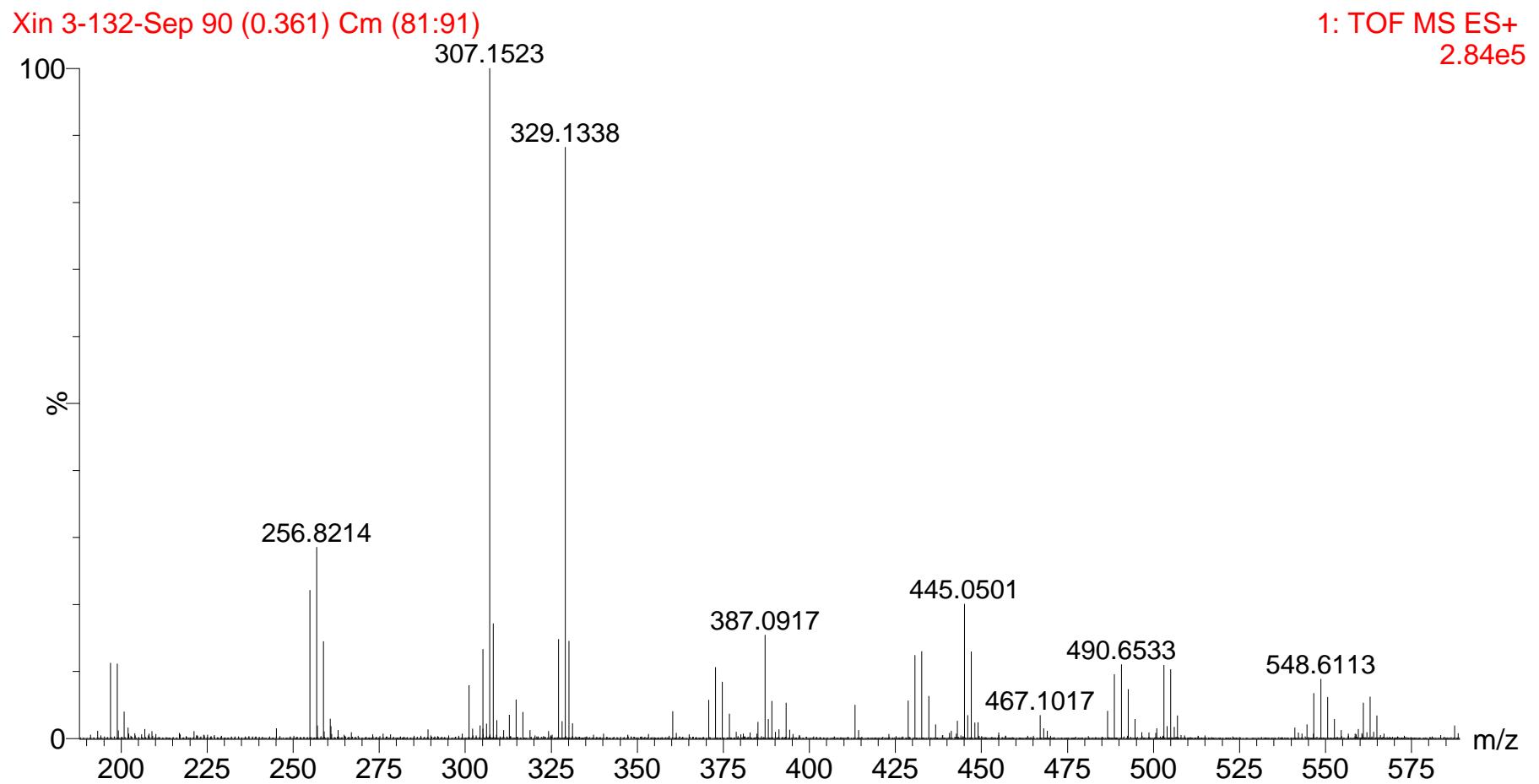
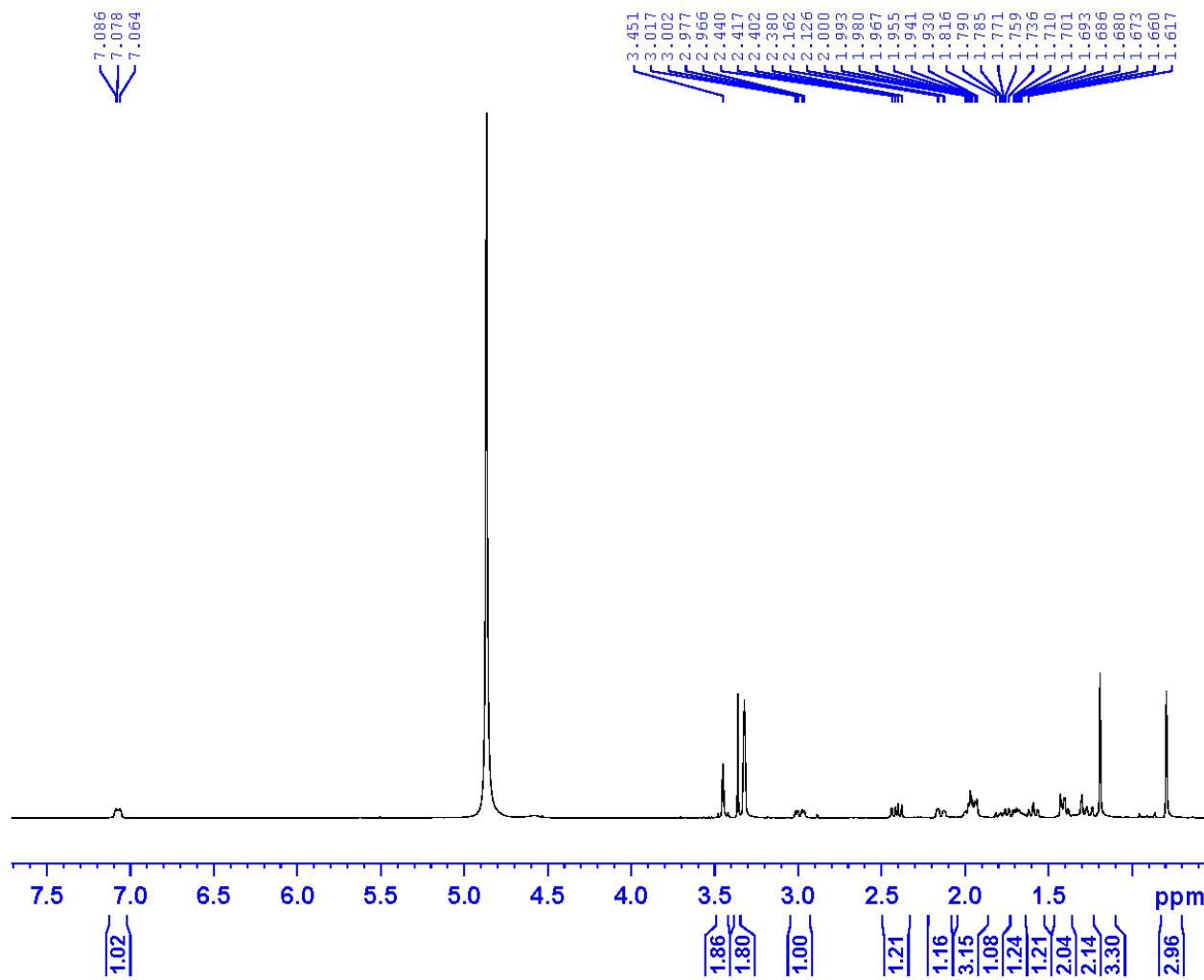


Figure S9. The HR-ESI-MS spectrum of **1**.

xin3-85 H



Current Data Parameters
NAME xin3-85
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180730
Time_ 11.27
INSTRUM spect
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PULPROG zg30
TD 65536
SOLVENT MeOD
NS 19
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 297.9 K
D1 1.0000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.09 usec
PL1 -1.00 dB
PL1W 12.14314651 W
SFO1 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1299974 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S10. ^1H NMR spectrum of **2** in CD_3OD .

xin3-85 C

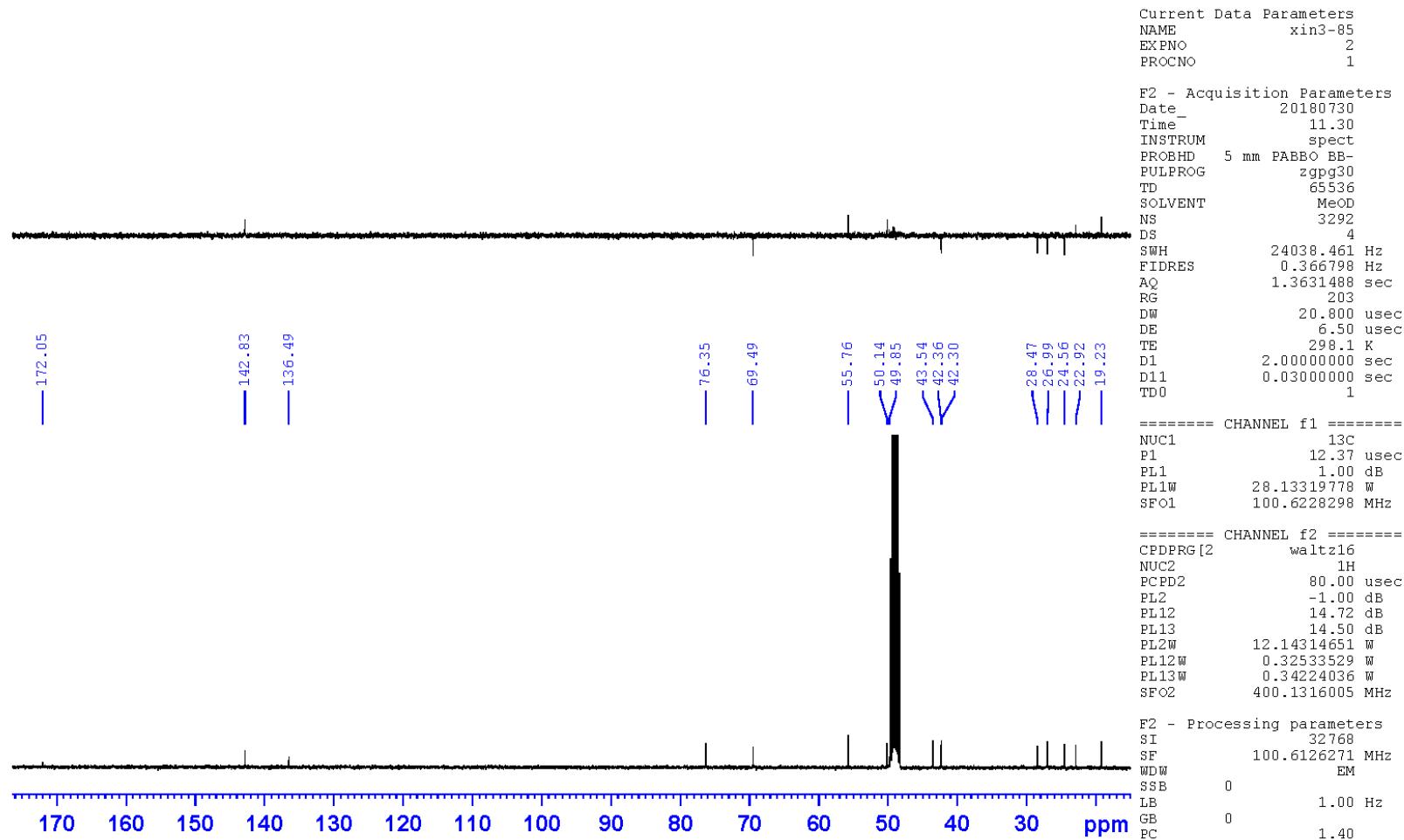


Figure S11. ^{13}C NMR spectrum of **2** in CD_3OD .

