Supporting Information

Evidence for catalyst association in the catalyst transfer polymerization of thieno[3,2-*b*]thiophene

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1 Reagents and Instrumentation

All reagents were purchased from Sigma-Aldrich, Acros Organics, Merck, TCI or Alfa Aesar. Tetrahydrofuran (THF) and diethylether (Et_2O) were dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). ^1H NMR and ^{13}C NMR measurements were carried out with a Bruker Avance 7 T (^1H: 300 MHz; ^{13}C: 75 MHz). ^{31}P NMR measurements were carried out with a Bruker Avance 9.4 T (162 MHz) .Gel permeation chromatography (GPC) measurements were done with a Shimadzu 10A apparatus with an absorbance detector and a differential refractometer in THF toward polystyrene standards. GC-MS spectra were performed on a device composed out of a GC with a Thermo-Finnigan oven with a Restek Rxi-5m (crossbond 5% diphenyl/ 95% dimethyl polysiloxane) column of 20 m, 0.18 mm internal diameter and an ion trap mass spectrometer ITQ900 with He carrier gas (0.3 mL/min). The measurements were started at an initial oven temperature of 60°C which was maintained for 1 minute. Afterwards a heating range of 15°C/min was applied until a temperature of 300°C was reached. Finally, the maximum temperature of 300°C was maintained for 2 minutes. The inlet temperature was 250°C. CI and ESI-MS spectra were recorded on a Thermo Electron LCQ Advantage ion trap apparatus with a mass range of 50-2000 amu. 2,5-dibromo-3,6-dioctylthienothiophene, 2,5-dibromo-3,6-di(2'-ethyl-hexyl)thienothiophene[1] and Ph-Pd(P*t*-Bu_3)-Br[2] were synthesized as described in literature.

2 Grignard metathesis optimization

2.1 Synthesis & characterization of 2-bromo-3,6-dioctylthiothieno[3,2-*b*]thiophene

2.1.1 Synthetic procedure

3,6-dioctylthiothieno[3,2-*b*]thiophene (6.00 mmol; 2.57 g) was dissolved in dry THF (100 mL), shielded from light and brought under an argon atmosphere. After the solution was cooled down to 0°C, *N*-bromosuccinimide (6.00 mmol; 1.07 g) was slowly added. After five minutes, the reaction mixture was allowed to reach room temperature and the reaction process was monitored on TLC (eluent: heptane). After 4 hours, the reaction mixture was extracted with heptane and washed with an aqueous $Na_2S_2O_3$ solution. Subsequently, the combined organic layers were dried using $MgSO_4$ and after filtration, the solvent was evaporated under reduced pressure. The crude product was further purified using column chromatography (silica, eluent: heptane). The pure product was isolated as a white solid. (1.85 g; 61%)

δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.30 (1H, s), 2.89 (4H, q), 1.60 (4H, m), 1.43 (4H, m), 1.25 (16H, m), 0.87 (6H, t); δ_C (75 MHz, $CDCl_3$, Me_4Si) 141.1, 139.1, 126.2, 125.6, 124.9, 119.1, 34.8, 34.6, 31.8, 30.0, 29.7, 29.6, 29.1, 28.5, 28.4, 22.6, 14.1; CI-MS: 509 [M^+]; 363 [M^+-SC_8H_{17}]; 284 [M^+-SC_8H_{17}-Br]

2.1.2 ^{1}H NMR spectrum

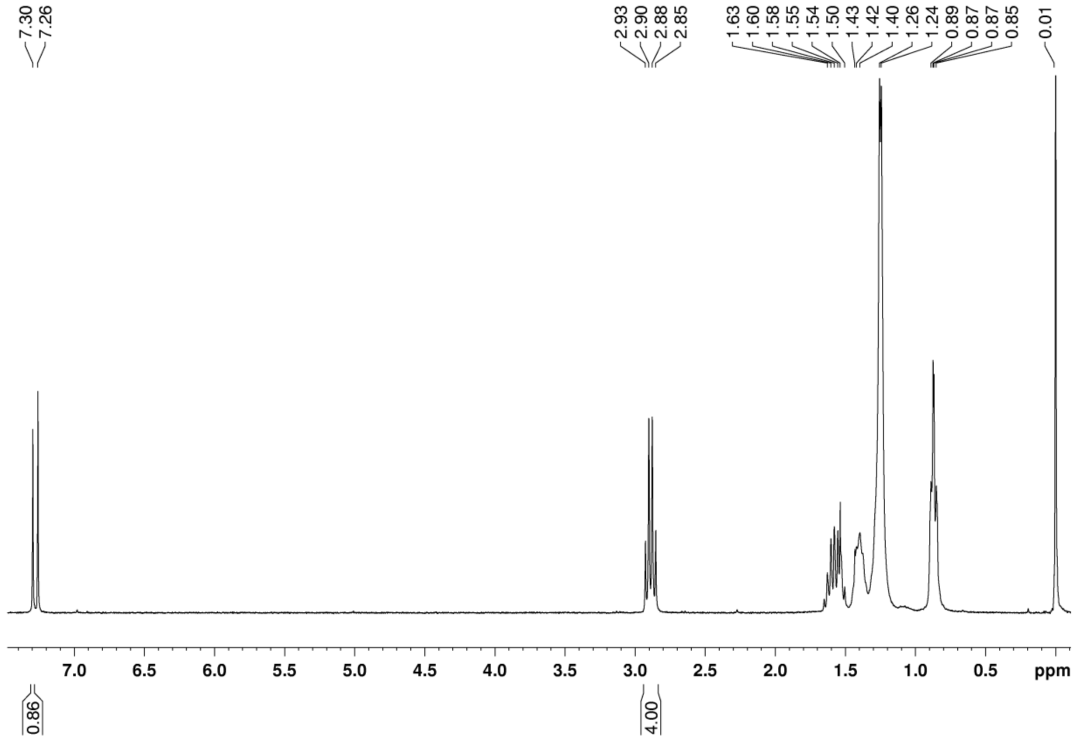

Figure S1. ^{1}H NMR spectrum in $CDCl_3$ of 2-bromo-3,6-dioctylthiothieno[3,2-b]thiophene.

2.1.3 ^{13}C NMR spectrum

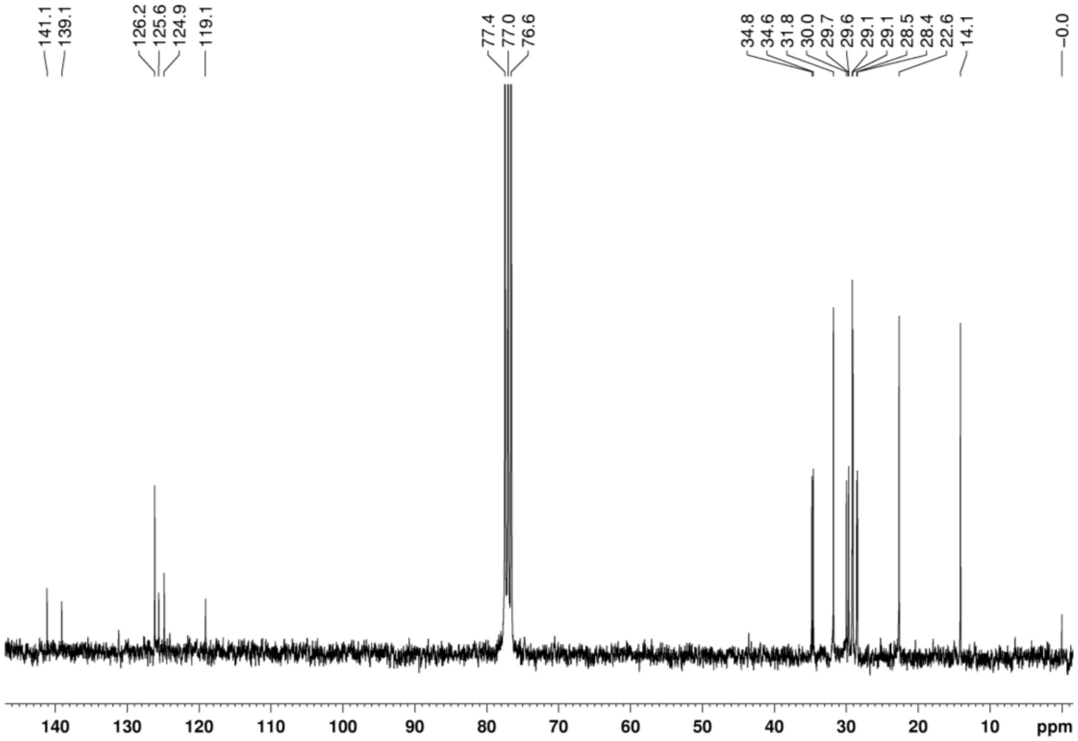

Figure S2. ^{13}C NMR spectrum in $CDCl_3$ of 2-bromo-3,6-dioctylthiothieno[3,2-b]thiophene.

2.2 GRIM results

2.2.1 Optimized GRIM test procedure

2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (0.100 mmol; 56.9 mg) was brought under argon atmosphere, after which dry THF (1.42 mL) was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.0782 mL; 1.27 M) was added at room temperature. After 45 minutes, the reaction mixture was quenched with H_2O. The mixture is then extracted with dichloromethane, dried with $MgSO_4$ and the solvent was evaporated under reduced pressure. The obtained crude product was analyzed in order to check the conversion.

2.2.2 ^{1}H NMR spectrum

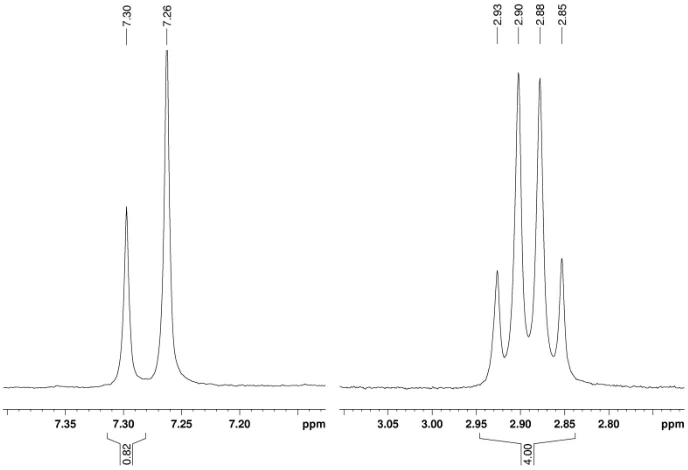

Figure S3. Relevant ^{1}H NMR signals in $CDCl_3$ of the GRIM quench. The signal of the β-methyl groups are calibrated to 4. The obtained aromatic integration value of 0.82 is 95.4% of the integration value of 2-bromo-3,6-dioctylthiothieno[3,2-b]thiophene.

