Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Boroxine Template for Macrocyclization and Postfunctionalization

Kosuke Ono,[a]* Satoru Onodera[b] and Hidetoshi Kawai[b]

School of Science, Tokyo Institute of Technology,
O-okayama, Meguro-ku, Tokyo 152-8551, Japan[a]
Faculty of Science, Tokyo University of Science
Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan[b]

*e-mail: k.ono@chem.titech.ac.jp

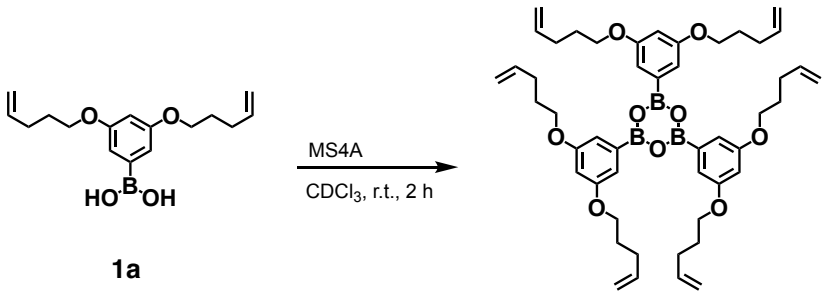
Table of Contents

1. General Methods

^{1}H NMR spectra were recorded on a Bruker BioSpin AVANCE DPX-400 (400 MHz) spectrometer and Bruker BioSpin AVANCE III (400 MHz) spectrometer and ^{13}C NMR spectra were recorded on a Bruker BioSpin AVANCE 400 M (100 MHz) spectrometer using residual $CHCl_3$ (^{1}H, 7.26 ppm), DMSO (^{1}H, 2.50 ppm), or DMSO-d_6 (^{13}C, 39.5 ppm) as an internal standard. All NMR spectra were recorded at 303 K unless otherwise noted. ^{11}B NMR spectra were recorded on a JEOL ECX-500 (160 MHz) spectrometer using BF_3•Et_2O (0.00 ppm) as an external standard. High-resolution mass analysis (MALDI^{+}) was performed on a JEOL JMS-S3000 mass spectrometer using DCTB (*trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile), DHB (2,5-dihydroxybenzoic acid) and Dithranol as matrix. IR spectra were recorded on a JASCO FT/IR-4600 plus spectrometer. The X-ray analysis data were obtained using a Rigaku R-AXIS RAPID charge-coupled device (CCD) apparatus (Cu κ α radiation, λ = 1.54178 Å). Preparative recycling gel permeation chromatography (GPC) was carried out on a JAI LC-908 equipped with JAIGEL -1HH and -2HH columns ($CHCl_3$ as an eluent; flow rate: 5.5 mL/min). All reactions except the catalytic hydrogen reduction were carried out under Ar unless otherwise noted. Tetrahydrofuran (THF) was purified by solvent purification system of Glass-Contour. Activated molecular sieves 4Å (MS 4A) was added 5 mg per 1 ml of solvent. All commercially available compounds were used without further purification unless otherwise indicated. Dehydrated dichloromethane was purchased from Kanto Chemical Co., Inc. 5-bromo-1-pentene was purchased from Kanto Chemical Co., Inc, 6-bromo-1-hexene was purchased from Oakwood Products, Inc, 7-bromo-1-heptene was purchased from Combi-Blocks, Inc. 5-bromoresorcinol[S1] and 3,5-bis(pent-5-en-1-yloxy)phenylboronic acid (**1a**)[S2] were prepared according to the literature procedures.

2. Synthesis of Macrocycle 4

2-1. Boroxine Formation from Boronic acid **1a** to **2a**



1a **2a**

To a $CDCl_3$ (600 μL) solution of boronic acid **1a** (1.76 mg) in an NMR tube was added MS4A. After standing at room temperature for 2 h, ^{1}H NMR spectrum of the solution revealed the quantitative formation of boroxine **2a**.

Physical data of **2a**

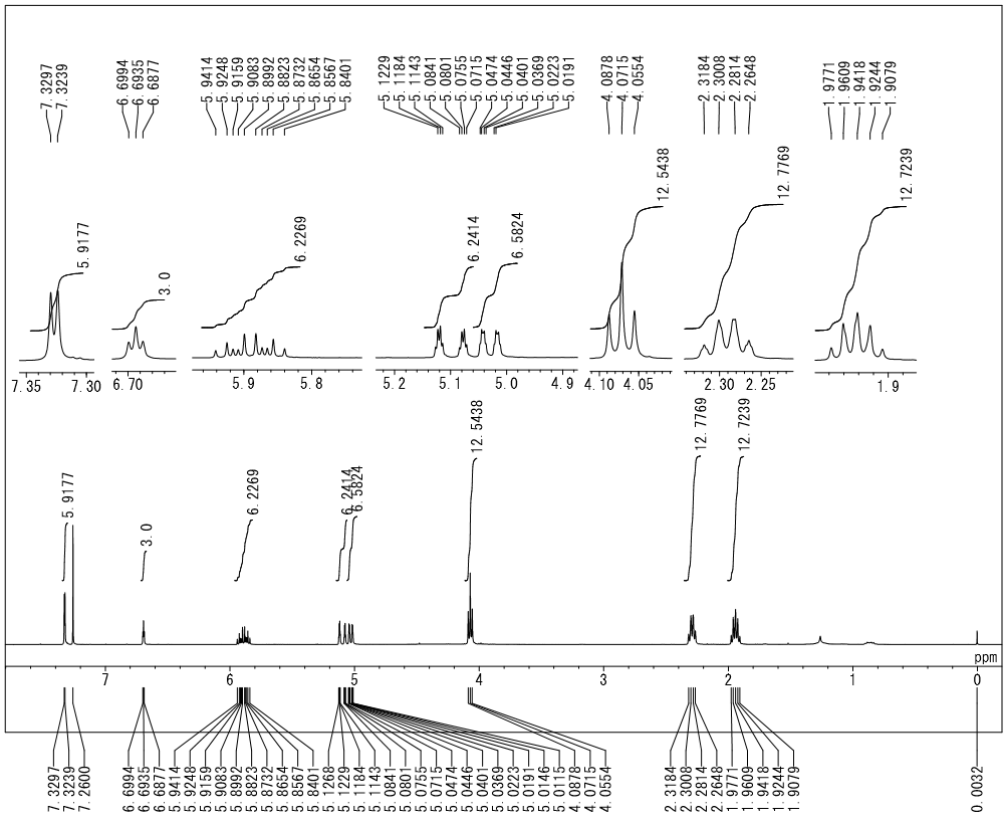
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, *J* = 2.3 Hz, 6H), 6.69 (t, *J* = 2.3 Hz, 3H), 5.89 (ddt, *J* = 17.0, 10.2, 6.6 Hz, 6H), 5.10 (dq, *J* = 17.0, 1.6 Hz, 6H), 5.05-5.02 (m, 6H), 4.07 (t, *J* = 6.5 Hz, 12H), 2.32-2.26 (m, 12H), 1.94 (quin, *J* = 6.9 Hz, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 137.9, 115.4, 113.8, 106.0, 67.5, 30.3, 28.6. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.2

HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{48}H_{63}B_3O_9Na$: 839.4666, found: 839.4651 $[M+Na]^+$.

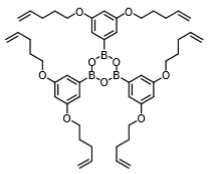
IR (ATR): 3077, 2920, 2872, 1641, 1585, 1433, 1332, 1297, 1162, 1057, 991, 908, 847, 725, 680 cm^{-1}.

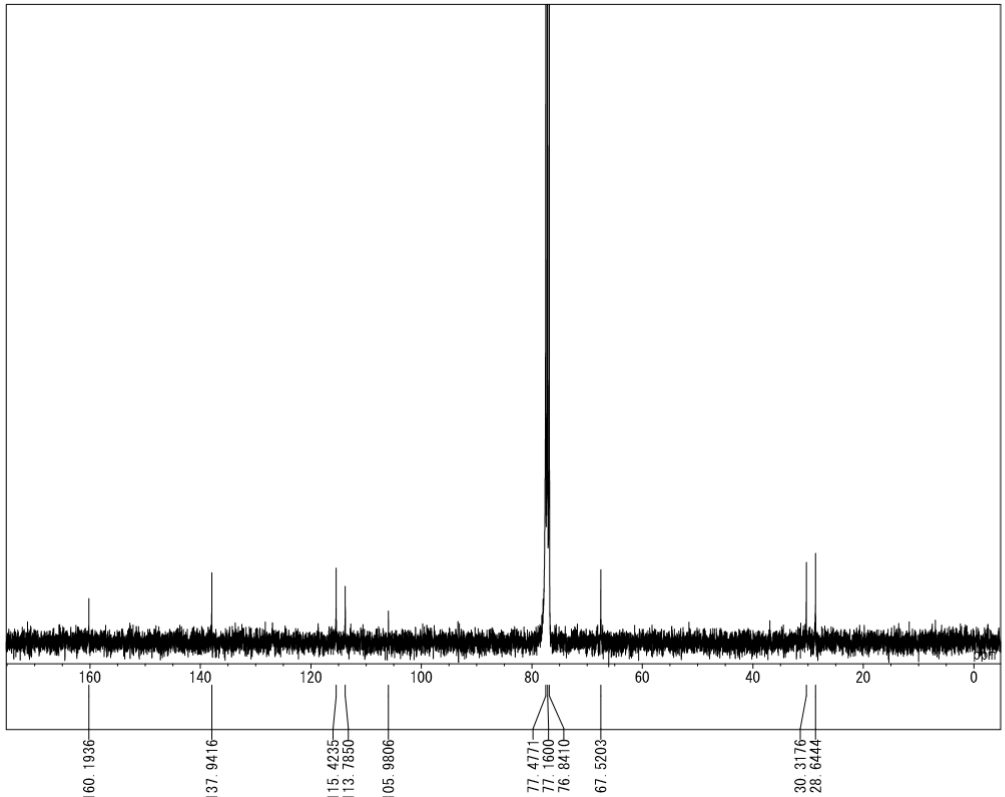


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C5 boroxine体\C5 boroxine 1H (SO330).rm1
DATIM 16/Dec/2019 19:32:41
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.13 MHz
OBSET	0.0 kHz
OBFIN	10003.76 Hz
POINT	65536
FREQU	8196.722 Hz
SCANS	16
ACQTM	7.9954 s
IRNUC	OFF
PROBHD	Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM	AVANCE
PULSPRG	ZG30
GRDPROG	
CTEMP	30.0027 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	101

^{1}H NMR

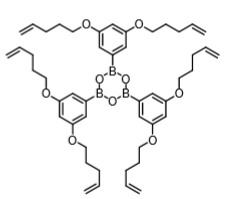


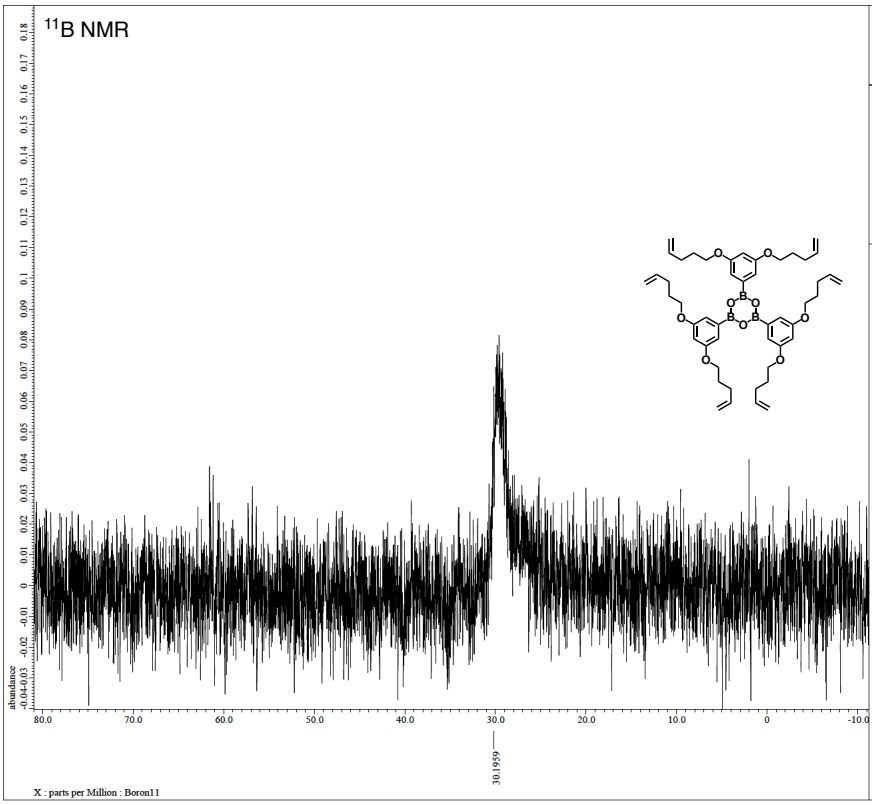


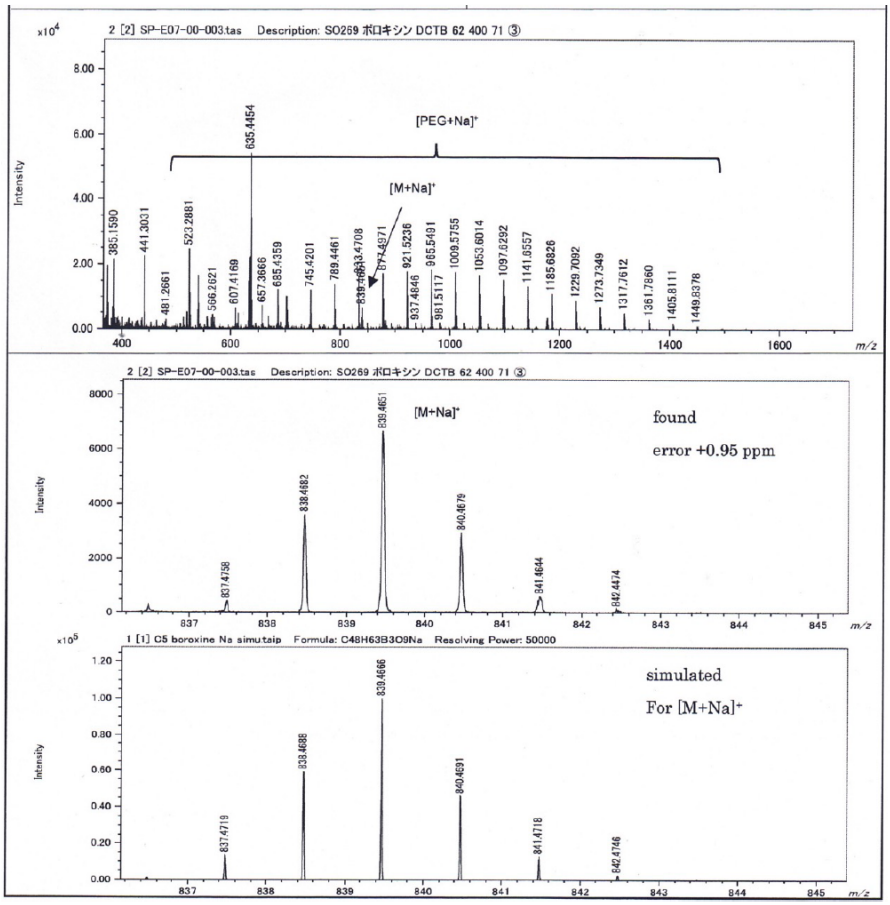
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C5 BOROXINE体\C5 BOROXINE 13C (SO330).RM1
DATIM 17/Dec/2019 09:52:05
COMNT

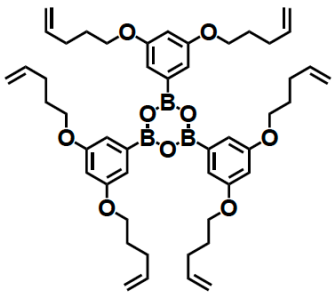
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.209 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	1024
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	64

^{13}C NMR

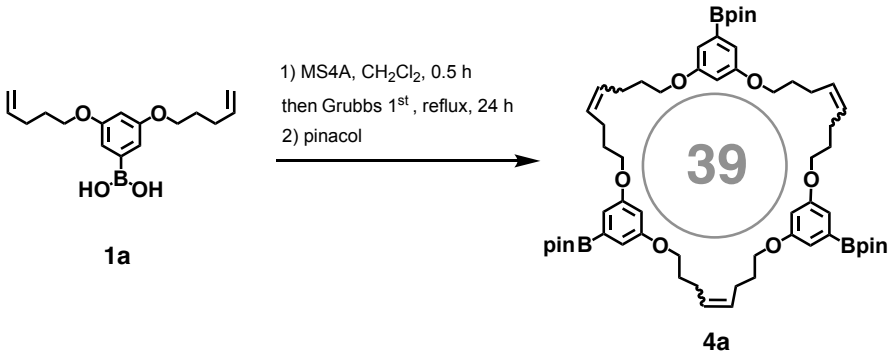



^{11}B NMR
abundance
30.1959
X : parts per Million : Boron11


2 [2] SP-E07-00-003.tas Description: SO269 ボロキシン DCTB 62 400 71 ③
[PEG+Na]+
[M+Na]+
Intensity
m/z
2 [2] SP-E07-00-003.tas Description: SO269 ボロキシン DCTB 62 400 71 ③
[M+Na]+
found
error +0.95 ppm
1 [1] C5 boroxine Na simutaip Formula: C48H63B3O9Na Resolving Power: 50000
simulated
For [M+Na]+



2-2. Synthesis of Macrocycle **4a**



1a **4a**

Boronic acid **1a** (69.0 mg, 0.238 mmol) was dissolved in dichloromethane (159 mL) with MS4A and the solution was stirred at room temperature for 0.5 h. Then Grubbs 1st Generation catalyst (19.6 mg, 23.8 μmol) was added and the resulting mixture was refluxed for 24 h under Ar. The reaction was quenched with ethyl vinyl ether (200 μL) and the solvent was evaporated to crude **3a**. The crude was treated with pinacol (28.1 mg, 0.238 mmol) in a mixture of methanol and chloroform and MS4A was removed by filtration. The filtrate was evaporated and the resulting crude product was purified by GPC to afford the desired **4a** (26.4 mg, 32%).

Physical data of **4a** (mixture of *cis*/*trans* isomers)

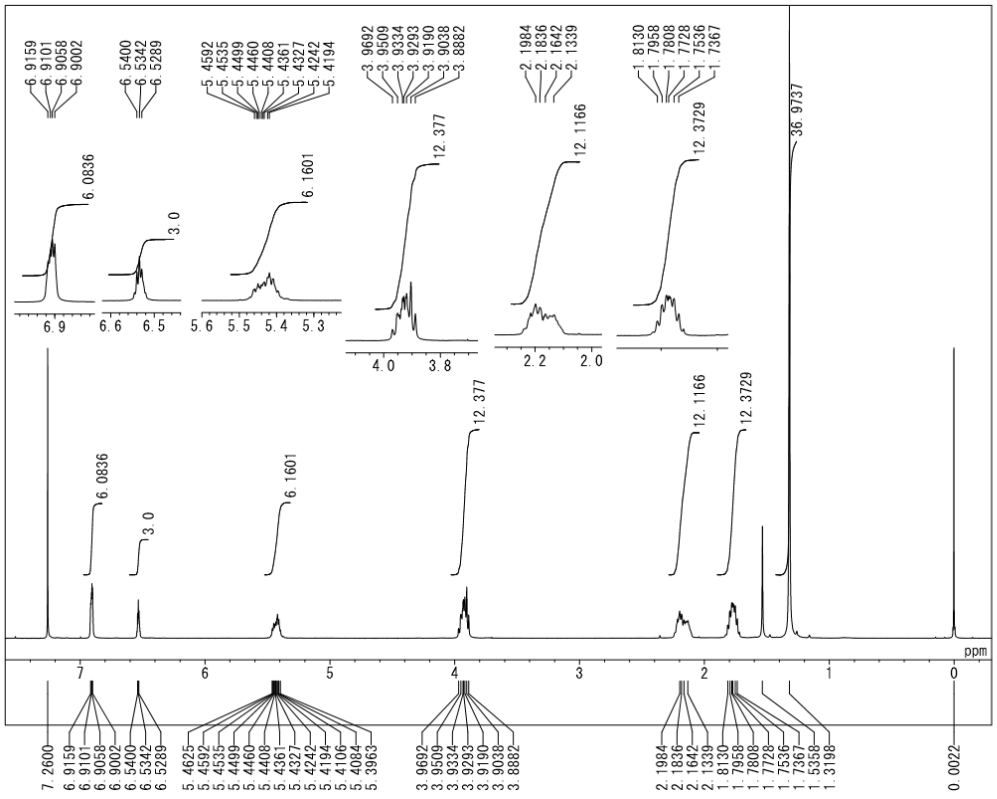
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92-6.90 (m, 6H), 6.54-6.53 (m, 3H), 5.46-5.42 (m, 6H), 3.97-3.89 (m, 12H), 2.20-2.13 (m, 12H), 1.81-1.74 (m, 12H), 1.32 (s, 36H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 130.4, 130.3, 130.2, 129.9, 129.8, 129.7, 113.1, 112.9, 112.8, 112.7, 112.6, 112.5, 112.5, 112.3, 105.2, 105.2, 105.1, 105.0, 83.9, 67.3, 67.2, 67.2, 67.2, 29.4, 29.3, 29.3, 29.2, 29.2, 29.2, 29.1, 29.0, 29.0, 28.9, 25.0, 23.8, 23.8, 23.7. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 29.7

HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{60}H_{87}B_3O_{12}Na$: 1055.6396, found: 1055.6317 $[M+Na]^+$.

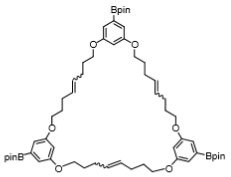
IR (ATR): 2977, 2931, 2871, 1716, 1586, 1469, 1429, 1362, 1308, 1164, 1146, 1056, 969, 851, 706 cm^{-1}.

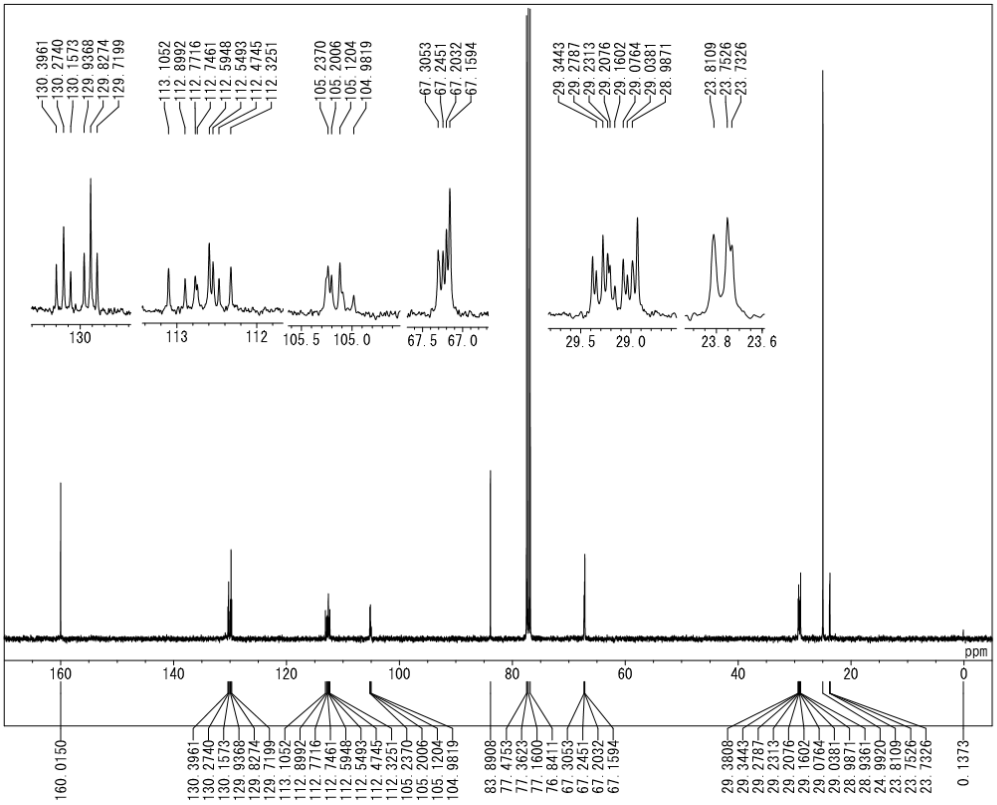


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C5 BpinMac\C5 BpinMac 1H (SO349).RM1
DATIM 23/Jan/2020 19:41:53
COMNT

OBNUC ^{1}H
EXMOD ZG30
OBFRQ 400.13 MHz
OBSET 0.0 kHz
OBFIN 10003.76 Hz
POINT 65536
FREQU 8196.722 Hz
SCANS 16
ACQTM 7.9954 s
IRNUC OFF
PROBHD Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM AVANCE
PULSPRG ZG30
GRDPROG
CTEMP 30.0087 °C
SLVNT $CDCl_3$
BF 0.25 Hz
RGAIN 101

^{1}H NMR

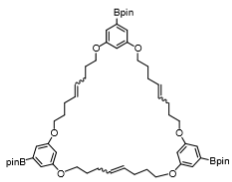


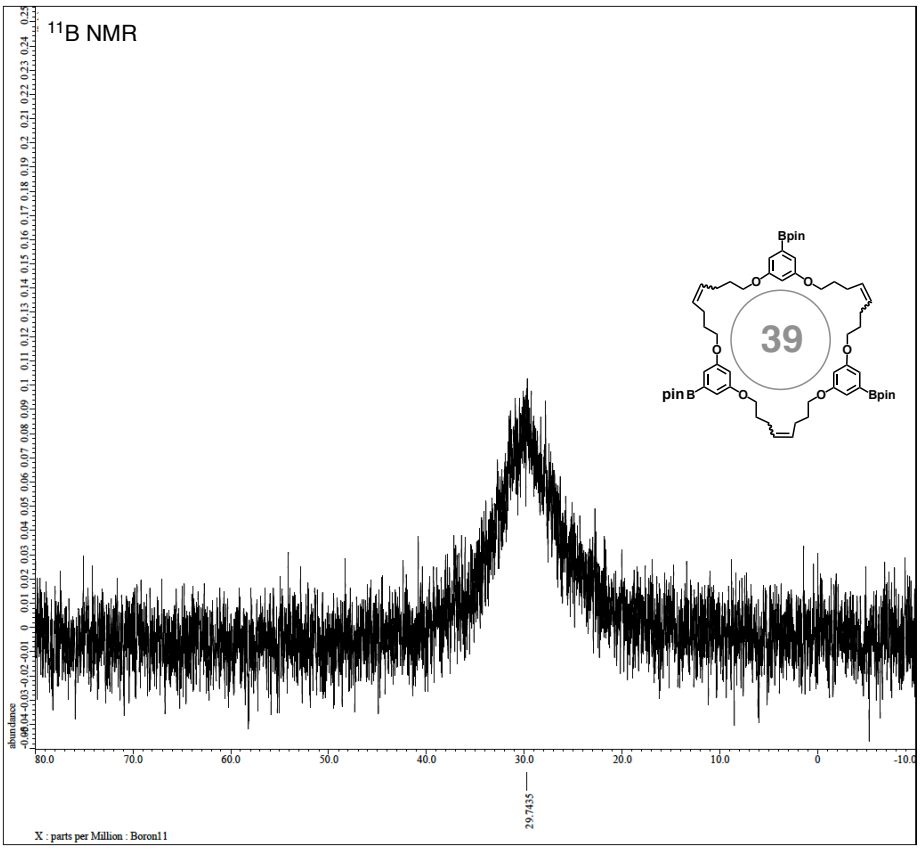


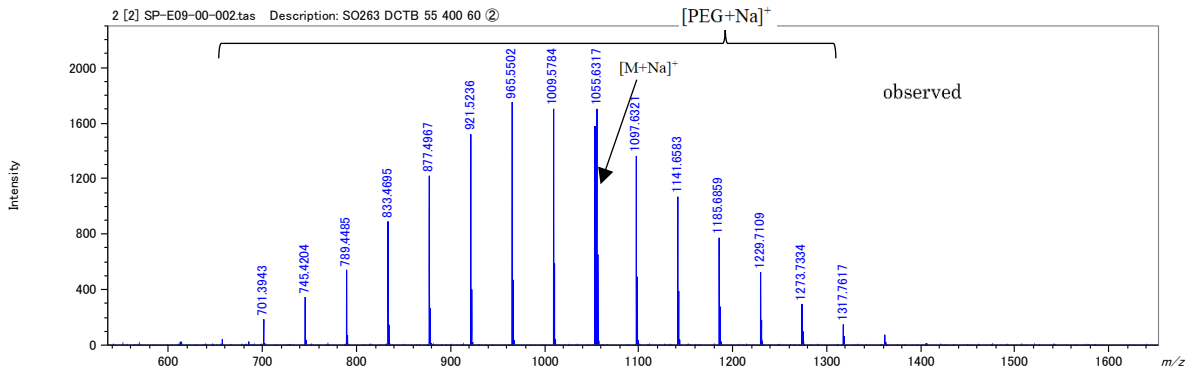
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C5 BPINMAC\C5 BPINMAC 13C (SO349).$RM1
DATIM 23/Jan/2020 22:58:14
COMNT

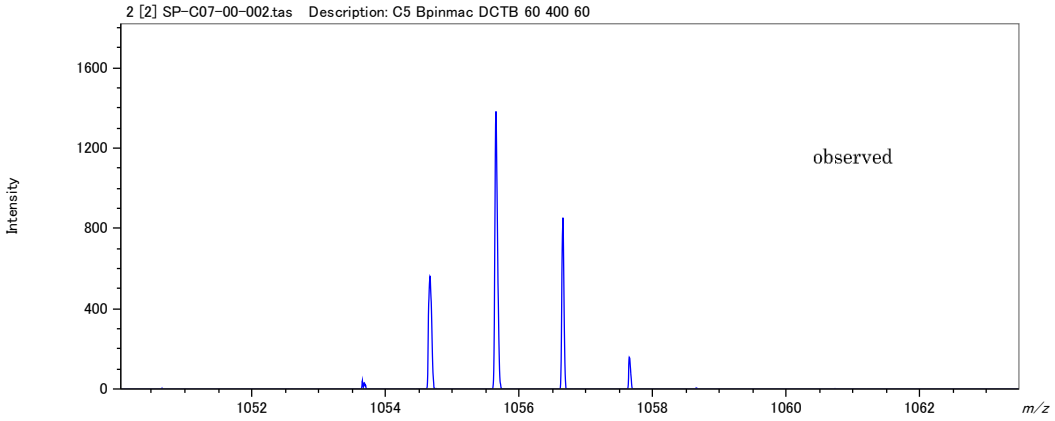
OBNUC ^{13}C
EXMOD ZGPG30
OBFRQ 100.63 MHz
OBSET 0.0 kHz
OBFIN 9999.211 Hz
POINT 32768
FREQU 24038.46 Hz
SCANS 1024
ACQTM 1.3631 s
IRNUC OFF
PROBHD 5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM SPECT
PULSPRG ZGPG30
GRDPROG
CTEMP 26.85 °C
SLVNT $CDCl_3$
BF 0.25 Hz
RGAIN 114

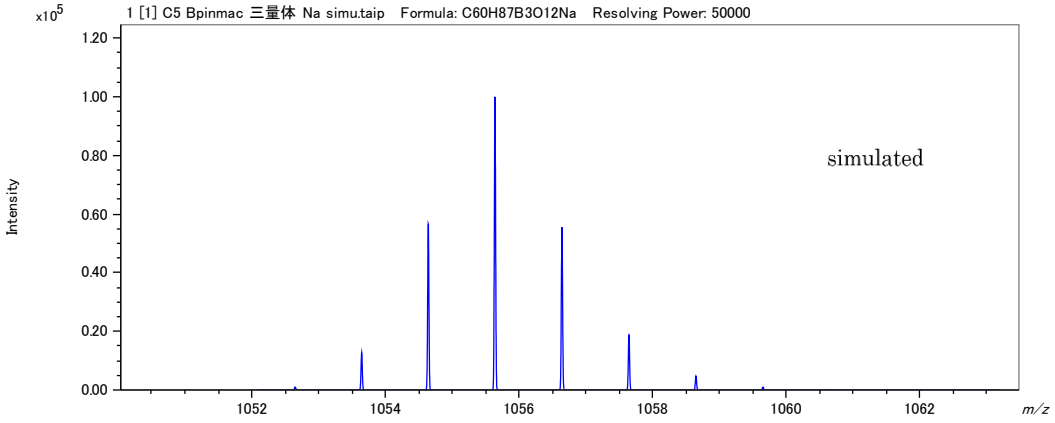
^{13}C NMR

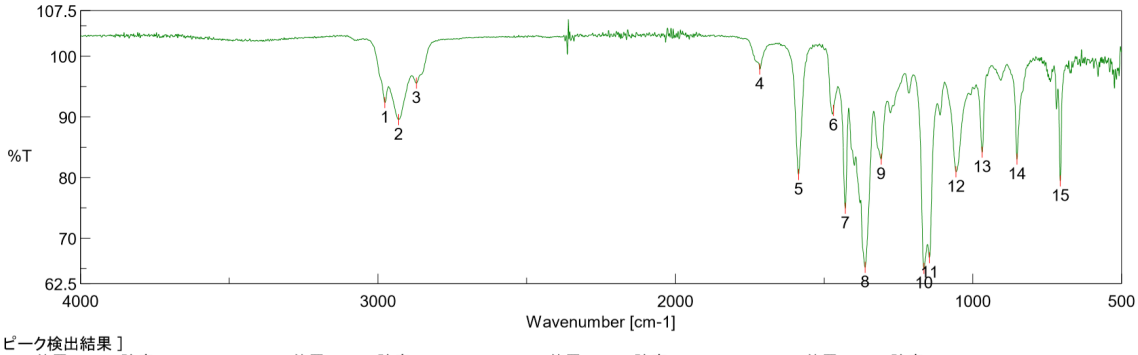



^{11}B NMR
Bpin
39
pin B
Bpin
abundance
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
29.7435
X : parts per Million : Boron11


2 [2] SP-E09-00-002.tas Description: SO263 DCTB 55 400 60 ②
[PEG+Na]+
[M+Na]+
observed
Intensity
701.3943
745.4204
789.4485
833.4695
877.4967
921.5236
965.5502
1009.5784
1055.6317
1097.6321
1141.6583
1185.6859
1229.7109
1273.7334
1317.7617
m/z


2 [2] SP-C07-00-002.tas Description: C5 Bpinmac DCTB 60 400 60
observed
Intensity
m/z


x10^5
1 [1] C5 Bpinmac 三量体 Na simu.taip Formula: C60H87B3O12Na Resolving Power: 50000
simulated
Intensity
m/z



［ピーク検出結果］

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2976.59	92.3246	2	2930.79	89.5201	3	2870.52	95.529	4	1716.34	97.8455
5	1586.16	80.4899	6	1469.01	91.0395	7	1428.99	74.9222	8	1361.98	65.1916
9	1308.46	83.0143	10	1164.31	65.0118	11	1145.99	66.7908	12	1056.32	80.9317
13	968.573	84.1554	14	851.418	83.0176	15	705.819	79.4385			

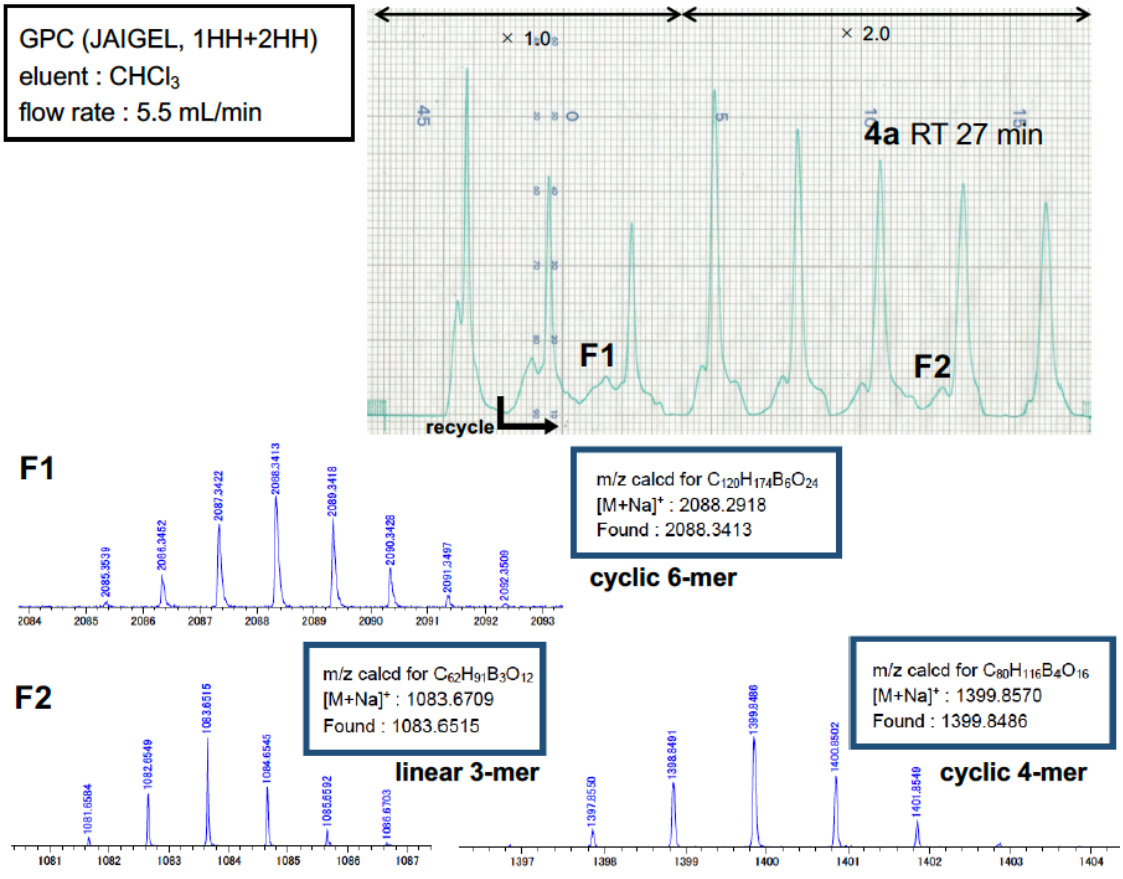


Fig. S1 GPC traces of crude **4a** and MALDI-TOF MS analysis of fractions F1 and F2.

