Supporting Information for:

*Chiro*-Inositols and related cyclitols as chiral monomers for polymerization: Expansion of a family of chiral polymers

John F. Trant, Hollich Ho, and Tomas Hudlicky*

Department of Chemistry and Centre for Biotechnology, Brock University, 500 Glenridge Avenue, St Catharines ON, L2S 3A1, Canada

Fax: 1-905-984-4841.
E-mail: thudicky@brocku.ca

Table of Contents

Experimental protocols and characterization data for new compounds.............................................................S2
General Reactions were carried out under argon atmosphere in flame-dried glassware unless otherwise stated. Solvents were distilled: methylene chloride, DMF, triethylamine, ortho-xylene, and pyridine from CaH₂; THF from Na/benzophenone. Other reagents were acquired from commercial sources (Sigma-Aldrich, Alfa Aesar, Acros Organics, Oakwood Products, Inc.) and were used without further purification.

Qualitative TLC was done with pre-coated silica gel aluminum sheets (EMD silica gel 60 F254), detection by UV or by spraying with Hanessian’s stain, vanillin or aqueous KMnO₄ solution followed by heating.

Melting points are uncorrected. Flash chromatography was performed using silica gel SiliaFlash P60 from Silicycle (40–66 μm). Optical rotation was measured in a 1-dm cell at 20-25 °C and 589 nm with a Perkin Elmer 341 polarimeter, concentration (c) is measured in g/100 mL. IR spectra were recorded in a KBr cell in solution using a Perkin Elmer Spectrum One Instrument. ¹H NMR and ¹³C NMR spectra were recorded at 300 or 600 MHz and 75 or 150 MHz, respectively on Bruker AVANCE spectrometers, and were calibrated on the solvent residual peak or TMS signal (CDCl₃ 7.26 ppm), the chemical shifts are reported in ppm. High resolution mass spectrometry was carried out using a Concept 1S Spectrometer (Dr. Tim Jones, Brock University) or on a Micromass GCT Spectrometer (Dr. Kirk Green, McMaster University).

Elemental analysis (carbon and hydrogen) was carried by Atlantic Microlab, Inc. 6180 Atlantic Blvd. Suite M, Norcross, Ga 30071. GPC analysis (Dr. Nicholas Burke, Dr. Harald Stöver, McMaster University) to determine average molecular weights was carries out on a Waters SEC system using a Waters 515 HPLC pump and a Water 717 plus autosampler connected to three Waters Styragel columns (HR2, HR3, HR4; 30 cm x 7.8 mm; 5 μm particles) connected in series and a Waters 2414 refractive index detector. THF was used as the mobile phase and the system was calibrated using polystyrene standards.

(1S, 2R, 3R, 4R)-1,2-diacetoxy-[3,4]-isopropylidenedioxycyclohexa-5-ene (5)

To a flame-dried, argon purged round-bottom flask was added diol 4 (137 mg, 0.742 mmol)¹ in anhydrous DCM (8 mL). Triethylamine (0.31 mL, 2.23 mmol) and acetic anhydride (0.21 mL, 2.23 mmol)
were added, then the mixture was cooled to 0°C. A catalytic amount of DMAP was added after which
the ice-bath was immediately removed and the reaction was allowed to stir at room temperature. TLC
analysis indicated starting material was consumed after 40 minutes and the reaction mixture was
quenched with saturated NH₄Cl (5 mL). The mixture was extracted with DCM (4 x 10 mL), and the
organics were dried (Na₂SO₄). The crude material was purified by silica-gel chromatography (3:1
hexanes/ethyl acetate) to obtain 190 mg (95% yield) of acetate-protected diol 5 as a white solid. mp 87–
89 °C (CHCl₃); Rₗ = 0.72 (1:4 hexanes/ethyl acetate); [α]₀²⁰ = -23 (c 1, CHCl₃); FT-IR (film) 3049, 2986,
2936, 2873, 1745, 1374, 1240, 1165, 1040 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 6.00 (ddd, J = 2.25,
3.6, 10 Hz, 1 H), 5.79 (d, J = 9.8 Hz, 1 H), 5.41 (d, J = 7.5 Hz, 1 H), 5.25 (t, J = 9.0 Hz, 1 H), 4.69(t, J = 4.9 Hz,
1 H), 4.26 (dd, J = 6.2, 9.2 Hz, 1 H), 2.12 (s, 1 H), 2.09 (s, 1 H), 1.55 (s, 1 H), 1.41 (s, 1 H); ¹³C NMR (CDCl₃,
75 MHz) δ 170.5, 170.2, 130.8, 124.9, 111.2, 75.4, 72.3, 72.1, 70.7, 27.8, 26.2, 21.0, 20.9; MS (EI⁺) m/z
255 (M-CH₃); HRMS calcd. for C₁₃H₁₈O₆: 270.1103, C₁₂H₁₅O₆ (M-CH₃): 255.0869. Found: 255.0868; Anal
calcd.: C 57.77, H 6.71. Found C 57.96, H 6.83. Characterization data is consistent with published data. ²

