

## Supplementary Information

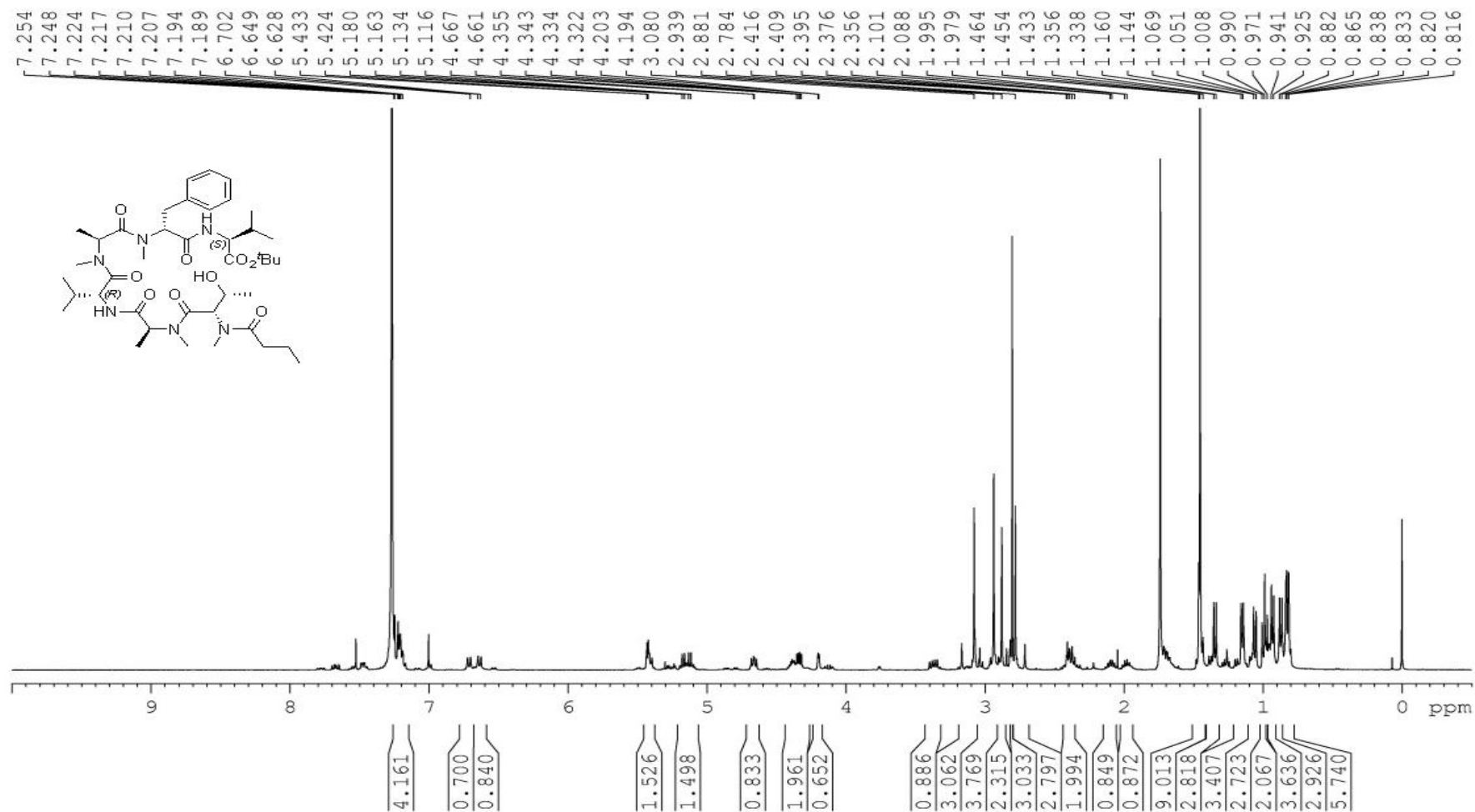


Figure S1. <sup>1</sup>H NMR of compound 19.

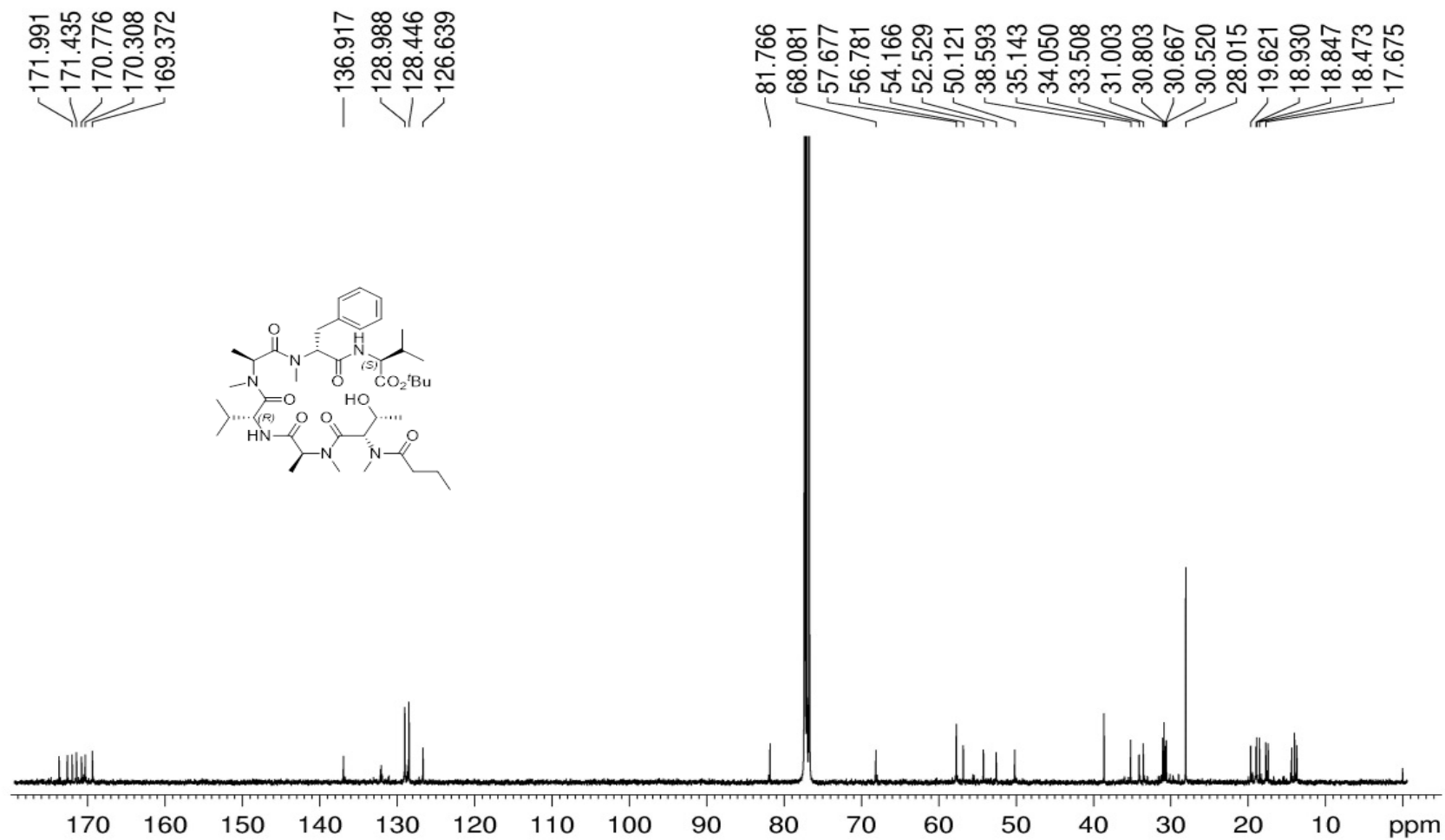


Figure S2.  $^{13}\text{C}$  NMR of compound 19.

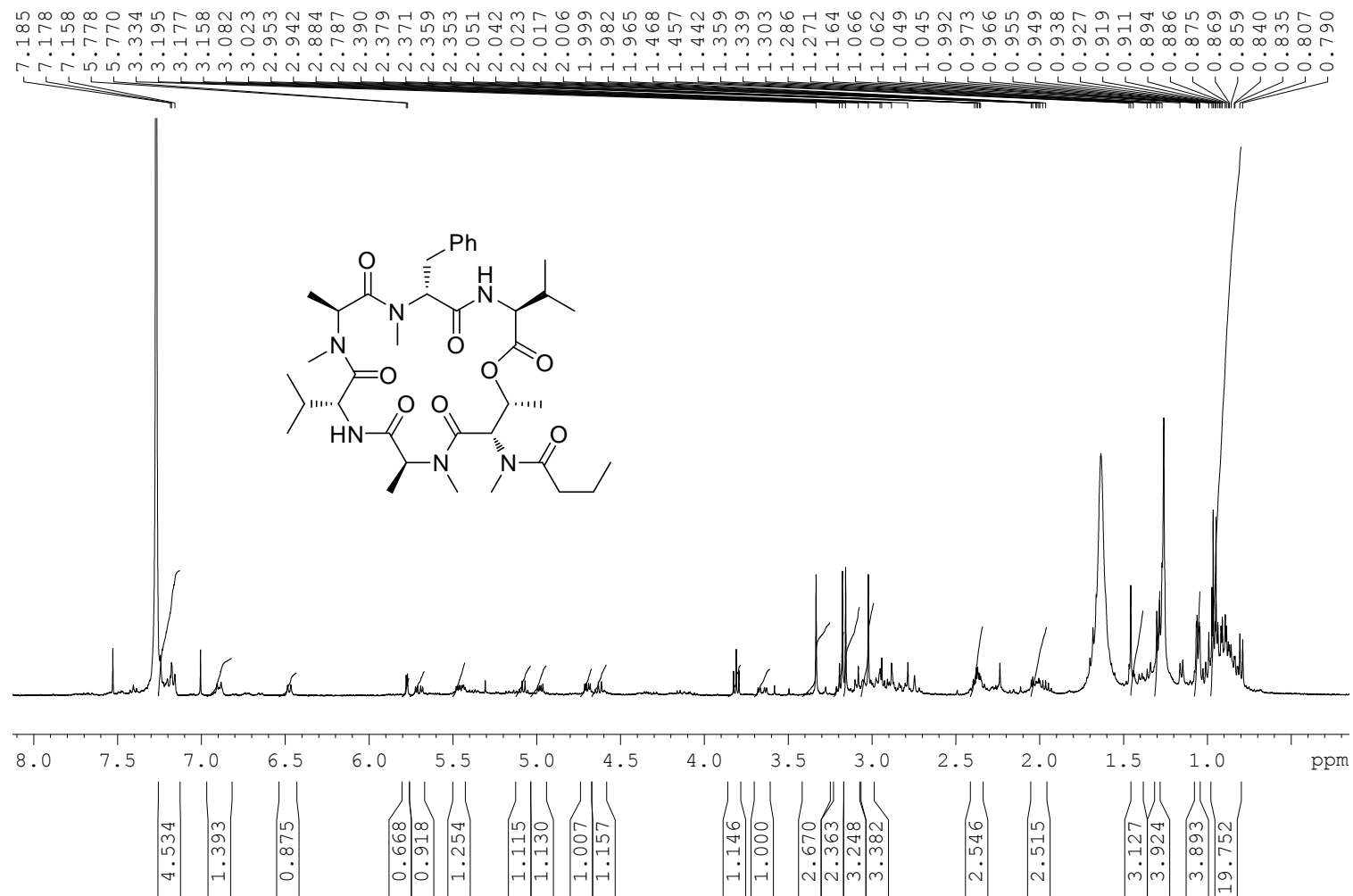


Figure S3.  $^1\text{H}$  NMR of compound 16.

