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Supplementary Information for

Ether Solvent-induced Chirality Inversion of Helical Poly(quinoxaline-2,3-diyl)s Containing L-Lactic Acid Derived Side Chains

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1. General

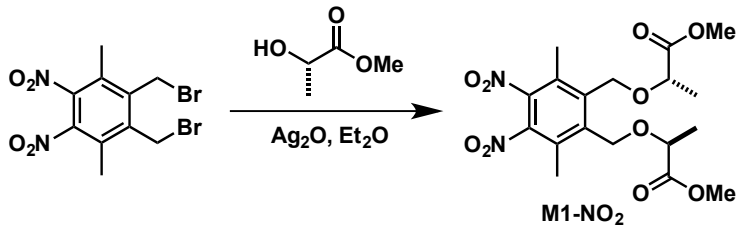
All reactions were carried out under an atmosphere of nitrogen with magnetic stirring. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 400-MR spectrometer at ambient temperature. ^{1}H NMR data are reported as follows: chemical shift in ppm downfield from tetramethylsilane (δ scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br = broad), coupling constant (Hz), and integration. ^{13}C NMR chemical shifts are reported in ppm downfield from tetramethylsilane (δ scale). All ^{13}C NMR spectra were obtained with complete proton decoupling. IR spectra were obtained using a Shimadzu FTIR-8400 Fourier transform infrared (FT-IR) spectrometer equipped with PIKE MIRacle attenuated total reflection (MIR-ATR) attachment. The GPC analysis was carried out with TSKgel GMH_{XL} ($CHCl_3$, polystyrene standards). Preparative GPC was performed on JAI LC-908 equipped with JAIGEL-1H and -2H columns in a series ($CHCl_3$). UV spectra were recorded on a JASCO V-500 spectrometer equipped with a JASCO ETC-505T temperature/stirring controller at 20 °C. CD spectra were recorded on a JASCO J-750 spectrometer equipped with a JASCO PTC-423L temperature/stirring controller at 20 °C. The chiral HPLC analysis was carried out on TOSOH 8020 series equipped with CHIRALCEL® OZ-H (hexane and 2-propanol). Flash chromatography was performed using a Biotage Isolera One flash purification system with silica gel flash cartridges.

Tetrahydrofurane (THF) and toluene were dried and deoxygenized using an alumina/catalyst column system (Glass Contour Co.). 1,2-Bis(bromomethyl)-3,6-dimethy-4,5-dinitrolbenzene, [1] acetic formic anhydride (AFA),[2] *o*-TolNiCl(PMe_3),[3] (2',3'-diisocyano-4'-methyl-[1,1'-biphenyl]-2-yl)diphenylphosphine sulfide **S1**, [4] and dimethyl (1-bromonaphthalen-2-yl)phosphonate **12**[5] were prepared according to the reported procedure. Other chemical reagents were purchased from the commercial sources. Primary alcohols (1-Propanol, 1-butanol, 1-pentanol, 1-hexanol, 1-heptanol, 1-octanol, 1-nonanol, and 1-decanol), $BF_3 \cdot Et_2O$, 1,2-dimethoxyethane (1,2-DME), and *tert*-butyl methyl ether (MTBE) were distilled over CaH_2 and degassed prior to use. Triethylamine (Et_3N) was distilled over KOH and degassed. Phosphoryl chloride ($POCl_3$) was distilled and degassed. K_3PO_4 was dried under reduced pressure at 150 °C for 5 h before use. Other chemicals were used without further purification.

2. Experimental Procedures and Spectral Data for New Compounds

Synthesis of M1-NO_2: To a mixture of 1,2-Bis(bromomethyl)-3,6-dimethyl -4,5-dinitrolbenzene (1.37 g, 3.58 mol) and Ag_2O (8.29 g, 35.8mol) was added a mixture of Et_2O (36 mL) and L-methyl lactate (1.37 mL, 14.3 mol) at room temperature. The mixture was stirred for 24 h at 40 °C. The reaction mixture was filtered. The filtrate was concentrated and dried under vacuum. The mixture was purified with silica gel flash column chromatography (hexane/AcOEt = 70/30 to 50/50) to give **M1-NO_2** as pale yellow solid (499 mg, 33%) ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.6 Hz), 4.55 (2H, d, J = 10.3 Hz), 4.16 (2H, q, J = 13.7 Hz), 3.79 (6H, s), 2.43 (6H, s), 1.44 (6H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 173.2, 144.3, 140.4, 130.8, 75.0, 65.3, 52.2, 18.9, 14.7; IR (ATR, neat) 1738, 1531, 1454, 1373, 1302, 1261, 1225, 1146, 1113, 1067, 1016, 972, 916, 868, 785, 754 cm^{-1}; HRMS (APCI) m/z calcd for $C_{18}H_{25}N_2O_{10}$ ($[M+NH_4]^+$): 429.1509, found: 429.1499; $[\alpha]^{26.6}_D$ −29.1 (*c* 7.97, $CHCl_3$).

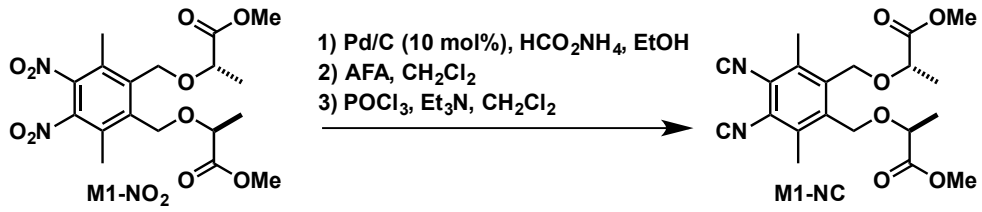
Scheme S1. Synthesis of **M1-NO_2**



Synthesis of M1-NC: A suspension of **M1-NO_2** (463 mg, 1.08 mmol), HCO_2NH_4 (449 mg, 7.13 mmol), and 10 wt% Pd/C (115 mg, 108 μmol) in EtOH (11 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (309 mg, 3.51 mmol) was added to the diamine dissolved in CH_2Cl_2 (8.8 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (226 μL, 372 mg, 2.42 mmol) was added to a solution of diformate in Et_3N (1.1 mL) and CH_2Cl_2 (12.1 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (CH_2Cl_2/MeOH = 98/2) to give **M1-NC** as white solid (198 mg, 47%). ^{1}H NMR (C_6D_6) δ 4.87 (2H, d, J = 10.6 Hz), 4.49 (2H, d, J = 10.3 Hz), 4.13 (2H, q, J = 14.0 Hz), 3.78 (6H, s), 2.53 (6H, s),

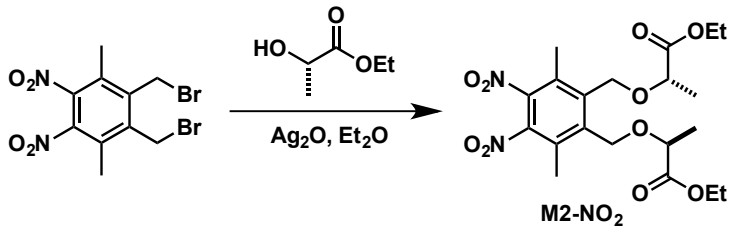
1.42 (6H, d, J = 7.1 Hz); ^{13}C NMR (C_6D_6) δ 173.1, 137.6, 134.5, 124.2, 74.7, 65.4, 52.0, 18.7, 15.6; IR (ATR, neat) 2118, 1736, 1454, 1261, 1229, 1144, 1113, 1016 cm^{-1}; HRMS (EI$^+$) m/z calcd for $C_{20}H_{24}N_2O_6$ (M^+): 388.1634, found: 388.1640; $[\alpha]^{27.9}_D$ −97.1 (*c* 9.49, CH_2Cl_2).

Scheme S2. Synthesis of **M1-NC**



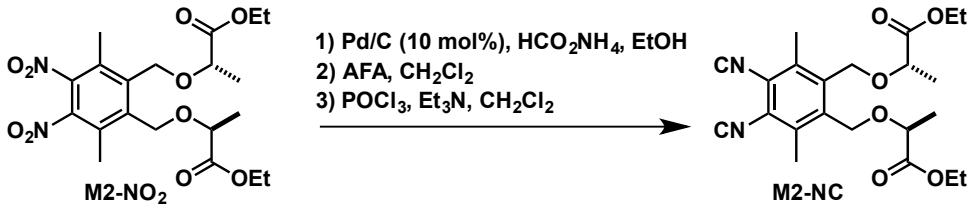
Synthesis of M2-NO_2: To a mixture of 1,2-Bis(bromomethyl)-3,6-dimethyl -4,5-dinitrolbenzene (9.97 g, 26.1 mol) and Ag_2O (60.5 g, 261mol) was added a mixture of Et_2O (261 mL) and L-ethyl lactate (12.3 g, 104 mol) at room temperature. The mixture was stirred for 24 h at 40 °C. The reaction mixture was filtered. The filtrate was concentrated and dried under vacuum. The mixture was purified with silica gel flash column chromatography (hexane/AcOEt = 80/20) to give **M2-NO_2** as pale yellow solid (6.12 g, 51%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.6 Hz), 4.55 (2H, d, J = 10.3 Hz), 4.27–4.21 (4H, m), 4.13 (2H, q, J = 6.8 Hz), 2.45 (6H, s), 1.44 (6H, d, J = 7.2 Hz), 1.32 (6H, t, J = 7.1 Hz); ^{13}C NMR ($CDCl_3$) 167.6, 139.1, 135.3, 125.7, 69.9, 60.1, 56.1, 13.8, 9.5, 9.2; IR (ATR, neat) 2984, 1738, 1541, 1447, 1366, 1300, 1265, 1202, 1140, 1111, 1067, 1018, 920, 860, 783, 754 cm^{-1}; HRMS (EI$^+$) m/z calcd for $C_{20}H_{29}N_2O_{10}$ (M^+): 457.1822, found: 457.1780; $[\alpha]^{23.6}_D$ −40.6 (*c* 6.80, $CHCl_3$).

Scheme S3. Synthesis of **M2-NO_2**



Synthesis of M2-NC: A suspension of **M2-NO$_2$** (470 mg, 1.20 mmol), HCO_2NH_4 (499 mg, 7.92 mmol), and 10 wt% Pd/C (127 mg, 120 μmol) in EtOH (12 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (452 mg, 5.14 mmol) was added to the diamine dissolved in CH_2Cl_2 (12 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (280 μL, 462 mg, 3.01 mmol) was added to a solution of diformate in Et_3N (1.40 mL) and CH_2Cl_2 (15 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (CH_2Cl_2/MeOH = 98/2) to give **M2-NC** as white solid (147 mg, 29%). ^{1}H NMR (C_6D_6) δ 4.73 (2H, d, J = 0.0 Hz), 4.12 (2H, d, J = 10.6 Hz), 4.02–3.97 (4H, m), 3.89 (2H, q, J = 6.8 Hz), 2.14 (6H, s), 1.29 (6H, d, J = 6.8 Hz), 0.98 (6H, t, J = 7.1 Hz); ^{13}C NMR (C_6D_6) δ 175.6, 172.6, 137.7, 134.3, 124.4, 75.0, 65.6, 60.8, 18.8, 15.3, 14.2; IR (ATR, neat) 2116, 1734, 1371, 1211, 1142, 1111, 1074, 1011, 918, 860 cm^{-1}; HRMS (NSI) m/z calcd for $C_{22}H_{29}N_2O_{10}$ ([M+H]$^+$): 417.2026, found: 417.2056; $[\alpha]^{25.5}_D$ −55.9 (*c* 6.72, CH_2Cl_2).

