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Synthesis, complexation, and photoisomerization studies on some chiral monocyclic stilbenophanes and bis-cyclophanes

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Abstract—Various chiral stilbenophanes with small and large rigid cavities have been synthesized. Bis-cyclophanes with a stilbene-bridging unit have also been synthesized. Some of the stilbenophanes form charge transfer complexes with either TCNQ or TCNE. Photoisomerization of the bis-cyclophanes has also been studied.

1. Introduction

Stilbenophanes are an important class of supramolecular structures in the cyclophane family since they can undergo functional group transformations and interesting photoisomerizations. The design and synthesis of stilbenophanes as molecular hosts continue to be of interest due to the size, shape, rigidity, and non-covalent interactions at the cavity. Synthesis of stilbenophanes using inter-[1] and intramolecular[2] McMurry coupling has been well explored in the literature. Stilbenophanes are known to form complexes with electron-deficient guest molecules.[3,4] Stilbenophanes with small cavity have complexing selectivity for lithium ions.[5] Stilbene-bridged cyclic compounds[6] have been found to be highly selective receptors for small electron-deficient molecules, and furthermore have photoswitching binding ability. Synthesis, photophysical, and photochemical properties of stilbenophanes tethered by silyl chains have also been reported.[7] Stilbenophanes are also important key intermediates for the synthesis of various acetylene-based cyclophanes.[8] Although the wide applicability of binaphthol as a chiral receptor[9] and a chiral discriminating agent in modern organic synthesis and asymmetric catalysis[10] has been exploited, the synthesis of chiral stilbenophanes and study of their asymmetric induction continue to be of interest. Also, chiral stilbenophanes may be useful for the synthesis of more rigid acetylenic chiral cyclophanes,[8] which are of specific interest for selective binding of disaccharides.[11] Although various chiral cyclophanes with binaphthol have been reported from our laboratory,[12] the synthesis of chiral stilbenophanes is still a rare observation. Herein, we wish to report the synthesis of chiral receptors with small cavity **1a–c** and with large cavity **3** and **4**, and their host–guest complexation studies with TCNQ or TCNE. Furthermore, we report herein the synthesis and photoisomerization of chiral bis-cyclophanes **5** and **6b**.

2. Results and discussion

The synthetic pathway leading to chiral cyclophanes **1a–c** is outlined in Scheme 1. Reaction of ethyl *p*-toluate **7a** with NBS in CCl_4 gave *p*-carbethoxybenzylbromide **8a** in 82% yield. O-Alkylation of **8a** with optically pure (*S*)-BINOL in DMF in the presence of K_2CO_3 gave chiral diester **9a** in 71% yield, which was then reduced to the corresponding chiral diol **10a** using $LiAlH_4$ in THF. Treatment of chiral diol **10a** with pyridinium chloro chromate (PCC) in CH_2Cl_2 at 25 °C afforded the corresponding dialdehyde **11a** in 73% yield. Addition of dialdehyde **11a** to a solution of 20 equiv of $TiCl_4$ and 40 equiv of Zn in THF followed by refluxing for 12 h resulted in the formation of chiral *cis*-stilbenophane **1a** (15%) along with chiral cyclic diol **2a** (50%) (Scheme 1).

The ^{1}H NMR spectrum of the stilbenophane **1a** showed two doublets at δ 4.70 and 4.97 for the *O*-methylene protons, a set of doublets at δ 6.40 and 6.49 for the *p*-xylyl protons, and a singlet at δ 6.81 for olefinic protons in addition to the aromatic protons of the binol unit at δ 7.00–7.86. In the ^{13}C NMR spectrum, chiral stilbenophane **1a** showed *O*-methylene carbon at δ 70.1 in addition to 15 peaks in the aromatic region. The ^{1}H NMR spectrum of chiral cyclic diol **2a** showed two doublets at δ 4.73 and 4.95 for *O*-methylene protons, a singlet at δ 4.40 for *O*-methine protons, and the aromatic protons appeared at δ 7.18–7.99. ^{13}C NMR spectrum of chiral diol **2a** showed the *O*–CH_2 carbon at δ 70.5 and *O*–CH carbon at δ 82.1, in addition to 14 aromatic

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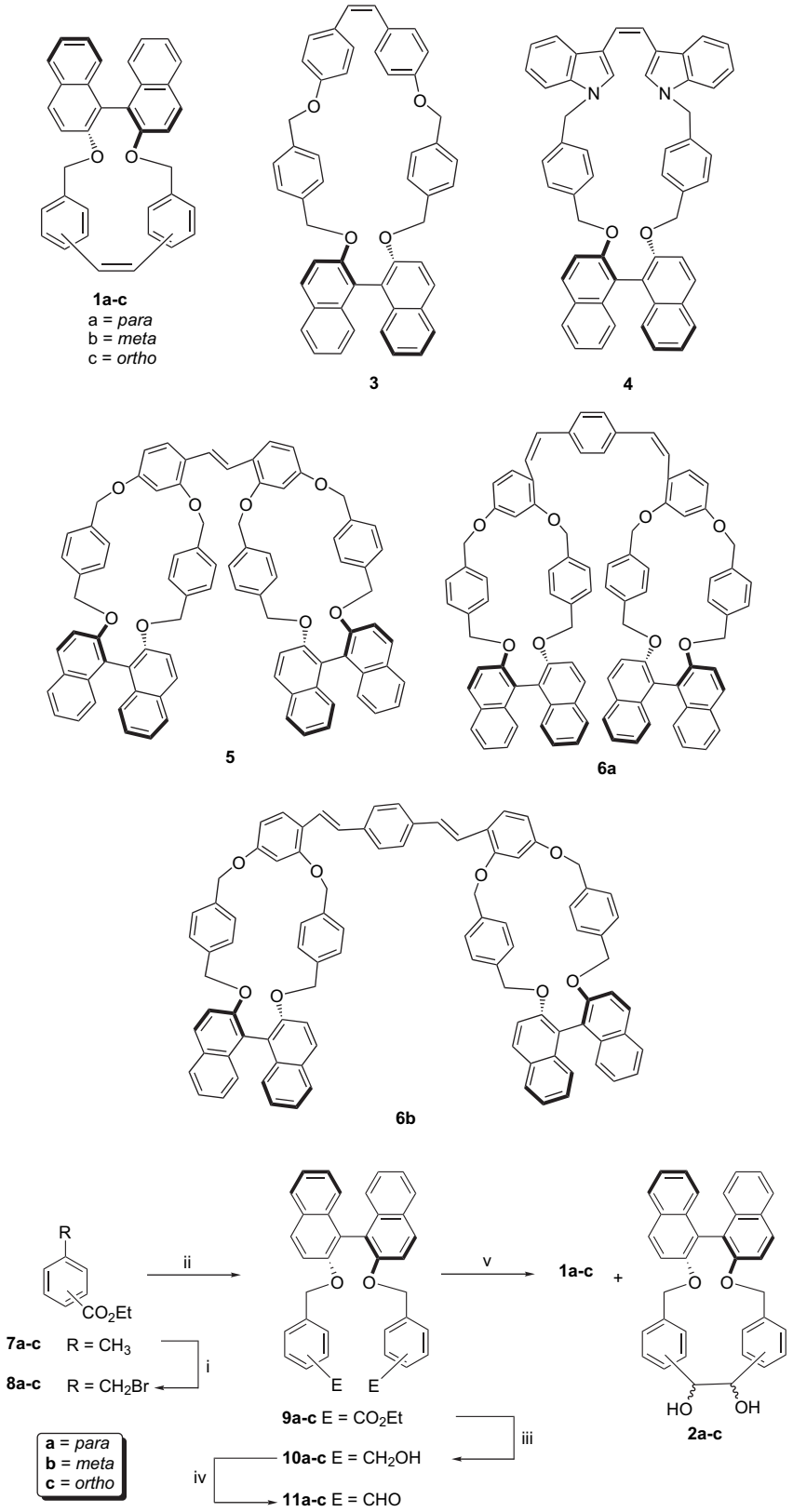


Scheme 1. Reagents and conditions: (i) NBS, CCl_4, reflux, 6 h, **8a** (82%), **8b** (84%), **8c** (88%); (ii) (*S*)-BINOL, K_2CO_3, DMF, 80 °C, 48 h, **9a** (71%), **9b** (65%), **9c** (82%); (iii) $LiAlH_4$, THF, reflux, 6 h, **10a** (85%), **10b** (75%), **10c** (82%); (iv) PCC, CH_2Cl_2, rt, 3 h, **11a** (73%), **11b** (78%), **11c** (69%); (v) $TiCl_4$ (20 equiv), Zn (40 equiv), THF, reflux, 12 h, **1a** (15%), **1b** (62%), **1c** (52%) and **2a** (50%), **2b** (7%), **2c** (8%).

carbons. Furthermore, the structure of the chiral diol **2a** was confirmed by the appearance of molecular ion peak at *m/z* 524 in the mass spectrum.

