SUPPORTING INFORMATION

Ni^0(cod)(dq) (COD: 1,5-cycloctadiene; DQ: duroquinone) complex as a catalyst precursor for oligothiophene and polythiophene synthesis

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Experimental Section

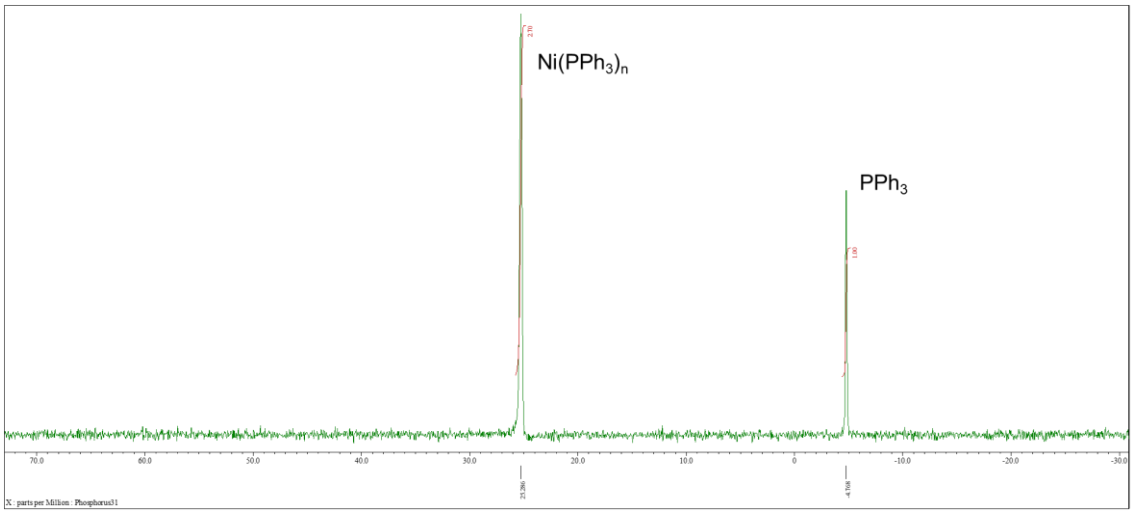
General. Unless otherwise specified, all the reactions were performed under argon or nitrogen atmosphere. The coupling reaction with Ni(cod)(dq) (**2**) was carried out without using glovebox with a standard Schlenk technique under nitrogen or argon atmosphere. ^{1}H NMR (400 MHz), ^{13}C{^{1}H} NMR (100 MHz) and ^{31}P{^{1}H} NMR (162 MHz) spectra were measured on JEOL ECZ400 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.00 ppm for ^{13}C) H_3PO_3 (0 ppm for ^{31}P) as internal standards. GCMS analysis was carried out on a Shimazu GCMS-PQ2010SE, equipped with EI-MS detector using helium as a carrier gas with Agilent DB-17 as a column with the flow rate of 1.81 mL/min, injection temp of 250 °C, and detector temp of 250 °C. For thin layer chromatography (TLC) analyses throughout the work, Fujifilm Wako precoated TLC plates (silica gel 70 F_{254}) were used. Flash column chromatography was performed on Wakogel 60N (63–212 μm , Fujifilm Wako Pure Chemical Industries, Ltd.) or high-efficiency irregular silica (25–40 μm, Santai Science Inc.) SEC (size exclusion chromatography) analyses were performed with a standard HPLC system equipped with UV detector at 40 °C using chloroform as an eluent with a Shodex GPC KH-404HQ or the related column. Molecular weights and molecular weight distributions were estimated on the basis of the calibration curve obtained by 6 standard polystyrenes (M_n = 2630-355000).

Materials. Unless otherwise specified, $Ni(cod)_2$ (**1**) was purchased from Sigma Aldrich Co. Ltd and used as received or stored in the freezer under argon atmosphere. Ni(cod)(dq) (**2**) was prepared by the procedure described in the literature[1] or purchased from TCI Co. Ltd. THF was purchased from Kanto Chemicals Co. Ltd. as an anhydrous grade and employed for the reaction after passed through alumina and copper columns (Nikko Hansen & Co. Ltd.) prior to use or alternatively employed after the distillation from sodium dispersion/benzophenone ketyl.[2] TMPMgCl·LiCl (chloromagnesium 2,2,6,6-tetrametylpiperidine-1-yl litium chloride salt) was prepared by the reaction of ^{i}PrMgCl·LiCl and 2,2,6,6-teteramethylpiperidine (TMPH) in THF and stored in a glove box as a ca. 1 M solution at room temperature.[3] The concentration of the TMPMgCl·LiCl solution was determined by the titration of 1-adamantane carboxylic acid with 4-phenylazodiphenyl amine as an indicator.[4] Other chemicals were purchased and used as received.

Ligand exchange experiments with PPh_3 procedure: A mixture of Ni(cod)(dq) (**2**) (33.1 mg, 0.1 mmol) and triphenylphosphine (131.2 mg, 0.5 mmol) was dissolved in 2

mL of toluene (anhydrous grade) at room temperature under argon atmosphere. An aliquot of the reaction mixture was taken and subjected to the measurement of $^{31}P\{^{1}H\}$ NMR in $CDCl_3$. For GC-MS analysis, the aliquot solution was poured into hexanes to form a precipitate. The supernatant was diluted with chloroform and the measurement of the resulting solution was performed to detect the liberated COD and DQ with 1,3,5-trimethoxybenzene as an internal standard. $^{31}P\{^{1}H\}$ NMR (80 °C, 2 h) δ 25.3 (lit.[5] 24.8 for $Ni(PPh_3)_4$), –4.8 (lit.[6] –4 for PPh_3); GC-MS (80 °C, 4 h) 4.14 min (COD), 8.21 min (DQ), 9.06 min (internal standard) (Figure S1).

