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Synthesis of Perfectly Alternating Copolymers for Polymers of Intrinsic Microporosity

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1. General Methods and Materials

General Methods:

Analytical thin-layer chromatography (TLC) was performed using Kieselgel F254 0.2 mm (Merck) silica plates with visualisation by ultraviolet irradiation (254 nm) followed by staining with alkaline potassium permanganate. NMR spectra, except ^{13}C NMR for polymers in this work, were recorded on a Bruker DRX400 spectrophotometer. Chemical shifts are reported in parts per million (ppm) referenced to δ 7.26 and 77.0 ppm from chloroform or δ 2.50 and 39.5 ppm from DMSO for ^{1}H and ^{13}C respectively. The multiplicities of ^{1}H signals are designated by the following abbreviations: s = singlet; d = doublet; dd= doublet of doublets; m = multiplet; br = broad. All ^{13}C NMR spectra were acquired using broadband decoupled mode, and assignments were determined using DEPT sequences. ^{13}C NMR spectra of PIM-A1 and PIM-S1 were obtained from a Varian Unity Plus 400 MHz spectrometer using the deuterated solvent ($CDCl_3$) as reference and a long relaxation delay (18.5s) was applied to obtain quantitative signal intensity. Mass spectra were obtained by ESI using a Bruker micrOTOF-Q mass spectrometer. GPC analyses were carried out using a PL-GPC 50 (A Varian, Inc. Company) integrated GPC system, coupled with UV and RI detectors. Two pL-gel 20 µm MIXED-A column (300×7.5mm) columns with pLgel 20 µm guard column (50×7.5 mm) were employed. $CHCl_3$ was used as the eluent with a flow rate of 1.0 ml/min at a constant temperature of 30 °C. The sample concentration was 2 mg of polymer in 1 mL of $CHCl_3$. 300 µL of the sample solution was injected in each run. The relative molecular weights (M_n) were determined by refractive index (RI) detection (with Normal or Inverse polarity) using polystyrene standard calibration curve. The data were analysed with Cirrus GPC software version 3.1. Infrared spectra were recorded on a Perkin Elmer Spectrum 100 FT-IR spectrometer using a diamond ATR sampling accessory. Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI-ToF) mass spectroscopy was performed on a Bruker Autoflex III Mass Spectrometer operating in positive linear mode; the analyte, matrix (DCTB) and cationisation agent (NaTFA) were dissolved in THF at concentrations of 10, 10 and 1 mg/ml, respectively, and then mixed in a ratio of 10:1:1. Then 0.8ul of this solution was spotted onto a ground steel target plate and the solvent was allowed to evaporate prior to analysis. FlexAnalysis (Bruker) was used to analyse the data. Shimadzu TGA-50 thermal gravimetric analyzer (TGA) was employed to analyze polymer thermal degradation. Samples for TG study were initially heated to 120 °C and maintained for 30min under argon flow and then heated to 800°C at heating rate of 5°C/min. Shimadzu DSC-60 differential scanning calorimetry was used to study phase transition. Samples for DSC was prepared in crimped aluminum sample cell and heated under argon flow to 220°C then cooled down to 50°C and re-heated to 330°C with all heating and cooling processes at a rate of 5°C/min. The DSC thermograms were from a second heating after quick cooling.

Materials:

5,5',6,6'-tetrahydroxy-3,3,3',3'- tetramethyl-1,1'-spirobisindane (96%), 1,2-dihydroxybenzene, 2,5-hexandione, potassium carbonate (99%) and anhydrous DMF (99.8%) purchased from Aldrich. 2,3,5,6-tetrafluoroterephthalonitrile (97%) was purchased from Manchester Organics. Potassium hydroxide (85%) was purchased from Scharlau. All the chemicals were used as received without further treatment.

2. Experimental Procedures

ABA monomer TFTTSBI

To a solution of 5,5',6,6'-tetrahydroxy-3,3,3',3'- tetramethyl-1,1'-spirobisindane (**TTSBI**) (5g, 14.7mmol) in DMF(70ml) was added KOH aq.(3M, 10ml) slowly under Ar atmosphere to give a dark blue solution. The solution was warmed at 50° C and dropwisely added to a solution of 2,3,5,6-tetrafluoroterephthalonitrile (**TFTPN**) (6g, 30.0mmol) in MeCN(150ml) at room temperature via cannula within 40 min. After addition, the mixture was stirred for another 10 min at room temperature, then cooled down in ice-bath for 30 min, filtered and washed with water to give yellow solid. The solid was dissolved in $CHCl_3$ and washed with water twice, dried over Na_2SO_4, evaporated to give ABA monomer (**TFTTSBI**) (8.0g, 12.1mmol, 82%) as a yellow solid. FTIR (ATR): ν_{max} cm^{-1} 2960, 2243, 1471, 1407, 1311, 1294, 1265, 1007, 877; ^1H NMR (400MHz, $CDCl_3$): δ ppm 6.88 (s, 2H), 6.46 (s, 2H), 2.39-2.16 (m, 4H), 1.40 (s, 6H), 1.34 (s, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ ppm 150.53, 147.54, 147.02-146.84(dd), 144.40-144.26(dd), 141.23-141.21(m), 139.06, 138.85, 112.50, 110.84, 107.75, 96.80-96.30(m), 58.74, 57.23, 43.78, 31.35, 29.87; ^{19}F NMR (376MHz, $CDCl_3$): δ ppm 134.85; HR-MS (ESI) calcd. for $C_{37}H_{20}F_4N_4NaO_4$ 683.1313, found 683.1324 $(M+Na)^+$.

9,10-Dimethyl-9,10-ethano-9,10-dihydro-2,3,6,7-tetrahydroxy-anthracene (DETA)[1]

Well-ground catechol (7g, 63.6mmol) was suspended in 70% H_2SO_4 aq. (140ml) and 2,5-Hexanedione(3.63g, 31.8mmol) was added dropwisely into the suspension at 0° C. The mixture was stirred at 0° C for another 1h and then at room temperature for 7d under inert atmosphere. The viscous brown mixture was diluted with water (30ml), filtered and washed with water several times. After drying, crude product was gained and recrystallized from EtOAc to give the title compound (6.3g, 21.1mmol, 66%) as off-white solid. FTIR (ATR): ν_{max} cm^{-1} 3288, 2965, 2936, 2860, 1599, 1447, 1291, 1134, 992, 881; ^1H NMR (400MHz, DMSO-d_6): δ ppm 8.41 (s, 4H), 6.61 (s, 4H), 1.69 (s, 6H), 1.41 (s, 4H); ^{13}C NMR (100MHz, DMSO-d_6): δ ppm 141.69,137.60, 108.73, 36.19, 18.49; HR-MS (ESI) calcd. for $C_{18}H_{18}NaO_4$ 321.1097, found 321.1087 $(M+Na)^+$.

Polymerization of PIM-S1

To a dry flask were added 5,5',6,6'-tetrahydroxy-3,3,3',3'- tetramethyl-1,1'-spirobisindane (**TTSBI**) (0.8000g, 2.35mmol), 9,10-Dimethyl-9,10-ethano-9,10-dihydro-2,3,6,7-tetrahydroxy-anthracene (**DETA**) (0.7011g, 2.35mmol), 2,3,5,6-tetrafluoroterephthalonitrile (**TFTPN**) (0.9405g, 4.70mmol) and anhydrous DMF(32ml) under Ar. Afterwards, well-ground K_2CO_3(5.2g, 37.6mmol) powder was added and the mixture was heated at 70° C for 72h under Ar. The yellow mixture was poured into water, stirred for 30min, filtered, washed with water to give crude polymer. The crude polymer was dissolved in $CHCl_3$ and precipitated from MeOH to give yellow solid which was filtered and dried in oven to give **TTSBI/TFTPN-*stat*-DETA/TFTPN** (**PIM-S1)** (1.95g, 95%) as yellow solid. FTIR (ATR): ν_{max} cm^{-1} 2959, 2240, 1606, 1441, 1312, 1266, 1135, 1008, 884; ^1H NMR (400MHz, $CDCl_3$): δ ppm 6.91 (br. s, 4H), 6.82 (br. s, 2H), 6.42 (br. s, 2H), 2.6-2.0 (br. m, 4H), 1.85 (br. s, 6H), 1.58(br. s, 4H), 1.37(br. s, 6H), 1.31 (br. s, 6H).

