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Configurationally defined sexi- and octinaphthalene derivatives: synthesis and optical properties☆

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Abstract—The copper mediated oxidative coupling of optically active quaternaphthalenes having a 2-hydroxynaphthyl moiety gave configurationally defined optically active octinaphthalenes. The absolute configuration was determined by comparison with products of [6+2] coupling. The CD spectra of bi-, ter-, quater-, sexi- and octinaphthalenes suggested that the absolute configuration of the chiral axis could be deduced from the intensity of their Cotton effects.

1. Introduction

Monodisperse, nanometer sized molecules having a unique three-dimensional structure such as a helix have become of great interest due to the possibility for their use as a specific molecular device for material sciences as well as for the architectural beauty of their molecular shape. 2,2′-Difunctionalized 1,1′-binaphthalenes have been used not only as an excellent chiral inducer for asymmetric synthesis but also for chiral recognition in host–guest chemistry. These molecules possess a relatively rigid but flexible twisted conformation around the axis between its aromatic rings. Therefore, these molecules could be used as a key structural element for introduction of a twisted conformation as well as chirality into larger molecules. On the other hand, the development of novel monodisperse π-conjugated oligomers has recently attracted much attention due to their potential application in material sciences.[2] Among them, oligo(*p*-phenylene)s have received special attention and have been used as backbones for artificial proton channels[3] and β-barrels[4] and as rigid spacer units in an artificial receptor of cyclic dipeptides.[5] Oligo(*p*-phenylene)s are also important model compounds for poly(*p*-phenylene)s since some poly(*p*-phenylene)s are remarkable organic conductors upon doping[6] and are also used as laser materials.[7] The rod can contain 15 or even l6 phenyl rings.[8,9] However, little attention has been paid to rod-shaped naphthalenes connected at the 1,4-positions, in which the 1,1′-binaphthyl moieties are directly coupled each other, although the partial incorporation of a 2,2′-difunctionalized 1,1′-binaphthyl into a large molecule such as a polymer have been reported.[2a] One example of monodisperse oligonaphthalene reported so far was sexinaphthalene.[10,11] Recently, we reported the preparation of stereochemically defined ter-, quarter-[12a] and higher oligonaphthalenes[12b] and quarternaphthalene **1** showed unique function as an organic zeolite (Fig. 1).[12c] Moreover, it has been reported that the *meso*-ternaphthalene **2** tethered by two crown ethers plays an interesting role as a ditopic receptor for recognition of the length of

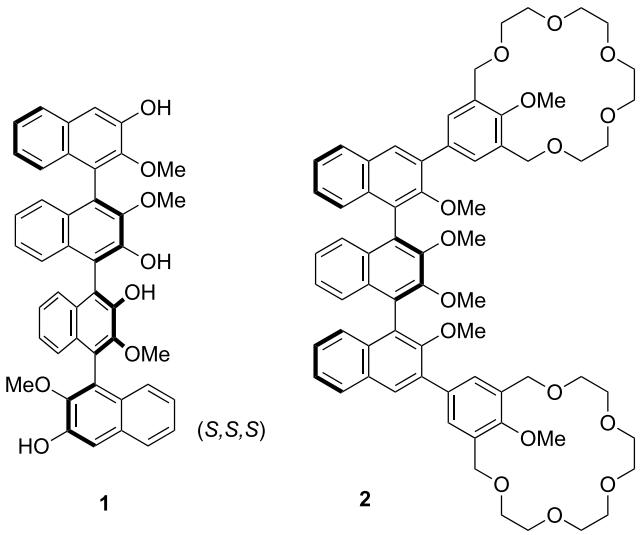

Figure 1. Ter- and quaternaphthalenes.

☆ See Ref. 1.

Keywords: Sexinaphthalene; Octinaphthalene; Atropisomerism; Oxidative coupling; CD spectra.

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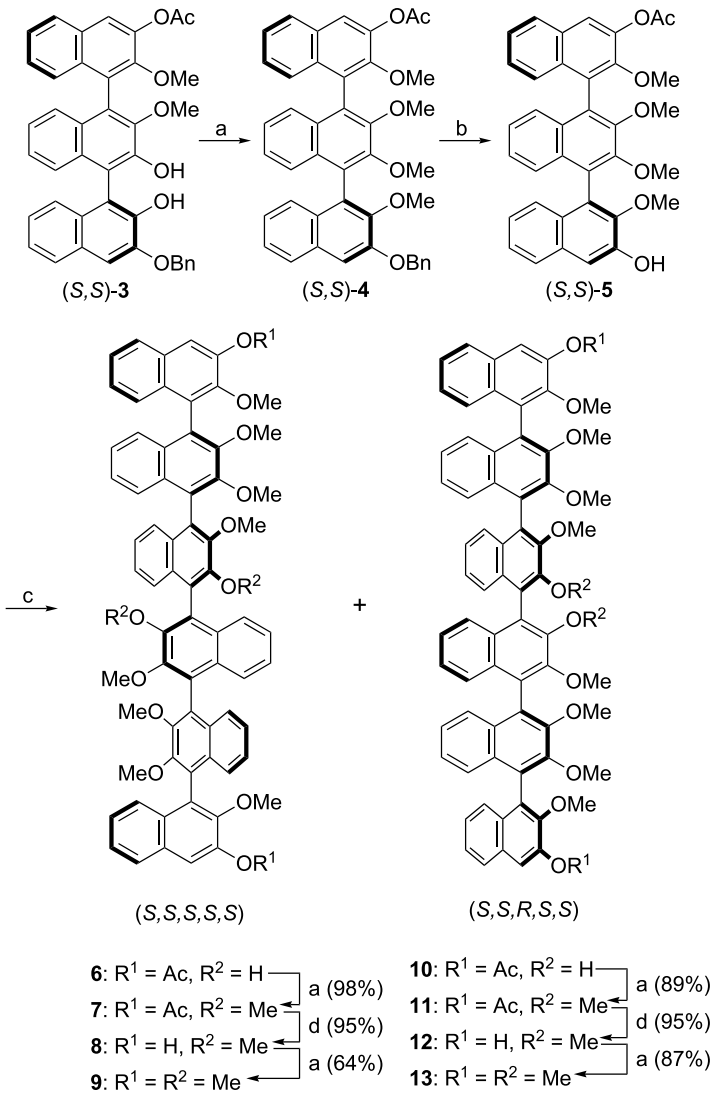
α,ω-diamines.[13] It would be interesting to determine whether higher oligonaphthalenes also show such specific characteristics. We report here the synthesis of optically active sexi- and octinaphthalenes as well as their CD spectra.[1]

2. Results and discussion

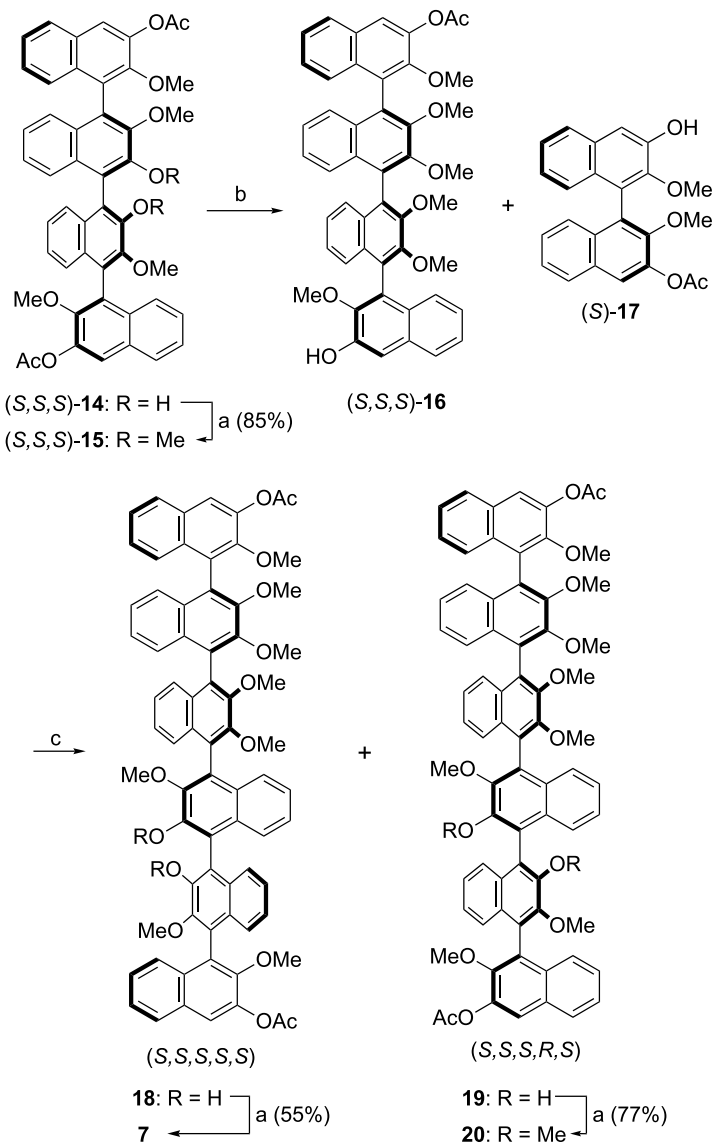
2.1. Synthesis of oligonaphthalenes and determination of their absolute configurations

