Supporting Information for:

Synthesis of helical π-conjugated polymers bearing pyridine *N*-oxide pendants and asymmetric allylation of aldehydes in the helical cavity

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1. Materials

Anhydrous solvents (acetonitrile, dichloromethane, tetrahydrofuran (THF) and *N*,*N*-dimethylformamide (DMF)) and common organic solvents were purchased from Kanto Kagaku (Tokyo, Japan). 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl) was purchased from Wako Pure Chemical Industries (Osaka, Japan). Copper (I) iodide (CuI), diisopropylamine (DIPA), benzaldehyde and *N*,*N*-dimethyl-4-aminopyridine (DMAP) were available from Sigma-Aldrich (St. Louis, MO, USA). Tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$) was purchased from Nacalai (Kyoto, Japan). 3-Hydroxypyridine *N*-oxide, 4-nitrobenzaldehyde, 4-methoxybenzaldehyde and *N*-ethyldiisopropylamine ($^iPr_2NEt$) were from Tokyo Kasei (TCI, Tokyo, Japan). An optically active diethynyl compound bearing a glucose-linked biphenyl unit (GLB-**1**),[S1] 4,6-diiodothieno[3,4-*b*]thiophene-2-carboxylic acid,[S2] 4,6-diiodothieno[3,4-*b*]thiophene-2-carboxylic acid ethyl ester (**3**)[S2] and thieno[3,4-*b*]thiophene-2-carboxylic acid[S3] were prepared according to the previously reported methods. CHIRALCEL OD-H (25 cm × 0.46 cm (i.d.)) and CHIRALPAK IG (25 cm × 0.46 cm (i.d.)) columns were purchased from Daicel (Tokyo, Japan).

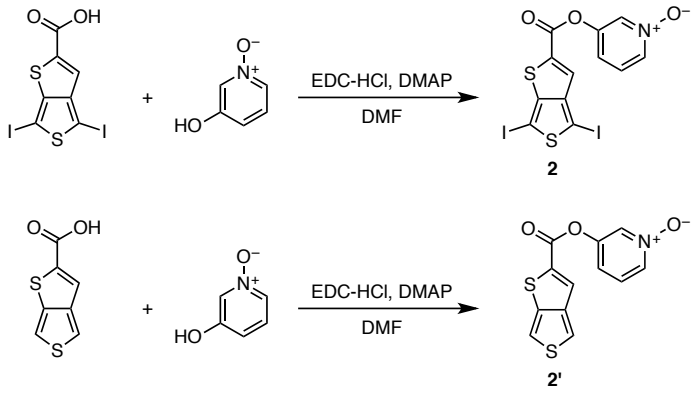
2. Instruments

The melting points were measured on a Yanako melting point apparatus (Yanako, Kyoto, Japan) and were uncorrected. The NMR spectra were measured using a JNM-ECA 500 (JEOL, Tokyo, Japan) operating at 500 MHz for ^1H and 126 MHz for ^{13}C using tetramethylsilane as the internal standard. The IR spectra were recorded on a JASCO Fourier Transform IR-4700 spectrophotometer (JASCO, Tokyo, Japan). The absorption and circular dichroism (CD) spectra were measured using a JASCO V-570 (a scanning rate of 200 nm min^{-1} and a bandwidth of 1.0 nm) and a JASCO J-725 (a scanning rate of 100 nm min^{-1} and a bandwidth of 1.0 nm) spectrometers, respectively, with a quartz cell of 1.0-mm path length (UV-grade) (GL Sciences, Tokyo, Japan). The temperature was controlled with JASCO ETC-505T and JASCO PTC-348WI apparatuses for absorption and CD measurements, respectively. The molar mass (M_n) and molar mass dispersity (M_w/M_n) of the polymer were estimated using size-exclusion chromatography (SEC) equipped with a TSKgel MultiporeH_{XL}-M column (Tosoh, Tokyo, Japan), a JASCO PU-2080 Intelligent HPLC pump and a JASCO UV-970 UV/VIS detector at 254 nm, where chloroform was used as the eluent. The molecular mass calibration curve was obtained with polystyrene standards (Tosoh). High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-700 spectrometer with fast atom bombardment (FAB) as the ionization technique. The determination of the enantiomeric excess (ee) of allyl alcohols was performed using HPLC equipped with a CHIRALCEL OD-H or a CHIRALPAK IG column, a JASCO PU-2080 Intelligent HPLC pump, a column oven (JASCO CO-1560), a JASCO MD-2018 multi-wavelength UV/VIS detector, a polarimetric detector (JASCO OR-990, Hg-Xe without filter) and a CD detector (JASCO CD-2095) (eluent, *n*-hexane–2-propanol; flow rate, 0.8 mL min^{-1}; temperature, *ca.* 20 °C).

