Supporting Information-OL

A Facile Synthesis of Complicated 9,9-Diarylfluorenes Based on $BF_3 \cdot Et_2O$-mediated Friedel-Crafts Reaction

Ling-Hai Xie,[†] Xiao-Ya Hou,[†] Yu-Ran Hua,[†] Chao Tang,[†] Feng Liu,[†] Qu-Li Fan,[†] and Wei Huang[†,‡,*]

[†] Institute of Advanced Materials (IAM), Fudan University, 220 Handan Raod, Shanghai 200433, People's Republic of China

[‡] Faculty of Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117576, Republic of Singapore

Email: wei-huang@fudan.edu.cn; chehw@nus.edu.sg

Experimental Section

Chemicals: magnesium turnings, thiophene, fluorenone, carbazole, pyrene, *tert*-butylbenzene, phenyl ether and tetrakistriphenylphosphine palladium(0) were obtained from Aldrich Chemical Co. and were used without further purification. 3,3-bithiophene, biphenyl boronic acid, 9-phenyl-fluoren-9-ol, [1] 2-bromo-9-phenyl-fluoren-9-ol, [1] and 2,7-dibromo-9-phenyl-fluoren-9-ol,[1] spiro[[8H]indeno[2,1-b]thiophene-8,9'-fluorene], [2] 9-(3-phenylthiophene-2-yl)-9-{spiro[[8H]indeno[2,1-b]thiophene-8,9'-fluorene]-2-yl}fluorene, [2] and spiro[cyclopenta[1,2-*b*:4,3-*b*']dithiophene-7,9'-fluorene][3] were prepared as previously reported. THF and diethyl ether were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior to use. All reactions involving organometallic reagents were carried out under nitrogen.

Procedures: Melting points were determined by a Fukai (Beijing) X-4 digital melting point instrument. ^{1}H- and ^{13}C-NMR in $CDCl_3$ was recorded at 400 MHz using a Varian

(1) Wong, K.-T.; Wang, Z.-J.; Chien, Y.-Y.; Wang, C.-L. *Org. Lett.* 2001, *3*(15), 2285-2288.
(2) Xie, L.-H.; Fu, T.; Hou, X.-Y.; Tang, C. Hua, Y.-R.; Wang, R.-J. Si, S.-M.; Fan, Q.-L.; Peng, B.; Wang, L.-H.; Wei, W.; Huang, W.. *Tetrahedron Lett.* Accepted.
(3) Xie, L.-H.; Hou, X.-Y.; Fu, T.; Tang, C. Hua, Y.-R.; Wang, R.-J. Si, S.-M.; Fan, Q.-L.; Peng, B.; Wang, L.-H.; Wei, W.; Huang, W. *Tetrahedron.* submitted.

Mercury 400 plus spectrometer. Chemical shifts are reported in parts per million (δ), and the signals have been designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Mass spectra were recorded on a Shimadzu GCMS-QP2010 plus equipped with DB-5 ms column or a Shimadzu AXIMA-CFR *plus* spectrometer. For the MALDI-TOF MS spectra, the spectra were recorded in reflective mode, and no substrates were used. Elemental analyses were carried out on an Elementar Analysensysteme GmbH Vario EL *III* Instrument. Absorption spectra (1 μM in CH_2Cl_2) were measured with a Shimadzu UV-3150 spectrometer at 25 ^oC, and emission spectra (1 μM in CH_2Cl_2) were recorded on a Shimadzu RF-530XPC luminescence spectrometer upon excitation at the absorption maxima in the degassed CH_2Cl_2 solvent after saturating with argon. Differential scanning calorimetry (DSC) analyses were performed on a Shimadzu DSC-60A Instrument. The sample was firstly heated (10 ^oC/min) to 360 ^oC, and then quenched with liquid nitrogen; the sample was secondly recorded by heating (10 ^oC/min) the quenched sample. Thermogravimetric analyses (TGA) were conducted on a Shimadzu DTG-60H thermogravimetric Analyzer under a heating rate of 10 ^oC/min and a nitrogen flow rate of 20 cm^3/min. Cyclic voltammetric (CV) studies were conducted using an Eco Chemie B. V. AUTOLAB potentiostat in a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode, and a silver/silver nitrate (Ag/Ag^+) reference electrode. All electrochemical experiments were carried out under a nitrogen atmosphere at room temperature in an electrolyte solution of 0.1 M tetrabutylammonium hexafluorophosphate ($Bu_4N^+PF_6^-$) in CH_2Cl_2 at a sweeping rate of 0.1V/s. According to the redox onset potentials of the CV measurements, the HOMO/LUMO energy levels of the materials are estimated based on the reference energy level of ferrocene (4.8 eV below the vacuum): HOMO/LUMO = -(E_{onset} - 0.0468 V) - 4.8 eV, where the value 0.0468 V is for FOC vs Ag/Ag^+. X-ray crystallographic data for **BSBF-SDTF** were collected on a P4 Bruker diffractometer equipped with a Bruker SMART 1K CCD area detector (employing the program SMART) and a rotating anode utilizing graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was carried out by use of the program SAINT, while the

program SADABS was utilized for the scaling of diffraction data, the application of a decay correction and an empirical absorption correction based on redundant reflections. The structures were solved by using the direct-methods procedure in the Bruker SHELXL program library and refined by full-matrix least-squares methods on F^2. All non-hydrogen atoms were refined using anisotropic thermal parameters and hydrogen atoms were added as fixed contributors at calculated positions, with isotropic thermal parameters based on the carbon atom to which they are bonded.

Synthesis

General procedure for reaction of 9-phenyl-fluoren-9-ol and its derivatives with aryl substrates:

A solution of boron trifluoride–diethyl ether complex in appropriate dichloromethane (20 mL) was added dropwise to a mixture solution of tertiary alcohols and aryl substrates in appropriate dichloromethane (100 mL). The reaction mixture was stirred at rt (25 ^{o}C) under nitrogen until starting material is no longer detectable by TLC (2 hours-2 days). Ethanol (50 mL) and water (150 mL) was successively added to quench the reaction. And then the phases were separated and the aqueous phase was extracted with dichloromethane. The combined dichloromethane layers were washed and dried ($MgSO_4$). After removal of the solvent, the remaining crude product was purified by silicon gel chromatography (petroleum ether–dichloromethane) to yield products.

Reaction of 9-phenyl-fluoren-9-ol and tert-butylbenzene (entry 10):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (0.88 g, 3.41 mmol, 2.1 equiv.), tert-butylbenzene (0.25 mL, 0.217 g, 1.6 mmol), and $BF_3{\cdot}OEt_2$ complex (0.439.4 mL, 3.46 mmol). The yield of 9-(4-tert-butylphenyl)-9-phenyl-fluorene (**P10**) is 0 %. The yield of byproduct 9-phenyl-fluorene is 70 %. m. p.: 143 °C. GC-MS(*m*/*z*):242 [M^+]. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.824-7.805 (d, J = 7.6 Hz, 4H), 7.41-7.373 (d, J = 7.6 Hz, 2H), 7.337-7.318 (d, J = 7.6 Hz, 2H), 7.296-7.233 (m, 5H), 7.114-7.094 (d, J = 8.0 Hz, 2H), 5.061 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 148.12, 141.819, 141.223, 128.911, 128.562, 127.531, 127.056, 125.559, 120.098, 54.664. Anal. Calcd for $C_{19}H_{14}$: C, 94.18; H, 5.82. Found: C, 94.22; H, 5.80.

Reaction of 9-phenyl-fluoren-9-ol and 1-phenoxybenzene (entry 8):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (0.88 g, 3.41 mmol, 2.1 equiv.), 1-phenoxybenzene (0.276 g, 1.6 mmol), and BF_3-Et_2O complex (0.439.4 mL, 3.46 mmol). The yield of 9-phenyl-fluoren-9-yl-phenyl ether (**P8**, 0.729 g) is 70%. m. p.: 358 °C. MALDI-TOF-MS (*m*/*z*): 650.3 (M^+), 650.4.^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.757-7.738 (d, *J* = 7.6 Hz, 4H), 7.384-7.326 (m, 8H), 7.324-7.233 (m, 4H), 7.191 (s, 5H), 7.125-7.103 (d, *J* = 8.8 Hz, 4H), 6.817-6.796 (d, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 156.038, 151.435, 146.099, 140.871, 140.268, 129.626, 128.428, 128.266, 127.931, 127.688, 126.854, 126.334, 120.381, 118.633, 65.135. Anal. Calcd for $C_{50}H_{34}O$: C, 92.28; H, 5.27; O, 2.46. Found: C, 92.22; H, 5.23; O, 2.44.

The yield of byproduct 9-(4-phenoxyphenyl)-9-phenyl-fluorene is 20%. m. p.: 140 °C. MALDI-TOF-MS (*m*/*z*): 410.2 (M^+), 410.3. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.778-7.759 (d, *J* = 7.6 Hz, 2H), 7.421-7.402 (d, *J* = 7.6 Hz, 2H), 7.383-7.345 (t, *J* = 7.6 Hz, 2H), 7.324-7.276 (m, 4H), 7.214 (s, 5H), 7.166-7.144 (d, *J* = 8.8 Hz, 2H), 7.093-7.056 (t, *J* = 7.6 Hz, 1H), 7.001-6.977 (d, *J* = 8.4 Hz, 2H), 6.856-6.834 (d, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 157.21, 156.237, 151.477, 146.159, 140.798, 140.301, 129.91, 129.694, 128.462, 128.298, 127.963, 127.726, 126.888, 126.379, 123.496, 120.419, 119.237, 118.484, 65.171. Anal. Calcd for $C_{31}H_{22}O$: C, 90.70; H, 5.40; O, 3.90. Found: C, 90.74; H, 5.39; O, 3.92.

Reaction of 9-phenyl-fluoren-9-ol and pyrene (entry 9):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (0.88 g, 3.41 mmol, 2.1 equiv.), pyrene (0.323 g, 1.6 mmol), and BF_3-Et_2O complex (0.439.4 mL, 3.46 mmol). The yield of 1-(9-phenyl-fluoren-9-yl)pyrene (**P9**, 0.212 g) is 30 %. m. p.: 280 °C. MALDI-TOF-MS (*m*/*z*): 442.2. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.156-8.137 (d, *J* = 7.6 Hz, 1H), 8.094-8.075 (d, *J* = 7.6 Hz, 1H), 8.034-7.924 (m, 5H), 7.863-7.844 (d, *J* = 7.6 Hz, 2H), 7.806-7.785 (d, 1H), 7.716-7.696 (d, 1H), 7.631-7.614 (d, 2H), 7.409-7.37 (t, *J* = 7.6 Hz, 2H), 7.245-7.207 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.264, 147.25, 140.199, 139.359, 131.634, 131.126, 130.528, 129.735, 128.941, 128.11, 127.861,

127.646, 127.49, 126.766, 126.633, 126.163, 126.141, 125.322, 125.164, 125.06, 124.875, 120.59, 66.997. Anal. Calcd for $C_{35}H_{22}$: C, 94.99; H, 5.01. Found: C, 94.96; H, 5.00.

