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FULL PAPER

Inherently Chiral Cavitands

Inherently Chiral Cavitand Curvature: Diastereoselective Oxidation of Tethered Allylsilanes

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Dedicated to Professor Julius Rebek Jr. on the occasion of his 75th birthday

Abstract: Syntheses of inwardly and outwardly directed allylsilanes those are tethered to new inherently chiral cavitands are described. Oxidized with mCPBA, these allylsilanes result in diastereomeric mixtures of epoxide molecules. Thus, it enables us to have comparative study of cavitand-structure diastereoselectivity relationship, which revealed that an inward allylsilane group flanked by a dibenzo[*f*, *h*]quinoxaline and two bridged methylene groups have the best chemical yield and diastereoselection.

Introduction

Synthetic organic compounds that contain an enforced cavity are defined as *cavitands*.[1] Cavitands impose a curved boundary that encloses an empty space.[2] The presence of such curvature can, in special circumstances, result in an asymmetric framework, that is "*inherent chirality*." Inherent chirality differs from point chirality, axial chirality, planar chirality, and helical chirality.[3] Cavitands that exist as enantiomers but lack other asymmetry elements (e.g. point chirality) have inherent chirality.[4,5] Inherently chiral cavitands have been synthetically difficult to prepare, even as racemates. Additionally, maximizing use of the curved space requires careful inwardly positioning of reactive centers.[6] Consequently, investigations on nature and potential of inherently chiral cavitands remains unexplored, even though they promise have strong potential for the progress of chiral science.[7]

Herein we report the syntheses and properties of new allylsilanes derived from the racemic diol *rac*-**1** (Figure 1). The *rac*-**1** possesses inherent chirality, which is stable because inversion of the resorcin[4]arene skeleton is impossible. Importantly, inwardly directed allylsilane *rac*-**2** and outwardly directed allylsilane *rac*-**3** were isolated. The epoxidation reaction of *rac*-**2** and *rac*-**3** would give rise to diastereomeric isomers (Scheme 1). The questions we pursue here are "*How effective can inherently chiral cavitands relay their chirality to prochiral substrates?*" "*Can this new asymmetric framework induce chiral diastereo-enriched compounds?*" In the pursuit of these questions, we also prepared *rac*-**4** to *rac*-**11** that possess different electronic and steric feature in an effort to more thoroughly understand the principles at work in inherently chiral spaces by studying the diastereoselection of allyl oxidation (Figure 2).

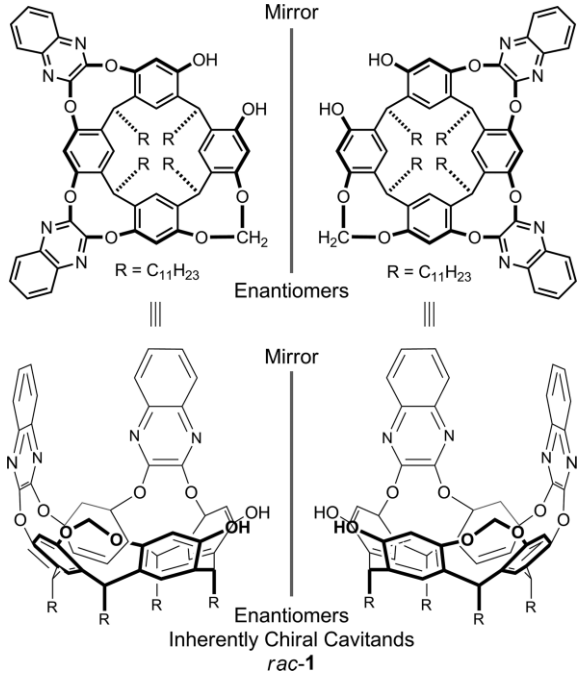

Figure 1. A mirror image of a resorcin[4]arene-based curvature molecule that represents an inherently chiral cavitand.

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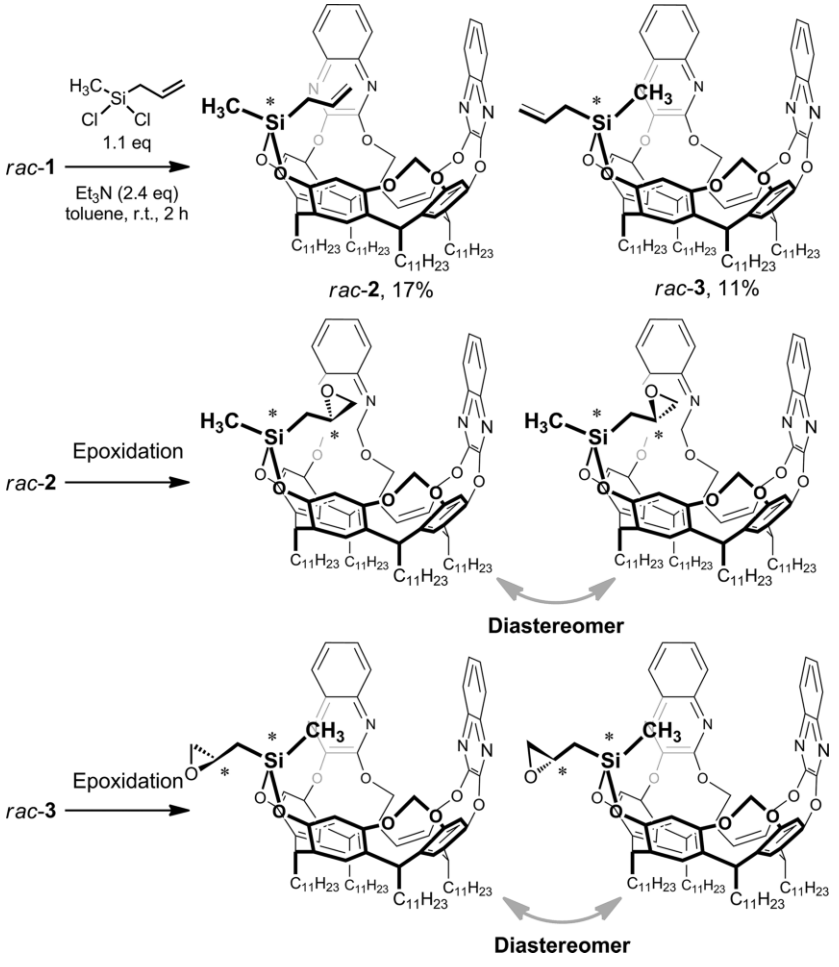


Scheme 1. Syntheses of allylsilanes *rac*-**2** and –**3**, and the following epoxidation reactions to give diastereomeric isomers.

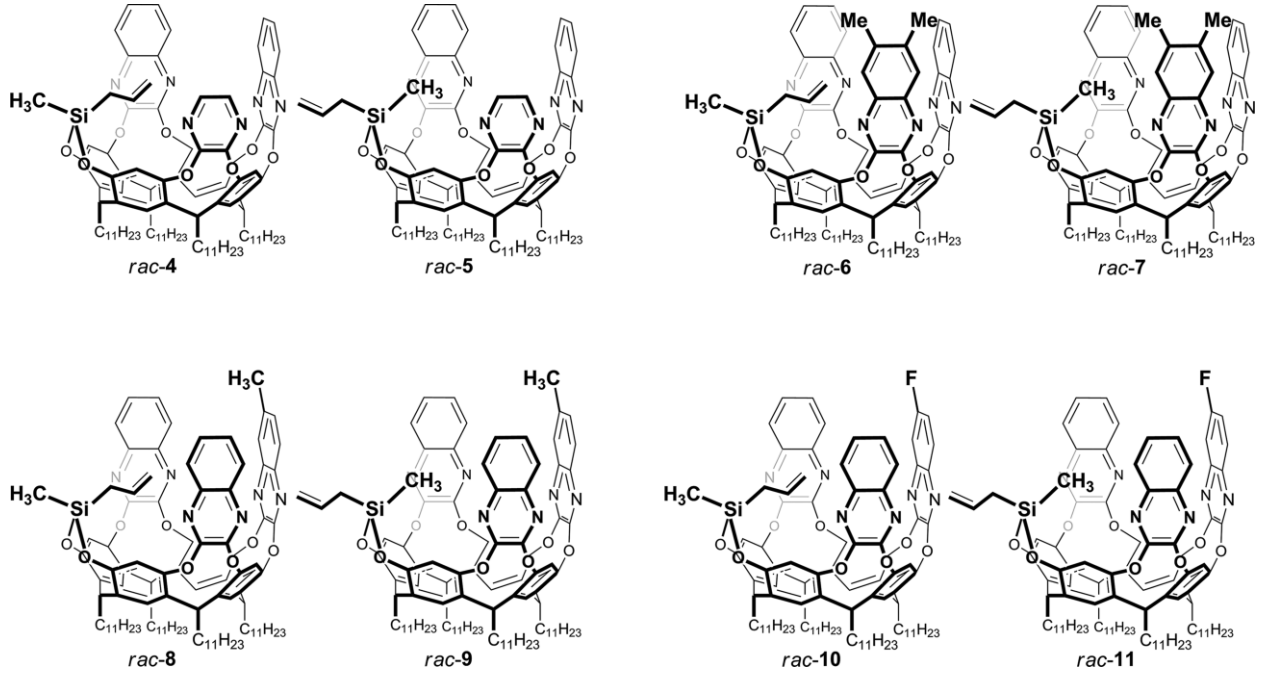


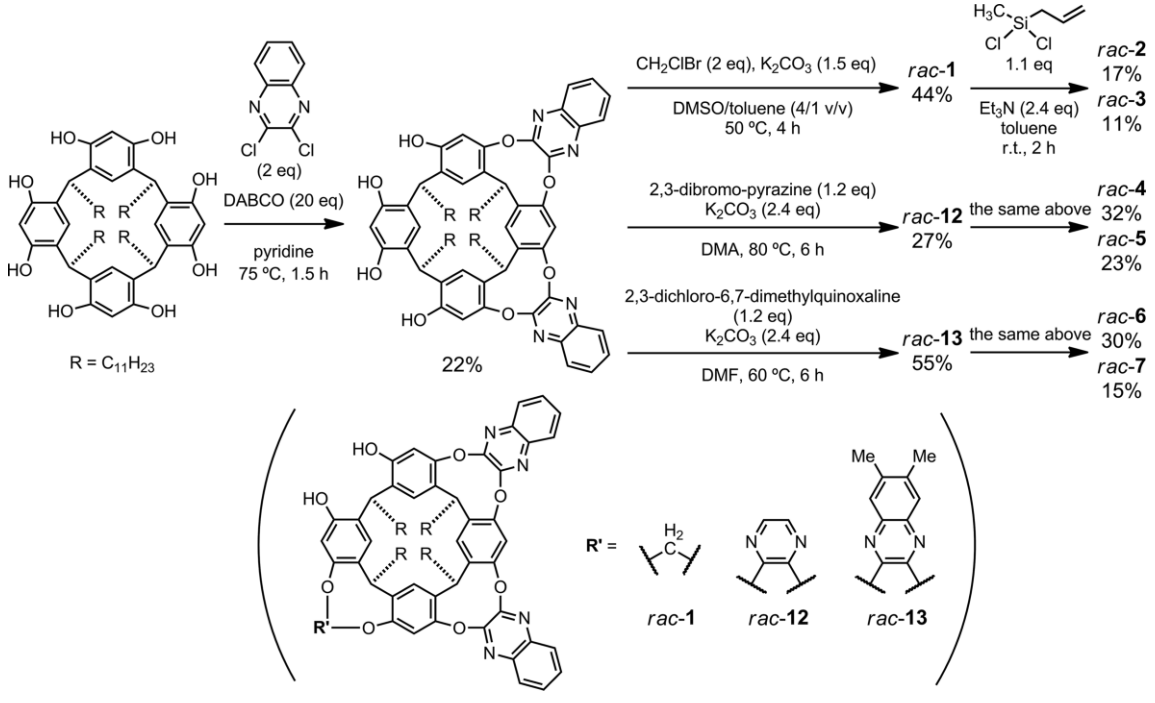
Figure 2. Four new pairs of isomers are *rac*-**4**/*rac*-**5**, *rac*-**6**/*rac*-**7**, *rac*-**8**/*rac*-**9**, and *rac*-**10**/*rac*-**11**. Introverted allylsilanes are *rac*-**4**, –**6**, –**8**, and –**10**, and extroverted allylsilanes correspond to *rac*-**5**, –**7**, –**9**, and –**11**.

Results and Discussion

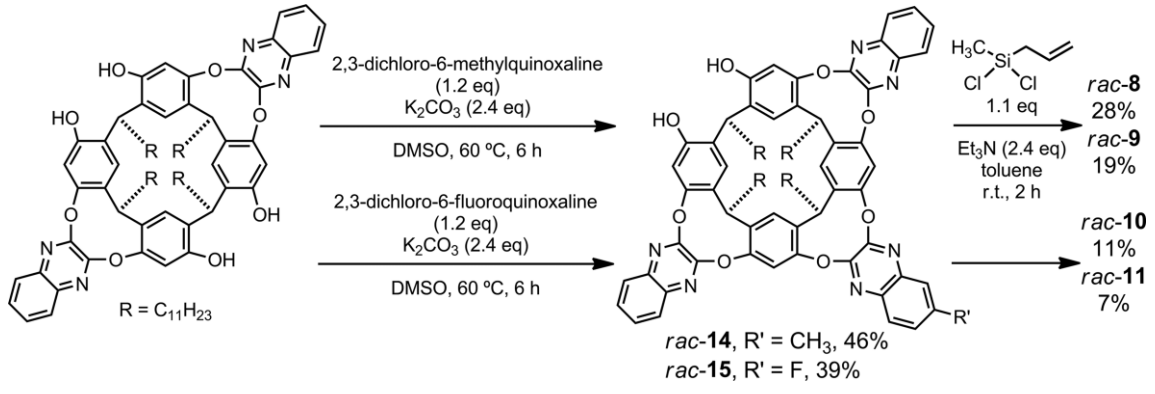
Routes for syntheses of *rac*-**1** and the corresponding allylsilanes *rac*-**2**–*rac*-**7** are illustrated in Scheme 2. Preparation of *cis*-positioned diquinoxaline-spanned resorcin[4]arene was laborious,[8] but the use of DABCO (1,4-diazabicyclo[2.2.2]octane) and pyridine pushed the chemical yield to 22 %. The *cis*-positioned tetra-ol is a prochiral platform for producing asymmetric molecules: the platform reacted with CH_2BrCl, 2,3-dibromopyrazine, and 2,3-dichloro-7,8-dimethylquinoxaline[9] to yield *rac*-**1** in 44 %, *rac*-**12** in 27 %, and *rac*-**13** in 55 %, respectively.[10,11] The resolution of *rac*-**1** was performed by analytical HPLC using a Chiralpak IG column singly eluted with CH_2Cl_2 in flow rate 1 mL/min at 25 °C, which afforded two peaks of t_R = 4.0 min and 7.4 min with perfect separation, confirming the presence of two enantiomers.[12] Then, the *rac*-**1**, *rac*-**12**, and *rac*-**13** reacted with commercially available allyl(dichloro)methylsilane, giving isomeric products of inward and outward allyl compounds those are *rac*-**2**/*rac*-**3**, *rac*-**4**/*rac*-**5**, and *rac*-**6**/*rac*-**7**, respectively.[13] The separation of these isomers (**2** from **3**, **4** from **5**, and **6** from **7**), which were prepared in roughly 1:1 ratios was an embarrassing operation.

