

Thiophene based hyperbranched polymers with tunable branching using direct arylation methods

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1. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of DB= 10% poly(3-hexylthiophene) in CDCl_3

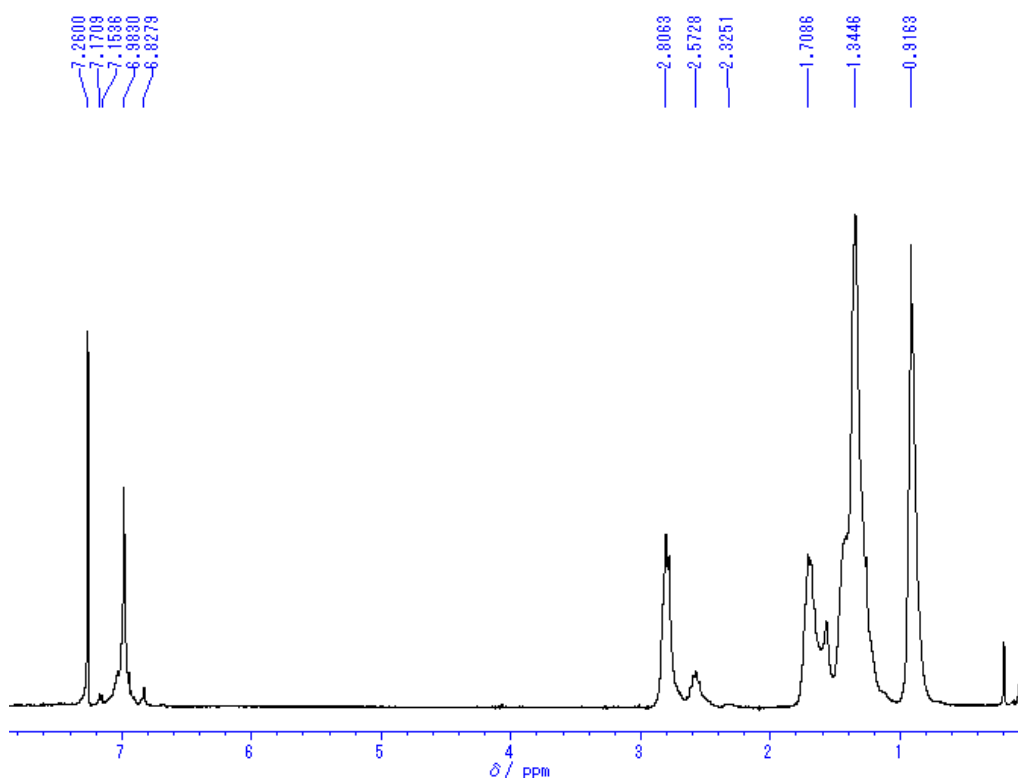


Fig. S1. ^1H NMR spectrum of DB = 10% poly(3-hexylthiophene) in CDCl_3 .

