Supporting Information

for

A Highly Efficient Catalytic System for Polycondensation of 2,7-Dibromo-9,9-dioctylfluorene and 1,2,4,5-Tetrafluorobenzene via Direct Arylation

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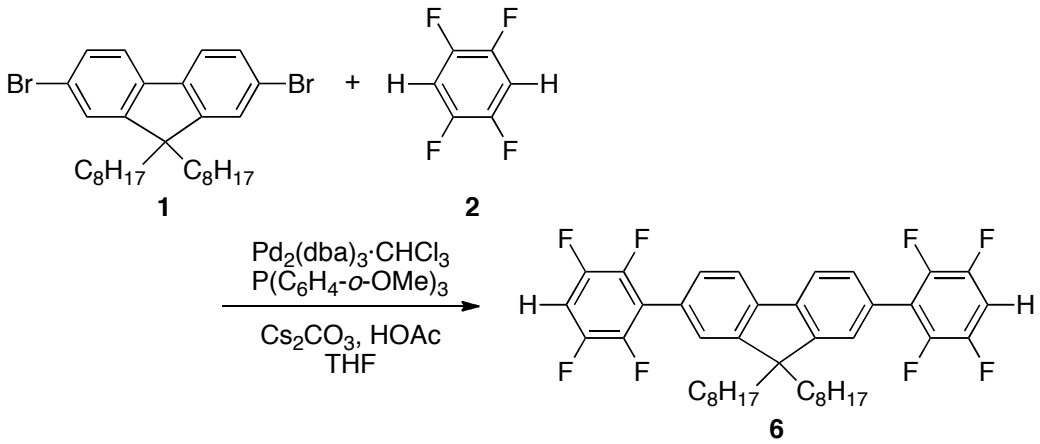
General Considerations. All manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Nitrogen gas was dried by passing through P_2O_5 (Merck, SICAPENT). NMR spectra were recorded on a Bruker Avance 400 spectrometer (^{1}H NMR 400.13 MHz, ^{13}C NMR 100.62 MHz, and ^{19}F NMR 376.46 MHz). Chemical shifts are reported in δ (ppm), referenced to ^{1}H (residual) and ^{13}C signals of deuterated solvents as internal standards or to the ^{19}F signal of C_6F_6 (δ – 163.0) as external standards. Analytical GPC was carried out on a JASCO GPC assembly consisting of a PU-980 pump, an RI-1530 detector, and three polystyrene gel columns (Shodex KF-801, KF-803L, KF-805L). THF was used as the mobile phase with a flow rate of 1.0 mL min^{-1} at 40 °C. The columns were calibrated against 9 standard polystyrene samples (Shodex; M_n = 980–1920000). Recycling preparative GPC was carried out on a JAI LC918U instrument equipped with two preparative GPC columns (JAIGEL-1H-A and -2H-A). Chloroform was used as the mobile phase with a flow rate 3.8 mL min^{-1}. IR spectra were recorded on a JASCO FT/IR-410 or FT/IR-4100 spectrometer in a KBr pellet. UV-vis absorption spectra were recorded on a JASCO V-560 spectrometer. High-resolution mass spectrometry data were obtained on a JEOL JMS-700 spectrometer. Elemental analysis was performed by ICR Analytical Laboratory, Kyoto University.

Toluene and DMF (Kanto, dehydrated) were used as received. THF and CPME were dried over Na/Ph_2CO, distilled, and stored over activated MS4A. DMA was dried over CaH_2, distilled, and stored over activated MS4A. Cs_2CO_3, K_2CO_3 and Na_2CO_3 were dried overnight at 120 °C under vacuum and handled in a glovebox. 2,7-Dibromo-9,9-dioctylfluorene (**1**),[1] Herrmann catalyst,[2] $Pd_2(dba)_3{\cdot}CHCl_3$,[3] $PdCl_2(MeCN)_2$,[4] $PdMe_2(tmeda)$,[5] CpPd(π-allyl),[6] $P(C_6H_4$-*o*-$NMe_2)_3$ (**L4**),[7] and 2-methoxypentafluorophenylbenzene (**5**)[8] were prepared according to the literature. All other chemicals were obtained from commercial suppliers and used without further purification.

Synthesis of Model Compounds (6, 8 and 9).

