

Supplementary Information

An Efficient Direct Arylation Polycondensation via C-S Bond Cleavage

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I. Materials and Methods

I-1. General methods

All reactions were carried out in flame-dried glassware under nitrogen atmosphere with the exclusion of air and moisture using standard Schlenk line techniques or in glovebox (Etelux, Lab 2000). All solvents were purified by FLEANO solvent purification systems (FL-MD-5). Reactions were stirred using Teflon-coated magnetic stir bars. Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. Analytical thin-layer chromatography (TLC) was performed on silica gel GF254 plates. The TLC plates were visualized by ultraviolet light ($\lambda = 254$ nm). Purification of products was accomplished by column chromatography on silica gel.

Nuclear magnetic resonance (NMR) spectra were taken with JEOL JNM-ECZ500R (500 MHz) at room temperature unless otherwise noted and reported in parts per million (ppm). ^1H NMR spectra were internally referenced to tetramethylsilane (0.00 ppm), CDCl_3 (7.26 ppm), or $\text{C}_2\text{D}_2\text{Cl}_4$ (5.97 ppm), or d^8 -toluene (7.09, 7.01, 6.97, and 2.08 ppm). ^{13}C NMR spectra were internally referenced to tetramethylsilane (0.0 ppm), CDCl_3 (77.0 ppm), $\text{C}_2\text{D}_2\text{Cl}_4$ (73.8 ppm). Data was reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), and integration. Gel permeation chromatography (GPC) was performed with Agilent Technologies PL-GPC 220 at 150 °C using 1,2,4-trichlorobenzene (TCB) as an eluent at the flow rate of 1.0 mL/min.

ESI-MS spectra was obtained on a Q Exactive Focus LC-MS (Thermo Scientific Company, USA). Elemental analysis (EA) was performed on a UNICUBE elemental analyzer. Gas-chromatographic mass (GC-MS) spectrometry was tested by SHIMADZU GCMS-QP2020 NX, which was using helium as carrier gas and using anthracene as standard substance. UV-Vis absorption spectra were measured on a Gary 60 UV-Vis spectrophotometer. All film samples were spin casted on glass substrates. The electrochemical cyclic voltammetry (CV) was performed in a 0.10 M of tetrabutylammonium hexafluorophosphate ($n\text{-Bu}_4\text{NPF}_6$), dichloromethane solution as the supporting electrolyte with a scan speed at 50 mV/s. A Pt wire, glassy carbon discs, and Ag/AgCl were used as the counter electrode, working electrode, and reference electrode, respectively. A ferrocene/ferrocenium redox couple was used as an external standard. Thermal gravimetric analyzer (TGA) was tested on a Q50 at a heating rate of

10 °C·min⁻¹ under nitrogen atmosphere. FT-IR tests were performed on an infrared spectrometer (NICOLET iS50, Thermo Scientific Company, USA), taking 32 scans for each sample. OFETs characteristics were carried out in ambient using a Keysight B1500A semiconductor characterization system. ICP analysis was performed on ThermoICPOES7200 (ThermoFisher, USA) equipment.

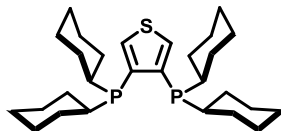
I-2. Materials

The *n*-butyllithium (2.5 M in hexane), KF, anthracene, 2-(methylthio)benzo[*d*]oxazole (**1c**), methyl(phenyl)sulfane (**1b**), 2-(methylthio)benzo[*b*]thiophene (**1f**), 2-bromobenzo[*b*]thiophene (**1g**), and benzo[*b*]thiophene (**2**) were purchased from Macklin Biochemical Technology Co., Ltd. The 3-hexylthiophene, 3,4-dibromothiophene, CuI, CuTc, K₂CO₃, 1,2-bis(dicyclohexylphosphanyl)benzene (dcypbz), 1,1'-bis(dicyclohexylphosphino)ferrocene (dcypf), *trans*-bis(acetato)bis[*o*-(di-*o*-tolylphosphino)benzyl]dipalladium(II) (Herrmann's Cat.), PdCl₂, Pd(PPh₃)₄, 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos), bromobenzene (**1e**), 1,4-dibromobenzene, 4,4'-dibromo-1,1'-biphenyl, 2,6-dibromonaphthalene, and thiophen-2-ylboronic acid, 2-bromo-3-dodecylthiophene were purchased from Bide Pharmatech Co., Ltd. The lithium diisopropylamide (2.0 M in hexane) was purchased from Beijing Inno Chem Science & Technology Co., Ltd. The chlorodicyclohexylphosphine was purchased from Shanghai Acme Biochemical Co., Ltd. The tris (dibenzylideneacetone)dipalladium (0) (Pd₂(dba)₃), bis(tri-*tert*-butylphosphine)palladium(0) (Pd(P^{*t*}Bu₃)₂), tris(2-methoxyphenyl)phosphane (P(*o*-MeOPh)₃), 3,3'-dihexyl-2,2'-bithiophene, and (*E*)-1,2-di(thiophen-2-yl)ethene (**N5**) were purchased from Tokyo Chemical Industry Co., Ltd. The 1,2-bis(dicyclohexylphosphino)ethane (dcype), KO^{*t*}Bu, CuBr₂, CuCl₂, Cu(OAc)₂, tricyclohexylphosphane (P(Cy)₃), tri(1-adamantyl)phosphine (P(Ad)₃), tri-*o*-tolylphosphane (P(*o*-tol)₃), 3,4-dibromothiophene, selenophene, thiazole, 2,2'-bithiophene, 3,3'''-didodecyl-2,2':5',2'':5'',2'''-quaterthiophene, *d*⁸-toluene, and D₂O were purchased from Anhui Zesheng Technology Co., Ltd. The Pd(MeCN)₂Cl₂, CuBr, CuCl, CuCN, 2,8-dibromodibenzo[*b,d*]thiophene, and benzo[1,2-*b*:4,5-*b'*]dithiophene (**N7**) were purchased from J&K Scientific Co., Ltd. The 2-bromo-3-(2-octyldodecyl)thiophene, and 4,4,9,9-tetrahexadecyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene (**N2**) were purchased from Derthon Optoelectronic Materials Science Technology Co., Ltd. The (*E*)-1,2-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)ethene was purchased from Solarmer Materials Inc Co., Ltd. Unless stated, all other reagents and chemicals were purchased from Suna Tech Inc Co., Ltd.

II. Preparation and Characterization of Substrates

II-1. Synthesis of ligands

3,4-Bis(dicyclohexylphosphino)thiophene (dcypt)



To a round-bottom glass flask containing a magnetic stirring bar was added a diethyl ether (15.0 mL) solution of 3,4-dibromothiophene (3.40 g, 14.0 mmol). After cooling to $-78\text{ }^{\circ}\text{C}$, a solution of *n*-butyllithium (*n*-BuLi) (14.0 mmol, 2.5 M in hexane, 5.6 mL) was added to the mixture in 20 min. After stirring the mixture at $-78\text{ }^{\circ}\text{C}$ for 1 h, a solution of chlorodicyclohexylphosphine (3.42 g, 14.7 mmol) in diethyl ether (10.0 mL) was added at $-78\text{ }^{\circ}\text{C}$ for 20 min. The resultant mixture was further stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. Then a solution of *n*-BuLi (14.0 mmol, 2.5 M in hexane, 5.6 mL) was added at $-78\text{ }^{\circ}\text{C}$ for 20 min. After stirring the mixture at $-78\text{ }^{\circ}\text{C}$ for 1 h, a solution of chlorodicyclohexylphosphine (3.42 g, 14.7 mmol) in diethyl ether (10.0 mL) was added at $-78\text{ }^{\circ}\text{C}$ for 20 min. The resultant mixture was further stirred at $-78\text{ }^{\circ}\text{C}$ for 30 min. After warming up to room temperature, the reaction was quenched with water, extracted with hexane. The combined organic phase was washed with brine, dried over Na_2SO_4 , and concentrated under reduced pressure, which was purified by reprecipitation from toluene (2.0 mL) in methanol (50.0 mL) to afford dcypt (3.62 g, 54%) as a white solid.

^1H NMR (500 MHz, CDCl_3): δ 7.39 (t, $J = 2.0\text{ Hz}$, 2H), 1.94-1.83 (m, 8H), 1.79-1.58 (m, 16H), 1.31-1.02 (m, 20H).

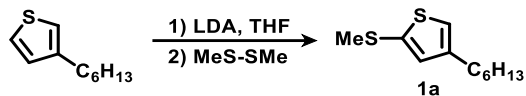
^{13}C NMR (125 MHz, CDCl_3): δ 141.5 (d, $J = 9.8\text{ Hz}$), 128.5, 34.4 (t, $J = 5.1\text{ Hz}$), 30.2 (t, $J = 8.3\text{ Hz}$), 28.9 (t, $J = 4.3\text{ Hz}$), 27.2-27.1 (m), 26.4.

^{31}P NMR (202 MHz, CDCl_3): δ -20.6.

The NMR spectra are matching with the reference¹.

II-2. Synthesis of monomers

4-Hexyl-2-(methylthio)thiophene (1a)



To a THF (20.0 mL) solution of 3-hexylthiophene (2.02 g, 12.0 mmol) was added lithium diisopropylamide (LDA) (13.2 mmol, 2.0 M in hexane, 6.6 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (1.36 g, 14.4 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane) to afford **1a** (2.36 g, 92%) as a colorless oil.

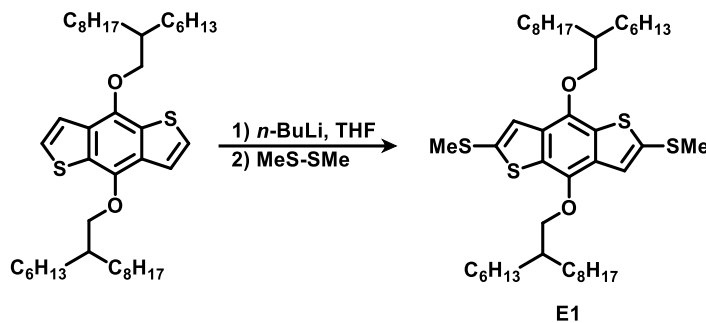
¹H NMR (500 MHz, CDCl₃): δ 6.90 (d, *J* = 1.5 Hz, 1H), 6.88 (s, 1H), 2.55 (t, *J* = 8.0 Hz, 2H), 2.48 (s, 3H), 1.61-1.55 (m, 2H), 1.35-1.26 (m, 6H), 0.90 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 143.7, 136.5, 132.2, 122.4, 31.6, 30.5, 30.3, 28.9, 22.6, 22.1, 14.1.

HRMS (ESI) *m/z* calcd for C₁₁H₁₈S₂ [M]⁺: 214.0844, found 214.0836.

The NMR spectra are matching with the reference².

4,8-Bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-bis(methylthio) (**E1**)



To a THF (50.0 mL) solution of 4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (6.71 g, 10.0 mmol) was added *n*-BuLi (30.0 mmol, 2.5 M in hexane, 12.0 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (3.30 g, 35.0 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 20:1, *v/v*) to afford **E1** (7.25

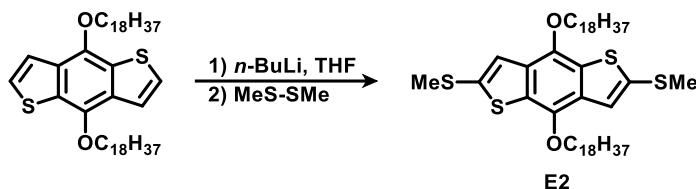
g, 95%) as a white solid.

^1H NMR (500 MHz, CDCl_3): δ 7.27 (s, 2H), 4.09 (d, J = 5.5 Hz, 4H), 2.62 (s, 6H), 1.84-1.80 (m, 2H), 1.63-1.56 (m, 4H), 1.50-1.25 (m, 44H), 0.91-0.87 (m, 12H).

^{13}C NMR (125 MHz, CDCl_3): δ 142.8, 138.8, 131.2, 130.6, 120.8, 76.3, 39.1, 31.9, 31.2, 30.1, 29.8, 29.7, 29.4, 27.0, 27.0, 22.7, 20.0, 14.1.

HRMS (ESI) m/z calcd for $\text{C}_{44}\text{H}_{74}\text{S}_4\text{O}_2 + \text{Na}$ $[\text{M} + \text{Na}]^+$: 785.4463, found 785.4434.

4,8-Bis(octadecyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-bis(methylthio) (E2)



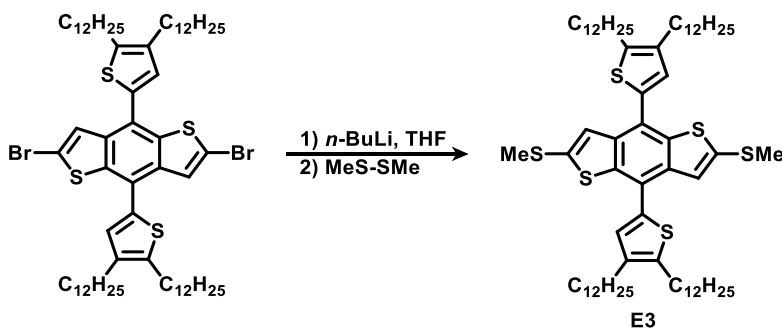
To a THF (25.0 mL) solution of 4,8-bis(octadecyloxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (3.64 g, 5.0 mmol) was added *n*-BuLi (15.0 mmol, 2.5 M in hexane, 6.0 mL) dropwise at $-78\text{ }^\circ\text{C}$ under nitrogen atmosphere. The reaction mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h before the slow addition of dimethyldisulfide (1.65 g, 17.5 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 15:1, v/v) to afford **E2** (3.77 g, 92%) as a dark yellow solid.

^1H NMR (500 MHz, CDCl_3): δ 7.28 (s, 2H), 4.21 (t, J = 7.0 Hz, 4H), 2.62 (s, 6H), 1.87-1.81 (m, 4H), 1.56-1.50 (m, 4H), 1.40-1.22 (m, 50H), 0.89-0.86 (m, 12H).

^{13}C NMR (125 MHz, CDCl_3): δ 142.7, 138.9, 131.3, 130.8, 120.9, 73.9, 31.9, 30.5, 29.7, 29.7, 29.6, 29.5, 29.4, 26.0, 22.7, 20.0, 14.1.

HRMS (ESI) m/z calcd for $\text{C}_{48}\text{H}_{82}\text{S}_4\text{O}_2$ $[\text{M}]^+$: 818.5192, found 818.5164.

4,8-Bis(4,5-didodecylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-bis(methylthio) (E3)



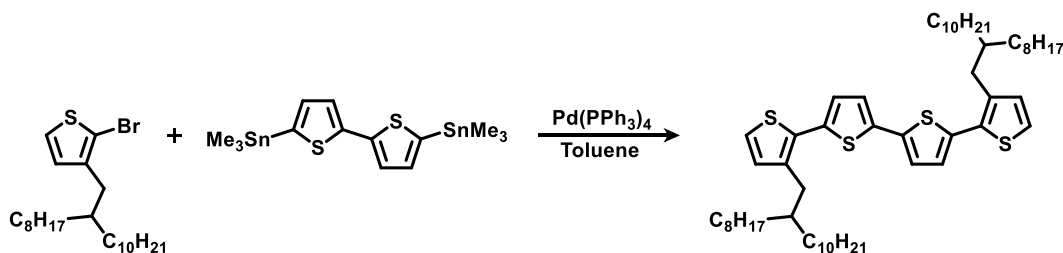
To a THF (30.0 mL) solution of 4,8-bis(4,5-didodecylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene-2,6-dibromo (2.37 g, 2.0 mmol) was added *n*-BuLi (6.0 mmol, 2.5 M in hexane, 2.4 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (0.66 g, 7.0 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 10:1, v/v) to afford **E3** (2.01 g, 90%) as a light yellow solid.

¹H NMR (500 MHz, CDCl₃): δ 7.48 (s, 2H), 7.14 (s, 2H), 2.82 (t, *J* = 7.5 Hz, 4H), 2.60 (t, *J* = 7.5 Hz, 4H), 2.57 (s, 6H), 1.75-1.69 (m, 4H), 1.66 (m, 4H), 1.47-1.27 (m, 72H), 0.89-0.86 (m, 12H).

¹³C NMR (125 MHz, CDCl₃): δ 140.3, 140.1, 139.7, 138.2, 136.0, 134.6, 129.8, 123.9, 122.4, 31.9, 31.8, 30.8, 29.7, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 28.3, 28.0, 22.7, 19.8, 14.1.

HRMS (ESI) *m/z* calcd for C₆₈H₁₁₀S₆+K [M+K]⁺: 1157.6563, found 1157.6604.

3,3'''-Bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene



Under nitrogen atmosphere, a mixture of 2-bromo-3-(2-octyldodecyl)thiophene (3.20 g, 7.2 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (1.78 g, 3.6 mmol), and Pd(PPh₃)₄ (231.2 mg, 0.2 mmol) in anhydrous toluene (36.0 mL) was stirred at 110 °C for 12 h. After cooling to room temperature, the solution was quenched with saturated KF solution and extracted with dichloromethane for three times.

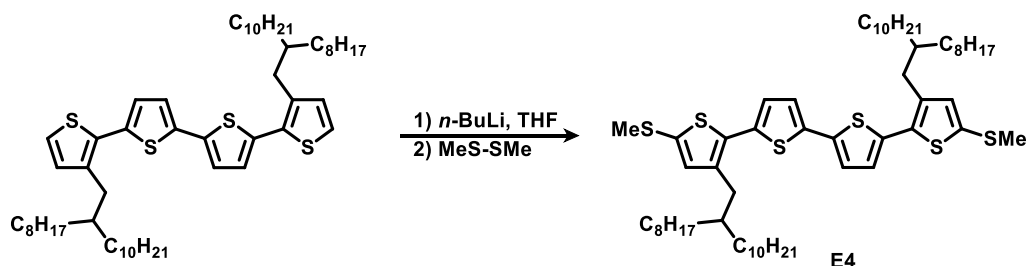
Afterwards, the combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 15:1, v/v) to afford 3,3'''-bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene (1.96 g, 61%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 7.19 (d, *J* = 6.5 Hz, 2H), 7.12 (d, *J* = 5.0 Hz, 2H), 7.02 (d, *J* = 5.0 Hz, 2H), 6.91 (d, *J* = 6.5 Hz, 2H), 2.73 (d, *J* = 9.0 Hz, 4H), 1.74-1.64 (m, 2H), 1.33-1.15 (m, 60H), 0.90-0.85 (m, 12H).

¹³C NMR (125 MHz, CDCl₃): δ 139.1, 136.9, 135.2, 130.8, 130.6, 126.8, 123.7, 123.6, 38.9, 33.7, 33.4, 31.9, 30.1, 29.7, 29.7, 29.4, 26.5, 22.7, 14.1.

The NMR spectra are matching with the reference³.

5,5'''-Bis(methylthio)-3,3'''-bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene (E4)



To a THF (30.0 mL) solution of 3,3'''-bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene (0.89 g, 1.0 mmol) was added *n*-BuLi (3.0 mmol, 2.5 M in hexane, 1.2 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (0.33 g, 3.5 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 10:1, v/v) to afford **E4** (0.69 g, 70%) as a yellow solid.

¹H NMR (500 MHz, CDCl₃): δ 7.09 (d, *J* = 4.0 Hz, 2H), 6.97 (d, *J* = 4.0 Hz, 2H), 6.85 (s, 2H), 2.65 (d, *J* = 7.0 Hz, 4H), 2.51 (s, 6H), 1.69-1.61 (m, 2H), 1.33-1.15 (m, 60H), 0.89-0.86 (m, 12H).

¹³C NMR (125 MHz, CDCl₃): δ 139.5, 136.9, 135.4, 134.7, 133.8, 132.7, 126.8, 123.7, 38.8, 33.8, 33.4, 31.9, 30.0, 29.7, 29.7, 29.6, 29.4, 29.3, 26.5, 22.7, 21.7, 14.1.

HRMS (ESI) m/z calcd for $C_{58}H_{94}S_6$ $[M]^+$: 982.5674, found 982.5629.

2,5-Bis(5-(methylthio)-3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene (E5)



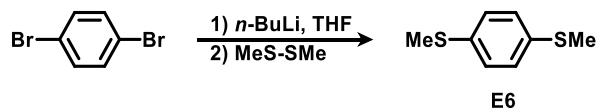
To a THF (20.0 mL) solution of 2,5-bis(3-tetradecylthiophen-2-yl)thieno[3,2-*b*]thiophene (0.91 g, 1.3 mmol) was added *n*-BuLi (4.0 mmol, 2.5 M in hexane, 1.6 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (0.43 g, 4.6 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 10:1, *v/v*) to afford **E5** (0.87 g, 85%) as a yellow solid.

1H NMR (500 MHz, $CDCl_3$): δ 7.19 (s, 2H), 6.90 (s, 2H), 2.73 (t, J = 7.5 Hz, 4H), 2.52 (s, 6H), 1.66-1.60 (m, 4H), 1.41-1.20 (m, 44H), 0.90-0.85 (m, 6H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 139.1, 137.2, 136.2, 133.1, 132.5, 117.9, 31.9, 30.6, 29.7, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 22.7, 21.6, 14.1.

HRMS (ESI) m/z calcd for $C_{44}H_{68}S_6$ $[M]^+$: 788.3639, found 788.3615.

1,4-bis(methylthio)benzene (E6)



To a THF (30.0 mL) solution of 1,4-dibromobenzene (1.18 g, 5.0 mmol) was added *n*-BuLi (15.0 mmol, 2.5 M in hexane, 6.0 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1h before the slow addition of dimethyldisulfide (1.41 g, 15.0 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane:

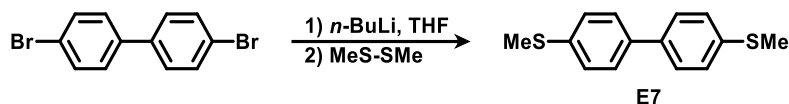
dichloromethane = 5:1, v/v) to afford **E6** (0.38 g, 45%) as a white solid.

^1H NMR (500 MHz, CDCl_3): δ 7.20 (dd, J = 4.5, 2.0 Hz, 4H), 2.47 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3): 134.2, 127.5, 17.0.

The NMR spectra are matching with the reference⁴.

4,4'-Bis(methylthio)-1,1'-biphenyl (**E7**)



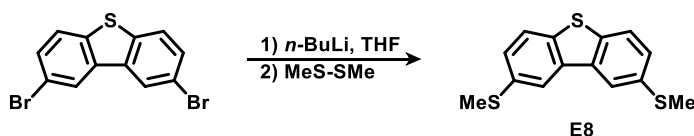
To a THF (30.0 mL) solution of 4,4'-dibromo-1,1'-biphenyl (0.94 g, 3.0 mmol) was added *n*-BuLi (9.0 mmol, 2.5 M in hexane, 3.6 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (0.99 g, 10.5 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 2:1, v/v) to afford **E7** (0.59 g, 80%) as a white solid.

^1H NMR (500 MHz, CDCl_3): δ 7.51-7.49 (m, 4H), 7.33-7.31 (m, 4H), 2.52 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3): δ 137.5, 137.3, 127.1, 126.9, 15.9.

The NMR spectra are matching with the reference⁵.

2,8-bis(methylthio)dibenzo[*b,d*]thiophene (**E8**)



To a THF (15.0 mL) solution of 2,8-dibromodibenzo[*b,d*]thiophene (0.34 g, 1.0 mmol) was added *n*-BuLi (3.0 mmol, 2.5 M in hexane, 1.2 mL) dropwise at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1 h before the slow addition of dimethyldisulfide (0.28 g, 3.0 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica

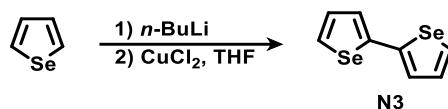
gel (hexane: dichloromethane = 5:1, v/v) to afford **E8** (0.17 g, 61%) as a white solid.

^1H NMR (500 MHz, CDCl_3): 8.01 (d, J = 1.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.41 (dd, J = 8.5, 2.0 Hz, 2H), 2.60 (s, 6H).

^{13}C NMR (125 MHz, CDCl_3): 137.1, 135.5, 134.6, 126.8, 124.1, 120.2, 16.5.

The NMR spectra are matching with the reference⁶.

2,2'-Biselenophene (**N3**)



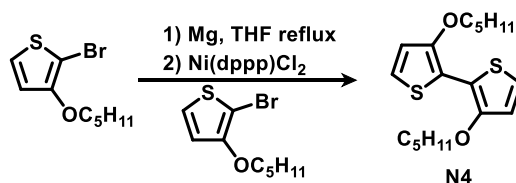
In a flame-dried three-neck-flask selenophene (0.92 g, 7.0 mmol) was dissolved in THF (30.0 mL) and cooled to $-78\text{ }^\circ\text{C}$. After a dropwise addition of $n\text{-BuLi}$ (7.0 mmol, 2.5 M in hexane, 2.8 mL), the reaction was stirred for 1 h at $0\text{ }^\circ\text{C}$. The solution was cooled again to $-78\text{ }^\circ\text{C}$ and CuCl_2 (1.41 g, 10.5 mmol) was added in small portions. After the reaction was stirred overnight at room temperature, the mixture was diluted with THF (15.0 mL), and then filtered over celite in THF (5.0 mL). Then the organic phase was washed with water, 1.0 M of HCl solution, NaHCO_3 (10 wt%) solution and water. Next, the solution was dried over anhydrous Na_2SO_4 , filtered, concentrated under reduced pressure and purified by flash column chromatography on silica gel (hexane only) to afford **N3** (0.46 g, 50%) as a colorless oil.

^1H NMR (500 MHz, CDCl_3): δ 7.88 (dd, J = 6.0, 1.0 Hz, 2H), 7.28 (dd, J = 4.0, 1.0 Hz, 2H), 7.24 (dd, J = 5.5, 3.5 Hz, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ 144.8, 130.2, 129.7, 126.7.

The NMR spectra are matching with the reference⁷.

3,3'-Bis(pentyloxy)-2,2'-bithiophene (**N4**)



A THF (5.0 mL) solution of 2-bromo-3-(pentyloxy)thiophene (0.75 g, 3.0 mmol) was added slowly over a period of 20 min to a mechanically stirred suspension of magnesium turnings (102.1 mg, 4.2 mmol) in THF (15.0 mL) in a round-bottomed flask (100 mL) under nitrogen atmosphere. The resultant mixture was stirred at room temperature for 1 h, then at $50\text{ }^\circ\text{C}$ for 20 min before cooling down to room temperature. The resultant mixture was then transferred via a cannula to a mixture of 2-bromo-3-(pentyloxy)thiophene

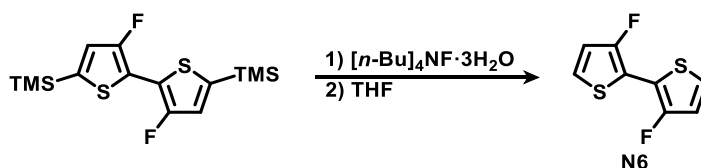
(0.75 g, 3.0 mmol) and [1,3-bis(diphenylphosphinoethane)]dichloronickel(II) (16.3 mg, 0.03 mmol) in THF (10.0 mL) in a 100 mL round-bottomed flask under an inert atmosphere, and refluxed overnight. Subsequently, the reaction mixture was diluted with dichloromethane (20.0 mL), washed twice with water and with 5 wt% aqueous HCl solution, and dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 10:1, v/v) to afford **N4** (0.41 g, 40%) as a pale yellow solid.

¹H NMR (500 MHz, CDCl₃): δ 7.08 (d, *J* = 5.5 Hz, 2H), 6.84 (d, *J* = 5.5 Hz, 2H), 4.11 (t, *J* = 6.5 Hz, 4H), 1.89-1.83 (m, 4H), 1.55-1.48 (m, 4H), 1.44-1.36 (m, 4H), 0.95 (t, *J* = 7.5 Hz, 6H).

¹³C NMR (125 MHz, CDCl₃): δ 151.9, 121.6, 116.0, 114.1, 72.0, 29.4, 28.2, 22.4, 14.0.

The NMR spectra are matching with the reference⁸.

3,3'-Difluoro-2,2'-bithiophene (N6)



To a THF (50.0 mL) solution of (3,3'-difluoro-[2,2'-bithiophene]-5,5'-diyl)bis(trimethylsilane) (1.04 g, 3.0 mmol) was added tetrabutylammonium fluoride trihydrate solution (6.0 mmol, 1.0 M in THF, 6.0 mL) at 0 °C. The mixture was allowed to warm to room temperature and stirred overnight. After quenching with water, the mixture was extracted with hexane, washed with water, dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane only) to afford **N6** (0.56 g, 92%) as a white solid.

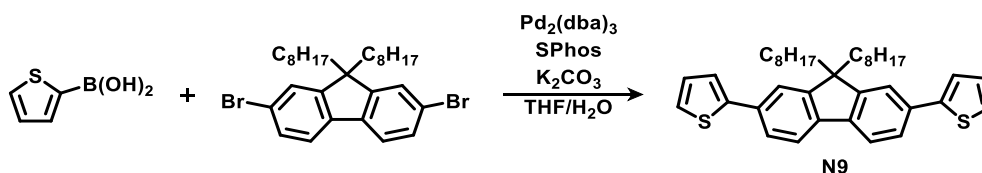
¹H NMR (500 MHz, CDCl₃): δ 7.19 (dd, *J* = 5.5, 3.0 Hz, 2H), 6.86 (d, *J* = 5.5 Hz, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 155.0, 152.9, 123.2 (t, *J* = 7.9 Hz), 117.3 (d, *J* = 26.6 Hz).

¹⁹F NMR (470 MHz, CDCl₃): δ -127.30.

The NMR spectra are matching with the reference⁹.

2,2'-(9,9-Dioctyl-9H-fluorene-2,7-diyl)dithiophene (N9)



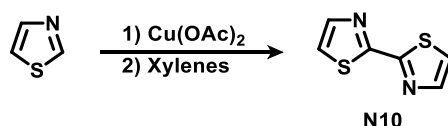
A degassed THF/H₂O (2:1, v:v, 10.0 mL) solution of 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (2.19 g, 4.0 mmol), thiophen-2-ylboronic acid (1.54 g, 12.0 mmol), K₂CO₃ (2.21 g, 16.0 mmol), Pd₂(dba)₃ (73.3 mg, 0.08 mmol), and SPhos (115.3 mg, 0.16 mmol) was stirred under nitrogen atmosphere at 70 °C for 18 h. After the reaction mixture was cooled to room temperature and extracted with ethyl acetate (20.0 mL × 3), the combined organic layers were dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. Next, the residue was purified by silica gel (hexane only) to afford **N9** (2.00 g, 90%) as a colorless oil.

¹H NMR (500 MHz, CDCl₃): δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.57 (s, 2H), 7.40 (d, *J* = 3.5 Hz, 2H), 7.30 (d, *J* = 5.0 Hz, 2H), 7.13 (t, *J* = 4.0 Hz, 2H), 2.04-2.01 (m, 4H), 1.20-1.06 (m, 20H), 0.81 (t, *J* = 7.0 Hz, 6H), 0.70-0.66 (m, 4H).

¹³C NMR (125 MHz, CDCl₃): δ 151.7, 145.1, 140.2, 133.2, 128.0, 124.9, 124.5, 122.9, 120.1, 120.0, 55.2, 53.4, 40.4, 31.8, 30.0, 29.2, 23.7, 22.6, 14.0.

The NMR spectra are matching with the reference¹⁰.

2,2'-Bithiazole (N10)



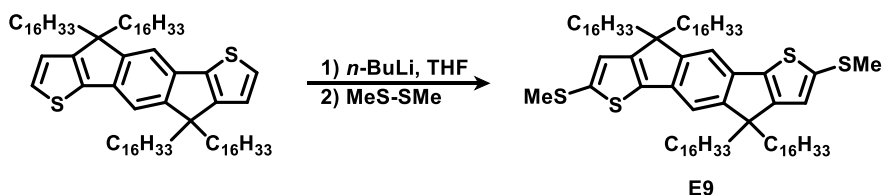
In a sealed, nitrogen-purged pressure vessel, thiazole (0.85 g, 10.0 mmol) and Cu(OAc)₂ (0.36 g, 2.0 mmol) were dissolved in xylenes (33.0 mL). Then the mixture was stirred at 140 °C for 16 h in a sealed pressure vial, then cooled to room temperature and depressurized in air for 10 min before being resealed and stirred at 140 °C for 16 h. Next, the reaction was concentrated and purified by silica gel (hexane: EtOAc = 4:1, v/v) to afford **N10** (0.46 g, 55%) as an off-white solid.

¹H NMR (500 MHz, CDCl₃): δ 7.89 (d, *J* = 3.0 Hz, 2H), 7.44 (d, *J* = 3.0 Hz, 2H).

¹³C NMR (125 MHz, CDCl₃): δ 161.6, 143.9, 120.9.

The NMR spectra are matching with the reference¹¹.

4,4,9,9-tetrahexadecyl-2,7-bis(methylthio)-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene (E9)



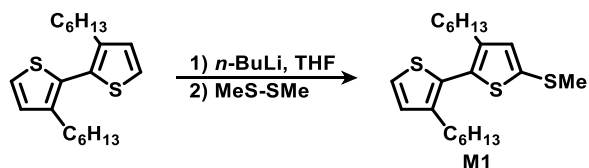
To a THF (20.0 mL) solution of 4,4,9,9-tetrahexadecyl-4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b'*]dithiophene (0.70 g, 0.6 mmol) was added *n*-BuLi (1.8 mmol, 2.5 M in hexane, 0.7 mL) dropwise at 0 °C under nitrogen atmosphere. The reaction mixture was stirred at 0 °C for 1h before the slow addition of dimethyldisulfide (0.20 g, 2.1 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane only) to afford **E9** (0.41 g, 54%) as a pale yellow solid.

¹H NMR (500 MHz, CDCl₃): δ 7.20 (s, 2H), 7.00 (s, 2H), 2.53 (s, 6H), 1.95-1.89 (m, 4H), 1.84-1.78 (m, 4H), 1.32-1.05 (m, 112H), 0.89-0.86 (m, 12H).

¹³C NMR (125 MHz, CDCl₃): δ 154.6, 152.6, 144.1, 137.8, 135.7, 127.1, 113.0, 54.2, 39.0, 31.9, 30.0, 29.7, 29.7, 29.6, 29.6, 29.4, 24.1, 23.3, 22.7, 14.1.

HRMS (ESI) *m/z* calcd for C₈₂H₁₄₂S₄ [M]⁺: 1254.9989, found 1254.9979.

3,3'-Dihexyl-5-(methylthio)-2,2'-bithiophene (**M1**)



To a THF (10.0 mL) solution of 3,3'-dihexyl-2,2'-bithiophene (1.00 g, 3.0 mmol) was added *n*-BuLi (3.3 mmol, 2.5 M in hexane, 1.3 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before slow addition of dimethyldisulfide (0.34 g, 3.6 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane only) to afford **M1** (0.96 g, 84%) as a colorless oil.

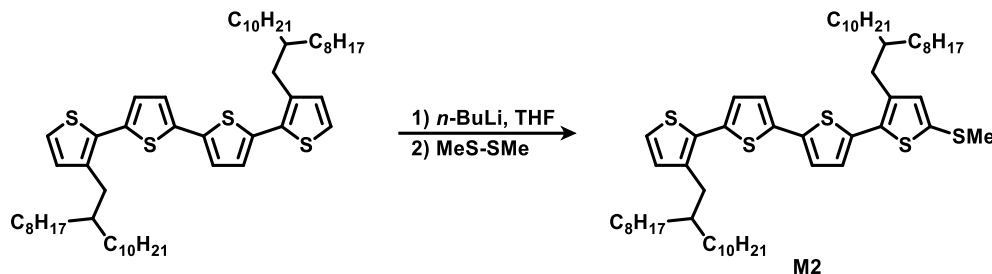
¹H NMR (500 MHz, CDCl₃): δ 7.28 (d, *J* = 5.0 Hz, 1H), 6.95 (d, *J* = 5.0 Hz, 1H), 6.91 (s, 1H), 2.51 (s, 3H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.44 (t, *J* = 7.5 Hz, 2H), 1.56-1.48 (m, 4H), 1.30-1.18 (m, 12H), 0.87-0.84 (m, 6H).

¹³C NMR (125 MHz, CDCl₃): δ 142.8, 142.5, 136.6, 131.8, 130.7, 128.6, 128.2, 125.4, 31.6, 31.6,

30.7, 30.6, 29.1, 29.1, 28.8, 28.8, 22.6, 22.5, 21.6, 14.1.

HRMS (ESI) m/z calcd for $C_{21}H_{32}S_3$ $[M]^+$: 380.1660, found 380.1644.

5-(Methylthio)-3,3'''-bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene (M2)



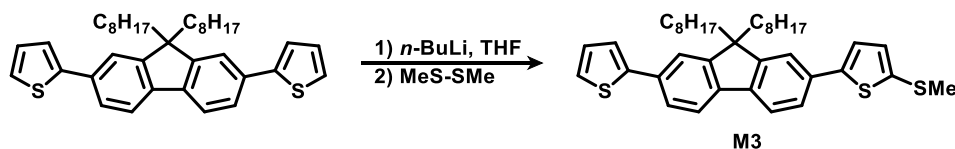
To a THF (20.0 mL) solution of 3,3'''-bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene (0.89 g, 1.0 mmol) was added *n*-BuLi (1.0 mmol, 2.5 M in hexane, 0.4 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (0.11 g, 1.2 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 15:1, v/v) to afford **M2** (0.59 g, 63%) as a yellow oil.

1H NMR (500 MHz, $CDCl_3$): δ 7.19 (d, J = 5.0 Hz, 1H), 7.11 (dd, J = 5.0, 4.0 Hz, 2H), 7.02 (d, J = 3.5 Hz, 1H), 6.98 (d, J = 3.5 Hz, 1H), 6.91 (d, J = 5.5 Hz, 1H), 6.86 (s, 1H), 2.73 (d, J = 7.5 Hz, 2H), 2.66 (d, J = 7.0 Hz, 2H), 2.52 (s, 3H), 1.74-1.62 (m, 2H), 1.33-1.15 (m, 60H), 0.90-0.86 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 139.5, 139.2, 137.1, 136.8, 135.4, 134.6, 133.8, 132.7, 130.7, 130.6, 126.8, 126.8, 123.7, 123.7, 123.6, 38.9, 38.8, 33.8, 33.7, 33.4, 31.9, 30.0, 29.7, 29.7, 29.6, 29.4, 29.4, 26.5, 22.7, 21.7, 14.1.

HRMS (ESI) m/z calcd for $C_{57}H_{92}S_5$ $[M]^+$: 936.5797, found 936.5789.

2-(9,9-Dioctyl-7-(thiophen-2-yl)-9H-fluoren-2-yl)-5-(methylthio)thiophene (M3)



To a THF (20.0 mL) solution of 2,2'-(9,9-dioctyl-9H-fluorene-2,7-diyl)dithiophene (1.11 g, 2.0 mmol) was added *n*-BuLi (2.3 mmol, 2.5 M in hexane, 0.9 mL) dropwise at -78 °C under nitrogen

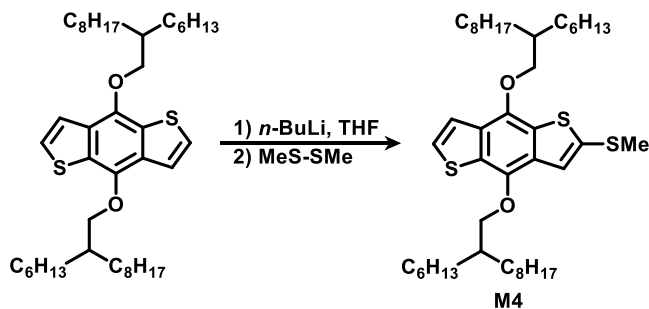
atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (0.23 g, 2.4 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane: dichloromethane = 30:1, v/v) to afford **M3** (0.73 g, 61%) as a yellow oil.

¹H NMR (500 MHz, CDCl₃): δ 7.68 (d, *J* = 2.5 Hz, 1H), 7.67 (d, *J* = 3.0 Hz, 1H), 7.61 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.56 (d, *J* = 1.0 Hz, 1H), 7.55 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.49 (d, *J* = 1.5 Hz, 1H), 7.39 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.30 (dd, *J* = 5.0, 0.5 Hz, 1H), 7.23 (d, *J* = 4.0 Hz, 1H), 7.12 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.08 (d, *J* = 3.5 Hz, 1H), 2.55 (s, 3H), 2.02-1.99 (m, 4H), 1.20-1.06 (m, 20H), 0.80 (t, *J* = 7.5 Hz, 6H), 0.72-0.61 (m, 4H).

¹³C NMR (125 MHz, CDCl₃): δ 151.7, 151.7, 147.4, 145.1, 140.4, 140.1, 136.2, 133.3, 132.8, 132.2, 128.0, 124.9, 124.6, 124.5, 123.0, 122.9, 120.1, 119.8, 55.3, 40.4, 31.8, 29.9, 29.2, 29.1, 23.7, 22.6, 22.3, 14.0.

HRMS (ESI) *m/z* calcd for C₃₈H₄₈S₃ [M]⁺: 600.2912, found 600.2888.

4,8-Bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene-2-(methylthio) (**M4**)



To a THF (20.0 mL) solution of 4,8-bis((2-hexyldecyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (0.94 g, 1.4 mmol) was added *n*-BuLi (1.5 mmol, 2.5 M in hexane, 0.6 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (0.16 g, 1.7 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified

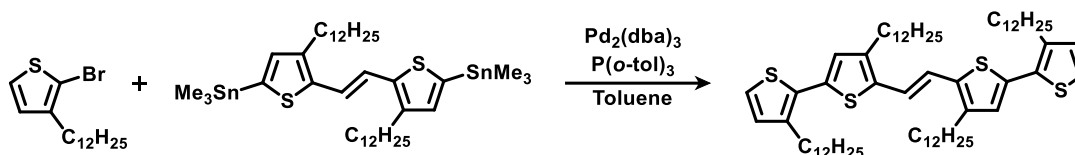
by flash column chromatography on silica gel (hexane: dichloromethane = 25:1, v/v) to afford **M4** (0.58 g, 58%) as a colorless oil.

^1H NMR (500 MHz, CDCl_3): δ 7.44 (dd, $J = 44.5, 5.5$ Hz, 2H), 7.31 (s, 1H), 4.13 (d, $J = 5.5$ Hz, 4H), 2.63 (s, 3H), 1.86-1.82 (m, 2H), 1.65-1.58 (m, 4H), 1.51-1.26 (m, 44H), 0.91-0.87 (m, 12H).

^{13}C NMR (125 MHz, CDCl_3): δ 143.9, 143.6, 138.9, 131.4, 131.2, 130.2, 130.1, 125.8, 120.7, 120.3, 76.3, 39.2, 31.9, 31.3, 30.1, 29.7, 29.7Z, 29.7Z, 29.4, 27.0, 27.0, 22.7, 19.9, 14.1.

HRMS(ESI) m/z calcd for $\text{C}_{43}\text{H}_{72}\text{S}_3\text{O}_2 + \text{Na}$ [$\text{M} + \text{Na}$] $^+$: 739.4586, found 739.4550.

(E)-1,2-Bis(3',4-didodecyl-[2,2'-bithiophen]-5-yl)ethene



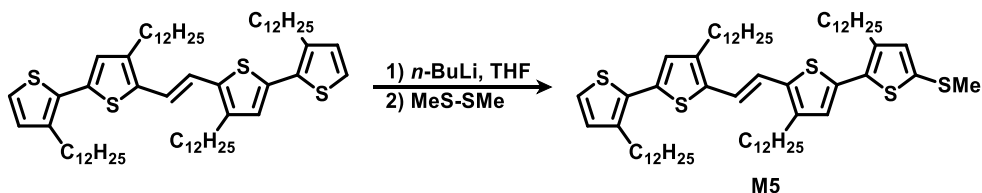
Under nitrogen atmosphere, a mixture of 2-bromo-3-dodecylthiophene (0.83 g, 2.5 mmol), (E)-1,2-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)ethene (0.85 g, 1.0 mmol), $\text{Pd}_2(\text{dba})_3$ (45.8 mg, 0.05 mmol), and $\text{P}(\text{o-tol})_3$ (30.4 mg, 0.1 mol) in toluene (10.0 mL) was stirred at 110 °C for 12 h. After cooling to room temperature, the solution was quenched with saturated KF solution, extracted with dichloromethane for three times. Afterwards, the organic layer was dried over anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (hexane only) to afford (E)-1,2-bis(3',4-didodecyl-[2,2'-bithiophen]-5-yl)ethene (0.67 g, 65%) as a red solid.

^1H NMR (500 MHz, CDCl_3): 7.15 (d, $J = 5.0$ Hz, 2H), 6.95 (s, 2H), 6.93 (d, $J = 5.0$ Hz, 2H), 6.87 (s, 2H), 2.80 (t, $J = 7.5$ Hz, 4H), 2.67 (t, $J = 7.5$ Hz, 4H), 1.68-1.60 (m, 8H), 1.43-1.18 (m, 72H), 0.88-0.83 (m, 12H).

^{13}C NMR (125 MHz, CDCl_3): 141.3, 140.2, 136.2, 133.3, 130.9, 130.1, 127.8, 122.7, 118.8, 31.9, 30.8, 30.6, 29.5, 29.5, 29.4, 29.3, 29.3, 28.4, 22.7, 14.1

HRMS(ESI) m/z calcd for $\text{C}_{66}\text{H}_{108}\text{S}_4$ [M] $^+$: 1028.7328, found 1028.7316.

(E)-5'-(2-(3',4-Didodecyl-[2,2'-bithiophen]-5-yl)vinyl)-3,4'-didodecyl-5-(methylthio)-2,2'-bithiophene (M5)



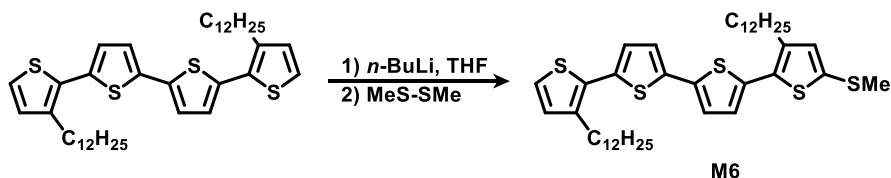
To a THF (20.0 mL) solution of (*E*)-1,2-bis(3',4-didodecyl-[2,2'-bithiophen]-5-yl)ethene (0.51 g, 0.5 mmol) was added *n*-BuLi (0.5 mmol, 2.5 M in hexane, 0.2 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (56.5 mg, 0.6 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane only) to afford **M5** (0.26 g, 48%) as a red solid.

¹H NMR (500 MHz, CDCl₃): 7.15 (d, *J* = 5.0 Hz, 1H), 6.94 (s, 2H), 6.93 (d, *J* = 5.0 Hz, 1H), 6.88 (d, *J* = 6.5 Hz, 2H), 6.82 (s, 1H), 2.80 (t, *J* = 8.0 Hz, 2H), 2.73 (t, *J* = 8.0 Hz, 2H), 2.66 (m, 4H), 2.50 (s, 3H), 1.68-1.58 (m, 8H), 1.42-1.19 (m, 72H), 0.88-0.84 (m, 12H).

¹³C NMR (125 MHz, CDCl₃): 141.5, 141.4, 139.9, 139.7, 136.5, 136.2, 135.1, 133.5, 133.4, 133.0, 132.7, 131.0, 130.2, 128.4, 128.3, 123.6, 119.0, 118.7, 32.0, 30.9, 30.9, 30.7, 30.5, 29.8, 29.7, 29.6, 29.6, 29.5, 29.5, 29.4, 29.4, 28.5, 28.5, 27.0, 22.8, 21.7, 14.2.

HRMS(ESI) *m/z* calcd for C₆₇H₁₁₀S₅+Na [M+Na]⁺: 1097.7103, found 1097.7092.

3,3'''-didodecyl-5-(methylthio)-2,2':5',2'':5'',2'''-quaterthiophene (**M6**)



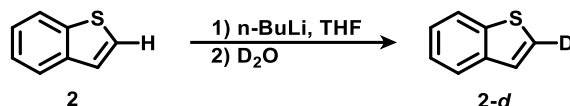
To a THF (25.0 mL) solution of 3,3'''-didodecyl-2,2':5',2'':5'',2'''-quaterthiophene (0.40 g, 0.6 mmol) was added *n*-BuLi (0.6 mmol, 2.5 M in hexane, 0.24 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of dimethyldisulfide (67.8 mg, 0.72 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were separated and the aqueous phase was extracted three times with dichloromethane. After the combined organic layers were dried over anhydrous Na₂SO₄,

filtered, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel (hexane only) to afford **M6** (0.22 g, 31%) as a yellow solid.

^1H NMR (500 MHz, CDCl_3): δ 7.19 (d, J = 4.0 Hz, 1H), 7.11 (m, 2H), 7.02 (d, J = 3.5 Hz, 1H), 6.98 (m, 1H), 6.94 (d, J = 5.0 Hz, 1H), 6.89 (s, 1H), 2.79 (m, 4H), 2.52 (s, 3H), 1.70-1.57 (m, 4H), 1.42-1.17 (m, 36H), 0.90-0.82 (m, 6H).

^{13}C NMR (125 MHz, CDCl_3): δ 140.2, 140.0, 136.9, 136.7, 135.6, 135.4, 134.7, 133.3, 132.3, 130.3, 130.1, 126.6, 126.5, 123.9, 123.8, 32.0, 30.7, 30.6, 29.7, 29.6, 29.6, 29.5, 29.4, 29.3, 22.8, 21.7, 14.2.

Benzo[*b*]thiophene-2-*d* (**2-d**)



To a THF (15.0 mL) solution of **2** (0.27 g, 2.0 mmol) was added *n*-BuLi (4.0 mmol, 2.5 M in hexane, 1.6 mL) dropwise at -78 °C under nitrogen atmosphere. The reaction mixture was stirred at -78 °C for 1 h before the slow addition of D_2O (0.1 mL, 5.0 mmol). Then the reaction mixture was allowed to warm up to room temperature overnight and quenched with water. Next, the organic layers were extracted three times in dichloromethane, combined, and dried over anhydrous Na_2SO_4 . Finally, the organic layers were filtered through a pad of Celite in dichloromethane, and concentrated under reduced pressure to afford **2-d** (0.26 g, 95%) as a colorless solid.

^1H NMR (500 MHz, CDCl_3): δ 7.92 (d, J = 7.5 Hz, 1H), 7.86 (d, J = 7.5 Hz, 1H), 7.41-7.35 (m, 3H).

The NMR spectra are matching with the reference¹².

III. Optimization in Small Molecule Reactions

General synthetic procedure. In a Schlenk flask under nitrogen atmosphere, a solvent (2.0 mL) of a mixture of compound **1a** (42.9 mg, 0.2 mmol) or **1b** (24.8 mg, 0.2 mmol), **2** (26.9 mg, 0.2 mmol), palladium source (if applicable), copper source (if applicable), phosphine ligand (if applicable), base (if applicable) was stirred at 120 °C for 24 h. After quenching the reaction, anthracene (35.6 mg, 0.20 mmol) in toluene (20.0 mL) was added into the reaction mixture. Then the solution was filtered through celite, washed with DCM and petroleum ether (1:1 v/v), and analyzed via GC using anthracene as an internal standard.

GC-MS assay parameters and retention times

4-Hexyl-2-(methylthio)thiophene (**1a**), retention time 10.20 min;

Benzo[*b*]thiophene (**2**), retention time 4.57 min;

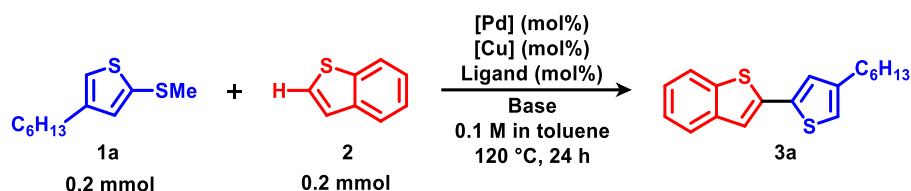
Anthracene, retention time 12.04 min;

2-(4-Hexylthiophen-2-yl)benzo[*b*]thiophene (**3a**), retention time 20.24 min.

2-Phenylbenzo[*b*]thiophene (**3b**), retention time 14.15 min.

3-Phenylbenzo[*b*]thiophene (**3d**), retention time 13.27 min.

Supplementary Table 1. Optimization in small molecule reaction using **1a** as the electrophile



Entry	[Pd] (mol%)	[Cu] (mol%)	Ligand (mol%)	Base (equiv)	Yield (%) ^a
1	Herrmann's Cat. (5)	—	P(<i>o</i> -MeOPh) ₃ (20)	KO ^t Bu (2.5)	5
2	Herrmann's Cat. (5)	—	dcype (10)	KO ^t Bu (2.5)	13
3	Herrmann's Cat. (5)	—	dcype (10)	KO ^t Bu (4)	36
4	Herrmann's Cat. (5)	—	dcype (10)	KO ^t Bu (5)	45
5	Herrmann's Cat. (5)	—	dcype (10)	KO ^t Bu (6)	37
6	Pd(OAc) ₂ (10)	—	dcype (10)	KO ^t Bu (5)	44
7	Herrmann's Cat. (5)	CuI (20)	dcype (10)	KO ^t Bu (5)	78
8	Pd ₂ (dba) ₃ (5)	CuI (20)	dcype (10)	KO ^t Bu (5)	91 ^b (85) ^c
9	Pd(MeCN) ₂ Cl ₂ (10)	CuI (20)	dcype (10)	KO ^t Bu (5)	80
10	Pd(P ^t Bu) ₃ (10)	CuI (20)	dcype (10)	KO ^t Bu (5)	72
11	—	CuI (20)	dcype (10)	KO ^t Bu (5)	0
12	Pd ₂ (dba) ₃ (5)	CuTc (20)	dcype (10)	KO ^t Bu (5)	82
13	Pd ₂ (dba) ₃ (5)	CuBr ₂ (20)	dcype (10)	KO ^t Bu (5)	64
14	Pd ₂ (dba) ₃ (5)	CuCl (20)	dcype (10)	KO ^t Bu (5)	75
15	Pd ₂ (dba) ₃ (5)	CuBr (20)	dcype (10)	KO ^t Bu (5)	54
16	Pd ₂ (dba) ₃ (5)	CuCN (20)	dcype (10)	KO ^t Bu (5)	78
17	Pd ₂ (dba) ₃ (5)	CuI (20)	P(Cy) ₃ (20)	KO ^t Bu (5)	58
18	Pd ₂ (dba) ₃ (5)	CuI (20)	P(Ad) ₃ (20)	KO ^t Bu (5)	0
19	Pd ₂ (dba) ₃ (2)	CuI (20)	dcype (4)	KO ^t Bu (5)	98 ^d
20	Pd ₂ (dba) ₃ (1)	CuI (20)	dcype (2)	KO ^t Bu (5)	96
21	Pd ₂ (dba) ₃ (0.5)	CuI (20)	dcype (1)	KO ^t Bu (5)	93
22	Pd ₂ (dba) ₃ (2)	—	dcype (4)	KO ^t Bu (5)	36
23	Pd ₂ (dba) ₃ (2)	CuI (10)	dcype (4)	KO ^t Bu (5)	53
24	Pd ₂ (dba) ₃ (2)	CuI (20)	dcype (8)	KO ^t Bu (5)	72
25	Pd ₂ (dba) ₃ (2)	CuI (20)	dcypt (4)	KO ^t Bu (5)	92
26	Pd ₂ (dba) ₃ (2)	CuI (20)	dcypbz (4)	KO ^t Bu (5)	82
27	Pd ₂ (dba) ₃ (2)	CuI (20)	dcypf (4)	KO ^t Bu (5)	47
28	Pd ₂ (dba) ₃ (2)	CuI (20)	dcype (4)	—	0
29 ^e	Pd ₂ (dba) ₃ (2)	CuI (20)	dcype (4)	KO ^t Bu (5)	30

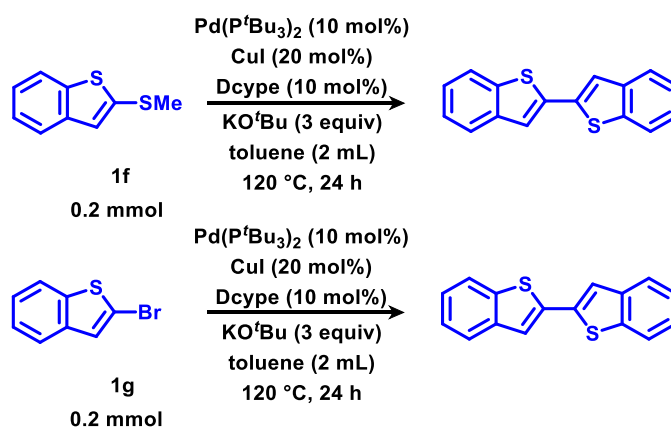
30^f	Pd₂(dba)₃ (2)	CuI (20)	dcype (4)	KO^tBu (5)	28
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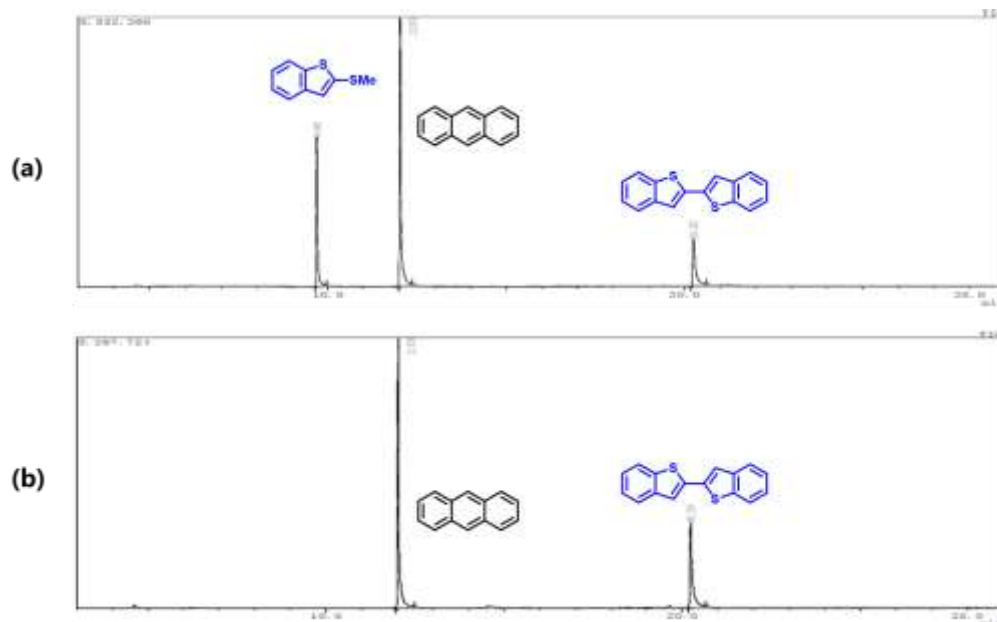
^aYields were determined by gas chromatography using anthracene as an internal standard. ^bThe homocoupling of **1a** produced 4,4'-dihexyl-2,2'-bithiophene in 2.0% yield. ^cIsolated yield in parentheses. ^dThe homocoupling of **1a** produced 4,4'-dihexyl-2,2'-bithiophene in 1.7% yield. ^eReaction temperature of 110 °C. ^fReaction temperature of 100 °C.

Supplementary Table 2. Optimization in small molecule reaction using **1b** as the electrophile

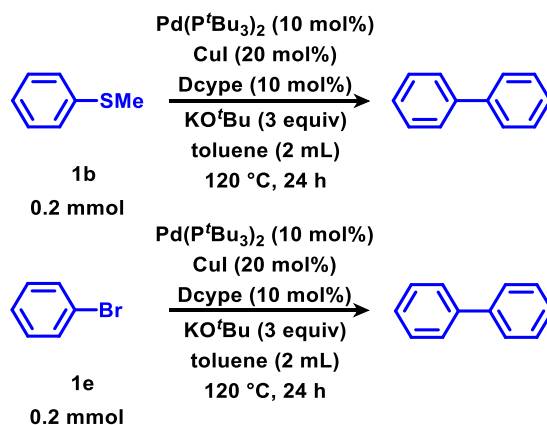
Entry	[Pd] (mol%)	[Cu] (mol%)	Ligand (mol%)	Base (equiv)	Yield (%) ^a
1	Pd ₂ (dba) ₃ (5)	CuI (20)	dcype (10)	KO ^t Bu (3)	45
2	Pd(MeCN) ₂ Cl ₂ (10)	CuI (20)	dcype (10)	KO ^t Bu (3)	77
3	Pd(P ^t Bu ₃) ₂ (10)	CuI (20)	dcype (10)	KO ^t Bu (3)	88 (86) ^b
4	Pd(P ^t Bu ₃) ₂ (5)	CuI (20)	dcype (5)	KO ^t Bu (3)	37

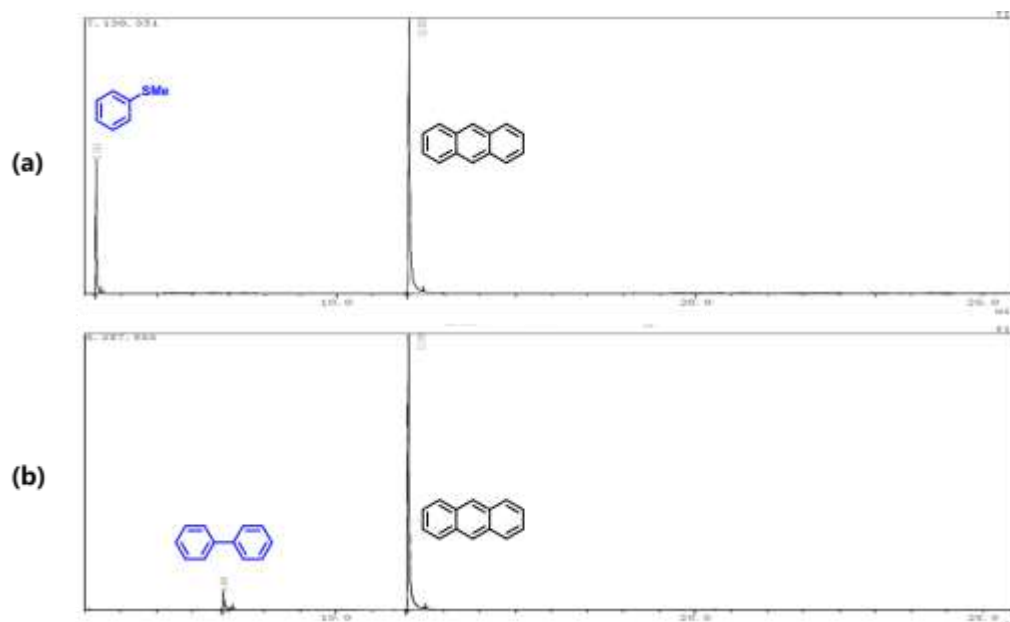
^aYields were determined by gas chromatography using anthracene as an internal standard. ^bYield was isolated.



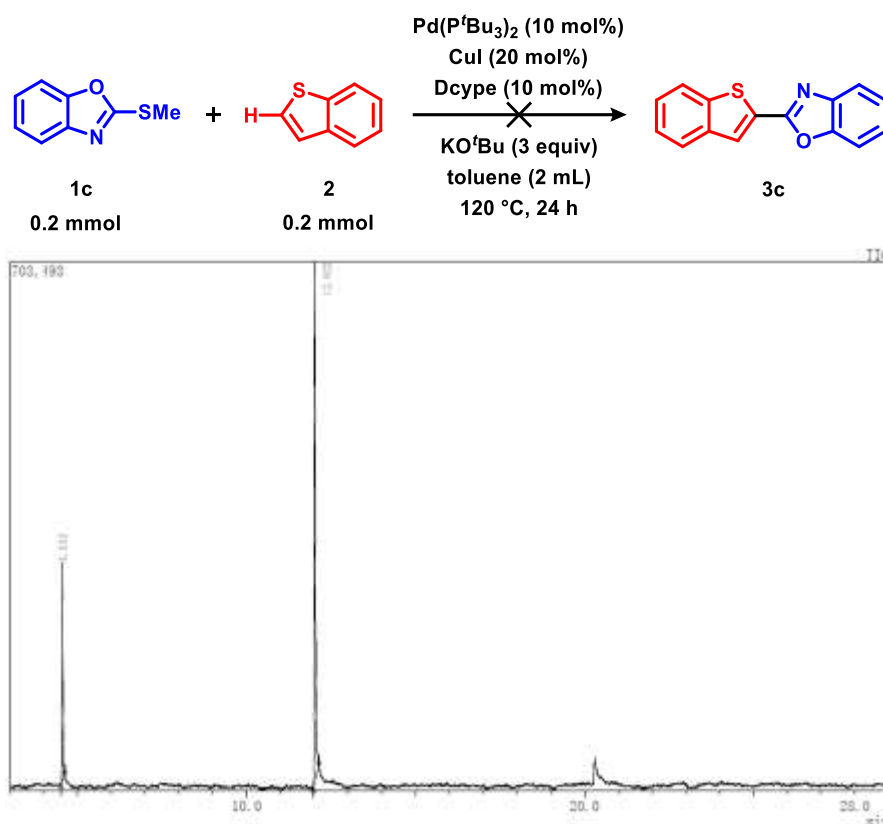


Supplementary Fig. 1. The homocoupling detection of benzothiophenyl based electrophiles by GC analysis. (a) The GC trace for the reaction of **1f** under the optimized condition. (b) The GC trace for the reaction of **1g** under the optimized condition.

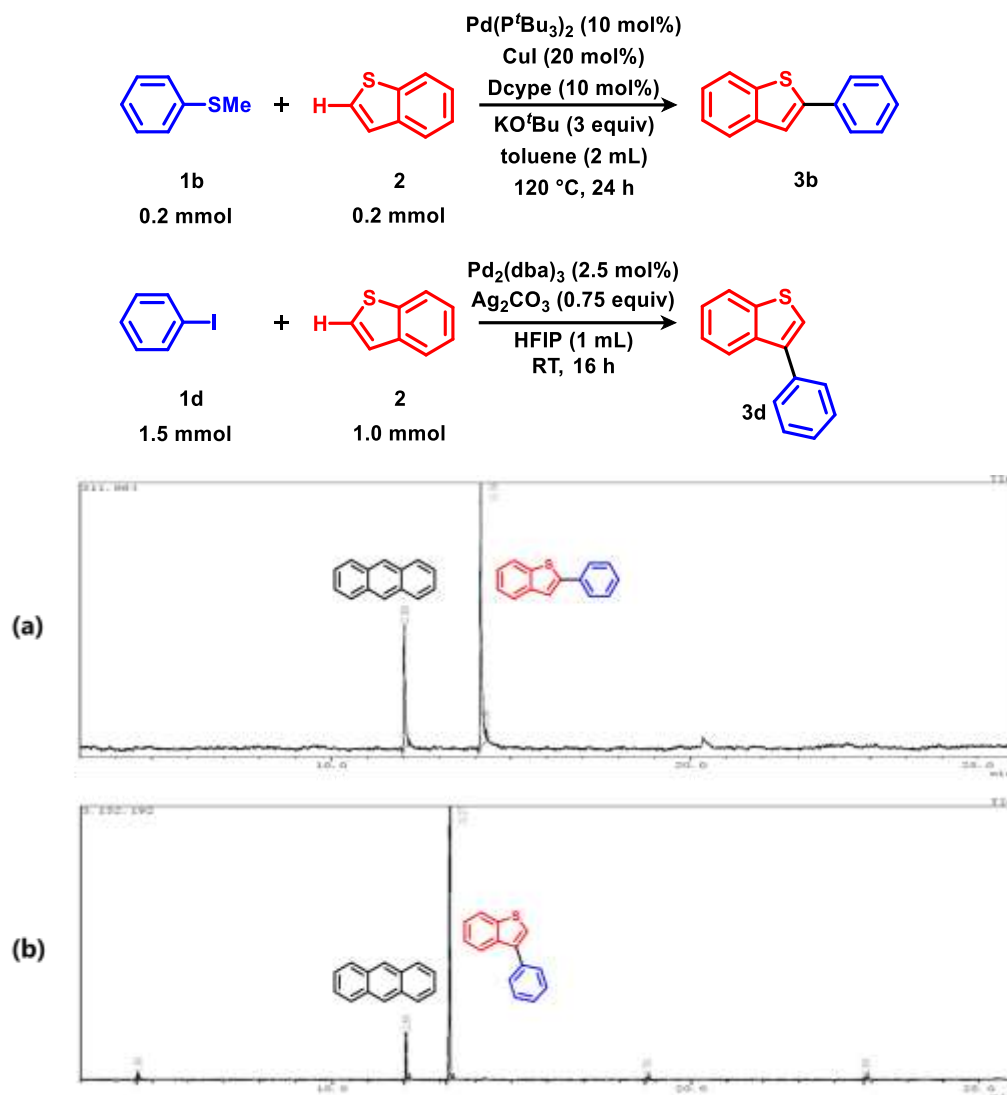




Supplementary Fig. 2. The homocoupling detection of phenyl based electrophiles by GC analysis. (a) The GC trace for the reaction of **1b** under the optimized condition. (b) The GC trace for the reaction of **1e** under the optimized condition.



Supplementary Fig. 3. The GC traces of the model reactions by cross-coupling **1c** and **2**.



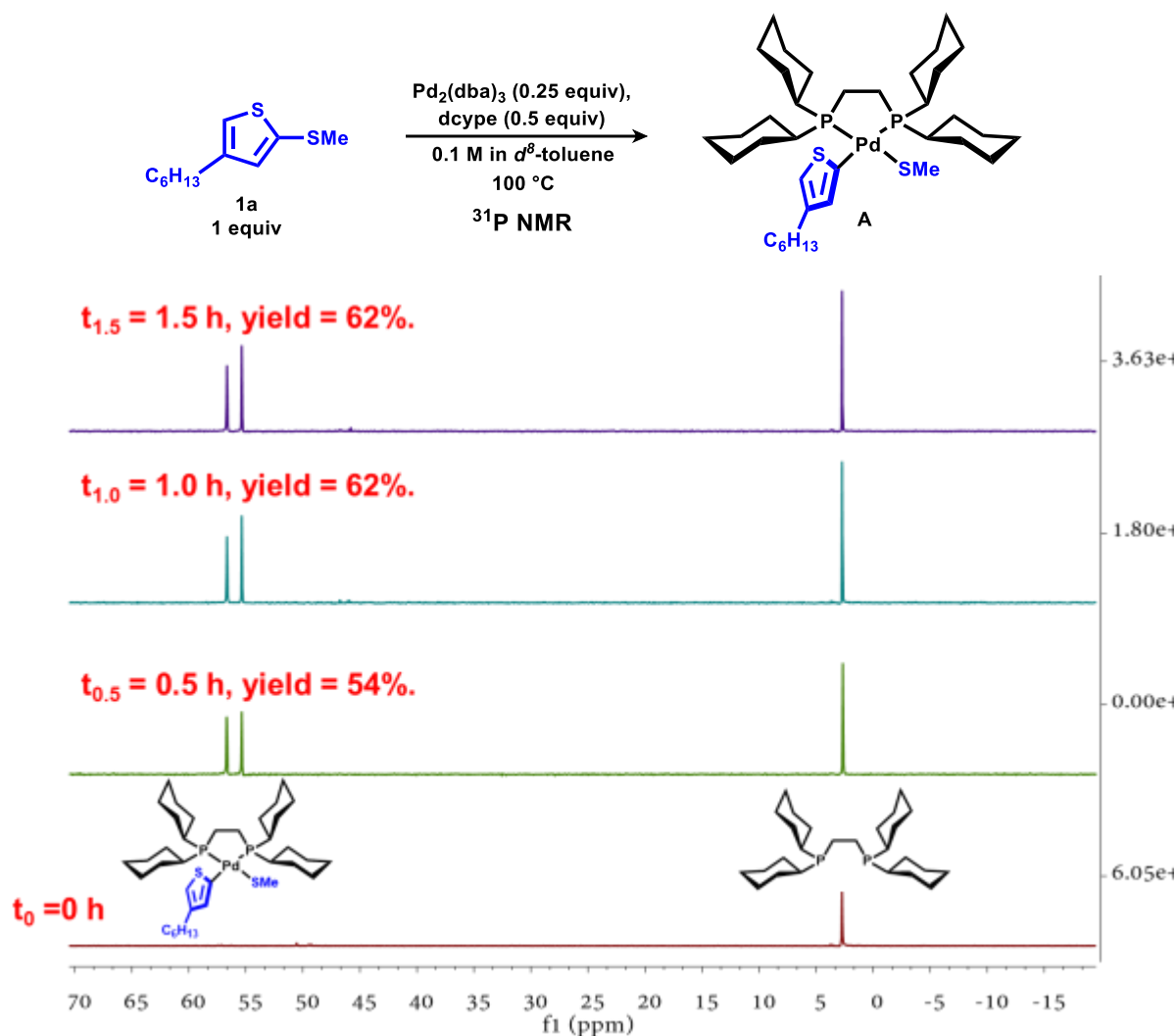
Supplementary Fig. 4. β -defects study of small molecule model reaction by GC analysis. (a) The GC trace of the reaction of **1b** and **2**. (b) The GC trace of the reaction of **1d** and **2**.¹³

IV. Mechanistic Studies

IV-1. Monitoring of the oxidative addition *in situ* ^{31}P NMR

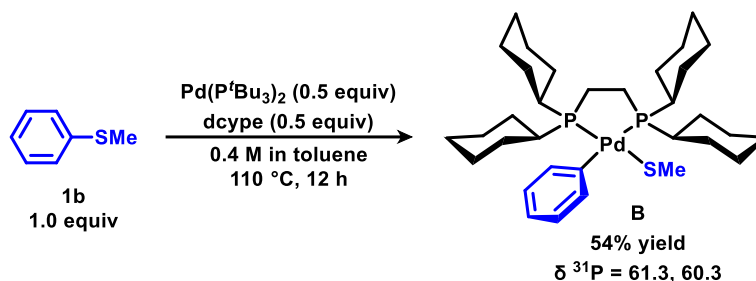
An NMR tube equipped with a screwed cap was dried with a heat-gun under reduced pressure and filled with nitrogen after cooling to room temperature, which was transferred into a glovebox. In the glovebox, **1a** (10.7 mg, 0.05 mmol), $\text{Pd}_2(\text{dba})_3$ (11.5 mg, 0.0125 mmol), dcype (10.6 mg, 0.025 mmol), and d^8 -toluene (0.5 mL) were added to this tube. The tube was capped, and was taken out of the glovebox. Afterwards, this tube was set into the NMR spectrometer, and the reaction was monitored by ^{31}P NMR

spectroscopy (0 h, 0.5 h, 1.0 h, 1.5 h) at 100 °C (**Supplementary Fig. 5**). ^{31}P NMR signals were conducted acquisition with a JEOL JNM-ECZ500R (202 MHz) spectrometer at 100 °C (each trace represents 200 scans). During the course of the reaction, two new downfield peaks ($\delta = 56.66$ and 55.36 ppm) appeared and strengthened on ^{31}P NMR. ^{31}P NMR yield was calculated based on $[\text{peak area } (\delta = 56.66 \text{ ppm}) \times 2]/[\text{peak area } (\delta = 56.66 \text{ ppm}) \times 2 + \text{peak area } (\delta = 2.14 \text{ ppm for dcype})]$.



Supplementary Fig. 5. The real time monitoring of the oxidative addition reaction in ^{31}P NMR.

IV-2. The synthesis of oxidative addition palladium (II) complex (B)



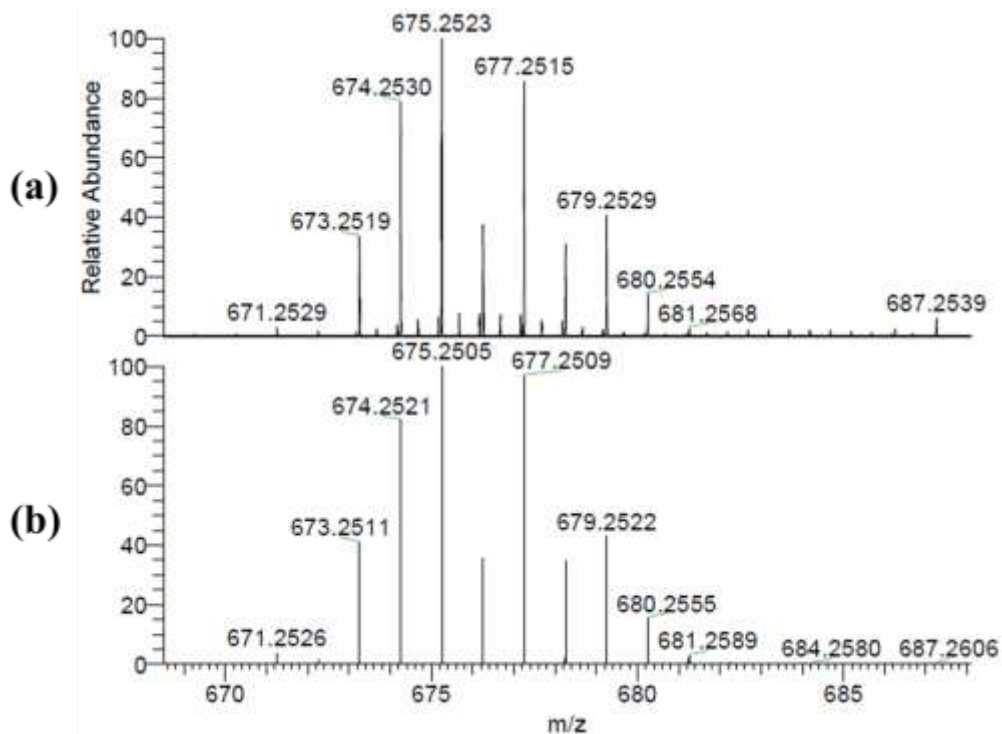
Under nitrogen atmosphere, a mixture of compound **1b** (99.4 mg, 0.8 mmol), $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (204.4 mg, 0.4 mmol), and dcype (169.1 mg, 0.4 mmol) were dissolved in toluene (2.0 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 110°C for 12 h. After cooling the reaction mixture to room temperature, this vessel was transferred into the glovebox. Next, the reaction mixture was filtered through a pad of Celite (toluene), and concentrated under reduced pressure to afford a crude solid. The title compound was obtained as a yellow acicular crystalline solid (141.1 mg, 54%) by recrystallization from the mixed solvent of toluene/hexane at -20°C .

^1H NMR (500 MHz, CDCl_3): δ 7.45 (t, $J = 7.0$ Hz, 2H), 7.04 (t, $J = 7.0$ Hz, 2H), 6.88 (t, $J = 7.0$ Hz, 1H), 2.35 (s, 3H), 2.24-2.11 (m, 2H), 2.09-1.98 (m, 2H), 1.88-1.59 (m, 18H), 1.48-1.12 (m, 24H), 0.81-0.76 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ 164.5 (dd, $J = 117.3, 7.4$ Hz), 137.7, 127.0 (d, $J = 7.3$ Hz), 121.9, 34.4 (dd, $J = 31.9, 22.6$ Hz), 28.9 (d, $J = 3.4$ Hz), 28.5, 28.0, 27.3, 27.2, 27.1, 27.0, 27.0, 26.9, 26.8, 26.0 (d, $J = 5.0$ Hz), 24.2 (t, $J = 21.5$ Hz), 21.1 (dd, $J = 19.1, 14.4$ Hz), 10.8 (dd, $J = 9.6, 2.1$ Hz).

^{31}P NMR (202 MHz, CDCl_3): δ 61.26 (d, $J = 21.8$ Hz), 60.28 (d, $J = 21.8$ Hz).

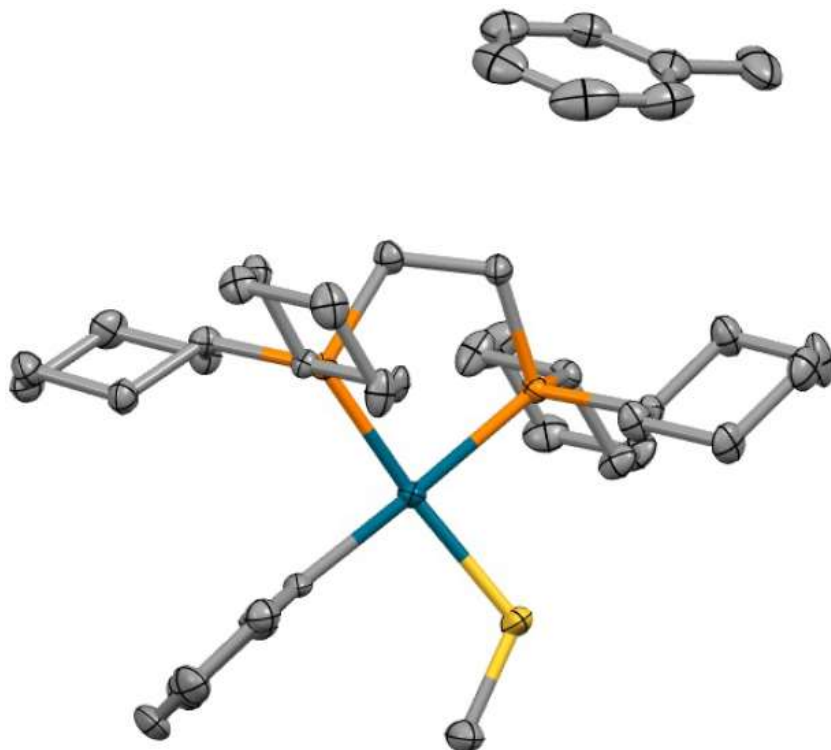
HRMS (ESI) m/z calcd for $\text{C}_{33}\text{H}_{56}\text{P}_2\text{SPd}+\text{Na}$ [$\text{M}+\text{Na}$] $^+$: 675.2505, found 675.2523.



Supplementary Fig. 6. The ESI-MS spectra of palladium (II) complex **B**. (a) Experimental isotopic distribution of **B**. (b) Computational isotopic distribution of **B**.

IV-3. X-ray crystal structure of palladium (II) complex (**B**)

Single crystals of palladium (II) complex **B** was isolated at room temperature by slow evaporation from toluene.



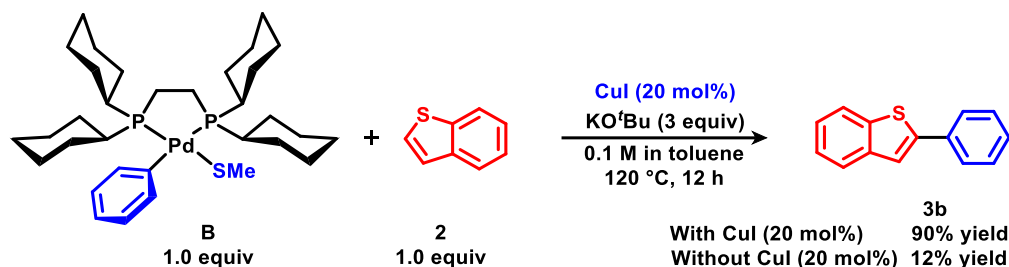
Crystal data and structure refinement

Identification code	CCDC 2203415
Empirical formula	C ₄₀ H ₆₄ P ₂ PdS
Formula weight	745.31
Temperature/K	113.15
Crystal system	Monoclinic
Space group	P2 ₁ /n
a/Å	11.7547(4)
b/Å	14.2287(5)
c/Å	22.6673(6)
α /°	90
β /°	93.288(3)
γ /°	90
Volume/Å ³	3785.0(2)
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.308
μ/mm^{-1}	0.656
F(000)	1584.0

Crystal size/mm ³	0.22 × 0.2 × 0.16
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	3.382 to 52.744
Index ranges	-14 ≤ h ≤ 14, -17 ≤ k ≤ 17, -2 ≤ l ≤ 18
Reflections collected	7729
Independent reflections	7729 [R_{sigma} = 0.0652]
Data/restraints/parameters	7729/0/400
Goodness-of-fit on F^2	1.237
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0817, wR_2 = 0.1904
Final R indexes [all data]	R_1 = 0.0919, wR_2 = 0.1954
Largest diff. peak/hole / e Å ⁻³	2.17/-1.41

Note: *B* and toluene were cocrystallized in a molar ratio 1:1.

IV-4. The reaction using stoichiometric amounts of palladium (II) complex (B)

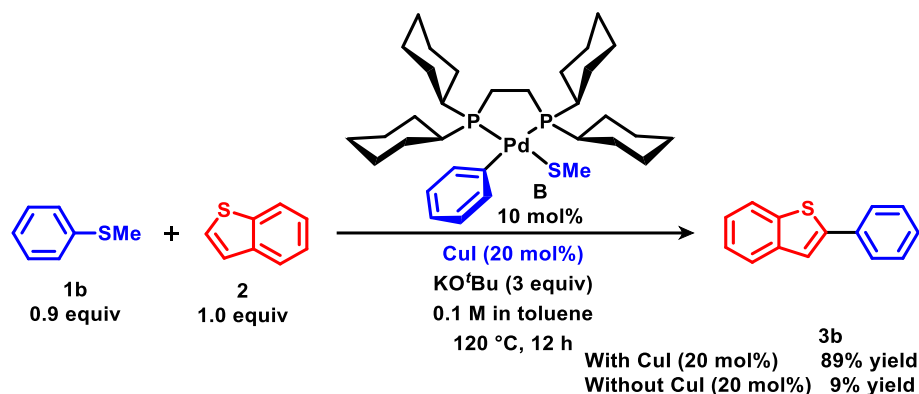


To a Schlenk flask under nitrogen atmosphere, a mixture of compound **B** (65.3 mg, 0.1 mmol), **2** (13.4 mg, 0.1 mmol), CuI (3.8 mg, 0.02 mmol, if applicable), and KO^tBu (33.7 mg, 0.3 mmol) were dissolved in toluene (1.0 mL). Then the mixture was stirred at 120 °C for 12 h. After the reaction was completed, anthracene (17.8 mg, 0.10 mmol) in toluene (5.0 mL) was added into the reaction solution. The solution was filtered through celite, washed with DCM and petroleum ether (1:1 v/v), and analyzed via GC using anthracene as an internal standard.

GC-MS assay parameters and retention times

Anthracene, retention time 12.04 min; 2-phenylbenzo[*b*]thiophene **3b**, retention time 14.14 min.

IV-5. The reaction using catalytic amounts of palladium (II) complex (B)

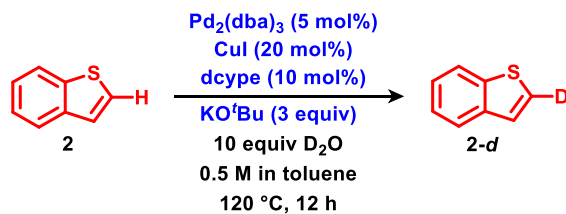


To a Schlenk flask under nitrogen atmosphere, a mixture of compound **1b** (11.2 mg, 0.09 mmol), **2** (13.4 mg, 0.1 mmol), **B** (6.5 mg, 0.01 mmol), CuI (3.8 mg, 0.02 mmol, if applicable), and KO^tBu (33.7 mg, 0.3 mmol) were dissolved in toluene (1.0 mL). Then the mixture was stirred at 120 °C for 12 h. After the reaction was completed, anthracene (17.8 mg, 0.10 mmol) in toluene (5.0 mL) was added into the reaction solution. The solution was filtered through celite, washed with DCM and petroleum ether (1:1 v/v), and analyzed via GC using anthracene as an internal standard.

IV-6. H/D exchange experiments

General procedure. To a Schlenk flask under nitrogen atmosphere, a mixture of compound **2** (107.4 mg, 0.8 mmol), Pd₂(dba)₃ (36.6 mg, 0.04 mmol), CuI (30.5 mg, 0.16 mmol), dcype (33.8 mg, 0.08 mmol), KO^tBu (269.3 mg, 2.4 mmol), and D₂O (0.16 mL, 8.0 mmol) were dissolved in toluene (1.6 mL). Then the mixture was stirred at 120 °C for 12 h. Next, the reaction mixture was cooled to room temperature, filtered through a pad of Celite (eluted with CH₂Cl₂), and then concentrated under reduced pressure. The amount of the deuteration **2-d** was determined by ¹H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard.

Supplementary Table 3. H/D exchange experiments of **2**



Entry	Pd ₂ (dba) ₃	CuI	dcype	KO ^t Bu	Deuteration (%)
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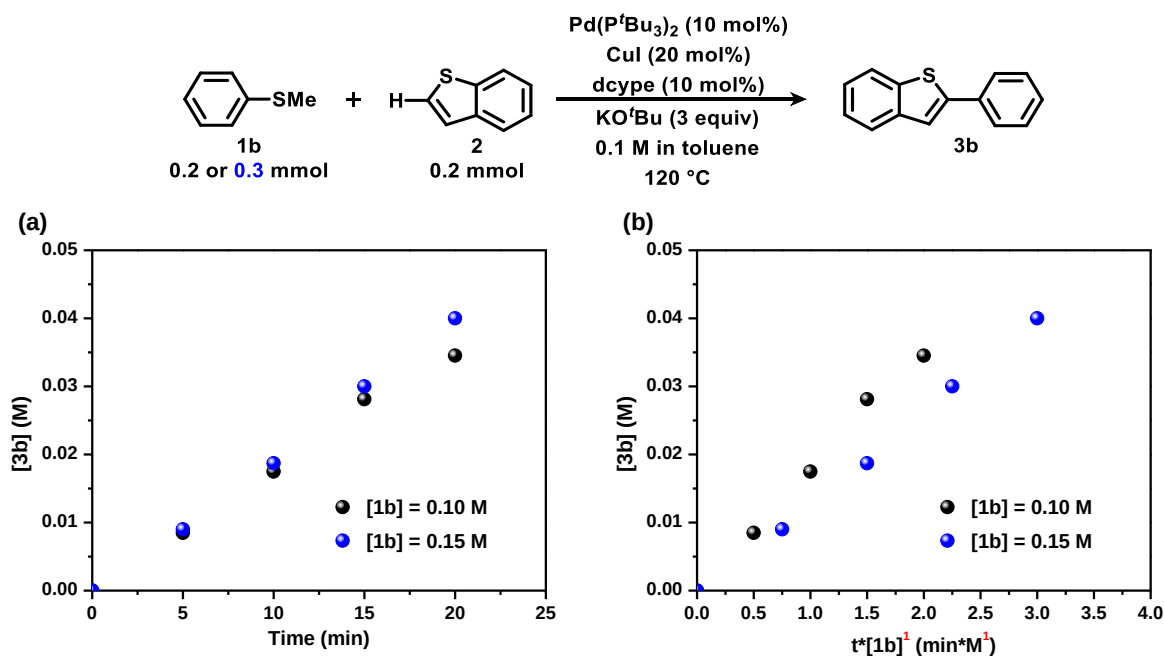
1	✓	✓	✓	✓	80
2	×	✓	✓	✓	73
3	✓	×	✓	✓	55
4	✓	✓	×	✓	53
5	✓	✓	✓	×	0
6	×	×	✓	✓	51
7	✓	×	×	✓	48
8	×	✓	×	✓	50
9	×	×	×	✓	47
10	×	✓	×	×	0

^aDeuteration yields were determined by ¹H NMR using 1,4-dimethoxybenzene as an internal standard.

IV-7. Kinetic analysis

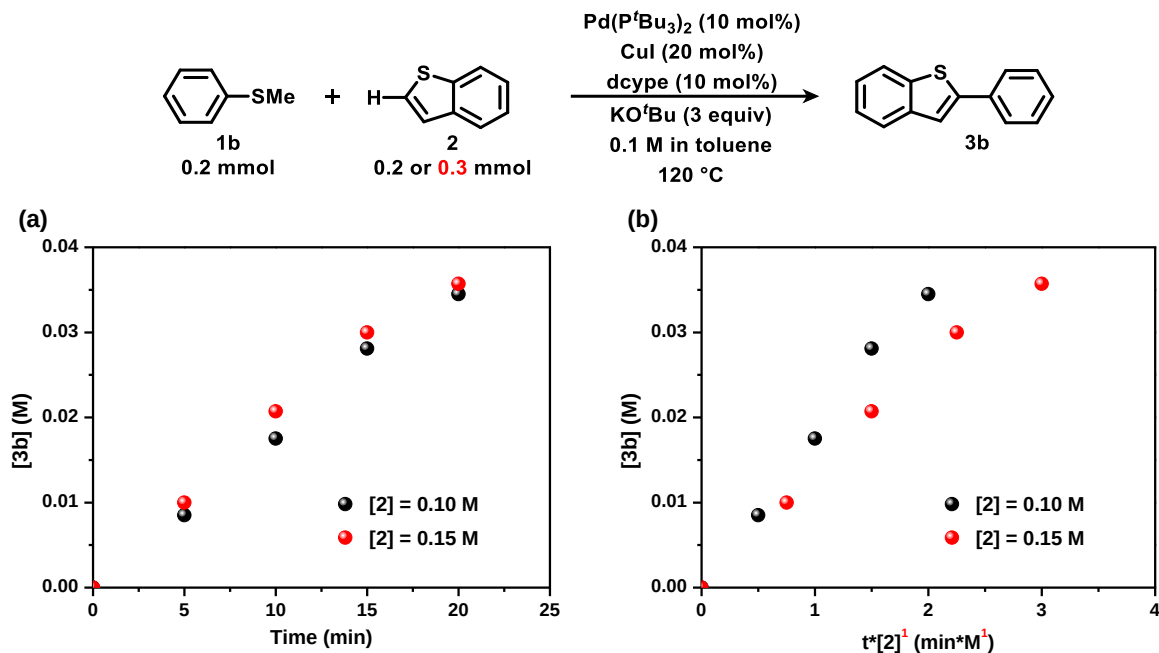
General procedure. To a Schlenk flask under nitrogen atmosphere, a mixture of compound **1b** (37.3 mg, 0.3 mmol), **2** (40.3 mg, 0.3 mmol), Pd(P^tBu₃)₂ (15.3 mg, 0.03 mmol), CuI (11.4 mg, 0.06 mmol), dcype (12.7 mg, 0.03 mmol), KO^tBu (101.0 mg, 0.9 mmol), and anthracene (53.4 mg, 0.3 mmol) were dissolved in toluene (3.0 mL). The reactions were heated at 120 °C. During the reaction, the aliquots (0.1 mL) were taken out during the reaction at various time points and filtered with celite plugs for GC analysis. This procedure was also applied to obtain all of the kinetic data.

Determination of order in **1b**



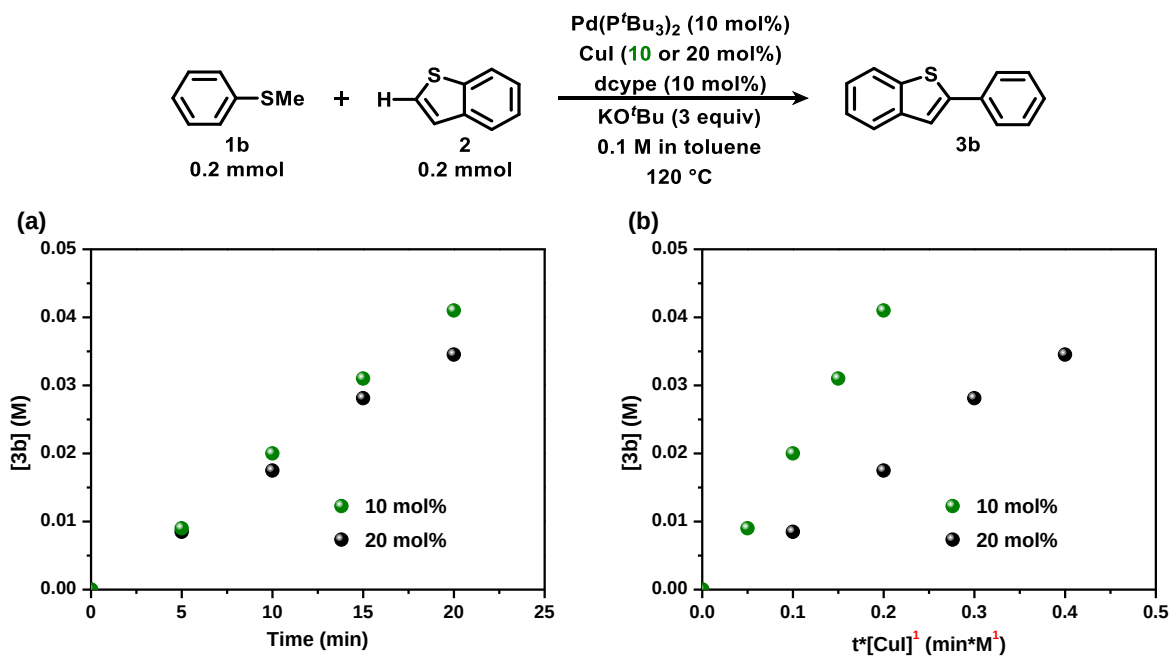
Supplementary Fig. 7. (a) Temporal reaction profiles with different concentrations of **1b**. (b) Normalized time scale profiles for order 1 in **1b**.

Determination of order in 2



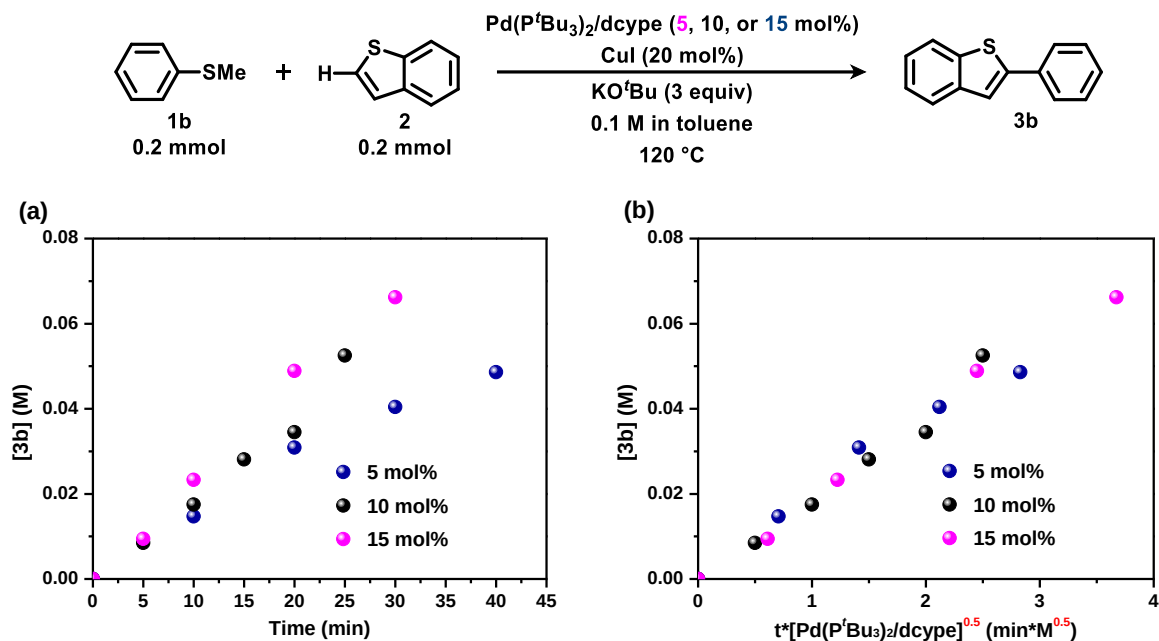
Supplementary Fig. 8. (a) Temporal reaction profiles in different concentrations of 2. (b) Normalized time scale profiles for order 1 in 2.

