Supporting Information

Oligoresorcinols fold into double helices in water

Hidetoshi Goto[1], Hiroshi Katagiri[1], Yoshio Furusho[1], and Eiji Yashima[1,2]

[1]Yashima Super-structured Helix Project. Exploratory Research for Advanced Technology (ERATO), Japan Science and Technology Agency (JST), Creation Core Nagoya 101, 2266-22 Anagahora, Shimoshidami, Moriyama-ku, Nagoya 463-0003, Japan.

[2]Institute for Advanced Research, Nagoya University, Chikusa-ku, Nagoya 464-8603, Japan.

*To whom correspondence should be addressed. E-mail: furusho@yp-jst.jp (Y.F.); yashima@apchem.nagoya-u.ac.jp (E.Y.).

Table of Contents

1. Instruments

The melting points were measured using a Yanaco MP-500D melting point apparatus (Kyoto, Japan) and were uncorrected. The solution pH was measured with a Horiba B-211 pH meter (Kyoto, Japan) or a DKK-TOA GST-5428S pH meter (Tokyo, Japan). The NMR spectra were obtained using a Varian UNITY INOVA 500AS spectrometer operating at 500 MHz for ^{1}H and 125 MHz for ^{13}C. Chemical shifts are reported in parts per million (δ) downfield from tetramethysilane (TMS) as the internal standard in $CDCl_3$ and from acetone or 1,4-dioxane dissolved in D_2O as the external standard in D_2O and CD_3OD. The electron spray ionization mass spectra (ESI-MS) were recorded using a Jeol JMS-T100CS spectrometer (Akishima, Japan). The matrix-assisted laser desorption-ionization time-of-flight mass spectra (MALDI-TOF-MS) were measured using a Shimadzu AXIMA-CFR Plus spectrometer (Kyoto, Japan). The elemental analyses were performed by the Nagoya University Analytical Laboratory in the Graduate School of Engineering. The IR spectra were recorded using a Jasco Fourier Transform IR-680 spectrophotometer (Hachioji, Japan). The absorption and CD spectra were measured in a 0.2- or 1.0-mm quartz cell on a Jasco V-570 spectrophotometer and a Jasco J-820 spectropolarimeter, respectively. The temperature was controlled by a Jasco PTC-423L apparatus (–10 to 90^{o}C). Optical rotations were taken using a Jasco P-1030 polarimeter in water and methanol in a 5-cm quartz cell equipped with a temperature controller (EYELA NCB-2100). The molecular weights of the oligomer aggregates in water were estimated using a Gonotec

070 vapor pressure osmometer (VPO) (Berlin, Germany) with NaCl (300 mOsmol/kg) as the standard. The samples were prepared in the range of 5–20 mmol/kg. The single crystal X-ray data were collected using a Bruker Smart Apex (153 K) or a Bruker Smart ApexII (90 K) CCD-based X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å).

2. Materials

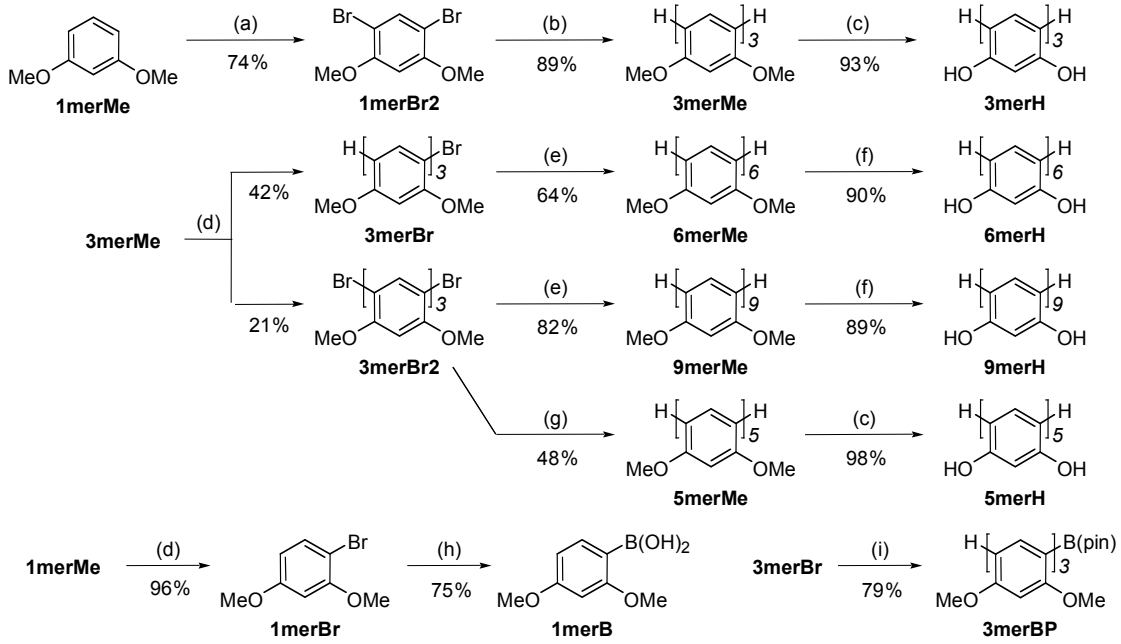
All starting materials and dehydrated solvents were purchased from Aldrich, Wako Pure Chemical Industries (Osaka, Japan), and Tokyo Kasei Kogyo (Tokyo, Japan). 1,3-Diiodo-5,5-dimethylhydantoin (DIH) was kindly supplied from Nippoh Chemicals Co., Ltd. (Tokyo, Japan). Triethylamine (NEt_3) was distilled over CaH_2 under Ar after being stirred with KOH pellets overnight under Ar. The distilled water and D_2O (99.9 atom %D) purchased from Wako and Cambridge Isotope Laboratories (Andover, MA, USA), respectively, were degassed with Ar and used throughout all the experiments. Silica gel (SiO_2) and aminopropyl-modified silica gel (NH_2-SiO_2) for the flash chromatography were purchased from Merck and Fuji Silysia Chemical Ltd. (Kasugai, Japan), respectively.

3. Synthetic Procedures

3-1. Synthesis of Achiral Oligoresorcinols

Achiral oligoresorcinols were synthesized according to Scheme S-1. **1merBr**,[1] **1merB**,[2] and **1merBr2**[3] were prepared by the previously reported methods. The reaction progresses were monitored by TLC or ESI-MS.

Scheme S-1. Synthesis of Resorcinol Oligomers (3–9merH)[a]



[a] Reagents and conditions: (a) HBr, DMSO, reflux, 1 day; (b) **1merB**, $Pd(PPh_3)_4$, Na_2CO_3, THF, H_2O, reflux, 1 week; (c) BBr_3, –78°C, 1 day; (d) DBH, THF, 0°C, 1 day; (e) **3merBP**, $Pd(PPh_3)_4$, K_2CO_3, THF, H_2O, reflux, 2 days; (f) BBr_3, 0°C, 1 day; (g) **1merB**, $Pd(PPh_3)_4$, K_2CO_3, THF, H_2O, reflux, 4 days; (h) (1) *n*-BuLi, THF, –78°C, 1 h, (2) B(O*i*-Pr)$_3$, –78°C, 1 day, (3) H_3O^+; (i) pinacolborane, $PdCl_2(PPh_3)_2$, NEt_3, 1,4-

dioxane, 80°C, 1 day.

3merMe [2,4,4',6',2'',4''-Hexamethoxy-1,1':3',1''-terphenyl][4]

To a solution of **1merBr2** (25.2 g, 85.3 mmol), **1merB** (31.1 g, 171 mmol) and $Pd(PPh_3)_4$ (5.9 g, 4.33 mmol, Aldrich) in dehydrated THF (1 L) was added a degassed solution of Na_2CO_3 (2 M, 200 mL, 400 mmol) through a cannula under Ar and the mixture was refluxed for 1 week. After most of the solvent had been removed by evaporation, the aqueous solution was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 chromatography with *n*-hexane/$CHCl_3$ (2/1 to 0/1, v/v) to obtain **3merMe** as a slightly yellow solid (31 g, 75.5 mmol, 88.8% yield). Mp: 112–113°C. IR (KBr, cm^{-1}): 2937, 1607, 1493, 1205, 1164, 1033, 930, 824. ^1H NMR ($CDCl_3$): δ 3.76 (s, OMe, 6H), 3.82 (s, OMe, 6H), 3.83 (s, OMe, 6H), 6.53 (dd, Ar-$H_{5 \text{ and } 5''}$, J = 8.0, 2.5 Hz, 2H), 6.54 (d, Ar-$H_{3 \text{ and } 3''}$, J = 2.5 Hz, 2H), 6.62 (s, Ar-$H_{5'}$, 1H), 7.12 (s, Ar-$H_{2'}$, 1H), 7.19 (d, Ar-$H_{6 \text{ and } 6''}$, J = 8.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 55.31, 55.64, 55.85, 96.02, 98.88, 104.14, 119.16, 120.20, 132.12, 134.56, 157.12, 158.10, 159.96. ESI-MS (CH_2Cl_2/CH_3OH (1/1, v/v), positive): Calcd for $C_{24}H_{26}O_6Na$ [**3merMe**+Na]$^+$: m/z = 433.16. Found: m/z = 433.20. Anal. Calcd for $C_{24}H_{26}O_6$: C, 70.23; H, 6.38. Found: C, 70.17; H, 6.36.

3merBr [5-Bromo-2,4,4',6',2'',4''-hexamethoxy-1,1':3',1''-terphenyl] and 3merBr2 [5,5''-Dibromo-2,4,4',6',2'',4''-hexamethoxy-1,1':3',1''-terphenyl][1]

To a solution of **3merMe** (20.5 g, 49.9 mmol) in THF (100 mL) was added 1,3-dibromo-5,5-dimethylhydantoin (DBH) (7.15 g, 25.0 mmol, Wako) at 0°C and the reaction mixture was stirred at that temperature overnight. After evaporation, the residue was dissolved in $CHCl_3$ and the solution was washed with sat. $Na_2S_2O_3$ aq., dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 chromatography with *n*-hexane/Et_2O (1/1, v/v) to obtain pure **3merBr** (10.2 g, 20.8 mmol, 41.6% yield) as a slightly yellow solid and crude **3merBr2**. The crude **3merBr2** was purified by SiO_2 chromatography with CH_2Cl_2 and by subsequent washing with Et_2O to obtain **3merBr2** (5.95 g, 10.5 mmol, 20.9% yield) as a white solid.

3merBr. Mp: 147–148°C. IR (KBr, cm^{-1}): 2945, 1600, 1492, 1457, 1359, 1204, 1028, 930, 813. ^1H NMR ($CDCl_3$): δ 3.76 (s, OMe, 3H), 3.79 (s, OMe, 3H), 3.82 (s, OMe, 3H), 3.83 (s, OMe, 6H), 3.93 (s, OMe, 3H), 6.53 (dd, Ar-$H_{5''}$, J = 8.0, 2.5 Hz, 1H), 6.54 (d, Ar-$H_{3''}$, J = 2.5 Hz, 1H), 6.56 (s, Ar-H_3, 1H), 6.61 (s, Ar-$H_{5'}$, 1H), 7.09 (s, Ar-$H_{2'}$, 1H), 7.18 (d, Ar-$H_{6''}$, J = 8.0 Hz, 1H), 7.43 (s, Ar-H_6, 1H). ^{13}C NMR ($CDCl_3$): δ 55.32, 55.65, 55.85, 55.86, 56.09, 56.36, 95.91, 97.09, 98.89, 101.67, 104.17, 117.82, 119.35, 119.99, 121.39, 132.06, 134.37, 135.39, 155.62, 156.99, 157.48, 158.09, 160.04. HRMS (ESI+): *m/z* calcd for $C_{24}H_{25}BrNaO_6$ ($M+Na^+$), 511.07322; found, 511.07221.

3merBr2. Mp: 204–205°C. IR (KBr, cm^{-1}): 2937, 1598, 1492, 1464, 1375, 1301, 1204, 1032, 935, 816. ^1H NMR ($CDCl_3$): δ 3.79 (s, OMe, 6H), 3.83 (s, OMe, 6H), 3.93 (s, OMe, 6H), 6.56 (s Ar-$H_{3 \text{ and } 3''}$, 2H), 6.60 (s, Ar-$H_{5'}$, 1H), 7.06 (s, Ar-$H_{2'}$, 1H), 7.42 (s, Ar-$H_{6 \text{ and } 6''}$, 2H). ^{13}C NMR ($CDCl_3$): δ 55.87, 56.10, 56.38, 95.79, 97.09,

101.70, 118.00, 121.18, 134.20, 135.33, 155.71, 157.36, 157.49. HRMS (ESI+): *m/z* calcd for $C_{24}H_{24}Br_2NaO_6$ ($M+Na^+$), 588.98373; found, 588.98923

3merBP [3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolyl)- 4,6,4',6',2'',4''-hexamethoxy-1,1':3',1''-terphenyl][5]

To a solution of **3merBr** (12 g, 24.5 mmol) and $PdCl_2(PPh_3)_2$ (1.72g, 2.45 mmol, Aldrich) in dehydrated 1,4-dioxane (100 mL) were added distilled NEt_3 (10.2 mL, 73.4 mmol) and pinacolborane (5.3 mL, 36.4 mmol, Aldrich) under Ar, and subsequently the mixture was heated at 80°C overnight. After concentration, the black residue was extracted with Et_2O (*ca*. 200 mL). The Et_2O-insoluble black precipitate was removed with Celite filtration. After concentration of the filtrate, the crude product was purified by SiO_2 chromatography with *n*-hexane/Et_2O (2/1 to 3/2, v/v) and by further recrystallization from Et_2O to obtain **3merBP** as a slightly gray powder (8.65 g, 16.1 mmol, 79.0% yield). Mp: 175–176°C. IR (KBr, cm^{-1}): 2975, 2937, 1602, 1571, 1493, 1460, 1333, 1205, 1033, 938, 833. ^1H NMR ($CDCl_3$): δ 1.30 (s, Me, 12H), 3.76 (s, OMe, 3H), 3.81 (2 x s, OMe, 2 x 3H), 3.82 (s, OMe, 3H), 3.83 (s, OMe, 3H), 3.88 (s, OMe, 3H), 6.49 (s, Ar-H_5, 1H), 6.52 (dd, Ar-$H_{5''}$, J = 8.0, 2.5 Hz, 1H), 6.54 (d, Ar-$H_{3''}$, J = 2.5 Hz, 1H), 6.60 (s, Ar-$H_{5'}$, 1H), 7.11 (s, Ar-$H_{2'}$, 1H), 7.19 (d, Ar-$H_{6''}$, J = 8.0 Hz, 1H), 7.60 (s, Ar-H_2, 1H). ^{13}C NMR ($CDCl_3$): δ 24.79, 55.31, 55.59, 55.92, 56.26, 82.97, 95.24, 96.05, 98.88, 104.11, 119.26, 119.49, 119.75, 120.29, 132.09, 134.41, 140.20, 157.16, 157.22, 158.10, 159.94, 160.93, 165.53.

