

Supporting Information for:

Template Ring-Opening Metathesis (T-ROM) of Cyclic Olefins Bound to Sequence-Controlled π -Conjugated Oligomers

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General Experimental:

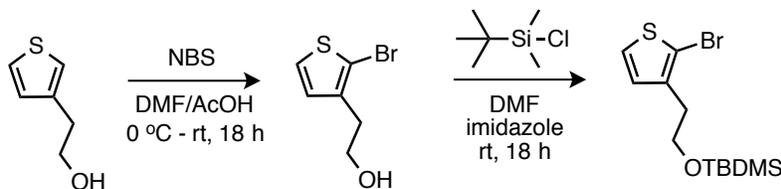
Reactants and reagents including 3-thiophene ethanol, 3-methyl thiophene, 3-hexyl thiophene, N-bromo succinimide (NBS), tert-butyldimethylsilyl chloride, imidazole, tributyltin chloride, n-butyllithium (1.6M in hexanes), diisopropylamine, tetrakis triphenylphosphine palladium, cyclooctadiene, exo-3 norbornyl carboxylic acid, diisopropyl carbodiimide, and 4-dimethyl aminopyridine were purchased from Sigma-Aldrich as ACS Reagent Plus grade and used without further purification, except where noted otherwise. Tributyltin chloride, n-BuLi(2.5M in THF), tetra-n-butylammonium fluoride (TBAF) (1.0 M solution in THF) and diisopropyl amide (LDA) were purchased from Sigma-Aldrich and stored in a glove box under N₂ atmosphere. Organic solvents: tetrahydrofuran(THF), dichloromethane (DCM), N,Ndimethylformamide (DMF), ethyl acetate, hexane, methanol (MeOH), and Toluene were obtained from Sigma-Aldrich (USA). Bio Beads SX-1 was purchased from Bio-Rad (USA). Deionized water was purified using EDM Millipore purification system. Flash-column chromatography was employed using silica gel (60 Å pore size, 40-63 µm technical grade, Sigma-Aldrich). Thin-layer chromatography was performed on IB2-F J.T. Baker silica gel TLC (Germany). All reactions were carried out under inert gas atmosphere under strictly anhydrous conditions, except where noted otherwise. Standard Schlenk line techniques using an inert gas/vacuum double manifold were employed for all reagent manipulations.

Instrumentation:

Proton nuclear magnetic resonance (¹H NMR) spectra were recorded using 500 MHz Agilent NMR spectrometer at 25 °C. NMR chemical shifts were reported in parts per million (ppm, δ) and referenced to tetramethylsilane ((CH₃)₄Si, 0.00 ppm) or to residual solvent signals (CDCl₃ (δ 7.27),). Data are expressed as chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances) and integration. Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded using 500 MHz Agilent NMR spectrometer at 25 °C. NMR chemical shifts were reported in parts per million (ppm, δ) and referenced to residual solvent signals (CDCl₃ (δ 77.0)).

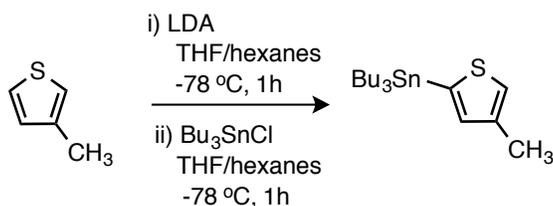
Mass spectrometric measurements were performed by the mass spectrometry service of the laboratory in the Center for Biotechnology and Interdisciplinary Studies (CBIS) on a Bruker Ultraflex III MALDI-TOF equipped with a nitrogen smart beam laser ($\lambda = 337$ nm, 150 μ J, 3 ns) at a pulse rate of 50 to 100 Hz using α -cyano-4-hydroxycinnamic acid (CHCA) as matrix. Ions were accelerated with pulsed ion extraction (PIE) by a voltage of 25 kV. The analyzer was operated in reflection mode and the ions were detected using a micro channel plate detector.

Synthetic Procedures



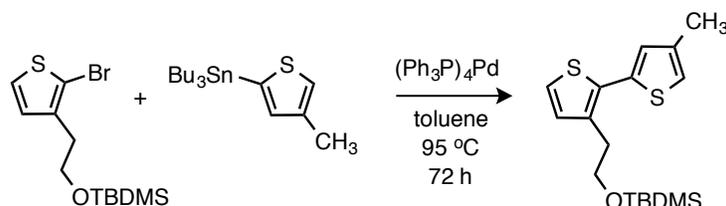
2-(2-bromothiophen-3-yl)ethan-1-ol. At 0 °C, recrystallized NBS (1.57g, 8.9mmol) was added to a solution of 2-(thiophen-3-yl)ethan-1-ol (1ml, 8.9mmol) in dry THF (20ml) under nitrogen atmosphere. The solution was allowed to warm to room temperature overnight. THF was removed under reduced pressure and mixture was dissolved in EtOAc (20ml), followed by washing with DI water (3 \times 20ml) brine (3 \times 20ml), drying over anhydrous sodium sulfate. After filtration, solvent was removed under high vacuum, the crude oil was purified by silica gel chromatography (Hex: EtOAc, 9:1) to give the product (1.18g, 64%). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.24$ (d, 1H), 6.87 (d, 1H), 3.84 (t, 2H), 2.86 (t, 2H)

(2-(2-bromothiophen-3-yl)ethoxy)(tert-butyl)dimethylsilane. Imidazole (0.86g, 12.6 mmol) and tert-butyldimethyl silyl chloride (0.92g, 6.08mmol) were dissolved in dry DMF and 2-(2-bromothiophen-3-yl)ethan-1-ol (1.05g, 5.07mmol) was added in a single portion. The reaction was stirred at 35 °C overnight. The mixture was quenched with saturated aq. Sodium carbonate and extracted with EtOAc (3 \times 20ml) followed by washing with DI water (3 \times 20 ml) and brine (3 \times 20 ml), drying over sodium sulfate. After filtration, solvent was removed under high vacuum, the crude oil was purified by silica gel chromatography (Hex) to give the product (0.97g, 60%). ¹H NMR (500 MHz, CDCl₃): $\delta = 7.18$ (d, 1H), 6.85 (d, 1H), 3.77 (t, 2H), 2.80 (t, 2H), 0.87(s, 9H), 0.00(s, 6H).

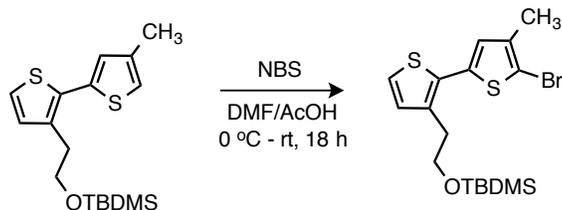


tributyl(4-methyl thiophen-2-yl) stannane (2). Lithium diisopropyl amide (LDA) was prepared by first mixing diisopropyl amine (7.15 mL, 51 mmol) with hexane (50 mL) and THF (50 mL) in a 250 mL oven-dried Schlenk flask, cooling to -78 °C, and injecting *n*-BuLi (2.5M solution, 20 mL, 50 mmol). Then, 3-methylthiophene (5 mL, 51 mmol) in THF (100 mL) was

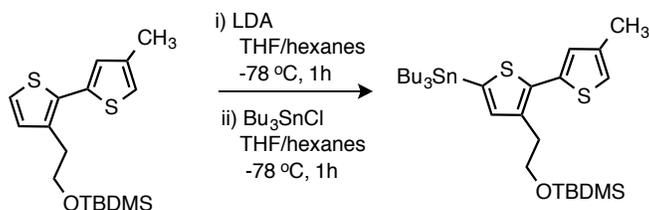
added dropwise via cannula transfer. After 30 min, tributyltin chloride (13.8 mL, 51 mmol) was injected via syringe and the reaction mixture was stirred for 1 h at $-78\text{ }^{\circ}\text{C}$. Upon warming to rt overnight, the reaction was quenched with saturated aq. sodium carbonate, and the crude reaction mixture was extracted with $3\times 50\text{ mL}$ EtOAc, followed by washing with DI water and brine, drying over magnesium sulfate, and evaporation under reduced pressure. The crude brown oil was purified by vacuum distillation (0.1 torr, $73\text{ }^{\circ}\text{C}$) to yield the pure product as a clear, colorless oil (15.3 g, 78 %).



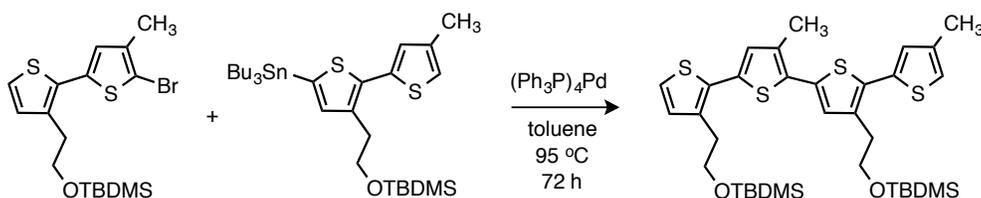
Stille Coupling, bithiophene parent “monomer” (3). In a 200 mL storage flask with a Teflon valve seal, **1** (1 g, 3.1 mmol) and **2** (1.33 g, 3.4 mmol) were dissolved in toluene (50 mL) and subjected to $3\times$ freeze/pump/thaw/cycles. $\text{Pd}(\text{Ph}_3\text{P})_4$ (36 mg, 0.031 mmol) as a slurry in toluene (1 mL) was added and subjected to another $3\times$ freeze/pump/thaw/cycles. The reaction vessel was sealed under vacuum with a Teflon valve, and then heated to $95\text{ }^{\circ}\text{C}$ for 24-72 h, or until the appearance of a black precipitate. The reaction mixture was cooled to rt, diluted with 50 mL THF, and stirred with 1M NaOH aq (100 mL) for 1 hr. The organic layer was washed with water and brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane:toluene, 9:1, $R_f = 0.35$) gave the title compd as a colorless oil (477 mg, 45%).



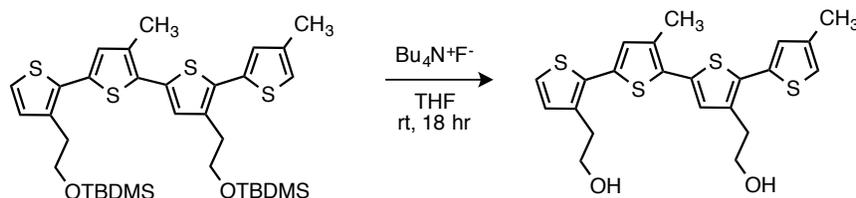
Bromination of bithiophene parent “monomer” (4). Same procedure as for **1(a)**. Amounts: Bithiophene **3** (477 mg, 1.4 mmol), NBS (0.25 g, 1.4 mmol), DMF (5 mL), AcOH (5 mL). Silica gel (EtOAc:toluene, 4:1), obtained 300 mg (49%).



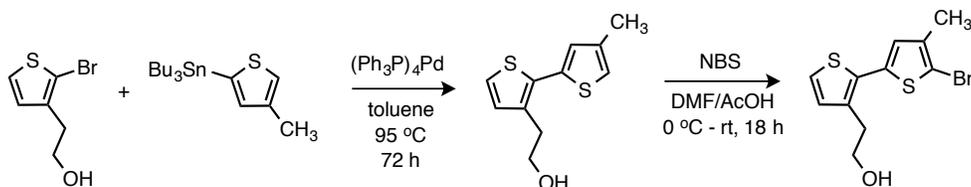
Stannylation of bithiophene parent “monomer” (5). Same procedure as for **2**. Amounts: diisopropyl amine (277 μ L, 2 mmol), *n*-BuLi (784 μ L, 1.95 mmol), bithiophene **3** (670 mg, 2 mmol), Bu₃SnCl (537 μ L, 2 mmol). No purification. Crude yield 1.03 g, 83%.



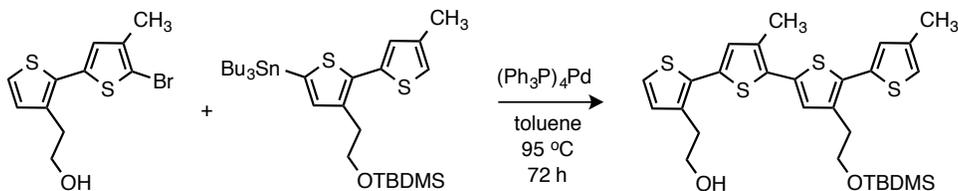
Stille Coupling, thiophene tetramer H/H (6). Same general procedure as for **3**. Amounts: **4** (100 mg, 0.24 mmol) and **5** (166 g, 0.26 mmol) in toluene (5 mL), Pd(Ph₃P)₄ (28 mg, 0.025 mmol). Purification on silica gel (hexane:toluene, 9:1) to give the pure product as a bright orange/yellow oil (136 mg, 84 %).



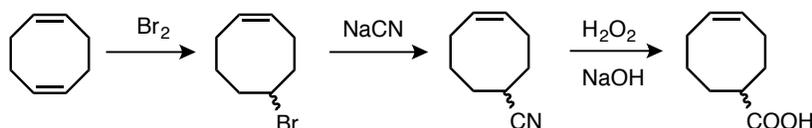
Deprotection of Side Chains. The protected template tetrathiophene (471 mg, 0.813 mmol) was dissolved in tetrabutylammonium fluoride (TBAF, 1M in THF, 2.5 mL 2.44 mmol) and stirred overnight at room temperature. Purified by silica gel column chromatography (toluene:hexanes = 4:1). Yield 92%.



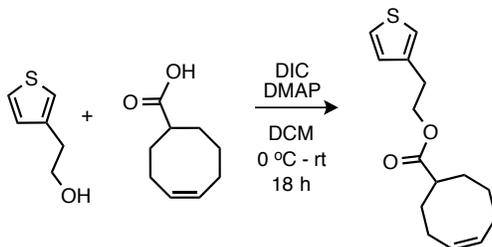
Brominated bithiophene, unprotected (7). Same procedures as for **3** and **4**. Purified by silica gel column chromatography (toluene:hexanes = 4:1), Yield 54%.



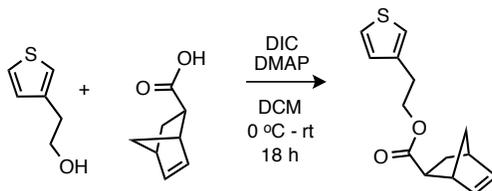
Hetero Template, n = 2 (8). Same general procedures as for **3**. Amounts: **7** (188 mg, 0.62) and **5** (433 mg, 0.69) in toluene (5 mL) with Pd(Ph₃P)₄ (72 mg, 0.06 mmol). Purification on silica gel (hexane:EtOAc, 2:1, R_f ~ 0.55) to give the pure product as a bright orange/yellow oil (295 mg, 85 %).