Determination of order in CuI



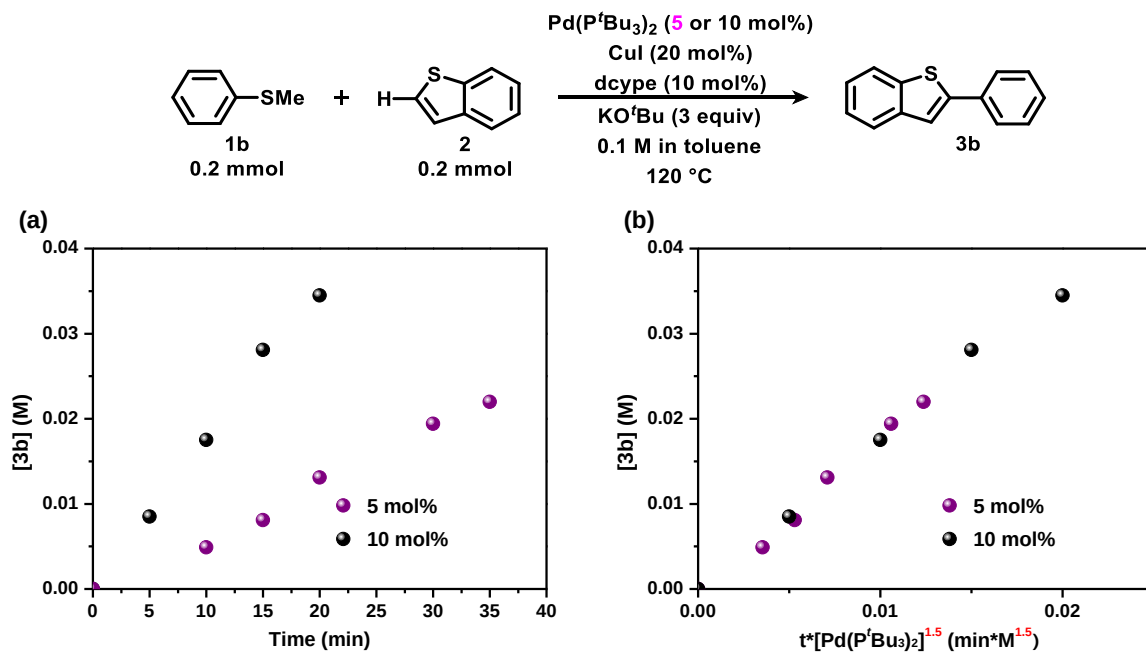
Supplementary Fig. 9. (a) Temporal reaction profiles with different loading of CuI. (b) Normalized time scale profiles for order 1 in CuI.

Determination of order in $[\text{Pd}(\text{P}^t\text{Bu}_3)_2/\text{dcype}]$



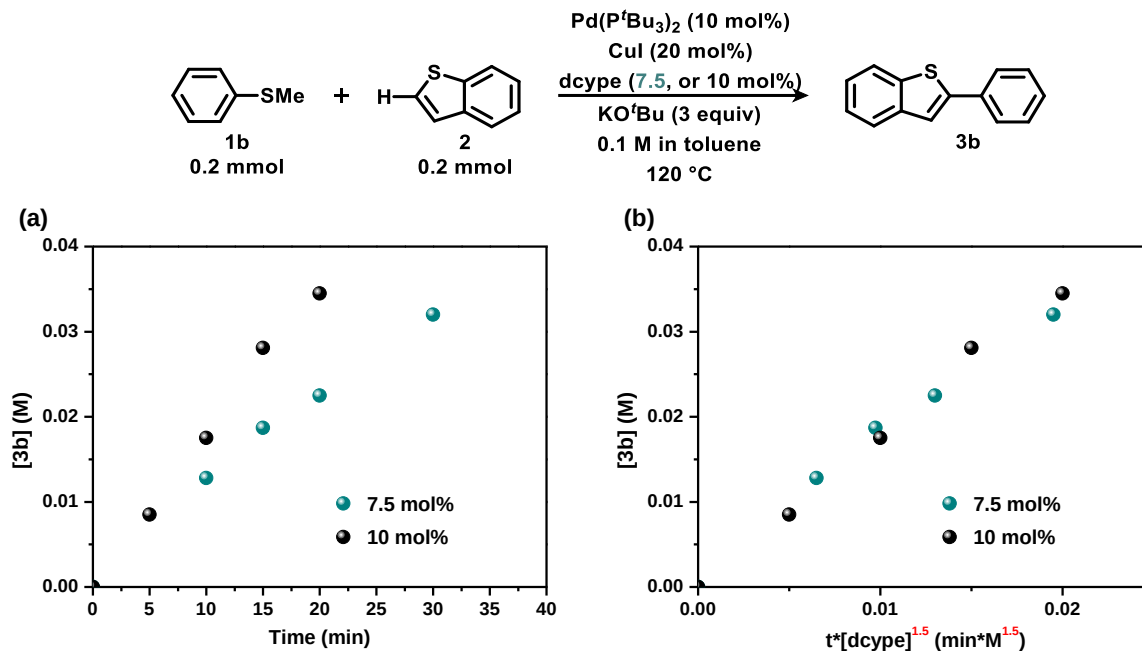
Supplementary Fig. 10. (a) Temporal reaction profiles with different loading of $[\text{Pd}(\text{P}^t\text{Bu}_3)_2/\text{dcype}]$. (b) Normalized time scale profiles for order 0.5 in $[\text{Pd}(\text{P}^t\text{Bu}_3)_2/\text{dcype}]$.

Determination of order in $\text{Pd}(\text{P}^t\text{Bu}_3)_2$



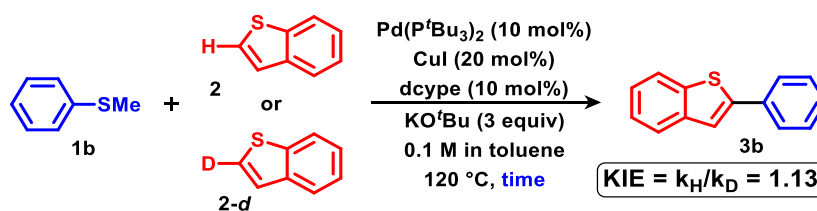
Supplementary Fig. 11. (a) Temporal reaction profiles with different loading of $\text{Pd}(\text{P}^t\text{Bu}_3)_2$. (b) Normalized time scale profiles for order 1.5 in $\text{Pd}(\text{P}^t\text{Bu}_3)_2$.

Determination of order in dcype



Supplementary Fig. 12. (a) Temporal reaction profiles with different loadings of dcype. (b) Normalized time scale profiles for order 1.5 in dcype.

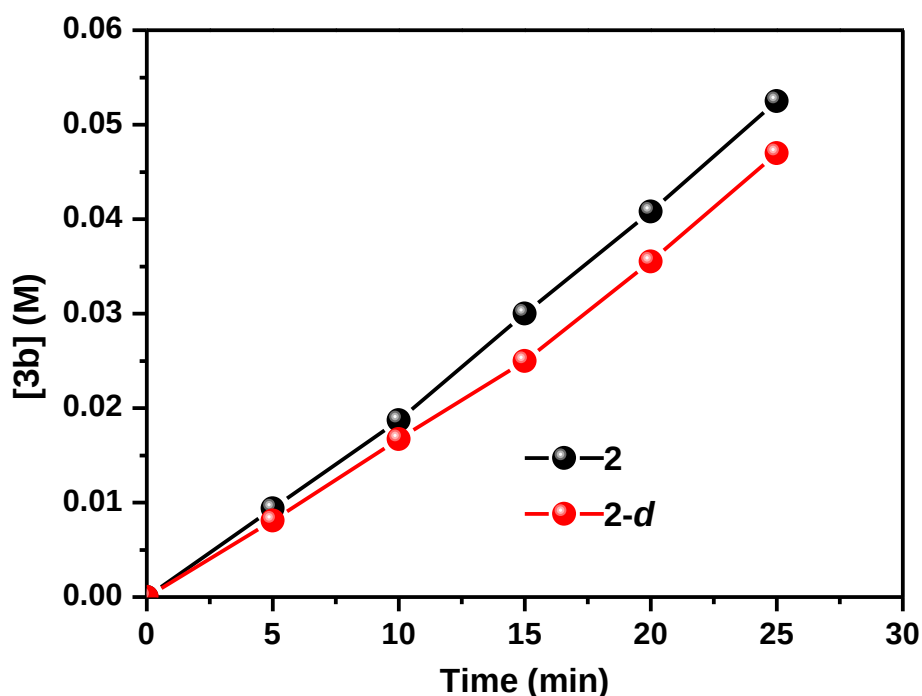
IV-8. Kinetic isotope effect



General procedure. To a Schlenk flask under nitrogen atmosphere, a mixture of compound **1b** (37.2 mg, 0.3 mmol), **2** (40.3 mg, 0.3 mmol) or **2-d** (40.5 mg, 0.3 mmol), Pd(P^tBu₃)₂ (15.3 mg, 0.03 mmol), CuI (11.4 mg, 0.06 mmol), dcype (12.7 mg, 0.03 mmol), KO^tBu (101.0 mg, 0.9 mmol), anthracene (53.4 mg, 0.3 mmol) were dissolved in toluene (1.0 mL). The reactions were heated at 120 °C. During the reaction, the aliquots (0.1 mL) were taken out every 5 min and filtered with celite plugs for GC analysis.

GC-MS assay parameters and retention times

Anthracene, retention time 12.04 min; 2-phenylbenzo[*b*]thiophene (**3b**), retention time 14.14 min.



Supplementary Fig. 13. Kinetic isotope effect experiment for the parallel reactions using **2** or **2-d** as the nucleophile.

KIE values were calculated by $\text{KIE} = k_{\text{H}}/k_{\text{D}}$. k_{H} and k_{D} were obtained via VTNA. **Supplementary Fig. 13** shows that $k_{\text{H}} = 2.10 \text{ mM/min}$, and $k_{\text{D}} = 1.86 \text{ mM/min}$. Therefore, $\text{KIE} = 2.10/1.86 = 1.13$. This shows that the deprotonation of **2** is not the turnover-limiting step.

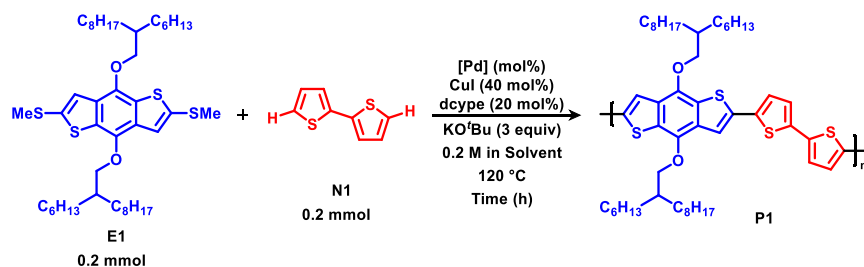
V. Synthesis of Polymers

V-1. Optimization in polycondensation reaction

General synthetic procedure. Under nitrogen atmosphere, a mixture of compound **4** (152.66 mg, 0.20 mmol), **5** (33.25 mg, 0.20 mmol), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (10.38 mg, 0.04 mmol, 20 mol%), CuI (15.24 mg, 0.08 mmol, 40 mol%), *dcype* (16.90 mg, 0.04 mmol, 20 mol%), and KO^tBu (67.33 mg, 0.60 mmol, 3.0 equiv) were dissolved in toluene (1.0 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 120 °C for 48 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL) for precipitation. The crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated, and precipitated in methanol.

Finally, the desired polymer was filtrated and dried over vacuum.

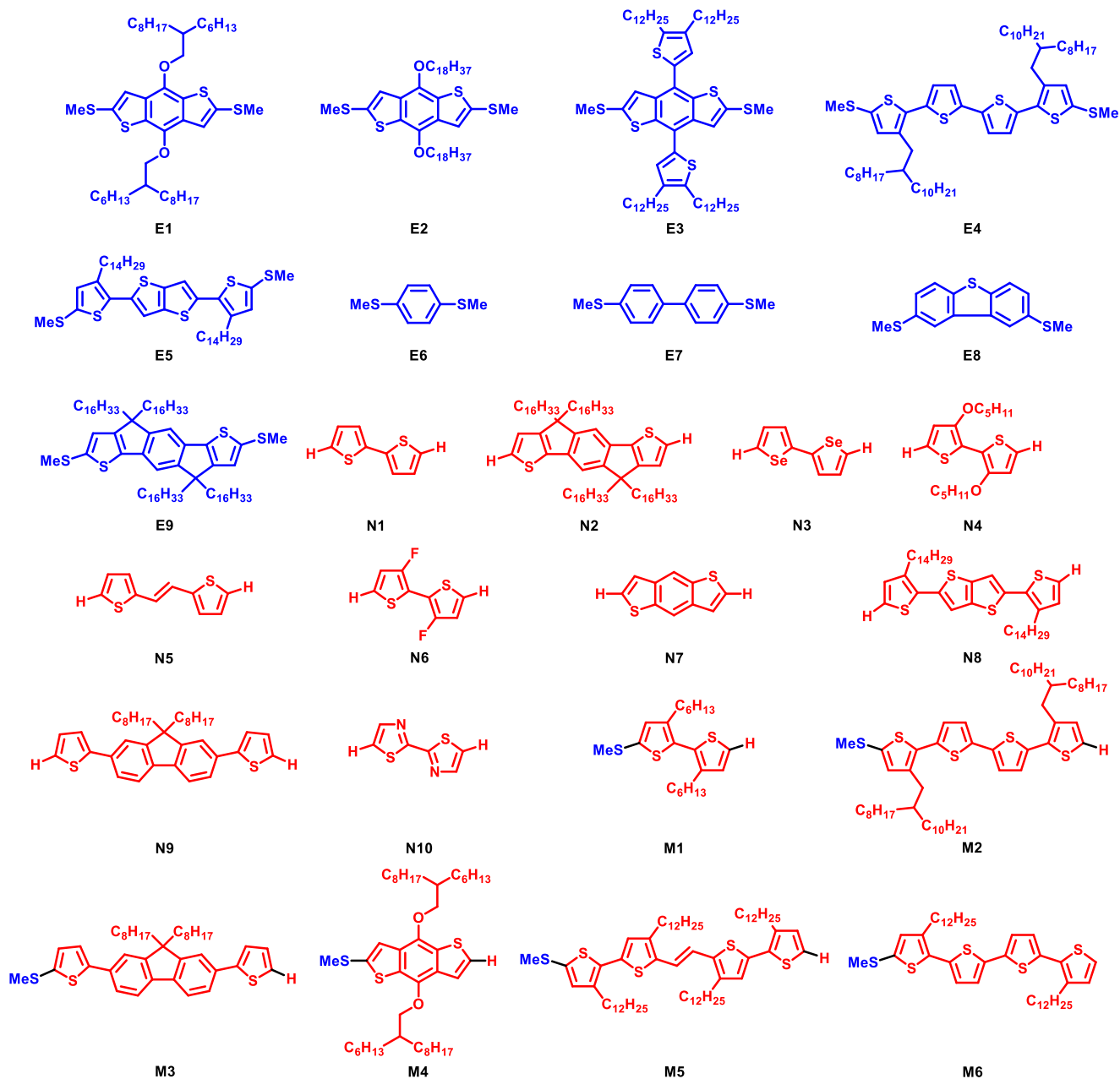
Supplementary Table 4. Optimization in polycondensation reaction



Entry	[Pd] (mol%)	Solvent	Time (h)	M_n (kg/mol) ^a	$\bar{D}$ ^a	Yield (%) ^b
1	Pd ₂ (dba) ₃ (10)	Toluene	24	6.3	1.66	31
2	Pd ₂ (dba) ₃ (10)	Toluene	48	16.5	1.66	68
3	Herrmann's Cat. (10)	Toluene	48	15.9	2.09	71
4	PdCl ₂ (20)	Toluene	48	4.3	1.77	39
5	Pd(PhCN) ₂ Cl ₂ (20)	Toluene	48	24.3	1.93	96
6	Pd(MeCN) ₂ Cl ₂ (20)	Toluene	48	51.6	1.88	98
7	Pd(MeCN) ₂ Cl ₂ (20)	<i>o</i> -Xylene	48	6.0	1.90	40
8	Pd(MeCN) ₂ Cl ₂ (20)	Chlorobenzene	48	4.0	1.85	27
9 ^c	Pd(MeCN) ₂ Cl ₂ (10)	Toluene	48	33.0	2.39	96
10 ^d	Pd(MeCN) ₂ Cl ₂ (5)	Toluene	48	12.4	2.01	88
11 ^e	Pd(MeCN) ₂ Cl ₂ (20)	Toluene	48	6.0	1.80	53
12 ^f	Pd(MeCN) ₂ Cl ₂ (20)	Toluene	48	5.3	1.75	41
13	Pd(MeCN) ₂ Cl ₂ (20)	Toluene	24	20.0	2.34	92

^a M_n and $\bar{D}$ were determined with GPC at 150 °C in 1,2,4-trichlorobenzene against a polystyrene standard. ^bIsolated yields of chloroform fraction. ^c10 mol% of dcype was used. ^d5 mol% of dcype was used. ^eReaction concentration of 0.1 M. ^fReaction concentration of 0.05 M.

V-2. General synthetic procedure for polycondensation reaction

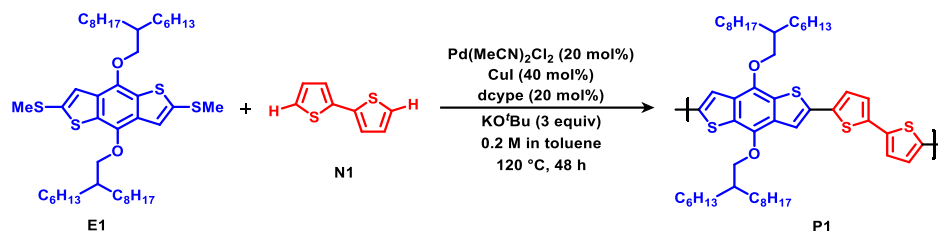


Supplementary Fig. 14. The chemical structures for electrophiles and nucleophiles in following polycondensation.

General synthetic procedure. Under nitrogen atmosphere, a mixture of monomers **E1-E8** (0.20 mmol, 1 equiv), **N1-N10** (0.20 mmol, 1 equiv), Pd(MeCN)₂Cl₂ (10.38 mg, 0.04 mmol, 20 mol%) or Pd(P^tBu₃)₂ (20.44 mg, 0.04 mmol, 20 mol%), CuI (15.24 mg, 0.08 mmol, 40 mol%), dcype (16.90 mg, 0.04 mmol, 20 mol%), and KO^tBu (67.33 mg, 0.60 mmol, 3.0 equiv) were dissolved in toluene (1.0 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 120 °C for 48 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL) for

precipitation. The crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated, and precipitated in methanol. Finally, the desired polymer was filtrated and dried over vacuum.

Synthesis of P1:



The title compound was obtained as a red solid (163.3 mg, 98%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

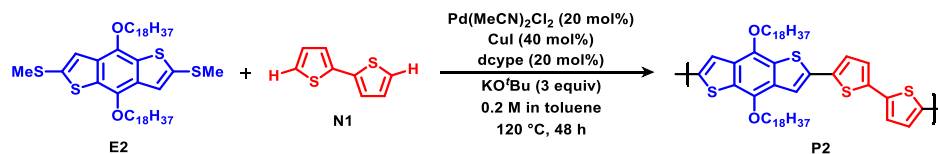
GPC (TCB, 150 °C): $M_n = 51.6$ kg/mol, $M_w = 97.1$ kg/mol, $D = 1.88$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.66-6.41 (m, 6H), 4.36-3.78 (br s, 4H), 0.68-1.55 (m, 62H).

IR (film), ν (cm^{-1}): 2918, 2849, 1653, 1632, 1457, 1430, 1358, 1229, 1164, 1034, 816, 781, 722.

Elemental analysis: Calculated for $((\text{C}_{50}\text{H}_{72}\text{O}_2\text{S}_4)_n)$: C, 72.06; H, 8.71; S, 15.39; found: C, 71.71; H, 9.02; S, 12.96.

Synthesis of P2:



The title compound was obtained as a dark red solid (158.9 mg, 97%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

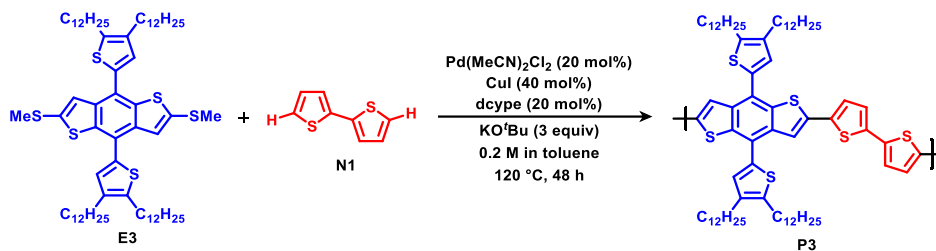
GPC (TCB, 150 °C): $M_n = 30.3$ kg/mol, $M_w = 59.3$ kg/mol, $D = 1.95$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.70-6.38 (m, 6H), 4.54-3.94 (br s, 4H), 2.14-1.82 (br s, 4H), 1.80-1.09 (br s, 64H), 1.09-0.76 (br s, 6H).

IR (film), ν (cm^{-1}): 2917, 2847, 1507, 1465, 1429, 1362, 1231, 1164, 1041, 820, 785, 721.

Elemental analysis: Calculated for $((\text{C}_{54}\text{H}_{80}\text{O}_2\text{S}_4)_n)$: C, 72.92; H, 9.07; S, 14.42; found: C, 67.59; H, 8.75; S, 13.29.

Synthesis of P3 (gram scale reaction):



Under nitrogen atmosphere, a mixture of **E3** (1.01 g, 0.90 mmol), **N1** (0.15 g, 0.90 mmol), Pd(MeCN)₂Cl₂ (46.70 mg, 0.18 mmol), CuI (68.56 mg, 0.36 mmol), dcype (76.07 mg, 0.18 mmol), and KO^tBu (0.3 g, 2.70 mmol) were dissolved in toluene (4.5 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 120 °C for 48 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL) for precipitation. Then, the crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated and precipitated in methanol, dried over vacuum. The title compound was obtained as a dark red solid (1.05 g, 98%).

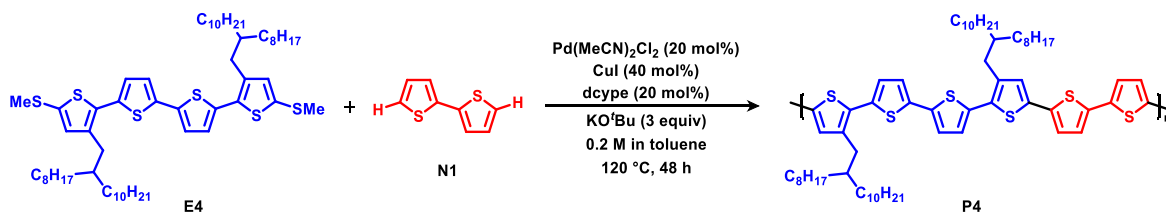
GPC (TCB, 150 °C): M_n = 76.0 kg/mol, M_w = 158.9 kg/mol, D = 2.09.

¹H NMR (500 MHz, C₂D₂Cl₄, 373 K): 7.89-6.89 (m, 8H), 3.06-2.50 (m, 8H), 1.96-1.63 (m, 8H), 1.62-1.09 (m, 72H), 0.98-0.88 (br s, 12H).

IR (film), ν (cm⁻¹): 2918, 2849, 1653, 1635, 1456, 1375, 1312, 1170, 820, 780, 719.

Elemental analysis: Calculated for ((C₇₄H₁₀₈S₆)_n): C, 74.69; H, 9.15; S, 16.16; found: C, 75.46; H, 9.29; S, 15.71.

Synthesis of P4:



The title compound was obtained as a dark red solid (174.9 mg, 83%). The reaction was performed according to general synthetic procedure using Pd(MeCN)₂Cl₂.

GPC (TCB, 150 °C): M_n = 35.4 kg/mol, M_w = 63.8 kg/mol, D = 1.80.

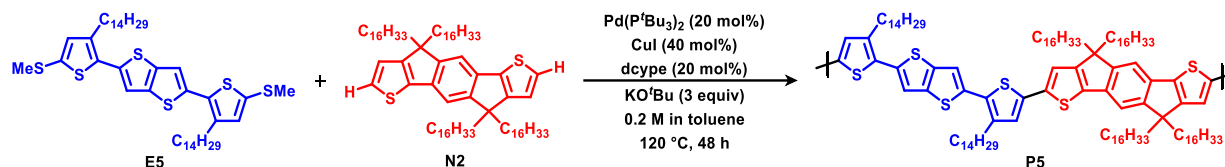
¹H NMR (500 MHz, C₂D₂Cl₄, 373 K): 7.36-6.76 (m, 10H), 3.08-2.38 (m, 4H), 2.12-1.95 (m, 2H), 1.85-

1.06 (m, 64H), 0.98-0.79 (br s, 12H).

IR (film), ν (cm^{-1}): 2917, 2849, 1654, 1633, 1492, 1457, 1430, 1376, 1066, 837, 787, 721.

Elemental analysis: Calculated for $((\text{C}_{64}\text{H}_{92}\text{S}_6)_n)$: C, 72.95; H, 8.80; S, 18.25; found: C, 73.56; H, 8.83; S, 18.15.

Synthesis of P5:



The title compound was obtained as a dark red solid (356.6 mg, 96%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$.

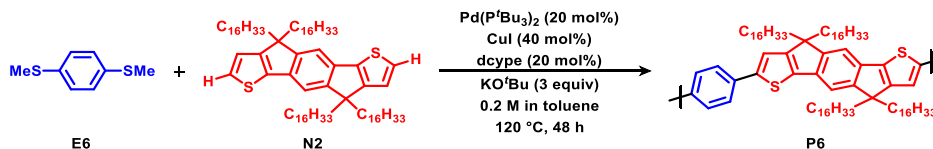
GPC (TCB, 150 °C): $M_n = 20.5$ kg/mol, $M_w = 42.0$ kg/mol, $D = 2.05$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.41-7.18 (m, 4H), 7.18-6.94 (m, 4H), 3.01-2.66 (m, 4H), 2.19-1.59 (m, 12H), 1.47-1.08 (m, 156H), 0.99-0.86 (m, 18H).

IR (film), ν (cm^{-1}): 2916, 2848, 2342, 1456, 1324, 869, 822, 716.

Elemental analysis: Calculated for $((\text{C}_{122}\text{H}_{198}\text{S}_6)_n)$: C, 78.90; H, 10.75; S, 10.36; found: C, 79.21; H, 10.68; S, 9.59.

Synthesis of P6:



The title compound was obtained as a yellow solid (235.2 mg, 95%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$.

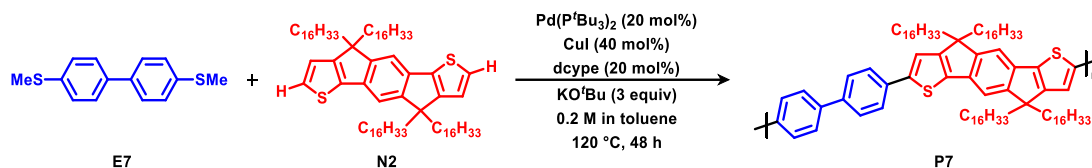
GPC (TCB, 150 °C): $M_n = 42.4$ kg/mol, $M_w = 75.4$ kg/mol, $D = 1.78$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.92-7.46 (m, 4H), 7.43-7.18 (m, 4H), 2.26-1.76 (m, 8H), 1.49-1.01 (m, 112H), 1.00-0.82 (m, 12H).

IR (film), ν (cm^{-1}): 2917, 2848, 1659, 1632, 1534, 1466, 870, 818, 719.

Elemental analysis: Calculated for $((\text{C}_{86}\text{H}_{142}\text{S}_2)_n)$: C, 83.42; H, 11.40; S, 5.18; found: C, 83.58; H, 11.41; S, 4.94.

Synthesis of P7:



The title compound was obtained as an orange solid (252.3 mg, 96%). The reaction was performed according to general synthetic procedure using $\text{Pd(P}^t\text{Bu}_3)_2$.

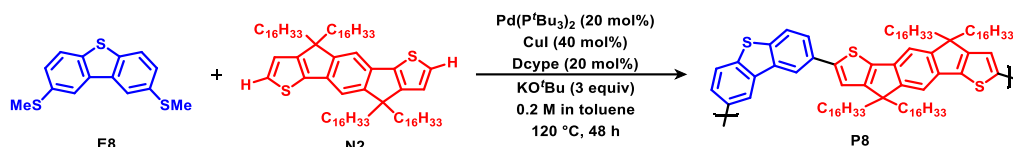
GPC (TCB, 150 °C): $M_n = 50.9$ kg/mol, $M_w = 99.9$ kg/mol, $D = 1.96$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.97-7.52 (m, 8H), 7.40-7.24 (m, 4H), 2.29-1.60 (m, 8H), 1.40-1.01 (m, 112H), 1.00-0.82 (m, 12H).

IR (film), ν (cm^{-1}): 2916, 2847, 1465, 870, 813, 720.

Elemental analysis: Calculated for $((\text{C}_{92}\text{H}_{144}\text{S}_2)_n)$: C, 84.08; H, 11.04; S, 4.88; found: C, 84.32; H, 10.94; S, 4.78.

Synthesis of P8:



The title compound was obtained as a yellow solid (250.0 mg, 93%). The reaction was performed according to general synthetic procedure using $\text{Pd(P}^t\text{Bu}_3)_2$.

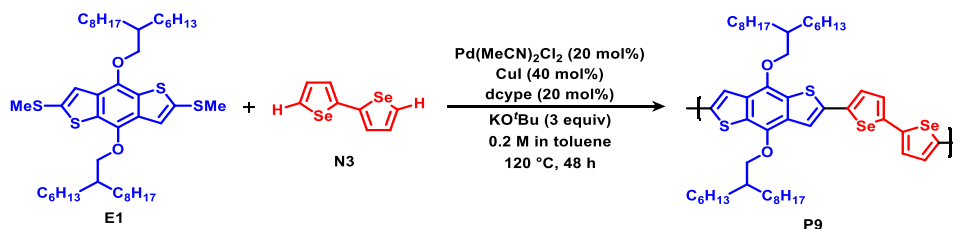
GPC (TCB, 150 °C): $M_n = 16.7$ kg/mol, $M_w = 26.0$ kg/mol, $D = 1.55$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 8.64-8.28 (m, 2H), 8.08-7.64 (m, 6H), 7.51-7.17 (m, 2H), 2.26-1.79 (m, 8H), 1.45-0.95 (m, 112H), 0.92-0.69 (m, 12H).

IR (film), ν (cm^{-1}): 2919, 2848, 1457.

Elemental analysis: Calculated for $((\text{C}_{92}\text{H}_{142}\text{S}_3)_n)$: C, 82.20; H, 10.65; S, 7.15; found: C, 82.54; H, 10.52; S, 7.06.

Synthesis of P9:



The title compound was obtained as a dark purple solid (146.5 mg, 79%). The reaction was performed

according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

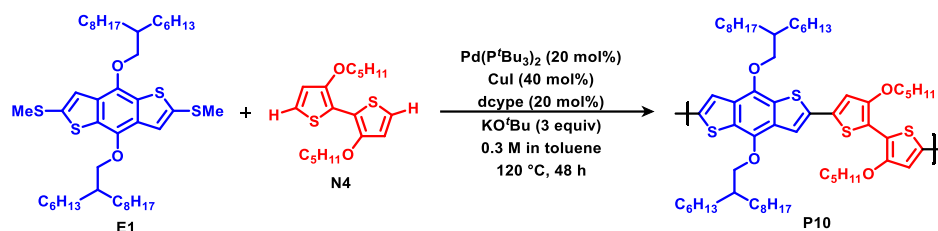
GPC (TCB, 150 °C): $M_n = 12.1$ kg/mol, $M_w = 19.9$ kg/mol, $D = 1.64$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.70-6.56 (m, 6H), 4.44-3.74 (m, 4H), 2.01-1.82 (m, 2H), 1.80-1.17 (m, 48H), 1.12-0.81 (m, 12H).

IR (film), ν (cm^{-1}): 2918, 2848, 1654, 1632, 1507, 1456, 1434, 1355, 1031, 780, 721.

Elemental analysis: Calculated for $((\text{C}_{50}\text{H}_{72}\text{O}_2\text{S}_2\text{Se}_2)_n)$: C, 64.77; H, 7.83; S, 6.92; found: C, 63.57; H, 7.74; S, 7.87.

Synthesis of P10:



The title compound was obtained as a dark purple solid (205.2 mg, 98%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (20.44 mg, 0.04 mmol), and toluene (0.67 mL).

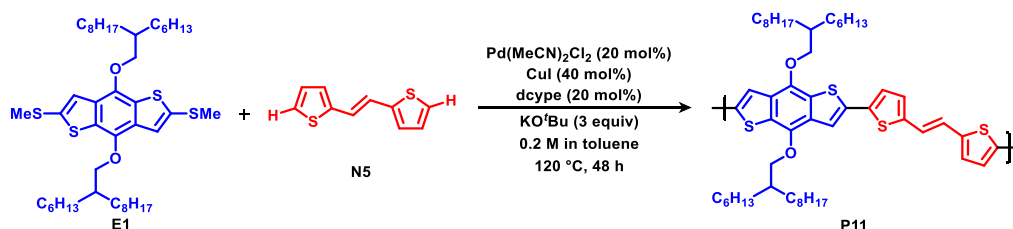
GPC (TCB, 150 °C): $M_n = 110.9$ kg/mol, $M_w = 174.8$ kg/mol, $D = 1.58$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.75-6.74 (m, 4H), 4.42-4.08 (m, 8H), 2.11-1.81 (br s, 8H), 2.11-1.81 (m, 54H), 1.13-0.77 (m, 18H).

IR (film), ν (cm^{-1}): 2919, 2851, 1508, 1457, 1424, 1356, 1339, 1260, 1181, 1055, 1033, 816, 796, 721.

Elemental analysis: Calculated for $((\text{C}_{60}\text{H}_{92}\text{O}_4\text{S}_4)_n)$: C, 71.66; H, 9.22; S, 12.75; found: C, 71.68; H, 9.51; S, 12.99.

Synthesis of P11:



The title compound was obtained as a dark purple solid (166.7 mg, 97%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

GPC (TCB, 150 °C): $M_n = 61.7$ kg/mol, $M_w = 127.9$ kg/mol, $D = 2.07$.

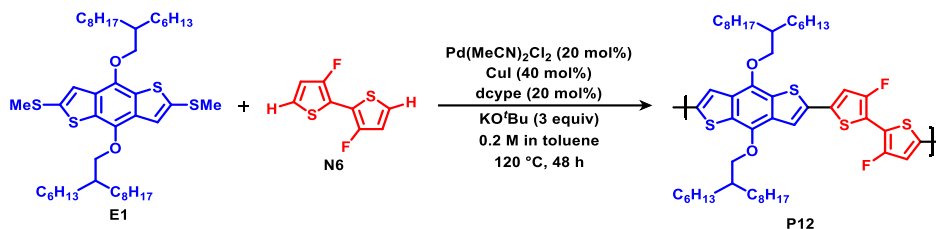
^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.71-6.57 (m, 8H), 4.42-4.02 (m, 4H), 2.06-1.81 (br s, 2H), 1.80-

1.20 (m, 48H), 1.10-0.77 (m, 12H).

IR (film), ν (cm^{-1}): 2918, 2849, 1654, 1634, 1456, 1435, 1356, 1243, 1163, 1032, 923, 816, 785, 720.

Elemental analysis: Calculated for $((\text{C}_{52}\text{H}_{74}\text{O}_2\text{S}_4)_n)$: C, 72.68; H, 8.68; S, 14.92; found: C, 73.13; H, 9.24; S, 14.42.

Synthesis of P12:



The title compound was obtained as a dark purple solid (121.7 mg, 70%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

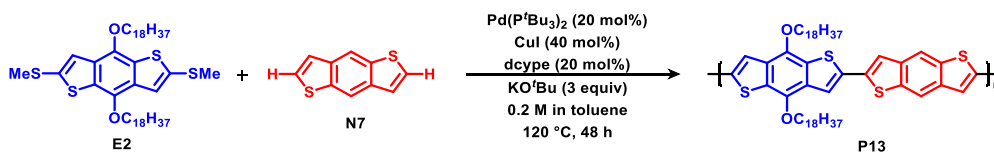
GPC (TCB, 150 °C): $M_n = 12.8$ kg/mol, $M_w = 18.9$ kg/mol, $D = 1.48$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.73-6.83 (m, 4H), 4.37-3.82 (m, 4H), 2.07-1.81 (br s, 2H), 1.77-1.10 (m, 48H), 1.07-0.77 (m, 12H).

IR (film), ν (cm^{-1}): 2919, 2851, 1647, 1516, 1457, 1360, 1261, 1229, 1162, 1037, 798.

Elemental analysis: Calculated for $((\text{C}_{50}\text{H}_{70}\text{F}_2\text{O}_2\text{S}_4)_n)$: C, 69.08; H, 8.12; S, 14.75; found: C, 67.48; H, 8.01; S, 15.56.

Synthesis of P13:



The title compound was obtained as a dark red solid (175.4 mg, 96%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$.

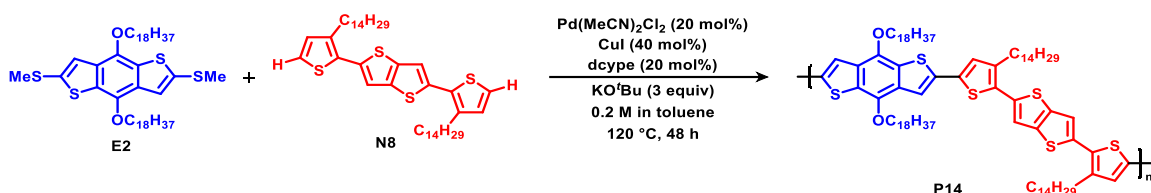
GPC (TCB, 150 °C): $M_n = 25.9$ kg/mol, $M_w = 86.4$ kg/mol, $D = 3.34$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 8.39-6.47 (m, 6H), 4.57-3.70 (m, 4H), 2.19-1.09 (m, 64H), 1.08-0.71 (m, 6H).

IR (film), ν (cm^{-1}): 2918, 2848, 1522, 1466, 1341, 1061, 852, 740.

Elemental analysis: Calculated for $((\text{C}_{56}\text{H}_{80}\text{O}_2\text{S}_4)_n)$: C, 73.63; H, 8.83; S, 14.04; found: C, 74.04; H, 8.82; S, 12.98.

Synthesis of P14:



The title compound was obtained as a dark red solid (272.7 mg, 96%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

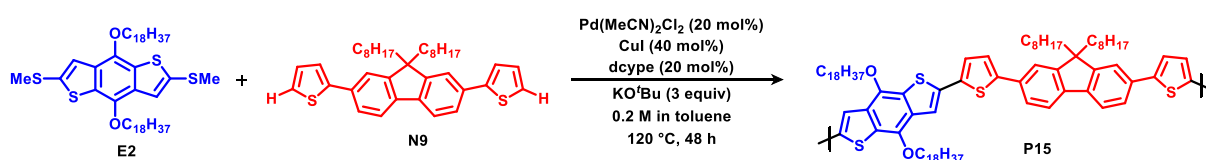
GPC (TCB, 150 °C): $M_n = 25.6$ kg/mol, $M_w = 44.3$ kg/mol, $D = 1.73$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.75-6.89 (m, 6H), 4.44-4.16 (m, 4H), 2.03-1.13 (m, 116H), 0.95-0.78 (m, 12H).

IR (film), ν (cm^{-1}): 2917, 2848, 1579, 1464, 1359, 1176, 1047, 813, 757, 719.

Elemental analysis: Calculated for $((\text{C}_{88}\text{H}_{138}\text{O}_2\text{S}_6)_n)$: C, 74.41; H, 9.79; S, 13.54; found: C, 75.38; H, 9.61; S, 12.75.

Synthesis of P15:



The title compound was obtained as a yellow orange solid (242.8 mg, 95%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

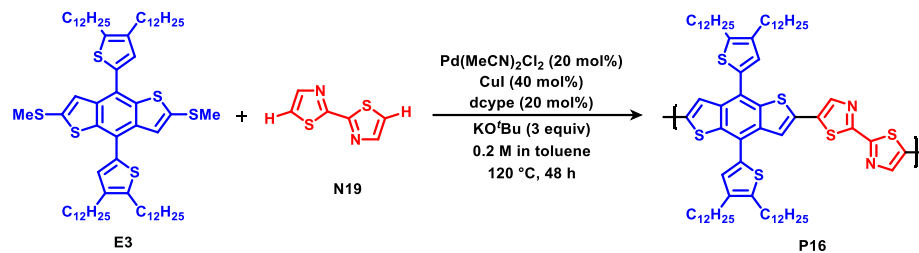
GPC (TCB, 150 °C): $M_n = 15.1$ kg/mol, $M_w = 26.1$ kg/mol, $D = 1.73$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.87-7.54 (m, 8H), 7.44-7.08 (m, 4H), 4.54-4.28 (m, 4H), 2.24-1.85 (m, 8H), 1.74-1.07 (m, 84H), 1.04-0.71 (m, 12H).

IR (film), ν (cm^{-1}): 2920, 2851, 2358, 2334, 1661, 1632, 1470.

Elemental analysis: Calculated for $((\text{C}_{83}\text{H}_{120}\text{O}_2\text{S}_4)_n)$: C, 78.00; H, 9.46; S, 10.03; found: C, 75.57; H, 8.63; S, 10.29.

Synthesis of P16:



The title compound was obtained as a red solid (226.9 mg, 95%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

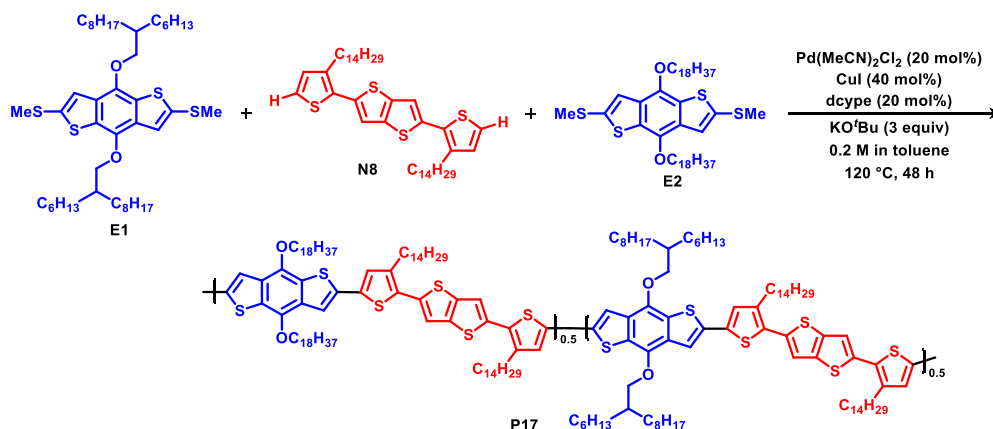
GPC (TCB, 150 °C): $M_n = 11.6$ kg/mol, $M_w = 22.0$ kg/mol, $D = 1.90$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 8.16-7.17 (m, 6H), 3.21-2.39 (m, 8H), 2.01-1.08 (m, 80H), 1.05-0.73 (m, 12H).

IR (film), ν (cm^{-1}): 2919, 2849, 1457, 1171, 921, 825, 719, 660, 610.

Elemental analysis: Calculated for $((\text{C}_{72}\text{H}_{106}\text{N}_2\text{S}_6)_n)$: C, 72.55; H, 8.96; N, 2.35; S, 16.14; found: C, 71.44; H, 9.35; N, 1.92; S, 15.08.

Synthesis of P17:



Under nitrogen atmosphere, a mixture of **E1** (53.43 mg, 0.07 mmol), **E2** (57.36 mg, 0.07 mmol), **N8** (97.61 mg, 0.14 mmol), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (7.26 mg, 0.028 mmol), CuI (10.67 mg, 0.056 mmol), dcype (11.83 mg, 0.028 mmol), and KOtBu (47.13 mg, 0.42 mmol) were dissolved in toluene (0.7 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and heated at 120 °C for 48 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL) for precipitation. Then, the crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated and precipitated in methanol, dried over vacuum. Finally, the title compound

was obtained as dark red solid (179.6 mg, 92%).

GPC (TCB, 150 °C): M_n = 17.9 kg/mol, M_w = 39.1 kg/mol, $\bar{D}$ = 2.19.

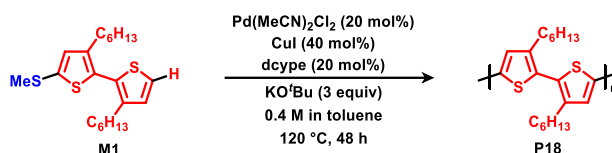
^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.78-6.90 (m, 6H), 4.54-3.93 (m, 4H), 3.04-2.54 (m, 4H), 2.17-0.56 (m, 120H).

IR (film), ν (cm^{-1}): 2923, 2851, 1468.

Elemental analysis: Calculated for $((\text{C}_{86}\text{H}_{134}\text{O}_2\text{S}_6)_n)$: C, 74.19; H, 9.70; S, 13.82; found: C, 72.98; H, 9.20; S, 12.93.

Procedure A: Under nitrogen atmosphere, a mixture of a monomer (0.40 mmol, 1 equiv), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (20.76 mg, 0.08 mmol, 20 mol%) or $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (40.88 mg, 0.08 mmol, 20 mol%), CuI (30.47 mg, 0.16 mmol, 40 mol%), dcype (33.81 mg, 0.08 mmol, 20 mol%), and KO^tBu (134.66 mg, 1.20 mmol, 3.0 equiv) were dissolved in toluene (1.0 or 2.0 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated to 120 °C for 48 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL) for precipitation. Then, the crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated and precipitated in methanol, dried over vacuum. Finally, the desired polymer was obtained.

Synthesis of P18:



The title compound was obtained as a yellow solid (129.0 mg, 97%). The reaction was performed according to Procedure A using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

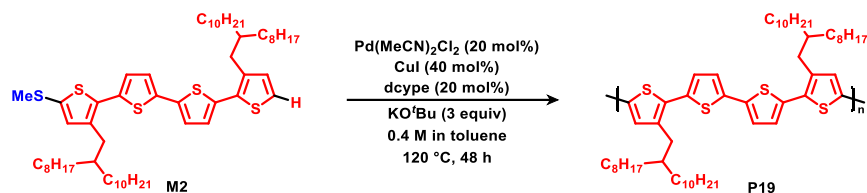
GPC (TCB, 150 °C): M_n = 33.6 kg/mol, M_w = 54.5 kg/mol, $\bar{D}$ = 1.62.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.28-6.96 (br s, 2H), 2.71-2.40 (br s, 4H), 1.77-1.49 (br s, 4H), 1.41-1.23 (m, 12H), 0.98-0.80 (br s, 6H).

IR (film), ν (cm^{-1}): 2919, 2849, 1653, 1635, 1456, 1376, 1176, 1112, 1015, 825, 722.

Elemental analysis: Calculated for $((\text{C}_{20}\text{H}_{28}\text{S}_2)_n)$: C, 72.23; H, 8.49; S, 19.28; found: C, 72.29; H, 8.24; S, 19.17.

Synthesis of P19:



The title compound was obtained as a dark red solid (348.7 mg, 98%). The reaction was performed according to Procedure A using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

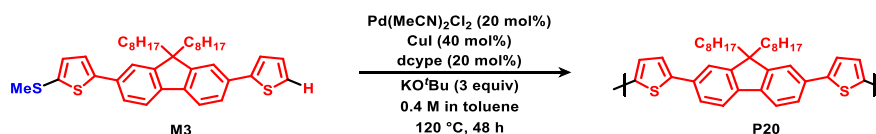
GPC (TCB, 150 °C): $M_n = 54.4$ kg/mol, $M_w = 79.8$ kg/mol, $D = 1.47$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.25-6.96 (m, 6H), 2.94-2.49 (br s, 4H), 1.86-1.68 (br s, 2H), 1.42-1.17 (m, 64H), 0.98-0.78 (m, 12H).

IR (film), ν (cm^{-1}): 2919, 2851, 1456, 1111, 1070, 782.

Elemental analysis: Calculated for $((\text{C}_{56}\text{H}_{88}\text{S}_4)_n)$: C, 75.61; H, 9.97; S, 14.42; found: C, 75.61; H, 9.57; S, 14.25.

Synthesis of P20:



The title compound was obtained as a yellow solid (214.5 mg, 97%). The reaction was performed according to Procedure A using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

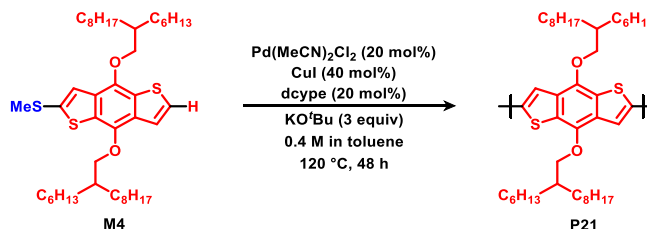
GPC (TCB, 150 °C): $M_n = 44.1$ kg/mol, $M_w = 62.5$ kg/mol, $D = 1.42$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.79-7.53 (m, 6H), 7.43-7.16 (m, 4H), 2.19-1.93 (m, 4H), 1.33-1.07 (m, 24H), 0.88-0.76 (m, 6H).

IR (film), ν (cm^{-1}): 2919, 2849, 1465, 1418, 791, 755.

Elemental analysis: Calculated for $((\text{C}_{37}\text{H}_{44}\text{S}_2)_n)$: C, 80.38; H, 8.02; S, 11.60; found: C, 78.14; H, 8.24; S, 11.21.

Synthesis of P21:



The title compound was obtained as a dark red solid (262.3 mg, 98%). The reaction was performed

according to Procedure A using $\text{Pd}(\text{MeCN})_2\text{Cl}_2$.

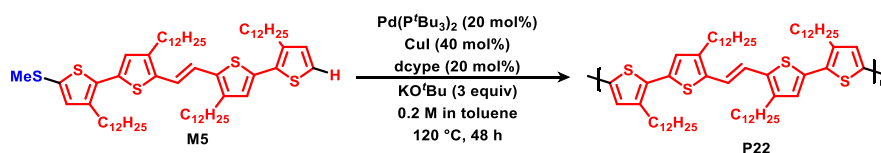
GPC (TCB, 150 °C): $M_n = 85.1$ kg/mol, $M_w = 139.7$ kg/mol, $D = 1.64$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.85-7.54 (m, 6H), 4.59-4.03 (m, 4H), 2.07-1.89 (m, 2H), 1.79-1.10 (m, 48H), 0.96-0.82 (m, 12H).

IR (film), ν (cm^{-1}): 2920, 2851, 1653, 1540, 1507, 1457, 1429, 1362, 1252, 1166, 1040, 817.

Elemental analysis: Calculated for $((\text{C}_{42}\text{H}_{68}\text{O}_2\text{S}_2)_n)$: C, 75.39; H, 10.24; S, 9.58; found: C, 74.49; H, 10.31; S, 9.60.

Synthesis of P22:



The title compound was obtained as a black solid (417.4 mg, 97%). The reaction was performed according to Procedure A using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$ (40.88 mg, 0.08 mmol), and toluene (2.0 mL).

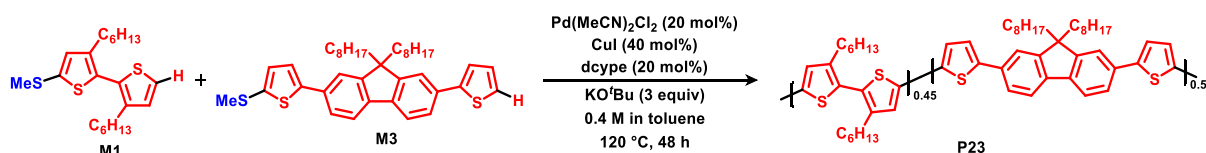
GPC (TCB, 150 °C): $M_n = 67.4$ kg/mol, $M_w = 121.4$ kg/mol, $D = 1.80$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.09-6.85 (m, 6H), 2.95-2.53 (m, 8H), 1.86-1.57 (m, 8H), 1.54-1.12 (m, 72H), 1.00-0.79 (m, 12H).

IR (film), ν (cm^{-1}): 2913, 2846, 1448, 920, 819.

Elemental analysis: Calculated for $((\text{C}_{66}\text{H}_{106}\text{S}_4)_n)$: C, 77.13; H, 10.40; S, 12.48; found: C, 77.90; H, 10.37; S, 11.83.

Synthesis of P23:



Under nitrogen atmosphere, a mixture of **M1** (54.24 mg, 0.142 mmol), **M3** (106.44 mg, 0.177 mmol), $\text{Pd}(\text{MeCN})_2\text{Cl}_2$ (16.75 mg, 0.064 mmol), CuI (24.35 mg, 0.128 mmol), dcype (27.11 mg, 0.064 mmol), and KO^tBu (107.72 mg, 0.96 mmol) were dissolved in toluene (0.8 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 120 °C for 48 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL). Then, the crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated and

precipitated in methanol, dried over vacuum. Finally, the title compound was obtained as a yellow orange solid (135.5 mg, 93%).

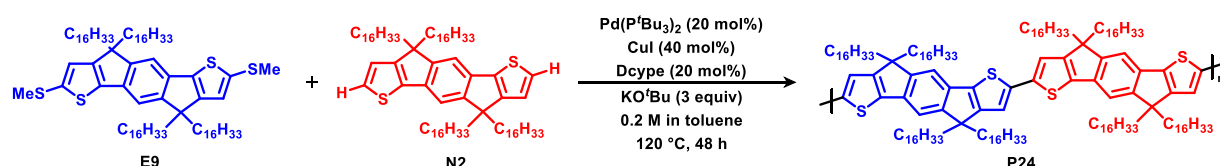
GPC (TCB, 150 °C): $M_n = 20.1$ kg/mol, $M_w = 32.7$ kg/mol, $D = 1.63$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.82-7.52 (m, 3.3H), 7.38-7.03 (m, 3.1H), 2.71-2.50 (m, 1.8H), 2.23-2.00 (m, 2.2H), 1.70-1.61 (m, 1.8H), 1.43-1.11 (m, 18.6H), 1.03-0.74 (m, 6H).

IR (film), ν (cm^{-1}): 2923, 2852, 1737, 1659, 1632, 1465, 1375, 1005, 948, 884, 747.

Elemental analysis: Calculated for $((\text{C}_{29.35}\text{H}_{36.80}\text{S}_2)_n)$: C, 74.18; H, 9.19; S, 16.63; found: C, 74.02; H, 8.89; S, 16.09.

Synthesis of P24:



The title compound was obtained as a red solid (441.5 mg, 95%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$.

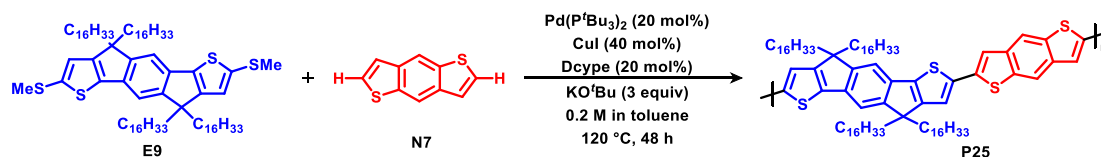
GPC (TCB, 150 °C): $M_n = 20.3$ kg/mol, $M_w = 35.3$ kg/mol, $D = 1.73$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.41-6.90 (m, 8H), 2.20-1.64 (m, 16H), 1.37-0.95 (m, 224H), 0.94-0.75 (m, 24H).

IR (film), ν (cm^{-1}): 2912, 2848, 1467, 1322, 871, 814, 716, 661, 626.

Elemental analysis: Calculated for $((\text{C}_{160}\text{H}_{272}\text{S}_4)_n)$: C, 82.69; H, 11.80; S, 5.51; found: C, 83.97; H, 11.85; S, 5.38.

Synthesis of P25:



The title compound was obtained as a dark red solid (259.3 mg, 96%). The reaction was performed according to general synthetic procedure using $\text{Pd}(\text{P}^t\text{Bu}_3)_2$.

GPC (TCB, 150 °C): $M_n = 41.1$ kg/mol, $M_w = 70.8$ kg/mol, $D = 1.72$.

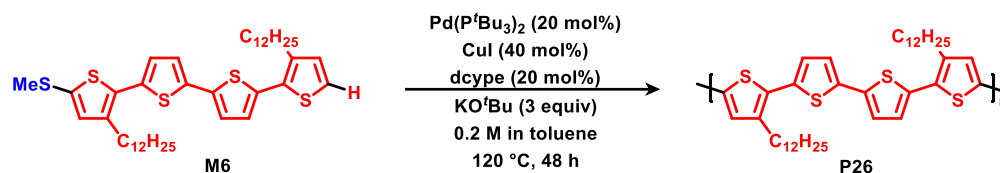
^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 8.24-8.06 (m, 2H), 7.70-6.90 (m, 6H), 2.69-1.70 (m, 8H), 1.44-

1.06 (m, 112H), 1.03-0.83 (m, 12H).

IR (film), ν (cm^{-1}): 2918, 2847, 2358, 1455.

Elemental analysis: Calculated for $((\text{C}_{90}\text{H}_{140}\text{S}_4)_n)$: C, 80.05; H, 10.45; S, 9.50; found: C, 80.88, H, 10.67, S, 8.35.

Synthesis of P26:



The title compound was obtained as a dark red solid (239 mg, 90%). The reaction was performed according to Procedure A using Pd(P^tBu₃)₂.

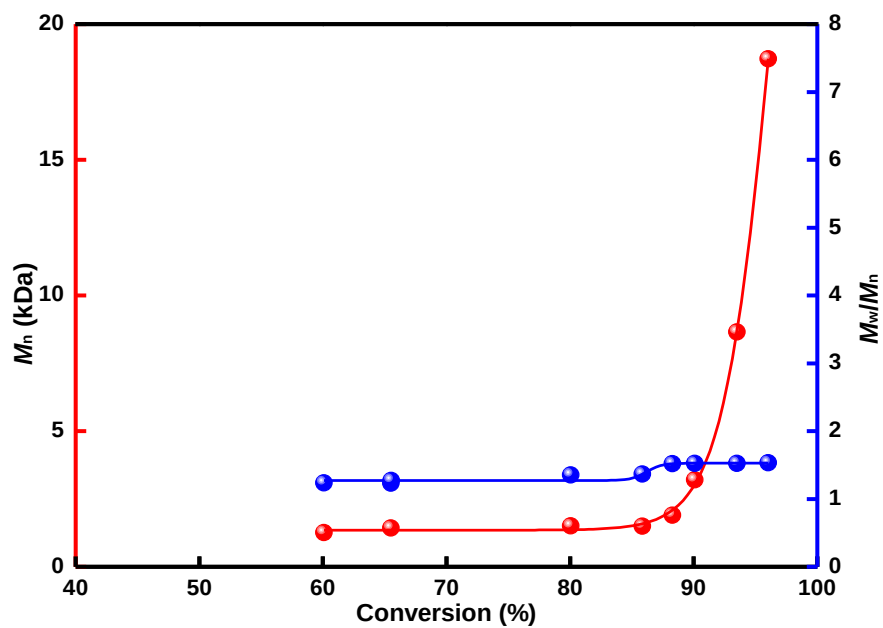
GPC (TCB, 150 °C): M_n = 26.5 kg/mol, M_w = 62.1 kg/mol, D = 2.34.

¹H NMR (500 MHz, C₂D₂Cl₄, 373 K): 7.17 (br s, 2H), 7.12-7.01 (m, 4H), 2.81 (br s, 4H), 1.73 (br s, 4H), 1.51-1.22 (m, 36H), 0.95-0.85 (m, 6H).

Elemental analysis: Calculated for $((\text{C}_{40}\text{H}_{56}\text{S}_4)_n)$: C, 72.23; H, 8.49; S, 19.28; found: C, 74.93; H, 9.00; S, 15.85.

V-3. Mechanistic studies on homopolycondensation

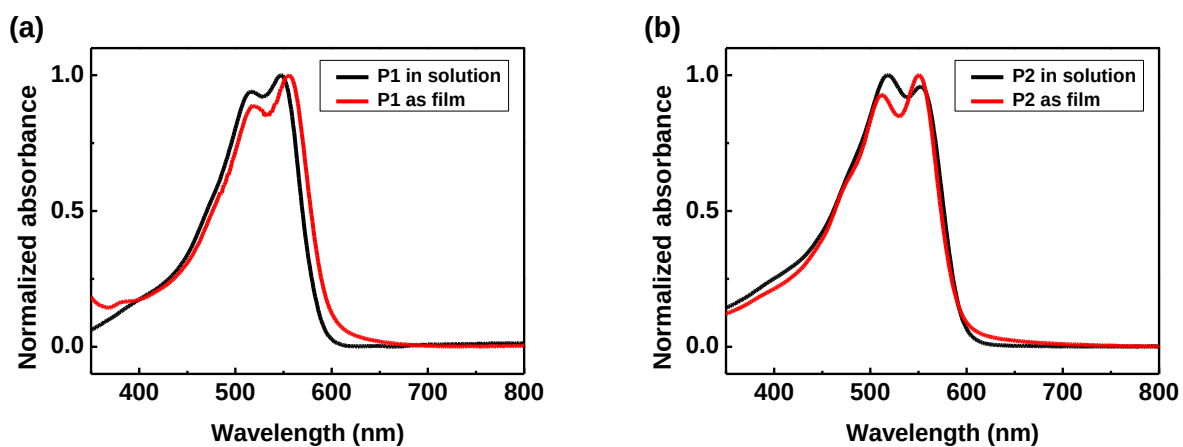
Under nitrogen atmosphere, a mixture of **M1** (76.08 mg, 0.20 mmol), Pd(MeCN)₂Cl₂ (10.38 mg, 0.04 mmol, 20 mol%), CuI (15.23 mg, 0.08 mmol, 40 mol%), dcype (16.90 mg, 0.04 mmol, 20 mol%), and KO^tBu (67.33 mg, 0.6 mmol, 3 equiv.) was dissolved in toluene (1.0 mL) in a Schlenk tube. The reaction was stirred at 120 °C, and taken portions out at the reaction time of 0.5, 1, 1.5, 2, 3, 4, 5, and 6 h. Then these samples were quenched by addition of chilled methanol (20.0 mL). The solid was collected by filtration, which was redissolved in dichloromethane and filtered through a pad of Celite. The collected solution was concentrated under reduced pressure, and analyzed by GPC.

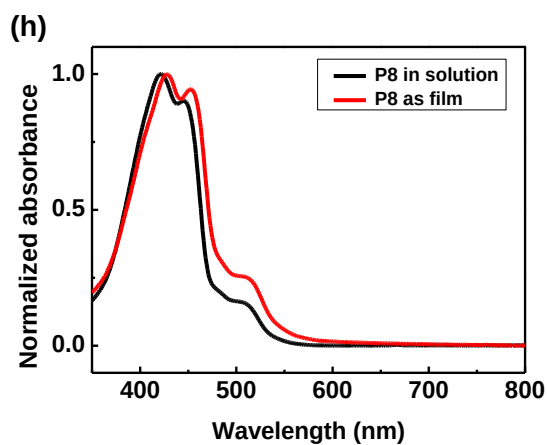
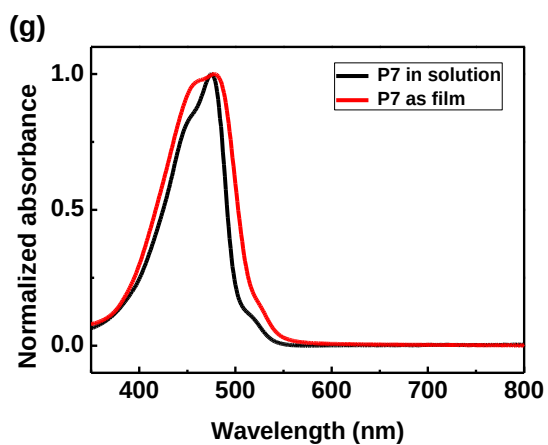
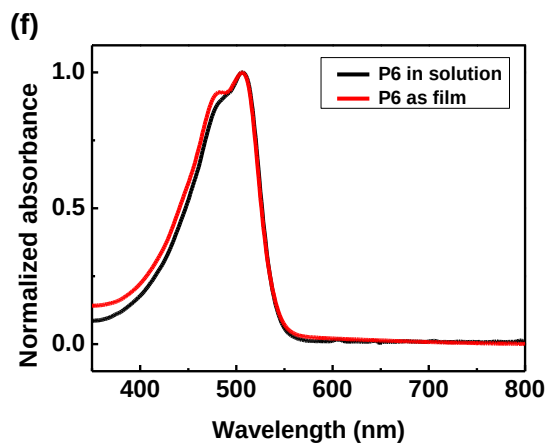
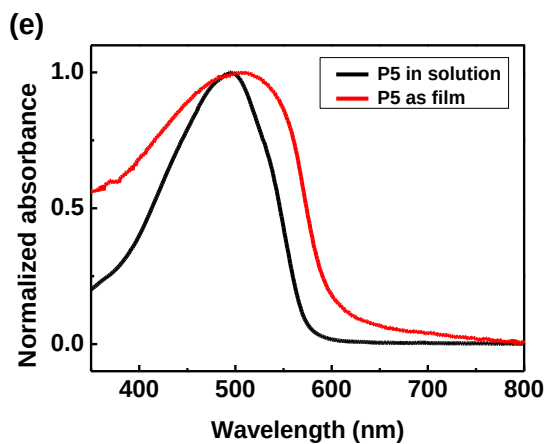
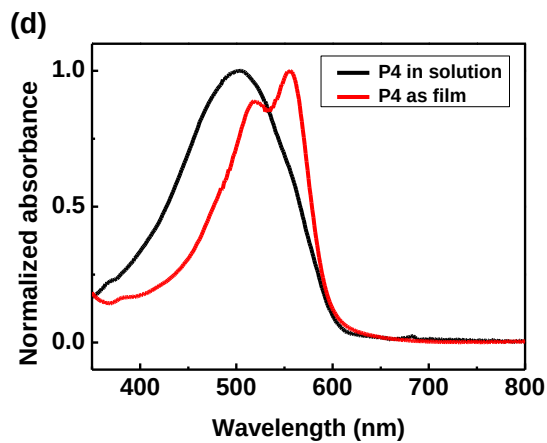
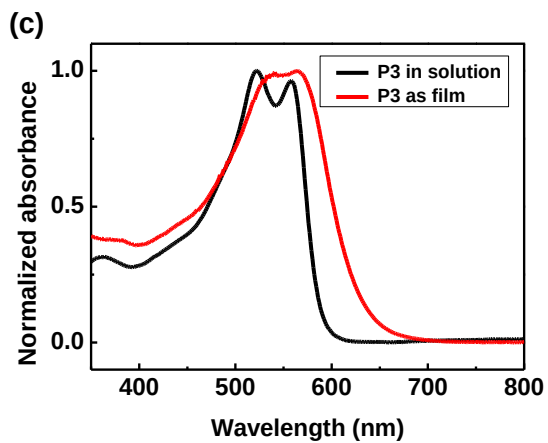


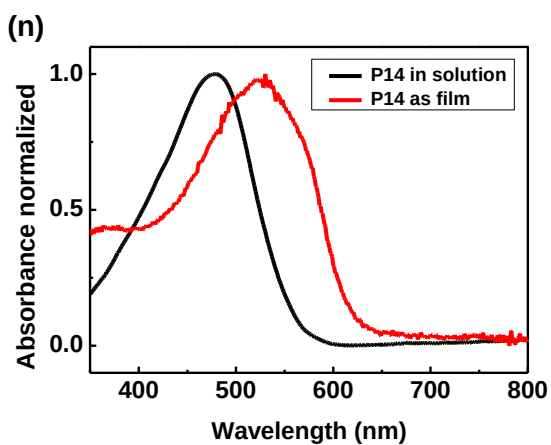
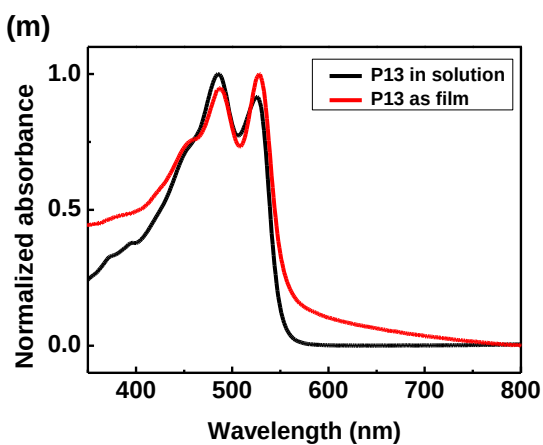
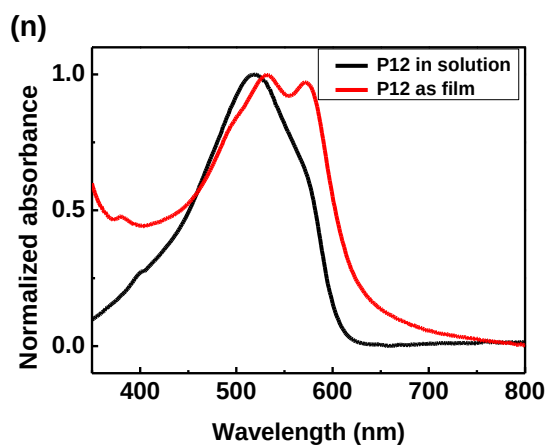
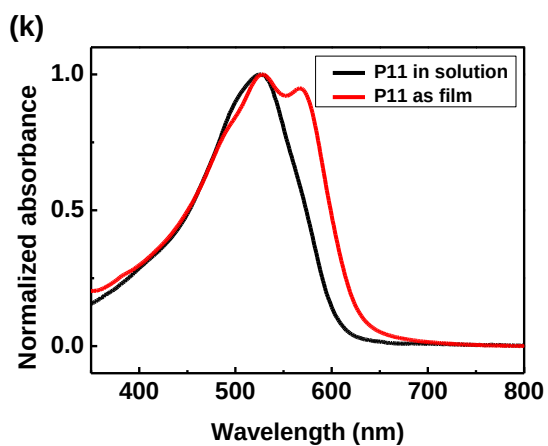
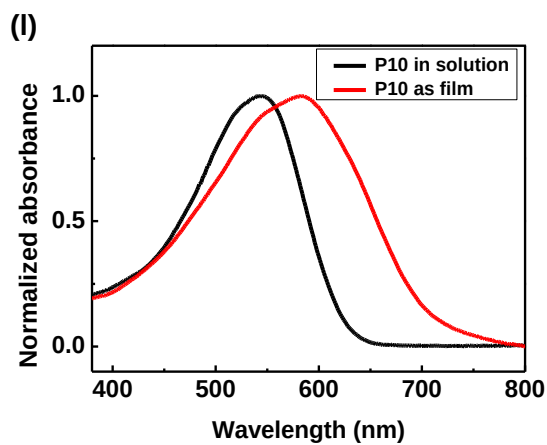
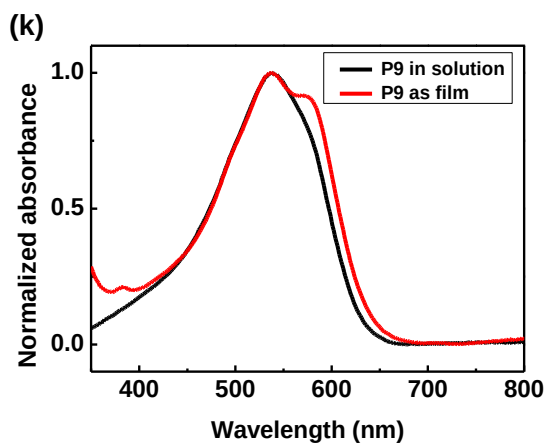
Supplementary Fig. 15. M_n and M_w/M_n values of **P18** as a function of monomer conversion.

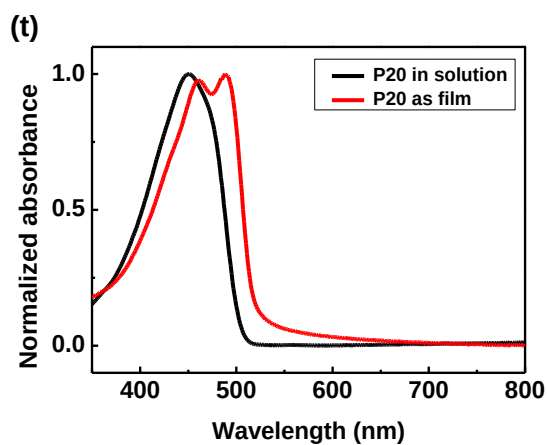
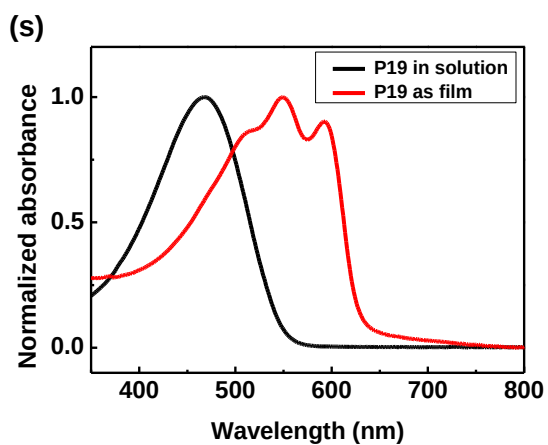
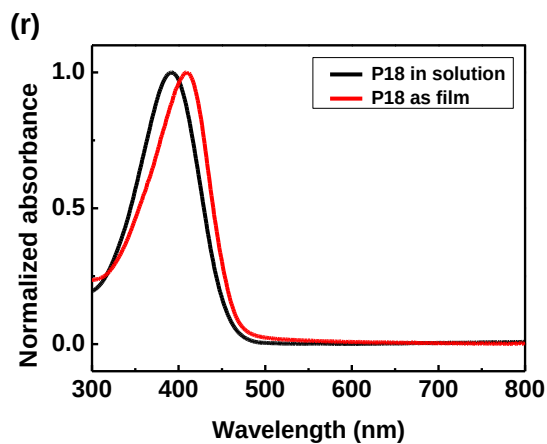
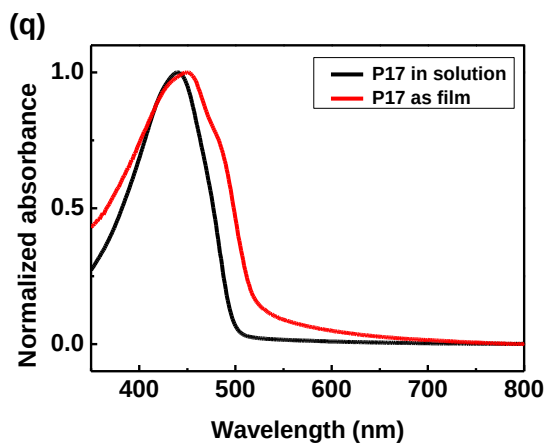
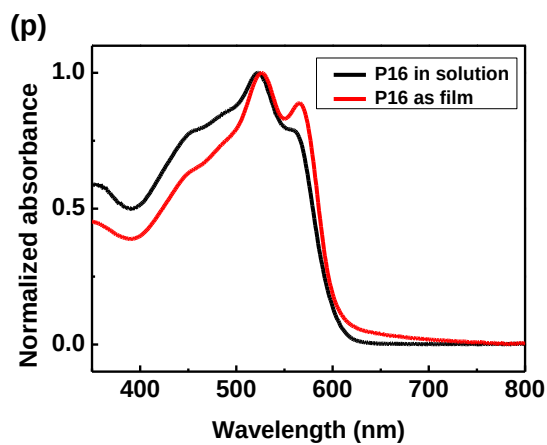
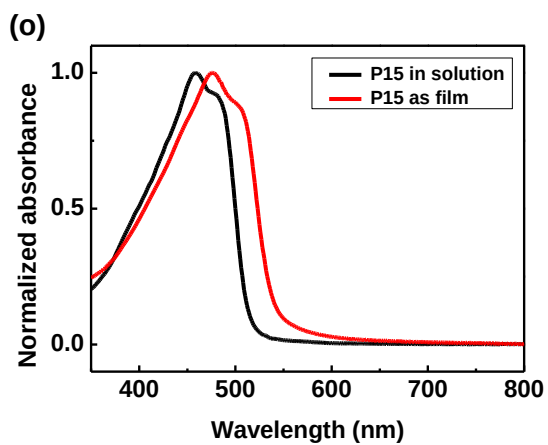
VI. Characterization

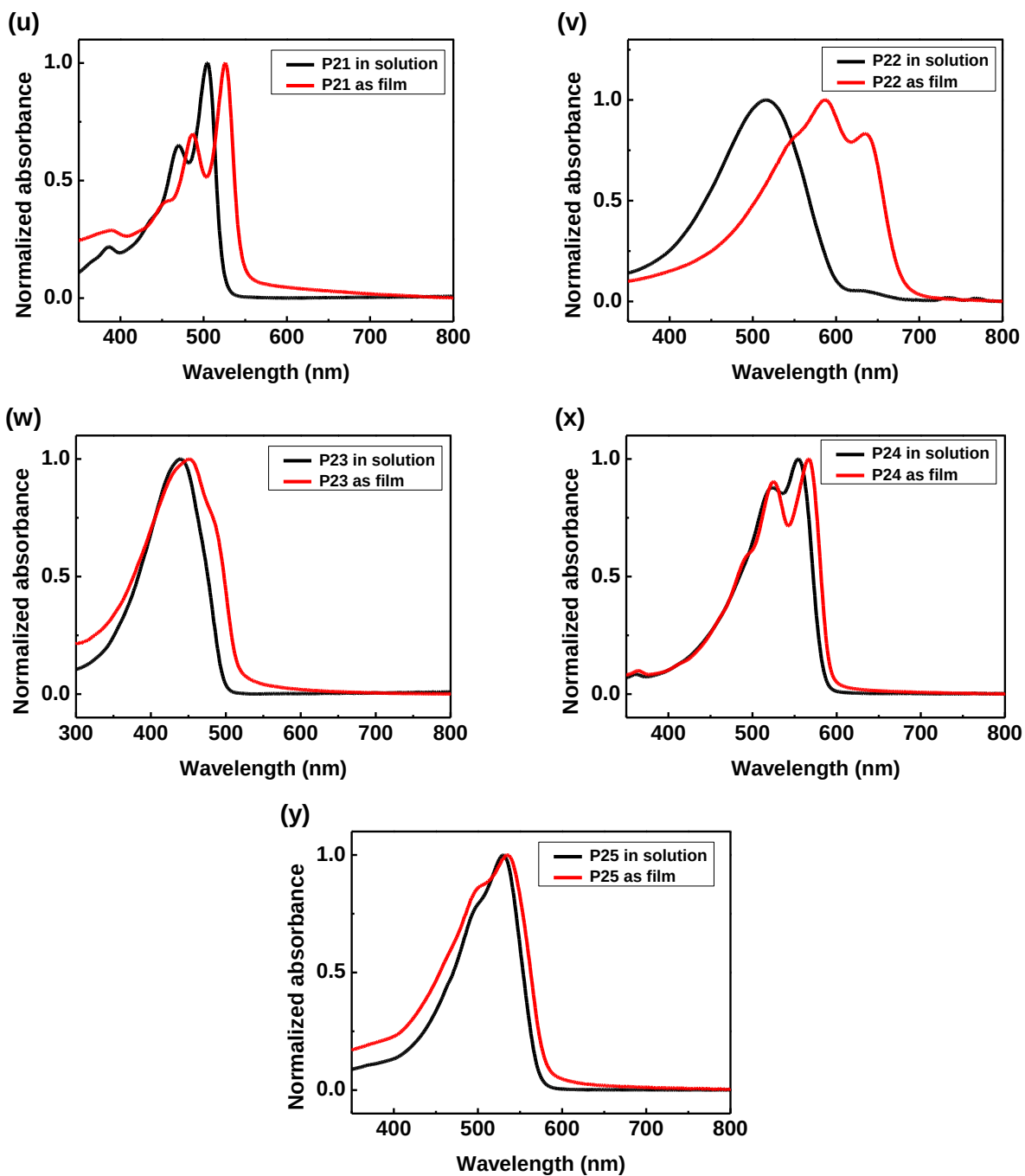
VI-1. Optical and electrochemical properties



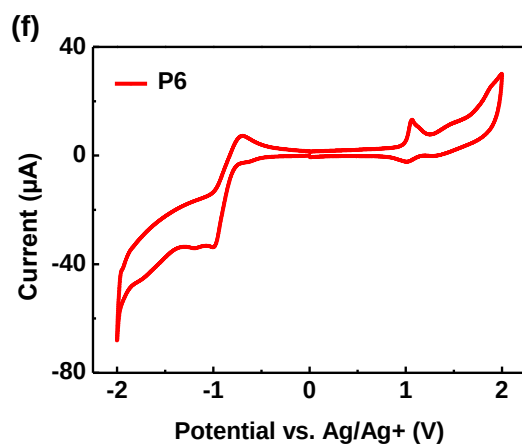
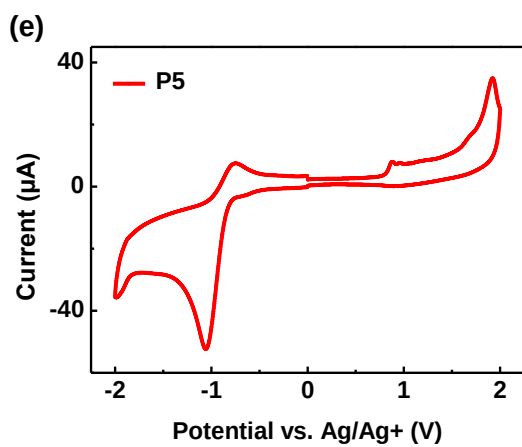
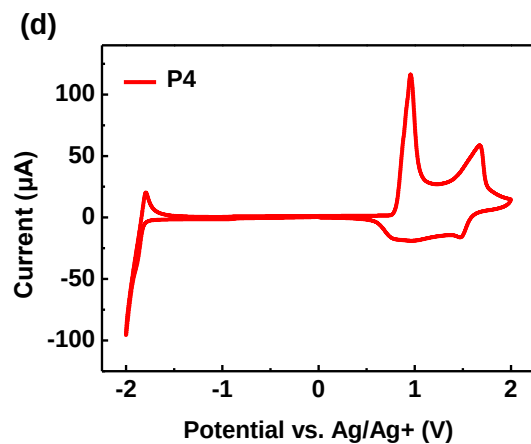
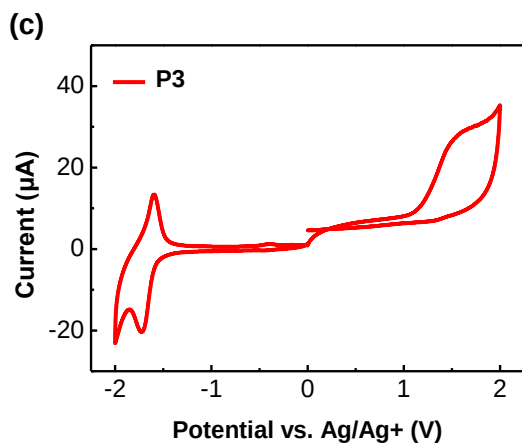
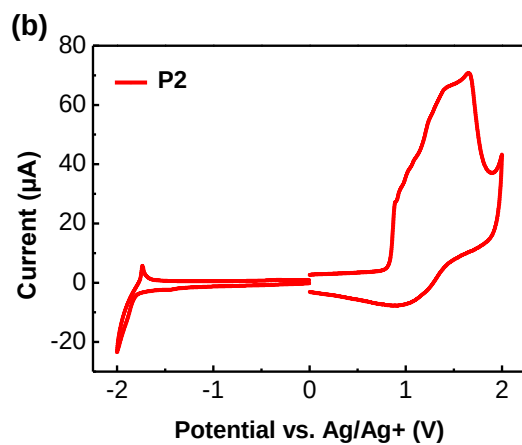
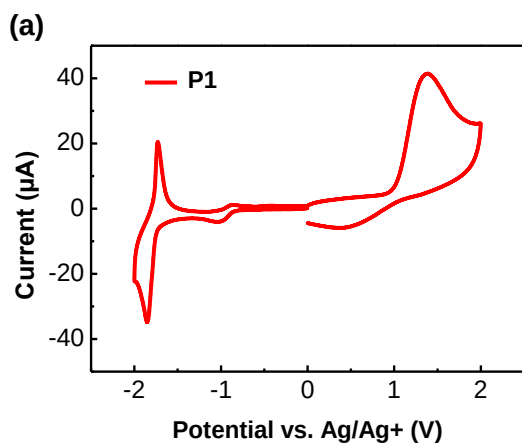


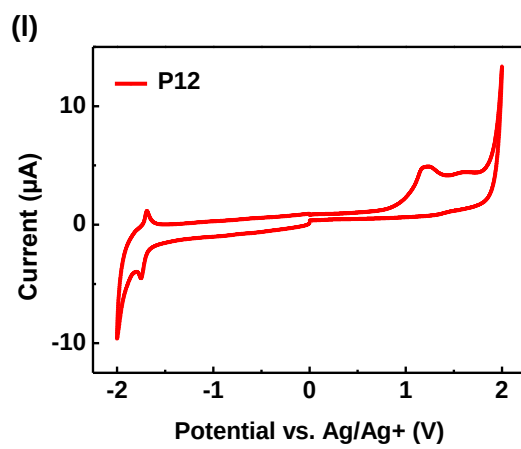
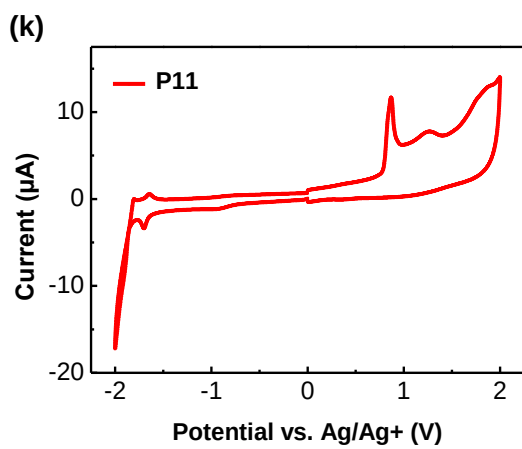
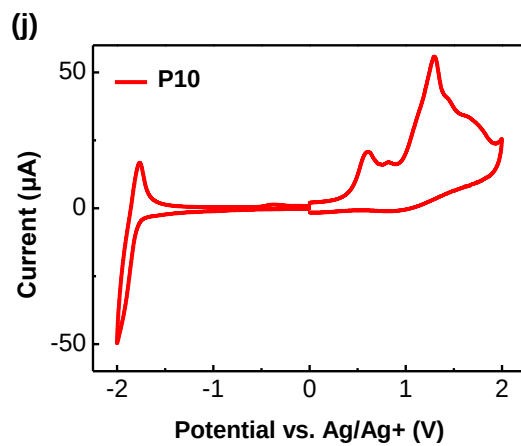
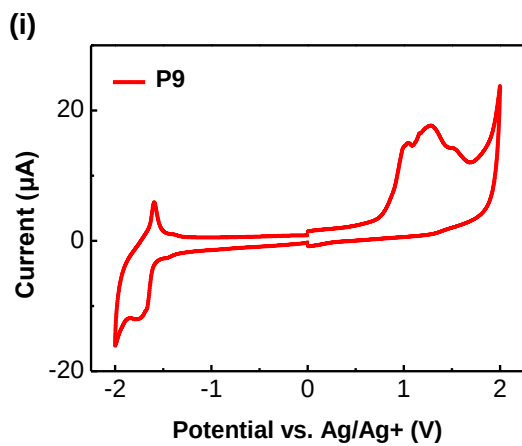
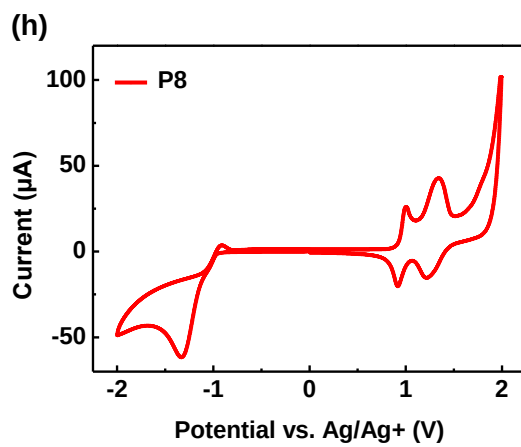
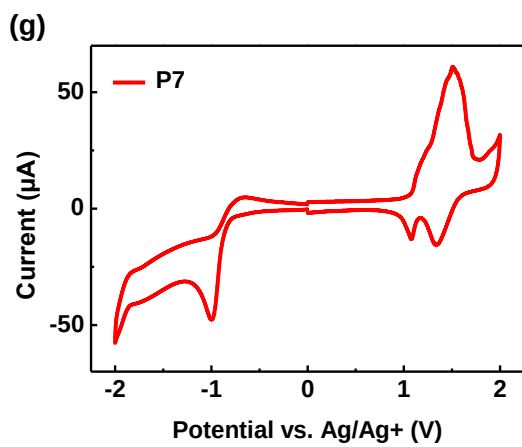


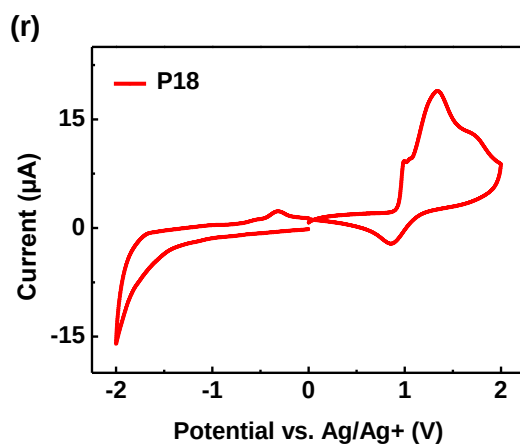
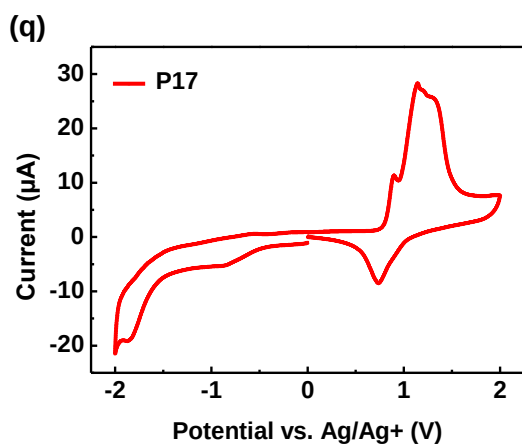
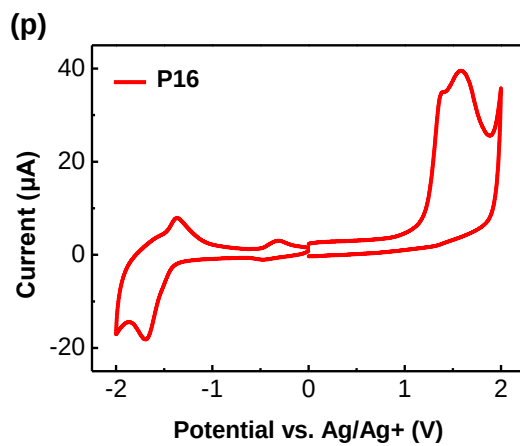
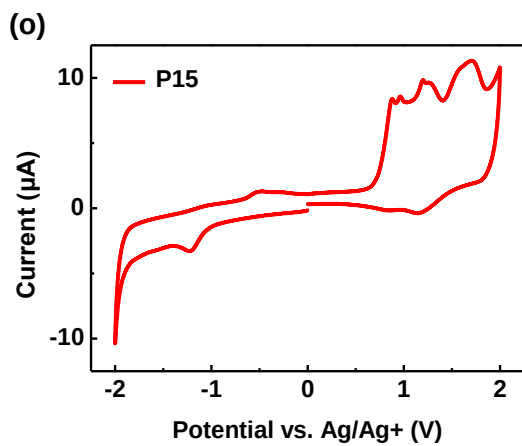
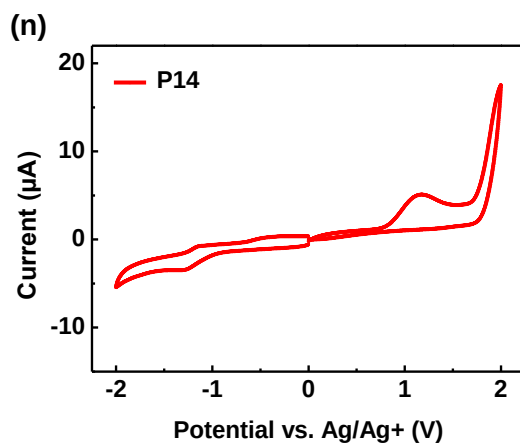
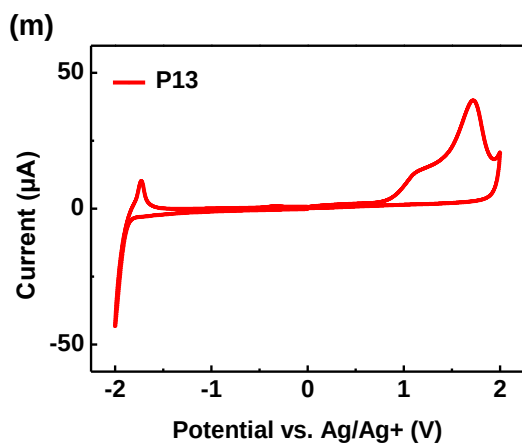


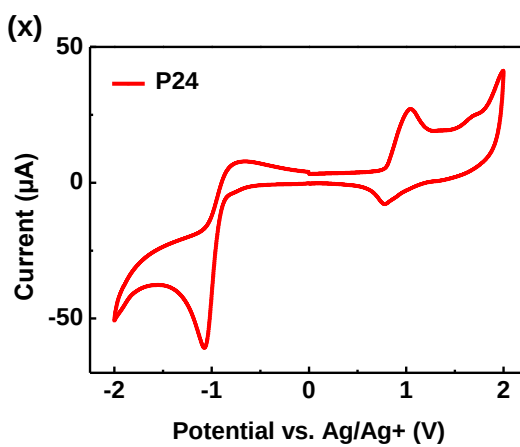
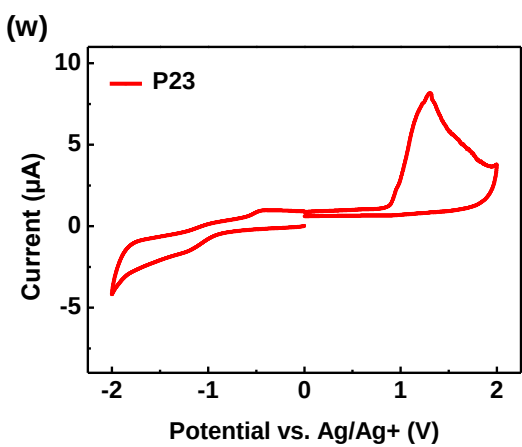
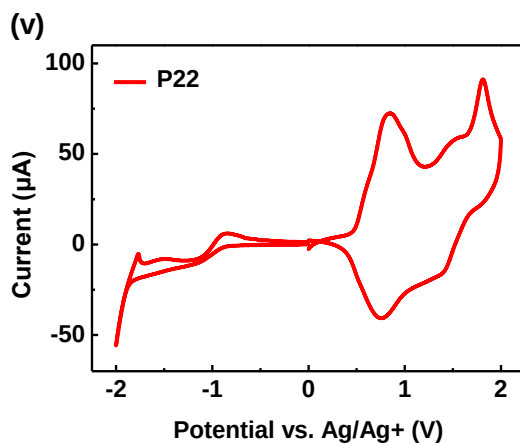
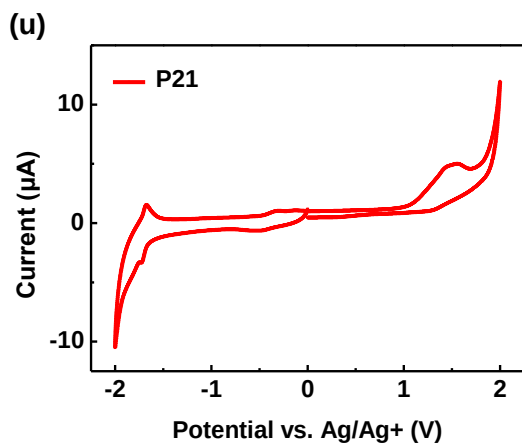
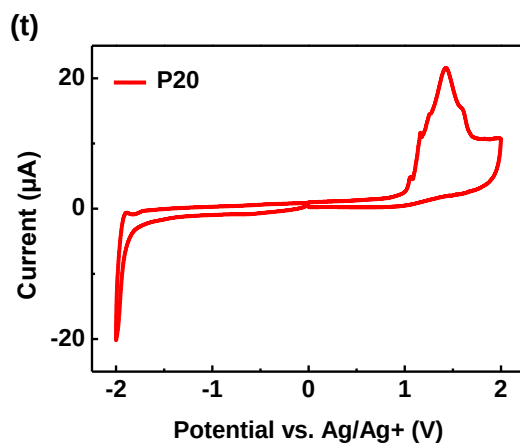
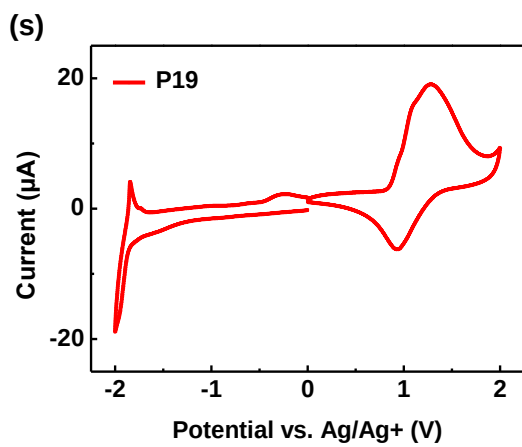


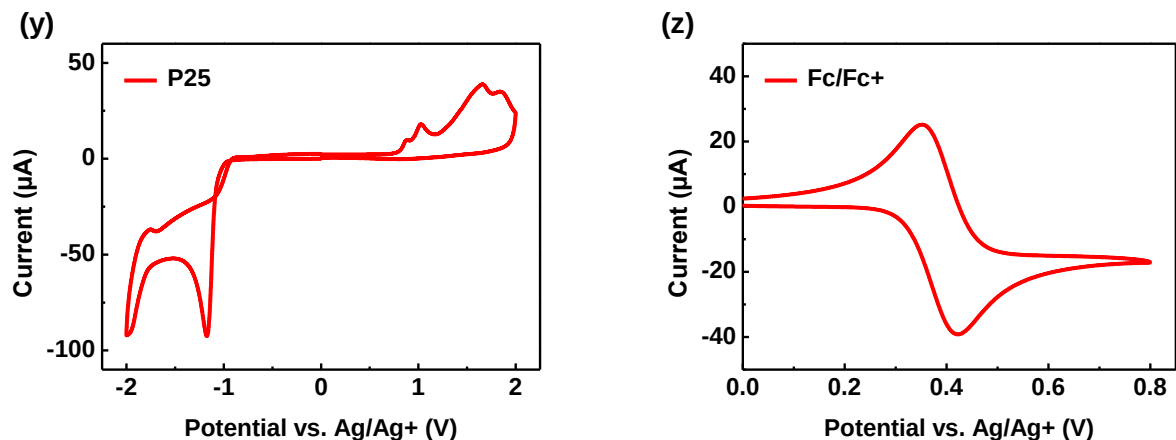
Supplementary Fig. 16. (a)-(y): UV-vis-NIR absorption spectra of **P1-P25** in chloroform solutions and as films.





