Electronic Supplementary Material (ESI) for Polymer Chemistry.

Suzuki-Miyaura Catalyst-Transfer Polymerization: New Mechanistic Insights

Mitchell T. Howell,[†] Peter Kei,[‡] Maksim V. Anokhin,[†] Yaroslav Losovyj,[§,#] Frank R. Fronczek,[‡] and Evgueni E. Nesterov[†,‡]*

[†]Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115, USA

[‡]Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA

[§]Department of Chemistry, Indiana University, Bloomington, Indiana 47401, USA

[#]Department of Physics and Astronomy, University of Nebraska, Lincoln, Nebraska 68588, USA

Supporting Information

I. Additional Figures

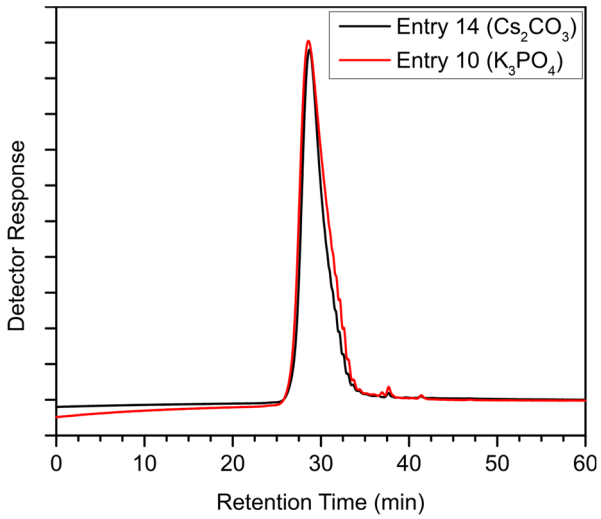


Fig. S1. GPC traces for the PF polymers obtained in Ag^+-mediated SCTP with K_2CO_3 (entry 10 in Table 1) and with Cs_2CO_3 (entry 14 in Table 1) as a base.

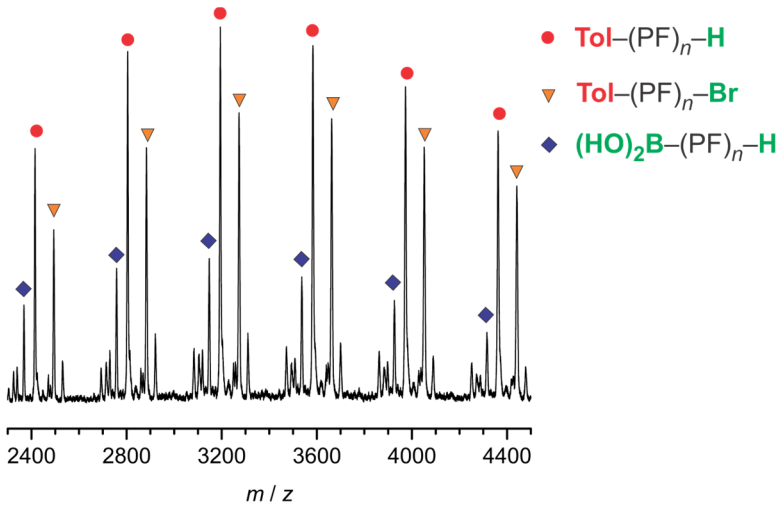


Fig. S2. A fragment of MALDI-TOF data for the PF polymer produced in SCTP of MIDA-boronate monomer **5** in Ag^+-mediated conditions at higher reaction temperature (40 °C) (entry 17 in Table 1). The chain composition corresponding to specific peaks is marked with colored symbols.

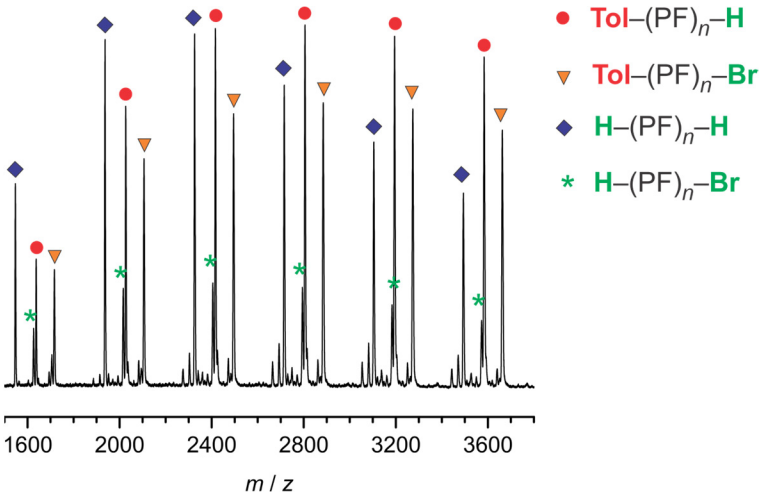


Fig. S3. A fragment of MALDI-TOF data for the PF polymer produced in SCTP of MIDA-boronate monomer **5** in the conditions of excess RuPhos ligand (entry 20 in Table 1). The chain composition corresponding to specific peaks is marked with colored symbols.

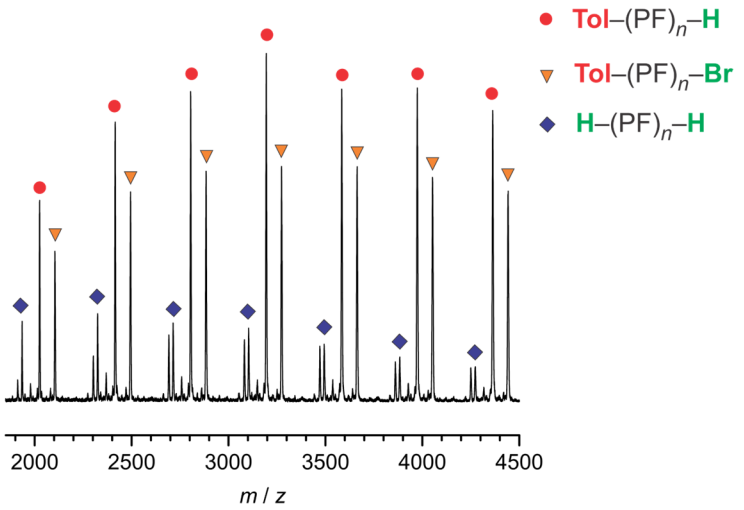


Fig. S4. A fragment of MALDI-TOF data for the PF polymer produced in SCTP of MIDA-boronate monomer **5** in in Ag^+-mediated conditions with excess RuPhos ligand (entry 19 in Table 1). The chain composition corresponding to specific peaks is marked with colored symbols.

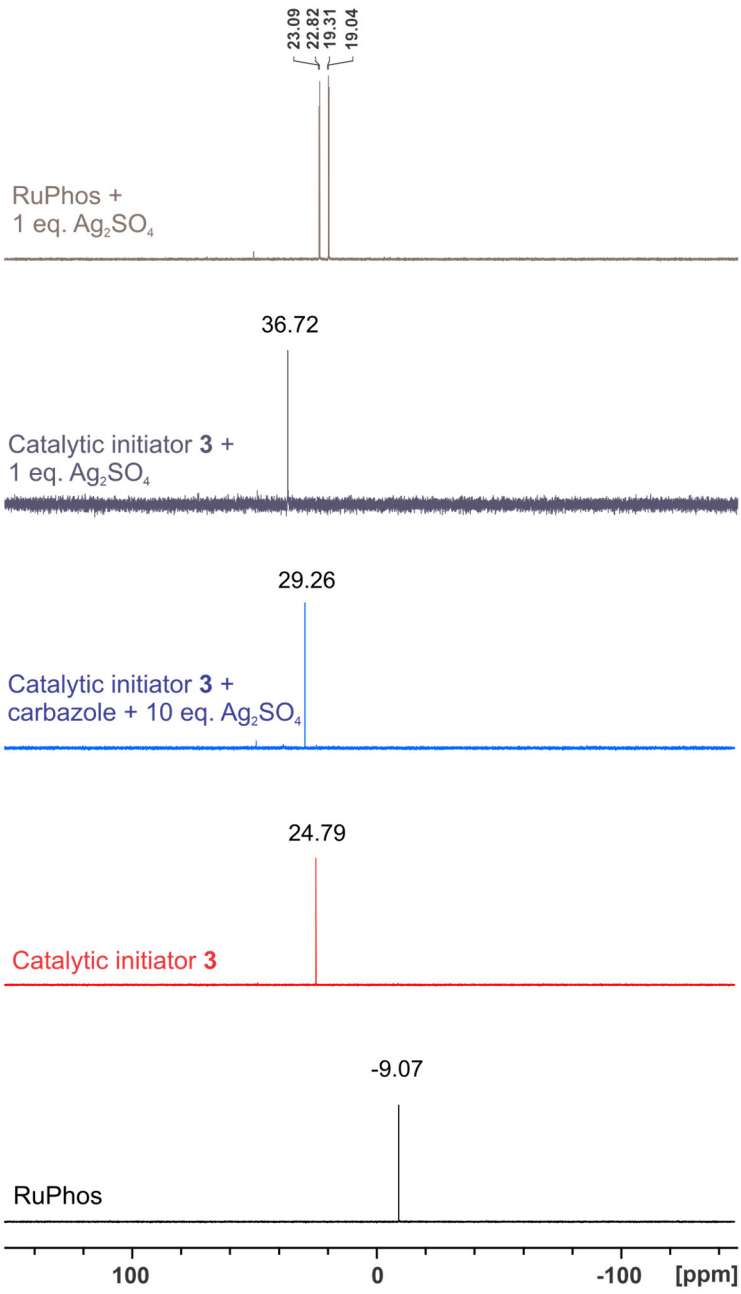


Fig. S5. ^{31}P NMR spectra (202 MHz) of (from bottom to top): RuPhos phosphine ligand, catalytic initiator **3**, catalytic initiator **3** containing carbazole upon addition of 10 eq. of Ag_2SO_4 and 10 eq. of Cs_2CO_3, carbazole-free catalytic initiator **3** upon addition of 1 eq. of Ag_2SO_4 and 10 eq. of Cs_2CO_3, and RuPhos ligand upon addition of 1 eq. of Ag_2SO_4 and 1 eq. of Cs_2CO_3. All spectra were acquired in 10% v/v D_2O in THF.

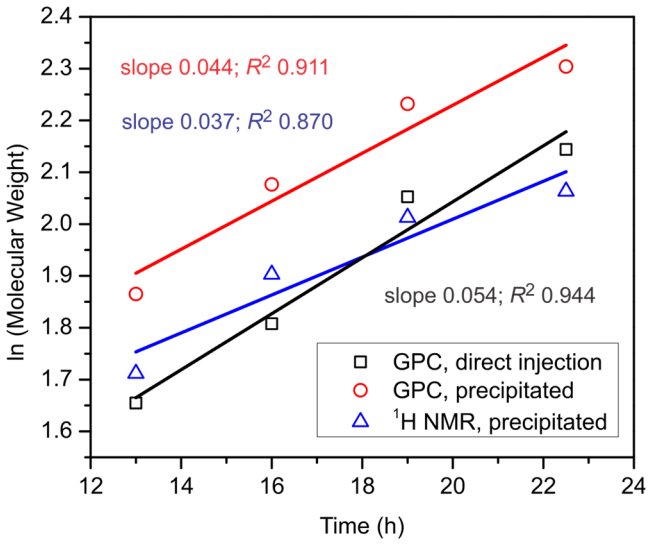


Fig. S6. Comparison of kinetic plots for polymerization of MIDA-boronate **5** in Ag^+-mediated conditions. The reaction conditions are listed in entry 12 of Table 1. "GPC, direct injection" data were obtained using GPC analysis (relative to polystyrene standards) prior to precipitation of withdrawn aliquots in acetone; "GPC, precipitated" data were obtained by GPC analysis using polymer samples after their precipitation in acetone; "^{1}H NMR, precipitated" data were obtained using end-group ^{1}H NMR analysis of the precipitated polymer samples.

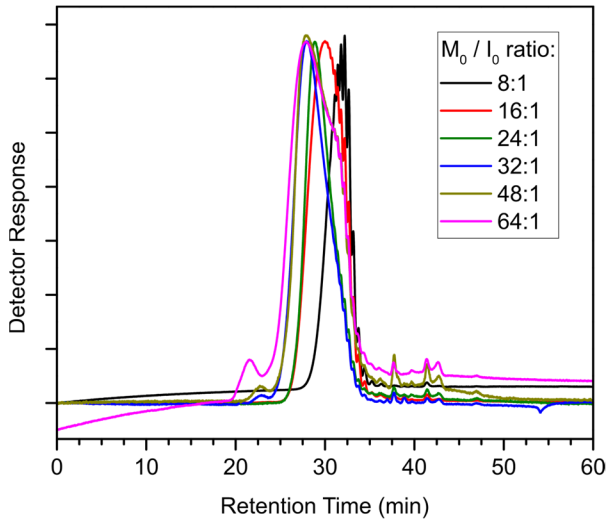


Fig. S7. GPC traces for the PF polymers obtained in Ag^+-mediated SCTP at varying M_0/I_0 ratio, in 72 h polymerization runs (entries 1-6 in Table 3).

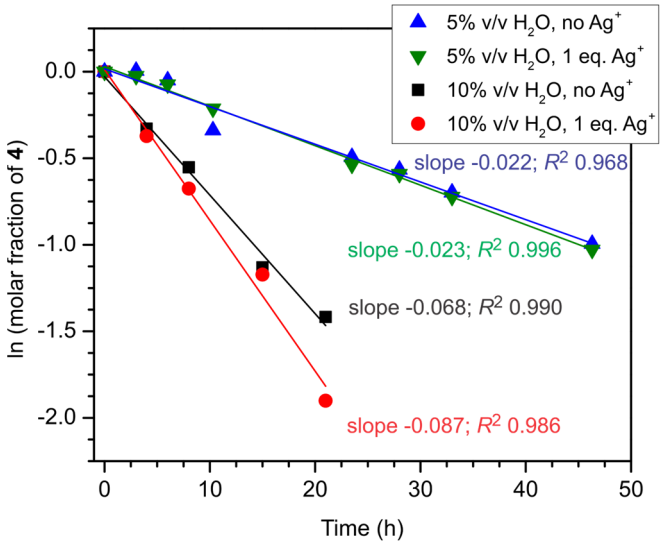


Fig. S8. Kinetic plots for hydrolysis of MIDA-boronate **5**. Reaction conditions: aqueous THF, Cs_2CO_3 (10 eq.), Ag_2SO_4 (0.5 eq., i.e. 1 eq. Ag^+, or not added), temperature 30 °C, percent amount of water and the presence or absence of Ag^+ is indicated in the graph legend.

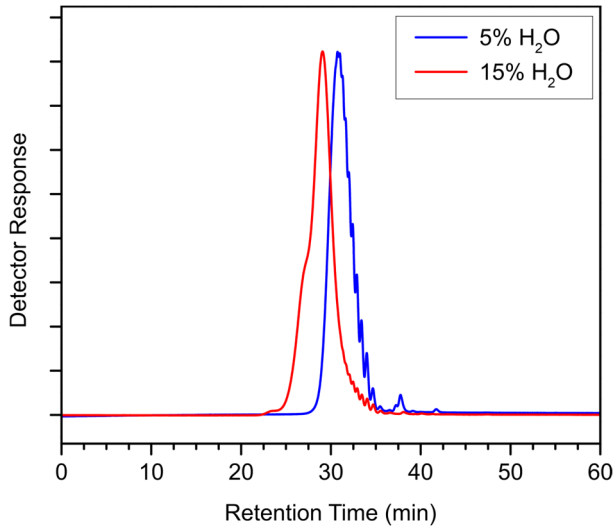


Fig. S9. GPC traces for PF polymer samples obtained in Ag^+-mediated SCTP of MIDA-boronate monomer **4** upon varying water content in the reaction medium (entries 3 and 7 in Table 4).