Reaction of 9-phenyl-fluoren-9-ol and thiophene (entry 1):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (3.224g, 12.48mmol, 2equiv.), thiophene (0.5 mL, 0.525g, 6.24 mmol), and BF_3-Et_2O complex (1.865 mL, 14.687mmol). The yield of 2,5-bis(9-phenyl-fluoren-9-yl)thiophene (**P1**, 3.414 g) is 97 %. m. p.: 254 °C. MALDI-TOF-MS (*m*/*z*): 564.2 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.755-7.737 (d, *J* = 7.6 Hz, 4H), 7.478-7.459 (d, *J* = 7.6 Hz, 4H), 7.384-7.344 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 4H), 7.291-7.251 (td, *J* = 7.6 Hz, *J* = 1.2 Hz, 4H), 7.173 (s, 5H), 6.624 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 151.092, 148.197, 145.761, 139.998, 128.346, 127.949, 127.89, 127.768, 127.096, 126.405, 125.817, 120.367, 62.559. Anal. Calcd for $C_{42}H_{28}S$: C, 89.32; H, 5.00; S, 5.68. Found: C, 89.34; H, 5.01.

Reaction of 2-bromo-9-phenyl-fluoren-9-ol and thiophene (entry 2):

This compound was prepared following the general procedures above using 2-bromo-9-phenyl-fluoren-9-ol (4.21 g, 12.48 mmol, 2 equiv.), thiophene (0.5 mL, 0.525 g, 6.24 mmol), and BF_3-Et_2O complex (1.865 mL, 14.687mmol). The yield of 2,5-bis(2-bromo-9-phenyl-fluoren-9-yl)thiophene (**P2**, 4.31 g) is 96 %. m. p.: 212 °C. MALDI-TOF-MS (*m*/*z*): .720.2 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.705-7.686 (d, *J* = 7.6 Hz, 2H), 7.602-7.582 (d, *J* = 8.0 Hz, 2H), 7.572 (s, 2H), 7.491-7.467 (d, *J* = 8.0 Hz, 2H), 7.436-7.417 (d, *J* = 7.6 Hz, 2H), 7.377-7.338 (t, *J* = 7.6 Hz, 2H), 7.303-7.264 (d, *J* = 7.6 Hz, 2H), 7.206-7.127 (m, 10H), 6.578-6.572 (d, *J* = 2.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.892, 150.76, 147.928, 144.802, 139.021, 138.878, 131.255, 129.571, 128.55, 128.361, 128.22, 127.721, 127.462, 126.375, 126.012, 121.786, 121.542, 120.474, 62.62. Anal. Calcd for $C_{42}H_{26}Br_2S$: C, 69.82; H, 3.63; Br, 22.12; S, 4.44. Found: C, 69.84; H, 3.65.

Reaction of 2,7-dibromo-9-phenyl-fluoren-9-ol and thiophene (entry 11):

This compound was prepared following the general procedures above using 2,7-dibromo-9-phenyl-fluoren-9-ol (5.19 g, 12.48 mmol, 2 equiv.), thiophene (0.5 mL,

0.525 g, 6.24 mmol), and BF_3-Et_2O complex (1.865 mL, 14.687 mmol). The yield of 2,5-bis(2,7- dibromo-9-phenyl-fluoren-9-yl)thiophene (**P11**, 4.94 g) is 90 %. m. p.: 338 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.572-7.552 (d, d, J = 8.0 Hz, J = 1.6 Hz, 8H), 7.5-7.475 (dd, J = 7.6 Hz, J = 1.6 Hz, 4H), 7.243-7.226 (m, 6H), 7.153-7.129 (m, 4H), 6.563 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$, ppm): δ 152.516, 147.658, 143.895, 137.904, 131.542, 129.569, 128.752, 127.814, 127.672, 126.159, 122.051, 121.88, 62.619. Anal. Calcd for $C_{42}H_{24}Br_4S$: C, 57.30; H, 2.75; Br, 36.31; S, 3.64. Found: C, 57.29; H, 2.76.

The yield of 9-phenyl-9-(thiophen-2-yl)-2,7-dibromofluorene is 9 %. GC-MS (EI-*m*/*z*): 480 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.604-7.579 (d, J = 8.0 Hz,3H), 7.519-7.495 (d, d, J = 8.0 Hz, J = 1.6 Hz, 2H), 7.269-7.253 (m, 3H), 7.202-7.163 (m, 3H), 6.932-6.91 (td, J = 3.6 Hz, J = 1.2 Hz, 1H), 6.865-6.853 (dd, J = 3.6 Hz, J = 1.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.997, 147.764, 144.018, 137.902, 131.532, 129.574, 128.763, 127.788, 127.697, 126.985, 126.803, 125.268, 122.023, 121.866, 62.472. Anal. Calcd for $C_{23}H_{14}Br_2S$: C, 57.29; H, 2.93; Br, 33.14; S, 6.65. Found: C, 57.25; H, 2.92.

Reaction of 9-phenyl-fluoren-9-ol with spiro[[8H]indeno[2,1-b]thiophene-8,9'-fluorene] (entry 5):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (0.76 g, 2.94 mmol), spiro[[8H]indeno[2,1-b] thiophene-8,9'-fluorene] (0.948 g, 2.94 mmol), and BF_3-Et_2O complex (439.4 μL, 3.46mmol). The yield of 9-(spiro[[8H]indeno[2,1-b]thiophene -8,9'-fluorene]-2-yl)-9-phenylfluorene (**P5**, 1.41 g) is 85 %. m. p.: 302 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.766-7.743 (d, J = 7.6 Hz, 2H), 7.54-7.521 (d, J = 7.2 Hz, 2H), 7.458-7.44 (d, J = 7.2 Hz, 1H), 7.397-7.357 (td, J = 7.6 Hz, J = 1.2 Hz, 2H), 7.355-7.315 (td, J = 7.6 Hz, J = 1.2 Hz, 2H), 7.306-7.266 (td, J = 7.6 Hz, J = 1.2 Hz, 2H), 7.248-7.2 (m, 6H), 7.137-7.097 (td, J = 7.6 Hz, J = 1.2 Hz, 2H), 6.939-6.898 (td, J = 7.6 Hz, J = 1.2 Hz, 1H), 6.829-6.81 (d, J = 7.6 Hz, 2H), 6.57-6.551 (d, J = 7.6 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.693, 152.603, 151.004, 147.944, 147.737, 146.808, 145.458, 141.604, 140.038, 139.442, 128.475, 128.149, 128.073, 127.955, 127.831, 127.594, 127.243, 126.431, 125.587, 124.179, 123.536, 120.439,

120.202, 119.323, 118.262, 64.52, 63.202. Anal. Calcd for $C_{42}H_{26}S$: C, 89.64; H, 4.66; S, 5.70. Found: C, 89.66; H, 4.64.

Reaction of 9-phenyl-fluoren-9-ol with spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene] (entry 6):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (0.800 g, 3.1 mmol, 2 equiv.), spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene] (0.5 g, 1.52 mmol, 1 equiv.), and BF_3-Et_2O complex (439.4 μL, 3.46 mmol). The yield of 2,5-bis(9-phenyl-fluoren-9-yl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene] (**P6**, 0.896 g) is 73 %. m. p.: > 400 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.712-7.693 (d, J = 7.6 Hz, 4H), 7.651-7.633 (d, J = 7.2 Hz, 2H), 7.449-7.43 (d, J = 7.6 Hz, 4H), 7.354-7.313 (t, J = 7.6 Hz, 4H), 7.304-7.260 (t, J = 7.6 Hz, 2H), 7.25-7.212 (t, J = 7.2 Hz, 4H), 7.17 (s, 10H), 7.13-7.093 (t, J = 7.6 Hz, 2H), 6.941(s, 2H), 6.881-6.861(d, J = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.351, 151.05, 147.944, 147.093, 145.432, 143.239, 141.084, 139.952, 128.374, 128.309, 128.114, 128.038, 127.862, 127.776, 127.154, 126.328, 124.266, 120.358, 120.174, 117.971, 63.029, 60.947. Anal. Calcd for $C_{59}H_{36}S_2$: C, 87.59; H, 4.49; S, 7.93. Found: C, 87.58; H, 4.48.

The yield of 2-(9-phenyl-fluoren-9-yl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene] is 20 %. m. p.: 311 °C. MALDI-TOF-MS (m/z): 568.1 (M^+), 567.3. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.74-7.711 (dd, J = 7.6 Hz, J = 7.2 Hz, 4H), 7.505-7.484 (d, J = 7.6 Hz, 2H), 7.38-7.316 (tt, J = 7.6 Hz, J = 7.2 Hz, 4H), 7.287-7.247 (m, 3H), 7.22-7.185 (m, 5H), 7.163-7.123 (tt, J = 7.6 Hz, J = 1.2 Hz, 2H), 7.068-7.056 (d, J = 4.2 Hz, 2H), 6.9-6.882 (d, J = 7.6 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 153.38, 151.061, 149.999, 148.502, 147.179, 145.526, 144.181, 142.933, 141.144, 139.991, 128.937, 128.429, 128.19, 128.086, 127.91, 127.814, 127.2, 126.392, 124.141, 120.403, 120.319, 118.235, 118.053, 77.45, 63.177, 63.072. Anal. Calcd for $C_{40}H_{24}S_2$: C, 84.47; H, 4.25; S, 11.28. Found: C, 84.46; H, 4.26.