Similarly, the chiral stilbenophanes **1b** (62%) and **1c** (52%) were obtained along with chiral diols **2b** and **2c** in 7 and 8% yields, respectively. The structure of stilbenophane **1b**

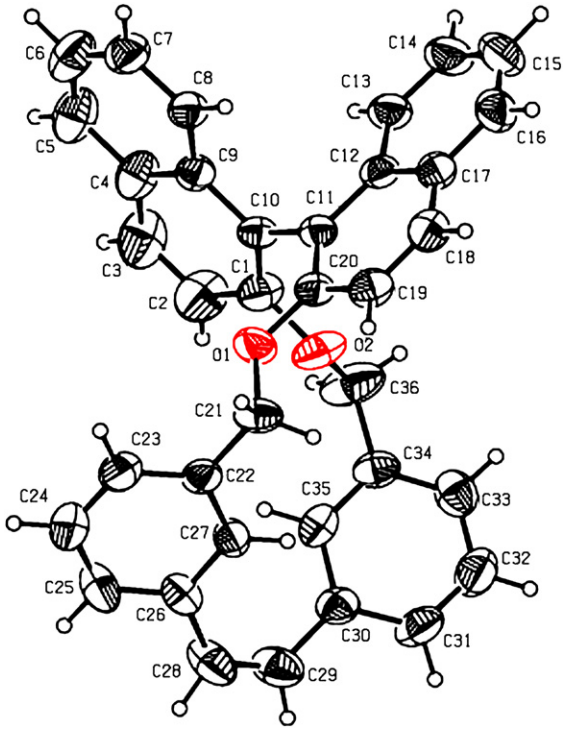
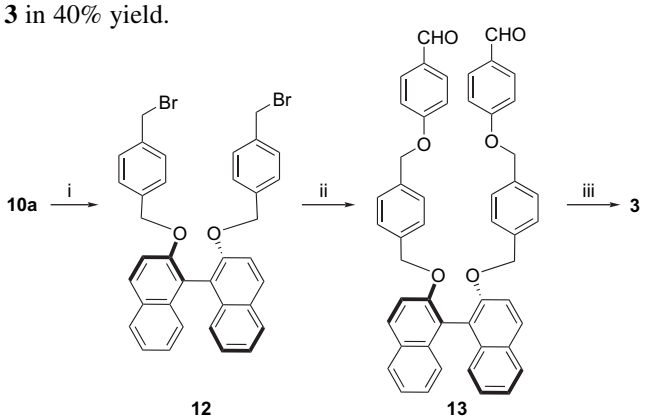


Figure 1. ORTEP diagram of chiral stilbenophane **1b**.

was also confirmed by spectral, analytical as well as by XRD studies.[13] The ORTEP diagram of chiral stilbenophane **1b** is shown in Figure 1. It is noteworthy to mention that the olefinic carbons in **1a–c** could function as a stereogenic center and the presence of (*S*)-BINOL moiety would facilitate asymmetric induction.

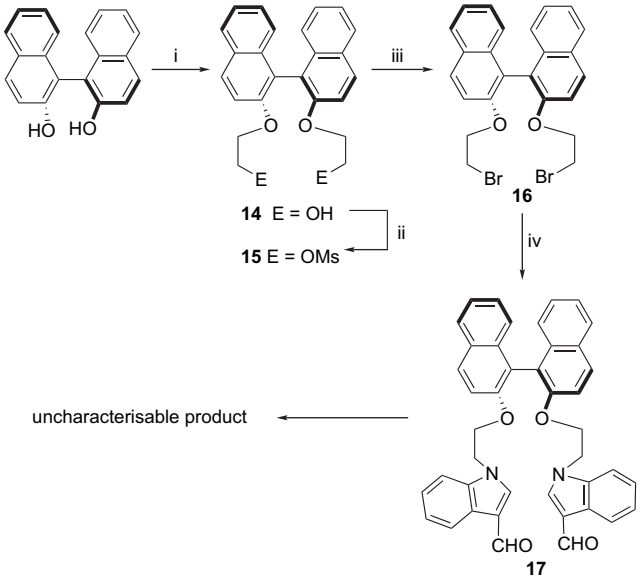
Electron-rich cyclophanes with large cavities[4] are known to bind electron-deficient guest molecules effectively. Hence, we focused our attention on the synthesis of chiral stilbenophane **3**, which has a large cavity. The synthetic pathway leading to stilbenophane **3** is outlined in Scheme 2. Treatment of chiral diol **10a** with PBr_3 in CH_2Cl_2 led to the chiral dibromide **12** in 72% yield. The O-alkylation reaction of *p*-hydroxybenzaldehyde with chiral dibromide **12** in DMF in the presence of K_2CO_3 gave chiral dialdehyde **13** in 84% yield. The chiral dialdehyde **13**, when subjected to McMurry coupling as shown in Scheme 1, lead to chiral stilbenophane **3** in 40% yield.



Scheme 2. Reagents and conditions: (i) PBr_3, CH_2Cl_2, 0 °C, 4 h, **12** (72%); (ii) *p*-hydroxybenzaldehyde (2.1 equiv), K_2CO_3, DMF, 80 °C, 48 h, **13** (84%); (iii) $TiCl_4$ (20 equiv), Zn (40 equiv), THF, reflux, 12 h, **3** (40%).

The ^1H NMR spectrum of the stilbenophane **3** showed a multiplet in the region of δ 4.96–5.12 for two different *O*-methylene protons, a singlet for olefinic proton at δ 6.42, and aromatic protons in the range of δ 6.64–7.95. In the ^{13}C NMR spectrum, chiral stilbenophane **3** showed two *O*-methylene carbons at δ 70.1 and 71.2 along with 19 peaks in the aromatic region. The structure of the stilbenophane **3** was further confirmed by FABMS.

Indole-based cyclophanes are known to form complexes with cobalt.[14] Hence, the synthesis of chiral stilbenophanes with an indole moiety having small and large cavities continues to be of interest. Chiral dibromide **16**[15] was reacted with indole-3-aldehyde using 25% aq NaOH in CH_3CN to give the chiral dialdehyde **17** in 63% yield. This chiral dialdehyde **17**, under McMurry coupling conditions, gave uncharacterizable product, instead of the corresponding indolophane. This may be due to the flexibility of chiral dialdehyde, which permits polymerization instead of giving cyclized product (Scheme 3).

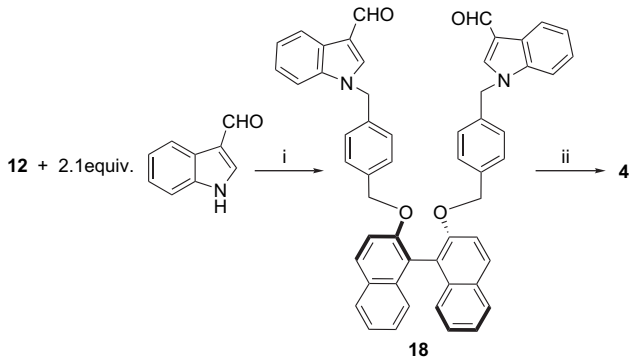


Scheme 3. Reagents and conditions: (i) 2-chloroethanol, K_2CO_3, DMF, 110 °C, reflux, 17 h, **14** (65%); (ii) methane sulfonyl chloride, DCM, DMAP, Et_3N, 0 °C, 20 h, **15** (80%); (iii) LiBr, DMSO, 60 °C, reflux, 24 h, **16** (72%); (iv) indole-3-aldehyde, 25% NaOH, CH_3CN, 48 h, **17** (63%); (v) $TiCl_4$ (20 equiv), Zn (40 equiv), THF, reflux, 12 h.

Similarly, chiral indolostilbenophane **4** with large cavity was synthesized in 15% yield by McMurry coupling of the chiral dialdehyde **18** with low-valent titanium (Scheme 4).

The formation of stilbenophane **4** was evident by the presence of a singlet at δ 4.85 for the *N*–CH_2 protons and two doublets at δ 4.88 and 5.06 with a coupling constant of 16.2 Hz for the *O*–CH_2 protons. The protons at the 2-position of indole ring and olefinic protons merged and appeared as a singlet at δ 6.50 for a total of four protons. The remaining protons appeared in the aromatic region δ 6.58–7.83.

Encouraged by the successful results, our attention focused on the synthesis of the chiral pyrrolostilbenophane **20**. However, the dialdehyde **19** when subjected to intramolecular



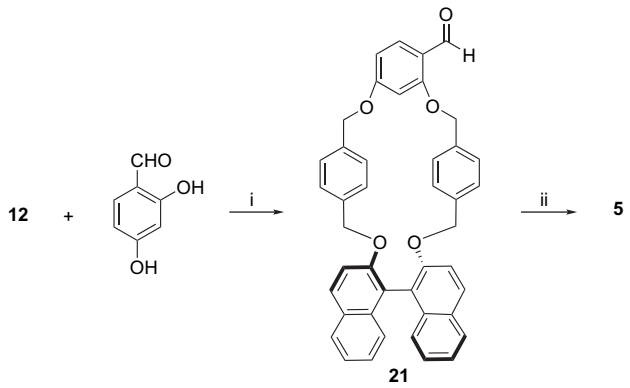
Scheme 4. Reagents and conditions: (i) 25% NaOH, CH_3CN, rt, 2 days, **18** (73%); (ii) $TiCl_4$ (20 equiv), Zn (40 equiv), THF, reflux, 12 h, **4** (15%).

McMurry coupling gave only uncharacterizable product rather than the pyrrolostilbenophane **20**. The product cannot be purified and decomposed before characterization (Scheme 5).

Stilbene double bonds are well known to exhibit *cis*/*trans* isomerization and photodimerization. Hence the synthesis of chiral bis-cyclophanes with a double bond continues to be of interest.

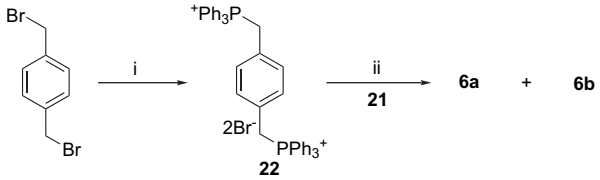
To synthesize cyclophane aldehyde **21**, the chiral dibromide **12** was stirred with 1 equiv of 2,4-dihydroxy benzaldehyde in the presence of K_2CO_3 in acetone at room temperature for 3 days. The ^1H NMR spectrum of cyclophane aldehyde **21** showed the *O*-methylene protons attached to the binol unit as two doublets at δ 5.00 and 5.18 and *O*-methylene protons attached to the 2,5-dihydroxy phenyl moiety appeared as two proton doublet at δ 5.08 and a two proton singlet at δ 5.14 in addition to the aromatic protons at δ 6.26–7.93 and the aldehydic proton appeared at δ 10.36. Furthermore, the structure of the aldehyde **21** was confirmed based on spectral and analytical data. Aldehyde **21**, when subjected to McMurry coupling afforded bis-cyclophanes **5** in 25% yield (Scheme 6).

