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Supporting Information

Inherently Chiral Cavitand Curvature: Diastereoselective Oxidation of Tethered Allylsilanes

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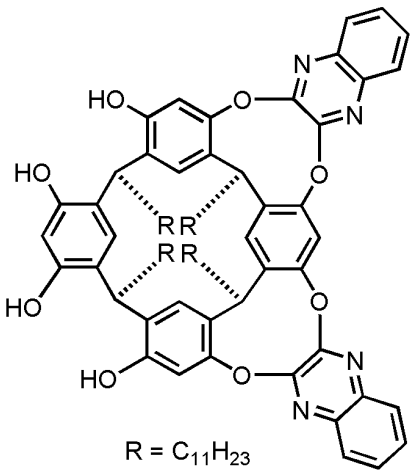
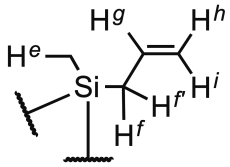
4. The analytical HPLC report for *rac*-**1**, which was helped by Daicel Corporation CPI Company.
5. ^{1}H NMR and ^{13}C NMR spectra for all new compounds of *rac*-**1**, *rac*-**2**, *rac*-**3**, *rac*-**4**, *rac*-**5**, *rac*-**6**, *rac*-**7**, *rac*-**8**, *rac*-**9**, *rac*-**10**, *rac*-**11**, *rac*-**12**, *rac*-**13**, *rac*-**14**, *rac*-**15**, *rac*-**16**, **17**, **18**, *rac*-**19**, and *rac*-**20**.

1. Synthesis of *cis*-formed di-quinoxaline-spanned resorcin[4]arene (Scheme S2): To a 50 mL flask charged with a suspension of resorcin[4]arene (1.99 g, 1.8 mmol) in freshly distilled pyridine (9 mL) was added 2,3-dichloroquinoxaline (716 mg, 3.6 mmol) and DABCO (4.04 g, 36 mmol) at ambient temperature. After stirred at 75 ºC for 1.5 h, the mixture was allowed to cool to ambient temperature, and filtered through a pad of celite. The filtrate was evaporated off, and the resultant residue was dissolved into toluene (50 mL) and neutralized with 1M aq. HCl (20 mL). The organic phase was carefully separated with the aid of centrifuge-apparatus, and dried over Na_2SO_4, concentrated *in vacuo* to give crude products of 2.45 g. Purification of short-plugged silica-gel column chromatography (CH_2Cl_2/EtOAc = 9/1) was followed by additional silica-gel column chromatography (toluene/EtOAc = 9/1), which yielded desired molecules of 392 mg (16%) as pale yellow solid materials. This operation was repeated ten times, giving 4.0 g of target molecules. The 4 g of sample was recrystallized from mixed solvents of 45 mL of EtOAc and 100 mL of CH_3CN, and 3.53 g of the white colored-desired molecules was obtained in pure form. For data of *cis*-diquinoxaline-spanned resorcin[4]arene: R_f values 0.5 (toluene/EtOAc = 2/1). ^{1}H NMR (400 MHz, $(CD_3)_2CO$) 8.74 (brs, 4H, -OH), 8.35 (s, 1H), 8.10 (d, J = 7.8 Hz, 2H), 7.94 (s, 1H), 7.81-7.74 (m, 6H), 7.66 (t, J = 7.7 Hz, 2H), 7.49 (s, 2H), 6.18 (s, 1H), 5.67 (t, J = 8.2 Hz, 2H), 4.29 (t, J = 7.9 Hz, 2H), 2.47-2.28 (m, 8H), 1.47-1.29 (m, 72H), 0.91-0.87 (m, 12H) ppm; ^{1}H NMR (400 MHz, $CDCl_3$) 8.32 (s, 1H), 7.95 (d, J = 7.9 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 7.59-7.51 (m, 4H), 7.33 (s, 1H), 7.21 (s, 2H), 7.13 (s, 2H), 7.03 (s, 1H), 7.00 (brs, 2H, -OH), 6.65 (brs, 2H, -OH), 6.10 (s, 1H), 5.55 (t, J = 8. 0 Hz, 2H), 4.22 (t, J = 7.7 Hz, 2H), 2.27-2.14 (m, 8H), 1.44-1.27 (m, 72H), 0.90-0.87 (m, 12H) ppm; ^{13}C NMR (100 MHz, $(CD_3)_2CO$) 153.75, 153.68, 153.2 (two peaks are



overlapped), 152.5, 140.71, 140.67, 138.2 (two peaks are overlapped), 131.3, 130.8, 130.5, 130.4, 129.0, 128.7, 126.0, 125.9, 125.4, 124.7, 119.0, 111.1, 103.8, 35.3, 34.7, 34.3, 32.81, 32.79, 30.7, 30.61, 30.57, 30.50 (many peaks are overlapped), 30.31 (many peaks are overlapped), 30.26, 30.18, 30.11 (many peaks are overlapped), 29.9, 29.7 (many peaks are overlapped), 29.5, 29.3, 29.2, 29.1, 23.5 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1358 $[MH]^+$; IR (neat) 3307 (-OH), 2913, 2849, 1487, 1412, 1332, 1148, 754 cm^{-1}; HRMS (MALDI-TOF) calcd for $C_{88}H_{117}N_4O_8$: 1357.8866 $[MH]^+$, Found: 1357.8853.

2. The ^{1}H NMR stacks (Figure S1) of allylsilane moieties for Table 2.



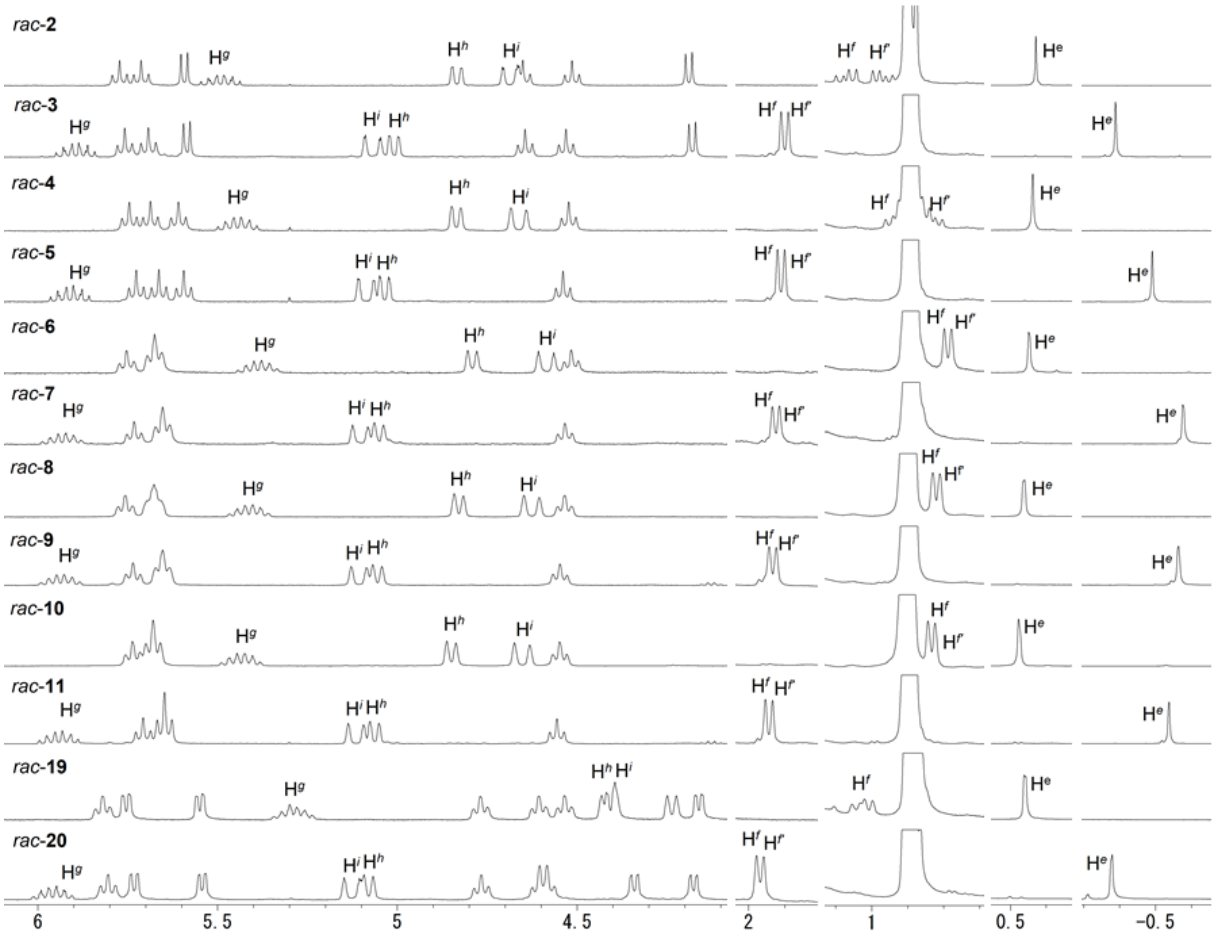


Figure S1. Portions of the ^{1}H NMR spectra (400 MHz, $CDCl_3$) for series of allylsilanes those include *rac*-**2**, -**3**, -**4**, -**5**, -**6**, -**7**, -**8**, -**9**, -**10**, -**11**, -**12**, -**19**, -**20** in Table 2. The resonance labelled with alphabetical letters of H^e ~ H^i corresponds to protons in allylsilane moieties.

3. ^{1}H NMR stacks (Figure S2 and S3) of diastereomeric mixtures of epoxides.

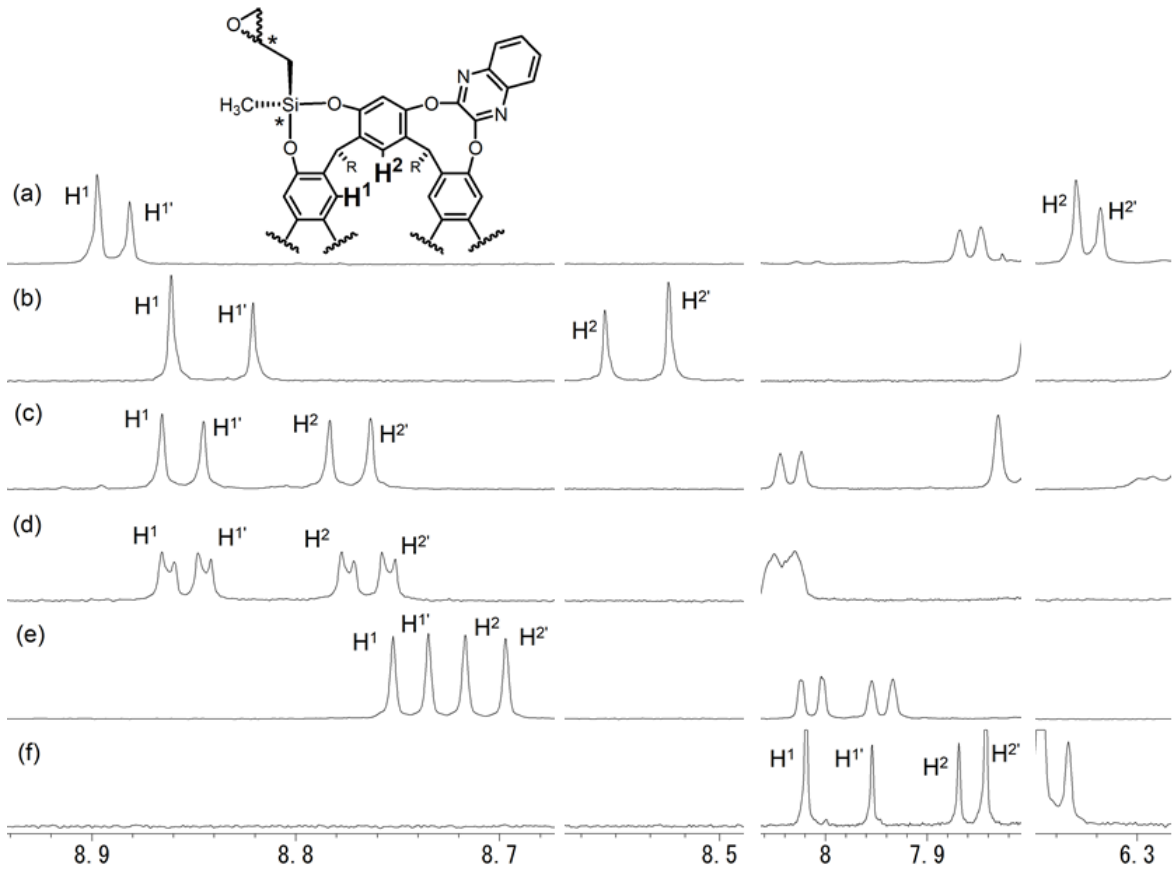


Figure S2. Portions of the ^{1}H NMR spectra (400 MHz, [D_6]benzene) for diastereomeric mixtures those are obtained in epoxidation reactions of (a) *rac*-**2** (Table 4, entry 1), (b) *rac*-**4** (Table 4, entry 3), (c) *rac*-**6** (Table 4, entry 5), (d) *rac*-**8** (Table 4, entry 8), (e) *rac*-**10** (Table 4, entry 10), and (f) *rac*-**19** (Table 7, entry 1). The resonance labelled with alphabetical letters of H^1, $H^{1'}$, H^2, and $H^{2'}$ corresponds to protons in resorcin[4]arene skeletons.

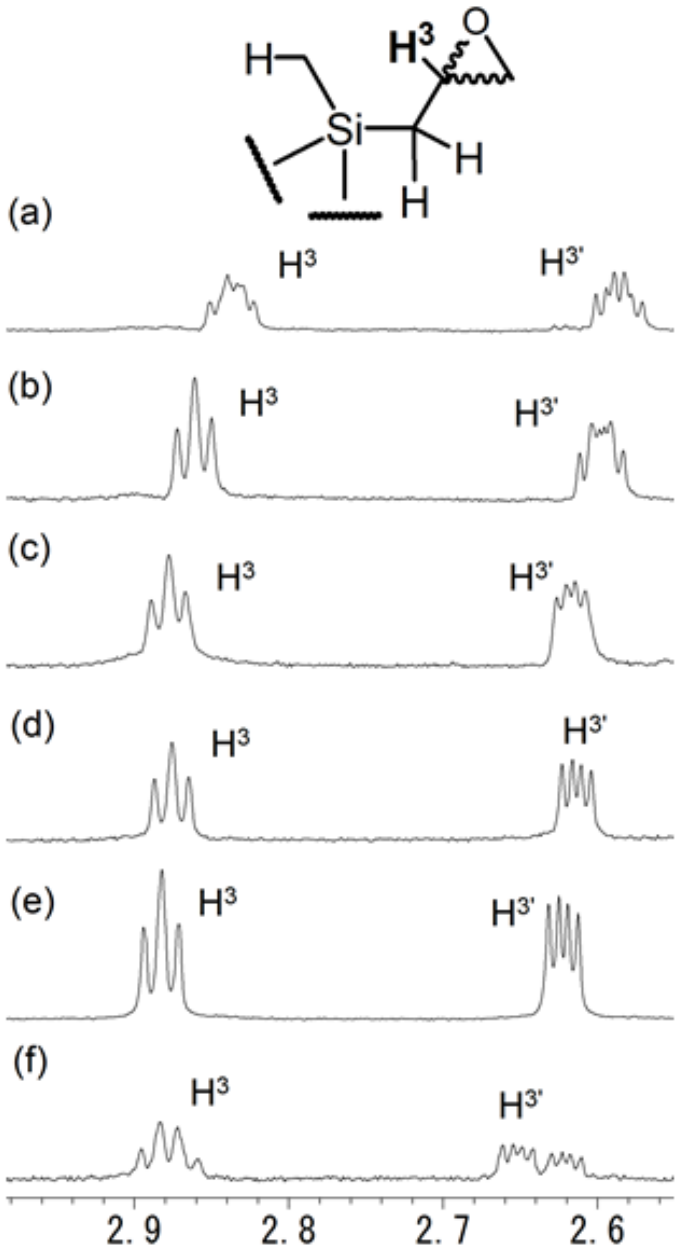


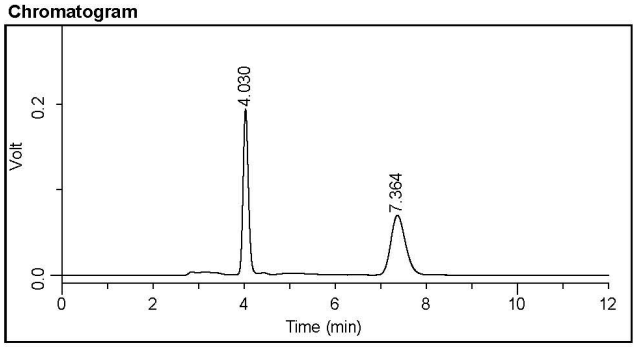
Figure S3. Portions of the ^{1}H NMR spectra (400 MHz, $CDCl_3$) for diastereomeric mixtures those are obtained in epoxidation reactions of (a) *rac*-**3** (Table 4, entry 2), (b) *rac*-**5** (Table 4, entry 4), (c) *rac*-**7** (Table 4, entry 9), (d) *rac*-**9** (Table 4, entry 11), (e) *rac*-**11** (Table 4, entry 13), and *rac*-**20** (Table 7, entry 2). The resonance labelled with alphabetical letters of H^3 and $H^{3'}$ corresponds to protons in resorcin[4]arene skeletons.

4. The analytical HPLC report for *rac*-**1**, which was helped by Daicel Corporation CPI Company.

Inherent Chiral Cavitand 片側メチレン体 推奨分析条件

Column: CHIRALPAK IG （0.46cmI.D. × 25cmL）
Eluent: DCM = 100
Flow Rate: 1.0mL/min.
Temp.: 25 ℃
Det.: 315 nm (UV)
Injection: 5 μL (1000mg/L in Eluent)

Chromatogram

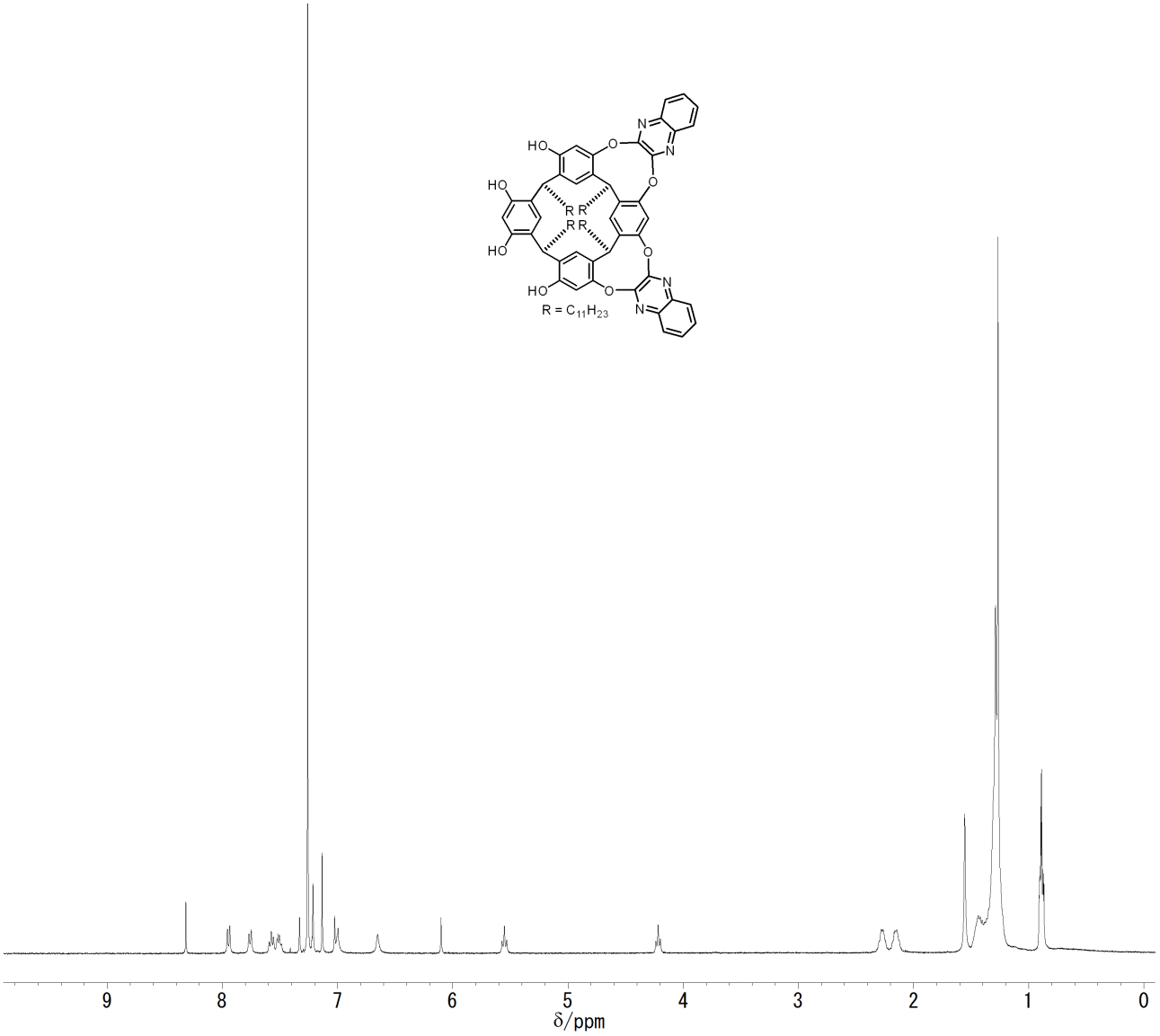


#	Time	Area	Area%	Height	Height%
1	4.030	1541911	49.86	192848	73.40
2	7.364	1550836	50.14	69872	26.60
		3092747	100.00	262720	100.00

