

## Supplementary Information

### Chiral, Cross-conjugated *iso*-Polydiacetylenes

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**General Experimental.** Reagents were purchased reagent grade from commercial suppliers and used without further purification. THF was distilled from sodium/benzophenone ketyl, and acetonitrile was distilled from CaH<sub>2</sub> immediately prior to use. Anhydrous MgSO<sub>4</sub> or Na<sub>2</sub>SO<sub>4</sub> were used as the drying agent after aqueous work-up. Evaporation and concentration *in vacuo* was done at H<sub>2</sub>O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of N<sub>2</sub>. Column chromatography: *silica gel-60* (230-400 mesh) from *General Intermediates of Canada*. Thin Layer Chromatography (TLC): aluminum sheets covered with *silica gel-60 F<sub>254</sub>* from *Macherey-Nagel*; visualization by UV light or KMnO<sub>4</sub> stain. IR spectra (cm<sup>-1</sup>): *Nicolet Magna-IR 750* (neat) or *Nic-Plan IR Microscope* (solids). <sup>1</sup>H- and <sup>13</sup>C-NMR: *Varian Gemini-300* or *500* instruments, at room temperature in CDCl<sub>3</sub>; solvent peaks (7.24 for <sup>1</sup>H and 77.0 for <sup>13</sup>C) as reference. UV/Vis spectra: *Varian Cary 400* at room temperature. CD spectra: OLIS DSM 1000 spectrophotometer. EI MS (*m/z*): *Kratos MS50* instrument. Elemental analyses were effected by Spectral Services at the University of Alberta.

**Bromo-butoxy Binap (R)-3.** Prepared as reported, J. C. Ostrowski, R. A. Hudack Jr., M. R. Robinson, S. J. Wang, and G. C. Bazan, *Chem. Eur. J.* **2001**, *7*, 4500.

**TMS-ethynyl Binap (R)-4.** A solution of Pd<sub>2</sub>(dba)<sub>3</sub> (0.077 g, 0.074 mmol), CuI (0.016 g, 0.084 mmol), PPh<sub>3</sub> (0.111 g, 0.423 mmol) in deoxygenated acetonitrile (24 mL) and Et<sub>3</sub>N (6 mL) was heated to 55 °C for 15 minutes in a sealed flask with stirring. After cooling to room temperature, compound

**(R)-3** (0.890 g, 1.59 mmol) and TMS-acetylene (1.13 mL, 0.78 g, 7.95 mmol) were added and the mixture was heated to 55 °C in the sealed flask. Two more equivalents of TMS-acetylene were added after 24 hr, and the reaction was worked up after 3 days by the addition of Et<sub>2</sub>O and washing with aqueous NH<sub>4</sub>Cl. The organic layer was separated and dried with MgSO<sub>4</sub>. The residue was purified by column chromatography (silica gel, hexane/CH<sub>2</sub>Cl<sub>2</sub> 2:1) and afforded **(R)-4** (0.573 g, 61%) as a yellow solid. R<sub>f</sub> = 0.40 (hexanes/CH<sub>2</sub>Cl<sub>2</sub> 3:1). [α]<sub>D</sub><sup>22</sup> -91.7 (c 1.13, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>, cast) 2958, 2872, 2150, 1619, 1589, 1465, 1339, 1273, 1248, 1168 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 1.5 Hz, 2H), 7.92 (d, *J* = 9.1 Hz, 2H), 7.44 (d, *J* = 9.1 Hz, 2H), 7.32 (dd, *J* = 1.5, 8.8 Hz, 2H), 7.15 (d, *J* = 8.8 Hz, 2H), 3.98 (m, 4H), 1.43 (m, 4H), 1.02 (m, 4H), 0.69 (t, *J* = 7.4 Hz, 6H), 0.32 (s, 18H). <sup>13</sup>C NMR (100.6 MHz, CDCl<sub>3</sub>, APT) δ 155.3, 133.6, 132.1, 129.2, 128.8, 128.5, 125.3, 120.0, 117.8, 115.8, 105.9, 93.6, 69.0, 31.3, 18.7, 13.5, 0.1. EI HRMS calcd for C<sub>38</sub>H<sub>46</sub>O<sub>2</sub>Si<sub>2</sub> (M<sup>+</sup>) *m/z* 590.3037, found 590.3028.

