

Kumada Catalyst-Transfer Polycondensation of Thiophene-Based Oligomers: Robustness of a Chain Growth Mechanism

Supporting Information

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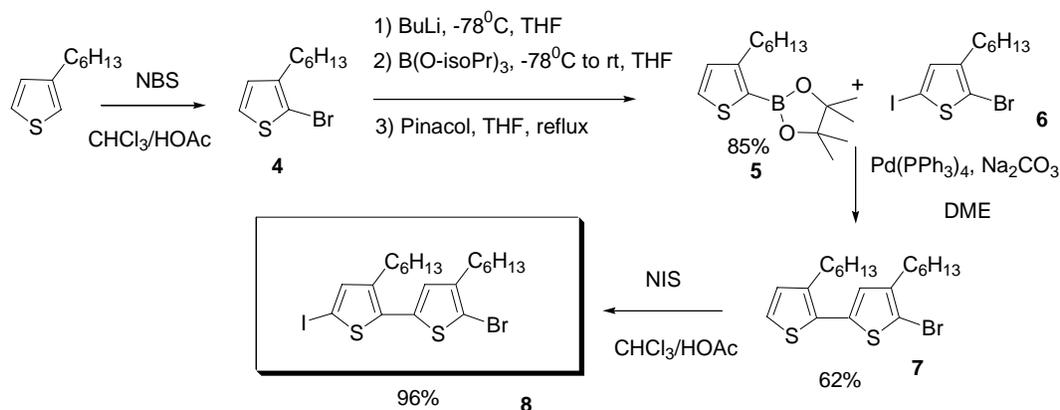
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Experimental Part.

Synthesis.

2-Bromo-3-hexyl-5-iodothiophene (6). NBS (37.38g, 0.21 mol) was added to the solution of 3-hexylthiophene (33.66 g, 0.2 mol) in 500 mL of a chloroform-acetic acid mixture (50/50 v/v) in the absence of light, under an argon atmosphere, at temperature 0°C. The mixture was allowed to reach room temperature, and stirred overnight, and hydrolyzed with 500 mL of ice-water, and the aqueous phase extracted with chloroform. The combined extracts were washed with water, 1 M sodium hydroxide solution (50 ml), again with water, dried (MgSO₄), and concentrated. The residue was purified by flash chromatography to give 44.45 g (0.18 mol) of monobromide **4** (90% yield). Iodination was performed in a similar manner. To this end, NIS (21.26 g, 95 mmol) was added to **4** (22.25 g, 90 mmol) in 500 mL of a chloroform-acetic acid mixture (50/50 v/v) in the absence of light, under an argon atmosphere, at temperature 0°C. The mixture was allowed to reach room temperature, stirred overnight,

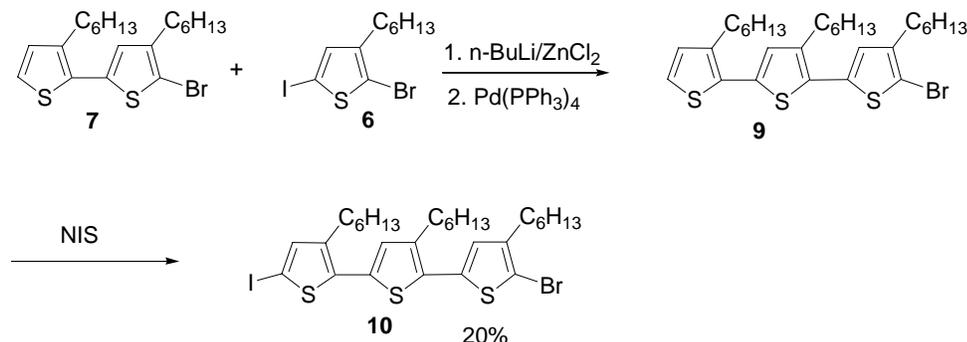
and then worked up according to above-described procedure. After vacuum distillation and purification by flash chromatography 28.54 g of **6** was obtained (85% yield).



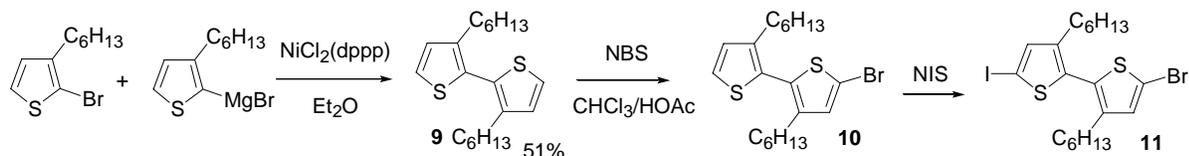
5'-bromo-3,4'-dihexyl-5-iodo-[2,2']bithiophenyl (8). To 4.94 g (20 mmol) of **4** in THF (20 ml) at -80 °C was added *n*-BuLi (13.2 ml, 21 mmol). After stirring at -80° C for one hour tri(isopropyl)borate (4.14 g, 22 mmol) was added and the solution was allowed to warm up to room temperature. After an additional two hours at room temperature, pinacol (2.84 g, 24 mmol) was added and the resulting suspension was stirred over night at room temperature. Next, THF was taken off and the residue was dissolved in petrol ether. After the white precipitate was filtered off the resulting solution was filtered over neutral aluminium oxide. The solvent was taken off and the product was dried in vacuum. Dioxaborolane **5** was obtained as a brownish oil (5.01 g, 85%).

To a solution of **6** (3.21 g, 10.9 mmol) in DME (48 ml) [Pd(PPh₃)₄] (0.504 g, 0.44 mmol) was added. After the mixture was stirred for 10 min at room temperature thiophene boronic ester **5** (4.07 g, 10.9 mmol) and a 1M aqueous solution of NaHCO₃ (33 ml) were added. The reaction mixture was refluxed under vigorous stirring for 24 hours. Then it was poured into water (150 ml) and the organic phase was separated while the aqueous phase was extracted with ether (3 times 30 ml). The combined extracts were dried over sodium sulphate and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (SiO₂, hexane) to yield bithiophene **7** (2.79 g, 62%) as a yellow liquid. **7** (2.79 g, 6.76 mmol) was further iodinated by NIS according to the protocol for the

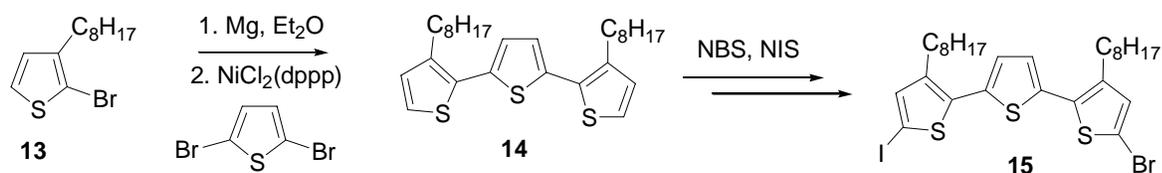
preparation of **6** from **4** and 3.28 g (6 mmol) of **8** was obtained after the flash chromatography purification step.



5''-bromo-3,4',4''-triethyl-5-iodo-[2,2';5',2'']terthiophene (10). Bithiophene **7** (829 mg, 2 mmol) was dissolved in THF (5 ml). At $-80\text{ }^{\circ}\text{C}$ *n*-BuLi (1.32 ml, 2.1 mmol) was added dropwise and the resulting solution was stirred for one hour at $-80\text{ }^{\circ}\text{C}$. After addition of zinc chloride (2.1 mmol as a 1 M solution in THF) the solution was allowed to warm up to room temperature. Next, this reaction mixture was transferred to a solution of **6** (783.5 mg, 2.1 mmol) and $[\text{Pd}(\text{PPh}_3)_4]$ (232 mg, 0.2 mmol) in THF (5 ml) *via* cannula. The resulting orange solution was stirred at room temperature for 24 h under light protection. Then the reaction mixture was poured into water (20 ml) and the organic layer was taken off while the water phase was extracted with CH_2Cl_2 (three times 20 ml). The combined organic phases were dried with MgSO_4 and the solvent was removed by rotary evaporation. The crude product was purified by flash column chromatography (SiO_2 , hexane). Terthiophene **9** was obtained as an orange viscous liquid (348 mg) and further iodinated by NIS according to the protocol for the preparation of **6** from **4** and (353 mg, 25% overall yield accounting from **7**).



5-bromo-3,3'-dihexyl-5'-iodo-[2,2']bithiophene (12). A solution of **4** (5 g, 0.0202 mol) in diethyl ether (75 ml) was added dropwise over 1 h to magnesium powder (0.72 g, 0.03 mol) suspended in diethyl ether (25 ml). The Grignard reagent was added in small portions to a mixture of **4** (5 g, 0.0202 mol) and Ni(dppp)Cl₂ (0.1 g) in diethyl ether (100 ml) and stirred for 3 h. The reaction was quenched with water (100 ml) and extracted with diethyl ether (3 × 50 ml). The combined organic layers were dried and the solvent removed under reduced pressure. Column chromatography (SiO₂, hexane) gave **11** (3.42 g, 51%) as a colourless liquid and further iodinated into **12** by NIS according to the protocol for the preparation of **6** from **4** and (2.71 g, 49% yield).



5-bromo-5'-iodo-3,3'-dioctyl-[2,2';5',2'']terthiophene (15). The Kumada coupling reaction between commercially available 2,5-dibromothiophene and Grignard reagent prepared from 2-bromo-3-octylthiophene (**13**) and Mg powder afforded 3,3'-dioctyl-2,2',5',2''-terthiophene (**14**). It was sequentially brominated and then iodinated into 5-bromo-5'-iodo-3,3'-dioctyl-[2,2';5',2'']terthiophene (**15**) using NBS and NIS, respectively.