(1S, 2R, 3S, 4S, 5R, 6R)-3,4-diacetoxy-[5,6]-isopropylidenedioxycyclohexa-1,2-diol (6)

To round-bottom flask was added N-methyl-morpholine-N-oxide (32 mg, 0.273 mmol) in a solution of
1:4 H₂O/acetone (1.1 mL). A catalytic amount of OsO₄ was added to the stirring reaction solution. A
solution of alkene 5 (67 mg, 0.248 mmol) was added to the reaction flask by addition funnel in 0.5 mL of
acetone. The reaction mixture was allowed to stir at room temperature under argon. The starting
material was consumed after 48 hours. The reaction mixture was then quenched with saturated NaHSO₃
(5 drops), extracted with DCM (3 x 10 mL) and the organics dried over Na₂SO₄. The crude material was
purified by silica-gel chromatography (1:2, hexanes/ethyl acetate) to obtain 38 mg (50% yield) of diol 6
as a white solid. mp 87–89 °C (CHCl₃); Rₗ = 0.47 (1:4 hexanes/ethyl acetate); [α]₀²⁰ = -93 (c 0.5, CHCl₃); FT-
IR (film) 3451, 2988, 1752, 1729, 1374, 1244, 1166, 1055, 1028 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 5.17
(m, J = 8.1 Hz, 1 H), 4.35 (s, 1 H), 4.01 (s, 1 H), 2.96 (d, J = 15.1 Hz, 1 H), 2.10 (s, 1 H), 1.56 (s, 1 H), 1.38 (s, 1 H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta\) 171.6, 170.1, 110.1, 76.4, 73.4, 72.4, 70.8, 69.4, 27.6, 25.9, 20.9; MS (EI+) \textit{m/z} 289 (M-CH\(_3\)); HRMS calcd. for C\(_{13}\)H\(_{20}\)O\(_8\): 304.1158, C\(_{13}\)H\(_{20}\)O\(_8\) (M-CH\(_3\)): 289.0923 Found: 289.0919; Anal calcd.: C: 51.31, H: 6.62. Found C: 51.36, H: 6.56.

\((1R, 2R, 3S, 4S, 5R, 6R)\)-3,4-diacetoxy-[1,2;5,6]-diisopropylidenedioxycyclohexane (7)

Diol 6 (0.8865 g, 2.89 mmol) was dissolved in acetone (12 mL) and 2,2 dimethoxypropane (0.71 mL, 5.79 mmol). A catalytic amount of pTsOH was added and the reaction was allowed to proceed at room temperature. The reaction was monitored by TLC (1:1 hexanes/ethyl acetate). Starting material was consumed after 24 hours upon which time the reaction mixture was concentrated under reduced pressure. The crude material was redissolved in ethyl acetate (60 mL) and washed sequentially with saturated NaHCO\(_3\), H\(_2\)O and brine. The organic layer was collected and dried over Na\(_2\)SO\(_4\). The crude material was purified by silica-gel chromatography (1:1 hexanes/ethyl acetate) to yield 0.88 g of diacetate 7 as a white solid in 88% yield. Characterization is consistent with previously published data for this compound.\(^3,\,4\)

\((1S, 2S, 3R, 4R, 5S, 6S)\)-3,4-dihydroxy-[1,2;5,6]-diisopropylidenedioxycyclohexane (8)

Diacetate 7 (2.15 g, 6.25 mmol) was dissolved in methanol (62 mL). 10% K\(_2\)CO\(_3\) (1.04 g, 7.50 mmol, 11 mL) was added dropwise at room temperature. The reaction mixture was allowed to stir for 24 hours, then concentrated under reduced pressure. The resulting aqueous solution was then adjusted to pH 4 with 1M HCl. The solution was then extracted with ethyl acetate (6 x 15 mL) and the organic layers were combined and dried over Na\(_2\)SO\(_4\) before concentration in the usual manner to provide 1.46 g of diol 8 in 90% yield. Spectral data is consistent with previously published data.\(^5,\,6\)