Elemental analyses were performed by the Research Institute for Instrumental Analysis of Advanced Science Research Center, Kanazawa University, Kanazawa, Japan.

3. Synthetic Procedures

Thieno[3,4-*b*]thiophene derivatives containing pyridine *N*-oxide units (**2** and **2'**) were prepared according to Scheme S1.



Scheme S1 Synthesis of thieno[3,4-*b*]thiophene derivatives **2** and **2'**.

Synthesis of 2. To a mixture of 4,6-diiodothieno[3,4-*b*]thiophene-2-carboxylic acid (79 mg, 0.18 mmol), 3-hydroxypyridine *N*-oxide (20 mg, 0.16 mmol) and DMAP (25 mg, 0.20 mmol) in anhydrous DMF (1.5 mL) was added EDC-HCl (38 mg, 0.20 mmol). The mixture was stirred at room temperature for 12 h and diluted with chloroform. The solution was washed with 1 N HCl aqueous solution, saturated $NaHCO_3$ aqueous solution, and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using chloroform–methanol (20:1, v/v) as the eluent to give the desired product as a reddish brown solid (31 mg, 36% yield). Mp: decomposed at >165 °C. IR (KBr, cm^{-1}): 1731 (C=O). ^1H NMR (500 MHz, DMSO-d_6, rt): δ 8.53 (t, J = 1.7 Hz, 1H), 8.22-8.24 (m, 1H), 7.95 (s, 1H), 7.53 (dd, J = 8.6, 6.3 Hz, 1H), 7.45-7.48 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6, rt): δ 159.74, 150.08, 148.67, 145.29, 137.45, 137.27, 133.96, 127.65, 126.35, 119.60, 75.37, 66.75. HRMS (FAB): *m*/*z* calcd for $C_{12}H_6I_2NO_3S_2$ ($M+H^+$), 529.7873; found 529.7881.

Synthesis of 2'. To a mixture of thieno[3,4-*b*]thiophene-2-carboxylic acid (100 mg, 0.54 mmol), 3-hydroxypyridine *N*-oxide (60 mg, 0.47 mmol) and DMAP (80 mg, 0.65 mmol) in anhydrous DMF (2.5 mL) was added EDC-HCl (125 mg, 0.65 mmol). The mixture was stirred at room temperature for 12 h and diluted with ethyl acetate. The solution was washed with 1 N HCl aqueous solution,

saturated $NaHCO_3$ aqueous solution, and water, and then dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography using chloroform–methanol (20:1, v/v) as the eluent to give the desired product as a yellow solid (31 mg, 36% yield). Mp: decomposed at >190 °C. IR (KBr, cm^{-1}): 1726 (C=O). ^1H NMR (500 MHz, $CDCl_3$, rt): δ 8.28 (t, J = 1.7 Hz, 1H), 8.15 (dt, J = 6.3, 1.4 Hz, 1H), 7.94 (s, 1H), 7.75 (d, J = 2.9 Hz, 1H), 7.37-7.38 (m, 1H), 7.33 (dd, J = 8.0, 6.3 Hz, 1H), 7.27-7.29 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$, rt): δ 160.08, 149.08, 145.45, 139.80, 137.10, 136.47, 134.21, 126.38, 125.46, 119.78, 118.35, 111.96. HRMS (FAB): m/z calcd for $C_{12}H_8NO_3S_2$ ($M+H^+$), 277.9940; found 277.9949.