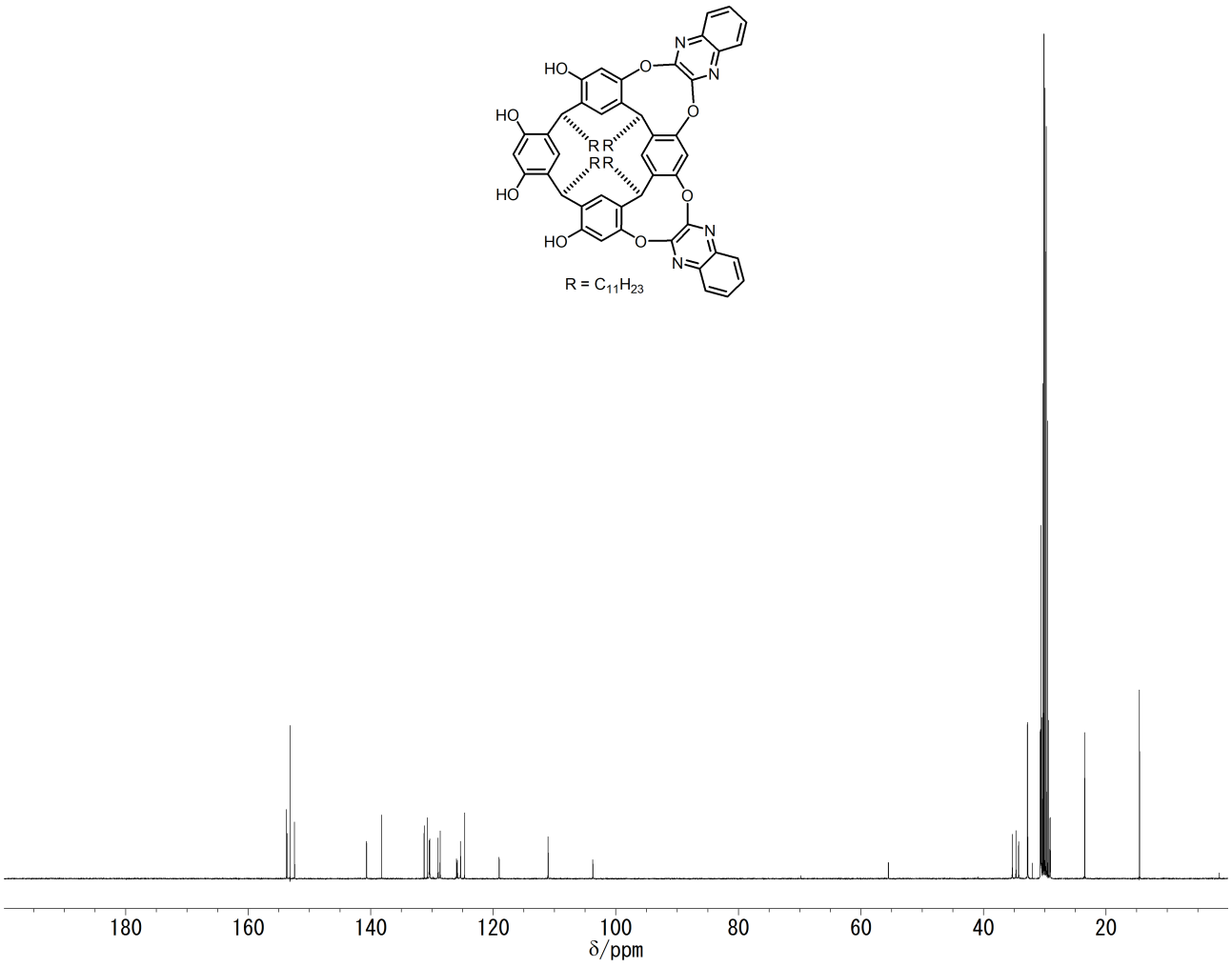
DCM=Dichloromethane

5. H NMR and ^{13}C NMR spectra for all new compounds of *rac*-**1**, *rac*-**2**, *rac*-**3**, *rac*-**4**, *rac*-**5**, *rac*-**6**, *rac*-**7**, *rac*-**8**, *rac*-**9**, *rac*-**10**, *rac*-**11**, *rac*-**12**, *rac*-**13**, *rac*-**14**, *rac*-**15**, *rac*-**16**, **17**, **18**, *rac*-**19**, and *rac*-**20**.

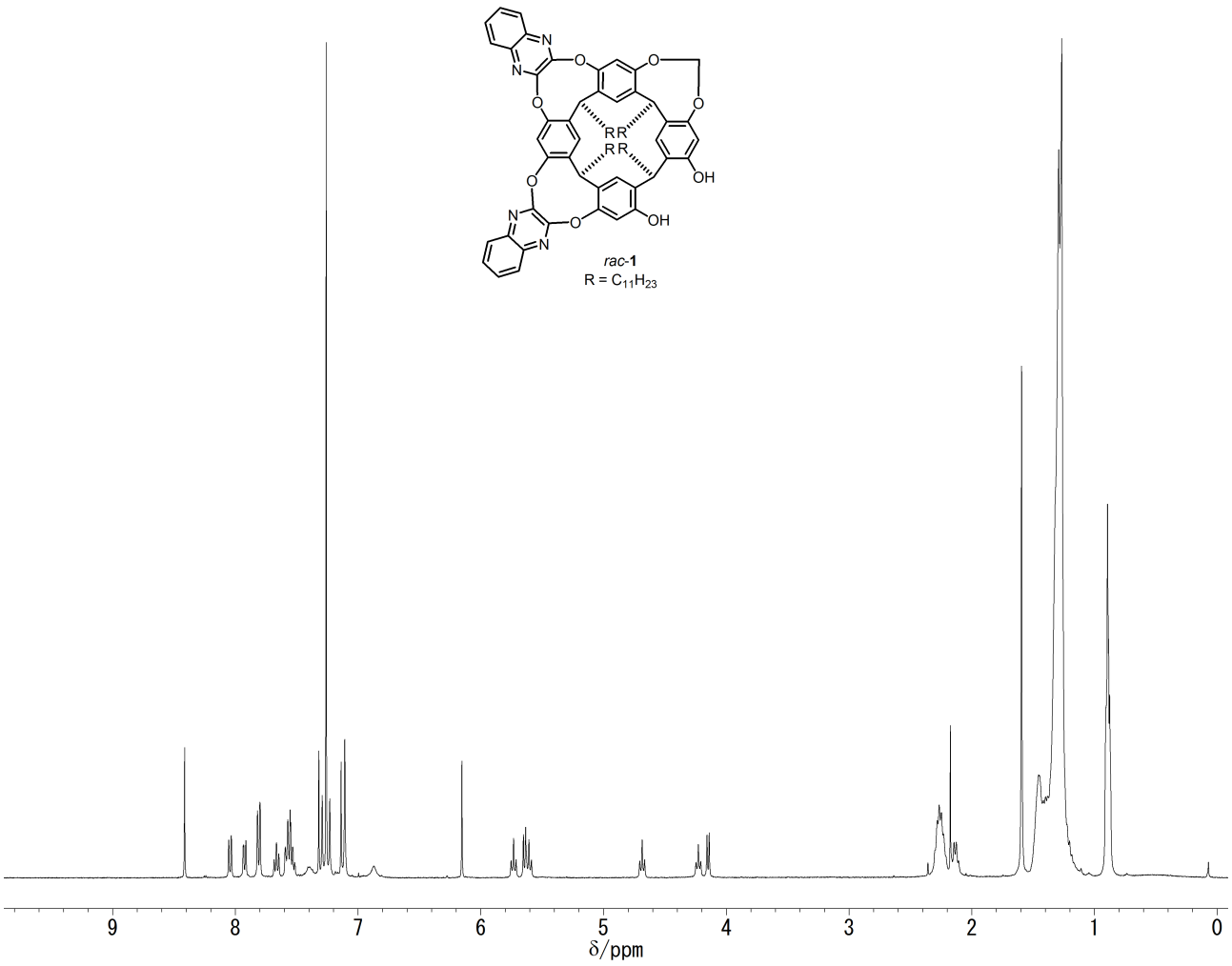
^{1}H NMR spectrum in $CDCl_3$ for *cis*-formed di-quinoxaline-spanned resorcin[4]arene.



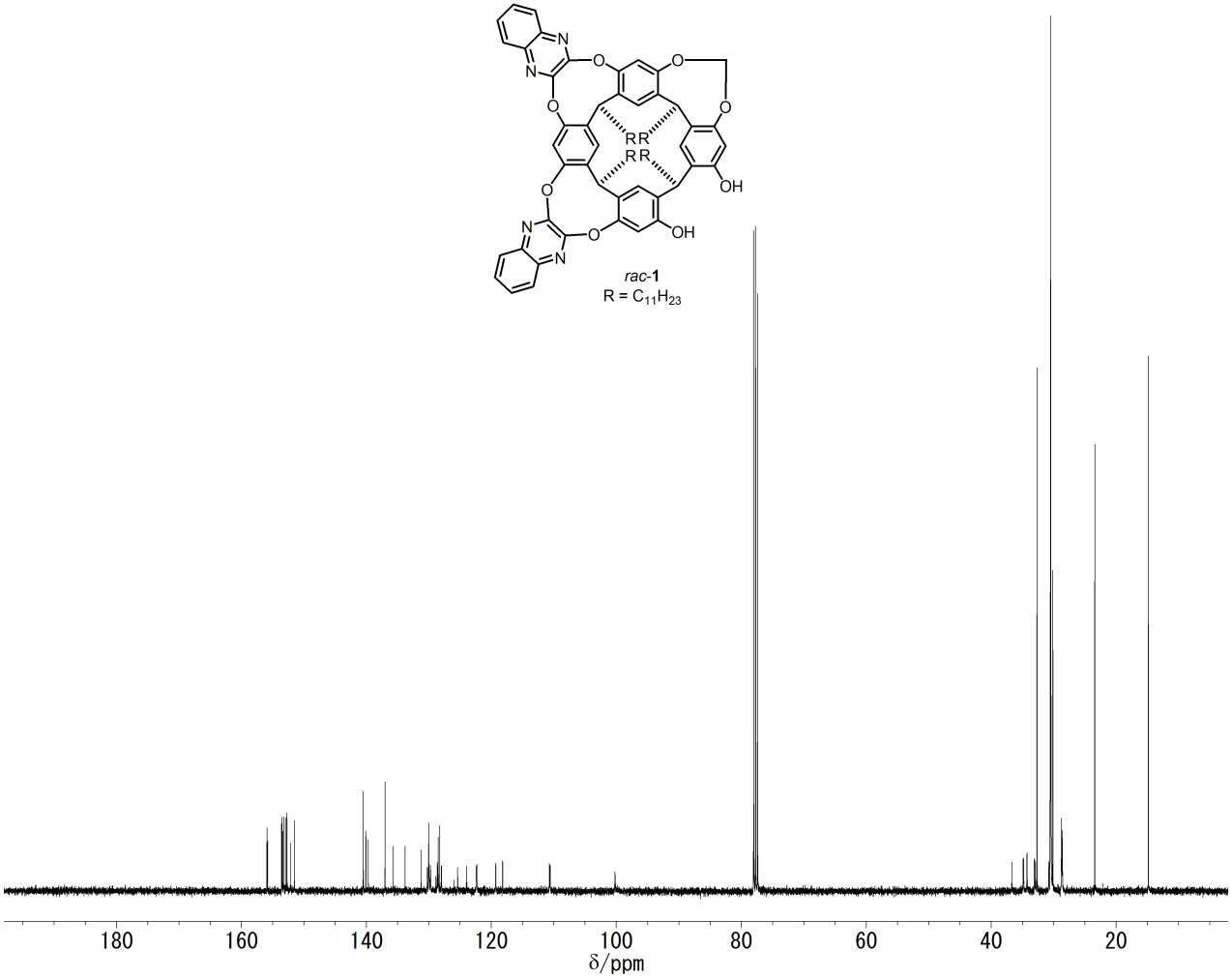
^{13}C NMR spectrum in $(CD_3)_2CO$ for *cis*-formed di-quinoxaline-spanned resorcin[4]arene.



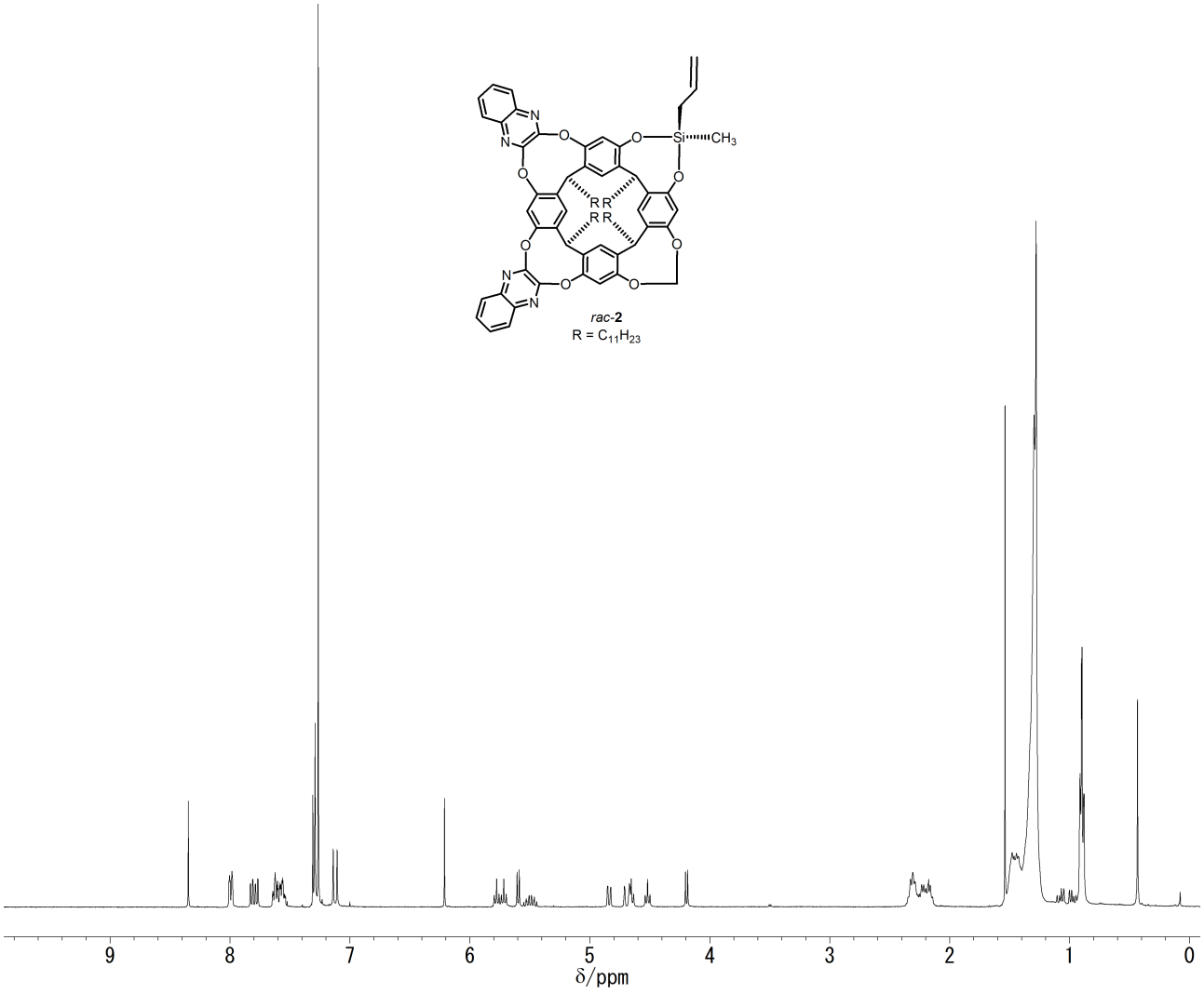
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**1**.



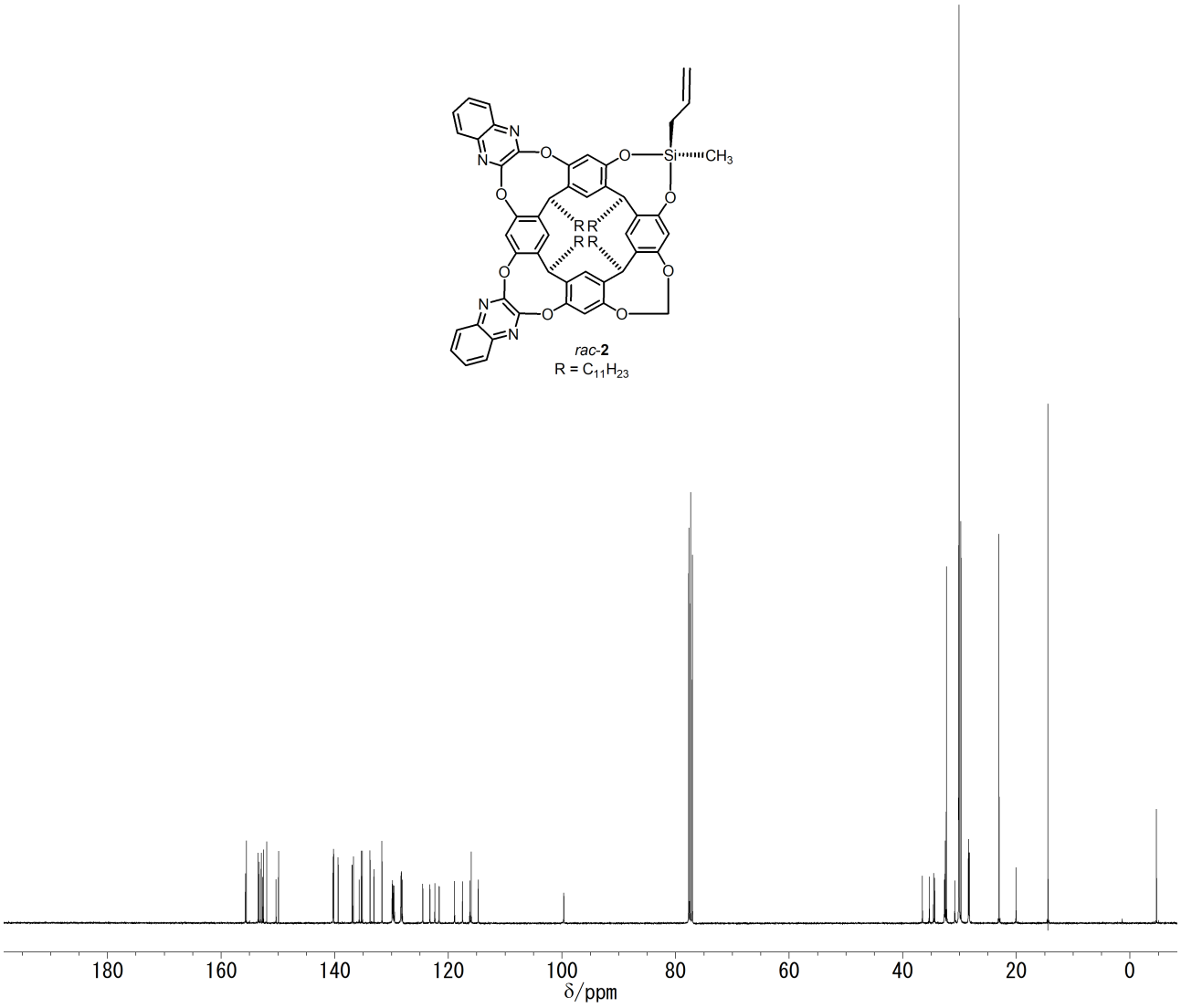
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**1**.



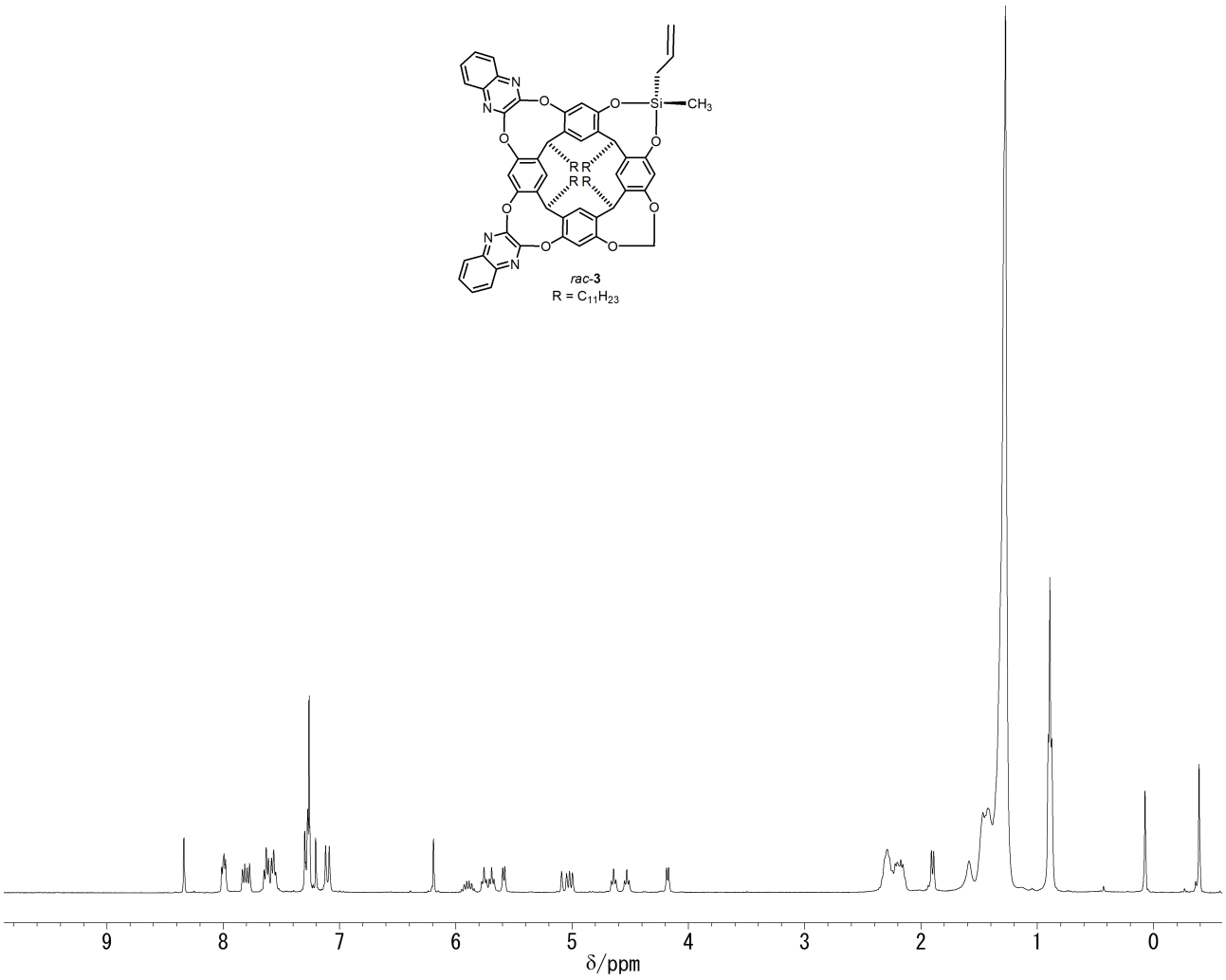
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**2**.