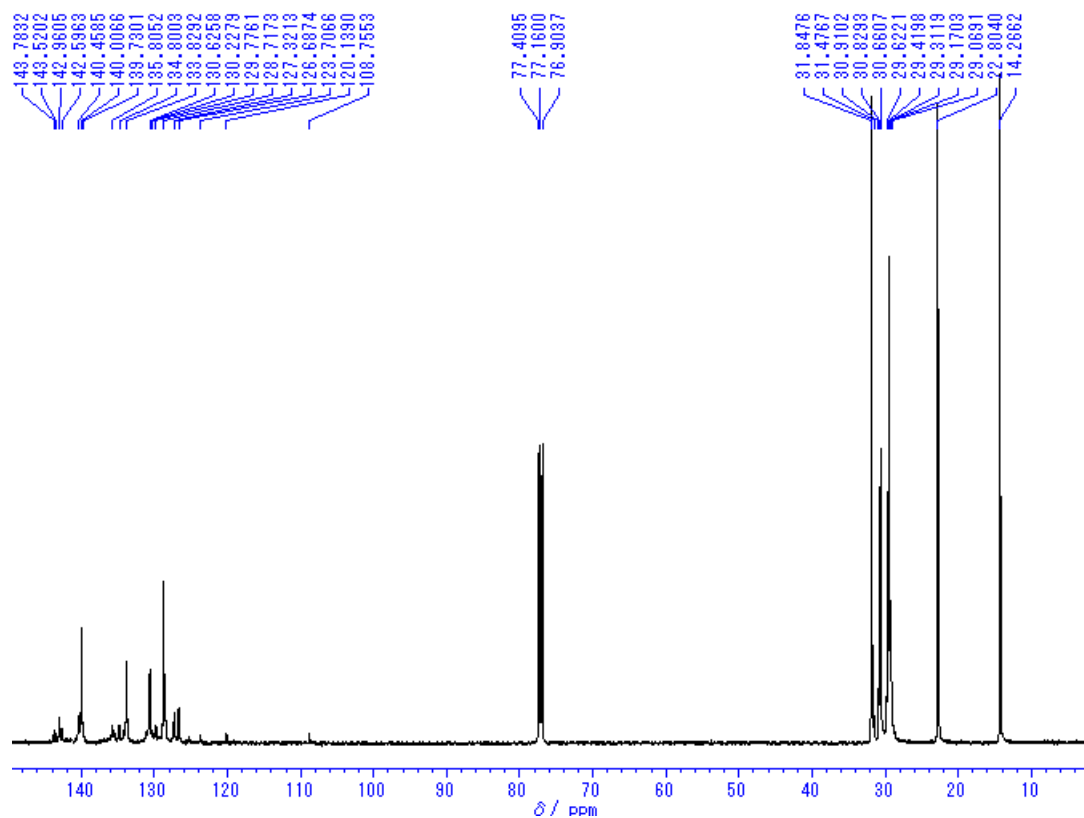


Fig. S2. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of DB = 10% poly(3-hexylthiophene) in CDCl_3 .