Polymerization of PIM-A1

To a dry flask were added 9,10-Dimethyl-9,10-ethano-9,10-dihydro-2,3,6,7-tetrahydroxy-anthracene (**DETA**) (0.4516g, 1.51mmol) and ABA monomer (**TFTTSBI**) (1.0000g, 1.51mmol) and anhydrous DMF(20ml) under Ar. Afterwards, well-ground K_2CO_3(1.67g, 12.1mmol) powder was added and the mixture was heated at 70° C for 72h under Ar. The yellow mixture was poured into water, stirred for 30min, filtered, washed with water to give crude polymer. The crude polymer was dissolved in $CHCl_3$ and precipitated from MeOH to give yellow solid which was filtered and dried in oven to give **TTSBI/TFTPN-*alt*-DETA/TFTPN** (**PIM-A1)** (1.17g, 88%) as yellow solid. FTIR (ATR): ν_{max} cm^{-1} 2960, 2240, 1606, 1442, 1312, 1271, 1135, 1008, 878; ^{1}H NMR (400MHz, $CDCl_3$): δ ppm 6.90 (br. s, 4H), 6.81 (br. s, 2H), 6.41 (br. s, 2H), 2.6-2.0 (br. m, 4H), 1.84 (br. s, 6H), 1.58(br. s, 4H), 1.37(br. s, 6H), 1.31 (br. s, 6H).

References

1. D. Fritsch, G. Bengtson, M. Carta and N. B. McKeown, *Macromol. Chem. Phys.*, 2011, **212**, 1137–1146.

3. Characterization

Figure S1: ^{1}H NMR of **TFTTSBI**.

Figure S2: ^{13}C NMR of **TFTTSBI**.

Figure S3: ^{19}F NMR of **TFTTSBI**.

Figure S4: ^{1}H NMR of **DETA**.

Figure S5: ^{13}C NMR of **DETA**.

Figure S6: ^{1}H NMR of **PIM-A1**.

Figure S7: ^{1}H NMR of **PIM-S1**.

Figure S8: ^{13}C NMR of **PIM-A1** and **PIM-S1**.

Figure S9: GPC analysis of **PIM-A1**.

Figure S10: GPC analysis of **PIM-S1**.

Figure S11: Robust films cast from **PIM-A1** and **PIM-S1.**

Figure S12: Single Crystal Structure of **TFTTSBI**.

Table S1: Bond lengths and angles data for the crystal structure of **TFTTSBI**.

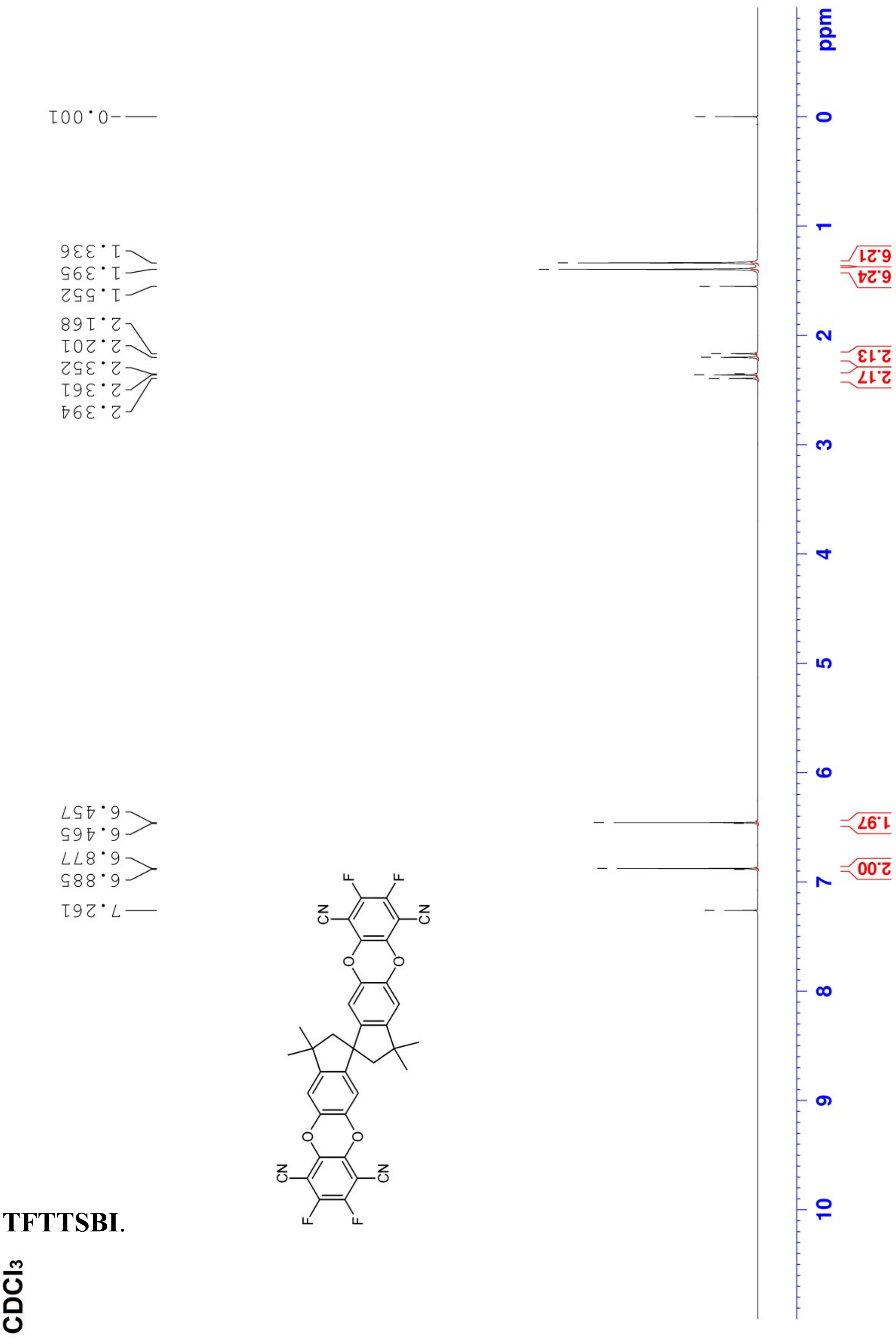


Figure S1: ^{1}H NMR of **TFTTSBI**.

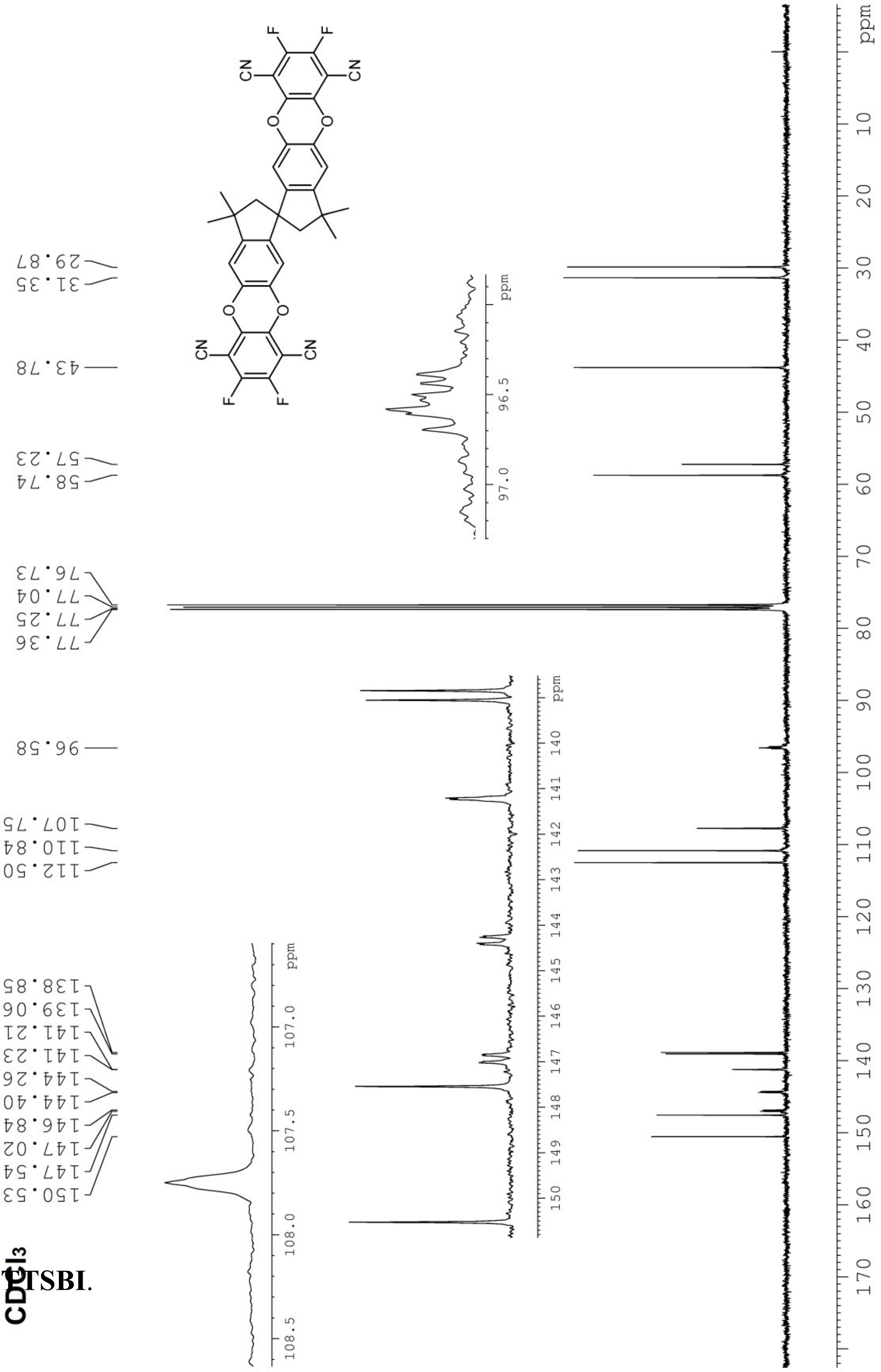


Figure S2: ^{13}C NMR of **TFPTSBI**.