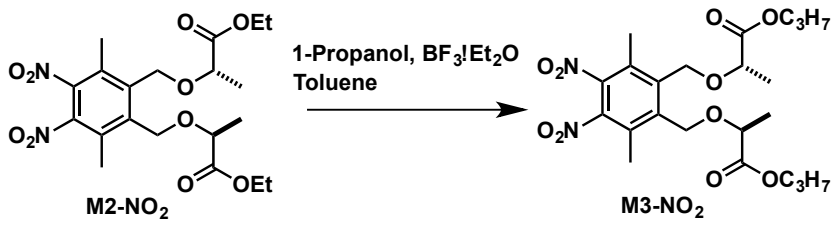
Scheme S4. Synthesis of **M2-NC**



Synthesis of M3-NO$_2$: To a solution of **M2-NO$_2$** (533 mg, 1.24 mmol) in toluene (25 mL) were added 1-propanol (25 mL) and $BF_3 \cdot Et_2O$ (7.42 mL). The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the mixture was added CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ aq (100 mL) to quench the reaction. The organic phase was washed with water (100 mL × 2) and brine (100 mL) and dried over Na_2SO_4. The residue was purified with silica gel column chromatography (hexane/AcOEt = 80/20) to give **M3-NO$_2$** as pale yellow solid (585 mg, 97%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.6 Hz), 4.56 (2H, d, J = 10.6 Hz), 4.19–4.09 (6H, m), 2.45 (6H, s), 1.75–1.66 (4H, m), 1.45 (6H, d, J = 6.9 Hz), 0.97 (6H, t, J = 7.4 Hz); ^{13}C NMR ($CDCl_3$) 172.8, 140.5, 130.8, 75.1, 66.8, 65.3, 22.1, 19.0, 14.7, 10.5; IR (ATR,

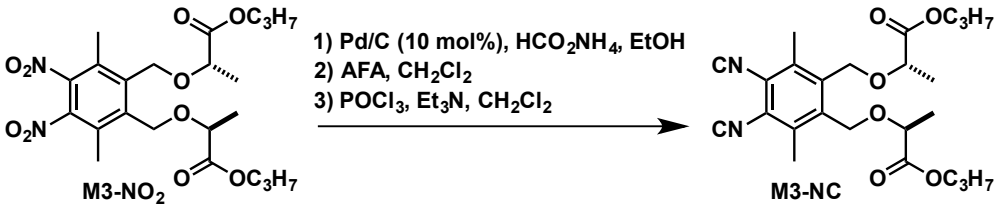
neat) 2970, 2881, 1740, 1541, 1456, 1416, 1362, 1302, 1269, 1200, 1140, 1111, 1065, 1016, 974, 943, 910, 862, 783, 756, 721, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{22}H_{36}N_3O_{10}$ ($[M+NH_4]^+$): 502.2401, found: 502.2383; $[\alpha]^{27.0}_D$ −36.1 (*c* 8.36, $CHCl_3$).

Scheme S5. Synthesis of **M3-NO$_2$**



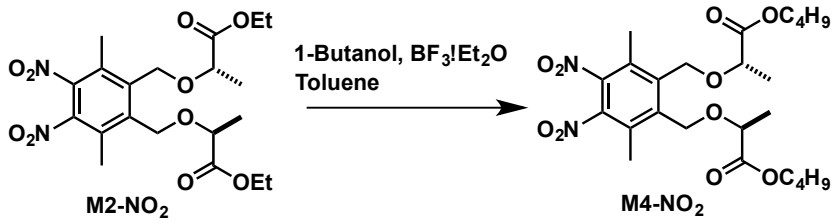
Synthesis of M3-NC: A suspension of **M3-NO$_2$** (554 mg, 1.14 mmol), HCO_2NH_4 (476 mg, 7.55 mmol), and 10 wt% Pd/C (122 mg, 114 μmol) in EtOH (11 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (403 mg, 4.58 mmol) was added to the diamine dissolved in CH_2Cl_2 (11 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (285 μL, 468 mg, 3.05 mmol) was added to a solution of diformate in Et_3N (1.41 mL) and CH_2Cl_2 (15 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (30 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25 to 25/75) to give **M3-NC** as white solid (252 mg, 50%). ^{1}H NMR (C_6D_6) δ 4.77 (2H, d, *J* = 10.6 Hz), 4.16 (2H, d, *J* = 10.6 Hz), 3.98 (4H, t, *J* = 6.7 Hz), 3.92 (2H, q, *J* = 6.9 Hz), 2.16 (6H, s), 1.48–1.39 (4H, m), 1.31 (6H, d, *J* = 6.9 Hz), 0.75 (6H, t, *J* = 7.4 Hz); ^{13}C NMR (C_6D_6) δ 175.6, 172.8, 137.8, 134.3, 75.0, 66.4, 65.6, 22.3, 18.9, 15.4, 10.4; IR (ATR, neat) 3744, 3647, 2120, 1747, 1732, 1653, 1558, 1506, 1456, 1204, 1142, 1059, 941 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{36}N_3O_6$ ($[M+NH_4]^+$): 462.2604, found: 462.2589; $[\alpha]^{27.6}_D$ −42.8 (*c* 9.12, CH_2Cl_2).

Scheme S6. Synthesis of **M3-NC**



Synthesis of M4-NO$_2$: To a solution of **M2-NO$_2$** (2.17 g, 4.76 mmol) in toluene (95 mL) were added 1-butanol (95 mL) and $BF_3 \cdot Et_2O$ (28.6 mL). The mixture was stirred for 24 h at 100 ^oC. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the mixture was added CH_2Cl_2 (200 mL) and saturated $NaHCO_3$ aq (200 mL) to quench the reaction. The organic phase was washed with water (200 mL × 2) and brine (200 mL) and dried over Na_2SO_4. The residue was purified with silica gel column chromatography (hexane/AcOEt = 80/20) to give **M4-NO$_2$** as yellow oil (2.04 g, 84%). ^1H NMR ($CDCl_3$,) δ 4.93 (2H, d, 10.6 Hz), 4.55 (2H, d, 10.6 Hz), 4.23–4.10 (6H, m), 2.44 (6H, s), 1.67–1.62 (4H, m), 1.45–1.37 (10H, m), 0.95 (6H, t, 7.3 Hz); ^{13}C NMR ($CDCl_3$) 172.8, 144.3, 140.5, 130.8, 75.1, 65.3, 65.1, 30.8, 19.2, 18.9, 14.7, 13.8; IR (ATR, neat) 2961, 2874, 1740, 1543, 1456, 1364, 1302, 1271, 1200, 1140, 1113, 1067, 1018, 939, 860, 783, 754, 719, 667 cm^{-1}; HRMS (ESI) m/z calcd for $C_{24}H_{40}N_3O_{10}$ ($[M+NH_4]^+$): 530.2714, found: 530.2709; $[\alpha]^{27.4}_D$ −46.3 (*c* 10.5, $CHCl_3$).

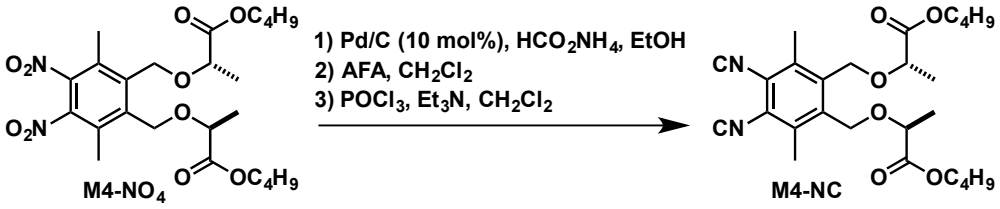
Scheme S7. Synthesis of **M4-NO$_2$**



Synthesis of M4-NC: A suspension of **M4-NO$_2$** (2.04 g, 3.98 mmol), HCO_2NH_4 (1.66 g, 26.2 mmol), and 10 wt% Pd/C (424 mg, 398 μmol) in EtOH (40 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (1.40 g, 15.9 mmol) was added to the diamine dissolved in CH_2Cl_2 (40 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (1.03 mL, 1.68 g, 11.0 mmol)

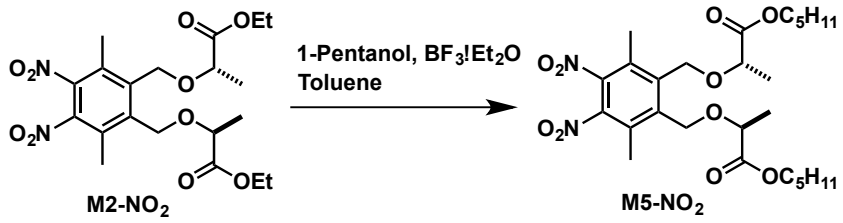
was added to a solution of diformate in Et_3N (5.10 mL) and CH_2Cl_2 (55 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (100 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25 to 25/75) to give **M4-NC** as pale yellow oil (936 mg, 50%). ^{1}H NMR (C_6D_6) δ 4.79 (2H, d, J = 10.6 Hz), 4.17 (2H, d, J = 10.6 Hz), 4.05 (4H, t, J = 6.7 Hz), 3.93 (2H, q, J = 6.9 Hz), 2.16 (6H, s), 1.45–1.39 (4H, m), 1.31 (6H, d, J = 6.8 Hz), 1.23–1.17 (6H, m), 0.80 (6H, t, J = 7.4 Hz); ^{13}C NMR (C_6D_6) δ 175.7, 172.6, 137.7, 134.3, 75.0, 65.6, 64.7, 30.9, 19.3, 18.8, 15.3, 13.7; IR (ATR, neat) 2961, 2874, 2116, 1742, 1456, 1385, 1306, 1269, 1198, 1140, 1113, 1059, 1016, 962, 939, 841, 812, 752, 640 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{40}N_3O_6$ ([M+NH_4]$^+$): 490.2917, found: 490.2902; $[\alpha]^{26.8}_D$ −49.9 (*c* 11.3, CH_2Cl_2).

Scheme S8. Synthesis of **M4-NC**



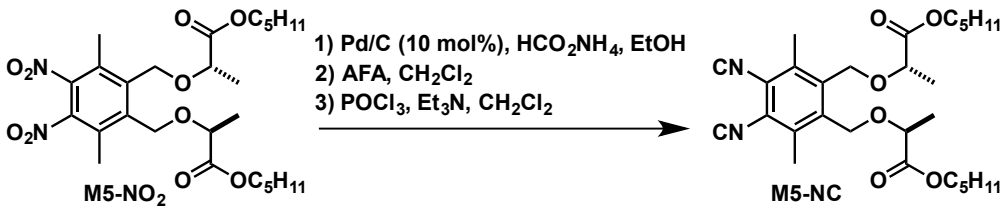
Synthesis of M5-NO_2: To a solution of **M2-NO_2** (1.23 g, 2.70 mmol) in toluene (54 mL) were added 1-pentanol (54 mL) and BF_3·Et_2O (16.3 mL). The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the mixture was added CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ aq (100 mL) to quench the reaction. The organic phase was washed with water (100 mL × 2) and brine (100 mL) and dried over Na_2SO_4. The mixture was heated at 70 °C and dried under vacuum to remove an alcohol. The residue was purified with silica gel column chromatography (hexane/AcOEt = 85/15) to give **M5-NO_2** as yellow oil (1.36 g, 93%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.3 Hz), 4.55 (2H, d, J = 10.6 Hz), 4.21–4.10 (6H, m), 2.45 (6H, s), 1.71–1.64 (4H, m), 1.44 (6H, d, J = 6.9 Hz), 1.37–1.33 (8H, m), 0.92 (6H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 172.8, 140.5, 130.8, 75.1, 65.4, 65.3, 28.4, 28.2, 22.4, 19.0, 14.7, 14.1; IR (ATR, neat) 3854, 3649, 2957, 1740, 1543, 1456, 1362, 1198, 1140, 1113, 1068, 1016, 964, 918, 860, 783 cm^{-1}; HRMS (ESI) m/z calcd for $C_{26}H_{44}N_3O_{10}$ ([M+NH_4]$^+$): 558.3027, found: 558.3013; $[\alpha]^{28.1}_D$ −39.3 (*c* 9.60, $CHCl_3$).