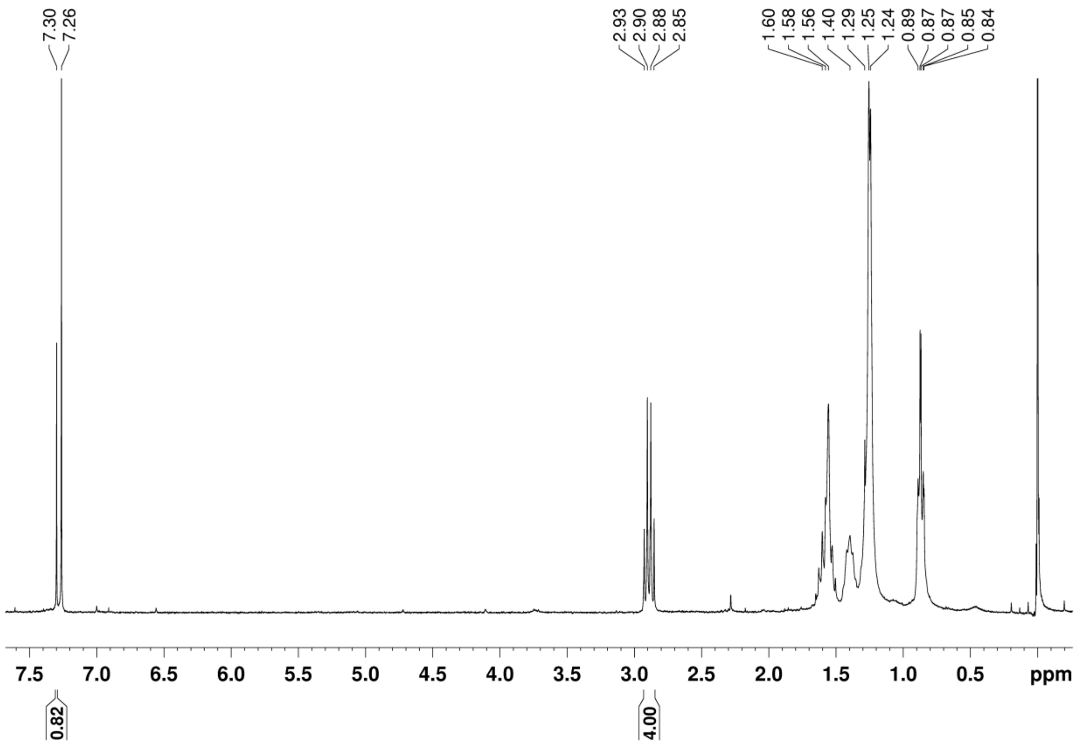

Figure S4. ^{1}H NMR in CDCl3 of the GRIM quench

2.2.3 ^{13}C NMR spectrum

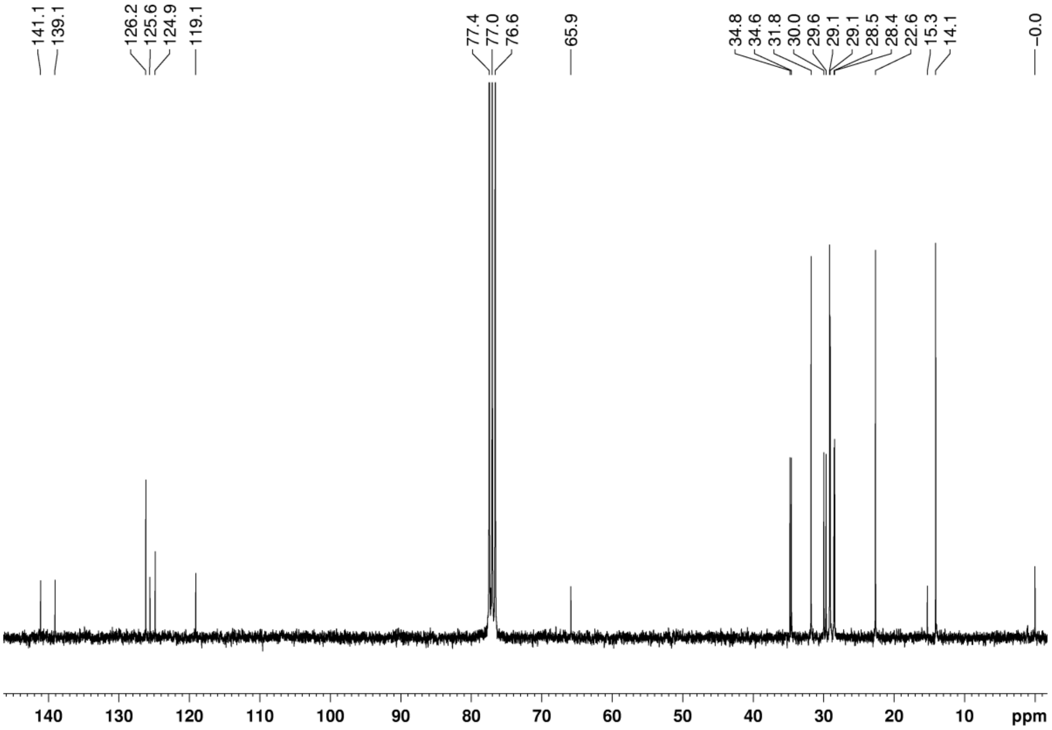

Figure S5. ^{13}C NMR spectrum in $CDCl_3$ of the GRIM quench. Signals at 65.9 and 15.3 ppm are ascribed to THF.

3 Synthesis & characterization of Pd(NHC)PPh_3

3.1 Synthetic procedure

Pd-PEPPSI-iPr (0.500 mmol; 0.340 g) and PPh_3 (0.500 mmol; 0.131 g) are combined in a flask which is brought under argon atmosphere and dry THF (15 mL) is subsequently added. The reaction mixture is then heated up to 60°C and stirred for 3 h. Afterwards, the solution is concentrated to a volume of ± 2 mL, precipitated in pentane (25 mL) at 0°C and left overnight at -20°C. Subsequently, the precipitate was filtered off and dried under vacuum. m= 0.120 g, yield= 58%. δ_H (300 MHz; $CDCl_3$; Me_4Si) 7.56 (2H, t), 7.36 (4H, d), 7.31-7.26 (9H, m), 7.19-7.14 (6H, d-d), 7.13 (2H, d), 3.20 (4H, quint), 1.30 (12H, d), 1.08 (12H, d); δ_C (75 MHz, $CDCl_3$, Me_4Si) 146.8, 135.5, 135.0, 134.9, 130.7, 130.1, 129.8, 129.7, 129.7, 127.6, 127.5, 124.3, 124.2, 123.8, 28.6, 26.3, 22.9; δ_P (162 MHz, $CDCl_3$, Me_4Si) 20.7.

3.1.1 ^{1}H NMR spectrum

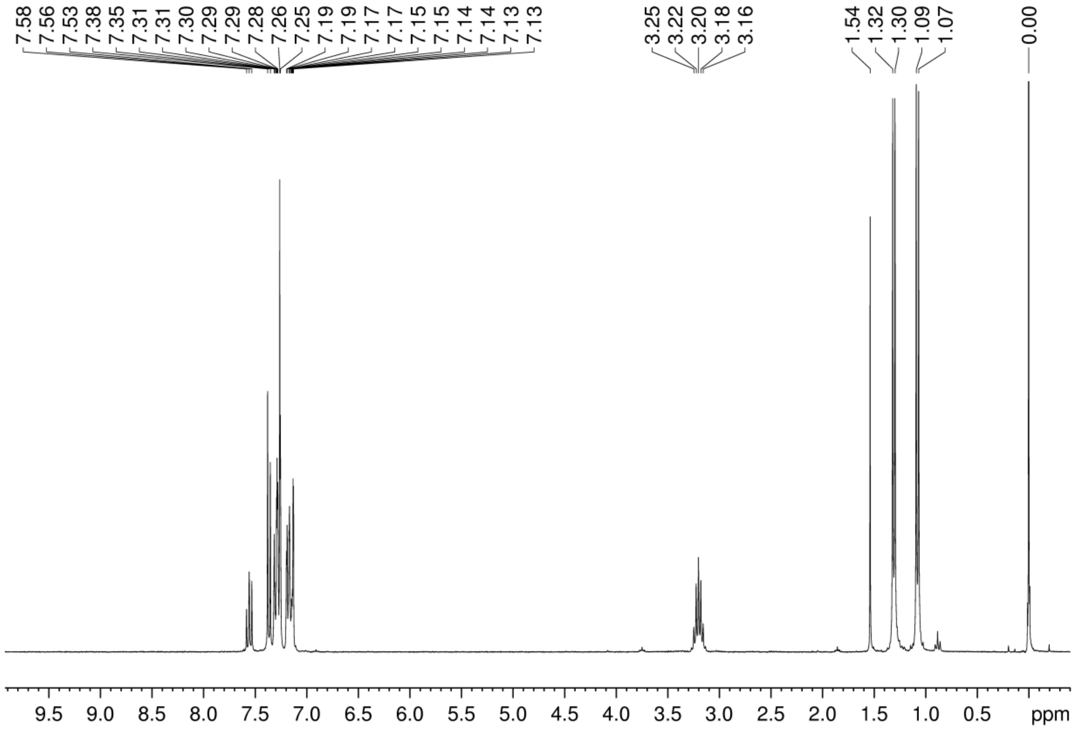

Figure S6. ^{1}H NMR spectrum in $CDCl_3$ of the Pd(NHC)PPh_3 catalyst.

3.2 ^{13}C NMR spectrum

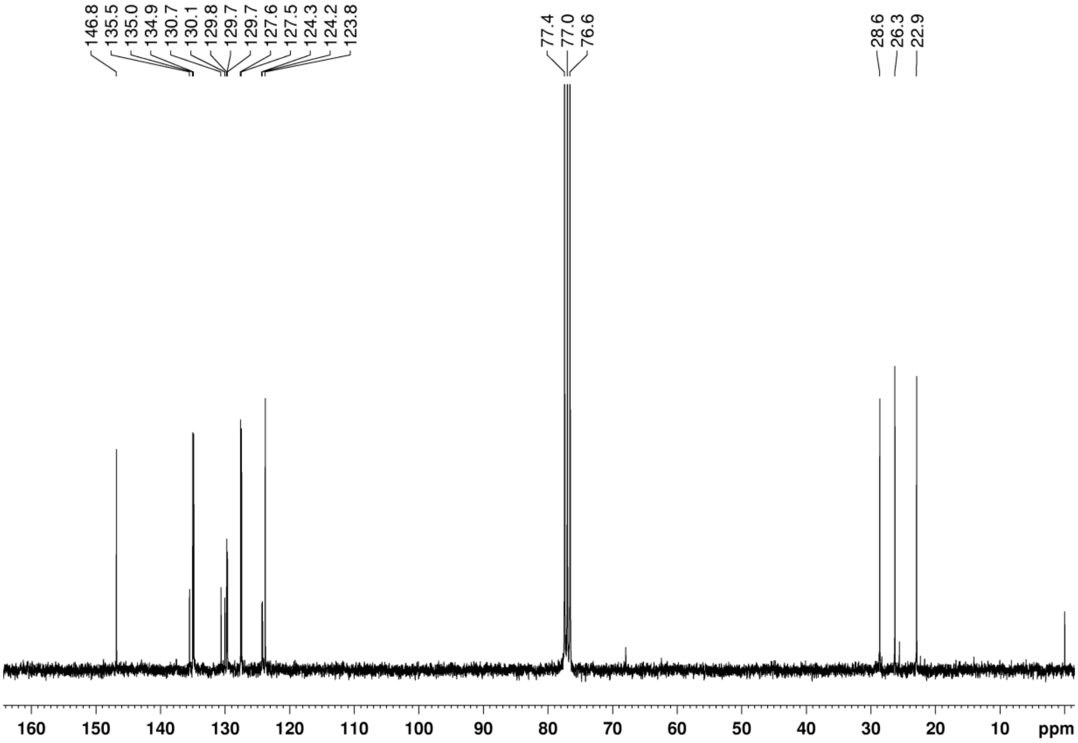

Figure S7. ^{13}C NMR spectrum in $CDCl_3$ of the $Pd(NHC)PPh_3$ catalyst.

