



## Supporting Information

for

### **Menthyl esterification allows chiral resolution for the synthesis of artificial glutamate analogs**

Kenji Morokuma, Shuntaro Tsukamoto, Kyosuke Mori, Kei Miyako, Ryuichi Sakai, Raku Irie and Masato Oikawa

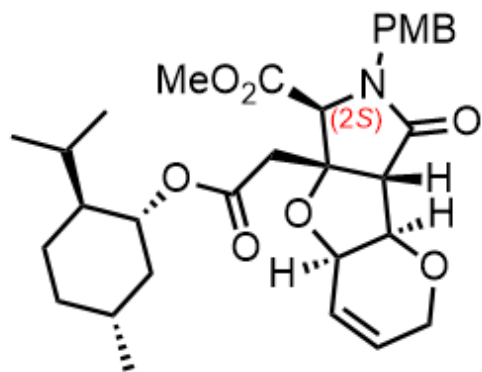
*Beilstein J. Org. Chem.* **2021**, *17*, 540–550. doi:10.3762/bjoc.17.48

### **NMR spectra of all new compounds**

**Contents:**

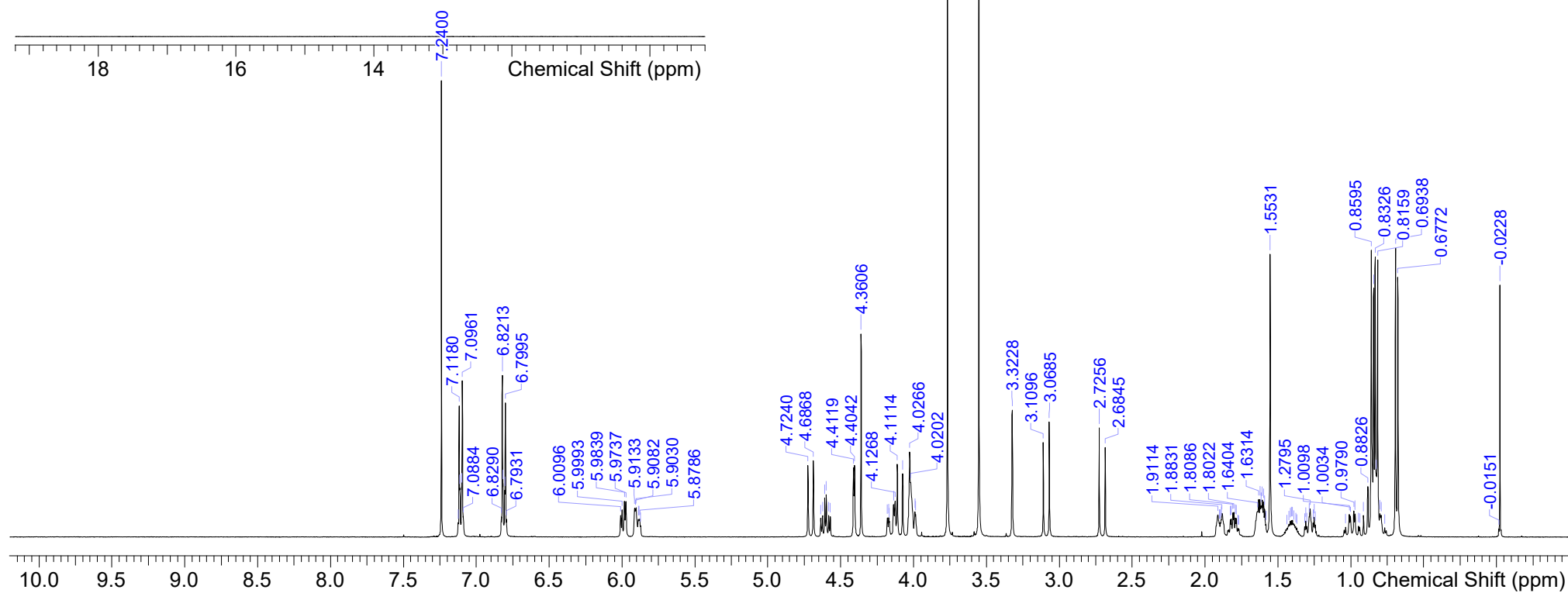
NMR spectra for all new compounds

**SII-2 ~ SII-39**



9\* (2S)

SII-2



Date 29 Jan 2018 20:04:36

AA70061-002

Nucleus 1H

Pulse Sequence zg30\_Bruker\_AVIIIHD400N-2

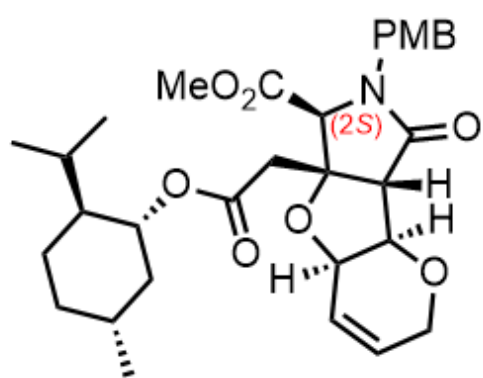
Solvent CHLOROFORM-d

Acquisition Time (sec) 1.9464

Frequency (MHz) 400.0300

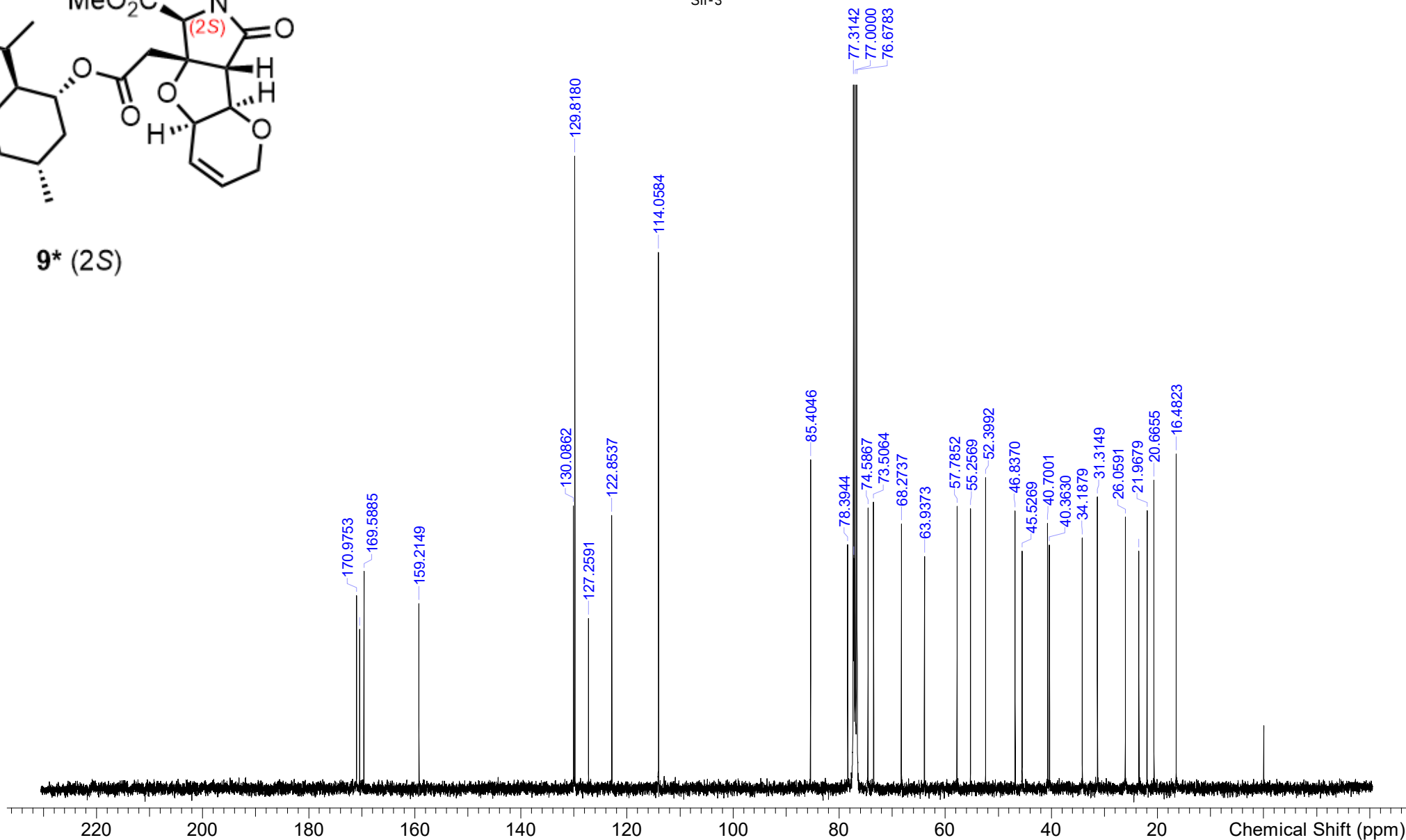
Receiver Gain 202.37

Sweep Width (Hz) 8417.00



**9\* (2S)**

SII-3



Date 30 Jan 2018 07:23:28

AA70061-002

Nucleus <sup>13</sup>C

Pulse Sequence zgpg30\_Bruker\_AVIIHD400N-2

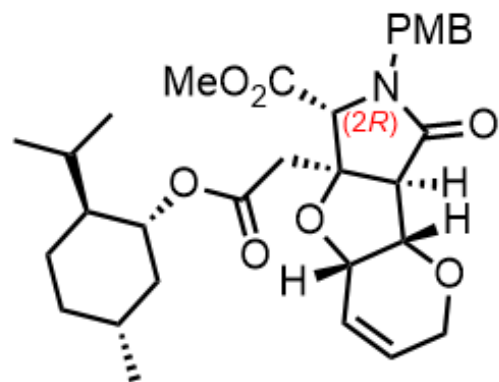
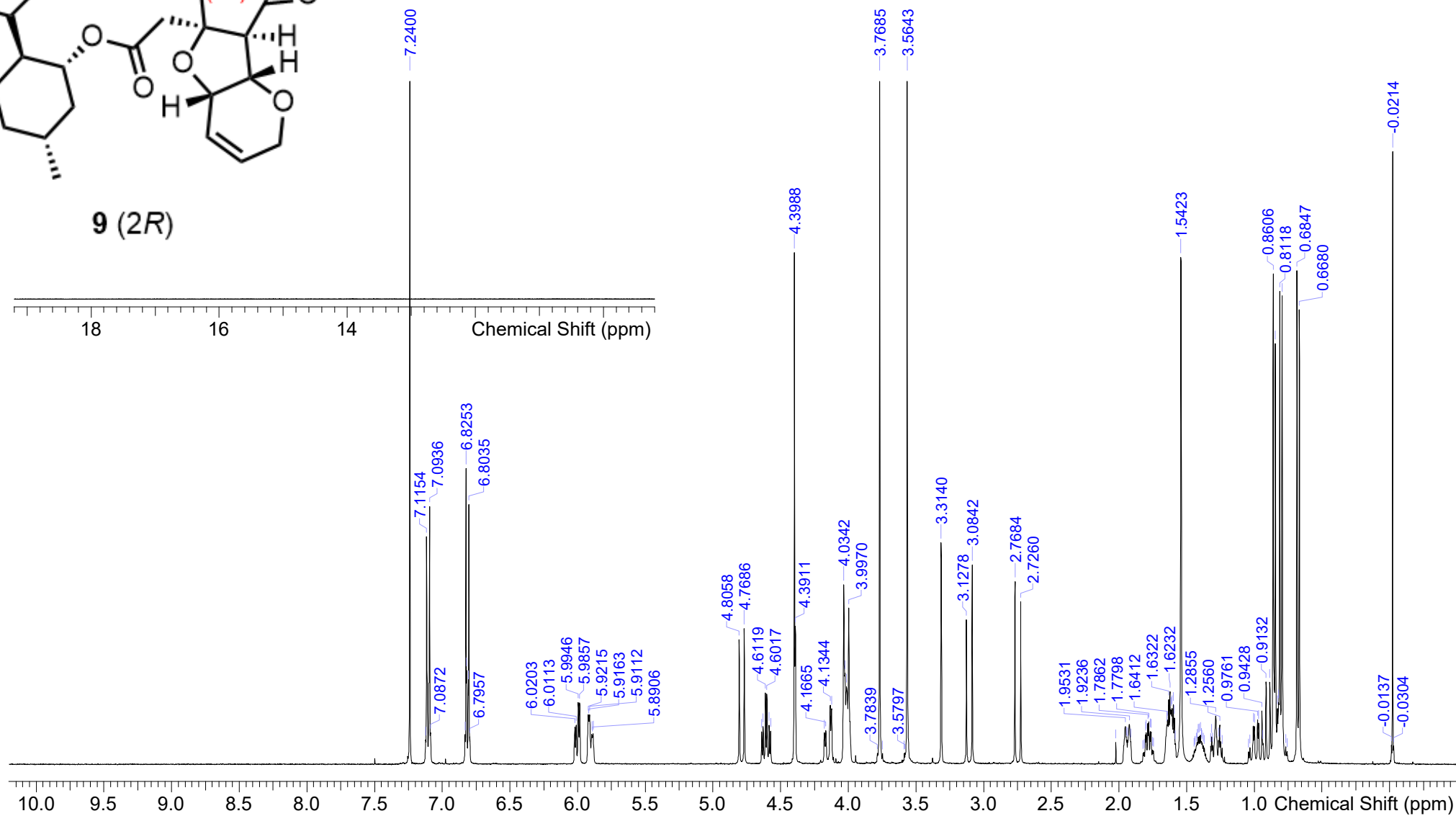
Solvent CHLOROFORM-d

