Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information:
A One-Pot Strategy to Improve End-Capping Efficacy in Stille Polycondensations

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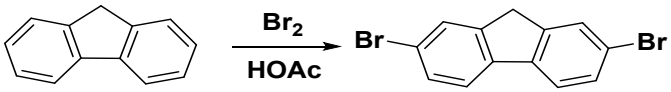
Contents:

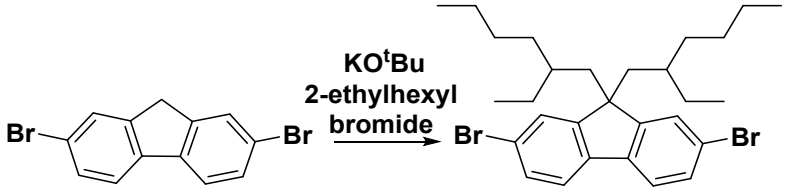
Synthetic Details:

2,7-dibromofluorene



Fluorene (5.01 g, 30.1 mmol, 1 eq.) was added to a clean, dry 250 mL round-bottomed flask with a stir bar and 30 mL $CHCl_3$. A clear, colorless solution formed. A septum sealed addition funnel containing 30 mL glacial acetic acid was fitted to the flask as it was cooled to 0 °C under N_2. The HOAc was slowly added to the stirred $CHCl_3$ solution over ~5 minutes. The solution was stirred for an additional 5 minutes. Br_2 (7.5 mL, 150.3 mmol, 5 eq.) was added to the addition funnel under positive N_2 pressure. Br_2 was then added to the reaction mixture dropwise over the course of 15 minutes. The mixture became dark brown/red and ppt eventually formed. The mixture was permitted to warm to room temperature over the course of 1 hr. After 1 hr., 30 mL 0.1 M $Na_2S_2O_{3(aq)}$ was added to the mixture, causing the formation of white ppt. The mixture was stirred for an additional hr. before vacuum filtration in a Büchner funnel. The ppt was washed with copius 0.1 M $Na_2S_2O_{3(aq)}$ until the orange/red color was removed. The hazy white/yellow filtrate was extracted with $CHCl_3$ and washed with 0.1 M $Na_2S_2O_{3(aq)}$ to gain a clear, off-white solution. The extracts were combined with the previously filtered ppt, dried over $MgSO_4$, gravity filtered, and solvent removed via rotary evaporation. The white crystalline residue was recrystallized from ~300 mL refluxing 2-propanol to yield 7.84 g (80.7 %) fine white needles. ^{1}H NMR (500.13 MHz, $CDCl_3$, Me_4Si): δ 7.67 (s, 2H), 7.60 (d, 2H, J =10.0 Hz), 7.50 (dd, 2H, J = 1.1 Hz, 8.7 Hz), 3.87 (s, 2H). ^{13}C NMR (125.76 MHz, $CDCl_3$, Me_4Si): δ 144.94, 139.85, 130.30, 128.46, 121.35, 121.09, 36.71.

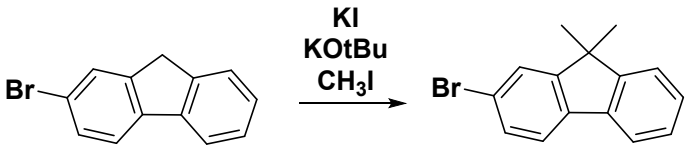
2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene



2,7-Dibromofluorene (3.00 g, 9.3 mmol, 1 eq.) was added to an oven dried 250 mL round-bottomed flask with a stir bar. The RBF was sealed with a septum and purged with N_2. Dry THF (~75 mL) was cannulated into the flask under N_2. The resulting colorless solution was stirred as it was chilled to 0 °C. Potassium *t*-butoxide (2.69 g, 23.9 mmol, 2.57 eq.) was added to the solution in one portion during N_2 positive pressure. The solution immediately became orange and ppt. formed. 2-Ethylhexyl bromide (6.75 mL, 38.0 mmol, 4.08 eq.) was added to the mixture dropwise via syringe over ~10 min. The mixture was permitted to warm to room temperature as it stirred overnight (14.5 hr.). Water (75 mL) was added to the pink/magenta mixture, stirred for another 15 min. The mixture was transferred to a separatory funnel and extracted with diethyl ether. The extracts were washed with 1 M $HCl_{(aq)}$ and brine yielding a yellow/orange organic layer. Extracts were dried with $MgSO_4$, gravity filtered, and solvent removed via rotary evaporation. The resulting orange oil was dissolved in hexanes and passed through a short SiO_2 column (~2"). Solvent was again removed via rotary evaporation. Remnant 2-ethylhexanol and 2-ethylhexyl bromide were removed from the colorless oil via Kugelrohr distillation at 120 °C and 145 °C, respectively. The product, a clear, colorless oil, remained in the still pot 4.32 g (84.7 %). ^{1}H NMR (500.13 MHz, $CDCl_3$, Me_4Si): δ 7.52 (d, 2H, J = 8.1 Hz), 7.49 (dt, 2H, J = 1.6, 5.9 Hz), 7.45 (dd, 2H, J = 1.7, 8.1 Hz), 1.93 (m, 4H), 0.96-0.66

(m, 22H), 0.54 (t, 3H, J = 7.3 Hz), 0.54 (t, 3H, J = 7.4 Hz), 0.47 (p, 2H, J = 5.6 Hz). ^{13}C NMR (125.76 MHz, $CDCl_3$, Me_4Si): δ 152.53, 139.32, 130.23, 127.53, 121.20, 121.07, 55.51, 44.46, 34.82, 33.75, 33.71, 28.17, 28.15, 27.21, 27.18, 22.86, 14.18, 10.47, 10.45.

2-bromo-9,9-dimethylfluorene



2-Bromofluorene (0.956 g, 3.90 mmol, 1 eq.) and potassium iodide (65.1 mg, 0.392 mmol, 0.1 eq.) were added to a 50 mL 2-neck RBF along with 10 mL DMSO under N_2 rich environment. Purged the resulting solution with N_2 for 5-10 min before adding methyl iodide (0.55 mL, 8.52 mmol, 2.19 eq.) via syringe. Potassium *t*-butoxide (1.751 g, 15.6 mmol, 4 eq.) was added in thirds at thirty minute intervals during N_2 over pressure. The resulting deep red mixture was stirred over night at room temperature. Reaction progress was monitored using SiO_2 TLC in hexanes. An additional portion of methyl iodide (0.55 mL, 8.52 mmol, 2.19 eq.) was added dropwise via syringe and the reaction was permitted to continue for another day. The reaction was quenched with 10 mL H_2O and stirred for ~1 hour before extracting with diethyl ether. The combined extracts were washed with water and brine. The ethyl ether solution was then dried over $MgSO_4$ and filtered. The solvent was removed via rotary evaporation to yield an amber oil. The oil was dissolved in hexanes and purified on a short SiO_2 column packed in hexanes to yield 0.683 g (64.2 %) colorless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$, Me_4Si): δ 7.69 (m, 1H), 7.58 (d, 1H, J = 8.0 Hz), 7.56 (d, 1H, J = 1.7 Hz), 7.46 (dd, 1H, J = 1.8, 8.1 Hz), 7.42 (m, 1H), 7.34 (m, 2H), 1.48 (s, 6H). ^{13}C NMR (100.61 MHz, $CDCl_3$, Me_4Si): δ 155.82, 153.38, 138.36, 138.29, 130.21, 127.80, 127.31, 126.30, 122.79, 121.52, 121.15, 120.20, 47.25, 27.15.

Table S1: Mass table used for end-capping reagent stock solutions in polymerizations.

	mass (mg)	conc. (mg mL^{-1})	μmol	eq.
bromobenzene	37.6	7.52	9.58	0.0958
p-bromotoluene	40.9	8.18	9.57	0.0956
4-bromobiphenyl	55.8	11.2	9.58	0.0957
4-(trifluoromethyl) bromobenzene	53.9	10.8	9.58	0.0958
iodobenzene	48.8	9.76	9.57	0.0956
p-iodotoluene	52.2	10.4	9.58	0.0957
4-iodobiphenyl	67.0	13.4	9.57	0.0956
2-bromo-9,9-dimethylfluorene	65.4	13.1	9.58	0.0957

Each solution diluted in 5.00 mL distilled, deoxygenated toluene.

Table S2: Summary of GPC data from all trials.

	M_n (kg mol^{-1})	M_w (kg mol^{-1})	Đ
P1 A	9.92	21.8	2.50
P1 B	17.0	32.0	2.15
P2 A	-	-	-
P2 B	-	-	-
P3 A	14.3	32.0	2.24
P3 B	14.8	35.6	2.41
P4 A	-	-	-
P4 B	-	-	-
P5 A	19.4	47.3	2.44
P5 B	17.3	39.0	2.25
P6 A	-	-	-
P6 B	-	-	-
P7 A	20.2	38.2	2.36
P7 B	12.6	28.5	2.26
P8 A	13.5	34.1	2.53
P8 B	13.5	35.3	2.62
P5$^{1.0}$ A^{a}	13.8	32.8	2.37
P5$^{1.0}$ B^{a}	11.6	23.4	2.02
P5$^{0.33}$ A^{b}	11.9	22.4	1.89
P5$^{0.33}$ B^{b}	8.86	18.9	2.53
P6* A^{c}	13.0	27.8	2.14
P6* B^{c}	13.7	29.1	2.12

[**TT**] was 0.50 M for all reactions unless otherwise indicated. a. [**TT**] = 1.0 M; b. [**TT**] = 0.33 M; c. ECR was added post-polymerization.

NMR Spectra:

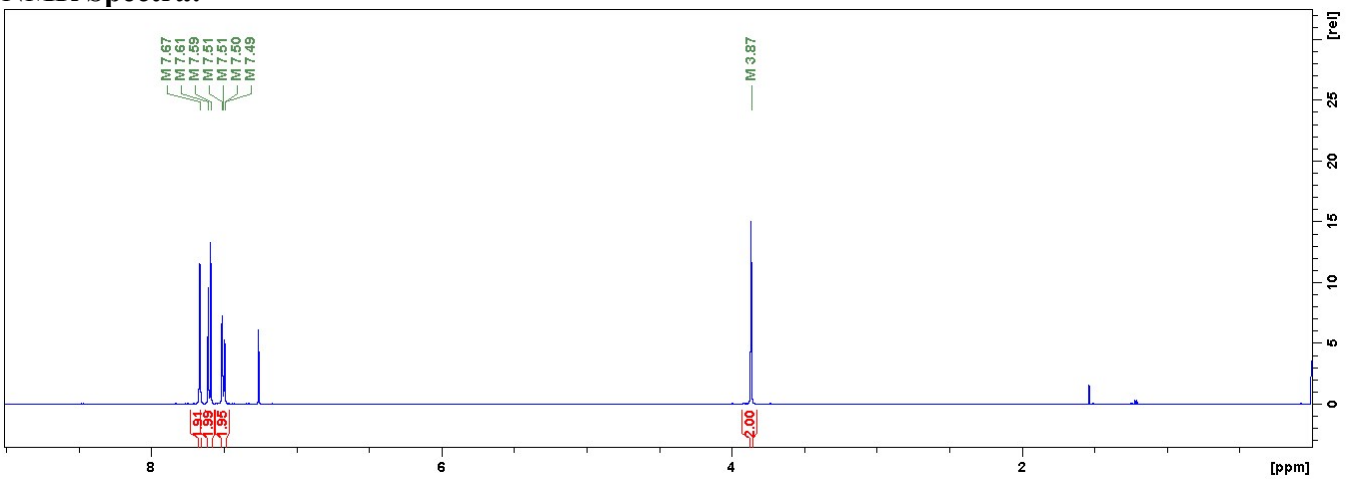


Figure S1: ^{1}H NMR spectrum of 2,7-dibromofluorene in $CDCl_3$, 500.13 MHz.