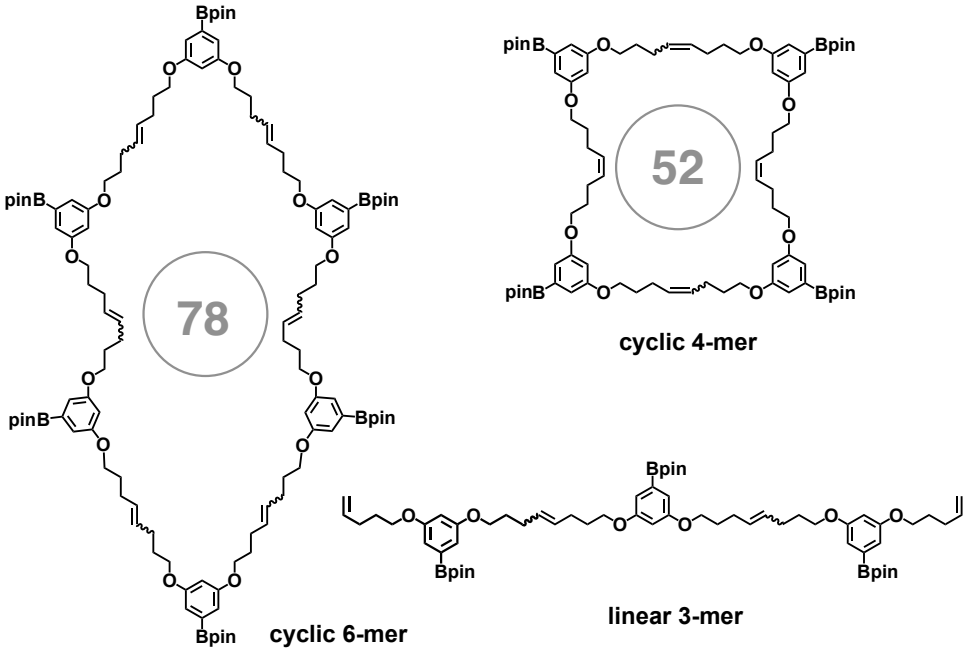
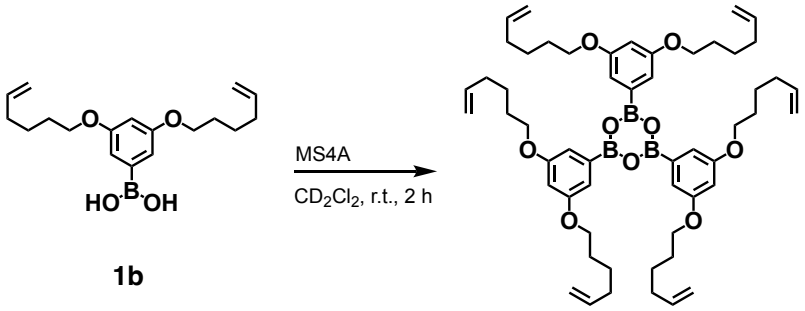


Fig. S2 Chemical structures of cyclic 6-mer, cyclic 4-mer and linear 3-mer.

2-3. Boroxine Formation from Boronic acid **1b** to **2b**



1b **2b**

To a $CDCl_3$ (600 μL) solution of boronic acid **1b** (2.1 mg) in an NMR tube was added MS4A. After standing at room temperature for 2 h, ^{1}H NMR spectrum of the solution revealed the quantitative formation of boroxine **2b**.

Physical data of **2b**

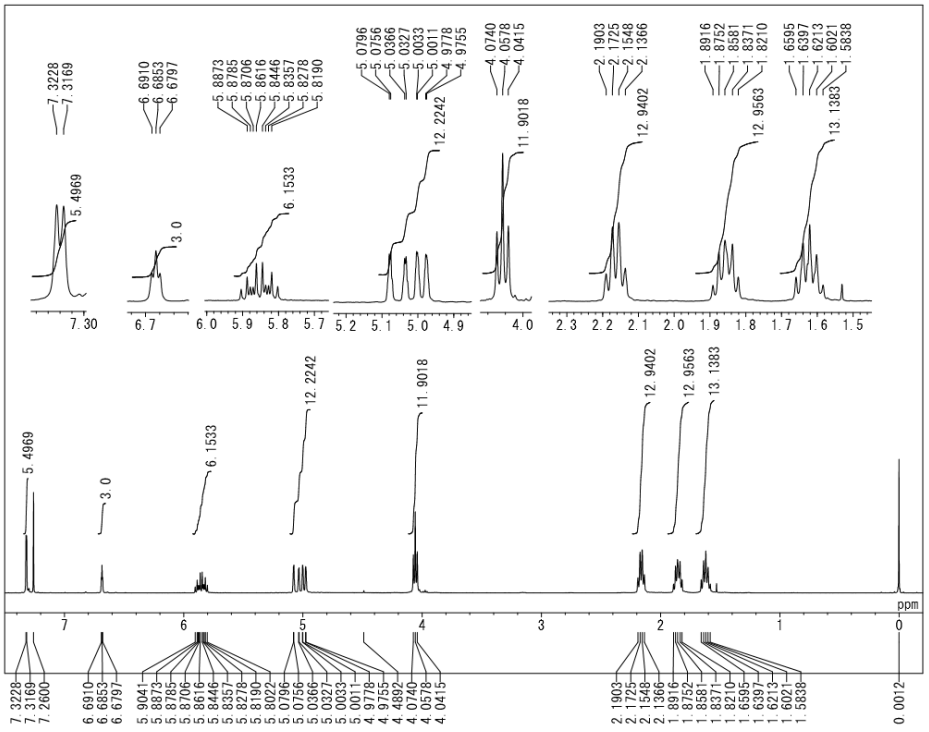
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 2.3 Hz, 6H), 6.69 (t, J = 2.3 Hz, 3H), 5.85 (ddt, J = 17.1, 10.3, 6.7 Hz, 6H), 5.08-5.03 (m, 6H), 5.00-4.98 (m, 6H), 4.06 (t, J = 6.5 Hz, 12H), 2.19-2.14 (m, 12H), 1.89-1.82 (m, 12H), 1.66-1.58 (m, 12H).

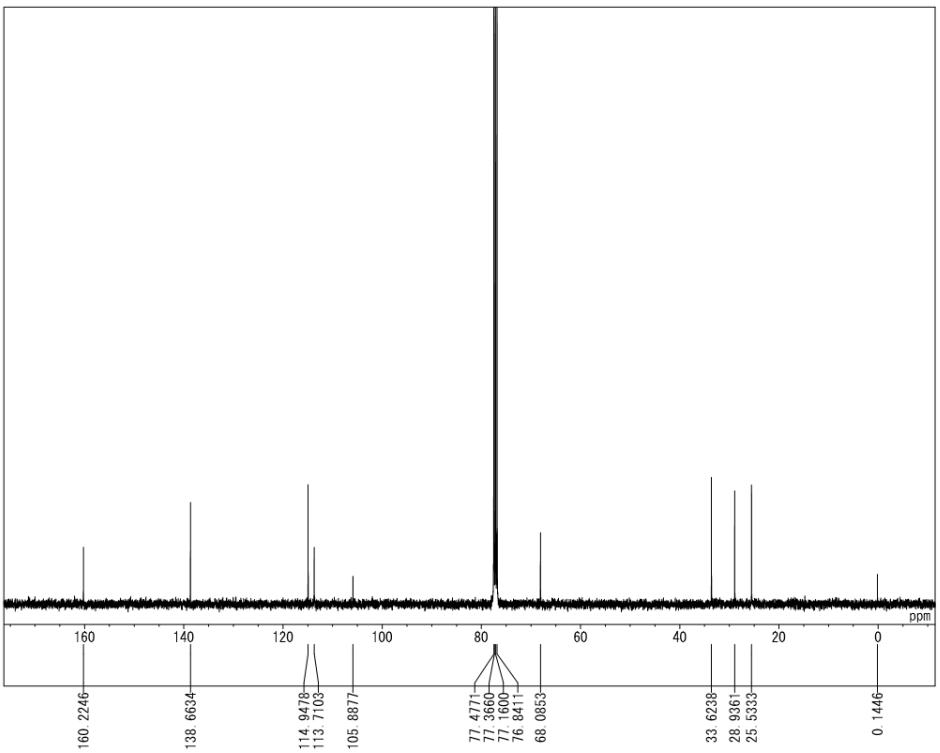
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 138.7, 114.9, 113.7, 105.9, 68.1, 33.6, 28.9, 25.5. The boron-bound carbons were not detected due to quadrupole relaxation.

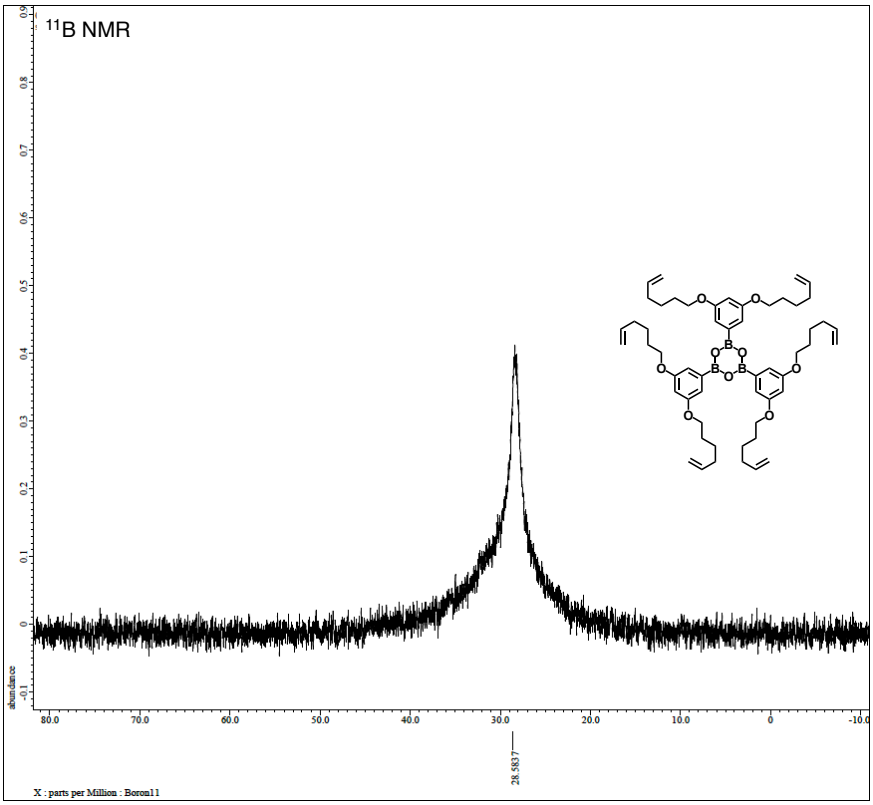
^{11}B NMR (160 MHz, $CDCl_3$): δ 28.6

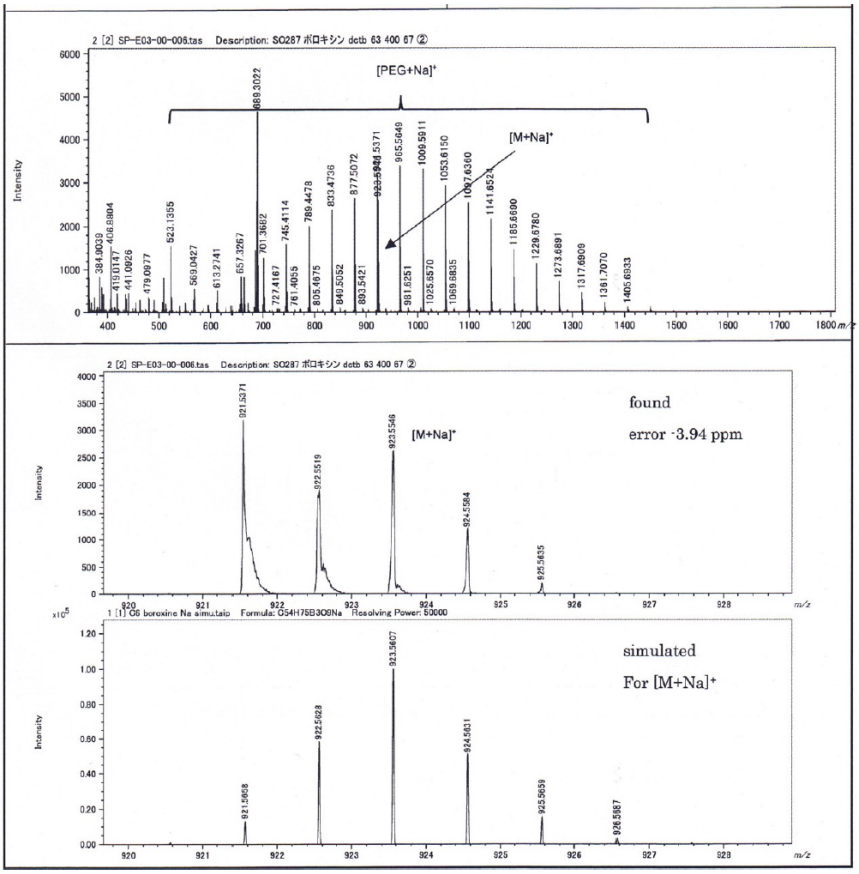
HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{54}H_{75}B_3O_9Na$: 923.5607, found: 923.5546 $[M+Na]^+$.

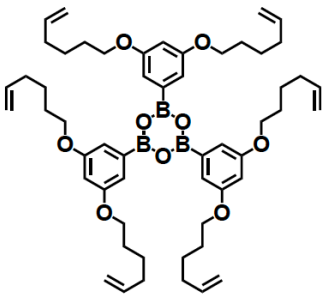
IR (ATR): 3075, 2942, 2912, 2871, 1641, 1585, 1432, 1393, 1332, 1295, 1168, 1043, 993, 909, 849, 728 678 cm^{-1}.



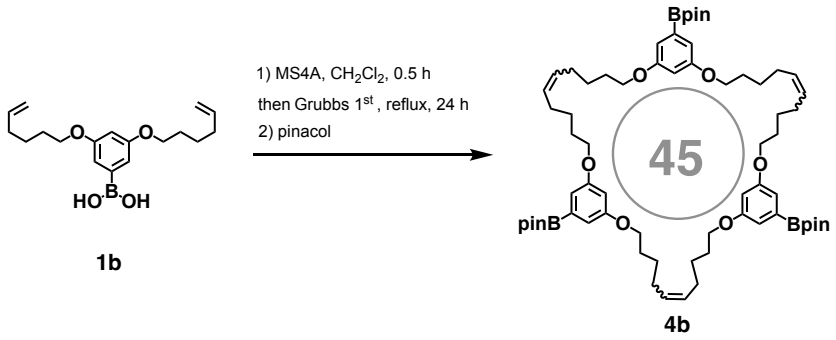



^{11}B NMR
X : parts per Million : Boron11


[PEG+Na]+
[M+Na]+
found
error -3.94 ppm
simulated
For [M+Na]+



2-4. Synthesis of Macrocycle **4b**



Boronic acid **1b** (79.6 mg, 0.25 mmol) was dissolved in dichloromethane (167 mL) with MS4A and the solution was stirred at room temperature for 0.5 h. Then Grubbs 1st Generation catalyst (20.6 mg, 0.025 mmol) was added and the resulting mixture was refluxed for 24 h under Ar. The reaction was quenched with ethyl vinyl ether (200 μL) and the solvent was evaporated to crude **3b**. The crude was treated with pinacol (29.5 mg, 0.25 mmol) in a mixture of methanol and chloroform and MS4A was removed by filtration. The filtrate was evaporated and the resulting crude product was purified by GPC to afford the desired **4b** (73.5 mg, 79%).

Physical data of **4b** (*cis*/*trans* isomers)

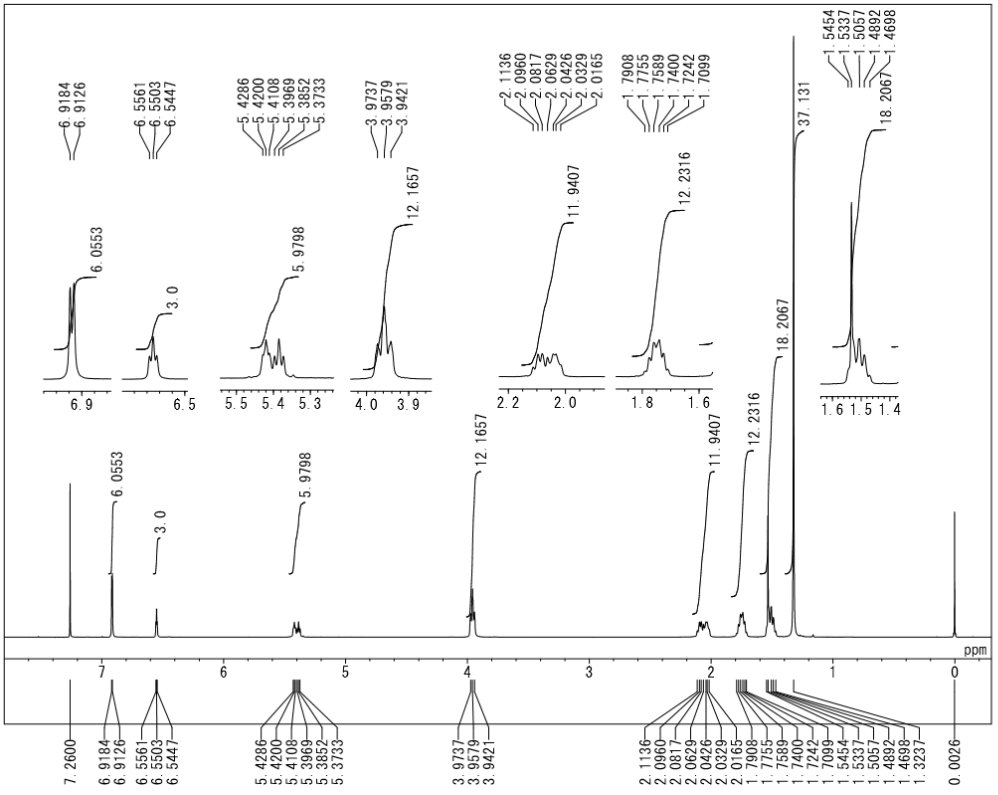
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, J = 2.3 Hz, 6H), 6.55 (t, J = 2.3 Hz, 3H), 5.43-5.37 (m, 6H), 3.96 (t, J = 6.3 Hz, 12H), 2.11-2.02 (m, 12H), 1.79-1.71 (m, 12H), 1.54-1.47 (m, 12H), 1.32 (s, 36H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 130.5, 130.0, 112.6, 105.3, 83.9, 68.0, 32.3, 29.0, 28.9, 27.0, 26.3, 26.1, 25.0. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 29.7

HRMS (MALDI$^+$): m/z calcd. for $C_{66}H_{99}B_3O_{12}Na$: 1139.7337, found: 1139.7288 $[M+Na]^+$.

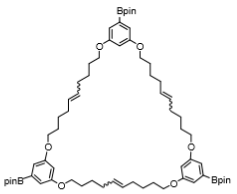
IR (ATR): 2976, 2931, 2867, 1716, 1585, 1428, 1359, 1308, 1145, 1060, 968, 851, 706 cm^{-1}.

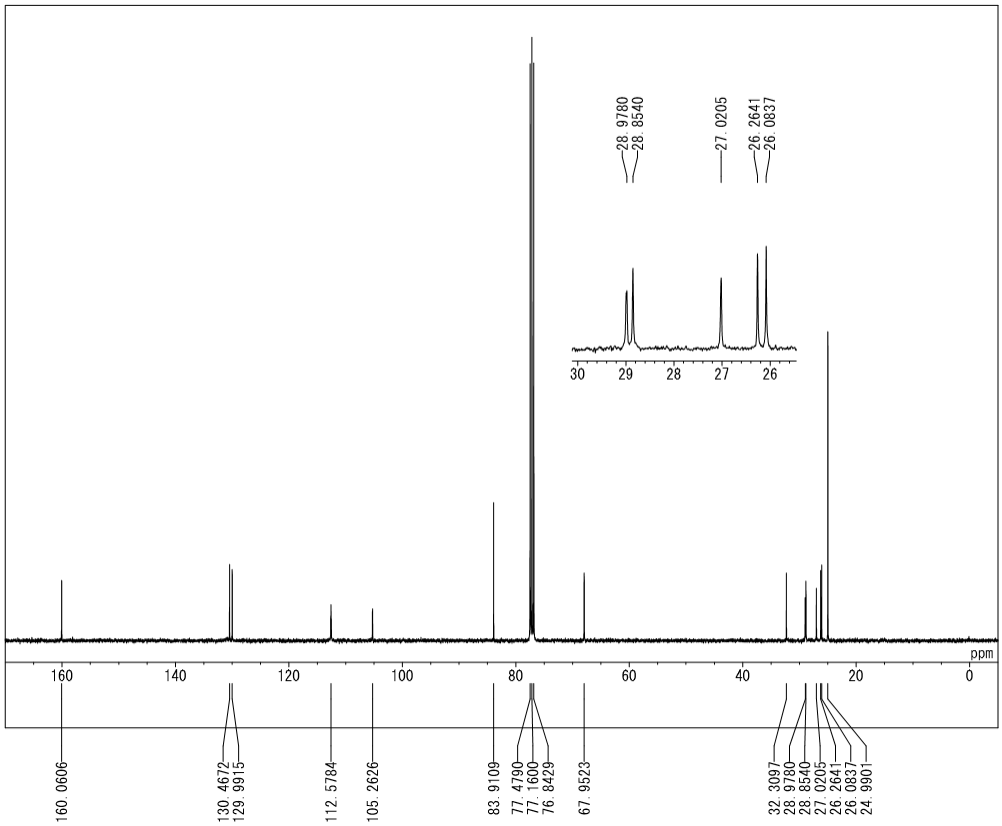


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C6 BpinMac\C6 BpinMac 1H (SO357).RM1
DATIM 19/Feb/2020 10:48:56
COMNT

OBNUC ^{1}H
EXMOD ZG30
OBFRQ 400.13 MHz
OBSET 0.0 kHz
OBFIN 10003.76 Hz
POINT 65536
FREQU 8196.722 Hz
SCANS 16
ACQTM 7.9954 s
IRNUC OFF
PROBHD Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM AVANCE
PULSPRG ZG30
GRDPROG
CTEMP 30.0101 °C
SLVNT $CDCl_3$
BF 0.25 Hz
RGAIN 101

^{1}H NMR

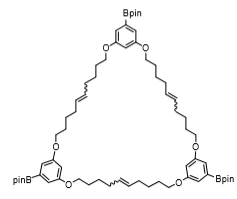


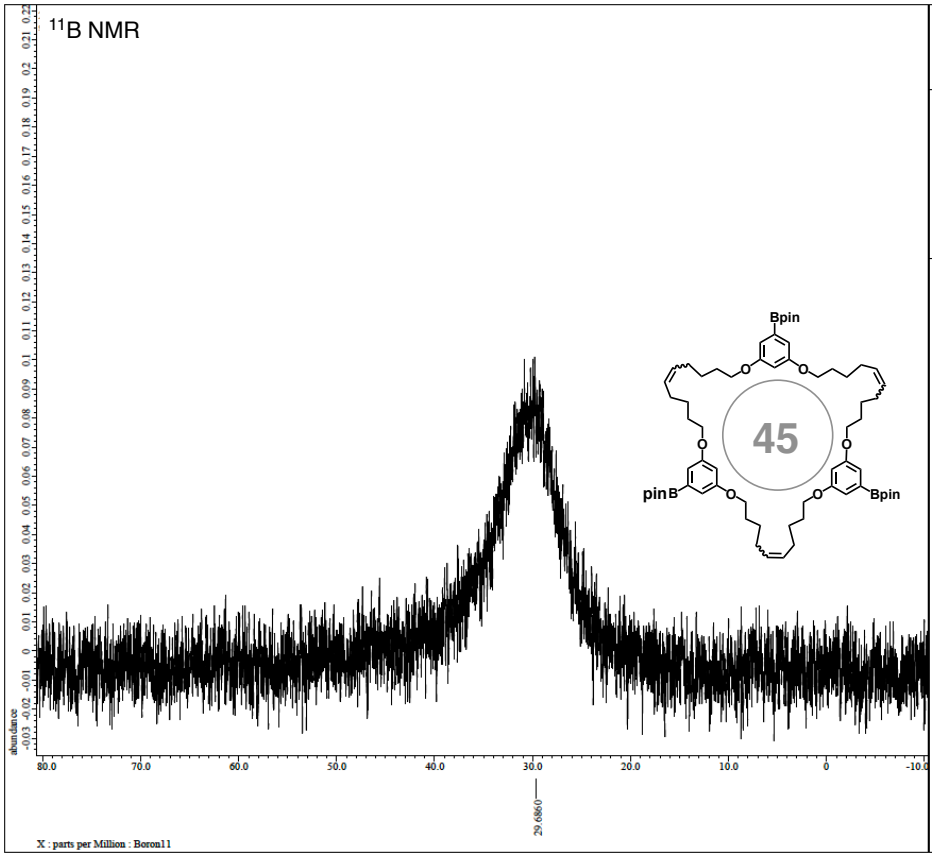


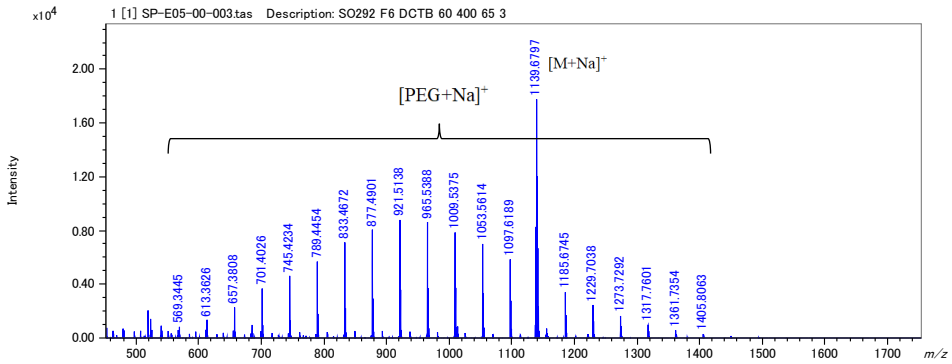
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 BPINMAC\C6 BPINMAC 13C (SO322).$RM1
DATIM 08/Nov/2019 23:59:26
COMNT

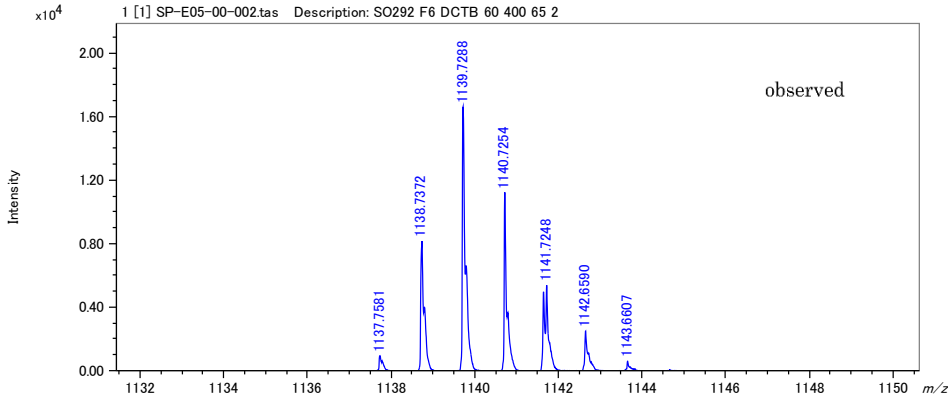
OBNUC ^{13}C
EXMOD ZGPG30
OBFRQ 100.63 MHz
OBSET 0.0 kHz
OBFIN 9999.214 Hz
POINT 32768
FREQU 24038.46 Hz
SCANS 2048
ACQTM 1.3631 s
IRNUC OFF
PROBHD 5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM SPECT
PULSPRG ZGPG30
GRDPROG
CTEMP 400.01 °C
SLVNT $CDCl_3$
BF 0.25 Hz
RGAIN 57

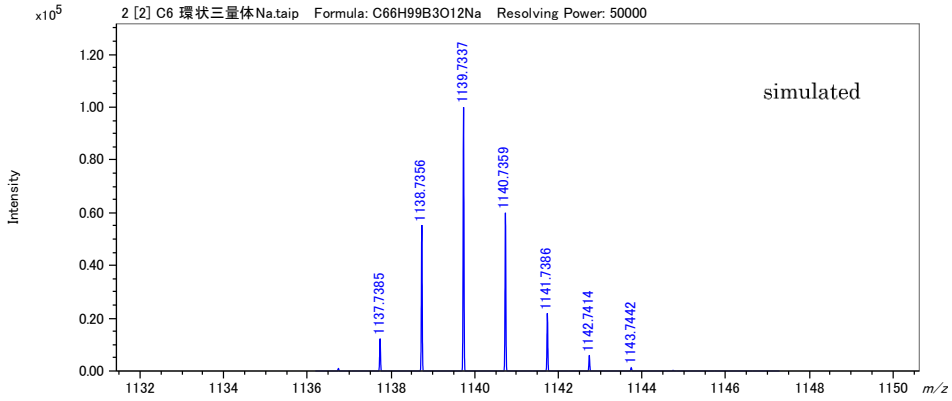
^{13}C NMR

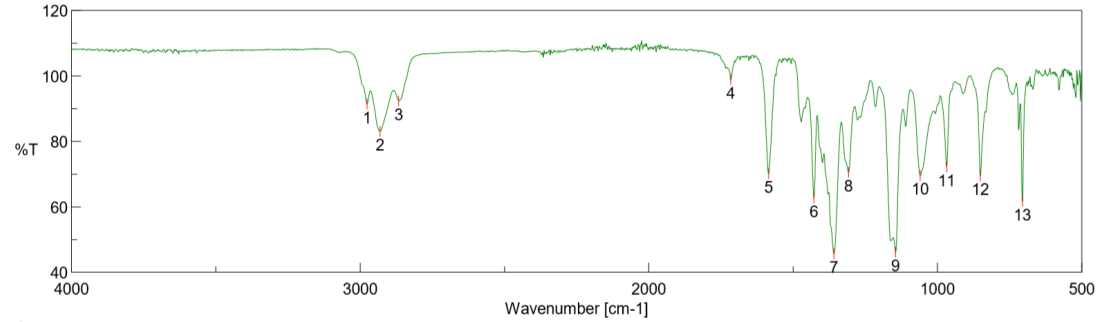



^{11}B NMR
Bpin
45
pinB
Bpin
abundance
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
29.6860
X : parts per Million : Boron11









[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2976.11	91.3758	2	2930.79	83.0276	3	2866.67	92.3136	4	1716.34	98.8583
5	1585.2	70.1169	6	1428.03	62.668	7	1358.6	45.6389	8	1308.46	70.4999
9	1145.03	46.1134	10	1059.69	69.5568	11	968.09	72.1463	12	851.418	69.4343
13	705.819	61.6279									

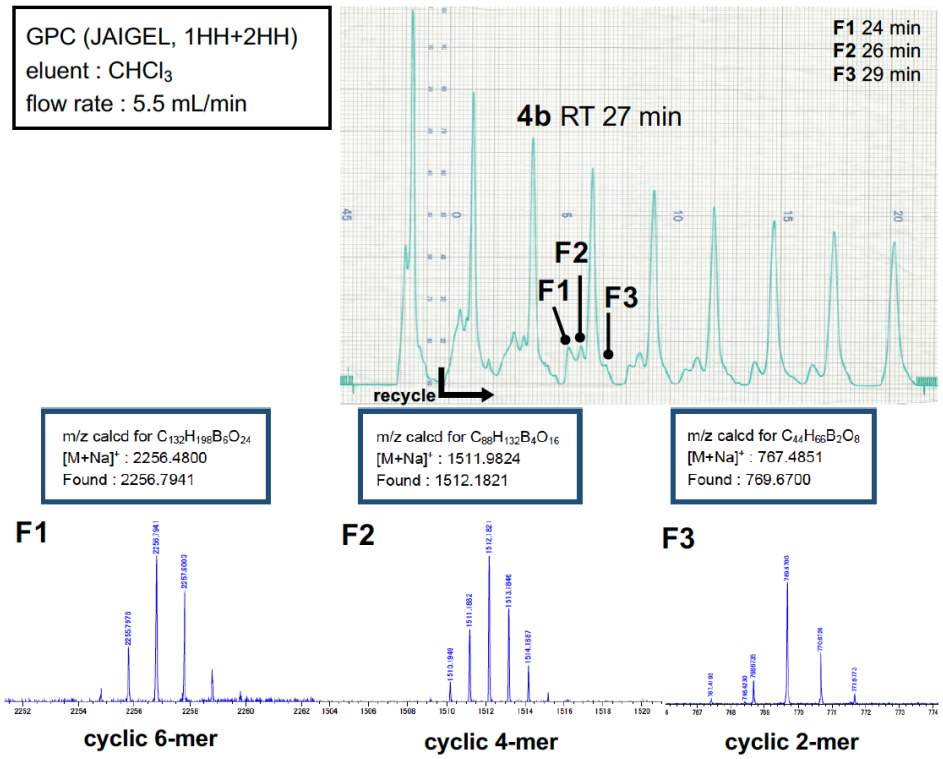


Fig. S3 GPC traces of crude **4b** and MALDI-TOF MS analysis of fractions F1, F2 and F3.