Synthesis of bis-cyclophanes **6a** and **6b** has been achieved by Wittig reaction. Treatment of phosphonium salt **22** with cyclophane aldehyde **21** in the presence of NaH in THF under reflux for 12 h afforded **6a** and **6b** in 8 and 75% yields, respectively. However, when the same reaction was carried out under refluxing conditions immediately after the



Scheme 6. Reagents and conditions: (i) K_2CO_3, acetone, rt, 3 days, **21** (34%); (ii) $TiCl_4$ (20 equiv), Zn (40 equiv), THF, reflux, 12 h, **5** (25%).

addition of the aldehyde **21** to the phosphonium salt **22** in THF gave **6b** in 80% yield (Scheme 7).

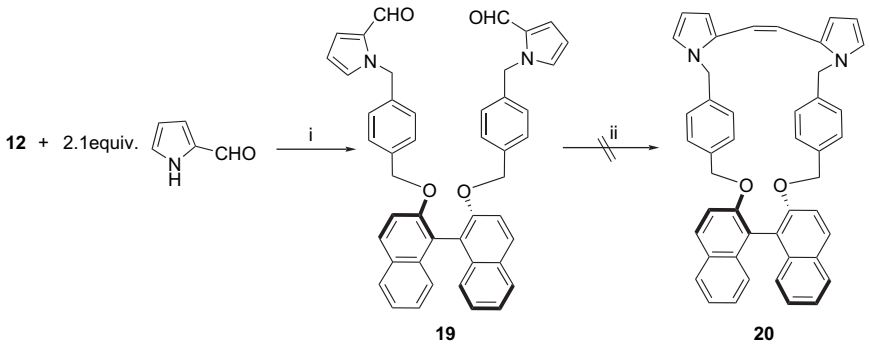


Scheme 7. Reagents and conditions: (i) PPh_3, CH_2Cl_2, 40 °C, 4 h, **22** (95%); (ii) NaH, THF, reflux, 12 h, **6a** (8%), **6b** (75%).

Theoretical calculations based on Molecular mechanics (MM2) on bis-cyclophanes **6a** and **6b** shows that the trans isomer **6b** has a smaller heat of formation (77.05 kcal mol^{-1}) than that of the corresponding cis isomer **6a** (98.93 kcal mol^{-1}), which is in accordance with our experimental observation (Fig. 2).

3. Complexation studies

Of the cyclophanes reported in this paper, compounds **1b**, **1c**, **3**, **5**, and **6b** formed charge transfer complexes with TCNQ. Cyclophanes **1b**, **1c**, **3**, **5**, and **6b** show UV–vis absorption maxima at 284, 286, 283, 282 and 378 nm, respectively. However, the acceptor TCNQ shows an absorption maximum at 274 nm. Cyclophanes **1b**, **1c**, **3**, **5**, and **6b** form a charge transfer complex with TCNQ as evidenced



Scheme 5. Reagents and conditions: (i) 25% NaOH, CH_3CN, rt, 2 days, **19** (60%); (ii) $TiCl_4$ (20 equiv), Zn (40 equiv), THF, reflux, 12 h.

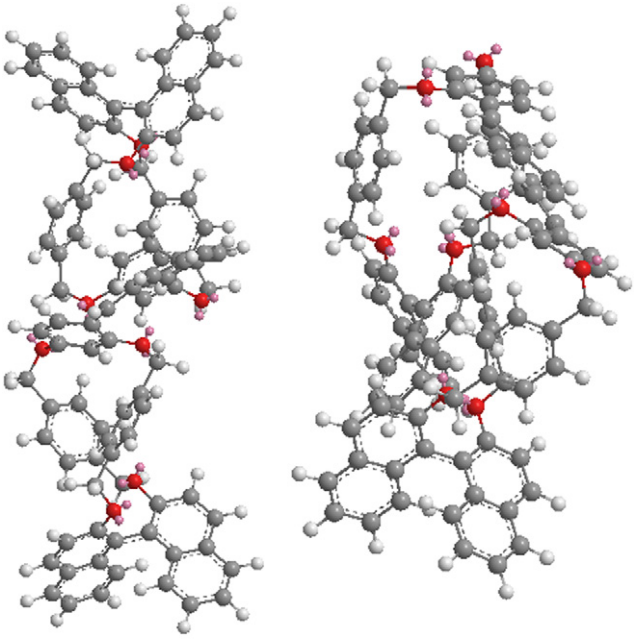


Figure 2. Energy minimized (MM2) structures and heat of formation of bis-cyclophanes **6a** and **6b**.

by the appearance of absorption maxima at 420, 424, 422, 422 and 382 nm, respectively. The studies were carried out as outlined below.

In a typical experiment, 3 mL of a standard stock solution of the cyclophane in DMF was placed in a quartz cuvette. A known amount of the electron-deficient guest molecule was added in incremental amounts and changes in absorbance of the CT bands were recorded. Table 1 shows the CT complexation studies of **1b** with various concentrations of TCNQ. Plot of [concn of cyclophane]/absorbance (*Y/A*) vs 1/concentration of guest (1/*X*) was linear. From the slope and the intercept values, K_a (K_a=intercept×slope^{-1}) and ε (ε=intercept^{-1}) were evaluated. The plot was linear suggesting that the predominant species in solution as a 1:1 complex (Fig. 3). K_a and ε values of the CT complexes formed from **1b**, **1c**, **3**, **5**, and **6b** with TCNQ are shown in Table 2.

All the compounds shown above effectively form charge transfer complexes with TCNQ. Compounds **1b**, **1c**, and **3** bind TCNQ more strongly than **5** and **6b**. Complexation studies of **1b**, **1c**, **3**, **5**, and **6b** with PQT were not successful. However, cyclophanes **3**, **5**, and **6b** form charge transfer complexes with TCNE unlike the other compounds reported

Table 1. Benesi–Hildebrand treatment data of the CT complex formed between the cyclophane **1b** and TCNQ

Concentration of guest, [*X*] (M)	Absorbance, *A*	[*Y*]/*A* (M)	1/[*X*] (M^{-1})
4.9×10^{-6}	0.388	0.0000257	204,081
9.8×10^{-6}	0.640	0.0000156	102,040
14.7×10^{-6}	0.873	0.0000115	68,027
19.6×10^{-6}	1.102	0.0000090	51,020
24.5×10^{-6}	1.331	0.0000075	40,816

λ_{max}=420 nm; concentration of cyclophane **1b**=10^{-5} M. K_a=3.03×10^4 M^{-1}; ε=3.33×10^5 M^{-1} cm^{-1}; SD=99.97 (%).

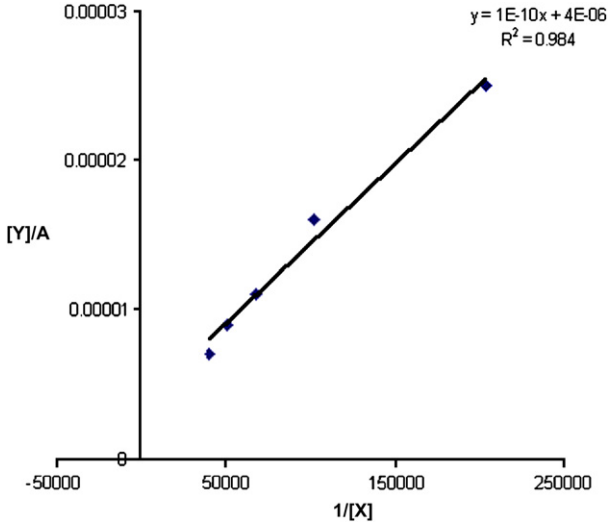


Figure 3. Plot between 1/*X* and *Y/A* for compound **1b**.

Table 2. Complexation of TCNQ with cyclophanes **1b**, **1c**, **3**, **5**, and **6b**

Cyclophane	K_a (mol^{-1} dm^3)	ε (M^{-1} cm^{-1})
1b	3.03×10^4	3.33×10^5
1c	4.00×10^4	2.50×10^5
3	2.00×10^4	2.50×10^5
5	3.50×10^3	1.43×10^6
6b	2.00×10^3	1.66×10^5

Table 3. Complexation of TCNE with cyclophanes **3**, **5**, and **6b**

Cyclophane	K_a (mol^{-1} dm^3)	ε (M^{-1} cm^{-1})
3	2.00×10^3	1.00×10^6
5	6.06×10^4	3.33×10^6
6b	3.10×10^4	1.66×10^5

in this paper. Compounds **5** and **6b** form complex with TCNE stronger than compound **3**. The acceptor TCNE shows absorption maxima at 287, cyclophanes **3**, **5**, and **7b** form charge transfer complexes at 488, 490, and 492 nm, respectively (Table 3).

4. *cis/trans* Isomerization

The photoisomerization behavior of the stilbene core in a variety of molecules, including dendrimers, is well known and has been thoroughly studied.[16] Recently, synthesis of photoresponsive stilbene dendrons and dendrimers has been reported from our laboratory.[17] However, the photoisomerization behavior of chiral bis-cyclophanes with a stilbene unit is still a rare observation. Hence, it is of interest to study the photoisomerization behavior of stilbene unit in chiral bis-cyclophanes **5** and **6b**.

On UV irradiation at 356 nm at room temperature in $CHCl_3$, the bis-cyclophanes **5** and **6b** underwent isomerization at the carbon–carbon double bond to give cis isomers as revealed by the decrease of absorbance[18] as shown in Figure 4.