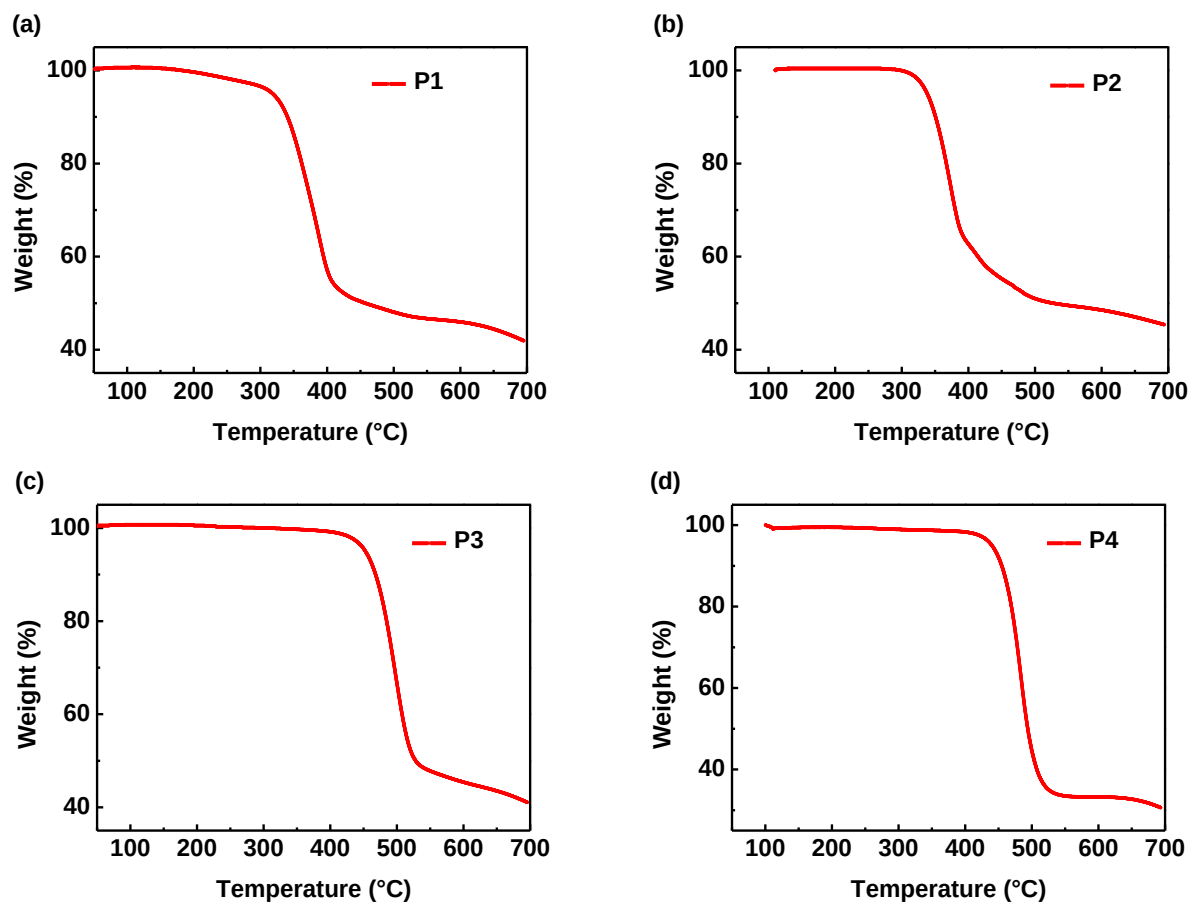


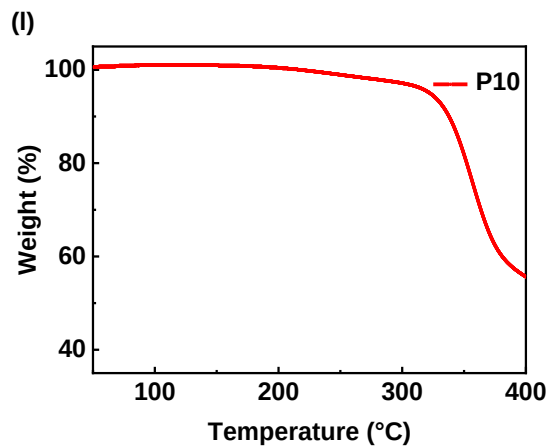
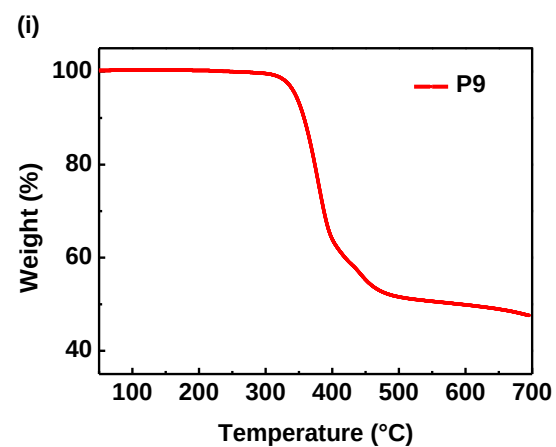
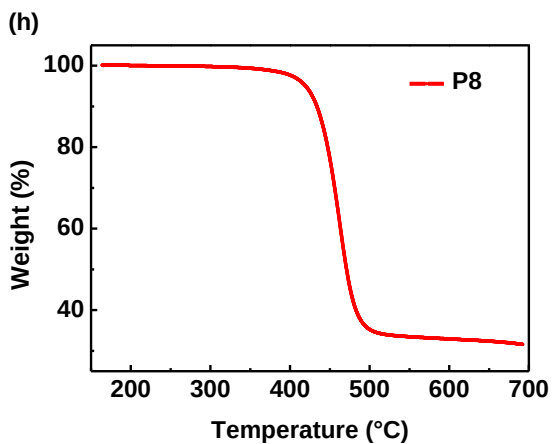
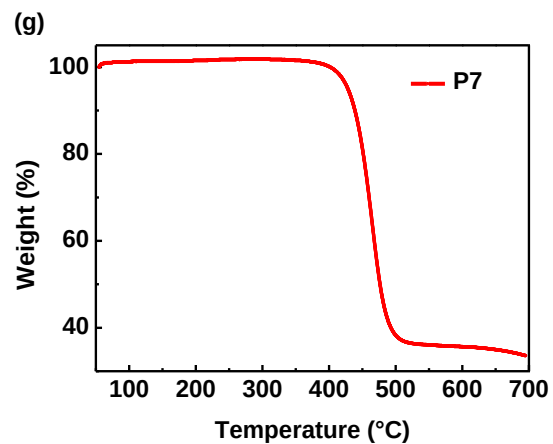
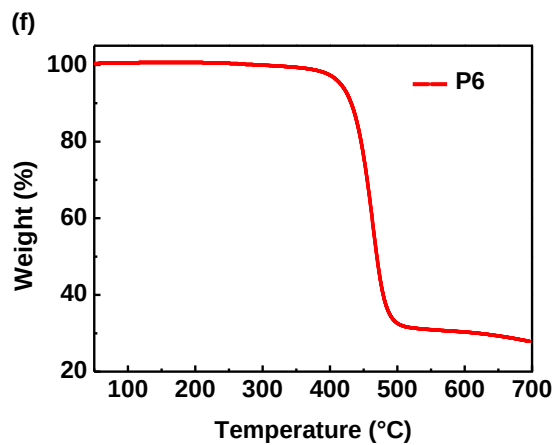
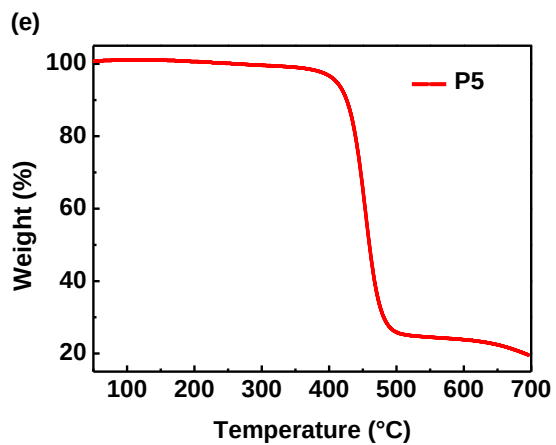


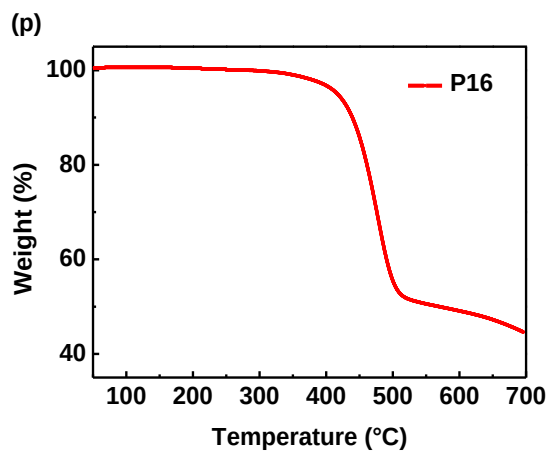
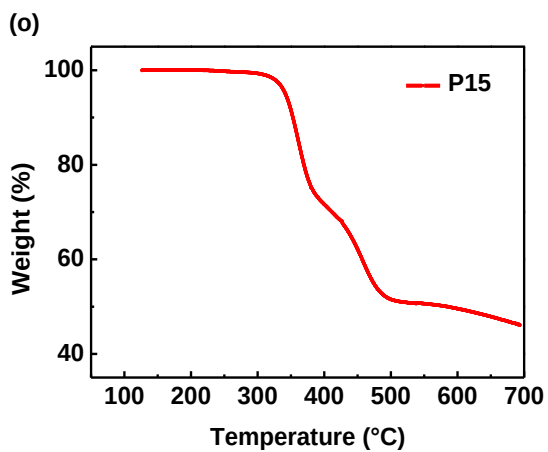
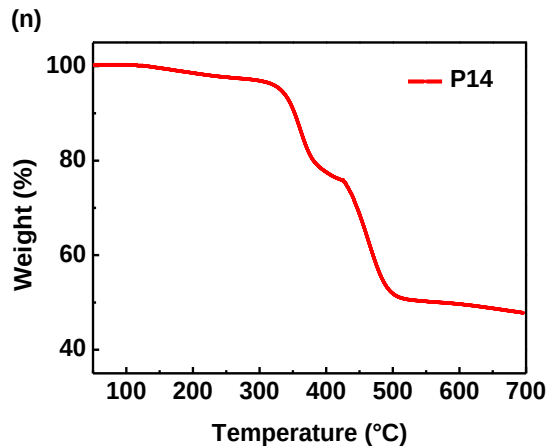
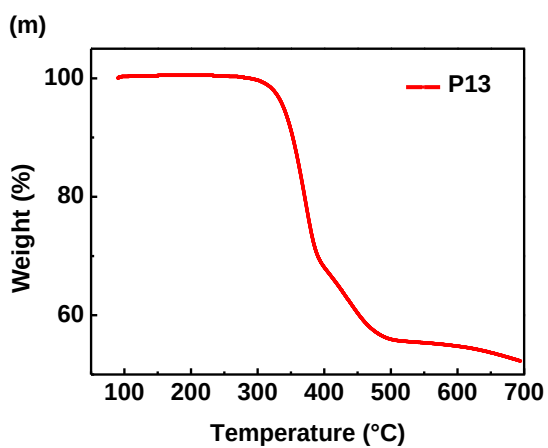
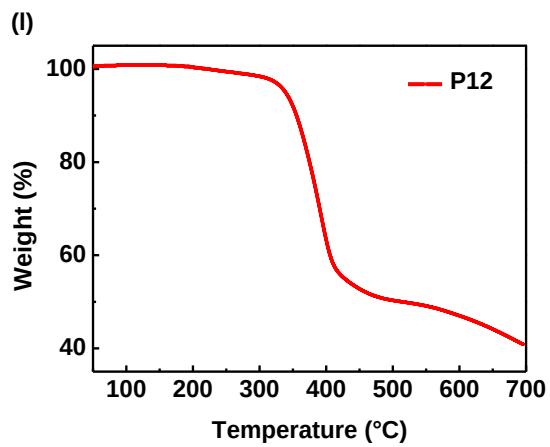
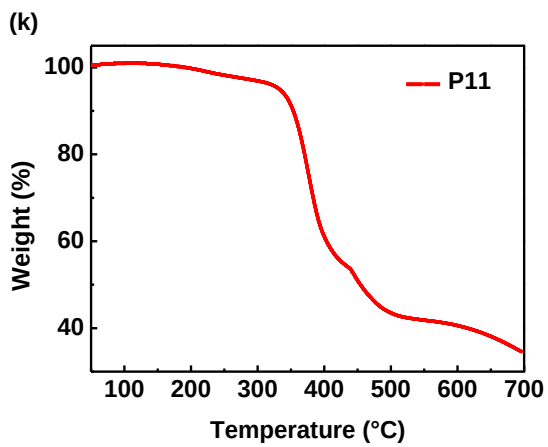


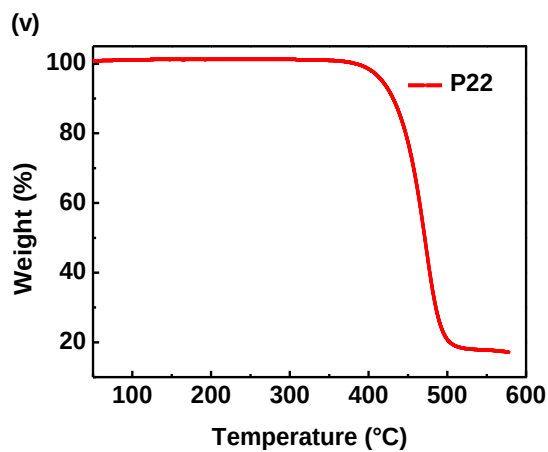
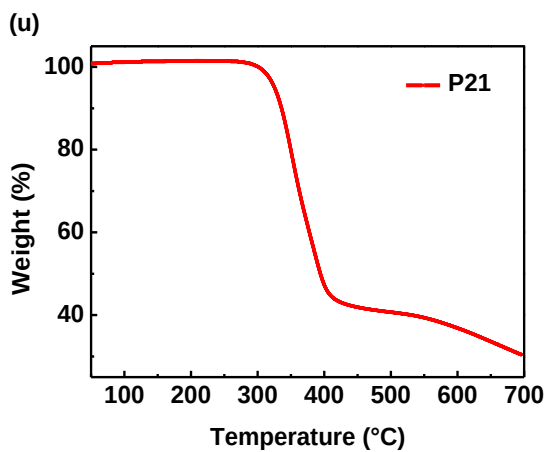
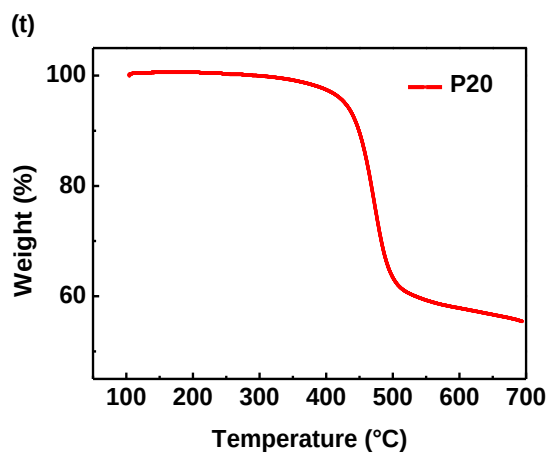
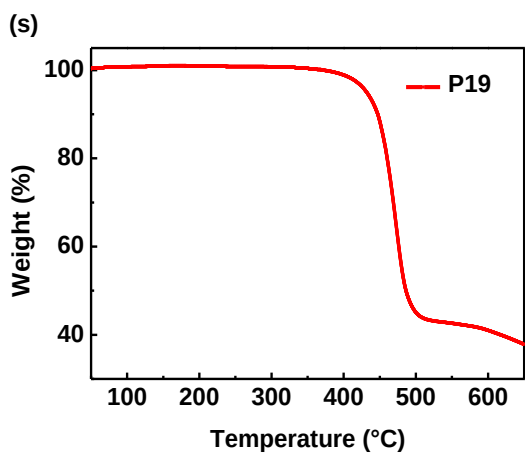
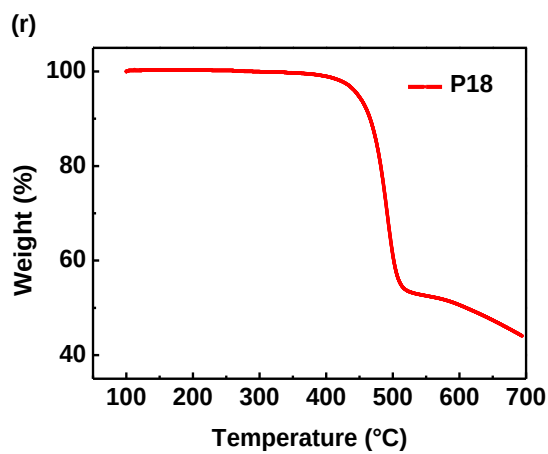
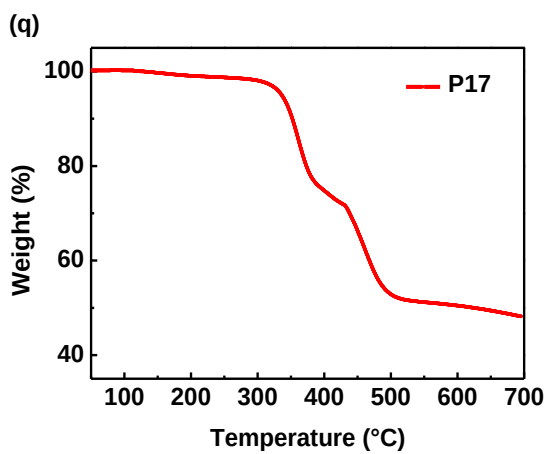
Supplementary Fig. 17. (a)-(z): Cyclic voltammograms of **P1-P25** thin films in CH₃CN/0.1 M [*n*-Bu₄N]⁺[PF₆]⁻ at 50 mV s⁻¹. Glassy carbon electrodes were used as the working electrodes, Pt electrodes as the counter electrodes, and with Ag/Ag⁺ (sat. NaCl) as the pseudoreference electrode. A ferrocene/ferrocenium (Fc/Fc⁺) redox couple was used as the internal standard and was assigned an absolute energy level of -4.80 eV vs vacuum.

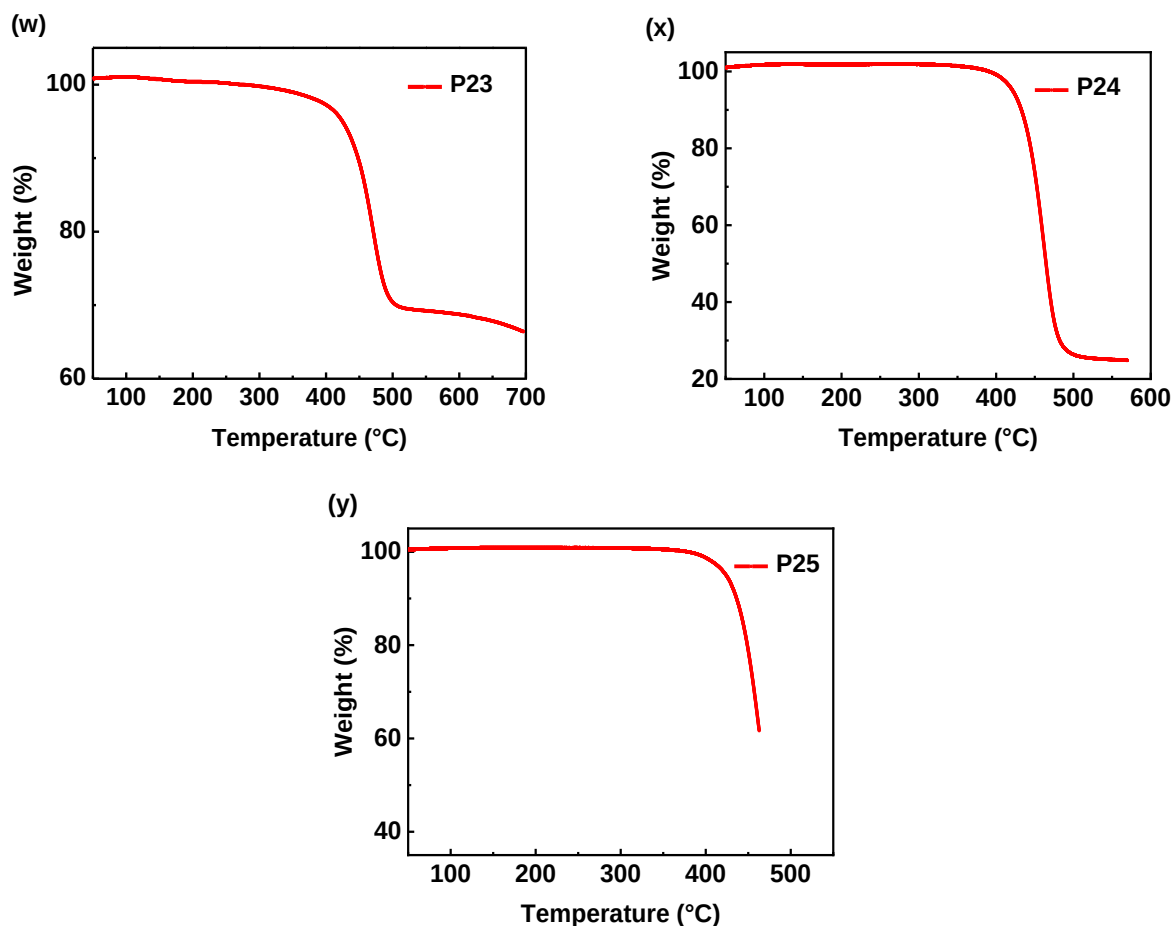
VI-2. Thermal properties











Supplementary Fig. 18. (a)-(y): Thermal gravimetric analysis (TGA) of the polymers **P1-P25**.

Supplementary Table 5. Optical, electrochemical, and thermal properties of the polymers **P1-P25**.

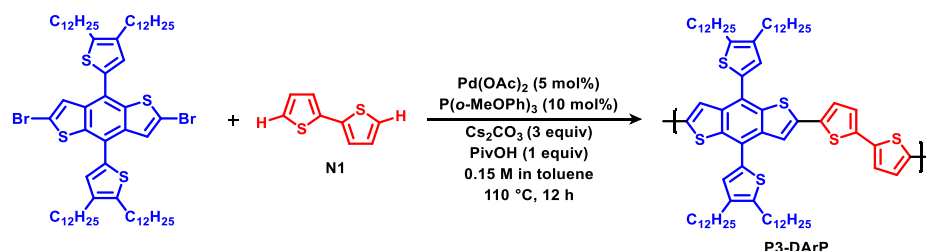
	Absorbance ^a		CV ^b				TGA ^c
	λ_{sol} (nm)	λ_{film} (nm)	E_{red} (V)	E_{ox} (V)	LUMO (eV)	HOMO (eV)	T_d (°C)
P1	592	596	-1.73	1.01	-2.68	-5.42	319
P2	600	592	-1.80	0.83	-2.61	-5.24	338
P3	593	637	-1.57	1.16	-2.84	-5.57	453
P4	603	599	-1.80	0.80	-2.61	-5.21	440
P5	576	601	-0.82	0.79	-3.59	-5.20	411
P6	547	545	-0.75	0.98	-3.66	-5.39	416
P7	539	545	-0.86	1.00	-3.55	-5.41	428
P8	539	550	-0.97	0.93	-3.44	-5.34	419
P9	632	638	-1.58	0.78	-2.83	-5.19	345
P10	626	702	-1.77	0.36	-2.64	-4.77	322
P11	609	628	-1.60	0.77	-2.81	-5.18	333

P12	608	626	-1.64	0.94	-2.77	-5.35	339
P13	552	557	-1.87	0.85	-2.54	-5.26	339
P14	565	615	-0.96	0.77	-3.45	-5.18	332
P15	513	541	-1.04	0.71	-3.37	-5.12	342
P16	605	602	-1.40	1.18	-3.01	-5.59	417
P17	498	519	-1.54	0.79	-2.87	-5.20	336
P18	457	466	-1.39	0.93	-3.02	-5.34	448
P19	547	628	-1.85	0.85	-2.56	-5.26	432
P20	504	518	-1.86	0.98	-2.55	-5.39	428
P21	526	548	-1.64	1.02	-2.77	-5.43	325
P22	598	677	-0.89	0.47	-3.52	-4.88	417
P23	499	515	-0.91	0.87	-3.50	-5.28	425
P24	587	594	-0.86	0.79	-3.55	-5.20	421
P25	577	581	-1.05	0.77	-3.36	-5.18	424

^aAbsorption maxima. ^bPolymer thin films on a glassy-carbon electrode in CH₃CN/0.1 M [*n*-Bu₄N]⁺[PF₆]⁻, versus ferrocenium/ferrocene at 50 mV s⁻¹. *E*_{ox} is the onset potential corresponding to oxidations, whereas *E*_{red} is the onset potential corresponding to reductions. HOMO and LUMO are estimated from the onset oxidation and reduction potentials, respectively, assuming the absolute energy level of ferrocene/ferrocenium to be 4.8 eV below vacuum. ^cTemperature at 5% weight loss measured by TGA at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

VII. Defect Analysis

Synthesis of P3-DArP:



Under nitrogen atmosphere, a mixture of 2,6-dibromo-4,8-bis(4,5-didodecylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (118.56 mg, 0.10 mmol), **N1** (16.63 mg, 0.10 mmol), Pd(OAc)₂ (1.12 mg, 0.005 mmol), P(*o*-MeOPh)₃ (3.52 mg, 0.01 mmol), Cs₂CO₃ (97.75 mg, 0.30 mmol), and PivOH (10.21 mg, 0.10 mmol) were dissolved in toluene (1.0 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 110 °C for 12 h¹⁴. After cooling to room temperature, the

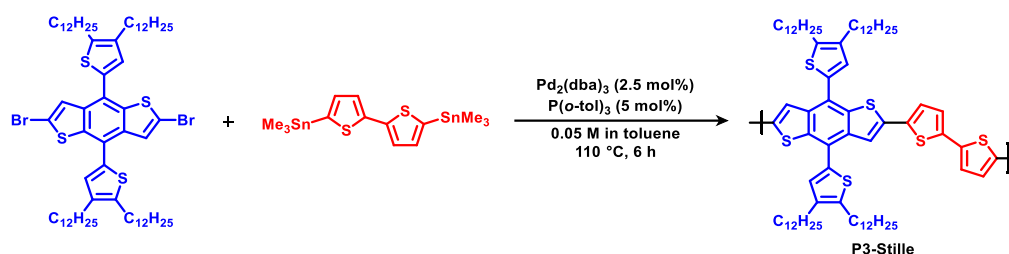
mixture was poured into chilled methanol (100.0 mL) for precipitation. Then, the crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated and precipitated in methanol, dried over vacuum. The title compound was obtained as a dark red solid (95.2 mg, 80%).

GPC (TCB, 150 °C): M_n = 15.8 kg/mol, M_w = 33.6 kg/mol, $\bar{D}$ = 2.12.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.89-6.84 (m, 8H), 2.98-2.47 (m, 8H), 1.87-1.61 (m, 8H), 1.60-0.98 (m, 72H), 0.97-0.73 (br s, 12H).

Elemental analysis: Calculated for $((\text{C}_{74}\text{H}_{108}\text{S}_6)_n)$: C, 74.69; H, 9.15; S, 16.16; found: C, 76.07; H, 8.92; S, 13.84.

Synthesis of P3-Stille:

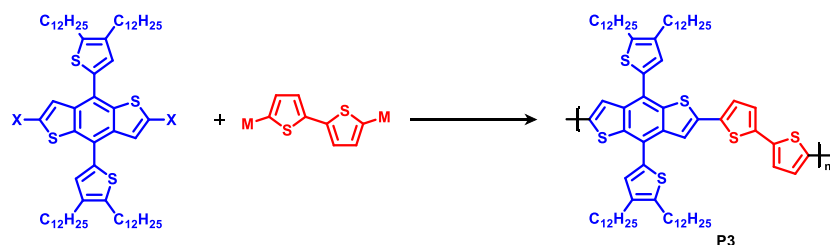


Under nitrogen atmosphere, a mixture of 2,6-dibromo-4,8-bis(4,5-didodecylthiophen-2-yl)benzo[1,2-*b*:4,5-*b'*]dithiophene (118.56 mg, 0.10 mmol), 5,5'-bis(trimethylstannyl)-2,2'-bithiophene (49.19 mg, 0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (2.29 mg, 0.0025 mmol), and $\text{P}(\text{o-tol})_3$ (1.52 mg, 0.005 mmol) were dissolved in toluene (2.0 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 110 °C for 6 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL) for precipitation. Then, the crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated and precipitated in methanol, dried over vacuum. The title compound was obtained as a dark red solid (115.4 mg, 97%).

GPC (TCB, 150 °C): M_n = 66.6 kg/mol, M_w = 191.3 kg/mol, $\bar{D}$ = 2.87.

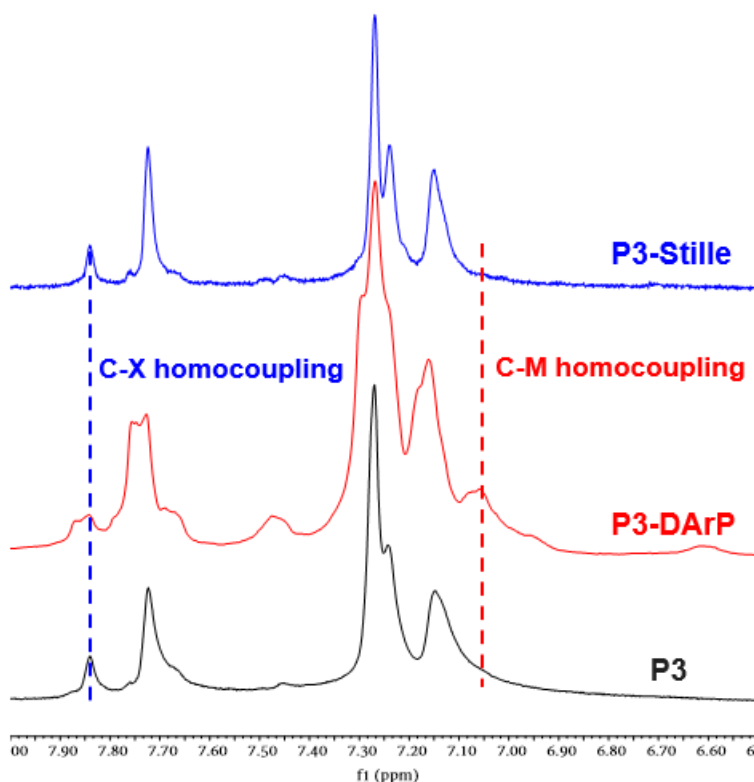
^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.94-6.91 (m, 8H), 3.04-2.50 (m, 8H), 1.95-1.67 (m, 8H), 1.64-1.08 (m, 72H), 1.03-0.72 (br s, 12H).

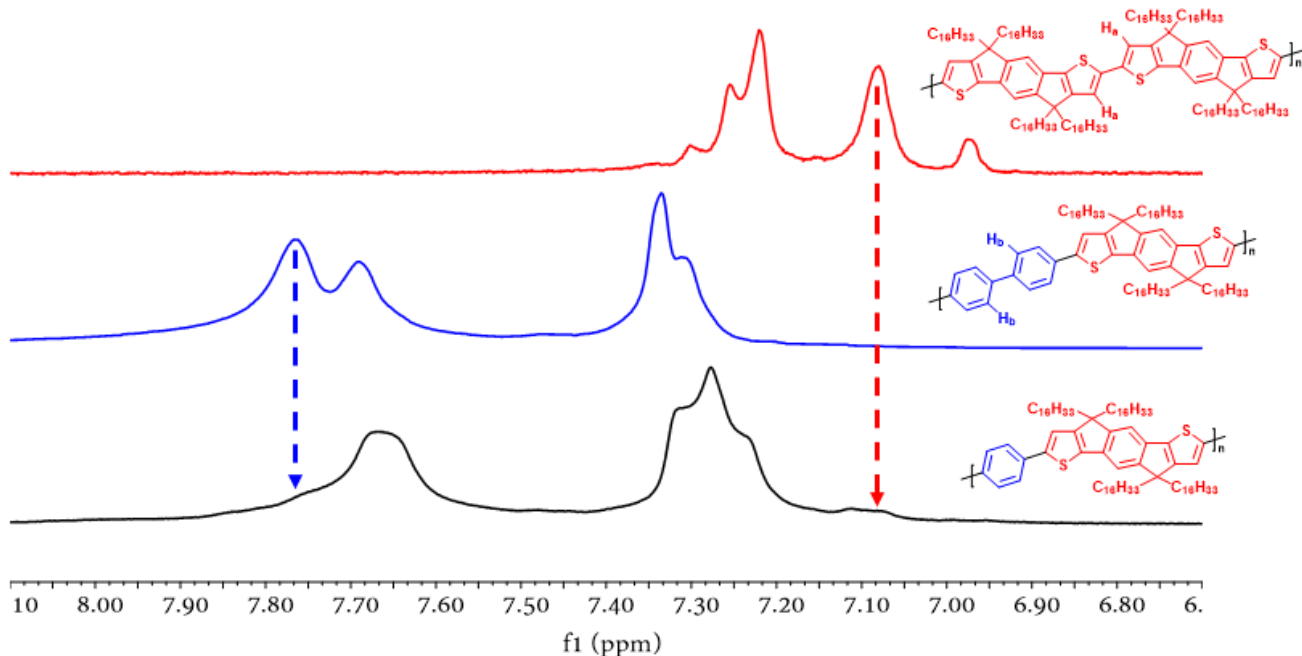
Elemental analysis: Calculated for $((\text{C}_{74}\text{H}_{108}\text{S}_6)_n)$: C, 74.69; H, 9.15; S, 16.16; found: C, 76.01; H, 8.95;

Supplementary Table 6. polycondensation of **P3**, **P3-DArP** and **P3-Stille**

Entry	Method (monomers)	M_n/M_w (kg/mol) ^a	$\bar{D}$ ^a	Yield (%)
1	DArP-CASP (X = SMe, M = H)	76.0/158.9	2.09	98
2^b	DArP (X = Br, M = H)	15.8/33.6	2.12	80
3^c	Stille (X = Br, M = SnMe ₃)	66.6/191.3	2.87	97

^a M_n , M_w , and $\bar{D}$ were determined with GPC at 150 °C in 1,2,4-trichlorobenzene against a polystyrene standard. ^bReaction conditions: Pd(OAc)₂ (5 mol%), P(*o*-MeOPh)₃ (10 mol%), Cs₂CO₃ (3.0 equiv), PivOH (1.0 equiv), 0.15 M in toluene, 12 h under nitrogen atmosphere (Mario Leclerc, et al. *ACS Macro Lett.* **2015**, 4, 21-24.). ^cReaction conditions: Pd₂(dba)₃ (2.5 mol%), P(*o*-tol)₃ (5 mol%), 0.05 M in toluene, 6 h under nitrogen atmosphere. This is a representative high M_w polymer from a Stille coupling polycondensation procedure.

**Supplementary Fig. 19.** The aromatic region of ¹H NMR for **P3**, **P3-DArP**, and **P3-Stille** from 8.00 to 6.50 ppm at 100 °C (C₂D₂Cl₄).



Supplementary Fig. 20. Defect analysis of **P6**. The aromatic region of ^1H NMR for **P6**, **P7**, and **P24** from 6.00 to 10.00 ppm at 100 °C ($\text{C}_2\text{D}_2\text{Cl}_4$).

VIII. Organic Field-Effect Transistors Fabrication and Characterization

Synthesis of P22-Stille: Under nitrogen atmosphere, a mixture of (*E*)-1,2-bis(3-dodecyl-5-(trimethylstannyl)thiophen-2-yl)ethene (85.46 mg, 0.10 mmol), 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene (66.07 mg, 0.10 mmol), $\text{Pd}_2(\text{dba})_3$ (4.58 mg, 0.005 mmol), and $\text{P}(\text{o-tol})_3$ (3.05 mg, 0.01 mmol) were dissolved in toluene (2.0 mL) in a Schlenk tube. The reaction was stirred at room temperature for 5 min and then heated at 110 °C for 12 h. After cooling to room temperature, the mixture was poured into chilled methanol (100.0 mL) for precipitation. Then, the crude polymer was collected by filtration and purified by successive Soxhlet extraction with acetone, hexane, and chloroform. Next, the chloroform fraction was filtered through a short silica gel (chloroform), concentrated and precipitated in methanol, dried over vacuum. The title compound was obtained as a dark red solid (92.5 mg, 90%).

GPC (TCB, 150 °C): $M_n = 49.0$ kg/mol, $M_w = 87.1$ kg/mol, $D = 1.77$.

^1H NMR (500 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 373 K): 7.11-6.77 (m, 6H), 2.87-2.53 (m, 8H), 1.79-1.50 (m, 8H), 1.48-1.03 (m, 72H), 0.96-0.75 (m, 12H).

Elemental analysis: Calculated for $((\text{C}_{66}\text{H}_{106}\text{S}_4)_n)$: C, 77.13; H, 10.40; S, 12.48; found: C, 78.07; H, 10.13; S, 11.58.

Supplementary Table 7. polycondensation of **P22** and **P22-Stille**

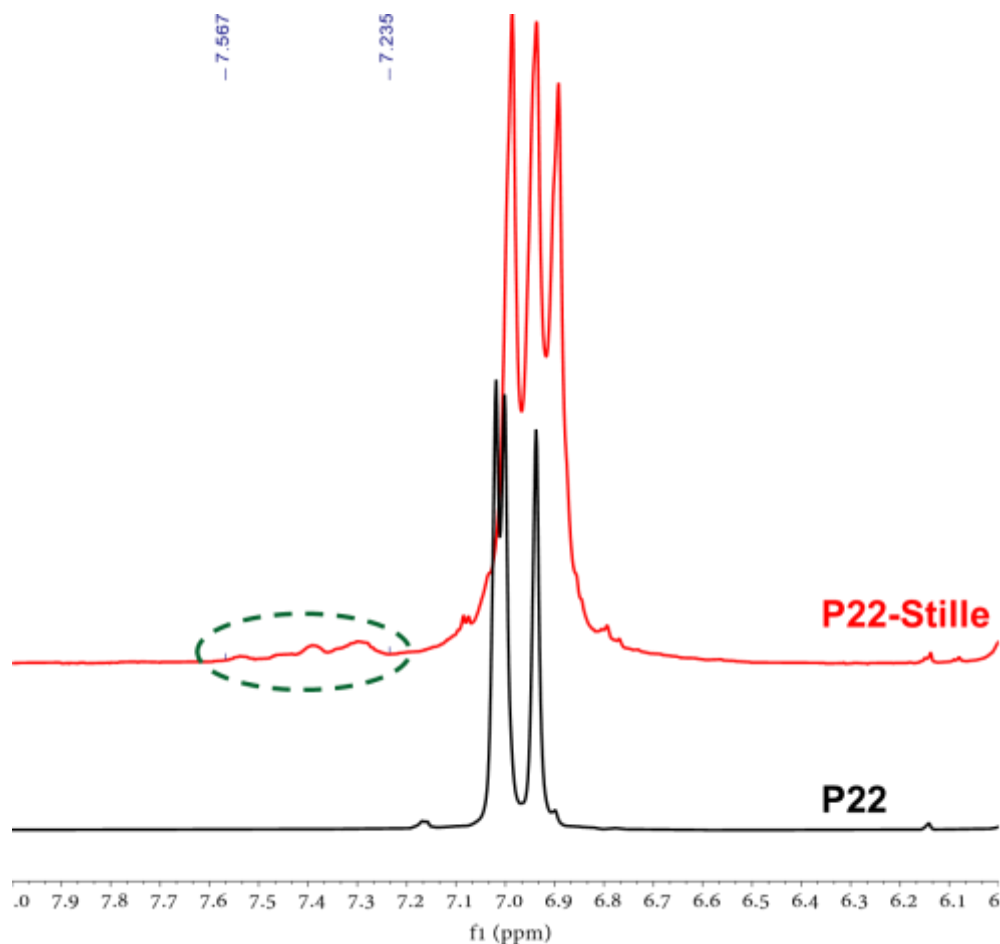
Polymer	M_n/M_w (kg/mol) ^a	$\bar{D}$ ^a	Yield (%)
P22-Stille ^b	49.0/87.1	1.77	90
P22	67.4/121.4	1.80	97

^a M_n , M_w , and $\bar{D}$ were determined with GPC at 150 °C in 1,2,4-trichlorobenzene against a polystyrene standard. ^bReaction conditions: $\text{Pd}_2(\text{dba})_3$ (5 mol%), $\text{P}(o\text{-tol})_3$ (10 mol%), 0.05 M in toluene, 12 h under nitrogen atmosphere. This is a representative high M_w polymer from a Stille coupling polycondensation procedure.

Supplementary Table 8. ICP analysis of **P22** and **P22-Stille**

	Residual element (ppm) ^a			
	Pd	P	Cu	K
P22	143	157	133	184
P22-Stille	21	128	—	—

^aCalculated based on [amount of residual element (mg)]/[amount of polymer (kg)].

**Supplementary Fig. 21.** The aromatic region of ^1H NMR for **P22-Stille** and **P22** from 8.0 to 6.0 ppm at 100 °C ($\text{C}_2\text{D}_2\text{Cl}_4$).

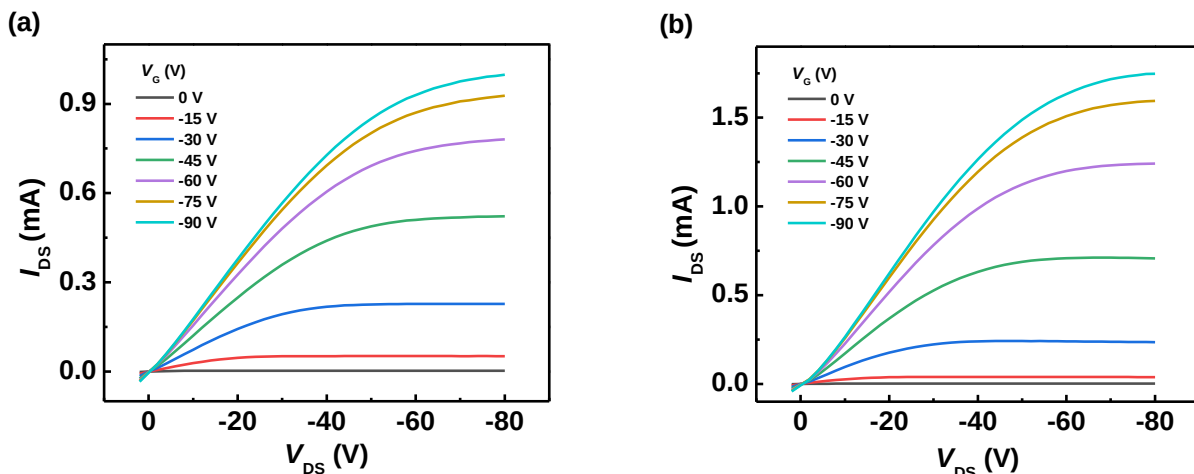
VIII-1. Organic field-effect transistors fabrication

Bottom gate bottom contact organic field effect transistors (OFETs) were fabricated on p++ Si/SiO₂ (300 nm) substrates. The interdigital Cr/Au (3/20 nm) source and drain electrodes (channel width 1400 μm, channel length 10-30 μm) were patterned onto the substrates using a conventional lift-off photolithography technique. To thoroughly remove residual photoresist, the substrates with electrodes were submerged in acetone for 3 h, dried in a vacuum oven, and processed with piranha solutions for 30 minutes. Then the substrates were sequentially rinsed in deionized water, acetone, and isopropanol in an ultrasonic cleaner, and dried with a filtered stream of nitrogen. Prior to polymer deposition, a single-molecular layer of octadecyltrichlorosilane (ODTS) was formed on the substrates in a vacuum oven at 120 °C, and excessive ODTS was washed off by sequentially rinsing in hexane, chloroform, and isopropanol. The polymers were dissolved in 1,2-dichlorobenzene (*o*-DCB) in a concentration of 5 mg mL⁻¹, spin-coated onto the substrates at a speed of 1500 rpm, and annealed at 150 °C for 30 minutes.

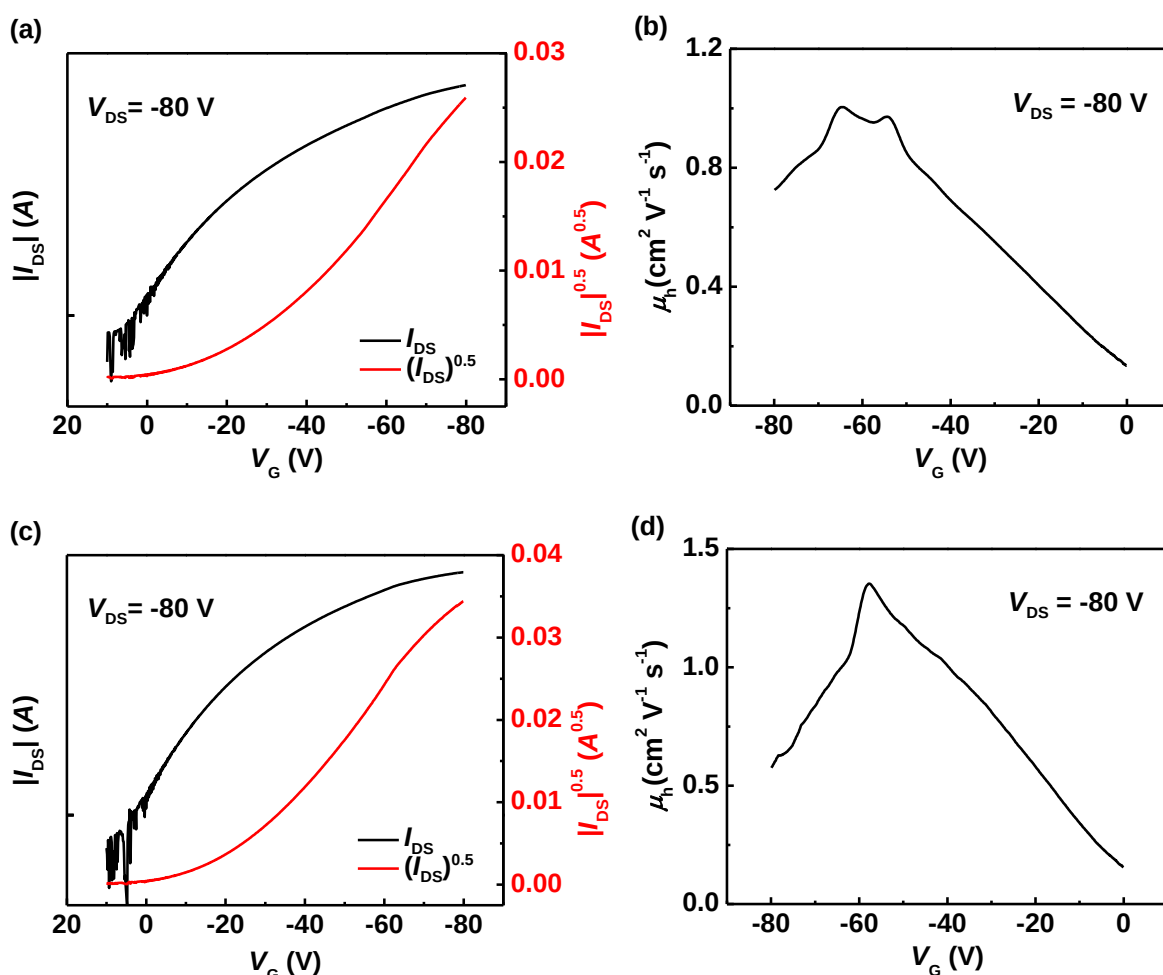
The electrical characteristics of the completed devices were measured in an ambient using a Keysight B1500A source meter. The hole mobilities (μ_h) were calculated from the source-drain current (I_{SD}) versus gate voltage (V_G) characteristics measured, following the formula:

$$I_{SD} = C_i \mu_h (W/2L)(V_G - V_{th})^2$$

in the saturated regime, where C_i is the capacitance per unit area of the gate dielectric layer; W and L are the semiconductor channel width and length, respectively; and V_{th} is the threshold voltage. Threshold voltages were obtained from the x-intercept of V_G vs $I_{SD}^{1/2}$ plots. 30 devices with channel lengths varying from 10 to 30 μm were measured for each polymer.



Supplementary Fig. 22. Output characteristics of (a) **P22-Stille** and (b) **P22** of OFETs devices.



Supplementary Fig. 23. (a) A typical *p*-type transfer characteristic of **P22-Stille** measured in the saturation regime. (b) Gate voltage dependent hole mobility of **P22-Stille** in the saturation regime, with a peak mobility of 1.09 cm² V⁻¹ s⁻¹. (c) A typical *p*-type transfer characteristic of **P22** measured in the saturation regime. (d) Gate voltage dependent hole mobility of **P22** in the saturation regime, with a peak mobility of 1.35 cm² V⁻¹ s⁻¹.

VIII-2. The trap density of states (tDOS) measurement

The trap density of states (tDOS) were performed on Keysight 4980A and analyzed by using the thermal admittance spectroscopy (TAS) method¹⁵. The configuration of the tested device was ITO/PEDOT:PSS/active layer/PDINN/Ag.

The thermal admittance spectroscopy (TAS) method was employed to check the trap density at varying energy depth. The angular frequency dependent capacitance can derive the energetic profile of trap density of states (tDOS) of solar cells according to the following equation:

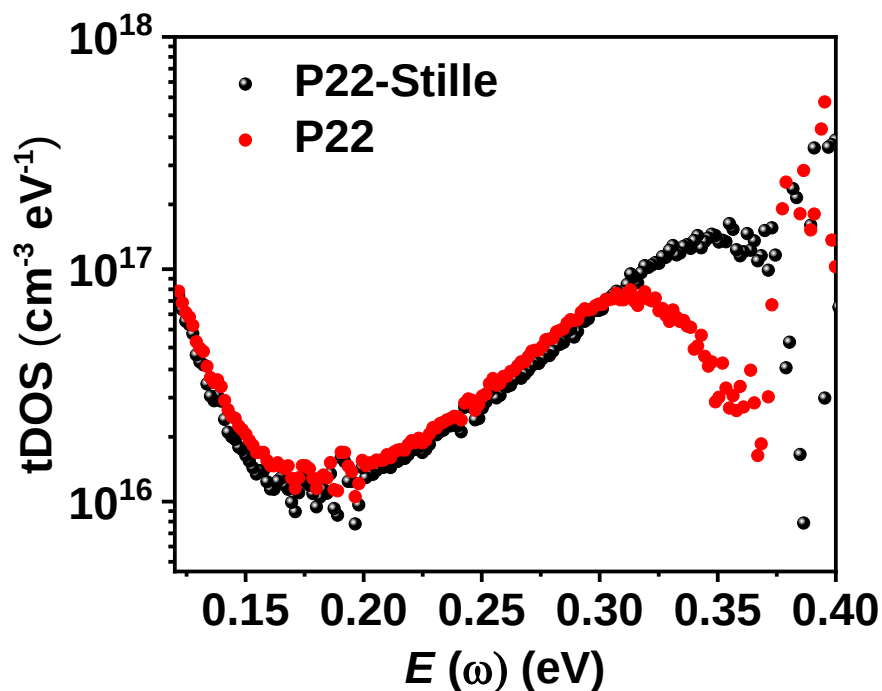
$$N_T(E_\omega) = -\frac{V_{bi}}{qW} \frac{dC}{d\omega} \frac{\omega}{k_B T}$$

where k_B is the Boltzmann's constant, q is the elementary charge, ω is the angular frequency, C is the capacitance, T is the absolute temperature (using the room temperature), W is the depletion width (using the thickness of the active layer), and V_{bi} is the built-in potential (extracted from the Mott-Schottky analysis). The applied angular frequency ω defined an energetic demarcation by the following formula:

$$E_\omega = k_B T \ln \frac{\omega_0}{\omega}$$

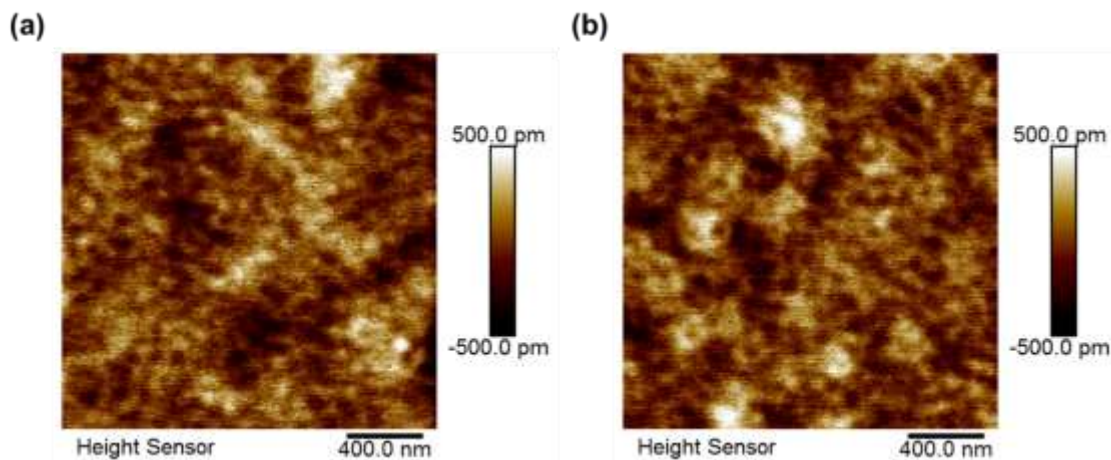
where ω_0 is the attempt-to-escape frequency. The trap states below the energy demarcation can capture or emit charges with the given ω and contribute to the capacitance.

ITO substrates were cleaned in deionized water, acetone, and isopropyl alcohol by sonication subsequently, and dried finally. The PEDOT:PSS (Clevios P VP AI 4083) layer was spin-coated onto precleaned ITO glass substrates at 4000 rpm for 30 s, and subsequently dried at 150 °C for 30 min in air. The active layer was dissolved in chloroform at 10 mg mL⁻¹, then deposited onto PEDOT:PSS layer through spin-coating at 3000 rpm for 30 s in the nitrogen glove box. The PDINN was dissolved in methanol at 1 mg mL⁻¹, then spin-coated on the active layer at 3000 rpm for 30 s. Ag electrode (*ca.* 100 nm) was slowly deposited onto the surface of the PDINN layer by the thermal evaporation method under vacuum (*ca.* 10⁻⁵ Pa). The thickness of the active film (*ca.* 95 nm) was measured via the Bruker Dektak-XT.



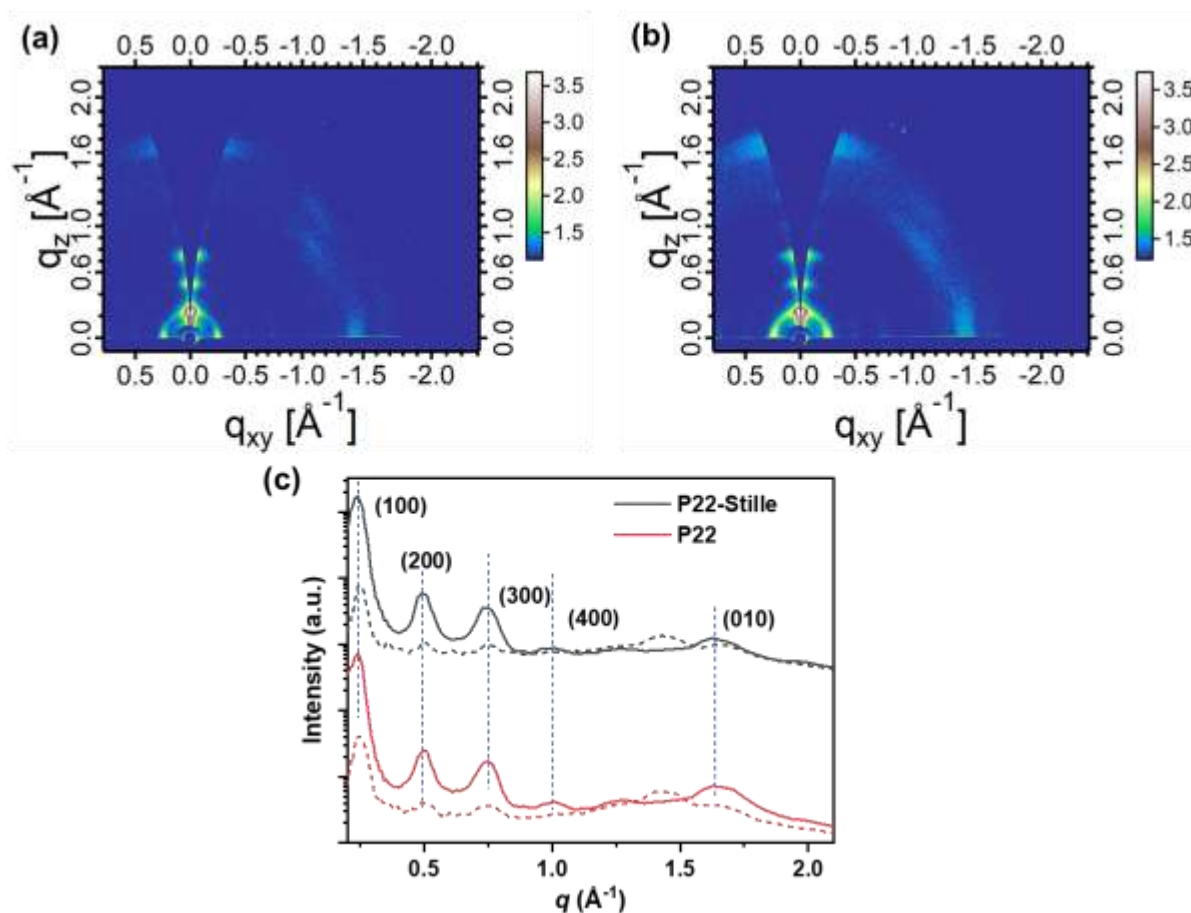
Supplementary Fig. 24. Energetic profile of trap density states (tDOS) of **P22-Stille** and **P22**.

VIII-3. AFM characterization



Supplementary Fig. 25. AFM height images of (a) **P22-Stille** (RMS = 0.166) and (b) **P22** (RMS = 0.165), scan size $2\ \mu\text{m} \times 2\ \mu\text{m}$.

VIII-4. 2D-GIWAXS characterization



Supplementary Fig. 26. 2D-GIWAXS patterns of (a) **P22-Stille** and (b) **P22** and the corresponding 1D line-cuts in the out-of-plane (solid line) and in-plane (dash line) directions (c).

Supplementary Table 9. OFETs parameters and π -stacking distances of the polymers

Polymer	μ_h^a [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	V_{th} (V)	$\text{Log}(I_{on}/I_{off})$	π - π^b [$\text{\AA}$]
P22-Stille	1.09 (0.88)	-6 to -33	4 to 5	3.86
P22	1.35 (1.16)	-15 to -32	5 to 6	3.84

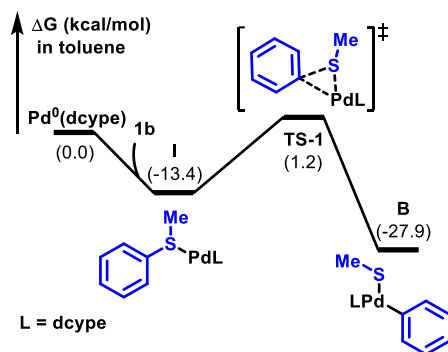
^aMaximum mobilities in the saturation regime; the average values are in parentheses (30 devices).

^b π - π stacking distances are calculated from out-of-plane (010) diffraction in 2D-GIWAXS patterns.

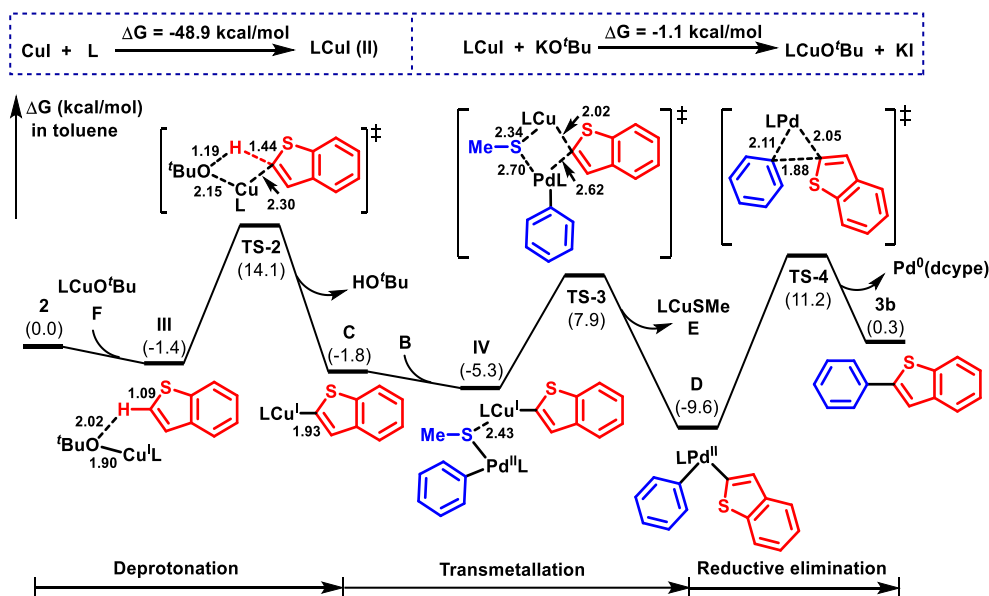
IX. Computational Details and Results

Computational Methods. All structures were optimized in toluene solvent with the implicit solvent model SMD¹⁶ at B3LYP¹⁷-D3(BJ)^{18,19}/BSI level, BSI denoting a basis set with SDD²⁰ for K, Cu, Pd and I atoms and 6-31G(d) for other atoms. At the same level, harmonic vibrational frequencies were calculated to verify that the minima have no imaginary frequency and transition states have unique one imaginary frequency, and simultaneously obtain the thermal corrections at the temperature of 298.15 K. With the

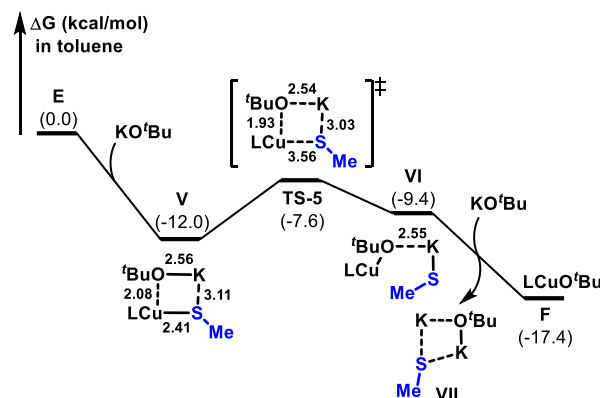
B3LYP-D3(BJ)/BSI geometrics, the electronic energies were further refined by single-point-energy calculations at the B3LYP-D3(BJ)/BSII level with SMD solvent model in toluene, BSII representing a basis set with SDD for K, Cu, Pd and I atoms and 6-311+G(d,p) for other atoms. A correction factor of 1.89 kcal/mol was employed for the standard state change from 1 atm to 1 M. All the calculations were carried out by Gaussian 16 program²¹. The selected calculated structures were illustrated using the CYLview²².



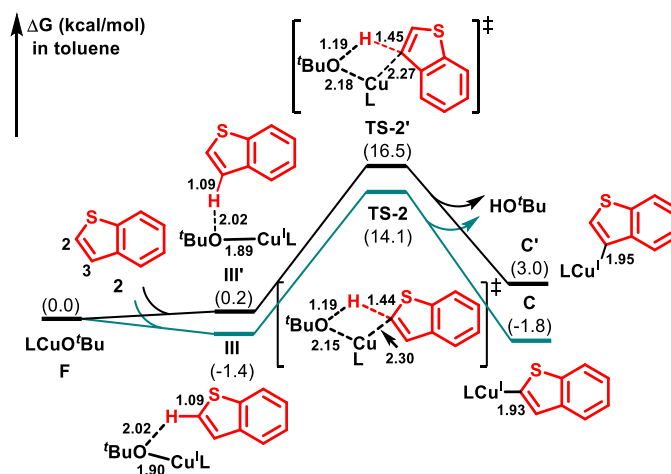
Supplementary Fig. 27. Free energy profile for oxidation addition of **1b**.



Supplementary Fig. 28. Free energy profile for the reaction of **2** to generate **3b** in the presence of CuI with dcype as its ligand. The bond lengths in the selected structures are given in angstroms.



Supplementary Fig. 29. Free energy profile for the regeneration of the intermediate F. The bond lengths in the selected structures are given in angstroms.



Supplementary Fig. 30. Comparing the energetics for C2-H and C3-H activations of 1 with copper active species F. The bond lengths in the selected structures are given in angstroms.

Cartesian coordinates (in Å), Gibbs free energy corrections (G_{corr} in a.u. at 298.15 K) and SCF energies (in a.u.) for all the optimized structures.

Pd ⁰ (Dcype)			
G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.643129 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -1830.931869 a.u.			
Pd	-0.028369	-0.344967	-1.547784
P	-1.716653	0.105595	-0.068141
P	1.734405	-0.203050	-0.095049
C	0.778130	0.429971	1.406595
C	-0.691819	-0.027612	1.511364
C	-2.479188	1.817422	0.034892
C	-3.257169	2.148470	1.319028

C	-3.891554	3.546264	1.237372
C	-2.841487	4.624321	0.940893
C	-2.048088	4.292699	-0.329659
C	-1.417718	2.896319	-0.246161
C	-3.140982	-1.033710	0.375749
C	-4.347919	-0.796292	-0.548740
C	-5.491127	-1.781107	-0.263182
C	-5.019732	-3.236836	-0.352251
C	-3.822723	-3.481933	0.573390
C	-2.679885	-2.500618	0.279334
C	3.112520	1.066317	-0.213016
C	3.885089	1.351312	1.086219
C	5.011425	2.370982	0.854828
C	4.475619	3.669465	0.239444
C	3.704237	3.389552	-1.056488
C	2.578242	2.371488	-0.830527
C	2.607320	-1.712831	0.591720
C	3.655963	-2.233525	-0.406610
C	4.325425	-3.525626	0.082834
C	3.289059	-4.610902	0.395388
C	2.256479	-4.103254	1.407879
C	1.581872	-2.812329	0.923733
H	0.810200	1.521878	1.337127
H	1.307045	0.158698	2.329420
H	-0.721933	-1.087357	1.780781
H	-1.181232	0.512579	2.331012
H	-3.187038	1.835630	-0.806229
H	-2.574625	2.118915	2.179064
H	-4.034204	1.398797	1.507069
H	-4.418574	3.773615	2.173012
H	-4.649102	3.549661	0.440136
H	-2.146360	4.692379	1.791021
H	-3.320771	5.607020	0.847186

H	-1.268761	5.046455	-0.500591
H	-2.721194	4.331263	-1.198531
H	-0.879298	2.655039	-1.170149
H	-0.672931	2.890070	0.561377
H	-3.444903	-0.829816	1.413227
H	-4.019675	-0.909075	-1.592611
H	-4.716824	0.229995	-0.444993
H	-6.317545	-1.602804	-0.963065
H	-5.886410	-1.590199	0.745478
H	-4.724475	-3.457825	-1.388349
H	-5.842023	-3.920275	-0.105127
H	-3.462493	-4.513324	0.468207
H	-4.142783	-3.364634	1.619285
H	-1.845364	-2.689032	0.964132
H	-2.293101	-2.678661	-0.734093
H	3.813170	0.630439	-0.939511
H	4.303658	0.425062	1.496766
H	3.194254	1.748461	1.842263
H	5.759353	1.932100	0.178350
H	5.527221	2.580143	1.800969
H	5.299029	4.369879	0.050701
H	3.803756	4.159100	0.960083
H	4.398673	2.995358	-1.812770
H	3.290336	4.320964	-1.463554
H	1.826286	2.813752	-0.162420
H	2.063545	2.148266	-1.772812
H	3.117857	-1.425847	1.522390
H	4.420937	-1.470083	-0.589895
H	3.161236	-2.420717	-1.370720
H	4.908067	-3.309941	0.990618
H	5.038680	-3.882514	-0.671034
H	3.783641	-5.514625	0.773448
H	2.773685	-4.896223	-0.533386

H	2.756712	-3.912442	2.368888
H	1.494886	-4.870817	1.596424
H	0.983795	-3.021230	0.025477
H	0.882367	-2.455776	1.687656

1b

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.095464 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -669.887224 a.u.

C	2.620043	0.000000	0.240809
C	1.933768	-1.208734	0.107503
C	0.563574	-1.210928	-0.157247
C	-0.128313	0.000000	-0.285988
C	0.563573	1.210928	-0.157247
C	1.933768	1.208734	0.107502
H	3.687199	0.000001	0.444352
H	2.464977	-2.151336	0.206502
H	0.026534	-2.148190	-0.266782
H	0.026533	2.148189	-0.266784
H	2.464977	2.151337	0.206501
S	-1.890360	-0.000001	-0.635045
C	-2.544019	0.000001	1.077649
H	-3.635876	0.000001	1.004233
H	-2.221471	-0.894607	1.617407
H	-2.221471	0.894609	1.617405

I

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.760652 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2500.859428 a.u.

Pd	0.119396	-0.337682	0.810417
P	2.157585	-0.221774	-0.272346

P	-0.845135	1.100624	-0.756117
C	0.590507	1.617573	-1.860418
C	1.739824	0.593965	-1.919985
C	3.483013	0.883575	0.459759
C	4.698871	1.187252	-0.429974
C	5.736593	2.036278	0.321653
C	5.117602	3.330330	0.865365
C	3.893256	3.035691	1.741792
C	2.859571	2.186924	0.990478
C	3.120097	-1.712448	-0.884046
C	3.952714	-2.334070	0.250440
C	4.667869	-3.617425	-0.196195
C	3.684598	-4.643513	-0.770195
C	2.862135	-4.033055	-1.910491
C	2.142031	-2.756854	-1.455260
C	-1.640487	2.747540	-0.350083
C	-1.943365	3.667214	-1.544211
C	-2.631512	4.964485	-1.091174
C	-1.804575	5.696599	-0.026978
C	-1.502729	4.781224	1.166427
C	-0.813827	3.485000	0.718705
C	-2.047131	0.330652	-1.969413
C	-3.412519	0.108696	-1.294654
C	-4.396874	-0.641030	-2.201820
C	-3.809967	-1.972461	-2.681582
C	-2.466989	-1.751583	-3.386046
C	-1.477246	-1.005694	-2.481285
H	0.965472	2.560212	-1.448288
H	0.236941	1.837332	-2.875694
H	1.457856	-0.228246	-2.584730
H	2.629961	1.056554	-2.362178
H	3.833241	0.317579	1.334613
H	4.371936	1.736424	-1.323380

H	5.163226	0.259119	-0.782790
H	6.582688	2.266074	-0.338885
H	6.140968	1.448965	1.158982
H	4.810199	3.964221	0.020166
H	5.865027	3.901259	1.430824
H	3.433518	3.972330	2.082674
H	4.214121	2.494591	2.643926
H	2.004582	1.951263	1.634525
H	2.465531	2.770182	0.147255
H	3.799544	-1.390799	-1.687356
H	3.282131	-2.560273	1.092494
H	4.691844	-1.616047	0.622266
H	5.220078	-4.047771	0.649191
H	5.414582	-3.365065	-0.963552
H	3.003160	-4.975514	0.026932
H	4.221971	-5.534821	-1.118402
H	2.129600	-4.759433	-2.285719
H	3.529337	-3.795039	-2.752062
H	1.570738	-2.335842	-2.290445
H	1.409456	-3.006094	-0.674752
H	-2.593935	2.467680	0.119850
H	-2.572713	3.149785	-2.277744
H	-1.004739	3.920496	-2.056034
H	-3.619882	4.719543	-0.675314
H	-2.807215	5.618066	-1.955489
H	-2.328986	6.600729	0.307551
H	-0.856048	6.029557	-0.474145
H	-2.444336	4.529904	1.676467
H	-0.876649	5.304353	1.900595
H	0.177836	3.730136	0.313679
H	-0.644899	2.820101	1.574106
H	-2.174796	1.007278	-2.827215
H	-3.850331	1.067441	-0.993699

H	-3.261088	-0.468709	-0.375607
H	-4.641889	-0.017178	-3.074494
H	-5.334890	-0.811235	-1.658847
H	-4.514172	-2.484285	-3.350230
H	-3.658659	-2.628232	-1.812583
H	-2.631633	-1.168680	-4.304549
H	-2.033223	-2.711306	-3.696191
H	-1.225410	-1.631042	-1.613441
H	-0.541166	-0.833207	-3.023999
S	-0.966492	-1.504358	2.542185
C	-0.442454	-3.250847	2.722784
H	0.563897	-3.208085	3.146651
H	-1.107650	-3.790616	3.403943
H	-0.390023	-3.755002	1.755232
C	-4.572448	-2.869246	1.121427
C	-3.221456	-2.829115	1.477088
C	-2.702099	-1.698169	2.116048
C	-3.546260	-0.614853	2.397595
C	-4.890154	-0.660722	2.036332
C	-5.411497	-1.789014	1.395571
H	-4.964797	-3.750782	0.621498
H	-2.582429	-3.672559	1.240558
H	-3.139898	0.266364	2.886376
H	-5.533472	0.186261	2.258878
H	-6.460162	-1.825024	1.115457

TS-1			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.761524 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -2500.837169 a.u.			
Pd	0.119642	-0.278780	0.878574
P	1.939799	0.389785	-0.511251

P	-1.236471	-0.215408	-1.044341
C	-0.218226	0.573073	-2.406072
C	1.296923	0.320695	-2.273673
C	2.497997	2.161254	-0.287433
C	3.559344	2.669860	-1.276267
C	3.981560	4.109321	-0.940856
C	2.775111	5.055343	-0.891762
C	1.706473	4.543212	0.082448
C	1.284344	3.107967	-0.256403
C	3.530277	-0.582865	-0.633688
C	4.387998	-0.352919	0.624892
C	5.658274	-1.215015	0.615871
C	5.328776	-2.702613	0.450890
C	4.485508	-2.938439	-0.807084
C	3.211556	-2.082720	-0.792980
C	-2.806280	0.789291	-1.020124
C	-3.570511	0.880193	-2.350898
C	-4.873190	1.678880	-2.187050
C	-4.612472	3.071671	-1.599720
C	-3.842123	2.979651	-0.276879
C	-2.537273	2.189914	-0.439513
C	-1.756209	-1.849698	-1.790467
C	-2.812892	-2.535042	-0.905651
C	-3.204773	-3.916880	-1.445390
C	-1.976714	-4.819641	-1.606582
C	-0.925799	-4.153992	-2.501555
C	-0.533183	-2.766651	-1.975425
H	-0.415198	1.647874	-2.347566
H	-0.567277	0.240755	-3.391405
H	1.532836	-0.683921	-2.636085
H	1.848854	1.018089	-2.913973
H	2.937167	2.167709	0.720161
H	3.152367	2.645824	-2.296560

H	4.438233	2.015310	-1.271809
H	4.715696	4.464199	-1.675449
H	4.485775	4.114796	0.036399
H	2.336798	5.132162	-1.898003
H	3.096194	6.066218	-0.610742
H	0.829799	5.203280	0.070112
H	2.106094	4.567229	1.106706
H	0.544145	2.740858	0.463299
H	0.796705	3.104588	-1.240708
H	4.094322	-0.246160	-1.515949
H	3.785888	-0.598726	1.510998
H	4.664156	0.703567	0.713635
H	6.224127	-1.048282	1.541087
H	6.306402	-0.893501	-0.212881
H	4.766680	-3.047161	1.330938
H	6.250994	-3.295995	0.410722
H	4.217469	-3.999001	-0.895354
H	5.082373	-2.688194	-1.696670
H	2.638829	-2.259401	-1.710565
H	2.569265	-2.394323	0.041554
H	-3.435932	0.263235	-0.289318
H	-3.798303	-0.120260	-2.736357
H	-2.936565	1.372396	-3.102069
H	-5.547465	1.125464	-1.517288
H	-5.386500	1.760371	-3.153866
H	-5.560307	3.605640	-1.455434
H	-4.024955	3.661370	-2.319311
H	-4.464223	2.480590	0.478876
H	-3.623668	3.983319	0.109759
H	-1.865007	2.745739	-1.108354
H	-2.028751	2.097616	0.523801
H	-2.194693	-1.654304	-2.779755
H	-3.704558	-1.904869	-0.812982

H	-2.400424	-2.646535	0.105792
H	-3.699776	-3.799300	-2.420537
H	-3.937842	-4.382178	-0.774303
H	-2.268080	-5.794072	-2.018198
H	-1.538070	-5.011930	-0.616209
H	-1.329938	-4.054538	-3.519741
H	-0.031489	-4.785506	-2.578058
H	-0.019465	-2.867339	-1.009551
H	0.183040	-2.306366	-2.664403
S	0.483835	-1.349399	3.010738
C	-0.447245	-2.923390	3.099764
H	0.238780	-3.671633	3.508697
H	-1.314232	-2.829031	3.762893
H	-0.771540	-3.254763	2.110396
C	-3.618089	0.022047	2.862904
C	-2.511084	-0.741524	2.501787
C	-1.213081	-0.178919	2.516648
C	-1.074829	1.149495	2.996948
C	-2.195188	1.908680	3.331100
C	-3.477888	1.356164	3.266124
H	-4.608617	-0.425273	2.807557
H	-2.658152	-1.752940	2.142518
H	-0.080929	1.571855	3.120042
H	-2.060400	2.933225	3.671120
H	-4.347975	1.942407	3.546650

B			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.768522 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -2500.890423 a.u.			
Pd	0.047145	-0.317411	0.784621
P	1.938676	0.156239	-0.555960

P	-1.221793	0.445196	-0.980078
C	-0.075157	1.222429	-2.235713
C	1.303950	0.551642	-2.268114
C	2.949119	1.618846	-0.017065
C	4.095328	2.019397	-0.960379
C	4.909057	3.179976	-0.366893
C	4.017159	4.384500	-0.040686
C	2.857432	3.985163	0.880659
C	2.044903	2.825951	0.290033
C	3.166648	-1.204303	-0.891662
C	4.156680	-1.399348	0.271980
C	5.129364	-2.552132	-0.014358
C	4.383447	-3.857790	-0.311141
C	3.393162	-3.671277	-1.466060
C	2.418611	-2.520330	-1.183088
C	-2.430289	1.793421	-0.578938
C	-3.167330	2.376003	-1.797772
C	-4.199626	3.425214	-1.357496
C	-3.554577	4.535021	-0.518012
C	-2.793392	3.955693	0.681425
C	-1.758828	2.913831	0.236114
C	-2.184206	-0.804887	-1.978263
C	-3.499539	-1.214180	-1.289580
C	-4.245755	-2.284476	-2.097764
C	-3.362885	-3.511418	-2.350780
C	-2.065869	-3.109627	-3.061089
C	-1.304268	-2.038113	-2.270614
H	0.031230	2.272781	-1.948690
H	-0.539442	1.205358	-3.228439
H	1.245906	-0.403355	-2.798454
H	2.022863	1.172875	-2.813661
H	3.377943	1.286879	0.938477
H	3.679707	2.332861	-1.928159

H	4.752974	1.166291	-1.160332
H	5.705182	3.471049	-1.063693
H	5.403630	2.834864	0.552232
H	3.609318	4.794263	-0.976915
H	4.612099	5.183254	0.419273
H	2.200668	4.844984	1.063652
H	3.255840	3.677482	1.857690
H	1.248821	2.524444	0.978407
H	1.560361	3.164351	-0.636760
H	3.729642	-0.912613	-1.791367
H	3.591948	-1.613818	1.187118
H	4.723151	-0.480301	0.455678
H	5.803005	-2.683064	0.841471
H	5.760706	-2.290300	-0.876908
H	3.833023	-4.169525	0.587681
H	5.094848	-4.660159	-0.544021
H	2.829234	-4.596158	-1.641117
H	3.948398	-3.458998	-2.391910
H	1.734166	-2.397500	-2.030073
H	1.799388	-2.767769	-0.311491
H	-3.162015	1.306250	0.077742
H	-3.663957	1.583944	-2.368546
H	-2.439894	2.846570	-2.473700
H	-4.980505	2.928297	-0.764158
H	-4.695774	3.851312	-2.238551
H	-4.318123	5.245478	-0.177975
H	-2.854025	5.102500	-1.148458
H	-3.505967	3.480533	1.370659
H	-2.296752	4.757003	1.242413
H	-0.994071	3.410620	-0.375861
H	-1.238326	2.489503	1.100732
H	-2.427089	-0.318614	-2.934461
H	-4.145942	-0.340848	-1.152236

H	-3.279205	-1.603041	-0.290897
H	-4.563573	-1.861561	-3.062603
H	-5.158999	-2.573281	-1.563144
H	-3.905706	-4.259122	-2.942365
H	-3.117277	-3.982772	-1.388291
H	-2.306340	-2.721394	-4.061848
H	-1.419900	-3.984239	-3.208560
H	-0.958801	-2.457066	-1.316945
H	-0.407558	-1.739815	-2.824316
S	1.407578	-0.880007	2.641555
C	0.369411	-1.244863	4.112912
H	1.046536	-1.426444	4.955078
H	-0.284705	-0.405390	4.362784
H	-0.249555	-2.132400	3.961454
C	-3.185346	-2.631635	2.487513
C	-2.031163	-2.201970	1.826085
C	-1.659891	-0.844979	1.793837
C	-2.494158	0.062177	2.465104
C	-3.651967	-0.358949	3.129993
C	-4.006809	-1.708452	3.140088
H	-3.442901	-3.688952	2.492898
H	-1.406035	-2.941117	1.329412
H	-2.239793	1.118885	2.484261
H	-4.274914	0.371435	3.642866
H	-4.905915	-2.038202	3.654396

CuI			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: -0.024839 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -208.835519 a.u.			
Cu	0.000000	0.000000	-1.577089
I	0.000000	0.000000	0.862935

Dcype			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.643233 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -1702.937520 a.u.			
P	1.759384	-0.124529	-0.423578
P	-1.772383	0.168077	-0.344534
C	-0.674021	-0.616201	0.967272
C	0.680990	0.095505	1.104484
C	3.152243	-1.194040	0.263584
C	3.959532	-0.623508	1.441356
C	5.067970	-1.590156	1.887732
C	4.503994	-2.974029	2.231025
C	3.706539	-3.551248	1.055214
C	2.596171	-2.590237	0.607281
C	2.563267	1.569930	-0.532748
C	3.778511	1.540852	-1.477550
C	4.407890	2.932533	-1.638028
C	3.378957	3.966210	-2.110951
C	2.162931	3.999219	-1.177391
C	1.535699	2.606368	-1.027025
C	-2.702332	-1.330192	-1.000567
C	-3.394751	-2.218910	0.045964
C	-4.129627	-3.398092	-0.610474
C	-3.189302	-4.224009	-1.496523
C	-2.507506	-3.341087	-2.548968
C	-1.767457	-2.163662	-1.898927
C	-3.055598	0.982227	0.762833
C	-4.269557	1.461235	-0.051832
C	-5.289797	2.201456	0.825583
C	-4.643232	3.371169	1.577147
C	-3.437395	2.898251	2.397714

C	-2.416186	2.163117	1.517928
H	-0.508999	-1.664580	0.697027
H	-1.198117	-0.622829	1.931895
H	0.529663	1.166981	1.271269
H	1.207303	-0.281197	1.989223
H	3.839511	-1.320265	-0.586102
H	3.290112	-0.434340	2.291608
H	4.401030	0.342050	1.171390
H	5.605237	-1.171704	2.748713
H	5.803902	-1.691512	1.076605
H	3.843541	-2.887333	3.106636
H	5.314681	-3.657127	2.514705
H	3.274754	-4.523312	1.326276
H	4.387154	-3.732562	0.210667
H	2.062622	-3.003452	-0.257953
H	1.858523	-2.499608	1.417772
H	2.905292	1.873345	0.467747
H	3.455151	1.171863	-2.461988
H	4.534583	0.836296	-1.112599
H	5.250246	2.882539	-2.340017
H	4.823008	3.251735	-0.670641
H	3.045664	3.704353	-3.125803
H	3.839359	4.960350	-2.176585
H	1.412955	4.707608	-1.552054
H	2.475444	4.364738	-0.187924
H	0.678425	2.654703	-0.346087
H	1.135803	2.278146	-1.996387
H	-3.479508	-0.904341	-1.652468
H	-4.101952	-1.630296	0.641533
H	-2.643927	-2.610593	0.745925
H	-4.955006	-3.009218	-1.224864
H	-4.584484	-4.032689	0.161312
H	-3.740289	-5.040447	-1.980582

H	-2.419340	-4.693102	-0.866036
H	-3.268348	-2.951154	-3.241013
H	-1.808681	-3.935160	-3.151767
H	-0.933164	-2.554664	-1.299966
H	-1.318162	-1.522172	-2.666100
H	-3.402778	0.252246	1.508384
H	-4.757133	0.612292	-0.545456
H	-3.922526	2.132084	-0.851412
H	-5.716069	1.495870	1.553822
H	-6.124312	2.558177	0.208332
H	-5.379504	3.861115	2.226941
H	-4.310212	4.126785	0.850596
H	-3.783179	2.220717	3.192191
H	-2.956809	3.749432	2.897052
H	-1.993643	2.868336	0.787512
H	-1.580464	1.812475	2.135550

II			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.640513 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -1911.870125 a.u			
P	1.606948	0.459669	-0.609028
P	-1.696394	0.102499	-0.616157
C	-0.848341	1.074797	-1.974573
C	0.633916	0.699513	-2.191531
C	2.403925	2.107516	-0.261739
C	3.321337	2.651384	-1.368782
C	3.962823	3.982741	-0.947375
C	2.903368	5.017772	-0.548964
C	1.979407	4.473792	0.548017
C	1.335341	3.145755	0.128189
C	2.994250	-0.666584	-1.133676

C	4.089989	-0.705166	-0.051248
C	5.205368	-1.695630	-0.414594
C	4.650684	-3.100622	-0.674892
C	3.559723	-3.069257	-1.751234
C	2.442176	-2.084693	-1.381731
C	-3.076739	1.224919	-0.066444
C	-3.978820	1.757580	-1.191972
C	-5.102779	2.641179	-0.629564
C	-4.542126	3.788388	0.219994
C	-3.642470	3.257828	1.343235
C	-2.514784	2.375244	0.790845
C	-2.532764	-1.312437	-1.491553
C	-3.422142	-2.090298	-0.502312
C	-4.050988	-3.328504	-1.156150
C	-2.984358	-4.245646	-1.764482
C	-2.112194	-3.479055	-2.764665
C	-1.475377	-2.240954	-2.118967
H	-0.916273	2.126297	-1.677521
H	-1.396728	0.977834	-2.919071
H	0.697089	-0.253777	-2.724722
H	1.113939	1.446030	-2.834089
H	3.015056	1.918211	0.631820
H	2.736358	2.811037	-2.284971
H	4.101896	1.922700	-1.614858
H	4.587613	4.369091	-1.762411
H	4.632508	3.802535	-0.094264
H	2.300920	5.275589	-1.432753
H	3.385287	5.945047	-0.215453
H	1.198870	5.206031	0.789503
H	2.559483	4.314620	1.468023
H	0.708149	2.752070	0.936662
H	0.674588	3.326912	-0.730987
H	3.428280	-0.286007	-2.069609

H	3.633429	-1.000375	0.903861
H	4.518890	0.291983	0.096929
H	5.950188	-1.721429	0.390261
H	5.725450	-1.337624	-1.315491
H	4.224948	-3.498671	0.257033
H	5.459305	-3.780494	-0.970854
H	3.135325	-4.070512	-1.895900
H	4.003186	-2.770886	-2.712683
H	1.683182	-2.071999	-2.172282
H	1.940461	-2.431001	-0.467288
H	-3.683855	0.594996	0.598045
H	-4.408542	0.927787	-1.765205
H	-3.374779	2.349332	-1.893565
H	-5.768113	2.023112	-0.009712
H	-5.713346	3.035482	-1.451628
H	-5.361081	4.386173	0.638754
H	-3.957069	4.461608	-0.424176
H	-4.247627	2.666661	2.045112
H	-3.215627	4.089220	1.917693
H	-1.842565	2.994944	0.181040
H	-1.913742	1.965482	1.611466
H	-3.161835	-0.906879	-2.296667
H	-4.212369	-1.440929	-0.108860
H	-2.811217	-2.399889	0.357061
H	-4.746660	-3.007787	-1.945602
H	-4.646146	-3.873177	-0.413102
H	-3.455371	-5.107935	-2.252477
H	-2.348436	-4.643025	-0.960512
H	-2.729553	-3.164257	-3.618838
H	-1.325276	-4.129520	-3.166585
H	-0.773199	-2.560346	-1.336411
H	-0.890738	-1.696250	-2.869050
Cu	0.022928	-0.350359	0.814236

I	0.131546	-1.493915	3.103515
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KO'Bu

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.088360 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -261.517910 a.u.

C	-0.563023	1.283683	-1.256749
C	0.300925	0.971932	0.000000
H	0.015523	1.059893	-2.162127
H	-1.455763	0.638544	-1.262825
H	-0.907377	2.326747	-1.317836
C	-0.563023	1.283683	1.256749
C	1.510969	1.946266	0.000000
H	0.015523	1.059893	2.162127
H	-0.907377	2.326747	1.317836
H	-1.455763	0.638544	1.262825
H	1.223424	3.008237	0.000000
H	2.131506	1.757243	0.885119
H	2.131506	1.757243	-0.885119
O	0.723894	-0.322758	0.000000
K	-0.563023	-2.363390	0.000000

KI

G_{corr} at B3LYP-D3BJ/BSI level in toluene: -0.025444 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -39.844270 a.u.

I	0.000000	0.000000	0.874623
K	0.000000	0.000000	-2.439737

F

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.759716 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2133.550852 a.u.			
P	-1.411189	-0.408806	-0.681190
P	1.801165	0.168923	-0.409786
C	1.156529	-0.712715	-1.933736
C	-0.335844	-0.443808	-2.216094
C	-2.023256	-2.159368	-0.472839
C	-2.726524	-2.777157	-1.691720
C	-3.243149	-4.188818	-1.372612
C	-2.115949	-5.098530	-0.868087
C	-1.401560	-4.480517	0.340730
C	-0.886606	-3.069707	0.026750
C	-2.899287	0.549188	-1.279400
C	-4.098124	0.359911	-0.331125
C	-5.299789	1.214051	-0.759938
C	-4.928050	2.696523	-0.875446
C	-3.741123	2.890360	-1.825745
C	-2.536887	2.043626	-1.392813
C	3.263546	-0.869077	0.104794
C	4.297524	-1.149788	-0.998059
C	5.474399	-1.978091	-0.460153
C	4.993068	-3.280192	0.191751
C	3.964282	-2.999694	1.294221
C	2.783030	-2.175453	0.764496
C	2.555631	1.739733	-1.077213
C	3.332654	2.466207	0.037210
C	3.882023	3.818363	-0.438439
C	2.769041	4.713192	-0.994779
C	2.008762	4.001157	-2.118926
C	1.452219	2.650251	-1.649344
H	1.306856	-1.782529	-1.756324
H	1.754470	-0.453123	-2.815457
H	-0.448327	0.544380	-2.672199

H	-0.716160	-1.166251	-2.946801
H	-2.755312	-2.082701	0.343409
H	-2.019752	-2.838810	-2.530253
H	-3.555900	-2.141652	-2.022962
H	-3.715932	-4.623159	-2.262585
H	-4.024728	-4.118607	-0.602356
H	-1.387160	-5.251412	-1.678071
H	-2.512809	-6.088532	-0.611192
H	-0.568268	-5.118671	0.660626
H	-2.100477	-4.425374	1.187610
H	-0.416451	-2.627470	0.912547
H	-0.108476	-3.137227	-0.745556
H	-3.178272	0.178732	-2.276466
H	-3.796330	0.640791	0.687050
H	-4.394271	-0.693977	-0.293029
H	-6.120688	1.079580	-0.044571
H	-5.667042	0.855663	-1.732953
H	-4.660085	3.080747	0.119156
H	-5.791495	3.280188	-1.218385
H	-3.452393	3.948043	-1.867664
H	-4.039872	2.603061	-2.844678
H	-1.710891	2.187536	-2.098747
H	-2.177640	2.393830	-0.415521
H	3.746941	-0.273110	0.891170
H	4.668085	-0.210437	-1.424821
H	3.815564	-1.701462	-1.817137
H	6.021591	-1.381692	0.284182
H	6.180700	-2.194027	-1.271949
H	5.845079	-3.839179	0.598400
H	4.533861	-3.919887	-0.576753
H	4.449107	-2.446235	2.111084
H	3.598097	-3.940200	1.724670
H	2.229284	-2.777828	0.030981

H	2.084094	-1.942768	1.576312
H	3.251411	1.483028	-1.888907
H	4.158010	1.841199	0.396419
H	2.660975	2.623708	0.892726
H	4.635376	3.648131	-1.221849
H	4.397224	4.318466	0.390999
H	3.185664	5.661521	-1.356668
H	2.067408	4.961802	-0.185531
H	2.687337	3.837530	-2.969103
H	1.188026	4.630020	-2.486549
H	0.694042	2.819597	-0.871989
H	0.946169	2.152192	-2.483891
Cu	-0.045109	0.363059	0.947453
C	-2.059843	2.153833	3.024153
C	-1.132769	1.034498	3.544083
H	-1.513675	3.104580	2.990844
H	-2.384084	1.917905	2.003389
H	-2.954525	2.290619	3.647679
C	-1.923933	-0.290952	3.586868
C	-0.668050	1.387005	4.971197
H	-1.272427	-1.100358	3.938750
H	-2.800441	-0.240027	4.247849
H	-2.268363	-0.551251	2.578183
H	-1.506104	1.507934	5.670822
H	-0.010195	0.597426	5.353812
H	-0.094885	2.321555	4.953994
O	0.000600	0.920444	2.738507

2

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.083626 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -706.801050 a.u.

C	0.111464	0.853887	0.000046
C	-0.061206	-0.553907	0.000256
C	1.029084	-1.428773	0.000291
C	2.309679	-0.886303	0.000003
C	2.502420	0.507479	-0.000140
C	1.418471	1.374681	-0.000154
C	-1.150715	1.550727	0.000262
C	-2.218842	0.712848	0.000000
H	0.880620	-2.504408	0.000233
H	3.170891	-1.548176	-0.000311
H	3.512358	0.907272	-0.000358
H	1.570465	2.450589	-0.000143
H	-1.237145	2.631882	0.000318
H	-3.268442	0.977736	-0.000381
S	-1.766930	-0.981170	-0.000172

III

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.863927 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2840.371632 a.u.