Scheme S9. Synthesis of **M5-NO$_2$**



Synthesis of M5-NC: A suspension of **M5-NO$_2$** (1.33 g, 2.45 mmol), HCO_2NH_4 (1.02 g, 16.2 mmol), and 10 wt% Pd/C (261 mg, 245 μmol) in EtOH (25 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (864 mg, 9.80 mmol) was added to the diamine dissolved in CH_2Cl_2 (25 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (671 μL, 1.10 g, 7.20 mmol) was added to a solution of diformate in Et_3N (3.34 mL) and CH_2Cl_2 (36 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25) to give **M5-NC** as pale yellow oil (656 mg, 54%). ^{1}H NMR (C_6D_6) δ 4.80 (2H, d, J = 10.3 Hz), 4.19 (2H, d, J = 10.6 Hz), 4.07 (4H, t, J = 6.7 Hz), 3.95 (2H, q, J = 7.2 Hz), 2.18 (6H, s), 1.50–1.46 (4H, m), 1.33 (6H, d, J = 6.8 Hz), 1.19–1.17 (8H, m), 0.83 (6H, t, J = 6.8 Hz); ^{13}C NMR (C_6D_6) δ 175.6, 172.7, 137.8, 134.3, 128.3, 75.0, 65.6, 65.0, 28.7, 28.3, 22.6, 18.9, 15.4, 14.1; IR (ATR, neat) 3854, 3736, 3676, 3649, 2928, 2118, 1747, 1732, 1508, 1458, 1389, 1290, 1215, 1200, 1138, 1119, 1051, 1018, 980, 918, 725 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{44}N_3O_6$ ([M+NH$_4$]$^+$): 518.3230, found: 518.3219; $[\alpha]^{29.4}_D$ −38.9 (*c* 9.30, CH_2Cl_2).

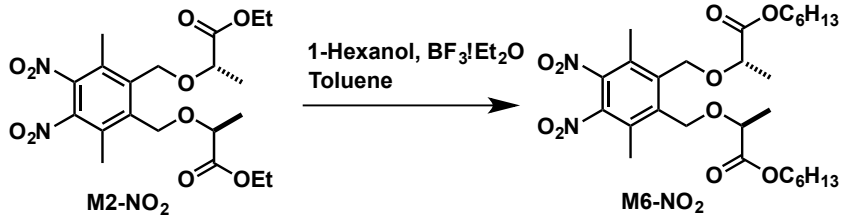
Scheme S10. Synthesis of **M5-NC**



Synthesis of M6-NO$_2$: To a solution of **M2-NO$_2$** (717 mg, 1.57 mmol) in toluene (31 mL) were added 1-hexanol (31 mL) and $BF_3 \cdot Et_2O$ (9.5 mL). The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated under

reduced pressure. To the mixture was added CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ aq (100 mL) to quench the reaction. The organic phase was washed with water (100 mL × 2) and brine (100 mL) and dried over Na_2SO_4. The mixture was heated at 70 °C and dried under vacuum to remove an alcohol. The residue was purified with silica gel column chromatography (hexane/AcOEt = 95/5 to 90/10) to give **M6-NO$_2$** as yellow oil (823 mg, 92%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.6 Hz), 4.55 (2H, d, J = 10.6 Hz), 4.18–4.12 (6H, m), 2.45 (6H, s), 1.70–1.63 (4H, m), 1.44 (6H, d, J = 6.9 Hz), 1.36–1.29 (12H, m), 0.90 (6H, t, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 172.8, 144.3, 140.5, 130.8, 75.1, 65.4, 65.3, 31.5, 28.7, 25.7, 22.7, 19.0, 14.7, 14.1; IR (ATR, neat) 2932, 1740, 1543, 1456, 1362, 1300, 1269, 1198, 1140, 1113, 1068, 1016, 860, 783, 723 cm^{-1}; HRMS (ESI) m/z calcd for $C_{28}H_{48}N_3O_{10}$ ([M+NH$_4$]$^+$): 586.3340, found: 586.3329; $[\alpha]^{30.3}_D$ −45.8 (*c* 10.8, $CHCl_3$).

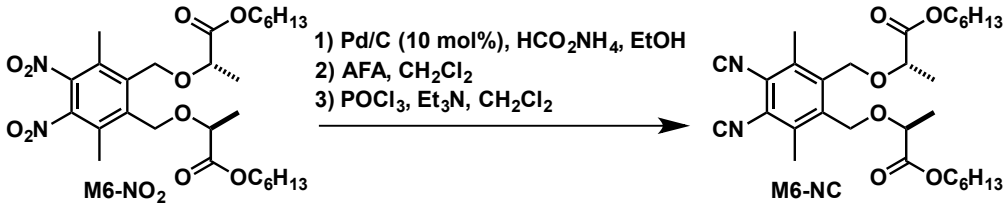
Scheme S11. Synthesis of **M6-NO$_2$**



Synthesis of M6-NC: A suspension of **M6-NO$_2$** (823 mg, 1.45 mmol), HCO_2NH_4 (602 mg, 9.55 mmol), and 10 wt% Pd/C (154 mg, 145 μmol) in EtOH (14 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (396 mg, 4.50 mmol) was added to the diamine dissolved in CH_2Cl_2 (11 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (427 μL, 703 mg, 4.58 mmol) was added to a solution of diformate in Et_3N (2.12 mL) and CH_2Cl_2 (23 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (50 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25) to give **M6-NC** as pale yellow oil (421 mg, 43%). ^{1}H NMR (C_6D_6) δ 4.79 (2H, d, J = 10.3 Hz), 4.23 (2H, d, J = 10.6 Hz), 4.10–4.06 (4H, m), 3.98 (2H, q, J = 6.9 Hz), 2.21 (6H, s), 1.51–1.48 (4H, m), 1.34 (6H, d, J = 6.9 Hz), 1.22–1.18 (8H, m), 0.86 (6H, t, J = 7.0 Hz); ^{13}C NMR (C_6D_6) δ 175.4, 172.7, 137.9, 134.4, 124.4, 75.0, 65.6, 65.0, 31.7, 29.0, 25.9, 22.9,

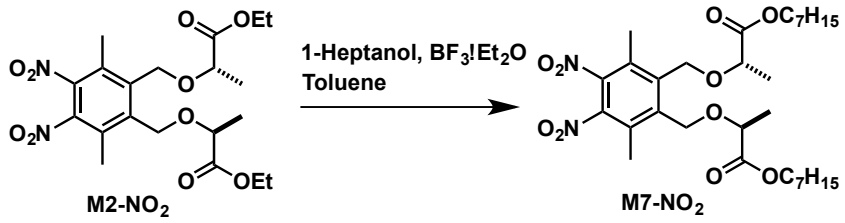
18.9, 15.4, 14.2; IR (ATR, neat) 2957, 2932, 2860, 2116, 1742, 1456, 1387, 1304, 1269, 1196, 1142, 1113, 1057, 1014, 926, 812, 754, 727, 642, 613 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{48}N_3O_6$ ($[M+NH_4]^+$): 546.3543, found: 546.3534; $[\alpha]^{27.3}_D$ −34.7 (*c* 8.54, CH_2Cl_2).

Scheme S12. Synthesis of **M6-NC**



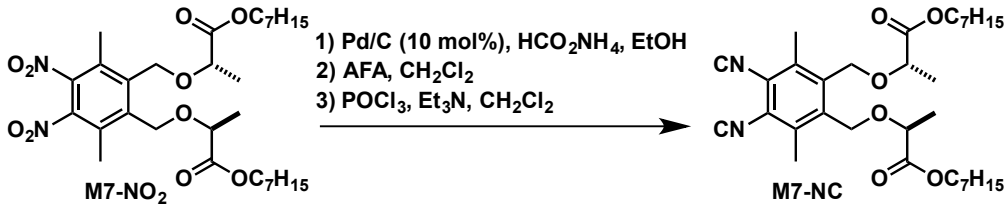
Synthesis of M7-NO_2: To a solution of **M2-NO_2** (1.03 g, 2.25 mmol) in toluene (45 mL) were added 1-heptanol (45 mL) and $BF_3 \cdot Et_2O$ (14 mL). The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the mixture was added CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ aq (100 mL) to quench the reaction. The organic phase was washed with water (100 mL × 2) and brine (100 mL) and dried over Na_2SO_4. The mixture was heated at 70 °C and dried under vacuum to remove an alcohol. The residue was purified with silica gel column chromatography (hexane/AcOEt = 90/10 to 80/20) to give **M7-NO_2** as yellow oil (1.10 g, 82%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, *J* = 10.6 Hz), 4.55 (2H, d, *J* = 10.3 Hz), 4.22–4.10 (6H, m), 2.44 (6H, s), 1.70–1.63 (4H, m), 1.44 (6H, d, *J* = 6.8 Hz), 1.37–1.29 (16H, m), 0.89 (6H, t, *J* = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 172.8, 144.3, 140.5, 130.8, 75.1, 65.4, 65.2, 31.8, 29.0, 28.7, 26.0, 22.7, 19.0, 14.7, 14.2; IR (ATR, neat) 2930, 2858, 1740, 1545, 1456, 1364, 1300, 1202, 1142, 1113, 1068, 1016, 860, 783, 756, 723 cm^{-1}; HRMS (ESI) m/z calcd for $C_{30}H_{52}N_3O_{10}$ ($[M+NH_4]^+$): 614.3653, found: 614.3637; $[\alpha]^{28.3}_D$ −39.2 (*c* 10.3, $CHCl_3$).

Scheme S13. Synthesis of **M7-NO_2**



Synthesis of M7-NC: A suspension of **M7-NO_2** (1.04 g, 1.74 mmol), HCO_2NH_4 (725 mg, 11.5 mmol), and 10 wt% Pd/C (185 mg, 174 μmol) in EtOH (17 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (609 mg, 6.91 mmol) was added to the diamine dissolved in CH_2Cl_2 (17 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (447 μL, 736 mg, 4.80 mmol) was added to a solution of diformate in Et_3N (2.22 mL) and CH_2Cl_2 (24 mL) at 0 °C. After stirring for 50 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (40 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25) to give **M7-NC** as pale yellow oil (213 mg, 22%). ^{1}H NMR (C_6D_6) δ 4.80 (2H, d, J = 10.6 Hz), 4.22 (2H, d, J = 10.6 Hz), 4.11–4.07 (4H, m), 3.98 (2H, q, J = 6.9 Hz), 2.21 (6H, s), 1.53–1.47 (4H, m), 1.35 (6H, d, J = 6.9 Hz), 1.28–1.18 (16H, m), 0.89 (6H, t, J = 7.0 Hz); ^{13}C NMR (C_6D_6) δ 175.5, 172.7, 137.9, 134.4, 124.4, 75.0, 65.7, 65.1, 32.1, 29.2, 29.1, 26.2, 23.0, 18.9, 15.4, 14.3; IR (ATR, neat) 2914, 2118, 1747, 1732, 1458, 1387, 1290, 1205, 1138, 1072, 1016, 926, 760, 719, 646 cm^{-1}; HRMS (ESI) m/z calcd for $C_{32}H_{52}N_3O_6$ ($[M+NH_4]^+$): 574.3856, found: 574.3840; $[\alpha]^{25.7}_D$ −34.9 (*c* 9.62, CH_2Cl_2).