5merMe [2,4,4',6',4'',6'',4''',6''',2'''',4''''-Decamethoxy-1,1':3',1'':3'',1''':3''',1'''':quinquephenyl][6]

A solution of **1merB** (362 mg, 2.00 mmol), **3merBr$_2$** (568 mg, 1.00 mmol), and $Pd(PPh_3)_4$ (115 mg, 0.10 mmol) in dehydrated THF (14 mL) was purged with Ar. An aqueous solution of K_2CO_3 (2 M, 4 mL, 8 mmol) purged with Ar was added to the solution by a syringe. The mixture was refluxed for 4 days and was then evaporated to dryness. The residue was partitioned between $CHCl_3$ (40 mL) and 10% aq. NaOH (10 mL). The $CHCl_3$ layer was separated, washed with H_2O (10 mL) and successively with brine (10 mL), and dried over $MgSO_4$. After filtration, the solvent was evaporated, and the residue was purified by column chromatography (SiO_2, 40 g, *n*-hexane/$CHCl_3$ = 1/1 to 0/1, v/v) and by preparative HPLC ($CHCl_3$) to afford **5merMe** as a yellow solid in 48% yield. Mp: 117–119°C. IR (KBr, cm^{-1}): 2995, 2936, 1604, 1491, 1204, 1161, 1034, 930, 822. ^{1}H NMR ($CDCl_3$): δ 3.74 (s, OMe, 6H), 3.80 (s, OMe, 6H), 3.82 (s, OMe, 12H), 3.83 (s, OMe, 6H), 6.51 (dd, J = 8.0, 2.5 Hz, Ar-H$_{5 \text{ and } 5''''}$, 2H), 6.52 (d, J = 2.5 Hz, Ar-H$_{3 \text{ and } 3''''}$, 2H), 6.60 (s, Ar-H$_{5' \text{ and } 5'''}$, 2H), 6.61 (s, Ar-H$_{5''}$, 1H), 7.15 (s, Ar-H$_{2' \text{ and } 2'''}$, 2H), 7.16 (d, J = 8.0 Hz, Ar-H$_{6 \text{ and } 6''''}$, 2H), 7.22 (s, Ar-H$_{2''}$, 1H). ^{13}C NMR ($CDCl_3$): δ 55.28, 55.62, 55.82, 55.83, 95.97, 98.82, 104.09, 119.13, 119.20, 119.25, 120.27, 132.12, 134.73, 134.88, 157.01, 157.04, 157.10, 158.08, 159.88. ESI-MS (CH_2Cl_2/CH_3OH (1/1, v/v), positive): Calcd for $C_{40}H_{42}O_{10}Na$ [**5merMe**+Na]$^+$: *m/z* = 705.27. Found: *m/z* = 705.34. Anal. Calcd for $C_{40}H_{42}O_{10}\cdot(CHCl_3)_{0.7}$: C, 63.79; H, 5.62. Found: C, 64.37; H, 5.67.

6merMe [2,4,4',6',4'',6'',4''',6''',4'''',6'''',2''''',4''''']-Dodecamethoxy-1,1':3',1'':3'',1''':3''',1'''':3'''',1''''':sexiphenyl][6]

A solution of **3merBP** (1.41 g, 2.62 mmol), **3merBr** (1.28 g, 2.62 mmol), and $Pd(PPh_3)_4$ (152 mg, 0.132 mmol) in dehydrated THF (24 mL) was purged with Ar. An aqueous solution of K_2CO_3 (2 M, 4 mL, 8 mmol) purged with Ar was added to the solution by a syringe and the mixture was refluxed for 2 days. After most of the solvent had been removed by evaporation, the aqueous solution was extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by NH_2-SiO_2 chromatography with *n*-hexane/CH_2Cl_2 (2/1 to 1/1, v/v) and then by recycling preparative SEC with $CHCl_3$ as the eluent to obtain **6merMe** as a white powder (1.38 g, 1.69 mmol, 64.3% yield). Mp: 138–140°C. IR (KBr, cm^{-1}): 2935, 1604, 1490, 1203, 1165, 1034, 930, 821. ^1H NMR ($CDCl_3$): δ 3.73 (s, OMe, 6H), 3.80 (s, OMe, 6H), 3.81 (s, OMe, 12H), 3.82 (s, OMe, 12H), 6.51 (dd, J = 8.0, 2.5 Hz, Ar-$H_{5 \text{ and } 5'''''}$, 2H), 6.52 (d, J = 2.5 Hz, Ar-$H_{3 \text{ and } 3'''''}$, 2H), 6.60 (s, Ar-$H_{5', 5'', 5''', \text{and } 5''''}$, 4H), 7.15 (s, Ar-$H_{5' \text{ and } 5''''}$, 2H), 7.17 (d, J = 8.0 Hz, Ar-$H_{6 \text{ and } 6'''''}$, 2H), 7.21 (s, Ar-$H_{2'' \text{ and } 2'''}$, 2H). ^{13}C NMR ($CDCl_3$): δ 55.29, 55.63, 55.82, 55.84, 95.99, 98.84, 104.09, 119.10, 119.17, 119.22, 119.31, 120.31, 132.14, 134.78, 134.95, 156.98, 157.00, 157.03, 157.12, 158.10, 159.86. ESI-MS (CH_2Cl_2/CH_3OH (1/1, v/v), positive): Calcd for $C_{48}H_{50}O_{12}Na$ [**6merMe**+Na]$^+$: m/z = 841.32. Found: m/z = 841.40. Anal. Calcd for $C_{48}H_{50}O_{12}$: C, 70.40; H, 6.15. Found: C, 70.48; H, 6.13.

9merMe

[2,4,4',6',4'',6'',4''',6''',4'''',6'''',4''''',6''''',4'''''',6'''''',4''''''',6''''''',2'''''''',4''''''''-

Octadecamethoxy1,1':3',1'':3'',1''':3''',1'''':3'''',1''''':3''''',1'''''':3'''''',1''''''':3''''''',1'''''''':3''''''',1'''''''''-noniphenyl][6]

A mixture of **3merBP** (4.51 g, 8.4 mmol), **3merBr2** (2.27 g, 4.0 mmol), and $Pd(PPh_3)_4$ (930 mg, 0.80 mmol) in dehydrated THF (80 mL) was purged with Ar. An aqueous solution of K_2CO_3 (2 M, 12 mL, 24 mmol) purged with Ar was added to the solution by a syringe and the mixture was refluxed for 2 days. After most of the solvent had been removed by evaporation, the aqueous solution was extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by NH_2-SiO_2 chromatography with *n*-hexane/CH_2Cl_2 (1/1, v/v) and then by recycling preparative SEC with $CHCl_3$ as the eluent to obtain **9merMe** as a white powder (4.0 g, 3.26 mmol, 81.5% yield). Mp: 180–182°C. IR (KBr, cm^{-1}): 2934, 1604, 1490, 1203, 1166, 1034, 930, 819. ^1H NMR ($CDCl_3$): δ 3.72 (s, OMe, 6H), 3.78 (s, OMe, 12H), 3.79 (s, OMe, 12H), 3.80 (s, OMe, 12H), 3.81 (2 x s, OMe, 2 x 6H), 6.49 (dd, J = 8.0, 2.5 Hz, Ar-$H_{5\text{ and }5''''''''}$, 2H), 6.51 (d, J = 2.5 Hz, Ar-$H_{3\text{ and }3''''''''}$, 2H), 6.58 (s, Ar, 3H), 6.59 (s, Ar, 4H), 7.14 (s, Ar, 2H), 7.16 (d, J = 8.0 Hz, Ar-$H_{6\text{ and }6''''''''}$, 2H), 7.20 (s, Ar-$H_{2''''}$, 1H, and 2 x s, Ar, 2 x 2H). ^{13}C NMR ($CDCl_3$): δ 55.26, 55.61, 55.81, 96.02, 98.81, 104.08, 119.09, 119.13, 119.18, 119.25, 119.32, 120.32, 132.12, 134.76, 134.94, 135.00, 135.01, 156.93, 156.94, 156.98, 157.03, 157.12, 158.09, 159.84. ESI-MS (CH_2Cl_2/CH_3OH (1/1, v/v), positive): Calcd for $C_{72}H_{74}O_{18}Na$ [**9merMe**+Na]$^+$: m/z = 1249.48. Found: m/z = 1249.61. Anal. Calcd for $C_{72}H_{74}O_{18}$:

C, 70.46; H, 6.08. Found: C, 70.40; H, 6.07.

3merH [2,4,4',6',2",4"-Hexahydroxy-1,1':3',1"-terphenyl]

To a solution of **3merMe** (410 mg, 1.00 mmol) in dehydrated CH_2Cl_2 (100 mL) was dropwise added BBr_3 (1 M in CH_2Cl_2, 20 mL, 20 mmol) at –78°C over 10 min, and the mixture was then stirred overnight at –78°C. After water (10 mL) was slowly added to the solution at that temperature to quench any excess BBr_3, the solution was slowly warmed to room temperature. After concentration, the resulting mixture was found to contain a considerable amount of HBr and water, which were repeatedly removed by evaporation as an azeotropic mixture with EtOH (20 mL) until the water was completely removed. The CH_3CN (*ca*. 10 mL)-insoluble part was removed by filtration and the filtrate was concentrated *in vacuo*. The EtOH (*ca*. 10 mL)-insoluble part was then removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was dissolved in water (*ca*. 10 mL) and dialyzed using a Spectra/Por membrane (MW = 100). The resulting aqueous solution was filtered by membrane filtration and the filtrate was lyophilized to obtain **3merH** as a slightly gray powder (314 mg, 0.931 mmol, 93.1% yield). Mp: 145–148°C. IR (KBr, cm^{-1}): 3389 ($\nu_{O\text{-}H}$), 1617, 1496, 1415, 1285, 1163, 971, 843. ^{1}H NMR (CD_3CN): δ 6.41 (d, J = 2.5 Hz, Ar-$H_{3\text{ and }3''}$, 2H), 6.42 (dd, J = 8.0, 2.5 Hz, Ar-$H_{5\text{ and }5''}$, 2H), 6.53 (s, Ar-$H_{5'}$, 1H), 6.97 (s, Ar-$H_{2'}$, 1H), 7.05 (d, J = 8.0 Hz, Ar-$H_{6\text{ and }6''}$, 2H), 6.0–8.0 (br, OH, 6H). ^{1}H NMR (CD_3OD): δ 7.12 (d, J = 2.5 Hz, Ar-$H_{3\text{ and }3''}$, 2H, and dd, J = 9.0, 2.5 Hz, Ar-$H_{5\text{ and }5''}$, 2H), 7.24 (s, Ar-$H_{5'}$, 1H), 7.73 (s, Ar-$H_{2'}$, 1H), 7.77 (d, J = 9.0 Hz, Ar-$H_{6\text{ and }6''}$, 2H).

^{13}C NMR (CD_3CN): δ 104.00, 104.79, 108.93, 117.97, 119.27, 133.32, 135.07, 155.00, 155.58, 158.59. ESI-MS (CH_3OH, negative): Calcd for $C_{18}H_{13}O_6$ [**3merH**–H]$^-$: *m/z* = 325.07. Found: *m/z* = 325.11. Anal. Calcd for $C_{18}H_{14}O_6 \cdot 4.3H_2O$: C, 61.63; H, 4.46. Found: C, 61.64; H, 4.51.

5merH [2,4,4',6',4'',6'',4''',6''',2'''',4''''-Decahydroxy-1,1':3',1'':3'',1''':3''',1'''':quinquephenyl]

To a solution of **5merMe** (250 mg, 0.366 mmol) in dehydrated CH_2Cl_2 (30 mL) was dropwise added BBr_3 (1 M in CH_2Cl_2, 10 mL, 10 mmol) at 0^{o}C under Ar, and the mixture was then stirred overnight at that temperature. After water (1 mL) was slowly added at 0^{o}C, the solution was slowly warmed to room temperature. After concentration, the resulting mixture was found to contain a considerable amount of HBr and water, which were repeatedly removed by evaporation as an azeotropic mixture with EtOH (20 mL) until the water was completely removed. The CH_3CN (*ca*. 10 mL)-insoluble part was removed by filtration and the filtrate was concentrated *in vacuo*. The EtOH (*ca*. 10 mL)-insoluble part was then removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was dissolved in water (*ca*. 10 mL) and dialyzed using a Spectra/Por membrane (MW = 100). The resulting aqueous solution was filtered by membrane filtration and the filtrate was lyophilized to obtain **5merH** as a slightly brown powder (195 mg, 0.359 mmol, 98.2% yield). Mp: 210^{o}C (dec). IR (KBr, cm^{-1}): 3366 ($\nu_{O\text{-}H}$), 1615, 1497, 1408, 1284, 1165, 972, 840. ^{1}H NMR (CD_3CN): δ 6.41 (d, *J* = 2.5 Hz, Ar-$H_{3 \text{ and } 3''''}$, 2H), 6.42 (dd, *J* = 8.0, 2.5 Hz, Ar-$H_{5 \text{ and } 5''''}$, 2H),

6.55 (s, Ar-$H_{5'\text{ and }5'''}$, 2H), 6.57 (s, Ar-$H_{5''}$, 1H), 7.04 (s, Ar-$H_{2''}$, 1H), 7.05 (d, J = 8.0 Hz, Ar-$H_{6\text{ and }6''''}$, 2H), 7.10 (s, Ar-$H_{2'\text{ and }2'''}$, 2H), 6.0–8.0 (m OH, 10H). ^{13}C NMR (CD_3CN): δ 104.00, 104.81, 104.83, 108.95, 117.92, 119.02, 119.09, 119.31, 133.36, 135.18, 135.23, 155.00, 155.07, 155.10, 155.54, 158.58. ESI-MS (CH_3OH, negative): Calcd for $C_{30}H_{21}O_{10}$ [**6merH**–H]$^-$: *m/z* = 541.11. Found: *m/z* = 541.18. ESI-MS: [**5merH**-H]$^-$ = $C_{30}H_{21}O_{10}$, Exact Mass = 541.18, m/z = 541.11. Anal. Calcd for $C_{30}H_{22}O_{10}\cdot 2.8H_2O$: C, 60.77; H, 4.69. Found: C, 60.61; H, 4.29.