2. ^1H spectrum of DB= 40% poly(3-hexylthiophene) in CDCl_3

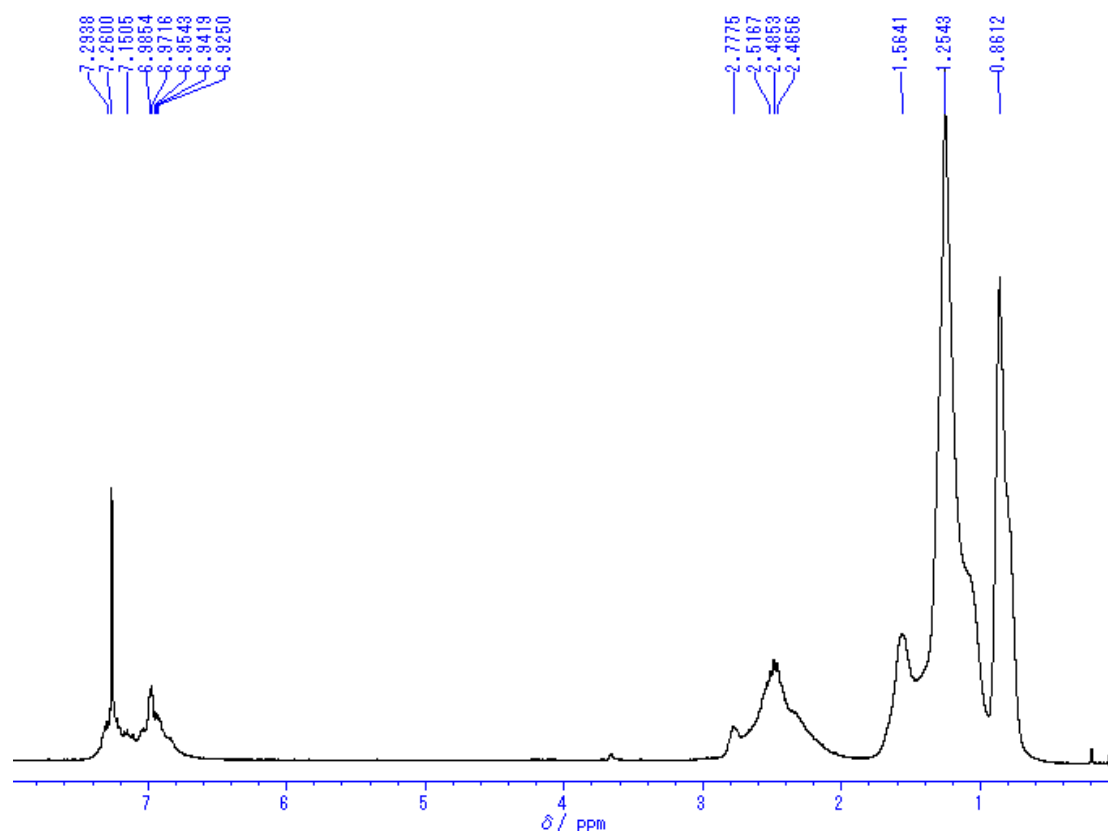
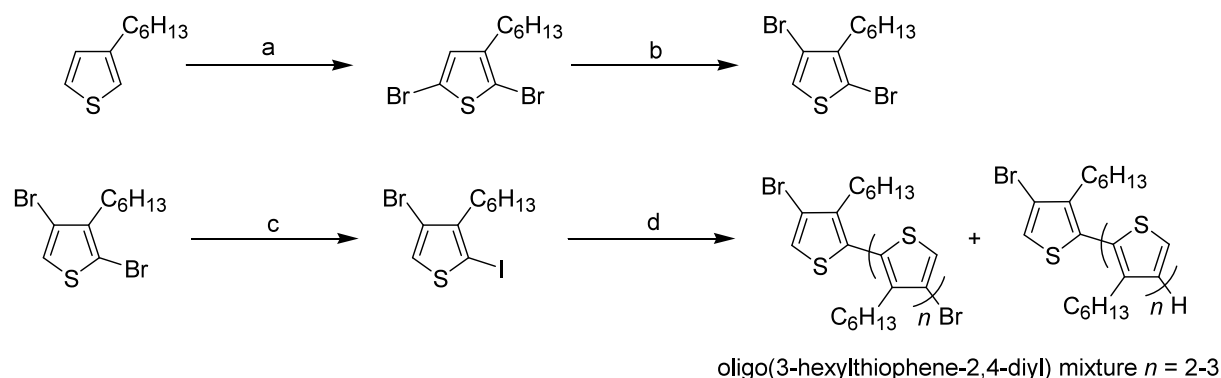


Fig. S3. ^1H NMR spectrum of DB = 40% poly(3-hexylthiophene) in CDCl_3 .

3. Synthetic procedures of oligo(3-hexylthiophene-2,4-diyl)s and branched 3-methylthiophene **2** (2,3-bis(3-methylthiophene-2-yl)-4-methylthiophene), branched monomer **3** (2,3-bis(2-bromo-4-methylthiophene-5-yl)-5-bromo-4-methylthiophene), model dendritic polymer, and regiorandom P3HT.



Scheme S1. Synthesis of oligo(3-hexylthiophene-2,4-diyl)s.

Reagent and conditions: (a) NBS, in $\text{CHCl}_3/\text{AcOH}$, reflux for 3 h, (b) 1. LDA $-78\text{ }^\circ\text{C}$ for 15 min, 2. quenched with MeOH at RT, in THF, (c) 1. $n\text{Bu}_3\text{MgLi-LiCl}$, $-15\text{ }^\circ\text{C}$, 2. I_2 , $-15\text{ }^\circ\text{C}$ in THF, (d) 1. $i\text{PrMgCl}$ at RT for 16 h, 2. Ni(dppp)Cl_2 , RT 48 h, reflux 24 h in THF

Oligo(3-hexylthiophene-2,4-diyl)s

Following Scheme S1, oligo(3-hexylthiophene-2,4-diyl)s were prepared.