Reaction of 9-phenyl-fluoren-9-ol with 9-(3-phenylthiophene-2-yl)-9-{spiro[[8H]indeno[2,1-b] thiophene-8,9'-fluorene]-2-yl}fluorene (entry 4):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (0.76 g, 2.94 mmol), 9-(3-phenylthiophene-2-yl)-9-{spiro[[8H]indeno[2,1-b] thiophene-8,9'-fluorene]-2-yl}fluorene (1.89 g, 2.94 mmol), and BF_3-Et_2O complex (439.4 μL, 3.46 mmol). The yield of

5-(2,7-dibromo-9-phenyl-fluoren-9-yl)-3-phenyl-2-(9-{spiro[[8H]indeno[2,1-b] thiophene-8,9'-fluorene]-2-yl}-fluoren-9-yl) thiophene (P4, 2.14 g) is 70 %. m. p.: 322 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.76-7.741(d, J = 7.6 Hz, 2H), 7.609-7.605(d, J = 1.6 Hz, 2H), 7.588-7.567(d, J = 8.0 Hz, 2H), 7.532-7.469 (m, 5H), 7.414-7.395 (d, J = 7.6 Hz, 3H), 7.346-7.308 (t, J = 7.6 Hz, 2H), 7.281-7.265 (m, 3H), 7.244-7.19 (m, 5H), 7.162-7.123 (t, J = 7.6 Hz, 2H), 7.098-7.06 (t, J = 7.6 Hz, 2H), 6.916-6.879 (t, J = 7.6 Hz, 1H), 6.854-6.817 (t, J = 7.6 Hz, 1H), 6.753-6.734 (d, J = 7.6 Hz, 2H), 6.716-6.678 (t, J = 7.6 Hz, 2H), 6.529-6.511(d, J = 7.2 Hz, 1H), 6.406 (s, 1H), 6.212-6.194 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 154.049, 152.67, 152.479, 150.083, 148.055, 147.667, 146.614, 144.058, 143.526, 143.125, 141.547, 139.928, 139.337, 138.733, 137.961, 136.446, 131.442, 131.235, 129.667, 128.914, 128.8, 128.124, 128.087, 127.749, 127.721, 127.553, 127.504, 126.938, 126.384, 126.162, 125.585, 124.261, 123.428, 122.021, 121.865, 120.222, 120.141, 119.496, 119.125, 64.422, 62.542, 59.499. Anal. Calcd for $C_{65}H_{38}Br_2S_2$: C, 74.86; H, 3.67; Br, 15.32; S, 6.15. Found: C, 74.86; H, 3.66.

Reaction of 9-phenyl-fluoren-9-ol with 3,3'-bithiophene (entry 3):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (2.054 g, 8.0 mmol, 4.4 equiv.), 3,3'-bithiophene (0.3 g, 1.8 mmol), and BF_3-Et_2O complex (1.195 mL, 9.14 mmol). The yield of 2,5,2',5'-tetrakis(9-phenyl-fluoren-9-yl)-3,3'-bithiophene (**P3**, 1.40 g) is 69 %. m. p.: 400 °C. MALDI-TOF-MS (m/z): 1126.1 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.905-7.887 (d, J = 7.6 Hz, 2H), 7.862-7.843 (d, J = 7.6 Hz, 2H), 7.513-7.474 (t, J = 7.6 Hz, 2H), 7.412-7.309 (m, 8H), 7.152-7 (m, 24H), 6.948-6.933 (m, 8H), 6.84-6.821 (d, J = 7.6 Hz, 2H), 6.728-6.693 (t, J = 7.6 Hz, 4H), 6.503-6.466 (t, J = 7.6 Hz, 2H), 5.344 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 150.129, 150.069, 149.797, 149.128, 147.175, 146.956, 143.133, 142.337, 140.837, 140.607, 139.762, 138.998, 132.122, 130.263, 128.059, 128.028, 127.894, 127.825, 127.798, 127.765, 127.73, 127.687, 127.612, 127.495, 127.157, 127.096, 127.066, 127.035, 126.85, 126.82, 126.37, 126.172, 120.365, 120.261, 119.858, 119.773, 62.698, 62.131. Anal. Calcd for $C_{84}H_{54}S_2$: C, 89.48; H, 4.83; S, 5.69. Found: C, 89.45; H, 4.81.

Reaction of 9-phenyl-fluoren-9-ol with carbazole (entry 7):

This compound was prepared following the general procedures above using 9-phenyl-fluoren-9-ol (0.88 g, 3.41 mmol, 3.1 equiv.), carbazole (0.190 g, 1.14 mmol),

and BF_3-Et_2O complex (439.4 μl, 3.46 mmol). The yield of 3,6-bis(9-phenyl-fluoren-9-yl)-carbazole (**P7**, 0.546 g) is 74 %. m. p.: 269 °C. MALDI-TOF-MS (*m*/*z*): 647 (M^+). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.86 (s, 1H), 7.781-7.763 (d, *J* = 7.6 Hz, 6H), 7.446-7.427 (d, *J* = 7.6 Hz, 4H), 7.365-7.325 (t, *J* = 7.6 Hz, 4H), 7.264-7.153 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.104, 147.001, 140.252, 138.948, 137.044, 128.419, 128.333, 127.908, 127.549, 126.762, 126.562, 123.387, 120.345, 120.013, 110.463, 65.817. Anal. Calcd for $C_{50}H_{33}N$: C, 92.70; H, 5.13; N, 2.16. Found: C, 92.74; H, 5.10; N, 2.14.

Synthesis of 2,5-bis(2,7,-bis([1,1'-biphenyl]-4-yl)-9-phenyl-fluoren-9-yl)thiophene (TBPFTF):

A mixture of 2,5-bis(2,7-dibromo-9-phenyl-fluoren-9-yl)thiophene (0.502 g, 0.57 mmol), 4-phenyl phenyl boronic acid (0.55 g, 2.7 mmol), $Pd(PPh_3)_4$ (157 mg, 0.135 mmol), Na_2CO_3 (2.0 M aqueous solution, 3.0 mL), and toluene (50 mL)/THF(30 mL) was stirred at 90 ^{o}C for 2 days. After it was cooled to room temperature, 200 mL of $CHCl_3$ was added to the reaction mixture. The organic portion was separated and washed with brine before dried over anhydrous $MgSO_4$. The solvent was evaporated off, and the solid residues were purified by column chromatography on silica gel with chloroform to afford TBPFTF as white solids (0.502 g, 75 %). m. p.: 419 °C. MALDI-TOF-MS (*m*/*z*): 1173.7 (M^+), ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.852-7.832 (d, *J* = 8.0 Hz,4H), 7.782 (s, 4H),7.694-7.671 (d, *J* = 8.0 Hz, 4H), 7.647-7.627 (d, *J* = 8.0 Hz, 8H), 7.58-7.559 (d, *J* = 8.4 Hz, 8H), 7.553-7.532 (d, *J* = 8.0 Hz,8H), 7.41-7.373 (t, *J* = 7.6 Hz,4H), 7.343-7.307 (t, 8H), 7.211-7.194 (m, 6H), 6.708 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 152.01, 148.95, 140.801, 140.335, 140.126, 138.989, 129, 128.504, 127.993, 127.72, 127.658, 127.22, 127.094, 125.784, 124.964, 124.33, 120.883, 62.816. Anal. Calcd for $C_{90}H_{60}S$: C, 92.11; H, 5.15; S, 2.73. Found: C, C, 92.13; H, 5.17.

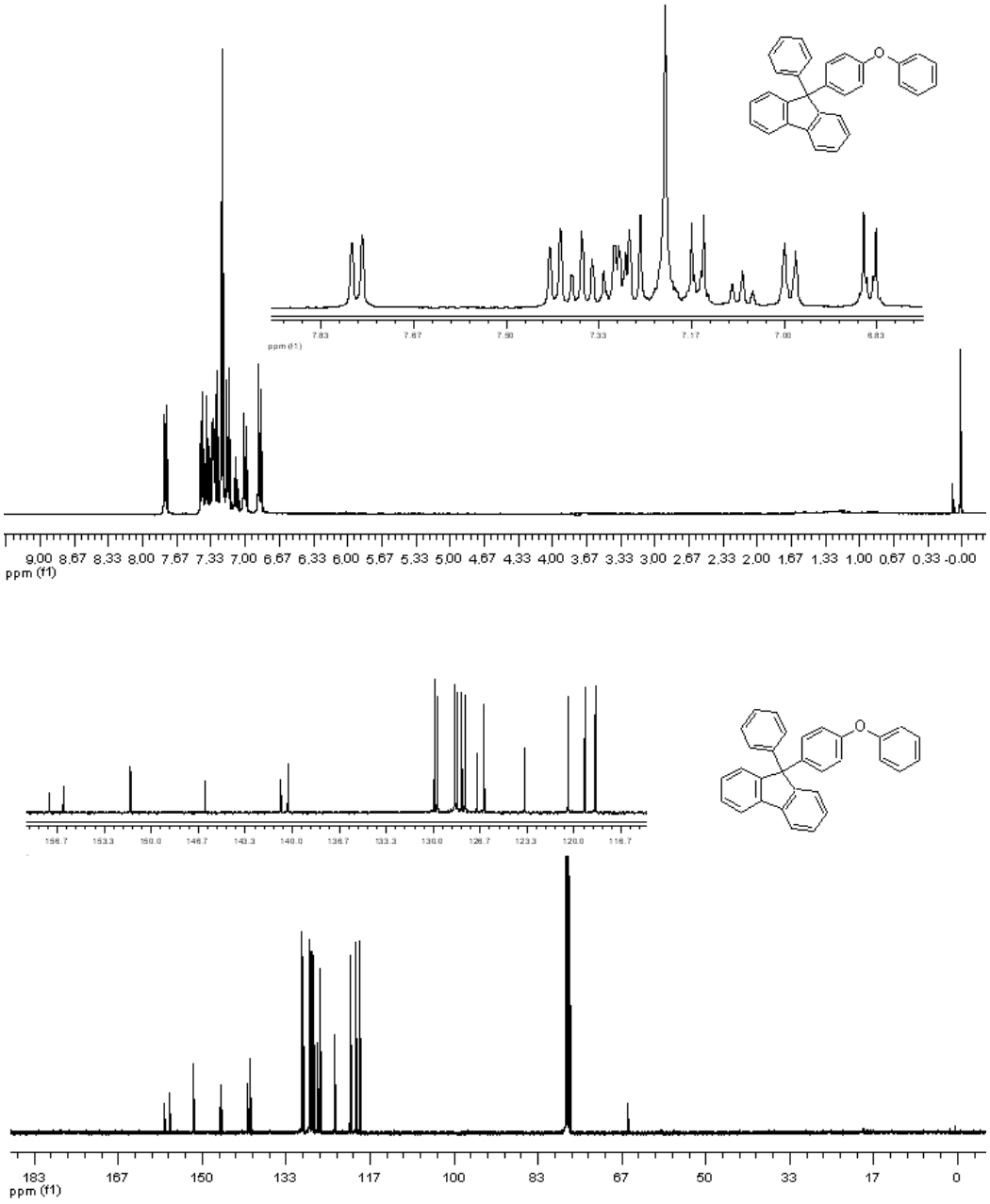


Figure SI-1: The ^{1}H-NMR and ^{13}C-NMR spectra of 9-(4-phenoxyphenyl)-9-phenyl-fluorene.