Polymerization.

Ternary copolymerizations of GLB-**1**, **2** and **3** were carried out according to Scheme 1 in a dry Schlenk flask under a dry nitrogen atmosphere using $Pd(PPh_3)_4$ and CuI as a catalyst in a similar way as reported previously.[S2]

A typical procedure for the ternary copolymerization is described below. GLB-**1** (500 mg, 0.650 mmol), **2** (35 mg, 0.065 mmol), **3** (272 mg, 0.585 mmol), CuI (37 mg, 0.20 mmol) and $Pd(PPh_3)_4$ (45 mg, 0.039 mmol) were placed in a Schlenk flask, which was then evacuated on a vacuum line and flushed with dry nitrogen. After this evacuation-flush procedure was repeated for three times, degassed THF/DIPA (5:1, v/v) (20 mL) was added with a syringe, and the mixture was stirred at 60 °C for 12 h. After cooling to room temperature, the reaction mixture was poured into a large amount of hexane, and the resulting polymer was collected by centrifugation, washed with ethanol and dried in vacuo to yield poly-**1**$(NO)_{0.10}$ as a yellow solid (630 mg, 98%). In the same way, poly-**1**$(NO)_{0.50}$ was prepared. The M_n and M_w/M_n of the polymers were determined by size exclusion chromatography (SEC) using polystyrene standards in chloroform. The polymerization results are summarized in Table S1.

Spectroscopic data of poly-**1**$(NO)_{0.10}$: IR (KBr, cm^{-1}): 2190 (C≡C), 1757 (C=O), 1711 (C=O). ^1H NMR (500 MHz, $CDCl_3$, 55 °C): δ 7.36-7.79 (m, 7H), 5.64 (t, J = 9.5 Hz, 1H), 5.31-5.38 (m, 2H), 5.00 (s, 1H), 4.18-4.38 (m, 8H), 4.09 (d, J = 8.6 Hz, 1H), 3.51-3.74 (m, 19H), 3.36 (s, 3H), 3.35 (s, 3H), 1.37 (t, J = 6.6 Hz, 3H). Calcd for $C_{48.3}H_{47.9}N_{0.1}O_{18.1}S_2 \cdot 1.4H_2O$: C, 57.51; H, 5.07. Found: C, 57.31; H, 4.83.

4. Asymmetric Allylation of Benzaldehydes

Typical procedure for asymmetric allylation of benzaldehyde with allyltrichlorosilane. Poly-**1**$(NO)_{0.10}$ (4.6 μmol based on the pyridine *N*-oxide residue of poly-**1**$(NO)_{0.10}$), tetrabutylammonium iodide (202 mg, 0.55 mmol), $^{i}Pr_2NEt$ (390 μL, 2.3 mmol) and allyltrichlorosilane (79 μL, 0.55 mmol) were dissolved in acetonitrile (0.90 mL) under a nitrogen atmosphere. To this was added **4a** (47 μL, 0.46 mmol) at 0 °C. The mixture was stirred at 0 °C for 48 h. After the addition of saturated $NaHCO_3$ aqueous solution (0.50 mL) and methanol (0.20 mL) to quench the reaction, the mixture was poured into hexane to remove the catalyst. The supernatant was evaporated under reduced pressure and the crude product was purified by silica gel chromatography with *n*-hexane–ethyl acetate (15:1, v/v) as the eluent. The enantiomeric excess (ee) value of the isolated product **5a** (26% ee, *R*-rich) was determined by chiral HPLC analysis using a CHIRALCEL OD-H column (*n*-hexane–2-propanol (99:1, v/v); flow rate 0.8 mL min^{-1}; temperature *ca.* 20 °C: t_r = 27.5 min (for *R*-isomer), t_r = 33.0 min (for *S*-isomer).[S4] Allylation reactions of **4b** and **4c** with allyltrichlorosilane were also performed in a similar manner and the results are summarized in Table 1.