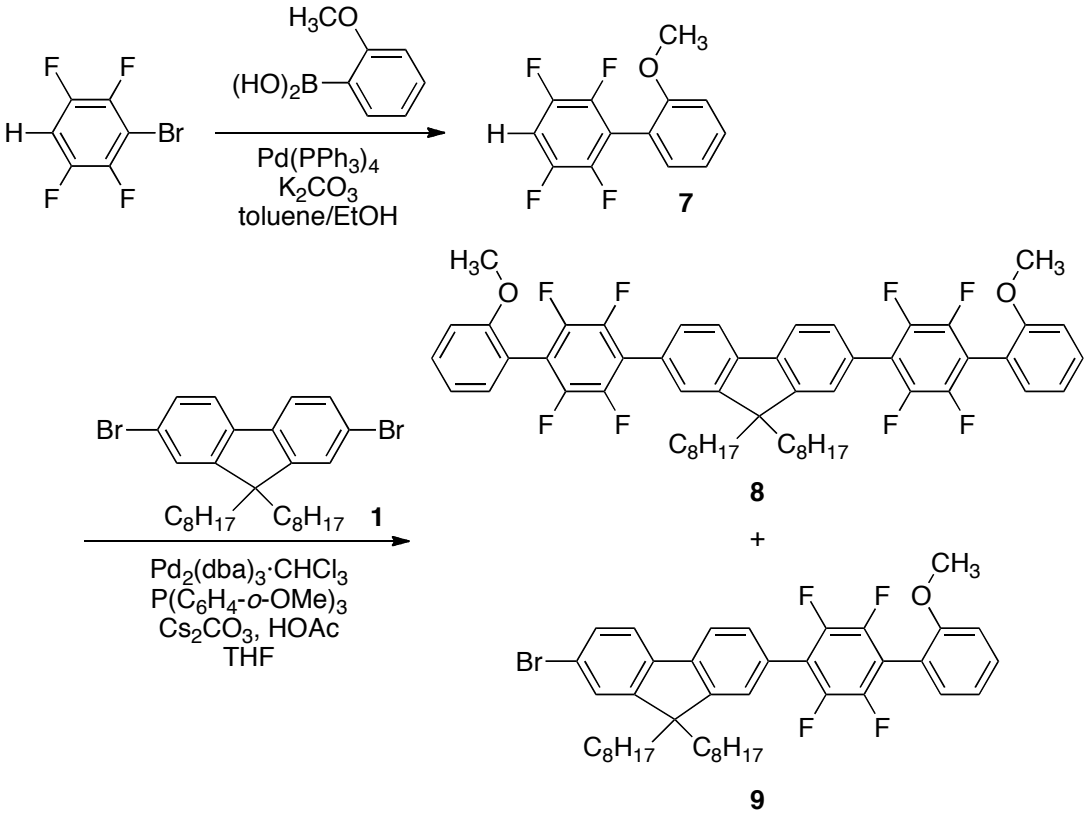
(a) Synthesis of 6.



A 10 mL Schlenk tube equipped with a Teflon cock was charged with 2,7-dibromo-9,9-dioctylfluorene (**1**; 274 mg, 0.50 mmol), 1,2,4,5-tetrafluorobenzene (**2**; 377 mg, 2.50 mmol), Cs_2CO_3

(489 mg, 1.5 mmol), AcOH (30.0 mg, 0.50 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (2.6 mg, 2.5 μmol), $P(C_6H_4$-*o*-$OMe)_3$ (**L1**; 3.5 mg, 10 μmol), and THF (1 mL). The mixture was stirred at room temperature for 0.5 h, and then at 100 °C for 24 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (5 mL), washed with water, passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)), and concentrated to dryness. The crude product was purified by flash column chromatography (SiO_2, hexane) to afford **3** as a colorless oily substance (115 mg, 33%). The NMR data were identical to those reported.[9] ^{1}H NMR ($CDCl_3$): δ 7.86 (d, J = 7.5 Hz, 2H), 7.50–7.44 (m, 4H), 7.08 (tt, J = 9.7, 7.3 Hz, 2H), 2.05–1.97 (m, 4H), 1.25–1.02 (m, 20H), 0.81 (t, J = 7.2 Hz, 6H), 0.73 (m, 4H). ^{19}F NMR ($CDCl_3$): δ –139.3 (ddd, J = 22.3, 12.2, 10.3 Hz, 4F), –143.6 (ddd, J = 22.3, 12.2, 7.4 Hz, 4F).

(b) Synthesis of 8 and 9.



