

Excited-State Engineering of Oligothiophenes via Phosphorus Chemistry towards Strong Fluorescent Materials

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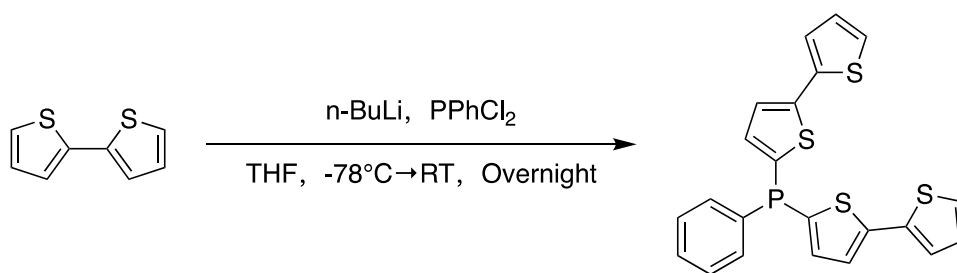
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Materials and Experiments

All manipulations were carried out under a dry nitrogen atmosphere employing standard Schlenk techniques. Reagents were purchased from Shanghai Titan Scientific, Energy Chemical, J&K Scientific, Sinopharm Chemical Reagent and TCI Shanghai, and were, unless otherwise noted, used as-received. Dichlorophenylphosphine was re-distilled before using in the experiments. Solvents were dried using an MBRAUN Solvent Purification System. NMR solvents were purchased from Cambridge Isotope Laboratories and J&K Scientific. ^1H NMR, ^{13}C $\{^1\text{H}\}$ NMR, and ^{31}P $\{^1\text{H}\}$ NMR were recorded on Bruker AVANCE NEO 400 and AVANCE III HD500 MHz spectrometers. High-resolution mass spectra were carried out on the Thermo Scientific ultimate 3000-Q Exactive Focus LC-MS spectrometer in atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI) mode. The single crystal structures of **T4** (CCDC2093209) were obtained at the X-ray Crystallography Facility using a Bruker D8 Venture diffractometer at the ShanghaiTech University. UV-vis experiments were carried out on the Agilent Cary 100 spectrophotometer. The fluorescence measurements were performed using a HORIBA Fluorolog-3 fluorescence spectrophotometer. Absolute quantum yields were obtained with a pre-calibrated Quanta- ϕ integrating sphere attached to a Fluorolog-3 instrument. Lifetime experiments were carried out on a HORIBA DeltaFlex-011x time-resolved fluorescence spectrometer. Melting point experiments were carried out on a TA Instruments Discovery 250 Differential Scanning Calorimeter. Theoretical calculations were carried out using the GAUSSIAN 03 suite of programs.^{S1}



Scheme S1. Synthesis of **D1**.

Compound **D1**.

Under N₂ atmosphere, 2,2'-Dithiophene (600 mg, 3.61 mmol) and 100 mL dry THF were added in a 200 mL flask, then the solution was cooled to -78°C in an acetone bath and stirred for 15 min, and n-butyllithium (2.39 mL, 1.6 M in hexane, 3.79 mmol) was added dropwise. The mixture was allowed up to room temperature slowly and stirred for 1 h, dichlorophenylphosphine (0.25 mL, 1.80 mmol) was slowly injected in one portion at -78°C. To complete the reaction, the mixture was allowed up to room temperature slowly and stirred for overnight. Finally, the solvent of mixture was removed under vacuum, a yellow oil derivative was obtained. At last, the residue was purified by silica gel column chromatography (CH₂Cl₂/petroleum ether 3:17). Yield: 500 mg of blue-green powder (63%). No melting point was observed due to the amorphous nature of **D1** (T_g = 1.8 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.49 – 7.45 (m, 2H), 7.38-7.35 (m, 3H), 7.29 (dd, J = 6.5, 3.6 Hz, 2H), 7.21 – 7.22 (dd, J = 5.1, 1.1 Hz, 2H), 7.17 (dd, J = 3.6, 1.3 Hz, 4H), 6.99 (dd, J = 5.1, 3.6 Hz, 2H) ppm. ¹³C NMR (126MHz, CDCl₃) δ 144.3, 138.2 (d, J = 6.1 Hz), 137.3 (d, J = 29.0 Hz), 137.0 (d, J = 26.9 Hz), 136.9, 132.1 (d, J = 19.2 Hz), 129.0, 128.6 (d, J = 6.8 Hz), 127.9, 125.0, 124.5, 124.4 ppm. ³¹P {¹H} NMR (162 MHz, CDCl₃) δ -32.1 ppm.

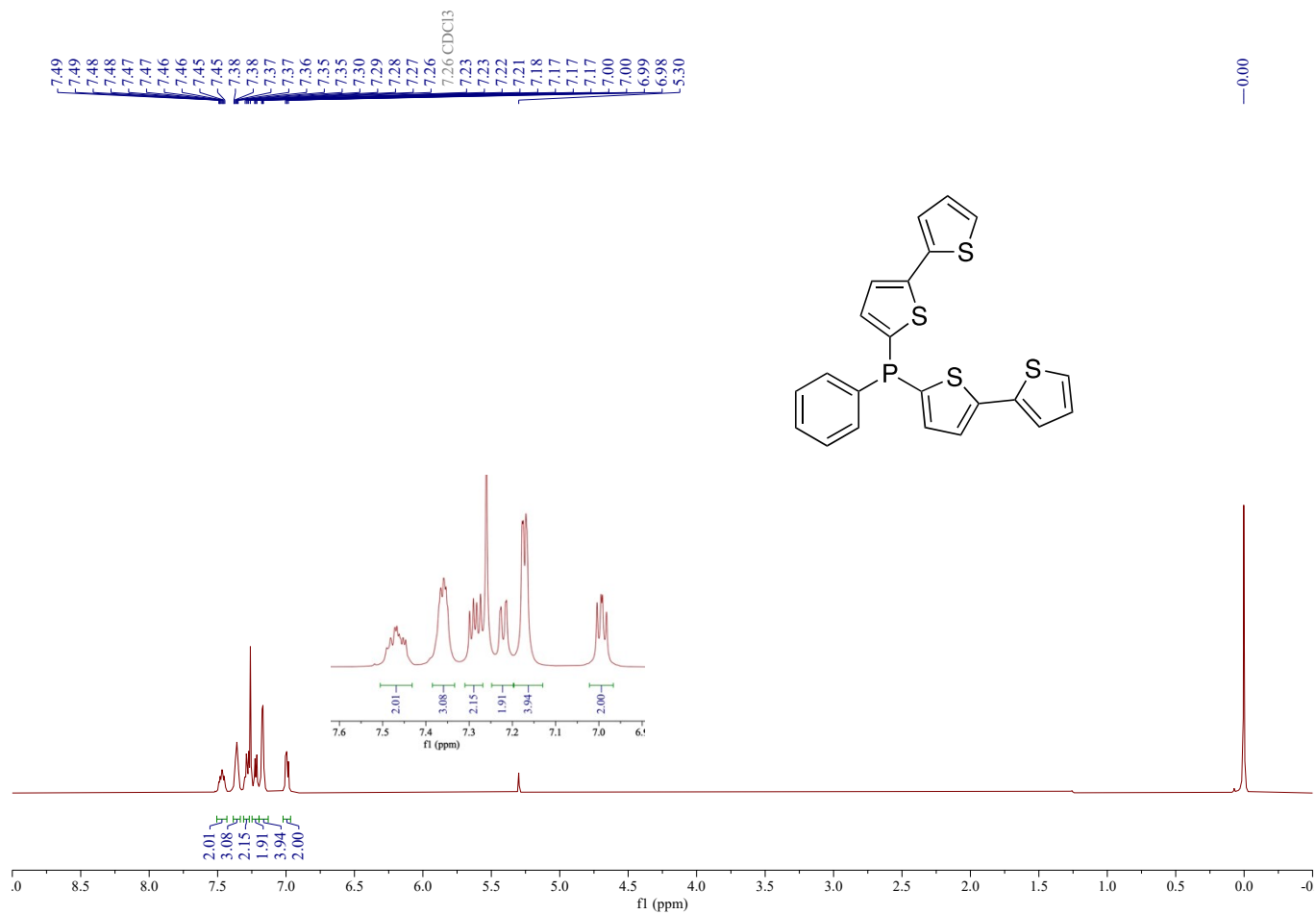


Figure S1. ¹H NMR (400 MHz, CDCl₃, 298K) of D1.

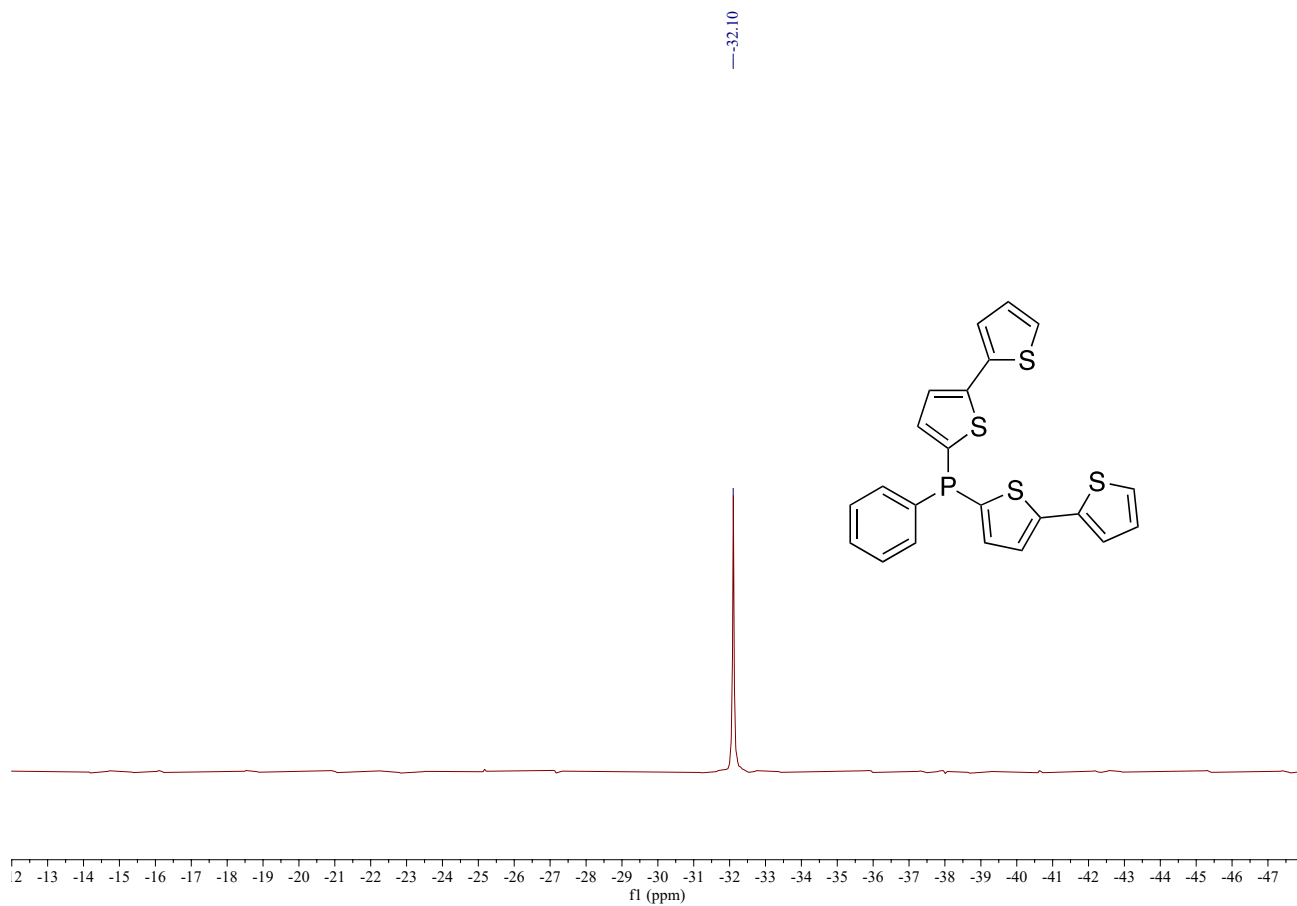


Figure S2. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, 298K) of **D1**.

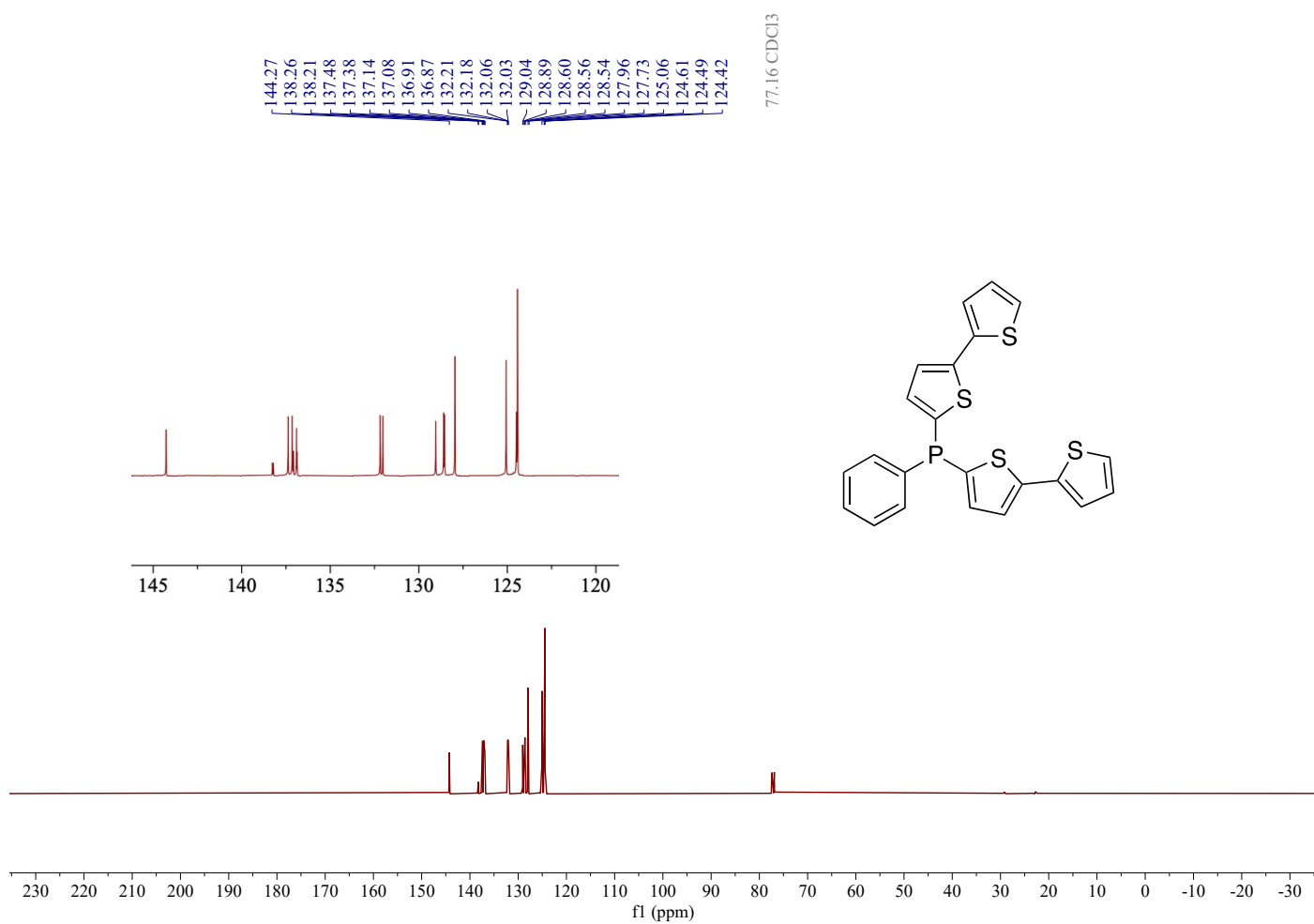
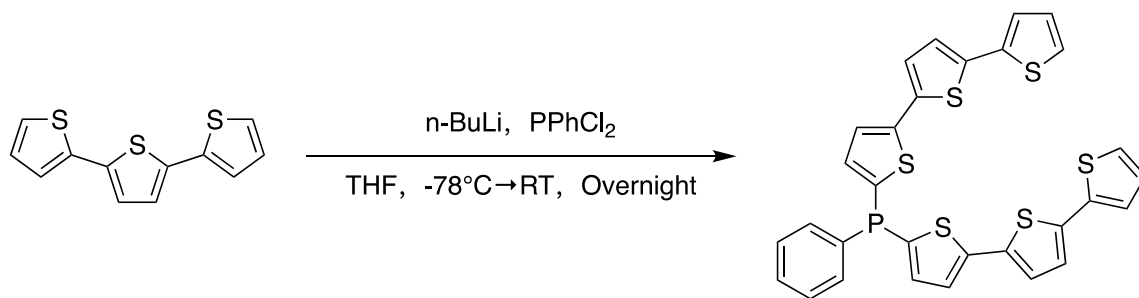


Figure S3. ^{13}C $\{^1\text{H}\}$ NMR (126 MHz, 298K) of **D1**.



Scheme S2. Synthesis of **T1**.

Compound T1.

Under N_2 atmosphere, 2,5-Bis(2-thienyl)thiophene (500 mg, 2.02 mmol) and 100 mL dry THF were added in a 200 mL flask, then the solution was cooled to -78°C in an acetone bath and stirred for 15 min, and *n*-butyllithium (1.32 mL, 1.6 M in hexane, 2.12 mmol) was added dropwise. The mixture was allowed up to room temperature slowly and stirred for 1 h, dichlorophenylphosphine (0.14 mL, 1.01 mmol) was slowly injected in one portion at -78°C . To complete the reaction, the mixture was allowed up to room temperature slowly and stirred for overnight. Finally, the solvent of mixture was removed under vacuum, a yellow oil derivative was obtained. The reaction mixture was purified by silica gel column chromatography (CH_2Cl_2 /petroleum ether 3:17). Yield: 475 mg of yellow powder (78%, $T_g = 30.0^\circ\text{C}$, $T_m = 155.1^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3) δ 7.51 – 7.45 (m, 2H), 7.37 (m, 3H), 7.29 (dd, $J = 6.5, 3.7$ Hz, 2H), 7.21 (dd, $J = 5.1, 1.3$ Hz, 2H), 7.17 (dd, $J = 3.7, 1.3$ Hz, 4H), 7.07 (q, $J = 3.8$ Hz, 4H), 7.02 (dd, $J = 5.1, 3.6$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 144.03, 137.52, 137.23, 137.12, 137.06, 137.03, 135.70, 132.31, 132.12, 129.19, 128.71, 128.64, 128.06, 125.10, 124.81, 124.50, 124.46, 124.37, 123.99 ppm. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ -31.9 ppm. HR LC-MS: Calcd: $[\text{M}+\text{H}]^+ = 602.9622$, found: $m/z = 602.9615$.

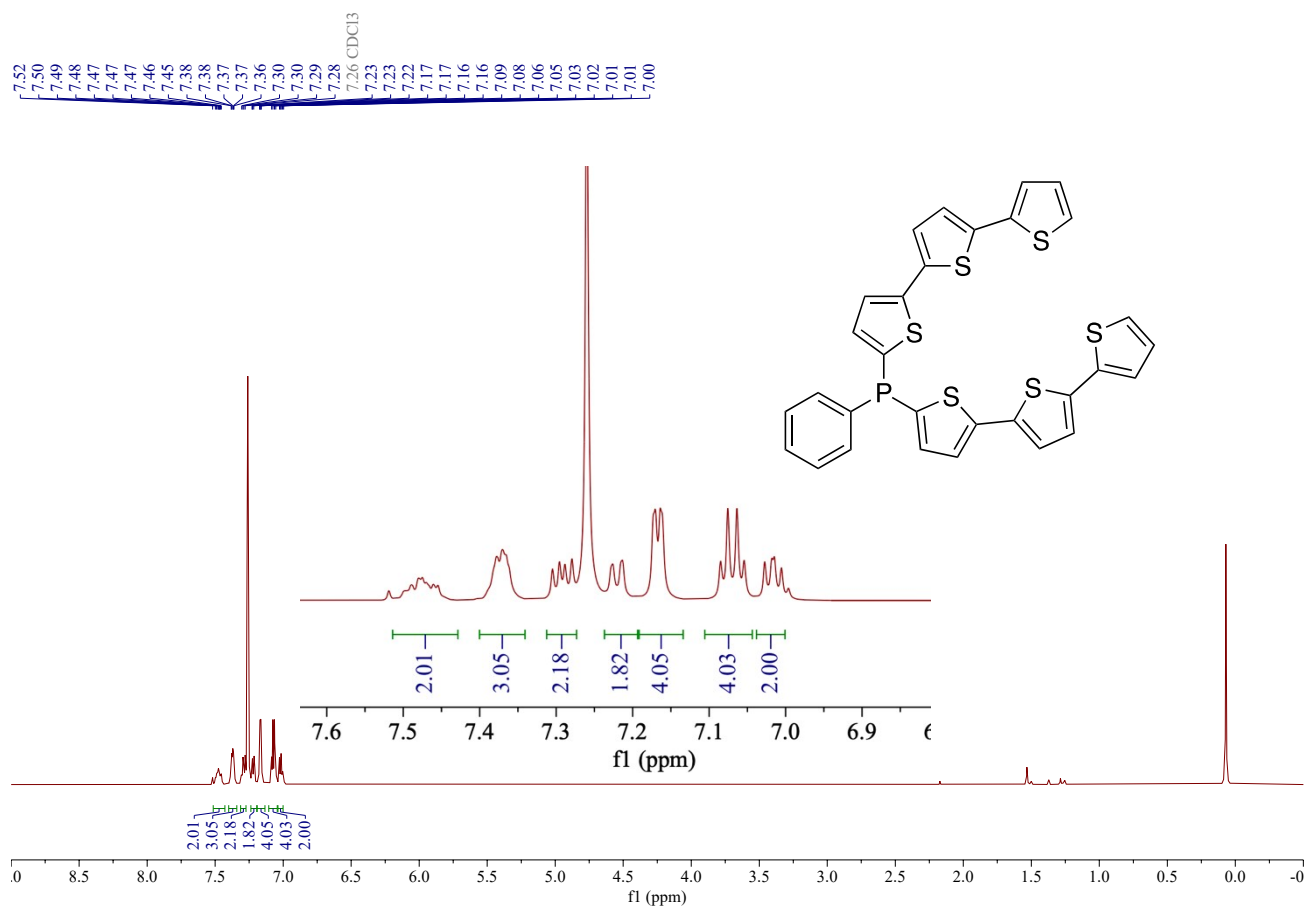


Figure S4. ¹H NMR (400 MHz, CDCl₃, 298K) of T1.

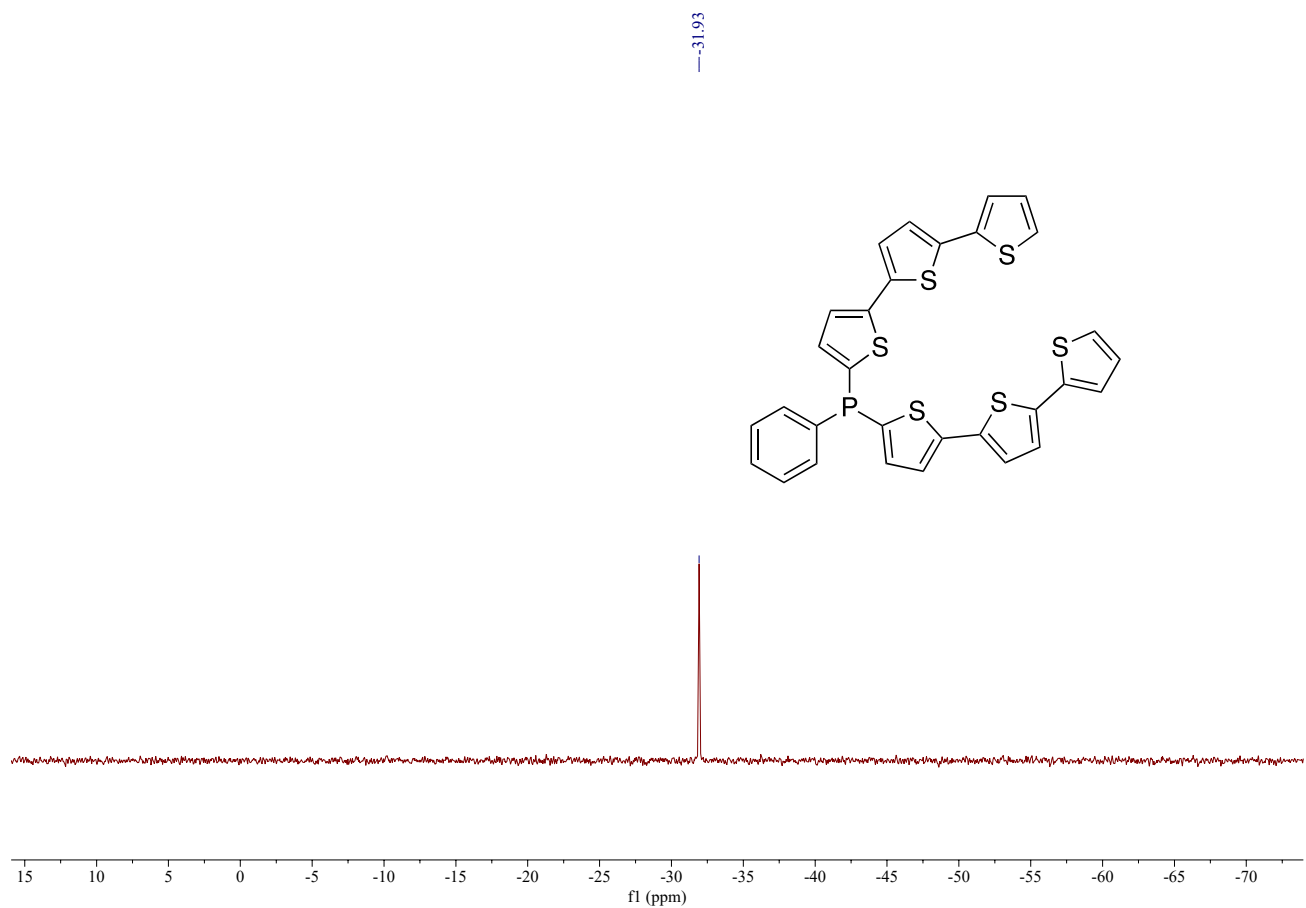


Figure S5. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298K) of **T1**.

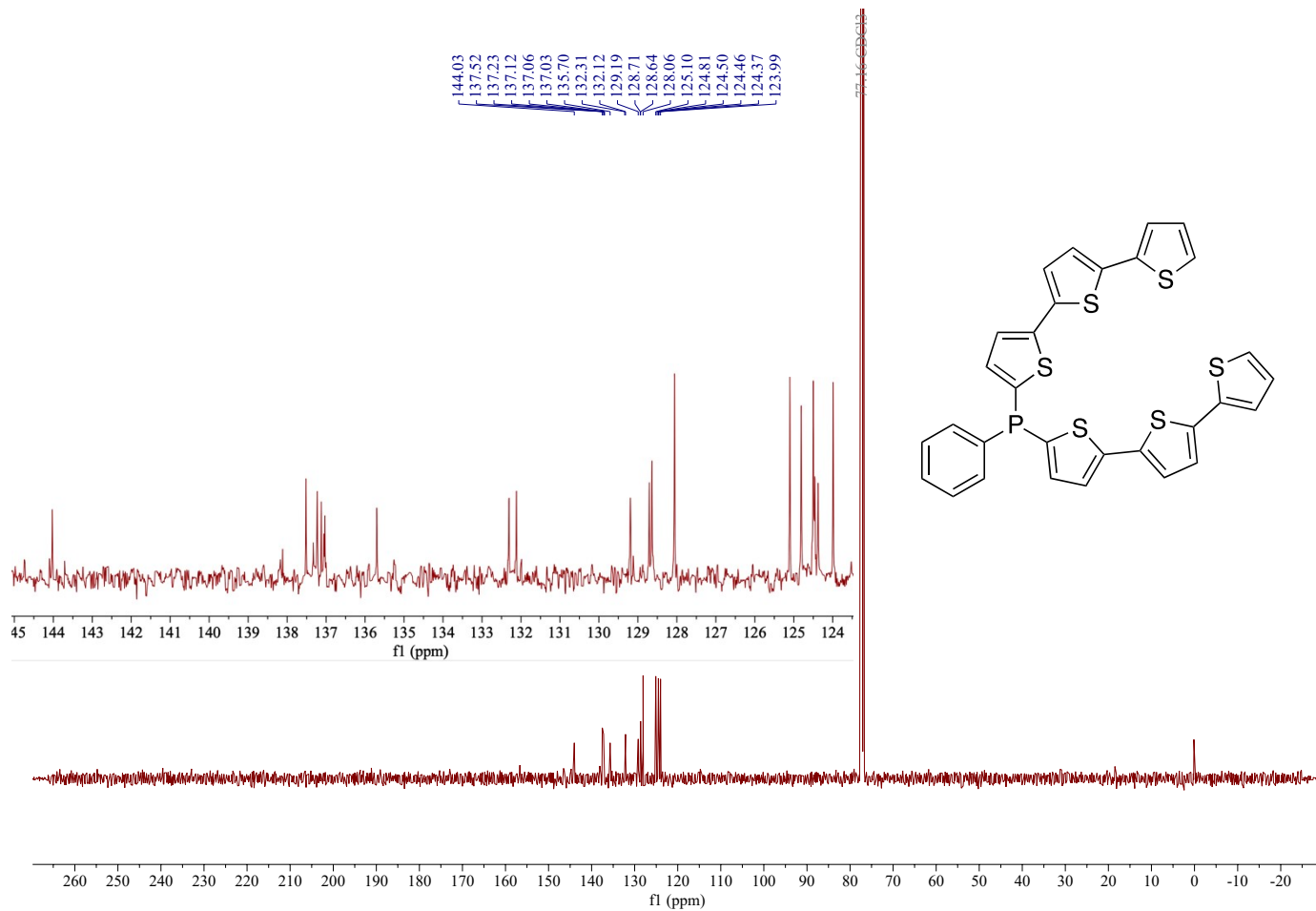
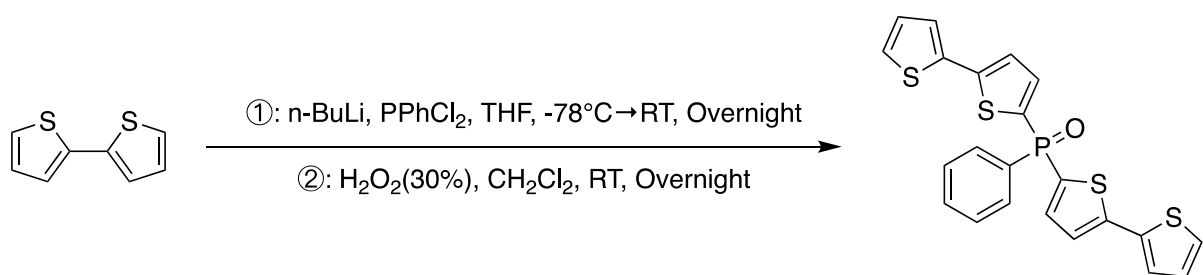


Figure S6. ^{13}C NMR (101 MHz, CDCl_3 , 298K) of **T1**.