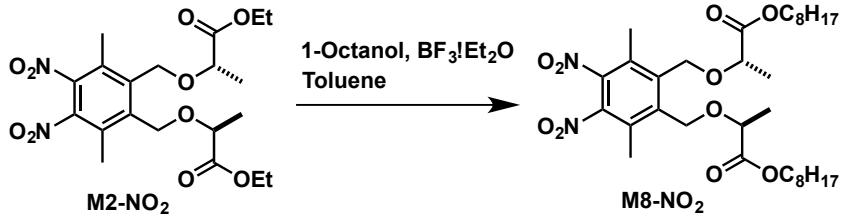
Scheme S14. Synthesis of **M7-NC**



Synthesis of M8-NO_2: To a solution of **M2-NO_2** (611 mg, 1.34 mmol) in toluene (27 mL) were added 1-octanol (27 mL) and $BF_3 \cdot Et_2O$ (8.2 mL). The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the mixture was added CH_2Cl_2 (100 mL) and saturated $NaHCO_3$ aq (100 mL) to quench the reaction. The organic phase was washed with water (100 mL × 2) and brine (100 mL) and dried over Na_2SO_4. The mixture was heated at 70 °C and dried under vacuum to remove an alcohol. The residue was purified with silica gel column

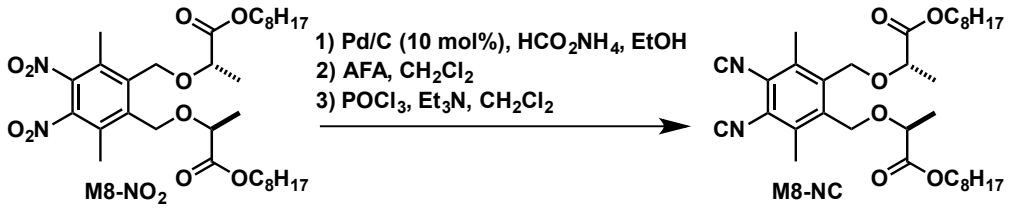
chromatography (hexane/AcOEt = 90/10 to 80/20) to give **M8-NO₂** as yellow oil (556 mg, 68%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.6 Hz), 4.55 (2H, d, J = 10.3 Hz), 4.21–4.12 (6H, m), 2.45 (6H, s), 1.69–1.65 (4H, m), 1.44 (6H, d, J = 6.9 Hz), 1.33–1.28 (20H, m), 0.89 (6H, t, J = 7.0 Hz); ^{13}C NMR ($CDCl_3$) δ 172.8, 140.5, 130.8, 75.1, 65.4, 65.3, 31.9, 29.3, 28.8, 26.0, 22.8, 19.0, 14.7, 14.2; IR (ATR, neat) 2926, 2856, 1742, 1545, 1456, 1362, 1200, 1142, 1113, 1068, 1016, 953, 860, 783, 721 cm^{-1}; HRMS (ESI) m/z calcd for $C_{32}H_{56}N_3O_{10}$ ([M+NH_4]$^+$): 642.3966, found: 642.3952; [α]$^{28.3}_D$ −38.4 (*c* 10.0, $CHCl_3$).

Scheme S15. Synthesis of **M8-NO₂**



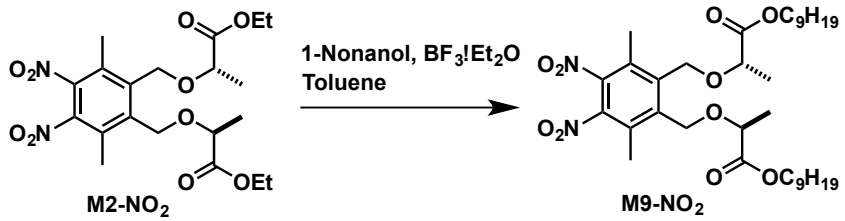
Synthesis of M8-NC: A suspension of **M8-NO₂** (577 mg, 0.92 mmol), HCO_2NH_4 (384 mg, 9.23 mmol), and 10 wt% Pd/C (98.2 mg, 92.3 μmol) in EtOH (9.2 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (260 mg, 2.95 mmol) was added to the diamine dissolved in CH_2Cl_2 (7.4 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (210 μL, 346 mg, 2.26 mmol) was added to a solution of diformate in Et_3N (11.3 mL) and CH_2Cl_2 (24 mL) at 0 °C. After stirring for 50 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (40 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25) to give **M8-NC** as pale yellow oil (235 mg, 27%). ^{1}H NMR (C_6D_6) δ 4.82 (2H, d, J = 10.6 Hz), 4.20 (2H, d, J = 10.6 Hz), 4.11 (4H, t, J = 6.7 Hz), 3.96 (2H, q, J = 6.8 Hz), 2.18 (6H, s), 1.54–1.50 (4H, m), 1.34 (6H, d, J = 6.9 Hz), 1.28–1.22 (20H, m), 0.91 (6H, t, J = 7.0 Hz); ^{13}C NMR (C_6D_6) δ 172.7, 137.7, 134.3, 75.0, 65.7, 65.1, 32.2, 29.6, 29.1, 26.3, 23.1, 18.9, 15.4, 14.3; IR (ATR, neat) 2922, 2851, 2118, 1747, 1732, 1470, 1387, 1292, 1202, 1138, 1119, 1076, 1053, 1022, 941, 918, 756, 719, 650, 621 cm^{-1}; HRMS (ESI) m/z calcd for $C_{34}H_{56}N_3O_6$ ([M+NH_4]$^+$): 602.4169, found: 602.4158; [α]$^{29.7}_D$ −34.0 (*c* 9.52, CH_2Cl_2).

Scheme S16. Synthesis of **M8-NC**



Synthesis of M9-NO_2: To a solution of **M2-NO_2** (1.16 g, 2.53 mmol) in toluene (51 mL) were added 1-nonanol (51 mL) and $BF_3 \cdot Et_2O$ (15.5 mL). The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the mixture was added CH_2Cl_2 (200 mL) and saturated $NaHCO_3$ aq (200 mL) to quench the reaction. The organic phase was washed with water (200 mL × 2) and brine (200 mL) and dried over Na_2SO_4. The mixture was heated at 90 °C and dried under vacuum to remove an alcohol. The residue was purified with silica gel column chromatography (hexane/AcOEt = 90/10 to 80/20) to give **M9-NO_2** as yellow oil (1.54 g, 93%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.3 Hz), 4.55 (2H, d, J = 10.6 Hz), 4.22–4.10 (6H, m), 2.44 (6H, s), 1.70–1.63 (4H, m), 1.44 (6H, d, J = 6.8 Hz), 1.33–1.27 (24H, m), 0.88 (6H, t, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 172.8, 144.3, 140.5, 130.8, 75.1, 65.4, 65.3, 32.0, 29.6, 29.4, 28.7, 26.0, 22.8, 19.0, 14.7, 14.2; IR (ATR, neat) 2926, 2854, 1742, 1545, 1456, 1364, 1300, 1269, 1200, 1142, 1113, 1067, 1018, 964, 922, 860, 783, 756, 721 cm^{-1}; HRMS (ESI) m/z calcd for $C_{34}H_{60}N_3O_{10}$ ($[M+NH_4]^+$): 670.4279, found: 670.4260; $[\alpha]^{28.7}_D$ −34.6 (*c* 9.72, $CHCl_3$).

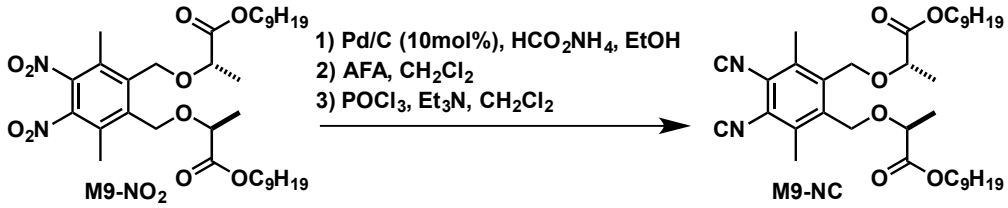
Scheme S17. Synthesis of **M9-NO_2**



Synthesis of M9-NC: A suspension of **M9-NO_2** (1.49 g, 2.28 mmol), HCO_2NH_4 (948 mg, 15.0 mmol), and 10 wt% Pd/C (242 mg, 228 μmol) in EtOH (23 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (802 mg, 9.11 mmol) was added to the diamine dissolved in CH_2Cl_2 (23 mL). After stirring for 14 h, removal of volatiles under reduced

pressure gave a diformate compound as white solid. $POCl_3$ (564 μL, 928 mg, 6.05 mmol) was added to a solution of diformate in Et_3N (2.80 mL) and CH_2Cl_2 (30 mL) at 0 °C. After stirring for 50 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (40 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25) to give **M9-NC** as pale yellow oil (498 mg, 36%). ^{1}H NMR (C_6D_6) δ 4.81 (2H, d, J = 10.6 Hz), 4.21 (2H, d, J = 10.3 Hz), 4.11 (4H, t, J = 6.9 Hz), 3.97 (2H, q, J = 6.9 Hz), 2.20 (6H, s), 1.36–1.23 (30H, m), 0.92 (6H, t, J = 6.9 Hz); ^{13}C NMR (C_6D_6) δ 175.3, 172.5, 137.6, 134.1, 124.2, 74.8, 65.4, 64.9, 32.0, 29.7, 29.4, 29.4, 28.8, 26.0, 22.9, 18.7; IR (ATR, neat) 2914, 2849, 2120, 1747, 1732, 1470, 1389, 1290, 1202, 1140, 1121, 1053, 1022, 920, 719 cm^{-1}; HRMS (ESI) m/z calcd for $C_{36}H_{60}N_3O_6$ ($[M+NH_4]^+$): 630.4482, found: 630.4475; $[\alpha]^{28.1}_D$ −40.4 (*c* 11.3, CH_2Cl_2).

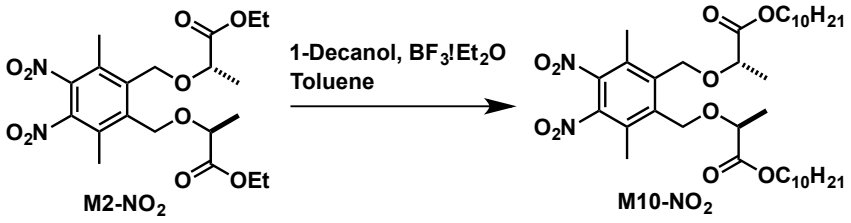
Scheme S18. Synthesis of **M9-NC**



Synthesis of M10-NO_2: To a solution of **M2-NO_2** (1.34 g, 2.93 mmol) in toluene (59 mL) were added 1-decanol (59 mL) and $BF_3 \cdot Et_2O$ (18.0 mL). The mixture was stirred for 24 h at 100 °C. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. To the mixture was added CH_2Cl_2 (200 mL) and saturated $NaHCO_3$ aq (200 mL) to quench the reaction. The organic phase was washed with water (200 mL × 2) and brine (200 mL) and dried over Na_2SO_4. The mixture was heated at 110 °C and dried under vacuum to remove an alcohol. The residue was purified with silica gel column chromatography (hexane/AcOEt = 92/8 to 80/20) to give **M10-NO_2** as yellow oil (1.76 g, 88%). ^{1}H NMR ($CDCl_3$) δ 4.93 (2H, d, J = 10.3 Hz), 4.55 (2H, d, J = 10.6 Hz), 4.21–4.12 (6H, m), 2.44 (6H, s), 1.70–1.63 (4H, m), 1.44 (6H, d, J = 6.8 Hz), 1.33–1.27 (28H, m), 0.88 (6H, t, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 172.8, 144.3, 140.5, 130.8, 75.1, 65.4, 65.3, 32.0, 29.7, 29.4, 29.4, 28.8. 26.0, 22.8,19.0, 14.7, 14.2; IR (ATR, neat) 3854, 3744, 3649, 3628, 2924, 2854, 1742, 1545, 1456, 1362, 1300, 1269, 1200, 1142, 1113, 1068, 1016, 974,

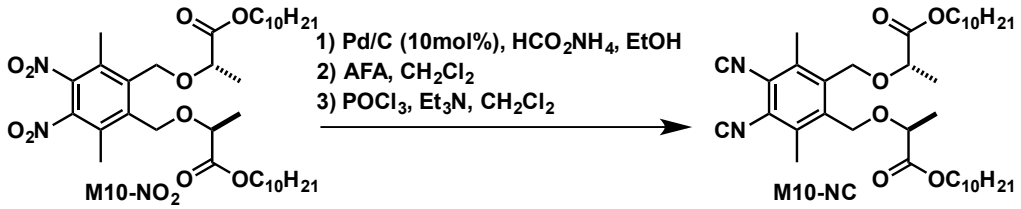
922, 860, 783, 721, 631 cm^{-1}; HRMS (ESI) m/z calcd for $C_{36}H_{64}N_3O_{10}$ ($[M+NH_4]^+$): 698.4592, found: 698.4585; $[\alpha]^{28.6}_D$ −28.5 (*c* 9.00, $CHCl_3$).