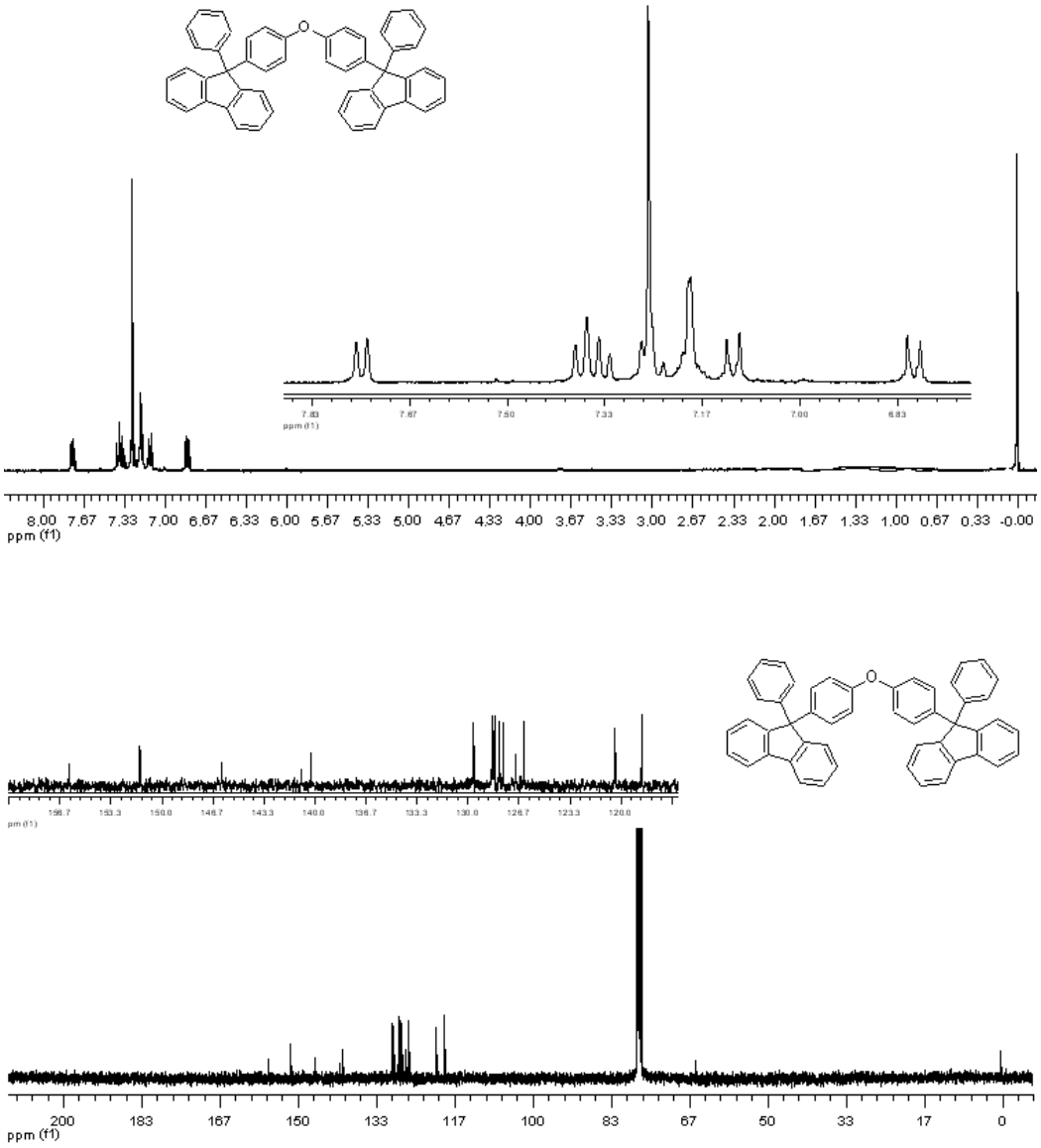


Figure SI-2: The ^{1}H-NMR and ^{13}C-NMR spectra of 9-phenyl-fluoren-9-yl-phenyl ether (**P8**).

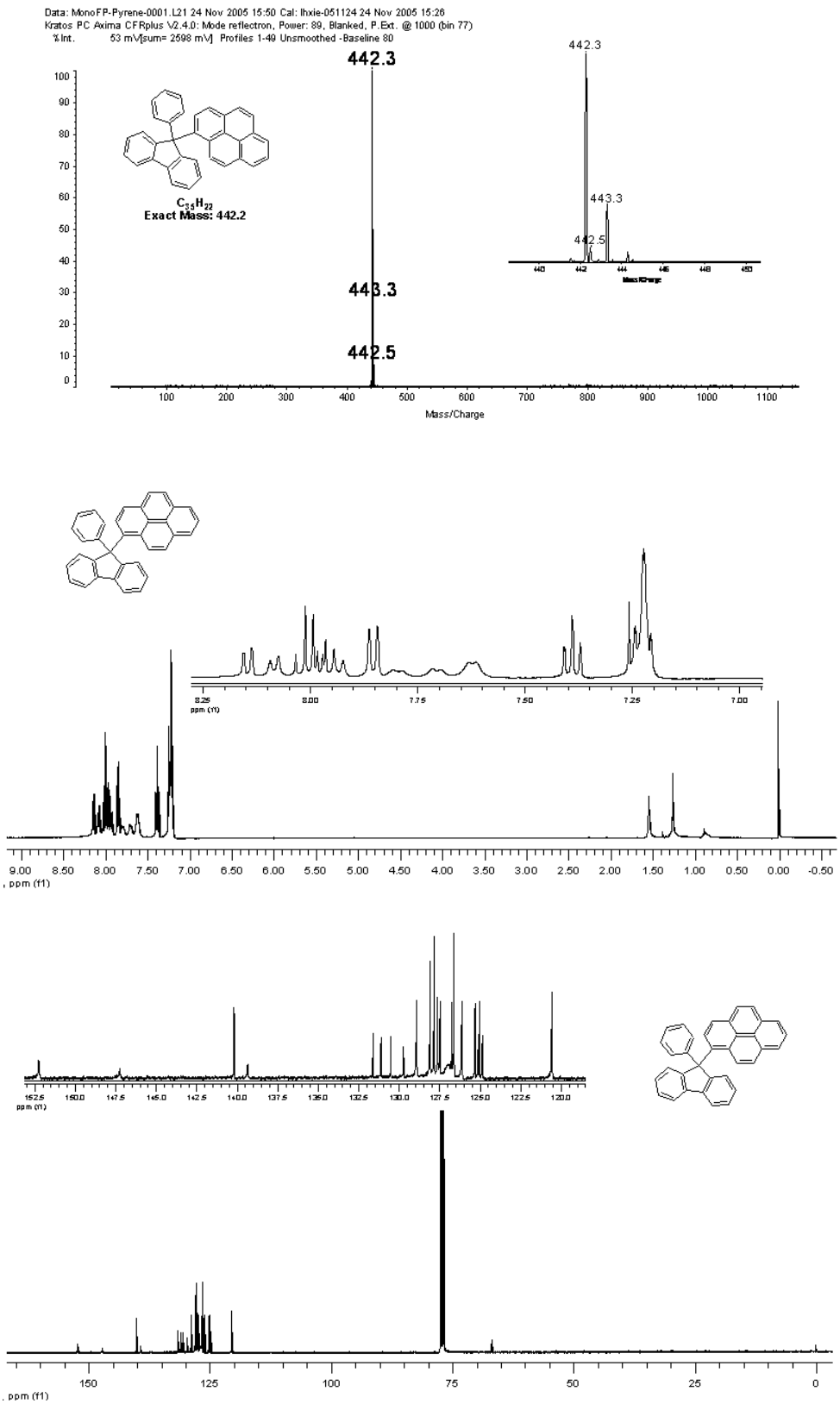


Figure SI-3: The MALDI-TOF-MS, ^{1}H-NMR and ^{13}C-NMR spectra of 9-phenyl-9-pyrenyl-fluorene (**P9**).

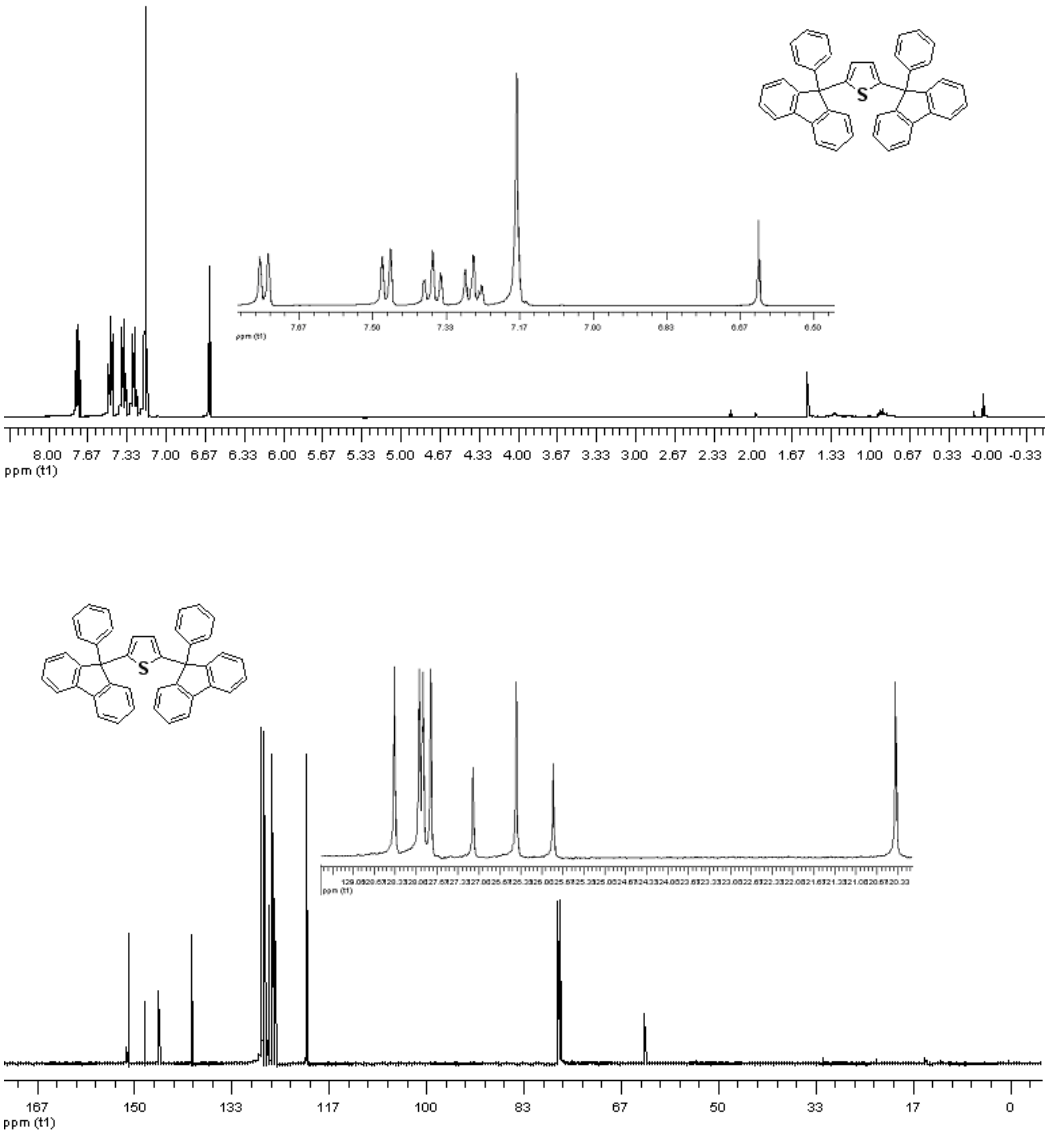


Figure SI-4: The ^{1}H-NMR and ^{13}C-NMR spectra of 2,5-bis(2-bromo-9-phenyl-fluoren-9-yl)thiophene (**P1**).