The synthetic pathway to sexinaphthalenes, starting from the optically active ternaphthalene **3**,[12a] is shown in Scheme 1. Methylation of (*S*,*S*)-**3** afforded (*S*,*S*)-**4**, which was converted into monohydroxyternaphthalene (*S*,*S*)-**5** by hydrogenolysis, in 82% overall yield. Oxidative coupling[14] of **5** in the presence of $CuCl_2$ and racemic α-phenylethylamine afforded sexinaphthalenes (*S*,*S*,*S*,*S*,*S*)-**6** and its diastereomer (*S*,*S*,*R*,*S*,*S*)-**10** in 31 and 38% yield, respectively. Methylation of **6** and **10** gave diastereomers **7** and **11**, which were converted into the permethylated derivatives **9** and **13**, respectively. The only difference of coupling products between **6** and **10** is the absolute stereochemistry around the newly created central bond, which was unambiguously determined by synthesis via an alternative synthetic route that included the [4+2] construction of sexinaphthalenes (Scheme 2).

Thus, the known quaternaphthalene (*S*,*S*,*S*)-**14**[12a] was methylated to give (*S*,*S*,*S*)-**15**, partial hydrolysis of which afforded (*S*,*S*,*S*)-**16** in 40% yield. In order to avoid homocoupling of **16**, the oxidative coupling between **16** and (*S*)-**17**[12a] was carried out in the presence of excess amount of **17** to give sexinaphthalenes (*S*,*S*,*S*,*S*,*S*)-**18** and (*S*,*S*,*S*,*R*,*S*)-**19** in respective yields of 18 and l6%, along with (*S*,*S*,*S*)-**14** and its isomer with an *R* configuration at the central bond. Methylation of **18** gave **7**, which was identical to one of the products of the homocoupling of **5**, while methylation of **19** gave **20**, which is distinct from both **7** and **11**. These findings clearly support the absolute



Scheme 1. The [3+3] construction of sexinaphthalenes. Reagents: (a) CH_3I, K_2CO_3, 85%; (b) 10% Pd–C, H_2, 97%; (c) α-phenylethylamine, $CuCl_2$, **6** (31%), **10** (38%); (d) K_2CO_3, MeOH.



Scheme 2. The [4+2] construction of sexinaphthalenes. Reagents: (a) CH_3I, K_2CO_3; (b) K_2CO_3, MeOH, 40%; (c) α-phenylethylamine, $CuCl_2$, **18** (18%), **19** (16%).

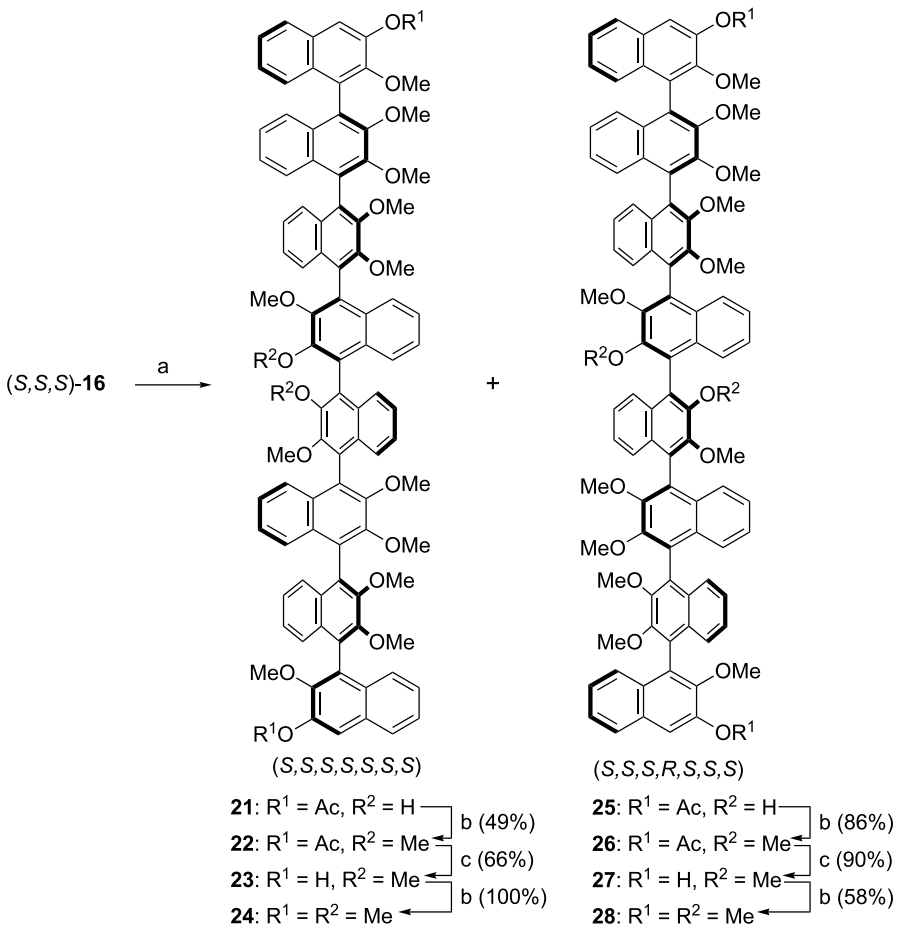
configurations of the coupling products **6**, **10**, **18** and **19** as depicted in Schemes 1 and 2.

A similar strategy to these transformations was used to synthesize octinaphthalenes as well as to determine their absolute stereochemistry (Schemes 3 and 4). Oxidative coupling of quaternaphthalene (*S*,*S*,*S*)-**16** gave (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**21** (22%) and (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**25** (30%). Methylation of **21** followed by hydrolysis gave **23**. Treatment of **23** with CH_3I/K_2CO_3 in acetone converted **23** into **24**, which has a methoxy group as a uniform substituent. The diastereomer **25** was transformed to **28** through the same sequence of reactions as those for **21** (Scheme 3). The [6+2] construction of octinaphthalenes is also shown in Scheme 4. Partial hydrolysis of (*S*,*S*,*S*,*S*,*S*)-**7** gave (*S*,*S*,*S*,*S*,*S*)-**29**, which was then subjected to the oxidative coupling in the presence of 5 equiv. of (*S*)-**17** to give (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**30** (13%) and (*S*,*S*,*S*,*S*,*S*,*R*,*S*)-**31** (22%). Methylation of **30** gave **22**, while that of **31** gave **32**, which resulted in determination of the absolute configuration of the products **30** and **31** as shown in Scheme 4.

For the CD study described below, (*S*)-tetramethoxybinaphthalene **33** was also prepared from binaphthalene **34**[12a] of known absolute configuration by methylation (Scheme 5).

2.2. Conformation of oligonaphthalenes

One of the most interesting aspects of oligonaphthalenes is their molecular shape, which is reminiscent of the banisters of a spiral staircase, and their π-system, which is totally different from that of helicenes.[15] An interesting question is how many naphthyl rings are required to complete a full turn of the helix. An X-ray crystal structural analysis of a quaternaphthalene **1** revealed that four naphthyl units are insufficient.[12a] Since none of the sexi- or octinaphthalenes gave fruitful crystals for X-ray analysis, the most stable



Scheme 3. The [4+4] construction of octinaphthalenes. Reagents: (a) α-phenylethylamine, $CuCl_2$, **21** (22%), **25** (30%); (b) CH_3I, K_2CO_3; (c) K_2CO_3, MeOH.