6merH [2,4,4',6',4'',6'',4''',6''',4'''',6'''',2''''',4''''']-Dodecahydroxy-1,1':3',1'':3'',1''':3''',1'''':3'''',1''''':sexiphenyl]

To a solution of **6merMe** (110 mg, 0.134 mmol) in dehydrated CH_2Cl_2 (20 mL) was dropwise added BBr_3 (1 M in CH_2Cl_2, 5 mL, 5 mmol) at 0^{o}C under Ar, and the mixture was then stirred overnight at that temperature. After water (2 mL) was slowly added at 0^{o}C, the solution was slowly warmed to room temperature. After concentration, the resulting mixture was found to contain a considerable amount of HBr and water, which were repeatedly removed by evaporation as an azeotropic mixture with EtOH (20 mL) until the water was completely removed. The CH_3CN (*ca*. 10 mL)-insoluble part was removed by filtration and the filtrate was concentrated *in vacuo*. The EtOH (*ca*. 10 mL)-insoluble part was then removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was dissolved in water (*ca*. 10 mL) and dialyzed using a Spectra/Por membrane (MW = 100). The resulting aqueous solution was filtered by membrane filtration and the filtrate was lyophilized to obtain **6merH** as

a slightly brown powder (78.8 mg, 0.121 mmol, 90.2% yield). Mp: 270°C (dec). IR (KBr, cm^{-1}): 3389 ($\nu_{O\text{-}H}$), 1615, 1492, 1406, 1281, 1163, 972, 843. ^1H NMR (CD_3CN): δ 6.40 (d, J = 2.5 Hz, Ar-$H_{3\text{ and }3''''''}$, 2H, and dd, J = 8.0, 2.5 Hz, Ar-$H_{5\text{ and }5''''''}$, 2H), 6.54 (s, Ar, 2H), 6.55 (s, Ar, 2H), 7.02 (s, Ar, 2H), 7.03 (d, J = 8.0 Hz, Ar-$H_{6\text{ and }6''''''}$, 2H), 7.09 (s, Ar, 2H), 6.0–8.0 (m OH, 12H). ^1H NMR (CD_3OD): δ 7.10 (d, J = 2.5 Hz, Ar-$H_{3\text{ and }3''''''}$, 2H, and dd, J = 9.0, 2.5 Hz, Ar-$H_{5\text{ and }5''''''}$, 2H), 7.24 (s, Ar, 2H), 7.26 (s, Ar, 2H), 7.76 (d, J = 9.0 Hz, Ar-$H_{6\text{ and }6''''''}$, 2H), 7.78 (s, Ar, 2H), 7.84 (s, Ar, 2H). ^{13}C NMR (CD_3CN): δ 104.01, 104.80, 108.97, 117.92, 118.99, 119.00, 119.02, 119.27, 133.34, 135.18, 135.24, 155.02, 155.06, 155.13, 155.52, 158.55. ESI-MS (CH_3OH, negative): Calcd for $C_{36}H_{25}O_{12}$ [**6merH**–H]$^-$: m/z = 649.13. Found: m/z = 649.20. Anal. Calcd for $C_{36}H_{26}O_{12}\cdot 2.2H_2O$: C, 62.64; H, 4.44. Found: C, 62.65; H, 4.47.

9merH

[2,4,4',6',4'',6'',4''',6''',4'''',6'''',4''''',6''''',4'''''',6'''''',4''''''',6''''''',2'''''''',4''''''''-Octadecahydroxy-1,1':3',1'':3'',1''':3''',1'''':3'''',1''''':3''''',1'''''':3'''''',1''''''':3''''''',1'''''''':3''''''',1''''''''-noniphenyl]

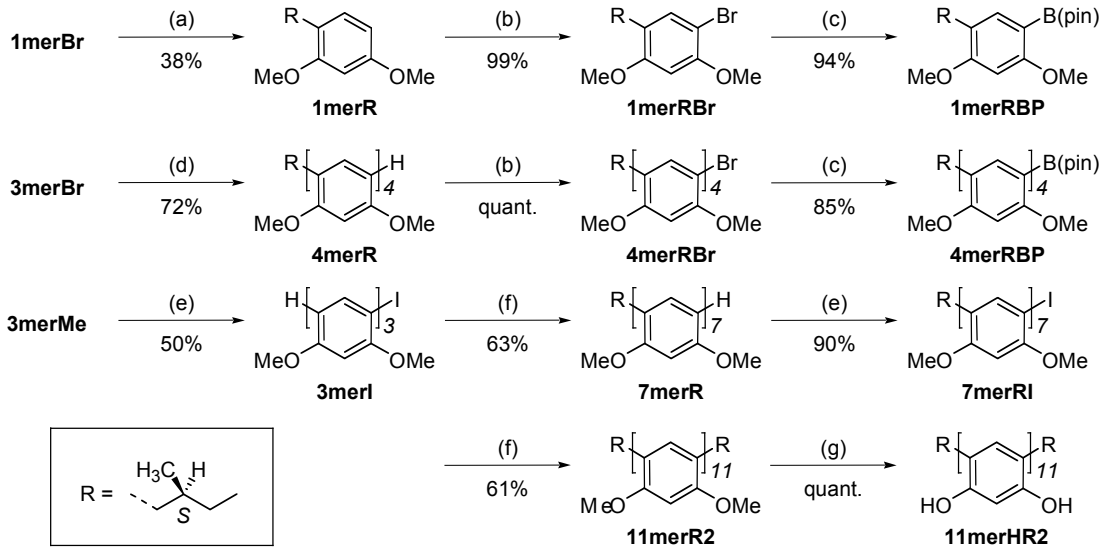
To a solution of **9merMe** (800 mg, 0.652 mmol) in dehydrated CH_2Cl_2 (50 mL) was dropwise added BBr_3 (1 M in CH_2Cl_2, 30 mL, 30 mmol) at 0°C under Ar over 10 min, and the mixture was then stirred overnight at that temperature. After water (10 mL) was slowly added to the solution at 0°C, the solution was slowly warmed to room temperature. After concentration, the resulting mixture was found to contain a

considerable amount of HBr and water, which were repeatedly removed by evaporation as an azeotropic mixture with EtOH (20 mL) until the water was completely removed. The CH_3CN (*ca*. 10 mL)-insoluble part was removed by filtration and the filtrate was concentrated *in vacuo*. The EtOH (*ca*. 10 mL)-insoluble part was then removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was dissolved in water (*ca*. 10 mL) and dialyzed using a Spectra/Por membrane (MW = 500). The resulting aqueous solution was filtered by membrane filtration and the filtrate was lyophilized to obtain **9merH** as a slightly brown powder (610 mg, 0.579 mmol, 88.8% yield). Mp: 300°C (dec). IR (KBr, cm^{-1}): 3399 ($\nu_{O\text{-}H}$), 1616, 1492, 1405, 1279, 1161, 976, 841. ^1H NMR (CD_3CN): δ 6.38 (dd, J = 8.0, 2.5 Hz, Ar-$H_{5\text{ and }5''''''''}$, 2H), 6.40 (d, J = 2.5 Hz, Ar-$H_{3\text{ and }3''''''''}$, 2H), 6.54 (2 x s, Ar, 2H and 3H), 6.55 (s, Ar, 2H), 6.99 (s, Ar, 2H), 7.00 (d, J = 8.0 Hz, Ar-$H_{6\text{ and }6''''''''}$, 2H), 7.05 (s, Ar, 2H), 7.06 (s, Ar, 3H), 6.0–8.0 (br, OH, 18H). ^1H NMR (CD_3OD): δ 7.10 (d, J = 2.5 Hz, Ar-$H_{3\text{ and }3''''''''}$, 2H, and dd, J = 9.0, 2.5 Hz, Ar-$H_{5\text{ and }5''''''''}$, 2H), 7.23 (s, Ar, 2H), 7.24 (2 x s, Ar, 3H and 2H), 7.76 (d, J = 9.0 Hz, Ar-$H_{6\text{ and }6''''''''}$, 2H), 7.77 (s, Ar, 2H), 7.83 (2 x s, Ar, 2H and 3H). ^{13}C NMR (CD_3CN): δ 104.02, 104.75, 104.78, 104.81, 104.83, 108.98, 117.92, 118.86, 118.88, 118.90, 118.97, 118.99, 119.27, 133.33, 135.13 135.19, 135.22, 135.24, 154.96, 155.00, 155.07, 155.10, 155.11, 155.14, 155.47, 158.51. ESI-MS (CH_3OH, negative): Calcd for $C_{54}H_{37}O_{18}$ [**9merH**–H]$^-$: m/z = 973.20. Found: m/z = 973.24. Anal. Calcd for $C_{54}H_{38}O_{18}\cdot 4.4H_2O$: C, 64.13; H, 4.54. Found: C, 64.03; H, 4.52.

3-2. Synthesis of Chiral Oligoresorcinols

Chiral oligoresorcinols were synthesized according to Scheme S-2. The reaction progresses were monitored by TLC or ESI-MS.

Scheme S-2. Synthesis of Chiral Oligomers[a]



[a] Reagents and conditions: (a) (1) *t*-BuLi, THF, –78°C, 25 min, (2) $MgBr_2 \cdot Et_2O$, –78°C, 30 min, (3) (*S*)-1-bromo-2-methyl-butane, $CuCl_2$, reflux, 2 days; (b) DBH, 0°C, 1 day; (c) pinacolborane, $PdCl_2(PPh_3)_2$, NEt_3, 1,4-dioxane, 80°C, 1 day; (d) **1merRBP**, $Pd(PPh_3)_4$, K_2CO_3, toluene, H_2O, 80°C, 2 days; (e) DIH, 0°C, 1 day; (f) **4merRBP**, $Pd(PPh_3)_4$, K_2CO_3, toluene, H_2O, 80°C, 2 days; (g) BBr_3, 0°C, 4 days.

1merR [4-((*S*)-2-Methylbutyl)-1,3-dimethoxybenzene][7]

To a solution of **1merBr** (9.7 g, 44.7 mmol) in dehydrated THF (90 mL) was slowly added *t*-BuLi (1.45 M in *n*-pentane, 61 mL, 88.5 mmol, Kanto Chemical) over 15 min at –78°C under Ar, and then the solution was further stirred for 10 min at room temperature. The solution was again cooled to –78°C and $MgBr_2 \cdot Et_2O$ (12.7 g, 49.2 mmol, Aldrich) was then added at one time. After being stirred at room temperature for 30 min, the resulting suspension became an almost clear yellow solution. (*S*)-1-Bromo-2-methylbutane (8.1 g, 53.6 mmol, Aldrich) and copper(II) chloride (180 mg, 1.34 mmol, Aldrich) were subsequently added to the solution at –78°C. The solution was stirred at room temperature for 30 min and then refluxed for 2 days. After evaporation, the residue was dissolved in *n*-hexane and the solution was washed with brine. The organic layer was washed with an aqueous EDTA solution, dried over Na_2SO_4, and filtered. After concentrated *in vacuo*, the crude product was purified by short NH_2-SiO_2 chromatography (CH_2Cl_2) and then by subsequent SiO_2 chromatography (*n*-hexane) to obtain **1merR** as a colorless oil (3.53 g, 16.9 mmol, 37.9% yield). IR (neat, cm^{-1}): 2998, 2958, 1613, 1506, 1464, 1288, 1208, 1156, 1040, 927, 834. ^{1}H NMR ($CDCl_3$): δ 0.82 (d, CHC*H*$_3$, J = 7.0 Hz, 3H), 0.89 (t, CH_2C*H*$_3$, J = 7.5 Hz, 3H), 1.14 (m, C*H*CH_3, 1H), 1.38 (m, C*H*CH_3, 1H), 1.62 (m, CH, 1H), 2.29 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.55 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.78 (s, OMe, 3H), 3.79 (s, OMe, 3H), 6.41 (dd, Ar-H_6, J = 8.0, 2.5 Hz, 1H), 6.44 (d, Ar-H_2, J = 2.5 Hz, 1H), 6.98 (d, Ar-H_5, J = 8.0 Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 11.51, 19.01, 29.35, 35.20, 36.77, 55.25, 55.30, 98.41, 103.55, 122.62, 130.91, 158.54, 158.92.

1merRBr [4-Bromo-6-((*S*)-2-methylbutyl)-1,3-dimethoxybenzene]

To a solution of **1merR** (3.48 g, 16.7 mmol) in THF (50 mL) was added DBH (2.50 g, 8.74 mmol) at 0°C and the mixture was stirred overnight at that temperature. After evaporation, the residue was dissolved in *n*-hexane and the solution was washed with sat. $Na_2S_2O_3$ aq., dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by short SiO_2 chromatography with *n*-hexane/ethyl acetate (4/1, v/v) to give **1merRBr** as a colorless oil (4.75 g, 16.5 mmol, 99.0% yield). IR (neat, cm^{-1}): 3001, 2958, 1602, 1503, 1463, 1289, 1204, 1161, 1036, 891, 813. ^{1}H NMR ($CDCl_3$): δ 0.82 (d, CHCH_3, J = 7.0 Hz, 3H), 0.89 (t, CH_2CH_3, J = 7.5 Hz, 3H), 1.14 (m, CHCH$_3$, 1H), 1.36 (m, CHCH$_3$, 1H), 1.60 (m, CH, 1H), 2.27 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.53 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.81 (s, OMe, 3H), 3.89 (s, OMe, 3H), 6.45 (s, Ar-H$_2$, 1H), 7.21 (s, Ar-H$_5$, 1H). ^{13}C NMR ($CDCl_3$): δ 11.48, 18.92, 29.29, 35.21, 36.38, 55.63, 56.41, 96.67, 101.22, 124.08, 134.25, 154.58, 157.83.

1merRBP [5-((*S*)-2-Methylbutyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-2,4-dimethoxybenzene]

To a solution of **1merRBr** (4.70 g, 16.3 mmol) and $PdCl_2(PPh_3)_2$ (564 mg, 0.804 mmol) in dehydrated 1,4-dioxane (50 mL) were added distilled NEt_3 (6.9 mL, 49.2 mmol) and pinacolborane (3.5 mL, 24.6 mmol) under Ar, and subsequently the mixture was heated at 80°C overnight. After concentration, the black residue was extracted with Et_2O (*ca*. 100 mL). The Et_2O-insoluble black precipitate was removed with Celite filtration. After concentration of the filtrate, the crude product was purified by

SiO_2 chromatography with *n*-hexane/Et_2O (2/1, v/v) to obtain **1merRBP** as a white solid (5.13 g, 15.4 mmol, 93.6% yield). Mp: 53–54°C. IR (KBr, cm^{-1}): 3367, 2999, 2956, 1609, 1507, 1468, 1413, 1334, 1260, 1209, 1146, 1035, 864, 815. ^{1}H NMR ($CDCl_3$): δ 0.81 (d, CHCH_3, J = 6.5 Hz, 3H), 0.89 (t, CH_2CH_3, J = 7.5 Hz, 3H), 1.14 (m, CHCH_3, 1H), 1.33 (s, Me, 12H), 1.37 (m, CHCH_3, 1H), 1.63 (m, CH, 1H), 2.30 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.54 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.82 (s, OMe, 3H), 3.83 (s, OMe, 3H), 6.38 (s, Ar-H_3, 1H), 7.39 (s, Ar-H_6, 1H). ^{13}C NMR ($CDCl_3$): δ 11.54, 18.96, 24.81, 29.43, 35.38, 36.55, 55.15, 56.37, 82.98, 94.95, 121.92, 138.91, 161.32, 164.62.