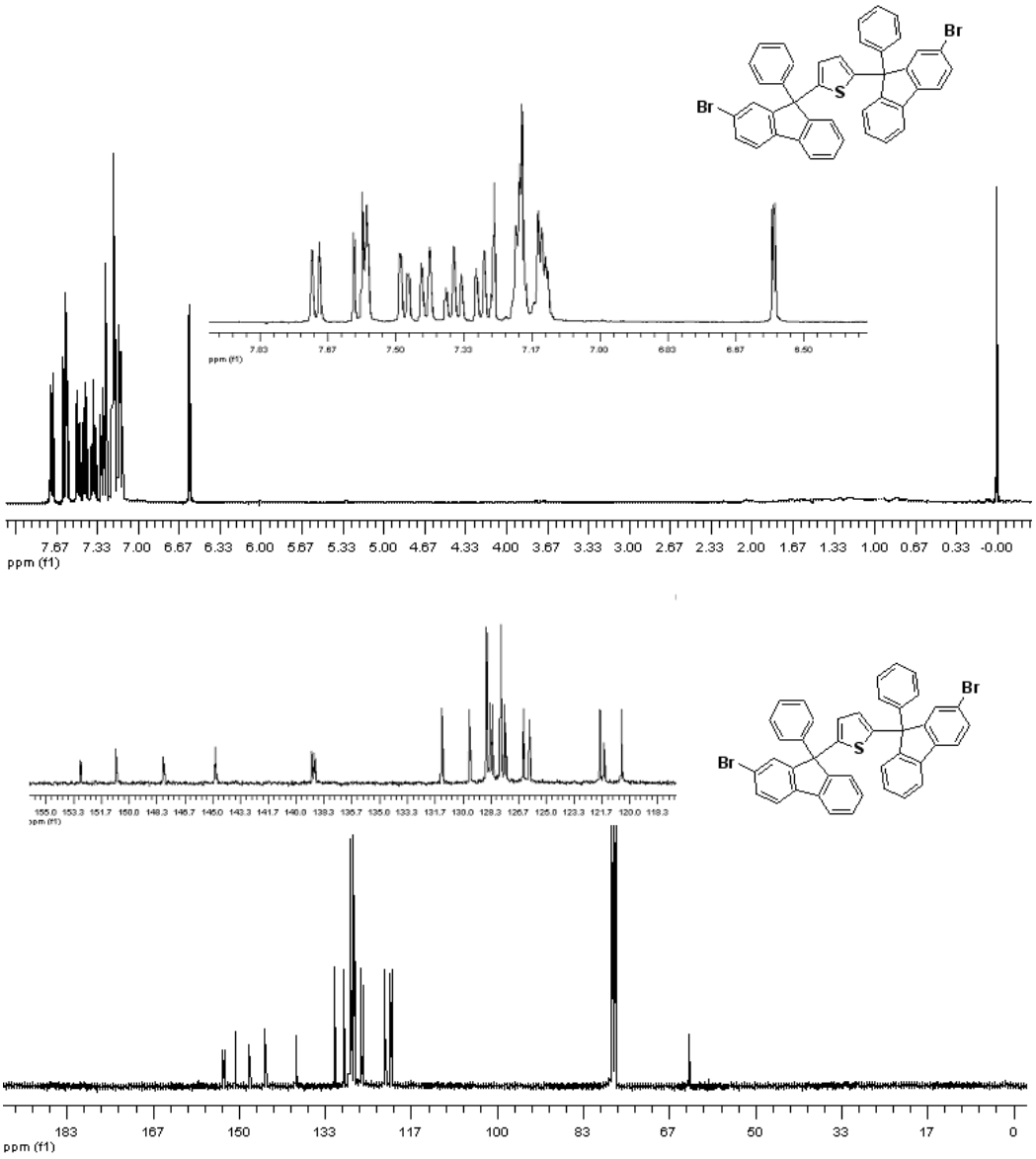


Figure SI-5: The ^{1}H-NMR and ^{13}C-NMR spectra of

2,5-bis(2-bromo-9-phenyl-fluoren-9-yl)thiophene (**P2**).

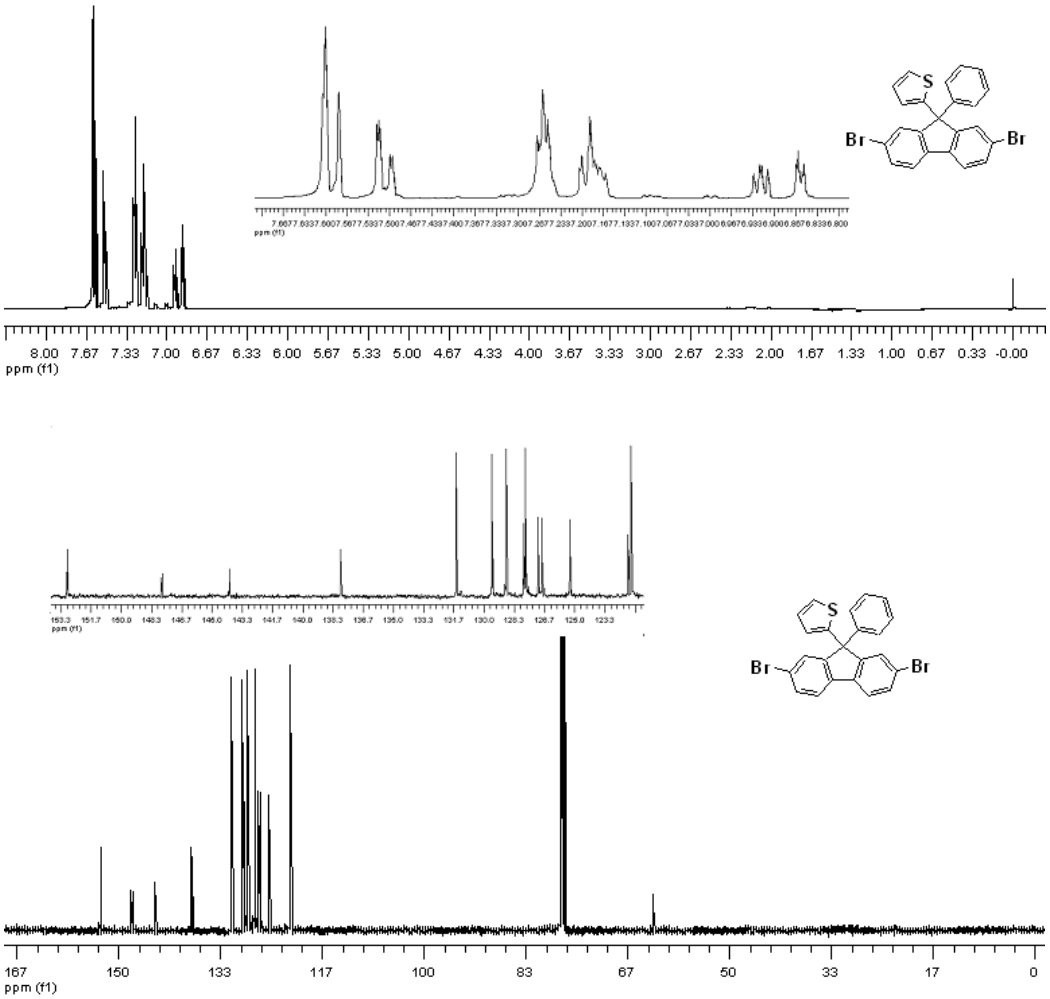


Figure SI-6: The ^{1}H-NMR and ^{13}C-NMR spectra of

9-phenyl-9-(thiophen-2-yl)-2,7-dibromofluorene.

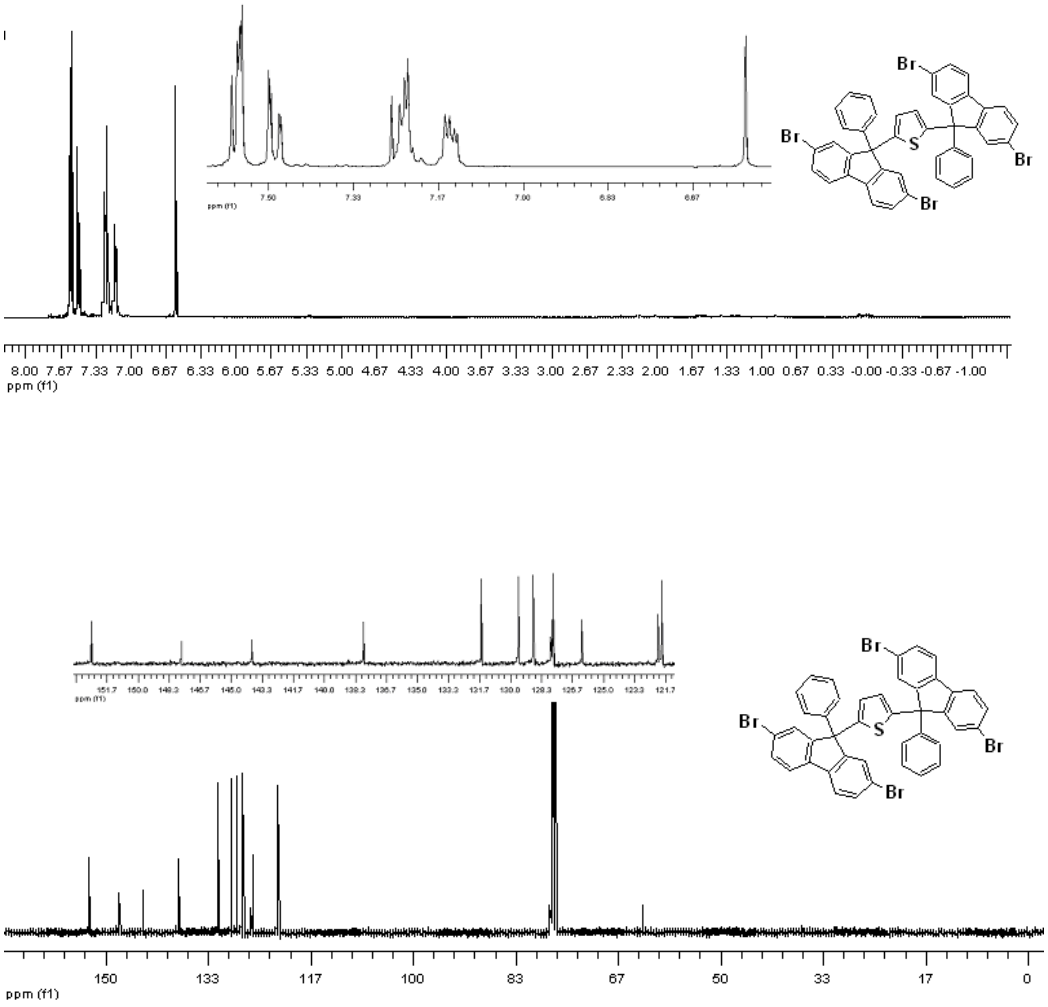


Figure SI-7: The ^{1}H-NMR and ^{13}C-NMR spectra of

2,5-bis(2,7-dibromo-9-phenyl-fluoren-9-yl)thiophene (**P11**).