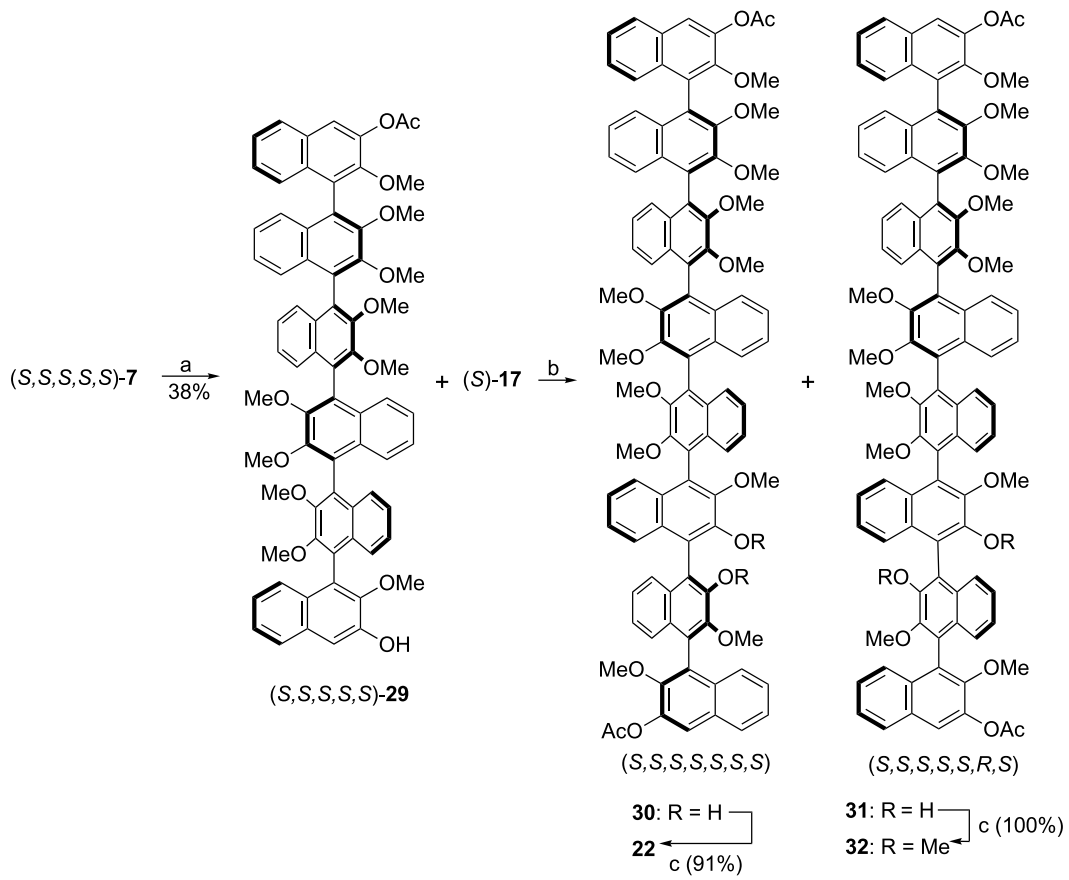
conformation of **24** was calculated by MacroModel/MM2 (version 6.0). The calculation results indicated that at least five to six naphthyls are necessary for a turn (Fig. 2a). The dihedral angles between each naphthyl unit are nearly 80° and the length of molecule including hydrogen atoms is 35 Å. These results are consistent with the X-ray analysis of quaternaphthalene **1**, in which the dihedral angles between each naphthalene are 74.7, 79.7 and 113.0°.[12a] The top view of **24** showed the cylindrical shape of molecule having around 9 Å diameter (Fig. 2b). The calculation for the corresponding 24-mer revealed that the helix repeated a full turn every five to six naphthyls (Fig. 2c). The central eight naphthalene units of the 24-mer were extracted and compared with octinaphthalene **24** (Fig. 2a and d). While the two conformations are quite similar, a slight lag was observed for a turn.

2.3. CD spectra of oligonaphthalenes

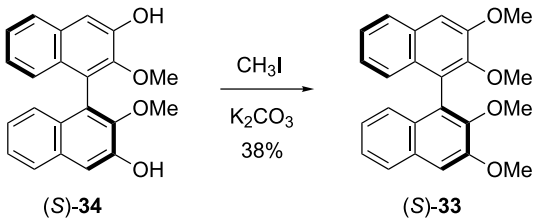
The CD spectra of permethylated, configurationally defined bi-, ter-, quater-, sexi- and octinaphthalenes **33**, **35**,[12a] **36**,[12a] **9** and **24**, possessing *aS* configuration around each axis, were taken (Fig. 3 and Table 1). All compounds showed strong split Cotton effects of positive exciton chirality.[16] The intensity of their Cotton effect around 240 nm are obviously increased in accordance with the increase of the number of naphthyl units, Δε 12.8, 68.8, 83.8, 102.7, 136.8 for **33**, **35**, **36**, **9** and **24**, respectively (Table 1). These results suggest an additivity relationship between the intensity of Cotton effect and the number of naphthalene chromophores.

Taking this hypothesis into account, the CD spectra of quater-, sexi-, and octinaphthalenes **37**,[12a] **13** and **28** possessing *aR* configuration at the central axis were measured and compared with the spectra of their diastereomers **36**, **9** and **24**, respectively. The quaternaphthalene **37** showed a smaller positive Cotton effect (Δε 27.7) at 233.7 nm than that of its isomer **36** (Fig. 4a). Also, the sexinaphthalene **13** exhibited a smaller positive Cotton effect (Δε 86.4) at 239.9 nm than that of **9** (Fig. 4b). The same tendency was observed in octinaphthalenes (Fig. 4c). Moreover, the intensity of Cotton effect of **13** around 240 nm is similar to that of **36**. This could be explained by the partial cancellation of Cotton effect owing to *R* axis of **13**. The same relationship was observed between **9** and **28**. These results clearly showed that the intensity of Cotton effect depends on the absolute configuration due to each axis. Therefore, it could be concluded that the intensity of Cotton effect could be useful informative source for the determination of the absolute configuration of such kinds of oligonaphthalenes.

The development of specific functions and the further study of optical properties of synthesized oligonaphthalenes are currently under investigation.



Scheme 4. The [6+2] construction of octinaphthalenes. Reagents: (a) K_2CO_3, MeOH; (b) α-phenylethylamine, $CuCl_2$, **30** (13%), **31** (22%); (c) CH_3I, K_2CO_3.



Scheme 5. Preparation of tetramethoxybinaphthalene.

3. Experimental

3.1. General

Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were taken in $CDC1_3$ at 200 or 400 MHz for ^1H NMR and at 50 MHz for ^{13}C NMR, with chemical shifts being reported as δ ppm from tetramethylsilane as an internal standard. FT-IR, UV and CD spectra were obtained

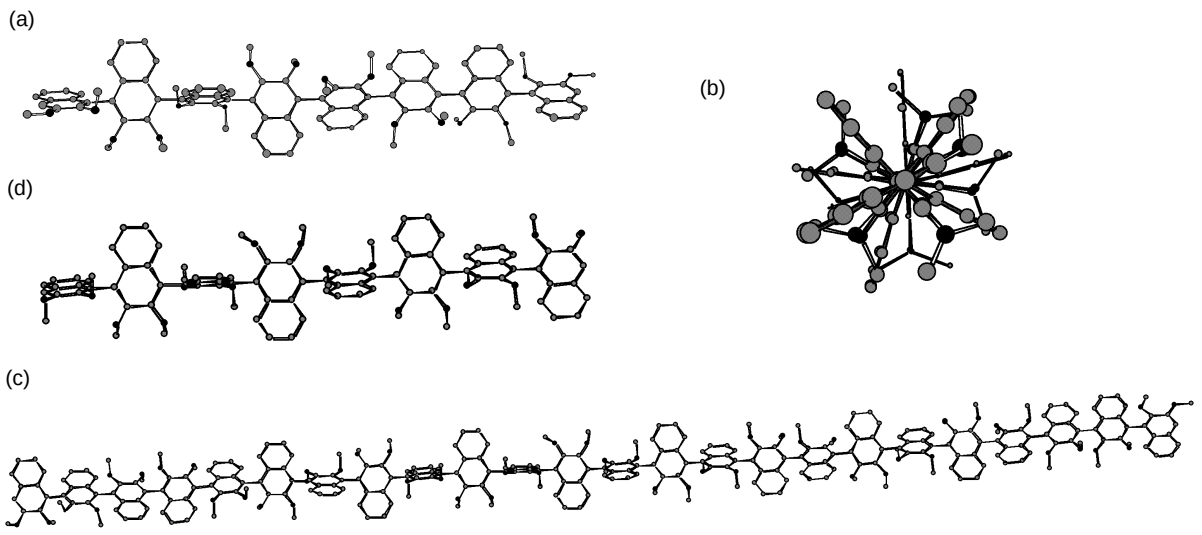


Figure 2. (a) The most stable conformation of octinaphthalene **24** calculated by MacroModel (version 6.0). (b) The top view of octinaphthalene **24**. (c) The most stable conformation of the 24-mer calculated by MacroModel (version 6.0). (d) The central eight naphthalenes of the 24-mer.