4merR [5-((*S*)-2-Methylbutyl)-2,4,4',6',4'',6'',2''',4'''-octamethoxy-1,1':3',1'':3'',1'''-quarterphenyl]

To a solution of **3merBr** (2.45 g, 5.0 mmol), **1merRBP** (1.67 g, 5.0 mmol), and $Pd(PPh_3)_4$ (289 mg, 0.25 mmol) in dehydrated toluene (30 mL) was added a degassed K_2CO_3 aqueous solution (2 M, 7.5 mL, 15 mmol) under Ar and the mixture was heated at 80°C for 2 days. After most of the solvent had been removed by evaporation, the aqueous solution was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by NH_2-SiO_2 chromatography with CH_2Cl_2 and subsequent by SiO_2 chromatography with THF/*n*-hexane (1/3 to 1/0, v/v) to obtain a mixture of **3merBr** and **4merR**. *n*-BuLi (1.6 M in *n*-hexane, 10 mL, 160 mmol) was slowly added to a solution of the mixture (**3merBr** and **4merR**) in THF (20 mL) over 10 min at –78°C and the mixture was

stirred at that temperature for 1 h. After methanol (10 mL) was slowly added to the mixture over 5 min at –78°C, the solution was warmed to room temperature. After evaporation, the residue was dissolved in ethyl acetate and the solution was washed with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 chromatography with THF/*n*-hexane (1/3 to 1/0, v/v) and subsequently by NH_2-SiO_2 chromatography with CH_2Cl_2/ethyl acetate (1/1, v/v) to obtain **4merR** as a white solid (2.21 g, 3.58 mmol, 71.6% yield). Mp: 173–175°C. IR (KBr, cm^{-1}): 2995, 2954, 1605, 1492, 1462, 1300, 1203, 1158, 1032, 931, 815. ^{1}H NMR ($CDCl_3$): δ 0.84 (d, CHCH_3, J = 6.5 Hz, 3H), 0.88 (t, CH_2CH_3, J = 7.5 Hz, 3H), 1.14 (m, CHCH_3, 1H), 1.40 (m, CHCH_3, 1H), 1.63 (m, CH, 1H), 2.30 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.55 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.75 (s, OMe, 3H), 3.77 (s, OMe, 3H), 3.81 (2 x s, OMe, 2 x 3H), 3.82 (s, OMe, 3H), 3.83 (s, OMe, 6H), 3.84 (s, OMe, 3H), 6.50 (s, Ar, 1H), 6.52 (dd, J = 8.0, 2.5 Hz, Ar-$H_{5'''}$, 1H), 6.53 (d, Ar-$H_{3'''}$, J = 2.5 Hz, 1H), 6.62 (2 x s, Ar, 2 x 1H), 6.98 (s, Ar, 1H), 7.18 (d, J = 8.0 Hz, Ar-$H_{6'''}$, 1H, and s, Ar, 1H), 7.19 (s, Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 11.53, 19.15, 29.38, 35.14, 36.69, 55.30, 55.45, 55.64, 55.81, 55.85, 56.00, 95.71, 96.01, 96.10, 98.85, 104.12, 118.87, 119.16, 119.26, 119.33, 119.59, 120.26, 121.63, 132.14, 133.89, 134.74, 134.76, 156.00, 157.04, 157.14, 157.48, 158.10, 159.92. HRMS (ESI+): *m/z* calcd for $C_{37}H_{44}NaO_8$ ($M+Na^+$), 639.29339; found, 639.29149.

4merRBr [5-Bromo-5'''-((*S*)-2-methylbutyl)-2,4,4',6',4'',6'',2''',4'''-octamethoxy-1,1':3',1'':3'',1'''-quaterphenyl]

To a solution of **4merR** (1.09 g, 1.77 mmol) in THF (20 mL) was added DBH (304 mg, 1.06 mmol) at 0°C and the mixture was stirred overnight at that temperature. After evaporation, the residue was dissolved in $CHCl_3$ and the solution was washed with sat. $Na_2S_2O_3$ aq., dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by NH_2-SiO_2 chromatography with $CHCl_3$/*n*-hexane (1/2 to 1/1, v/v) to obtain **4merRBr** as a white solid (1.24 g, 1.78 mmol, 100% yield). Mp: 96–99°C. IR (KBr, cm^{-1}): 2995, 2955, 1601, 1491, 1462, 1282, 1203, 1168, 1034, 932, 816. ^{1}H NMR ($CDCl_3$): δ 0.84 (d, CHC*H*$_3$, J = 6.5 Hz, 3H), 0.88 (t, CH_2C*H*$_3$, J = 7.5 Hz, 3H), 1.14 (m, C*H*CH_3, 1H), 1.40 (m, C*H*CH_3, 1H), 1.63 (m, CH, 1H), 2.30 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.56 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.77 (s, OMe, 3H), 3.78 (s, OMe, 3H), 3.81 (s, OMe, 3H), 3.82 (s, OMe, 3H), 3.84 (3 x s, OMe, 3 x 3H), 3.92 (s, OMe, 3H), 6.51 (s, Ar, 1H), 6.55 (s, Ar, 1H), 6.61 (s, Ar, 1H), 6.62 (s, Ar, 1H), 6.99 (s, Ar, 1H), 7.15 (s, Ar, 1H), 7.17 (s, Ar, 1H), 7.42 (s, Ar-H_6, 1H). ^{13}C NMR ($CDCl_3$): δ 11.53, 19.14, 29.38, 35.14, 36.69, 55.45, 55.83, 55.85, 55.87, 56.00, 56.09, 56.36, 95.71, 95.90, 96.13, 97.10, 101.66, 117.80, 118.81, 119.04, 119.50, 119.64, 121.45, 121.64, 133.87, 134.60, 134.66, 135.43, 155.59, 155.99, 156.90, 157.01, 157.13, 157.47, 157.50. HRMS (ESI+): *m/z* calcd for $C_{37}H_{43}BrNaO_8$ ($M+Na^+$), 717.20390; found, 717.19747.

4merRBP [5'''-((*S*)-2-Methylbutyl)-4,6,4',6',4'',6'',2''',4'''-octamethoxy-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolyl)-1,1':3',1'':3'',1'''-quaterphenyl]

To a solution of **4merRBr** (1.21 g, 1.74 mmol) and $PdCl_2(PPh_3)_2$ (61 mg, 0.087 mmol) in dehydrated 1,4-dioxane (20 mL) were added distilled NEt_3 (1.46 mL, 10.4

mmol) and pinacolborane (0.75 mL, 5.21 mmol) under Ar, and subsequently the mixture was heated at 80°C overnight. After concentration, the black residue was extracted with Et_2O (*ca*. 100 mL). The Et_2O-insoluble black precipitate was removed with Celite filtration. After concentration of the filtrate, the crude product was purified by SiO_2 chromatography with Et_2O/*n*-hexane (4/1, v/v) to obtain **4merRBP** as a slightly brown solid (1.10 g, 1.48 mmol, 85.1% yield). Mp: 113–115°C. IR (KBr, cm^{-1}): 2992, 2956, 1603, 1493, 1463, 1437, 1334, 1269, 1203, 1168, 1145, 1034, 931, 818. ^1H NMR ($CDCl_3$): δ 0.84 (d, CHCH_3, J = 7.0 Hz, 3H), 0.88 (t, CH_2CH_3, J = 7.5 Hz, 3H), 1.14 (m, CHCH$_3$, 1H), 1.30 (s, Me, 12H), 1.40 (m, CHCH$_3$, 1H), 1.64 (m, CH, 1H), 2.30 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.55 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.77 (s, OMe, 3H), 3.80 (2 x s, OMe, 2 x 3H), 3.81 (s, OMe, 3H), 3.83 (2 x s, OMe, 6H and 3H), 3.87 (s, OMe, 3H), 6.47 (s, Ar, 1H), 6.50 (s, Ar, 1H), 6.60 (s, Ar, 1H), 6.61 (s, Ar, 1H), 6.99 (s, Ar, 1H), 7.16 (s, Ar, 1H), 7.18 (s, Ar, 1H), 7.60 (s, Ar-H_2, 1H). ^{13}C NMR ($CDCl_3$): δ 11.53, 19.15, 24.79, 29.38, 35.13, 36.68, 55.45, 55.58, 55.83, 55.88, 55.91, 55.99, 56.23, 82.95, 95.18, 95.68, 96.01, 96.13, 118.85, 119.33, 119.43, 119.54, 119.78, 121.58, 133.90, 134.64, 134.71, 140.30, 155.98, 157.00, 157.01, 157.11, 157.17, 157.45, 160.90, 165.46.

3merI [5-Iodo-2,4,4',6',2'',4''-hexamethoxy-1,1':3',1''-terphenyl]

To a solution of **3merMe** (4.1 g, 10 mmol) in THF (100 mL) was added DIH (5.7 g, 15 mmol) at 0°C and the solution was stirred at that temperature for 1 day. To the solution was added a 20 w% aqueous $Na_2S_2O_3$ solution (50 mL) at 0°C to quench any

excess DIH. After most of the solvent had been removed by evaporation, the aqueous solution was extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 chromatography with THF/*n*-hexane (1/2, v/v) to obtain **3merI** as a slightly brown solid (2.70 g, 5.02 mmol, 50.2% yield). Mp: 83–85°C. IR (KBr, cm^{-1}): 2997, 2936, 1606, 1489, 1463, 1358, 1282, 1205, 1160, 1032, 930, 818. ^1H NMR ($CDCl_3$): δ 3.77 (s, OMe, 3H), 3.80 (s, OMe, 3H), 3.82 (s, OMe, 3H), 3.83 (s, OMe, 6H), 3.91 (s, OMe, 3H), 6.50 (s, Ar-H_3, 1H), 6.53 (dd, Ar-$H_{5''}$, J = 8.0, 2.5 Hz, 1H), 6.54 (d, Ar-$H_{3''}$, J = 2.5 Hz, 1H), 6.60 (s, Ar-$H_{5'}$, 1H), 7.08 (s, Ar-$H_{2'}$, 1H), 7.18 (d, Ar-$H_{6''}$, J = 8.0 Hz, 1H), 7.63 (s, Ar-H_6, 1H). ^{13}C NMR ($CDCl_3$): δ 55.33, 55.65, 55.86, 55.88, 55.96, 56.46, 74.16, 95.94, 96.27, 98.90, 104.18, 117.83, 119.38, 120.01, 122.29, 132.06, 134.33, 141.17, 156.99, 157.49, 158.10, 158.14, 158.67, 160.05. HRMS (ESI+): *m/*z calcd for $C_{24}H_{25}INaO_6$ ($M+Na^+$), 559.05935; found, 559.05786.

7merR [5-((*S*)-2-methylbutyl)-2,4,4',6',4'',6'',4''',6''',4'''',6'''',4''''',6''''',2''''''',4''''''-tetradecamethoxy-1,1':3',1'':3'',1''':3''',1'''':3'''',1''''':3''''',1'''''':3'''''-septiphenyl]

To a solution of **3merI** (320 mg, 0.60 mmol), **4merRBP** (446 mg, 0.60 mmol), and $Pd(PPh_3)_4$ (21 mg, 0.018 mmol) in dehydrated toluene (10 mL) was added a degassed aqueous K_2CO_3 solution (2 M, 2 mL, 4 mmol) under Ar and the mixture was heated at 80°C for 2 days. After most of the solvent had been removed by evaporation at room temperature, the aqueous solution was extracted with $CHCl_3$. The organic layer was

dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 chromatography with THF/*n*-hexane (1/1 to 2/1, v/v) and subsequently by NH_2-SiO_2 chromatography with CH_2Cl_2/*n*-hexane (1/3 to 2/1, v/v) to obtain **7merR** as a white solid (387 mg, 0.378 mmol, 62.9% yield). Mp: 143–145°C. IR (KBr, cm^{-1}): 2994, 2953, 1604, 1491, 1463, 1282, 1202, 1167, 1034, 931, 818. ^1H NMR ($CDCl_3$): δ 0.83 (d, CHCH_3, J = 6.5 Hz, 3H), 0.88 (t, CH_2CH_3, J = 7.5 Hz, 3H), 1.13 (m, CHCH$_3$, 1H), 1.40 (m, CHCH$_3$, 1H), 1.63 (m, CH, 1H), 2.30 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.55 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.72 (s, OMe, 3H), 3.75 (s, OMe, 3H), 3.80 (s, OMe, 24H), 3.82 (s, OMe, 9H), 3.83 (s, OMe, 3H), 6.49 (s, Ar, 1H), 6.50 (dd, Ar-$H_{5'''''''}$, J = 8.0, 2.5 Hz, 1H), 6.52 (d, Ar-$H_{3'''''''}$, J = 2.5 Hz, 1H), 6.59 (s, Ar, 1H), 6.60 (2 x s, Ar, 3H and 1H), 6.98 (s, Ar, 1H), 7.15 (s, Ar, 1H), 7.16 (s, Ar, 1H), 7.17 (d, Ar-$H_{6'''''''}$, J = 8.0 Hz, 1H), 7.21 (2 x s, Ar, 2 x 1H), 7.22 (s, Ar, 1H). ^{13}C NMR ($CDCl_3$): δ 11.53, 19.14, 29.37, 35.11, 36.68, 55.26, 55.42, 55.61, 55.78, 55.79, 55.80, 55.82, 55.84, 55.99, 95.71, 95.97, 96.08, 98.82, 104.08, 118.91, 119.07, 119.11, 119.15, 119.16, 119.21, 119.29, 119.31, 119.46, 120.32, 121.52, 132.13, 133.90, 134.78, 134.96, 134.99, 135.01, 155.99, 156.92, 156.96, 157.00, 157.02, 157.11, 157.40, 158.09, 159.84. HRMS (ESI+): *m/z* calcd for $C_{61}H_{68}NaO_{14}$ ($M+Na^+$), 1047.45067; found, 1047.44546.

