

Supplementary information for

A Palladium Precatalyst for Direct Arylation Polymerization

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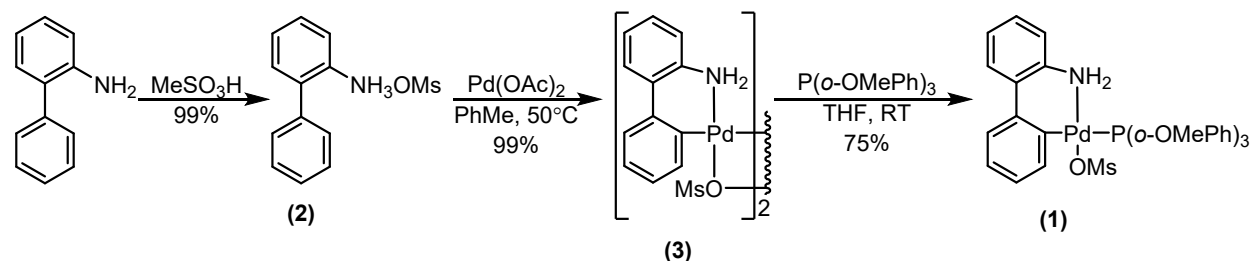
General: ^1H , ^{13}C and ^{31}P NMR were recorded on a Bruker 300 or 500 MHz ultrashield NMR spectrometer in deuterated chloroform. Number average (M_n) and weight average (M_w) molecular weights were determined by size exclusion chromatography using a Viscotek GPC Max VE2001 at 35°C equipped with a Ve 3580 RI detector and two PAS- 104 styrene-divinylbenzene gel columns. The flow rate was fixed at 1.0 mL/min using THF as the eluent. All GPC samples were prepared nominally at 2mg/mL in THF and were filtered through a 0.22 μm PTFE filter into a 1ml chromatography vial. The GPC was calibrated against polystyrene standards ranging from 300g/mol to 600000g/mol. Differential scanning calorimetry (DSC) was performed on q2000 DSC from TA instruments using a rate of 10°C/min under N_2 .

Materials: All materials were purchased from Millipore-Sigma and utilized without any further purification. Solvents were obtained from a JC Meyer solvent system and used without any further purification.

Synthetic Procedures:

Synthesis of P(*o*-OMePh)₃ Precatalyst (1):

Compounds (2) and (3) were synthesized according to the procedure outlined in Buchwald et al.¹



P(*o*-OMePh)₃ Palladium Precatalyst (1): A flame dried 2ml microwave vial was charged with a magnetic stir bar, compound 3 50mg (0.068mmol, 1eq), and P(*o*-OMePh)₃ 47.71mg (0.135mmol, 2eq). The vial was then capped and purged with argon gas 3 times. THF (1.1mL) was then added under a protective atmosphere and the reaction was allowed to proceed for 1 hour or until an off-white precipitate formed. After the allotted reaction time, 90% of the solvent was removed under vacuum and the remaining residue was triturated with pentane and isolated via suction filtration. The off-white solid was then further dried under high vacuum for 24 hours. Yield 71.42 mg (73%). Single crystal suitable for X-ray diffraction was grown through slow evaporation in CHCl_3 .

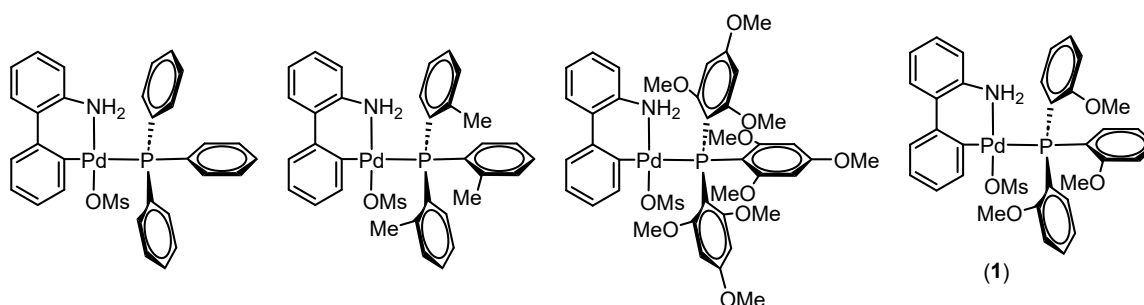
^1H NMR (300MHz, CDCl_3 , 293K, CHCl_3): 7.44 (m, 3H), 7.33 (m, 5H), 7.21 (m, 6H), 6.83 (m, 5H), 6.70 (broad s, 3H), 6.45 (m, 2H), 4.43 (s, 1H), 3.35 (s, 9H), 2.15 (s, 3H)

^{13}C NMR (300MHz, CDCl_3 , 293K, CHCl_3): 160.8, 140.2, 138.7, 136.5,

135.5, 135.3, 132.2, 128.0, 127.4, 126.8, 125.4, 125.1, 124.8, 120.6, 120.6, 120.4, 120.2
 116.8, 111.0, 55.3, 38.5
³¹P NMR (300MHz, CDCl₃, 293K, H₃PO₄): 19.9

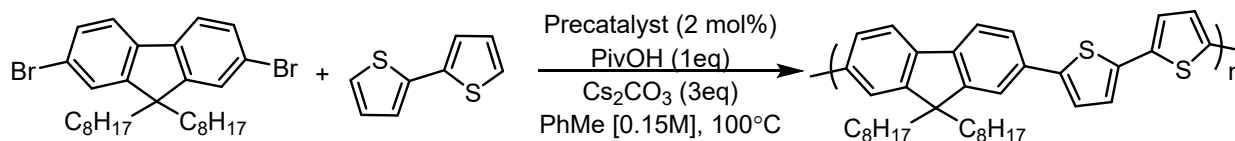
Buchwald-type catalysts screen in Direct Arylation Polymerization to make of Poly(9,9-dioctyl-2,7-fluorene-alt-2,2'- bithiophene) (PFBT).

The following catalysts were screened the direct arylation polymerization to make of Poly(9,9-dioctyl-2,7-fluorene-alt-2,2'- bithiophene) (PFBT). Only (1) gave appreciable molecular weight, all others yielded either no reaction or only produced oligomers.



Time vs. Molecular weight experiments for of Poly(9,9-dioctyl-2,7-fluorene-alt-2,2'- bithiophene) (PFBT).

PFBT Synthesized using precatalyst (1):



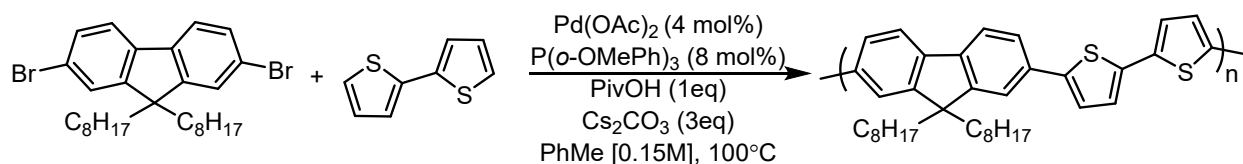
The polymerization of PFBT was done according to the procedure outlined by LeClerc et al.² A flame dried 5mL microwave vial with a magnetic stir bar was charged with 75.3mg (0.45mmol, 1eq) of 2,2'-bithiophene, 246.8mg of 9,9-dioctyl-2,7- dibromofluorene (0.45mmol, 1eq), 46.0mg of pivalic acid (0.45mmol, 1eq), 6.5mg of P(*o*-OMePh)₃ palladium pre-catalyst (0.009mmol, 0.02eq), and 439.86mg of Cs₂CO₃ (1.35mmol, 3eq). The vial was sealed and freeze-dried by repeatedly cooling with liquid nitrogen and then drying under high vacuum. The reaction vessel was then purged twice with argon gas. After purging, dry toluene 5mL [0.15M] was added to the reaction vessel under a protective atmosphere and then the reaction was set to stir at 100°C. At the time intervals listed below an aliquot of approximately 0.01mL was extracted from the reaction mixture and without further purification analyzed by GPC. The reaction was then repeated as listed above without removing any aliquots in order to obtain the reaction yield. Upon completing the reaction time (720 min) as determined by the kinetic experiment, the reaction mixture was cooled to room temperature and the PFBT was precipitated by adding the entire reaction mixture to vigorously stirring cold methanol revealing a fibrous yellow polymer. (96%)