Into a thoroughly dried round-bottom flask supplied with refrigerator under argon atmosphere Mg powder (1.0 g, 41 mmol) and I₂ was added, and heated to form violet cloud for activation of the Mg powder. After that 10 mL of dry THF in one portion and 2-bromo-3-octylthiophene (**13**) (8.26 g, 30 mmol) in 30 mL of THF were added dropwise during 30 min and stirred for 2 hours. Thus-obtained Grignard reagent was added into the dry round-bottom flask supplied with refrigerator and contained 2,5-dibromothiophene (3.14 g, 13 mmol) and Ni(dppp)Cl₂ (0.1 g) in 50 mL dry THF. The reaction was carried out during 2 days at 65 °C. The reaction mixture was quenched by water and extracted with chloroform; the organic solution was washed with diluted HCl, water and dried over MgSO₄. Then the

solution was filtrated, evaporated and purified by column chromatography to release a yellow oil of 3,3''-dioctyl-2,2',5',2''-terthiophene (**14**) (5.22 g, 85 % yield). **14** was iodinated into **15** by NIS according to the protocol for the preparation of **6** from **4** and (5.14 g, 69% yield).

Preparation of the initiators.¹⁶ To a solution of Ni(PPh₃)₄ (222 mg, 0.2 mmol) in dry toluene (3.5 ml, glove-box, argon atmosphere) bromobenzene or *o*-bromotoluene (0.95 mmol) was added at room temperature. The homogeneous mixture was stirred for 15 min and was allowed to stand unperturbed overnight. The original deep red color of the reaction mixture gradually changes to brownish-yellow together with precipitation of Ph-Ni(PPh₃)₂-Br or *o*-Tol-Ni(PPh₃)₂-Br crystals, which were separated by filtration, washed with dry hexane and dried in vacuum. Yield: 0.07 - 0.08 g, 40-50%.

Preparation of *o*-Tol-(3HT)₆-Br. *o*-Tol-(3HT)₆-H was prepared by the standard polycondensation procedure (see Experimental part of the main text) of the monomer **1** initiated by the *o*-Tol-Ni(PPh₃)₂-Br at the monomer-to-initiator ratio of 6, followed by the bromination of the *o*-Tol-(3HT)₆-H by NBS (¹H NMR S9 and S10).

Figure S1. ^1H NMR of P3HT obtained upon the Ph-Ni(PPh₃)₂-Br mediated polymerization of **1** prepared by GRIM at **6** to *t*-BuMgCl ratio of 0.75 (entry 1 of Table1). The Ph-P3HT to H/Br P3HT ratio is estimated as follows: $1/[(I_{\text{Hf}}+ I_{\text{Hg}}-1)/2]=1/[(0.9+1.47-1)/2]= 1 / 0.685$, that corresponds to the percentage of Ph-P3HT of $1/1 + 0.685 \sim 60\%$, whereas of H/Br P3HT of $\sim 40\%$. On the other hand, Mn_{GPC} is equal to 3000, whereas Mn_{NMR} determined assuming that all polymer chains are Ph-terminated (by setting the integral of Hd=1) $Mn_{\text{NMR}} \sim 6000$. The observed discrepancy between Mn_{GPC} and Mn_{NMR} is mostly due to presence of **P3HT** without Ph-termination. $Mn_{\text{GPC}}/Mn_{\text{NMR}}$ ratio of 0.5 corresponding to 50% content of Ph-**P3HT** is not too far from the content of Ph-**P3HT** determined by the direct integration of the ^1H NMR spectrum.

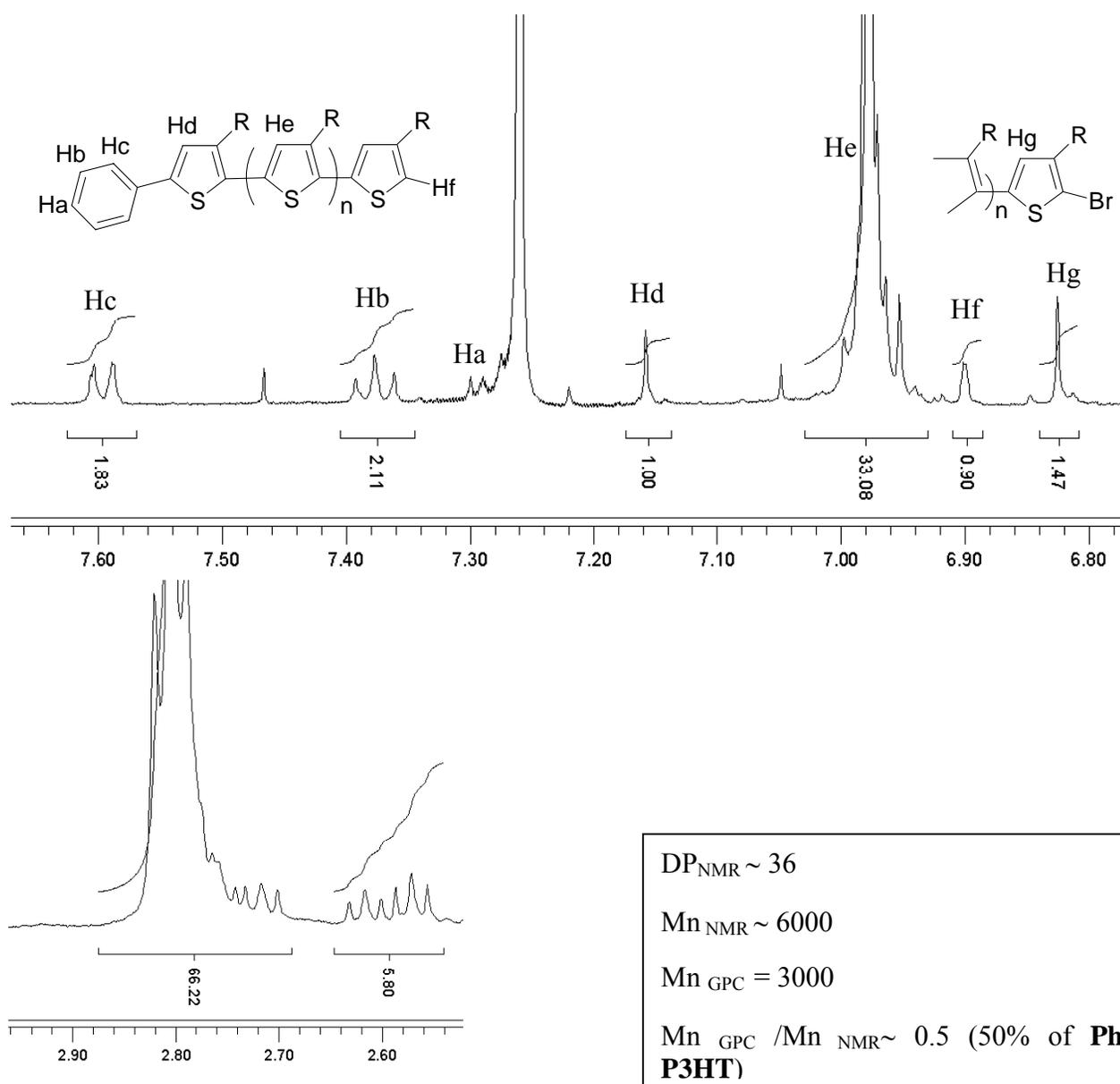


Figure S2. ^1H NMR of P3HT obtained upon the Ph-Ni(PPh₃)₂-Br mediated polymerization of **1** prepared by GRIM at **6** to *t*-BuMgCl ratio of 0.9 (entry 2 of Table1). The Ph-P3HT to H/Br P3HT ratio is estimated as follows: $1/[(I_{\text{Hf}}+ I_{\text{Hg}}-1)/2]=1/[(1.01+0.76-1)/2]= 1/0.385$, that corresponds to the percentage of Ph-P3HT of $1/1 + 0.385 \sim 72\%$, whereas of H/Br P3HT of $\sim 28\%$. On the other hand, Mn_{GPC} is equal to 4300, whereas Mn_{NMR} determined assuming that all polymer chains are Ph-terminated (by setting the integral of Hd=1) $Mn_{\text{NMR}} \sim 6650$. The observed discrepancy between Mn_{GPC} and Mn_{NMR} is mostly due to presence of **P3HT** without Ph-termination.

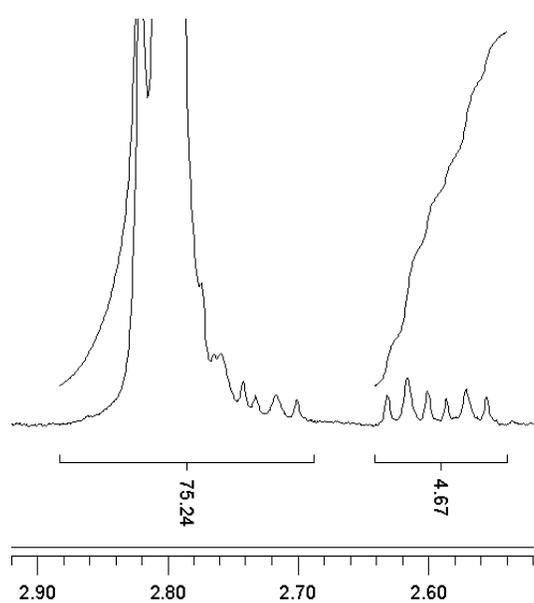
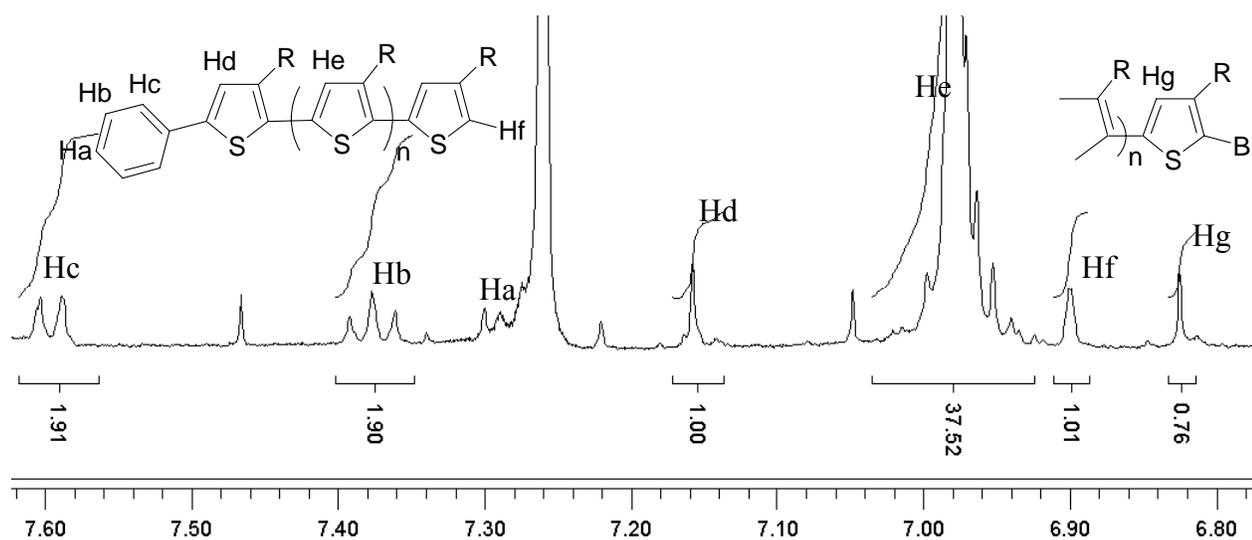