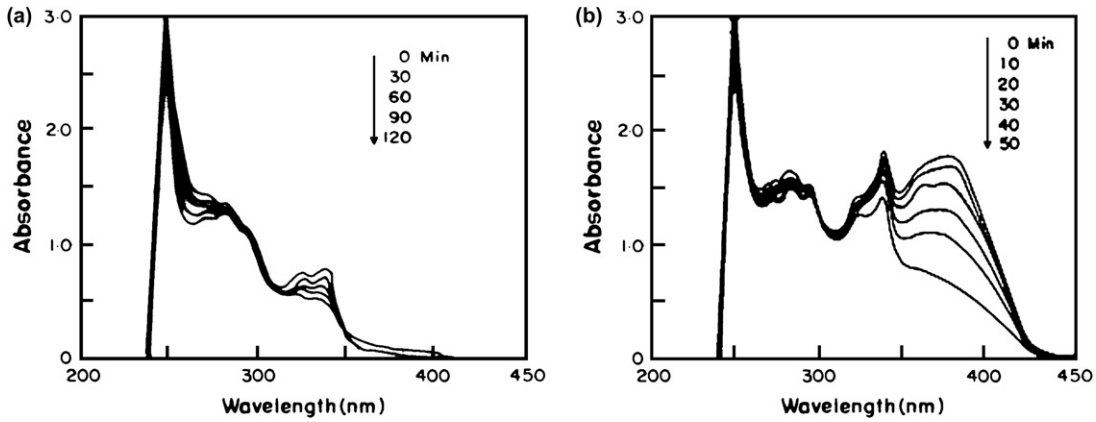


Figure 4. Change of absorption spectrum of (a) *trans*-**5** and (b) *trans*-**6b** upon irradiation of 356 nm light in 1×10^{-5} M $CHCl_3$ solution at room temperature.

5. Conclusion

In conclusion, we have synthesized various chiral stilbenophanes with small and large cavities. Synthesis of chiral stilbenophanes with indole moiety and chiral bis-cyclophanes with stilbene units has also been studied. Complexation studies were carried out for various chiral cyclophanes with TCNE and TCNQ. Photoisomerization behavior of bis-cyclophanes with a stilbene unit was also studied by the irradiation of UV light at room temperature in $CHCl_3$.

6. Experimental

6.1. General

All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ from Jeol GSX 400 (400 MHz) and Jeol ECA 500 (500 MHz) NMR spectrometers. Mass spectra were recorded from Jeol DX 303, Jeol SX 102/DA-600 (6 kV, 10 mA), and FABMS. The rotations were recorded using Autopol II (Automatic Polarimeter) at 25 °C. Column chromatography was performed using silica gel (100–200 mesh).

6.2. General procedure for McMurry coupling reaction

A solution of zero-valent titanium was prepared from $TiCl_4$ (20 equiv) with zinc (40 equiv) in dry THF (75 mL) under a nitrogen atmosphere at 0 °C and was allowed to attain room temperature after 0.5 h and then refluxed for 1 h. Dialdehyde was added in one batch to the freshly prepared low-valent titanium. After the addition, the reaction mixture was refluxed overnight, cooled, and then quenched with saturated K_2CO_3 solution. The precipitated inorganic material was removed by filtration, thoroughly washed with THF for several times, and the combined THF extract was removed under reduced pressure. The residue was then dissolved in water and extracted in $CHCl_3$ (200 mL), washed with water (2×200 mL), brine (100 mL), and dried over Na_2SO_4. Crude product obtained after evaporation of $CHCl_3$ was purified by column chromatography.

6.2.1. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-tricyclo[14.2^{9,10}.2^{19,20}.2^{21,22}]docosa-2,4,8,10,12,14,16,19,21-nonaene (1a). White solid; yield: 15%; hexane/$CHCl_3$ (7:3); mp 110 °C; $[\alpha]_D^{25}$ −130.0 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{26}O_2$: C, 88.14; H, 5.34. Found: C, 88.21; H, 5.42] δ_H (400 MHz, $CDCl_3$) 7.86 (d, 2H, *J* 9.3 Hz, Ar), 7.78 (d, 2H, *J* 9.9 Hz, Ar), 7.44 (d, 2H, *J* 11.3 Hz, Ar), 7.23 (t, 2H, *J* 8.8 Hz, Ar), 7.00–7.18 (m, 4H, Ar), 6.81 (s, 2H, C*H*=C*H*), 6.49 (d, 4H, *J* 9.9 Hz, Ar), 6.40 (d, 4H, *J* 9.9 Hz, Ar), 4.97 (d, 2H, *J*=14.9 Hz, OCH_2), 4.70 (d, 2H, *J* 14.9 Hz, OCH_2); δ_C (100 MHz, $CDCl_3$) 153.5 138.2, 133.7, 135.5, 134.5, 129.3, 129.1, 128.8, 127.8, 127.7, 126.2, 125.6, 123.5, 120.7, 115.8, 70.1; *m*/*z* (EI, 70 eV) 490 (M^+).

6.2.2. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-tricyclo[16.3$^{9-11}$.1^{21}.1^{22}]docosa-2,4,8,10,12(22),13,15(21),16,18-nonaene (1b). White solid; yield: 62%; hexane/$CHCl_3$ (7:3); mp 174 °C; $[\alpha]_D^{25}$ −149.1 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{26}O_2$: C, 88.14; H, 5.34. Found: C, 88.04; H, 5.23] δ_H (500 MHz, $CDCl_3$) 7.51 (s, 2H, Ar), 7.87 (t, 4H, *J* 9.7 Hz. Ar), 7.40 (d, 2H, *J* 8.6 Hz, Ar), 7.32–7.35 (m, 2H, Ar), 7.22–7.26 (m, 2H, Ar), 7.14–7.19 (m, 4H, Ar), 7.07–7.09 (m, 2H, Ar), 6.93 (d, 2H, *J* 7.4 Hz, Ar), 6.56 (s, 2H, C*H*=C*H*), 4.99 (d, 2H, *J* 12.6 Hz, OCH_2), 4.79 (d, 2H, *J* 12.6 Hz, OCH_2); δ_C (125 MHz, $CDCl_3$) 154.5 137.6, 137.3, 134.3, 130.3, 129.4, 129.3, 128.5, 128.0, 127.4, 126.9, 126.3, 125.7, 123.6, 120.3, 115.8, 71.5; *m*/*z* (EI, 70 eV) 490 (M^+).

6.2.3. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-tricyclo[18.4$^{9-12}$.0^{8,13}.0^{16,21}]docosa-2,4,8,10,12,14,16,18,20-nonaene (1c). White solid; yield: 52%; hexane/$CHCl_3$ (7:3); mp 175 °C; $[\alpha]_D^{25}$ −702.5 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{26}O_2$: C, 88.14; H, 5.34. Found: C, 88.25; H, 5.41] δ_H (500 MHz, $CDCl_3$) 7.90 (d, 2H, *J* 9.2 Hz, Ar), 7.79 (d, 2H, *J* 8.4 Hz, Ar), 7.48 (d, 2H, *J* 9.2 Hz, Ar), 7.39 (d, 2H, *J* 7.6 Hz, Ar), 7.31 (s, 2H, Ar), 7.20–7.29 (m, 6H, Ar), 7.12–7.15 (m, 4H, Ar), 6.95 (d, 2H, *J* 8.4 Hz, C*H*=C*H*), 4.99–5.02 (m, 4H, OCH_2); δ_C NMR (125 MHz, $CDCl_3$) 170.5, 154, 140.1, 134.8, 133.2, 132.0, 131.7, 129.3, 129.0, 128.9, 127.8, 127.7, 127.1, 126.2, 125.5, 123.3, 118.6, 113.5; *m*/*z* (EI, 70 eV) 490 (M^+).

6.2.4. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-tricyclo[14.2^{9,10}.2^{19,20}.2^{21,22}]docosa-2,4,8,10,14,16,19,21-octaene-12,13-diol (2a). Pale green solid; yield: 50%; hexane/$CHCl_3$ (3:7); mp 210–212 °C; $[\alpha]_D^{25}$ −168.4 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{28}O_4$: C, 82.42; H, 5.38.

Found: C, 82.55; H. 5.49] δ_H (500 MHz, $CDCl_3$) 7.99 (d, 2H, *J* 9.2 Hz, Ar), 7.87 (d, 2H, *J* 8.4 Hz, Ar), 7.52 (d, 2H, *J* 9.2 Hz, Ar), 7.18–7.35 (m, 14H, Ar), 5.66–5.70 (m, 2H, O*H*), 4.95 (d, 2H, *J* 12.2 Hz, OCH_2), 4.73 (d, 2H, *J* 12.2 Hz, OCH_2), 4.40 (s, 2H, OC*H*); δ_C (125 MHz, $CDCl_3$) 153.9, 139.2, 136.6, 134.6, 129.4, 129.1, 128.5, 128.1, 127.7, 126.5, 125.7, 123.8, 121.2, 116.4, 82.1, 70.5; *m*/*z* 524 (M^+).

6.2.5. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-tricyclo[16.3$^{9-11}$.1^{21}.1^{22}]docosa-2,4,8,10,12(22),15(21),16,18-octaene-13,14-diol (2b). Pale green solid; yield: 7%; hexane/$CHCl_3$ (3:7); mp 110 °C; $[\alpha]_D^{25}$ −56.2 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{28}O_4$: C, 82.42; H, 5.38. Found: C, 82.53; H. 5.46] δ_H (500 MHz, $CDCl_3$) 7.81–7.84 (m, 2H, Ar), 7.76–7.78 (m, 2H, Ar), 7.47–7.50 (m, 2H, Ar), 7.22–7.25 (m, 2H, Ar), 7.06–7.12 (m, 6H, Ar), 7.00–7.06 (m, 4H, Ar), 6.54–6.58 (m, 2H, Ar), 5.21–5.24 (m, 2H, O*H*), 4.50–4.62 (m, 4H, OCH_2), 4.38–4.52 (m, 2H, C*H*); δ_C (125 MHz, $CDCl_3$) 153.6, 139.4, 136.5, 134.6, 129.2, 129.0, 128.3, 127.8, 127.4, 126.0, 125.7, 123.5, 121.0, 116.3, 82.0, 70.1; *m*/*z* 524 (M^+).