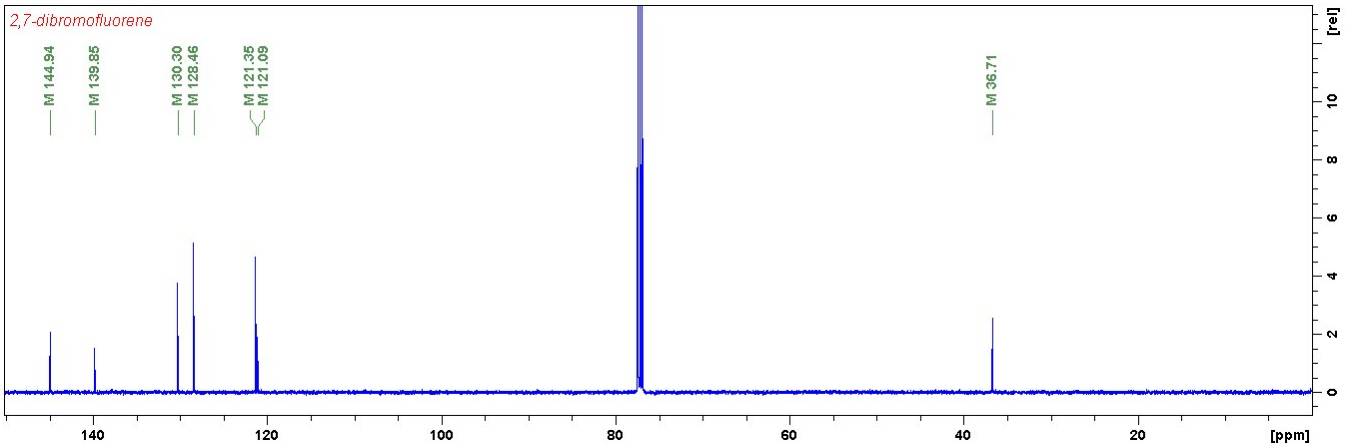


Figure S2: ^{13}C NMR spectrum of 2,7-dibromofluorene in $CDCl_3$, 125.76 MHz.

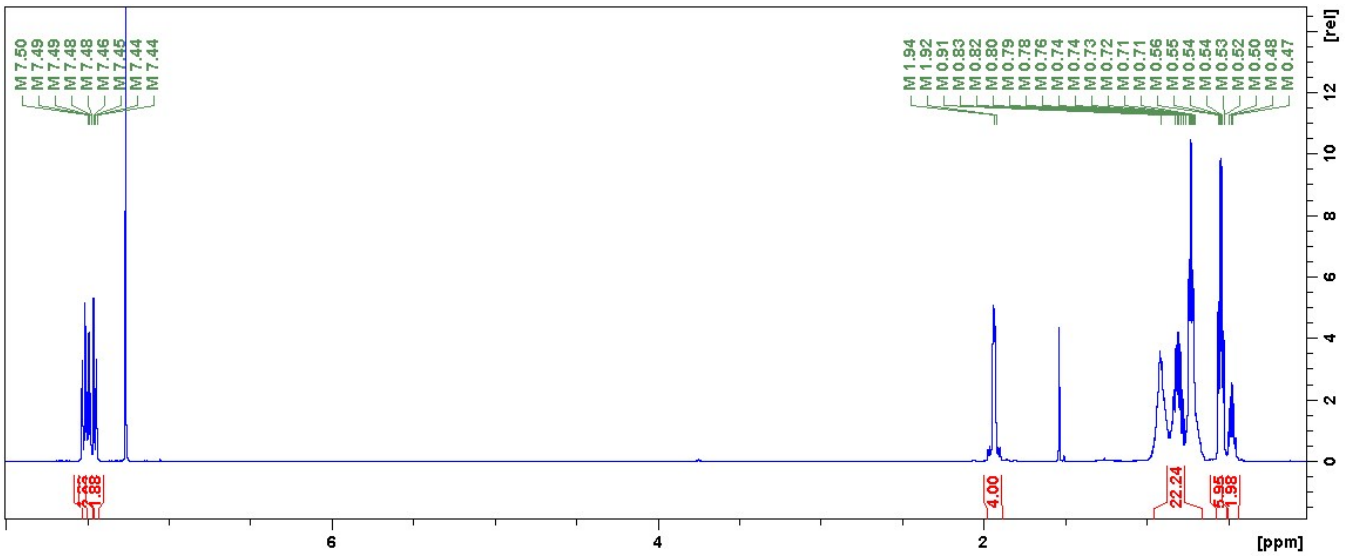


Figure S3: ^{1}H NMR of 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene in $CDCl_3$, 500.13 MHz.

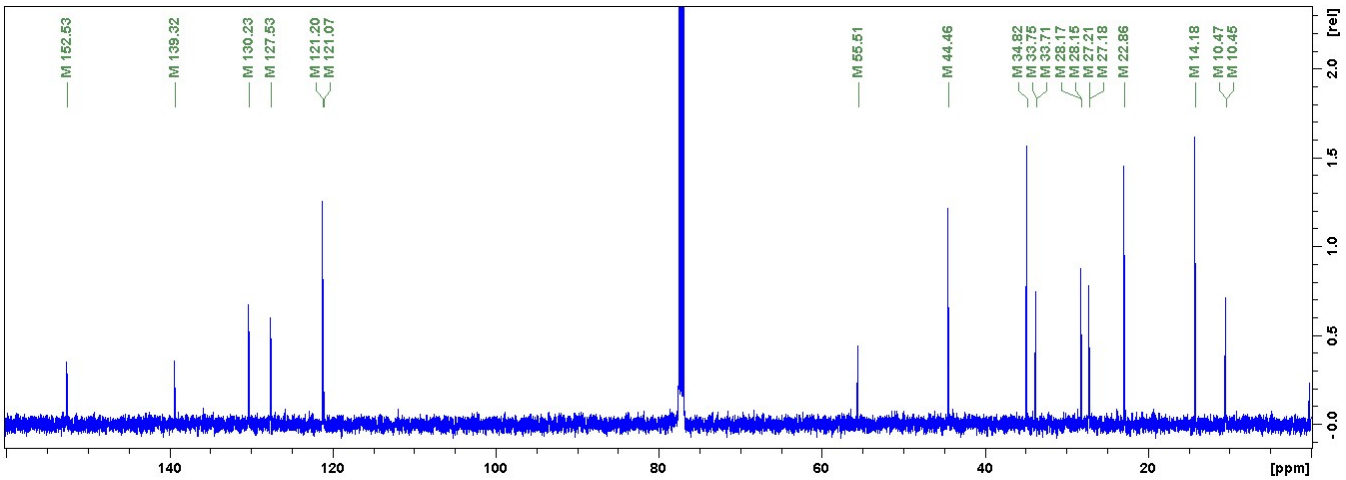


Figure S4: ^{13}C NMR of 2,7-dibromo-9,9-bis(2-ethylhexyl)fluorene in $CDCl_3$, 125.76 MHz.

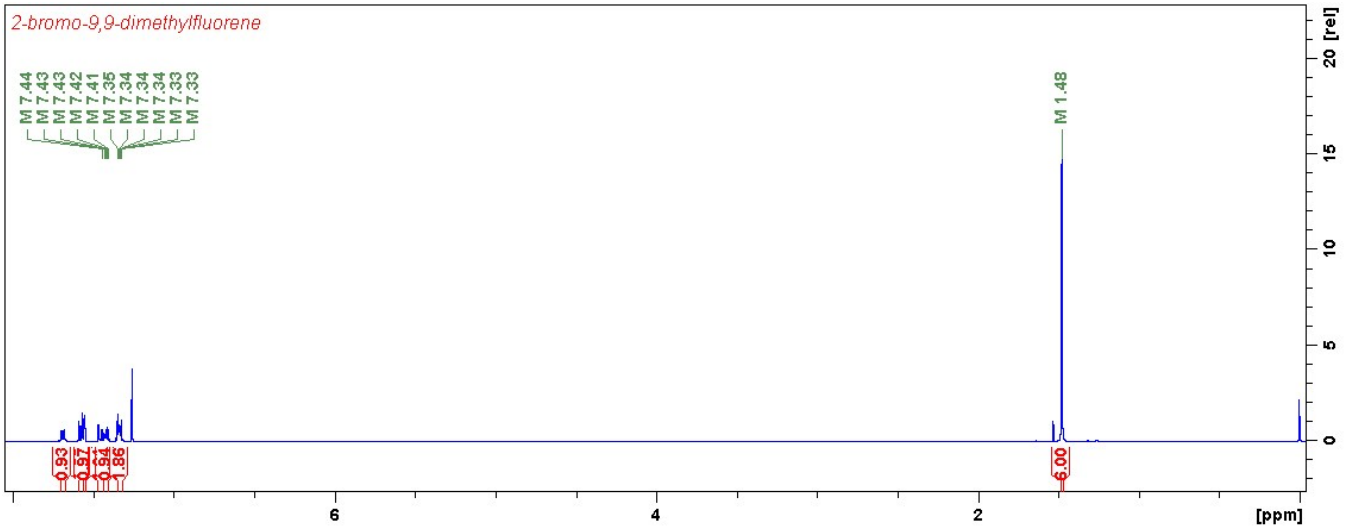


Figure S5: ^{1}H NMR of 2-bromo-9,9-dimethylfluorene in $CDCl_3$, 400.13 MHz.