Figure S3. ^1H NMR of P3HT obtained upon the Ph-Ni(PPh₃)₂-Br mediated polymerization of **1** prepared by GRIM at **6** to *t*-BuMgCl ratio of 1.5 (entry 3 of Table1). The Ph-P3HT to H/Br P3HT ratio is estimated as follows: $1/[(I_{\text{Hf}}+ I_{\text{Hg}}-1)/2]=1/[(1.07+0.56-1)/2]= 1/0.315$, that corresponds to the percentage of Ph-P3HT of $1/1 + 0.315 \sim 76 \%$, whereas of H/Br P3HT of $\sim 24 \%$. On the other hand, M_n_{GPC} is equal to 3800, whereas $M_{n\text{NMR}}$ determined assuming that all polymer chains are Ph-terminated (by setting the integral of Hd=1) $M_{n\text{NMR}} \sim 6000$. The observed discrepancy between M_n_{GPC} and $M_{n\text{NMR}}$ is mostly due to presence of **P3HT** without Ph-termination.

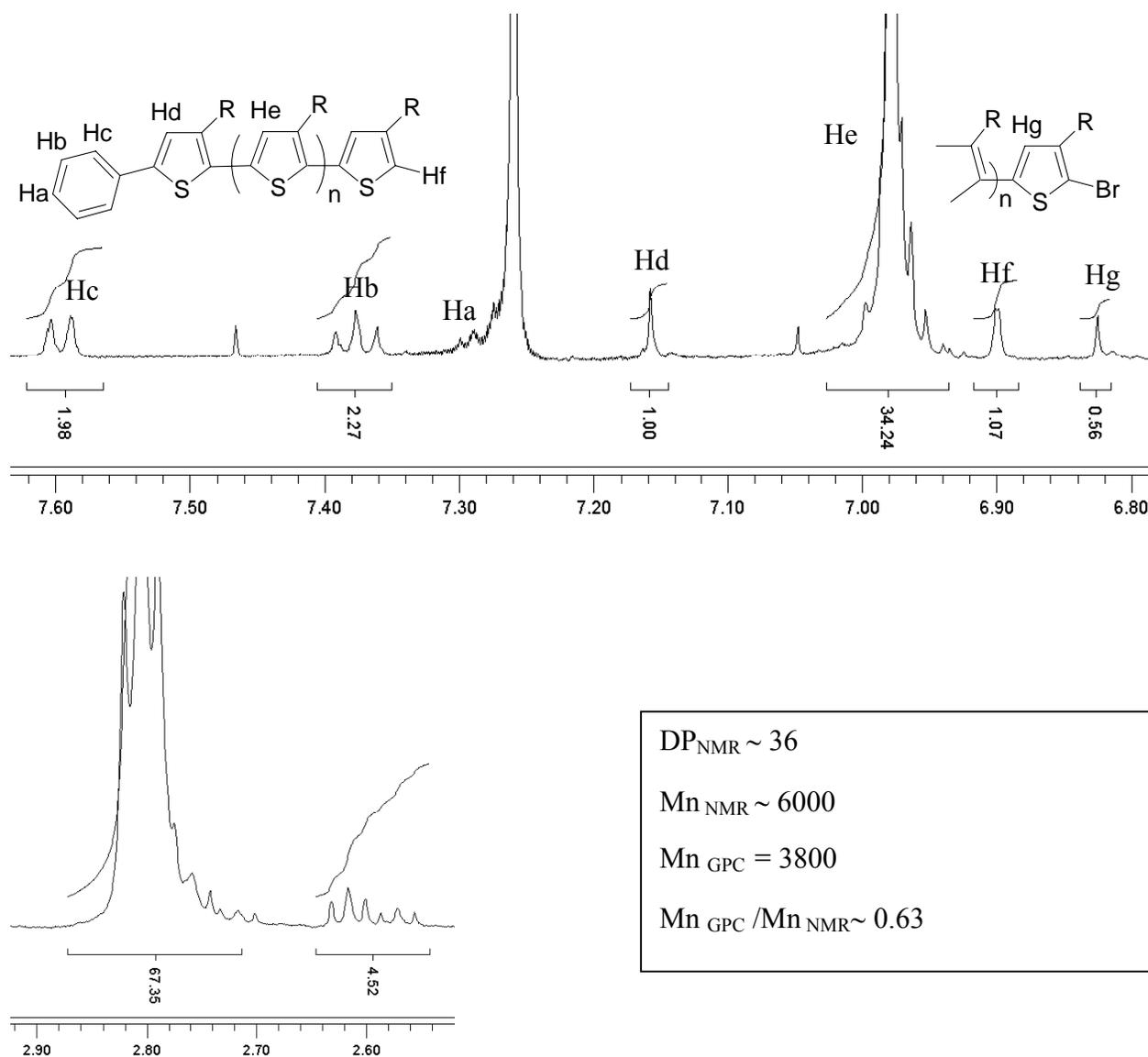


Figure S4. ^1H NMR of P3HT obtained upon the $\text{Ph-Ni}(\text{PPh}_3)_2\text{-Br}$ mediated polymerization of **1** prepared by GRIM at **6** to $t\text{-BuMgCl}$ ratio of 1.05 (entry 4 of Table1). The spectrum is nicely fitted by Ph/H P3HT and only traces of Br/H P3HT are recognizable (close to the detection limit of NMR of 5%), so we estimate that Ph/H P3HT content to be $\sim 95\%$. A calculation of Mn_{GPC} from the NMR spectrum assuming that all polymer chains are Ph-terminated (by setting the integral of Hd=1) gives essentially the same value that gives GPC ($\text{Mn}_{\text{NMR}} \sim 6000$; $\text{Mn}_{\text{GPC}} = 6100$).

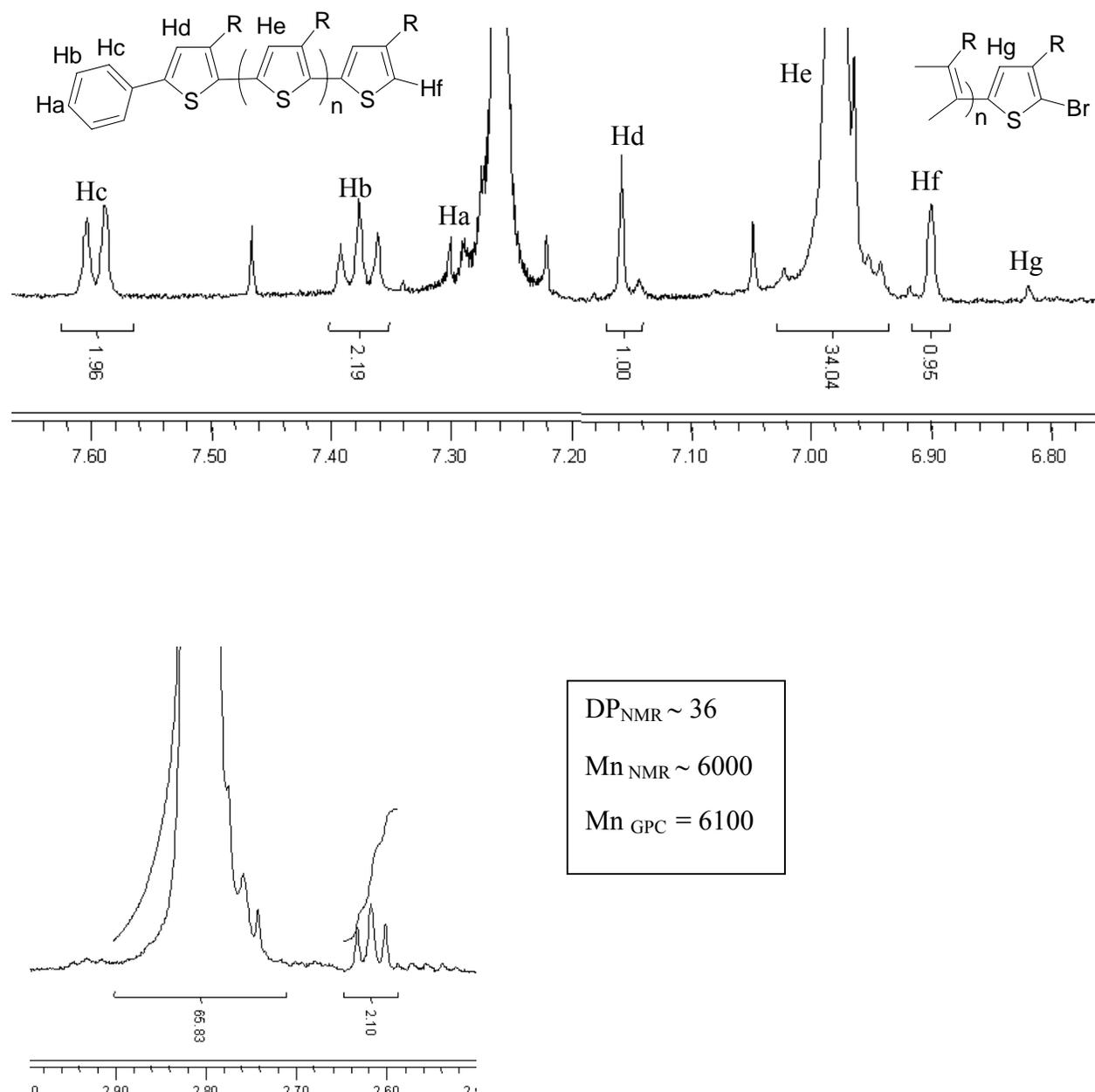


Figure S5. ^1H NMR of P3HT obtained upon the Ph-Ni(PPh_3) $_2$ -Br mediated polymerization of **2a** (entry 5 of Table1). The Ph-P3HT to H/Br P3HT ratio is estimated as follows: $1/[(I_{\text{Hf}} + I_{\text{Hg}} - 1)/2] = 1/[(1.3 - 1)/2] = 1/0.15$, that corresponds to the percentage of Ph- **poly2a** of $1/1 + 0.15 \sim 87\%$, whereas of H/H **poly2a** of $\sim 13\%$. A calculation of $M_{\text{n GPC}}$ from the NMR spectrum assuming that all polymer chains are Ph-terminated (by setting the integral of Hd=1) gives the value close to one obtained by GPC ($M_{\text{n NMR}} \sim 4500$; $M_{\text{n GPC}} = 5300$).