xin3-85-QC

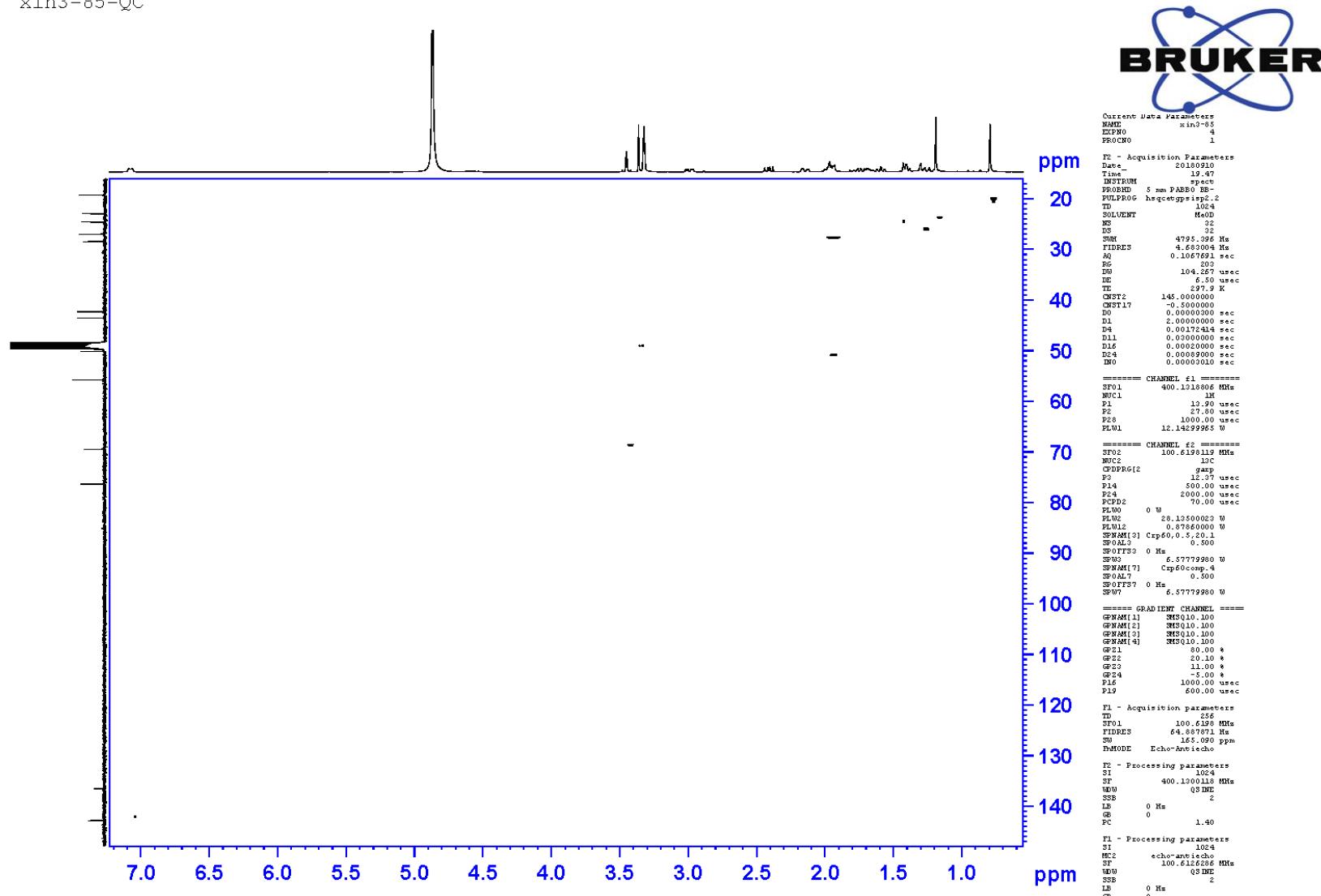


Figure S12. HSQC spectrum of **2** in CD₃OD.

xin3-85-COSY

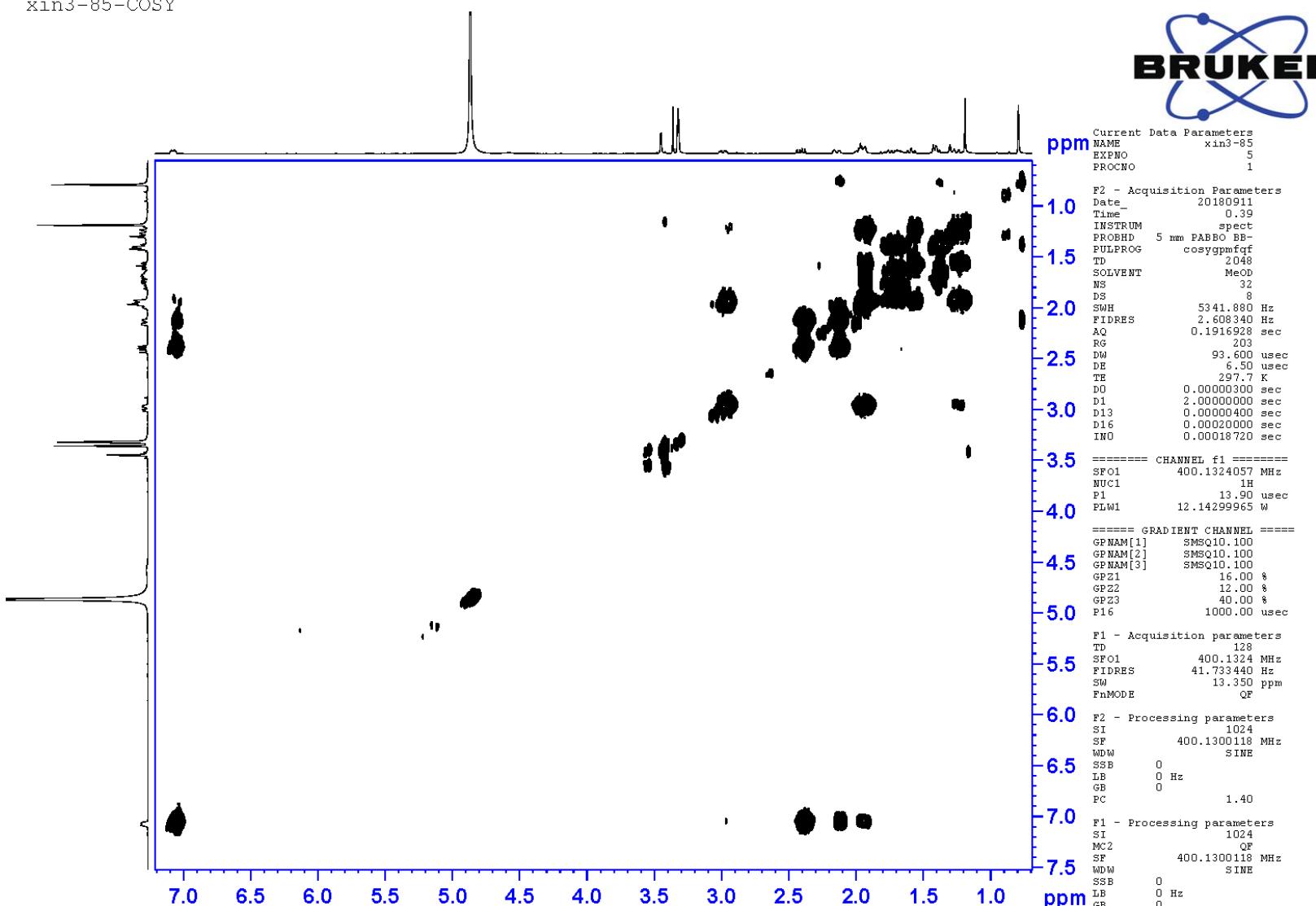


Figure S13. COSY NMR spectrum of **2** in CD₃OD.

xin3-85-BC

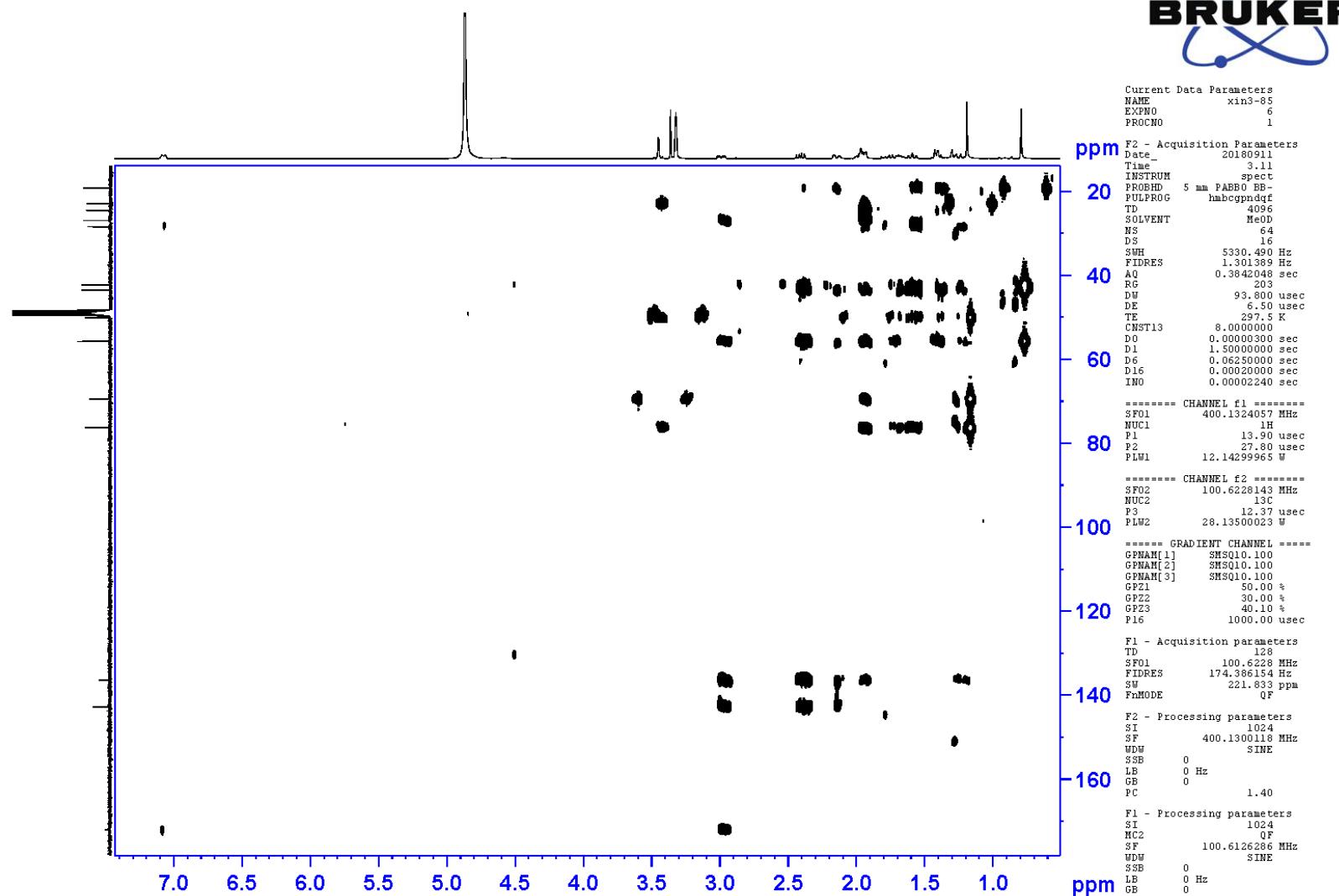


Figure S14. HMBC NMR spectrum of 2 in CD_3OD .