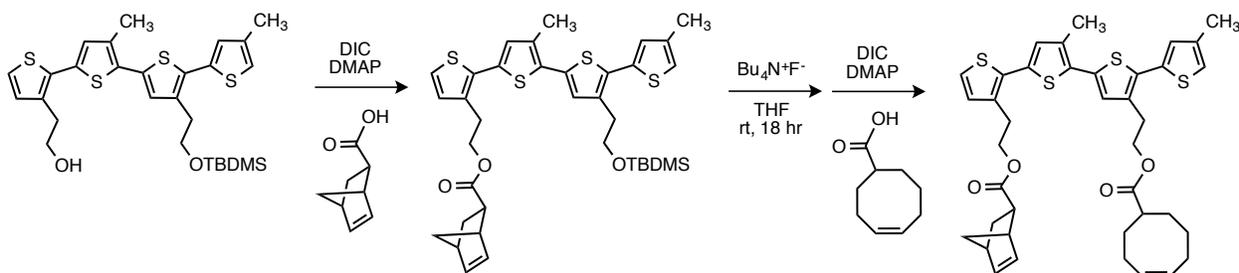
Z-cyclooct-4-ene carboxylic acid. Cyclooctadiene (COD, 25 mL, 0.2 mol) and HBr (37 mL) were mixed in a r.b. flask at room temperature overnight. The mixture was extracted with EtOAc and washed with water and brine. The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a dark brown, *malodorous* oil. The crude was distilled (40 °C, 0.4 torr) to give a non-malodorous and colorless oil (27.5 g). Then, the brominated intermediate was dissolved in DMSO (100mL), sodium cyanide was added, and the mixture was heated at 110 °C for 2 h in a r.b. flask equipped with a reflux condenser. The product was extracted with EtOAc (3×500 mL) washed with DI water (3×500 mL) and brine (500 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a dark brown oil, that was distilled (50 °C, 0.1 torr) to give a colorless oil. This intermediate (~10g) was mixed with 33 mL of aq. KOH (30% w/v) and 2.1 mL of H₂O₂ and heated to 120 °C for 48 h. Organics were extracted with EtOAc (3×200 mL) and the organic layer was set aside. The aqueous phase (containing the conjugate base of the product) was acidified with 40% phosphoric acid to pH 4 and extracted with EtOAc (3×200 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to give a brown oil. Purification by distillation (120 °C, 0.15 torr) gave the pure product as a clear, colorless oil that slowly solidifies to a waxy consistency upon standing at 4 °C for a few days. Yield 12.7 g (41 %).



(Z)-2-(thiophen-3-yl) ethyl cyclooct-4-ene carboxylate (12). In a 10 mL oven-dried Schlenk flask, the cyclooctene monomer *Z*-cyclooct-4-ene carboxylic acid (158 mg, 1 mmol) and 2-(thiophen-3-yl)ethanol (115 μ L, 1 mmol) were dissolved in anhydrous DCM (5 mL) under nitrogen and DMAP (15 mg, 0.1 mmol) was added in one portion. The solution was cooled to 0 $^{\circ}$ C and stirred for 10 min before injection of neat DIC (190 μ L, 1.5 mmol). The reaction mixture was allowed to warm to rt and stirred overnight. A white precipitate (urea byproduct) was filtered from the yellow solution. Then, the solution was diluted with ethyl acetate (50 mL) and washed with water (3x50mL) and brine (50 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure to yield a yellow viscous oil. This crude oil was purified by silica gel column chromatography (EtOAc:hexanes, 9:1, $R_f \sim 0.4$) to give the title compd (182 mg, 67%).



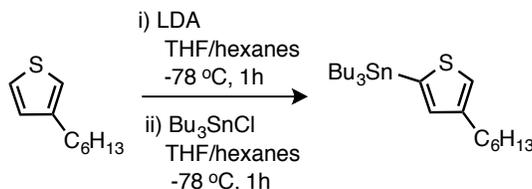
(Z)-2-(thiophen-3-yl) ethyl *exo*-norbornene carboxylate (13). Same procedure as **12**. Amounts: 2-(thiophen-3-yl)ethanol (516 μ L, 4.6 mmol), *exo*-norbornene carboxylic acid (700 mg, 5 mmol), DMAP (56 mg, 0.46 mmol), DIC (1 mL, 6.9 mmol). Purified by silica gel column chromatography (EtOAc:hexanes, 9:1, $R_f \sim 0.5$) to give the title compd (895 mg, 78%).



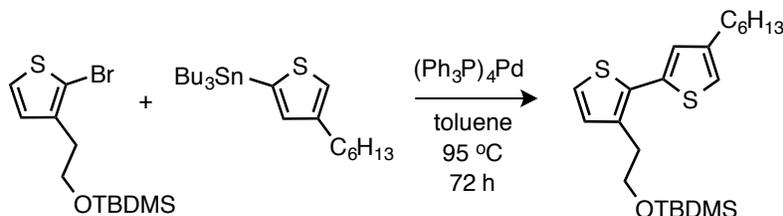
Heterodimer Parent Template. Same general procedure as **12**. Briefly, the hetero-template **8** (295 mg, 0.53 mmol) was coupled to *exo*-norbornene carboxylic acid (80 mg, 0.58 mmol), using

DMAP (6 mg, 0.053 mmol) and DIC (122 μ L, 0.79 mmol) in DCM (5 mL) yielded 290 mg (89%). Deprotection with TBAF (1.5 mL of 1M soln in THF, 1.5 mmol) yielded 210 mg (72%). Coupling with Z-cyclooct-4-ene carboxylic acid (63 mg, 0.4 mmol) using DMAP (5 mg, 0.037 mmol) and DIC (86 μ L, 0.56 mmol) in DCM (3 mL). Silica gel column (hexanes:EtOAc, 4:1) gave the pure product as a bright orange oil (220 mg, 84%).

For R₁ = hexyl side chain:

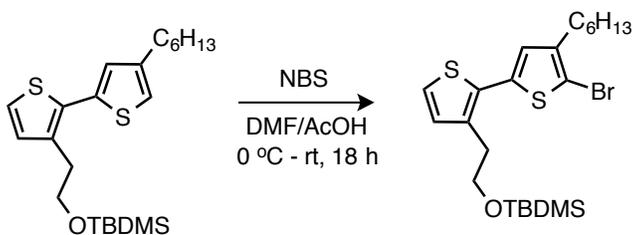


tributyl(4-hexylthiophen-2-yl)stannane. Lithium diisopropyl amide (LDA) was prepared by mixing diisopropyl amine (0.78ml, 5.56mmol) with hexane (10ml) and THF (10ml) in a 100ml oven-dried Schlenk flask, cooling to -78°C, and injecting n-BuLi (2.5M solution, 2.2ml, 5.50mmol). Then, 3-hexylthiophene (1ml, 5.56mmol) in THF (20ml) was added dropwise via cannula transfer. After 30 minutes, tributyltin chloride (1.66ml, 6.11mmol) was injected via syringe and the reaction mixture was stirred for 1 hour at -78°C. Upon warming up to room temperature overnight, the reaction was quenched with saturated aq. Sodium carbonate, and the crude reaction mixture was extracted with EtOAc (3×20ml), followed by washing with DI water (3 ×20 ml) and brine (3 ×20 ml), drying over sodium sulfate. After filtration, solvent was removed under high vacuum, the crude oil was purified by vacuum distillation (0.16mmHg, 120°C) to yield pure ptd (2.03g, 77%). ¹H NMR (500 MHz, CDCl₃): δ = 7.19 (d, 1H), 6.96 (s, 1H), 2.65 (t, 2H), 1.63-1.51(m, 8H), 1.34-1.28(m, 12H), 1.11-1.05(m, 6H), 0.91-0.86(m, 12H).

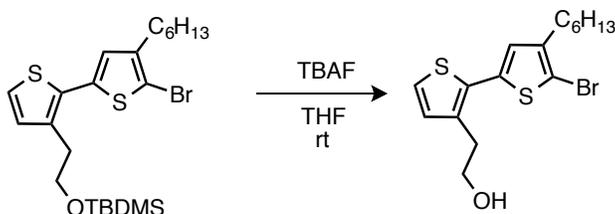


(3HT)₂-1OTBDMS. In a 200ml storage flask with a Teflon valve seal, (2-(2-bromothiophen-3-yl)ethoxy)(tert-butyl)dimethylsilane (1g, 3.1mmol) and tributyl(4-hexylthiophen-2-yl)stannane (1.56g, 3.4mmol) were dissolved in dry toluene (50ml) and subjected to 3× freeze/pump/thaw/cycles. Pd(Ph₃P)₄ (36mg, 0.031mmol) as a slurry in toluene (1ml) was added and subjected to another 3× freeze/pump/thaw/ cycles. The reaction vessel was sealed under vacuum with a Teflon valve, and then heated to 90 °C for 72 hours, or until the appearance of a black precipitate. The reaction mixture was cooled to room temperature. The organic layer was washed with water (3×50ml) and brine (3×50ml), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (Hex: Toluene, 9:1) gave pure product (727mg, 70%). ¹H NMR (500 MHz,

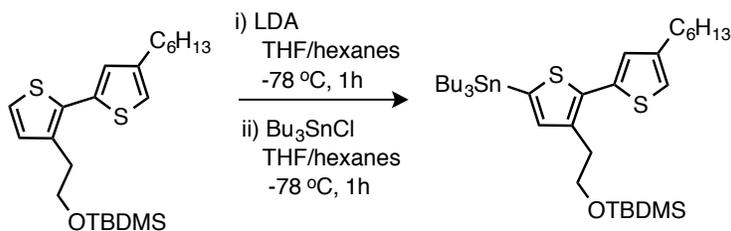
CDCl₃): δ = 7.15 (d, 1H), 6.98 (d, 1H), 6.95 (s, 1H), 6.88(s, 1H), 3.83(t, 2H), 2.98(t, 2H), 2.60(t, 2H), 1.60(m,2H) 1.33-1.31(m, 6H), 0.91-0.86(m, 12H), 0.00(s, 6H)



(3HT)₂-Br-1OTBDMS. At 0 °C, recrystallized NBS(140mg, 0.78mmol) was added to a solution of (3HT)₂-1OTBDMS (325mg, 0.79mmol) in dry THF (4ml) under nitrogen atmosphere. The solution was allowed to warm to room temperature overnight. THF was removed under reduced pressure and mixture was dissolved in EtOAc (20ml), followed by washing with DI water (3×20ml) brine (3×20ml), drying over anhydrous sodium sulfate. After filtration, solvent was removed under high vacuum, the crude oil was purified by silica gel chromatography (Hex: Toluene, 4:1) to give the product (272mg, 70%). ¹H NMR (500 MHz, CDCl₃): δ = 7.14 (d, 1H), 6.93 (d, 1H), 6.81(s, 1H), 3.80(t, 2H), 2.91(t, 2H), 2.52(t, 2H), 1.57(m, 2H) 1.31-1.29(m, 6H), 0.87-0.83(m, 12H), 0.00(s, 6H)

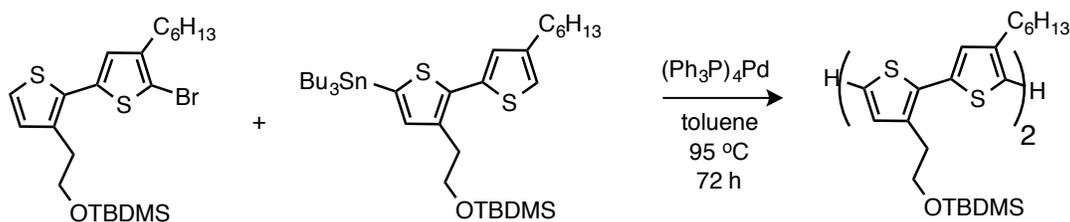


(3HT)₂-Br-1OH. Tetrabutylammonium fluoride (1M in THF, 1.23ml, 2.3mmol) was added into (3HT)₂-3OTBDMS (200mg, 0.41mmol) THF solution (2ml) and stirred at room temperature overnight. The mixture was purified by silica gel column (Hex:EtOAc,4:1) to yield pure product (137mg, 90%). ¹H NMR (500 MHz, CDCl₃): δ = 7.20 (d, 1H), 6.96(d, 1H), 6.90(s, 1H), 3.88(t, 2H), 3.05(t, 2H), 2.60(t, 2H), 1.63(m, 2H) 1.36-1.31(m, 6H), 0.87-0.83(m, 12H), 0.00(s, 6H)

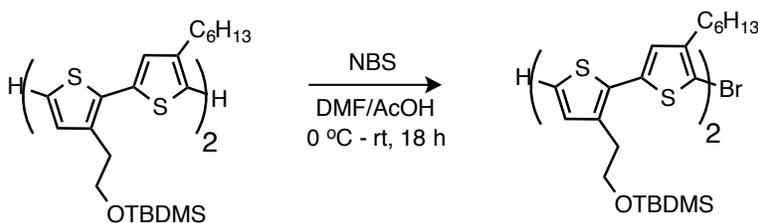


(3HT)₂-Bu₃Sn-1OTBDMS. Lithium diisopropyl amide (LDA) was prepared by mixing diisopropyl amine (0.25ml, 1.78mmol) with hexane (10ml) and THF (10ml) in a 100ml oven-

dried Schlenk flask, cooling to $-78\text{ }^{\circ}\text{C}$, and injecting $n\text{-BuLi}$ (2.5M solution, 0.71ml, 1.78mmol). Then, $(3\text{HT})_2\text{-1OTBDMS}$ (728mg, 1.78mmol) in THF (10ml) was added dropwise via cannula transfer. After 1 hour, tributyltin chloride (0.483ml, 1.78mmol) was injected via syringe and the reaction mixture was stirred for 1 hour at $-78\text{ }^{\circ}\text{C}$. Upon warming up to room temperature overnight, the reaction was quenched with saturated aq. Sodium carbonate, and the crude reaction mixture was extracted with EtOAc ($3 \times 20\text{ ml}$), followed by washing with DI water ($3 \times 20\text{ ml}$) and brine ($3 \times 20\text{ ml}$), drying over sodium sulfate. Solvent was removed over high vacuum. The product was obtained (822.5mg, 70 %) and used without purification. $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 6.96$ (s, 1H), 6.93 (s, 1H), 6.82 (s, 1H), 3.82(t, 2H), 2.98(t, 2H), 2.55(t, 2H), 1.59-1.51(m, 8H), 1.33-1.28(m, 12H), 1.09-1.04(m, 6H), 0.90-0.83(m, 18H), 0.00(s, 6H)