**Monomer 6.** Compound **(R)-4** (0.450 g, 0.773 mmol) was reacted in wet methanol (15 mL) with K<sub>2</sub>CO<sub>3</sub> (20 mg) until TLC analysis showed complete desilylation (about 2 hr). The resulting mixture was washed with NH<sub>4</sub>Cl (aq) and Et<sub>2</sub>O, the organic layer was dried with MgSO<sub>4</sub> and the concentrated to dryness. The product was immediately dissolved in deoxygenated THF:diisopropyl amine (10:1, 8 mL) and placed in a flask. CuI (0.090 g, 0.47 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.045 g, 0.039 mmol) along with triflate **5** (0.740 g, 1.59 mmol) were added and the reaction mixture was heated to 55 °C for 2 days. The reaction was cooled to room temperature and then worked up with NH<sub>4</sub>Cl (aq) and Et<sub>2</sub>O with the organic layer then dried with MgSO<sub>4</sub>. The residue was purified by column chromatography (silica gel, hexane/Et<sub>2</sub>O 8:1) and afforded **(R)-6** (0.440 g, 53%) as a yellow solid. R<sub>f</sub> = 0.70 (hexane/Et<sub>2</sub>O 4:1). [α]<sub>D</sub><sup>22</sup> -208 (c 3.74, CHCl<sub>3</sub>). IR (CHCl<sub>3</sub>, cast) 3054, 2955, 2194, 2141, 1269 cm<sup>-1</sup>. UV-vis (NCCH<sub>3</sub>): λ<sub>max</sub> (ε) 359 (59 600), 253 (101 000) nm. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> (ε) 366 (53 600), 256 (82 100) nm. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 8.8 Hz, 4H), 7.53-7.48 (m, 8H), 7.38-7.28 (m, 14H), 7.04 (dd, *J* = 1.4, 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.92 (m, 4H), 1.39 (m, 4H), 1.02-0.94 (m, 4H), 0.94

(t,  $J = 7.6$  Hz, 18H), 0.67-0.53 (m, 18H).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , APT)  $\delta$  156.1, 155.4, 140.5, 140.4, 133.6, 131.4, 130.4, 129.2, 128.6, 128.5, 128.44, 128.36, 127.6, 125.3, 120.2, 118.0, 115.9, 104.6, 102.5, 95.6, 92.7, 88.8, 69.2, 31.3, 18.8, 13.6, 7.5, 4.3 (two coincident signals not observed). ESI MS  $m/z$  1079.6 ( $[\text{M} + \text{H}]^+$ , 100). EA calcd for  $\text{C}_{76}\text{H}_{78}\text{O}_2\text{Si}_2$ : C, 84.55; H, 7.28; found: C, 84.17; H, 7.40.