7merRI [5-Iodo-5’’’’’’-((*S*)-2-methylbutyl)-2,4,4’,6’,4’’,6’’,4’’’,6’’’,4’’’’,6’’’’,4’’’’’,6’’’’’,2’’’’’’,4’’’’’’-tetradecamethoxy-1,1’:3’,1’’:3’’,1’’’:3’’’,1’’’’:3’’’’,1’’’’’:3’’’’’,1’’’’’’-septiphenyl]

To a solution of **7merR** (350 mg, 0.34 mmol) in THF (20 mL) was added DIH

(2.28 g, 6.0 mmol) at 0°C and the mixture was stirred at that temperature for 1 day. To the solution was added a 20 w% aqueous $Na_2S_2O_3$ solution (20 mL) at 0°C. After most of the solvent had been removed by evaporation, the aqueous solution was extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 chromatography with THF/*n*-hexane (1/1 to 2/1, v/v) to obtain **7merRI** as a white solid (354 mg, 0.308 mmol, 90.3% yield). Mp: 148–150°C. IR (KBr, cm^{-1}): 2994, 2952, 2934, 1604, 1490, 1463, 1355, 1263, 1202, 1167, 1033, 931, 817. ^{1}H NMR ($CDCl_3$): δ 0.84 (d, CHCH_3, J = 6.5 Hz, 3H), 0.88 (t, CH_2CH_3, J = 7.5 Hz, 3H), 1.14 (m, CHCH$_3$, 1H), 1.40 (m, CHCH$_3$, 1H), 1.64 (m, CH, 1H), 2.30 (dd, CH_2, J = 13.5, 8.0 Hz, 1H), 2.55 (dd, CH_2, J = 13.5, 6.0 Hz, 1H), 3.74 (2 x s, OMe, 2 x 3H), 3.79 (s, OMe, 12H), 3.80 (s, OMe, 12H), 3.81 (s, OMe, 6H), 3.82 (s, OMe, 3H), 3.87 (s, OMe, 3H), 6.47 (s, Ar, 1H), 6.49 (s, Ar, 1H), 6.58 (s, Ar, 1H), 6.60 (2 x s, Ar, 3H and 1H), 6.98 (s, Ar, 1H), 7.11 (s, Ar, 1H), 7.16 (s, Ar, 1H), 7.18 (s, Ar, 1H), 7.19 (s, Ar, 1H), 7.21 (s, Ar, 1H), 7.61 (s, Ar-H$_6$, 1H). ^{13}C NMR ($CDCl_3$): δ 11.46, 19.07, 29.29, 35.04, 36.61, 55.35, 55.70, 55.73, 55.75, 55.76, 55.82, 55.91, 56.31, 73.94, 95.62, 95.81, 95.87, 95.91, 96.00, 96.15, 117.66, 118.81, 118.87, 119.03, 119.09, 119.18, 119.22, 119.40, 121.40, 122.27, 133.79, 134.44, 134.66, 134.75, 134.84, 141.04, 155.92, 156.75, 156.88 (x 2), 156.90, 156.93, 157.05, 157.33, 157.39, 157.94, 158.58. HRMS (ESI+): *m/z* calcd for $C_{61}H_{67}INaO14$ ($M+Na^+$), 1173.34732; found, 1173.34595.

11merR2 [5,5’’’’’’’’’’-Bis((*S*)-2-methylbutyl)-2,4,4’,6’,4’’,6’’,4’’’,6’’’,4’’’’,6’’’’,4’’’’’,6’’’’’,4’’’’’’,6’’’’’’,4’’’’’’’,6’’’’’’’,4’’’’’’’’,6’’

’’’’’’,4’’’’’’’’’,6’’’’’’’’’,2’’’’’’’’’’,4’’’’’’’’’’-docosamethoxy-1,1’:3’,1’’:3’’,1’’’:3’’’,1’’’’:3’’’’,1’’’’’:3’’’’’,1’’’’’’:3’’’’’’,1’’’’’’’:3’’’’’’’,1’’’’’’’’:3’’’’’’’,1’’’’’’’’’:3’’’’’’’’’,1’’’’’’’’’’-undeciphenyl]

To a solution of **7merRI** (320 mg, 0.278 mmol), **4merRBP** (309 mg, 0.417 mmol), and $Pd(PPh_3)_4$ (16 mg, 0.014 mmol) in dehydrated toluene (6 mL) was added a degassed aqueous K_2CO_3 solution (2 M, 1.5 mL, 3 mmol) and the mixture was stirred at 80°C for 2 days. After most of the toluene had been removed by evaporation at room temperature, the residue was extracted with $CHCl_3$. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified successively by short NH_2-SiO_2 chromatography with $CHCl_3$, by SiO_2 chromatography with $CHCl_3$/ethyl acetate (10/1, v/v), and by recycled preparative SEC chromatography with $CHCl_3$. The $CHCl_3$ solution was evaporated and the residue was dissolved in benzene and freeze-dried to obtain **11merR2** as a slightly brownish white solid (278 mg, 0.170 mmol, 61.2% yield). **11merR2**: $[\alpha]_D^{25}$: +2.9° (*c* = 1.11, $CHCl_3$). Mp: 299–301°C. IR (KBr, cm^{-1}): 2994, 2952, 1604, 1508, 1490, 1459, 1355, 1263, 1202, 1167, 1035, 930, 897, 818. ^{1}H NMR ($CDCl_3$): δ 0.83 (d, CHCH_3, *J* = 6.5 Hz, 6H), 0.88 (t, CH_2CH_3, *J* = 7.5 Hz, 6H), 1.14 (m, C*H*CH_3, 2H), 1.40 (m, C*H*CH_3, 2H), 1.64 (m, CH, 2H), 2.30 (dd, CH_2, *J* = 13.5, 8.0 Hz, 2H), 2.55 (dd, CH_2, *J* = 13.5, 6.0 Hz, 2H), 3.74 (s, OMe, 6H), 3.77 (s, OMe, 12H), 3.78 (s, OMe, 12H), 3.79 (2 x s, OMe, 2 x 12H), 3.81 (2 x s, OMe, 2 x 6H), 6.49 (s, Ar, 2H), 6.58 (s, Ar, 5H), 6.59 (s, Ar, 4H), 6.98 (s, Ar, 2H), 7.17 (s, Ar, 2H), 7.19 (s, Ar, 2H), 7.21 (s, Ar, 3H), 7.22 (s, Ar, 2H). ^{13}C NMR ($CDCl_3$): δ 11.48, 19.09, 29.32, 35.06, 36.64, 55.35, 55.72, 55.75, 55.78, 55.91, 95.65,

95.95, 95.98, 96.05, 118.85, 118.99, 119.01, 119.05, 119.08, 119.13, 119.24, 119.40, 121.43, 133.83, 134.72, 134.92, 134.99, 135.00, 155.95, 156.85, 156.87, 156.89, 156.92, 156.96, 157.35. ESI-MS (CH_2Cl_2/CH_3OH (1/1, v/v), positive): Calcd for $C_{98}H_{110}O_{22}Na$ [**11merR2**+Na]$^+$: *m/z* = 1662.74. Found: *m/z* = 1662.89. Anal. Calcd for $C_{98}H_{110}O_{22}\cdot 0.7H_2O$: C, 71.23; H, 6.79. Found: C, 71.26; H, 6.75.

11merHR2; [5,5’’’’’’’’’’-Bis((*S*)-2-methylbutyl)-2,4,4’,6’,4’’,6’’,4’’’,6’’’,4’’’’,6’’’’,4’’’’’,6’’’’’,4’’’’’’,6’’’’’’,4’’’’’’’,6’’’’’’’,4’’’’’’’’,6’’’’’’’’,4’’’’’’’’’,6’’’’’’’’’,2’’’’’’’’’’,4’’’’’’’’’’-docosahydroxy-1,1’:3’,1’’:3’’,1’’’:3’’’,1’’’’:3’’’’,1’’’’’:3’’’’’,1’’’’’’:3’’’’’’,1’’’’’’’:3’’’’’’’,1’’’’’’’’:3’’’’’’’’,1’’’’’’’’’:3’’’’’’’’’,1’’’’’’’’’’-undeciphenyl]

To a solution of **11merR2** (101 mg, 0.062 mmol) in dehydrated CH_2Cl_2 (20 mL) was dropwise added BBr_3 (1.0 M in CH_2Cl_2, 4.0 mL, 4.0 mmol) over 10 min at 0^{o}C under Ar, and the mixture was then stirred overnight at that temperature. After water (0.5 mL) was slowly added at the same temperature, the solution was slowly warmed to room temperature. After concentration, the resulting mixture was found to contain a considerable amount of HBr and water, which were repeatedly removed by evaporation as an azeotropic mixture with EtOH (20 mL) until the water was completely removed. The CH_3CN (*ca*. 10 mL)-insoluble part was removed by filtration, and the filtrate was concentrated *in vacuo*. The EtOH (*ca*. 10 mL)-insoluble part was then removed by filtration, and the filtrate was concentrated *in vacuo*. The residue was dissolved in water (*ca*. 10 mL) and dialyzed using a Spectra/Por membrane (MW = 500). The

resulting aqueous solution was filtered by membrane filtration and the filtrate was lyophilized to obtain **11merHR2** as a slightly brown powder (82.6 mg, 0.062 mmol, 100% yield). $[\alpha]_D^{25}$: +4.6 (c = 1.06, CH_3OH) and +107° (c = 0.27, H_2O). Mp: 270°C (dec). IR (KBr, cm^{-1}): 3399 (ν_{O-H}), 2959, 1611, 1497, 1408, 1280, 1163, 982, 841. ^1H NMR (CD_3CN): δ 0.76 (d, $CHCH_3$, J = 7.0 Hz, 6H), 0.82 (t, CH_2CH_3, J = 7.5 Hz, 6H), 1.08 (m, $CHCH_3$, 2H), 1.33 (m, $CHCH_3$, 2H), 1.57 (m, CH, 2H), 2.23 (dd, CH_2, J = 13.5, 8.0 Hz, 2H), 2.47 (dd, CH_2, J = 13.5, 6.0 Hz, 2H), 6.39 (s, Ar, 2H), 6.51 (s, Ar-$H_{5'''''}$, 1H, and s, Ar, 2H), 6.52 (2 x s, Ar, 2 x 2H), 6.53 (s, Ar, 2H), 6.85 (s, Ar, 2H), 6.98 (s, Ar, 2H), 7.01 (s, Ar-$H_{2'''''}$, 1H, and s, Ar, 2H), 7.03 (s, Ar, 2H), 7.05 (s, Ar, 2H), 6.0–8.0 (br, OH, 22H). ^1H NMR (CD_3OD): δ 1.51 (d, $CHCH_3$, J = 6.5 Hz, 6H), 1.56 (t, CH_2CH_3, J = 7.5 Hz, 6H), 1.82 (m, $CHCH_3$, 2H), 2.09 (m, $CHCH_3$, 2H), 2.34 (m, CH, 2H), 2.98 (dd, CH_2, J = 13.5, 8.0 Hz, 2H), 3.23 (dd, CH_2, J = 13.5, 6.0 Hz, 2H), 7.10 (s, Ar, 2H), 7.22 (s, Ar-$H_{2'''''}$, 1H), 7.23 (2 x s, Ar, 2 x 2H), 7.24 (s, Ar, 2H), 7.25 (s, Ar, 2H), 7.59 (s, Ar, 2H), 7.78 (s, Ar, 2H), 7.83 (3 x s, Ar, 2H, 3H and 2H). ^{13}C NMR (CD_3CN): δ 11.79, 19.21, 29.97, 36.07, 37.13, 104.00, 104.78, 104.81, 104.87, 117.48, 118.75, 118.77, 118.78, 118.81, 118.82, 118.93, 119.00, 119.57, 121.52, 134.65, 135.08, 135.19, 135.20, 153.02, 154.88, 154.92, 155.12, 155.13, 155.15, 155.16, 156.07. ESI-MS (CH_3OH, negative): Calcd for $C_{76}H_{65}O_{22}$ [**11merHR2**–H]$^-$: m/z = 1329.40. Found: m/z = 1329.51. Anal. Calcd for $C_{76}H_{66}O_{22}\cdot 7.7H_2O$: C, 62.09; H, 5.58. Found: C, 62.19; H, 5.20.

References

1. Chassaing, C.; Haudrechy, A.; Langlois, Y. *Tetrahedron Lett*. **1997**, *38*, 4415–4416.

2. Narioka, T.; Ishikawa, T. *Heterocycles* **2002**, *56*, 413–420.

3. Majetich, G.; Hicks, R.; Reister, S. *J. Org. Chem*. **1997**, *62*, 4321–4326.

4. Monkman, A. P.; Palsson, L.-O.; Higgins, R. W. T.; Wang, C.; Bryce, M.; Batsanov, A. S.; Howard, J. A. K. *J. Am. Chem. Soc*. **2002**, *124*, 6049–6055.

5. Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *J. Org. Chem*. **2000**, *65*, 164–168.

6. Neuteboom, E. E.; Meskers, S. C. J.; van Hal, P. A.; van Duren, J. K. J.; Meijer, E. W.; Janssen, R. A. J.; Dupin, H.; Pourtois, G.; Cornil, J.; Lazzaroni, R.; Brédas, J.-L.; Beljonne, D. *J. Am. Chem. Soc*. **2003**, *125*, 8625–8638.

7. Terao, J.; Ikumi, A.; Kuniyasu, H.; Kambe, N. *J. Am. Chem. Soc.* **2003**, *125*, 5646–5647.

4. Investigation of Double Helix Formation of Oligoresorcinols

4-1. Concentration Effect

The ^{1}H NMR (500 MHz, 25°C) spectra of **9merH** in D_2O exhibited almost no change in the range of 0.1 to 8 mM, suggesting that **9merH** forms the stable double helix within the concentration range.