Scheme S19. Synthesis of **M10-NO$_2$**



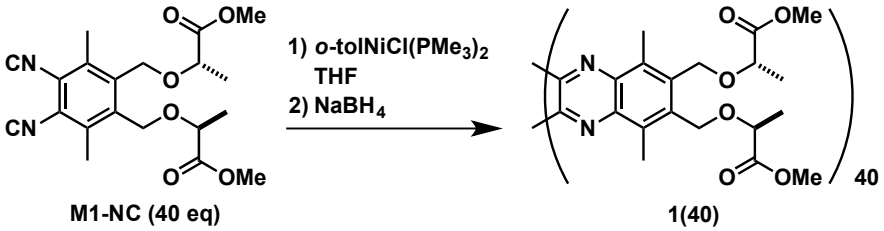
Synthesis of M10-NC: A suspension of **M10-NO$_2$** (1.64 g, 2.41 mmol), HCO_2NH_4 (1.00 g, 15.9 mmol) and 10 wt% Pd/C (257 mg, 241 μmol) in EtOH (24 mL) was stirred for 3 h. The mixture was filtered through a pad of Celite and evaporated under vacuum to give a diamine compound as yellow oil. AFA (843 mg, 9.57 mmol) was added to the diamine dissolved in CH_2Cl_2 (24 mL). After stirring for 14 h, removal of volatiles under reduced pressure gave a diformate compound as white solid. $POCl_3$ (589 μL, 969 mg, 6.32 mmol) was added to a solution of diformate in Et_3N (2.80 mL) and CH_2Cl_2 (32 mL) at 0 °C. After stirring for 30 min at 0 °C, the reaction mixture was washed with saturated $NaHCO_3$ aq (40 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (hexane/Et_2O = 75/25) to give **M10-NC** as pale yellow oil (383 mg, 26%). ^{1}H NMR (C_6D_6) δ 4.82 (2H, d, *J* = 10.6 Hz), 4.20 (2H, d, *J* = 10.6 Hz), 4.12 (4H, t, *J* = 6.7 Hz), 3.97 (2H, q, *J* = 6.9 Hz), 2.18 (6H, s), 1.53–1.52 (4H, m), 1.35 (6H, d, *J* = 6.8 Hz), 1.28–1.24 (28H, m), 0.93 (6H, t, *J* = 6.7 Hz); ^{13}C NMR (C_6D_6) δ 176.2, 173.2, 138.3, 134.9, 125.0, 75.6, 66.2, 65.6, 32.9, 30.5, 30.3, 30.2, 29.6, 26.8, 23.7, 19.5, 15.9, 14.9; IR (ATR, neat) 2914, 2849, 2118, 1749, 1732, 1470, 1389, 1292, 1215, 1200, 1138, 1119, 1053, 1022, 966, 920, 719, 650, 609 cm^{-1}; HRMS (ESI) m/z calcd for $C_{38}H_{64}N_3O_6$ ($[M+NH_4]^+$): 658.4795, found: 658.4778; $[\alpha]^{27.8}_D$ −37.5 (*c* 9.72, CH_2Cl_2).

Scheme S20. Synthesis of **M10-NC**



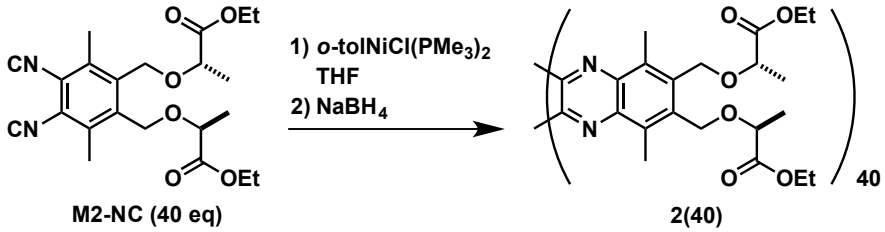
Synthesis of 1(40): M1-NC (128 mg, 329 μmol) was dissolved in THF (13 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 826 μL, 8.24 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (49.8 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (20 mL) was added and extracted with CH_2Cl_2 (20 mL). The organic phase was washed with water (20 mL) and brine (20 mL) and dried over Na_2SO_4 followed by preparative GPC gave **1(40)** as a beige solid (126 mg, 98%). ^{1}H NMR ($CDCl_3$) δ 4.98 (2H, br s), 4.63 (2H, br s), 4.12 (2H, br s), 3.71–3.66 (6H, m), 2.38–2.26 (6H, m), 1.36 (6H, br s); GPC ($CHCl_3$, g/mol): M_n = 9.6 × 10^3, M_w/M_n = 1.17.

Scheme S21. Synthesis of polymer **1(40)**



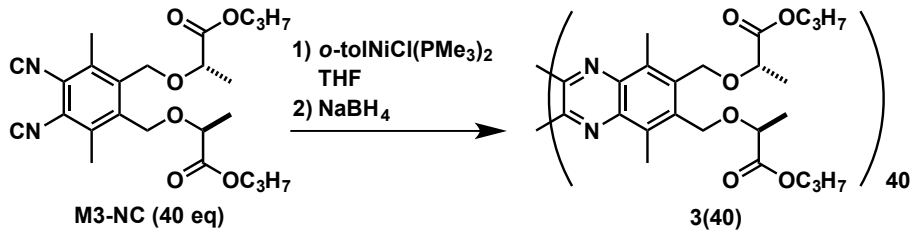
Synthesis of 2(40): M2-NC (23.0 mg, 55.1 μmol) was dissolved in THF (2.2 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 138 μL, 1.38 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (8.34 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **2 (40)** as a beige solid (21.6 mg, 94%). ^{1}H NMR ($CDCl_3$) δ 5.00 (2H, br s), 4.61 (2H, br s), 4.15–4.09 (6H, m), 2.38 (6H, br s), 1.35 (6H, br s), 1.19–1.16 (6H, m); GPC ($CHCl_3$, g/mol): M_n = 9.6 × 10^3, M_w/M_n = 1.13.

Scheme S22. Synthesis of polymer **2(40)**



Synthesis of 3(40): M3-NC (23.9 mg, 53.7 μmol) was dissolved in THF (2.2 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 135 μL, 1.34 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (20.3 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **3(40)** as a beige solid (19.9 mg, 84%). ^{1}H NMR ($CDCl_3$) δ 5.00 (2H, br s), 4.59 (2H, br s), 4.10 (6H, br s), 2.37 (6H, br s), 1.62–1.57 (4H, m), 1.35 (6H, br s), 0.84–0.81 (6H, m), GPC ($CHCl_3$, g/mol): $M_n = 8.0 \times 10^3$, $M_w/M_n = 1.17$.

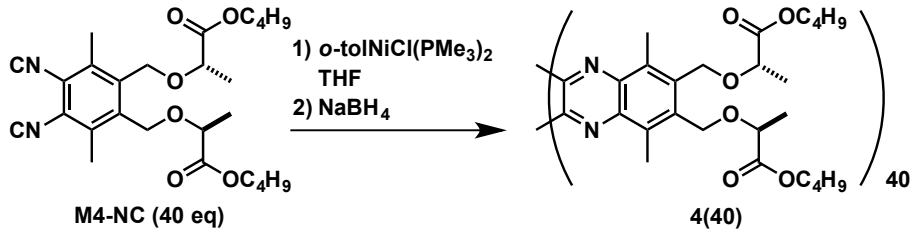
Scheme S23. Synthesis of polymer **3(40)**



Synthesis of 4(40): M4-NC (30.7 mg, 65.0 μmol) was dissolved in THF (2.6 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 163 μL, 1.63 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (24.6 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **4(40)** as a beige solid (26.9 mg, 87%). ^{1}H NMR ($CDCl_3$) δ 4.99 (4H, br s), 4.58 (4H, br s), 4.11–4.07

(6H, m), 2.41–2.31 (6H, m), 1.57 (4H, br s), 1.36–1.29 (10H, m), 0.85–0.82 (6H, m); GPC ($CHCl_3$, g/mol): $M_n = 8.8 \times 10^3$, $M_w/M_n = 1.15$.

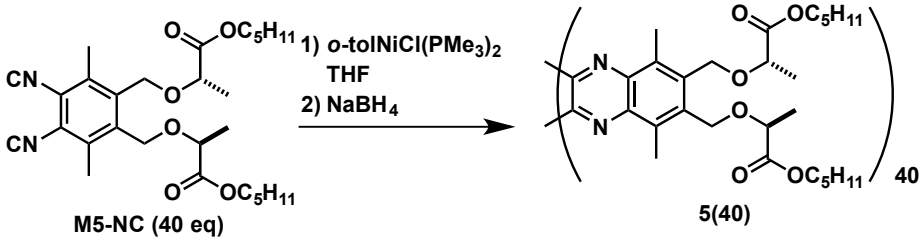
Scheme S24. Synthesis of polymer **4(40)**



M4-NC (40 eq) 4(40)

Synthesis of 5(40): M5-NC (22.0 mg, 43.9 μmol) was dissolved in THF (1.8 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 110 μL, 1.10 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (16.6 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(40)** as a beige solid (21.0 mg, 96%). ^{1}H NMR ($CDCl_3$) δ 5.00 (2H, br s), 4.58 (2H, br s), 4.22–4.05 (6H, m), 2.38 (6H, br s), 1.72–1.58 (4H, m), 1.35–1.22 (14H, m), 0.81 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 1.2 \times 10^4$, $M_w/M_n = 1.11$.

Scheme S25. Synthesis of polymer **5(40)**

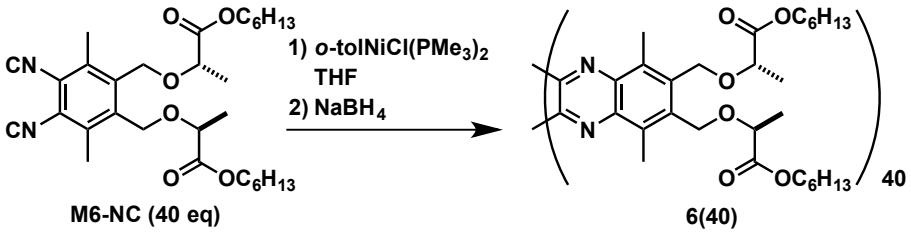


M5-NC (40 eq) 5(40)

Synthesis of 6(40): M6-NC (39.1 mg, 74.0 μmol) was dissolved in THF (3.0 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 186 μL, 1.85 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (28.0 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (15 mL) was added and extracted with CH_2Cl_2 (15 mL). The organic phase was washed with water (15 mL) and brine (15 mL) and dried over Na_2SO_4 followed by preparative GPC gave **6(40)** as a beige solid (35.1 mg, 90%). ^{1}H NMR ($CDCl_3$) δ 5.00 (2H, br s), 4.58 (2H, br s), 4.10–4.03

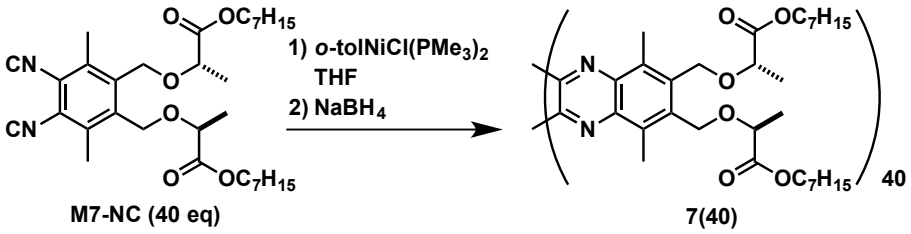
(6H, m), 2.38 (6H, br s), 1.58 (4H, br s), 1.36–1.22 (18H, m), 0.81 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 1.2 \times 10^4$, $M_w/M_n = 1.13$.

