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 CaH₂ immediately prior to use. Anh. MgSO₄ or Na₂SO₄ were used as the drying agent after aqueous work-up. Evaporation and concentration *in vacuo* was done at H₂O-aspirator pressure. All reactions were performed in standard, dry glassware under an inert atmosphere of N₂. Column chromatography: *silica gel*-60 (230-400 mesh) from General Intermediates of Canada. Thin Layer Chromatography (TLC): aluminum sheets covered with *silica gel*-60 F₂₅₄ from Macherey-Nagel; visualization by UV light or KMnO₄ stain. IR spectra (cm⁻¹): Nicolet Magna-IR 750 (neat) or Nic-Plan IR Microscope (solids). ¹H- and ¹³C-NMR: Varian Gemini-300 or 500 instruments, at room temperature in CDCl₃; solvent peaks (7.24 for ¹H and 77.0 for ¹³C) 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.


**TMS-ethynyl Binap (R)-4.** A solution of Pd₂(dba)₃ (0.077 g, 0.074 mmol), CuI (0.016 g, 0.084 mmol), PPh₃ (0.111 g, 0.423 mmol) in deoxygenated acetonitrile (24 mL) and Et₃N (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 Et₂O and washing with aqueous NH₄Cl. The organic layer was separated and dried with MgSO₄. The residue was purified by column chromatography (silica gel, hexane/CH₂Cl₂ 2:1) and afforded (R)-4 (0.573 g, 61%) as a yellow solid. Rₐ = 0.40 (hexanes/CH₂Cl₂ 3:1). [α]²²D –91.7 (c 1.13, CHCl₃). IR (CHCl₃, cast) 2958, 2872, 2150, 1619, 1589, 1465, 1339, 1273, 1248, 1168 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) 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). ¹³C NMR (100.6 MHz, CDCl₃, 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 C₃₈H₄₆O₂Si₂ (M⁺) 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 K₂CO₃ (20 mg) until TLC analysis showed complete desilylation (about 2 hr). The resulting mixture was washed with NH₄Cl (aq) and Et₂O, the organic layer was dried with MgSO₄ 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(PPh₃)₄ (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 NH₄Cl (aq) and Et₂O with the organic layer then dried with MgSO₄. The residue was purified by column chromatography (silica gel, hexane/Et₂O 8:1) and afforded (R)-6 (0.440 g, 53%) as a yellow solid. Rₐ = 0.70 (hexane/Et₂O 4:1). [α]²²D –208 (c 3.74, CHCl₃). IR (CHCl₃, cast) 3054, 2955, 2194, 2141, 1269 cm⁻¹. UV-vis (NCCH₃): λₘₐₓ (ε) 359 (59 600), 253 (101 000) nm. UV-vis (CHCl₃): λₘₐₓ (ε) 366 (53 600), 256 (82 100) nm. ¹H NMR (300 MHz, CDCl₃) 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). \(^{13}\)C NMR (75.5 MHz, 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 ([M + H]\(^+\), 100). EA calcd for C\(_{76}\)H\(_{78}\)O\(_2\)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 K\(_2\)CO\(_3\) (20 mg) until TLC analysis showed complete desilylation (about 16 hr). The resulting mixture was washed with NH\(_4\)Cl (aq) and Et\(_2\)O, the organic layer was dried with 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. CuI (0.040 g, 0.21 mmol) and Pd(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 °C for 2 days. The reaction was cooled to room temperature and worked up with NH\(_4\)Cl (aq) and Et\(_2\)O with the organic layer then dried with MgSO\(_4\). The residue was purified by column chromatography (silica gel, hexane/Et\(_2\)O 8:1) and afforded (R)-7 (0.370 g, 73%) as a yellow solid. \( R_f = 0.40 \) (hexane/Et\(_2\)O 8:1). \([\alpha]^{22}_D \) –147 (c 1.27, CHC\(_3\)). UV-vis (NCCH\(_3\)): \( \lambda_{max} \) (\( \varepsilon \)) 355 (70 200), 256 (117 000) nm. UV-vis (CHCl\(_3\)): \( \lambda_{max} \) (\( \varepsilon \)) 359 (65 300), 260 (102 000) nm. \(^1\)H NMR (300 MHz, 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). \(^{13}\)C NMR (125.7 MHz, CDCl\(_3\), APT) \( \delta \) 156.8, 155.4, 154.9, 140.8, 140.5, 140.1, 140.0, 133.6, 131.6, 130.6, 130.4, 130.2, 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 (M\(^+\), 100). EA calcd for C\(_{108}\)H\(_{93}\)O\(_2\)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
The resulting mixture was washed with NH₄Cl (aq) and Et₂O, the organic layer was dried with MgSO₄ and then concentrated to dryness. The product was immediately dissolved in deoxygenated THF:diisopropyl amine (10:1, 8 mL) and placed in a flask. CuI (0.030 g, 0.160 mmol) and Pd(PPh₃)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 NH₄Cl (aq) and Et₂O with the organic layer then dried with MgSO₄. The residue was purified by column chromatography (silica gel, hexane/CHCl₃ 1:1) and afforded compound (R,R)-11 (vide infra) and (R)-8 (0.355 g, 75%) as a yellow solid. Rᵣ = 0.60 (hexane/Et₂O 2:1). [α]²²D –117 (c 1.93, CHCl₃).