**Dimer (R)-7.** Compound **(R)-6** (0.370 g, 0.343 mmol) was reacted in wet methanol (15 mL) and THF (5 mL) with  $\text{K}_2\text{CO}_3$  (20 mg) until TLC analysis showed complete desilylation (about 16 hr). The resulting mixture was washed with  $\text{NH}_4\text{Cl}$  (aq) and  $\text{Et}_2\text{O}$ , the organic layer was dried with  $\text{MgSO}_4$  and then concentrated to dryness. The product was immediately dissolved in deoxygenated THF:diisopropyl amine (10:1, 8 mL) and placed in a flask.  $\text{CuI}$  (0.040 g, 0.21 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.020 g, 0.017 mmol) along with triflate **5** (0.328 g, 0.703 mmol) were added and the reaction mixture was heated to  $55^\circ\text{C}$  for 2 days. The reaction was cooled to room temperature and worked up with  $\text{NH}_4\text{Cl}$  (aq) and  $\text{Et}_2\text{O}$  with the organic layer then dried with  $\text{MgSO}_4$ . The residue was purified by column chromatography (silica gel, hexane/ $\text{Et}_2\text{O}$  8:1) and afforded **(R)-7** (0.370 g, 73%) as a yellow solid.  $R_f = 0.40$  (hexane/ $\text{Et}_2\text{O}$  8:1).  $[\alpha]_D^{22} -147$  (c 1.27,  $\text{CHCl}_3$ ). UV-vis ( $\text{NCCH}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 355 (70 200), 256 (117 000) nm. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 359 (65 300), 260 (102 000) nm.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 9.1$  Hz, 2H), 7.74 (s, 2H), 7.49-7.40 (m, 18H), 7.34-7.21 (m, 24H), 6.99 (m, 4H), 3.95 (m, 4H), 1.40-1.34 (m, 4H), 1.09-0.90 (m, 4H), 0.88 (t,  $J = 8.0$  Hz, 18H), 0.65 (t,  $J = 7.3$  Hz, 6H), 0.53 (q,  $J = 8.0$  Hz, 12H).  $^{13}\text{C}$  NMR (125.7 MHz,  $\text{CDCl}_3$ , APT)  $\delta$  156.8, 155.4, 154.9, 140.8, 140.5, 140.1, 140.0, 133.6, 131.6, 130.6, 130.5, 130.4, 129.2, 128.7, 128.6, 128.5 (2 $\times$ ), 128.4, 128.3, 127.8, 127.7, 127.63, 127.60, 125.3, 120.2, 118.0, 115.9, 104.0, 102.4, 102.2, 95.3, 92.6, 90.9, 90.8, 88.4, 69.2, 31.3, 18.8, 13.6, 7.5, 4.3 (one coincident signal not observed). ESI MS  $m/z$  1483.7 ( $\text{M}^+$ , 100). EA calcd for  $\text{C}_{108}\text{H}_{98}\text{O}_2\text{Si}_2$ : C, 87.40; H, 6.66; found: C, 86.87; H, 6.60.

**Trimer (R)-8.** Compound **(R)-7** (0.371 g, 0.250 mmol) was deprotected using TBAF (0.25 mL, 0.25 mmol, 1 M in THF) and wet THF (10 mL) until TLC analysis showed complete desilylation (about 10

min). The resulting mixture was washed with  $\text{NH}_4\text{Cl}$  (aq) and  $\text{Et}_2\text{O}$ , the organic layer was dried with  $\text{MgSO}_4$  and then concentrated to dryness. The product was immediately dissolved in deoxygenated THF:diisopropyl amine (10:1, 8 mL) and placed in a flask.  $\text{CuI}$  (0.030 g, 0.160 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.020 g, 0.017 mmol) along with triflate **5** (0.239 g, 0.512 mmol) were added and the reaction mixture was heated to 55 °C for 36 hours. The reaction was cooled to room temperature and worked up with  $\text{NH}_4\text{Cl}$  (aq) and  $\text{Et}_2\text{O}$  with the organic layer then dried with  $\text{MgSO}_4$ . The residue was purified by column chromatography (silica gel, hexane/ $\text{CHCl}_3$  1:1) and afforded compound (**R,R**)-**11** (vide infra) and (**R**)-**8** (0.355 g, 75%) as a yellow solid.  $R_f = 0.60$  (hexane/ $\text{Et}_2\text{O}$  2:1).  $[\alpha]_D^{22} -117$  (c 1.93,  $\text{CHCl}_3$ ). UV-vis ( $\text{NCCH}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 355 (95 900), 253 (153 000) nm. UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 363 (89 000), 260 (135 000) nm.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 9.1$  Hz, 2H), 7.78 (s, 2H), 7.48-7.46 (m, 4H), 7.41-7.18 (m, 58H), 6.99 (s, 4H), 3.92 (m, 4H), 1.41-1.37 (m, 4H), 1.0-0.90 (m, 4H), 0.87 (t,  $J = 8.1$  Hz, 18H), 0.63 (t,  $J = 7.2$  Hz, 6H), 0.52 (q,  $J = 7.2$  Hz, 12H).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , APT)  $\delta$  156.7, 155.4, 155.0, 140.8, 140.5, 140.2, 140.1, 140.0, 139.9, 133.6, 131.6, 130.6, 130.5, 130.4, 130.3, 129.2, 128.7, 128.6, 128.5 (2 $\times$ ), 128.4, 128.3, 127.82, 127.77, 127.70, 127.67, 127.64, 127.59, 125.3, 120.2, 118.1, 115.9, 104.1, 102.3, 102.2, 95.4, 92.7, 90.8, 90.7, 90.3, 90.2, 88.5, 69.2, 31.3, 18.8, 13.6, 7.5, 4.3 (six coincident signals not observed). ESI MS  $m/z$  1911 ( $[\text{M} + \text{Na}]^+$ , 100).