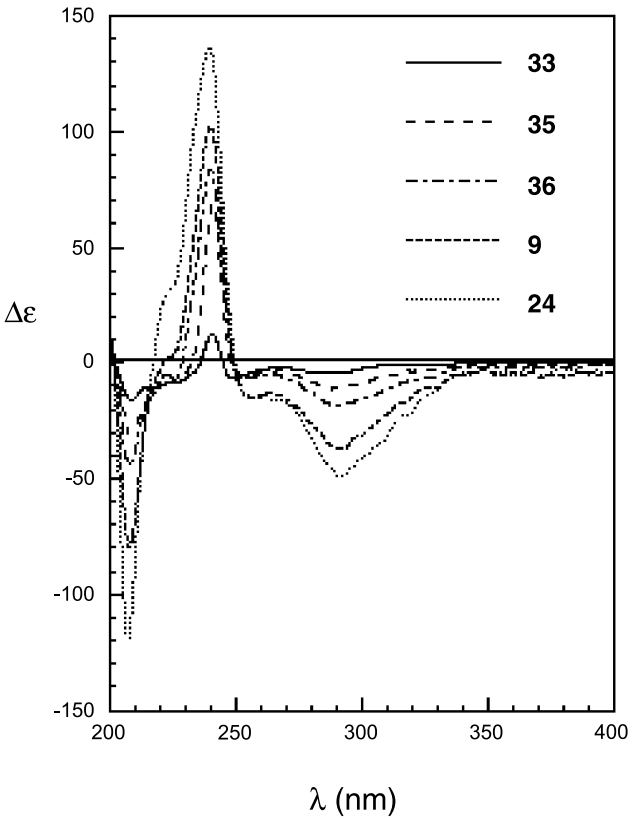
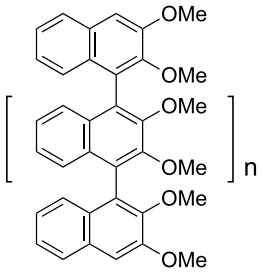


Figure 3. CD spectra of oligonaphthalenes in 0.4% dioxane–MeOH.

Table 1. CD Spectral data of oligonaphthalenes

Compound	λ_{ext} (nm) ($\Delta\varepsilon$)
33	286.1 (−4.4), 240.3 (12.8), 208.2 (−16.0)
35	286.3 (−11.3), 240.3 (68.8), 208.2 (−30.7)
36	288.9 (−18.3), 239.6 (83.8), 207.4 (−43.7)
9	291.9 (−36.8), 239.5 (102.7), 207.4 (−79.8)
24	291.6 (−48.8), 239.2 (136.8), 206.9 (−119.4)
37	285.7 (−6.9), 245.5 (−15.0), 233.7 (27.7), 209.3 (−27.9)
13	292.6 (−21.2), 239.9 (86.4), 207.7 (−63.4)
28	291.9 (−30.7), 239.5 (108.8), 207.1 (−84.0)



n = 0: **33** (*S*)
n = 1: **35** (*S,S*)
n = 2: **36** (*S,S,S*)
37 (*S,R,S*)
n = 4: **9** (*S,S,S,S,S*)
13 (*S,S,R,S,S*)
n = 6: **24** (*S,S,S,S,S,S,S*)
28 (*S,S,S,R,S,S,S*)

on a JASCO FT/IR-300, Shimadzu UV-2200 and JASCO J-720W, respectively. All extractive organic solutions were dried over anhydrous $MgSO_4$. Flash column chromatography was carried out with silica gel 60 spherical (150–325 mesh) and Kiesel gel 60 F_{254} plates (Merck) were used for preparative TLC (pTLC).

3.1.1. (*S,S*)-Ternaphthalene 4. To a mixture of (*S,S*)-**3** (500 mg, 0.79 mmol) and potassium carbonate (1.6 g, 12 mmol) in acetone (15 mL) was added dropwise methyl iodide (1.0 mL, 16 mmol) at room temperature. The mixture was refluxed for 2 h. After cooling, the reaction mixture was evaporated under reduced pressure, and the residue was added to a mixture of ethyl acetate and aq. 2 N HCl. The organic layer was separated, dried and then evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2, *n*-hexane/EtOAc=2/1) to afford (*S,S*)-**4** as colorless powder (445 mg, 85%), which was recrystallized from CH_2Cl_2/EtOAc/pet. ether to give colorless prisms. Mp 206–208 °C; $[\alpha]_D^{20}=-113.7$ (*c* 2.3, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.0–7.1 (m, 19H), 5.37 (s, 2H), 3.79 (s, 3H), 3.67 (s, 3H), 3.64 (s, 3H), 3.60 (s, 3H), 2.42 (s, 3H); IR ($CHCl_3$): 3063, 3029, 3010, 2940, 1766, 1597, 1503, 1467, 1016 cm^{-1}; EI MS *m/z* 664 (M^+). Anal. Calcd for $C_{43}H_{36}O_7$: C, 77.69; H, 5.46. Found: C, 77.39; H, 5.45.

3.1.2. (*S,S*)-Ternaphthalene 5. To a suspension of palladium on carbon (10%, 296 mg) in $CHCl_3$, a solution of (*S,S*)-**4** (320 mg, 0.48 mmol) in $CHCl_3$ (15 mL) and AcOH (0.75 mL) was added. The mixture was stirred at room temperature for 29 h under hydrogen. After the catalyst was filtered off, the filtrate was evaporated under reduced pressure to give a residue, which was purified by the recrystallization from CH_2Cl_2/EtOAc/pet. ether to give (*S,S*)-**5** as colorless plates (268 mg, 97%). Mp 161–162 °C; $[\alpha]_D^{20}=-73.4$ (*c* 0.6, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.0–7.1 (m, 14H), 6.18 (s, 1H), 3.65 (s, 3H), 3.63 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 2.43 (s, 3H); IR ($CHCl_3$): 3522, 3009, 3010, 2941, 1631, 1506, 1468, 1221 cm^{-1}; EI MS *m/z* 574 (M^+); HRMS *m/z* Calcd for $C_{36}H_{30}O_7$ (M^+) 574.1992. Found 574.2007.

3.1.3. Oxidative coupling to sexinaphthalenes (*S,S,S,S,S,S*)-6 and (*S,S,R,S,S*)-10. A mixture of $CuCl_2$ (126 mg, 0.94 mmol) and α-phenylethylamine (0.30 mL, 2.4 mmol) in MeOH (0.5 mL) was stirred for 20 min, to which was added a solution of (*S,S*)-**5** (268 mg, 0.47 mmol) in CH_2Cl_2 (20 mL). After being stirred for 23 h under nitrogen, the reaction mixture was acidified with conc. HCl, concentrated, and extracted with EtOAc. The organic layer was washed with water, dried, and evaporated to give a residue. The residue was purified by column chromatography (SiO_2, *n*-hexane/CH_2Cl_2/EtOAc=8/5/1) to afford (*S,S,S,S,S,S*)-**6** (83 mg, 31%) and (*S,S,R,S,S*)-**10** (102 mg, 38%).

Compound (*S,S,S,S,S,S*)-**6**. Mp >300 °C; colorless powder (from CH_2Cl_2/Et_2O/pet. ether); $[\alpha]_D^{20}=-190.6$ (*c* 0.4, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J*=8.4 Hz), 7.79 (s, 2H), 7.6–7.1 (m, 22H), 6.33 (s, 2H), 3.79 (s, 6H), 3.74 (s, 12H), 3.67 (s, 6H), 2.45 (s, 6H); IR ($CHCl_3$): 3511, 3009, 2941, 1767, 1507, 1453, 1391, 1237, 1201, 1014 cm^{-1}; FAB MS *m/z* 1147 $(M+H)^+$. Anal. Calcd for $C_{72}H_{58}O_{14}$: C, 75.38; H, 5.10. Found: C, 75.15; H, 5.05.

Compound (*S,S,R,S,S*)-**10**. Mp >300 °C; colorless prisms (from benzene); $[\alpha]_D^{20}=-117.0$ (*c* 0.3, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 7.93 (d, 2H, *J*=8.4 Hz), 7.79 (s, 2H), 7.6–7.1 (m, 22H), 6.23 (s, 2H), 3.78 (s, 6H), 3.76 (s, 6H), 3.72 (s, 6H), 3.68 (s, 6H), 2.45 (s, 6H); IR ($CHCl_3$): 3518, 3010, 2941, 1766, 1602, 1453, 1393, 1350, 1014 cm^{-1}; FAB MS *m/z* 1147 $(M+H)^+$. Anal. Calcd for $C_{72}H_{58}O_{14}\cdot 1/2H_2O$. Anal. Calcd for C, 74.79; H, 5.14. Found: C, 74.78; H, 5.09.