\((1S, 2S, 3R, 4R, 5S, 6S)\)-3,4-di(pent-4-enoxy)-[1,2;5,6]-diisopropylidenedioxycyclohexane (9)
A flame-dried flask was charged with NaH (60% in mineral oil, 0.24 g, 29.22 mmol) in DMF (25 mL) and a magnetic stirring bar under argon. Diol 8 (1.52 g, 5.84 mmol) in DMF (33 mL) was added dropwise to the NaH at 0°C and the mixture was allowed to stir at this temperature for 50 minutes when 5-bromo-1-pentene (3.5 mL, 29.22 mmol) was added dropwise over 5 minutes. The reaction mixture was stirred at room temperature for an additional 15 hours then quenched with water and the aqueous mixture was extracted with diethyl ether (6 x 20 mL). The organic layers were collected, dried over anhydrous MgSO₄, and concentrated under reduced pressure. The crude material was purified by silica-gel chromatography (9:1 to 4:1; hexane: ethyl acetate) to provide 1.80 g of diene monomer 9 (78% yield). Rf = 0.85 (2:1 hexane/ethyl acetate); [α]D20 = 2.0 (c 1, CHCl₃); FT-IR (film) 3077, 2980, 2936, 2030, 1862, 1732, 1641, 1455, 1415, 1381, 1370, 1244, 1217, 1181, 1111 cm⁻¹; 1H NMR (CDCl₃, 300 MHz) δ 5.79 (m, J = 5.8 Hz, 1 H), 5.02 (s, 1 H), 4.94 (t, J = 8.8 Hz, 1 H), 4.15 (s, 1 H), 3.69 (m, J = 7.5 Hz, 1 H), 3.28 (s, 1 H), 2.11 (q, J = 7.0 Hz, 1 H), 1.66 (q, J = 7.0 Hz, 1 H), 1.47 (s, 1 H), 1.30 (s, 1 H); 13C NMR (CDCl₃, 75 MHz) δ 138.3, 114.6, 109.4, 80.1, 79.2, 76.5, 71.4, 30.2, 29.3, 27.8, 25.3; MS (EI+) m/z 396 (M), 381 (M-CH₃); HRMS calcd. for C₂₂H₃₆O₆ (M)+: 396.2512, Found: 396.2516; Anal calcd.: C: 66.64, H: 9.15. Found C: 66.90, H: 9.39. Spectral data is consistent with that published for the enantiomer.⁷

Poly-[(1S, 2S, 3R, 4R, 5S, 6S)-3,4-di(pent-4-enoxy)-[1,2;5,6]-diisopropylidenedioxycyclohexane] (10)

Diene 9 (402 mg, 1.01 mmol) was added to a flame-dried flask equipped with a stir bar followed by several freeze-pump thaw cycles. Grubbs’ I (45 mg, 0.05 mmol) was added at room temperature to vacuum was applied where bubbling was observed. This proceeded for 2 days at which point the reaction mixture became too viscous for stirring to continue. The reaction was slowly heated to 45°C to facilitate stirring and bubbling was again observed when high vacuum was applied. The heated reaction with consistent vacuum was allowed to proceed for an additional 7 days; this resulted in a brown viscous oil. The reaction was quenched by exposure to air. The TLC (2:1 hexanes/ethyl acetate) profile
revealed a series of spots. The crude polymer was furnished by silica-gel chromatography (2:1 hexanes/ethyl acetate). The column was flushed with ethyl acetate to obtain baseline material. The ethyl acetate flush was concentrated under reduced pressure to obtain 200 mg of protected polymer 10 as brown viscous oil. SEC: 7500 g/mol, PDI = 1.35. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{ppm}$ 5.50-5.40 (m, 2 H), 4.25-4.15 (m, 4 H), 3.80-3.65 (m, 4 H), 3.31 (m, 2 H), 2.20-1.80 (m, 4 H), 1.75-1.55 (m, 4 H), 1.50 (s, 6 H), 1.33 (s, 6 H). Spectral data is consistent with the previously published enantiomer.\footnote{7}