Scheme 3 shows synthetic routes to allylsilanes *rac*-**8**–*rac*-**11** that are based on trans-positioned diquinoxaline-spanned resorcin[4]arene. The *trans*-positioned tetra-ol reacted with 2,3-dichloro-6-methylquinoxaline and 2,3-dichloro-6-fluoroquinoxaline in 46 % of *rac*-**14** and 39 % of *rac*-**15** yields, respectively.[14] The racemates of *rac*-**14** and *rac*-**15** comprises two enantiomers bearing inherent chirality like *rac*-**1**, which lead to the corresponding allylsilanes of *rac*-**8**, –**9**, –**10**, and –**11**.

We made the following observations about the solution dynamics of these allylsilanes derivatives.[15] Typically, chemical shifts of the methine protons below the quinoxaline moieties, like H^a and H^b (Table 1), explain the behaviour: the protons around 5.5 ppm are indicative vase conformers, whereas



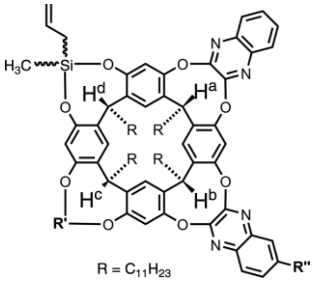
Scheme 2. Synthetic routes to intro- and extroverted allylsilanes *rac*-**2**–*rac*-**7**.



Scheme 3. Synthetic route to intro- and extroverted allylsilanes *rac*-**8**–*rac*-**11**.

3.7 ppm indicates the kite form.[16] Protons H^c and H^d reside in an electronic different from the other protons H^a and H^b. The summarized chemical shifts of the methines H^a–H^d are found in Table 1. H^a and H^b in both $CDCl_3$ and [D_8]toluene are found between 5.6 and 6.2 ppm, respectively. This observation is in agreement with the vase-kite switching cavitands, in which a class of quinoxaline walled cavitands prefer vase conformers.

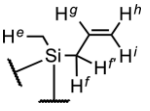
Table 1. NMR chemical shifts of the methine protons H^a–H^d for the allylsilanes of *rac*-**n** (***n*** = **2**–**11**).



Entry	Cavitand	Solvent	Chemical shifts [ppm]			
			H^a	H^b	H^c	H^d
1	*rac*-**2**	$CDCl_3$	5.71	5.77	4.64	4.51
2		C_7D_8	6.15	6.17	5.10	4.77
3	*rac*-**3**	$CDCl_3$	5.69	5.76	4.64	4.53
4		C_7D_8	6.12	6.18	5.07	4.80
5	*rac*-**4**	$CDCl_3$	5.69	5.75	5.61	4.52
6		C_7D_8	6.11	6.17	6.03	4.73
7	*rac*-**5**	$CDCl_3$	5.66	5.72	5.59	4.53
8		C_7D_8	6.12	6.18	6.04	4.77
9	*rac*-**6**	$CDCl_3$	5.68	5.75	5.67	4.52
10		C_7D_8	6.16	6.19	6.05	4.74
11	*rac*-**7**	$CDCl_3$	5.66	5.73	5.66	4.54
12		C_7D_8	6.12	6.15	6.06	4.79
13	*rac*-**8**	$CDCl_3$	5.68	5.76	5.68	4.53
14		C_7D_8	6.18	6.07	6.18	4.73
15	*rac*-**9**	$CDCl_3$	5.65	5.73	5.65	4.55
16		C_7D_8	6.16	6.08	6.16	4.77
17	*rac*-**10**	$CDCl_3$	5.66	5.72	5.66	4.53
18		C_7D_8	6.17	6.02	6.17	4.73
19	*rac*-**11**	$CDCl_3$	5.64	5.70	5.64	4.55
20		C_7D_8	6.13	6.03	6.13	4.76

The chemical shift difference between in- and out-isomeric allylsilanes is also documented (Table 2). Protons H^e–H^i belong to methyl and allyl groups on silicon, and because of the magnetic shielding caused by the cavity, inwardly directed protons shift *upfield*.[17–19] These chemical shifts are summarized in Table 2. The CH_3 protons H^e of *rac*-**2**, –**4**, –**6**, –**8**, –**10** nearly positioned at 0.45 ppm, although those of *rac*-**3**, –**5**, –**7**, –**9**, –**11** shifted upfield to around - 0.50 ppm. On the other hand, the CH_2 protons H^f of *rac*-**2**, –**4**, –**6**, –**8**, –**10** shifted to more upfield ca. 1.0 ppm than those of *rac*-**3**, –**5**, –**7**, –**9**, –**11** nearly at 2.0 ppm. These mean that H^f of *rac*-**2**, –**4**, –**6**, –**8**, –**10** and H^e of *rac*-**3**, –**5**, –**7**, –**9**, –**11** are enclosed by the interior space: thus, the orientation of the substituents on the silicon atoms was determined. In addition, we summarized the difference in chemical shifts ($\Delta\delta$ values) between each two-isomeric allylsilanes (Table 3). The protons of the H^e (CH_3) and H^f/$H^{f'}$ (CH_2) directly bonded to the silicon atoms show relatively large values of approximately 0.82 – 1.84 as compared to the corresponding values of H^g, H^h, and H^i. This means the closest position to the silicon atom is most sufficiently covered by the anisotropic effect of the strong π-surrounding induced by the inner space. In addition, it is especially noteworthy that only geminal protons H^f/$H^{f'}$ of *rac*-**2** and *rac*-**4** reflect the asymmetry and are distinguishable from each other. The corresponding H^f protons of other cavitands are free from influence of the dissymmetrical π-space, even if they are placed inside or not and partitioned or not.

Table 2. The chemical shifts (400 MHz) of H^e, H^f, $H^{f'}$, H^g, H^h, and H^i for allylsilane moieties tethered to *rac*-**n** (***n*** = **2** –**11**).



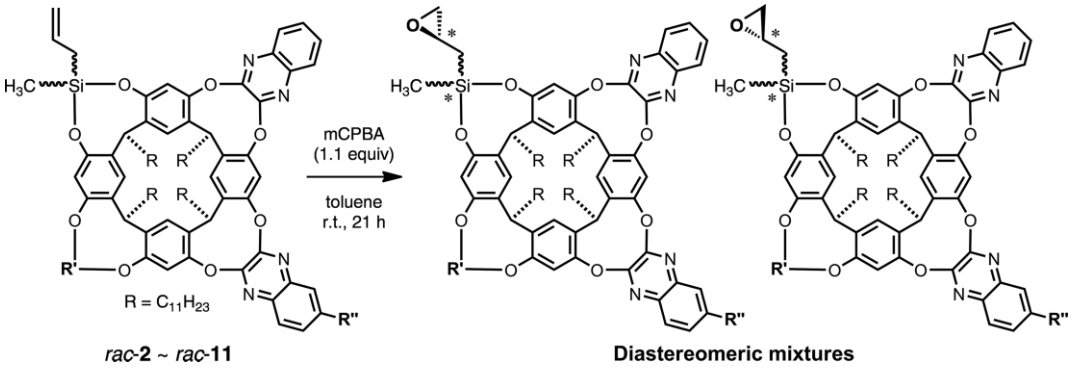
Entry	Solvent	Cavitand *rac*-**n**	Chemical shifts [ppm]					
			H^e	H^f	$H^{f'}$	H^g	H^h	H^i
1	$CDCl_3$	*rac*-**2**	0.43	1.07	0.97	5.49	4.83	4.68
2		*rac*-**3**	–0.39	1.90		5.89	5.01	5.06
3		*rac*-**4**	0.44	0.95	0.81	5.45	4.83	4.66
4		*rac*-**5**	–0.49	1.90		5.91	5.03	5.08
5		*rac*-**6**	0.45	0.79		5.39	4.79	4.59
6		*rac*-**7**	–0.58	1.93		5.94	5.05	5.11
7		*rac*-**8**	0.46	0.82		5.41	4.83	4.63
8		*rac*-**9**	–0.56	1.93		5.94	5.06	5.11
9		*rac*-**10**	0.46	0.82		5.42	4.84	4.64
10		*rac*-**11**	–0.54	1.94		5.94	5.06	5.11
11	C_7D_8	*rac*-**2**	0.31	0.39	0.20	5.13	4.67	4.28
12		*rac*-**3**	–1.0	1.71		5.82	4.94	4.96
13		*rac*-**4**	0.27	0.036	–0.13	4.99	4.59	4.11
14		*rac*-**5**	–1.26	1.65		5.78	4.90	4.92
15		*rac*-**6**	0.28	–0.13		4.96	4.57	4.12
16		*rac*-**7**	–1.29	1.66		5.80	4.92	4.94
17		*rac*-**8**	0.28	–0.19		4.94	4.59	4.12
18		*rac*-**9**	–1.38	1.65		5.81	4.93	4.94
19		*rac*-**10**	0.27	–0.24		4.91	4.58	4.11
20		*rac*-**11**	–1.43	1.63		5.80	4.93	4.93

Table 3. The differences in chemical shifts ($\Delta\delta$) between the inwardly and outwardly directed allyl protons. The $\Delta\delta$ values are standardized as (δ of *rac*-**2**, –**4**, –**6**, –**8**, –**10**) – (δ of *rac*-**3**, -**5**, -**7**, -**9**, -**11**), respectively.

Entry	Solvent	Cavitands *rac*-**n**		$\Delta\delta$ H^e	H^f	$H^{f'}$	H^g	H^h	H^i
1	$CDCl_3$	**2**	**3**	0.82	–0.83	–0.93	–0.40	–0.18	–0.38
2		**4**	**5**	0.93	–0.95	–1.09	–0.46	–0.20	–0.42
3		**6**	**7**	1.03	–1.14		–0.55	–0.26	–0.52
4		**8**	**9**	1.02	–1.11		–0.53	–0.23	–0.48
5		**10**	**11**	1.00	–1.12		–0.52	–0.22	–0.47
6	C_7D_8	**2**	**3**	1.31	–1.32	–1.51	–0.69	–0.27	–0.68
7		**4**	**5**	1.53	–1.61	–1.78	–0.79	–0.31	–0.81
8		**6**	**7**	1.57	–1.79		–0.84	–0.35	–0.82
9		**8**	**9**	1.66	–1.84		–0.87	–0.34	–0.82
10		**10**	**11**	1.70	–1.87		–0.89	–0.35	–0.82

With the success in structural evaluation of series of cavitands,[20] we eventually set out to study the diastereomeric ratios that result from epoxidation of allylsilanes *rac*-**2**–*rac*-**11**. The results are summarized in Table 4. MCPBA (*meta*-Chloroperbenzoic acid) in toluene was used at room temperature. After 12 hours reaction showed completion by TLC. Inwardly directed allyl groups were more reactive than their outward counter-

Table 4. Evaluation of reactivities and selectivities of allylsilanes *rac*-**n** (***n*** = **2** – **1ba1**) on the epoxidation.[a]



Entry	Allylsilanes	Allyl orientation	Yield[%][b]	Product ratios[c]
1	*rac*-**2**	in	86	60:40
2	*rac*-**3**	out	41	51:49
3	*rac*-**4**	in	52	60:40
4	*rac*-**5**	out	42	51:49
5			67	51:49
6[d]	*rac*-**6**	in	60	52:48
7[e]			20	51:49
8	*rac*-**7**	out	40	51:49
9	*rac*-**8**	in	80	51:49
10	*rac*-**9**	out	52	50:50
11	*rac*-**10**	in	70	51:49
12	*rac*-**11**	out	50	51:49

[a] Conditions: allylsilanes (0.019 mmol, 30 mg), mCPBA (25 % water contained, 0.028 mmol, 6.4 mg), dry toluene (1 mL). [b] Isolated yields of diastereomeric mixtures of resultant epoxides. [c] Determined in ^{1}H NMR spectra (400 MHz, C_6D_6) on the basis of singlet peaks those are corresponding to the aromatic protons in resorcin[4]arene skeletons (for *rac*-**2**, -**4**, -**6**, -**8**, -**10**) and protons in epoxide ring moieties (for *rac*-**3**, -**5**, -**7**, -**9**, -**11**). These peaks were totally separated between diastereomeric isomers. ^{1}H NMR stacks are summarized in Figure S2 and Figure S3 of Supporting Information. [d] CH_2Cl_2 was used as a solvent. [e] 1,3,5-mesitylene was used as a solvent.

parts: these phenomena were observed in our previous report,[13] in which the inside π-cloud actively stabilizes the reaction. For diastereomeric ratios, better distributions of ca. 60:40 were observed with inwardly directed allyl groups found in *rac*-**2** and *rac*-**4**. These variants have two short walls compared to the others in the series (entries 1 and 3). The larger walls of *rac*-**6**–*rac*-**11** gave almost ca. 50:50 diastereomeric ratios, independent allyl group orientation (entries 5–12). This indicates that having one opening (or low height wall) is advantageous for diastereoselection of the prochiral allyl group.

Using this data, we designed a final candidate *rac*-**16** that is bridged with two methylenes and one wider dibenzo[*f*,*h*]quinoxaline (Figure 3). A straightforward synthetic route to *rac*-**16** and its derivative allylsilanes *rac*-**19**/*rac*-**20** are illustrated in Scheme 4. The tetra-ol platform was bridged with two methylene units in 79 % yield of **17**, and this was followed by removal of two quinoxaline walls in 68 % yield of **18**. Then, reaction of **18** with 2,3-dichloro-dibenzo[*f*,*h*]quinoxaline afforded *rac*-**16** in 41 % yield, although a side-product of two-walled cavitand was accompanied in 15 %. Finally, *rac*-**16** was converted into inward allyl *rac*-**19** in 26 % yield and an outward allyl *rac*-**20** in 12 % yield. Chemical shift analysis is consistent with our prior cavitands above, meaning that *rac*-**19** and *rac*-**20** are in the *vase* shape (Table 5 and Table 6).