Acquisition Time (sec) 1.2976

Frequency (MHz) 100.5876

Receiver Gain 202.37

Sweep Width (Hz) 25251.75

**9 (2R)**

Date 23 Jan 2018 17:52:55

AA70051-003

Nucleus <sup>1</sup>H

Pulse Sequence zg30\_Bruker\_AVANCEIII400N

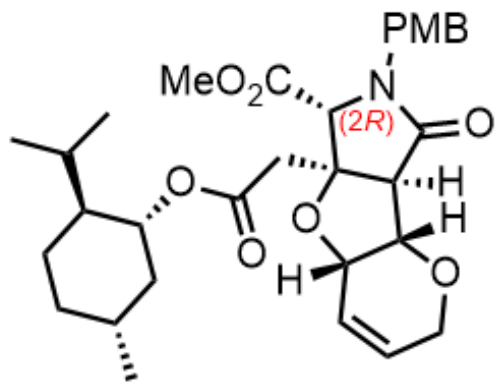
Solvent CHLOROFORM-d

Acquisition Time (sec) 1.9464

Frequency (MHz) 400.1800

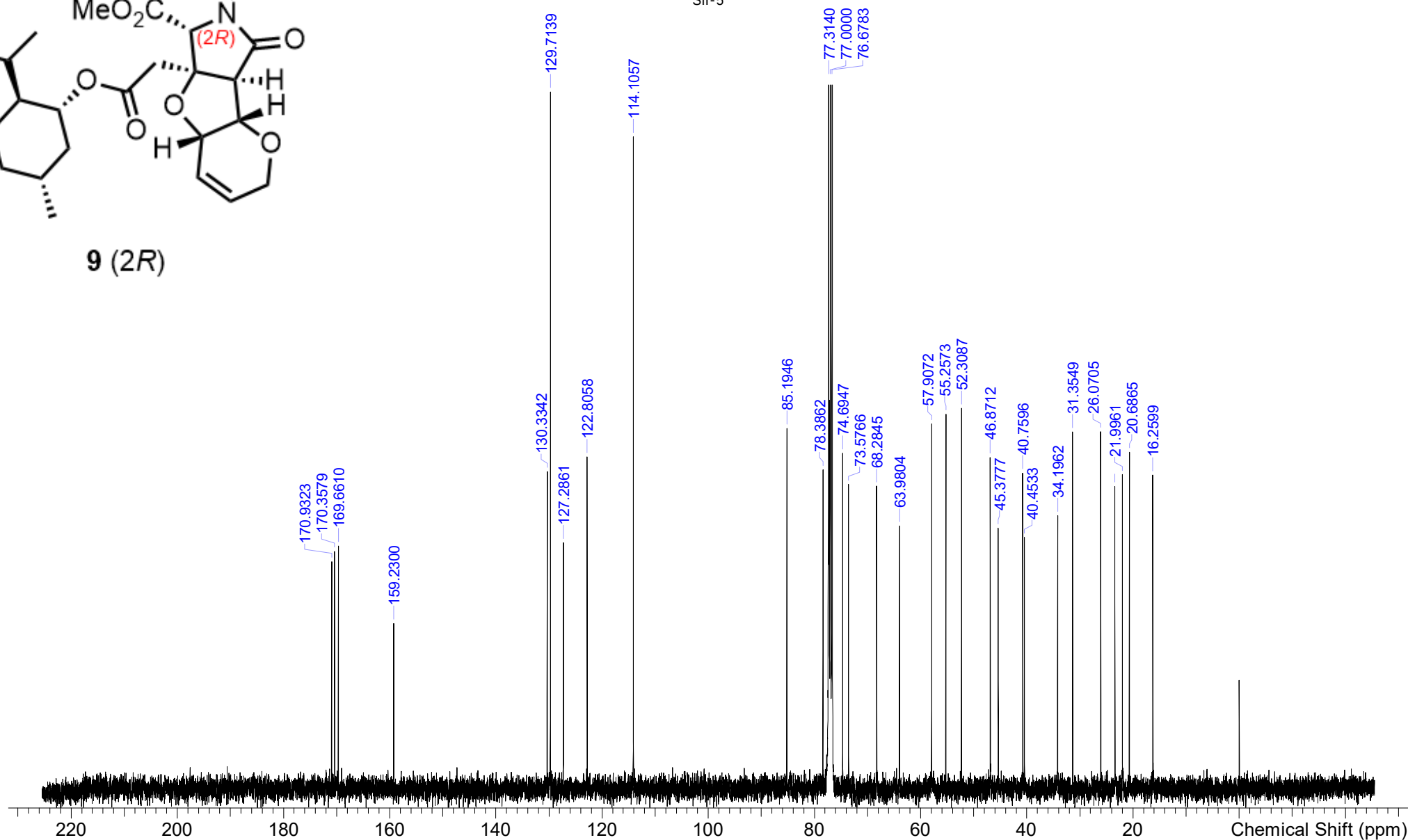
Receiver Gain 128.00

Sweep Width (Hz) 8417.00



**9 (2R)**

SII-5



**Date** 24 Jan 2018 05:25:30

AA70051-003

**Nucleus**  $^{13}\text{C}$

**Pulse Sequence** zgpg30\_Bruker\_AVANCEIII400N

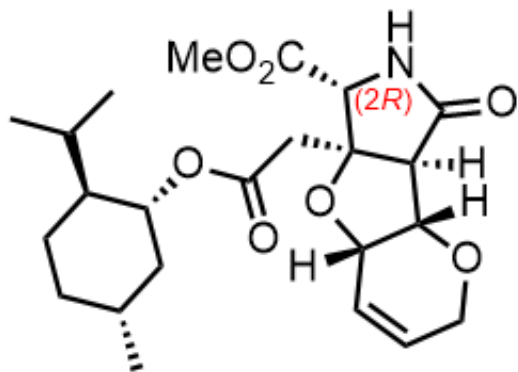
**Solvent** CHLOROFORM-d

**Acquisition Time (sec)** 1.2976

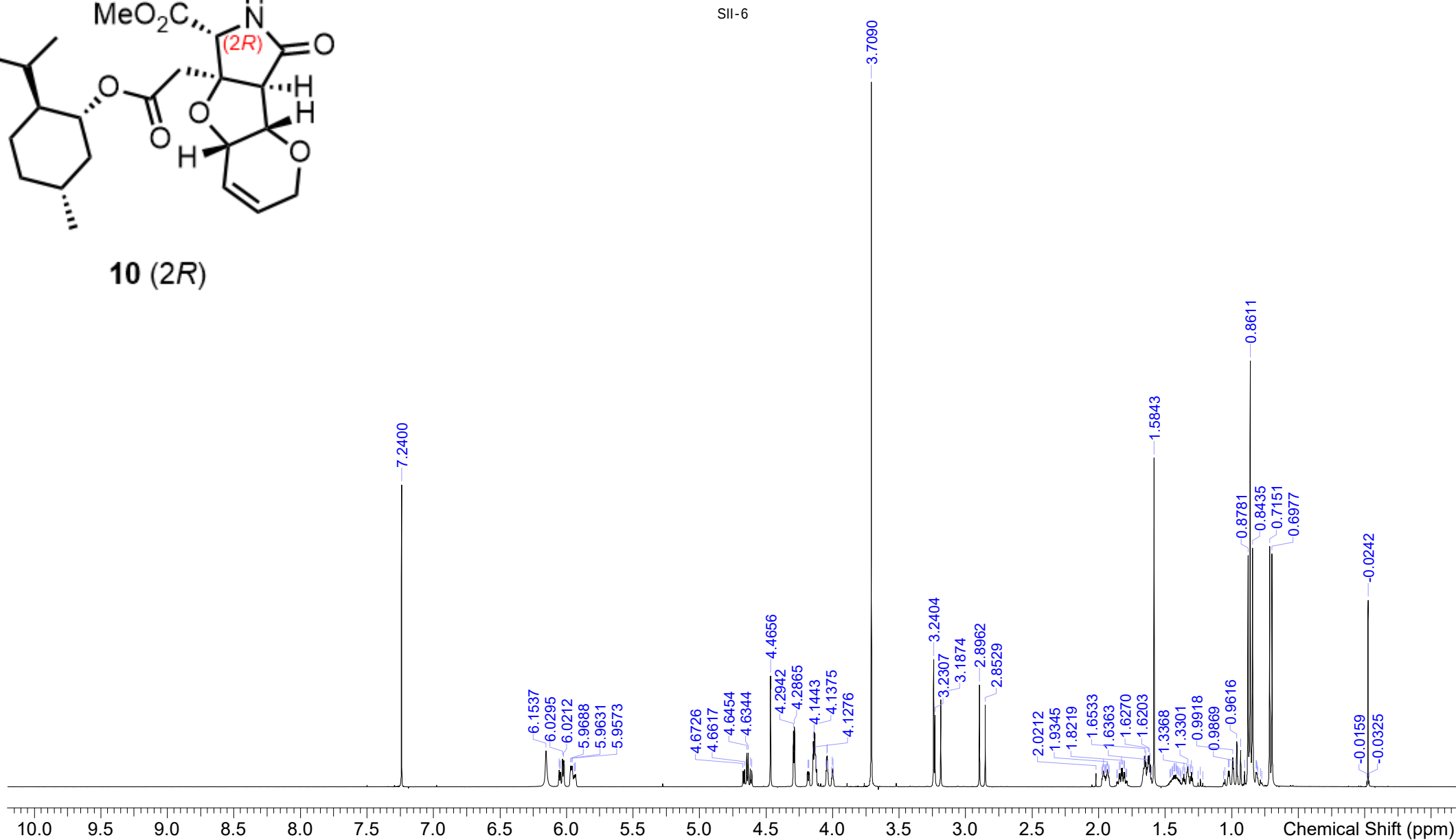
**Frequency (MHz)** 100.6253

**Receiver Gain** 203.00

**Sweep Width (Hz)** 25251.75



**10 (2R)**



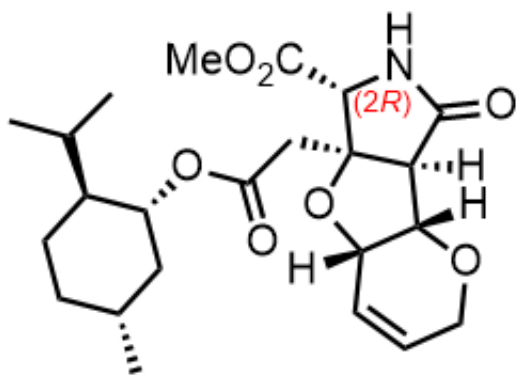
Date 16 Nov 2020 22:05:37

Kenji Morokuma  
AA70065-002

Nucleus 1H  
Pulse Sequence zg30\_Bruker\_AVANCEII400M  
Solvent CHLOROFORM-d

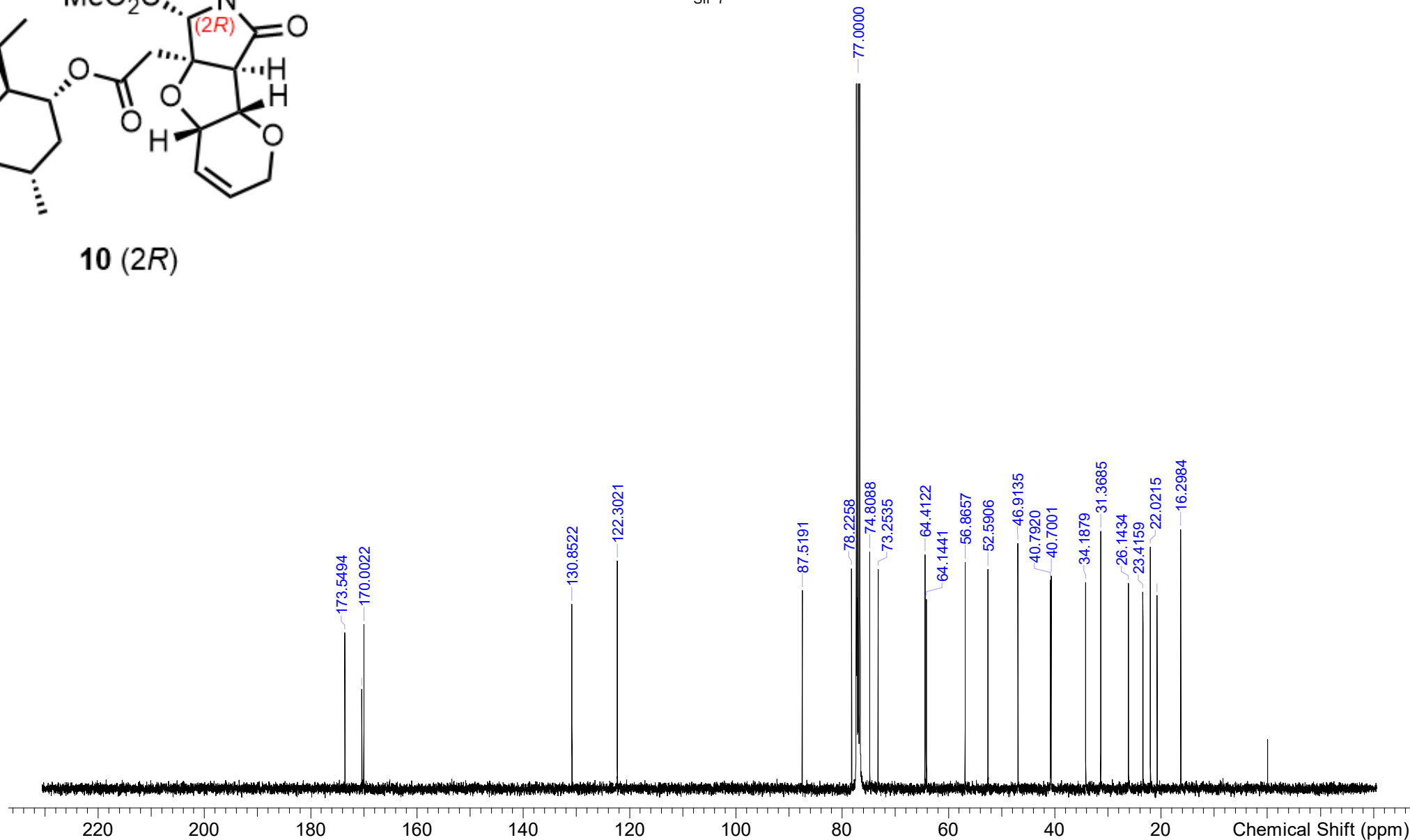
Acquisition Time (sec) 3.8928  
Frequency (MHz) 400.1300  
Receiver Gain 406.00  
Sweep Width (Hz) 8417.38

D1 1  
NS 32  
SI 65536  
TD 65536



**10 (2R)**

SII-7



Date 24 Jan 2018 07:30:39

AA70052-001

Nucleus <sup>13</sup>C

Pulse Sequence zgpg30\_Bruker\_AVIIHD400N-2

Solvent CHLOROFORM-d

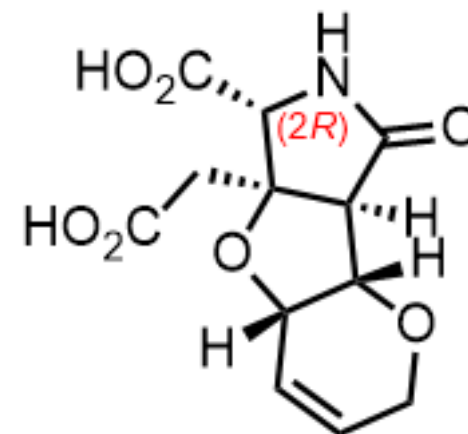
Acquisition Time (sec) 1.2976

Frequency (MHz) 100.5876

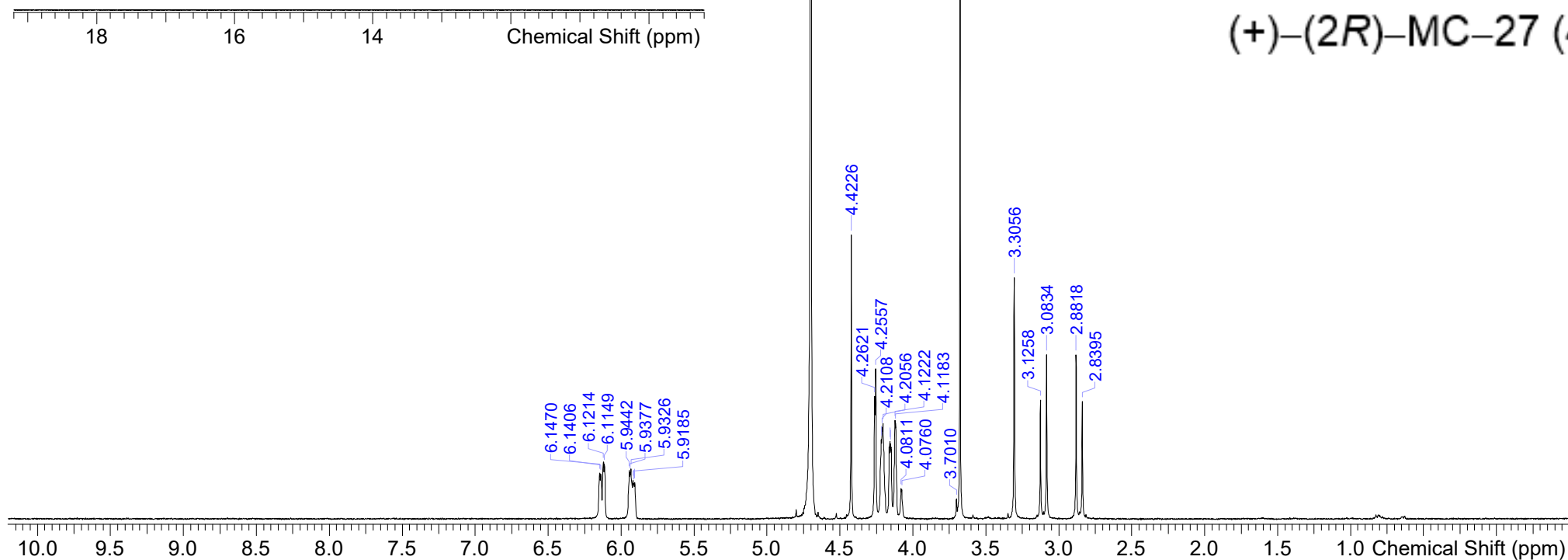
Receiver Gain 202.37

Sweep Width (Hz) 25251.75

SII-8



(+)-(2R)-MC-27 (4)



Date 23 Jan 2018 13:48:34

AA70069-001

Nucleus 1H

Pulse Sequence zg30\_Bruker\_AVANCEII400M

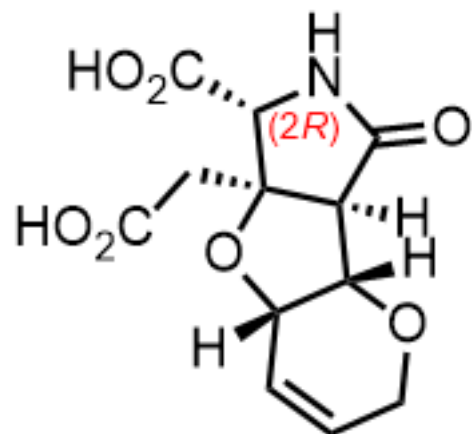
Solvent DEUTERIUM OXIDE

Acquisition Time (sec) 1.9464

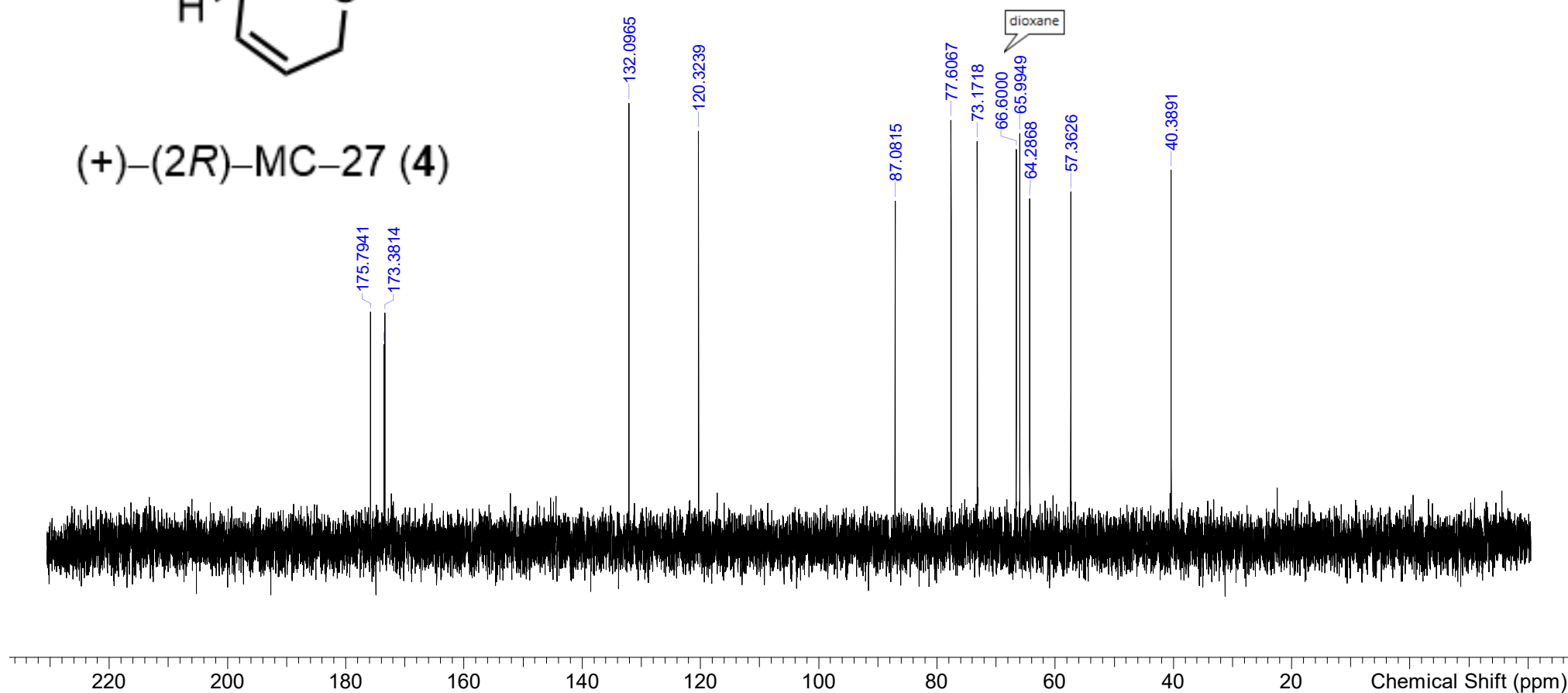
Frequency (MHz) 400.1300

Receiver Gain 724.00

Sweep Width (Hz) 8417.00



(+)-(2R)-MC-27 (4)