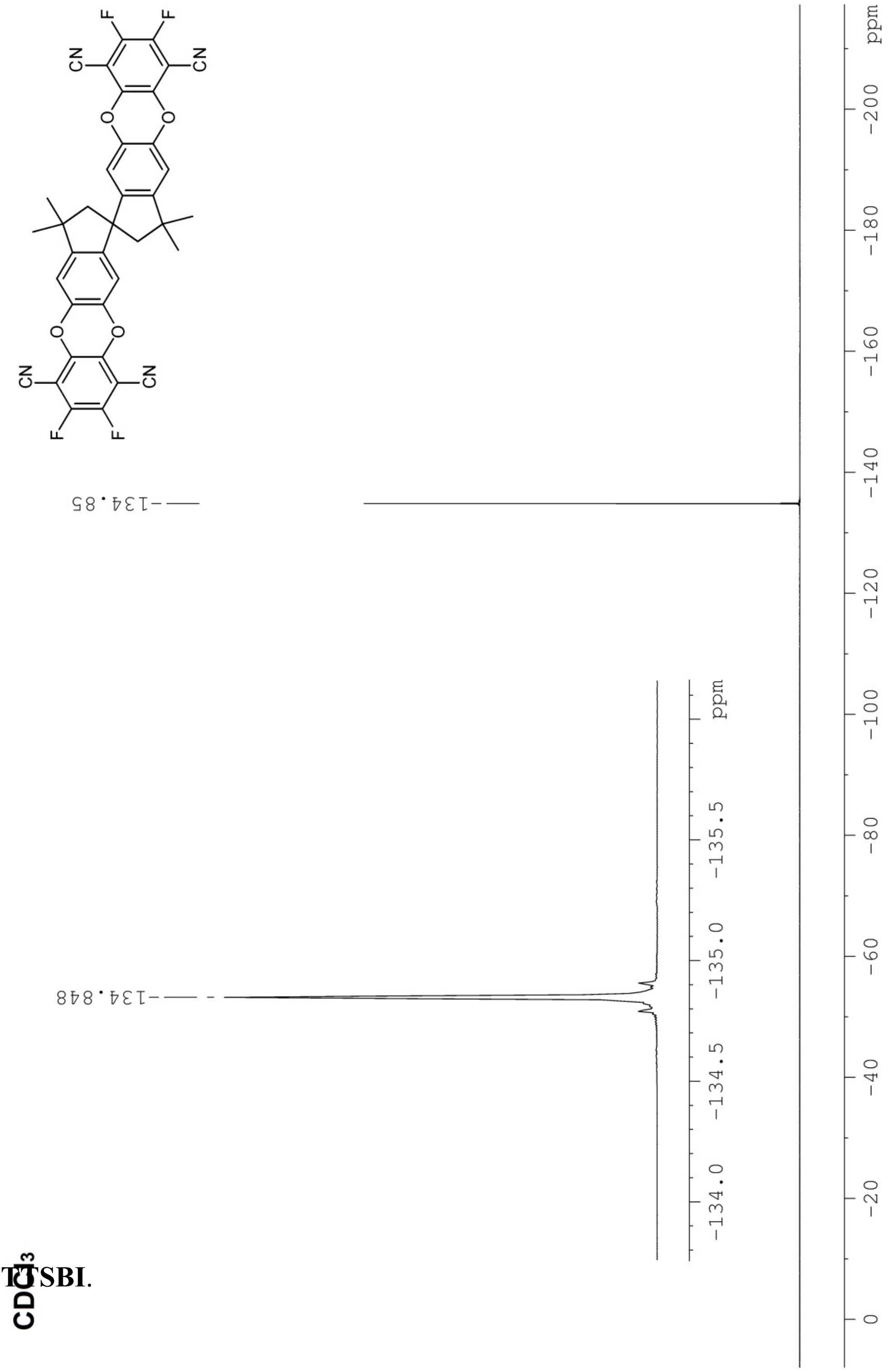


Figure S3: ^{19}F NMR of **TFTCSBI**.

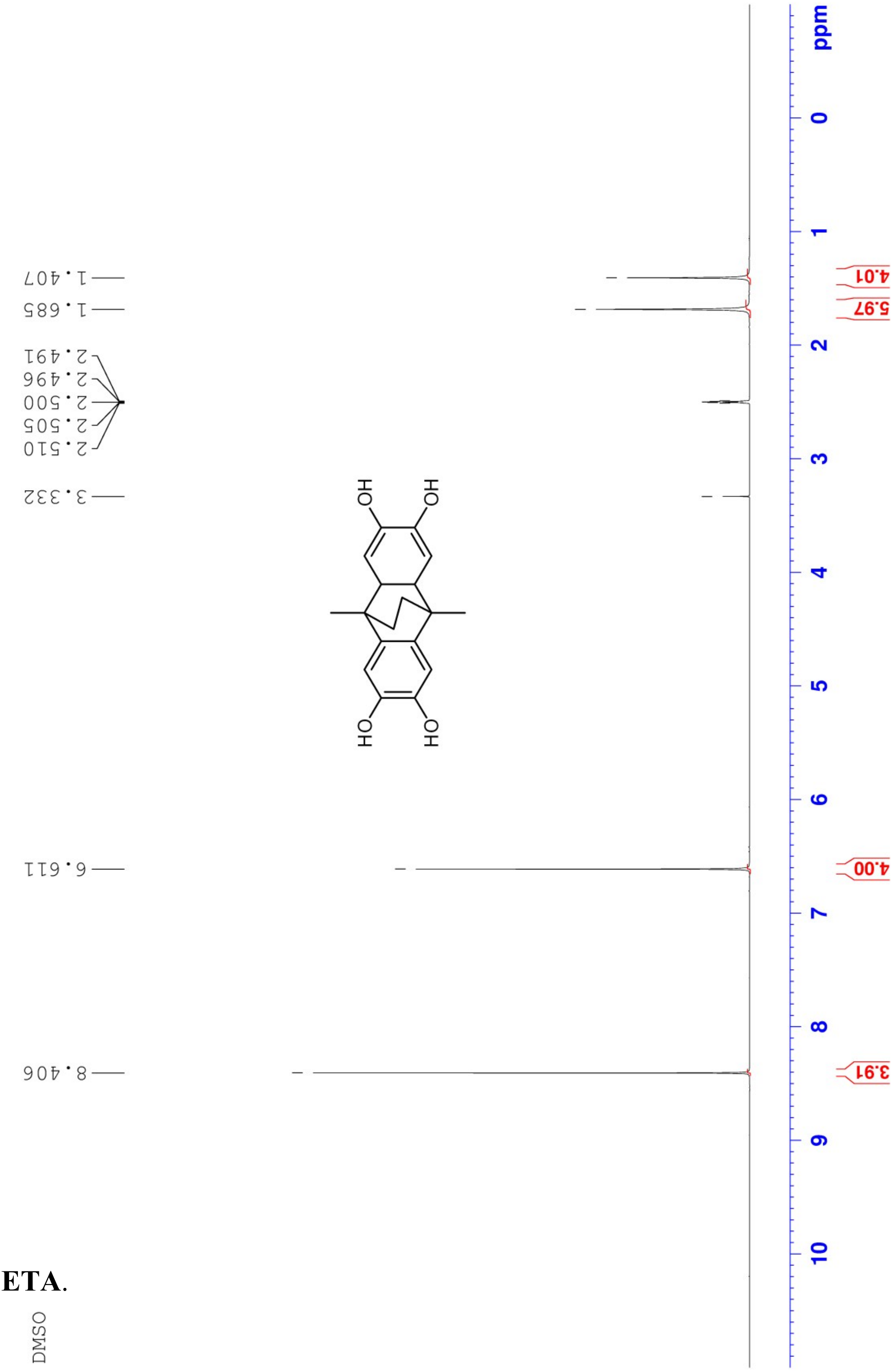


Figure S4: ^{1}H NMR of **DETA**.