Scheme S26. Synthesis of polymer **6(40)**



Synthesis of 7(40): M7-NC (60.3 mg, 108 μmol) was dissolved in THF (4.3 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 272 μL, 2.71 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (41.0 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (20 mL) was added and extracted with CH2Cl2 (20 mL). The organic phase was washed with water (20 mL) and brine (20 mL) and dried over Na_2SO_4 followed by preparative GPC gave **7(40)** as a beige solid (54.8 mg, 91%). ^{1}H NMR ($CDCl_3$) δ 5.00 (2H, br s), 4.57 (2H, br s), 4.11–4.06 (6H, m), 2.37 (6H, br s), 1.59 (4H, br s), 1.37–1.21 (22H, m), 0.87–0.81 (6H, m); GPC ($CHCl_3$, g/mol): $M_n = 1.3 \times 10^4$, $M_w/M_n = 1.12$.

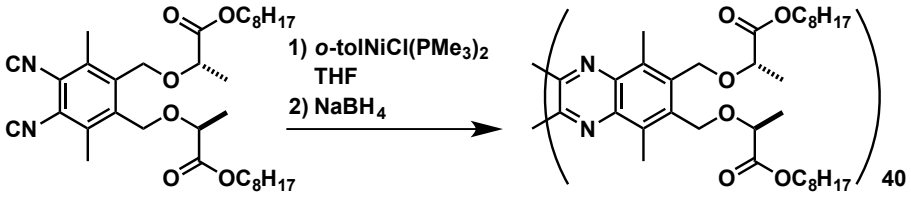
Scheme S27. Synthesis of polymer **7(40)**



Synthesis of 8(40): M8-NC (28.1 mg, 48.1 μmol) was dissolved in THF (1.9 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (9.97 mM, 120 μL, 1.20 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (18.1 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **8(40)** as

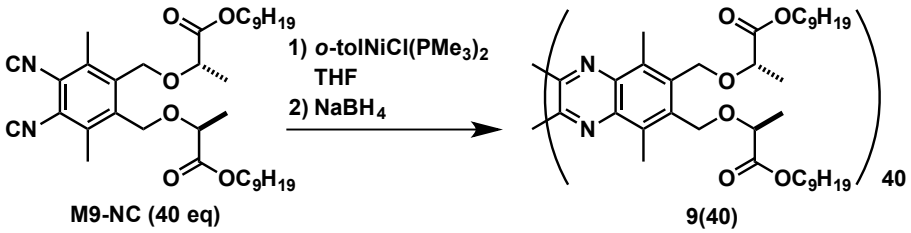
a beige solid (24.5 mg, 87%). ^{1}H NMR ($CDCl_3$) δ 4.99 (2H, br s), 4.57 (2H, br s), 4.11–4.03 (6H, m), 2.37 (6H, br s), 1.60 (4H, br s), 1.41–1.22 (26H, m), 0.85–0.82 (6H, m); GPC ($CHCl_3$, g/mol): $M_n = 1.2 \times 10^4$, $M_w/M_n = 1.13$.

Scheme S28. Synthesis of polymer 8**(40)**



Synthesis of 9(40): M9-NC (32.6 mg, 53.1 μmol) was dissolved in THF (2.1 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 152 μL, 1.33 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (20.1 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **9(40)** as a beige solid (30.1 mg, 92%). ^{1}H NMR ($CDCl_3$) δ 4.99 (2H, br s), 4.57 (2H, br s), 4.19–4.03 (6H, m), 2.36 (6H, br s), 1.60–1.58 (4H, m), 1.43–1.22 (28H, m), 0.89–0.83 (6H, m); GPC ($CHCl_3$, g/mol): $M_n = 1.1 \times 10^4$, $M_w/M_n = 1.16$.

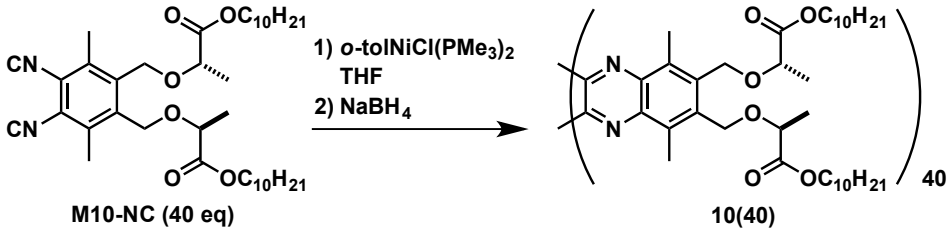
Scheme S29. Synthesis of polymer **9(40)**



Synthesis of 10(40): M10-NC (37.4 mg, 58.4 μmol) was dissolved in THF (2.3 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 167 μL, 1.50 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (22.1 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **10(40)** as

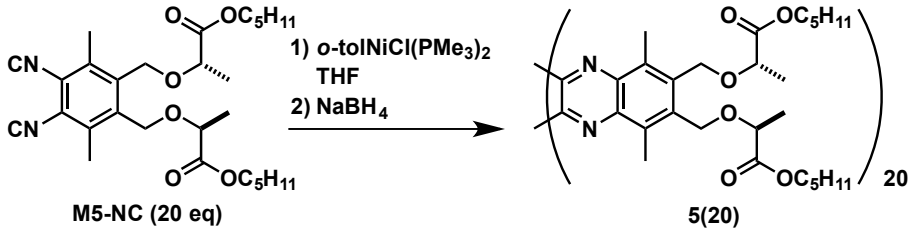
a beige solid (31.0 mg, 83%). ^{1}H NMR ($CDCl_3$) δ 4.99 (2H, br s), 4.57 (2H, br s), 4.12–4.02 (6H, m), 2.36 (6H, br s), 1.60 (4H, br s), 1.37–1.23 (32H, m), 0.86–0.83 (6H, m); GPC ($CHCl_3$, g/mol): $M_n = 1.0 \times 10^4$, $M_w/M_n = 1.14$.

Scheme S30. Synthesis of polymer **10(40)**



Synthesis of 5(20): M5-NC (28.9 mg, 57.6 μmol) was dissolved in THF (2.3 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 330 μL, 2.88 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (43.6 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(20)** as a beige solid (25.3 mg, 88%). ^{1}H NMR ($CDCl_3$) δ 4.97 (2H, br s), 4.55 (2H, br s), 4.16–4.04 (6H, m), 2.33–2.21 (6H, m), 1.57 (4H, br s), 1.40–1.22 (14H, m), 0.92–0.80 (6H, m); GPC ($CHCl_3$, g/mol): $M_n = 6.3 \times 10^3$, $M_w/M_n = 1.16$.

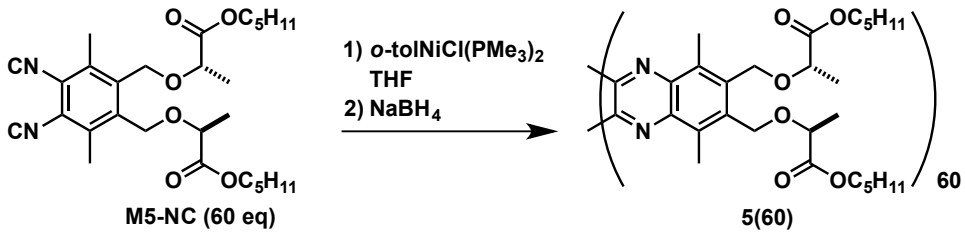
Scheme S31. Synthesis of polymer **5(20)**



Synthesis of 5(60): M5-NC (27.0 mg, 53.9 μmol) was dissolved in THF (2.2 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 103 μL, 0.898 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (13.6 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10

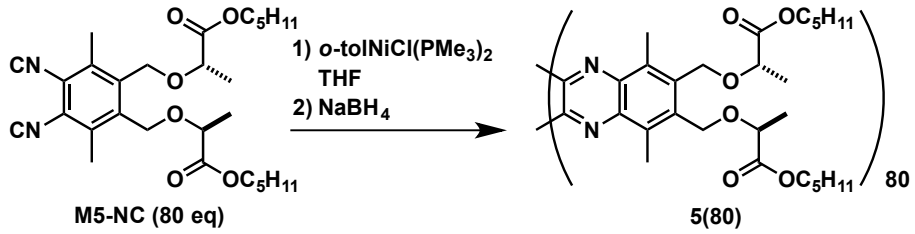
mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(60)** as a beige solid (25.5 mg, 95%). ^{1}H NMR ($CDCl_3$) δ 5.01 (2H, br s), 4.59 (2H, br s), 4.10–4.03 (6H, m), 2.39 (6H, br s), 1.58 (4H, br s), 1.37–1.22 (14H, m), 0.81 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 1.6 \times 10^4$, $M_w/M_n = 1.11$.

Scheme S32. Synthesis of polymer **5(60)**



Synthesis of 5(80): M5-NC (29.1 mg, 58.0 μmol) was dissolved in THF (2.3 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 83.1 μL, 0.726 μmol) was added to the solution. After stirring for 2 h, $NaBH_4$ (11.0 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(80)** as a beige solid (25.1 mg, 86%). ^{1}H NMR ($CDCl_3$) δ 5.01 (2H, br s), 4.59 (2H, br s), 4.10–4.01 (6H, m), 2.39 (6H, br s), 1.58 (4H, br s), 1.37–1.23 (14H, m), 0.81 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 2.6 \times 10^4$, $M_w/M_n = 1.10$.

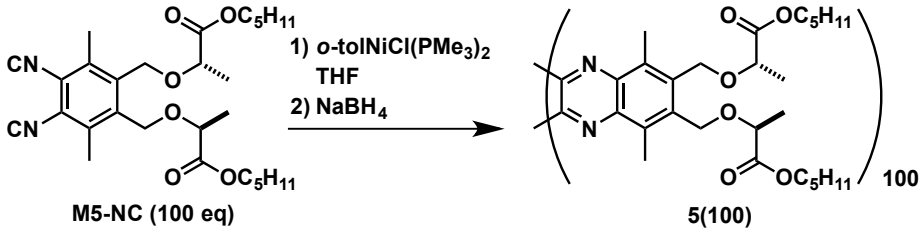
Scheme S33. Synthesis of polymer **5(80)**



Synthesis of 5(100): M5-NC (28.8 mg, 57.5 μmol) was dissolved in THF (2.3 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 65.8 μL, 0.575 μmol) was added to the solution. After stirring for 10 h, $NaBH_4$ (8.70 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was

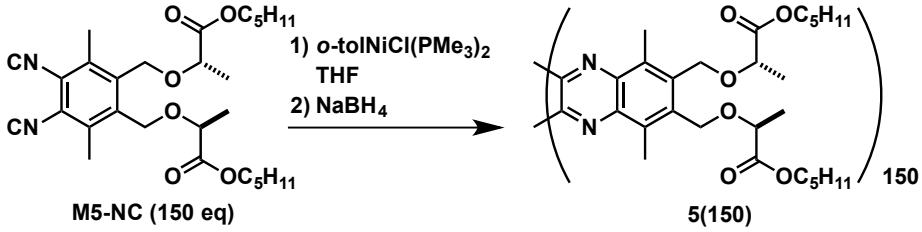
added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(100)** as a beige solid (24.7 mg, 86%). ^{1}H NMR (CDCl3)) δ 5.01 (2H, br s), 4.59 (2H, br s), 4.10–4.01 (6H, m), 2.39 (6H, br s), 1.58 (4H, br s), 1.43–1.23 (14H, m), 0.93 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 3.7 \times 10^4$, $M_w/M_n = 1.11$.