**Poly-[(1$R$, 2$R$, 3$S$, 4$S$, 5$R$, 6$R$)-3,4-di(pent-4-enoxy)-(1,2,5,6)-tetrahydroxycyclohexane] (11)**

Protected polymer 10 (140 mg) was dissolved in THF (4 mL) and H$_2$O (1 mL). TFA (1 mL) was added dropwise at room temperature and the reaction was allow to stir for 4 days at which point the reaction appeared cloudy. Toluene was used to azeotrope off the TFA. The resulting sludge was washed with CH$_2$Cl$_2$ (3 x 2 mL). The left over sludgy material was placed into a vial followed by several CH$_2$Cl$_2$ and ethyl acetate washes until a white solid was obtained. The material was dried under high vacuum and the sides of the vial were gently scraped to obtain 35 mg of deprotected polymer 11 as an off-white solid. SEC: $M_w = 6$ kg/mol, $D = 1.35$. $\alpha_{o}^{27} = -25$ (c 2.0, CH$_3$OH). Consistent with previously reported optical rotation of enantiomer.\footnote{7}

**[(1$S$,2$R$,3$R$,6$R$)-[2,3]-isopropylidenedioxy-7-oxabicyclo[4.1.0]hept-4-ene (12)]**

Epoxide 2 (22.03 g, 90 mmol), prepared as previously described,\footnote{8} was dissolved in anhydrous benzene (200 mL) and tributyltin hydride (31.2 mL, 116 mmol) and the solution was deoxygenated using argon. The reaction mixture was then heated to reflux and 1,1’-Azobis(cyclohexanecarbonitrile) (5.4 g, 36 mmol) was then added portionwise, 500 mg at a time, over the following 12 hours. Following completion the reaction was cooled to ambient and concentrated to dryness. The material was purified by dry vacuum chromatography (100 to 80% hexanes in ethyl acetate in 2% gradient steps) to provide 11g of the dehalogenated olefin 12 in 73% yield. Over three runs, on scales varying from 10g to 22g of
material, yields of 55, 73 and 82% were obtained respectively. $\alpha_0^{}\text{D} = -8.2$ (c 2.0, CHCl$_3$); $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{\text{ppm}}$ 6.04 (ddd, $J = 10.1$, 3.9, 1.5 Hz, 1H), 5.78 ($\text{pseudo-d}$, $J = 10.2$ Hz, 1H), 4.76 (dd, $J = 7.0$, 1.1 Hz, 1H), 4.44 (m, 1H), 3.53 (dd, $J = 3.6$, 1.9 Hz, 1H), 3.32 (dd, $J = 3.8$, 3.8 Hz, 1H), 1.38 (s, 6H). Spectral data is consistent with that previously published for the compound.9

(1R,2R,3R,6R)-[2,3]-isopropylidenedioxy-7-oxabicyclo[4.1.0]heptane (13)

Olefin 12 (3.0 g, 17.9 mmol) was dissolved in methanol (30 mL) in a 250mL two-necked flask equipped with a magnetic stirring bar and a 100 mL dropping funnel. The reaction mixture was cooled to 0 °C in an ice bath, and potassium azodicarboxylate (PAD, 17 g, 90 mmol) was added at once. A mixture of methanol (12 mL) and acetic acid (24 mL) was then added dropwise via the funnel. The reaction solution was then kept at 0 °C for 2 hours, and then allowed to warm to ambient and stirred for an additional 16 hours. NaHCO$_3$ was then added as a saturated solution until the pH reached 7. The reaction mixture was then extracted 6 times with ethyl acetate, the combined organics were dried, filtered and concentrated in the usual manner and purified by flash chromatography (10:1 hexanes: ethyl acetate) to provide 1.7 g of the product as a white solid in 55% yield. $^1$H NMR (CDCl$_3$, 300 MHz) $\delta_{\text{ppm}}$ 4.25 (d, $J = 5.9$ Hz, 1H), 4.18-4.12 (m, 1H), 3.22-3.17 (m, 1H), 2.94 (m, 1H), 2.10-1.97 (m, 1H), 1.89 (tdd, $J = 14.9$, 5.0, 2.6, 2.6 Hz, 1H), 1.70-1.59 (m, 2H), 1.39 (s, 3H), 1.32 (s, 3H). Spectral data is identical with that found for the enantiomer, 14 (below).