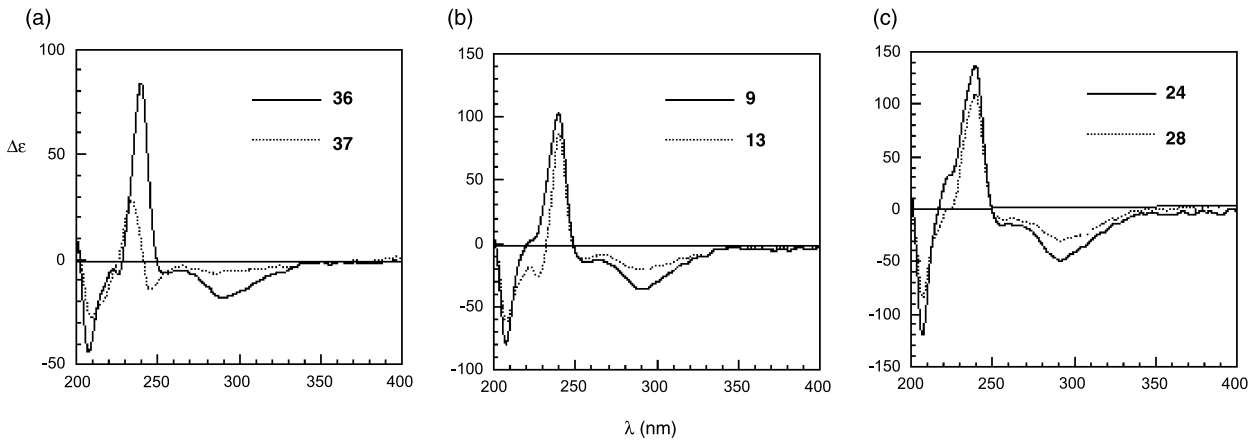


Figure 4. (a) CD spectra of quaternaphthalenes **36** and **37** in 0.4% dioxane–MeOH. (b) CD spectra of sexinaphthalenes **9** and **13** in 0.4% dioxane–MeOH. (c) CD spectra of octinaphthalenes **24** and **28** in 0.4% dioxane–MeOH.

3.1.4. (*S*,*S*,*S*,*S*,*S*)-Sexinaphthalene 7. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*S*,*S*)-**6** (73 mg, 64 μmol) was treated with potassium carbonate (128 mg, 0.93 mmol) and methyl iodide (82 μL, 1.3 mmol) in acetone (10 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (6/3/1) gave (*S*,*S*,*S*,*S*,*S*)-**7** (74 mg, 98%). Mp >300 °C; colorless powder (from CH_2Cl_2/Et_2O/pet. ether); $[\alpha]_D^{20}=-196.7$ (*c* 0.3, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.91 (d, 2H, *J*=8.1 Hz), 7.78 (s, 2H), 7.6–7.2 (m, 22H), 3.90 (s, 12H), 3.83 (s, 6H), 3.77 (s, 6H), 3.65 (s, 6H), 2.44 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.5, 151.0, 150.9, 150.8, 149.2, 143.6, 132.4, 131.2, 131.1, 131.0, 130.7, 127.9, 127.0, 126.7, 126.5, 126.3, 126.1, 125.9, 125.7, 125.6, 125.4, 120.9, 77.2, 61.1, 60.8, 60.7, 20.7; IR ($CHCl_3$): 3062, 3010, 2940, 2828, 1766, 1504, 1453, 1390, 1347, 1239, 1220, 1210, 1016 cm^{-1}; FAB MS *m*/*z* 1175 $(M+H)^+$. Anal. Calcd for $C_{74}H_{62}O_{14}$: C, 75.62; H, 5.32. Found: C, 75.75; H, 5.26.

3.1.5. (*S*,*S*,*S*,*S*,*S*)-Sexinaphthalene 8. To a mixture of (*S*,*S*,*S*,*S*,*S*)-**7** (43 mg, 37 μmol) and potassium carbonate (73 mg, 0.53 mmol) in CH_2Cl_2 (5 mL) was added MeOH (0.20 mL) at room temperature. After being stirred for 4 h, the reaction mixture was concentrated under reduced pressure, and then acidified with aq. 2 N HCl. The mixture was extracted with CH_2Cl_2, dried and evaporated in vacuo to give a residue. The residue was purified by column chromatography (SiO_2, *n*-hexane/CH_2Cl_2/EtOAc=6/3/1) to afford (*S*,*S*,*S*,*S*,*S*)-**8** (38 mg, 95%). Mp >300 °C; orange powder (from CH_2Cl_2/Et_2O/pet. ether); $[\alpha]_D^{20}=-146.5$ (*c* 1.2, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.84 (d, 2H, *J*=8.1 Hz), 7.54 (s, 2H), 7.56–7.2 (m, 22H), 6.22 (s, 2H), 3.911 (s, 6H), 3.907 (s, 6H), 3.82 (s, 6H), 3.75 (s, 6H), 3.64 (s, 6H); IR ($CHCl_3$): 3520, 3009, 2938, 2854, 1766, 1507, 1452, 1390, 1348, 1112, 1017 cm^{-1}; FAB MS *m*/*z* 1091 $(M+H)^+$; HRMS *m*/*z* Calcd for $C_{70}H_{59}O_{12}$ $(M+H)^+$ 1091.4007. Found 1091.3986.

3.1.6. (*S*,*S*,*S*,*S*,*S*)-Sexinaphthalene 9. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*S*,*S*)-**8** (29 mg, 26 μmol) was treated with potassium carbonate (52 mg, 0.37 mmol) and methyl iodide (63 μL, 1.0 mmol) in acetone (10 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (6/3/1) gave (*S*,*S*,*S*,*S*,*S*)-**9** (19 mg, 64%). Mp >300 °C; colorless powder (from CH_2Cl_2/Et_2O/pet. ether); $[\alpha]_D^{20}=-194.9$ (*c* 0.9, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J*=8.1 Hz), 7.5–7.1 (m, 24H), 4.12 (s, 6H), 3.90 (s, 6H), 3.88 (s, 6H), 3.85 (s, 6H), 3.77 (s, 6H), 3.76 (s, 6H); IR ($CHCl_3$): 3062, 3010, 2939, 1463, 1390, 1346, 1019 cm^{-1}; CD (0.4% dioxane in MeOH): see Table 1; UV (0.4% dioxane in MeOH) λ_{max} 302.6 nm (ε 40187), 230.8 (301685); FAB MS *m*/*z* 1119 $(M+H)^+$. Anal. Calcd for $C_{72}H_{62}O_{12}$: C, 77.26; H, 5.58. Found: C, 77.14; H, 5.49.

3.1.7. (*S*,*S*,*R*,*S*,*S*)-Sexinaphthalene 11. Following the procedure for the preparation of **4**, (*S*,*S*,*R*,*S*,*S*)-**10** (92 mg, 81 μmol) was treated with potassium carbonate (158 mg, 1.1 mmol) and methyl iodide (0.1 mL, 1.6 mmol) in acetone (20 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (6/3/1) gave (*S*,*S*,*R*,*S*,*S*)-**11** (84 mg, 89%). Mp >300 °C; colorless prisms (recrystallized from *n*-hexane/CH_2Cl_2/EtOAc); $[\alpha]_D^{20}=-95.0$ (*c* 1.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, 2H, *J*=8.2 Hz), 7.82 (s, 2H), 7.6–7.2 (m, 22H), 3.95 (s, 6H), 3.86 (s, 6H), 3.77 (s, 12H), 3.70 (s, 6H), 2.48 (s, 6H); IR ($CHCl_3$): 3063, 3013, 2940, 1766, 1453, 1390, 1015 cm^{-1}; FAB MS *m*/*z* 1175 $(M+H)^+$. Anal. Calcd for $C_{74}H_{62}O_{14}$: C, 75.62; H, 5.32. Found: C, 75.55; H, 5.31.

3.1.8. (*S*,*S*,*R*,*S*,*S*)-Sexinaphthalene 12. Following the procedure for the preparation of **8**, (*S*,*S*,*R*,*S*,*S*)-**11** (65 mg, 56 μmol) was treated with potassium carbonate (109 mg, 0.79 mmol) and MeOH (0.2 mL) in CH_2Cl_2 (5 mL) for 7 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/EtOAc (2/1) gave (*S*,*S*,*R*,*S*,*S*)-**12** (58 mg, 95%). Mp >300 °C; orange powder (from *n*-hexane/EtOAc); $[\alpha]_D^{20}=-63.8$ (*c* 1.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.83 (d, 2H, *J*=8.0 Hz), 7.6–7.1 (m, 24H), 6.22

(s, 2H), 3.92 (s, 6H), 3.82 (s, 6H), 3.72 (s, 12H), 3.65 (s, 6H); IR ($CHCl_3$): 3520, 3008, 2940, 2359, 1631, 1579, 1507, 1452, 1390, 1111, 1017, 908 cm^{-1}; FAB MS *m/z* 1091 $(M+H)^+$. Anal. Calcd for $C_{70}H_{58}O_{12}$: C, 77.05; H, 5.36. Found: C, 76.81; H, 5.09.