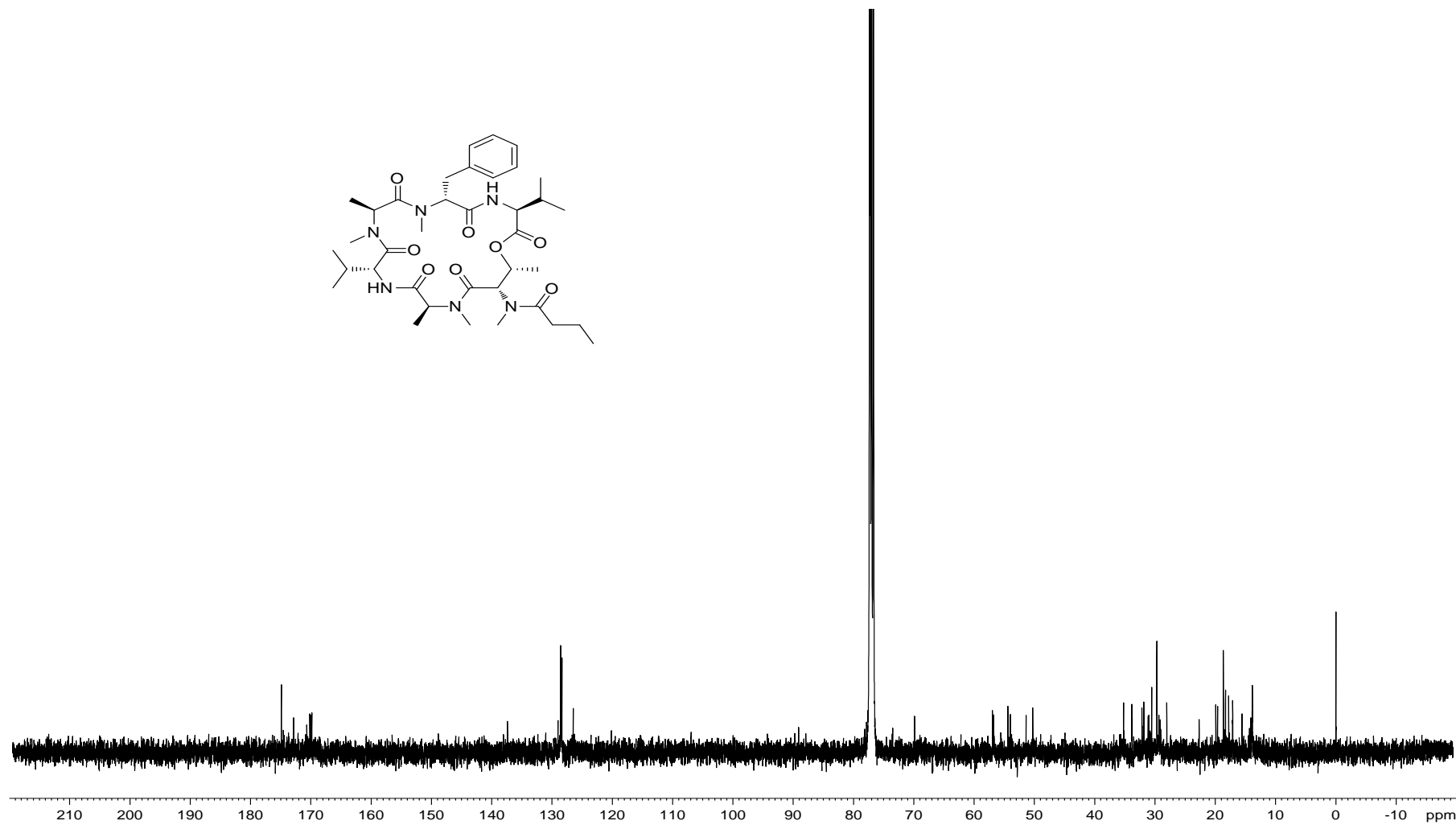
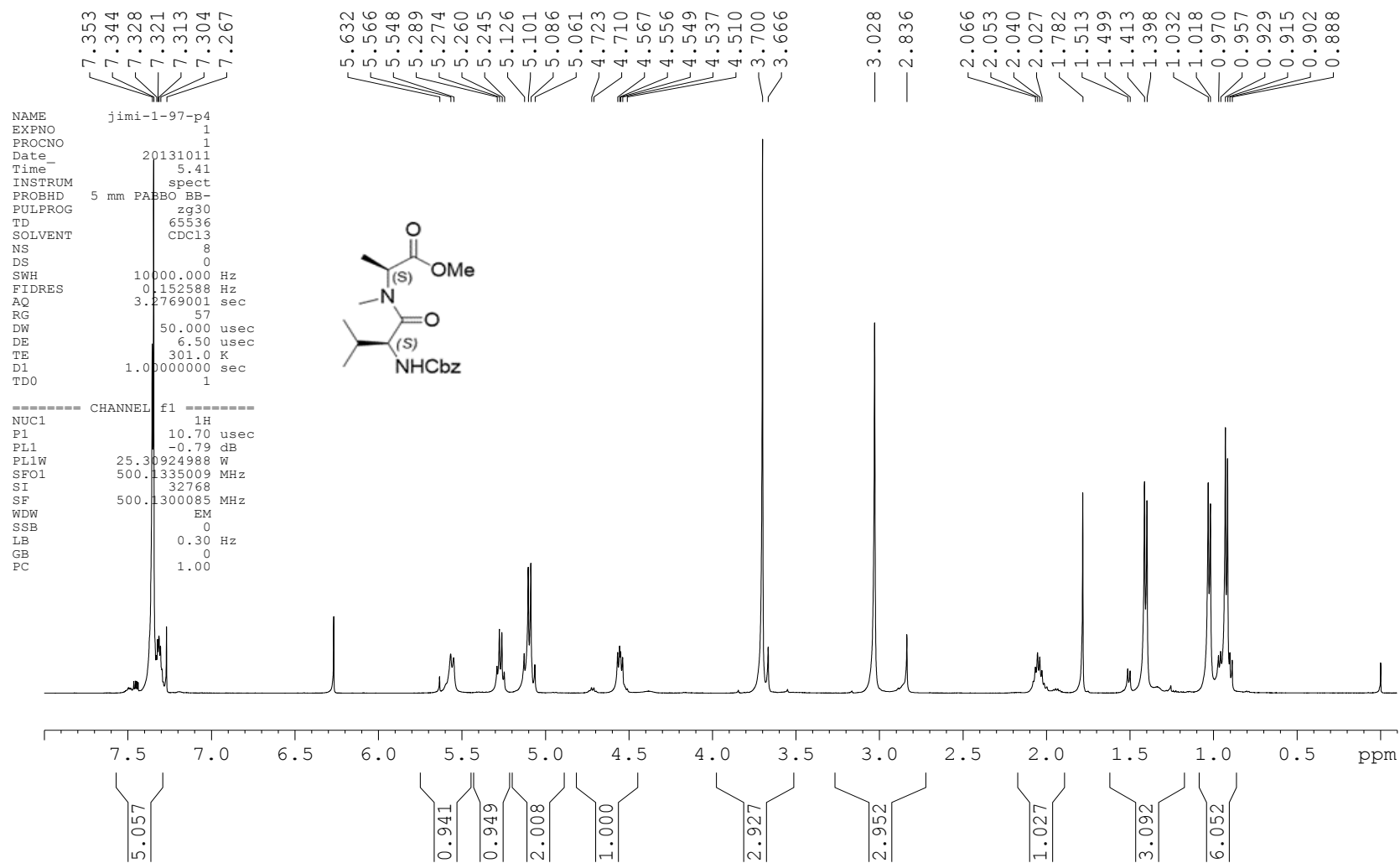
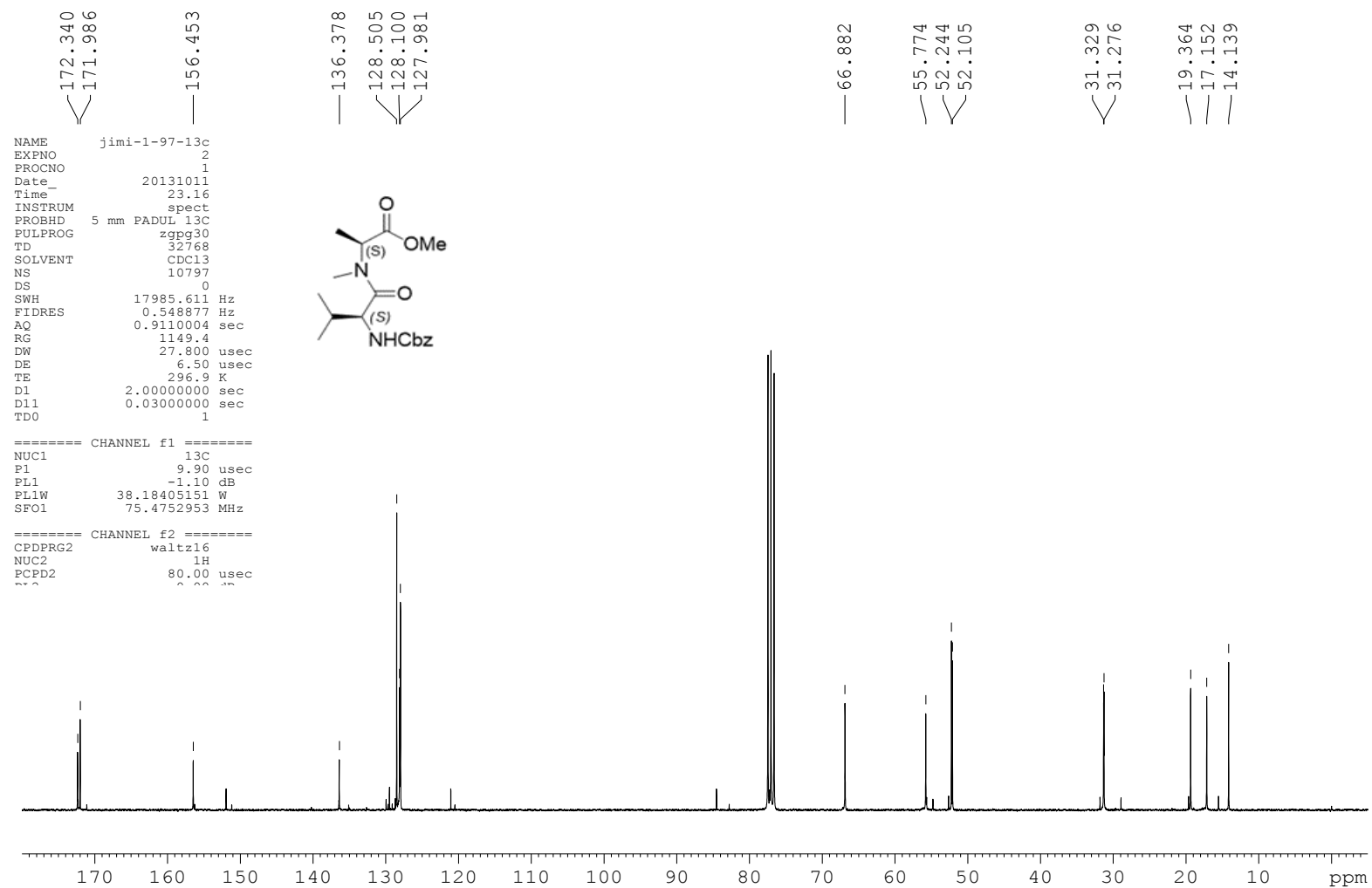


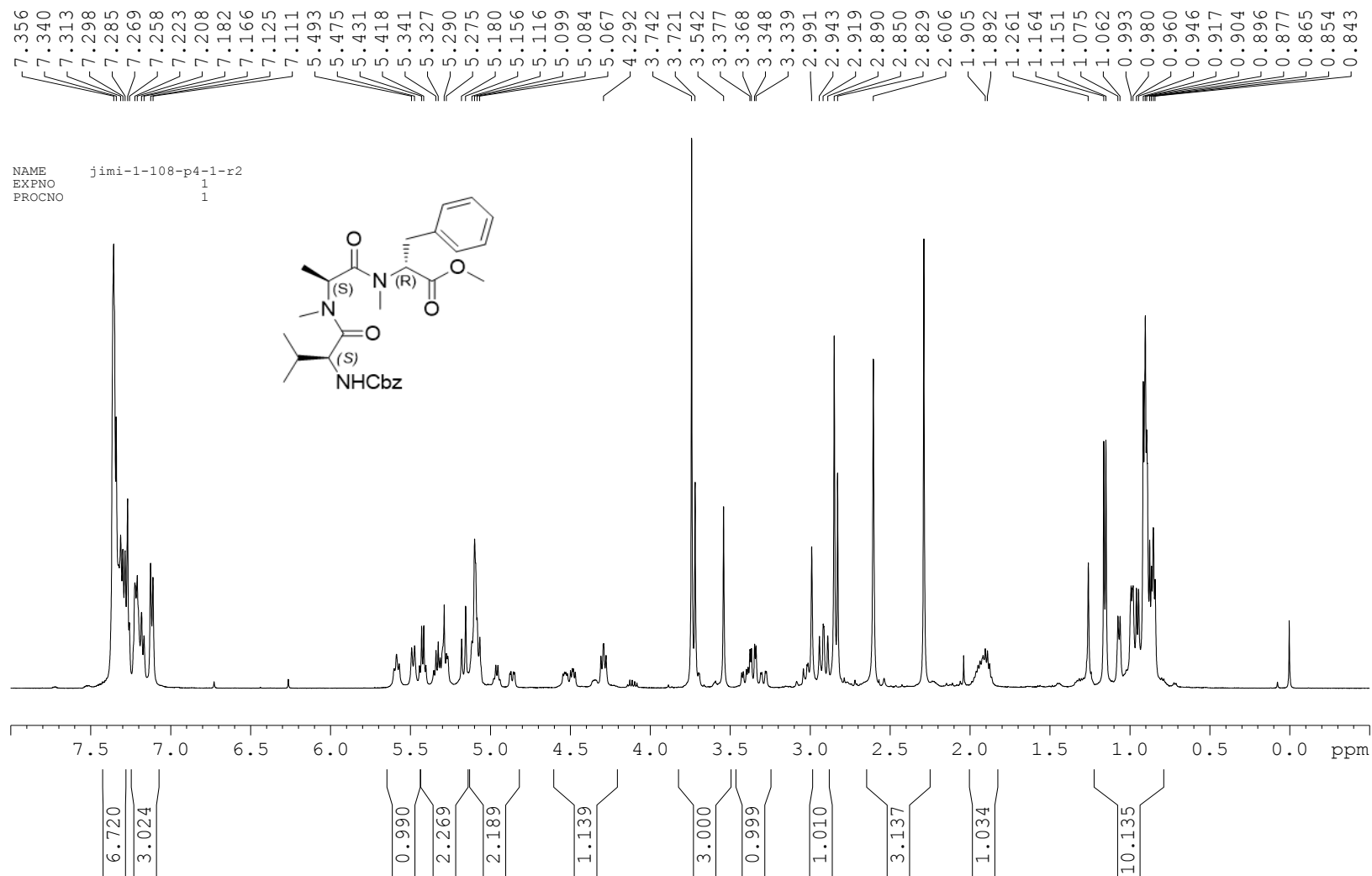
Figure S4. <sup>13</sup>C NMR of compound 16.