xin3-85-NOESY

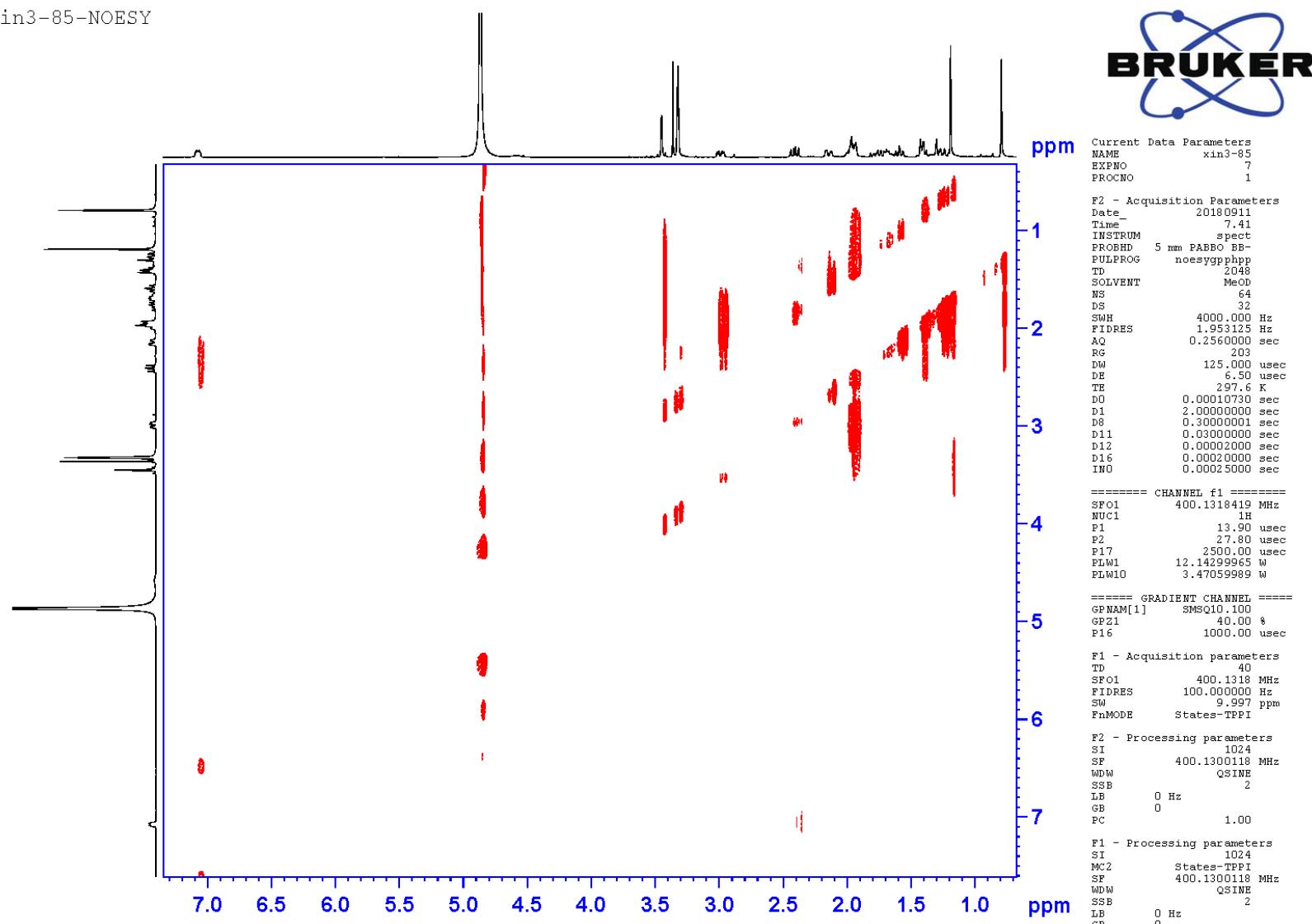


Figure S15. NOESY NMR spectrum of **2** in CD₃OD.

Xin 3-74-Aug 118 (0.461) Cm (101:139)

1: TOF MS ES+
1.50e7

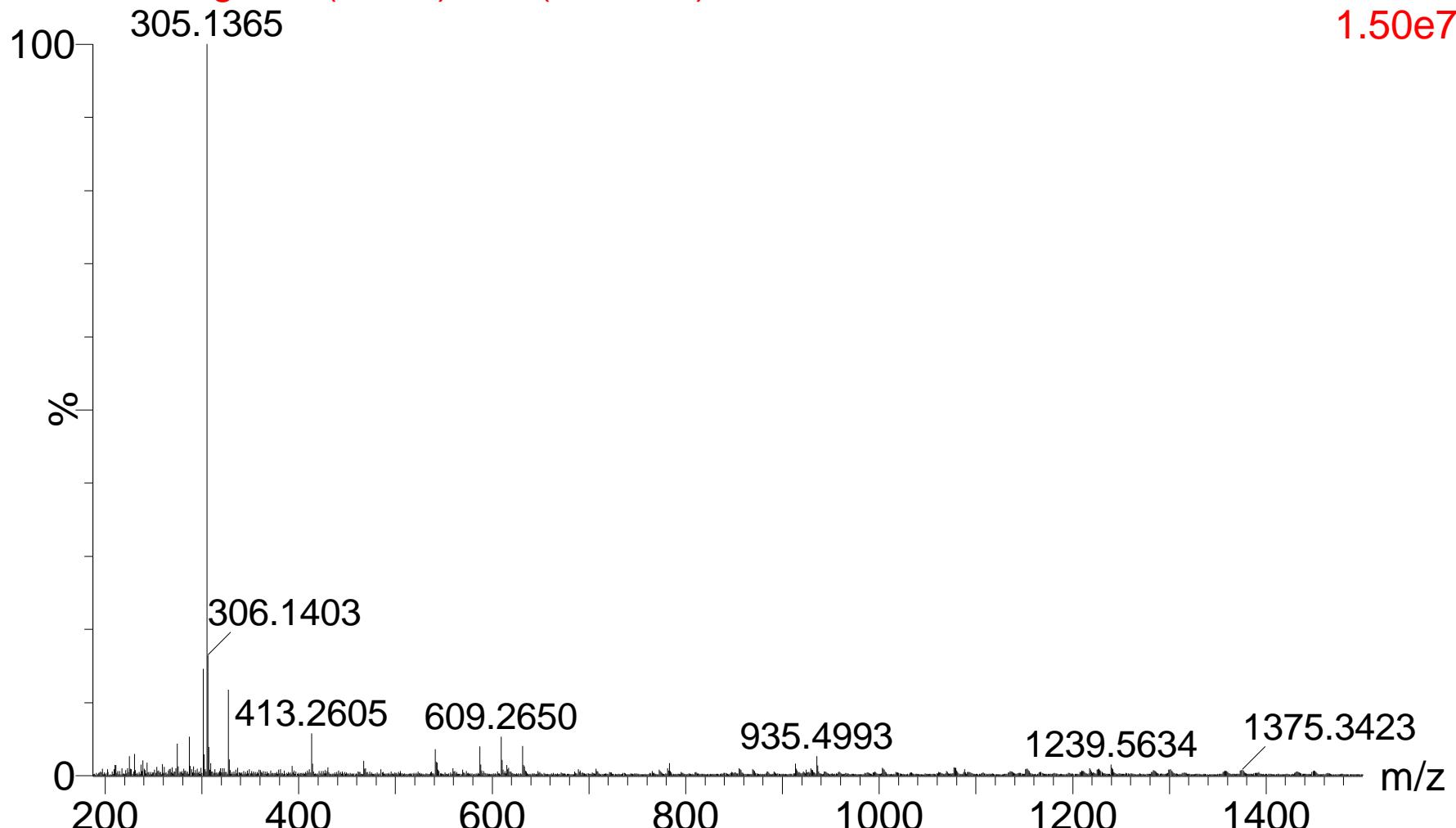
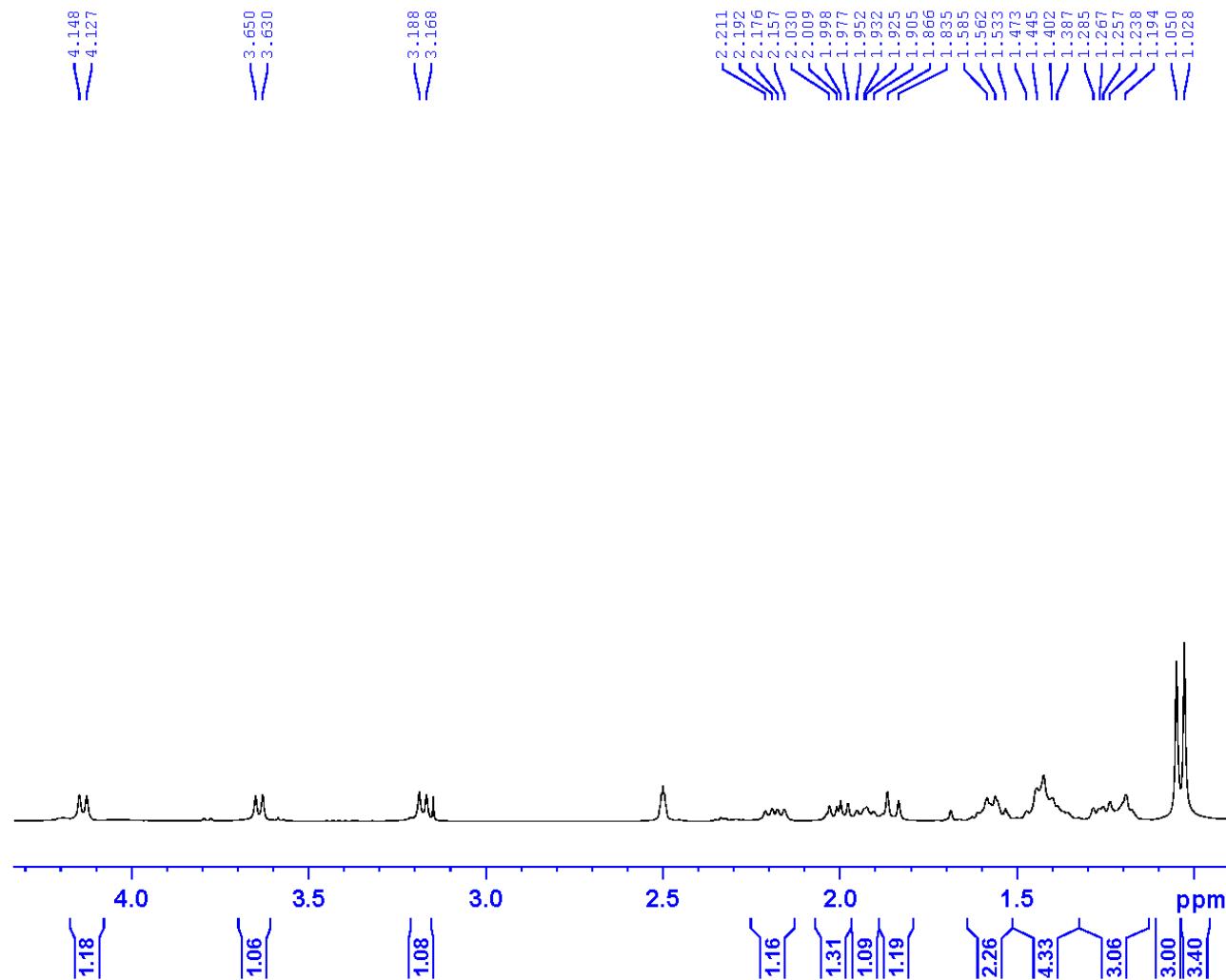