Reaction time (min)	M _n (g/mol)	M _w (g/mol)	Đ
60	1600	1636	1.0

120	1743	1808	1.0
180	1999	2219	1.1
240	2273	2687	1.2
300	2652	3440	1.3
360	3629	5226	1.4
420	6173	10719	1.7
480	13592	26376	1.9
540	22629	53992	2.4
600	31447	73154	2.3
660	34371	76634	2.2
720	25594	75424	2.9
780	25594	75424	2.9

Table S1- Time vs. Molecular weight data for PFBT using precatalyst (1)

PFBT synthesized using Pd(OAc)₂/ P(*o*-OMePh)₃:



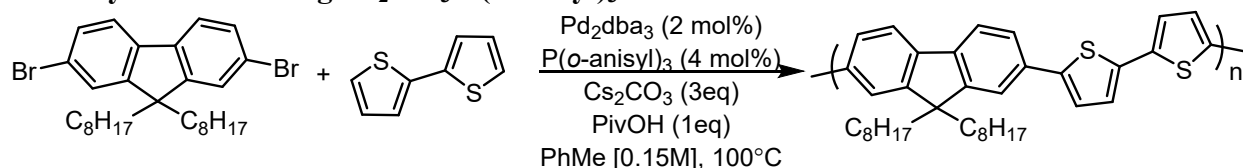
The polymerization of PFBT was done according to the procedure outlined by LeClerc et al.² A flame dried 5mL microwave vial with a magnetic stir bar was charged with 50.40mg (0.30mmol, 1eq) of 2,2'-bithiophene, 164.5mg of 9,9-dioctyl-2,7- dibromofluorene (0.30mmol, 1eq), 30.3mg of pivalic acid (0.30mmol, 1eq), 8.6mg of P(*o*-OMePh)₃ (0.02mmol, 0.08eq), 3.1mg of Pd(OAc)₂ (0.01mmol, 0.05eq) and 293.4mg of Cs₂CO₃ (0.9mmol, 3eq). The vial was sealed and freeze-dried by repeatedly cooling with liquid nitrogen and then drying under high vacuum. The reaction vessel was then purged twice with argon gas. After purging, dry toluene 2mL [0.15M] was added to the reaction vessel under a protective atmosphere and then the reaction was set to stir at 100°C. At the time intervals listed below an aliquot of approximately 0.01mL was extracted from the reaction mixture and without further purification analyzed by GPC. The reaction was then repeated as listed above without removing any aliquots in order to obtain the reaction yield. Upon completing the reaction time (210 min) as determined by the kinetic experiment, the reaction mixture was cooled to room temperature and the PFBT was precipitated by adding the entire reaction mixture to vigorously stirring cold methanol a fibrous yellow polymer. (89%) If the reaction was allowed to proceed past 210 min it will result in the formation of a dark brown gummy insoluble solid.

Reaction time (min)	M _n (g/mol)	M _w (g/mol)	Đ
10	1536	1568	1.0
20	1866	2124	1.1

30	2001	2441	1.2
40	2454	3287	1.3
60	3803	4925	1.3
90	5534	9388	1.7
120	10584	25016	2.4
150	10733	37372	3.5
210	7918	20446	2.6

Table S2- Time vs. Molecular weight data for PFBT using Pd(OAc)₂/P(*o*-OMePh)₃

PFBT synthesized using Pd₂dba₃/P(*o*-anisyl)₃

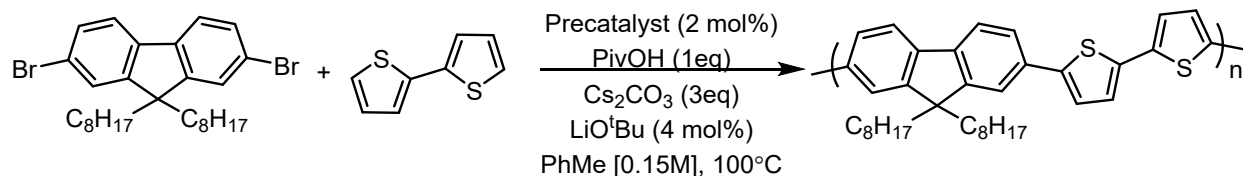


The polymerization of PFBT was done according to the procedure outlined by LeClerc et al.³ A flame dried 5mL microwave vial with a magnetic stir bar was charged with mg (0.45mmol, 1eq) of 2,2'-bithiophene, mg of 9,9-dioctyl-2,7- dibromofluorene (0.45mmol, 1eq), 46.0mg of pivalic acid (0.45mmol, 1eq), 6.5mg Pd₂dba₃ (0.009mmol, 0.02eq), and 439.86mg of Cs₂CO₃ (1.35mmol, 3eq). The vial was sealed and freeze-dried by repeatedly cooling with liquid nitrogen and then drying under high vacuum. The reaction vessel was then purged twice with argon gas. After purging, dry toluene 5mL [0.15M] was added to the reaction vessel under a protective atmosphere and then the reaction was set to stir at 100°C. At the time intervals listed below an aliquot of approximately 0.01mL was extracted from the reaction mixture and without further purification analyzed by GPC. The reaction was then repeated as listed above without removing any aliquots in order to obtain the reaction yield. Upon completing the reaction time (210 min) as determined by the kinetic experiment, the reaction mixture was cooled to room temperature and the PFBT was precipitated by adding the entire reaction mixture to vigorously stirring cold methanol revealing a fibrous yellow polymer. (93%) If the reaction was allowed to proceed past 210 min it will result in the formation of an insoluble dark yellow brittle solid.

Reaction time (min)	M _n (g/mol)	M _w (g/mol)	Đ
60	1472	3375	2.3
120	5841	21013	3.6
150	12838	47026	3.7
180	10679	44448	4.2
210	8789	41363	4.7

Table S3- Time vs. Molecular weight data for PFBT using Pd₂dba₃/P(*o*-anisyl)₃

PFBT synthesized using Precatalyst (1) and LiO^tBu



The polymerization of PFBT was done according to the procedure outlined by LeClerc et al.² A flame dried 5mL microwave vial with a magnetic stir bar was charged with 25.4mg (0.15mmol, 1eq) of 2,2'-bithiophene, 83.4mg of 9,9-dioctyl-2,7- dibromofluorene (0.15mmol, 1eq), 15.7mg of pivalic acid (0.15mmol, 1eq), 2.3mg of P(*o*-OMePh)₃ palladium pre-catalyst (0.003mmol, 0.02eq), 0.5mg of LiO^tBu (0.006mmol, 0.04eq) and 149.9mg of Cs₂CO₃ (0.45mmol, 3eq). The vial was sealed and freeze-dried by repeatedly cooling with liquid nitrogen and then drying under high vacuum. The reaction vessel was then purged twice with argon gas. After purging, dry toluene 1mL [0.15M] was added to the reaction vessel under a protective atmosphere and then the reaction was set to stir at 100°C. At the time intervals listed below an aliquot of approximately 0.01mL was extracted from the reaction mixture and without further purification analyzed by GPC. The reaction was then repeated as listed above without removing any aliquots in order to obtain the reaction yield. Upon completing the reaction time (330 min) as determined by the kinetic experiment, the reaction mixture was cooled to room temperature and the PFBT was precipitated by adding the entire reaction mixture to vigorously stirring cold methanol revealing a fibrous yellow polymer. (87%)

Reaction time (min)	M _n (g/mol)	M _w (g/mol)	Đ
60	1294	1465	1.1
120	2136	3210	1.5
180	3877	7457	1.9
240	6488	14097	2.2
300	20417	54769	2.6
330	17737	65315	3.7

Table S4- Time vs. Molecular weight data for PFBT using precatalyst (1) with LiO^tBu as an additive.