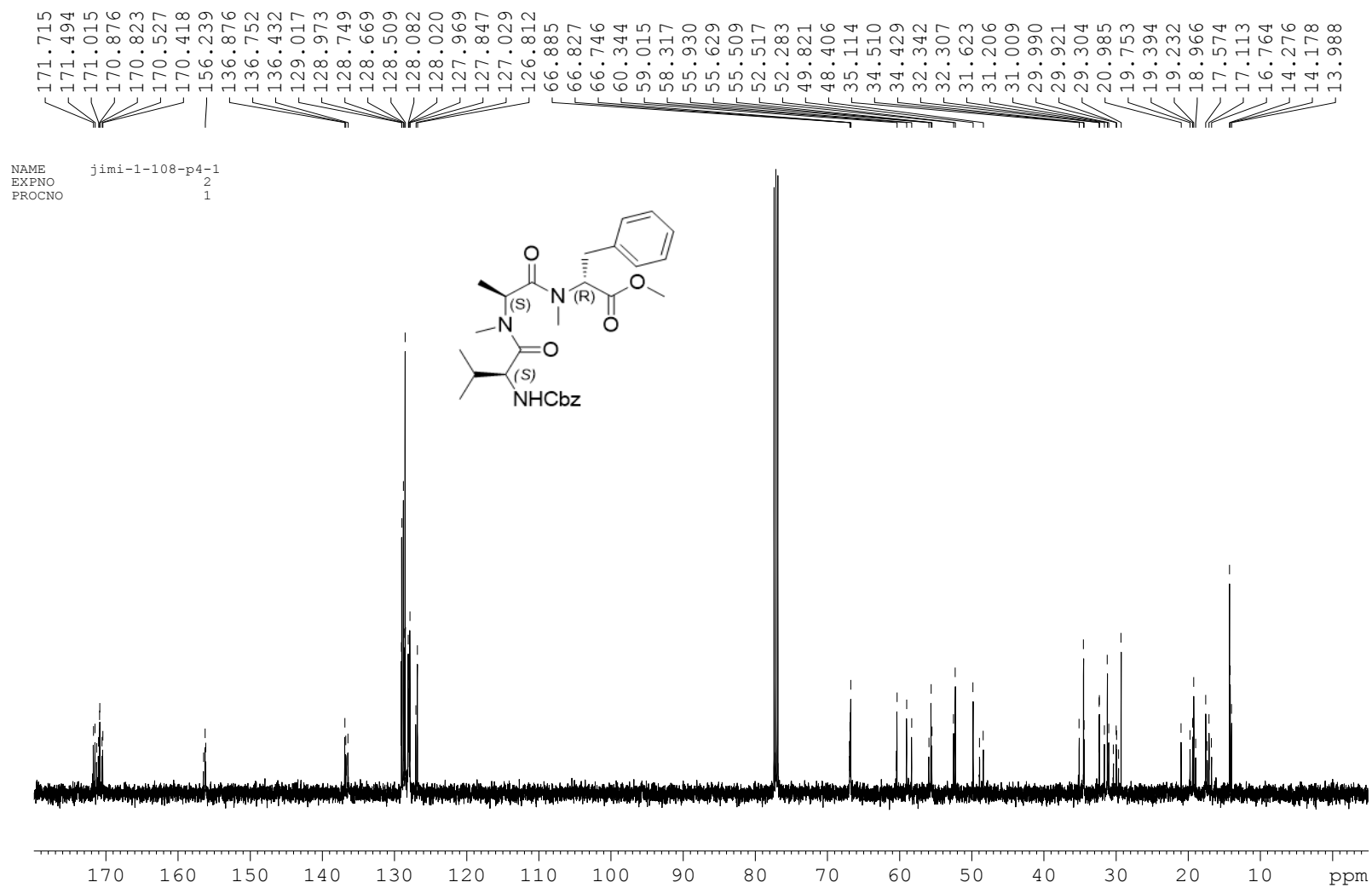


**Figure S5.**  $^1\text{H}$  NMR of dipeptide Cbz-L-Val-N(Me)-Ala-OMe.

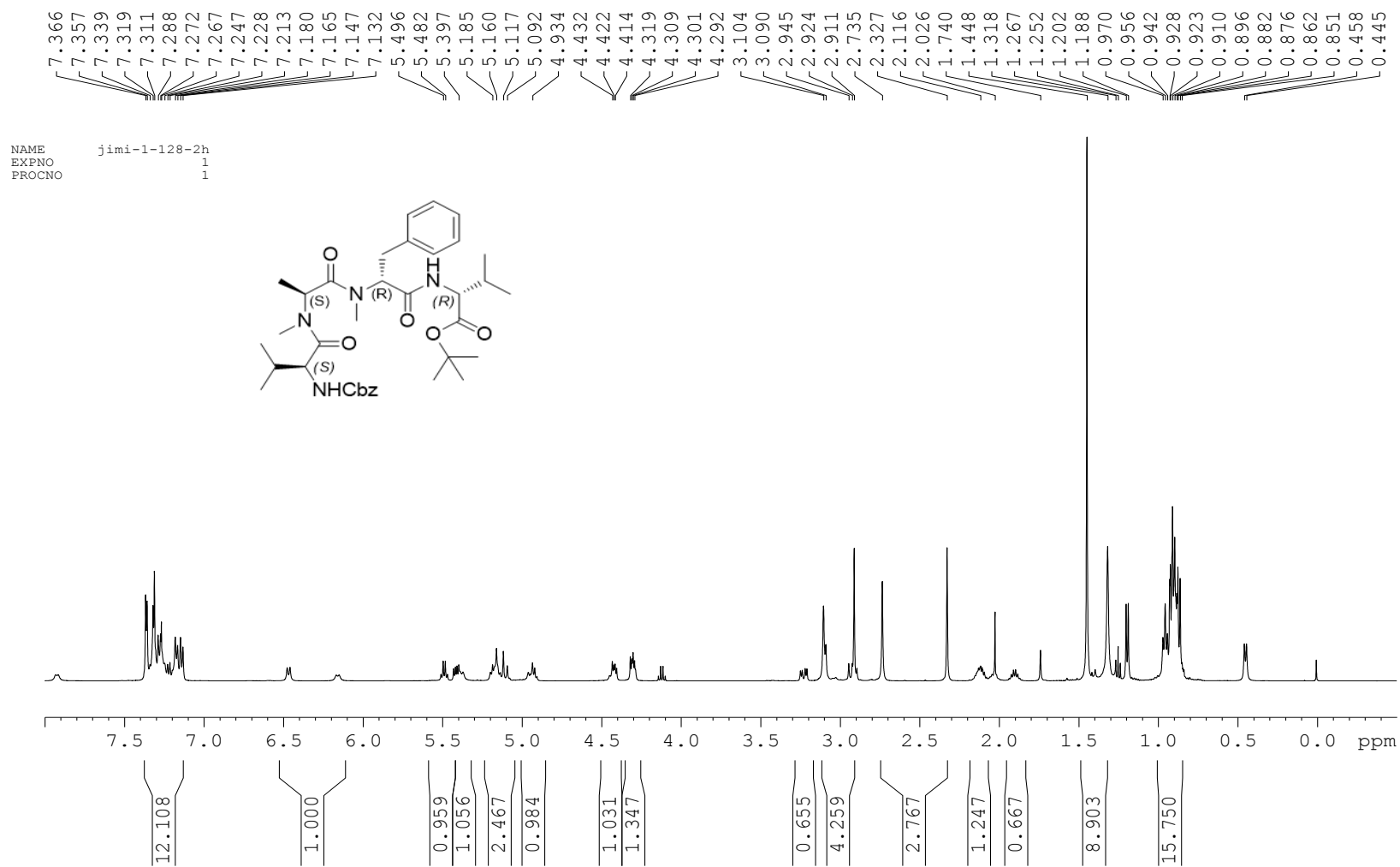


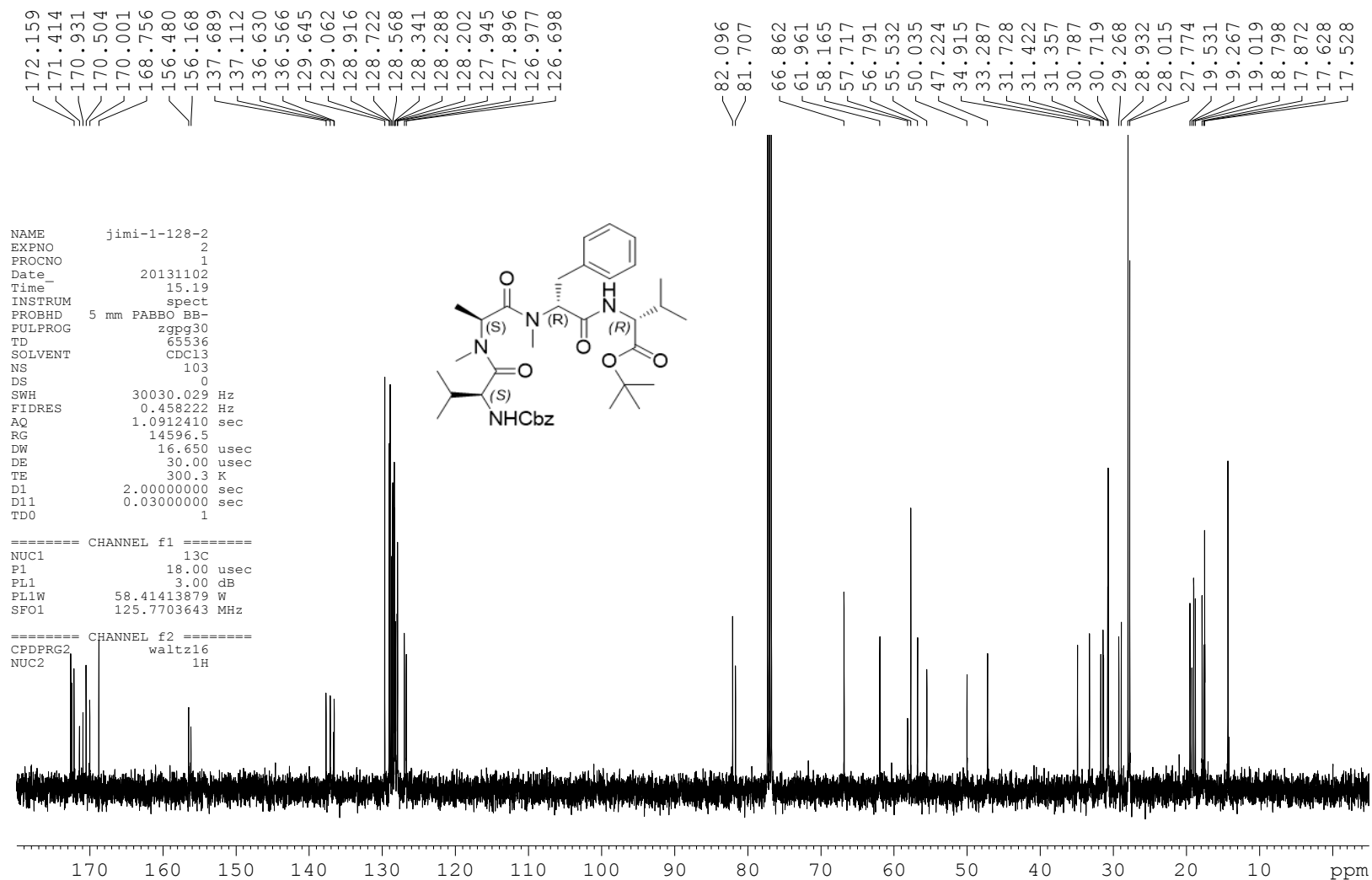
**Figure S6.**  $^{13}\text{C}$  NMR of dipeptide Cbz-L-Val-N(Me)-Ala-OMe.