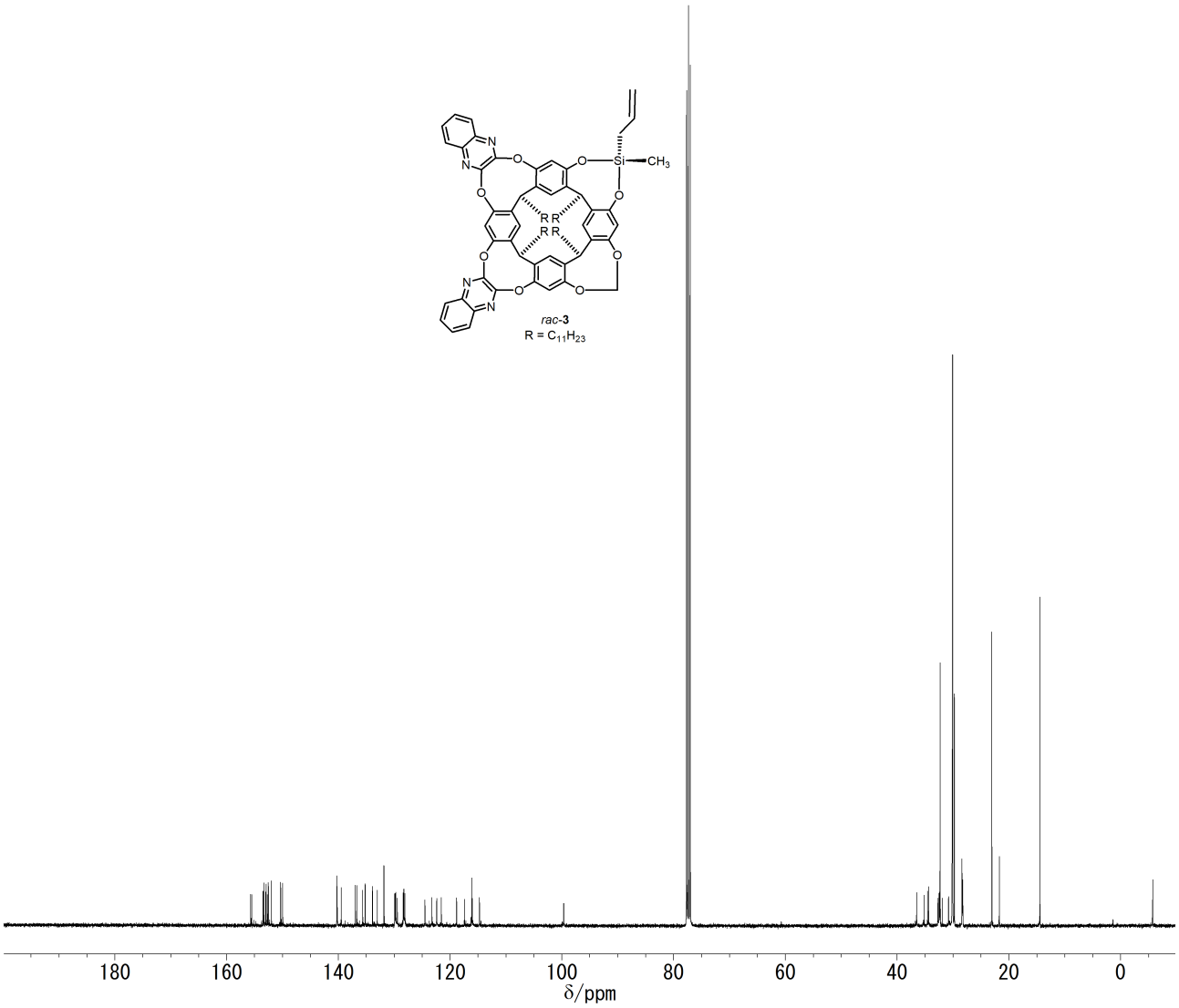
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**2**.



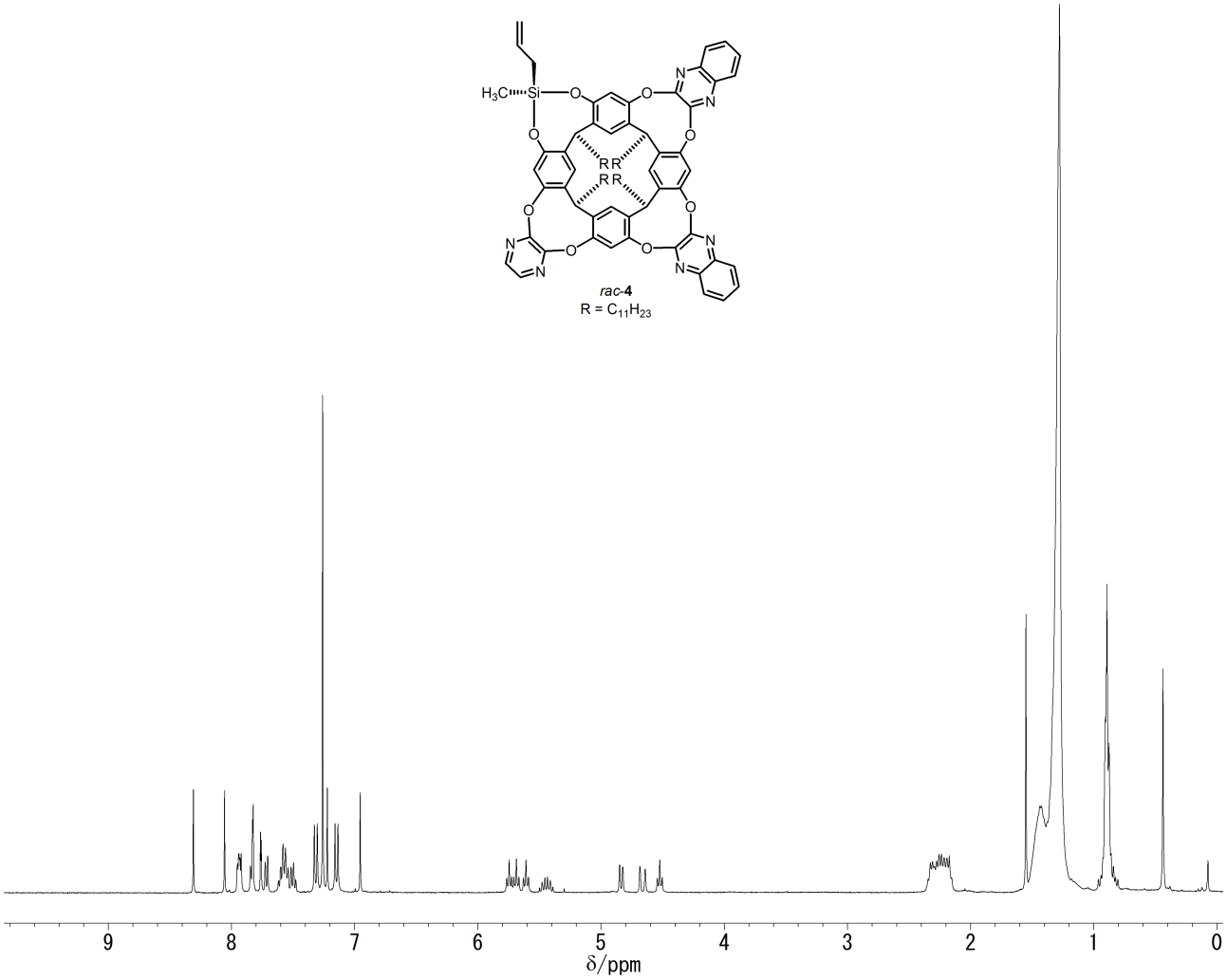
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**3**.



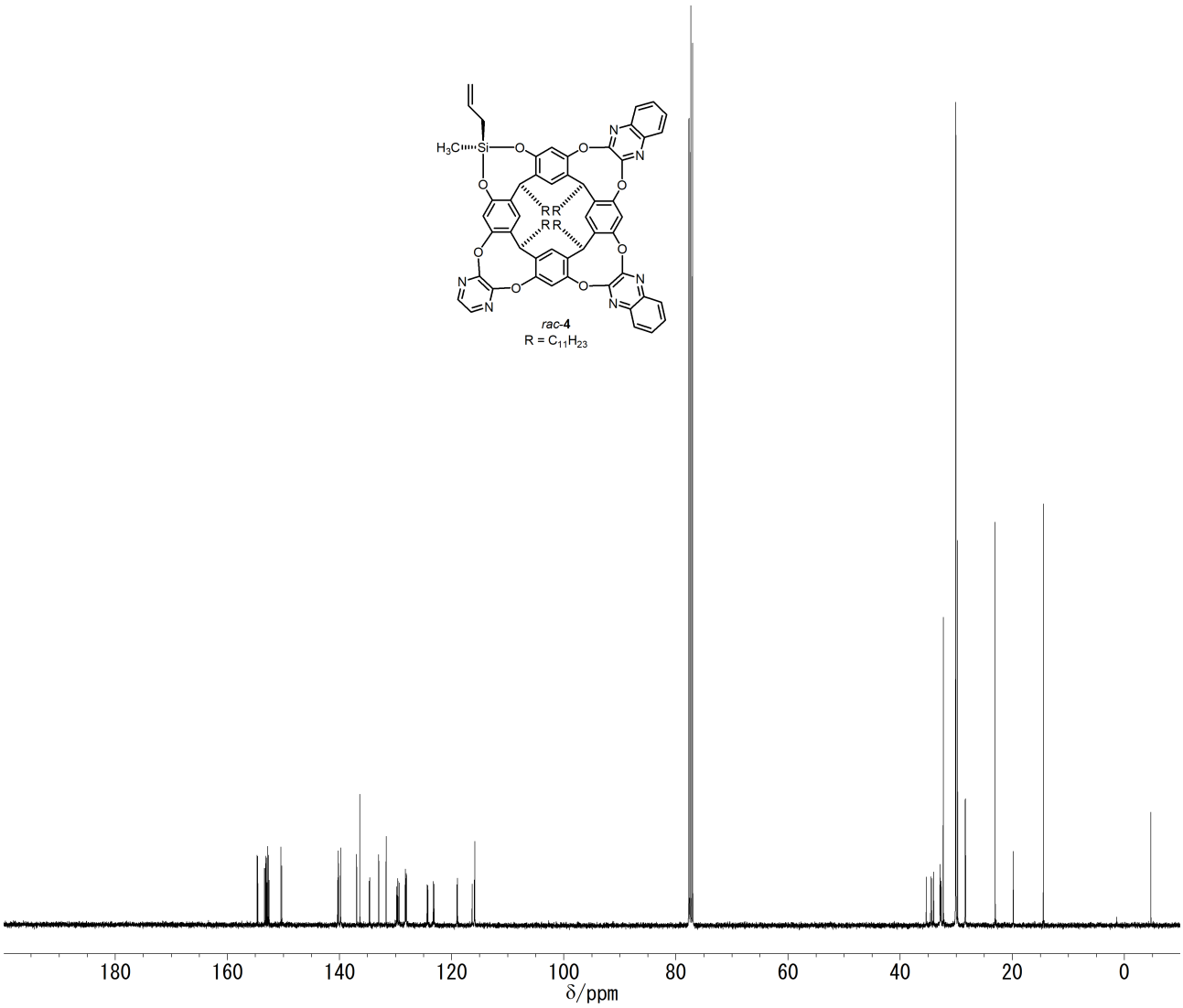
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**3**.



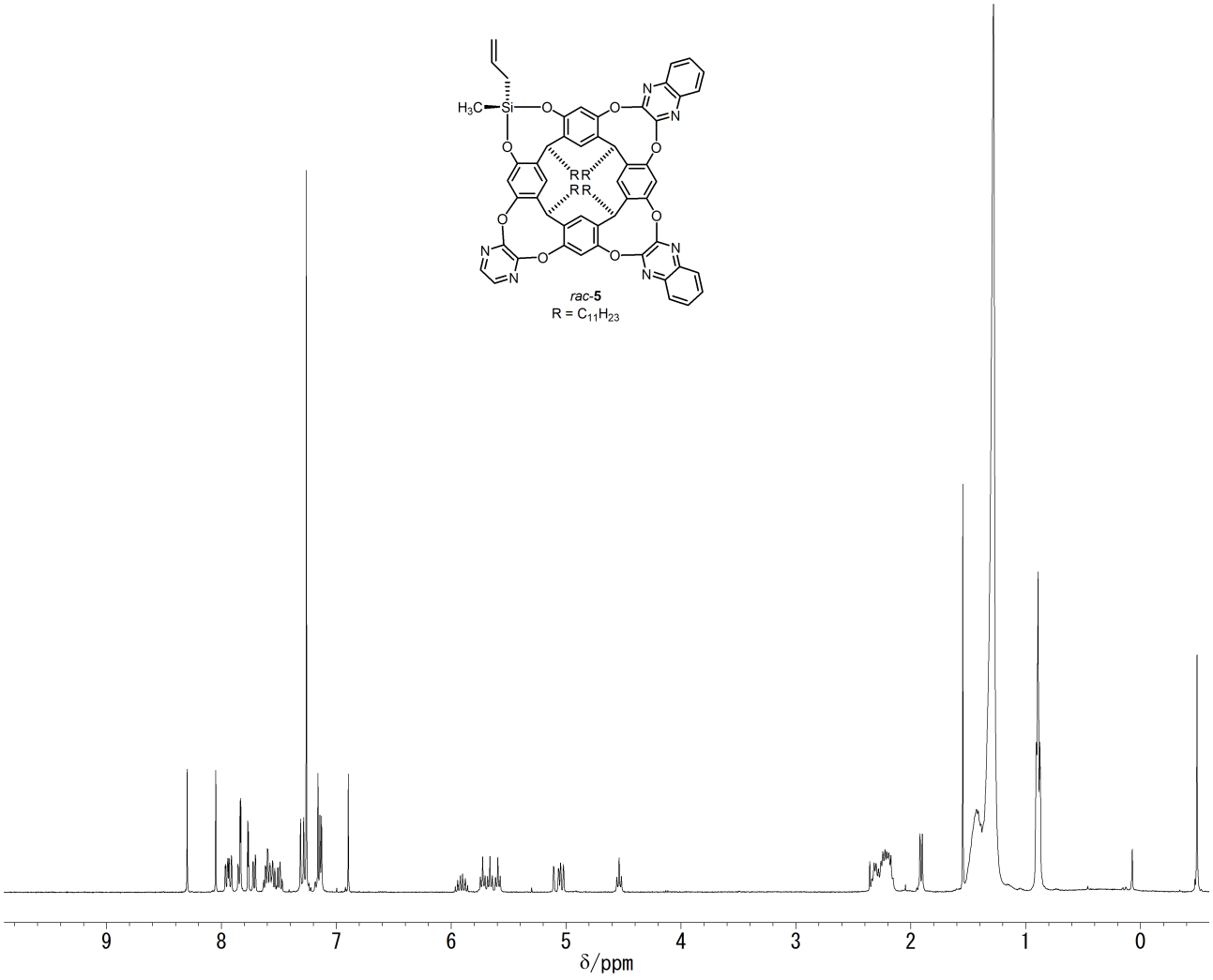
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**4**.



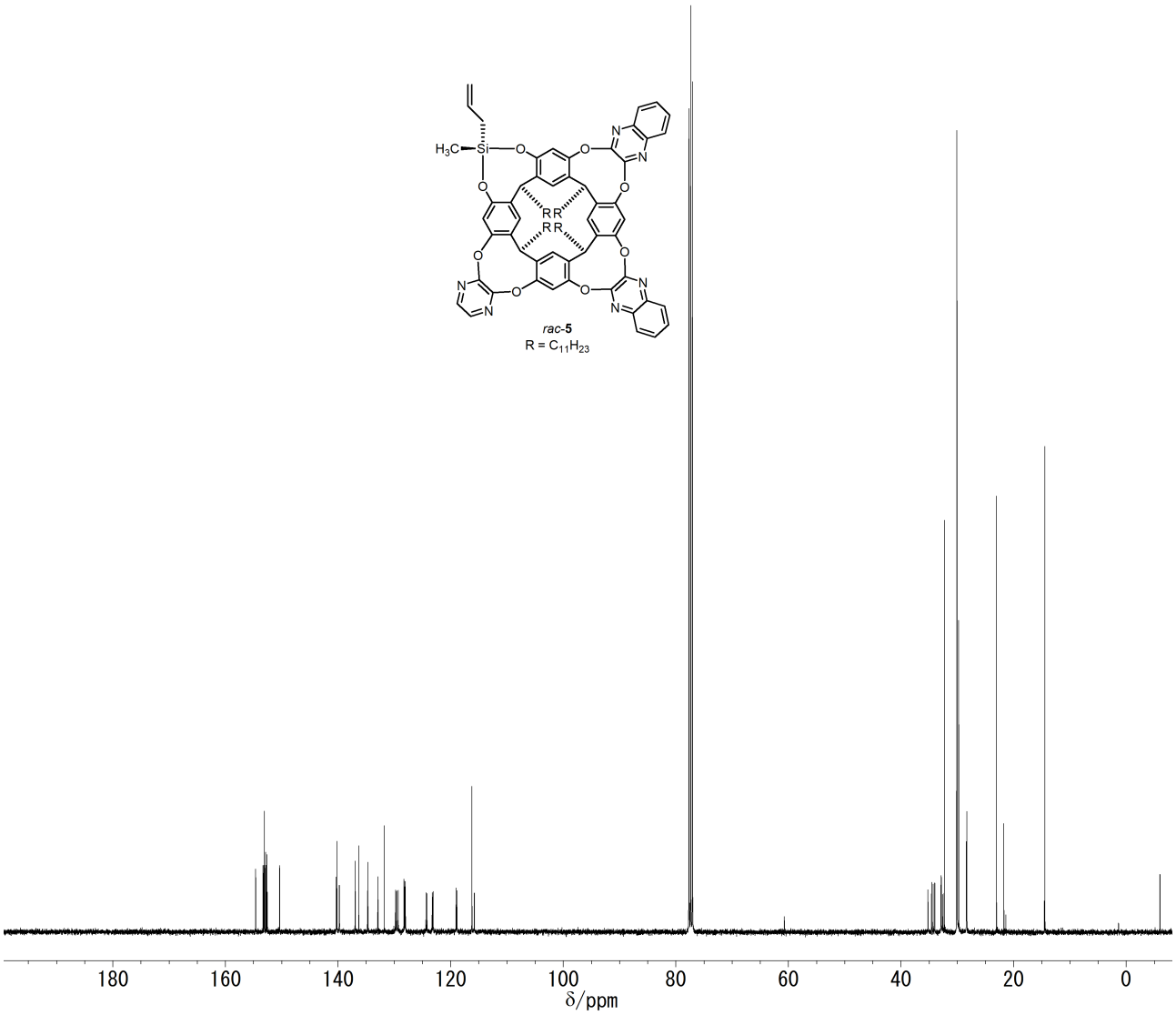
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**4**.