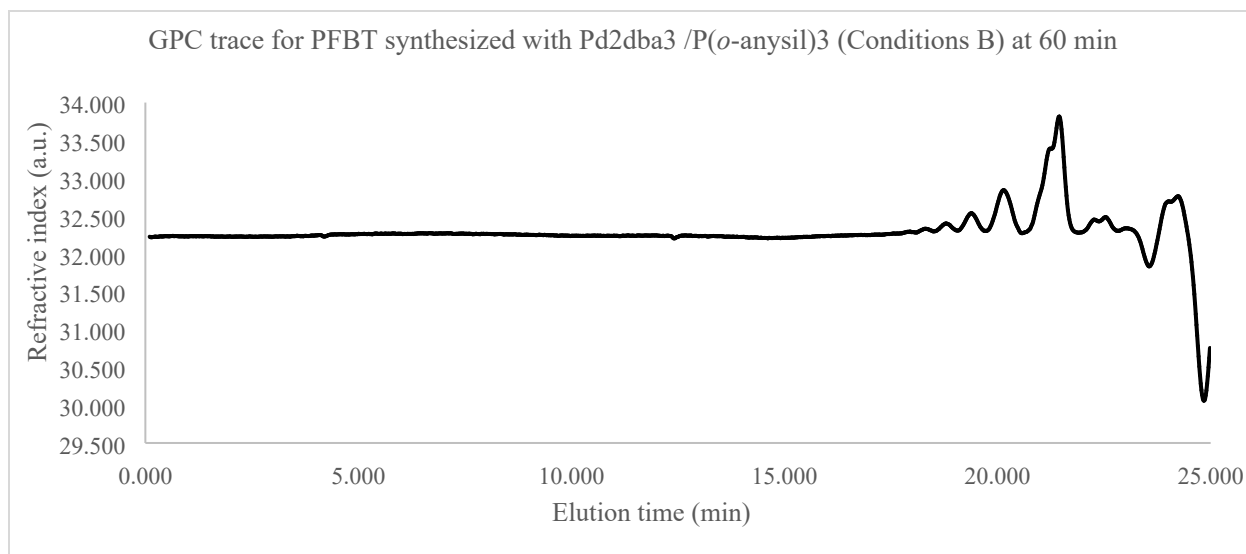


Figure S1. Representative GPC trace for PFBT synthesized with Pd₂dba₃/P(*o*-anysil)₃ at 60 min.

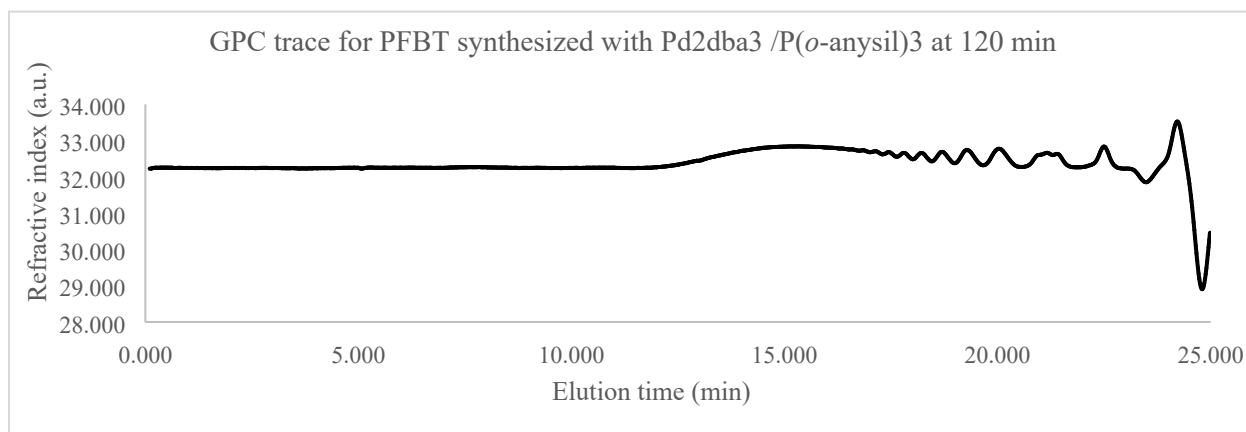


Figure S2. Representative GPC trace for PFBT synthesized with Pd₂dba₃/P(*o*-anysil)₃ at 120 min.

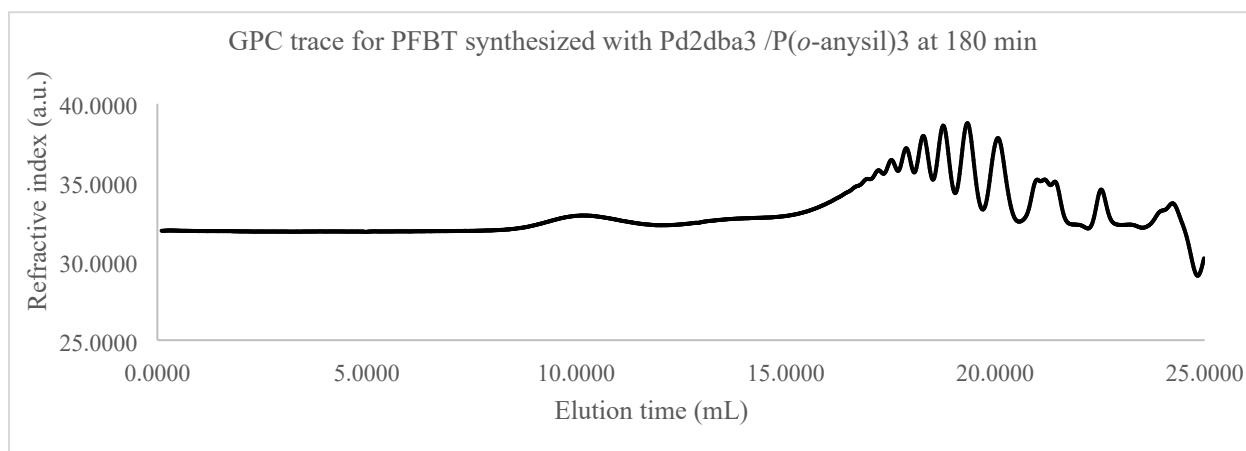


Figure S3. Representative GPC trace for PFBT synthesized with Pd₂dba₃/P(*o*-anysil)₃ at 180 min.