(i) A mixture of 2,3,5,6-tetrafluorobromobenzene (1.15 g, 5.0 mmol), 2-methoxyphenylboronic acid (912 mg, 6.0 mmol), $Pd(PPh_3)_4$ (57.8 mg, 50 μmol), K_2CO_3 (2.07 g, 15 mmol), toluene (12 mL) and EtOH (10 mL) was stirred under reflux for 5 h. Water (50 mL) was added, and the mixture was extracted with diethyl ether (4 × 30 mL). The combined extracts were washed with brine (50 mL), dried over $MgSO_4$, evaporated under reduced pressure, and then purified by flash column chromatography (SiO_2, hexane) to afford **7** as a white solid (762 mg, 59% yield). ^{1}H NMR ($CDCl_3$): δ 7.45 (t, J = 7.5 Hz, 1H), 7.26 (d, J = 7.4 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 8.4 Hz, 1H), 7.11–7.01 (m, 1H), 7.08 (tt, J = 9.7, 7.3 Hz, 2H), 3.82 (s, 3H). ^{19}F NMR ($CDCl_3$): δ –140.1 (ddd, J =

22.9, 12.4, 10.2 Hz, 2F), –140.9 (ddd, J = 22.9, 10.2, 7.2 Hz, 2F). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.0 (s), 147.1 (dddd, J = 246, 14, 11, 4 Hz), 144.0 (dddd, J = 246, 14, 5, 5 Hz), 131.5 (s), 130.9 (s), 120.5 (s), 118.5 (t, J = 19 Hz), 116.3 (s), 111.2 (s), 104.8 (t, J = 23 Hz), 55.6 (s). Anal. Calcd. for $C_{13}H_8F_4O$: C, 60.95; H, 3.15. Found: C, 60.81; H, 3.05.

(ii) A 10 mL Schlenk tube equipped with a Teflon cock was charged with **1** (1.10 g, 2.00 mmol), **7** (256 mg, 0.50 mmol), Cs_2CO_3 (489 mg, 1.5 mmol), AcOH (30.0 mg, 0.50 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (5.2 mg, 5.0 μmol), $P(C_6H_4$-*o*-$OMe)_3$ (**L1**; 7.0 mg, 20 μmol), and THF (2 mL). The mixture was stirred at room temperature for 0.5 h, and then at 100 °C for 15 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 (5 mL), washed with water, passed through a short column (SiO_2, hexane/CH_2Cl_2 (1/1)), and concentrated to dryness. The residue was subjected to flash column chromatography (SiO_2, hexane and then hexane/CH_2Cl_2 (5/1)). The crude product was purified by recycle GPC to afford **8** (381 mg, 85% yield) and **9** (10.3 mg, 2% yield) as a white solid and a colorless oily substance, respectively.

8: ^1H NMR ($CDCl_3$): δ 7.90 (d, J = 8.3 Hz, 2H), 7.60–7.55 (m, 4H), 7.49 (td, J = 7.9, 1.6 Hz, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.12 (t, J = 7.5 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 3.89 (s, 6H), 2.08–2.02 (m, 4H), 1.30–1.08 (m, 20H), 0.83 (t, J = 7.1 Hz, 6H), 0.80 (m, 4H). ^{19}F NMR ($CDCl_3$): δ –141.3 (dd, J = 23.4, 12.2 Hz, 4F), –144.8 (dd, J = 23.4, 12.2 Hz, 4F). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.2 (s), 151.3 (s), 144.5 (dddd, J = 246, 14, 6, 4 Hz), 143.9 (dddd, J = 246, 15, 5, 4 Hz), 141.1 (s), 131.7 (s), 130.9 (s), 126.7 (s), 125.0 (s), 120.1 (s), 120.0 (t, J = 17 Hz), 116.4 (s), 116.4 (t, J = 19 Hz), 111.3 (s), 55.7 (s), 55.5 (s), 40.1 (s), 31.7 (s), 29.9 (s), 29.1 (s), 23.8 (s), 22.6 (s), 14.0 (s). Anal. Calcd. for $C_{55}H_{54}F_8O_2$: C, 73.48; H, 6.05. Found: C, 73.56; H, 6.09.