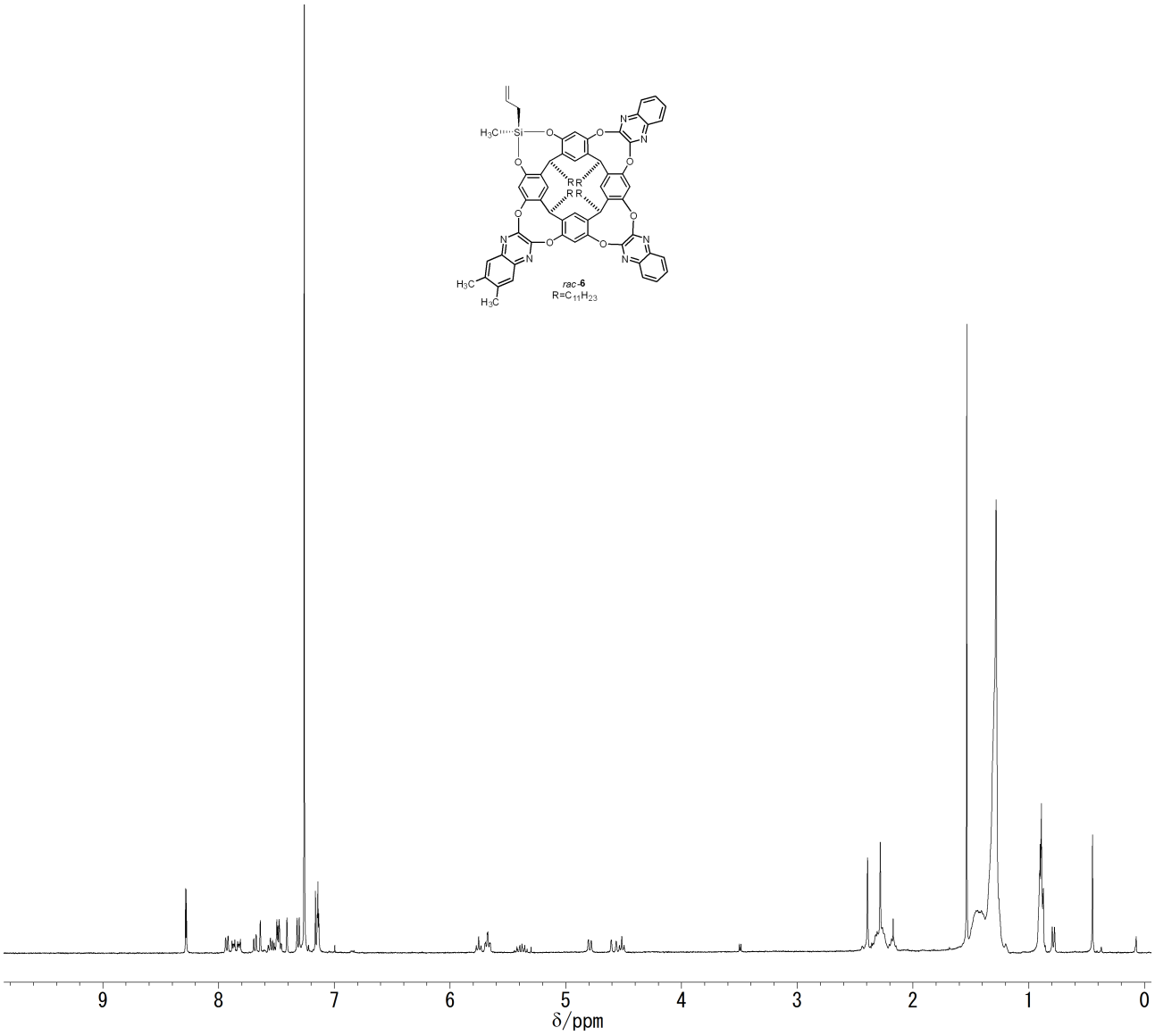
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**5**.



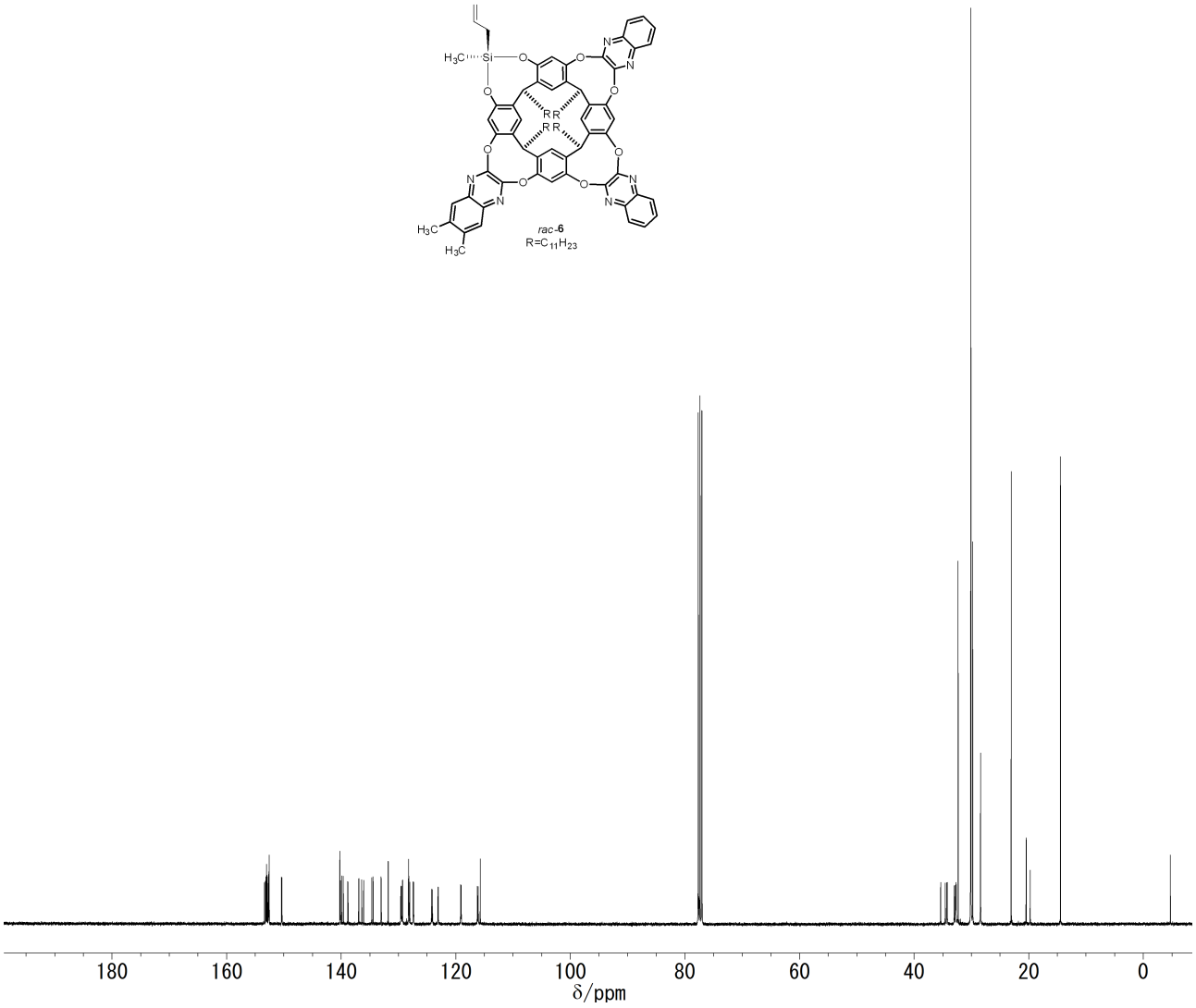
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**5**.



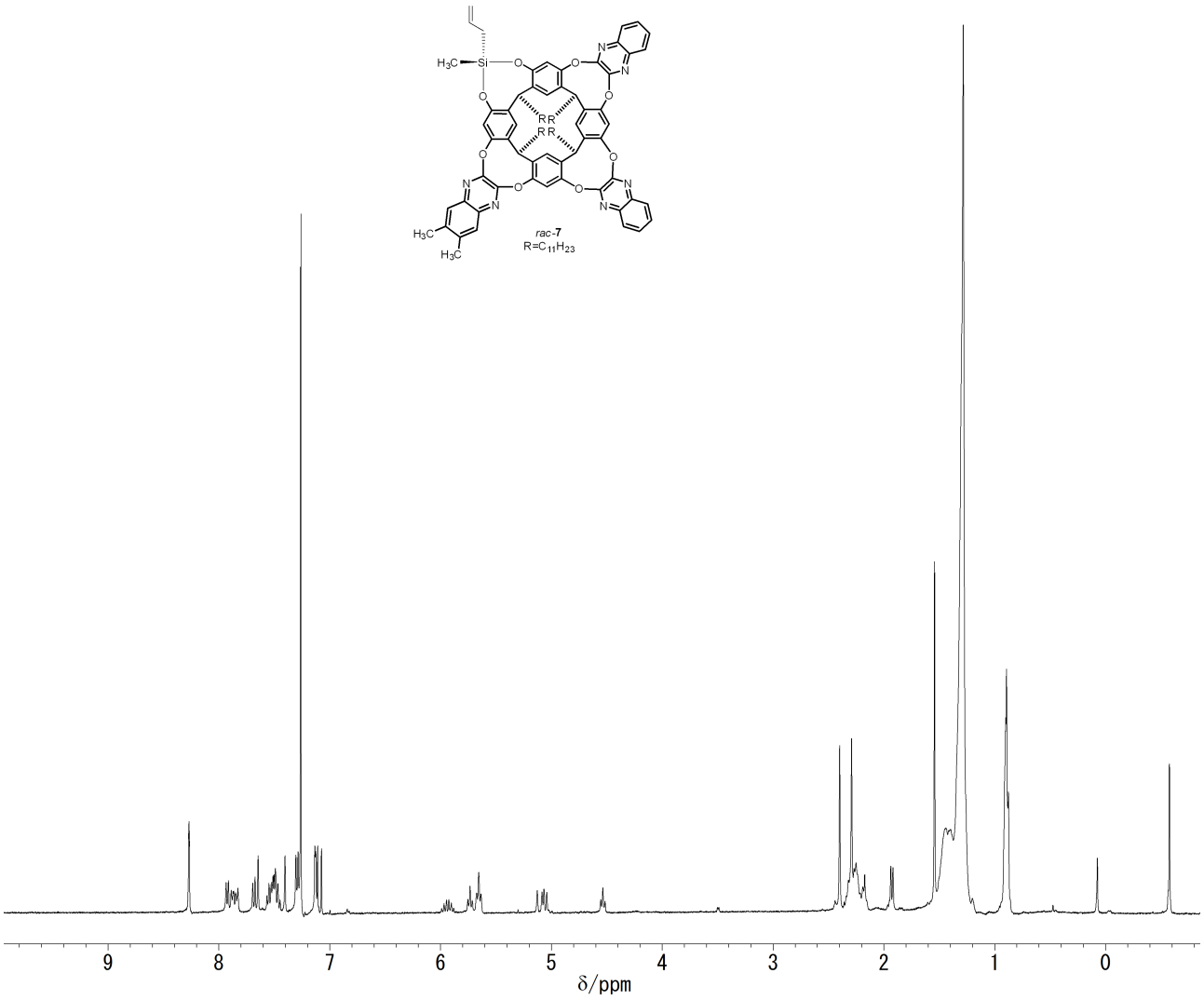
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**6**.



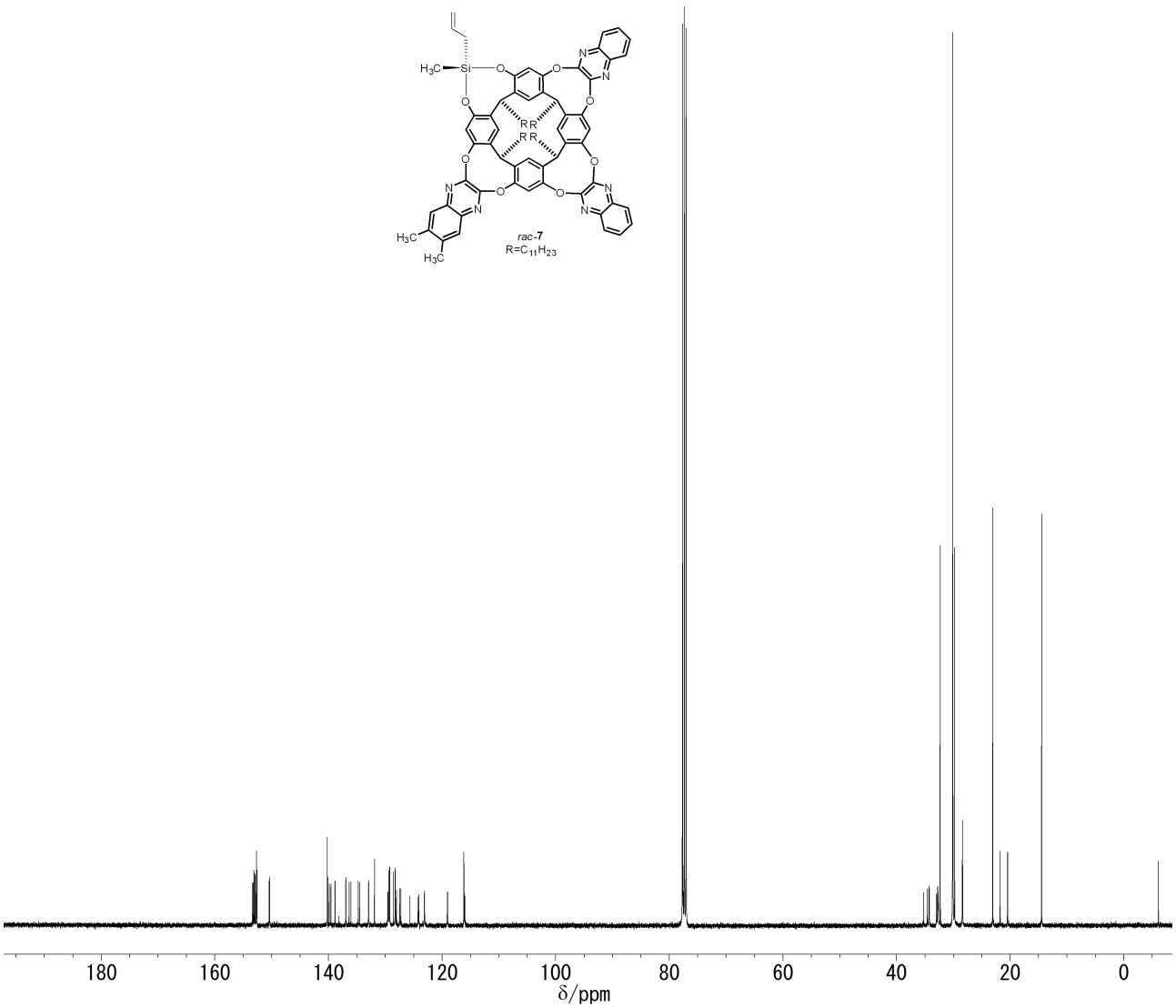
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**6**.



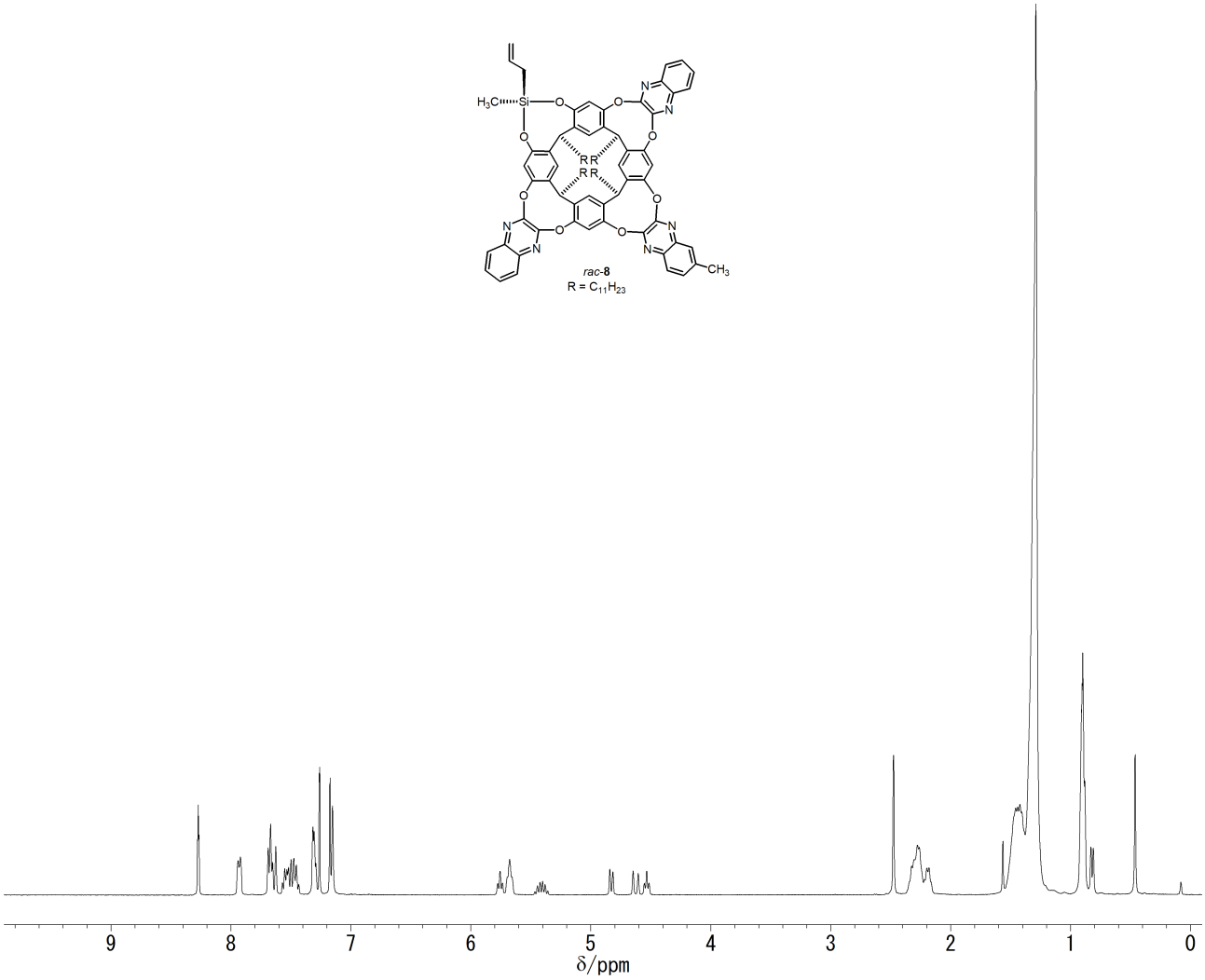
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**7**.



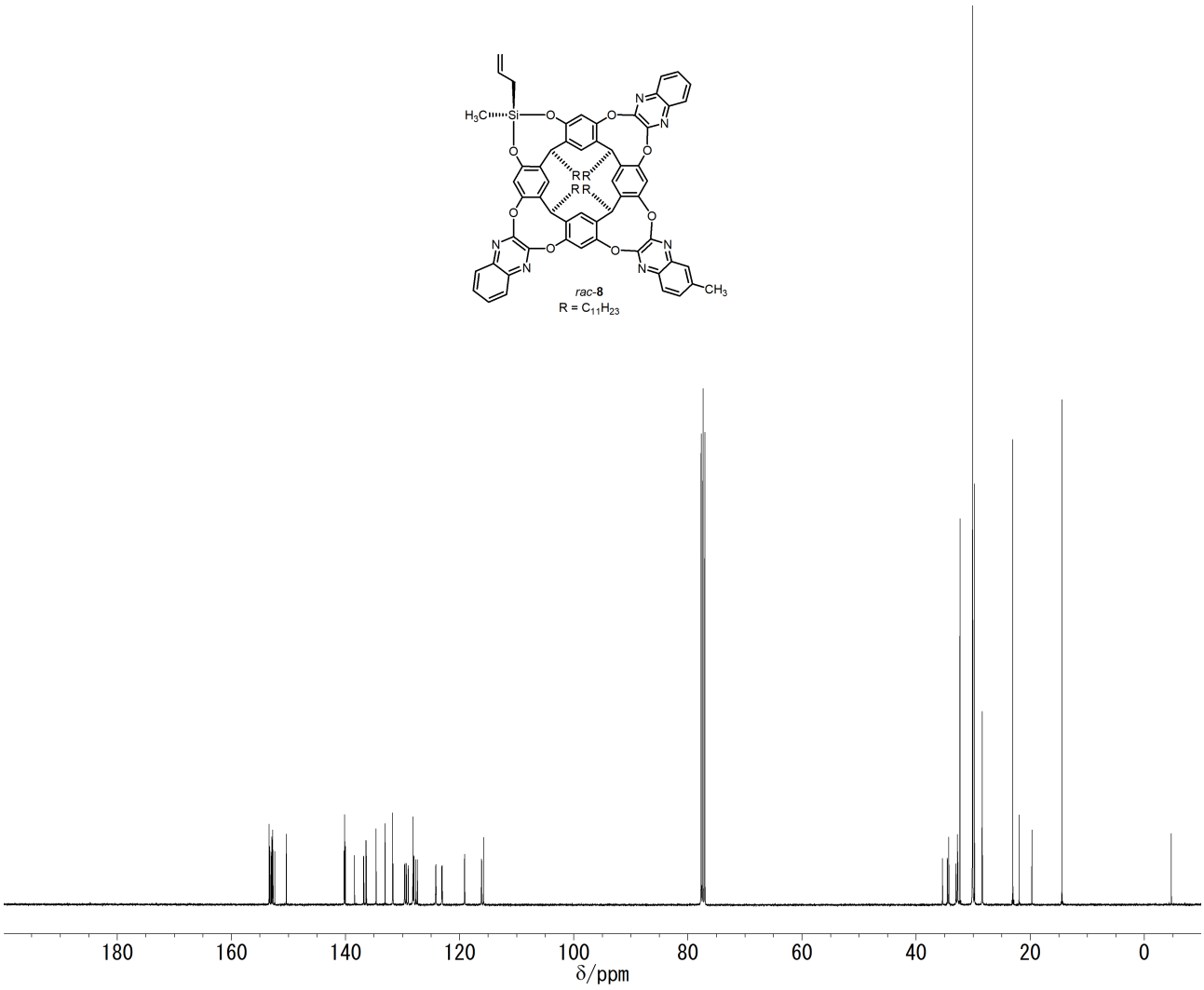
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**7**.