(a)



(b)

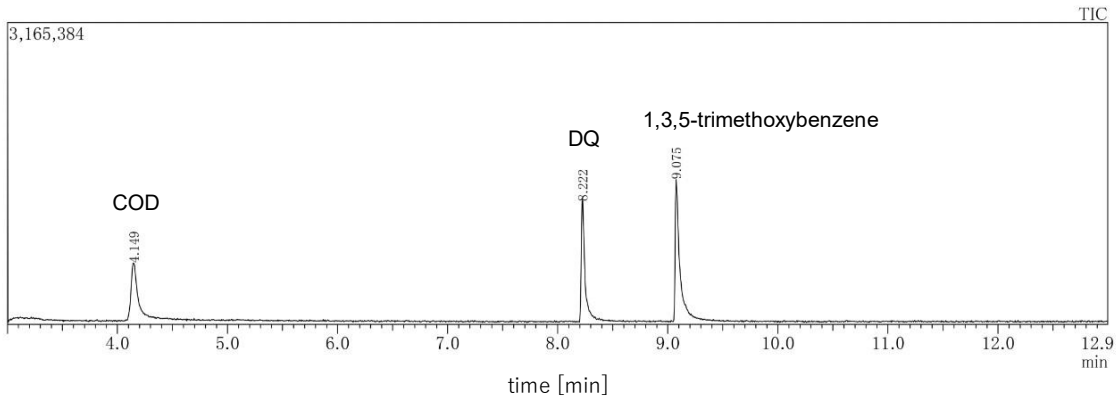


Figure S1. Ligand exchange of **2** with PPh_3 (a) $^{31}P\{^{1}H\}$ NMR spectrum after the reaction period of 2 h at 80 °C (b) GC-MS profile at 80 °C for 4 h (column temperature: 35 °C, 3 min; 35–200 °C at the rate of 20 °C/min; 200–250 °C at the rate of 10 °C/min 200; 250 °C, 10 min).

Ligand exchange experiments with IPr procedure: The measurement was carried out in a manner shown above in THF. GC-MS (60 °C, 4 h) 4.14 min (COD, 81%), 8.21 min (DQ, 49%), 9.06 min (internal standard).

In-situ generation of a THF solution of nickel catalyst: NaO^{t}Bu (5.4 mg, 0.055 mmol) and 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride (17.3 mg, 0.05 mmol) were dissolved in 0.5 mL of THF at room temperature. After stirring at room temperature for 30 min, Ni(cod)(dq) (**2**) (8.6 mg, 0.025 mmol) was added to the resulting suspension and stirring was continued at 60 °C for 4 h to form the nickel complex. The solution of the obtained nickel complex was directly employed for the catalytic reactions shown below.

5-(3-Hexylthiophen-2-yl)-3-hexylthiophene (5): To a solution of TMPMgCl·LiCl (0.78 mmol) in 0.65 mL of anhydrous THF was added 3-hexylthiophene (**3**) (0.11 mL, 0.6 mmol) at room temperature. The solution was stirred at room temperature for 6 h. To the resulting solution were added 2-choloro-3-hexylthiophene (0.10 mL, 0.5 mmol) (**4a**) and 0.5 mL of anhydrous THF. The catalyst solution prepared above was transferred via cannula into the mixture of the in-situ formed metalated thiophene **3'** and **4a**. The resulting solution was stirred at room temperature for 24 h. The reaction was terminated by the addition of saturated aqueous solution of ammonium chloride (1.0 mL). The solution was poured into the mixture of diethyl ether/water and two phases were separated. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude mixture of **5** and the corresponding homocoupling byproduct **6**, which was subjected to ^{1}H NMR analysis after the addition of 1,1,2,2-tetrachloroethane (32.6 mg, 0.19 mmol) as an internal standard. (Figure S2). ^{1}H NMR δ 7.14 (d, J = 5.0 Hz, 1H), 6.93 (d, J = 1.4 Hz, 1H), 6.92 (d, J = 5.0 Hz, 1H), 6.89 (s, 1H), 2.74 (t, J = 8.0 Hz, 2H), 2.60 (t, J = 7.8 Hz, 2H), 1.70-1.57 (m, 4H), 1.40-1.25 (m, 12H), 0.96-0.82 (m, 6H) The spectroscopic properties were identical with the authentic sample.[7] (Figure S2)

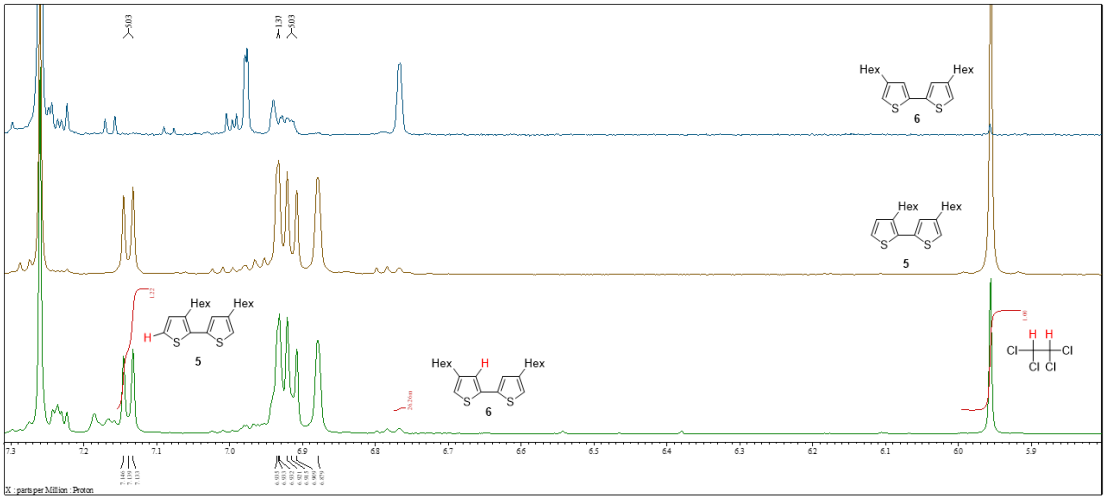


Figure S2. ^{1}H NMR spectrum for the determination of the ratio of **5** and **6** for Table 1, entry 4 (5.8–7.3 ppm expanded). Bottom: the reaction mixture (green); middle: authentic **5** (brown); top: authentic **6** (blue)

Synthesis of 3T$^{\prime}$: To a mixture of EtMgCl (1.5 M THF solution, 0.50 mL, 0.75 mmol) and TMPH (2,2,6,6-tetramethylpiperidine) (0.09 mL, 0.05 mmol) in 0.38 mL of THF was added thiophene dimer **5** (179.1 mg, 0.5 mmol) at room temperature. The mixture was heated at 60 °C and stirring was continued for 24 h. The resulting solution was cooled to room temperature and addition of 2-chloro-3-hexylthiophene (0.15 mL, 0.75 mmol) and 0.5 mL of THF followed. To the solution was transferred the in-situ formed catalyst solution via cannula and stirring was continued at room temperature for 24 h. The termination of the reaction was carried out in a similar manner to the preparation of thiophene dimer **5**. Yield of **3T$^{\prime}$** (90%) accompanied by homocoupling byproduct **7** (trace). (Figure S3) ^{1}H NMR δ 7.15 (d, J = 5.0 Hz, 1H), 6.96 (d, J = 0.9 Hz, 1H), 6.922 (s, 1H), 6.921 (d, J = 5.0 Hz, 1H), 6.89 (d, J = 0.9 Hz, 1H), 2.80-2.71(m, 4H), 2.61 (t, J = 7.8 Hz, 2H), 1.73-1.60 (m, 6H), 1.46-1.19 (m, 18H), 0.95-0.82 (m, 9H) The spectroscopic properties were identical with the authentic sample.[7] (Figure S3)