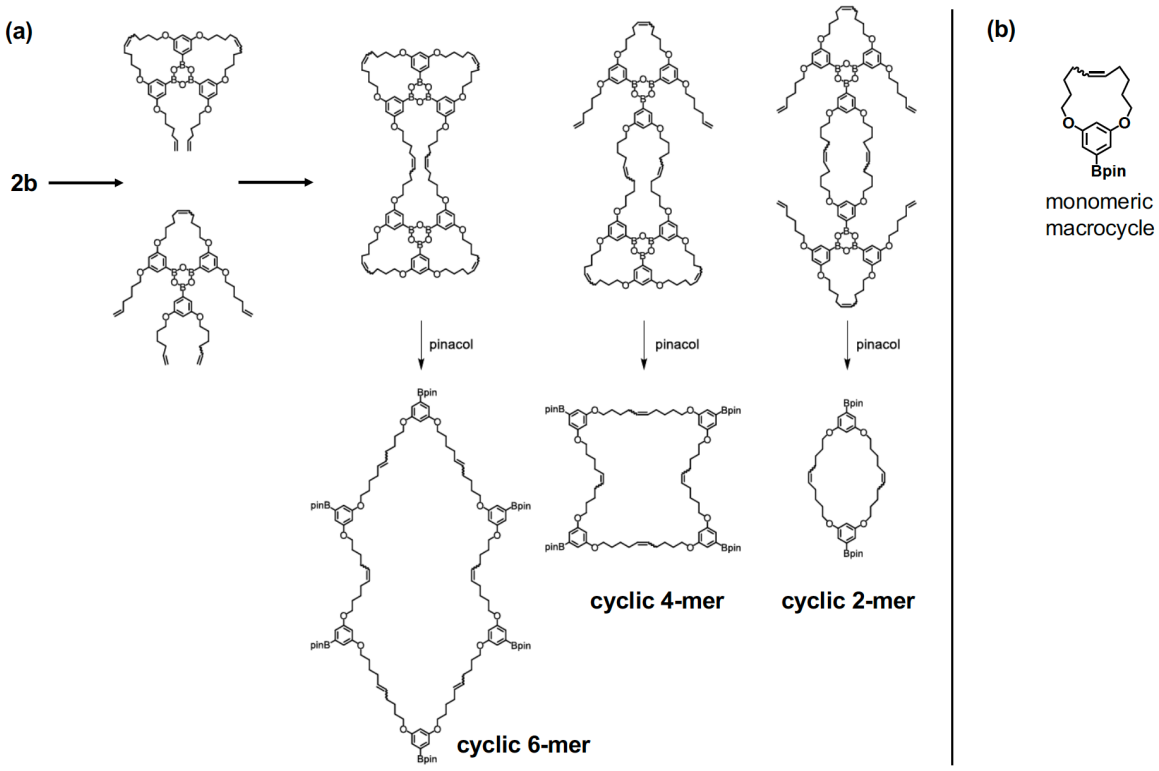


Fig. S4 (a) Chemical structures of cyclic 6-mer, cyclic 4-mer and cyclic 2-mer and their plausible formation mechanism from **2b**. (b) Chemical structure of monomeric macrocycle formed by self-cyclization of **1b**.

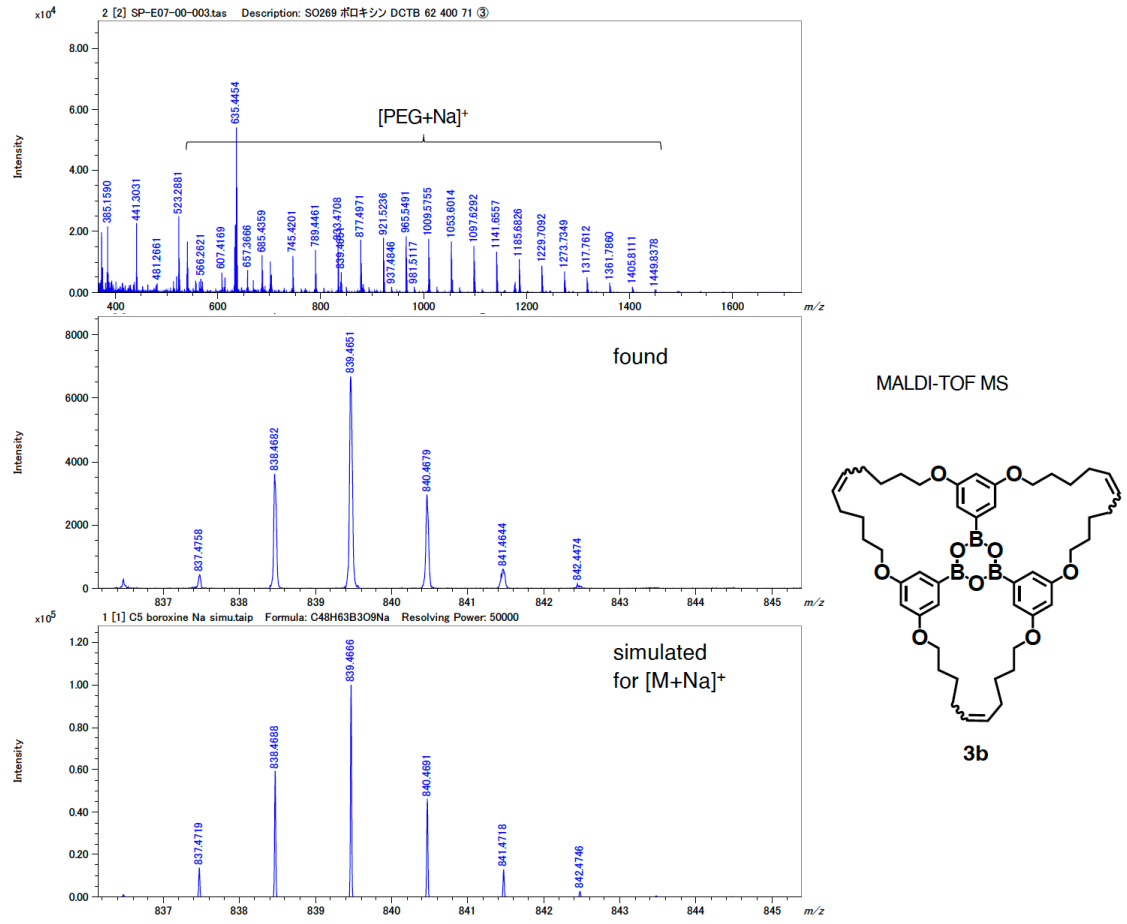
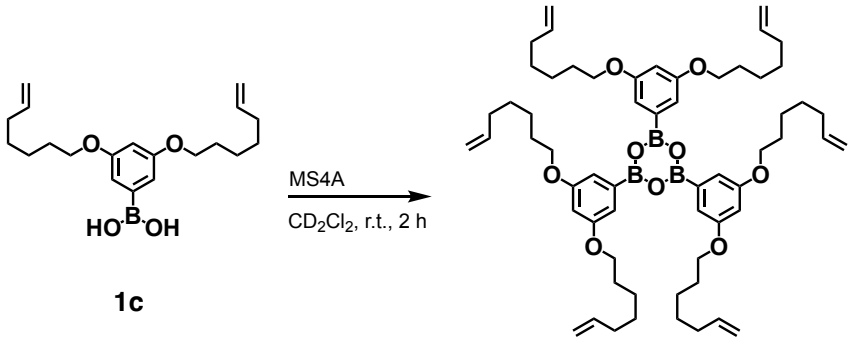


Fig. S5 MALDI-TOF MS spectra of crude **3b**

2-5. Boroxine Formation from Boronic acid **1c** to **2c**



To a $CDCl_3$ (600 µL) solution of boronic acid **1c** (2.4 mg) in an NMR tube was added MS4A. After standing at room temperature for 2 h. ^{1}H NMR spectrum of the solution revealed the quantitative formation of boroxine **2c**.

Physical data of **2c**

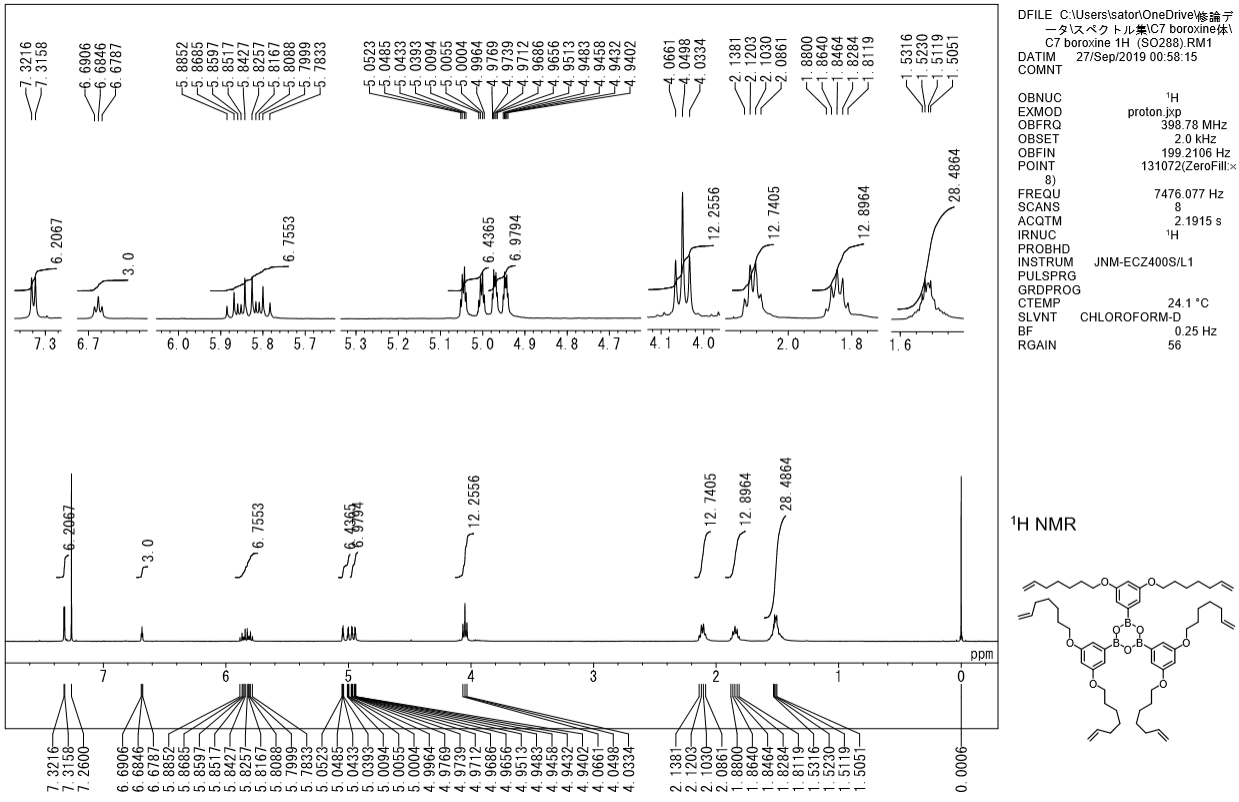
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 2.3 Hz, 6H), 6.68 (t, *J* = 2.3 Hz, 3H), 5.83 (ddt, *J* = 17.1, 10.3, 6.7 Hz, 6H), 5.05-5.00 (m, 6H), 4.98-4.94 (m, 6H), 4.05 (t, *J* = 6.5 Hz, 12H), 2.13-2.09 (m, 12H), 1.85 (quin, *J* = 6.8 Hz, 12H), 1.53-1.51 (m, 24H).

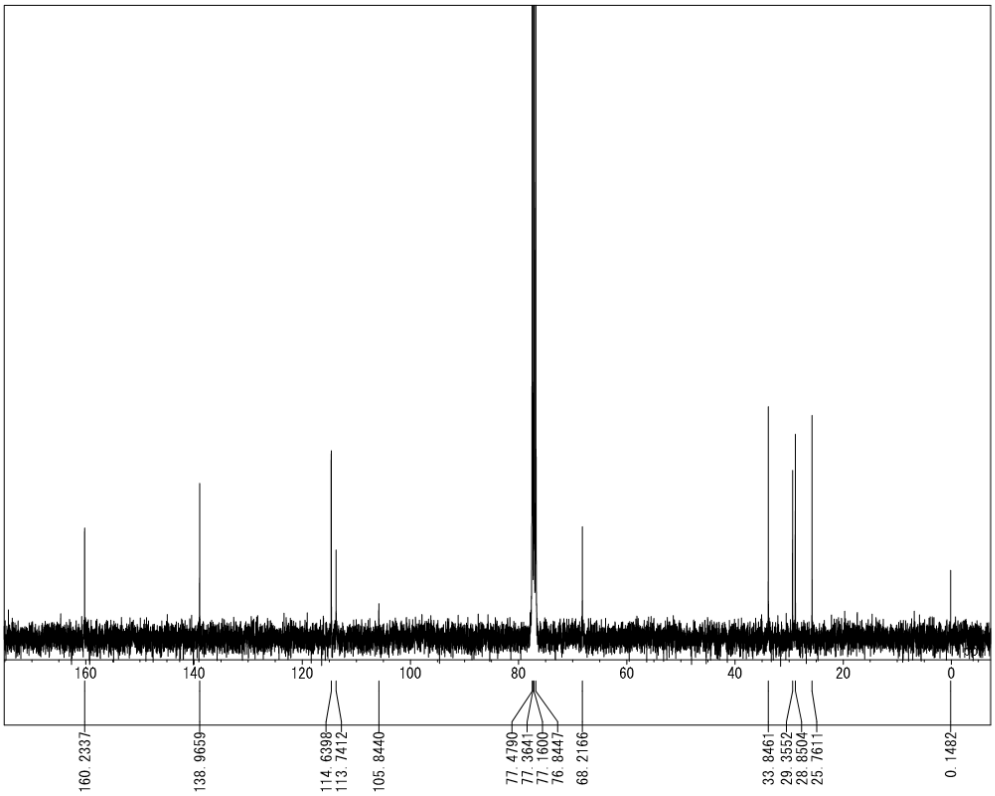
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 139.0, 114.6, 113.7, 105.8, 68.2, 33.8, 29.4, 28.9, 25.8. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 29.4

HRMS (MALDI^{+}): *m*/*z* calcd. for $C_{60}H_{87}B_3O_9Na$: 1007.6548, found: 1007.6484 $[M+Na]^{+}$.

IR (ATR): 3074, 2927, 2856, 1640, 1586, 1462, 1431, 1338, 1259, 1162, 1053, 993, 908, 844, 729, cm^{-1}.

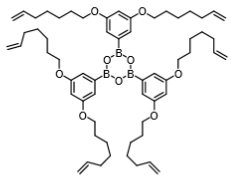


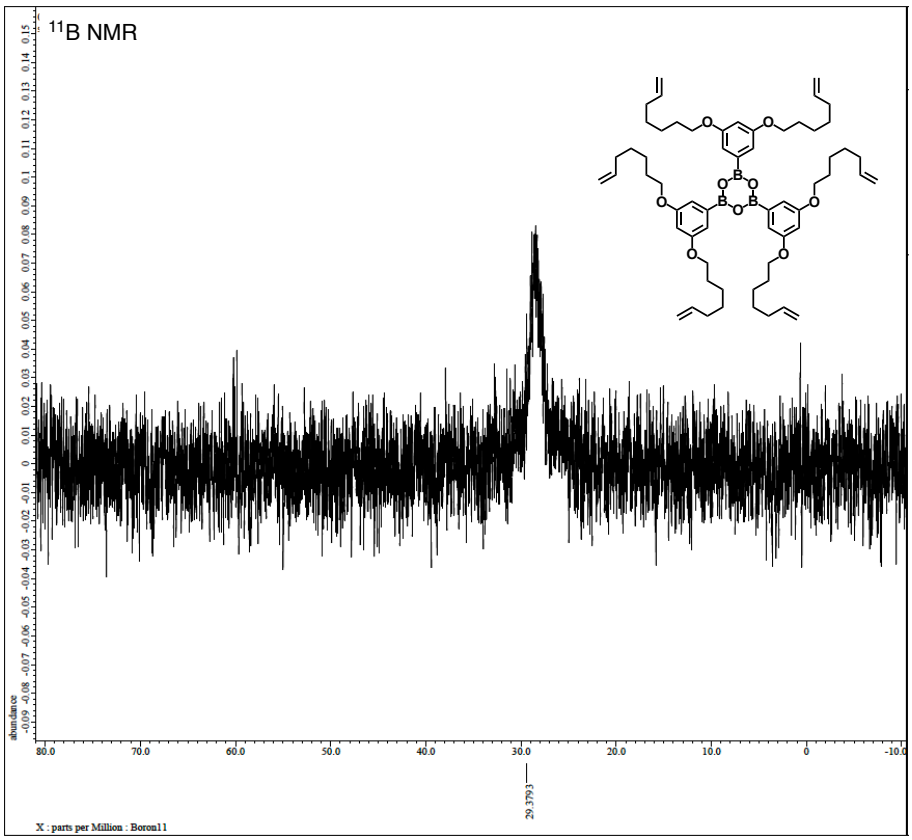


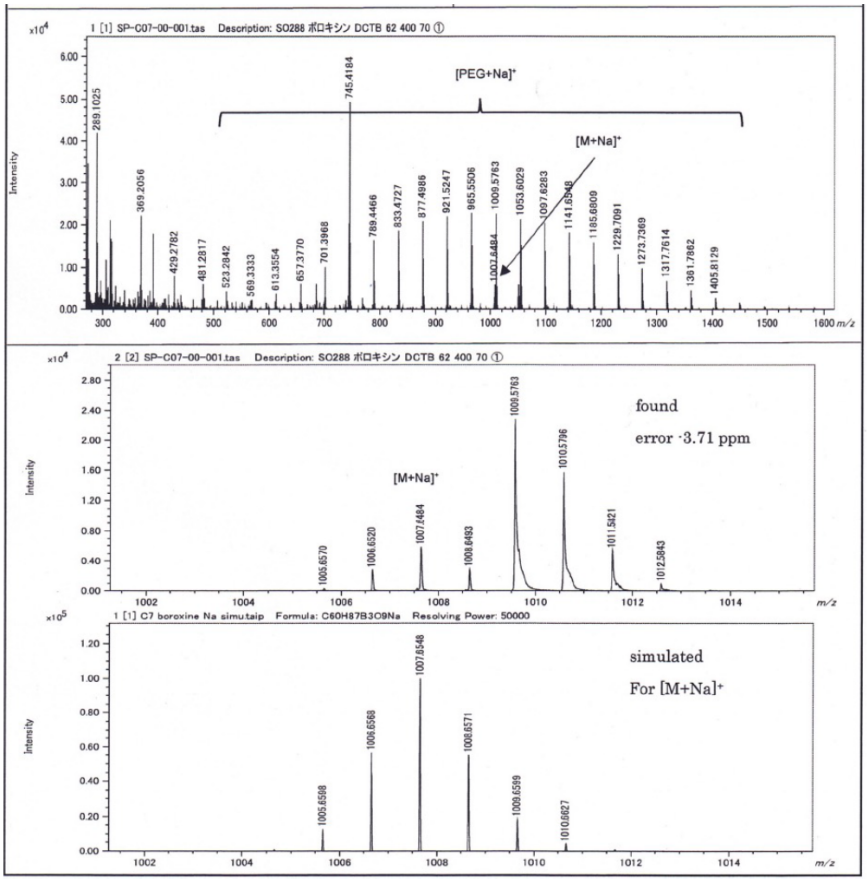
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C7 BOROXINE体\C7 BOROXINE 13C (SO 288).$RM1
DATIM 27/Sep/2019 02:09:39
COMNT

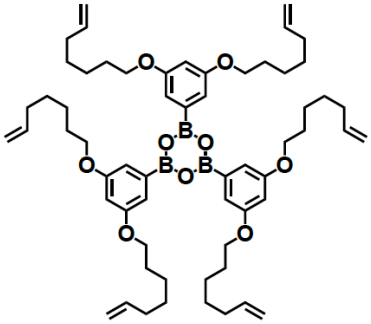
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.214 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	2048
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	25.61 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	81

^{13}C NMR

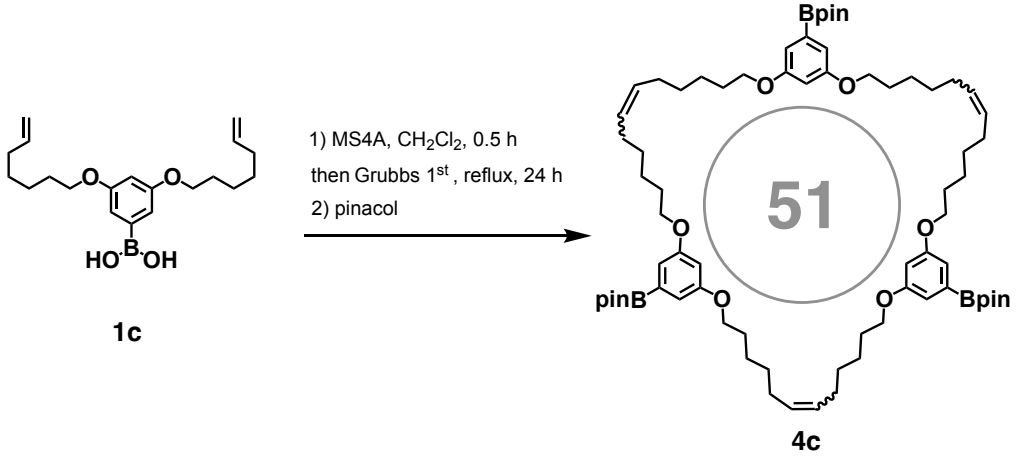








2-6. Synthesis of Macrocycle **4c**



1c

4c

Boronic acid **1c** (92.9 mg, 0.268 mmol) was dissolved in dichloromethane (340 mL) with MS4A and stirred at room temperature for 2 h. Then Grubbs 1st Generation catalyst (22.1 mg, 27.0 μmol) was added and the resulting mixture was refluxed for 40 h. Ethyl vinyl ether (400 μL) was added and the mixture was stirred at room temperature for 2 h. After MS4A was removed and solvent was evaporated to crude **3c**, the crude

was treated with 3.0 equivalent pinacol (31.7 mg, 270 μmol) in a mixture of methanol and chloroform. After solvent was evaporated, the residue was purified by GPC to afford the desired **4c** (39.2 mg, 38%).

Physical data of **4c** (mixture of *cis*/*trans* isomers)

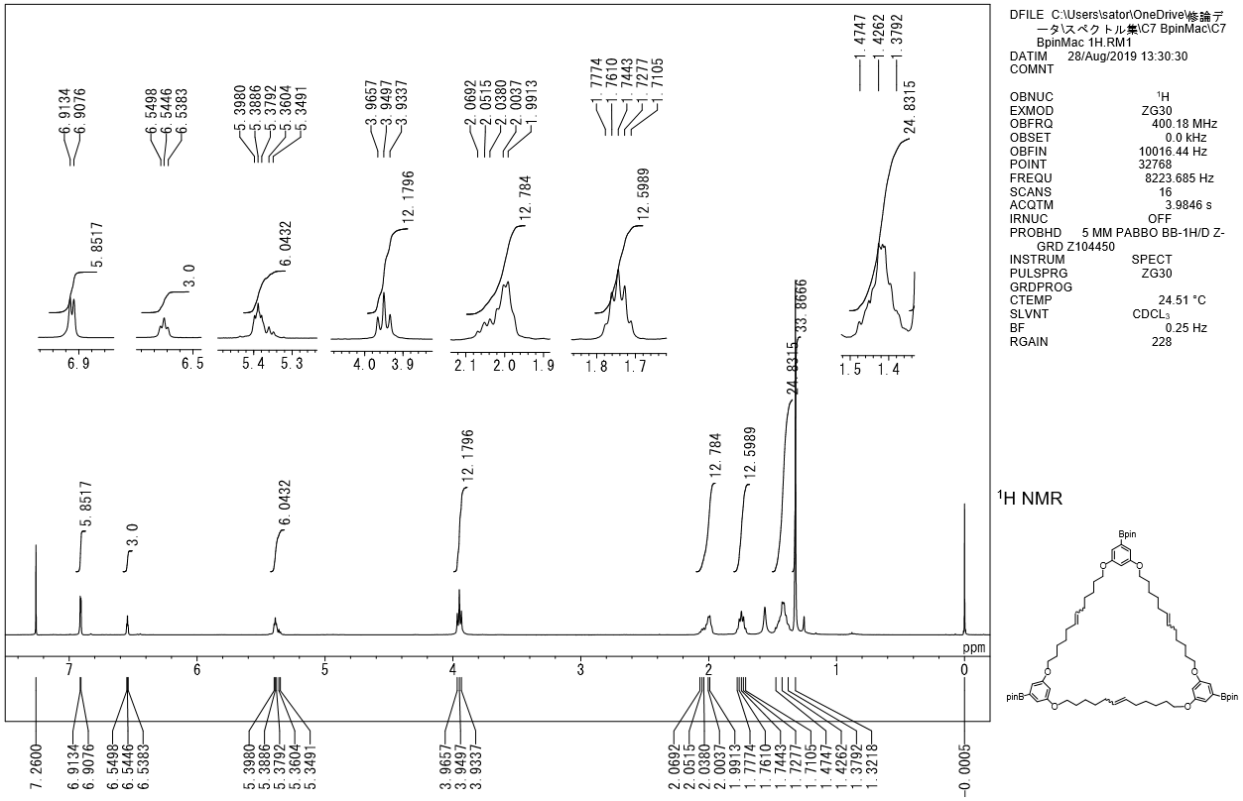
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, J = 2.3 Hz, 6H), 6.54 (t, J = 2.3 Hz, 3H), 5.40-5.35 (m, 6H), 3.95 (t, J = 6.4 Hz ,12H), 2.07-1.99 (m, 12H), 1.74 (quin, J = 6.7 Hz, 12H), 1.47-1.38 (m, 24H), 1.32 (s, 36 H).

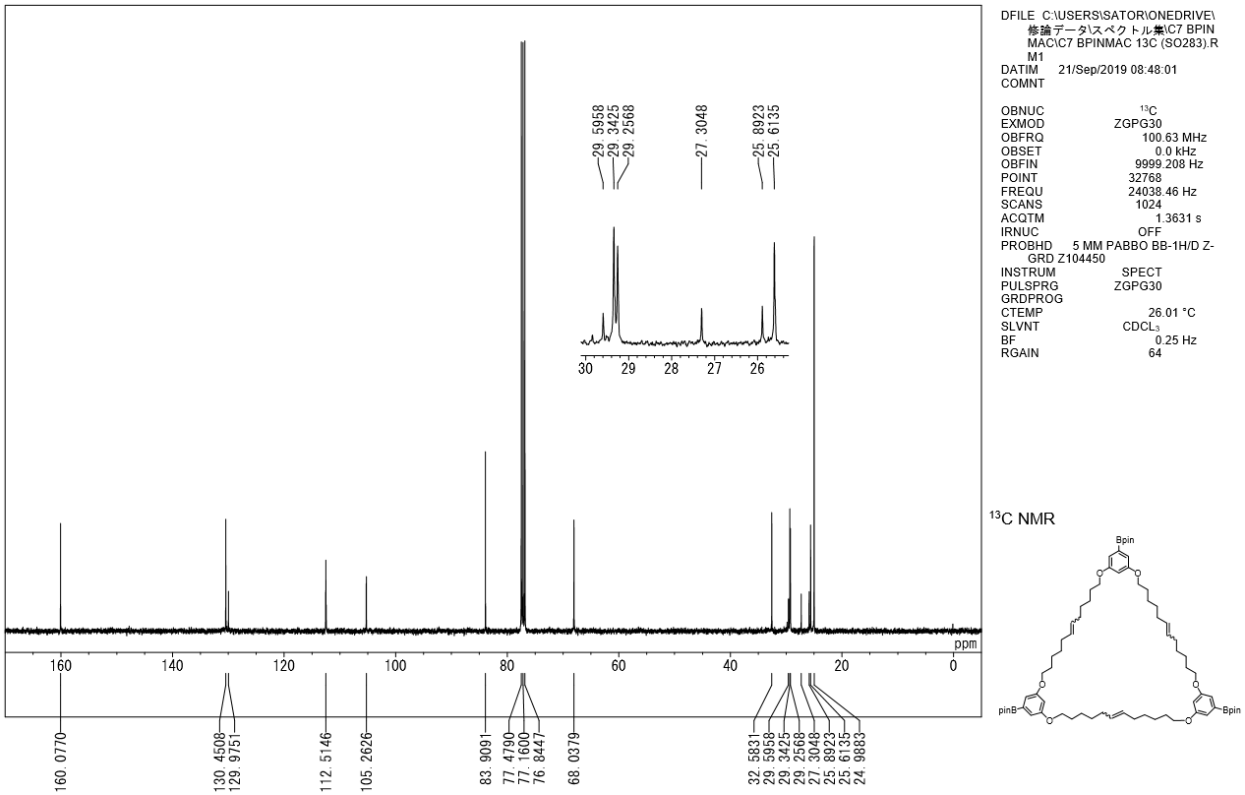
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 130.5, 130.0, 112.5, 105.3, 83.9, 68.0, 32.6, 29.6, 29.3, 29.3, 27.3, 25.9, 25.6, 25.0. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.1

HRMS (MALDI^{+}): m/z calcd. for $C_{72}H_{111}B_3O_{12}Na$: 1223.8278, found: 1223.8221 $[M+Na]^{+}$.

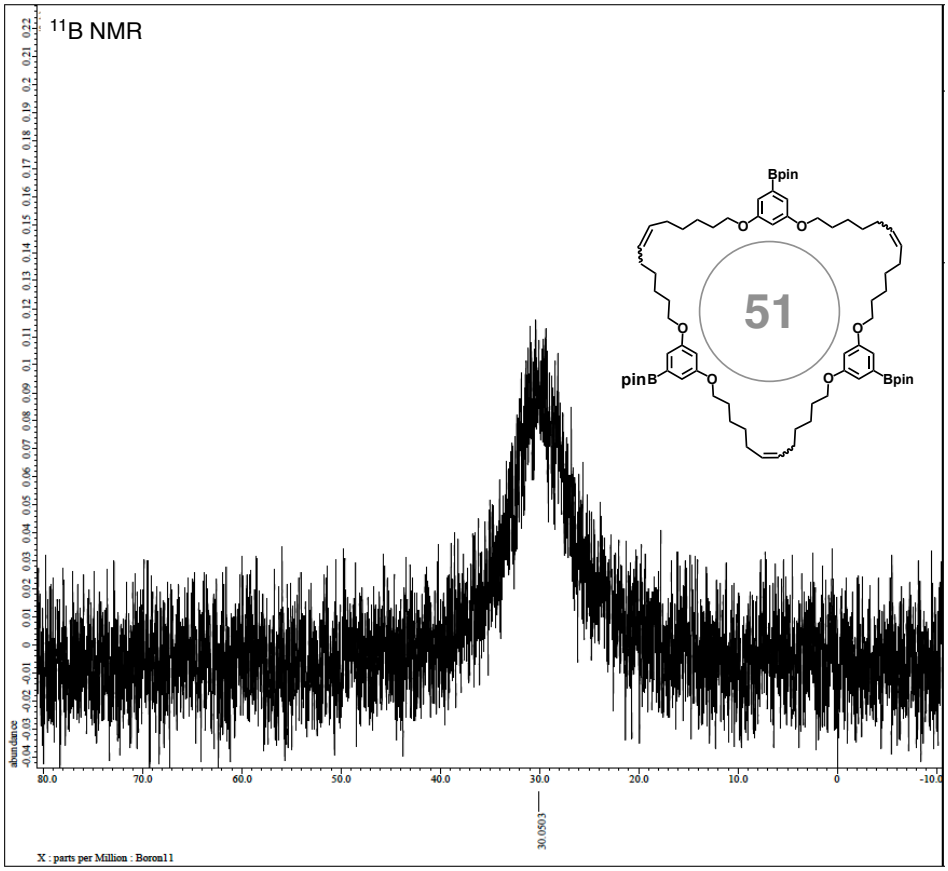
IR (ATR): 2977, 2929, 2855, 1715, 1585, 1428, 1357, 1308, 1144, 1052, 967, 851, 705 cm^{-1}.

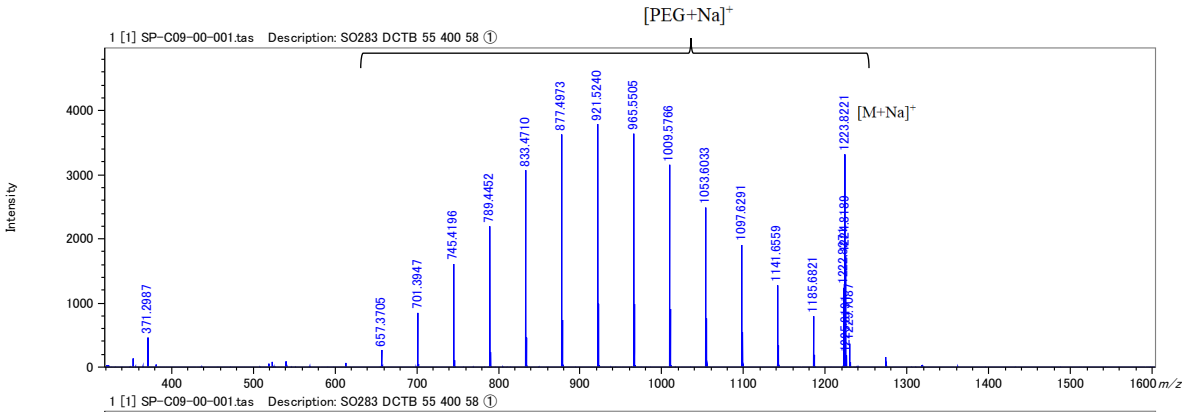


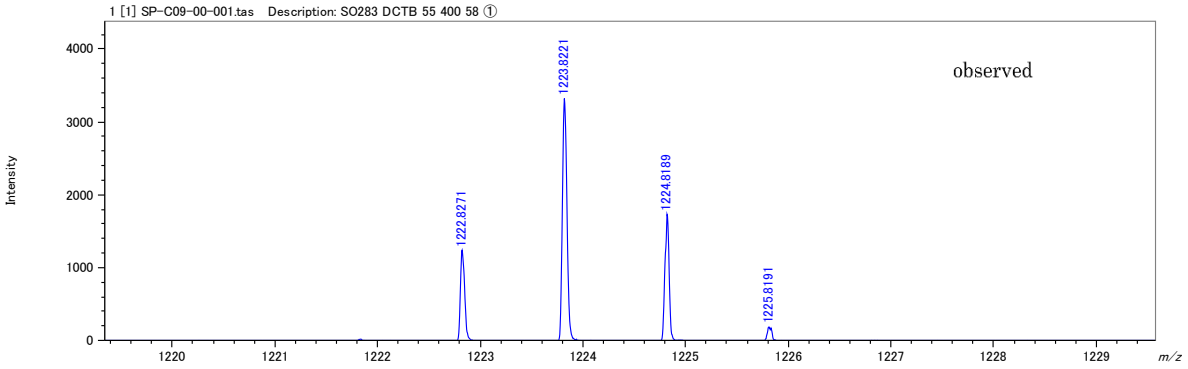

DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C7 BPIN MAC\C7 BPINMAC 13C (SO283).R M1
DATIM 21/Sep/2019 08:48:01
COMNT
OBNUC 13C
EXMOD ZGPG30
OBFRQ 100.63 MHz
OBSET 0.0 kHz
OBFIN 9999.208 Hz
POINT 32768
FREQU 24038.46 Hz
SCANS 1024
ACQTM 1.3631 s
IRNUC OFF
PROBHD 5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM SPECT
PULSPRG ZGPG30
GRDPROG
CTEMP 26.01 °C
SLVNT CDCL3
BF 0.25 Hz
RGAIN 64
29.5958
29.3425
29.2568
27.3048
25.8923
25.6135
ppm
160.0770
130.4508
129.9751
112.5146
105.2626
83.9091
77.4790
77.1600
76.8447
68.0379
32.5831
29.5958
29.3425
29.2568
27.3048
25.8923
25.6135
24.9883

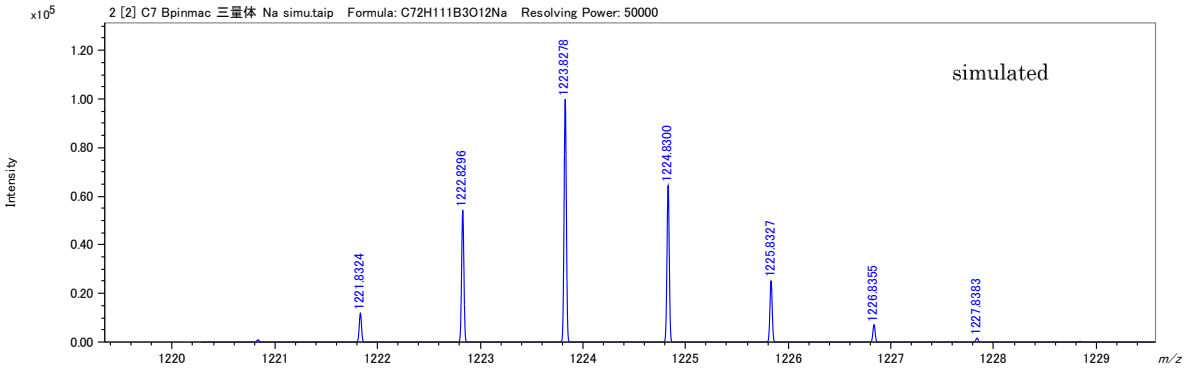
^{13}C NMR

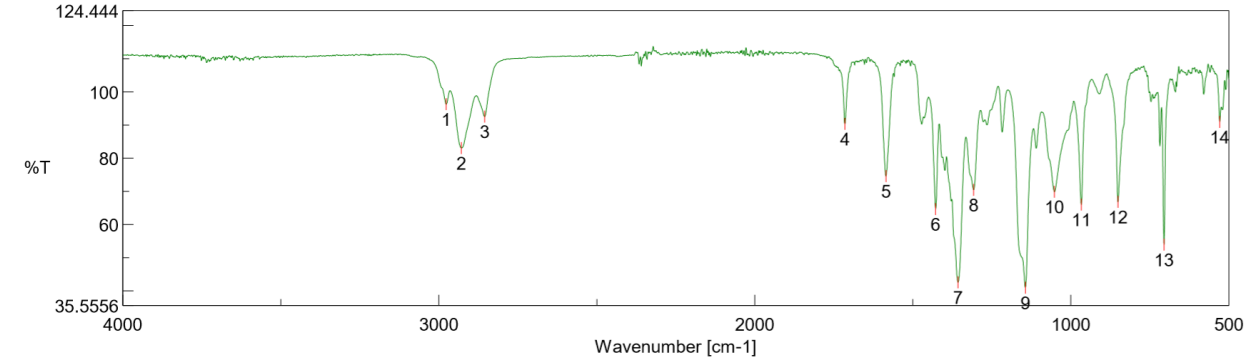
Bpin
pinB
Bpin


11B NMR
51
Bpin
pinB
Bpin
abundance
30.0503
X : parts per Million : Boron11









[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2976.59	96.2067	2	2928.86	83.0285	3	2855.1	92.4623	4	1714.89	90.2743
5	1585.2	74.5577	6	1428.03	64.6067	7	1357.16	42.5525	8	1307.5	70.3996
9	1144.06	40.9239	10	1051.98	69.8376	11	967.126	65.9684	12	850.936	66.7748
13	705.337	53.8714	14	529.364	90.8534						

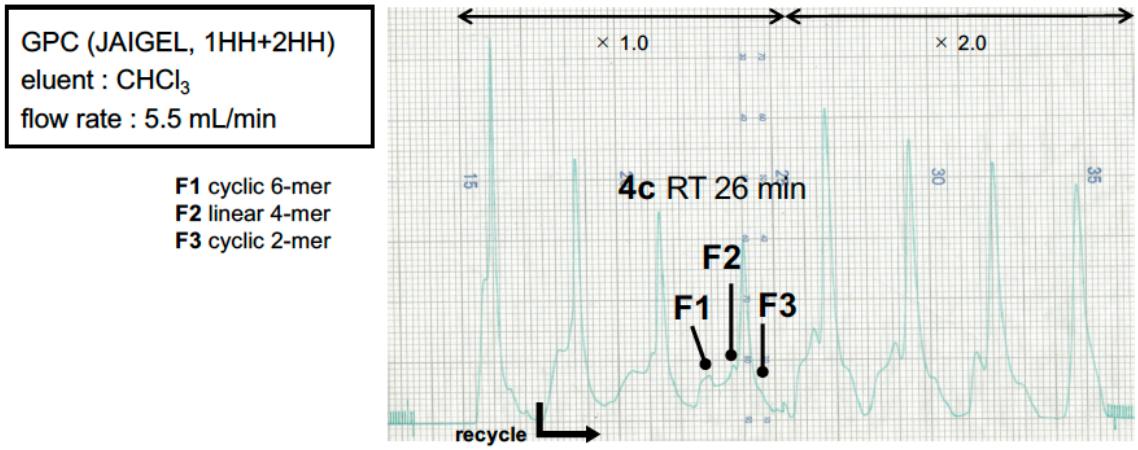
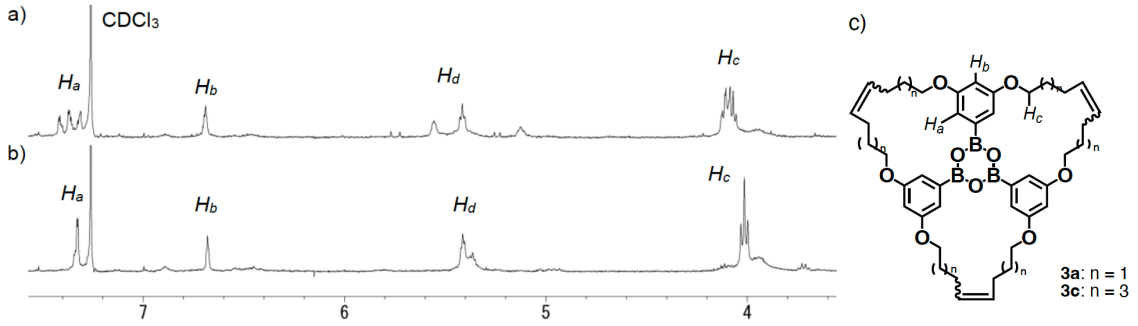


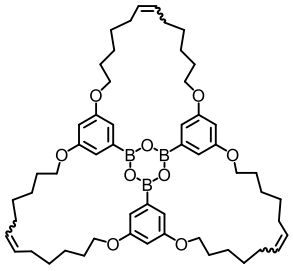
Fig. S6 GPC traces of crude **4c**.