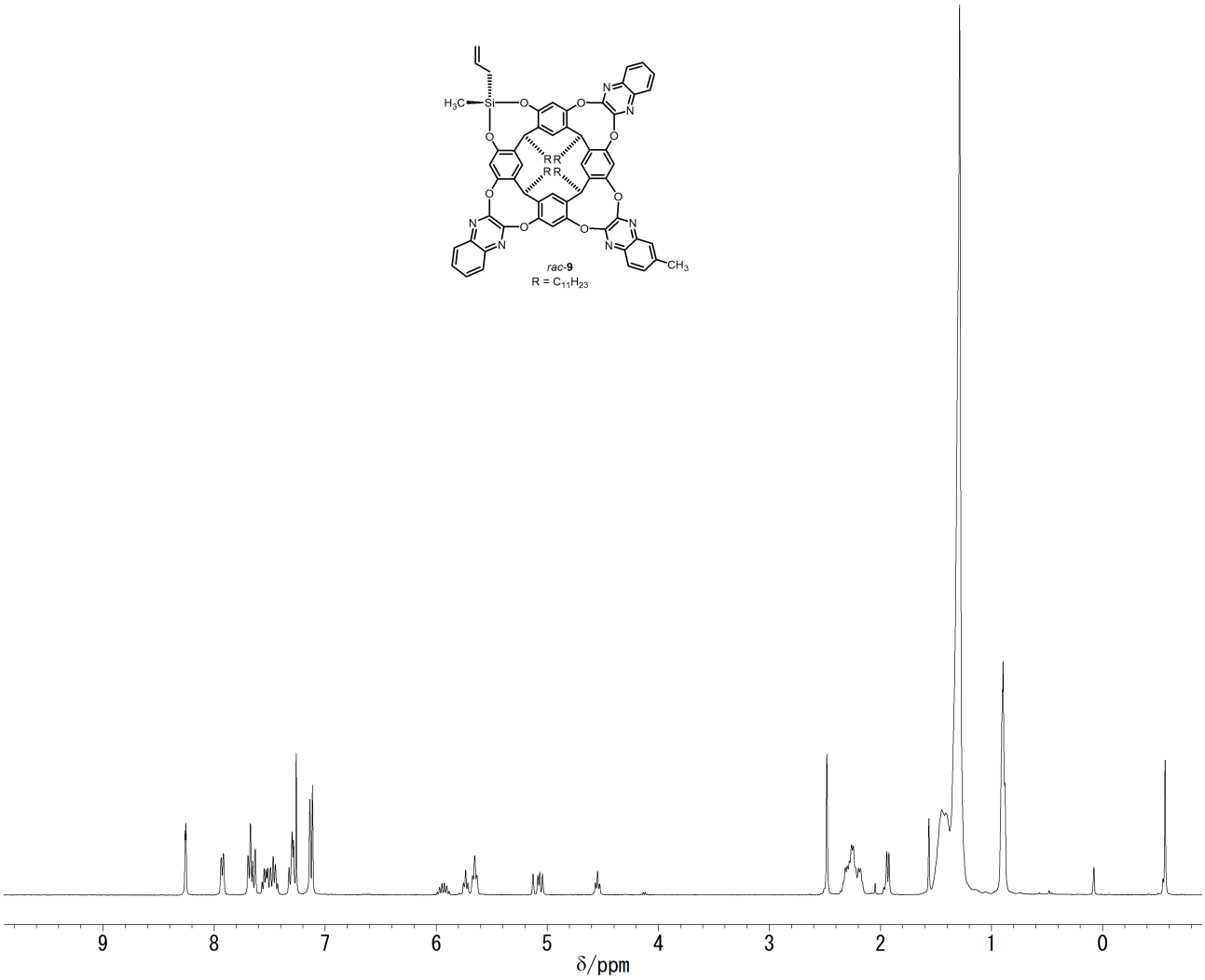
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**8**.



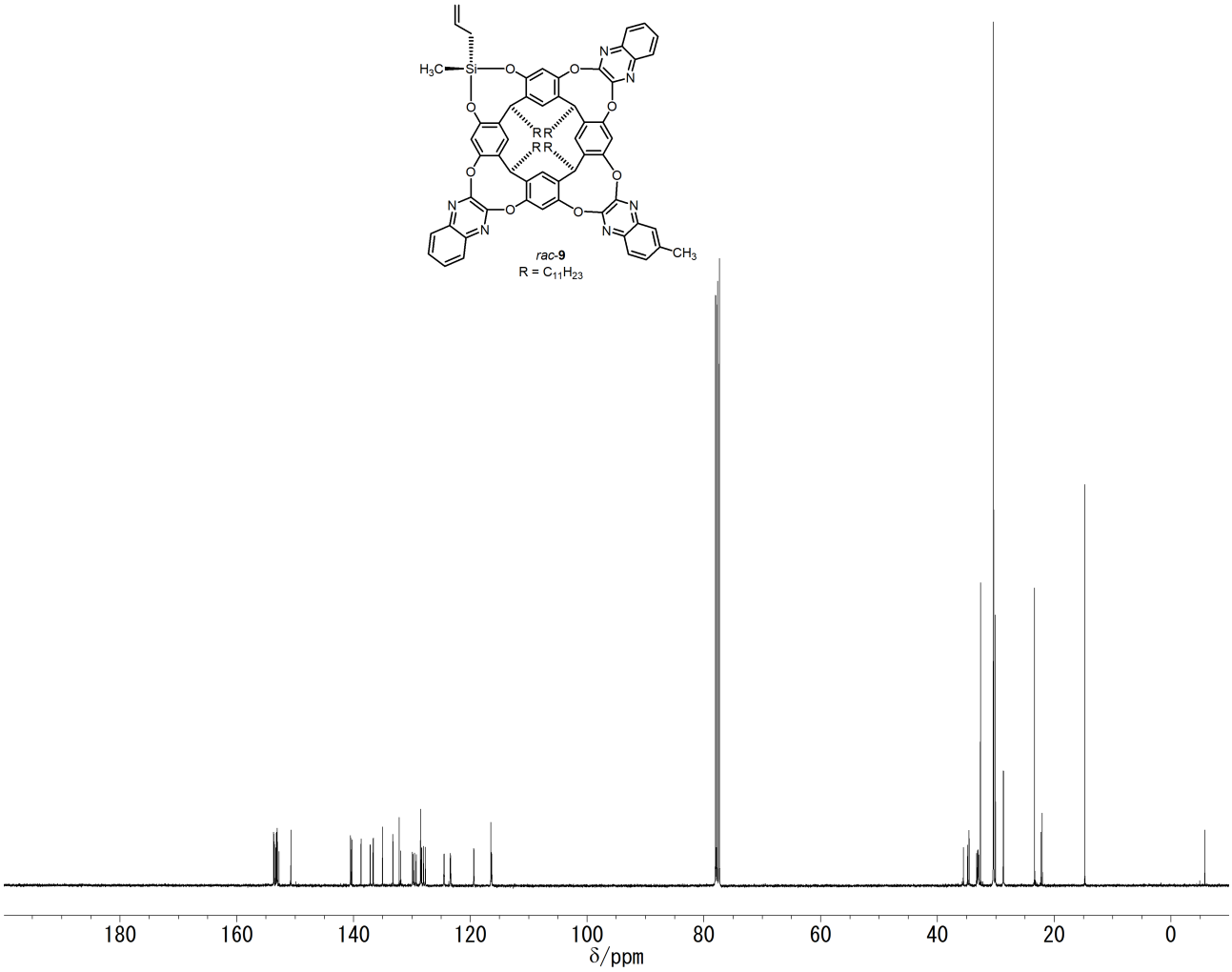
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**8**.



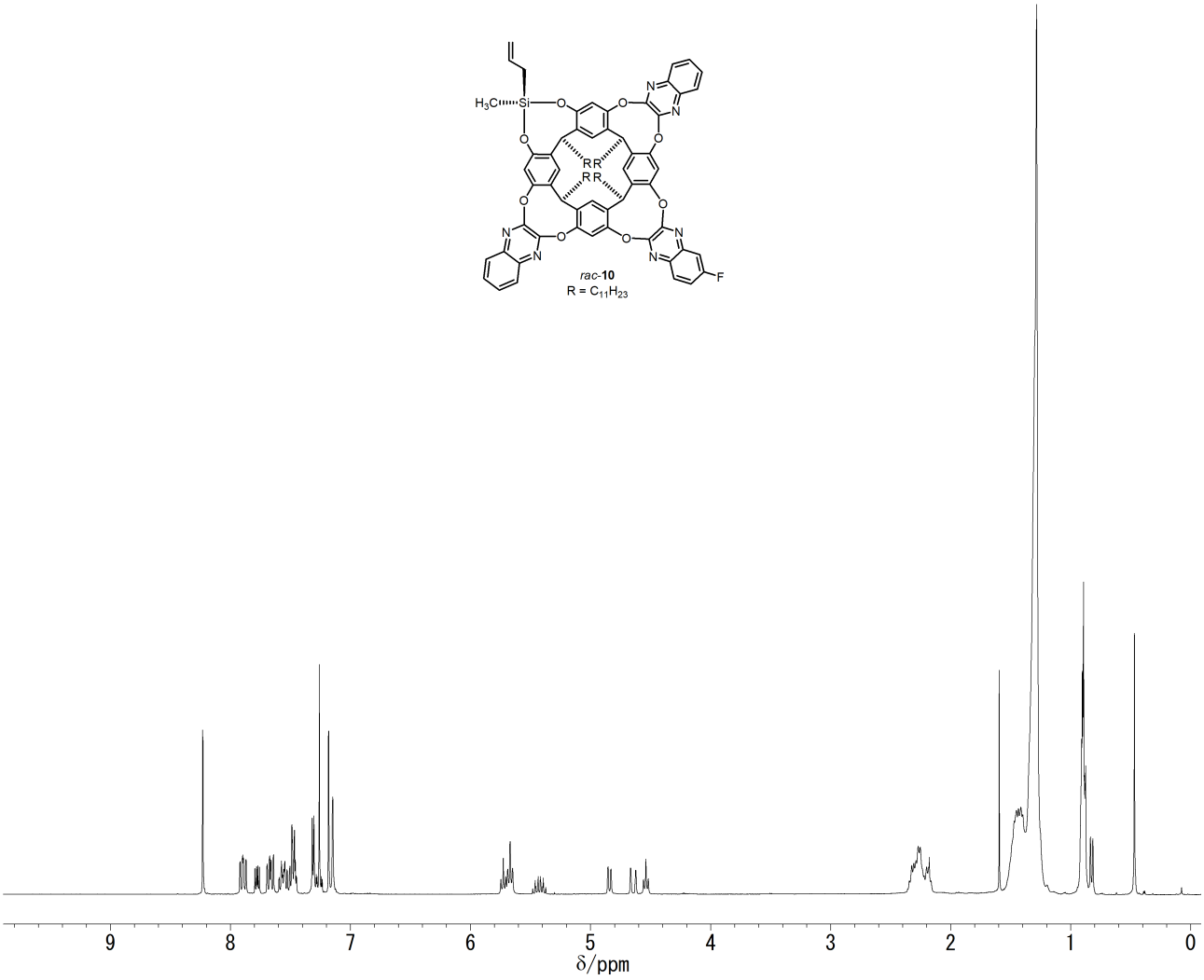
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**9**.



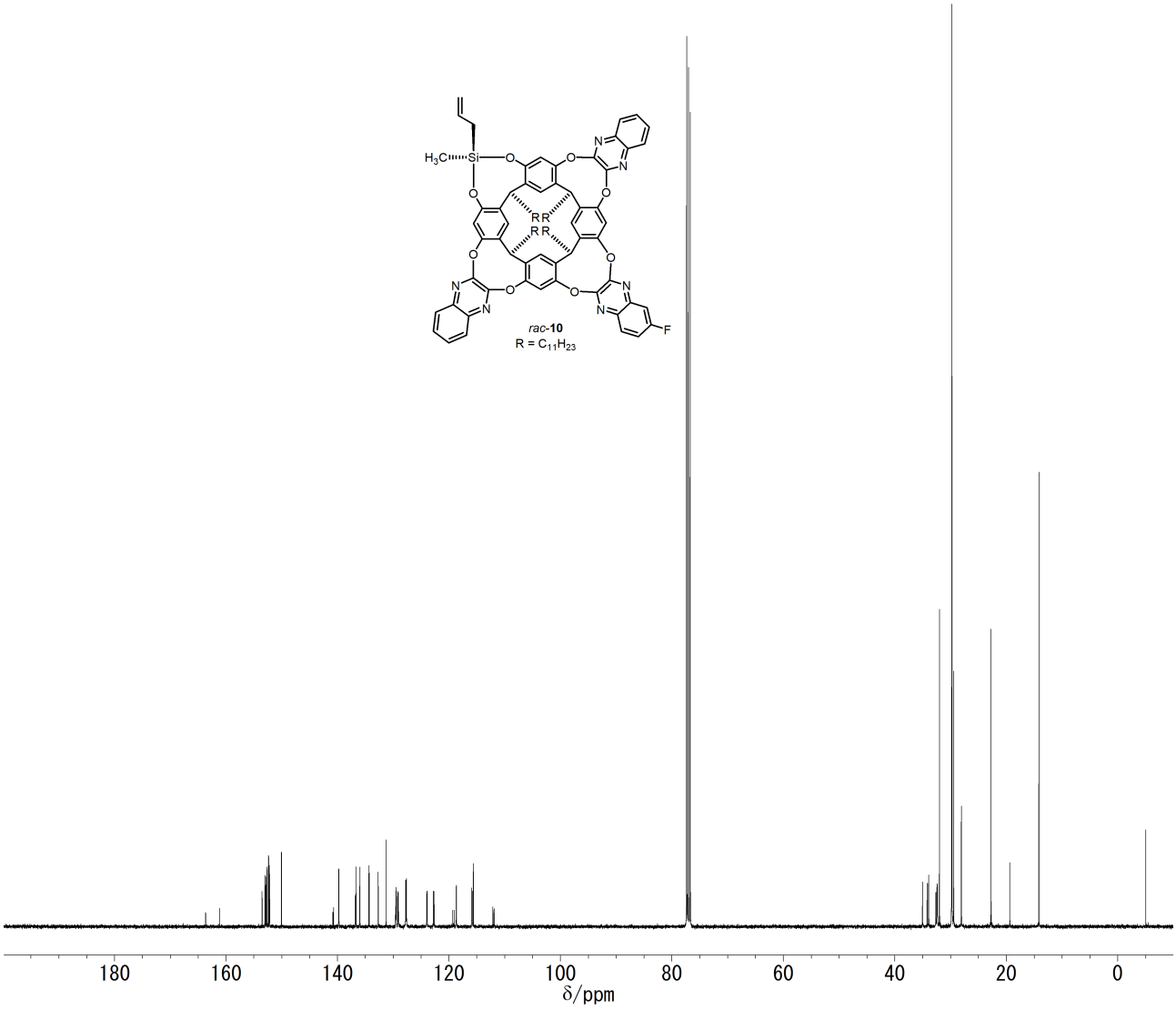
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**9**.



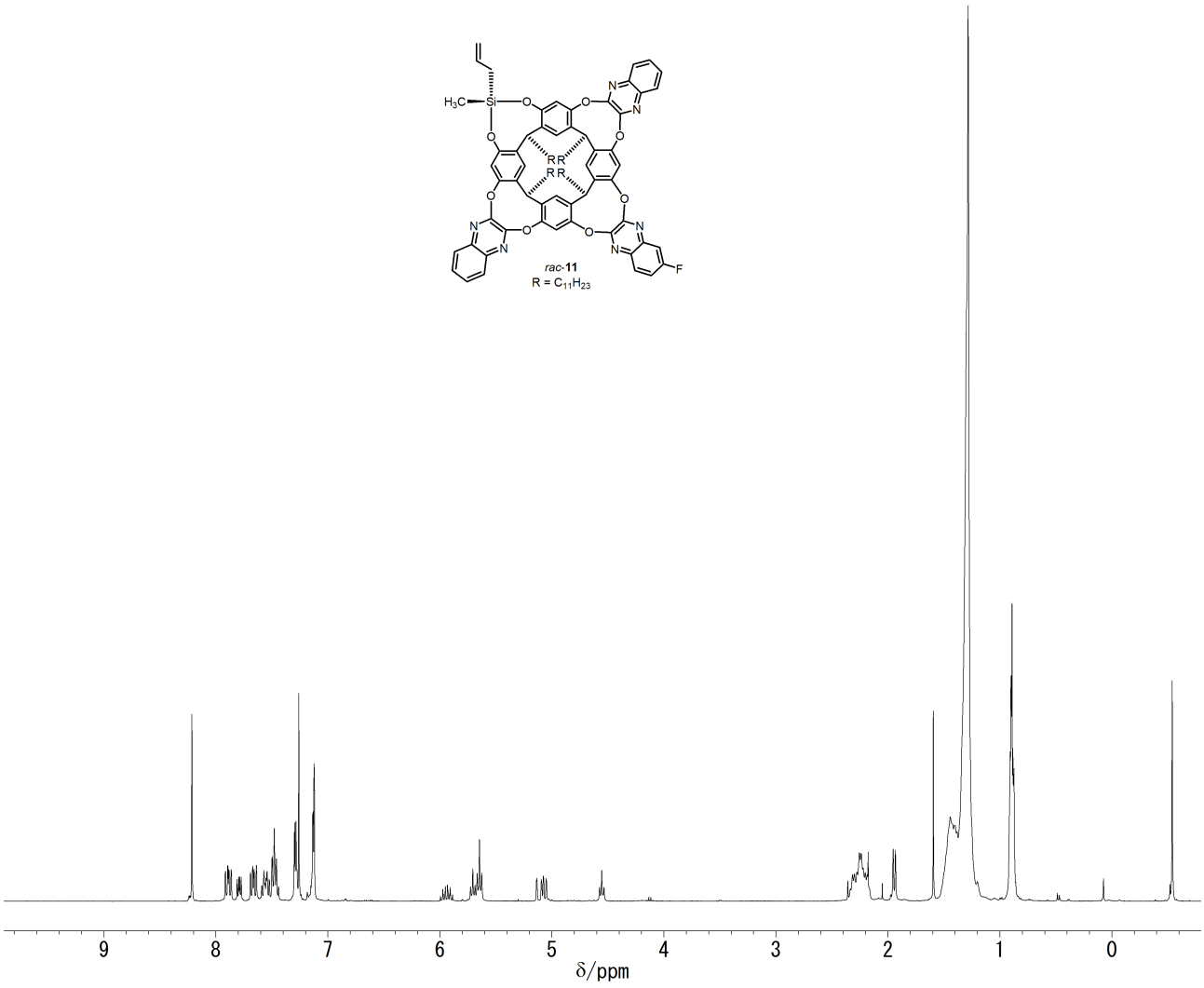
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**10**.



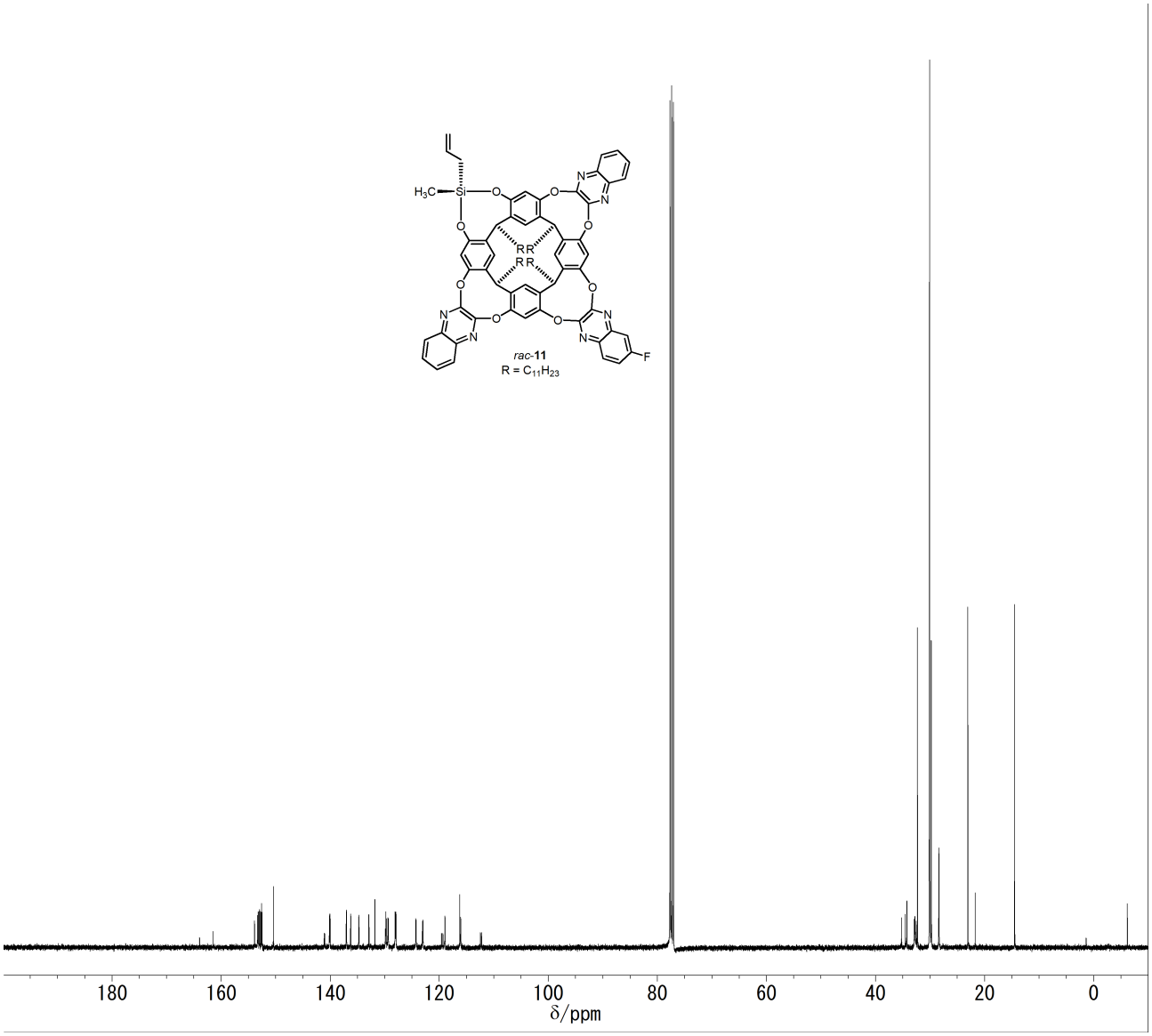
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**10**.