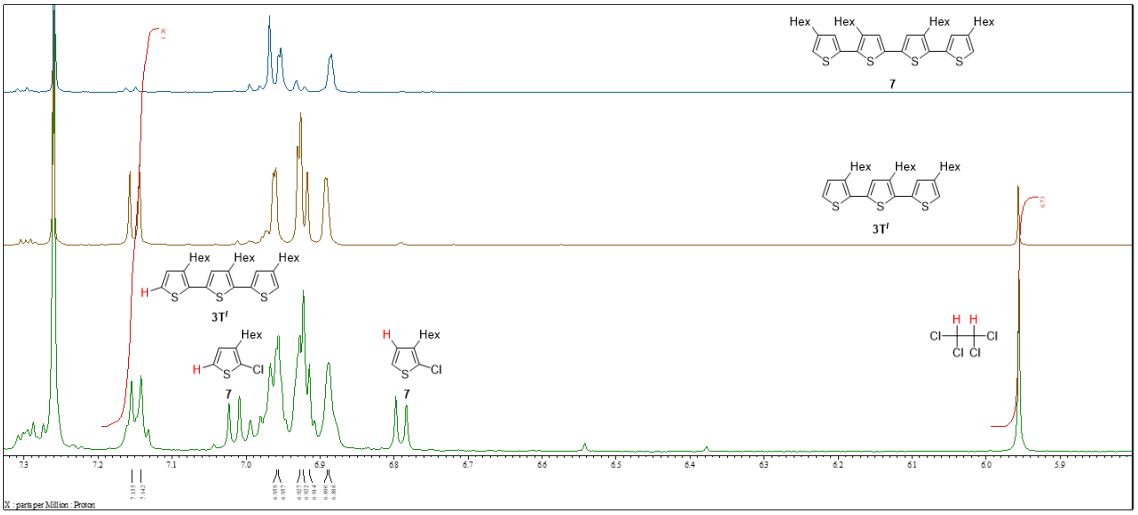


Figure S3. ^{1}H NMR spectrum for the determination of the ratio of **3T*'*** and **7** (5.8–7.3 ppm expanded). Bottom: the reaction mixture (green); middle: authentic **3T*'*** (brown); top: authentic **7** (blue)

Synthesis of 3T*b*: Preparation of **3T*b*** was carried out in a similar manner to that of **3T*'*** with 2,3-dibromothiophene (**7**, 0.06 mL, 0.5 mmol) and 3-hexylthiophene (**3**, 0.18 mL, 1.0 mmol) to yield **3T*b*** (92%). ^{1}H NMR δ 7.23 (d, J = 5.5 Hz, 1H), 7.14 (d, J = 5.5 Hz, 1H), 6.96 (d, J = 1.4 Hz, 1H), 6.90-6.87 (m, 2H), 6.83 (d, J = 1.4 Hz, 1H), 2.59-2.51 (m, 4H), 1.66-1.51 (m, 4H), 1.39-1.24 (m, 12H), 0.92-0.85 (m, 6H) The spectroscopic properties were identical with the authentic sample.[8] (Figure S4)

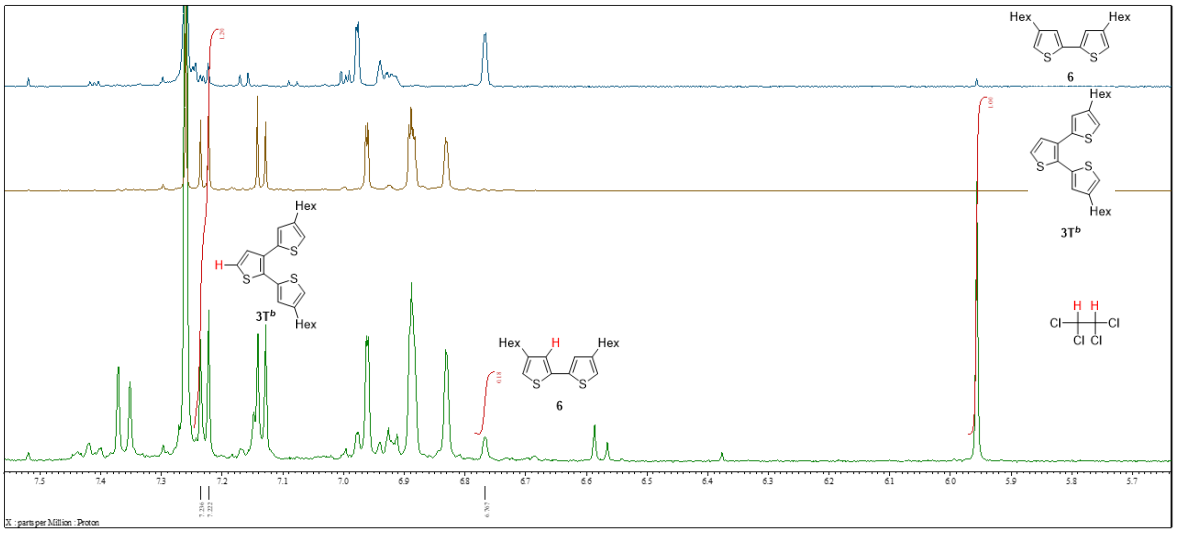


Figure S4. ^{1}H NMR spectrum for the determination of the ratio of **3T*b*** and **6** (5.8–7.3 ppm expanded). Bottom: the reaction mixture (green); middle: authentic **3T*b*** (brown); top: authentic **6** (blue).