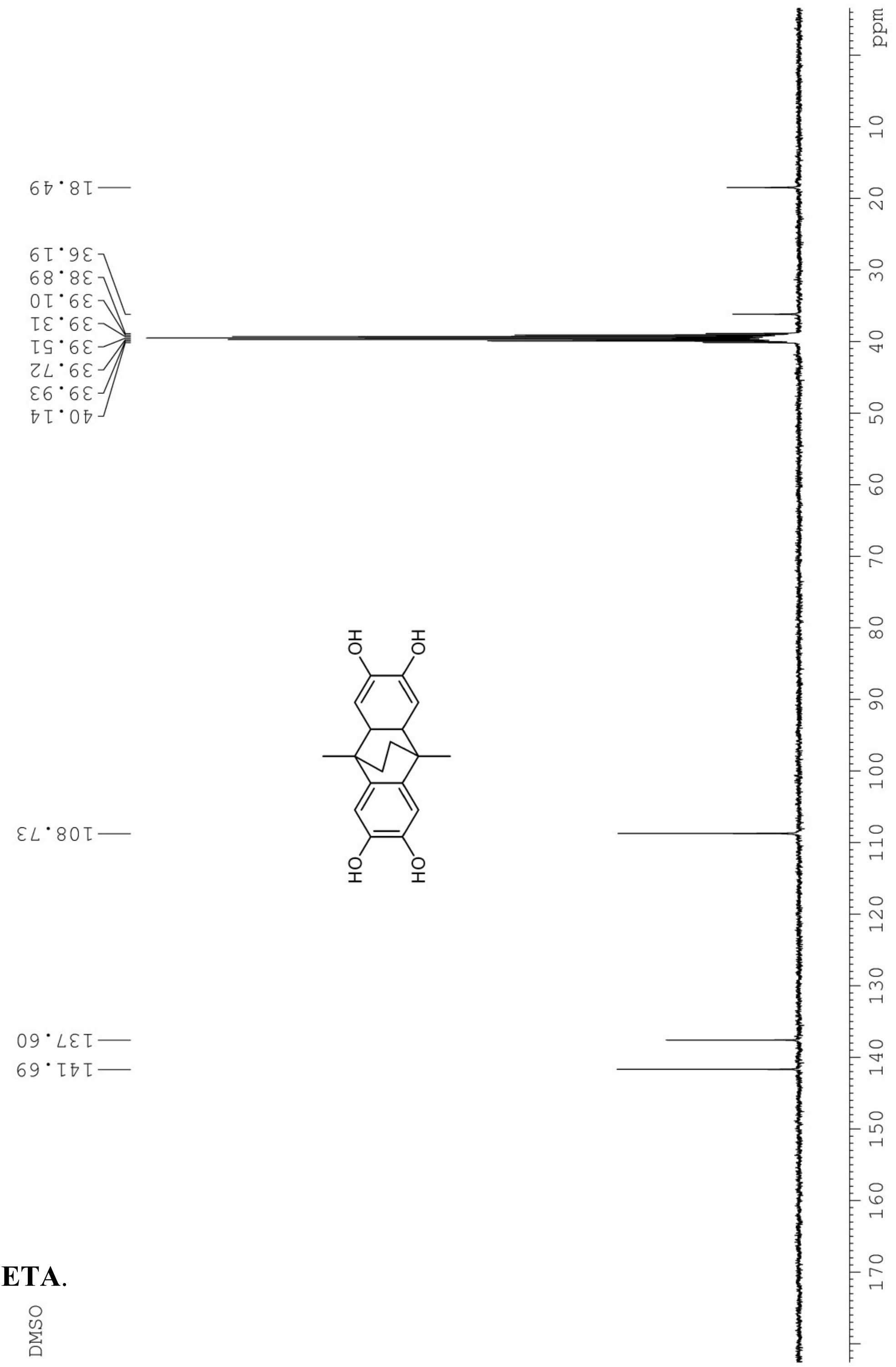


Figure S5: ^{13}C NMR of **DETA**.

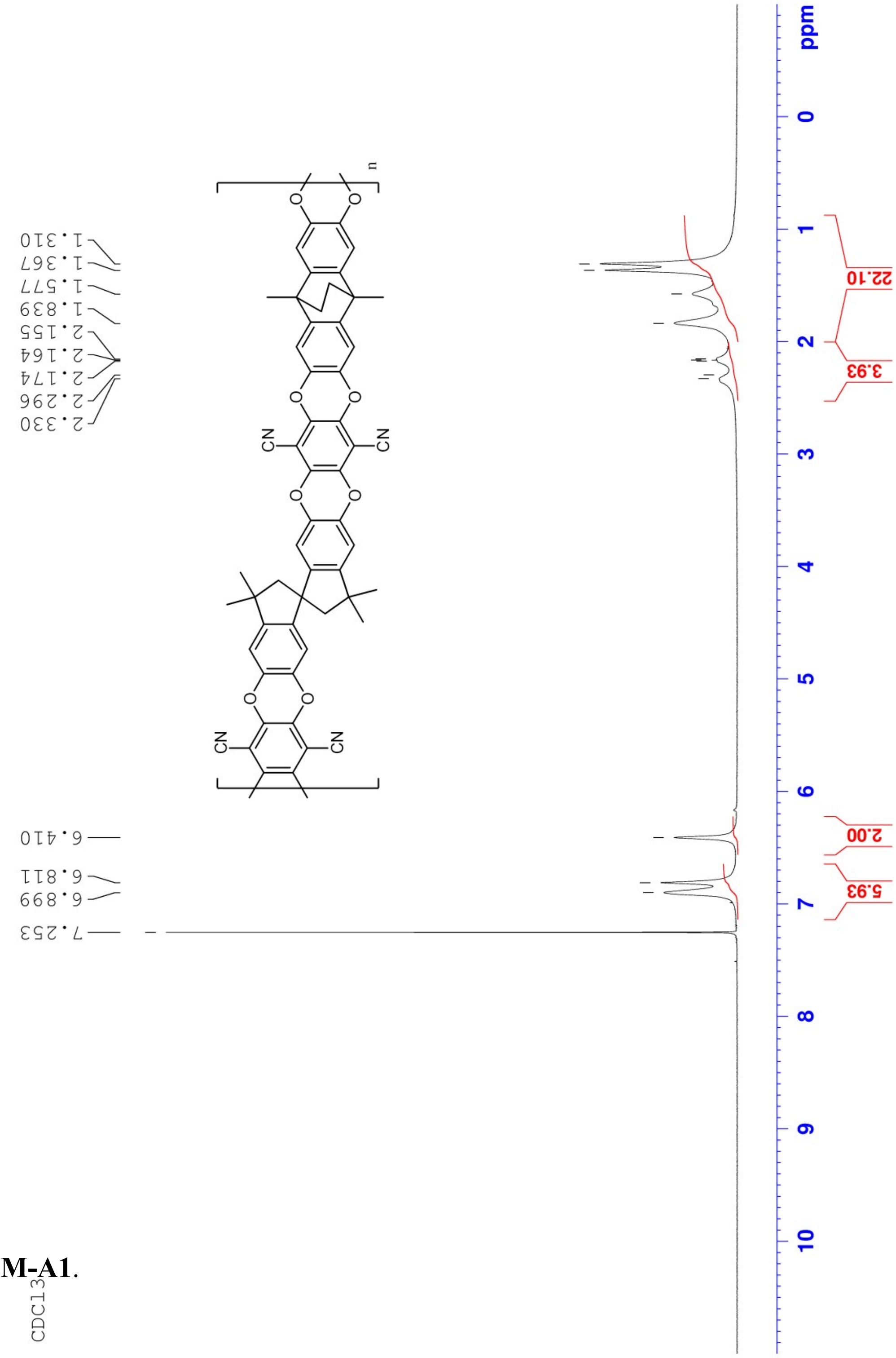


Figure S6: ^{1}H NMR of **PIM-A1**.