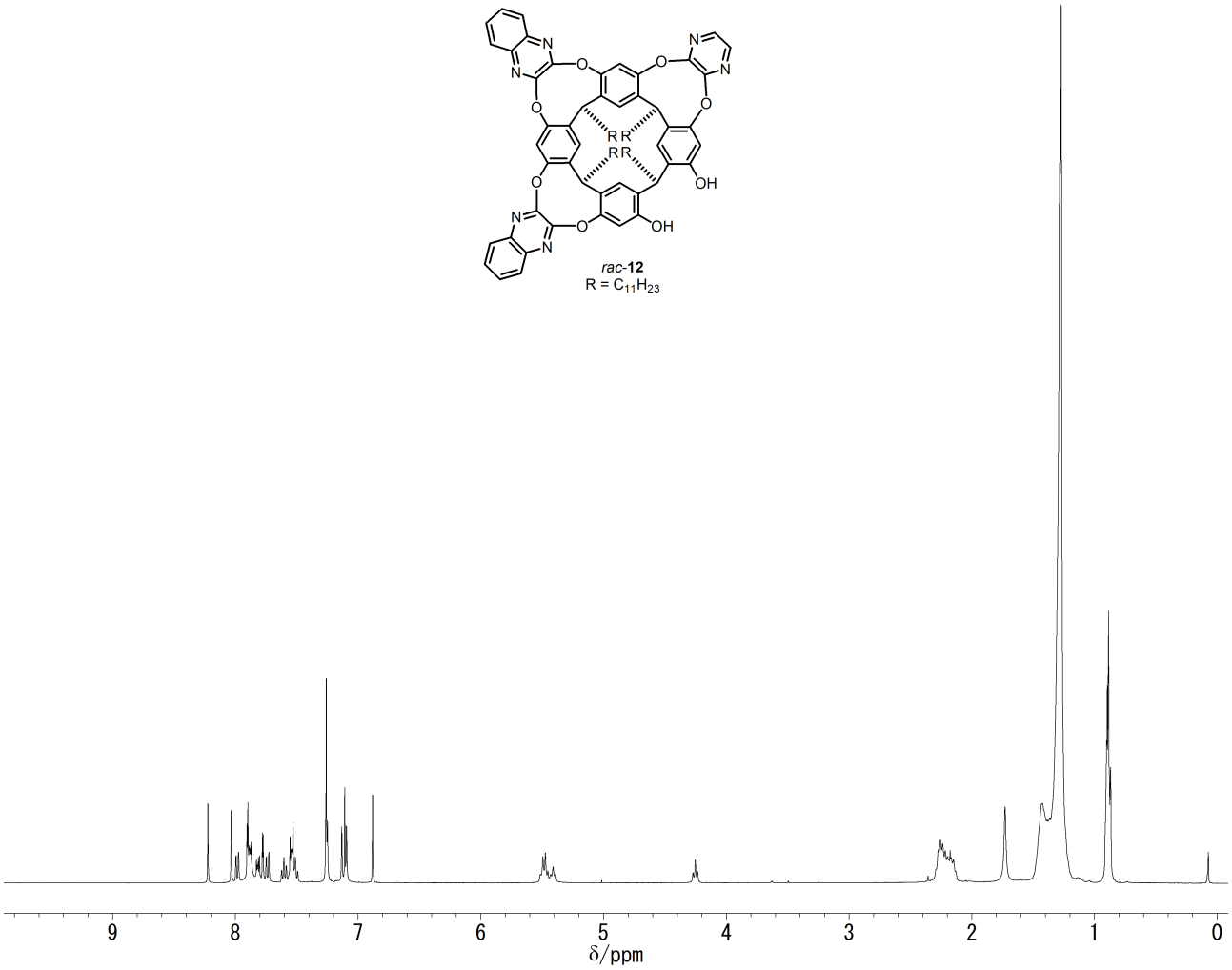
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**11**.



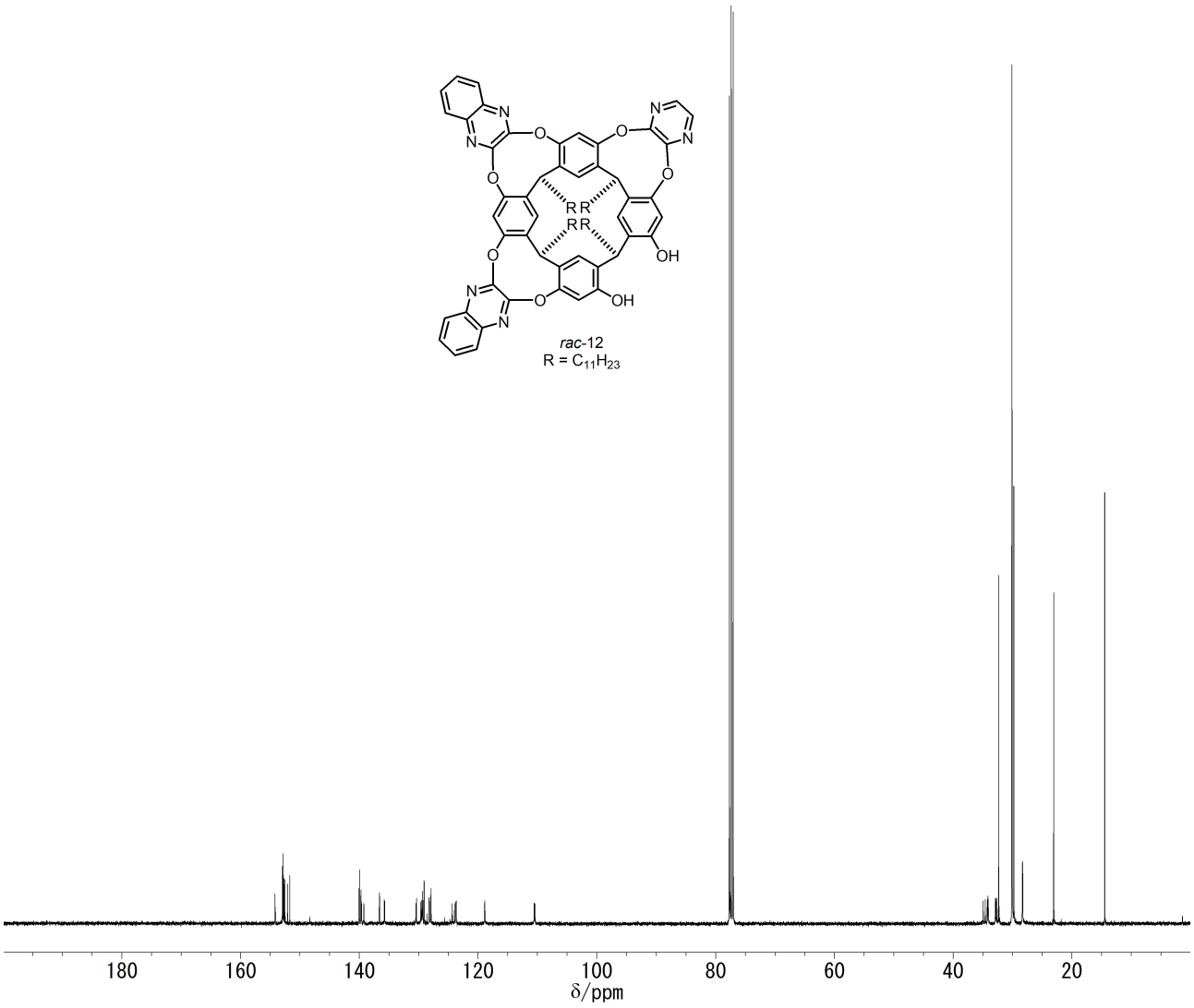
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**11**.



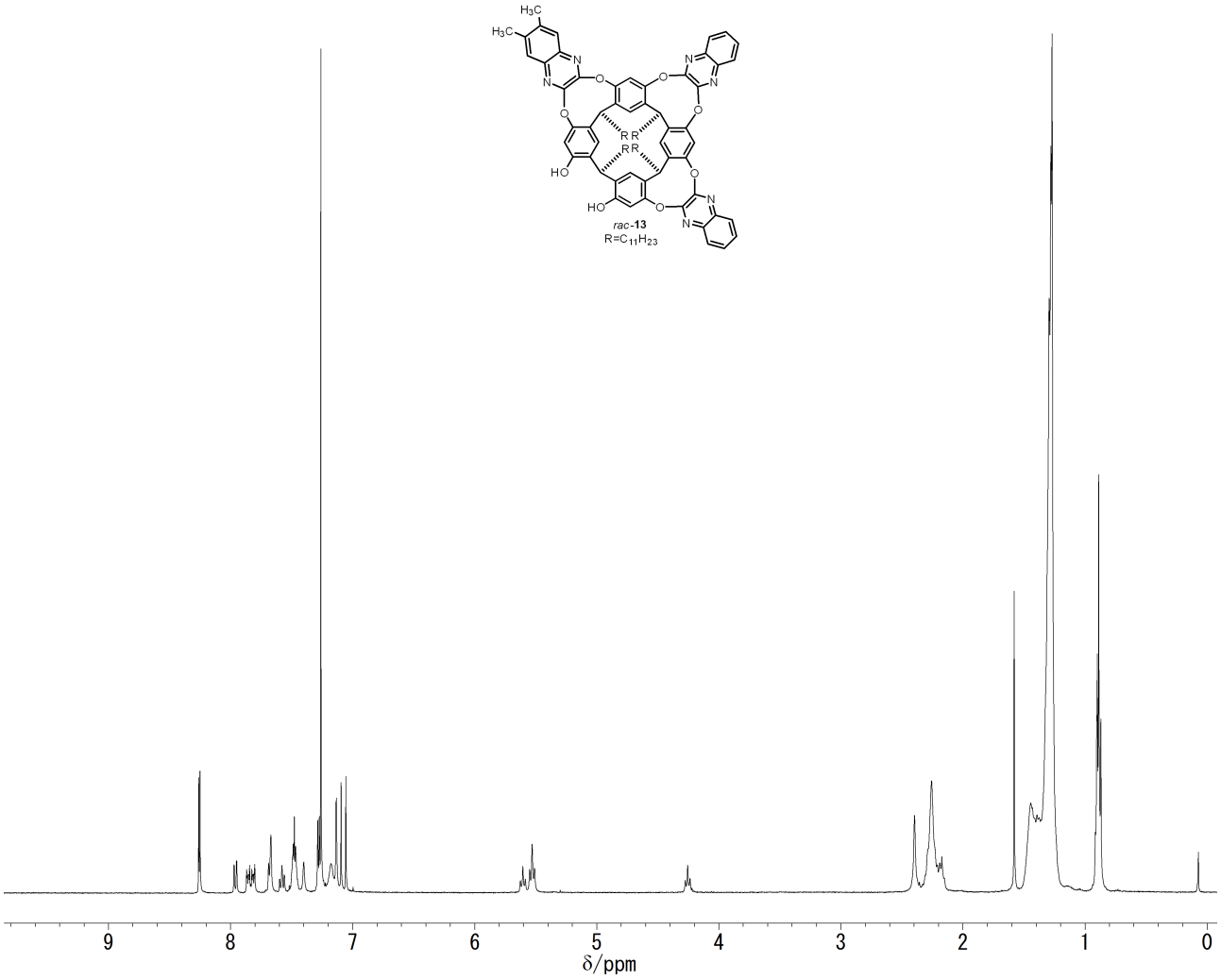
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**12**.



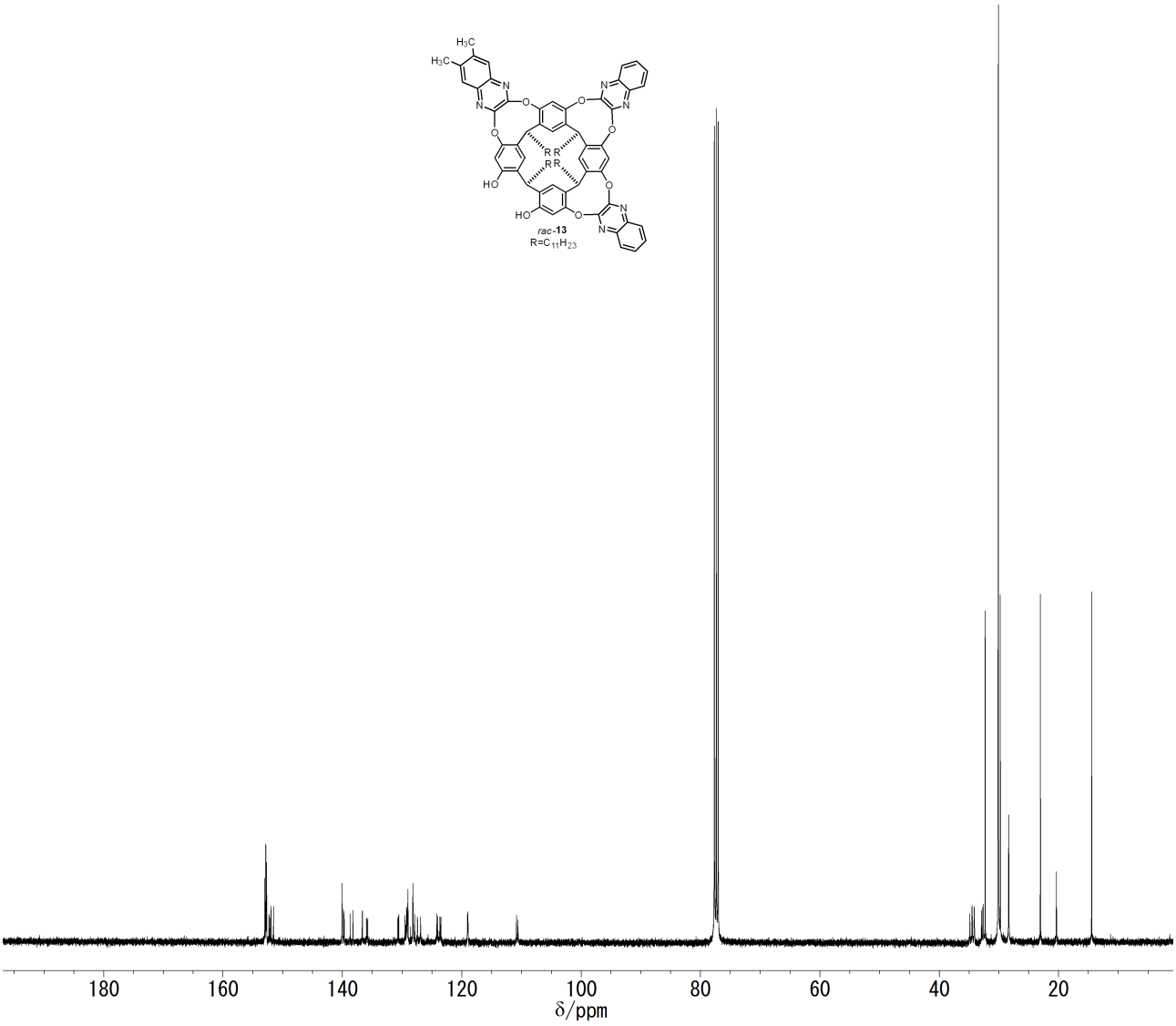
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**12**.



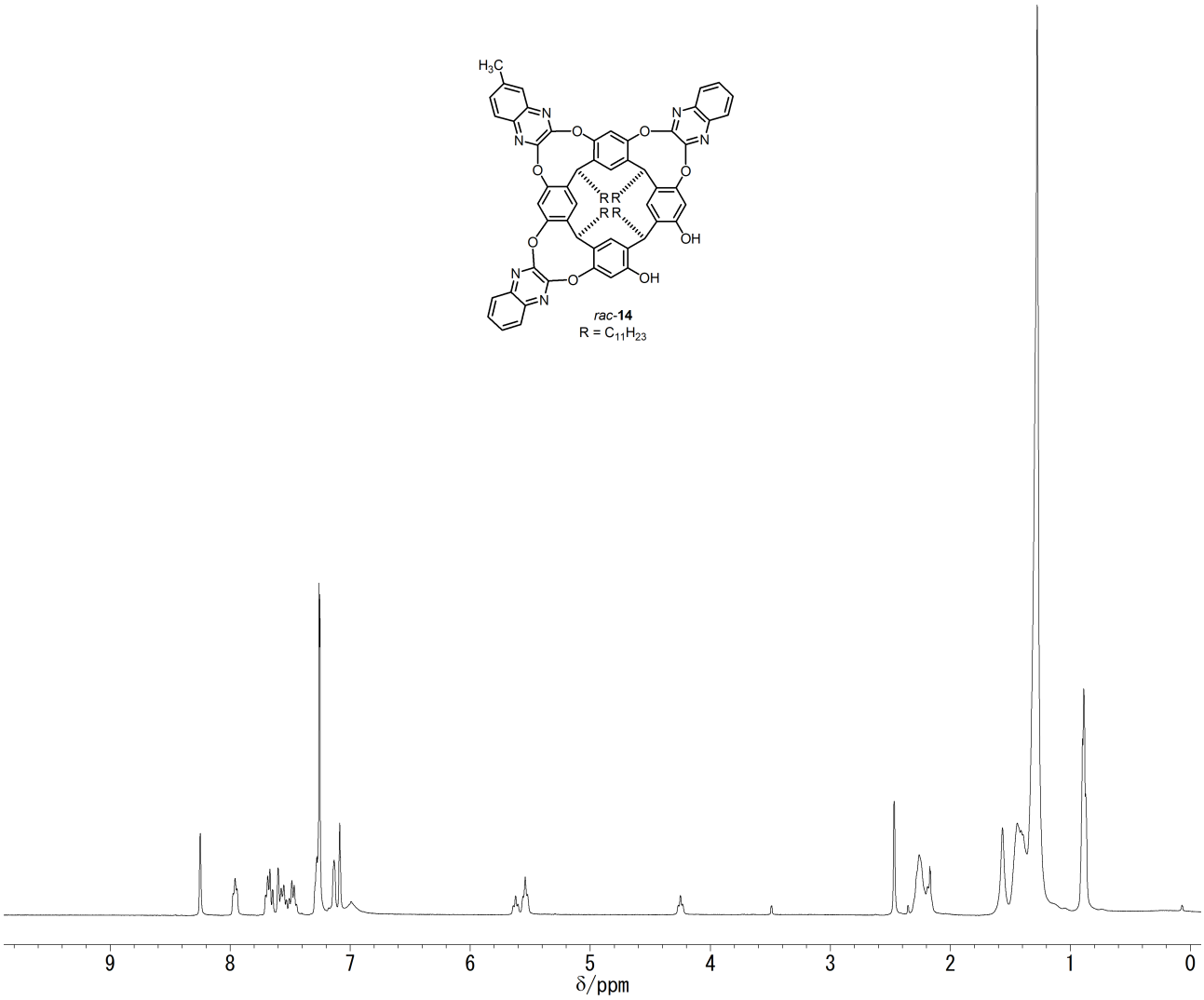
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**13**.



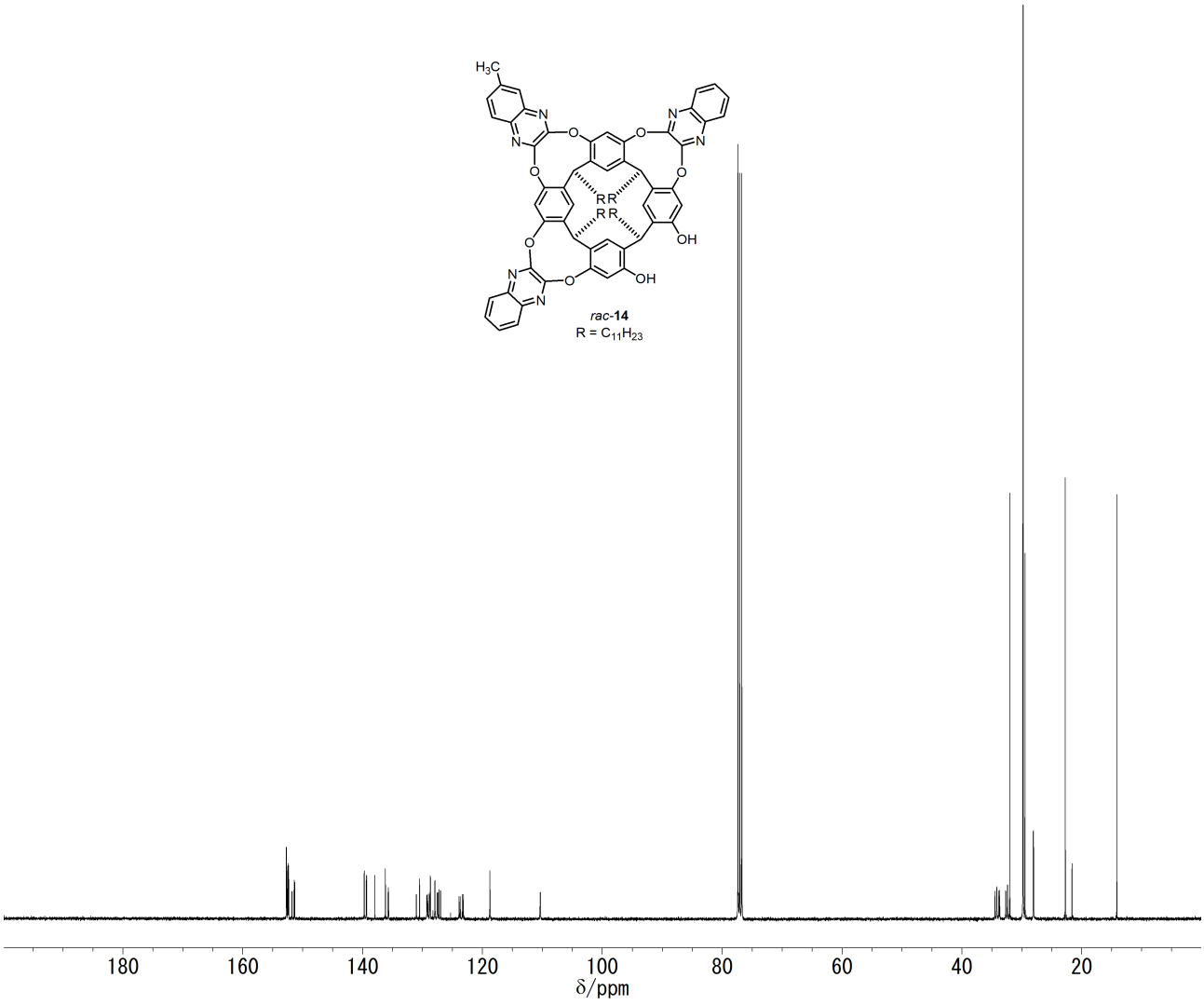
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**13**.