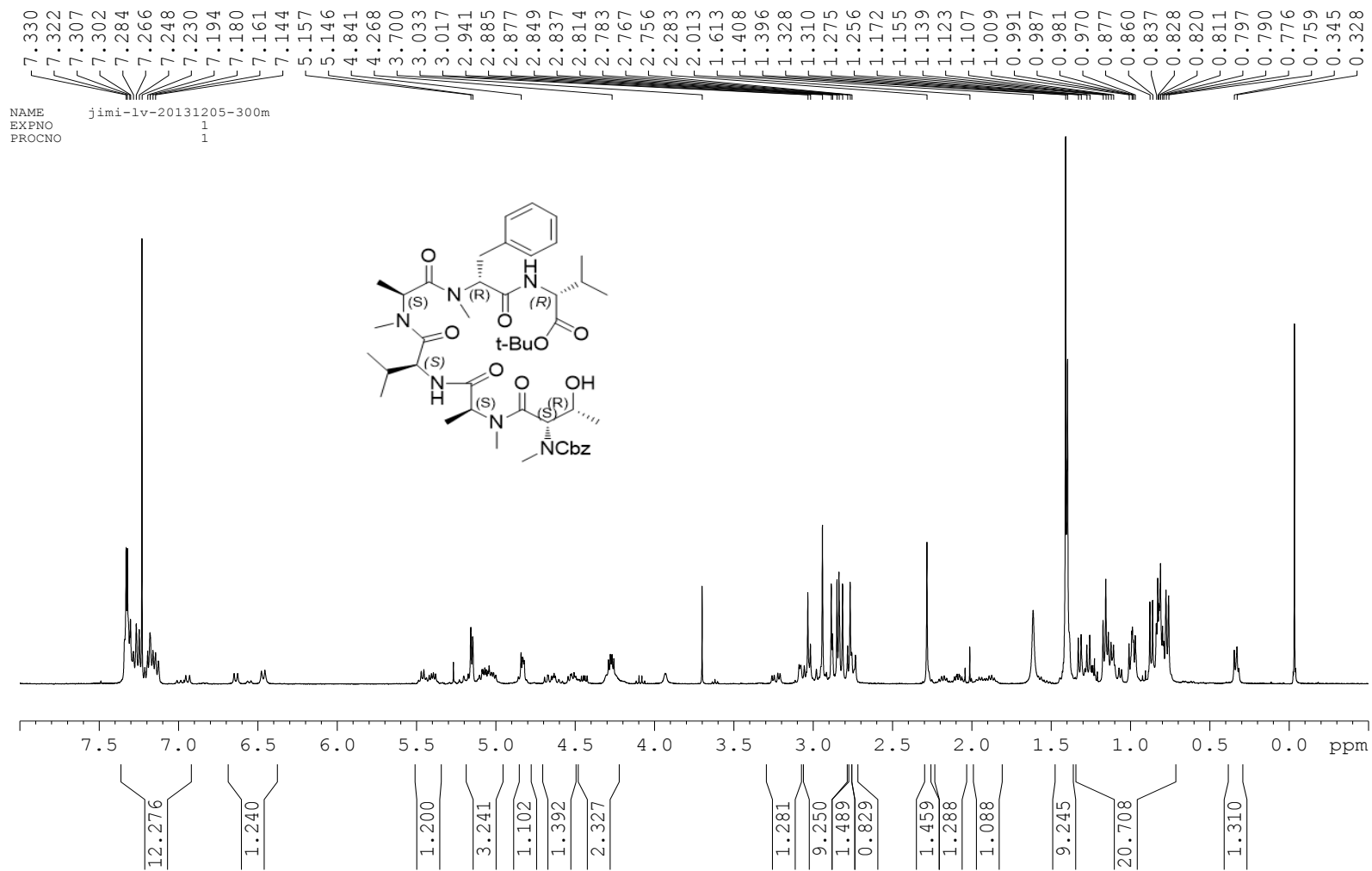
Figure S7. <sup>1</sup>H NMR of compound 28.

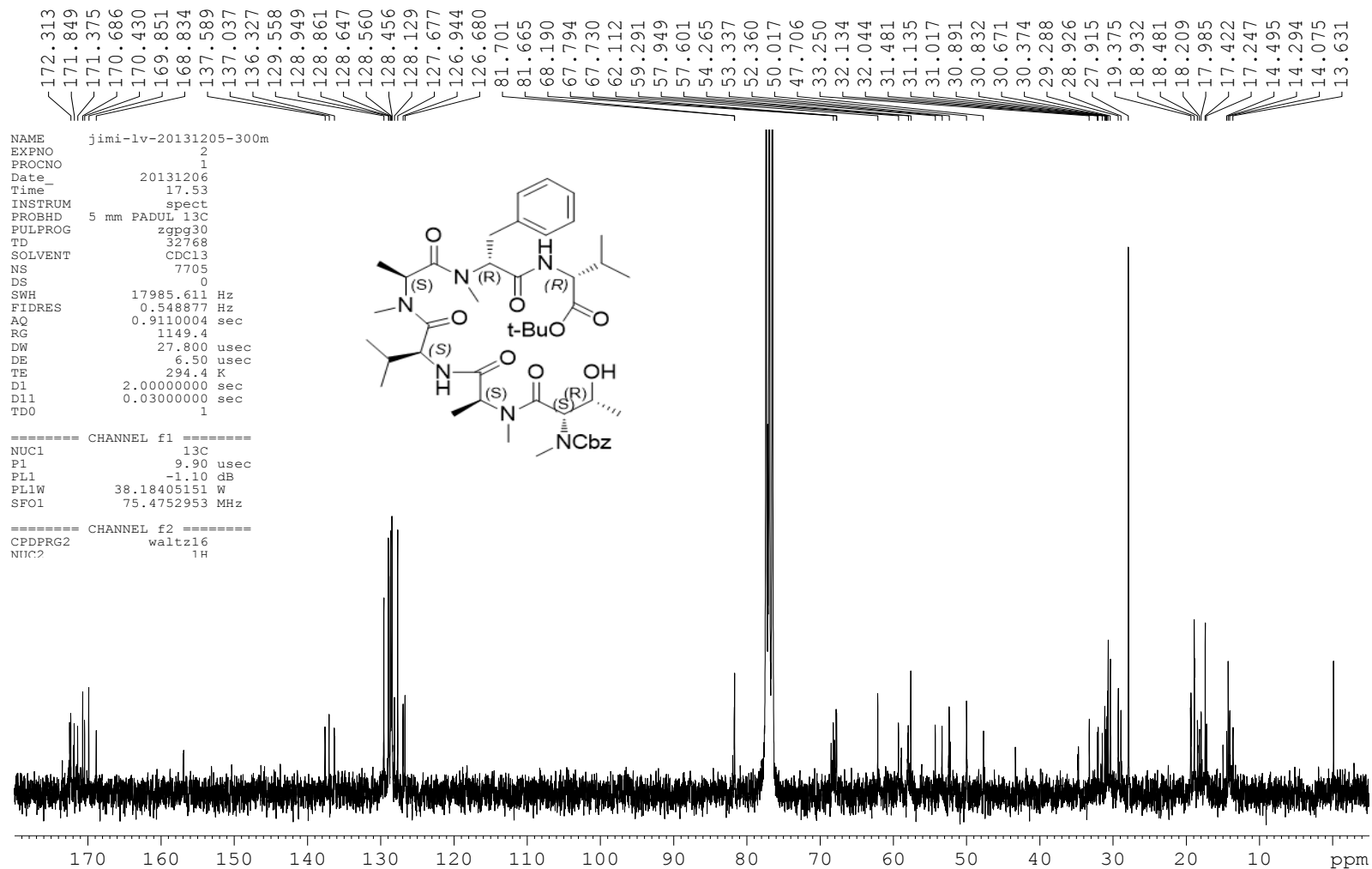
Figure S8. <sup>13</sup>C NMR of compound 28.