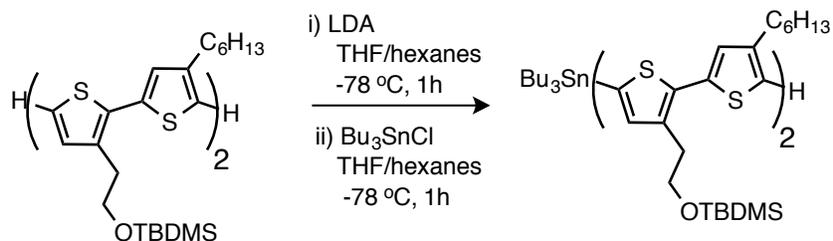


$(3\text{HT})_4\text{-2OTBDMS}$: In a 200ml storage flask with a Teflon valve seal, $(3\text{HT})_2\text{-Br-1OTBDMS}$ (522mg, 1.07mmol) and $(3\text{HT})_2\text{-Bu}_3\text{Sn-1OTBDMS}$ (822mg, 1.17mmol) were dissolved in dry toluene (15ml) and subjected to $3 \times$ freeze/pump/thaw/cycles. $\text{Pd}(\text{Ph}_3\text{P})_4$ (124mg, 0.107mmol) as a slurry in toluene (1ml) was added and subjected to another $3 \times$ freeze/pump/thaw/ cycles. The reaction vessel was sealed under vacuum with a Teflon valve, and then heated to $90\text{ }^{\circ}\text{C}$ for 72 hours, or until the appearance of a black precipitate. The reaction mixture was cooled to room temperature. The organic layer was washed with water ($3 \times 30\text{ ml}$) and brine ($3 \times 30\text{ ml}$), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (Hex: Toluene, 4:1) gave pure product (820mg, 94%). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 7.16$ (d, 1H), 7.02-6.98 (m, 4H), 6.90 (s, 1H), 3.89-3.85(m, 4H), 3.05-2.99(m, 4H), 2.77(t, 2H), 2.62(t, 2 H), 1.67-1.63(m, 4H), 1.37-1.33(m, 12H), 0.91-0.86(m, 24H), 0.00(m, 12H)

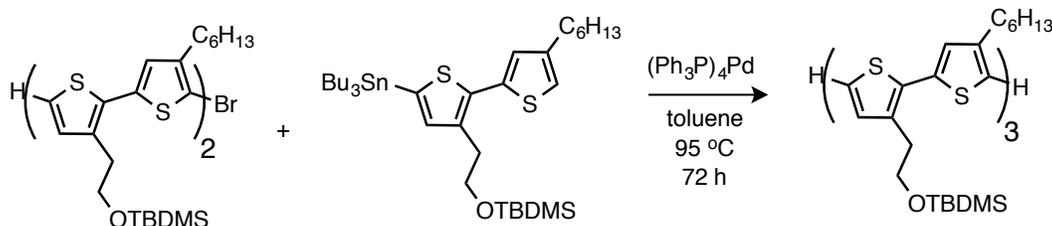


$(3\text{HT})_4\text{-Br-2OTBDMS}$: At $0\text{ }^{\circ}\text{C}$, recrystallized NBS(140mg, 0.78mmol) was added to a solution of $(3\text{HT})_2\text{-1OTBDMS}$ (325mg, 0.79mmol) in dry THF (4ml) under nitrogen atmosphere. The solution was allowed to warm to room temperature overnight. THF was removed under reduced pressure and mixture was dissolved in EtOAc (20ml), followed by washing with DI water ($3 \times 20\text{ ml}$) brine ($3 \times 20\text{ ml}$), drying over anhydrous sodium sulfate. After filtration, solvent was removed under high vacuum, the crude oil was purified by silica gel chromatography (Hex: Toluene, 4:1) to give the product (272mg, 70%). $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 7.16$ (d, 1H),

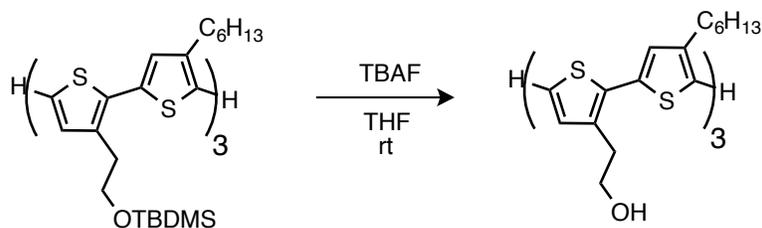
7.02-6.98 (t, 3H), 6.88 (s, 1H), 3.88-3.85(m, 4H), 3.02(t, 2H), 2.75(t, 2H), 2.56(t,2 H), 1.72-1.58(m, 4H), 1.43-1.25(m, 12H), 0.91-0.87(m,24H), 0.00(m,12H)



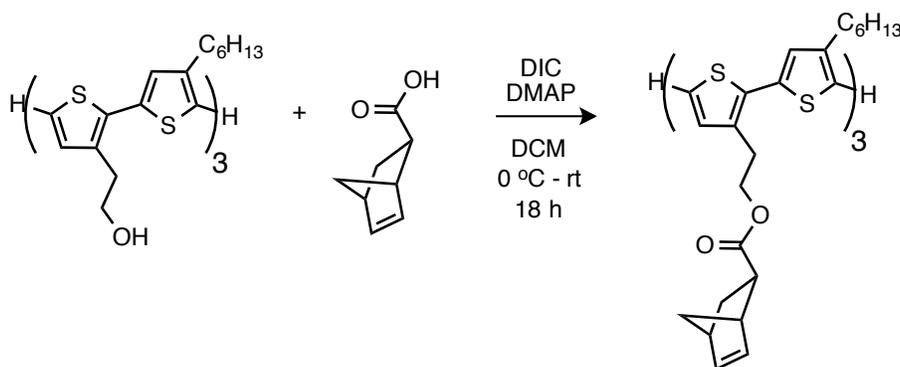
(3HT)₄-Bu₃Sn-2OTBDMS: Lithium diisopropyl amide (LDA) was prepared by mixing diisopropyl amine (0.074ml, 0.529mmol) with hexane (10ml) and THF (10ml) in a 100ml oven-dried Schlenk flask, cooling to -78.C, and injecting n-BuLi (2.5M solution, 0.21ml, 0.529mmol). Then, (3HT)₄-2OTBDMS (432mg, 0.529mmol) in THF (10ml) was added dropwise via cannula transfer. After 1 hour, tributyltin chloride (0.143ml,0.529mmol) was injected via syringe and the reaction mixture was stirred for 1 hour at -78.C. Upon warming up to room temperature overnight, the reaction was quenched with saturated aq. Sodium carbonate, and the crude reaction mixture was extracted with EtOAc (3×20ml), followed by washing with DI water(3 ×20 ml) and brine(3 ×20 ml), drying over sodium sulfate. Solvent was removed over high vacuum. The product was obtained (313mg, 55%) and used without purification. ¹H NMR (500 MHz, CDCl₃): δ =7.01-6.97 (t, 4H), 6.87 (s, 1H), 3.88-3.82(m, 4H), 3.08(t, 2H), 2.87(t, 2H), 2.76(t,2H), 2.60(t,2H) 1.70-1.57(m, 6H), 1.36-1.25(m, 25H), 1.18(m, 6H) 0.91-0.87(m,30H), 0.00(m,12H)



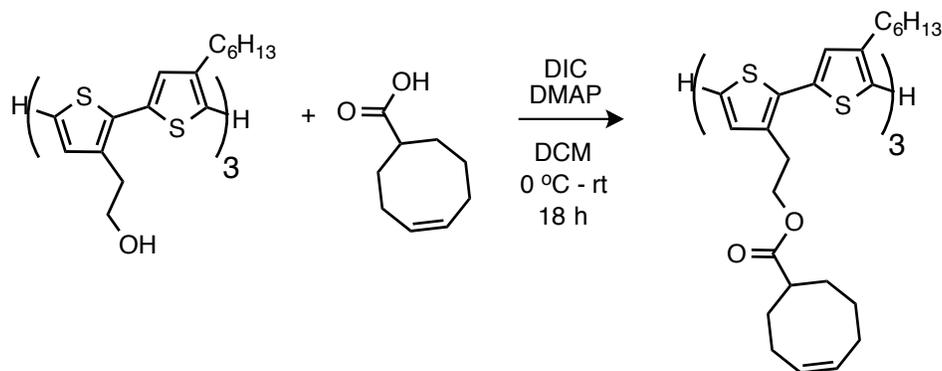
(3HT)₆-3OTBDMS: In a 50ml storage flask with a Teflon valve seal, (3HT)₄-Br-2OTBDMS (412mg, 0.46mmol) and (3HT)₂-Bu₃Sn-1OTBDMS (378mg, 0.54mmol) were dissolved in dry toluene (15ml) and subjected to 3× freeze/pump/thaw/cycles. Pd(Ph₃P)₄ (53mg, 0.046mmol) as a slurry in toluene (1ml) was added and subjected to another 3×freeze/pump/thaw/ cycles. The reaction vessel was sealed under vacuum with a Teflon valve, and then heated to 90° C for 72 hours, or until the appearance of a black precipitate. The reaction mixture was cooled to room temperature. The organic layer was washed with water (3×30ml) and brine (3×30ml), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (Hex: Toluene, 4:1) gave pure product (384mg, 68%). ¹H NMR (500 MHz, CDCl₃): δ = 7.16 (d, 1H), 7.01-6.97 (m, 6H), 6.90 (s, 1H), 3.90-3.84(m, 6H), 3.05-2.99(m, 6H), 2.79-2.76(m, 4H), 2.60(t,2 H), 1.69-1.64(m, 6H), 1.42-1.32(m, 21H), 0.91-0.88(m,33H), 0.03-0.00(m,18H)



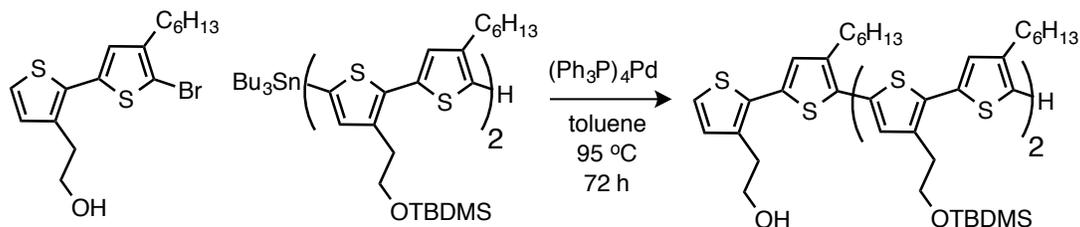
(3HT)₆-3OH: Tetreabutylammonium fluoride (1M in THF, 0.4ml, 0.39mmol) was added into (3HT)₆-3OTBDMS (80mg, 0.064mmol) THF solution (4ml) and stirred at room temperature overnight. The mixture was purified by SX1 biobeads column (THF) to yield pure product (50mg, 90%). ¹H NMR (500 MHz, CDCl₃): δ = 7.15 (d, 1H), 7.00-6.97 (m, 6H), 6.88 (s, 1H), 3.98-3.87(m, 6H), 3.05-2.99(m, 6H), 2.79-2.76(m, 4H), 2.60(t, 2 H), 1.68-1.64(m, 6H), 1.41-1.34(m, 21H), 0.88-0.83(m, 6H)



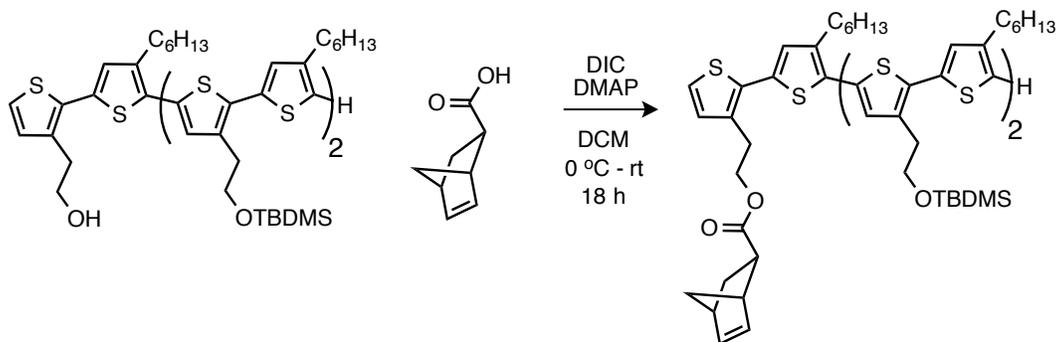
(3HT)₆-3exo-norbornene: In a 4ml oven-dried vial, the exo-norbornene carboxylic acid (13.75mg, 0.1mmol) and (3HT)₆-3OH (25mg, 0.028mmol) were dissolved in dry THF (2ml) under nitrogen and DMAP (1mg, 0.0084mmol) was added in one portion. The solution was cooled to 0°C and stirred 30 minutes before injection of neat DIC (0.018ml, 0.1mmol). The reaction was allowed to warm to room temperature and stirred overnight. The solution was diluted with EtOAc (20ml) and washed with DI water (3×20ml) and brine (3×20ml). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by SX1 biobeads column (THF) to yield the pure product (31mg, 88%). ¹H NMR (500 MHz, CDCl₃): δ = 7.21 (d, 1H), 7.01-6.98 (m, 6H), 6.92 (s, 1H), 6.11-6.08(m, 6H) 4.37-4.35(m, 6H), 3.15-3.12(m, 6H), 3.01-2.99(m, 3H), 2.89(m, 3H), 2.79-2.76(m, 4H), 2.60(t, 2 H), 2.21(m, 3H), 1.90(m, 3H) 1.68-1.64(m, 6H), 1.49-1.41(m, 27H), 0.89(m, 9H). ¹³C-NMR (500 MHz, CDCl₃): δ = 176.10, 143.92, 140.18, 138.03, 135.72, 134.67, 132.89, 130.83, 130.55, 130.46, 130.24, 130.13, 129.97, 129.28, 129.13, 128.78, 128.46, 127.75, 124.25, 120.50, 68.14, 63.95, 63.82, 46.59, 46.38, 43.16, 41.63, 38.73, 31.66, 30.49, 30.36, 29.67, 29.42, 29.23, 29.01, 29.60, 28.73, 28.59, 23.74, 22.96, 22.60, 14.07, 10.94. MS (Maldi-ToF, m/z): M⁺ Calc. 1238.7, Found 1238.5