Synthesis of 7T*b*: Preparation of **7T*b*** was carried out in a similar manner to that of **3T*b*** with 2,3-dibromothiophene (0.06 mL, 0.5 mmol) and **3T*b*** (521.1 mg, 1.25 mmol) to yield **7T*b*** (93% yield). NMR δ 7.30 (d, J = 5.5 Hz, 1H), 7.24 (s, 1H), 7.19 (d, J = 5.5 Hz, 1H), 6.98 (d, J = 1.8 Hz, 1H), 6.97 (s, 1H), 6.91 (s, 1H), 6.89 (s, 2H), 6.87(s, 1H), 6.84 (s, 1H), 2.59-2.49 (m, 8H), 1.66-1.49 (m, 8H), 1.40-1.21 (m, 24H), 0.95-0.77 (m, 12H). The spectroscopic properties were identical with the authentic sample.[8] (Figure S5)

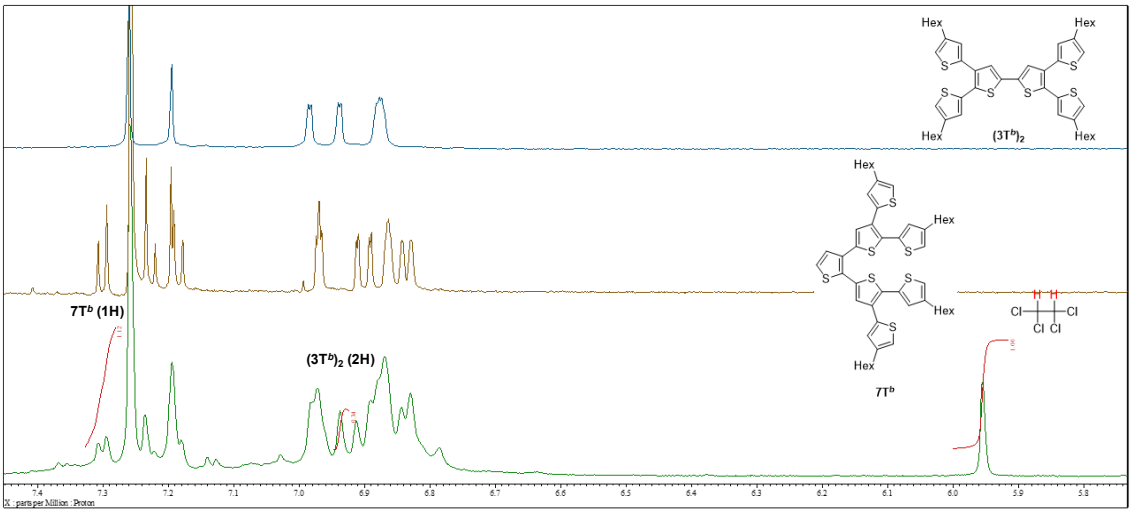


Figure S5. ^{1}H NMR spectrum for the determination of the ratio of **7T^b** and **(3T^b)$_2$** (5.8–7.4 ppm expanded). Bottom: the reaction mixture (green); middle: authentic **7T^b** (brown); top: authentic **(3T^b)$_2$** (blue)

Bis-triphenylphosphine(3-methylthiophen-2-yl)nickel(II) chloride (10): To a solution of Ni(cod)(dq) (**2**) (33.0 mg, 0.1 mmol) in 0.8 mL of anhydrous toluene was added PPh_3 (12.5 mg, 0.5 mmol) and stirring of the mixture was continued at 80 °C for 2 h. After cooling the resulting mixture to room temperature, 2-chloro-3-methylthiophene (0.055 mL, 0.5 mg) was added. Further stirring was continued for 2 h. The reaction mixture was diluted by hexane to form a precipitate, which was filtered off. The residue was washed with hexane to afford nickel complex **10** (0.51 g, 71%). The spectroscopic properties were identical with the authentic sample. $^{31}P\{^1H\}$ NMR (162 MHz, Benzene-d6) δ 20.3 ppm (lit.[9] 19.7 ppm).

One-pot polymerization of 2-bromo-3-hexylthiophene (11): A mixture of 2-bromo-3-hexylthiophene (**4b**, 0.057 mL, 0.3 mmol), Ni(cod)(dq) (**2**, 2.5 mg, 0.006 mmol) and PPh_3 (9.3 mg, 0.03 mmol) in 3 mL of THF was heated at 80 °C for 2 h. Addition of DPPP (2.5 mg, 0.006 mmol) followed and stirring was continued at 80 °C for 2 h. After cooling to room temperature, TMPMgCl·LiCl (1.0 M THF solution, 0.3 mL, 0.3 mmol) was added to the reaction mixture. Further stirring was continued at room temperature for 24 h. The mixture was poured into a mixture of 1 M hydrochloric acid (1.0 mL) and methanol (1.0 mL) to form a precipitate, which was filtered off to leave a crude solid. The residue was washed with methanol and hexanes repeatedly and dried under reduced pressure to afford 32.4 mg of **11** (65%). M_n = 16000, M_w/M_n = 2.0 (SEC). ^{1}H NMR δ 6.98 (s, 1H), 2.80 (t,

J = 7.6 Hz, 2H), 1.78-1.60 (m, 2H), 1.50-1.25 (m, 6H), 0.91 (t, J = 6.6 Hz, 3H). The spectroscopic properties were identical with the authentic sample.[10]