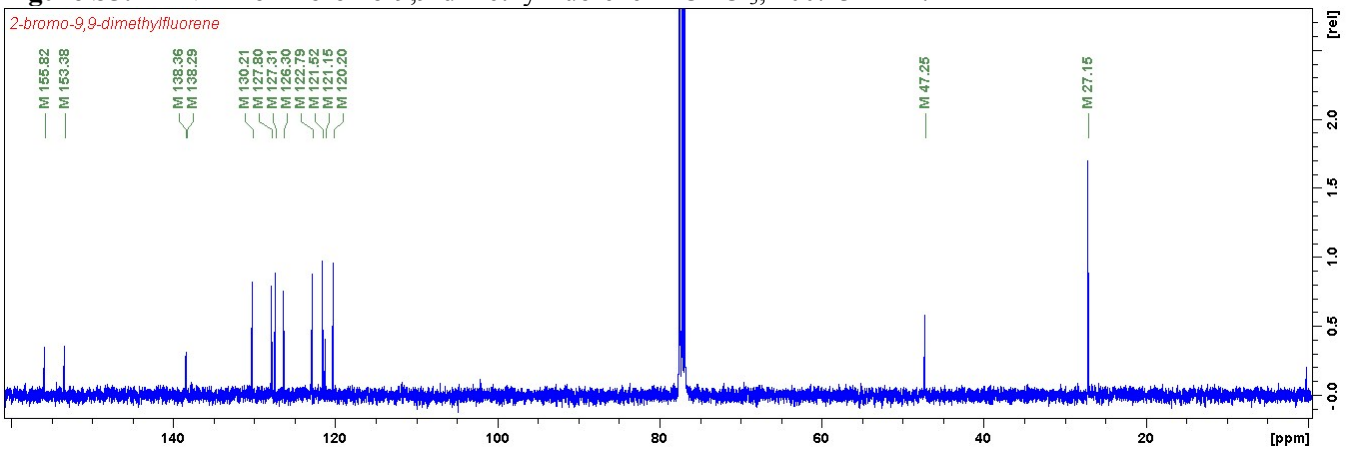


Figure S6: ^{13}C NMR of 2-bromo-9,9-dimethylfluorene in $CDCl_3$, 100.61 MHz.

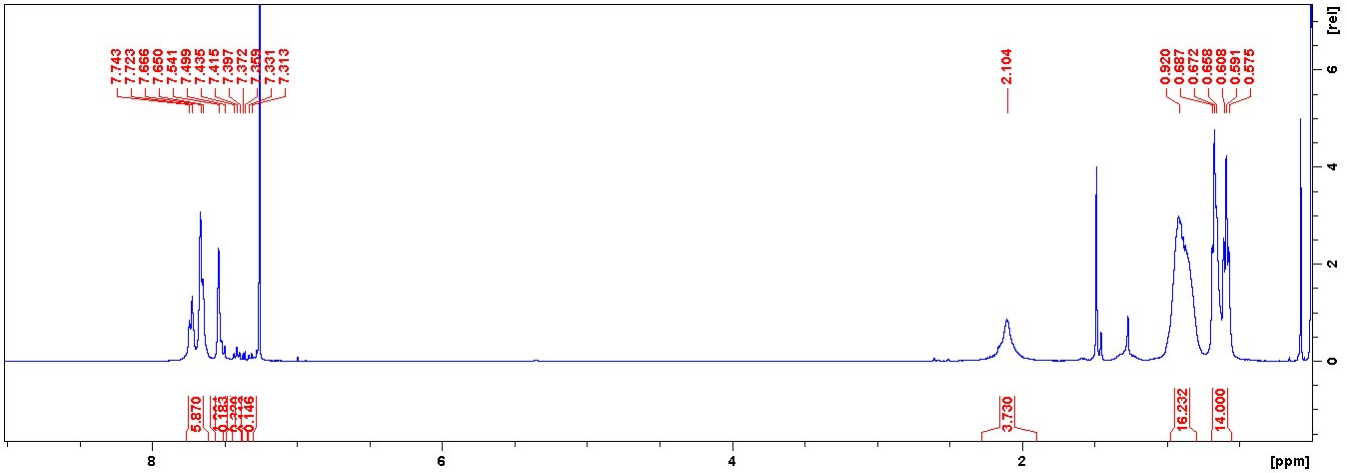


Figure S7: Representative ^{1}H NMR spectrum of **P1** in $CDCl_3$ at 318 K.

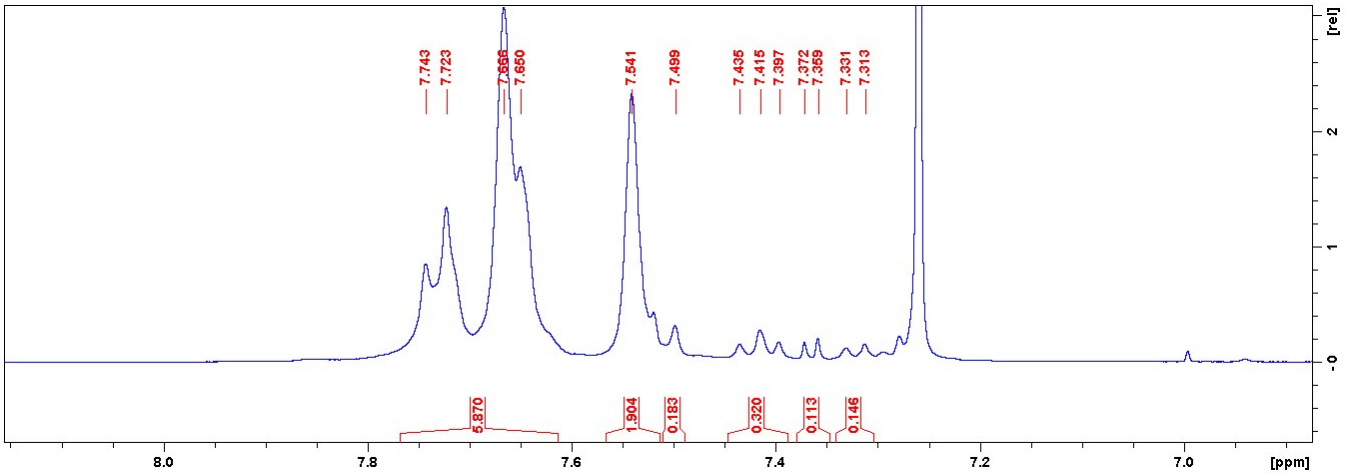


Figure S8: Expanded view of the aromatic region found in **Figure S7**.

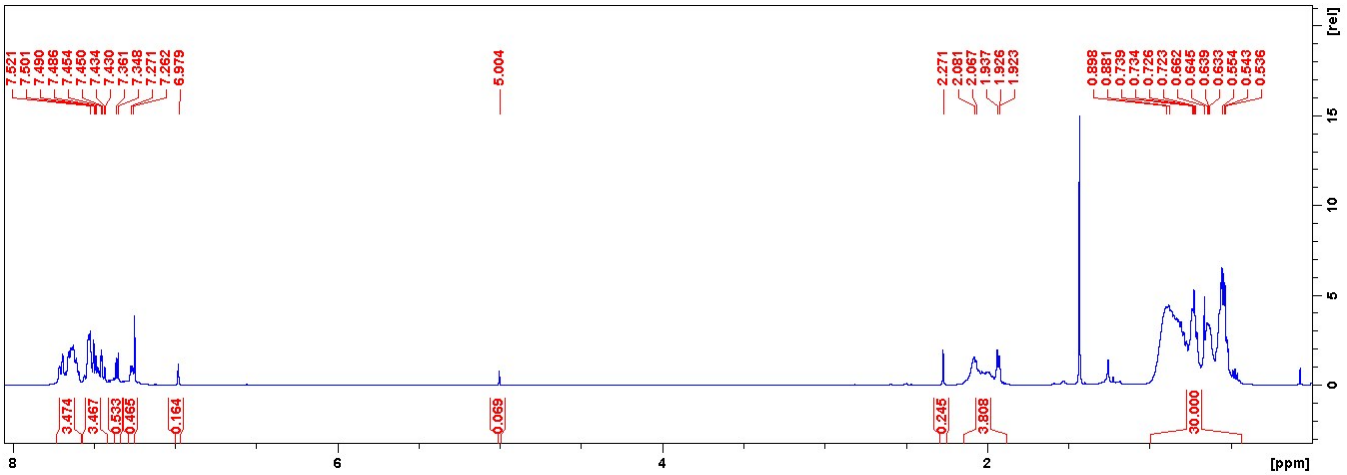


Figure S9: Representative ^{1}H NMR spectrum of **P2** in $CDCl_3$ at 298 K.

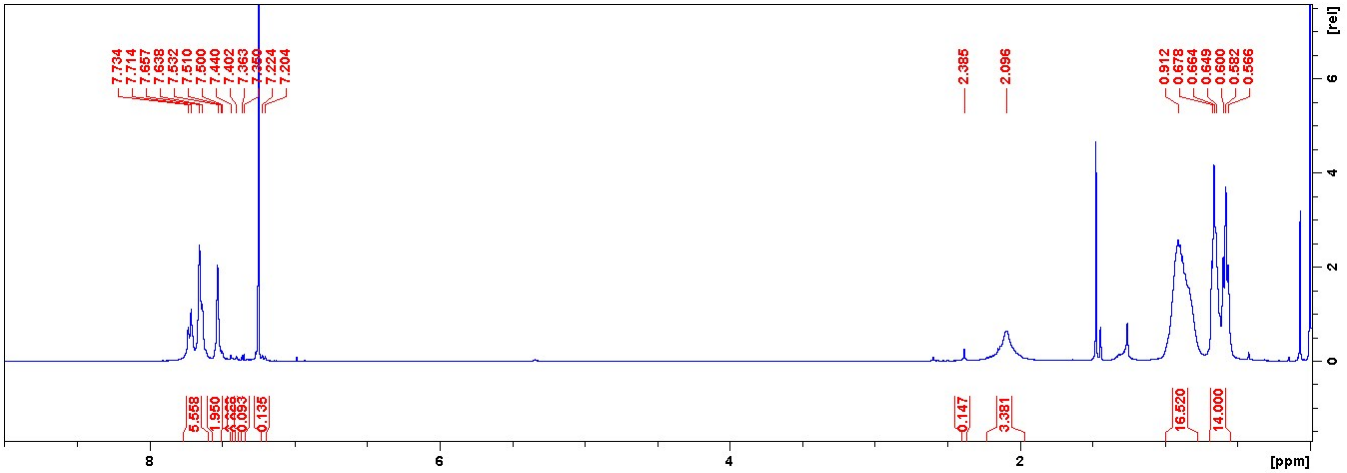


Figure S10: Representative ^{1}H NMR spectrum of **P3** in $CDCl_3$ at 318 K.