3.1.9. (*S*,*S*,*R*,*S*,*S*)-Sexinaphthalene 13. Following the procedure for the preparation of **4**, (*S*,*S*,*R*,*S*,*S*)-**12** (39 mg, 36 μmol) was treated with potassium carbonate (71 mg, 0.51 mmol) and methyl iodide (90 μL, 1.4 mmol) in acetone (20 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (6/3/1) gave (*S*,*S*,*R*,*S*,*S*)-**13** (35 mg, 87%). Mp >300 °C; colorless powder (from *n*-hexane/CH_2Cl_2/EtOAc); $[\alpha]_D^{20}=-89.3$ (*c* 0.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J*=8.1 Hz), 7.6–7.1 (m, 24H), 4.13 (s, 6H), 3.89 (s, 6H), 3.82 (s, 6H), 3.78 (s, 6H), 3.75 (s, 6H), 3.73 (s, 6H); IR ($CHCl_3$): 3063, 3010, 2939, 1463, 1391, 1350, 1019 cm^{-1}; CD (0.4% dioxane in MeOH): see Table 1; UV (0.4% dioxane in MeOH) λ_{max} 302.6 nm (ε 42700), 230.8 (302330); FAB MS *m/z* 1119 $(M+H)^+$. Anal. Calcd for $C_{72}H_{62}O_{12}\cdot 1/2H_2O$: C, 76.65; H, 5.63. Found: C, 76.69; H, 5.61.

3.1.10. (*S*,*S*,*S*)-Quaternaphthalene 15. Following the procedure for the preparation of **4**, (*S*,*S*,*S*)-**14** (203 mg, 0.26 mmol) was treated with potassium carbonate (257 mg, 1.9 mmol) and methyl iodide (0.33 mL, 5.2 mmol) in acetone (7.0 mL) for 1.5 h. After extraction with EtOAc, the organic layer was dried and evaporated to give a residue. The residue was purified by recrystallization from *n*-hexane/CH_2Cl_2/Et_2O to give (*S*,*S*,*S*)-**15** as colorless plates (177 mg, 85%). Mp 298–300 °C; $[\alpha]_D^{20}=-131.0$ (*c* 0.8, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.91 (d, 2H, *J*=7.8 Hz), 7.77 (s, 2H), 7.6–7.1 (m, 14H), 3.80 (s, 6H), 3.75 (s, 6H), 3.62 (s, 6H), 2.44 (s, 6H); IR ($CHCl_3$): 3062, 3011, 2941, 1766, 1504, 1466, 1453, 1370, 1155, 1105, 1015 cm^{-1}; EI MS *m/z* 802 (M^+). Anal. Calcd for $C_{50}H_{42}O_{10}$: C, 74.80; H, 5.27. Found: C, 74.63; H, 5.16.

3.1.11. (*S*,*S*,*S*)-Quaternaphthalene 16. Following the procedure for the preparation of **8**, (*S*,*S*,*S*)-**15** (30 mg, 37 μmol) was treated with potassium carbonate (7.4 mg, 54 μmol) and MeOH (0.13 mL) in CH_2Cl_2 (5 mL) for 8 h. After extraction with EtOAc, the organic layer was dried and evaporated to give a residue, which was subjected to pTLC. Developing with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*)-**16** (11 mg, 40%). Mp 170–171 °C; colorless needles (recrystallized from CH_2Cl_2/EtOAc/Et_2O/pet. ether); $[\alpha]_D^{20}=-129.9$ (*c* 0.6, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 8.0–7.2 (m, 18H), 6.21 (s, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.63 (s, 3H), 3.61 (s, 3H), 2.44 (s, 3H); IR ($CHCl_3$): 3522, 3010, 2940, 1767, 1602, 1467, 1453, 1390, 1155, 1110, 1016 cm^{-1}; EI MS *m/z* 760 (M^+). Anal. Calcd for $C_{48}H_{40}O_9$: C, 75.78; H, 5.30. Found: C, 75.61; H, 5.44.

3.1.12. Oxidative coupling to sexinaphthalenes (*S*,*S*,*S*,*S*,*S*)-18 and (*S*,*S*,*S*,*R*,*S*)-19. A mixture of $CuCl_2$ (210 mg, 1.6 mmol) and α-phenylethylamine (0.25 mL, 2.0 mmol) in MeOH (0.6 mL) was stirred for 20 min, to which was added a solution of (*S*,*S*,*S*)-**16** (96 mg, 0.13 mmol) and (*S*)-**17** (252 mg, 0.65 mmol) in CH_2Cl_2 (12 mL). After being stirred for 27 h under nitrogen, the reaction mixture was acidified with conc. HCl, concentrated, and extracted with EtOAc. The organic layer was washed with water, dried, and evaporated to give a residue, which was subjected to column chromatography. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*)-**14** (66 mg), its isomer possessing (*S*,*R*,*S*)-configuration (51 mg) and a separable mixture of **18** and **19**, from which **18** (27 mg, 18%) and **19** (24 mg, 16%) were afforded after pTLC with *n*-hexane/acetone (3/2).

Compound (*S*,*S*,*S*,*S*,*S*)-**18**. Amorphous; $[\alpha]_D^{20}=-144.1$ (*c* 1.2, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J*=8.8 Hz), 7.80 (s, 1H), 7.78 (s, 1H), 7.6–7.1 (m, 22H), 6.34 (s, 2H), 3.87 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H), 3.57 (s, 3H), 3.54 (s, 3H), 2.45 (s, 6H); IR ($CHCl_3$): 3508, 3063, 3009, 2940, 2854, 1766, 1506, 1454, 1392, 1348, 1014 cm^{-1}; FAB MS *m/z* 1147 $(M+H)^+$; HRMS *m/z* Calcd for $C_{72}H_{59}O_{14}$ $(M+H)^+$ 1147.3905. Found 1147.3885.

Compound (*S*,*S*,*S*,*R*,*S*)-**19**. Amorphous; $[\alpha]_D^{20}=-95.8$ (*c* 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.93 (d, 2H, *J*=7.0 Hz), 7.80 (s, 1H), 7.79 (s, 1H), 7.6–7.1 (m, 22H), 6.27 (s, 2H), 3.86 (s, 3H), 3.85 (s, 6H), 3.78 (s, 3H), 3.75 (s, 3H), 3.65 (s, 3H), 3.59 (s, 3H), 3.57 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H); IR ($CHCl_3$): 3517, 3063, 3026, 3009, 2941, 2855, 1766, 1731, 1504, 1453, 1391, 1014 cm^{-1}; FAB MS *m/z* 1147 $(M+H)^+$; HRMS *m/z* Calcd for $C_{72}H_{59}O_{14}$ $(M+H)^+$ 1147.3905. Found 1147.3915.

3.1.13. Methylation of (*S*,*S*,*S*,*S*,*S*)-18 to (*S*,*S*,*S*,*S*,*S*)-7. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*S*,*S*)-**18** (23 mg, 20 μmol) was treated with potassium carbonate (40 mg, 0.30 mmol) and methyl iodide (0.13 mL, 2.0 mmol) in acetone (15 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*S*,*S*)-**7** (13 mg, 55%), which was identical with the product obtained from the methylation of (*S*,*S*,*S*,*S*,*S*)-**6** in terms of the spectroscopic data as well as the retention time in HPLC analysis with chiral stationary phase (Chiralpak AS, 14% *i*-PrOH/*n*-hexane, 0.7 mL/min, t_R=23.9 min).

3.1.14. (*S*,*S*,*S*,*R*,*S*)-Sexinaphthalene 20. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*R*,*S*)-**19** (10 mg, 8.7 μmol) was treated with potassium carbonate (17 mg, 0.12 mmol) and methyl iodide (0.11 mL, 1.7 mmol) in acetone (10 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to pTLC. Developing with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*R*,*S*)-**20** (7.9 mg, 77%). Mp >300 °C; colorless powder (from CH_2Cl_2/benzene); $[\alpha]_D^{20}=-91.6$ (*c* 0.3, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J*=8.0 Hz), 7.78 (s, 2H), 7.6–7.2 (m, 22H), 3.91 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.81 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.77 (s, 3H), 3.76 (s, 3H), 3.64 (s, 3H), 3.56 (s, 3H), 2.45 (s, 3H), 2.44 (s, 3H); IR ($CHCl_3$): 3063, 3009, 2940, 2854, 1766, 1729, 1577, 1502, 1466, 1453, 1390, 1016 cm^{-1}; FAB MS *m/z* 1175 $(M+H)^+$; HRMS *m/z*

Calcd for $C_{72}H_{63}O_{14}$ $(M+H)^+$ 1175.4218. Found 1175.4221.

3.1.15. Oxidative coupling to octinaphthalenes (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-21 and (*S*,*S*,*S*,*R*,*S*,*S*,*S*,*S*)-25. A mixture of $CuCl_2$ (135 mg, 1.0 mmol) and α-phenylethylamine (0.16 mL, 1.3 mmol) in MeOH (0.4 mL) was stirred for 20 min, to which was added a solution of (*S*,*S*,*S*)-**16** (383 mg, 0.50 mmol) in CH_2Cl_2 (8 mL). After being stirred for 36 h under nitrogen, the reaction mixture was acidified with conc. HCl, concentrated, and extracted with EtOAc. The organic layer was washed with water, dried, and evaporated to give a residue. The residue was purified by column chromatography (SiO_2, *n*-hexane/CH_2Cl_2/EtOAc=4/5/1) to afford (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**21** (84 mg, 22%) and (*S*,*S*,*S*,*R*,*S*,*S*,*S*,*S*)-**25** (114 mg, 30%).