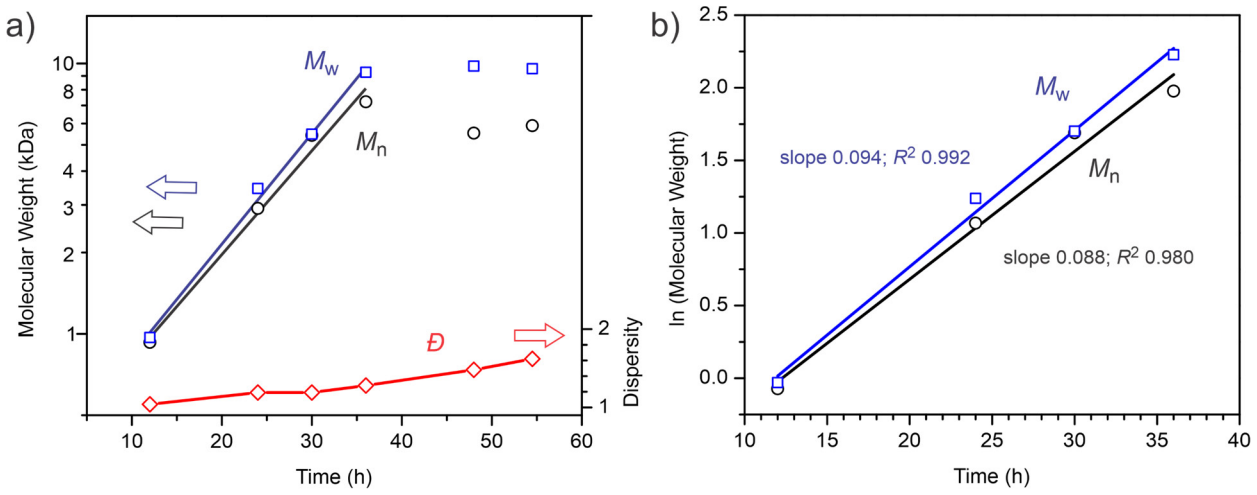


Fig. S10. a) Kinetic study of Ag^+-mediated SCTP of monomer **5** (M_0/I_0 48:1, 10% v/v H_2O in THF, Cs_2CO_3 (10 eq.), Ag_2SO_4 (0.5 eq.), temperature 30 °C). b) First-order kinetic plot for the linear portion of the kinetic data in (a).

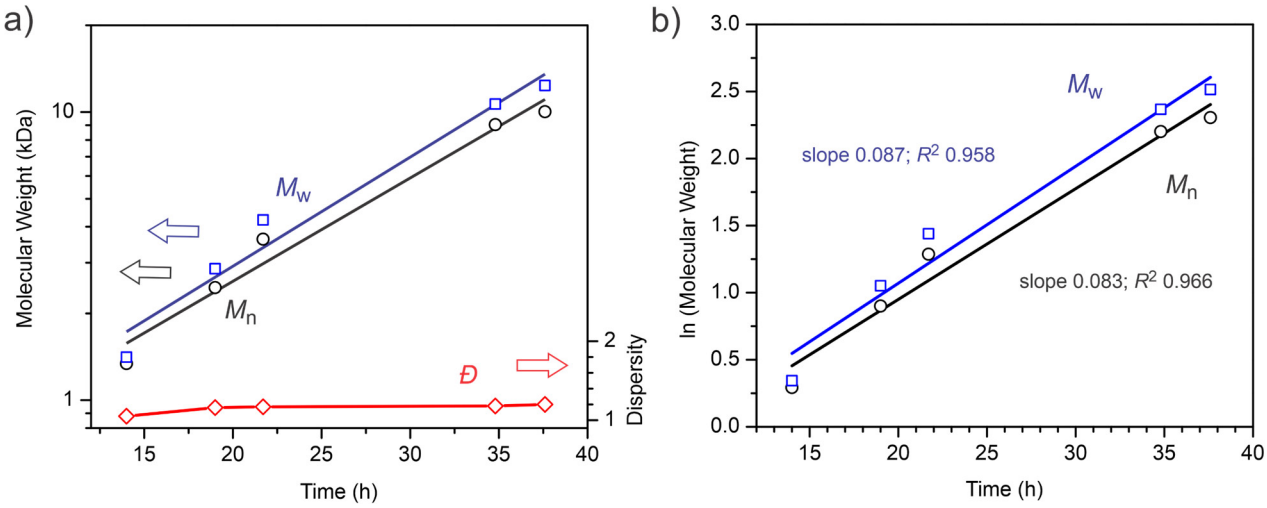


Fig. S11. a) Kinetic study of Ag^+-mediated SCTP of monomer **5** (M_0/I_0 48:1, 10% v/v H_2O in THF, Cs_2CO_3 (10 eq.), Ag_2SO_4 (1.0 eq.), temperature 30 °C). b) First-order kinetic plot for the linear portion of the kinetic data in (a).

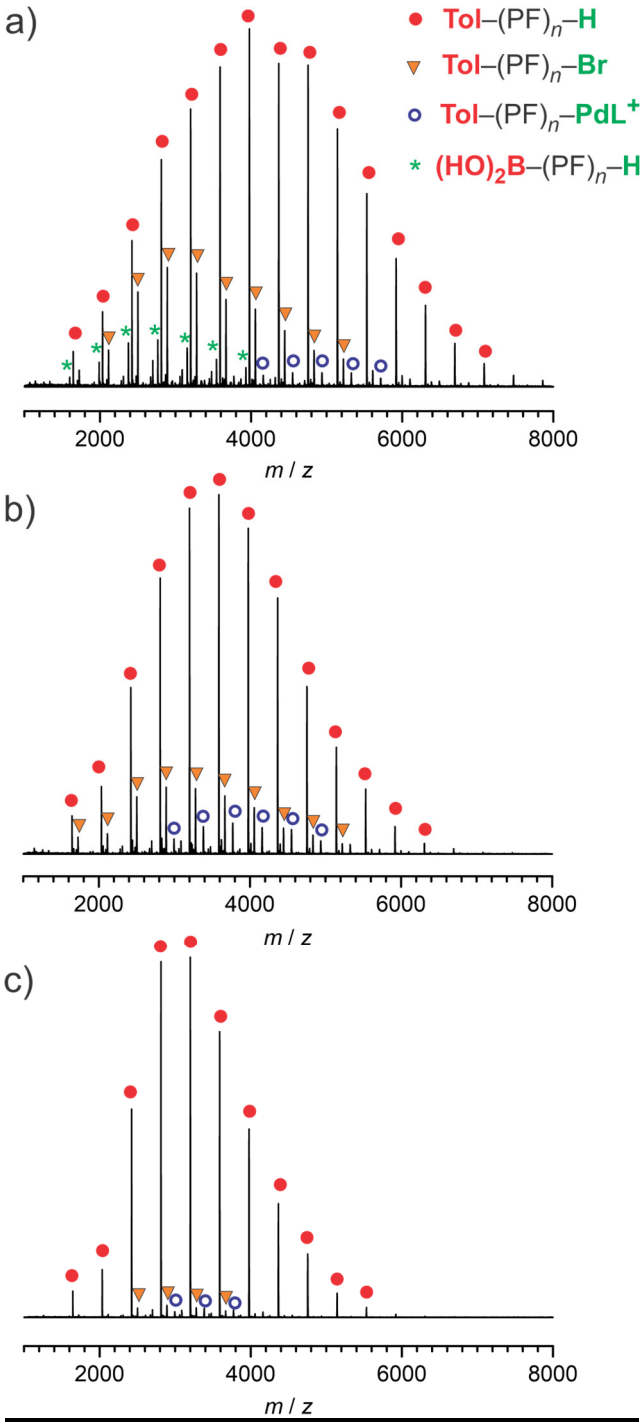


Fig. S12. MALDI-TOF data for the PF polymer produced in Ag^+-mediated SCTP in the conditions of varying Ag^+ amount at 10% v/v water content: a) 1 eq. of Ag^+ (entry 8 in Table 4), b) 2 eq. of Ag^+ (entry 9 in Table 4), and c) 3 eq. of Ag^+ (entry 10 in Table 4). The chain composition corresponding to specific peaks is marked with colored symbols.

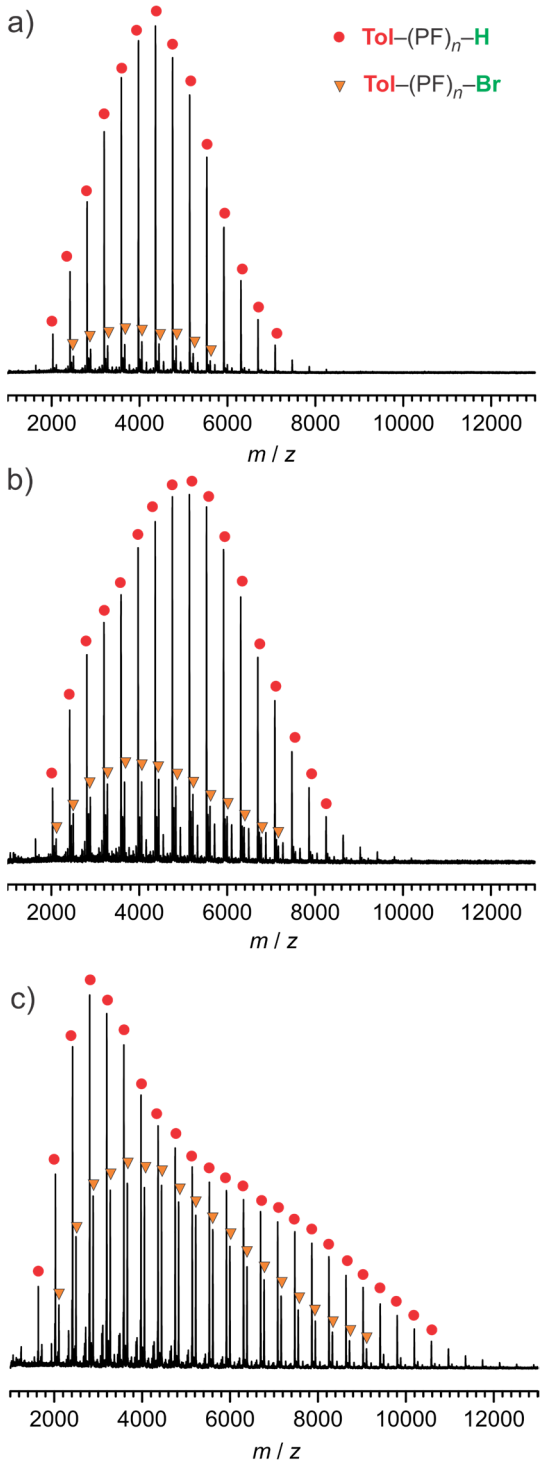


Fig. S13. MALDI-TOF data for the PF polymer produced via SCTP of cyclic triolboronate monomer **13**: a) in the reaction conditions with no water, no base, and no Ag^+ (entry 11 in Table 4); b) in the reaction conditions with water, no base and no Ag^+ (entry 12 in Table 4); and c) in the reaction conditions with water, Cs_2CO_3 base, and 1 eq. of Ag^+ (entry 15 in Table 4). The chain composition corresponding to specific peaks is marked with colored symbols.

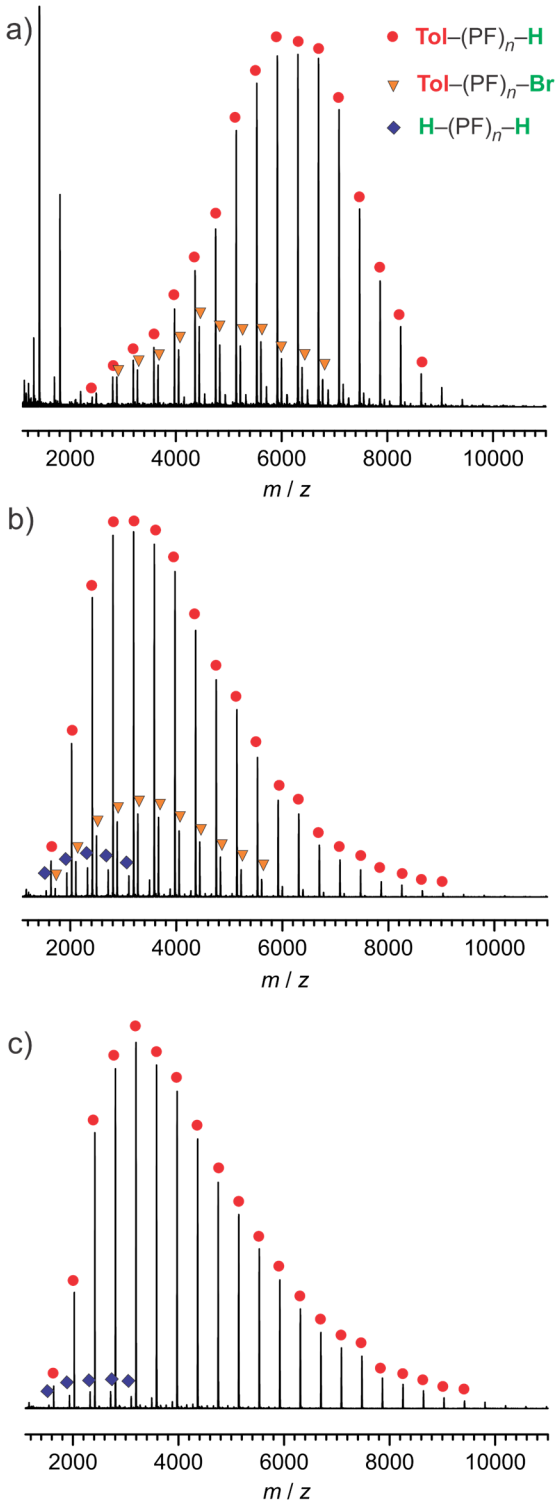


Fig. S14. MALDI-TOF data for the PF polymer produced in SCTP of boronic acid monomer **9**: a) in the reaction conditions with no added Ag^+ (entry 16 in Table 4); b) in the reaction conditions with 1 eq. of Ag^+ (entry 17 in Table 4); and c) in the reaction conditions with 3 eq. of Ag^+ (entry 18 in Table 4). The chain composition corresponding to specific peaks is marked with colored symbols.

