Electronic Supplementary Material (ESI) for Materials Advances.

Supporting Information

Two-dimensional benzo[1,2-*b*:4,5-*b'*]difurans as donor building blocks for the formation of novel donor−acceptor copolymers

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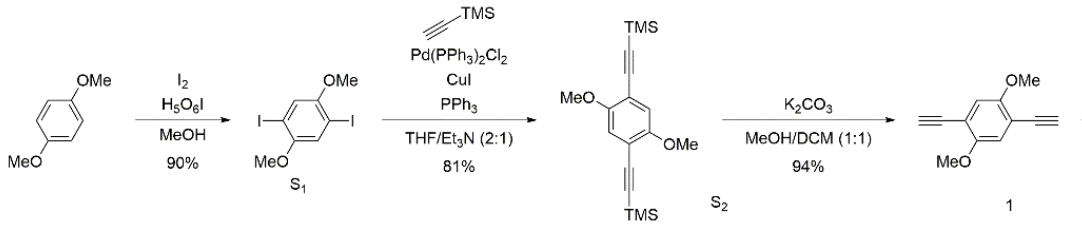
Supplementary Synthesis

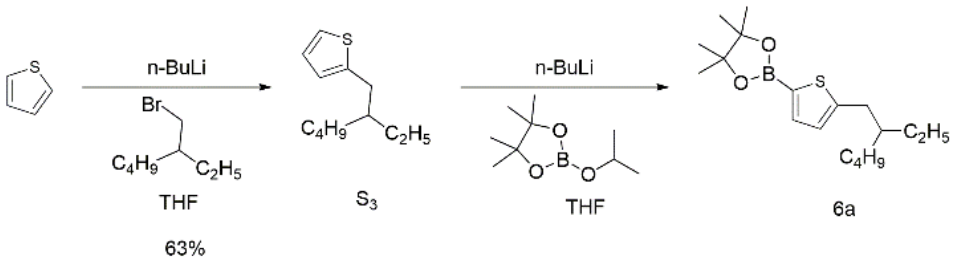


1,4-diiodo-2,5-dimethoxybenzene (S1).[1] In a 500mL round bottom flask, a solution of H_5IO_6 (20.51g, 90mmol) and I_2 (45.69g, 180mmol) in CH_3OH (200mL) was stirred for 10 min before 1,4-dimethoxybenzene (20.72g, 150mmol) was added in one portion and heated to reflux overnight. The resulting suspension was cooled, filtered, and the solid washed with cold CH_3OH before being dissolved in CH_2Cl_2. The solution was then dried with $MgSO_4$, filtered, and the solvent evaporated to afford a white crystalline solid (52.64g, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (2H, s), δ 3.82 (6H, s).

1,4-Dimethoxy-2,5-bis[2-(trimethylsilyl)ethynyl]benzene (S2). In a dry round bottom flask attached to a condenser under nitrogen environment, **S1** (19.03g, 50mmol) was added along with $Pd(PPh_3)_2Cl_2$ (0.01 equiv.), CuI (0.02 equiv.), and PPh_3 (0.02 equiv.). The flask was purged and backfilled three times before adding deoxygenated THF/*i*-Pr_2NH (2:1) and TMSA (2.2eq) then stirred overnight at room temperature. The reaction mixture was then poured into ice and extracted three times with dichloromethane. The combined organic layers were then washed with saturated aqueous NH_4Cl, water, and brine. The organic layer was then dried with $MgSO_4$, evaporated, then purified using a silica plug (Hex: DCM (4:1)). The resulting solid was then recrystallized with ethanol to yield a light yellow-white crystalline solid (13.39g, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 (2H, s), δ 3.83

(6H, s), δ 0.27 (18H, s).

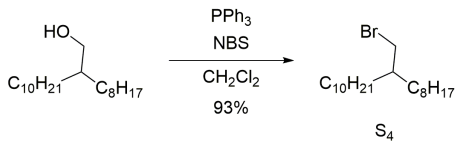
1,4-diethynyl-2,5-dimethoxybenzene (1). In a 500mL round bottom flask, **S2** (13.25g, 40 mmol) was dissolved in a 2:1 mixture of dichloromethane and methanol. Then, four equivalence of K_2CO_3 was added to the flask in one portion. The reaction mixture was stirred overnight then filtered, poured into water, and extracted with dichloromethane three times. The combined organic layers were washed with water, brine, dried with $MgSO_4$, and solvent evaporated. The resulting solid was recrystallized using ethanol to yield a light yellow solid (7g, 94% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (2H, s), δ 3.85 (6H, s), δ 3.39 (2H, s).



2-(2-ethylhexyl)thiophene (S3). A solution of thiophene (1.91g, 22.7mmol) and dry THF was added to a in a dry round bottom flask under nitrogen. The solution was cooled to -78°C and 10mL of *n*-BuLi solution (2.5 M in hexanes) was added dropwise. The solution was stirred at -78°C for one hour then quenched with 2-ethylhexyl bromide (4.83g, 25mmol). The reaction was brought to room temperature and stirred overnight. The reaction was then poured into ice, extracted with hexanes three times, washed with water, brine, then dried with $MgSO_4$. The solution was then removed via rotary evaporation, and the residue was purified by vacuum distillation to give the title compound. Colorless liquid

(2.81g, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, J = 6.3 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.76 (d, J = 3.4 Hz, 1H), 2.76 (d, J = 6.8 Hz, 2H), 1.58 (m, 1H), 1.30 (m, 8H), 0.89 (t, J = 7.2 Hz, 6H).

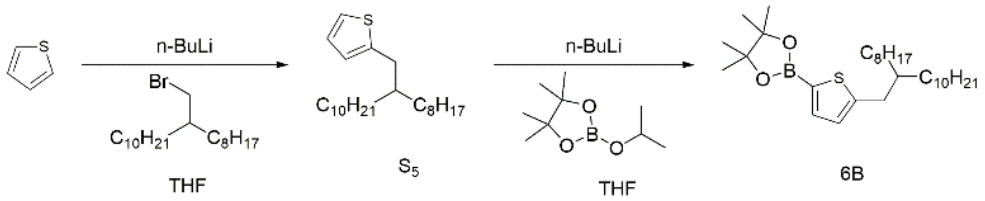
2-(5-(2-ethylhexyl)thiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6a). A solution of **S3** (2.78g, 14.31mmol) in anhydrous THF was cooled to −78°C before n-butyl lithium (2.5 M in hexane, 1.2 equiv) was added dropwise. The reaction mixture was allowed to come to 0 °C and stirred for 1h at this temperature. The mixture was cooled again to −78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 equiv) was added. The reaction mixture was allowed to come to room temperature overnight. The solvent was then removed under reduced pressure and the residue dissolved in CH_2Cl_2. The organic layer was then washed with water and brine. The solvent was removed in vacuo and the resulting product was used without further purification. Product was a clear oil (3.67g, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.47 (d, J= 3.4 Hz, 1H), 6.84 (d, J= 3.4 Hz, 1H), 2.79 (d, J= 6.9 Hz, 2H), 1.64-1.56 (m, 1H), 1.37-1.24 (m, 20H), 0.88 (dd, J= 8.4, 6.4 Hz, 6H).



S4

9-(bromomethyl)nonadecane (S4).[2] N-bromosuccinimide (1.5 equiv) was slowly added to a solution of 2-Octyldodecanol (10g, 33.5mmol) and triphenyl phosphine (2 equiv) at 0˚C in DCM (200mL). The reaction was stirred overnight then poured into water and extracted with dichloromethane three times. The organic solution was then washed with

water, dried over $MgSO_4$ and the solvent evaporated. Product S4 was purified by flash chromatography in hexanes to afford colorless oil (11.25g, 93% yield). The NMR was consistent with previously reported values. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.44 (d, J = 4.8 Hz, 2H), 1.38 – 1.23 (m, 32H), 0.88 (t, J = 6.8 Hz, 6H).



2-(2-octyldodecyl)thiophene (S5). A solution of thiophene (1.91g, 22.7mmol) and dry THF was added to a in a dry round bottom flask under nitrogen. The solution was cooled to -78°C and 10mL of *n*-BuLi solution (2.5 M in hexanes) was added dropwise. The solution was stirred at -78°C for one hour then quenched with 9-(bromomethyl)nonadecane (25mmol). The reaction was brought to room temperature and then refluxed overnight. The reaction was then poured into ice, extracted with hexanes three times, washed with water, brine, then dried with $MgSO_4$. The solution was then removed via rotary evaporation, and the residue was purified by vacuum distillation to give the title compound. Colorless liquid (4.80g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J=5.0 Hz, 1H), 6.93 (dd, J=4.9 Hz, 3.5 Hz, 1H), 6.78 (d, J=3.3 Hz, 1H), 2.79 (d, J=6.7 Hz, 2H), 1.65 (bs, 1H), 1.47 – 1.12 (m, 32 H), 0.92 (t, J=6.5 Hz, 6H).

4,4,5,5-tetramethyl-2-(5-(2-octyldodecyl)thiophen-2-yl)-1,3,2-dioxaborolane (6b). A solution of S5 (4.56g, 12.5mmol) in anhydrous THF was cooled to −78°C before *n*-butyl lithium (2.5 M in hexane, 1.2 equiv) was added dropwise. The reaction mixture was

allowed to come to 0°C and stirred for 1h at this temperature. The mixture was cooled again to −78°C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.2 equiv) was added. The reaction mixture was allowed to come to room temperature overnight. The solvent was then removed under reduced pressure and the residue dissolved in CH_2Cl_2. The organic layer was then washed with water and brine. The solvent was removed in vacuo and the resulting product was used without further purification. Product was a clear oil (4.78g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 3.4 Hz, 1H), 6.83 (d, J = 3.3 Hz, 1H), 2.78 (d, J = 6.6 Hz, 2H), 1.37 – 1.12 (m, 45H), 0.89 (m, 6H).