9: ^1H NMR ($CDCl_3$): δ 7.99 (d, J = 7.9 Hz, 1H), 7.61 (dd, J = 7.5, 1.2 Hz, 2H), 7.54–7.48 (m, 4H), 7.48 (td, J = 7.6, 1.7 Hz, 2H), 7.32 (d, J = 8.5 Hz, 1H), 7.10 (td, J = 8.4, 0.9 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 3.87 (s, 6H), 2.08–1.90 (m, 4H), 1.30–1.03 (m, 20H), 0.82 (t, J = 7.1 Hz, 6H), 0.68 (m, 4H). ^{19}F NMR ($CDCl_3$): δ –141.3 (dd, J = 23.3, 12.3 Hz, 2F), –144.9 (dd, J = 23.3, 12.3 Hz, 2F). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 157.2 (s), 153.4, (s), 150.5 (s), 144.5 (dddd, J = 247, 15, 6, 3 Hz), 143.8 (dddd, J = 246, 15, 5, 4 Hz), 140.8 (s), 139.4 (s), 131.7 (s), 130.9 (s), 130.1 (s), 129.1 (s), 126.5 (s), 126.3 (s), 125.0 (s), 121.7 (s), 121.4 (s), 120.6 (s), 119.9 (t, J = 17 Hz), 119.8 (s), 116.5 (t, J = 19 Hz), 116.4 (s), 111.3 (s), 55.7 (s), 55.6 (s), 40.1 (s), 31.7 (s), 29.9 (s), 29.1 (s), 23.7 (s), 22.6 (s), 14.0 (s). HRMS (FAB): m/z calcd for $C_{42}H_{47}BrF_4O$ 722.2746 ($[M]^+$), found 722.2746.

References

(1) Lee, J.-I.; Klaerner, G.; Miller, R. D. *Chem. Mater.* **1999**, *11*, 1083–1088.

(2) Herrmann, W. A.; Brossmer, C.; Reisinger, C.-P.; Riermeier, T. H.; Öfele, K.; Beller, M. *Chem.–Eur. J.* **1997**, *3*, 1357–1364.

(3) Ukai, T.; Kawazura, H.; Ishii, Y. *J. Organomet. Chem.* **1974**, *65*, 253–266.

(4) Schlosser, M. Ed. *Organometallics in Synthesis. A Manual*, 2nd ed.; John Wiley & Sons Ltd.: New York, 2010; p. 1126.

(5) de Graaf, W.; Boersma, J.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *Organometallics* **1989**, *8*, 2907–2917.

(6) Tatsuno, Y.; Yoshida, T.; Otsuka, S. *Inorg. Synth.* **1979**, *19*, 220–223.

(7) Fritz, H. P.; Gordon, I. R.; Schwarzhans, K. E.; Venanzi, L. M. *J. Chem. Soc.* **1965**, 5210–5216.

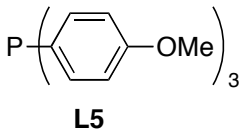
(8) Mu, H.-L.; Ye, W.-P.; Song, D.-P.; Li, Y.-S. *Organometallics* **2010**, *29*, 6282–6290.

(9) Lu, W.; Kuwabara, J.; Kanbara, T. *Macromolecules* **2011**, *44*, 1252–1255.

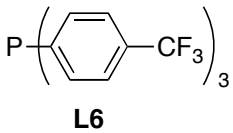
Table S1. Effects of Ligands on Copolymerization of 1 and 2 in THF (Supplementary)[a]

entry	ligand[b]	yield (%)	M_n[c]	PDI[c]
1	P(*t*-Bu)$_3$	86	7,700	2.04
2	P(*t*-Bu)$_2$Me	63	5,300	1.71
3	PCy$_3$	1	—	—
4	**L5**	53	3,100	1.42
5	**L6**	17	1,500	1.09
6	**L7**	1	—	—
7	**L8**	2	—	—
8	**L9**	11	2,200	1.22
9	**L10**	11	1,200	1.85
10	**L11** (XPhos)	49	2,900	1.31
11	**L12**	0	—	—

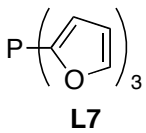
[a]Reactions were carried out at 100 °C for 24 h in THF (1 mL) using **1** (0.50 mmol), **2** (0.50 mmol), Cs_2CO_3 (1.5 mmol), AcOH (0.5 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.5 mol%), and ligand (2.0 mol%). [b]The structures of **L5**–**L12** are shown below. [c]Estimated by GPC calibration based on polystyrene standards.