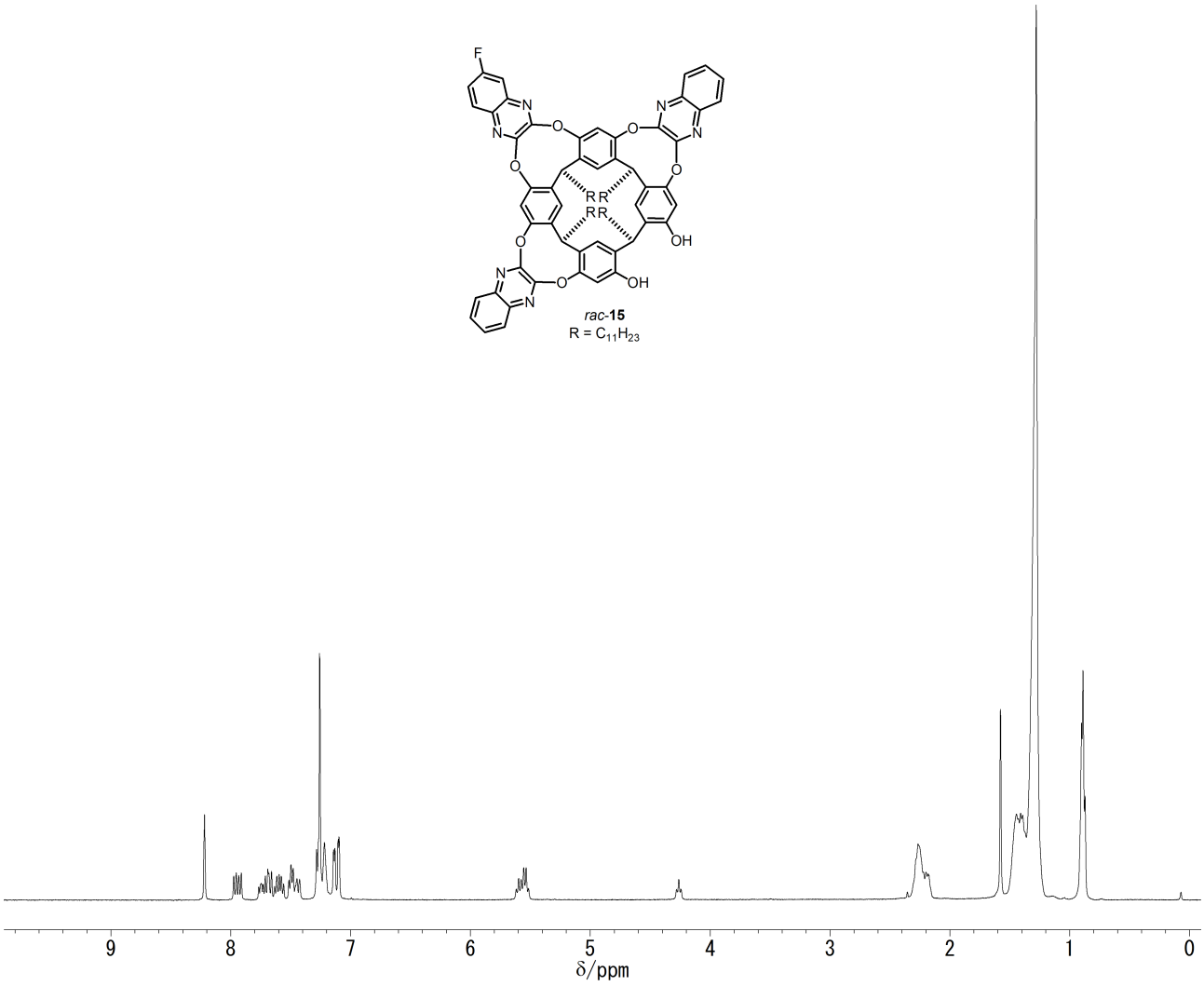
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**14**.



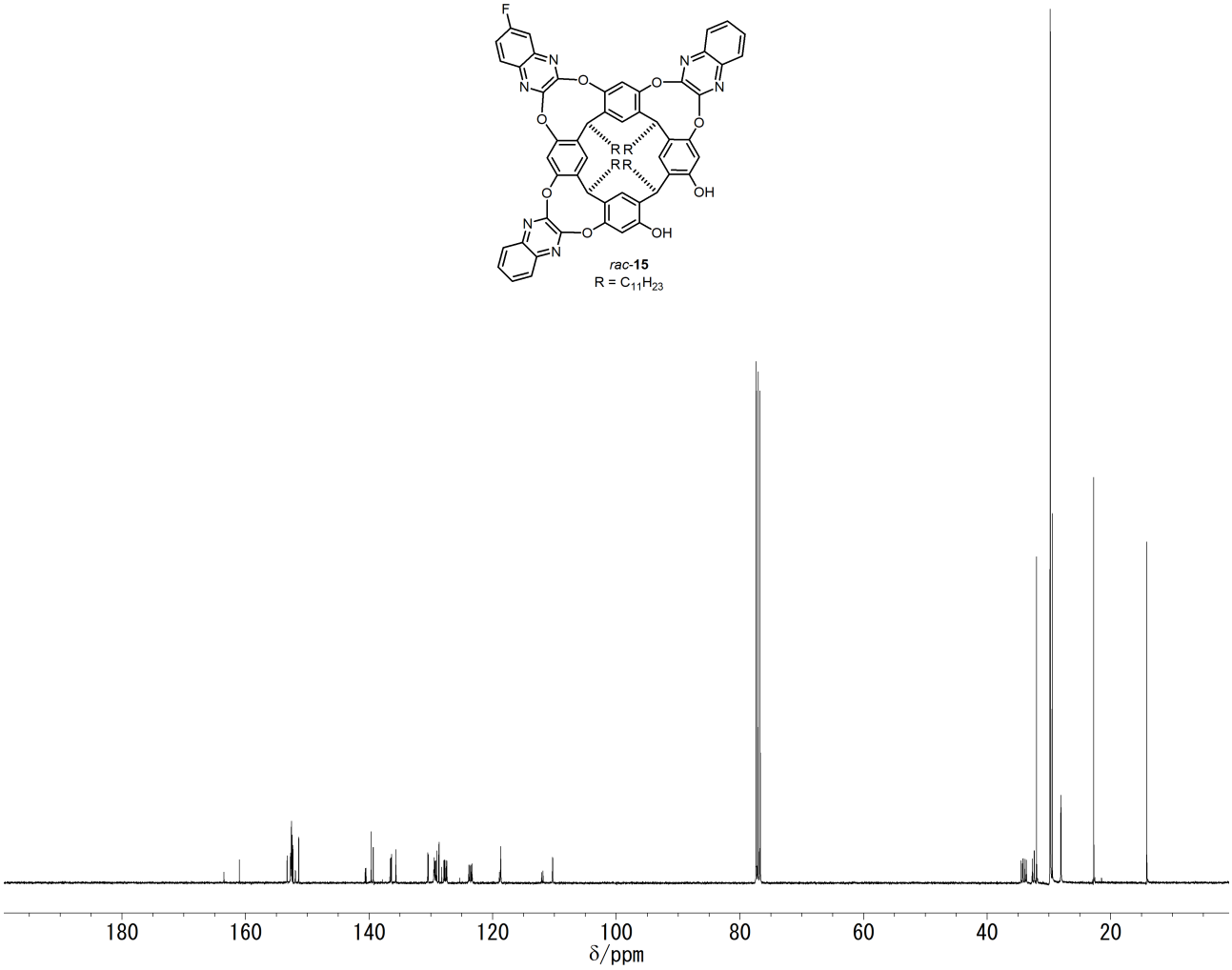
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**14**.



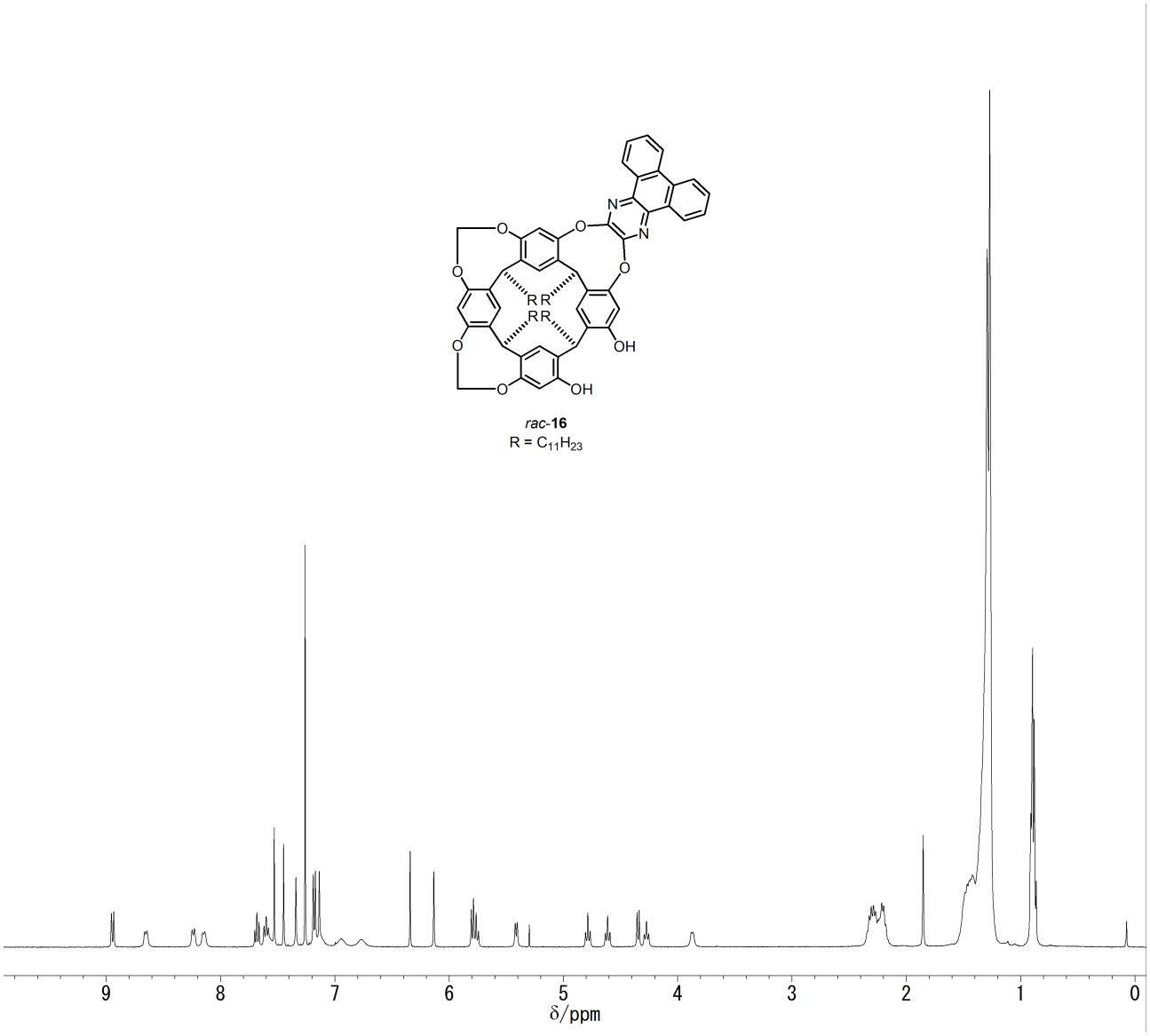
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**15**.



^{13}C NMR spectrum in $CDCl_3$ for *rac*-**15**.

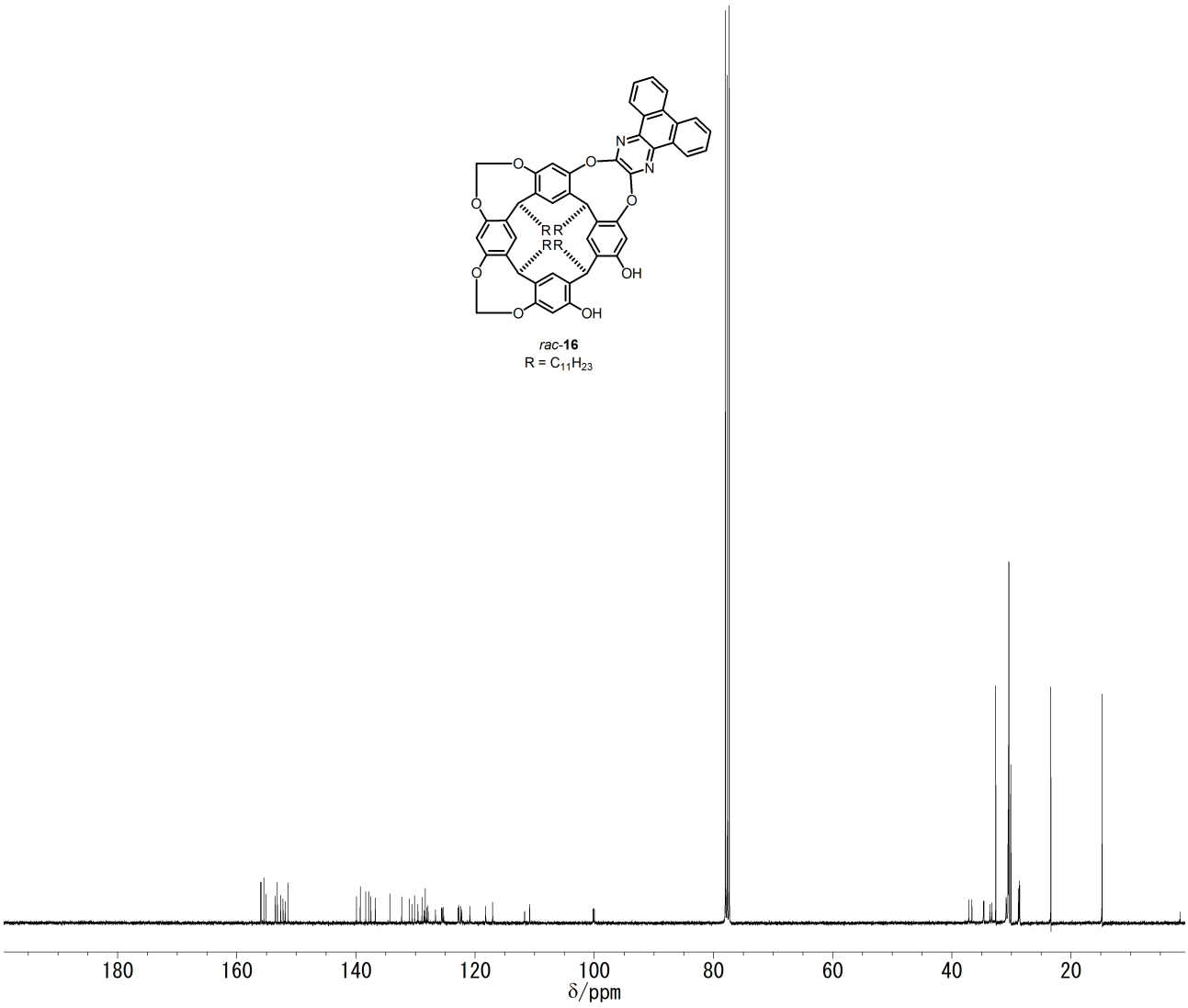


^{1}H NMR spectrum in $CDCl_3$ for *rac*-**16**.

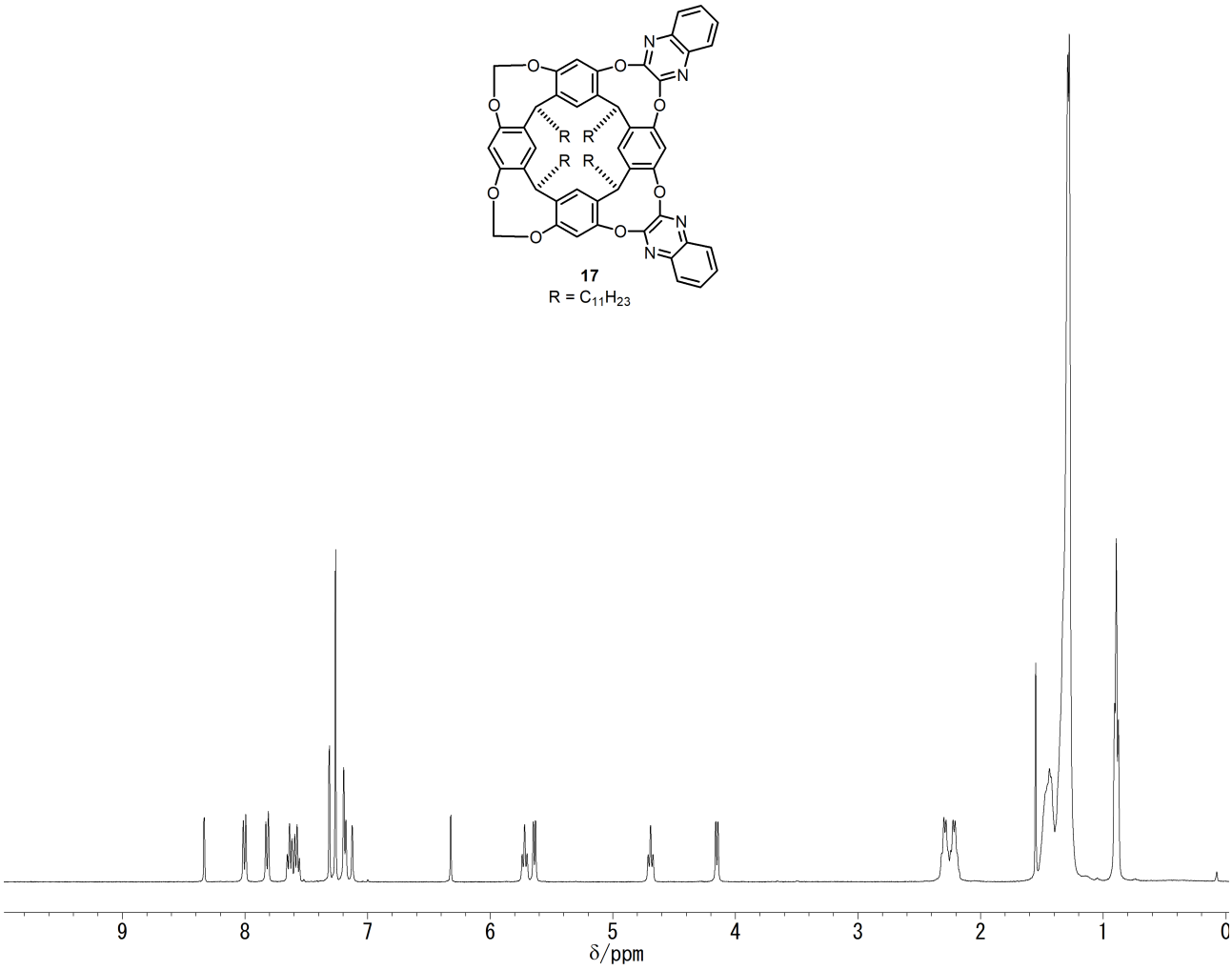


rac-**16**
R = $C_{11}H_{23}$

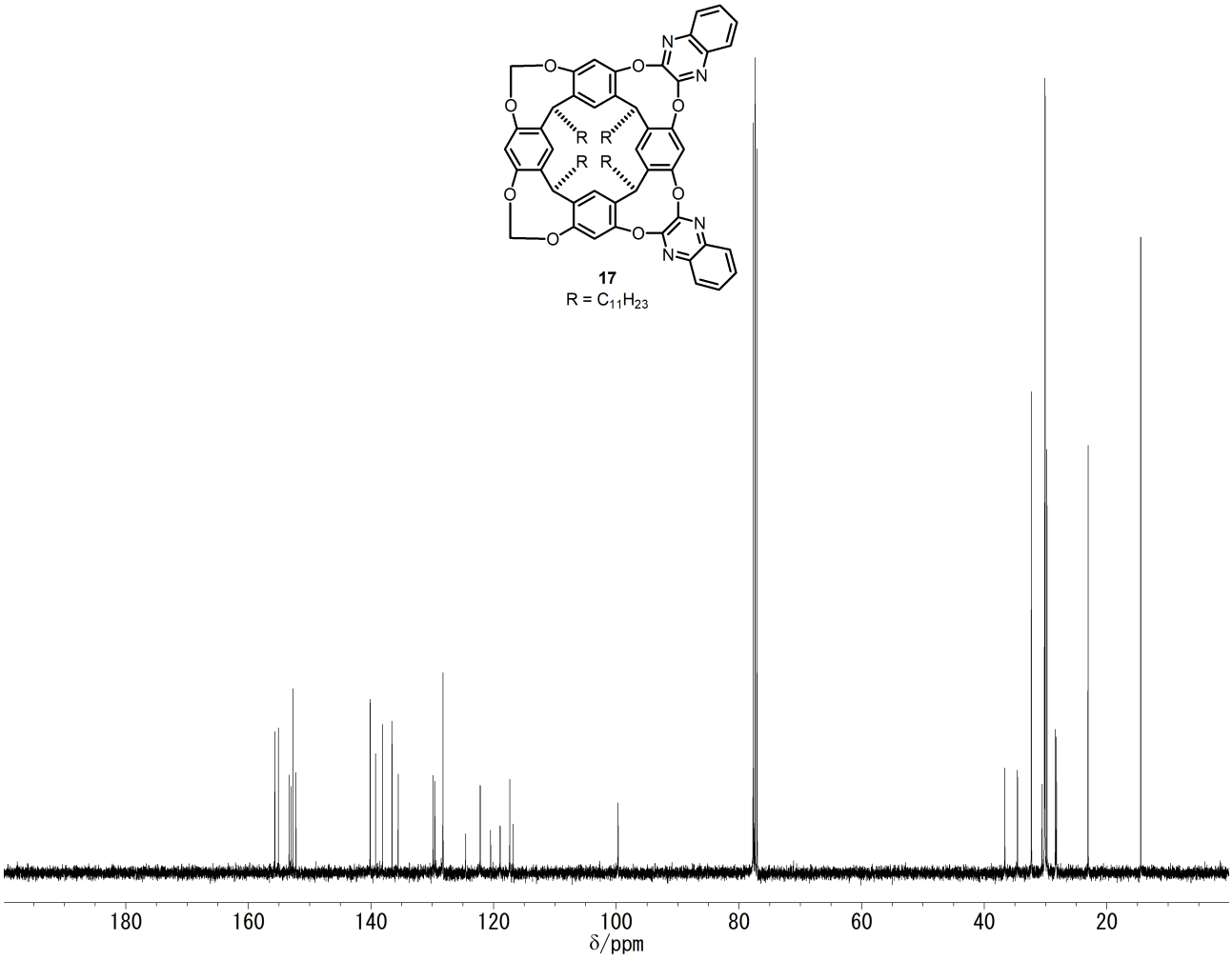
^{13}C NMR spectrum in $CDCl_3$ for *rac*-**16**.