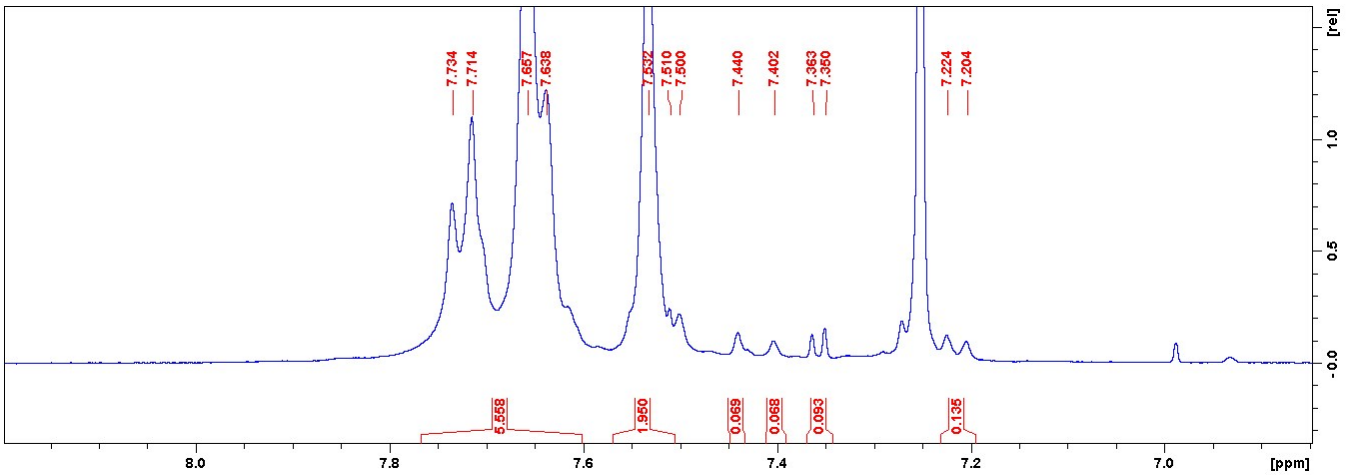


Figure S11: Expanded view of the aromatic region found in **Figure S10**.

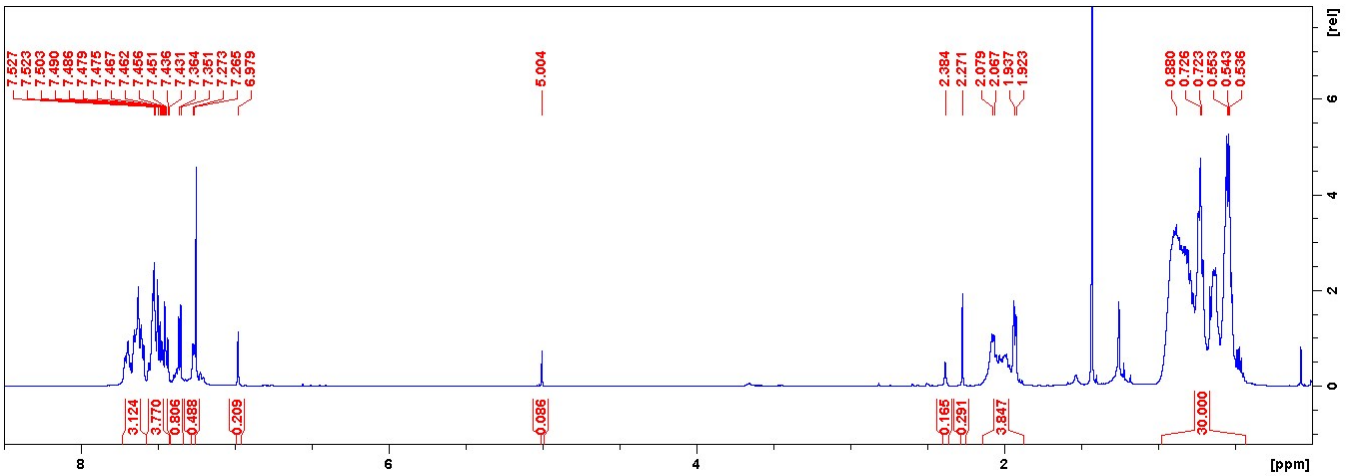


Figure S12: Representative ^{1}H NMR spectrum of **P4** in $CDCl_3$ at 298 K.

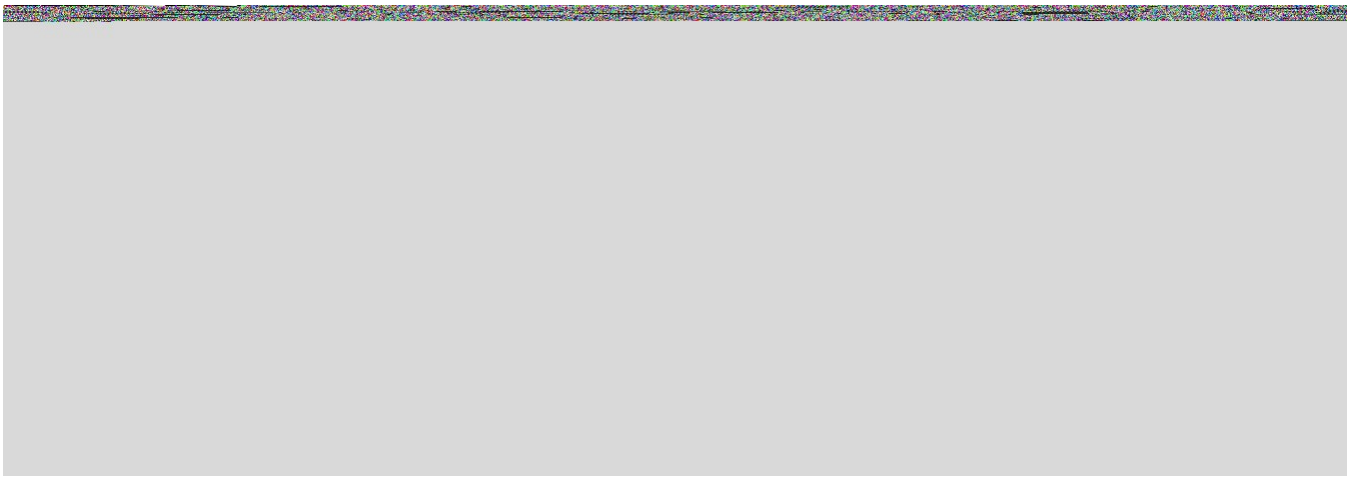


Figure S13: Representative ^{1}H NMR spectrum of **P5** in $CDCl_3$ at 318 K.

Figure S14: Expanded view of the aromatic region found in **Figure S13**.

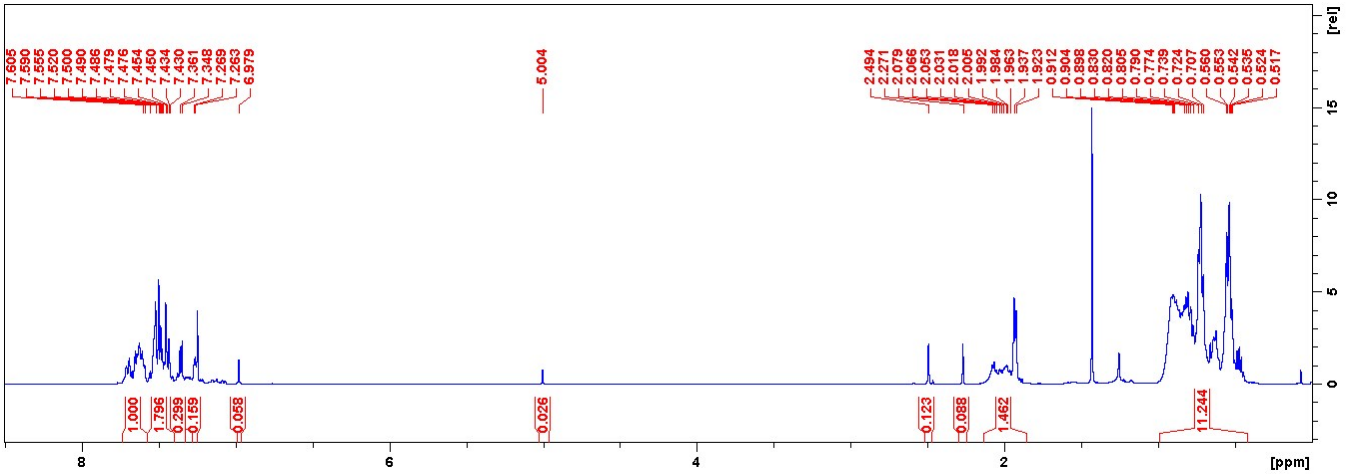


Figure S15: Representative ^{1}H NMR spectrum of **P6** in $CDCl_3$ at 298 K.

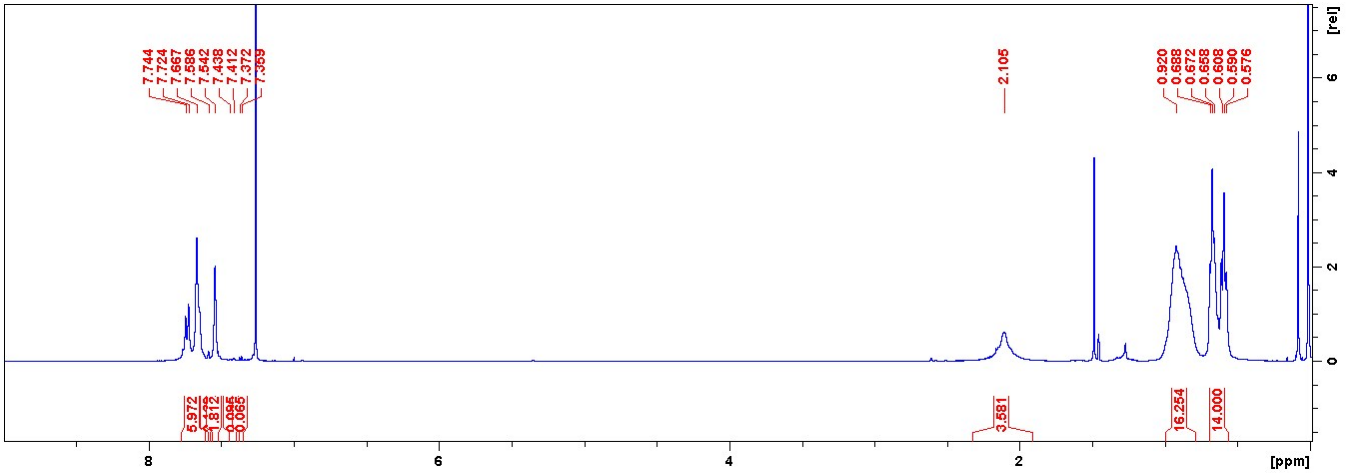


Figure S16: Representative ^{1}H NMR spectrum of **P7** in $CDCl_3$ at 318 K.