3.3 ^{31}P NMR spectrum

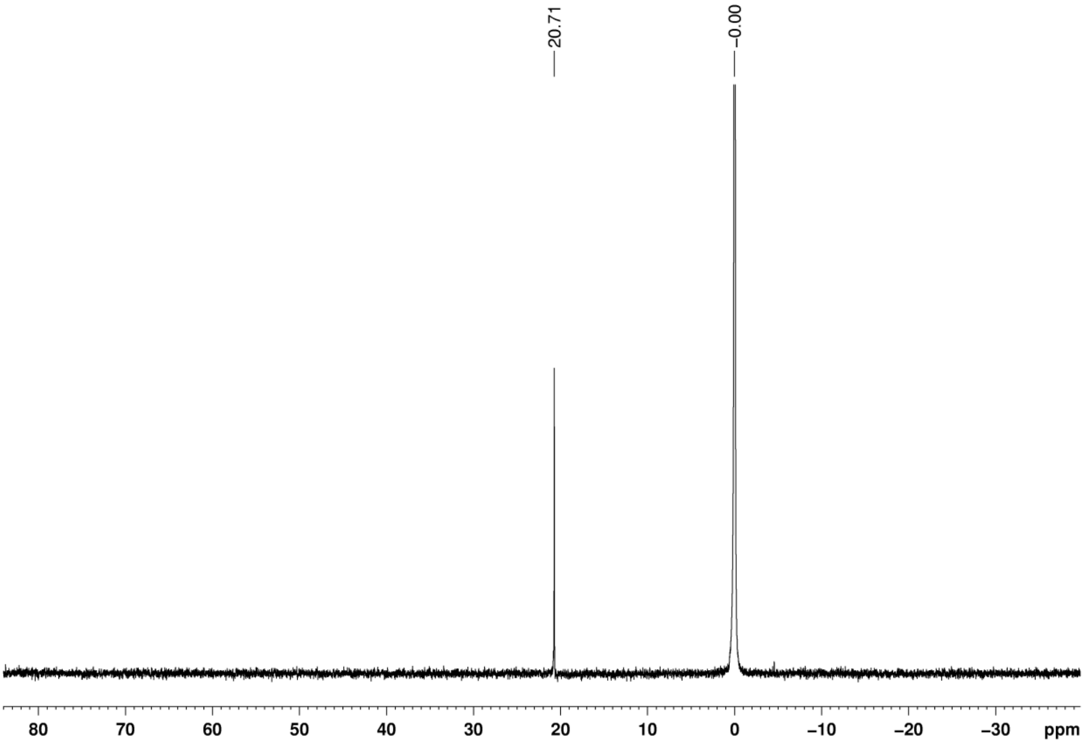

Figure S8. ^{31}P NMR spectrum of the $Pd(NHC)PPh_3$ catalyst. Spectrum measured in THF-d8 relative to a H_3PO_4 (80%) reference.

4 Polymerization results

4.1 Ni-catalyzed polymerizations results

4.1.1 General polymerization procedure for Ni-catalyzed polymerizations

2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (0.100 mmol; 56.9 mg) was brought under argon atmosphere, after which dry THF (1.42 mL) was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.0782 mL; 1.27 M) was added at room temperature. After 45 minutes, the reaction mixture was cannulated to an argon purged flask containing the Ni-catalyst (5.00 mol%, 5.00 µmol) in dry THF (1.5 mL). After a polymerization time of 2 h, the reaction mixture was terminated with acidified THF(HCl) and investigated with GPC.

Catalyst	Quantity used
Ni(dppp)Cl$_2$	2.71 mg
Ni(dppe)Cl$_2$	2.64 mg
Ni(depe)Cl$_2$	1.68 mg
Ni(NHC)PPh$_3$	3.90 mg

4.1.2 GPC results of the Ni-catalyzed polymerizations

4.1.2.1 Ni(dppp)Cl$_2$

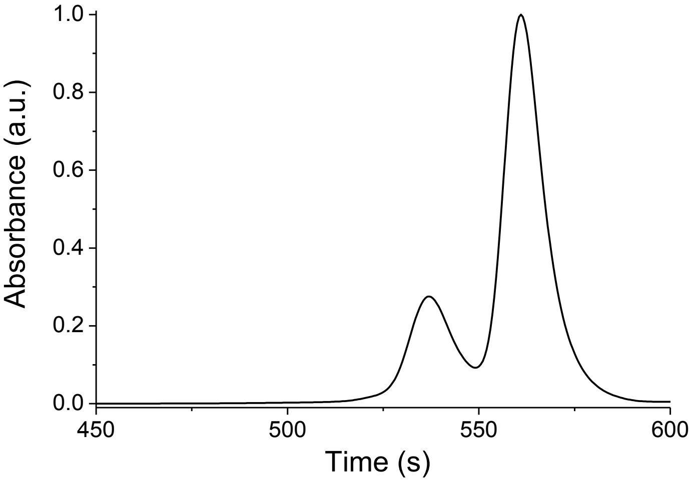

Figure S9. GPC spectrum of the Ni(dppp)Cl$_2$ catalyzed polymerization.

4.1.2.2 Ni(dppe)Cl$_2$

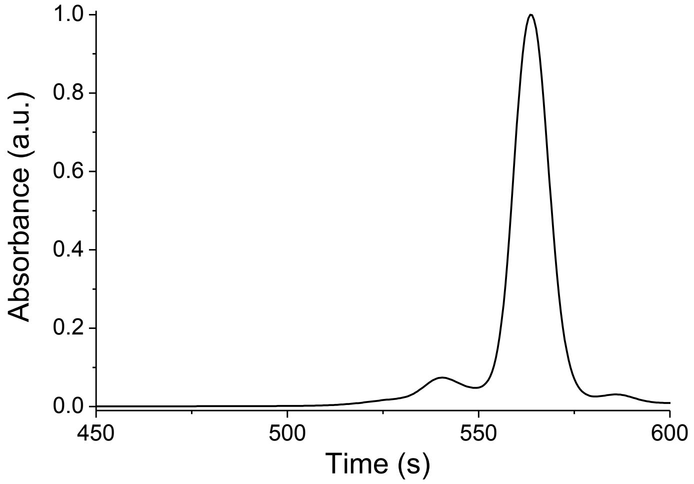

Figure S10. GPC spectrum of the Ni(dppe)Cl$_2$ catalyzed polymerization.

4.1.2.3 Ni(depe)Cl$_2$

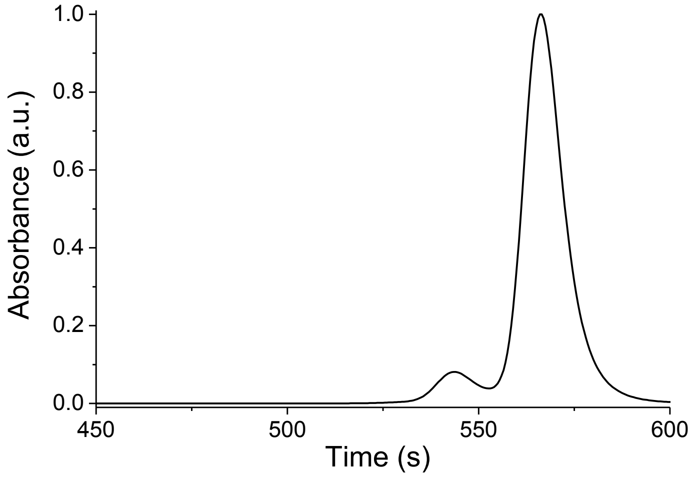

Figure S11. GPC spectrum of the Ni(depe)Cl$_2$ catalyzed polymerization.

4.1.2.4 Ni(NHC)PPh$_3$

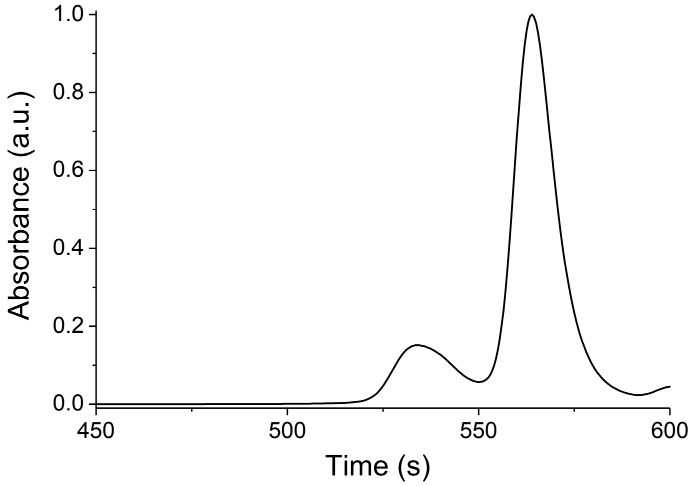

Figure S12. GPC spectrum of the Ni(NHC)PPh$_3$ catalyzed polymerization.

4.2 Pd-catalyzed polymerizations results

4.2.1 General polymerization procedure for Pd-catalyzed polymerizations

2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (0.100 mmol; 56.9 mg) was brought under argon atmosphere, after which dry THF (1.42 mL)was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.0782 mL; 1.27 M) was added at room temperature. After 45 minutes, the reaction mixture was cannulated to an argon purged flask containing Schlenk dried $ZnBr_2$ (0.200 mmol; 45.0 mg). After 15 minutes, the monomer mixture was added to an argon purged flask containing the Pd-catalyst (4 mol%, 4.00 µmol) dissolved in dry THF (8.5 mL). After a polymerization time of 2 h, the reaction mixture was terminated with acidified THF (HCl) and investigated with GPC.

Catalyst	Quantity used
Pd-PEPPSI-iPr	2.72 mg
Pd(NHC)PPh_3	3.31 mg
PhPd(P*t*-Bu_3)	1.86 mg

4.2.2 GPC results of the Pd-catalyzed polymerizations

4.2.2.1 *Pd-PEPPSI-iPr*

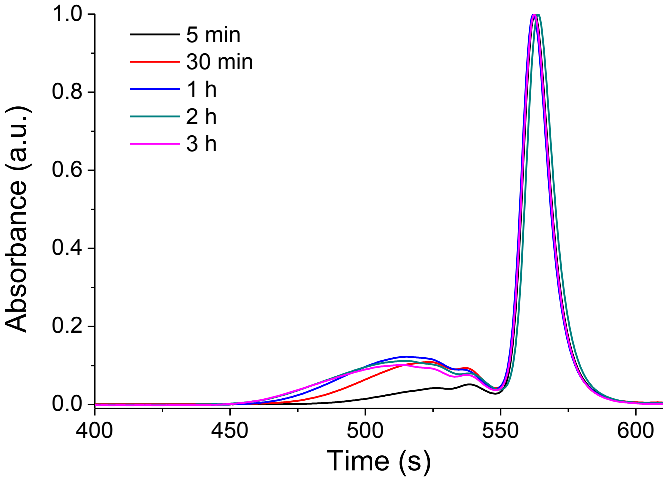

Figure S13. GPC spectra recorded during the Pd-PEPPSI-iPr catalyzed polymerization.

4.2.2.2 *Evolution of $\overline{M}_n$ and Đ in function of time for the Pd-PEPPSI-iPr polymerization*

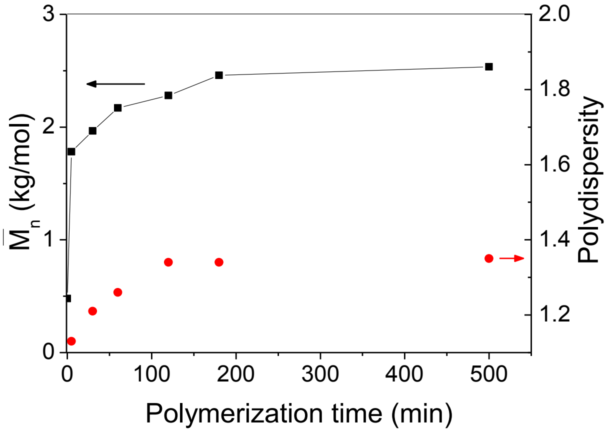

Figure S14. Overview of the evolution of the molar mass and polydispersity in function of the polymerization time.