Compound (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**21**. Mp >300 °C; pale yellow powder (from CH_2Cl_2/Et_2O); $[\alpha]_D^{20}=-155.7$ (*c* 0.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.93 (d, 2H, *J*=7.9 Hz), 7.79 (s, 2H), 7.7–7.1 (m, 30H), 6.37 (s, 2H), 3.89 (s, 6H), 3.88 (s, 6H), 3.86 (s, 6H), 3.79 (s, 6H), 3.76 (s, 6H), 3.66 (s, 6H), 2.45 (s, 6H); IR ($CHCl_3$): 3510, 3063, 3009, 2940, 2854, 2360, 2341, 1766, 1155, 1111 cm^{-1}; FAB MS *m*/*z* 1519 $(M+H)^+$; HRMS *m*/*z* Calcd for $C_{96}H_{79}O_{18}$ $(M+H)^+$ 1519.5266. Found 1519.5240.

Compound (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**25**. Mp >300 °C; colorless powder (from toluene); $[\alpha]_D^{20}=-150.6$ (*c* 2.2, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.96 (d, 2H, *J*=8.0 Hz), 7.83 (s, 2H), 7.7–7.1 (m, 30H), 6.34 (s, 2H), 3.92 (s, 6H), 3.90 (s, 12H), 3.82 (s, 12H), 3.69 (s, 6H), 2.49 (s, 6H); IR ($CHCl_3$): 3519, 3009, 2940, 2854, 1766, 1155, 1110 cm^{-1}; FAB MS *m*/*z* 1519 $(M+H)^+$; HRMS *m*/*z* Calcd for $C_{96}H_{79}O_{18}$ $(M+H)^+$ 1519.5266. Found 1519.5259.

3.1.16. (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-Octinaphthalene 22. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**21** (6.0 mg, 4.0 μmol) was treated with potassium carbonate (16 mg, 0.12 mmol) and methyl iodide (0.10 mL, 1.6 mmol) in acetone (5 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**22** (3.0 mg, 49%). Mp >300 °C; colorless powder (from CH_2Cl_2/Et_2O/pet. ether); $[\alpha]_D^{20}=-215.7$ (*c* 0.4, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J*=7.9 Hz), 7.79 (s, 2H), 7.6–7.1 (m, 30H), 3.93 (s, 12H), 3.92 (s, 12H), 3.84 (s, 6H), 3.78 (s, 6H), 3.66 (s, 6H), 2.45 (s, 6H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 169.6, 151.0, 150.9, 149.2, 143.6, 132.5, 131.3, 131.2, 131.1, 130.7, 127.9, 127.1, 126.8, 126.7, 126.6, 126.3, 126.1, 126.0, 125.7, 125.5, 121.0, 61.1, 60.9, 60.7, 20.8; IR ($CHCl_3$): 3063, 3009, 2938, 1765, 1453, 1389, 1222, 1017 cm^{-1}; FAB MS *m*/*z* 1547 $(M+H)^+$. Anal. Calcd for $C_{98}H_{82}O_{18}$: C, 76.05; H, 5.34. Found: C, 75.79; H, 5.24.

3.1.17. (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-Octinaphthalene 23. Following the procedure for the preparation of **8**, (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**22** (16 mg, 10 μmol) was treated with potassium carbonate (60 mg, 0.43 mmol) and MeOH (0.4 mL) in CH_2Cl_2 (5 mL) for 3 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**23** (9.7 mg, 66%). Mp >300 °C; orange powder (from *n*-hexane/CH_2Cl_2/EtOAc); $[\alpha]_D^{20}=-190.3$ (*c* 0.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.84 (d, 2H, *J*=8.3 Hz), 7.6–7.1 (m, 32H), 6.23 (s, 2H), 3.94 (s, 6H), 3.92 (s, 18H), 3.83 (s, 6H), 3.76 (s, 6H), 3.65 (s, 6H); IR ($CHCl_3$): 3521, 3017, 2939, 2854, 1452, 1389, 1221, 1210 cm^{-1}; FAB MS *m*/*z* 1463 $(M+H)^+$; HRMS *m*/*z* Calcd for $C_{94}H_{79}O_{16}$ $(M+H)^+$ 1463.5368. Found 1463.5372.

3.1.18. (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-Octinaphthalene 24. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**23** (12 mg, 8.1 μmol) was treated with potassium carbonate (32 mg, 0.23 mmol) and methyl iodide (0.10 mL, 1.6 mmol) in acetone (5 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**24** (12 mg, 100%). Mp >300 °C; colorless powder (from CH_2Cl_2/Et_2O/pet. ether); $[\alpha]_D^{20}=-177.8$ (*c* 0.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J*=8.1 Hz), 7.5–7.1 (m, 32H), 4.13 (s, 6H), 3.92 (s, 6H), 3.914 (s, 6H), 3.912 (s, 6H), 3.88 (s, 6H), 3.85 (s, 6H), 3.77 (s, 6H), 3.76 (s, 6H); IR ($CHCl_3$): 3008, 2935, 2854, 1454, 1389, 1115, 1019 cm^{-1}; CD (0.4% dioxane in MeOH): see Table 1; UV (0.4% dioxane in MeOH) λ_{max} 305.4 nm (ε 72533), 229.8 (407143); FAB MS *m*/*z* 1491 $(M+H)^+$. Anal. Calcd for $C_{96}H_{82}O_{16}$: C, 77.30; H, 5.54. Found: C, 77.07; H, 5.43.

3.1.19. (*S*,*S*,*S*,*R*,*S*,*S*,*S*,*S*)-Octinaphthalene 26. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**25** (14 mg, 9.2 μmol) was treated with potassium carbonate (37 mg, 0.26 mmol) and methyl iodide (0.23 mL, 3.7 mmol) in acetone (10 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to pTLC. Developing with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**26** (12 mg, 86%). Mp >300 °C; colorless prisms (from *n*-hexane/CH_2Cl_2/EtOAc); $[\alpha]_D^{20}=-139.2$ (*c* 1.5, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.92 (d, 2H, *J*=8.1 Hz), 7.79 (s, 2H), 7.6–7.1 (m, 30H), 3.93 (s, 6H), 3.88 (s, 6H), 3.859 (s, 6H), 3.856 (s, 6H), 3.83 (s, 6H), 3.79 (s, 6H), 3.65 (s, 6H), 2.45 (s, 6H); IR ($CHCl_3$): 3063, 3010, 2940, 2854, 1766, 1577, 1504, 1453, 1390, 1017 cm^{-1}; FAB MS *m*/*z* 1547 $(M+H)^+$. Anal. Calcd for $C_{98}H_{82}O_{18}$: C, 76.05; H, 5.34. Found: C, 76.09; H, 5.41.

3.1.20. (*S*,*S*,*S*,*R*,*S*,*S*,*S*,*S*)-Octinaphthalene 27. Following the procedure for the preparation of **8**, (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**26** (36 mg, 23 μmol) was treated with potassium carbonate (91 mg, 0.66 mmol) and MeOH (0.4 mL) in CH_2Cl_2 (5 mL) for 25 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (6/3/1) gave (*S*,*S*,*S*,*R*,*S*,*S*,*S*,*S*)-**27** (30 mg, 90%). Mp >300 °C; orange powder (from CH_2Cl_2/EtOAc); $[\alpha]_D^{20}=-115.4$ (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.84 (d, 2H, *J*=8.1 Hz), 7.6–7.1 (m, 32H), 6.23 (s, 2H), 3.94 (s, 6H), 3.89 (s, 6H), 3.86 (s, 6H), 3.84 (s, 12H), 3.77 (s, 6H), 3.64 (s, 6H); IR ($CHCl_3$): 3521, 3063, 3009, 2940, 2853, 1507, 1467, 1452, 1389, 1111,

1071 cm^{-1}; FAB MS *m/z* 1463 $(M+H)^+$; HRMS *m/z* Calcd for $C_{94}H_{79}O_{16}$ $(M+H)^+$ 1463.5368. Found 1463.5370.

3.1.21. (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-Octinaphthalene 28. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**27** (20 mg, 14 μmol) was treated with potassium carbonate (55 mg, 0.40 mmol) and methyl iodide (0.17 mL, 2.8 mmol) in acetone (4 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*R*,*S*,*S*,*S*)-**28** (12 mg, 58%). Mp >300 °C; colorless powder (from CH_2Cl_2/EtOAc); $[\alpha]_D^{20}=-129.6$ (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H, *J*=8.0 Hz), 7.6–7.1 (m, 32H), 4.13 (s, 6H), 3.93 (s, 6H), 3.87 (s, 6H), 3.85 (s, 12H), 3.82 (s, 6H), 3.772 (s, 6H), 3.768 (s, 6H); IR ($CHCl_3$): 3017, 2939, 1390, 1221 cm^{-1}; CD (0.4% dioxane in MeOH): see Table 1; UV (0.4% dioxane in MeOH) λ_{max} 305.2 nm (ε 72244), 230.6 (392756); FAB MS *m/z* 1491 $(M+H)^+$. Anal. Calcd for $C_{96}H_{82}O_{16}$: C, 77.30; H, 5.54. Found: C, 77.43; H, 5.52.

