2. The $^1$H NMR stacks (Figure 1S) of allylsilane moieties for Table 2 and of resultant epoxide compounds for Table 4.
3. $^1$H NMR stacks (Figure 2S and 3S) of diastereomeric mixtures of epoxides (see Table 4).
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 2): 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 °C 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$_2$SO$_4$, concentrated in vacuo to give crude products of 2.45 g. Purification of short-plugged silica-gel column chromatography (CH$_2$Cl$_2$/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$_3$CN, 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$_3$)$_2$CO) 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$_3$)$_2$CO) 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 C₈₈H₁₁₇N₄O₈: 1357.8866 [MH]+, Found: 1357.8853.
2. The $^1$H NMR stacks (Figure 1S) of allylsilane moieties for Table 2.

Figure 1S. 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 2S and 3S) of diastereomeric mixtures of epoxides.

![Image of NMR spectra](image)

**Figure 2S.** 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 3S. 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 \textit{rac-1}, which was helped by Daicel Corporation CPI Company.

\begin{center}
\textbf{Inherent Chiral Cavitand 片側メチレン体 推奨分析条件}
\end{center}

\begin{itemize}
\item \textbf{Column:} CHIRALPAK IG (0.46cm.i.D. \times 25cmL)
\item \textbf{Eluent:} DCM = 100
\item \textbf{Flow Rate:} 1.0mL/min.
\item \textbf{Temp.:} 25 \degree C
\item \textbf{Det.:} 315 nm (UV)
\item \textbf{Injection:} 5 \mu L (1000mg/L in Eluent)
\end{itemize}

\begin{center}
\textbf{Chromatogram}
\end{center}

\begin{center}
\begin{tabular}{cccccc}
\hline
\# & Time & Area & Area\% & Height & Height\% \\
\hline
1 & 4.030 & 1541911 & 49.66 & 192846 & 73.40 \\
2 & 7.364 & 1550836 & 50.14 & 69872 & 26.60 \\
\hline
& 3052747 & 100.00 & 262720 & 100.00 \\
\hline
\end{tabular}
\end{center}

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$_3$)$_2$CO 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.
$^{13}\text{C}$ 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.
$^{13}$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.
$^{13}$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.