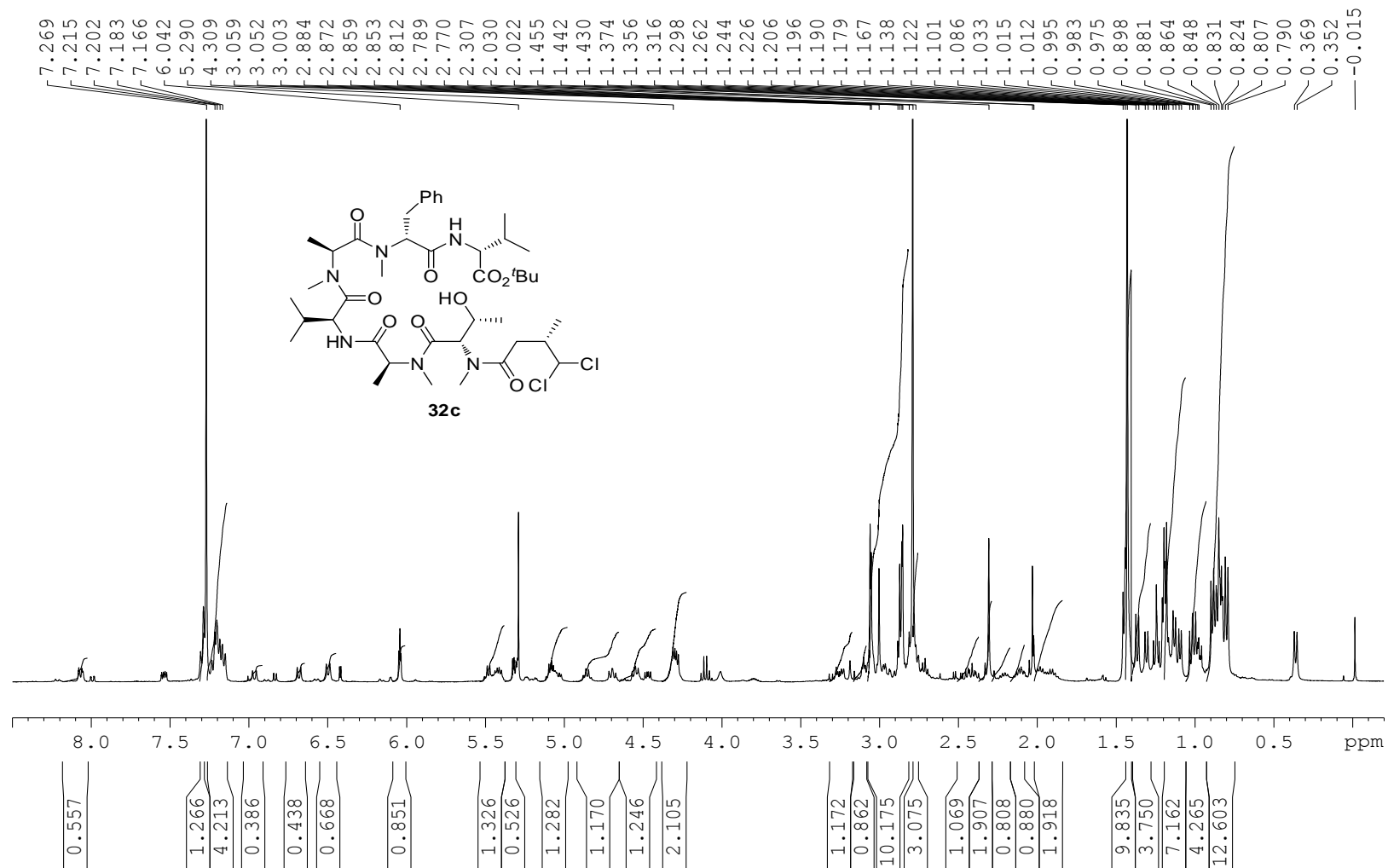


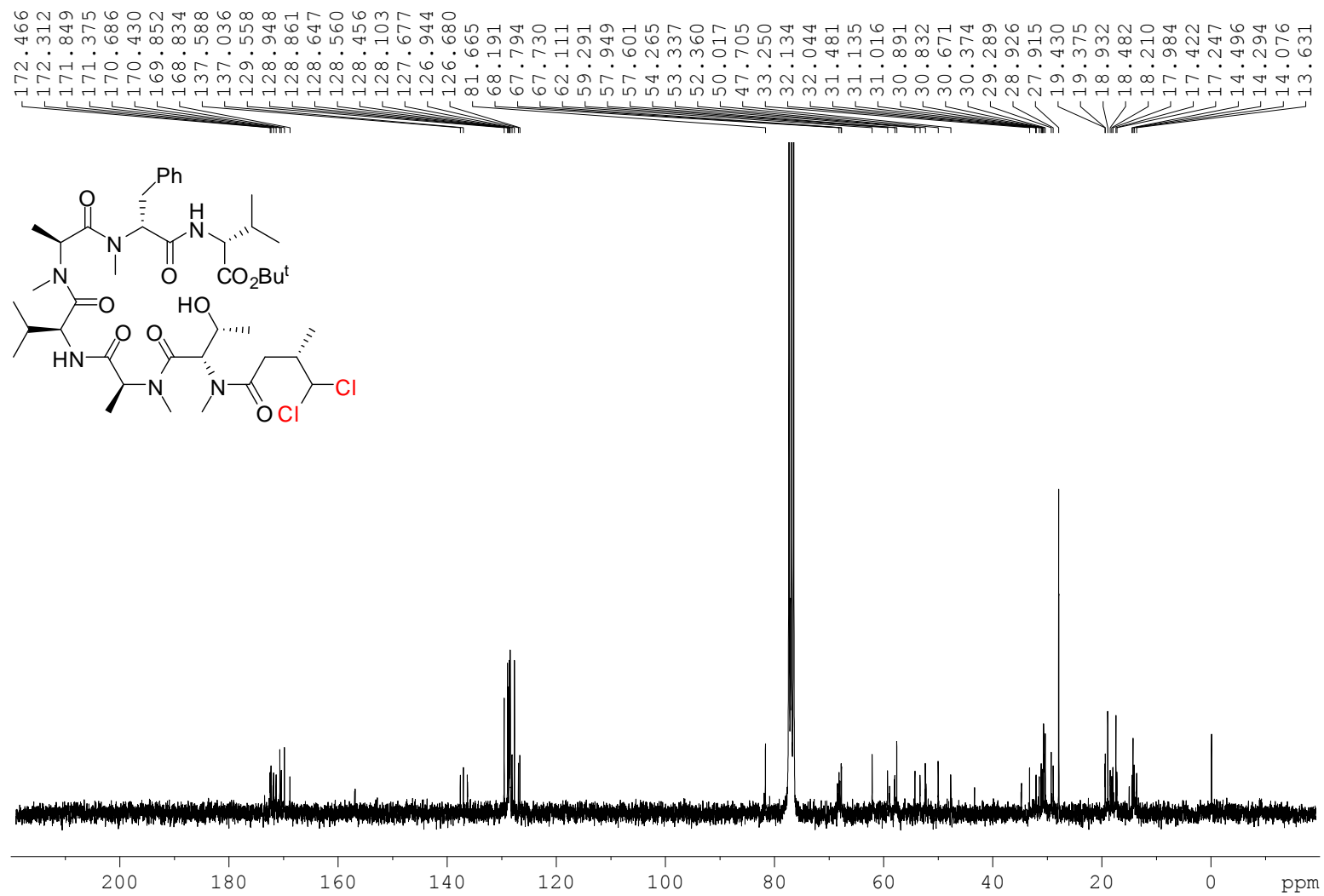
Figure S9. <sup>1</sup>H NMR of compound 30.

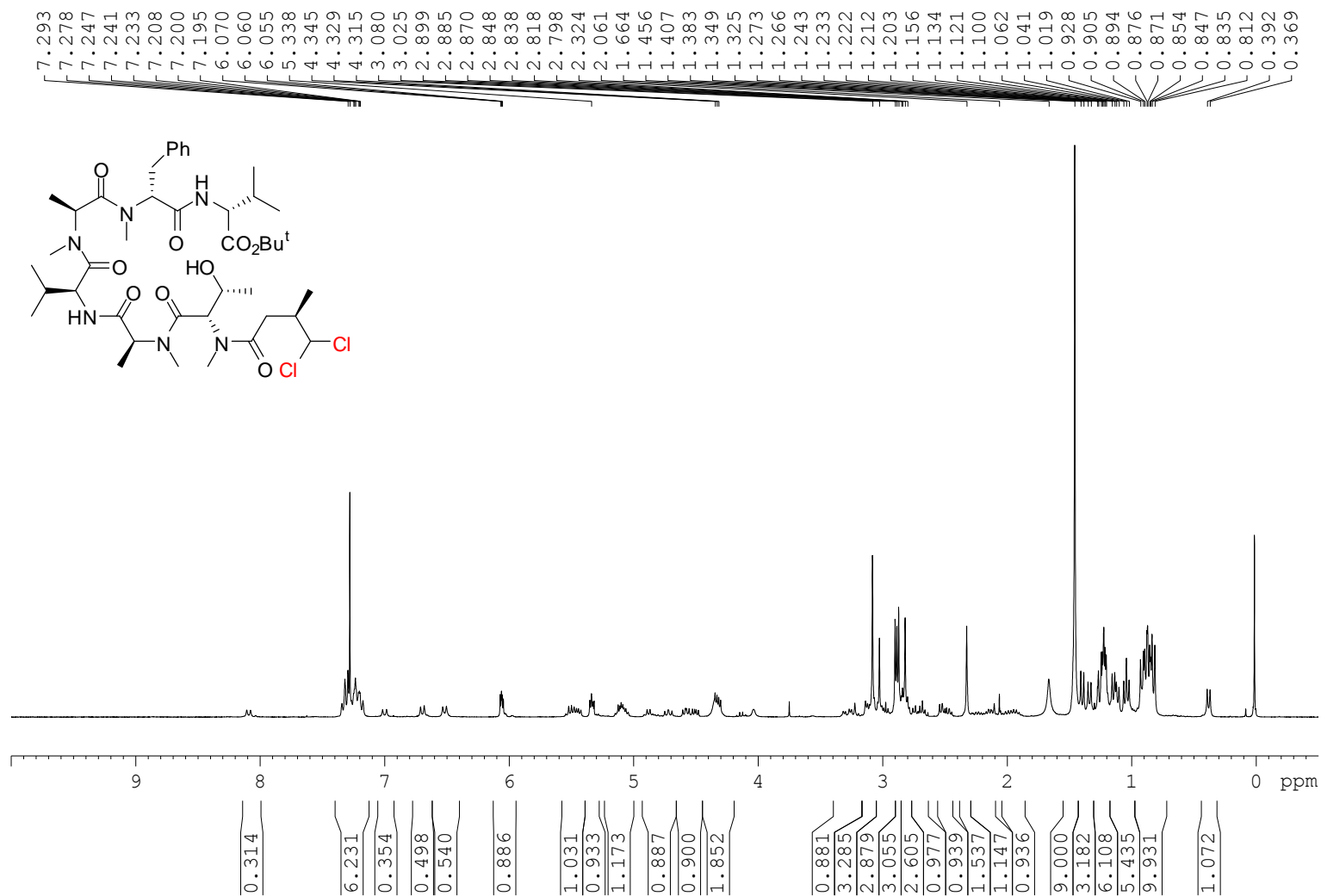
Figure S10. <sup>13</sup>C NMR of compound 30.

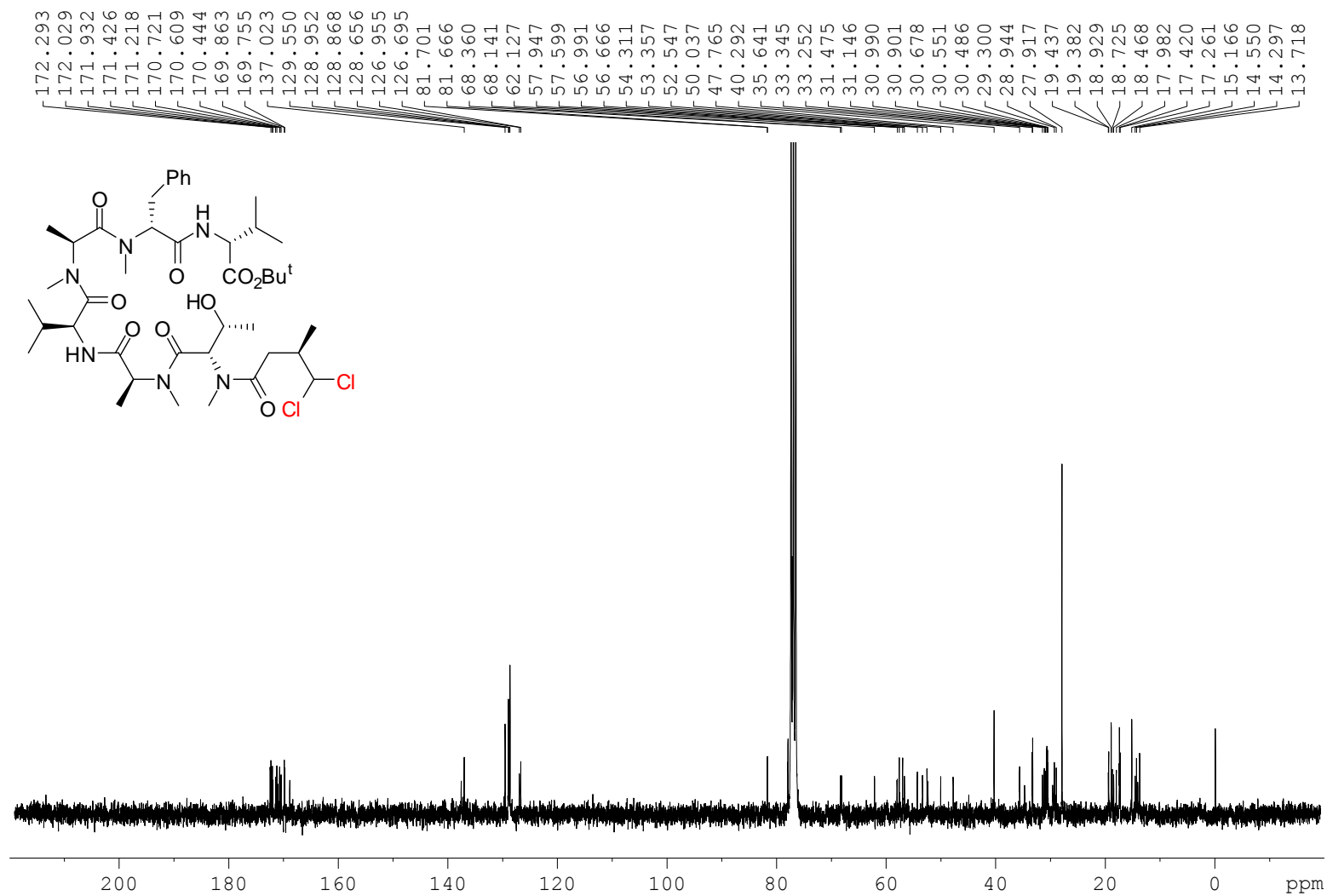
Figure S11. <sup>1</sup>H NMR of compound 31.