Chromatographic condition for the ee determination of **5b**: CHIRALCEL IG column (*n*-hexane–2-propanol (99:1, v/v); flow rate 0.8 mL min^{-1}; temperature *ca.* 20 °C: t_r = 100.8 min (for *R*-isomer), t_r = 111.0 min (for *S*-isomer).[S4]

Chromatographic condition for the ee determination of **5c**: CHIRALPAK OD-H column (*n*-hexane–2-propanol (99:1, v/v); flow rate 0.8 mL min^{-1}; temperature *ca.* 20 °C: t_r = 37.4 min (for *R*-isomer), t_r = 46.0 min (for *S*-isomer).[S4]

5. Supporting Data

Table S1 Polymerization result

Polymer	Yield (%)[a]	M_n (10^4)[b]	PDI[b]
poly-**1**$(NO)_{0.10}$	98	1.3	2.2

[a] Ethanol and hexane insoluble part. [b] Determined by SEC (eluent: chloroform; polystyrene standards).

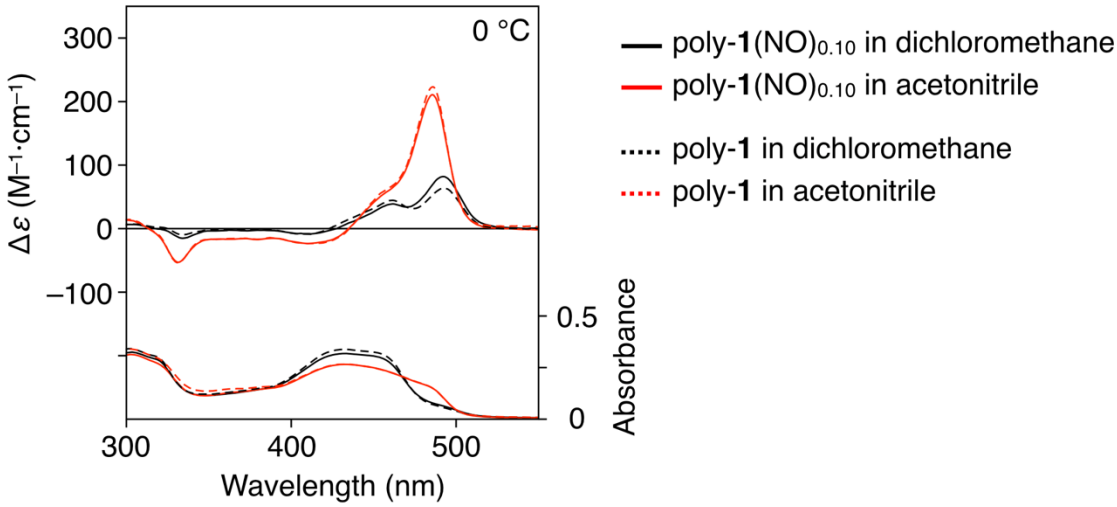


Fig. S1 CD and absorption spectra of poly-**1**$(NO)_{0.10}$ and poly-**1** in dichloromethane and acetonitrile at 0 °C. [Glucose unit] = 1.0×10^{-4} M.