2-7. ^{1}H NMR spectra of crude **3a** and **3c**



^{1}H NMR spectra (400 MHz, $CDCl_3$, r.t.) of a) crude **3a** and b) **3c**. c) Chemical structures of **3a** and **3c**.

2-8. Purification procedure and spectral data of **3c**



3c

In a 50 mL flask, the crude of **3c** (72 mg) was dissolved in water saturated $CHCl_3$ and stirred at room temperature for 7 h. After that, a white precipitate was obtained (14.8 mg). Diffusion of toluene to a THF solution of the precipitate gave a small amount of solid **3c** including single crystals.

Physical data of **3c** (mixture of *cis*/*trans* isomers)

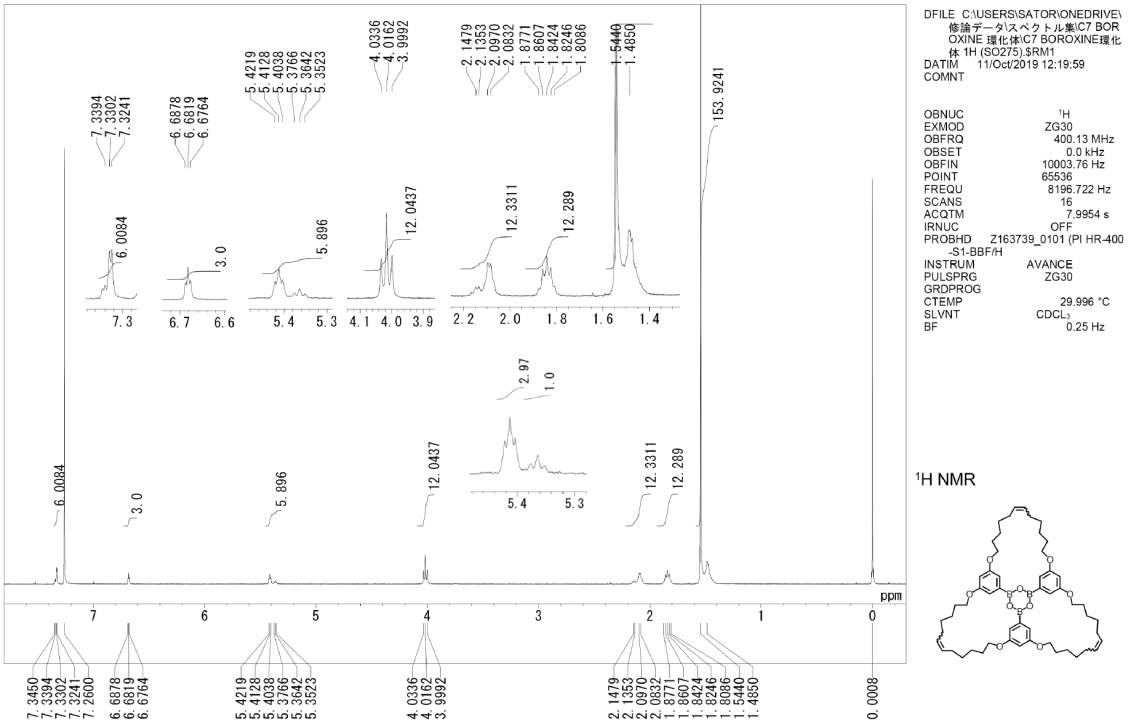
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.33 (m, 6H), 6.68 (t, J = 2.3 Hz, 3H), 5.42-5.40, 5.38-5.35 (m, 6H), 4.02 (t, J = 6.9 Hz, 12H), 2.15-2.08 (m, 12H), 1.84 (quin, J = 6.9 Hz, 12H), 1.48 (m, 24H).

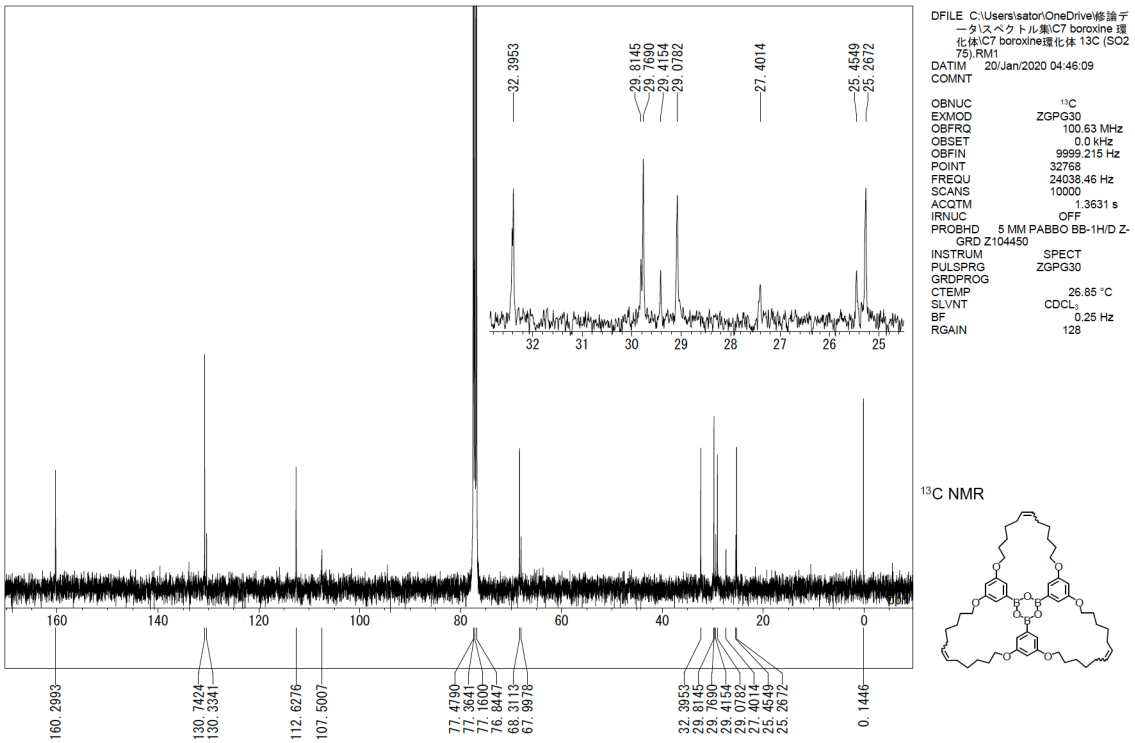
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 130.7, 130.3, 112.6, 107.5, 68.3, 68.0, 32.4, 29.8, 29.8, 29.4, 29.1, 27.4, 25.5, 25.3. The boron-bound carbons were not detected due to quadrupole relaxation.

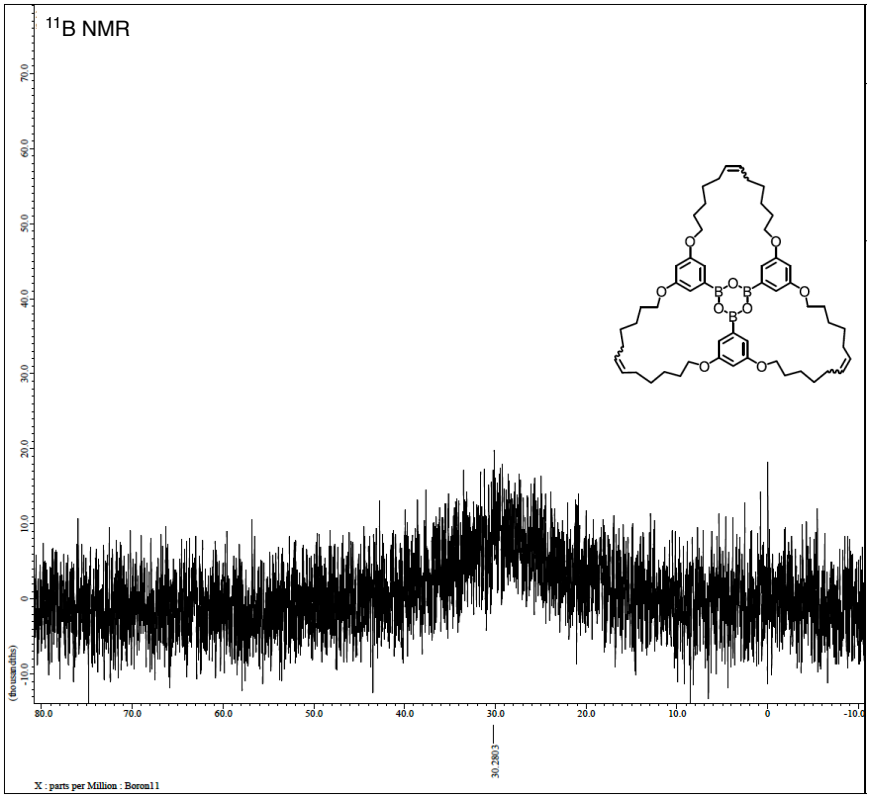
^{11}B NMR (160 MHz, $CDCl_3$): δ 30.3

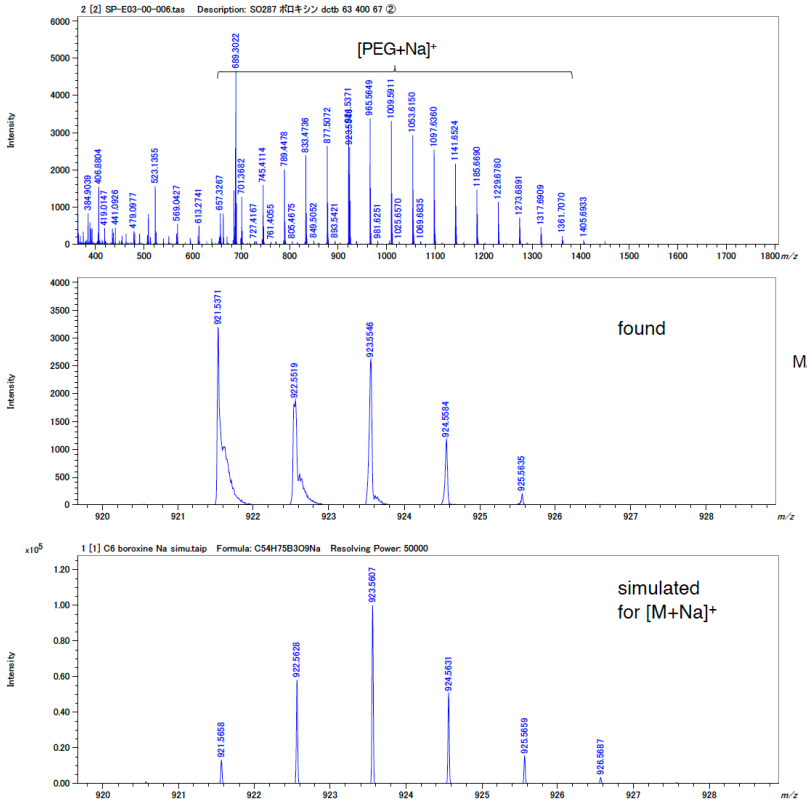
MS (MALDI$^+$): *m*/*z* calcd. for $C_{54}H_{75}B_3O_9Na$: 923.5607, found: 923.5546 $[M+Na]^+$.

IR (ATR): 2933, 2913, 2851, 1594, 1428, 1322, 1257, 1159, 1059, 963, 846, 736, 670, 582.

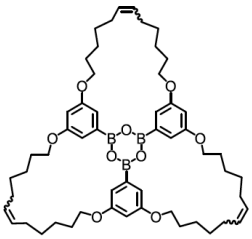



32.3953
29.8145
29.7690
29.4154
29.0782
27.4014
25.4549
25.2672
160.2993
130.7424
130.3341
112.6276
107.5007
77.4790
77.3841
77.1600
76.8447
68.3113
67.9978
32.3953
29.8145
29.7690
29.4154
29.0782
27.4014
25.4549
25.2672
0.1446
DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C7 boroxine 環化体\C7 boroxine環化体 13C (SO2 75).RM1
DATIM 20/Jan/2020 04:46:09
COMNT
OBNUC 13C
EXMOD ZGPG30
OBFRQ 100.63 MHz
OBSET 0.0 kHz
OBFIN 9999.215 Hz
POINT 32768
FREQU 24038.46 Hz
SCANS 10000
ACQTM 1.3631 s
IRNUC OFF
PROBHD 5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM SPECT
PULSPRG ZGPG30
GRDPROG
CTEMP 26.85 °C
SLVNT CDCl3
BF 0.25 Hz
RGAIN 128
13C NMR

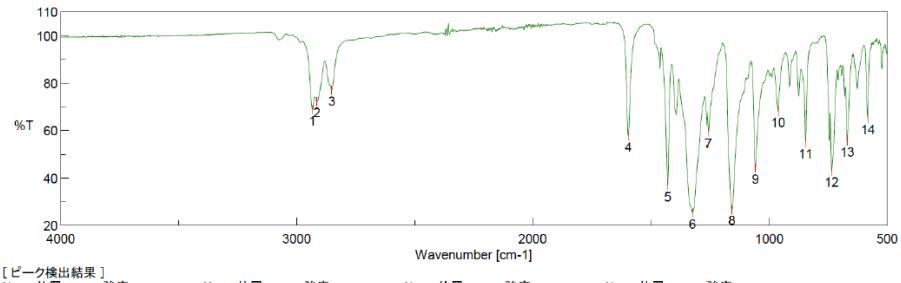

11B NMR
30.2803
X : parts per Million : Boron11



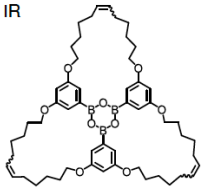
MALDI-TOF MS



3c



IR



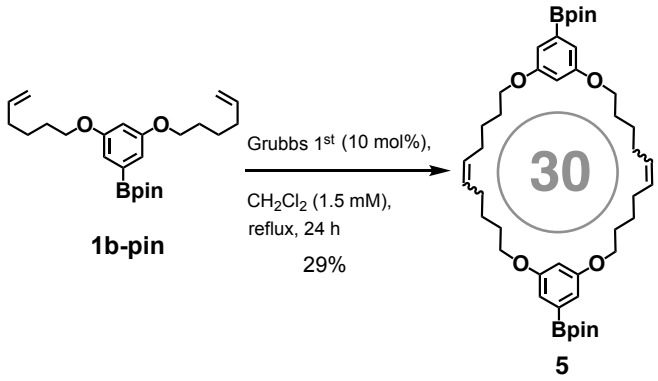
3c

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2932.72	68.737	2	2913.43	72.074	3	2850.76	76.9041	4	1594.36	57.5267
5	1427.55	36.7389	6	1321.96	25.294	7	1257.36	59.3392	8	1159.01	26.726
9	1058.73	44.1204	10	982.787	67.9512	11	846.115	54.852	12	735.71	42.7695
13	669.66	55.4771	14	582.397	64.9391						

3. Control experiments

3-1. Olefin metathesis of boronic ester **1b-pin**



Boronic ester **1b-pin** (5.65 mg, 14 μmol) was dissolved in dichloromethane (9.0 mL) and allowed to react with Grubbs 1st Generation catalyst (1.15 mg, 1.4 μmol). The resulting mixture was refluxed for 24 h. Ethyl vinyl ether (50 μL) was added and the mixture was stirred at room temperature for 2 h. After solvent was evaporated, the residue was purified by GPC to give **5** (3.02 mg, 58%).

Physical data of **5** (mixture of *cis*/*trans* isomers)

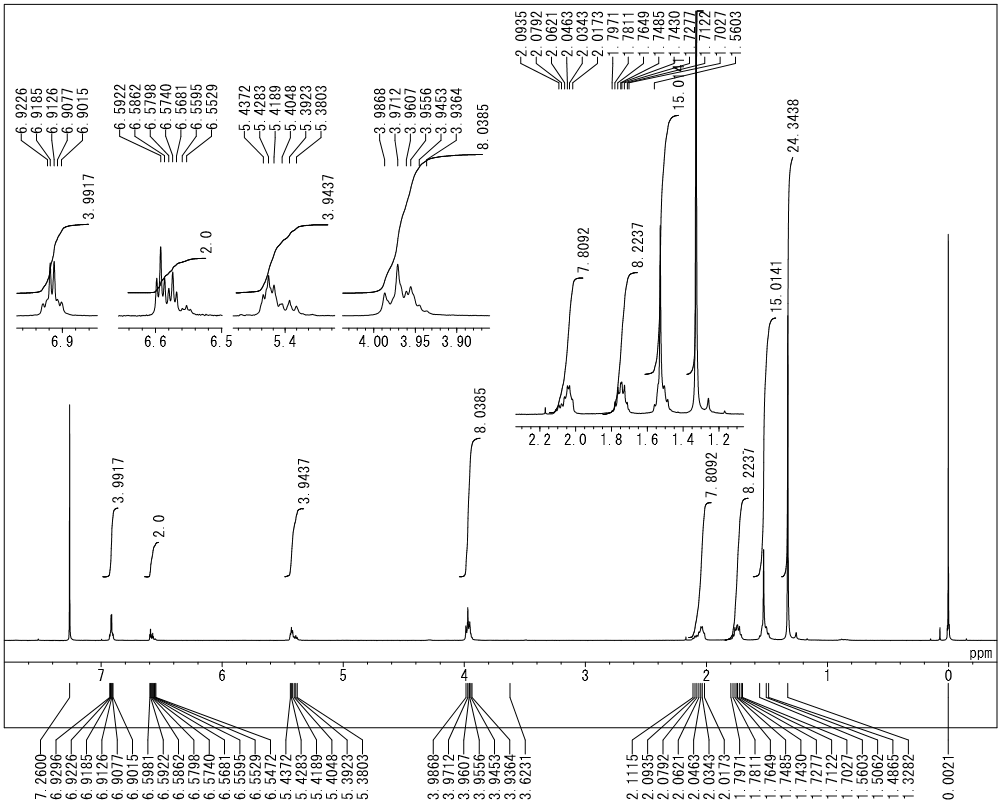
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92-6.90 (m, 4H), 6.60-6.55 (m, 2H), 5.43-5.38 (m, 4H), 3.99-3.94 (m, 8H), 2.11-2.02 (m, 8H), 1.79-1.70 (m, 8H), 1.56-1.49 (m, 8H), 1.33 (s, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 130.5, 130.5, 130.0, 130.0, 112.9, 112.2, 112.0, 105.7, 105.4, 83.9, 67.9, 32.2, 32.2, 29.0, 28.8, 28.7, 27.0, 26.3, 26.2, 26.0, 25.0. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 29.5

HRMS (MALDI^{+}): *m*/*z* calcd. for $C_{44}H_{66}B_2O_8Na$: 767.4851, found: 767.4839 $[M+Na]^{+}$.

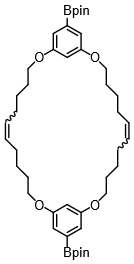
IR (ATR): 2927, 2855, 1727, 1587, 1429, 1361, 1308, 1277, 1164, 1146, 1061, 969, 851, 706, cm^{-1}.

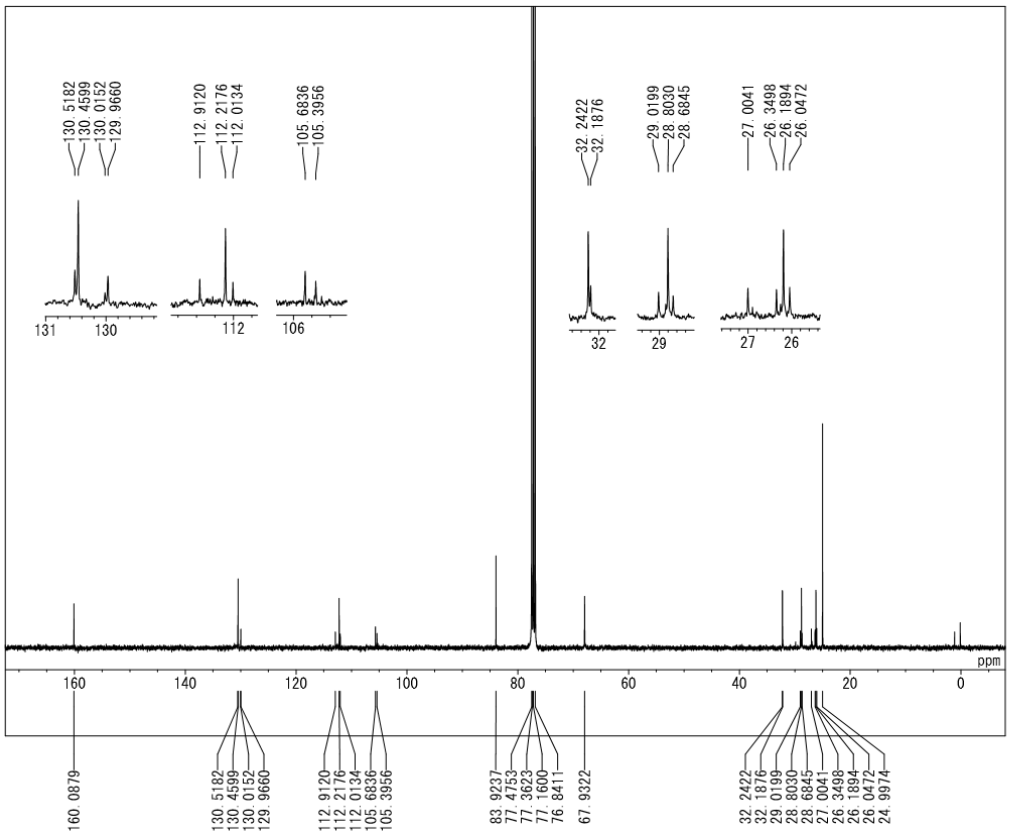


DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 BPIN環状二量体\C6 BPIN環状二量体 1H (SO335).RM1
DATIM 27/Dec/2019 16:55:00
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.13 MHz
OBSET	0.0 kHz
OBFIN	10003.76 Hz
POINT	65536
FREQU	8196.722 Hz
SCANS	16
ACQTM	7.9954 s
IRNUC	OFF
PROBHD	Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM	AVANCE
PULSPRG	ZG30
GRDPROG	
CTEMP	29.989 °C
SLVNT	$CDCl_3$
BF	0.25 Hz

^{1}H NMR

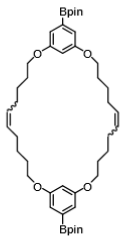


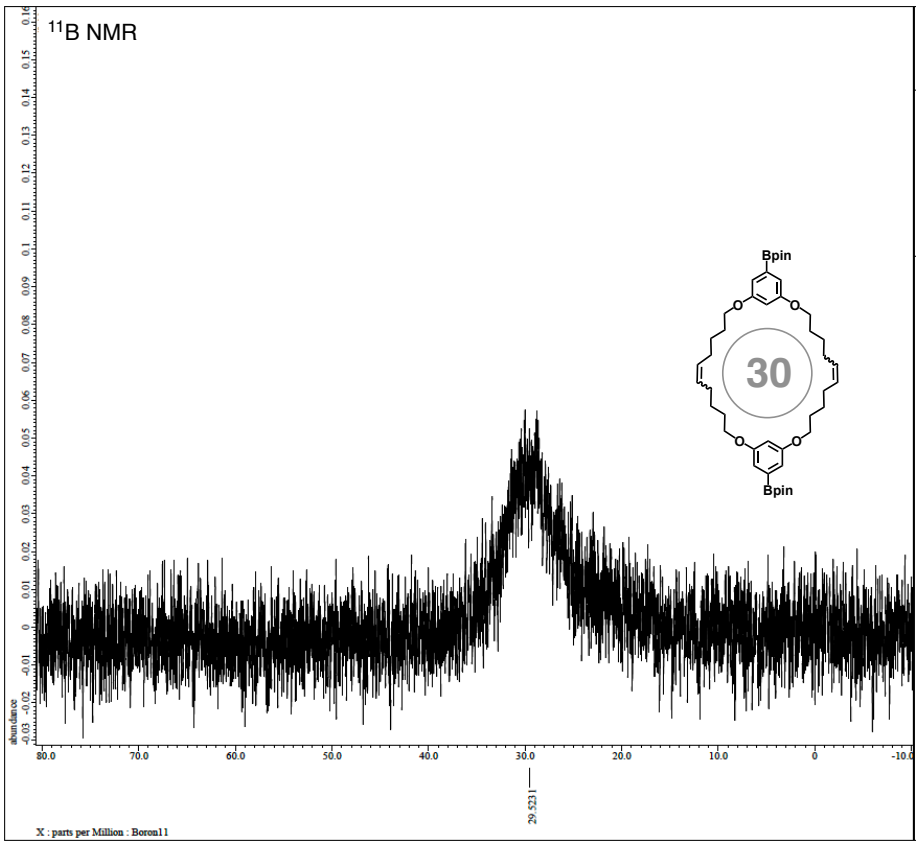


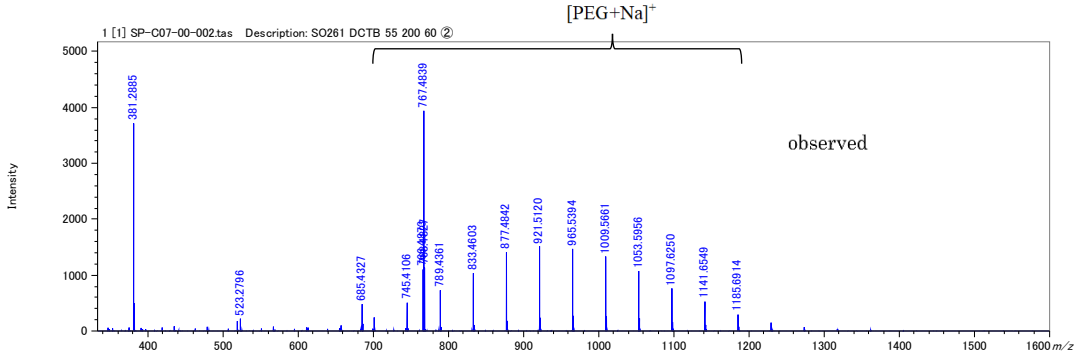
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 BPIN環状二量体\C6 BPIN環状二量体 13C (335).RM1
DATIM 13/Jan/2020 09:40:36
COMNT

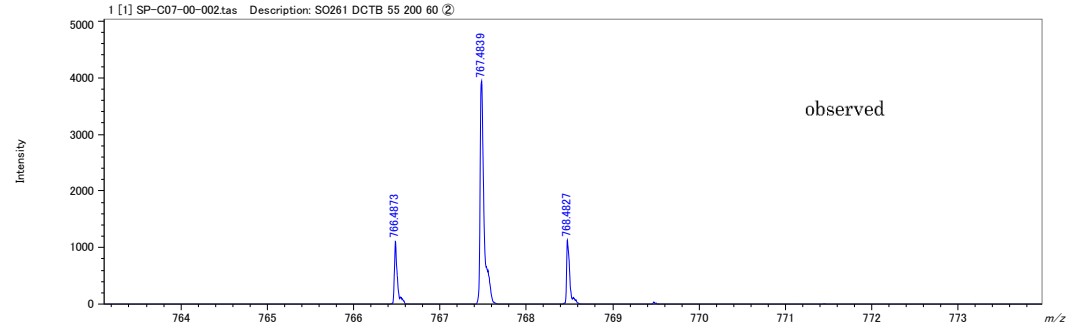
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.209 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	8192
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	72

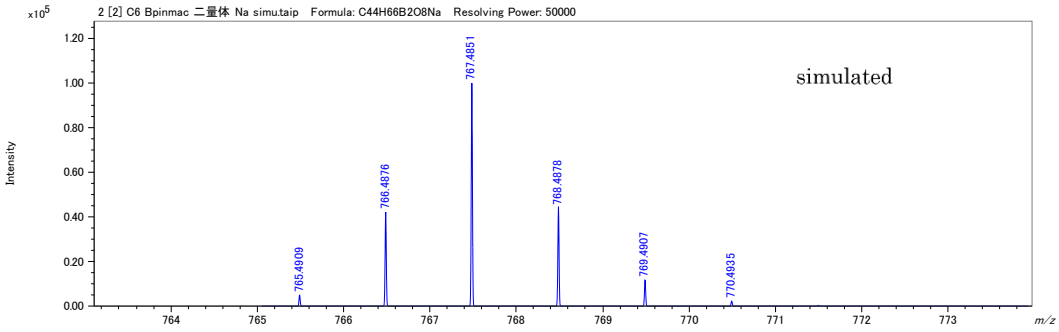
^{13}C NMR

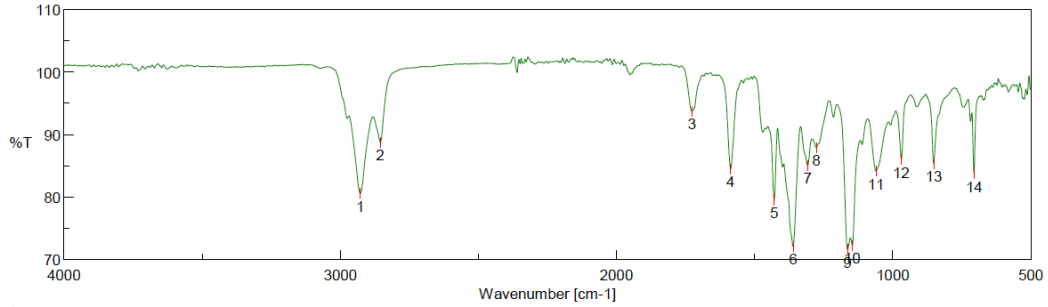



11B NMR
Bpin
30
Bpin
29.5231
X : parts per Million : Boron11


[PEG+Na]+
1 [1] SP-C07-00-002.tas Description: SO261 DCTB 55 200 60 ②
observed
Intensity
381.2885
523.2796
685.4327
745.4106
767.4839
789.4361
833.4603
877.4842
921.5120
965.5394
1009.5661
1053.5956
1097.6250
1141.6549
1185.6914
m/z


1 [1] SP-C07-00-002.tas Description: SO261 DCTB 55 200 60 ②
observed
Intensity
766.4873
767.4839
768.4827
m/z





[データ情報]

作成日時	2020/02/20 13:32
データタイプ	等間隔データ
横軸	Wavenumber [cm-1]
縦軸	%T
スタート	499.473 cm-1
エンド	4000.6 cm-1
データ間隔	0.964233 cm-1
データ数	3632

[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2927.41	80.5796	2	2855.1	88.7321	3	1726.94	93.765	4	1587.13	84.4521
5	1428.99	79.5234	6	1360.53	72.0969	7	1308.46	85.0571	8	1276.65	87.9349
9	1163.83	71.5782	10	1146.47	72.2464	11	1060.66	84.1537	12	969.055	86.007
13	851.418	85.3279	14	705.819	83.7107						

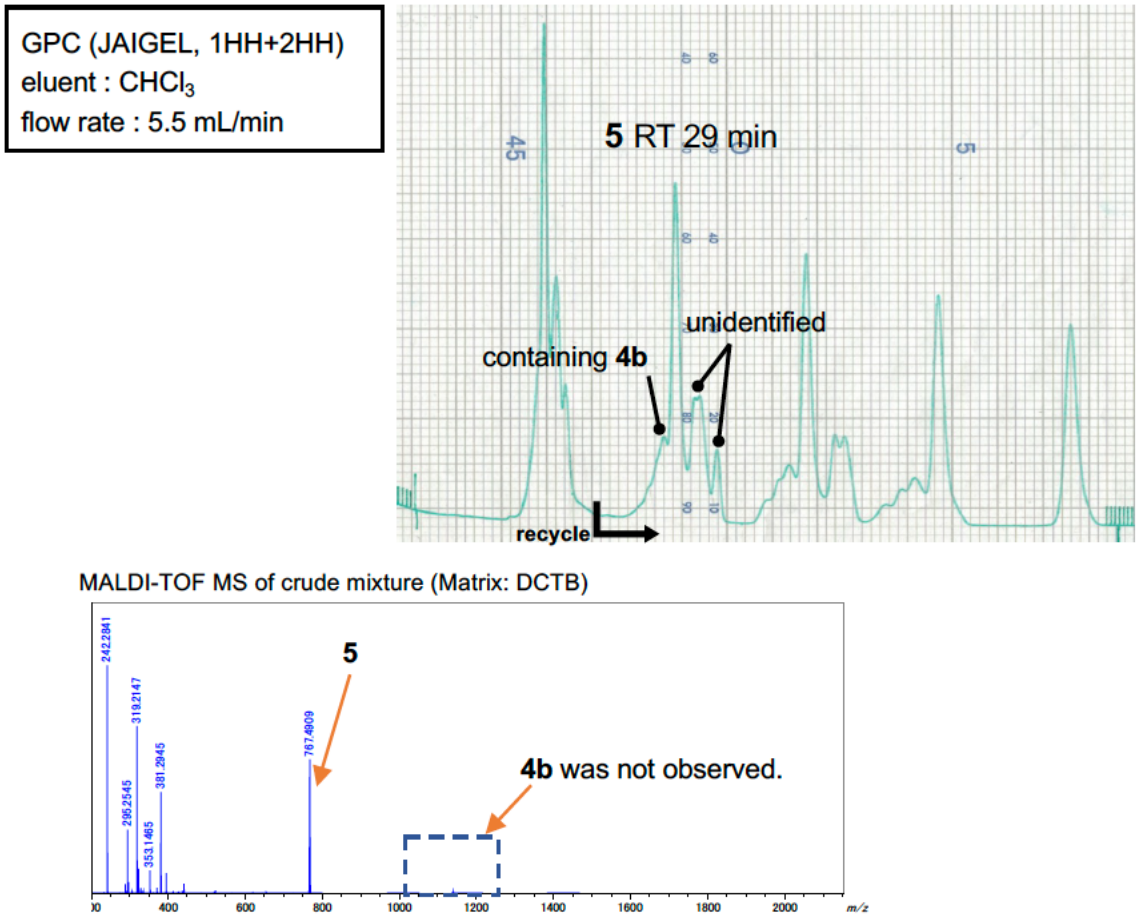
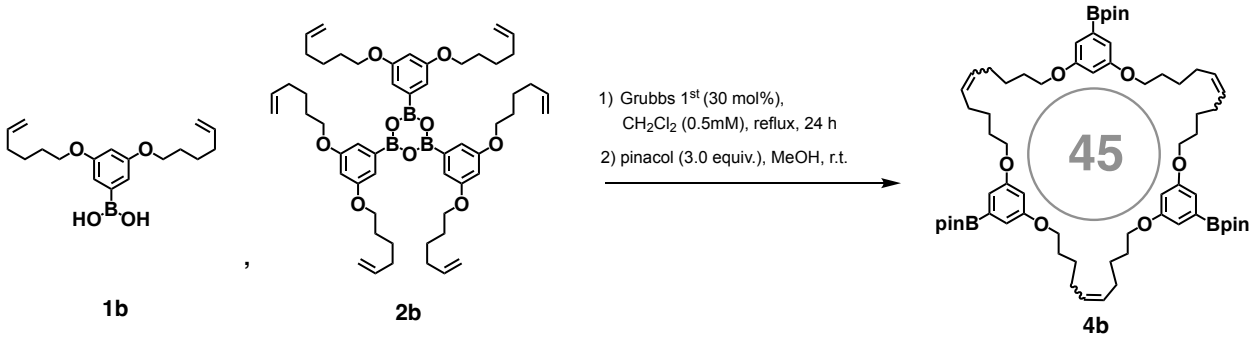


Fig. S7 GPC traces of crude **5** and MALDI-TOF MS analysis of crude mixture.