P	-0.962805	-1.342978	-1.148281
P	-0.409264	1.866711	-0.843164
C	-0.474173	1.130151	-2.565402
C	-1.198082	-0.231936	-2.638603
C	0.621340	-2.279092	-1.469537
C	0.657222	-3.079028	-2.782382
C	1.977784	-3.851463	-2.926798
C	3.190814	-2.919892	-2.815473
C	3.153140	-2.125022	-1.505524
C	1.840572	-1.346136	-1.361000
C	-2.308288	-2.614097	-1.402915
C	-2.092994	-3.816009	-0.463550

C	-3.223958	-4.846370	-0.587635
C	-4.596500	-4.208762	-0.346515
C	-4.819607	-3.021322	-1.289430
C	-3.694062	-1.986450	-1.158784
C	1.059143	3.024230	-0.926394
C	1.001620	4.108335	-2.015830
C	2.225597	5.035205	-1.940294
C	3.541026	4.249034	-2.009139
C	3.592113	3.159065	-0.931279
C	2.374848	2.230125	-1.021859
C	-1.881890	3.010595	-0.765792
C	-1.879827	3.730308	0.597851
C	-3.120727	4.615525	0.776929
C	-4.411839	3.810394	0.592354
C	-4.426922	3.107288	-0.769402
C	-3.189625	2.218590	-0.955826
H	0.563969	1.006868	-2.886752
H	-0.937784	1.830142	-3.270803
H	-2.277188	-0.064532	-2.699198
H	-0.914907	-0.757499	-3.557515
H	0.681793	-2.986386	-0.630905
H	0.553021	-2.390968	-3.632578
H	-0.186535	-3.776120	-2.834856
H	1.990870	-4.388537	-3.883749
H	2.034150	-4.613767	-2.136216
H	3.188795	-2.221361	-3.665665
H	4.121047	-3.497604	-2.885274
H	4.002880	-1.435016	-1.443477
H	3.253616	-2.815131	-0.658215
H	1.819841	-0.810973	-0.407256
H	1.790553	-0.588567	-2.152842
H	-2.262282	-2.964860	-2.443789
H	-2.043861	-3.451114	0.571931

H	-1.132353	-4.299135	-0.672549
H	-3.052857	-5.667512	0.119547
H	-3.200799	-5.287136	-1.595191
H	-4.654466	-3.858426	0.694134
H	-5.391511	-4.953884	-0.474950
H	-5.784960	-2.542965	-1.081979
H	-4.862176	-3.383540	-2.327151
H	-3.872906	-1.158182	-1.853608
H	-3.711513	-1.558954	-0.148177
H	1.050528	3.520726	0.054592
H	0.085663	4.702331	-1.924077
H	0.971139	3.627685	-3.003876
H	2.188991	5.595485	-0.994752
H	2.181420	5.777638	-2.747365
H	4.395542	4.929755	-1.907545
H	3.628800	3.778327	-2.999584
H	3.612498	3.631234	0.062005
H	4.514122	2.571238	-1.020706
H	2.414457	1.695740	-1.980519
H	2.413814	1.471032	-0.236574
H	-1.810747	3.755058	-1.571386
H	-0.974757	4.341308	0.702073
H	-1.847186	2.971056	1.391157
H	-3.096539	5.434684	0.042534
H	-3.100368	5.081391	1.770113
H	-5.288552	4.462546	0.694062
H	-4.481507	3.055284	1.388016
H	-4.453544	3.863534	-1.568044
H	-5.335362	2.501093	-0.878346
H	-3.219772	1.399229	-0.225034
H	-3.214419	1.761784	-1.951822
Cu	-0.924790	0.056800	0.590428
C	-3.615957	-0.102324	2.700903

C	-2.172505	-0.112445	3.240805
H	-3.957611	0.930961	2.566789
H	-3.650975	-0.597476	1.723335
H	-4.321355	-0.613804	3.370117
C	-1.709663	-1.572472	3.423214
C	-2.141613	0.601448	4.605863
H	-0.705509	-1.602082	3.863237
H	-2.380107	-2.147320	4.076345
H	-1.664249	-2.071839	2.447485
H	-2.794226	0.119529	5.345939
H	-1.119387	0.608148	5.002616
H	-2.463416	1.643068	4.488404
O	-1.320329	0.583192	2.373193
C	3.927539	0.002254	1.903081
C	3.710348	-1.398586	1.984932
C	4.731626	-2.314784	1.715905
C	5.980063	-1.826783	1.343208
C	6.210750	-0.442364	1.244209
C	5.199670	0.468344	1.523403
C	2.735417	0.746921	2.224179
C	1.667718	-0.041152	2.519427
H	4.553677	-3.383674	1.789699
H	6.784494	-2.523673	1.126093
H	7.192969	-0.083286	0.950038
H	5.382942	1.537025	1.452402
H	2.686776	1.830471	2.224381
H	0.641326	0.258420	2.738912
S	2.049240	-1.752133	2.436168

TS-2

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.863764 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2840.346919 a.u.			
P	-0.426201	-1.343493	-1.241099
P	-0.564975	1.923426	-0.748363
C	-0.361355	1.262534	-2.489839
C	-0.831166	-0.196319	-2.665963
C	1.299304	-1.970293	-1.576853
C	1.515284	-2.626471	-2.949787
C	2.947314	-3.169243	-3.080531
C	3.991055	-2.074979	-2.822657
C	3.768254	-1.409592	-1.459464
C	2.340948	-0.865615	-1.329917
C	-1.528358	-2.803305	-1.629142
C	-1.100101	-4.046740	-0.826783
C	-2.044567	-5.232328	-1.070310
C	-3.502793	-4.866381	-0.772527
C	-3.934247	-3.639347	-1.583440
C	-2.998176	-2.450033	-1.331546
C	0.708904	3.287332	-0.644150
C	0.551397	4.425761	-1.666530
C	1.602723	5.523490	-1.437717
C	3.029013	4.959472	-1.450615
C	3.180865	3.813063	-0.443104
C	2.138061	2.715271	-0.688853
C	-2.198817	2.818755	-0.780568
C	-2.415585	3.539456	0.564091
C	-3.788393	4.223161	0.625076
C	-4.921984	3.226862	0.356995
C	-4.717744	2.510129	-0.982452
C	-3.345060	1.826876	-1.052859
H	0.704056	1.333394	-2.725998
H	-0.884316	1.906707	-3.206905
H	-1.922355	-0.217614	-2.743263

H	-0.445619	-0.600537	-3.608978
H	1.451905	-2.729319	-0.797884
H	1.342898	-1.883257	-3.740588
H	0.794837	-3.435788	-3.114429
H	3.089303	-3.608805	-4.076131
H	3.088232	-3.981885	-2.353231
H	3.917360	-1.314340	-3.614561
H	5.003088	-2.494690	-2.883366
H	4.488836	-0.598299	-1.300155
H	3.944804	-2.140078	-0.659744
H	2.191632	-0.424560	-0.341565
H	2.200362	-0.062492	-2.064476
H	-1.433991	-3.028651	-2.701377
H	-1.093137	-3.799401	0.243200
H	-0.076322	-4.335879	-1.086323
H	-1.730066	-6.085143	-0.455957
H	-1.958832	-5.550657	-2.119763
H	-3.609121	-4.645937	0.299421
H	-4.160975	-5.717438	-0.987583
H	-4.964515	-3.356811	-1.333122
H	-3.925749	-3.889303	-2.654528
H	-3.318981	-1.592153	-1.933982
H	-3.080624	-2.143014	-0.281784
H	0.557101	3.705139	0.361491
H	-0.451631	4.862552	-1.609725
H	0.664610	4.019353	-2.681617
H	1.411762	6.000067	-0.465221
H	1.494271	6.307148	-2.198325
H	3.753428	5.755676	-1.238282
H	3.259513	4.583775	-2.458537
H	3.058090	4.205245	0.577113
H	4.189211	3.384321	-0.497730
H	2.324816	2.270444	-1.675239

H	2.248196	1.911433	0.042861
H	-2.184889	3.561747	-1.590242
H	-1.626328	4.282574	0.729239
H	-2.333972	2.801447	1.373261
H	-3.827609	5.028036	-0.123965
H	-3.921001	4.697824	1.605273
H	-5.892367	3.738949	0.370340
H	-4.943974	2.481687	1.164269
H	-4.800630	3.240390	-1.800968
H	-5.508061	1.765726	-1.142690
H	-3.299822	1.021260	-0.309301
H	-3.218075	1.362452	-2.037465
Cu	-0.581696	0.037079	0.549202
C	-3.958611	-0.488440	2.229438
C	-2.623936	-0.700681	2.951991
H	-4.290133	0.549535	2.343645
H	-3.849079	-0.692954	1.159116
H	-4.742446	-1.145753	2.626499
C	-2.159884	-2.156843	2.784822
C	-2.776333	-0.369000	4.444451
H	-1.232625	-2.338225	3.339503
H	-2.915448	-2.863945	3.149285
H	-1.967423	-2.370403	1.728632
H	-3.517381	-1.015375	4.932126
H	-1.817754	-0.496833	4.960427
H	-3.091274	0.673364	4.568426
O	-1.673581	0.197574	2.391195
C	3.201836	0.154939	2.220742
C	3.248744	-1.265517	2.217501
C	4.464933	-1.954143	2.151208
C	5.645054	-1.220364	2.071183
C	5.616724	0.186779	2.061239
C	4.410885	0.872258	2.138028

C	1.845543	0.640294	2.286933
C	0.859544	-0.318385	2.310604
H	4.488552	-3.040476	2.156167
H	6.597483	-1.740250	2.014172
H	6.549483	0.740555	1.996594
H	4.393466	1.959362	2.136329
H	1.612144	1.701557	2.314352
H	-0.539521	-0.105165	2.568087
S	1.620401	-1.920978	2.285532

HO'Bu			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.107305 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -233.776528 a.u.			
H	-0.970077	0.000405	1.712203
C	-0.681881	1.262695	-0.517765
C	0.006137	-0.000007	0.015197
H	-1.742466	1.277026	-0.233476
H	-0.206445	2.158739	-0.104457
H	-0.630974	1.315770	-1.611587
C	1.492282	-0.000532	-0.340269
C	-0.682888	-1.262051	-0.518026
H	1.983319	-0.887827	0.073751
H	1.632997	-0.000513	-1.426421
H	1.983954	0.886356	0.073862
H	-0.632010	-1.315028	-1.611840
H	-0.208174	-2.158501	-0.104759
H	-1.743473	-1.275562	-0.233697
O	-0.033568	-0.000187	1.453949

C

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.733667 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2606.575819 a.u.

C	-4.325886	0.536073	-1.680357
C	-4.390822	-0.878212	-1.801433
C	-5.551381	-1.521404	-2.242476
C	-6.664284	-0.749485	-2.565446
C	-6.619670	0.652171	-2.450857
C	-5.466050	1.292056	-2.014533
C	-3.034933	0.977223	-1.210375
C	-2.106373	-0.005608	-0.960670
H	-5.585589	-2.604108	-2.331066
H	-7.574450	-1.234257	-2.908614
H	-7.498011	1.238803	-2.707686
H	-5.437467	2.376041	-1.929013
H	-2.812216	2.031506	-1.060911
S	-2.852558	-1.581566	-1.322272
P	1.176232	1.697909	0.356519
P	1.113110	-1.555210	0.604829
C	2.655950	-0.632096	1.137297
C	2.401707	0.847880	1.491878
C	2.206008	2.478740	-0.988039
C	3.304449	3.446934	-0.521145
C	4.036951	4.068976	-1.720584
C	4.607620	2.992423	-2.652568
C	3.515539	2.017932	-3.111428
C	2.785744	1.393914	-1.914725
C	0.570890	3.120039	1.401474
C	-0.146649	4.166249	0.527975
C	-0.748772	5.296563	1.374582
C	-1.692112	4.753988	2.453717
C	-0.980212	3.718794	3.331783
C	-0.387845	2.584844	2.484645

C	1.778165	-2.947613	-0.441628
C	2.890560	-3.785351	0.209990
C	3.342333	-4.925751	-0.715009
C	3.777895	-4.396449	-2.087038
C	2.666537	-3.563450	-2.737891
C	2.212445	-2.418945	-1.821588
C	0.509047	-2.380905	2.163922
C	-0.619470	-3.376873	1.835434
C	-1.219280	-3.997369	3.104702
C	-1.714999	-2.919635	4.074939
C	-0.588838	-1.939599	4.421768
C	0.015169	-1.312298	3.158250
H	3.348415	-0.688196	0.291428
H	3.143020	-1.139838	1.978088
H	1.970859	0.915249	2.495590
H	3.351709	1.392863	1.526265
H	1.472515	3.047126	-1.576898
H	4.031652	2.904870	0.098555
H	2.880093	4.237374	0.108393
H	4.836998	4.731056	-1.366123
H	3.332314	4.698417	-2.282940
H	5.389848	2.431946	-2.119193
H	5.091176	3.458858	-3.519801
H	3.946360	1.227500	-3.738713
H	2.786434	2.554495	-3.735141
H	1.985049	0.728758	-2.258247
H	3.495882	0.774777	-1.349766
H	1.431976	3.596469	1.892262
H	-0.946637	3.666218	-0.036470
H	0.543286	4.589984	-0.209707
H	-1.277940	6.002606	0.722497
H	0.065451	5.859540	1.854248
H	-2.559337	4.280801	1.971199

H	-2.080206	5.575396	3.068850
H	-1.674587	3.301611	4.071663
H	-0.174377	4.211463	3.895605
H	0.124519	1.866284	3.134590
H	-1.201867	2.036226	1.990622
H	0.906126	-3.595427	-0.605911
H	2.549996	-4.194644	1.168273
H	3.751647	-3.139130	0.429663
H	2.509511	-5.631429	-0.847137
H	4.159118	-5.486904	-0.243598
H	4.063124	-5.228886	-2.742210
H	4.674150	-3.770198	-1.964273
H	1.805517	-4.211973	-2.953869
H	3.004912	-3.158077	-3.699592
H	3.041936	-1.708271	-1.701124
H	1.385313	-1.865691	-2.282349
H	1.345440	-2.927075	2.623247
H	-0.248029	-4.171674	1.178794
H	-1.408181	-2.851135	1.279959
H	-0.456105	-4.612409	3.604302
H	-2.039319	-4.672414	2.830600
H	-2.114098	-3.380436	4.987157
H	-2.543166	-2.367596	3.607943
H	0.199397	-2.472508	4.973812
H	-0.958885	-1.147554	5.084944
H	-0.744055	-0.691298	2.662560
H	0.838980	-0.645438	3.436298
Cu	-0.308414	0.050427	-0.250631

IV

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 1.534367 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -5107.501050 a.u.			
Pd	-2.120309	-0.633708	0.052347
P	-2.147395	-0.702129	-2.329434
P	-4.266019	0.196068	-0.066623
C	-4.703826	0.438213	-1.868410
C	-3.948033	-0.520876	-2.796567
C	-1.236995	0.567629	-3.345844
C	-1.488022	0.443559	-4.860747
C	-0.691883	1.491424	-5.651003
C	-1.023339	2.907963	-5.170674
C	-0.759651	3.039821	-3.668247
C	-1.530223	1.995452	-2.850399
C	-1.709888	-2.342836	-3.107450
C	-0.194095	-2.486669	-3.343453
C	0.161160	-3.869076	-3.905826
C	-0.354821	-4.992917	-3.000995
C	-1.867817	-4.865591	-2.789063
C	-2.232637	-3.488954	-2.218767
C	-4.551412	1.857329	0.703524
C	-5.959227	2.434626	0.471391
C	-6.119963	3.777990	1.199507
C	-5.037837	4.779803	0.777737
C	-3.631644	4.199562	0.973216
C	-3.472235	2.856047	0.251834
C	-5.645896	-0.891056	0.561519
C	-5.859023	-0.783933	2.082719
C	-6.974189	-1.726824	2.555869
C	-6.695856	-3.177185	2.145902
C	-6.508380	-3.287018	0.628738
C	-5.399150	-2.350471	0.132393
H	-4.449833	1.472794	-2.115249
H	-5.786586	0.333791	-2.003559

H	-4.377986	-1.524971	-2.725870
H	-4.053392	-0.206639	-3.840156
H	-0.177524	0.365450	-3.140128
H	-2.556153	0.595757	-5.066266
H	-1.240035	-0.561463	-5.217462
H	-0.901625	1.383718	-6.722952
H	0.383676	1.305609	-5.517412
H	-2.081346	3.123393	-5.384343
H	-0.432716	3.647836	-5.725545
H	-1.011113	4.045030	-3.312373
H	0.310316	2.905083	-3.479491
H	-1.266338	2.079389	-1.791945
H	-2.605509	2.201140	-2.938899
H	-2.226754	-2.387615	-4.078004
H	0.318694	-2.333779	-2.388165
H	0.164235	-1.711808	-4.027518
H	1.249190	-3.945580	-4.028651
H	-0.276385	-3.982987	-4.909088
H	0.150989	-4.931785	-2.026766
H	-0.108262	-5.973522	-3.427396
H	-2.228349	-5.651433	-2.113071
H	-2.382335	-5.014055	-3.750110
H	-3.319275	-3.412655	-2.092041
H	-1.791831	-3.377615	-1.222023
H	-4.410493	1.681093	1.778183
H	-6.732303	1.734516	0.806416
H	-6.115218	2.588180	-0.605497
H	-6.053443	3.605030	2.283359
H	-7.119164	4.188331	1.005852
H	-5.147474	5.715271	1.340479
H	-5.176766	5.032792	-0.283885
H	-3.439612	4.054806	2.046343
H	-2.874311	4.900912	0.605991

H	-3.554065	3.023725	-0.830175
H	-2.474776	2.444814	0.428457
H	-6.558725	-0.534586	0.061880
H	-6.107619	0.245401	2.360780
H	-4.928984	-1.034149	2.600161
H	-7.933683	-1.406590	2.122807
H	-7.078197	-1.649983	3.645170
H	-7.511507	-3.831956	2.477165
H	-5.783273	-3.525776	2.650370
H	-7.453034	-3.028287	0.128046
H	-6.272563	-4.319967	0.343145
H	-4.431629	-2.677704	0.532166
H	-5.321765	-2.415036	-0.958760
S	0.077549	-1.594387	0.161019
C	-0.111480	-3.068313	1.235548
H	-0.810249	-3.777157	0.776737
H	0.854012	-3.564136	1.341638
H	-0.483960	-2.808930	2.226300
C	1.299702	4.041653	-1.162263
C	0.469034	4.248823	-0.028668
C	-0.062827	5.507322	0.267720
C	0.223950	6.576199	-0.580338
C	1.040109	6.388780	-1.710179
C	1.575880	5.138426	-2.000551
C	1.734029	2.668925	-1.264055
C	1.317521	1.802881	-0.277726
H	-0.682311	5.652501	1.148492
H	-0.180166	7.561161	-0.361854
H	1.256706	7.232385	-2.360794
H	2.205964	5.001529	-2.876830
H	2.374192	2.346049	-2.078244
S	0.288160	2.731128	0.839273
P	3.599824	-1.162439	-0.768238

P	3.258645	0.079927	2.239806
C	4.723337	-1.030983	1.851599
C	5.095298	-1.090517	0.354623
C	3.321619	-2.996056	-1.056639
C	4.228005	-3.702438	-2.076887
C	3.813840	-5.172956	-2.254503
C	3.781916	-5.931684	-0.922114
C	2.906710	-5.207088	0.108126
C	3.362030	-3.753597	0.281683
C	4.231590	-0.550205	-2.420017
C	3.026293	-0.530017	-3.382737
C	3.385407	0.045338	-4.757475
C	3.993127	1.445935	-4.626710
C	5.212199	1.425436	-3.696957
C	4.877893	0.842932	-2.314933
C	2.726482	-0.524497	3.927445
C	3.841615	-0.671150	4.974508
C	3.275576	-1.130249	6.327338
C	2.474043	-2.430873	6.187298
C	1.359175	-2.282849	5.144743
C	1.910328	-1.819090	3.790474
C	4.089292	1.718936	2.623201
C	3.130070	2.652448	3.385718
C	3.724122	4.052344	3.594897
C	4.156986	4.683854	2.267783
C	5.158437	3.776547	1.545934
C	4.574800	2.376486	1.316362
H	4.440925	-2.029420	2.198668
H	5.600900	-0.728608	2.436335
H	5.637066	-0.181090	0.085202
H	5.778979	-1.927845	0.167055
H	2.287116	-3.040336	-1.422569
H	5.272927	-3.652323	-1.736999

H	4.188534	-3.201290	-3.049319
H	4.492871	-5.669327	-2.959746
H	2.812742	-5.203061	-2.707751
H	4.805646	-6.012624	-0.527709
H	3.422711	-6.956735	-1.078373
H	2.937867	-5.730608	1.072459
H	1.859337	-5.218743	-0.225741
H	2.747595	-3.238865	1.024926
H	4.390566	-3.752019	0.667501
H	4.986952	-1.244763	-2.810533
H	2.230106	0.074073	-2.928410
H	2.617963	-1.540995	-3.495037
H	2.490691	0.072581	-5.393366
H	4.106745	-0.618551	-5.256682
H	3.235770	2.131154	-4.220068
H	4.274496	1.836179	-5.613074
H	5.619576	2.437589	-3.578792
H	6.004142	0.819313	-4.161584
H	5.797786	0.788499	-1.722352
H	4.202249	1.519354	-1.781057
H	2.026734	0.248817	4.272636
H	4.382492	0.274643	5.097938
H	4.574868	-1.411252	4.625189
H	2.619200	-0.343178	6.726538
H	4.090959	-1.258254	7.051302
H	2.054471	-2.725026	7.157978
H	3.153658	-3.239982	5.879496
H	0.622578	-1.547743	5.496137
H	0.818004	-3.229980	5.022367
H	2.540587	-2.614564	3.365782
H	1.094269	-1.648057	3.085832
H	4.964209	1.519514	3.260184
H	2.874141	2.218786	4.359050

H	2.195303	2.740867	2.819645
H	4.595605	3.983593	4.263828
H	2.987749	4.689726	4.101118
H	4.593580	5.676097	2.440533
H	3.274295	4.829241	1.629764
H	6.077156	3.700618	2.147629
H	5.446505	4.214456	0.581561
H	3.730589	2.446717	0.621778
H	5.327167	1.741457	0.835505
Cu	1.904597	0.005863	0.327144
C	-2.211828	-0.650534	2.106483
C	-1.810421	0.472208	2.847785
C	-2.617095	-1.784119	2.831331
C	-1.795472	0.459638	4.247181
H	-1.479886	1.366392	2.330801
C	-2.610058	-1.805652	4.230585
H	-2.941317	-2.676454	2.300858
C	-2.198041	-0.680343	4.947616
H	-1.463144	1.343559	4.788062
H	-2.928748	-2.702438	4.758300
H	-2.188746	-0.692597	6.034571

TS-3			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 1.534920 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -5107.480616 a.u.			
Pd	-1.679934	-0.059548	0.558584
P	-1.563817	-2.197821	1.668348
P	-3.952595	-0.257583	0.762959
C	-4.377894	-1.932687	1.469052
C	-3.271632	-2.499347	2.362835
C	-1.239785	-3.699325	0.597429

C	-1.209917	-5.047841	1.337160
C	-0.877521	-6.196210	0.370537
C	-1.856615	-6.249688	-0.807096
C	-1.884891	-4.908015	-1.546127
C	-2.213923	-3.752233	-0.592318
C	-0.471856	-2.498005	3.154351
C	1.010167	-2.491420	2.725869
C	1.947096	-2.703290	3.921617
C	1.686872	-1.667492	5.019876
C	0.223839	-1.720984	5.473698
C	-0.740175	-1.501469	4.298796
C	-5.009094	-0.157868	-0.761299
C	-6.508951	-0.411784	-0.521739
C	-7.302122	-0.198830	-1.820867
C	-6.770701	-1.078407	-2.960291
C	-5.263834	-0.877024	-3.168334
C	-4.488255	-1.095812	-1.863632
C	-4.752818	0.910830	1.988692
C	-5.163026	2.264960	1.382510
C	-5.772926	3.189586	2.445599
C	-4.819260	3.392932	3.628017
C	-4.427514	2.047077	4.247559
C	-3.821503	1.104004	3.200858
H	-4.551534	-2.593105	0.616519
H	-5.323216	-1.864718	2.019625
H	-3.301851	-2.007502	3.338113
H	-3.428499	-3.569073	2.542137
H	-0.244169	-3.511929	0.186081
H	-2.186725	-5.242413	1.802724
H	-0.470804	-5.033604	2.144316
H	-0.876630	-7.148610	0.916233
H	0.140479	-6.050526	-0.017702
H	-2.863634	-6.485880	-0.430628

H	-1.578337	-7.058038	-1.494975
H	-2.620253	-4.931157	-2.360769
H	-0.909170	-4.730251	-2.008280
H	-2.193952	-2.799714	-1.127345
H	-3.235926	-3.896243	-0.217668
H	-0.722167	-3.502762	3.523275
H	1.240298	-1.530023	2.256680
H	1.187786	-3.269866	1.974954
H	2.988659	-2.651028	3.582663
H	1.798504	-3.713527	4.332657
H	1.906607	-0.665597	4.626830
H	2.357887	-1.835967	5.872195
H	0.033962	-0.964826	6.246390
H	0.026803	-2.700662	5.935517
H	-1.771152	-1.604993	4.657162
H	-0.622440	-0.485183	3.912648
H	-4.875460	0.872734	-1.113391
H	-6.902542	0.240112	0.265048
H	-6.651245	-1.445284	-0.177176
H	-7.227351	0.858746	-2.112350
H	-8.365931	-0.403371	-1.645523
H	-7.317346	-0.867080	-3.887812
H	-6.959949	-2.134319	-2.716546
H	-5.076222	0.144606	-3.528893
H	-4.890335	-1.559517	-3.941953
H	-4.613909	-2.139511	-1.546160
H	-3.417258	-0.948569	-2.019930
H	-5.665357	0.399960	2.330137
H	-5.881248	2.120241	0.569296
H	-4.287068	2.748739	0.943760
H	-6.715291	2.755377	2.811993
H	-6.027144	4.153712	1.987707
H	-5.279078	4.042115	4.383689

H	-3.913262	3.907449	3.276477
H	-5.320282	1.579022	4.688305
H	-3.711749	2.193786	5.066349
H	-2.864130	1.502573	2.846567
H	-3.592438	0.136901	3.661371
S	0.344607	0.961834	2.023558
C	0.063619	2.550244	2.905421
H	0.720116	2.578873	3.782569
H	0.284365	3.426250	2.290787
H	-0.967910	2.630437	3.267163
C	1.091245	-2.804038	-2.039098
C	0.230839	-2.468500	-3.119519
C	0.136794	-3.274767	-4.257304
C	0.904192	-4.436603	-4.321151
C	1.750946	-4.793326	-3.255751
C	1.846408	-3.989982	-2.124673
C	1.015421	-1.837714	-0.975137
C	0.161484	-0.770911	-1.165689
H	-0.526101	-3.005031	-5.074967
H	0.843459	-5.073792	-5.199126
H	2.335734	-5.707283	-3.318100
H	2.493934	-4.275390	-1.300351
H	1.624240	-1.918807	-0.082514
S	-0.627251	-0.984699	-2.749655
P	3.852749	0.087670	0.510392
P	2.022724	2.414176	-1.440191
C	3.755788	2.678153	-0.781491
C	4.652298	1.462040	-0.487168
C	4.307750	0.570290	2.277957
C	5.785007	0.481600	2.695590
C	5.950884	0.798148	4.191691
C	5.359609	2.164184	4.562119
C	3.900179	2.281112	4.104144

C	3.766387	1.973776	2.607847
C	5.060274	-1.318583	0.174750
C	4.738116	-2.498277	1.112614
C	5.671884	-3.692216	0.872713
C	5.627329	-4.152575	-0.588599
C	5.915632	-2.990022	-1.545669
C	4.988989	-1.791920	-1.289438
C	1.430456	4.193932	-1.539504
C	2.271611	5.125893	-2.430395
C	1.673052	6.539409	-2.483253
C	1.524746	7.133926	-1.078314
C	0.681273	6.214187	-0.188746
C	1.257748	4.792824	-0.132589
C	2.296647	1.972190	-3.239299
C	1.003820	2.189442	-4.048543
C	1.172845	1.771114	-5.516151
C	1.651990	0.320589	-5.642555
C	2.944265	0.101784	-4.849588
C	2.783958	0.518100	-3.381544
H	3.611955	3.247842	0.139950
H	4.285234	3.339611	-1.478215
H	4.979854	1.017965	-1.430075
H	5.564780	1.818713	0.009315
H	3.738374	-0.143222	2.891395
H	6.376267	1.195188	2.103479
H	6.198400	-0.511329	2.492538
H	7.012279	0.754707	4.469503
H	5.441386	0.016064	4.773894
H	5.950311	2.954878	4.075714
H	5.440428	2.332113	5.643910
H	3.513204	3.285908	4.319347
H	3.278225	1.573965	4.672027
H	2.724330	2.051782	2.288053

H	4.344697	2.721360	2.047591
H	6.088984	-0.984745	0.374080
H	3.697529	-2.810243	0.943280
H	4.798911	-2.187623	2.161251
H	5.402232	-4.519095	1.542686
H	6.700586	-3.400433	1.130845
H	4.629885	-4.558287	-0.807460
H	6.341214	-4.969627	-0.754588
H	5.810885	-3.321235	-2.586700
H	6.960521	-2.670090	-1.418605
H	5.262224	-0.979856	-1.971680
H	3.955660	-2.067197	-1.534460
H	0.425416	4.112207	-1.973018
H	2.353306	4.723385	-3.445488
H	3.293446	5.192885	-2.034003
H	0.684634	6.493783	-2.963460
H	2.300123	7.186014	-3.110649
H	1.073799	8.133118	-1.131093
H	2.522715	7.260152	-0.632565
H	-0.338491	6.167922	-0.591009
H	0.604683	6.623817	0.826989
H	2.225954	4.826483	0.384921
H	0.604015	4.142402	0.453834
H	3.076778	2.640003	-3.633891
H	0.692302	3.238415	-4.003483
H	0.199897	1.601731	-3.592299
H	1.902824	2.437819	-6.000202
H	0.222151	1.907755	-6.048010
H	1.801898	0.058858	-6.698157
H	0.877891	-0.350913	-5.251010
H	3.755845	0.686483	-5.309443
H	3.244868	-0.952453	-4.895934
H	2.072934	-0.147781	-2.886991

H	3.736771	0.387805	-2.864834
Cu	0.661922	0.983340	-0.294119
C	-2.024841	1.729592	-0.418389
C	-2.327170	1.779906	-1.790066
C	-2.001642	2.955978	0.266519
C	-2.567105	2.989202	-2.451125
H	-2.376434	0.864749	-2.366218
C	-2.259158	4.168408	-0.379900
H	-1.796108	2.970871	1.327763
C	-2.538414	4.195290	-1.747748
H	-2.780860	2.982081	-3.517855
H	-2.245599	5.092205	0.193106
H	-2.732720	5.136941	-2.254686

E			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.676262 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -2338.561405 a.u.			
S	-0.045856	-0.828292	3.365223
C	-1.837251	-1.148814	3.694435
H	-2.468088	-0.343726	3.303821
H	-2.161450	-2.093191	3.244840
H	-1.999699	-1.215453	4.776306
P	1.683205	0.185620	-0.273690
P	-1.587628	-0.056907	-0.365654
C	-0.675457	0.670751	-1.833306
C	0.801873	0.234746	-1.927476
C	2.505715	1.851690	-0.111500
C	3.492570	2.225419	-1.229076
C	4.147109	3.588298	-0.953304
C	3.096798	4.688088	-0.752770
C	2.103431	4.312658	0.354018

C	1.446717	2.953685	0.078110
C	3.075729	-1.018007	-0.573419
C	4.117822	-0.921969	0.557247
C	5.233501	-1.963086	0.388622
C	4.669753	-3.385007	0.291751
C	3.634603	-3.487957	-0.833953
C	2.515933	-2.452095	-0.658411
C	-2.961374	1.168577	-0.063589
C	-3.794340	1.545616	-1.300206
C	-4.915642	2.530649	-0.935595
C	-4.360565	3.780050	-0.240669
C	-3.530912	3.405012	0.993623
C	-2.406433	2.422969	0.637834
C	-2.443094	-1.563719	-1.054112
C	-3.357187	-2.186581	0.017786
C	-4.009903	-3.485366	-0.475162
C	-2.958284	-4.497067	-0.944458
C	-2.057162	-3.887130	-2.023746
C	-1.399647	-2.588377	-1.537627
H	-0.726259	1.757507	-1.711237
H	-1.194703	0.434579	-2.769682
H	0.858729	-0.781572	-2.328230
H	1.335620	0.877746	-2.636218
H	3.063896	1.774493	0.831893
H	2.959353	2.273059	-2.188516
H	4.265556	1.455892	-1.335050
H	4.823060	3.850466	-1.777014
H	4.767204	3.510422	-0.048686
H	2.547901	4.837937	-1.694488
H	3.585887	5.641818	-0.518758
H	1.331511	5.085994	0.454424
H	2.630919	4.265549	1.317261
H	0.768311	2.682775	0.895116

H	0.837378	3.032307	-0.832935
H	3.561123	-0.769853	-1.528368
H	3.610137	-1.080260	1.519290
H	4.556080	0.081372	0.592280
H	5.937376	-1.886708	1.226623
H	5.803443	-1.735362	-0.524381
H	4.191301	-3.649156	1.245553
H	5.480737	-4.106685	0.132431
H	3.201828	-4.495700	-0.865420
H	4.131170	-3.326280	-1.802174
H	1.798817	-2.540340	-1.482511
H	1.961664	-2.667276	0.265742
H	-3.619999	0.661371	0.654987
H	-4.222301	0.649047	-1.763665
H	-3.141038	2.009720	-2.051747
H	-5.628960	2.030103	-0.264926
H	-5.474306	2.809987	-1.837902
H	-5.179538	4.453649	0.040687
H	-3.725381	4.333841	-0.948011
H	-4.186570	2.941691	1.744869
H	-3.106290	4.303825	1.457725
H	-1.688520	2.927677	-0.023497
H	-1.853180	2.130630	1.537997
H	-3.056957	-1.260460	-1.914172
H	-4.133780	-1.474436	0.319429
H	-2.757398	-2.396171	0.913929
H	-4.690414	-3.256051	-1.308397
H	-4.624898	-3.915353	0.325058
H	-3.443656	-5.405776	-1.321691
H	-2.340305	-4.799143	-0.086639
H	-2.657766	-3.674341	-2.920306
H	-1.281505	-4.602089	-2.325720
H	-0.713141	-2.814775	-0.709996

H	-0.795175	-2.158969	-2.344343
Cu	0.046775	-0.337950	1.221404

D			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.823658 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -2768.915026 a.u.			
Pd	0.181588	-0.322145	-0.250836
P	-0.750692	1.285366	1.199657
P	2.257509	0.337669	0.595736
C	1.993412	1.815496	1.714554
C	0.602819	1.826548	2.368013
C	-1.394911	2.822752	0.381914
C	-1.826111	3.948490	1.335241
C	-2.430349	5.122989	0.550050
C	-1.458264	5.644547	-0.515929
C	-1.003449	4.519394	-1.454283
C	-0.403400	3.344066	-0.672329
C	-2.099594	0.733788	2.359689
C	-3.479936	0.705952	1.674810
C	-4.564706	0.173173	2.621114
C	-4.203205	-1.210447	3.171741
C	-2.837761	-1.180359	3.867587
C	-1.746100	-0.656483	2.925533
C	3.517497	0.910997	-0.638677
C	4.818953	1.451510	-0.021738
C	5.826693	1.830934	-1.117299
C	5.226870	2.830339	-2.114386
C	3.917851	2.301167	-2.714298
C	2.910274	1.931863	-1.617746
C	3.141872	-0.905603	1.664257
C	3.876589	-1.967714	0.823348

C	4.523463	-3.038626	1.712521
C	3.495227	-3.696345	2.639142
C	2.785732	-2.642706	3.496406
C	2.131198	-1.564788	2.623274
H	2.113218	2.704552	1.088069
H	2.777764	1.855597	2.479146
H	0.577662	1.116995	3.201040
H	0.381848	2.813100	2.789748
H	-2.279681	2.464841	-0.160399
H	-0.952623	4.308057	1.896596
H	-2.547847	3.578900	2.072400
H	-2.708829	5.928930	1.240582
H	-3.357628	4.788004	0.063833
H	-0.577405	6.077452	-0.018550
H	-1.924500	6.454451	-1.090437
H	-0.271534	4.897705	-2.178919
H	-1.864259	4.156506	-2.033528
H	-0.125299	2.532680	-1.353186
H	0.519857	3.674400	-0.176726
H	-2.132147	1.454941	3.190336
H	-3.427013	0.065063	0.789393
H	-3.757183	1.707444	1.329973
H	-5.522478	0.133523	2.088278
H	-4.694991	0.874606	3.458996
H	-4.171345	-1.929652	2.341652
H	-4.977769	-1.559232	3.866238
H	-2.565606	-2.181847	4.224266
H	-2.895484	-0.533246	4.755497
H	-0.784266	-0.624647	3.450715
H	-1.624331	-1.350532	2.085411
H	3.747341	0.006141	-1.215959
H	5.264096	0.712944	0.654130
H	4.592107	2.339784	0.584180

H	6.128540	0.920047	-1.653885
H	6.734999	2.244013	-0.660884
H	5.948780	3.051332	-2.910227
H	5.027280	3.780425	-1.596804
H	4.129237	1.409244	-3.321163
H	3.477543	3.045815	-3.388918
H	2.624359	2.842914	-1.075082
H	1.991424	1.529265	-2.056632
H	3.883523	-0.353732	2.260124
H	4.645345	-1.496415	0.201931
H	3.165541	-2.444567	0.141063
H	5.317447	-2.579651	2.320566
H	5.006193	-3.793073	1.079342
H	3.979119	-4.445602	3.277991
H	2.750670	-4.228554	2.029999
H	3.515952	-2.171955	4.171127
H	2.024586	-3.111696	4.132611
H	1.325913	-2.013417	2.027491
H	1.663733	-0.805196	3.259991
C	-3.726359	-1.990819	-1.292547
C	-3.941206	-0.846554	-2.105342
C	-5.143865	-0.643184	-2.785130
C	-6.157809	-1.589093	-2.646748
C	-5.967137	-2.726400	-1.842855
C	-4.766476	-2.931069	-1.171943
C	-2.417017	-1.984690	-0.683327
C	-1.639167	-0.898261	-0.976932
H	-5.288429	0.236080	-3.407188
H	-7.102042	-1.445170	-3.164821
H	-6.768252	-3.454593	-1.746541
H	-4.624447	-3.815014	-0.554634
H	-2.083325	-2.783258	-0.027059
S	-2.509055	0.179262	-2.082484

C	1.029892	-1.783450	-1.423183
C	1.754995	-1.508272	-2.594110
C	0.945002	-3.130078	-1.027145
C	2.388873	-2.522342	-3.321343
H	1.833973	-0.485176	-2.953939
C	1.580313	-4.149494	-1.742365
H	0.378742	-3.394487	-0.136118
C	2.312831	-3.848741	-2.893484
H	2.942261	-2.272962	-4.224805
H	1.500607	-5.179964	-1.401460
H	2.807419	-4.638078	-3.453867

TS-4			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.821288 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -2768.879477 a.u.			
Pd	0.173827	-0.321296	-0.235818
P	-0.643103	1.430337	1.124229
P	2.318101	0.160620	0.657664
C	2.141043	1.706945	1.706008
C	0.731815	1.892718	2.306601
C	-1.108825	3.004824	0.244915
C	-1.556254	4.168566	1.143536
C	-1.985012	5.380584	0.301519
C	-0.875294	5.818965	-0.662453
C	-0.418819	4.655018	-1.551402
C	0.013329	3.446670	-0.710862
C	-2.095754	1.056868	2.231131
C	-3.382014	0.988808	1.382338
C	-4.596202	0.531078	2.201381
C	-4.330729	-0.802532	2.906924
C	-3.073452	-0.717424	3.778946

C	-1.855517	-0.284559	2.952628
C	3.713165	0.565838	-0.506898
C	5.011491	1.056862	0.153497
C	6.106015	1.308688	-0.895137
C	5.631496	2.281583	-1.981863
C	4.334132	1.791828	-2.637758
C	3.236728	1.547027	-1.593642
C	3.034779	-1.099528	1.831249
C	3.552443	-2.322119	1.049688
C	4.018159	-3.446842	1.984544
C	2.916082	-3.854210	2.968335
C	2.434467	-2.643132	3.774316
C	1.956735	-1.514856	2.851386
H	2.369272	2.550274	1.046629
H	2.892801	1.717730	2.504171
H	0.613421	1.234683	3.173002
H	0.611287	2.917975	2.674687
H	-1.960235	2.703072	-0.380509
H	-0.726206	4.464768	1.800061
H	-2.380318	3.857739	1.795639
H	-2.269406	6.211182	0.959969
H	-2.881965	5.114104	-0.275925
H	-0.016508	6.185651	-0.080524
H	-1.218380	6.658733	-1.279565
H	0.405688	4.971555	-2.202808
H	-1.245693	4.353799	-2.210463
H	0.298721	2.609449	-1.357510
H	0.904673	3.718056	-0.128435
H	-2.199335	1.852297	2.983610
H	-3.223345	0.286325	0.556988
H	-3.594089	1.964570	0.932500
H	-5.465475	0.442938	1.538388
H	-4.841136	1.297223	2.952289

H	-4.194207	-1.584986	2.148150
H	-5.198367	-1.093306	3.512661
H	-2.869630	-1.684907	4.255680
H	-3.240395	0.005856	4.590996
H	-0.971570	-0.220942	3.597989
H	-1.639684	-1.050278	2.196324
H	3.915754	-0.389925	-1.009889
H	5.365666	0.330088	0.893902
H	4.811607	1.990792	0.697158
H	6.380619	0.351507	-1.361587
H	7.010825	1.692229	-0.406606
H	6.414398	2.416607	-2.738591
H	5.456154	3.269223	-1.529824
H	4.530157	0.853763	-3.176716
H	3.984888	2.517607	-3.383036
H	2.962185	2.506180	-1.133793
H	2.332123	1.154330	-2.070888
H	3.873717	-0.642094	2.375619
H	4.378133	-2.029171	0.391620
H	2.752117	-2.696365	0.398308
H	4.899121	-3.108821	2.550086
H	4.338832	-4.310183	1.388183
H	3.275352	-4.643257	3.640741
H	2.068515	-4.275561	2.407803
H	3.259010	-2.275771	4.402872
H	1.623038	-2.931048	4.454787
H	1.062556	-1.842938	2.303678
H	1.653845	-0.649336	3.451632
C	-3.677721	-1.915664	-1.043108
C	-3.831595	-0.891468	-2.018309
C	-5.076314	-0.566768	-2.554354
C	-6.201077	-1.262998	-2.107376
C	-6.073256	-2.275697	-1.142557

C	-4.829420	-2.607688	-0.615982
C	-2.318795	-2.066708	-0.619452
C	-1.416215	-1.185195	-1.193328
H	-5.171978	0.216704	-3.301122
H	-7.179923	-1.017286	-2.509334
H	-6.958303	-2.807811	-0.803899
H	-4.738661	-3.394077	0.129064
H	-2.011533	-2.827353	0.090381
S	-2.277218	-0.136495	-2.364727
C	0.272889	-1.858752	-1.679800
C	0.743583	-1.476656	-2.954422
C	0.577698	-3.167550	-1.238438
C	1.516223	-2.342461	-3.728861
H	0.499738	-0.491091	-3.341892
C	1.346593	-4.028735	-2.012957
H	0.207437	-3.505599	-0.274204
C	1.828333	-3.622307	-3.264617
H	1.871105	-2.015705	-4.703780
H	1.576431	-5.024455	-1.640083
H	2.422015	-4.299688	-3.871925

3b

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.157565 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -937.947527 a.u.

C	-1.837639	0.768849	0.110997
C	-2.017297	-0.623455	-0.092059
C	-3.288491	-1.196972	-0.173310
C	-4.396770	-0.364718	-0.047982
C	-4.240335	1.018201	0.157223
C	-2.976210	1.586208	0.237999
C	-0.448970	1.129839	0.164996

C	0.407033	0.075270	0.011041
H	-3.410079	-2.264589	-0.329926
H	-5.394213	-0.790213	-0.108812
H	-5.120510	1.647355	0.253366
H	-2.858054	2.654474	0.397607
H	-0.108566	2.144032	0.342029
S	-0.472319	-1.446945	-0.220131
C	1.873088	0.093258	0.012456
C	2.621446	-1.044364	0.361206
C	2.564709	1.268027	-0.336021
C	4.014162	-1.007163	0.366130
H	2.109825	-1.958022	0.649983
C	3.956153	1.304745	-0.321445
H	2.004852	2.147534	-0.638050
C	4.688421	0.167385	0.028262
H	4.572754	-1.897196	0.641670
H	4.471072	2.221221	-0.595832
H	5.774216	0.195867	0.033095

V			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.793718 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -2600.124450 a.u.			
S	-0.751669	2.361918	1.781018
C	0.413967	2.783371	3.144692
H	0.535603	1.957975	3.854899
H	1.406387	3.033182	2.751125
H	0.045850	3.654614	3.698399
P	-1.565601	-0.276823	-0.875622
P	1.649212	0.419002	-0.825733
C	0.865850	-0.185288	-2.417544
C	-0.653774	0.043999	-2.480485

C	-2.006248	-2.096073	-0.917275
C	-2.706987	-2.613619	-2.182122
C	-3.069966	-4.100681	-2.041903
C	-1.840108	-4.951773	-1.698700
C	-1.132107	-4.426419	-0.443222
C	-0.766345	-2.943167	-0.576882
C	-3.190107	0.576856	-1.274973
C	-4.317881	0.143257	-0.322643
C	-5.633263	0.875465	-0.622916
C	-5.449398	2.396445	-0.577105
C	-4.325186	2.842425	-1.519034
C	-3.013390	2.106938	-1.213443
C	3.206890	-0.613614	-0.727455
C	4.197806	-0.483514	-1.895407
C	5.459826	-1.324103	-1.641127
C	5.121857	-2.793350	-1.356381
C	4.113397	-2.921969	-0.207192
C	2.853817	-2.092983	-0.486236
C	2.271373	2.125215	-1.254984
C	3.045956	2.694546	-0.051635
C	3.493319	4.143345	-0.286288
C	2.302818	5.040901	-0.642666
C	1.554956	4.491699	-1.862637
C	1.094919	3.046022	-1.630246
H	1.073112	-1.257381	-2.477790
H	1.348137	0.278365	-3.286930
H	-0.852485	1.094079	-2.711855
H	-1.090630	-0.542413	-3.297112
H	-2.705915	-2.212535	-0.074223
H	-2.036717	-2.492096	-3.043885
H	-3.608341	-2.027478	-2.398882
H	-3.538863	-4.460942	-2.966695
H	-3.820484	-4.212419	-1.245104

H	-1.137684	-4.923683	-2.545082
H	-2.131158	-6.001811	-1.566902
H	-0.229504	-5.015929	-0.237318
H	-1.793360	-4.554604	0.427341
H	-0.315507	-2.564392	0.347544
H	-0.024509	-2.832355	-1.379238
H	-3.485537	0.297507	-2.297181
H	-4.020797	0.384018	0.710582
H	-4.475983	-0.939738	-0.367927
H	-6.406870	0.558793	0.088670
H	-5.983773	0.579163	-1.622025
H	-5.197450	2.698804	0.450108
H	-6.389394	2.900737	-0.833689
H	-4.168076	3.924929	-1.437346
H	-4.623268	2.642363	-2.558963
H	-2.237396	2.434493	-1.913661
H	-2.657732	2.387189	-0.213833
H	3.704464	-0.246247	0.181424
H	4.481864	0.563200	-2.050049
H	3.714459	-0.821924	-2.822989
H	5.996008	-0.904027	-0.777627
H	6.139422	-1.248610	-2.499805
H	6.036710	-3.355294	-1.129435
H	4.690823	-3.245361	-2.262195
H	4.575517	-2.573716	0.727830
H	3.843048	-3.974326	-0.052238
H	2.360571	-2.501346	-1.378614
H	2.134144	-2.179192	0.332528
H	2.948955	2.056475	-2.117918
H	3.917806	2.067299	0.172124
H	2.390550	2.655014	0.827654
H	4.227246	4.170740	-1.105776
H	4.005023	4.521523	0.607994

H	2.641347	6.067905	-0.831073
H	1.612549	5.080734	0.211561
H	2.216735	4.531029	-2.741366
H	0.685848	5.121220	-2.092569
H	0.357741	3.023813	-0.817799
H	0.600245	2.671219	-2.534194
Cu	0.022828	0.326165	0.760306
C	0.244131	-1.172157	4.537014
C	0.845117	-1.520969	3.148329
H	0.021526	-0.098005	4.595797
H	-0.683129	-1.741717	4.703654
H	0.921348	-1.410131	5.367463
C	1.156981	-3.033712	3.129989
C	2.164043	-0.733999	2.997967
H	1.601438	-3.313743	2.168395
H	1.848690	-3.336862	3.928194
H	0.227772	-3.606596	3.244400
H	2.860468	-0.928157	3.825543
H	2.663666	-1.007849	2.065410
H	1.957654	0.340630	2.961772
O	-0.063895	-1.224934	2.136634
K	-2.282634	-0.135126	2.818737

TS-5			
G _{corr} at B3LYP-D3BJ/BSI level in toluene: 0.791544 a.u.			
B3LYP-D3BJ/BSII SCF energy in toluene: -2600.115272 a.u.			
S	1.341817	-3.373450	0.684324
C	0.247340	-4.007847	2.030367
H	-0.075967	-3.206454	2.709091
H	-0.661614	-4.463080	1.616889
H	0.746881	-4.777339	2.631907

P	1.403529	0.880158	-0.834416
P	-1.692789	-0.261450	-0.842614
C	-1.081684	0.765895	-2.283586
C	0.451334	0.757081	-2.441195
C	1.573507	2.713095	-0.500101
C	2.174838	3.559246	-1.632857
C	2.339747	5.024865	-1.200445
C	1.014427	5.620961	-0.709075
C	0.403563	4.770329	0.411855
C	0.236512	3.309046	-0.023496
C	3.118589	0.368696	-1.392111
C	4.171849	0.766516	-0.341620
C	5.571658	0.245353	-0.692263
C	5.568419	-1.269232	-0.922384
C	4.554099	-1.650774	-2.005349
C	3.148391	-1.150605	-1.651111
C	-3.377096	0.467306	-0.486371
C	-4.325233	0.578348	-1.692839
C	-5.697637	1.125537	-1.270228
C	-5.570991	2.471714	-0.546486
C	-4.614969	2.370218	0.648532
C	-3.244932	1.826601	0.223063
C	-2.078058	-1.933730	-1.567159
C	-2.523058	-2.876937	-0.432845
C	-2.793461	-4.296607	-0.948112
C	-1.568456	-4.860437	-1.677226
C	-1.145417	-3.934700	-2.823416
C	-0.864094	-2.513382	-2.315527
H	-1.425877	1.788451	-2.099966
H	-1.552494	0.437615	-3.217562
H	0.763560	-0.193144	-2.882886
H	0.760087	1.544138	-3.138771
H	2.258824	2.751974	0.359389

H	1.513304	3.517739	-2.509020
H	3.142710	3.153666	-1.949422
H	2.739874	5.617360	-2.033016
H	3.082293	5.077410	-0.390816
H	0.307394	5.667851	-1.550697
H	1.165593	6.652674	-0.367685
H	-0.566517	5.181142	0.719155
H	1.056390	4.807694	1.295991
H	-0.165036	2.707190	0.798430
H	-0.494653	3.263896	-0.841278
H	3.355554	0.893472	-2.328925
H	3.875330	0.357813	0.637691
H	4.202496	1.853986	-0.218216
H	6.276711	0.516574	0.104172
H	5.919825	0.749288	-1.605284
H	5.301689	-1.781491	0.014916
H	6.573183	-1.614880	-1.194963
H	4.528942	-2.738537	-2.139439
H	4.871056	-1.216797	-2.965418
H	2.451732	-1.414515	-2.454159
H	2.788388	-1.677641	-0.758744
H	-3.819691	-0.235742	0.234053
H	-4.451210	-0.395323	-2.178740
H	-3.884122	1.252105	-2.440556
H	-6.181010	0.398900	-0.601207
H	-6.346554	1.223725	-2.149770
H	-6.557781	2.821488	-0.218301
H	-5.187340	3.224692	-1.251004
H	-5.046931	1.699156	1.405020
H	-4.494839	3.350133	1.127573
H	-2.769873	2.549415	-0.454315
H	-2.585351	1.731074	1.091168
H	-2.904317	-1.816136	-2.282659

H	-3.417949	-2.481957	0.064673
H	-1.723454	-2.910832	0.315667
H	-3.654793	-4.280408	-1.633612
H	-3.072059	-4.945250	-0.107730
H	-1.781556	-5.867576	-2.058534
H	-0.732828	-4.944300	-0.970198
H	-1.940790	-3.904127	-3.584471
H	-0.247890	-4.328219	-3.316964
H	-0.008722	-2.546209	-1.629477
H	-0.601813	-1.867990	-3.162563
Cu	-0.071075	-0.108658	0.696521
C	0.030760	-0.294813	4.898498
C	-0.611854	0.251084	3.604085
H	0.262356	-1.362899	4.783621
H	0.962755	0.246612	5.111278
H	-0.623581	-0.191300	5.773199
C	-0.972526	1.735350	3.811842
C	-1.894598	-0.551170	3.315581
H	-1.417527	2.141658	2.896428
H	-1.683279	1.887357	4.635326
H	-0.066009	2.314319	4.027228
H	-2.611051	-0.496923	4.146308
H	-2.385286	-0.170532	2.413400
H	-1.648031	-1.604132	3.138374
O	0.322559	0.134990	2.568252
K	2.462397	-1.237008	2.514129

VI

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.789405 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2600.116126 a.u.

S	2.552565	-3.432482	0.337725
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C	1.321031	-4.132940	1.529070
H	0.739295	-3.350343	2.037477
H	0.598187	-4.777637	1.013838
H	1.802747	-4.747161	2.300920
P	1.095902	1.346283	-0.746985
P	-1.664466	-0.433216	-0.845974
C	-1.329958	0.804026	-2.209409
C	0.158029	1.182926	-2.359505
C	0.909102	3.137932	-0.249533
C	1.355044	4.178810	-1.288183
C	1.212815	5.606747	-0.737958
C	-0.216139	5.885253	-0.255202
C	-0.666653	4.843194	0.776219
C	-0.528469	3.417441	0.227186
C	2.870740	1.201083	-1.321052
C	3.831581	1.658685	-0.207859
C	5.302837	1.422357	-0.574595
C	5.561830	-0.036493	-0.964918
C	4.636631	-0.465715	-2.107930
C	3.162433	-0.253097	-1.742071
C	-3.470535	-0.169935	-0.458008
C	-4.423597	-0.211588	-1.664739
C	-5.884679	-0.038059	-1.221832
C	-6.079019	1.249838	-0.412139
C	-5.123562	1.300436	0.786666
C	-3.663768	1.128622	0.346544
C	-1.598907	-2.103192	-1.666514
C	-1.838610	-3.203264	-0.614345
C	-1.745737	-4.605034	-1.233310
C	-0.407498	-4.813493	-1.952218
C	-0.173455	-3.722836	-3.002841
C	-0.250197	-2.324252	-2.375324
H	-1.911710	1.696246	-1.956859

H	-1.715846	0.437030	-3.167532
H	0.676636	0.397373	-2.915056
H	0.250895	2.098390	-2.954596
H	1.559866	3.229638	0.632207
H	0.737239	4.081666	-2.191310
H	2.391945	3.999982	-1.594839
H	1.505135	6.332978	-1.506820
H	1.910852	5.738208	0.101602
H	-0.899228	5.857432	-1.117187
H	-0.284372	6.895290	0.167527
H	-1.705484	5.026915	1.078024
H	-0.052398	4.938342	1.683211
H	-0.816512	2.684942	0.989802
H	-1.222607	3.291044	-0.614198
H	3.015163	1.858383	-2.190424
H	3.599311	1.107055	0.716980
H	3.673328	2.717018	0.025762
H	5.944118	1.720760	0.264774
H	5.567010	2.074707	-1.419305
H	5.382291	-0.688536	-0.096357
H	6.612837	-0.173456	-1.247118
H	4.797946	-1.521715	-2.353127
H	4.882689	0.115496	-3.009222
H	2.532540	-0.536096	-2.592333
H	2.891086	-0.940989	-0.929464
H	-3.722792	-1.007395	0.207909
H	-4.312329	-1.153788	-2.212692
H	-4.161713	0.595356	-2.362991
H	-6.176446	-0.900891	-0.605742
H	-6.542813	-0.041031	-2.099863
H	-7.119437	1.333274	-0.074320
H	-5.887555	2.116624	-1.062114
H	-5.381358	0.496918	1.491617

H	-5.240103	2.246574	1.329961
H	-3.373565	1.990004	-0.271241
H	-2.999333	1.128993	1.217683
H	-2.398751	-2.146924	-2.419591
H	-2.816708	-3.071989	-0.135102
H	-1.081816	-3.102780	0.172995
H	-2.572343	-4.740544	-1.947533
H	-1.881123	-5.360530	-0.448964
H	-0.379681	-5.806004	-2.420056
H	0.414398	-4.771122	-1.226523
H	-0.925233	-3.807952	-3.802820
H	0.809618	-3.856094	-3.470430
H	0.565270	-2.223158	-1.647003
H	-0.103146	-1.565998	-3.153088
Cu	-0.094481	-0.020890	0.706185
C	0.190587	-1.007868	4.794833
C	-0.578637	-0.441906	3.582788
H	0.646962	-1.973236	4.536413
H	0.985867	-0.311459	5.092738
H	-0.456430	-1.171268	5.665502
C	-1.252614	0.883509	3.984918
C	-1.658247	-1.455412	3.161196
H	-1.795788	1.297935	3.127053
H	-1.962606	0.761657	4.813792
H	-0.492475	1.614904	4.285269
H	-2.357904	-1.674415	3.978712
H	-2.232052	-1.065690	2.313153
H	-1.192009	-2.395243	2.844409
O	0.346806	-0.206620	2.554213
K	2.715742	-1.105783	2.278136

VII

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.119151 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -728.09698 a.u.

S	-3.042997	-0.000218	0.011077
C	-2.105884	-0.000067	1.619878
H	-1.016119	0.000060	1.462519
H	-2.357139	0.879497	2.225871
H	-2.356923	-0.879670	2.225904
C	3.259778	-0.000814	-0.939809
C	2.163815	0.000065	0.153614
H	3.143913	-0.886376	-1.578502
H	3.144571	0.884271	-1.579274
H	4.281768	-0.001018	-0.534988
C	2.366644	1.253873	1.046349
C	2.365813	-1.253058	1.047514
H	1.589710	1.285717	1.821882
H	3.345098	1.286122	1.544635
H	2.281887	2.164987	0.434777
H	3.344199	-1.285433	1.545924
H	1.588791	-1.283733	1.823009
H	2.280604	-2.164706	0.436794
O	0.909450	0.000234	-0.409323
K	-0.688606	1.941581	-0.639361
K	-0.688184	-1.941480	-0.639401

III'

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.86773 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2840.373019 a.u.

P	-2.194807	-0.832835	-0.664246
P	0.501754	0.882194	-1.344389
C	-0.375563	-0.001352	-2.746541

C	-1.843635	-0.368845	-2.444393
C	-1.833950	-2.657953	-0.524789
C	-2.572301	-3.570972	-1.515602
C	-2.247756	-5.048974	-1.245257
C	-0.736088	-5.311070	-1.268294
C	0.004895	-4.387939	-0.292492
C	-0.317054	-2.914836	-0.569166
C	-4.057736	-0.709756	-0.602856
C	-4.601674	-1.372999	0.676516
C	-6.123710	-1.213872	0.797968
C	-6.545337	0.257851	0.728125
C	-6.017520	0.916379	-0.551204
C	-4.494652	0.767521	-0.669415
C	2.306851	0.571118	-1.723224
C	2.777557	1.055100	-3.105768
C	4.277593	0.791690	-3.308641
C	4.619424	-0.688486	-3.102627
C	4.159291	-1.163559	-1.720281
C	2.661308	-0.911909	-1.506839
C	0.267898	2.700144	-1.695652
C	1.057700	3.508145	-0.645857
C	0.820924	5.017835	-0.787395
C	-0.672575	5.355834	-0.720693
C	-1.454165	4.577050	-1.784484
C	-1.228136	3.065444	-1.648240
H	0.195198	-0.916485	-2.930042
H	-0.327479	0.588122	-3.669786
H	-2.480371	0.498556	-2.640520
H	-2.181560	-1.159927	-3.123421
H	-2.172967	-2.909032	0.490443
H	-2.268382	-3.319012	-2.540967
H	-3.655154	-3.411126	-1.457918
H	-2.756639	-5.683029	-1.982244

H	-2.648511	-5.327362	-0.259781
H	-0.356107	-5.136189	-2.285789
H	-0.530223	-6.362464	-1.032184
H	1.088063	-4.549077	-0.356644
H	-0.290696	-4.633799	0.738079
H	0.197918	-2.268018	0.147887
H	0.068387	-2.647654	-1.561340
H	-4.469745	-1.235912	-1.476242
H	-4.115618	-0.913221	1.548406
H	-4.343084	-2.437468	0.695606
H	-6.467402	-1.667372	1.735994
H	-6.609740	-1.769081	-0.017799
H	-6.143399	0.791484	1.601291
H	-7.637877	0.344181	0.779441
H	-6.285899	1.979960	-0.573837
H	-6.497072	0.450141	-1.424489
H	-4.152478	1.230309	-1.601882
H	-4.011013	1.317060	0.148398
H	2.843708	1.141267	-0.953636
H	2.571663	2.124122	-3.230334
H	2.211690	0.529848	-3.888210
H	4.846818	1.395567	-2.587234
H	4.581902	1.123121	-4.309876
H	5.698457	-0.849336	-3.221498
H	4.122876	-1.286471	-3.881699
H	4.723992	-0.628931	-0.948441
H	4.376265	-2.230764	-1.585119
H	2.095068	-1.535702	-2.211787
H	2.366172	-1.219852	-0.500559
H	0.649750	2.936200	-2.698616
H	2.129682	3.293246	-0.732446
H	0.744092	3.180243	0.354864
H	1.228722	5.364593	-1.748707

H	1.369052	5.551443	-0.000806
H	-0.827533	6.434820	-0.847012
H	-1.057087	5.091239	0.274700
H	-1.131530	4.904260	-2.784149
H	-2.526953	4.796764	-1.711083
H	-1.648343	2.722816	-0.692546
H	-1.770053	2.539085	-2.442356
Cu	-0.819547	0.437266	0.546646
C	-2.637989	1.947016	2.932658
C	-1.231532	1.408672	3.259208
H	-2.560523	2.946336	2.486870
H	-3.125445	1.289809	2.203186
H	-3.282186	2.012425	3.820331
C	-1.359253	-0.018111	3.834367
C	-0.569876	2.320568	4.309966
H	-0.370251	-0.408716	4.100981
H	-1.994033	-0.055386	4.730260
H	-1.794111	-0.682772	3.076189
H	-1.144906	2.371088	5.244088
H	0.435599	1.951787	4.544690
H	-0.470665	3.337183	3.910847
O	-0.420097	1.411671	2.117319
C	3.456527	-0.111375	1.902769
C	4.269011	-1.273765	1.848557
C	5.640252	-1.200548	1.586305
C	6.203073	0.051780	1.358632
C	5.411403	1.214968	1.389718
C	4.050951	1.140879	1.662047
C	2.077911	-0.414165	2.199133
C	1.863181	-1.747554	2.347028
H	6.251243	-2.097714	1.553086
H	7.266452	0.129834	1.150760
H	5.872818	2.181068	1.205527

H	3.438564	2.037606	1.696669
H	1.284954	0.333032	2.280170
H	0.927926	-2.241521	2.577250
S	3.313122	-2.720588	2.139592

TS-2'

G_{corr} at B3LYP-D3BJ/BSI level in toluene: 0.863071 a.u.

B3LYP-D3BJ/BSII SCF energy in toluene: -2840.342297 a.u.

P	-1.654093	-0.989604	-0.880668
P	0.969729	0.992202	-1.240733
C	0.306372	0.062502	-2.727150
C	-1.159582	-0.400073	-2.588563
C	-1.199835	-2.801220	-0.830880
C	-1.840218	-3.681844	-1.916419
C	-1.456784	-5.157986	-1.725542
C	0.064845	-5.347678	-1.689290
C	0.708583	-4.456149	-0.620404
C	0.328233	-2.984098	-0.817792
C	-3.519160	-0.989620	-1.007868
C	-4.143500	-1.780014	0.158321
C	-5.677338	-1.722082	0.128541
C	-6.188635	-0.277375	0.114871
C	-5.581648	0.505544	-1.054607
C	-4.048448	0.457005	-1.020944
C	2.816246	0.737741	-1.376527
C	3.429446	1.180117	-2.716781
C	4.950541	0.966448	-2.736422
C	5.317470	-0.487502	-2.417349
C	4.716968	-0.918725	-1.074871
C	3.195935	-0.717892	-1.045943
C	0.718523	2.788167	-1.666637

C	1.352569	3.670841	-0.574246
C	1.113962	5.161991	-0.848836
C	-0.381074	5.471400	-0.986635
C	-1.029624	4.592893	-2.062771
C	-0.783524	3.100849	-1.798407
H	0.953549	-0.810198	-2.852316
H	0.415346	0.665833	-3.636187
H	-1.825120	0.442213	-2.800018
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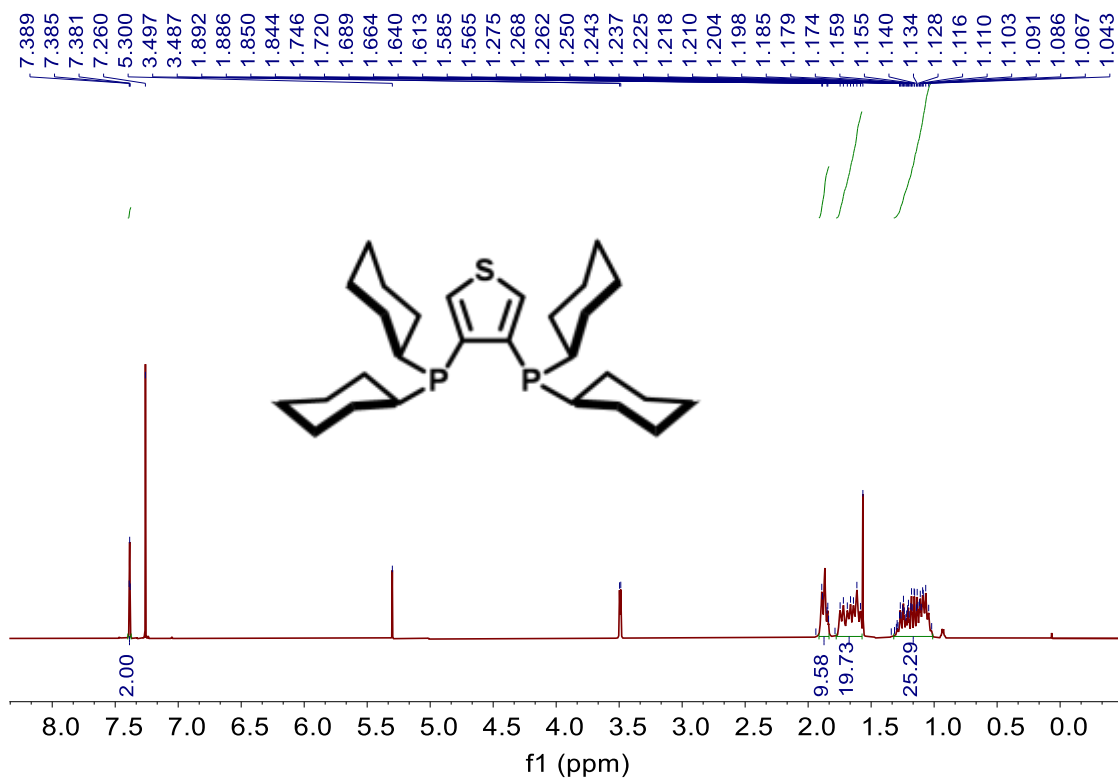
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H	4.982852	4.022663	2.998403
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H	2.034734	2.999708	0.818498

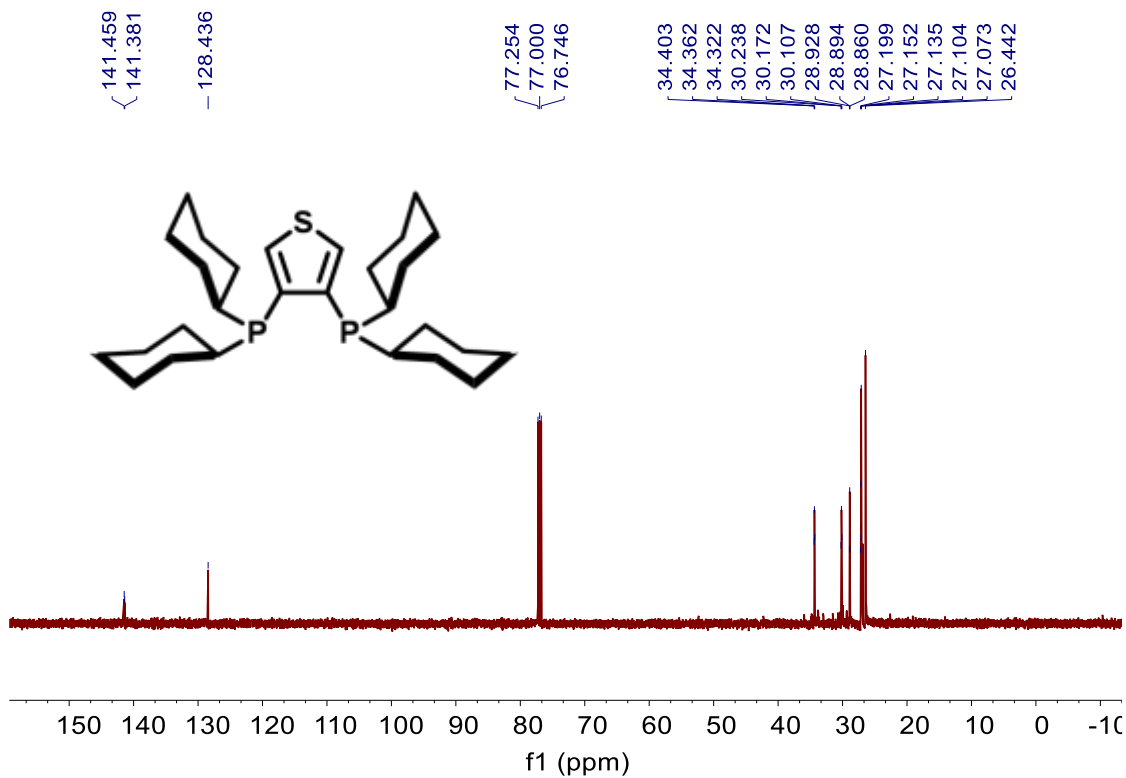
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H	3.260751	-4.491106	-0.716676
H	4.711870	-4.763593	-1.680854
H	2.826110	-3.841573	-3.071295
H	4.213410	-2.753305	-3.055250
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H	-2.698811	3.316282	-2.192878
H	-1.335254	4.200926	-1.513309
H	-4.211968	4.232134	-0.460424
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H	-1.774322	5.793272	0.548780
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H	-1.986267	4.444871	2.623967
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C	-4.468601	-1.058566	2.151313
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C	-0.809816	-1.876275	1.420853
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H	-2.873169	0.044063	1.205735
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S	-1.282296	-4.234759	2.591248

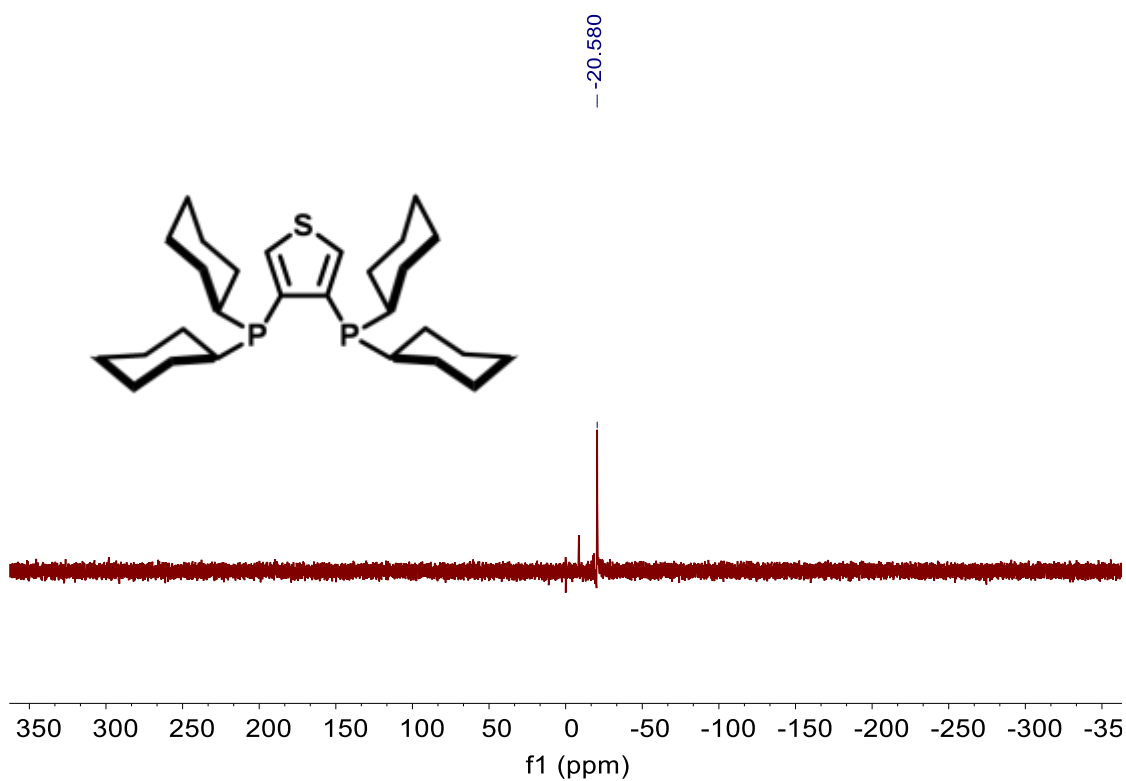
X. NMR, FT-IR Spectra and GPC Traces



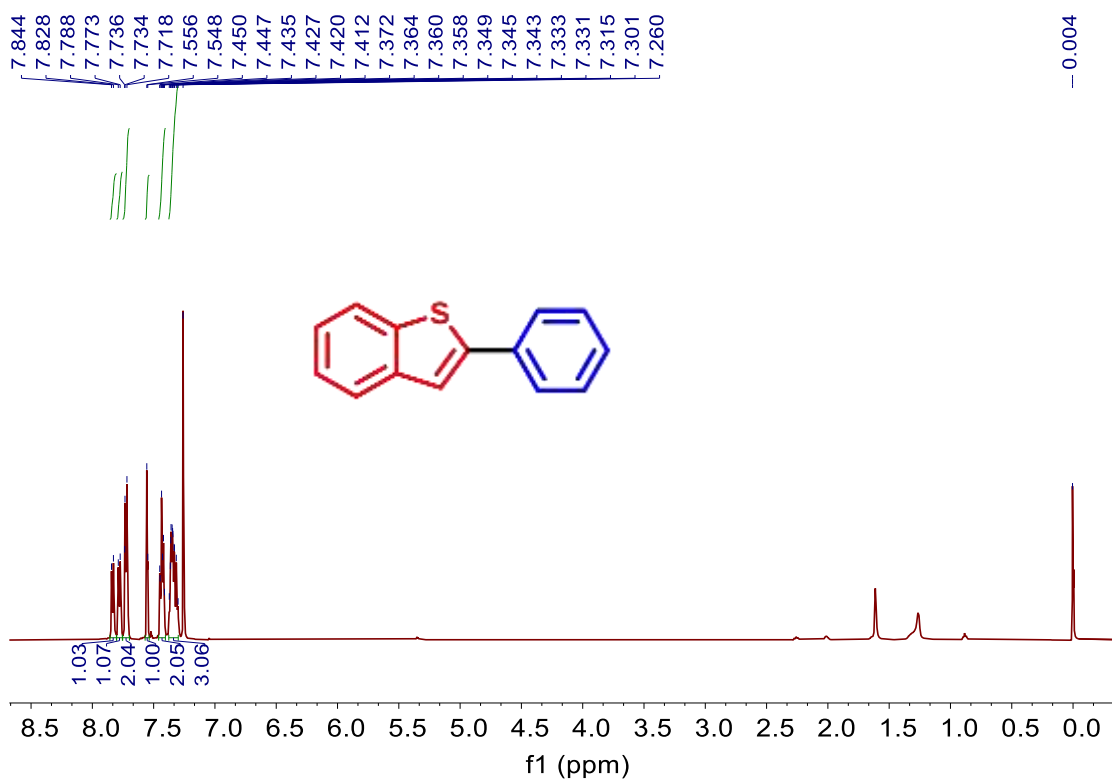
Supplementary Fig. 31. ¹H NMR (500 MHz) spectra of **dcypt** in CDCl₃ at 298 K.



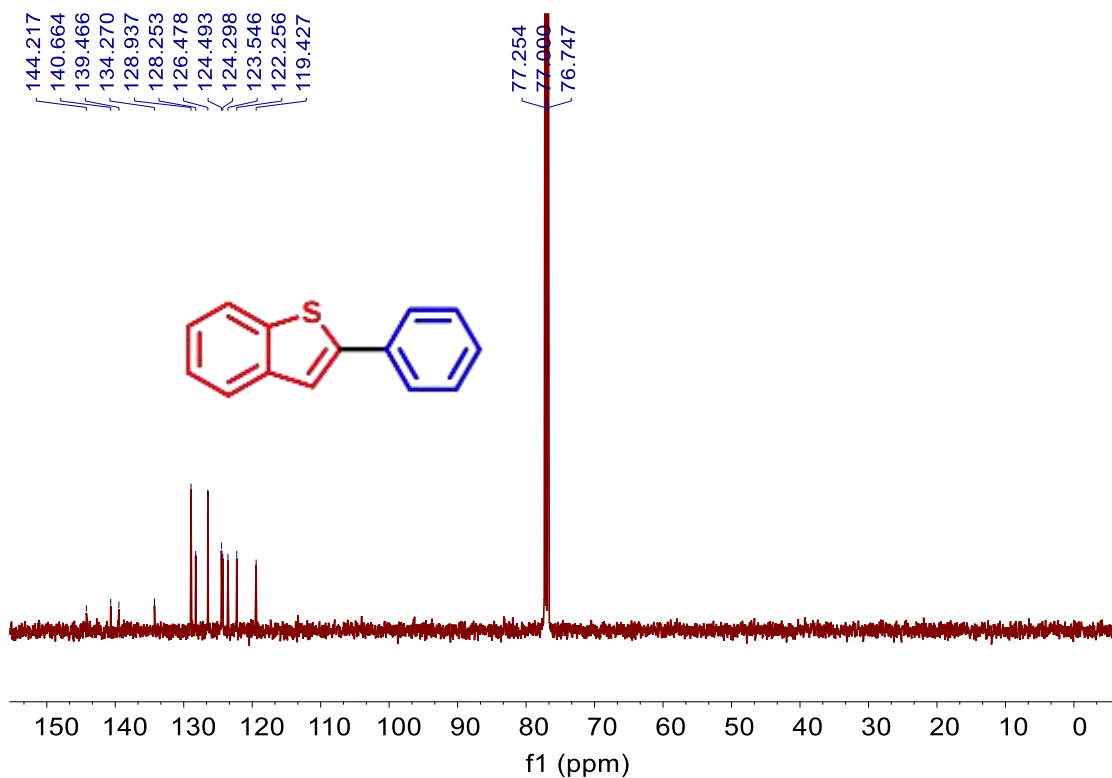
Supplementary Fig. 32. ¹³C NMR (125 MHz) spectra of **dcypt** in CDCl₃ at 298 K.



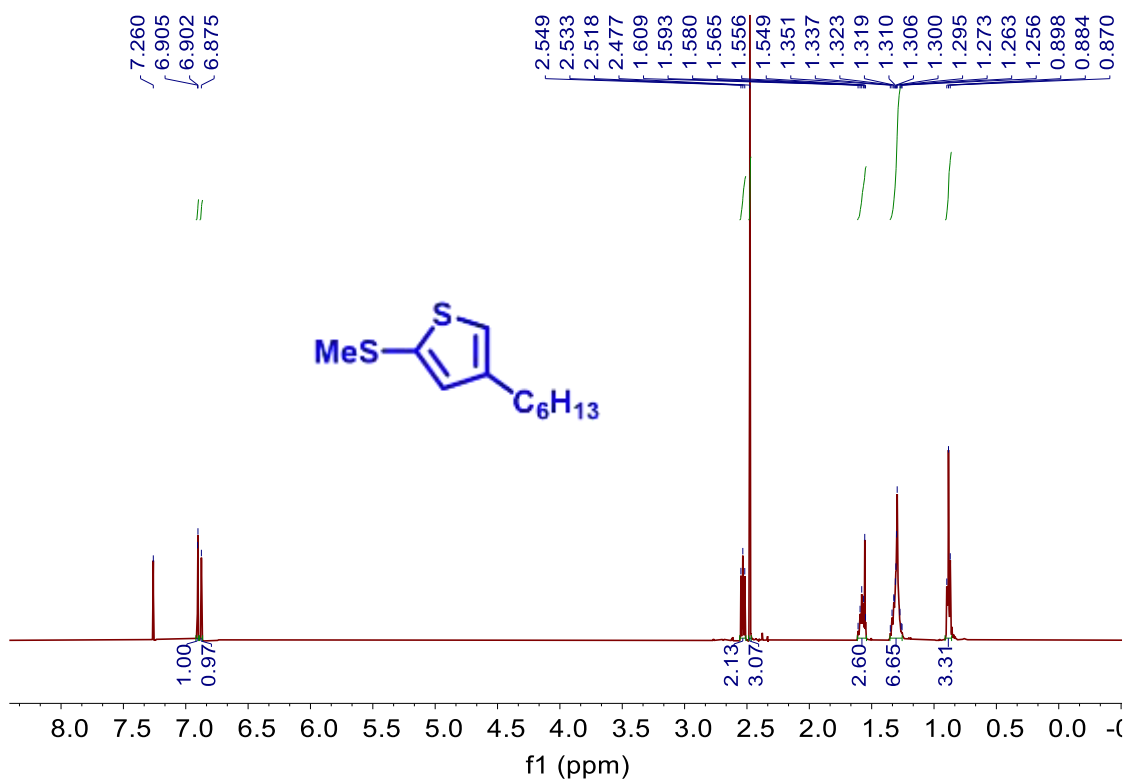
Supplementary Fig. 33. ^{31}P NMR (202 MHz) spectra of **dcypt** in CDCl_3 at 298 K.



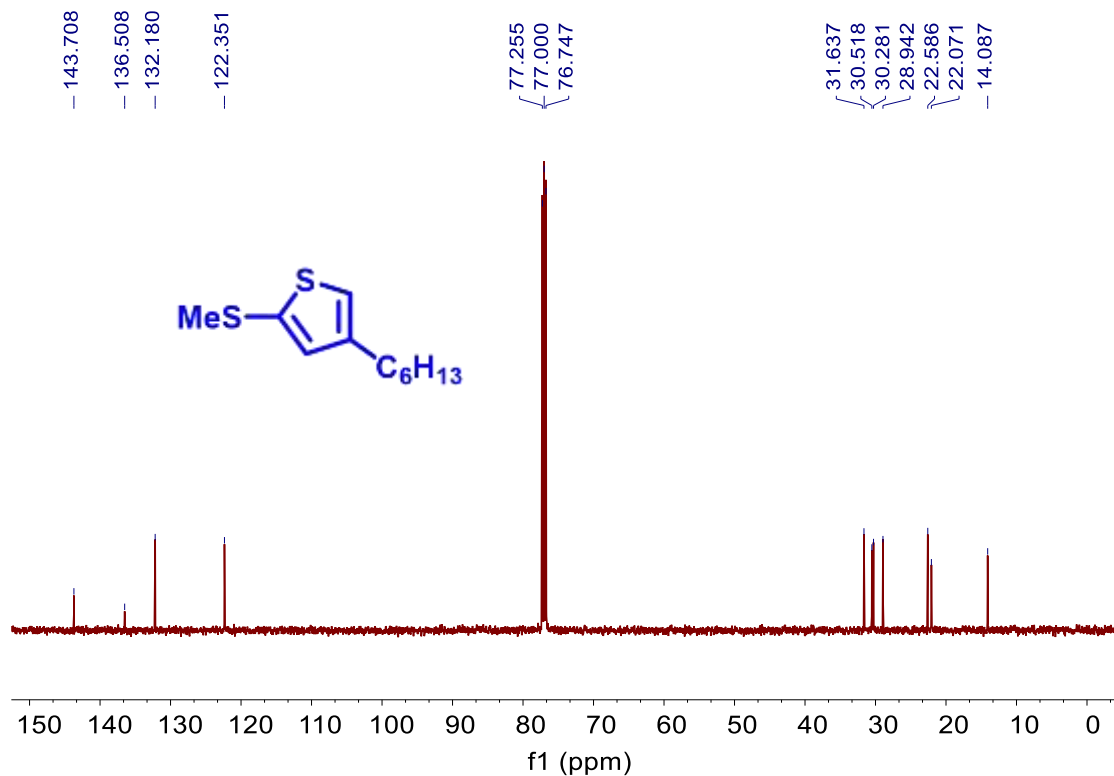
Supplementary Fig. 34. ^1H NMR (500 MHz) spectra of **3b** in CDCl_3 at 298 K.



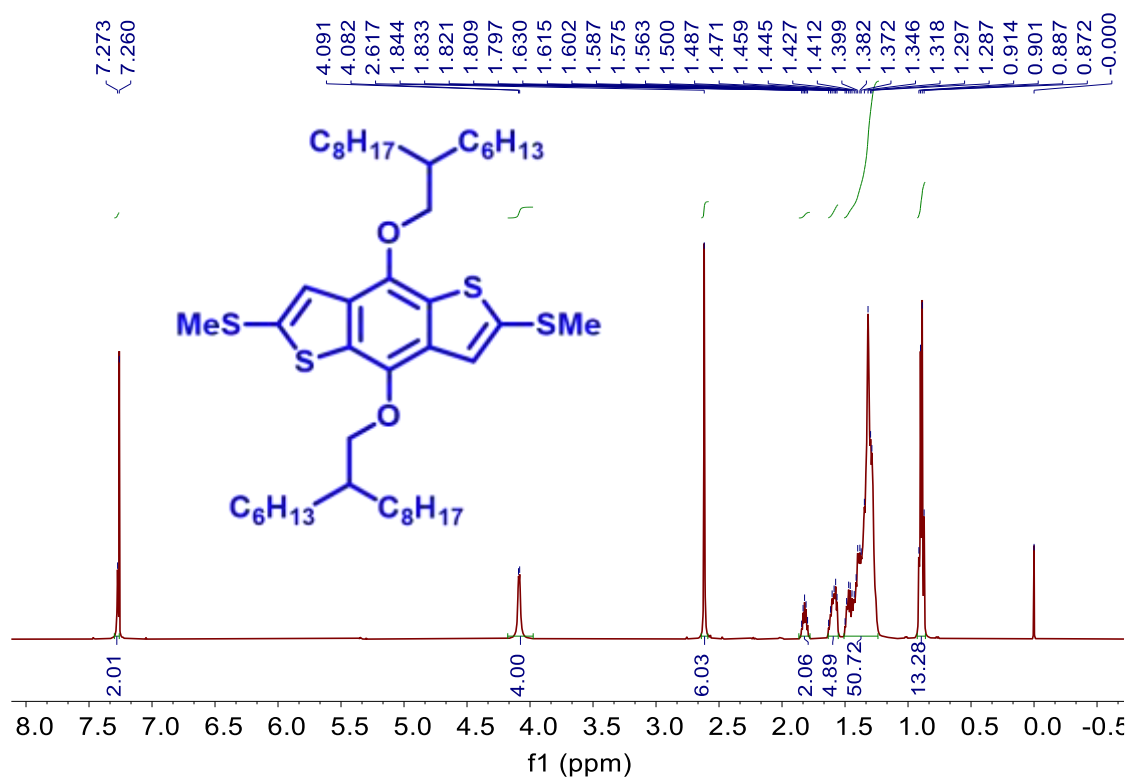
Supplementary Fig. 35. ¹³C NMR (125 MHz) spectra of **3b** in CDCl₃ at 298 K.



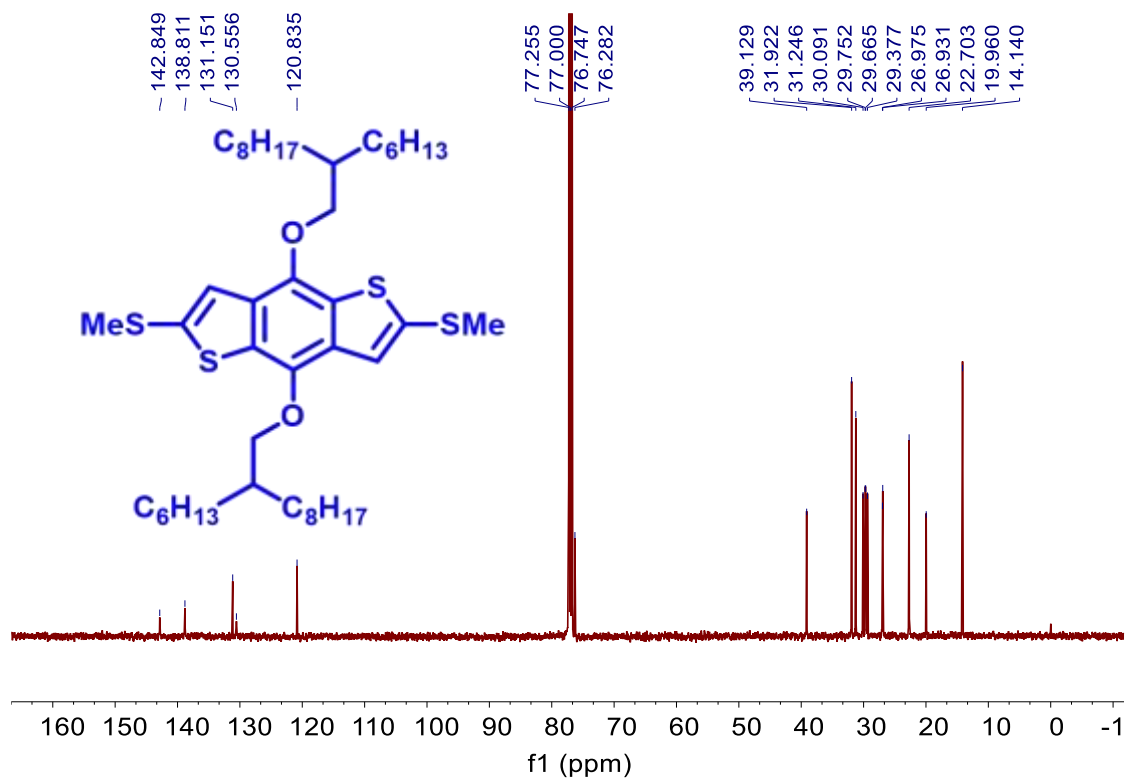
Supplementary Fig. 36. ¹H NMR (500 MHz) spectra of **1a** in CDCl₃ at 298 K.



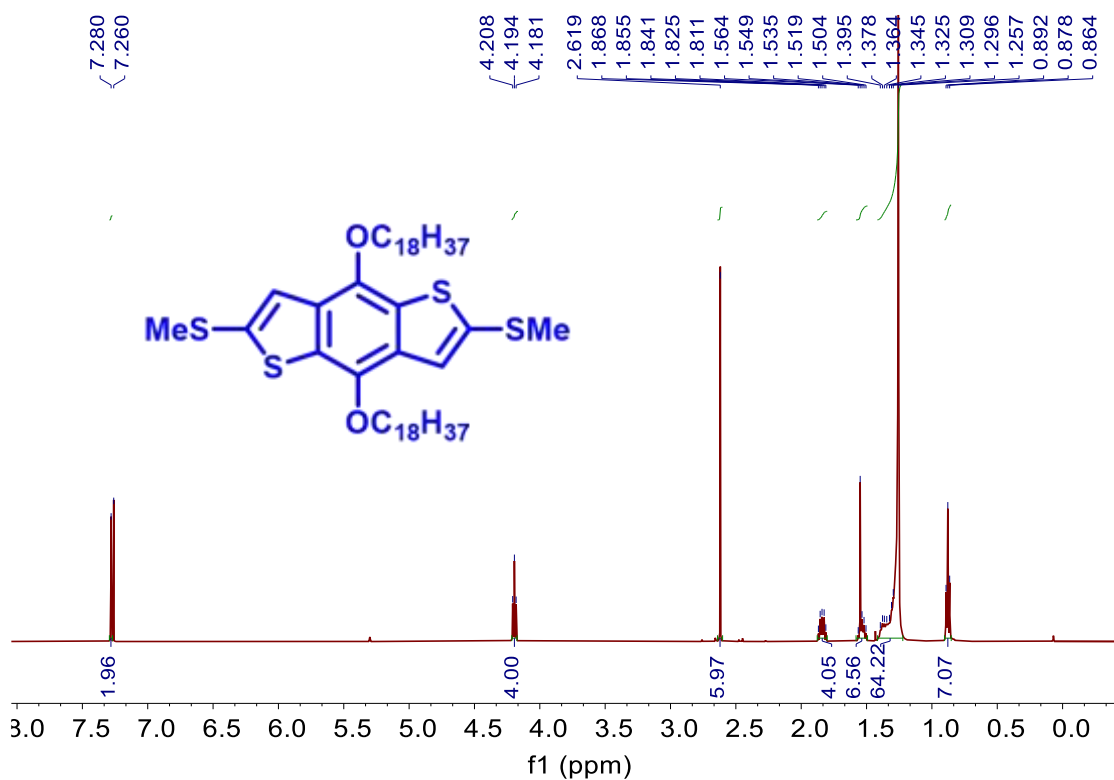
Supplementary Fig. 37. ¹³C NMR (125 MHz) spectra of **1a** in CDCl₃ at 298 K.



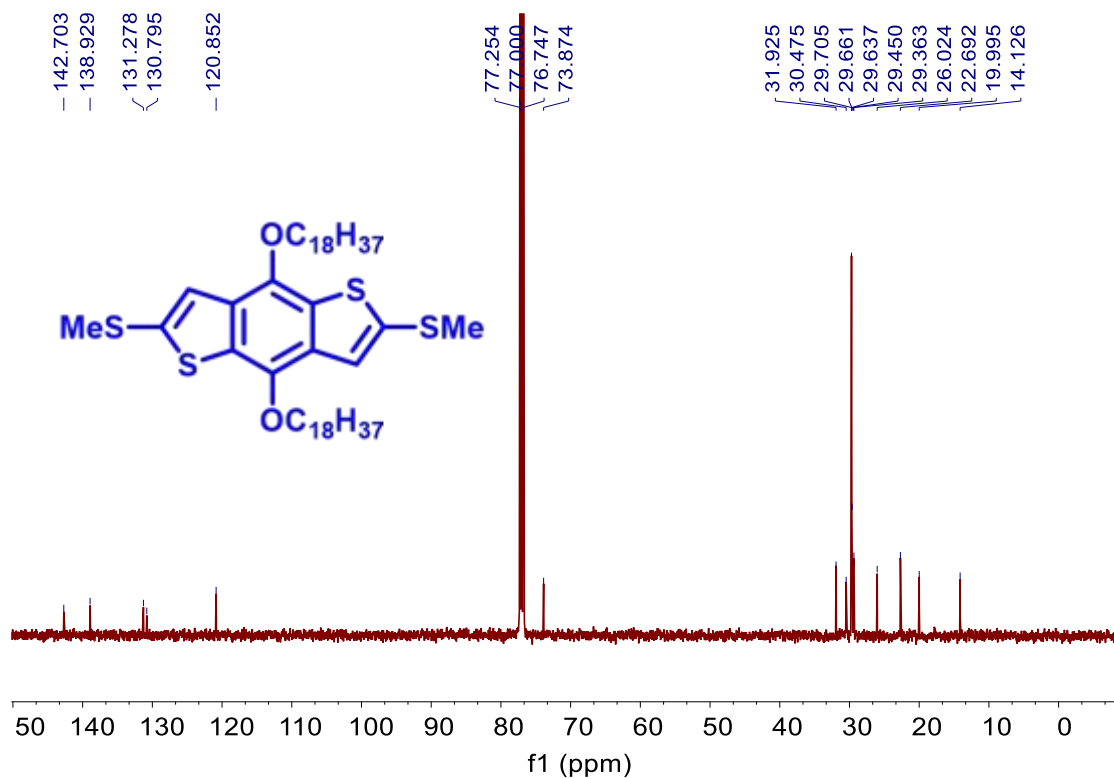
Supplementary Fig. 38. ¹H NMR (500 MHz) spectra of **E1** in CDCl₃ at 298 K.



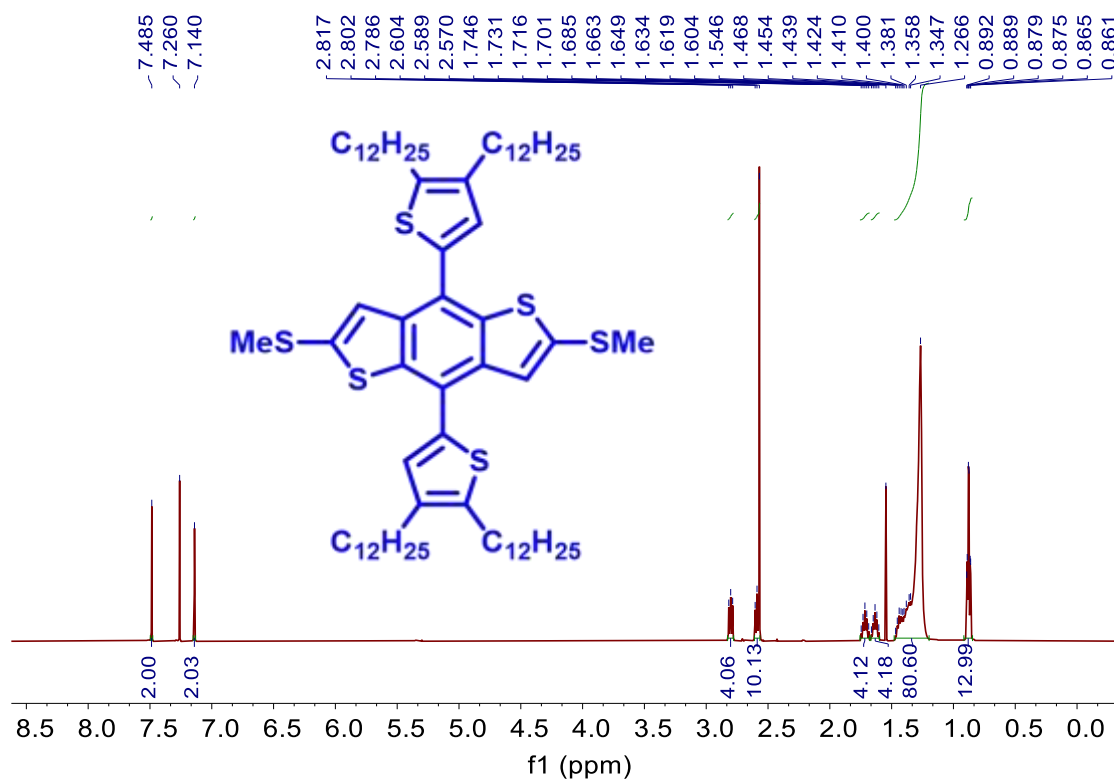
Supplementary Fig. 39. ¹³C NMR (125 MHz) spectra of **E1** in CDCl₃ at 298 K.



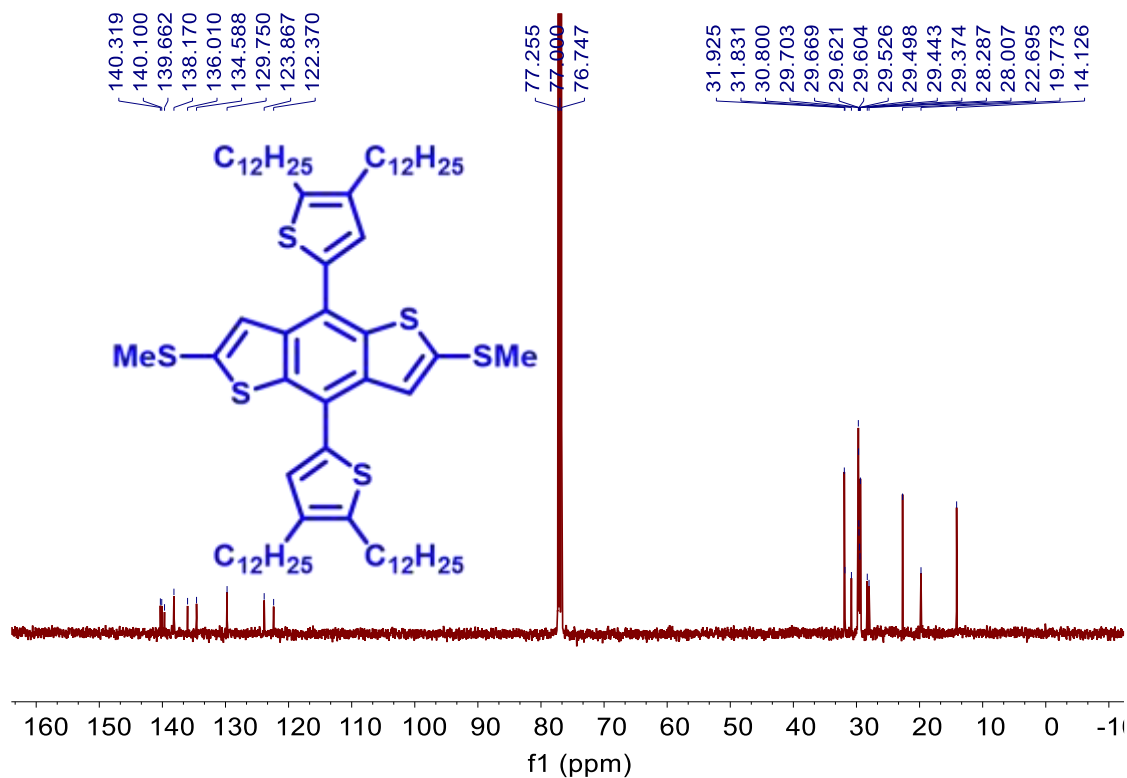
Supplementary Fig. 40. ¹H NMR (500 MHz) spectra of **E2** in CDCl₃ at 298 K.