Scheme S34. Synthesis of polymer **5(100)**



Synthesis of 5(150): M5-NC (32.6 mg, 65.2 μmol) was dissolved in THF (2.3 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 49.8 μL, 0.435 μmol) was added to the solution. After stirring for 14 h, $NaBH_4$ (6.58 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(150)** as a beige solid (28.3 mg, 86%). ^{1}H NMR ($CDCl_3$) δ 5.02 (2H, br s), 4.63 (2H, br s), 4.10–4.01 (6H, m), 2.39 (6H, br s), 1.59 (4H, br s), 1.36–1.23 (14H, m), 0.81 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 5.6 \times 10^4$, $M_w/M_n = 1.15$.

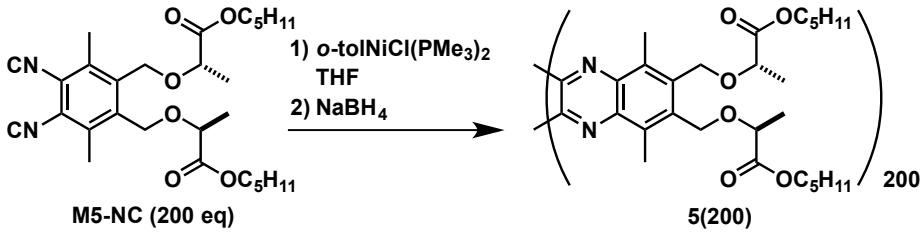
Scheme S35. Synthesis of polymer **5(150)**



Synthesis of 5(200): M5-NC (34.6 mg, 69.2 μmol) was dissolved in THF (2.8 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 39.6 μL, 0.346 μmol) was added to the solution. After stirring for 14 h, $NaBH_4$ (5.24 mg) was added to the reaction mixture at room

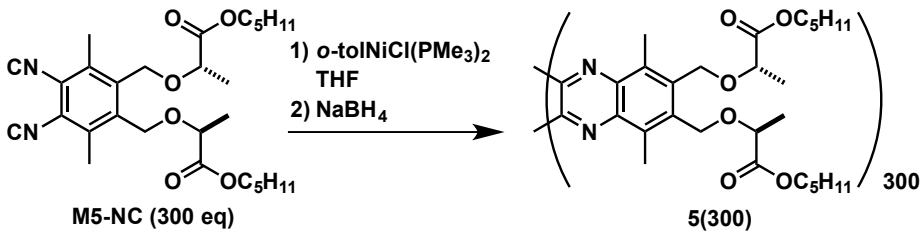
temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(200)** as a beige solid (31.6 mg, 91%). ^{1}H NMR ($CDCl_3$) δ 5.01 (2H, br s), 4.60 (2H, br s), 4.10–4.03 (6H, m), 2.39 (6H, br s), 1.58 (4H, br s), 1.36–1.23 (14H, m), 0.81 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 8.5 \times 10^4$, $M_w/M_n = 1.09$.

Scheme S36. Synthesis of polymer **5(200)**



Synthesis of 5(300): M5-NC (34.2 mg, 68.2 μmol) was dissolved in THF (2.8 mL). A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 26.1 μL, 0.227 μmol) was added to the solution. After stirring for 14 h, $NaBH_4$ (3.44 mg) was added to the reaction mixture at room temperature. After stirring for 1 h at room temperature, saturated NH_4Cl aq (10 mL) was added and extracted with CH_2Cl_2 (10 mL). The organic phase was washed with water (10 mL) and brine (10 mL) and dried over Na_2SO_4 followed by preparative GPC gave **5(300)** as a beige solid (29.7 mg, 87%). ^{1}H NMR ($CDCl_3$) δ5.03 (2H, br s), 4.68 (2H, br s), 4.10–4.03 (6H, m), 2.39 (6H, br s), 1.56 (4H, br s), 1.37–1.23 (14H, m), 0.81 (6H, br s); GPC ($CHCl_3$, g/mol): $M_n = 8.7 \times 10_4$, $M_w/M_n = 1.17$.

Scheme S37. Synthesis of polymer **5(300)**

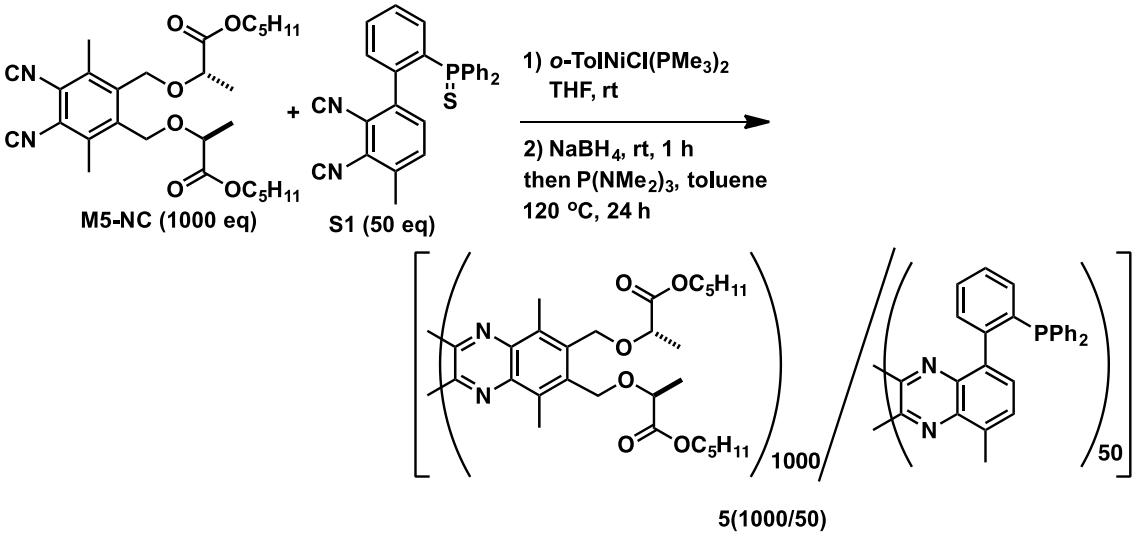


Synthesis of 5(1000/50):

[Polymerization] A THF solution of *o*-TolNiCl(PMe_3)$_2$ (8.73 mM, 134 μL, 1.17 μmol) was added to THF (29 mL). To the solution was added a mixture of monomer **M5-NC** (587 mg, 1.17 mmol) and **S1** (58.7 μmol) in THF (20 mL) at room temperature. The mixture was stirred for 24 h at room temperature. To the reaction mixture was added $NaBH_4$ (17.8 mg,), and the mixture was stirred for 1 h. The solvent was then evaporated until approximately half of the original volume. The mixture was poured into vigorously stirred MeOH (600 mL), and precipitated polymer was collected by centrifugation followed by washing with MeOH × 2. After drying in vacuo, fibriform polymer was obtained.

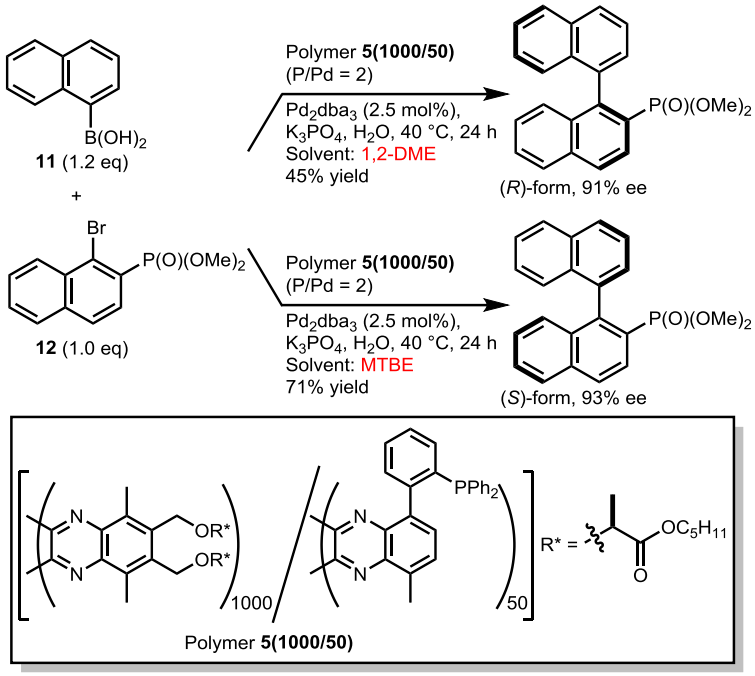
[Reduction of Phosphine Sulfide] A mixture of the obtained polymer (56.1 μmol P) and $P(NMe_2)_3$ (0.408 mL, 2.24 mmol) in toluene (5.3 mL) was stirred at 110 °C for 24 h. The mixture was diluted with THF (1 mL) and poured into vigorously stirred MeOH (600 mL). Precipitated material was collected by filtration and washed with MeOH × 2 to give **5(1000/50)** as fibriform solid (531 mg, 91%). ^{1}H NMR ($CDCl_3$) δ 4.96–4.10 (10H, m), 2.38 (6H, br s), 1.59–1.23 (18H, m), 0.81 (6H, br s); ^{31}P NMR ($CDCl_3$) δ −15.2; Molecular weight could not be determined by GPC, because of the exclusion limit of the column.

Scheme S38. Synthesis of random copolymer **5(1000/50)**



3. Use of Polymer 5(1000/50) as a Chiral Ligand in the Asymmetric Suzuki-Miyaura coupling (SMC) Reaction

Scheme S39. Asymmetric SMC of **11** and **12** in the presence of **5(1000/50)** in 1,2-DME or MTBE