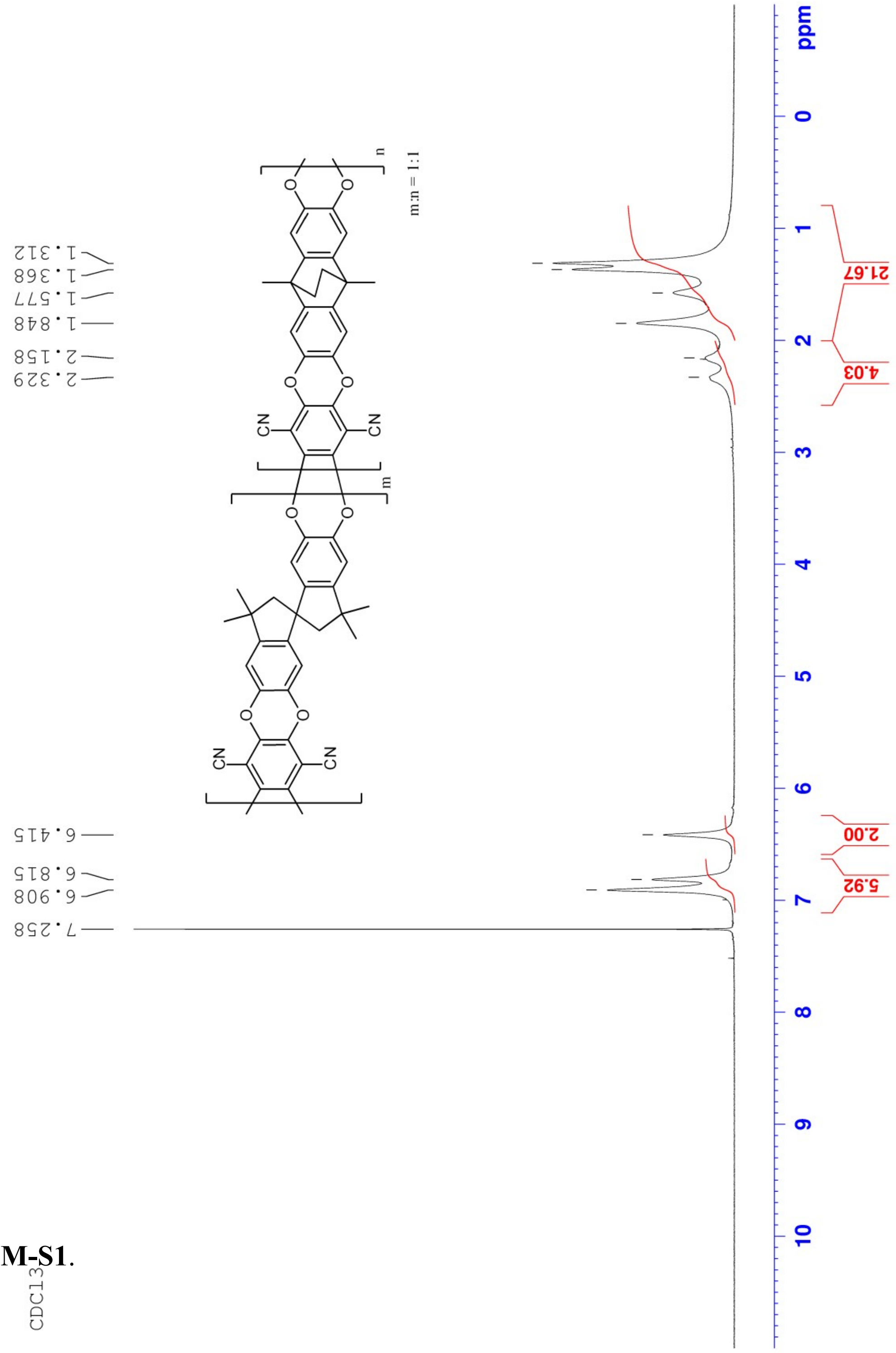


Figure S7: ^{1}H NMR of **PIM-S1**.

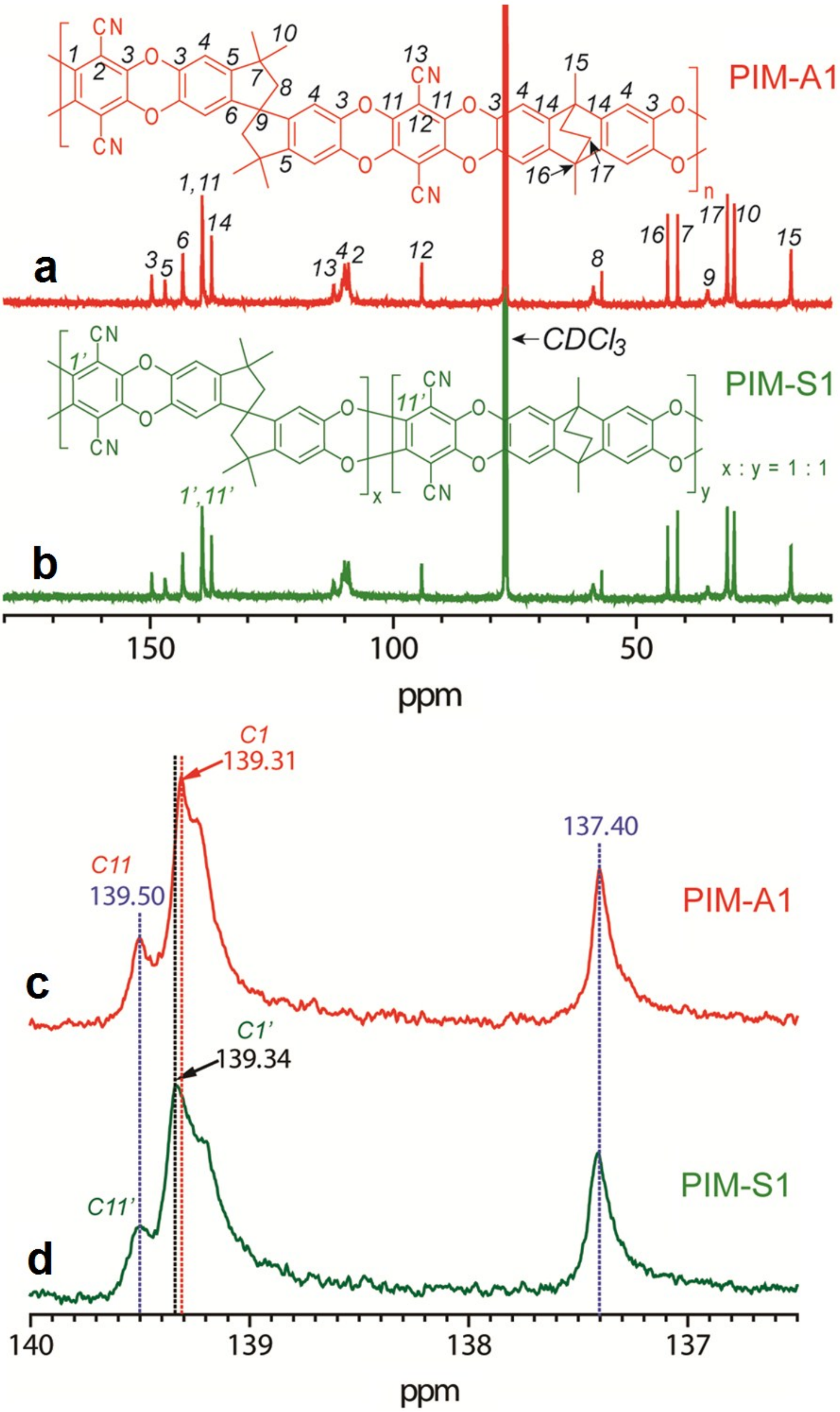


Figure S8: ^{13}C NMR spectra of (a) **PIM-A1** and (b) **PIM-S1**. Enlarged partial ^{13}C NMR spectra of (c) **PIM-A1** and (d) **PIM-S1** were also shown.