4.2.2.3 Pd(NHC)PPh$_3$

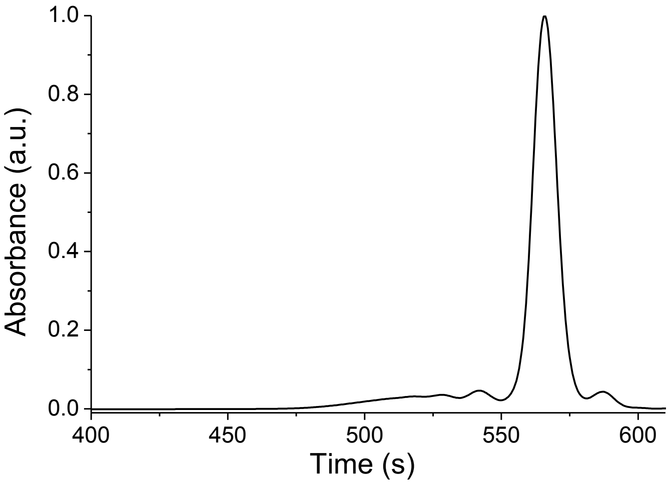

Figure S15. GPC spectrum of the Pd(NHC)PPh$_3$ catalyzed polymerization.

4.2.2.4 Pd(Pt-Bu$_3$)

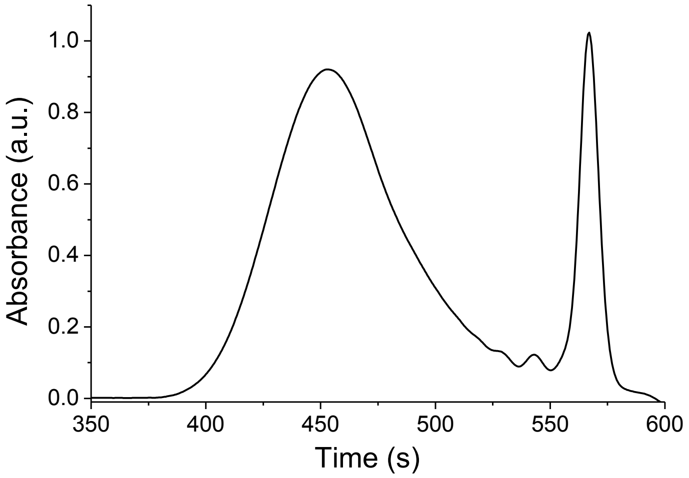

Figure S16. GPC spectrum of the Pd(P*t*-Bu$_3$) catalyzed polymerization.

4.3 Further investigation of the Pd(P*t*-Bu$_3$) catalyzed polymerization

4.3.1 Polymerization procedure of 2,5-dibromo-3,6-di(2'-ethylhexylthio) thieno[3,2-*b*]thiophene with a Pd(P*t*-Bu$_3$) catalyst

2,5-dibromo-3,6-di(2-ethylhexylthio)thieno[3,2-*b*]thiophene (0.100 mmol; 56.9 mg) was brought under argon atmosphere, after which dry THF (1.42 mL) was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.0782 mL; 1.27 M) was added at room temperature. After 45 minutes, the reaction mixture was cannulated to an argon purged flask containing Schlenk dried ZnBr$_2$ (0.200 mmol; 45.0 mg). After 15 minutes, the monomer mixture was added to an argon purged flask containing Ph-Pd(P*t*-Bu$_3$)-catalyst (4 mol%; 1.86 mg) dissolved in dry THF (8.5 mL). After a polymerization time of 2 h, the reaction mixture was terminated with acidified THF (HCl) and investigated with GPC. ($\overline{M}_n$= 5.9 kg/mol; Đ= 1.7)

4.3.2 GPC spectrum of poly(3,6-di(2’-ethylhexylthio) thieno[3,2-*b*]thiophene)

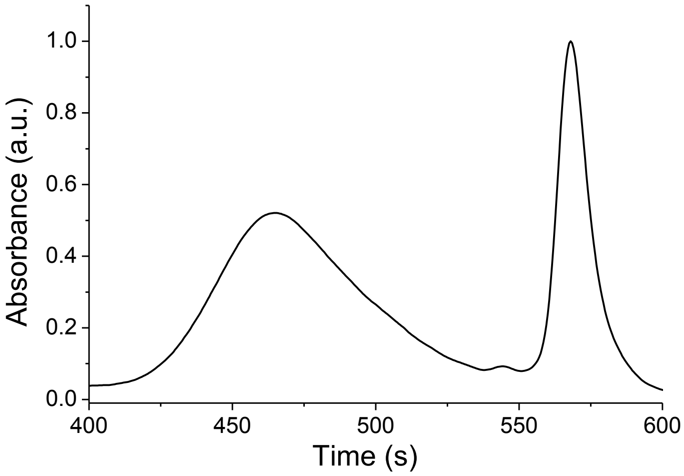

Figure S17. GPC spectrum of the Pd(P*t*-Bu$_3$) catalyzed polymerization of poly(3,6-di(2’-ethylhexylthio) thieno[3,2-*b*]thiophene).

4.3.3 Chain extension experiment of 2,5-dibromo-3,6-dioctylthieno[3,2-*b*]thiophene with a Pd(P*t*-Bu$_3$) catalyst

2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (0.150 mmol; 85.3 mg) was brought under argon atmosphere, after which dry THF (2.14 mL) was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.11 mL; 1.32 M) was added at room temperature. After 45 minutes, the reaction mixture was cannulated to an argon purged flask containing Schlenk dried ZnBr$_2$ (0.30 mmol; 67.6 mg). After 15 minutes, part of the monomer mixture (1.5 mL) was added to an argon purged flask containing the Ph-Pd(P*t*-Bu$_3$)-catalyst (4 mol%, 1.86 mg) dissolved in dry THF (8.5 mL). After a polymerization time of 5 min, half of the polymerization mixture (0.75 mL) was quenched in acidified THF (HCl), while the second part of the monomer mixture (0.75 mL) was added to the remaining polymerization mixture. After an additional polymerization time of 1 h, this polymerization mixture was terminated with acidified THF (HCl) and both samples were investigated with GPC.

4.3.4 GPC spectrum of the chain extension experiment

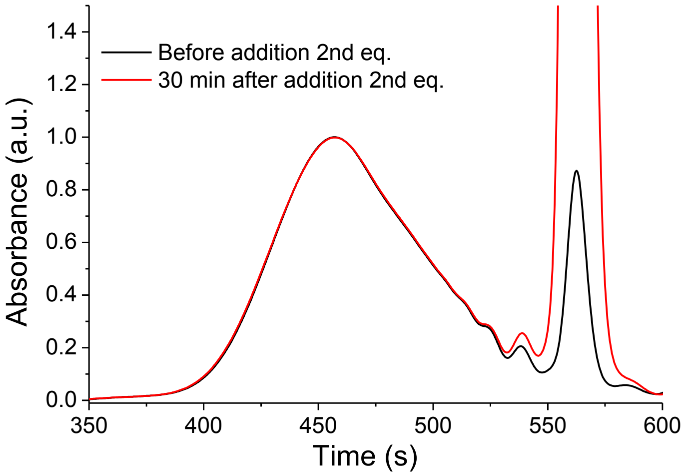

Figure S18. GPC spectra of the chain extension experiment on the Pd(P*t*-Bu$_3$) catalyzed polymerization. The peak at 570 s originates from the monomer.

4.3.5 Polymerization procedure of 2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene with varying mol% of initiator with a Pd(P*t*-Bu$_3$) catalyst

2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (0.400 mmol; 0.228 g) was brought under argon atmosphere, after which dry THF (5.69 mL) was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.31 mL; 1.27 M) was added at room temperature. After 45 minutes, the reaction mixture was cannulated to an argon purged flask containing Schlenk dried ZnBr$_2$ (0.200 mmol; 45.0 mg). After 15 minutes, the monomer mixture was divided in four equal parts (1.5 mL) and each part was added to an argon purged flask containing the appropriate amount of the Ph-Pd(P*t*-Bu$_3$)-catalyst dissolved in dry THF (8.5 mL). After a polymerization time of 2 h, the reaction mixtures were terminated with acidified THF (HCl) and investigated with GPC.

Mol%	Catalyst mass	$\bar{M}_n$ (kg/mol)	Đ
2	0.931 mg	8.4	2.0
4	1.86 mg	5.8	2.0
10	4.66 mg	4.9	1.8
20	9.31 mg	3.4	1.6

4.3.6 Polymerization procedure of 2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene with varying mol% of transfer agent with a Pd(P*t*-Bu$_3$) catalyst

2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (0.400 mmol; 0.228 g) was brought under argon atmosphere, after which dry THF (5.69 mL) was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.31 mL; 1.27 M) was added at room temperature. After 45 minutes, the reaction mixture was cannulated to an argon purged flask containing Schlenk dried ZnBr$_2$ (0.200 mmol; 45.0 mg). After 15 minutes, the monomer mixture was divided in four equal parts (1.5 mL) and each part was added to an argon purged flask containing the Ph-Pd(P*t*-Bu$_3$)-catalyst (4 mol%, 1.86 mg) and the appropriate amount of bromobenzene dissolved in dry THF (8.5 mL). After a polymerization time of 2 h, the reaction mixtures were terminated with acidified THF (HCl) and investigated with GPC.

Mol% bromobenzene	mass	$\bar{M}_n$ (kg/mol)	Đ
0	-	5.9	1.83
20	3.14 mg	5.2	1.77
100	15.7 mg	4.9	1.75
200	31.4 mg	4.6	1.77

5 Mechanistic KCTP study

5.1 Protocol of the Ni(dppp)Cl₂ polymerizations with different catalyst loading

2,5-dibromo-3,6-dioctylthiothieno[3,2-*b*]thiophene (0.100 mmol; 56.9 mg) was brought under argon atmosphere, after which dry THF (1.42 mL) was added. To the reaction mixture, *i*-PrMgCl.LiCl (0.0782 mL; 1.27 M) was added at room temperature. After 45 minutes, the reaction mixture was cannulated to an argon purged flask containing Ni(dppp)Cl_2 in dry THF (1.5 mL). After a polymerization time of 2 h, the reaction mixture was terminated with acidified THF (HCl) and investigated with GPC.

Mol%	Quantity used
5	2.71 mg
10	5.42 mg
25	13.6 mg
30	16.3 mg

5.2 GPC spectrum of the isolated dimer species

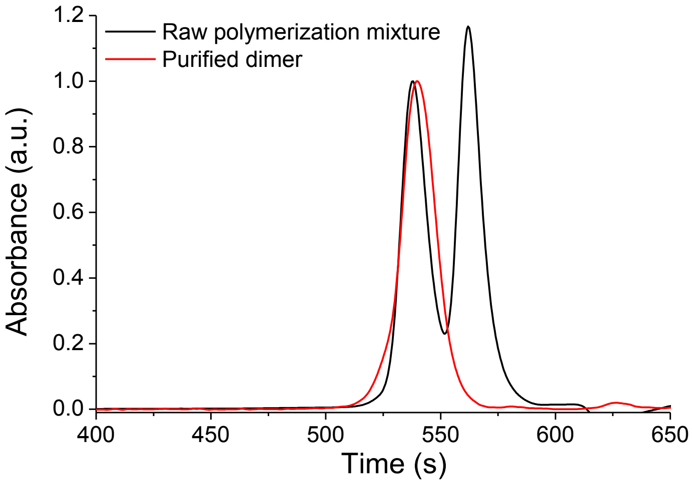

Figure S19. GPC spectra of the raw polymerization mixture (25 mol% Ni(dppp)Cl_2) and the purified dimer.