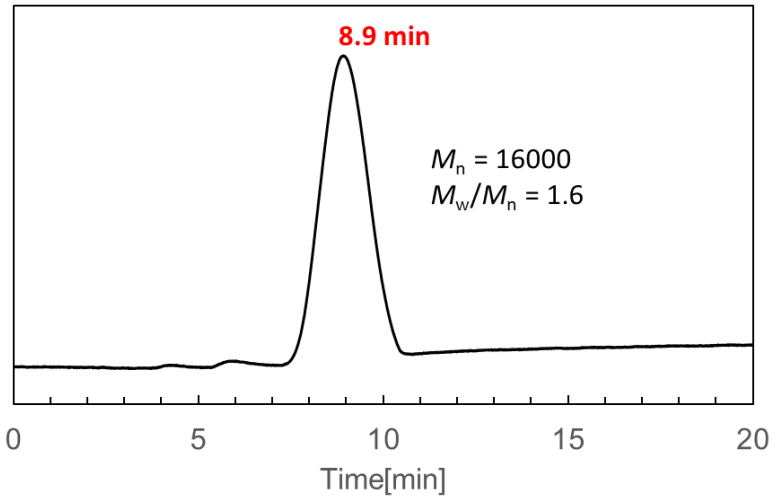
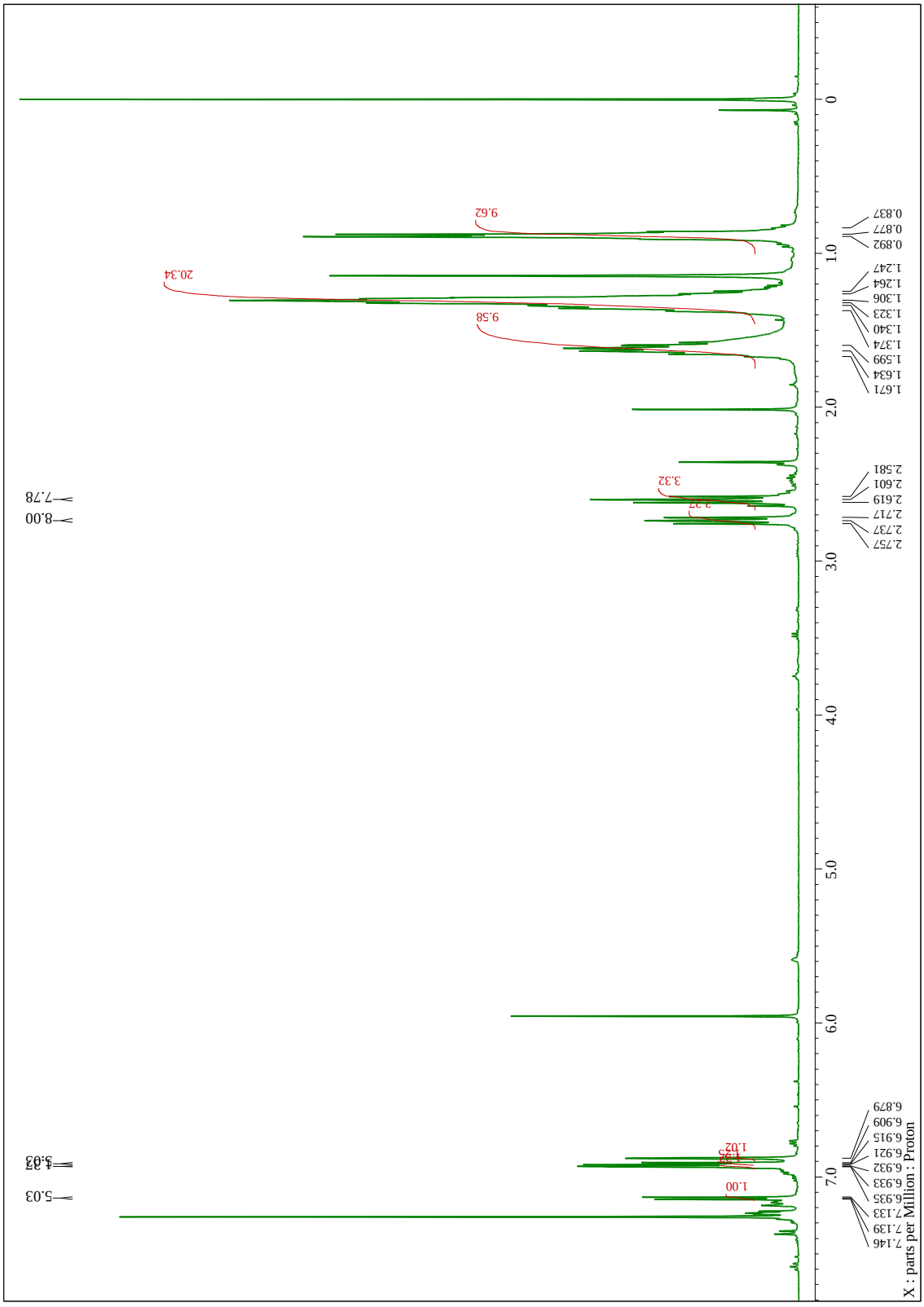
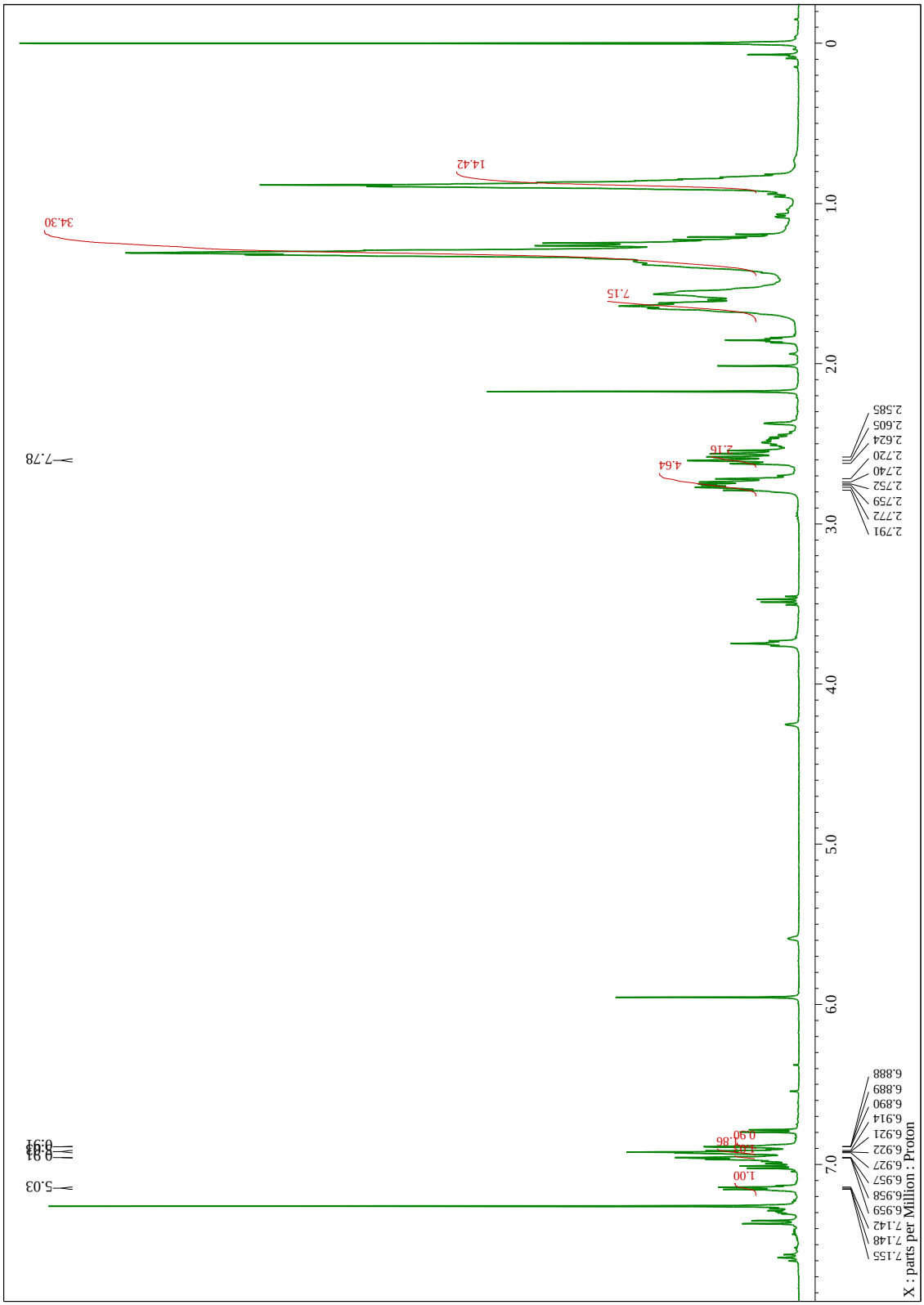