Figure S16. The HR-ESI-MS spectrum of **2**.

xin3-132-H



Current Data Parameters
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EXPNO 1
PROCNO 1

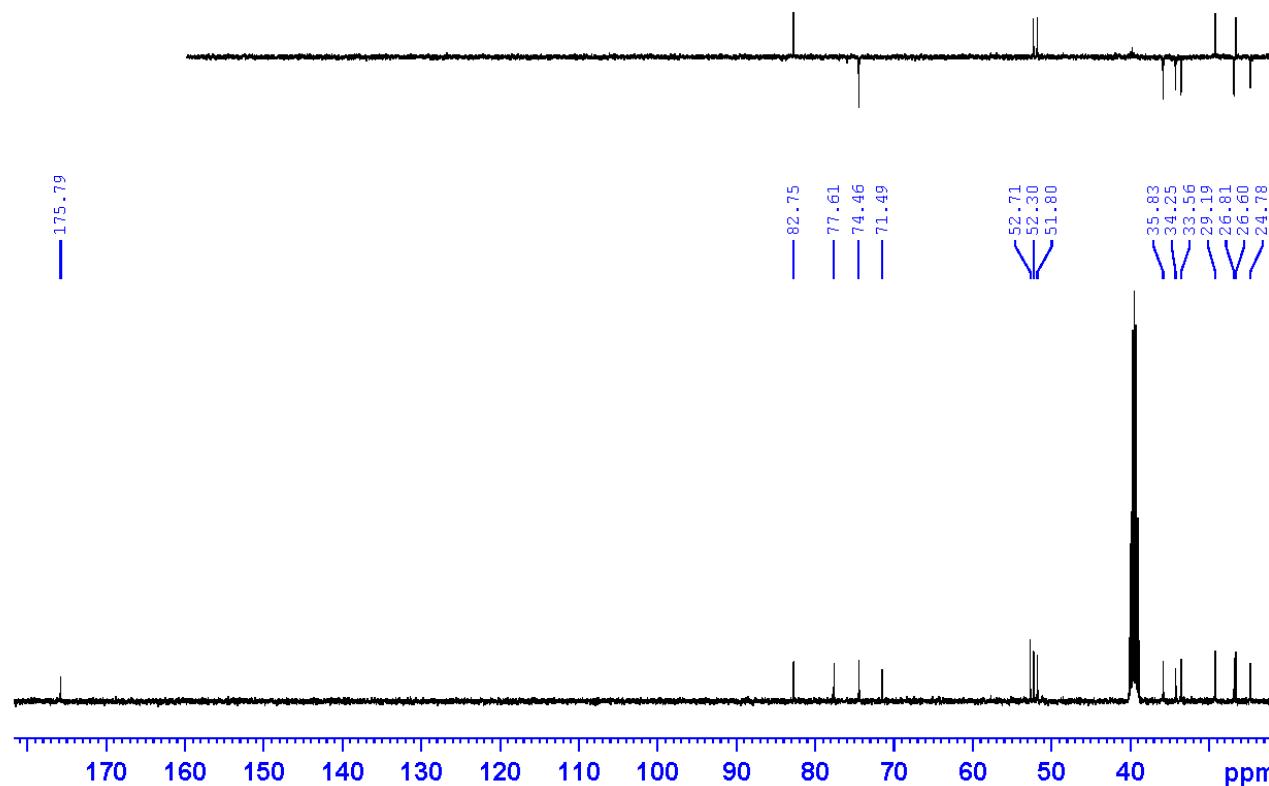
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Time_ 21.06
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PULPROG zg30
TD 65536
SOLVENT DMSO
NS 15
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894465 sec
RG 90.5
DW 62.400 usec
DE 6.50 usec
TE 296.5 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 ======
SFO1 400.1324710 MHz
NUC1 1H
P1 13.90 usec
PLW1 12.14299965 W

F2 - Processing parameters
SI 32768
SF 400.1300035 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S17. ^1H NMR spectrum of **3** in $\text{DMSO}-d_6$.

xin3-132-C



Current Data Parameters
NAME xin3-132
EXPNO 2
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180923
Time 21.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zpgpg30
TD 65536
SOLVENT DMSO
NS 115
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 297.2 K
D1 2.0000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 ======
SFO1 100.6228298 MHz
NUC1 ¹³C
P1 12.37 usec
PLW1 28.13500023 W

===== CHANNEL f2 ======
SFO2 400.1316005 MHz
NUC2 ¹H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 12.14299965 W
PLW12 0.28964999 W
PLW13 0.23461001 W

F2 - Processing parameters
SI 32768
SF 100.6128132 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Figure S18. ^{13}C NMR spectrum of **3** in $\text{DMSO}-d_6$.

xin3-132-QC

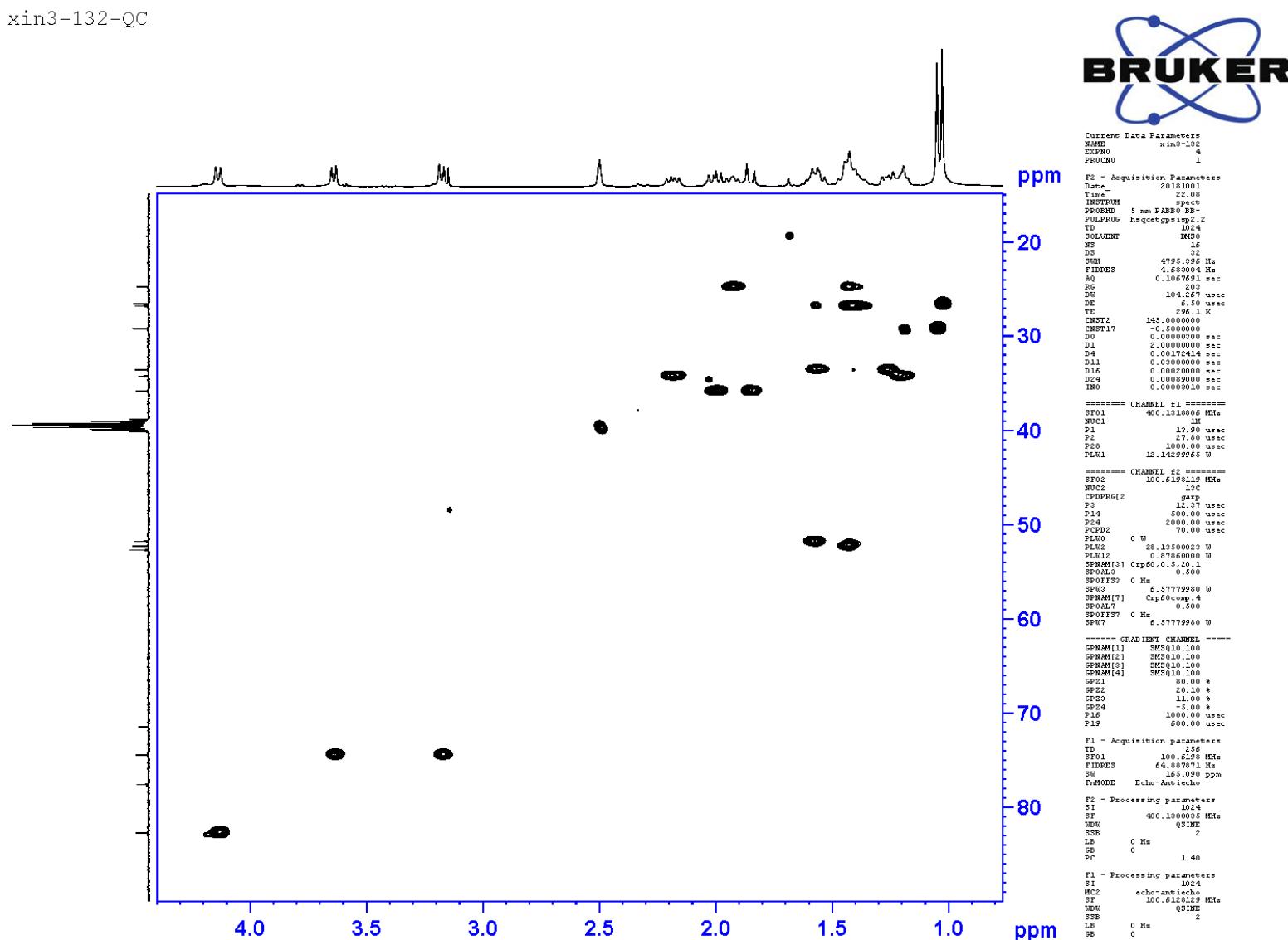


Figure S19. HSQC spectrum of **3** in DMSO-*d*₆.