(1S,2S,3S,6S)-[2,3]-isopropylidenedioxy-7-oxabicyclo[4.1.0]heptane (14)

Olefin 19 (6.0 g, 39 mmol) was dissolved in CH$_2$Cl$_2$. mCPBA (77%, 13.1 g, 58.5 mmol) was dissolved in CH$_2$Cl$_2$, dried with magnesium sulfate, and filtered directly into the flask containing 19. Sodium hydrogen carbonate (100 mg) was then added and the reaction mixture was allowed to stir at ambient temperature for 16 hours. The reaction was then diluted with additional CH$_2$Cl$_2$ and a saturated solution of sodium metabisulfite, stirred an additional ten minutes, then the layers were separated, and the
organic phase washed sequentially with saturated sodium bicarbonate and brine. Following drying, filtration and concentration in the usual fashion, the product was purified by flash chromatography (10:1, hexanes: ethyl acetate) to provide 4.7 g of the title compound in 71 % yield. ¹H NMR (CDCl₃, 300 MHz) δ ppm 4.25 (d, J = 5.9 Hz, 1H), 4.18-4.12 (m, 1H), 3.22-3.17 (m, 1H), 2.94 (m, 1H), 2.10-1.97 (m, 1H), 1.89 (tdd, J = 14.9, 5.0, 2.6, 2.6 Hz, 1H), 1.70-1.59 (m, 2H), 1.39 (s, 3H), 1.32 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ ppm 108.8, 70.7, 70.6, 52.2, 51.8, 27.6, 25.6, 17.7, 17.3. Spectral data is consistent with that previously published for this compound.¹⁰

(1R,2S,3R)-(2,3)-isopropylidenedioxycclohexanol (16)

Vinyl bromide 12 (400 mg, 2.3 mmol) was dissolved in a mixture of methanol (8 mL) and triethylamine (2 mL) and sodium bicarbonate (20 mg). Argon was bubbled through the reaction mixture for 1 hour, followed by the addition of palladium on carbon (40 mg); the reaction mixture was then evacuated, then charged with hydrogen gas and stirred at ambient temperature for 8 hours. The reaction mixture was then filtered through a celite pad, and the filtrate was concentrated to dryness. The residue was partitioned between ethyl acetate and 10 % HCl. The organic phase was washed with brine, and then dried filtered and concentrated. The reaction was passed through a silica column to recover 135 mg of the product as the only isolatable compound as a clear oil in 36 % yield. Clear, colourless liquid; Rf = 0.22 (4:1 hexanes:ethyl acetate, vanillin); [α]²⁰D = -100.5° (c = 1.2, CHCl₃); b.p. = 190-193 ºC/60 mmHg; ¹H NMR (300 MHz, CDCl₃): δ ppm 4.22 (dd, J = 7.4, 3.9 Hz, 1H), 3.72 (dd, J = 7.3, 5.2 Hz, 1H), 3.60 (ddd, J = 11.6, 7.3, 4.5 Hz, 1H), 3.19 (bs, 1H-OH), 1.98 (d, J = 13.9 Hz, 1H), 1.84-1.71 (m, 1H), 1.65-1.46 (m, 3H), 1.43 (s, 3H), 1.29 (s, 3H), 1.22-1.04 (m, 1H); ¹³C NMR (75 MHz, CDCl₃): δ ppm 108.4, 81.6, 74.4, 72.5, 30.5, 28.4, 26.8, 26.3, 18.7; IR νmax. (CHCl₃) 3600, 3024, 2990, 2941, 1453, 1383,1248, 1053, 1037, 753 cm⁻¹; HRMS (El) Calculated for C₈H₁₁O₂ (M-15)⁺: 157.0865. Found: 157.0867.

(1S,2S)-3-bromocyclohex-3-ene-1,2-diol (17)
Diene 1 (20.0 g, 105 mmol) was dissolved in methanol (60 mL) in a 1L two-necked flask equipped with a mechanical overhead stirrer and a 250 mL dropping funnel. The reaction mixture was cooled to 0 °C in an ice bath, and potassium azodicarboxylate (PAD, 60.0 g, 315 mmol) was added at once. A mixture of methanol (50 mL) and acetic acid (64 mL) was then added dropwise via the funnel. The reaction solution was then kept at 0 °C for 5 hours, and then allowed to warm to ambient and stirred for an additional 16 hours. NaHCO₃ was then added as a saturated solution until the pH reached 7. The reaction mixture was then extracted 6 times with ethyl acetate, the combined organics were dried, filtered and concentrated in the usual manner to provide 16.7 g of the product as a white solid in 83% yield. $^1$H NMR (CDCl₃, 300 MHz) δ ppm 6.16 (dd, $J = 4.5$, 3.6 Hz, 1H), 4.16 (d, $J = 4.0$ Hz, 1H), 3.88 (td, $J = 9.2$, 4.0, 4.0 Hz, 1H), 3.11 (bs, 2H), 2.30-2.14 (m, 1H), 2.10-2.00 (m, 1H), 1.84-1.65 (m, 2H). Spectral data is consistent with that previously published for the compound.¹¹