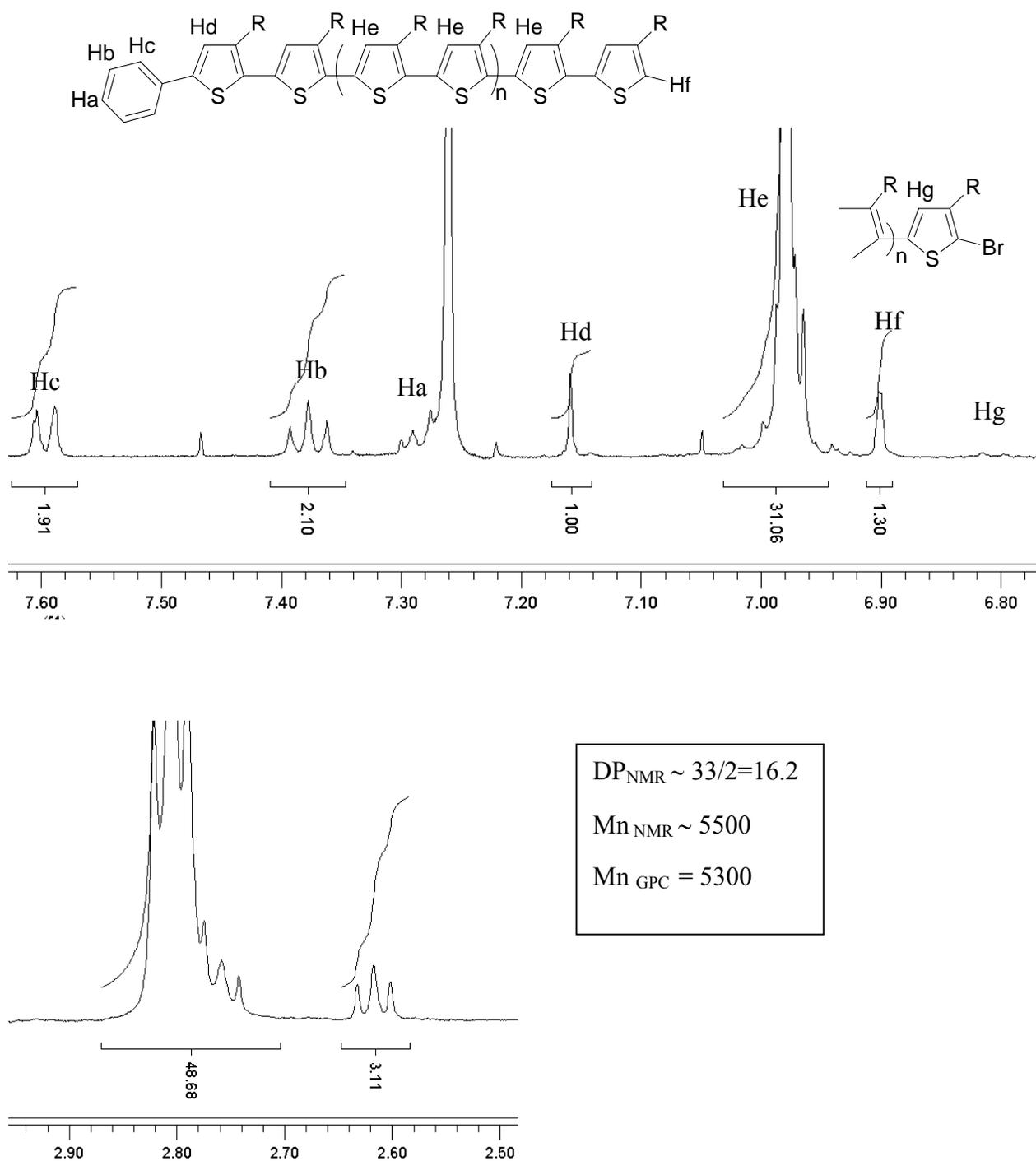


Figure S5a. ^1H NMR of crude reaction mixture obtained upon the $\text{Ph-Ni}(\text{PPh}_3)_2\text{-Br}$ mediated polymerization of **2a** (entry 5 of Table1) highlights the co-existence of the **poly2a** and a product of the protonation of the **2a** monomer suggesting the chain growth polycondensation mechanism.. The conversion of 87% can be deduced from the spectra ($7/7+1=0.87$).

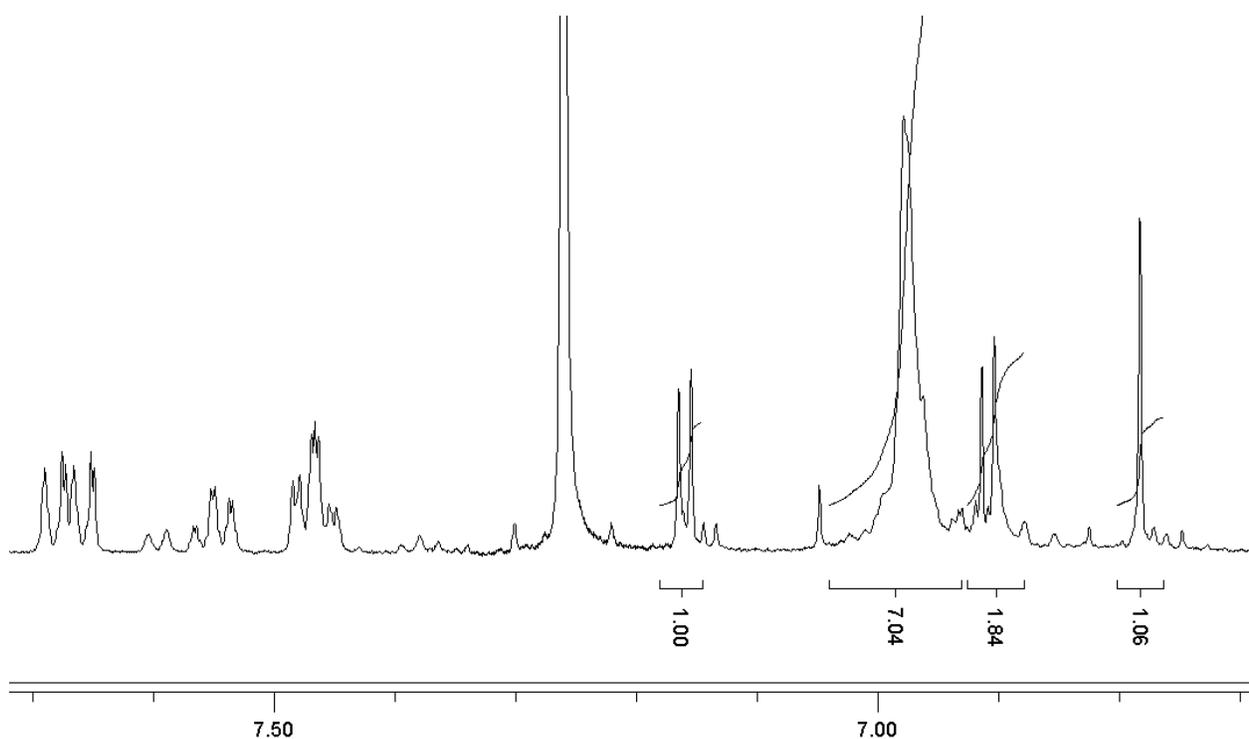


Figure S6. ^1H NMR of P3HT obtained upon the $\text{Ph-Ni}(\text{PPh}_3)_2\text{-Br}$ mediated polymerization of **3a** (entry 6 of Table1). The Ph-P3HT to H/Br P3HT ratio is estimated as follows: $1/[(I_{\text{Hf}}+ I_{\text{Hg}}-1)/2]=1/[(1.01+0.85-1)/2]= 1/0.43$, that corresponds to the percentage of Ph-P3HT of $1/1 + 0.43 \sim 69\%$, and of H/Br **poly3b** of $\sim 31\%$. On the other hand, $M_n_{\text{GPC}} = 5700$, whereas M_n_{NMR} determined assuming that all polymer chains are Ph-terminated (by setting the integral of Hb=2) $M_n_{\text{NMR}} \sim 8200$. The observed discrepancy between M_n_{GPC} and M_n_{NMR} is mostly due to presence of **poly3b** without Ph-termination. $M_n_{\text{GPC}}/M_n_{\text{NMR}}$.