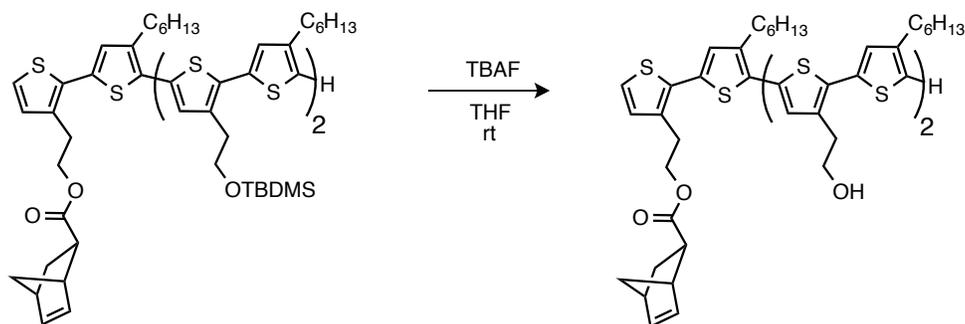
(3HT)₆-3cyclooctene: In a 4ml oven-dried vial, the Z-cyclooct-4-ene carboxylic acid (15.34mg, 0.1mmol) and (3HT)₆-3OH (25mg, 0.028mmol) were dissolved in dry THF (2ml) under nitrogen and DMAP (1mg, 0.0084mmol) was added in one portion. The solution was cooled to 0°C and stirred 30 minutes before injection of neat DIC (0.018ml, 0.1mmol). The reaction was allowed to warm to room temperature and stirred overnight. The solution was diluted with EtOAc (20ml) and washed with DI water (3×20ml) and brine (3×20ml). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by SX1 biobeads column (THF) to yield the pure product (32mg, 87%). ¹H NMR (500 MHz, CDCl₃): δ = 7.21 (d, 1H), 7.01-6.99 (m, 6H), 6.93 (s, 1H), 5.69-5.62(m,6H) 4.35-4.30(m, 6H), 3.15-3.11(m, 6H), 2.81-2.78(m,4H), 2.64(t,2H), 2.47(m, 3H), 2.37(m,3H), 2.15-2.11(m, 9H), 2.02-1.99(m,3H) 1.85-1.82(m, 3H), 1.72-1.55(m, 18H), 1.44-1.34(m,24H), 0.92-0.89(m,9H). ¹³C-NMR (500 MHz, CDCl₃): δ = 177.47, 143.91, 140.18, 134.69, 132.28, 130.50, 129.98, 129.55, 129.24, 129.10, 128.61, 128.49, 127.73, 124.24, 120.49, 63.82, 63.77, 43.38, 31.66, 31.56, 30.50, 30.38, 29.42, 29.33, 29.23, 29.01, 28.59, 27.83, 27.82, 25.88, 24.14, 24.13, 23.74, 22.60, 14.07. MS (Maldi-ToF, m/z): M⁺ Calc. 1286.2, Found 1286.8



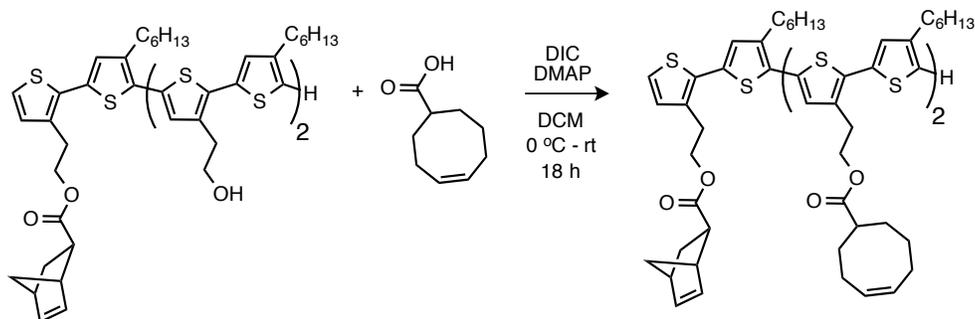
(3HT)₆-1OH-2OTBDMS: In a 50ml storage flask with a Teflon valve seal, (3HT)₂-Br-1OH (19mg, 0.05mmol) and (3HT)₄-Bu₃Sn-2OTBDMS (64mg, 0.058mmol) were dissolved in dry toluene (4ml) and subjected to 3× freeze/pump/thaw/cycles. Pd(PPh₃)₄ (6mg, 0.005mmol) as a slurry in toluene (1ml) was added and subjected to another 3×freeze/pump/thaw/ cycles. The reaction vessel was sealed under vacuum with a Teflon valve, and then heated to 90° C for 72 hours, or until the appearance of a black precipitate. The reaction mixture was cooled to room temperature. The organic layer was washed with water (3×30ml) and brine (3×30ml), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel column chromatography (Hex:EtOAc, 4:1) gave pure product (50mg, 78%).



(3HT)₆-1exo-norbornene-2OTBDMS: In a 4ml oven-dried vial, the exo-norbornene carboxylic acid (7.2mg, 0.05mmol) and (3HT)₆-1OH-2OTBDMS (48mg, 0.043mmol) were dissolved in dry THF (2ml) under nitrogen and DMAP (1mg, 0.0084mmol) was added in one portion. The solution was cooled to 0°C and stirred 30 minutes before injection of neat DIC (0.010ml, 0.065mmol). The reaction was allowed to warm to room temperature and stirred overnight. The solution was diluted with EtOAc (20ml) and washed with DI water (3×20ml) and brine (3×20ml). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by SX1 biobeads column (THF) to yield the pure product (47mg, 88%). ¹H NMR (500 MHz, CDCl₃): δ = 7.20 (d, 1H), 7.02-6.99 (m, 6H), 6.91(s, 1H), 6.13 (t, 1H), 6.09(t, 1H), 4.35(t, 2H), 3.91-3.85(m, 4H), 3.16(t, 3H), 3.04-3.00(m, 4H), 2.91(t, 2H), 2.79(s, 1H), 2.62(t, 3H), 2.56(t, 2H), 2.22(m, 1H), 1.69-1.62(m, 6H), 1.44-1.33(m, 24H), 0.92-0.88(m, 27H), 0.03-0.01(d, 12H).



(3HT)₆-1exo-norbornene-2OH: Tetreabutylammonium fluoride (1M in THF, 0.16ml, 0.16mmol) was added into (3HT)₆-1exo-norbornene-2OTBDMS (47mg, 0.038mmol) THF solution (2ml) and stirred at room temperature overnight. The mixture was purified by SX1 biobeads column (THF) to yield pure product (36mg, 95%). ¹H NMR (500 MHz, CDCl₃): δ=7.20(d, 1H), 7.02-6.98(m, 6H), 6.88(s, 1H), 6.02(t, 1H), 5.99(t, 1H), 4.25(t, 2H), 3.83(m, 4H), 3.65(t, 4H), 3.07(m, 2H), 3.01(t, 2H), 2.93(t, 2H), 2.90(s, 1H), 2.80(s, 1H), 2.50(t, 2H), 2.12(m, 1H), 1.32-1.16(m, 18H), 0.89-0.94(m, 9H).



(3HT)₆-1exo-norbornene-2cyclooctene: In a 4ml oven-dried vial, the Z-cyclooct-4-ene carboxylic acid (12mg, 0.078mmol) and (3HT)₆-1exo-norbornene-2OH(36mg,0.036mmol) were dissolved in dry THF (2ml) under nitrogen and DMAP (1mg, 0.0084mmol) was added in one portion. The solution was cooled to 0°C and stirred 30 minutes before injection of neat DIC (0.015ml, 0.1mmol). The reaction was allowed to warm to room temperature and stirred overnight. The solution was diluted with EtOAc (20ml) and washed with DI water (3×20ml) and brine (3×20ml). The organic layer was dried over sodium sulfate, filtered, and concentrated under reduced pressure. The crude product was purified by SX1 biobeads column (THF) to yield the pure product (40mg, 87%). ¹H NMR (500 MHz, CDCl₃): δ = 7.20 (d, 1H), 7.00-6.99 (m, 6H), 6.92 (s, 1H), 6.12 (t,1H), 6.08 (t,1H), 5.65-5.61 (m,4H), 4.34-4.30 (m,6H), 3.15-3.09 (m,6H), 2.99 (m,1H), 2.89 (m,1H), 2.78 (t,4H), 2.46 (m,2H), 2.38 (m,2H), 2.13-2.11 (m,7H), 2.01-1.97 (m,2H) 1.86-1.83 (m, 4H), 1.68-1.61 (m, 12H), 1.46-1.33 (m,22H), 0.91-0.89 (m,9H). ¹³C-NMR (500MHz, CDCl₃): δ = 167.72, 138.04, 132.45, 130.84, 130.67, 130.50, 130.47, 130.21, 129.98, 129.55, 128.78, 127.72, 124.22, 68.14, 63.94, 63.71, 46.55, 46.35, 43.38, 43.13, 41.62, 38.73,31.66,31.56,30.88,30.49,30.35,30.32,29.67,29.43,29.22,29.01,28.91,28.60,27.82,25.87,24.13,23.74,22.96,22.60,14.08,14.01,10.93. MS (Maldi-ToF, m/z): M+ Calc. 1270.2, Found 1270.9

Preliminary Model Studies.

Before delving into the templated TROM studies, we first examined the reactivity of model monomers attached to single thiophene units, *i.e.* without any polythiophene template. The COE monomer attached to a single thiophene unit (which does not have any template effect) was firstly subjected to conventional ROMP conditions in dilute solution; specifically, COE in anhydrous DCM under nitrogen at 0 °C for 1 h, with a monomer to catalyst ratio of 10:1, at concentrations varying from 10⁻³ to 10⁻¹ M (Figure S1).

We observed a distribution of MALDI peaks indicating a disperse population of cyclic oligomers (from n = 3 to 11, Fig. 3). An initial monomer concentration of 10⁻³ M is sufficiently dilute to yield only cyclic oligomers, suggesting that this concentration regime is a reasonable starting point for template synthesis in which we aim to avoid inter-template metathesis. Low MW fragments that result from back-biting secondary metathesis were not observed in significant quantity, perhaps because they fall below the lower limit of our MALDI detection range.

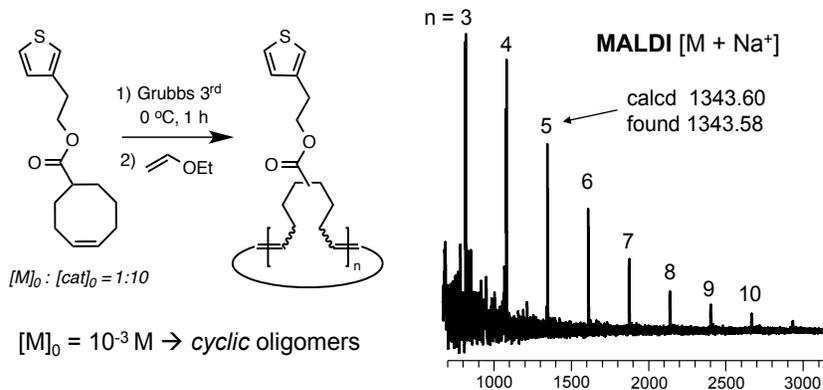


Figure S1. Conventional ROMP of *cis*-cyclooctene (COE) attached to a single thiophene unit (no template effect, negative control experiment).

Next, we examined copolymerization of COE with other cyclic olefin model monomers. We hypothesize that using a high ring strain monomer at the alpha position of a template would favor initiation at the alpha site, followed by propagation of lower ring strain monomer along the backbone of the template. Batch copolymerization of norbornene and cyclooctene (1:1 mol ratio) derivatives bearing thiophene side chains, in dilute conditions (10^{-3} M), gave a series of peaks in the ESI ms that are indicative of NB/COE cyclic co-oligomers. Presumably the NB monomer is consumed first, followed by consumption of the COE substrate, to form blocky co-oligomers. Importantly, this phenomenon is later exploited in our template polymerization efforts; a template bearing a single NB unit at the alpha position, with all remaining sites bearing COE monomers will putatively enable predominate initiation at the alpha position, followed by end-to-end chain growth polymerization of the COEs.

Templated Ring-Opening Metathesis (T-ROM). We began our first exploration of T-ROM with the simplest possible template: a thiophene oligomer bearing two pendant COE monomers covalently attached to the side chains, dubbed **C₂** (Figure S2). The MALDI spectrum of this compound shows a single peak at the expected mass of 622 g/mol. Upon fragmentation of this molecular ion by ms/ms, two signals appear: a major peak corresponding to the template with the loss of one COE monomer by the McLafferty rearrangement (m/z 468), and a very minor peak indicating concurrent loss of two COEs (m/z 314).

The template **C₂** was subjected to T-ROM with the Grubb's 3rd generation catalyst (cat:template = 1:1) in dilute conditions (10^{-3} M in DCM), at low temperature (0 °C), and for short reaction time (10 min) to give product **PC₂**. The ¹H NMR spectrum of the crude product revealed complete conversion of the COE olefinic protons (δ 5.7 ppm) to their ring-opened analogue (δ 5.3 ppm).

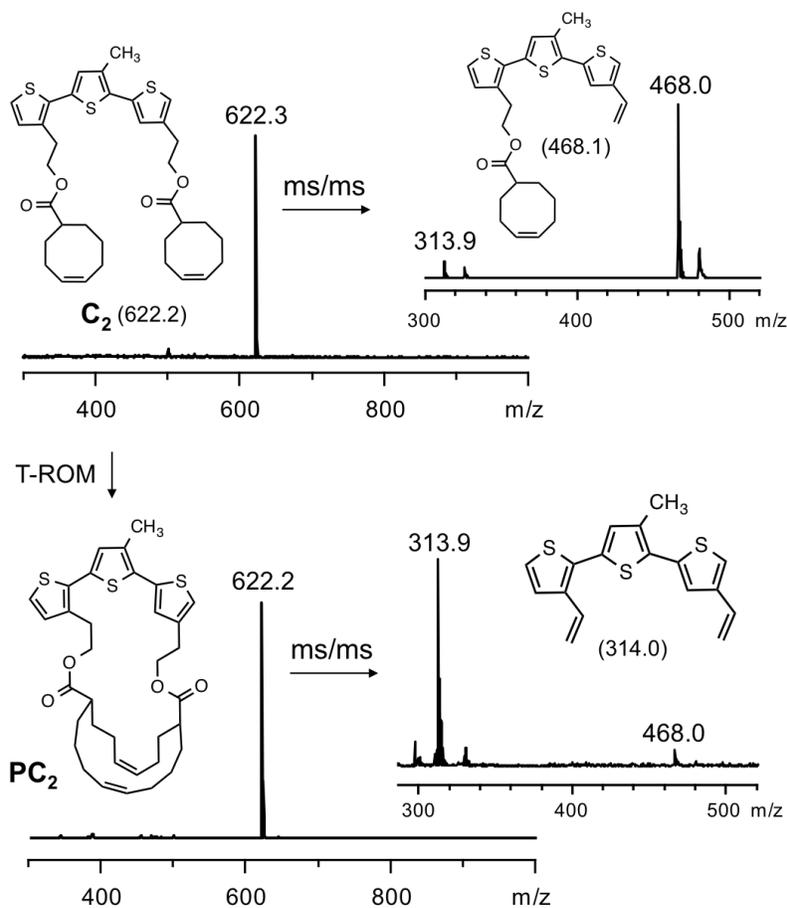


Figure S2. Templated ring-opening metathesis (T-ROM) confined to the side chains of a π -conjugated thiophene trimer bearing two COE units. MALDI with *ms/ms* fragmentation confirms that the template metathesis occurred.