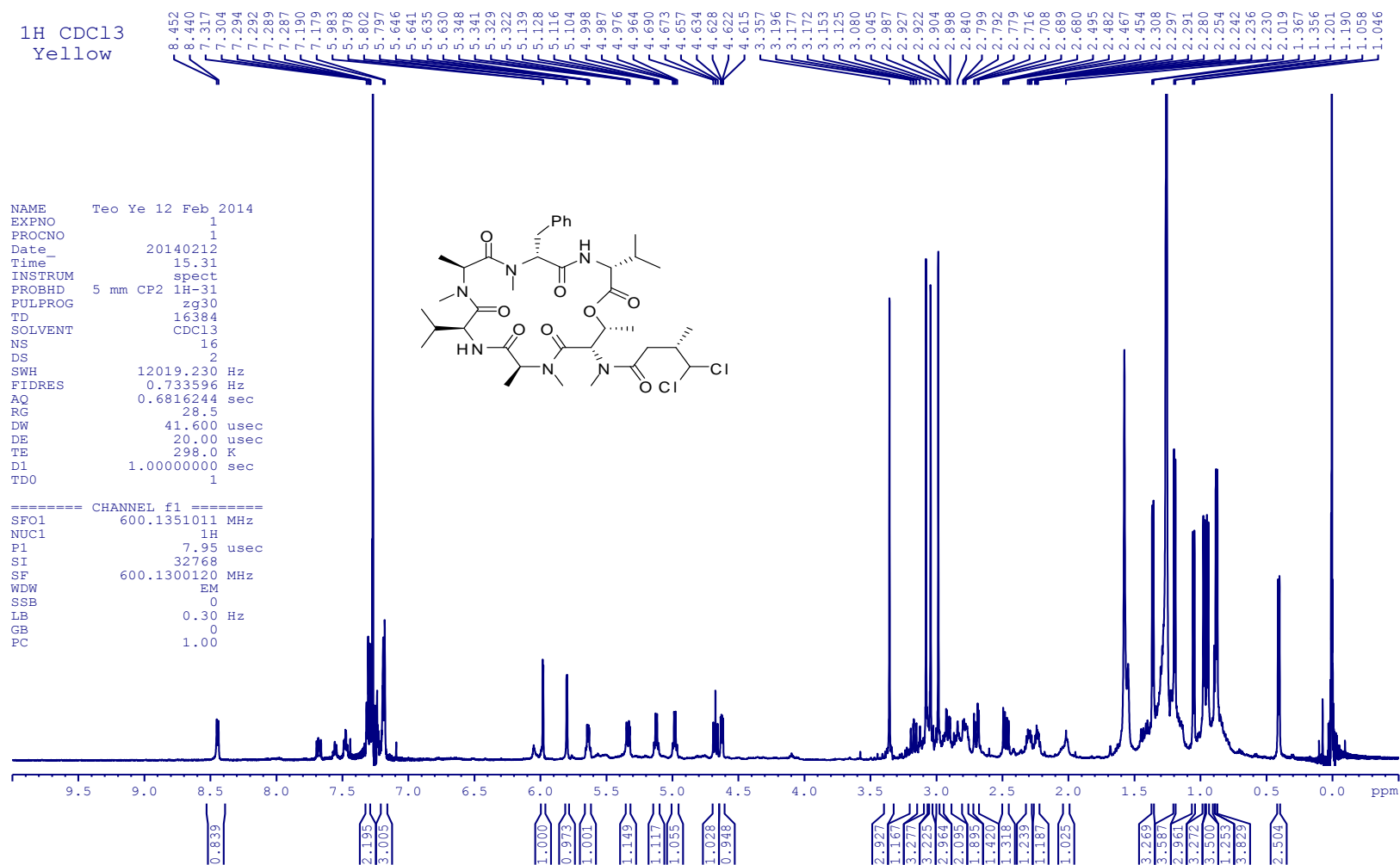
Figure S13. <sup>1</sup>H NMR of compound 32c.

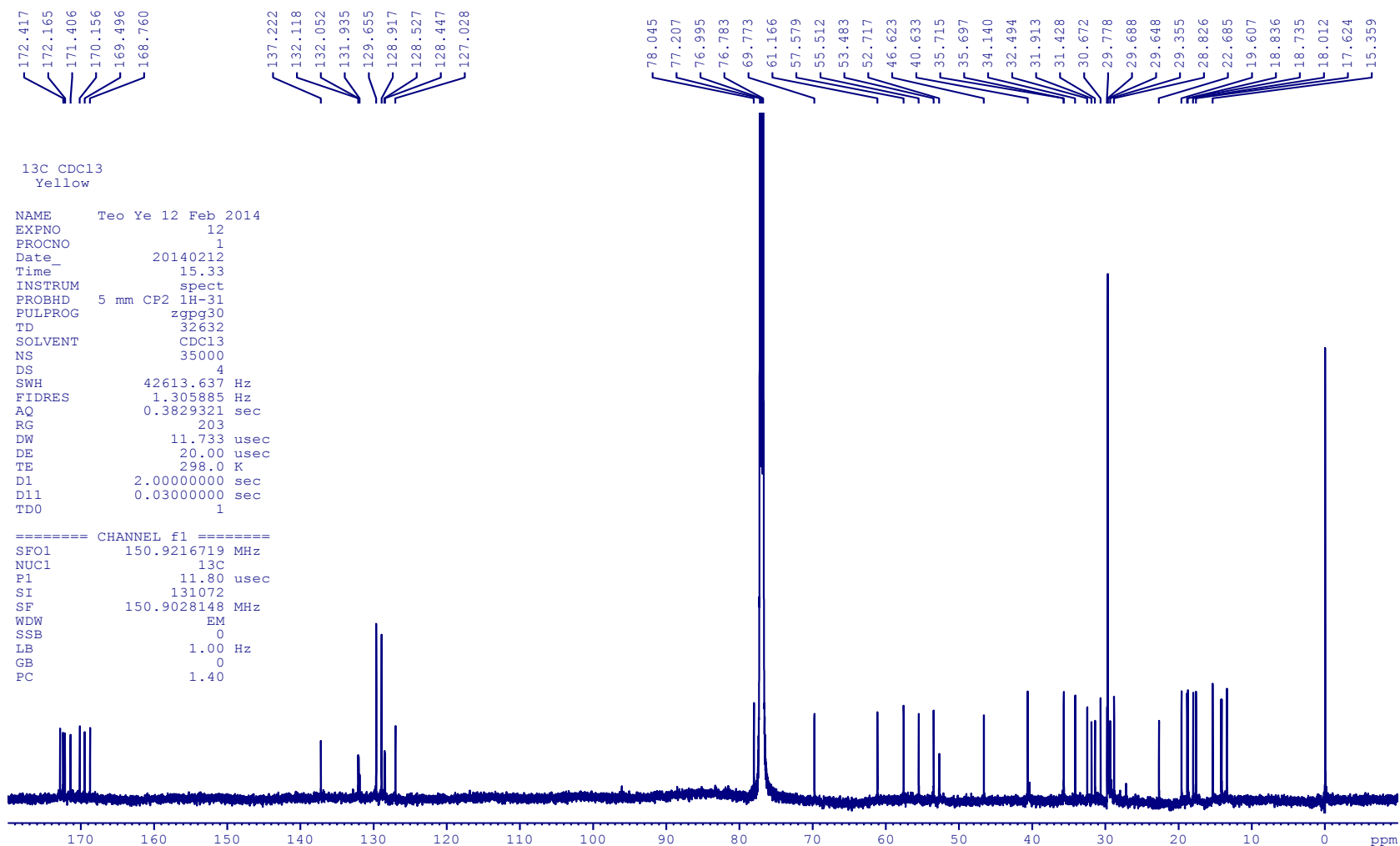
Figure S14. <sup>13</sup>C NMR of compound 32c.

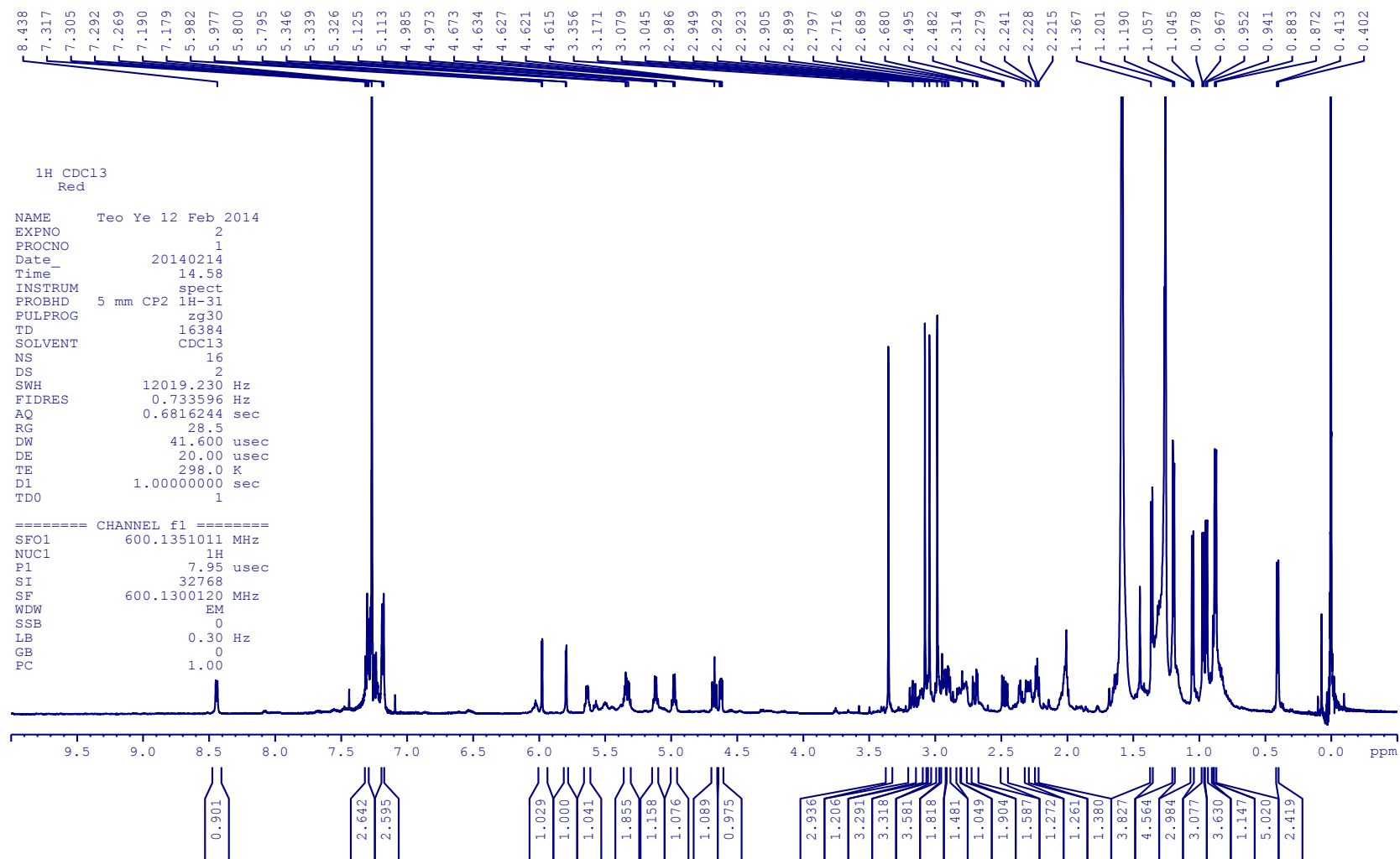
Figure S15. <sup>1</sup>H NMR of compound 32d.