6.2.6. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-tricyclo[18.4$^{9-12}$.0^{8,13}.0^{16,21}]docosa-2,4,8,10,12,16,18,20-octaene-14,15-diol (2c). Pale green solid; yield: 8%; hexane/$CHCl_3$ (3:7); mp 150–152 °C; $[\alpha]_D^{25}$ −35.4 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{28}O_4$: C, 82.42; H, 5.38. Found: C, 82.33; H. 5.30] δ_H (500 MHz, $CDCl_3$) 7.85–7.90 (m, 2H, Ar), 7.78–7.80 (m, 2H, Ar), 7.48–7.52 (m, 2H, Ar), 7.29–7.31 (m, 4H, Ar), 7.12–7.25 (m, 4H, Ar), 7.02–7.08 (m, 4H, Ar), 6.53–6.58 (m, 2H, Ar), 5.29–5.32 (m, 2H, O*H*), 4.66–4.85 (m, 4H, OCH_2), 4.39–4.54 (m, 2H, C*H*); δ_C (125 MHz, $CDCl_3$) 153.5, 139.4, 136.6, 134.8, 129.4, 127.9, 127.7, 127.4, 126.0, 123.8, 125.6, 120.9, 116.5, 82.9, 69.7; *m*/*z* 524 (M^+).

6.2.7. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6,13,24-tetraoxa-pentocyclo[26.2^{9,10}.2^{31,32}.2^{33,34}.2^{35,36}.2^{37,38}]octatriconta-2,4,8,10,14,16,18,20,22,26,28,31,33,35,37-pentadecaene (3). White solid; yield 40%; hexane/$CHCl_3$ (1:1); mp 118–120 °C; $[\alpha]_D^{25}$ −97.6 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{50}H_{38}O_4$: C, 85.44; H, 5.45. Found: C, 85.32; H, 5.56] δ_H (500 MHz, $CDCl_3$) 7.92–7.95 (m, 2H, Ar), 7.87 (d, 2H, *J* 8.4 Hz, Ar), 7.39–7.42 (m, 2H, Ar), 7.34 (t, 2H, *J* 6.9 Hz, Ar), 7.21–7.25 (m, 4H, Ar), 7.15 (d, 2H, *J* 8.4 Hz, Ar), 7.06–7.09 (m, 4H, Ar), 6.99–7.01 (m, 4H, Ar), 6.64–6.68 (m, 4H, Ar), 6.59 (d, 2H, *J* 9.2 Hz, Ar), 6.42 (s, 2H, C*H*=C*H*), 4.96–5.12 (m, 8H, OCH_2); δ_C (125 MHz, $CDCl_3$) 157.4, 156.6, 154.3, 137.2, 137.0, 134.3, 130.4, 129.9, 129.6, 128.8, 128.1, 127.0, 126.9, 126.8, 126.5, 125.6, 123.9, 115.4, 115.1, 71.2, 70.1; *m*/*z* (FABMS) 702 (M^+).

6.2.8. (*S*)-(−)-2,3:4,5-Di(1,2-naphtho)-1,6-dioxa-13,22-diaza-14,15,20,21-bis(1,2-benzo)pentocyclo[24.2^{9,10}.2^{29,30}.2^{33,34}.1^{31}.1^{32}]tetratriconta-2,4,8,10,16(32),17,19(31),24,26,29,33-undecaene (4). White solid; yield: 15%; hexane/$CHCl_3$ (1:1); mp 155 °C; $[\alpha]_D^{25}$ −98.1 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{54}N_{40}N_2O_2$: C, 86.60; H, 5.38; N, 3.74. Found: C, 86.73; H, 5.46; N, 3.91] δ_H (500 MHz, $CDCl_3$) 7.83 (d, 4H, *J* 9.3 Hz, Ar), 7.78 (d, 4H, *J* 7.8 Hz, Ar), 7.49 (d, 4H, *J* 7.8 Hz, Ar), 7.26–7.28 (m, 2H, Ar), 7.07–7.18 (m, 6H, Ar), 6.71 (d, 4H, *J* 7.8 Hz, Ar), 6.58 (d, 4H, *J* 7.8 Hz, Ar), 6.50 (s, 4H, Ar and C*H*=C*H*), 5.06 (d, 2H, *J* 16.2 Hz, OCH_2), 4.88 (d, 2H, *J* 16.2 Hz, OCH_2), 4.85 (s, 4H, NCH_2); δ_C (125 MHz, $CDCl_3$) 152.5, 139.9, 136.5, 133.6, 129.8, 129.3, 128.4, 126.9, 125.2, 125.4, 124.5, 123.8, 122.8, 122.5, 120.3, 116.8, 115.6, 109.2, 67.5, 49.4; *m*/*z* (FABMS) 748 (M^+).

6.2.9. *trans*-1′2′-Di-[(*S*)-(−)-2,3:4,5-di(1,2-naphtho)-1,6,13,19-tetraoxa-quadricyclo[21.2^{9,10}.2^{26,27}.2^{29,30}.1^{28}]-triaconta-2,4,8,10,14(28),15,17,21,23,26,29-undece]-ethene (5). White solid; yield 25%; hexane/$CHCl_3$ (7:3); $[\alpha]_D^{25}$ −272.5 (*c* 0.1, $CHCl_3$); mp 155 °C; [Elemental anal. calcd for $C_{86}H_{64}O_8$: C, 84.29; H, 5.26. Found: C, 84.42; H, 5.34] δ_H (500 MHz, $CDCl_3$) 7.94 (t, 4H, *J* 9.1 Hz, Ar), 7.87–7.89 (m, 4H, Ar), 7.54 (d, 2H, *J* 8.4 Hz, Ar), 7.32–7.40 (m, 10H, Ar), 7.23–7.25 (m, 8H, Ar), 6.93 (d, 4H, *J* 7.7 Hz, Ar), 6.89 (d, 4H, *J* 7.7 Hz, Ar), 6.84 (d, 4H, *J* 7.7 Hz, Ar), 6.78 (d, 4H, *J* 8.4 Hz, Ar), 6.58 (d, 2H, *J* 6.9 Hz, Ar), 6.26 (s, 2H, Ar), 4.98–5.20 (m, 16H, OCH_2); δ_C (125 MHz, $CDCl_3$) 158.6, 156.2, 153.8, 153.7, 137.0, 136.4, 134.3, 129.4, 128.1, 126.9, 126.7, 126.5, 125.4, 123.7, 121.3, 120.9, 120.4, 120.2, 115.4, 115.2, 110.6, 100.2, 70.1, 69.9, 69.8, 69.7; *m*/*z* (FABMS) 1225 (M^+).

6.3. General procedure for Wittig reaction

To the stirred suspension of NaH (1.65 mmol) in THF (40 mL) at 0 °C under nitrogen atmosphere, was added bisphosphonium salt (0.17 mmol) followed by aldehyde (0.35 mmol) in THF (30 mL). The reaction mixture was allowed to reflux for 12 h. Then the reaction mixture was quenched by using saturated NH_4Cl solution. The reaction mixture was then dissolved in water and extracted with $CHCl_3$ (2×100 mL), washed with water (2×200 mL), brine (100 mL), and dried over Na_2SO_4. The solvent was evaporated under vacuum to obtain the crude product, which was purified by column chromatography using hexane/chloroform (2:3) as a eluant.

6.3.1. 1′4′-Di-[(*S*)-(−)-2,3:4,5-di(1,2-naphtho)-1,6,13,19-tetraoxa-quadricyclo[21.2^{9,10}.2^{26,27}.2^{29,30}.1^{28}]-15-*cis*-ethenyl-triaconta-2,4,8,10,14(28),15,17,21,23,26,29-undece]benzene (6a). Light green solid; yield: 8%; hexane/$CHCl_3$ (7:3); mp 189 °C; $[\alpha]_D^{25}$ −390.3 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{94}H_{70}O_8$: C, 85.04; H, 5.31. Found: C, 84.91; H, 5.38] δ_H (500 MHz, $CDCl_3$) 7.90–7.95 (m, 8H, Ar), 7.38–7.51 (m, 6H, Ar), 7.30–7.37 (m, 6H, Ar), 7.20–7.25 (m, 8H, Ar), 7.13–7.18 (m, 4H, Ar), 7.00–7.08 (m, 2H, Ar), 6.88–6.93 (m, 8H, Ar), 6.75–6.83 (m, 8H, Ar), 6.51–6.62 (m, 2H, Ar), 6.25 (s, 2H, Ar), 5.11–5.20 (m, 6H, OCH_2), 4.98–5.05 (m, 10H, OCH_2); δ_C (125 MHz, $CDCl_3$) 163.5, 159.1, 156.6, 153.8, 153.6, 136.8, 136.4, 136.3, 134.3, 129.4, 128.1, 127.1, 127.0, 126.9, 126.8, 126.6, 125.4, 125.2, 123.9, 123.6, 122.9, 115.3, 115.2, 110.5, 100.2, 70.2, 69.9, 69.8, 69.5; *m*/*z* (FABMS) 1328 (M^+).

6.3.2. 1′4′-Di-[(*S*)-(−)-2,3:4,5-di(1,2-naphtho)-1,6,13,19-tetraoxa-quadricyclo[21.2^{9,10}.2^{26,27}.2^{29,30}.1^{28}]-15-*cis*-ethenyl-triaconta-2,4,8,10,14(28),15,17,21,23,26,29-undece]benzene (6b). Light green solid; yield 75%; hexane/$CHCl_3$ (7:3); mp 246 °C; $[\alpha]_D^{25}$ −411.9 (*c* 0.1, $CHCl_3$);

[Elemental anal. calcd for $C_{94}H_{70}O_8$: C, 85.04; H, 5.31. Found: C, 85.13; H, 5.18] δ_H (500 MHz, $CDCl_3$) 4.99–5.08 (m, 10H, OCH_2), 5.11–5.19 (m, 6H, OCH_2), 6.26 (s, 2H, Ar), 6.58 (d, 2H, *J* 8.4 Hz, Ar), 6.75–6.94 (m, 16H, Ar), 7.20–7.23 (m, 6H, Ar), 7.30–7.40 (m, 8H, Ar), 7.45–7.56 (m, 8H, Ar), 7.65–7.69 (m, 4H, Ar), 7.85–7.95 (m, 8H, Ar); δ_C (125 MHz, $CDCl_3$) 163.3, 159.0, 156.5, 153.8, 153.7, 136.9, 136.4, 136.3, 134.3, 129.4, 127.0, 126.9, 126.7, 126.6, 126.5, 125.5, 125.3, 123.8, 123.6, 122.8, 115.3, 115.1, 110.7, 100.2, 70.1, 69.9, 69.8, 69.6; *m*/*z* (FABMS) 1328 (M^+).