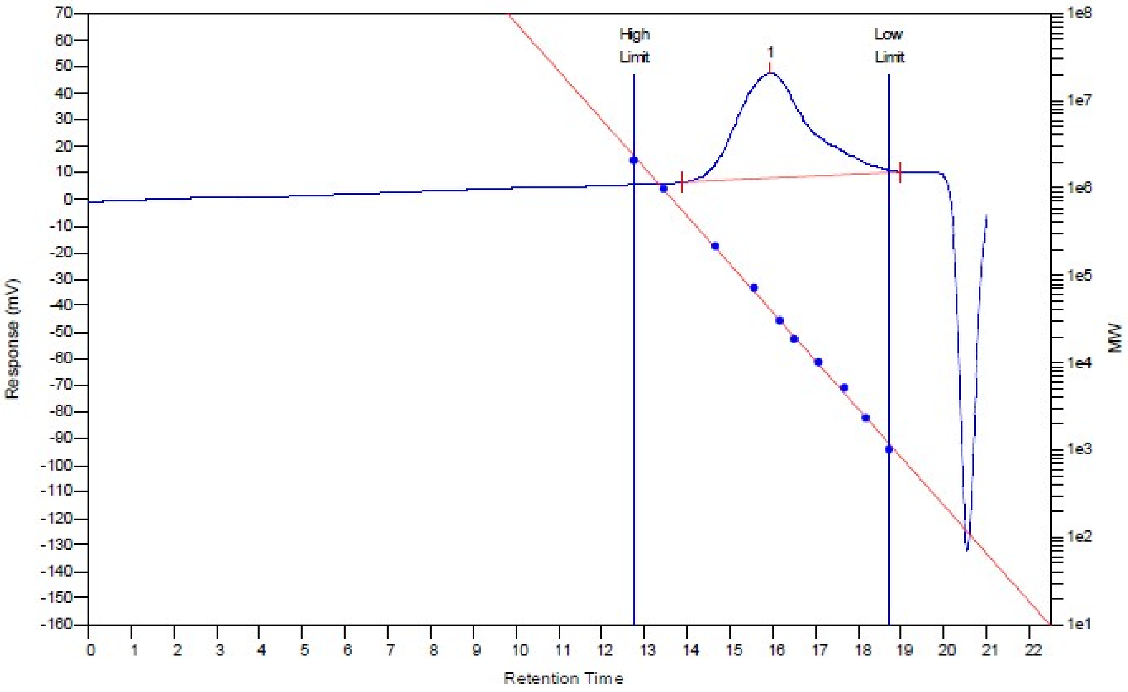


Figure S9: GPC analysis of **PIM-A1**.

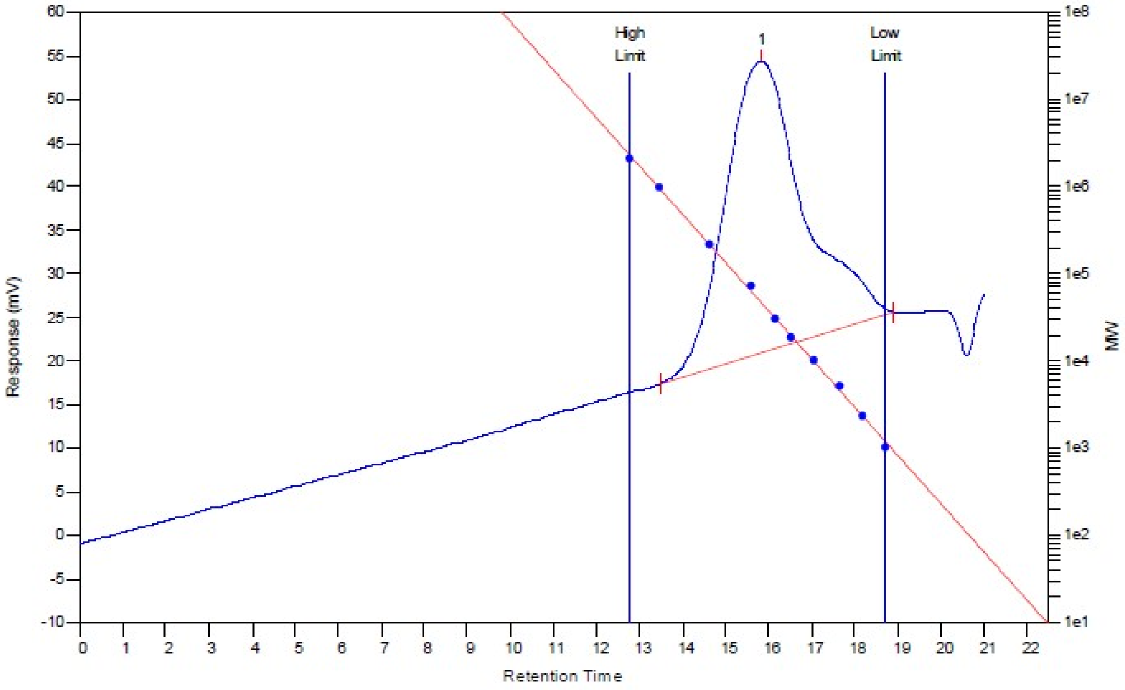


Figure S10: GPC analysis of **PIM-S1**.