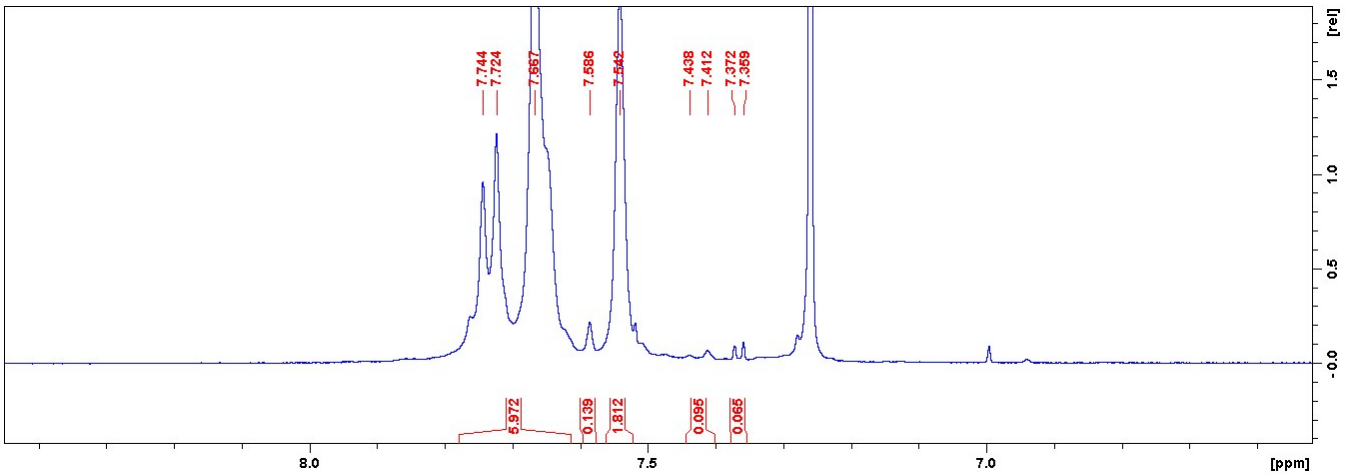


Figure S17: Expanded view of the aromatic region found in **Figure S16**.

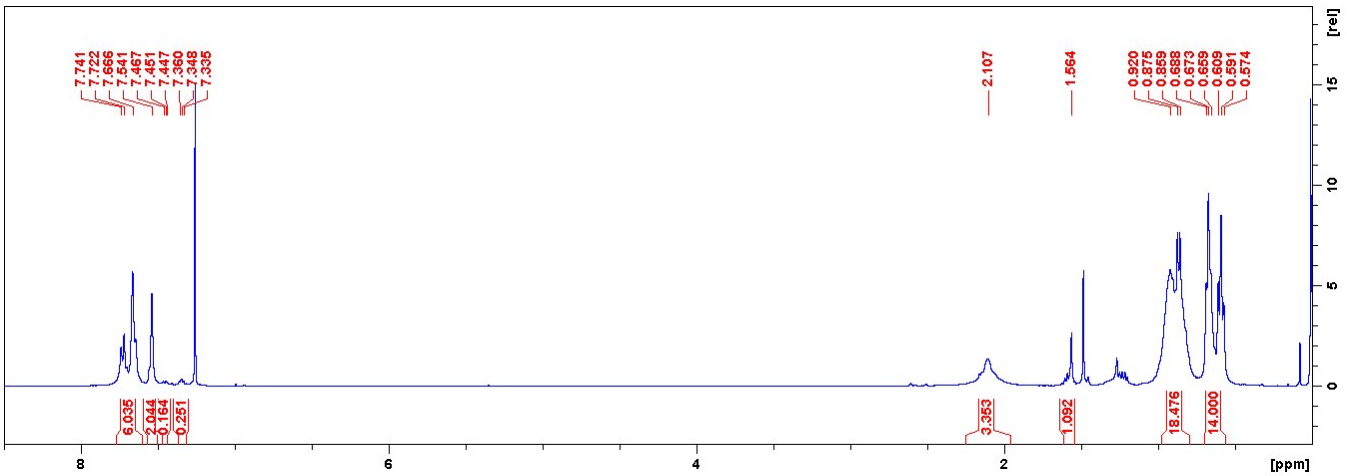


Figure S18: Representative ^{1}H NMR spectrum of **P8** in $CDCl_3$ at 318 K.

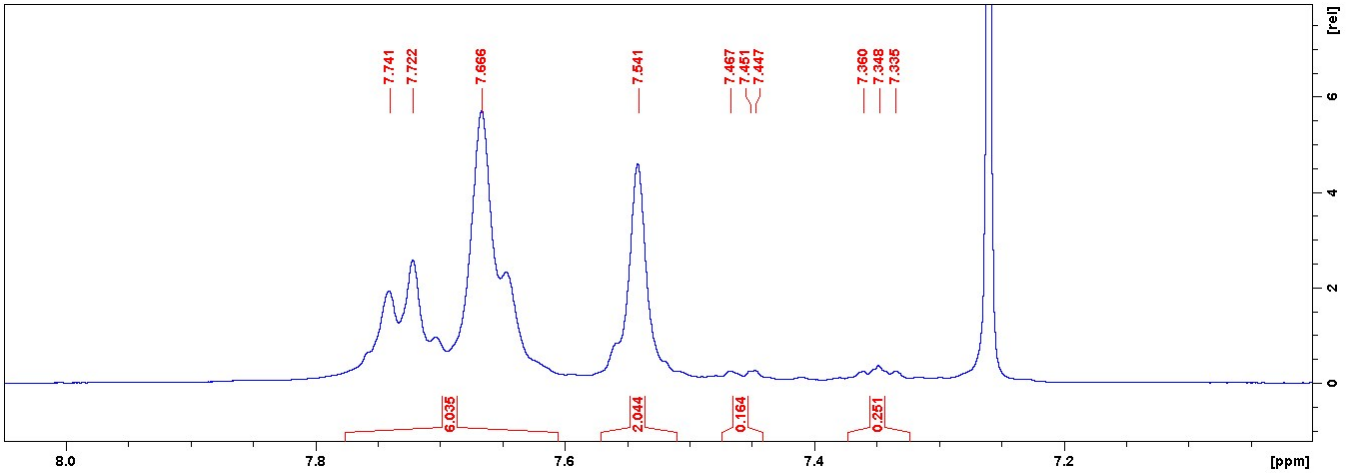


Figure S19: Expanded view of the aromatic region found in **Figure S18**.

MALDI-ToF MS Spectra:

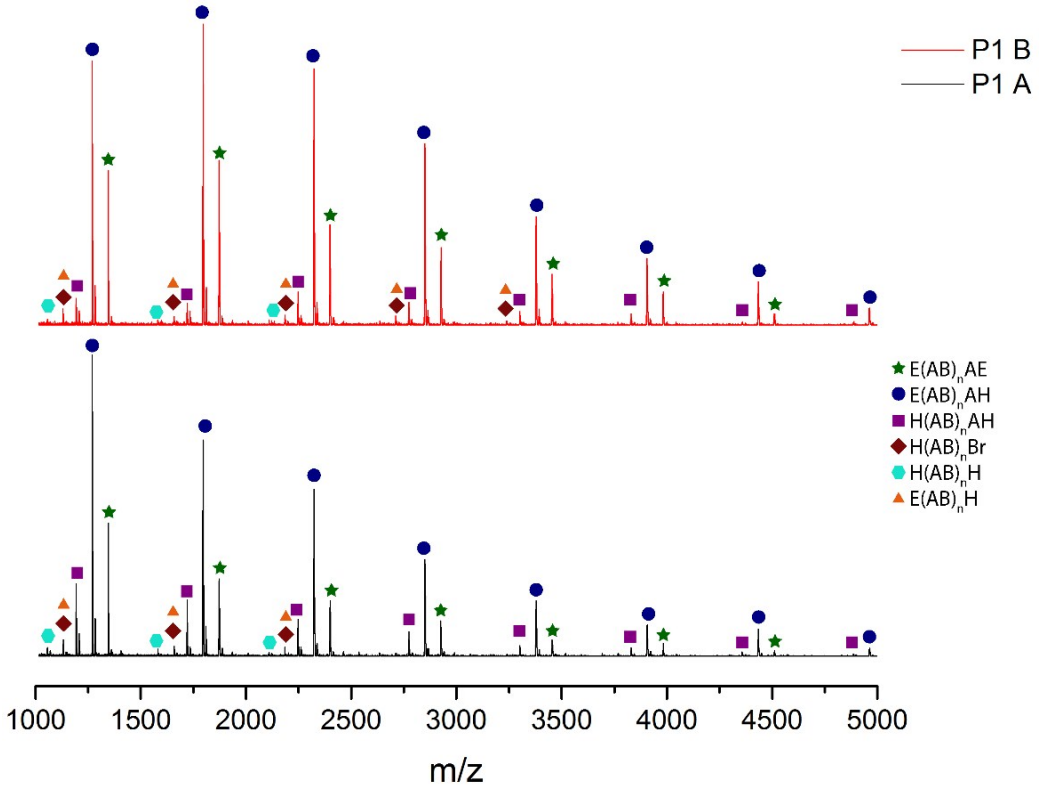


Figure S20: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P1**. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

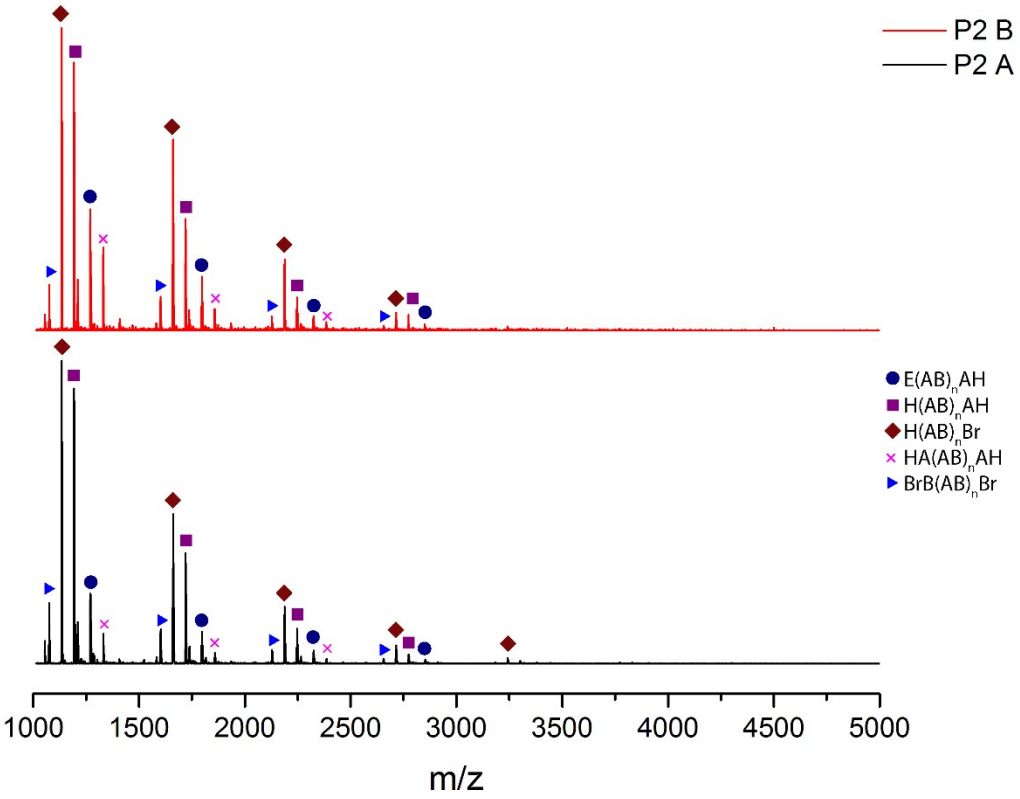


Figure S21: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P2**. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