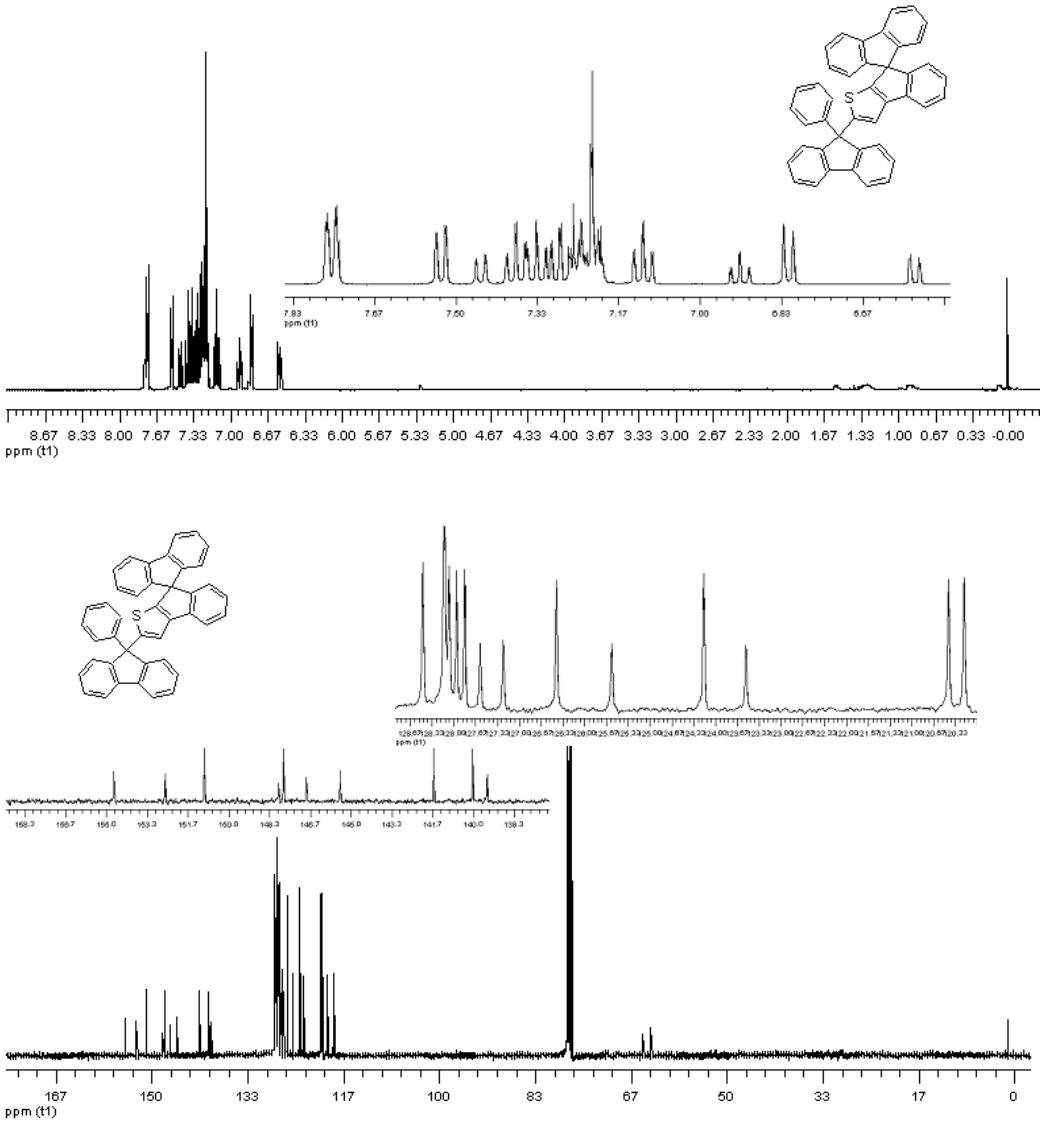


Figure SI-8: The ^{1}H-NMR and ^{13}C-NMR spectra of

9-(spiro[[8H]indeno[2,1-b]thiophene-8,9'-fluorene]-2-yl)-9- phenylfluorene (**P5**).

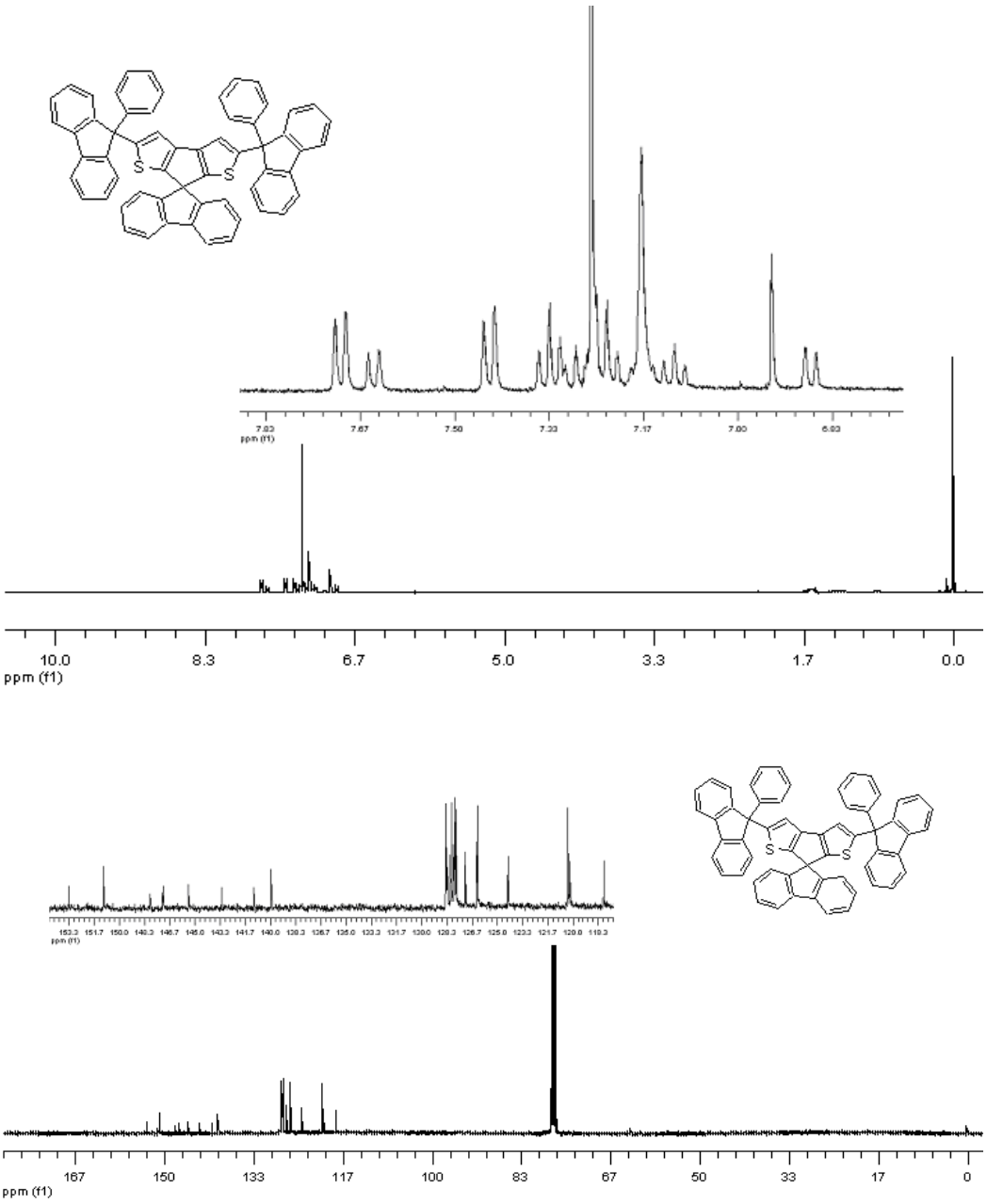
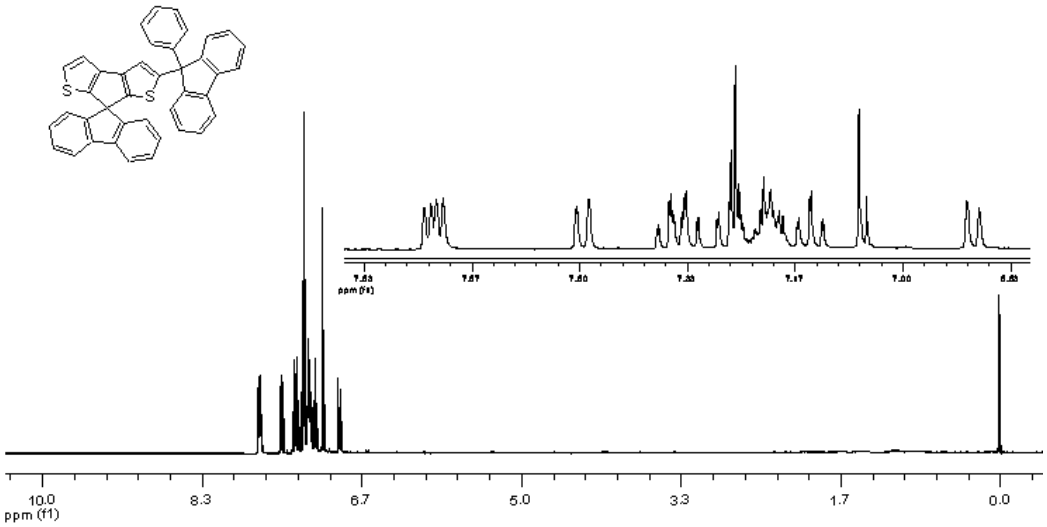


Figure SI-9: The ^{1}H-NMR and ^{13}C-NMR spectra of 2,5-bis(9-phenyl-fluoren-9-yl) -spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene] (**P6**).