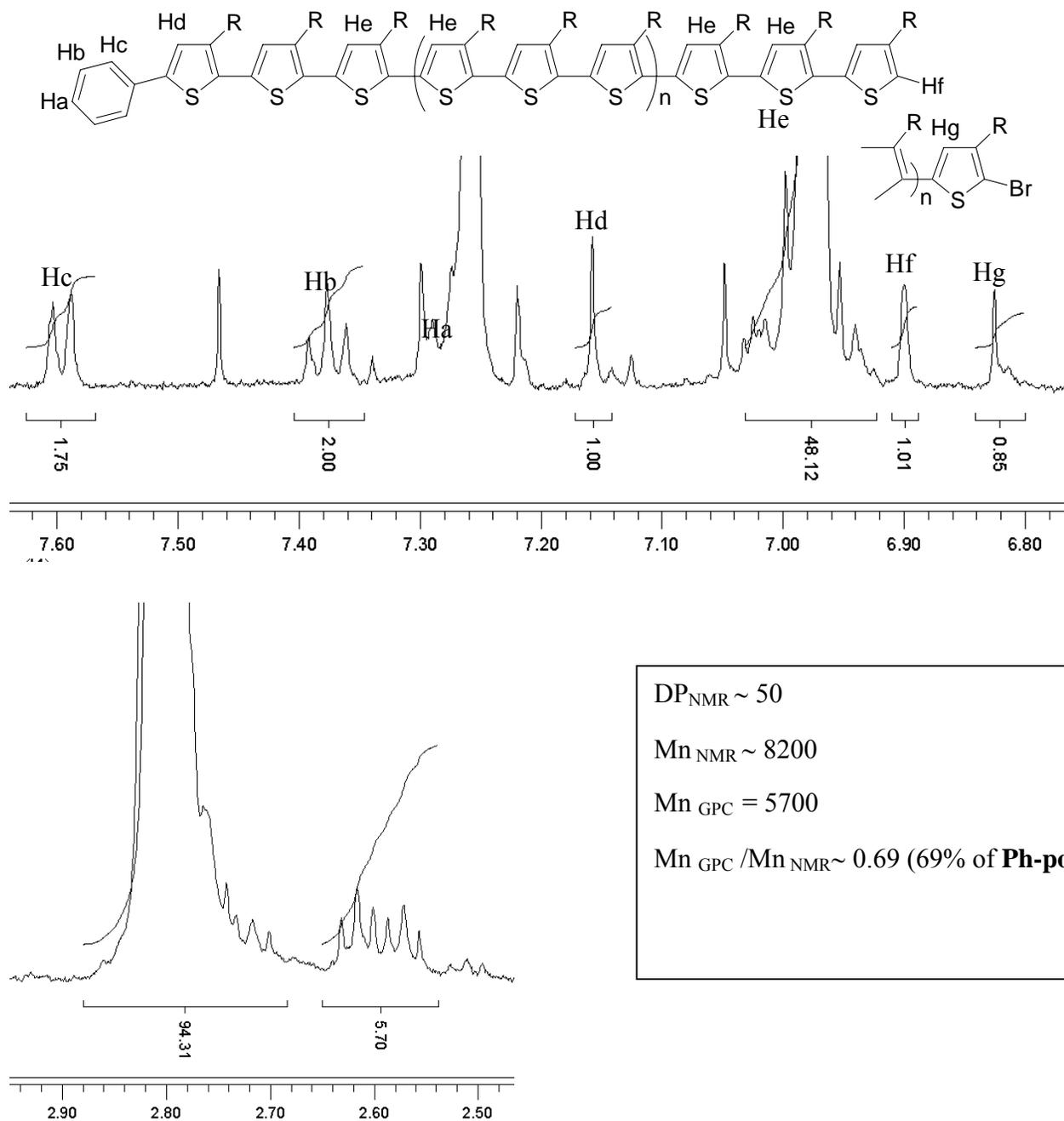


Figure S6a. ^1H NMR of crude reaction mixture obtained upon the $\text{Ph-Ni}(\text{PPh}_3)_2\text{-Br}$ mediated polymerization of **3a** (entry 6 of Table1) highlights the co-existence of the **poly3a** and a product of the protonation of the **3a** monomer (Figure S6b) suggesting the chain growth polycondensation mechanism.. The conversion of 85% can be deduced from the spectra ($5.7/5.7+1=0.85$).

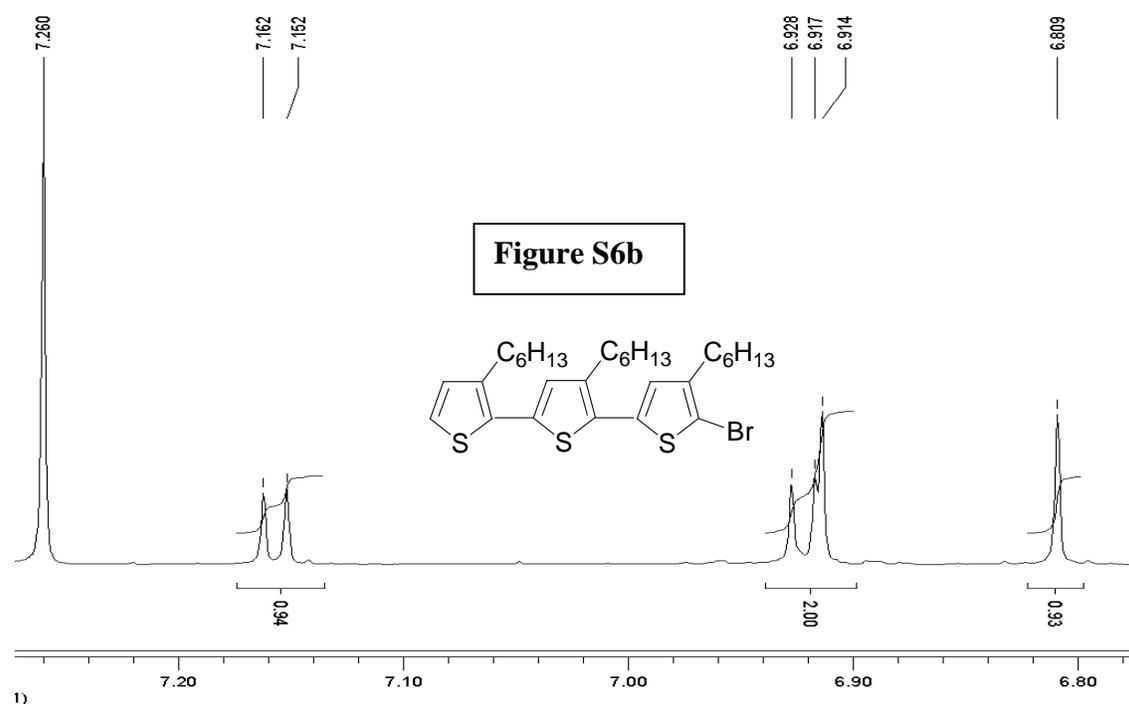
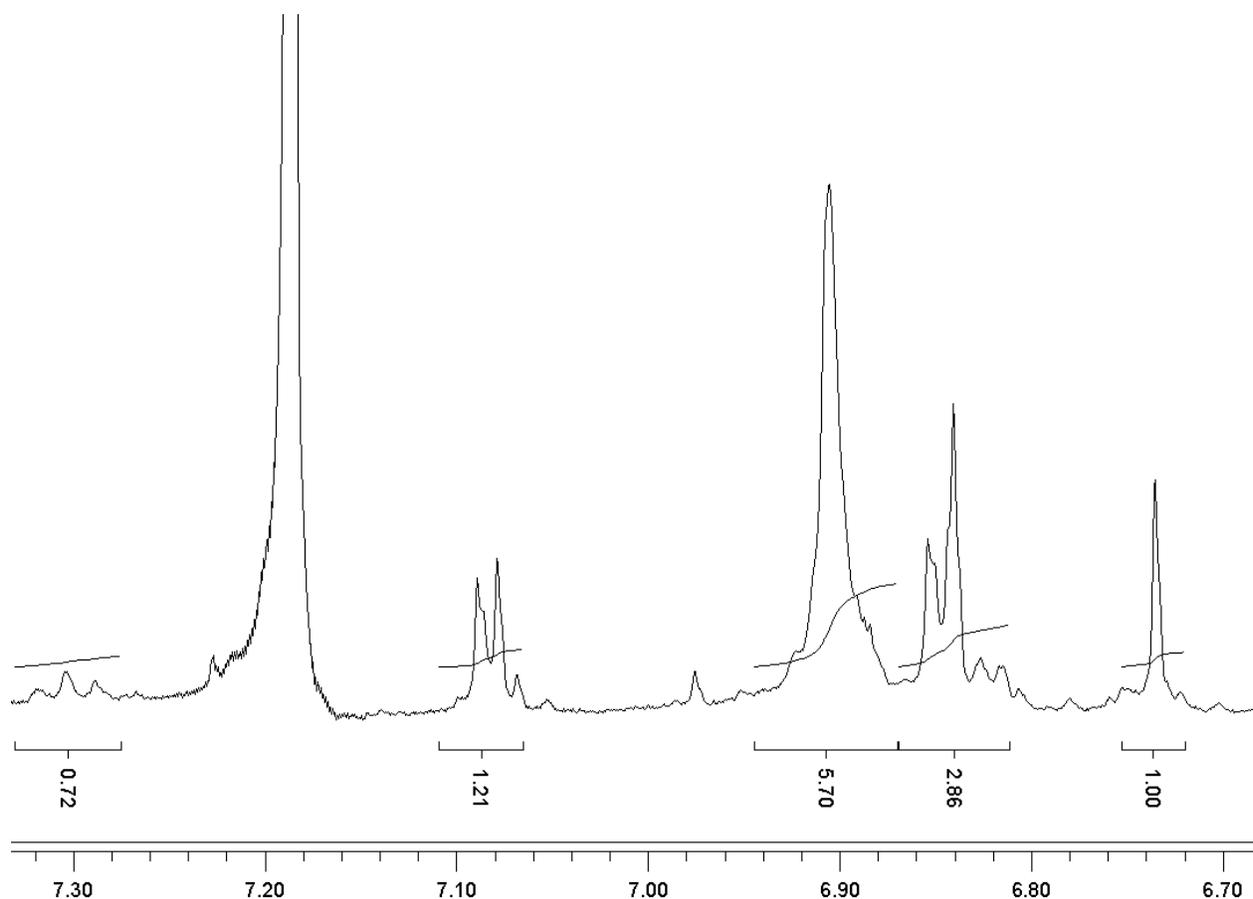


Figure S7. ^1H NMR of P3HT obtained upon the Ph-Ni(PPh₃)₂-Br mediated polymerization of **2b** prepared by GRIM at **6** to *t*-BuMgCl ratio of 0.9 (entry 3 of Table1). The Ph-poly**2b** to H/Br poly**2b** ratio is estimated as follows: $1/[(I_{\text{Hg}} + I_{\text{Hi}} - 1)/2] = 1/[(1.22 + 2.18 - 1)/2] = 1/1.2$, that corresponds to the percentage of Ph-poly**2b** of $1/1 + 1.2 \sim 45\%$, and of H/Br poly**2b** of $\sim 55\%$. On the other hand, $Mn_{\text{GPC}} = 3300$, whereas Mn_{NMR} determined assuming that all polymer chains are Ph-terminated (by setting the integral of Hb=2) $Mn_{\text{NMR}} \sim 7500$. The observed discrepancy between Mn_{GPC} and Mn_{NMR} is due to presence of poly**2b** without Ph-termination.