xin3-132-COSY

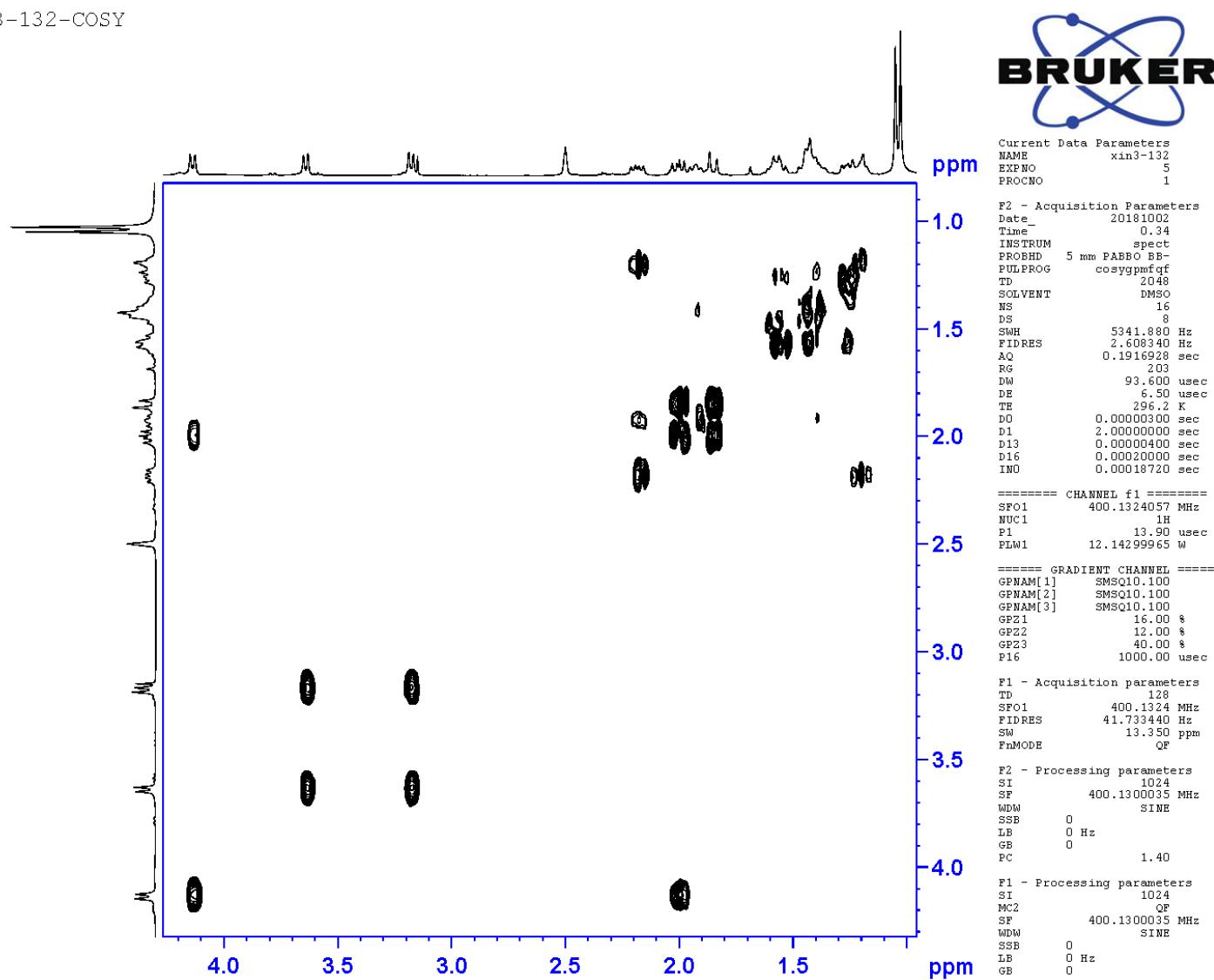


Figure S20. COSY NMR spectrum of **3** in DMSO-*d*₆.

xin3-132-BC

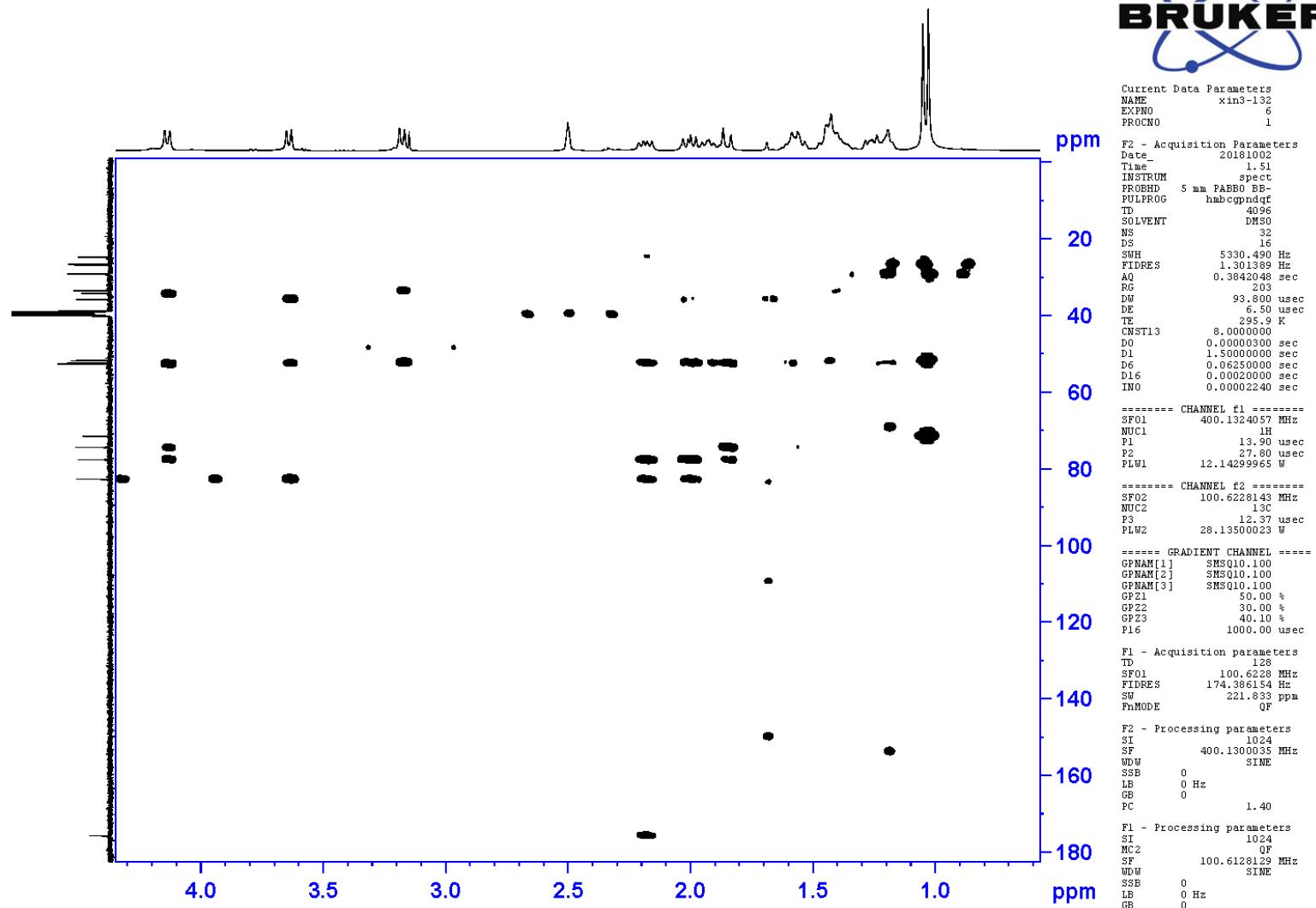


Figure S21. HMBC NMR spectrum of **3** in DMSO-*d*₆.

xin3-132-NOE

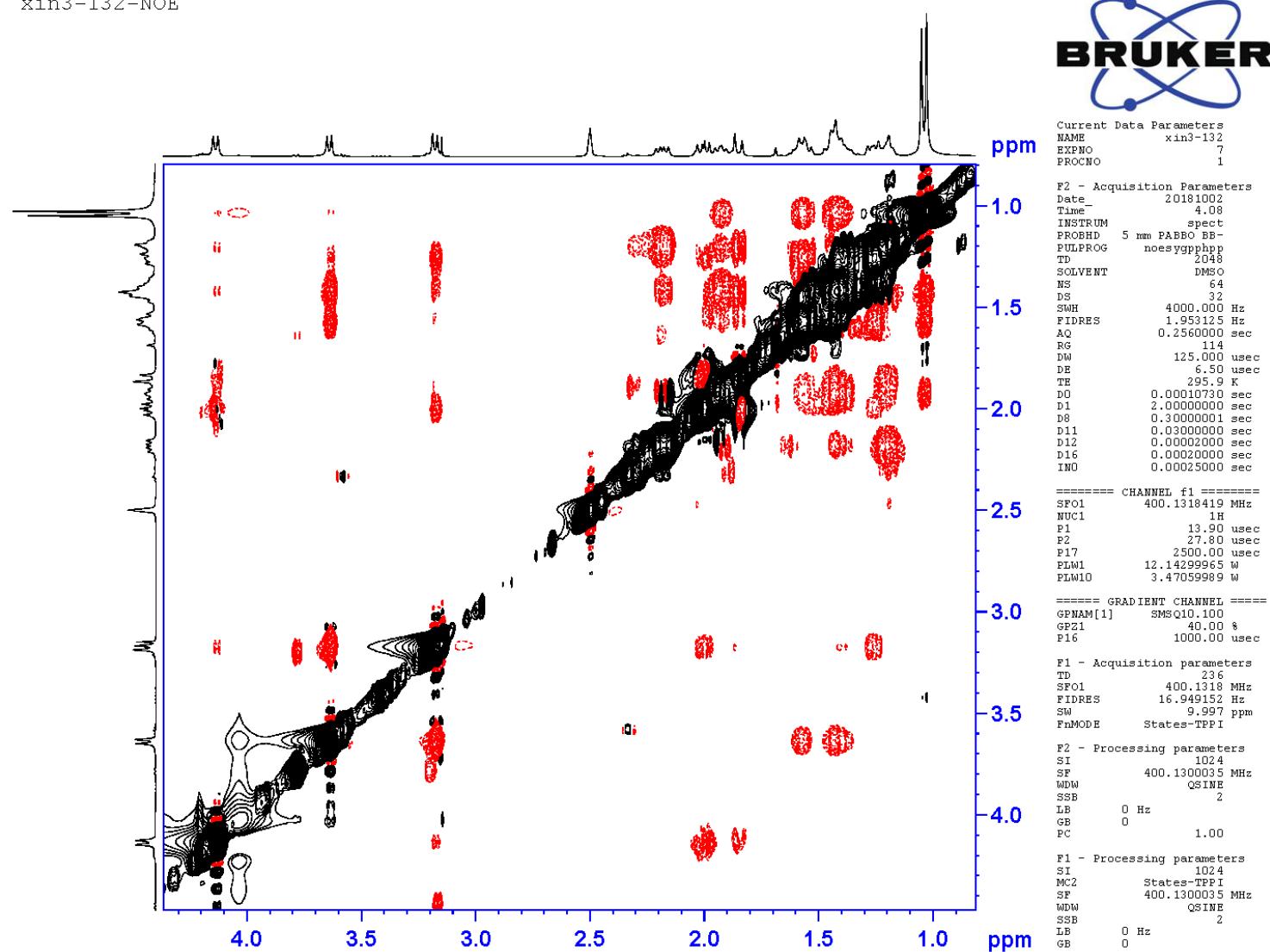


Figure S22. NOESY NMR spectrum of **3** in $\text{DMSO}-d_6$.