The MALDI spectra of the resulting product **PC₂** exhibited a single major peak with the same mass as the starting compound (m/z 622). Combined, these data suggest that the two COE monomers underwent T-ROM followed by macrocyclic ring-closing to give a 16-membered macrocycle bound to the template. Indeed, this hypothesis was confirmed by *ms/ms* fragmentation, which showed a major peak consistent with loss of the 16-membered macrocycle, presumably via two McLafferty rearrangements (m/z 314). The peak that corresponds to loss of one COE monomer (468) is dramatically reduced in intensity relative to the *ms/ms* data for the unreacted template **C₂**. Since the loss of one COE from the template backbone is statistically much more likely than simultaneous loss of two, the marked change in the ratio of peak intensities at 468/314 strongly suggests that the dimer of COE must have formed on the template (thus suppressing the possibility of fragmenting off a single COE). Furthermore, no traces of any higher degrees of polymerization were detected by MALDI or GPC, confirming that the dilute conditions suppressed inter-template metathesis in these specific conditions. It is noteworthy that at higher concentrations (above 10^{-2} M) or longer reaction times (hours), substantial extents of intra-template metathesis do occur, as evidenced by higher MW peaks in the MALDI spectra, which correspond to double (and triple, quadruple, etc...) the mass of the expected T-ROM product. At still higher concentration (10^{-1} M), an insoluble gel was obtained in a few minutes.

These observations highlight the necessity of careful optimization of the T-ROM conditions, especially the use of highly dilute conditions.

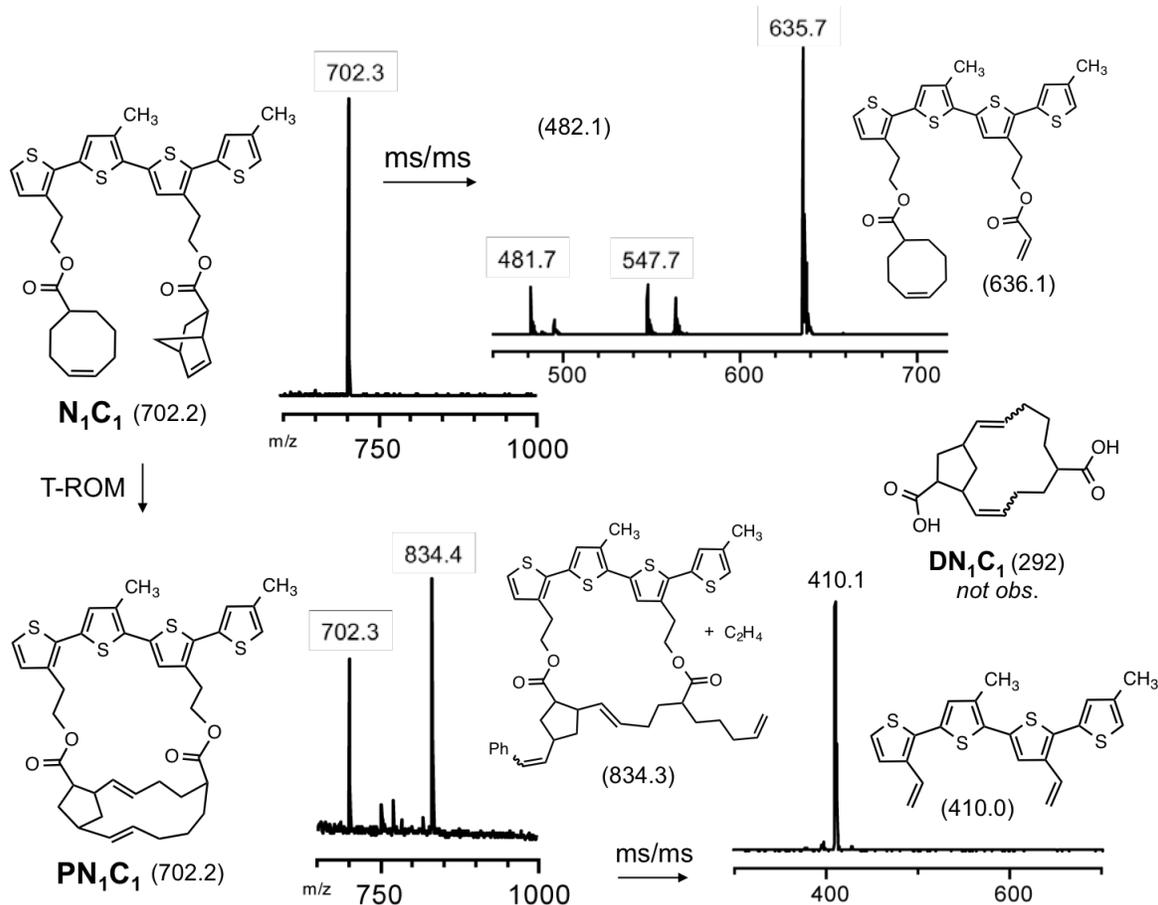
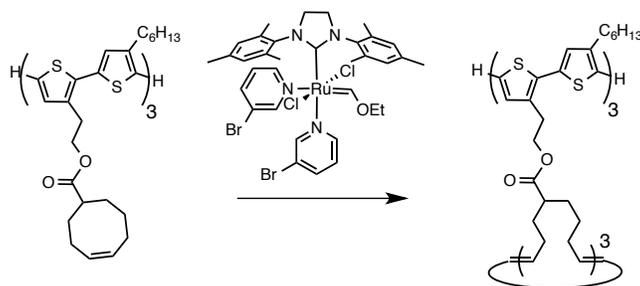


Figure S3. Templated ring-opening metathesis (T-ROM) confined to the side chains of a π -conjugated thiophene trimer bearing one COE monomer and one norbornene monomer.

An oligothiophene template containing one NBE unit and one COE unit in the side chains (N_1C_1) was then investigated to probe the extent to which this monomer pair may undergo cross-metathesis when co-localized on a template (Figure S3). Optimized T-ROM conditions (10^{-3} M in DCM, 0 °C, 10 min) were employed for N_1C_1 to give the product PN_1C_1 . NMR confirmed complete disappearance of olefinic signals for COE and NBE monomers, replaced by a feature corresponding to the ring-opened olefin. The MALDI spectrum of PN_1C_1 has two peaks: one appears near m/z 702, which matches the expectation for the cyclic dimer. A second, slightly more intense peak appears at m/z 834, which corresponds to the mass of the product plus the mass of styrene end groups (+104), as expected for the linear heterodimer, plus the mass of ethylene (+28), the latter of which was unanticipated. We speculate that the quenching of the ROM process with ethyl vinyl ether (EVE) leads to ethenolysis of the daughter product, although the details remain unclear at present. We had initially suspected that the EVE was thermally degraded over time and was thus contaminated with ethylene; however, repeating the experiment with a fresh bottle of EVE gave the same result. Curiously, this effect is only seen in the case of templates bearing both norbornene and cyclooctene. As shown below, the template bearing

multiple norbornenes only gives the expected linear product peak at mass $M+104$, with no evidence of ethenolysis. Again, judicious tuning of the T-ROM conditions (10^{-3} M in DCM, 0°C , 10 min) was critical for success. When N_1C_1 is subjected to T-ROM for 10 min, the expected daughter product is obtained. But if allowed to react for 30 min or longer, higher MW products corresponding to undesired metathesis between multiple templates start to appear in the MALDI spectra (supporting information). Hence, not only dilute conditions but also short reaction times are required in order to access the desired daughter dimer as the sole product.



Optimized procedure for PC_3 by T-ROM: $(3\text{HT})_6$ -3cyclooctene (8mg, 0.0062mmol) was dissolved in anhydrous DCM (32ml) under a nitrogen flow in an oven-dried 10ml Schlenk flask, and cooled to 0°C on ice water bath. Then, the Grubbs 3rd generation catalyst (5.5mg, 0.0062mmol) dissolved in DCM (8ml) was injected via syringe, to give an initial template concentration of 1.5×10^{-4} M. After 60 minutes, ethyl vinyl ether (0.1ml) was injected via syringe and the reaction was stirred for an additional 30 minutes before warming to room temperature. The solvent was evaporated under reduced pressure and the residue was extracted with 1ml of THF. The catalyst was removed by passing SX1 biobeads column. NMR shows around 92% conversion and MALDI shows single peak (MW=1286).

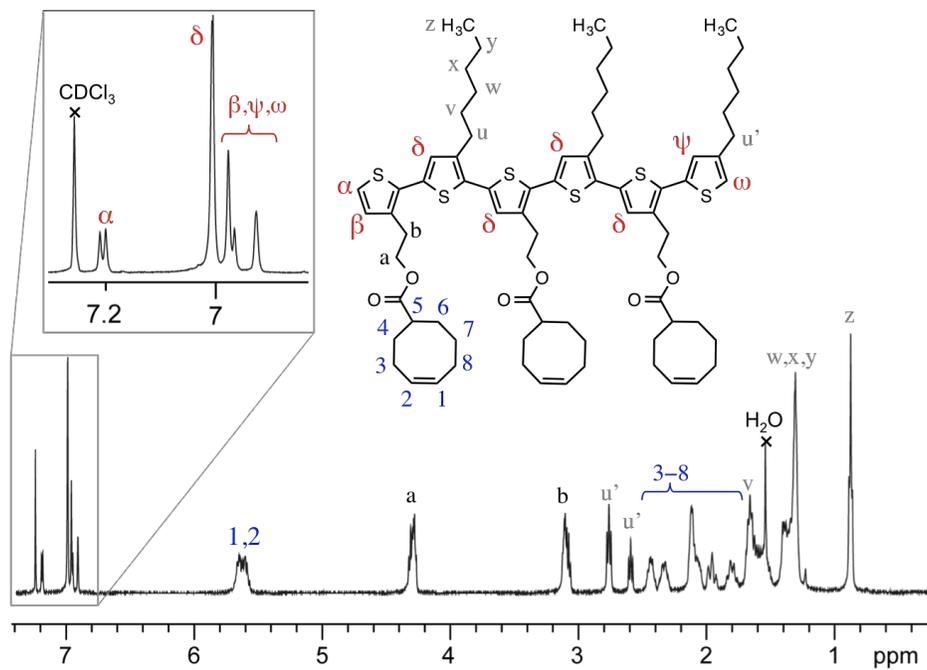


Figure S4. NMR of C₃ with peak assignments.

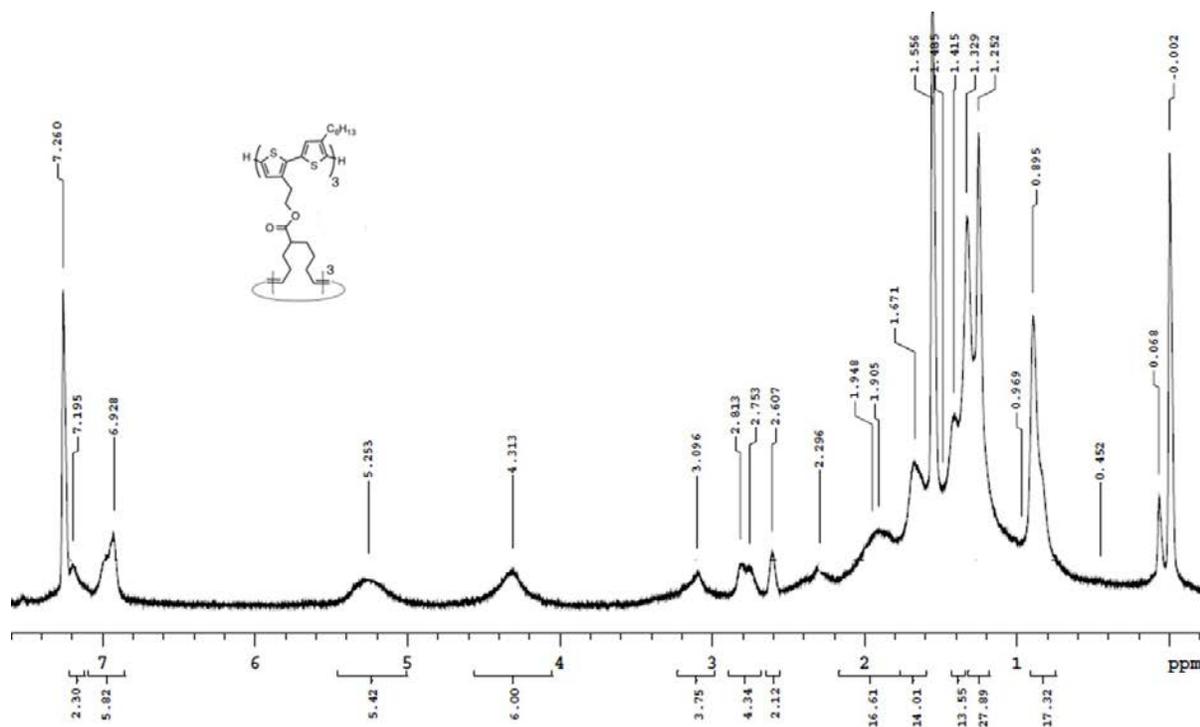


Figure S5. NMR Spectra for the product PC₃.

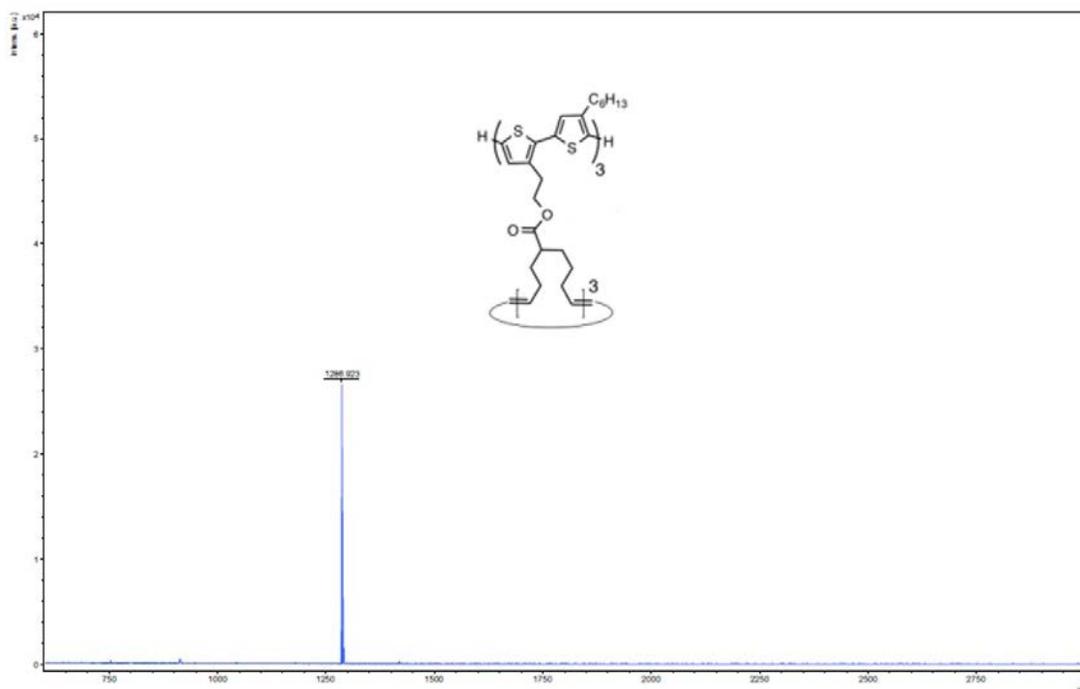


Figure S6. MALDI spectra for the product PC3.