Date 24 Jan 2018 07:32:40

AA70069-001

Nucleus  $^{13}\text{C}$

Pulse Sequence zgpg30\_Bruker\_AVANCEII400M

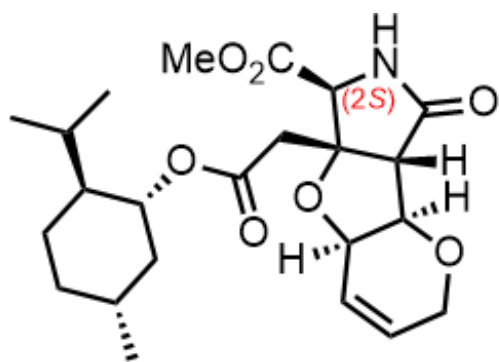
Solvent DEUTERIUM OXIDE

Acquisition Time (sec) 1.2976

Frequency (MHz) 100.6128

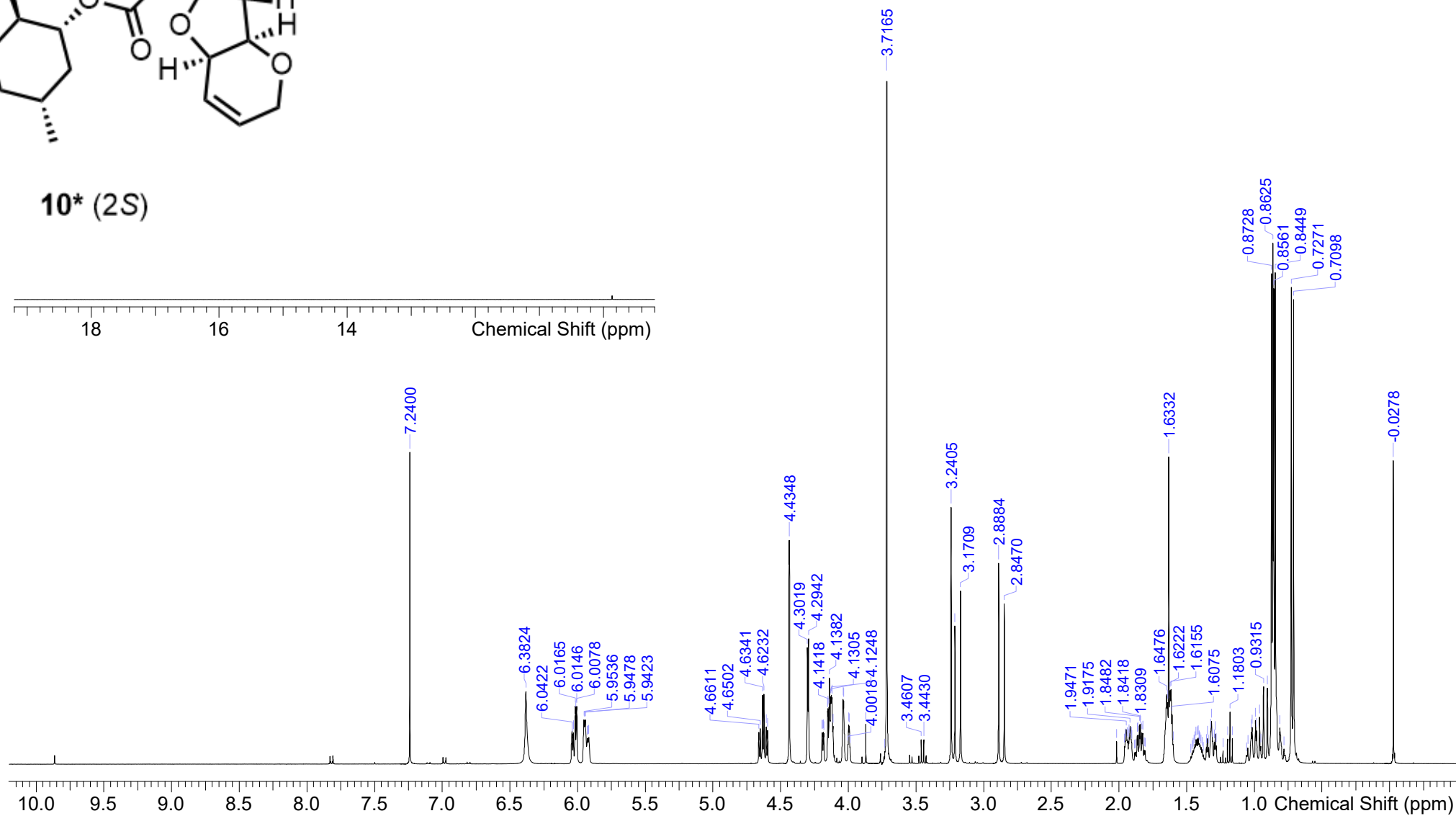
Receiver Gain 2050.00

Sweep Width (Hz) 25251.75



**10\* (2S)**

SII-10



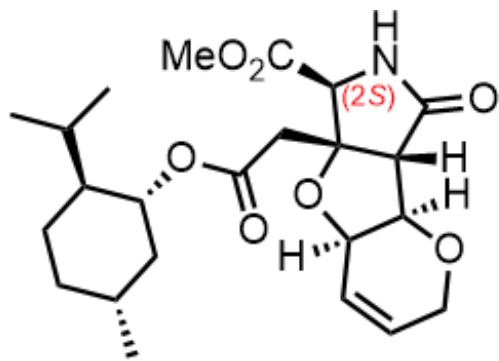
Date 20 Mar 2019 20:14:25

Kenji Morokuma  
AA70071-001

Nucleus 1H  
Pulse Sequence zg30\_Bruker\_AVANCEIII400N  
Solvent CHLOROFORM-d

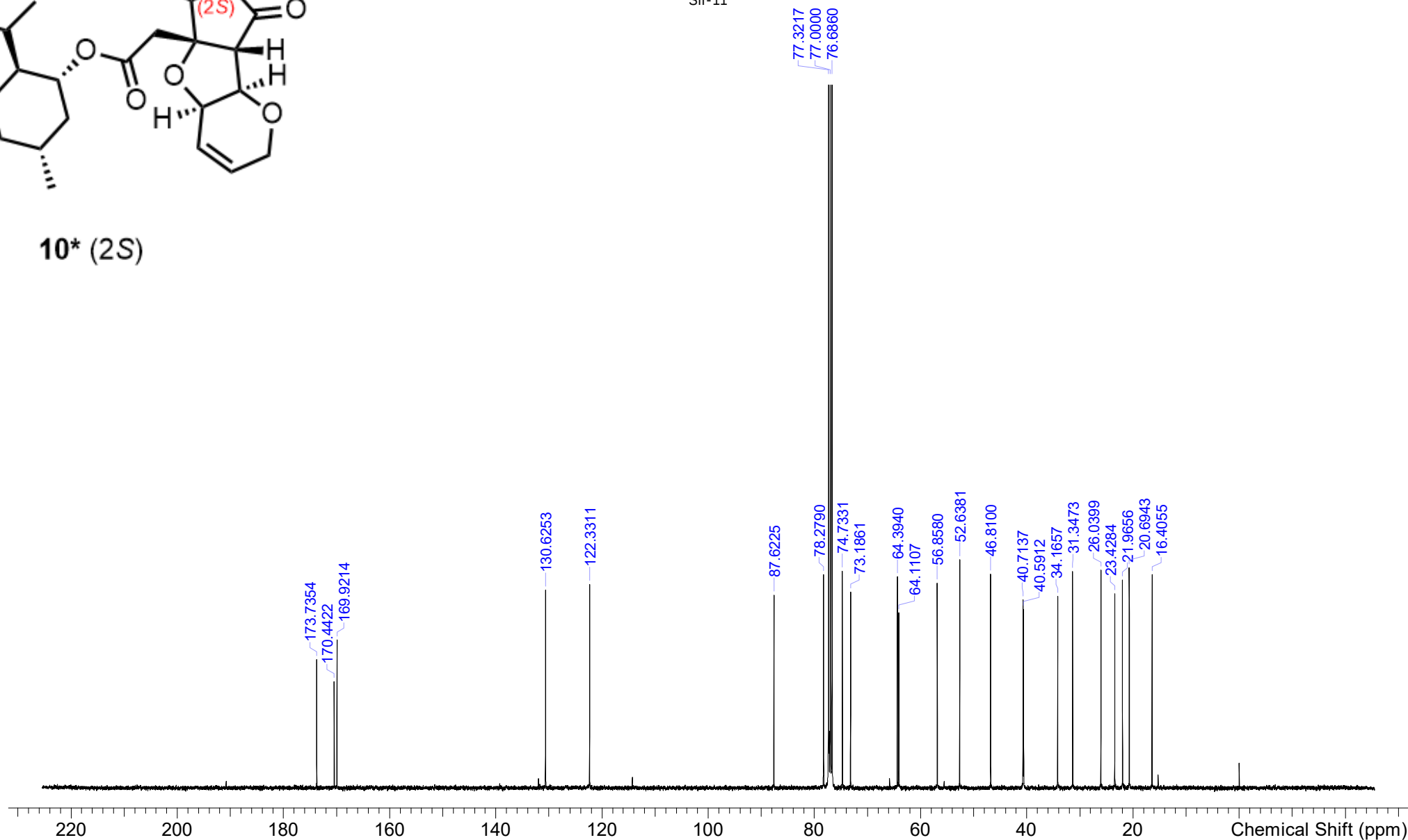
Acquisition Time (sec) 3.8928  
Frequency (MHz) 400.1800  
Receiver Gain 71.80  
Sweep Width (Hz) 8417.38

D1 1  
NS 16  
SI 65536  
TD 65536



10\* (2S)

SII-11



Date 21 Mar 2019 03:54:45

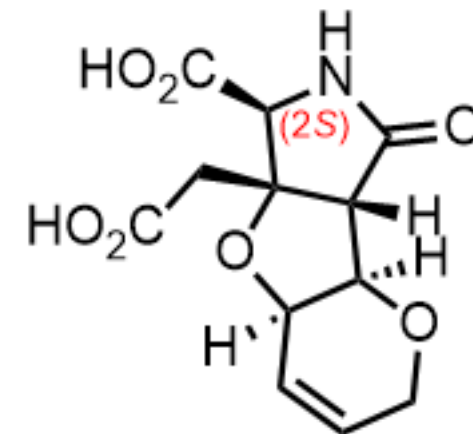
Kenji Morokuma  
AA70071-001

Nucleus  $^{13}\text{C}$   
Pulse Sequence zgpg30\_Bruker\_AVANCEIII400N  
Solvent CHLOROFORM-d

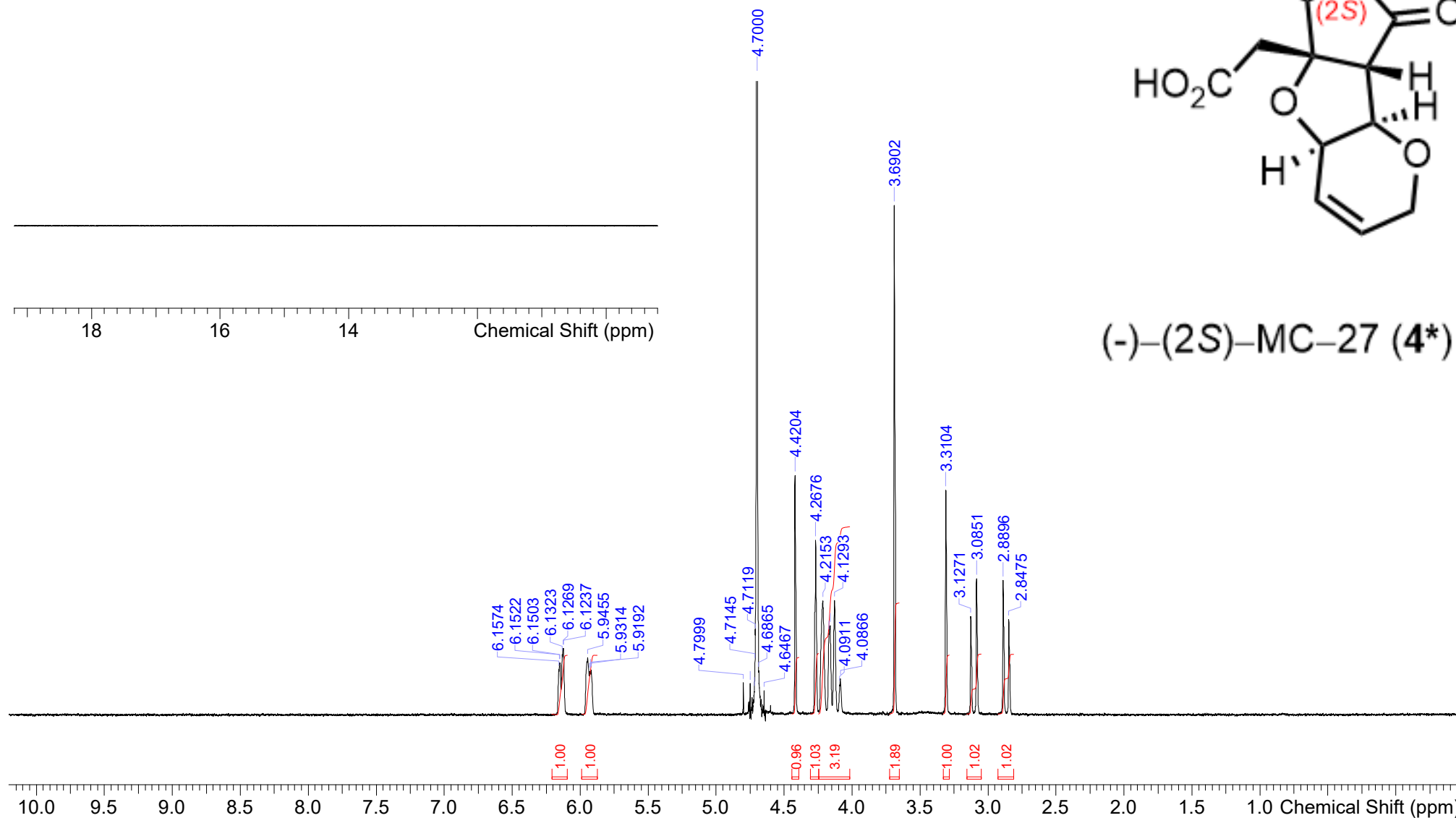
Acquisition Time (sec) 1.2976  
Frequency (MHz) 100.6253  
Receiver Gain 203.00  
Sweep Width (Hz) 25251.75

D1 2  
NS 8192  
SI 32768  
TD 65536

SII-12



(-)-(2S)-MC-27 (4\*)



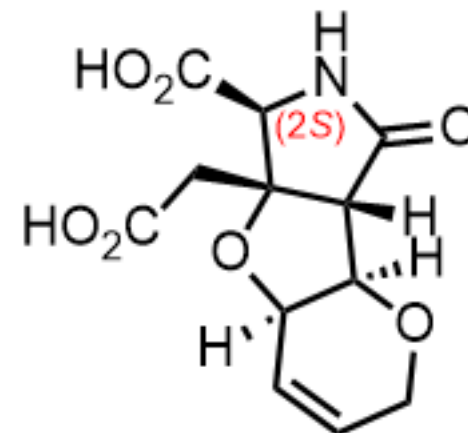
Date 17 Jan 2020 16:34:58

Kenji Morokuma  
AA70073-001

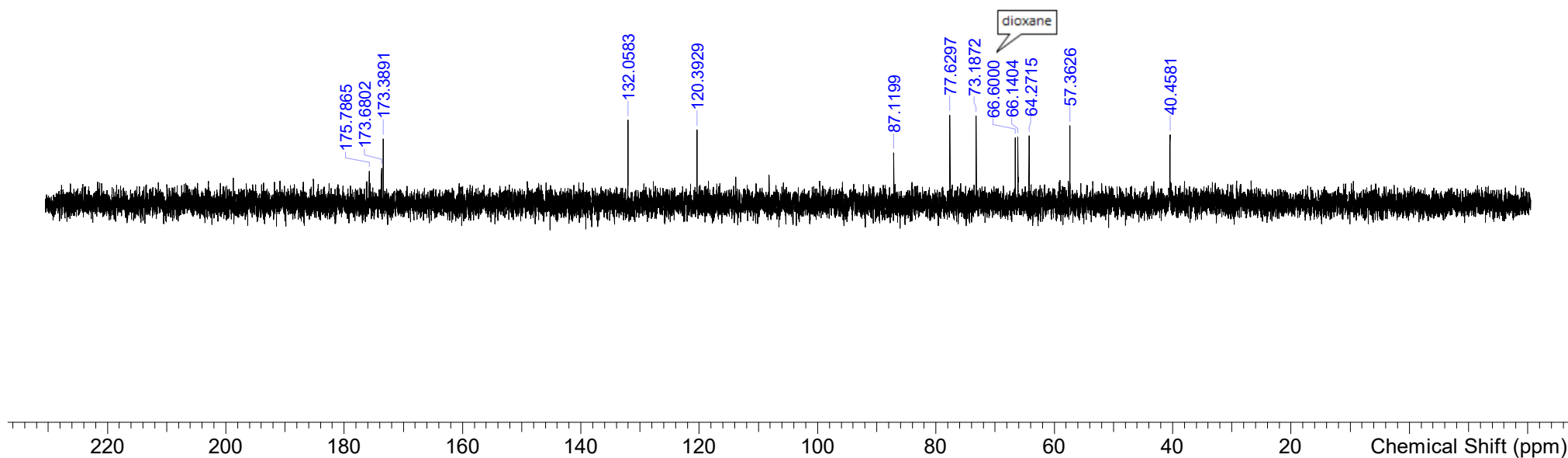
Nucleus 1H  
Pulse Sequence zg30\_Bruker\_AVANCEII400M  
Solvent DEUTERIUM OXIDE

Acquisition Time (sec) 3.8928  
Frequency (MHz) 400.1300  
Receiver Gain 724.00  
Sweep Width (Hz) 8417.38

D1 1  
NS 64  
SI 65536  
TD 65536



(-)-(2S)-MC-27 (4\*)



Date 18 Jan 2020 01:55:11

Kenji Morokuma  
AA70073-001

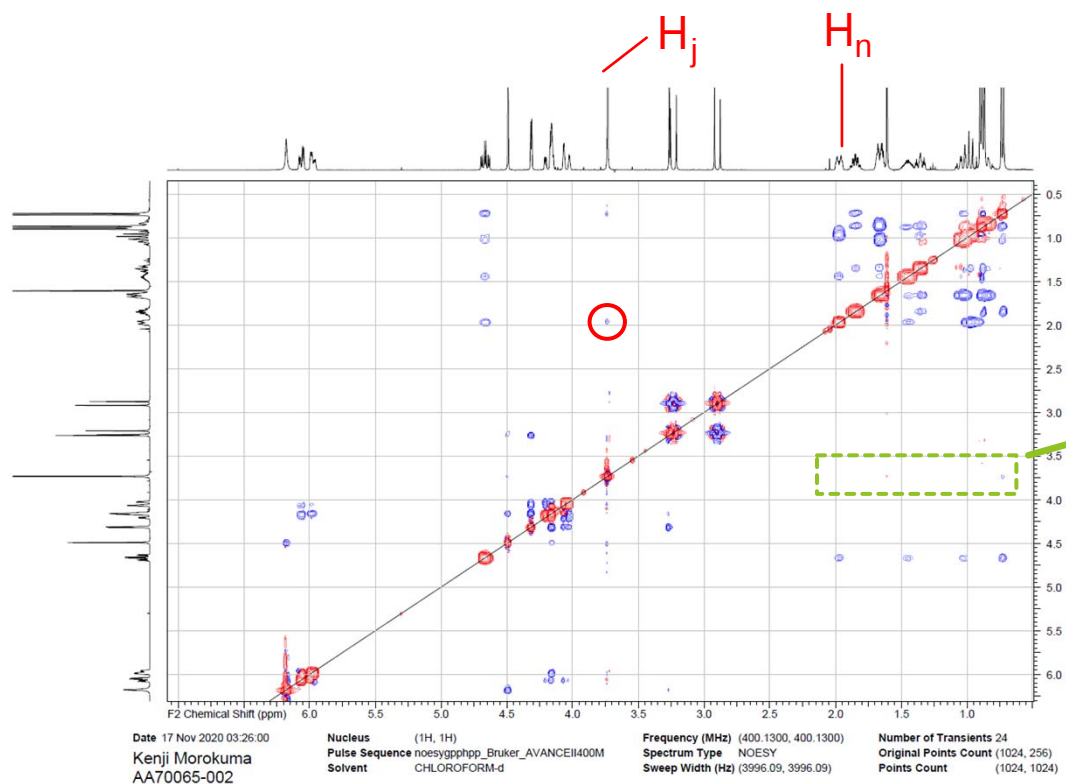
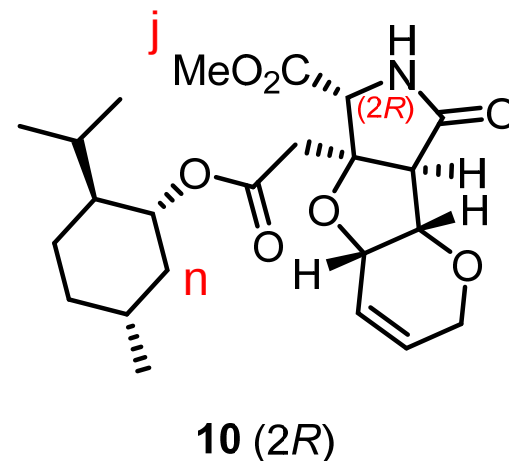
Nucleus 13C  
Pulse Sequence zgpg30\_Bruker\_AVANCEII400M  
Solvent DEUTERIUM OXIDE

Acquisition Time (sec) 1.2976  
Frequency (MHz) 100.6128  
Receiver Gain 512.00  
Sweep Width (Hz) 25251.75

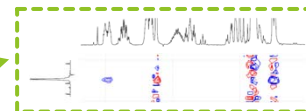
D1 2  
NS 4096  
SI 32768  
TD 65536

# NOESY spectrum of menthyl ester diastereomer 10

fig. NOESY (400 MHz, CDCl<sub>3</sub>)

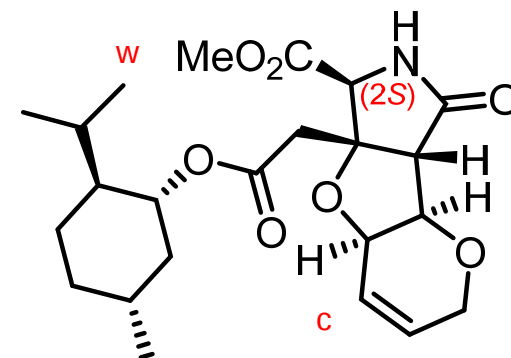


a spectrum deeply digged by a low threshold

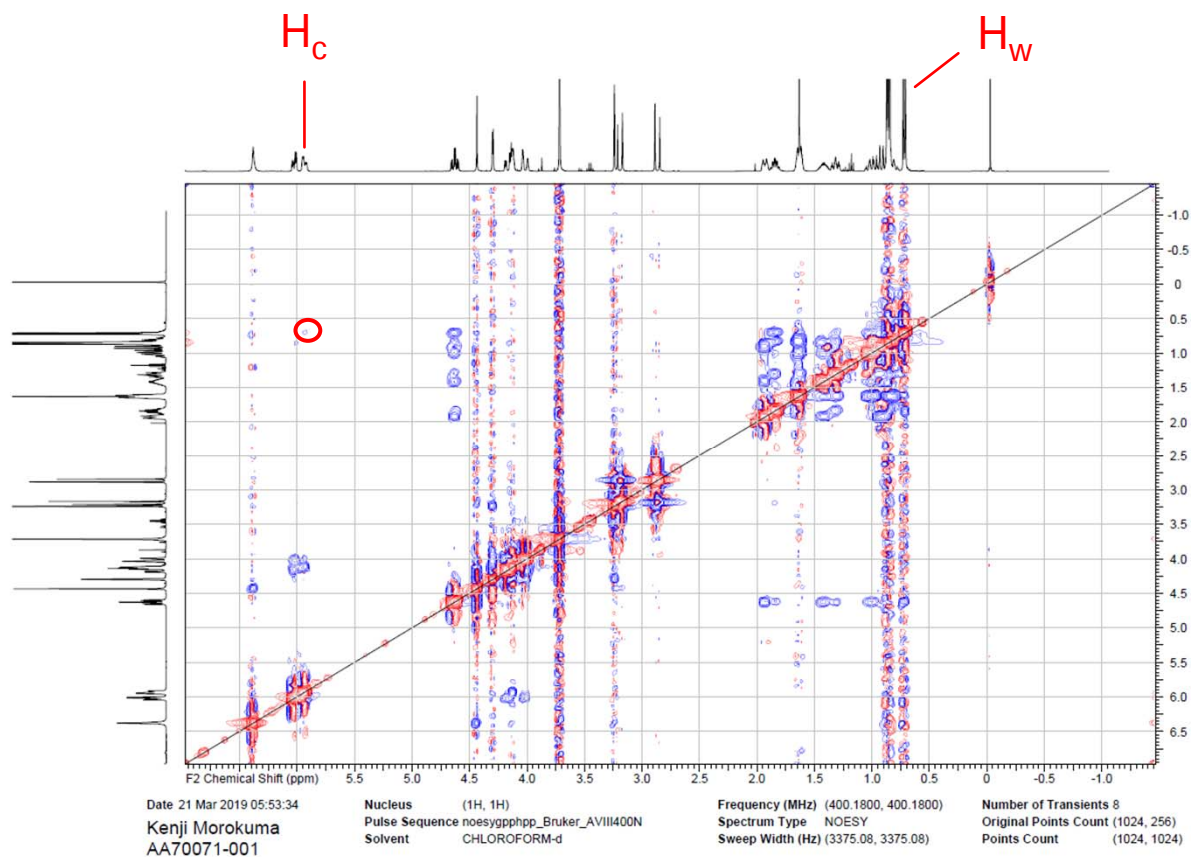


# NOESY spectrum of menthyl ester diastereomer 10\*

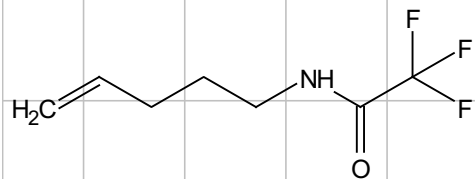
fig. NOESY (400 MHz, CDCl<sub>3</sub>)