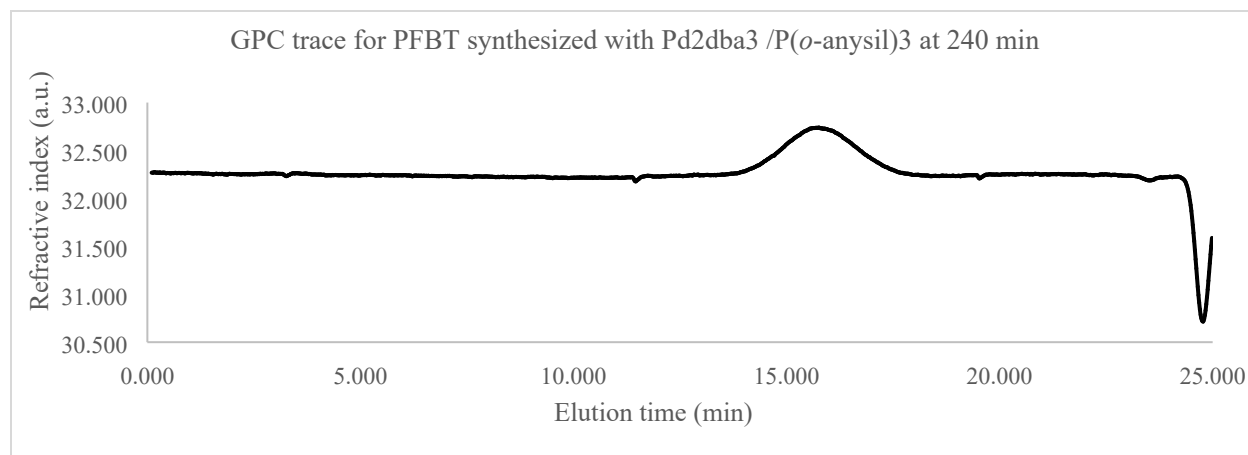


Figure S4. Representative GPC trace for PFBT synthesized with Pd₂dba₃/P(*o*-anysil)₃ at 240 min.

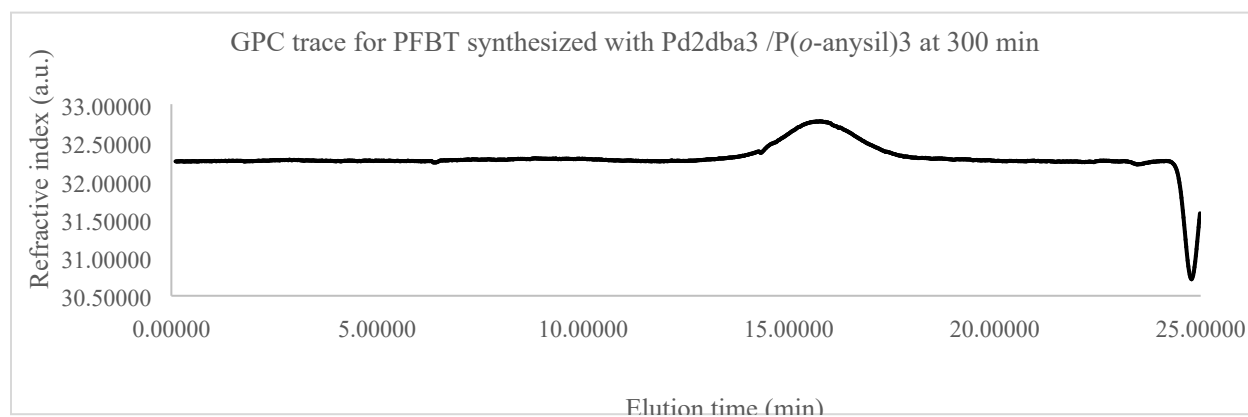


Figure S5. Representative GPC trace for PFBT synthesized with Pd₂dba₃/P(*o*-anysil)₃ at 300 min

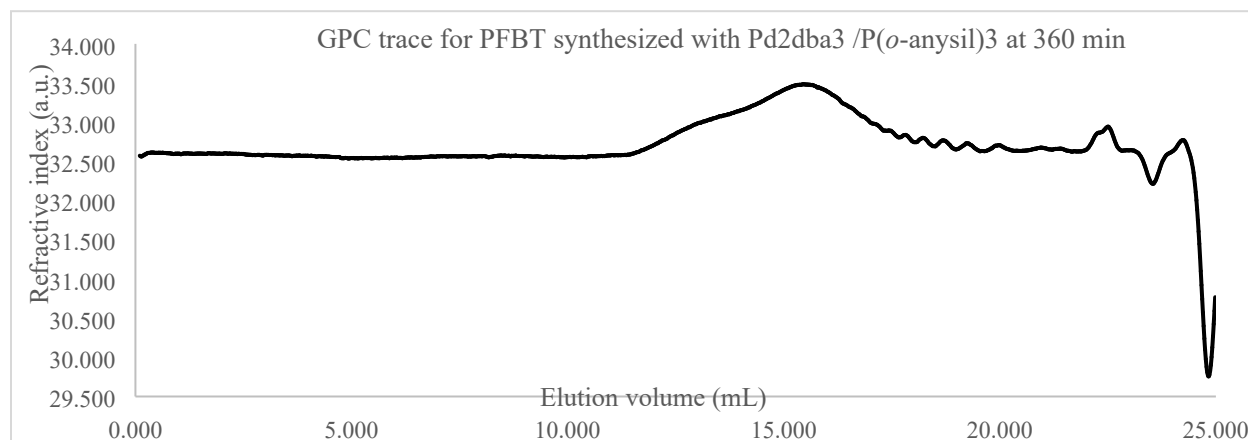


Figure S6. Representative GPC trace for PFBT synthesized with Pd₂dba₃/P(*o*-anysil)₃ at 360 min