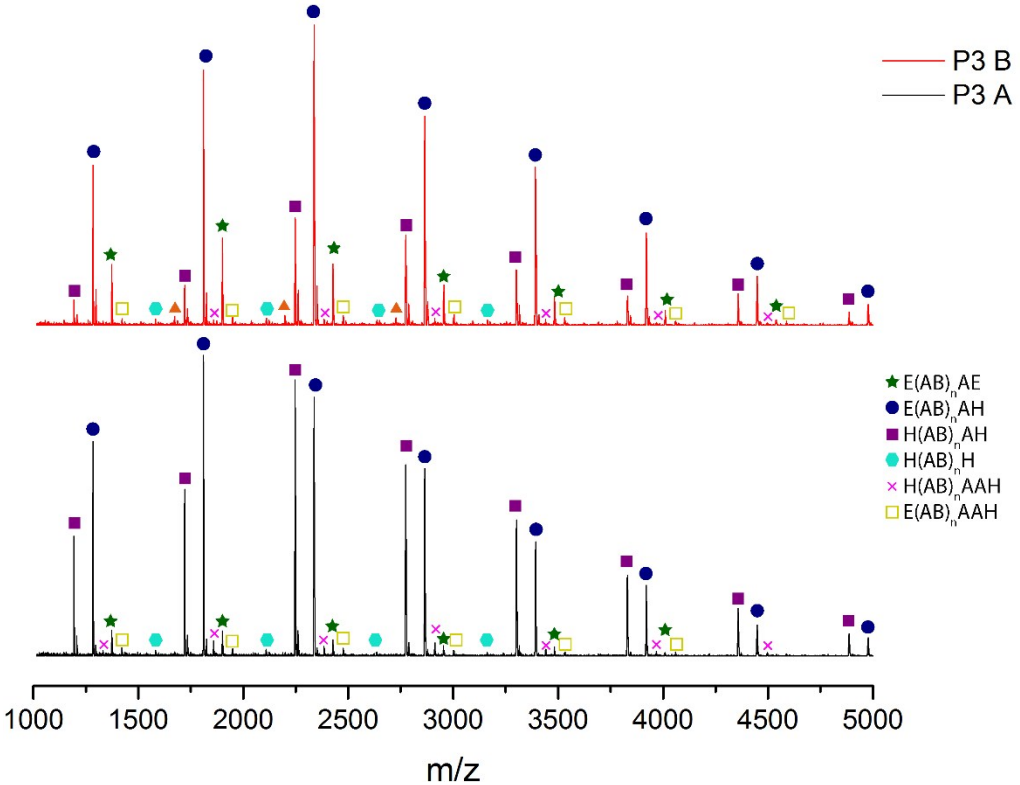


Figure S22: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P3**. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

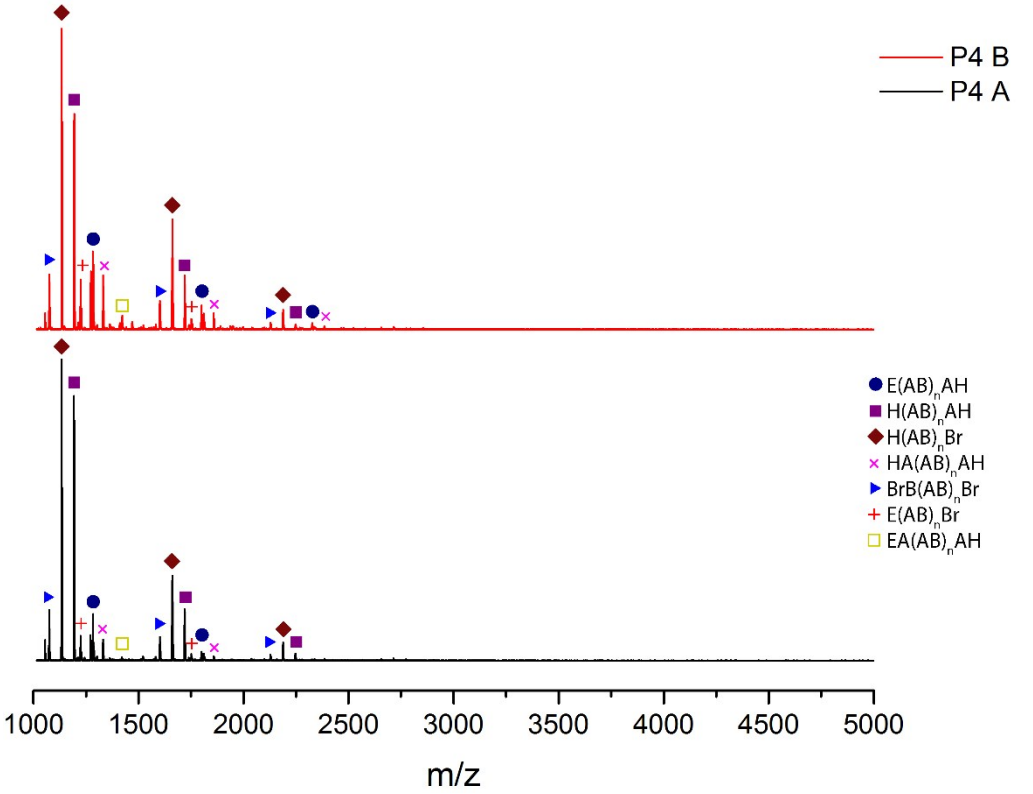


Figure S23: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P4**. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

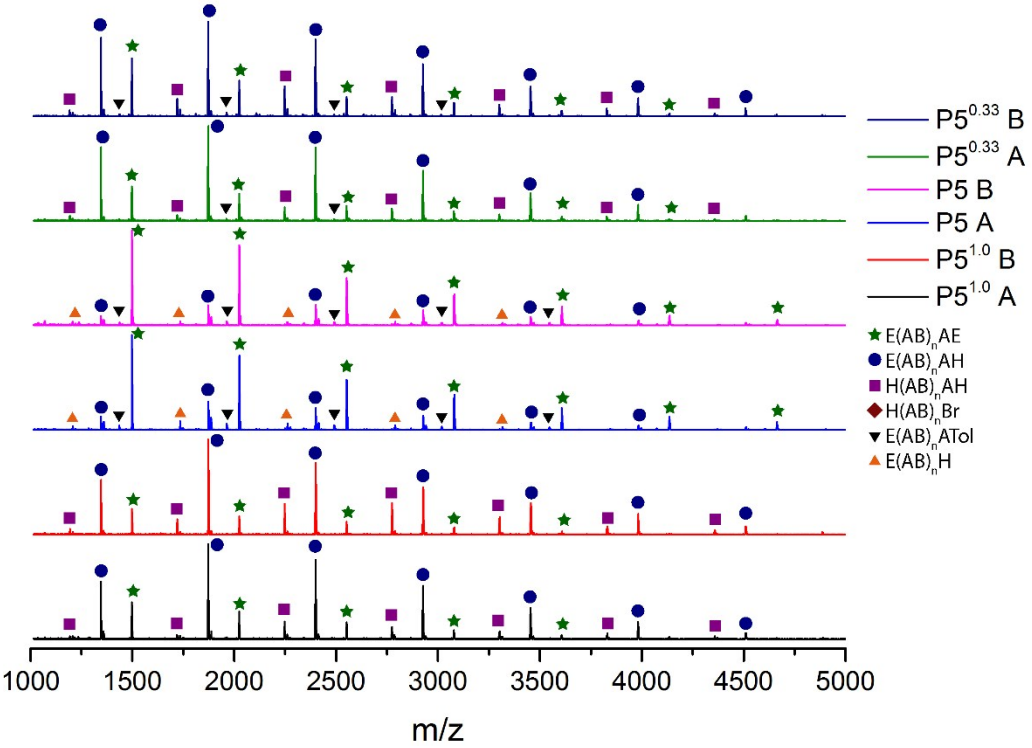


Figure S24: MALDI-ToF MS spectra for both (A and B) trials of **P5$^{0.33}$** (second green and top navy), **P5** (fourth blue and third pink), and **P5$^{1.0}$** (bottom black and fifth red). Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

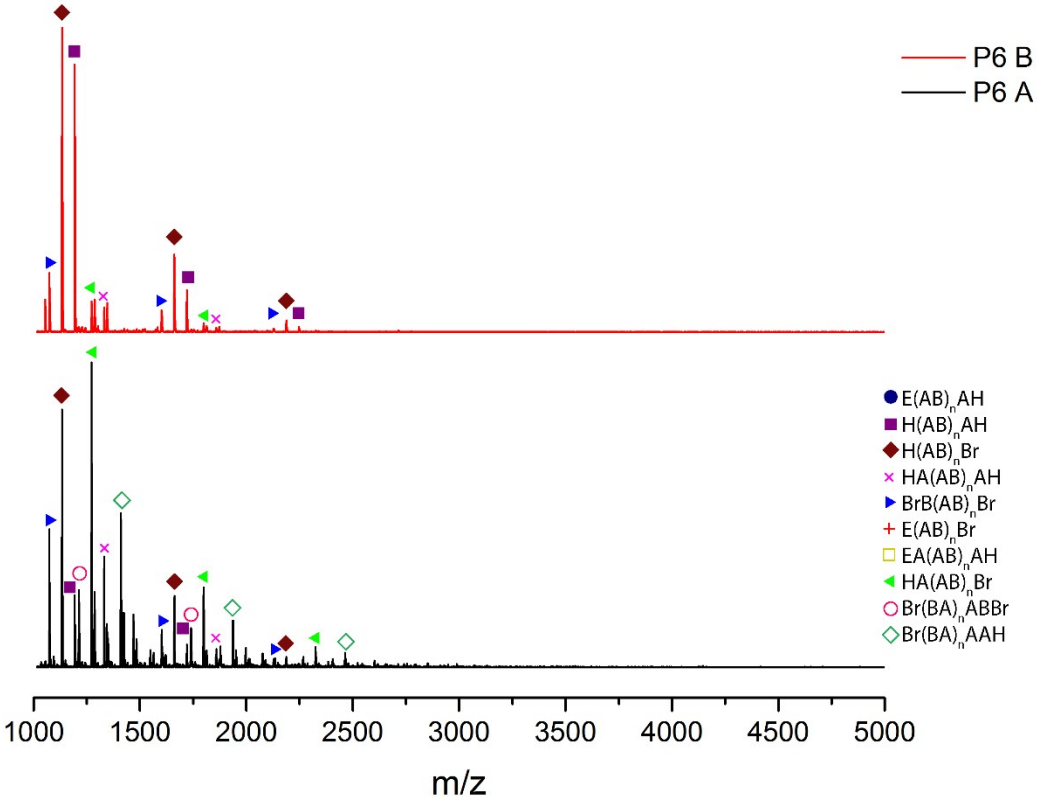


Figure S25: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P6**. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