**10\* (2S)**

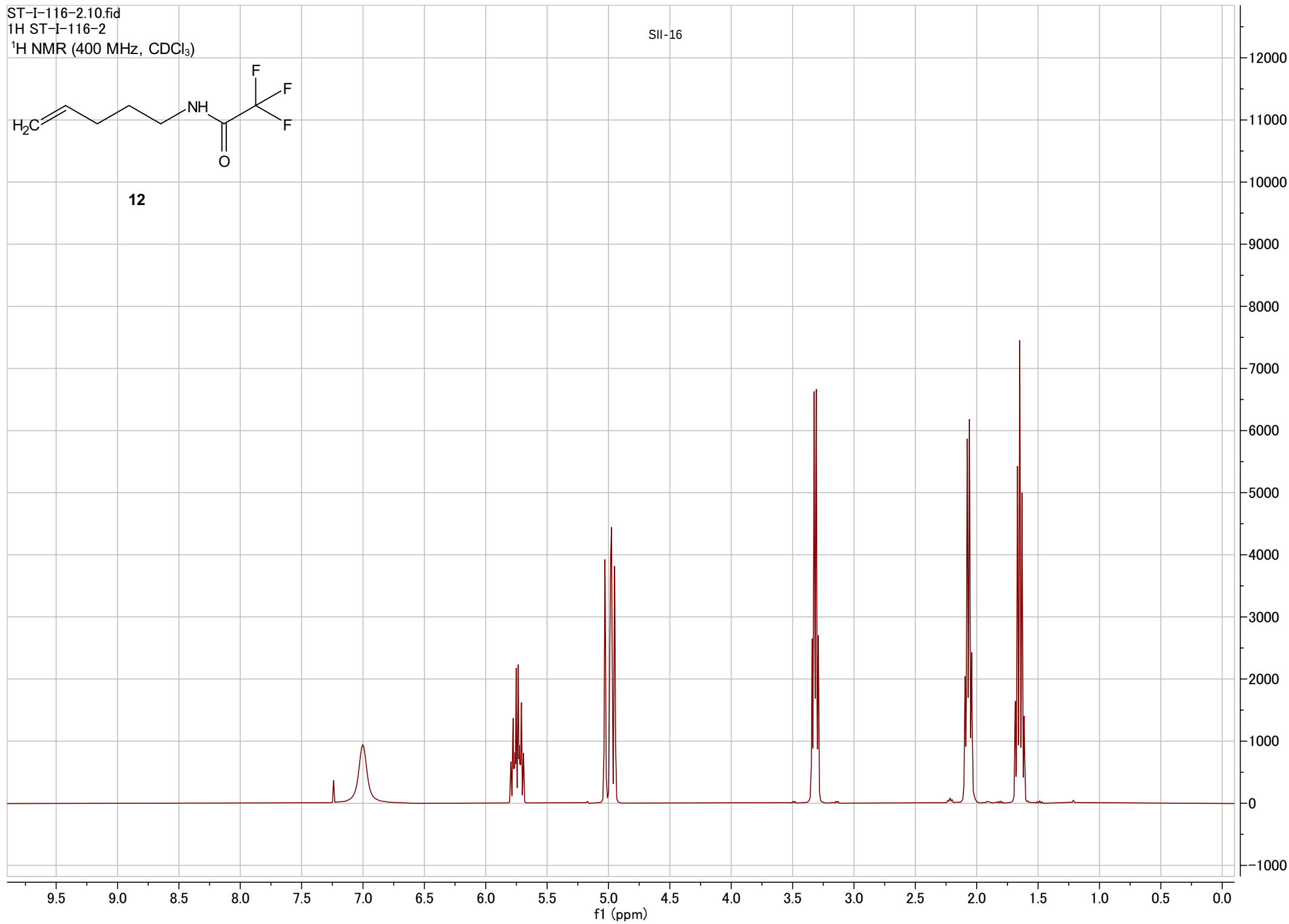


ST-I-116-2.10.fid  
1H ST-I-116-2  
1H NMR (400 MHz, CDCl<sub>3</sub>)

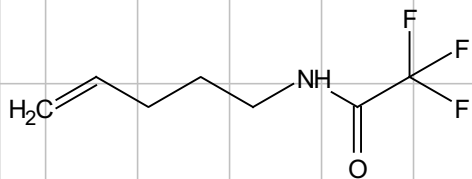


12

SII-16

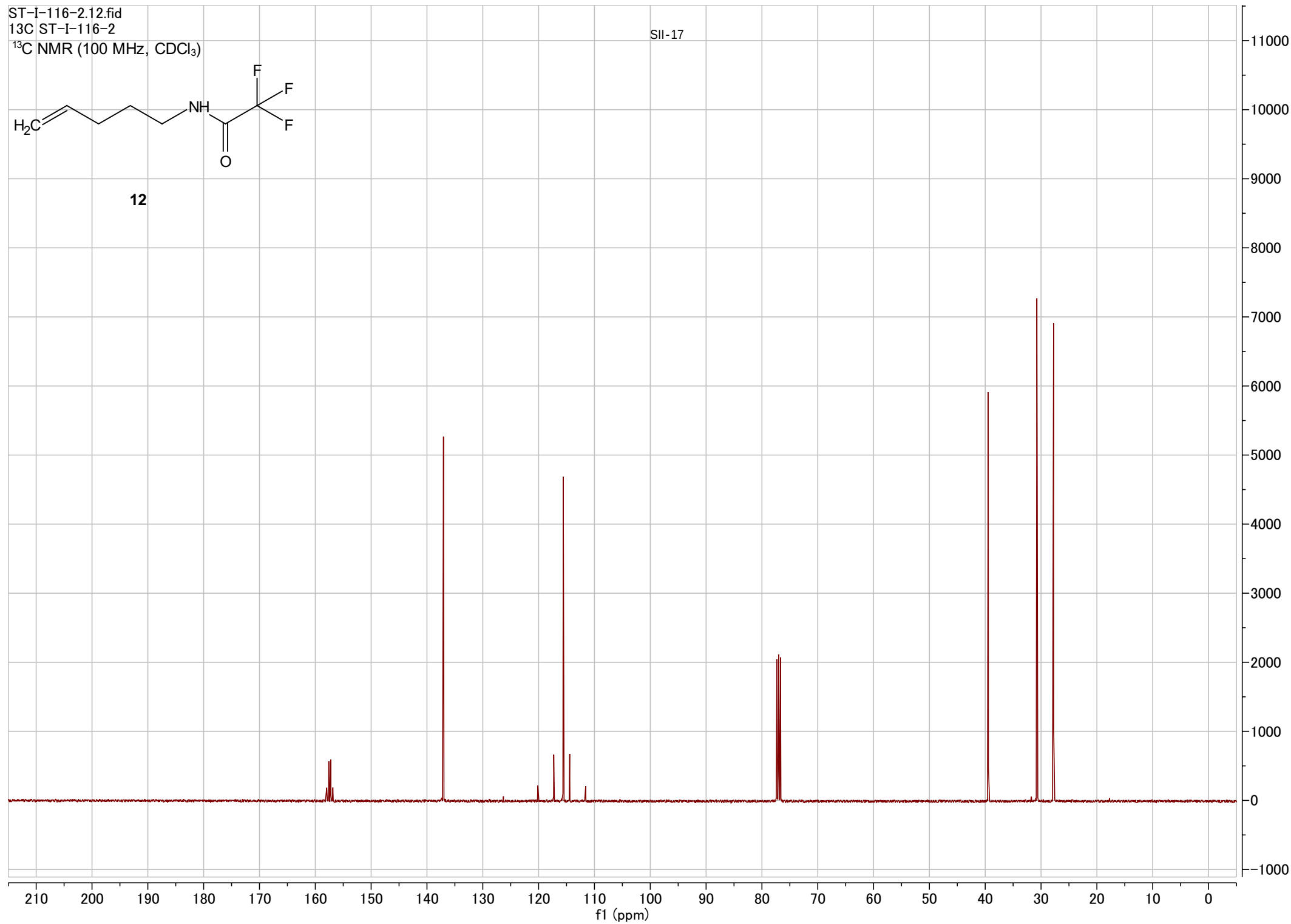


ST-I-116-2.12.fid  
13C ST-I-116-2  
13C NMR (100 MHz, CDCl<sub>3</sub>)



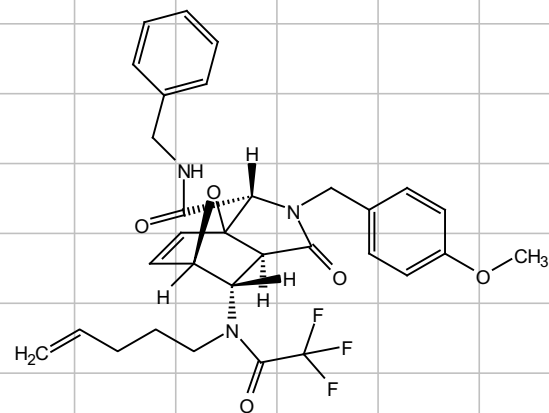
12

SII-17

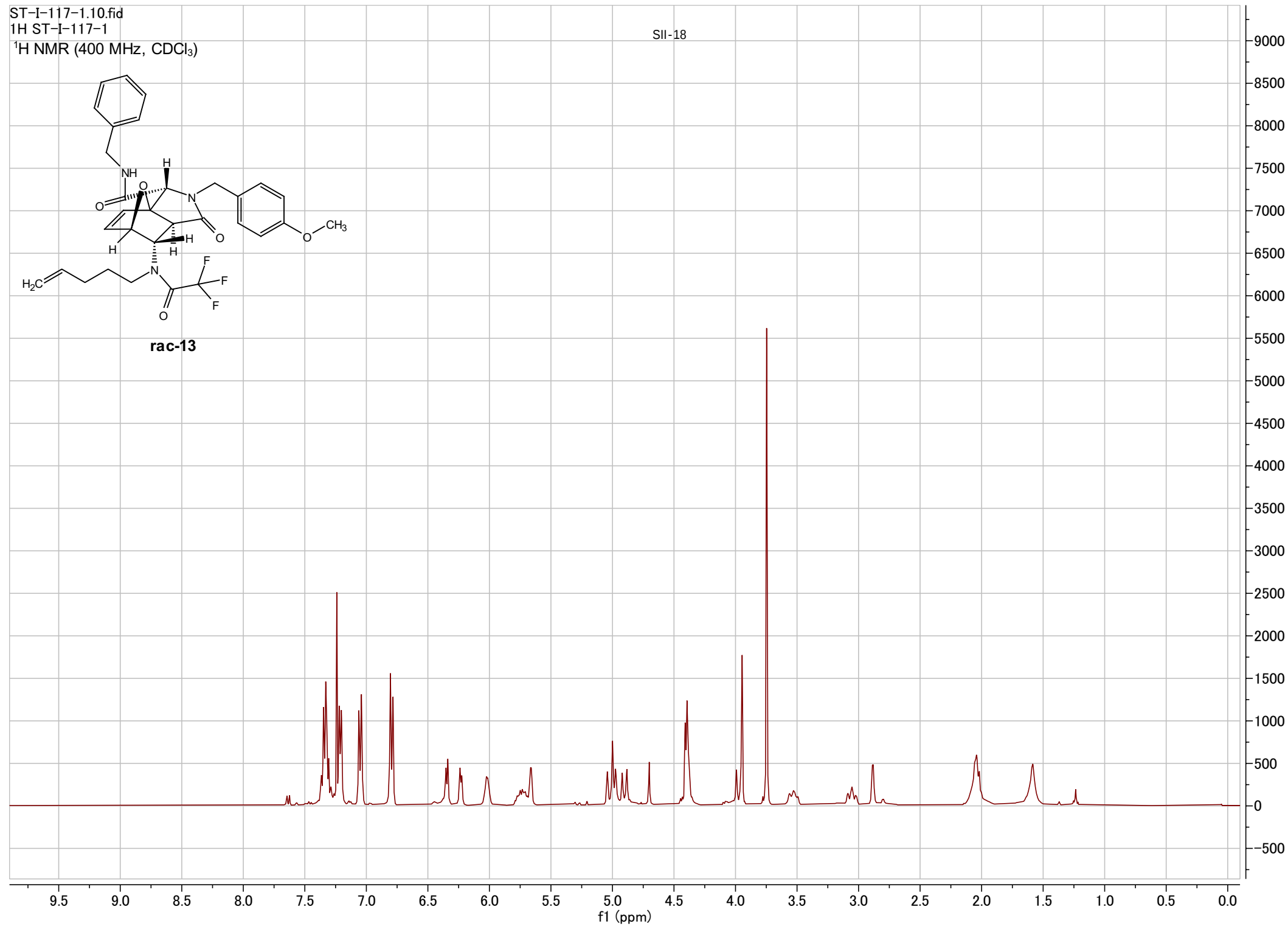


ST-I-117-1.10.fid  
1H ST-I-117-1  
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

SII-18

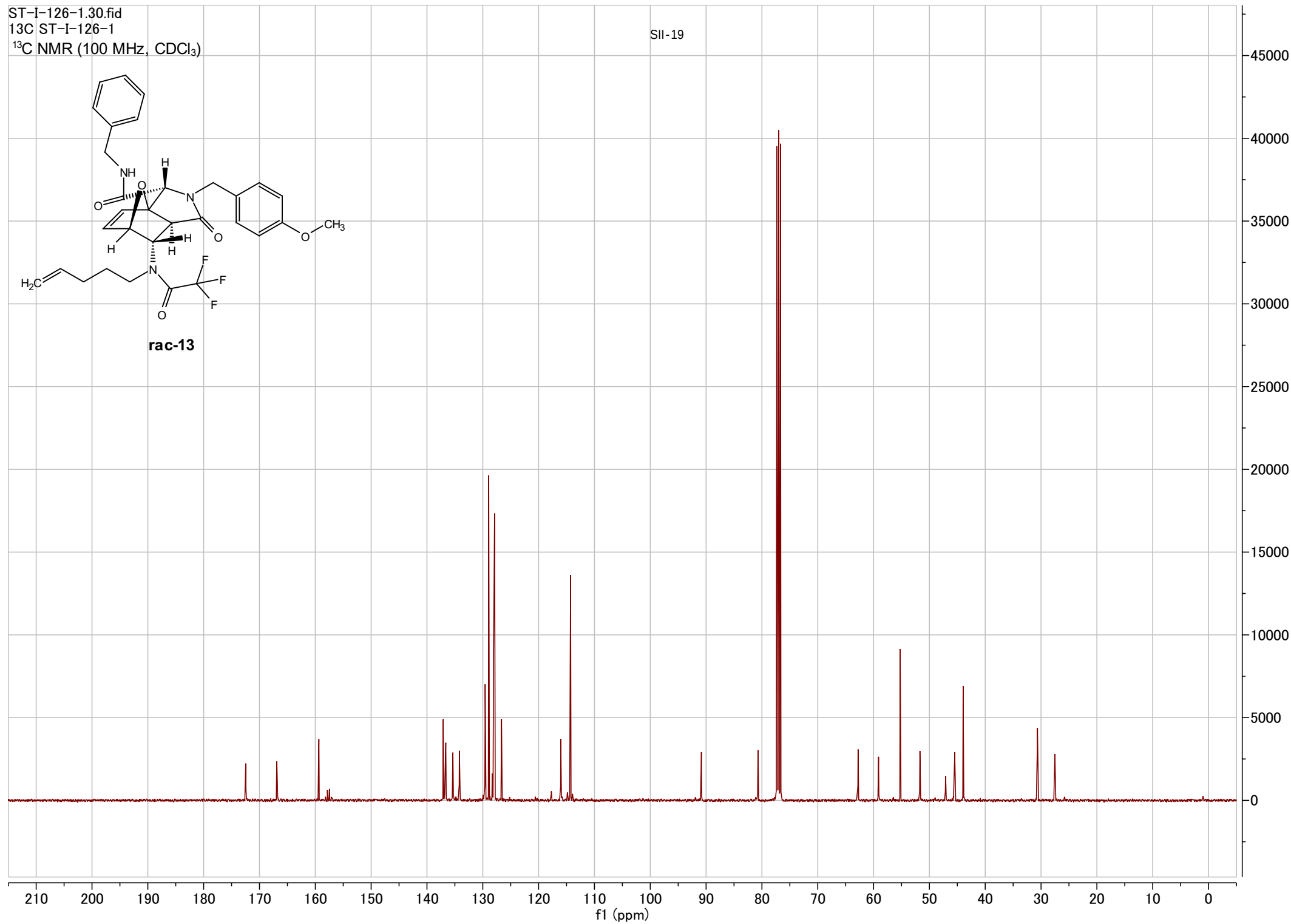
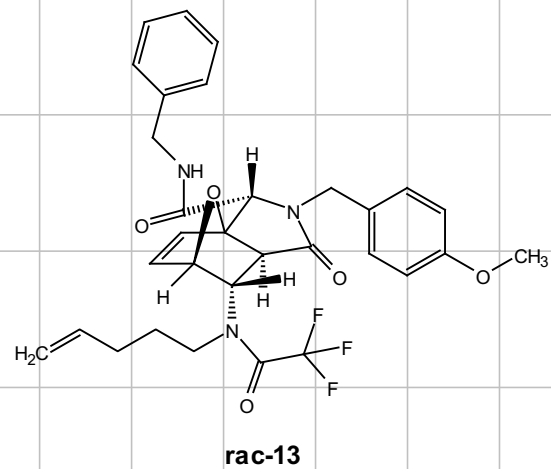


**rac-13**



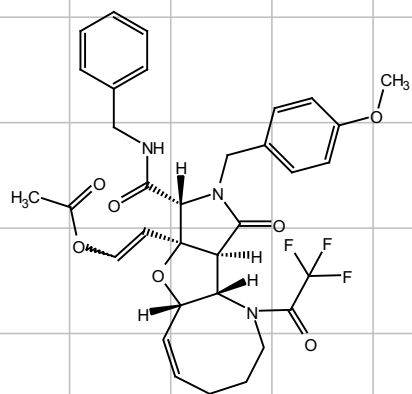
ST-I-126-1.30.fid  
13C ST-I-126-1  
13C NMR (100 MHz, CDCl<sub>3</sub>)

SII-19

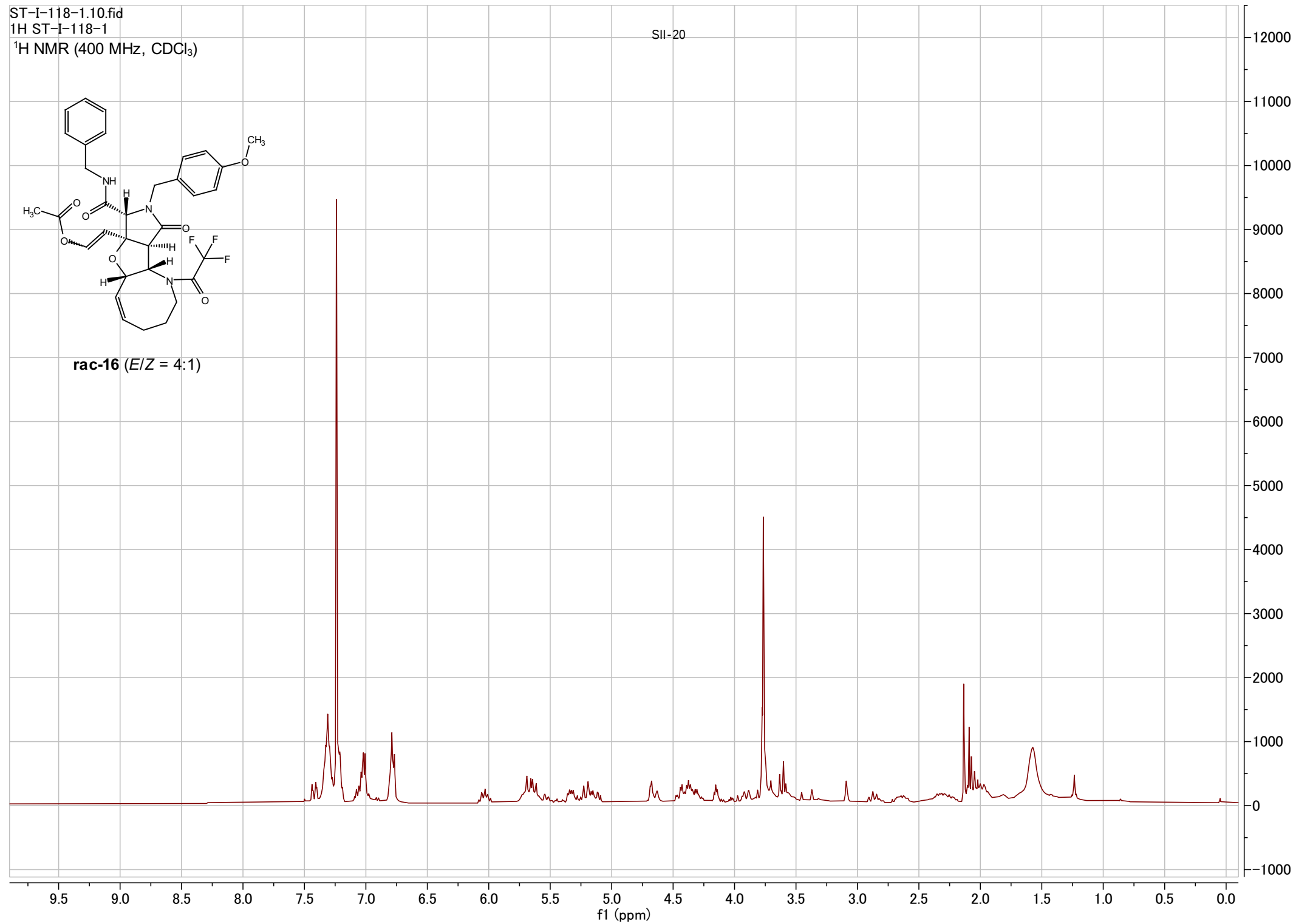


ST-I-118-1.10.fid  
1H ST-I-118-1  
1H NMR (400 MHz, CDCl<sub>3</sub>)