Xin 3-14-Sep 130 (0.504) Cm (110:147)

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4.47e3

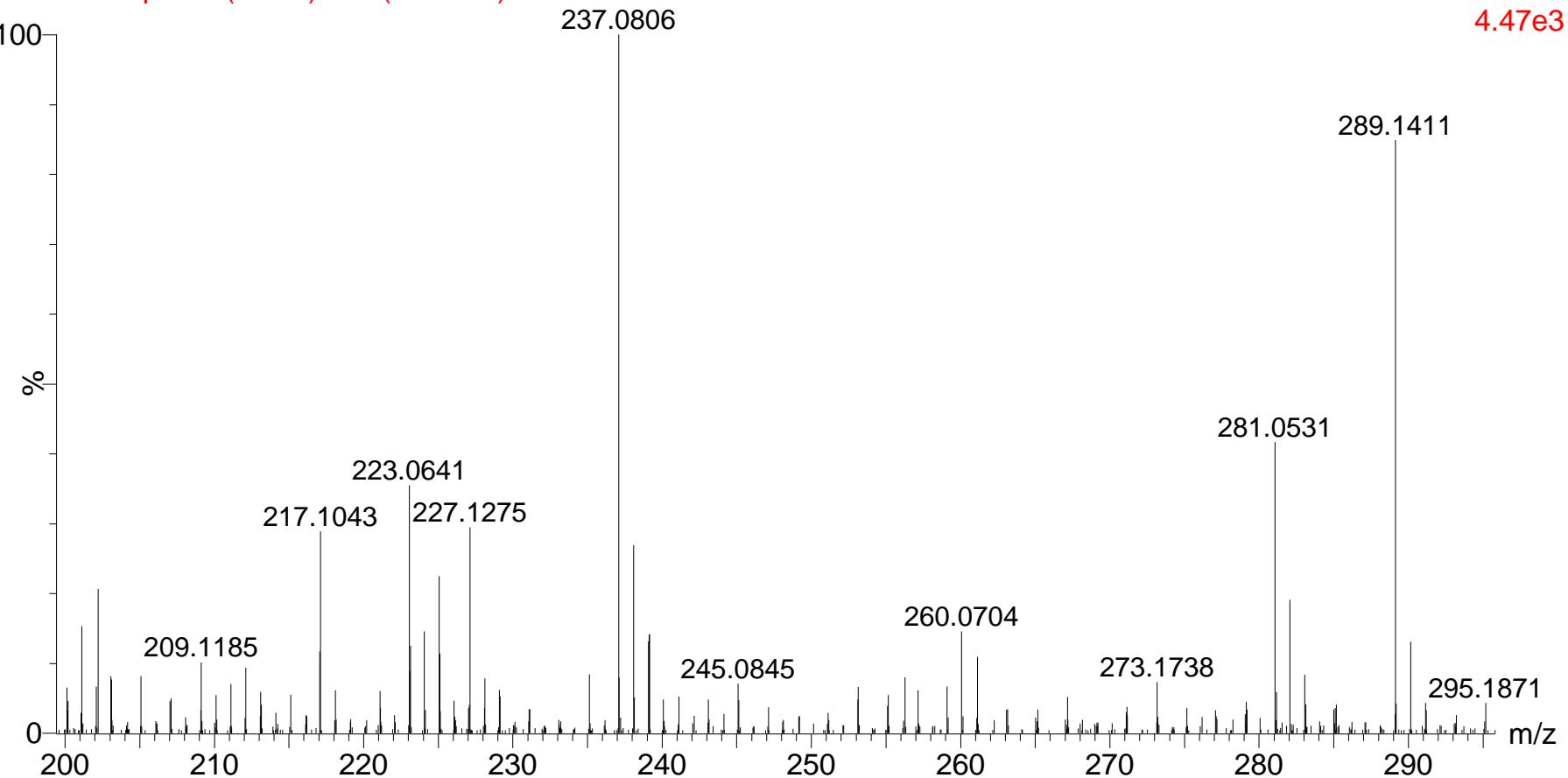
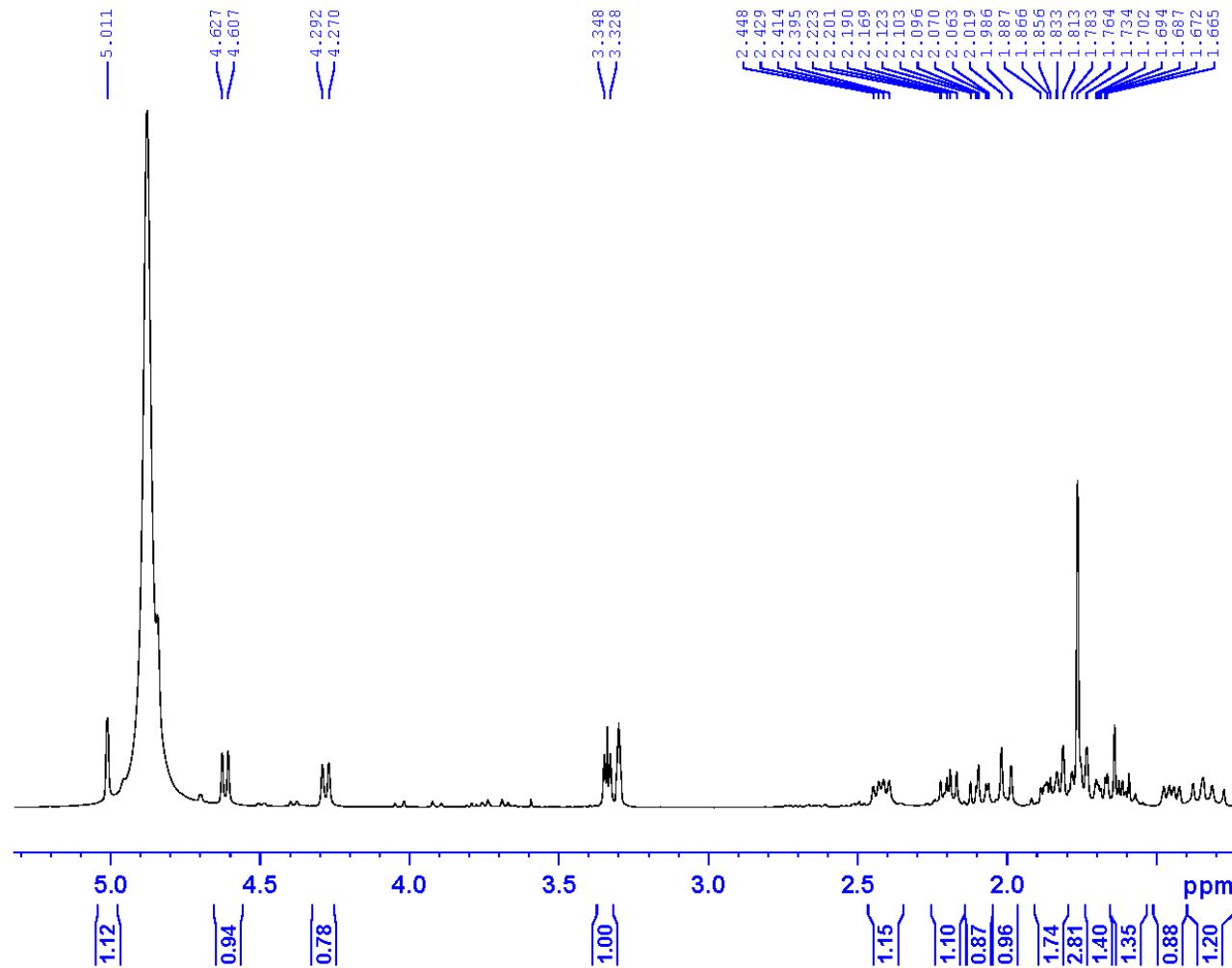


Figure S23. The HR-ESI-MS spectrum of **3**.

xin3-74 H



Current Data Parameters
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EXPNO 1
PROCNO 1

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DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9845889 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 296.2 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.09 usec
PL1 -1.00 dB
PL1W 12.14314651 W
SF01 400.1324710 MHz

F2 - Processing parameters
SI 32768
SF 400.1300066 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Figure S24. ^1H NMR spectrum of **4** in CD_3OD .

xin3-74 C

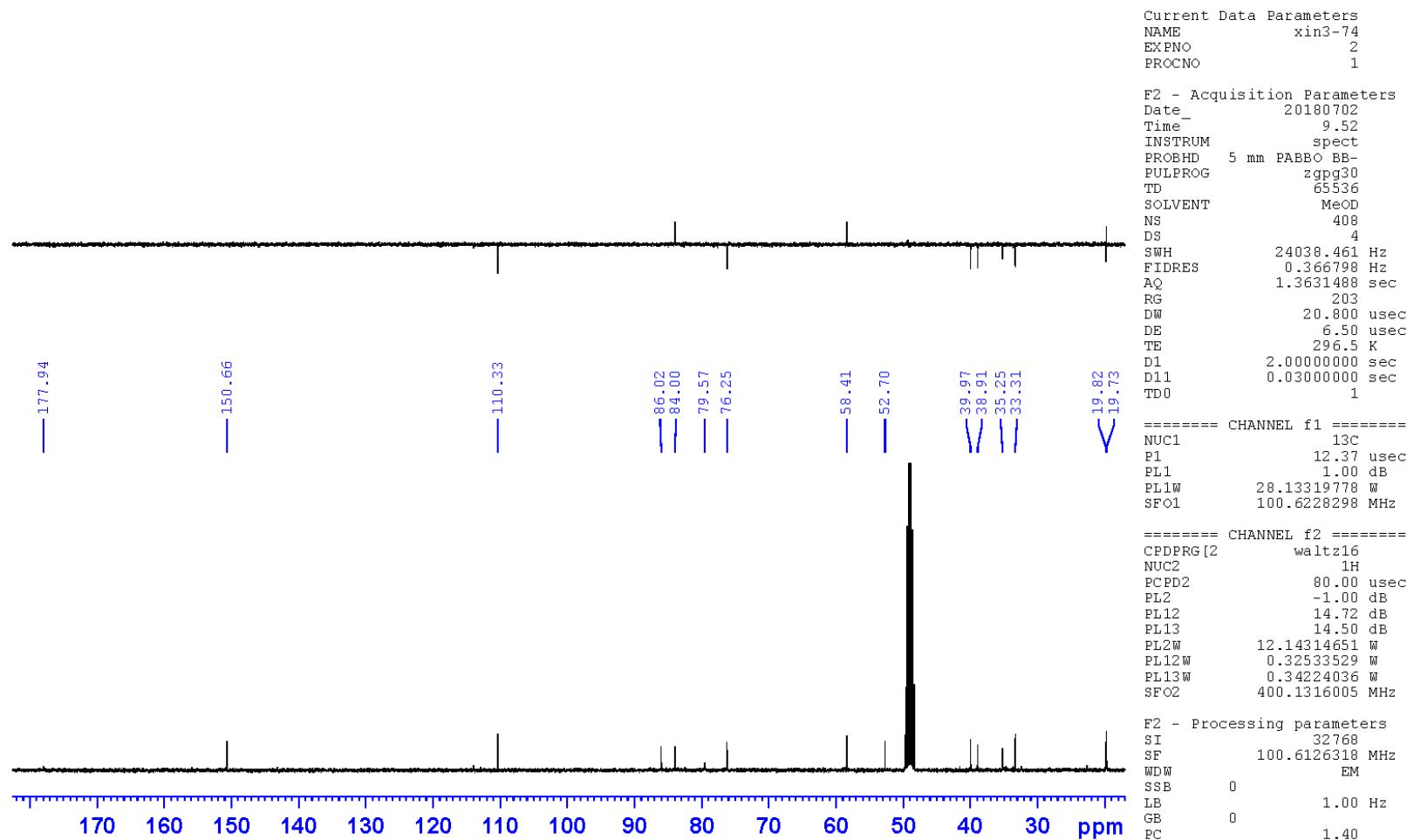
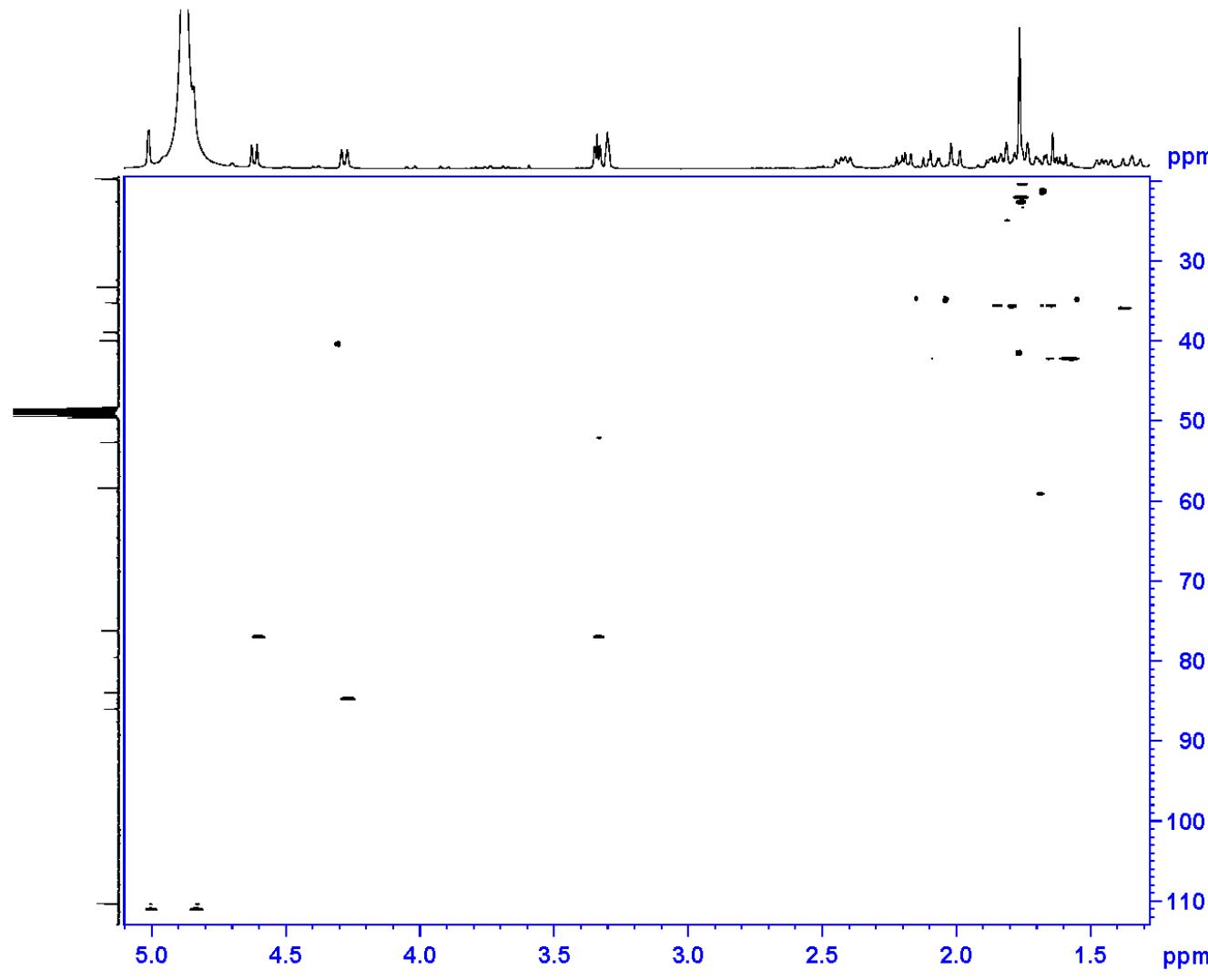