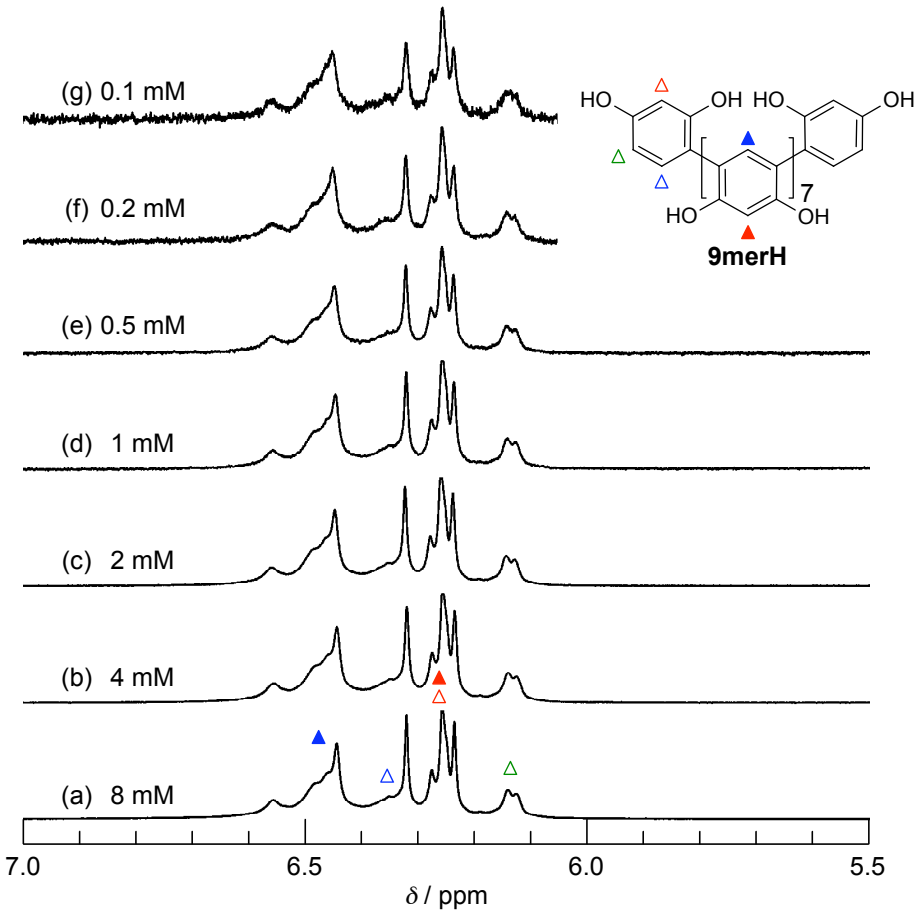


Figure S-1. ^{1}H NMR spectra of **9merH** in D_2O at 25°C. 1,4-Dioxane in D_2O was used as the external standard. [**9merH**] = 8 (a), 4 (b), 2 (c), 1 (d), 0.5 (e), 0.2 (f), and 0.1 mM (g).

4-2. Temperature Effect

The ^{1}H NMR signals of **9merH** in D_2O slightly shifted downfield and became sharper with an increase in temperature, suggesting that the double helix of **9merH** dissociates into the corresponding single strands to a lesser extent at high temperatures.

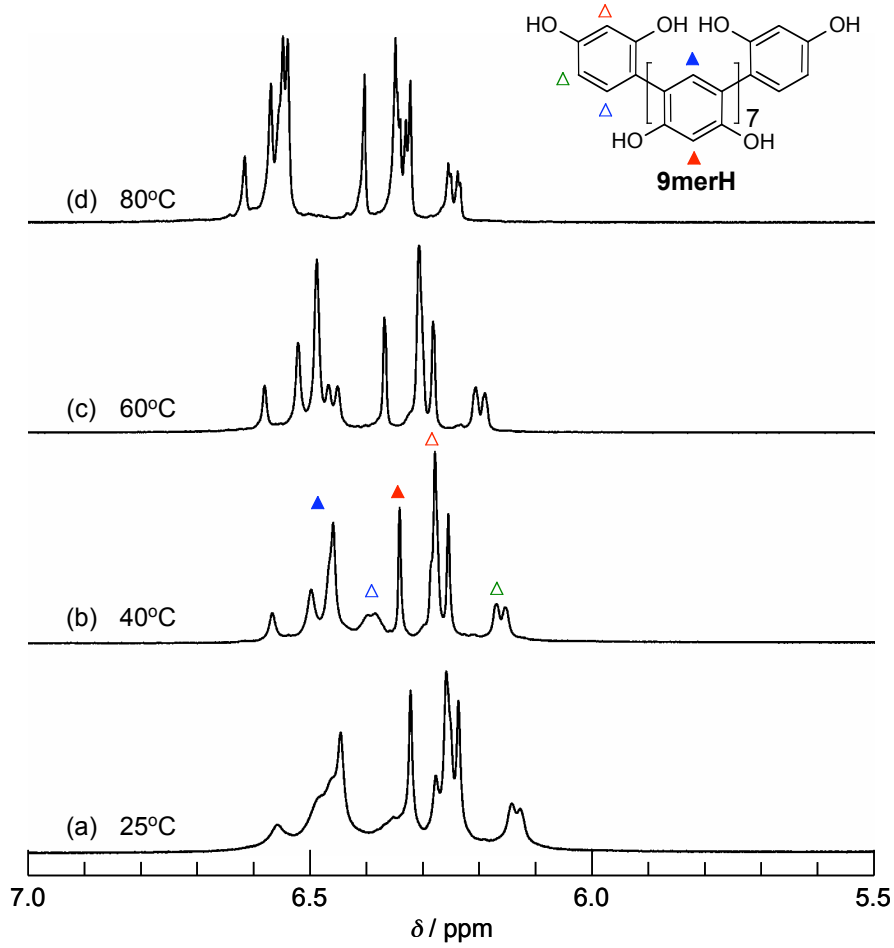


Figure S-2. ^{1}H NMR spectra of **9merH** in D_2O at various temperatures. 1,4-Dioxane in D_2O was used as the external standard.

The ^{1}H NMR signals of **9merH** in D_2O/CD_3OD (72/28, v/v) largely shifted downfield and were quite broadened compared with those in D_2O, suggesting that most of **9merH** exists as a single strand at high temperatures

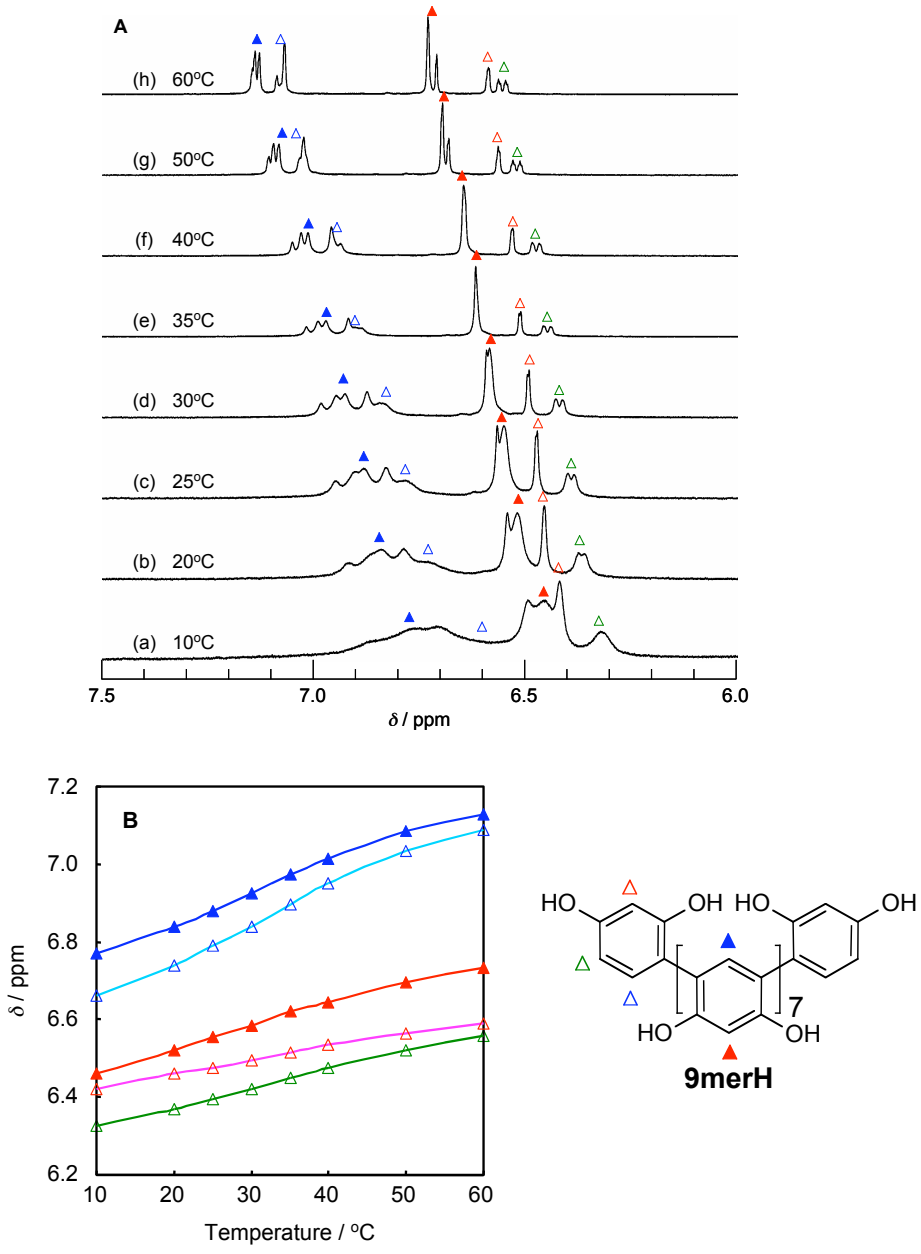


Figure S-3. **(A)** ^{1}H NMR spectral changes of **9merH** in D_2O/CD_3OD (72/28, v/v). [**9merH**] = 1 mM. (B) Plots of the chemical shifts of the marked signals *vs*. temperature.

The ^{1}H NMR signals of **6merH** in D_2O shifted downfield with an increase in temperature, indicating that the double helix of **6merH** favorably dissociates into the single strands at high temperatures in D_2O.

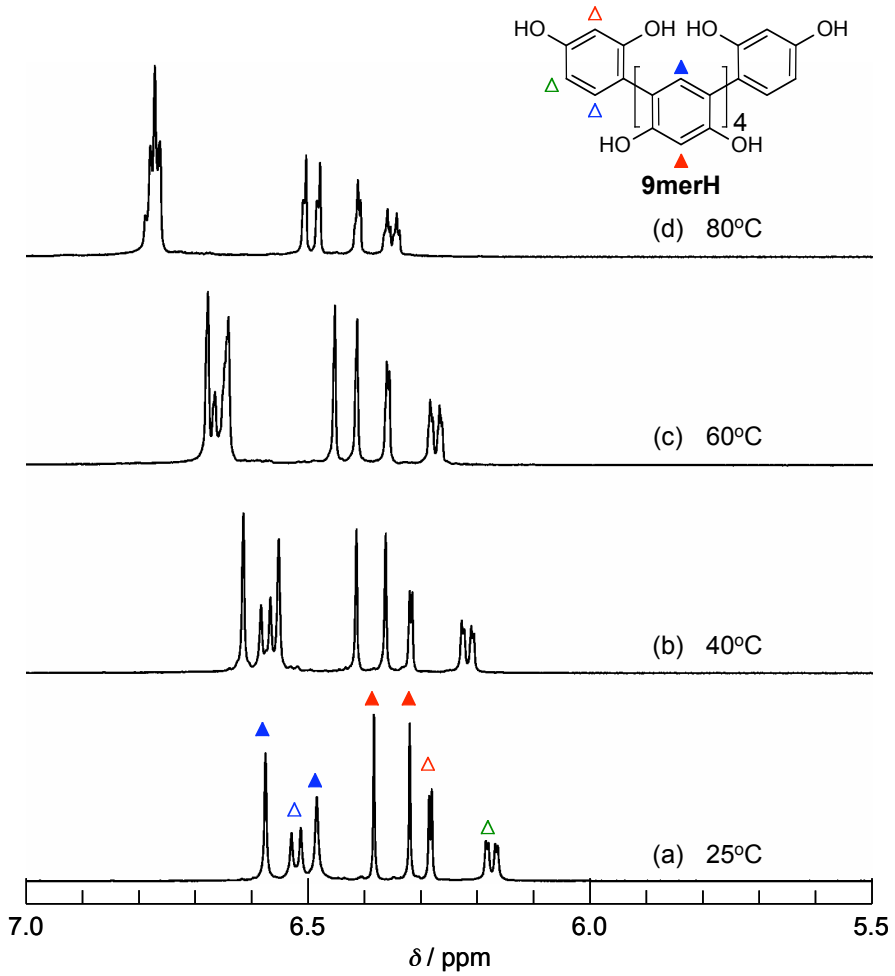


Figure S-4. ^{1}H NMR spectra of **6merH** in D_2O at various temperatures. 1,4-Dioxane in D_2O was used as the external standard.

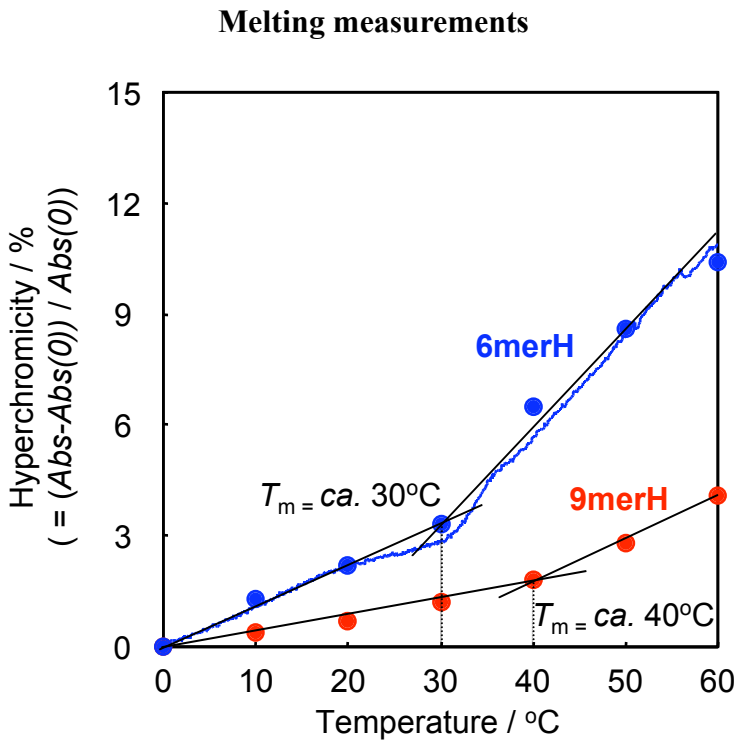


Figure S-5. UV melting profiles of **6merH** (blue line (heating rate 0.5 °C/min) and blue circles) and **9merH** (red circles) in H_2O. [**6merH**] = 1.5 mM, [**9merH**] = 1 mM.