6.4. General procedure for O-alkylation

A mixture of (*S*)-BINOL (6.98 mmol), carbethoxybenzylbromide (14.67 mmol), and potassium carbonate (41.91 mmol) in anhydrous DMF (60 mL) was stirred at 80 °C for 48 h under nitrogen. The reaction mixture was then allowed to cool at room temperature and poured into ice water (1 L) and extracted with CH_2Cl_2 (5×100 mL). The organic layer was washed with water (3×100 mL) and brine (1×100 mL), and dried over anhydrous Na_2SO_4. The crude product obtained after the removal of solvent under reduced pressure was subjected to column chromatography over SiO_2 using hexane/$CHCl_3$ (1:2) as eluant to give the corresponding diester.

6.4.1. (*S*)-(−)-2,2′-Bis(ethyl-*p*-oxymethyl benzoate)-1,1′-binaphthyl (9a). Yellow pasty liquid; yield: 71%; hexane/$CHCl_3$ (1:4); $[\alpha]_D^{25}$ −130.0 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{40}H_{34}O_6$: C, 78.67; H, 5.61. Found: C, 78.73; H, 5.55] δ_H (400 MHz, $CDCl_3$) 7.92 (d, 4H, *J* 8.9 Hz, Ar), 7.87 (d, 2H, *J* 8.2 Hz, Ar), 7.72 (d, 4H, *J* 8.1 Hz, Ar), 7.37 (d, 2H, *J* 9.0 Hz, Ar), 7.21–7.35 (m, 4H, Ar), 6.93 (d, 4H, *J* 8.1 Hz, Ar), 5.04 (s, 4H, OCH_2), 4.30 (q, 4H, *J* 7.1 Hz, CH_2), 1.33 (t, 6H, *J* 7.1 Hz, CH_3); δ_C (100 MHz, $CDCl_3$) 166.4, 153.8, 142.5, 134.1, 130.2, 129.4, 128.0, 126.5, 126.4, 125.5, 125.1, 124.0, 120.7, 115.6, 70.5, 60.9, 14.3; *m*/*z* (EI, 70 eV) 610 (M^+).

6.4.2. (*S*)-(−)-2,2′-Bis(ethyl-*m*-oxymethyl benzoate)-1,1′-binaphthyl (9b). Yellow pasty liquid; yield: 65%; hexane/$CHCl_3$ (1:4); $[\alpha]_D^{25}$ −109.5 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{40}H_{34}O_6$: C, 78.67; H, 5.61. Found: C, 78.61; H, 5.51] δ_H (400 MHz, $CDCl_3$) 7.89 (d, 4H, *J* 8.8 Hz, Ar), 7.84–7.85 (m, 2H, Ar), 7.79 (s, 2H, Ar), 7.45 (d, 2H, *J* 8.8 Hz, Ar), 7.35–7.38 (m, 2H, Ar), 7.23–7.27 (m, 4H, Ar), 7.09–7.12 (m, 4H, Ar), 5.12 (t, 4H, *J* 8.0 Hz, OCH_2), 4.36 (q, 4H, *J* 8.0 Hz, CH_2), 1.38 (t, 6H, *J* 7.0 Hz, OCH_3); δ_C (100 MHz, $CDCl_3$) 166.4, 153.9, 137.9, 134.1, 131.3, 130.4, 129.4, 128.6, 128.2, 127.9, 127.8, 126.4, 125.5, 123.9, 120.8, 116.0, 70.9, 60.9, 14.3; *m*/*z* (EI, 70 eV) 610 (M^+).

6.4.3. (*S*)-(−)-2,2′-Bis(ethyl-*o*-oxymethyl benzoate)-1,1′-binaphthyl (9c). Yellow pasty liquid; yield: 82%; hexane/$CHCl_3$ (1:4); $[\alpha]_D^{25}$ −153.0 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{40}H_{34}O_6$: C, 78.67; H, 5.61. Found: C, 78.77; H, 5.53] δ_H (400 MHz, $CDCl_3$) 7.91 (d, 4H, *J* 8.8 Hz, Ar), 7.82–7.84 (m, 2H, Ar), 7.76–7.79 (m, 2H, Ar), 7.42 (d, 2H, *J* 8.6 Hz, Ar), 7.33–7.36 (m, 2H, Ar), 7.19–7.23 (m, 4H, Ar), 7.06–7.09 (m, 4H, Ar), 5.02 (t, 4H, *J* 8.0 Hz, OCH_2), 4.32 (q, 4H, *J* 8.2 Hz, CH_2), 1.39 (t, 6H, *J* 7.2 Hz, CH_3); δ_C (100 MHz, $CDCl_3$) 166.5, 153.7, 137.8, 134.2, 131.3, 130.3, 129.6, 128.6, 128.2, 128.1, 127.6, 126.4, 125.4, 123.7, 120.5, 116.1, 70.7, 60.8, 14.3; *m*/*z* (EI, 70 eV) 610 (M^+).

6.5. General procedure for $LiAlH_4$ reduction of diester

To a stirred suspension of LAH (8.18 mmol) in dry THF (25 mL) was added a solution of diester (3.27 mmol) in dry THF (50 mL) dropwise at room temperature under nitrogen atmosphere. The reaction mixture was heated under reflux for 6 h, after which it was cooled to 0–10 °C and the excess LAH was quenched by the cautious dropwise addition of 10% NaOH solution. Anhydrous Na_2SO_4 was added to the reaction mixture, stirred, and filtered. THF (20 mL) was added to the residue, digested on a steam bath, and filtered. The process was repeated for five times. The combined THF fractions were evaporated under reduced pressure to give the crude alcohol, which was purified by column chromatography using hexane/ethyl acetate (2:3) as eluant.

6.5.1. (*S*)-(−)-2,2′-Bis(*p*-hydroxymethyl benzyloxy)-1,1′-binaphthyl (10a). Yellow pasty liquid; yield: 85%; $[\alpha]_D^{25}$ −190.0 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{30}O_4$: C, 82.11; H, 5.74. Found: C, 82.19; H, 5.65] δ_H (400 MHz, $CDCl_3$) 7.81 (d, 2H, *J* 9.0 Hz, Ar), 7.77 (d, 2H, *J* 8.1 Hz, Ar), 7.30 (d, 2H, *J* 9.0 Hz, Ar), 7.21–7.25 (m, 2H, Ar), 7.09–7.16 (m, 4H, Ar), 6.86 (d, 4H, *J* 8.0 Hz, Ar), 6.81 (d, 4H, *J* 8.0 Hz, Ar), 4.97 (d, 2H, *J* 12.6 Hz, OCH_2), 4.90 (d, 2H, *J* 12.6 Hz, OCH_2), 4.40 (d, 2H, *J* 12.8 Hz, CH_2), 4.37 (d, 2H, *J* 12.8 Hz, CH_2), 1.95–2.14 (m, 2H, O*H*); δ_C (100 MHz, $CDCl_3$) 153.9, 139.9, 136.8, 134.2, 129.4, 129.3, 127.9, 127.2, 127.0, 126.8, 126.3, 125.5, 123.7, 120.7, 70.7, 65.0; *m*/*z* (EI, 70 eV) 526 (M^+).

6.5.2. (*S*)-(−)-2,2′-Bis(*m*-hydroxymethyl benzyloxy)-1,1′-binaphthyl (10b). Yellow pasty liquid; yield: 75%; $[\alpha]_D^{25}$ −120.1 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{30}O_4$: C, 82.11; H, 5.74. Found: C, 82.23; H, 5.83] δ_H (500 MHz, $CDCl_3$) 8.12 (d, 2H, *J* 8.6 Hz, Ar), 7.98 (d, 2H, *J* 8.0 Hz, Ar), 7.60 (d, 2H, *J* 9.1 Hz, Ar), 7.42–7.47 (m, 2H, Ar), 7.31–7.35 (m, 4H, Ar), 7.21 (d, 2H, *J* 8.0 Hz, Ar), 7.09 (t, 2H, *J* 7.45 Hz, Ar), 6.89 (d, 2H, *J* 8.0 Hz, Ar), 6.75 (s, 2H, Ar), 5.08 (d, 2H, *J* 11.8 Hz, OCH_2), 5.01 (d, 2H, *J* 11.8 Hz, OCH_2), 4.41 (d, 2H, *J* 12.5 Hz, CH_2), 4.38 (d, 2H, *J* 12.5 Hz, CH_2), 1.94–2.02 (m, 2H, O*H*); δ_C (125 MHz, $CDCl_3$) 153.8, 138.2, 137.6, 135.1, 129.7, 128.3, 128.0, 127.5, 126.4, 126.7, 125.5, 123.6, 121.9, 120.5, 115.8, 70.6, 65.3; (EI, 70 eV) 526 (M^+).

6.5.3. (*S*)-(−)-2,2′-Bis(*o*-hydroxymethyl benzyloxy)-1,1′-binaphthyl (10c). Yellow pasty liquid; yield: 89%; $[\alpha]_D^{25}$ −160.3, [Elemental anal. calcd for $C_{36}H_{30}O_4$: C, 82.11; H, 5.74. Found: C, 82.06; H, 5.68] δ_H (500 MHz, $CDCl_3$) 7.82 (d, 2H, *J* 8.4 Hz, Ar), 7.62 (d, 2H, *J* 8.4 Hz, Ar), 7.45–7.49 (m, 4H, Ar), 7.32–7.41 (m, 6H, Ar), 7.22–7.26 (m, 4H, Ar), 6.75 (s, 2H, Ar), 5.06 (d, 2H, *J* 11.5 Hz, OCH_2), 5.00 (d, 2H, *J* 11.5 Hz, OCH_2), 4.43 (d, 2H, *J* 12.1 Hz, CH_2), 4.40 (d, 2H, *J* 12.1 Hz, CH_2), 1.98–2.13 (m, 2H, O*H*); δ_C (125 MHz, $CDCl_3$) 153.8, 138.0, 137.5, 134.0, 129.3, 128.6, 128.0, 127.5, 126.2, 126.8, 126.6, 125.1, 123.7, 120.9, 115.5, 70.9, 65.1; (EI, 70 eV) 526 (M^+).