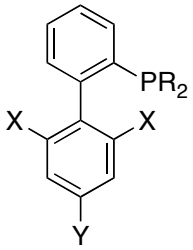
L5



L6



L7



L8: R = *t*-Bu, X = Y = H
L9: R = *t*-Bu, X = Y = *i*-Pr
L10: R = Cy, X = Y = H
L11: R = Cy, X = Y = *i*-Pr (XPhos)
L12: R = Cy, X = OMe, Y = H

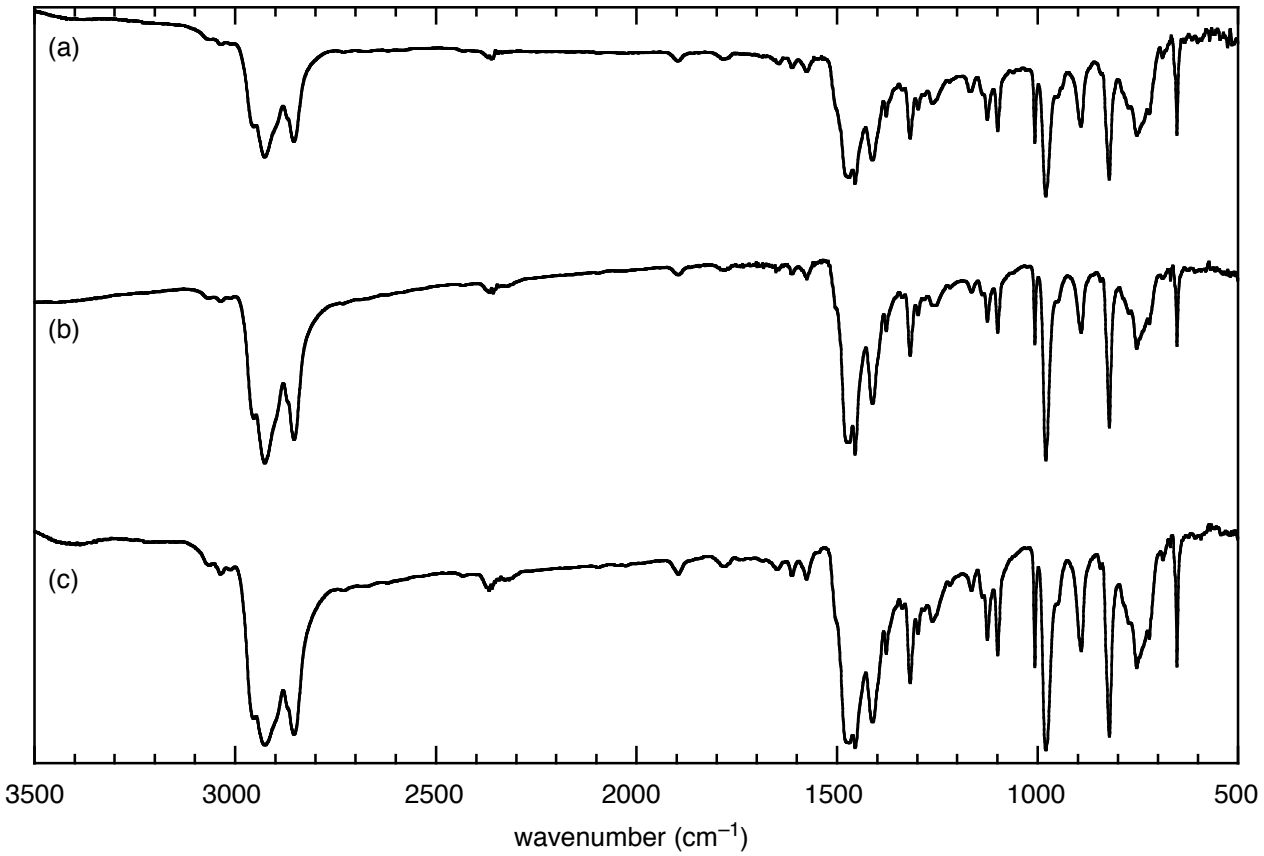


Figure S1. FT-IR spectra of PDOF-TP: (a) entry 4 in Table 1 (catalyst = $PdCl_2(MeCN)_2$, M_n = 85,600), (b) entry 3 in Table 1 (catalyst = $Pd_2(dba)_3 \cdot CHCl_3$, M_n = 132,800), (c) entry 6 in Table 2 (catalyst = $Pd_2(dba)_3 \cdot CHCl_3$, M_n = 347,700).