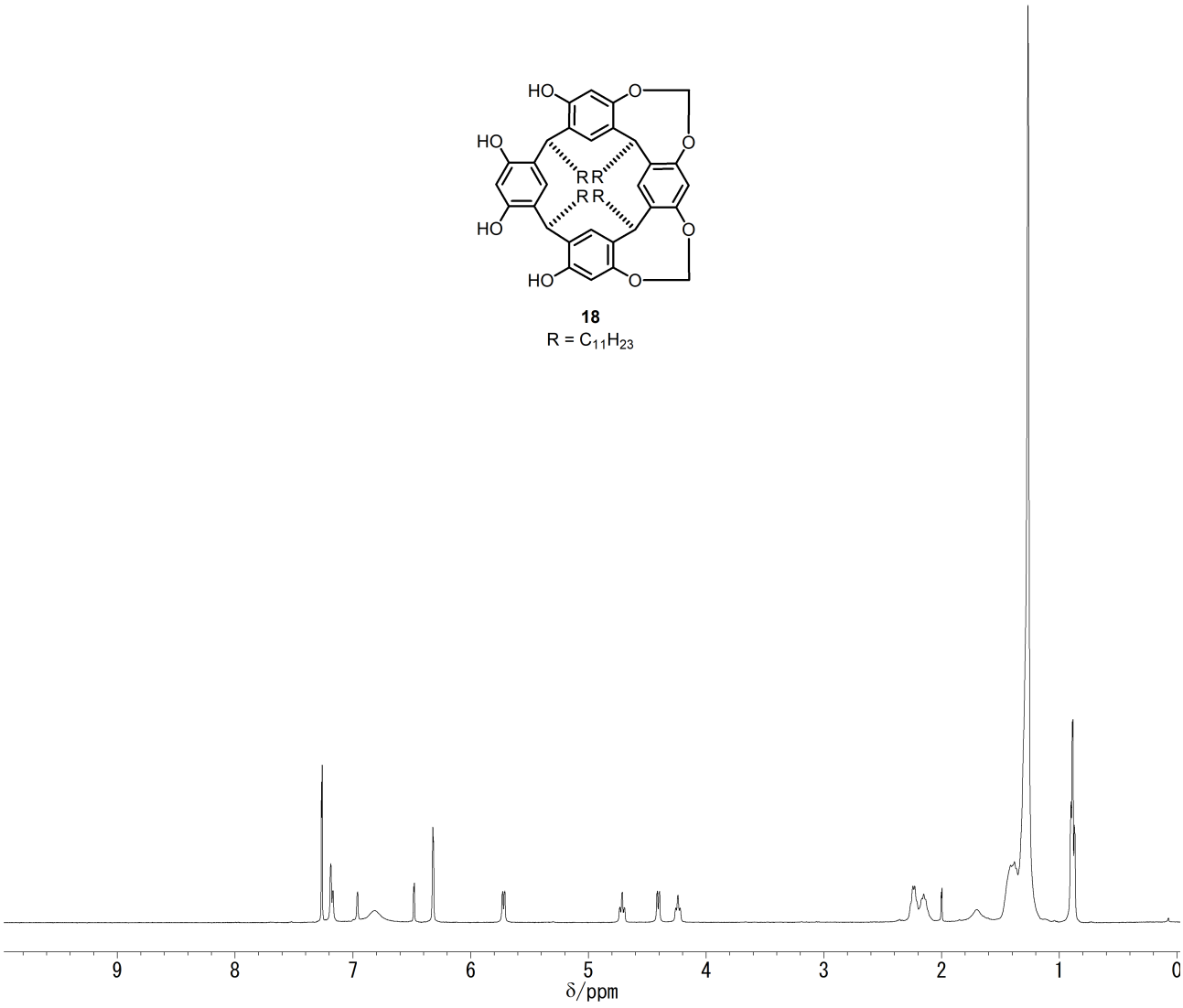
^{1}H NMR spectrum in $CDCl_3$ for **17**.



^{13}C NMR spectrum in $CDCl_3$ for **17**.

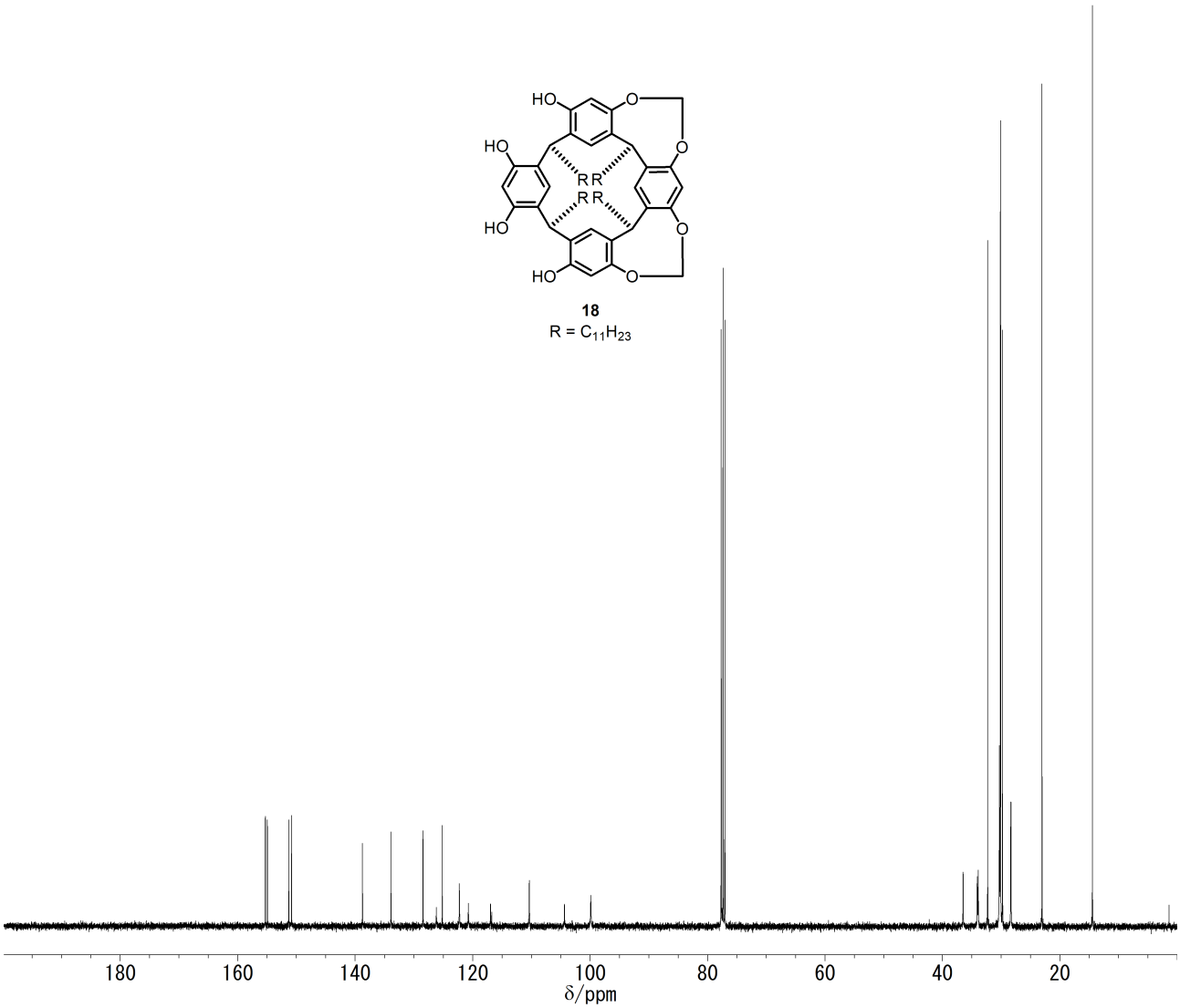


^{1}H NMR spectrum in $CDCl_3$ for **18**.

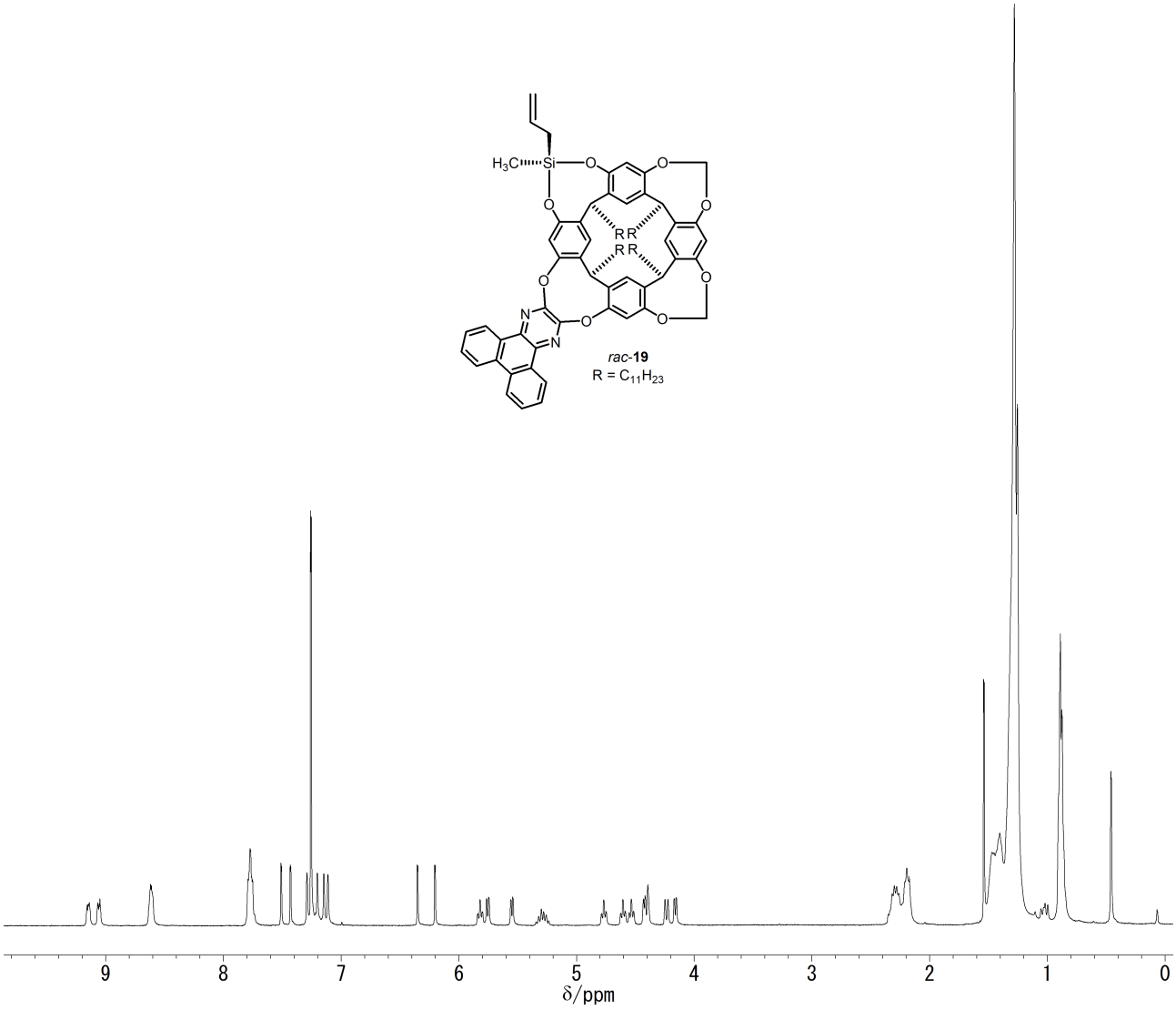


18
R = $C_{11}H_{23}$

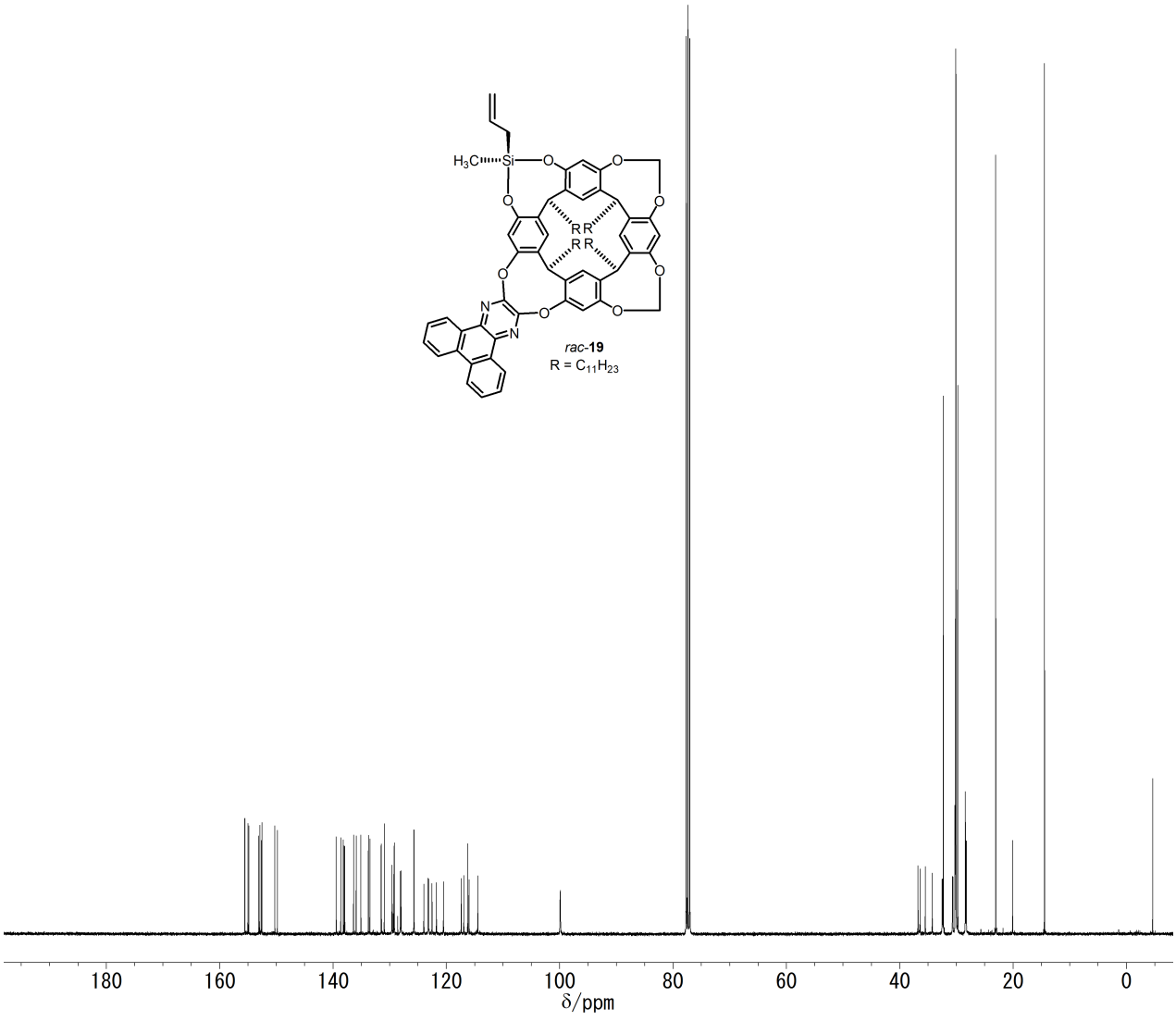
^{13}C NMR spectrum in $CDCl_3$ for **18**.



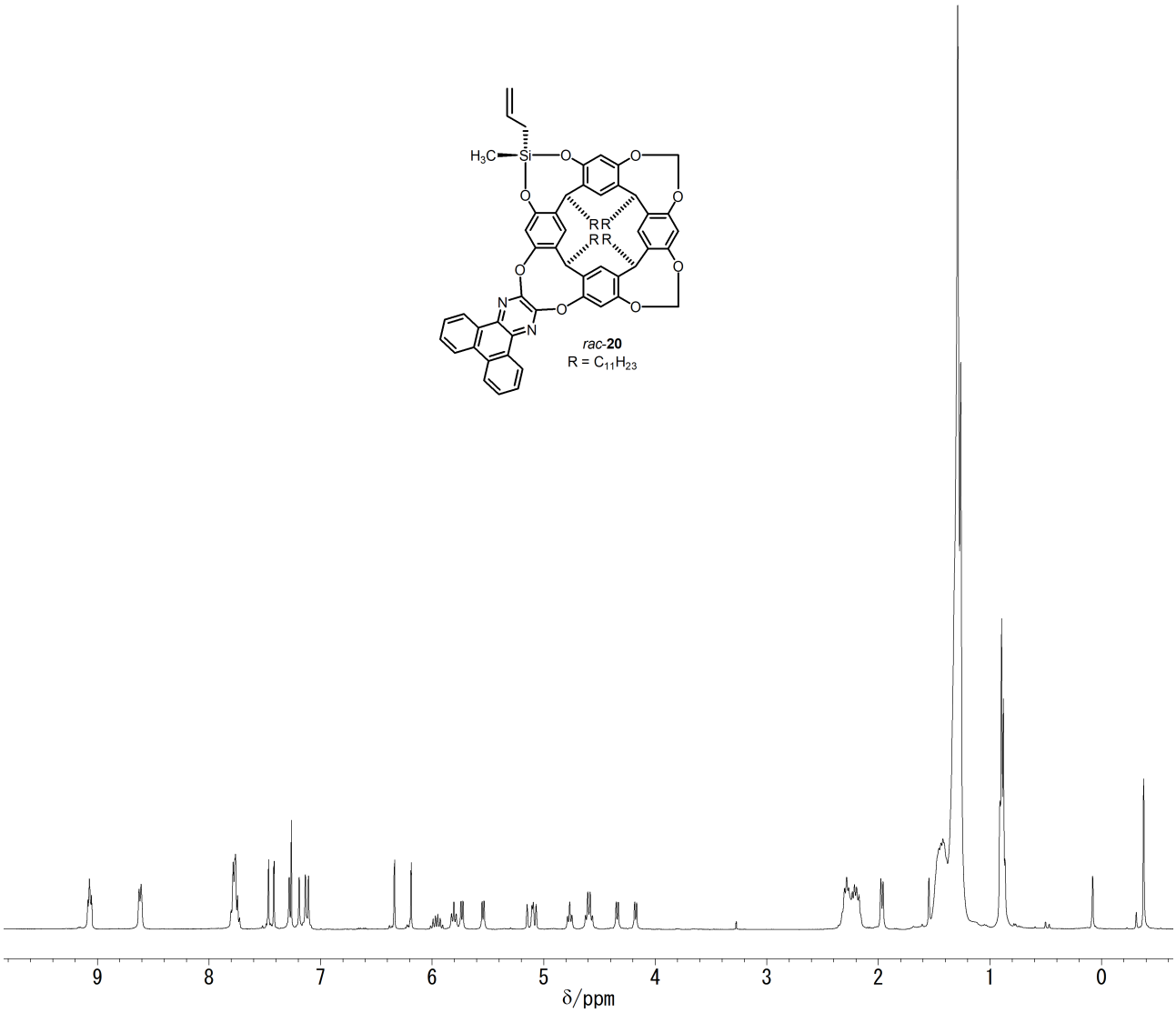
^{1}H NMR spectrum in $CDCl_3$ for *rac*-**19**.



^{13}C NMR spectrum in $CDCl_3$ for *rac*-**19**.



^{1}H NMR spectrum in $CDCl_3$ for *rac*-**20**.



^{13}C NMR spectrum in $CDCl_3$ for *rac*-**20**.