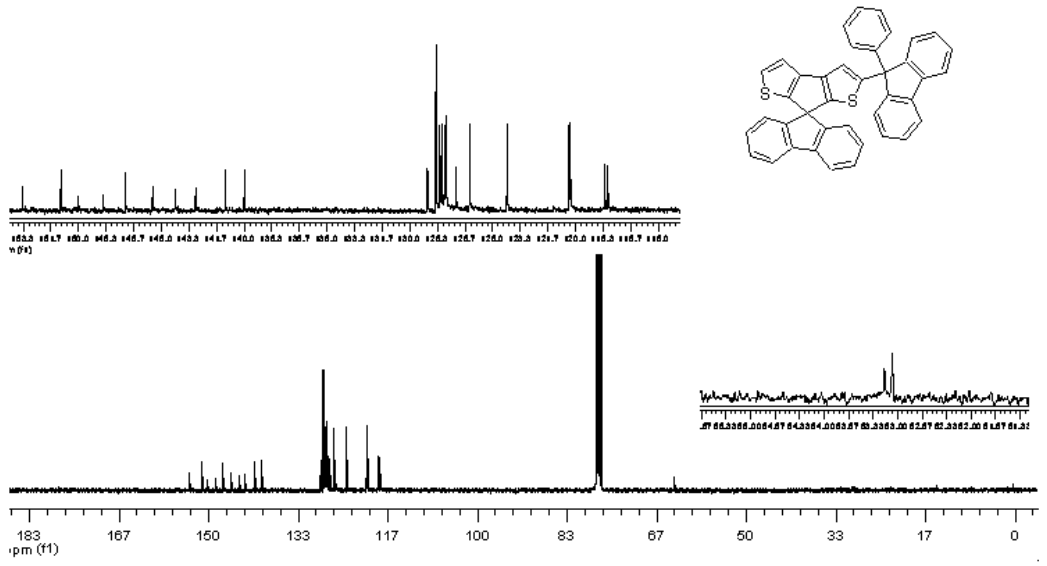


Figure SI-10: The ^{1}H-NMR and ^{13}C-NMR spectra of 2-(9-phenyl-fluoren-9-yl)-spiro[cyclopenta[1,2-b:4,3-b']dithiophene-7,9'-fluorene]

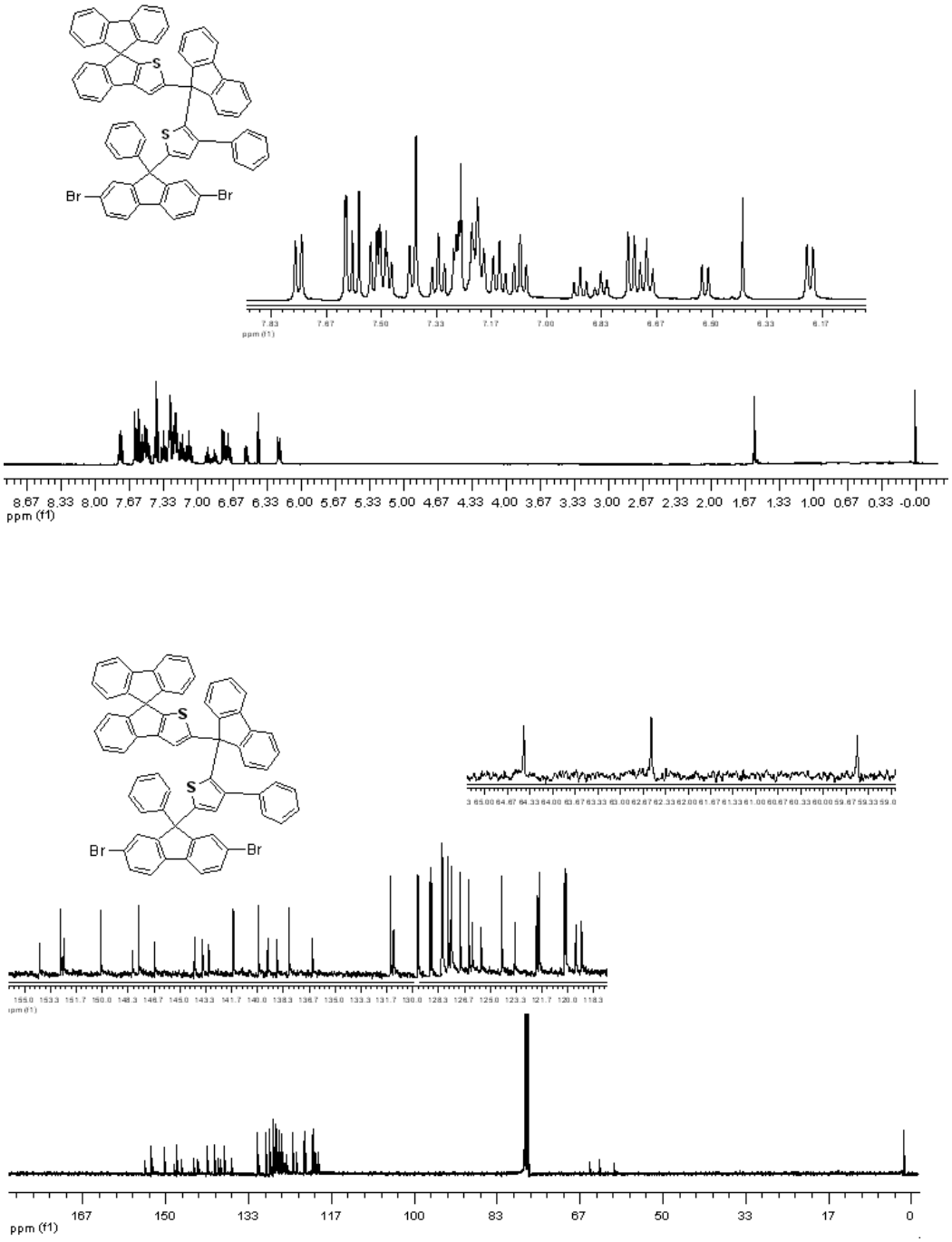


Figure SI-11: The ^{1}H-NMR and ^{13}C-NMR spectra of

5-(2,7-dibromo-9-phenyl-fluoren-9-yl)-3-phenyl- 2-(9-{spiro[[8H]indeno[2,1-b]

thiophene-8,9'-fluorene]-2-yl}-fluoren-9-yl)thiophene (**P4**).

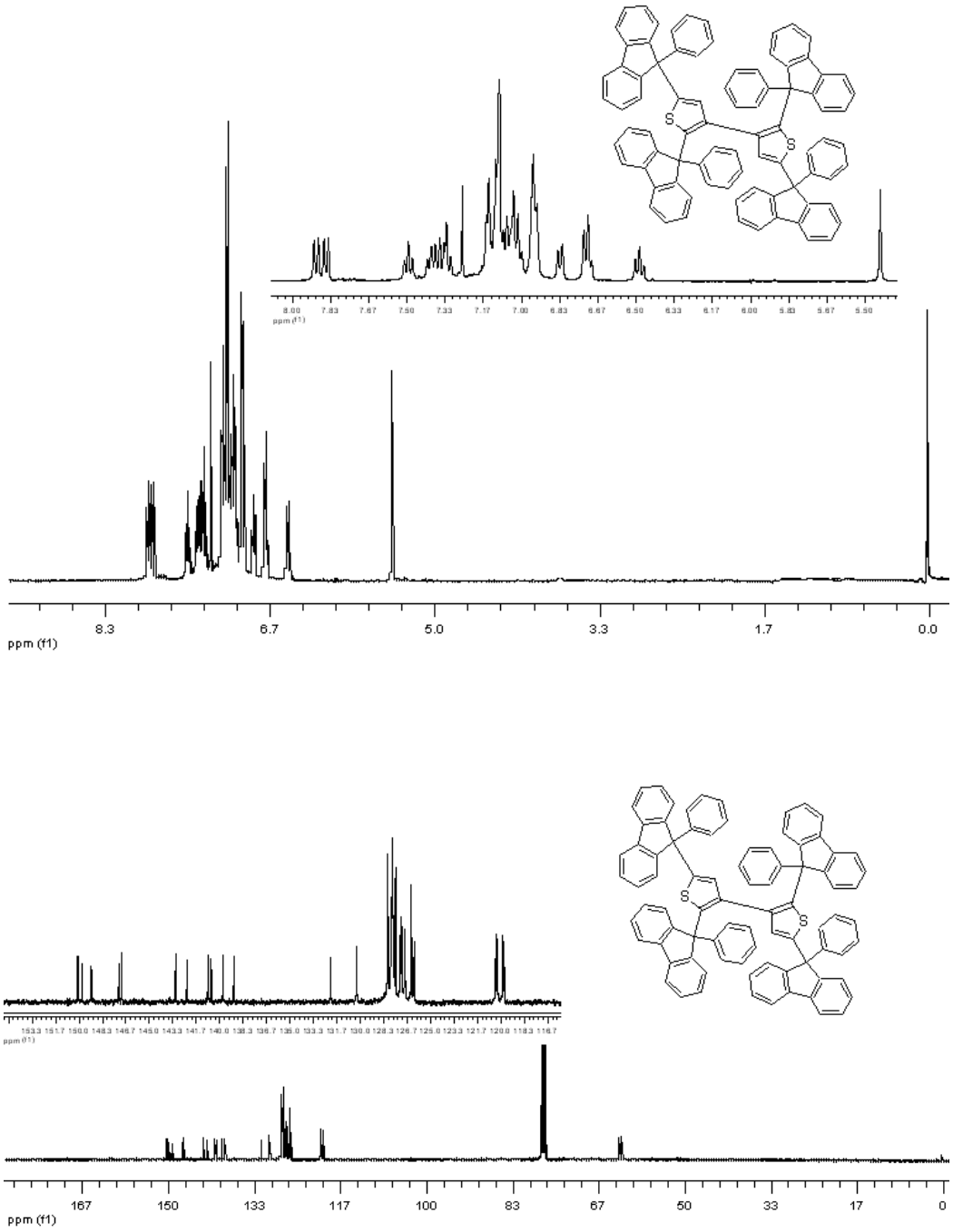


Figure SI-12: The ^{1}H-NMR and ^{13}C-NMR spectra of

2,5,2',5'-tetrakis(9-phenyl-fluoren-9-yl)-3,3'-bithiophene (**P3**).