Figure S25. ^{13}C NMR spectrum of **4** in CD_3OD .

xin3-74-COSY



```

Current Data Parameters
DPPM1      xin3-74
EXPNO        4
PRSWNO        1
P1          10.00
P2          5.00 PABW135
PULPROG    hsqcetprsp12
TD          1024
SOLVENT      ND
MS          32
DS          32
JW          4779.39 Hz
PRDRES     4.653044 Hz
AQ          0.1067691 sec
RG          200
DE          10.40 usec
D1          6.50 usec
TE          298.0 K
CNUST1     145.000000
CNUST1?    -0.500000
D0          0.00000300 sec
D1          2.00000000 sec
D4          0.00000414 sec
D11         0.03000000 sec
D16         0.00020000 sec
D24         0.00089000 sec
D90         0.00003010 sec

===== CHANNEL f1 =====
ST01      400.1218806 MHz
NUC1      1H
F1          13.90 usec
P2          27.80 usec
P12        10.00 usec
PLM1      12.14239930 0

===== CHANNEL f2 =====
ST02      100.6190119 MHz
NUC2      13C
CPDPFG[2]  gARP
P1          1.00 usec
P14        500.00 usec
P24        2000.00 usec
PFD2        70.00 usec
PLM0        0 0
PLM2      28.12500023 0
PLM3      0.97860000 0
SP0M1[3] Crp60.0;3;20.1
SP0AL5      0.500
SP0FT33      0 0
SP0M7      6.57779980 0
SP0M1[7]      Crp60.0;3;4
SP0AL5      0.500
SP0FT37      0 0
SP07      6.57779980 0

===== GRADIENT CHANNEL =====
GPMM1[1]  SHSQ10.100
GPMM1[2]  SHSQ10.100
GPMM1[3]  SHSQ10.100
GPMM1[4]  SHSQ10.100
GP21        80.00 *
GP22        20.00 *
GP23        11.00 *
GP24        -5.00 *
P16        1000.00 usec
P17        200.00 usec

F1 - Acquisition parameters
TD          1024
ST01      100.6190119 MHz
FIDRES     64.887871 Hz
SW0        165.090 ppm
P1MODE    Echo-anti-echo

F2 - Processing parameters
SI          1024
MC2      echo-anti-echo
SF          400.1200118 MHz
WDW        Q3INE
SSB          2
LB          0 Hz
GB          0
PC          1.40

F1 - Processing parameters
SI          1024
MC2      echo-anti-echo
SF          100.6120112 MHz
WDW        Q3INE
SSB          2
LB          0 Hz
GB          0

```

Figure S26. HSQC spectrum of **4** in CD₃OD.

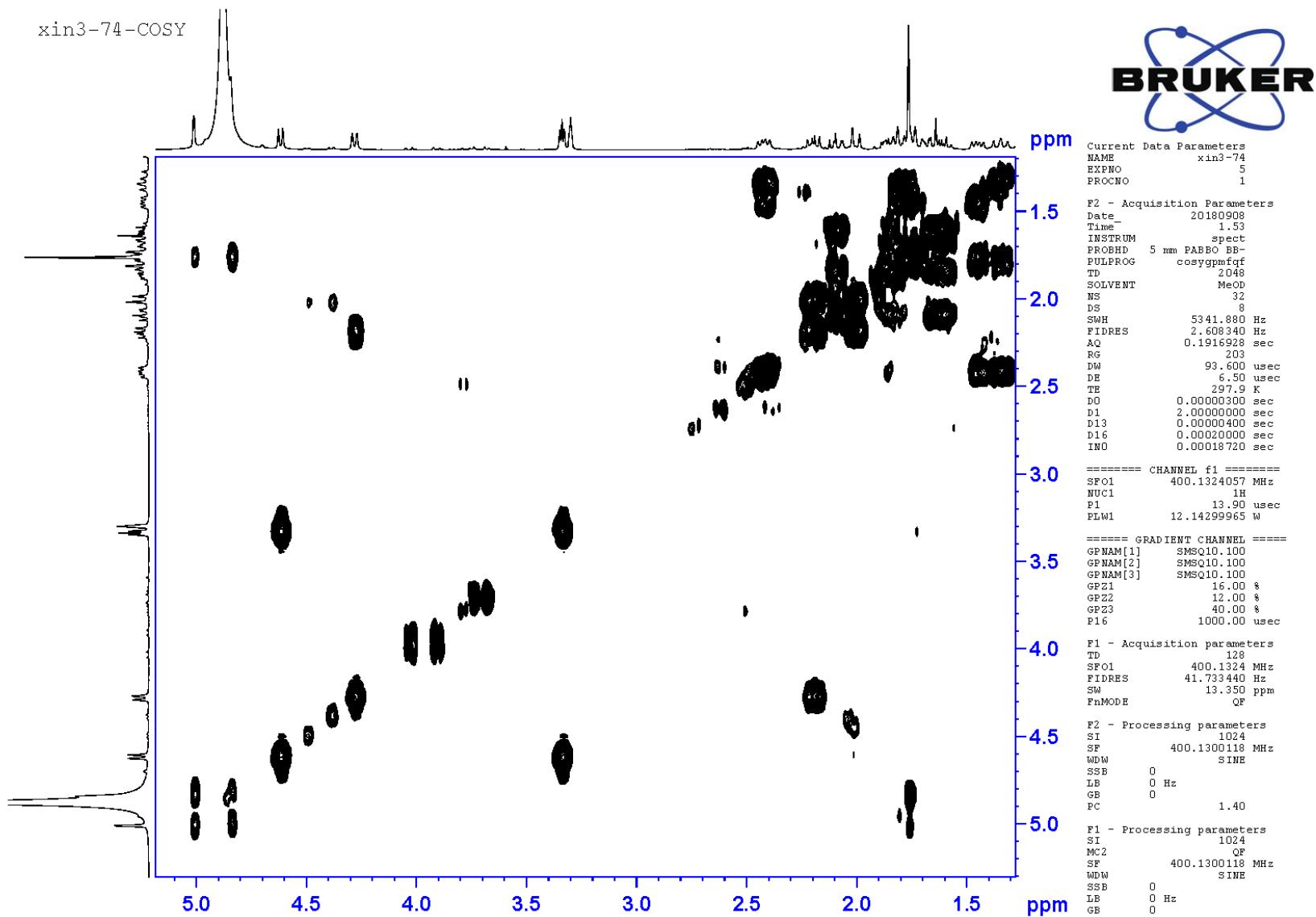


Figure S27. COSY NMR spectrum of **4** in CD_3OD .