5.3 Characterization of the isolated TT dimer

5.3.1 ^{1}H NMR

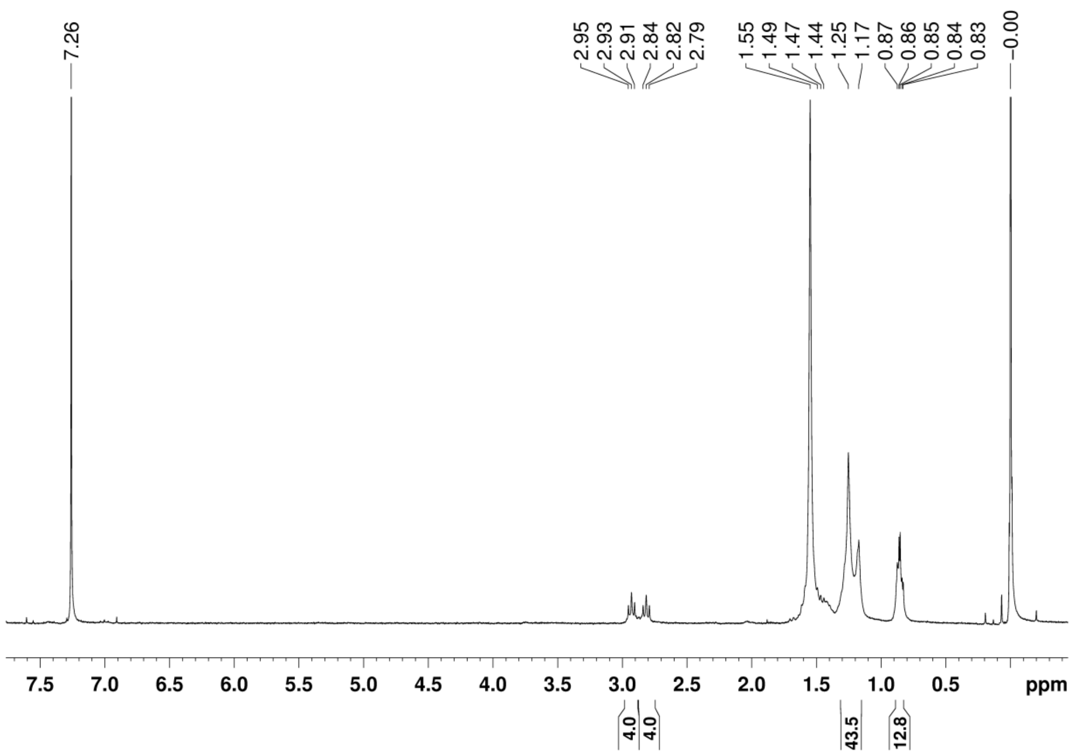

Figure S20. ^{1}**H NMR spectrum in CDCl$_3$ of the isolated TT dimer. Two different environments are observed for the β-methyl protons of the side-chains, corresponding to a symmetrical dimer. Furthermore, no aromatic signals are present, confirming formation of the dibromo-substituted TT dimer.**

5.3.2 ^{13}C NMR

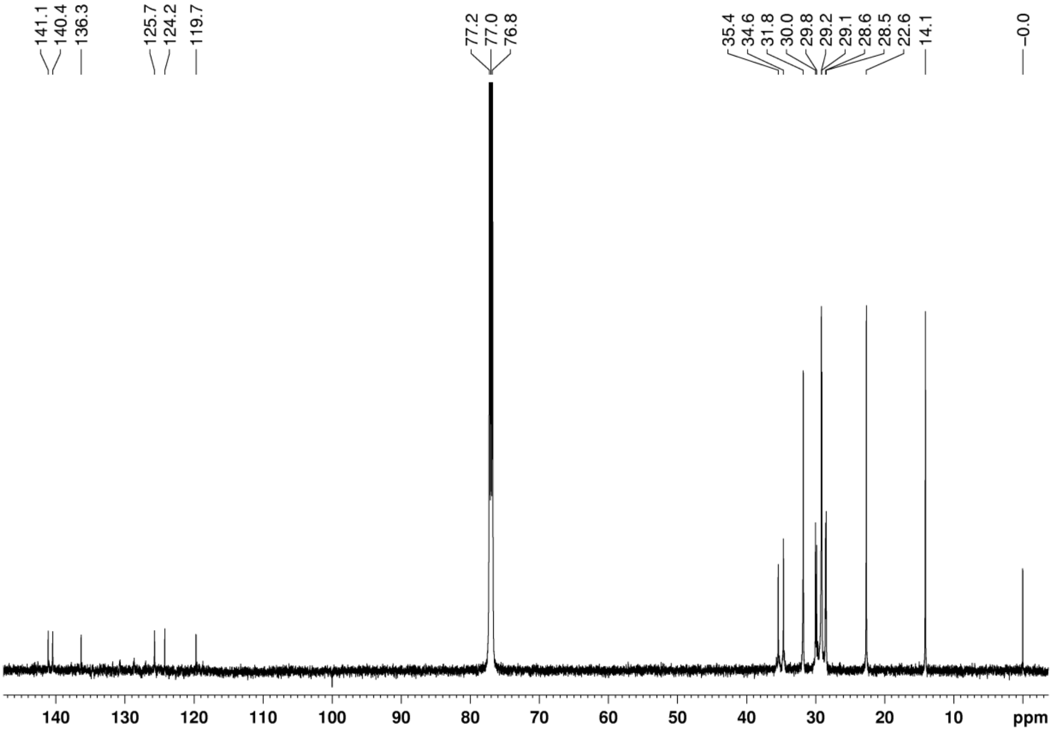

Figure S21. ^{13}**C NMR spectrum in CDCl$_3$ of the isolated TT dimer. The presence of six aromatic signals indicates a symmetric dimer molecule, *i.e.* the dibromo substituted dimer.**

5.3.3 ESI-MS

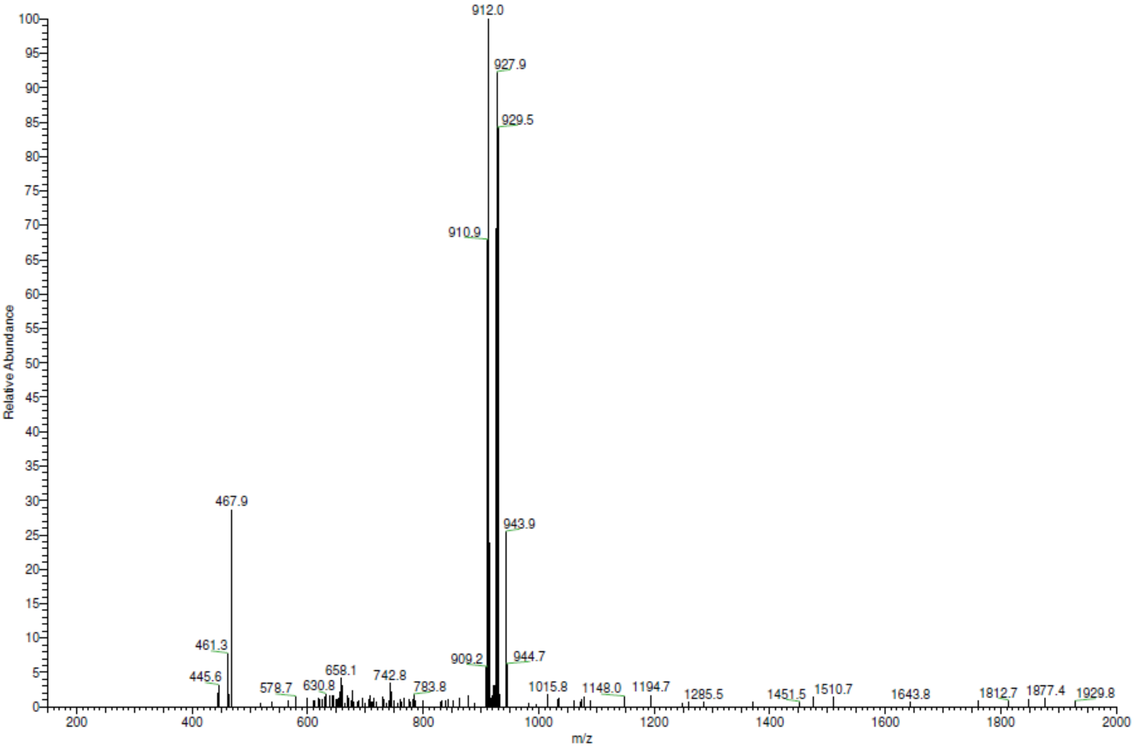

Figure S22. ESI-MS spectrum of the isolated TT dimer. Fragmentation of the dibromo TT dimer is observed. The main observed peaks at 944, 929 and 912 correspond to the dibromo dimer with loss of a sidechain fragment of respectively 5, 6 or 7 carbon atoms.

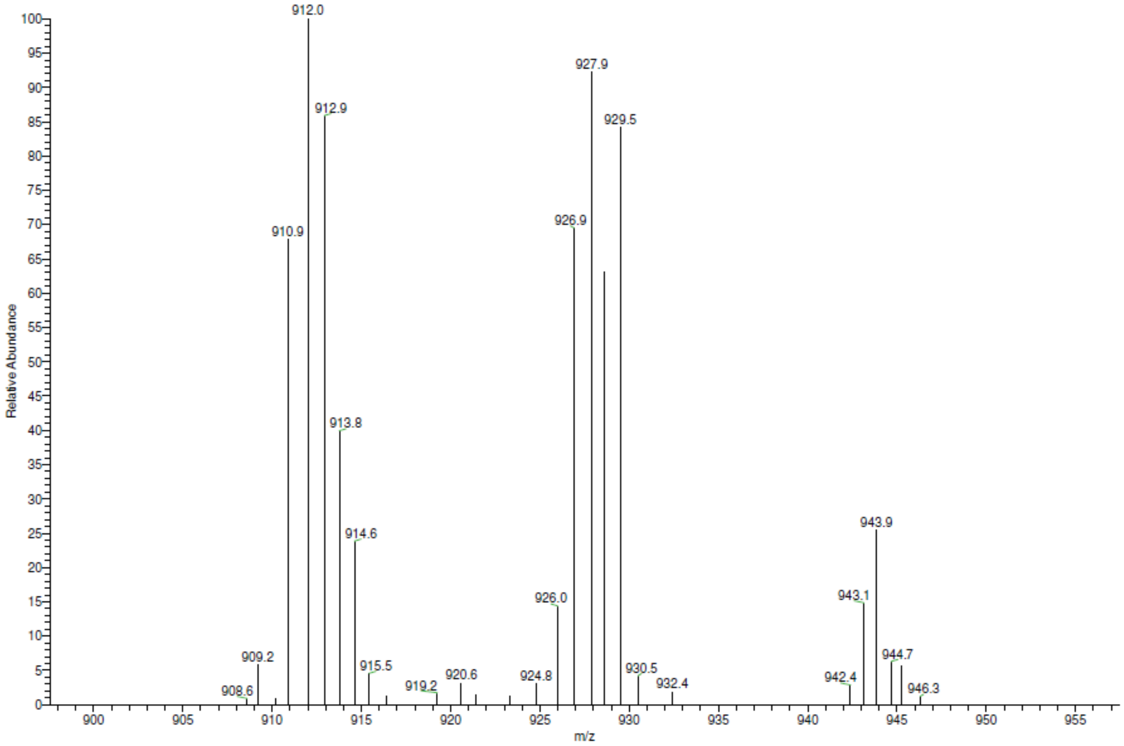

Figure S23 Zoom of the ESI-MS spectrum of the isolated TT dimer. The observed isomer pattern is in line with a dibromo substitution.