UV-vis (NCCH₃): λ_max (ε) 355 (95 900), 253 (153 000) nm. UV-vis (CHCl₃): λ_max (ε) 363 (89 000), 260 (135 000) nm. ¹H NMR (300 MHz, CDCl₃) δ 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). ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 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 (2x), 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 ([M + 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/Et₂O 1:1) afforded (R)-11 (up to 15%) as a yellow solid. Rᵣ = 0.10 (hexane/Et₂O 2:1). ¹H NMR (500 MHz, CDCl₃) δ 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 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 ([M + 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 NH₄Cl (aq) and Et₂O, the organic layer was dried with
MgSO$_4$ 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$_3$)$_4$ (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$_4$Cl (aq) and Et$_2$O with the organic layer then dried with MgSO$_4$. The residue was purified by size exclusion chromatography (Bio-Beads XS1 200-400 mesh, CHCl$_3$) and afforded (R)-9 (0.405 g, 57%) as a yellow solid. $R_f$ = 0.70 (hexane/Et$_2$O 1:1). [α]$^{22}_D$ -95.4 (c 1.09, CHCl$_3$). UV-vis (NCCH$_3$): $\lambda_{\text{max}}$ (ε) 358 (113 000), 256 (180 000) nm. UV-vis (CHCl$_3$): $\lambda_{\text{max}}$ (ε) 367 (105 000), 261 (159 000) nm. $^1$H NMR (300 MHz, CDCl$_3$) 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). $^{13}$C NMR (125 MHz, CDCl$_3$, 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 $m/\text{z}$ 2293 (M$^+$, 30). MALDI MS (retinoic acid) $m/\text{z}$ 2294 ([M + H]$^+$, 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$_4$Cl (aq) and Et$_2$O, the organic layer was dried with MgSO$_4$ 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$_3$)$_4$ (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$_4$Cl (aq) and Et$_2$O with the organic layer then dried with MgSO$_4$. The reaction was purified by size exclusion chromatography (Bio-Beads XS1 200-400 mesh, CHCl$_3$) and afforded (R)-10 (0.455 g, 71%) as a yellow solid. $R_f$ = 0.70 (hexane/Et$_2$O 1:1). [α]$^{22}_D$ -95.4 (c 1.09, CHCl$_3$). UV-vis (NCCH$_3$): $\lambda_{\text{max}}$ (ε) 358 (113 000), 256 (180 000) nm. UV-vis (CHCl$_3$): $\lambda_{\text{max}}$ (ε) 367 (105 000), 261 (159 000) nm. $^1$H NMR (300 MHz, CDCl$_3$) 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). $^{13}$C NMR (125 MHz, CDCl$_3$, 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 $m/\text{z}$ 2293 (M$^+$, 30). MALDI MS (retinoic acid) $m/\text{z}$ 2294 ([M + H]$^+$, 100).
exclusion chromatography (Bio-Beads XS1 200-400 mesh, CHCl₃) and afforded (R)-10 (0.161 g, 39%) as a yellow solid. Rᵣ = 0.70 (hexane/CH₂Cl₂ 1:1). UV-vis (CHCl₃): λₓₜₜ (ε) 370 (128 000), 262 (193 000) nm. ¹H NMR (300 MHz, CDCl₃) δ 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). ¹³C NMR (75.5 MHz, CDCl₃, APT) δ 156.9, 155.31, 155.30, 155.2, 154.95, 154.87, 140.7, 140.5, 140.2, 140.0 (2×), 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×), 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 ([M + 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 CHCl₃.
Figure s3. Monomer (6), dimer (7), trimer (8), and tetramer (9), and pentamer (11) taken in CHCl₃.

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