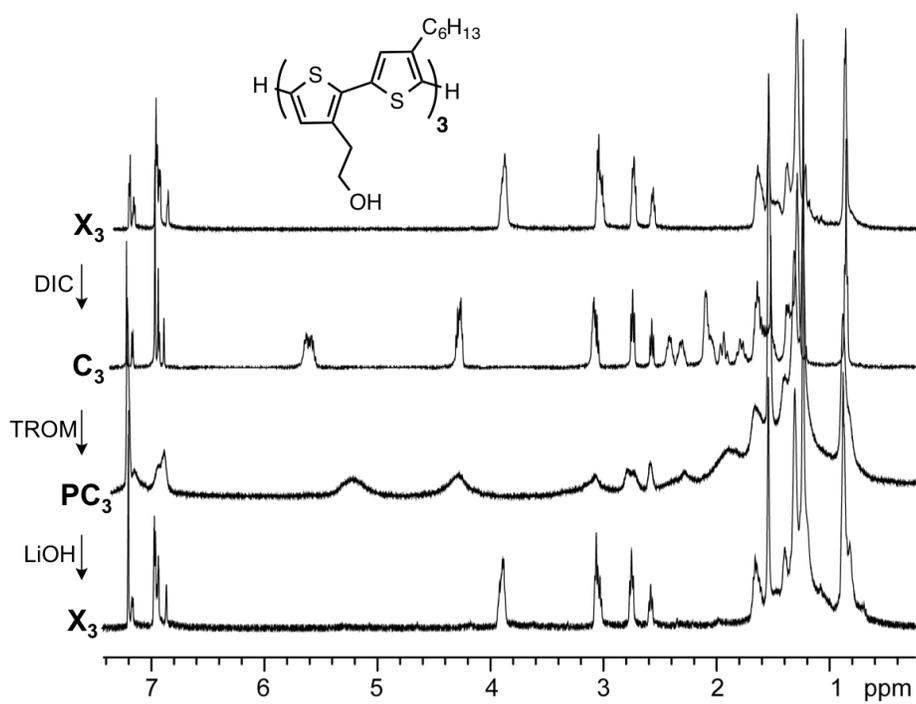


Figure S7. NMR of X₃, C₃, PC₃, and hydrolyzed X

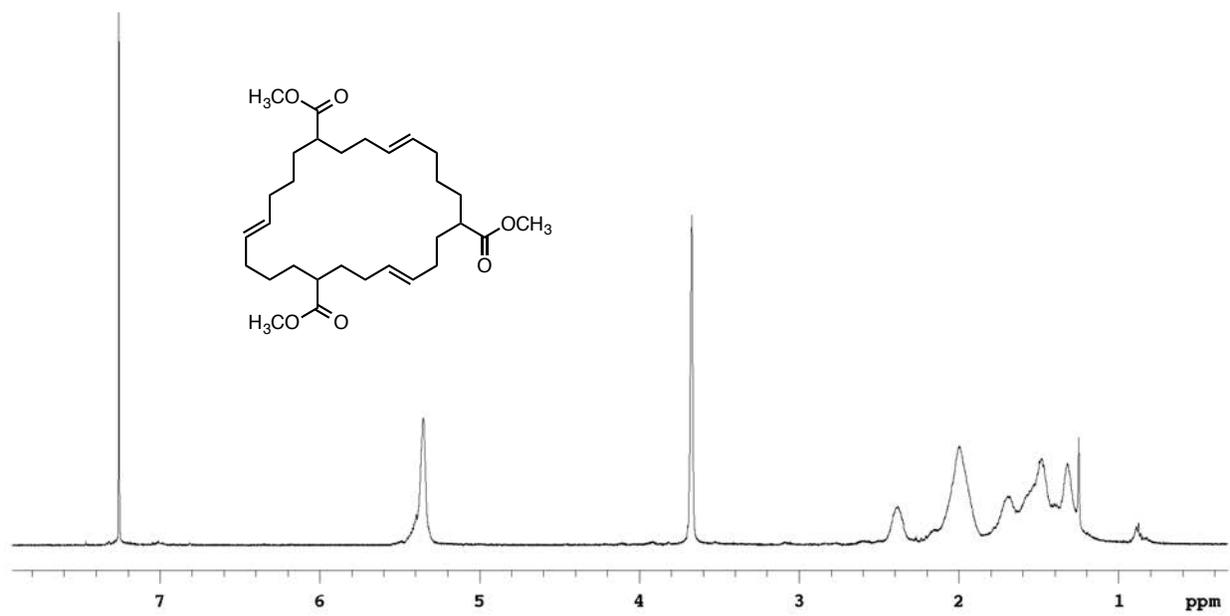


Figure S7b. ^1H NMR of DC₃.

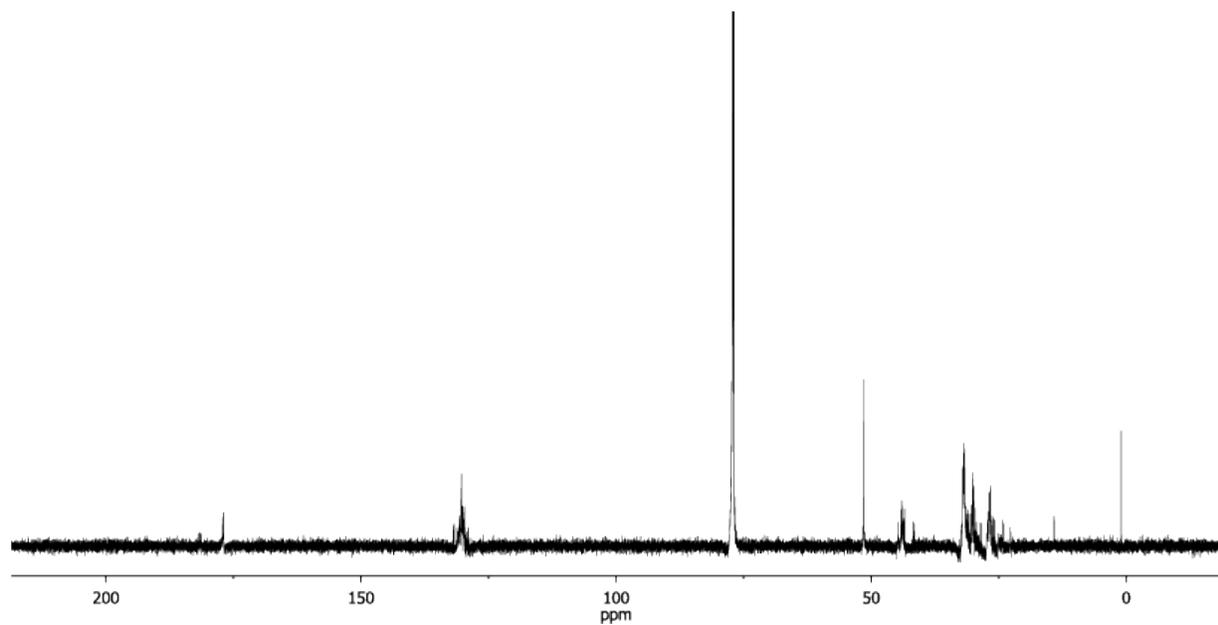


Figure S7c. ^{13}C NMR of DC₃.

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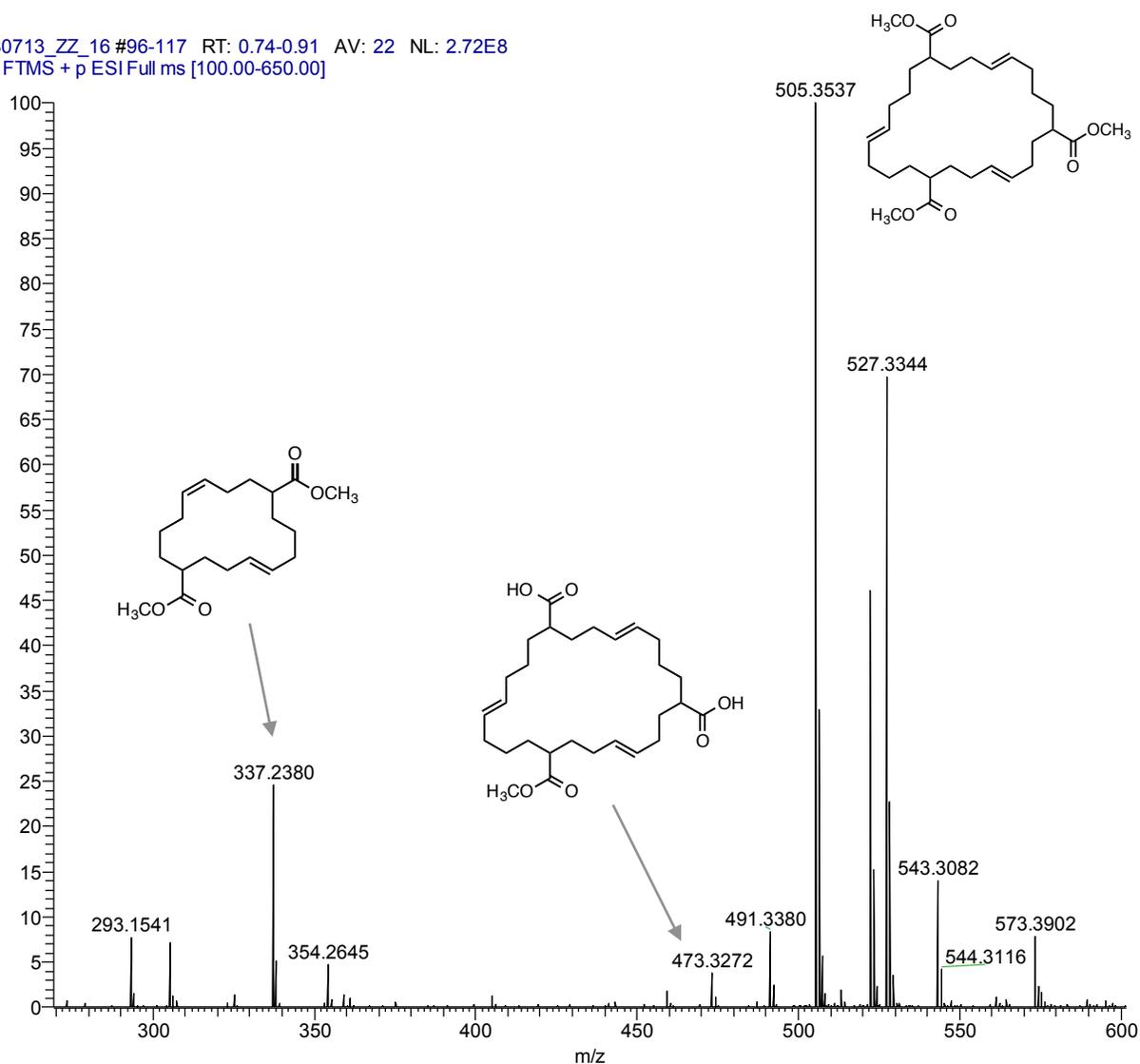


Figure S7c. ESI mass spec of DC3

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T: FTMS + p ESI Full ms [100.00-650.00]

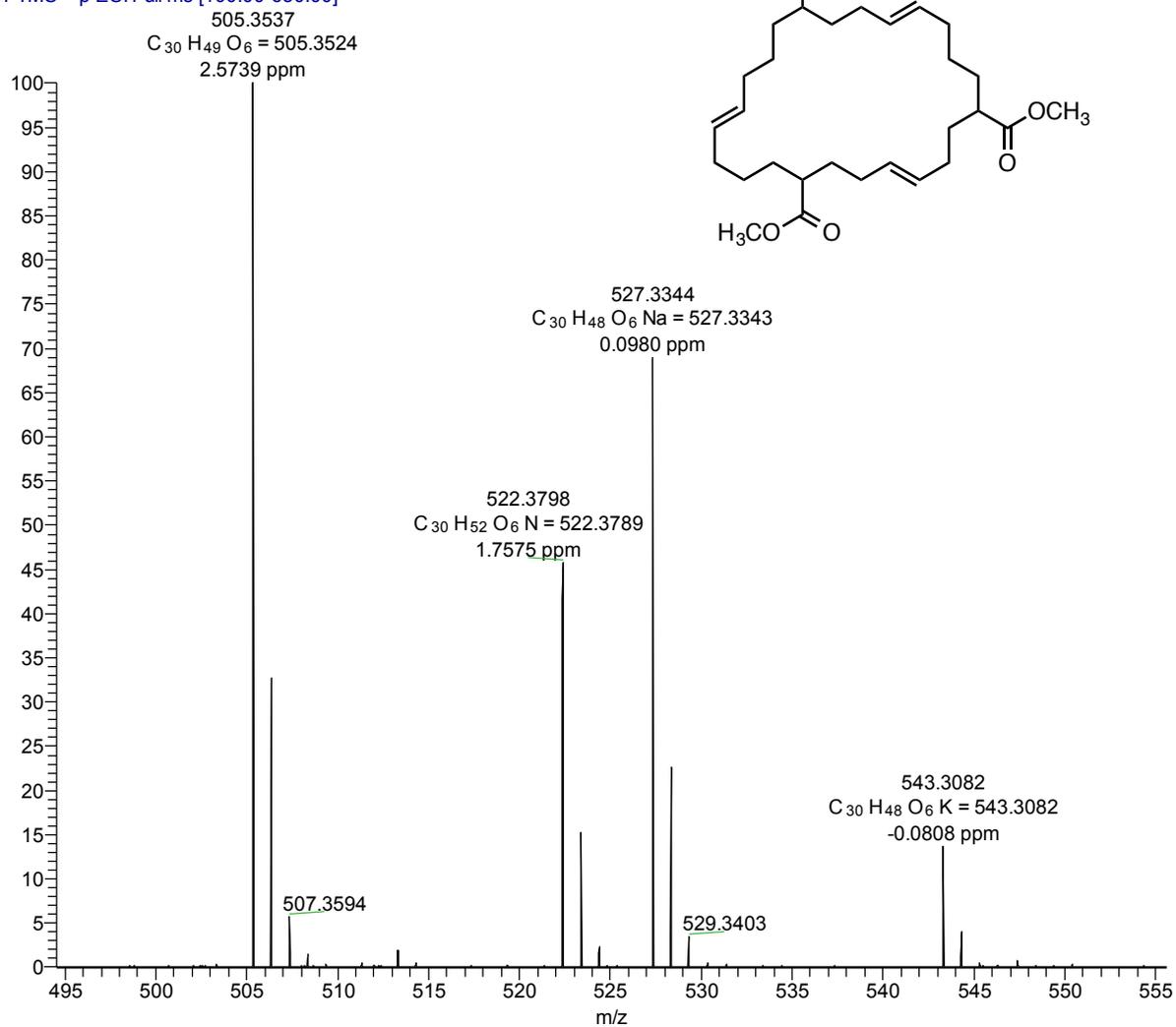
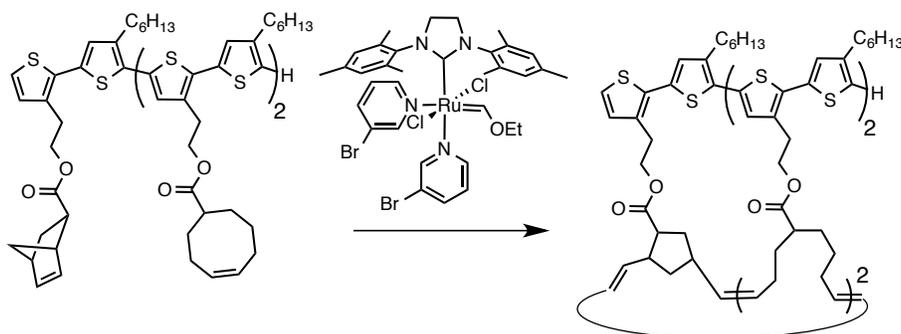


Figure S7c. HR-ESI mass spec of DC₃, selected molecular ion region.