3-2. Olefin metathesis of a 1.1:1.0 mixture of **1b** and **2b**



1b , **2b** (1.1 : 1.0)

A 1.1:1.0 mixture of **1b** and **2b** (1.75 mg) was dissolved in dichloromethane (4.0 mL) and allowed to react with Grubbs 1st Generation catalyst (0.469 mg, 0.57 μmol). The resulting mixture was refluxed for 24 h. Ethyl vinyl ether (25 μL) was added and the mixture was stirred at room temperature for 2 h. After solvent was evaporated, the residue was purified by GPC to give **4b** (1.72 mg, 76%).

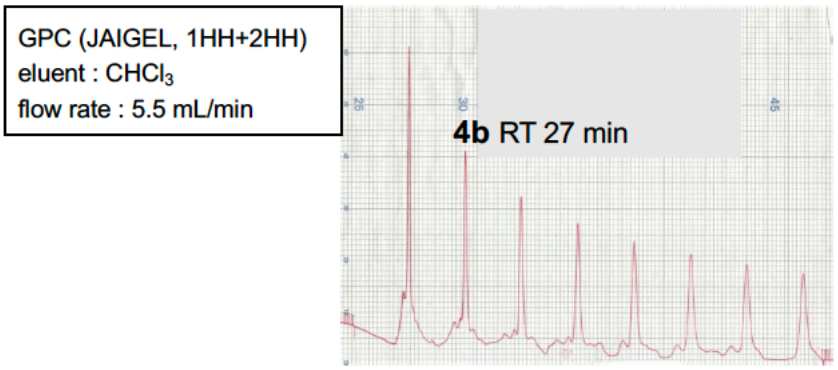
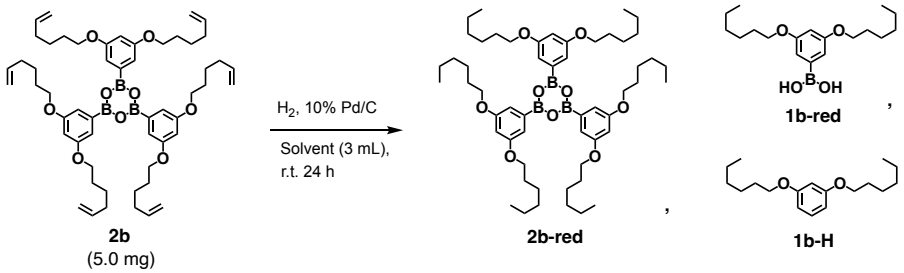


Fig. S8 GPC traces of crude **4b** prepared from a 1.1:1.0 mixture of **1b** and **2b**.

3-3. Hydrogenation of boroxine **2b**

a)



entry	solvent	1b-H
1	EtOAc	31%
2	THF	30%
3*	EtOAc	quant.

*MS4A was added.

b)

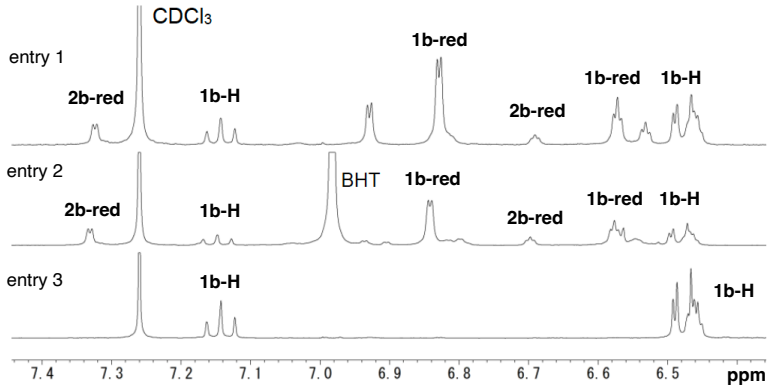
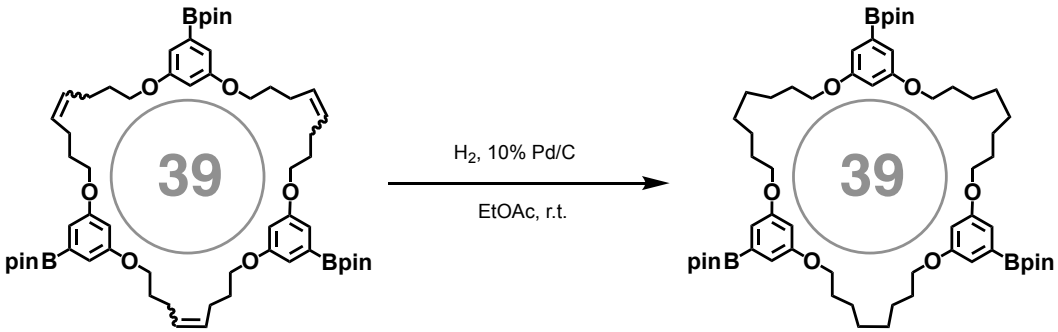


Fig. S9 a) Examination of reaction solvents of hydrogenation of **2b**. b) ^{1}H NMR spectra (400 MHz, 303 K, $CDCl_3$,) of crude of entry 1, 2, and 3.

4. Post-modification of Macrocycles

4-1. Hydrogenation of Macrocycle **4a** to **6a**



4a **6a**

Macrocycle **4a** (1.75 mg, 1.69 μmol) and palladium (10%) on charcoal were mixed in EtOAc (1.0 mL). Under hydrogen, the solution was stirred for 18 h and then filtered through Celite. The solvent was evaporated to afford the desired **6a** quantitatively.

Physical data of **6a**

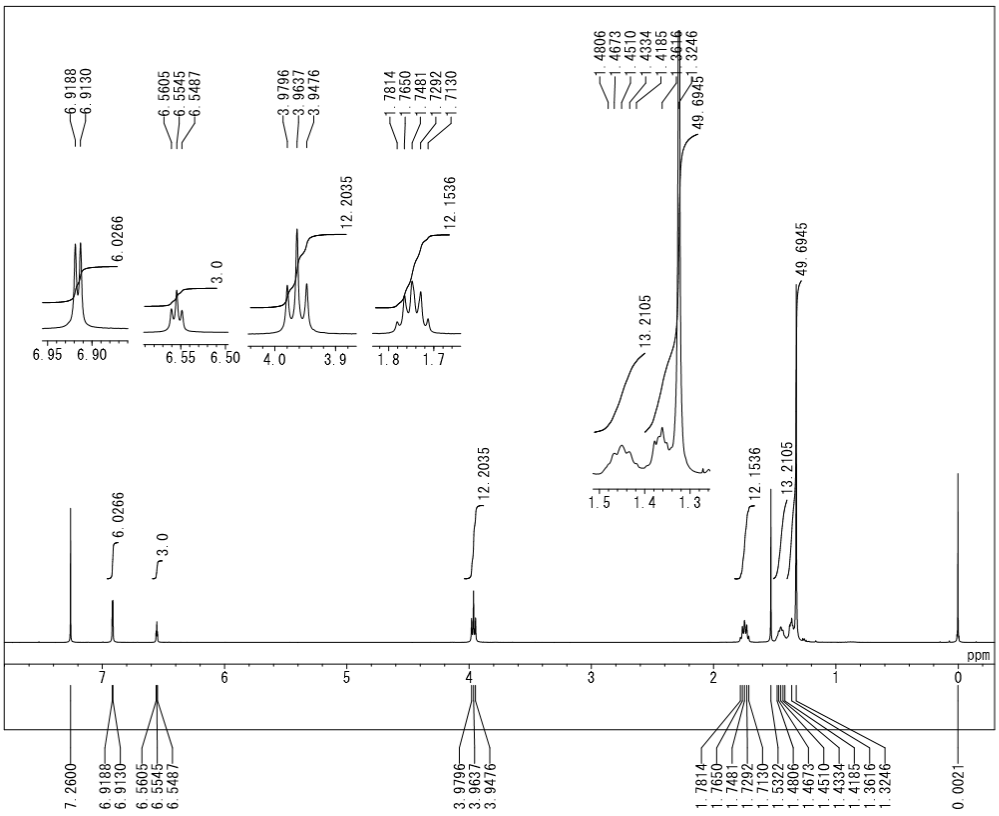
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, J = 2.3 Hz, 6H), 6.55 (t, J = 2.4 Hz, 3H), 3.96 (t, J = 6.4 Hz, 12H), 1.75 (quin, J = 6.8 Hz, 12H), 1.48-1.42 (m, 12H) 1.40-1.36 (m, 12H), 1.32 (s, 36H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 112.6, 105.3, 83.9, 68.0, 29.4, 29.3, 26.0, 25.0. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.2

HRMS (MALDI^{+}): m/z calcd. for $C_{60}H_{93}B_3O_{12}Na$: 1061.6865, found: 1061.6793 $[M+Na]^{+}$.

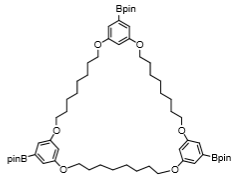
IR (ATR): 2926, 2855, 1715, 1586, 1466, 1429, 1360, 1308, 1263, 1146, 1050, 968, 851, 819, 706 cm^{-1}.

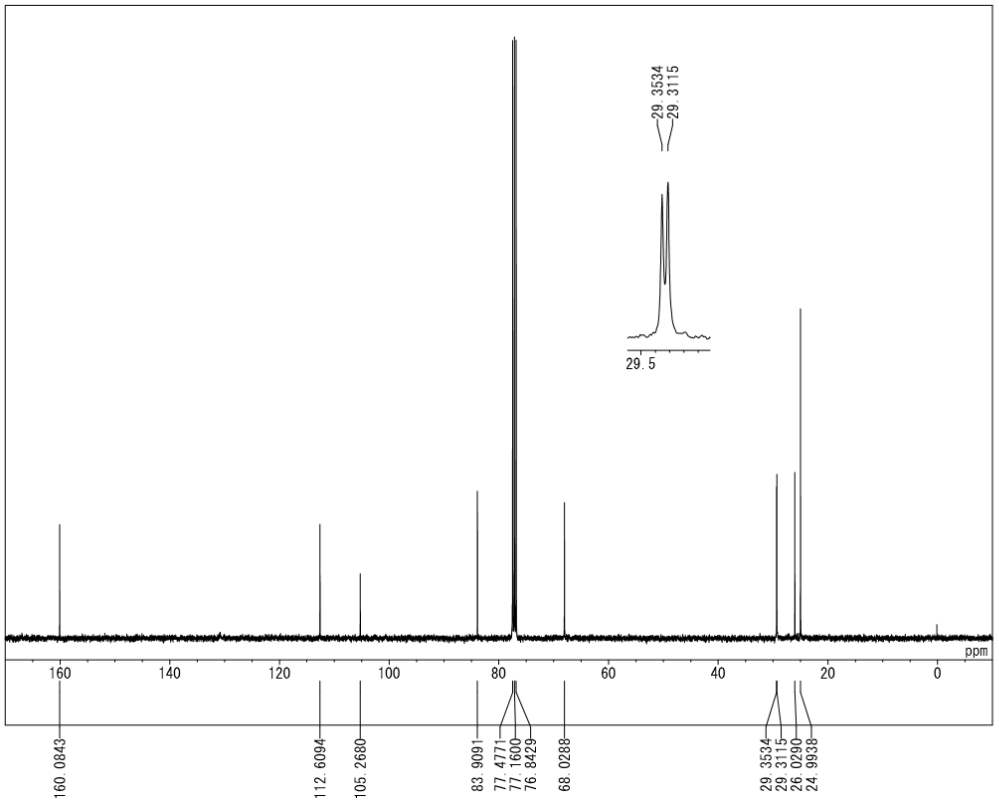


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C5 BpinMac 還元体\C5 BpinMac 還元体 1H (SO352).RM1
DATIM 26/Jan/2020 18:00:09
COMNT

OBNUC ^{1}H
EXMOD ZG30
OBFRQ 400.13 MHz
OBSET 0.0 kHz
OBFIN 10003.76 Hz
POINT 65536
FREQU 8196.722 Hz
SCANS 16
ACQTM 7.9954 s
IRNUC OFF
PROBHD Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM AVANCE
PULSPRG ZG30
GRDPROG
CTEMP 29.9062 °C
SLVNT $CDCl_3$
BF 0.25 Hz

^{1}H NMR

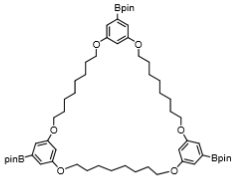


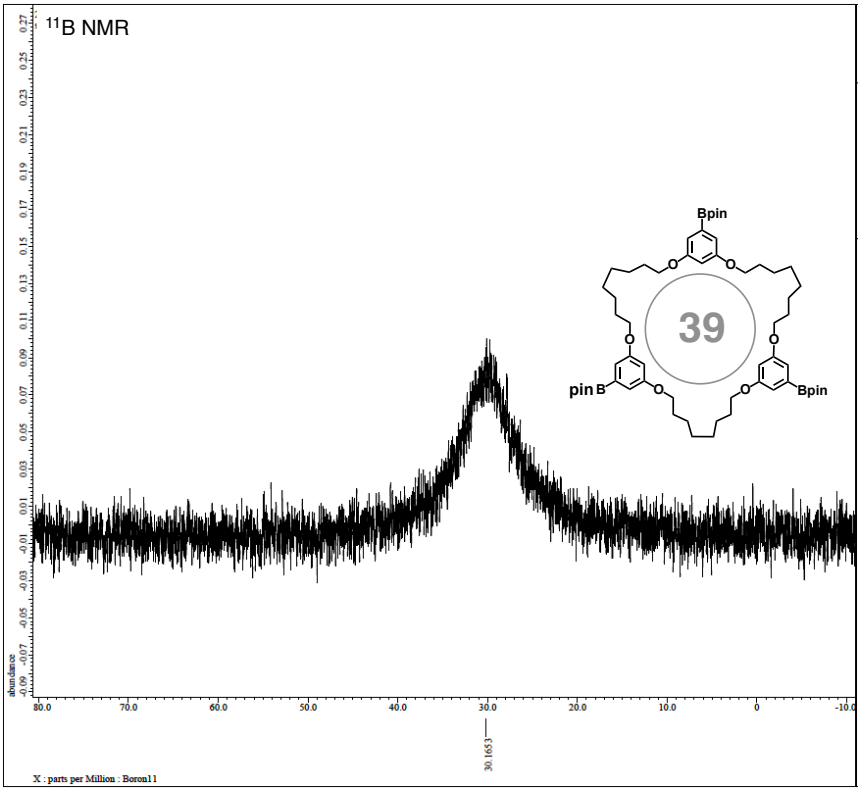


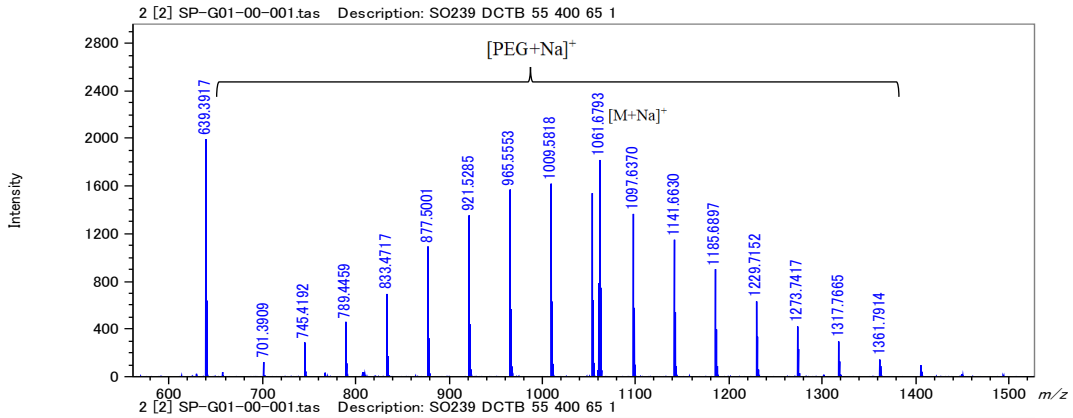
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C5 BPINMAC 還元体\C5 BPINMAC 還元体 13C (SO352).$RM1
DATIM 27/Jan/2020 02:24:07
COMNT

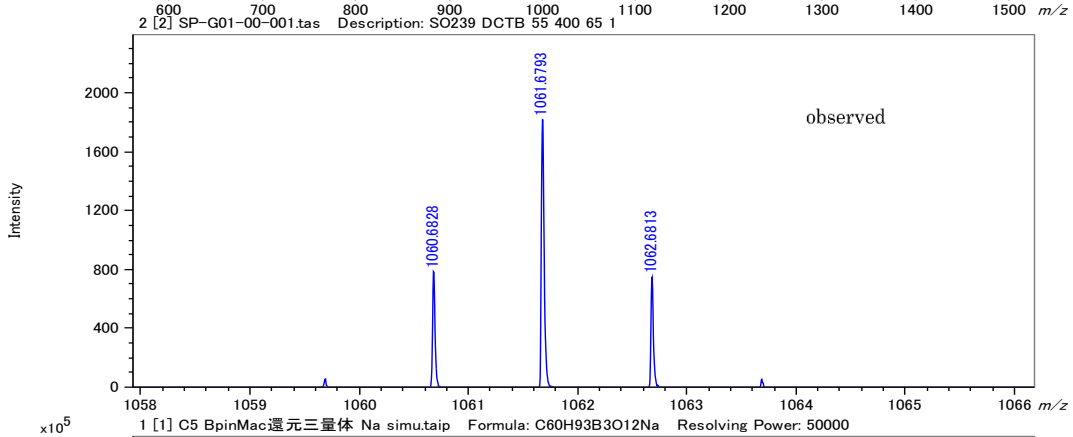
OBNUC ^{13}C
EXMOD ZGPG30
OBFRQ 100.63 MHz
OBSET 0.0 kHz
OBFIN 9999.211 Hz
POINT 32768
FREQU 24038.46 Hz
SCANS 1024
ACQTM 1.3631 s
IRNUC OFF
PROBHD 5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM SPECT
PULSPRG ZGPG30
GRDPROG
CTEMP 26.85 °C
SLVNT $CDCl_3$
BF 0.25 Hz
RGAIN 114

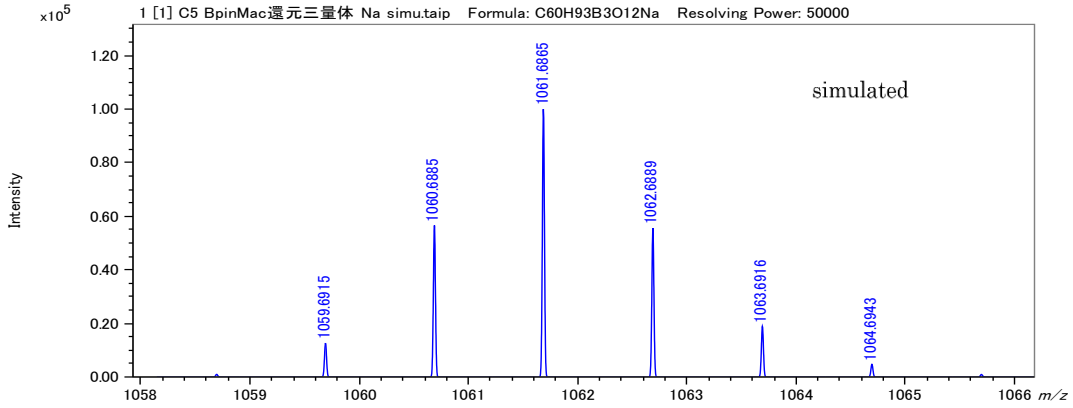
^{13}C NMR

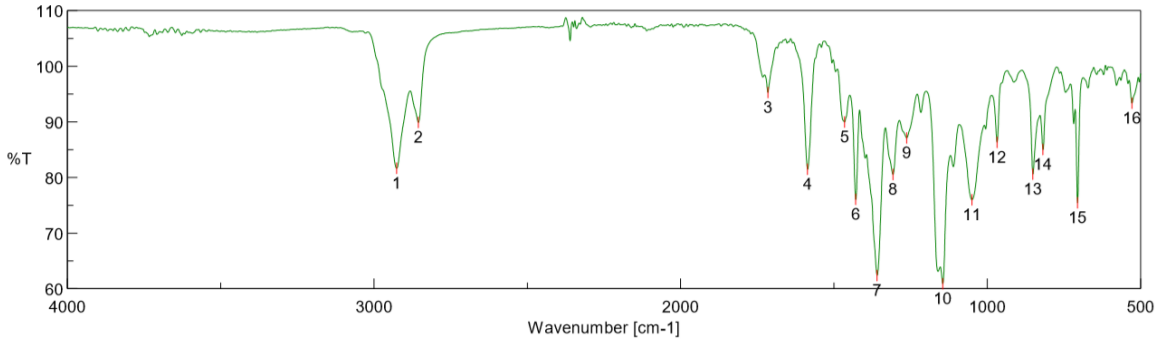



^{11}B NMR
Bpin
39
pin B
Bpin
abundance
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
30.1653
X : parts per Million : Boron11





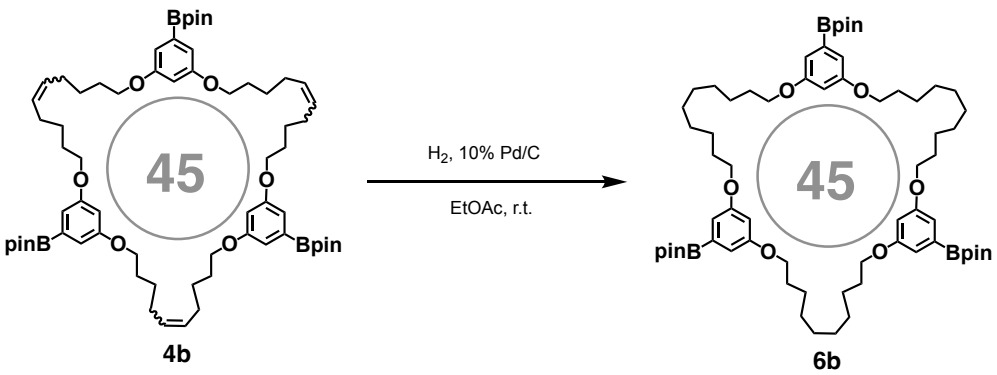




[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2926.45	81.6267	2	2855.1	89.8704	3	1715.37	95.2507	4	1586.16	81.4512
5	1465.63	89.9518	6	1428.99	76.0516	7	1359.57	62.3601	8	1307.5	80.5168
9	1263.15	87.1004	10	1145.51	60.8808	11	1050.05	75.9675	12	968.09	86.3026
13	851.418	80.5877	14	818.634	85.0107	15	705.819	75.4471	16	528.4	93.3206

4-2. Hydrogenation of Macrocycle **4b** to **6b**



Macrocycle **4b** (72 mg, 64.5 μmol) and palladium (10%) on charcoal were mixed in EtOAc (8.0 mL). Under hydrogen, the solution was stirred for 24 h and then filtered through Celite. The solvent was evaporated to afford the desired **6b** quantitatively.

Physical data of **6b**

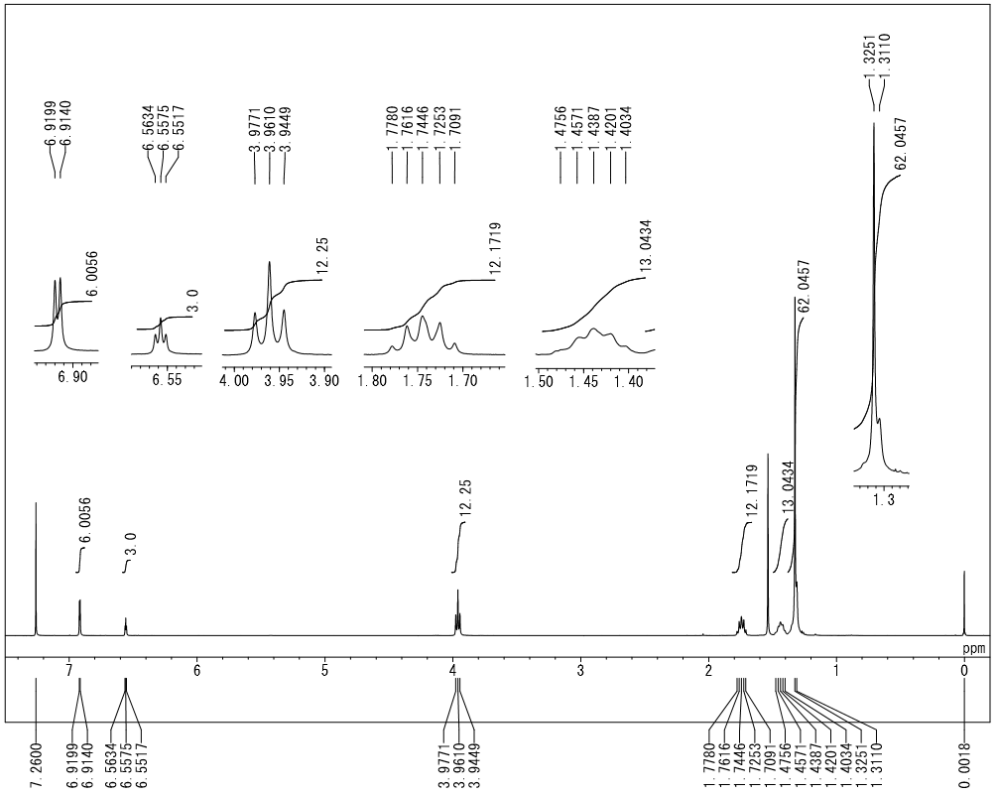
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, J = 2.4 Hz, 6H), 6.56 (t, J = 2.3 Hz, 3H), 3.96 (t, J = 6.4 Hz, 12H), 1.74 (quin, J = 6.9 Hz, 12H), 1.44 (quin, J = 7.2 Hz, 12H), 1.33 (s, 36H), 1.33-1.31 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 112.6, 105.3, 83.9, 68.1, 29.5, 29.4, 29.4, 26.1, 25.0. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.1

HRMS (MALDI^{+}): m/z calcd. for $C_{66}H_{105}B_3O_{12}Na$: 1145.7806, found: 1145.7764 $[M+Na]^{+}$.

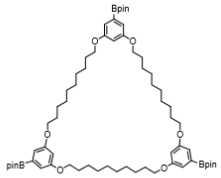
IR (ATR): 2977, 2929, 2855, 1586, 1472, 1429, 1361, 1308, 1165, 1146, 1052, 968, 852, 707 cm^{-1}.

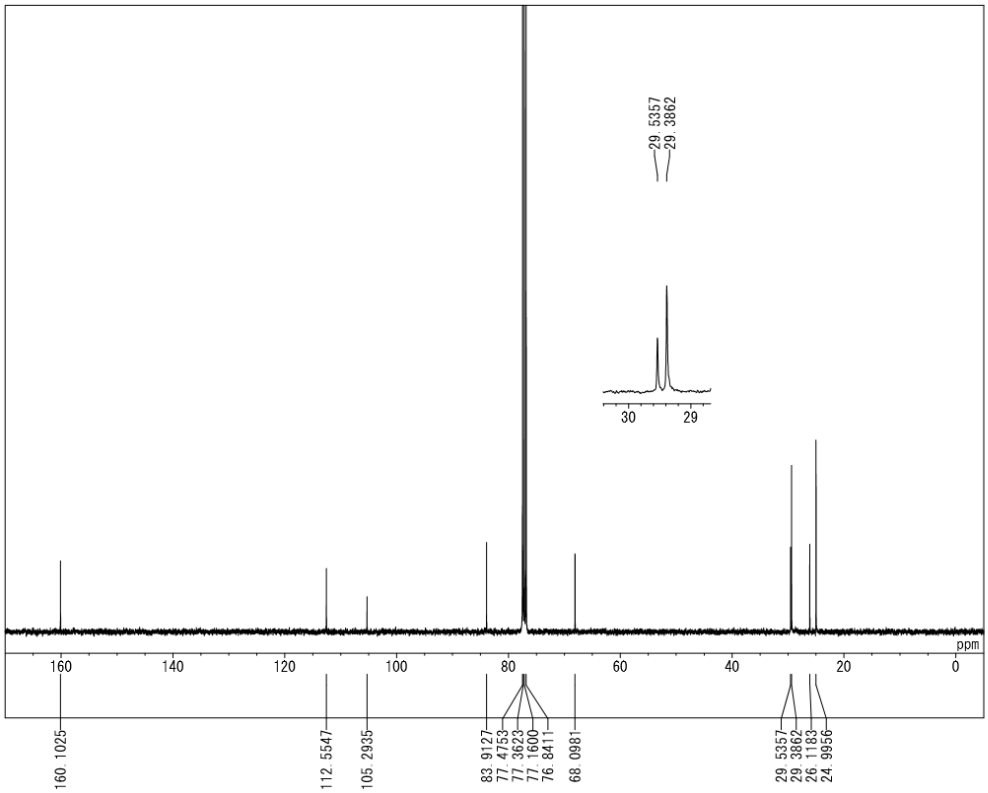


DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 BPINMAC 還元体\C6 BPINMAC 還元体 1H (SO323).RM1
DATIM 12/Nov/2019 20:18:56
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.13 MHz
OBSET	0.0 kHz
OBFIN	10003.76 Hz
POINT	65536
FREQU	8196.722 Hz
SCANS	16
ACQTM	7.9954 s
IRNUC	OFF
PROBHD	Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM	AVANCE
PULSPRG	ZG30
GRDPROG	
CTEMP	29.988 °C
SLVNT	$CDCl_3$
BF	0.25 Hz

^{1}H NMR

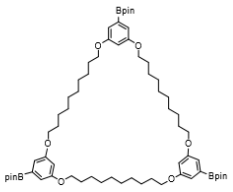


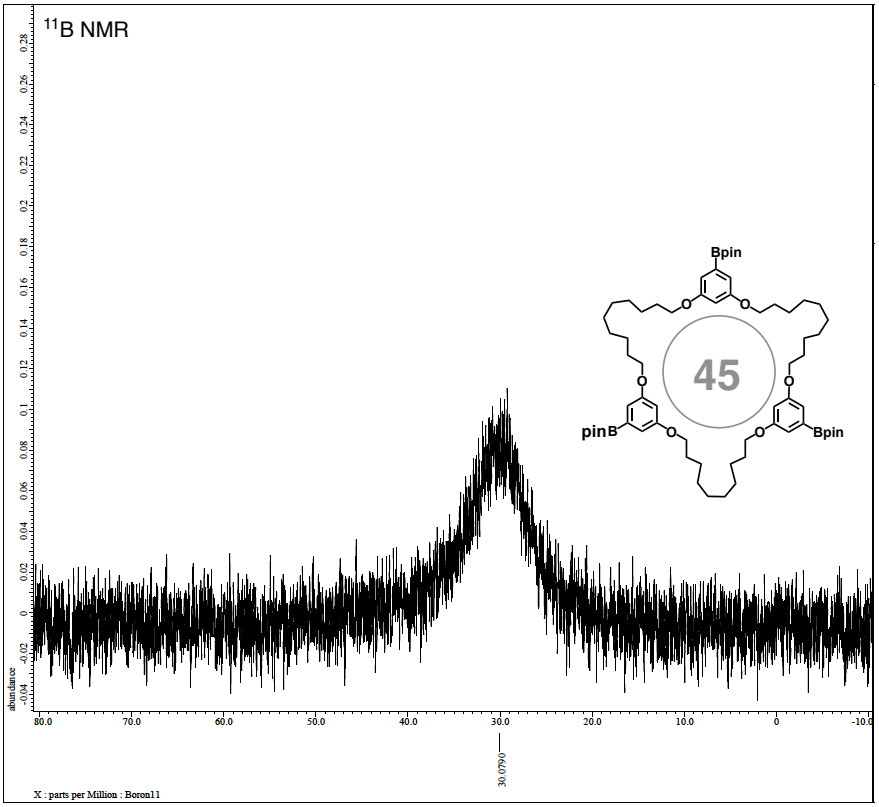


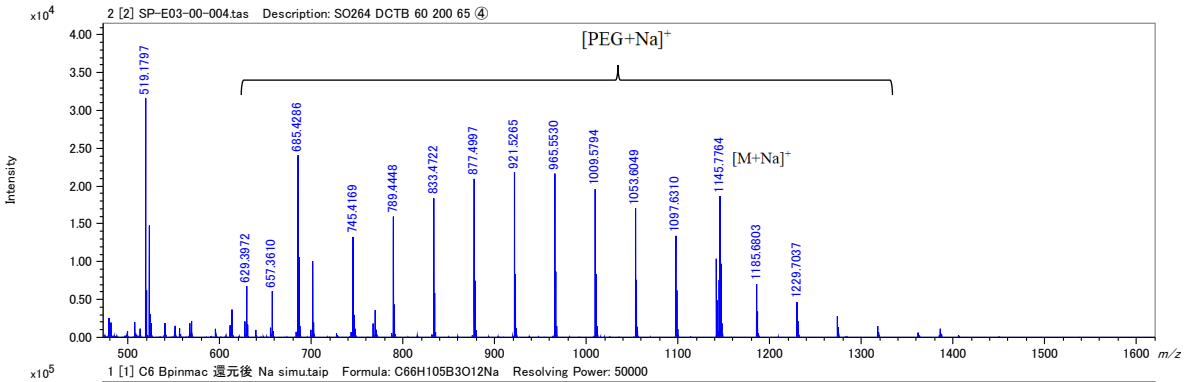
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 BPINMAC 還元体\C6 BPINMAC 還元体 13C (SO323).$RM1
DATIM 15/Nov/2019 04:05:56
COMNT