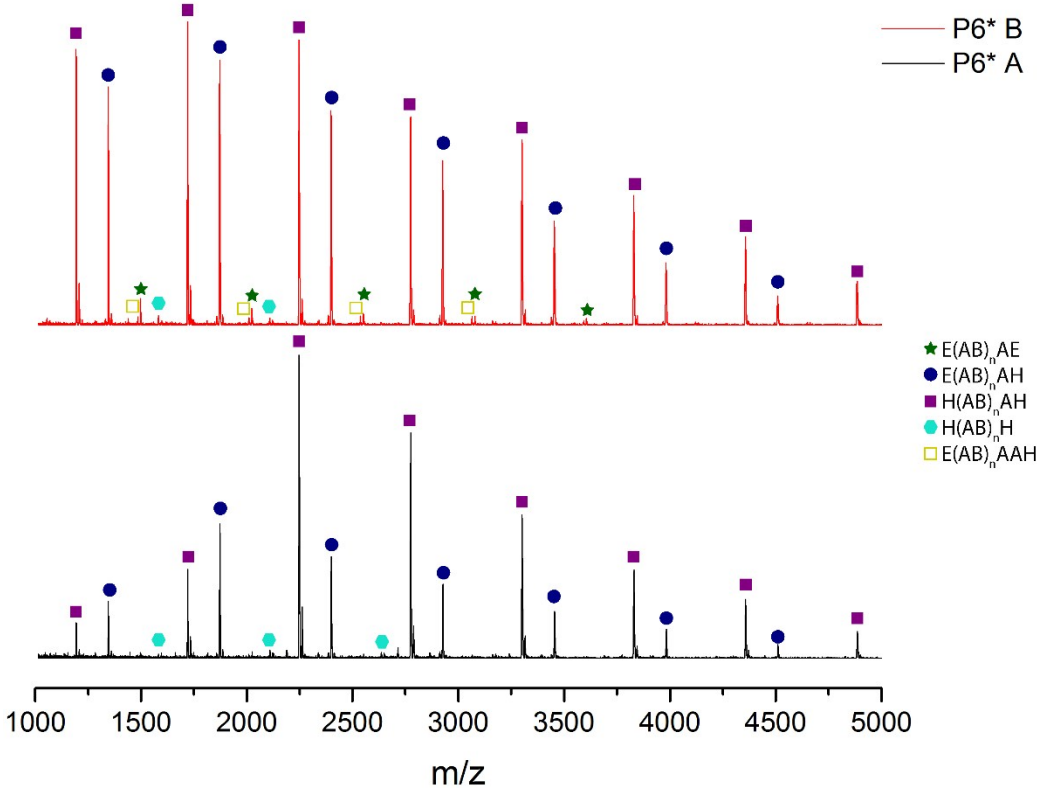


Figure S26: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P6***. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

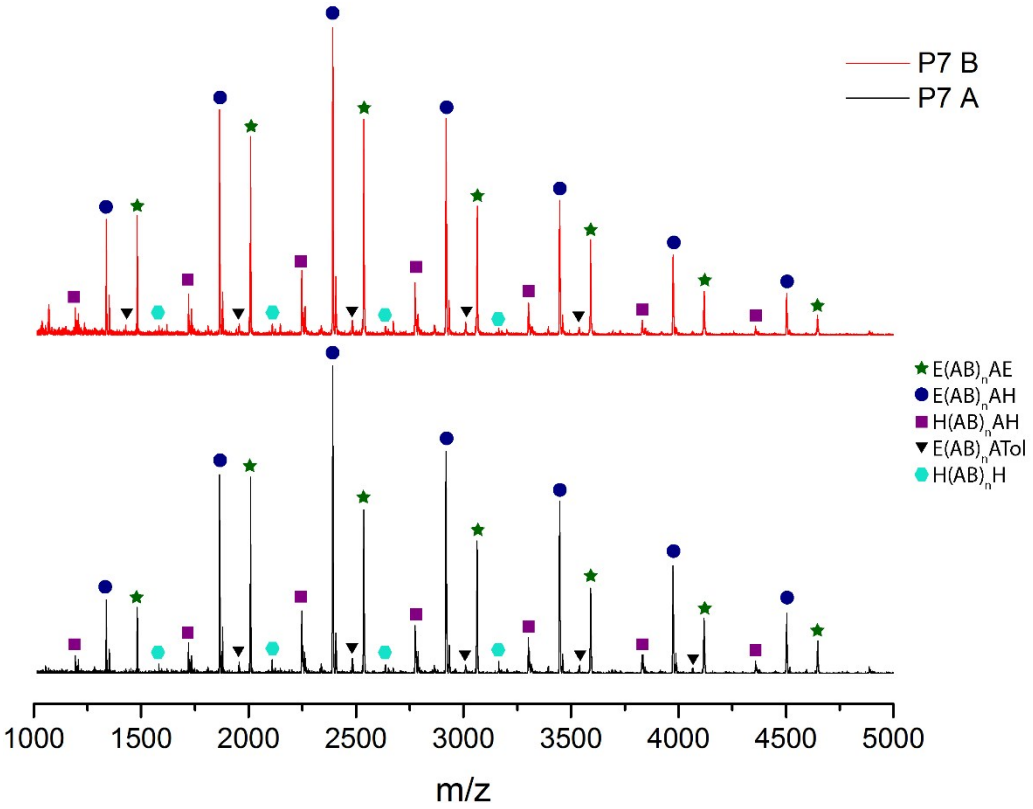


Figure S27: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P7**. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

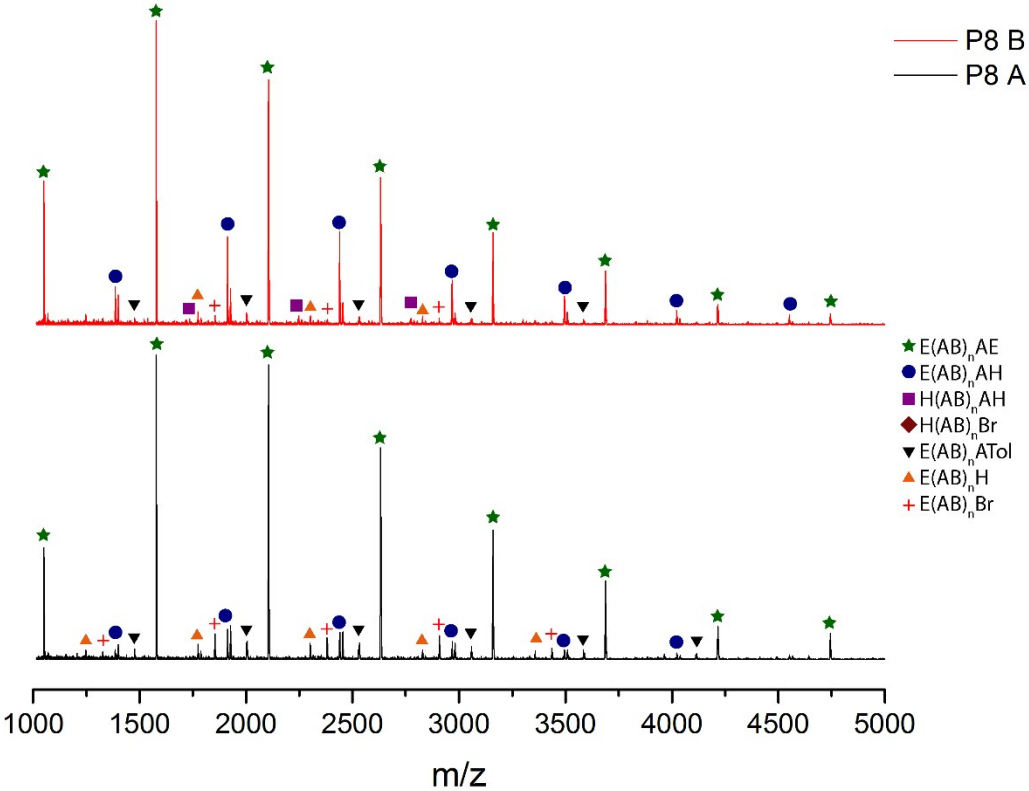


Figure S28: MALDI-ToF MS spectra for both (A, bottom black and B, top red) trials of **P8**. Samples were prepared at 5 mg ml^{-1} in THF and mixed with a 50 mg ml^{-1} terthiophene (matrix) solution 1:15 (v:v).

Table S3: Distribution of chain-types as determined by MALDI-ToF MS.

	P1	P2	P3	P4	$P5^{0.33}$	P5	$P5^{1.0}$	P6	P6*	P7	P8
$E(AB)_nAE$	25	-	9	-	25	64	16	-	2	29	67
$E(AB)_nAH$	55	-	51	7	61	19	63	8	36	40	14
$H(AB)_nAH$	9	31	28	29	7	-	15	30	52	8	1
$E(AB)_nAMe$	6	-	4	-	4	7	4	-	-	7	8
$H(AB)_nAMe$	2	-	5	-	-*	-*	-*	-	-*	4	-
$E(AB)_nATol$	-	-	-	< 1	1	4	-	-	-	2	3
$H(AB)_nATol$	-	-	-	-	< 1	-	-	-	-	2	-
$E(AB)_nBr$	-	5	-	5	-	1	-	4	-	-	4
$E(AB)_nH$	2	-	1	-	3*	5*	3*	-	7*	4	4
$H(AB)_nBr$	-	41	-	42	-	-	-	45	1	-	-
$H(AB)_nH$	1	2	1	2	-	-	-	4	1	2	-
$HA(AB)_nBr$	-	11	-	6	-	-	-	5	-	-	-
$HA(AB)_nAH$	-	5	1	5	-	-	-	3	1	-	-
$EA(BA)_nAH$	-	-	2	1	-	-	-	-	1	1	-
other	-	5	< 1	3	-	< 1	-	3	< 1	2	1

Distributions are based on peak heights for species where n = 2-6, are averages of two runs, and presented out of 100. Threshold for to distinguish peaks from noise was 2% of principle peak. *For biphenyl endgroups, the chain-types $E(AB)_nH$ and $H(AB)_nAMe$ are indistinguishable by mass (calc. 1207.88 and 1207.93 g mol^{-1}, respectively, for n = 2). Thus, peaks at these m/z are given as $E(AB)_nH$ although there is likely contribution from $H(AB)_nAMe$.