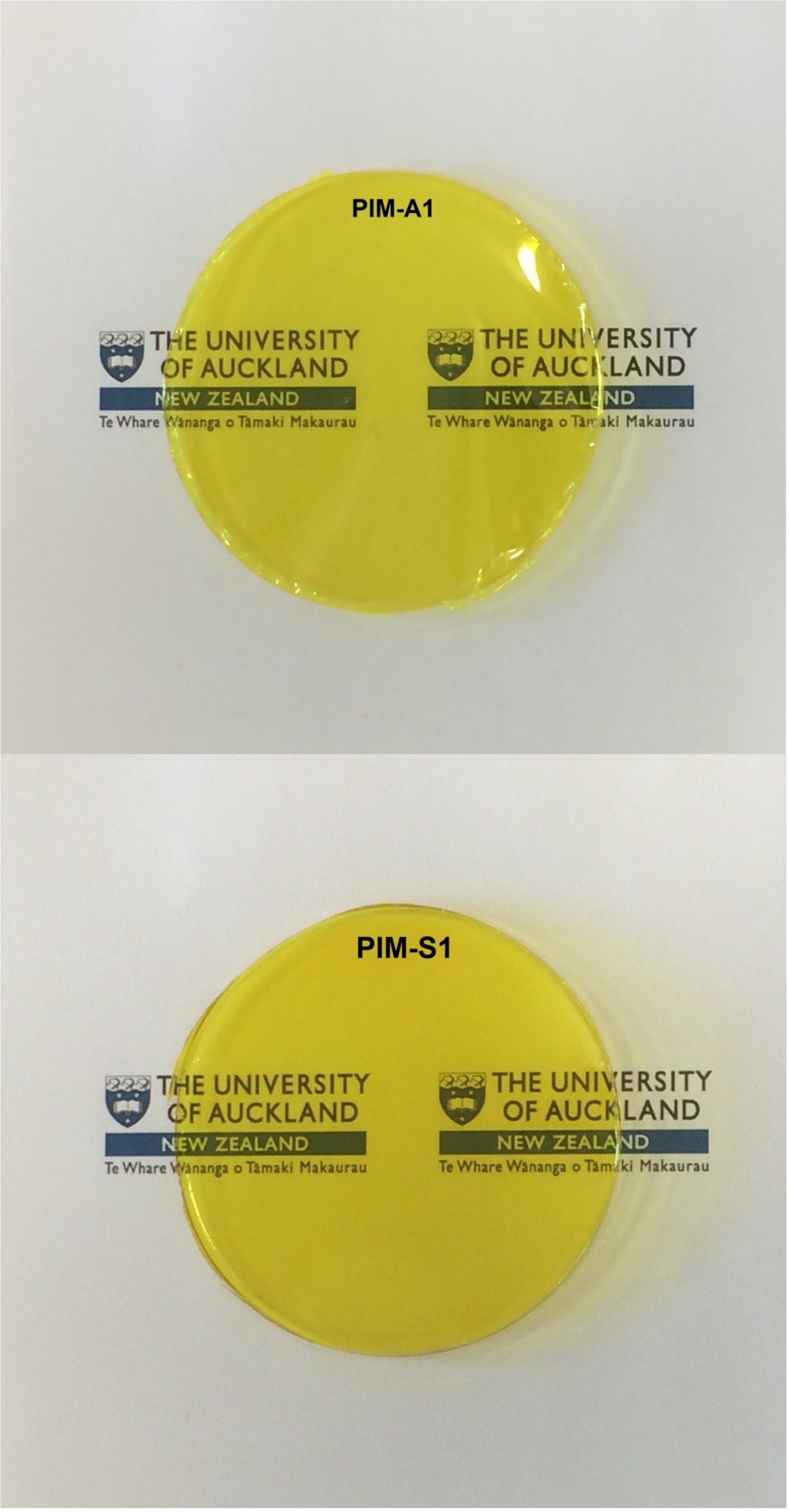


Figure S11: Robust films cast from **PIM-A1** and **PIM-S1.**

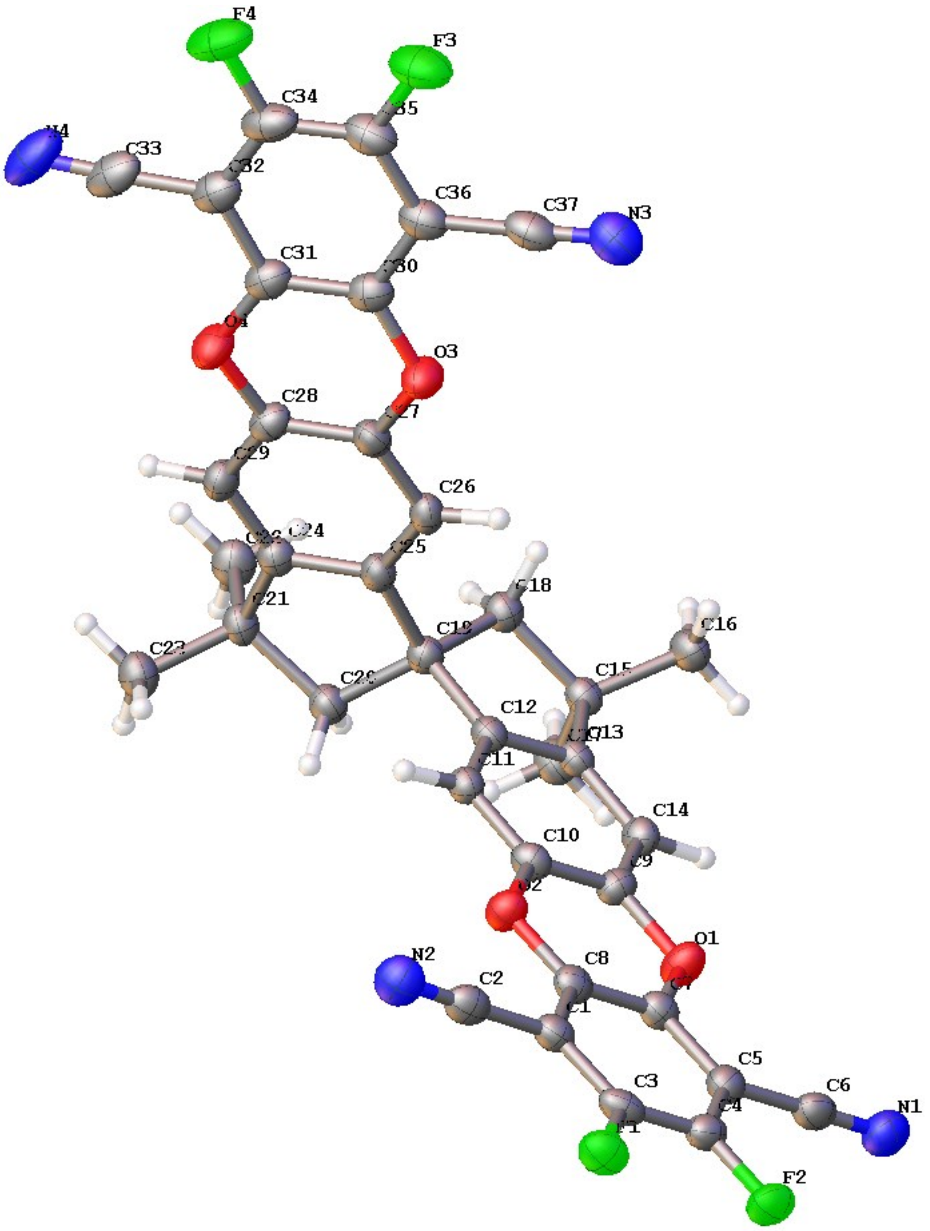
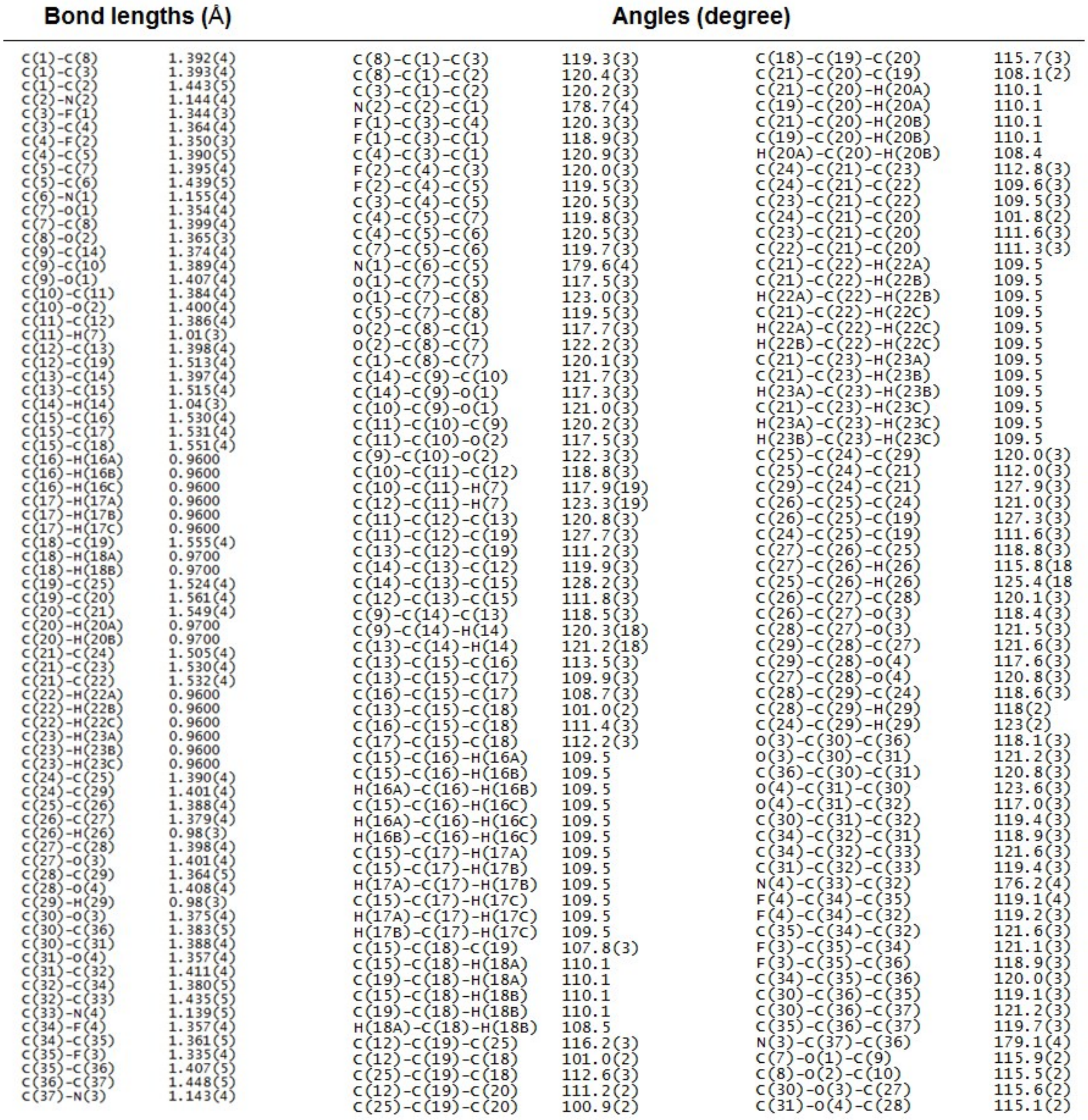


Figure S12. Single Crystal Structure of **TFTTSBI**.

Table S1. Bond lengths and angles data for the crystal structure of **TFTTSBI**.