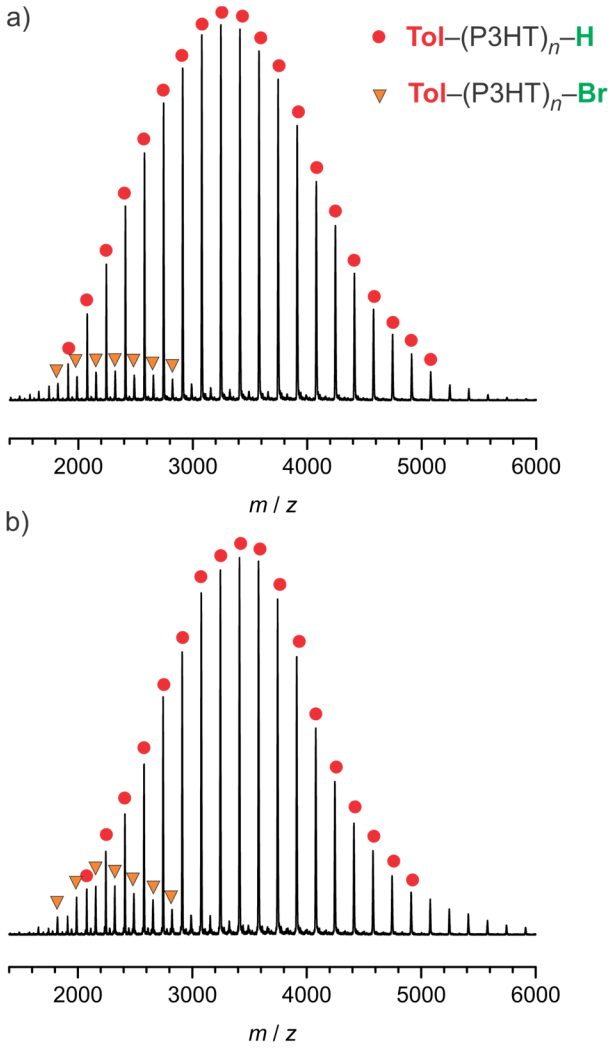


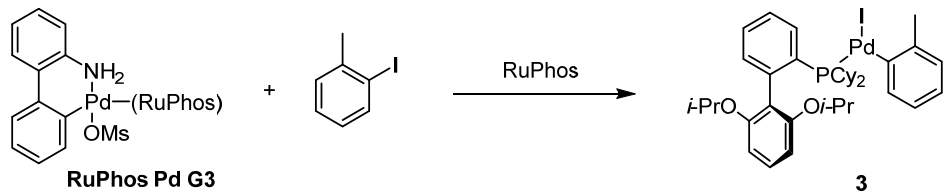
Fig. S15. MALDI-TOF data for the P3HT polymers produced in SCTP polymerization of monomer **1** initiated with catalytic initiator **3** in (a) Ag^{+}-mediated conditions (entry 20 in Table 4) and (b) without added Ag_2SO_4 (entry 19 in Table 4). The chain composition corresponding to specific peaks is marked with colored symbols.

II. Experimental Section

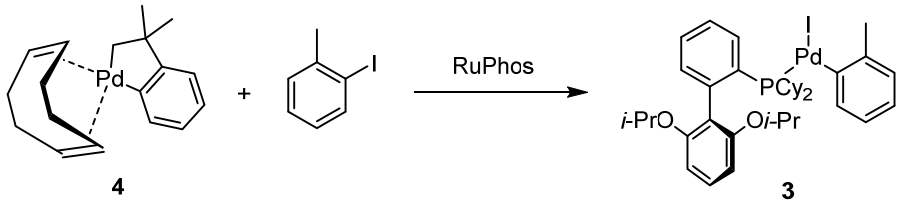
General Procedures

All reactions were performed under an atmosphere of dry nitrogen (unless mentioned otherwise). Column chromatography was performed on silica gel (Sorbent Technologies, 60 Å, 40-63 μm) slurry packed into glass columns. Tetrahydrofuran (THF), ether, toluene, and hexanes were dried by passing through activated alumina, and *N,N*-dimethylformamide (DMF) was dried by passing through molecular sieves, using a PS-400 Solvent Purification System from Innovative Technology, Inc. The water content of the solvents was periodically controlled by Karl Fischer titration (using a DL32 coulometric titrator from Mettler Toledo). All other reagents and solvents were obtained from Aldrich, Alfa Aesar, or TCI America, and used without further purification. Butyllithium was titrated with salicylaldehyde phenylhydrazone prior to use.[1] ^{1}H NMR spectra were recorded at 300 MHz or 500 MHz, and are reported in ppm downfield from tetramethylsilane; ^{31}P NMR spectra were obtained at 202 MHz and are reported in ppm relative to 80% aqueous H_3PO_4 as external standard. ^{11}B NMR spectra were acquired at 160 MHz using quartz NMR tubes and are reported in ppm relative to $BF_3 \cdot Et_2O$ as external standard. GPC analysis of polymers was performed with an Agilent 1100 chromatograph equipped with two PLgel 5 μm MIXED-C and one PLgel 5 μm 1000 Å columns connected in series, using THF as a mobile phase at a flow rate of 0.7 ml min^{-1}, and calibrated against polystyrene standards. MALDI-TOF data were acquired with Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer using DCTB matrix. Calibration was performed using standard polyalanine mixture to verify intensity and resolution benchmarks; the mass error was estimated at 50-100 ppm at 5700 Da. High-resolution ESI-TOF data were obtained using Bruker Maxis Plus QqTOF mass spectrometer.

Synthetic Details



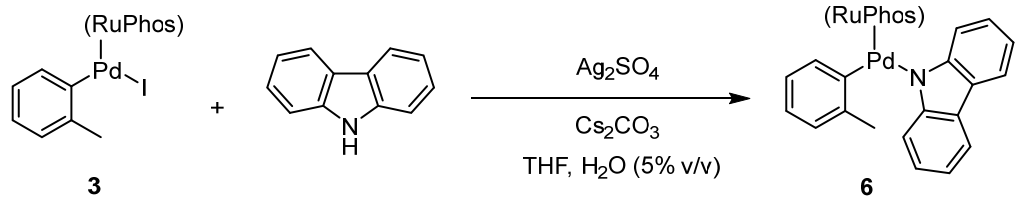
Catalytic initiator 3 (with equimolar carbazole). The preparation of this compound was done inside a glovebox with nitrogen atmosphere. A mixture of 0.34 g (1.56 mmol) of 2-iodotoluene, 1.0 g (1.2 mmol) of RuPhos Pd G3, 1.0 g (2.4 mmol) of RuPhos, 1.27 g (6.0 mmol) of K_3PO_4 in 35 ml of THF and 2 ml of water (degassed using a freeze-thaw procedure) was stirred in a sealed 45 ml pressure tube at 50 °C for 4 h. Upon completion, the tube was allowed to cool to room temperature, the reaction mixture was poured in water and extracted with hexanes, and the organic phase was dried over Na_2SO_4. The organic phase was concentrated *in vacuo* using a rotary evaporator backfilled with argon, the residual yellow material was dissolved in 10 ml of THF and passed through a celite plug to remove black Pd nanoparticles. Hexanes (430 ml) were added to the filtrate, and the resulting solution was placed in the freezer for 5 days resulting in formation of golden yellow crystals. The crystals were collected by filtration and dried *in vacuo* to yield 0.88 g (92%) of **3** as co-crystals with carbazole (in 1:1 ratio). ^{1}H NMR (300 MHz, THF-d_8) δ 10.27 (br. s, 1H), 8.06 (d, J = 7.8 Hz, 2H), 7.76 – 7.69 (m, 1H), 7.62 (t, J = 8.2 Hz, 1H), 7.46 - 7.31 (m, 6H), 7.14 (t, J = 7.8 Hz, 2H), 6.91-6.79 (m, 2H), 6.77 – 6.62 (m, 5H), 4.69 – 4.55 (m, 2H), 2.55 (s, 3H), 2.38 – 2.19 (m, 2H), 1.95 – 1.43 (m, 12H), 1.38 (d, J = 6.0 Hz, 6H), 1.30 – 1.00 (m, 10H), 1.00 – 0.84 (m, 3H), 0.55 – 0.36 (m, 1H). ^{31}P NMR (202 MHz, THF with 10% D_2O) δ 24.79.



4 3

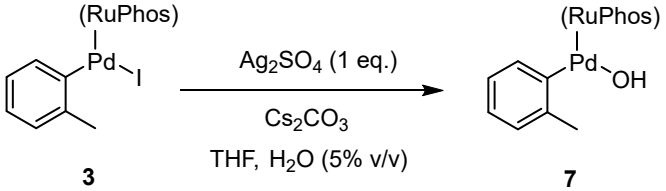
Catalytic initiator 3 (carbazole-free). Inside a glove box with nitrogen atmosphere, 150 mg (0.42 mmol, 1.0 eq.) of the palladacycle **4** (prepared according to procedure in ref. 2), 204 mg (0.44 mmol, 1.05 eq.) of RuPhos and 110 mg (0.50 mmol, 1.2 eq.) of *o*-iodotoluene were added to an oven dried pressure tube followed by 4.5 ml of hexanes. The reaction mixture in the sealed tube was heated at 60 °C upon stirring for 4 h producing a yellow precipitate. The reaction mixture was allowed to cool to room temperature, the precipitate was collected with a fritted funnel, washed with hexanes, and dried *in vacuo*, yielding 243 mg (75%) of **3** as a yellow solid. ^{1}H NMR (500 MHz, C_6D_6) δ 7.70 (t, J = 7.5 Hz, 1H), 7.29 (t, J = 7.5 Hz, 1H), 7.21 (d, J = 7.5 Hz, 1H), 7.06

(t, J = 8.0 Hz, 1H), 6.98 – 6.95 (m, 1H), 6.92 -6.83 (m, 3H), 6.73 – 6.71 (m, 1H), 6.57 – 6.52 (m, 2H), 4.25 – 4.20 (m, 2H), 2.87 (s, 3H), 2.71 – 2.63 (m, 1H), 2.33 – 2.25 (m, 1H), 2.10 – 2.05 (m, 1H), 1.80 – 1.43 (m, 10H), 1.41 – 0.90 (m, 14H), 0.86 (d, J = 6.0 Hz, 3H), 0.70 (d, J = 6.0 Hz, 3H), 0.66 – 0.52 (m, 1H). ^{31}P NMR (202 MHz, THF with 10% D_2O) δ 24.79.



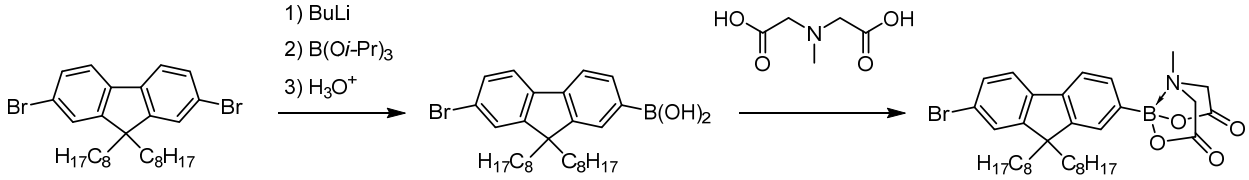
3 **6**

Pd-carbazolide complex 6. The preparation of this compound was done inside a glovebox with nitrogen atmosphere. In a 20 ml vial, 158 mg (505 μmol) of Ag_2SO_4, 40 mg (50 μmol) of the carbazole-containing complex **3** and 165 mg (505 μmol) of Cs_2CO_3 were mixed with 2 ml of THF, followed by addition of 0.1 ml of degassed H_2O. The mixture was heated at 30 °C for 3 h, resulting in formation of a yellow precipitate while the liquid phase turned amber orange. The liquid phase was collected with a syringe, passed through a 0.2 μm PTFE syringe filter, and concentrated *in vacuo* to yield an orange amorphous material. Recrystallization via slow evaporation from a THF-hexanes solution (0.05 ml of THF and 2.0 ml of hexanes) yielded red-orange crystals. ^{1}H NMR (500 MHz, C_6D_6) δ 8.24 (t, J = 7.5 Hz, 2H), 8.03 (d, J = 8.0 Hz, 1H), 7.94 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.68 – 7.51 (m, 2H), 7.40 – 7.20 (m, 3H), 7.09 – 6.95 (m, 2H), 6.69 – 6.57 (m, 1H), 6.54 – 6.46 (m, 3H), 5.93 (d, J = 8.5 Hz, 1H), 5.67 (t, J = 8.5 Hz, 1H), 5.59 (d, J = 8.5 Hz, 1H), 4.41 – 4.34 (m, 2H), 2.94 (s, 3H), 2.69 – 2.59 (m, 1H), 2.37 – 1.40 (m, 15H), 1.33 (d, J = 6.5 Hz, 3H), 1.27 (d, J = 6.5 Hz, 3H), 1.20 – 0.90 (m, 6H), 0.71 (d, J = 6.0 Hz, 3H), 0.65 (d, J = 6.0 Hz, 3H). ^{31}P NMR (202 MHz, C_6D_6) δ 28.38.



3 **7**

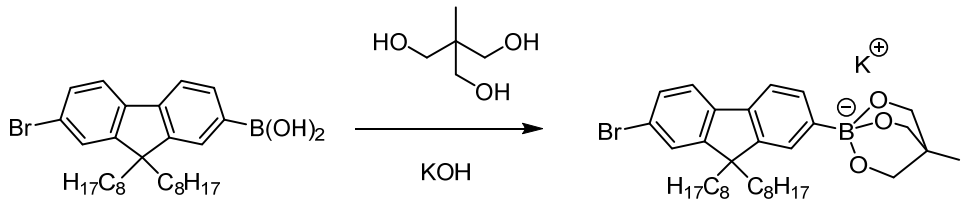
Hydroxo-Pd complex 7. The preparation of this compound was done inside a glovebox with nitrogen atmosphere. In a 20 ml vial, 8 mg (25 μmol) of Ag_2SO_4, 20 mg (25 μmol) of the carbazole-free complex **3** and 83 mg (253 μmol) of Cs_2CO_3 were mixed with 2 ml of THF followed by addition of 0.1 ml of degassed water. The mixture was heated 30 °C for 10 h, resulting in formation of a yellow precipitate while the liquid phase turned green. The liquid phase was collected with a syringe, passed through a 0.2 μm PTFE syringe filter and concentrated *in vacuo* to produce a green solid. Recrystallization upon slow evaporation from hexanes-THF solution produced **7** as colorless crystals. ^{1}H NMR (500 MHz, C_6D_6) δ 8.84 (br. s, 1H), 7.65 – 7.48 (m, 1H), 7.15 – 7.00 (m, 2H), 6.82 – 6.62 (m, 5H), 6.49 (br. s, 1H), 6.32 (d, *J* = 7.5 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.88 – 3.80 (m, 1H), 3.09 (s, 3H), 1.92 – 1.65 (m, 6H), 1.59 – 1.30 (m, 10H), 1.15 – 0.70 (m, 9H), 0.68 (d, *J* = 6.0 Hz, 3H), 0.56 (d, *J* = 6.0 Hz, 3H), 0.52 (d, *J* = 6.0 Hz, 3H), –2.10 (br. s, 1H). ^{31}P NMR (202 MHz, THF with 5% D_2O) δ 36.72 (s).