6. ^{1}H and ^{13}C NMR Spectra of Monomers and Polymers

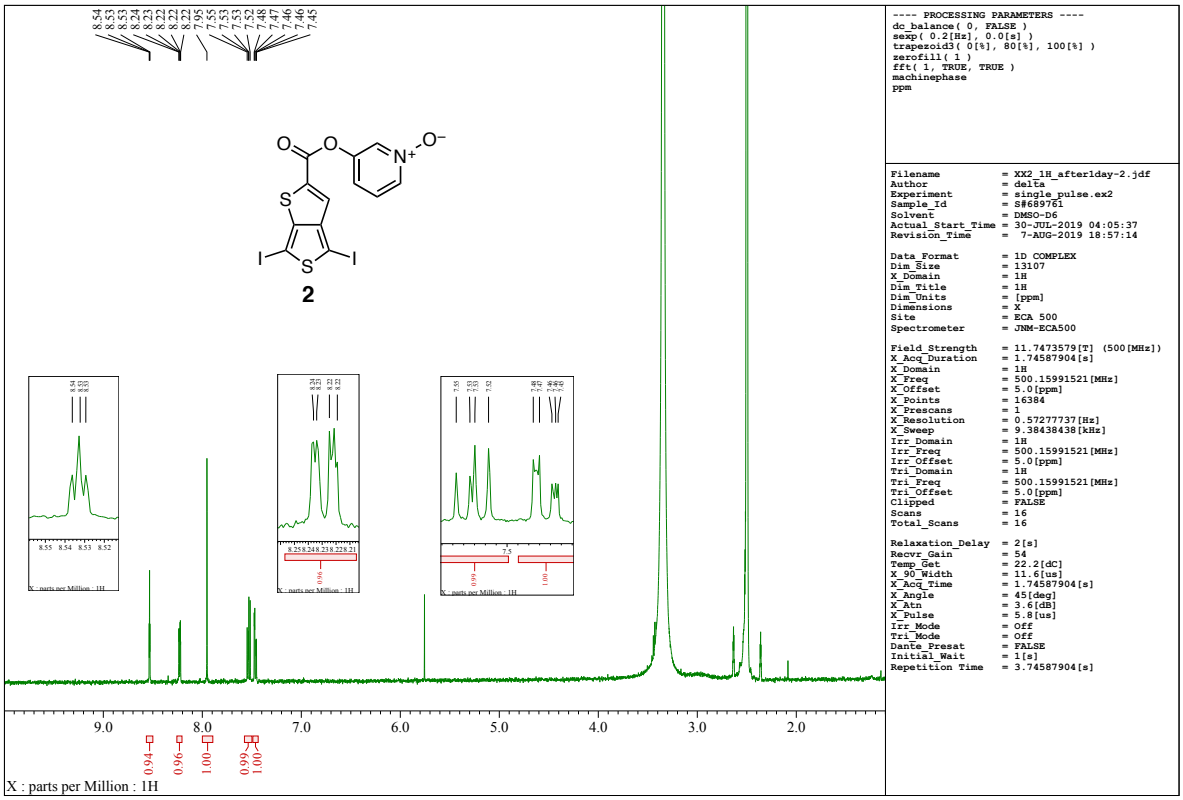


Fig. S2 ^{1}H NMR (500 MHz, DMSO-d_6, rt) spectrum of **2**.