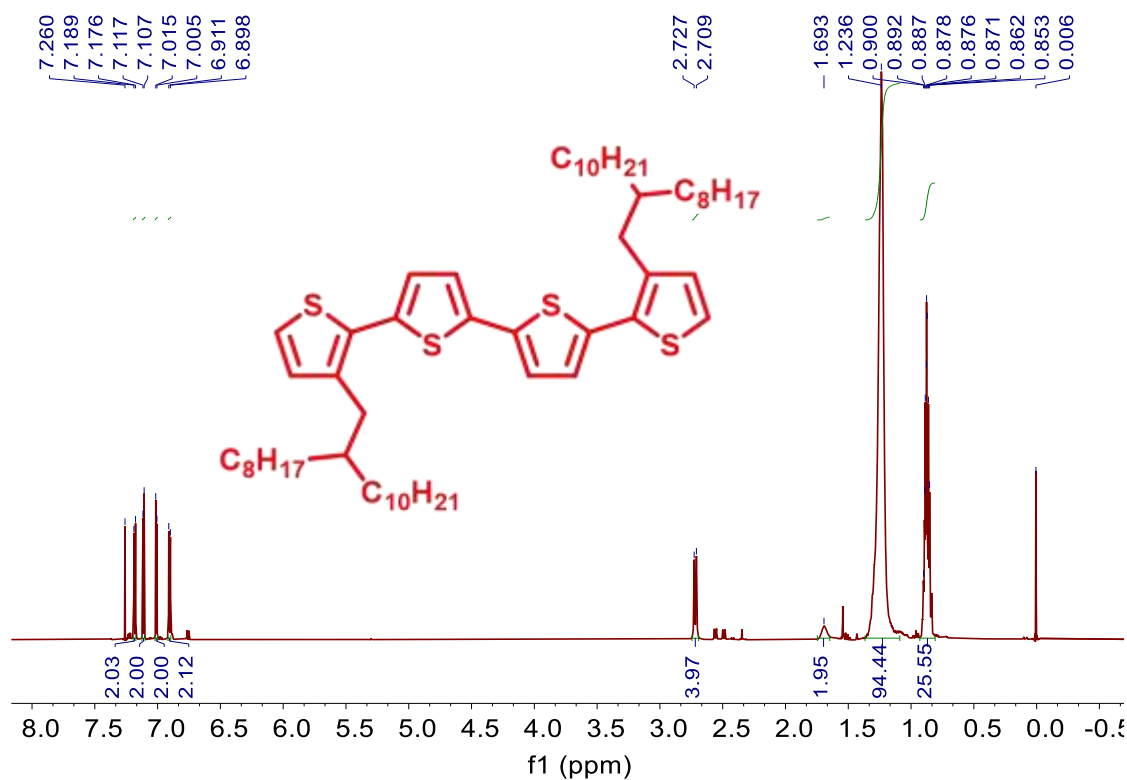
Supplementary Fig. 41. ¹³C NMR (125 MHz) spectra of **E2** in CDCl₃ at 298 K.



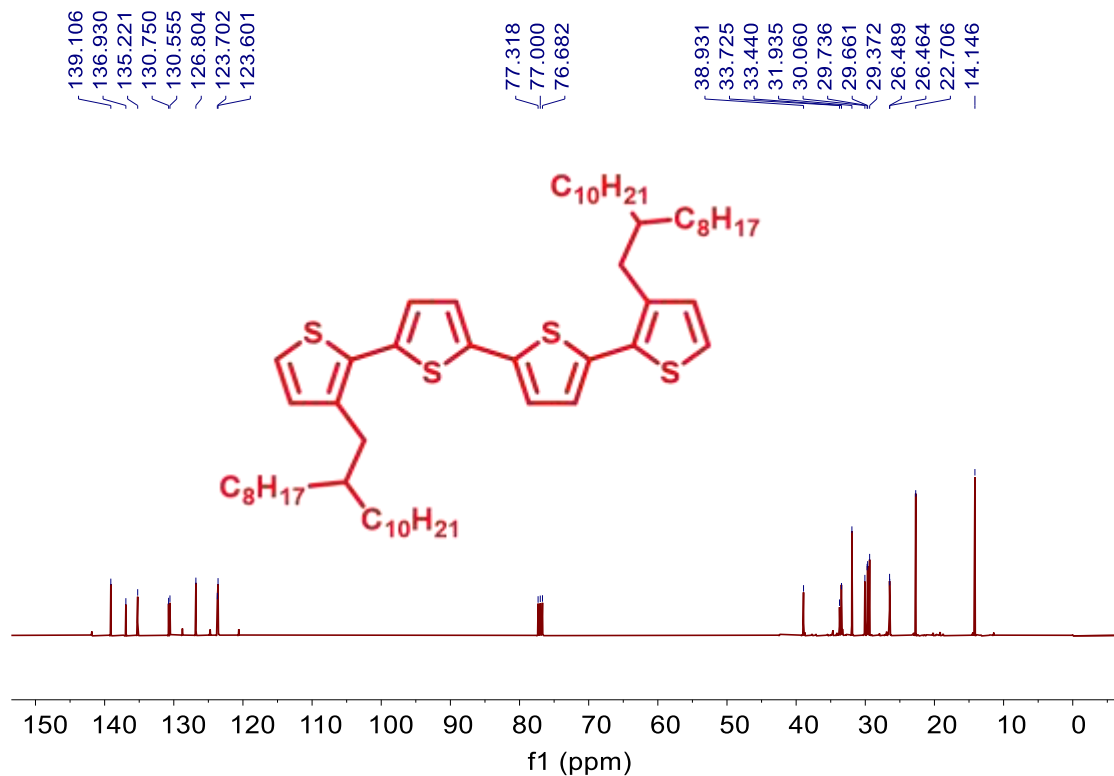
Supplementary Fig. 42. ¹H NMR (500 MHz) spectra of **E3** in CDCl₃ at 298 K.



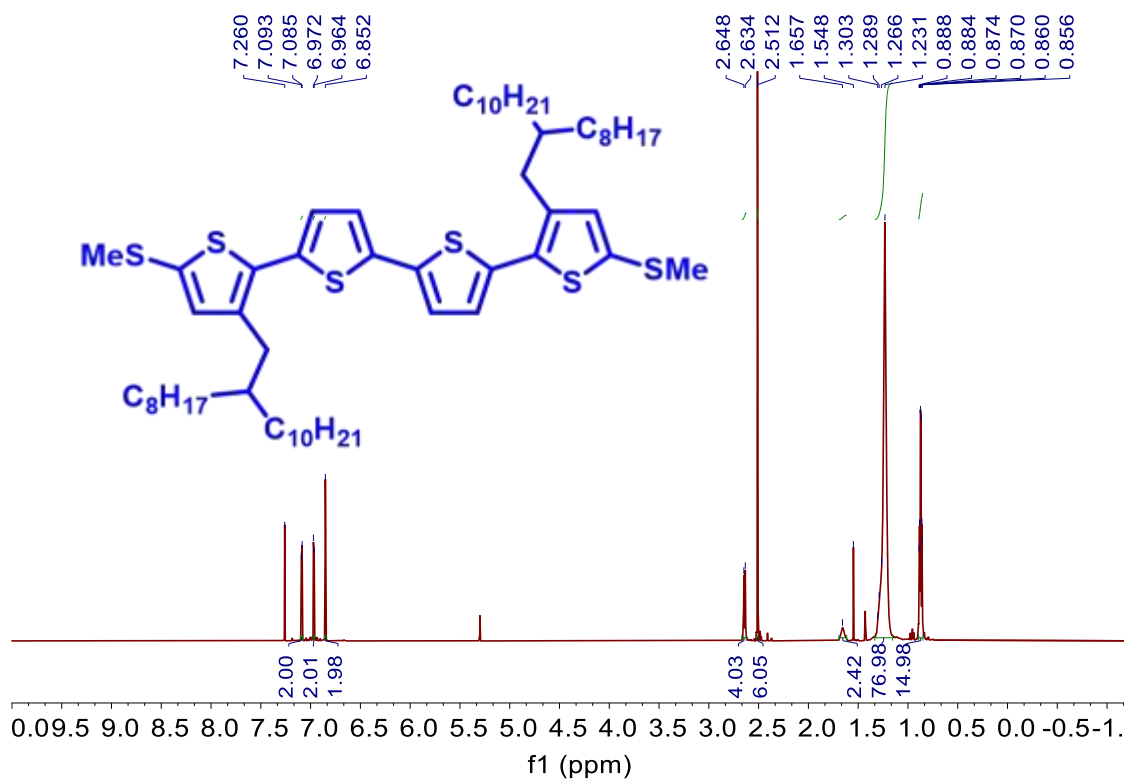
Supplementary Fig. 43. ^{13}C NMR (125 MHz) spectra of **E3** in CDCl_3 at 298 K.



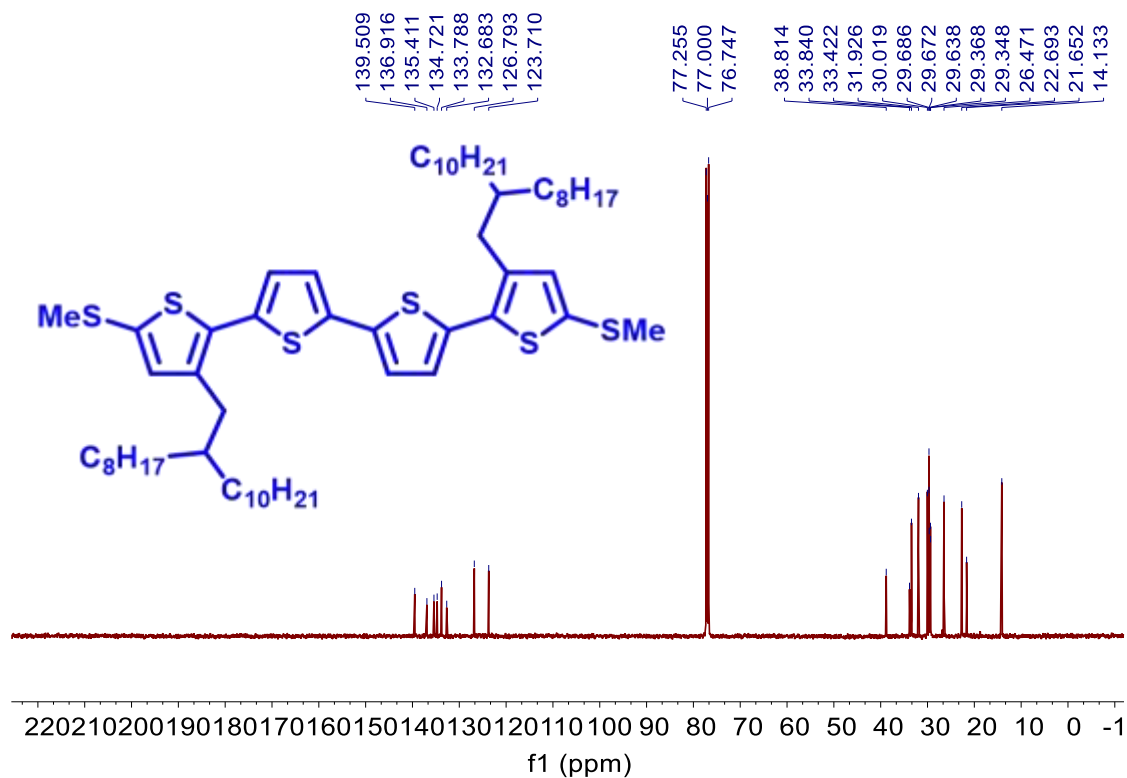
Supplementary Fig. 44. ^1H NMR (500 MHz) spectra of **3,3'''-bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene** in CDCl_3 at 298 K.



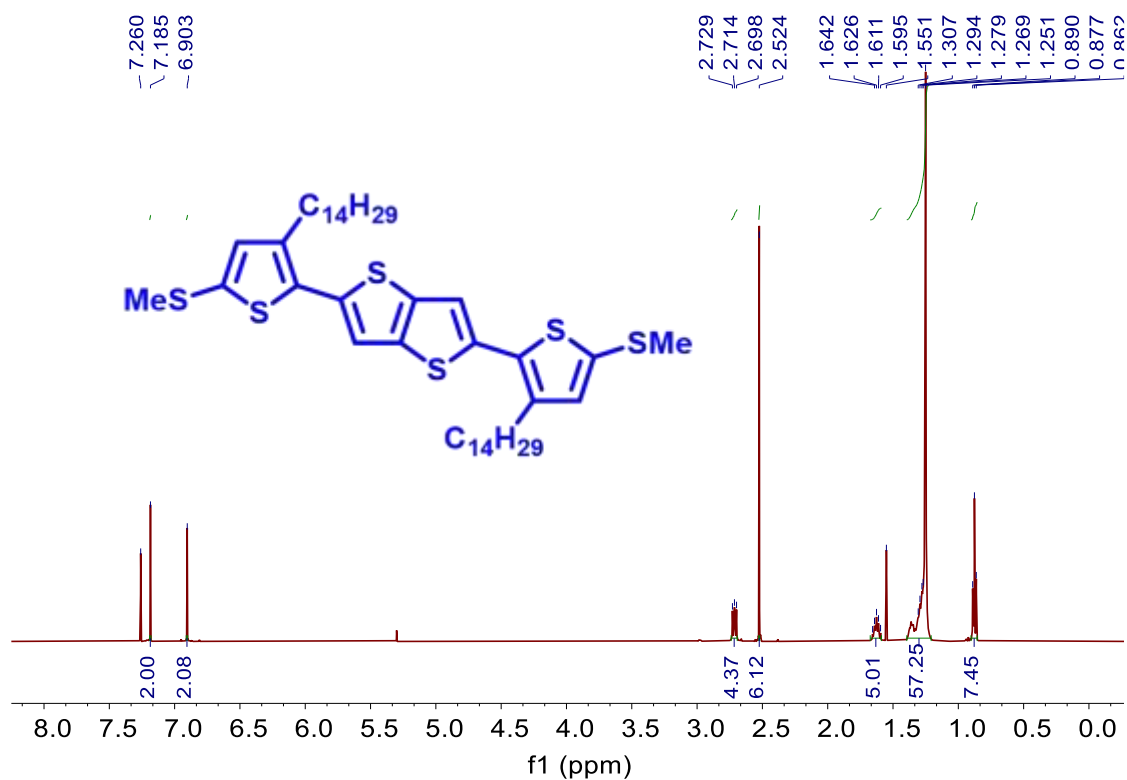
Supplementary Fig. 45. ¹³C NMR (125MHz) spectra of 3,3'''-bis(2-octyldodecyl)-2,2':5',2'':5'',2'''-quaterthiophene in CDCl₃ at 298 K.



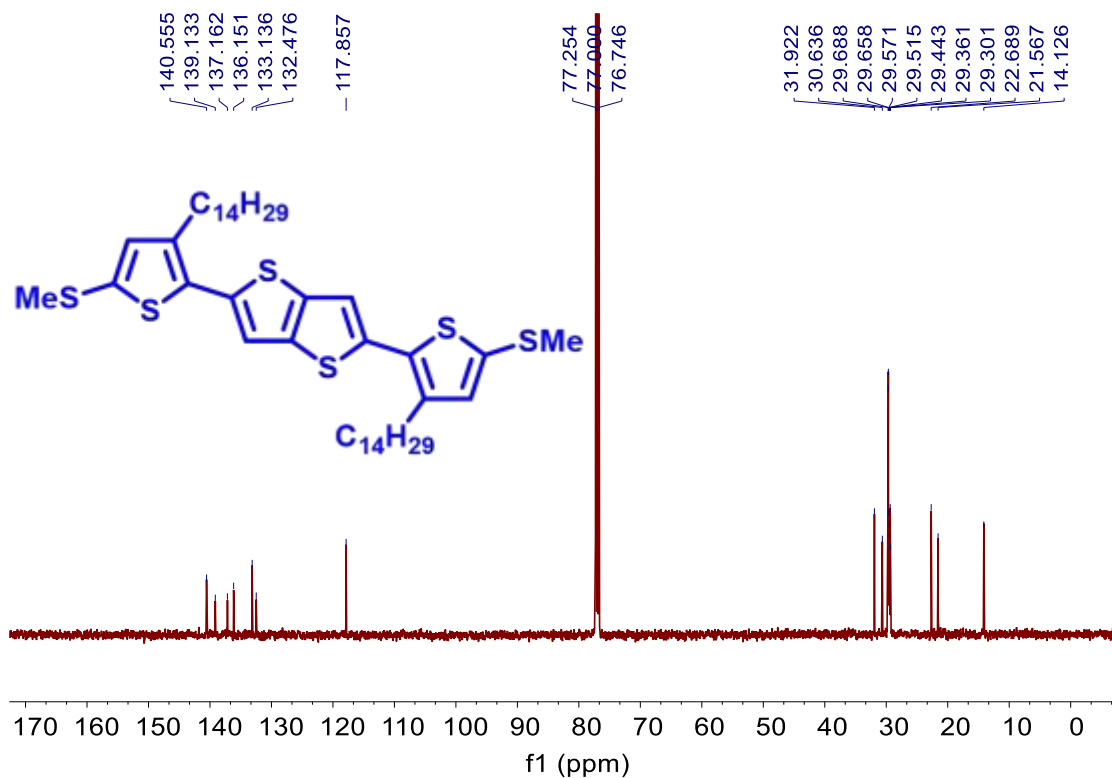
Supplementary Fig. 46. ¹H NMR (500 MHz) spectra of E4 in CDCl₃ at 298 K.



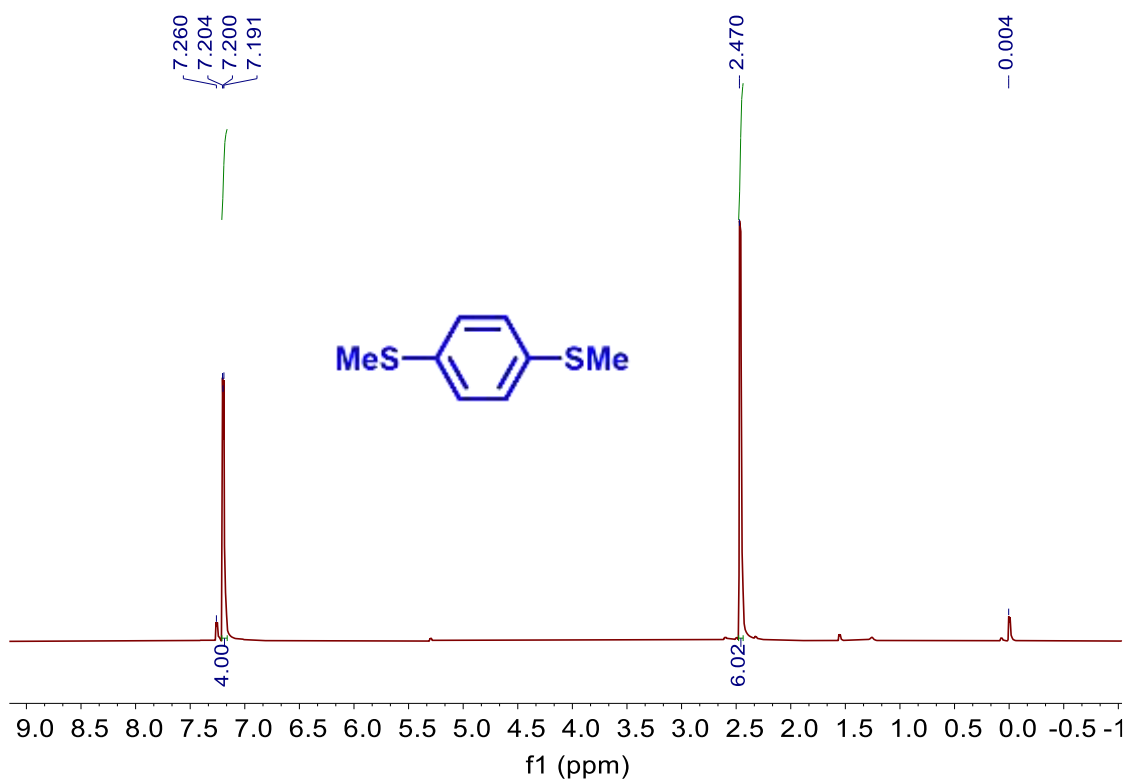
Supplementary Fig. 47. ^{13}C NMR (125 MHz) spectra of **E4** in CDCl_3 at 298 K.



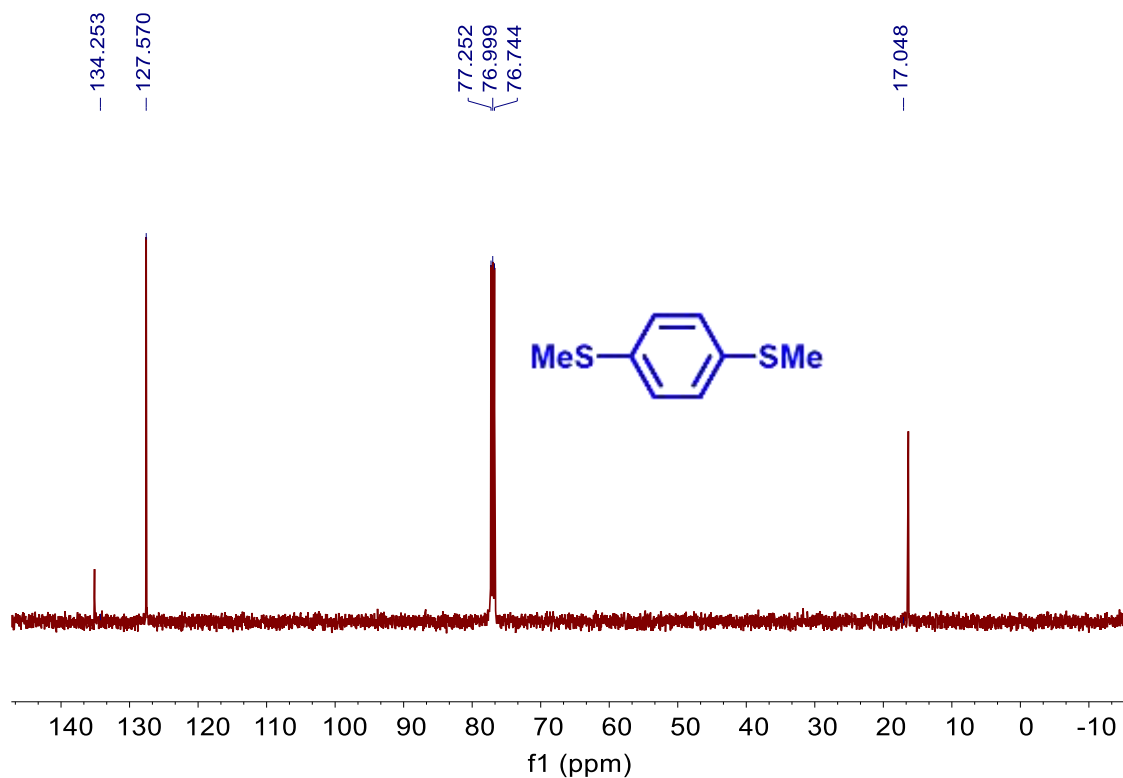
Supplementary Fig. 48. ^1H NMR (500 MHz) spectra of **E5** in CDCl_3 at 298 K.



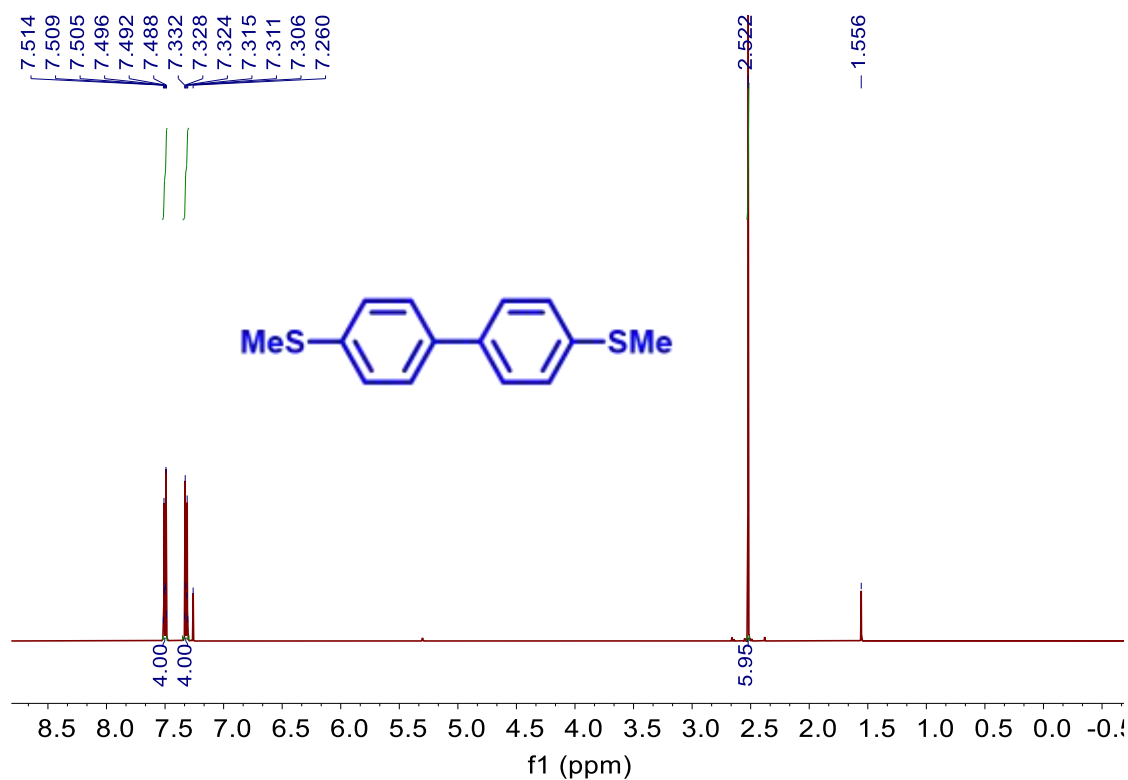
Supplementary Fig. 49. ¹³C NMR (125 MHz) spectra of **E5** in CDCl₃ at 298 K.



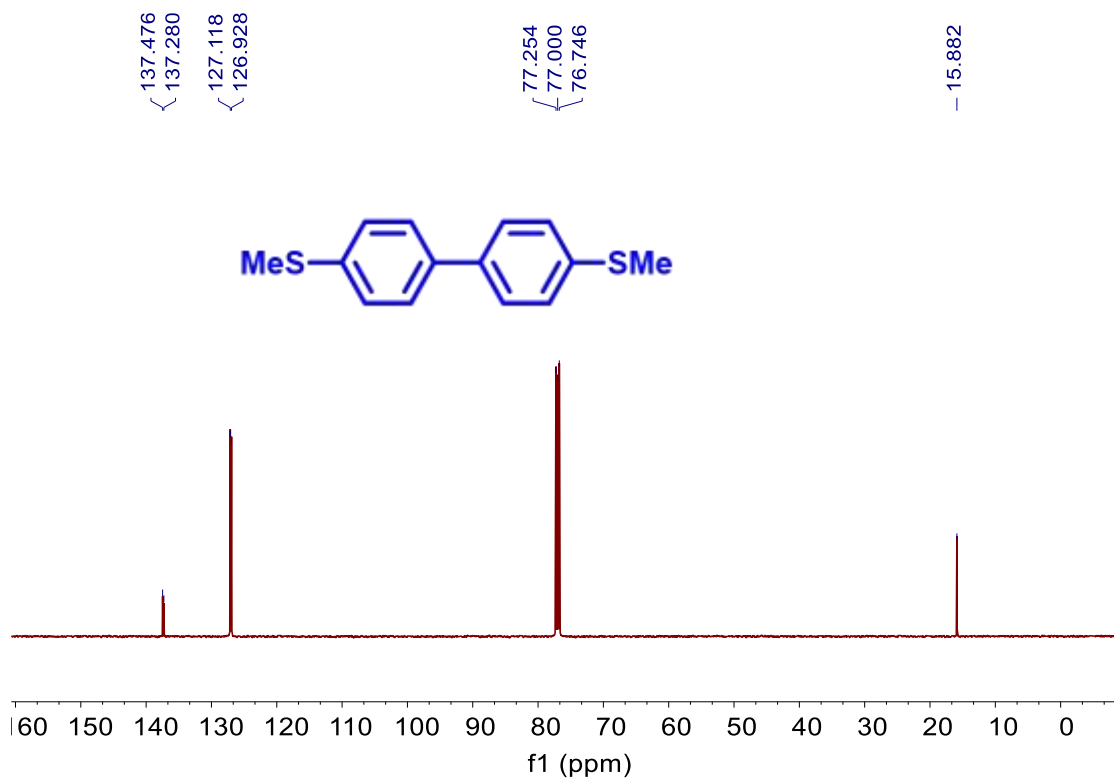
Supplementary Fig. 50. ¹H NMR (500 MHz) spectra of **E6** in CDCl₃ at 298 K.



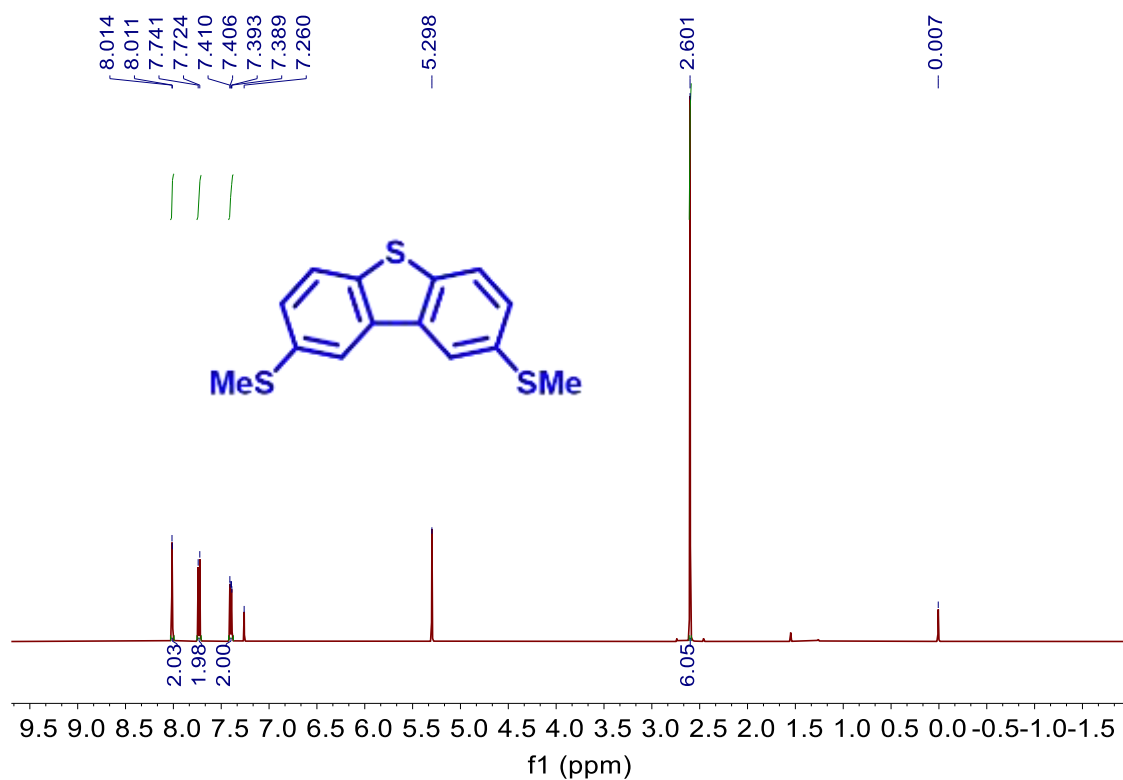
Supplementary Fig. 51. ¹³C NMR (125 MHz) spectra of **E6** in CDCl₃ at 298 K.



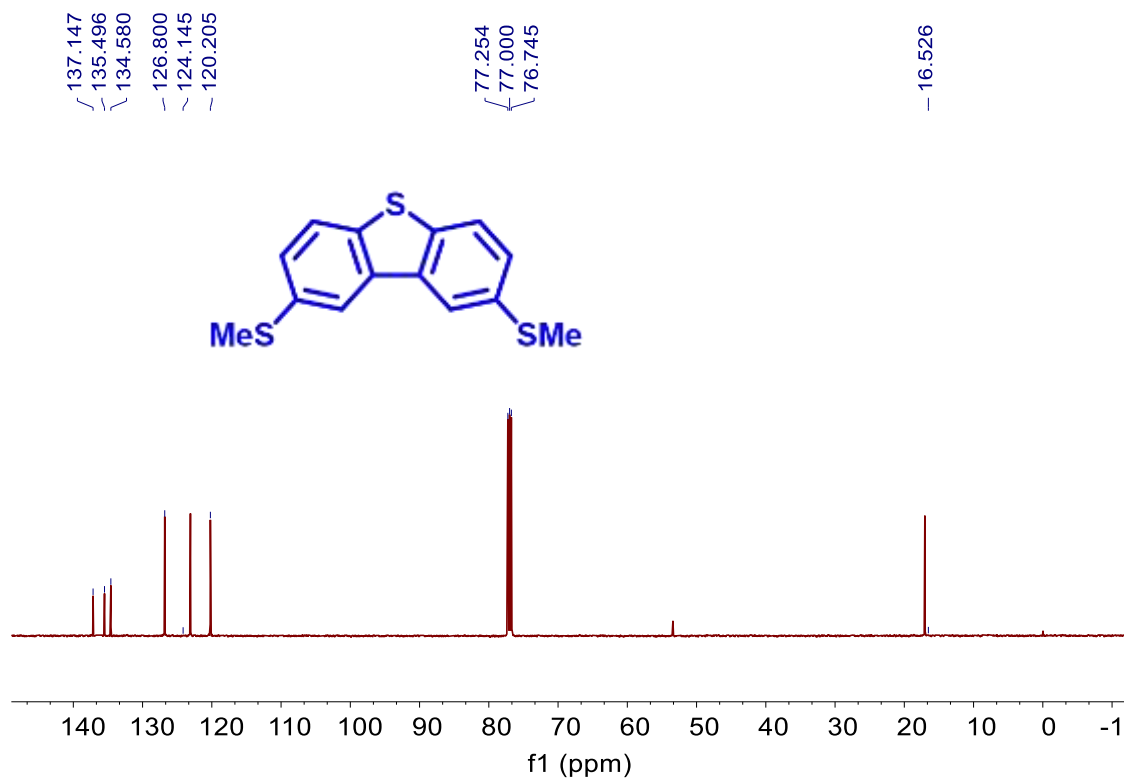
Supplementary Fig. 52. ¹H NMR (500 MHz) spectra of **E7** in CDCl₃ at 298 K.



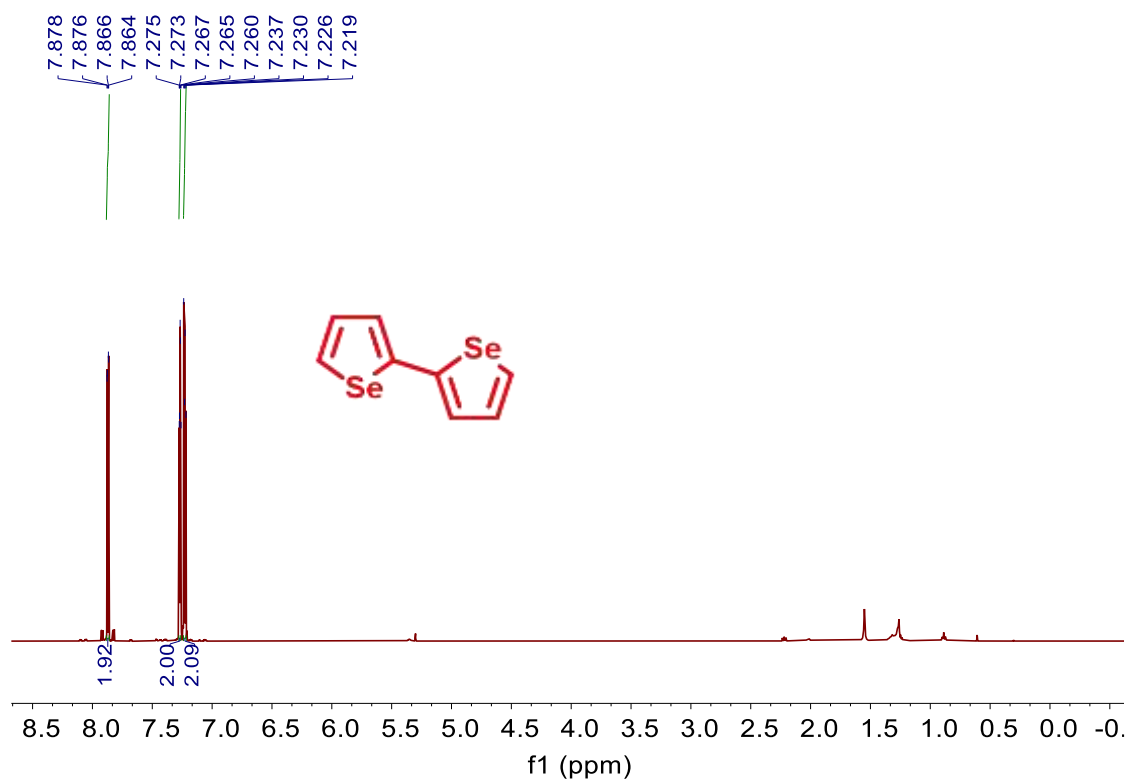
Supplementary Fig. 53. ^{13}C NMR (125 MHz) spectra of **E7** in CDCl_3 at 298 K.



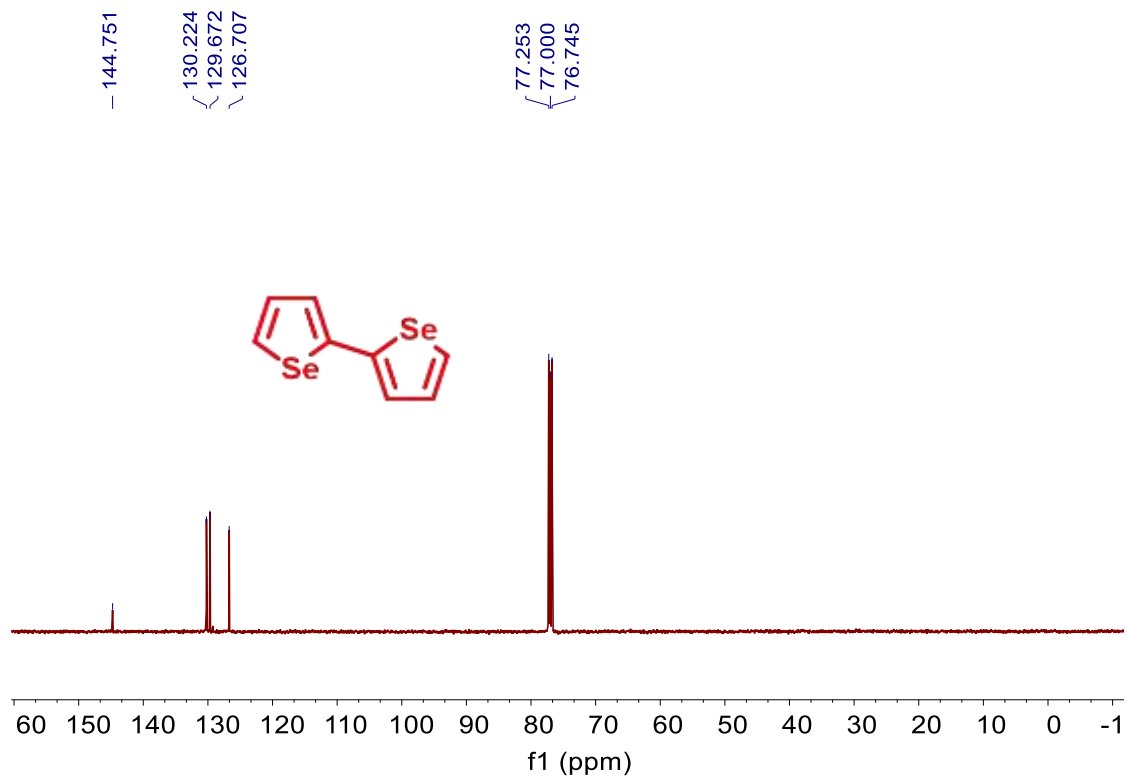
Supplementary Fig. 54. ^1H NMR (500 MHz) spectra of **E8** in CDCl_3 at 298 K.



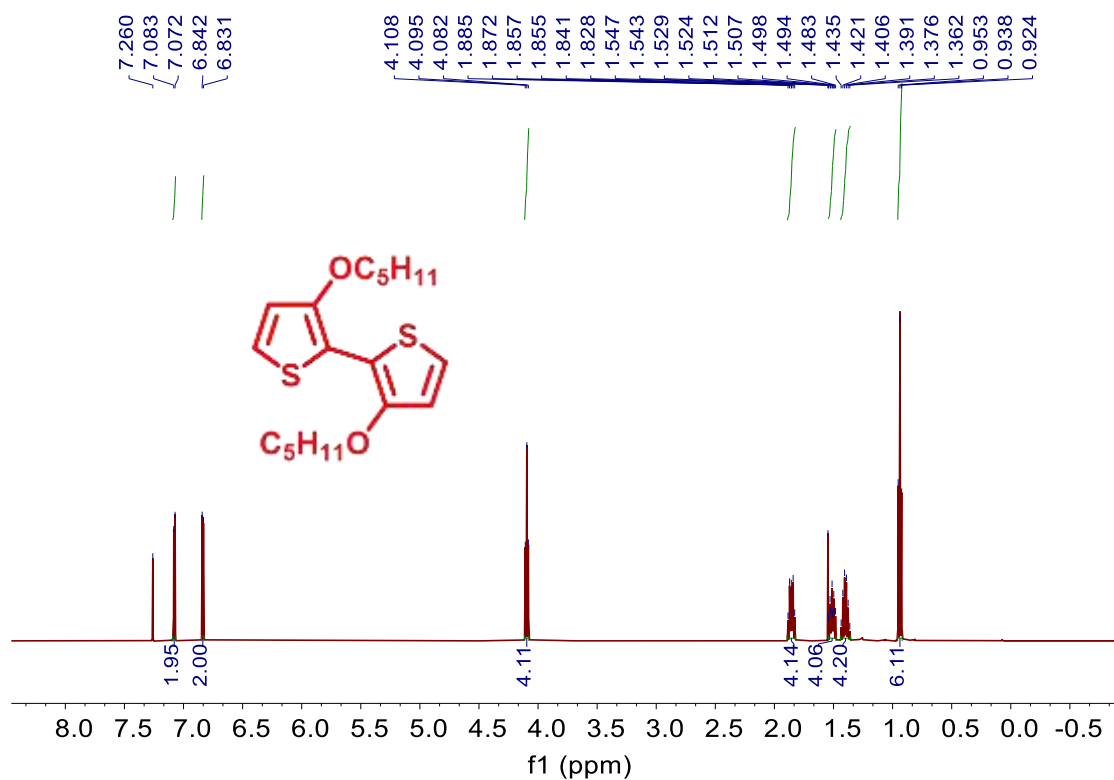
Supplementary Fig. 55. ¹³C NMR (125 MHz) spectra of **E8** in CDCl₃ at 298 K.



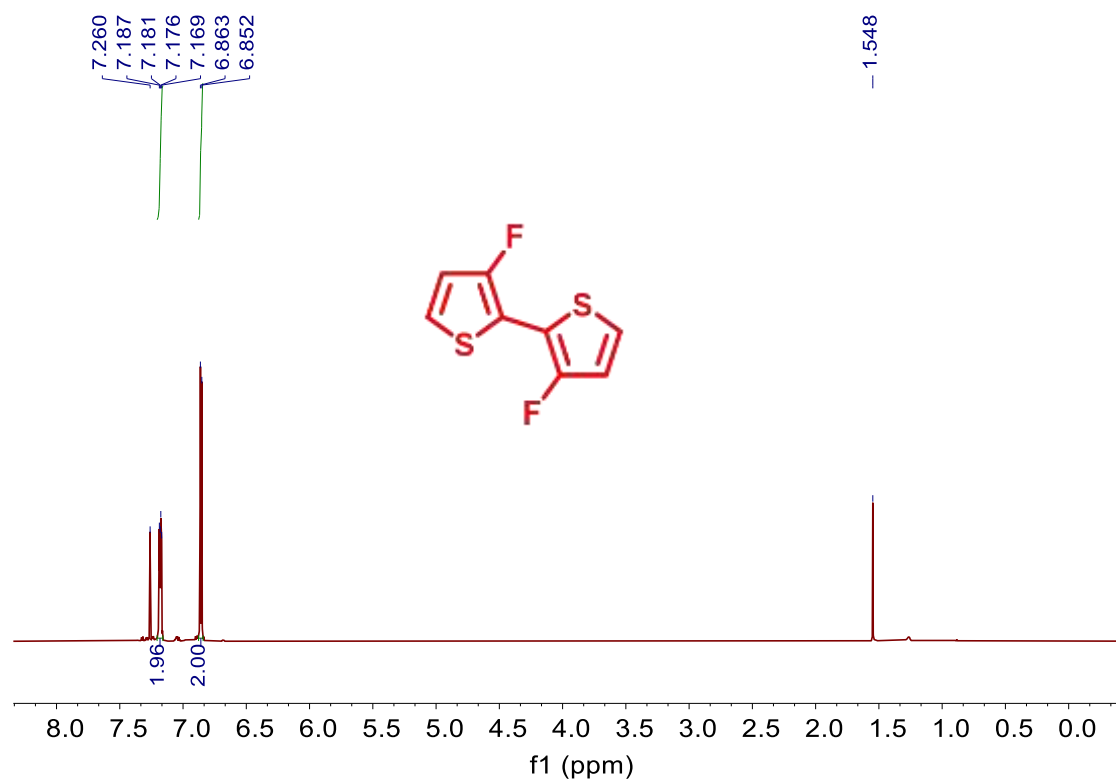
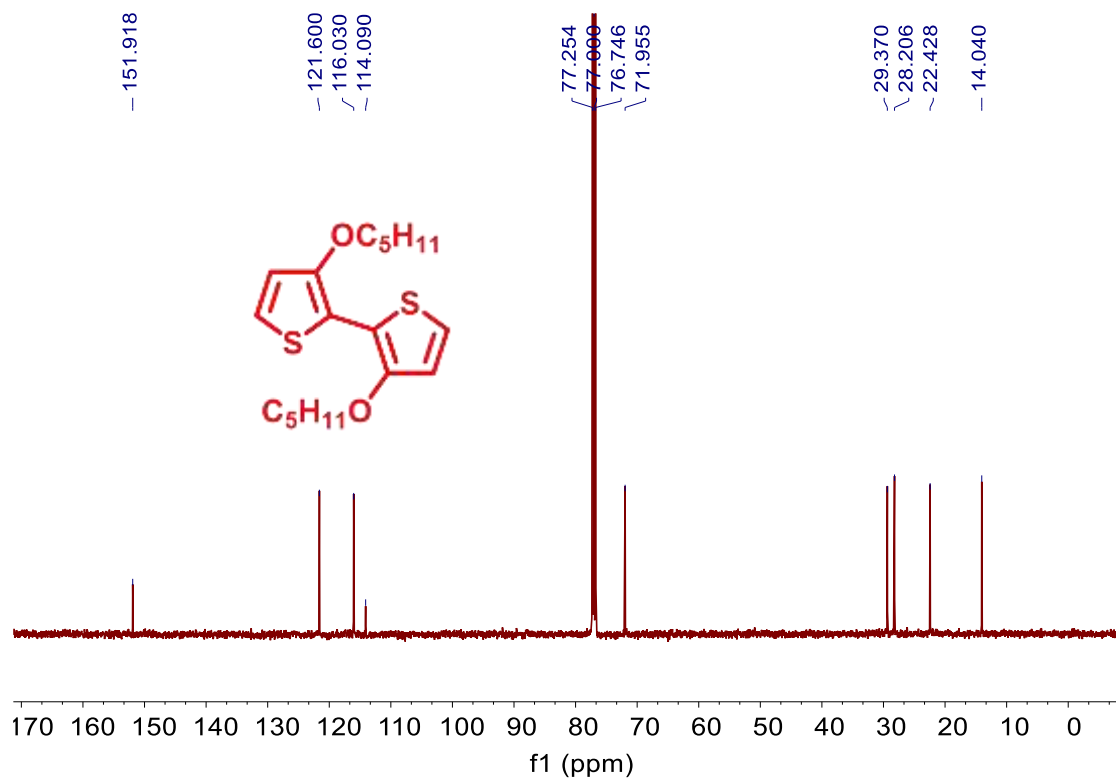
Supplementary Fig. 56. ¹H NMR (500 MHz) spectra of **N3** in CDCl₃ at 298 K.

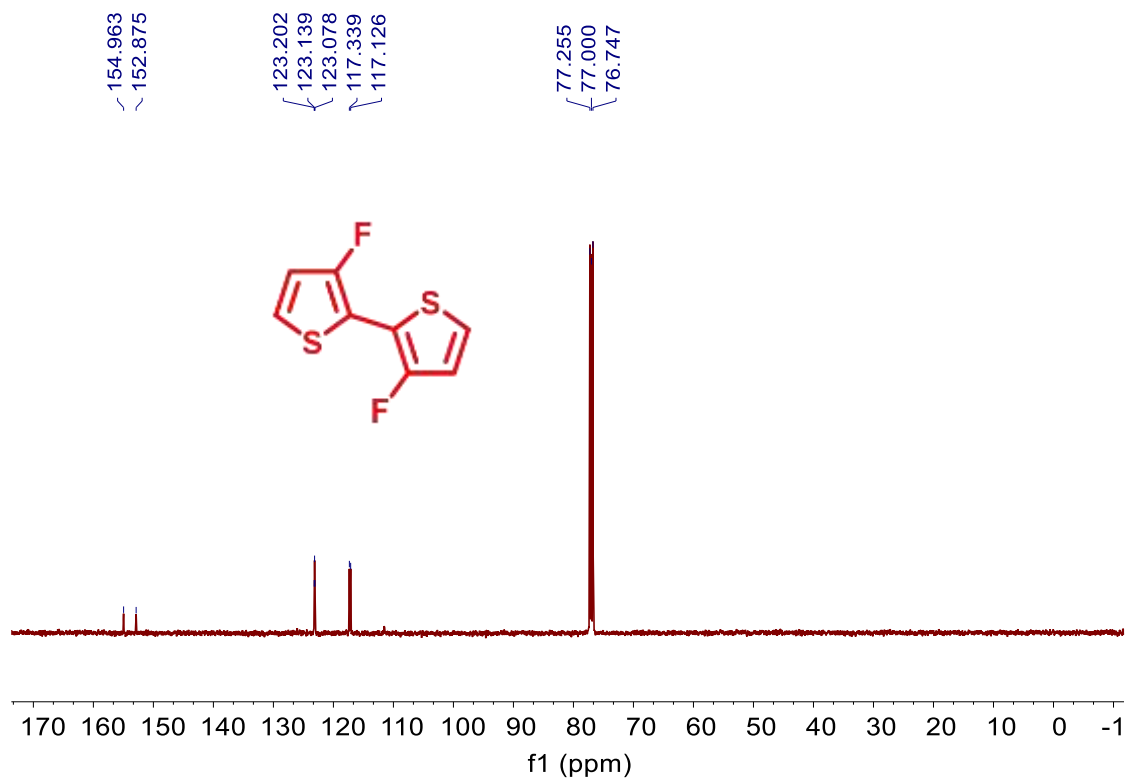


Supplementary Fig. 57. ¹³C NMR (125 MHz) spectra of **N3** in CDCl₃ at 298 K.

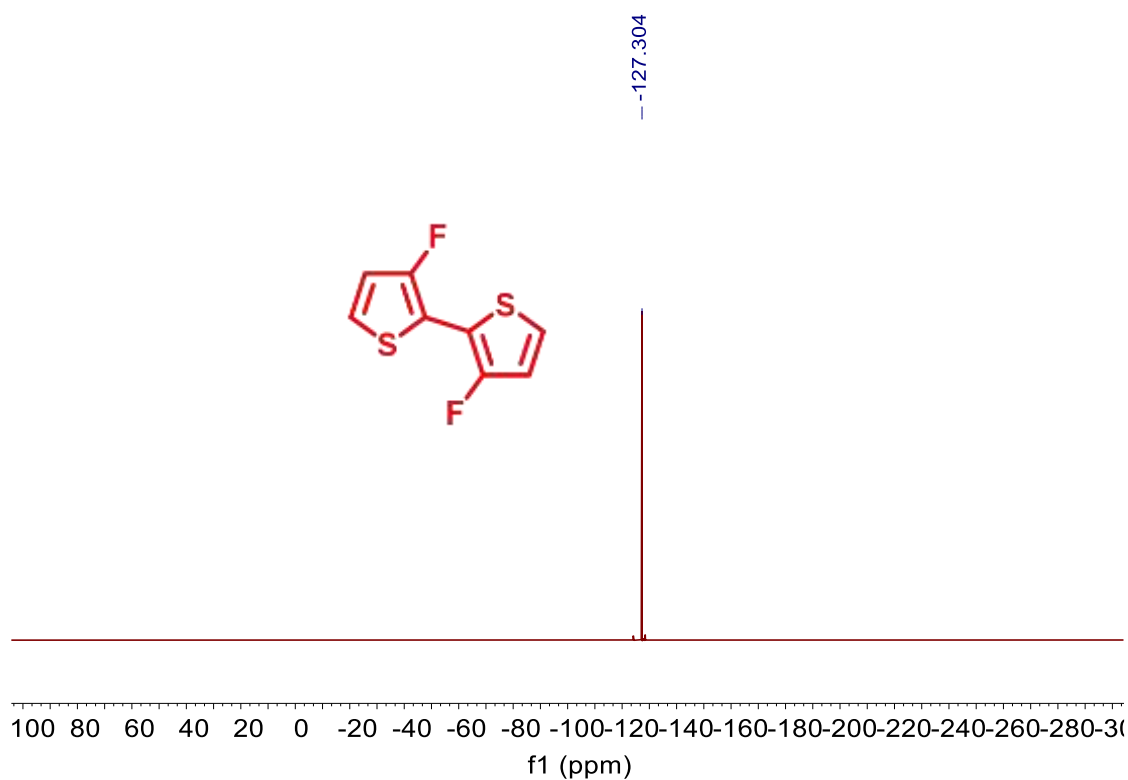


Supplementary Fig. 58. ¹H NMR (500 MHz) spectra of **N4** in CDCl₃ at 298 K.

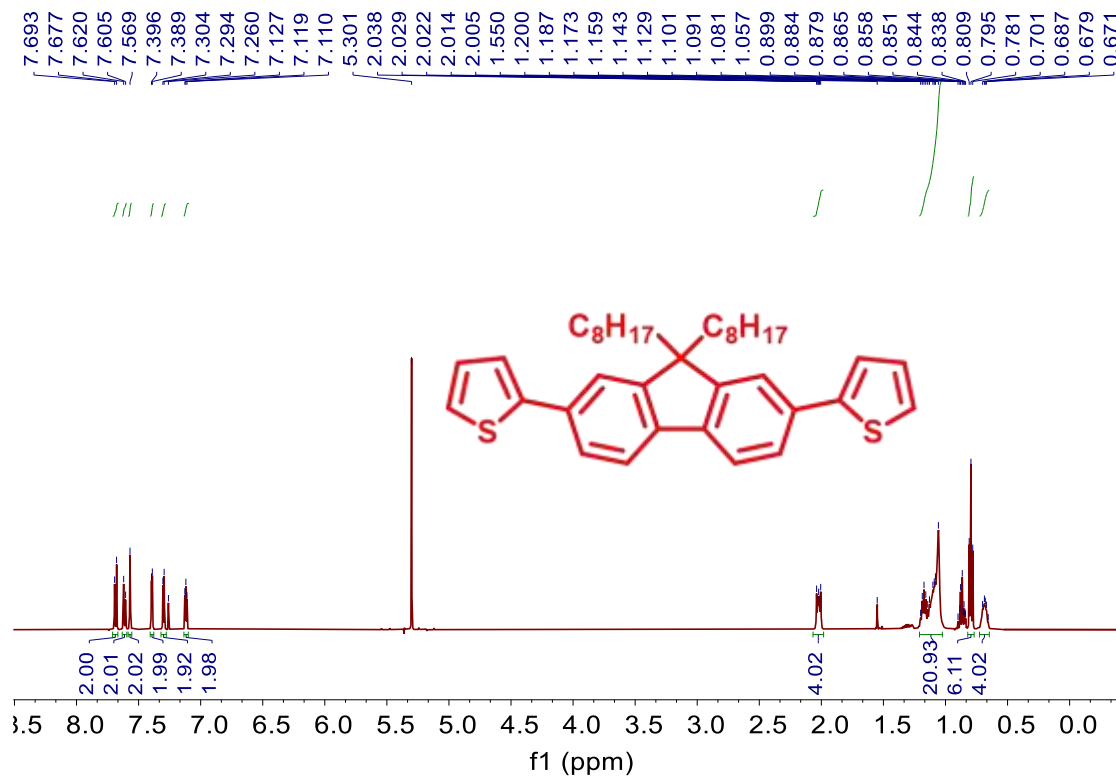




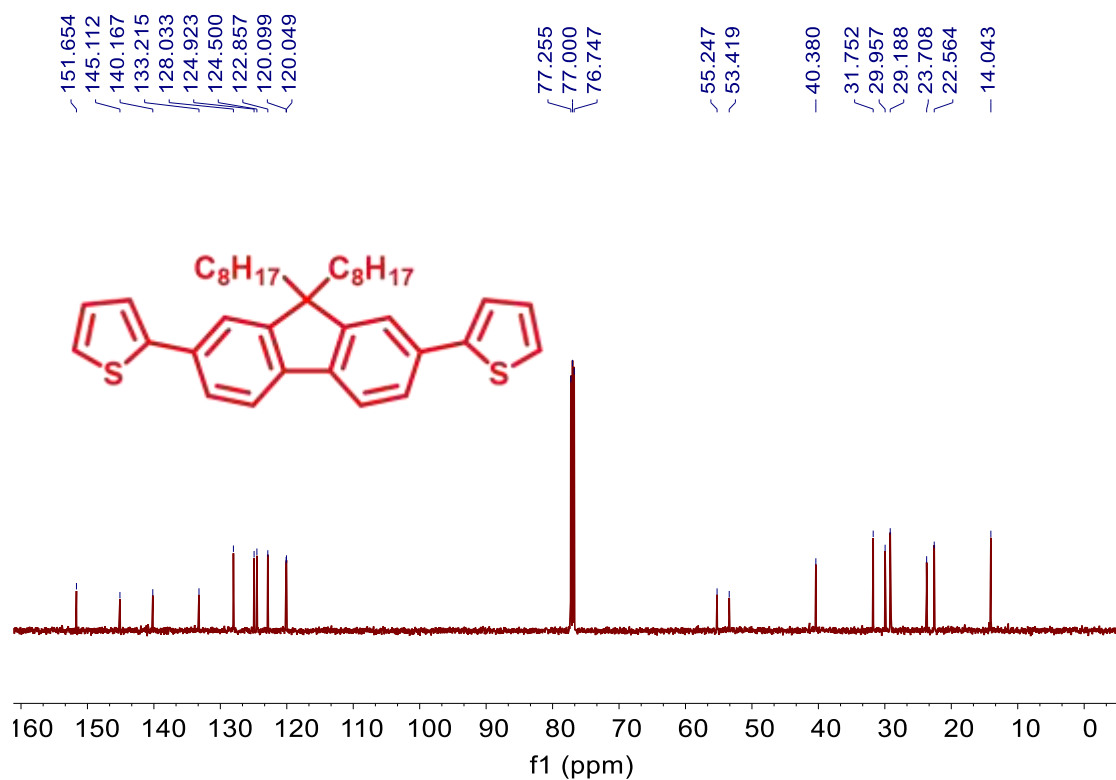
Supplementary Fig. 61. ¹³C NMR (125 MHz) spectra of **N6** in CDCl₃ at 298 K.



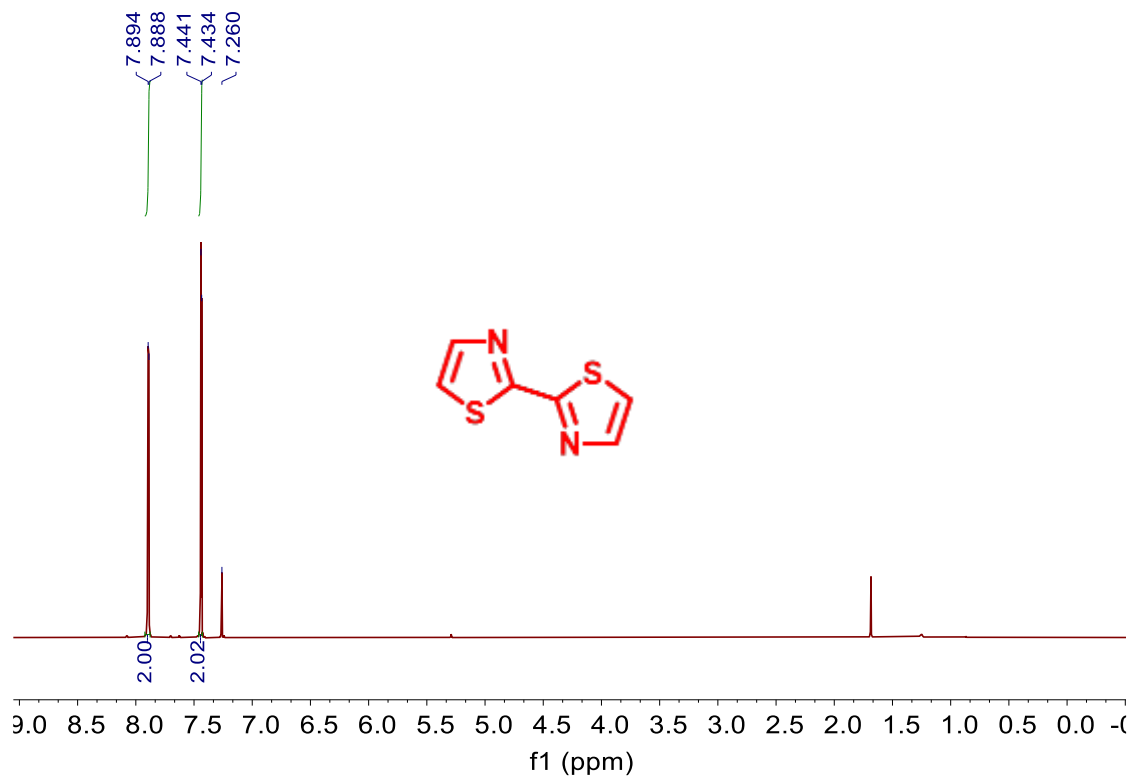
Supplementary Fig. 62. ¹⁹F NMR (470 MHz) spectra of **N6** in CDCl₃ at 298 K.



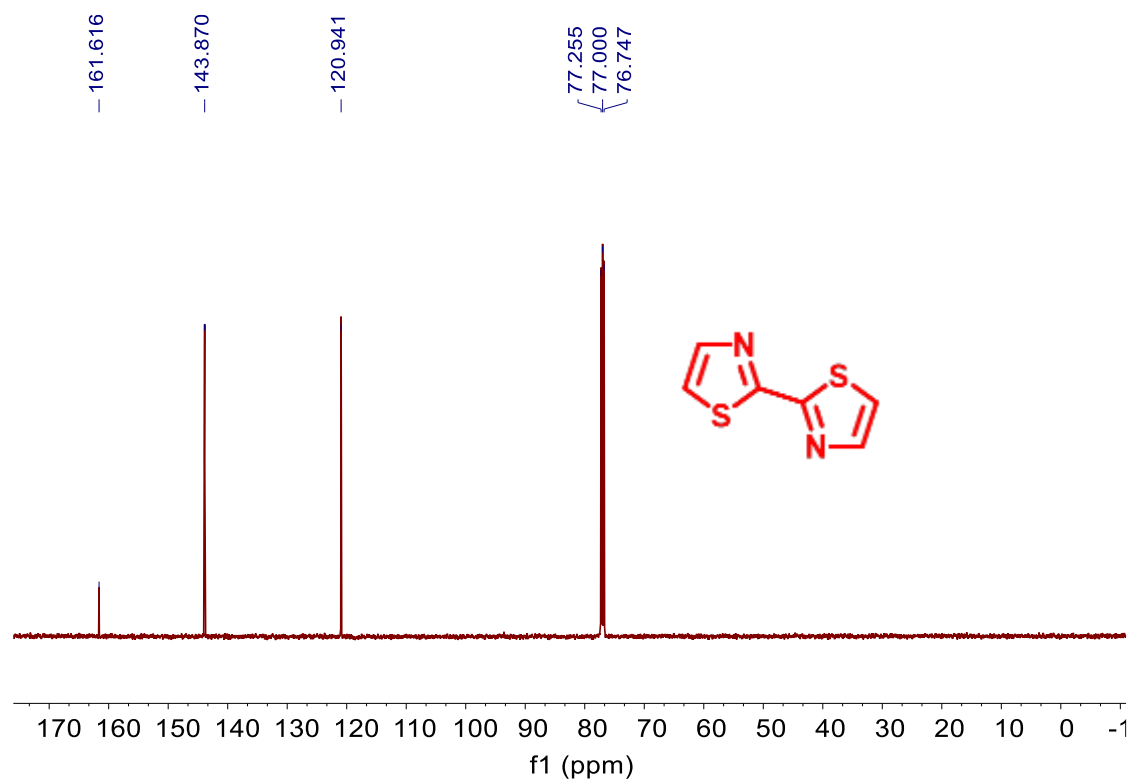
Supplementary Fig. 63. ¹H NMR (500 MHz) spectra of **N8** in CDCl₃ at 298 K.



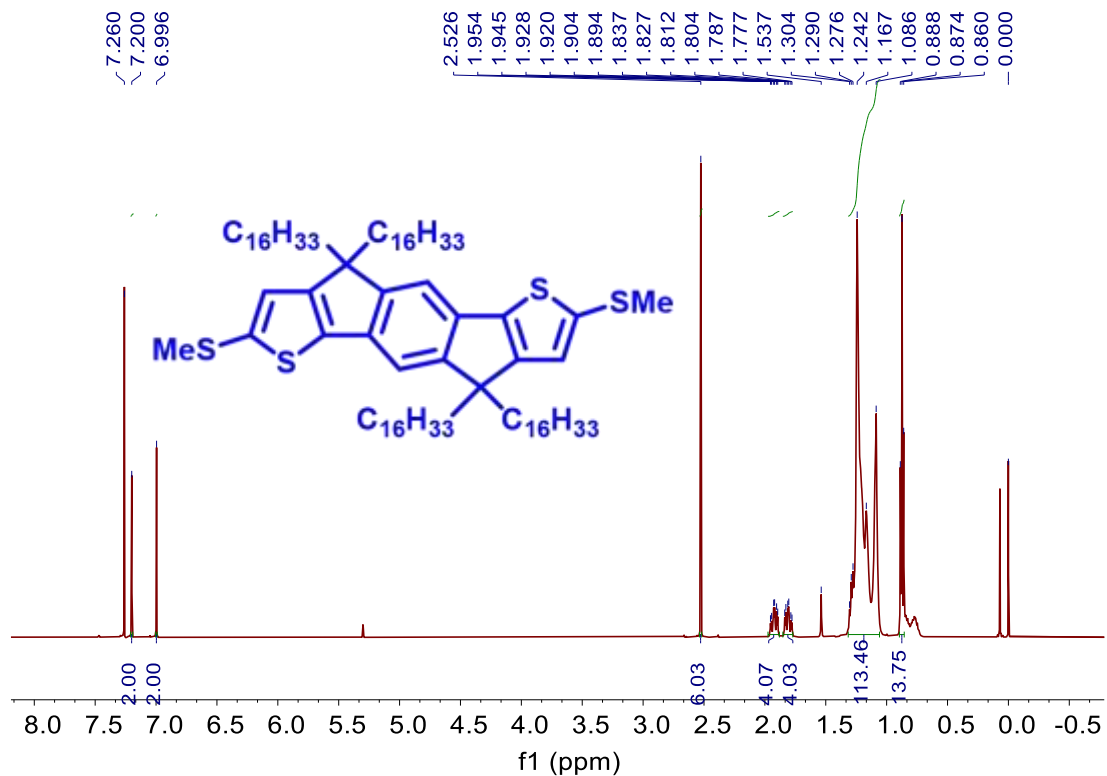
Supplementary Fig. 64. ¹³C NMR (125 MHz) spectra of **N8** in CDCl₃ at 298 K.



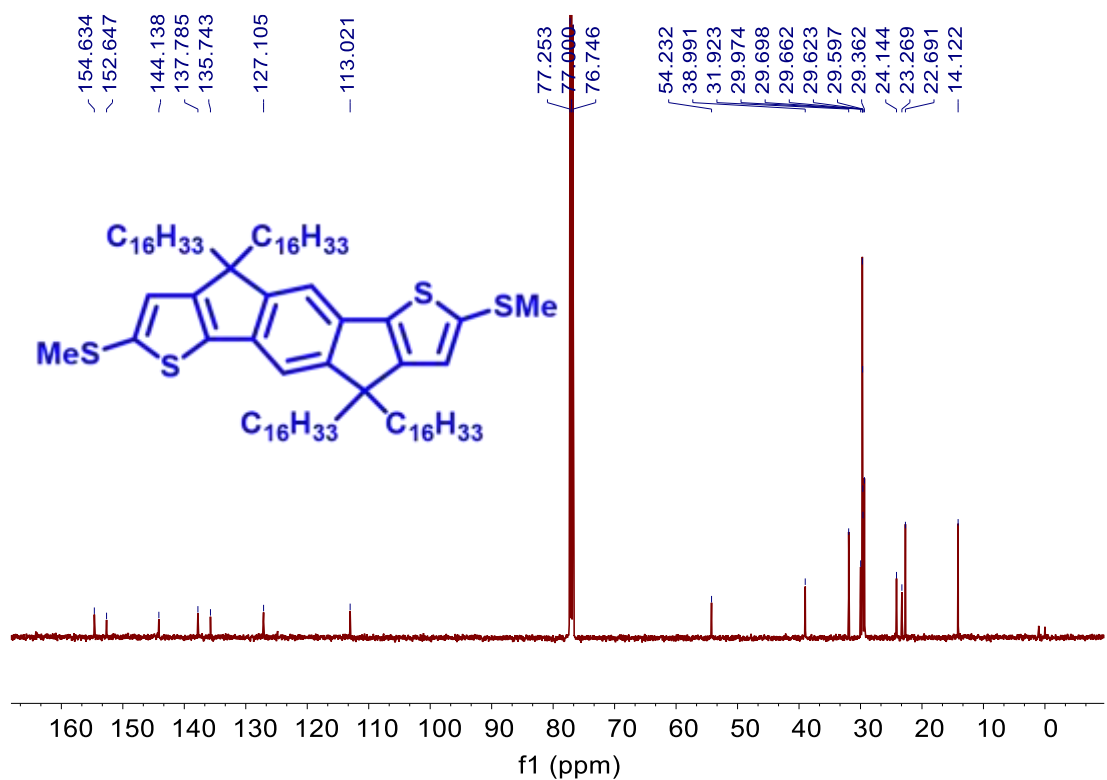
Supplementary Fig. 65. ¹H NMR (500 MHz) spectra of **N9** in CDCl₃ at 298 K.



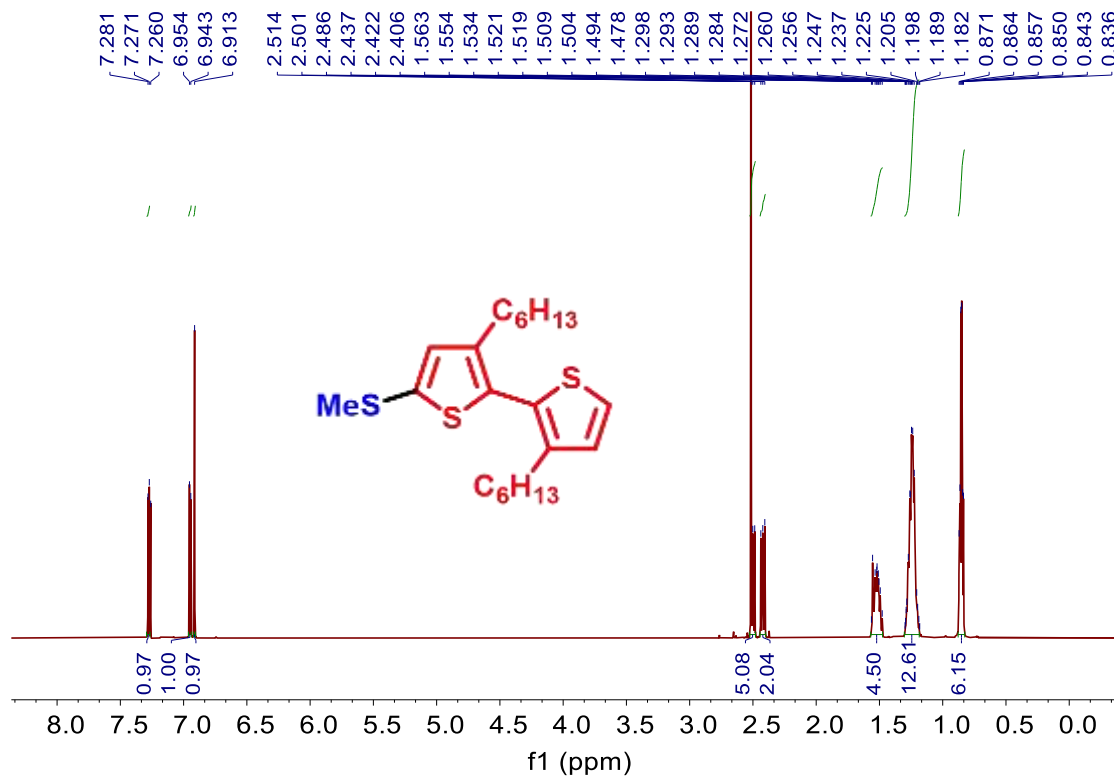
Supplementary Fig. 66. ¹³C NMR (125 MHz) spectra of **N9** in CDCl₃ at 298 K.



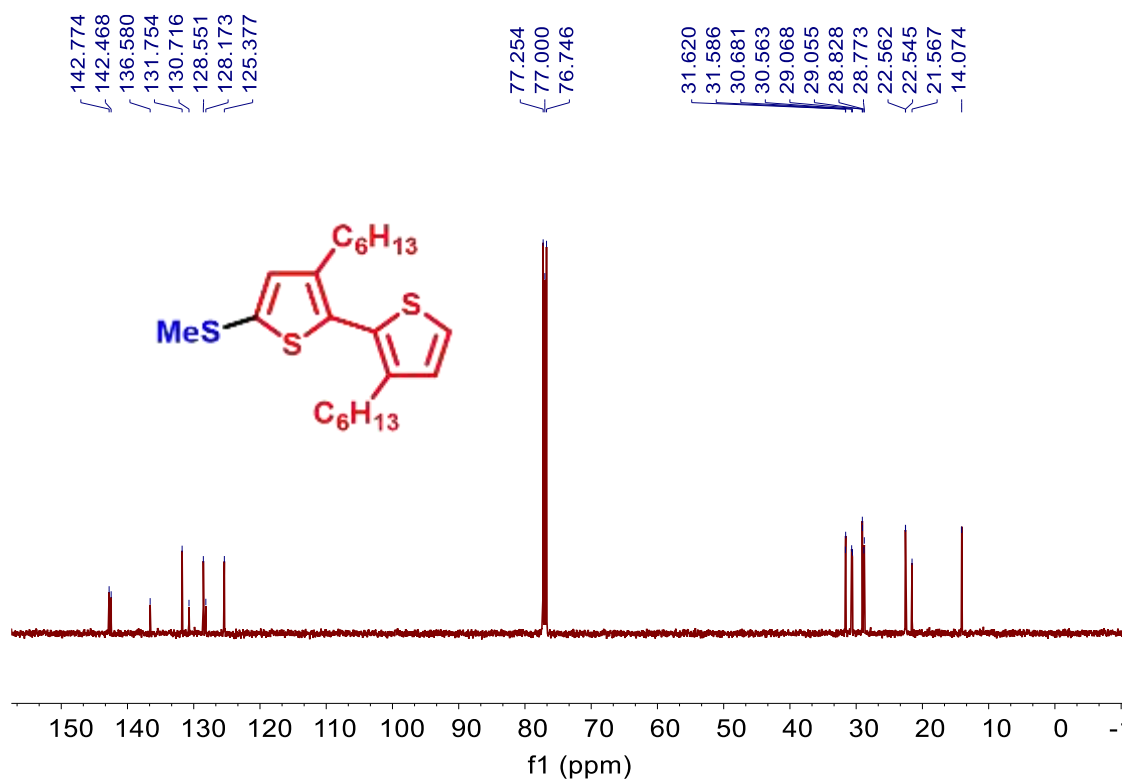
Supplementary Fig. 67. ¹H NMR (500 MHz) spectra of **E9** in CDCl₃ at 298 K.



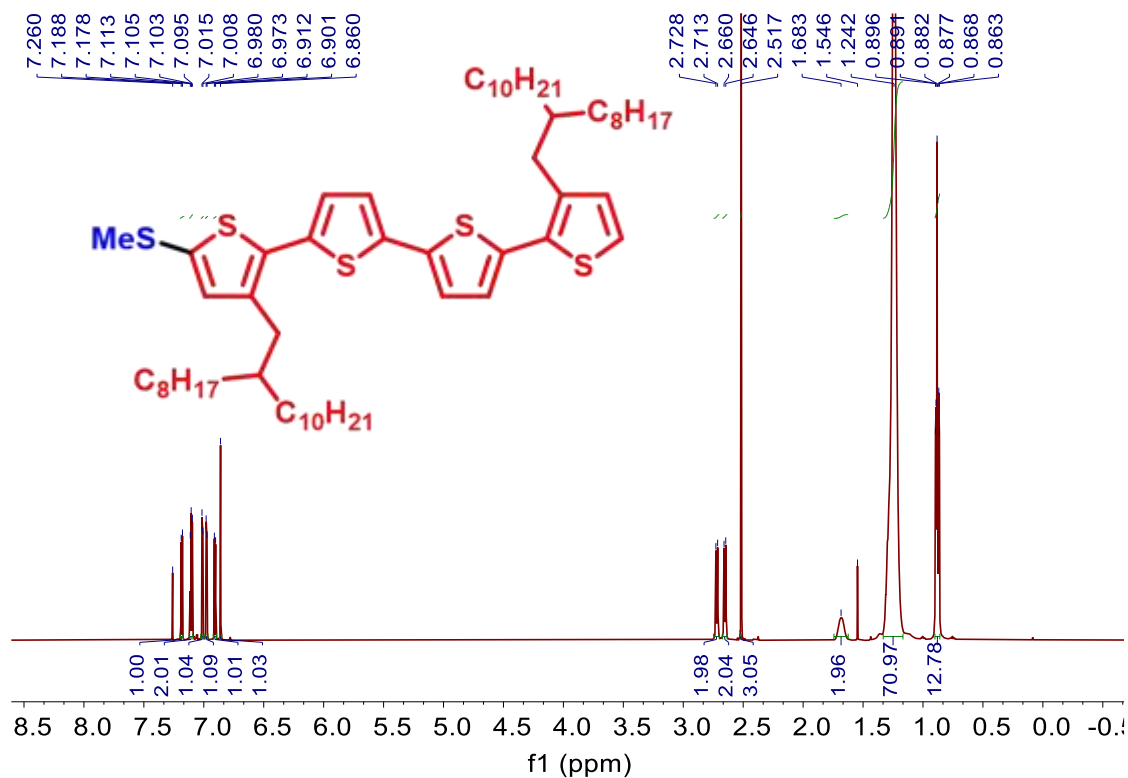
Supplementary Fig. 68. ¹³C NMR (125 MHz) spectra of **E9** in CDCl₃ at 298 K.



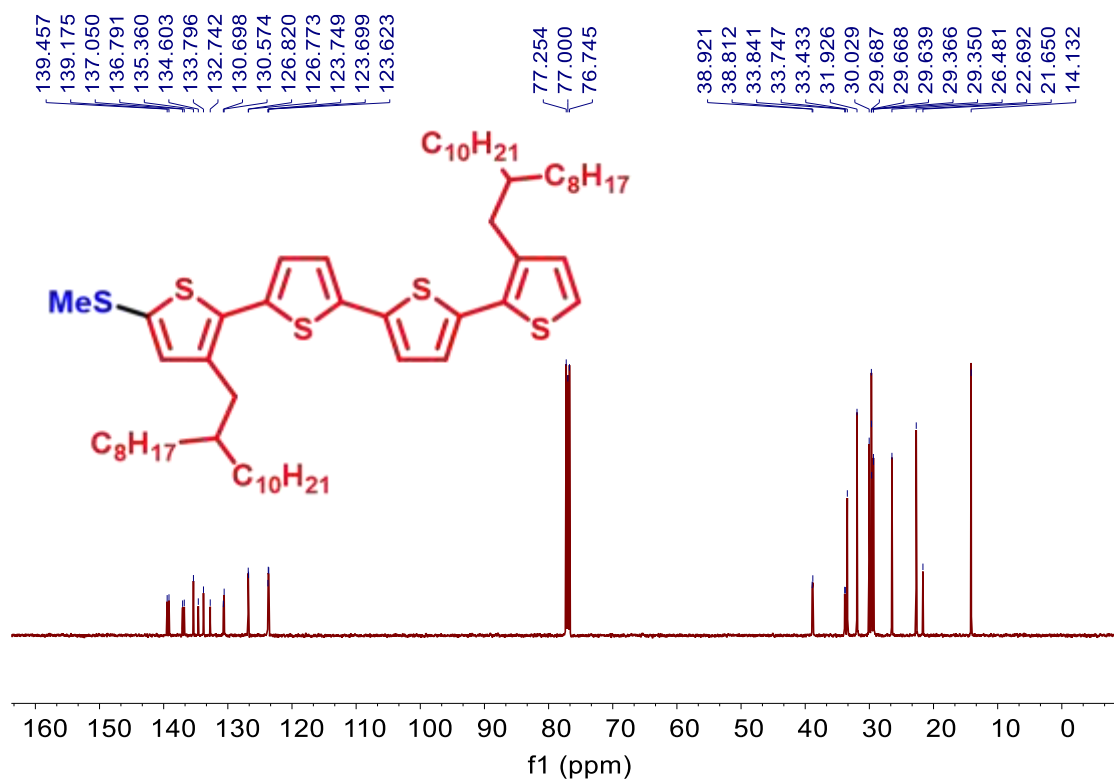
Supplementary Fig. 69. ¹H NMR (500 MHz) spectra of **M1** in CDCl₃ at 298 K.



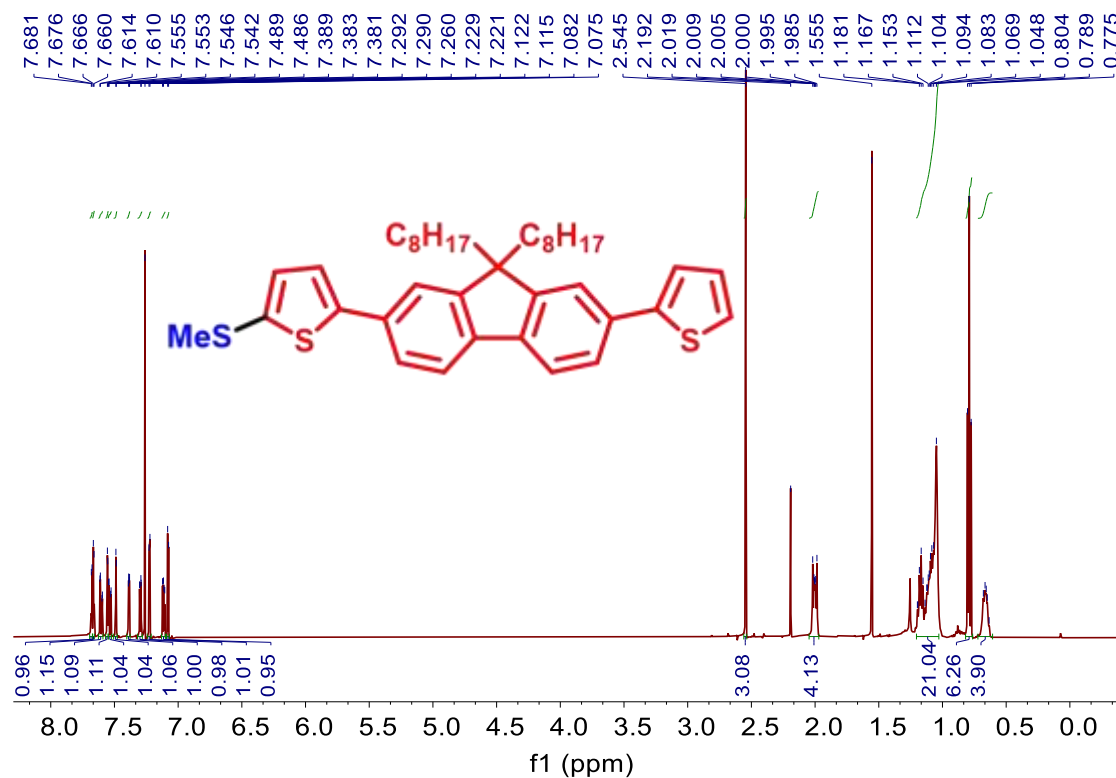
Supplementary Fig. 70. ¹³C NMR (125 MHz) spectra of **M1** in CDCl₃ at 298 K.



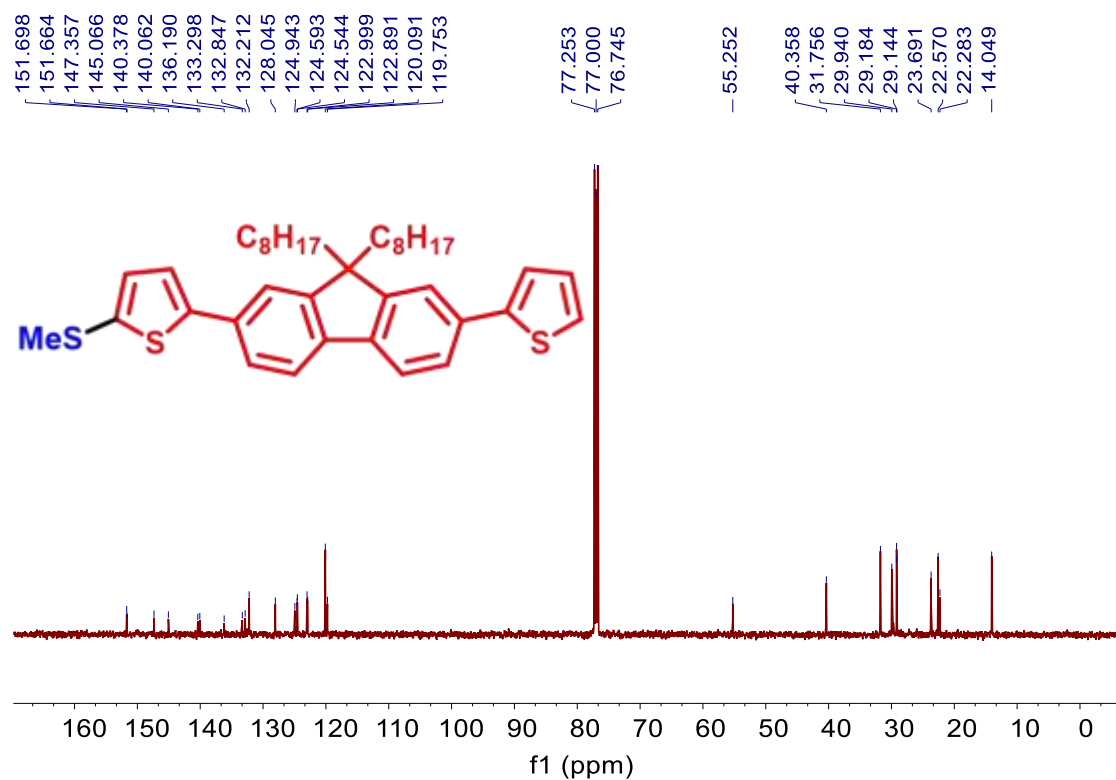
Supplementary Fig. 71. ¹H NMR (500 MHz) spectra of **M2** in CDCl₃ at 298 K.



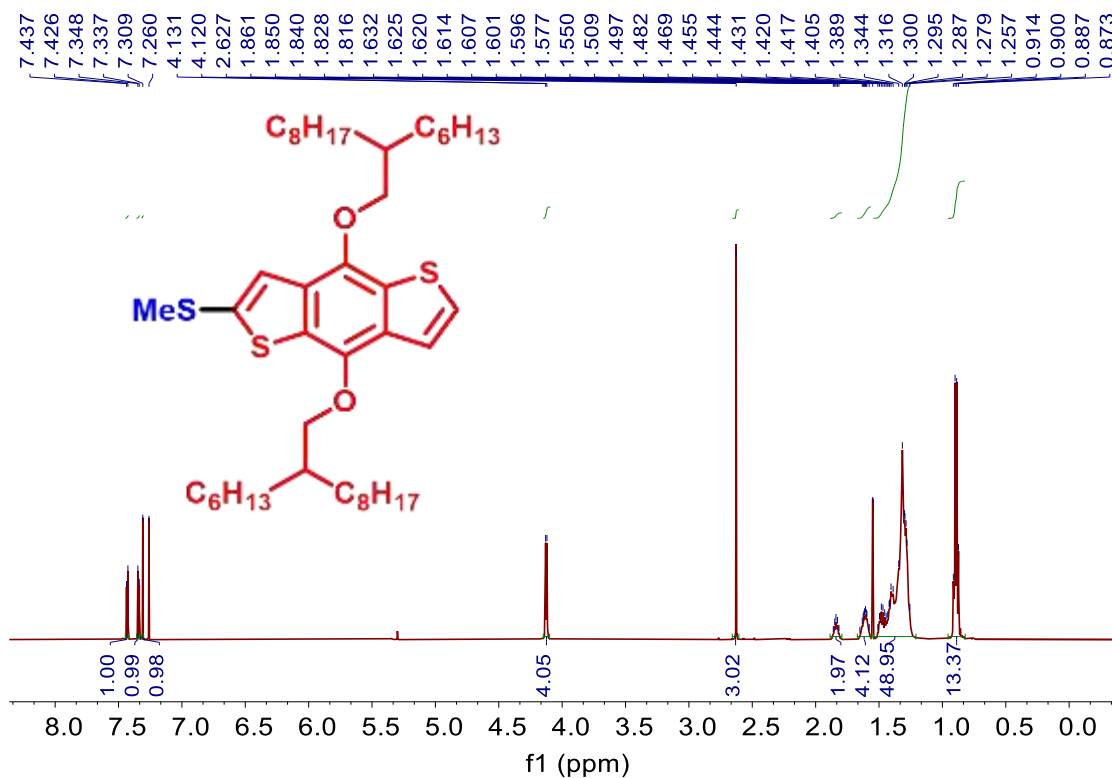
Supplementary Fig. 72. ¹³C NMR (125 MHz) spectra of **M2** in CDCl₃ at 298 K.



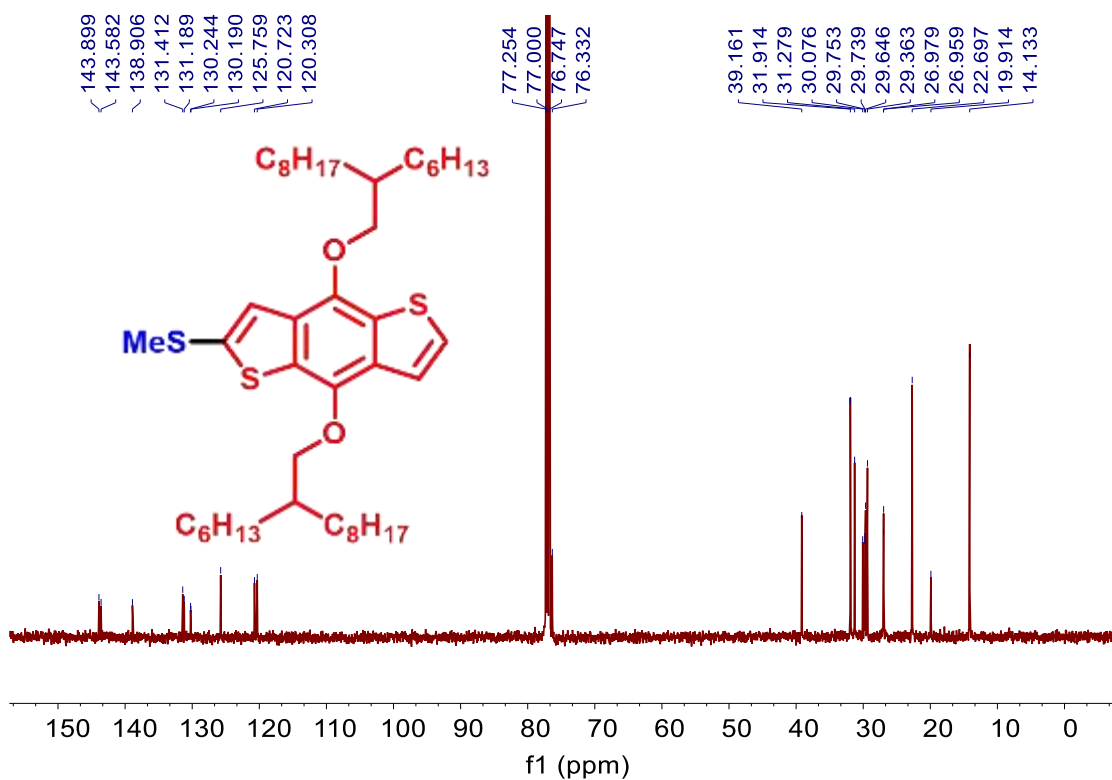
Supplementary Fig. 73. ¹H NMR (500 MHz) spectra of **M3** in CDCl₃ at 298 K.



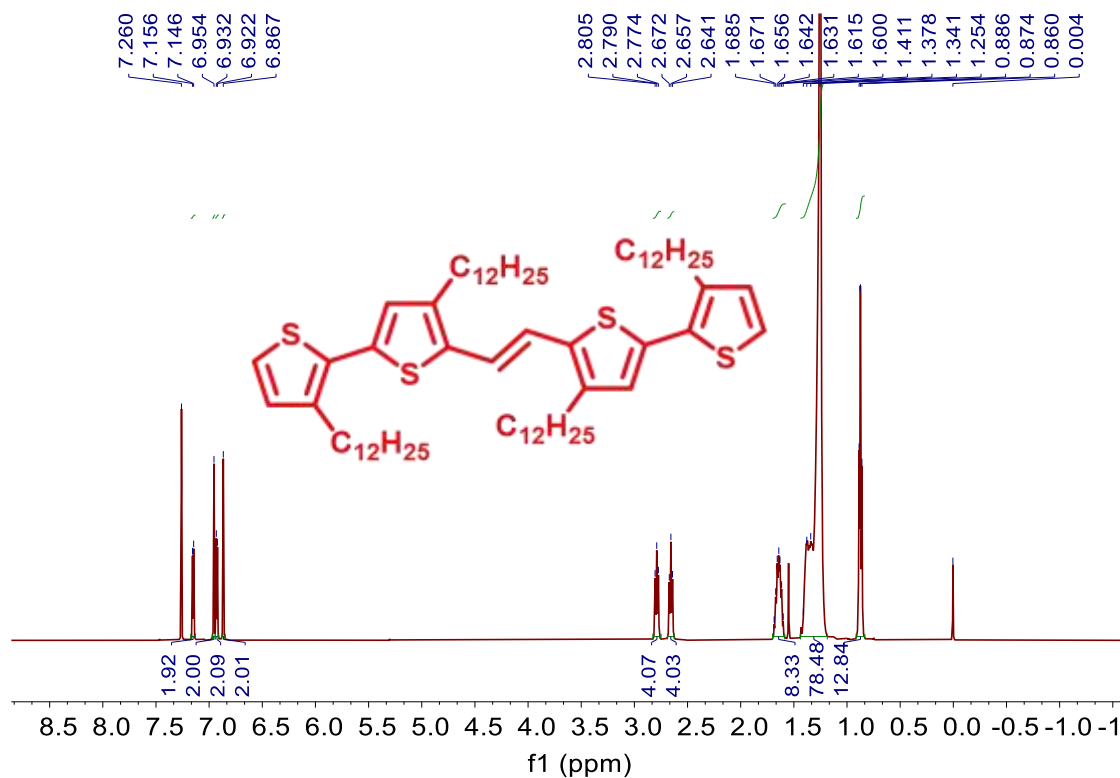
Supplementary Fig. 74. ¹³C NMR (125 MHz) spectra of **M3** in CDCl₃ at 298 K.



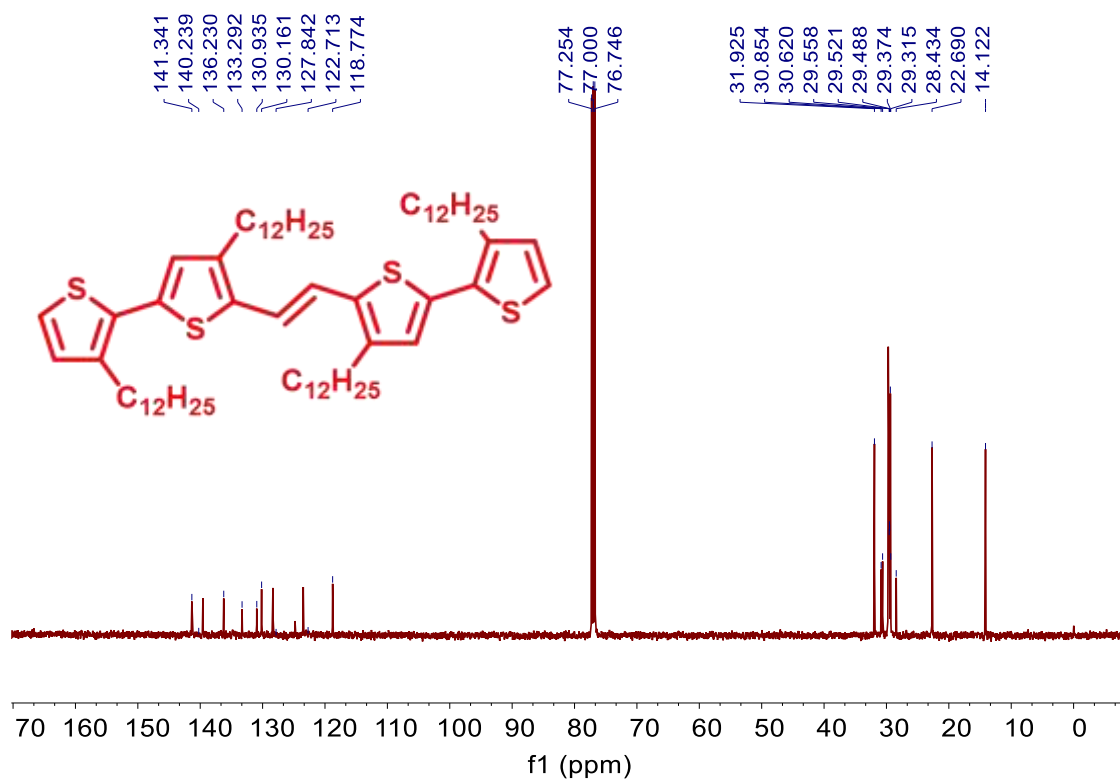
Supplementary Fig. 75. ¹H NMR (500 MHz) spectra of **M4** in CDCl₃ at 298 K.