5.4 ^{31}P NMR spectra recorded during the KCTP reaction

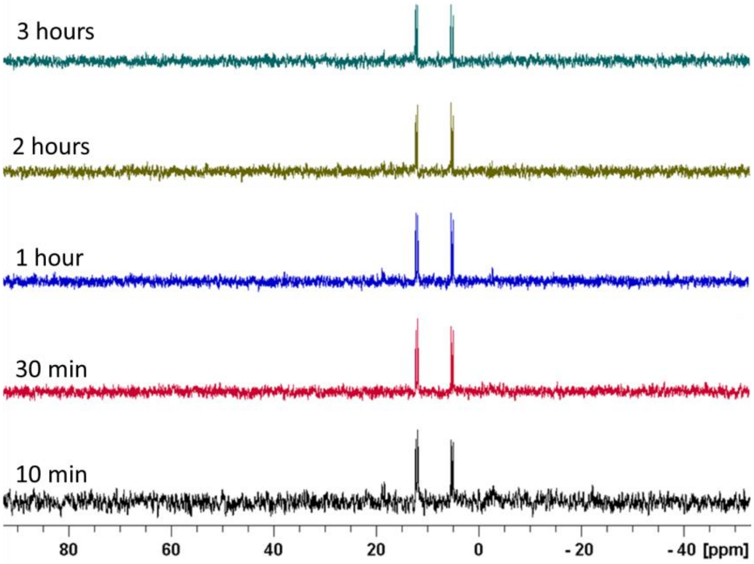

Figure S24. Overview of the ^{31}P NMR spectra recorded during the KCTP reaction. Spectra recorded in THF. Locking and calibration occurred by a prior measurement of a H_3PO_4 (80%) reference in THF-d8.

5.5 Kumada coupling of 3,6-dibromothieno[3,2-*b*]thiophene

5.5.1 Reaction protocol

3,6-dibromothieno[3,2-*b*]thiophene (0.220 mmol; 66.2 mg) and Ni(dppp)Cl_2 (2 mol%; 2.39 mg) were combined in a flask, brought under argon atmosphere and dissolved in dry Et_2O (2.00 mL). To this mixture, *n*-butylmagnesiumchloride (0.22 mL; 2.00 M in THF) was added dropwise. After a reaction time of 2 hours, an aliquot of the reaction was washed with water to remove the salts and the organic layer was analyzed with GC-MS.

5.5.2 GC-MS results

5.5.2.1 Reference 3,6-dibromothieno[3,2-b]thiophene

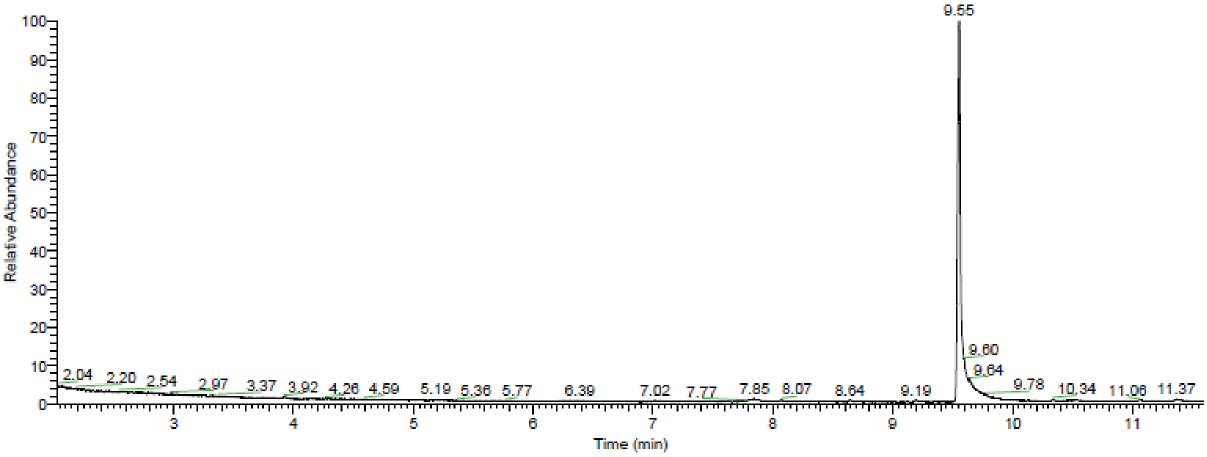

Figure S25. GC spectrum of 3,6-dibromothieno[3,2-*b*]thiophene.

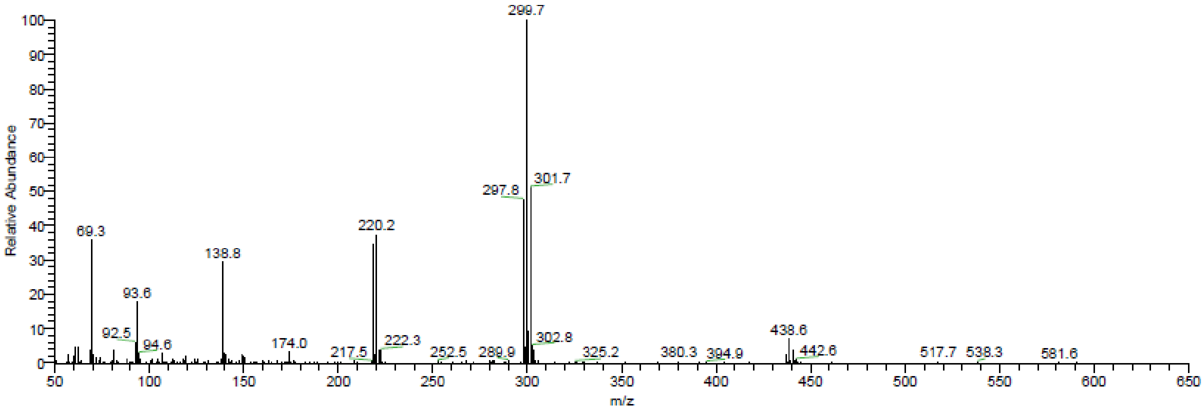

Figure S26. Mass spectrum corresponding to the GC signal at 9.55 min. The spectrum is assigned to 3,6-dibromothieno[3,2-*b*]thiophene.

5.5.2.2 *Crude reaction mixture*

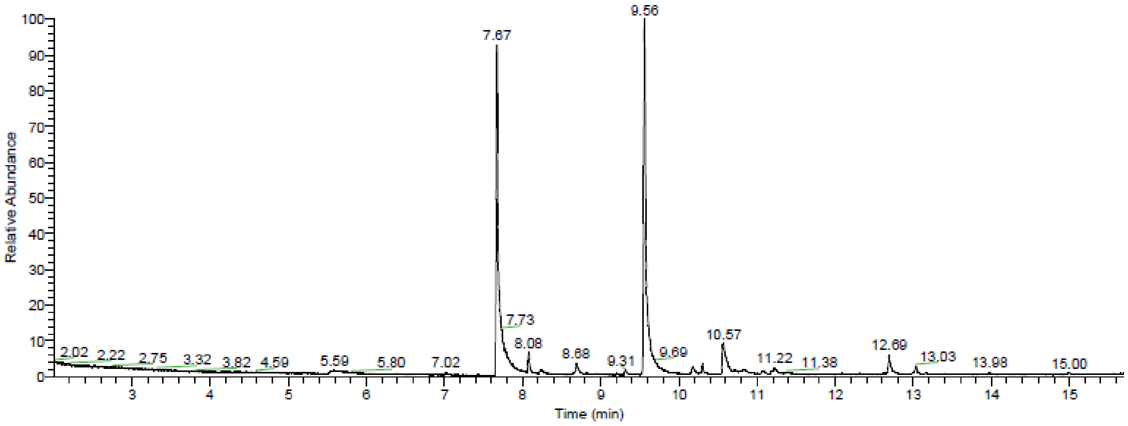

Figure 27. GC spectrum of the crude reaction mixture of the Kumada alkylation reaction of 3,6-dibromothieno[3,2-*b*]thiophene.

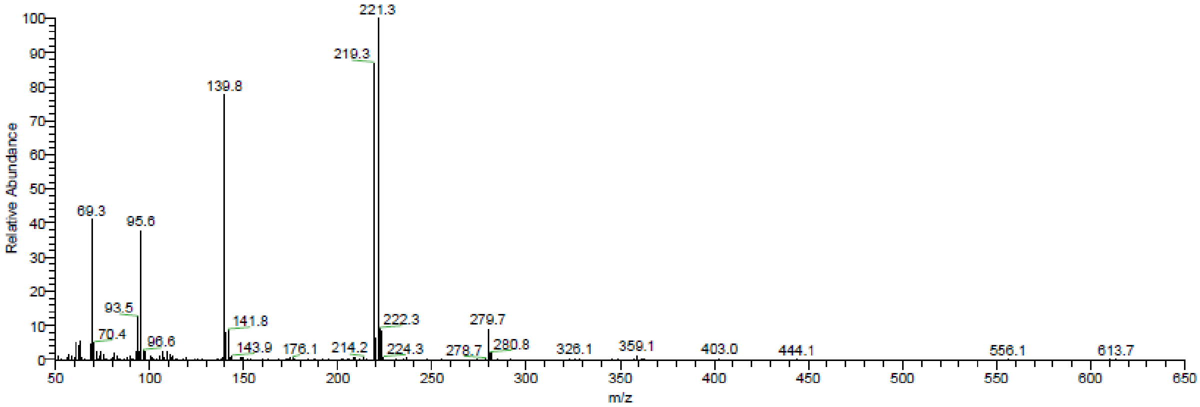

Figure S28. Mass spectrum corresponding to the GC signal at 7.67 min. The spectrum is assigned to 3-bromothieno[3,2-*b*]thiophene.

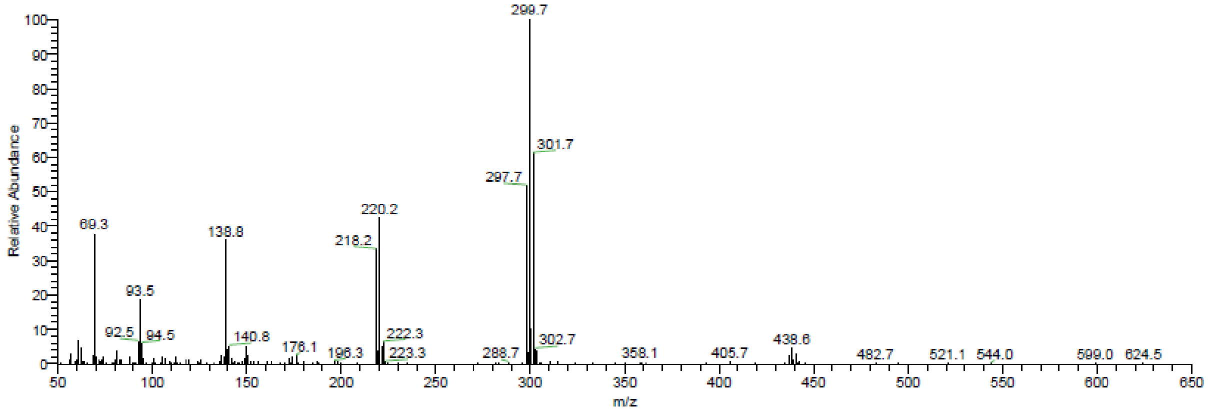

Figure S29. Mass spectrum corresponding to the GC signal at 9.56 min. The spectrum is assigned to 3,6-dibromothieno[3,2-*b*]thiophene.