Scheme S3. Synthesis of **D2**.

Compound **D2**.

Under N₂ atmosphere, 2,2'-Dithiophene (500 mg, 3.01 mmol) and 100 mL dry THF were added in a 200 mL flask, then the solution was cooled to -78°C in an acetone bath and stirred for 15 min, and n-butyllithium (1.97 mL, 1.6 M in hexane, 3.16 mmol) was added dropwise. The mixture was allowed up to room temperature slowly and stirred for 1 h, dichlorophenylphosphine (0.21 mL, 1.51 mmol) was slowly injected in one portion at -78°C. To complete the reaction, the mixture was allowed up to room temperature slowly and stirred for overnight. Finally, the solvent of mixture was removed under vacuum, the residue was purified by flash silica gel column chromatography (CH₂Cl₂/petroleum ether 3:17). After that, the solid was dissolved in 50 ml CH₂Cl₂, and 5 ml H₂O₂ (30% in H₂O) was added. The solution was stirred for overnight at room temperature. Then, the mixture was separated and the aqueous phase was extracted with CH₂Cl₂ (3 × 30 mL), organic layer was dried over anhydrous Na₂SO₄. The solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1:9), Yield: 433 mg of white powder (63%). No melting point was observed due to the amorphous nature of **D2** (T_g = 22.4 °C). ¹H NMR (400 MHz, CDCl₃) δ 7.93 – 7.83 (m, 2H), 7.60 (td, *J* = 7.3, 1.7 Hz, 1H), 7.52 (td, *J* = 7.6, 3.3 Hz, 2H), 7.46 (dd, *J* = 7.9, 3.8 Hz, 2H), 7.29 (dd, *J* = 5.1, 1.1 Hz, 2H), 7.25 – 7.22 (m, 4H), 7.03 (dd, *J* = 5.1, 3.6 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 146.4 (d, *J* = 6.1 Hz), 137.8 (d, *J* = 10.1 Hz), 135.8 (d, *J* = 2.0 Hz), 132.8 (d, *J* = 117.2 Hz), 132.7 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 120.2 Hz), 131.6 (d, *J* = 11.1 Hz), 128.7 (d, *J* = 13.1 Hz), 128.2, 126.2, 125.4, 124.6 (d, *J* = 13.1 Hz) ppm. ³¹P {¹H} NMR (162 MHz, CDCl₃) δ 13.0 ppm. HR LC-MS: Calcd: [M+H]⁺ = 454.9817, found: *m/z* = 454.9817.

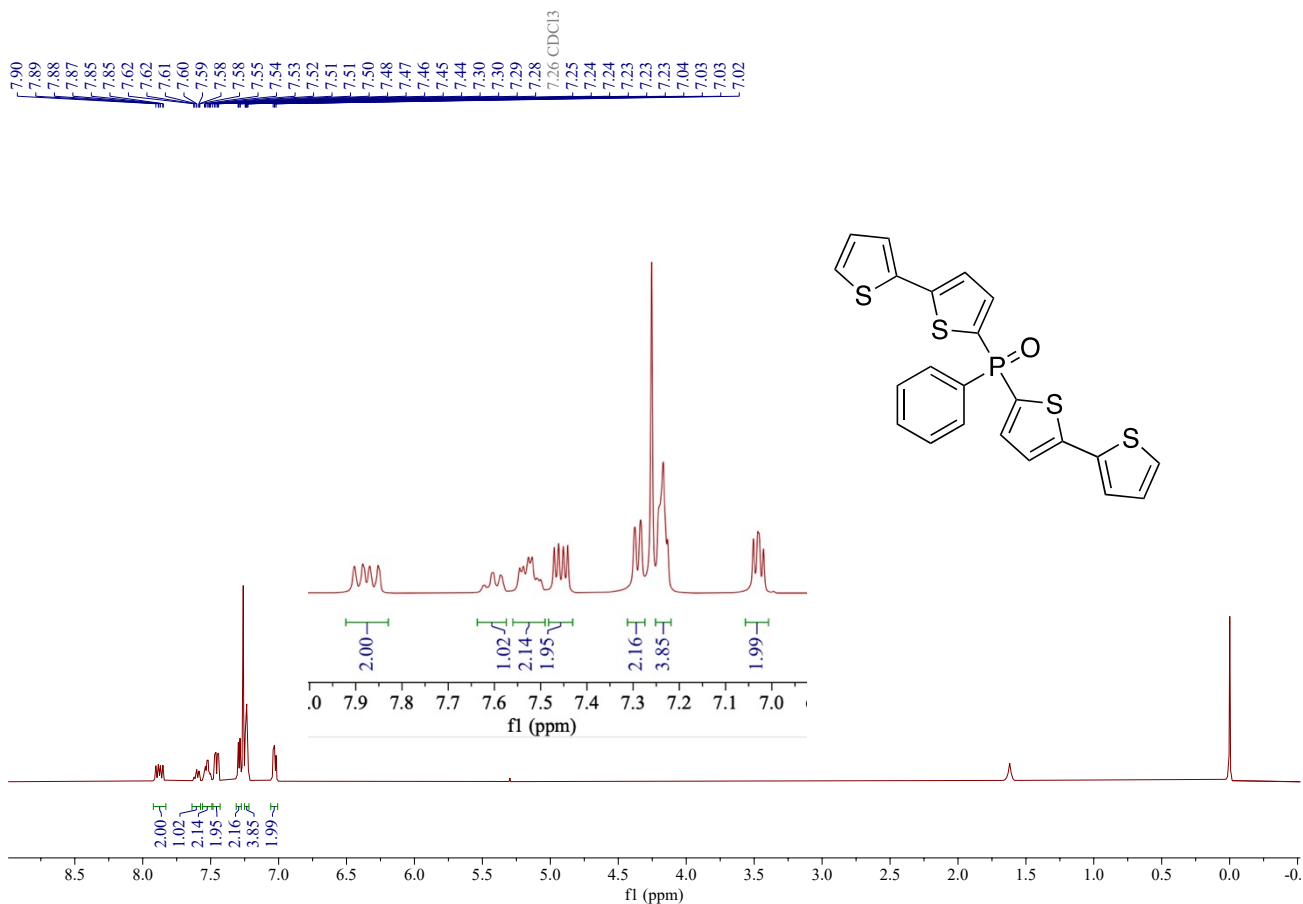


Figure S7. ¹H NMR (400 MHz, CDCl₃, 298K) of D2.

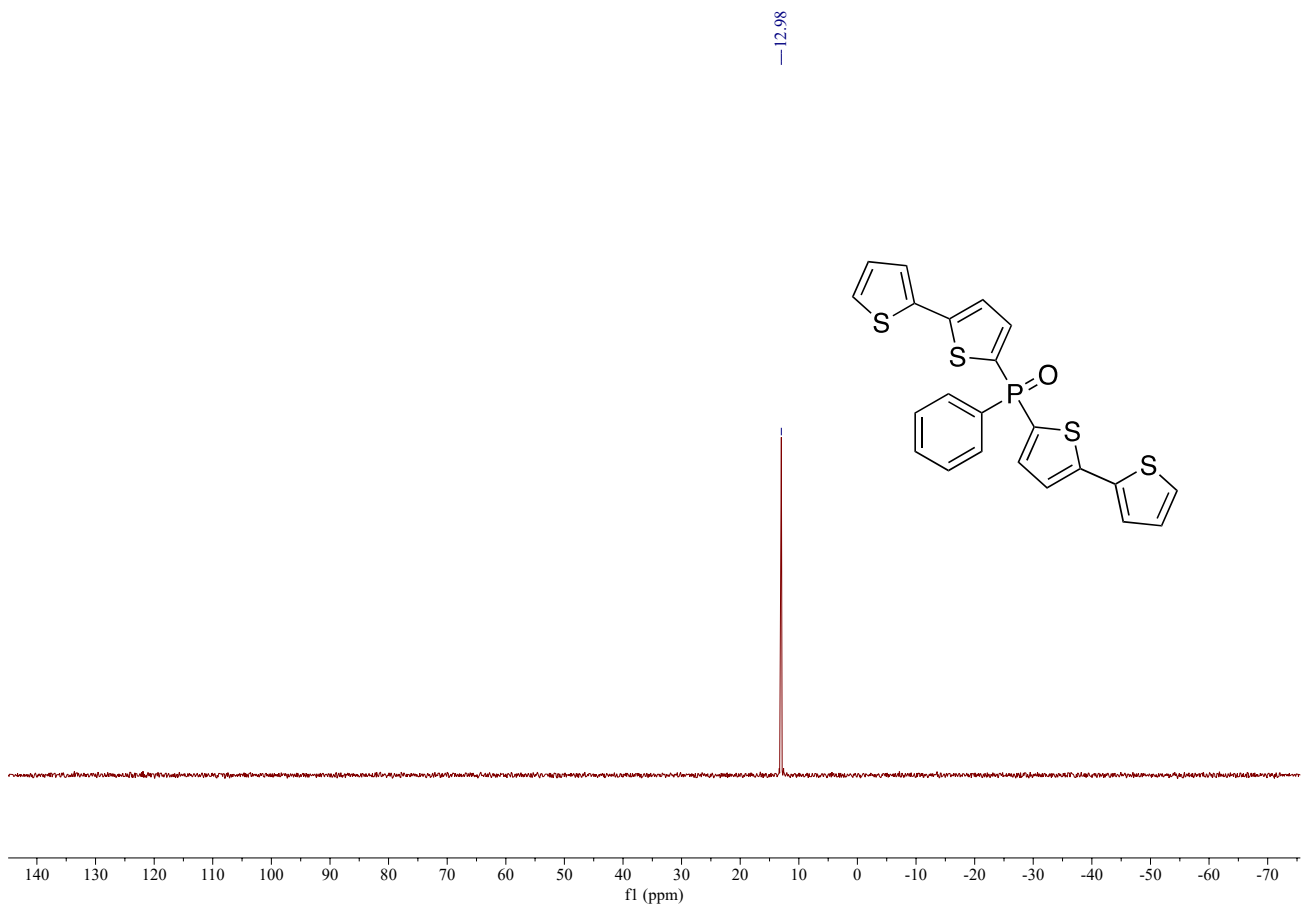


Figure S8. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298K) of **D2**.

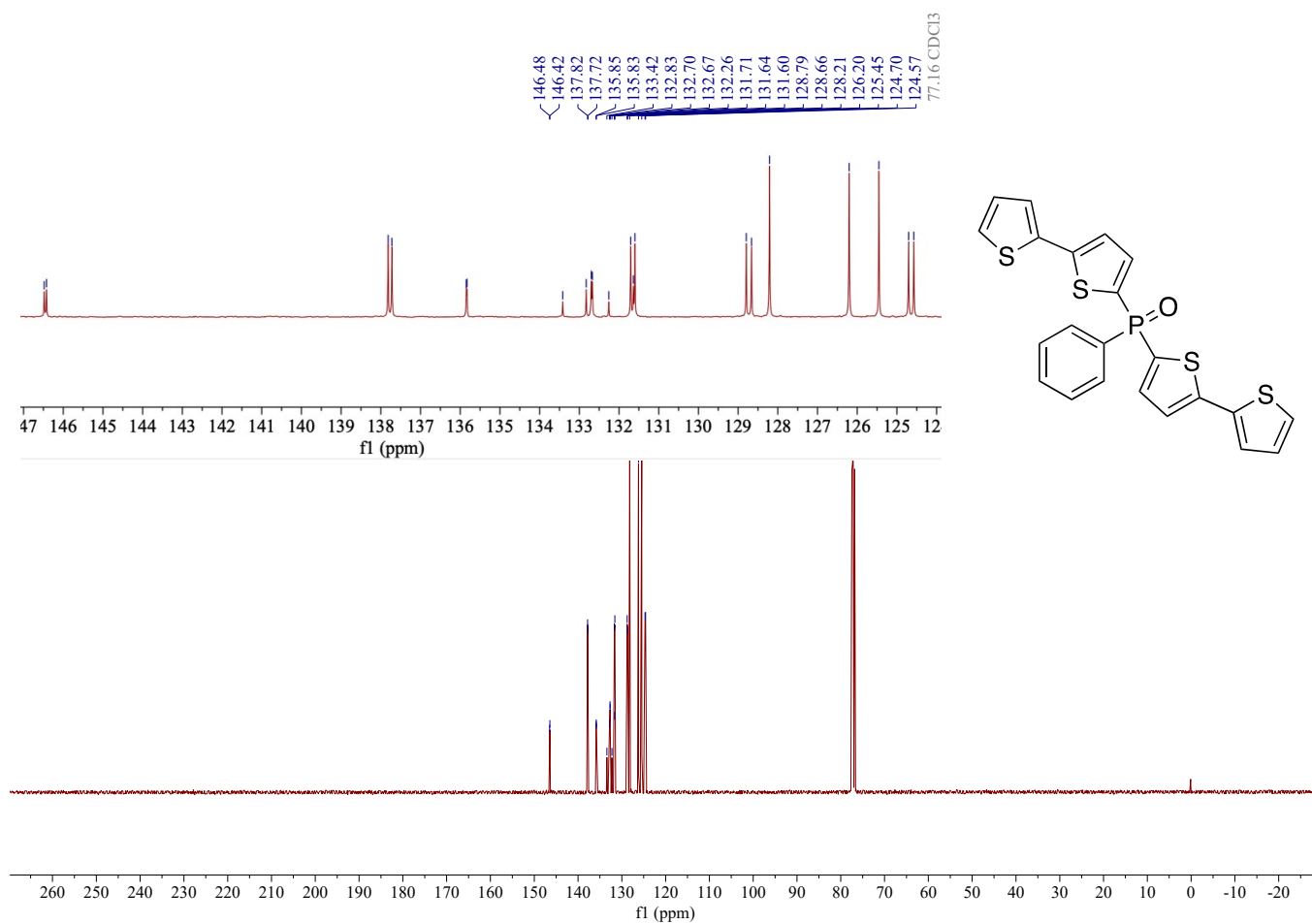
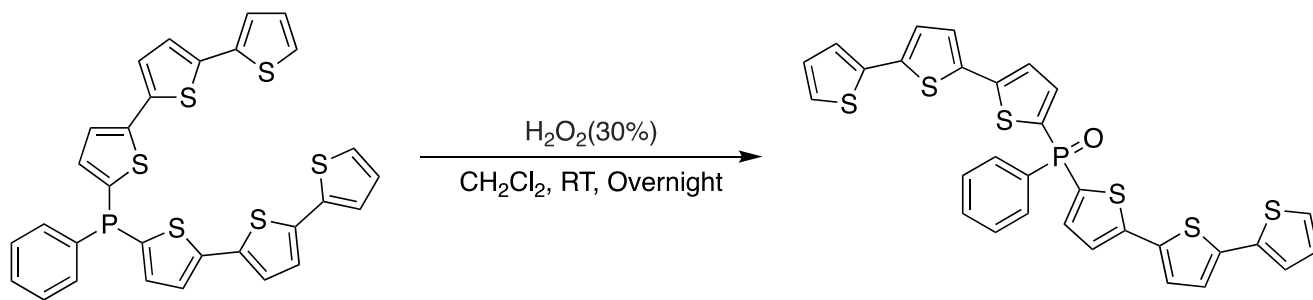


Figure S9. ^{13}C NMR (101 MHz, CDCl_3 , 298K) of **D2**.



Scheme S4. Synthesis of **T2**.

Compound T2

Compound **T1** (70.9 mg, 0.11 mmol) was dissolved in 30 ml CH_2Cl_2 , and 3 ml H_2O_2 (30% in H_2O) was added. The solution was stirred for overnight at room temperature. Then, the mixture was separated and the aqueous phase was extracted with CH_2Cl_2 (3×30 mL), organic layer was dried over anhydrous Na_2SO_4 . The solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether 1:19), Yield: 57.4 mg of green powder (79%, $T_g = 51.5$ °C, $T_m = 217.4$ °C). ^1H NMR (400 MHz, CDCl_3) δ 7.93 – 7.83 (m, 2H), 7.61 (dd, $J = 7.5, 1.7$ Hz, 1H), 7.54 (dt, $J = 7.6, 3.7$ Hz, 2H), 7.47 (dd, $J = 7.9, 3.8$ Hz, 2H), 7.25 – 7.22 (m, 2H), 7.19 (dd, $J = 3.6, 1.2$ Hz, 2H), 7.15 (d, $J = 3.8$ Hz, 2H), 7.09 (d, $J = 3.8$ Hz, 2H), 7.03 (dd, $J = 5.1, 3.6$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 146.2 (d, $J = 6.1$ Hz), 138.1 (d, $J = 28.28$ Hz), 137.9, 136.8 (d, $J = 168.7$ Hz), 134.5, 133.9 (d, $J = 106.8$ Hz), 132.2 (d, $J = 120.2$ Hz), 132.8, 132.8, 132.2 (d, $J = 114.1$ Hz), 131.7 (d, $J = 11.1$ Hz), 128.8 (d, $J = 13.13$ Hz), 128.1, 126.1, 125.1, 124.5 (d, $J = 27.27$ Hz), 124.5 (d, $J = 14.1$ Hz) ppm. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3) δ 12.9 ppm. HR LC-MS: Calcd: $[\text{M}+\text{H}]^+ = 618.9571$, found: $m/z = 618.9568$.

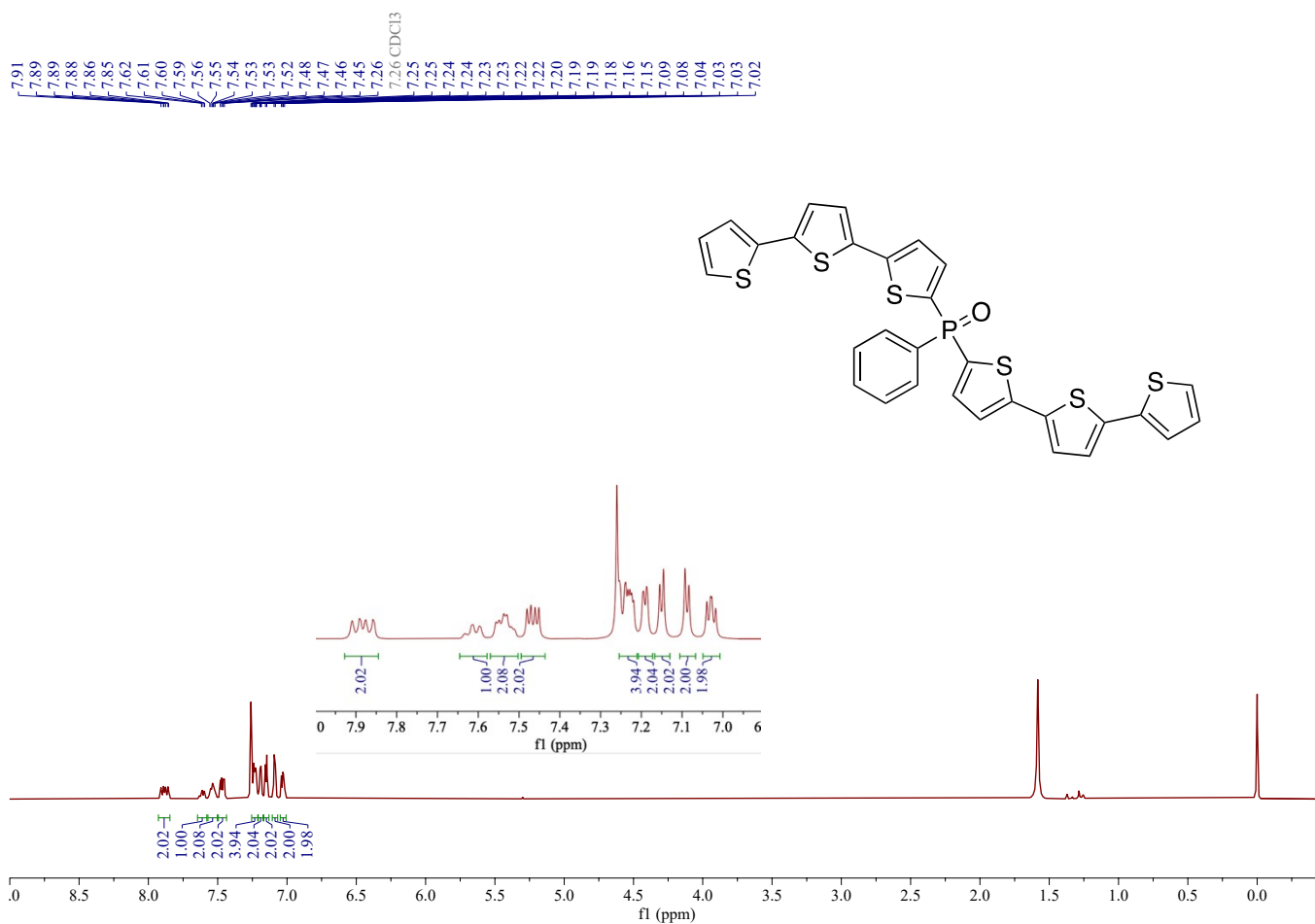


Figure S10. ¹H NMR (400 MHz, CDCl₃, 298K) of **T2**.

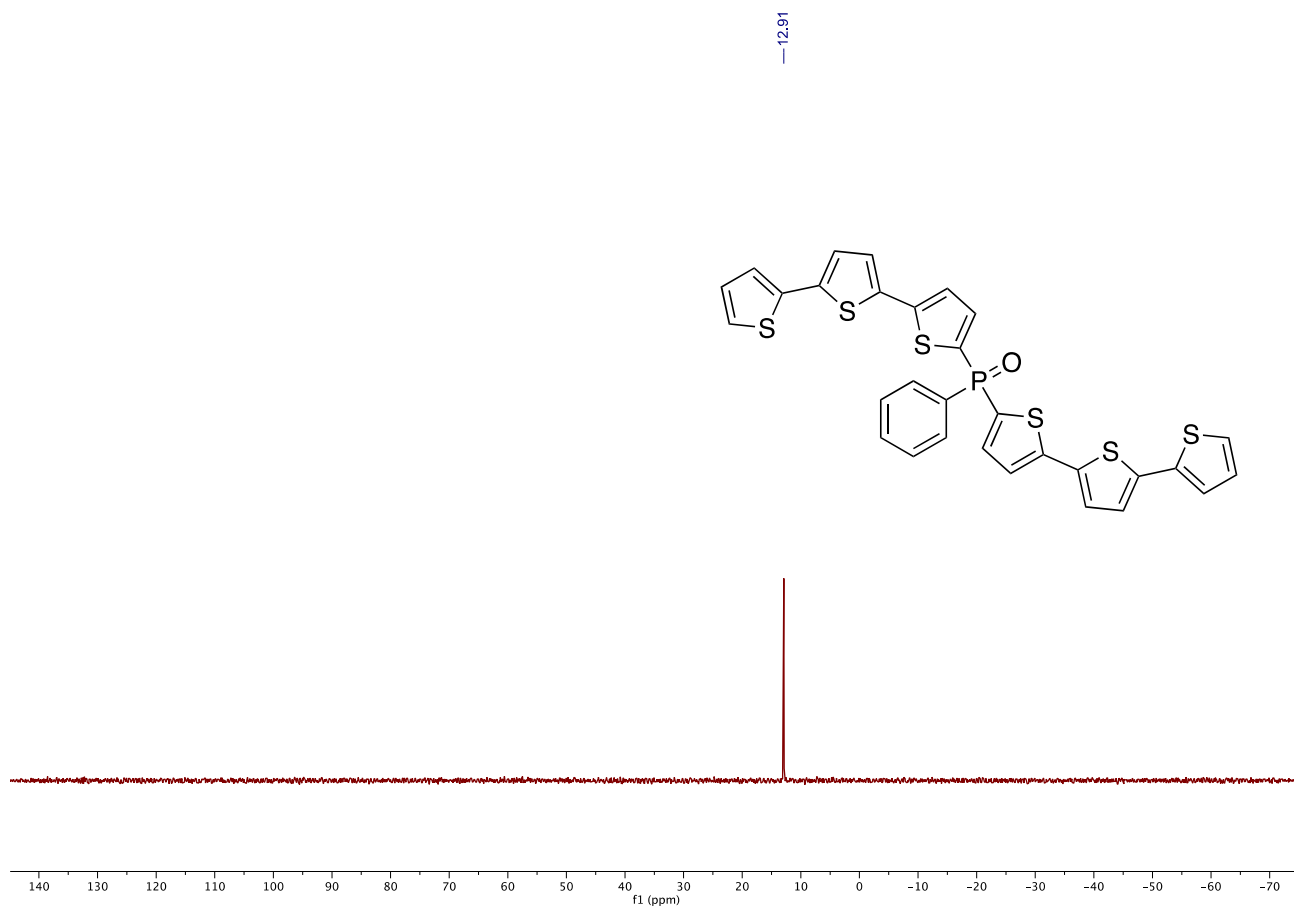
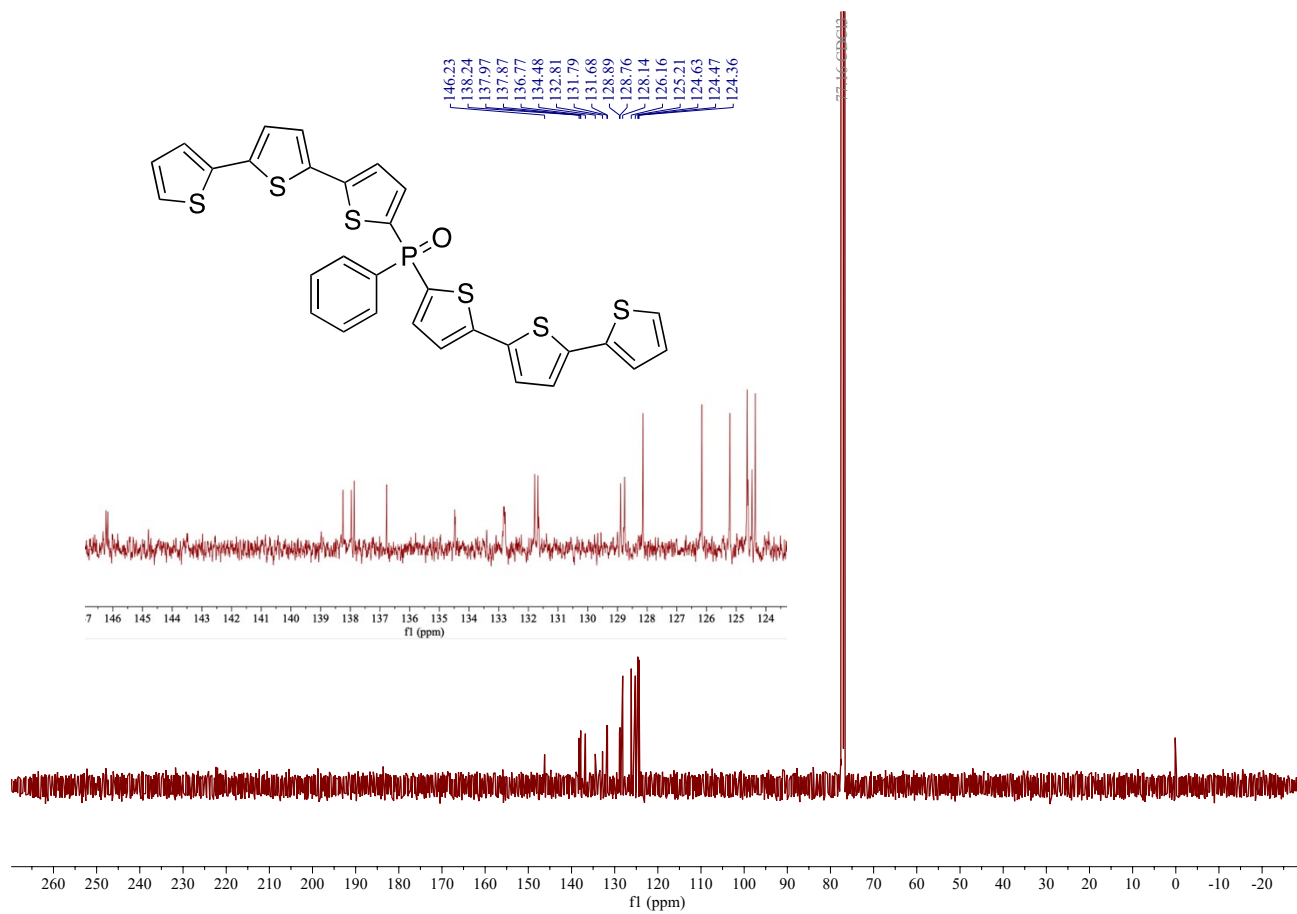
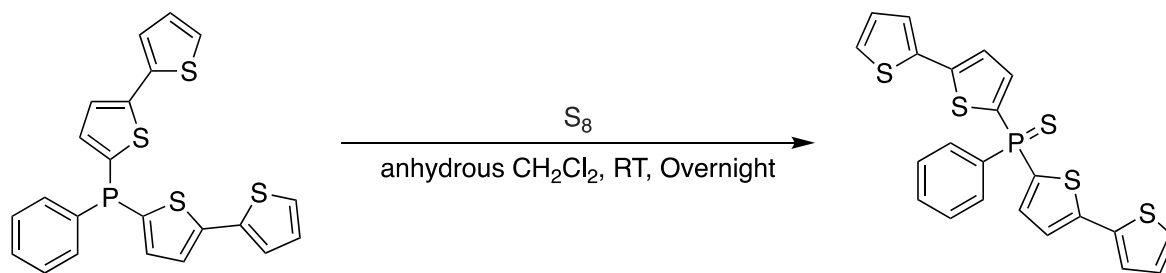


Figure S11. ³¹P {¹H} NMR (162 MHz, CDCl₃, 298K) of **T2**.





Scheme S5. Synthesis of **D3**.

Compound **D3**.

Under N_2 atmosphere, Compound **D1** (530 mg, 1.21 mmol) was dissolved in 15 ml anhydrous CH_2Cl_2 , and sublimed sulfur (194 mg, 6.04 mmol) was added. The solution was stirred for overnight at room temperature. After that, the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (CH_2Cl_2 /petroleum ether 1:1), Yield: 315 mg of green powder (55%) No melting point was observed due to the amorphous nature of **D3** ($T_g = 20.7\text{ }^\circ C$). 1H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.87 (m, 2H), 7.60 – 7.54 (m, 1H), 7.52 – 7.48 (m, 2H), 7.43 (dd, $J = 8.8, 3.7$ Hz, 2H), 7.29 (dd, $J = 5.1, 1.2$ Hz, 2H), 7.23 (dd, $J = 3.7, 1.2$ Hz, 2H), 7.20 (dd, $J = 3.8, 2.0$ Hz, 2H), 7.03 (dd, $J = 5.1, 3.6$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6 (d, $J = 6.1$ Hz), 137.6 (d, $J = 9.1$ Hz), 135.9 (d, 2.0 Hz), 133.9 (d, $J = 99.0$ Hz), 132.3 (d, $J = 4.0$ Hz), 131.5 (d, $J = 12.1$ Hz), 128.8 (d, $J = 13.1$ Hz), 128.2, 126.2, 125.4, 124.6 (d, $J = 7.1$) ppm. ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 23.1 ppm. HR LC-MS: Calcd: $[M+H]^+ = 470.9588$, found: $m/z = 470.9584$.