(7-Bromo-9,9-dioctyl-9*H*-fluoren-2-yl)boronic acid (9). A solution of 11.7 ml (18.8 mmol) of 1.6 M n-butyllithium in hexanes was added dropwise to a solution of 10.0 g (18.2 mmol) of 2,7-dibromo-9,9-dioctylfluorene in 125 ml of THF at –78 °C, and the reaction mixture was stirred for 1 h at this temperature resulting in a yellow solution. Triisopropyl borate (6.26 ml, 27.3 mmol) was added, and the reaction mixture was allowed to reach room temperature, and stirred for additional 16 h. Then, the reaction mixture was cooled in an ice bath, quenched with 100 ml of 10% HCl, and stirred for 1 h. The organic phase was extracted with ethyl acetate, washed with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. Concentration *in vacuo* using a rotary evaporator (the temperature of water bath was kept below 35 °C) yielded quantitative yield of crude **9** as a colorless foamy solid, which was used for the synthesis of **5**. For polymerization and for the synthesis of **13**, the crude material was purified by column chromatography on silica gel (eluent ethyl acetate – CH_2Cl_2 1:10) to yield 5.43 g (58%) of **9** as a colorless foamy solid, R_f 0.5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, *J* = 7.5 Hz, 1H), 8.21 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.70

(d, J = 8.0 Hz, 1H), 7.58 – 7.53 (m, 2H), 2.21 – 2.11 (m, 2H), 2.09 – 2.0 (m, 2H), 1.26 – 1.02 (m, 20H), 0.81 (t, J = 7.0 Hz, 6H), 0.77 – 0.64 (m, 4H). HRMS (ESI-TOF) *m/z* 535.2359 [M+Na^+] (calcd. for $C_{29}H_{42}BBrNaO_2$ 535.2359).

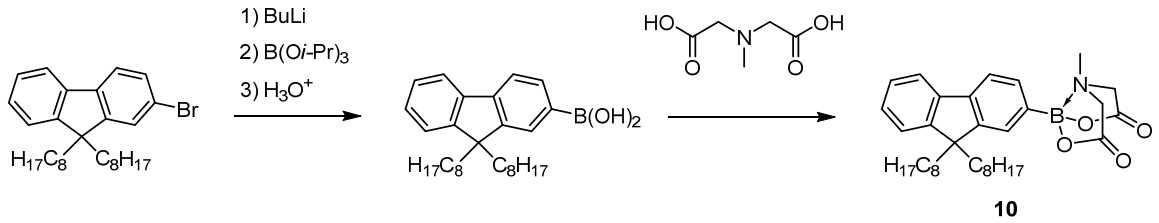
(7-Bromo-9,9-dioctyl-9*H*-fluoren-2-yl)boronic acid MIDA ester (5). The crude boronic acid **9** obtained as described above was mixed with 2.76 g (18.7 mmol) of *N*-methyliminodiacetic acid (MIDA) and 320 ml of benzene-DMSO (10:1 v/v) in a 500 ml flask equipped with a Dean-Stark adapter. The mixture was stirred upon reflux at 115 °C for 16 h until no more water was separated in the Dean-Stark adapter. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate, and washed with small portions of water at least 10 times to remove DMSO. The organic fraction was then dried over Na_2SO_4, and concentrated *in vacuo* to produce a crude product as a colorless sticky solid. It was further purified by column chromatography on silica gel (eluent ethyl acetate – hexanes 3:2) to yield 8.5 g (75%) of **5** as a colorless solid, R_f 0.35. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 7.7 Hz, 1H), 7.58 (d, J = 7.7 Hz, 1H), 7.52 (s, 1H), 7.49 – 7.45 (m, 3H), 4.00 (d, J = –16.5 Hz, 2H), 3.81 (d, J = –16.5 Hz, 2H), 2.54 (s, 3H), 1.98 – 1.92 (m, 4H), 1.27 – 0.95 (m, 20H), 0.84 (t, J = 7.0 Hz, 6H), 0.66-0.44 (m, 4H). HRMS (ESI-TOF) *m/z* 626.2837 [M+H^+] (calcd. for $C_{34}H_{48}BBrNO_4$ 624.2853).



9 **13**

Cyclic triolboronate monomer 13. A mixture of boronic acid **9** (2.99 g, 5.84 mmol) and trimethylolethane (0.702 g, 5.84 mmol) was refluxed in toluene for 8 h in a flask equipped with a Dean-Stark adapter to remove water. Then, freshly ground KOH (0.327 g, 5.84 mmol) was added, and the mixture was refluxed with the Dean-Stark adapter for 12 h. Upon cooling to room temperature, the reaction mixture was concentrated in vacuo to yield 3.7 g (100%) of compound **13** as a white foam which was used directly without further purification. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.58 (d, J = 8.0 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.42 (d, J = 7.5 Hz, 1H), 7.39 (dd, J_1 = 8.0, J_2 = 2.0 Hz, 1H), 7.34 – 7.30 (m, 2H), 3.59 (s, 6H), 1.99 – 1.83 (m, 4H), 1.23 – 0.92 (m,

20H), 0.79 (t, J = 7.0 Hz, 6H), 0.57 – 0.31 (m, 7H). HRMS (ESI-TOF) *m/z* 634.2528 [M^+] (calcd. for $C_{34}H_{49}BBrKO_3$ 634.2595).



10

(9,9-Dioctyl-9*H*-fluoren-2-yl)boronic acid MIDA ester (10). A solution of 0.69 ml (1.10 mmol) of 1.6 M n-butyllithium in hexanes was added dropwise to a solution of 500 mg (1.06 mmol) of 2-bromo-9,9-dioctylfluorene in 50 ml of THF at –78 °C, and the reaction mixture was stirred for 1 h at this temperature resulting in a yellow solution. Triisopropyl borate (0.37 ml, 1.60 mmol) was added, and the reaction mixture was allowed to reach room temperature and stirred for additional 16 h. Then, the reaction mixture was cooled in an ice bath, quenched with 3.1 ml of 10% HCl, and stirred for 1 h. The organic phase was extracted with ethyl acetate, washed with saturated $NaHCO_3$ solution, and dried over Na_2SO_4. Concentration *in vacuo* using a rotary evaporator (the temperature of water bath was kept below 35 °C) gave boronic acid as a colorless solid. The crude product was then dissolved in 20 ml of benzene-DMSO (10:1 v/v) mixture and 162 mg (1.10 mmol) of *N*-methyliminodiacetic acid was added. The reaction mixture was then refluxed at 120 °C for 16 h with a Dean-Stark trap filled with benzene. The reaction mixture was then allowed to cool to room temperature. An extraction with ethyl acetate and several washes with water were done to remove DMSO. The organic phase was dried with anhydrous Na_2SO_4, concentrated *in vacuo* and dried in high vacuum yielding a white solid. The solid was then dissolved in CH_2Cl_2, and loaded into a short column with silica gel which was eluted with CH_2Cl_2. This was followed by elution with ethyl acetate to result in the product fraction that was concentrated *in vacuo* yielding 482 mg (83%) of **10** as a colorless powder. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.81 – 7.72 (m, 2H), 7.56 (s, 1H), 7.48 (dd, J_1 = 7.5, J_2 = 1 Hz, 1H), 7.43 – 7.34 (m, 3H), 3.97 (d, J = –16.0 Hz, 2H), 3.83 (d, J = –16.0 Hz, 2H), 2.54 (s, 3H), 2.05 – 2.02 (m, 4H), 1.25 – 1.04 (m, 20H), 0.85 (t, J = 7.0 Hz, 6H), 0.59 – 0.54 (m, 4H). HRMS (ESI-TOF) *m/z* 568.3578 [M+Na^+] (calcd. for $C_{34}H_{48}BBrNNaO_4$ 568.3574).

General polymerization procedure with monomer 5

A representative polymerization procedure is provided for the entry 9 in Table 3. The polymerization was carried out in nitrogen atmosphere inside a glovebox. Ag_2SO_4 (12 mg, 38 μmol) was placed in a 20 ml glass scintillation vial used as the reaction vessel. MIDA-boronate monomer **5** (47 mg, 75.3 μmol) and catalytic initiator **3** (2.5 mg, 3.2 μmol) were added to the vial via respective THF stock solutions. More THF was added to bring the total THF volume to 4 ml, and a magnetic stir bar was placed in the vial. A solution of 247 mg (0.76 mmol) of Cs_2CO_3 in 0.20 ml of freeze-thawed degassed, deionized H_2O was added to reaction mixture. The vial was capped and placed into a heating block preheated to 30 °C, and the reaction mixture was stirred for 42 h at this temperature. It was then taken outside of the glovebox, and quenched with 3 ml of 12 N HCl, and the resulting mixture was stirred at 45 °C for 1 h. Upon cooling to room temperature, the reaction mixture was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4, and concentrated *in vacuo*. The crude solid was then dissolved in ~0.5 ml of CH_2Cl_2 and added into acetone (~6 ml) in a glass centrifuge tube inducing precipitation of a yellow (sometimes with a blue hue) polymer. The tube was then placed into a freezer for at least 1 h. The chilled tube was centrifuged at 4000 rpm for 5 min. The supernatant was decanted from the tube leaving a spongy puck of polymer material. The polymer was then dried *in vacuo* yielding 13 mg (42%) of PF polymer as a yellow brittle solid. GPC (eluent THF, calibrated against polystyrene standards): M_n 4.7 kDa, $Đ$ 1.11. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.94 – 7.86 (m, 2H), 7.79 – 7.71 (m, 4H), 7.45 – 7.28 (m, 0.31H), 2.37 (s, 0.23H), 2.28 – 2.05 (m, 4H), 1.30 – 1.15 (m, 24H), 0.88 – 0.83 (m, 6H).

Polymerization of monomer 1. Polymerization of thiophene monomer **1** was carried out using a general procedure outlined above for monomer **5**. In brief, 31 mg (76 μmol) of monomer **1** (prepared as described in ref. 3), 2.5 mg (3.2 μmol) of **3**, and 12 mg (38 μmol) of Ag_2SO_4 were pre-mixed in 4 ml of THF at 30 °C. Then a solution of 247 mg (760 μmol) of Cs_2CO_3 in 0.2 ml of degassed H_2O was added and the reaction mixture was stirred for 24 h at 30 °C. A 12 N solution of HCl (3 ml) was added to the mixture and it was stirred for 1 h yielding a dark brown solution. The mixture was extracted with CH_2Cl_2, washed with water, dried over Na_2SO_4 and concentrated *in vacuo*. The residual solid was dissolved in a small amount of CH_2Cl_2, reprecipitated into 15% MeOH in acetone, the solid was separated by centrifugation and dried *in vacuo* yielding 6.7 mg

(53%) of P3HT as a red-purple solid. GPC (eluent THF, calibrated against polystyrene standards): M_n 4.41 kDa, $Đ$ 1.09. ^{1}H NMR spectrum was identical to the previously published data.[4] The second polymerization run was done exactly following the procedure above but without Ag_2SO_4: yield 42%, GPC (eluent THF, calibrated against polystyrene standards): M_n 4.92 kDa, $Đ$ 1.09.

Kinetic studies

Polymerization kinetics (representative procedure). The reaction was carried out in nitrogen atmosphere inside a glovebox. Ag_2SO_4 (47.0 mg, 151 μmol) was placed in the reaction flask followed by stock solutions in THF of 5.0 mg (6 μmol) of catalytic initiator **3** and 190 mg (304 μmol) of MIDA-boronate **5**. The mixture was diluted to 16 ml total volume with additional THF, and a solution of 0.97 g (3.04 mmol) of Cs_2CO_3 in 0.80 ml of freeze-thawed degassed, deionized H_2O was added to the reaction mixture. The addition of base to the reaction was considered the reaction initiating step and designated as zero reaction time. The reaction flask was sealed and placed into a heating block pre-heated to 30 °C placed on top of a hotplate magnetic stirrer. The reaction mixture was stirred at 500 rpm for 72 h. Aliquots of 1 ml were taken at specified times via syringe and transferred into 4 ml glass vials. The collected aliquot was immediately quenched with 1 ml of 12 N HCl, taken outside of glovebox, and heated at 45 °C for 1 h. Then the reaction mixture was extracted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*. The residual material was used without further purification for GPC analysis to determine M_n, M_w and polydispersity index. To obtain pure polymer samples for the comparison analysis (e.g. for the data shown in Figs. 8 and S5) the polymer samples were additionally reprecipitated (by dissolving the samples in ~0.5 ml of CH_2Cl_2, dropwise adding the solution to 6-10 ml of acetone, and centrifuging at 4000 rpm to separate solid precipitate which was then dried *in vacuo*). The reprecipitated samples were analyzed by GPC, and the absolute M_n values were also determined by end-group ^{1}H NMR analysis (using integrated intensities of the signal from CH_3 protons of *o*-tolyl end-group at 2.4 ppm and a signal of two CH_2 groups from the octyl substituents of fluorenyl at ~2.2 ppm (see representative ^{1}H NMR spectrum in Fig. S26). The reliability of the determination was also checked by using integrated intensity of the fluorenyl aromatic ^{1}H signals as an alternative reference.

Checking for accuracy and reproducibility of polymerization kinetic data. It was important to check the accuracy and reproducibility of the kinetic measurements since the GPC

analysis used for the experiment described above (and for other polymerization kinetic experiments in this work) did not produce the absolute molecular weights but their values relative to polystyrene standards. We also wanted to check if precipitation of the polymer samples in acetone prior to GPC analysis could also affect the kinetic data. Therefore, we carried out the first stage of polymerization run again, and analyzed the results both before and after aliquot sample precipitation in acetone. In addition, we compared the M_n values derived from GPC analysis with the absolute M_n values obtained by the end-group ^{1}H NMR analysis (as described in the representative example above). The comparison kinetic plots from this experiment are shown in Fig. S6. Although GPC-derived M_n values obtained with the precipitated polymer samples were generally higher than the absolute M_n values obtained using ^{1}H NMR analysis and the values obtained from the samples analyzed by GPC prior to precipitation, the obtained values for the polymerization rate constants were expectedly close to each other (i.e. GPC-derived rate constant k_{polym} from precipitated samples was 0.044 h^{-1}, the value obtained from the end-group ^{1}H NMR analysis was 0.037 h^{-1}, and the value obtained from GPC analysis of the non-precipitated aliquot samples was 0.054 h^{-1}). The invariance of the k_{polym} could be anticipated considering that in the semilogarithmic kinetic plots, the pseudo first-order rate constant is the slope of the linear relationship between ln(M_n) vs. time, and thus depends on the change of the polymer molecular weight over time rather than on the absolute M_n values. Therefore, with this experiment we confirmed that using molecular weight values obtained by GPC calibrated relative to polystyrene standards provided sufficiently accurate data for subsequent kinetic analysis.

Hydrolysis kinetics of MIDA-boronate monomer 5 (representative procedure). The reaction was performed in nitrogen atmosphere inside a glovebox. Ag_2SO_4 (47.0 mg, 151 μmol) was placed in the reaction flask followed by a stock solution in THF of 190 mg (304 μmol) of MIDA-boronate **5**. The reaction mixture was diluted to 16 ml total volume with additional THF, and a solution of 0.97 g (3.04 mmol) of Cs_2CO_3 dissolved in 0.80 ml of freeze-thawed degassed, deionized H_2O was added. The addition of base to the reaction was considered the reaction initiating step and designated as zero reaction time. The reaction flask was sealed and placed into a heating block pre-heated to 30 °C placed on top of a hotplate magnetic stirrer. The reaction mixture was stirred at 500 rpm for 48 h. Aliquots of 0.5 ml were taken at specified times via syringe and transferred into 4 ml glass vials. They were immediately washed with water, extracted

with CH_2Cl_2, dried over Na_2SO_4, concentrated *in vacuo*, and the residue was redissolved in 0.6 ml of $CDCl_3$ and analyzed by ^1H NMR.