Kinetic Data:

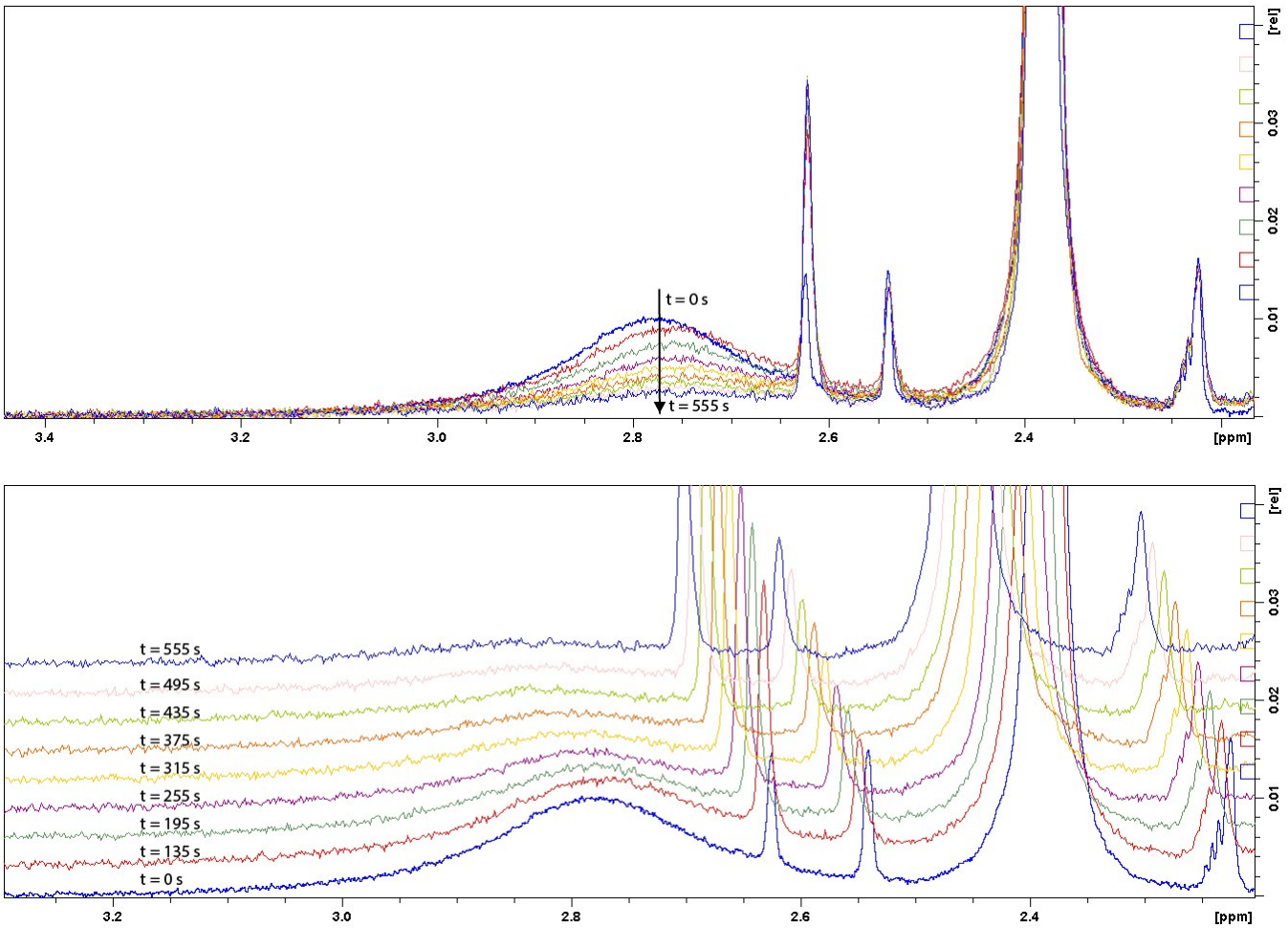


Figure S29: Alternate views of representative kinetic evolution plots focused on the *o*-tolyl peak of the Pd-bound P(*o*-tol)$_3$ ligand. As oxidative addition proceeds, this resonance becomes buried in the free ligand's *o*-tolyl proton peak (2.38 ppm).

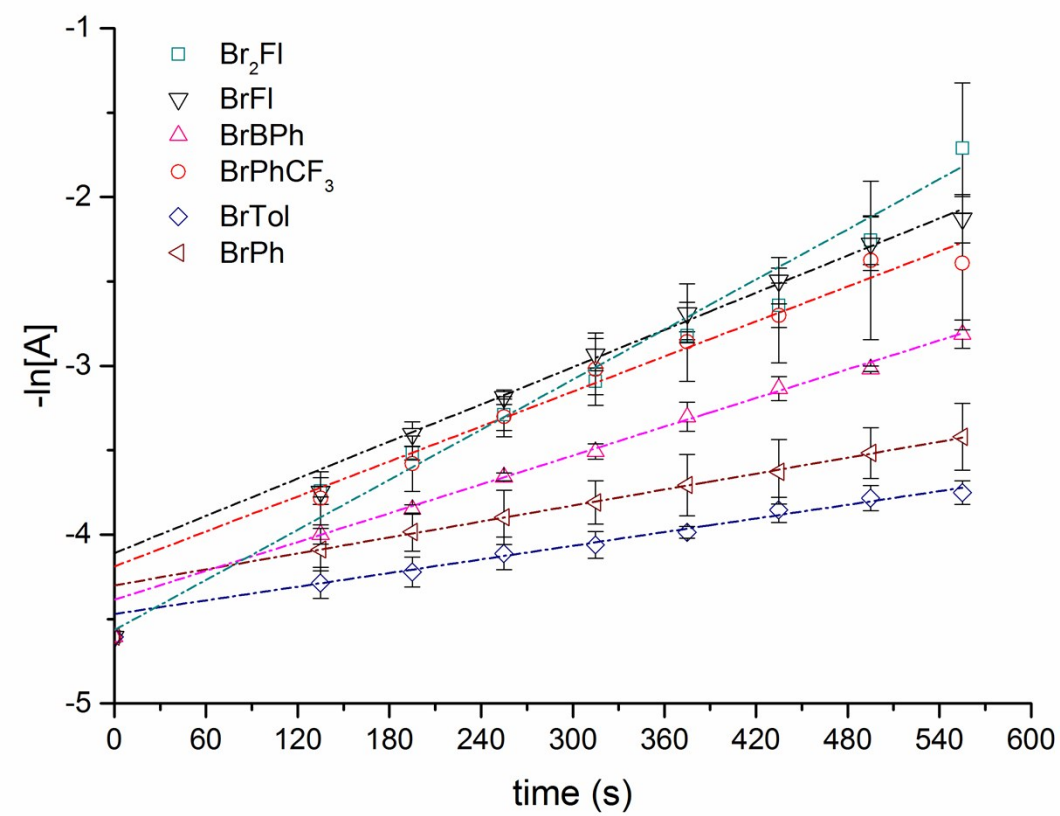


Figure S30: Kinetic plots for the decay of Pd-bound P(*o*-tol)$_3$ (A). Concentration of Pd^0 catalyst is defined as 100 at t = 0 s. Each experiment was done in triplicate, error bars represent standard deviation of the three trials. Dashed lines indicate the linear fit used to calculate k_{obs}.

Table S4: Experimental rate constants[a] for ECRs and monomer.

Substrate	**k_{obs}** (x 10^{-3} s^{-1})	**$k/k_{monomer}$**
Br_2Fl	1.99	1.0
BrFl	1.47	0.74
BrBPh	1.14	0.57
$BrPhCF_3$	1.39	0.70
BrTol	0.539	0.27
BrPh	0.630	0.32

[a]Measured via decay of Pd-bound P(*o*-tol)$_3$ via ^{1}H NMR.

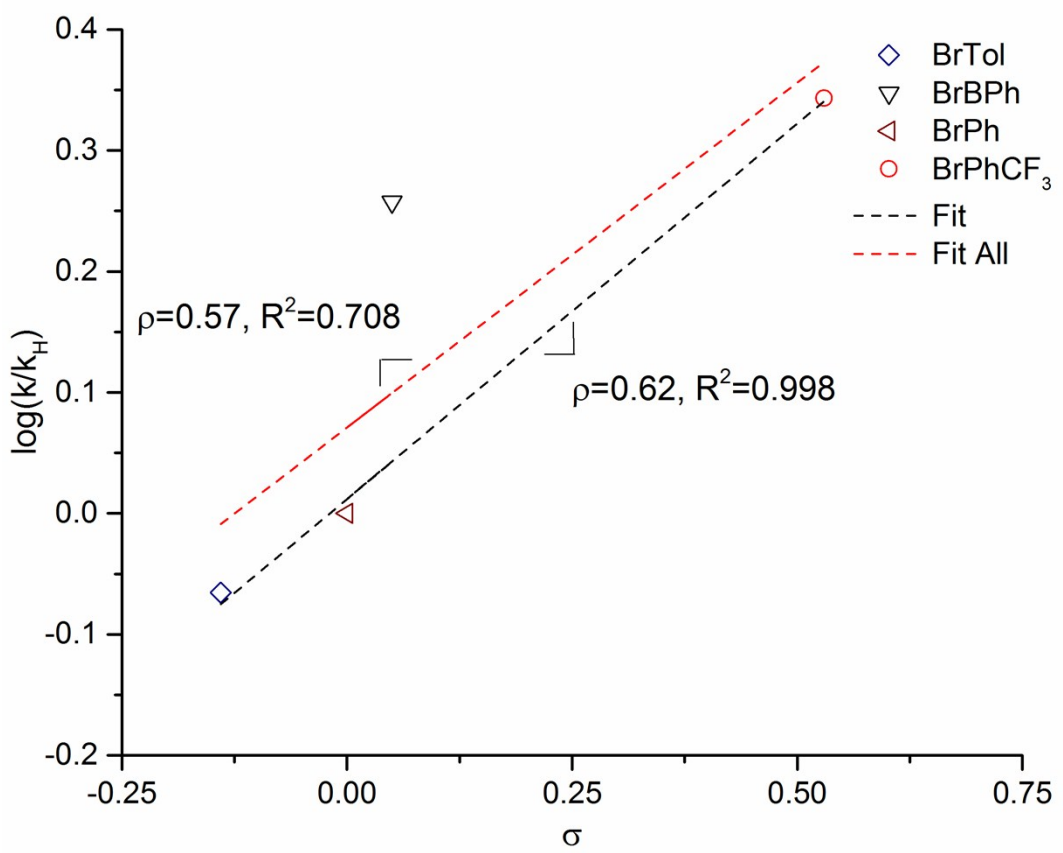


Figure S31: A Hammett analysis for the oxidative addition of bromobenzene, *p*-bromotoluene, 4,4'-bromobiphenyl, and 4-(trifluoromethyl) bromobenzene to Pd[P(*o*-tol)$_3$]$_2$. σ values obtained from Ritchie and Sager.[2] The red dashed line represents a linear fit including all four substrates where the black dashed line shows a linear fit excluding 4,4'-bromobiphenyl.

References:

1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I., NMR chemical shifts of trace impurities: Common laboratory solvents, organics, and gases in deuterated solvents relevant to the organometallic chemist. *Organometallics* **2010,** *29*, 2176-2179.

2. Ritchie, C. D.; Sager, W. F., An Examination of Structure-Property Relationships. In *Progress in Physical Organic Chemistry*, Cohen, S. G.; Streitweiser, A.; Taft, R. W., Eds. Wiley & Sons: New York, 1964; Vol. 2, pp 323-400.