6.6. General procedure for oxidation of diol to dialdehyde

To a stirred suspension of pyridinium chloro chromate (10.1 mmol) in CH_2Cl_2 (30 mL) was added a solution of diol (2.9 mmol) in CH_2Cl_2 (10 mL) at room temperature. The reaction mixture was allowed to stir at room temperature for 3 h and then filtered through Celite. The residue was washed with CH_2Cl_2 (2×10 mL). The filtrate was evaporated under vacuum and the crude product was purified by column chromatography using hexane/$CHCl_3$ (1:9).

6.6.1. (*S*)-(−)-2,2′-Bis(*p*-benzyloxy carboxaldehyde)-1,1′-binaphthyl (11a). Light yellow solid; yield: 73%; $[\alpha]_D^{25}$ −29.9 (*c* 0.2, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{26}O_4$: C, 82.74; H, 5.01. Found: C, 82.68; H, 5.09] δ_H (500 MHz, $CDCl_3$) 9.74 (s, 2H, C*H*O), 7.86 (d, 2H, *J* 9.0 Hz, Ar), 7.79 (d, 2H, *J* 8.1 Hz, Ar), 7.44 (d, 4H, *J* 8.1 Hz, Ar), 7.22–7.31 (m, 4H, Ar), 7.12–7.14 (m, 4H, Ar), 6.90 (d, 4H, *J* 8.1 Hz, Ar), 4.98 (s, 4H, OCH_2); δ_C (125 MHz, $CDCl_3$) 191.8, 153.7, 144.4, 135.5, 134.1, 129.6, 128.1, 127.0, 126.7, 125.5, 124.1, 120.7, 115.6, 70.5; *m*/*z* (EI, 70 eV) 522 (M^+).

6.6.2. (*S*)-(−)-2,2′-Bis(*m*-benzyloxy carboxaldehyde)-1,1′-binaphthyl (11b). Yellow pasty liquid in 78% yield; mp semisolid; $[\alpha]_D^{25}$ −42.3 (*c* 0.2, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{26}O_4$: C, 82.74; H, 5.01. Found: C, 82.80; H, 5.11] δ_H (500 MHz, $CDCl_3$) 9.61 (s, 2H, C*H*O), 7.98 (d, 2H, *J* 8.6 Hz, Ar), 7.91 (d, 2H, *J* 8.6 Hz, Ar), 7.60–7.62 (m, 2H, Ar), 7.46 (d, 2H, *J* 9.2 Hz, Ar), 7.34–7.39 (m, 2H, Ar), 7.23–7.26 (m, 6H, Ar), 7.19–7.22 (m, 2H, Ar), 7.15–7.17 (m, 2H, Ar), 5.12 (d, 2H, *J* 12.6 Hz, OCH_2), 5.07 (d, 2H, *J* 12.6 Hz, OCH_2); δ_C (125 MHz, $CDCl_3$) 192.3, 153.8, 138.6, 136.4, 134.2, 132.6, 129.7, 128.9, 128.8, 128.2, 127.9, 126.8, 125.6, 124.2, 120.9, 115.9, 70.5; *m*/*z* (EI, 70 eV) 522 (M^+).

6.6.3. (*S*)-(−)-2,2′-Bis(*o*-benzyloxy carboxaldehyde)-1,1′-binaphthyl (11c). Yellow pasty liquid; yield: 69%; $[\alpha]_D^{25}$ −39.7 (*c* 0.2, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{26}O_4$: C, 82.74; H, 5.01. Found: C, 82.66; H, 5.09] δ_H (500 MHz, $CDCl_3$) 9.92 (s, 2H, C*H*O), 7.92 (d, 2H, *J* 8.4 Hz, Ar), 7.81 (d, 2H, *J* 8.4 Hz, Ar), 7.51–7.55 (m, 4H, Ar), 7.33–7.39 (m, 6H, Ar), 7.21–7.24 (m, 4H, Ar), 6.96 (d, 2H, *J* 8.4 Hz, Ar), 5.14 (d, 2H, *J* 13.0 Hz, OCH_2), 5.10 (d, 2H, *J* 13.0 Hz, OCH_2); δ_C (125 MHz, $CDCl_3$) 192.4, 153.6, 138.5, 136.3, 134.1, 132.8, 129.9, 128.9, 128.7, 128.1, 127.9, 126.7, 125.5, 124.1, 120.7, 115.8, 70.4; *m*/*z* (EI, 70 eV) 522 (M^+).

6.7. (*S*)-(−)-2,2′-Bis(*p*-bromomethyl benzyloxy)-1,1′-binaphthyl (12)

To a stirred suspension of diol **10a** (3.80 mmol) in CH_2Cl_2 (50 mL) was added dropwise a solution of PBr_3 (7.60 mmol) in CH_2Cl_2 (25 mL) at 0 °C. The reaction mixture was allowed to stir at room temperature for 4 h and then quenched by addition of ice water. The organic layer was separated, washed with water (3×100 mL), brine (1×100 mL), and dried over Na_2SO_4. The solvent was evaporated under vacuum and the crude product was purified by column chromatography over SiO_2 using hexane/$CHCl_3$ (3:2) to afford the dibromide as a white solid in 72% yield; mp 110 °C; $[\alpha]_D^{25}$ −156.9 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{36}H_{28}Br_2O_2$: C, 66.27; H, 4.33. Found: C, 66.33; H, 4.39] δ_H (400 MHz, $CDCl_3$), 7.82 (d, 2H, *J* 8.6 Hz, Ar), 7.77 (d, 2H, *J* 8.1 Hz, Ar), 7.28 (d, 2H, *J* 9.0 Hz, Ar), 7.21–7.25 (m, 2H, Ar), 7.11–7.12 (m, 4H, Ar), 6.96 (d, 4H, *J* 8.0 Hz, Ar), 6.77 (d, 4H, *J* 8.0 Hz, Ar), 4.90 (t, 4H, *J* 13.7 Hz, OCH_2), 4.25 (s, 4H, CH_2); δ_C (100 MHz, $CDCl_3$) 153.9, 137.9, 136.7, 134.2, 129.5, 129.4, 128.9, 128.0, 127.1, 126.5, 125.5, 123.9, 120.7, 115.8, 70.7, 33.5; *m*/*z* (EI, 70 eV) 652 (M^+).

6.8. (*S*)-(−)-2,2′-Bis(4-formyl oxymethyl-*p*-benzyloxy)-1,1′-binaphthyl (13)

A mixture of *p*-hydroxybenzaldehyde (4.2 mmol) and dibromide **12** (2 mmol) and K_2CO_3 (10.8 mmol) in dry DMF (30 mL) was stirred under nitrogen for 48 h at 80 °C. The reaction mixture was poured into water (1 L) and stirred. The resulting precipitate was filtered, washed with water (3×150 mL), and dissolved in CH_2Cl_2 (350 mL). The organic layer was washed with NaOH solution (5% w/v, 2×100 mL) and dried over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure to give a residue, which was column chromatographed using hexane/$CHCl_3$ (1:9) to give the dialdehyde **13** as a white solid in 84% yield; mp 110 °C; $[\alpha]_D^{25}$ −105.7 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{50}H_{38}O_6$: C, 81.72; H, 5.21. Found: C, 81.65; H, 5.27] δ_H (500 MHz, $CDCl_3$) 9.86 (s, 2H, C*H*O), 7.94 (d, 2H, *J* 9.2 Hz, Ar), 7.89 (d, 2H, *J* 8.4 Hz, Ar), 7.80 (d, 4H, *J* 9.2 Hz, Ar), 7.43 (d, 2H, *J* 9.2 Hz, Ar), 7.33–7.36 (m, 2H, Ar), 7.21–7.25 (m, 4H, Ar), 7.14 (d, 4H, *J* 8.4 Hz, Ar), 7.00 (d, 4H, *J* 9.2 Hz, Ar), 6.97 (d, 4H, *J* 8.4 Hz, Ar), 5.04 (t, 4H, *J* 13.0 Hz, OCH_2), 4.98 (s, 4H, OCH_2); δ_C (125 MHz, $CDCl_3$) 190.9, 163.7, 154.0, 137.8, 135.0, 134.3, 132.1, 130.2, 129.6, 129.5, 128.1, 127.5, 127.2, 126.5, 125.6, 124.0, 120.8, 116.0, 115.2, 70.9, 70.1; *m*/*z* (FABMS) 734 (M^+).

6.9. (*S*)-(−)-2,2′-Bis(2-hydroxyethoxy)-1,1′-binaphthyl (14)

Following the procedure,[15] chiral diol **14** was obtained as white solid in 65% yield; hexane/ethyl acetate (7:3); mp 130–134 °C $[\alpha]_D^{25}$ −52.6 (*c* 0.2, DMSO); δ_H (500 MHz, $CDCl_3$) 7.98 (d, 2H, *J* 9.2 Hz, Ar), 7.90 (d, 2H, *J* 8.4 Hz, Ar), 7.44 (d, 2H, *J* 8.4 Hz, Ar), 7.37 (t, 2H, *J* 8.4 Hz, Ar), 7.25 (t, 2H, *J* 7.6 Hz, Ar), 7.17 (d, 2H, *J* 8.5 Hz, Ar), 4.17–4.21 (m, 2H, OCH_2), 3.99–4.02 (m, 2H, OCH_2), 3.50–3.60 (m, 4H, CH_2), 2.46 (s, 2H); δ_C (125 MHz, $CDCl_3$) 153.7, 134.0, 129.9, 129.8, 128.3, 126.9, 125.4, 124.3, 120.4, 116.1, 71.78, 61.3; *m*/*z* (EI, 70 eV) 373 (M^+).