Optimized procedure for PN1C2 by T-ROM: (3HT)₆-1exo-norbornene-2cyclooctene (7mg, 0.0055mmol) was dissolved in anhydrous DCM (28ml) under a nitrogen flow in an oven-dried 10ml Schlenk flask, and cooled to 0°C on ice water bath. Then, the Grubbs 3rd generation catalyst (4.9mg, 0.0055mmol) dissolved in DCM (7ml) was injected via syringe, to give an initial template concentration of 1.5×10^{-4} M. After 60 minutes, ethyl vinyl ether (0.1ml) was injected via syringe and the reaction was stirred for an additional 30 minutes before warming to room temperature. The solvent was evaporated under reduced pressure and the residue was extracted with 1ml of THF. The catalyst was removed by passing SX1 biobeads column. NMR shows 100% conversion and MALDI shows two peaks, one peak gives 1270 Mw which is cyclic polymerized monomer, the other peak gives Mw equals 1403 which means liner polymerized monomer.

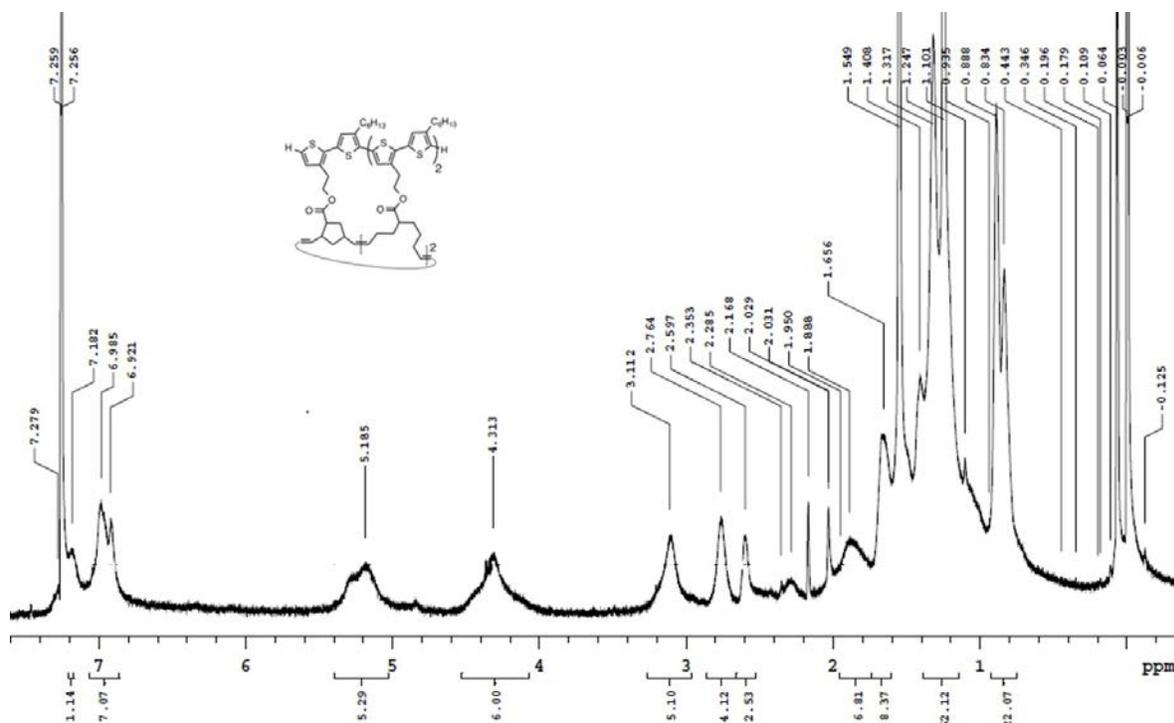


Figure S8. NMR spectra for PN₁C₂

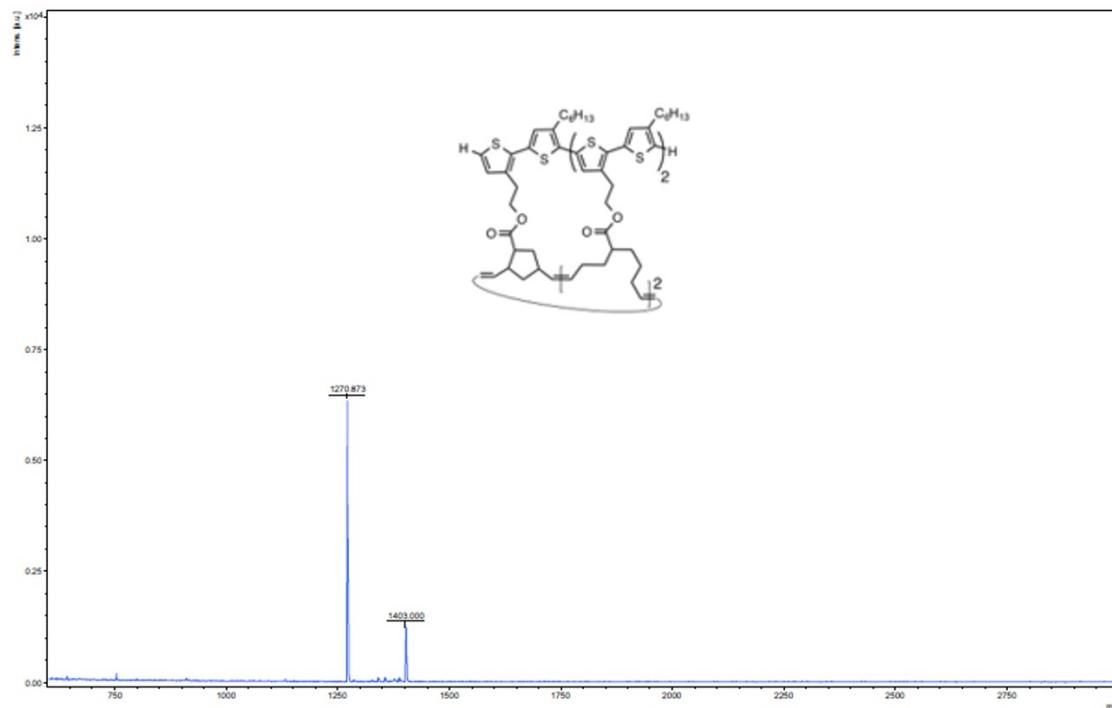
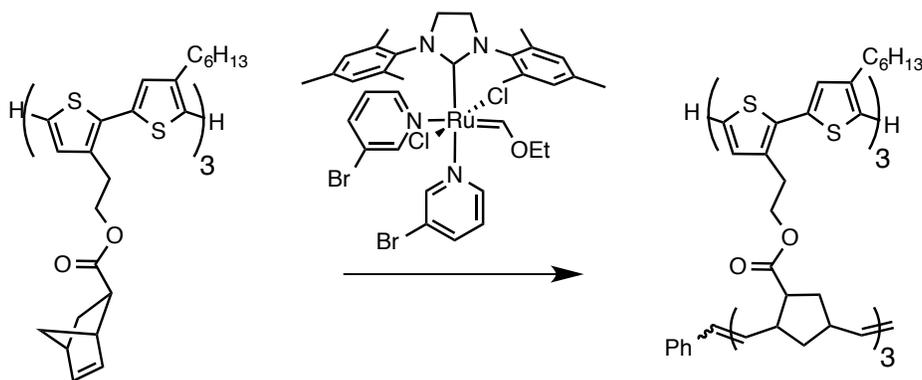


Figure S9. MALDI spectra for PN_1C_2



Optimized procedure for PN3 by T-ROM: $(3\text{HT})_6$ -3exo-norbornene (6mg, 0.0048mmol) was dissolved in anhydrous DCM (25ml) under a nitrogen flow in an oven-dried 10ml Schlenk flask, and cooled to 0°C on ice water bath. Then, the Grubbs 3rd generation catalyst (4.3mg, 0.0048mmol) dissolved in DCM (7ml) was injected via syringe, to give an initial template concentration of $1.5 \times 10^{-4}\text{M}$. After 60 minutes, ethyl vinyl ether (0.1ml) was injected via syringe and the reaction was stirred for an additional 30 minutes before warming to room temperature. The solvent was evaporated under reduced pressure and the residue was extracted with 1ml of THF. The catalyst was removed by passing SX1 biobeads column. NMR shows 100% conversion and MALDI shows three peaks, the dominate one gives Mw equals 1344 which is

liner polymerized monomer, the lower peak gives $2 \cdot M_w$ equals 2583 which means crosslinked polymerization happened between two chains.

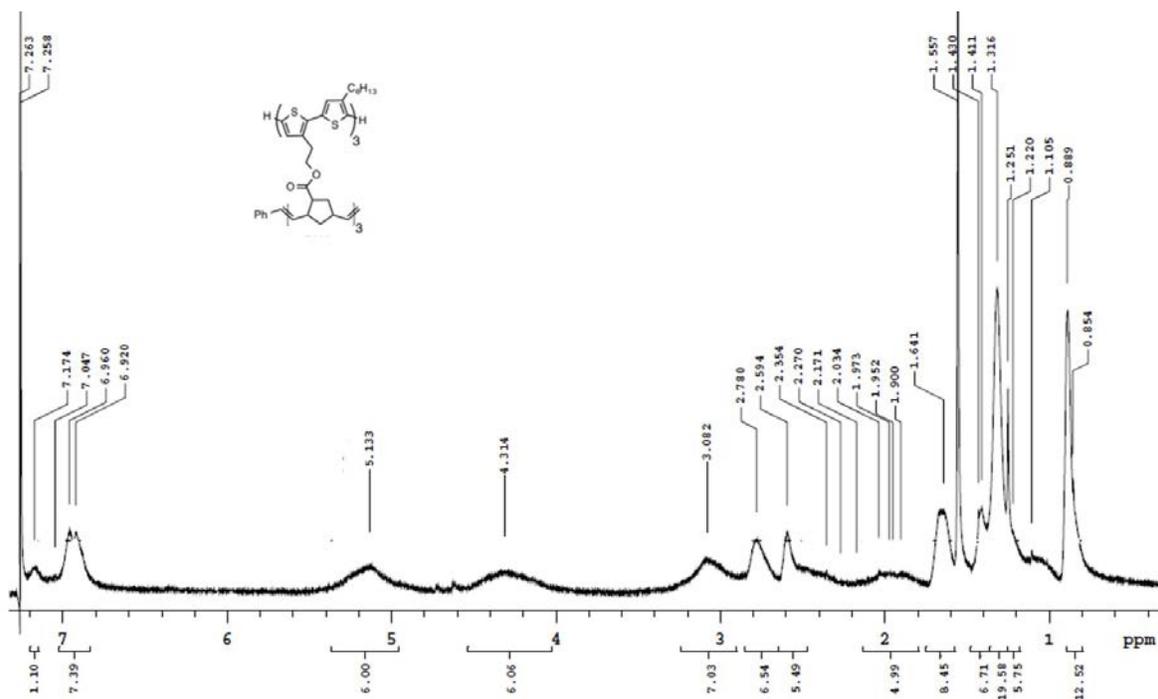


Figure S10. NMR spectra of PN₃.

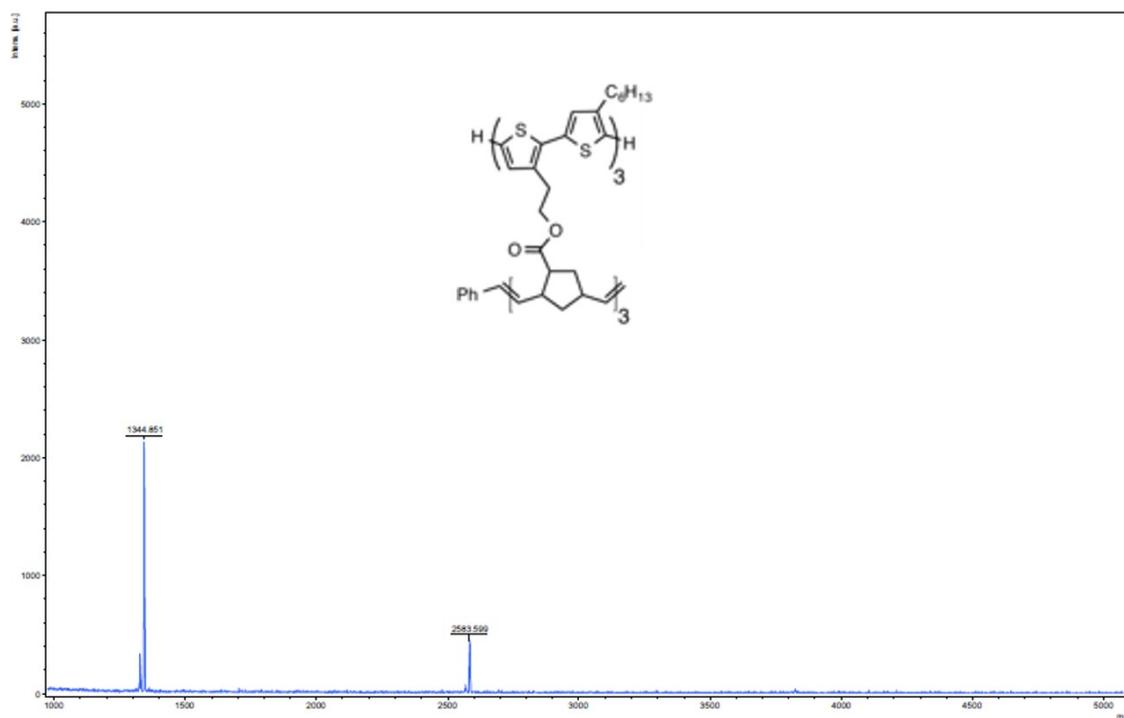
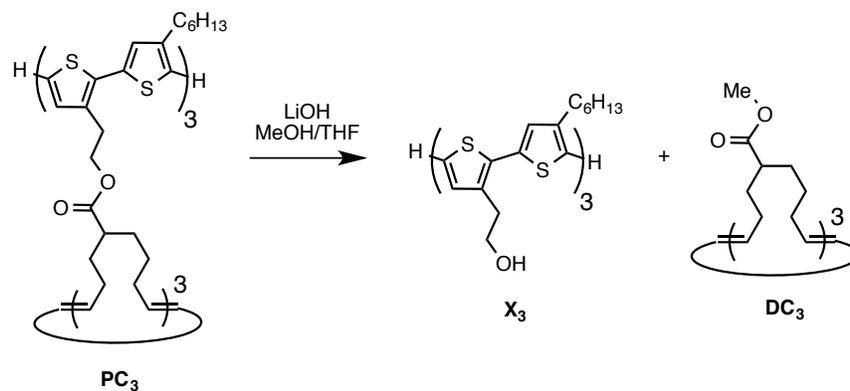


Figure S11. MALDI spectrum for PN₃

Hydrolysis of the template/daughter conjugate:



Lithium hydroxide(1M in MeOH,2ml) was added into PC₃ (8mg, 0.0062mmol) THF solution (1ml) and stirred at room temperature 2 hours. The mixture was purified by silica gel column chromatography (Hex: EA, 4:1) to yield pure product (5mg,90%).