NMR Spectra

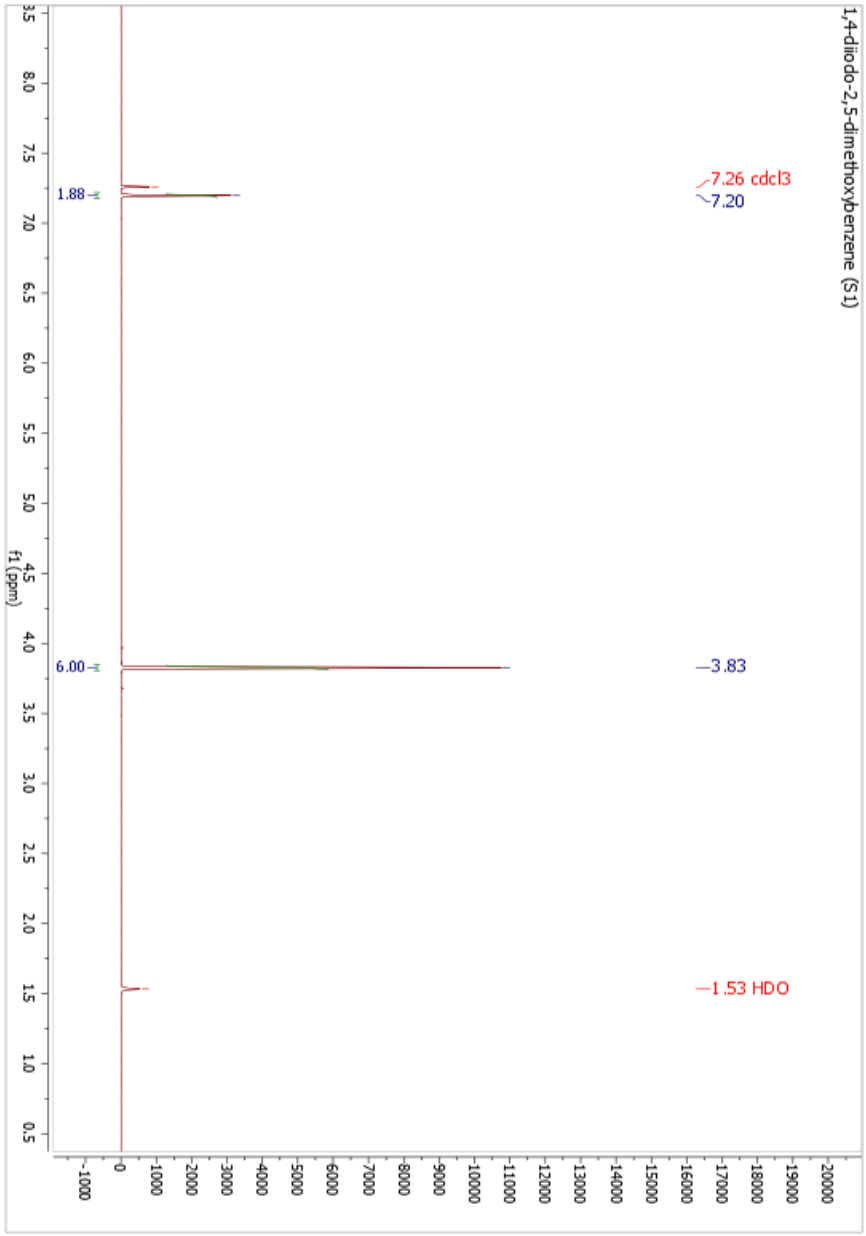


Figure 0.1 - ^{1}H NMR Compound S1

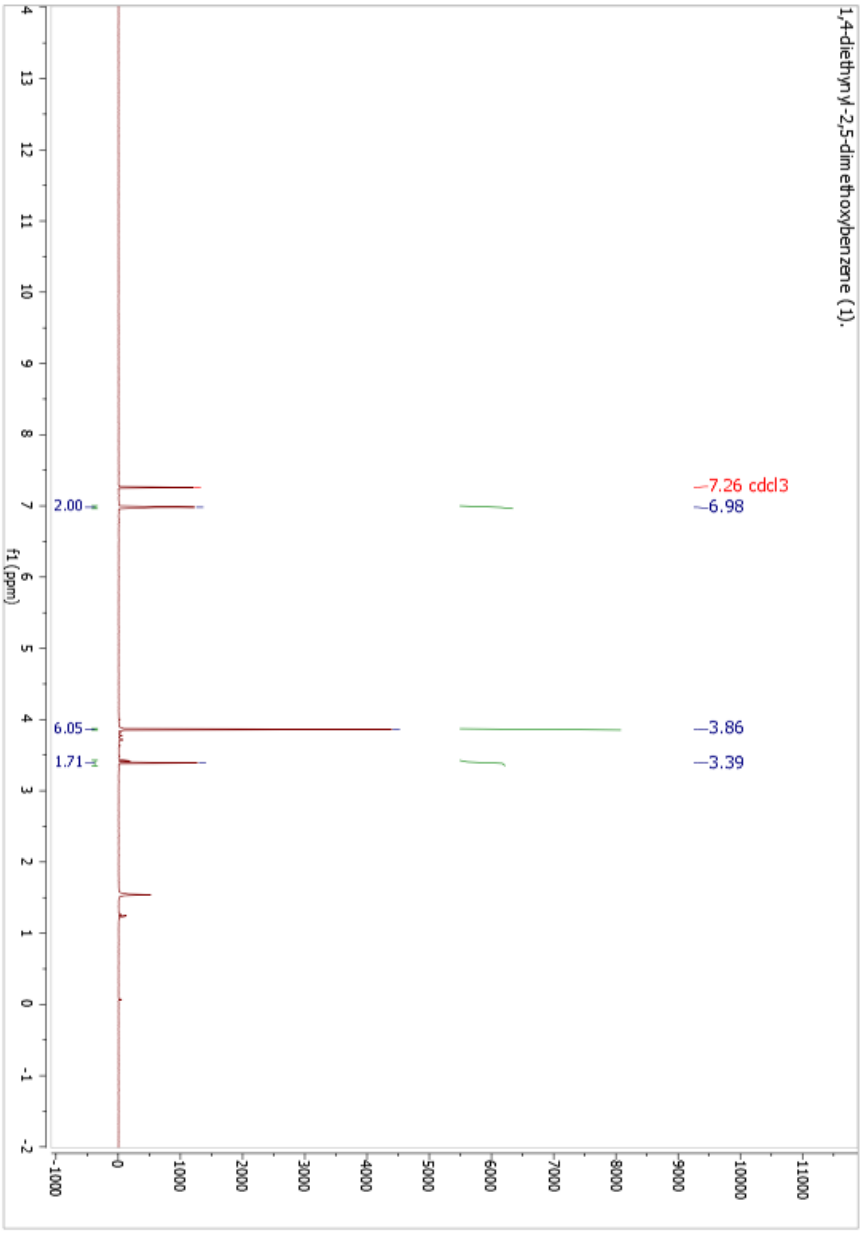


Figure 0.2 - ^{1}H NMR Compound 1

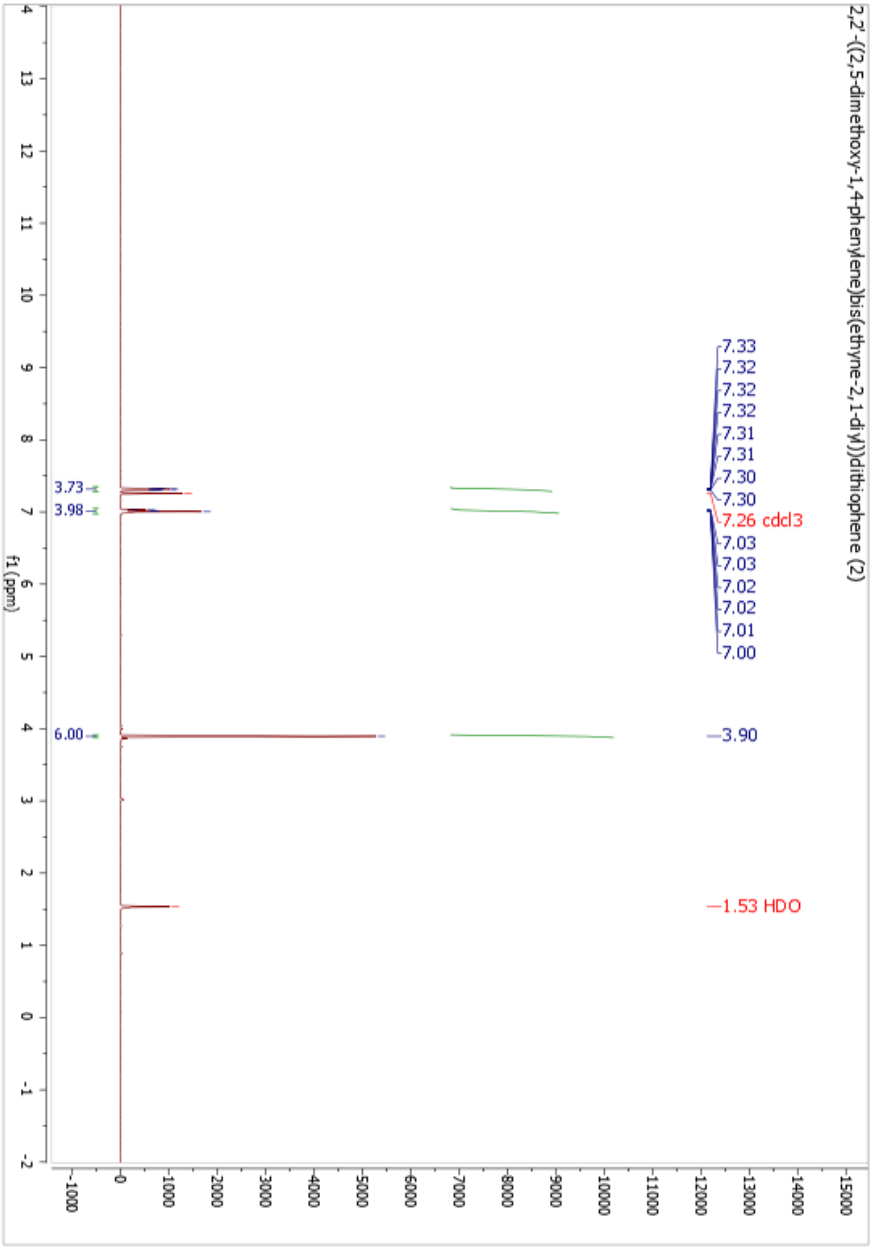


Figure 0.3 - ^{1}H NMR Compound 2

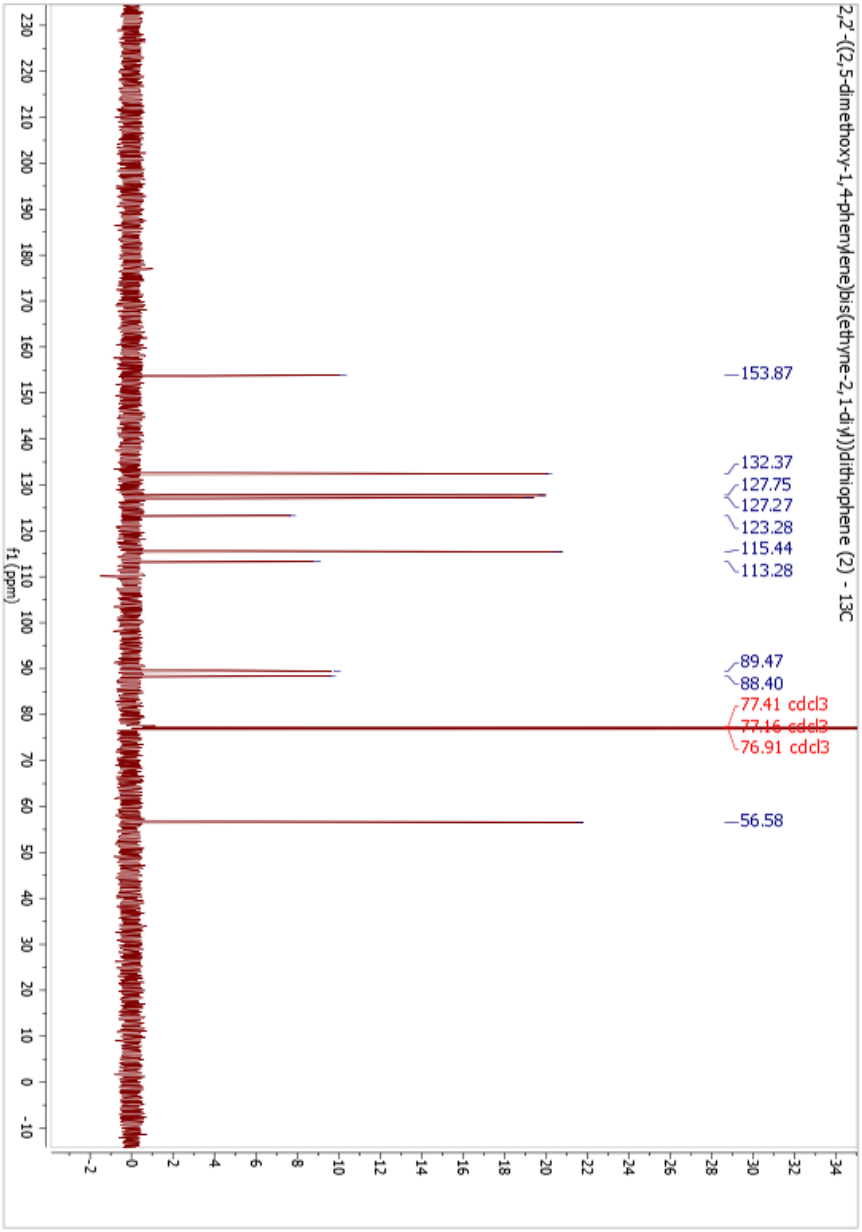