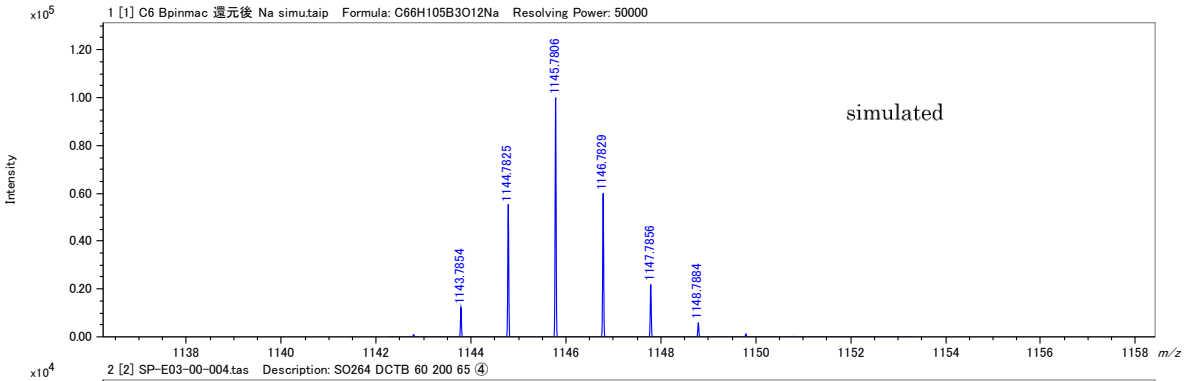
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.209 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	2048
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	400.01 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	64

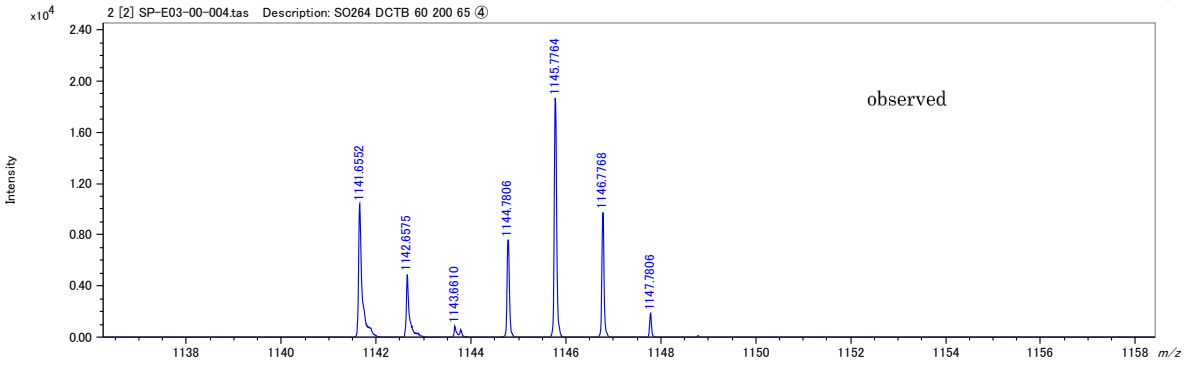
^{13}C NMR

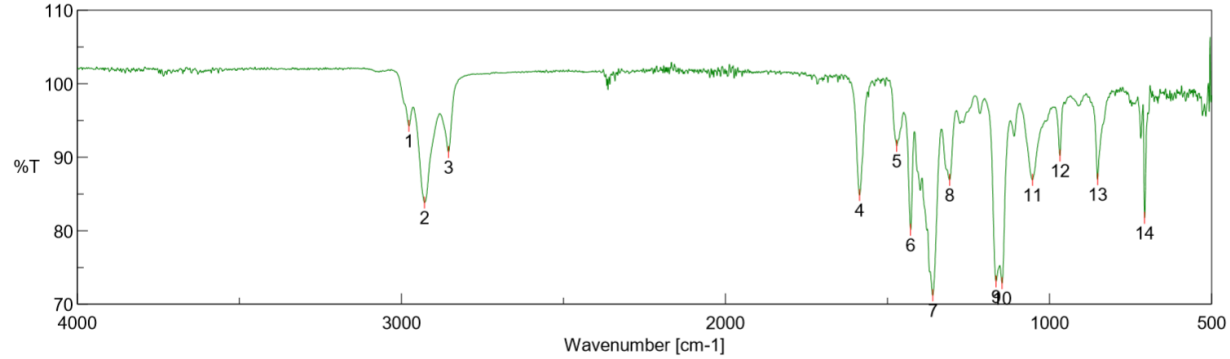



11B NMR
Bpin
45
pinB
Bpin
30.0790
X : parts per Million : Boron11





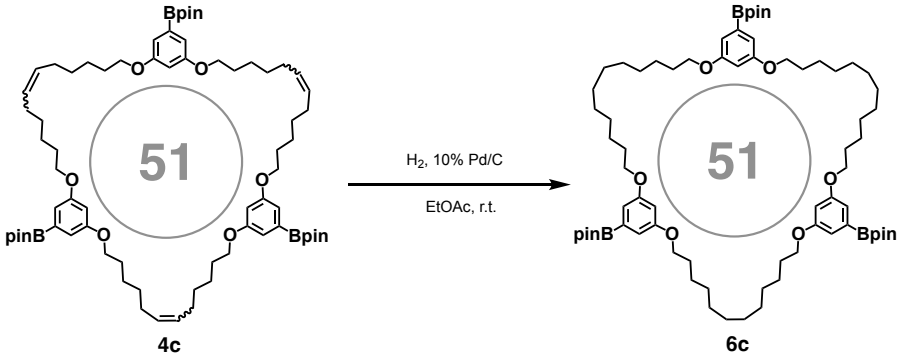




[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2976.59	94.2534	2	2928.86	83.825	3	2854.61	90.6917	4	1586.16	84.8302
5	1471.9	91.5132	6	1428.99	80.1069	7	1360.53	71.1812	8	1308.46	86.9014
9	1165.28	73.0807	10	1146.47	72.8554	11	1052.46	86.9144	12	968.09	90.2161
13	851.9	86.9928	14	706.783	81.7383						

4-3. Hydrogenation of Macrocycle **4c** to **6c**



Macrocycle **4c** (39.2 mg, 32.6 μmol) and palladium (10%) on charcoal were mixed in EtOAc (8.0 mL). Under hydrogen, the solution was stirred for 19 h and then filtered through Celite. The solvent was evaporated to afford the desired **6c** quantitatively.

Physical data of **6c**

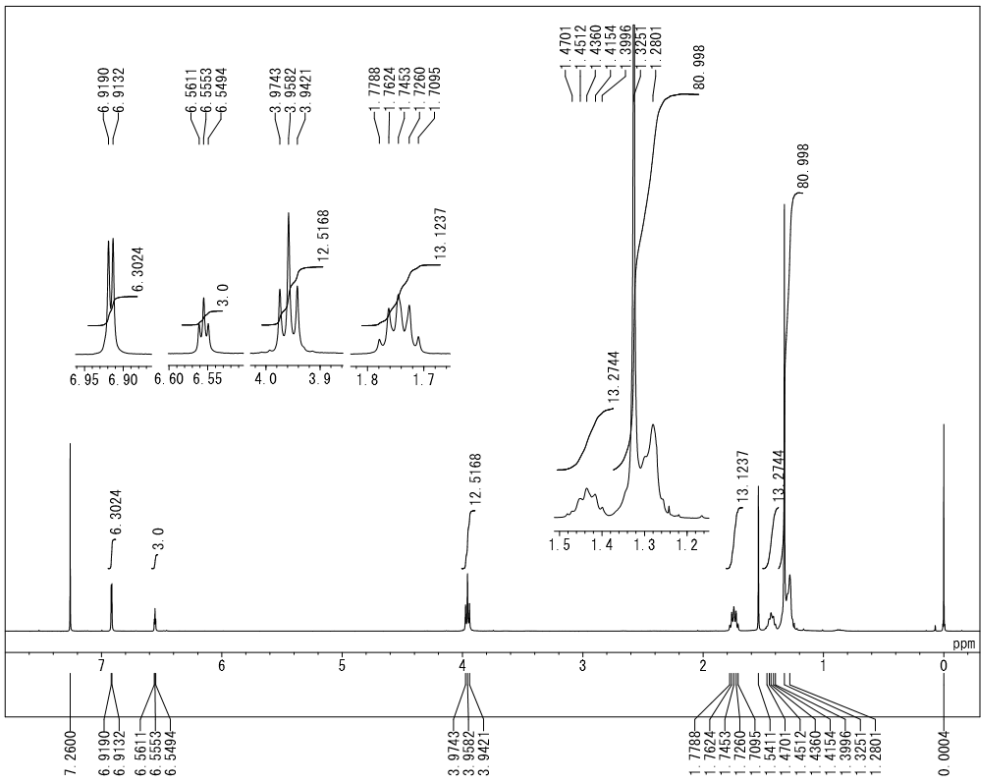
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, J = 2.3 Hz, 6H), 6.56 (t, J = 2.3 Hz, 3H), 3.96 (t, J = 6.4 Hz, 12H), 1.75 (quin, J = 6.9 Hz, 12H), 1.47-1.40 (m, 12H), 1.33 (s, 36H), 1.33-1.28 (m, 36H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 112.5, 105.3, 83.9, 68.1, 29.6, 29.6, 29.4, 29.4, 26.1, 25.0. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.4

HRMS (MALDI^{+}): *m*/*z* calcd. for $C_{72}H_{117}B_3O_{12}Na$: 1229.8747, found: 1229.8778 $[M+Na]^{+}$.

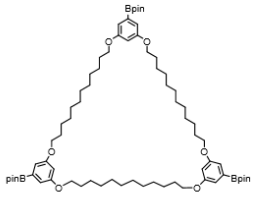
IR (ATR): 2925, 2853, 1715, 1586, 1428, 1360, 1308, 1163, 1146, 1053, 968, 851, 706 cm^{-1}.

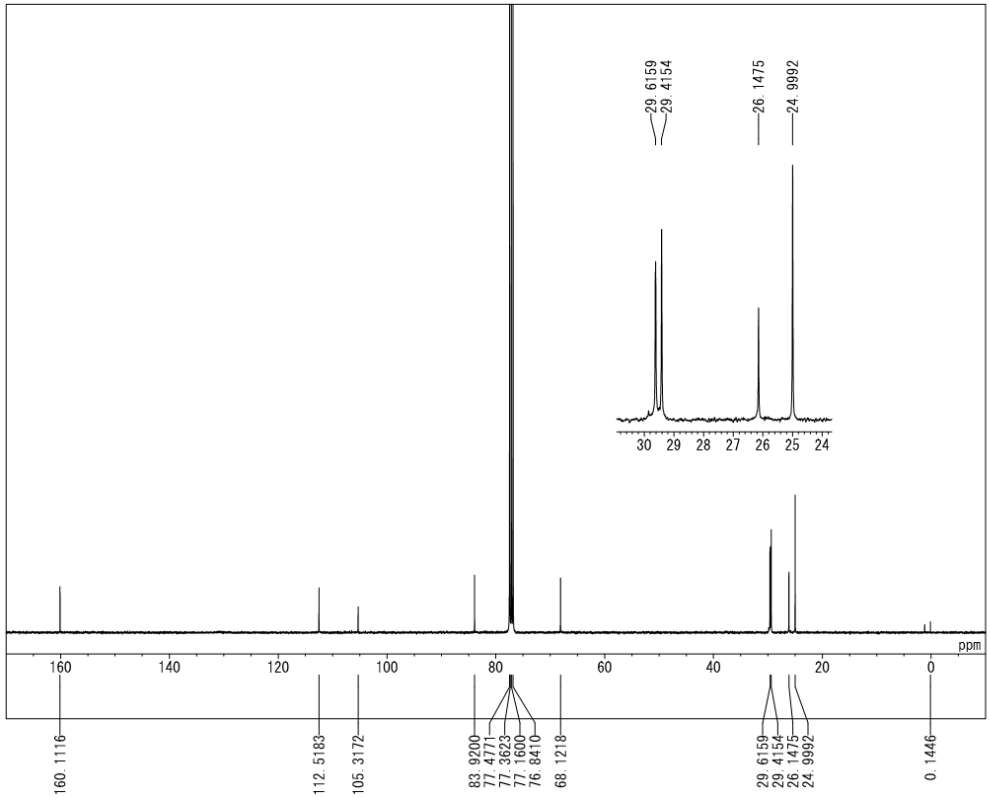


DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C7 BPINMAC 還元体\C7 BPINMAC 還元体 (SO354).$RM1
DATIM 04/Feb/2020 19:03:36
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.13 MHz
OBSET	0.0 kHz
OBFIN	10003.76 Hz
POINT	65536
FREQU	8196.722 Hz
SCANS	16
ACQTM	7.9954 s
IRNUC	OFF
PROBHD	Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM	AVANCE
PULSPRG	ZG30
GRDPROG	
CTEMP	26.227 °C
SLVNT	$CDCl_3$
BF	0.25 Hz

^{1}H NMR

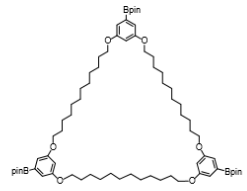


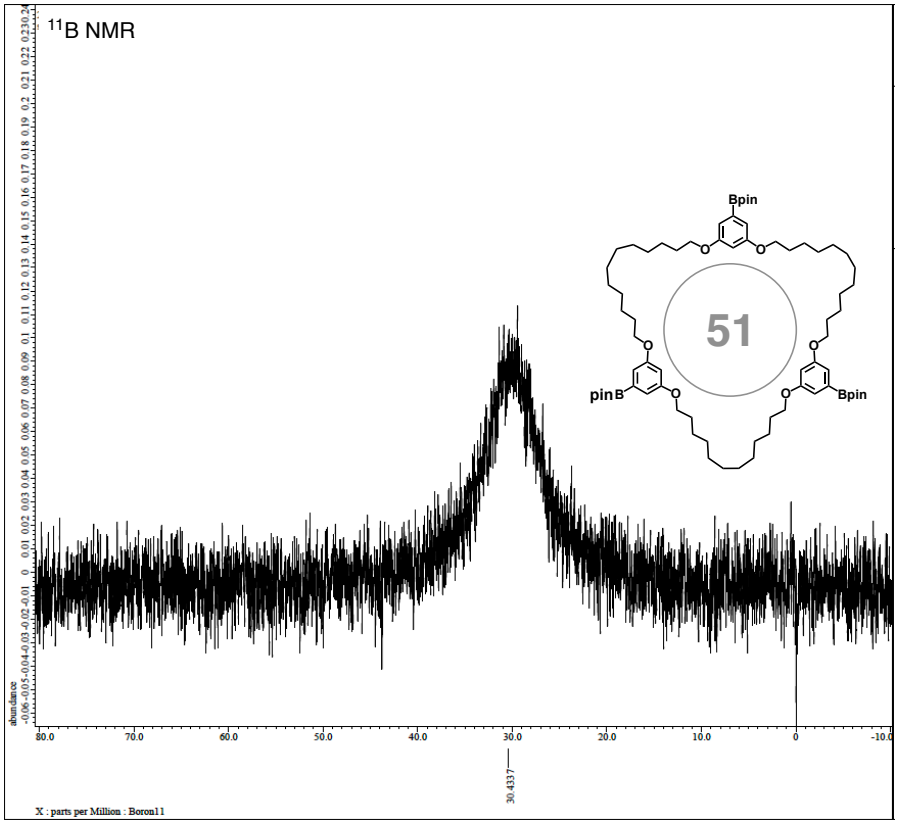


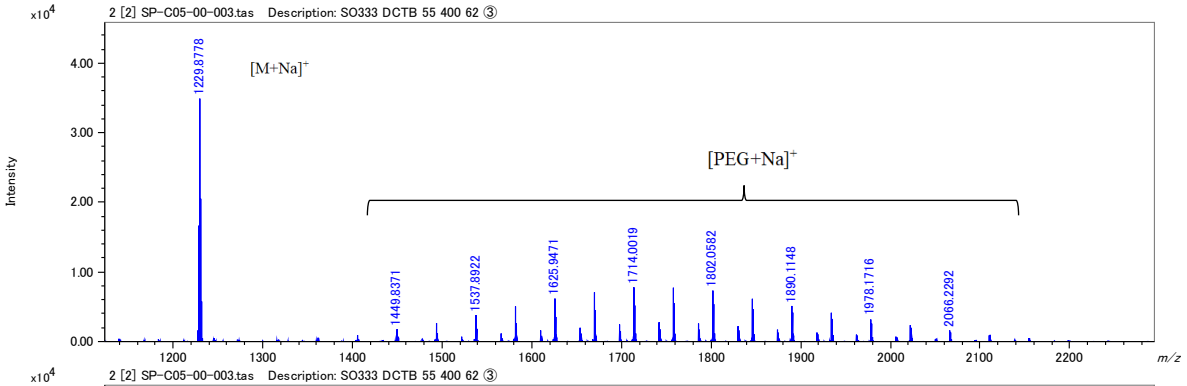
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C7 BPINMAC 還元体\C7 BPINMAC 還元体 13C (SO333).$RM1
DATIM 24/Jan/2020 08:37:55
COMNT

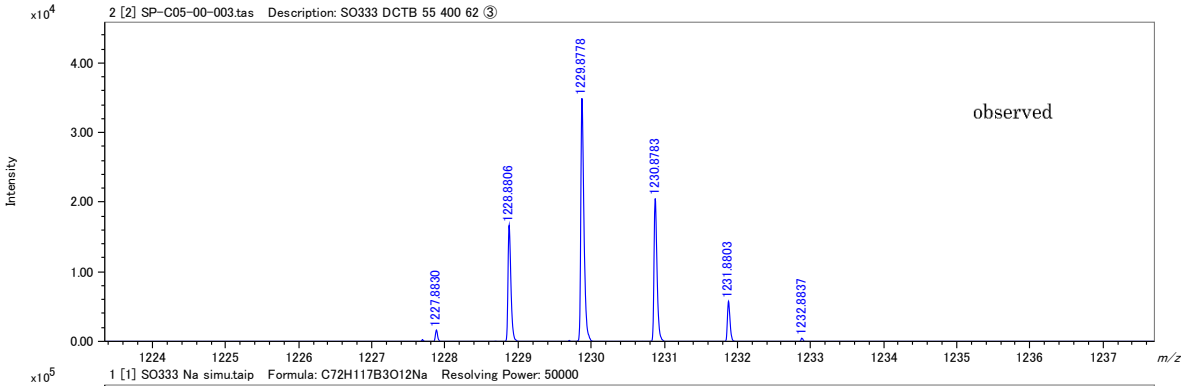
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.209 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	10000
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	72

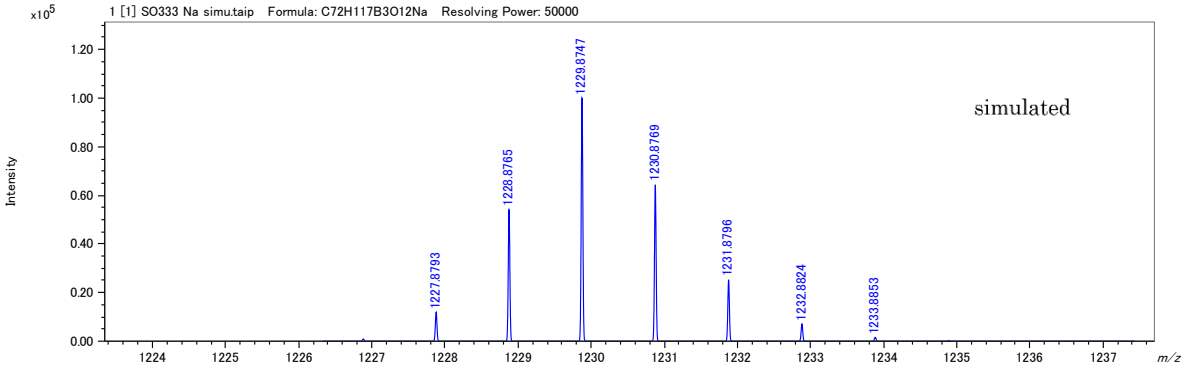
^{13}C NMR

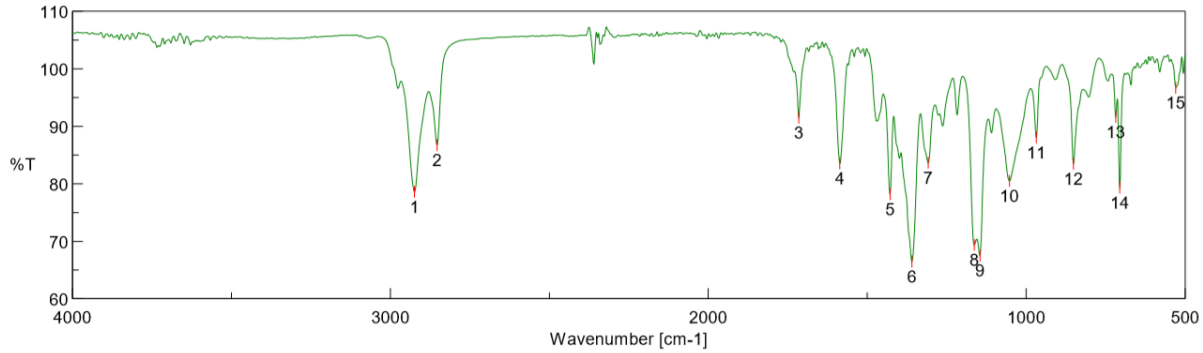



11B NMR
Bpin
51
pinB
Bpin
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
30.4337
X : parts per Million : Boron11





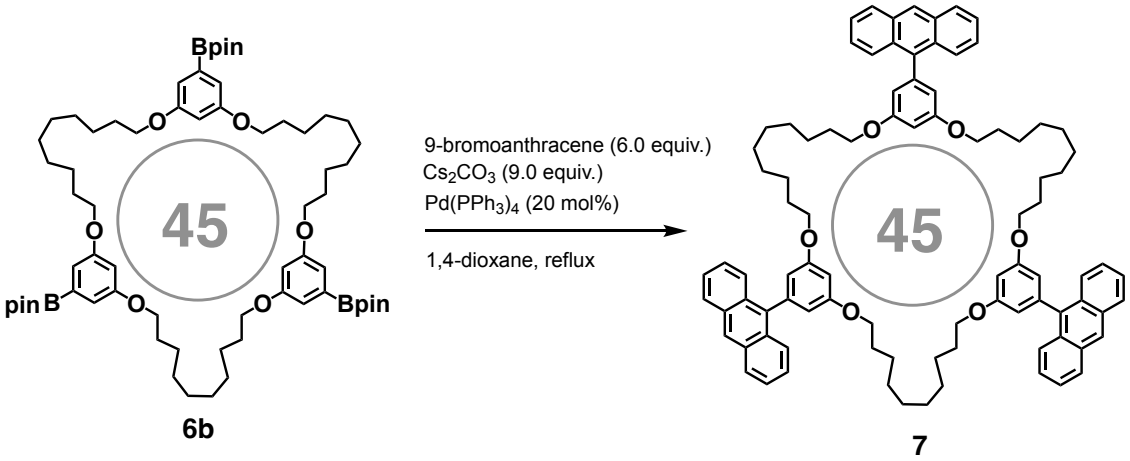




[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2924.52	78.6038	2	2853.17	86.7387	3	1715.37	91.4753	4	1586.16	83.5199
5	1428.03	78.1427	6	1359.57	66.4531	7	1308.46	83.643	8	1162.87	69.3532
9	1145.51	67.5313	10	1052.94	80.4953	11	968.09	88.0362	12	851.418	83.4435
13	718.354	91.6253	14	705.819	79.3017	15	529.364	96.7214			

4-4. Suzuki-Miyaura coupling of Macrocycle **6b** and 9-bromoanthracence



Macrocycle **6b** (11.0 mg, 9.8 μmol), 9-bromoanthracene (15.1 mg, 58.7 μmol), $Pd(PPh_3)_4$ (2.3 mg, 2.0 μmol), Cs_2CO_3 (28.7 mg, 88.1 μmol) were added to a test tube and the test tube was filled with Ar. Degassed 1,4-dioxane (0.5 mL) were added to the test tube and the resulting mixture was refluxed for 24 h. The reaction mixture was treated with water and the organic material was extracted with $CHCl_3$. The organic layer was washed with brine and dried over Na_2SO_4. The crude product was purified by silica gel column chromatography ($CHCl_3$/*n*-hexane = 3:2) to afford **7** (8.1 mg, 65% yield).

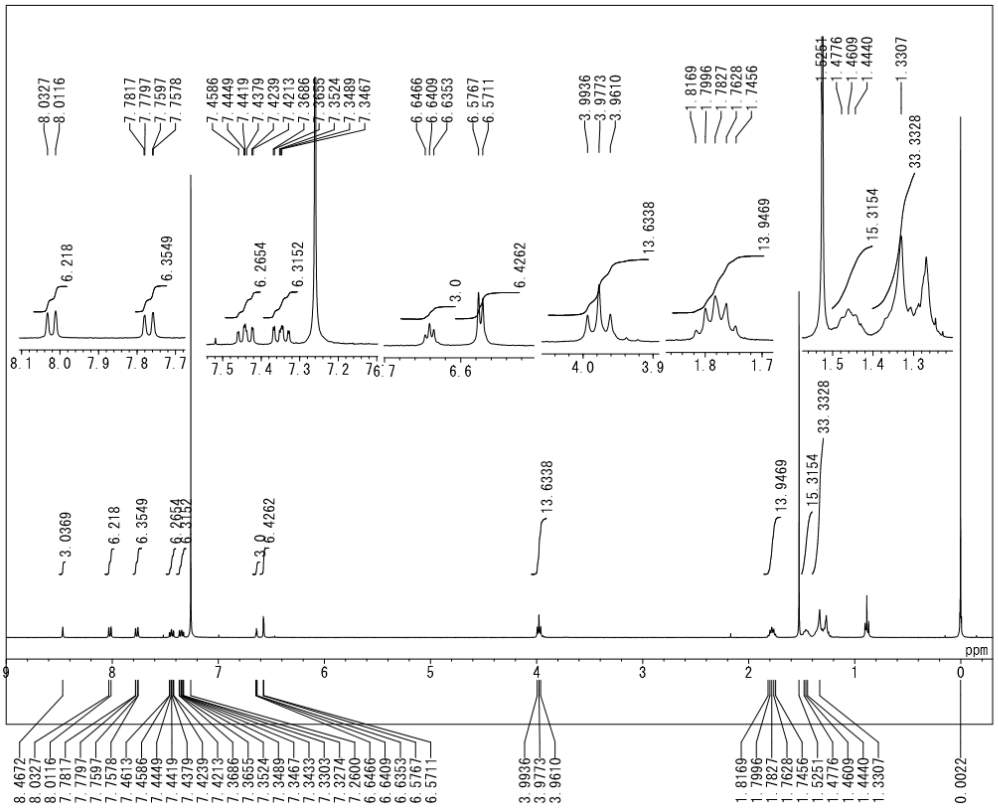
Physical data of **7**

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 3H), 8.02 (dd, *J* = 8.4 Hz, 6H), 7.77 (dd, *J* = 8.8, 0.8 Hz, 6H), 7.44 (ddt, *J* = 8.4, 6.6, 1.4 Hz, 6H), 7.35 (ddt, *J* = 8.8, 6.6, 1.4 Hz, 6H), 6.64 (t, *J* = 2.3 Hz, 3H), 6.57 (d, *J* = 2.3 Hz, 6H), 3.98 (t, *J* = 6.5 Hz, 12H), 1.78 (quin, *J* = 7.1 Hz, 12H), 1.50-1.44 (m, 12H), 1.38-1.30 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 140.8, 137.3, 131.5, 130.1, 128.4, 127.2, 126.6, 125.4, 125.2, 110.0, 100.9, 68.3, 29.5, 29.4, 29.4, 26.1.

HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{90}H_{96}O_6$: 1272.7201, found: 1272.7219 $[M]^+$.

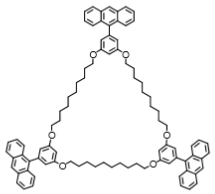
IR (ATR): 2925, 2853, 1712, 1589, 1442, 1362, 1220, 1161, 1056, 885, 833, 758, 738, 701 cm^{-1}.

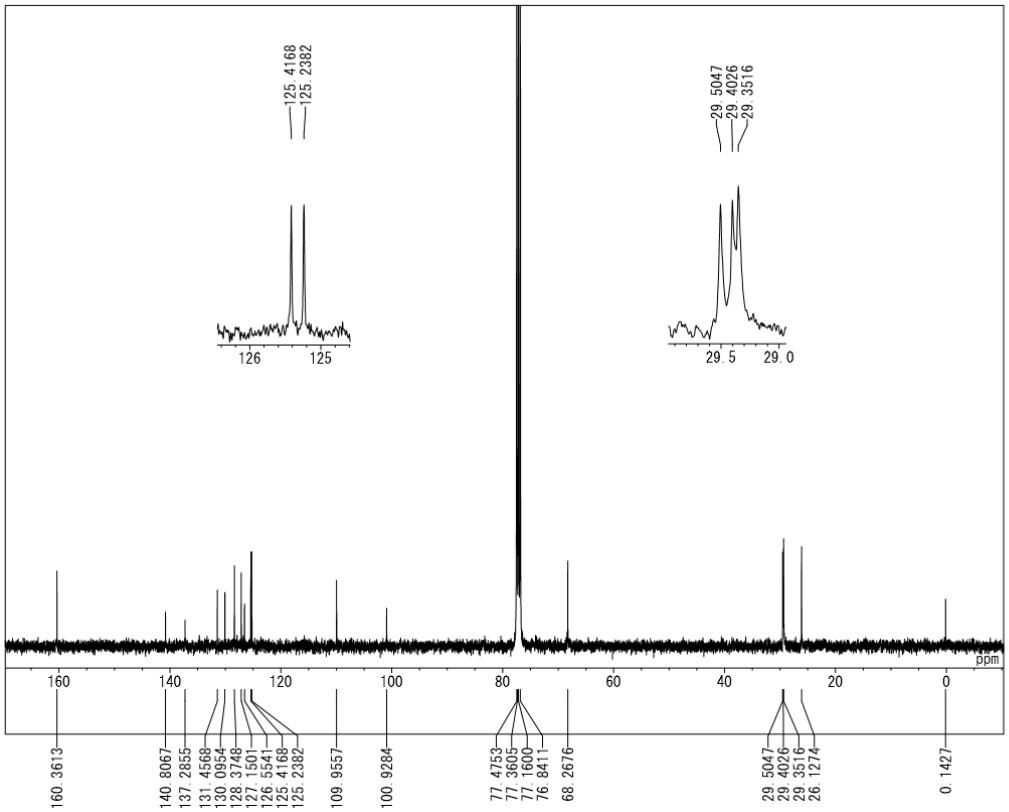


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C6 anthraMac\C6 anthraMac 1H (SO345).RM1
DATIM 07/Jan/2020 13:28:58
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.13 MHz
OBSET	0.0 kHz
OBFIN	10003.76 Hz
POINT	65536
FREQU	8196.722 Hz
SCANS	16
ACQTM	7.9954 s
IRNUC	OFF
PROBHD	Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM	AVANCE
PULSPRG	ZG30
GRDPROG	
CTEMP	29.984 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	101

^{1}H NMR

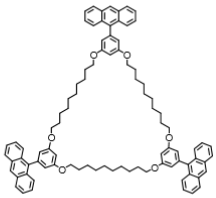


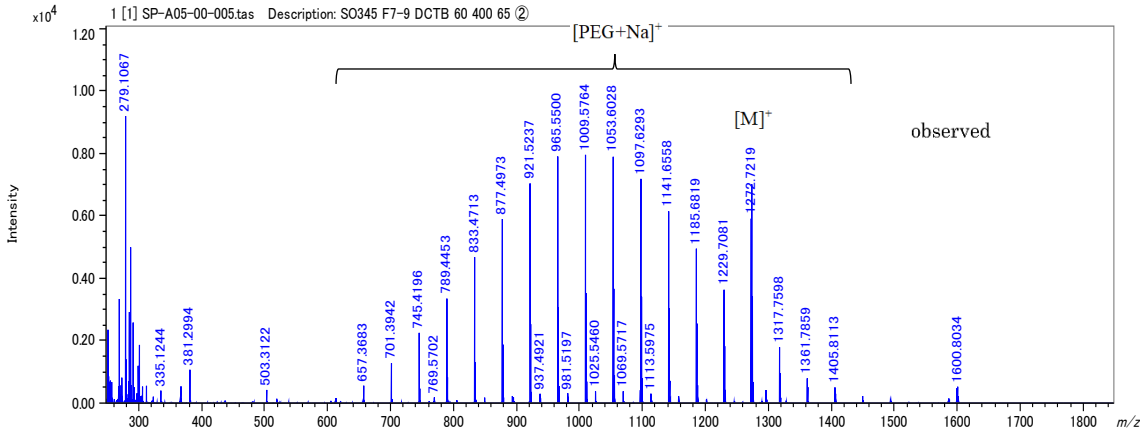


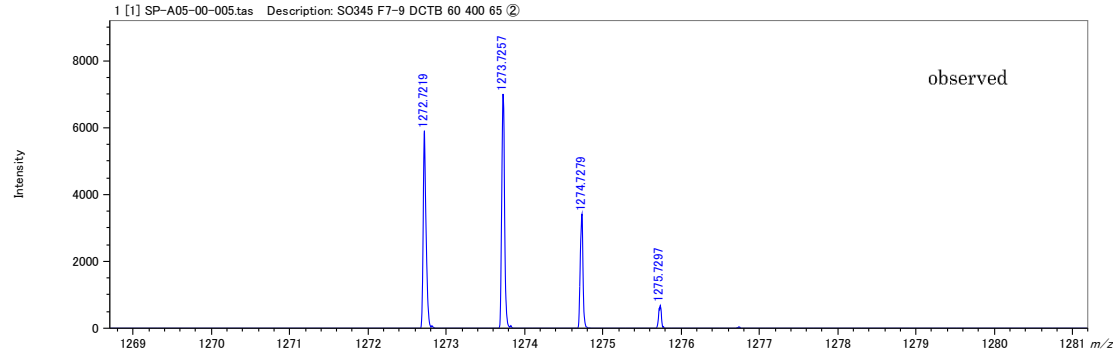
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 ANTHRAMAC\C6 ANTHRAMAC 13C (SO345).RM1
DATIM 15/Feb/2020 07:28:29
COMNT

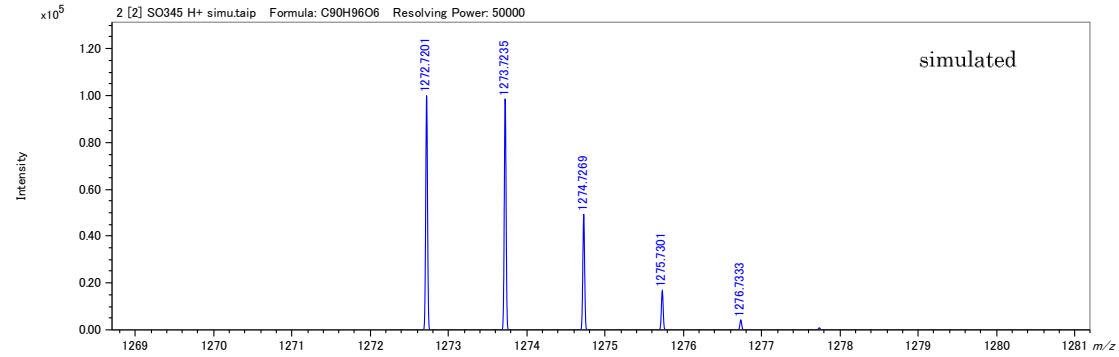
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.211 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	10000
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	72

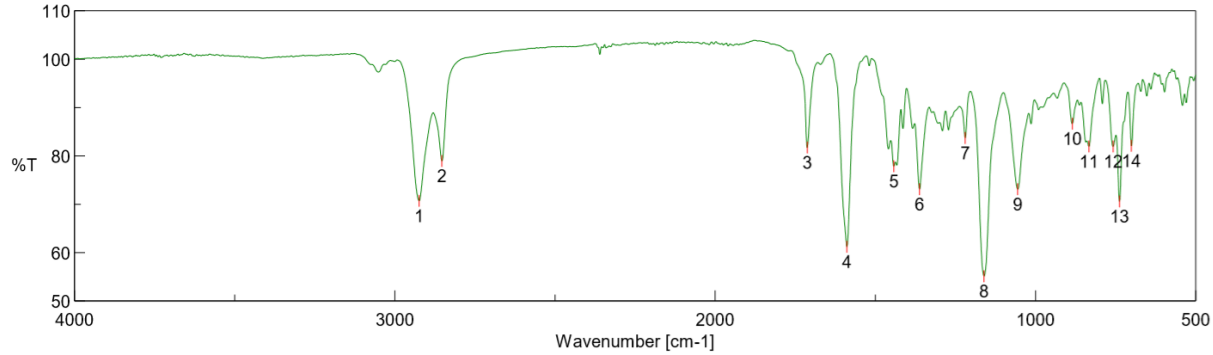
^{13}C NMR







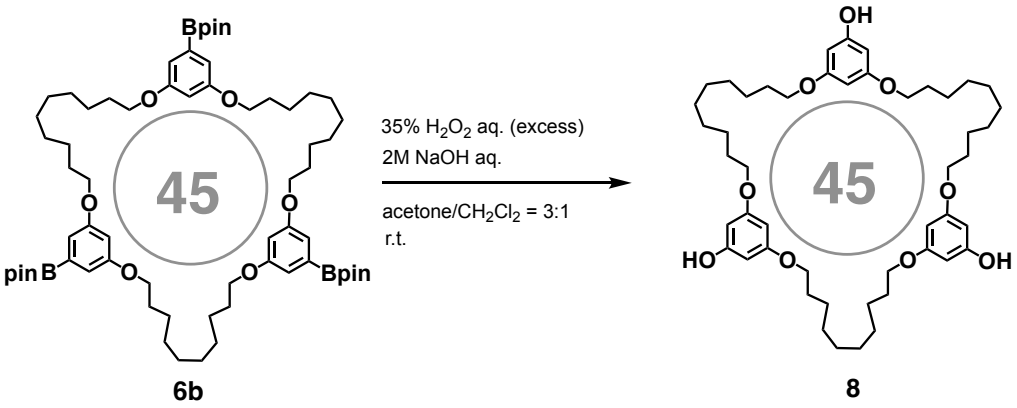




[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	2924.52	70.6847	2	2853.17	78.9375	3	1712.48	81.7224	4	1589.06	61.2174
5	1442.49	77.8298	6	1362.46	73.0868	7	1219.76	83.6846	8	1160.94	55.1092
9	1055.84	73.0851	10	885.166	86.6278	11	833.098	81.941	12	757.888	81.9401
13	737.639	70.5535	14	700.998	82.0879						

4-5. Oxidation of Macrocycle **6b** to **8**



Macrocycle **6b** (17.9 mg, 15.9 μmol) was dissolved in a mixture of acetone (8.6 mL) and CH_2Cl_2 (2.9 mL). 2 M NaOH aq. (90 equiv.) and 35% H_2O_2 aq. (excess) was added and stirred at room temperature. After 22 h, the reaction mixture was quenched by 1 N HCl aq. and the organic solvents were evaporated. The residue was treated with water and the organic materials was extracted with $CHCl_3$. The organic layer was washed with brine and dried over $MgSO_4$. The crude product was washed with hexane to afford **8** (10.1 mg, 80% yield).