(1S,2S)-3-bromo-[1,2]-isopropylidenedioxycyclohex-3-ene (18)

Diol 17 (16.7 g, 87.2 mmol) was dissolved in acetone (200 mL) and 2,2 dimethoxypropane (40 mL, 326 mmol). A catalytic amount of pTsOH was added and the reaction was allowed to proceed at room temperature. The reaction was monitored by TLC (1:1 hexanes/ethyl acetate), and deemed complete after 2 hours, and the mixture was concentrated to dryness. The crude material was redissolved in ethyl acetate (60mL) and washed sequentially with saturated NaHCO₃, H₂O and brine. The organic layer was collected and dried over Na₂SO₄. The crude material was purified by silica-gel chromatography (1:1 hexanes/ethyl acetate, silica pre-neutralized with triethylamine) to yield 20 g of vinyl bromide 18 as a white solid in quantitative yield. Characterization is consistent with previously published data for this compound.¹¹

(3R,4S)-[3,4]-isopropylidenedioxycyclohexene (19)
Vinyl bromide 18 (13.0g, 56.0 mmol) was dissolved in anhydrous benzene and argon was bubbled through the solution for 15 minutes. The reaction flask was then fitted with a water-cooled condenser, and the combined apparatus was purged with argon, prior to being heated to reflux under an argon balloon. At this point tributyltin hydride (21.2 g, 72.8 mmol) was added in one batch followed by ABCN (2.7 g, 11.2 mmol) in portions over 3 hours. After a total of 4 hours under reflux, the reaction was determined to be complete by TLC (vanillin 4:1 hexanes: ethyl acetate) and allowed to cool to ambient temperature. Benzene was removed under reduced pressure, and the product was then distilled from the reaction mixture (120 ºC, 100 mm Hg) to provide 6.2 g of pure product and 2.3 g of material contaminated with tributyltin byproducts. An additional 500 mg of product was obtained following a second fractional distillation of the contaminated material providing a total of 6.7 g of the cyclohexene product as a clear, colourless liquid in 78 % yield. Clear, colourless liquid; Rf = 0.62 (4:1 hexanes:ethyl acetate, vanillin); [α]_D^20 = -8.25º (c = 2.0, CHCl₃); b.p. = 90 ºC/35 mmHg; _1H NMR (300 MHz, CDCl₃): δ ppm 5.91 (ddd, J = 9.4, 3.7, 3.7 Hz, 1H), 5.71 (ddd, J = 9.4, 3.3, 2.2 Hz, 1H), 4.44 (ddd, J = 4.2, 2.6, 1.0 Hz, 1H), 4.27 (ddd, J = 5.8, 5.7, 3.8 Hz, 1H), 2.24-2.09 (m, 1H), 1.96-1.63 (m, 3H), 1.42 (s, 3H), 1.37 (s, 3H); _13C NMR (75 MHz, CDCl₃): δ ppm 131.1, 125.3, 108.2, 73.0, 71.3, 28.0, 26.4, 25.5, 20.7; IR _ν_max_: (CHCl₃) 3025, 3011, 2988, 2935, 1453, 1380, 1238, 1049, 908, 867, 755 cm⁻¹; HRMS (EI) Calculated for C₈H₁₄O₂ (M-15)⁺: 139.0759. Found: 139.0757.