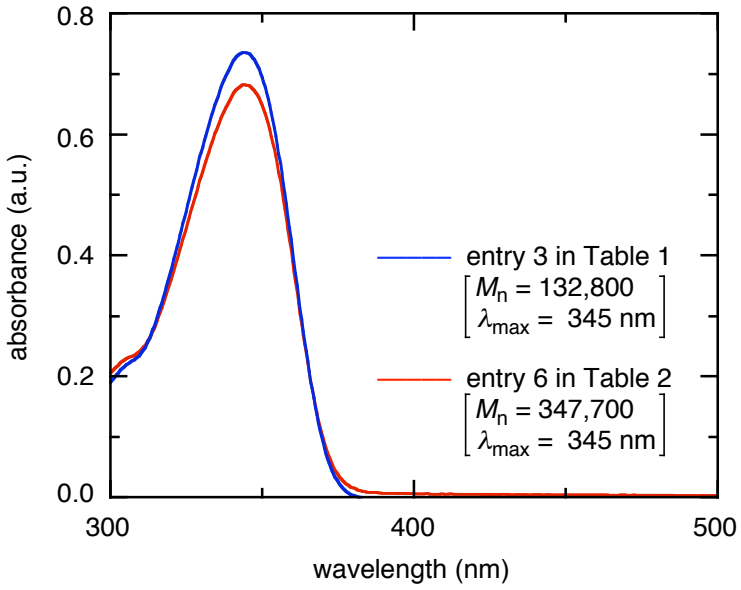


Figure S2. UV-vis absorption spectra of PDOF-TP in $CHCl_3$ (10 mg L^{-1}).