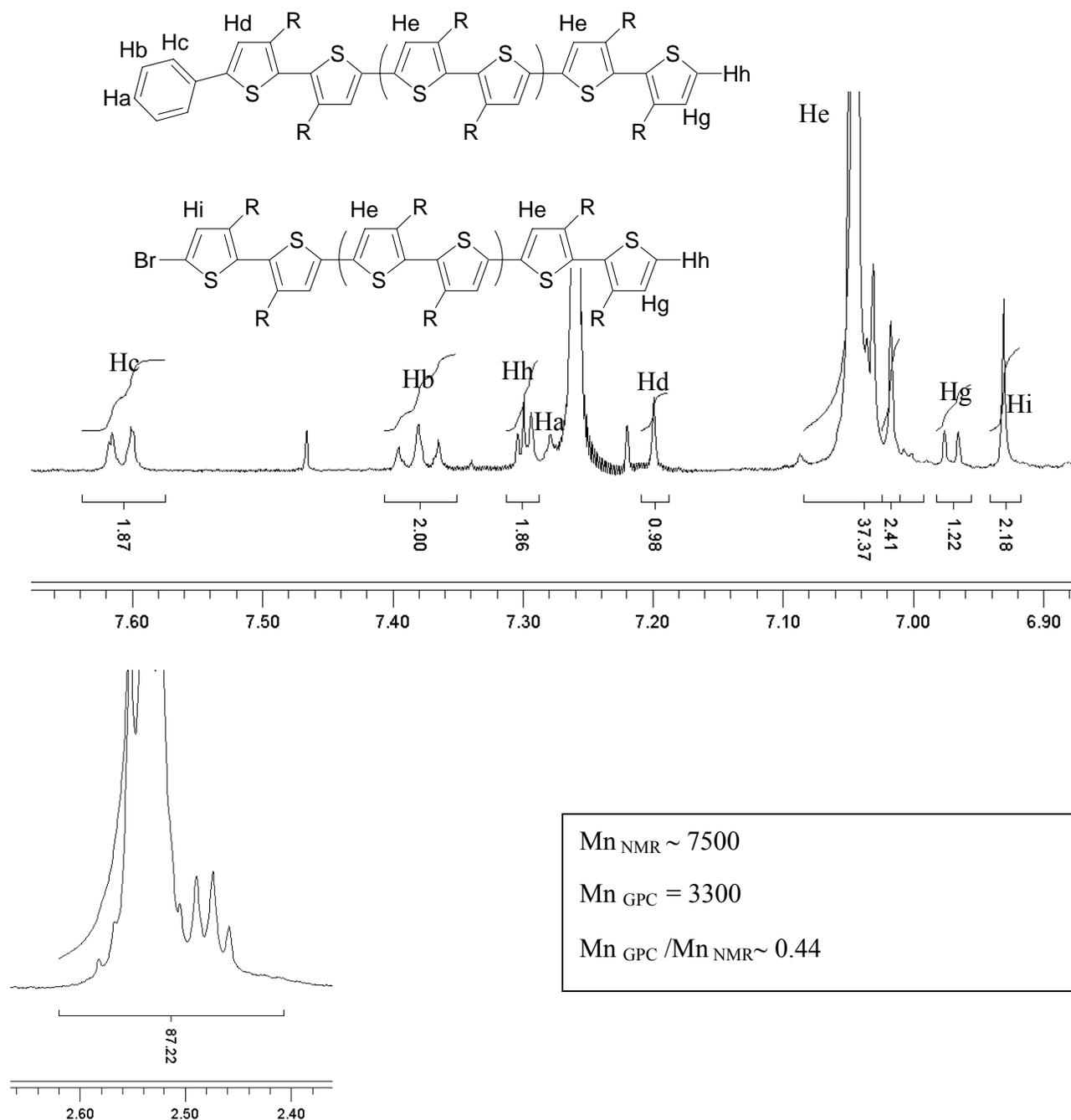


Figure S7a. ^1H NMR of crude reaction mixture obtained upon the $\text{Ph-Ni}(\text{PPh}_3)_2\text{-Br}$ mediated polymerization of **2b** (entry 7 of Table1) highlights the co-existence of the **poly2b** and a product of the protonation of the **2b** monomer (Figure S7b) suggesting the chain growth polycondensation mechanism.. The conversion of 75% can be deduced from the spectra ($1/1+0.34=0.75$).

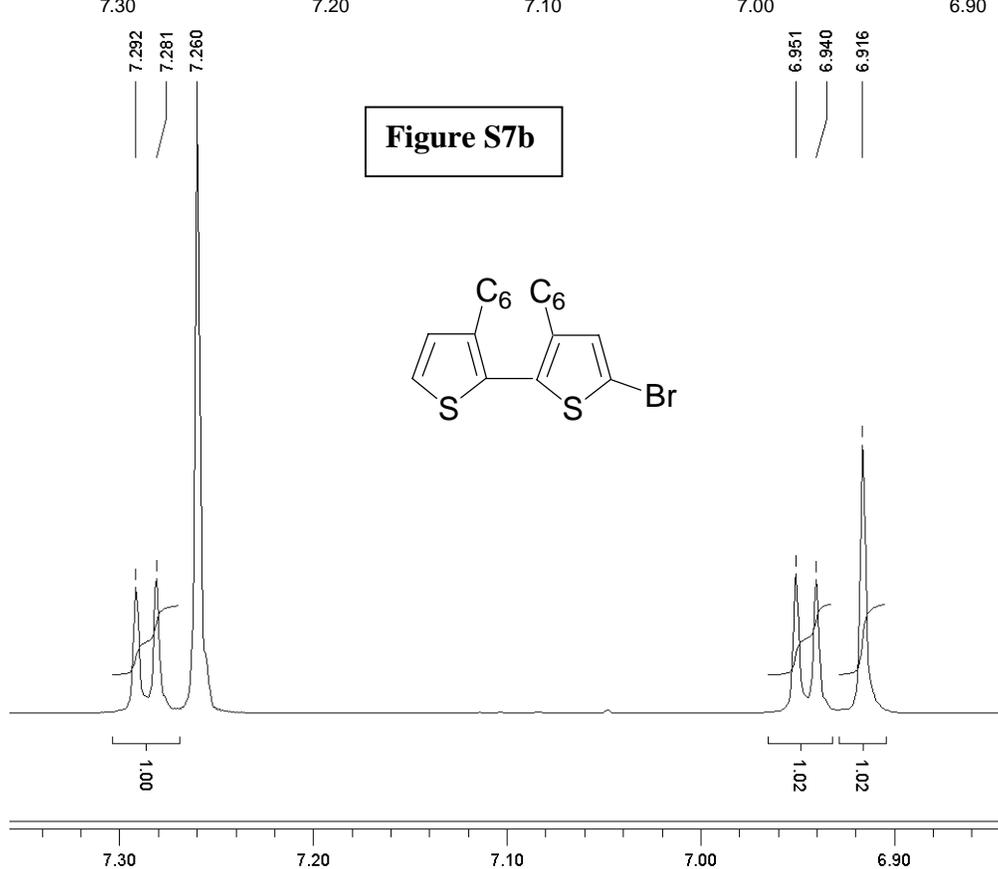
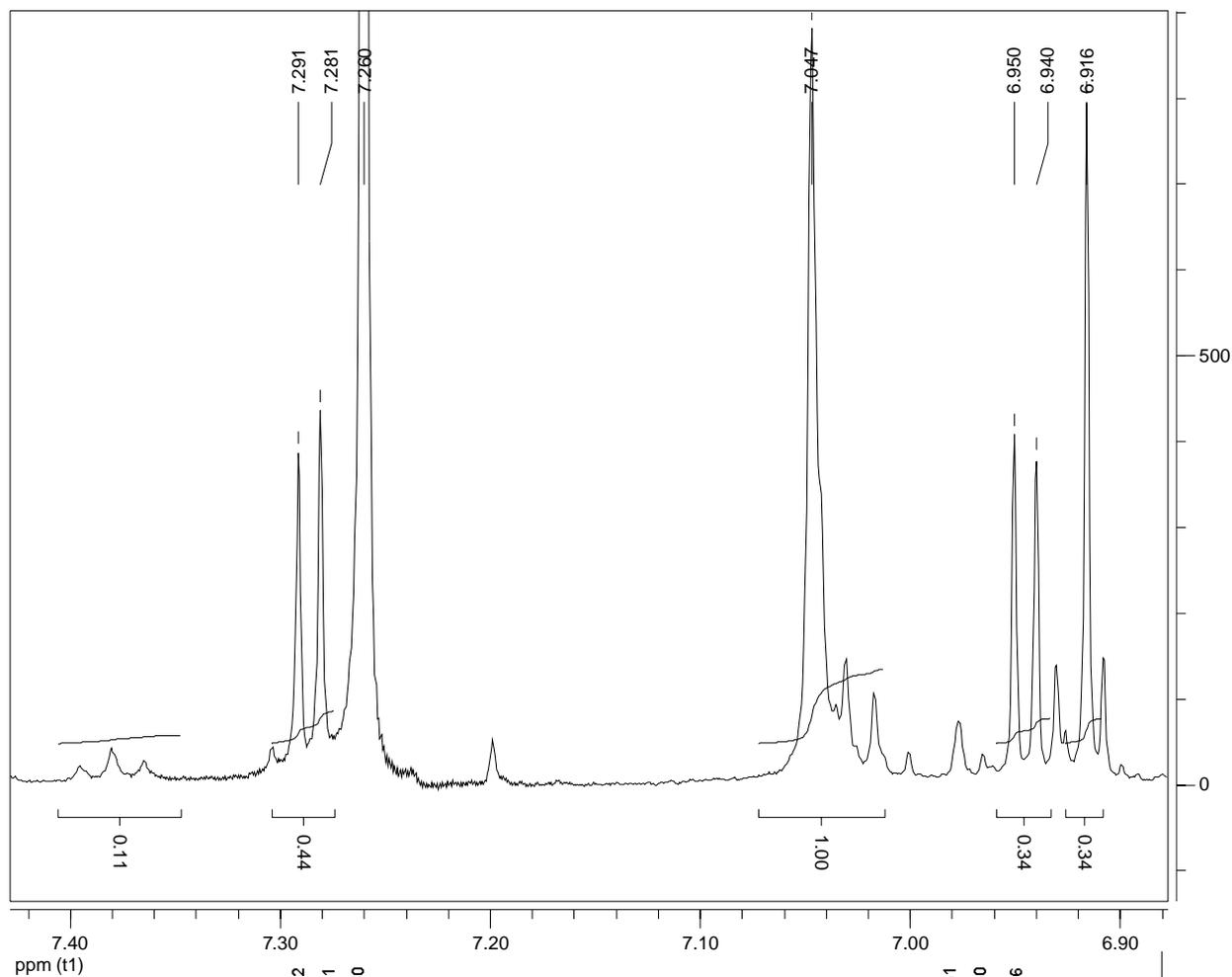