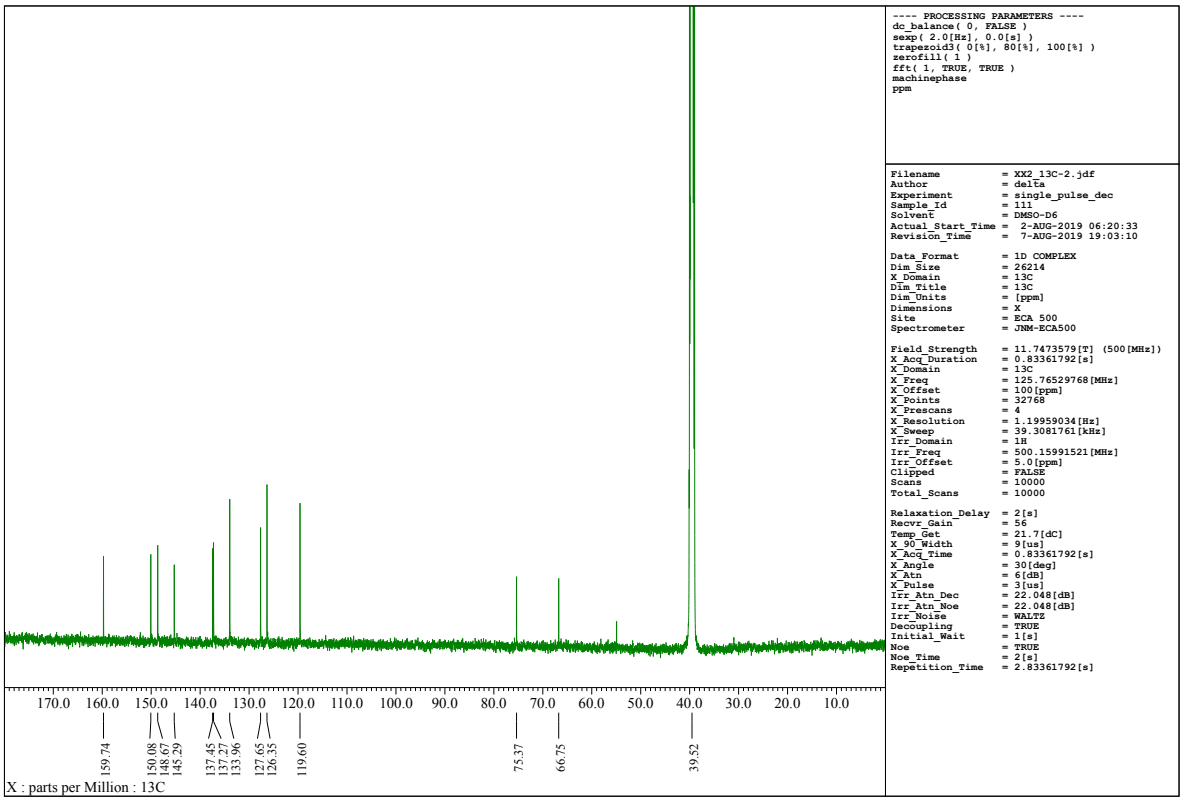


Fig. S3 ^{13}C NMR (126 MHz, DMSO-d_6, rt) spectrum of **2**.