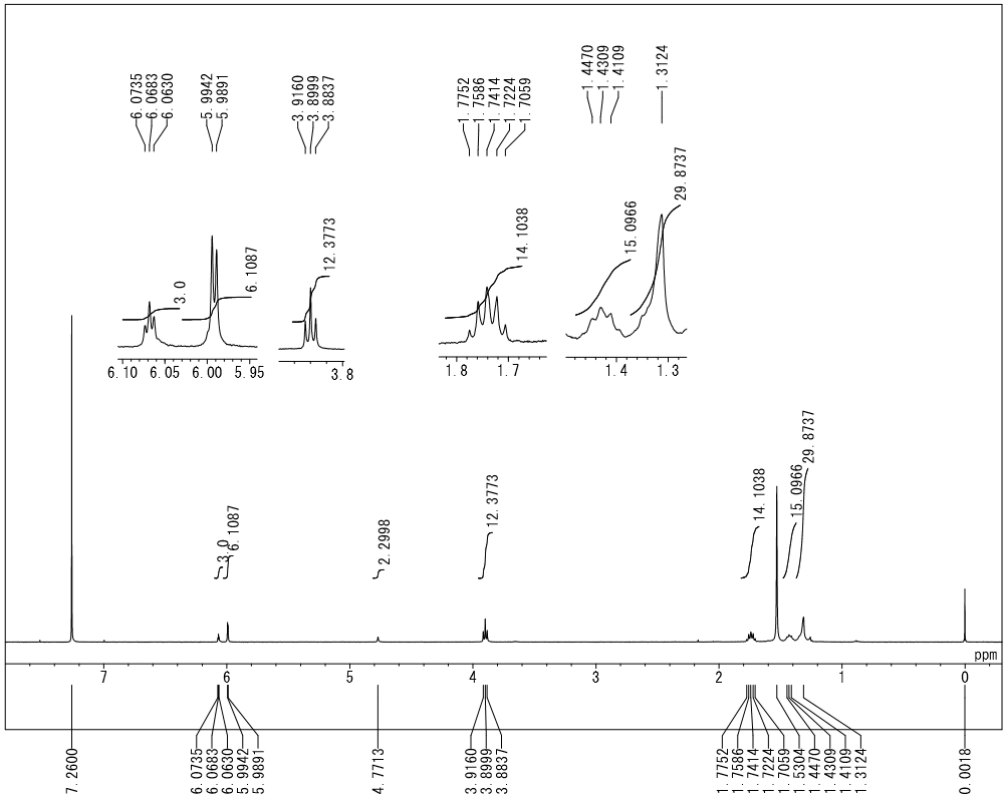
Physical data of **8**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.07 (t, *J* = 2.1 Hz, 3H), 5.99 (d, *J* = 2.1 Hz, 6H), 4.77 (s, 3H), 3.90 (t, *J* = 6.5 Hz, 12H), 1.74 (quin, *J* = 6.9 Hz, 12H), 1.45-1.41 (m, 12H), 1.38-1.30 (m, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 157.4, 94.8, 94.4, 68.1, 29.3, 29.2, 26.0.

HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{48}H_{72}O_9Na$: 815.5069, found: 815.5080 $[M+Na]^+$.

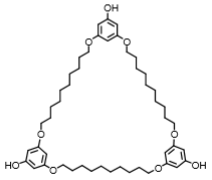
IR (ATR): 3348, 2922, 2851, 1594, 1497, 1463, 1387, 1145, 1092, 821, 593 cm^{-1}.

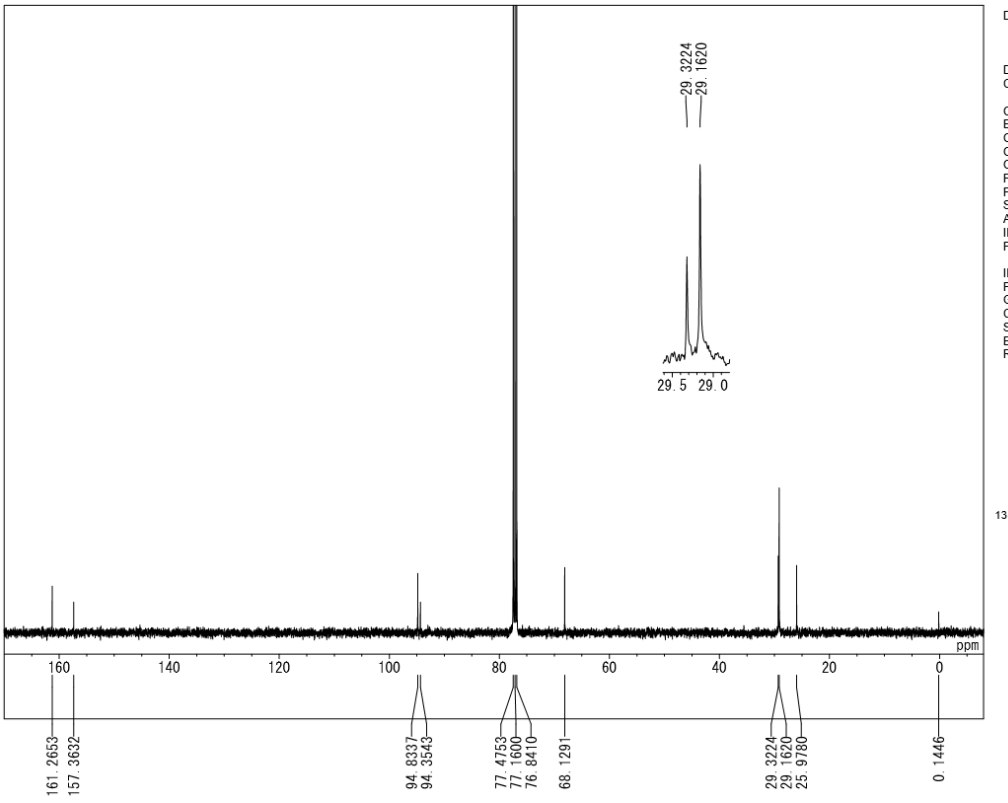


DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 OHM AC\C6 OH MAC 1H (SO334).$RM1
DATIM 13/Dec/2019 16:01:56
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.13 MHz
OBSET	0.0 kHz
OBFIN	10003.76 Hz
POINT	65536
FREQU	8196.722 Hz
SCANS	16
ACQTM	7.9954 s
IRNUC	OFF
PROBHD	Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM	AVANCE
PULSPRG	ZG30
GRDPROG	
CTEMP	29.9775 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	101

^{1}H NMR

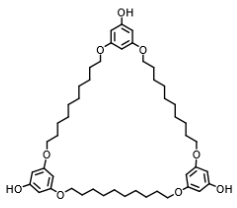


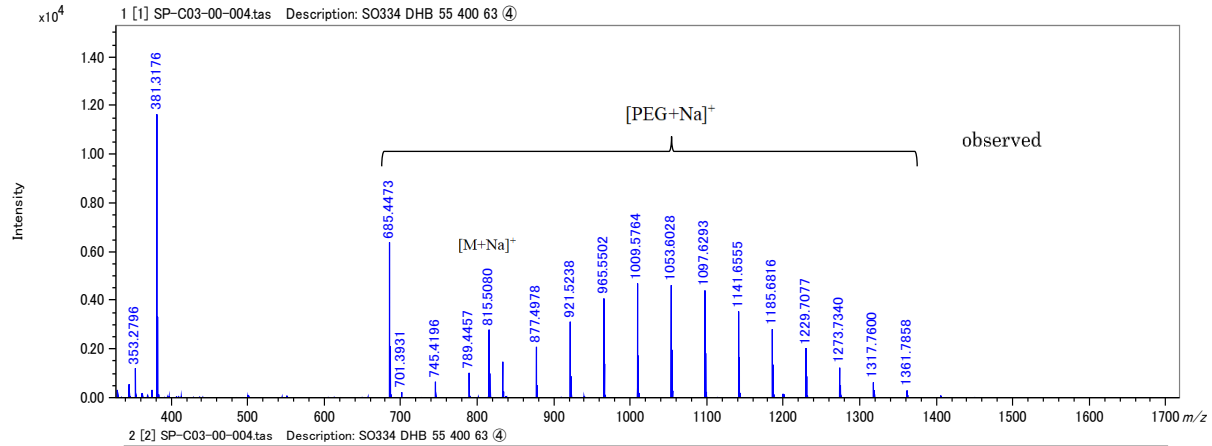


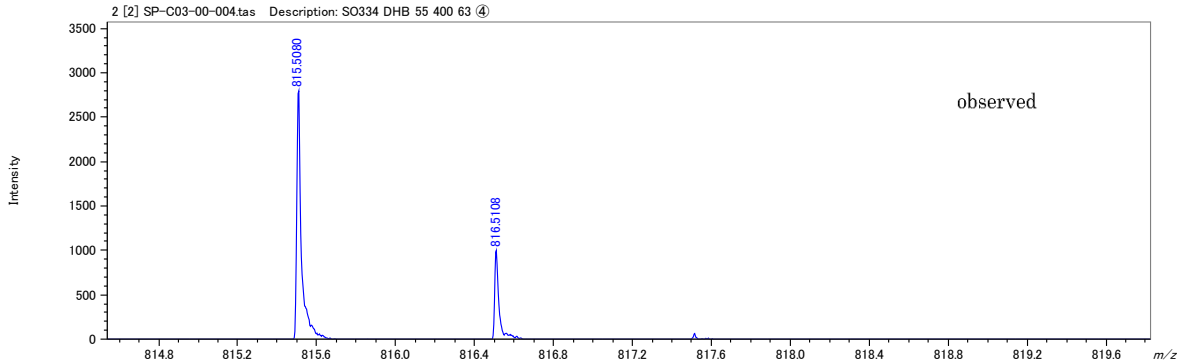
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 OHM AC\C6 OH MAC 13C (SO334).$RM1
DATIM 19/Jan/2020 17:51:58
COMNT

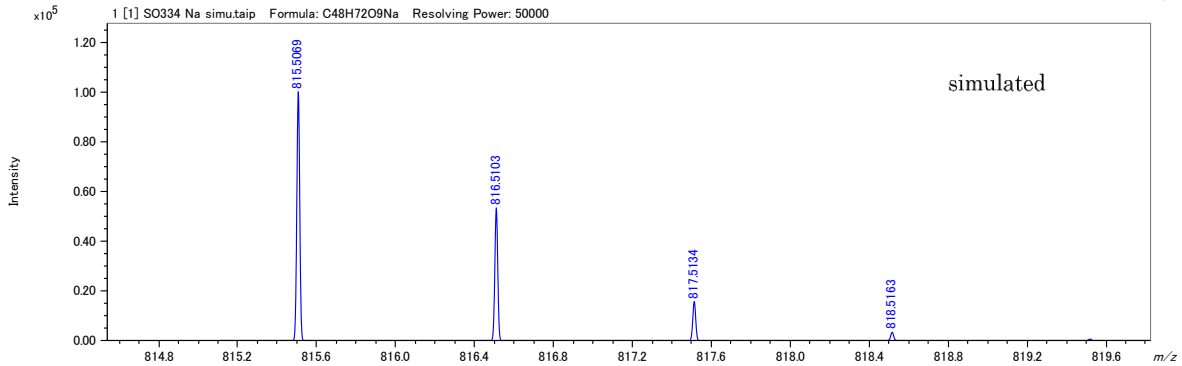
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.217 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	1024
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	26.85 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	72

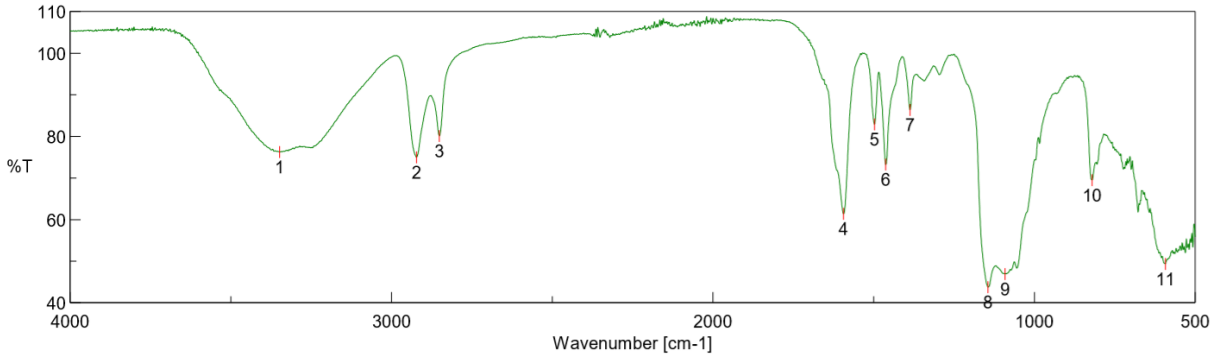
^{13}C NMR







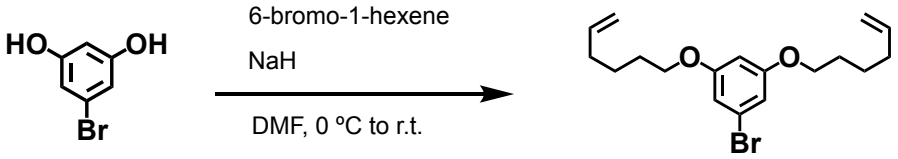




[ピーク検出結果]

No.	位置	強度	No.	位置	強度	No.	位置	強度	No.	位置	強度
1	3347.82	76.2095	2	2922.11	74.9486	3	2851.24	80.0639	4	1593.88	61.3322
5	1497.45	82.8395	6	1462.74	73.1704	7	1387.05	86.3188	8	1144.55	43.7068
9	1091.51	46.8521	10	820.563	69.4463	11	592.521	49.2967			

5. Synthetic Procedures and Characterization of New Compounds



S1

Under an Ar atmosphere, NaH (60% in oil; 320 mg, 8.0 mmol) was dissolved in dry DMF (13.3 mL) and then 5-bromoresorcinol (756 mg, 4.0 mmol) was added at 0 ºC. The mixture was stirred at 0 ºC for 1 h, and then 6-bromo-1-hexene (1.6 mL, 12.0 mmol) was added slowly and further stirred at room temperature. After 12 h, water was added and the product was extracted with *n*-hexane/EtOAc = 4:1 and then combined extract was washed with brine and dried over $MgSO_4$. After solvent was evaprated, the residue was purified by column chromatography (*n*-hexane/EtOAc = 9:1) to give **S1** (1.41 g, quant.).

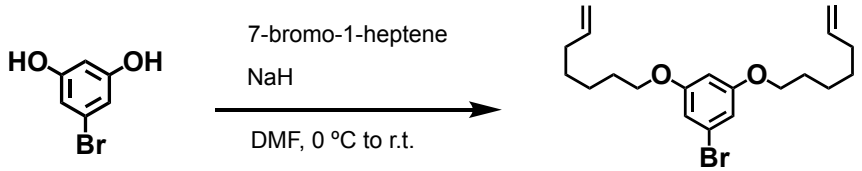
Physical data of **S1**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.64 (d, *J* = 2.2 Hz, 2H), 6.36 (t, *J* = 2.2 Hz, 1H), 5.82 (ddt, *J* = 17.1, 10.2, 6.7 Hz, 2H), 5.06-5.01 (m, 2H), 4.99-4.96 (m, 2H), 3.91 (t, *J* = 6.44 Hz, 4H), 2.15-2.09 (m, 4H), 1.78 (quin, *J* = 7.0 Hz, 4H), 1.59-1.51 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 138.6, 123.0, 115.0, 110.4, 100.8, 68.2, 33.5, 28.7, 25.4.

HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{18}H_{25}BrO_2Na$: 375.0930, found: 375.0929 $[M+Na]^+$.

IR (ATR): 3077, 2924, 2871, 1597, 1575, 1451, 1439, 1386, 1278, 1053, 990, 911, 833, 677 cm^{-1}.



S2

Under an Ar atmosphere, NaH (60% in oil; 240 mg, 6.0 mmol) was dissolved in dry DMF (10.0 mL) and then 5-bromoresorcinol (567 mg, 3.0 mmol) was added at 0 ºC. The mixture was stirred at 0 ºC for 1 h, and then 7-bromo-1-heptene (1.37 mL, 9.0 mmol) was added slowly and further stirred at room temperature. After 22 h, water was added and the product was extracted with hexane/EtOAc = 4:1 and then combined extract was washed by brine and dried over $MgSO_4$. The solvent was evaporated to give **S2** (1.14 g, quant.).

Physical data of **S2**

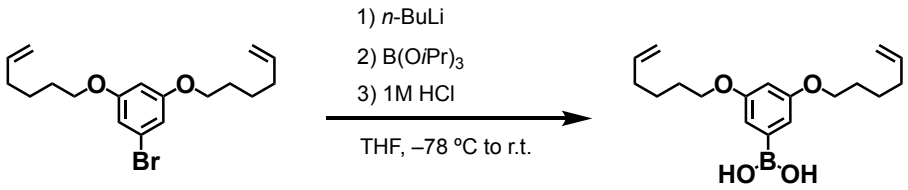
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.63 (d, *J* = 2.2 Hz, 2H), 6.36 (t, *J* = 2.2 Hz, 1H), 5.82 (ddt, *J* = 17.1, 10.3,

6.8 Hz, 2H), 5.03-4.98 (m, 2H), 4.97-4.94 (m, 2H), 3.90 (t, J = 6.5 Hz, 4H), 2.10-2.06 (m, 4H), 1.76 (quin, J = 6.9 Hz, 4H), 1.47-1.43 (m, 8H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 138.9, 123.0, 114.6, 110.4, 100.8, 68.3, 33.8, 29.1, 28.7, 25.6.

HRMS (MALDI$^+$): m/z calcd. for $C_{20}H_{29}BrO_2Na$: 403.1243, found: 403.1258 $[M+Na]^+$.

IR (ATR): 3075, 2926, 2857, 1597, 1575, 1438, 1387, 1278, 1165, 1052, 991, 911, 831, 676 cm^{-1}.



S1 **1b**

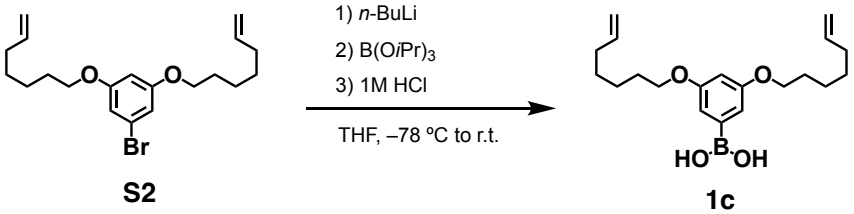
Under an Ar atmosphere, **S1** (700 mg, 19.8 mmol) was dissolved in dry THF (6.6 mL) and then *n*-BuLi (1.57 M in hexane, 1.39 mL, 2.18 mmol) was added dropwise to the solution at –78 ºC. The mixture was stirred at –78 ºC for 1 h, and then B(O*i*Pr)$_3$ (500 μL, 2.18 mmol) was added and warmed up to room temperature over 2 h. After warmed up, 1N HCl aq. was added and the product was extracted with *tert*-butyl methyl ether and then combined extract was washed with brine and dried over $MgSO_4$. The solvent was evaporated and the solid was washed with CH_3CN to give **1b** (397 mg, 63%).

Physical data of **1b**

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99 (s, 2H), 6.92 (d, J = 2.2 Hz, 2H), 6.48 (t, J = 2.2 Hz, 1H), 5.82 (ddt, J = 17.1, 10.3, 6.7 Hz, 2H), 5.06-5.01 (m, 2H), 4.98-4.96 (m, 2H), 3.93 (t, J = 6.5 Hz, 4H), 2.11-2.05 (m, 4H), 1.70 (quin, J = 6.9 Hz, 4H), 1.53-1.46 (m, 4H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 159.2, 138.6, 114.9, 112.0, 103.1, 67.1, 32.8, 28.2, 24.8. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, DMSO-d_6): δ 28.5



S2 **1c**

Under an Ar atmosphere, **S2** (1.07 g, 2.8 mmol) was dissolved in dry THF (9.3 mL) and then *n*-BuLi (1.57 M in hexane, 1.96 mL, 3.08 mmol) was added dropwise to the solution at –78 ºC. The mixture was stirred at –78 ºC for 1 h, and then B(O*i*Pr)$_3$ (775 μL, 3.36 mmol) was added and warmed up to room temperature

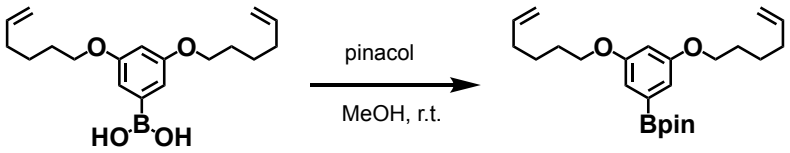
over 2 h. After warmed up, 1N HCl aq. was added and the product was extracted with *tert*-butyl methyl ether and then combined extract was washed by brine and dried over $MgSO_4$. After solvent was evaporated, the residue was purified by column chromatography (*n*-hexane/EtOAc = 9:1, then EtOAc only) to give **1c** (405 mg, 40%).

Physical data of **1c**

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.99 (s, 2H), 6.91 (d, J = 2.3 Hz, 2H), 6.47 (t, J = 2.3 Hz, 1H), 5.81 (ddt, J = 17.1, 10.2, 6.7 Hz, 2H), 5.04-4.99 (m, 2H), 4.97-4.93 (m, 2H), 3.92 (t, J = 6.6 Hz, 4H), 2.07-2.02 (m, 4H), 1.73-1.66 (m, 4H), 1.43-1.39 (m, 8H).

^{13}C NMR (100 MHz, DMSO-d_6): δ 159.3, 138.7, 114.8, 112.0, 103.1, 67.2, 33.2, 28.6, 28.0, 25.1. The boron-bound carbons were not detected due to quadrupole relaxation.

^{11}B NMR (160 MHz, DMSO-d_6): δ 28.3



1b **1b-pin**

Boronic acid **1b** (5.5 mg, 17 μmol) was treated with pinacol (6.0 mg, 51 μmol) in methanol. After the mixture was evaporated, the residue was purified by GPC to give **1b-pin** (4.29 mg, 71%).

Physical data of **1b-pin**

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.92 (d, J = 2.4 Hz, 2H), 6.55 (t, J = 2.3 Hz, 1H), 5.83 (ddt, J = 17.0, 10.3, 6.7 Hz, 2H), 5.05-5.00 (m, 2H), 4.98-4.95 (m, 2H), 3.97 (t, J = 6.4 Hz, 4H), 2.15-2.09 (m, 4H), 1.78 (quin, J = 7.0 Hz, 4H), 1.57-1.52 (m, 4H), 1.33 (s, 12H).

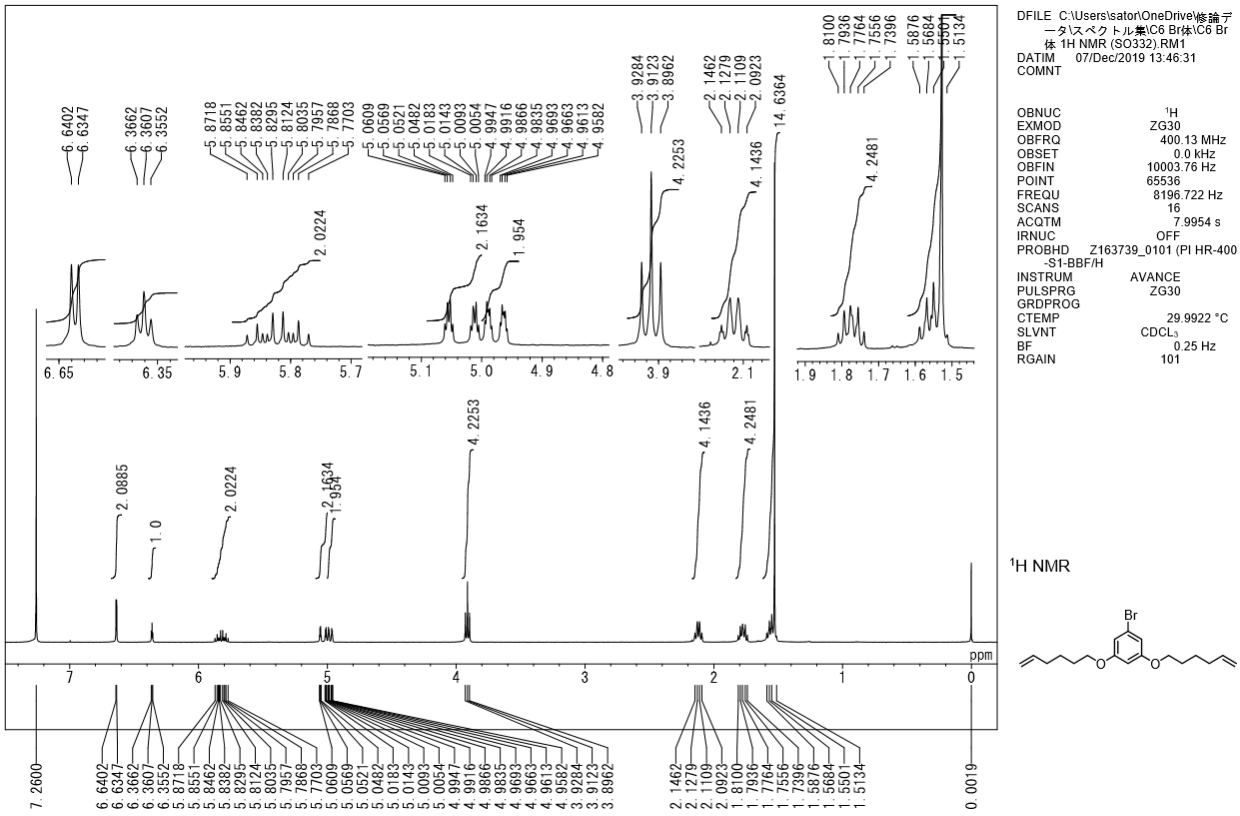
^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 138.8, 114.8, 112.5, 105.3, 84.0, 67.9, 33.6, 28.9, 25.5, 25.0. The boron-bound carbons were not detected due to quadrupole relaxation.

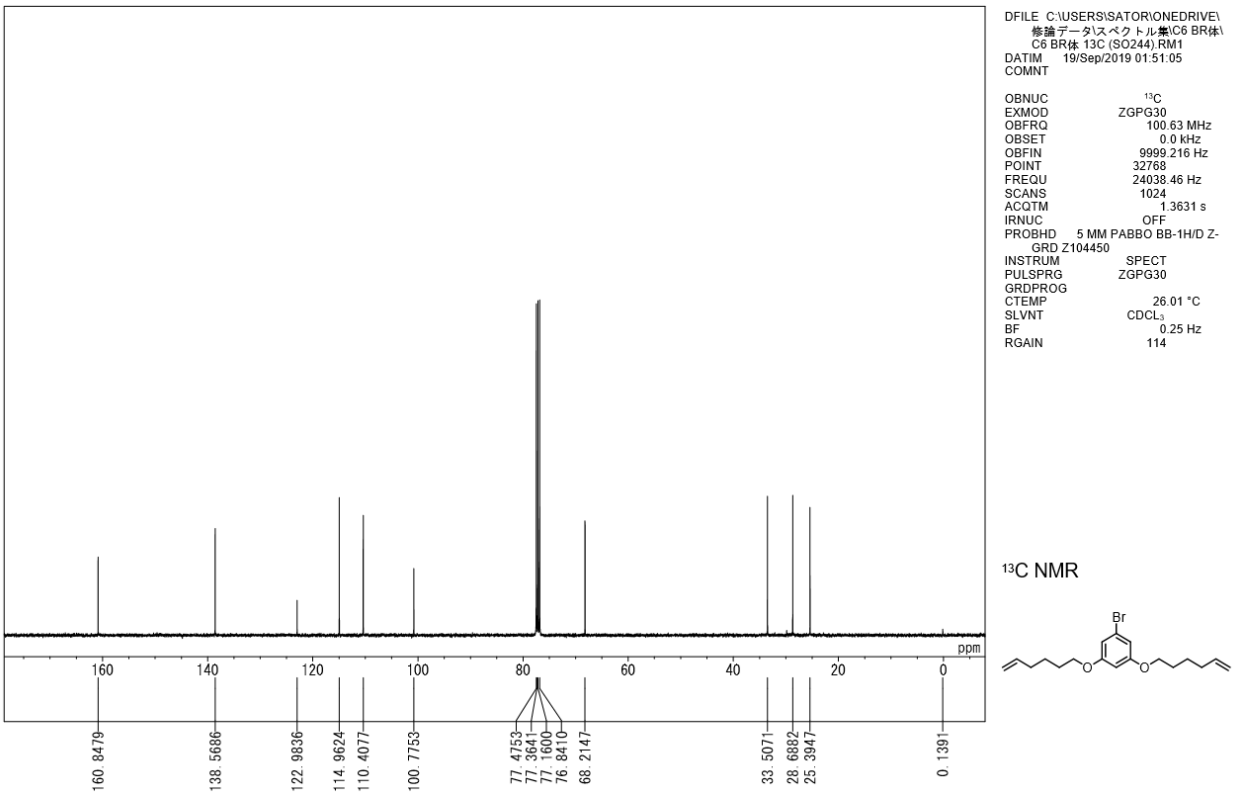
^{11}B NMR (160 MHz, $CDCl_3$): δ 32.2

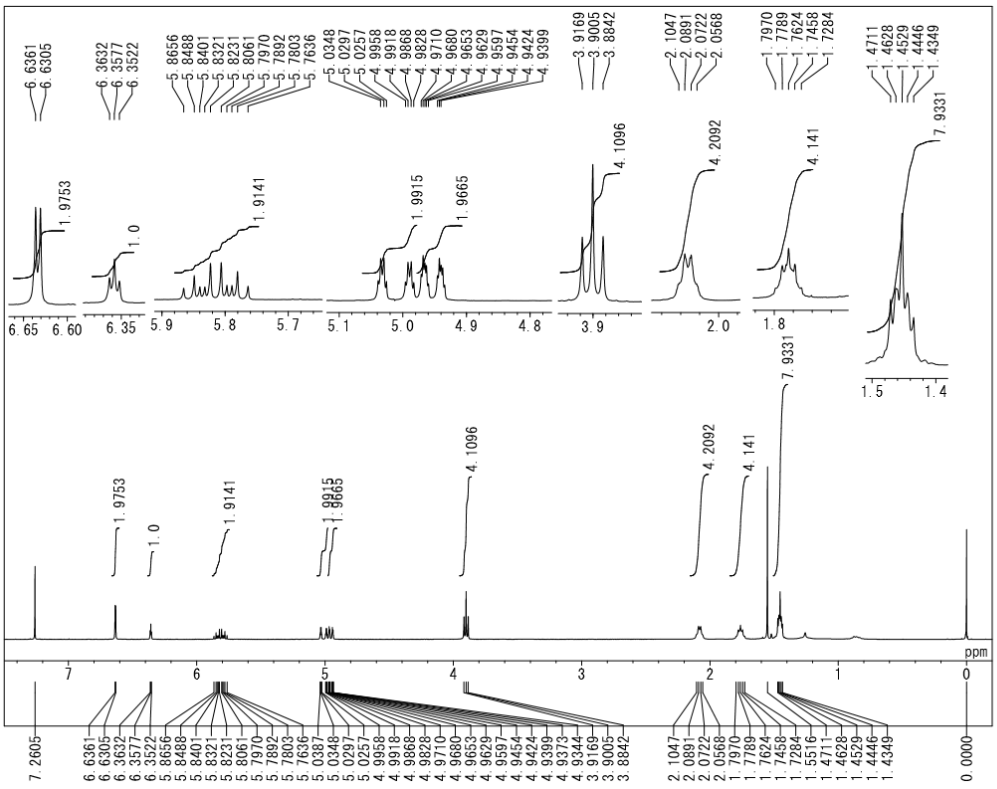
HRMS (MALDI$^+$): *m*/*z* calcd. for $C_{24}H_{37}BO_4Na$: 423.2681, found: 423.2678 $[M+Na]^+$.

IR (ATR): 3075, 2977, 2934, 2868, 1641, 1586, 1429, 1356, 1308, 1164, 1138, 1052, 910, 851, 706 cm^{-1}.