Crystal Data

Formula

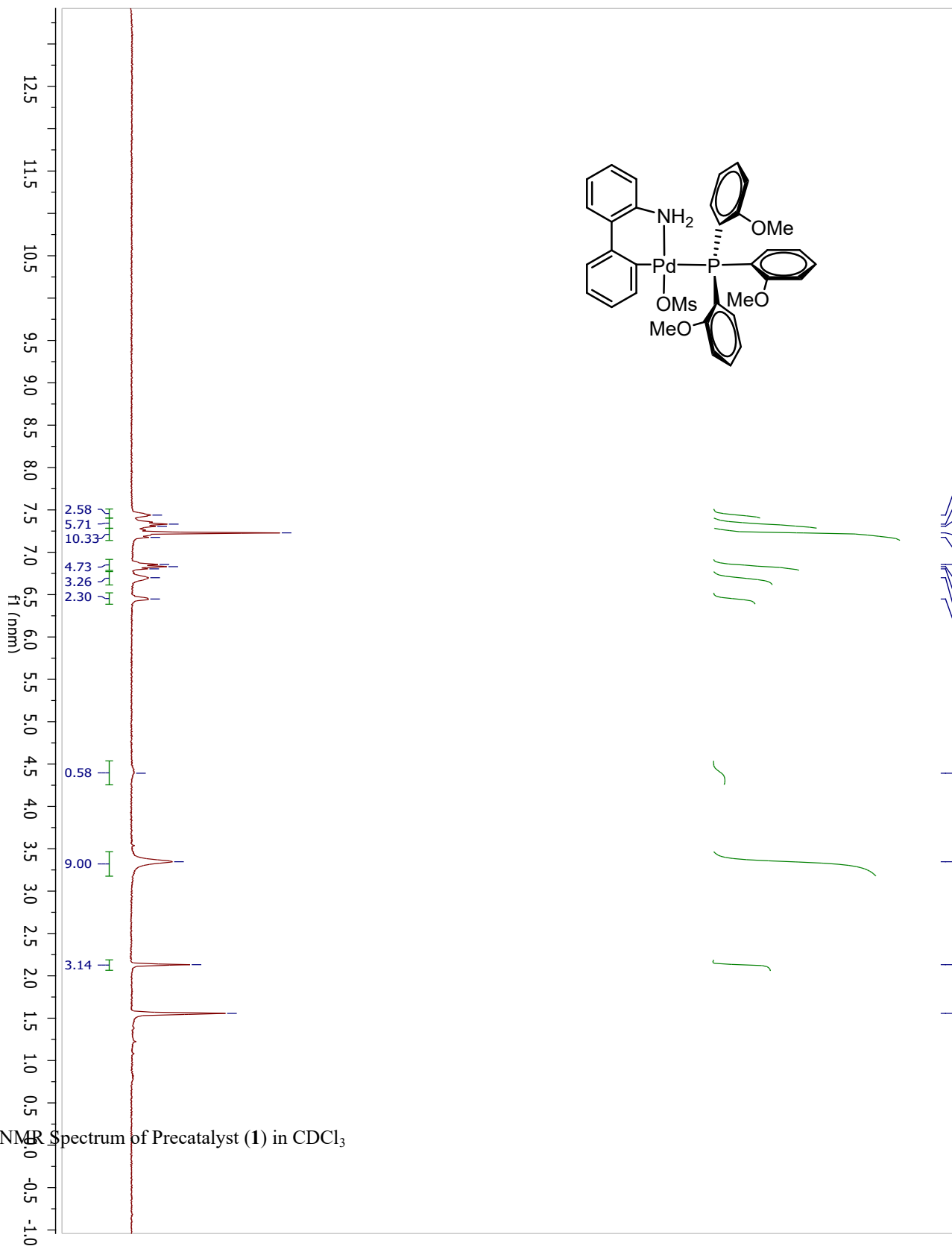
C₃₄ H₃₄ N₀₆ P Pd S. 0.5 C₆ H₁₂

Formula Weight

764.13

Crystal System	monoclinic
Space group	C2/c (No. 15)
a, b, c [Angstrom]	27.2958(11) 10.3051(4) 25.7535(10)
alpha, beta, gamma [deg]	90 109.1286(17) 90
V [Ang**3]	6844.1(5)
Z	8
D(calc) [g/cm**3]	1.401
Mu(MoKa) [/mm]	0.697
F(000)	2960
Crystal Size [mm]	0.04 x 0.11 x 0.14
<u>Data Collection</u>	
Temperature (K)	296
Radiation [Angstrom]	MoKa 0.71073
Theta Min-Max [Deg]	1.6, 26.0
Dataset	-27: 33 ; -11: 12 ; -31: 31
Tot., Uniq. Data, R(int)	6711, 6711, 0.040
Observed Data [I > 2.0 sigma(I)]	4692
<u>Refinement</u>	
Nref, Npar	6711, 403
R, wR2, S	0.0424, 0.0847, 1.33
$w = \frac{1}{\sigma^2(F_o^2) + (0.0257P)^2}$ WHERE $P = \frac{(F_o^2 + 2F_c^2)}{3}$	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.41, 0.91

Table **S5**- Crystal and structure refinement data for 1. Crystal structure of material was elucidated with the aid of the SQUEEZE function.