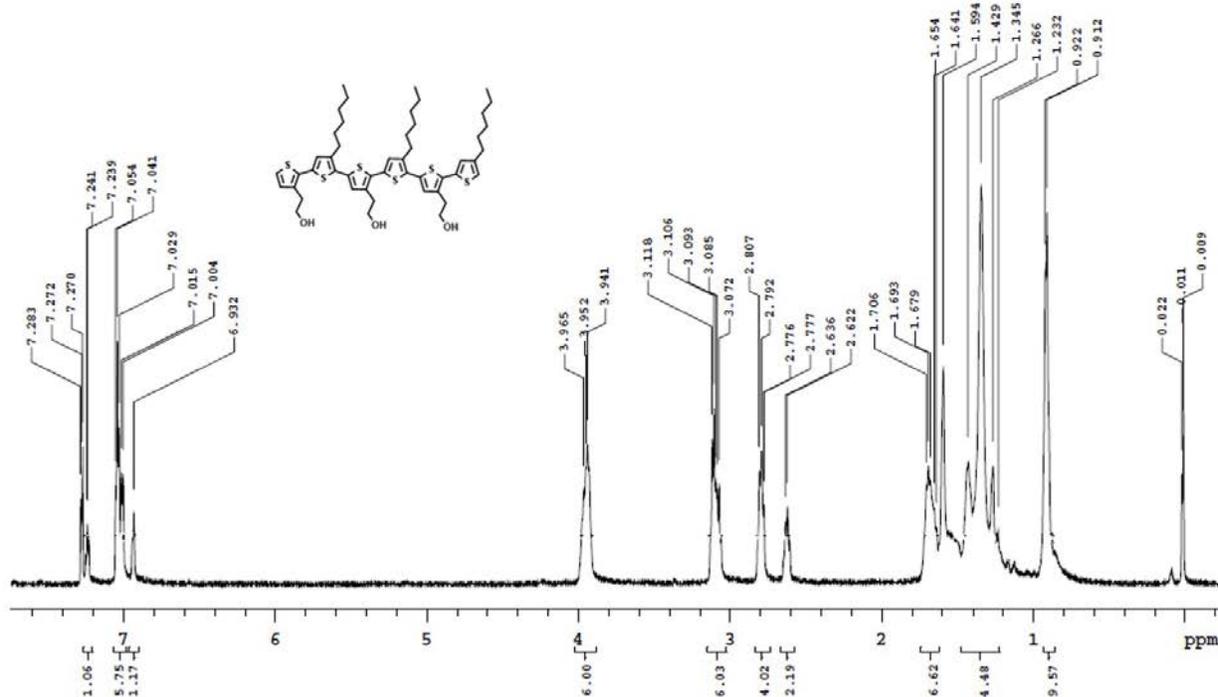


Figure S12. NMR of hydrolyzed template X₃.

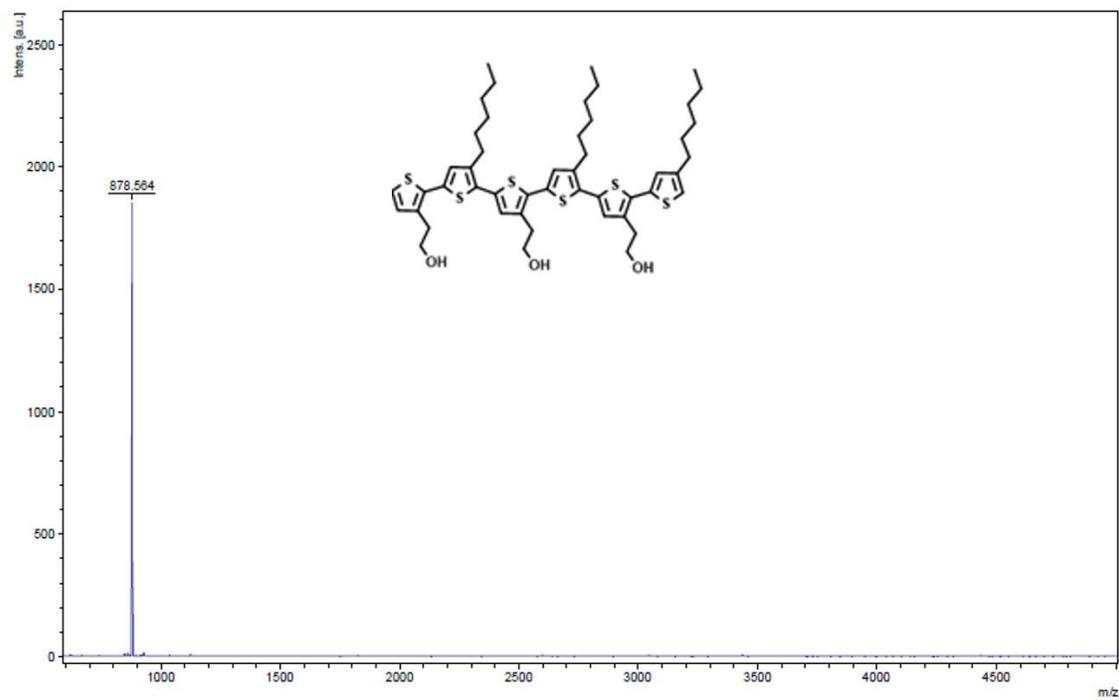


Figure S13. MALDI of hydrolyzed template X₃.

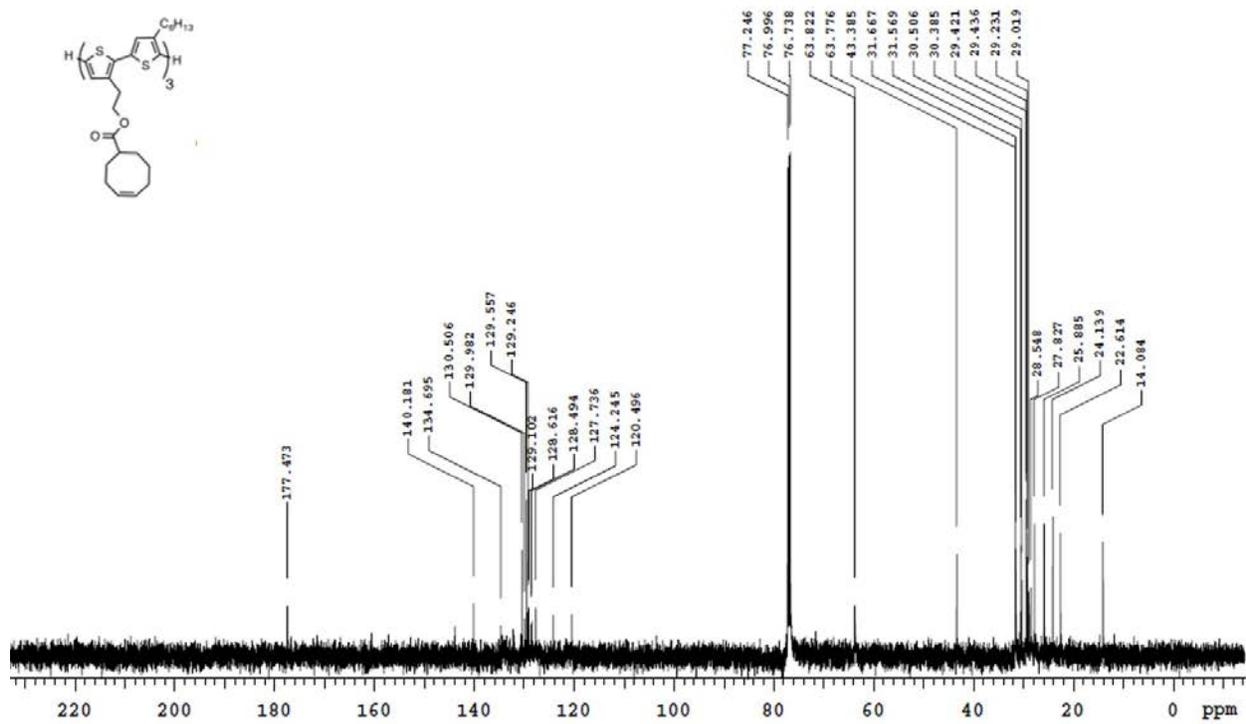
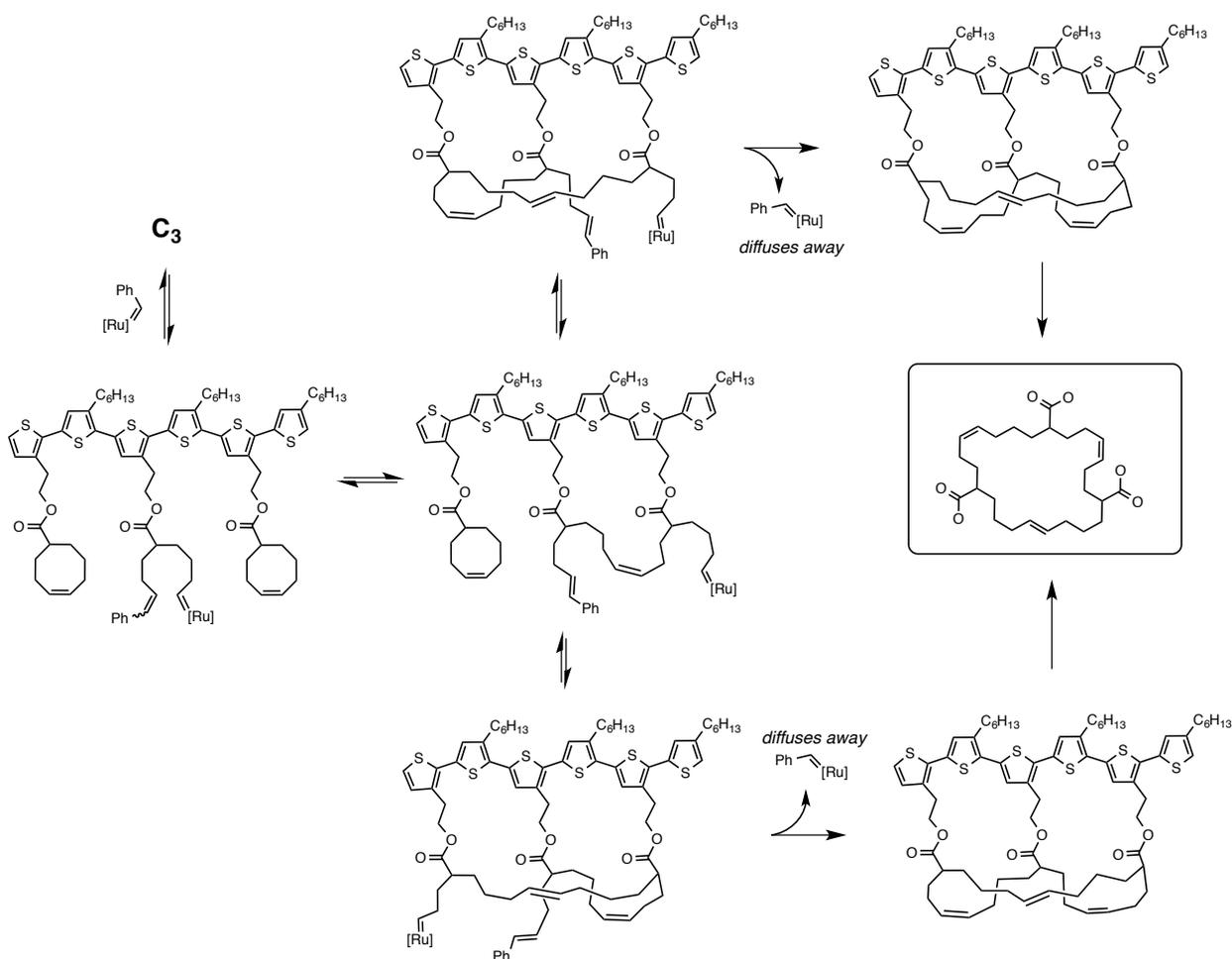


Figure S16. ^{13}C NMR of C_3

Appendix:

Consider a single template with three COE monomers in dilute solution. Initiation may occur at any of the three possible sites along the backbone (let's call them alpha, beta, omega). There is no reason to suppose that ring-opening will necessarily occur only at the alpha position, in this case (when norbornene occupies the alpha position, with COE at beta and omega, there *is* reason to favor such a mechanism). Shown is the example of initiation at the beta site, followed by ROM with the monomer at the omega position, as just one example of many possible pathways:



Next, the lone monomer at the alpha position is available for ROM propagation, again without any regioselectivity. 3D models show that ROM between the 1st and 3rd position is reasonable from the viewpoint of sterics, bond angles, etc. Since all steps in the ROM catalytic cycle are reversible in principle, the system is inherently "self-correcting." In other words, regardless of the order of the ROM and secondary metathesis events, the cyclic trimer is the observed product in all cases.

The *only* metathesis event that results in a structure for which the ruthenium center is not bonded to the template is the final RCM, which expels an equivalent of the 3rd gen catalyst. Once the catalyst is not bound to template, *it can diffuse away* into the very dilute solution. Thus, perhaps the reverse of the RCM is kinetically sluggish, even if thermodynamically the equilibrium would lie far towards the ring-opened pdt.