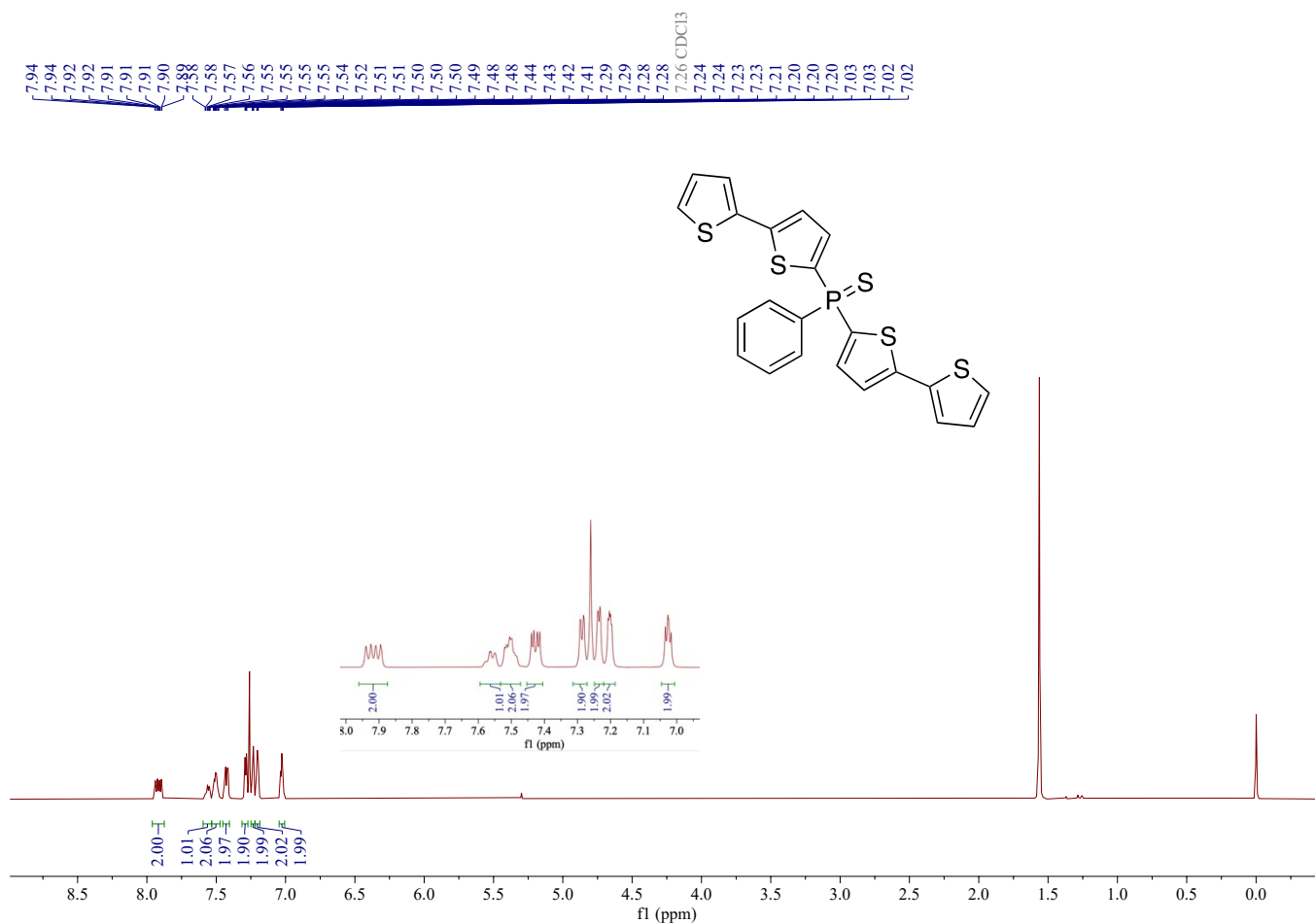


Figure S13. ¹H NMR (500 MHz, CDCl₃, 298K) of D3.

-23.08

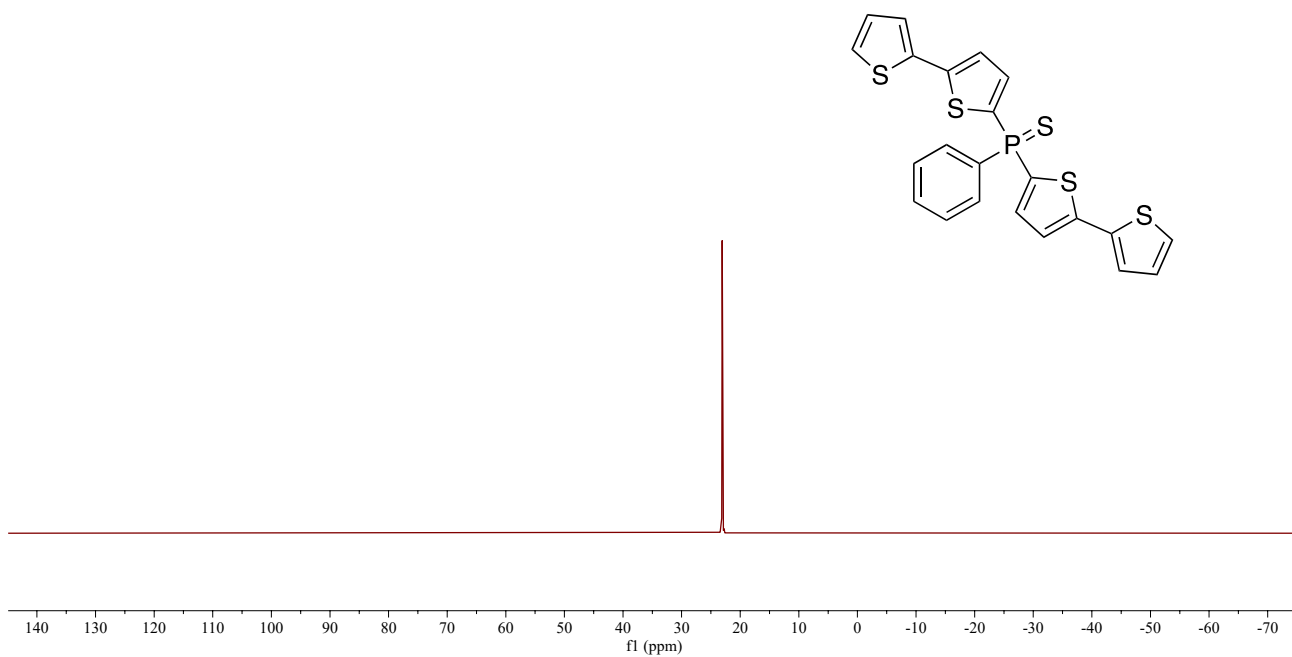


Figure S14. ³¹P {¹H} NMR (162 MHz, CDCl₃, 298K) of D3.

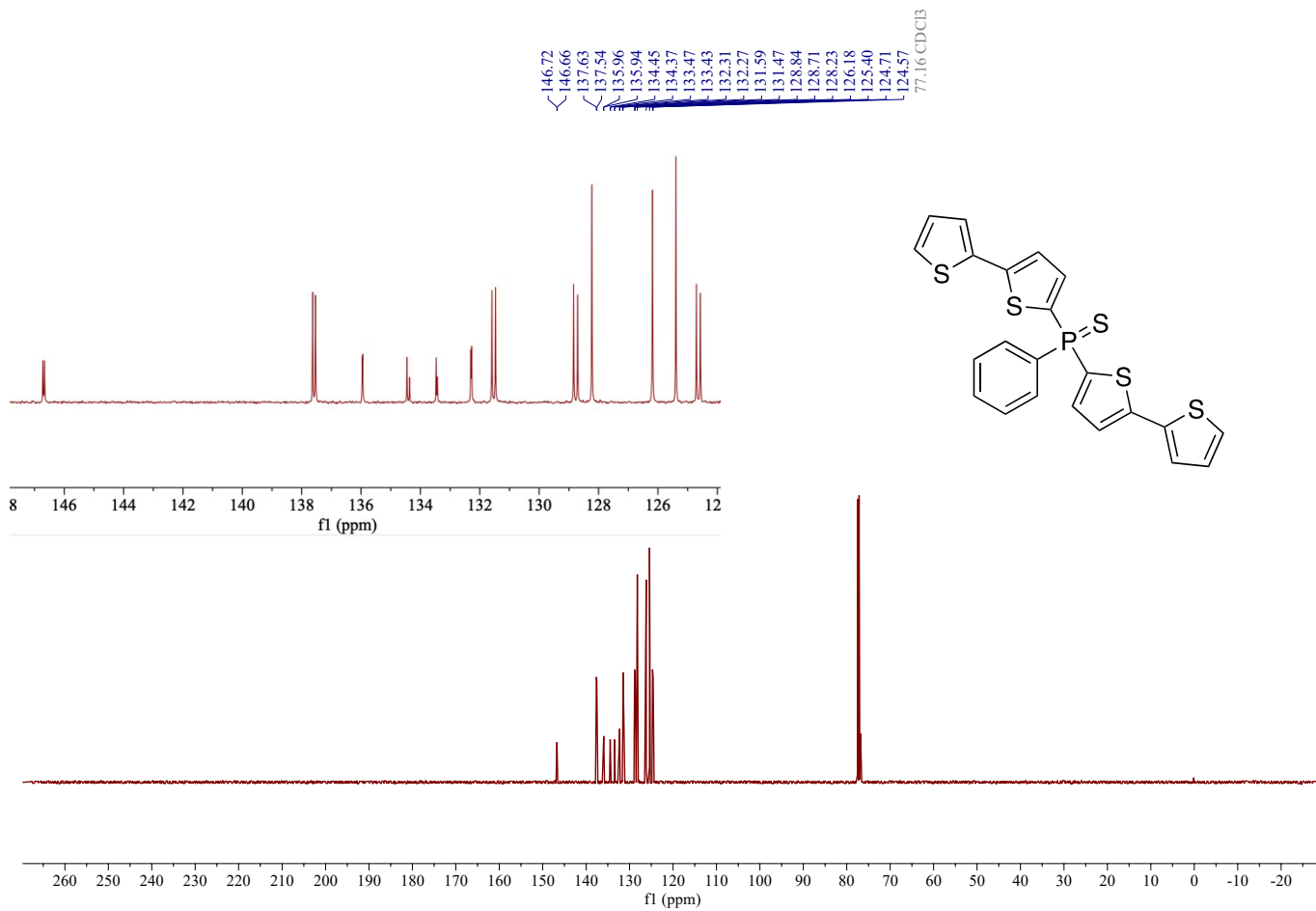
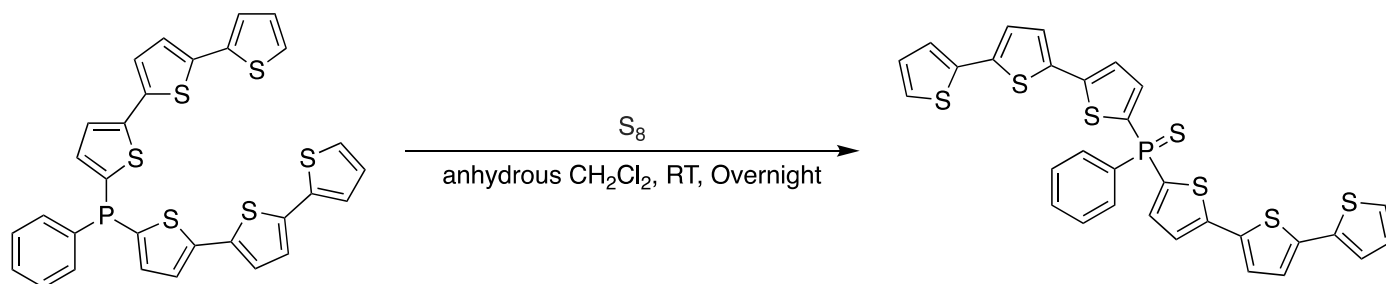


Figure S15. ¹³C NMR (101 MHz, CDCl₃, 298K) of **D3**.



Scheme S6. Synthesis of **T3**.

Compound **T3**.

Under N_2 atmosphere, Compound **T1** (285 mg, 0.473 mmol) was dissolved in 15 ml anhydrous CH_2Cl_2 , and sublimed sulfur (76 mg, 2.365 mmol) was added. The solution was stirred for overnight at room temperature. After that, the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (CH_2Cl_2 /petroleum ether 1:1), Yield: 144 mg of green powder (48%). No melting point was observed due to the amorphous nature of **D1** ($T_g = 47.6\text{ }^\circ\text{C}$). ^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.90 (m, 2H), 7.60 – 7.55 (m, 1H), 7.54 – 7.47 (m, 2H), 7.43 (dd, $J = 8.8, 3.8$ Hz, 2H), 7.24 (dd, $J = 5.1, 1.2$ Hz, 2H), 7.18 (dt, $J = 4.0, 1.8$ Hz, 4H), 7.14 (d, $J = 3.9$ Hz, 2H), 7.08 (d, $J = 3.9$ Hz, 2H), 7.02 (dd, $J = 5.1, 3.6$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 146.4 (d, $J = 5.0$ Hz), 138.1, 137.7 (d, $J = 9.1$ Hz), 136.7, 134.5 (d, $J = 1.0$ Hz), 133.9 (d, $J = 99.0$ Hz), 133.8 (d, $J = 93.9$ Hz), 132.3 (d, $J = 3.0$ Hz), 131.6 (d, $J = 12.1$ Hz), 128.8 (d, $J = 13.1$ Hz), 128.1, 120.0, 125.2, 124.6, 124.5 (d, $J = 14.1$ Hz), 124.3 ppm. ^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ 23.0 ppm. HR LC-MS: Calcd: $[\text{M}+\text{H}]^+ = 634.9343$, found: $m/z = 634.9344$.

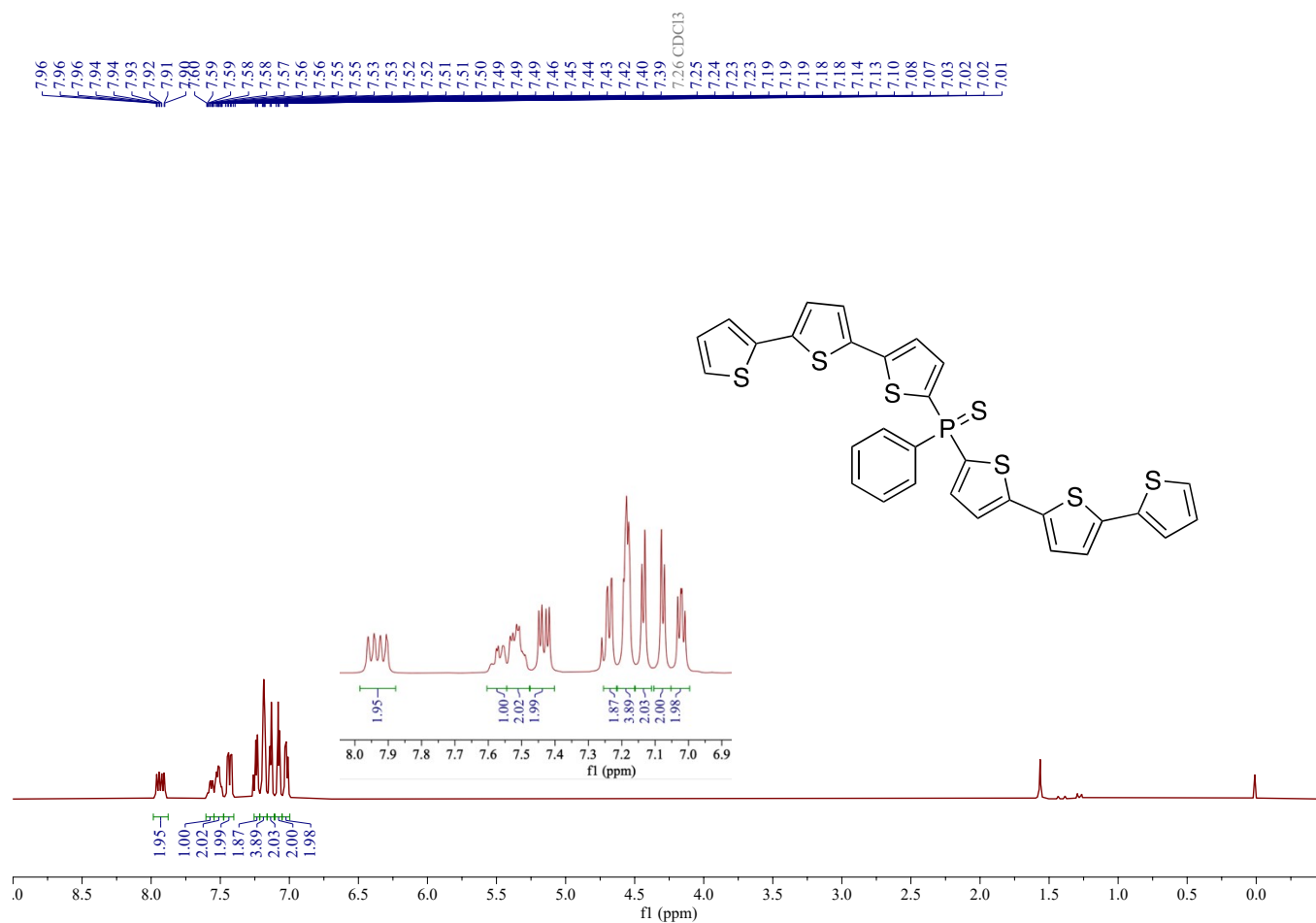


Figure S16. ^1H NMR (400 MHz, CDCl_3 , 298K) of T3.

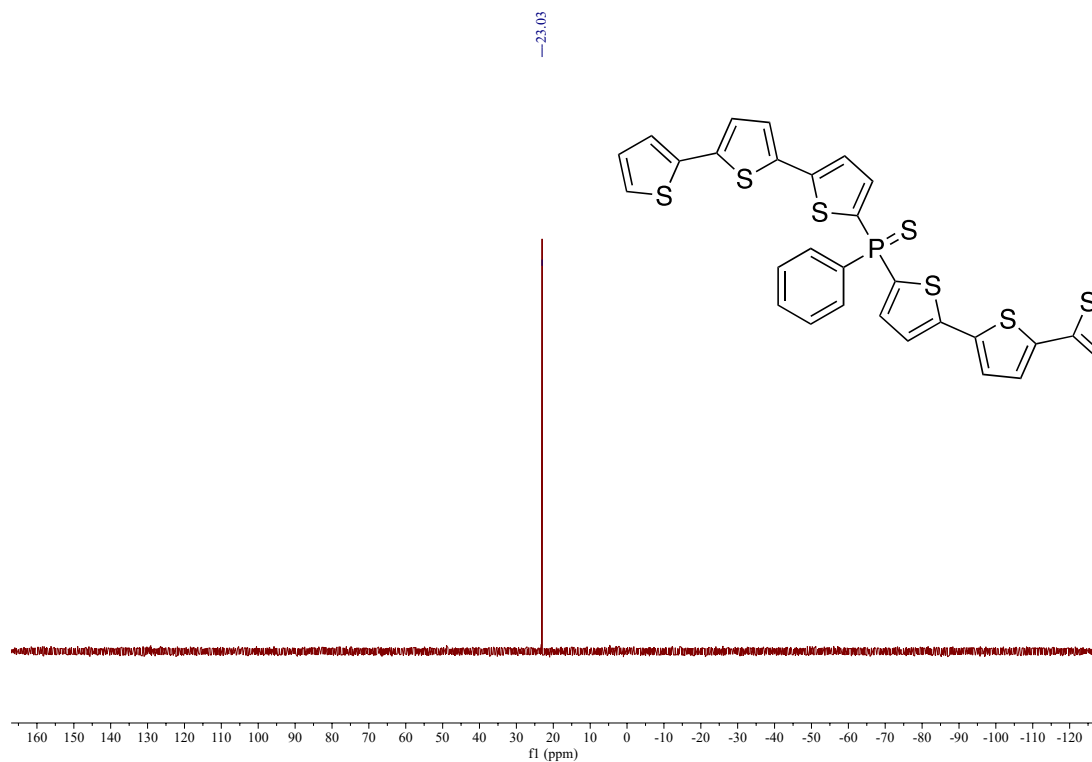


Figure S17. ^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298K) of T3.

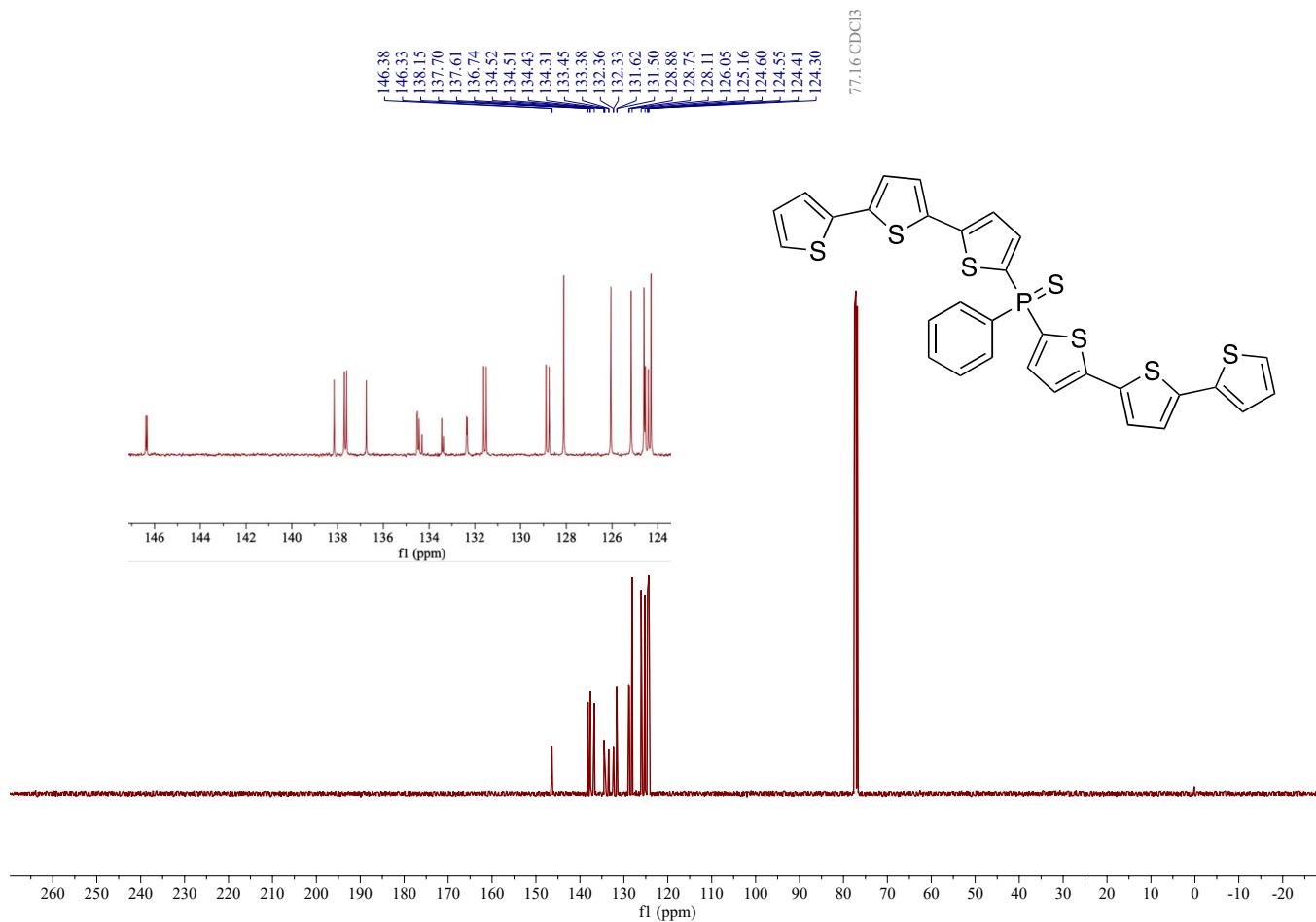
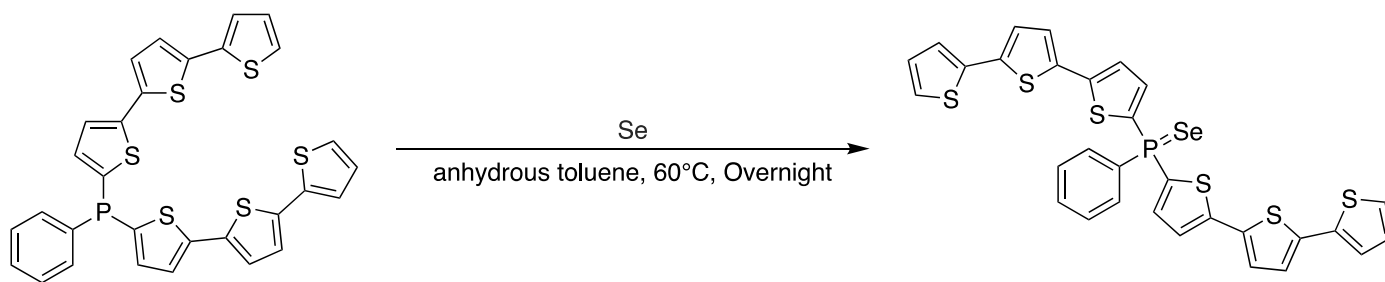


Figure S18. ^{13}C NMR (101 MHz, CDCl_3 , 298K) of T3.



Scheme S7. Synthesis of **T4**.

Compound **T4**.

Under N_2 atmosphere, Compound **T1** (280 mg, 0.465 mmol) was dissolved in 20 ml anhydrous toluene, and selenium powder (75 mg, 0.950 mmol) was added. The solution was stirred for overnight at 60°C . After cooling to room temperature, the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (CH_2Cl_2 /petroleum ether 3:7), Yield: 294.7 mg of yellow powder (93 %). No melting point was observed due to the amorphous nature of **T4** ($T_g = 48.2^\circ\text{C}$). ^1H NMR (500 MHz, CDCl_3) δ 7.96 – 7.88 (m, 2H), 7.57 – 7.54 (m, 1H), 7.52 – 7.49 (m, 2H), 7.44 (dd, $J = 9.0, 3.8$ Hz, 2H), 7.24 (d, $J = 1.1$ Hz, 2H), 7.21 (dd, $J = 3.8, 1.8$ Hz, 2H), 7.20 – 7.17 (m, 2H), 7.15 (d, $J = 3.8$ Hz, 2H), 7.09 (d, $J = 3.8$ Hz, 2H), 7.03 (dd, $J = 5.1, 3.6$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 146.5 (d, $J = 5.0$ Hz), 138.2 (d, $J = 3.0$ Hz), 128.1, 136.8, 134.5 (d, $J = 1.0$ Hz), 133.0 (d, $J = 84.8$ Hz), 132.7 (d, $J = 89.9$ Hz), 132.4 (d, $J = 3.0$ Hz), 131.9 (d, $J = 12.1$ Hz), 128.8 (d, $J = 14.1$ Hz), 128.1, 126.1, 125.2, 124.6, 124.5 (d, $J = 14.1$ Hz), 124.3 ppm. ^{31}P { ^1H } NMR (202 MHz, CDCl_3) δ 8.4 ppm. HR LC-MS: Calcd: $[\text{M}+\text{H}]^+ = 682.8787$, found: $m/z = 682.8772$.

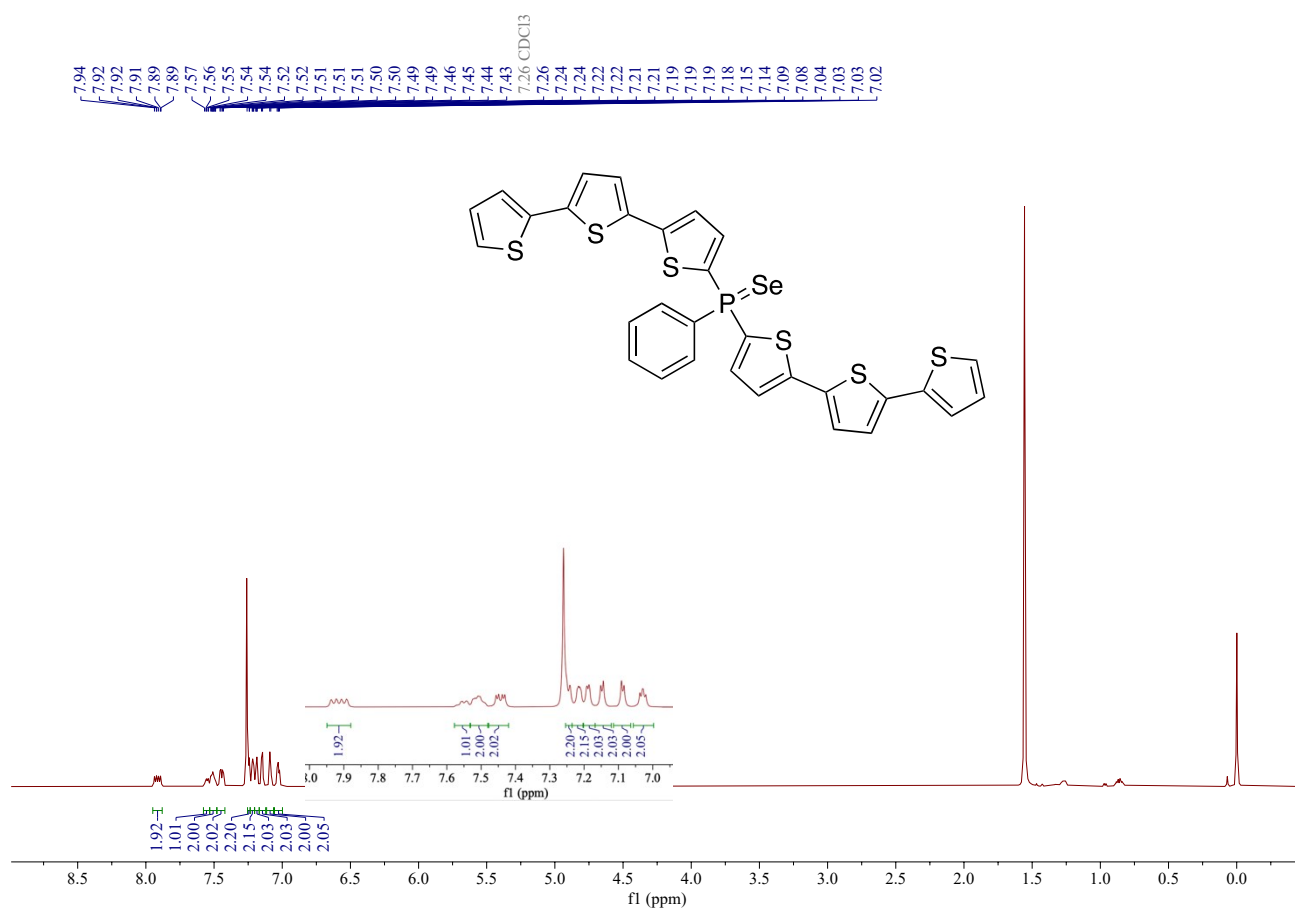


Figure S19. ^1H NMR (500 MHz, CDCl_3 , 298K) of T4.