The concentration of MIDA-boronate **5** and corresponding boronic acids were determined through integrated intensity of the two doublets corresponding to CH_2 protons within the BMIDA unit (δ 4.00 and 3.81 ppm), $I(\mathbf{5}, CH_2)$, whereas the relatives amounts of MIDA-boronate **5** and boronic acid **9** were determined via integrated intensities of the CH_2 protons of octyl groups (δ 1.98-1.92 ppm for **5** and 2.21-2.0 ppm for **9**). The accuracy of determination (and the absence of protodeboronation product) was confirmed via integrated intensity of the octyl CH_3 protons (triplet at δ 0.84 ppm). The mole fraction of MIDA-boronate **5** at a given time *t* was defined as the ratio of the $I(\mathbf{5}, CH_2)$ integrated intensities at the given time to that before initiation of hydrolysis:

$$x_{\text{MIDA-boronate } \mathbf{5}} = \frac{I(\mathbf{5}, \mathrm{CH_2})(t)}{I(\mathbf{5},\ \mathrm{CH_2})(0)}$$

The hydrolysis kinetics of MIDA-boronate 10 was studied using the same approach as described above for compound **5**.

Small-molecule coupling kinetics. The reaction was carried out in nitrogen atmosphere inside a glovebox. Ag_2SO_4 (14.8 mg, 47.3 μmol) was placed in the reaction flask followed by stock solutions in THF of 75.0 mg (94.8 μmol) of carbazole-free catalytic initiator **3** and 51.7 mg (94.8 μmol) of MIDA-boronate **10**. The mixture was diluted to 5 ml total volume with additional THF, and a solution of 0.31 g (0.95 mmol) of Cs_2CO_3 in 0.25 ml of freeze-thawed degassed, deionized H_2O was added to the reaction mixture. The addition of base to the reaction was considered the reaction initiating step and designated as zero reaction time. The reaction flask was sealed and placed into a heating block pre-heated to 30 °C placed on top of a hotplate magnetic stirrer. The reaction mixture was stirred at 600 rpm for 40 h. Aliquots of 0.5 ml were taken at specified times via syringe and transferred into 4 ml glass vials. Then the reaction mixture was extracted with CH_2Cl_2, washed with water and brine, dried over Na_2SO_4 and concentrated *in vacuo*, the residue was redissolved in 0.6 ml of $CDCl_3$ and analyzed by ^1H NMR.

The total concentration of unreacted MIDA-boronate **10** in specific aliquots was determined using the same approach as described for the hydrolysis kinetics above. However, the concentration of MIDA-boronate **10** that has participated in the cross-coupling reaction (rather than in hydrolysis) was determined through the integrated intensity of the singlet corresponding to

the CH_3 protons of the *o*-tolyl group belonging to the coupling product **11** [δ 2.33 ppm], *I*(**12**, CH_3). The calibration reference for concentration determination was the integrated intensity of the octyl CH_3 protons (triplet at δ 0.84 ppm) as this signal remained unchanged for all the species present in the reaction mixture at any given time (i.e. for MIDA-boronate **10**, its hydrolysis product boronic acid, and the coupling product **11**). The mole fraction of coupled MIDA-boronate **10** at a given time *t* was defined as one minus the ratio of the *I*(**11**, CH_3) integrated intensities at the given time to that before initiation of cross-coupling:

$$x_{\text{MIDA-boronate } \mathbf{11}} = 1 - \frac{I(\mathbf{11}, \text{CH}_3)(t)}{I(\mathbf{11},\ \text{CH}_3)(0)}$$

Isolation and characterization of 2-(2-methylphenyl)-9,9-dioctyl-9*H*-fluorene (11). Column chromatography on silica gel (eluent CH_2Cl_2) of the combined aliquots from the small-molecule coupling kinetic experiment yielded 16 mg (35%) of **11** as a colorless solid, R_f 1.00. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.38 – 7.27 (m, 9H), 2.33 (s, 3H), 1.99 (t, *J* = 8.3 Hz, 4H), 1.29 – 1.06 (m, 20H), 0.85 (t, *J* = 7.3 Hz, 6H), 0.75 -0.70 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.93, 150.50, 142.54, 140.92, 140.67, 139.79, 135.46, 130.36, 129.84, 127.76, 127.15, 126.93, 126.75, 125.75, 123.89, 122.85, 119.63, 119.26, 55.07, 40.38, 31.77, 30.02, 29.71, 29.18, 23.81, 22.59, 20.57, 14.05.

X-ray photoelectron spectroscopy (XPS)

The XPS experiments were carried out using PHI *VersaProbe II* instrument equipped with a focused monochromatic Al K(alpha) source. Instrument base pressure was ca. 2-4×10^{-10} Torr. The X-ray power of 25 W at 15 kV was used for all experiments with 100 micron beam size at the X-ray incidence of 90° and take off of 45° angles. The instrument work function was calibrated to give a binding energy (BE) of 84.0 eV for Au 4*f*$_{7/2}$ line for metallic gold and the spectrometer dispersion was adjusted to give a BE's of 284.8 eV, 932.7 eV and of 368.3 eV for the C 1*s* line of adventitious (aliphatic) carbon presented on the non-sputtered samples, Cu 2*p*$_{3/2}$ and Ag 3*d*$_{5/2}$ photoemission lines, respectively. The patented PHI dual charge neutralization system was used on all samples. The high resolution Pd 3*d* and P 2*p* spectra were taken with a minimum of 10-60 s scans using 0.1 eV steps and 93.6 eV pass energy. Signal above background measurement and Shirley background subtraction was made using *MultiPak* v9.0 PHI software. At the ultimate *Versa Probe II* instrumental resolution the temperature spread (at 14/86%) of the metallic silver

Fermi edge was less than 120 meV. All XPS spectra were recorded using PHI software *SmartSoft –XPS* v2.0 and processed using PHI *MultiPack* v9.0 and/or *CasaXPS* v.2.3.14. The relative sensitivity factors from *MultiPack* library were used to determine atomic percentages. Peaks were fitted using GL line shapes a combination of Gaussians and Lorentzians. Wherever possible, conclusions were drawn from the number of resolved signals for a given element, so as to minimize reliance on absolute binding energies for the nonconductive molecular materials. A given sample was examined at 5-6 different spots on the mounted specimen to assure that consistent, reproducible results were obtained.

The high resolution XPS spectra have been deconvoluted into Pd^0 and Pd^{II} 3*d* components and P $2p_{1/2}$ and $2p_{3/2}$ components which generated reasonably good fits (red curves in Figures 6c and d). The fitting parameters are presented in Table S1.

Table S1. Fitting parameters for high-resolution XPS spectra in Figs. 6c and d.

Band	Position, eV	Position separation, eV	FWHM, eV	% Gauss	% Area	Chi squared
Pd 3*d* components (Fig. 6c)						
1 blue	335.48	0.00	1.27	95	5.46	0.91
2 green	337.18	1.70	1.89	77	54.78	
3 blue	340.78	5.30	1.20	76	3.60	
4 green	342.44	6.96	1.80	85	36.16	
P 2*p* components (Fig. 6d)						
1 green	131.1	0.00	2.16	90	66.67	1.08
2 magenta	131.94	0.84	2.16	90	33.33	

Single-crystal X-ray data for compound 3 (co-crystallized with carbazole): CCDC deposit number 2176971

Crystal data

$C_{37}H_{50}IO_2PPd \cdot C_{12}H_9N$	$F(000) = 1960$
$M_r = 958.24$	$D_x = 1.475$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 9.435$ (2) Å	Cell parameters from 9836 reflections
$b = 15.715$ (4) Å	$\theta = 2.6–28.2°$
$c = 29.428$ (6) Å	$\mu = 1.22$ mm^{-1}
$\beta = 98.613$ (6)°	$T = 90$ K
$V = 4314.0$ (16) Å^3	Needle, yellow
$Z = 4$	0.18 × 0.09 × 0.07 mm

Data collection

Bruker Kappa APEX-II DUO diffractometer	17342 independent reflections
Radiation source: fine-focus sealed tube	11838 reflections with $I > 2\sigma(I)$
TRIUMPH curved graphite monochromator	$R_{int} = 0.099$
ϕ and ω scans	$\theta_{max} = 33.9°$, $\theta_{min} = 1.4°$
Absorption correction: multi-scan *SADABS* (Krause *et al.*, 2015)	$h = -14 – 14$
$T_{min} = 0.799$, $T_{max} = 0.919$	$k = -24 – 23$
127212 measured reflections	$l = -46 – 46$

Refinement

Refinement on F^2	192 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.057$	H-atom parameters constrained
$wR(F^2) = 0.109$	$w = 1/[\sigma^2(F_o^2) + (0.0229P)^2 + 15.6455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.08$	$(\Delta/\sigma)_{max} = 0.001$
17342 reflections	$\Delta\rho_{max} = 2.38$ e Å^{-3}
619 parameters	$\Delta\rho_{min} = -1.72$ e Å^{-3}

Single-crystal X-ray data for compound 6: CCDC deposit number 2239393

Crystal data

$C_{49}H_{58}NO_2PPd \cdot 0.25(C_6H_{14})$	$F(000) = 3588$
$M_r = 851.87$	$D_x = 1.315$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 24.539$ (3) Å	Cell parameters from 4065 reflections
$b = 9.9099$ (13) Å	$\theta = 2.2–22.6°$
$c = 35.394$ (4) Å	$\mu = 0.51$ mm^{-1}
$\beta = 90.752$ (2)°	$T = 100$ K
$V = 8606.5$ (19) Å^3	Needle fragment, orange
$Z = 8$	0.14 × 0.08 × 0.07 mm

Data collection

Bruker Kappa APEX-II DUO diffractometer	17561 independent reflections
Radiation source: fine-focus sealed tube	9799 reflections with $I > 2\sigma(I)$
TRIUMPH curved graphite monochromator	$R_{int} = 0.112$
ϕ and ω scans	$\theta_{max} = 26.4°$, $\theta_{min} = 1.2°$
Absorption correction: multi-scan *SADABS* (Krause *et al.*, 2015)	$h = -30 – 30$
$T_{min} = 0.847$, $T_{max} = 0.965$	$k = -9 – 12$
52823 measured reflections	$l = -44 – 43$

Refinement

Refinement on F^2	32 restraints
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.063$	H-atom parameters constrained
$wR(F^2) = 0.131$	$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 6.1953P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} = 0.003$
17561 reflections	$\Delta\rho_{max} = 1.11$ e Å^{-3}
989 parameters	$\Delta\rho_{min} = -0.94$ e Å^{-3}

Single-crystal X-ray data for compound 8: CCDC deposit number 2245647

Crystal data

$C_{74}H_{102}O_6P_2Pd_2$	$F(000) = 2864$
$M_r = 1362.29$	$D_x = 1.318$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 15.2700$ (9) Å	Cell parameters from 9907 reflections
$b = 16.0942$ (9) Å	$\theta = 2.5–34.2°$
$c = 28.5954$ (17) Å	$\mu = 0.62$ mm^{-1}
$\beta = 102.271$ (2)°	$T = 100$ K
$V = 6867.0$ (7) Å^3	Prism, colourless
$Z = 4$	0.29 × 0.26 × 0.18 mm

Data collection

Bruker Kappa APEX-II DUO diffractometer	28225 independent reflections
Radiation source: fine-focus sealed tube	21192 reflections with $I > 2\sigma(I)$
TRIUMPH curved graphite monochromator	$R_{int} = 0.047$
ϕ and ω scans	$\theta_{max} = 35.0°$, $\theta_{min} = 1.4°$
Absorption correction: multi-scan *SADABS* (Krause *et al.*, 2015)	$h = -24 – 24$
$T_{min} = 0.836$, $T_{max} = 0.897$	$k = -25 – 25$
101718 measured reflections	$l = -43 – 45$

Refinement

Refinement on F^2	2 restraints
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.048$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.097$	$w = 1/[\sigma^2(F_o^2) + (0.0321P)^2 + 7.5853P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.04$	$(\Delta/\sigma)_{max} = 0.001$
28225 reflections	$\Delta\rho_{max} = 3.42$ e Å^{-3}
773 parameters	$\Delta\rho_{min} = -1.28$ e Å^{-3}

III. NMR Spectra for Key Compounds

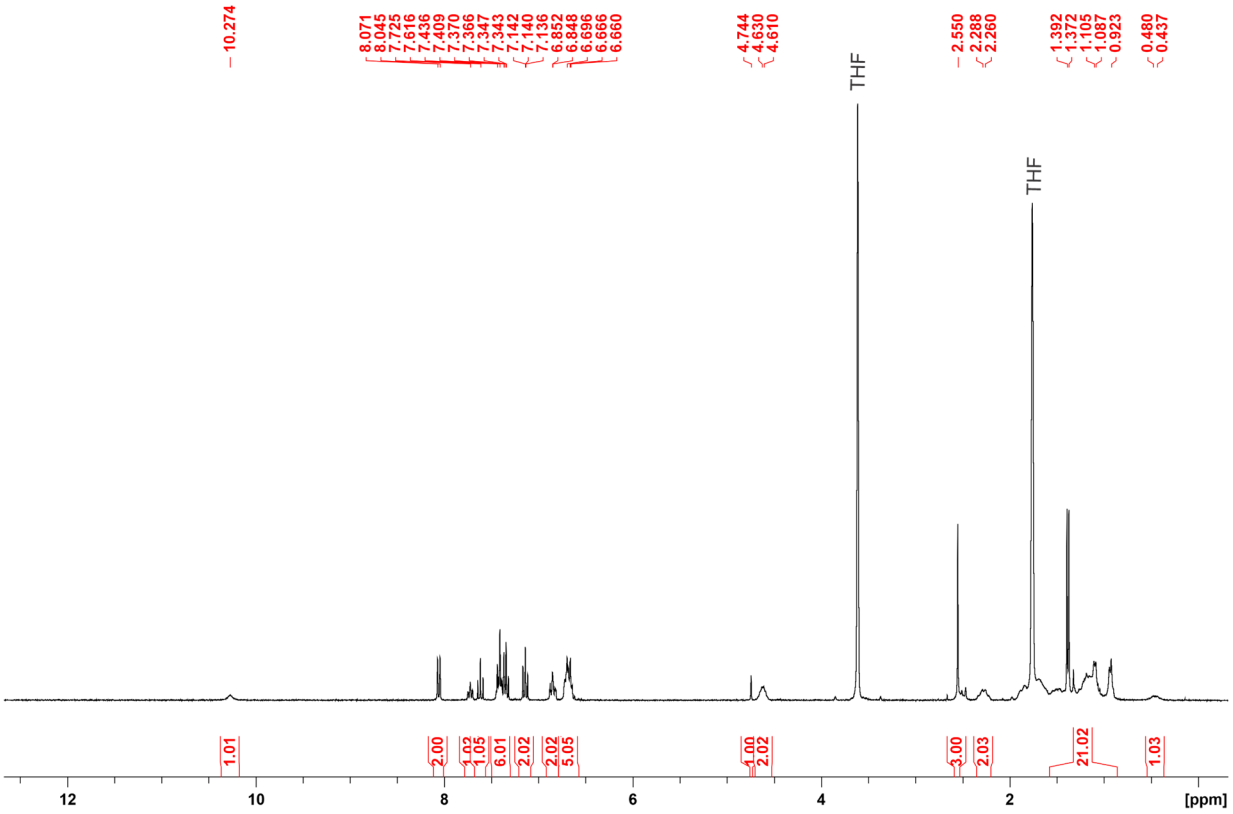


Fig. S16. ^{1}H NMR spectrum (300 MHz, THF-d_8) of compound **3** (co-crystallized with carbazole).