7. ^{1}H NMR, ^{13}C NMR and ^{11}B NMR spectra



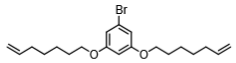


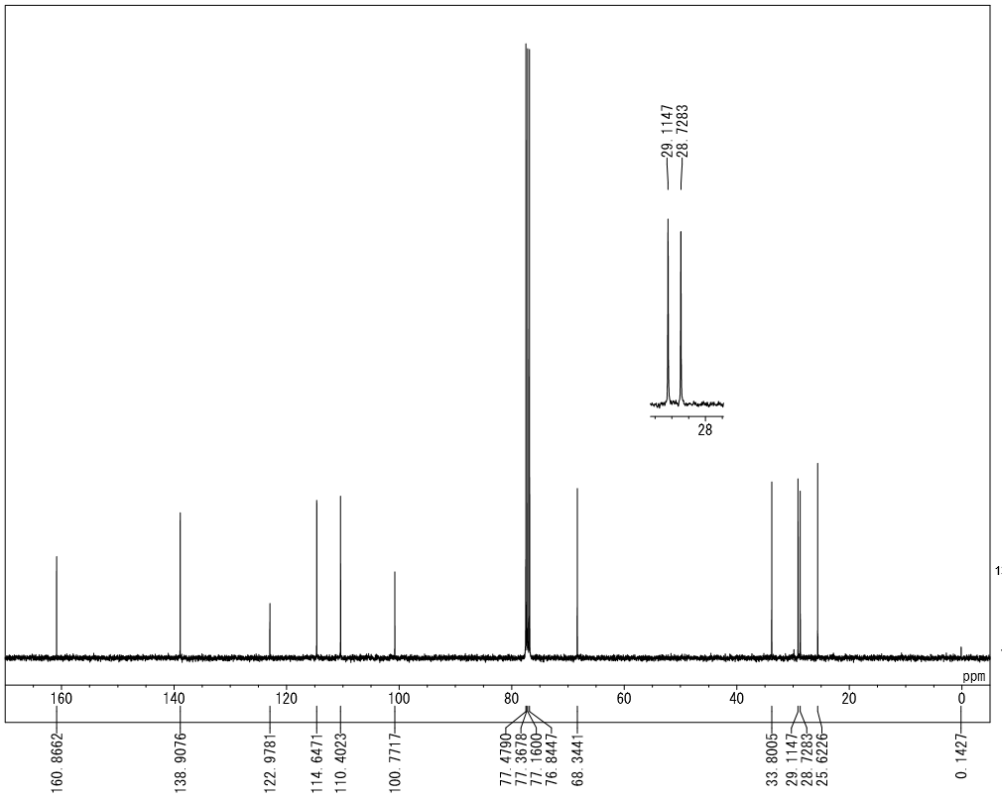


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C7 Br体\C7 Br体 1H (SO270).RM1
DATIM 03/Sep/2019 10:29:13
COMNT

OBNUC	^{1}H
EXMOD	proton.jxp
OBFRQ	398.78 MHz
OBSET	2.0 kHz
OBFIN	199.2106 Hz
POINT	131072(ZeroFill:×8)
FREQU	7476.077 Hz
SCANS	8
ACQTM	2.1915 s
IRNUC	^{1}H
PROBHD	
INSTRUM	JNM-ECZ400S/L1
PULSPRG	
GRDPROG	
CTEMP	24.1 °C
SLVNT	CHLOROFORM-D
BF	0.25 Hz
RGAIN	56

^{1}H NMR

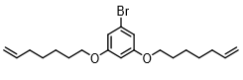


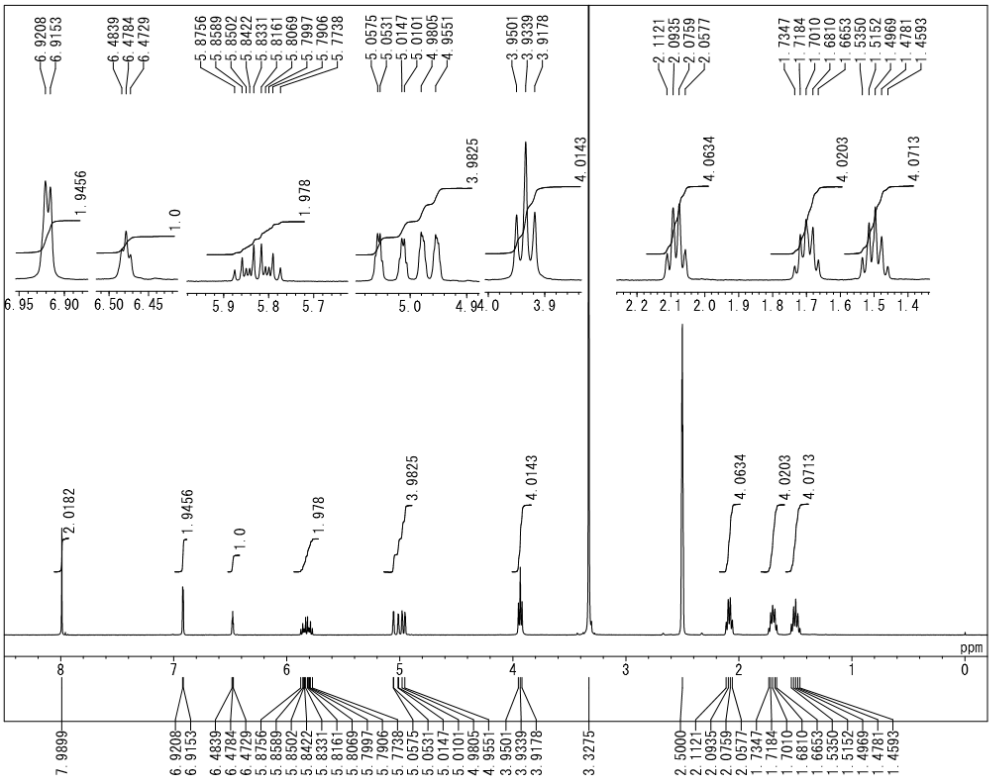


DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C7 BR体\C7 BR体 13C (SO270).$RM1
ORGFILE D:\カーボンNMR\編集前\SO270 C7BR体 13C\PDATA1\1\1
DATIM 21/Sep/2019 05:37:41
COMNT

OBNUC	^{13}C
OFR	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.216 Hz
PW1	7.1 µs
PW2	7.1 µs
PW3	14.2 µs
PI1	2.0 ms
PI2	0.0035 ms
PI3	0.0 ms
LOOP1	0
POINT	32768
SCANS	1024
DUMMY	4
FREQU	24038.46 Hz
ACQTM	1.3631 s
PD	2.0 s
RGAIN	64

^{13}C NMR

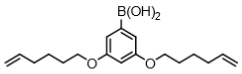


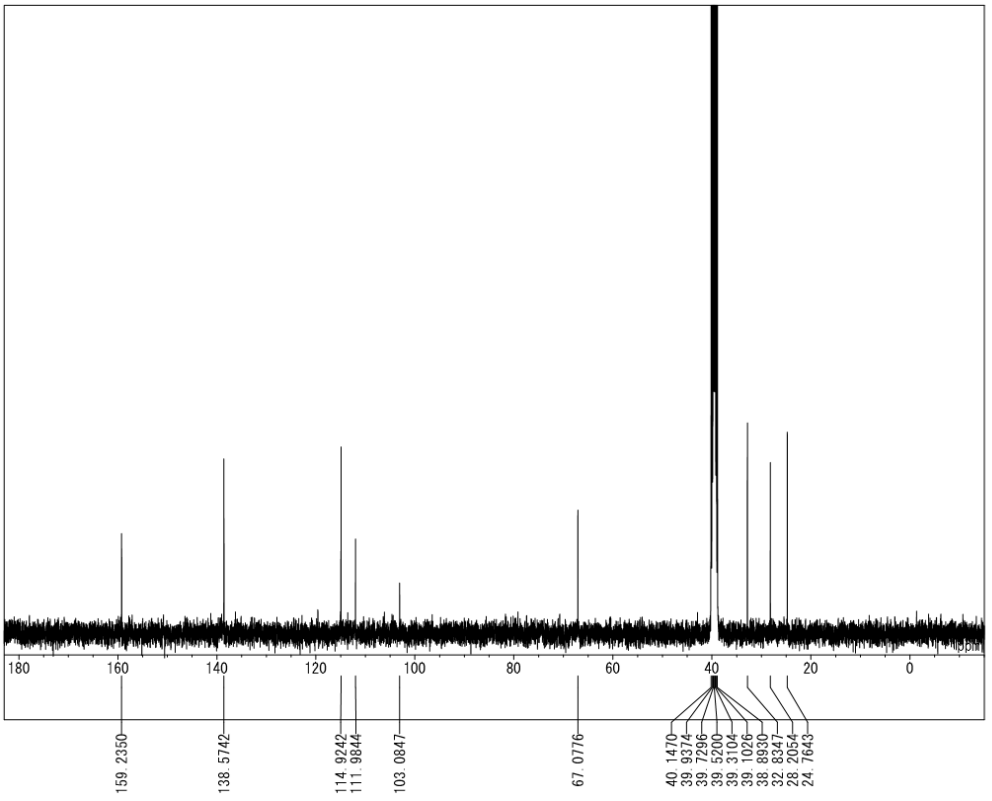


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C6 B(OH)2体\C6 B(OH)2 DMSO (SO287).RM1
DATIM 29/Sep/2019 12:54:58
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.18 MHz
OBSET	0.0 kHz
OBFIN	10016.44 Hz
POINT	32768
FREQU	8223.685 Hz
SCANS	16
ACQTM	3.9846 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZG30
GRDPROG	
CTEMP	24.61 °C
SLVNT	DMSO
BF	0.25 Hz
RGAIN	228

^{1}H NMR

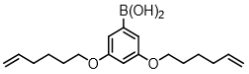




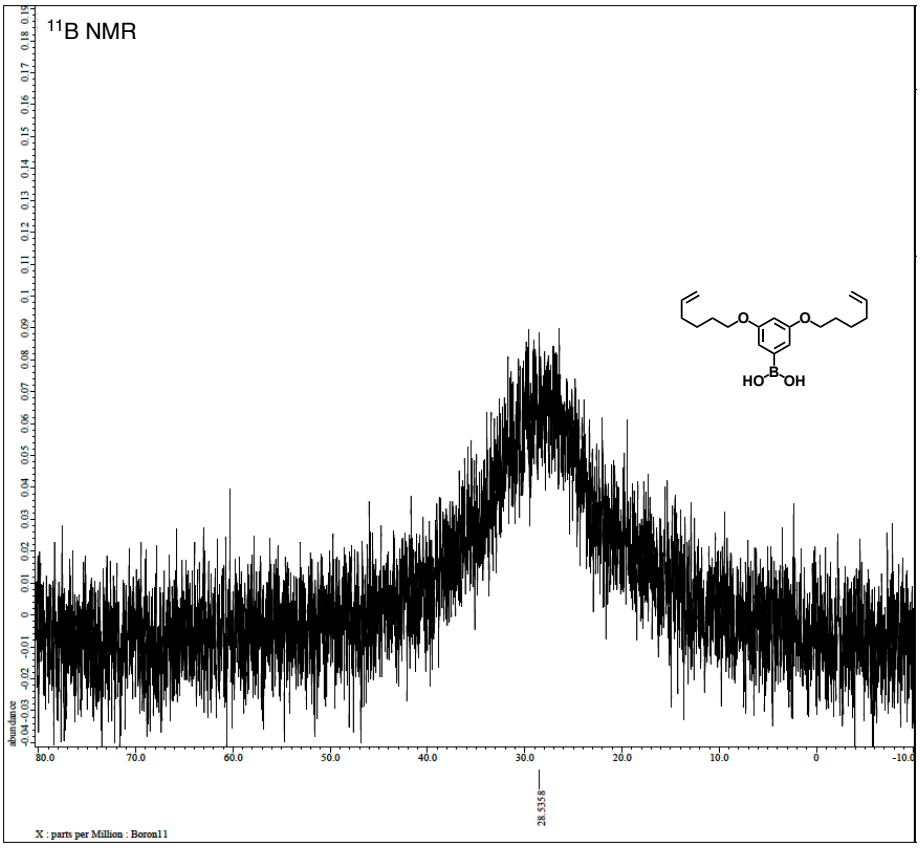
DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 B(OH)2体\C6 B(OH)2 DMSO 13C (SO287).$RM1
DATIM 29/Sep/2019 21:59:47
COMNT

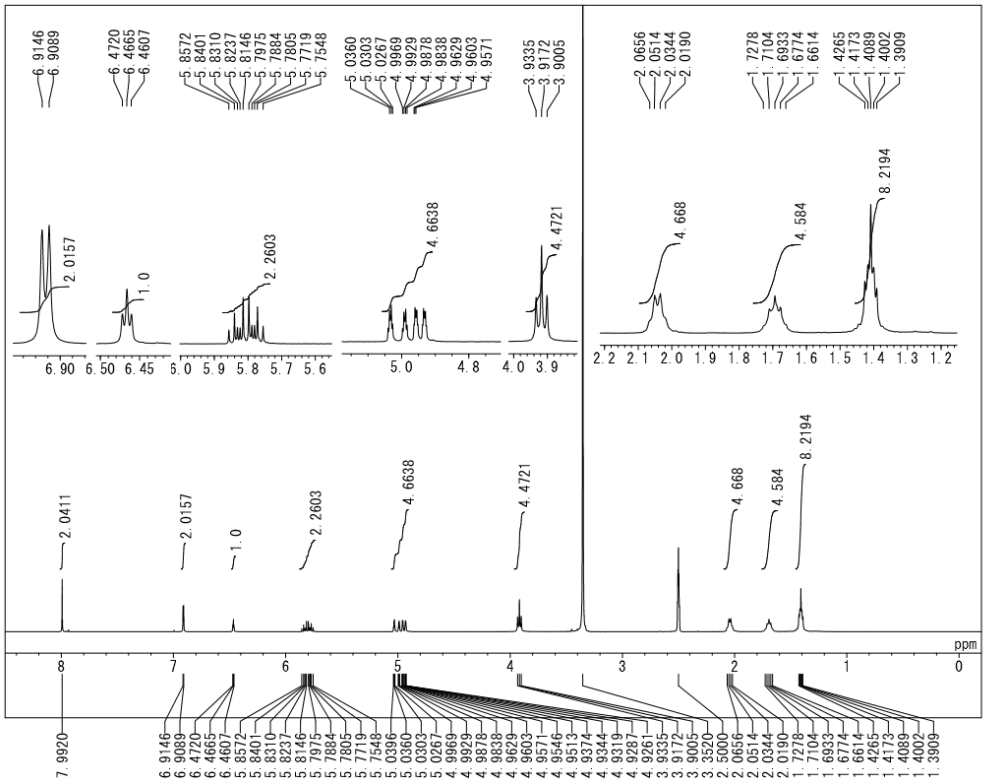
OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.211 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	2048
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	25.81 °C
SLVNT	DMSO
BF	0.25 Hz
RGAIN	81

^{13}C NMR



^{11}B NMR

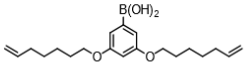


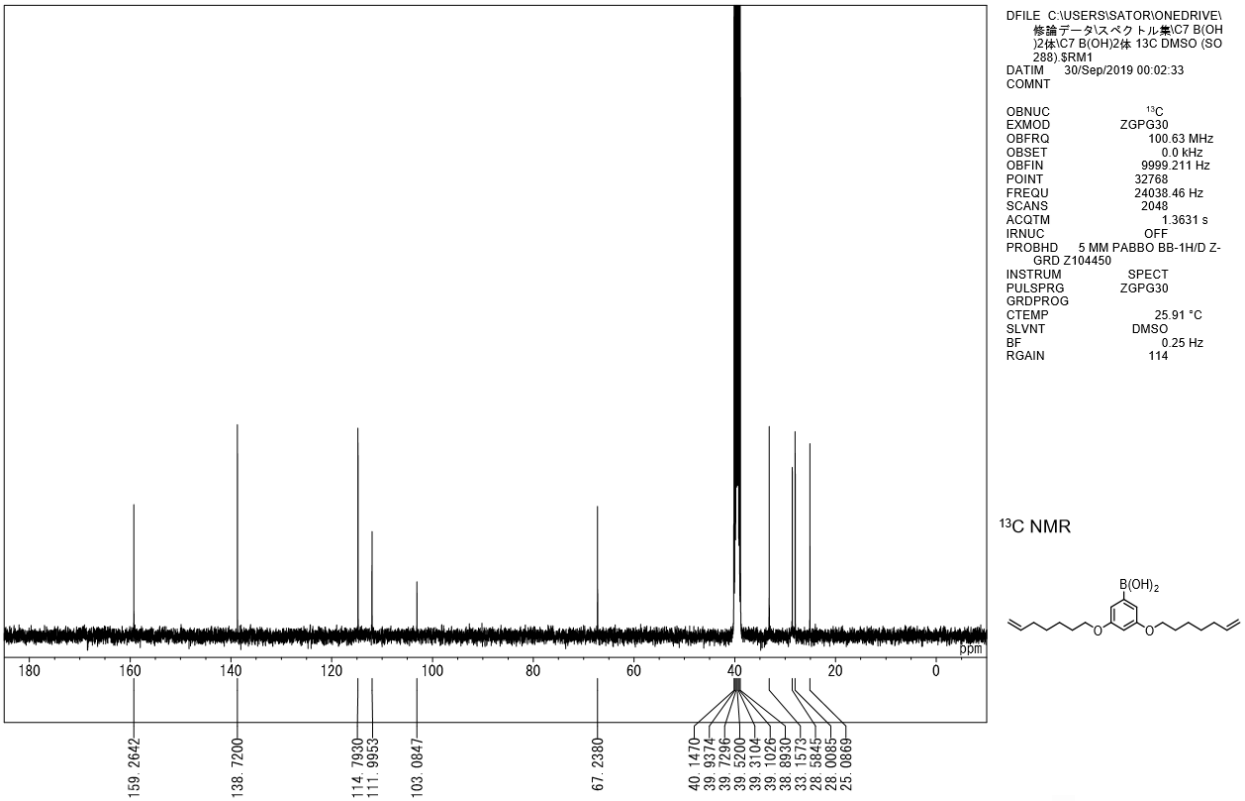


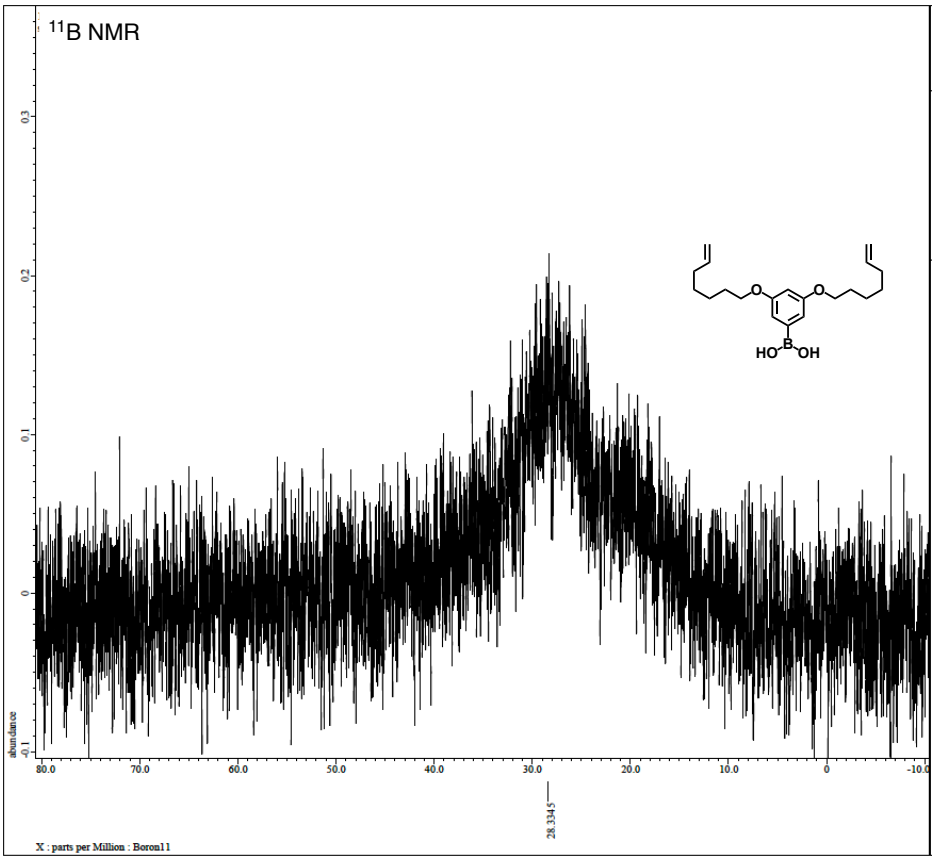
DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C7 B(OH)2体\C7 B(OH)2体 1H DMSO (SO288).R M1
DATIM 29/Sep/2019 19:31:39
COMNT

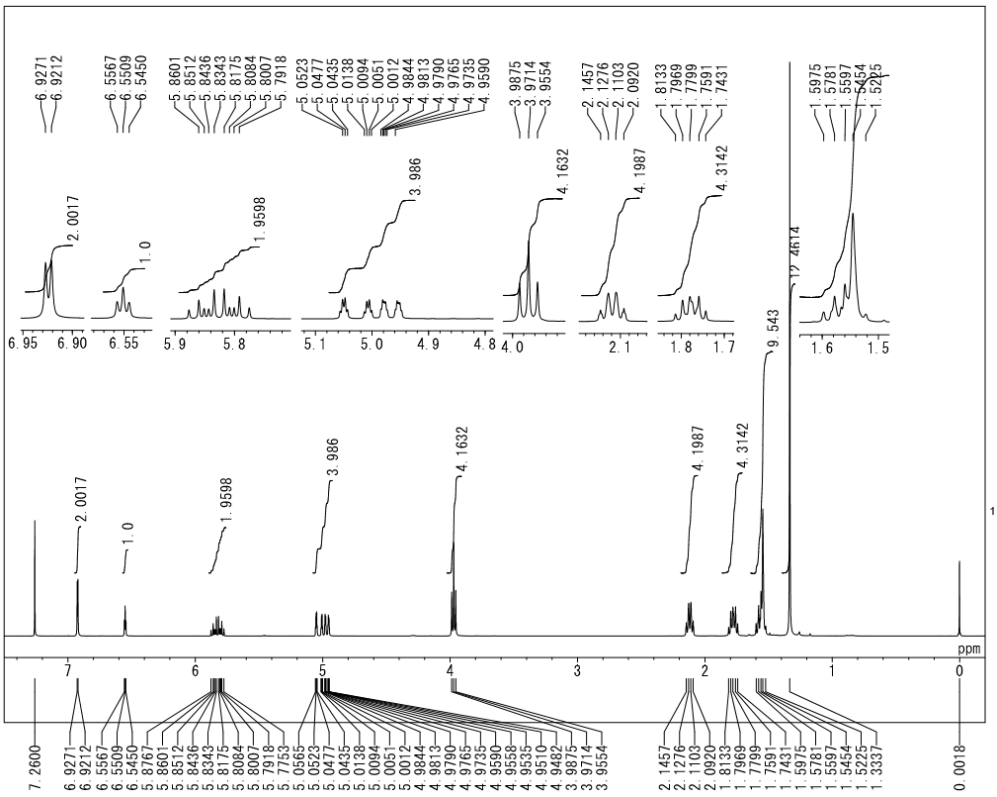
OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.18 MHz
OBSET	0.0 kHz
OBFIN	10016.44 Hz
POINT	32768
FREQU	8223.685 Hz
SCANS	16
ACQTM	3.9846 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZG30
GRDPROG	
CTEMP	24.51 °C
SLVNT	DMSO
BF	0.25 Hz
RGAIN	161

^{1}H NMR




DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C7 B(OH)2体\C7 B(OH)2体 13C DMSO (SO 288).$RM1
DATIM 30/Sep/2019 00:02:33
COMNT
OBNUC 13C
EXMOD ZGPG30
OBFRQ 100.63 MHz
OBSET 0.0 kHz
OBFIN 9999.211 Hz
POINT 32768
FREQU 24038.46 Hz
SCANS 2048
ACQTM 1.3631 s
IRNUC OFF
PROBHD 5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM SPECT
PULSPRG ZGPG30
GRDPROG
CTEMP 25.91 °C
SLVNT DMSO
BF 0.25 Hz
RGAIN 114
13C NMR
B(OH)2
ppm
180
160
140
120
100
80
60
40
20
0
159.2642
138.7200
114.7930
111.9953
103.0847
67.2380
40.1470
39.9374
39.7296
39.5200
39.3104
39.1026
38.8930
33.1573
28.5845
28.0085
25.0869

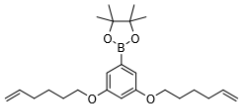

11B NMR
HO
B
OH
abundance
0.3
0.2
0.1
0
-0.1
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
28.3345
X : parts per Million : Boron11

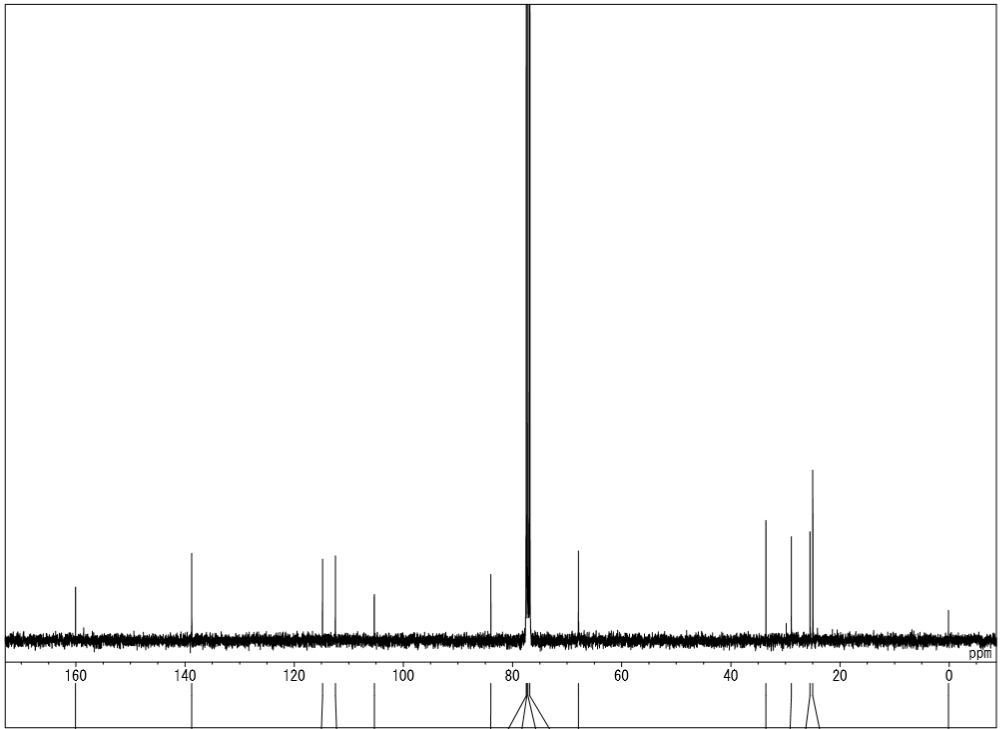


DFILE C:\Users\sator\OneDrive\修論データ\スペクトル集\C6 Bpin体\C6 Bpin体 1H.RM1
DATIM 01/Nov/2019 19:26:32
COMNT

OBNUC	^{1}H
EXMOD	ZG30
OBFRQ	400.13 MHz
OBSET	0.0 kHz
OBFIN	10003.76 Hz
POINT	65536
FREQU	8196.722 Hz
SCANS	16
ACQTM	7.9954 s
IRNUC	OFF
PROBHD	Z163739_0101 (PI HR-400-S1-BBF/H
INSTRUM	AVANCE
PULSPRG	ZG30
GRDPROG	
CTEMP	30.0035 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	101

^{1}H NMR

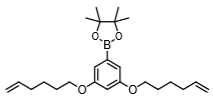


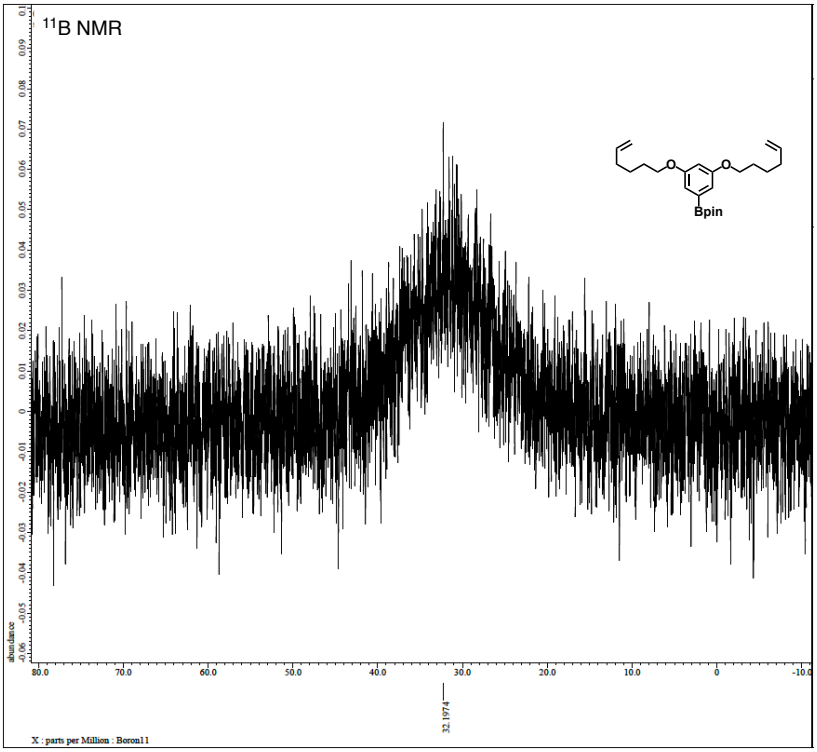


DFILE C:\USERS\SATOR\ONEDRIVE\修論データ\スペクトル集\C6 BPIN体\C6 BPIN体 13C.$RM1
DATIM 21/Sep/2019 07:42:16
COMNT

OBNUC	^{13}C
EXMOD	ZGPG30
OBFRQ	100.63 MHz
OBSET	0.0 kHz
OBFIN	9999.213 Hz
POINT	32768
FREQU	24038.46 Hz
SCANS	2048
ACQTM	1.3631 s
IRNUC	OFF
PROBHD	5 MM PABBO BB-1H/D Z-GRD Z104450
INSTRUM	SPECT
PULSPRG	ZGPG30
GRDPROG	
CTEMP	26.01 °C
SLVNT	$CDCl_3$
BF	0.25 Hz
RGAIN	81

^{13}C NMR




11B NMR
Bpin
abundance
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
32.1974
X : parts per Million : Boron11

6. X-ray Crystallographic Analysis of 3c

Single crystals of **3c** for X-ray diffraction analysis were obtained as colorless block by diffusion of toluene to a THF solution of the crude product of **3c**.

The single X-ray structure determination was performed on Rigaku RAPID (CuKα radiation, λ = 1.54187 Å). A numerical absorption correction (μ) was applied. The structure was solved by direct methods and refined by the full-matrix least-squares method on F^2 with anisotropic temperature factors for non-hydrogen atoms. All the hydrogen atoms were located at the calculated positions and refined with riding. The disordered alkylene chains of **3c** were restricted by DFIX and DELU. Crystallographic data collection and refinement information is listed in Table S1. CCDC reference number 2195814.

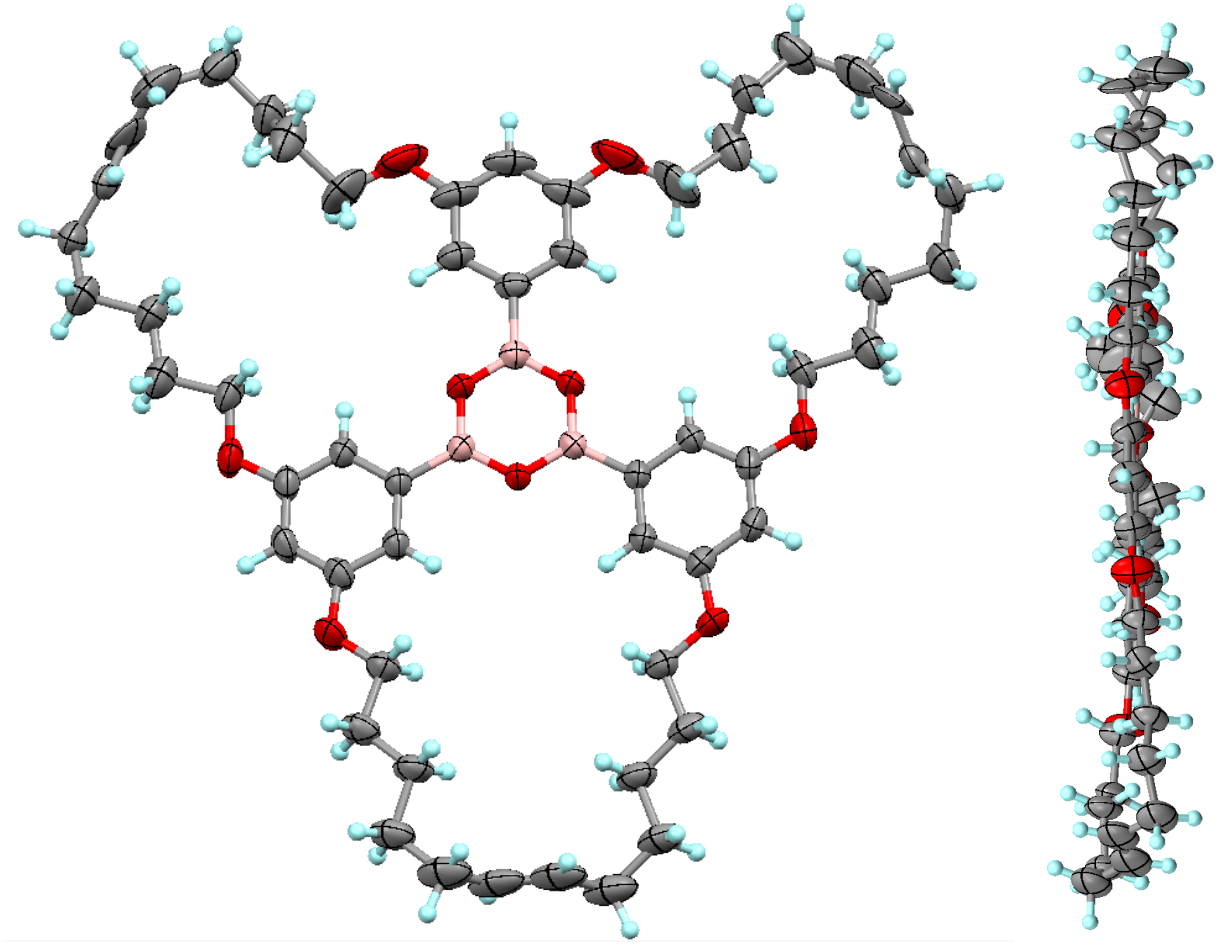


Table S1. Crystal data and structure refinement for 3c

CCDC number	2195814
Identification code	191002os
Empirical formula	$C_{54}H_{75}B_3O_9$
Formula weight	900.61
Temperature	193 K
Wavelength	1.54187 Å
Crystal system	monoclinic
Space group	*C*2/c
Unit cell dimensions	a = 15.6791(3) Å α = 90°.
	b = 19.9517(4) Å β = 110.201(8)°.
	c = 18.0668(3) Å γ = 90°.
Volume	5304.1(3) Å^3
Z	4
Density (calculated)	1.128 Mg/m^3
Absorption coefficient	0.587 mm^{-1}
F(000)	1944.00
Crystal size	0.30 x 0.30 x 0.15 mm^3
Theta range for data collection	3.73 to 68.30°.
Index ranges	-18<=h<=18, -24<=k<=24, -21<=l<=21
Reflections collected	30762
Independent reflections	4866 [R(int) = 0.0566]
Completeness to theta = 25.24°	99.8 %
Absorption correction	multi-scan
Max. and min. transmission	0.916 and 0.632
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4866 / 36 / 381
Goodness-of-fit on F^2	1.054
Final R indices [I>2sigma(I)]	R_1 = 0.0830, wR_2 = 0.1690
R indices (all data)	R_1 = 0.1492, wR_2 = 0.1976
Largest diff. peak and hole	0.24 and -0.19 e/Å^{-3}

9. References

S1) R. El-Haggar, K. Kamikawa, K. Machi, Z. Ye, Y. Ishino, T. Tsumuraya, I. Fujii, *Bioorg. Med. Chem. Lett.* **2010**, *20*, 1169–1172.

S2) C. Simocko, T. C. Young, K. B. Wagener, *Macromolecules*, **2015**, *48*, 5470-5473.