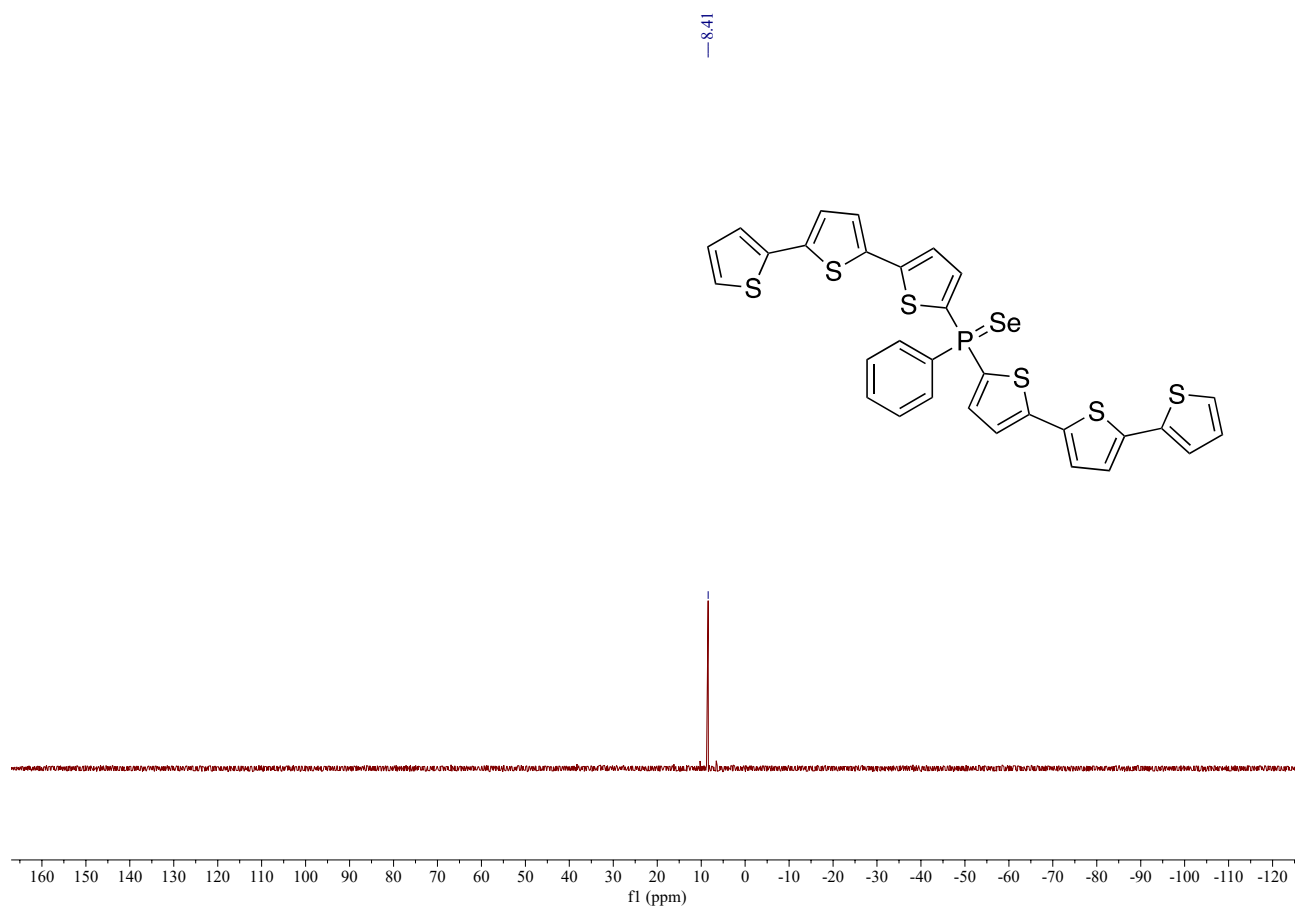


Figure S20. ^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298K) of T4.

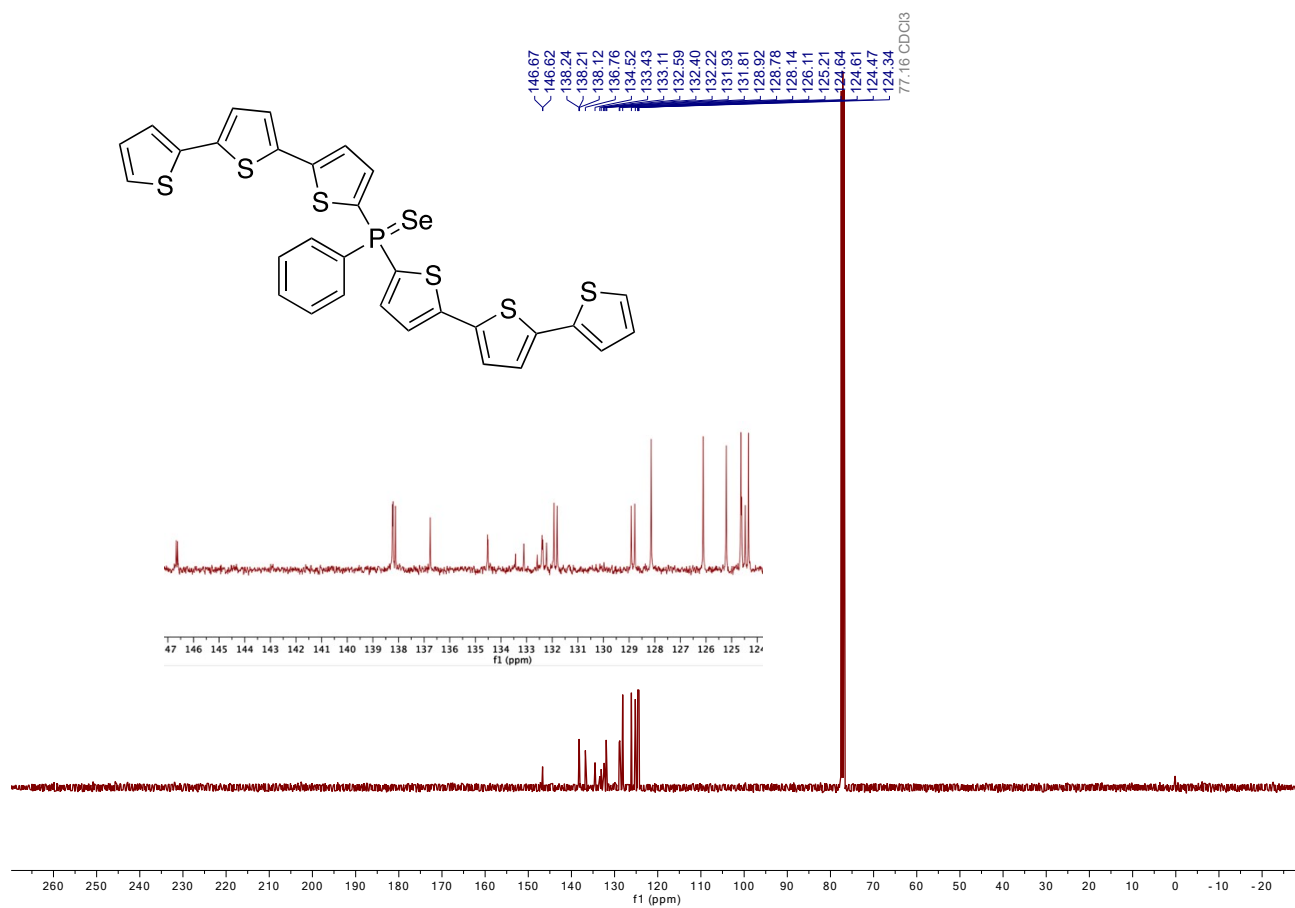
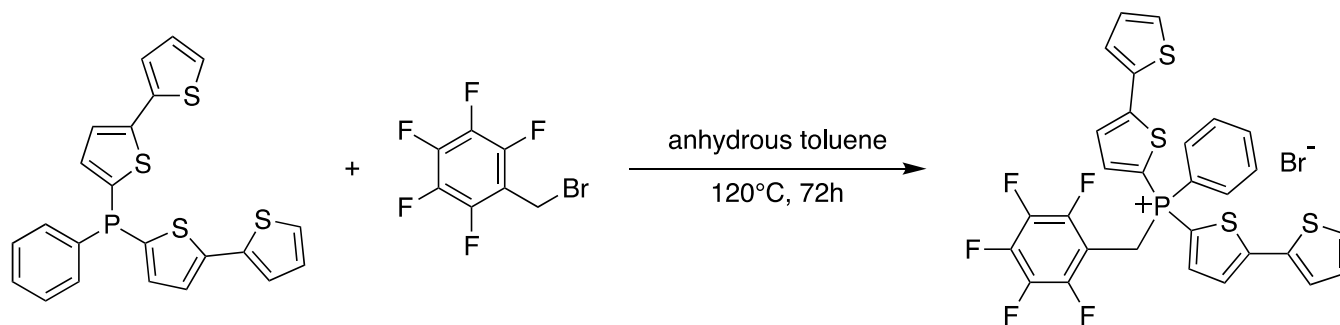


Figure S21. ^{13}C NMR (101 MHz, CDCl_3 , 298K) of T4.



Scheme S8. Synthesis of **D5-Br**.

Compound **D5-Br**.

Under N₂ atmosphere, Compound **D1** (511.6 mg, 1.17 mmol) was dissolved in 20 ml anhydrous toluene, and 1-(Bromomethyl)-2,3,4,5,6-pentafluorobenzene (2.33 g, 8.93 mmol) was added. The solution was stirred for 72h at 120°C. After cooling to room temperature, the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (MeOH/CH₂Cl₂ 3:97). Yield: 323 mg of pale-yellow powder (40 %). No melting point was observed due to the amorphous nature of **D1** ($T_g = 97.7$ °C). ¹H NMR (400 MHz, CDCl₃) δ 8.42 – 8.33 (m, 2H), 8.02 (dd, $J = 14.1, 7.7$ Hz, 2H), 7.86 (t, $J = 7.3$ Hz, 1H), 7.75 – 7.69 (m, 2H), 7.49 (t, $J = 3.2$ Hz, 2H), 7.43 (d, $J = 5.0$ Hz, 2H), 7.33 (d, $J = 3.7$ Hz, 2H), 7.09 (dd, $J = 5.1, 3.6$ Hz, 2H), 5.78 (d, $J = 14.1$ Hz, 2H) ppm. ³¹P {¹H} NMR (162 MHz, CDCl₃) δ 9.4 ppm. ¹⁹F {¹H} NMR (376 MHz, CDCl₃) δ -135.8 (db, $J = 21.0$ Hz), -150.0 – -151.0 (m), -159.5 (d, $J = 19.7$ Hz) ppm. HR LC-MS: Calcd: [M-Br]⁺ = 618.9866, found: $m/z = 618.9865$.

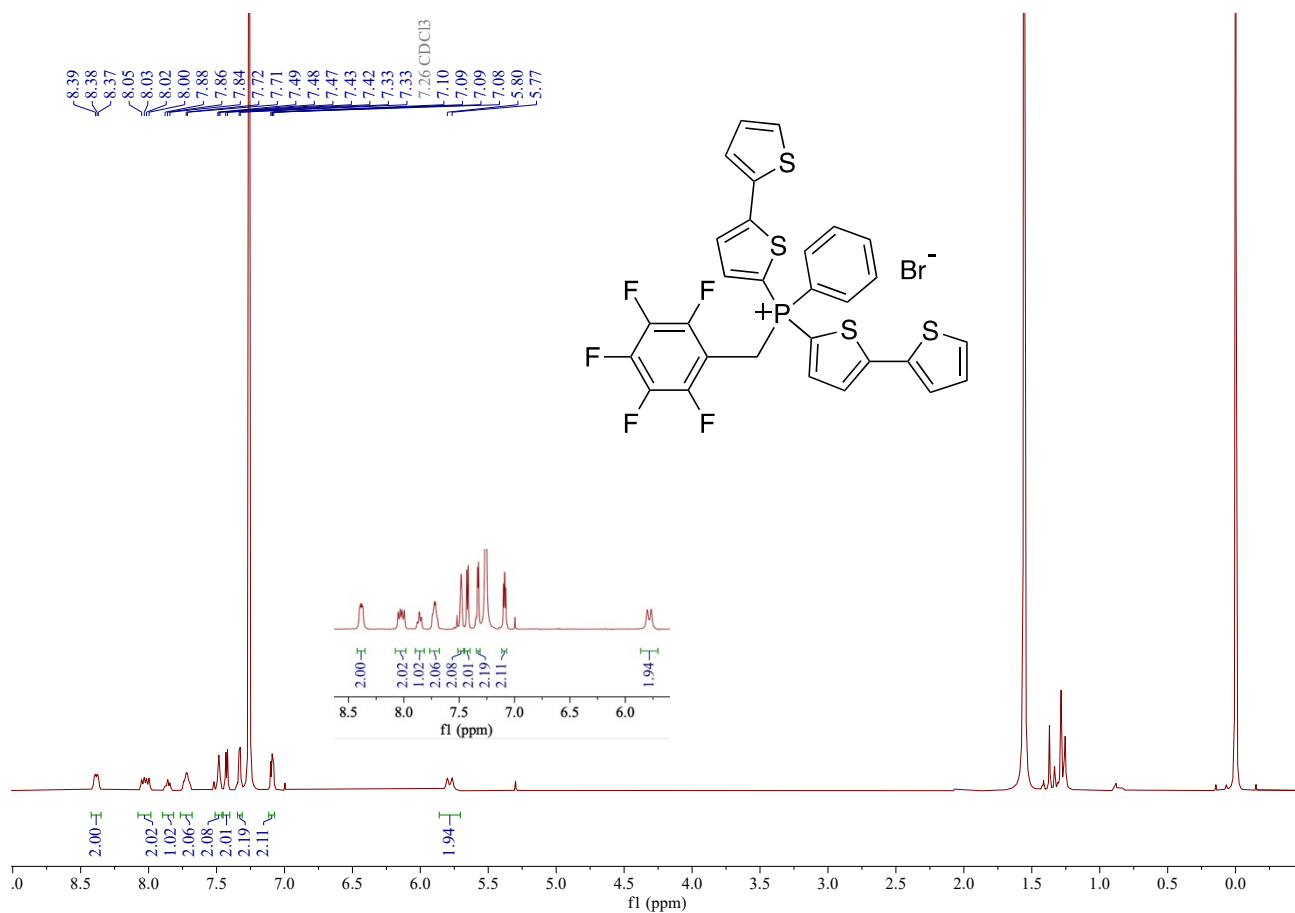


Figure S22. ^1H NMR (400 MHz, CDCl_3 , 298K) of D5-Br.

9.44

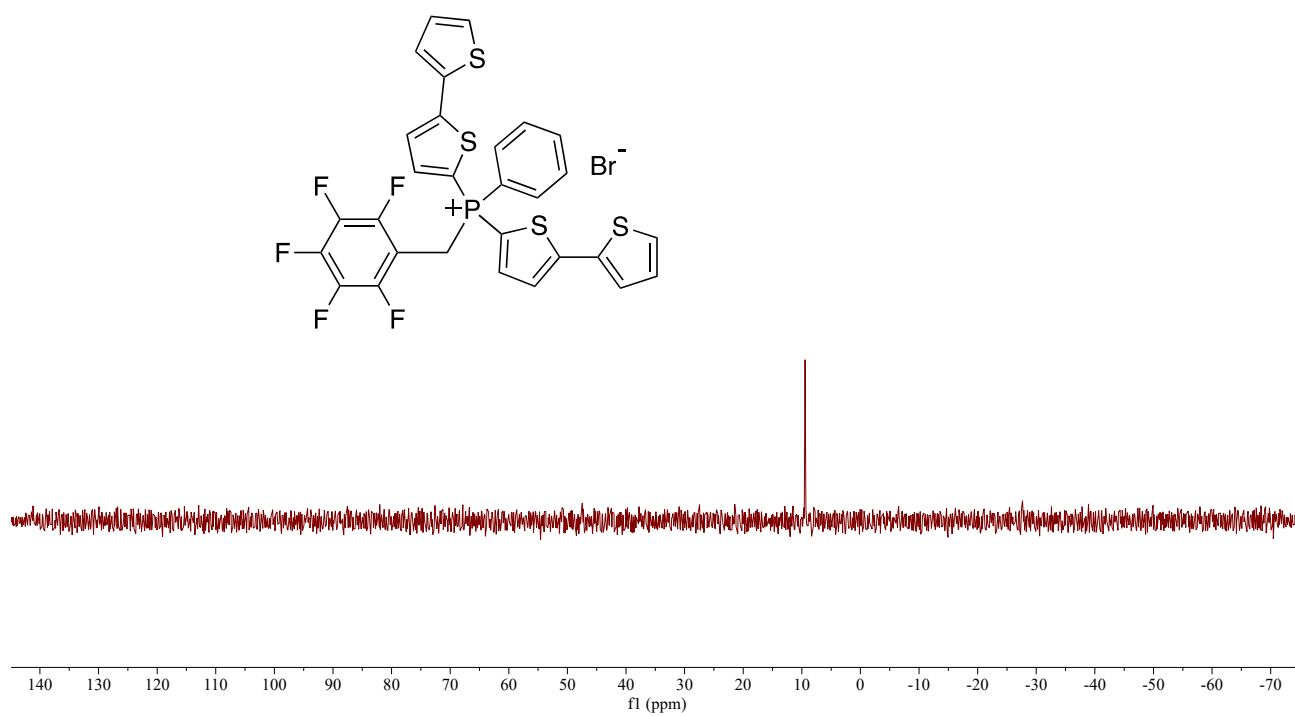


Figure S23. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298K) of D5-Br.

135.73
135.78
150.46
150.49
150.51
150.57
159.49
159.53
159.54
159.59

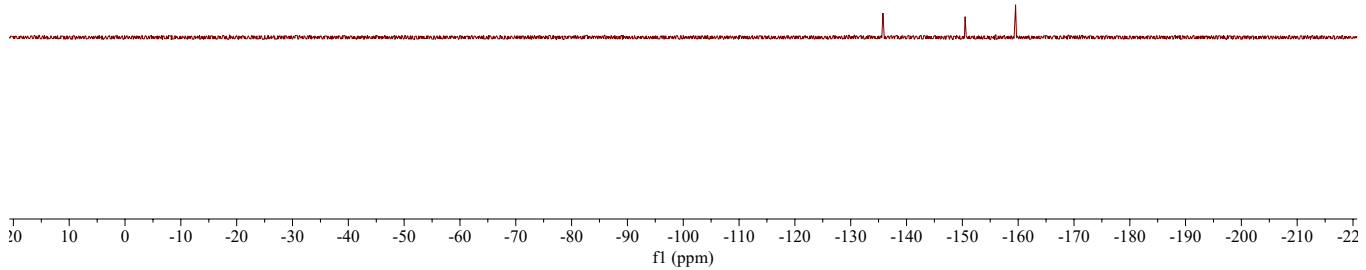
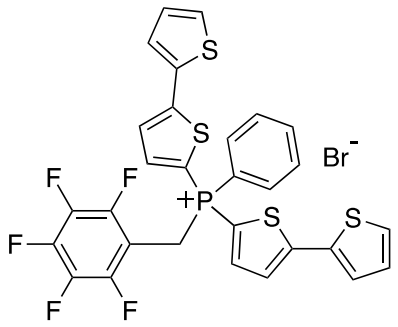
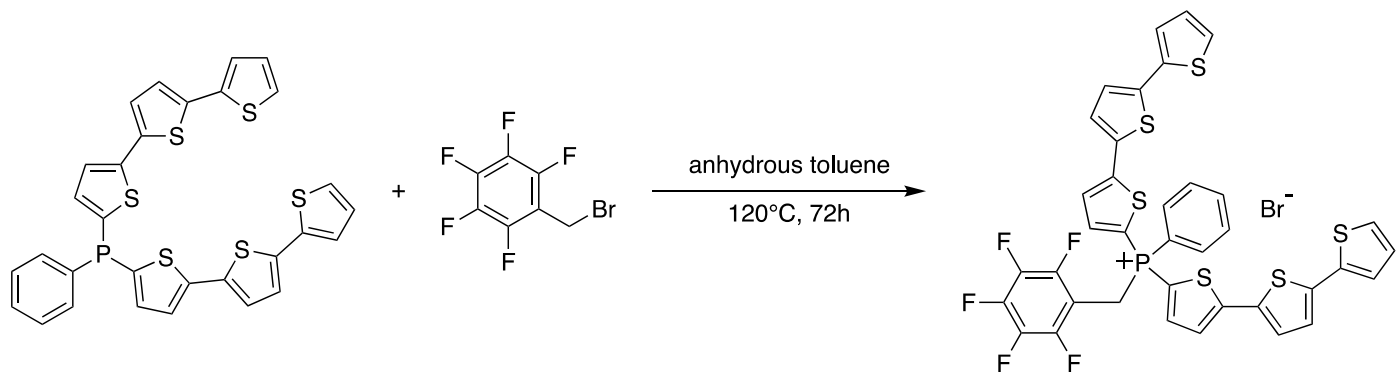


Figure S24. ¹⁹F {¹H} NMR (376 MHz, CDCl₃, 298K) of **D5-Br**.



Scheme S9. Synthesis of **T6-Br**.

Compound T6-Br.

Under N₂ atmosphere, Compound **T1** (475 mg, 0.788 mmol) was dissolved in 20 ml anhydrous toluene, and 1-(Bromomethyl)-2,3,4,5,6-pentafluorobenzene (1.03 g, 3.94 mmol) was added. The solution was stirred for 72h at 120°C. After cooling to room temperature, the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (MeOH/CH₂Cl₂ 3:97). Yield: 320.4 mg of yellow powder (47 %). No melting point was observed due to the amorphous nature of **T6-Br** ($T_g = 108.5$ °C). ¹H NMR (500 MHz, CDCl₃) δ 8.39 (dd, $J = 8.2, 4.1$ Hz, 2H), 8.02 (dd, $J = 14.2, 7.8$ Hz, 2H), 7.90 – 7.83 (m, 1H), 7.73 (dt, $J = 11.4, 5.7$ Hz, 2H), 7.46 (dd, $J = 4.1, 2.5$ Hz, 2H), 7.30 (dd, $J = 5.1, 1.2$ Hz, 2H), 7.25 – 7.23 (m, 4H), 7.13 (d, $J = 3.8$ Hz, 2H), 7.05 (dd, $J = 5.1, 3.6$ Hz, 2H), 5.79 (d, $J = 14.1$ Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃) δ 152.2 (d, $J = 6.1$ Hz), 145.2 (d, $J = 10.1$ Hz), 140.6, 136.2 (d, $J = 3.0$ Hz), 136.0, 133.5 (d, $J = 12.1$ Hz), 132.2 (d, $J = 1.0$ Hz), 130.5 (d, $J = 14.1$ Hz), 128.3, 128.1, 126.4 (d, $J = 15.1$ Hz), 126.0, 125.1, 124.9, 119.9 (d, $J = 92.9$ Hz), 111.7 (d, $J = 107.1$ Hz), 25.0 (d, $J = 55.5$ Hz) ppm. ³¹P {¹H} NMR (162 MHz, CDCl₃) δ 9.3 ppm. ¹⁹F {¹H} NMR (471 MHz, CDCl₃) δ -135.9 (db, $J = 18.6$ Hz), -150.4 (td, $J = 20.9, J = 6.8$ Hz), -159.5 (t, $J = 20.4$ Hz) ppm. HR LC-MS: Calcd: [M-Br]⁺ = 782.9620, found: m/z = 782.9609.

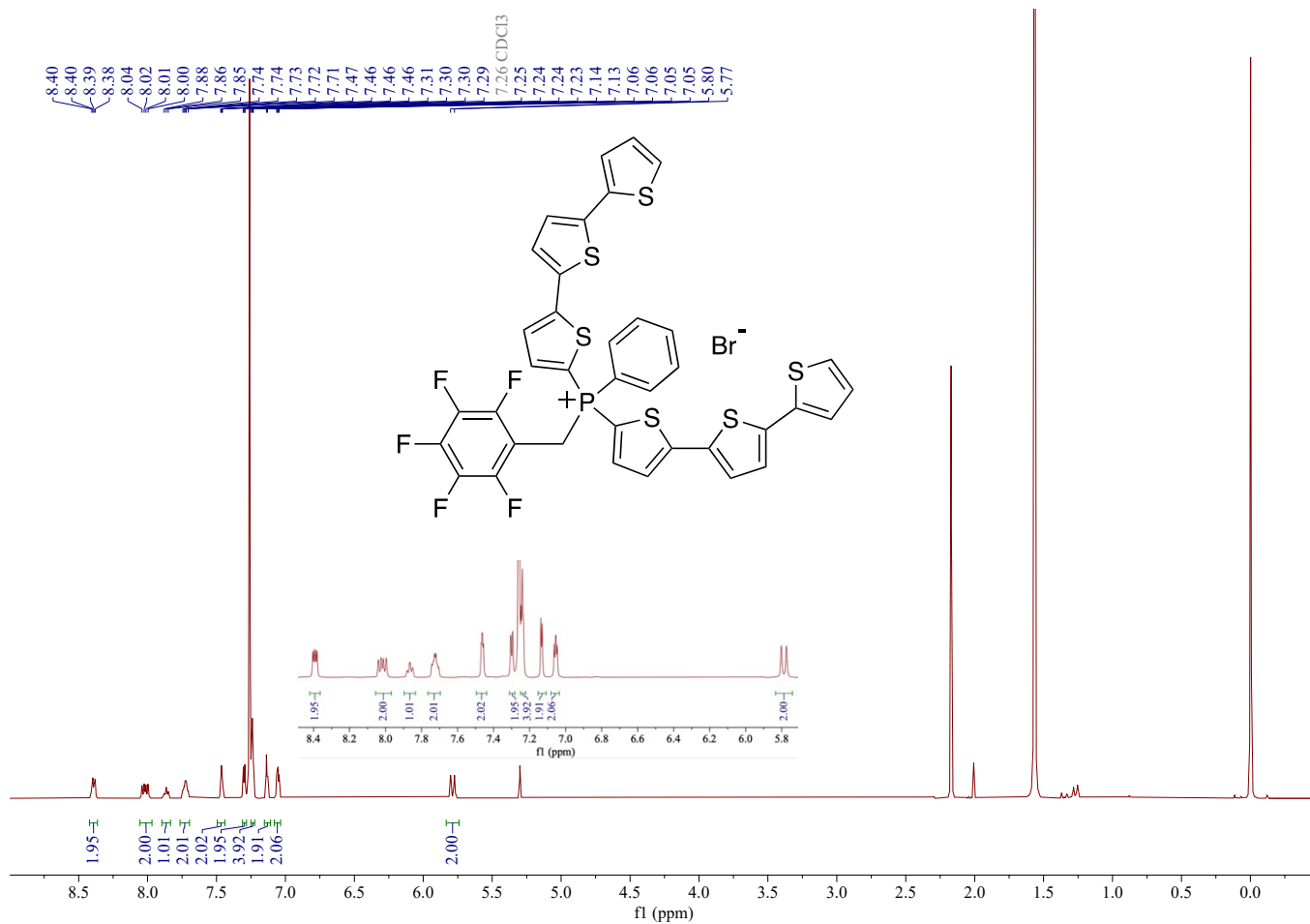


Figure S25. ¹H NMR (500 MHz, CDCl₃, 298K) of T6-Br.

—9.26

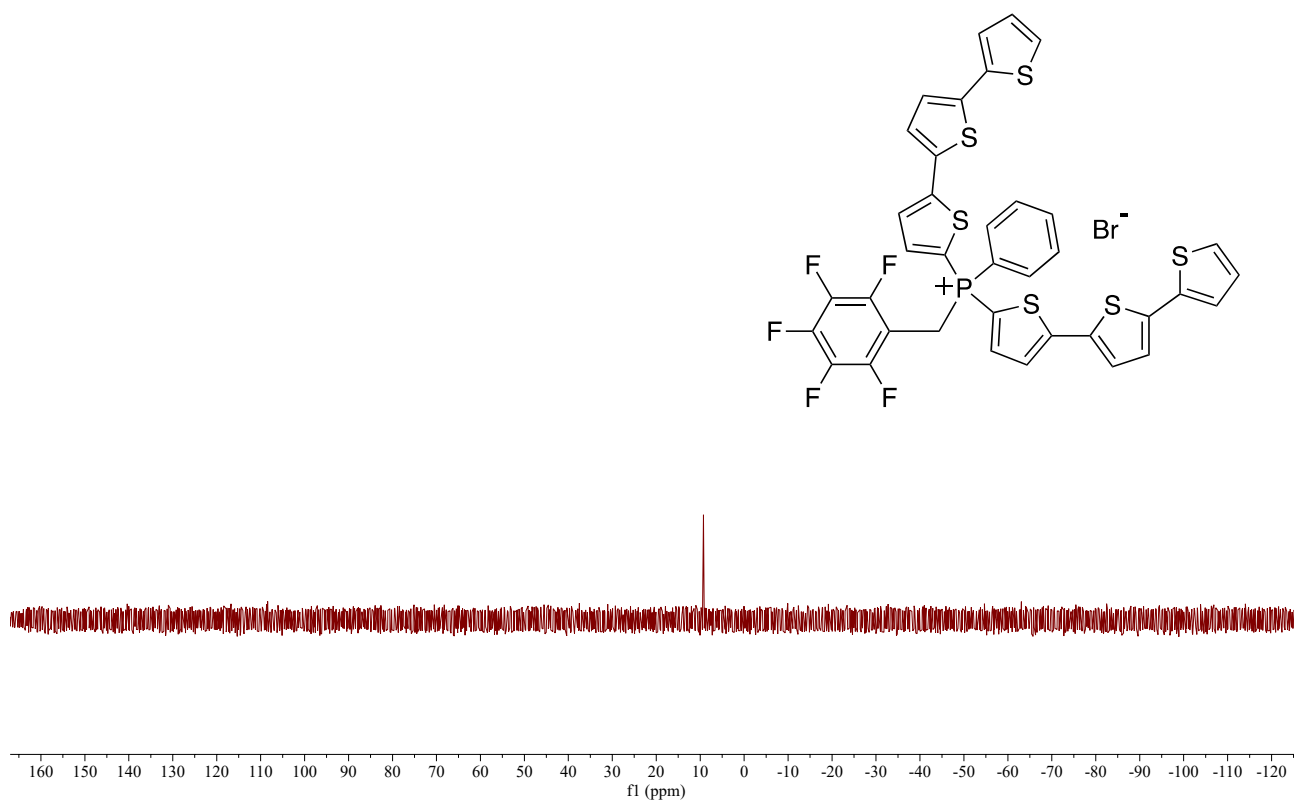


Figure S26. ³¹P {¹H} NMR (162 MHz, CDCl₃, 298K) of T6-Br.