Figure 0.4 - ^{13}C NMR Compound 2

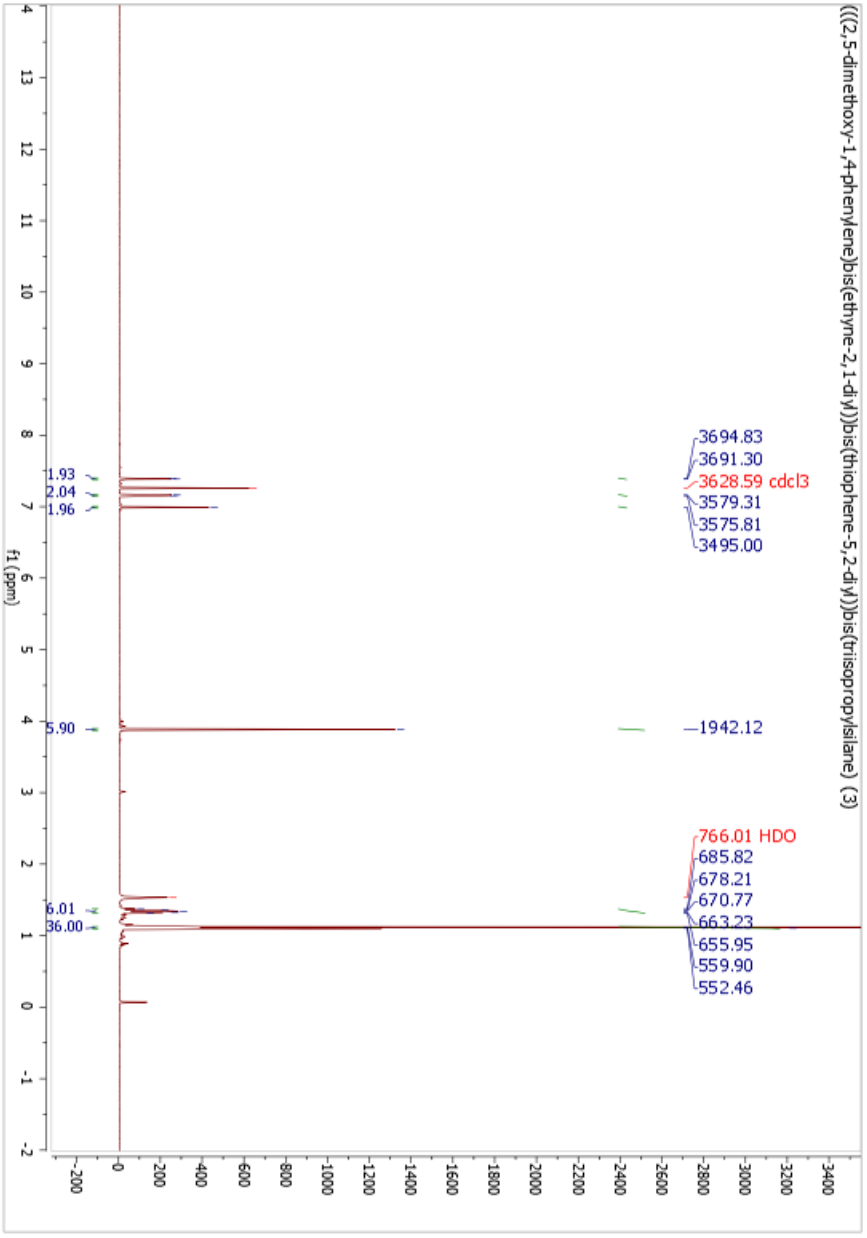


Figure 0.5 - 1H NMR Compound 3

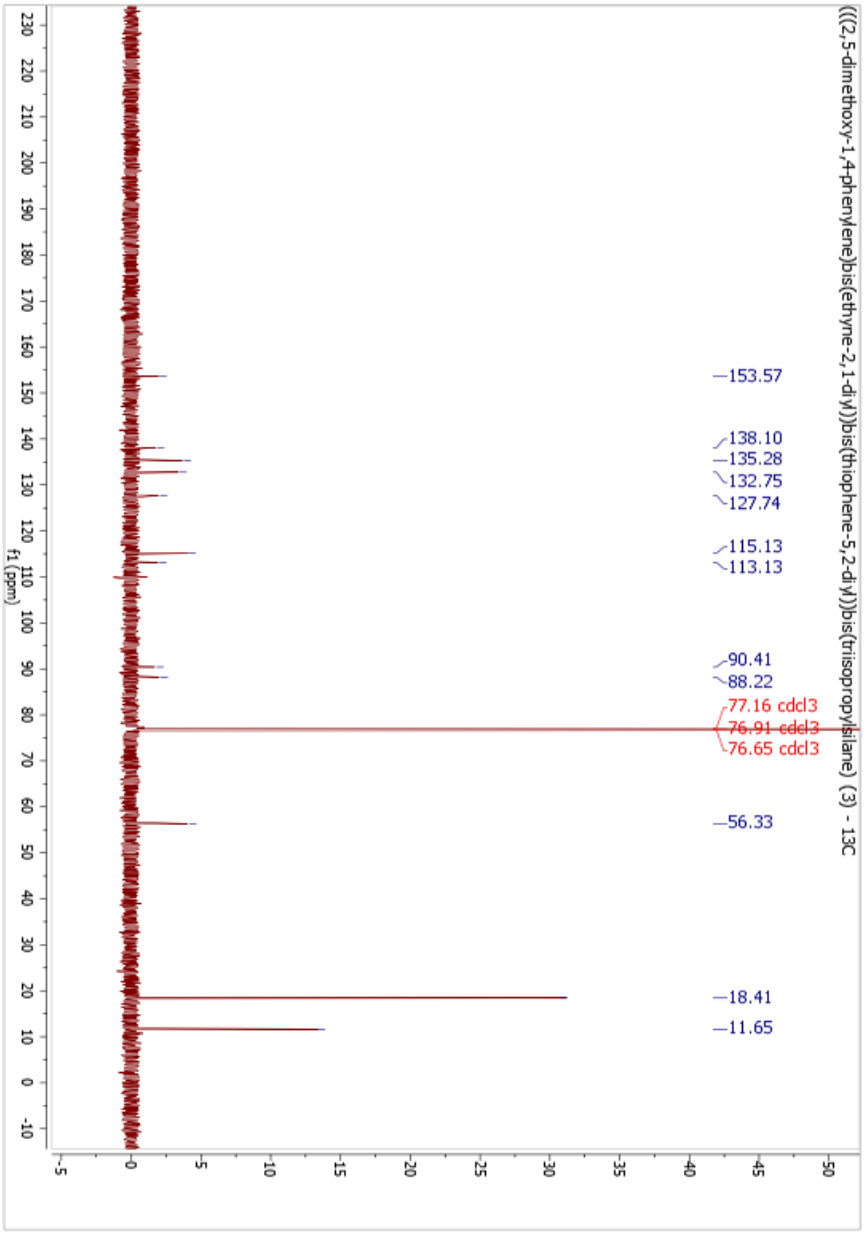


Figure 0.6 - ^{13}C NMR Compound 3

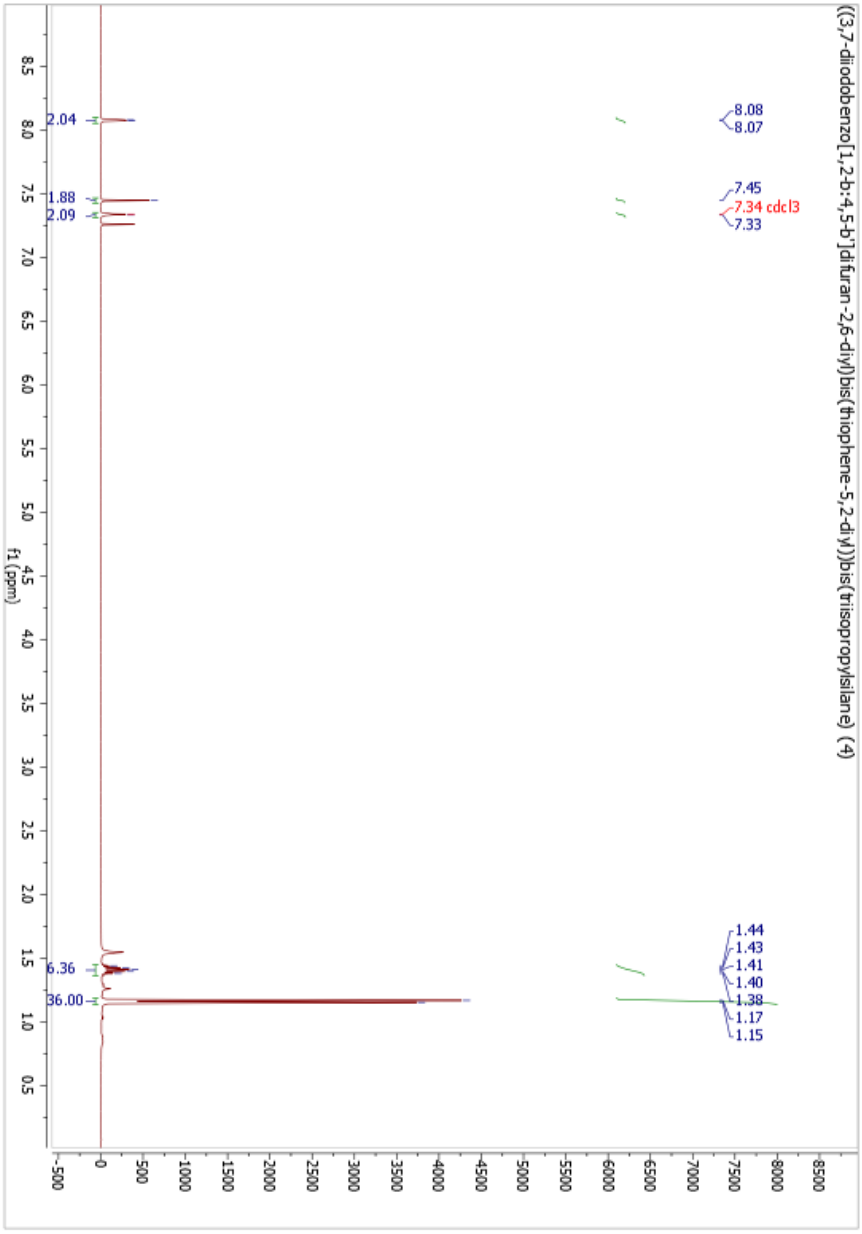


Figure 0.7 - ^{1}H NMR Compound 4