Figure S6. SEC profile of polythiophene **11**

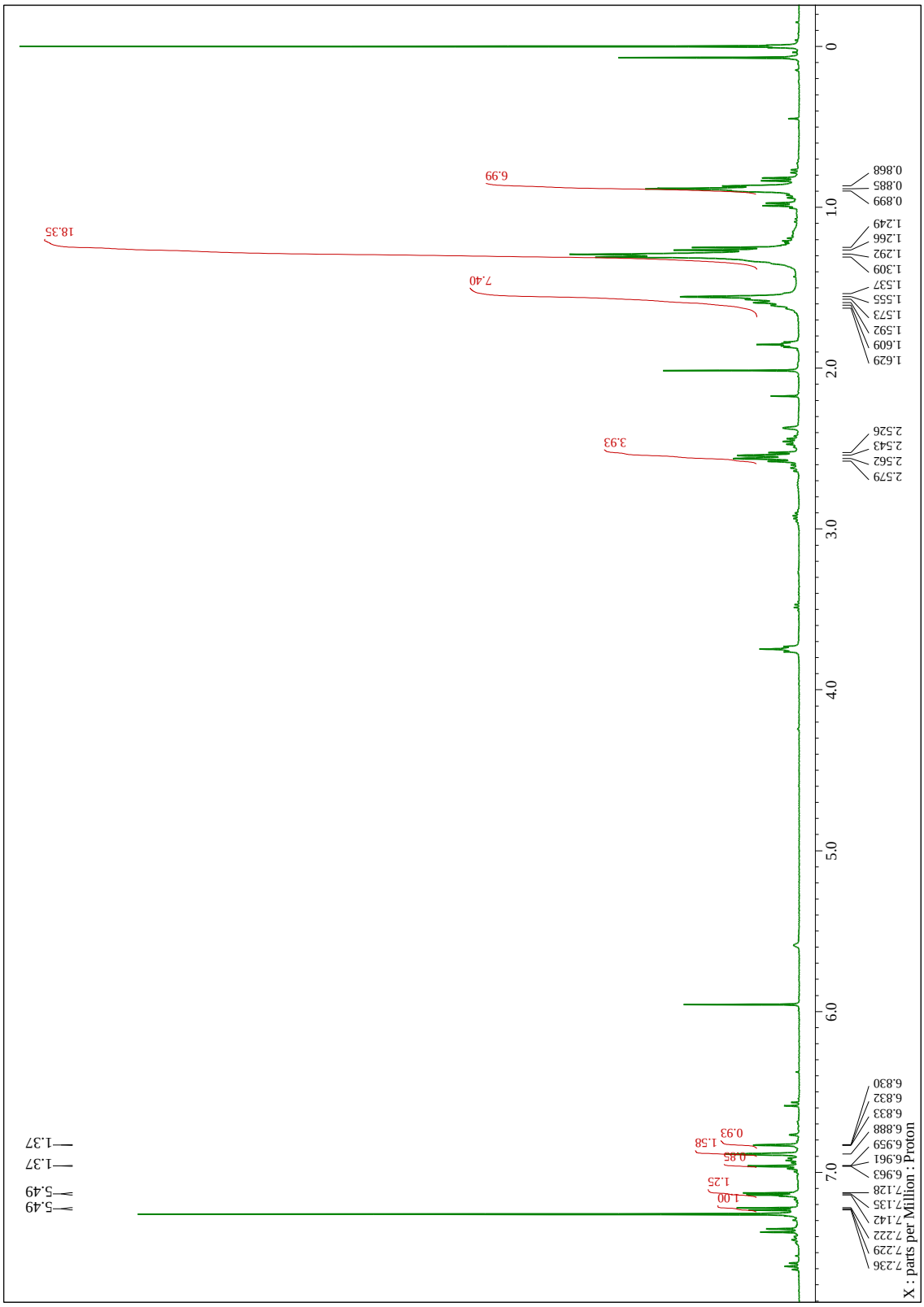
Copies of NMR spectra



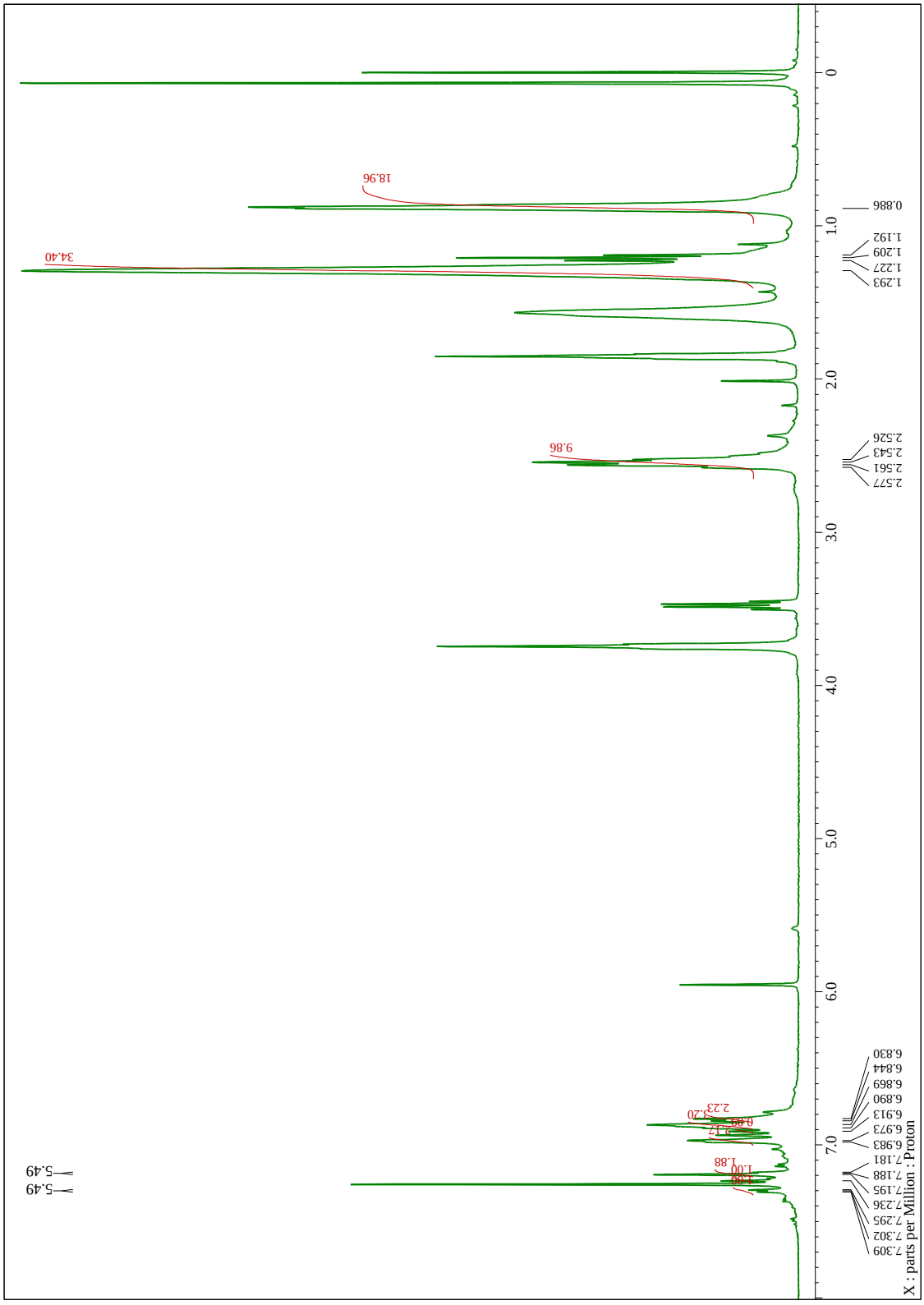
^{1}H NMR spectrum of **5**



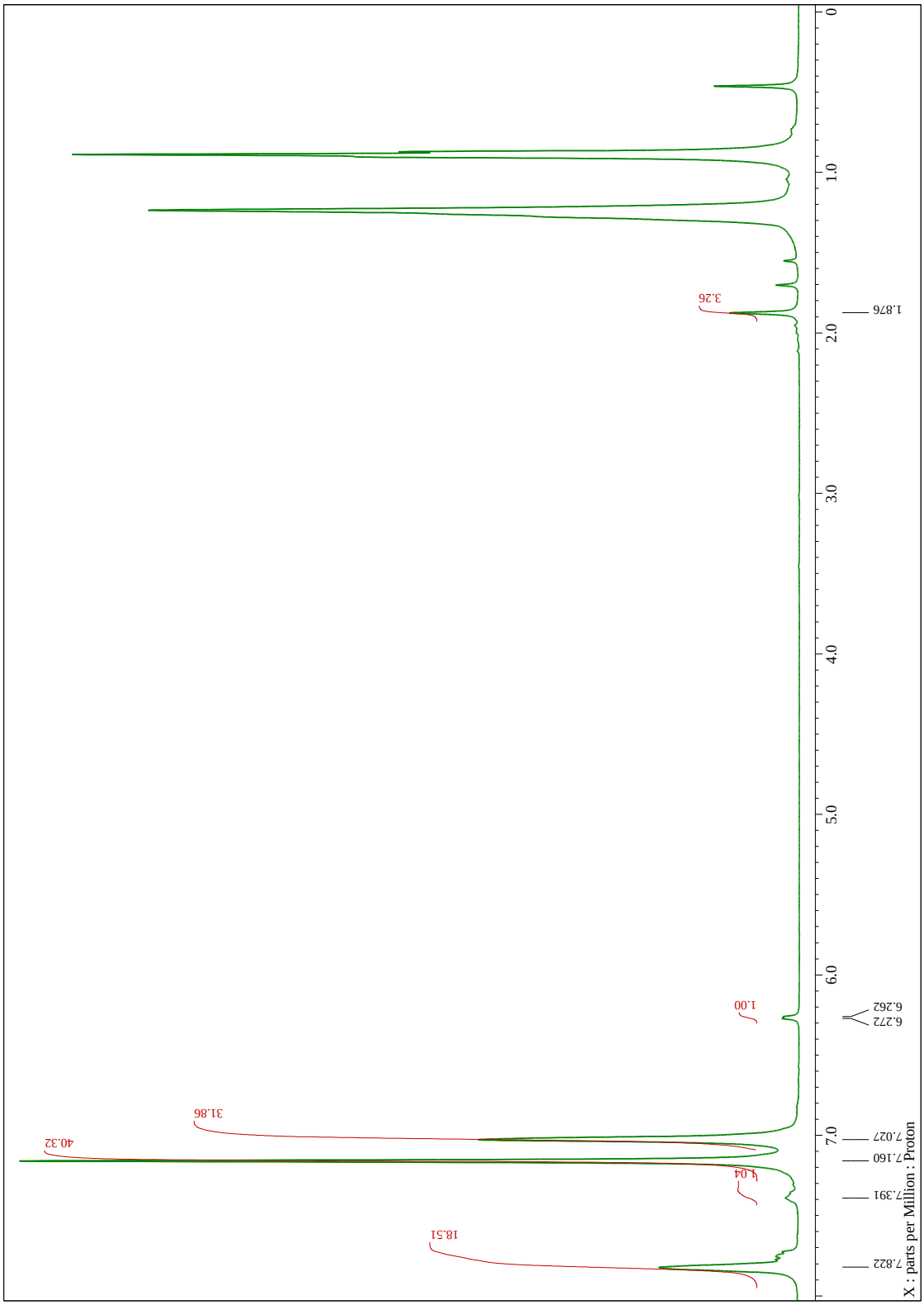