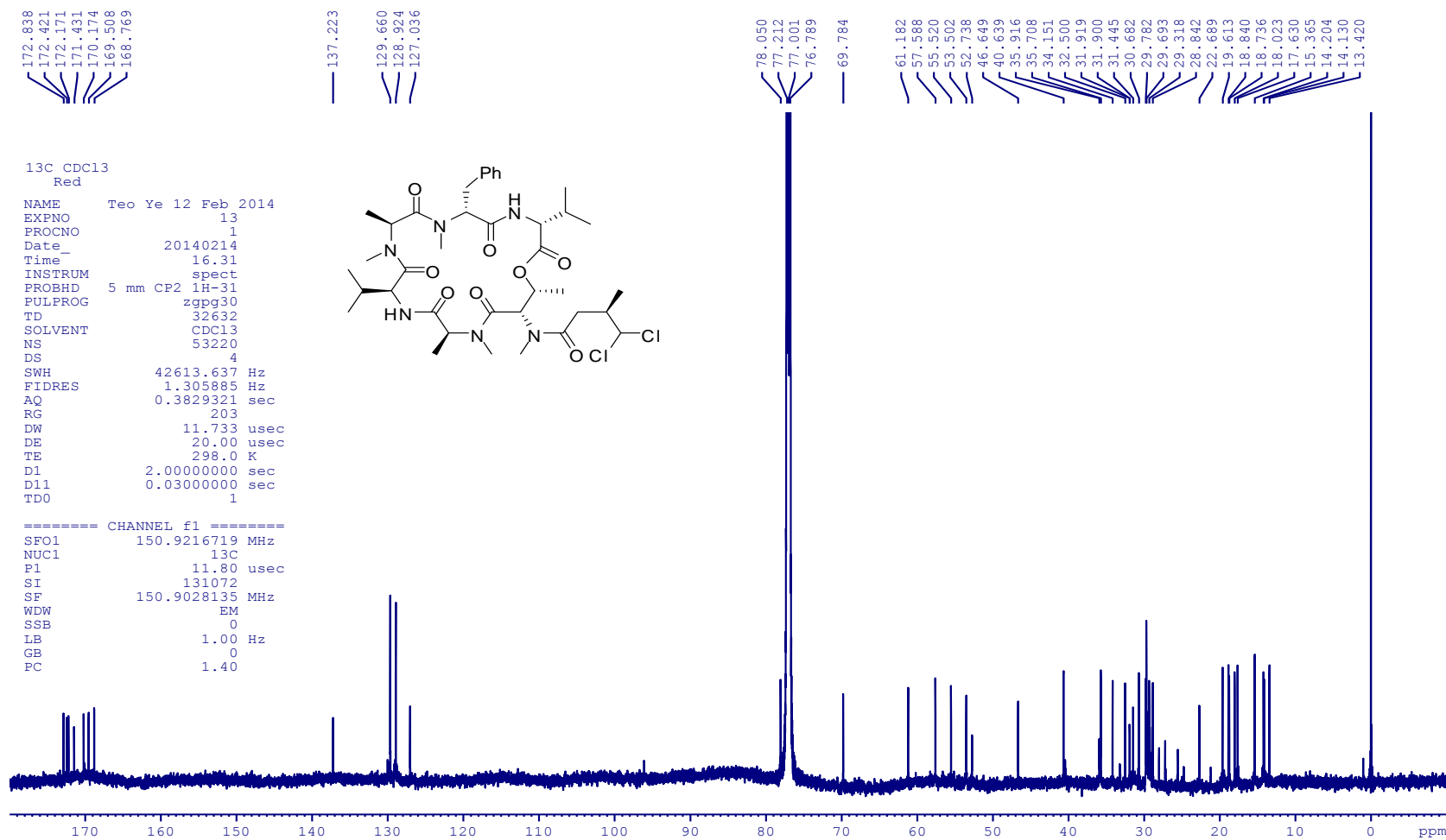
Figure S16. <sup>13</sup>C NMR of compound 32d.



Figure S17. <sup>1</sup>H NMR of itralamide B 1c.

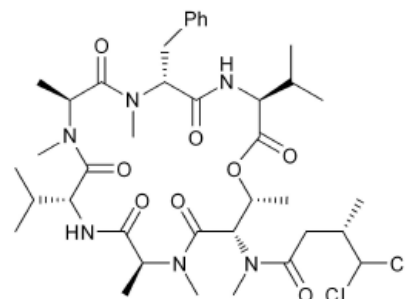
Figure S18. <sup>13</sup>C NMR of itralamide B 1c.

Figure S19.  $^1\text{H}$  NMR of itralamide B **1d**.

Figure S20. <sup>13</sup>C NMR of itralamide B 1d.

NAME lcs-04-JJ-130624-final-1  
EXPNO 1  
PROCNO 1  
Date\_ 20130624  
Time 22.36  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zg30  
TD 65536  
SOLVENT CDCl3  
NS 16  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 195.79  
DW 62.400 usec  
DE 6.50 usec  
TE 298.1 K  
D1 1.0000000 sec

lcs-04-JJ-130624-final-1  
400NMR CDC13



S-Itralamide B 1

===== CHANNEL f1 =====  
NUC1 1H  
P1 15.00 usec  
SI 65536  
SF 400.1300071 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

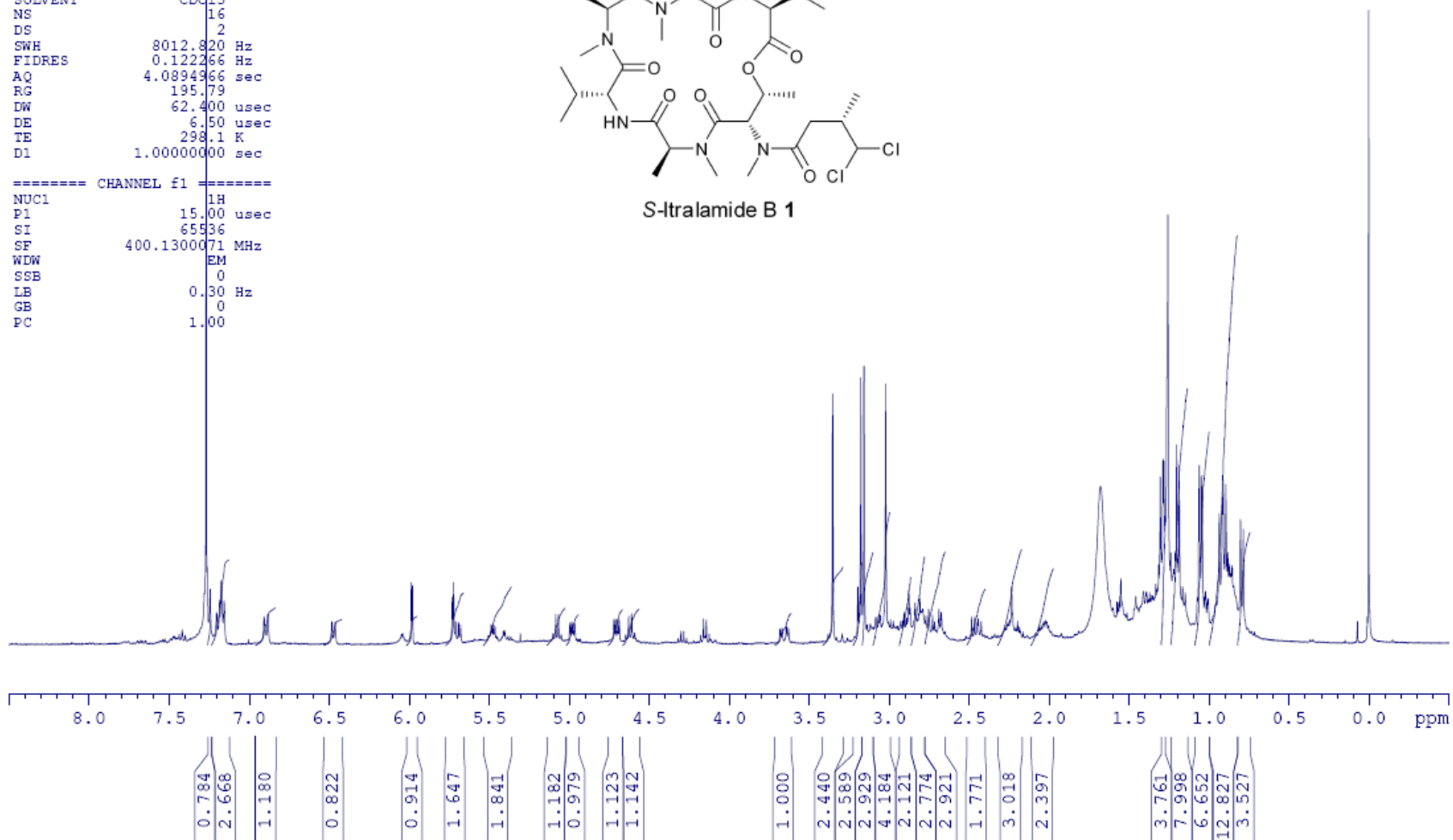
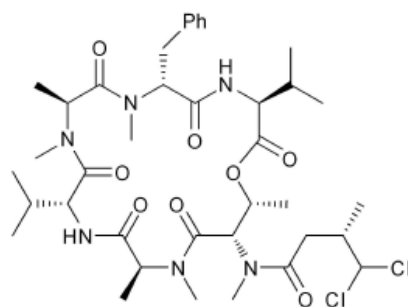


Figure S21. <sup>1</sup>H NMR of itralamide B 1a.

NAME lcs-04-JJ-130624-final-1  
EXPNO 2  
PROCNO 1  
Date\_ 20130624  
Time 22.39  
INSTRUM spect  
PROBHD 5 mm PABBO BB-  
PULPROG zgpg30  
TD 65536  
SOLVENT CDC13  
NS 11894  
DS 4  
SWH 24038.461 Hz  
FIDRES 0.366798 Hz  
AQ 1.3631988 sec  
RG 195.79  
DW 20.800 usec  
DE 6.50 usec  
TE 298.2 K  
D1 2.00000000 sec  
D11 0.03000000 sec

=====  
CHANNEL f1  
NUC1 13C  
P1 10.00 usec  
SI 32768  
SF 100.6127710 MHz  
WDW EM  
SSB 0  
LB 1.00 Hz  
GB 0  
PC 1.40

lcs-04-JJ-130624-final-1  
400NMR CDC13



S-Itralamide B 1

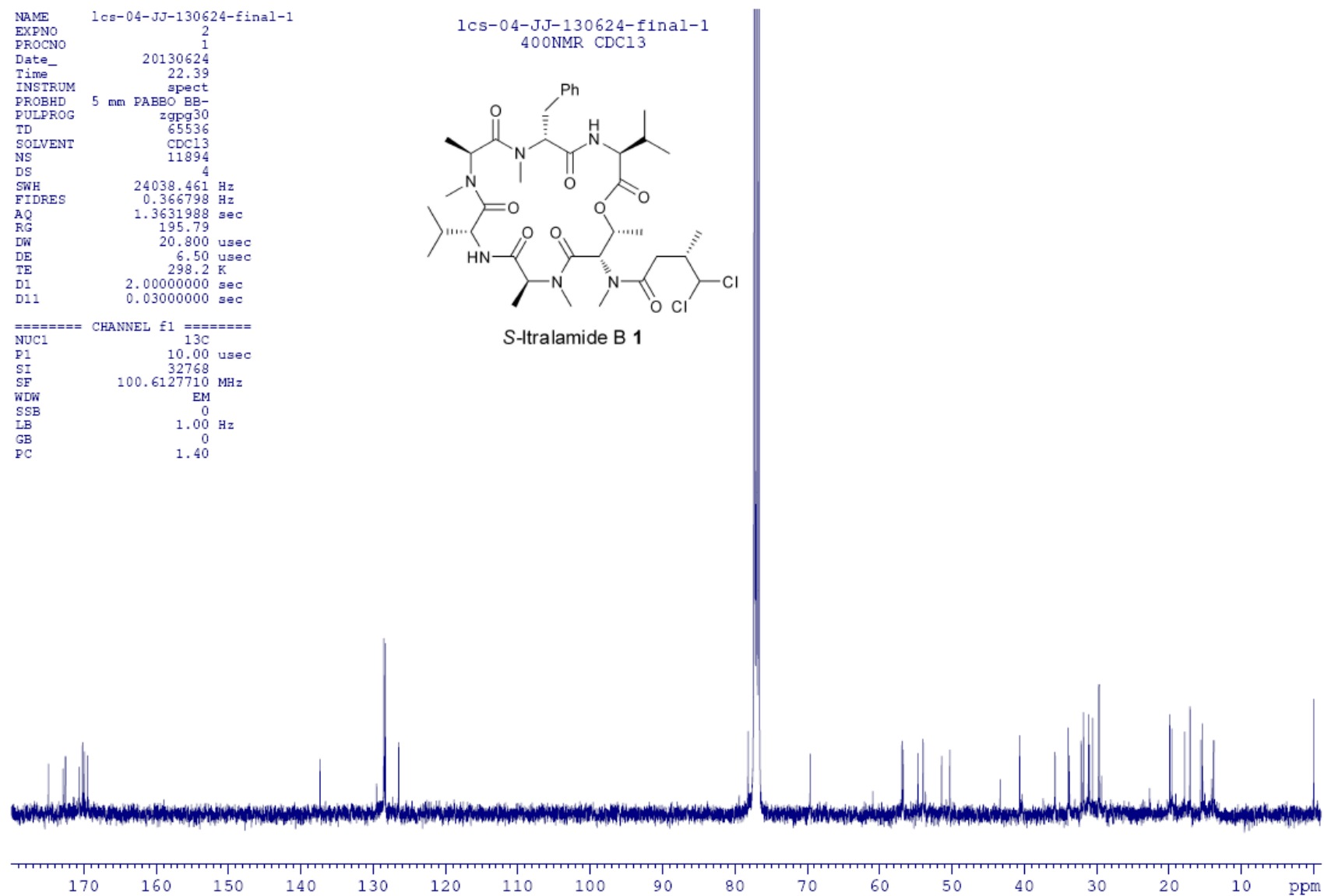
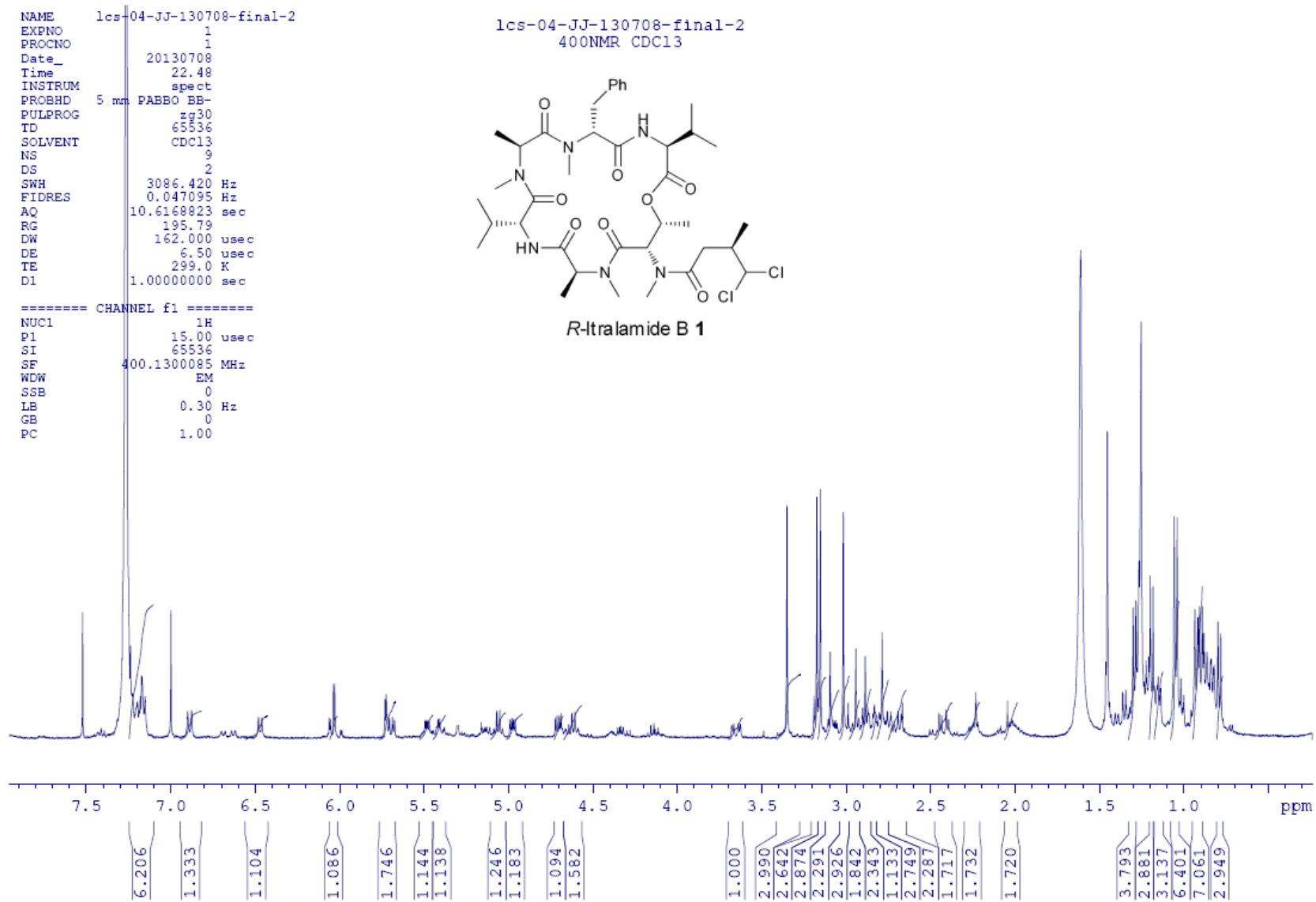