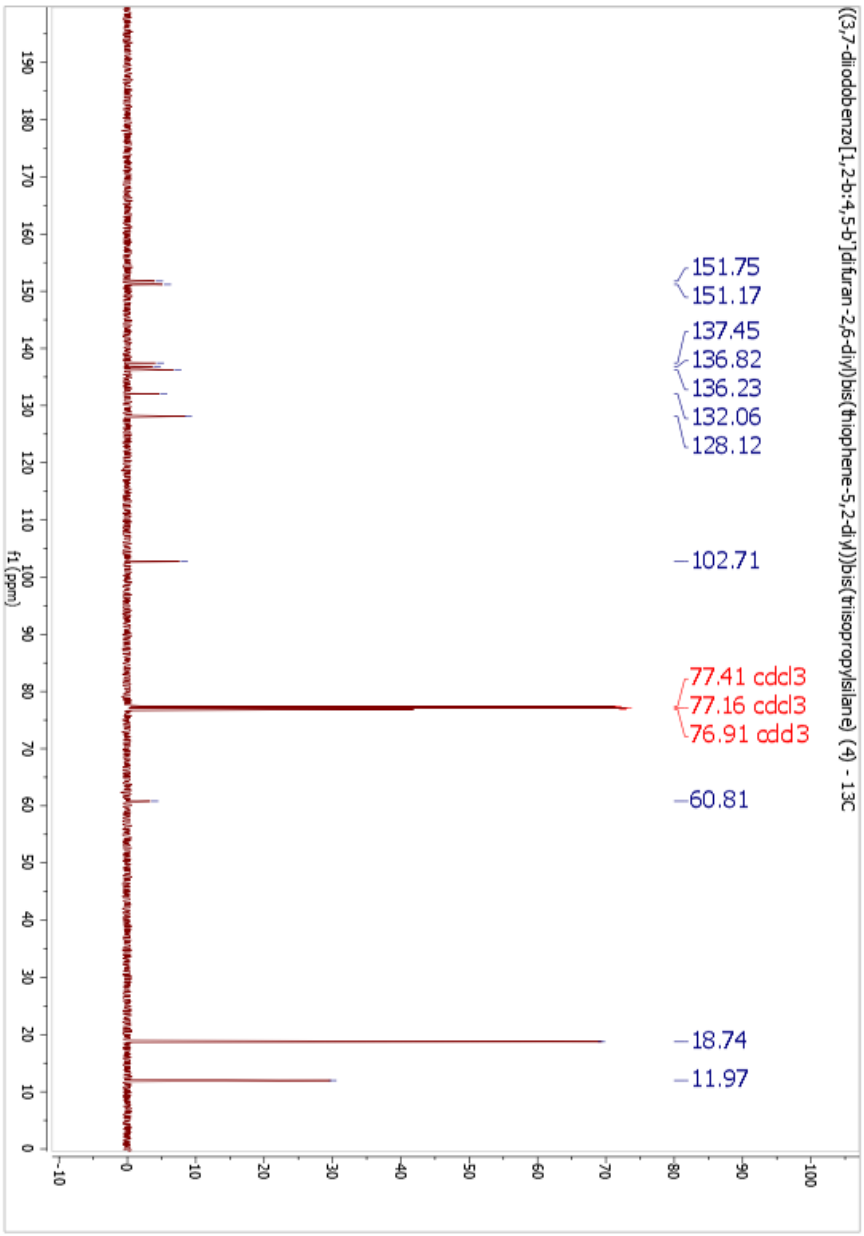


Figure 0.8 - ^{13}C NMR Compound 4

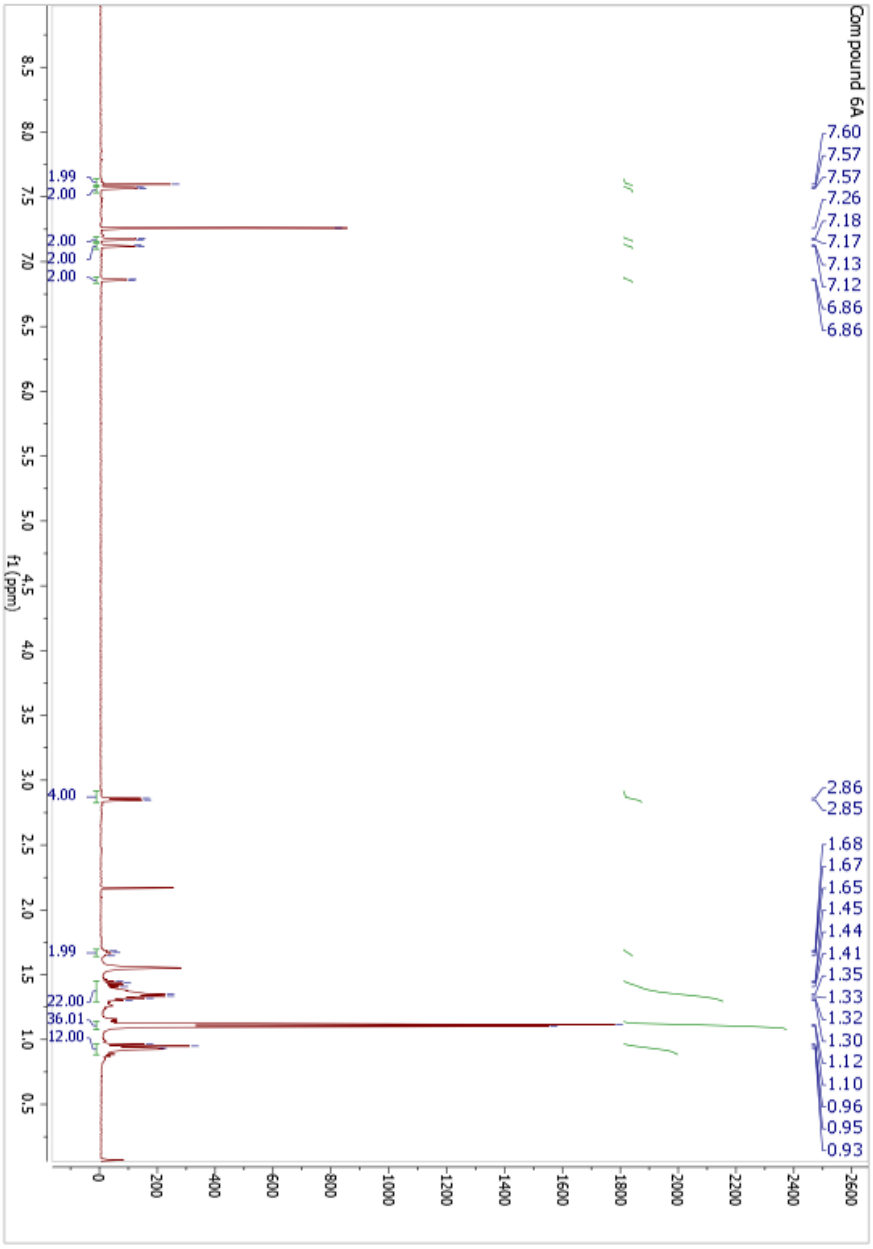


Figure 0.9 - ^{1}H NMR Compound 6A

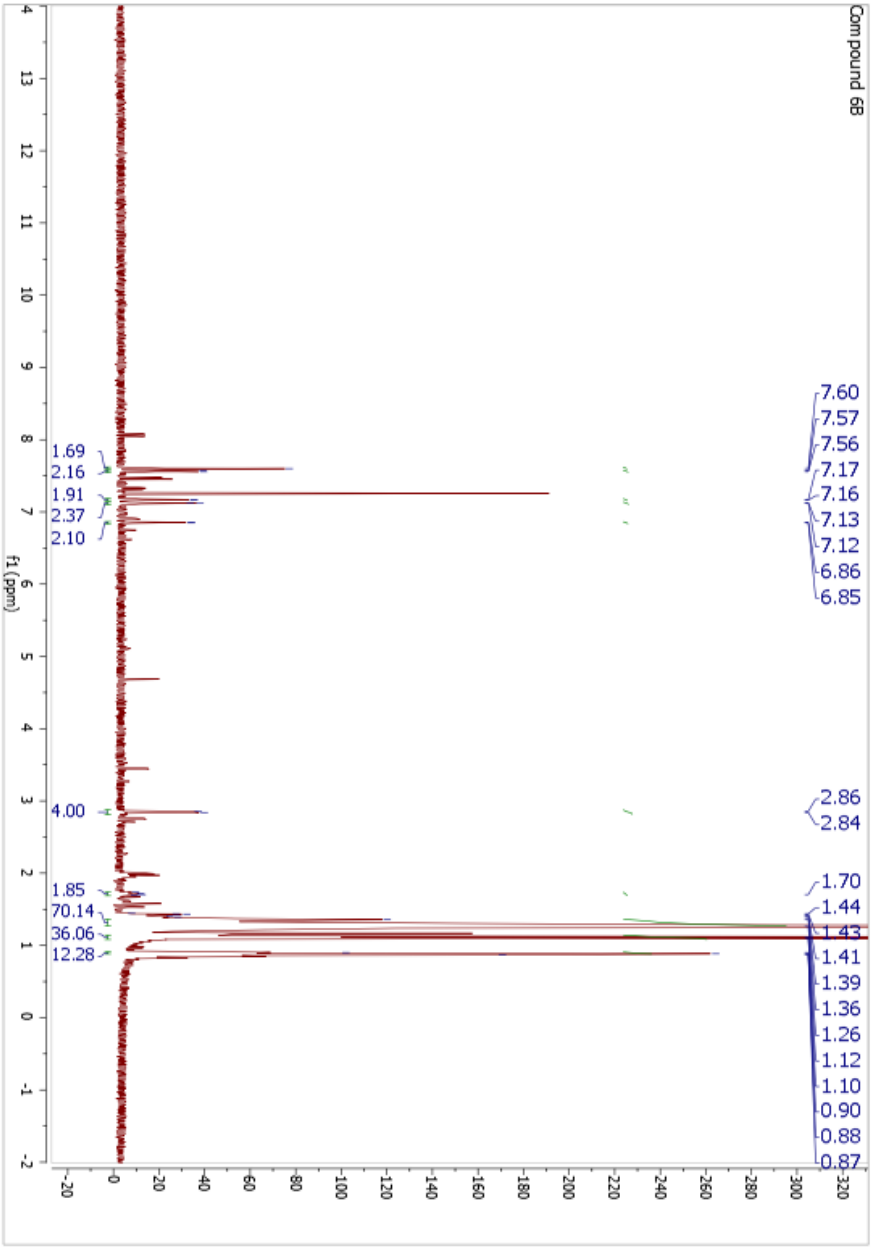


Figure 0.10 - ^{1}H NMR Compound 6B

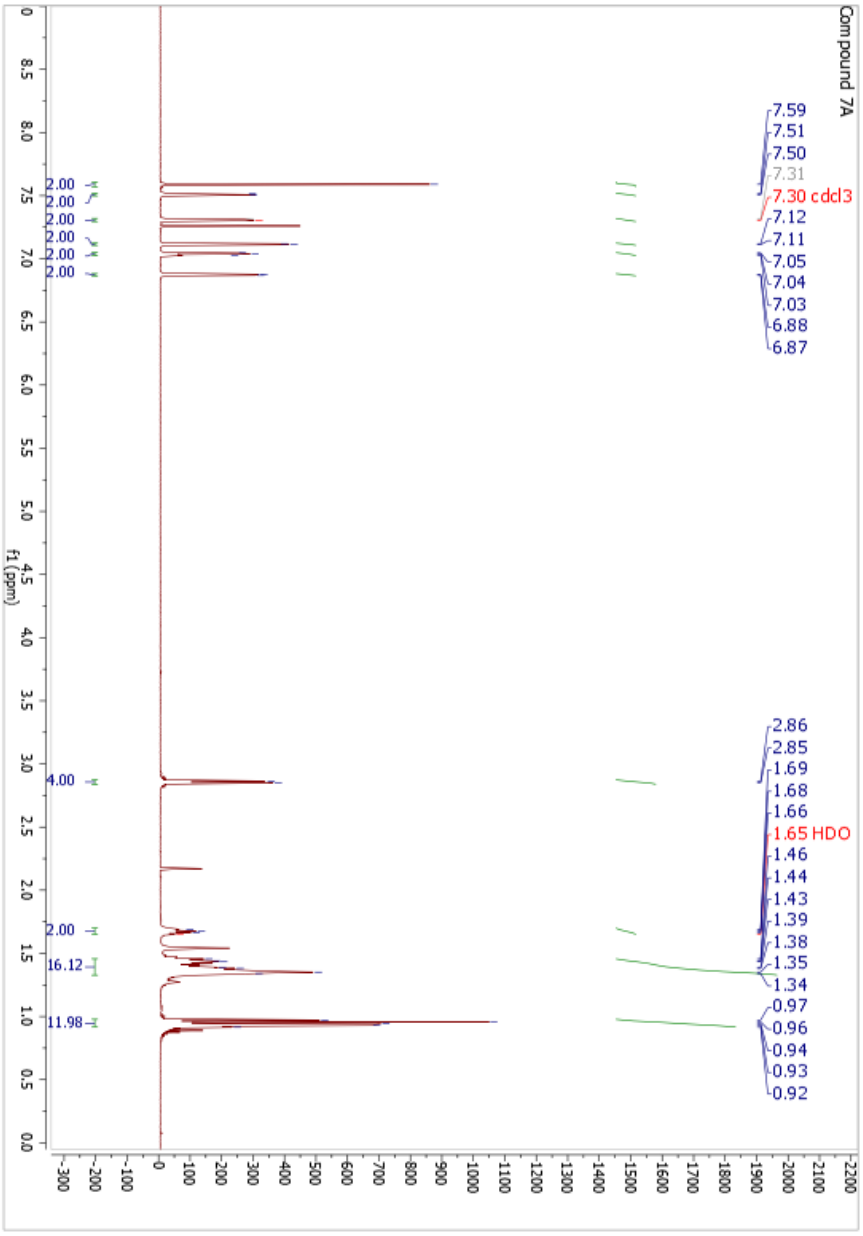