4-3. VPO Measurement

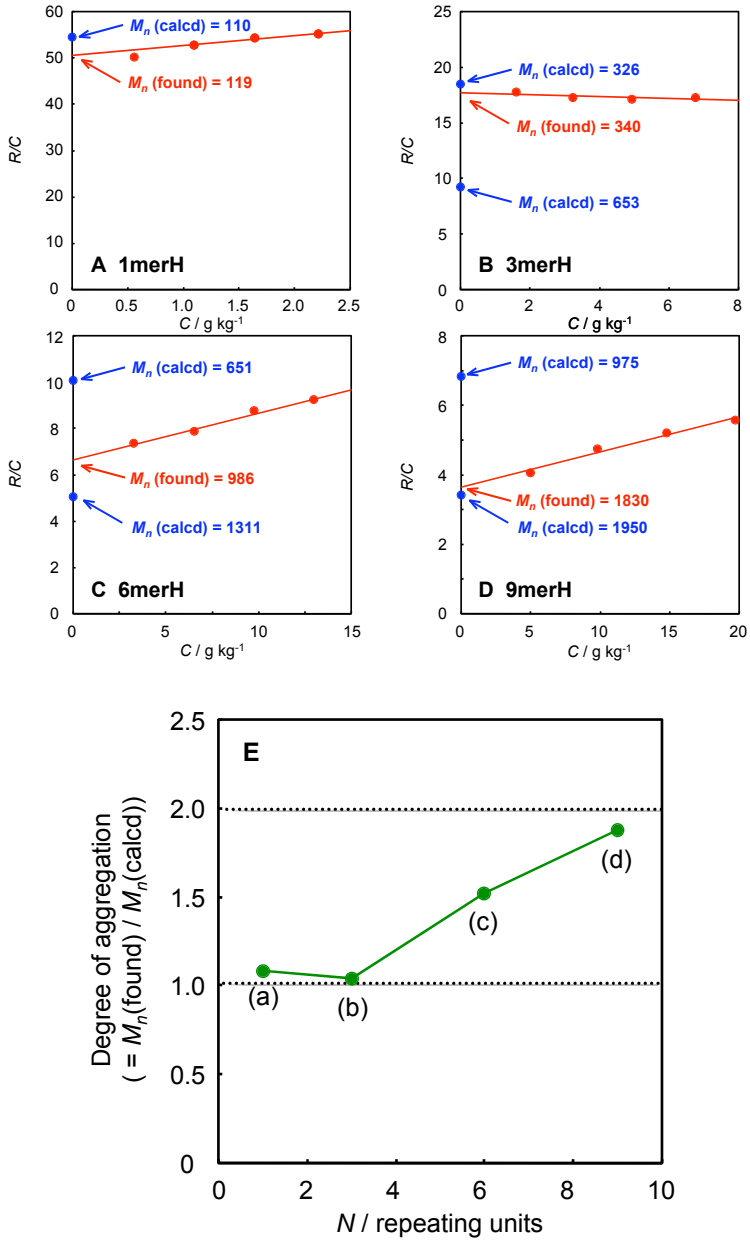


Figure S-6. (A–D) Plots of *R*/*C vs.* concentration of oligoresorcinols (**1merH** (A), **3merH** (B), **6merH** (C), and **9merH** (D)) in H_2O at 40°C (*R*: VPO response, arbitrary unit; *C*: initial concentration of oligomer). [Oligomers] = 5, 10, 15, and 20 mmol/kg. (E) Plots of the degree of aggregation of the oligomers (M_n (found) / M_n (calcd)) in H_2O.

4-4. Chain Length Dependence of Absorption Spectra

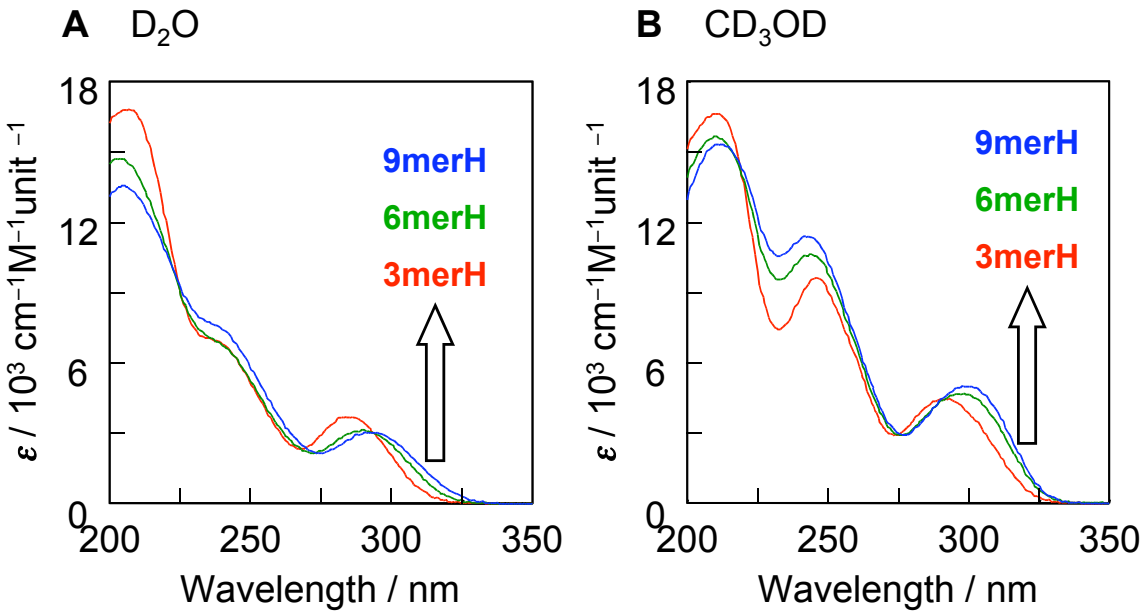


Figure S-7. Absorption spectra of oligoresorcinols (**3merH**, **6merH**, and **9merH**) in D_2O (A) and CD_3OD (B) at 25 °C.

4-5. Molecular Modeling and Calculations

Molecular modeling and molecular mechanics calculations were performed using the Compass Force Field as implemented in the Materials Studio software (version 3.0; Accerlys Inc.). The models of the single strands of **9merH** and **11merHR2** were constructed using Materials Visualizer in the Materials Studio. The parameter, "relative electric" was set to 4 that is the recommended value for calculations in water. The initial conformations of the main chains of **9merH** and **11merHR2** were constructed based on the crystal structures of the poly- or oligo(*m*-phenylene) that adopt the 5_1-helical conformation.[1] Charges on the atoms of the oligomers were calculated using the charge equilibration (QEq) in the Materials Studio; the total charge of the molecule was set to 0. The structures of the double helices of **9merH** and **11merHR2** were constructed by duplicating the initial structures of the single strands of **9merH** and **11merHR2.** The energy minimization was conducted using the Smart Minimizer of the Discover module until the root-mean-square (rms) value became less than 0.1 kcal mol^{-1} $Å^{-1}$. Molecular dynamics calculations were run for 1 ns at a constant volume and temperature (300 K) (NVT MD using the Nosé temperature thermostat[2]) with a step size of 1 fs, and the trajectory structures were obtained at 20 ps intervals.

The double helices of both **9merH** and **11merHR2** were calculated to be more stable than their single strands by energy minimization. Furthermore, the MD simulations showed that the double helical structures were retained after the 1 ns MD calculations at 300 K, while the single helices were broken.

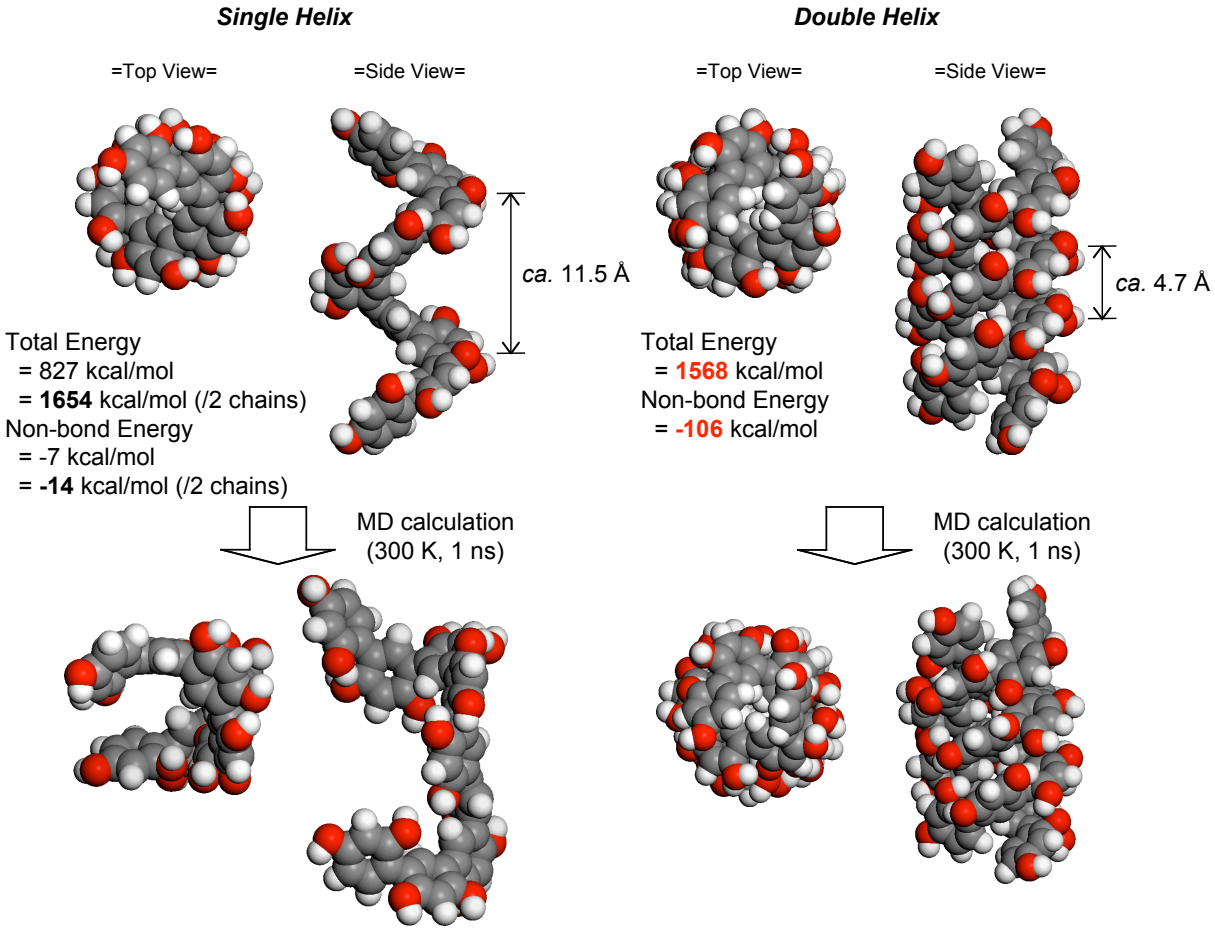


Figure S-8. Possible models for single and double helices of **9merH.**

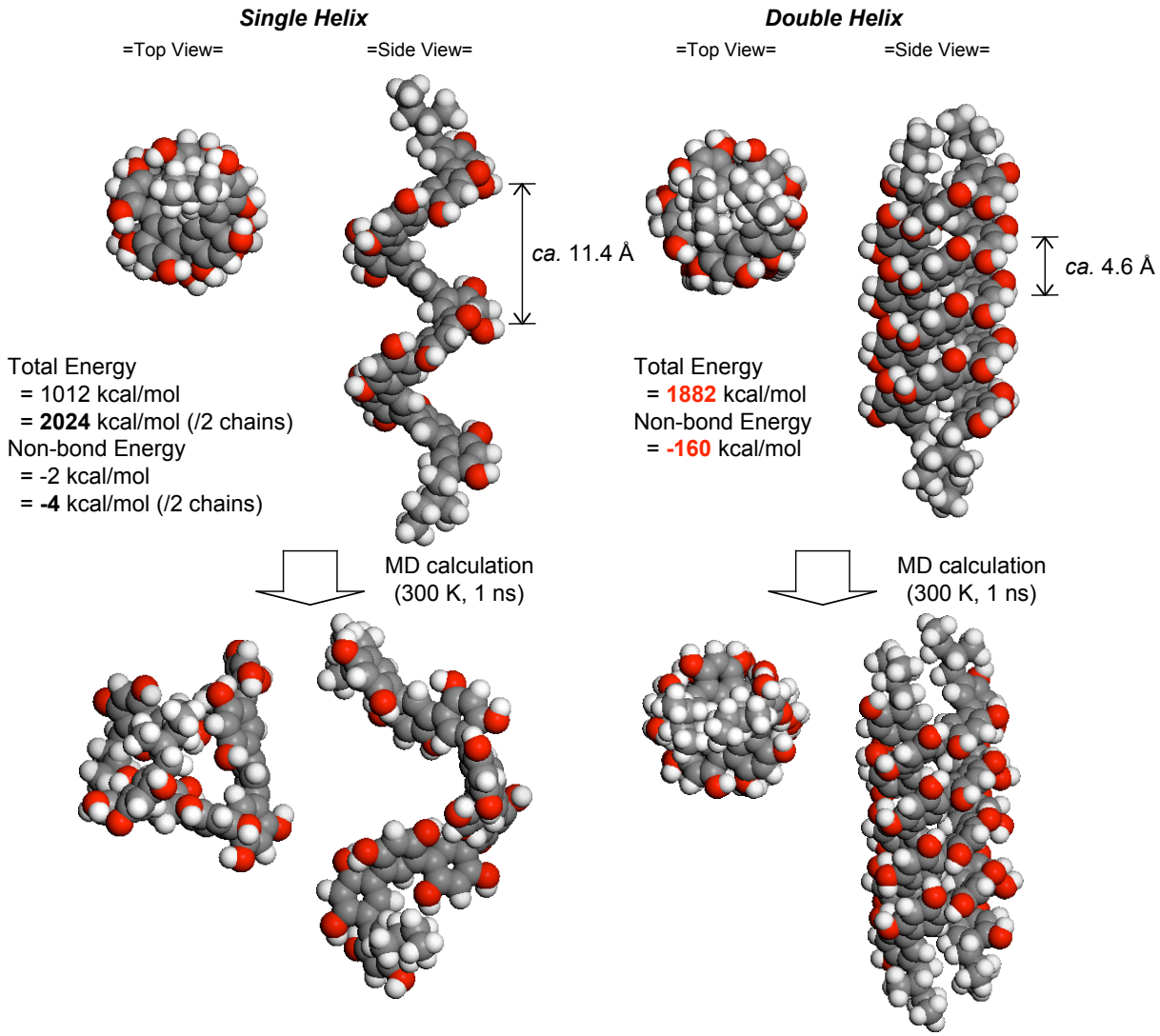


Figure S-9. Possible models for single and double helices of **11merHR2.**

References

1. (a) Williams, D. J.; Colquhoun, H. M.; O'Mahoney, C. A. *J. Chem. Soc., Chem. Commun*. **1994**, 1643–1644. (b) Kobayashi, N.; Sasaki, S.; Abe, M.; Watanabe, S.; Fukumoto, H.; Yamamoto, T. *Macromolecules* **2004**, *37*, 7986–7991.