^{1}H NMR spectrum of **3T^{I}**



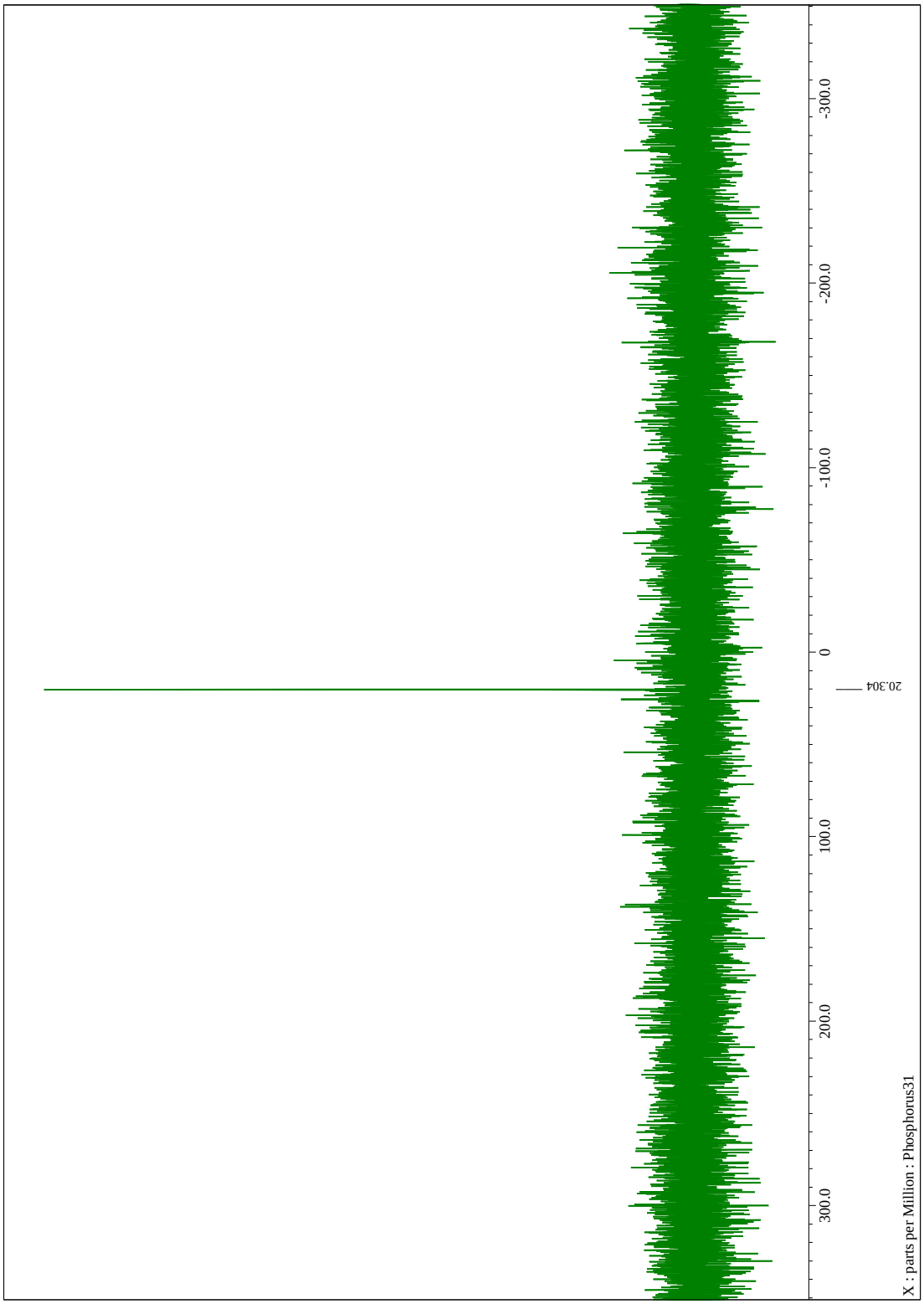
^{1}H NMR spectrum of **3T**^{b}



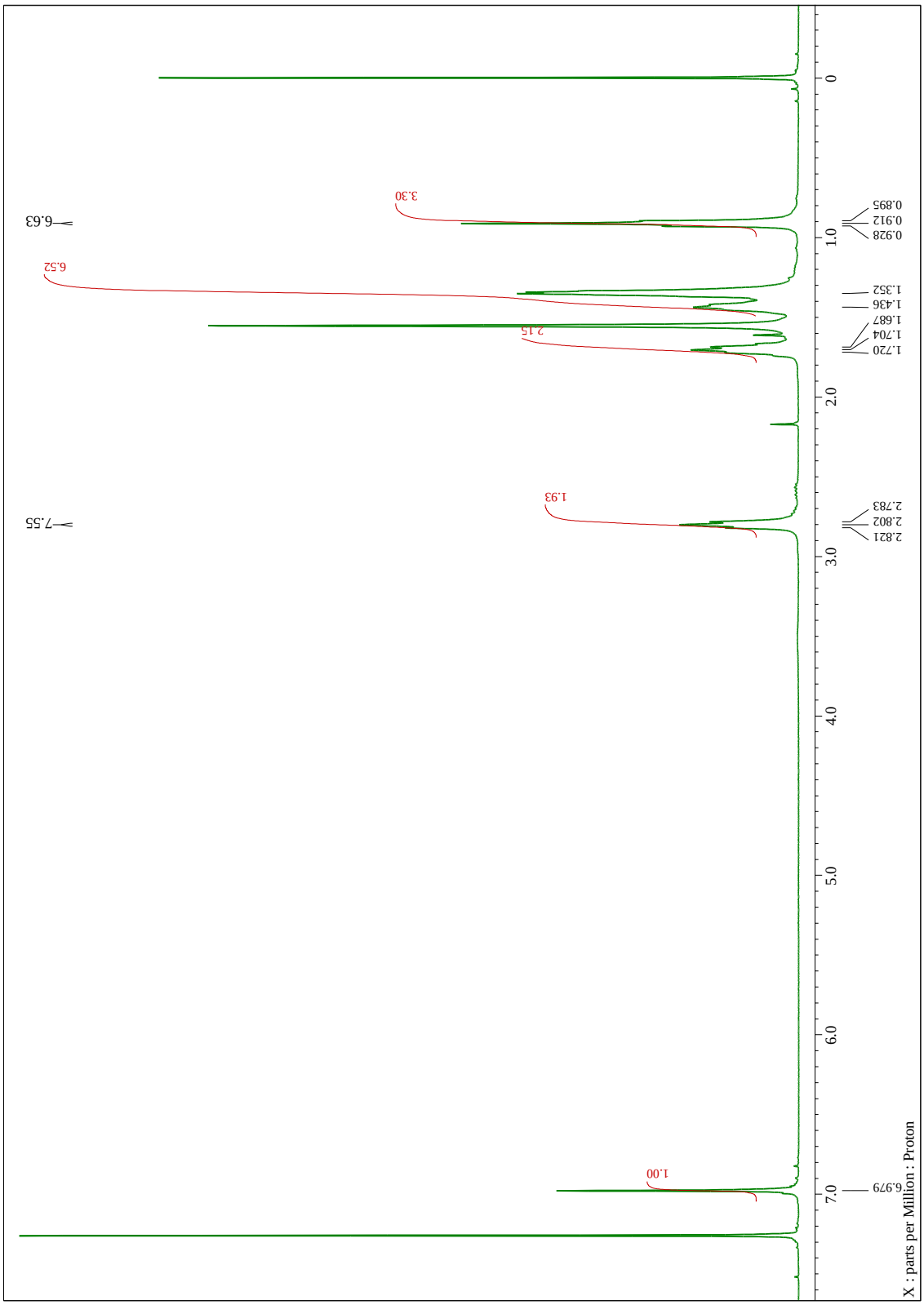
^{1}H NMR spectrum of **7T*b***



^{1}H NMR spectrum of the nickel complex (3-methylthiophen-2-yl)NiCl(PPh_3)$_2$ (**10**)



$^{31}P\{^{1}H\}$ NMR spectrum of the nickel complex (3-methylthiophen-2-yl)NiCl(PPh_3)$_2$ (**10**)



^{1}H NMR spectrum of poly(3-hexylthiophen-2,5-diyl) (**11**)

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