Figure 0.11 - ^{1}H NMR Compound 7A

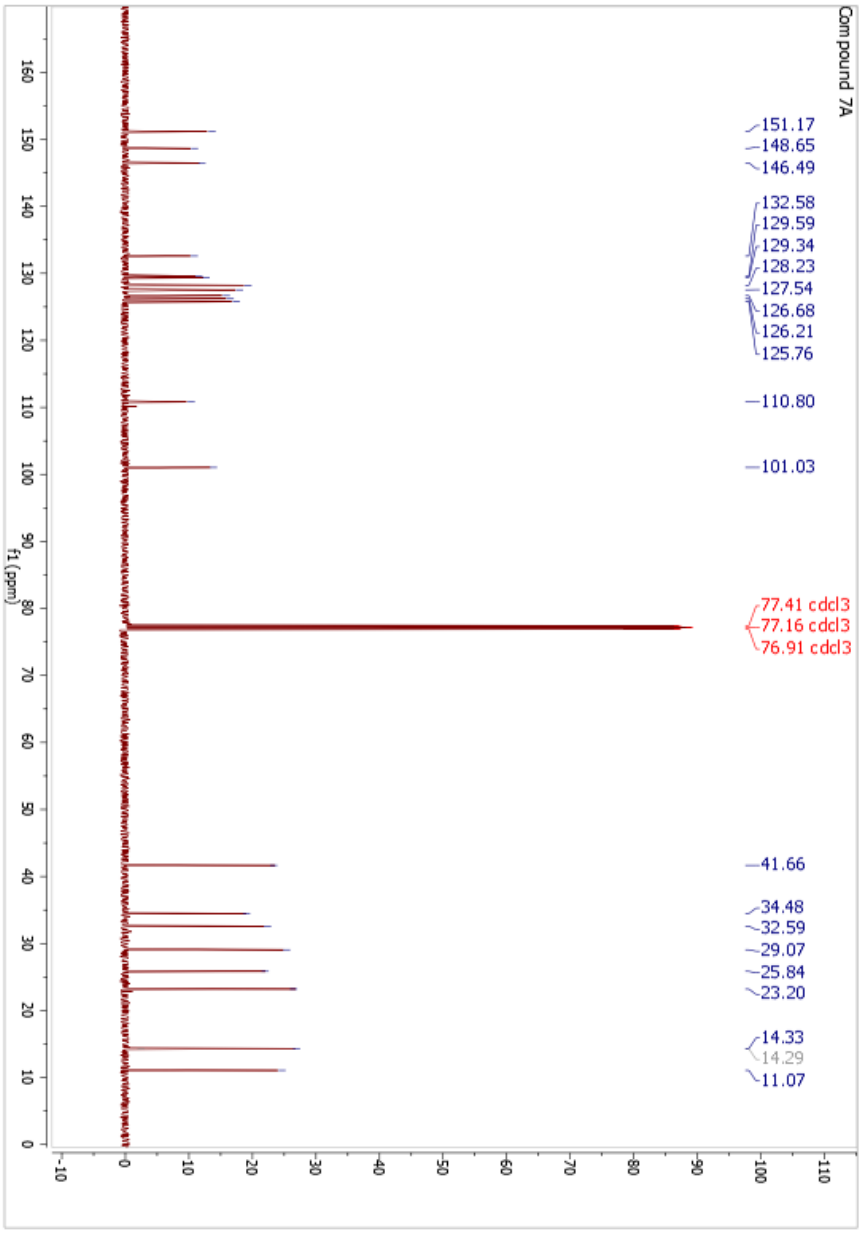


Figure 0.12 - ^{13}C NMR Compound 7A

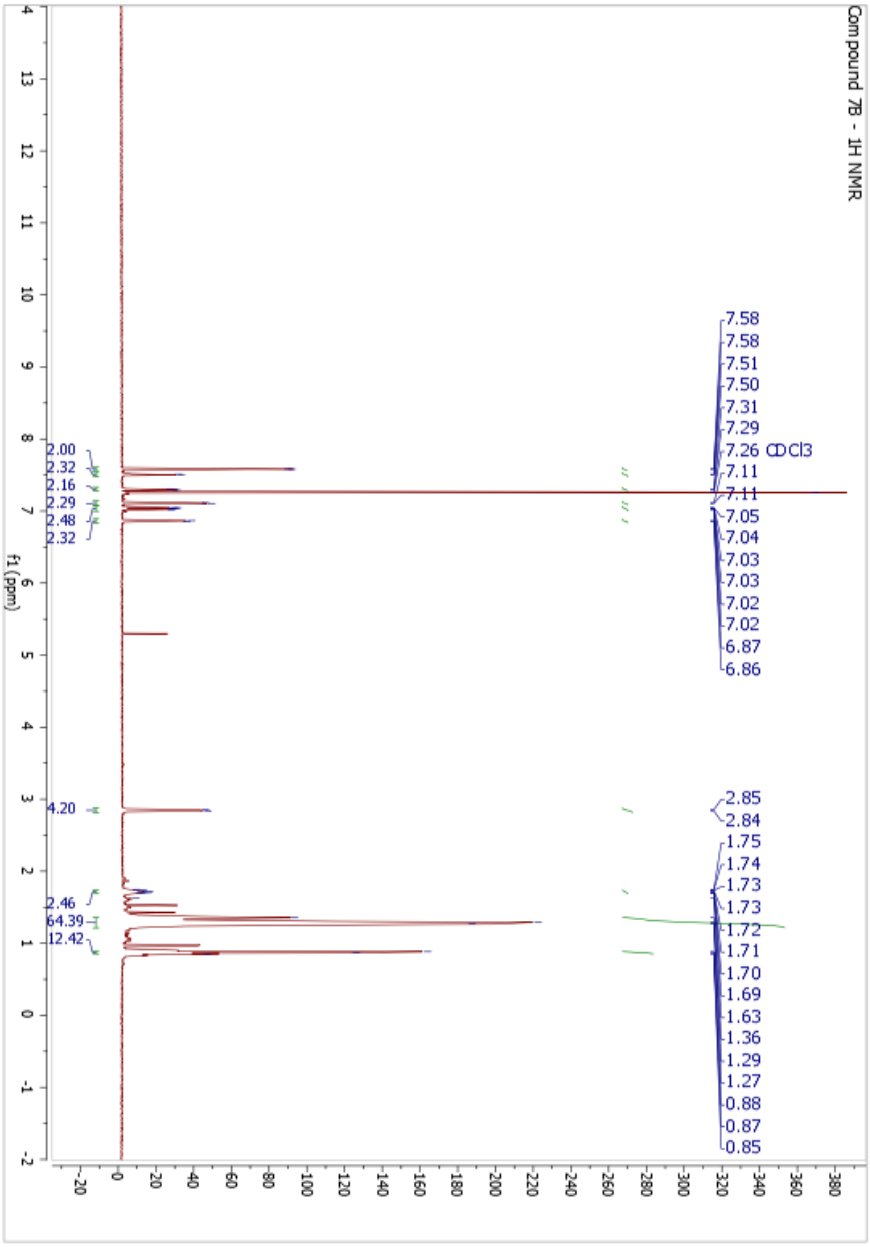


Figure 0.13 - ^{1}H NMR Compound 7B

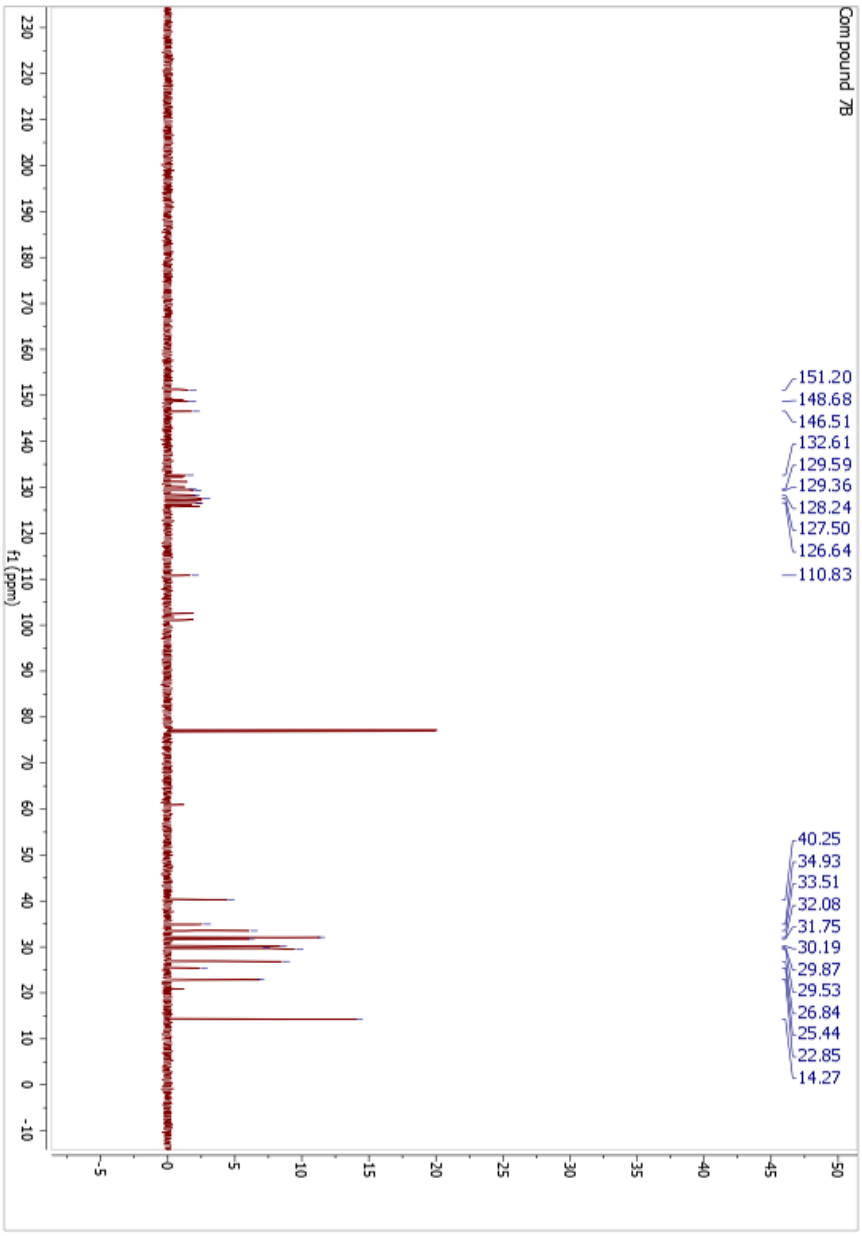


Figure 0.14 - ^{13}C NMR Compound 7B