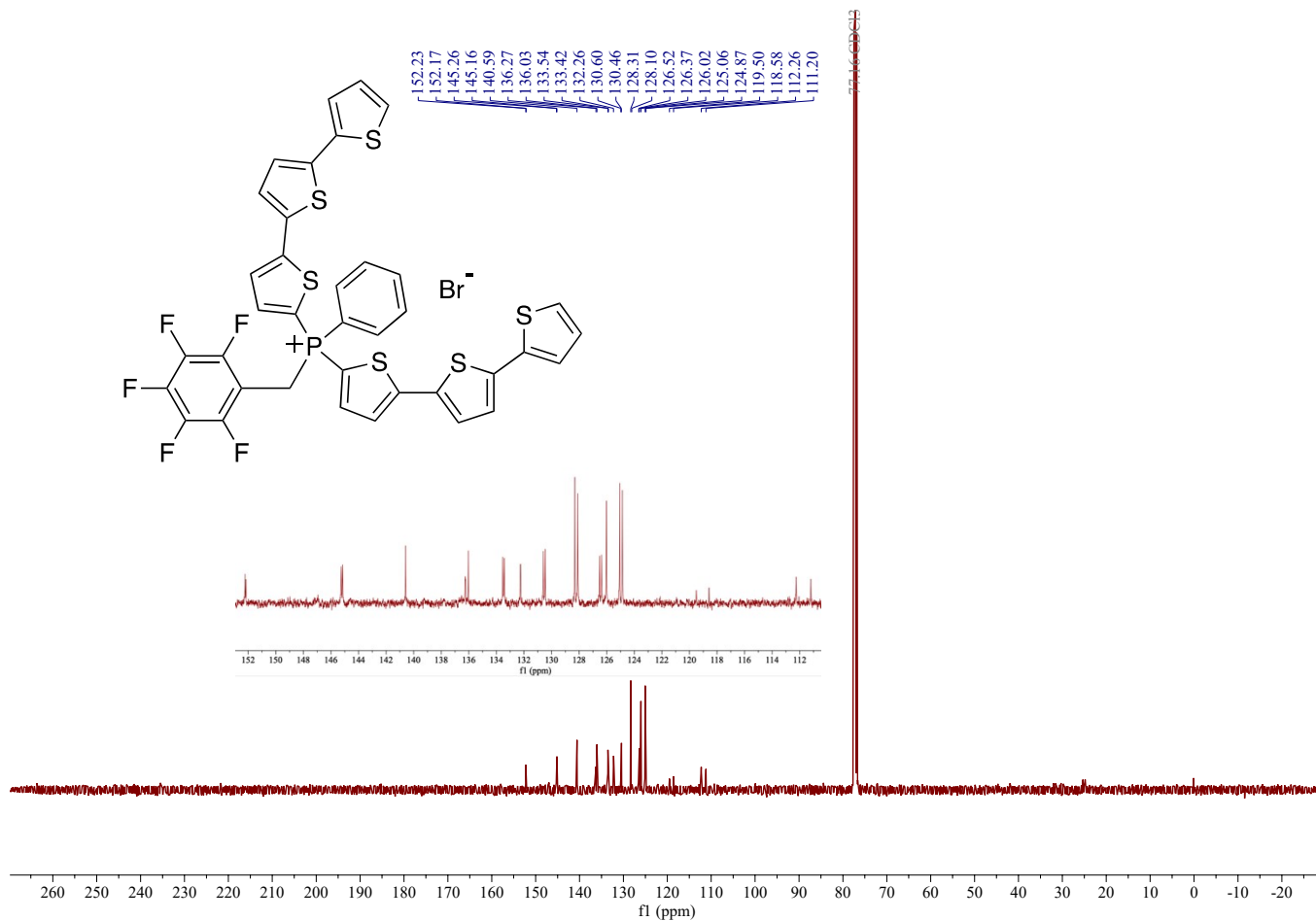


Figure S27. ¹³C NMR (101 MHz, CDCl₃, 298K) of T6-Br.

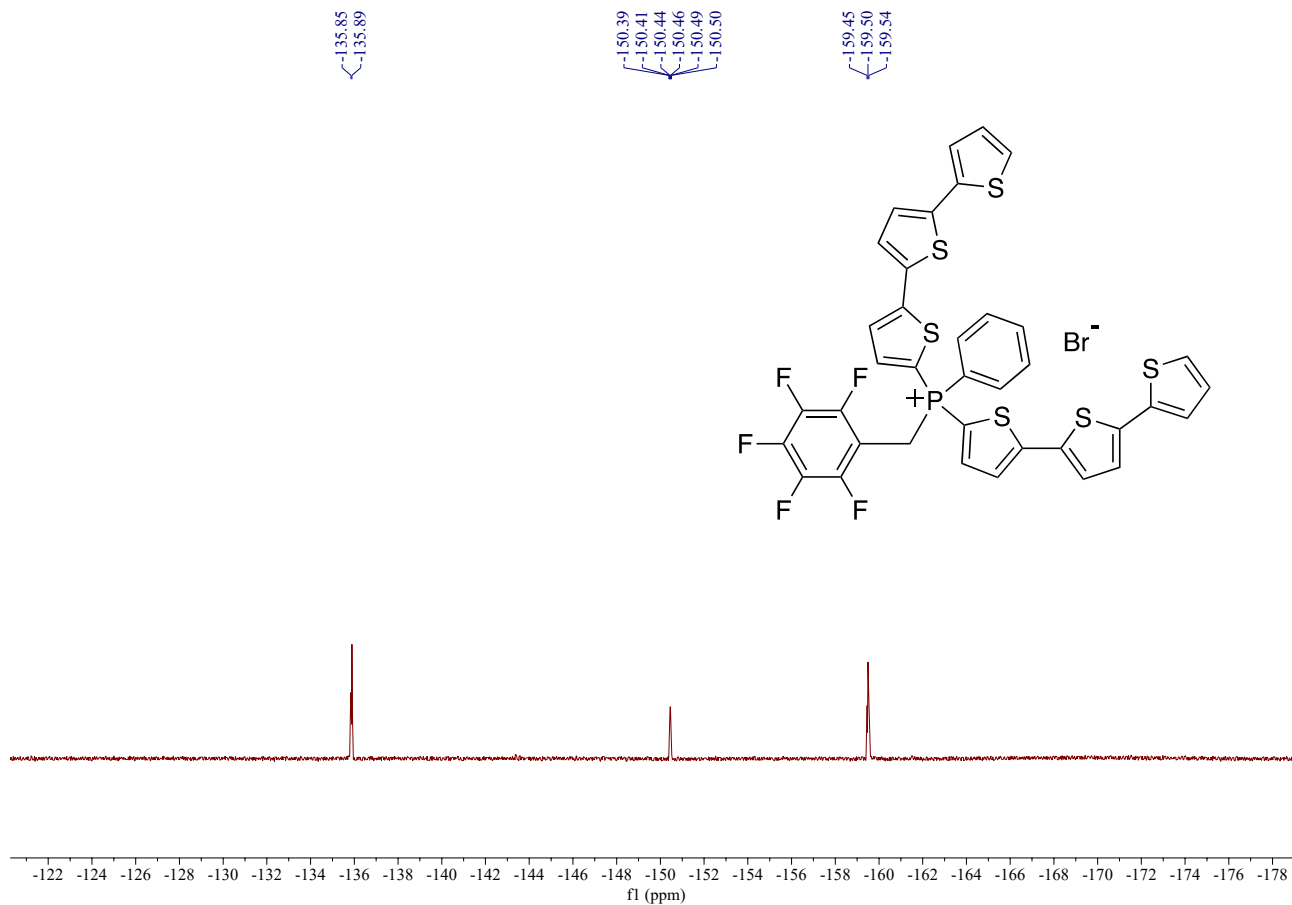
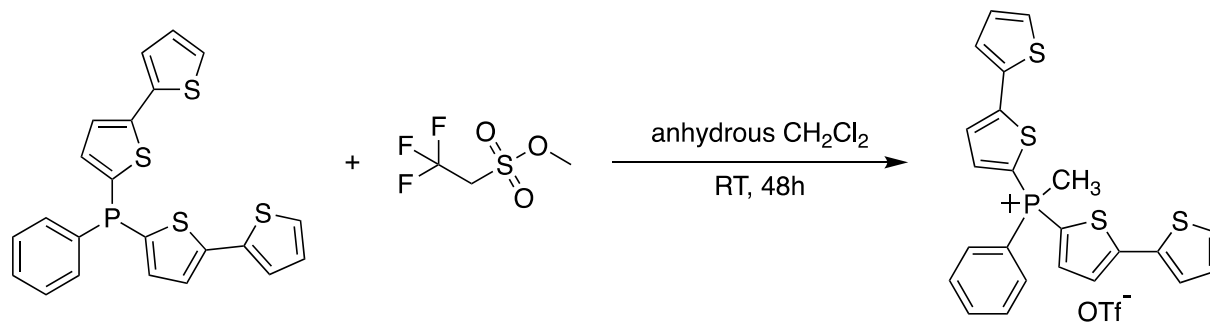


Figure S28. ¹⁹F {¹H} NMR (471 MHz, CDCl₃, 298K) of T6-Br.



Scheme S10. Synthesis of **D4**.

Compound **D4**.

Under N_2 atmosphere, Compound **D1** (442 mg, 1.01 mmol) was dissolved in 50 ml anhydrous CH_2Cl_2 , and Methyl trifluoromethanesulfate (182 mg, 1.11 mmol) was added. The solution was stirred for 48h at room temperature. Then the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (MeOH/ CH_2Cl_2 2:98). Yield: 443.4 mg of white powder (73 %). No melting point was observed due to the amorphous nature of **D4** ($T_g = 31.6$ °C). 1H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.80 (m, 5H), 7.72 (td, $J = 7.8, 3.8$ Hz, 2H), 7.46 – 7.42 (m, 2H), 7.42 – 7.39 (m, 2H), 7.37 – 7.32 (m, 2H), 7.08 (dd, $J = 5.1, 3.6$ Hz, 2H), 3.06 (d, $J = 13.7$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.6 (d, $J = 6.1$ Hz), 143.0 (d, $J = 10.1$ Hz), 135.8 (d, $J = 3.0$ Hz), 134.1, 132.4 (d, $J = 12.1$ Hz), 130.5 (d, $J = 14.1$ Hz), 128.7, 128.1, 127.1, 126.4 (d, $J = 15.1$ Hz), 120.9 (d, $J = 322.2$ Hz), 120.7 (d, $J = 96.0$ Hz), 12.6 (d, $J = 61.6$ Hz) ppm. ^{31}P { 1H } NMR (202 MHz, $CDCl_3$) δ 8.6 ppm. ^{19}F { 1H } NMR (471 MHz, $CDCl_3$) δ -78.2 ppm. HR LC-MS: Calcd: $[M-OTf]^+ = 453.0024$, found: $m/z = 453.0021$.

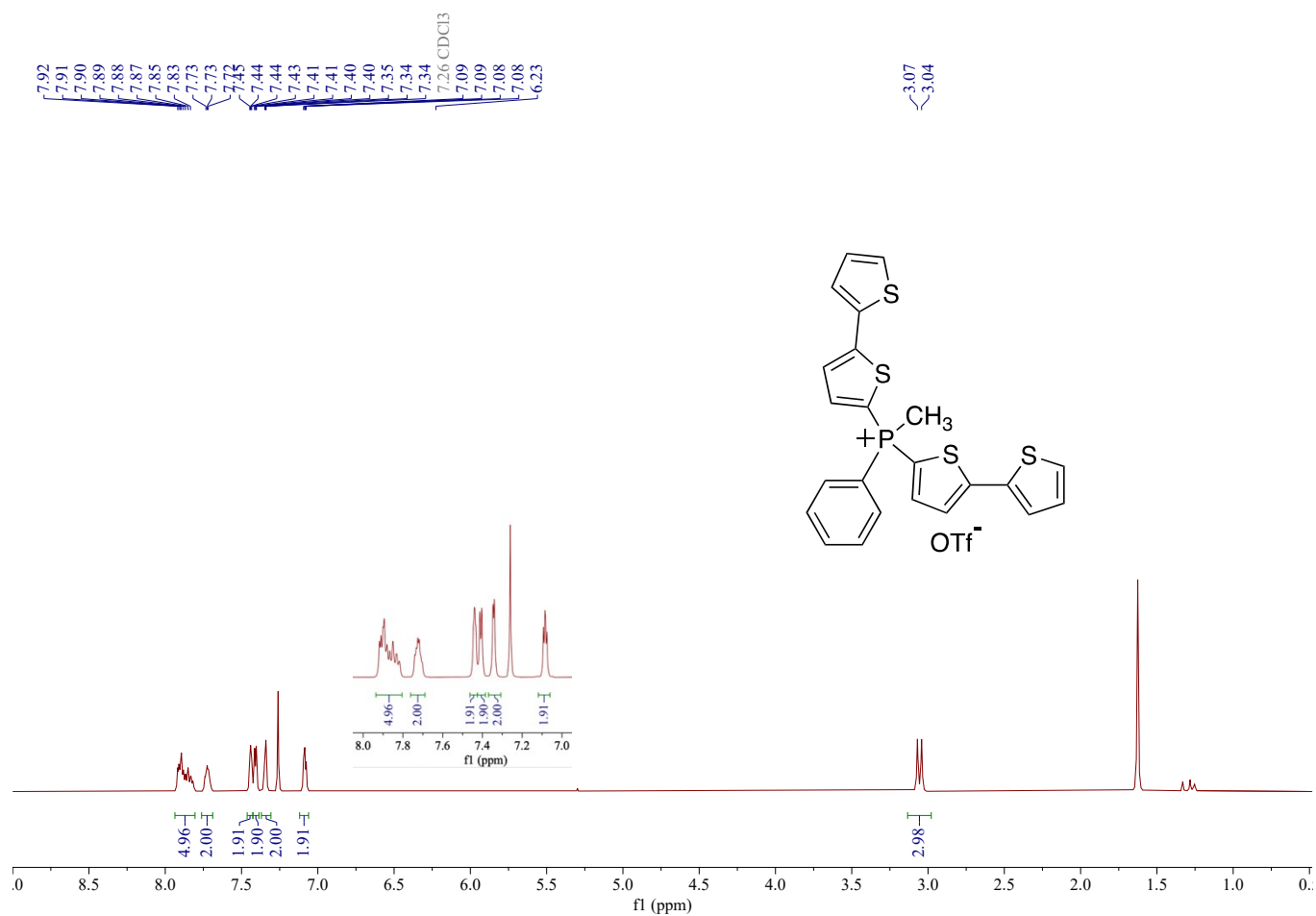


Figure S29. ¹H NMR (500 MHz, CDCl₃, 298K) of D4.

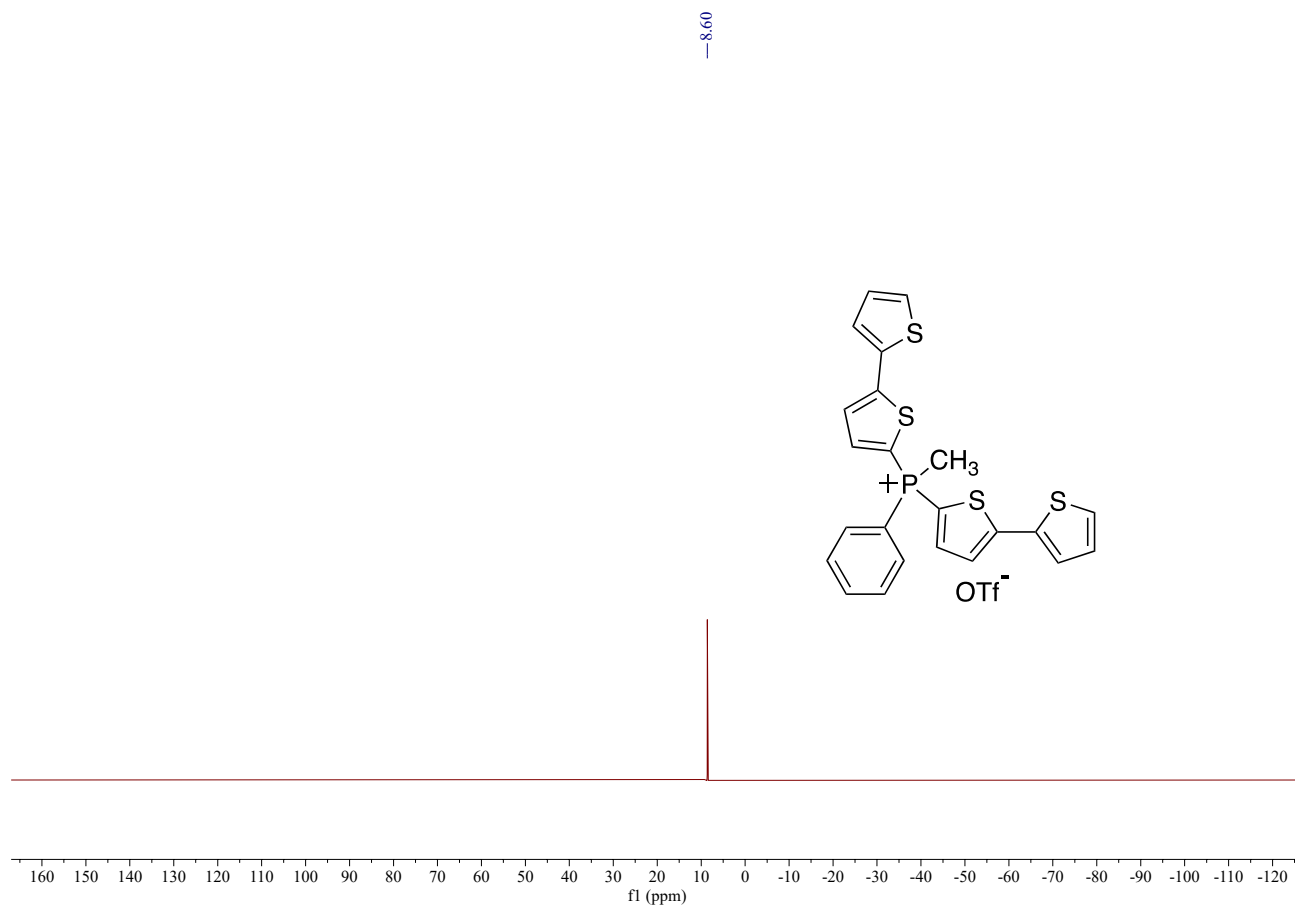


Figure S30. ³¹P {¹H} NMR (202 MHz, CDCl₃, 298K) of D4.

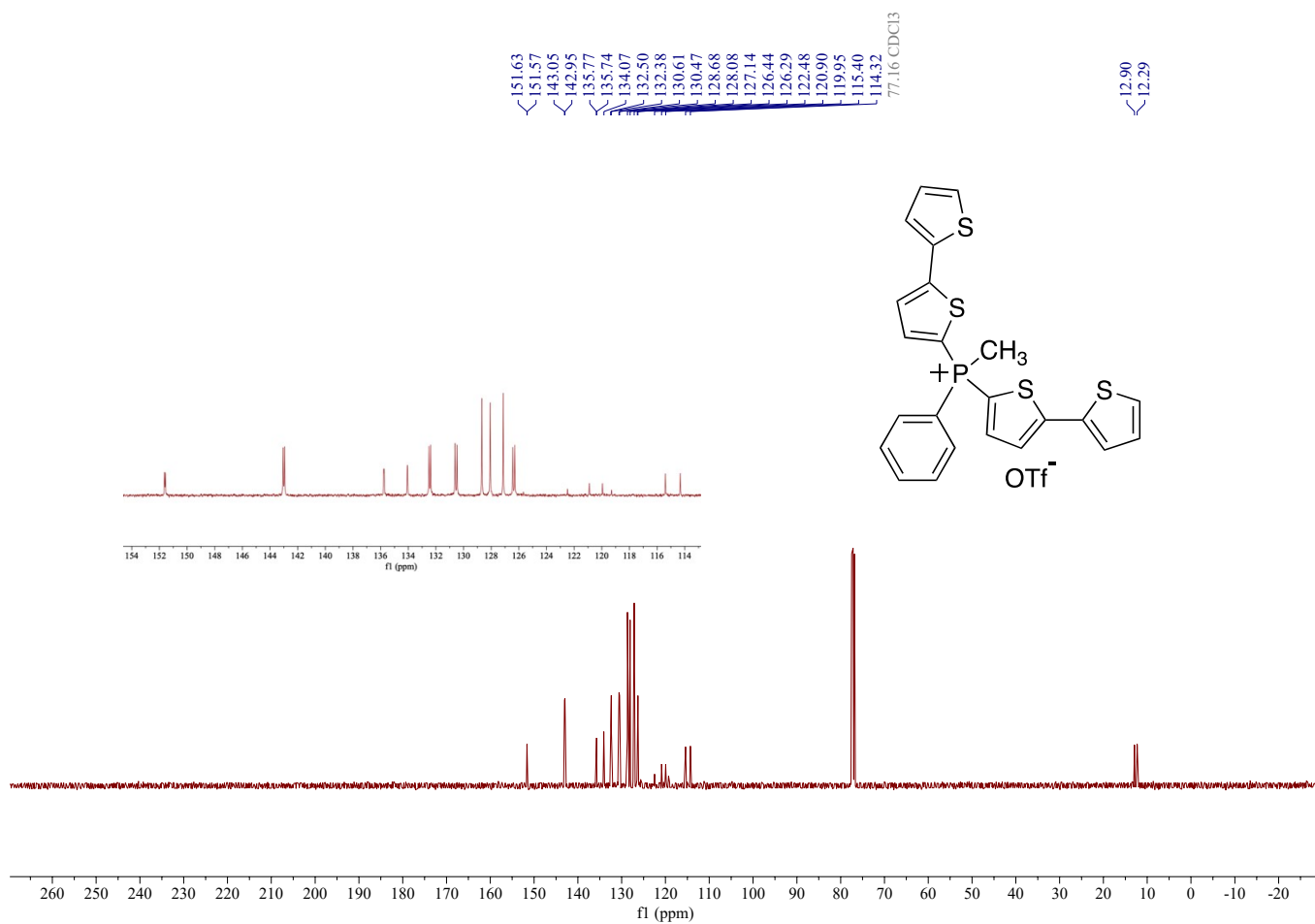


Figure S31. ¹³C NMR (101 MHz, CDCl₃, 298K) of D4.

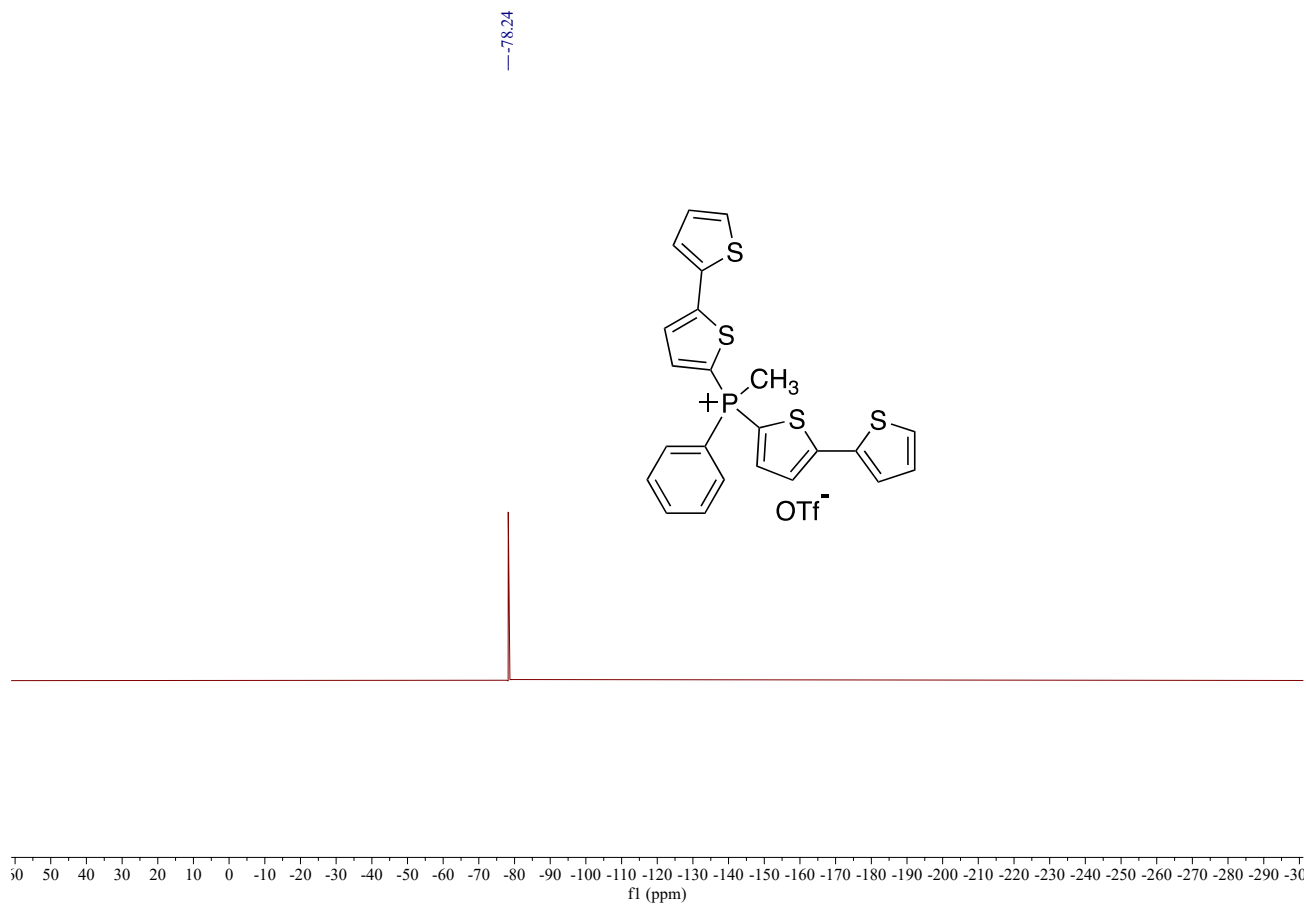
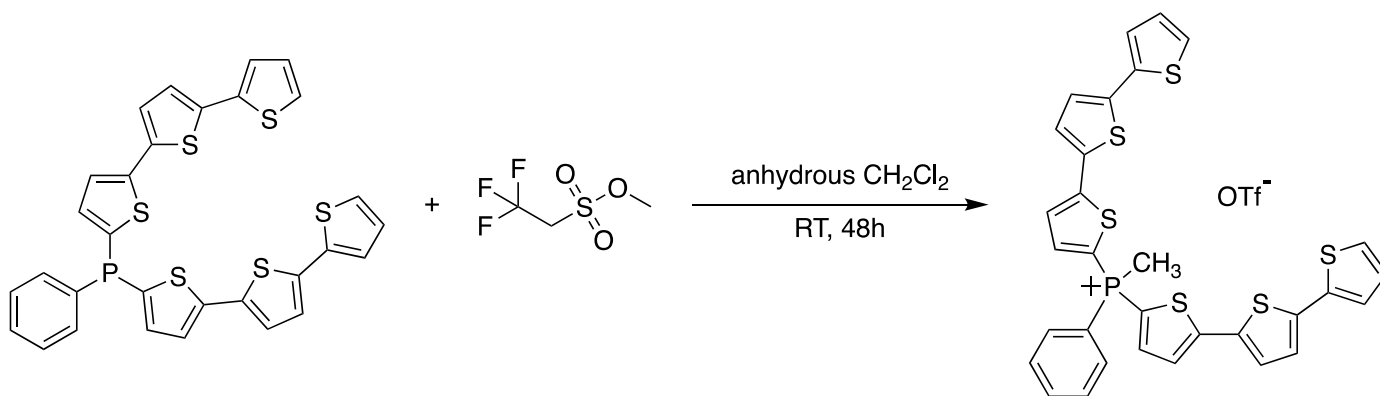


Figure S32. ¹⁹F {¹H} NMR (471 MHz, CDCl₃, 298K) of D4.



Scheme S11. Synthesis of **T5**.

Compound **T5**.

Under N_2 atmosphere, Compound **T1** (310 mg, 0.515 mmol) was dissolved in 50 ml anhydrous CH_2Cl_2 , and Methyl trifluoromethanesulfate (93 mg, 0.567 mmol) was added. The solution was stirred for 48h at room temperature. Then the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography ($\text{MeOH}/\text{CH}_2\text{Cl}_2$ 2:98). Yield: 131.4 mg of yellow powder (33 %). No melting point was observed due to the amorphous nature of **T5** ($T_g = 61.7$ °C). ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.88 (m, 3H), 7.88 – 7.81 (m, 2H), 7.73 (td, $J = 7.7, 3.7$ Hz, 2H), 7.42 (dd, $J = 4.0, 2.3$ Hz, 2H), 7.29 (dd, $J = 5.1, 1.2$ Hz, 2H), 7.23 (dd, $J = 3.7, 1.2$ Hz, 2H), 7.13 (d, $J = 3.9$ Hz, 2H), 7.05 (dd, $J = 5.1, 3.6$ Hz, 2H), 3.06 (d, $J = 13.7$ Hz, 3H) ppm. ^{13}C NMR (101 MHz, CDCl_3) δ 151.3 (d, $J = 6.1$ Hz), 143.1 (d, $J = 11.1$ Hz), 140.1, 136.1, 135.8 (d, $J = 3.0$ Hz), 132.6, 132.5, 130.6 (d, $J = 14.1$ Hz), 128.3, 128.0, 126.1 (d, $J = 14.1$ Hz), 125.8, 124.9, 124.8, 120.9 (d, $J = 322.2$ Hz), 120.6 (d, $J = 96.0$ Hz), 114.7 (d, $J = 109.1$ Hz), 12.7 (d, $J = 61.6$ Hz) ppm. ^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3) δ 8.5 ppm. ^{19}F $\{^1\text{H}\}$ NMR (471 MHz, CDCl_3) δ -78.2 ppm. HR LC-MS: Calcd: $[\text{M-OTf}]^+ = 616.9778$, found: $m/z = 616.9775$.

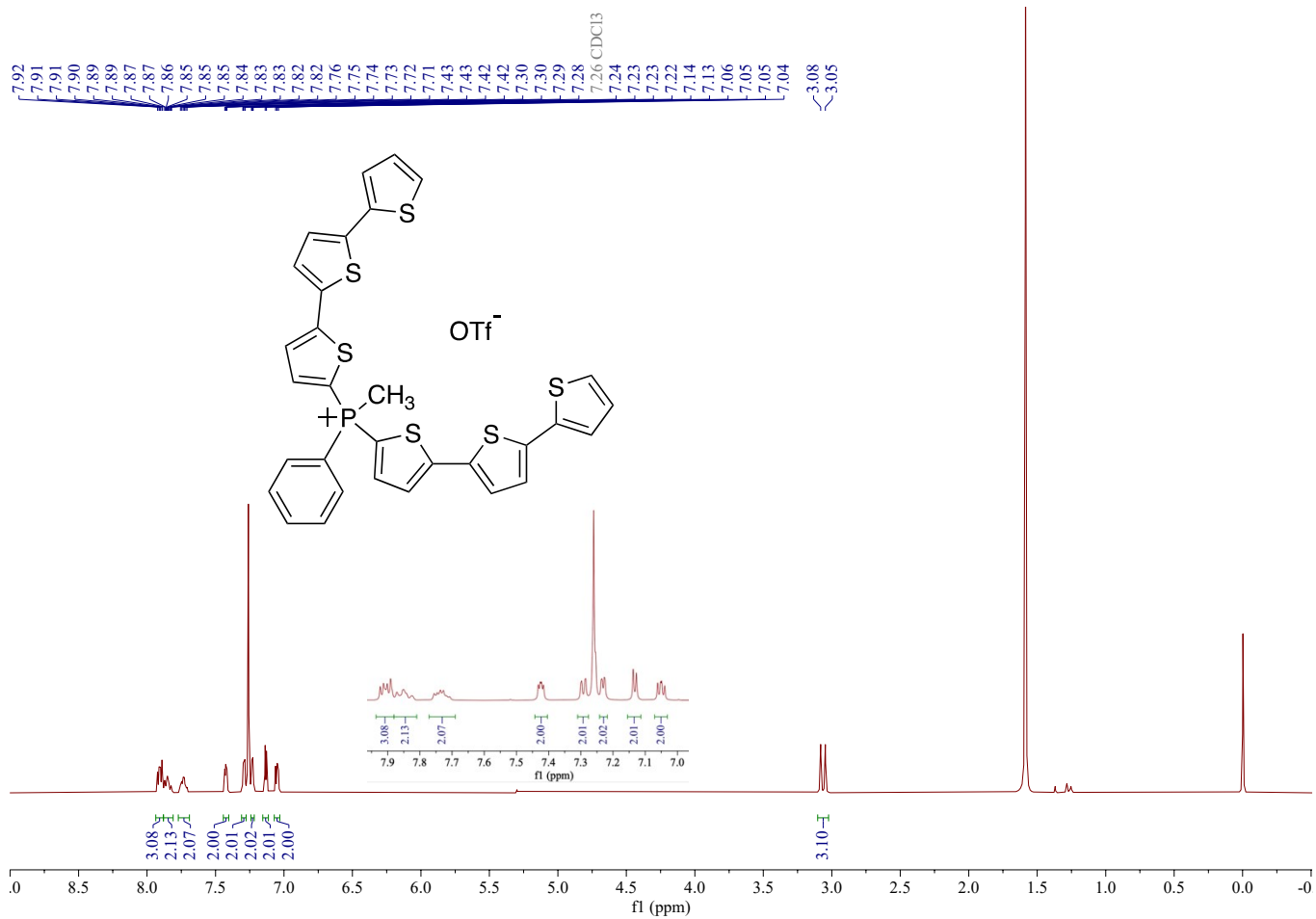


Figure S33. ^1H NMR (400 MHz, CDCl_3 , 298K) of **T5**.