Given the stereo-defined synthesis of allylsilanes *rac*-**19**, and –**20**, we then investigated structural effects on diastereo-

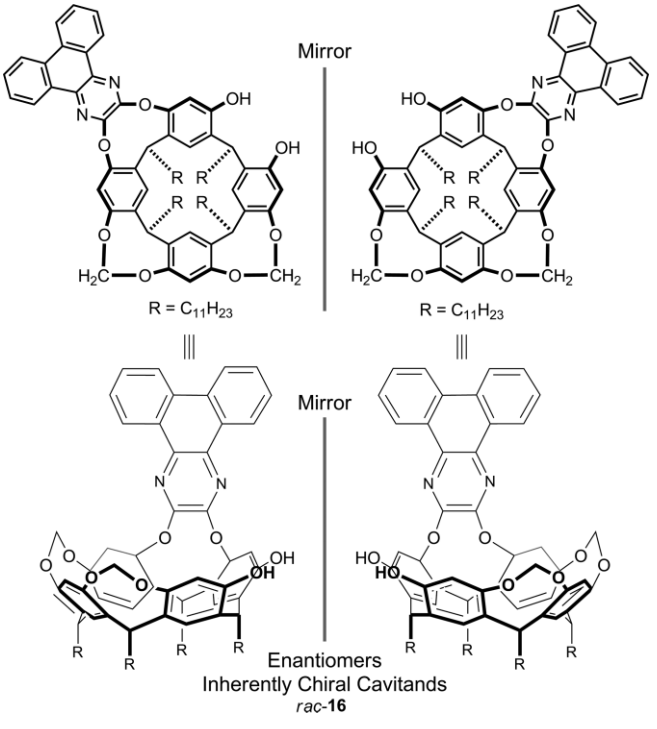
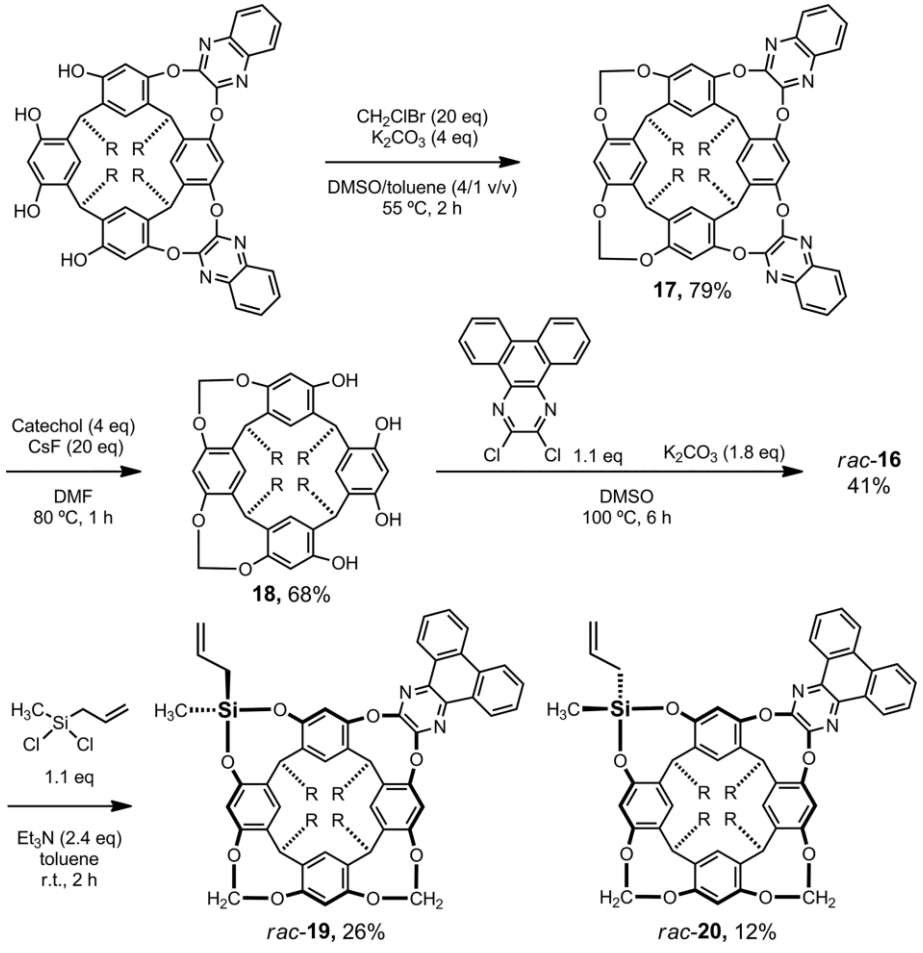
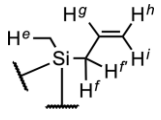


Figure 3. Inherently chiral cavitands *rac*-**16** that is featured with two methylene bridges and one dibenzo[*f*,*h*]quinoxaline.



Scheme 4. A synthetic route to isomeric allylsilanes of *rac*-**19** and *rac*-**20**.

Table 5. The chemical shifts (400 MHz) of H^e, H^f, $H^{f'}$, H^g, H^h and H^i for allylsilane moieties tethered to *rac*-**n** (***n*** = **19**–**20**).



Entry	Solvent	Cavitands *rac*-**n**	Chemical shifts [ppm] H^e	H^f	$H^{f'}$	H^g	H^h	H^i
1	$CDCl_3$	*rac*-**19**	0.46	1.03	1.34[a]	5.29	4.23	4.41
2		*rac*-**20**	–0.38	1.97		5.95	5.08	5.13
3	C_7D_8	*rac*-**19**	0.37	0.73	0.61	5.24	4.37	4.26
4		*rac*-**20**	–0.56	1.84		5.97	5.08	5.04

[a] This $H^{f'}$ peak overlaps with many peaks of aliphatic protons 72H (1.41–1.26 ppm) and doesn't give an accurate value. Thus, we inferred this chemical shift as a median value of the amplitude.

Table 6. The differences in chemical shifts ($\Delta\delta$) between the inwardly and outwardly directed allyl protons. The $\Delta\delta$ values are standardized as (δ of *rac*-**19**) – (δ of *rac*-**20**).

Entry	Solvent	Cavitands *rac*-**n**		$\Delta\delta$ H^e	H^f	$H^{f'}$	H^g	H^h	H^i
1	$CDCl_3$	**19**	**20**	0.84	–0.94	–0.63	–0.66	–0.85	–0.72
2	C_7D_8	**19**	**20**	0.93	–1.11	–1.23	–0.73	–0.71	–0.78

selective production in epoxidation reactions (Table 7). The *rac*-**19** afforded the highest diastereomeric ratio of 64:36 with excellent chemical yield of 84 % (entry 1). In contrast, the reaction of *rac*-**20** resulted in an even 50:50 diastereomeric ratio with low 42 % yield (entry 2). These results confirm our earlier observation: the asymmetric compartment partitioned is effective when a mix of tall/wide groups and much smaller bridging groups provides for the inherent chirality of the system. Very likely, this will result in a strong preference for selective approach of mCPBA to the more accessible prochiral face of the allyl carbon–carbon double bond.

Table 7. Evaluation of reactivities and selectivities of allylsilanes *rac*-**19**/*rac*-**20** on the mCPBA-mediated epoxidation.[a]

Entry	Allylsilanes	Yield[%][b]	Product ratios[c]
1	*rac*-**19** (in)	84	64:36
2	*rac*-**20** (out)	42	50:50

[a] Conditions: allylsilanes (0.019 mmol, 30 mg), mCPBA (25 % water contained, 0.028 mmol, 6.4 mg), dry toluene (1 mL). [b] Isolated yields of diastereomeric mixtures of resultant epoxides. [c] Determined in ^1H NMR spectra (400 MHz, C_6D_6) on the basis of singlet peaks those are corresponding to the aromatic protons in resorcin[4]arene skeletons (for *rac*-**19**), and protons in epoxide ring moiety (for *rac*-**20**). These peaks were totally separated between diastereomeric isomers. ^1H NMR stacks are summarized in Figure S2 and 3S of Supporting Information.

Conclusions

In summary, we have studied syntheses of racemic cavitand compounds having inherent chirality. These compounds were further elaborated by the covalent insertion of an allylsilane that exists as a pair of in-out isomers that were separable. Oxidation of this suite of compounds allowed us to directly observe diastereomeric ratios and relate those to the features that give rise to inherent chirality of the cavitand species. Comparative study of structure-diastereoselectivity relationships strongly suggests several salient features that will direct future study. Firstly, the *cis*-diquinoxaline-spanned resorcin[4]arene works as a platform for diverse syntheses of inherently chiral cavitands. Second, a mixture of small bridging methylene groups and much taller, flatter walls gave higher diastereomeric ratios and good conversion of the starting allyl substrates when they were inwardly directed. This confirms both reaction stabilization and effective blocking of one pi-face of the allyl group. Third, one large dibenzo-[*f*,*h*]quinoxaline walls is sufficient to have diastereoselection and resulted in the best chemical yield and stereoselection. Finally, outwardly directed allyl groups did not experience any effects from the inherent chirality that the cavitands possess under these reaction conditions. These features illustrate relevance of the quinoxaline resorcin[4]arene cavitands to the design of new asymmetric reactors, reactions, and catalysis.[21,22] Further development along these avenues is in progress.

Experimental Section

General Methods: All reactions sensitive to air or moisture were carried out under an argon or a nitrogen atmosphere and anhydrous conditions unless otherwise noted. Dry solvents were purchased and used without further purification and dehydration. All reagents were purchased and used without further purification. Analytical thin layer chromatography was carried out on Merck silica $60F_{254}$. Column chromatography was carried out with silica gel 60_N (Kanto Chemical Co.). LRMS and HRMS were reported on the basis of TOF (time of flight)-MS (MADI-TOF or LCMS-IT-TOF), and DART (Direct Analysis in Real Time)-MS. ^{1}H and ^{13}C NMR spectra were recorded with a 5 mm QNP probe at 400 MHz and 100 MHz, respectively. Chemical shifts are reported in d (ppm) with reference to residual solvent signals [^{1}H NMR: $CHCl_3$ (7.26), C_7H_8 (2.08), C_6H_6 (7.16), CH_2Cl_2 (5.32); ^{13}C NMR: $CDCl_3$ (77.0)]. Signal patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad.

Synthesis of di-ol platform *rac*-1: (see Scheme 2) *rac*-**1**: Under an argon atmosphere, a solution of the *cis*-diquinoxaline spanned resorcin[4]arene (1.22 g, 0.9 mmol) in toluene (4 mL) and DMSO (16 mL) was stirred 55 °C for 10 min, and followed by addition of K_2CO_3 (187 mg, 1.35 mmol) and CH_2BrCl (0.12 mL, 1.8 mmol). After 4 h the mixture was cooled to room temperature and filtered through a pad of Celite with eluent of toluene, and the filtrate was evaporated off. The residue dissolved into toluene was transferred into a separatory funnel, and washed with water (10 mL) and brine (10 mL × 3), dried with Na_2SO_4, and concentrated in vacuo to give a crude of 1.20 g as a brown solid material. Purification by silica-gel column chromatography (toluene/EtOAc = 9:1) afforded *rac*-**1** of 485 mg as white solid materials (39 %). R_f values 0.35 (hexane/EtOAc = 2:1). ^{1}HNMR (400 MHz, $CDCl_3$) 8.41 (s, 1H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.59–7.52 (m, 3H), 7.41 (brs, 1H, -OH), 7.32 (s, 1H), 7.29 (s, 1H), 7.23 (s, 1H), 7.14 (s, 1H), 7.11 (s, 2H), 6.87 (brs, 1H, -OH), 6.15 (s, 1H), 5.73 (t, *J* = 8.0 Hz, 1H), 5.64 (d, *J* = 7.2 Hz, 1H), 5.61 (t, *J* = 8.0 Hz, 1H), 4.69 (t, *J* = 8.0 Hz, 1H), 4.23 (t, *J* = 8.0 Hz, 1H), 4.15 (d, *J* = 7.2 Hz, 1H), 2.30–2.11 (m, 8H), 1.46–1.27 (m, 72H), 0.91–0.87 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.6, 155.5, 153.3, 153.22, 153.15, 153.0, 152.9, 152.6, 152.40, 152.35, 151.8, 151.2, 140.17, 140.16, 139.7, 139.4, 136.7 (two peaks are overlapped), 135.4, 133.5, 130.9, 129.9, 129.7 (two peaks are overlapped), 129.6, 129.42, 129.37, 128.6, 128.3, 128.2, 127.9, 127.6, 125.1, 123.6, 122.04, 121.98, 118.9, 117.9, 110.4, 110.2, 99.9, 36.3, 34.51, 34.45, 33.9, 32.7, 32.5, 32.32, 32.30 (many peaks are overlapped), 30.4, 30.3, 30.2, 30.13, 30.09 (many peaks are overlapped), 30.0, 29.9, 29.8, 28.4, 28.3, 28.2, 23.1 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1392 $[M + Na]^+$; IR (neat) 3327 (-OH), 2925, 2849, 1483, 1408, 1328, 1152, 957, 754 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{89}H_{116}N_4NaO_8$: 1391.8685 $[M + Na]^+$, found 1391.8703.

Synthesis of di-ol platform *rac*-12: (see Scheme 2) A solution of the *cis*-diquinoxaline spanned resorcin[4]arene (200 mg, 0.15 mmol) in DMA (2 mL) under an argon atmosphere was stirred 80 °C for 10 min, and followed by addition of K_2CO_3 (41 mg, 0.29 mmol) and 1,2-dibromopyrazine (42 mg, 0.18 mmol). After 6 h the reaction mixture was cooled to room temperature, and filtered through a pad of Celite with eluent of toluene, and the filtrate was evaporated off. The residue dissolved into toluene was transferred into a separatory funnel, washed with water (10 mL) and brine (10 mL × 3), dried with Na_2SO_4, and concentrated to give a crude of 197 mg as a brown solid material. Purification by silica-gel column chromatography (toluene/EtOAc = 9:1) afforded *rac*-**12** of 57 mg as white solid materials (27 %). R_f values 0.42 (hexane/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.22 (s, 1H), 8.15 (brs, 2H, -OH), 8.03 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.90–7.87 (m, 2H), 7.81–7.80 (m, 2H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.62–7.49 (m, 4H), 7.25 (s, 1H), 7.13 (s, 1H), 7.11 (s, 3H), 7.09 (s, 1H), 6.88 (s, 1H), 5.51–5.45 (m, 2H), 5.41 (t, *J* = 7.4 Hz, 1H), 4.25 (t, *J* = 7.4 Hz, 1H), 2.26–2.18 (m, 8H), 1.28–1.27 (m, 72H), 0.90–0.87 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 154.2, 154.1, 153.0, 152.91, 158.7 (two peaks are overlapped), 152.84, 152.82, 152.74, 152.69, 152.5, 152.1, 151.7, 140.04, 139.96 (two peaks are overlapped), 139.7, 139.6, 139.2, 136.63, 136.58, 135.8, 135.7, 130.5, 130.4, 129.7, 129.5, 129.4, 129.3, 129.11 (two peaks are overlapped), 129.07 (two peaks are overlapped), 128.3, 128.2, 127.9, 124.4, 124.0, 123.8, 123.7, 118.91, 118.87, 110.5, 110.4, 34.9, 34.6, 34.3, 34.14, 34.09, 32.9, 32.8, 32.6, 32.3 (many peaks are overlapped), 30.12, 30.08, 29.8 (many peaks are overlapped), 28.3, 23.1 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1434 $[MH]^+$; IR (neat) 3267, 2917, 2845, 1606, 1578, 1483, 1408, 1324, 1152, 759 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{92}H_{118}N_6O_8$: 1430.8351 $[MH]^+$, found 1433.8938.