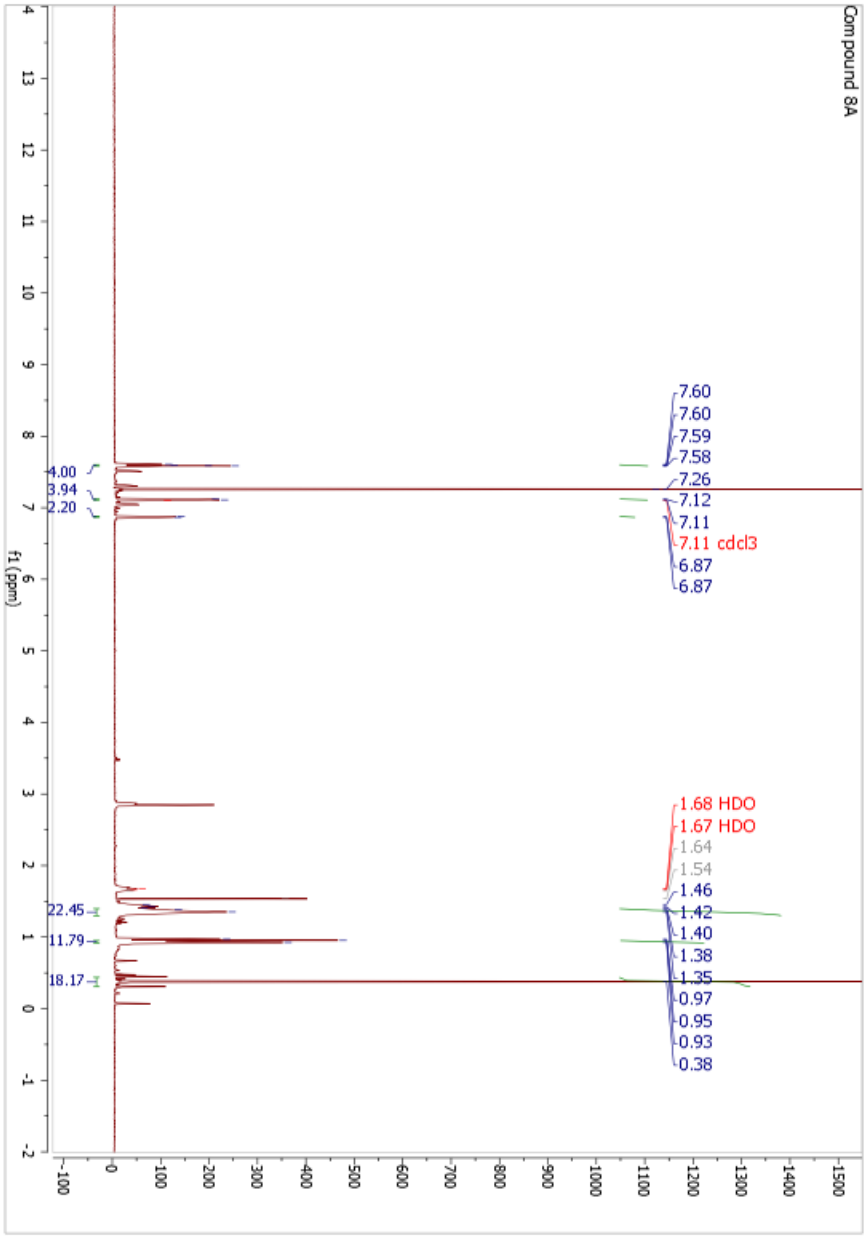


Figure 0.15 - ^{1}H NMR Compound 8A

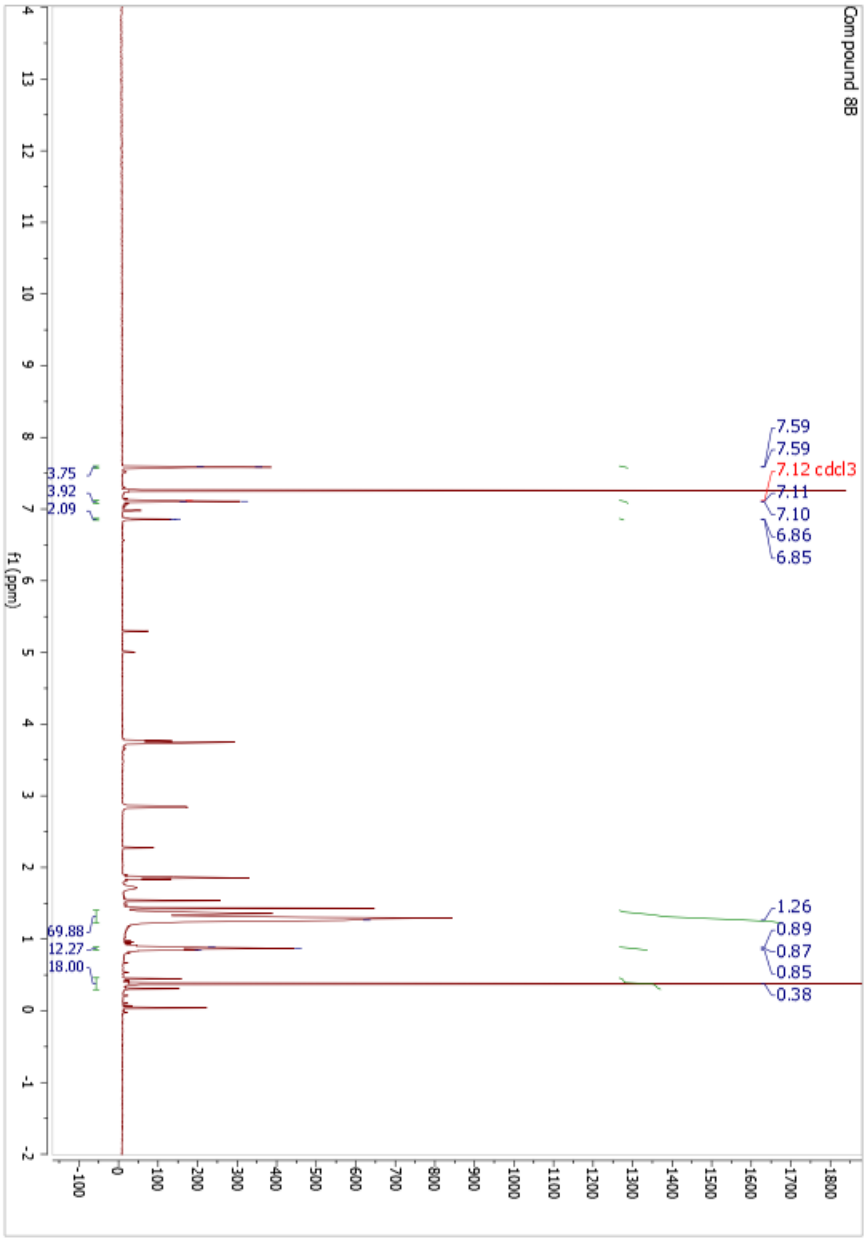


Figure 0.16 - 1H NMR Compound 8B

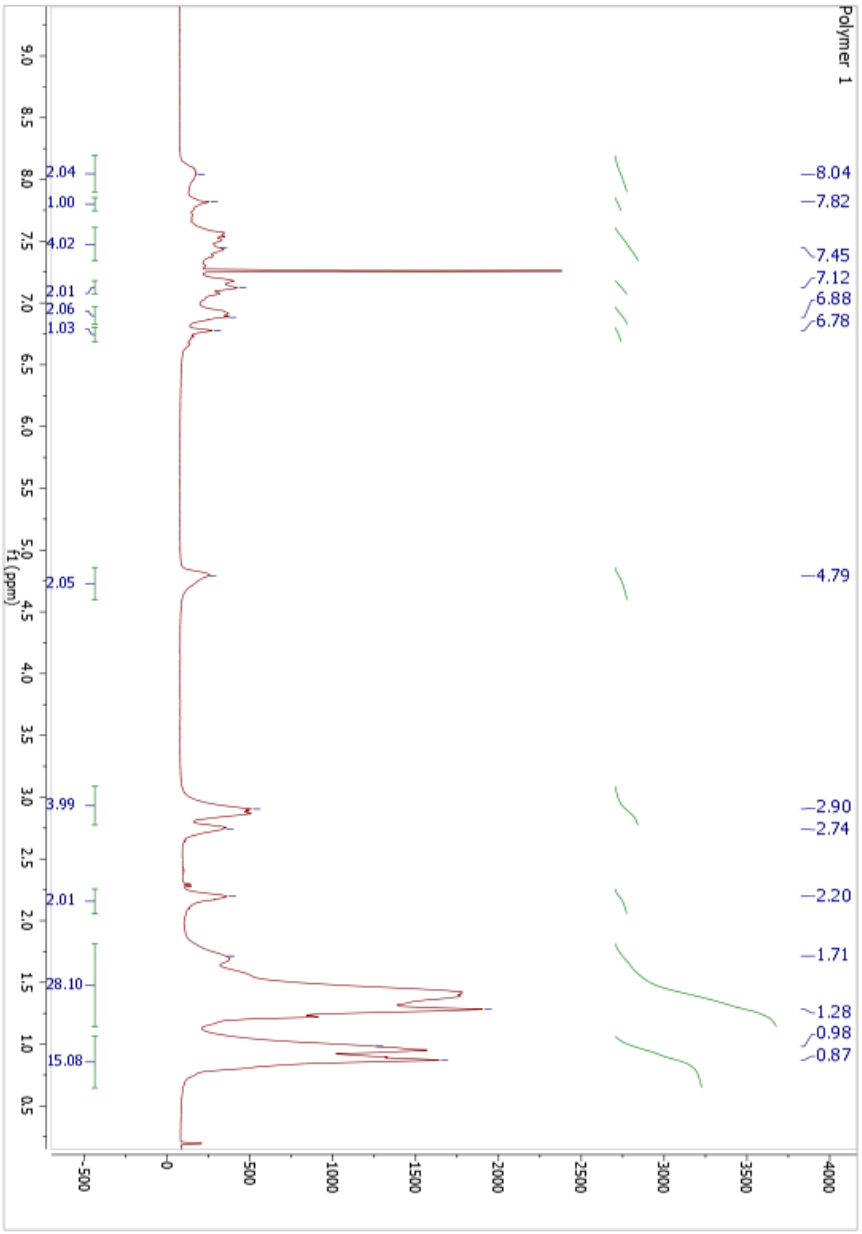


Figure 0.17 - ^{1}H NMR Polymer P1

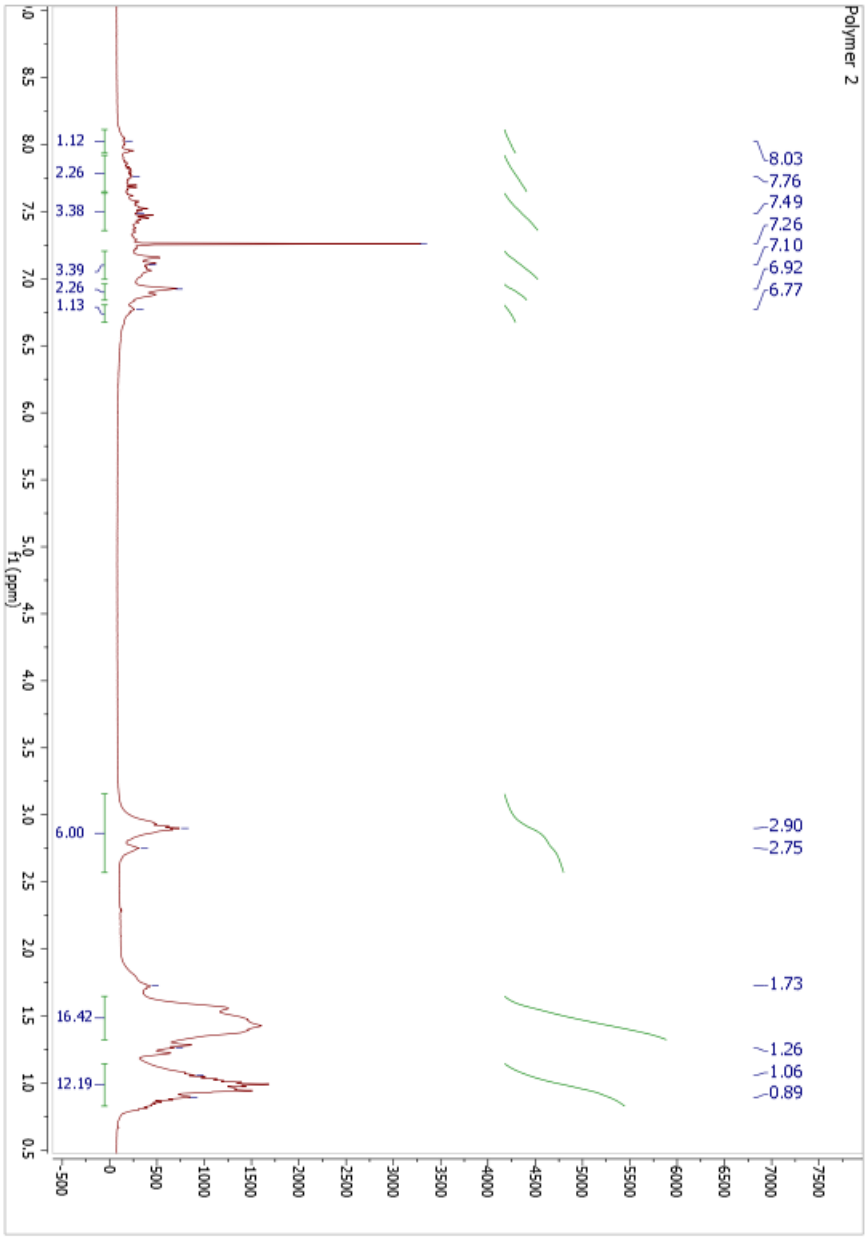