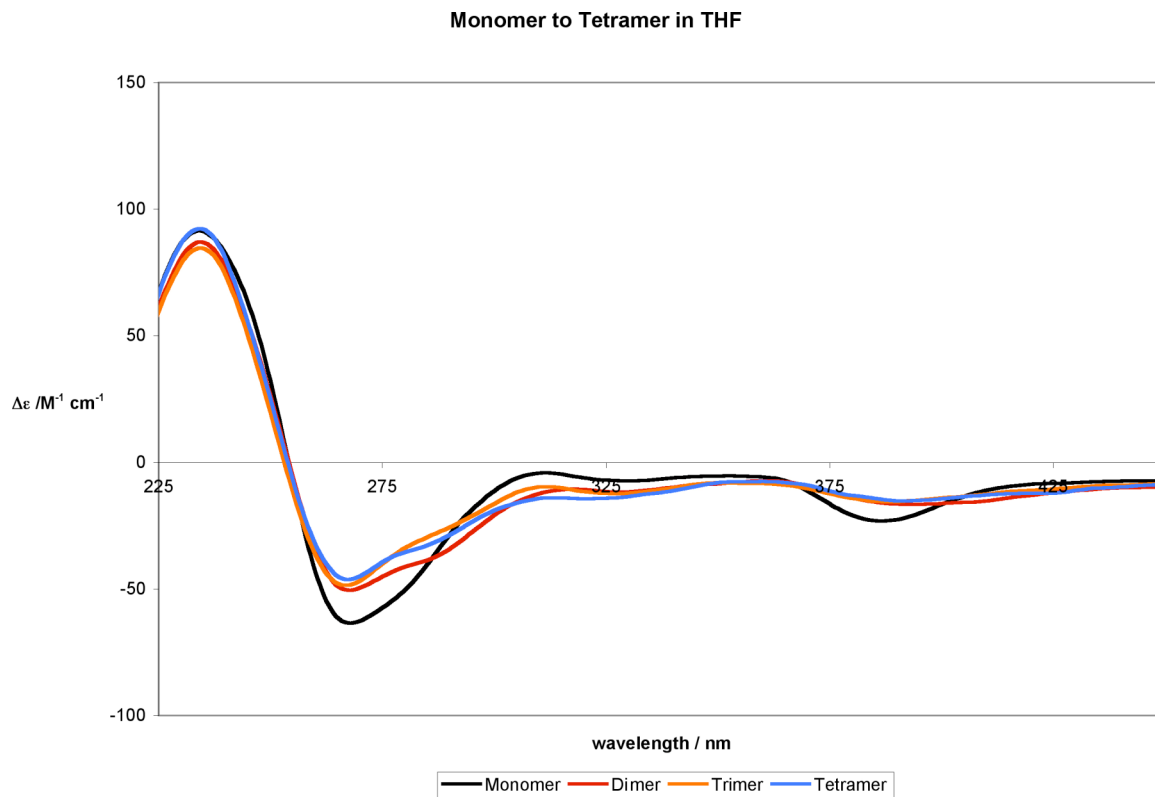
**Dimer of Trimer (R,R)-11.** The dimer of the trimer was isolated as a side-product during the production of **9** and was purified by column chromatography (silica gel, hexane/ $\text{Et}_2\text{O}$  1:1) afforded (**R**)-**11** (up to 15%) as a yellow solid.  $R_f = 0.10$  (hexane/ $\text{Et}_2\text{O}$  2:1).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 9.1$  Hz, 4H), 7.80 (s, 2H), 7.75 (s, 2H), 7.54-7.18 (m, 104H), 7.03-6.96 (m, 8H), 3.85-4.00 (m, 8H), 1.46-1.30 (m, 8H), 1.06-0.94 (m, 8H), 0.90 (t,  $J = 7.4$  Hz, 18H), 0.65 (t,  $J = 8.0$  Hz, 12H), 0.54 (q,  $J = 7.0$  Hz, 12H). MALDI-MS (retinoic acid)  $m/z$  3142 ( $[\text{M} + \text{H}]^+$ ).