Bond lengths (Å)		Angles (degree)			
C(1)-C(8)	1.392(4)	C(8)-C(1)-C(3)	119.3(3)	C(18)-C(19)-C(20)	115.7(3)
C(1)-C(3)	1.393(4)	C(8)-C(1)-C(2)	120.4(3)	C(21)-C(20)-C(19)	108.1(2)
C(1)-C(2)	1.443(5)	C(3)-C(1)-C(2)	120.2(3)	C(21)-C(20)-H(20A)	110.1
C(2)-N(2)	1.144(4)	N(2)-C(2)-C(1)	178.7(4)	C(19)-C(20)-H(20A)	110.1
C(3)-F(1)	1.344(3)	F(1)-C(3)-C(4)	120.3(3)	C(21)-C(20)-H(20B)	110.1
C(3)-C(4)	1.364(4)	F(1)-C(3)-C(1)	118.9(3)	C(19)-C(20)-H(20B)	110.1
C(4)-F(2)	1.350(3)	C(4)-C(3)-C(1)	120.9(3)	H(20A)-C(20)-H(20B)	108.4
C(4)-C(5)	1.390(5)	F(2)-C(4)-C(3)	120.0(3)	C(24)-C(21)-C(23)	112.8(3)
C(5)-C(7)	1.395(4)	F(2)-C(4)-C(5)	119.5(3)	C(24)-C(21)-C(22)	109.6(3)
C(5)-C(6)	1.439(5)	C(3)-C(4)-C(5)	120.5(3)	C(23)-C(21)-C(22)	109.5(3)
C(6)-N(1)	1.155(4)	C(4)-C(5)-C(7)	119.8(3)	C(24)-C(21)-C(20)	101.8(2)
C(7)-O(1)	1.354(4)	C(4)-C(5)-C(6)	120.5(3)	C(23)-C(21)-C(20)	111.6(3)
C(7)-C(8)	1.399(4)	C(7)-C(5)-C(6)	119.7(3)	C(22)-C(21)-C(20)	111.3(3)
C(8)-O(2)	1.365(3)	N(1)-C(6)-C(5)	179.6(4)	C(21)-C(22)-H(22A)	109.5
C(9)-C(14)	1.374(4)	O(1)-C(7)-C(5)	117.5(3)	C(21)-C(22)-H(22B)	109.5
C(9)-C(10)	1.389(4)	O(1)-C(7)-C(8)	123.0(3)	H(22A)-C(22)-H(22B)	109.5
C(9)-O(1)	1.407(4)	C(5)-C(7)-C(8)	119.5(3)	C(21)-C(22)-H(22C)	109.5
C(10)-C(11)	1.384(4)	O(2)-C(8)-C(1)	117.7(3)	H(22A)-C(22)-H(22C)	109.5
C(10)-O(2)	1.400(4)	O(2)-C(8)-C(7)	122.2(3)	H(22B)-C(22)-H(22C)	109.5
C(11)-C(12)	1.386(4)	C(1)-C(8)-C(7)	120.1(3)	C(21)-C(23)-H(23A)	109.5
C(11)-H(7)	1.01(3)	C(14)-C(9)-C(10)	121.7(3)	C(21)-C(23)-H(23B)	109.5
C(12)-C(13)	1.398(4)	C(14)-C(9)-O(1)	117.3(3)	H(23A)-C(23)-H(23B)	109.5
C(12)-C(19)	1.513(4)	C(10)-C(9)-O(1)	121.0(3)	C(21)-C(23)-H(23C)	109.5
C(13)-C(14)	1.397(4)	C(11)-C(10)-C(9)	120.2(3)	H(23A)-C(23)-H(23C)	109.5
C(13)-C(15)	1.515(4)	C(11)-C(10)-O(2)	117.5(3)	H(23B)-C(23)-H(23C)	109.5
C(14)-H(14)	1.04(3)	C(9)-C(10)-O(2)	122.3(3)	C(25)-C(24)-C(29)	120.0(3)
C(15)-C(16)	1.530(4)	C(10)-C(11)-C(12)	118.8(3)	C(25)-C(24)-C(21)	112.0(3)
C(15)-C(17)	1.531(4)	C(10)-C(11)-H(7)	117.9(19)	C(29)-C(24)-C(21)	127.9(3)
C(15)-C(18)	1.551(4)	C(12)-C(11)-H(7)	123.3(19)	C(26)-C(25)-C(24)	121.0(3)
C(16)-H(16A)	0.9600	C(11)-C(12)-C(13)	120.8(3)	C(26)-C(25)-C(19)	127.3(3)
C(16)-H(16B)	0.9600	C(11)-C(12)-C(19)	127.7(3)	C(24)-C(25)-C(19)	111.6(3)
C(16)-H(16C)	0.9600	C(13)-C(12)-C(19)	111.2(3)	C(27)-C(26)-C(25)	118.8(3)
C(17)-H(17A)	0.9600	C(14)-C(13)-C(12)	119.9(3)	C(27)-C(26)-H(26)	115.8(18
C(17)-H(17B)	0.9600	C(14)-C(13)-C(15)	128.2(3)	C(25)-C(26)-H(26)	125.4(18
C(17)-H(17C)	0.9600	C(12)-C(13)-C(15)	111.8(3)	C(26)-C(27)-C(28)	120.1(3)
C(18)-C(19)	1.555(4)	C(9)-C(14)-C(13)	118.5(3)	C(26)-C(27)-O(3)	118.4(3)
C(18)-H(18A)	0.9700	C(9)-C(14)-H(14)	120.3(18)	C(28)-C(27)-O(3)	121.5(3)
C(18)-H(18B)	0.9700	C(13)-C(14)-H(14)	121.2(18)	C(29)-C(28)-C(27)	121.6(3)
C(19)-C(25)	1.524(4)	C(13)-C(15)-C(16)	113.5(3)	C(29)-C(28)-O(4)	117.6(3)
C(19)-C(20)	1.561(4)	C(13)-C(15)-C(17)	109.9(3)	C(27)-C(28)-O(4)	120.8(3)
C(20)-C(21)	1.549(4)	C(16)-C(15)-C(17)	108.7(3)	C(28)-C(29)-C(24)	118.6(3)
C(20)-H(20A)	0.9700	C(13)-C(15)-C(18)	101.0(2)	C(28)-C(29)-H(29)	118(2)
C(20)-H(20B)	0.9700	C(16)-C(15)-C(18)	111.4(3)	C(24)-C(29)-H(29)	123(2)
C(21)-C(24)	1.505(4)	C(17)-C(15)-C(18)	112.2(3)	O(3)-C(30)-C(36)	118.1(3)
C(21)-C(23)	1.530(4)	C(15)-C(16)-H(16A)	109.5	O(3)-C(30)-C(31)	121.2(3)
C(21)-C(22)	1.532(4)	C(15)-C(16)-H(16B)	109.5	C(36)-C(30)-C(31)	120.8(3)
C(22)-H(22A)	0.9600	H(16A)-C(16)-H(16B)	109.5	O(4)-C(31)-C(30)	123.6(3)
C(22)-H(22B)	0.9600	C(15)-C(16)-H(16C)	109.5	O(4)-C(31)-C(32)	117.0(3)
C(22)-H(22C)	0.9600	H(16A)-C(16)-H(16C)	109.5	C(30)-C(31)-C(32)	119.4(3)
C(23)-H(23A)	0.9600	H(16B)-C(16)-H(16C)	109.5	C(34)-C(32)-C(31)	118.9(3)
C(23)-H(23B)	0.9600	C(15)-C(17)-H(17A)	109.5	C(34)-C(32)-C(33)	121.6(3)
C(23)-H(23C)	0.9600	C(15)-C(17)-H(17B)	109.5	C(31)-C(32)-C(33)	119.4(3)
C(24)-C(25)	1.390(4)	H(17A)-C(17)-H(17B)	109.5	N(4)-C(33)-C(32)	176.2(4)
C(24)-C(29)	1.401(4)	C(15)-C(17)-H(17C)	109.5	F(4)-C(34)-C(35)	119.1(4)
C(25)-C(26)	1.388(4)	H(17A)-C(17)-H(17C)	109.5	F(4)-C(34)-C(32)	119.2(3)
C(26)-C(27)	1.379(4)	H(17B)-C(17)-H(17C)	109.5	C(35)-C(34)-C(32)	121.6(3)
C(26)-H(26)	0.98(3)	C(15)-C(18)-C(19)	107.8(3)	F(3)-C(35)-C(34)	121.1(3)
C(27)-C(28)	1.398(4)	C(15)-C(18)-H(18A)	110.1	F(3)-C(35)-C(36)	118.9(3)
C(27)-O(3)	1.401(4)	C(19)-C(18)-H(18A)	110.1	C(34)-C(35)-C(36)	120.0(3)
C(28)-C(29)	1.364(5)	C(15)-C(18)-H(18B)	110.1	C(30)-C(36)-C(35)	119.1(3)
C(28)-O(4)	1.408(4)	C(19)-C(18)-H(18B)	110.1	C(30)-C(36)-C(37)	121.2(3)
C(29)-H(29)	0.98(3)	H(18A)-C(18)-H(18B)	108.5	C(35)-C(36)-C(37)	119.7(3)
C(30)-O(3)	1.375(4)	C(12)-C(19)-C(25)	116.2(3)	N(3)-C(37)-C(36)	179.1(4)
C(30)-C(36)	1.383(5)	C(12)-C(19)-C(18)	101.0(2)	C(7)-O(1)-C(9)	115.9(2)
C(30)-C(31)	1.388(4)	C(25)-C(19)-C(18)	112.6(3)	C(8)-O(2)-C(10)	115.5(2)
C(31)-O(4)	1.357(4)	C(12)-C(19)-C(20)	111.2(2)	C(30)-O(3)-C(27)	115.6(2)
C(31)-C(32)	1.411(4)	C(25)-C(19)-C(20)	100.9(2)	C(31)-O(4)-C(28)	115.1(2)
C(32)-C(34)	1.380(5)				
C(32)-C(33)	1.435(5)				
C(33)-N(4)	1.139(5)				
C(34)-F(4)	1.357(4)				
C(34)-C(35)	1.361(5)				
C(35)-F(3)	1.335(4)				
C(35)-C(36)	1.407(5)				
C(36)-C(37)	1.448(5)				
C(37)-N(3)	1.143(4)				