Synthesis of di-ol platform *rac*-13: (see Scheme 2) To a 25 mL flask charged with a suspension of *cis*-diquinoxaline-spanned resorcin[4]arene (400 mg, 0.3 mmol) in DMSO (8 mL) was added K_2CO_3 (74 mg, 0.53 mmol) and 2,3-dichloro-6,7-dimethylquinoxaline (74 mg, 0.32 mmol) at ambient temperature. After stirred at 60 °C for 6 h, the mixture was cooled to room temperature, and filtered through a pad of Celite. The filtrate was evaporated off, and the residue dissolved into toluene was transferred into a separatory funnel, washed with water (10 mL) and brine (10 mL × 2), dried with Na_2SO_4, and concentrated in vacuo to give a crude of 434 mg as a brown solid material. Purification by silica-gel column chromatography (toluene/EtOAc = 19:1) afforded *rac*-**13** of 243 mg as white solid materials (55 %). R_f values 0.45 (toluene/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.26 (s, 1H), 8.25 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.86–7.80 (m, 1H), 7.82–7.80 (m, 1H), 7.69–7.67 (m, 2H), 7.58 (dd, *J* =

8.2, 8.2 Hz, 1H), 7.49–7.47 (m, 3H), 7.40 (s, 1H), 7.29 (s, 1H), 7.28 (s, 1H), 7.14 (s, 2H), 7.09 (s, 1H), 7.06 (s, 1H), 5.61 (t, *J* = 8.0 Hz, 1H), 5.53 (t, *J* = 8.0 Hz, 2H), 4.26 (t, *J* = 8.0 Hz, 1H), 2.40 (s, 3H), 2.26–2.17 (m, 11H), 1.44–1.27 (m, 72H), 0.90–0.87 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.0 (two peaks are overlapped), 152.48 (two peaks are overlapped), 152.83, 152.81, 152.7 (two peaks are overlapped), 152.30, 152.28, 152.1, 152.0, 151.5, 140.1, 140.01, 139.98, 139.8, 139.7, 138.7, 138.2, 136.7, 136.6, 136.0, 135.8, 135.7, 130.7, 130.6, 129.5, 129.4, 129.24, 129.20, 129.1, 129.0, 128.58, 128.56, 128.2 (two peaks are overlapped), 128.1, 127.9, 127.4, 124.2, 124.0, 123.7, 123.5, 119.0, 118.9, 110.8, 110.6, 34.9, 34.5 (many peaks are overlapped), 34.1 (many peaks are overlapped), 32.9 (many peaks are overlapped), 32.6 (many peaks are overlapped), 32.3, 30.1 (many peaks are overlapped), 29.8, 28.4, 23.1, 20.4 (two peaks are overlapped), 14.5 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1513 $[MH]^+$; IR (neat): $\tilde{\nu}$ = 3363, 2921, 2849, 1412, 1332, 1161, 759 cm^{-1}; HRMS (MALDI-TOF) calcd. for: $C_{99}H_{123}N_6O_8$: 1512.9436 $[MH]^+$, found 1512.9208.

Synthesis of allylsilanes *rac*-2/*rac*-3, *rac*-4/*rac*-5, and *rac*-6/*rac*-7: (see Scheme 2) Under an argon atmosphere, to the one-neck flask charged with *rac*-**1** (411 mg, 0.3 mmol) was added anhydrous toluene (3 mL), triethylamine (0.1 mL, 0.72 mmol), and allyl(dichloro)methylsilane (0.048 mL, 0.33 mmol). After stirred at ambient temperature for 2.5 h, the mixture was filtered through a pad of Celite, and the filtrate was concentrated in vacuo to give a crude of 429 mg as a white solid material. Purification by silica-gel column chromatography (hexane/EtOAc = 9:1) afforded *rac*-**2** of 73 mg as white solid materials (17 %), and *rac*-**3** of 48 mg as white solid materials (11 %). For data of *rac*-**2**: R_f values 0.57 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.34 (s, 1H), 8.01–7.98 (m, 2H), 7.82–7.76 (m, 2H), 7.65–7.54 (m, 4H), 7.31 (s, 1H), 7.29 (s, 3H), 7.13 (s, 1H), 7.10 (s, 1H), 6.40 (s, 1H), 5.77 (t, *J* = 8.0 Hz, 1H), 5.71 (t, *J* = 8.0 Hz, 1H), 5.59 (d, *J* = 7.2 Hz, 1H), 5.49 (dddd, *J* = 17.0, 10.1, 8.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.83 (dd, *J* = 10.1, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.68 (dd, *J* = 17.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.64 (t, *J* = 8.0 Hz, 1H), 4.51 (t, *J* = 8.0 Hz, 1H), 4.18 (d, *J* = 7.2 Hz, 1H), 2.32–2.16 (m, 8H), 1.47–1.27 (m, 72H), 1.05 (dd, *J* = 8.0, 8.0 Hz, 1H, $SiCH_2CH$=CH_2), 0.97 (dd, *J* = 8.0, 8.0 Hz, 1H, $SiCH_2CH$=CH_2), 0.91–0.87 (m, 12H), 0.43 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D$_8$]toluene) 8.76 (s, 1H), 8.02 (d, *J* = 8.3 Hz, 2H), 7.76–7.70 (m, 5H), 7.60–7.58 (m, 2H), 7.54–7.50 (m, 2H), 7.32–7.28 (m, 1H), 7.26–7.16 (m, 1H), 7.09–6.97 (m, 3H), 6.25 (s, 1H), 6.17 (t, *J* = 8.0 Hz, 1H), 6.15 (t, *J* = 8.0 Hz, 1H), 6.10 (d, *J* = 7.2 Hz, 1H), 5.13 (dddd, *J* = 17.4, 10.1, 8.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 5.10 (t, *J* = 8.0, 1H), 4.77 (t, *J* = 8.0 Hz, 1H), 4.67 (dd, *J* = 10.1, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.44 (d, *J* = 7.2 Hz, 1H), 4.28 (dd, *J* = 17.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 2.46–2.23 (m, 8H), 1.49–1.29 (m, 72H), 0.96–0.93 (m, 12H), 0.39–0.36 (m, 1H, $SiCH_2CH$=CH_2), 0.31 (s, 3H, $SiCH_3$), 0.26–0.17 (m, 1H, $SiCH_2CH$=CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.7, 155.5, 153.5, 153.31, 153.28, 152.97, 152.9, 152.7, 152.5, 152.0, 150.3, 149.9, 140.29, 140.26, 140.23, 140.19, 139.4, 136.9, 136.7, 135.7, 135.3, 135.1, 133.8, 133.1, 131.7, 129.9, 129.8, 129.7, 129.5, 128.4, 128.30, 128.27, 128.1, 124.5, 123.2, 122.4, 121.6, 118.9, 117.5, 116.2, 116.0, 114.7, 99.7, 36.5, 35.3, 34.6, 34.4, 32.7, 32.5, 32.3 (many peaks are overlapped), 30.8, 30.14, 30.09 (many peaks are overlapped), 30.07 (many peaks are overlapped), 29.77, 29.75, 28.44, 28.42 (many peaks are overlapped), 28.38, 28.30, 23.1 (many peaks are overlapped), 20.1, 14.4 (many peaks are overlapped), –4.66 ppm; MS (MALDI-TOF) *m/z*: 1454 $[MH]^+$; IR (neat) 2917, 2849, 1603, 1571, 1483, 1404, 1328, 1148, 759 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{93}H_{123}N_4O_8Si$: 1453.9172 $[MH]^+$, found 14539178. For data of *rac*-**3**: R_f values 0.55 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.34 (s, 1H), 8.01–7.98 (m, 2H), 7.84–7.77 (m, 2H), 7.65–7.55 (m, 4H), 7.30 (s, 1H), 7.26 (s, 1H), 7.25 (s, 1H), 7.20 (s, 1H), 7.12 (s, 1H), 7.19 (s, 1H), 6.19 (s, 1H), 5.89 (dddd, *J* = 17.0, 10.1, 7.8, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 5.76 (t, *J* = 7.8 Hz, 1H), 5.69 (t, *J* = 7.8 Hz, 1H), 5.58 (d, *J* = 7.2 Hz, 1H), 5.07 (dd, *J* = 17.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 5.01 (dd, *J* = 10.1, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.64 (t, *J* = 7.8 Hz, 1H), 4.53 (t, *J* = 7.8 Hz, 1H), 4.18 (d, *J* = 7.2 Hz, 1H), 2.29–2.16 (m, 8H), 1.90 (d, *J* = 7.8 Hz, 2H, $SiCH_2CH$=CH_2), 1.43–1.27 (m, 72H), 0.91–0.88 (m, 12H), –0.39 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D$_8$]toluene) 8.77 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.72–7.66 (m, 6H), 7.58 (s, 1H), 7.56 (s, 1H), 7.52 (s, 1H), 7.27–7.25 (m, 1H), 7.15–7.12 (m, 3H), 6.19 (s, 1H), 6.18 (t, *J* = 7.8 Hz, 1H), 6.12 (t, *J* = 7.8 Hz, 1H), 5.82 (dddd, *J* = 16.9, 10.0, 7.9, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 5.51 (d, *J* = 7.2 Hz, 1H), 5.07 (t, *J* = 7.8 Hz, 1H), 4.96 (dd, *J* = 17.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.94 (dd, *J* = 10.3, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.80 (t, *J* = 7.8 Hz, 1H), 4.33 (d, *J* = 7.2 Hz, 1H), 2.46–2.35 (m, 8H), 1.71 (dd, *J* = 7.9, 7.9 Hz, 2H, $SiCH_2CH$=CH_2), 1.49–1.29 (m, 72H), 0.96–0.93 (m, 12H), –1.00 (s, 3H, $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.7, 155.5, 153.5, 153.3 (two peaks are overlapped), 153.0, 152.9, 152.7, 152.5, 152.0, 150.3, 150.0, 140.3 (two peaks are overlapped), 140.23, 140.20, 139.5, 136.9, 136.7, 135.6, 135.2 (two peaks are overlapped), 133.9, 133.0, 131.8, 129.9, 129.8, 129.7, 129.5, 128.4, 128.31, 128.27, 128.1, 124.5, 123.3, 122.4, 121.6, 118.8, 117.4, 116.1, 116.0, 114.7, 99.7, 36.5, 35.3, 34.6 (many peaks are overlapped), 34.4 (many peaks are overlapped), 32.7, 32.5, 32.4, 32.3 (many peaks are overlapped), 31.9, 30.8, 30.1, 29.8, 28.4, 28.33, 28.25, 23.1 (many peaks are overlapped), 21.7, 14.5 (many peaks are overlapped), –5.73 ppm; MS (MALDI-TOF) *m/z*: 1593 $[MH]^+$; IR (neat) 2922, 2851, 1607, 1576, 1485, 1406, 1332, 1158, 910, 759 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{93}H_{123}N_4O_8Si$: 1452.9138 $[MH]^+$, found 1452.9119.

Allylsilanes *rac*-4/*rac*-5 (see Scheme 2) For data of *rac*-**4**: R_f values 0.43 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.31 (s, 1H), 8.06 (s, 1H), 7.98–7.95 (m, 2H), 7.85–7.82 (m, 2H), 7.76–7.75 (m, 1H), 7.71 (d, *J* = 8.2 Hz, 1H), 7.62–7.48 (m, 4H), 7.33 (s, 1H), 7.30 (s, 1H), 7.22 (s, 1H), 7.16 (s, 1H), 7.14 (s, 1H), 6.96 (s, 1H), 5.75 (t, *J* = 8.1 Hz, 1H), 5.69 (t, *J* = 8.1 Hz, 1H), 5.61 (t, *J* = 8.1 Hz, 1H), 5.45 (dddd, *J* = 17.0, 10.0, 7.9, 1.4 Hz, 1H, $SiCH_2CH$=CH_2), 4.83 (dd, *J* = 10.0, 1.4 Hz, 1H, $SiCH_2CH$=CH_2), 4.66 (dd, *J* = 17.0, 1.4 Hz, 1H, $SiCH_2CH$=CH_2), 4.52 (t, *J* = 8.1 Hz, 1H), 2.33–2.17 (m, 8H), 1.43–1.28 (m, 72H), 0.95 (d, *J* = 7.9 Hz, 1H, $SiCH_2CH$=CH_2), 0.90–0.88 (m, 12H), 0.81 (d, *J* = 7.9 Hz, 1H, $SiCH_2CH$=CH_2), 0.44 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D$_8$]toluene) 8.72 (s, 1H), 8.47 (s, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.76 (s, 1H), 7.73 (s, 1H), 7.71 (s, 1H), 7.63 (s, 3H), 7.61 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.50 (s, 1H), 7.46–7.45 (m, 1H), 7.32–7.28 (m, 1H), 7.27 (s, 1H), 7.19–7.09 (m, 3H), 6.17 (t, *J* = 8.1 Hz, 1H), 6.11 (t, *J* = 8.1 Hz, 1H), 6.03 (t, *J* = 8.1 Hz, 1H), 4.99 (dddd, *J* = 17.0, 10.0, 8.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.73 (t, *J* = 8.1 Hz, 1H), 4.59 (dd, *J* = 10.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.11 (dd, *J* = 17.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 2.47–2.33 (m, 8H), 1.46–1.29 (m, 72H), 0.96–0.92 (m, 12H), 0.27 (s, 3H, $SiCH_3$), 0.036 (dd, *J* = 8.0, 8.0 Hz, 1H, $SiCH_2CH$=CH_2), –0.13 (dd, *J* = 8.0, 8.0 Hz, 1H, $SiCH_2CH$=CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 154.7, 154.6, 153.4, 153.19, 153.18, 153.05, 153.03, 153.02, 152.9, 152.8, 152.7, 152.5, 150.4, 150.3, 140.33, 140.26, 140.21, 140.17, 139.8 (two peaks are overlapped), 137.0, 136.9, 136.4 (two peaks are overlapped), 134.7, 134.6, 133.03, 132.9, 131.7, 129.8, 129.63, 129.59, 129.4, 128.27, 128.24, 128.13, 128.07, 124.4, 124.2, 123.3, 123.1, 119.1, 119.0, 116.3, 115.9, 115.8, 35.4, 34.6, 34.3, 34.0, 32.9, 32.7, 32.3 (many peaks are overlapped), 30.13, 30.09, 29.8 (many peaks are overlapped), 28.4, 28.3, 23.1 (many peaks are overlapped), 19.8, 14.5 (many peaks are overlapped), –4.71 ppm; MS (MALDI-TOF) *m/z*: 1516 $[MH]^+$; IR (neat): $\tilde{\nu}$ = 2917, 2849, 1603, 1571, 1479, 1404, 1328, 1157, 1145, 763 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{96}H_{123}N_6O_8Si$: 1515.9166 $[MH]^+$, found 1515.9224. For data of *rac*-**5**: R_f values 0.38 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.30 (s, 1H), 8.05 (s, 1H), 7.96–7.91 (m, 2H), 7.86–7.83 (m, 2H), 7.77–