3.1.22. (*S*,*S*,*S*,*S*,*S*)-Sexinaphthalene 29. Following the procedure for the preparation of **8**, (*S*,*S*,*S*,*S*,*S*)-**7** (40 mg, 34 μmol) was treated with potassium carbonate (9.9 mg, 72 μmol) and MeOH (0.44 mL) in CH_2Cl_2 (5 mL) for 5 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to pTLC. Developing with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*S*,*S*)-**29** (15 mg, 38%). Amorphous; $[\alpha]_D^{20}=-191.6$ (*c* 0.3, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 8.0–7.8 (m, 3H), 7.6–7.2 (m, 23H), 6.27 (s, 1H), 3.94 (s, 12H), 3.93 (s, 12H), 3.86 (s, 3H), 3.85 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 3.67 (s, 3H), 2.48 (s, 3H); IR ($CHCl_3$): 3521, 3063, 3010, 2939, 2854, 1766, 1505, 1467, 1452, 1389, 1347, 1240, 1017 cm^{-1}; FAB MS *m/z* 1133 $(M+H)^+$; HRMS *m/z* Calcd for $C_{72}H_{61}O_{13}$ $(M+H)^+$ 1133.4112. Found 1133.4086.

3.1.23. Oxidative coupling to octinaphthalenes (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-30 and (*S*,*S*,*S*,*S*,*S*,*R*,*S*)-31. A mixture of $CuCl_2$ (51 mg, 0.38 mmol) and α-phenylethylamine (61 μL, 0.47 mmol) in MeOH (0.4 mL) was stirred for 20 min, to which was added a solution of (*S*,*S*,*S*,*S*,*S*)-**29** (35 mg, 31 μmol) and (*S*)-**17** (61 mg, 0.16 mmol) in CH_2Cl_2 (15 mL). After being stirred for 16 h under nitrogen, the reaction mixture was acidified with conc. HCl, concentrated, and extracted with EtOAc. The organic layer was washed with water, dried, and evaporated to give a residue, which was subjected to pTLC. Developing with *n*-hexane/acetone (3/2) afforded a mixture of **30** and **31** as a polar fraction and **14** and its isomer as less polar fraction. From a polar and less polar fractions, **30** (6.2 mg, 13%) and **31** (11 mg, 22%), and **14** (15 mg) and its isomer (18 mg) were isolated, respectively, after the second separation by pTLC with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1).

Compound (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**30**. Amorphous; $[\alpha]_D^{20}=-254.9$ (*c* 0.1, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, 2H, *J*=8.8 Hz), 7.83 (s, 1H), 7.81 (s, 1H), 7.7–7.1 (m, 30H), 6.40 (s, 1H), 6.38 (s, 1H), 3.97 (s, 3H), 3.95 (s, 6H), 3.94 (s, 3H), 3.91 (s, 6H), 3.86 (s, 3H), 3.80 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 3.61 (s, 3H), 3.57 (s, 3H), 2.48 (s, 6H); IR ($CHCl_3$): 3693, 3510, 3063, 3026, 3009, 2940, 2854, 1766, 1505, 1453, 1390, 1347, 1016 cm^{-1}; FAB MS *m/z* 1519 $(M+H)^+$; HRMS *m/z* Calcd for $C_{96}H_{79}O_{18}$ $(M+H)^+$ 1519.5266. Found 1519.5251.

Compound (*S*,*S*,*S*,*S*,*S*,*R*,*S*)-**31**. Amorphous; $[\alpha]_D^{20}=-186.8$ (*c* 0.3, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, 2H, *J*=8.5 Hz), 7.82 (s, 1H), 7.81 (s, 1H), 7.6–7.2 (m, 30H), 6.27 (brs, 2H), 3.97 (s, 3H), 3.95 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 3.86 (s, 3H), 3.79 (s, 6H), 3.67 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 2.47 (s, 3H), 2.46 (s, 3H); IR ($CHCl_3$): 3673, 3518, 3023, 3009, 2940, 1731, 1505, 1453, 1389, 1374, 1249, 1045, 1015 cm^{-1}; FAB MS *m/z* 1519 $(M+H)^+$; HRMS *m/z* Calcd for $C_{96}H_{79}O_{18}$ $(M+H)^+$ 1519.5266. Found 1519.5245.

3.1.24. Methylation of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-30 to (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-22. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**30** (5.1 mg, 3.4 μmol) was treated with potassium carbonate (14 mg, 0.10 mmol) and methyl iodide (85 μL, 1.4 mmol) in acetone (10 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**22** (4.8 mg, 91%), which was identical with the product obtained from the methylation of (*S*,*S*,*S*,*S*,*S*,*S*,*S*)-**21** in terms of the spectroscopic data as well as the retention time in HPLC analysis with chiral stationary phase (Chiralpak AS, 25% *i*-PrOH/*n*-hexane, 0.8 mL/min, t_R=32.0 min).

3.1.25. (*S*,*S*,*S*,*S*,*S*,*R*,*S*)-Octinaphthalene 32. Following the procedure for the preparation of **4**, (*S*,*S*,*S*,*S*,*S*,*R*,*S*)-**31** (5.0 mg, 3.3 μmol) was treated with potassium carbonate (13 mg, 94 μmol) and methyl iodide (81 μL, 1.3 mmol) in acetone (5 mL) for 2 h. After extraction with CH_2Cl_2, the organic layer was dried and evaporated to give a residue, which was subjected to column chromatography on silica gel. Elution with *n*-hexane/CH_2Cl_2/EtOAc (4/5/1) gave (*S*,*S*,*S*,*S*,*S*,*R*,*S*)-**32** (5.1 mg, 100%). Mp >300 °C; colorless powder (from CH_2Cl_2/benzene); $[\alpha]_D^{20}=-113.0$ (*c* 0.2, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.95 (d, 2H, *J*=8.0 Hz), 7.81 (s, 2H), 7.6–7.2 (m, 30H), 3.97 (s, 3H), 3.96 (s, 3H), 3.95 (s, 3H), 3.94 (s, 3H), 3.93 (s, 3H), 3.91 (s, 3H), 3.86 (s, 3H), 3.84 (s, 6H), 3.80 (s, 6H), 3.79 (s, 3H), 3.68 (s, 3H), 3.59 (s, 3H), 2.47 (s, 3H), 2.46 (s, 3H); IR ($CHCl_3$): 3062, 3007, 2939, 2854, 1766, 1728, 1577, 1503, 1453, 1390, 1349, 1239, 1017, 909 cm^{-1}; FAB MS *m/z* 1547 $(M+H)^+$; HRMS *m/z* Calcd for $C_{98}H_{83}O_{18}$ $(M+H)^+$ 1547.5579. Found 1547.5582.

3.1.26. (*S*)-2,3,2′,3′-Tetramethoxy-1,1′-binaphthalene (33). Following the procedure for the preparation of **4**, (*S*)-**34** (551 mg, 1.6 mmol) was treated with potassium carbonate (3.2 g, 23 mmol) and methyl iodide (2.0 mL, 32 mmol) in acetone (25 mL) for 1.5 h. After extraction with EtOAc, the organic layer was dried and evaporated to give a residue, which was purified by recrystallization from EtOAc to give (*S*)-**33** as colorless prisms (230 mg, 38%). Mp 204–206 °C; $[\alpha]_D^{20}=-52.2$ (*c* 1.0, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): δ 7.80 (d, 2H, *J*=8.3 Hz), 7.5–7.0 (m, 8H), 4.08 (s, 6H), 3.63 (s, 6H); IR ($CHCl_3$): 3011, 2940, 1597, 1464, 1420, 1251, 1117 cm^{-1}; CD (0.4% dioxane in

MeOH): see Table 1; UV (0.4% dioxane in MeOH) λ_{max} 325.6 nm (ε 5193), 290.6 (10559), 280.2 (11193), 232.0 (119248). Anal. Calcd for $C_{24}H_{22}O_4$: C, 76.99; H, 5.92. Found: C, 76.89; H, 5.89.

3.2. Molecular modeling of octinaphthalene 24 and corresponding 24-mer

The lowest energy conformations of octinaphthalene **24** and corresponding 24-mer were obtained by MacroModel (version. 6.0) using MM2 force field. The calculations were started from the structures **24** and 24-mer, in which the absolute configuration of each axis was prefixed as *aS*.

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