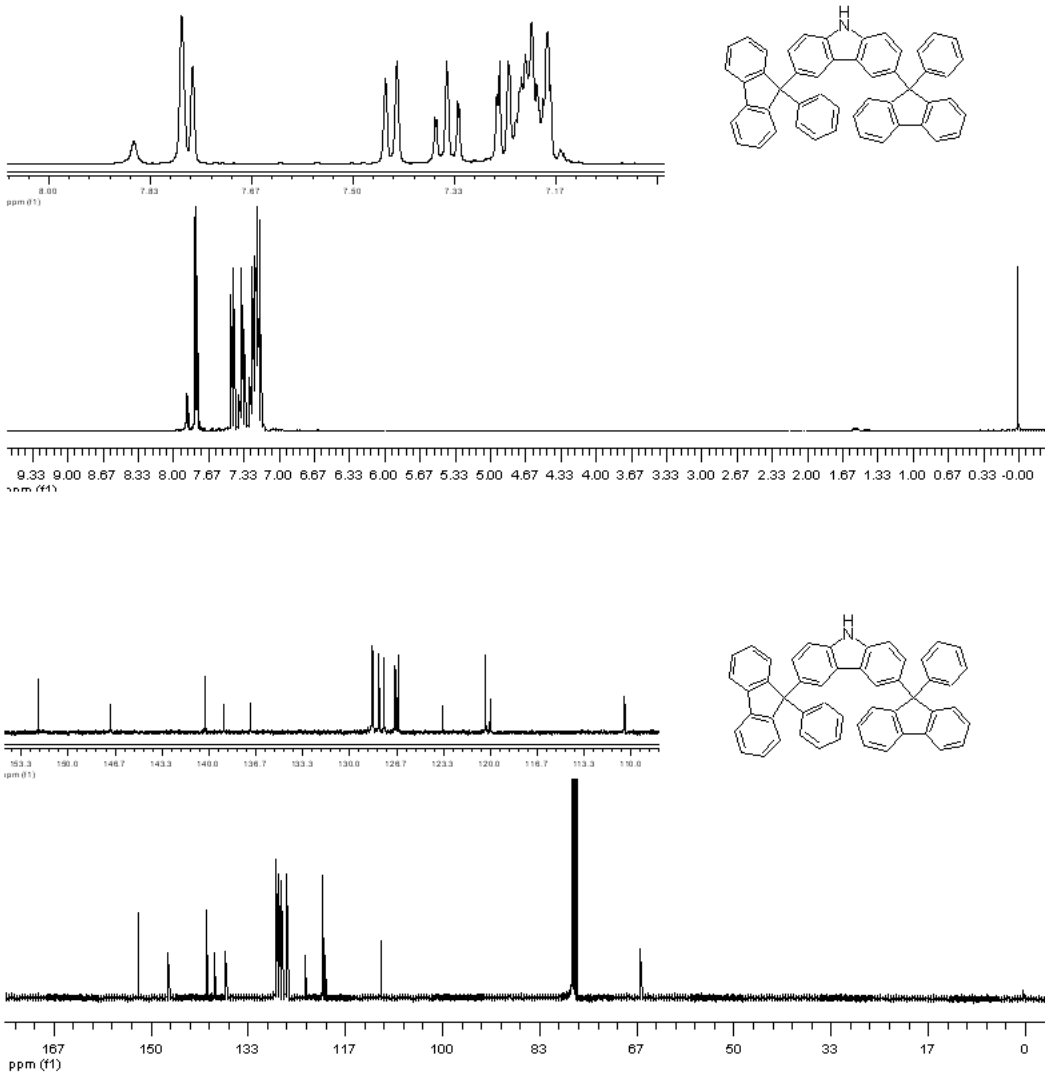


Figure SI-13: The ^{1}H-NMR and ^{13}C-NMR spectra of 3,6-bis(9-phenyl-fluoren-9-yl)-carbazole (**P7**).

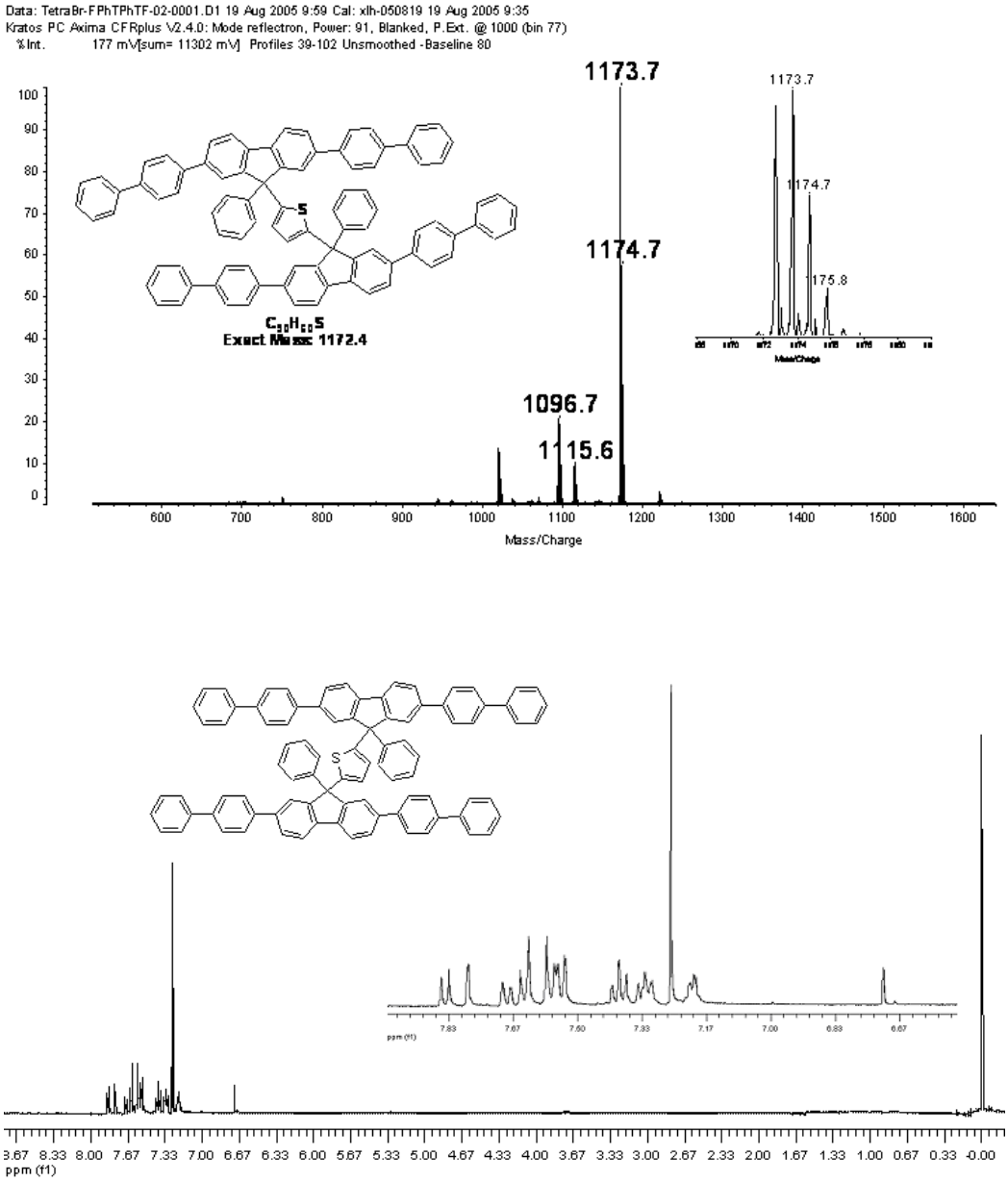


Figure SI-14: The MALDI-TOF-MS and ^{1}H-NMR spectra of

2,5-bis(2,7,-bis([1,1'-biphenyl]-4-yl)-9-phenyl-fluoren-9-yl)thiophene (TBPFTF).

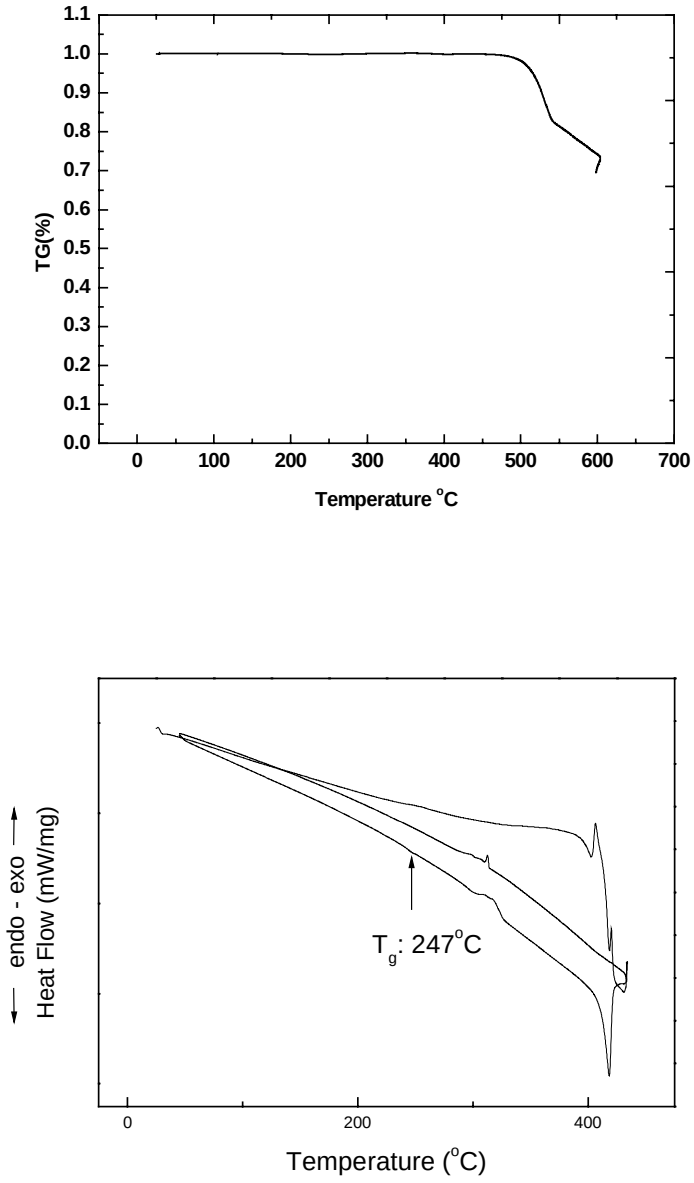


Figure SI-15: The TGA and DSC curves of TBPFTF.