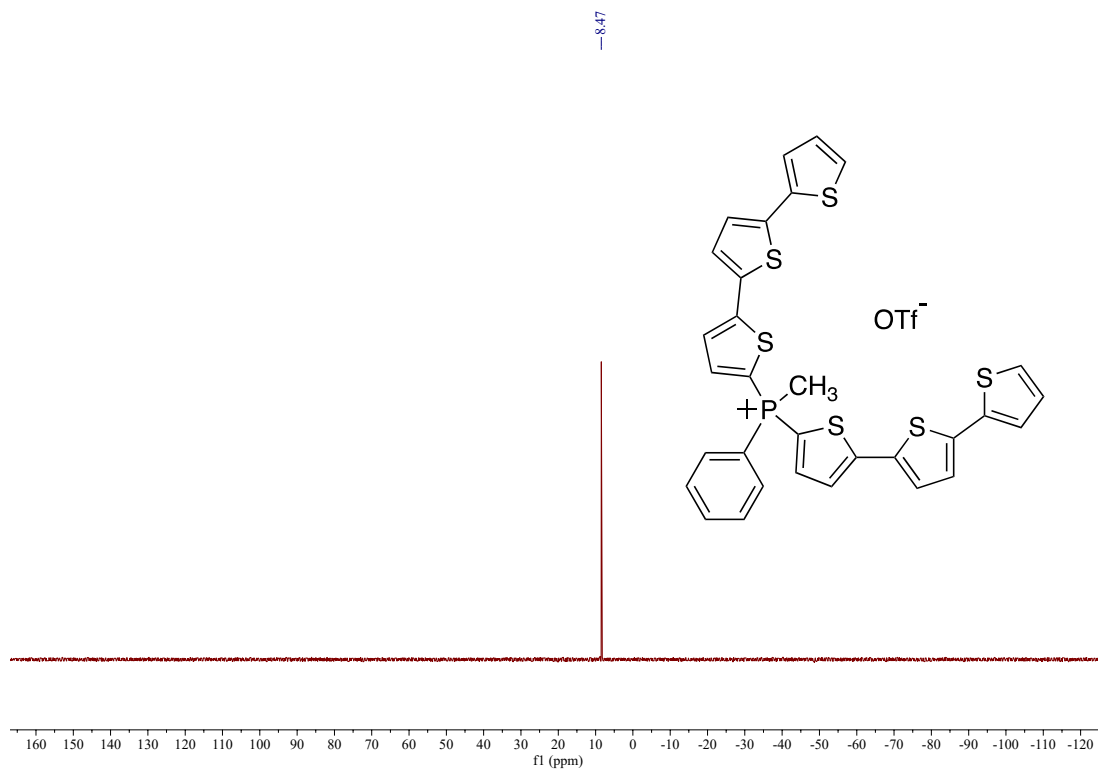


Figure S34. ^{31}P $\{^1\text{H}\}$ NMR (202 MHz, CDCl_3 , 298K) of **T5**.

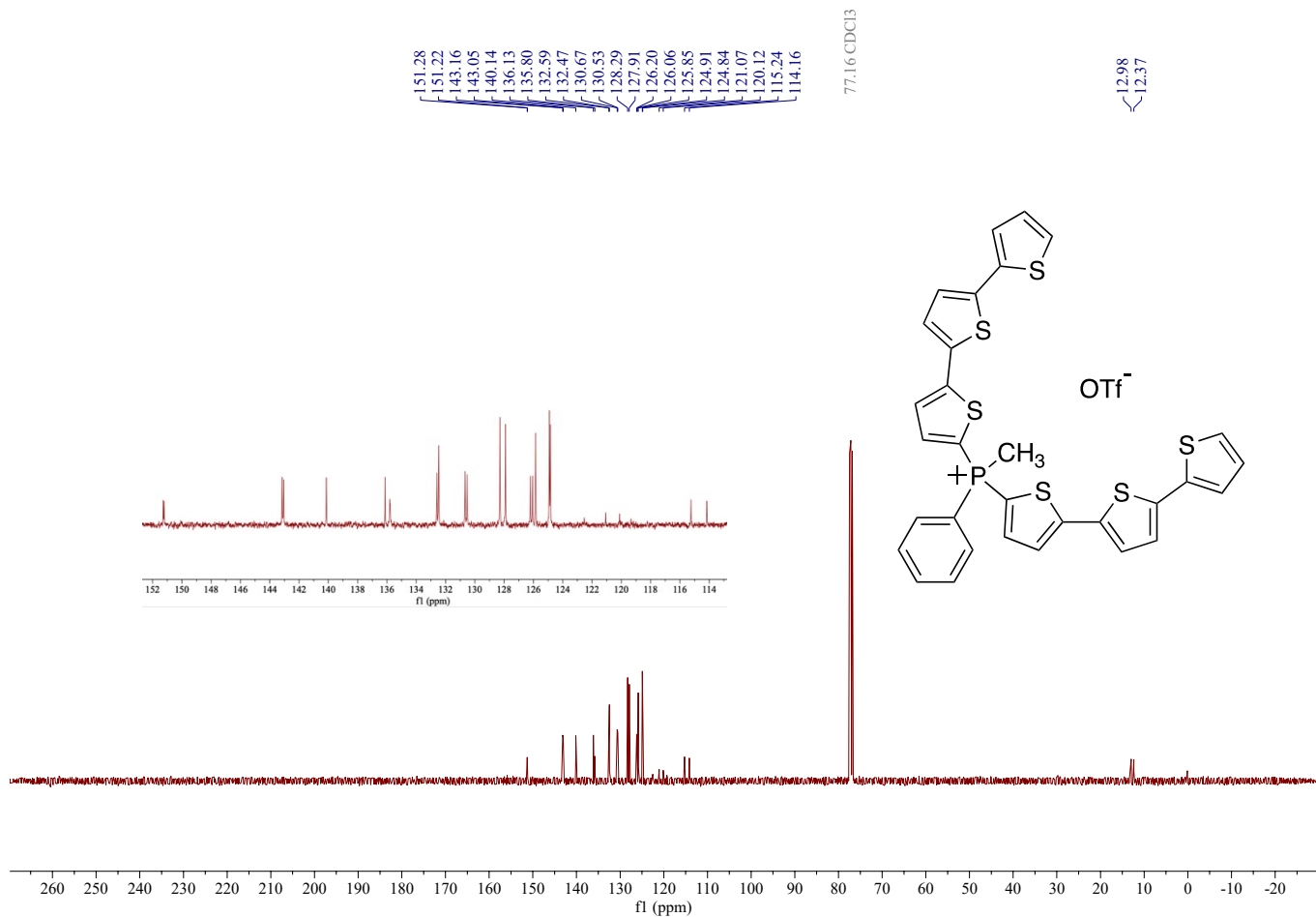


Figure S35. ¹³C NMR (101 MHz, CDCl₃, 298K) of T5.

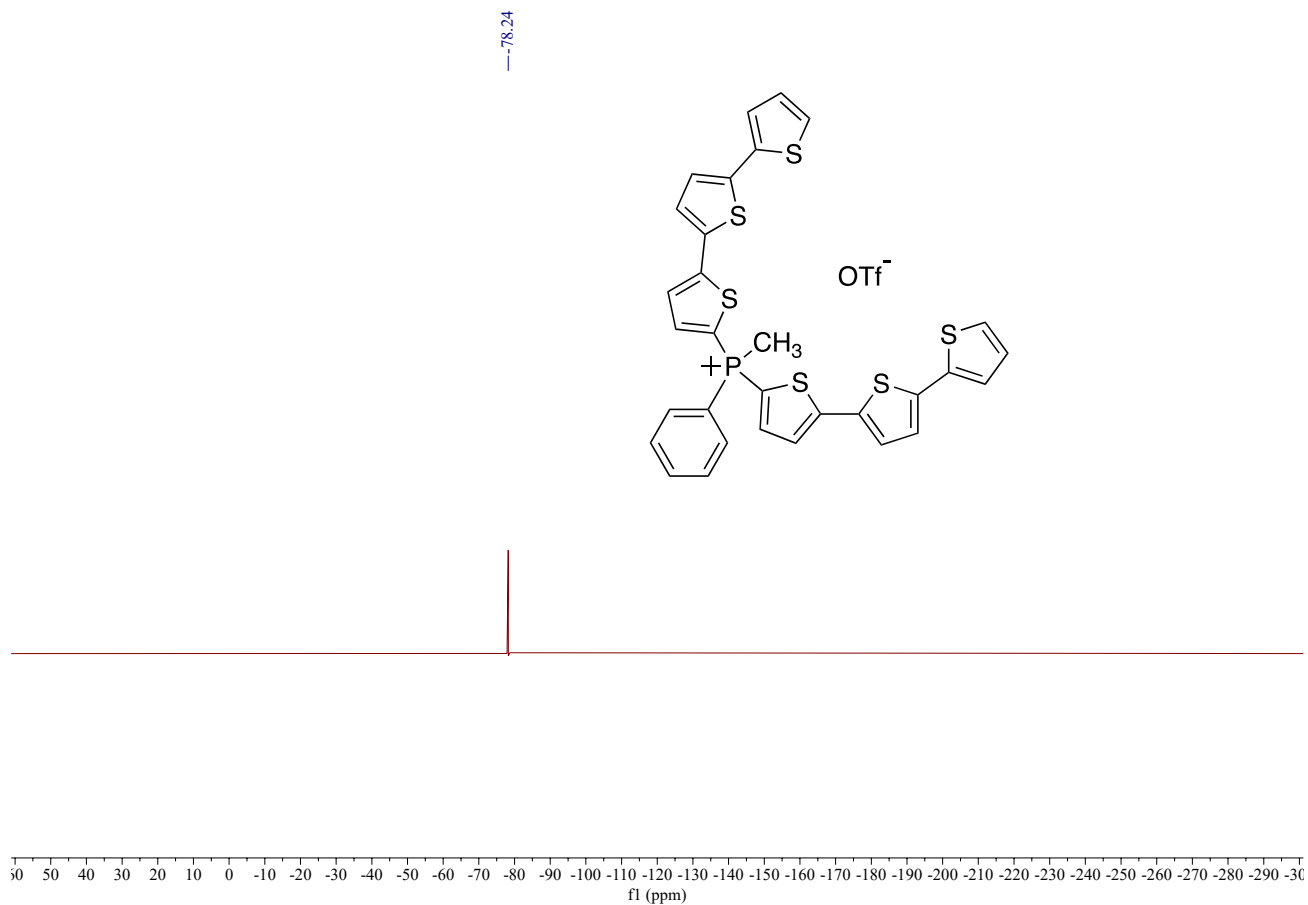
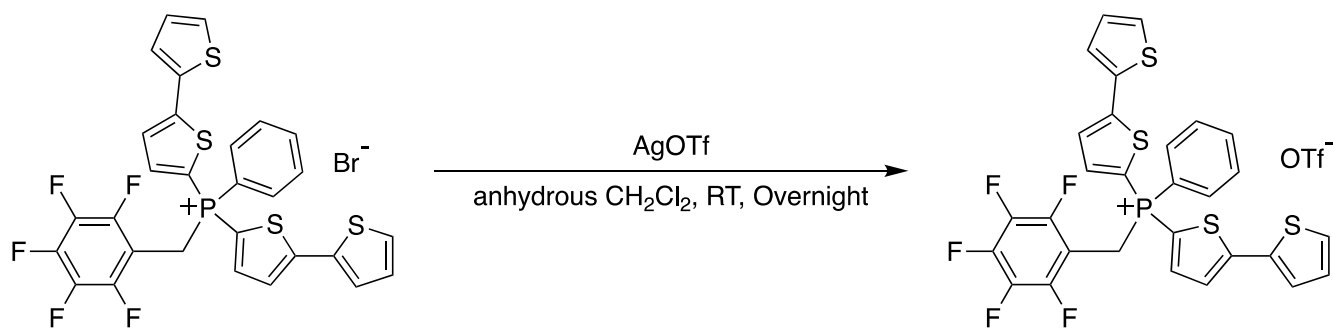


Figure S36. ¹⁹F {¹H} NMR (471 MHz, CDCl₃, 298K) of T5.



Scheme S12. Synthesis of **D5**.

Compound **D5**.

Under N_2 atmosphere, Compound **D5-Br** (155 mg, 0.222 mmol) was dissolved in 10 ml anhydrous CH_2Cl_2 , and Silver trifluoromethanesulfonate (72.7 mg, 0.283 mmol) was added. The solution was stirred for overnight at room temperature. Then the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (MeOH/ CH_2Cl_2 2:98), Yield: 125.5 mg of pale-yellow powder (73%). No melting point was observed due to the amorphous nature of **D5** ($T_g = 47.4$ °C). 1H NMR (400 MHz, $CDCl_3$) δ 8.08 – 7.97 (m, 2H), 7.94 – 7.83 (m, 3H), 7.80 – 7.68 (m, 2H), 7.48 (t, $J = 3.2$ Hz, 2H), 7.44 (d, $J = 5.1$ Hz, 2H), 7.34 (d, $J = 3.6$ Hz, 2H), 7.10 (t, $J = 4.4$ Hz, 2H), 5.11 (d, $J = 13.9$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0 (d, $J = 6.1$ Hz), 144.4 (d, $J = 10.1$ Hz), 136.4 (d, $J = 3.0$ Hz), 133.9 (d, $J = 1.01$ Hz), 133.2 (d, $J = 12.1$ Hz), 128.8, 128.6, 127.5, 126.7 (d, $J = 18.2$ Hz), 120.9 (d, $J = 321.2$ Hz), 118.5 (d, $J = 92.9$ Hz), 111.6 (d, $J = 108.1$ Hz), 23.4 (d, $J = 57.6$ Hz) ppm. ^{31}P $\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ 9.1 ppm. ^{19}F $\{^1H\}$ NMR (376 MHz, $CDCl_3$) δ -78.4, -136.6 (d, $J = 20.6$ Hz), -150.0 – 150.2 (m), -159.3 (d, $J = 20.0$ Hz) ppm. HR LC-MS: Calcd: $[M-OTf]^+ = 618.9866$, found: $m/z = 618.9863$.

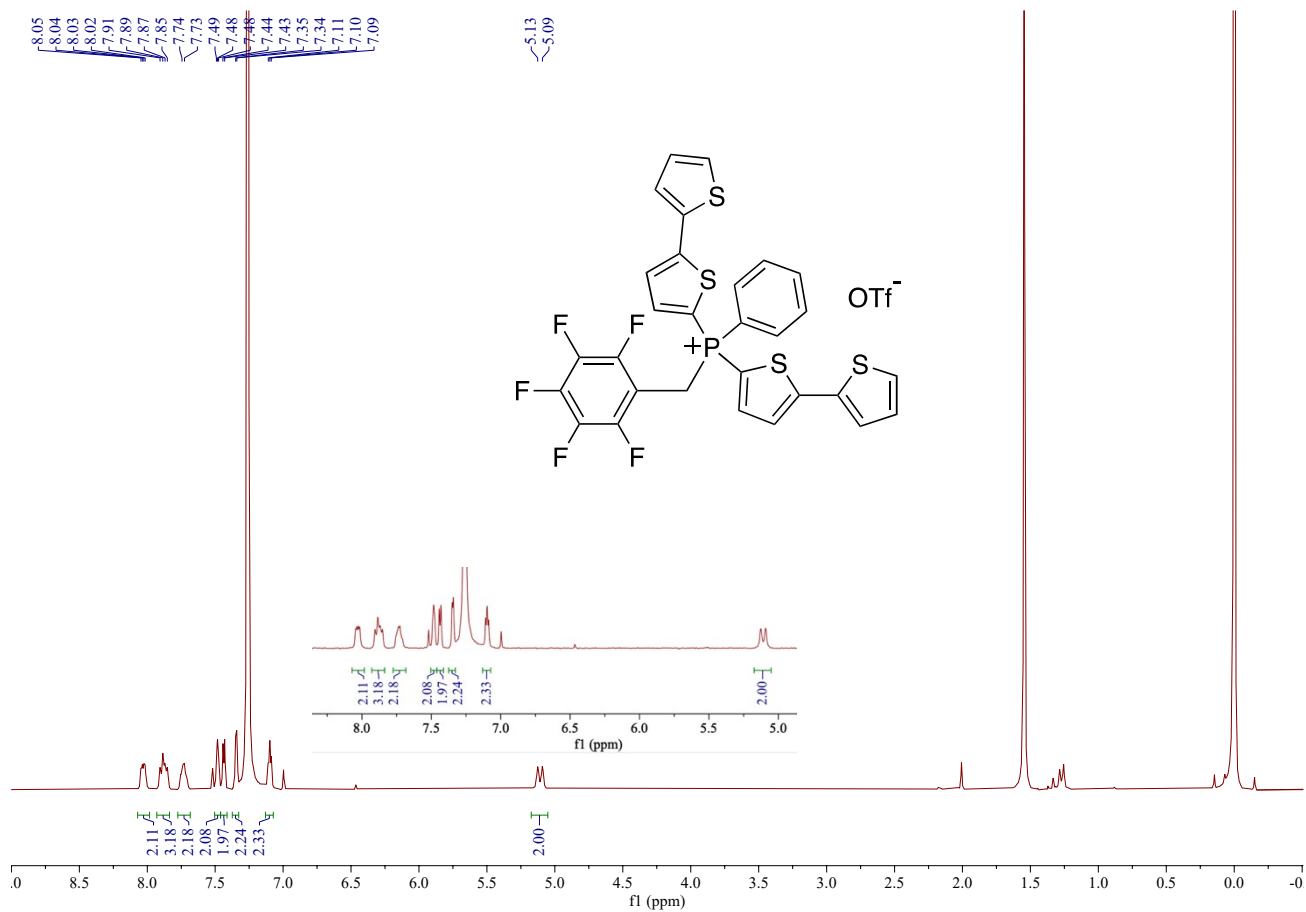


Figure S37. ¹H NMR (400 MHz, CDCl₃, 298K) of **D5**.

-9.09

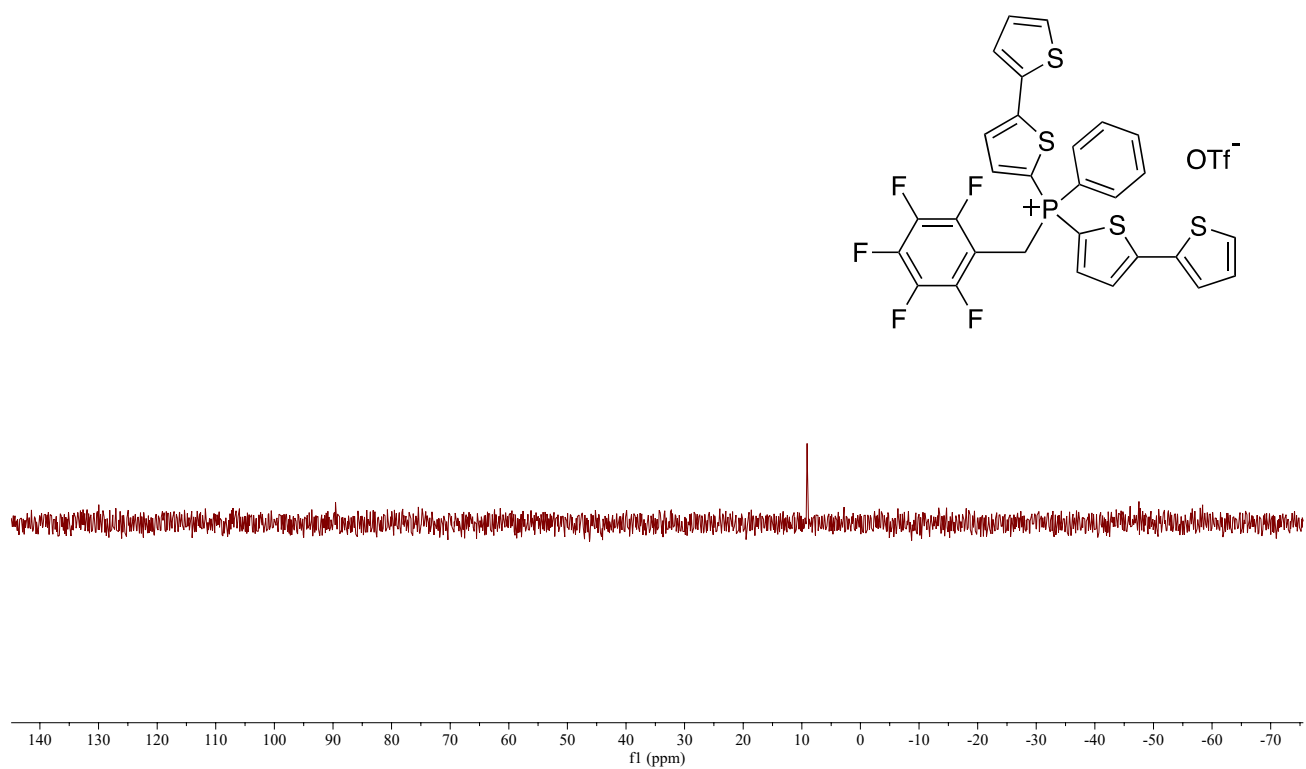


Figure S38. ³¹P {¹H} NMR (162 MHz, CDCl₃, 298K) of **D5**.

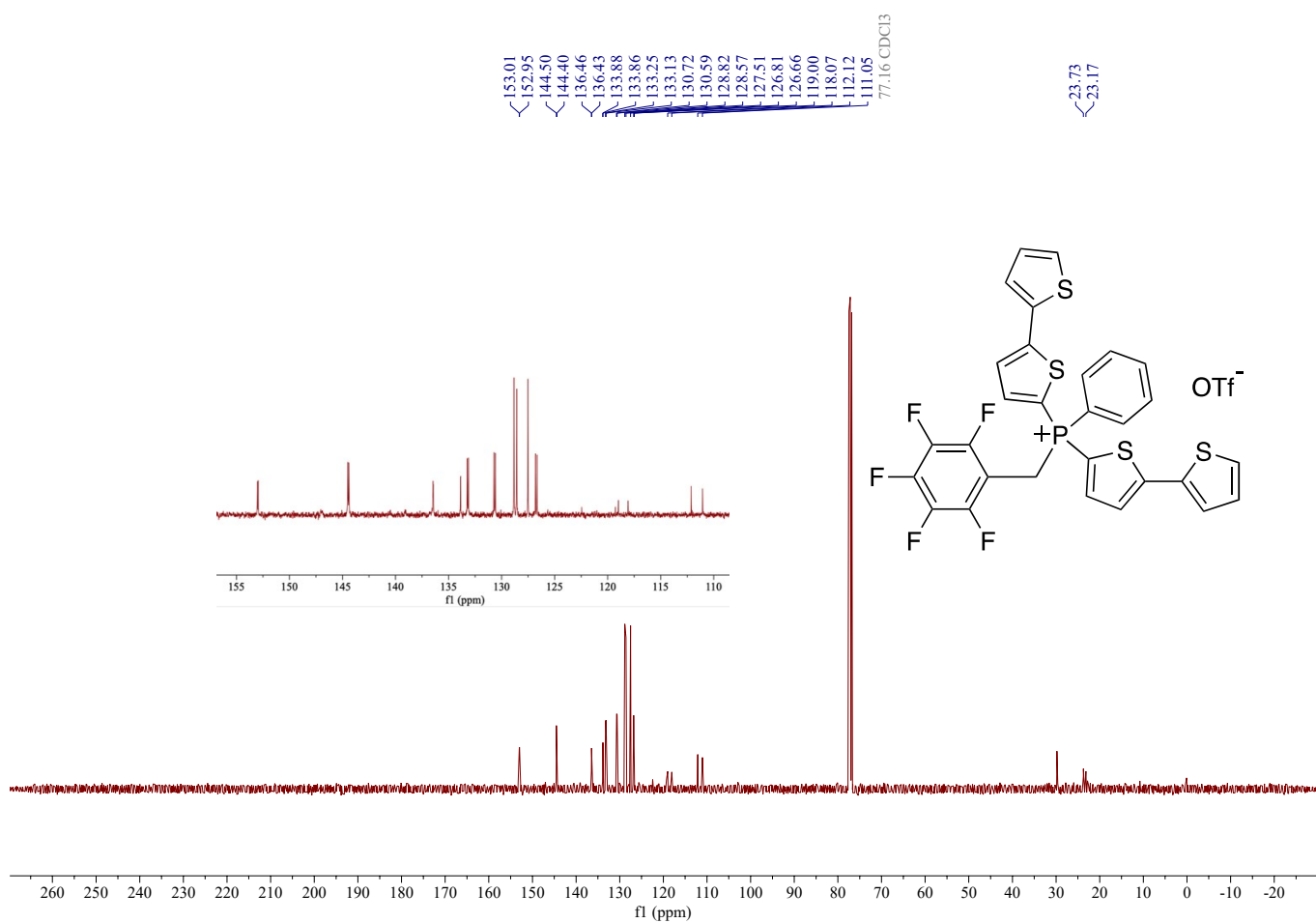


Figure S39. ^{13}C NMR (101 MHz, $CDCl_3$, 298K) of **D5**.

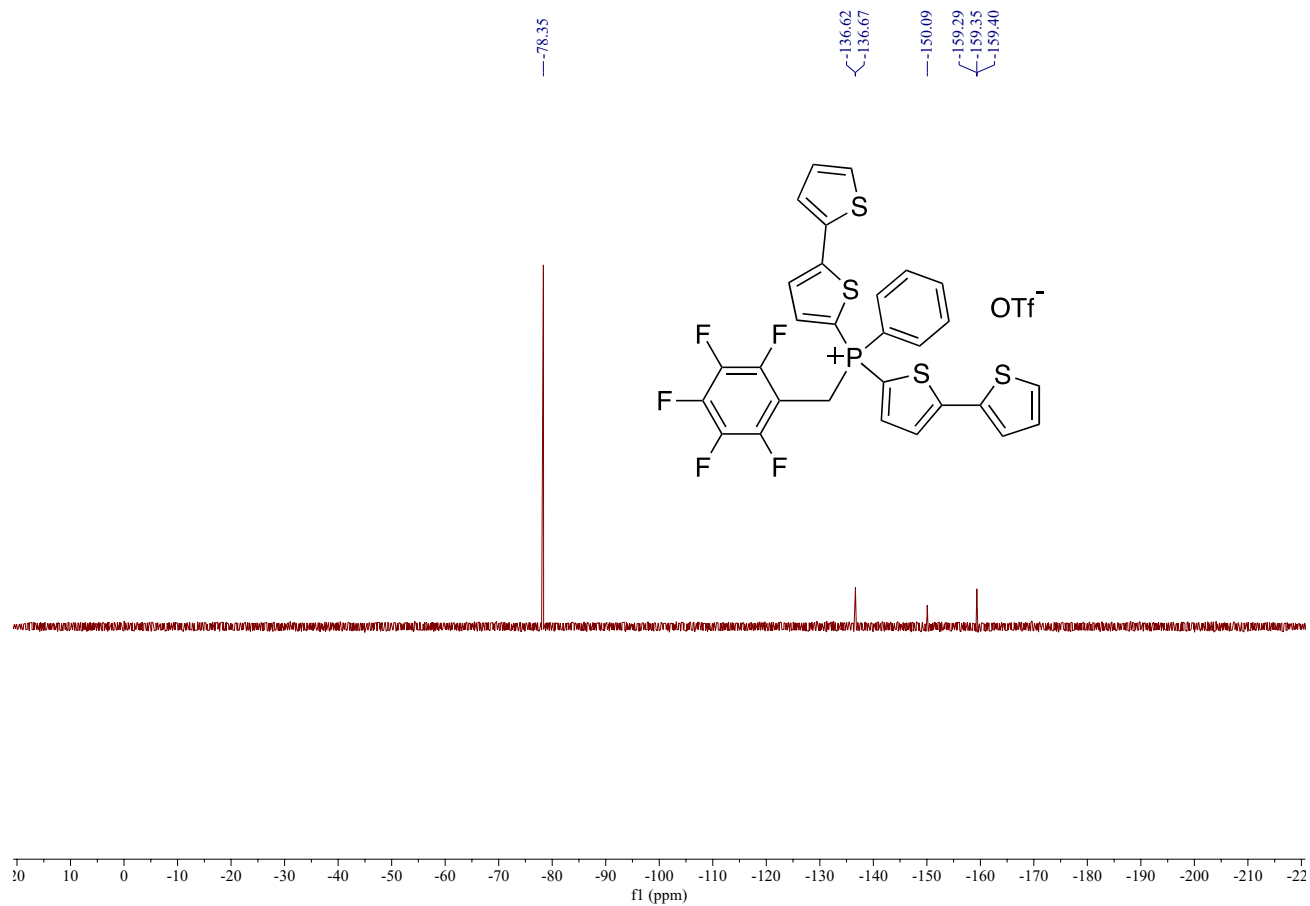
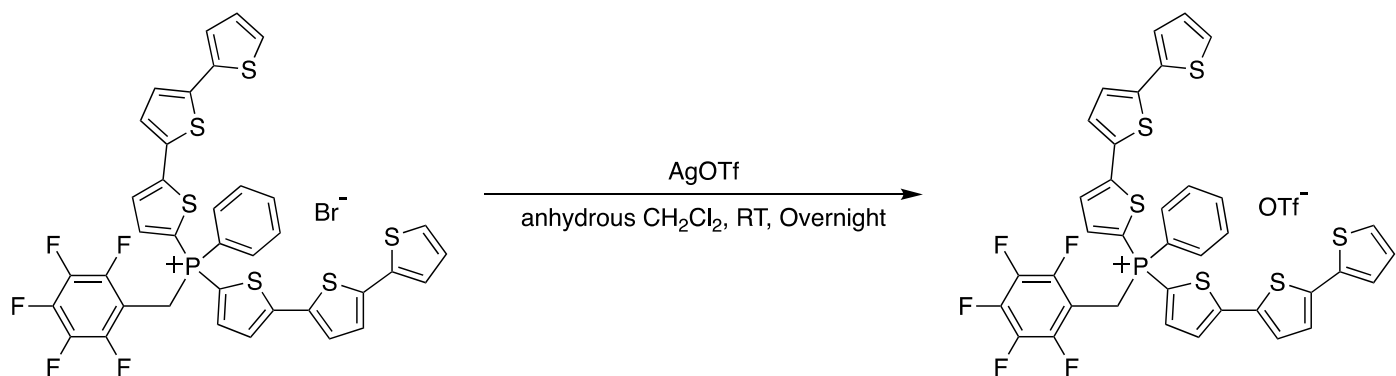


Figure S40. ^{19}F $\{^1H\}$ NMR (376 MHz, $CDCl_3$, 298K) of **D5**.