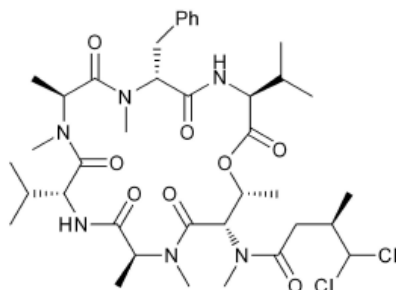
Figure S22. <sup>13</sup>C NMR of itralamide B 1a.

Figure S23. <sup>1</sup>H NMR of itralamide B 1b.

```
NAME      lcs-04-JJ-130708-final-2
EXPNO     2
PROCNO    1
Date_     20130708
Time      22.53
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zgpg30
TD         65536
SOLVENT   CDC13
NS         9156
DS         4
SWH        18115.941 Hz
FIDRES    0.276427 Hz
AQ         1.8088436 sec
RG         195.79
DW         27.600 usec
DE         6.50 usec
TE         299.1 K
D1         2.00000000 sec
D11        0.03000000 sec
```

```
===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
SI         32768
SF         100.6127716 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
```

lcs-04-JJ-130708-final-2  
400NMR CDC13



R-Italamide B 1

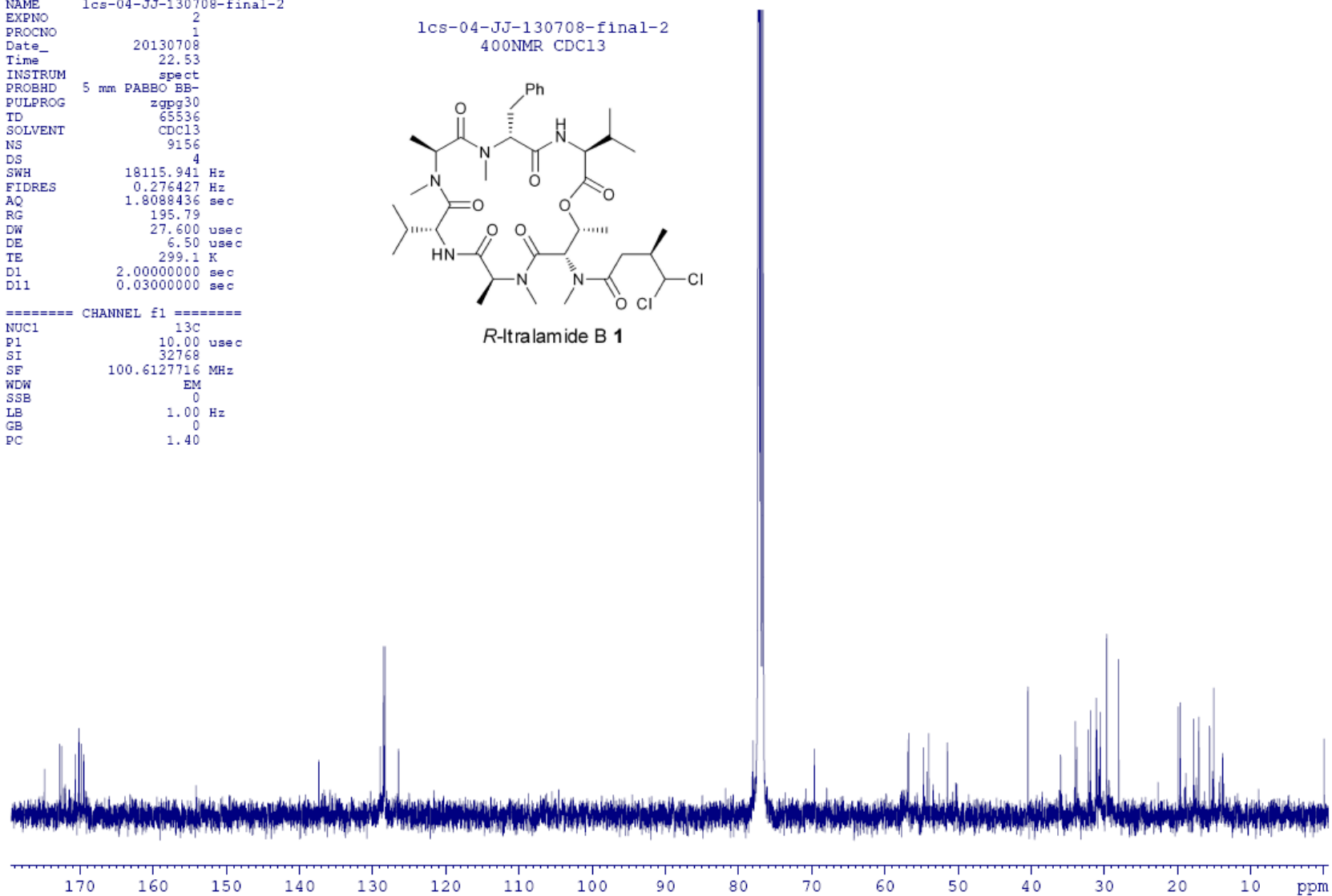


Figure S24. <sup>13</sup>C NMR of itralamide B 1b.



**Table S1.** Comparison of  $^{13}\text{C}$  NMR data of natural itralamide B with synthetic samples.

Carbon No.	$\delta_{\text{Natural product}}$	$\delta_{1a}$	$\delta_{\text{NP}}-\delta_{1a}$	$\delta_{1b}$	$\delta_{\text{NP}}-\delta_{1b}$	$\delta_{1c}$	$\delta_{\text{NP}}-\delta_{1c}$	$\delta_{1d}$	$\delta_{\text{NP}}-\delta_{1d}$
2	173.9	174.89	-0.99	174.88	-0.98	172.83	1.07	172.84	1.06
3	56.6	56.75	-0.15	56.75	-0.15	57.6	-1	57.59	-0.99
3a	32	32.15	-0.15	32.18	-0.18	32.49	-0.49	32.5	-0.5
3b	20.5	19.63	0.87	19.63	0.87	19.61	0.89	19.61	0.89
3c	16.6	17.1	-0.5	17.09	-0.49	17.62	-1.02	17.63	-1.03
5	-	169.47	-	169.51	-	168.76	-	168.77	-
6	56.7	56.92	-0.22	56.88	-0.18	61.17	-4.47	61.18	-4.48
6a	33.4	33.77	-0.37	33.78	-0.38	34.14	-0.74	34.15	-0.75
6b	137.5	137.35	0.15	137.37	0.13	137.22	0.28	137.22	0.28
6c/6c'	128.5	128.54	-0.04	128.55	-0.05	129.66	-1.16	129.66	-1.16
6d/6d'	128.3	128.34	-0.04	128.34	-0.04	128.92	-0.62	128.92	-0.62
6e	126.3	126.48	-0.18	126.48	-0.18	127.03	-0.73	127.04	-0.74
7a	31.5	31	0.5	31.02	0.48	30.67	0.83	30.68	0.82
8	172.7	172.84	-0.14	172.83	-0.13	172.42	0.28	172.42	0.28
9	51.6	51.43	0.17	51.47	0.13	46.62	4.98	46.65	4.95
9a	13	13.82	-0.82	13.83	-0.83	13.43	-0.43	13.42	-0.42
10a	31.6	31.12	0.48	31.12	0.48	31.43	0.17	31.45	0.15
11	172.1	170.65	1.45	170.68	1.42	171.41	0.69	171.43	0.67
12	54.9	54.69	0.21	54.75	0.15	55.51	-0.61	55.52	-0.62
12a	30.9	30.54	0.36	30.55	0.35	29.78	1.12	29.69	1.21
12b	20.8	19.9	0.9	19.89	0.91	22.69	-1.89	22.69	-1.89
12c	16.3	15.61	0.69	17.07	-0.77	14.21	2.09	14.2	2.1
14	170.4	170.17	0.23	170.17	0.23	170.16	0.24	170.17	0.23
15	53.5	53.98	-0.48	53.99	-0.49	52.72	0.78	52.74	0.76
15a	13.5	14.1	-0.6	15.05	-1.55	14.13	-0.63	14.13	-0.63

Table S1. Cont.

16a	31.7	31.83	-0.13	31.85	-0.15	31.91	-0.21	31.92	-0.22
17	169.9	169.9	0	169.85	0.05	169.5	0.4	169.51	0.39
18	54.8	54.68	0.12	54.22	0.58	53.48	1.32	53.5	1.3
18a	68.8	69.62	-0.82	69.64	-0.84	69.77	-0.97	59.78	-0.98
18b	17.7	17.82	-0.12	17.82	-0.12	18.01	-0.31	18.02	-0.32
19a	34.1	33.92	0.18	33.97	0.13	35.7	-1.6	35.71	-1.61
20	172.6	172.53	0.07	172.56	0.04	172.17	0.43	172.17	0.43
21	35.8	35.75	0.05	35.98	-0.18	35.72	0.08	35.92	-0.12
22	40.5	40.65	-0.15	40.45	0.05	40.63	-0.13	40.64	-0.14
22a	15.1	15.35	-0.25	15.6	-0.5	15.37	-0.27	15.36	-0.26
23	77.8	78.18	-0.38	78.02	-0.22	78.05	-0.25	78.05	-0.25

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