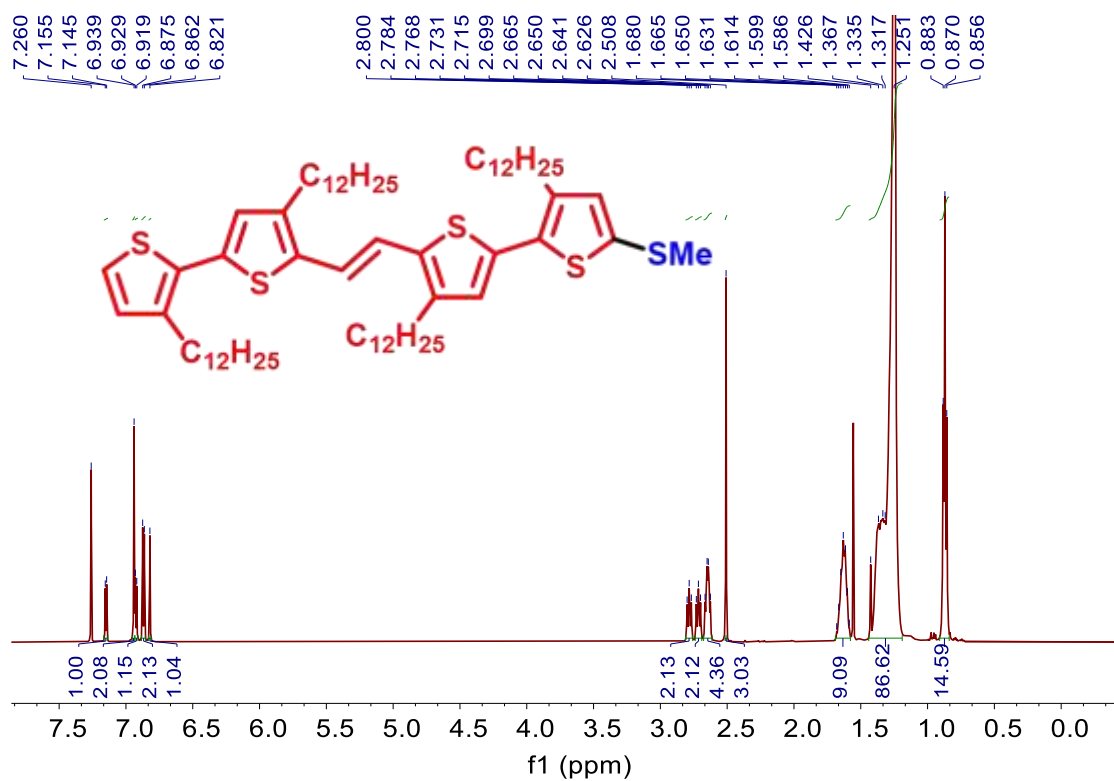
Supplementary Fig. 76. ¹³C NMR (125 MHz) spectra of **M4** in CDCl₃ at 298 K.



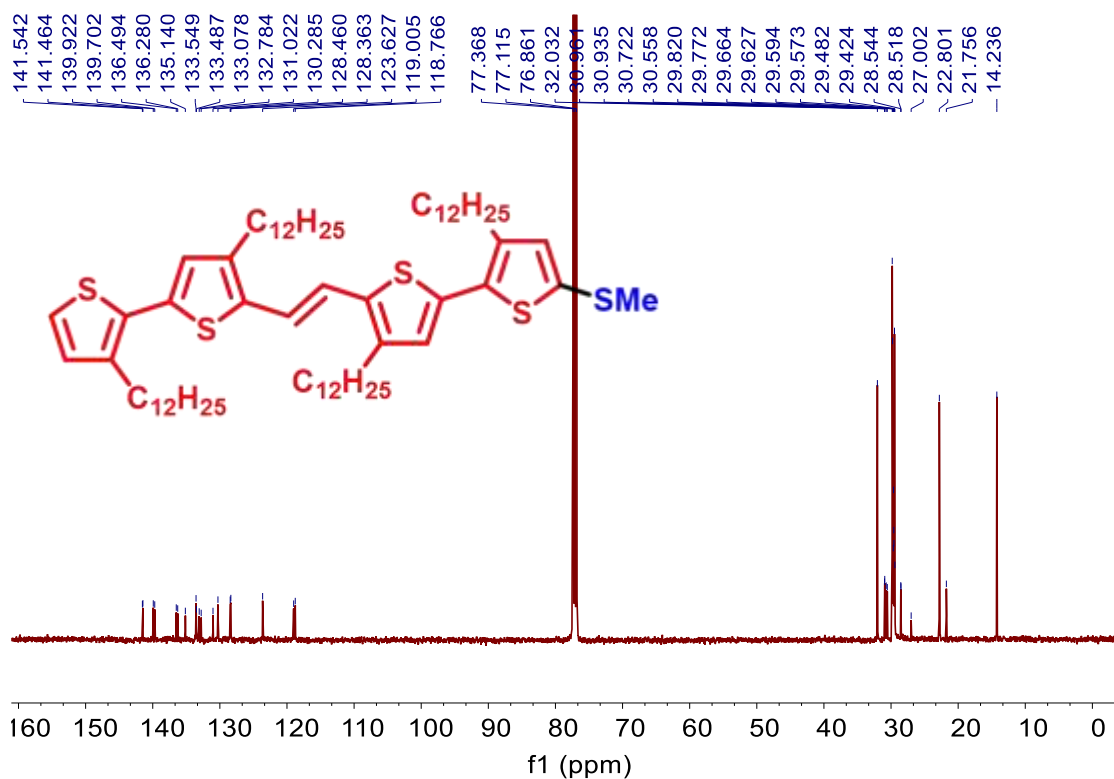
Supplementary Fig. 77. ¹H NMR (500 MHz) spectra of *(E)*-1,2-bis(3',4-didodecyl-[2,2'-bithiophen]-5-yl)ethene in CDCl₃ at 298 K.



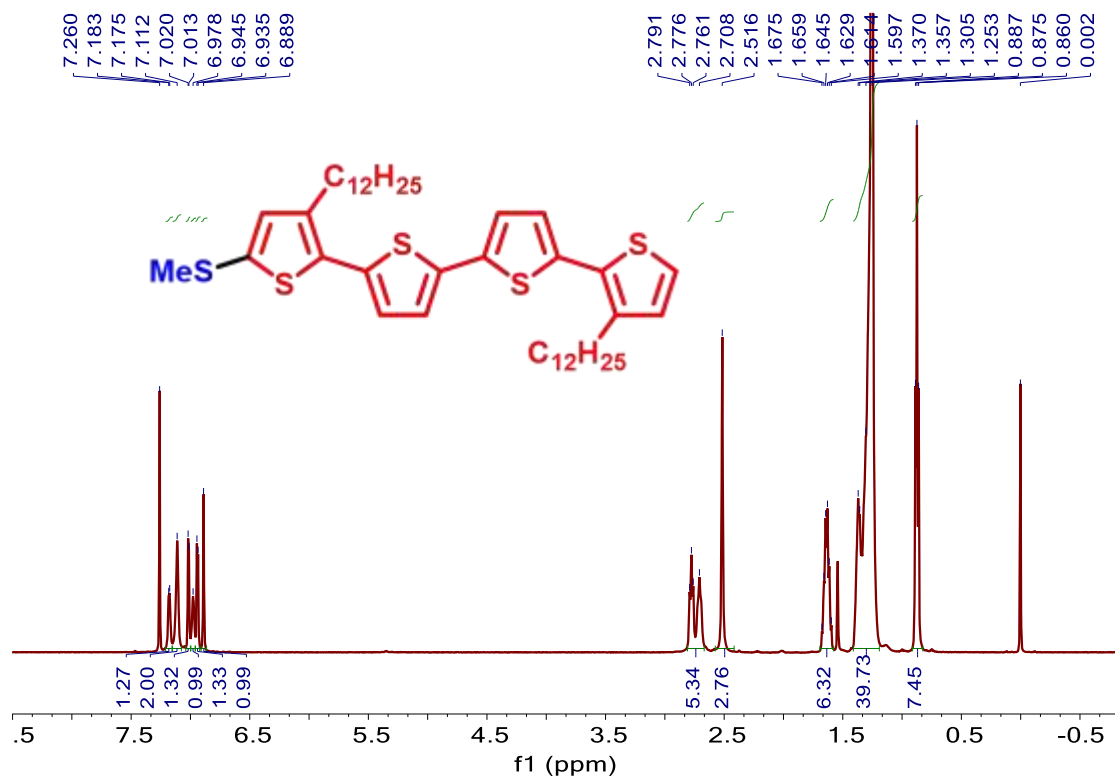
Supplementary Fig. 78. ¹³C NMR (125 MHz) spectra of *(E)*-1,2-bis(3',4-didodecyl-[2,2'-bithiophen]-5-yl)ethene in CDCl₃ at 298 K.



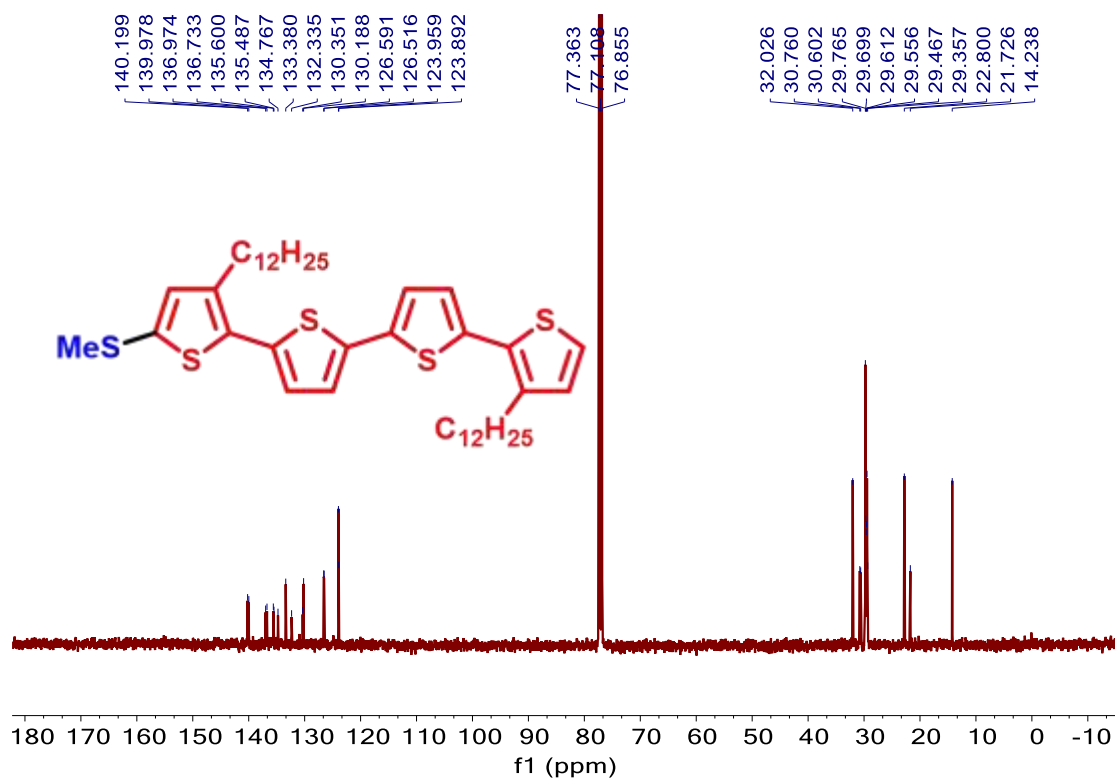
Supplementary Fig. 79. ¹H NMR (500 MHz) spectra of **M5** in CDCl₃ at 298 K.



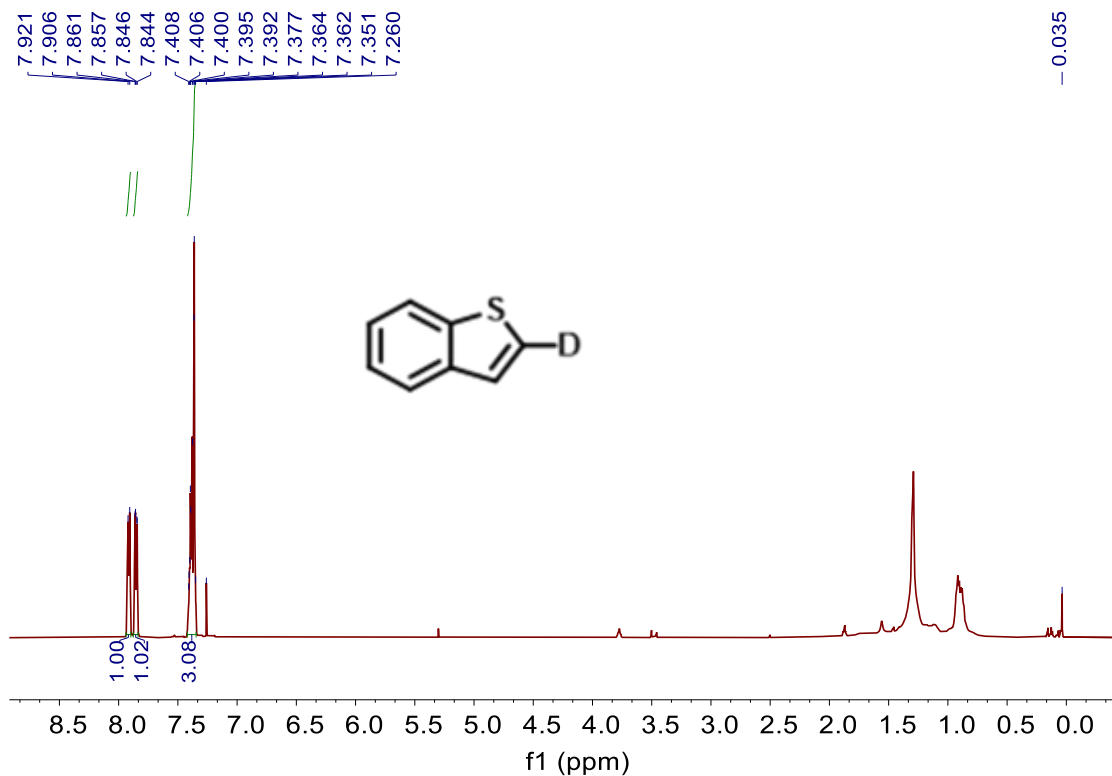
Supplementary Fig. 80. ¹³C NMR (125 MHz) spectra of **M5** in CDCl₃ at 298 K.



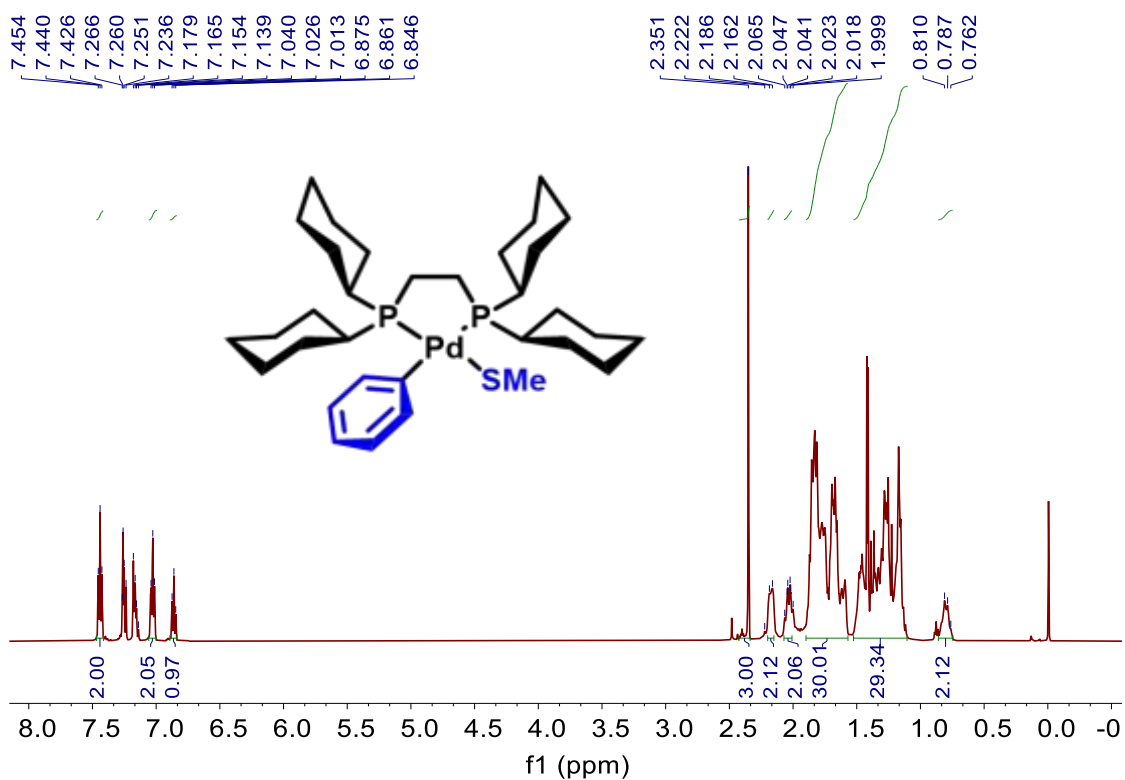
Supplementary Fig. 81. ¹H NMR (500 MHz) spectra of **M6** in CDCl₃ at 298 K.



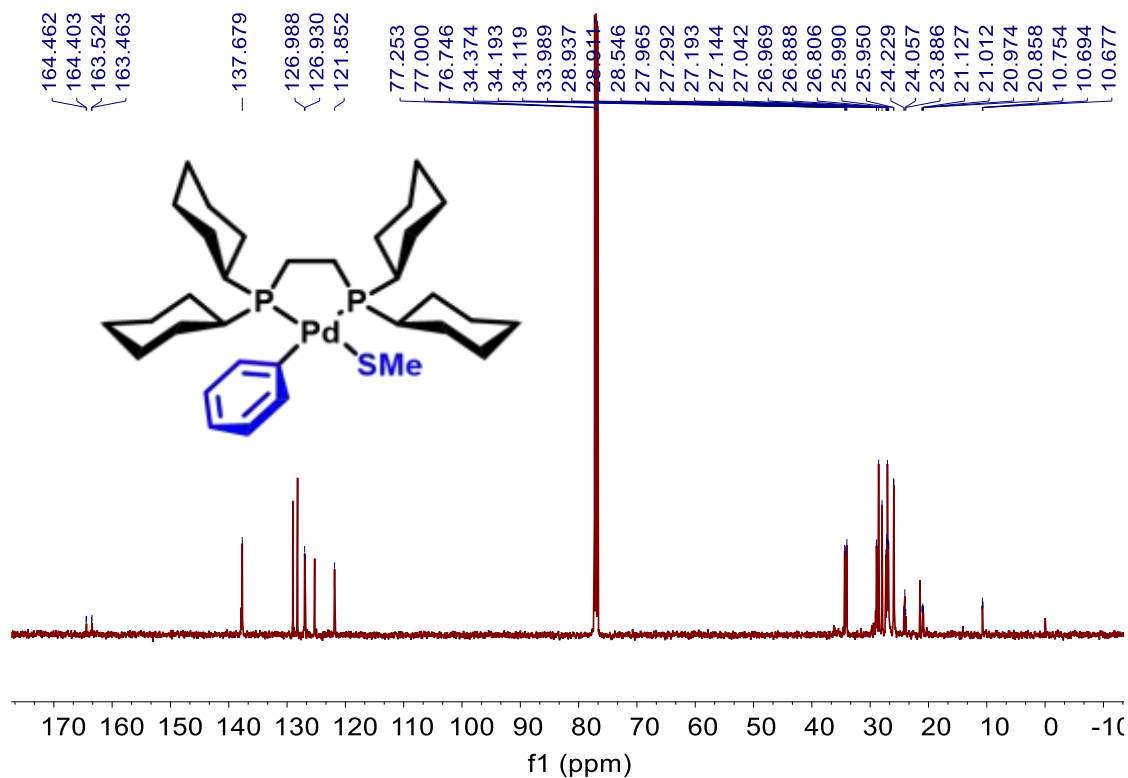
Supplementary Fig. 82. ¹³C NMR (125 MHz) spectra of **M6** in CDCl₃ at 298 K.



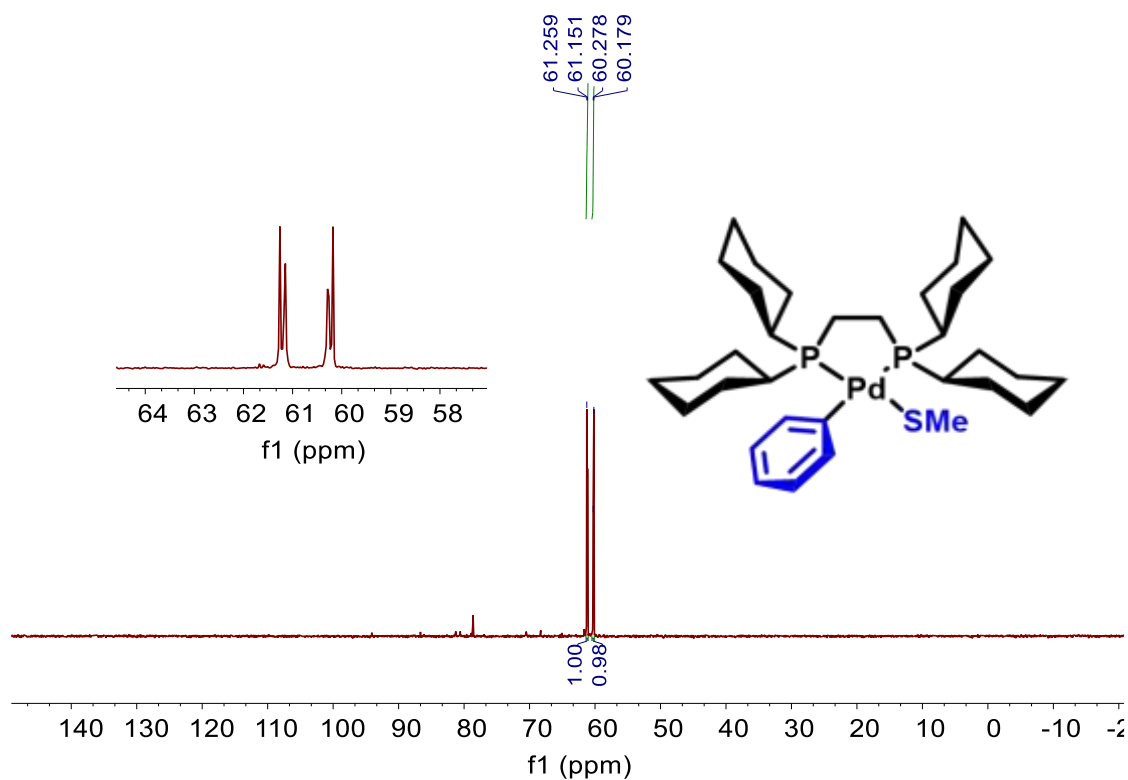
Supplementary Fig. 83. ¹H NMR (500 MHz) spectra of **2-d** in CDCl₃ at 298 K.



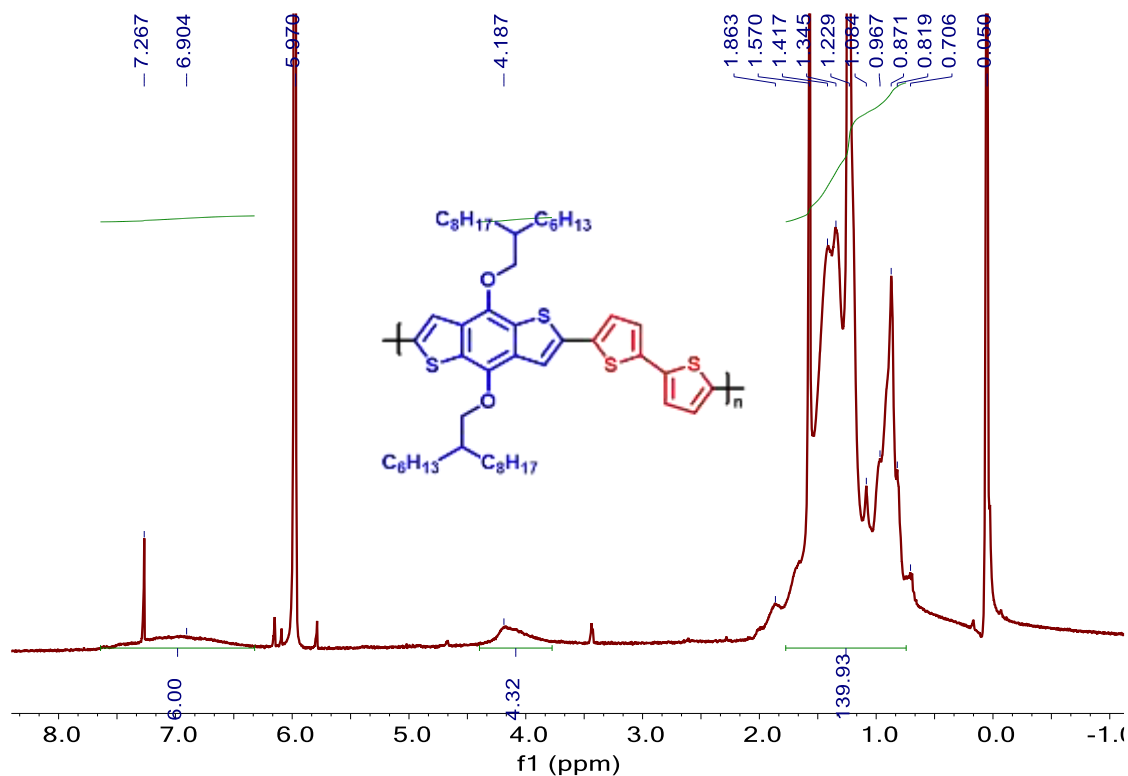
Supplementary Fig. 84. ¹H NMR (500 MHz) spectra of **B** in CDCl₃ at 298 K.



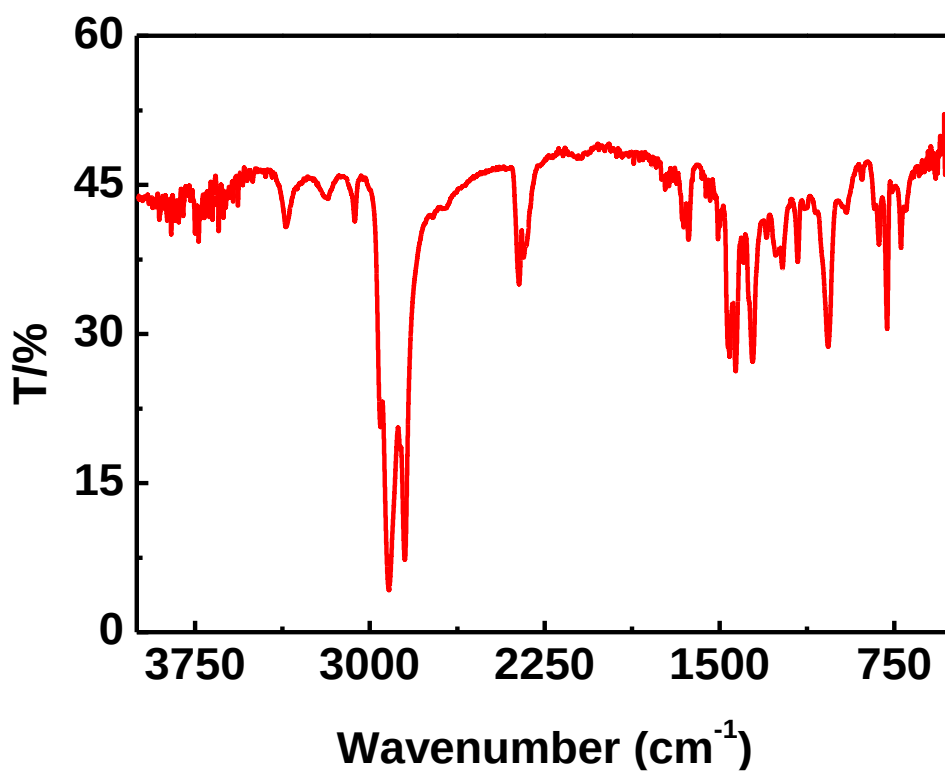
Supplementary Fig. 85. ^{13}C NMR (125 MHz) spectra of **B** in CDCl_3 at 298 K.



Supplementary Fig. 86. ^{31}P NMR (202 MHz) spectra of **B** in CDCl_3 at 298 K.

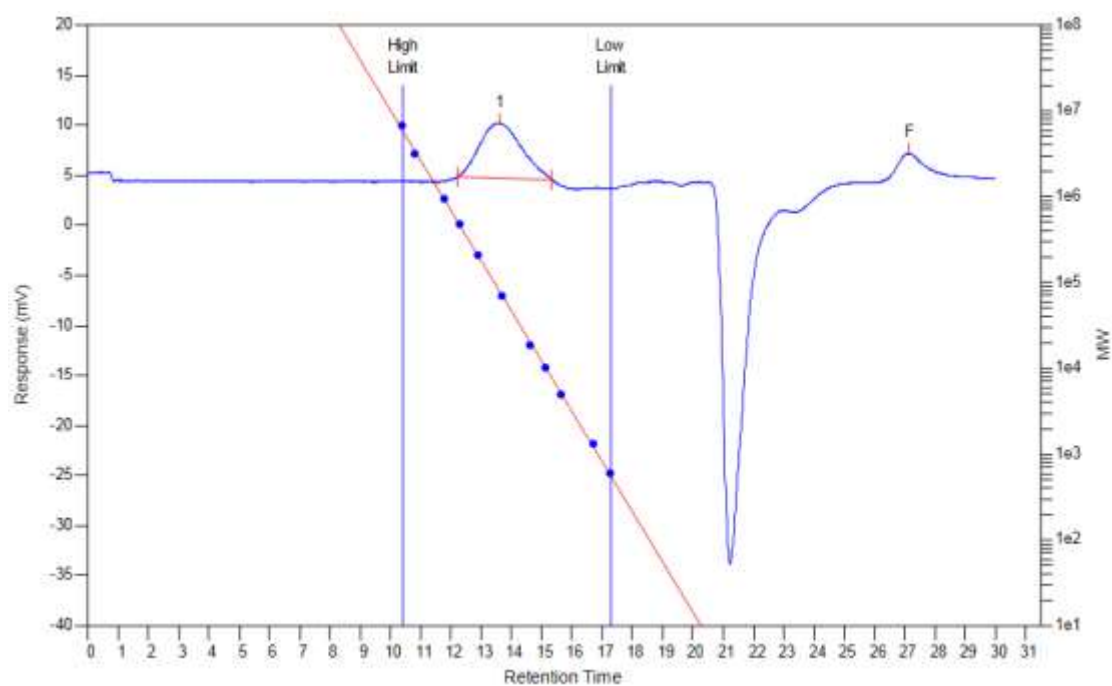


Supplementary Fig. 87. 1H NMR (500 MHz) spectra of **P1** in $C_2D_2Cl_4$ at 373 K.



Supplementary Fig. 88. FT-IR spectrum of **P1** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 79954

Mn: 51570

Mv: 89343

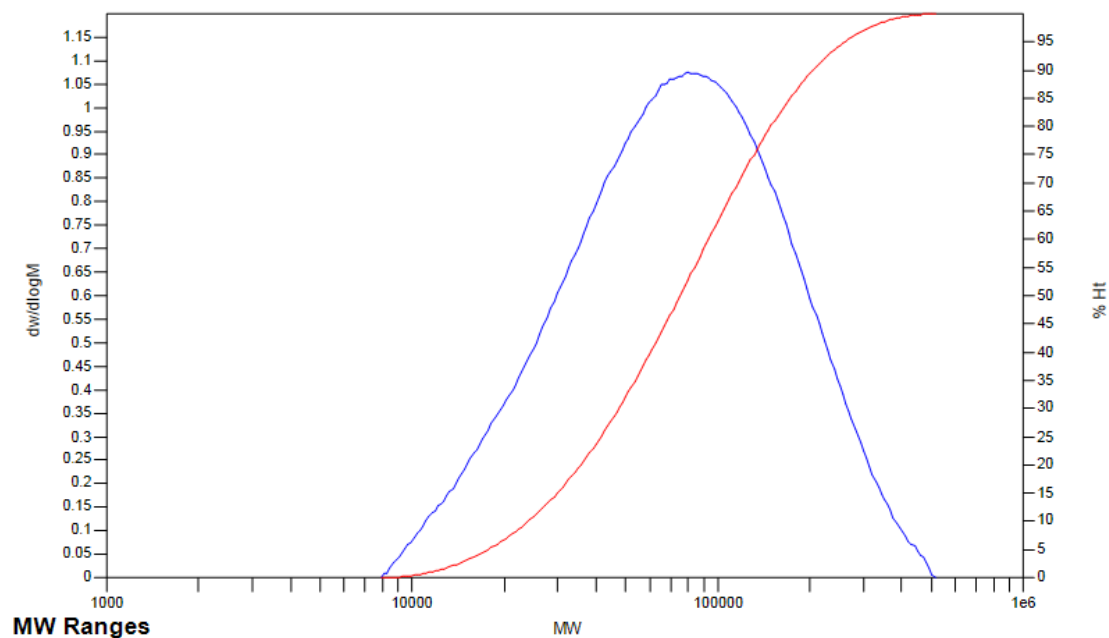
Mw: 97112

Mz: 158890

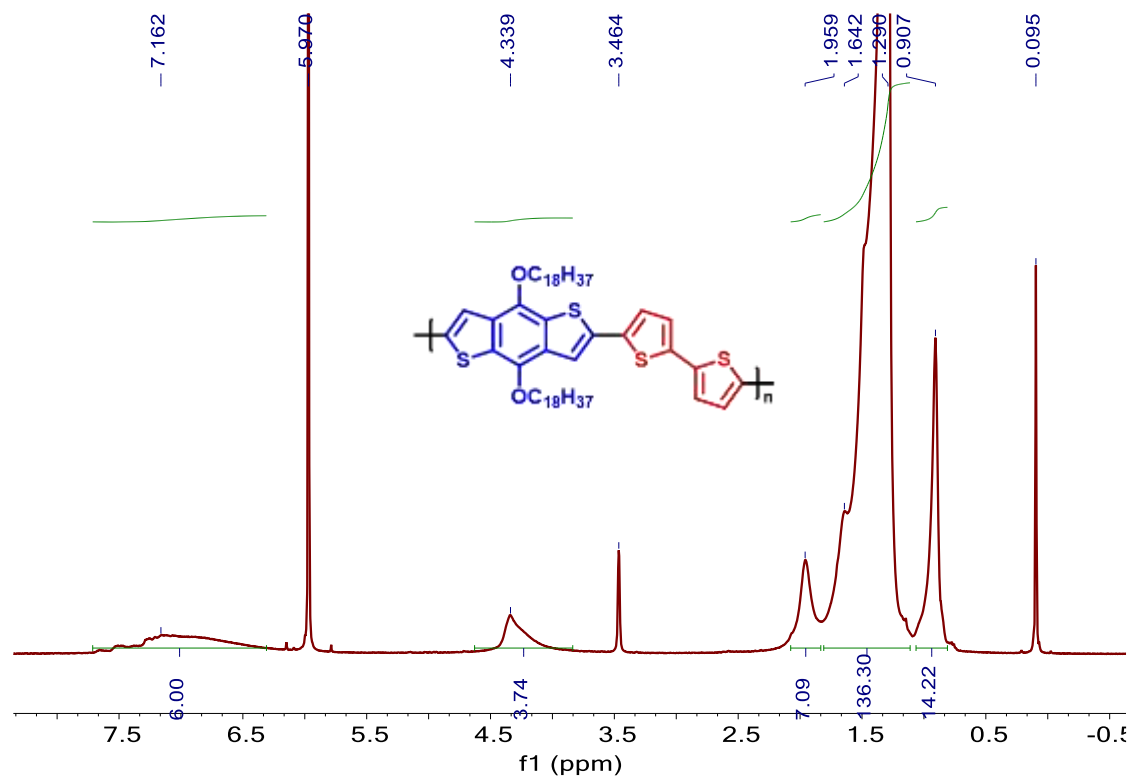
Mz+1: 220807

PD: 1.8831

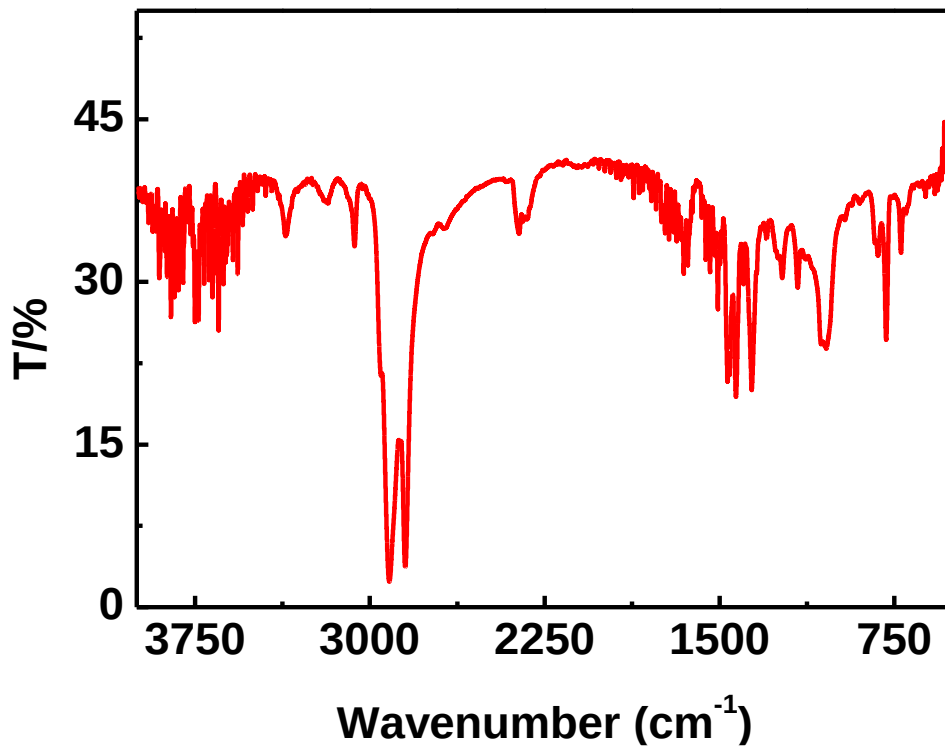
Distribution Plots



Supplementary Fig. 89. Gel permeation chromatography (GPC) trace of **P1**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P1**.

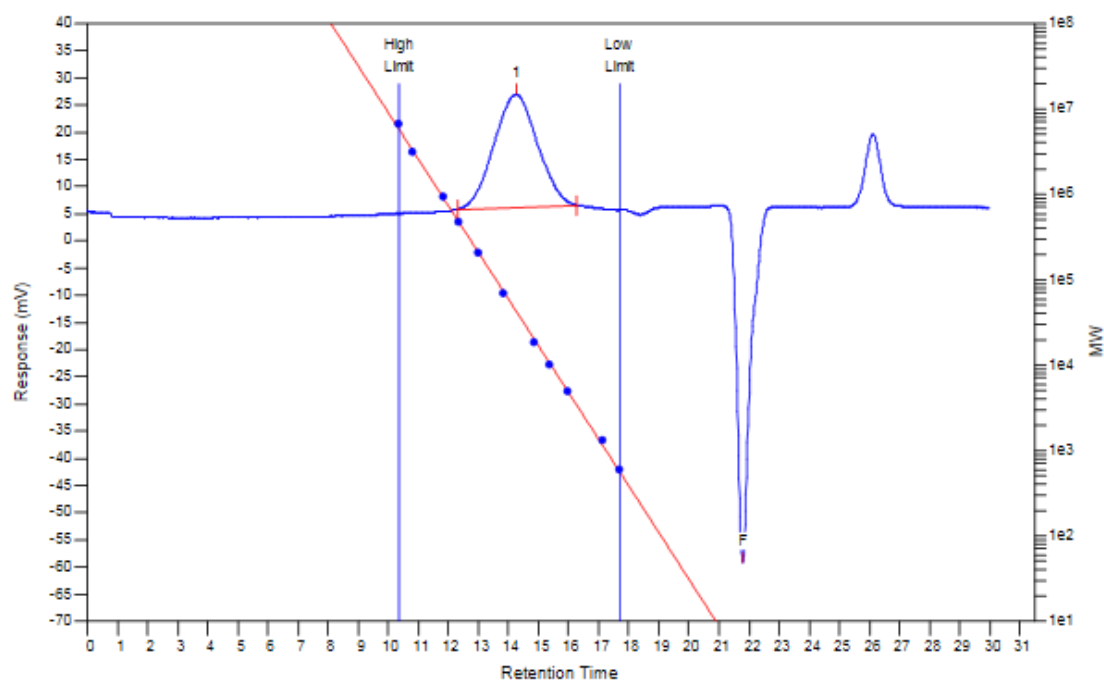


Supplementary Fig. 90. ^1H NMR (500 MHz) spectra of **P2** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 91. FT-IR spectrum of **P2** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 43306

Mn: 30344

Mv: 53990

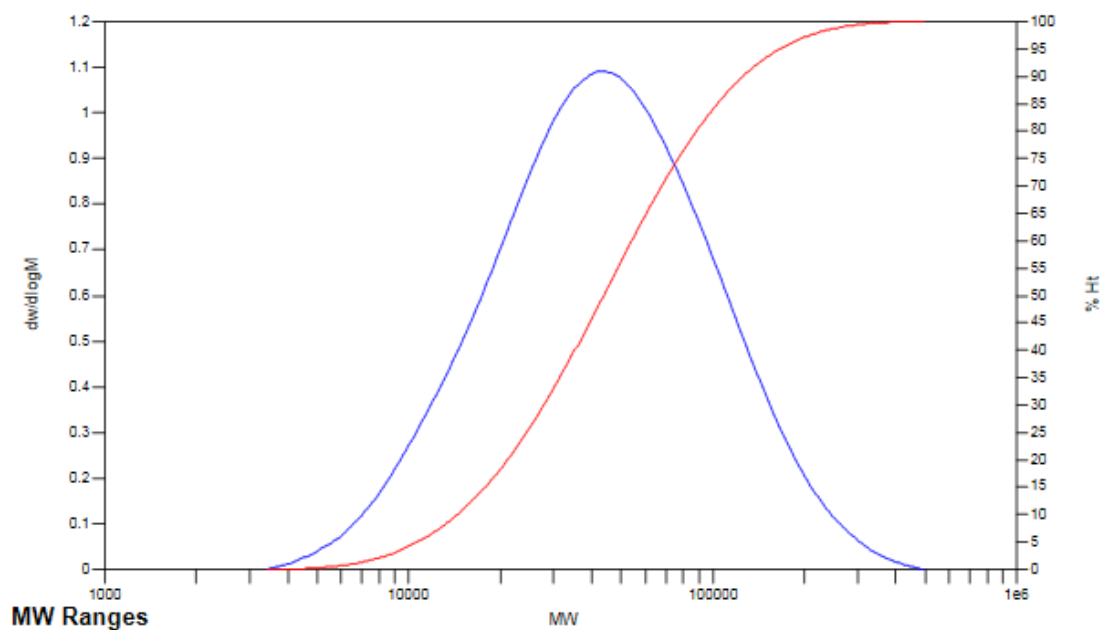
Mw: 59279

Mz: 106062

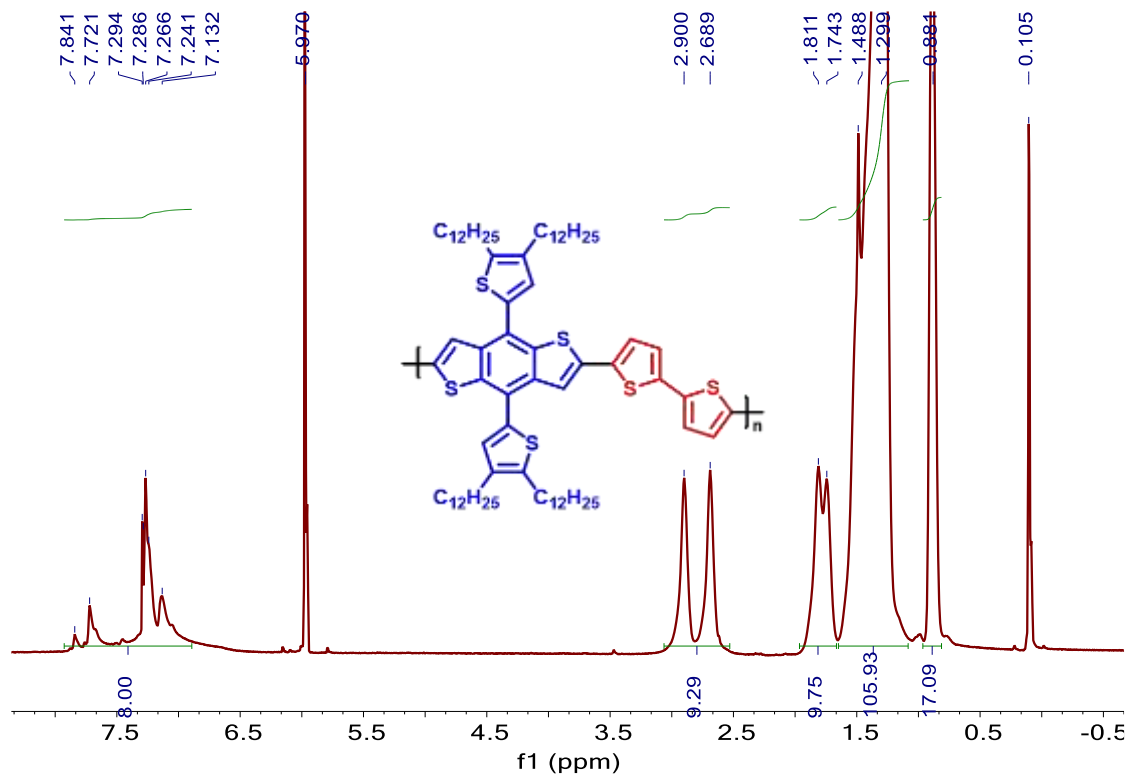
Mz+1: 163545

PD: 1.9536

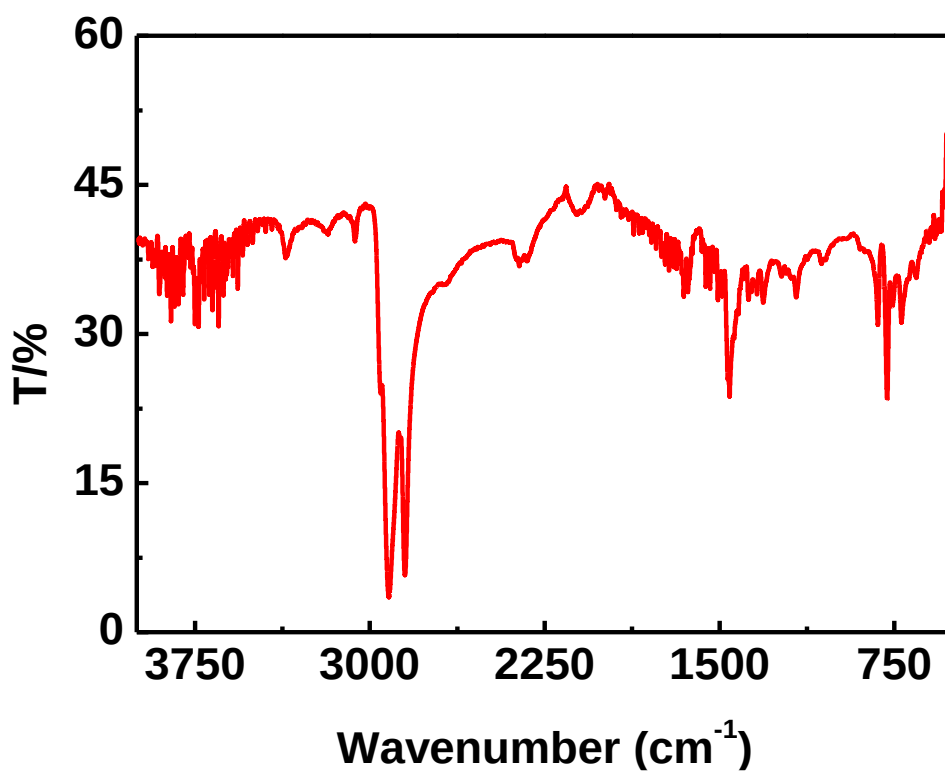
Distribution Plots



Supplementary Fig. 92. Gel permeation chromatography (GPC) trace of **P2**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P2**.

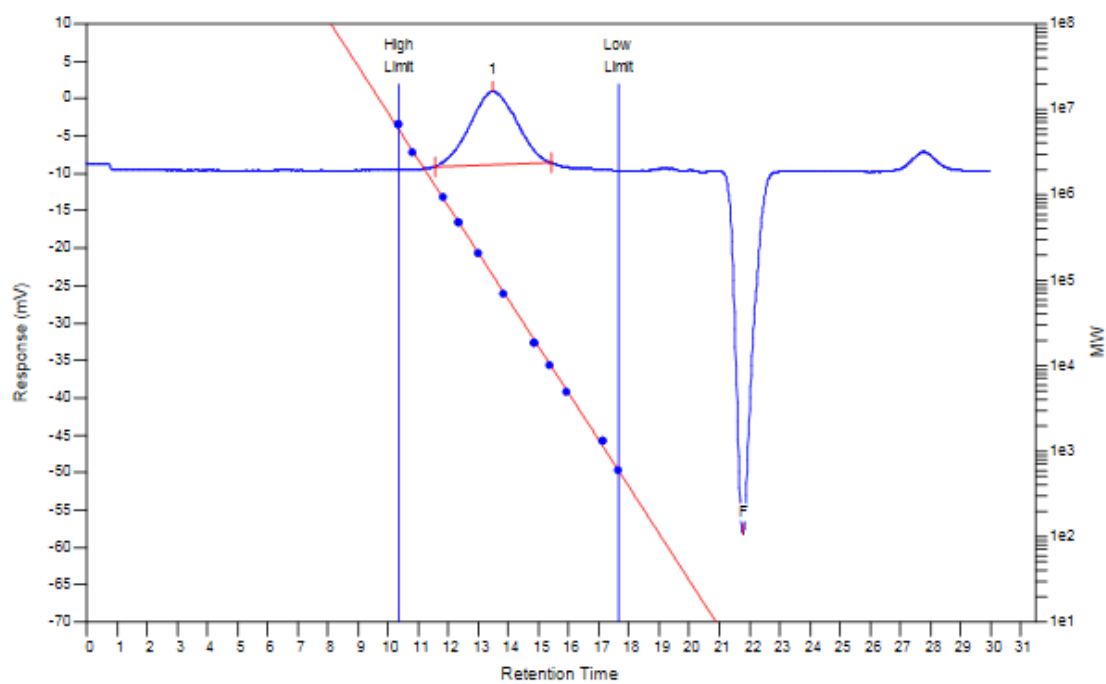


Supplementary Fig. 93. ¹H NMR (500 MHz) spectra of **P3** in C₂D₂Cl₄ at 373 K.



Supplementary Fig. 94. FT-IR spectrum of **P3** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 113474

Mn: 76028

Mv: 143073

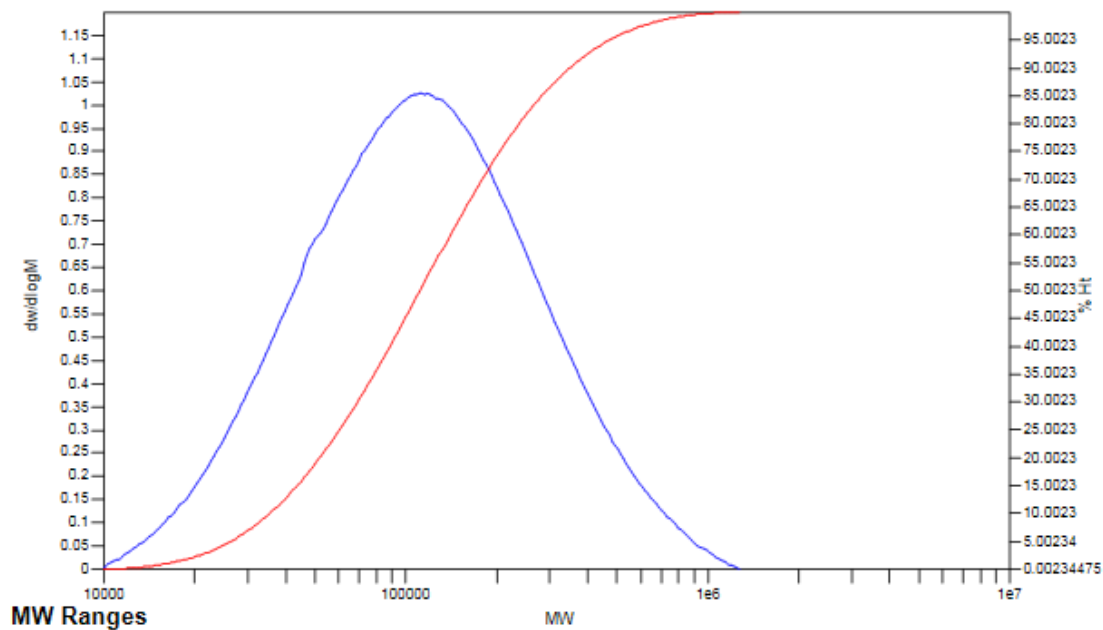
Mw: 158904

Mz: 302840

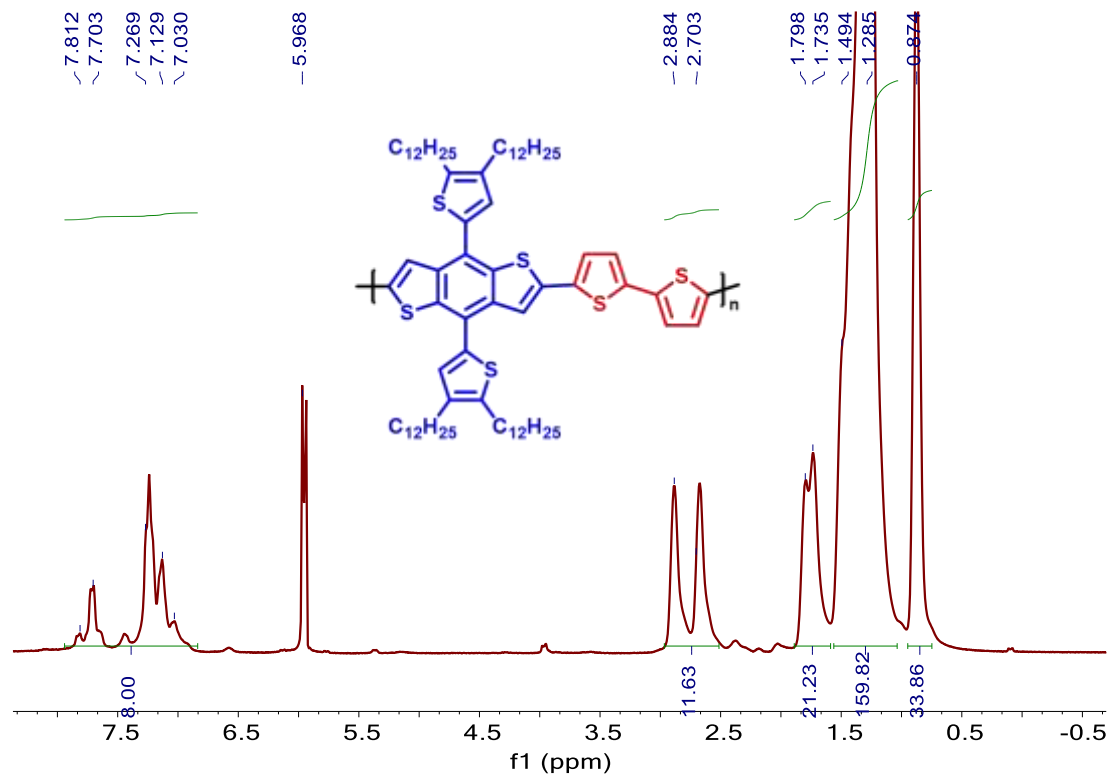
Mz+1: 474602

PD: 2.0901

Distribution Plots

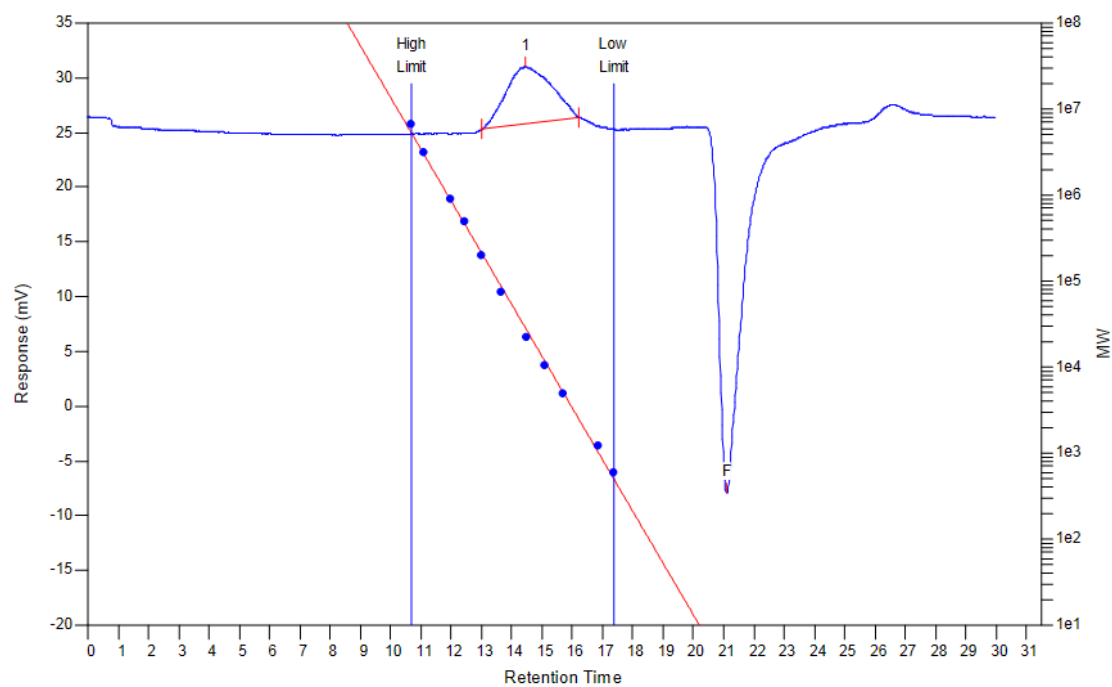


Supplementary Fig. 95. Gel permeation chromatography (GPC) trace of **P3**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P3**.

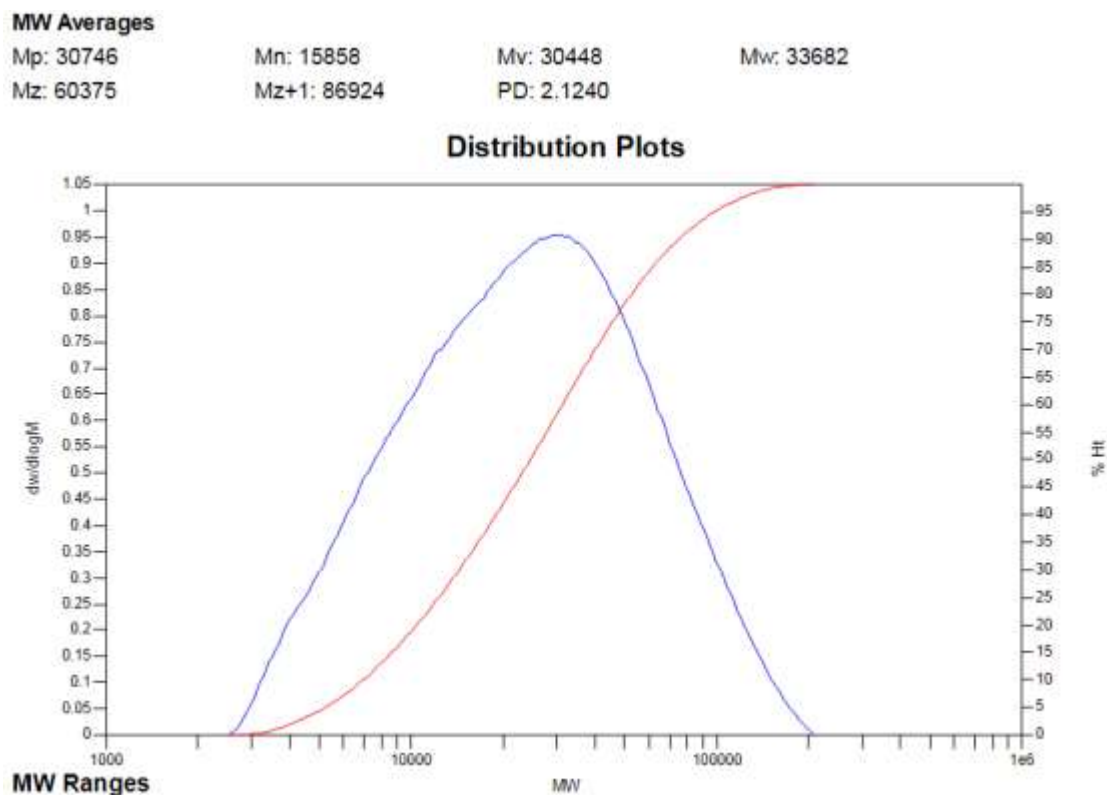


Supplementary Fig. 96. ^1H NMR (500 MHz) spectra of **P3-DArP** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.

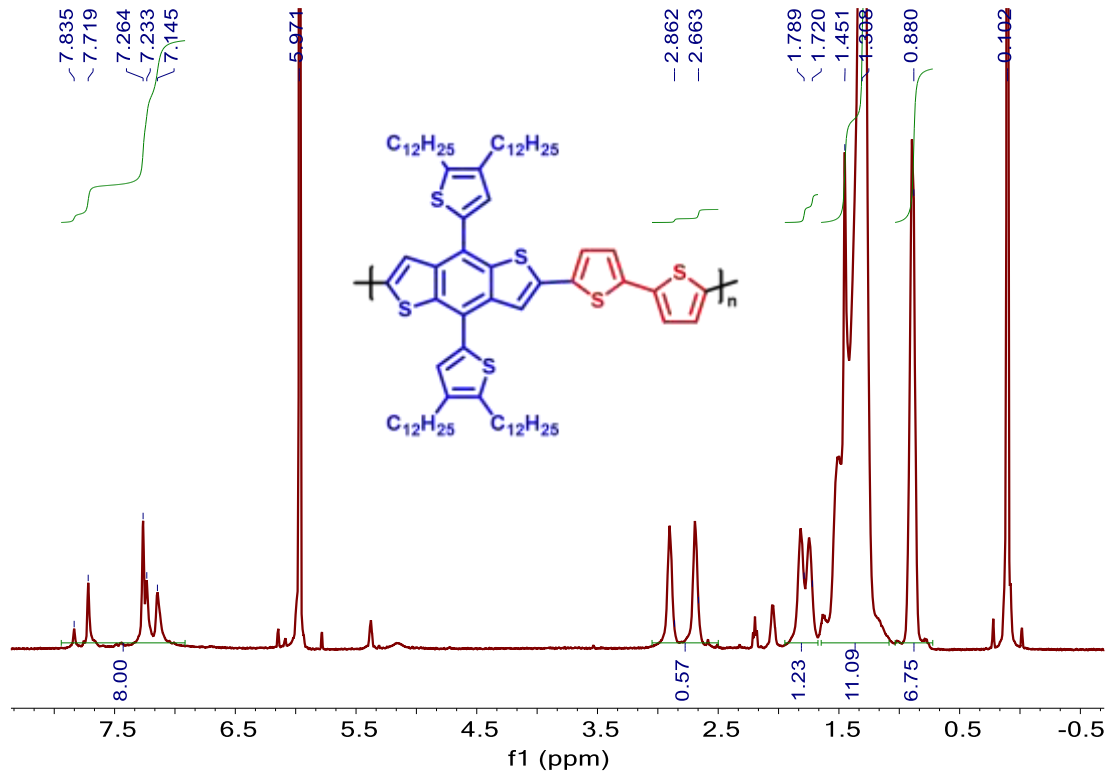
(a)



(b)



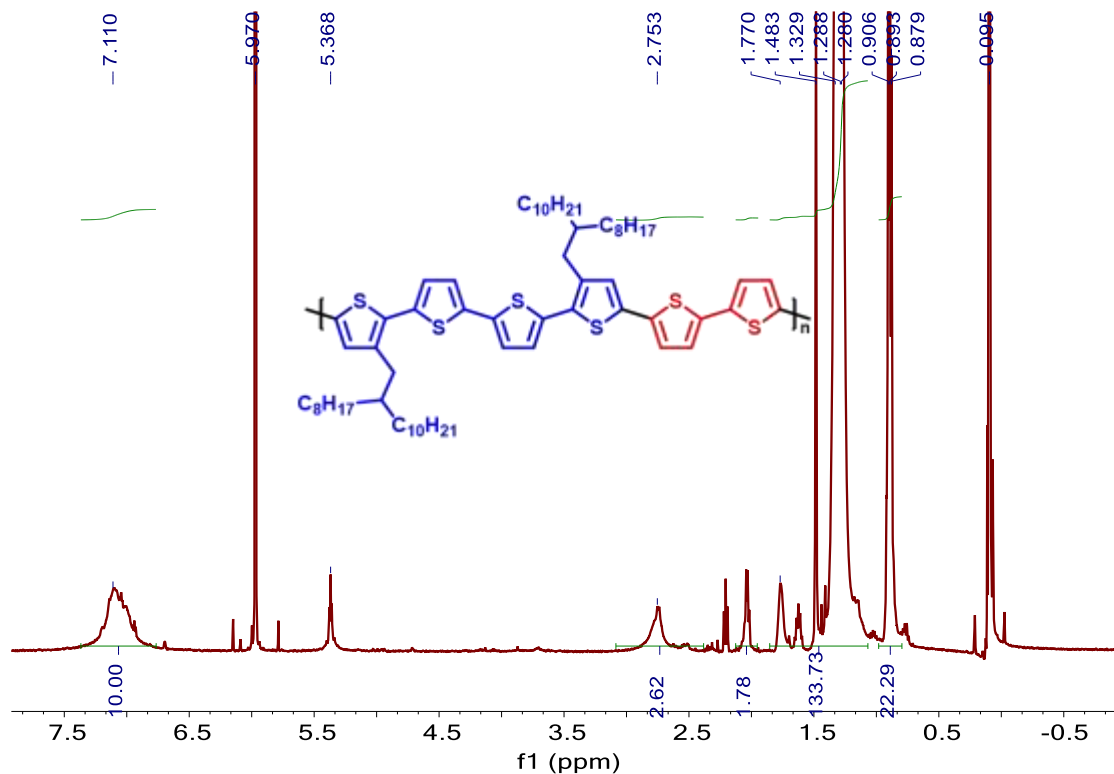
Supplementary Fig. 97. Gel permeation chromatography (GPC) trace of **P3-DArP**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P3-DArP**.



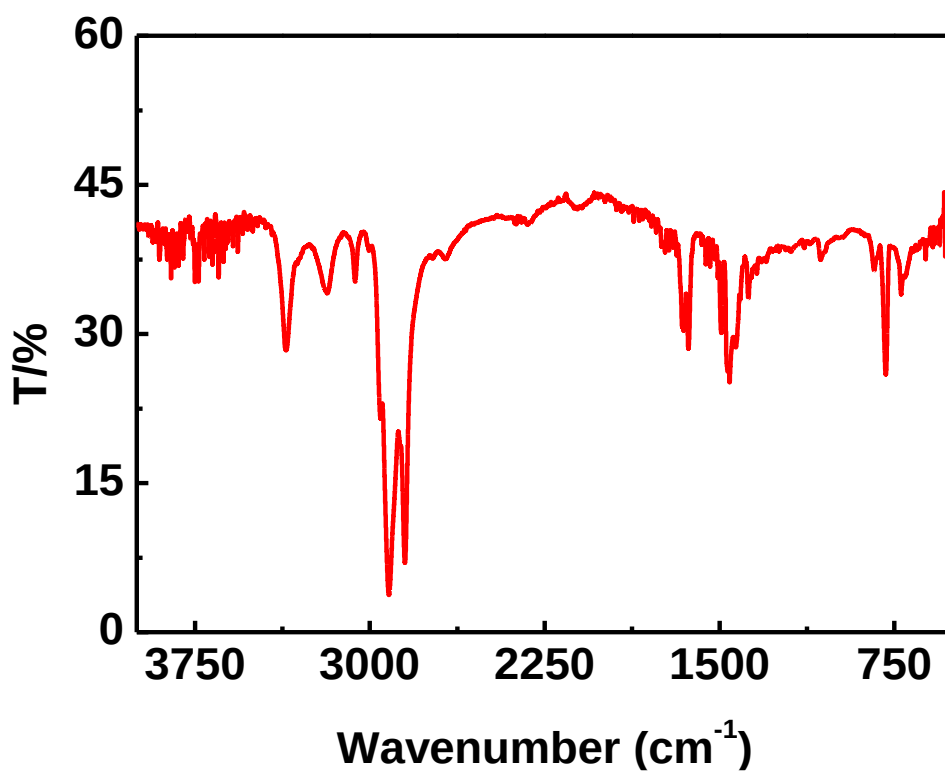
Supplementary Fig. 98. ^1H NMR (500 MHz) spectra of **P3-Stille** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.

PD: 2.8736

S189

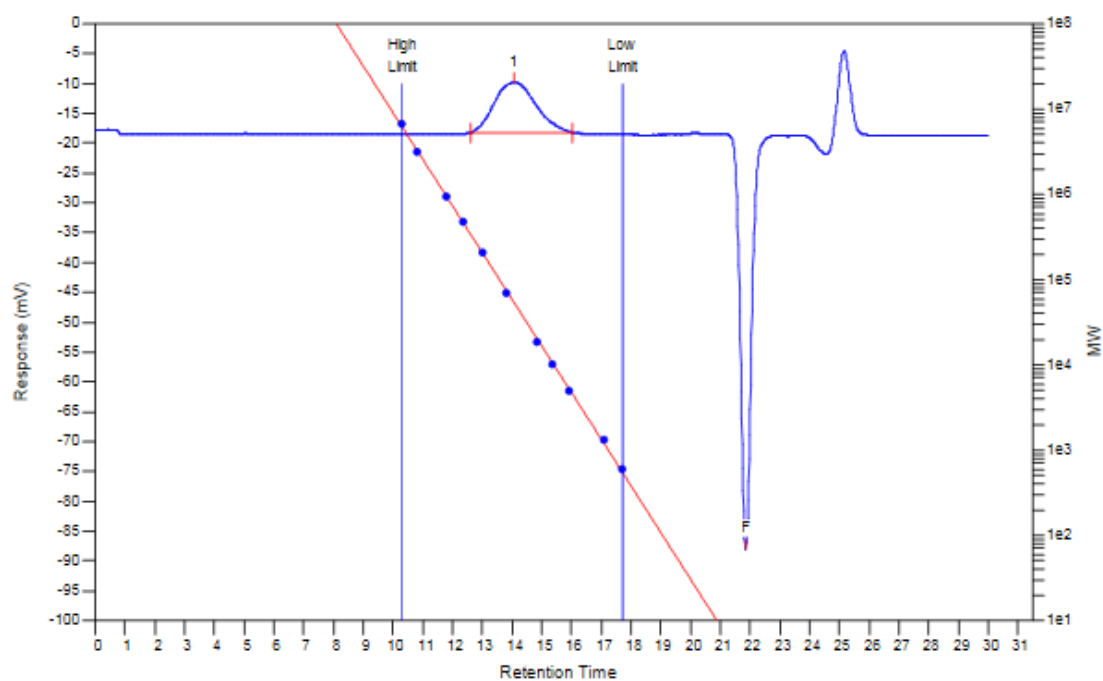


Supplementary Fig. 100. ^1H NMR (500 MHz) spectra of **P4** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 101. FT-IR spectrum of **P4** in thin film at 298 K.

(a)

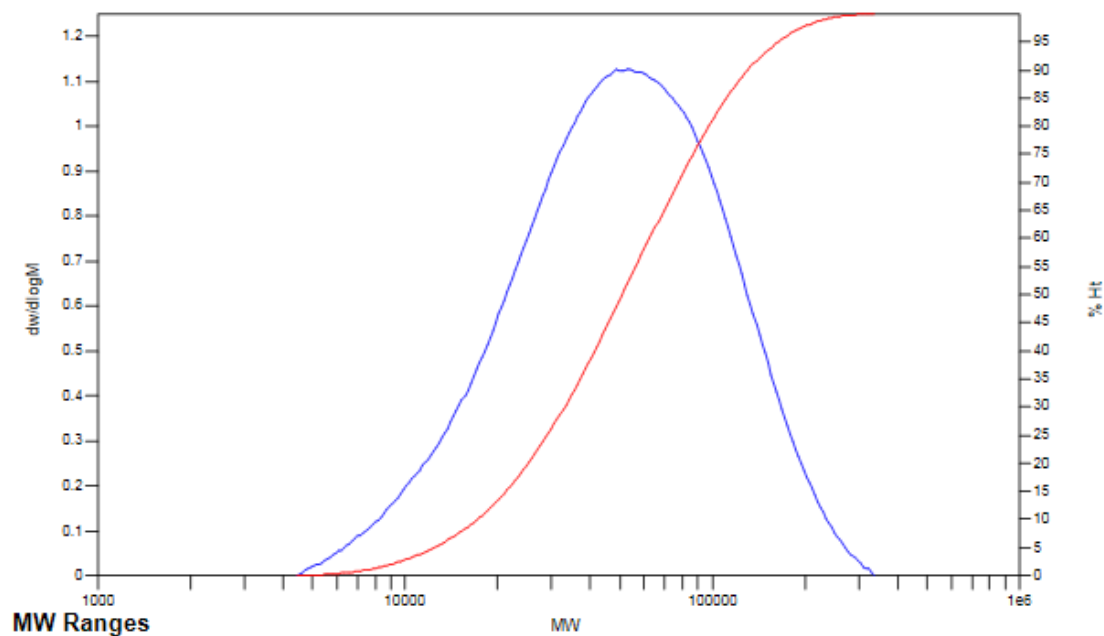


(b)

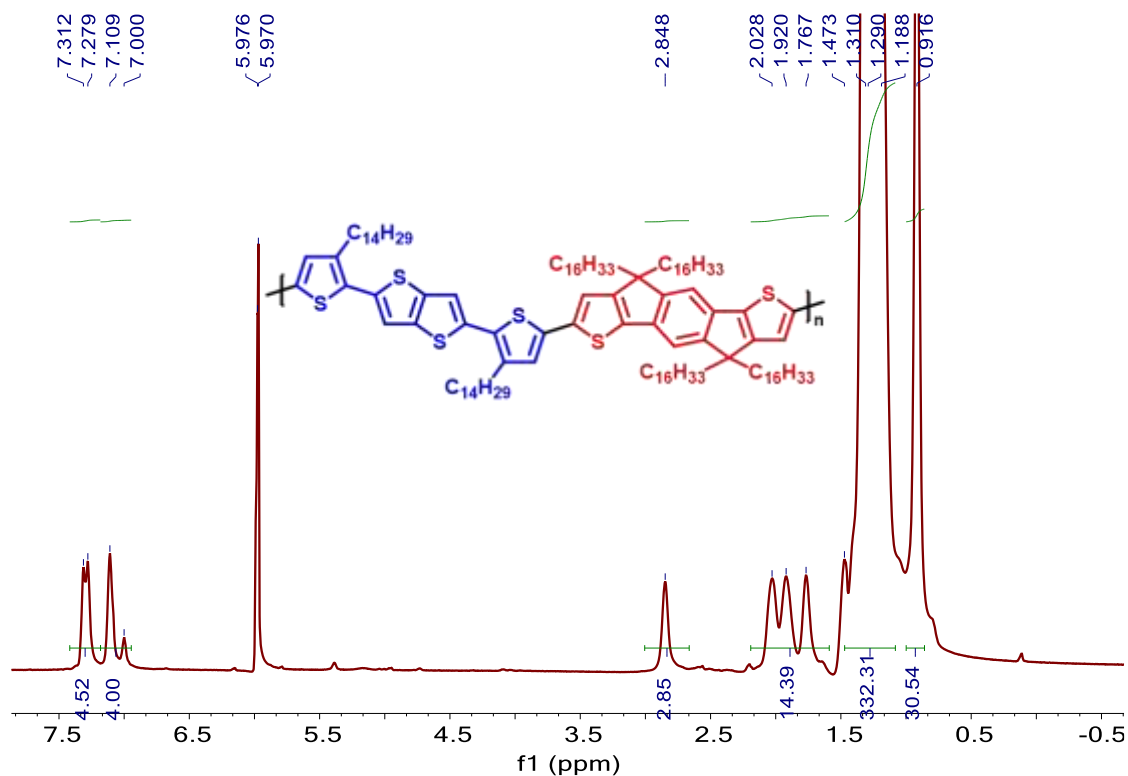
MW Averages

Mp: 54028	Mn: 35369	Mv: 59181	Mw: 63849
Mz: 100214	Mz+1: 136805	PD: 1.8052	

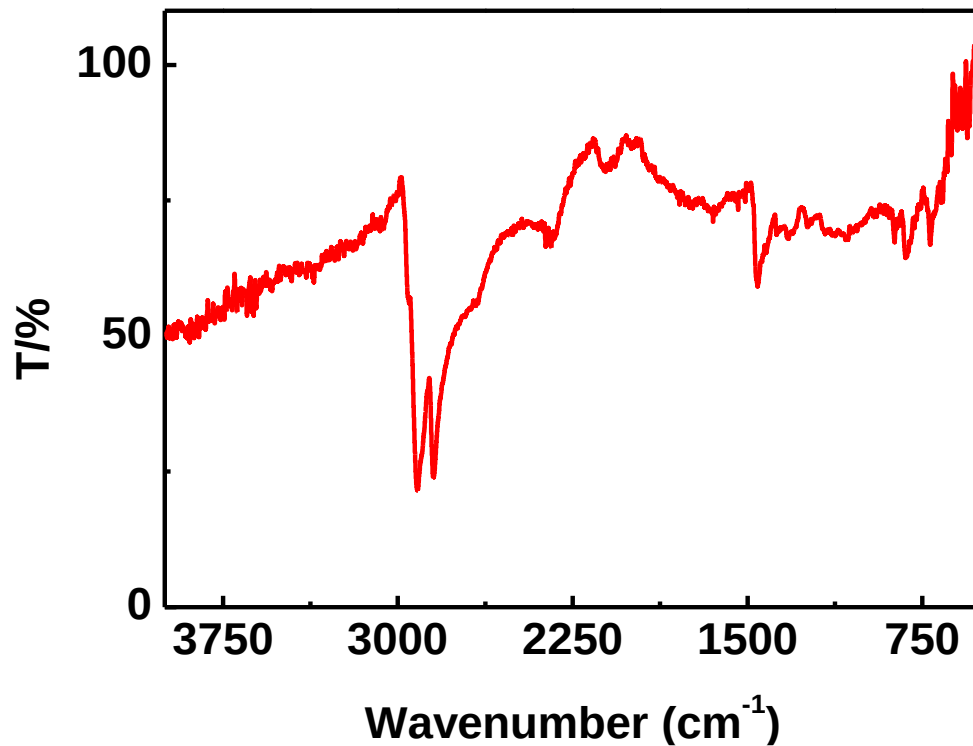
Distribution Plots



Supplementary Fig. 102. Gel permeation chromatography (GPC) trace of **P4**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P4**.

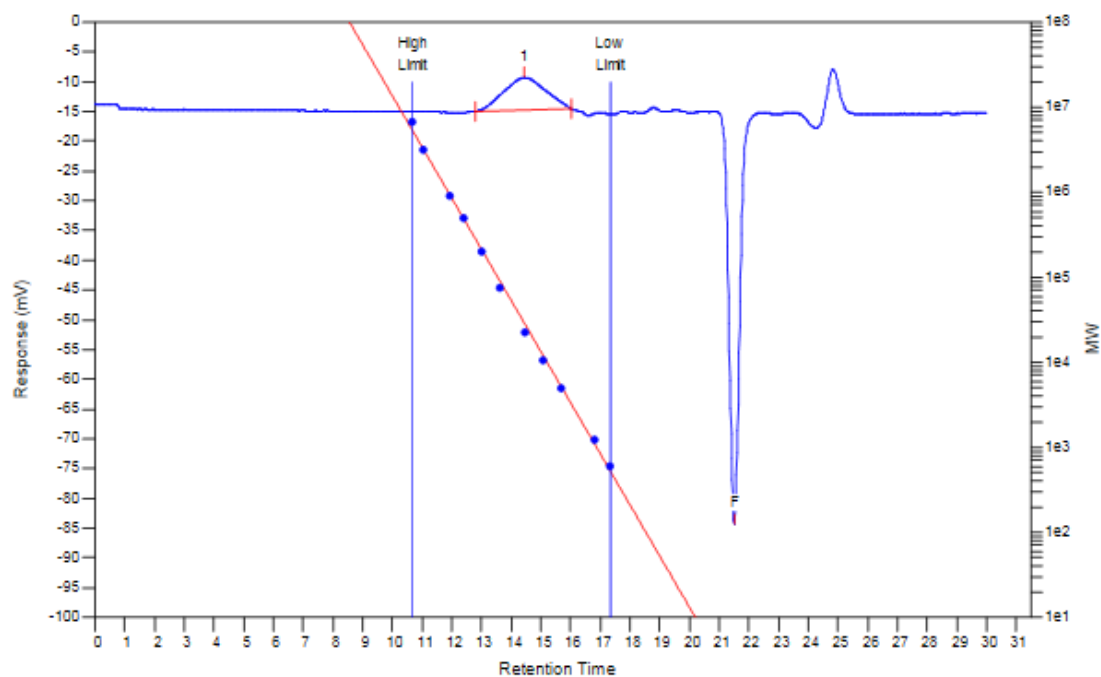


Supplementary Fig. 103. ¹H NMR (500 MHz) spectra of **P5** in $C_2D_2Cl_4$ at 373 K.



Supplementary Fig. 104. FT-IR spectrum of **P5** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 30085

Mn: 20548

Mv: 38012

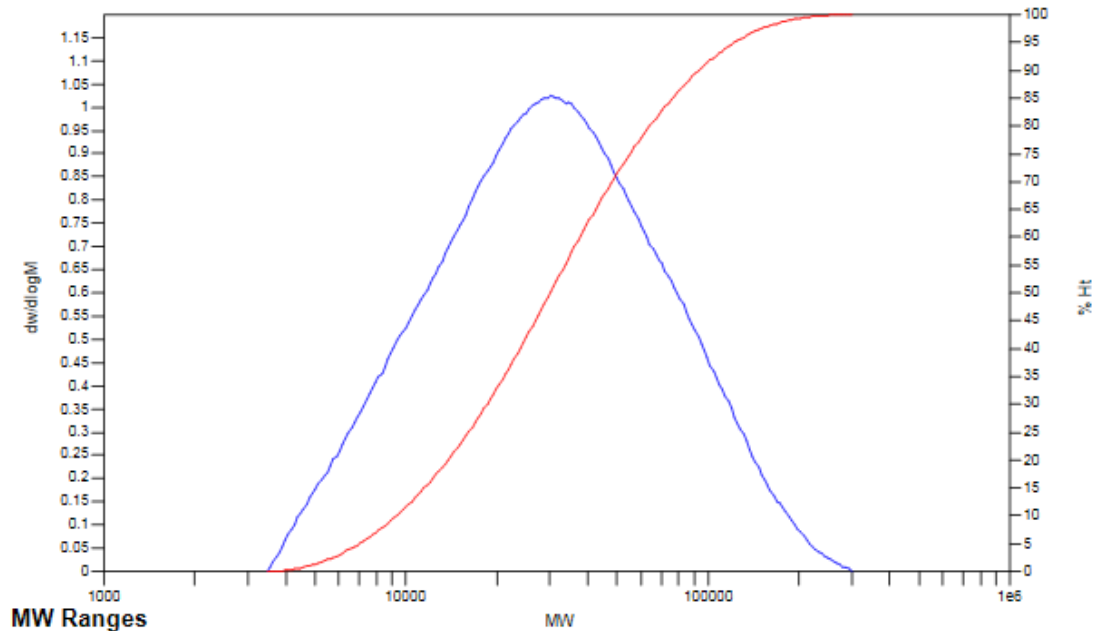
Mw: 42021

Mz: 76659

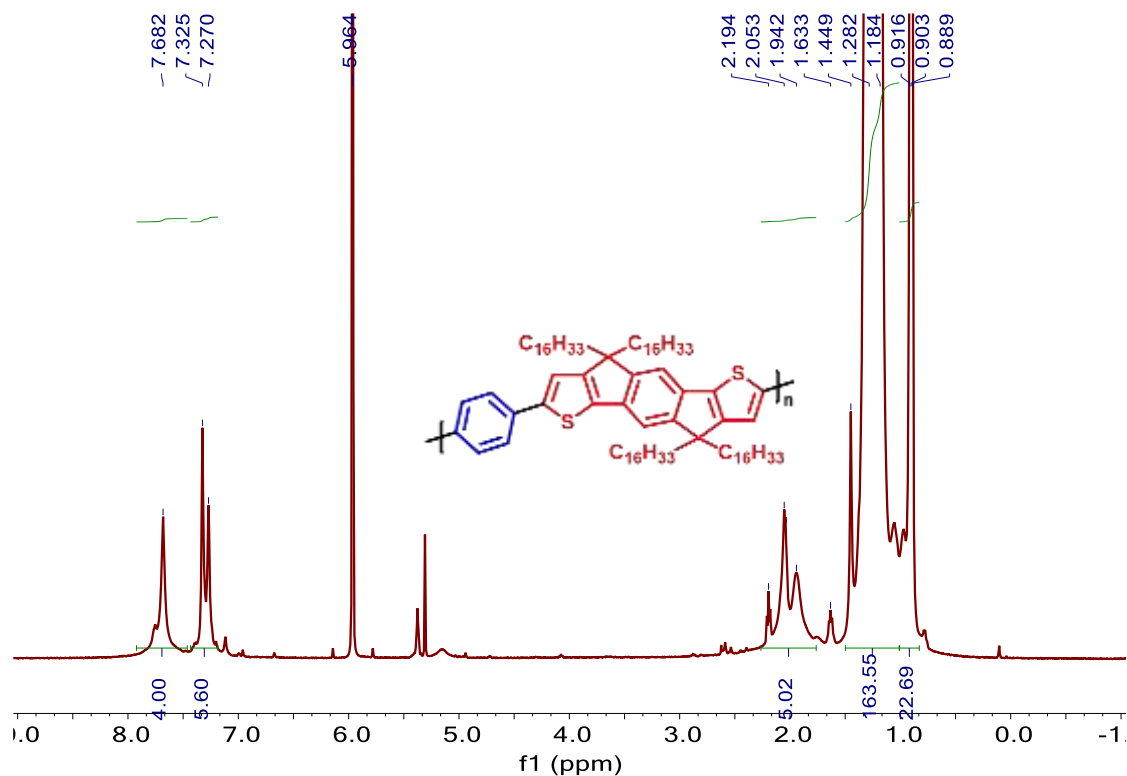
Mz+1: 114442

PD: 2.0450

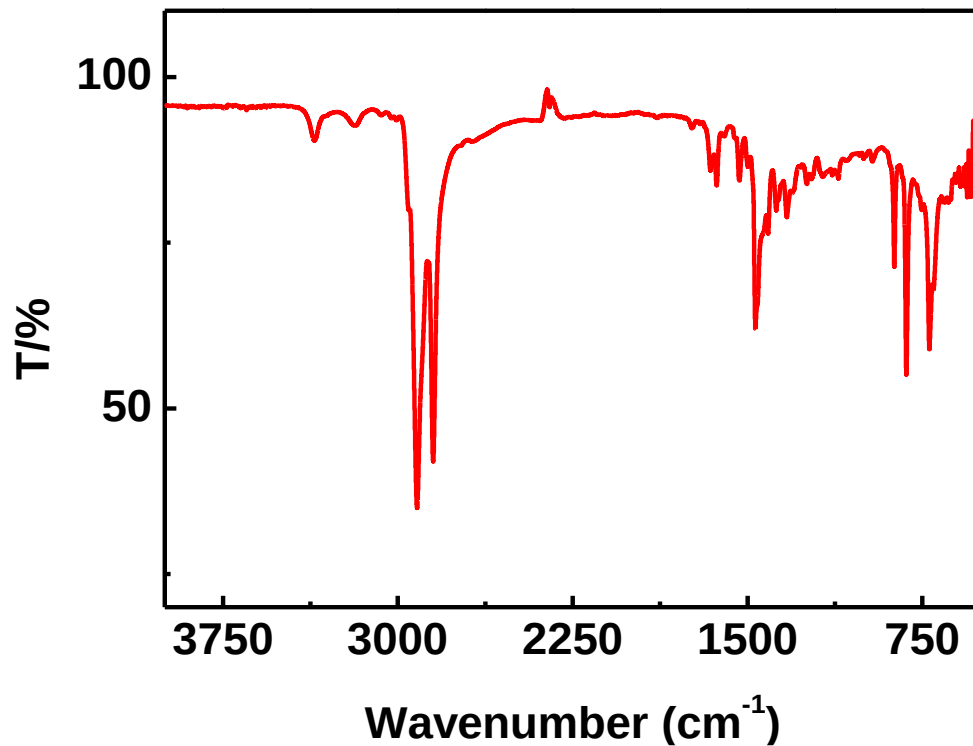
Distribution Plots



Supplementary Fig. 105. Gel permeation chromatography (GPC) trace of **P5**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P5**.

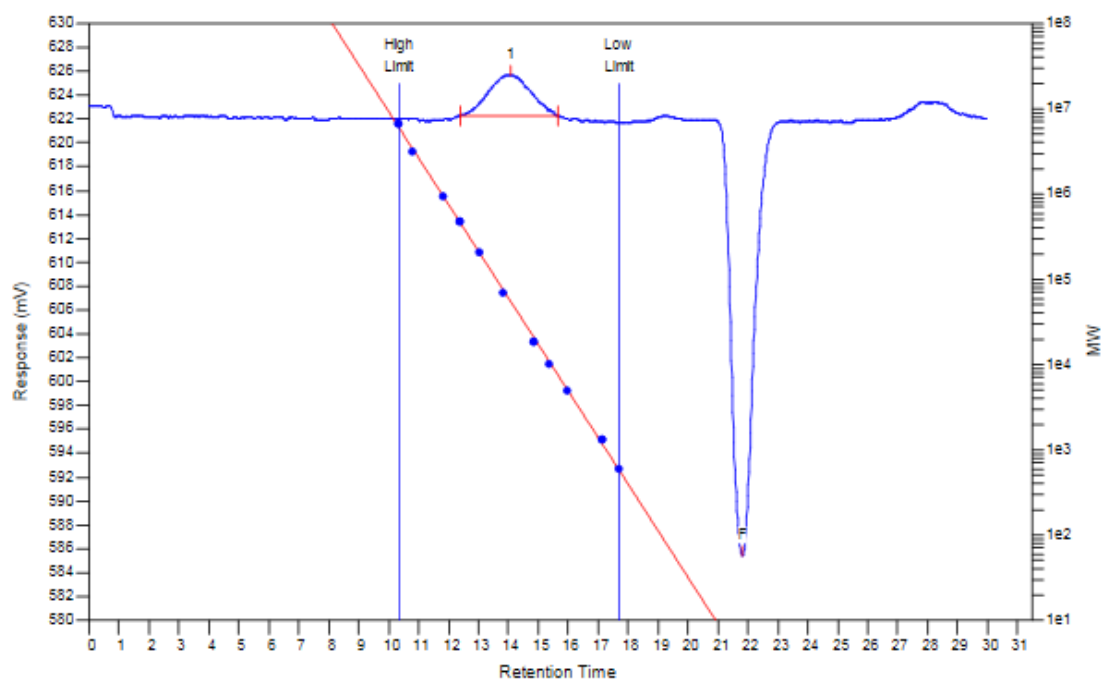


Supplementary Fig. 106. ¹H NMR (500 MHz) spectra of **P6** in C₂D₂Cl₄ at 373 K.



Supplementary Fig. 107 FT-IR spectrum of **P6** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 54723

Mn: 42371

Mv: 69537

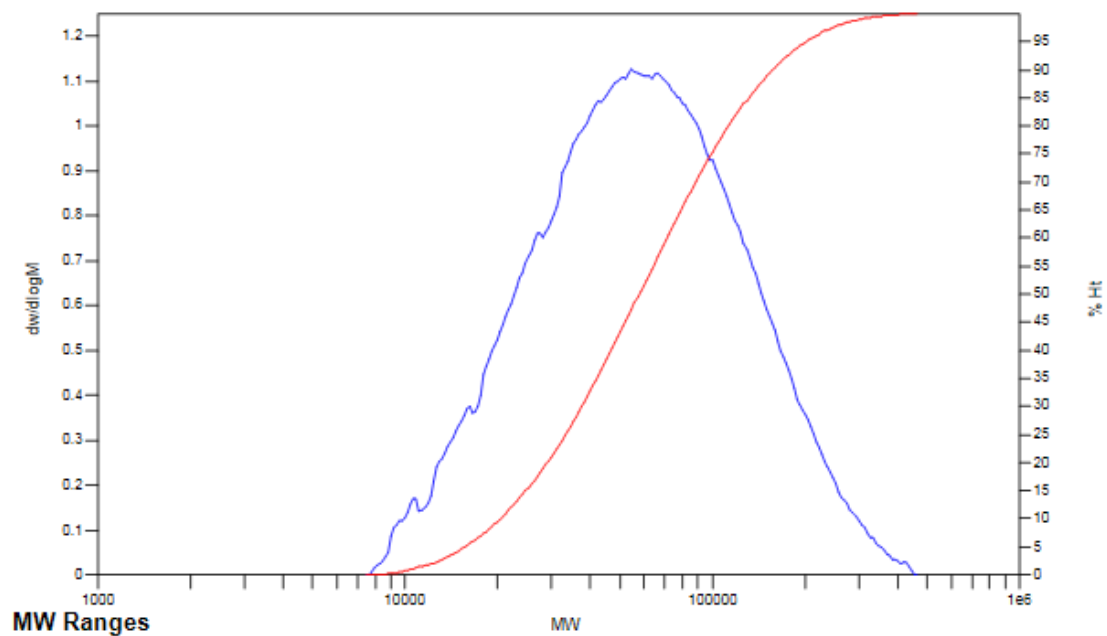
Mw: 75417

Mz: 124443

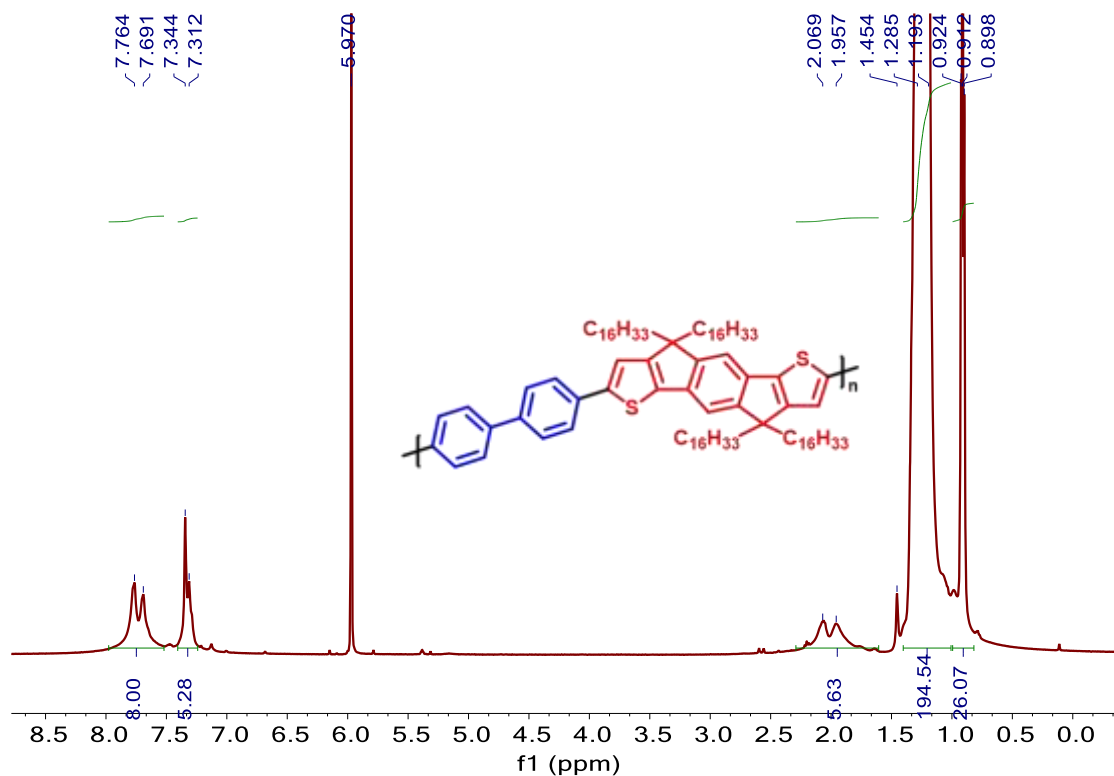
Mz+1: 179119

PD: 1.7799

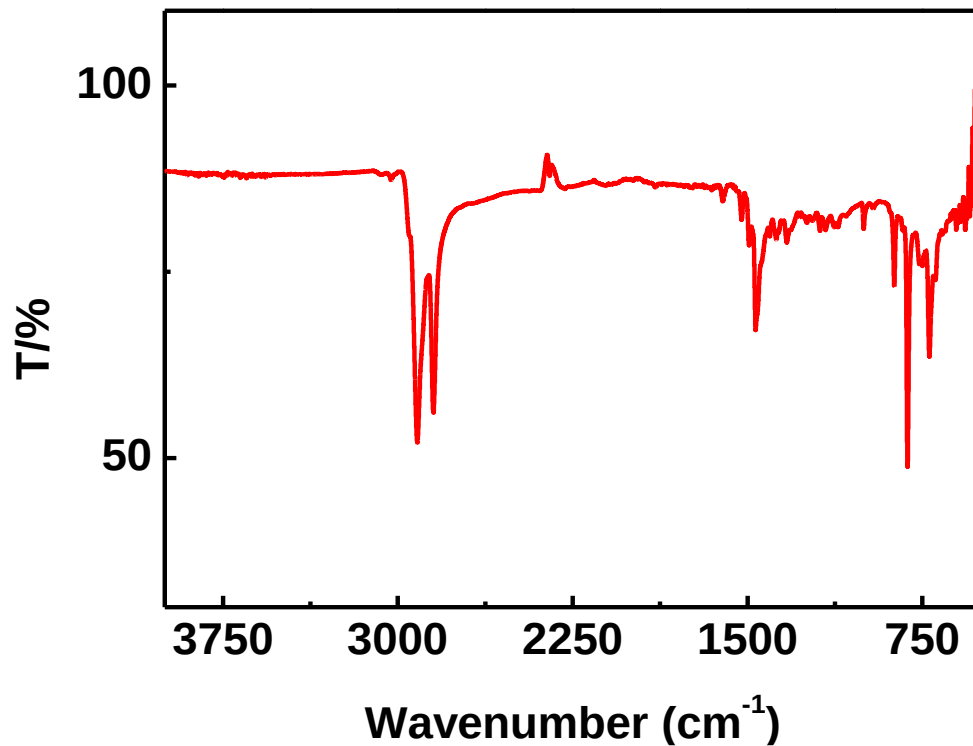
Distribution Plots



Supplementary Fig. 108. Gel permeation chromatography (GPC) trace of **P6**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P6**.