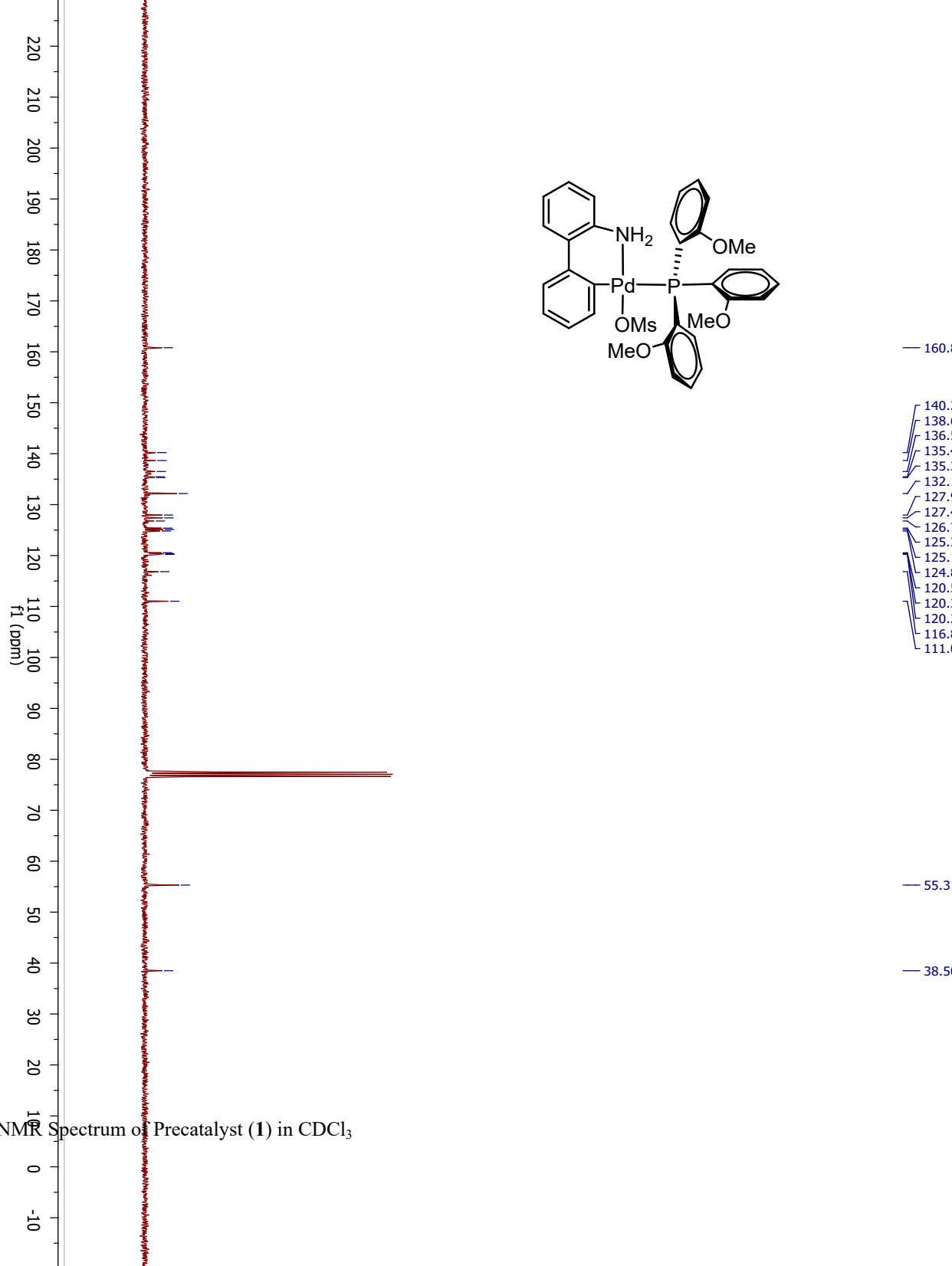


Figure S8- ^{13}C NMR Spectrum of Precatalyst (1) in CDCl_3

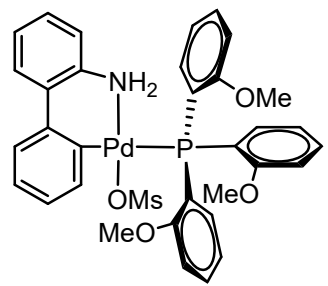
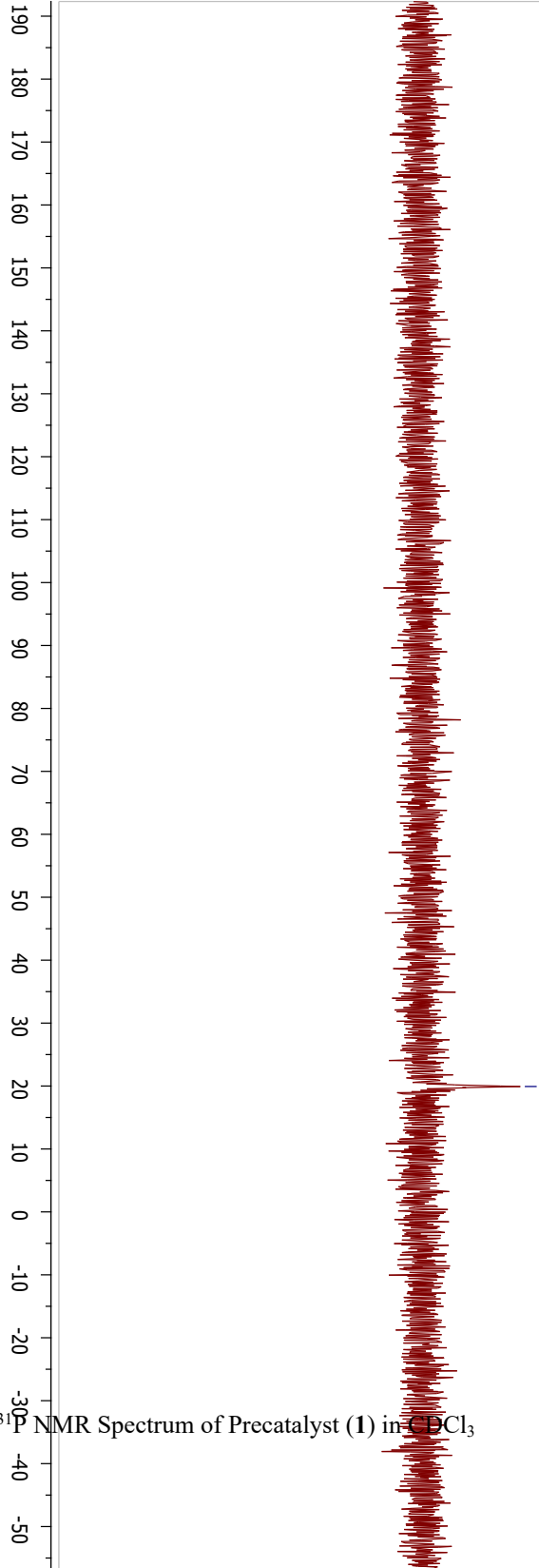
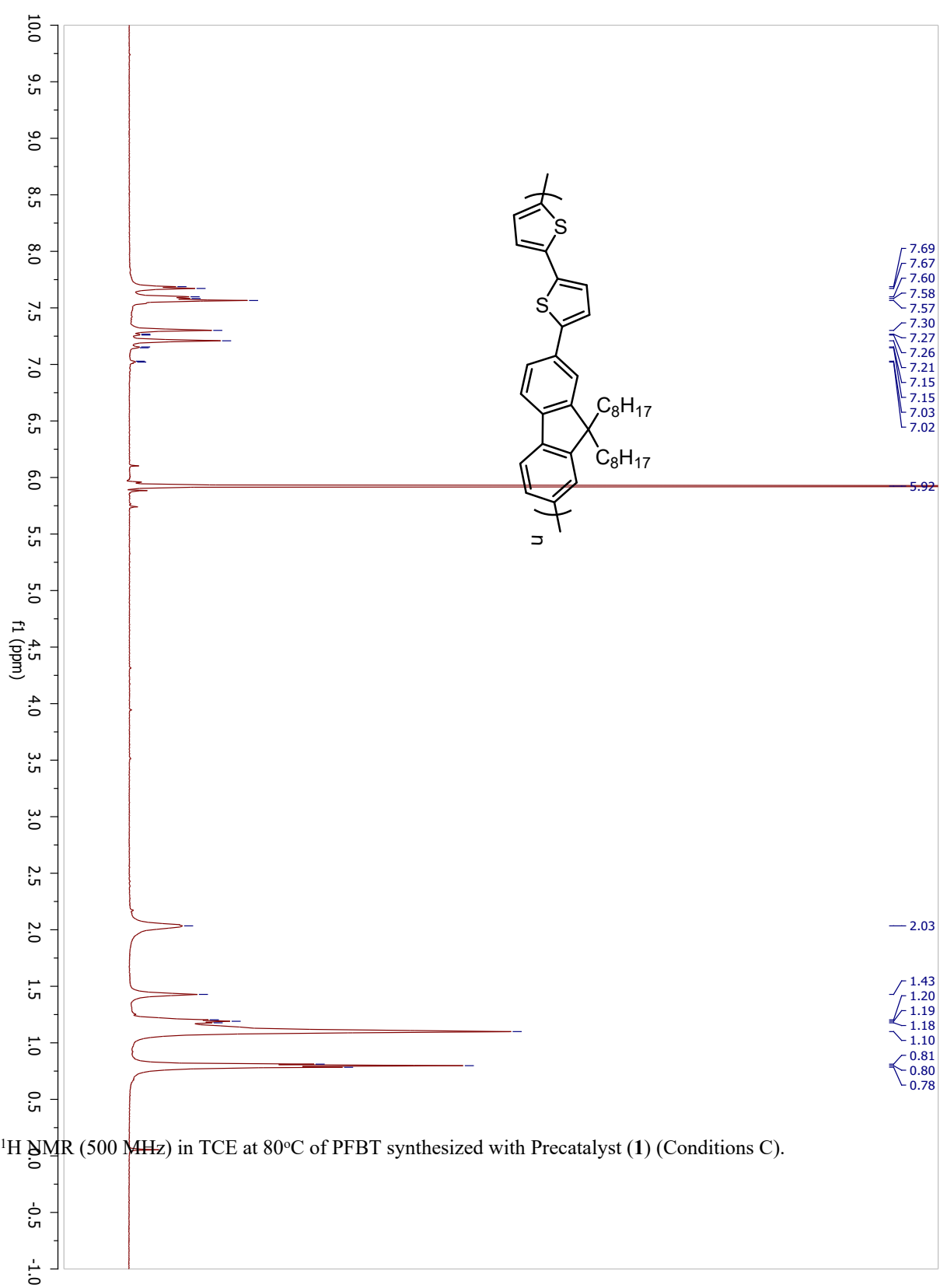