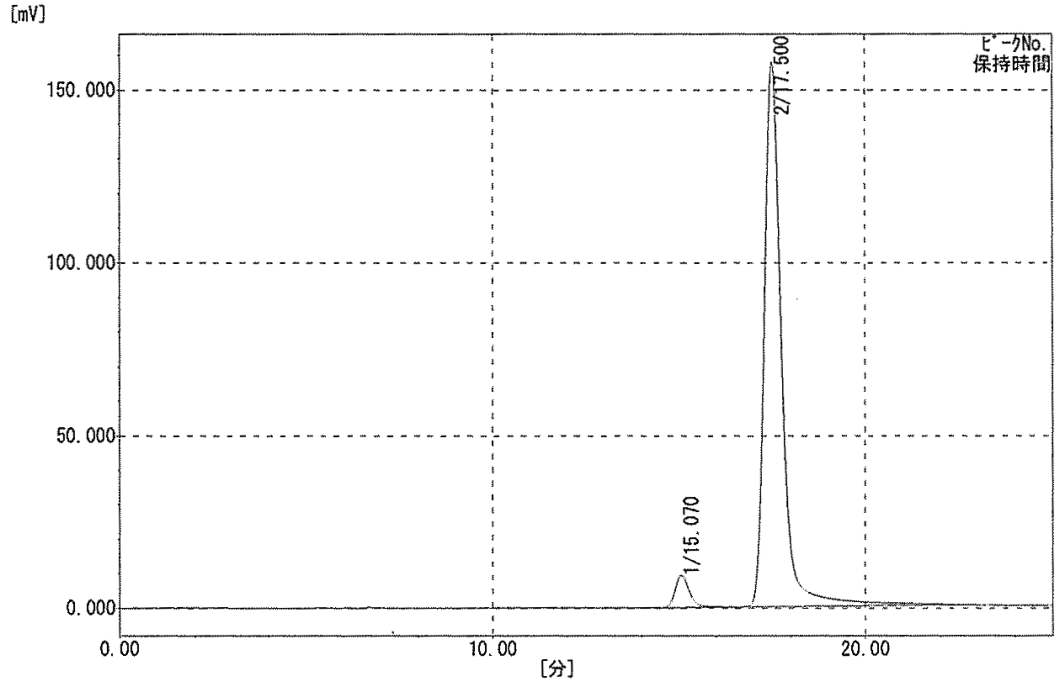


Asymmetric SMC of 11 and 12 in the Presence of *P*-helical Polymer 5(1000/50) as a ligand in 1,2-DME: A solution of **5(1000/50)** (104 mg, 10 μmol phosphorous atom) in 1,2-DME (1.1mL) was stirred for 24 h at 60 °C. To the solution was added Pd_2dba_3 (5.0 mM in 1,2-DME, 500 μL, 2.5 μmol). The mixture was stirred at room temperature for 10 min. To the mixture were added K_3PO_4 (63.7 mg, 0.3 mmol), 1-naphthylboronic acid **11** (30.0 mg, 0.2 mmol), aryl bromide **12** (31.5 mg, 0.1 mmol), and H_2O (160 μL). The mixture was stirred at 40 °C for 24 h. To the mixture was added 1,2-bis(diphenylphosphino)ethane (5 mg) to dissolve the gelled polymer. Subsequent addition of acetonitrile (10 mL) resulted in precipitation of polymer **5(1000/50)**. The suspension was passed through a pad of Celite using MeCN as an eluent. The filtrate was dried over Na_2SO_4 and subjected to PTLC (hexane/AcOEt = 1/4). Further purification was made by GPC. The corresponding product (+)-(*R*)-form was isolated in 45% yield. The enantiomeric excess of the product was determined to be 91% by HPLC with CHIRALCEL® OZ-H (Eluent: Hexane/2-PrOH =

80/20, Flow rate: 0.6 mL/min, Retention time: t_R of (+)-isomer = 17.3 min, t_R of (−)-isomer = 14.9 min).

Asymmetric SMC of 11 and 12 in the Presence of *P*-helical Polymer 5(1000/50) as a ligand in MTBE: A solution of **5(1000/50)** (104 mg, 10 μmol phosphorous atom) in MTBE (1.1mL) was stirred for 24 h at 60 °C. To the solution was added Pd_2dba_3 (5.0 mM in MTBE, 500 μL, 2.5 μmol). The mixture was stirred at room temperature for 10 min. To the mixture were added K_3PO_4 (63.7 mg, 0.3 mmol), 1-naphthylboronic acid **11** (30.0 mg, 0.2 mmol), aryl bromide **12** (31.5 mg, 0.1 mmol), and H_2O (160 μL). The mixture was stirred at 40 °C for 24 h. To the mixture was added 1,2-bis(diphenylphosphino)ethane (5 mg) to dissolve the gelled polymer. Subsequent addition of acetonitrile (10 mL) resulted in precipitation of polymer **5(1000/50)**. The suspension was passed through a pad of Celite using MeCN as an eluent. The filtrate was dried over Na_2SO_4 and subjected to PTLC (hexane/AcOEt = 1/4). Further purification was made by GPC. The corresponding product (−)-(*S*)-form was isolated in 71% yield. The enantiomeric excess of the product was determined to be 93% by HPLC with CHIRALCEL® OZ-H (Eluent: Hexane/2-PrOH = 80/20, Flow rate: 0.6 mL/min, Retention time: t_R of (+)-isomer = 17.3 min, t_R of (−)-isomer = 14.9 min).

タイトル　　：
データ　　：C:¥HPLCData¥data_kuroda.mdb　TK0422　TK0422
日時　　：収集 2014/04/30 11:03:16　計算 2014/04/30 11:40:03
カップ番号　：28
収集属性　　：独立　0.00 - 25.00 min
計算方法　　：百分率法

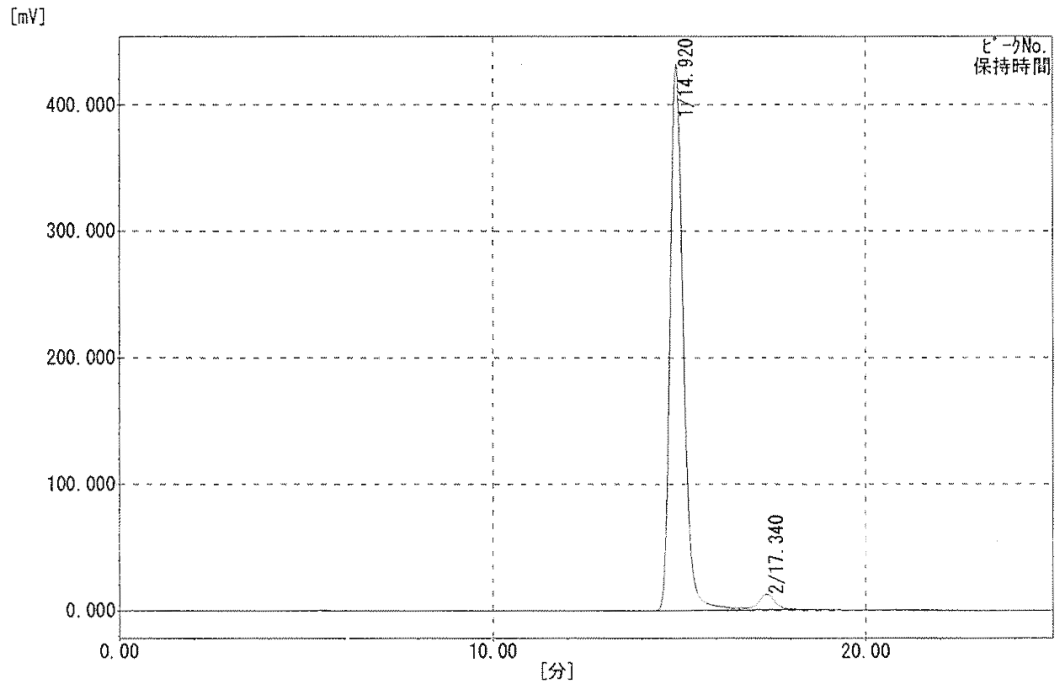


No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	15.070	9.30	23.56	245.60	4.63	8157	0.00	1.35
2	1	17.500	157.85	27.36	5063.99	95.37	8159	3.37	1.36

CH.1 Peak Not Found.

Figure S1. HPLC trace of the product of the asymmetric SMC of **11** and **12** in 1,2-DME. Enantiomeric excess was found to be 91% (*R*).

タイトル　　：
データ　　：C:¥HPLCData¥data_kuroda.mdb　TK0416　TK0416
日時　　：収集 2014/04/17 22:47:57　計算 2014/04/17 23:14:45
カップ番号　：28
収集属性　　：独立　0.00 - 25.00 min
計算方法　　：百分率法



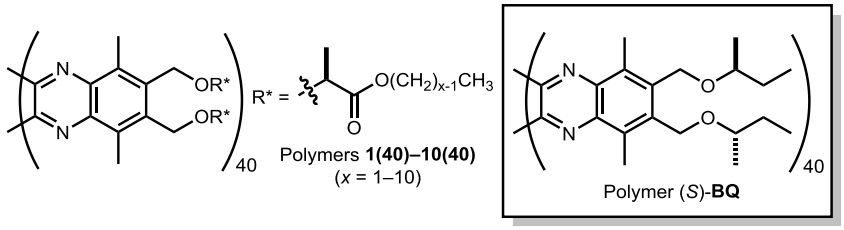
No.	Ch	時間[分]	高さ[mV]	半値幅[秒]	面積[mVx秒]	面積%	理論段数	分離能	非対称係数
1	1	14.920	432.17	22.15	10653.26	96.43	9048	0.00	1.35
2	1	17.340	12.27	26.85	394.21	3.57	8318	3.49	0.00

CH.1 Peak Not Found.

Figure S2. HPLC trace of the product of the asymmetric SMC of **11** and **12** in MTBE. Enantiomeric excess was found to be 93% (*S*).

4. Summary of CD and UV Measurements of Polymer Solutions

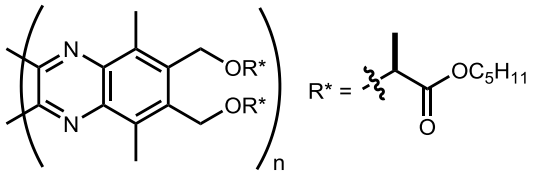
Table S1. Structures and screw-sense induction properties (g_{abs}) of polymers containing chiral side chains



	The g_{abs} values (/10^{-3}, 363.5 nm) of polymers containing varied length of alkyl side chains *x*										
Solvent	*x* = 1	*x* = 2	*x* = 3	*x* = 4	*x* = 5	*x* = 6	*x* = 7	*x* = 8	*x* = 9	*x* = 10	(*S*)-**BQ**
$CHCl_3$	–2.28	–2.38	–2.14	–2.18	–2.18	–2.07	–2.12	–2.16	–2.10	–2.11	–2.36
CH_2Cl_2	–2.06	–2.01	– [a]	– [a]	– [a]	– [a]	– [a]	– [a]	– [a]	– [a]	–2.06
1,1,2-TCE	–2.64	–2.70	–2.57	–2.47	–2.83	–2.37	–2.58	–2.52	–2.41	–2.29	+2.81
Toluene	–1.97	–1.73	– [a]	– [a]	– [a]	– [a]	– [a]	– [a]	– [a]	– [a]	–1.97
THF	–1.49	–0.18	–1.69	–0.77	–1.88	–1.71	–1.85	–1.78	–1.75	–1.71	–1.90
1,4-Dioxane	–1.64	+0.48	–1.65	+0.18	–1.90	–1.74	–1.89	–1.68	–1.48	–1.22	–2.10
2-MeTHF	–0.30	+1.33	–0.97	+1.34	–1.92	–1.75	–1.87	–1.41	–1.10	–0.63	– [a]
1,2-DME	–0.17	+1.29	–1.30	–0.08	–2.03	–1.84	–1.99	–1.81	–1.51	–1.26	–1.90
CPME	+1.26	+2.01	+0.75	+1.94	–1.54	–1.73	–1.57	+0.21	+1.06	+1.46	– [a]
Et_2O	+1.38	+1.96	+0.71	+1.78	–1.57	–1.66	–1.45	+0.50	+1.29	+1.64	–2.01
MTBE	+1.54	+1.98	+1.76	+2.14	+1.81	+0.54	+1.69	+2.08	+2.03	+2.04	–1.93
EtOAc	+0.74	+1.55	+0.24	+1.35	–1.47	–1.46	–1.34	+0.20	+0.78	+1.19	– [a]

[a] Not measured

Table S2. Structures and screw-sense induction properties (g_{abs}) of polymers with varied degrees of polymerization



Polymers **5(*n*)** (*n* = 20, 40, 60, 80, 100, 150, 200, and 300)

	The g_{abs} values (/10^{-3}, 363.5 nm) of polymers **5(*n*)**		
n	1,2-DME	MTBE	CPME
20	–1.13	+1.03	–0.51
40	–1.86	+1.49	–1.40
60	–1.96	+1.76	–1.76
80	–2.16	+1.94	–1.96
100	–2.20	+1.95	–2.03
150	–2.28	+2.11	–2.12
200	–2.31	+2.10	–2.13
300	–2.33	+2.10	–2.19

5. References

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