Figure 0.18 - ^{1}H NMR Polymer P2

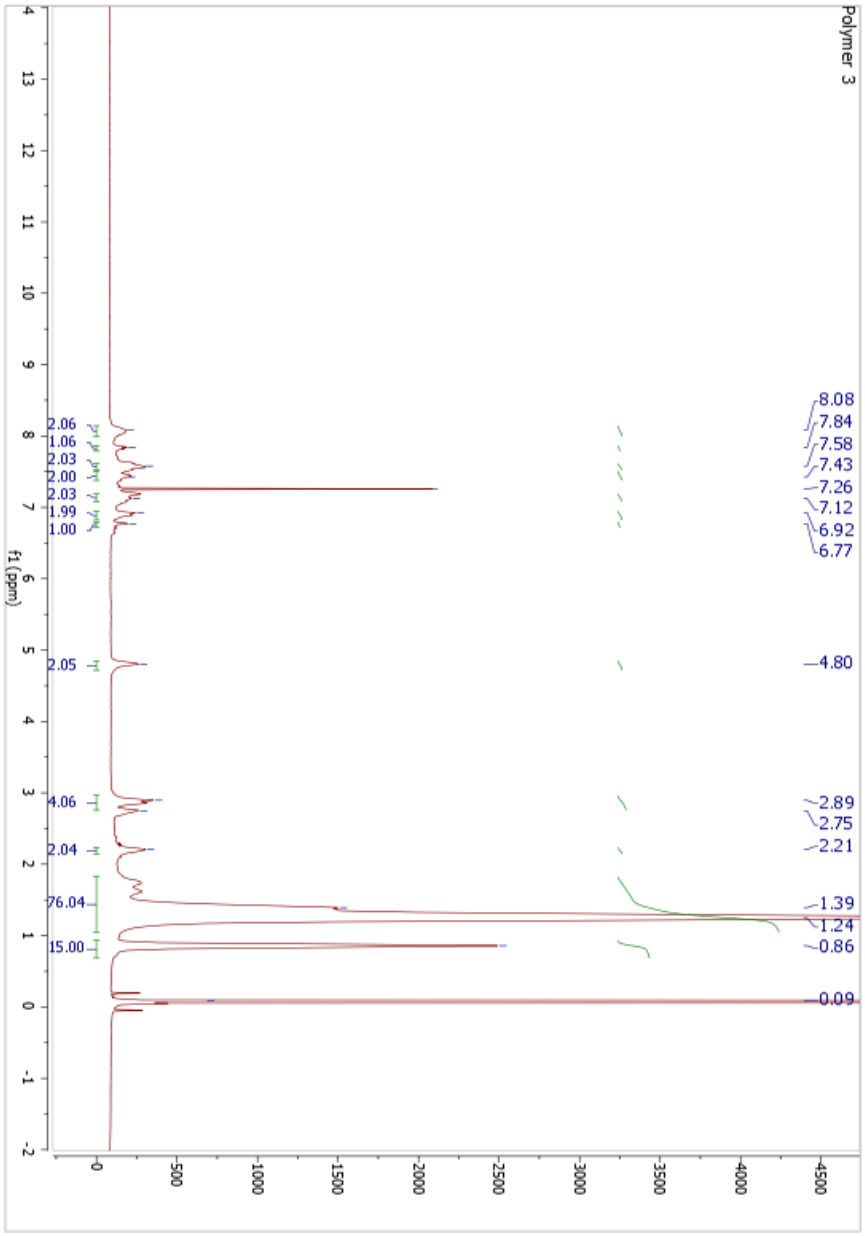


Figure 0.19 - ^{1}H NMR Polymer P3

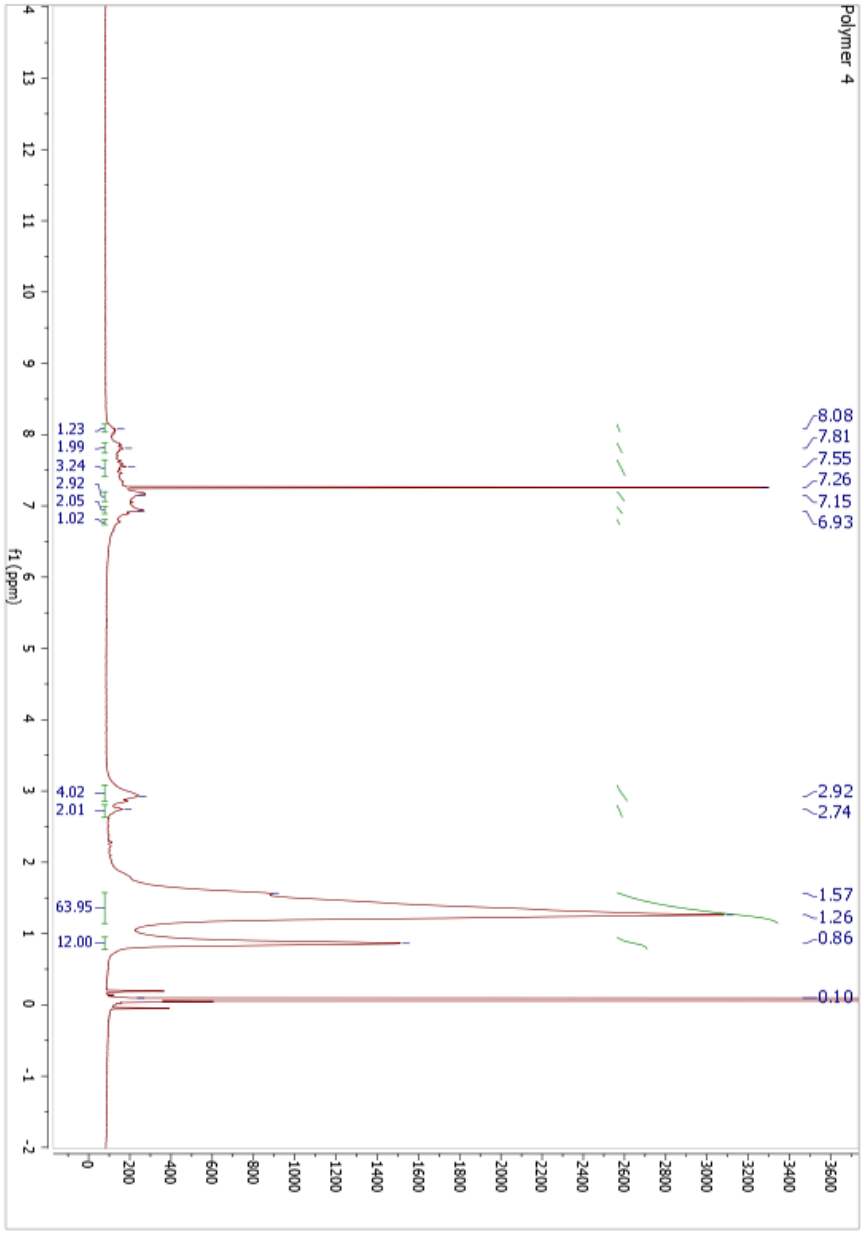
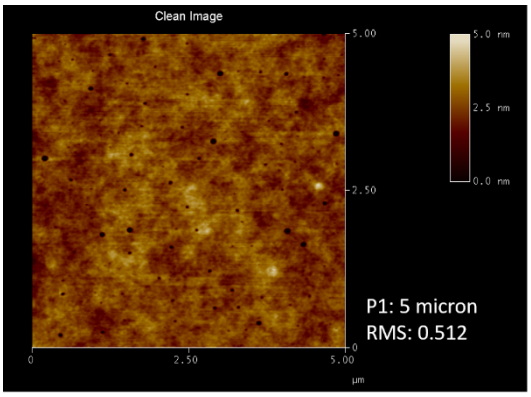
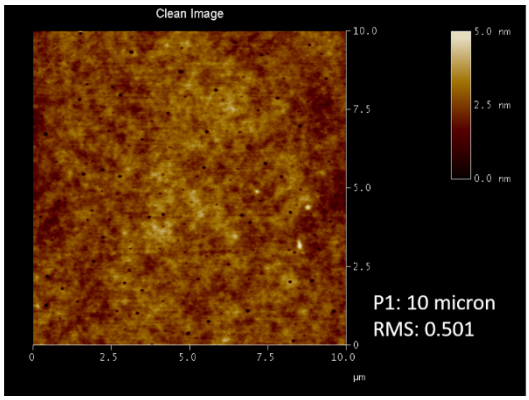
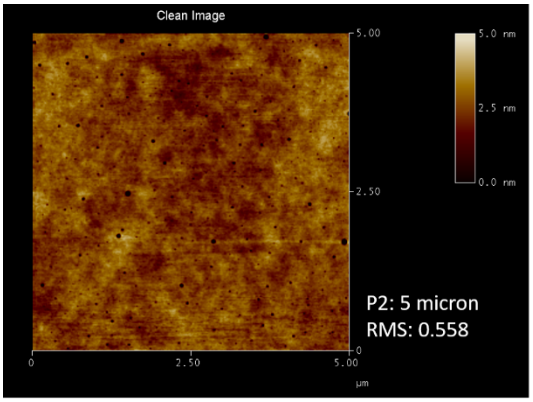