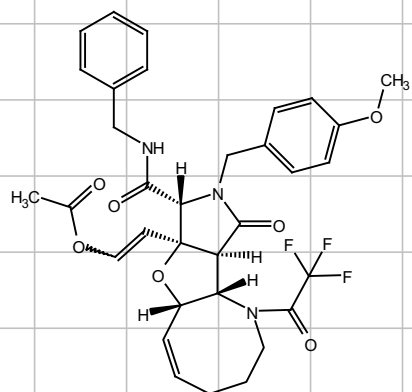
SII-20



**rac-16** (*E/Z* = 4:1)

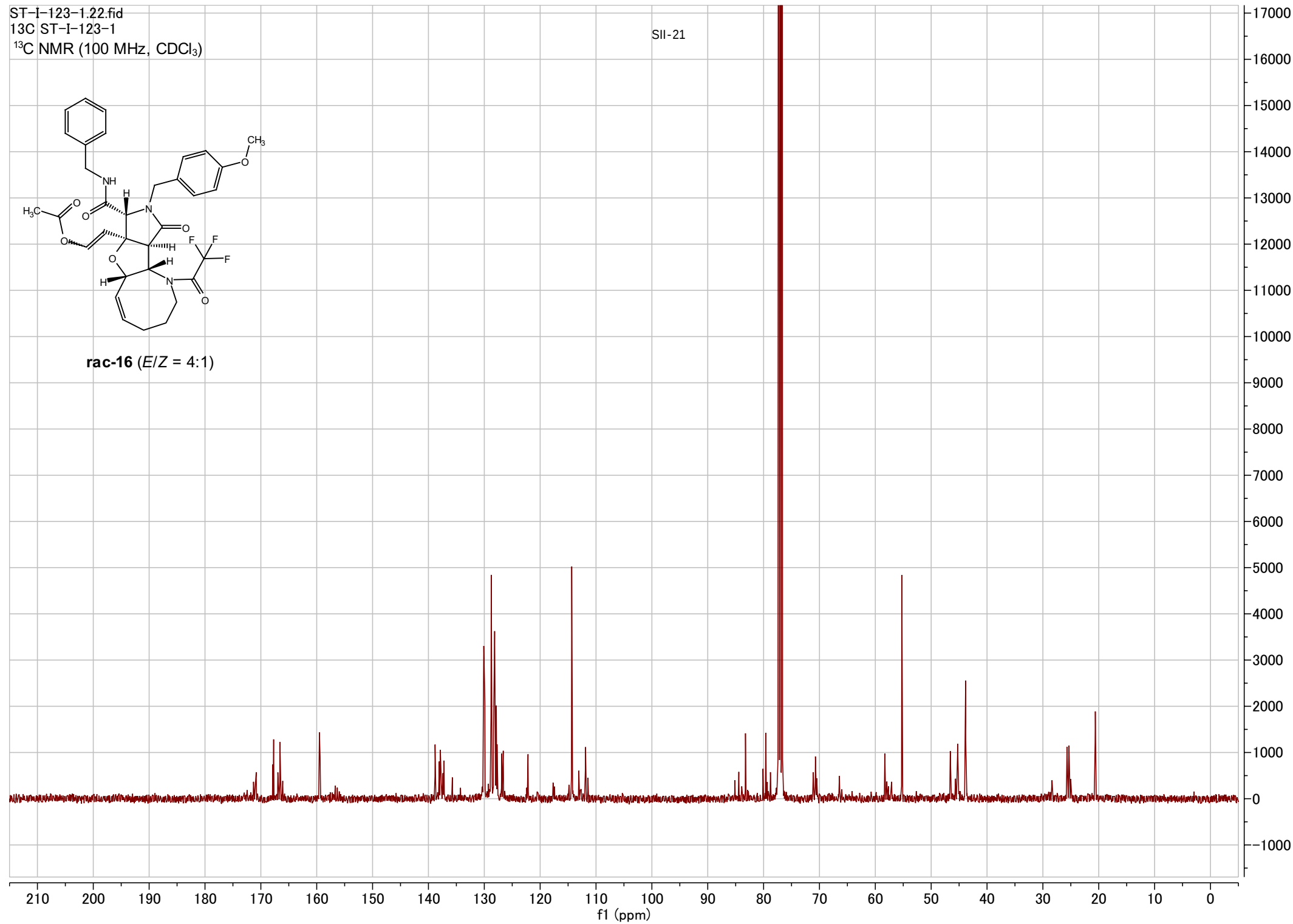


ST-I-123-1.22.fid  
13C ST-I-123-1  
13C NMR (100 MHz, CDCl<sub>3</sub>)



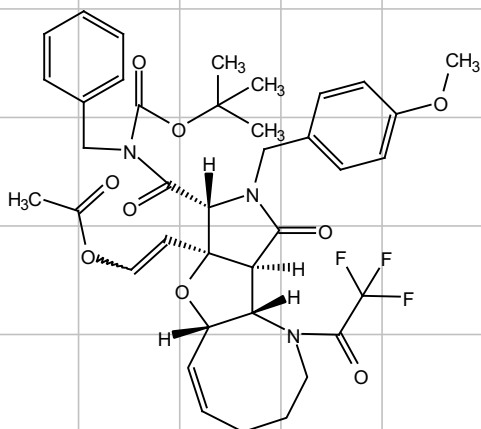
**rac-16** (*E/Z* = 4:1)

SII-21

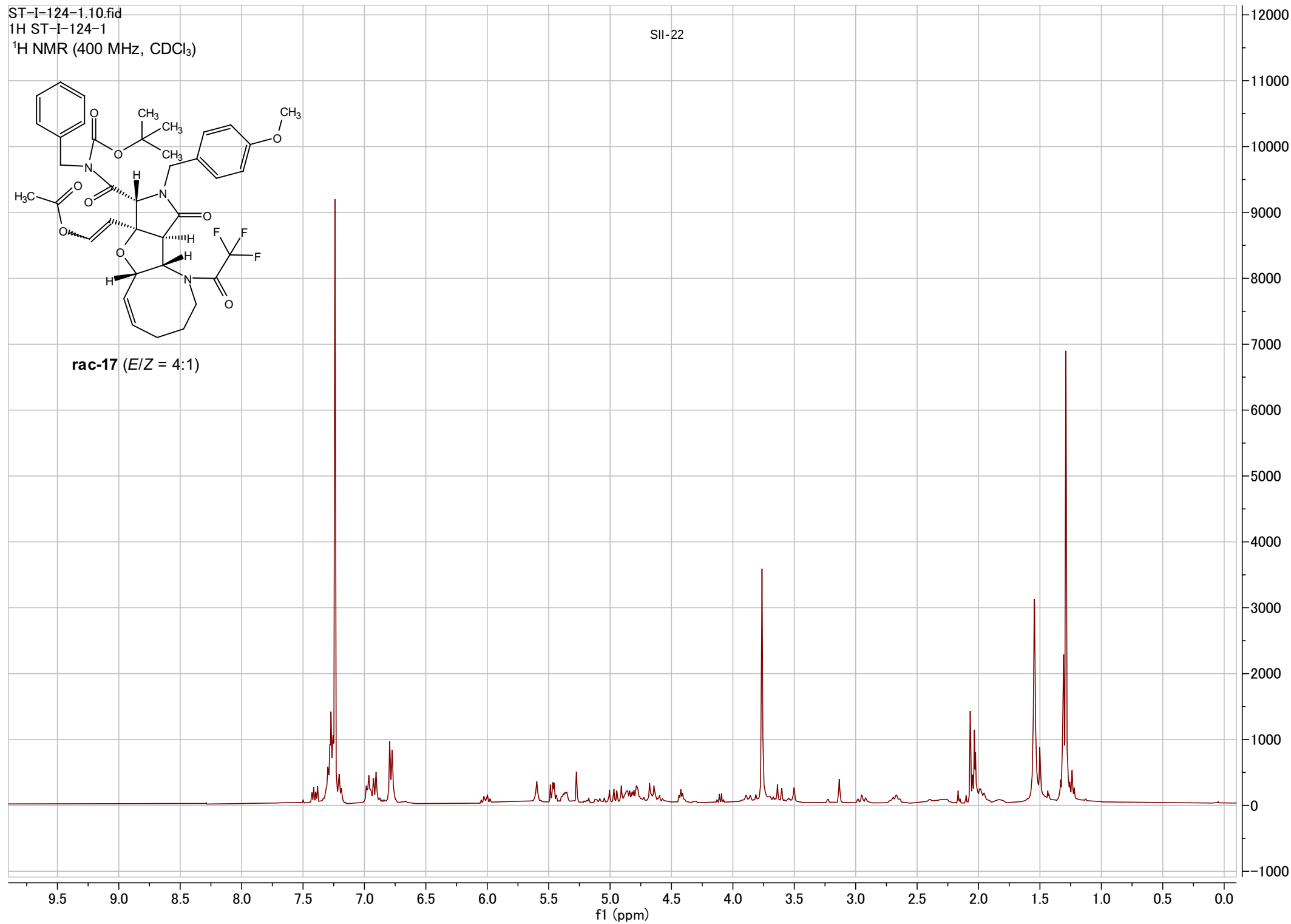


ST-I-124-1.10.fid  
1H ST-I-124-1  
1H NMR (400 MHz, CDCl<sub>3</sub>)

SII-22



**rac-17** (*E/Z* = 4:1)

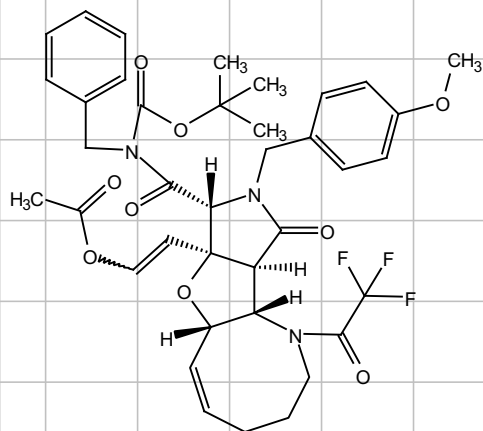


ST-II-016-1.23.fid

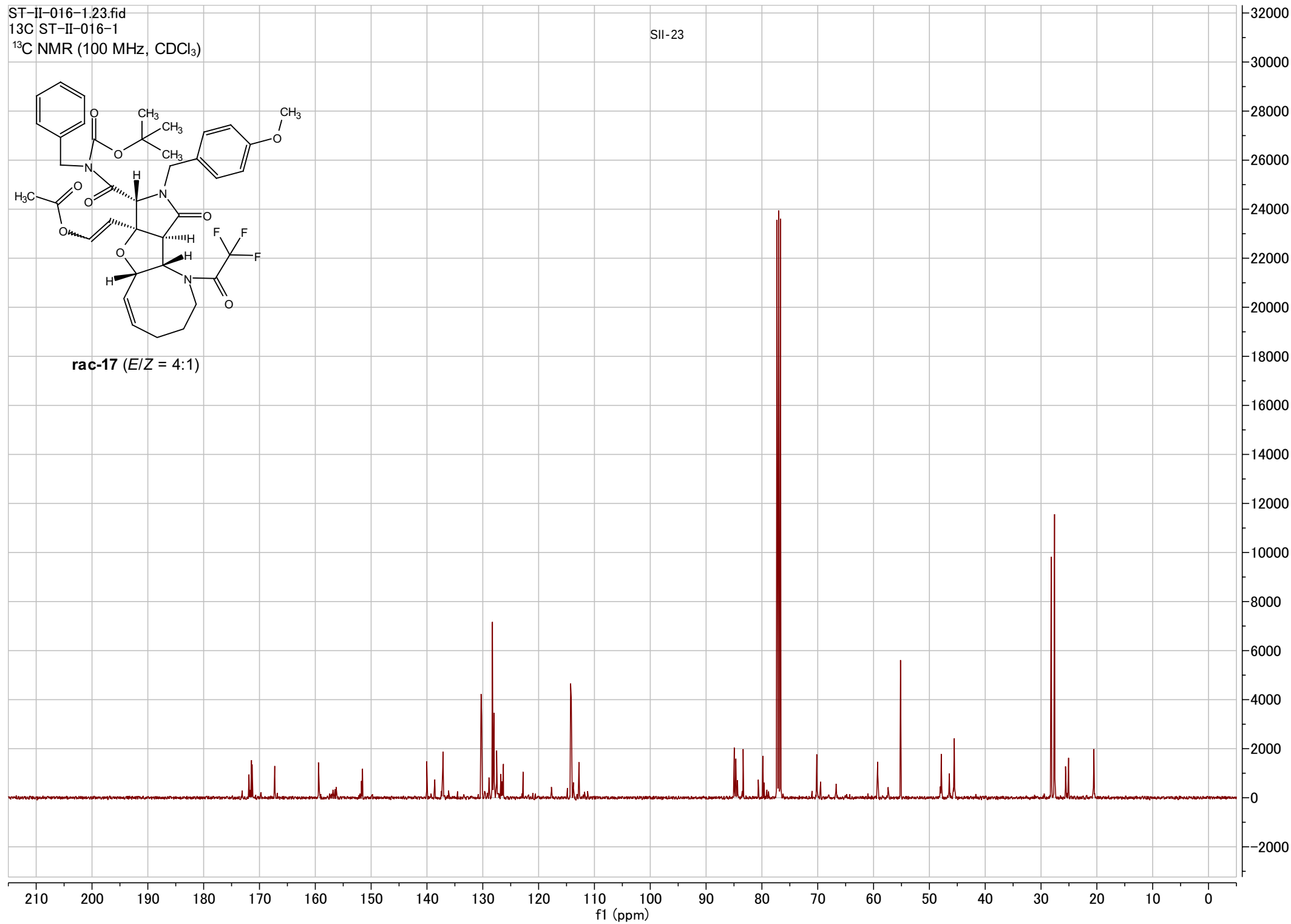
<sup>13</sup>C ST-II-016-1

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

SII-23

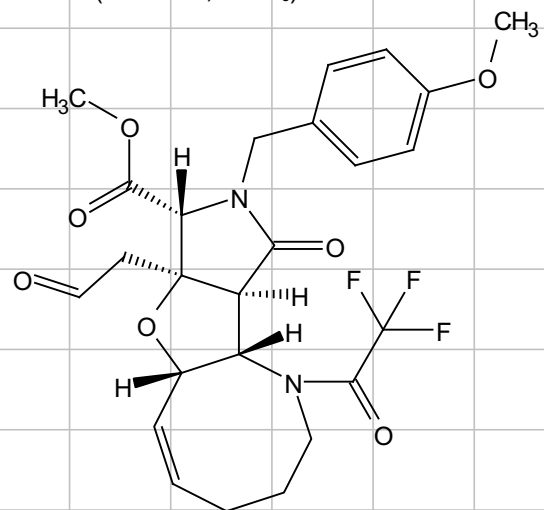


**rac-17** (*E/Z* = 4:1)

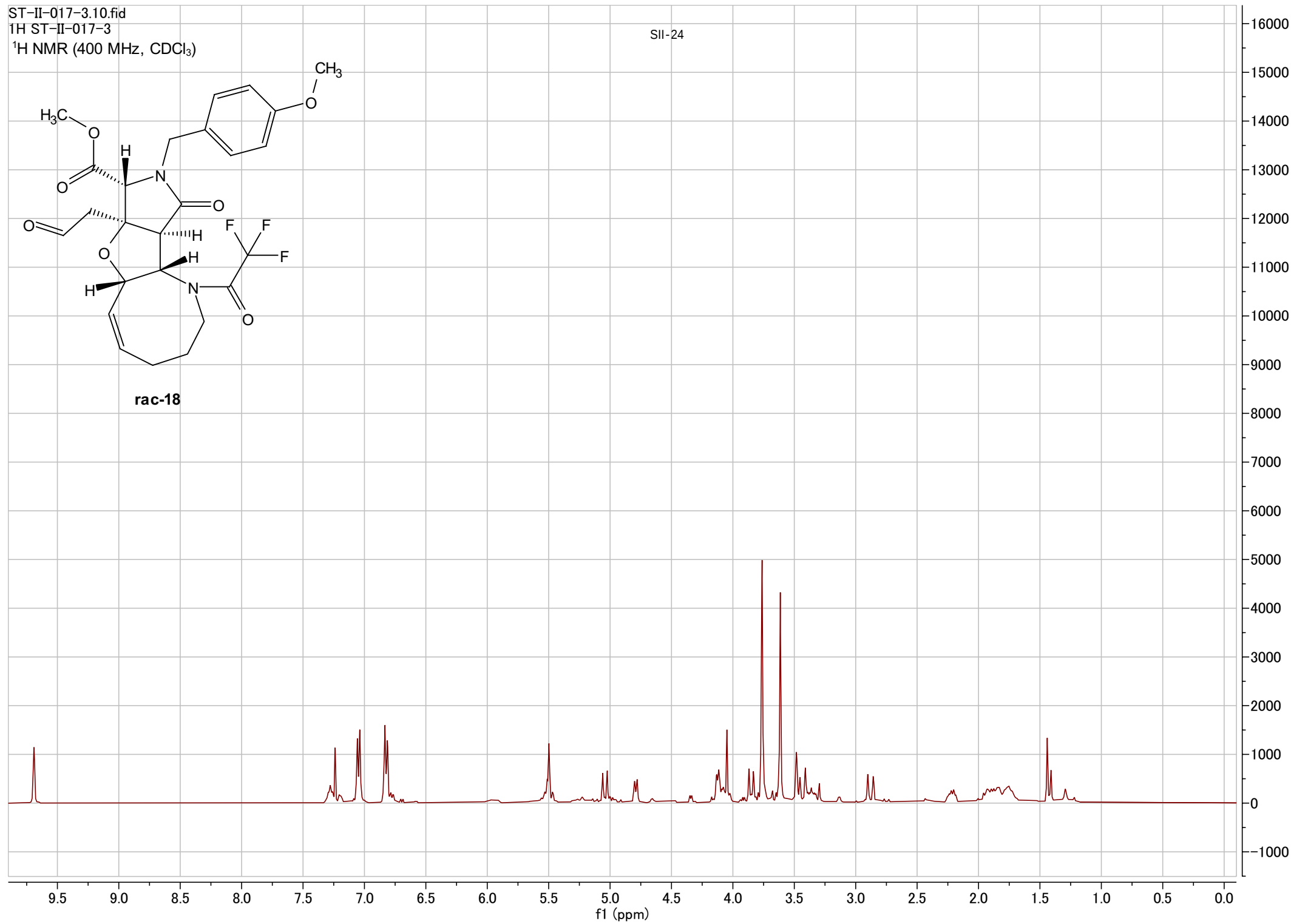


ST-II-017-3.10.fid  
1H ST-II-017-3  
1H NMR (400 MHz, CDCl<sub>3</sub>)