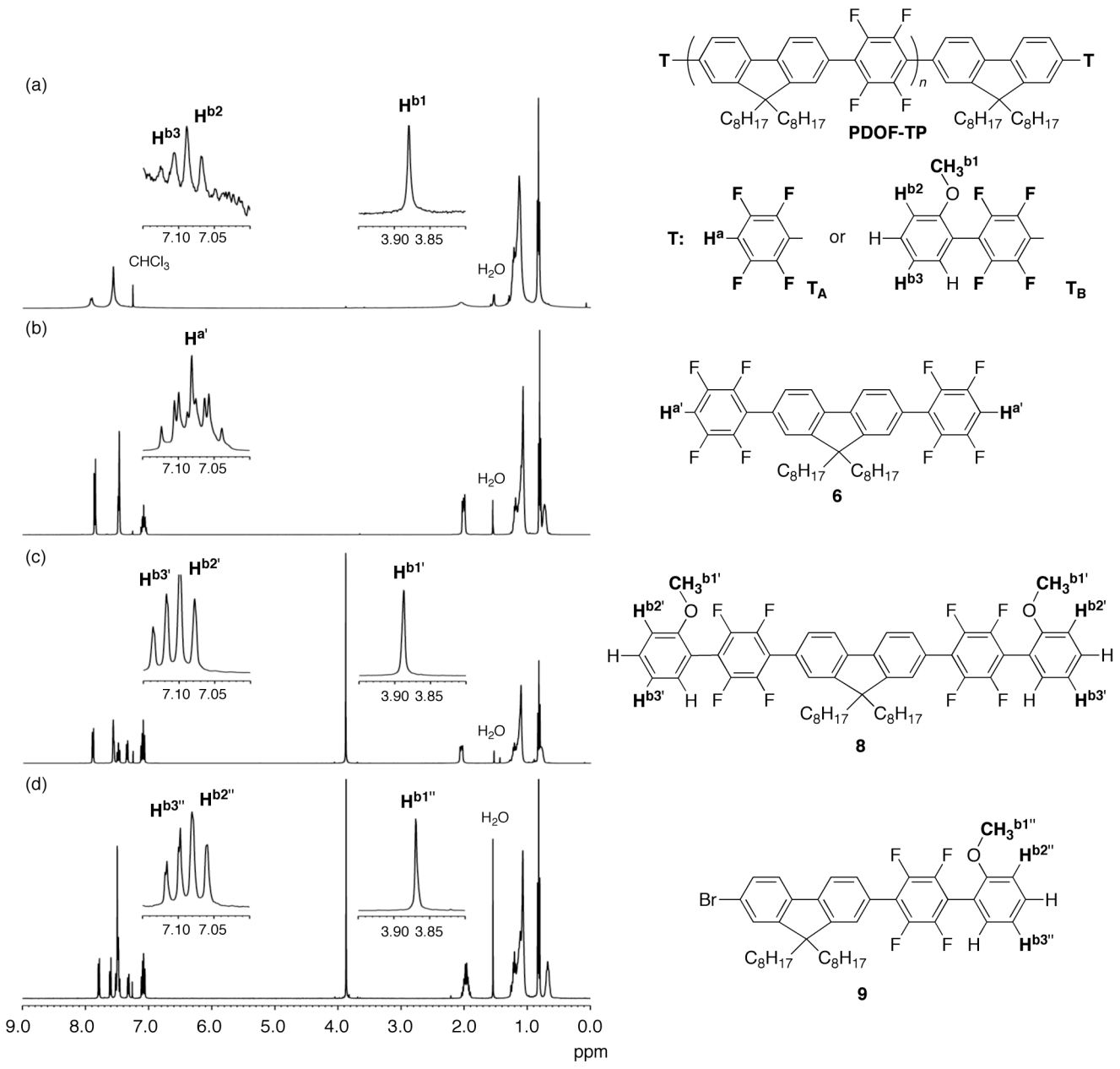


Figure S3. ^{1}H NMR spectra of (a) PDOF-TP (entry 3 in Table 1, M_n = 132,800), (b) **6**, (c) **8**, and (d) **9** in $CDCl_3$.