Figure S8. ^1H NMR of P3HT obtained upon the $\text{Ph-Ni}(\text{PPh}_3)_2\text{-Br}$ mediated polymerization of **3b** (entry 8 of Table1). The Ph-poly3b to H/Br poly3b ratio is estimated as follows: $1/[(I_{\text{Hg}} + I_{\text{Hi}} - 1)/2] = 1/[(2.22 + 3.33 - 1)/2] = 1/2.275$, that corresponds to the percentage of Ph/H P3HT of $1/1 + 2.275 \sim 31\%$, whereas of H/Br poly3b of $\sim 69\%$. On the other hand, $M_n_{\text{GPC}} = 4200$, whereas M_n_{NMR} determined assuming that all polymer chains are Ph-terminated (by setting the integral of $\text{Hb}=2$) $M_n_{\text{NMR}} \sim 15500$. The observed discrepancy between M_n_{GPC} and M_n_{NMR} is mostly due to presence of **poly3b** without Ph-termination . $M_n_{\text{GPC}}/M_n_{\text{NMR}}$ ratio of 0.27 corresponding to 27% content of Ph-poly3b is quite close to the content determined by the direct integration of the ^1H NMR spectrum.

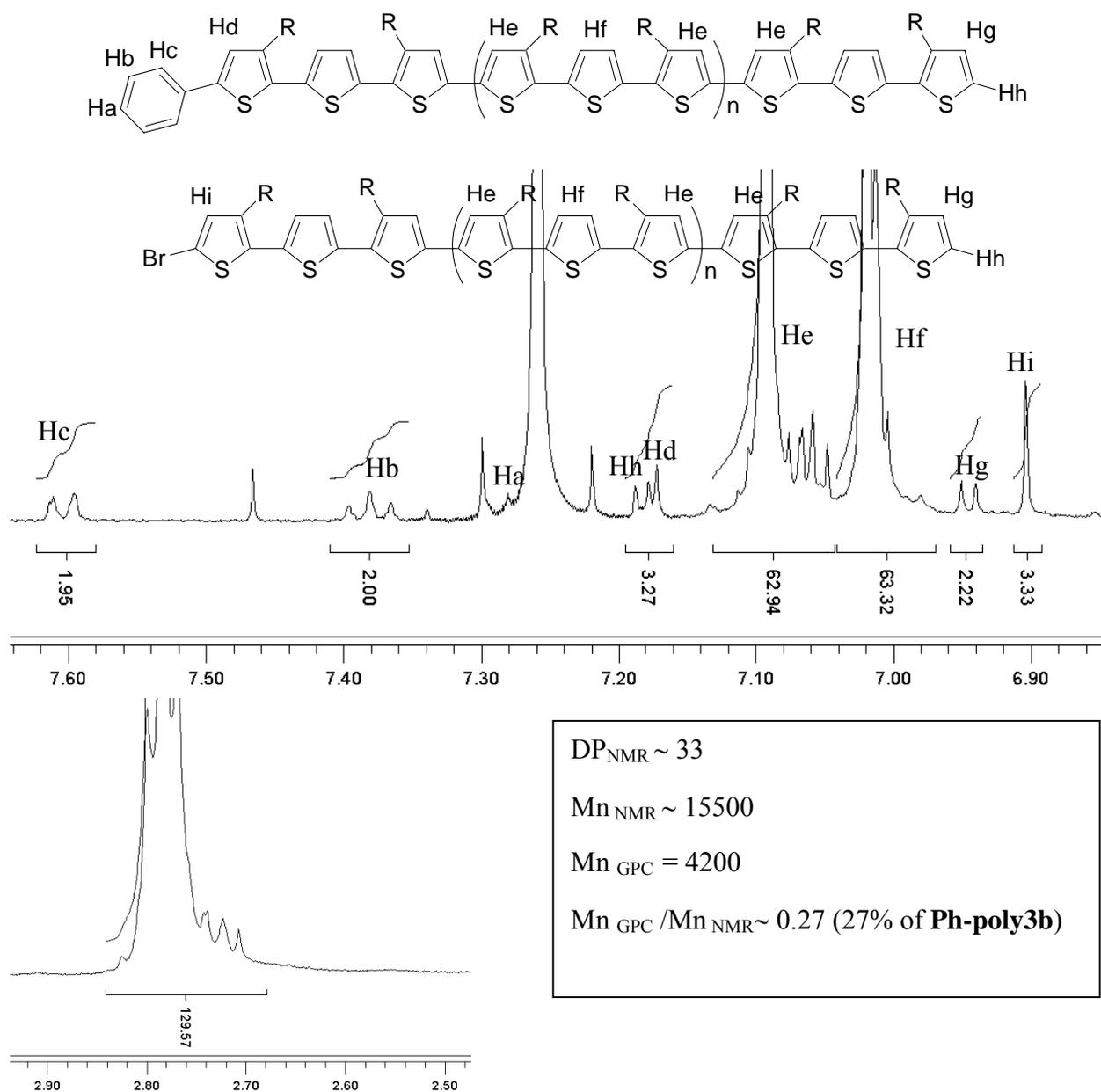


Figure S8a. ^1H NMR of crude reaction mixture obtained upon the $\text{Ph-Ni}(\text{PPh}_3)_2\text{-Br}$ mediated polymerization of **3b** (entry 7 of Table1) highlights the co-existence of the **poly3b** and a product of the protonation of the **3b** monomer (Figure S8b) suggesting the chain growth polycondensation mechanism.. The conversion of 68% can be deduced from the spectra ($2/2+0.92=0.68$).

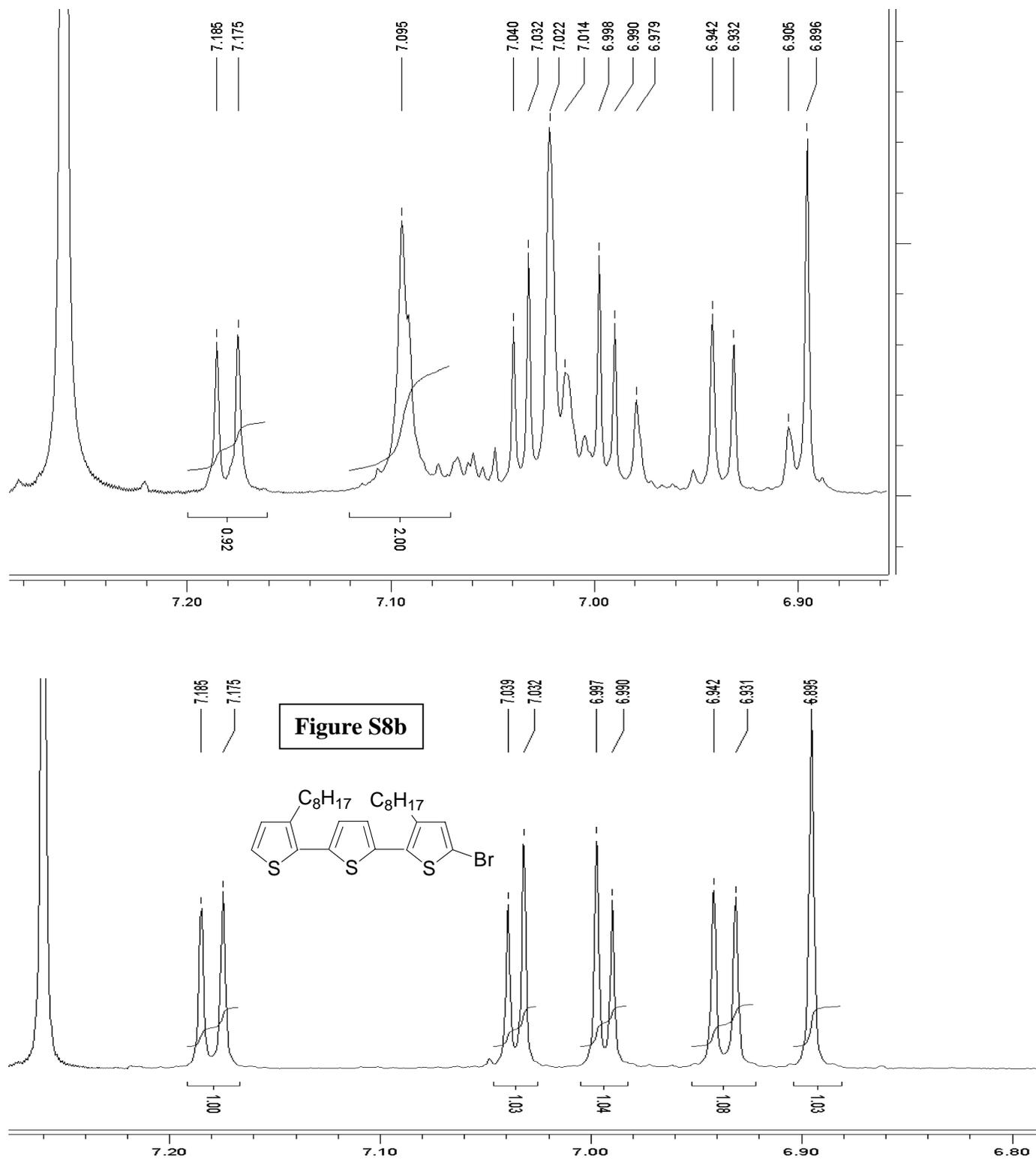


Figure S9. ^1H NMR of *o*-Tol/H sexi-3HT.