7.76 (m, 1H), 7.71 (d, *J* = 7.9 Hz, 1H), 7.62–7.49 (m, 4H), 7.31 (s, 1H), 7.28 (s, 1H), 7.16 (s, 1H), 7.14 (s, 1H), 7.13 (s, 1H), 6.90 (s, 1H), 5.91 (dddd, *J* = 17.0, 10.1, 8.2, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 5.72 (t, *J* = 8.2 Hz, 1H), 5.66 (t, *J* = 8.2 Hz, 1H), 5.59 (t, *J* = 8.2 Hz, 1H), 5.08 (dd, *J* = 17.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 5.03 (dd, *J* = 10.1, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.53 (t, *J* = 8.2 Hz, 1H), 2.32–2.18 (m, 8H), 1.90 (d, *J* = 8.2 Hz, 2H, $SiCH_2CH$=CH_2), 1.43–1.28 (m, 72H), 0.91–0.88 (m, 12H), –0.49 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D$_8$]toluene) 8.71 (s, 1H), 8.45 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.74 (s, 1H), 7.72 (s, 1H), 7.67–7.58 (m, 6H), 7.48 (s, 1H), 7.39–7.38 (m, 1H), 7.30–7.27 (m, 1H), 7.24 (s, 1H), 7.15–7.09 (m, 3H), 6.18 (t, *J* = 8.2 Hz, 1H), 6.12 (t, *J* = 8.2 Hz, 1H), 6.04 (t, *J* = 8.2 Hz, 1H), 5.78 (dddd, *J* = 16.2, 9.9, 8.2, 1.7 Hz, 1H, $SiCH_2CH$=CH_2), 4.92 (dd, *J* = 16.2, 1.7 Hz, 1H, $SiCH_2CH$=CH_2), 4.90 (dd, *J* = 9.9, 1.7 Hz, 1H, $SiCH_2CH$=CH_2), 4.77 (t, *J* = 8.2 Hz, 1H), 2.42–2.34 (m, 8H), 1.67–1.64 (m, 2H, $SiCH_2CH$=CH_2), 1.47–1.22 (m, 72H), 0.96–0.88 (m, 12H), –1.26 (s, 3H, $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 154.7, 154.6, 153.3, 153.2, 153.15, 153.07 (two peaks are overlapped), 153.04, 152.9, 152.8, 152.7 (two peaks are overlapped), 152.6, 150.39, 150.36, 140.3, 140.2 (two peaks are overlapped), 140.16, 139.78, 139.75, 137.0, 136.9, 136.3 (two peaks are overlapped), 134.8, 134.7, 132.94, 132.90, 131.8, 129.8, 129.62, 129.56, 129.3, 128.3, 128.2, 128.1, 128.0, 124.4, 124.2, 123.3, 123.1, 119.0, 118.9, 116.2, 115.8, 35.2, 34.6, 34.3, 32.9 (many peaks are overlapped), 32.6, 32.3 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8, 28.4, 28.3, 23.1 (many peaks are overlapped), 21.7, 14.5 (many peaks are overlapped), –5.98 ppm; MS (MALDI-TOF) *m/z*: 1516 [MH]$^+$; IR (neat) 2925, 2849, 1606, 1567, 1483, 1408, 1328, 1148, 754 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{96}H_{123}N_6O_8Si$: 1515.9166 [MH]$^+$, found 1515.9273.

Allylsilanes *rac*-6/*rac*-7 (see Scheme 2) For data of *rac*-**6**: R_f values 0.51 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.284 (s, 1H), 8.278 (s, 1H), 7.93 (d, *J* = 8.3 Hz, 1H), 7.88–7.86 (m, 1H), 7.84–7.81 (m, 1H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.64 (s, 1H), 7.55 (dd, *J* = 8.3 Hz, 8.3 Hz, 1H), 7.52–7.46 (m, 3H), 7.41 (s, 1H), 7.32 (s, 1H), 7.30 (s, 1H), 7.16 (s, 1H), 7.15 (s, 1H), 7.14 (s, 1H), 7.13 (s, 1H), 5.75 (t, *J* = 7.8 Hz, 1H), 5.68 (t, *J* = 8.0 Hz, 1H), 5.67 (t, *J* = 8.0 Hz, 1H), 5.39 (dddd, *J* = 17.1, 10.2, 7.9, 1.4 Hz, 1H, $SiCH_2CH$=CH_2), 4.79 (dd, *J* = 10.2, 1.4 Hz, 1H, $SiCH_2CH$=CH_2), 4.59 (dd, *J* = 17.1, 1.4 Hz, 1H, $SiCH_2CH$=CH_2), 4.52 (t, *J* = 8.0 Hz, 1H), 2.39 (s, 3H), 2.28–2.17 (m, 11H), 1.44–1.28 (m, 72H), 0.90–0.87 (m, 12H), 0.79 (d, *J* = 7.9 Hz, 2H), 0.45 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D$_8$]toluene) 8.77 (s, 1H), 8.69 (s, 1H), 7.99 (d, *J* = 8.3 Hz, 1H), 7.76 (s, 1H), 7.75 (s, 2H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.63 (s, 1H), 7.62 (s, 1H), 7.58 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.53 (dd, *J* = 7.0, 7.0 Hz, 1H), 7.48 (s, 1H), 7.46 (s, 1H), 7.45 (s, 1H), 7.27–7.24 (m, 1H), 7.13–7.04 (m, 1H), 6.19 (t, *J* = 8.2 Hz, 1H), 6.16 (t, *J* = 8.2 Hz, 1H), 6.05 (t, *J* = 8.2 Hz, 1H), 4.96 (dddd, *J* = 16.1, 9.2, 7.8, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.74 (t, *J* = 8.2 Hz, 1H), 4.57 (dd, *J* =9.2, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.11 (dd, *J* = 16.1, 1.4 Hz, 1H, $SiCH_2CH$=CH_2), 2.47–2.35 (m, 8H), 2.13 (s, 3H), 1.97 (s, 3H), 1.57–1.29 (m, 72H), 0.95–0.92 (m, 12H), 0.28 (s, 3H, $SiCH_3$), –0.13 (d, *J* = 7.8 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.4, 153.2, 153.1, 153.0 (two peaks are overlapped), 152.94, 152.88, 152.74, 152.66, 152.63, 152.57 (two peaks are overlapped), 150.4, 150.3, 140.24 (two peaks are overlapped), 140.17, 140.1, 139.9, 139.6, 138.9, 138.8, 137.0, 136.9, 136.4, 136.1, 134.7, 134.4, 133.1, 133.0, 131.8, 129.6, 129.5, 129.31, 129.28, 128.24 (two peaks are overlapped), 128.19, 128.0, 127.45, 127.36, 124.2, 124.1, 123.11, 123.07, 119.1, 116.2, 116.1, 115.7, 35.4, 34.6, 34.3, 34.2, 33.0, 32.8, 32.7, 32.3 (many peaks are overlapped), 30.1 (many peaks are overlapped), 28.4, 23.1 (many peaks are overlapped), 20.5, 20.4, 19.7, 14.5 (many peaks are overlapped), –4.72 ppm; MS (MALDI-TOF) *m/z*: 1594 [MH]$^+$; IR (neat): $\tilde{\nu}$ = 2925, 2849, 1483, 1412, 1332, 1157, 759 cm^{-1}; HRMS (MALDI-TOF) calcd. for: $C_{102}H_{129}N_6O_8Si$: 1593.9636 [MH]$^+$, found 1593.9610. For data of *rac*-**7**: R_f values 0.48 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.27 (s, 2H), 7.92 (d, *J* = 8.1 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.1 Hz, 1H), 7.65 (s, 1H), 7.57–7.45 (m, 4H), 7.40 (s, 1H), 7.31 (s, 1H), 7.29 (s, 1H), 7.134 (s, 1H), 7.126 (s, 1H), 7.11 (s, 1H), 7.07 (s, 1H), 5.94 (dddd, *J* = 17.0, 10.0, 8.0, 1.3 Hz, 1H, $SiCH_2CH$=CH_2), 5.73 (t, *J* = 8.0 Hz, 1H), 5.66 (t, *J* = 7.5, 7.5 Hz, 2H, overlapped), 5.11 (dd, *J* = 17.0, 1.3 Hz, 1H, $SiCH_2CH$=CH_2), 5.06 (dd, *J* = 10.0, 1.3 Hz, 1H, $SiCH_2CH$=CH_2), 4.54 (t, *J* = 7.8 Hz, 1H), 2.40 (s, 3H), 2.29–2.17 (m, 11H), 1.93 (d, *J* = 8.0 Hz, 2H, $SiCH_2CH$=CH_2), 1.44–1.28 (m, 72H), 0.90–0.88 (m, 12H), –0.58 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D$_8$]toluene) 8.77 (s, 1H), 8.69 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.75 (s, 1H), 7.74 (s, 1H), 7.72 (s, 1H), 7.62–7.55 (m, 5H), 7.46 (s, 1H), 7.44 (s, 1H), 7.38 (s, 1H), 7.25–7.22 (m, 1H), 7.09–7.05 (m, 3H), 6.15 (t, *J* = 8.2 Hz, 1H), 6.12 (t, *J* = 8.2 Hz, 1H), 6.06 (t, *J* = 8.2 Hz, 1H), 5.80 (dddd, *J* = 16.2, 10.4, 7.8, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.92 (dd, *J* = 16.2, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.91 (dd, *J* = 10.4, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.79 (t, *J* = 8.2 Hz, 1H), 2.46–2.35 (m, 8H), 2.12 (s, 3H), 1.91 (s, 3H), 1.65 (d, *J* = 7.8 Hz, 2H, $SiCH_2CH$=CH_2), 1.49–1.30 (m, 72H), 0.95–0.93 (m, 12H), –1.29 (s, 3H, $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.4, 153.2, 153.12, 153.10, 153.08, 152.93, 152.88, 152.68, 152.64, 152.59, 152.57, 150.43, 150.35, 140.22, 140.17, 140.1, 139.9, 139.6, 138.9, 138.8, 137.0, 136.9, 136.4, 136.0, 134.8, 134.5, 133.0, 132.9, 131.9, 129.5, 129.43, 129.39, 129.2, 128.6, 128.3 (two peaks are overlapped), 128.2, 128.0, 127.5, 127.2, 125.7, 124.2, 124.1, 123.11, 123.07, 119.1, 119.0, 116.2, 116.1, 116.0, 35.2, 34.8, 34.3, 32.9, 32.8, 32.7, 32.6, 32.3 (many peaks are overlapped), 30.1 (many peaks are overlapped), 28.4, 23.1 (many peaks are overlapped), 21.7, 20.5, 20.4, 14.5 (many peaks are overlapped), –6.10 ppm; MS (MALDI-TOF) *m/z*: 1594 [MH]$^+$; IR (neat): $\tilde{\nu}$ = 2922, 2851, 1607, 1574, 1482, 1414, 1159, 759 cm^{-1}; HRMS(MALDI-TOF) calcd. for: $C_{102}H_{129}N_6O_8Si$: 1593.9636 [M]$^+$, found 1593.9690.

Synthesis of diol platforms *rac*-14: (see Scheme 3) A solution of the di-quinoxaline-spanned resorcin[4]arene (200 mg, 0.15 mmol) in DMSO (4 mL) under an argon atmosphere was stirred 60 °C for 10 min, and followed by addition of K_2CO_3 (37 mg, 0.27 mmol) and 2,3-dichloro-6-methyl quinoxaline (35 mg, 0.16 mmol). After 6 h the reaction mixture was cooled to room temperature, and filtered through a pad of Celite with eluent of toluene, and the filtrate was evaporated off. The residue dissolved into toluene was transferred into a separatory funnel, washed with water (10 mL) and brine (10 mL × 3), dried with Na_2SO_4, and concentrated to give a crude of 189 mg as a brown solid material. Purification by silica-gel column chromatography (toluene/EtOAc = 19:1) afforded *rac*-**14** of 107 mg as white solid materials (49 %). R_f values 0.51 (hexane/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.25 (s, 2H), 7.97–7.94 (m, 2H), 7.71–7.67 (m, 3H), 7.60–7.45 (m, 6H), 7.82–7.80 (m, 1H), 7.69–7.67 (m, 2H), 7.29–7.25 (m, 2H), 7.13 (s, 2H), 7.09 (s, 2H), 6.70 (brs, 2H, -OH), 5.62 (t, *J* = 7.6 Hz, 1H), 5.56–5.52 (m, 2H), 4.25 (t, *J* = 7.6 Hz, 1H), 2.47 (s, 3H), 2.26–2.17 (m, 8H), 1.44–1.28 (m, 72H), 0.90–0.87 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 152.74 (two peaks are overlapped), 152.72, 152.69, 152.65, 152.60, 152.51, 152.48, 152.41, 152.39, 152.34, 151.8, 151.4, 151.3, 139.8, 139.7, 139.42, 139.36, 139.34, 138.0 (two peaks are overlapped), 136.2 (two peaks are overlapped), 135.74, 135.66, 131.0, 130.51, 130.49, 129.3, 129.2, 129.1, 129.0, 128.8, 128.73, 128.69, 127.9 (two peaks are overlapped), 127.6, 127.5, 127.3, 127.0, 123.9, 123.7, 123.4, 123.2, 118.8 (two peaks are overlapped), 110.4, 110.3, 34.5, 34.2 (many peaks are overlapped), 33.8, 33.7, 32.7, 32.4 (many peaks are overlapped), 32.0, 29.8 (many peaks are overlapped), 29.5, 28.1, 28.0, 22.7 (many peaks are overlapped), 21.6, 14.2 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1499 [MH]$^+$; IR (neat): $\tilde{\nu}$ = 3339 (-OH), 2917, 2849, 1610, 1578, 1412, 1328, 1152 cm^{-1}; HRMS (MALDI-TOF) calcd. for: $C_{97}H_{121}N_6O_8$: 1498.9274 [MH]$^+$, found 1498.9244.