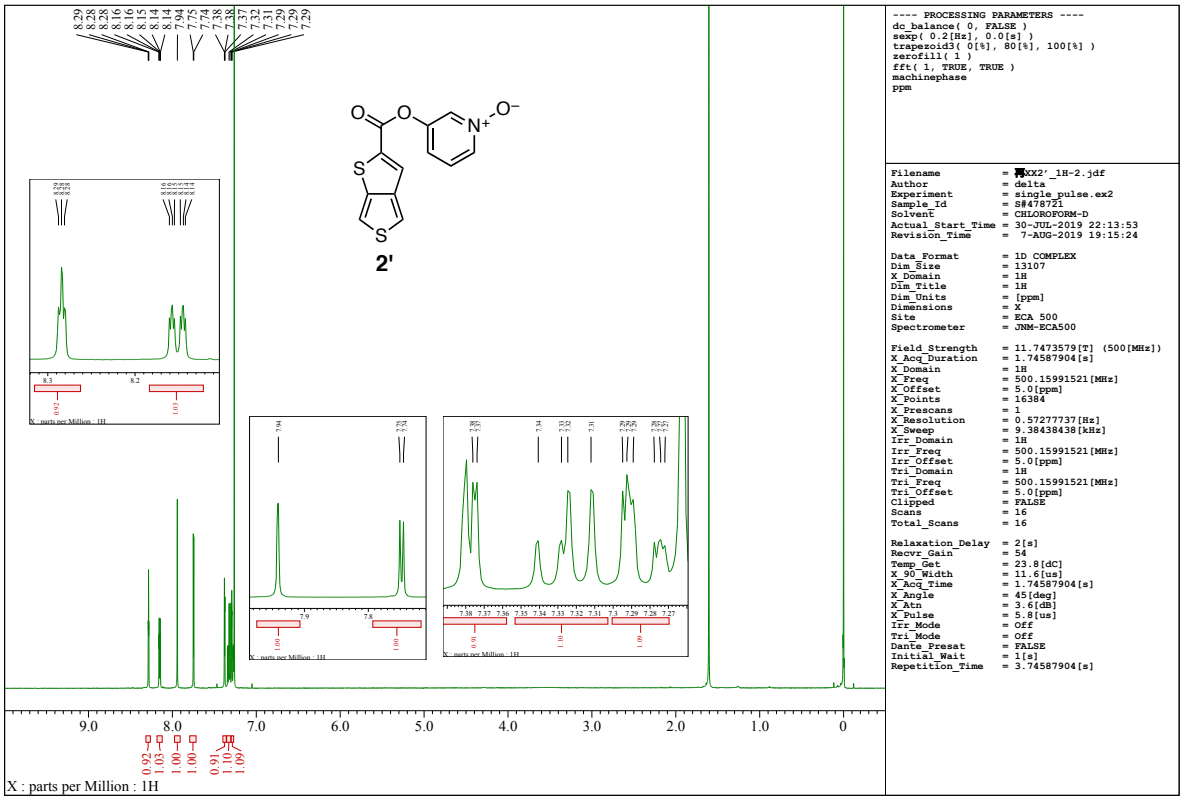


Fig. S4 ^{1}H NMR (500 MHz, $CDCl_3$, rt) spectrum of **2'**.

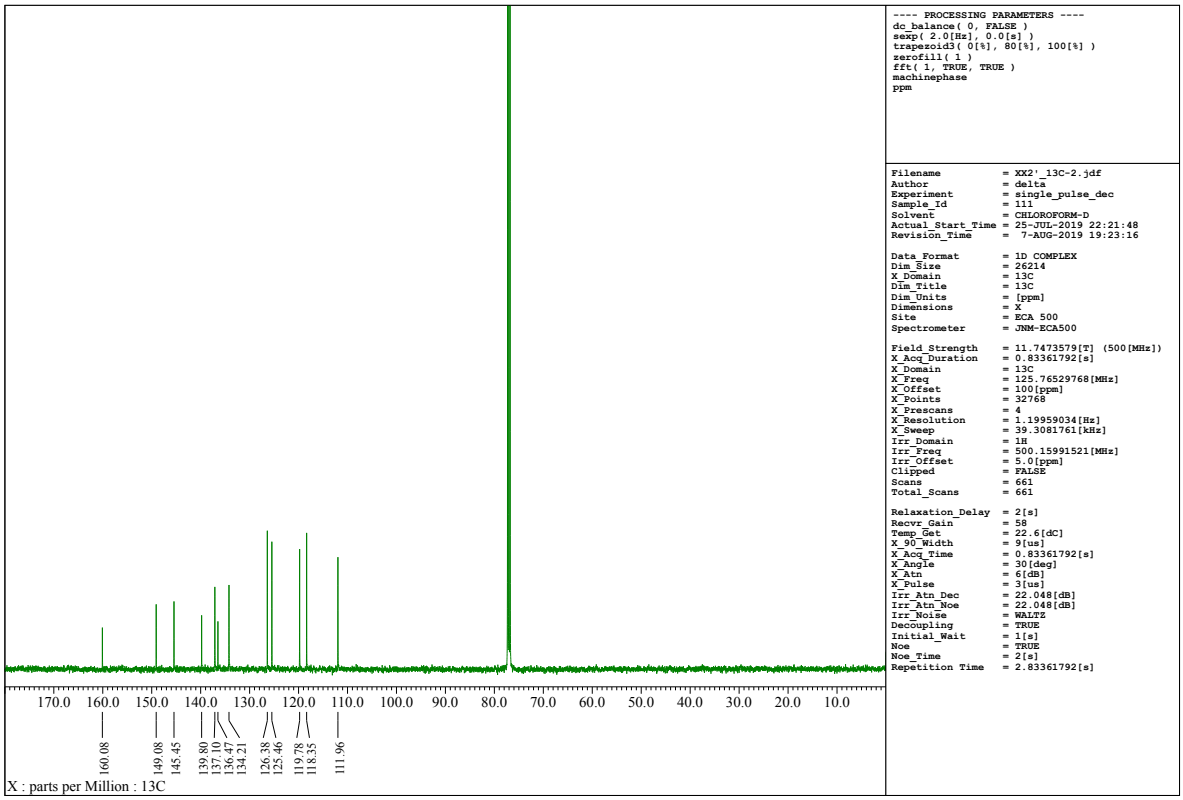


Fig. S5 ^{13}C NMR (126 MHz, $CDCl_3$, rt) spectrum of **2'**.