2. (a) Nosé, S. *Molec. Phys*. **1984**, *52*, 255–268, (b) Nosé, S. *J. Chem. Phys.* **1984**, *81*, 511–519, (c) Nosé, S. *Prog. Theoret. Phys. Supplement* **1991**, *103*, 1–46.

4-6. Single-Crystal X-ray Analysis

4-6-1. Single Helix of 5merH

X-ray diffraction data for the single helix of **5merH** were collected on a Bruker Smart Apex CCD-based X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 153 K.

Single crystals of the single helix of **5merH** [$C_{30}H_{22}O_{10}\cdot 1.2(CHCl_3)\cdot 2(H_2O)$, Mw = 721.75] suitable for X-ray analysis were grown by slow liquid diffusion of $CHCl_3$ into an CH_3CN solution of **5merH**, and a single colorless crystal with dimensions 0.30 × 0.20 × 0.05 mm was selected for intensity measurements. The unit cell was orthorhombic with the space group *Pbcn*. The lattice constants with Z = 4, ρ_{calcd} = 1.387 g cm^{-3}, μ(Mo-Kα) = 0.37 cm^{-1}, F(000) = 1486, $2\theta_{max}$ = 55.0° were a = 14.0511(5), b = 10.1199(4), c = 24.3010(8) Å, and V = 3455.5(2) Å^3. A total of 22005 reflections were collected, of which 3958 reflections were independent (R_{int} = 0.0360). The structure was refined to final R_1 = 0.0875 for 3958 data [$I>2\sigma(I)$] with 240 parameters and wR_2 = 0.2782 for all data, GOF = 1.060, and residual electron density max./min. = 1.420/ –0.372 e·Å^{-3}.

Data collection, indexing, and initial cell refinements were carried out using the program SMART.[1] Frame integration and final cell refinements were performed using SAINT software.[2] A multiple absorption correction for each data set was applied using the program SADABS.[3] The structure was solved by direct methods and Fourier

techniques using the program SHELXS-97,[4] and refined by full-matrix least squares methods on F^2 using SHELXL-97[5] incorporated in SHELXTL-PC.[6]

All non-hydrogen atoms were refined anisotropically. The C13, C16, H11, and H12 sit on special positions with an occupancy of 0.5. The H11 and H12 were found by differential-Fourier analysis and refined with U_{iso}(H) values of 1.2U_{eq}(C). The water hydrogen atoms were also located in differential-Fourier syntheses, but their positional and displacement parameters were refined with O-H distance restraints of 0.9 Å, and with U_{iso}(H) values of 1.5U_{eq}(O). The positions of other hydrogen atoms were calculated geometrically and refined as a riding model with U_{iso}(H) values of 1.2U_{eq}(C) or 1.3U_{eq}(O). A molecule of solvent $CHCl_3$ that was gradually lost during data collection, was determined to have an occupancy of *ca.* 0.6 based on a trial refinement of occupancy parameters. This value was fixed in the subsequent refinement.

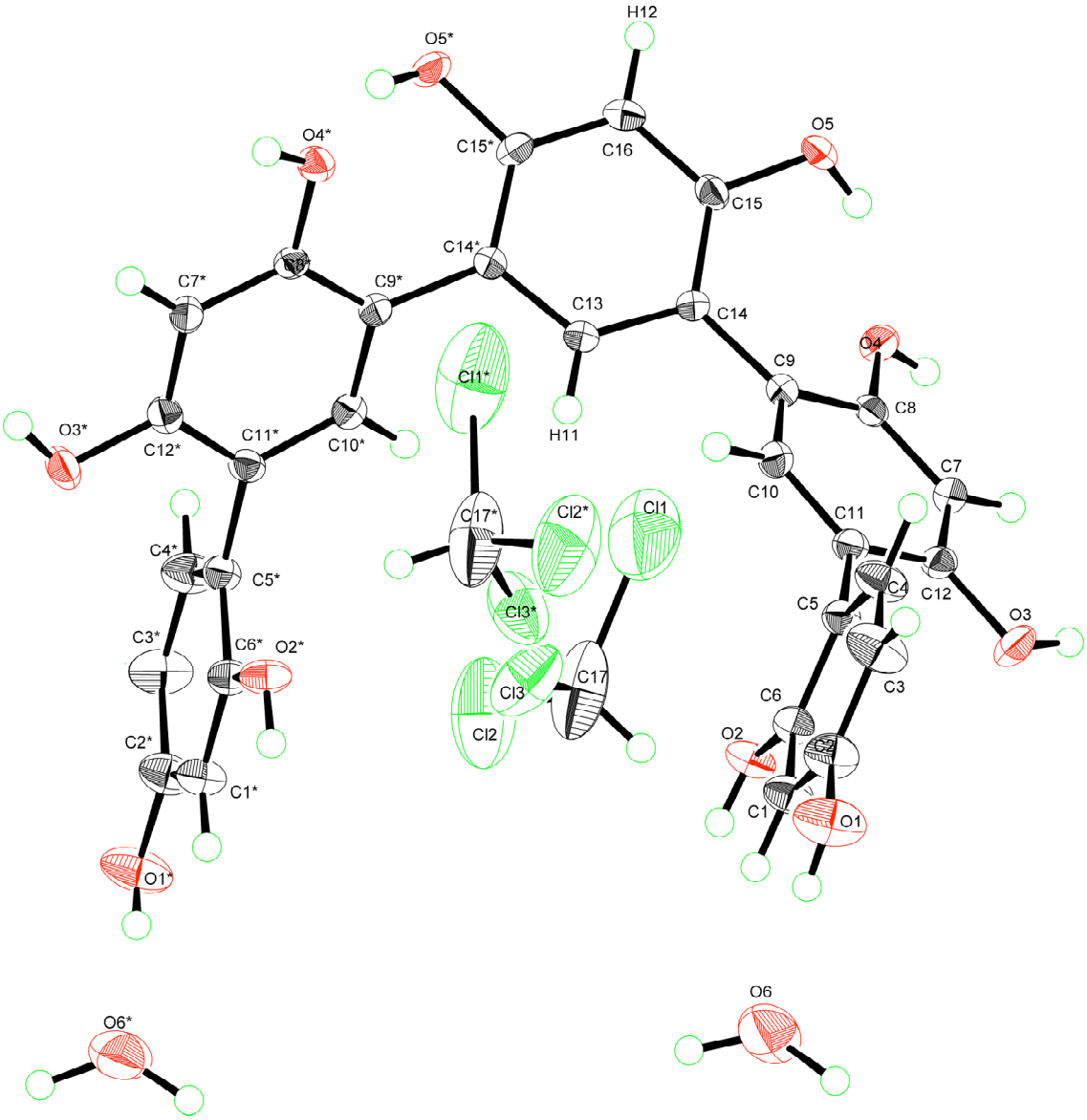


Figure S-10. ORTEP drawing of the single helix of **5merH** with thermal ellipsoids at 50% probability.

Table S-1. Crystal data and structure refinement for the single helix of **5merH** (CIF file is available in a separate file.).

Identification code	297375	
Empirical formula	C31.2 H27.2 Cl3.6 O12	
Formula weight	721.75	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal system	*Orthorhombic*	
Space group	*Pbcn*	
Unit cell dimensions	a = 14.0511(5) Å	α = 90°
	b = 10.1199(4) Å	β = 90°
	c = 24.3010(8) Å	γ = 90°
Volume	3455.5(2) $Å^3$	
Z	4	
Density (calculated)	1.387 g/cm^3	
Absorption coefficient	0.371 mm^{-1}	
F(000)	1486	
Crystal size	0.30 x 0.20 x 0.05 mm^3	
Theta range for data collection	2.22 to 27.50°.	
Index ranges	–18<=h<=16, –13<=k<=6, –28<=l<=31	
Reflections collected	22005	

Independent reflections	3958 [R(int) = 0.0360]
Completeness to theta = 27.50°	99.8%
Absorption correction	Empirical
Max. and min. transmission	0.979 and 0.904
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3958 / 1 / 240
Goodness-of-fit on F^2	1.060
Final R indices [I>2sigma(I)]	R_1 = 0.0875, wR_2 = 0.2515
R indices (all data)	R_1 = 0.1095, wR_2 = 0.2782
Largest diff. peak and hole	1.420 and –0.372 e·Å^{-3}

4-6-2. Double Helix of 5merH

X-ray diffraction data for the double helix of **5merH** were collected on a Bruker Smart ApexII CCD-based X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å) at 90 K.

Single crystals of the double helix of **5merH** [$2(C_{30}H_{22}O_{10})\cdot 5(H_2O)$, Mw = 1164.95] suitable for X-ray analysis were grown by slow evaporation of an aqueous solution of **5merH**, and a single colorless crystal with dimensions 0.06 × 0.04 × 0.02 mm was selected for intensity measurements. The unit cell was orthorhombic with the space group *P-1*. The lattice constants with Z = 2, ρ_{calcd} = 1.507 g cm^{-3}, μ(Mo-Kα) = 0.12 cm^{-1}, F(000) = 1208, $2\theta_{max}$ = 50.9° were a = 11.4241(19), b = 12.300(2), c = 19.998(3) Å, and V = 2567.3(7) Å^3. A total of 25368 reflections were collected, of which 9416 reflections were independent (R_{int} = 0.0459). The structure was refined to final R_1 = 0.0715 for 5901 data [$I>2\sigma(I)$] with 787 parameters and wR_2 = 0.2133 for all data, *GOF* = 1.038, and residual electron density max / min = 1.552 / –0.846 e·Å^{-3}.

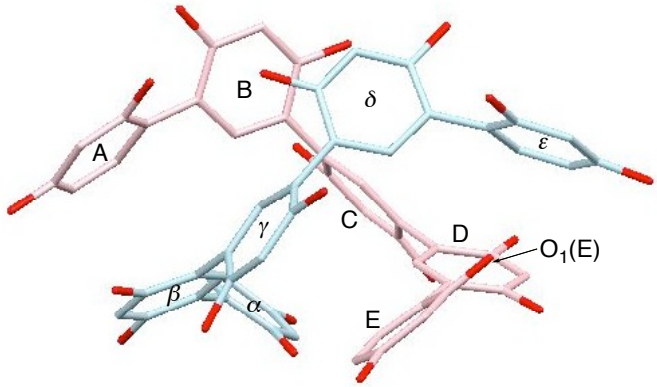
Data collection, indexing, and initial cell refinements were carried out using the program SMART.[1] Frame integration and final cell refinements were performed using SAINT software.[7] A multiple absorption correction for each data set was applied using the program SADABS.[3] The structure was solved by direct methods and Fourier techniques using the program SHELXS-97[4] and refined by full-matrix least squares methods on F^2 using SHELXL-97[5] incorporated in SHELXTL-PC.[6]

All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were

calculated geometrically and refined as a riding model with U_{iso}(H) values of 1.2U_{eq}(C) or 1.3U_{eq}(O). The water hydrogen atoms were not located because they have disordered configurations.

Figure S-11. ORTEP drawing of the double helix of **5merH** with thermal ellipsoids at 50% probability.

Table S-2. Centroid–Centroid Separations for Pairs of Aromatic Rings



Interaction	Mode	Distance / Å	Angle / deg[a)]
A···β	π–π	3.937	17.92
C···α	π–π	4.016	19.75
D···ε	π–π	4.324	35.86
E···γ	π–π	4.189	18.99
B –› β	CH–π	5.675	58.16
C –› δ	CH–π	5.593	81.90
β –› C	CH–π	5.886	63.94
γ –› B	CH–π	5.754	80.38
δ –› E	CH–π	5.776	70.04
O_1(E) –› ε	OH–π	3.426	–

a) Defined by the two mean planes of the aromatic rings.

Table S-3. Crystal data and structure refinement for the double helix of **5merH** (CIF file is available in a separate file.).

Identification code	297376	
Empirical formula	C60 H44 O25	
Formula weight	1164.95	
Temperature	90(2) K	
Wavelength	0.71073 Å	
Crystal system	*Triclinic*	
Space group	*P–1*	
Unit cell dimensions	a = 11.4241(19) Å	α = 98.767(2)°
	b = 12.300(2) Å	β = 105.237(2)°
	c = 19.998(3) Å	γ = 103.483(2)°
Volume	2567.3(7) $Å^3$	
Z	2	
Density (calculated)	1.507 g/cm^3	
Absorption coefficient	0.119 mm^{-1}	
F(000)	1208	
Crystal size	0.06 x 0.04 x 0.02 mm^3	
Theta range for data collection	1.08 to 25.43°.	
Index ranges	–13<=h<=13, –14<=k<=14, –24<=l<=24	
Reflections collected	25368	

Independent reflections	9416 [R(int) = 0.0459]
Completeness to theta = 27.50°	99.2%
Absorption correction	Empirical
Max. and min. transmission	0.9976 and 0.9929
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9416 / 0 / 787
Goodness-of-fit on F^2	1.038
Final R indices [I>2sigma(I)]	R_1 = 0.0715, wR_2 = 0.1822
R indices (all data)	R_1 = 0.1219, wR_2 = 0.2133
Largest diff. peak and hole	1.556 and –0.849 e·Å^{-3}

References

1. Bruker. SMART Version 5.624: Program for collecting frames of data, indexing reflection, and determination of lattice parameters; Bruker AXS, Inc., Madison, Wisconsin, USA, 2000.
2. Bruker. SAINT Version 6.02: Program for integration of the intensity of reflections and scaling; Bruker AXS, Inc., Madison, Wisconsin, USA, 2000.
3. Sheldrick, G. M. SADABS Version 2.03: Program for Performing Absorption Corrections to Single-Crystal X-ray Diffraction Patterns; University of Göttingen, Göttingen, Germany, 2001.
4. Sheldrick, G. M. SHELXS-97: Program for the Solution of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

5. Sheldrick, G. M. SHELXL-97: Program for the Refinement of Crystal Structures; University of Göttingen, Göttingen, Germany, 1997.

6. Bruker. SHELXTL Version 5.10: Suite of Programs for Crystal Structure Analysis, Incorporating Structure Solution (XS), Least-Squares Refinement (XL), and Graphics (XP); Bruker AXS, Inc., Madison, Wisconsin, USA, 2000.

7. Bruker. SAINT Version 7.12: Program for integration of the intensity of reflections and scaling; Bruker AXS, Inc., Madison, Wisconsin, USA, 2000.