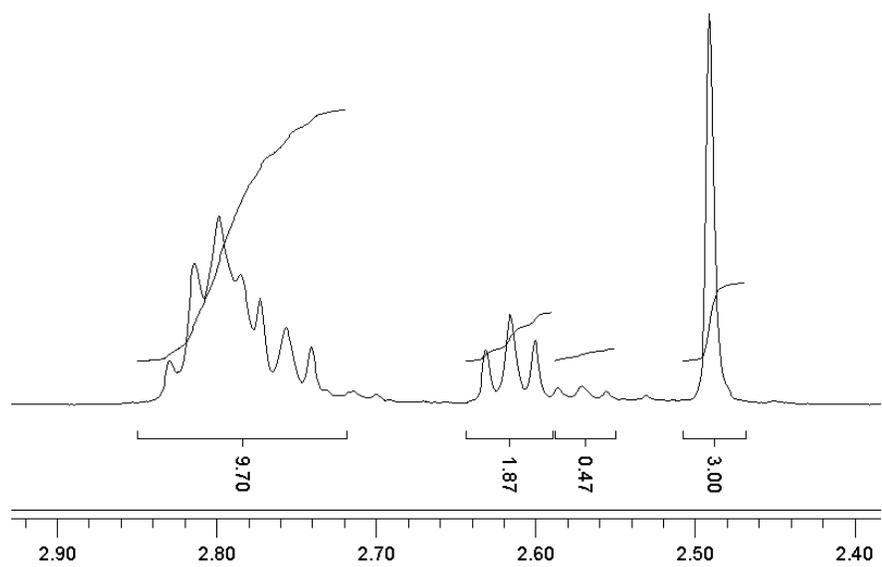
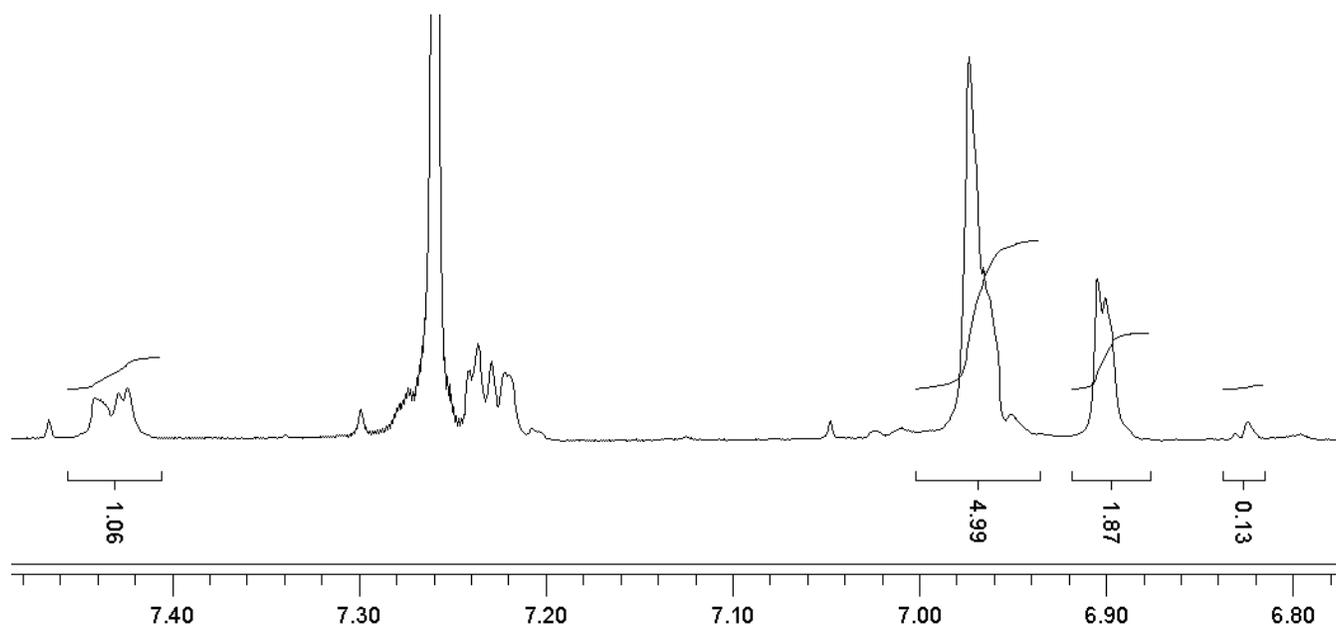
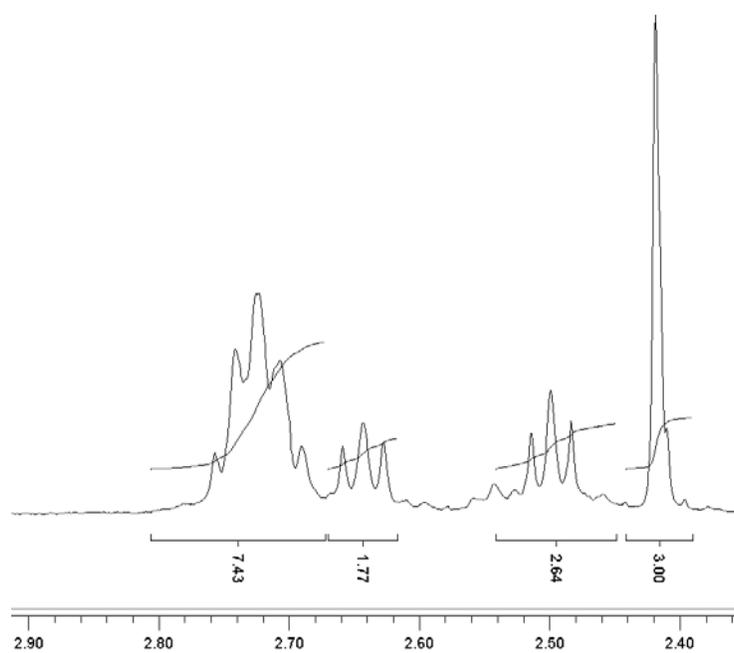
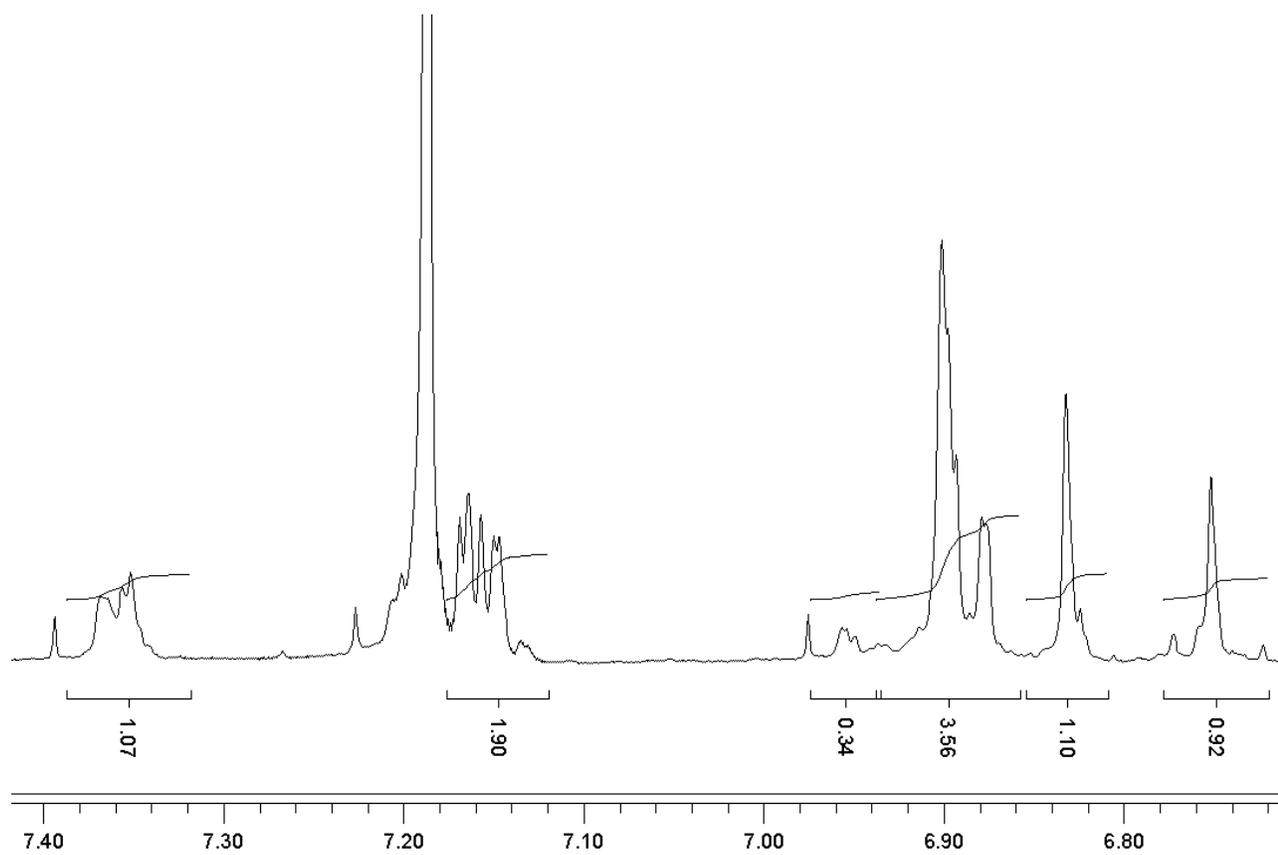


Figure S10. ^1H NMR of *o*-Tol/Br sexi-3HT.



Monomer precursors.