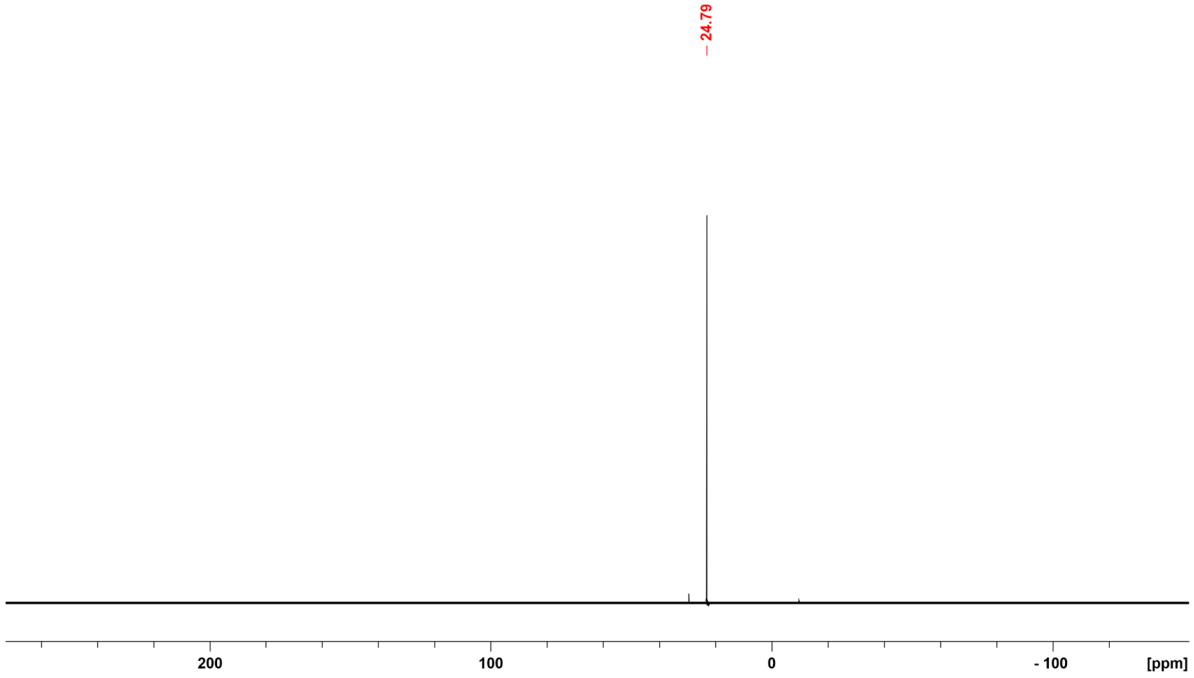


Fig. S17. ^{31}P NMR spectrum (202 MHz, THF with 10% D_2O) of compound **3**.

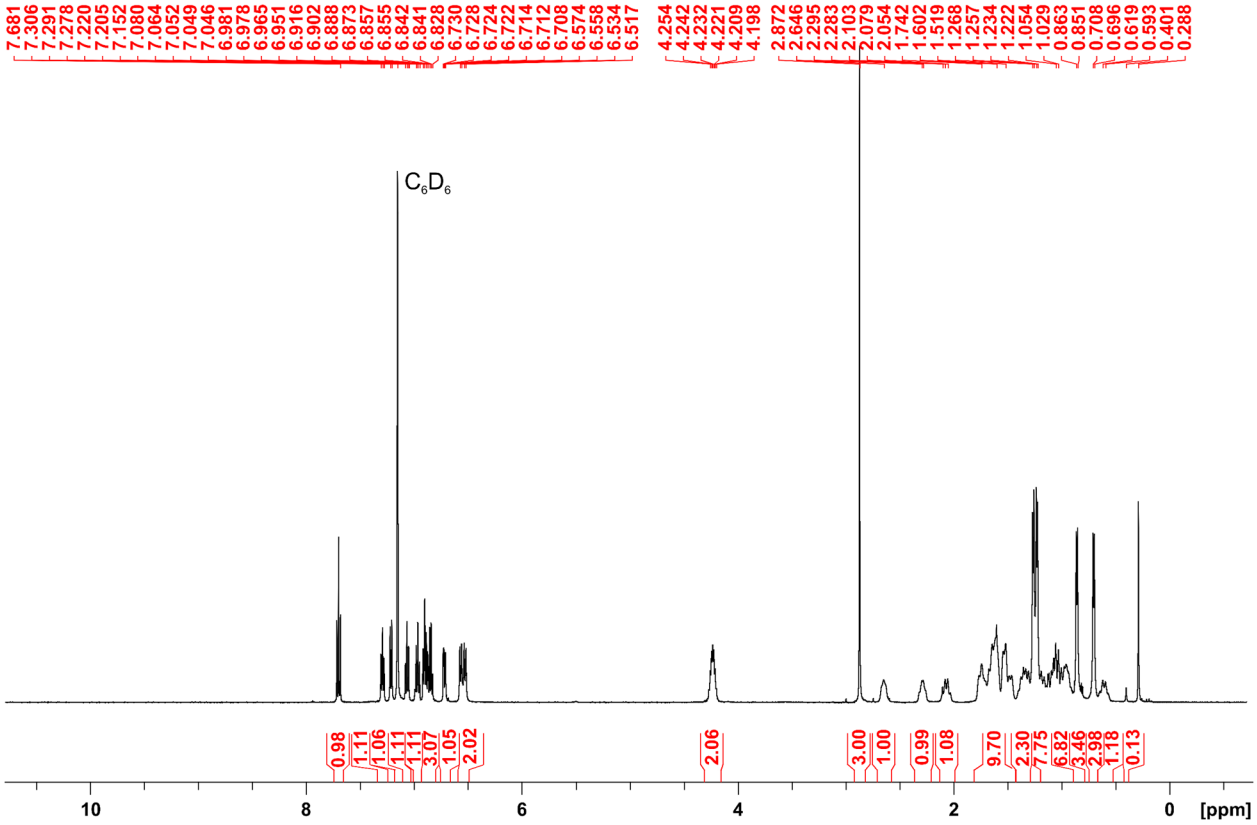


Fig. S18. ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **3** (carbazole-free).

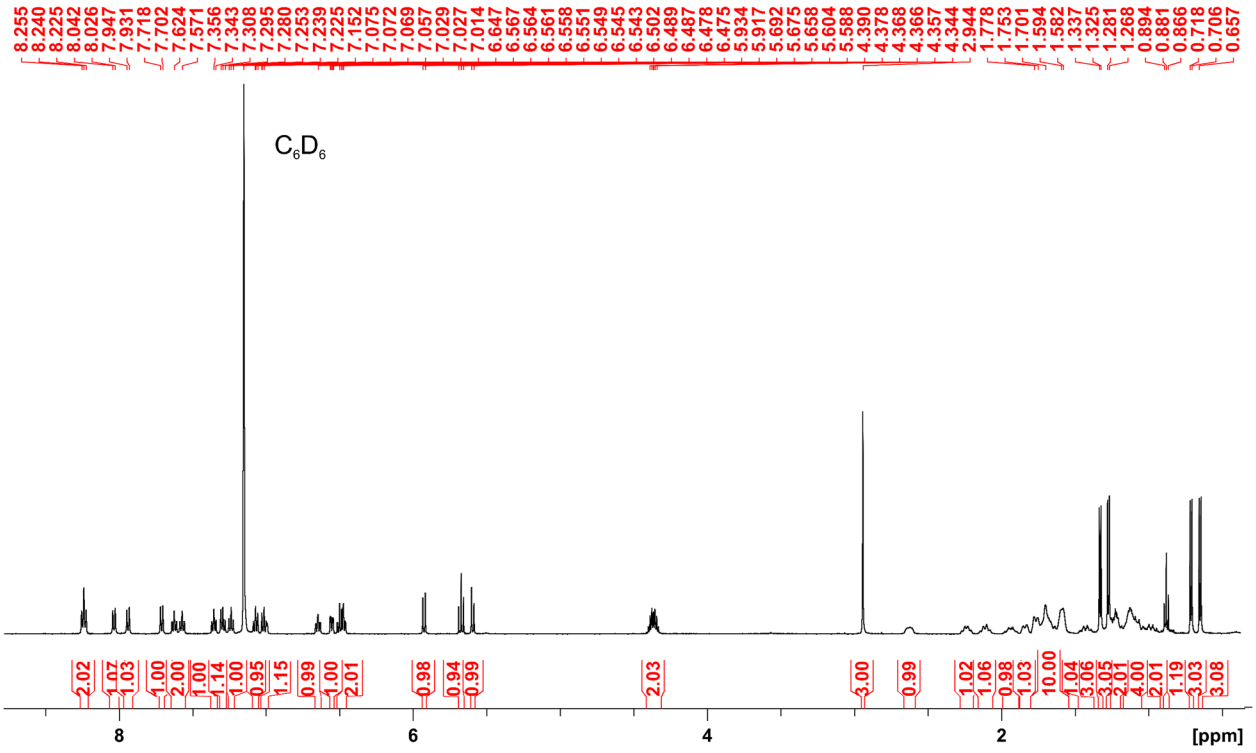


Fig. S19. ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **6**.

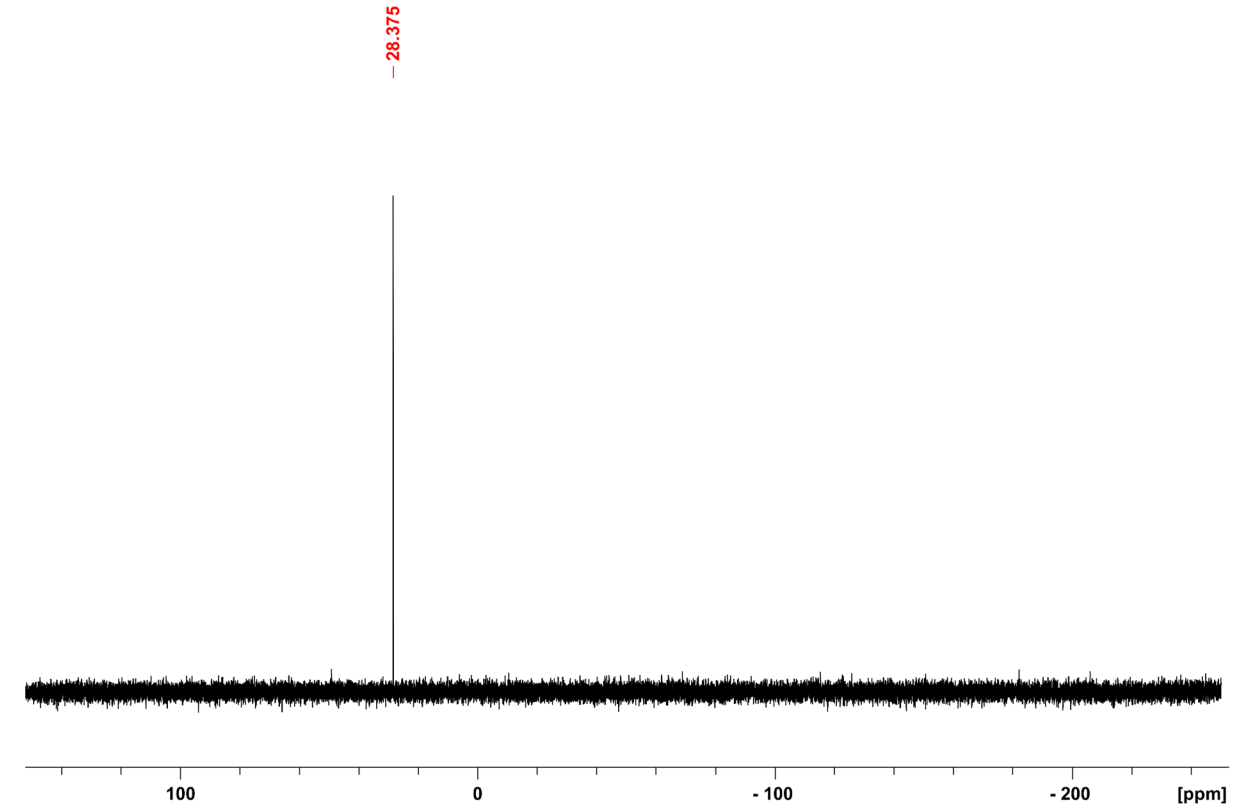


Fig. S20. ^{31}P NMR spectrum (202 MHz, C_6D_6) of compound **6**.

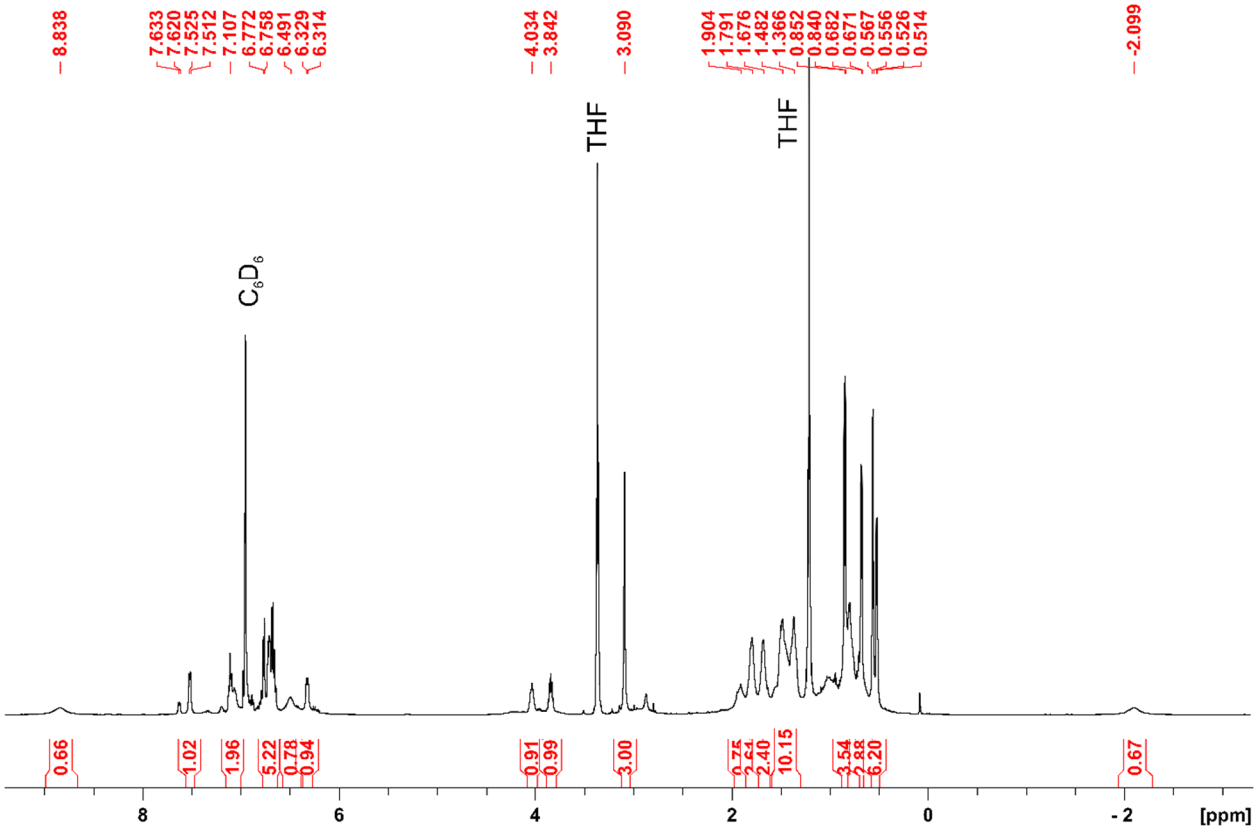


Fig. S21. ^{1}H NMR spectrum (500 MHz, C_6D_6) of compound **7**.