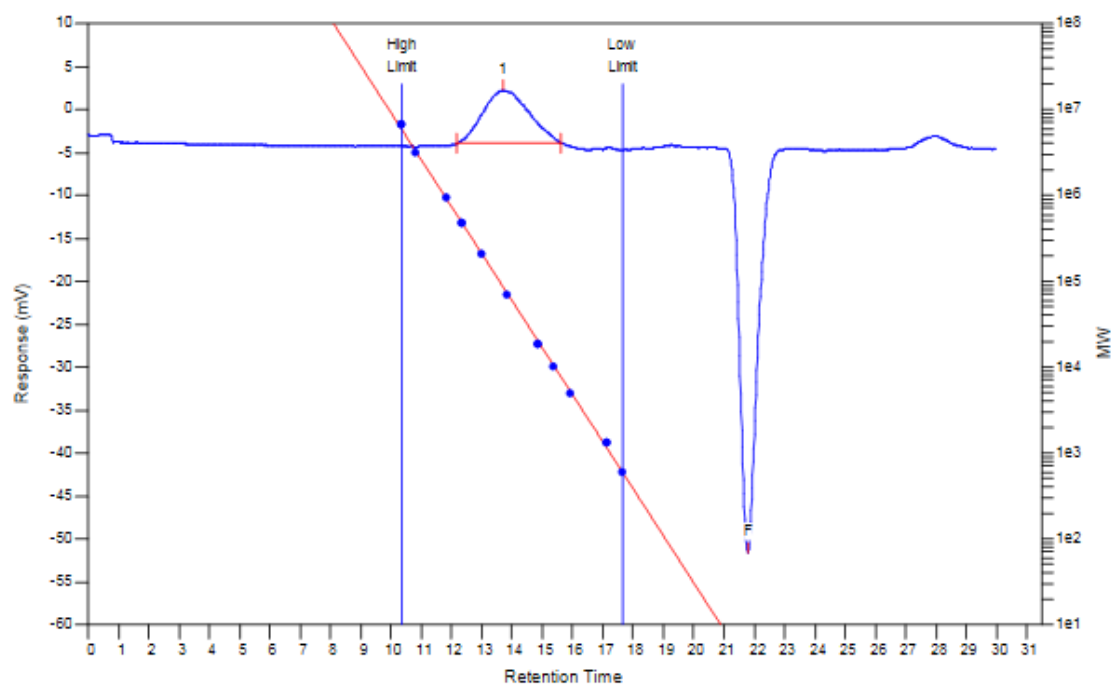


Supplementary Fig. 109. 1H NMR (500 MHz) spectra of **P7** in $C_2D_2Cl_4$ at 373 K.



Supplementary Fig. 110. FT-IR spectrum of **P7** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 86351

Mn: 50910

Mv: 91318

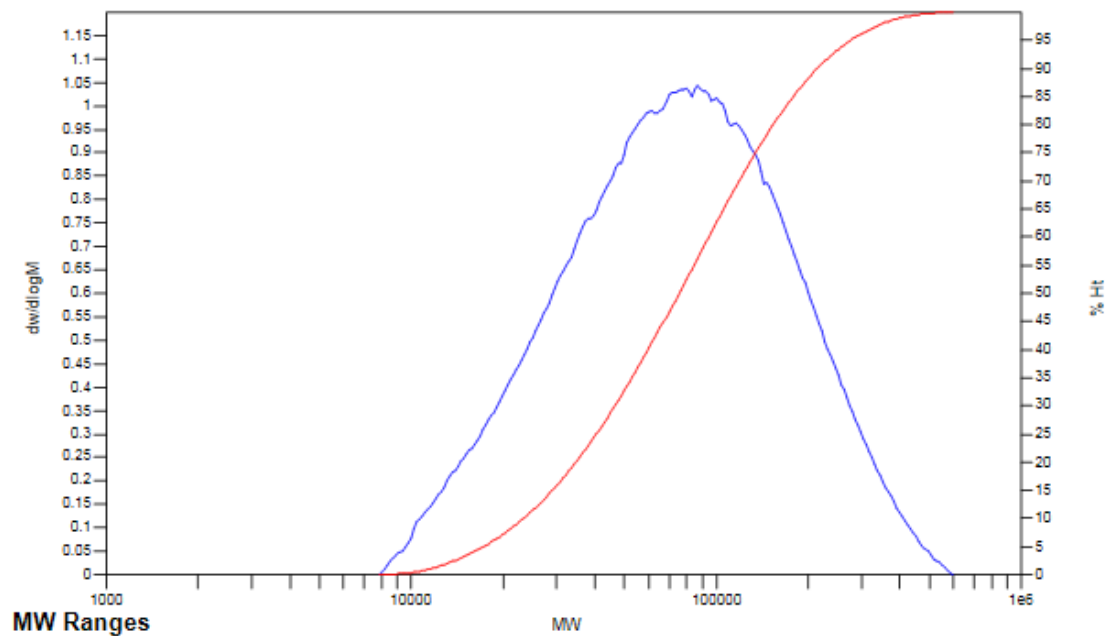
Mw: 99921

Mz: 170070

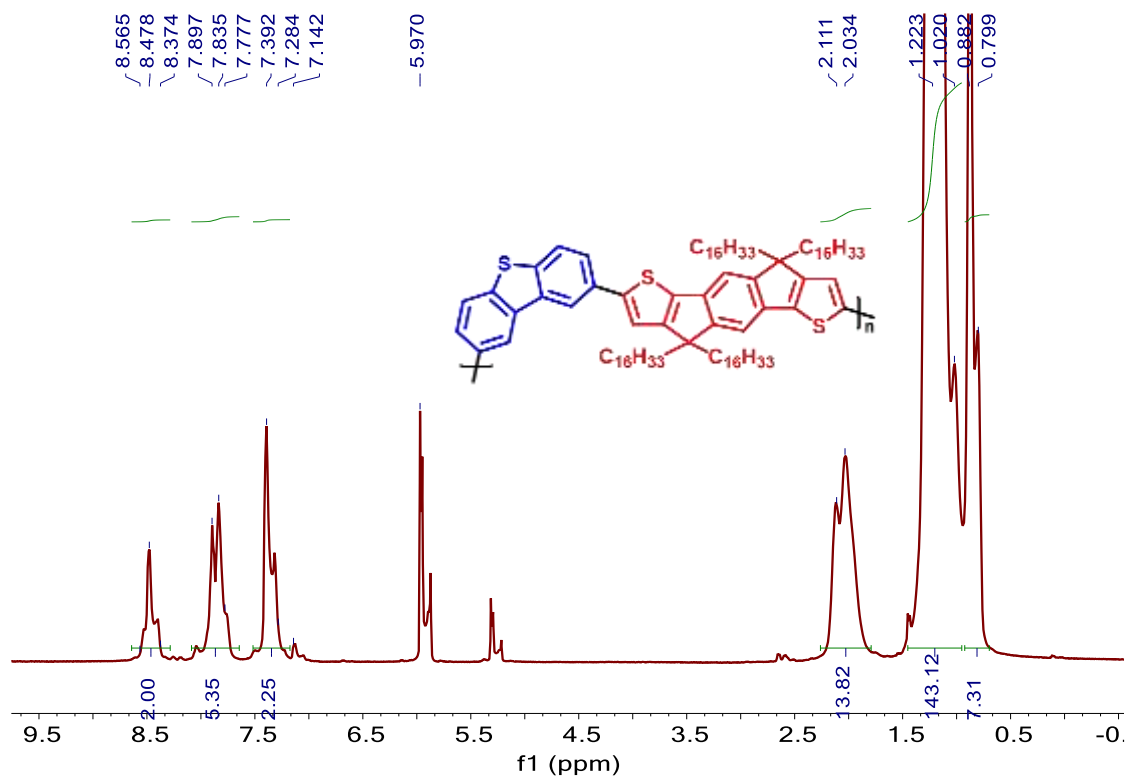
Mz+1: 242051

PD: 1.9627

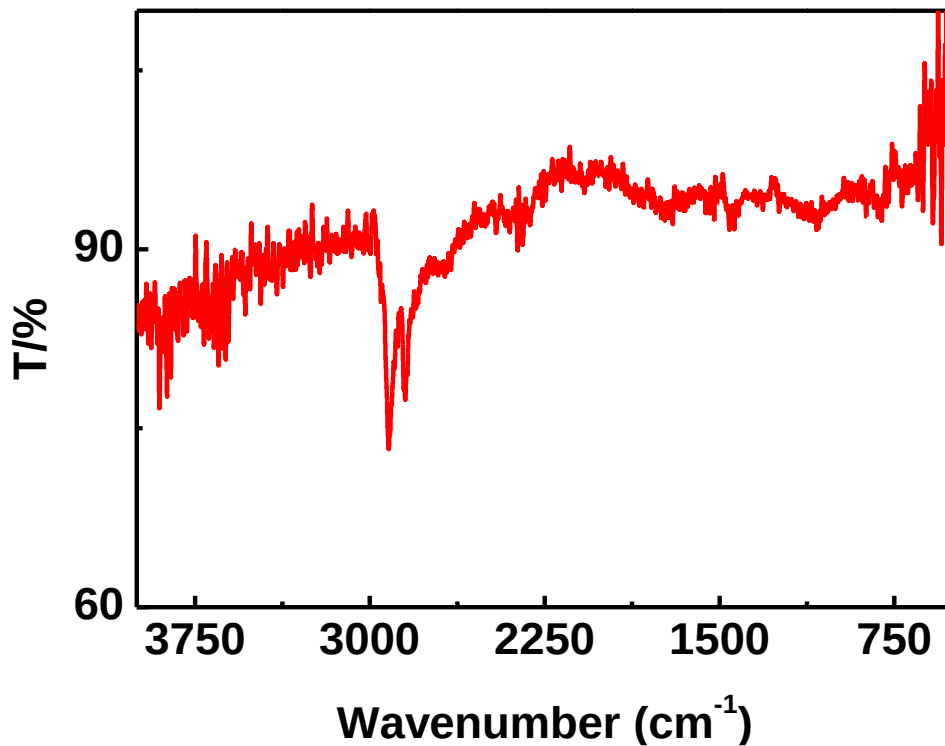
Distribution Plots



Supplementary Fig. 111. Gel permeation chromatography (GPC) trace of **P7**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P7**.

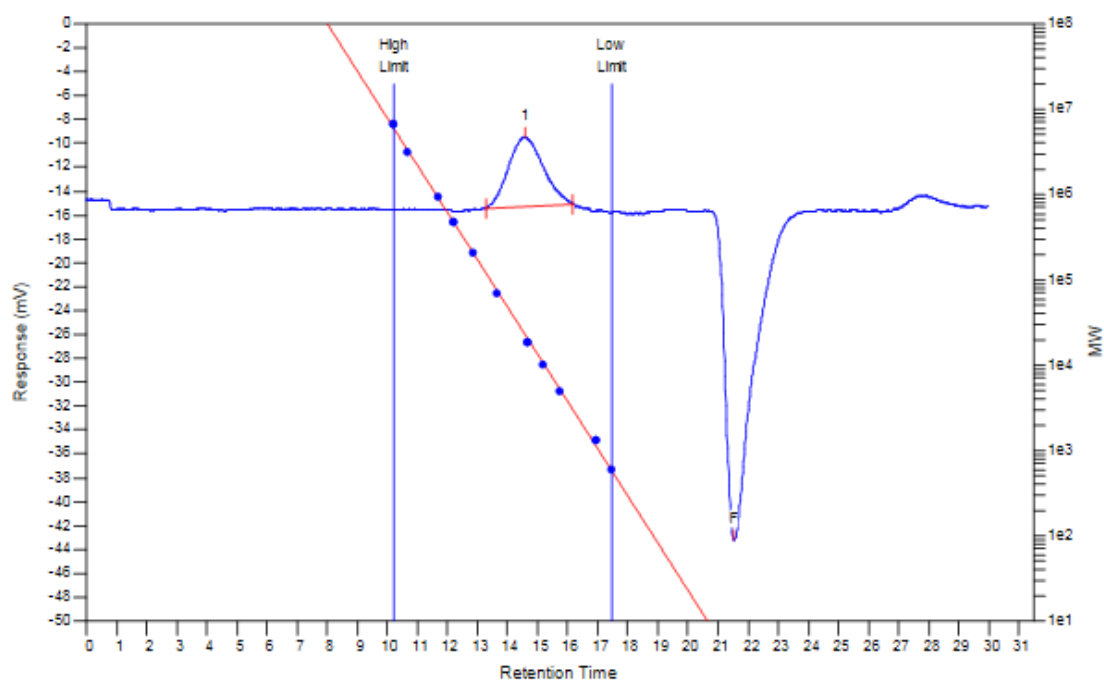


Supplementary Fig. 112. ¹H NMR (500 MHz) spectra of **P8** in $C_2D_2Cl_4$ at 373 K.



Supplementary Fig. 113. FT-IR spectrum of **P8** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 23397

Mn: 16739

Mv: 24516

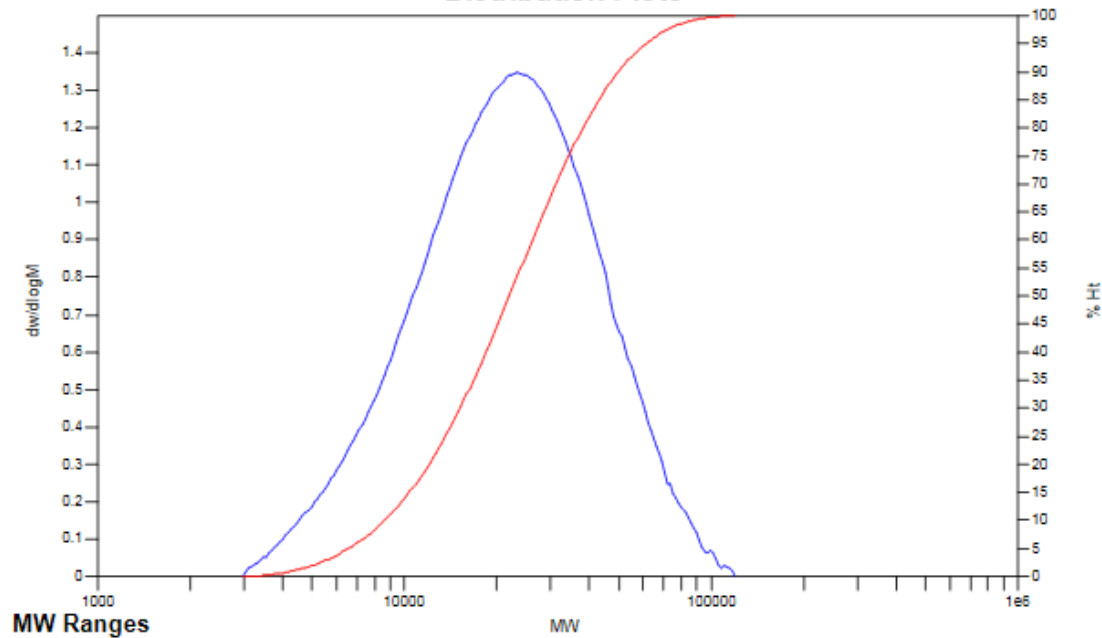
Mw: 26003

Mz: 37392

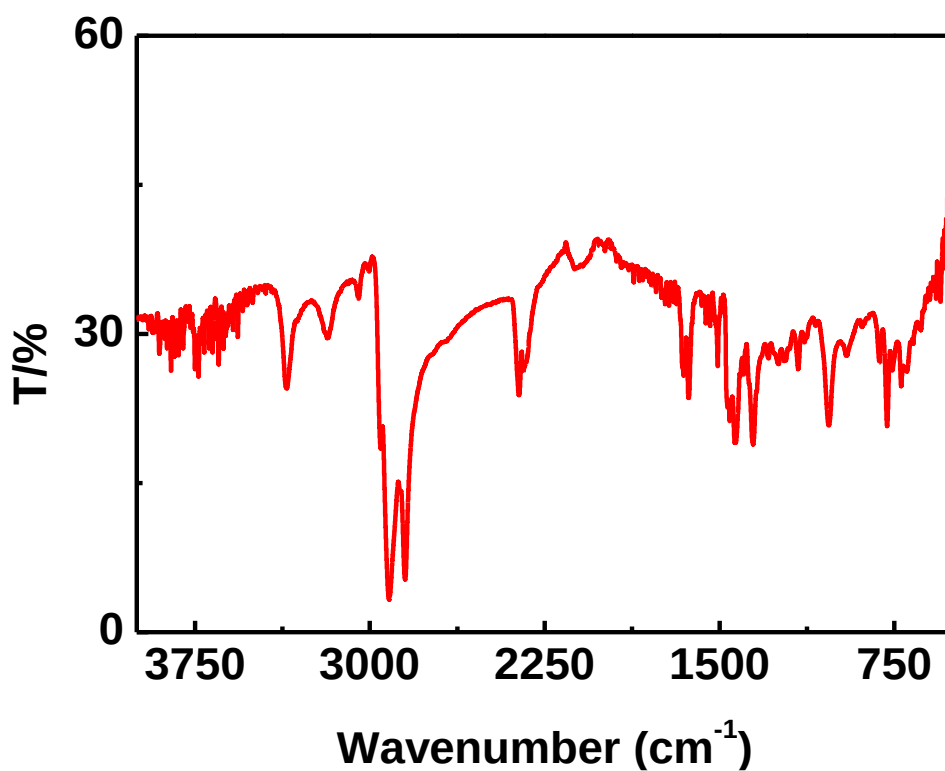
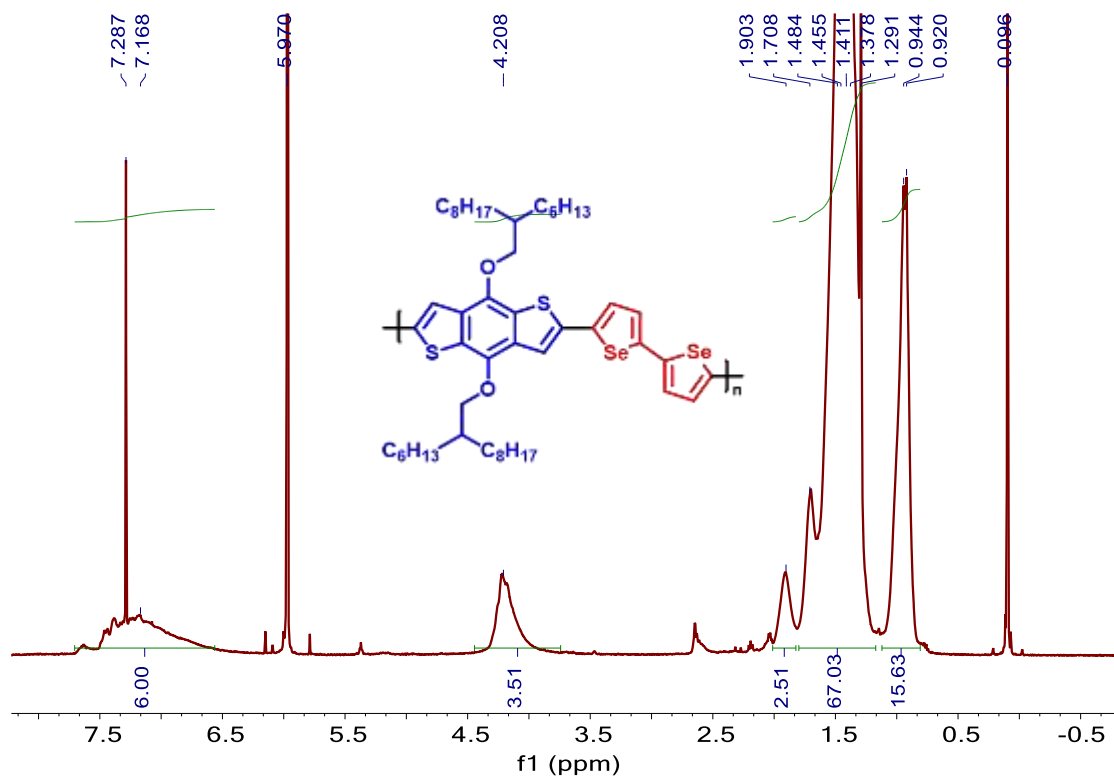
Mz+1: 49251

PD: 1.5534

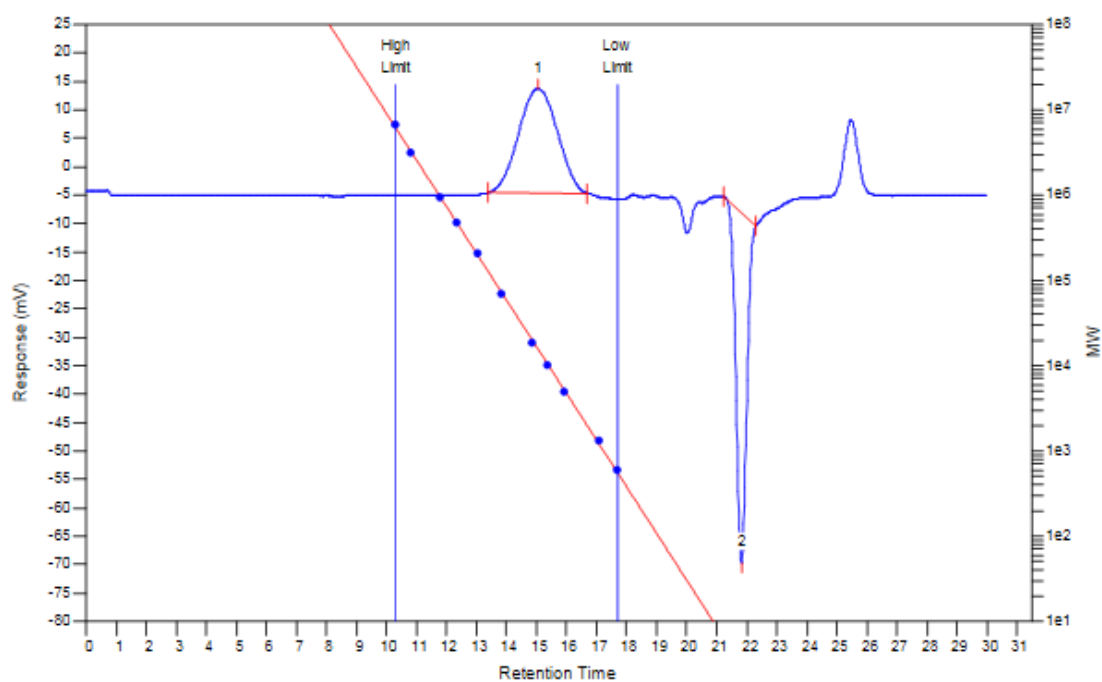
Distribution Plots



Supplementary Fig. 114. Gel permeation chromatography (GPC) trace of **P8**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P8**.



(a)



(b)

MW Averages

Mp: 15639

Mn: 12123

Mv: 18549

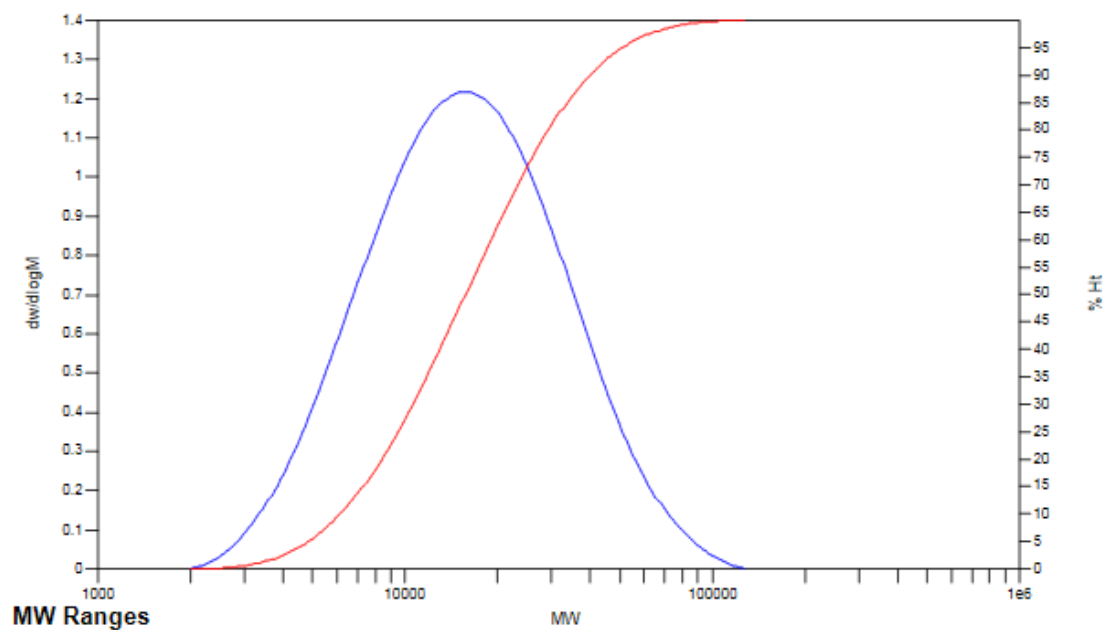
Mw: 19930

Mz: 31491

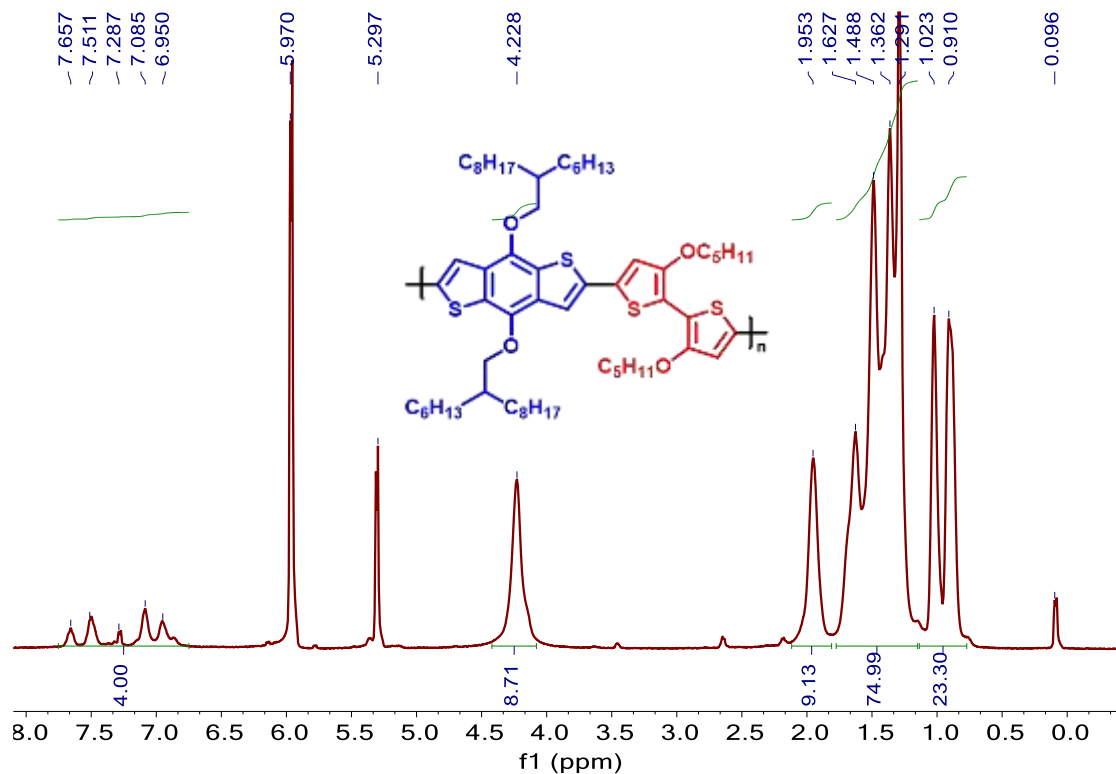
Mz+1: 45163

PD: 1.6440

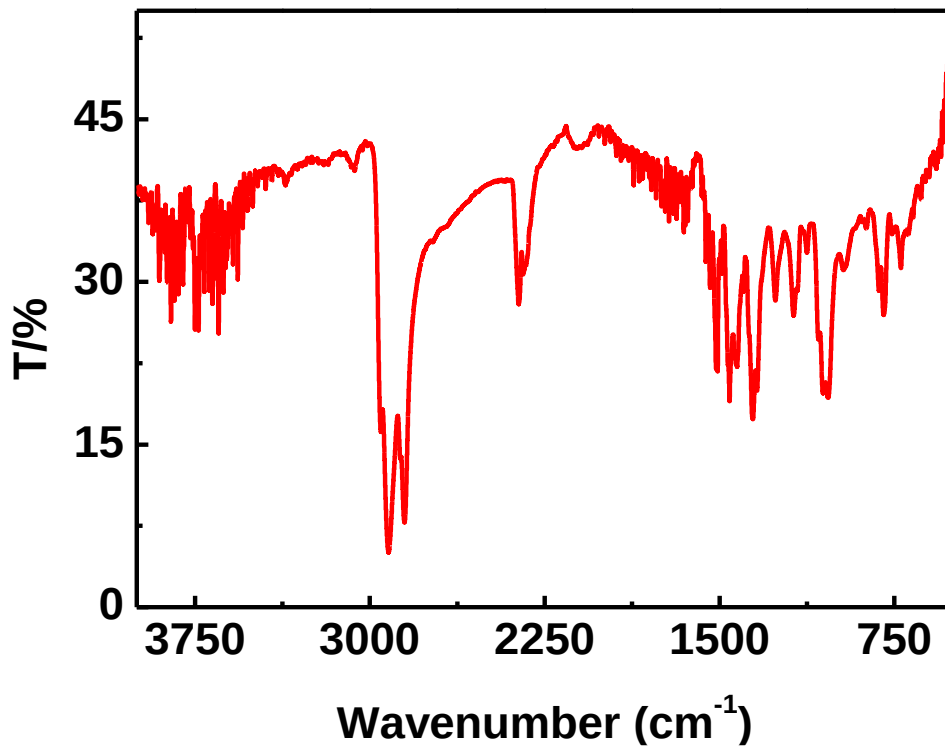
Distribution Plots



Supplementary Fig. 117. Gel permeation chromatography (GPC) trace of **P9**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P9**.

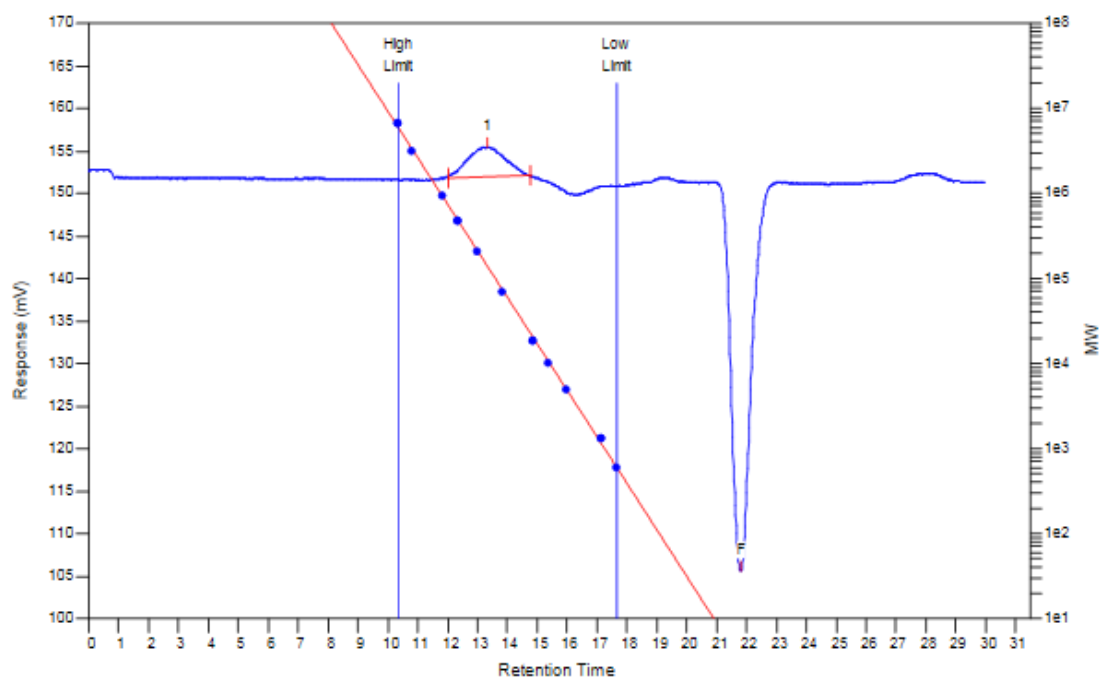


Supplementary Fig. 118. 1H NMR (500 MHz) spectra of **P10** in $C_2D_2Cl_4$ at 373 K.



Supplementary Fig. 119. FT-IR spectrum of **P10** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 138866

Mn: 110850

Mv: 164121

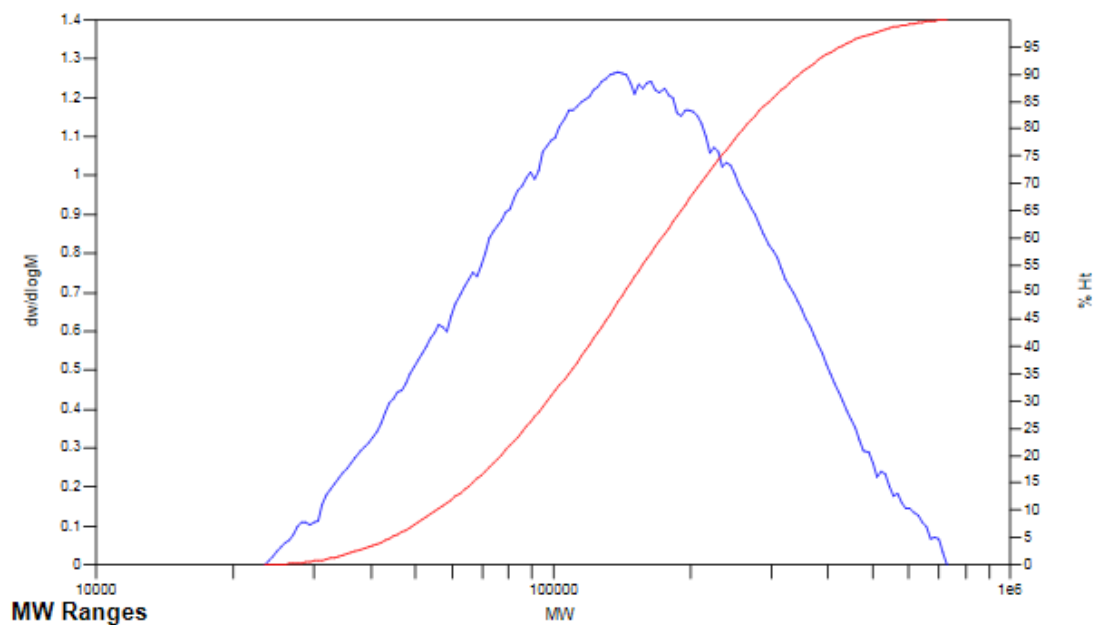
Mw: 174775

Mz: 256940

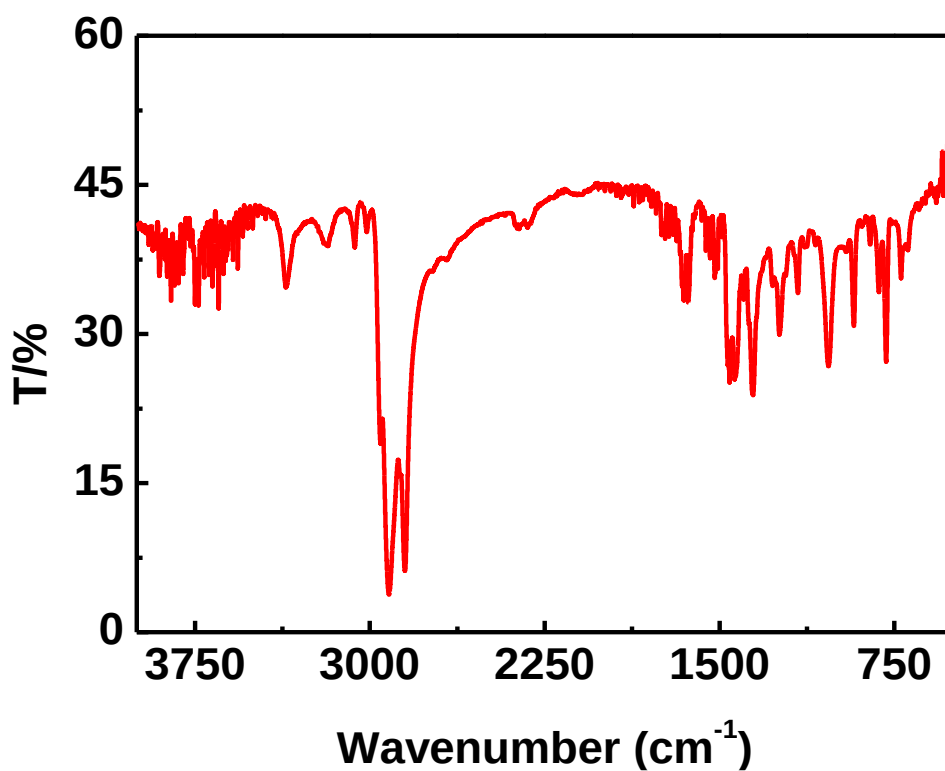
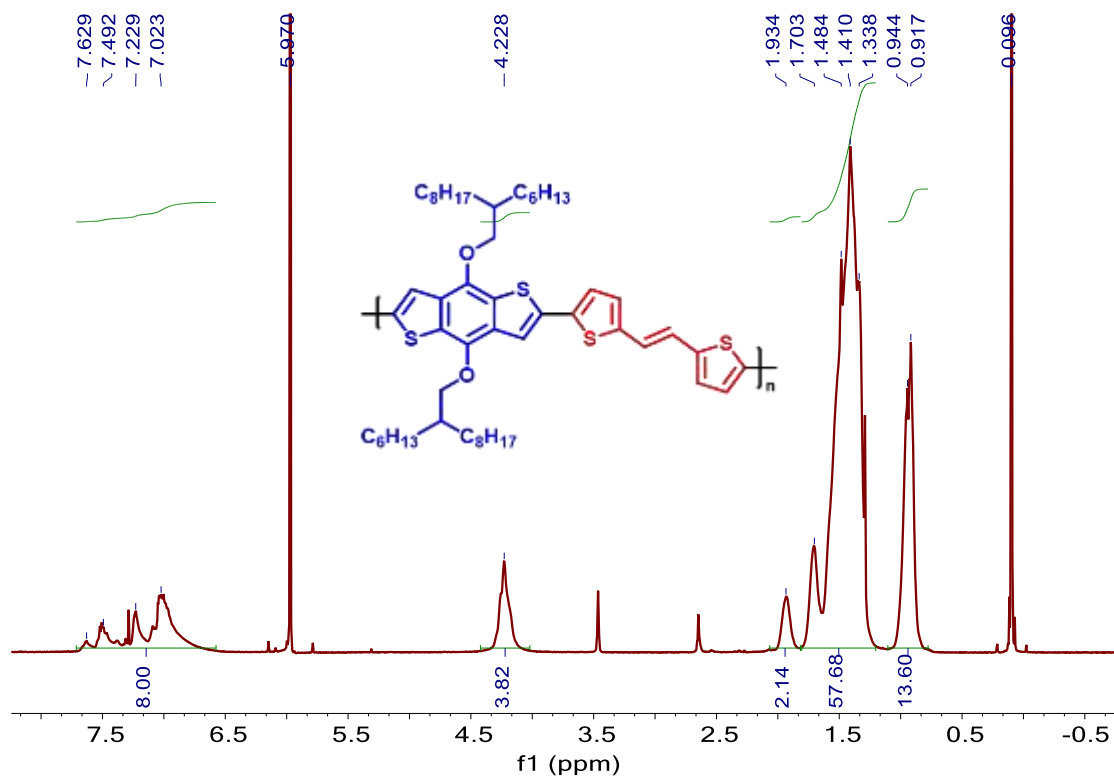
Mz+1: 339347

PD: 1.5767

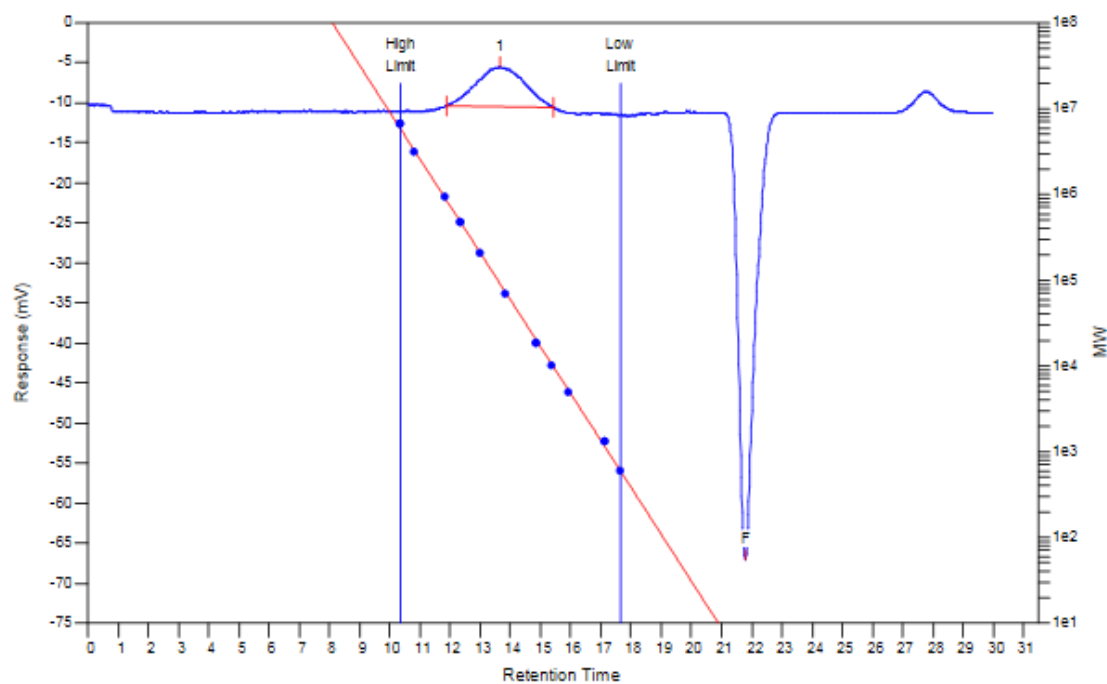
Distribution Plots



Supplementary Fig. 120. Gel permeation chromatography (GPC) trace of **P10**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P10**.



(a)



(b)

MW Averages

Mp: 91969

Mn: 61651

Mv: 115338

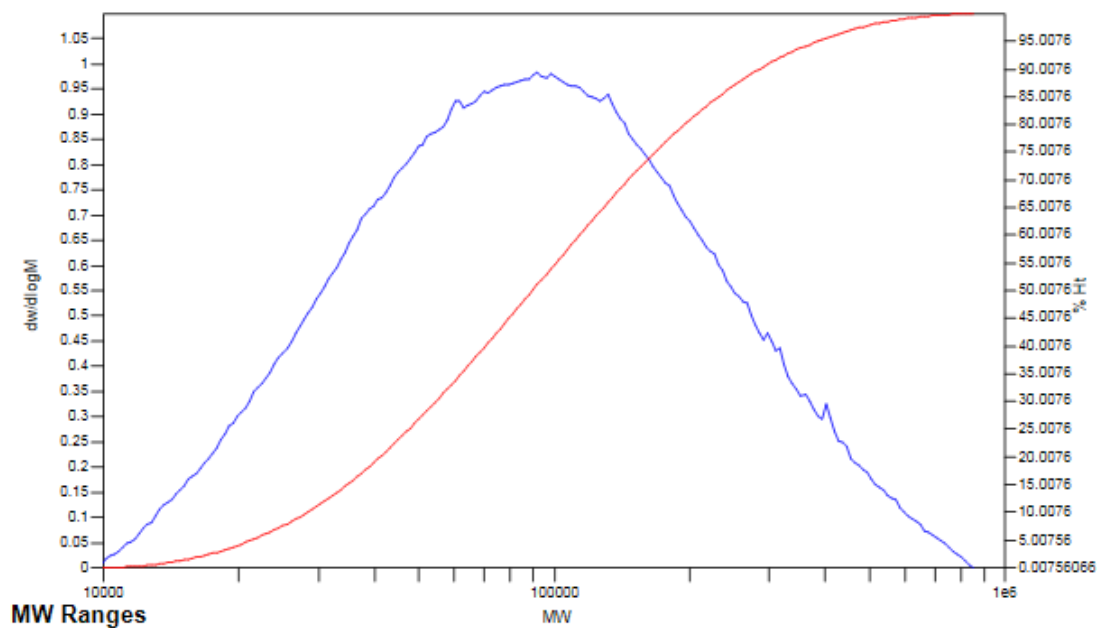
Mw: 127941

Mz: 238195

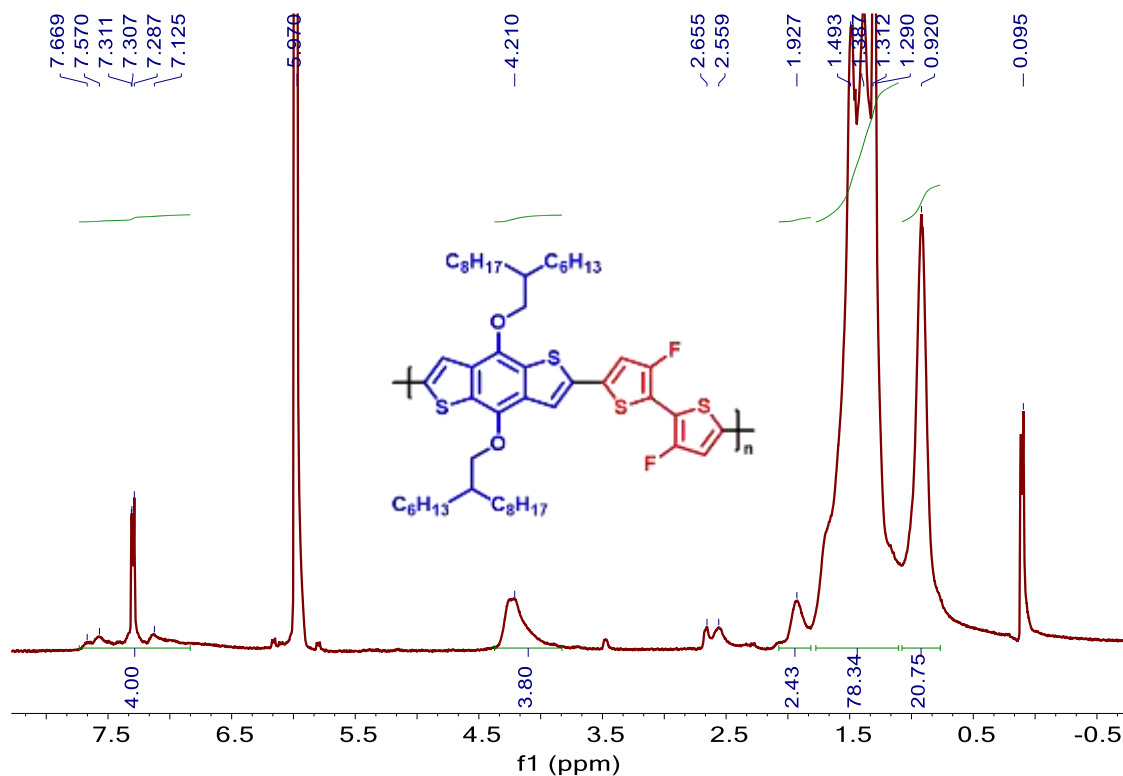
Mz+1: 357416

PD: 2.0752

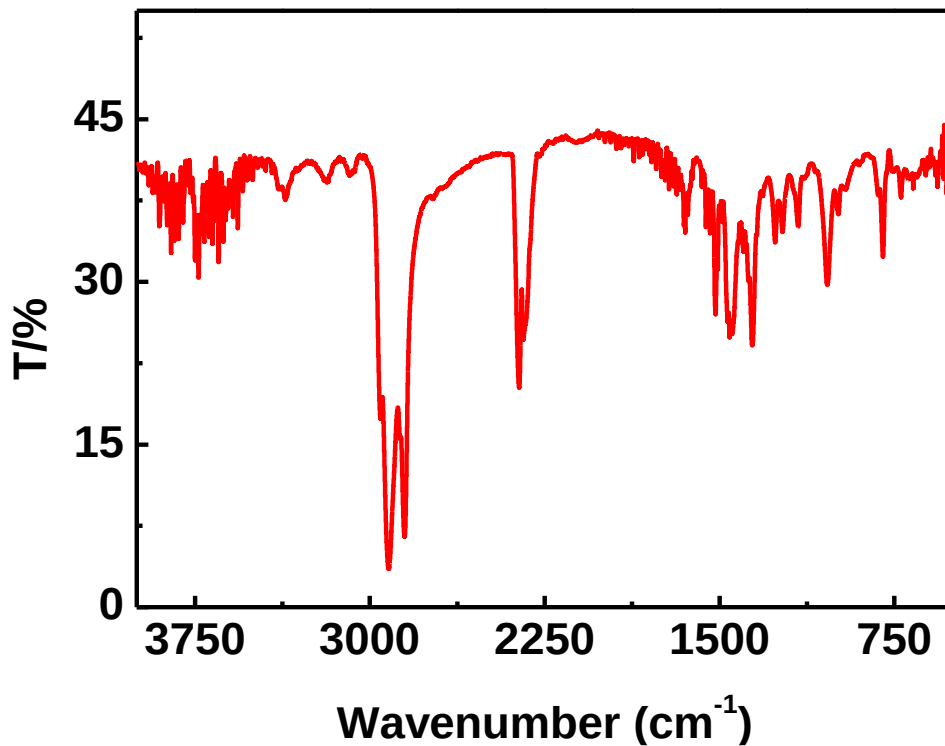
Distribution Plots



Supplementary Fig. 123. Gel permeation chromatography (GPC) trace of **P11**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P11**.

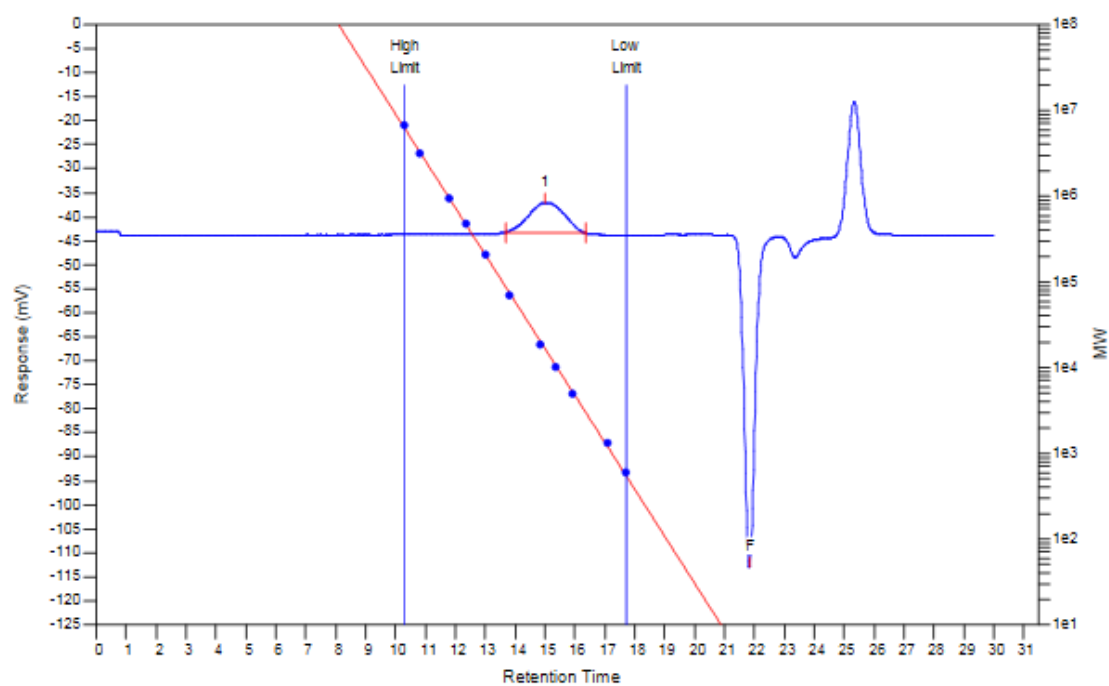


Supplementary Fig. 124. ¹H NMR (500 MHz) spectra of **P12** in C₂D₂Cl₄ at 373 K.



Supplementary Fig. 125. FT-IR spectrum of **P12** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 16311

Mn: 12767

Mv: 17855

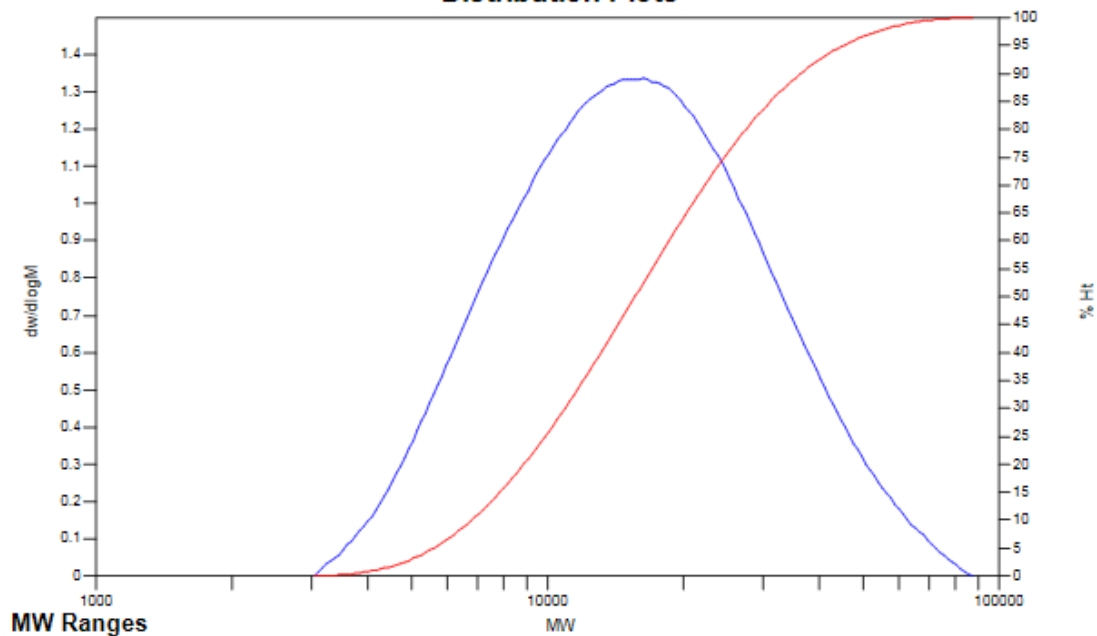
Mw: 18908

Mz: 27287

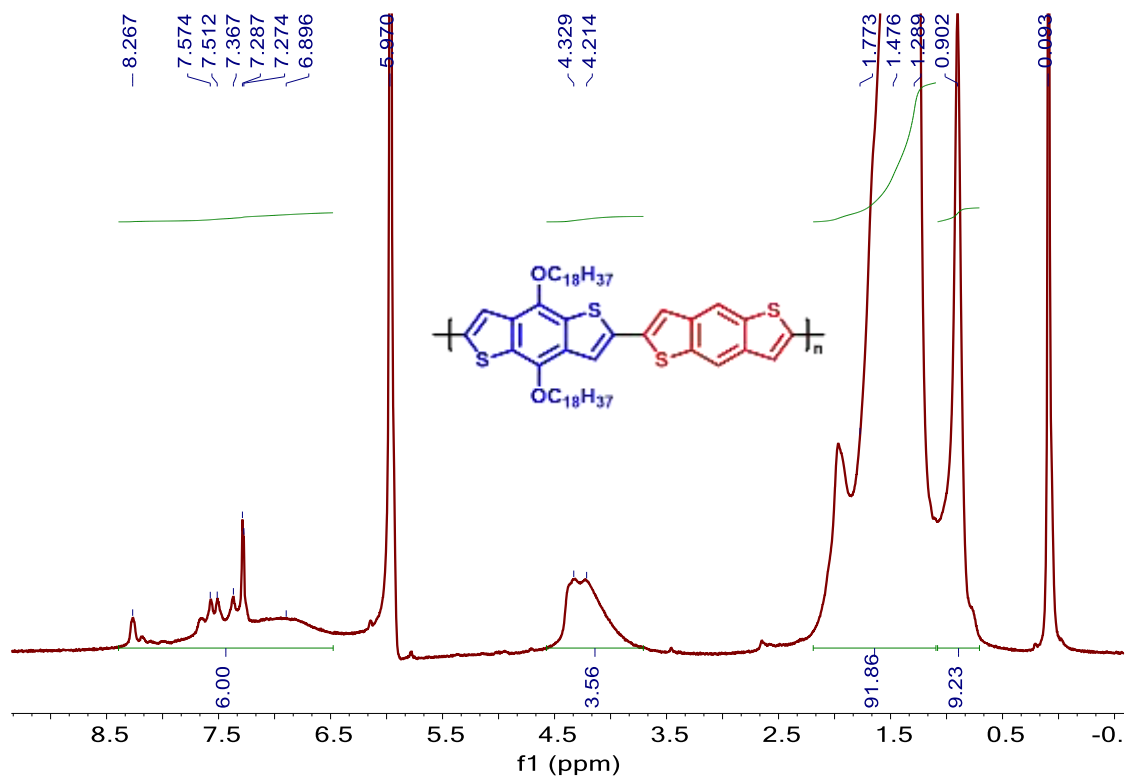
Mz+1: 36441

PD: 1.4810

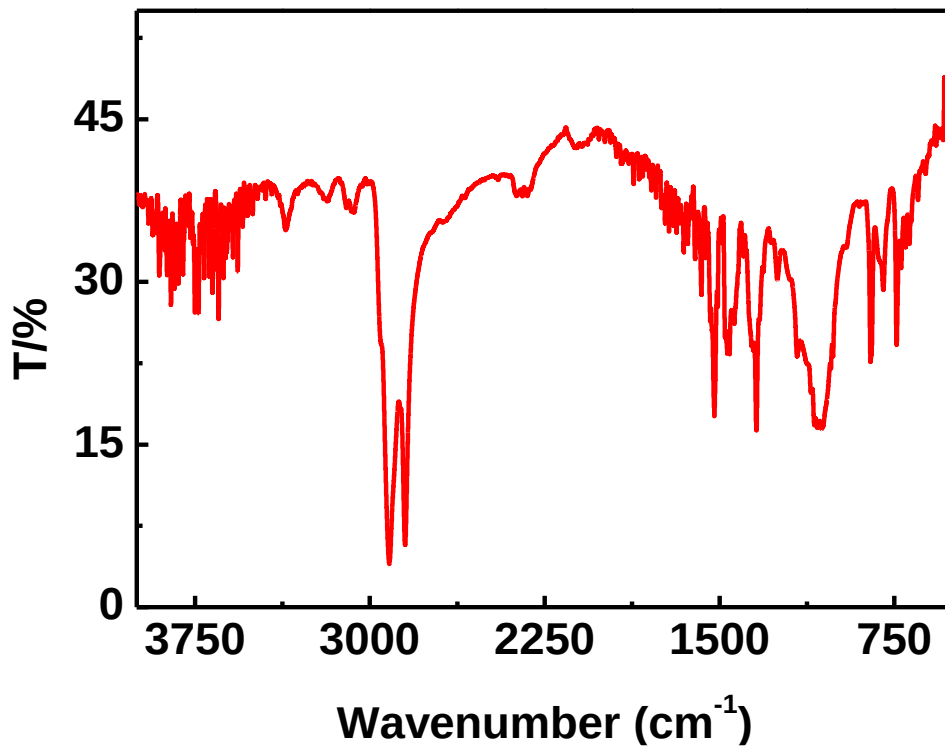
Distribution Plots



Supplementary Fig. 126. Gel permeation chromatography (GPC) trace of **P12**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P12**.

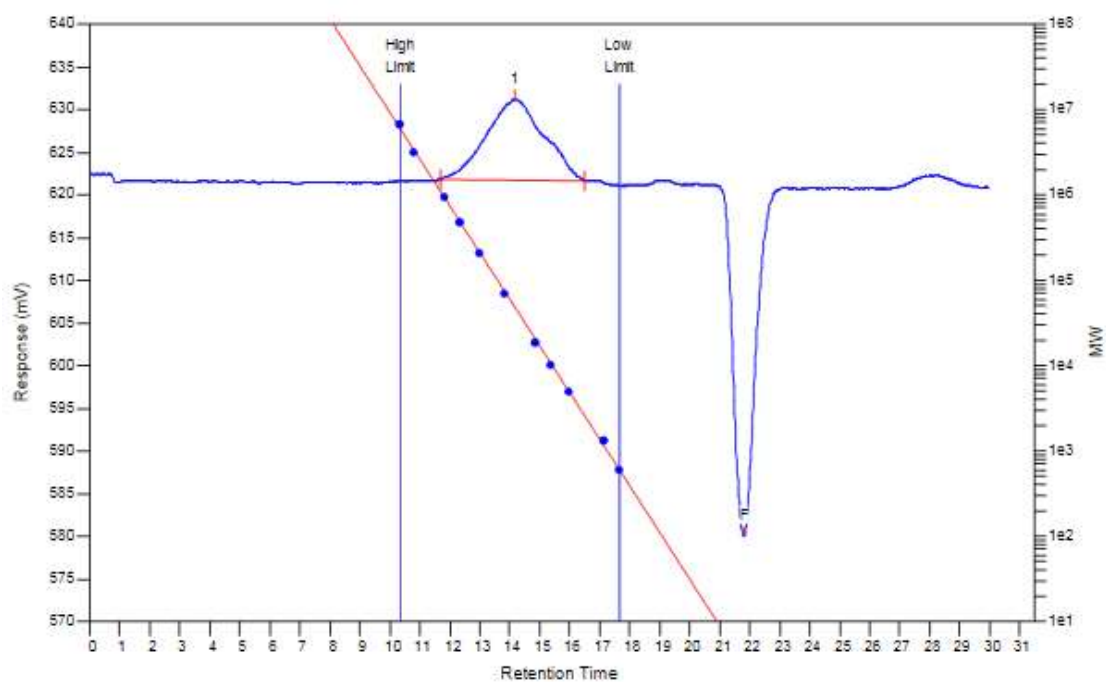


Supplementary Fig. 127. ^1H NMR (500 MHz) spectra of **P13** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 128. FT-IR spectrum of **P13** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 47596

Mn: 25888

Mv: 72780

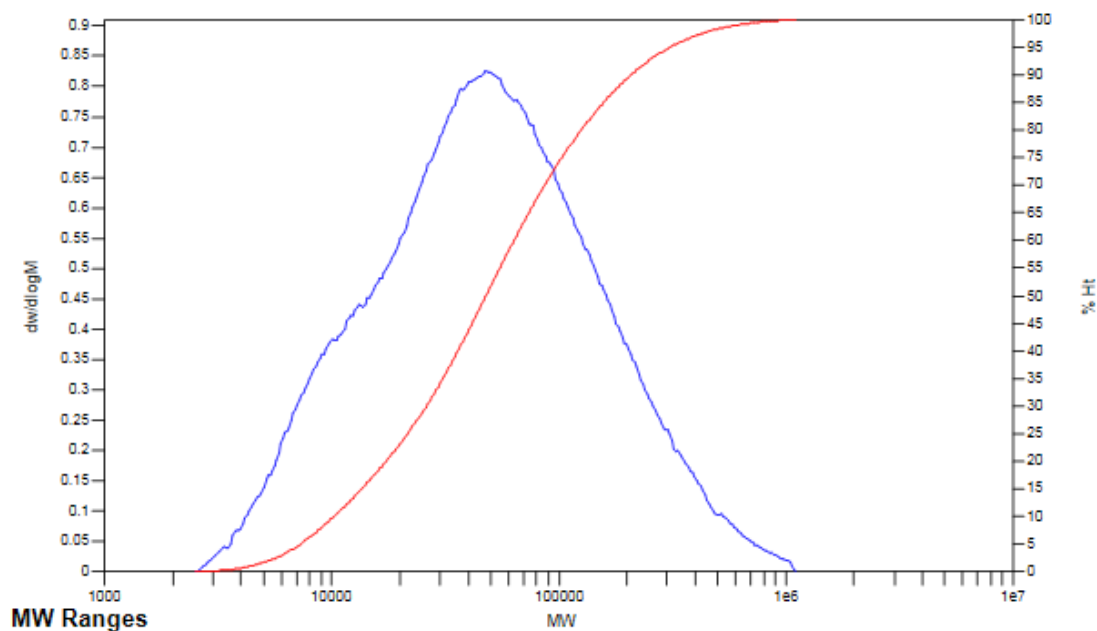
Mw: 86435

Mz: 237374

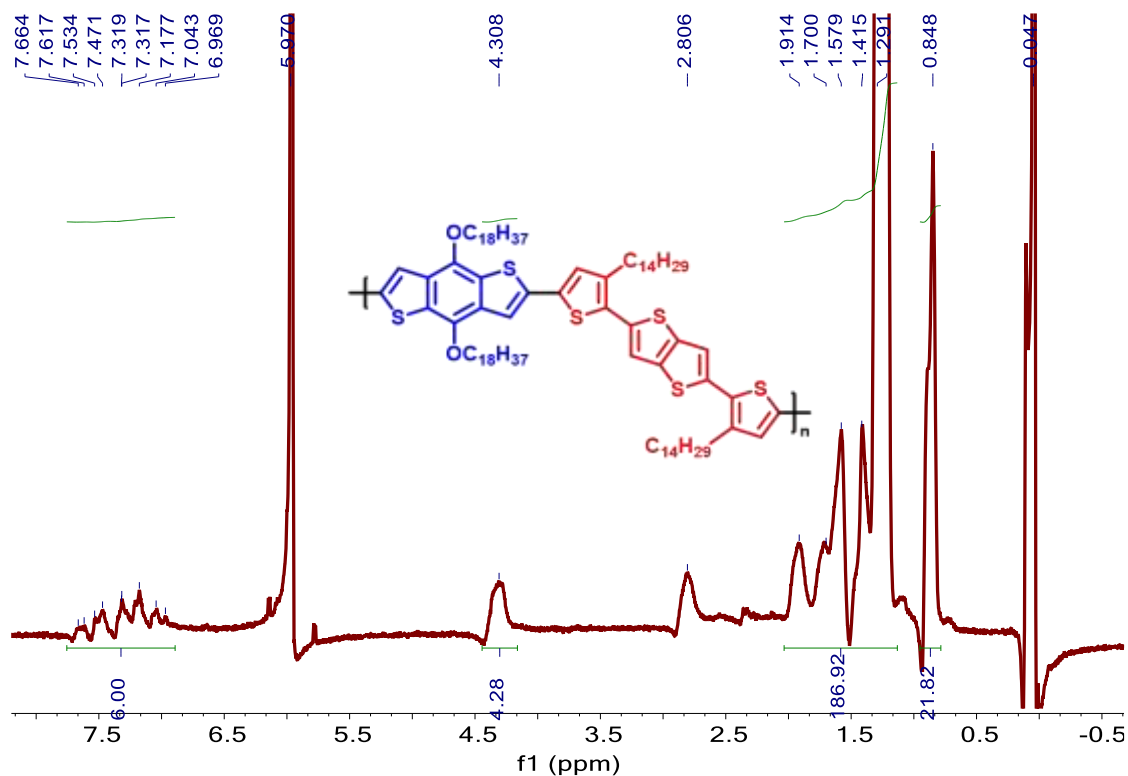
Mz+1: 435279

PD: 3.3388

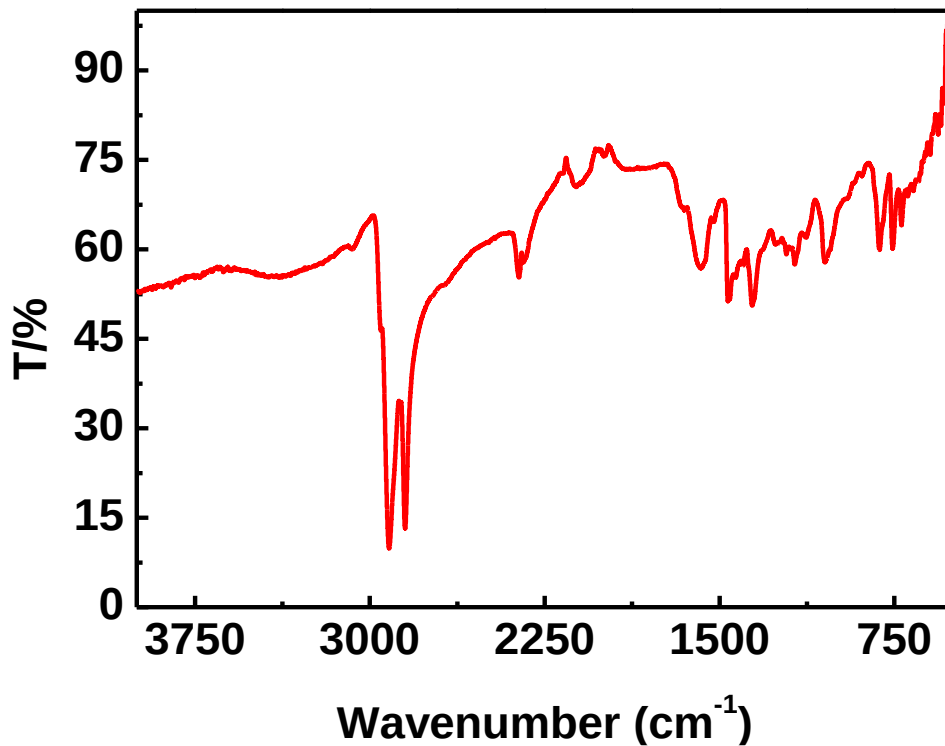
Distribution Plots



Supplementary Fig. 129. Gel permeation chromatography (GPC) trace of **P13**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P13**.

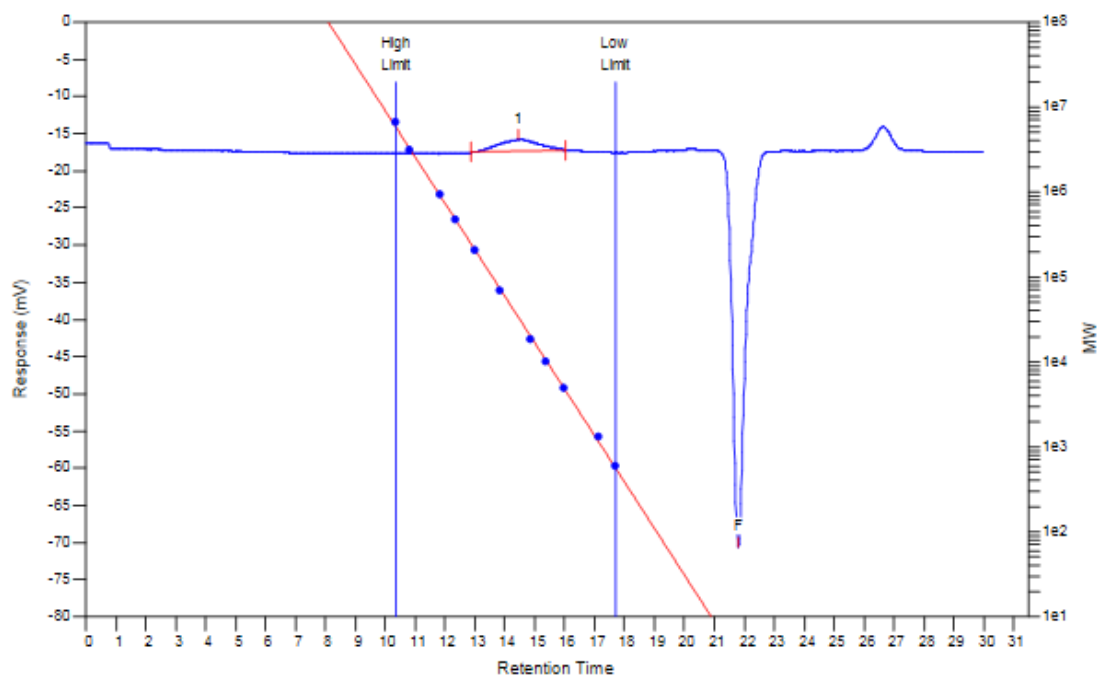


Supplementary Fig. 130. ¹H NMR (500 MHz) spectra of **P14** in $C_2D_2Cl_4$ at 373 K.



Supplementary Fig. 131. FT-IR spectrum of **P14** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 33662

Mn: 25641

Mv: 41029

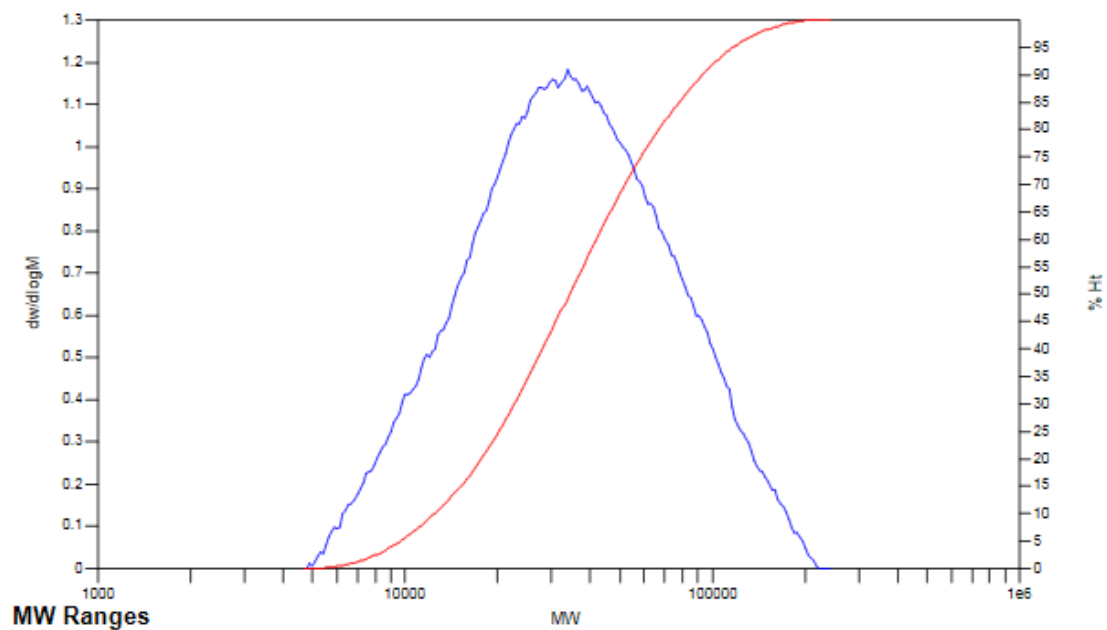
Mw: 44296

Mz: 70688

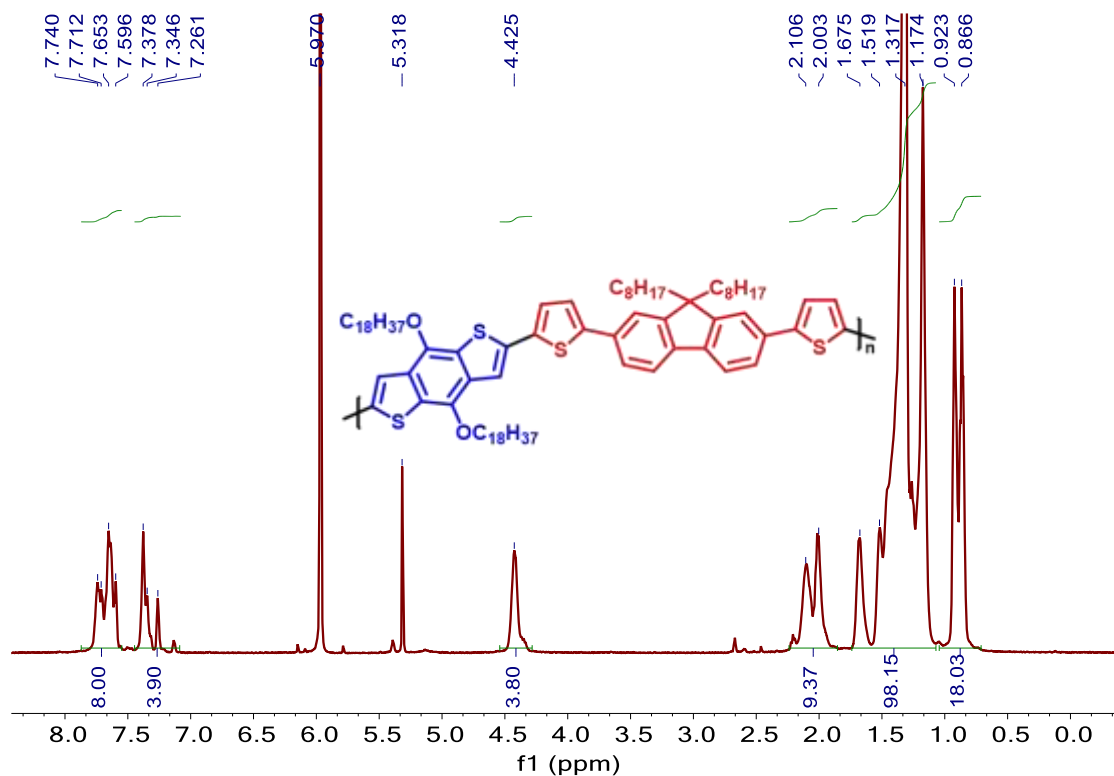
Mz+1: 97881

PD: 1.7275

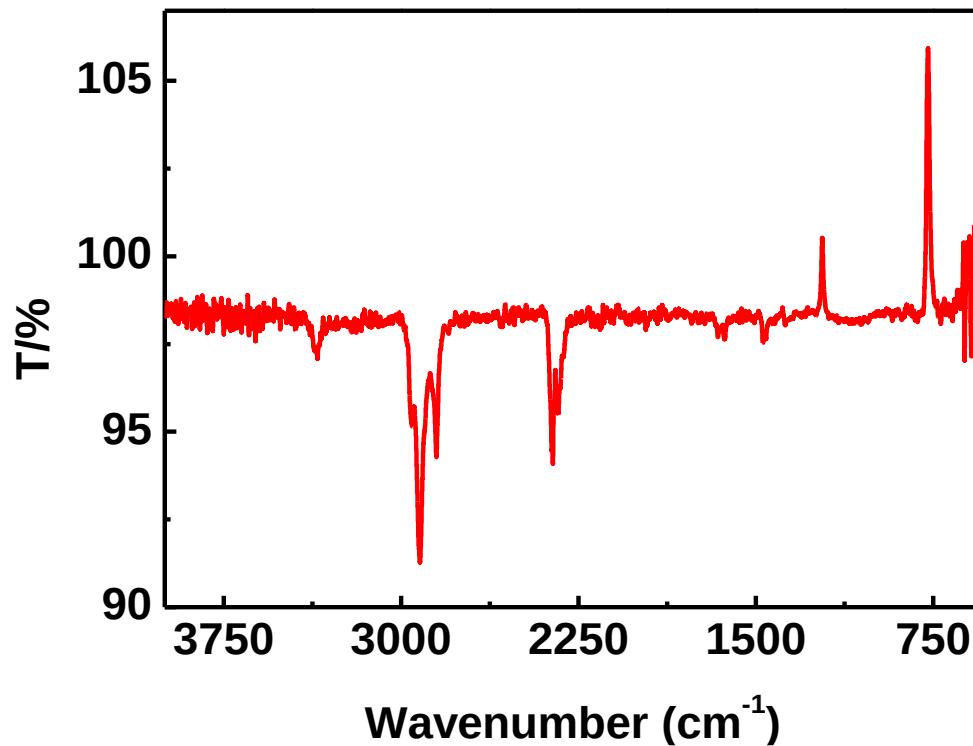
Distribution Plots



Supplementary Fig. 132. Gel permeation chromatography (GPC) trace of **P14**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P14**.

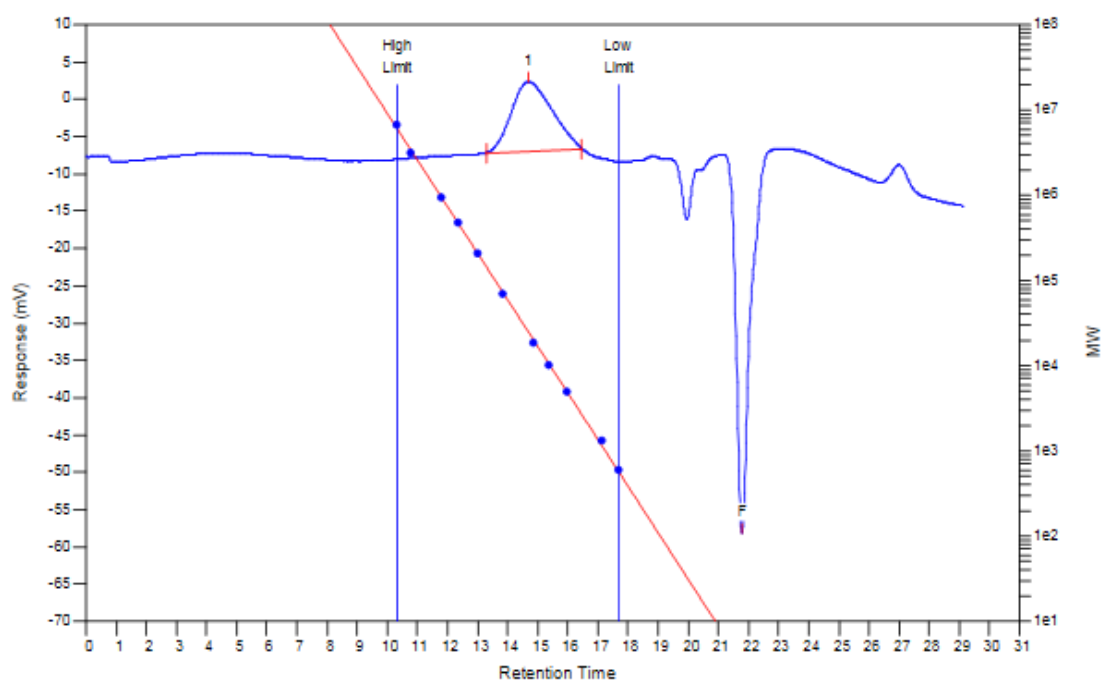


Supplementary Fig. 133. ¹H NMR (500 MHz) spectra of **P15** in C₂D₂Cl₄ at 373 K.



Supplementary Fig. 134. FT-IR spectrum of **P15** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 25090

Mn: 15131

Mv: 24307

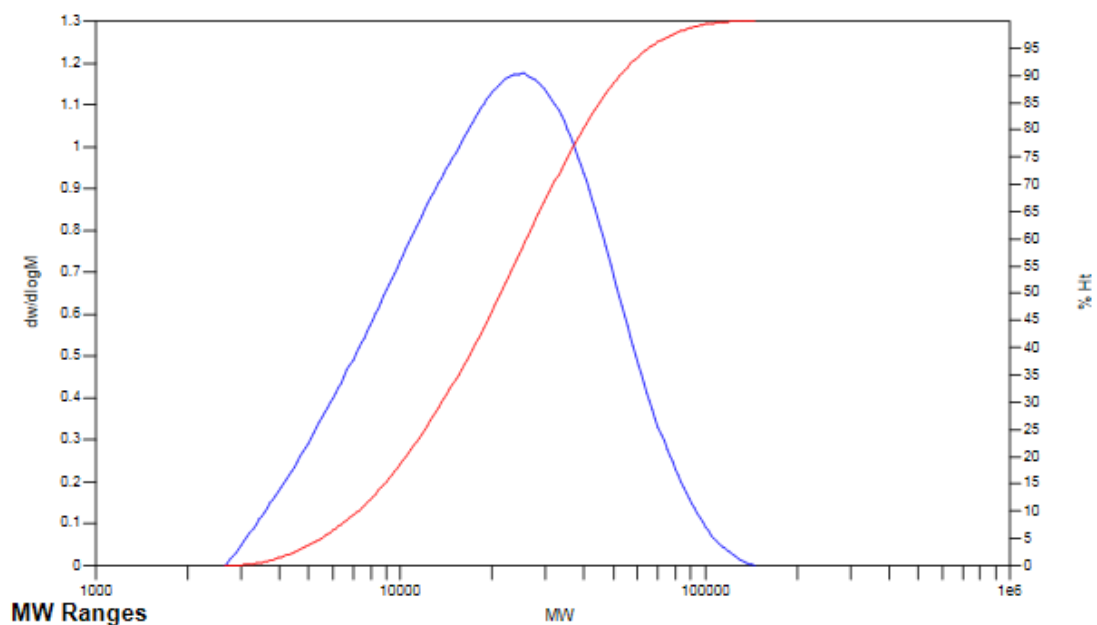
Mw: 26128

Mz: 40304

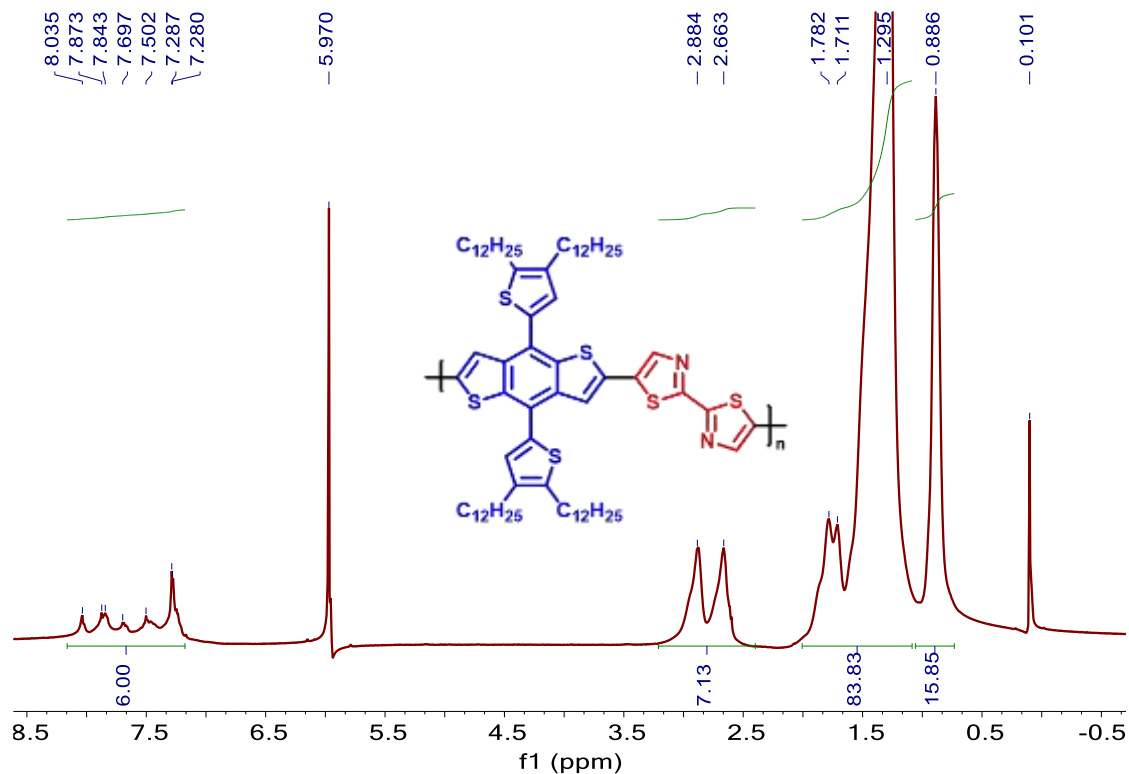
Mz+1: 54833

PD: 1.7268

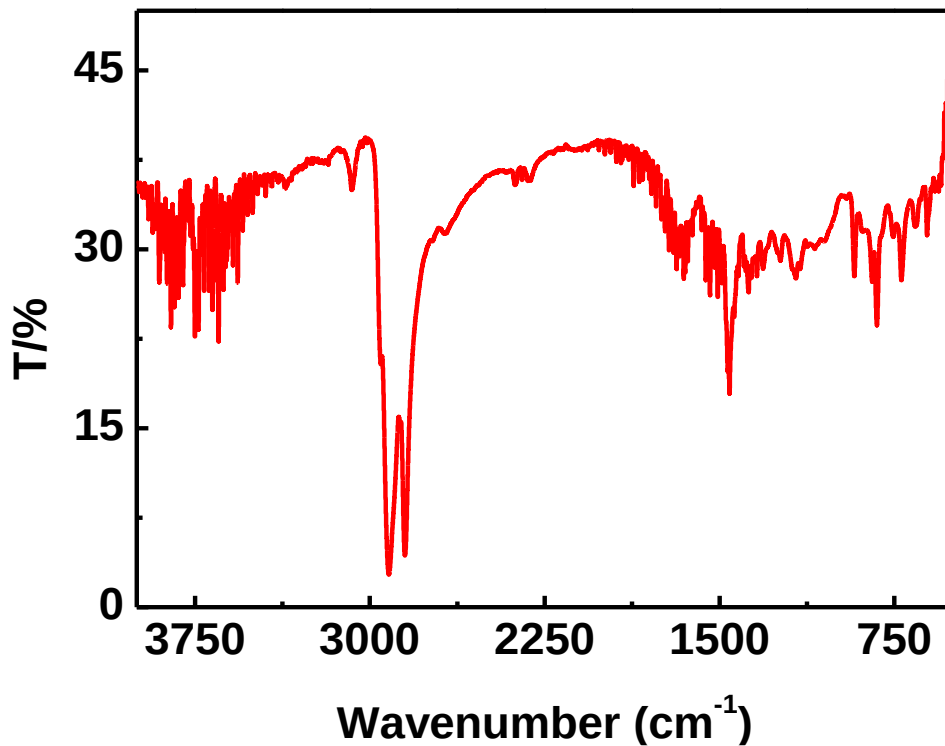
Distribution Plots



Supplementary Fig. 135. Gel permeation chromatography (GPC) trace of **P15**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P15**.

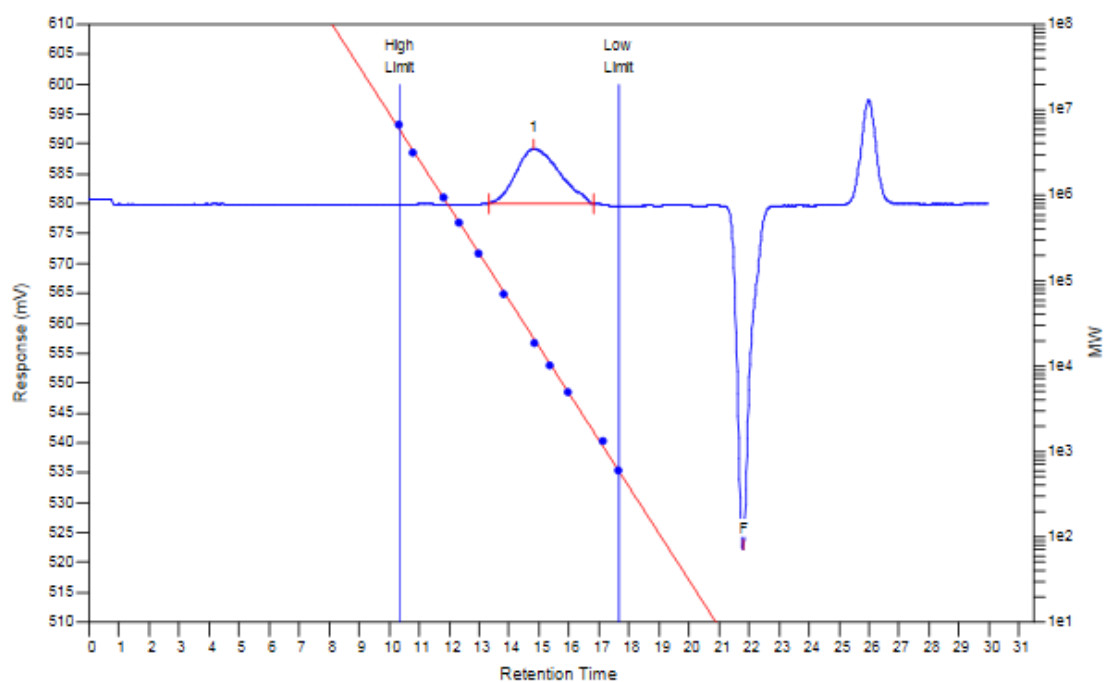


Supplementary Fig. 136. ¹H NMR (500 MHz) spectra of **P16** in $C_2D_2Cl_4$ at 373 K.



Supplementary Fig. 137. FT-IR spectrum of **P16** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 21211

Mn: 11600

Mv: 20231

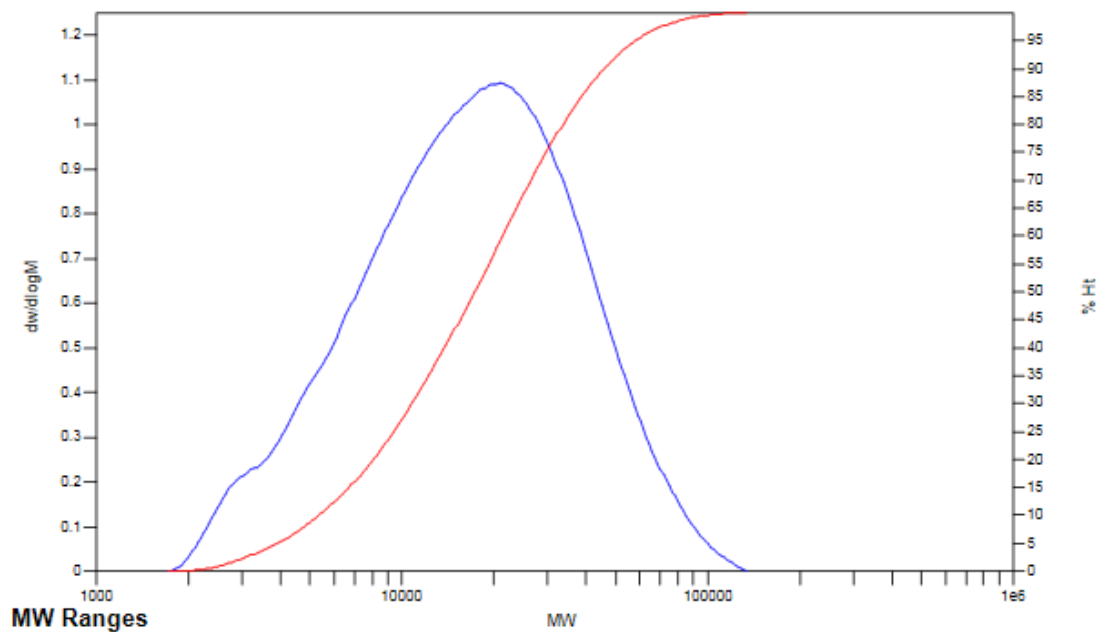
Mw: 21992

Mz: 36095

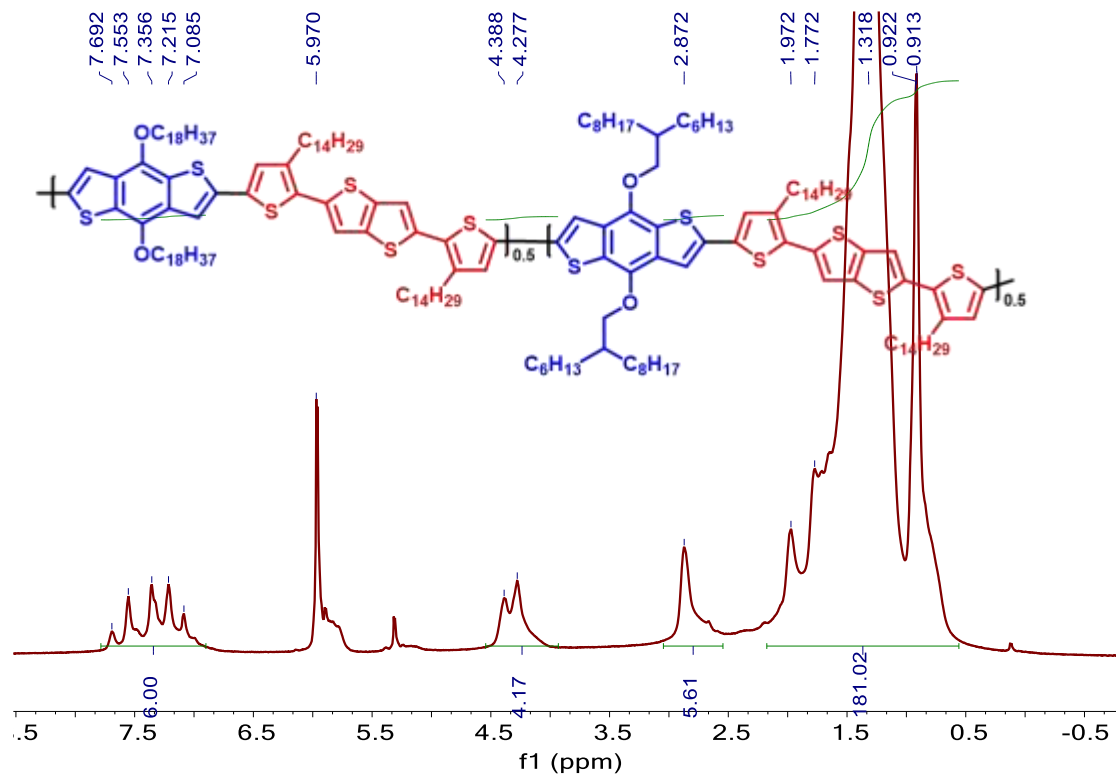
Mz+1: 50893

PD: 1.8959

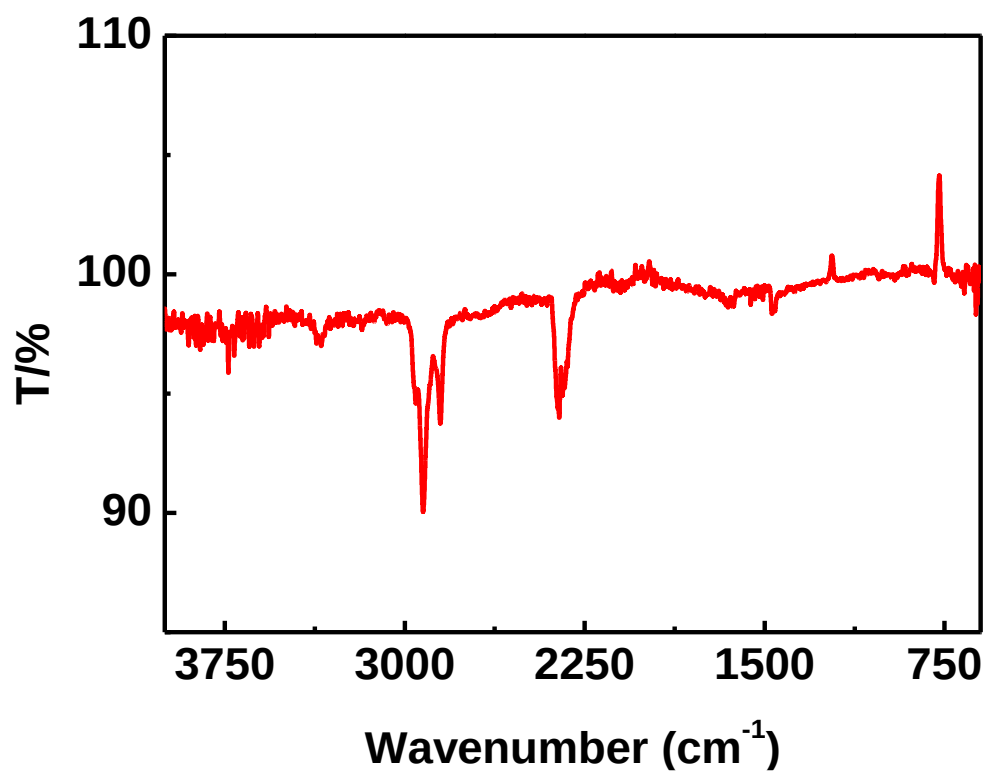
Distribution Plots



Supplementary Fig. 138. Gel permeation chromatography (GPC) trace of **P16**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P16**.