SII-24

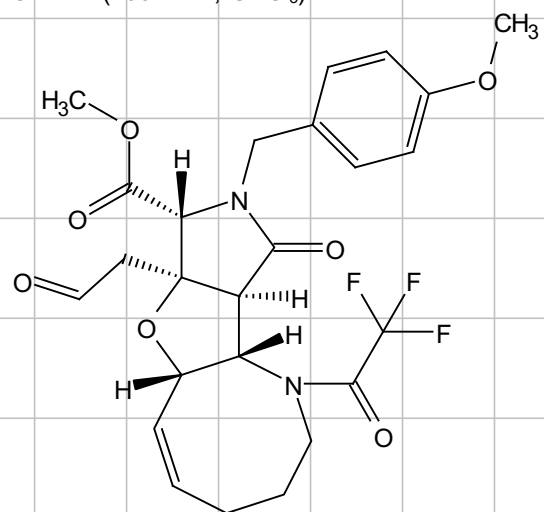


rac-18

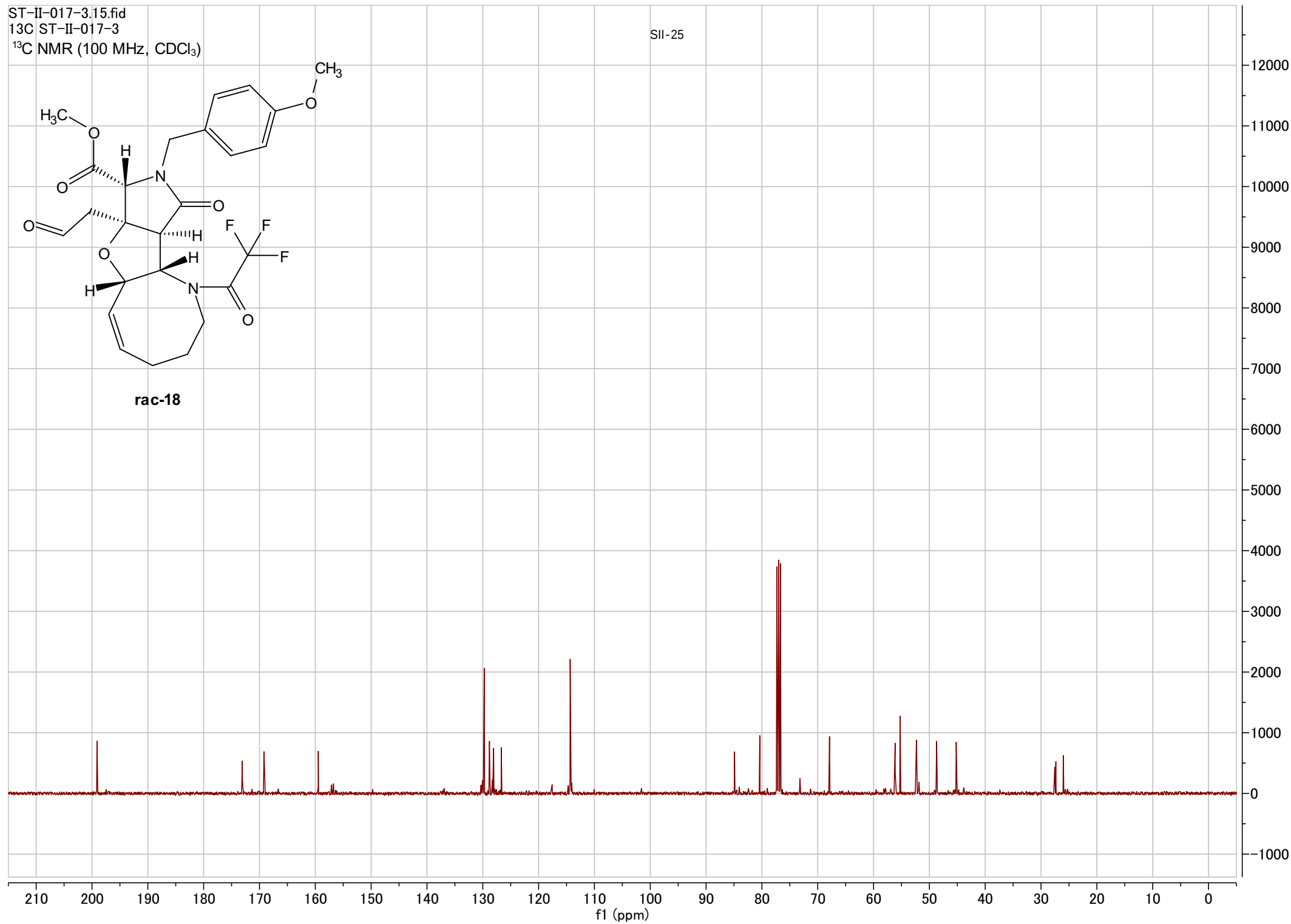


ST-II-017-3.15.fid  
13C ST-II-017-3  
13C NMR (100 MHz, CDCl<sub>3</sub>)

SII-25

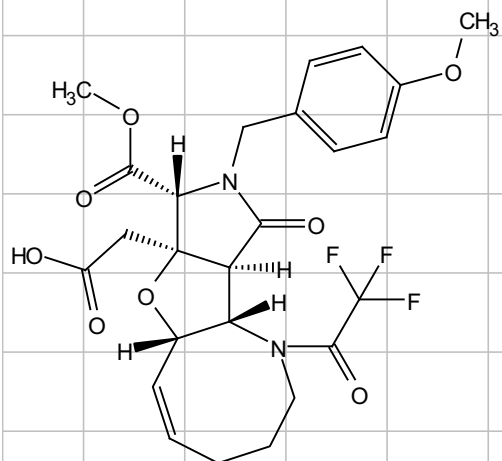


rac-18

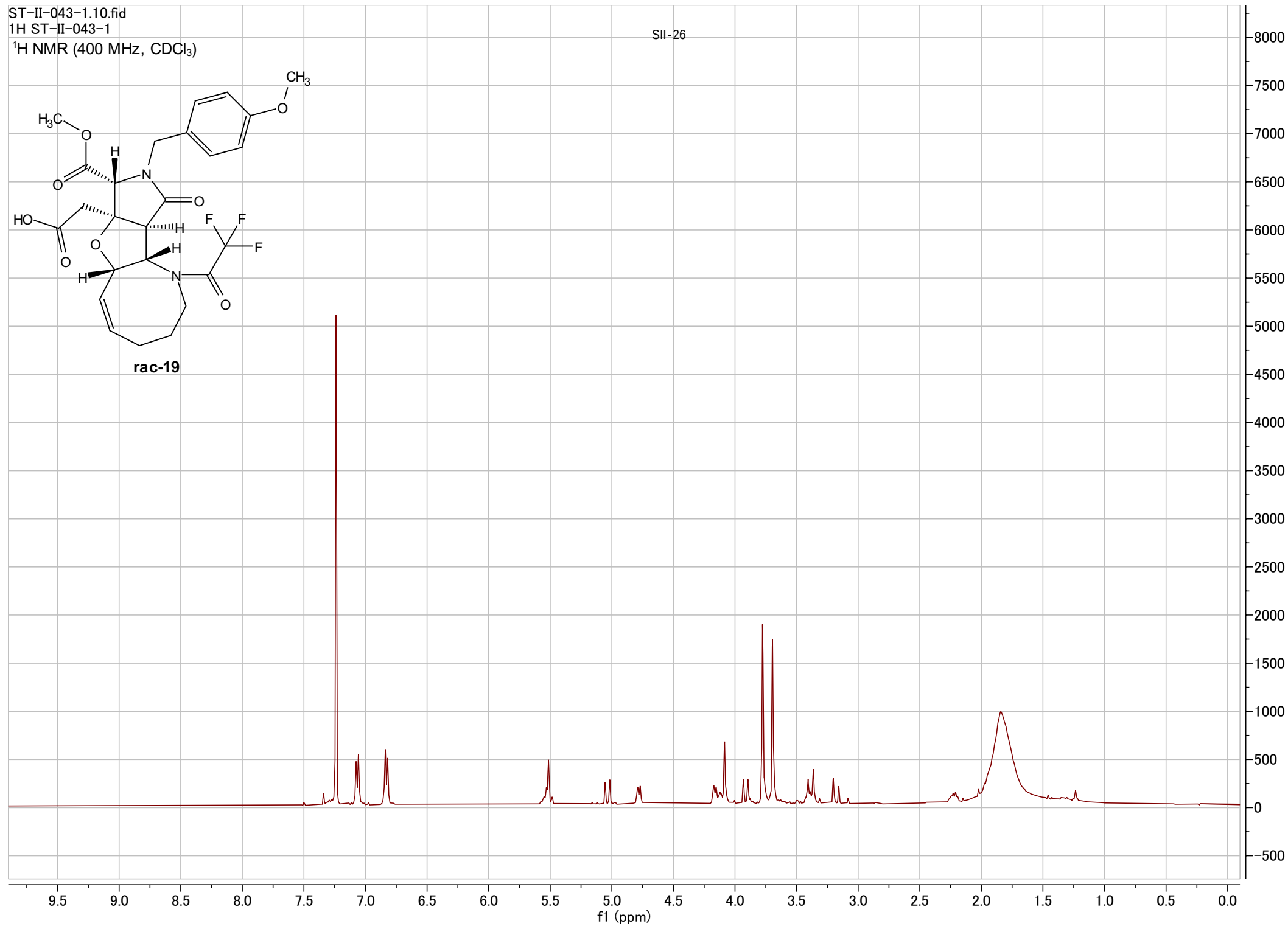


ST-II-043-1.10.fid  
1H ST-II-043-1  
1H NMR (400 MHz, CDCl<sub>3</sub>)

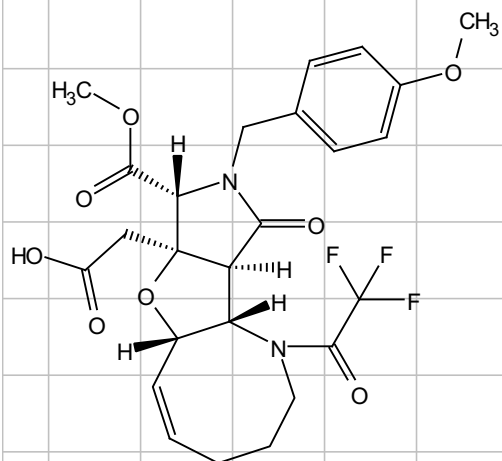
SII-26



**rac-19**

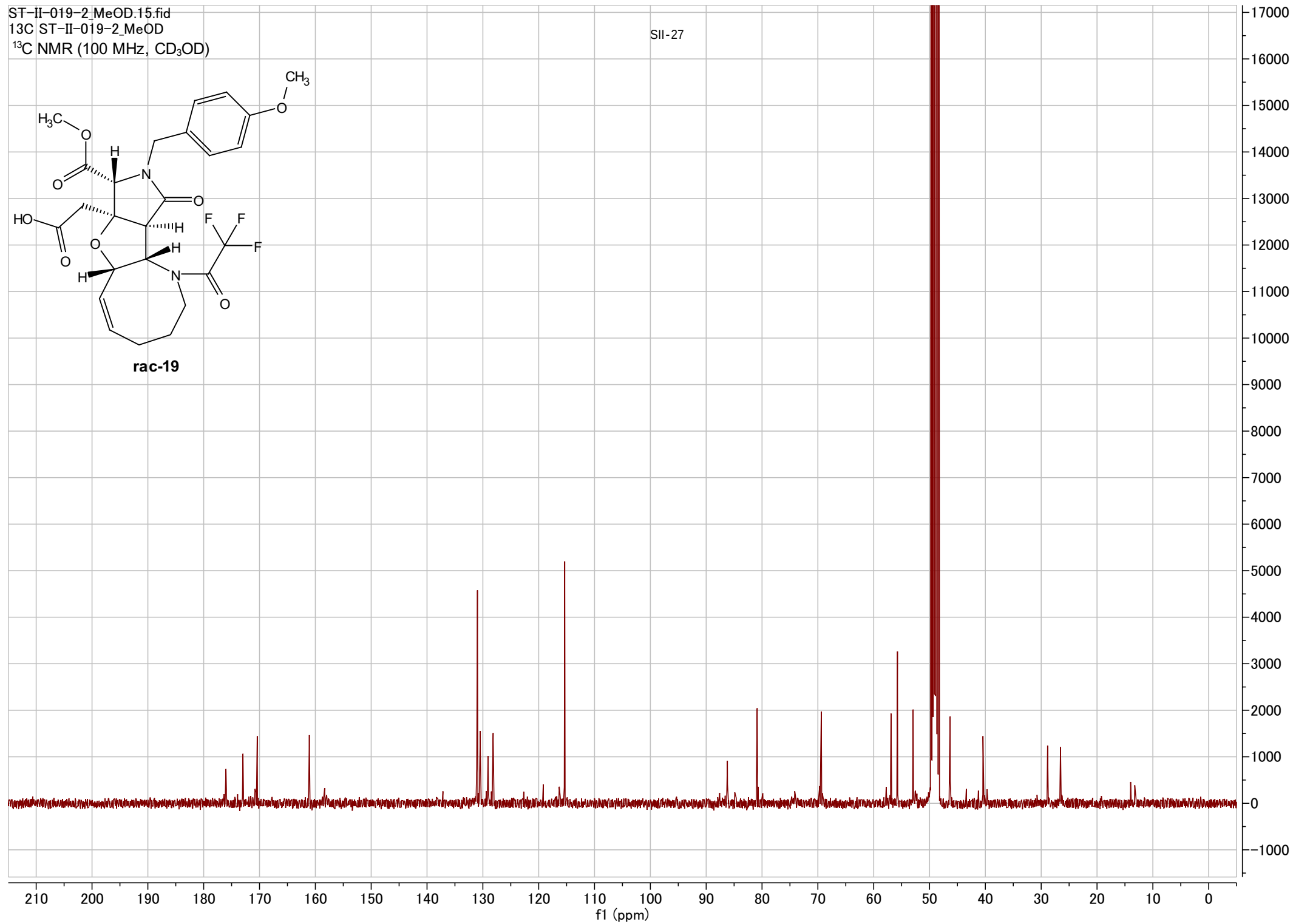


ST-II-019-2\_MeOD.15.fid  
13C ST-II-019-2\_MeOD  
13C NMR (100 MHz, CD<sub>3</sub>OD)



**rac-19**

SII-27



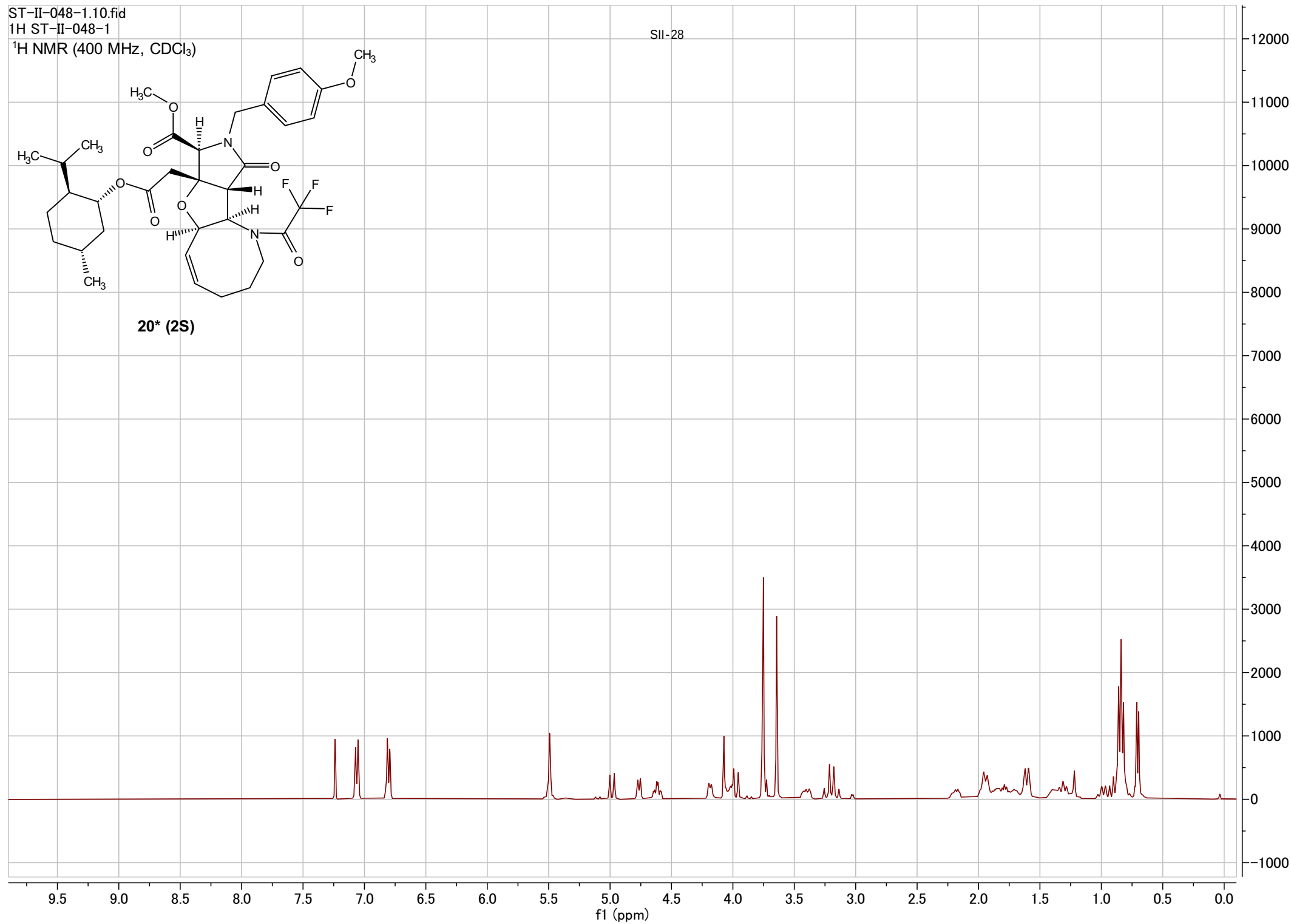
ST-II-048-1.10.fid

1H ST-II-048-1

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)

SII-28

**20\* (2S)**

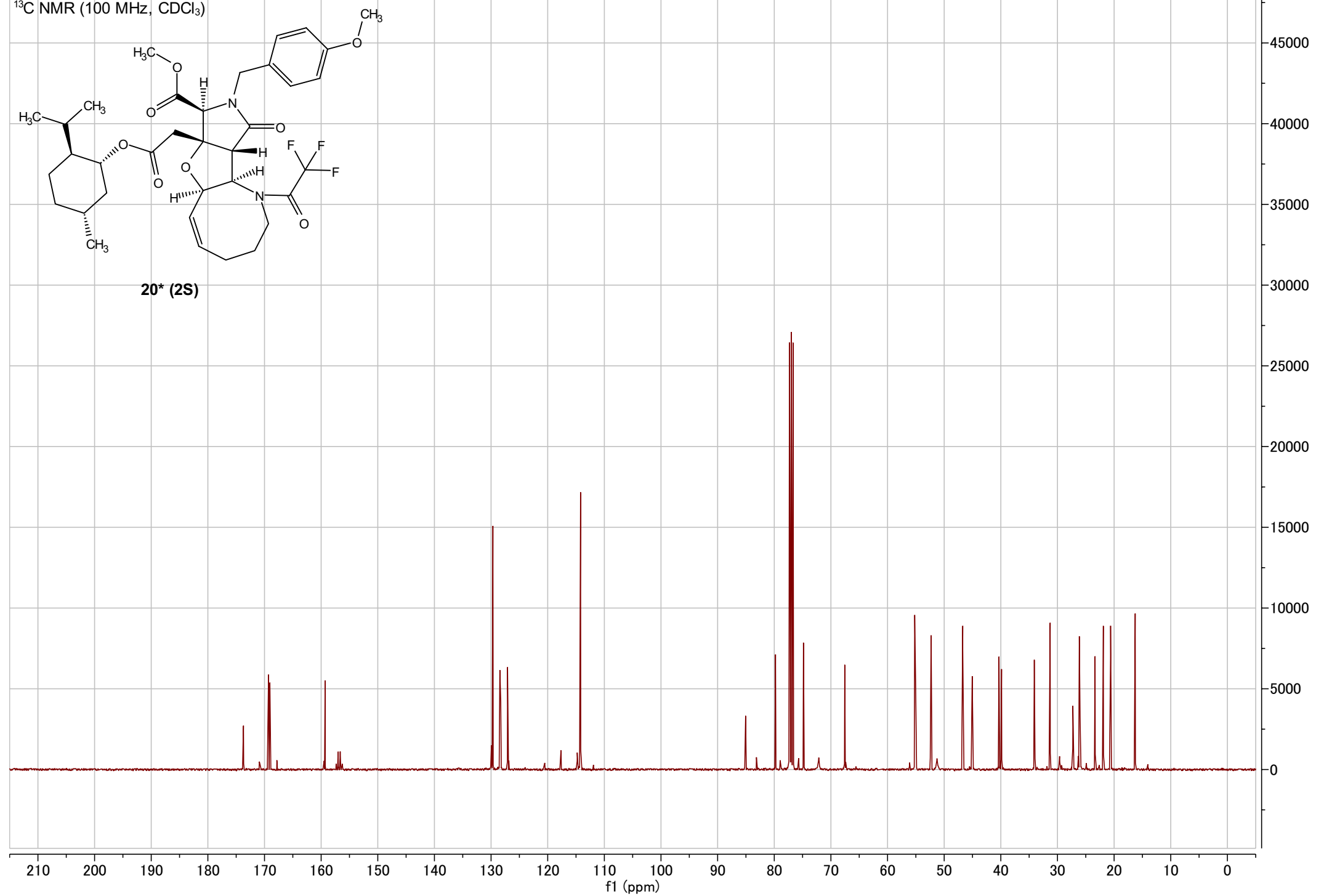


ST-II-048-1.11.fid

13C ST-II-048-1

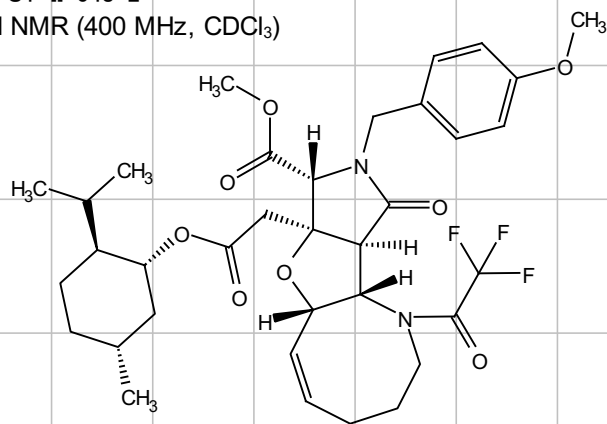
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