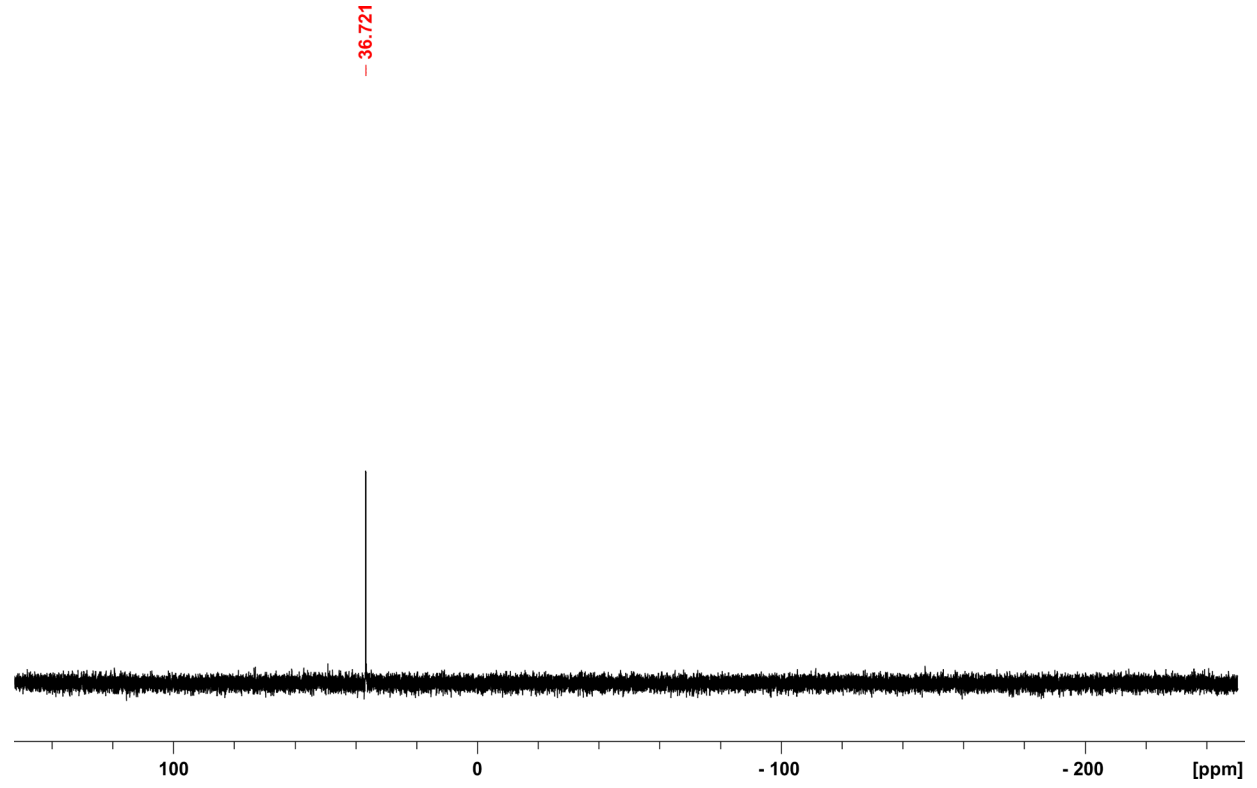


Fig. S22. ^{31}P NMR spectrum (202 MHz, THF with 5% D_2O) of compound **7**.

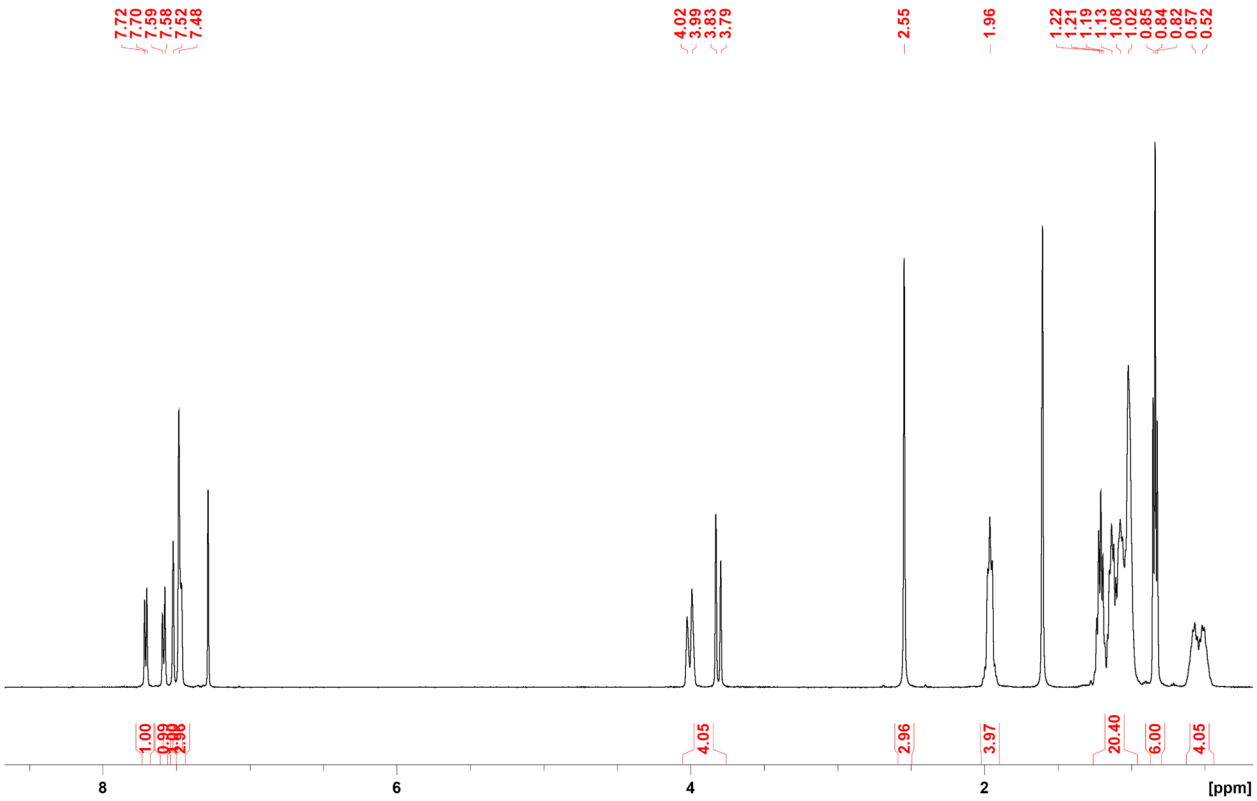


Fig. S23. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **5**.

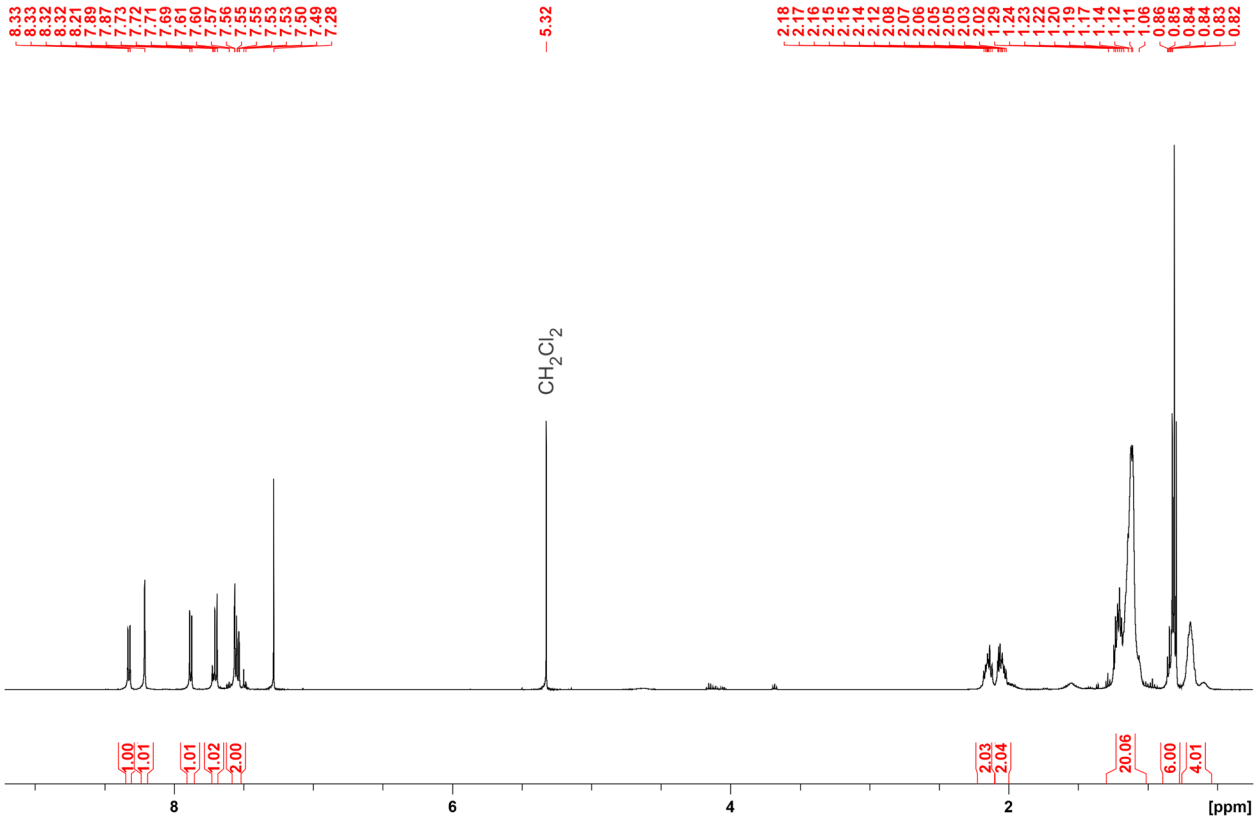


Fig. S24. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **9**.

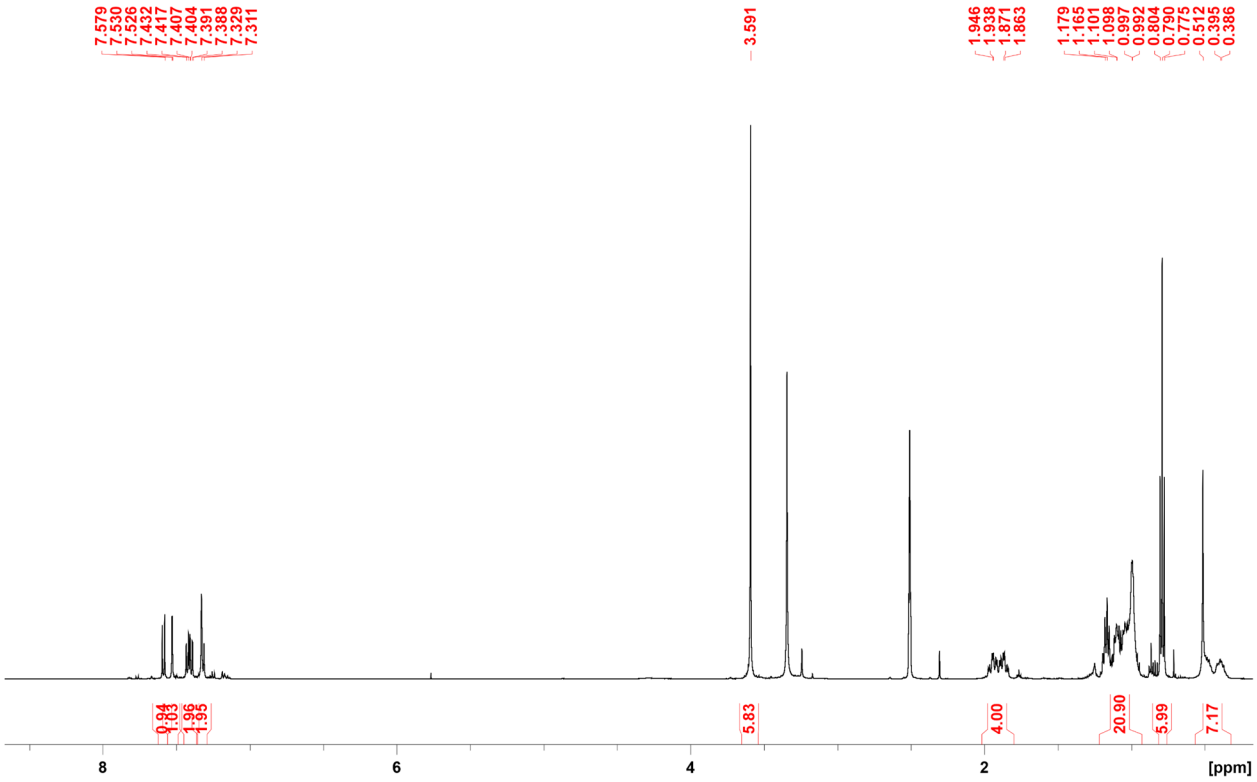


Fig. S25. ^{1}H NMR spectrum (500 MHz, DMSO-d_6) of compound **13**.