2,5-dibromo-3-hexylthiophene and 2,4-dibromo-3-hexylthiophene were prepared according to reported methods.^{1,2} A modified literature procedure was used for preparation of 4-bromo-2-iodo-3-hexylthiophene.^{3,4} The Grignard reagent formed from 4-bromo-2-iodo-3-hexylthiophene (1 mmol), LiCl (2 mmol) and $i\text{PrMgCl}$ (1 mmol) in 0.75 mL THF for 16 hours was slowly added to a Ni(dppp)Cl_2 (4mol% to monomer) at room temperature and then stirred for 48 hours. The mixed solution was then refluxed for 24 hours. The reaction was quenched by 5 M HCl. The mixture was extracted with CHCl_3 (2×10 mL) and the combined organic layers were dried with anhydrous Na_2SO_4 , filtered and the solvent evaporated. The residue was run through a silica gel column using a hexane as eluent, colorless liquid was obtained (DP = <3, 98%, DP = ≥ 3 , 2%). The DP values for the separately collected fractions were estimated by MALDI-TOF-MS (e.g. Fig. S9).

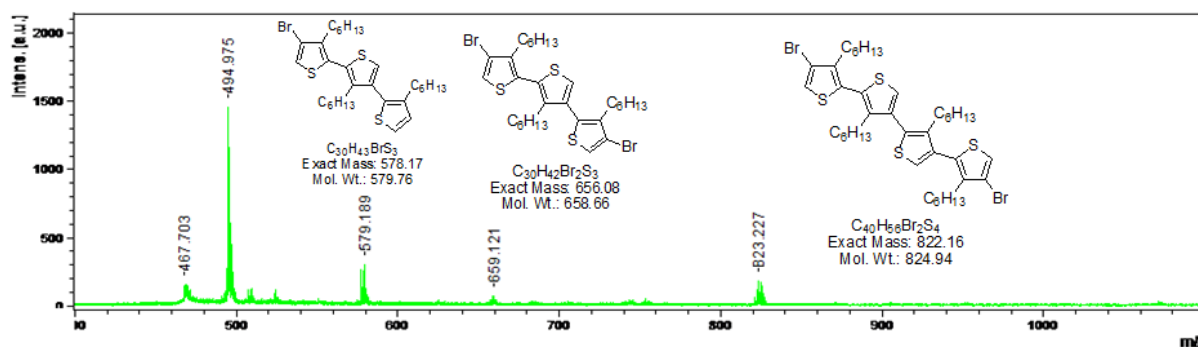


Fig. S4. MALDI-TOF-MS spectra of oligo(3-hexylthiophene-2,4-diyl)s.

2,3-bis(3-methylthiophene-2-yl)-4-methylthiophene (2).

The Grignard reagent formed from 2-bromo-3-methylthiophene (24 mmol) and magnesium (24 mmol) was slowly added to a mixture of 2,3-dibromo-4-methylthiophene (4 mmol), Ni(dppp)Cl₂ (5mol% to 2,3-dibromo-4-methylthiophene) and 10 mL ether at 0 °C to room temperature for 48 hours. The reaction was quenched by dil. HCl. The mixture was extracted with ether (3 × 15 mL) and the combined organic layers were dried with anhydrous Na₂SO₄, filtered and the solvent evaporated. The residue was run through a silica gel column using hexane as eluent and a colorless liquid was obtained (yield 10%).

¹H NMR (CDCl₃ δ ppm) 7.24 (d, J = 5.4 Hz, 1H), 7.12 (d, J = 5.1 Hz, 1H), 7.04 (s, 1H), 6.85 (d, J = 5.4 Hz, 1H), 6.77 (d, J = 5.0 Hz, 1H), 2.14 (s, 3H), 2.12 (s, 3H), 1.93 (s, 3H).