Poly-[(1R,2R,3R,4R)-[3,4]-isopropylidenedioxy-cyclohexenoxide] (21)

Triethyl aluminum (1M in hexanes, 130 µL, 0.13 mmol) was added to a flame-dried, argon-charged round-bottomed flask equipped with a magnetic stirring bar. The Lewis acid was cooled to 0 ºC, and water (0.087 mmol, 1.6 µL) was added and the catalyst stirred for 30 minutes. Epoxide 13,12 was then added dropwise (250 mg, 1.6 mmol) as a solution in anhydrous toluene (400 µL). The material was then warmed to ambient, stirred 24 hours, then heated to 50 ºC for 12 hours, then to 70 ºC for a final 12 hours. After cooling to room temperature, the solution had noticeably thickened, and the reaction was
quenched with 100 μL of methanol. The volatiles were then removed, and the residue was then triturated thrice each with diethyl ether and methanol successively. The resulting 80 mg of brown residue was sparingly soluble in THF, and chloroform. $^1$H NMR (CDCl$_3$, 300 MHz) δ ppm 4.32-4.08 (m, 2H), 4.01-3.82 (m, 1H), 3.65-3.53 (m, 1H), 2.15-1.86 (m, 2H), 1.71-1.58 (m, 2H), 1.50-1.42 (m, 3H), 1.36-1.22 (m, 3H). SEC: $M_w = 11.2$ kg/mol, PDI = 2.3. MALDI (Masses correspond to [M$_n$+AlEtOH]$^+$) = 5164 (30 repeats), 4995, 4823, 4654, 4485, 4311.

**Poly-[(1S,2S,3S,4S)-[3,4]-isopropylidenedioxy-cyclohexenoxide] (22)**

Triethyl aluminum (1M in hexanes, 130 μL, 0.13 mmol) was added to a flame-dried, argon-charged round-bottomed flask equipped with a magnetic stirring bar. The Lewis acid was cooled to 0 °C, and water (0.087 mmol, 1.6 μL) was added and the catalyst stirred for 30 minutes. Epoxide 14$^{10}$ was then added dropwise (200 mg, 1.3 mmol) as a solution in anhydrous toluene (400 μL). The material was then warmed to ambient, stirred 24 hours, then heated to 50 °C for 12 hours, then to 70 °C for a final 12 hours. After cooling to room temperature, the solution had noticeably thickened, and the reaction was quenched with 100 μL of methanol. The volatiles were then removed, and the residue was then triturated thrice each with diethyl ether and methanol successively. The resulting 71 mg of brown residue was sparingly soluble in THF, and chloroform. $^1$H NMR (CDCl$_3$, 300 MHz) δ ppm 4.30-4.09 (m, 2H), 4.01-3.80 (m, 1H), 3.65-3.50 (m, 1H), 2.17-1.83 (m, 2H), 1.73-1.55 (m, 2H), 1.53-1.42 (m, 3H), 1.35-1.24 (m, 3H); SEC: $M_w = 12.2$ kg/mol, PDI = 2.4. MALDI (Masses correspond to [M$_n$+AlEtOH]$^+$) = 5846 (34 repeats), 5675, 5505, 5334.

**Poly-[(1R,2R,3R,4R)-[3,4]-isopropylidenedioxy-1,2-epoxy-cyclohex-5-ene] (23)**

Diethyl aluminum chloride (1M in hexanes, 130 μL, 0.13 mmol) was added to a flame-dried, argon-charged round-bottomed flask equipped with a magnetic stirring bar. The Lewis acid was cooled to 0 °C, and water (0.087 mmol, 1.6 μL) was added and the catalyst stirred for 30 minutes. Epoxide 12$^{13}$
was then added dropwise (200 mg, 1.3 mmol) as a solution in anhydrous toluene (200 μL). The material was then warmed to ambient, stirred 24 hours, then heated to 50 °C for 12 hours, then to 70 °C for a final 12 hours. After cooling to room temperature, the solution had thickened to the point where stirring was no longer possible, and the reaction was quenched with 100 μL of methanol. The volatiles were then removed, and the residue was then triturated thrice each with diethyl ether and methanol successively. The resulting 32 mg of brown powder was sparingly soluble in THF, and mostly insoluble in chloroform. A small portion of the material was consequently deprotected (dissolved in TFA:THF:H2O 4:1:1 and stirred for 6 hours then concentrated to dryness) for 1H analysis (DMSO-d6). SEC and MALDI were carried out on the THF soluble protected title compound. 1H NMR (DMSO-d6, 300 MHz) δ ppm 6.00-5.59 (m, 2H), 4.53-4.32 (m, 1H), 4.13-3.91 (m, 1H), 3.88-3.69 (m, 2H); SEC: Mw = 3.0 kg/mol, PDI = 2.7. MALDI (Masses correspond to [Mn-CH3]+= 2505 (15 repeats), 2169 (13 repeats), 2002, 1833 (11 repeats), 1665, 1497.