**Tetramer (R)-9.** Compound (**R**)-**8** (0.588 g, 0.311 mmol) was deprotected using TBAF (0.35 mL, 0.35 mmol, 1 M in THF) and wet THF (20 mL) until TLC analysis showed complete desilylation (about 10 min). The resulting mixture was washed with  $\text{NH}_4\text{Cl}$  (aq) and  $\text{Et}_2\text{O}$ , the organic layer was dried with

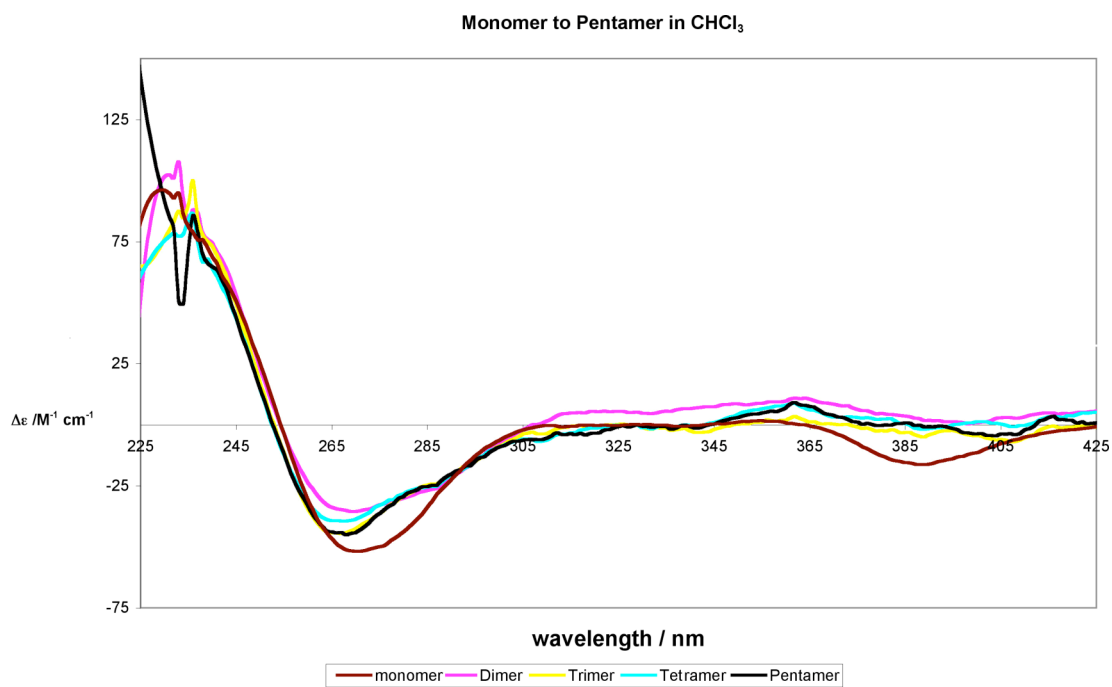
MgSO<sub>4</sub> and then concentrated to dryness. The product was immediately dissolved in deoxygenated THF:diisopropyl amine (25:2, 27 mL) and placed in a flask. CuI (0.037 g, 0.018 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.019 g, 0.017 mmol) along with triflate **5** (0.313 g, 0.672 mmol) were added and the reaction mixture was heated to 55 °C for 2 days. The reaction was cooled to room temperature and worked up with NH<sub>4</sub>Cl (aq) and Et<sub>2</sub>O with the organic layer then dried with MgSO<sub>4</sub>. The residue was purified by size exclusion chromatography (Bio-Beads XS1 200-400 mesh, CHCl<sub>3</sub>) and afforded (**R**)-**9** (0.405 g, 57%) as a yellow solid. R<sub>f</sub> = 0.70 (hexane/Et<sub>2</sub>O 1:1). [α]<sub>D</sub><sup>22</sup> -95.4 (c 1.09, CHCl<sub>3</sub>). UV-vis (NCCH<sub>3</sub>): λ<sub>max</sub> (ε) 358 (113 000), 256 (180 000) nm. UV-vis (CHCl<sub>3</sub>): λ<sub>max</sub> (ε) 367 (105 000), 261 (159 000) nm. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 9.1 Hz, 2H), 7.75 (s, 2H), 7.52-7.48 (m, 4H), 7.43-7.18 (m, 78H), 7.02-6.99 (m, 4H), 3.93 (m, 4H), 1.42-1.39 (m, 4H), 1.08-0.98 (m, 4H), 0.89 (t, *J* = 7.9 Hz, 18H), 0.64 (t, *J* = 7.5 Hz, 6H), 0.53 (q, *J* = 7.5 Hz, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, APT) δ 157.0, 155.4, 155.3, 155.2, 154.8, 140.7, 140.5, 140.3, 140.13, 140.12, 140.06, 140.00, 139.9, 133.6, 131.6, 130.6, 130.52, 130.49, 130.46, 130.44, 130.41, 130.37, 130.32, 129.3, 128.7 (2×), 128.65, 128.58, 128.55, 128.52, 128.4, 128.3, 127.85, 127.84, 127.77, 127.72, 127.68, 127.67, 127.62, 127.56, 125.3, 120.2, 118.1, 115.9, 104.0, 102.3, 102.2, 102.1, 95.3, 92.7, 91.0, 90.9, 90.5, 90.4, 90.13, 90.09, 88.4, 69.2, 31.3, 18.8, 13.6, 7.5, 4.3 (three coincident signals not observed). ESI MS *m/z* 2293 (M<sup>+</sup>, 30). MALDI MS (retinoic acid) *m/z* 2294 ([M + H]<sup>+</sup>, 100).

**Pentamer (R)-10.** A mixture of (**R**)-**9** (0.350 g, 0.153 mmol) was deprotected using TBAF (0.46 mL, 0.461 mmol, 1 M in THF) and wet THF (20 mL) until TLC analysis showed complete desilylation (about 20 min). The resulting mixture was washed with NH<sub>4</sub>Cl (aq) and Et<sub>2</sub>O, the organic layer was dried with MgSO<sub>4</sub> and then concentrated to dryness. The product was immediately dissolved in THF:diisopropyl amine (10:1, 25 mL) and placed in a flask. CuI (0.017 g, 0.089 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.090 g, 0.078 mmol) along with triflate **5** (0.154 g, 0.330 mmol) were added and the reaction mixture was heated to 55 °C for 2 days. The reaction was cooled to room temperature and worked up with NH<sub>4</sub>Cl (aq) and Et<sub>2</sub>O with the organic layer then dried with MgSO<sub>4</sub>. The reaction was purified by size