2,3-bis(2-bromo-4-methylthiophene-5-yl)-5-bromo-4-methylthiophene (3).

A round bottom flask was charged with **2** (0.35 mmol, 0.101 g) and AcOH:THF 1:1 mixed solution (3.0 mL). The colorless solution was cooled in an ice bath and NBS (0.123 mmol, 0.218 g) was added in one portion. The mixed solution was heated up reflux at 1h and poured into a 10% KOH(aq) solution. The aqueous layer was extracted with hexane (3 × 15 mL) and the combined organic layers were dried with anhydrous Na₂SO₄, filtered and the solvent evaporated. The residue was run through a silica gel column using a hexane as eluent, colorless liquid was obtained (quant.).

¹H NMR (CDCl₃ δ ppm) 6.85 (s, 1H), 6.76 (s, 1H), 2.12 (s, 3H), 2.03 (s, 3H), 1.91 (s, 3H).

Model dendritic polymer.

To a Schlenk flask of **3** (62 mg, 0.12 mmol) stirring at 0 °C in dry THF (5 mL) under nitrogen was added 0.12 mL of a 2.0 M *i*PrMgCl (0.24 mmol, 2 eq) solution in hexanes dropwise. The mixture was left to stir at 0 °C for 1 hour, and 1.3 mg of Ni(dppp)Cl₂ (2mol%) was quickly added to the flask. The solution was left to polymerize for 24 h, then quenched with 5 M HCl (0.5 mL). The mixture was extracted with CHCl₃ (3 × 15 mL) into and the combined organic layers were dried with anhydrous Na₂SO₄, filtered and the solvent evaporated. The residue was washed with 100 mL of MeOH. A brown viscous fluid was obtained (62%). The resulting brown viscous fluid was analyzed via NMR and GPC.

Regiorandom P3HT.

Highly regiorandom P3HT was prepared according to reported method.⁵

4. ^1H NMR spectra of bent poly(3-hexylthiophene) (entry 5, Table 1 in main text) (Fig. S5)