5.6 Kumada coupling of 3-bromothiophene

5.6.1 Reaction protocol

3-bromothiophene (2.00 mmol; 0.326 g) and Ni(dppp)Cl_2 (2 mol%; 21.7 mg) were combined in a flask, brought under argon atmosphere and dissolved in dry Et_2O (10.0 mL). To this mixture, *n*-butylmagnesiumchloride (1.2 mL; 2.00 M in THF) was added dropwise. After a reaction time of 2 hours, an aliquot of the reaction was washed with water to remove the salts and the organic layer was analyzed with GC-MS.

5.6.2 GC-MS results

5.6.2.1 Reference 3-bromothiophene

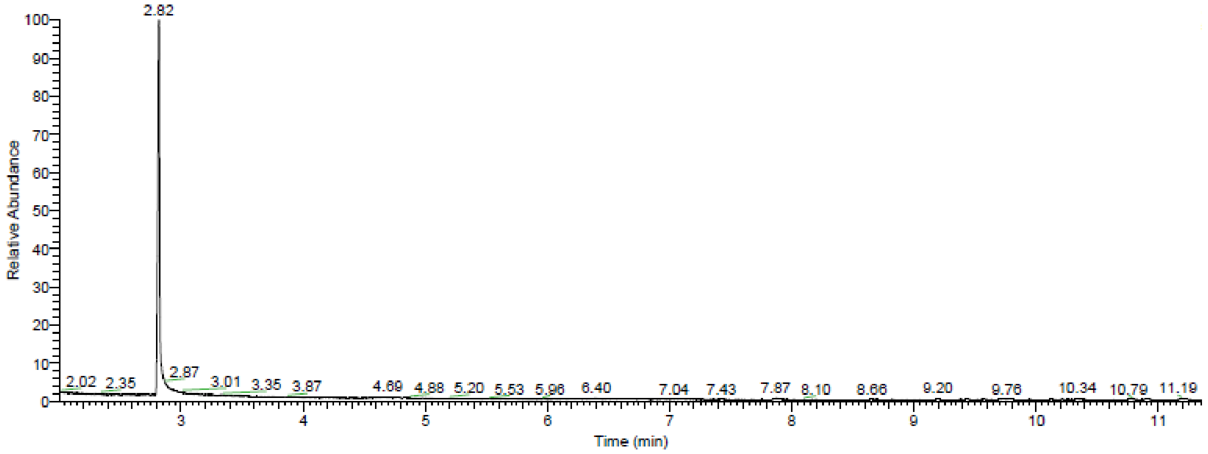

Figure S30. GC spectrum of 3-bromothiophene.

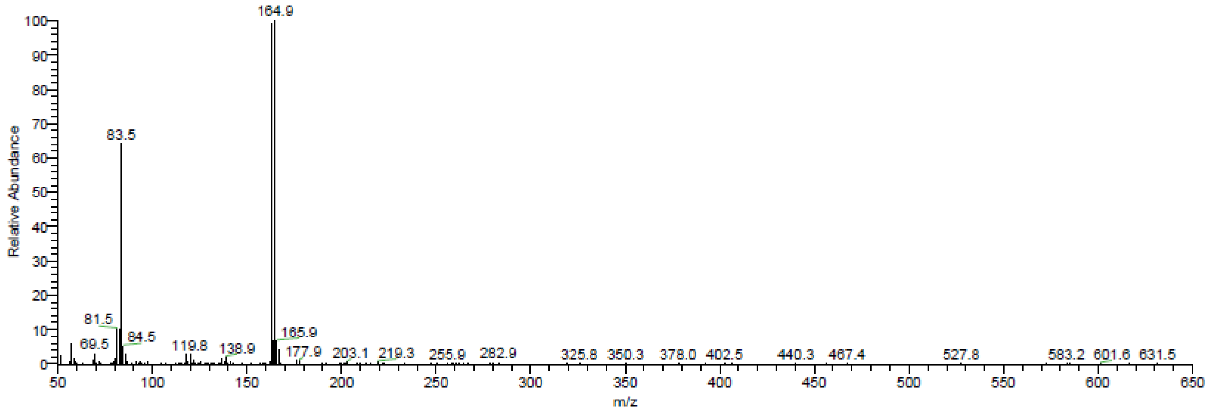

Figure S31. Mass spectrum corresponding to the GC signal at 2.82 min. The spectrum is assigned to 3-bromothiophene.

5.6.2.2 Crude reaction mixture

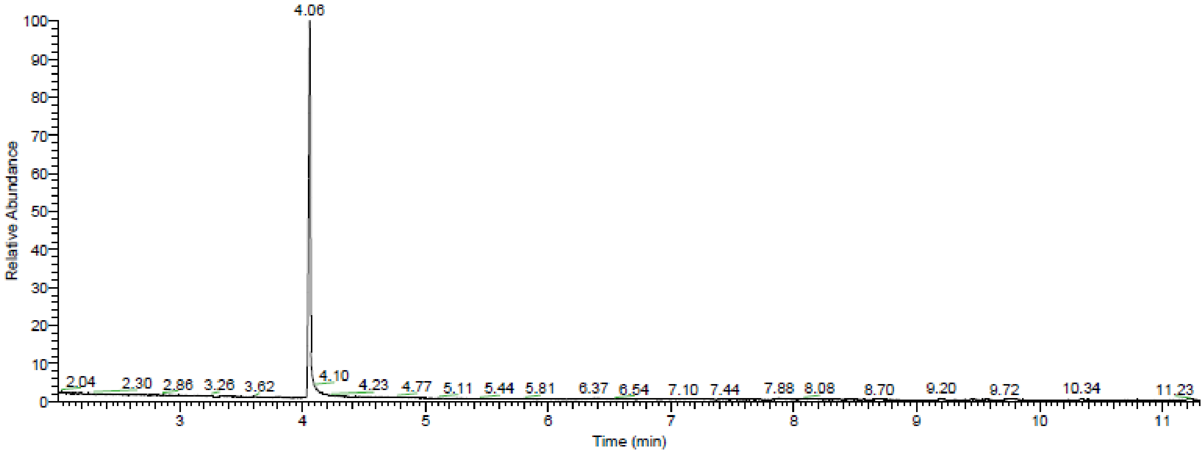

Figure S32. GC spectrum of the crude reaction mixture of the Kumada alkylation reaction of 3-bromothiophene.

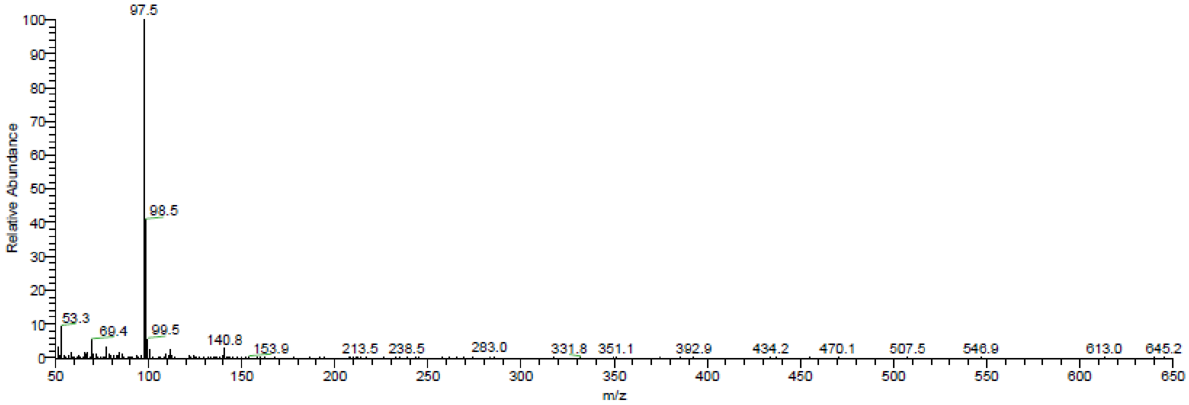

Figure S33. Mass spectrum corresponding to the GC signal at 4.06 min. The spectrum is assigned to 3-butylthiophene.

5.7 Kumada coupling of 3-bromothiophene in the presence of 3,6-dioctylthiothieno[3,2-*b*]thiophene

5.7.1 Reaction protocol

3-bromothiophene (0.1 mmol; 16.3 mg), 3,6-dioctylthiothieno[3,2-*b*]thiophene (0.1 mmol; 42.8 mg) and Ni(dppp)Cl_2 (2 mol%; 1.08 mg) were combined in a flask, brought under argon atmosphere and dissolved in dry Et_2O (10.0 mL). To this mixture, *n*-butylmagnesiumchloride (60 µL; 2.00 M in THF) was added dropwise. After a reaction time of 2 hours, an aliquot of the reaction was washed with water to remove the salts and the organic layer was analyzed with GC-MS.

5.7.2 GC-MS results

5.7.2.1 Reference 3,6-dioctylthiothieno[3,2-b]thiophene

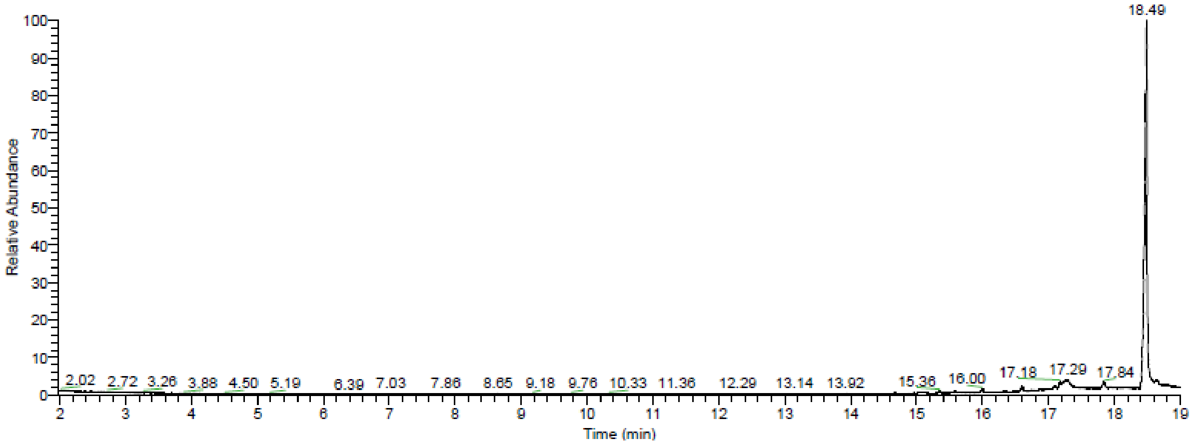

Figure S34. GC spectrum of 3,6-dioctylthio[3,2-*b*]thiophene.