Synthesis of diol platform *rac*-15: (see Scheme 3) A solution of the di-quinoxaline-spanned resorcin[4]arene (200 mg, 0.15 mmol) in DMSO (4 mL) under an argon atmosphere was stirred 60 °C for 10 min, and followed by addition of K_2CO_3 (37 mg, 0.27 mmol) and 2,3-dichloro-6-methyl quinoxaline (35 mg, 0.16 mmol). After 6 h the reaction mixture was cooled to room temperature, and filtered through a pad of Celite with eluent of toluene, and the filtrate was evaporated off. The residue dissolved into toluene was transferred into a separatory funnel, washed with water (10 mL) and brine (10 mL × 3), dried with Na_2SO_4, and concentrated to give a crude of 189 mg as a brown solid material. Purification by silica-gel column chromatography (toluene/EtOAc = 19:1) afforded *rac*-**15** of 92 mg as white solid materials (42 %). R_f values 0.55 (hexane/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.22 (s, 2H), 7.97 (d, J = 8.3 Hz, 1H), 7.92 (d, J = 8.3 Hz,1H), 7.77–7.69 (m, 3H), 7.66–7.56 (m, 2H), 7.52–7.43 (m, 3H), 7.28 (s, 1H), 7.26 (s, 1H), 7.22 (s, 1H), 7.14 (s, 1H), 7.13 (s, 1H), 7.103 (s, 1H), 7.098 (s, 1H), 5.60 (t, J = 8.2 Hz, 1H), 5.54 (t, J = 8.1 Hz, 1H), 5.52 (t, J = 7.7 Hz, 1H), 4.26 (t, J = 7.7 Hz, 1H), 2.26–2.20 (m, 8H), 1.44–1.28 (m, 72H), 0.97–0.90 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 163.8, 161.3 ($^1J_{C,F}$ = 249.6 Hz), 153.6, 153.0, 152.94, 152.91, 152.89, 152.86, 152.8, 152.70, 152.28, 152.25 ($^4J_{C,F}$ = 2.9 Hz), 151.73, 151.69, 140.9, 140.8, 140.0, 139.7, 139.6, 136.9, 136.8, 136.7, 136.0, 135.97, 130.84, 130.75 ($^3J_{C,F}$ = 8.8 Hz), 129.9, 129.8, 129.7, 129.6, 129.4, 129.1, 129.0, 128.6, 128.2, 128.1, 127.9, 127.7, 125.6, 124.2, 124.0, 123.8, 123.6, 119.2, 119.0 ($^2J_{C,F}$ = 20.7 Hz), 119.0 (two peaks are overlapped), 112.4, 112.2 ($^2J_{C,F}$ = 22.4 Hz), 110.64, 110.61, 34.8, 34.5, 34.2, 34.0, 33.0, 32.7 (many peaks are overlapped), 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.3 (many peaks are overlapped), 23.1 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1503 $[MH]^+$; IR (neat) 3343 (-OH), 2917, 2849, 1408, 1332, 1225, 1157, 759 cm^{-1}; HRMS (MALDI-TOF) calcd. for: $C_{96}H_{118}FN_6O_8$: 1502.9029 $[MH]^+$, found 1502.9047.

Synthesis of allylsilanes *rac*-8/*rac*-9: (see Scheme 3) Under an argon atmosphere, to the one-neck flask charged with *rac*-**14** (102 mg, 0.068 mmol) was added anhydrous toluene (2 mL), Et_3N (0.023 mL, 0.16 mmol), and allyl(dichloro)methylsilane (0.01 mL, 0.075 mmol). After stirred at ambient temperature for 2 h, the mixture was filtered through a pad of cotton and concentrated in vacuo to give a crude of 114 mg as a white solid material. Purification by silica-gel column chromatography (hexane/EtOAc = 9:1) afforded *rac*-**8** of 30 mg as white solid materials (28 %), and *rac*-**9** of 21 mg as white solid materials (19 %). For data of *rac*-**8**: R_f values 0.58 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.27 (s, 2H), 7.93 (d, J = 8.2 Hz, 2H), 7.69–7.63 (m, 4H), 7.57–7.44 (m, 4H), 7.32–7.29 (m, 3H), 7.18 (s, 1H), 7.17 (s, 1H), 7.15 (s, 2H), 5.76 (t, J = 7.9 Hz, 1H), 5.70–5.66 (m, 2H), 5.41 (dddd, J = 16.9, 10.2, 7.8, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 4.83 (dd, J =10.2, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 4.63 (dd, J = 16.9, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 4.53 (t, J = 7.9 Hz, 1H), 2.48 (s, 3H), 2.35–2.16 (m, 8H), 1.47–1.29 (m, 72H), 0.90–0.88 (m, 12H), 0.82 (d, J = 7.8 Hz, 2H, $SiCH_2CH$=CH_2), 0.46 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D_8]toluene) 8.76 (s, 1H), 8.72 (s, 1H), 8.01 (dd, J = 8.6, 8.6 Hz, 2H), 7.76 (s, 2H), 7.68 (dd, J = 8.6, 8.6 Hz, 2H), 7.63 (s, 2H), 7.47–7.41 (m, 3H), 7.28–7.26 (m, 4H), 7.09 (s, 1H), 6.88 (d, J = 8.5 Hz, 3H), 6.20–6.16 (m, 2H), 6.07 (t, J = 7.6 Hz, 1H), 4.93 (dddd, J = 17.0, 10.1, 7.8, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.73 (t, J = 8.1 Hz, 1H), 4.58 (dd, J = 10.1, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 4.11 (dd, J = 17.0, 1.5 Hz, 1H, $SiCH_2CH$=CH_2), 2.48–2.34 (m, 8H), 2.12 (s, 3H), 1.47–1.33 (m, 72H), 0.96–0.93 (m, 12H), 0.27 (s, 3H, $SiCH_3$), –0.18 (d, J = 7.8 Hz, 2H, $SiCH_2CH$=CH_2) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.4 (two peaks are overlapped), 153.2, 153.3, 153.0, 152.91, 152.90, 152.80, 152.78, 152.73, 152.69, 152.4, 150.39 (two peaks are overlapped), 150.37, 140.3, 140.19, 140.16 (two peaks are overlapped), 140.1, 140.0, 138.4, 136.84, 136.79, 136.4, 136.3, 134.6, 133.1 (two peaks are overlapped), 131.8, 131.7, 129.7, 129.6, 129.3, 129.0, 128.2 (two peaks are overlapped), 128.1, 128.0, 127.7, 127.4, 124.2, 124.1, 123.1, 123.0, 119.13, 119.11, 116.2, 116.1, 115.8, 35.4, 34.5, 34.3, 33.0, 32.8 (many peaks are overlapped), 32.7, 32.3, 30.1 (many peaks are overlapped), 29.8 (many peaks are overlapped), 28.4, 23.1 (many peaks are overlapped), 22.0, 19.7, 14.5 (many peaks are overlapped), –4.71 ppm; MS (MALDI-TOF) *m/z*: 1580 $[MH]^+$; IR (neat) 2917, 2875, 1479, 1408, 1328, 1157, 759 cm^{-1}; HRMS (ESI) calcd. for: $C_{101}H_{126}N_6O_8$ Si: 1579.9479 $[MH]^+$, found 1579.9450. For data of *rac*-**9**: R_f values 0.54 (hexane/EtOAc = 2:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.259 (s, 1H), 8.255 (s, 1H), 7.93 (d, J = 8.2 Hz, 2H), 7.70–7.63 (m, 4H), 7.57–7.43 (m, 4H), 7.33–7.29 (m, 3H), 7.14 (s, 2H), 7.11 (s, 2H), 5.94 (dddd, J = 16.9, 10.1, 7.8, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 5.73 (t, J = 7.8 Hz, 1H), 5.67–5.63 (m, 2H), 5.11 (dd, J =16.9, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 5.06 (dd, J = 10.1, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 4.55 (t, J = 7.8 Hz, 1H), 2.48 (s, 3H), 2.34–2.16 (m, 8H), 1.93 (d, J = 7.8 Hz, 2H), 1.47–1.29 (m, 72H), 0.90–0.88 (m, 12H), –0.56 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D_8]toluene) 8.77 (s, 1H), 8.72 (s, 1H), 7.99 (dd, J = 8.0, 8.0 Hz, 2H), 7.74 (s, 2H), 7.62–7.59 (m, 4H), 7.44–7.42 (m, 3H), 7.27–7.22 (m, 3H), 7.09–7.05 (m, 2H), 7.13–7.05 (m, 3H), 6.88 (d, J = 8.6 Hz, 1H), 6.18–6.14 (m, 2H), 6.08 (t, J = 8.3 Hz, 1H), 5.81 (dddd, J = 15.0, 10.0, 7.7, 1.9 Hz, 1H, $SiCH_2CH$=CH_2), 4.93 (dd, J = 15.0, 1.9 Hz, 1H), 4.92 (dd, J =10.0, 1.9 Hz, 1H, $SiCH_2CH$=CH_2), 4.77 (t, J = 8.3 Hz, 1H, $SiCH_2CH$=CH_2), 2.46–2.34 (m, 8H), 2.12 (s, 3H), 1.64 (d, J = 7.7 Hz, 2H), 1.48–1.29 (m, 72H), 0.96–0.93 (m, 12H), –1.37 (s, 3H, $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 153.7 (two peaks are overlapped), 153.60, 153.56, 153.3, 153.23, 153.21, 153.12, 153.09, 153.05, 153.0, 152.7, 150.7 (two peaks are overlapped), 140.53 (two peaks are overlapped), 140.49, 140.47, 140.44, 140.3, 138.7, 137.14, 137.11, 136.7, 136.6, 135.0 (two peaks are overlapped), 133.29, 133.27, 132.2, 131.9, 129.9, 129.8, 129.6, 129.3, 128.5 (two peaks are overlapped), 128.4, 128.3, 128.0, 127.7, 124.53, 124.46, 123.5, 123.4, 119.41, 119.38, 116.5, 116.4, 116.3, 35.6, 34.9, 34.6, 33.3, 33.12, 33.06, 32.9, 32.6 (many peaks are overlapped), 30.4 (many peaks are overlapped), 30.1, 28.74, 28.71, 28.67, 23.4 (many peaks are overlapped), 22.3, 22.1, 14.8 (many peaks are overlapped), –5.79 ppm; MS (MALDI-TOF) *m/z*: 1580 $[MH]^+$; IR (neat) 2921, 2849, 1479, 1412, 1328, 1157, 759 cm^{-1}; HRMS (ESI) calcd. for: $C_{101}H_{126}N_6O_8$ Si: 1579.9479 $[MH]^+$, found 1579.9456.

Synthesis of allylsilanes *rac*-10/*rac*-11 (see Scheme 3) Under an argon atmosphere, to the one-neck flask charged with *rac*-**15** (305 mg, 0.20 mmol) was added anhydrous toluene (2 mL), Et_3N (0.07 mL, 0.48 mmol), and allyl(dichloro)methylsilane (0.03 mL, 0.22 mmol). After stirred at ambient temperature for 2 h, the mixture was filtered through a pad of cotton and concentrated in vacuo to give a crude of 114 mg as a white solid material. Purification by silica-gel column chromatography (hexane/EtOAc = 9:1) afforded *rac*-**10** of 34 mg as white solid materials (11 %), and *rac*-**11** of 20 mg as white solid materials (6 %). For data of *rac*-**10**: R_f values 0.45 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 8.23 (s, 1H), 8.22 (s, 1H), 7.90 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 8.5 Hz, 1H), 7.78 (d, J = 7.4 Hz, $^4J_{H,F}$ = 5.6 Hz, 1H), 7.68 (d, J = 8.3 Hz, 1H), 7.65 (d, J = 8.3 Hz, 1H), 7.46–7.59 (m, 6H), 7.31 (s, 1H), 7.30 (s, 1H), 7.18 (s, 2H), 7.14 (s, 2H), 5.72 (t, J = 8.4 Hz, 1H), 5.66 (d, J = 8.2 Hz, 2H), 5.42 (dddd, J = 17.0, 9.9, 7.9, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 4.84 (dd, J = 9.9, 1.2 Hz, $SiCH_2CH$=CH_2), 4.64 (dd, J = 17.0, 1.2 Hz, 1H, $SiCH_2CH$=CH_2), 4.53 (t, J = 7.8 Hz, 1H), 2.17–2.32 (m, 8H), 1.28–1.45 (m, 72H), 0.87–0.90 (m, 12H), 0.82 (d, J = 7.9 Hz, 2H, $SiCH_2CH$=CH_2), 0.46 (s, 3H, $SiCH_3$) ppm; ^{1}H NMR (400 MHz, [D_8]toluene) 8.70 (s, 1H), 8.68 (s, 1H), 7.96 (dd, J = 7.4, 7.4 Hz, 2H), 7.75 (s, 2H), 7.68 (d, J = 7.4 Hz, 2H), 7.61 (s, 2H), 7.47 (s, 1H), 7.46 (s, 1H), 7.36–7.30 (m, 2H), 7.25–7.21 (m, 1H), 7.12–7.07 (m, 3H), 6.78–6.73 (m, 1H), 6.20–6.00 (m, 2H), 6.02 (t, J = 8.2 Hz,