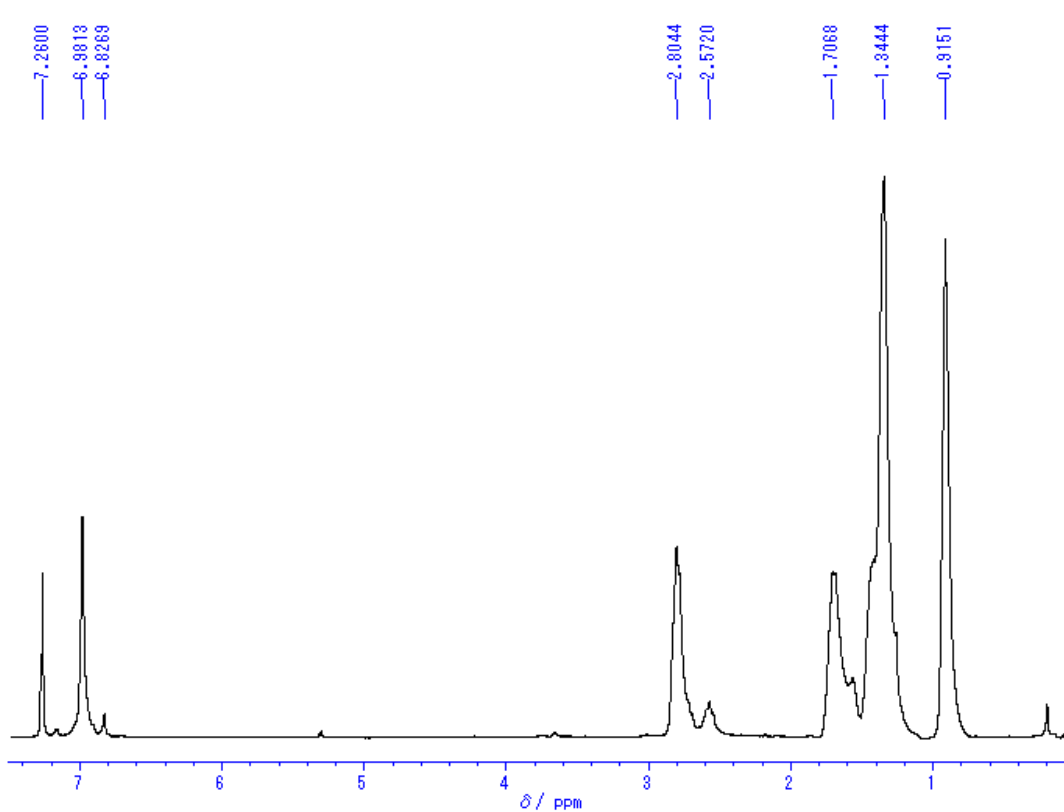


Fig. S5. ^1H NMR spectrum of bent poly(3-hexylthiophene) in CDCl_3 .

5. ^1H NMR spectra of oligothiophene (Fig. S6, S7)