Figure S9-³¹P NMR Spectrum of Precatalyst (1) in CDCl₃



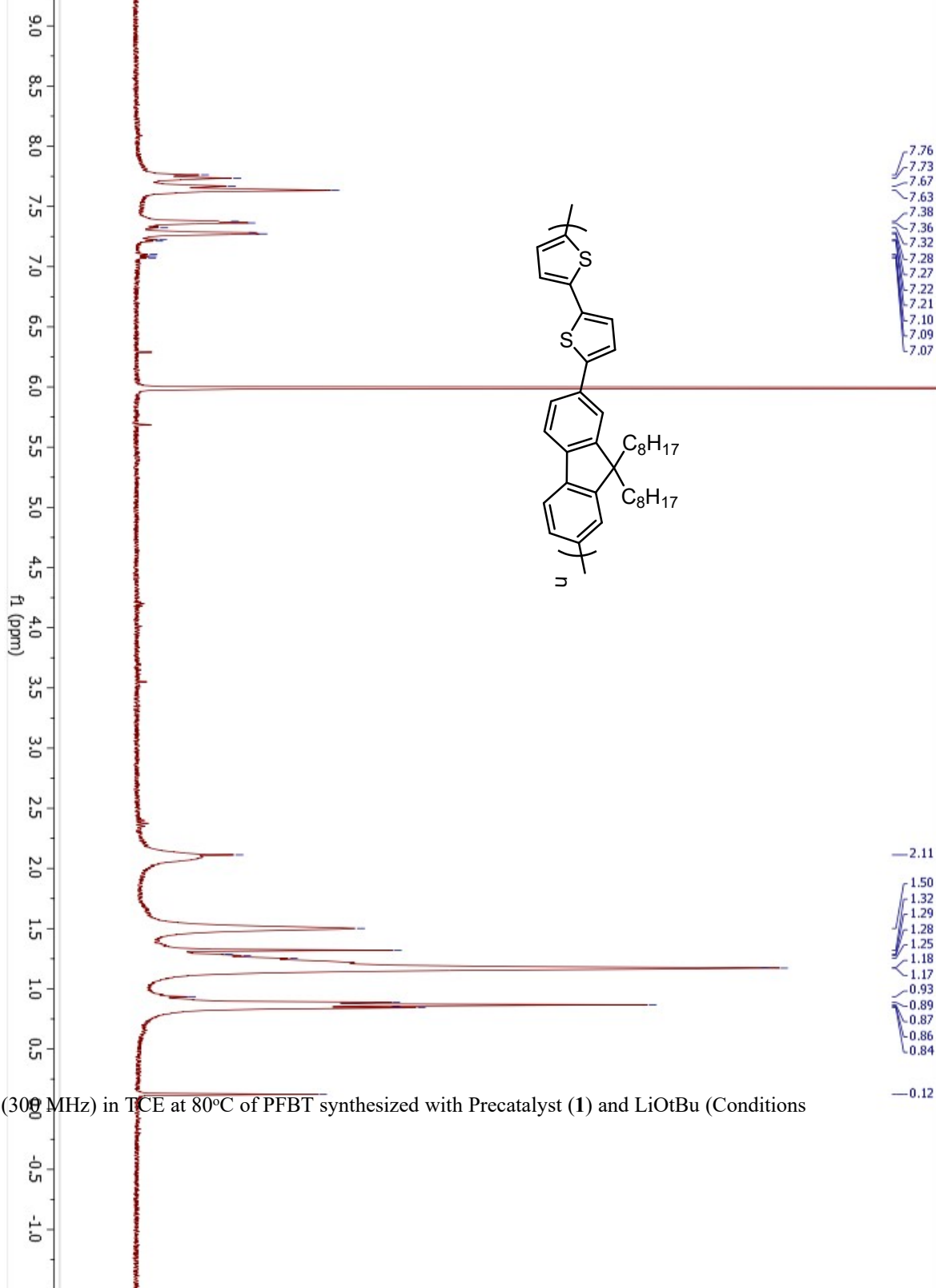


Figure S11- ^1H NMR (300 MHz) in TCE at 80°C of PFBT synthesized with Precatalyst (1) and LiOtBu (Conditions D).

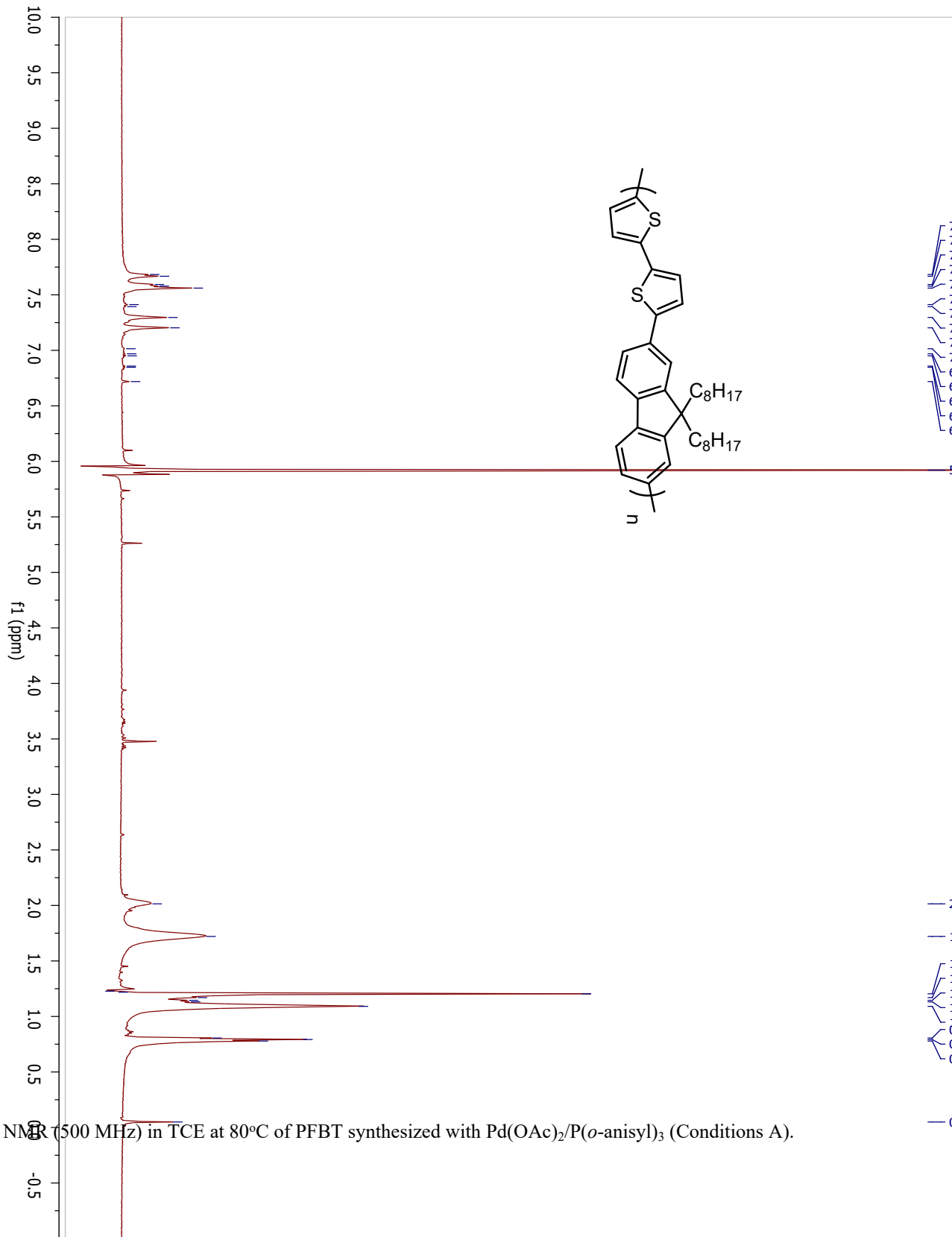


Figure S12- ¹H NMR (500 MHz) in TCE at 80°C of PFBT synthesized with Pd(OAc)₂/P(*o*-anisyl)₃ (Conditions A).