SII-29

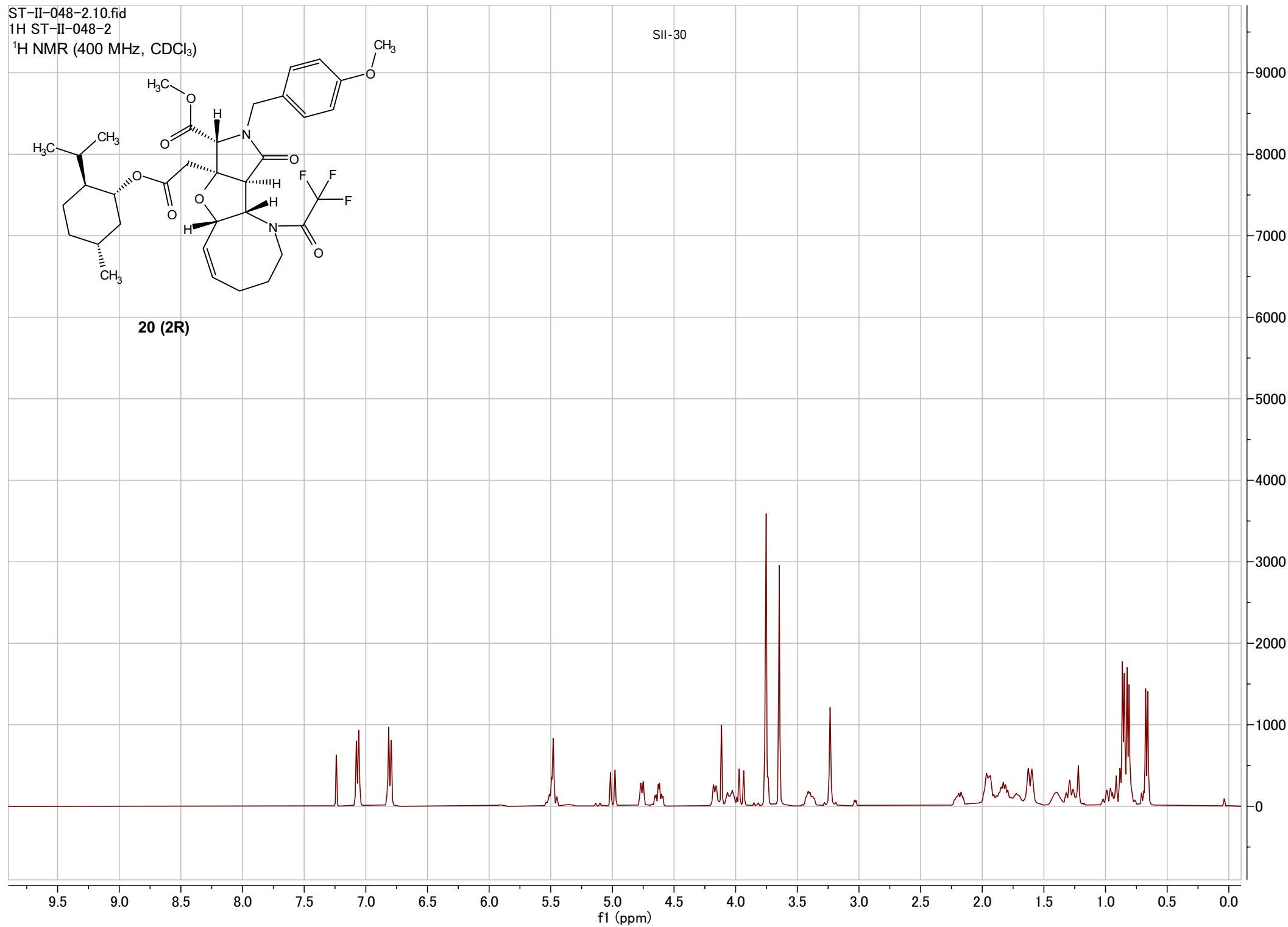


ST-II-048-2.10.fid  
1H ST-II-048-2  
1H NMR (400 MHz, CDCl<sub>3</sub>)

SII-30



20 (2R)

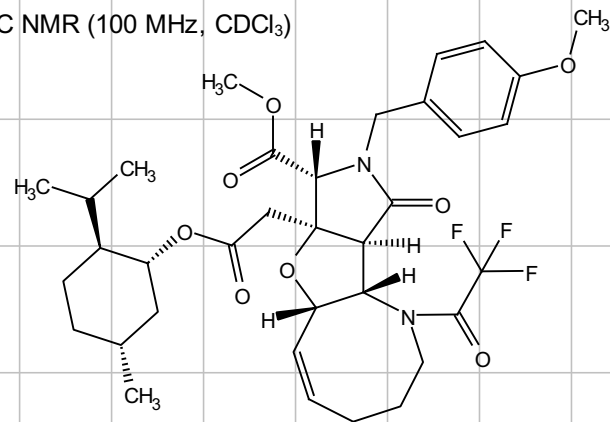


ST-II-048-2.11.fid

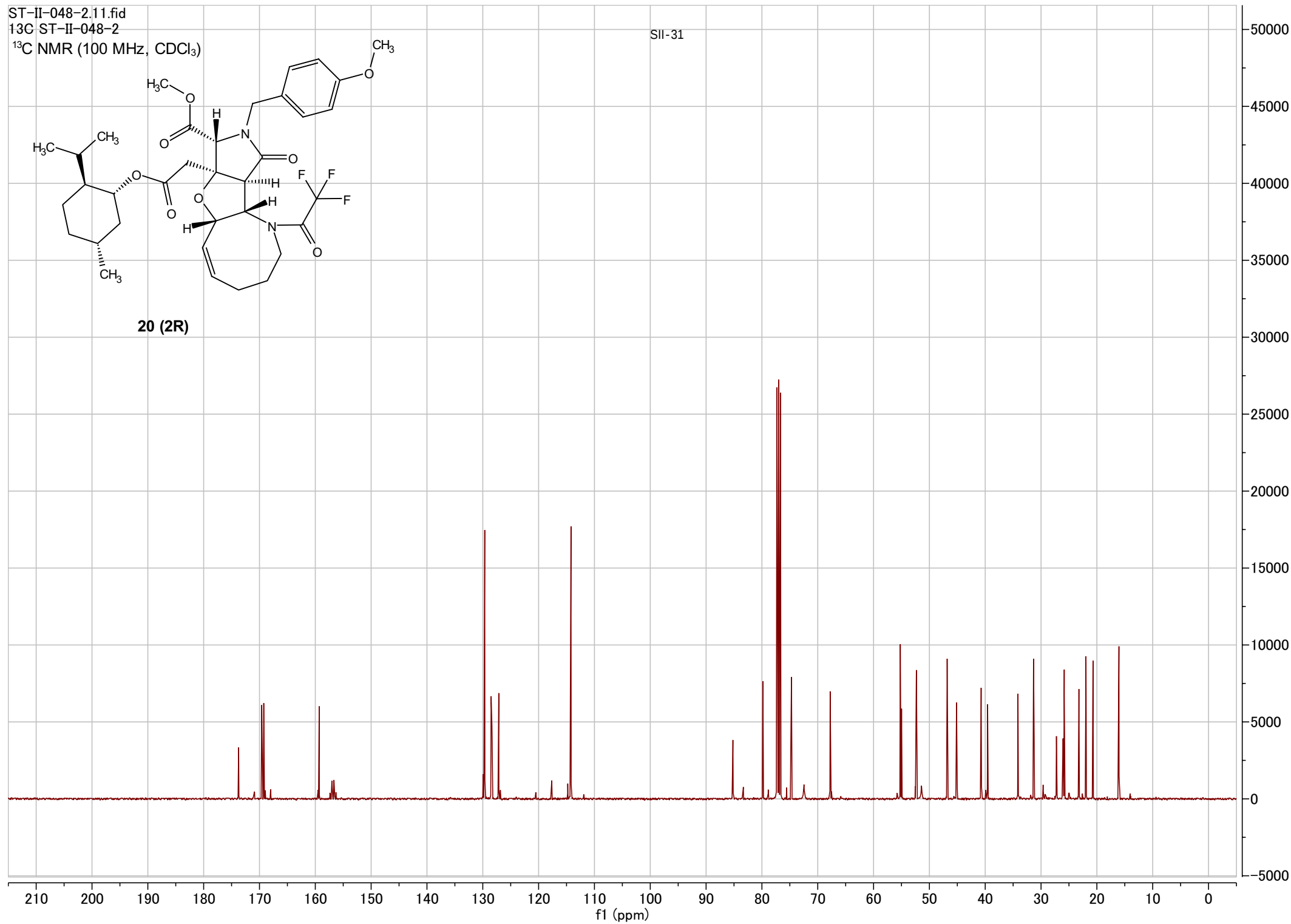
13C ST-II-048-2

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

SII-31



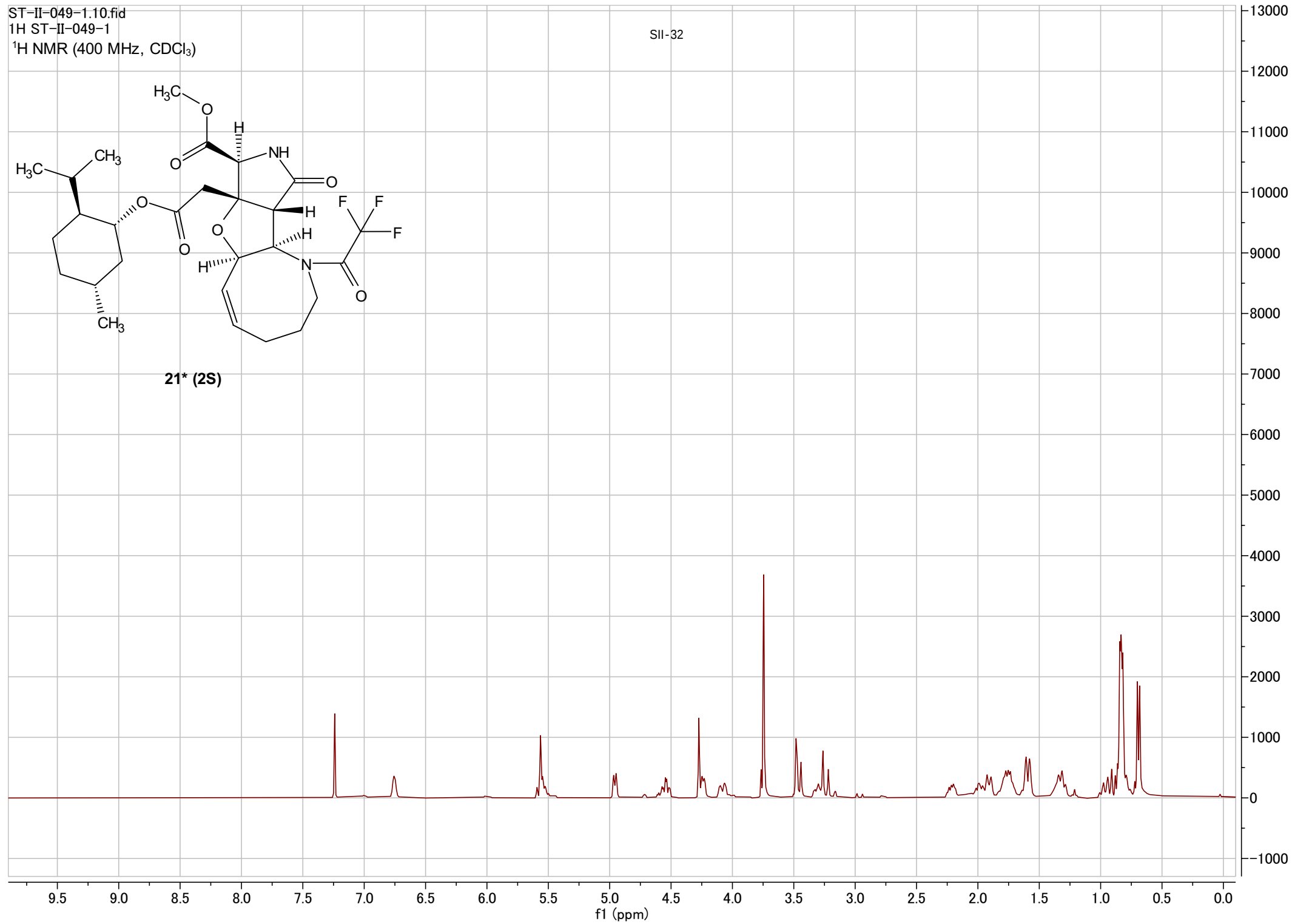
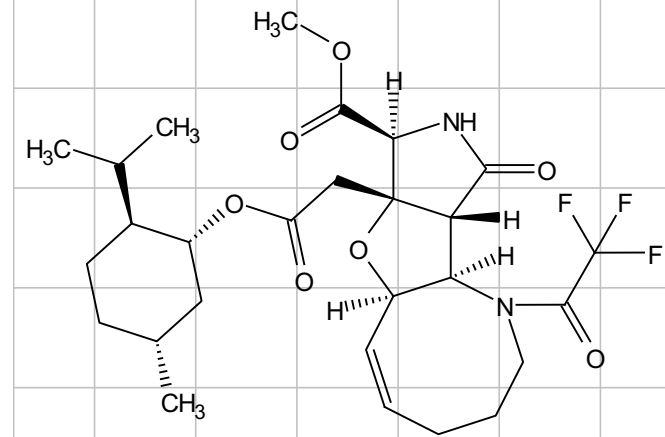
**20 (2R)**



ST-II-049-1.10.fid  
1H ST-II-049-1  
1H NMR (400 MHz, CDCl<sub>3</sub>)

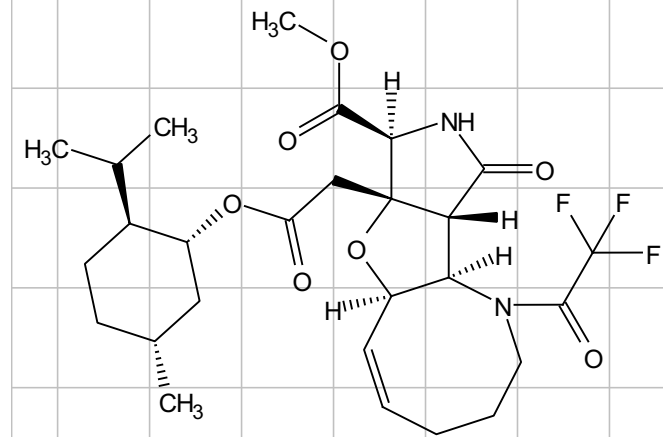
SII-32

21\* (2S)

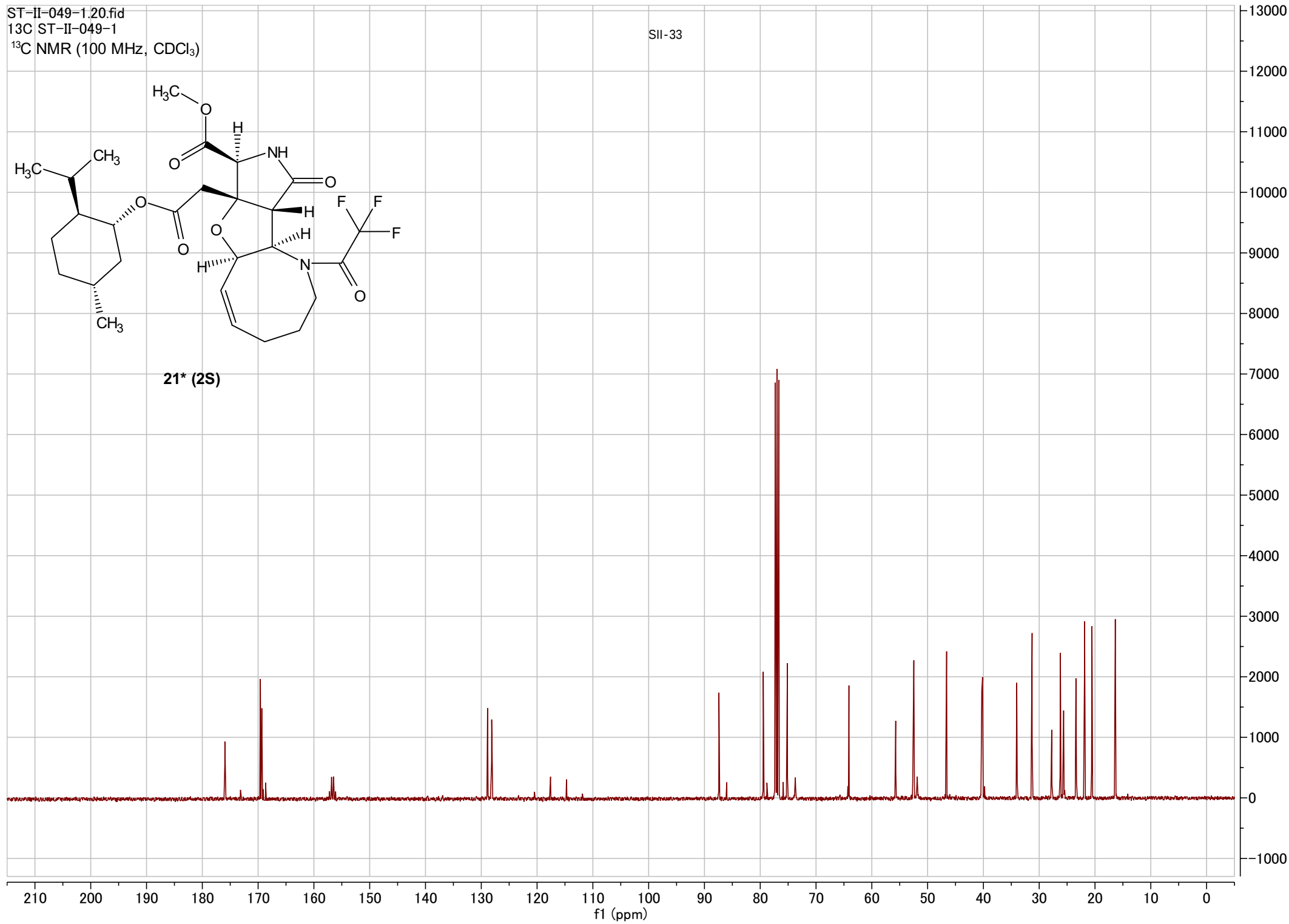


ST-II-049-1.20.fid  
13C ST-II-049-1  
13C NMR (100 MHz, CDCl<sub>3</sub>)