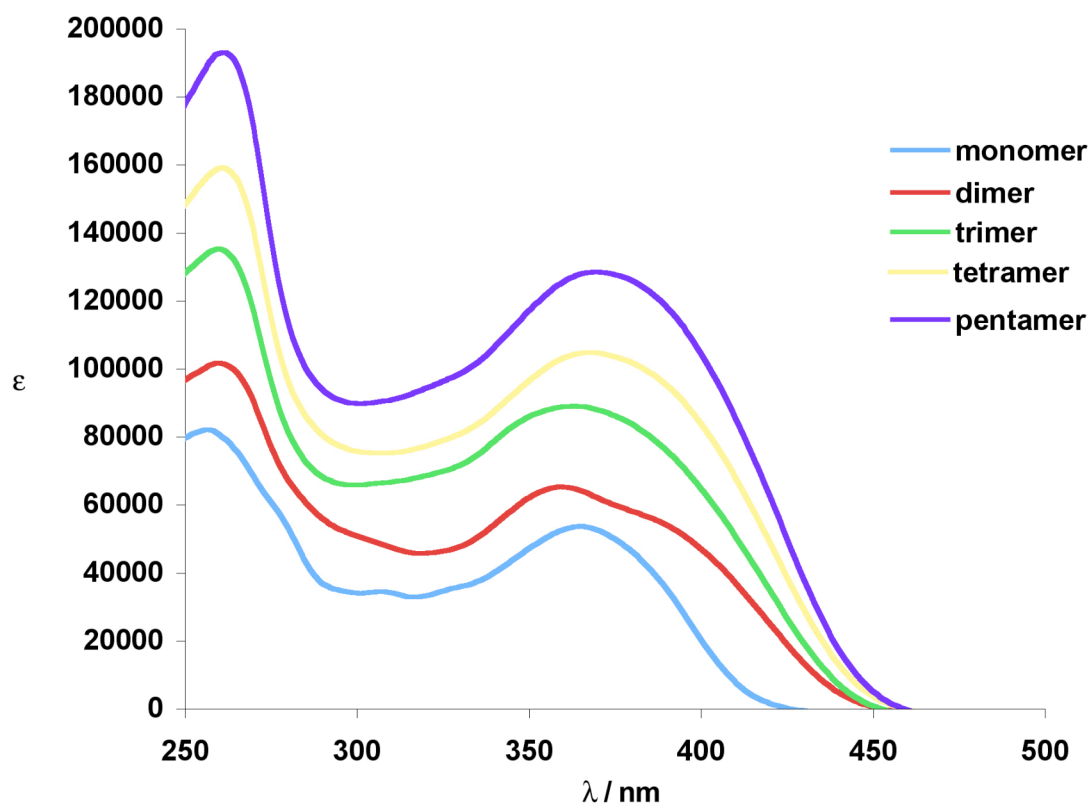
exclusion chromatography (Bio-Beads XS1 200-400 mesh,  $\text{CHCl}_3$ ) and afforded (**R**)-**10** (0.161 g, 39%) as a yellow solid.  $R_f = 0.70$  (hexane/ $\text{CH}_2\text{Cl}_2$  1:1). UV-vis ( $\text{CHCl}_3$ ):  $\lambda_{\text{max}}$  ( $\epsilon$ ) 370 (128 000), 262 (193 000) nm.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.82 (d,  $J = 9.1$  Hz, 2H), 7.81 (s, 2H), 7.54-7.51 (m, 4 H), 7.45-7.18 (m, 98H), 7.06-7.04 (m, 4H), 4.00-3.95 (m, 4H), 1.49-1.42 (m, 4H), 1.02-0.98 (m, 4H), 0.94 (t,  $J = 8.1$  Hz, 18H), 0.68 (t,  $J = 7.2$  Hz, 6H), 0.58 (q,  $J = 7.2$  Hz, 12H).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , APT)  $\delta$  156.9, 155.31, 155.30, 155.2, 154.95, 154.87, 140.7, 140.5, 140.2, 140.0 (2 $\times$ ), 139.99, 139.96, 139.90, 139.85, 133.6, 131.5, 130.6, 130.44, 130.40, 130.35, 130.32, 130.29, 130.22, 129.2, 128.7, 128.53, 128.45, 128.33, 128.27, 127.8, 127.7 (2 $\times$ ), 127.6, 127.55, 127.51, 125.2, 120.1, 118.0, 115.9, 104.0, 102.2, 102.12, 102.06, 102.03, 102.00, 95.2, 92.6, 90.8, 90.7, 90.4, 90.4, 90.19, 90.17, 88.5, 69.1, 31.3, 18.7, 13.6, 7.4, 4.3 (17 coincident signals not observed). ESI MS  $m/z$  2720.2 ( $[\text{M} + \text{Na}]^+$ ).