Poly-[(1R,2R,3S,4S)-5-bromo-[3,4]-isopropylidenedioxy-1,2-epoxy-cyclohex-5-ene] (24)

Triethyl aluminum (1M in hexanes, 130 μL, 0.13 mmol) was added to a flame-dried, argon-charged round-bottomed flask equipped with a magnetic stirring bar. The Lewis acid was cooled to 0 °C, and water (0.087 mmol, 1.6 μL) was added and the catalyst stirred for 30 minutes. Epoxide 2,8 was then added dropwise (200 mg, 1.3 mmol) as a solution in anhydrous toluene (200 μL). The material was then warmed to ambient, stirred 24 hours, then heated to 50 °C for 12 hours, then to 70 °C for a final 12 hours. After cooling to room temperature, the solution had thickened to the point where stirring was no longer possible, and the reaction was quenched with 100 μL of methanol. The volatiles were then removed, and the residue was then triturated thrice each with diethyl ether and methanol successively. The resulting 32 mg of brown powder was sparingly soluble in THF, and mostly insoluble in chloroform. A small portion of the material was consequently deprotected (dissolved in TFA:THF:H2O 4:1:1 and
stirred for 6 hours then concentrated to dryness) for $^1$H analysis (DMSO-d6). SEC and MALDI were carried out on the THF soluble protected title compound. $^1$H NMR (DMSO-d6, 300 MHz) $\delta_{ppm}$ 6.00-5.86 (m, 1H), 4.53-4.33 (m, 2H), 4.22-4.04 (m, 2H); SEC: $M_w$ = 4.0 kg/mol, PDI = 2.5. MALDI (Masses correspond to $[M+n+AlOH_2-CH_3]^+$): 2719 (11 repeats), 2492, 2268, 2044, 1820.

Poly-[2,2,7,7-Tetramethyl-5-cinnamyloxy-6-(3,5-hexadienyloxy)-hexahydrobenzo[1,2-d;3,4-d']bis[1,3]dioxol-4-ol] (27)

Janus diene/dienophile 24 (400 mg, 0.85 mmol), 14 was dissolved in anhydrous xylene in a Schlenk pressure tube equipped with a magnetic stirring bar under argon, and the reaction was stirred under high vacuum at 0 °C for 1 hour. The vessel was then isolated under vacuum and heated to 141 °C in an oil bath for 92 hours. After cooling, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (7.5:1 hexanes:ethyl acetate, 0.1 % triethylamine) to provide 80 mg of previously reported cycloadduct 26 in 20 % yield. 14 The column was then eluted using 3:2 hexanes: ethyl acetate to recover four different fractions of oligomeric material, fractions 1 (70 mg), 2 (67 mg), 3 (82 mg) and 4 (63 mg) respectively as off white solids. End group analysis by NMR, using the olefin of the cinnamyl moiety, MALDI, and SEC(THF) were used to estimate the molecular weight and number of monomeric repeats present in each of the fractions.

$^1$H NMR$_{Fraction 3}$ (CDCl$_3$, 300 MHz) $\delta_{ppm}$ 7.50-7.01 (m, 75H), 6.54 (d, $J = 16.0$ Hz, 1H), 5.30-4.87 (m, 23 H), 4.70-4.26 (m, 42 H), 3.32-2.80 (m, 23H), 2.40-2.12 (m, 20H), 1.54-1.28 (m, 120H).

Fraction 1: $^1$H NMR : 2.5 repeats (implies $M_w$ of 1172 g/mol); MALDI: 767 (2 repeats-200), 1203 (3 repeats-200), 1688 (4 repeats-200). SEC: $M_w$ = 1110, PDI = 1.14.

Fraction 2: $^1$H NMR: 3.6 repeats (implies $M_w$ of 1742 g/mol); MALDI: 1203, 1689, 2174 SEC: $M_w$ = 1708, PDI = 1.22.
Fraction 3: $^1$H NMR: 10 repeats (implies $M_w$ of 4890 g/mol); MALDI: 1600, 2085, 2570, 3039, 3538, 4023.
SEC: $M_w = 2070$, PDI = 1.28.

Fraction 4: $^1$H NMR: 17 repeats (implies $M_w$ of 8300 g/mol); MALDI: 1600, 2086; SEC: $M_w = 2506$, PDI = 1.42.