Scheme S13. Synthesis of **T6**.

Compound **T6**.

Under N_2 atmosphere, Compound **T6-Br** (96 mg, 0.111 mmol) was dissolved in 20 ml anhydrous CH_2Cl_2 , and Silver trifluoromethanesulfonate (68.7 mg, 0.267 mmol) was added. The solution was stirred for overnight at room temperature. Then the solvent of mixture was removed under vacuum, the residue was purified by silica gel column chromatography (Acetone/ CH_2Cl_2 3:17), Yield: 98 mg of yellow powder (94%). No melting point was observed due to the amorphous nature of **T6** ($T_g = 61.9\text{ }^\circ C$). 1H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, $J = 8.3, 4.1$ Hz, 2H), 7.91 – 7.83 (m, 3H), 7.74 (td, $J = 7.7, 3.9$ Hz, 2H), 7.49 – 7.44 (m, 2H), 7.31 (dd, $J = 5.1, 1.2$ Hz, 2H), 7.26 – 7.22 (m, 2H), 7.14 (d, $J = 3.9$ Hz, 2H), 7.06 (dd, $J = 5.2, 3.7$ Hz, 2H), 5.09 (d, $J = 13.9$ Hz, 2H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.4 (d, $J = 6.1$ Hz), 144.3 (d, $J = 10.1$ Hz), 140.5, 136.4, 135.9, 133.0 (d, $J = 11.1$ Hz), 132.0 (d, $J = 2.02$ Hz), 130.7, 130.5, 128.2, 126.3 (d, $J = 15.1$ Hz), 125.9, 124.9, 124.8, 120.8 (d, $J = 350.5$ Hz), 118.2 (d, $J = 92.9$ Hz), 111.0 (d, $J = 108.1$ Hz), 23.4 (d, $J = 57.6$ Hz) ppm. ^{31}P { 1H } NMR (162 MHz, $CDCl_3$) δ 8.9 ppm. ^{19}F { 1H } NMR (376 MHz, $CDCl_3$) δ -78.34, -136.7 (db, $J = 18.8$ Hz), -150.0 – -150.1 (m), -159.2 – -159.4 (m) ppm. HR LC-MS: Calcd: $[M-OTf]^+ = 782.9620$, found: $m/z = 782.9608$.

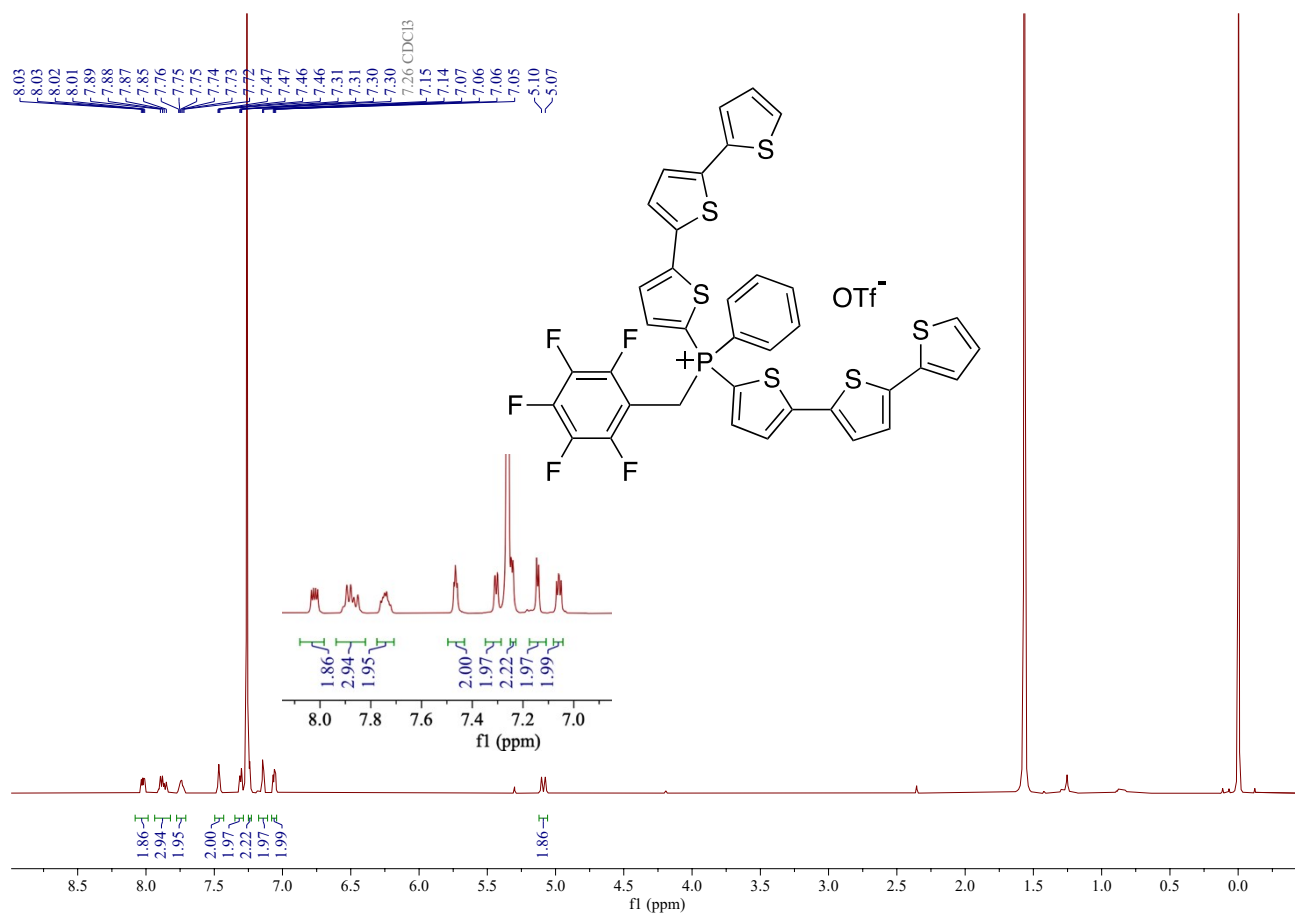


Figure S41. ^1H NMR (500 MHz, CDCl_3 , 298K) of T6.

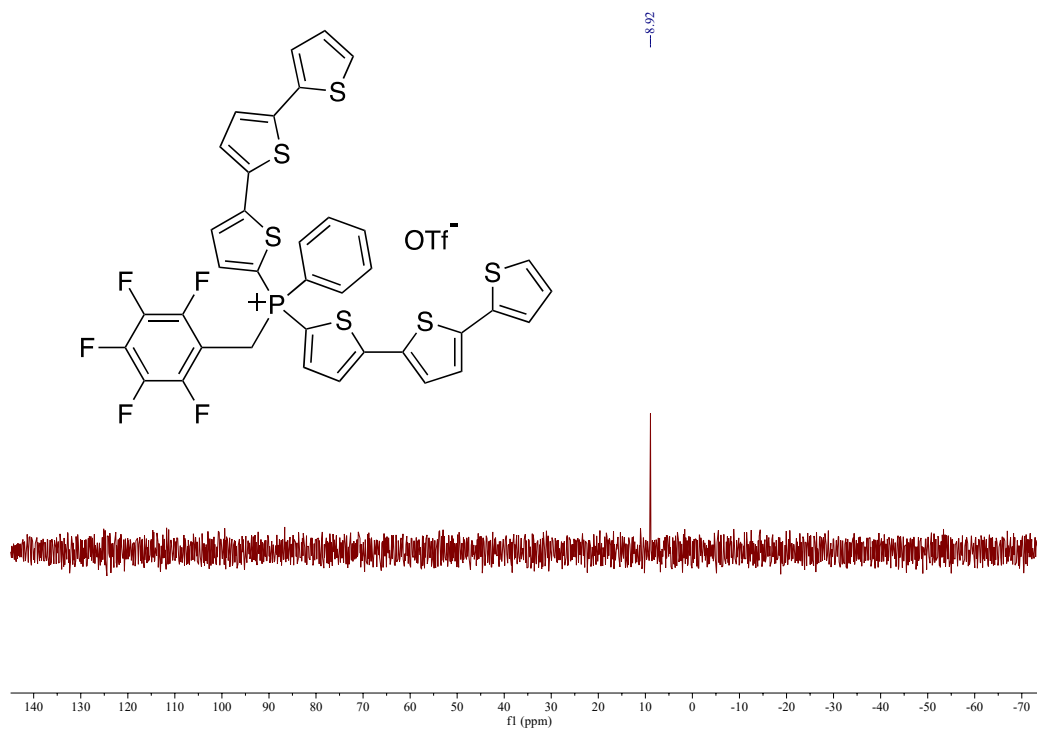


Figure S42. ^{31}P $\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 298K) of T6.

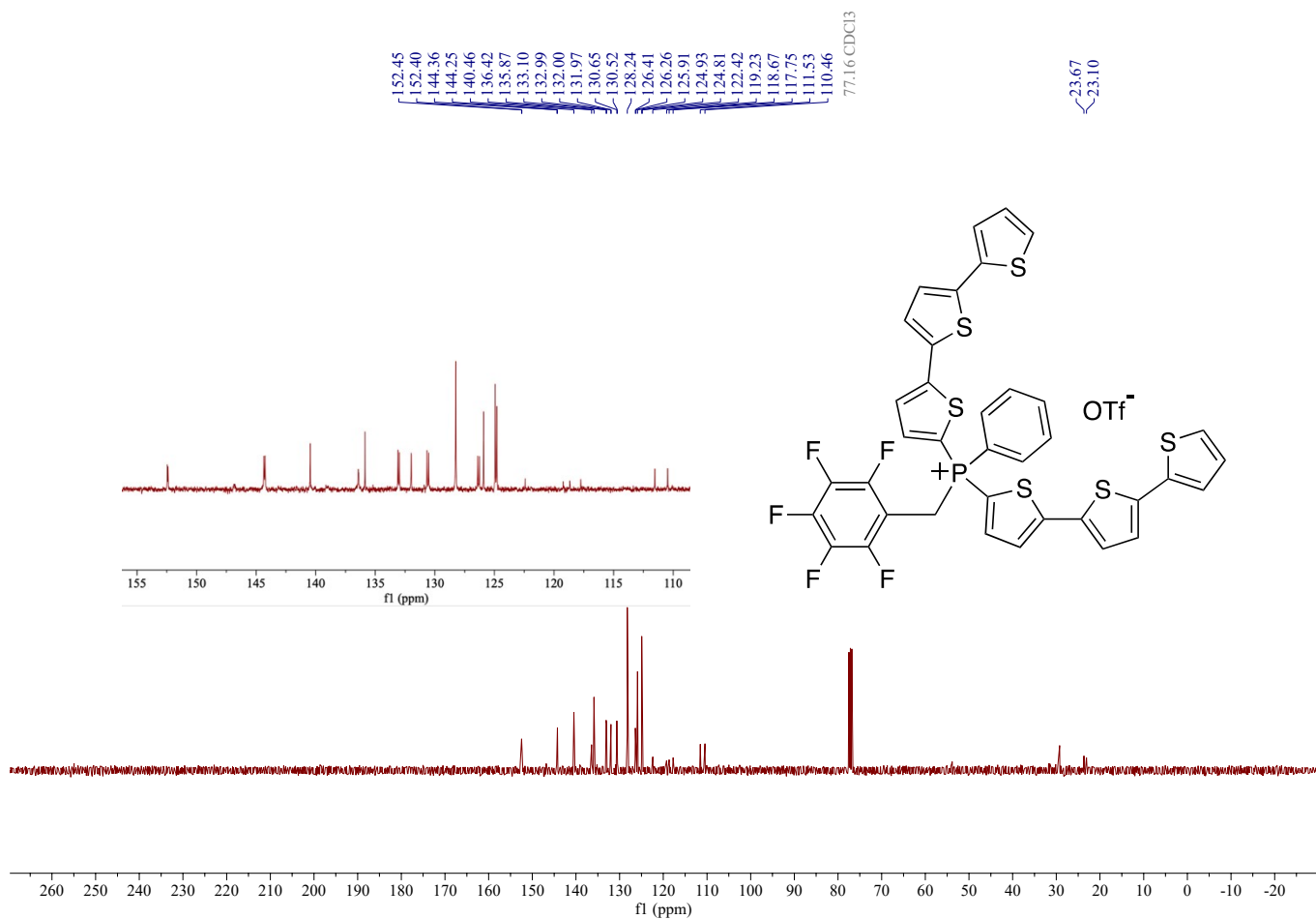


Figure S43. ¹³C NMR (101 MHz, CDCl₃, 298K) of T6.

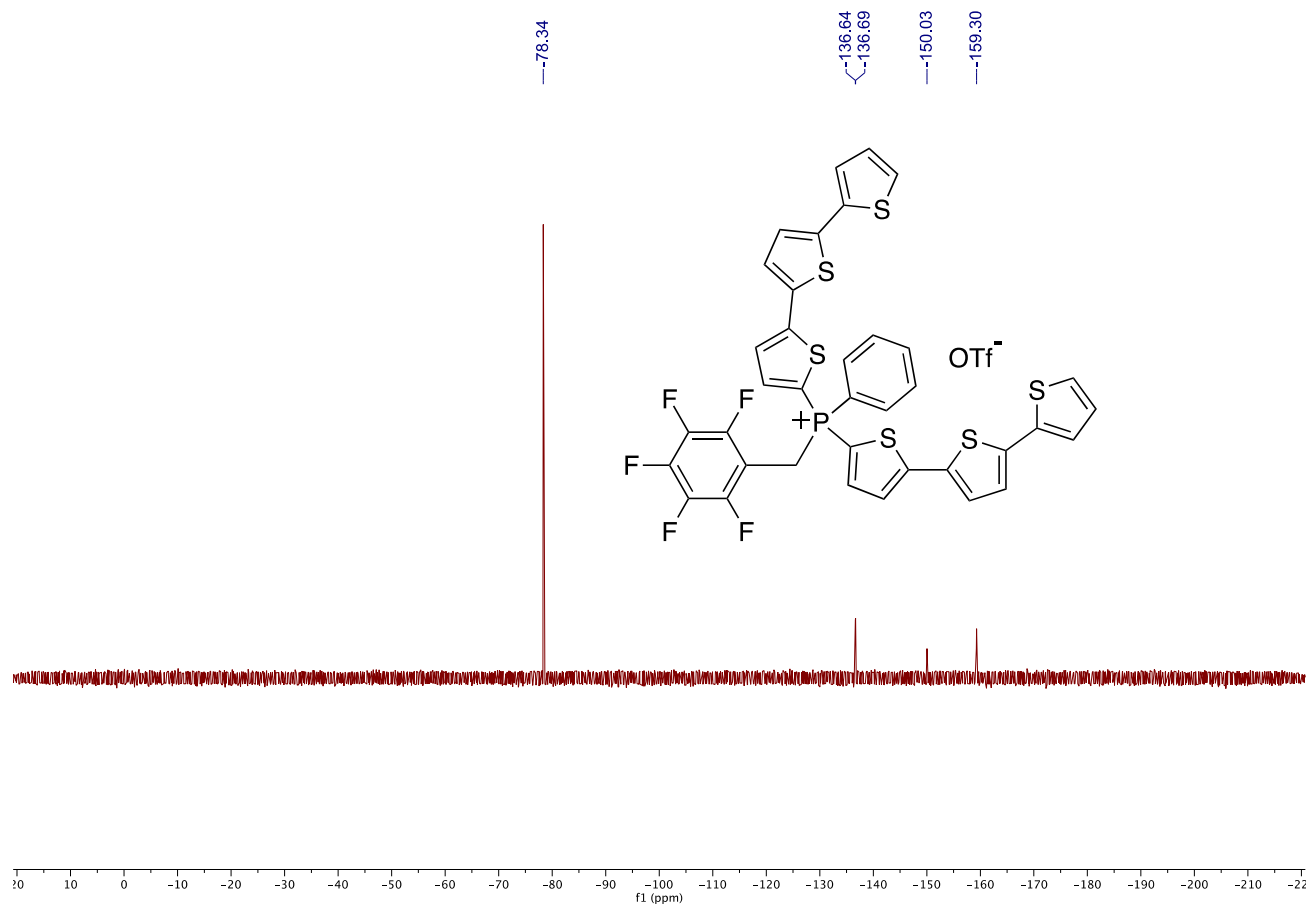


Figure S44. ¹⁹F {¹H} NMR (376 MHz, CDCl₃, 298K) of T6.

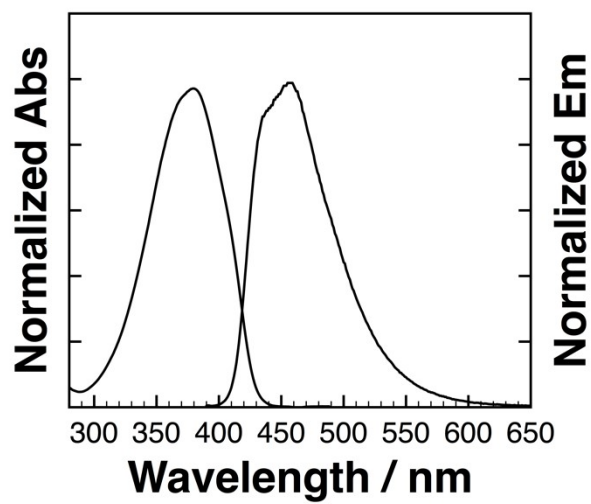


Figure S45. UV-vis spectra of T3 in DCM.

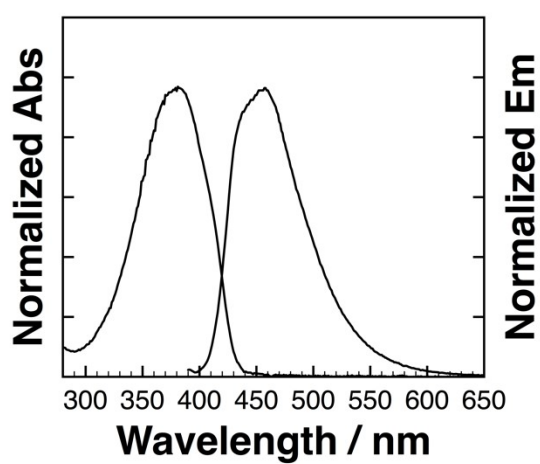


Figure S46. UV-vis spectra of T4 in DCM.

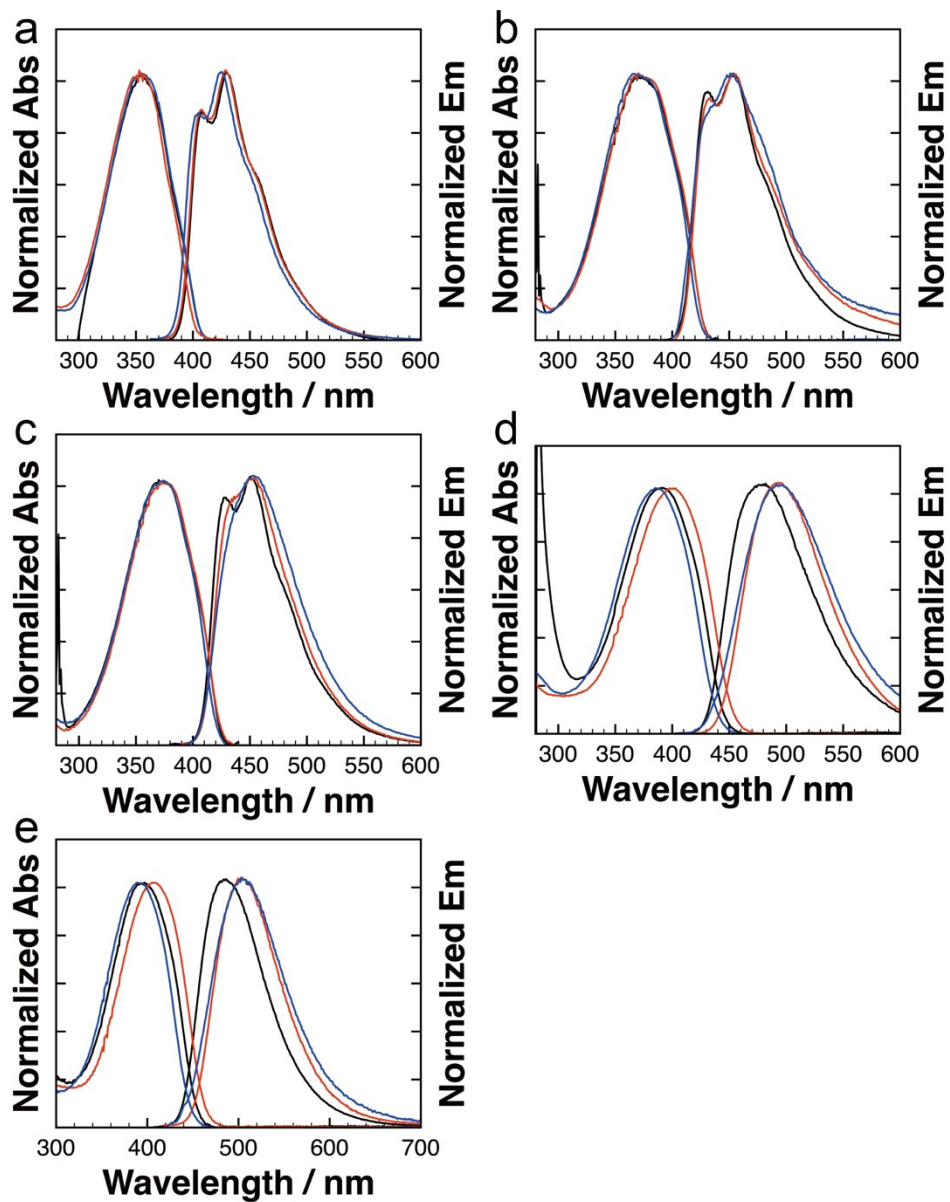


Figure S47. UV-vis spectra of a) terTh, b) T1, c) T2, d) T5, and e) T6 in toluene (black), DCM (red) and acetonitrile (blue).

Table S1. Photophysical data of **P-terThs** in toluene

Compound	λ_{abs} [nm] ^a	λ_{em} [nm] ^a	Φ [%] ^a	τ_{PL} [ps]
terTh	355	407, 429, 458	6.0	τ_1 : 150 (0.8) τ_2 : 230 (0.2) τ_{average} : 170
T1	370	431, 454, 485	4.9	τ_1 : 40 (0.17) τ_2 : 170 (0.83) τ_{average} : 150
T2	370	409, 429, 450	7.6	τ_1 : 100 (0.11) τ_2 : 180 (0.89) τ_{average} : 170
T5	392	480	30.4	τ_1 : 180 (0.46) τ_2 : 950 (0.54) τ_{average} : 590
T6	397	487	41.3	τ_1 : 450 (0.34) τ_2 : 450 (0.66) τ_{average} : 1110

Table S2. Photophysical data of **P-terThs** in DCM

Compound	λ_{abs} [nm] ^a	λ_{em} [nm] ^a	Φ [%] ^a	τ_{PL} [ps]
terTh	353	407, 428, 458	1.5	τ_1 : 0.160(0.95) τ_2 : 0.350(0.05) τ_{average} : 170
T1	370	432, 455	0	τ_1 : 110 τ_2 : 200(0.75) τ_{average} : 180
T2	377	434, 454	8.7	τ_1 : 110 (0.11) τ_2 : 190 (0.89) τ_{average} : 180
T3	381	436, 456	9.0	τ_1 : 110 (0.21) τ_2 : 210 (0.79) τ_{average} : 190
T4	381	437, 457	0	τ_1 : 20 (0.98) τ_2 : 190 (0.02) τ_{average} : 30
T5	398	492	69.5	τ_1 : 740 (0.26) τ_2 : 1890 (0.74) τ_{average} : 1590
T6	408	505	71.2	τ_1 : 1020 (0.15) τ_2 : 2030 (0.85) τ_{average} : 1880

Table S3. Photophysical data of **P-terThs** in acetonitrile.

Compound	λ_{abs} [nm] ^a	λ_{em} [nm] ^a	Φ [%] ^a	τ_{PL} [ps]
terTh	353	405, 425, 450	12.4	τ_1 : 150 (1.0)
T1	366	430, 450	0	τ_1 : 150 (0.04) τ_2 : 380 (0.01) τ_3 : 10 (0.96) τ_{average} : 20
T2	374	453	1.8	τ_1 : 60 (0.54) τ_2 : 330 (0.46) τ_{average} : 190
T5	385	492	3.6	τ_1 : 210 (0.11) τ_2 : 350 (0.03) τ_3 : 10 (0.86) τ_{average} : 40
T6	388	507	0.3	τ_1 : 60 (0.68) τ_2 : 240 (0.32) τ_3 : 1290 (0.0) τ_{average} : 120

Table S4. Photophysical data of **P-biThs** in DCM.

Compound	λ_{abs} [nm] ^a	λ_{em} [nm] ^a	Φ [%] ^a	τ_{PL} [ps]
D2	328	391	3.4	τ_1 : 470 (0.03) τ_2 : 900 (0.97) τ_{average} : 890
D5	353	423	32.5	τ_1 : 1150 (1.0)

Table S5. Photophysical data of **P-biThs** in toluene.

Compound	λ_{abs} [nm] ^a	λ_{em} [nm] ^a	Φ [%] ^a	τ_{PL} [ps]
D2	327	384	35.66	τ_1 : 730 (1.0)
D5	338	420	9.55	τ_1 : 100 (0.61) τ_2 : 860 (0.39) τ_{average} : 400

Table S6. Photophysical data of **P-biThs** in acetonitrile.

Compound	λ_{abs} [nm] ^a	λ_{em} [nm] ^a	Φ [%] ^a	τ_{PL} [ps]
D2	324	393	1.86	τ_1 : 30 (0.78) τ_2 : 320 (0.22) τ_{average} : 90
D5	340	425	0.24	τ_1 : 20 (0.87) τ_2 : 260 (0.13) τ_{average} : 50

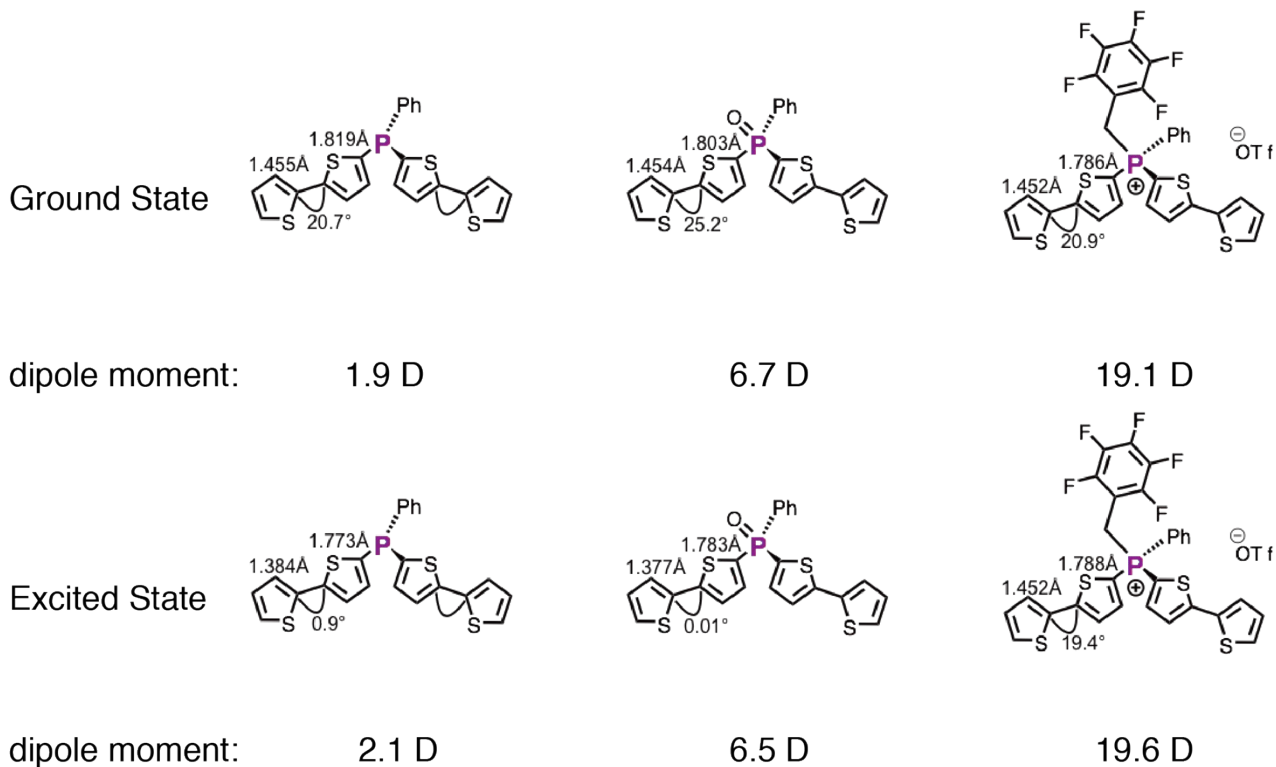


Figure S48. Structure information of P-biThs in both ground state and excited state.

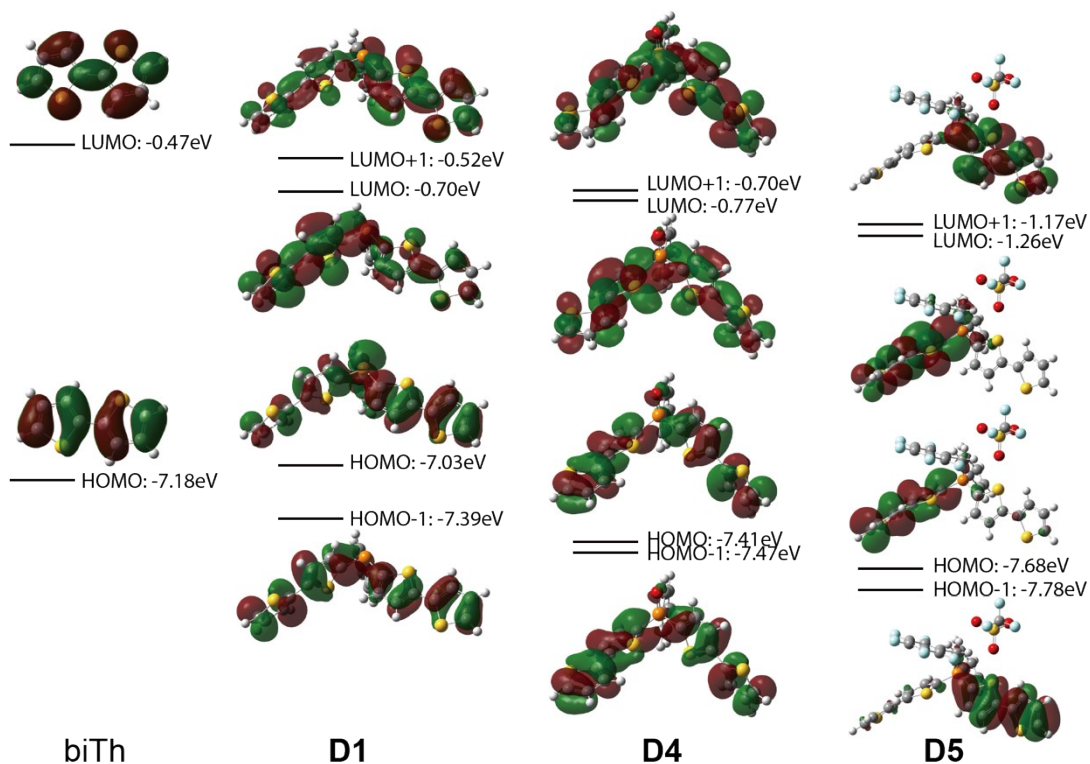


Figure S49. MOs of P-biThs in S_0 .