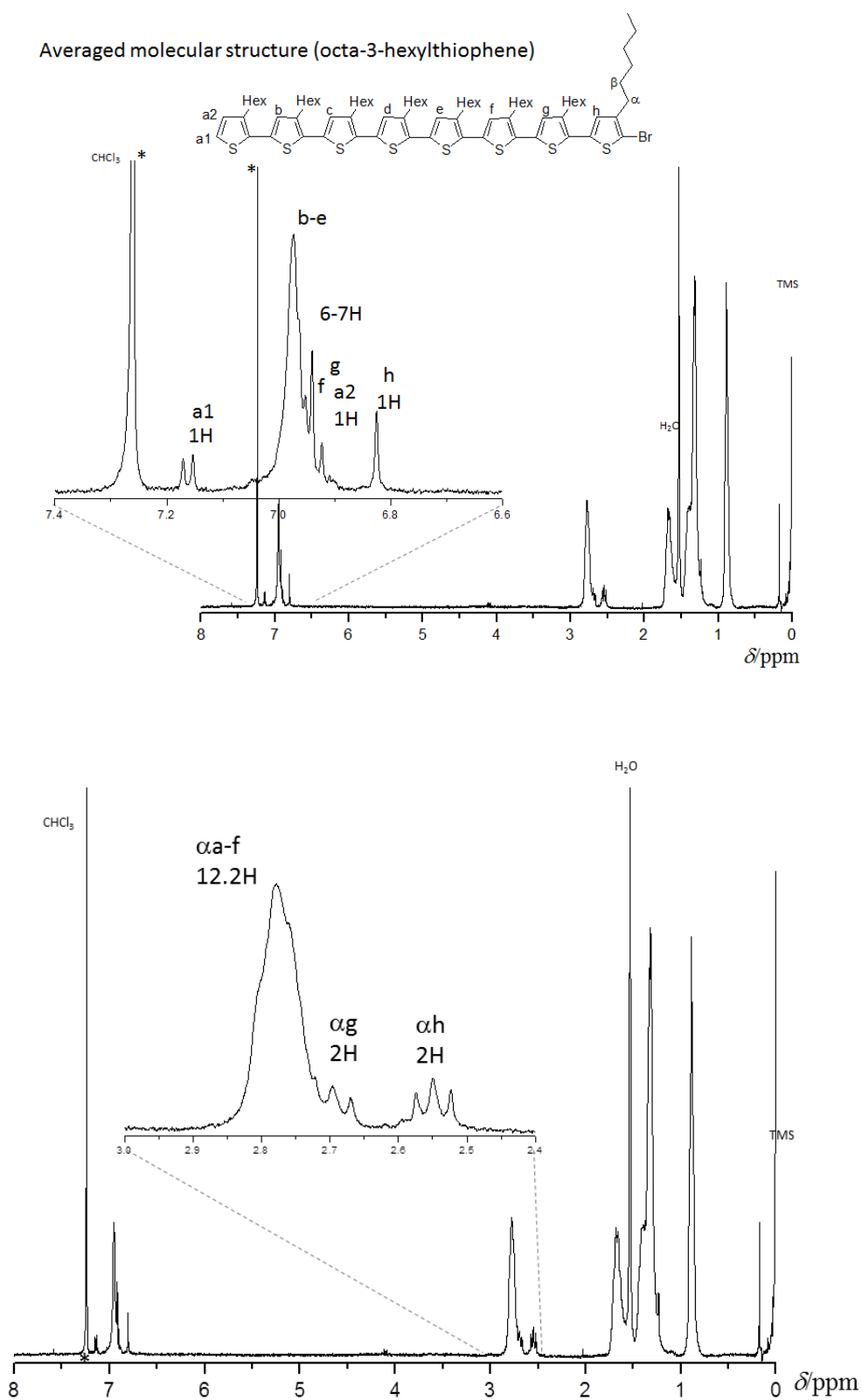


Fig. S6. Long oligomer (entry 6 in Table 1).