6.10. (*S*)-(−)-2,2′-Bis(2-(mesyloxy)ethoxy)-1,1′-binaphthyl (15)

Following the procedure,[15] chiral dimesylate **15** was obtained as white solid in 80% yield; hexane/$CHCl_3$ (7:3); mp 149–150 °C; $[\alpha]_D^{25}$ −68.8 (*c* 0.1, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 7.94–7.98 (m, 2H, Ar), 7.87 (d, 2H, *J* 8.4 Hz, Ar), 7.41 (d, 2H, *J* 9.2 Hz, Ar), 7.35 (t, 2H, *J* 7.7 Hz, Ar), 7.23–7.25 (m, 2H, Ar), 7.09–7.16 (m, 2H, Ar), 4.16–4.25 (m, 8H, OCH_2 and CH_2), 2.10–2.12

(m, 6H, CH_2); δ_C (125 MHz, $CDCl_3$) 153.5, 134.0, 129.9, 129.6, 128.1, 127.0, 125.4, 124.4, 120.0, 115.0, 69.0, 67.2, 36.2; *m*/*z* (EI, 70 eV) 530 (M^+).

6.11. (*S*)-(−)-2,2′-Bis(2-bromoethoxy)-1,1′-binaphthyl (16)

Following the procedure,[15] chiral dibromide **16** was obtained as a white solid in 72% yield; hexane/$CHCl_3$ (7:3); mp 91–92 °C; $[\alpha]_D^{25}$ −43.7 (*c* 0.17, $CHCl_3$); δ_H (500 MHz, $CDCl_3$) 7.98 (d, 2H, *J* 8.4 Hz, Ar), 7.90 (d, 2H, *J* 8.4 Hz, Ar), 7.43 (d, 2H, *J* 9.2 Hz, Ar), 7.36–7.39 (m, 2H, Ar), 7.24–7.27 (m, 2H, Ar), 7.17 (d, 2H, Ar), 4.17–4.30 (m, 4H, OCH_2), 3.23–3.25 (m, 4H, CH_2); δ_C (125 MHz, $CDCl_3$) 134.1, 129.9, 129.8, 128.1, 126.7, 125.5, 124.3, 121.2, 116.5, 70.2, 70.0; *m*/*z* (EI, 70 eV) 500 (M^+).

6.12. General procedure for N-alkylation

To a solution of aldehyde (7.5 mmol) in CH_3CN (50 mL), NaOH (25%) solution was added and stirred for 10 min. The bromide (15.9 mmol) in acetonitrile (20 mL) was added at once and stirred at room temperature for 48 h. After completion of the reaction, CH_3CN was removed under reduced pressure and the reaction mixture was extracted with CH_2Cl_2 (300 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and residue was chromatographed using hexane/chloroform (1:4) as eluant.

6.12.1. (*S*)-(−)-2,2′-Bis(3-formyl-*N*-oxyethyl indolyl)-1,1′-binaphthyl (17). Light brown solid; yield: 40%; hexane/$CHCl_3$ (1:9); mp 185 °C; $[\alpha]_D^{25}$ −143.0 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{42}H_{32}N_2O_4$: C, 80.24; H, 5.13; N, 4.46. Found: C, 80.15; H, 5.09; N, 4.53] δ_H (500 MHz, $CDCl_3$) 9.39 (s, 2H, C*H*O), 8.20 (d, 2H, *J* 7.7 Hz Ar), 7.86–7.90 (m, 4H, Ar), 7.33–7.37 (m, 2H, Ar), 7.21–7.25 (m, 2H, Ar), 7.16–7.19 (m, 2H, Ar), 7.12–7.14 (m, 2H, Ar), 7.09–7.11 (m, 2H, Ar), 7.01 (d, 2H, *J* 8.4 Hz, Ar), 6.83 (d, 2H, *J* 8.4 Hz, Ar), 6.35 (s, 2H, Ar), 3.99–4.03 (m, 2H, OCH_2), 3.77–3.87 (m, 4H, NCH_2, OCH_2), 3.65–3.69 (m, 2H, NCH_2); δ_C (125 MHz, $CDCl_3$) 185.1, 46.4, 152.3, 139.9, 136.5, 133.7, 129.9, 129.6, 128.2, 126.8, 125.2, 125.1, 124.4, 123.9, 122.8, 122.3, 120.1, 117.7, 115.0, 109.4, 67.0; *m*/*z* (EI, 70 eV) 628 (M^+).

6.12.2. (*S*)-(−)-2,2′-Bis(3-formyl *N*-*p*-oxymethyl benzyl-indolyl)-1,1′-binaphthyl (18). Light brown solid; yield: 73%; hexane/$CHCl_3$ (1:9); mp 110 °C; $[\alpha]_D^{25}$ −193.1 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{54}H_{40}N_2O_4$: C, 83.05; H, 5.16; N, 3.59. Found: C, 83.12; H, 5.04; N, 3.66] δ_H (500 MHz, $CDCl_3$) 9.90 (s, 2H, C*H*O), 8.31 (d, 2H, *J* 7.5 Hz, Ar), 7.90 (d, 2H, *J* 9.2 Hz, Ar), 7.84 (d, 2H, *J* 8.0 Hz, Ar), 7.50 (s, 2H, Ar), 7.36 (d, 2H, *J* 8.6 Hz, Ar), 7.28–7.32 (m, 4H, Ar), 7.24 (t, 2H, *J* 6.9 Hz, Ar), 7.20 (s, 2H, Ar), 7.16–7.19 (m, 4H, Ar), 6.84 (d, 4H, *J* 8.6 Hz, Ar), 6.81 (d, 4H, *J* 8.6 Hz, Ar), 5.10 (s, 4H, NCH_2), 4.97 (d, 2H, *J* 12.6 Hz, OCH_2), 4.94 (d, 2H, *J* 12.6 Hz, OCH_2); δ_C (125 MHz, $CDCl_3$) 184.7, 154.0, 137.8, 137.4, 134.4, 134.2, 129.6, 129.5, 128.1, 127.5, 127.1, 125.6, 125.5, 124.2, 124.0, 123.2, 122.2, 120.8, 118.5, 115.9, 110.5, 70.8, 50.6; *m*/*z* (FABMS) 780 (M^+).

6.12.3. (*S*)-(−)-2,2′-Bis(3-formyl *N*-*p*-oxymethyl benzyl-pyrolyl)-1,1′-binaphthyl (19). Light brown solid; yield: 60%; hexane/$CHCl_3$ (1:4); mp 110 °C; $[\alpha]_D^{25}$ −169.9 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{46}H_{36}N_2O_4$: C, 81.15; H, 5.33; N, 4.11. Found: C, 81.19; H, 5.29; N, 4.21] δ_H (500 MHz, $CDCl_3$) 9.53 (s, 2H, C*H*O), 7.93 (d, 2H, *J* 9.2 Hz, Ar), 7.87 (d, 2H, *J* 8.4 Hz, Ar), 7.40 (d, 2H, *J* 9.2 Hz, Ar), 7.32–7.35 (m, 2H, Ar), 7.19–7.21 (m, 4H, Ar), 6.94–6.95 (m, 2H, Ar), 6.88 (br s, 10H, Ar), 6.24 (br s, 2H, Ar), 5.43 (s, 4H, NCH_2), 4.98 (s, 4H, OCH_2); δ_C (125 MHz, $CDCl_3$) 179.6, 154.1, 137.2, 136.6, 134.2, 131.6, 131.5, 129.6, 129.5, 128.0, 127.3, 127.1, 126.5, 125.6, 124.9, 120.9, 110.2, 116.1, 71.0, 51.7; *m*/*z* (EI, 70 eV) 680 (M^+).

6.13. (*S*)-(−)-2,3:4,5-Di(1,2-naptho)-1,6,13,19-tetraoxaquadricyclo[21.2^{9,10}.2^{26,27}.2^{29,30}.1^{28}]triaconta-2,4,8,10,14(28),15,17,21,23,26,29-undecaene (21)

A mixture of 1 equiv of chiral dibromide **12** (0.76 mmol) and 1 equiv of methyl 3,5-dihydroxybenzoate (0.76 mmol) was stirred at room temperature in the presence of K_2CO_3 (15.2 mmol) in acetone (250 mL) under high dilution condition for 3 days. After completion of the reaction, solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 (300 mL), washed with water, brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and residue was column chromatographed using hexane/chloroform (2:3) as eluant to afford the cyclophane aldehyde as a white solid in 34% yield; mp 171 °C; $[\alpha]_D^{25}$ −382.9 (*c* 0.1, $CHCl_3$); [Elemental anal. calcd for $C_{43}H_{32}O_5$: C, 82.15; H, 5.13. Found: C, 82.30; H, 5.20] δ_H (500 MHz, $CDCl_3$) 10.36 (s, 1H, C*H*O), 7.93 (d, 2H, *J* 9.2 Hz, Ar), 7.88 (d, 2H, *J* 8.4 Hz, Ar), 7.75 (d, 1H, *J* 8.4 Hz, Ar), 7.32–7.35 (m, 4H, Ar), 7.19–7.25 (m, 4H, Ar), 6.92–6.95 (m, 4H, Ar), 6.76–6.79 (m, 4H, Ar), 6.59 (d, 1H, *J* 10.7 Hz, Ar), 6.26 (s, 1H, Ar), 5.18 (d, 2H, *J* 13.8 Hz, OCH_2), 5.14 (s, 2H, OCH_2), 5.08 (d, 2H, *J* 4.6 Hz, OCH_2), 5.00 (d, 2H, *J* 13.8 Hz, OCH_2); δ_C (125 MHz, $CDCl_3$) 188.5, 164.8, 153.7, 137.4, 135.3, 134.3, 130.0, 129.5, 129.4, 128.1, 127.0, 126.7, 126.6, 126.5, 125.4, 123.8, 119.4, 115.2, 111.4, 99.0, 69.8, 69.7; *m*/*z* (FABMS) 628 (M^+).

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13. Crystallographic data for the structure (cyclophane **1b**) in this paper have been deposited with the Cambridge Crystallographic Data centre as supplemental publication CCDC 638654. Copies of the data can be obtained, free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 01223 336033 or email deposit@ccdc.cam.ac.uk).
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