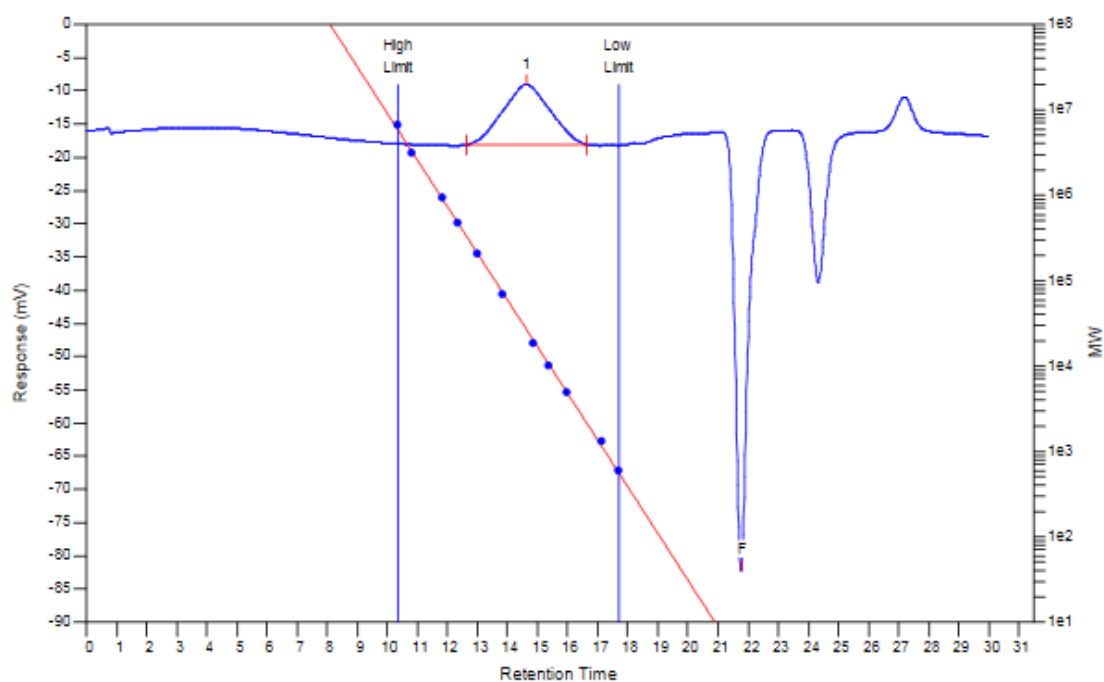


Supplementary Fig. 139. ¹H NMR (500 MHz) spectra of **P17** in C₂D₂Cl₄ at 373 K.



Supplementary Fig. 140. FT-IR spectrum of **P17** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 26721

Mn: 17856

Mv: 35020

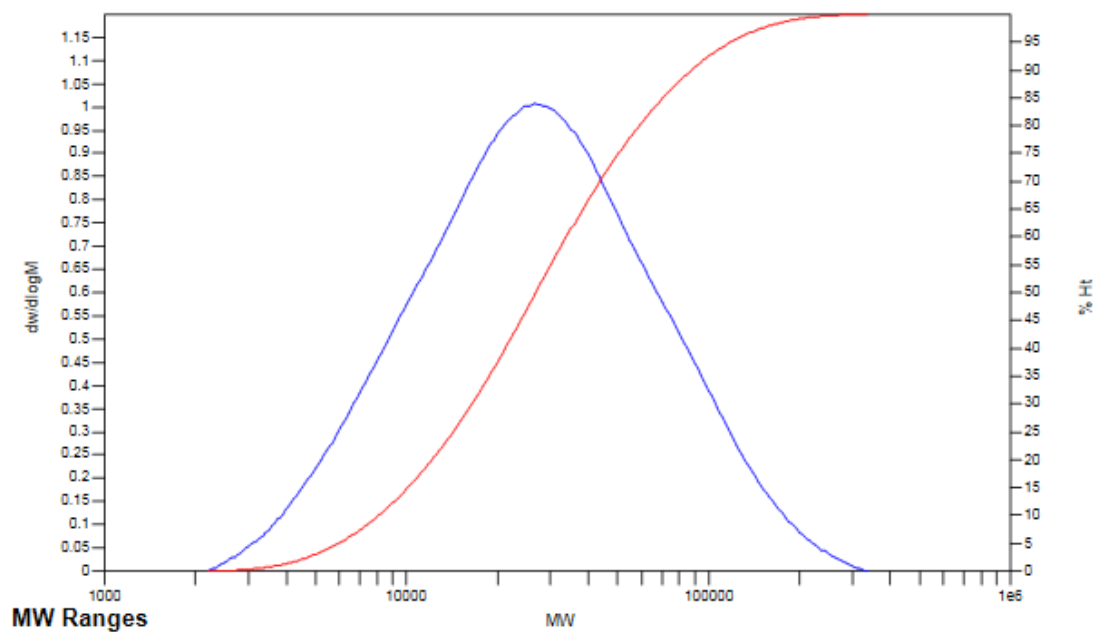
Mw: 39120

Mz: 76623

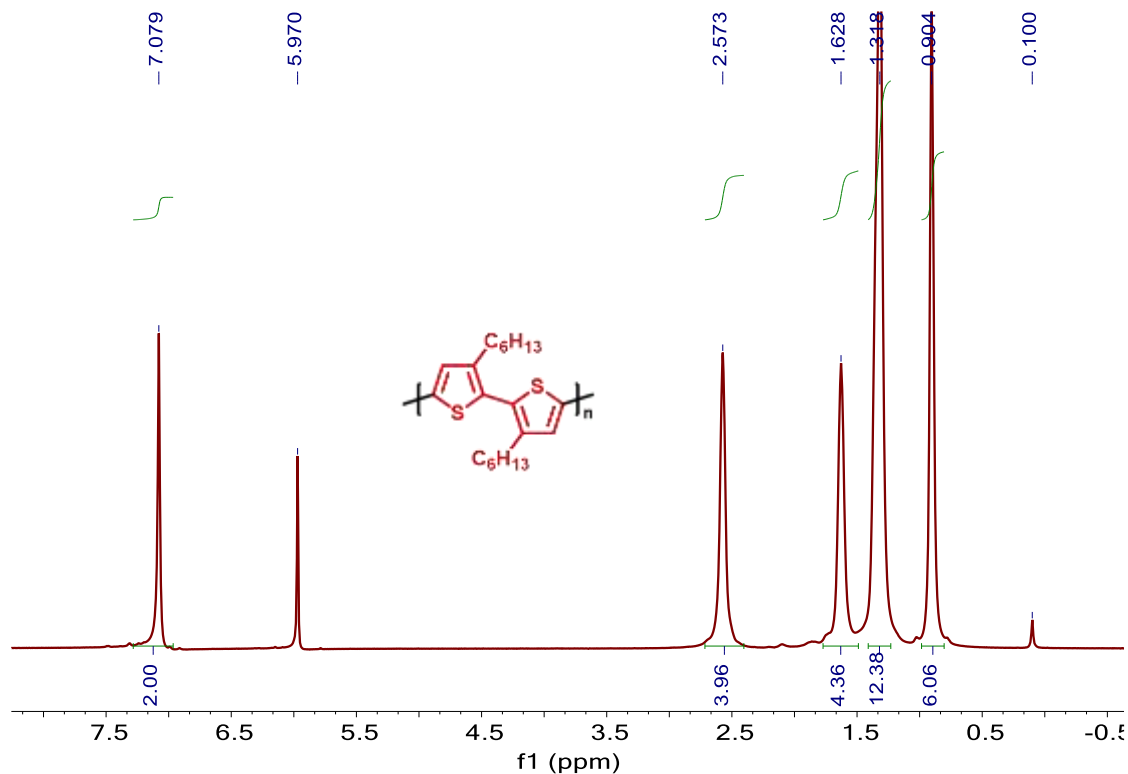
Mz+1: 121079

PD: 2.1909

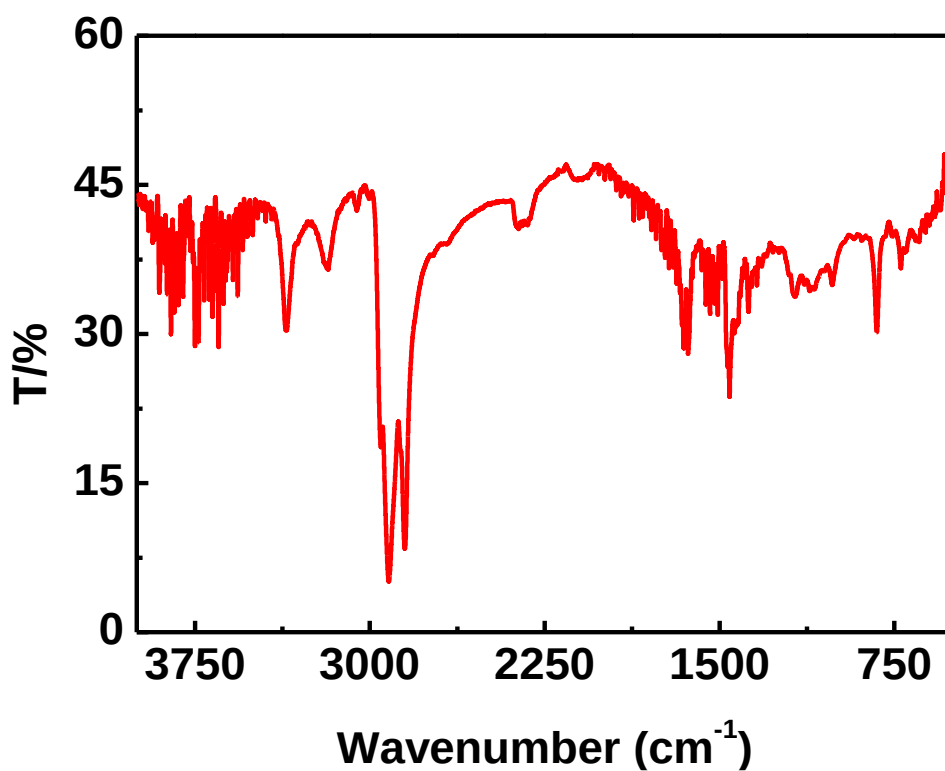
Distribution Plots



Supplementary Fig. 141. Gel permeation chromatography (GPC) trace of **P17**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P17**.

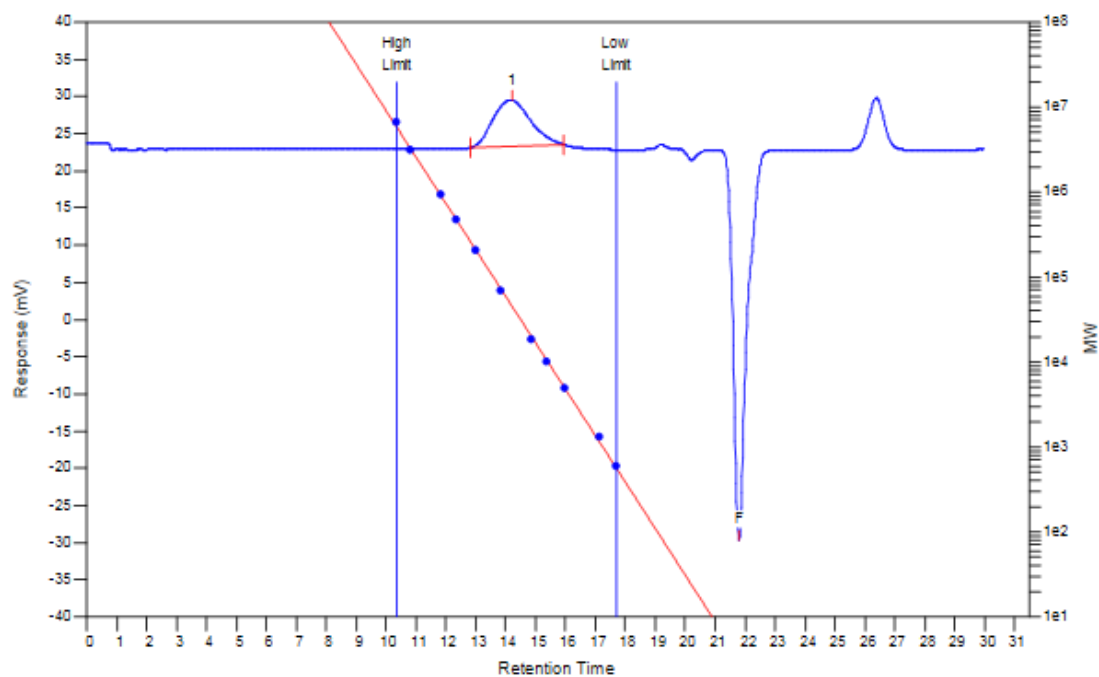


Supplementary Fig. 142. ^1H NMR (500 MHz) spectra of **P18** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 143. FT-IR spectrum of **P18** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 47099

Mn: 33599

Mv: 51185

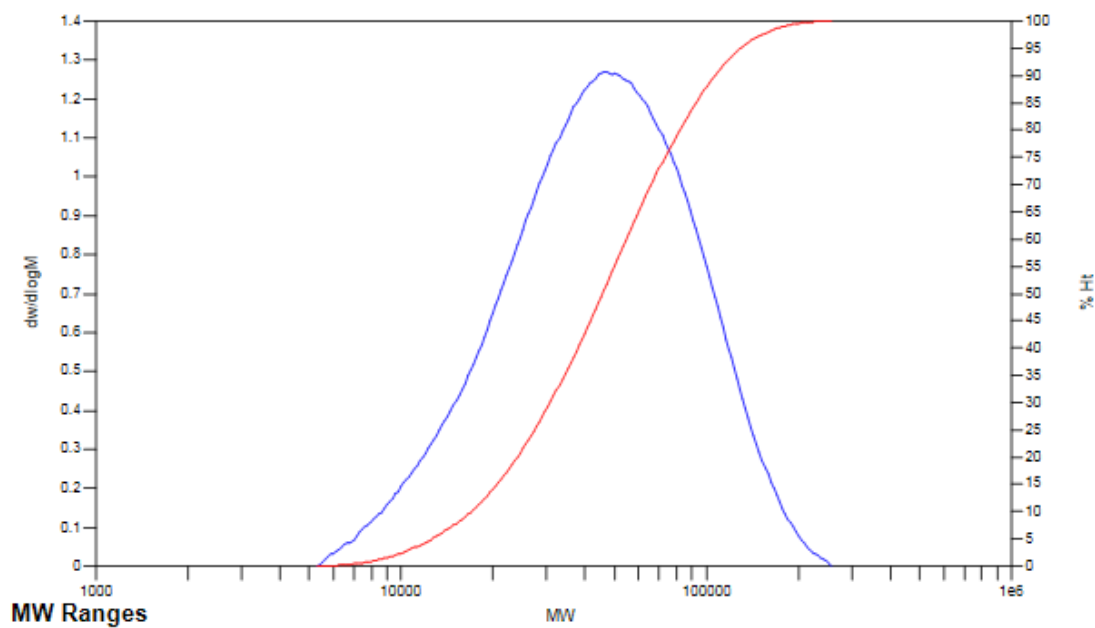
Mw: 54509

Mz: 79644

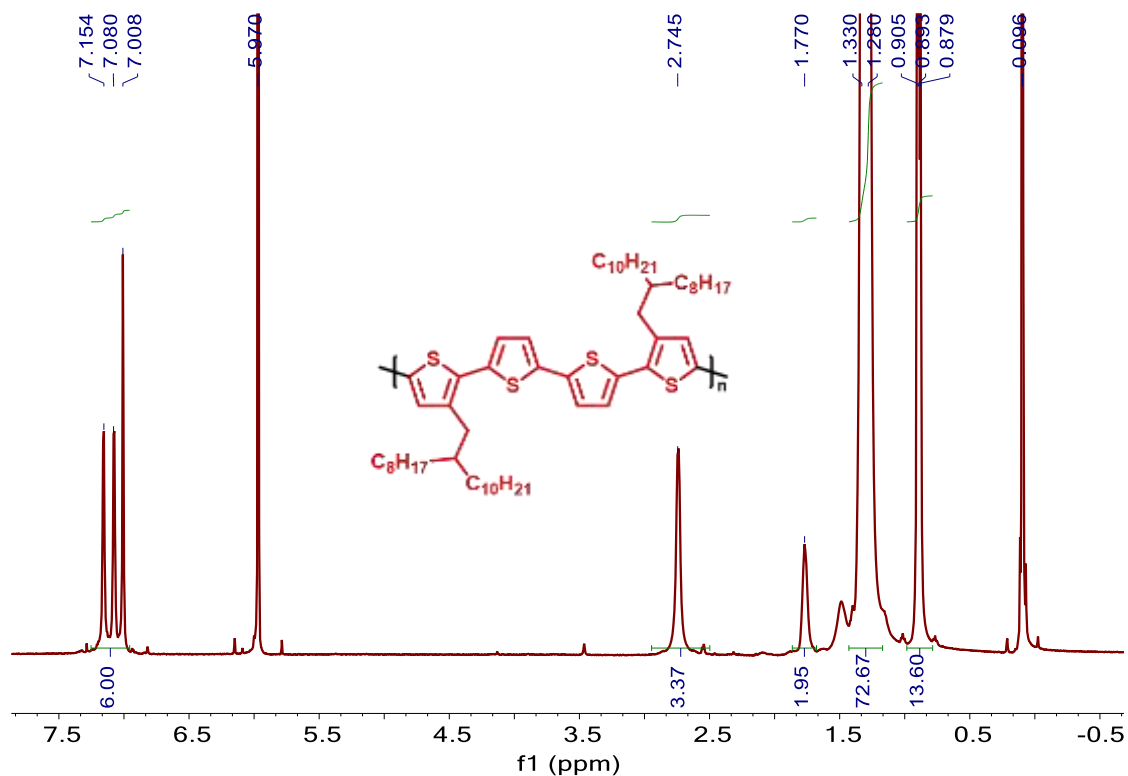
Mz+1: 104683

PD: 1.6223

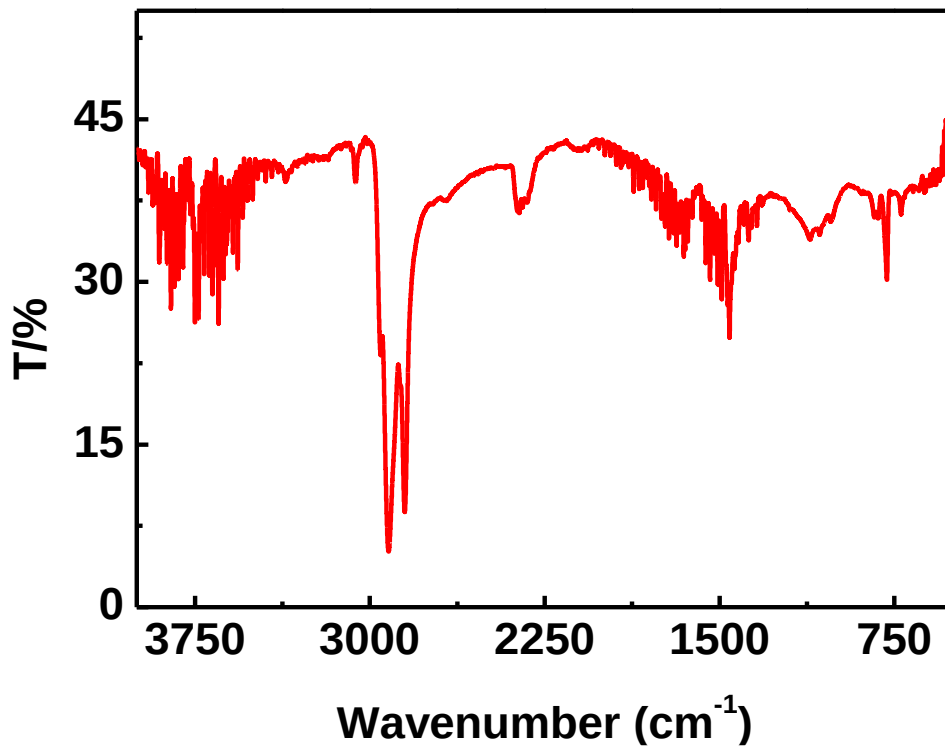
Distribution Plots



Supplementary Fig. 144. Gel permeation chromatography (GPC) trace of **P18**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P18**.

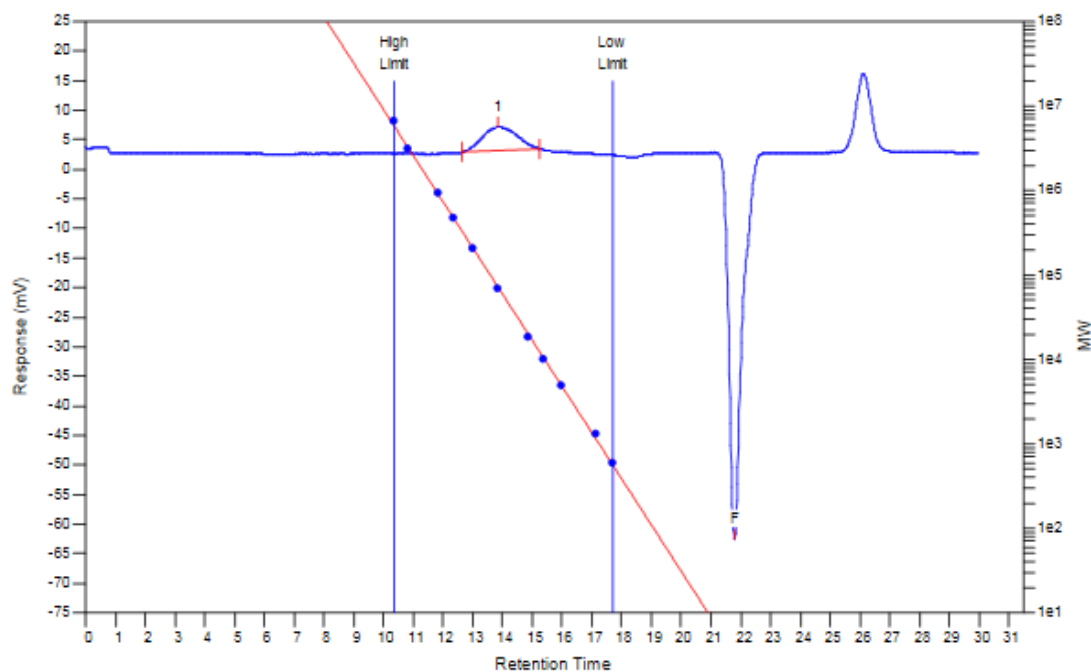


Supplementary Fig. 145. ^1H NMR (500 MHz) spectra of **P19** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 146. FT-IR spectrum of **P19** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 73194

Mn: 54428

Mv: 75573

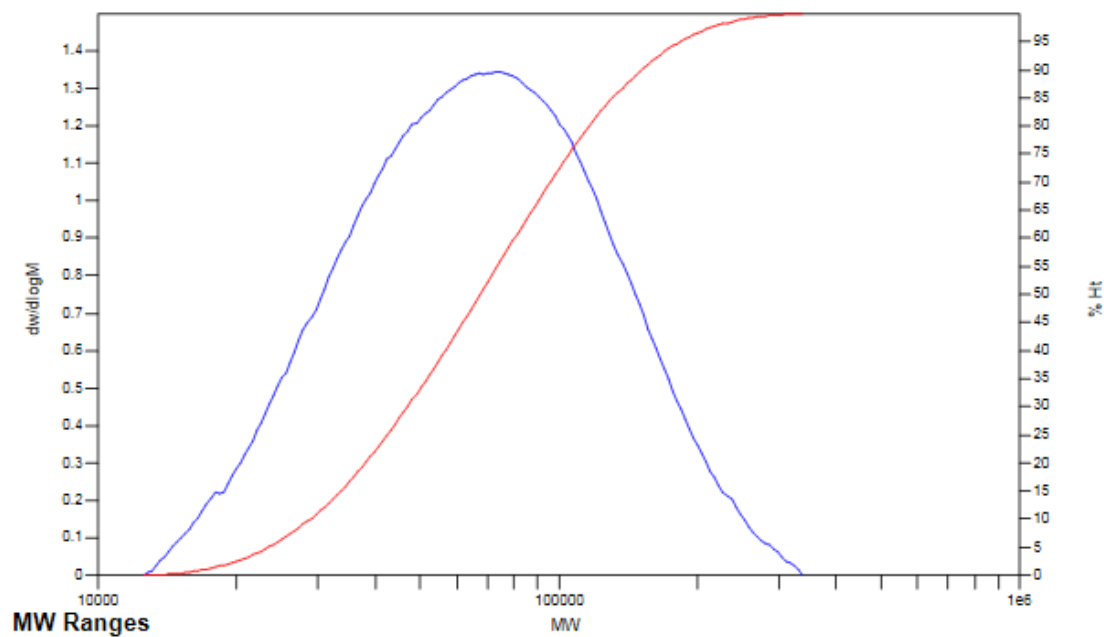
Mw: 79758

Mz: 111920

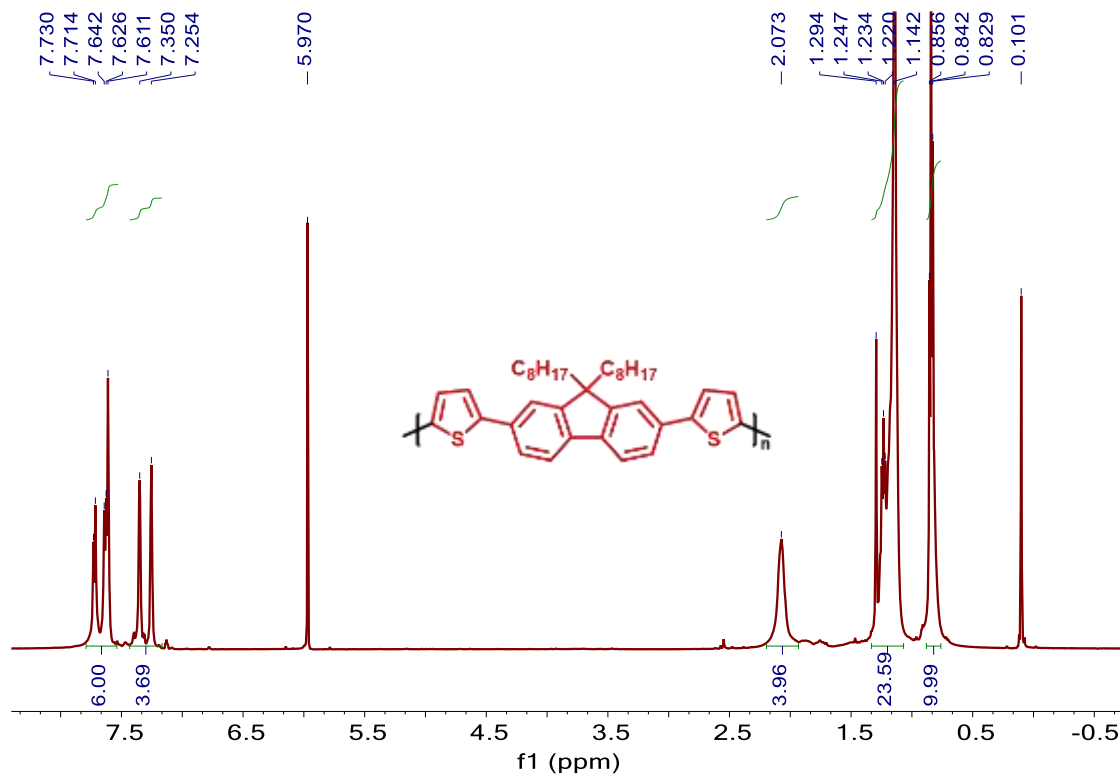
Mz+1: 145462

PD: 1.4654

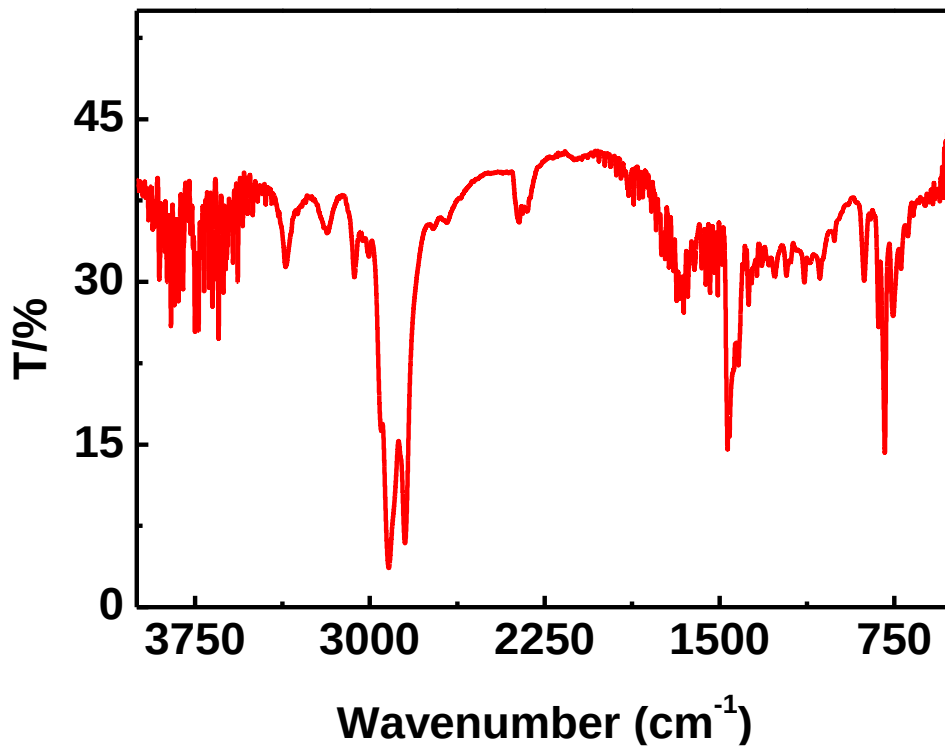
Distribution Plots



Supplementary Fig. 147. Gel permeation chromatography (GPC) trace of **P19**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P19**.

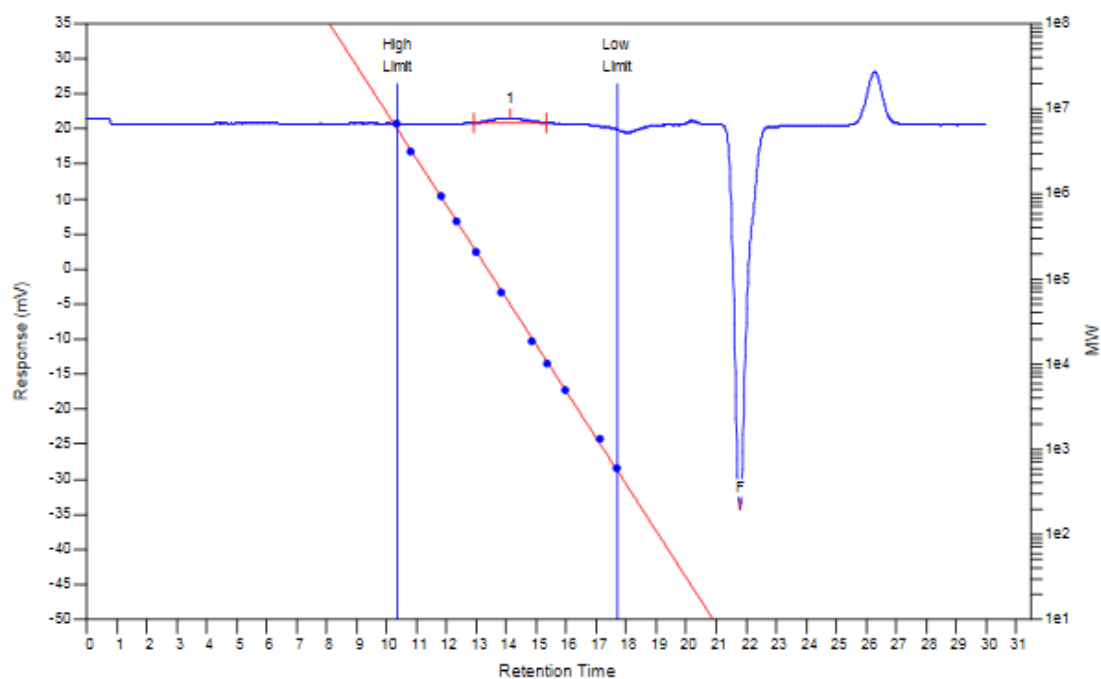


Supplementary Fig. 148. ¹H NMR (500 MHz) spectra of **P20** in C₂D₂Cl₄ at 373 K.



Supplementary Fig. 149. FT-IR spectrum of **P20** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 51225

Mn: 44076

Mv: 59510

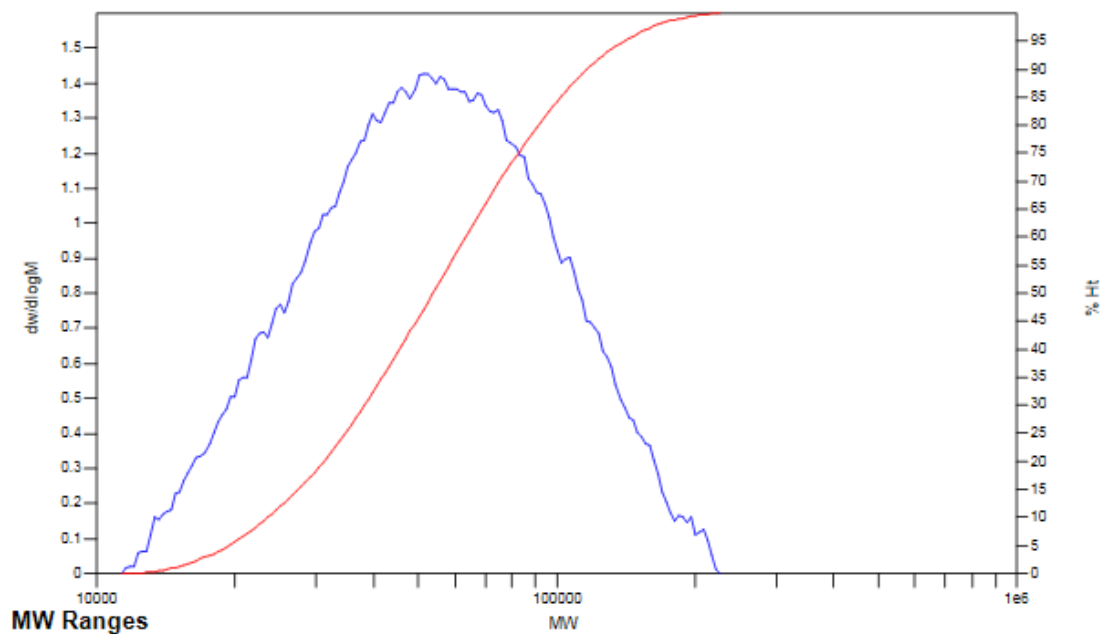
Mw: 62502

Mz: 84994

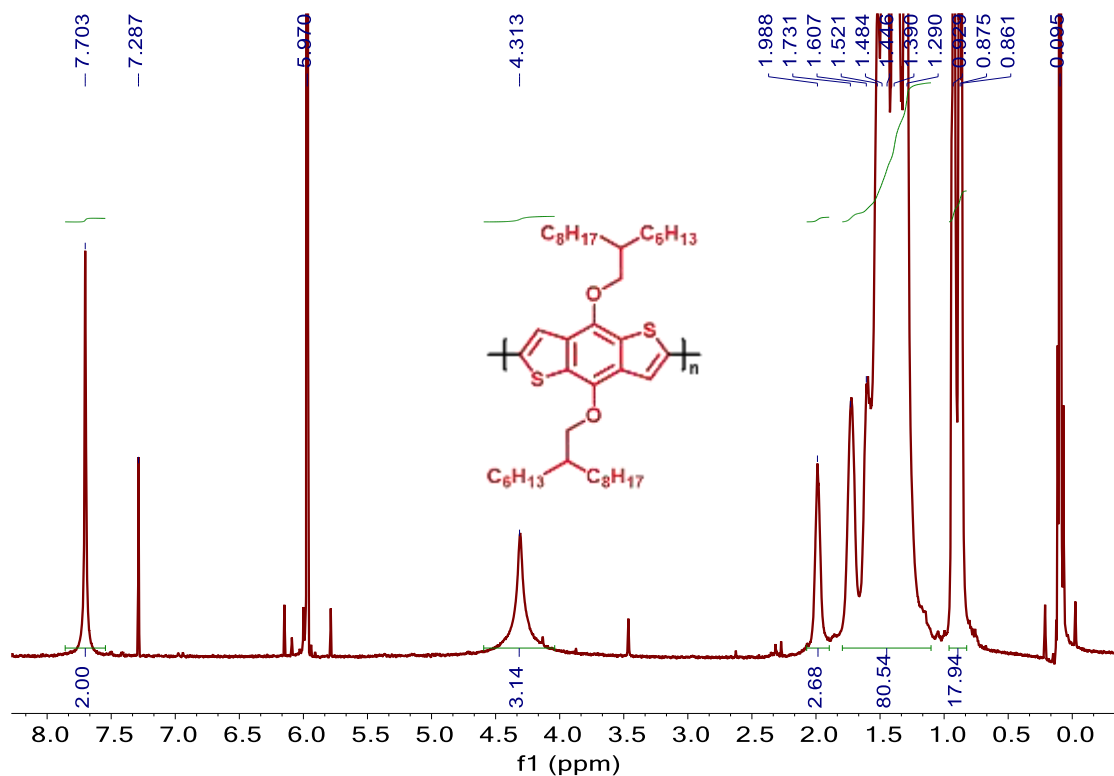
Mz+1: 107558

PD: 1.4181

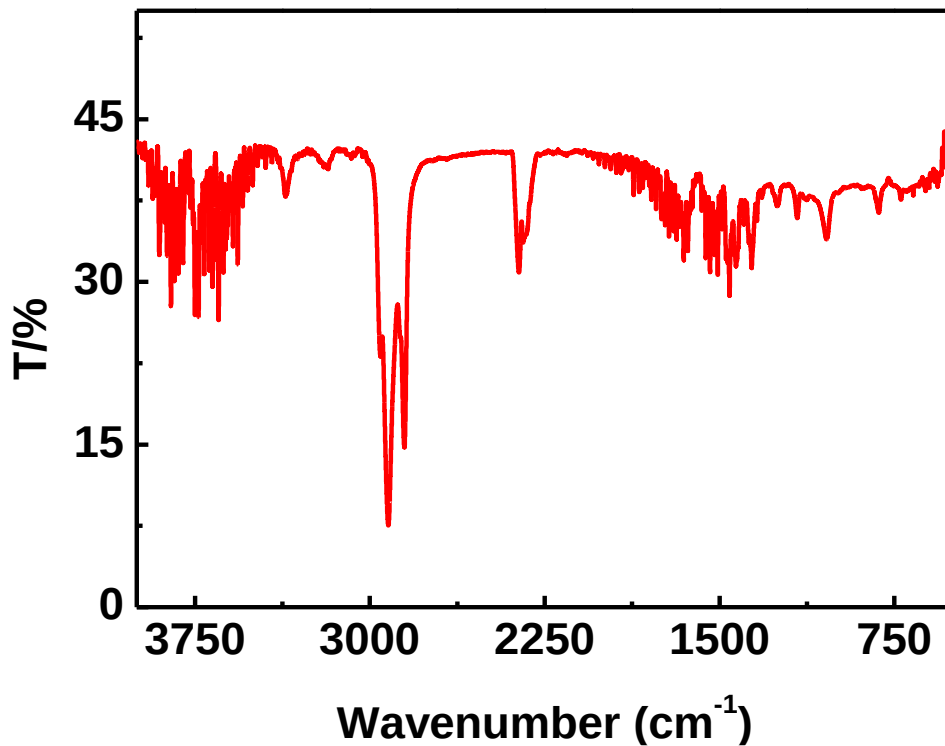
Distribution Plots



Supplementary Fig. 150. Gel permeation chromatography (GPC) trace of **P20**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P20**.

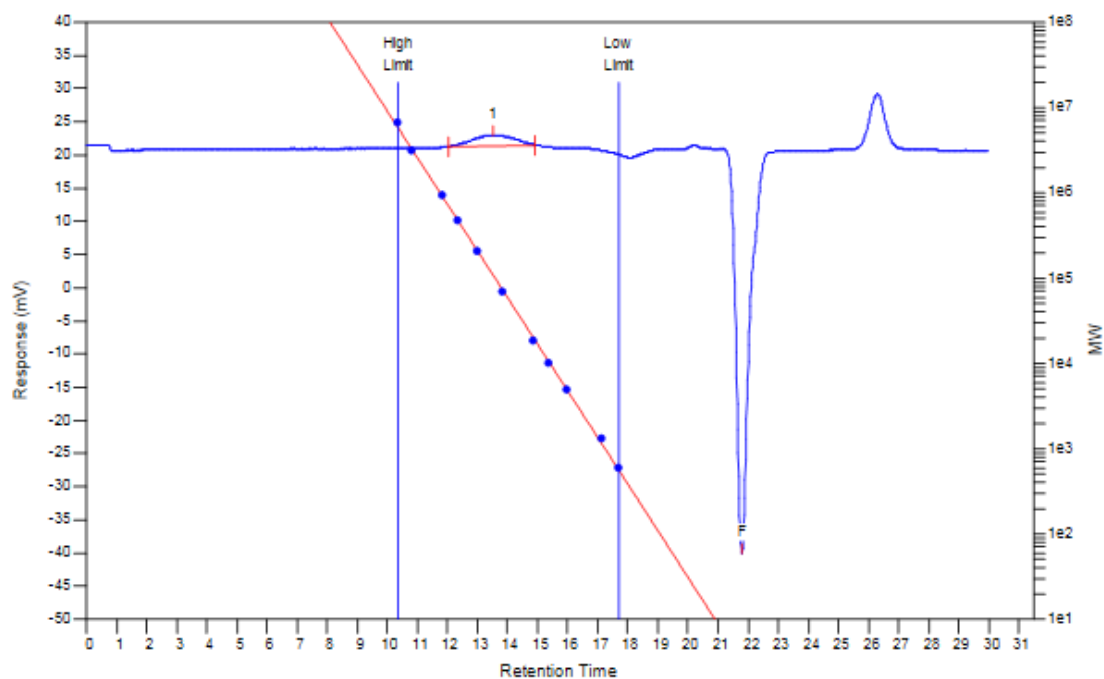


Supplementary Fig. 151. ^1H NMR (500 MHz) spectra of P21 in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 152. FT-IR spectrum of P21 in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 109069

Mn: 85050

Mv: 129995

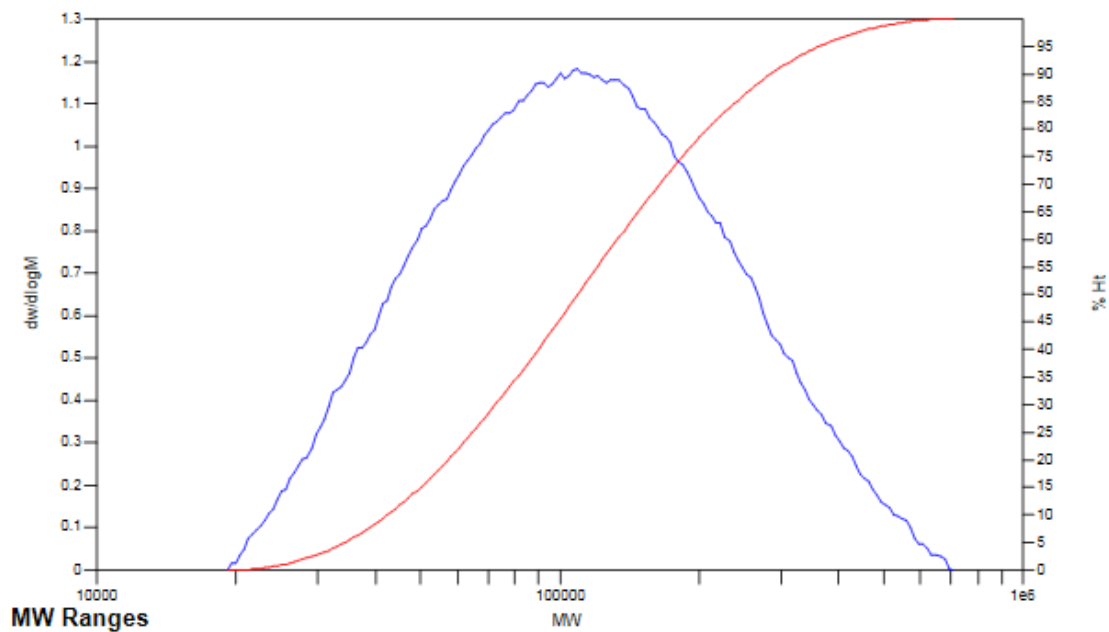
Mw: 139706

Mz: 218844

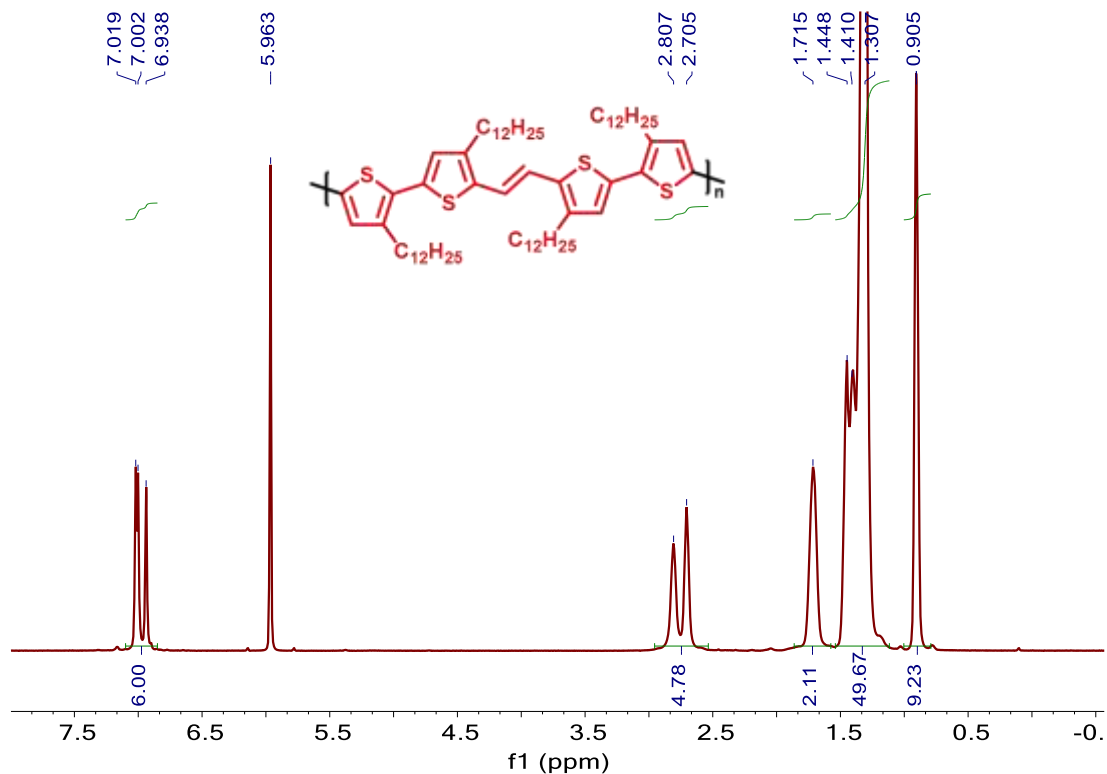
Mz+1: 303335

PD: 1.6426

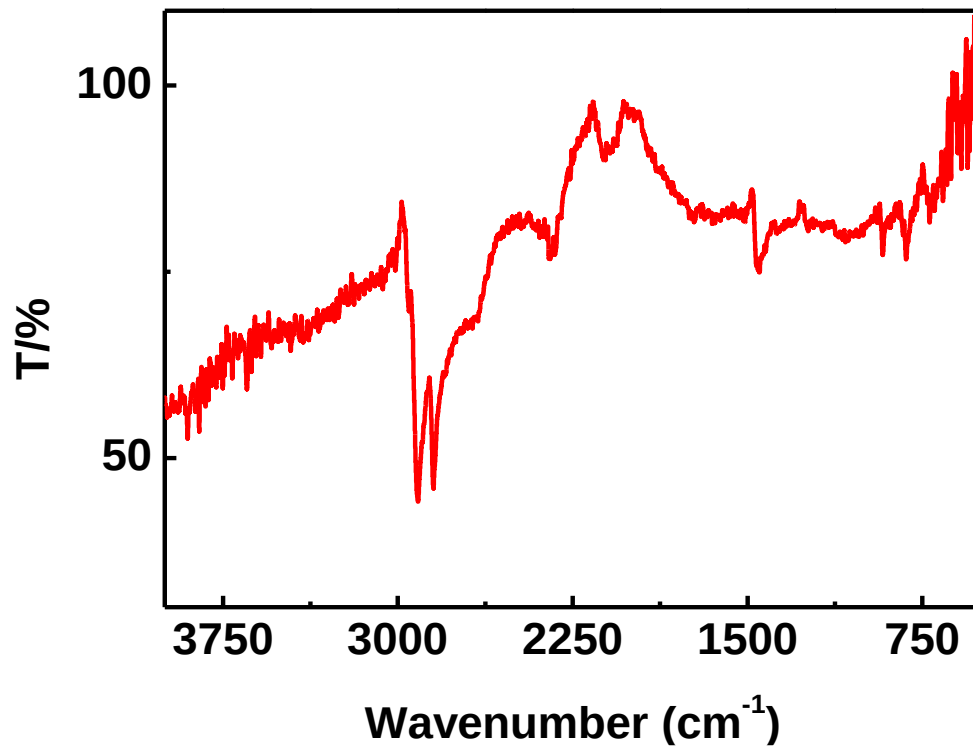
Distribution Plots



Supplementary Fig. 153. Gel permeation chromatography (GPC) trace of **P21**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P21**.

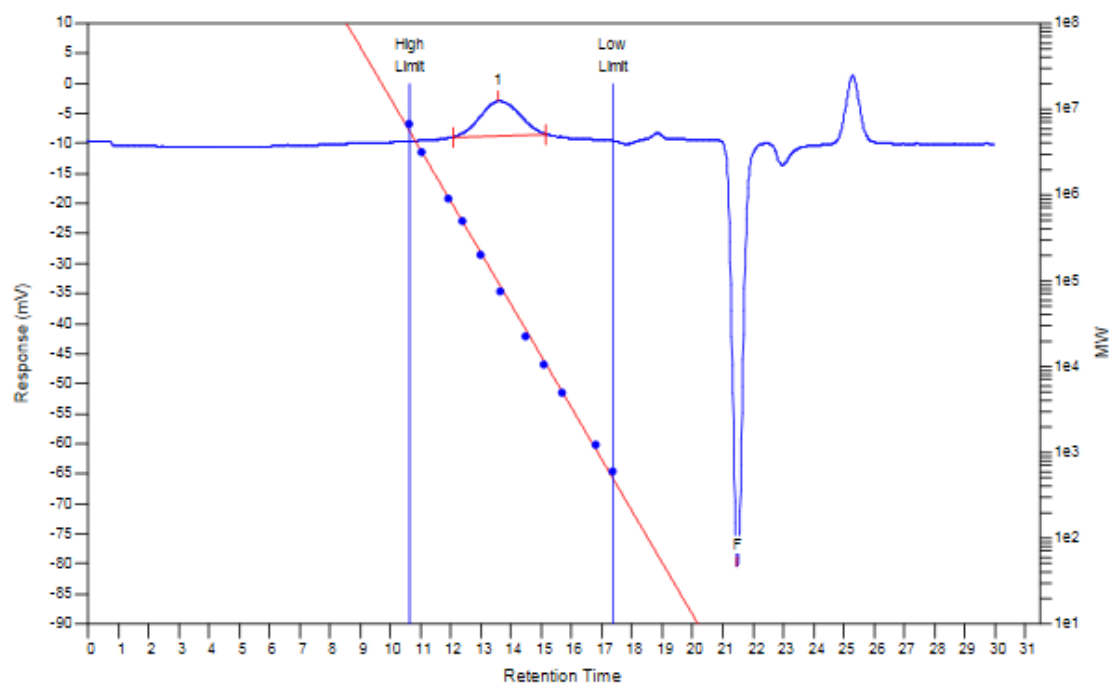


Supplementary Fig. 154. ^1H NMR (500 MHz) spectra of **P22** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 155. FT-IR spectrum of **P22** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 97993

Mn: 67407

Mv: 111646

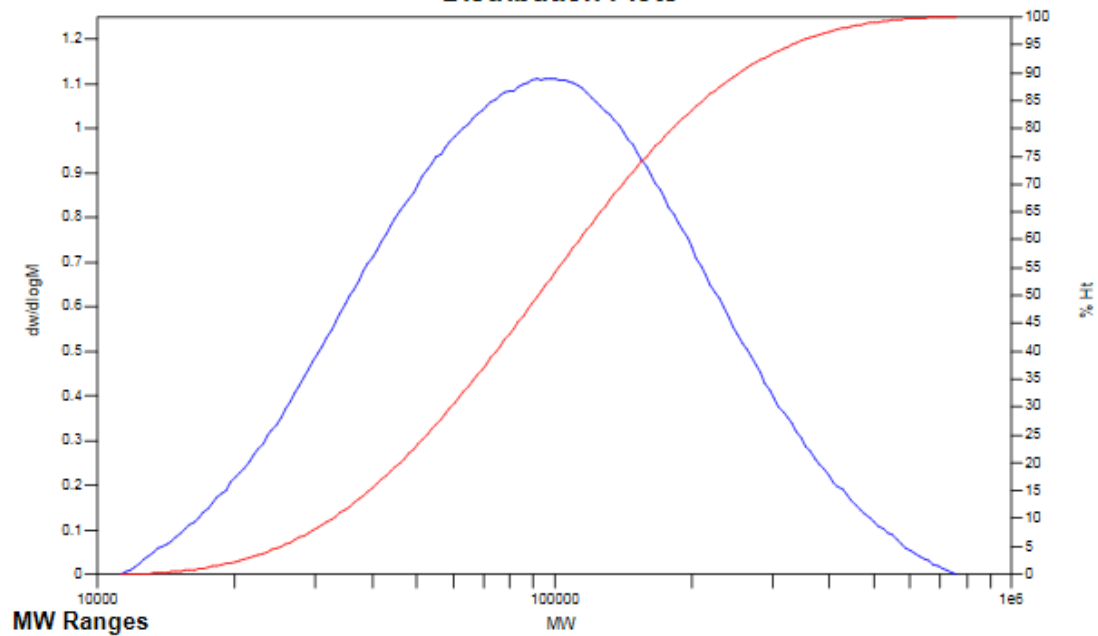
Mw: 121385

Mz: 203692

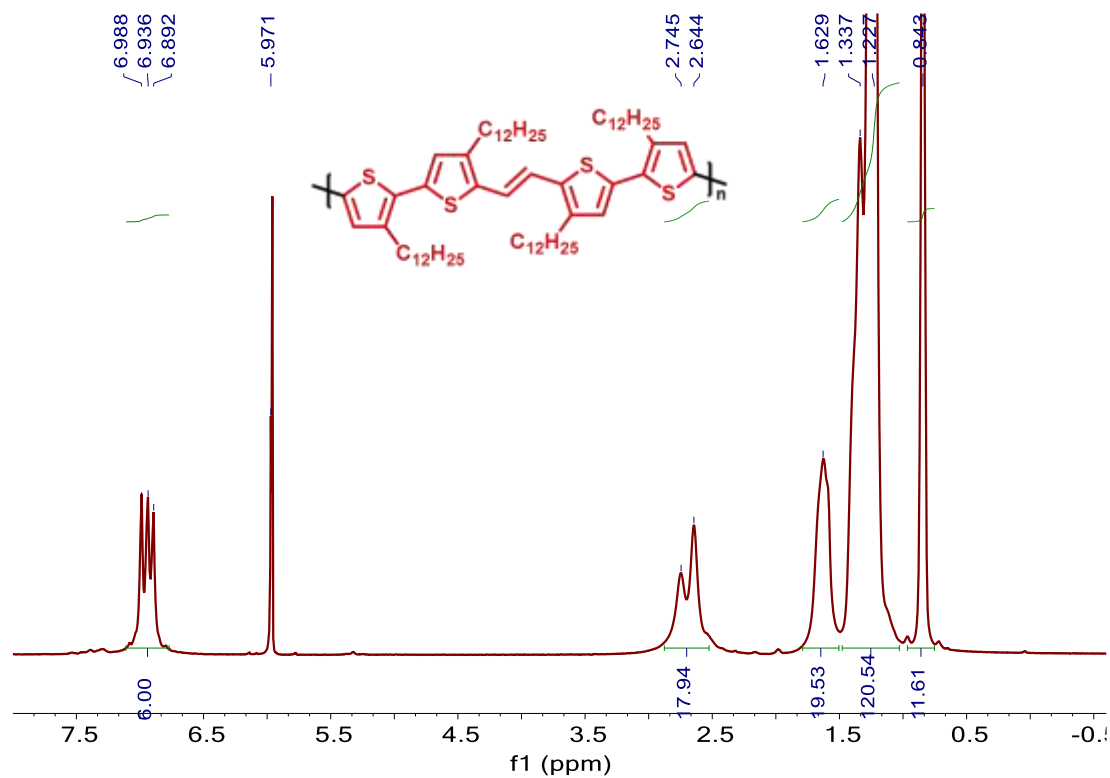
Mz+1: 296193

PD: 1.8008

Distribution Plots

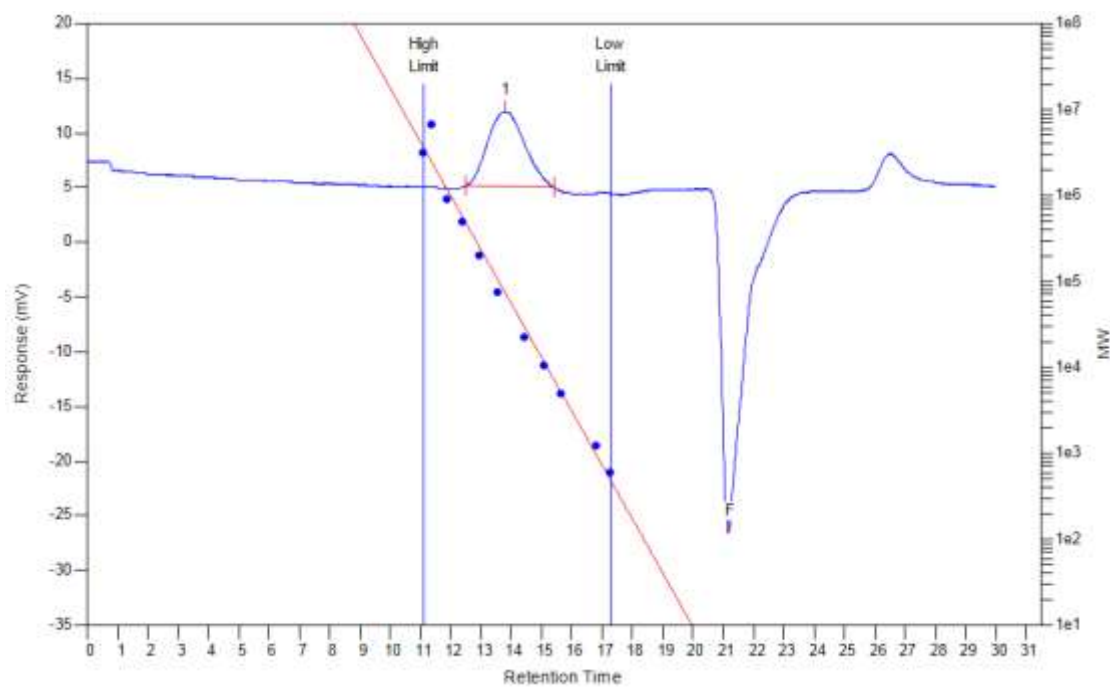


Supplementary Fig. 156. Gel permeation chromatography (GPC) trace of **P22**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P22**.



Supplementary Fig. 157. ¹H NMR (500 MHz) spectra of **P22-Stille** in C₂D₂Cl₄ at 373 K.

(a)



(b)

MW Averages

Mp: 75586

Mn: 49045

Mv: 80784

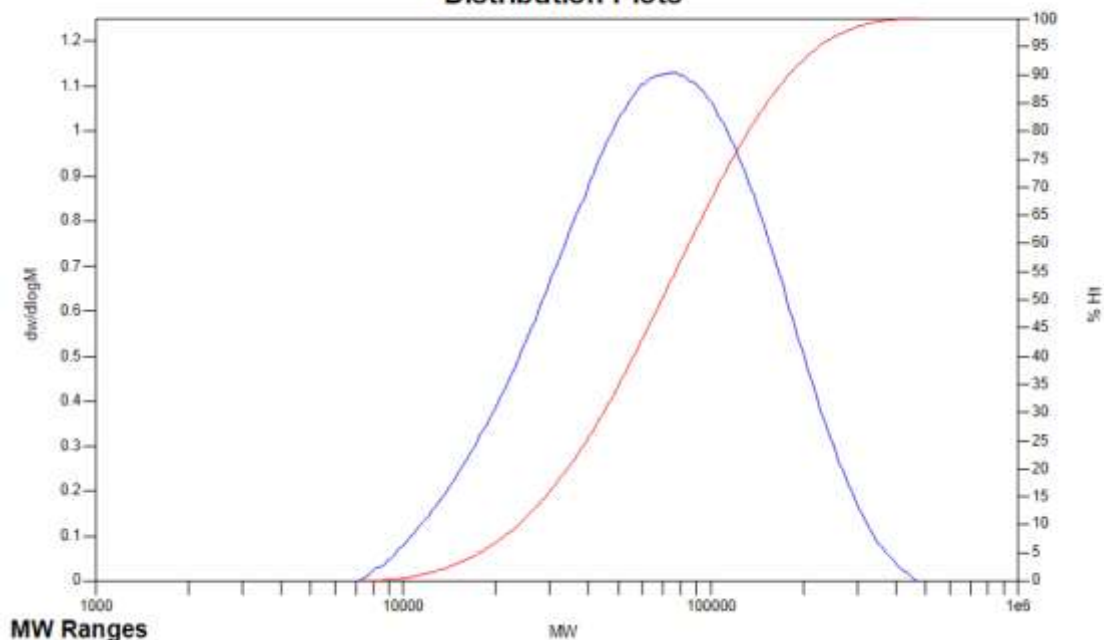
Mw: 87158

Mz: 137244

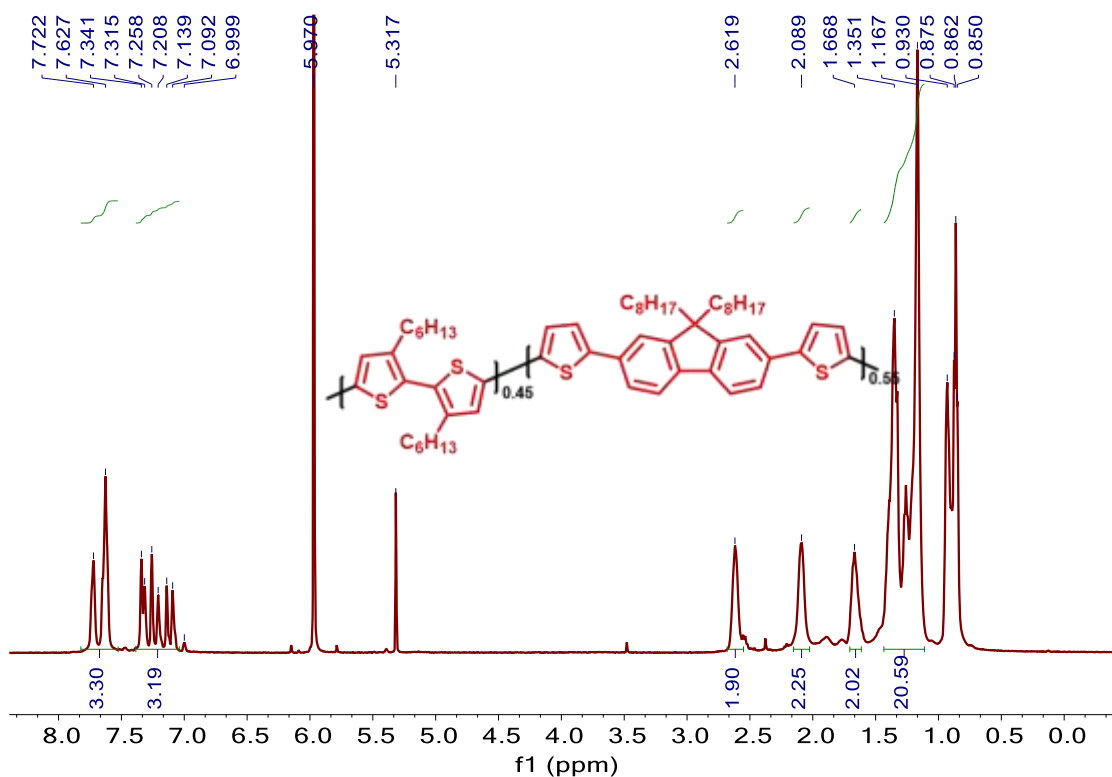
Mz+1: 188066

PD: 1.7771

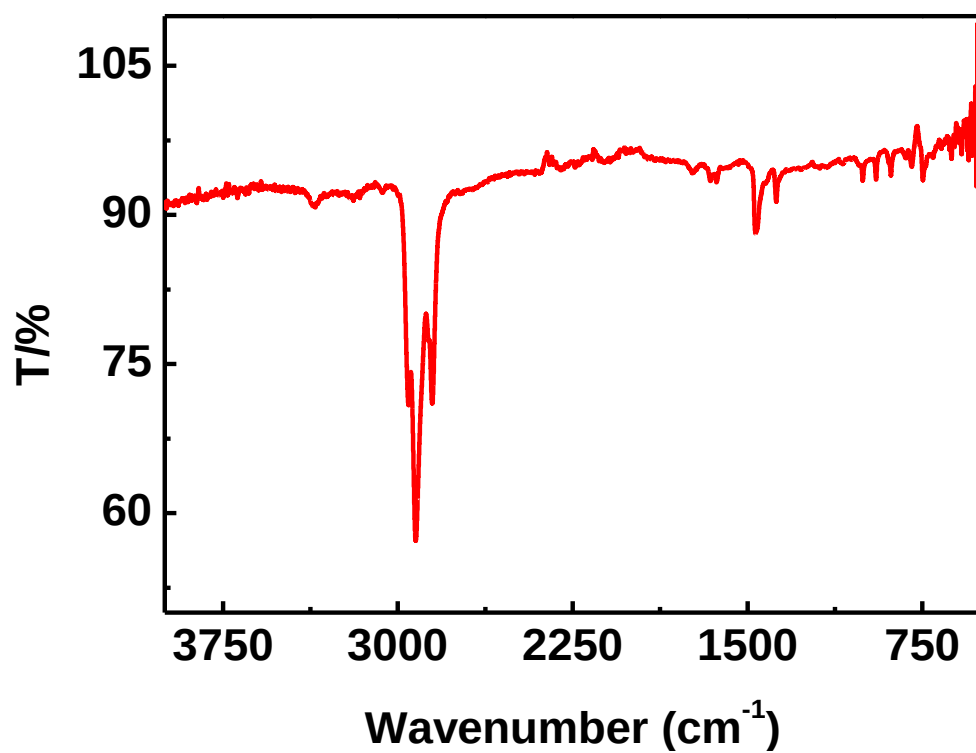
Distribution Plots



Supplementary Fig. 158. Gel permeation chromatography (GPC) trace of **P22-Stille**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P22-Stille**.

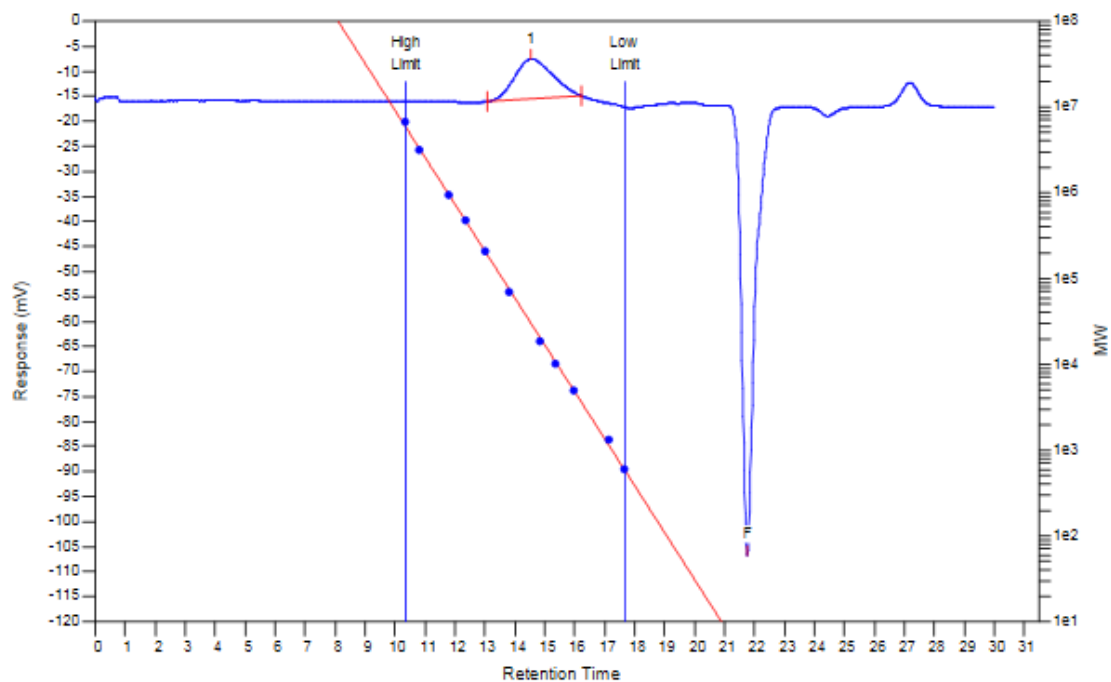


Supplementary Fig. 159. ¹H NMR (500 MHz) spectra of **P23** in C₂D₂Cl₄ at 373 K.



Supplementary Fig. 160. FT-IR spectrum of P23 in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 30308

Mn: 20066

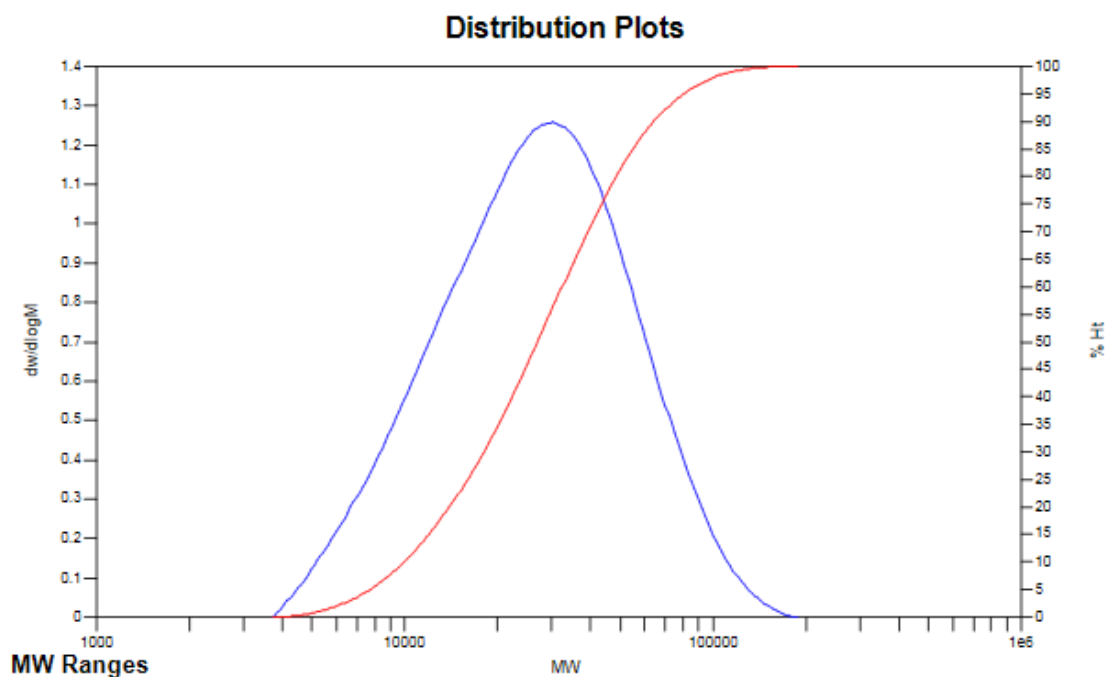
Mv: 30614

Mw: 32717

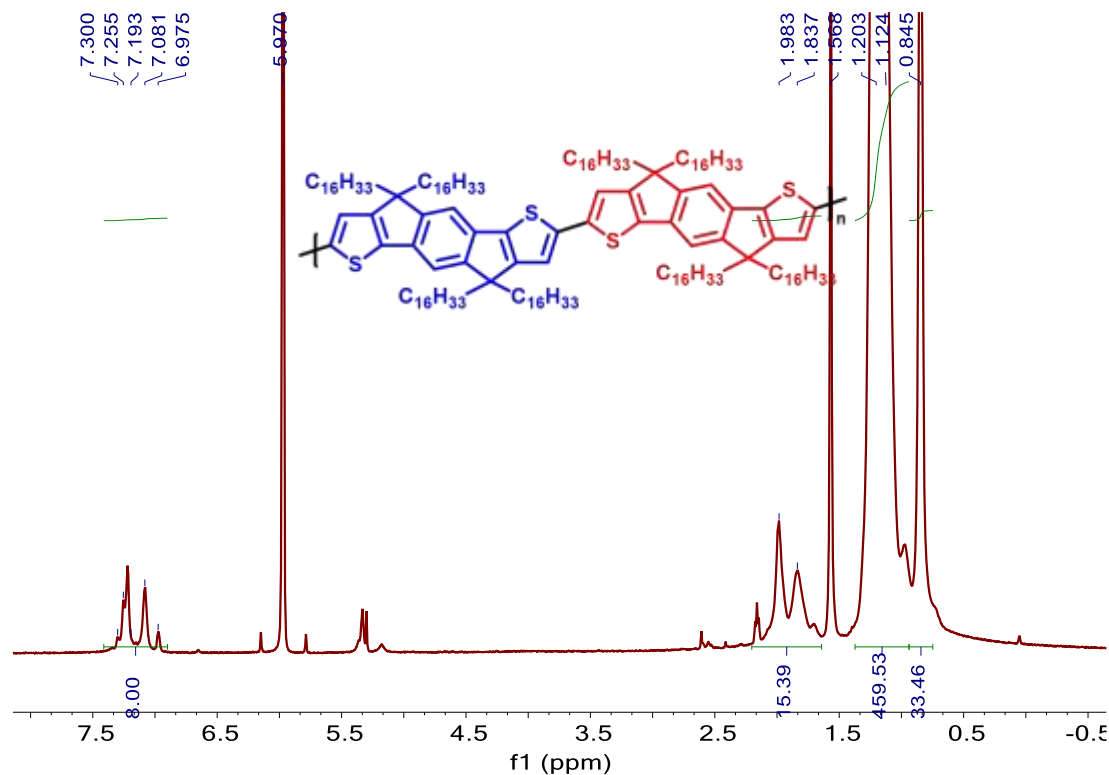
Mz: 49265

Mz+1: 67030

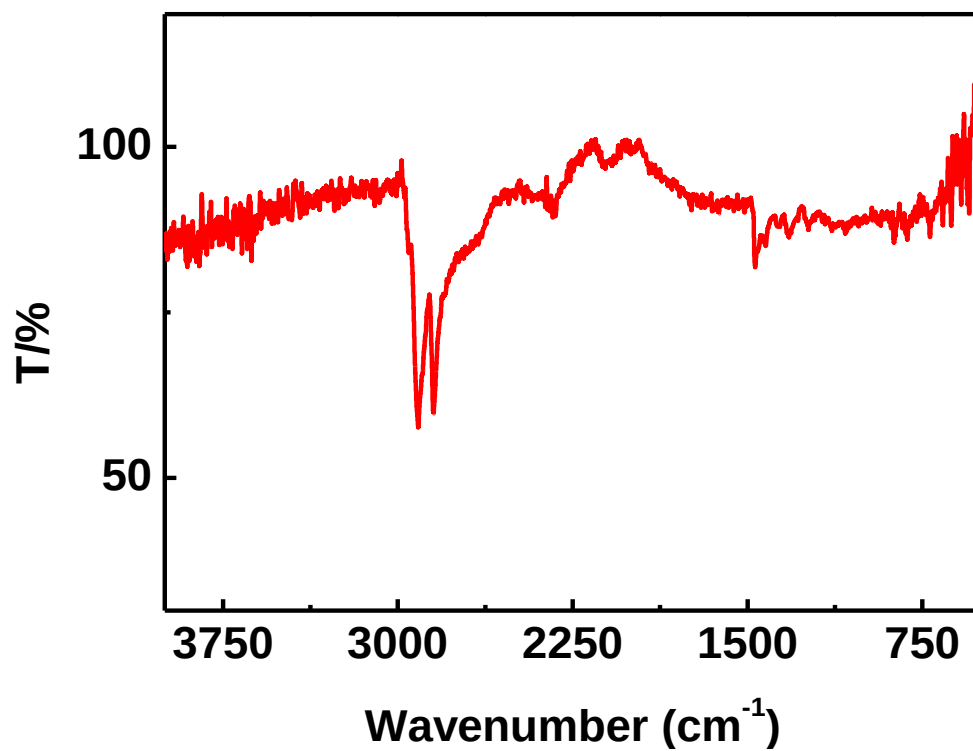
PD: 1.6305



Supplementary Fig. 161. Gel permeation chromatography (GPC) trace of **P23**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P23**.

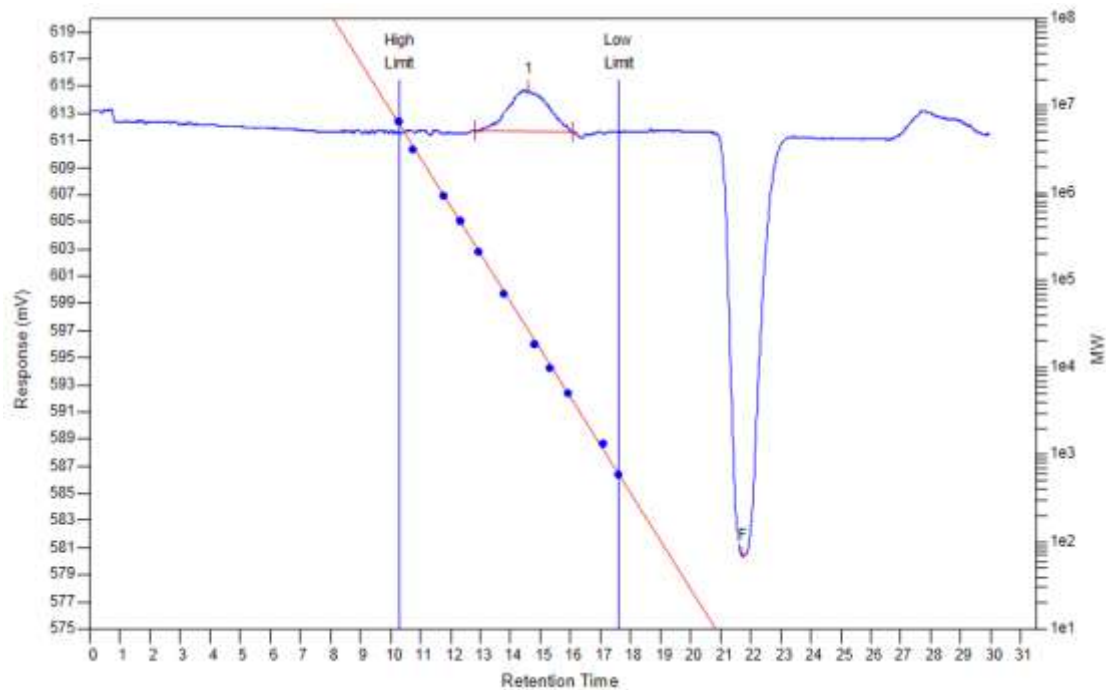


Supplementary Fig. 162. ^1H NMR (500 MHz) spectra of **P24** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.

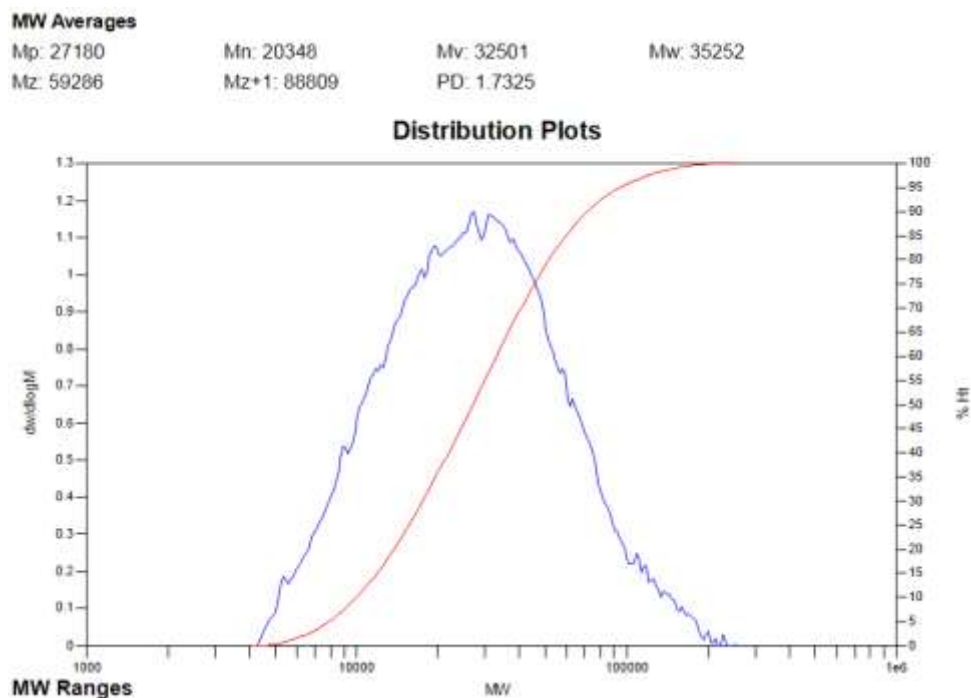


Supplementary Fig. 163. FT-IR spectrum of P24 in thin film at 298 K.

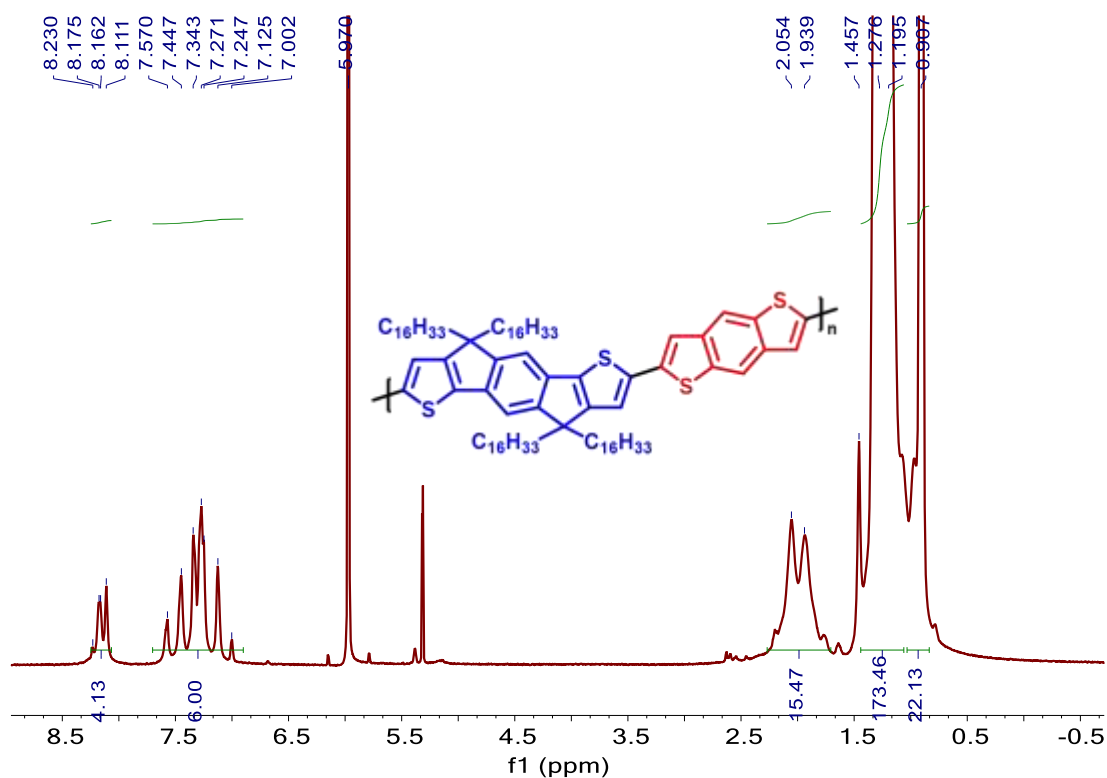
(a)



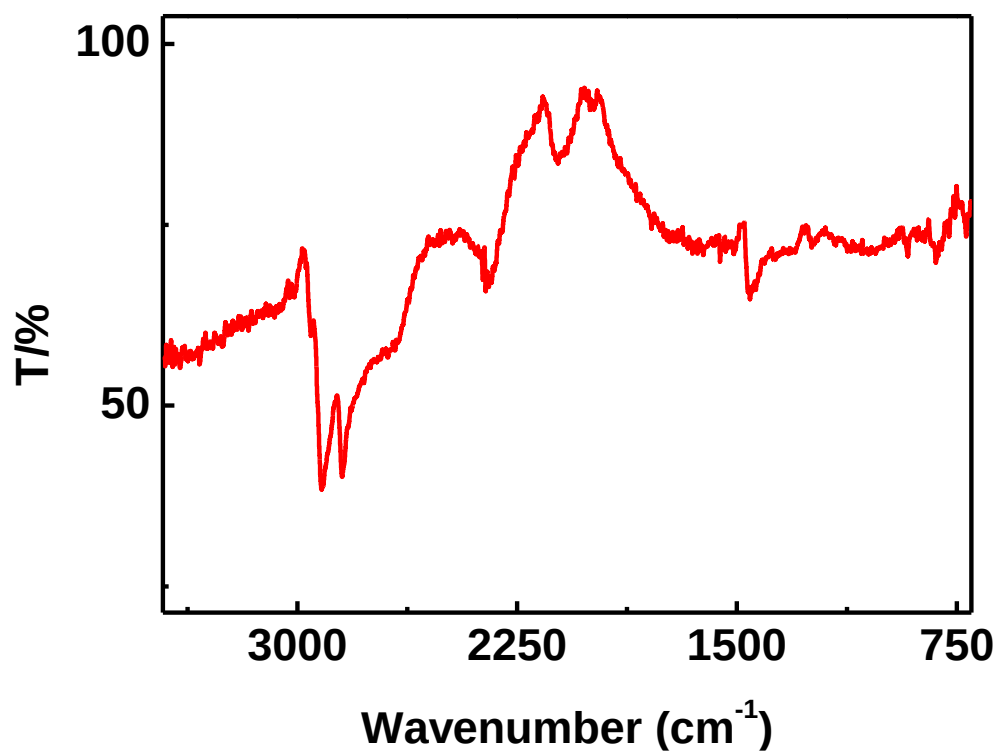
(b)



Supplementary Fig. 164. Gel permeation chromatography (GPC) trace of **P24**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P24**.

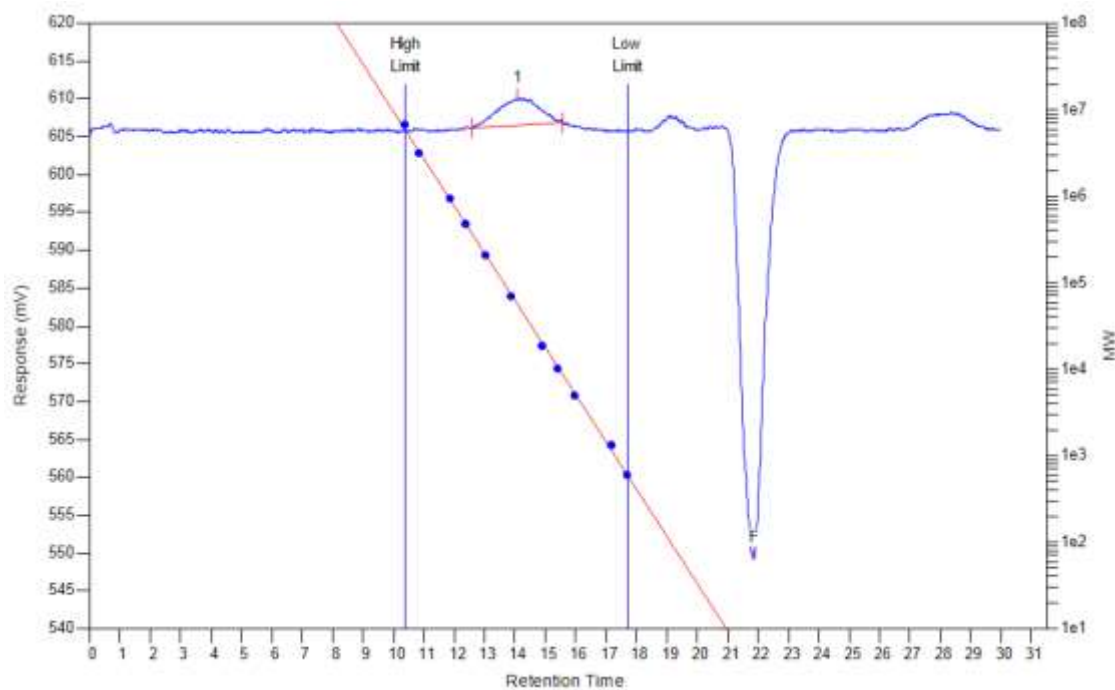


Supplementary Fig. 165. ^1H NMR (500 MHz) spectra of **P25** in $\text{C}_2\text{D}_2\text{Cl}_4$ at 373 K.



Supplementary Fig. 166. FT-IR spectrum of **P25** in thin film at 298 K.

(a)



(b)

MW Averages

Mp: 56223

Mn: 41062

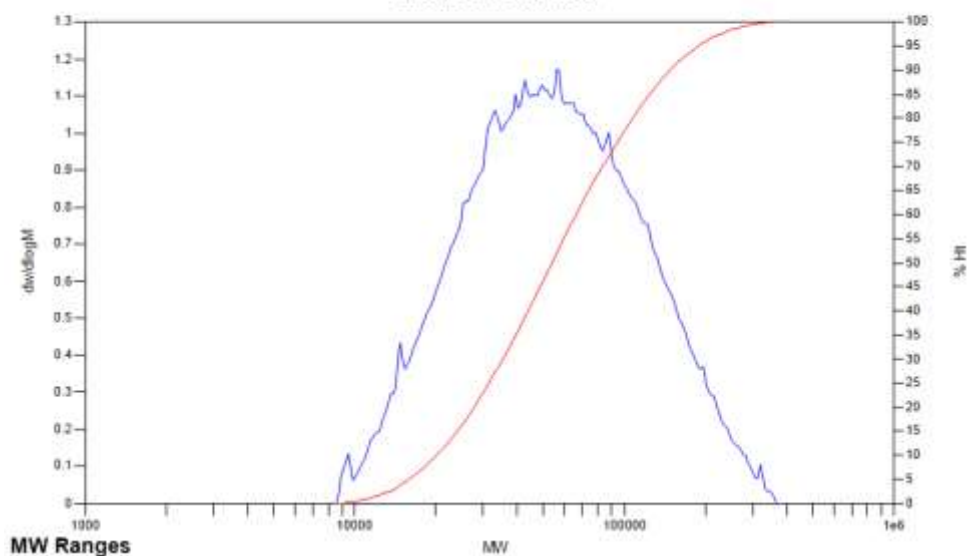
Mv: 65492

Mw: 70816

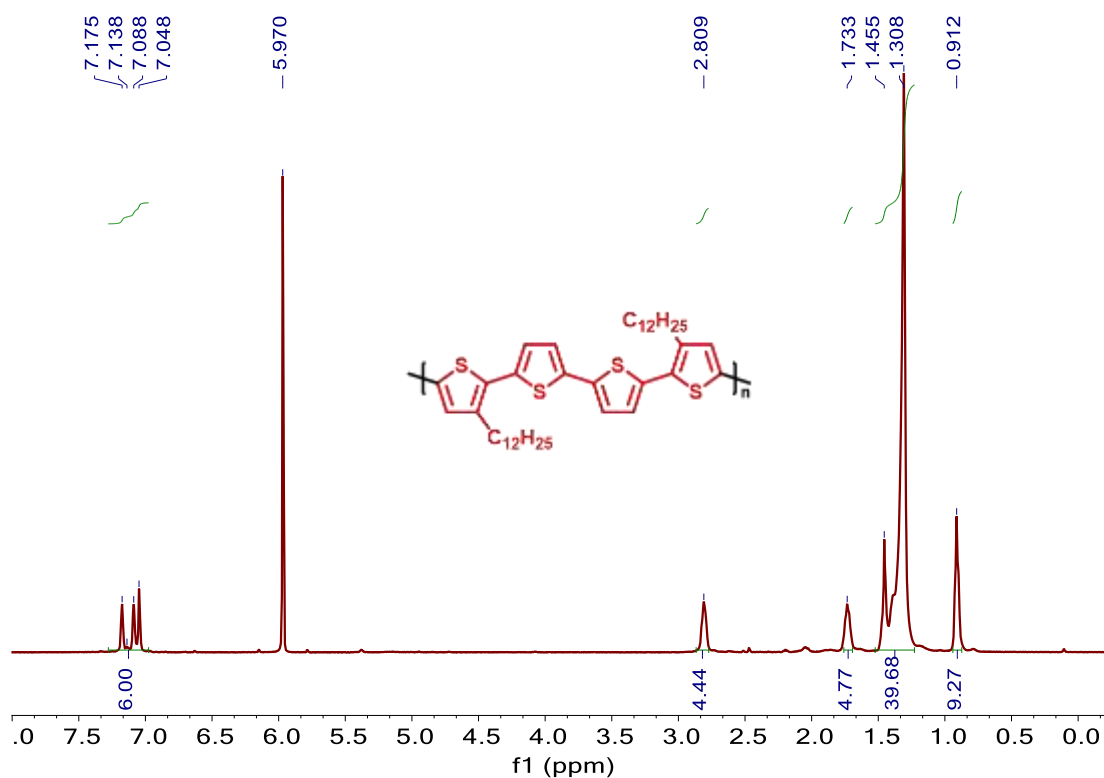
Mz: 114491

Mz+t: 160539

PD: 1.7246

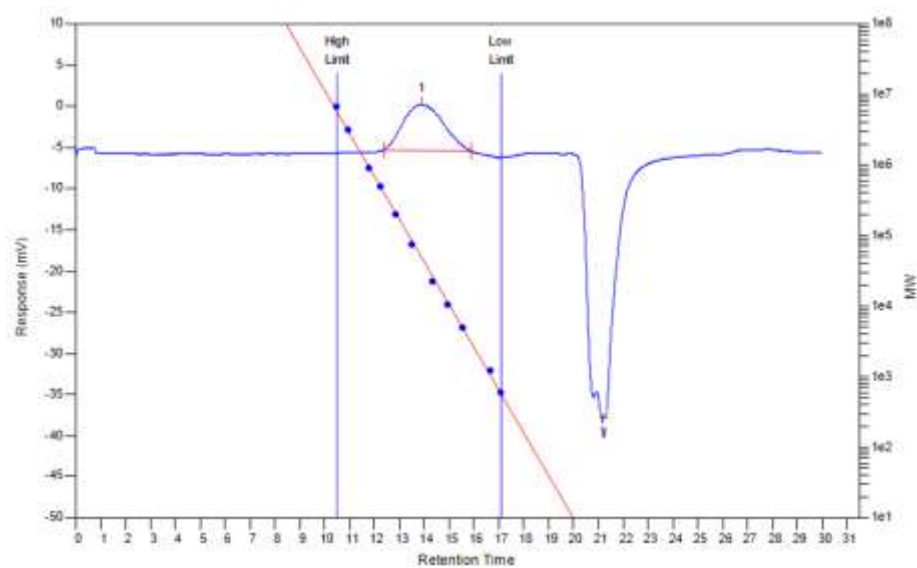
Distribution Plots

Supplementary Fig. 167. Gel permeation chromatography (GPC) trace of **P25**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P25**.



Supplementary Fig. 168. ¹H NMR (500 MHz) spectra of **P26** in C₂D₂Cl₄ at 373 K.

(a)



(b)

MW Averages

Mp: 50241

Mn: 26549

Mv: 55743

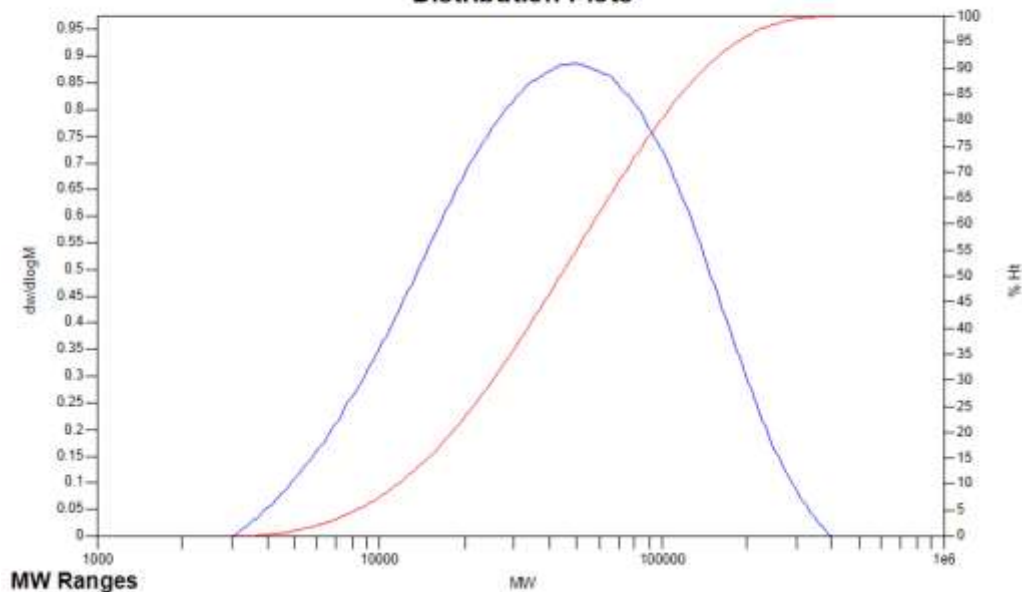
Mw: 62170

Mz: 115036

Mz+1: 165860

PD: 2.3417

Distribution Plots



Supplementary Fig. 169. Gel permeation chromatography (GPC) trace of **P26**. (a) Trace data from refractive index (RI) detector. (b) Molecular weight distribution plots of **P26**.

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