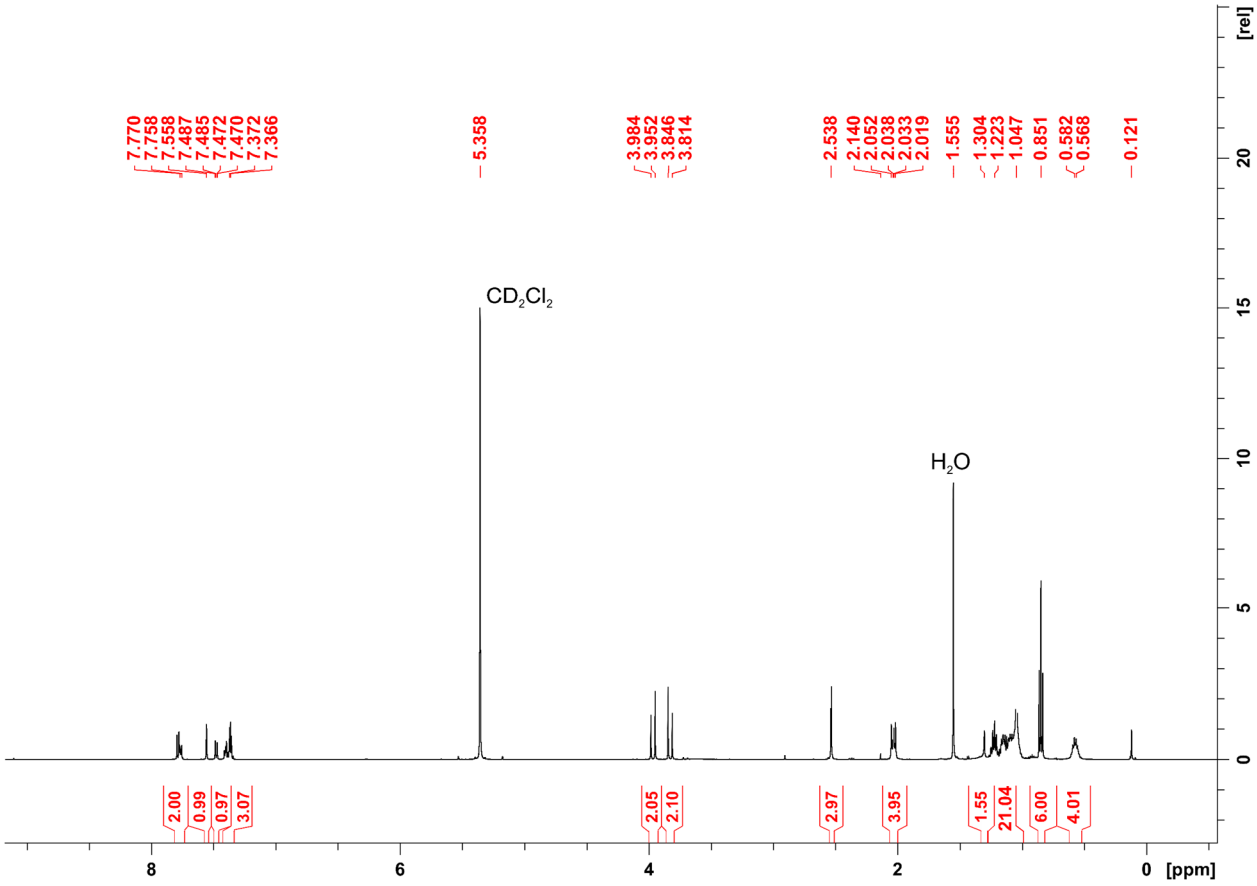


Fig. S26. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of compound **10**.

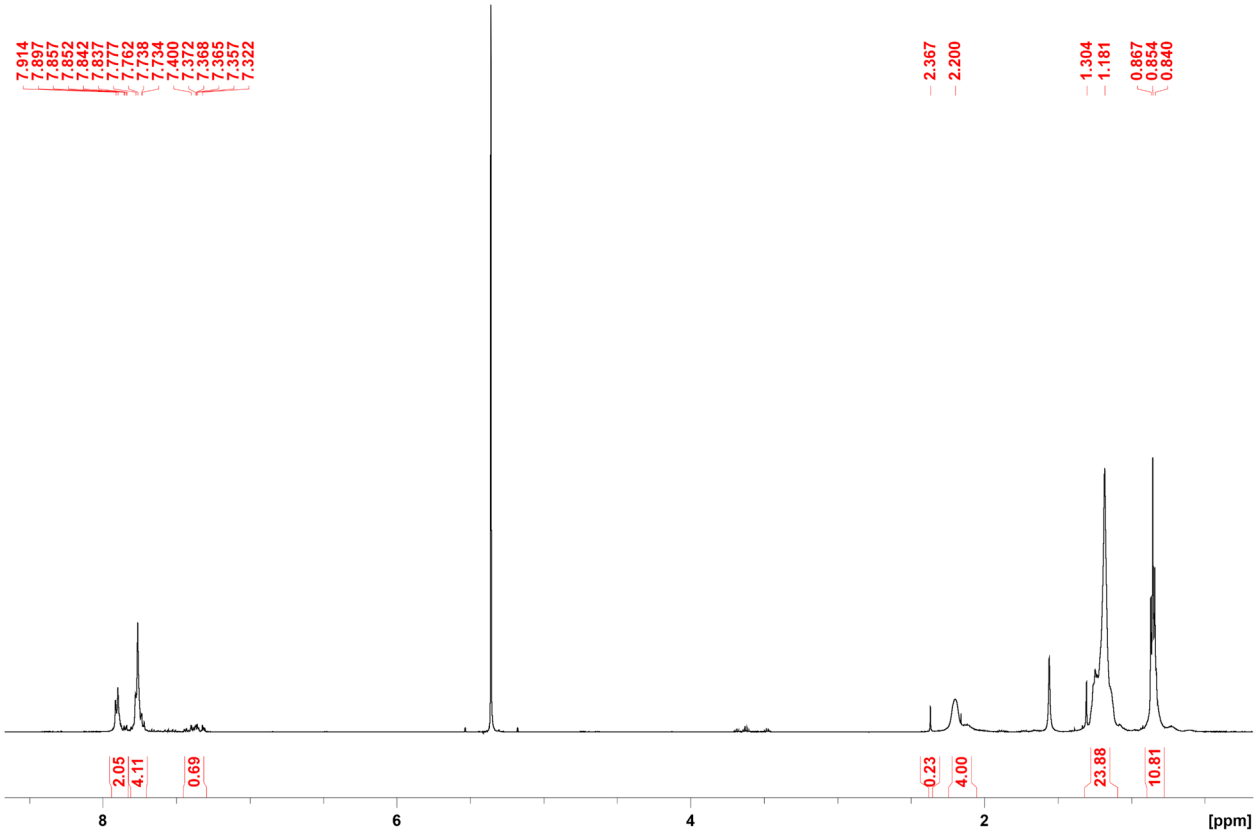


Fig. S27. Representative ^{1}H NMR spectrum (500 MHz, CD_2Cl_2) of PF polymer (sample from entry 9 in Table 3).

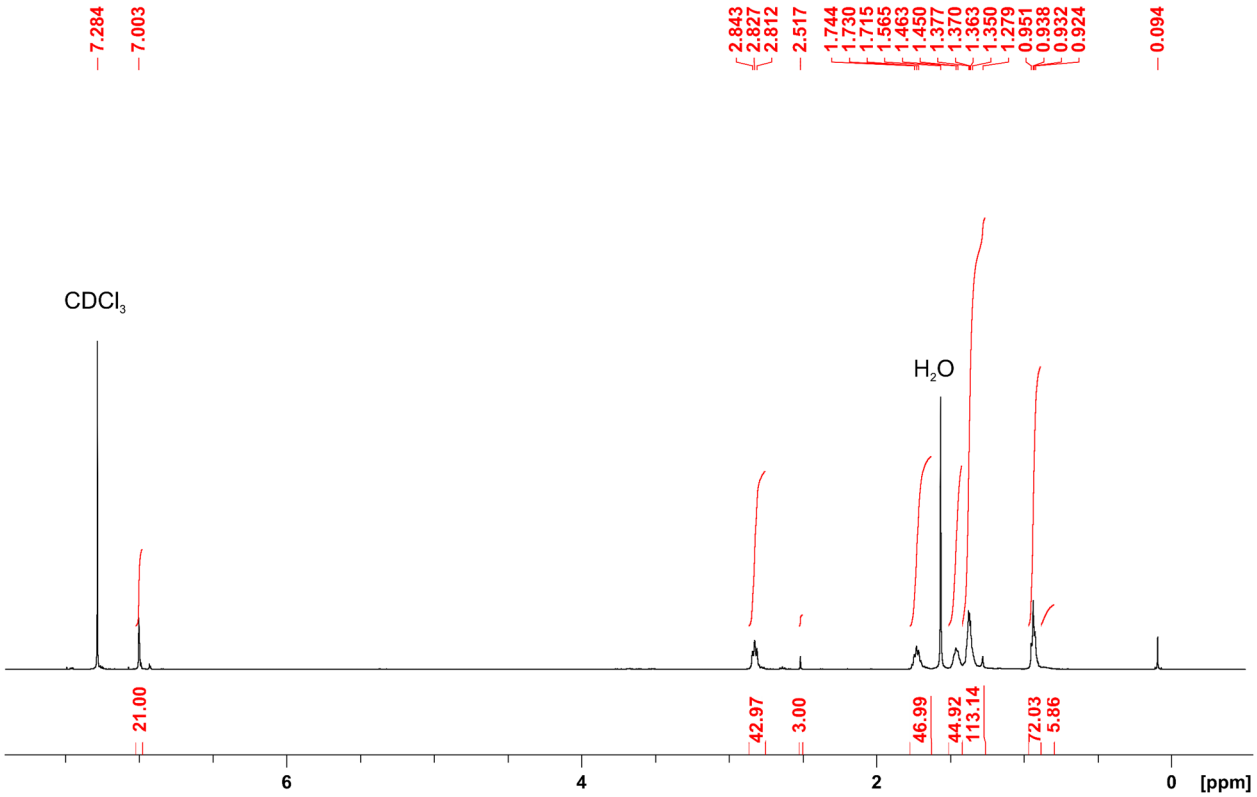


Fig. S28. Representative ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of P3HT polymer (sample from entry20 in Table 4).

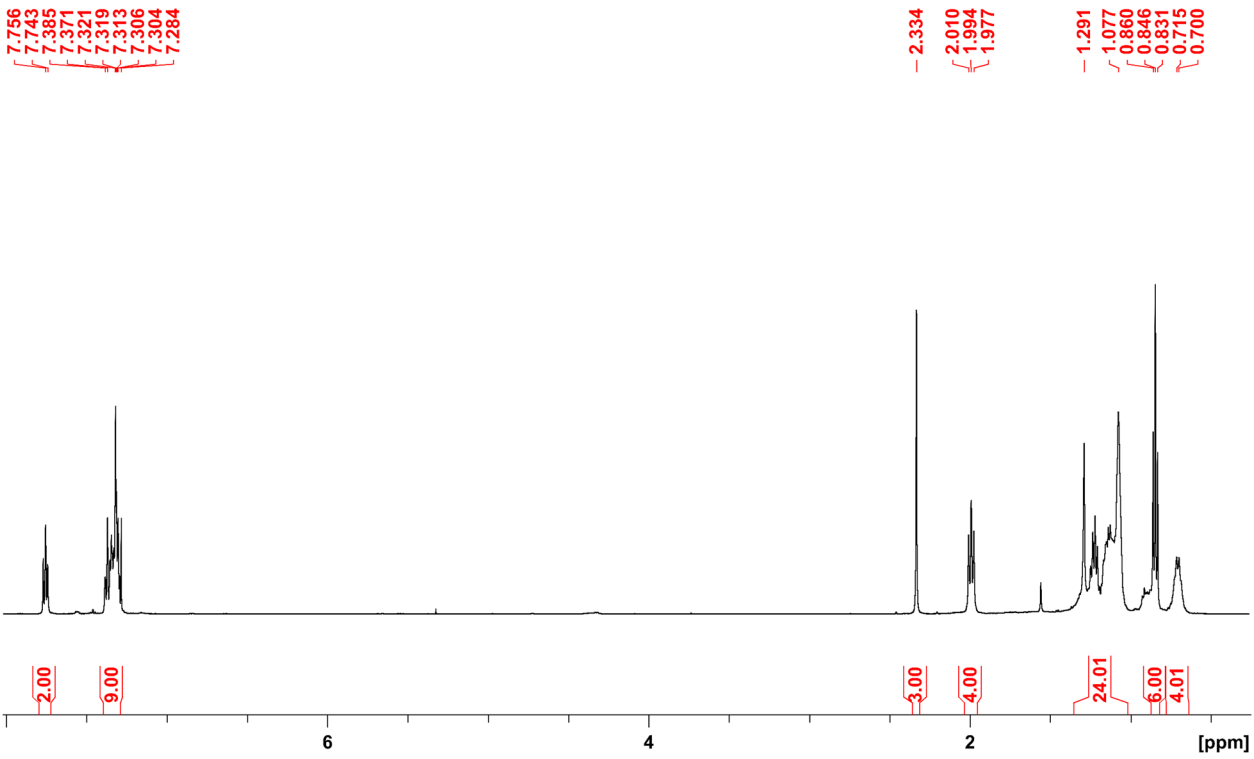


Fig. S29. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **11**.

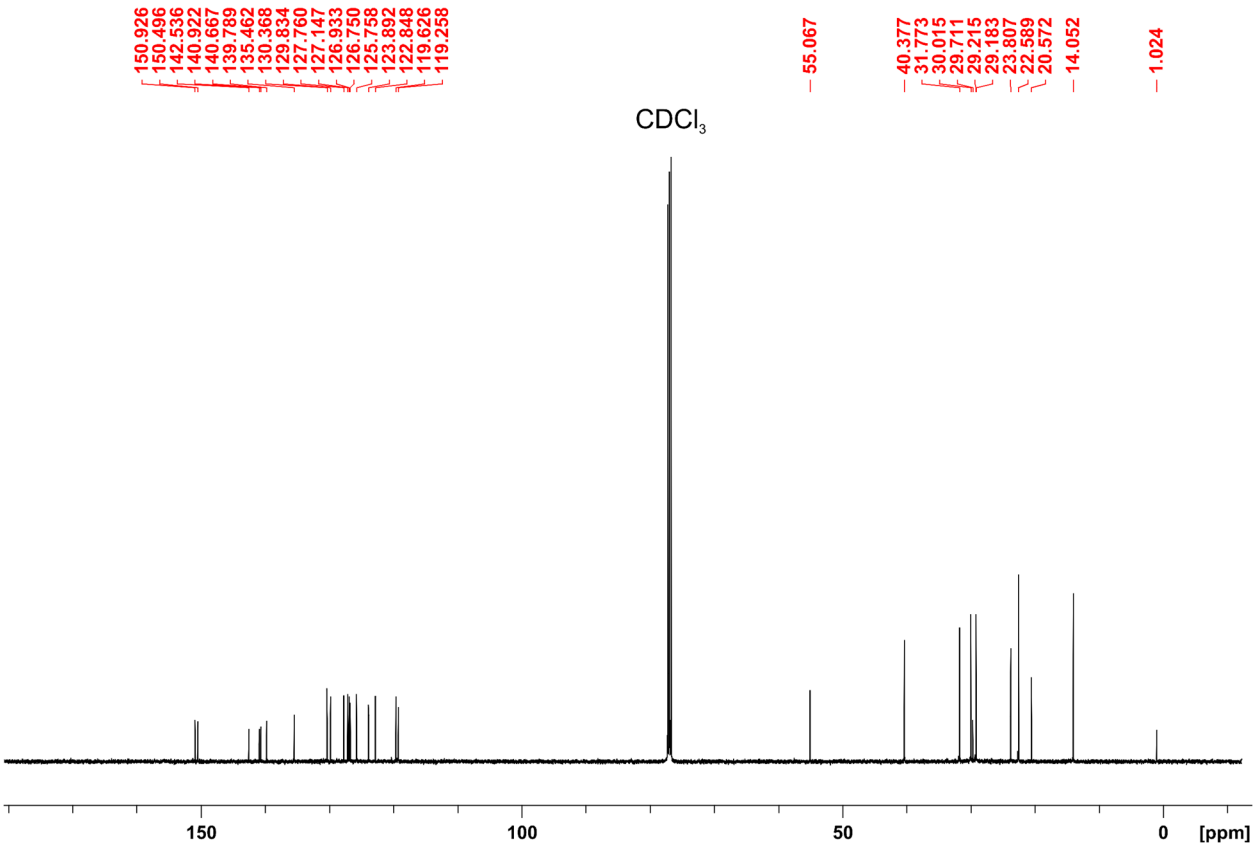


Fig. S30. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **11**.

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