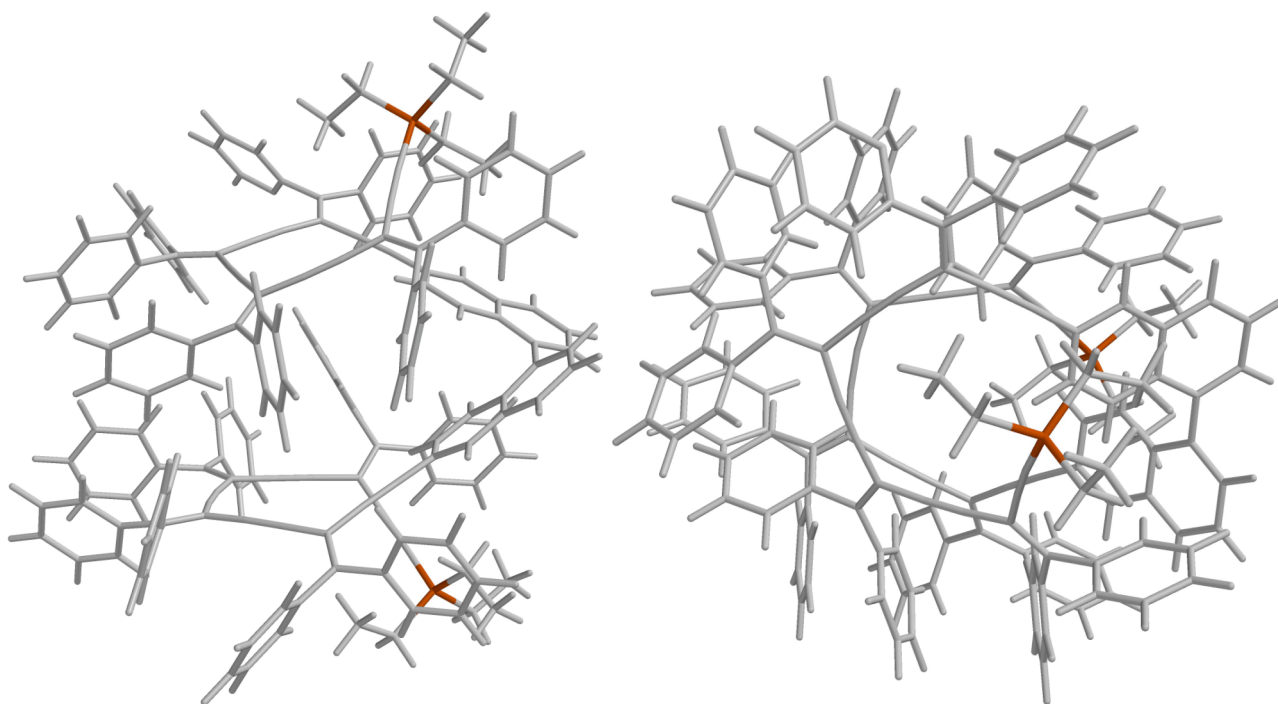
**Figure s1.** CD spectra of monomer (6), dimer (7), trimer (8), and tetramer (9) taken in THF.



**Figure s2.** CD spectra of monomer (6), dimer (7), trimer (8), and tetramer (9), and pentamer (11) taken in CHCl<sub>3</sub>.



**Figure s3.** monomer (6), dimer (7), trimer (8), and tetramer (9), and pentamer (11) taken in  $\text{CHCl}_3$ .



**Figure s4.** Molecular mechanics geometry minimization of tetramer (9) using Spartan 02 (edge on and from top) showing helical conformation.