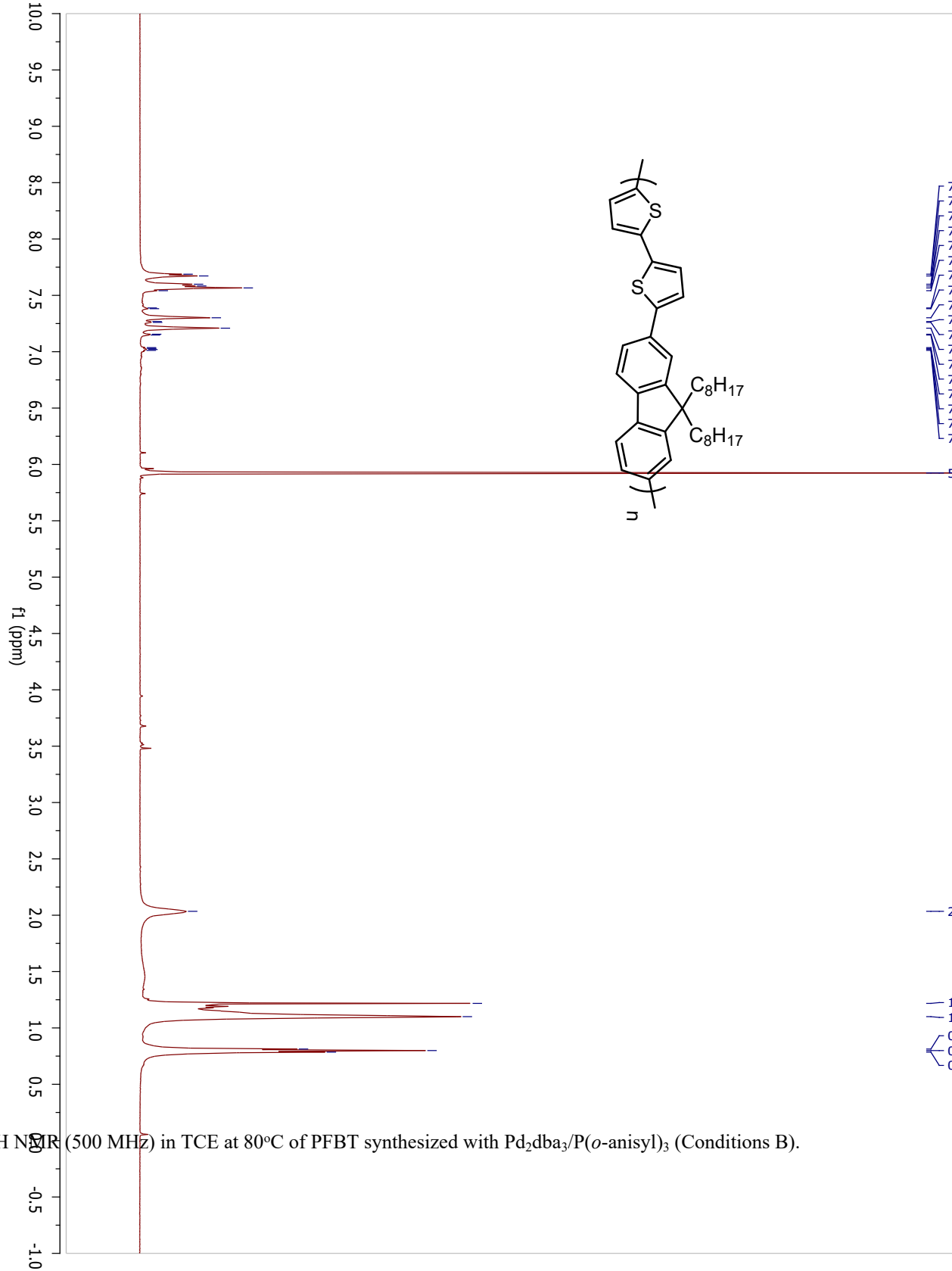


Figure S13- ^1H NMR (500 MHz) in TCE at 80°C of PFBT synthesized with $\text{Pd}_2\text{dba}_3/\text{P}(o\text{-anisyl})_3$ (Conditions B).

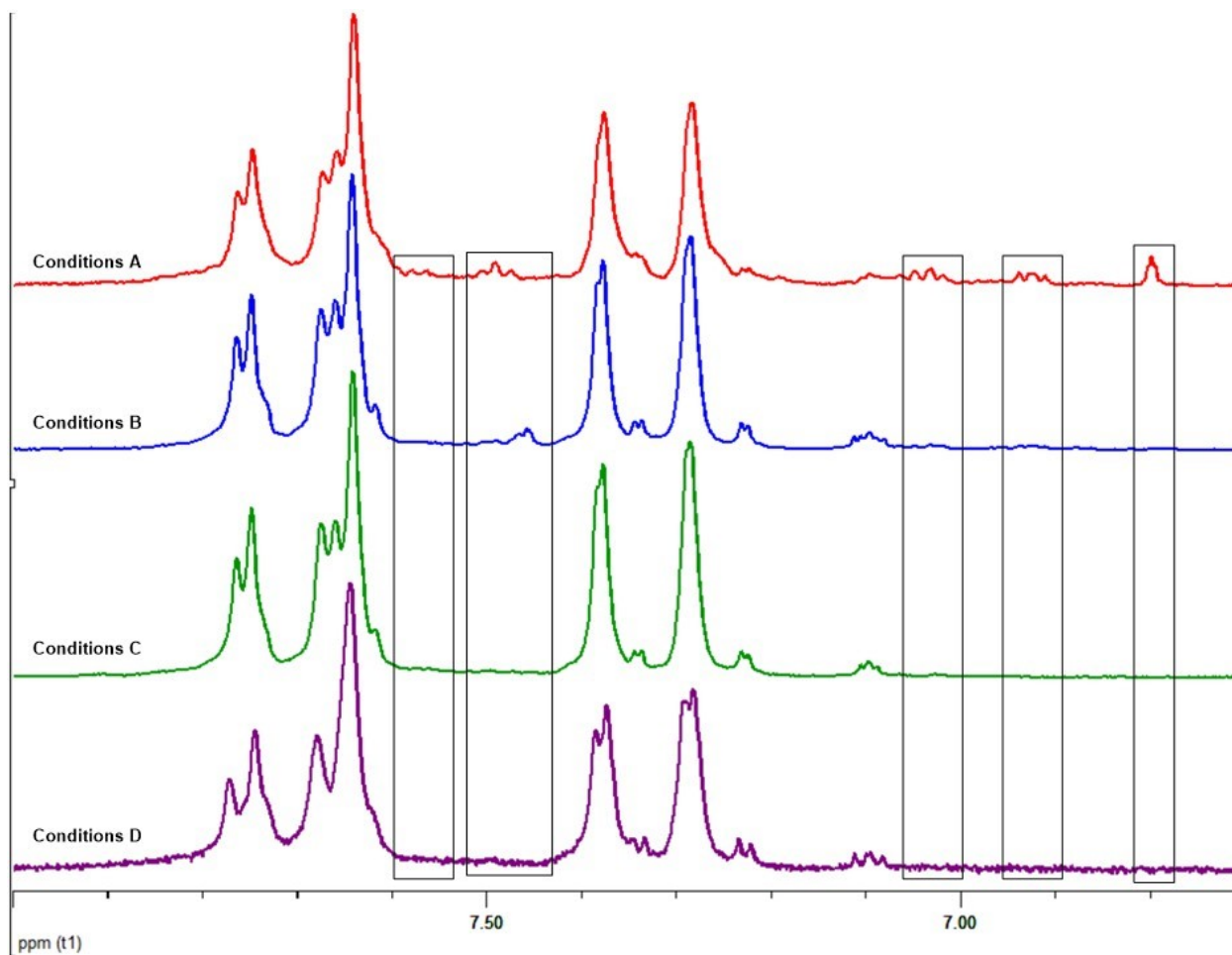


Figure S14- ^1H NMR spectra of the aromatic region of PFBT made with conditions A (red), B (blue), C (green) and D (purple). Chemical shift ranges of common defects are highlighted in black rectangles.

¹ Bruno, N.C.; Tudge, M. T.; Buchwald, S. L. *Chem. Sci.*, **2013**, 4, 916-920

² Morin, P.O.; Bura, T.; Sun. B.; Gorelsky, S. I.; Li, Y.; Leclerc, M.; *ACS Macro Lett.* **2015**, 4, 21-24.

³ Morin, P.O.; Bura, T.; Sun. B.; Gorelsky, S. I.; Li, Y.; Leclerc, M.; *ACS Macro Lett.* **2015**, 4, 21-24.