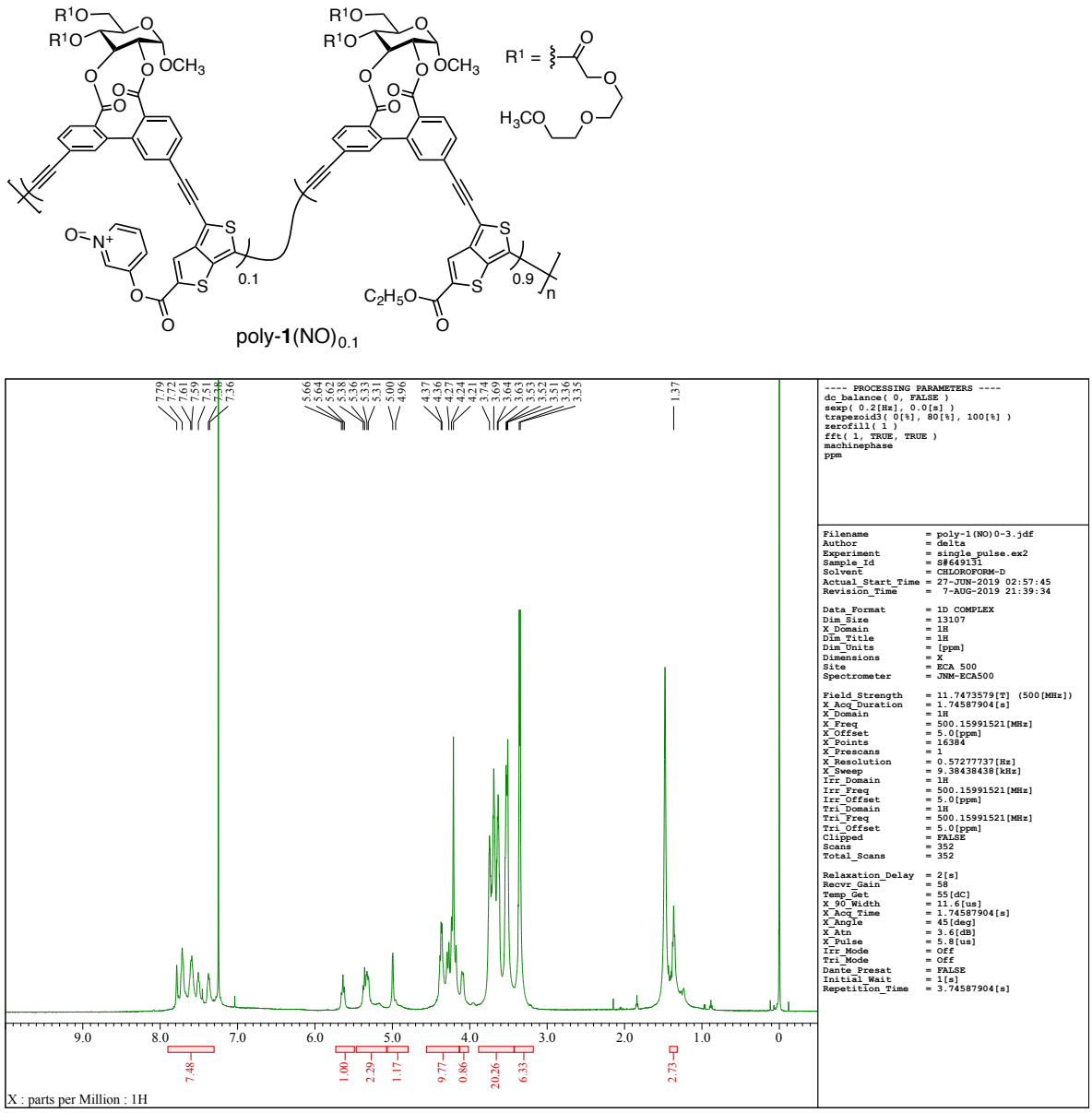


Fig. S6 ^{1}H NMR (500 MHz, $CDCl_3$, 55 °C) spectrum of poly-**1**$(NO)_{0.10}$.

Supporting References

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