1H), 4.91 (dddd, *J* = 17.0, 10.3, 7.8, 1.4 Hz, 1H, $SiCH_2CH{=}CH_2$), 4.72 (t, *J* = 8.2 Hz, 1H), 4.58 (dd, *J* =10.3, 1.4 Hz, 1H, $SiCH_2CH{=}CH_2$), 4.11 (dd, *J* = 17.0, 1.4 Hz, 1H, $SiCH_2CH{=}CH_2$), 2.46–2.33 (m, 8H), 2.13 (s, 3H), 1.46–1.29 (m, 72H), 0.97–0.93 (m, 12H), 0.27 (s, 3H, $SiCH_3$), –0.24 (d, *J* = 7.8 Hz, 2H, $SiCH_2CH{=}CH_2$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 163.7, 161.2 ($^1J_{C,F}$ = 249.8 Hz), 153.5, 153.0, 152.97, 152.85, 152.83, 152.7, 152.6, 152.4, 152.34, 152.25, 152.23, 152.19 ($^4J_{C,F}$ = 3.8 Hz), 152.17, 150.1, 140.8, 140.7, 139.80, 139.77, 139.76, 139.73, 136.8, 136.70, 136.68, 136.01, 135.96, 134.4, 134.3, 132.70, 132.67, 131.3 ($SiCH_2CH{=}CH_2$), 129.6, 129.51, 129.48, 129.44, 129.2, 129.1 ($^3J_{C,F}$ = 9.5 Hz), 127.77, 127.74, 127.65, 127.62, 124.0, 123.9, 122.8, 122.7, 119.3, 119.1 ($^2J_{C,F}$ = 24.8 Hz), 118.69, 118.67, 115.9, 115.8, 115.6 ($SiCH_2CH{=}CH_2$), 112.1, 112.0 ($^2J_{C,F}$ = 22.2 Hz), 35.1, 34.2, 33.9 (many peaks are overlapped), 32.6, 32.5, 32.4 (many peaks are overlapped), 32.0, 29.8 (many peaks are overlapped), 29.5, 28.1, 22.7 (many peaks are overlapped), 19.4 ($SiCH_2CH{=}CH_2$), 14.2 (many peaks are overlapped), –5.03 ppm; MS (MALDI-TOF) *m/z*: 1584 $[MH]^+$; IR (neat) 2921, 2849, 1479, 1412, 1328, 1165 cm^{-1}; HRMS (ESI) calcd. for: $C_{100}H_{124}FN_6O_8Si$: 1583.9228 $[MH]^+$, found 1583.9204. For data of *rac*-**11**: R_f values 0.45 (hexane/EtOAc = 2:1). ^1H NMR (400 MHz, $CDCl_3$) 8.21 (s, 2H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.79 (dd, *J* = 7.4 Hz, $^4J_{H,F}$ = 5.5 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.44–7.59 (m, 6H), 7.29 (s, 1H), 7.28 (s, 1H), 7.13 (s, 2H), 7.119 (s, 1H), 7.116 (s, 1H), 5.94 (dddd, *J* = 17.0, 9.8, 8.1, 1.5 Hz, 1H, $SiCH_2CH{=}CH_2$), 5.70 (t, *J* = 8.1 Hz, 1H), 5.64 (t, *J* = 8.2 Hz, 2H), 5.11 (dd, *J* = 17.0, 1.5 Hz, 1H, $SiCH_2CH{=}CH_2$), 5.06 (dd, *J* = 9.8, 1.5 Hz, 1H, $SiCH_2CH{=}CH_2$), 4.55 (t, *J* = 8.0 Hz, 1H), 2.17–2.33 (m, 8H), 1.94 (d, *J* = 8.1 Hz, 2H, $SiCH_2CH{=}CH_2$), 1.28–1.44 (m, 72H), 0.87–0.90 (m, 12H), –0.54 (s, 3H, $SiCH_3$) ppm; ^1H NMR (400 MHz, [D_8]toluene) 8.70 (s, 1H), 8.68 (s, 1H), 7.94 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.73 (s, 2H), 7.61–7.60 (m, 4H), 7.45 (s, 1H), 7.43 (s, 1H), 7.37–7.29 (m, 2H), 7.24–7.20 (m, 1H), 7.13–7.05 (m, 3H), 6.79–6.74 (m, 1H), 6.18–6.13 (m, 2H), 6.03 (t, *J* = 8.2 Hz, 1H), 5.80 (dddd, *J* = 15.7, 11.8, 7.7, 1.6 Hz, 1H, $SiCH_2CH{=}CH_2$), 4.72 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.93 (dd, *J* =11.8, 1.6 Hz, 1H, $SiCH_2CH{=}CH_2$), 4.76 (t, *J* = 8.2 Hz, 1H, $SiCH_2CH{=}CH_2$), 2.45–2.33 (m, 8H), 1.63 (d, *J* = 7.7 Hz, 2H), 1.47–1.29 (m, 72H), 0.96–0.93 (m, 12H), –1.43 (s, 3H, $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 164.0, 161.5 ($^1J_{C,F}$ = 249.8 Hz), 153.9, 153.3, 153.24, 153.19, 153.17, 153.0, 152.9, 152.72, 152.67,152.57 (two peaks are overlapped), 142.5, 150.4, 140.10, 140.97, 140.15, 140.11, 140.05, 140.0, 137.1, 137.01, 136.98, 136.3, 136.2, 134.8, 134.7, 132.91, 132.87, 131.8, 129.9, 129.8 (two peaks are overlapped), 129.71, 129.4, 129.3 ($^3J_{C,F}$ = 9.8 Hz), 128.1, 128.04, 127.97, 127.93, 124.3, 124.2, 123.1, 123.0, 119.6, 119.3 ($^2J_{C,F}$ = 25.8 Hz), 119.0, 118.9, 116.2 ($SiCH_2CH{=}CH_2$), 116.1, 116.0, 112.4, 112.2 ($^2J_{C,F}$ = 22.6 Hz), 35.2, 34.5, 34.2, 32.9, 32.8, 32.7, 32.5, 32.3 (many peaks are overlapped), 30.1,30.0 (many peaks are overlapped), 29.8, 29.7 (many peaks are overlapped), 28.3 (many peaks are overlapped), 23.0 (many peaks are overlapped), 21.7 ($SiCH_2CH{=}CH_2$), 14.5 (many peaks are overlapped), –6.18 ppm; MS (MALDI-TOF) *m/z*: 1585 $[MH]^+$; IR (neat) 2921, 2849, 1479, 1408, 1324, 1148, 754 cm^{-1}; HRMS (ESI) calcd. for:$C_{100}H_{124}FN_6O_8Si$: 1584.9267 $[MH]^+$, found 1584.9288.

Synthesis of 17: (see Scheme 4) A solution of *cis*-diquinoxaline-spanned resorcin[4]arene (500 mg, 0.37 mmol) in toluene (2 mL) and DMSO (8 mL) was stirred at 55 °C for 5 min, and followed by addition of K_2CO_3 (205 mg, 1.48 mmol) and CH_2BrCl (0.5 mL, 1.48 mmol). After the mixture was stirred 2 h cooled to room temperature. The reaction mixture was poured into 10 mL of cold water, and the mixture was transferred into a 50 mL separatory funnel. The aqueous phase was extracted with CH_2Cl_2 (10 mL × 3), and the combined organic phases were washed with water (10 mL × 3) and brine (10 mL), and dried with Na_2SO_4, and filtered off, and concentrated to give a crude of 1.08 g as a yellow solid material. After column chromatography (hexane/EtOAc = 9:1), afforded **17** of 814 mg as a white solid material (79 %). R_f values 0.42 (hexane/EtOAc = 2:1). ^1H NMR (400 MHz, $CDCl_3$) 8.33 (s, 1H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 7.4 Hz, 2H), 7.65–7.56 (m, 4H), 7.31 (s, 2H), 7.19 (s, 2H), 7.17 (s, 1H), 7.12 (s, 1H), 6.32 (s, 1H), 5.72 (t, *J* = 8.0 Hz, 2H), 5.64 (d, *J* = 7.2 Hz, 2H), 4.69 (t, *J* = 8.0 Hz, 2H), 4.15 (d, *J* = 7.2 Hz, 2H), 2.30–2.21 (m, 8H), 1.49–1.26 (m, 72H), 0.91–0.85 (m, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.7, 155.1, 153.7, 153.1, 152.7, 152.2, 140.1, 139.3, 138.1, 136.6, 135.6, 129.9, 129.6, 128.3 (two peaks are overlapped), 124.6, 122.2 (two peaks are overlapped), 120.5, 118.9, 117.4, 116.8, 99.7, 36.6, 34.6, 32.3 (many peaks are overlapped), 30.6 (many peaks are overlapped), 29.8, 28.4, 28.2, 23.1 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1382 $[MH]^+$; IR (neat) 2922, 2851, 1578, 1486, 1413, 1332, 1282, 1158, 959, 756 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{90}H_{116}N_4O_8$: 1381.8866 $[MH]^+$, found 1381.8808.

Synthesis of 18: (see Scheme 4) To a solution of **17** (600 mg, 0.43 mmol) in DMF (5 mL) at 80 °C was added CsF (1.31 g, 8.6 mmol), and the resultant mixture was followed by addition of a solution of catechol (192 mg, 1.74 mmol) in DMF (2.5 mL). After the reaction mixture was stirred at 80 °C for 1 h, the mixture was cooled to room temperature, and followed by quenching with slow addition of 1 M aqueous HCl (20 mL). The precipitates was filtered off, and washed thoroughly with water (300 mL), and dried up at ambient temperature. The filter cake was dissolved into $CHCl_3$ (100 mL), and the solution was washed with brine (40 mL), and dried with Na_2SO_4, and filtered, and concentrated in vacuo to give a crude of 1.25 g as a brown solid material. Purification by column chromatography ($CHCl_3$/EtOAc = 3:1), and the following reprecipitation from CH_2Cl_2 (1.5 mL)/CH_3OH (12 mL) afforded **18** of 608 mg as whitish brown solid materials (68 %). For data of **17**: R_f values 0.42 (hexane/EtOAc = 2:1). ^1H NMR (400 MHz, $CDCl_3$) 7.19 (s, 2H), 7.17(s, 1H), 6.96 (s, 1H), 6.81 (brs, 2H, -OH), 6.66 (brs, 2H, -OH), 6.48 (s, 1H), 6.32 (s, 2H), 6.31 (s, sH), 5.72 (d, *J* = 7.2 Hz, 2H), 4.72 (t, *J* = 8.1 Hz, 2H), 4.40 (d, *J* = 7.2 Hz, 2H), 4.23 (t, *J* = 7.7 Hz, 2H), 2.26–2.11 (m, 8H), 1.38–1.26 (m, 72H), 0.88 (t, *J* = 6.8 Hz, 12H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.3, 154.9, 151.3, 150.8, 138.8, 133.9, 128.4, 126.2, 125.2, 122.3, 120.7, 117.0, 110.4, 104.4, 99.9, 36.4, 34.1, 33.9 (many peaks are overlapped), 32.3, 30.3, 30.3, 30.08, 29.98 (many peaks are overlapped), 28.4, 23.0, 14.5 (many peaks are overlapped) ppm; MS (ESI) *m/z*: 1130 $[MH]^+$; IR (neat) 3291 (-OH), 2921, 2849, 1615, 1582, 1491, 1288, 1169, 958 cm^{-1}; HRMS (ESI) calcd. for: $C_{74}H_{113}O_8$: 1129.8430 $[MH]^+$, found 1129.8420.

Synthesis of *rac*-16: (see Scheme 4) A solution of the bis methylene tetra-ol cavitand (100 mg, 0.09 mmol) in DMSO (1 mL) under an argon atmosphere was stirred 100 °C for 10 min, and followed by addition of K_2CO_3 (22 mg, 0.16 mmol) and 2,3-dichlorodibenzo[*f,h*]quinoxaline (30 mg, 0.1 mmol). After 8 h the reaction mixture was cooled to room temperature, and filtered through a pad of Celite with eluent of toluene, and the filtrate was evaporated off. The residue dissolved into toluene was transferred into a separatory funnel, washed with water (10 mL) and brine (10 mL × 3), dried with Na_2SO_4, and concentrated to give a crude of 682 mg as a brown solid material. Purification by short-plugged silica-gel column chromatography (CH_2Cl_2 only) afforded *rac*-**16** of 319 mg as white solid materials (41 %). R_f values 0.50 (hexane/EtOAc = 2:1). ^1H NMR (400 MHz, $CDCl_3$) 8.94 (d, *J* = 8.0 Hz, 1H), 8.63 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 8.0 Hz, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.59 (dd, *J* = 8.0, 8.0 Hz, 2H), 7.53 (s, 1H), 7.45 (s, 1H), 7.34 (s, 1H), 7.19 (s, 1H), 7.17 (s, 1H), 7.13 (s, 1H), 6.34 (s, 1H), 6.13 (s, 1H), 5.80 (d, *J* = 7.4 Hz, 1H), 5.76 (t, *J* = 8.2 Hz, 1H), 5.41 (d, *J* = 7.4 Hz, 1H), 4.78 (t, *J* = 7.9 Hz, 1H), 4.61 (t, *J* = 8.2 Hz, 1H), 4.35

(d, *J* = 7.4 Hz, 1H), 4.28 (t, *J* = 7.8 Hz, 1H), 3.86 (d, *J* = 7.4 Hz, 1H), 2.17–2.31 (m, 8H), 1.27–1.41 (m, 72H), 0.88–0.91 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) 155.7, 155.6, 155.1, 154.8, 153.2, 152.9, 152.3, 151.9, 151.6, 151.1, 139.6, 139.0, 138.1, 137.5, 137.2, 136.4, 134.0, 132.0, 130.7, 130.2, 129.8, 129.3, 128.6, 128.3, 128.1, 127.8, 127.6, 126.3, 125.3, 125.2, 125.0, 122.5, 122.4, 122.1, 121.9, 120.6, 117.9, 116.8, 111.4, 110.5, 99.9, 99.7, 36.8, 36.3, 34.4, 34.2, 33.3, 33.0, 32.3 (many peaks are overlapped), 30.5 (many peaks are overlapped), 30.2 (many peaks are overlapped), 30.0 (many peaks are overlapped), 28.4, 28.3 (many peaks are overlapped), 23.0 (many peaks are overlapped), 14.5 (many peaks are overlapped) ppm; MS (MALDI-TOF) *m/z*: 1356 $[MH]^+$; IR (neat) 3248, 2925, 2849, 1491, 1380, 1169, 965, 722 cm^{-1}; HRMS (MALDI-TOF) calcd. for: $C_{90}H_{119}N_2O_8$: 1355.8966 $[MH]^+$, found 1355.8978.