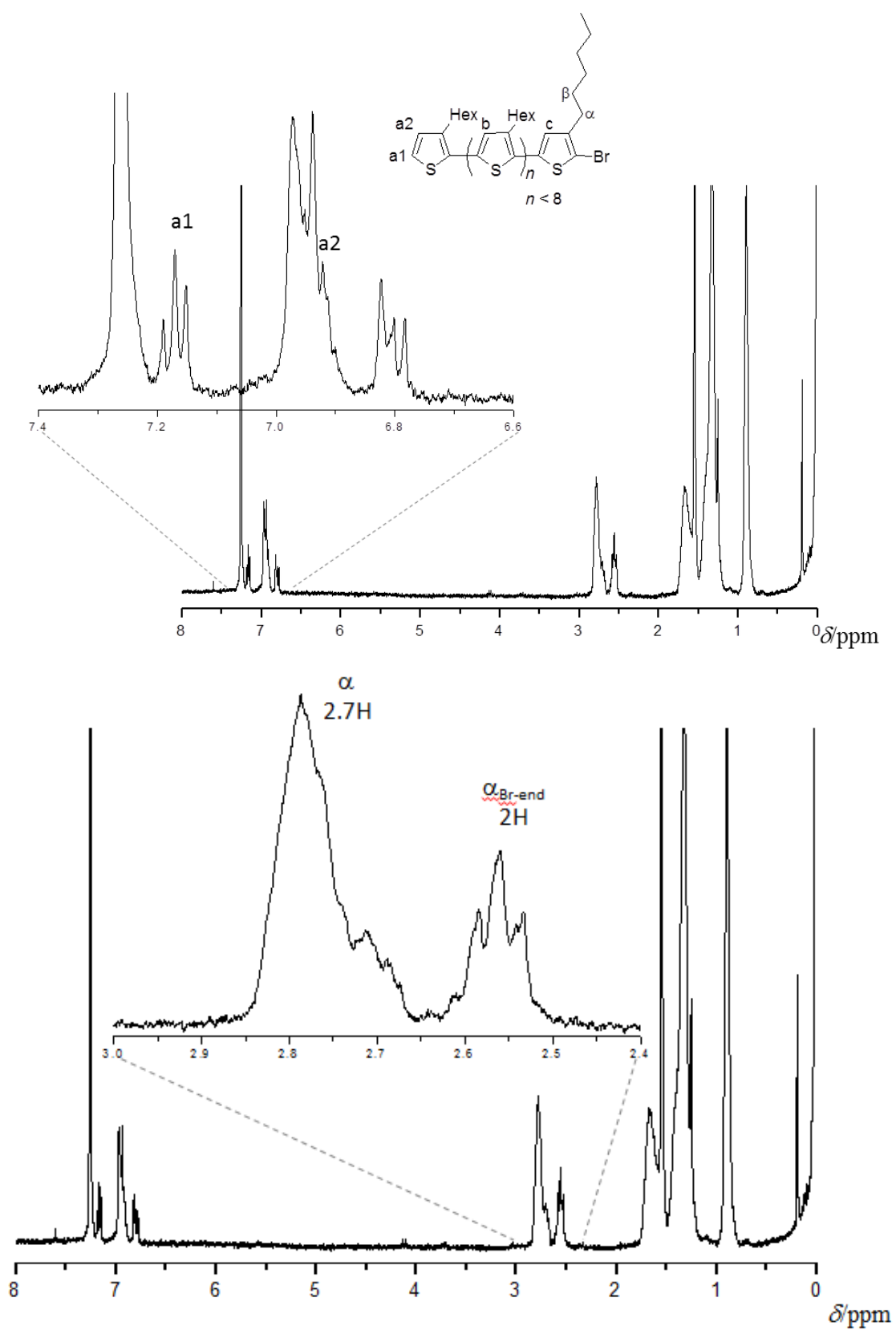


Fig. S7. Short oligomer (entry 6 in Table 1).

6. ^1H NMR spectra of fraction 2 from condition B in CDCl_3 (Fig. S8)

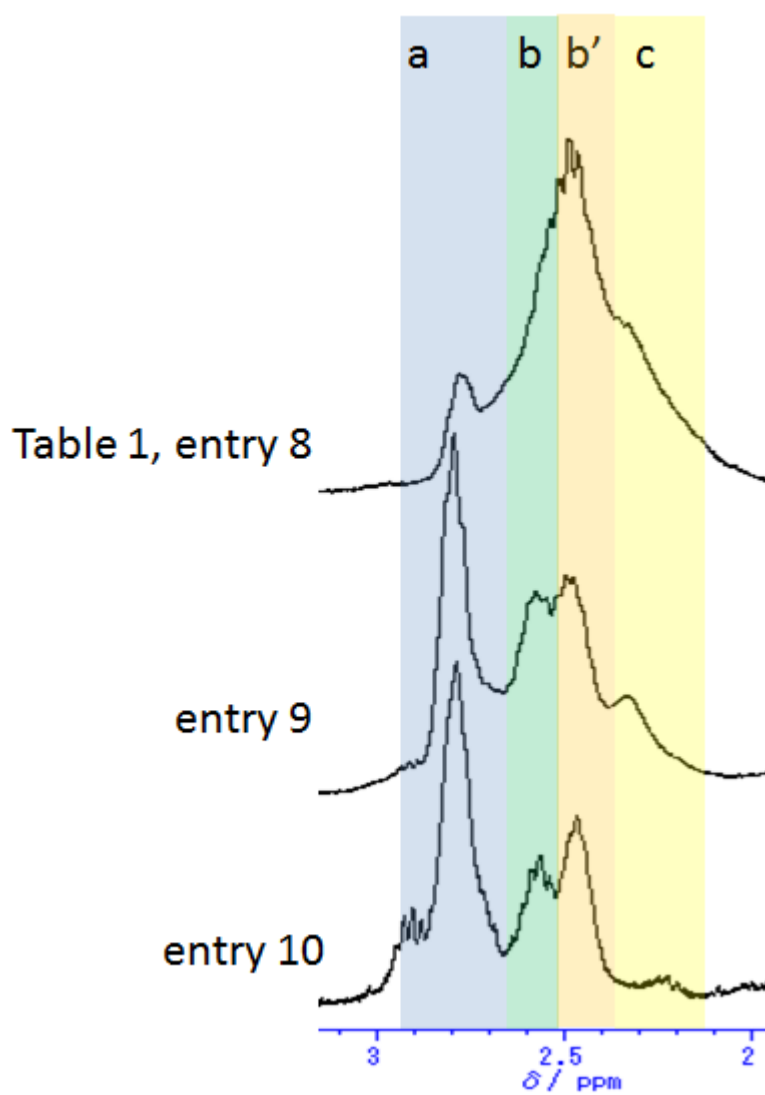


Fig. S8. ^1H NMR spectra of fraction 2 from condition B in CDCl_3

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