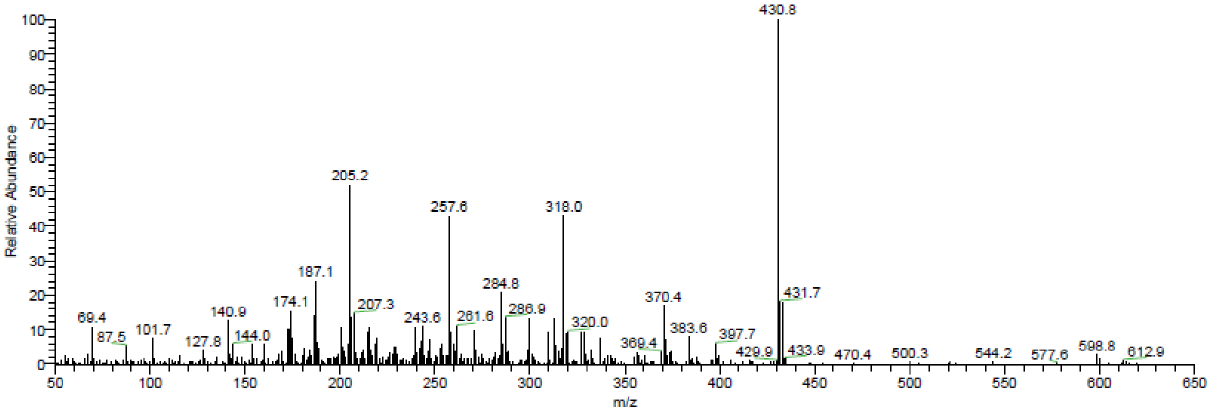

Figure S35. Mass spectrum corresponding to the GC signal at 18.49 min. The spectrum is assigned to 3,6-dioctylthio[3,2-*b*]thiophene.

5.7.2.2 *Crude reaction mixture*

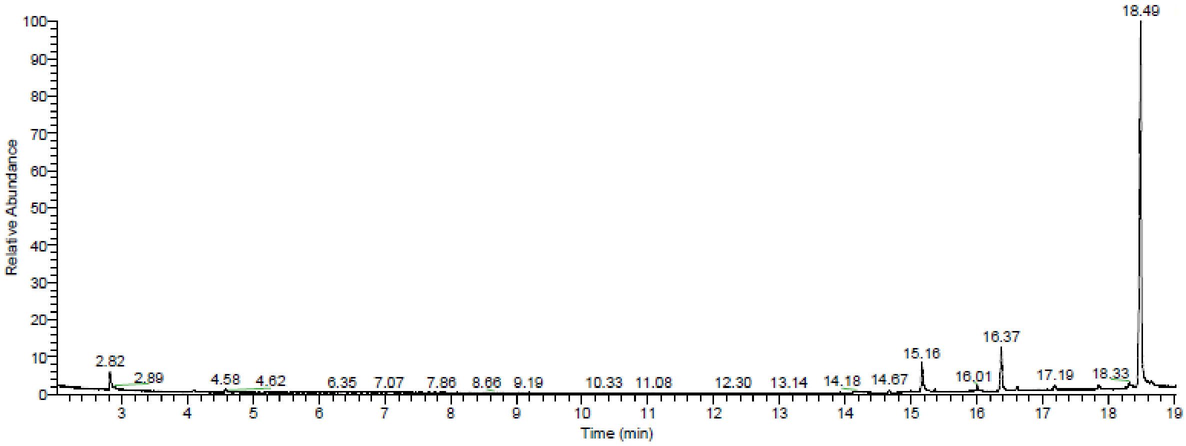

Figure S36. GC spectrum of the crude reaction mixture of the Kumada alkylation reaction of 3-bromothiophene in the presence of 3,6-dioctylthiothieno[3,2-*b*]thiophene.

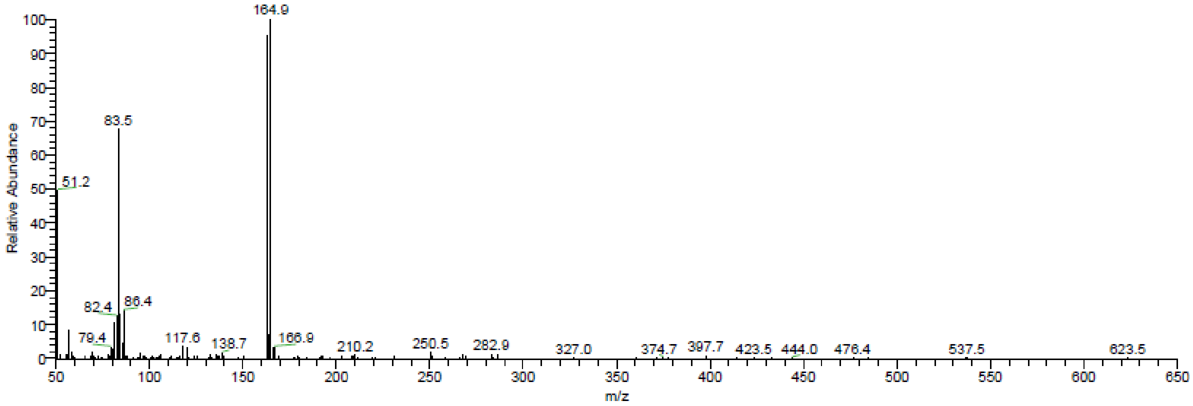

Figure S37. Mass spectrum corresponding to the GC signal at 2.82 min. The spectrum is assigned to 3-bromothiophene.

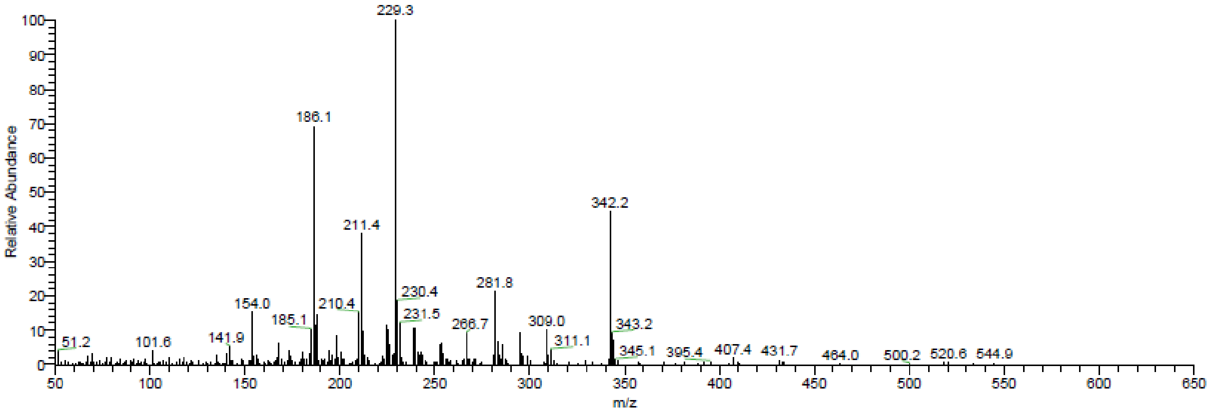

Figure S38. Mass spectrum corresponding to the GC signal at 15.16 min.

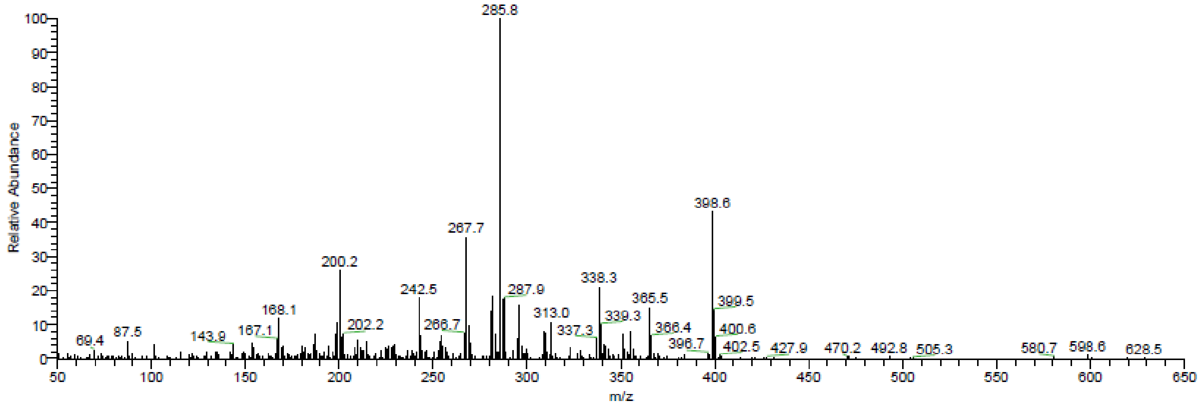

Figure S39. Mass spectrum corresponding to the GC signal at 16.37 min.

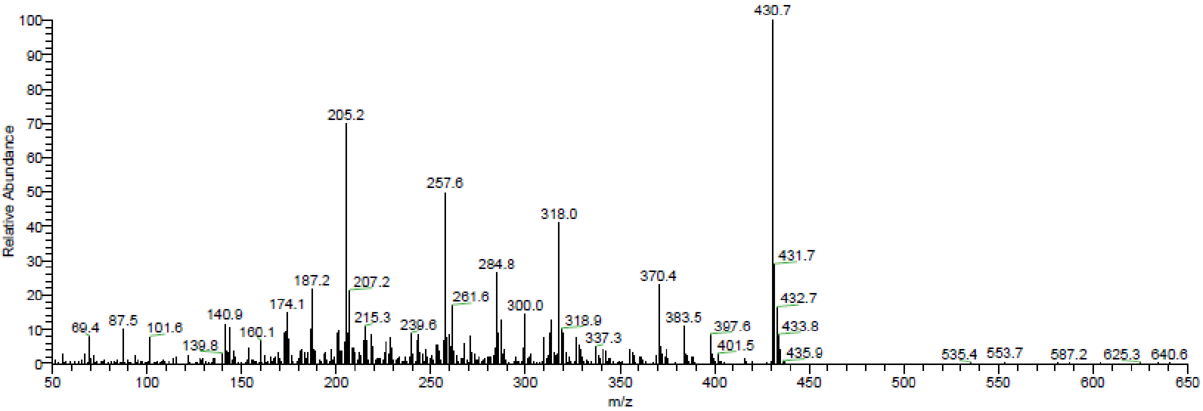

Figure S40. Mass spectrum corresponding to the GC signal at 18.49 min. The spectrum is assigned to 3,6-dioctylthio[3,2-*b*]thiophene.

The notable lower intensity of the thiophene related signals can be ascribed to the formation of thiophene through a competing GRIM reaction, as is also the observed in the Kumada reaction of 3,6-dibromothieno[3,2-*b*]thiophene. The volatile thiophene is not measured by the GC-MS as it evaporates in the same temperature region as the solvents.

The small GC signals at 15.16 min and 16.37 min are unidentified side-products, which cannot be ascribed to an expected reaction product. The molar masses indicate these signals can be ascribed to side-reactions of the 3,6-dioctylthieno[3,2-*b*]thiophene, rather than side-reactions of 3-bromothiophene.

5.8 Polymerization of P3HT-ref and P3HT-TT

5.8.1 Polymerization protocol

2-bromo-5-iodo-3-hexylthiophene (0.400 mmol; 0.152 g) is dissolved in dry THF (3.68 mL) under an argon atmosphere. To this mixture, *i*-PrMgCl.LiCl (0.319 mL; 1.27 M) is added dropwise and the reaction mixture is stirred for 1 h at room temperature. Subsequently, the monomer mixture is divided in two equal parts (2 mL). A first part is added to an argon purged flask containing Ni(dppp)Cl_2 (4 mol%; 4.34 mg) and dry THF (1.5 mL), while the second part is cannulated to an argon purged flask containing Ni(dppp)Cl_2 (4 mol%; 4.34 mg), 2,5-dibromo-3,6-dioctylthiothieno[3,2-b]thiophene (0.200 mmol; 0.114 g) and dry THF (1.5 mL). After a polymerization time of 1 h, both polymerization mixtures are quenched with acidified THF (HCl) and investigated with GPC.

6 References

(1) De Cremer, L.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2008**, *41*, 568–578.

(2) Yokoyama, A.; Suzuki, H.; Kubota, Y.; Ohuchi, K.; Higashimura, H.; Yokozawa, T. *J. Am. Chem. Soc.* **2007**, *129*, 7236–7237.