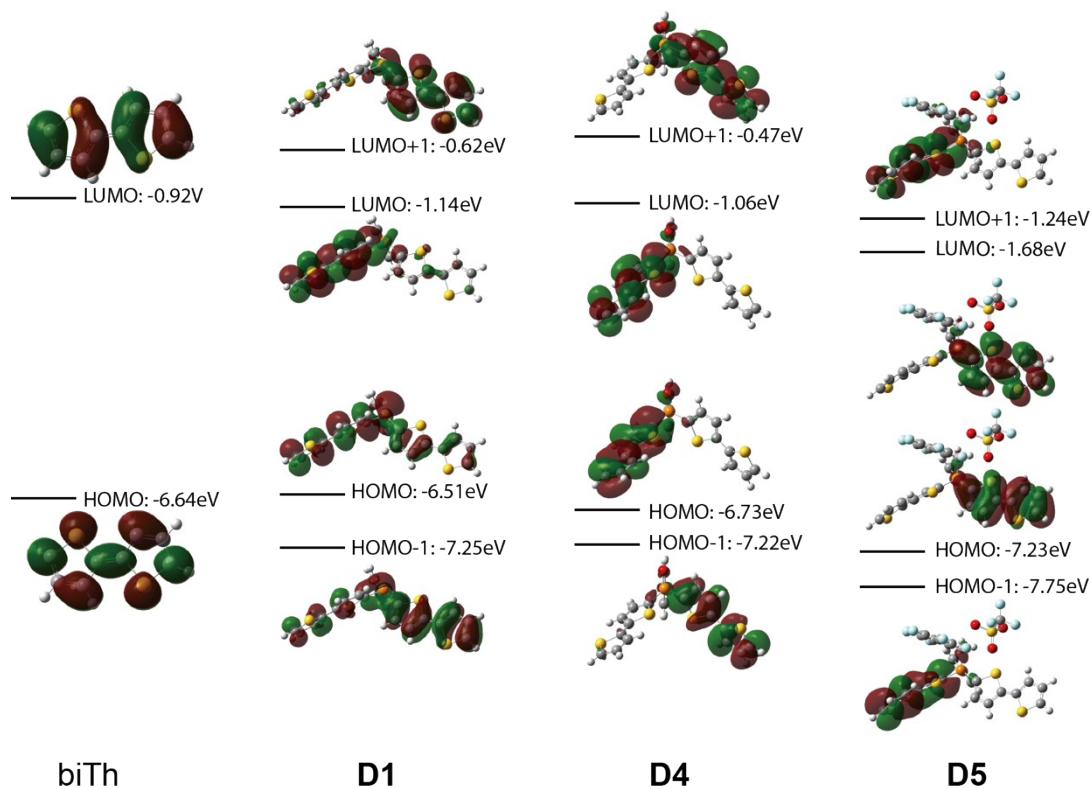


Figure S50. MOs of P-biThs in S_{SBCT}^* .

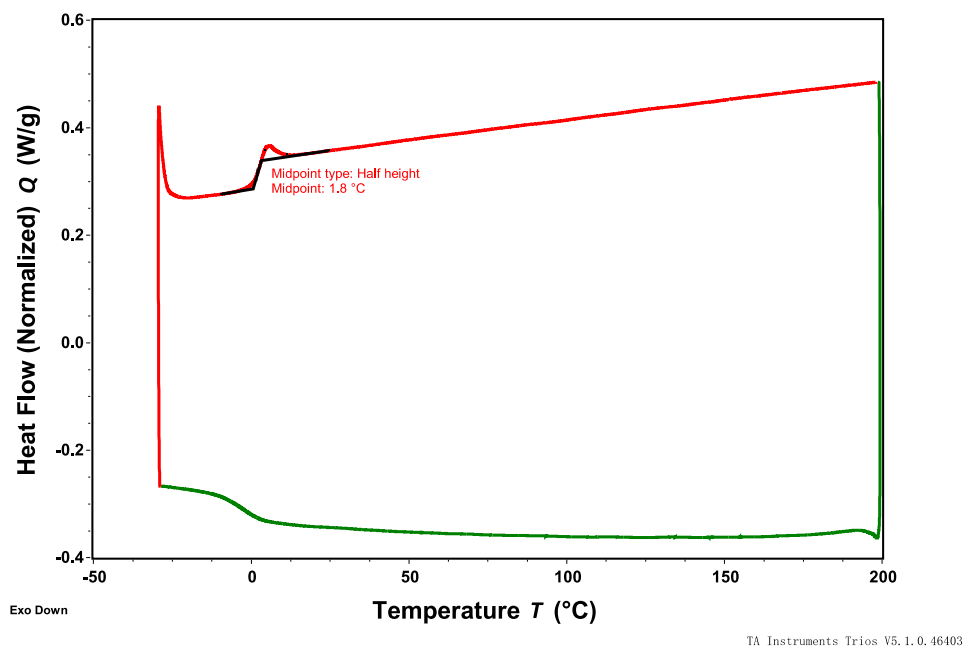


Figure S51. DSC data of **D1** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min).

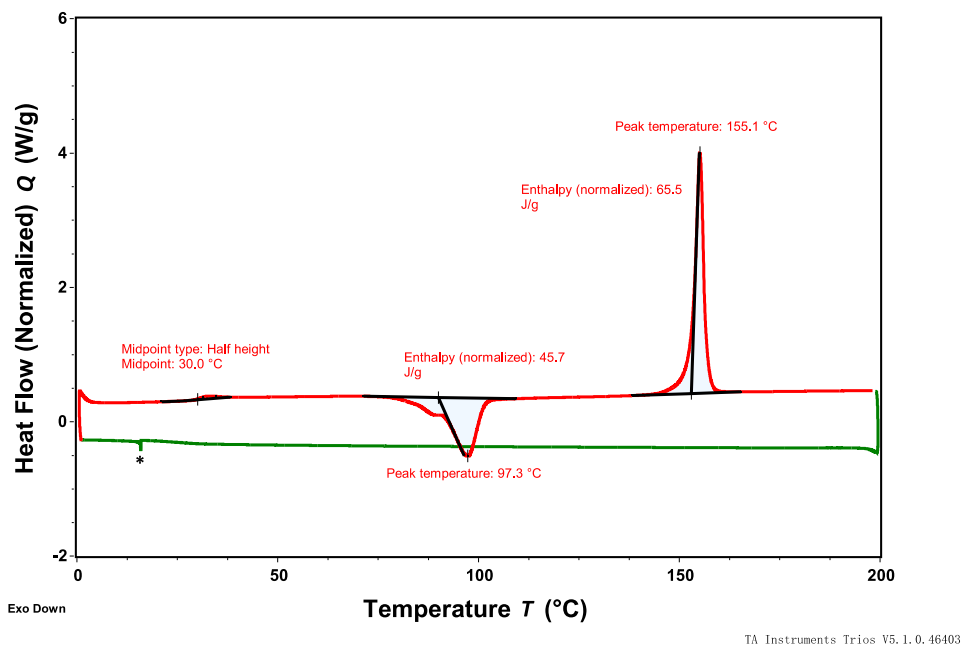


Figure S51. DSC data of **T1**(red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10 $^{\circ}\text{C}/\text{min}$, * means artifact).

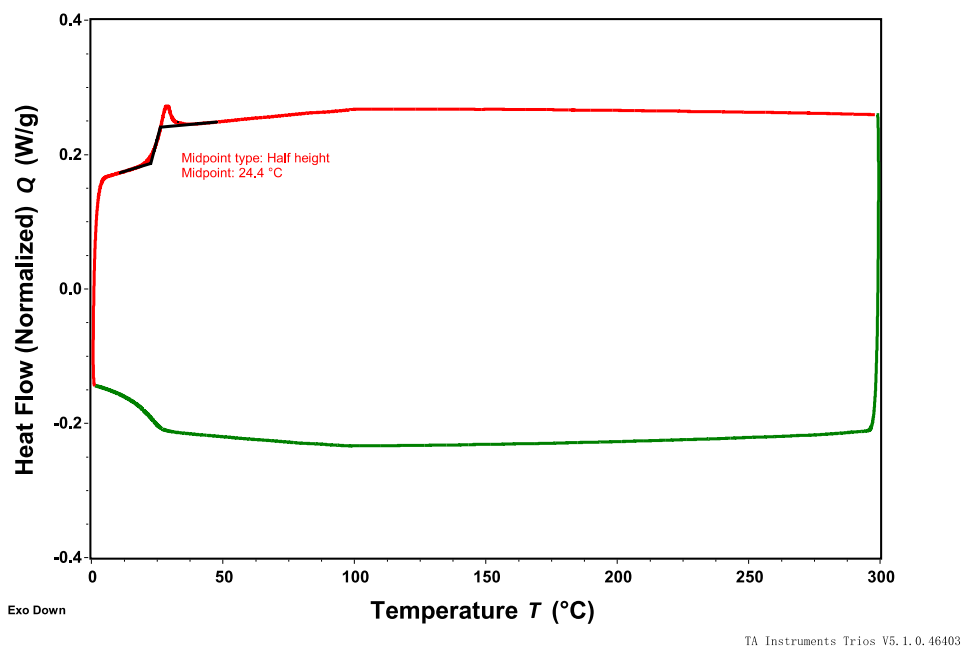


Figure S51. DSC data of **D2** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10 $^{\circ}\text{C}/\text{min}$).

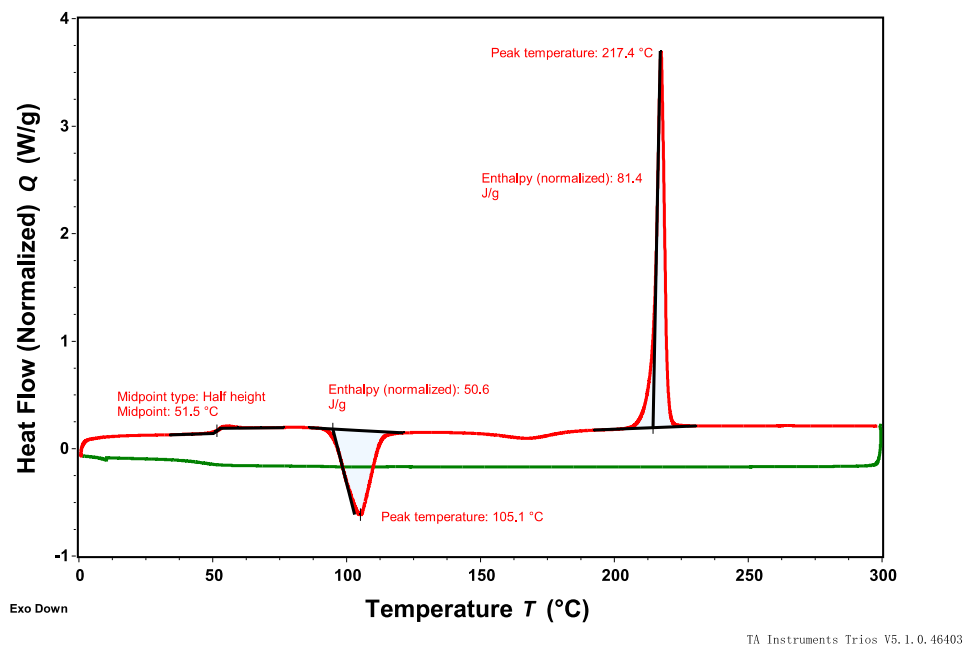


Figure S51. DSC data of **T2** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min).

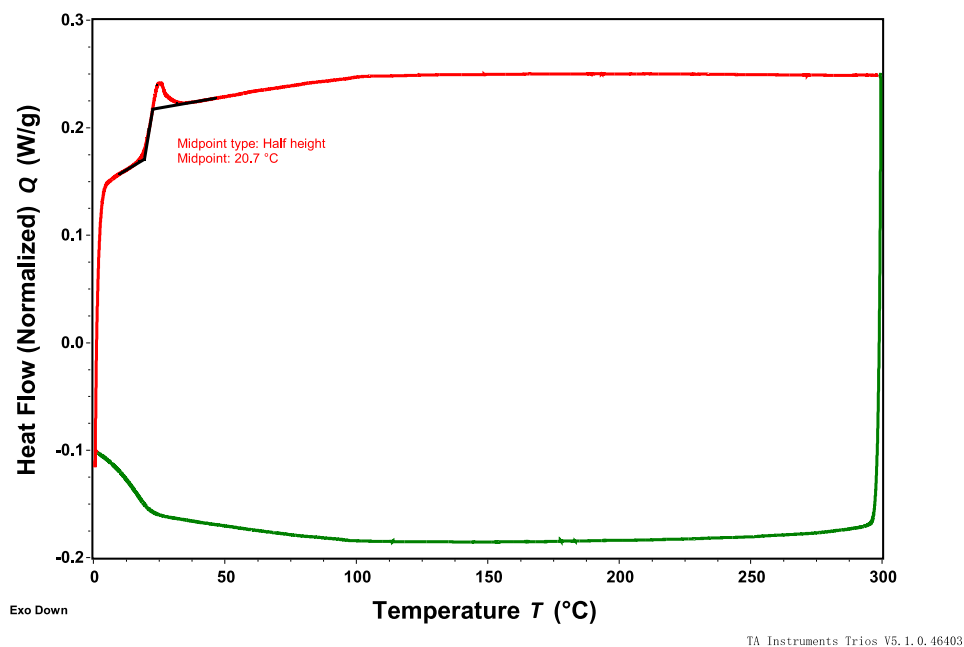


Figure S51. DSC data of **D3** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min).

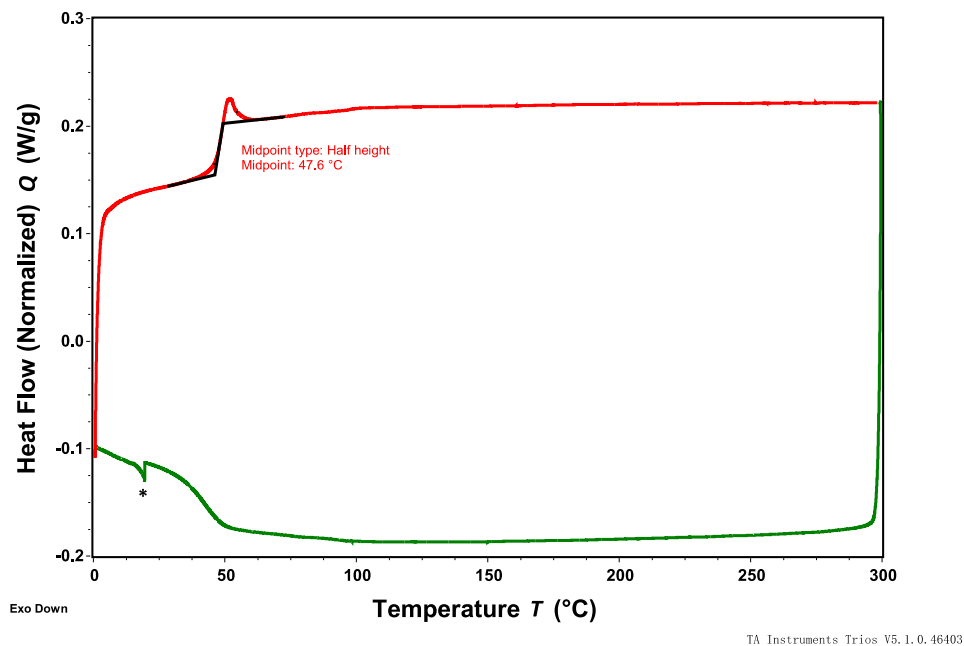


Figure S51. DSC data of T3 (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min, * means artifact).

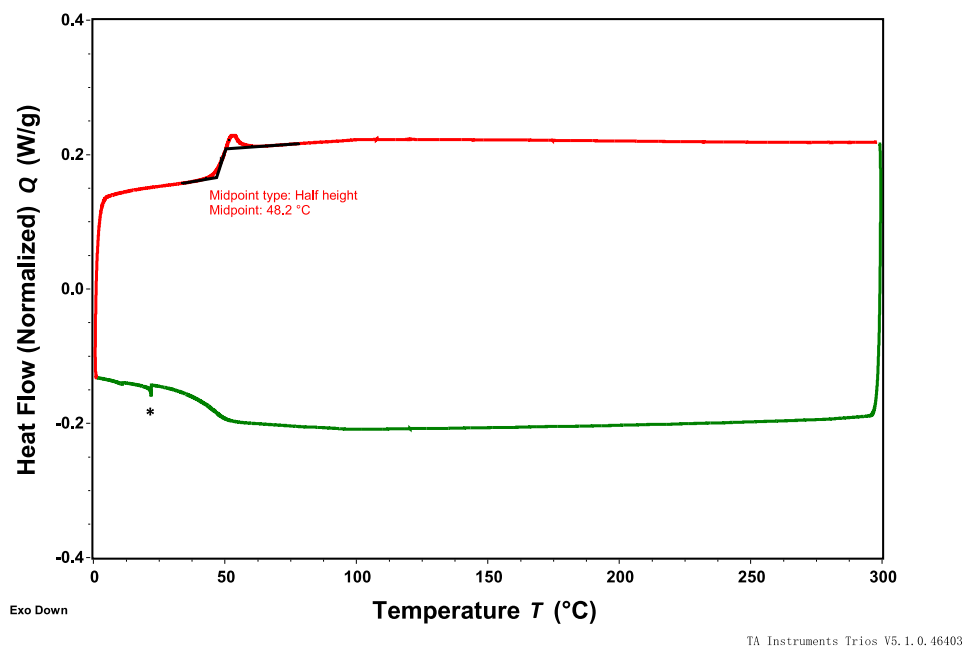


Figure S51. DSC data of T4 (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min, * means artifact).

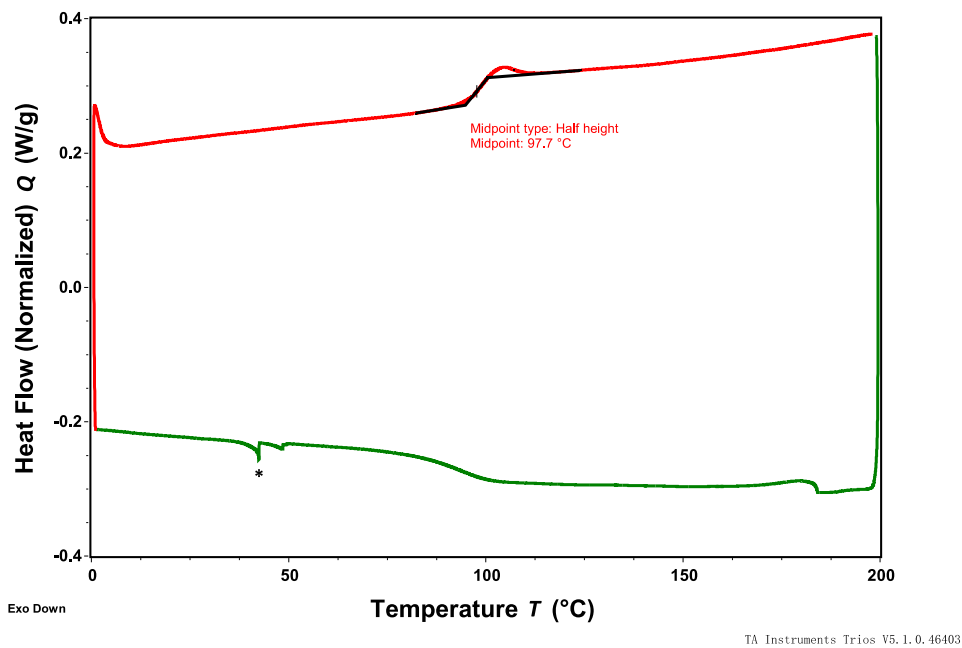


Figure S51. DSC data of **D5-Br** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min, * means artifact).

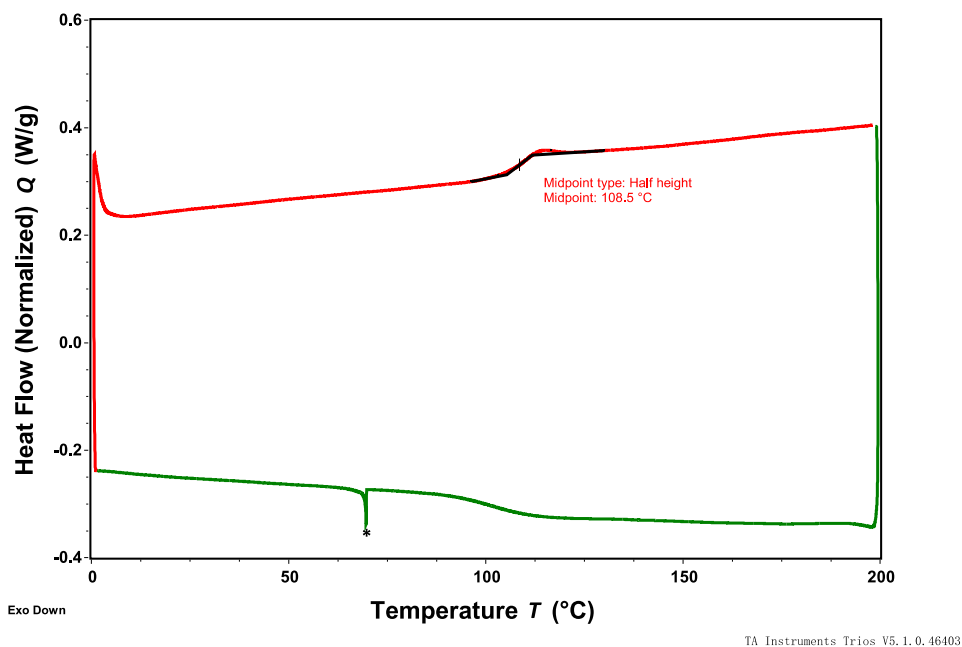


Figure S51. DSC data of **T6-Br** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min, * means artifact).

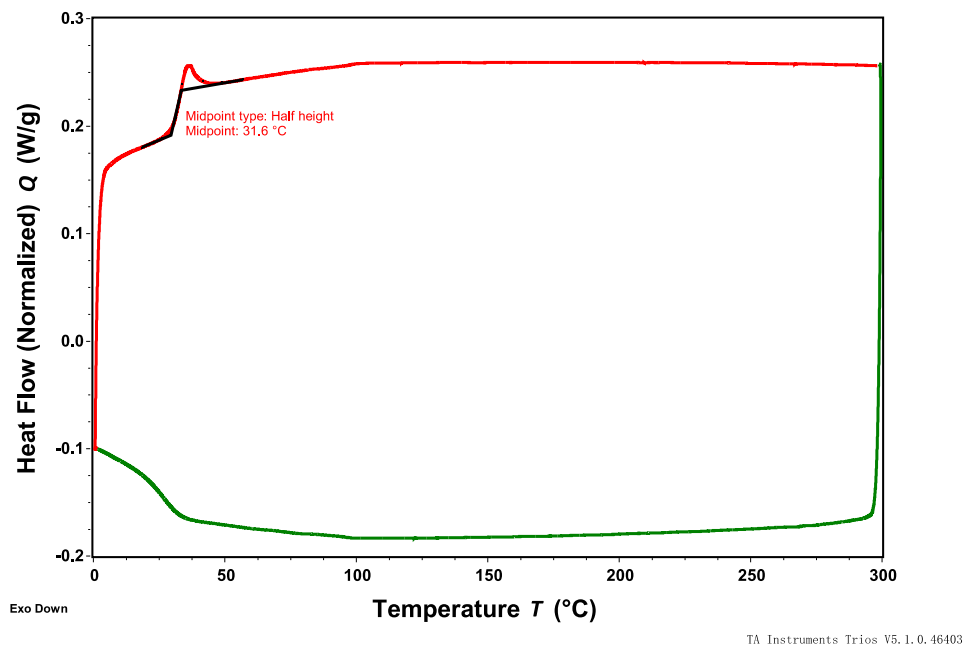


Figure S51. DSC data of **D4** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min).

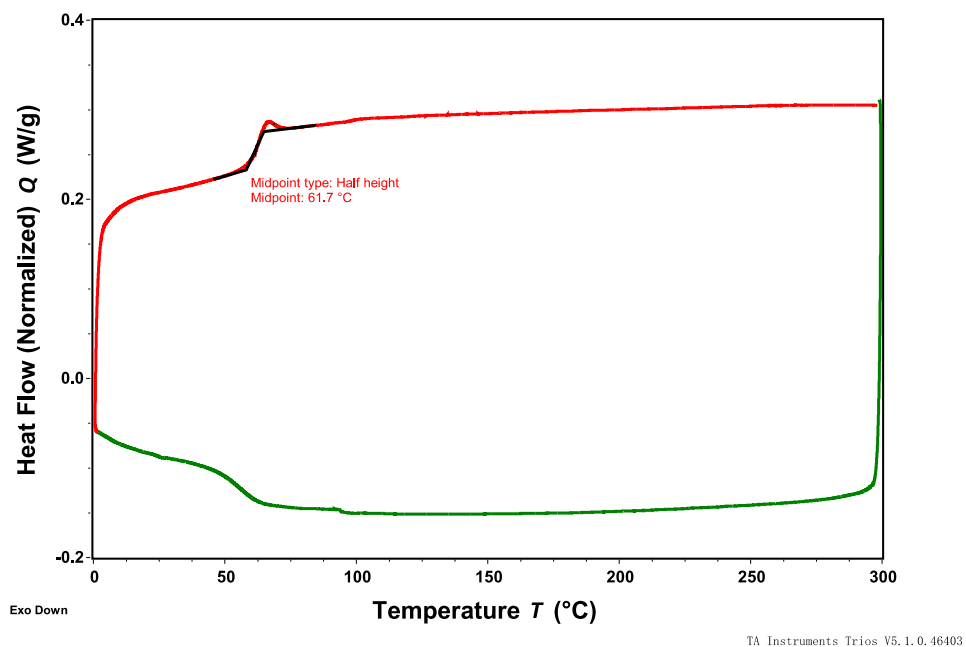


Figure S51. DSC data of **T5** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min).

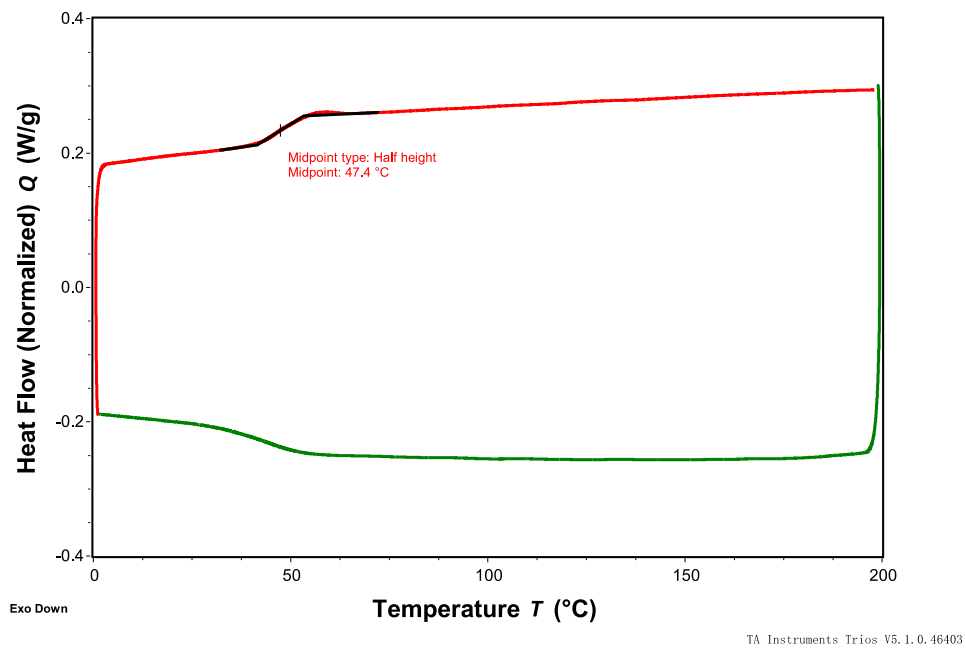


Figure S51. DSC data of **D5** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min).

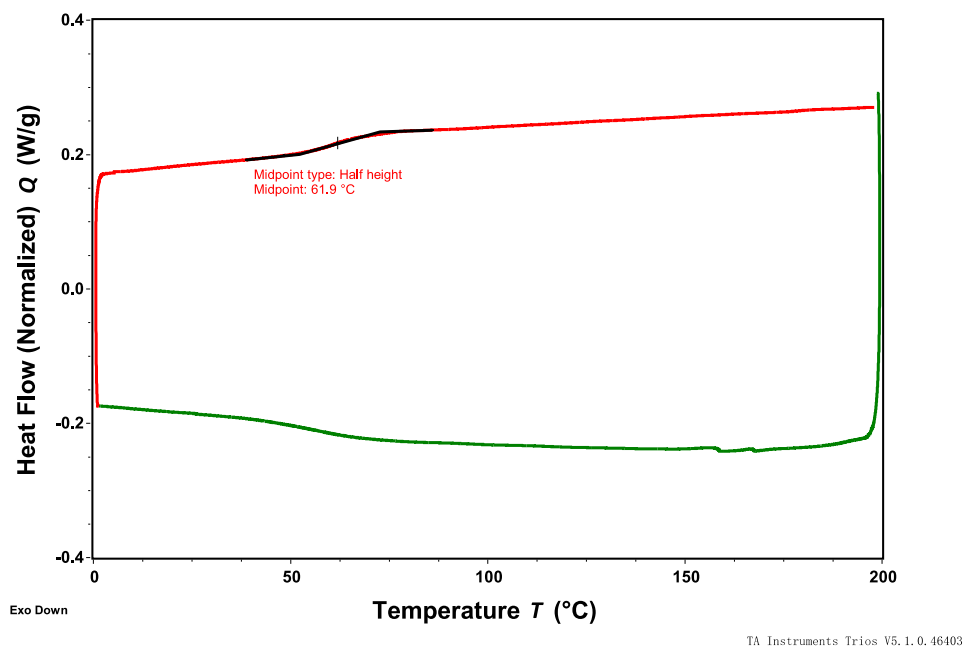


Figure S51. DSC data of **T6** (red line: the 2nd heating, green line: the 1st cooling, heating/cooling rate: 10°C/min).

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S1. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision E.01*, Gaussian Inc., Wallingford, CT, **2007**.