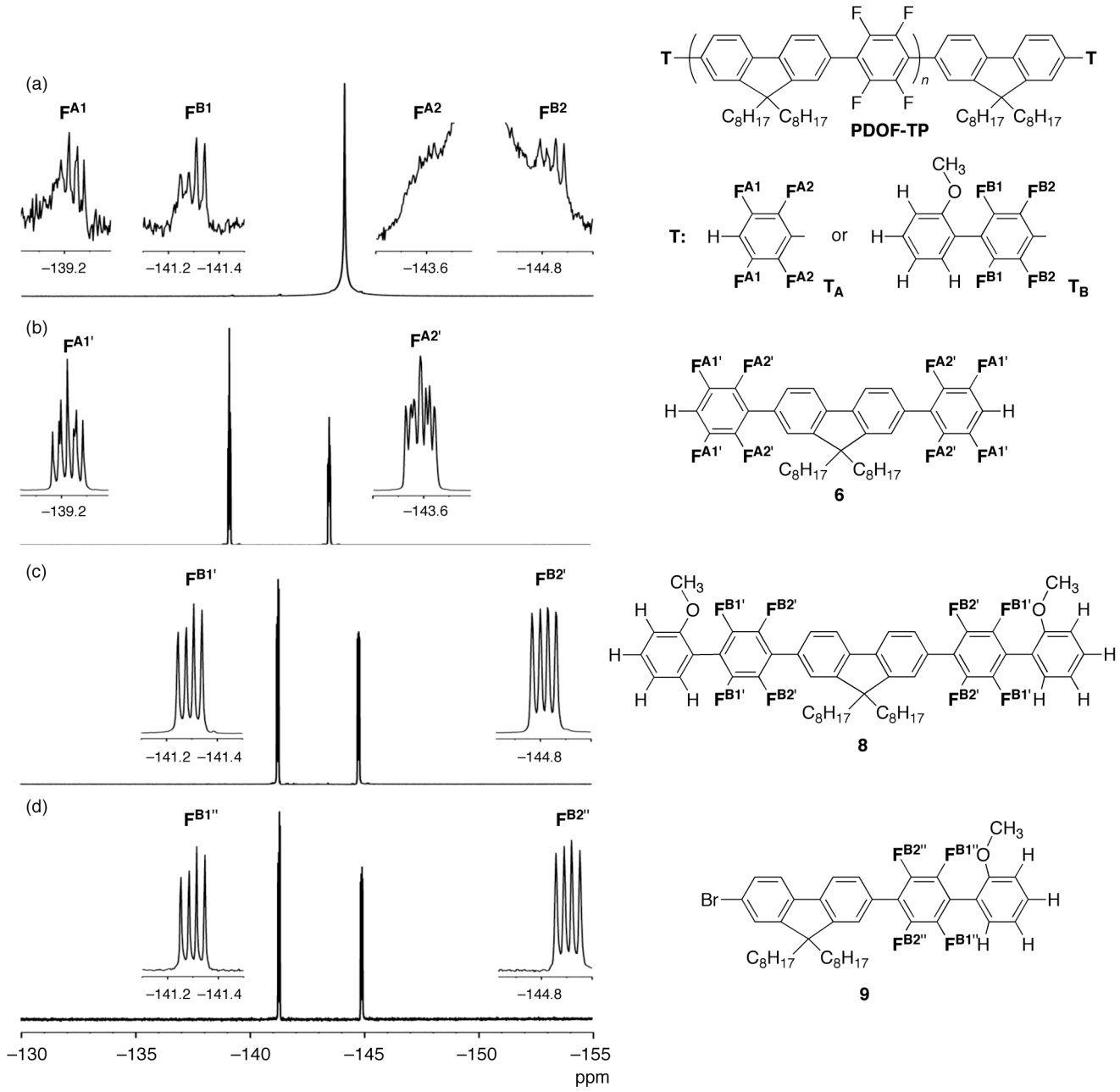


Figure S4. ^{19}F NMR spectra of (a) PDOF-TP (entry 3 in Table 1, M_n = 132,800), (b) **6**, (c) **8**, and (d) **9** in $CDCl_3$.

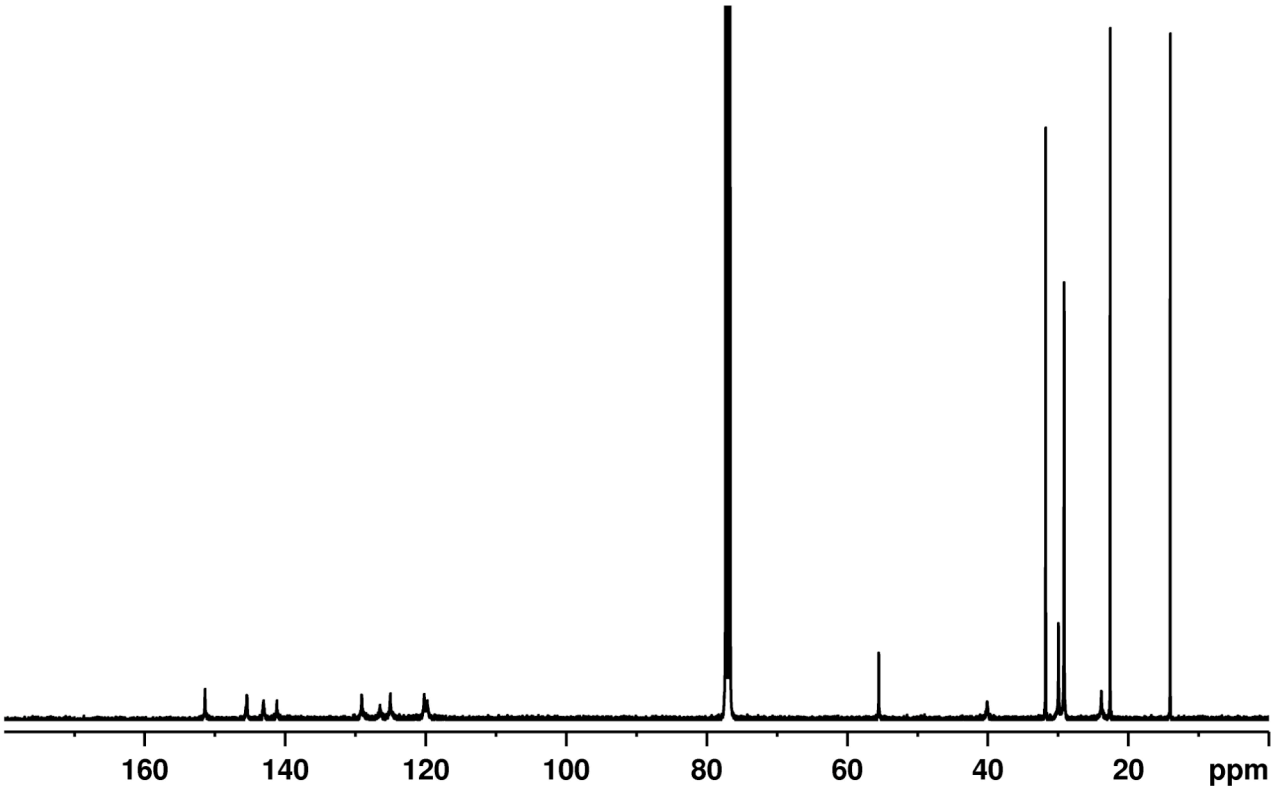


Figure S5. $^{13}C\{^{1}H\}$ NMR spectra of PDOF-TP in $CDCl_3$ (entry 3 in Table 1, M_n = 132,800).