xin3-74-BC

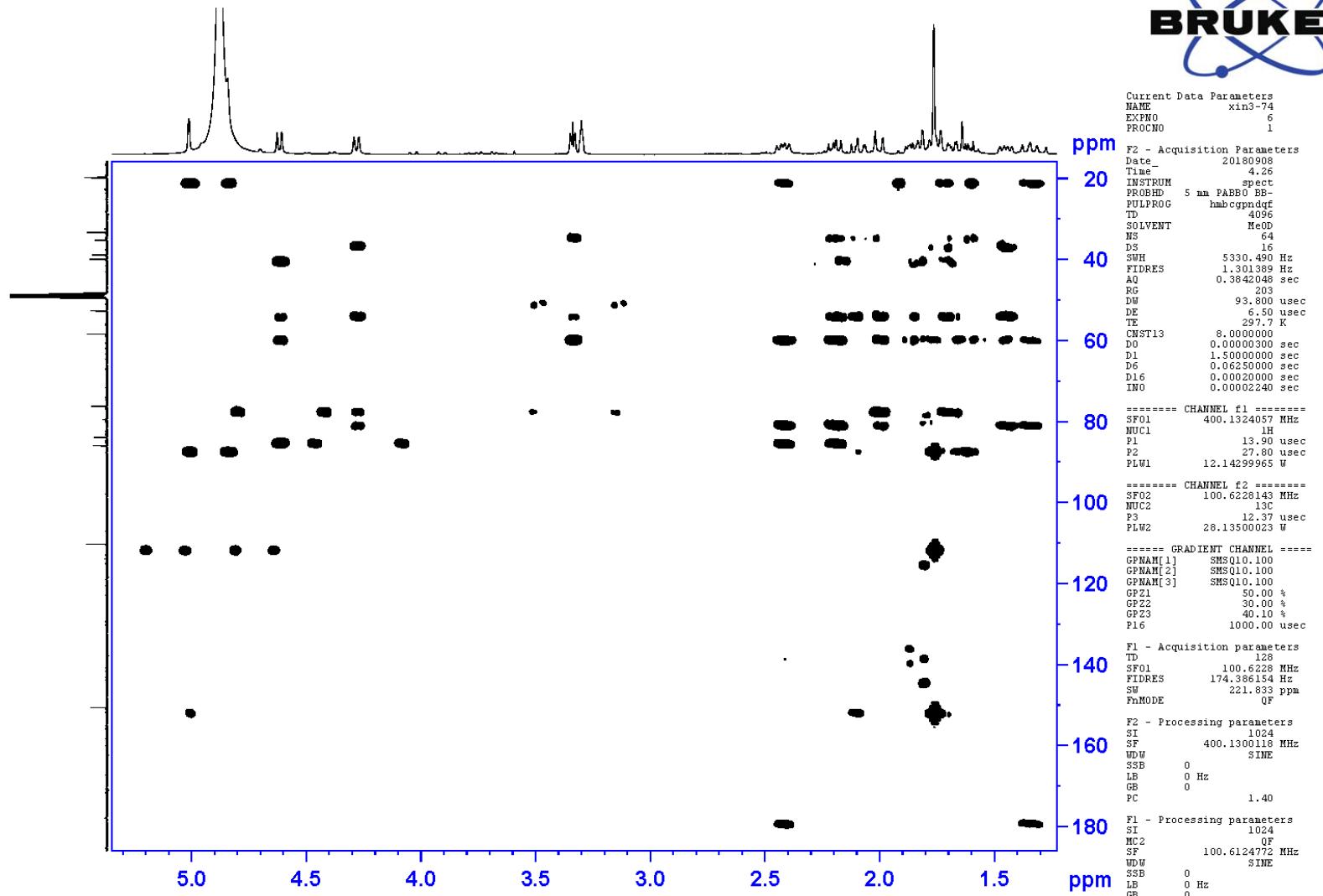
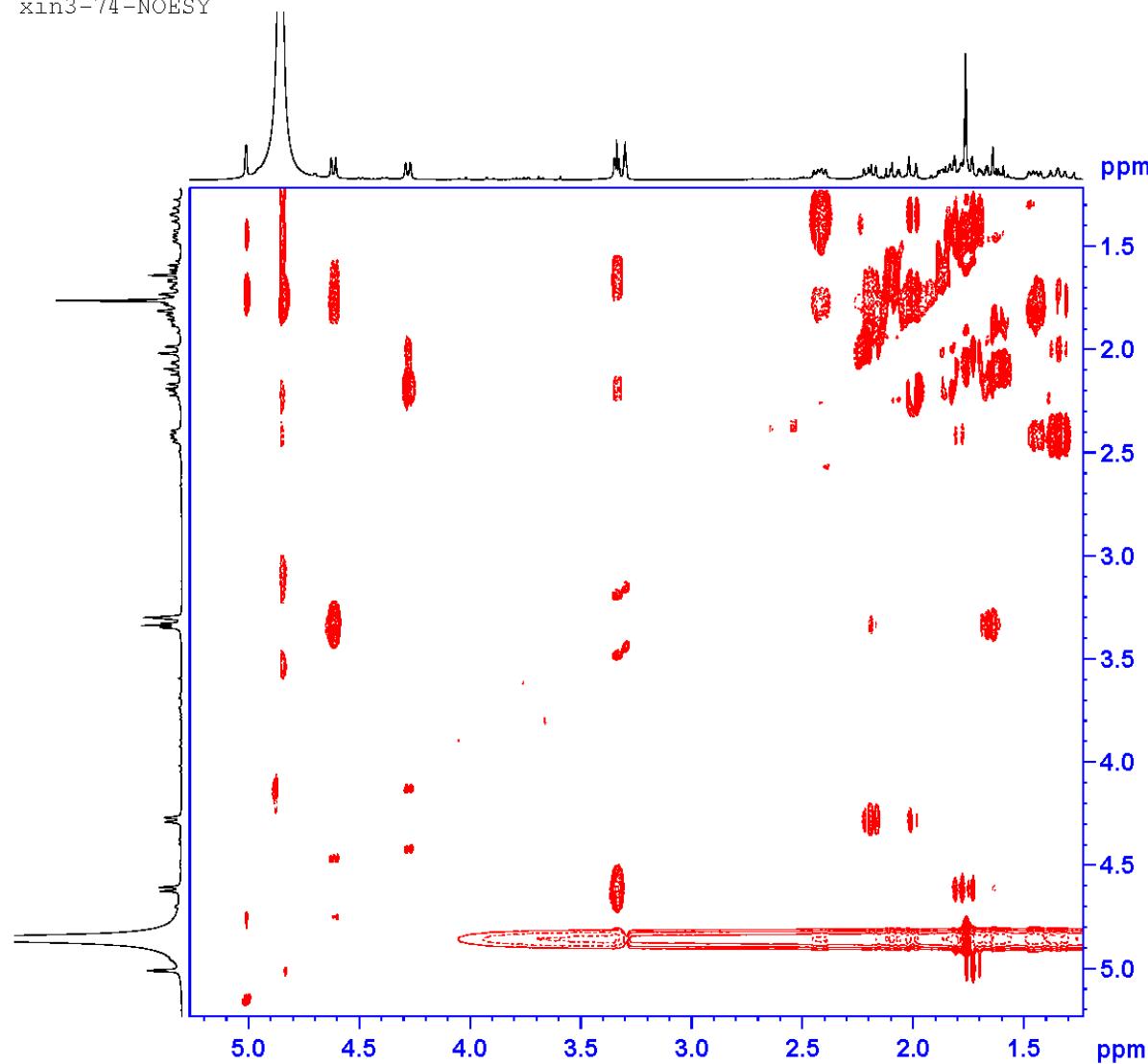


Figure S28. HMBC NMR spectrum of **4** in CD₃OD.

xin3-74-NOESY



Current Data Parameters
NAME xin3-74
EXPNO 7
PROCNO 1

P2 - Acquisition Parameters
Date_ 20180910
Time 9.05
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG noeugpphp
TD 2048
SOLVENT MeOD
NS 64
DS 32
SWH 4000.000 Hz
FIDRES 1.953125 Hz
AQ 0.2560000 sec
RG 64
DW 125.000 usec
DE 6.50 usec
TE 297.6 K
DO 0.00010730 sec
D1 2.0000000 sec
D8 0.3000001 sec
D11 0.0300000 sec
D12 0.00002000 sec
D16 0.00020000 sec
INO 0.00025000 sec

===== CHANNEL f1 =====
SFO1 400.1318419 MHz
NUC1 1H
P1 13.90 usec
P2 27.80 usec
P17 2500.00 usec
PLW1 12.1429965 W
PLW10 3.47059989 W

===== GRADIENT CHANNEL =====
GPNAME[1] SMSQ10.100
GPZ1 40.00 %
P16 1000.00 usec

F1 - Acquisition parameters
TD 173
SFO1 400.1318 MHz
FIDRES 23.121387 Hz
SW 9.997 ppm
FnMODE States-TPPI

F2 - Processing parameters
SI 1024
SF 400.1300117 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0
PC 1.00

F1 - Processing parameters
SI 1024
MC2 States-TPPI
SF 400.1300117 MHz
WDW QSINE
SSB 2
LB 0 Hz
GB 0

Figure S29. NOESY NMR spectrum of **4** in CD_3OD .

Xin 3-85-Sep 117 (0.458) Cm (116:136)

1: TOF MS ES+
6.99e3

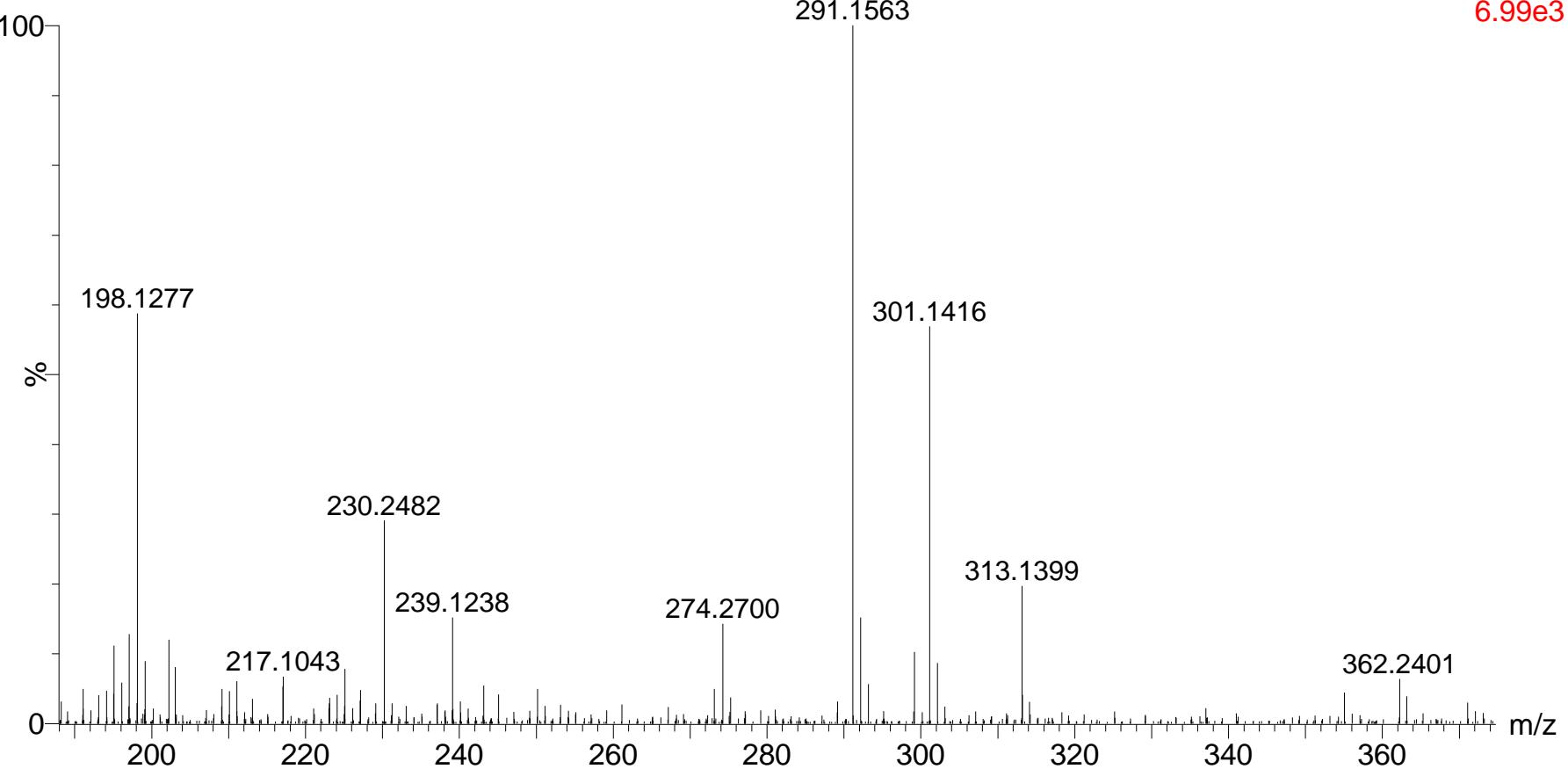


Figure S30. The HR-ESI-MS spectrum of 4.