SII-33

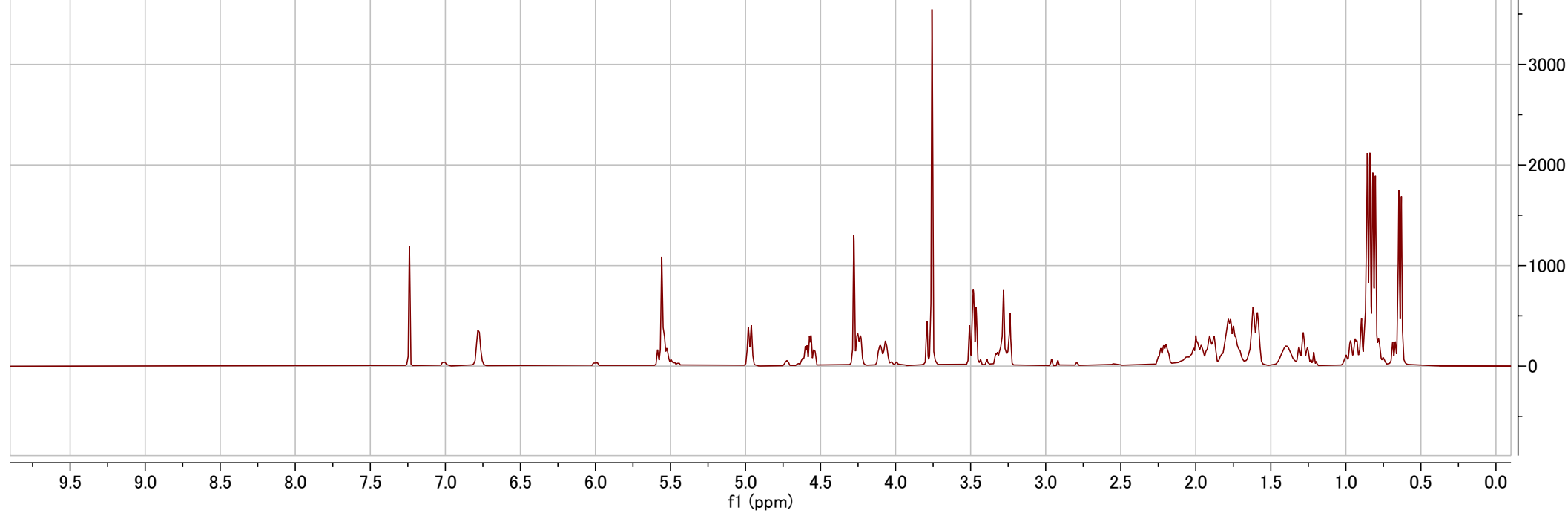
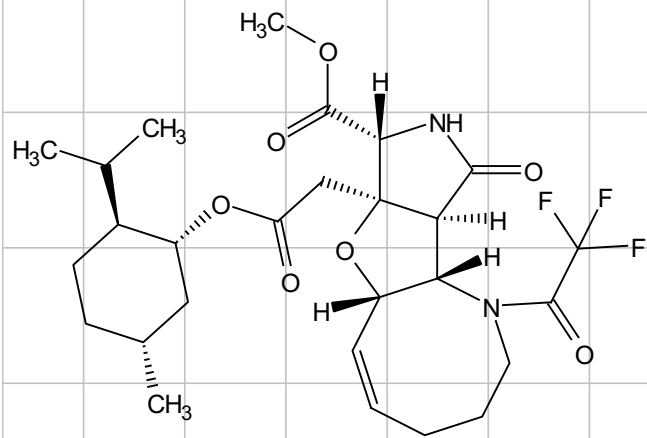


21\* (2S)



ST-II-050-1.10.fid  
1H ST-II-050-1  
1H NMR (400 MHz, CDCl<sub>3</sub>)

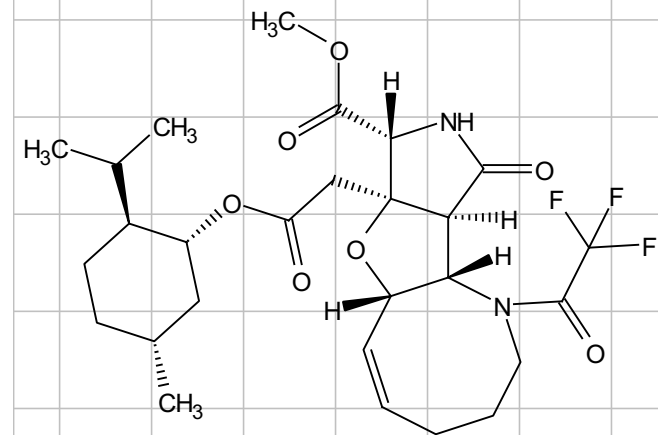
SII-34



ST-II-050-1.13.fid

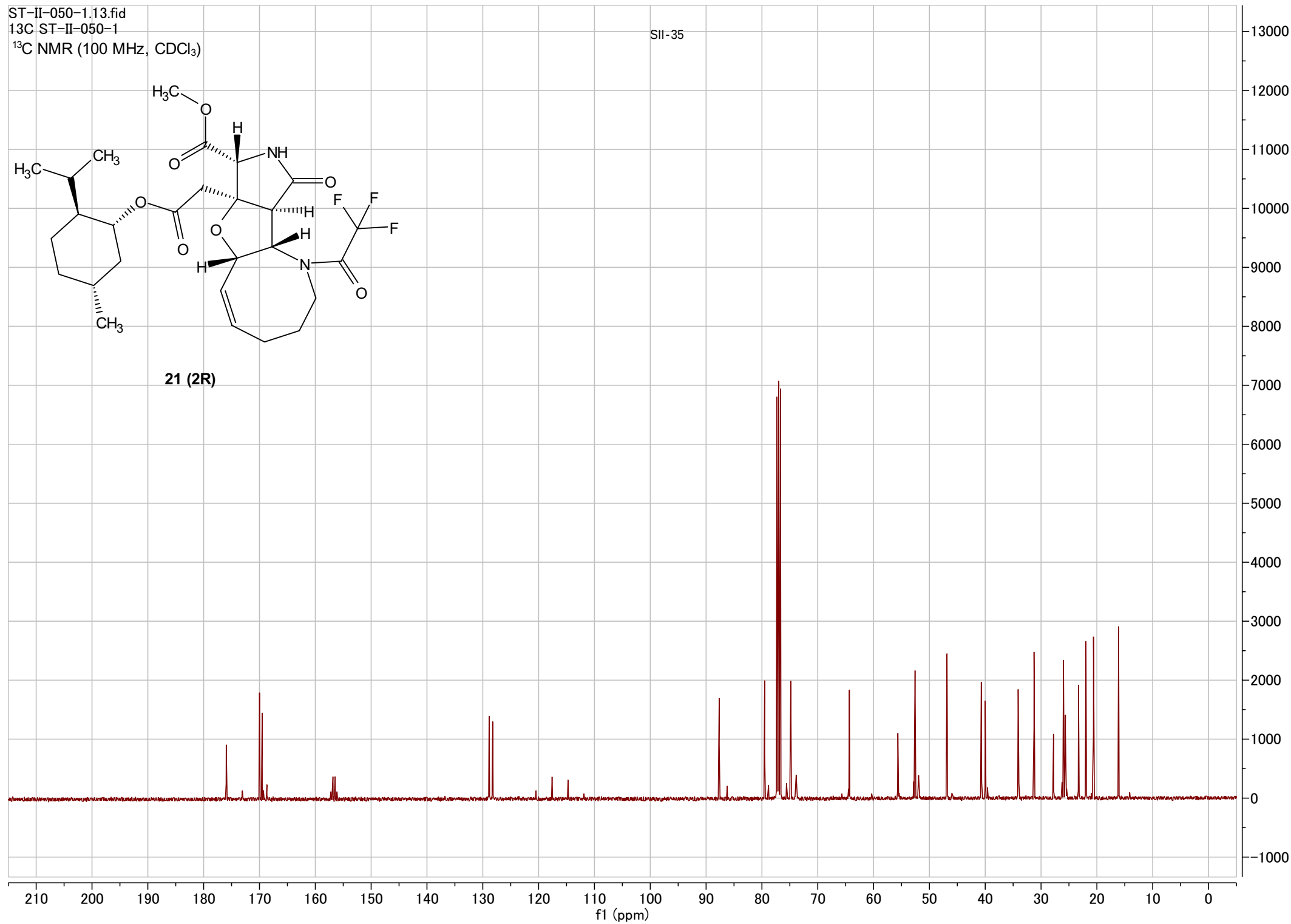
13C ST-II-050-1

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

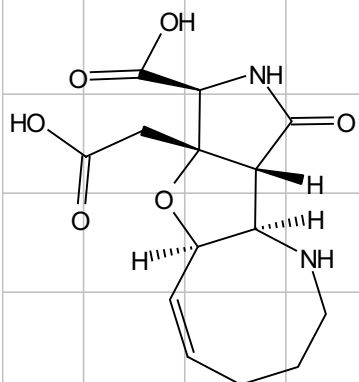


**21 (2R)**

SII-35

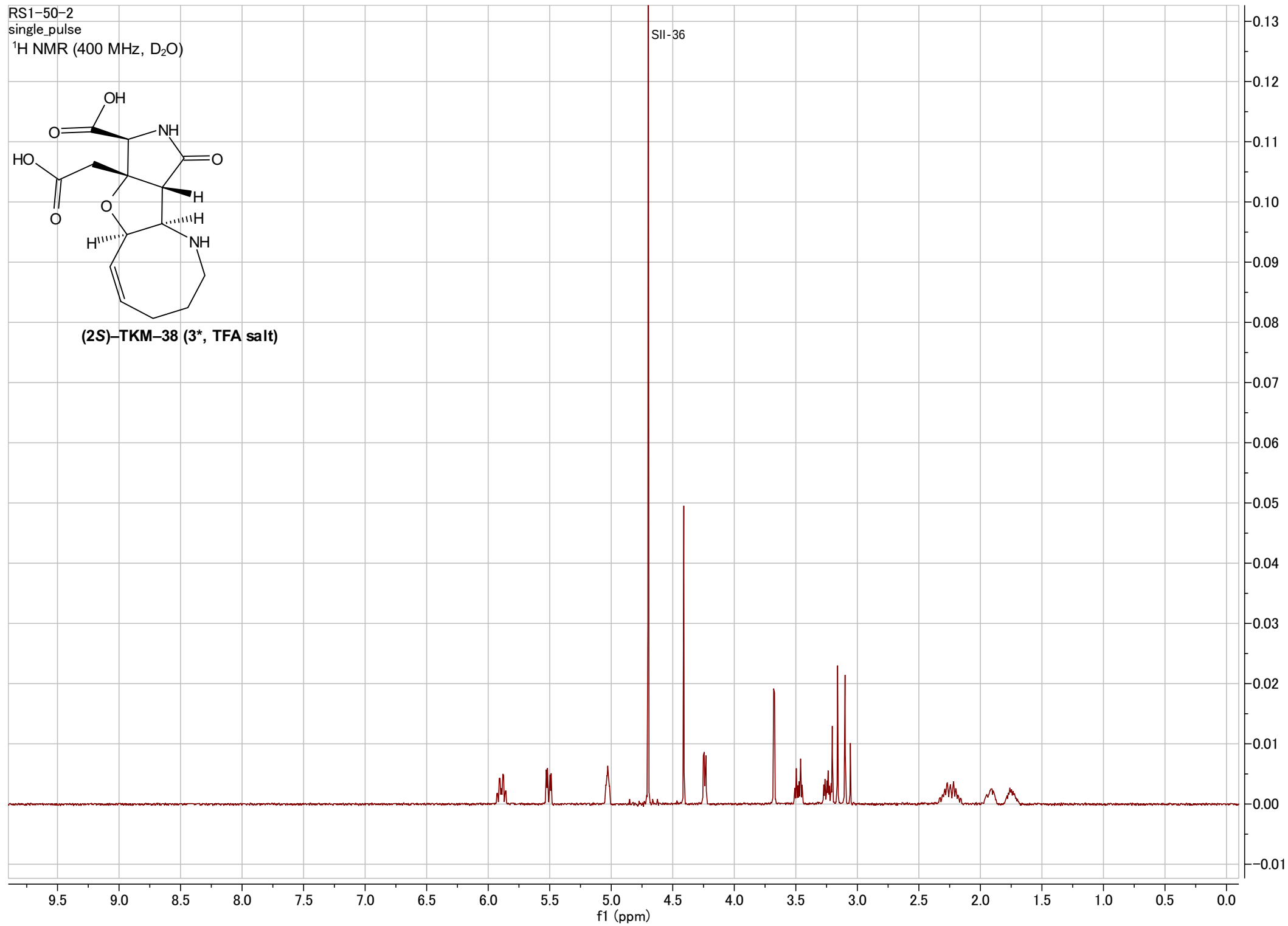


RS1-50-2  
single\_pulse  
<sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O)

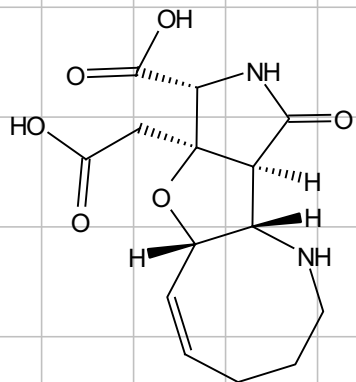


**(2S)-TKM-38 (3\*, TFA salt)**

SII-36

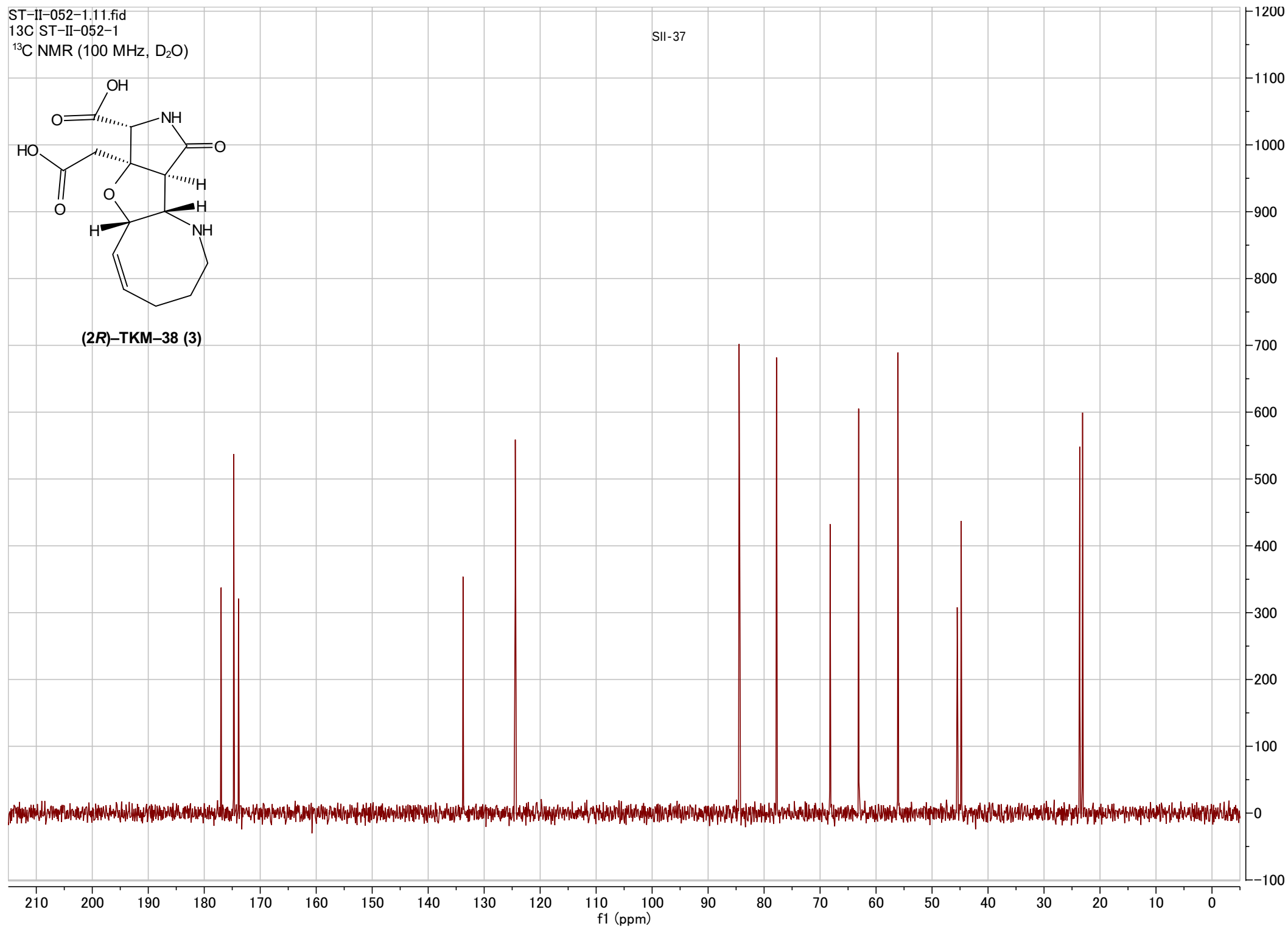


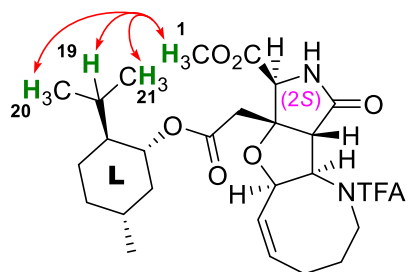
ST-II-052-1.11.fid  
13C ST-II-052-1  
13C NMR (100 MHz, D<sub>2</sub>O)



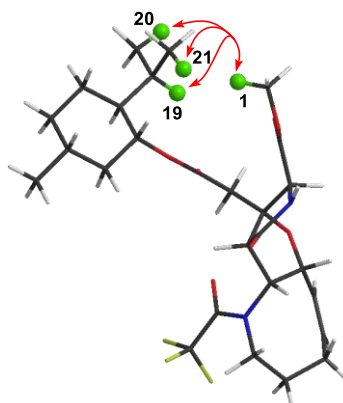
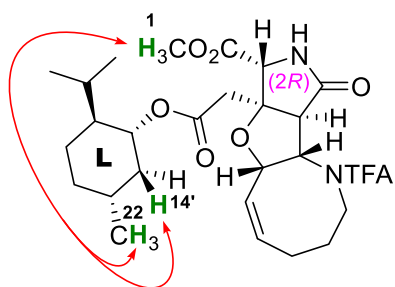
(2R)-TKM-38 (3)

SII-37

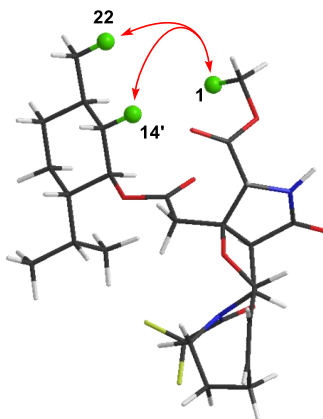


**21\* (2S)**

NOESY

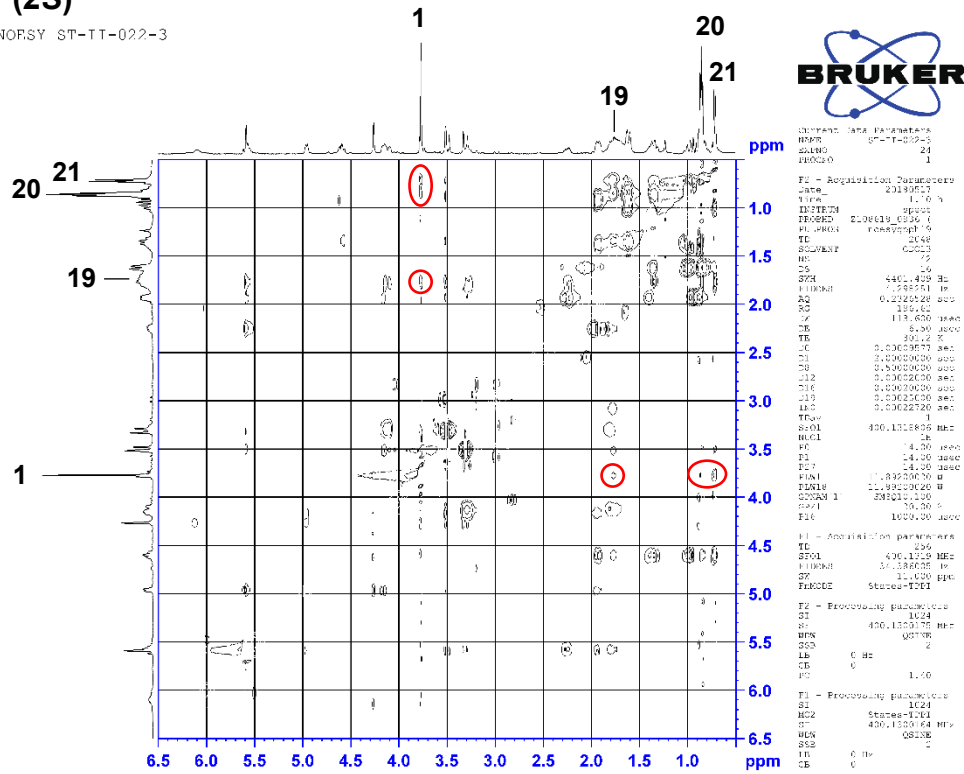
CONFLEX  
population 89%**21 (2R)**

NOESY

CONFLEX  
population 77%

**21\* (2S)**

NORSY ST-TT-022-3

**21 (2R)**

NORSY ST-II-024-3