Synthesis of *rac*-19/*rac*-20: (Scheme 4) Under an argon atmosphere, to the one-neck flask charged with *rac*-**16** (100 mg, 0.074 mmol) was added anhydrous toluene (2 mL), Et_3N (0.025 mL, 0.18 mmol), and allyl(dichloro)methylsilane (0.012 mL, 0.081 mmol). After stirred at ambient temperature for 2 h, the mixture was filtered through a pad of cotton and concentrated in vacuo to give a crude of 107 mg as a white solid material. Purification by silica-gel column chromatography (hexane/EtOAc = 9:1) afforded *rac*-**19** of 28 mg as white solid materials (26 %), and *rac*-**20** of 13 mg as white solid materials (12 %). For data of *rac*-**19**: R_f values 0.59 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 9.15 (d, *J* = 7.2 Hz, 1H), 9.06 (d, *J* = 7.2 Hz, 1H), 8.62 (m, 2H), 7.77 (m, 4H), 7.51 (s, 1H), 7.43 (s, 1H), 7.29 (s, 1H), 7.20 (s, 1H), 7.15 (s, 1H), 7.11 (s, 1H), 6.35 (s, 1H), 6.21 (s, 1H), 5.82 (t, *J* = 7.7 Hz, 1H), 5.76 (d, *J* = 7.0 Hz, 1H), 5.55 (d, *J* = 7.0 Hz, 1H), 5.29 (dddd, *J* = 15.0, 10.2, 7.1, 1.7 Hz, 1H), 4.77 (t, *J* = 7.7 Hz, 1H), 4.61 (t, *J* = 7.6 Hz, 1H), 4.53 (t, *J* = 8.0 Hz, 1H), 4.41 (dd, *J* = 15.0, 1.7 Hz, 1H), 4.40 (d, *J* = 8.0 Hz, 1H), 4.23 (dd, *J* = 10.2, 1.7 Hz, 1H), 4.16 (d, *J* = 7.0 Hz, 1H), 2.17–2.38 (m, 8H), 1.40–1.54 (m, 72H), 1.03 (dd, *J* = 14.0, 7.1 Hz, 1H), 0.88–0.89 (m, 12H), 0.46 (s, 3H) ppm; ^{1}H NMR (400 MHz, [D_8]toluene) 9.12 (d, *J* = 7.9 Hz, 1H), 9.09 (d, *J* = 7.9 Hz, 1H), 8.25 (d, *J* = 7.9 Hz, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.69 (s, 1H), 7.61 (s, 1H), 7.56 (s, 1H), 7.52 (s, 1H), 7.36–7.48 (m, 4H), 6.34 (s, 1H), 6.33 (s, 1H), 5.56 (d, *J* = 7.1 Hz, 1H), 5.24 (dddd, *J* = 17.0, 9.3, 8.2, 2.1 Hz, 1H), 5.23 (d, *J* = 7.1 Hz, 1H), 5.08 (t, *J* = 8.4 Hz, 1H), 5.05 (t, *J* = 8.2 Hz, 1H), 4.87 (t, *J* = 8.1 Hz, 1H), 4.38 (t, *J* = 6.9 Hz, 1H), 4.37 (dd, *J* = 9.3, 2.1 Hz, 1H), 4.26 (dd, *J* = 17.0, 2.1 Hz, 1H), 3.73 (d, *J* = 7.5 Hz, 1H), 2.49 (d, *J* = 7.5 Hz, 1H), 2.33–2.39 (m, 8H), 1.29–1.51 (m, 72H), 0.94–0.95 (m, 12H), 0.73 (dd, *J* = 8.4, 8.4 Hz, 1H), 0.61 (dd, *J* = 8.4, 8.4 Hz, 1H), 0.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.6, 155.5, 155.0, 154.9, 153.1, 152.9, 152.64, 152.55, 150.3, 149.8, 139.4, 138.6, 138.2, 138.0, 137.9, 136.4, 135.9, 135.1, 133.8, 133.5, 131.51, 131.45, 131.0, 129.59, 129.57, 129.23, 129.15, 128.1, 128.0, 125.8 (two peaks are overlapped), 124.0, 123.2, 123.1, 122.5, 121.8, 120.5, 117.4, 116.9, 116.2, 116.0, 114.4, 99.93, 99.85, 36.8, 36.4, 35.5, 34.3, 32.5, 32.4, 32.34, 32.33, 32.29, 32.28 (many peaks are overlapped), 30.7, 30.69, 30.61, 30.3, 30.18, 30.17, 30.17, 30.15, 30.1, 30.08, 30.06 (many peaks are overlapped), 29.81, 29.80, 29.79, 29.78, 29.76, 29.75 (many peaks are overlapped), 28.4, 28.3, 28.2 (many peaks are overlapped), 23.1, 23.09, 23.08, 23.06, 23.05, 23.03, 23.02 (many peaks are overlapped), 20.1, 14.5, 14.49, 14.48, 14.47, 14.4 (many peaks are overlapped), –4.53 ppm; MS (DART-IT-TOF) *m/z*: 1438 $[MH]^+$; IR (neat): $\tilde{\nu}$ = 2922, 2851, 1487, 1381, 1174, 961, 761, 725, 562 cm^{-1}; HRMS (DART-IT-TOF) calcd. for $C_{94}H_{125}N_2O_8Si$: 1437.9199 $[MH]^+$, found 1437.9172. For data of *rac*-**20**: R_f values 0.55 (hexane/EtOAc = 4:1). ^{1}H NMR (400 MHz, $CDCl_3$) 9.05–9.08 (m, 2H), 8.62 (d, *J* = 7.6 Hz, 2H), 7.74–7.78 (m, 4H), 7.46 (s, 1H), 7.42 (s, 1H), 7.28 (s, 1H), 7.19 (s, 1H), 7.14 (s, 1H), 7.11 (s, 1H), 6.34 (s, 1H), 6.19 (s, 1H), 5.95 (dddd, *J* = 16.8, 10.0, 8.0, 1.9 Hz, 1H), 5.81 (t, *J* = 7.7 Hz, 1H), 5.73 (d, *J* = 7.0 Hz, 1H), 5.55 (d, *J* = 7.0 Hz, 1H), 5.13 (dd, *J* = 16.8, 1.9 Hz, 1H), 5.08 (dd, *J* = 10.0, 1.9 Hz, 1H), 4.77 (t, *J* = 7.7 Hz, 1H), 4.60 (t, *J* = 8.0 Hz, 1H), 4.57 (t, *J* = 8.1 Hz, 1H), 4.34 (d, *J* = 7.7 Hz, 1H), 4.18 (d, *J* = 7.4 Hz, 1H), 2.17–2.30 (m, 8H), 1.97 (d, *J* = 8.0 Hz, 2H), 1.26–1.42 (m, 72H), 0.87–0.91 (m, 12H), –0.38 (s, 3H) ppm; ^{1}H NMR (400 MHz, [D_8]toluene) 8.70 (s, 1H), 8.68 (s, 1H), 7.94 (dd, *J* = 7.3, 7.3 Hz, 2H), 7.73 (s, 2H), 7.61–7.60 (m, 4H), 7.45 (s, 1H), 7.43 (s, 1H), 7.37–7.29 (m, 2H), 7.24–7.20 (m, 1H), 7.13–7.05 (m, 3H), 6.79–6.74 (m, 1H), 6.18–6.13 (m, 2H), 6.03 (t, *J* = 8.2 Hz, 1H), 5.80 (dddd, *J* = 15.7, 11.8, 7.7, 1.6 Hz, 1H, $SiCH_2CH{=}CH_2$), 4.72 (dd, *J* = 15.7, 1.6 Hz, 1H), 4.93 (dd, *J* =11.8, 1.6 Hz, 1H, $SiCH_2CH{=}CH_2$), 4.76 (t, *J* = 8.2 Hz, 1H, $SiCH_2CH{=}CH_2$), 2.45–2.33 (m, 8H), 1.63 (d, *J* = 7.7 Hz, 2H), 1.47–1.29 (m, 72H), 0.96–0.93 (m, 12H), –1.43 (s, 3H, $SiCH_3$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) 155.52, 155.47, 155.1, 154.8, 153.1, 153.0, 152.74, 152.67, 150.1, 149.9, 139.5, 138.7, 138.2, 137.94, 137.93, 136.3, 135.7, 135.2, 133.8, 133.6, 131.8, 131.52, 131.45, 129.6 (two peaks are overlapped), 129.3, 129.2, 128.1, 127.9, 125.8, 125.5, 124.0, 123.2, 123.2, 122.7, 121.7, 120.6, 117.4, 116.8, 116.2, 116.0, 114.4, 99.9 (two peaks are overlapped), 36.8, 36.4, 35.3, 34.2, 32.6, 32.31, 32.29, 32.28 (many peaks are overlapped), 30.6, 30.24, 30.18, 30.15, 30.13, 30.09, 30.07, 30.06 (many peaks are overlapped), 29.8, 29.7 (many peaks are overlapped), 28.41, 28.39, 28.2 (many peaks are overlapped), 23.09, 23.08, 23.06, 23.04, 23.03 (many peaks are overlapped), 20.7, 14.5, 14.49, 14.48, 14.47, 14.46 (many peaks are overlapped), –5.79 ppm; MS (MALDI-TOF) *m/z*: 1438 $[MH]^+$; IR (neat): $\tilde{\nu}$ = 2922, 2851, 1487, 1380, 1173, 960, 761, 725, 561 cm^{-1}; HRMS (MALDI-TOF) calcd. for $C_{94}H_{125}N_2O_8Si$: 1437.9200 $[MH]^+$, found 1437.9195.

Representative experimental sections for oxidation reactions of allylsilanes: (see Table 4) Under an argon atmosphere, to the one-neck flask charged with appropriate allylsilanes (*rac*-**n**, 0.019 mmol) and anhydrous toluene (1 mL) was added mCPBA (6.4 mg, 0.028 mmol). After the reaction mixture was stirred for overnight, saturated aqueous $NaHCO_3$ (3 mL) was added at 0 °C, and then toluene (10 mL) and water (10 mL) were also added. The aqueous phases were extracted with toluene, and the combined organic phases were washed with brine, and concentrated in vacuo to give crude products. Purification by short-plugged silica-gel column chromatography (hexane/EtOAc = 4:1) afforded diastereomeric mixtures of corresponding epoxides. ^{1}H NMR stacks (Figure S2, and S3) of diastereomeric mixtures of epoxides are given in Supporting Information.

Supporting Information (see footnote on the first page of this article): The ^{1}H and ^{13}C NMR spectra of all new compounds, and Figure S1, S2, and S3.

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[1] J. R. Moran, S. Karbach, D. J. Cram, *J. Am. Chem. Soc.* **1982**, *104*, 5826–5828.
[2] P. D. Frischmann, M. J. MacLachlan, *Chem. Soc. Rev.* **2013**, *42*, 871–890, and references cited therein.
[3] A. Dalla, L. Mandolini, C. Pasquini, L. Schiaffino, *New J. Chem.* **2004**, *28*, 1198–1199.
[4] a) V. Böhmer, D. Kraft, M. Tabatabai, *J. Inclusion Phenom. Mol. Recognit. Chem.* **1994**, *19*, 17–39; b) J. Vachon, S. Harthong, B. Dubessy, J.-P. Dutasta, N. Vanthuyne, C. Roussel, J.-V. Naubron, *Tetrahedron: Asymmetry* **2010**, *21*, 1534–1541.
[5] a) S. Shirakawa, S. Shimizu, *Inherently Chiral Calix[4]arenes as Supramolecular Catalysts in Designed Molecular Space in Material Science and Catalysis*, Springer, page 51–68, **2018**; b) A. Szumna, *Chem. Soc. Rev.* **2010**, *39*, 4274–4285.
[6] a) Mini-reviews, A. C. H. Jans, X. Caumes, J. N. H. Reek, *ChemCatChem* **2019**, *11*, 287–297; b) Digest review, T. Iwasawa, *Tetrahedron Lett.* **2017**, *58*, 4217–4226.
[7] a) S. Guieu, E. Zaborova, Y. Blériot, G. Poli, A. Jutand, D. Madec, G. Prestat, M. Sollogoub, *Angew. Chem. Int. Ed.* **2010**, *49*, 2314–2318; *Angew. Chem.* **2010**, *122*, 2364; b) See ref.[4b]; c) J. Vachon, S. Harthong, E. Jeanneau, C. Aronica, N. Vanthuyne, C. Roussel, J.-P. Dutasta, *Org. Biomol. Chem.* **2011**, *9*, 5086–5091; d) P. Soncini, S. Bonsignore, E. Dalcanale, F. Ugozzi, *J. Org. Chem.* **1992**, *57*, 4608–4612; e) D. J. Cram, L. M. Tunstad, C. B. Knobler, *J. Org. Chem.* **1992**, *57*, 528–535.
[8] P. P. Castro, G. Zhao, G. A. Masangkay, C. Hernandez, L. M. Gutierrez-Tunstad, *Org. Lett.* **2004**, *6*, 333–336.
[9] Y. Miura, H. Chiba, R. Katoono, H. Kawai, K. Fujiwara, S. Suzuki, K. Okada, T. Suzuki, *Tetrahedron Lett.* **2012**, *53*, 6561–6564.
[10] M. Kanaura, N. Endo, M. P. Schramm, T. Iwasawa, *Eur. J. Org. Chem.* **2016**, *2016*, 4970–4975.
[11] In each synthesis of *rac*-**1**, -**12**, -**13**, -**14**, and -**15**, two pieces of methylenes, pyrazines, and quinoxalines reacted with the tetra-ol platform to cause side-production of the corresponding symmetrical compounds which are summarized in Supporting Information. These over-reactions in ca. 20 % yields decreased each productivity of the desired di-ol molecules.
[12] We thank Daicel Corporation CPI for their help, the analytical report is attached in Electronic Supporting Information.
[13] K. Ohashi, K. Ito, T. Iwasawa, *Eur. J. Org. Chem.* **2014**, *2014*, 1597–1601.
[14] a) A. R. Renslo, D. M. Rudkevich, J. Rebek Jr., *J. Am. Chem. Soc.* **1999**, *121*, 7459–7460; b) A. R. Renslo, F. C. Tucci, D. M. Rudkevich, J. Rebek Jr., *J. Am. Chem. Soc.* **2000**, *122*, 4573–4582.
[15] J. R. Moran, J. L. Ericson, E. Dalcanale, J. A. Bryant, C. B. Knobler, D. J. Cram, *J. Am. Chem. Soc.* **1991**, *113*, 5707–5714.
[16] a) T. Gottschalk, P. D. Jarowski, F. Diederich, *Tetrahedron* **2008**, *64*, 8307–8317; b) A. V. Azov, B. Jaun, F. Diederich, *Helv. Chim. Acta* **2004**, *87*, 449–462; c) P. J. Skinner, A. G. Cheetham, A. Beeby, V. Gramlich, F. Diederich, *Helv. Chim. Acta* **2001**, *84*, 2146–2154.
[17] These stacks of ^{1}H NMR spectra were summarized in Supporting Information as Figure S1.
[18] T. Iwasawa, Y. Nishimoto, K. Hama, T. Kamei, Y. Nishiuchi, Y. Kawamura, *Tetrahedron Lett.* **2008**, *49*, 4758–4762.
[19] a) D. J. Cram, J. M. Cram, *Container Molecules and Their Guests*, *Monographs in Supramolecular Chemistry* (Ed.: J. F. Stoddart), RSC, Cambridge, **MA**, **1994**; b) T. Heinz, D. M. Rudkevich, J. Rebek Jr. *Nature* **1998**, *394*, 764–766.
[20] One reviewer thoughtfully gave us an advise that ROESY technique proves such a type of supramolecular structures, whereas herein we didn't use the spectra. For example, see: E. Botana, M. C. Lubinu, E. Da Silva, P. Espinet, J. de Mendoza, *Chem. Commun.* **2010**, *46*, 4752–4754.
[21] a) F. Maffei, G. Brancatelli, T. Barboza, E. Dalcanale, S. Geremia, R. Pinalli, *Supramol. Chem.* **2018**, *30*, 600–609; b) G. Brancatelli, C. Nicosia, T. Barboza, L. Guy, J.-P. Dutasta, R. De Zorzi, N. Demitri, E. Dalcanale, S. Geremia, R. Pinalli, *CrystEngComm* **2017**, *19*, 3355–3361.
[22] F. Diederich, *Angew. Chem. Int. Ed.* **2007**, *46*, 68–69; *Angew. Chem.* **2007**, *119*, 68.

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