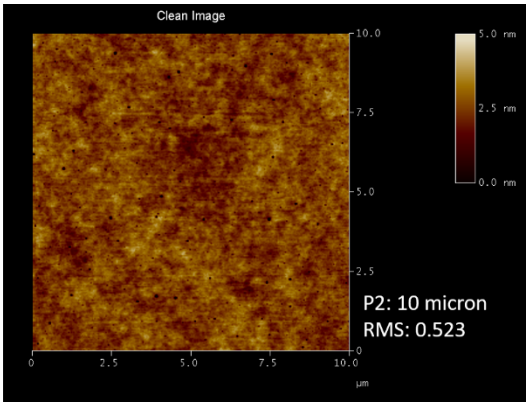
Figure 0.20 - ^{1}H NMR Polymer P4

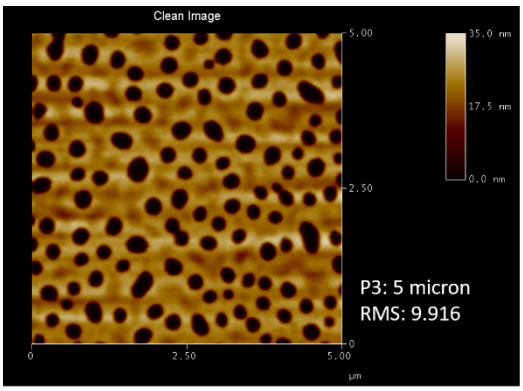
Atomic Force Microscopy

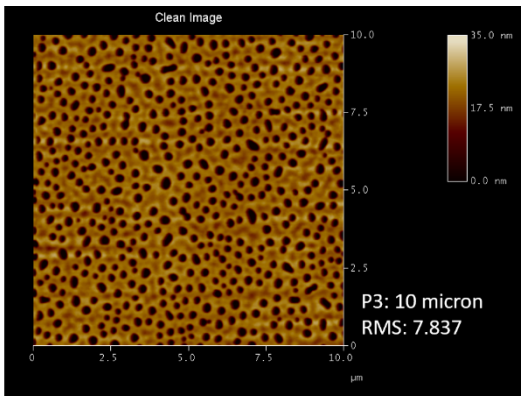












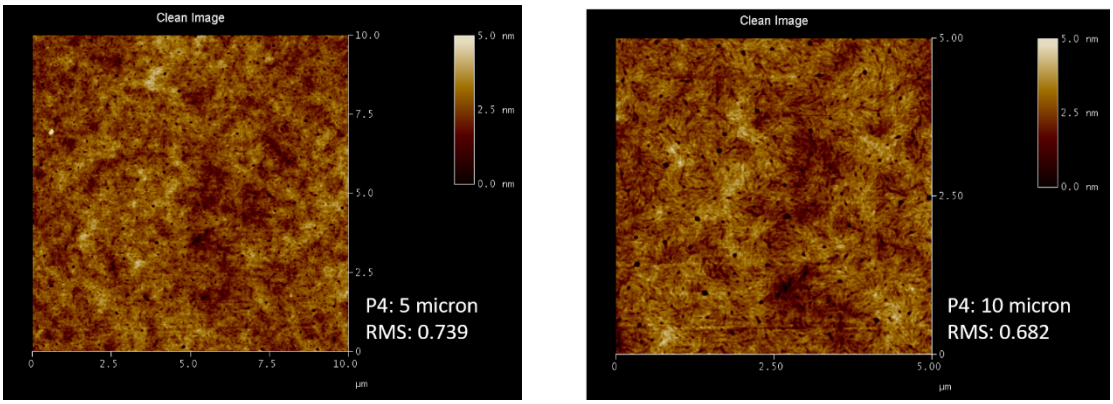


Figure 0.1 - AFM Images Active Layers P1 - P4 at 5 and 10 microns

Cyclic Voltammetry

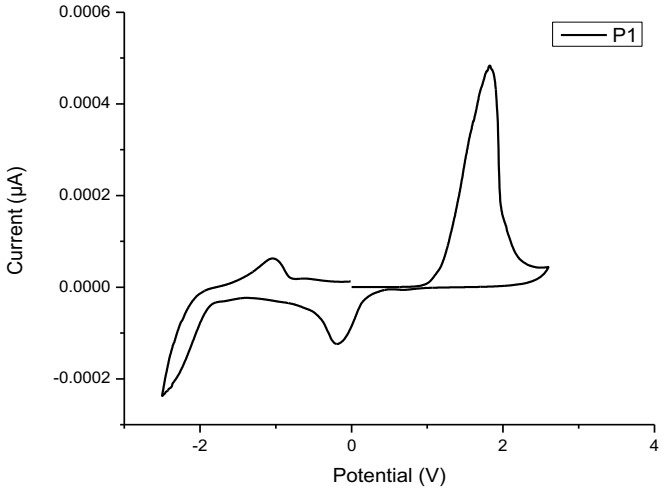


Figure 0.1 - CV Polymer 1

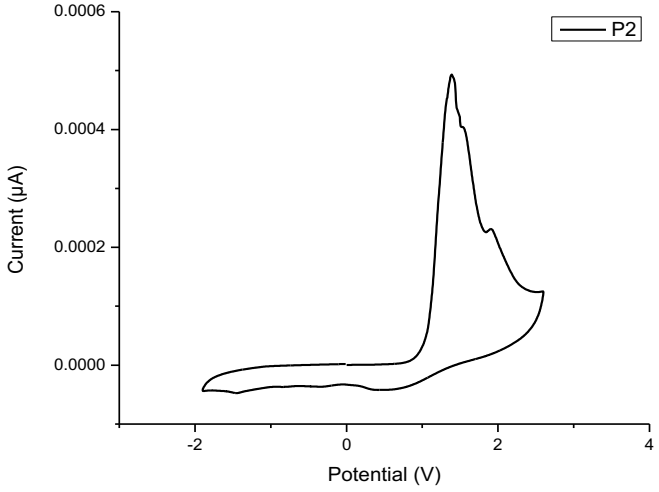


Figure 0.2 - CV Polymer 2

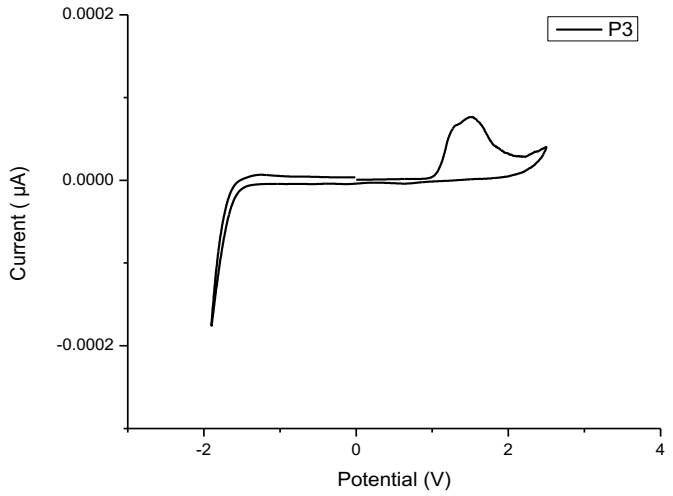


Figure 0.3 - CV Polymer 3

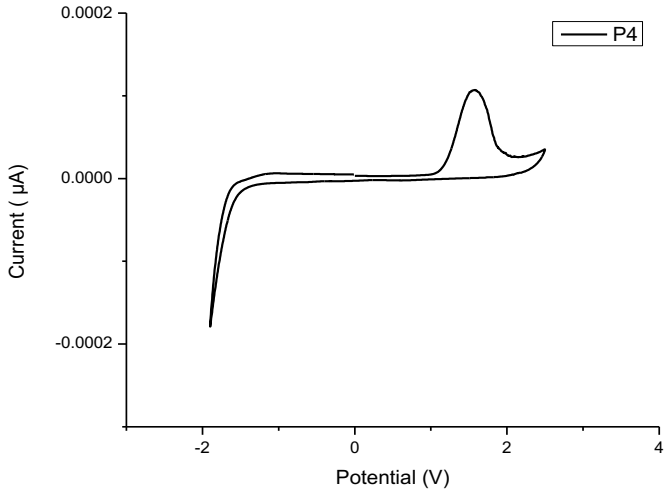


Figure 0.4 - CV Polymer 4

Differential Scanning Calorimetry of P1-P4

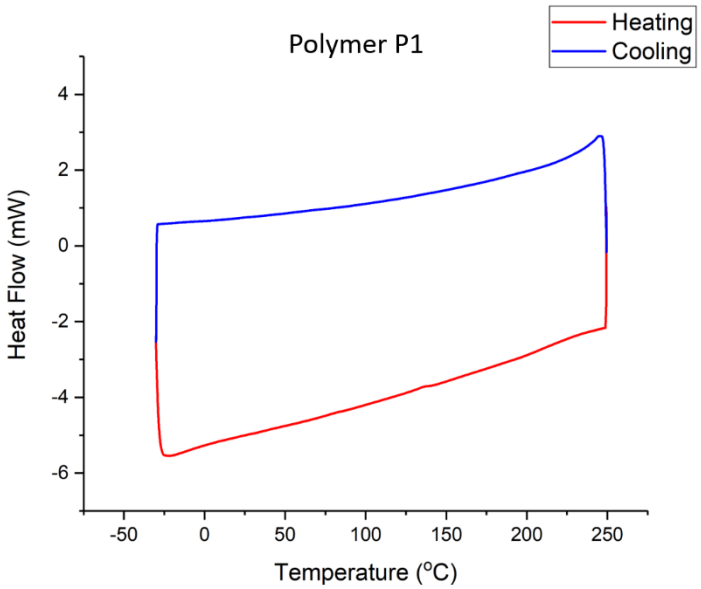


Figure 0.1 - DSC Polymer P1

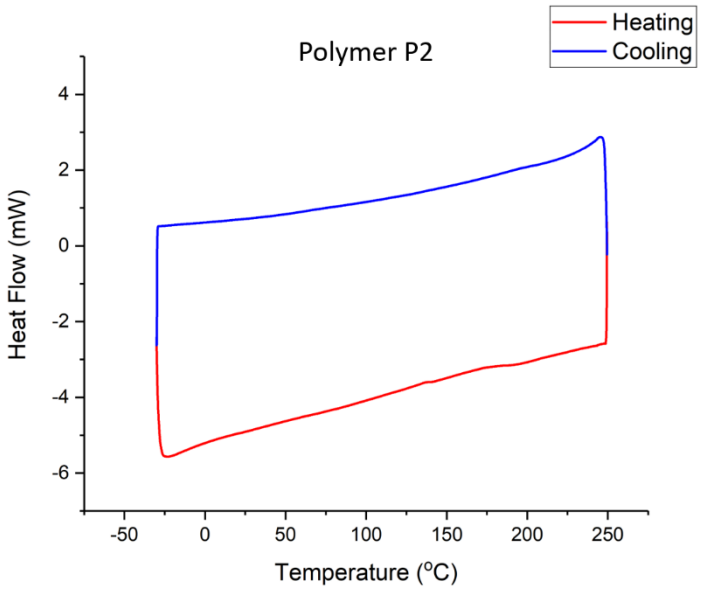


Figure 0.2 - DSC Polymer P2

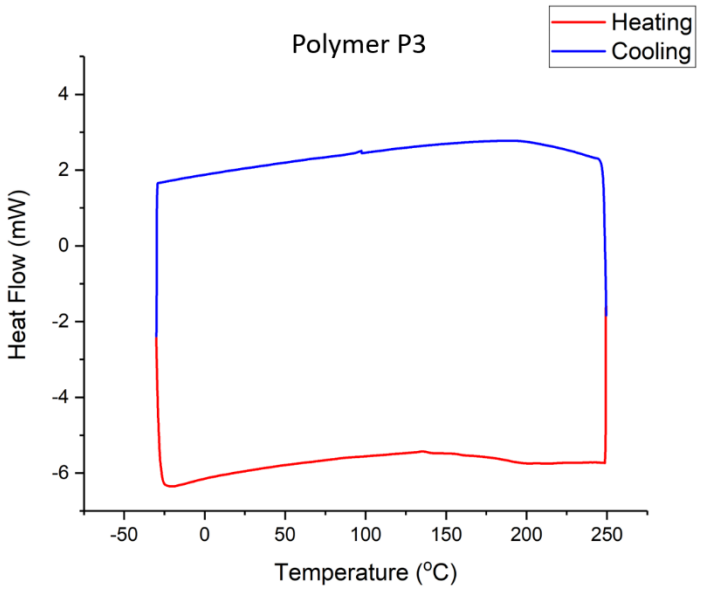


Figure 0.3 - DSC Polymer P3

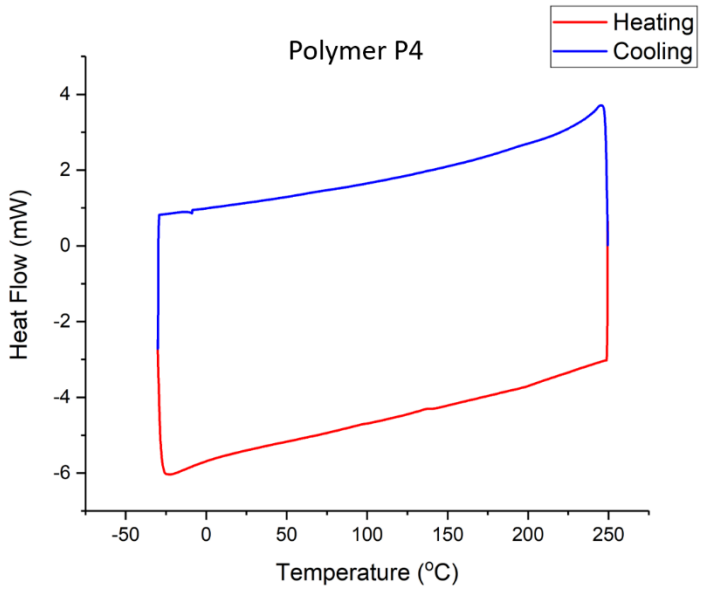


Figure 0.4 - DSC Polymer P4

Thermogravimetric Analysis of P1-P4

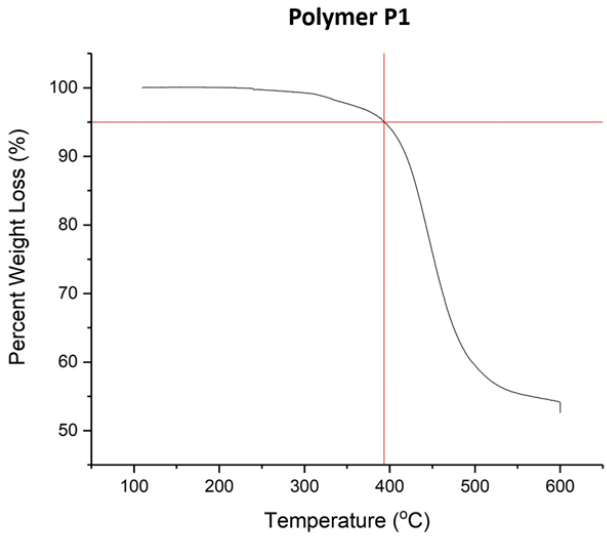


Figure 0.1 - TGA Polymer P1

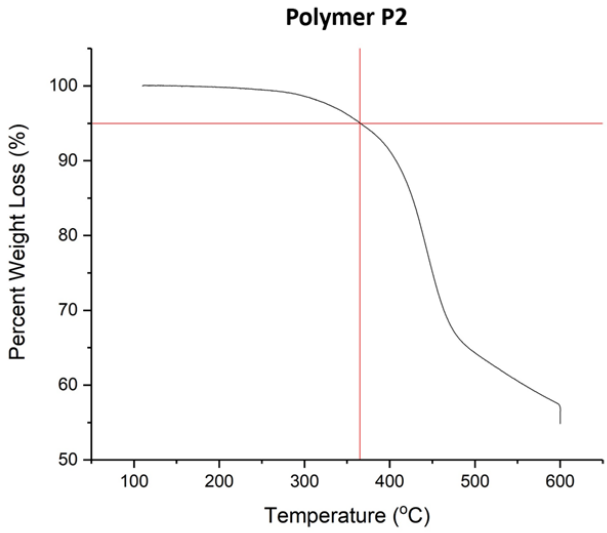


Figure 0.2 - TGA Polymer P2

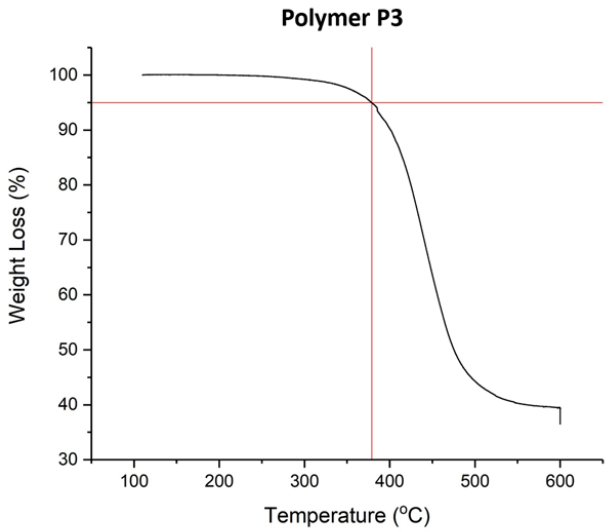


Figure 0.3 - TGA Polymer P3

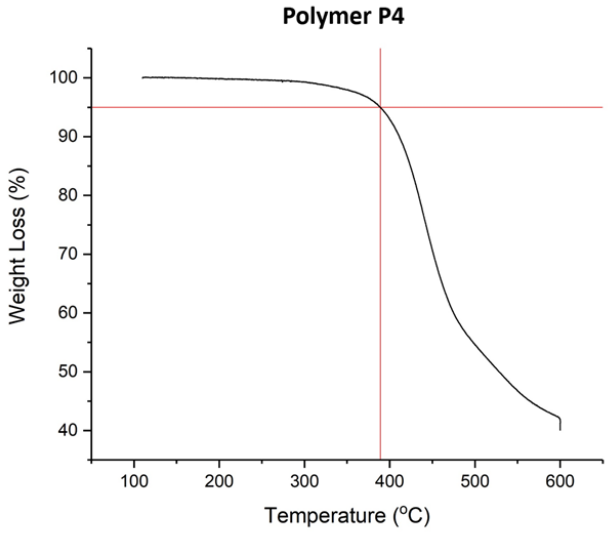


Figure 0.4 - TGA Polymer P3

Average Device Data

	Solution	*Acceptor*	*Spin Coating speed [rpm]*	*Annealing Temp °C*	*D/A*	*J_{sc} [mA/cm²]*	*V_{oc} [V]*	*FF*	*PCE [%]*
	oDCB	$PC_{71}BM$	1000	100	1:2	5.25 (4.84 ± 0.28)	0.70 (0.63 ± 0.07)	47.75 (45.11 ± 3.44)	1.78 (1.42 ± 0.30)
P3	oDCB	$PC_{71}BM$	1000	100	1:3	4.82 (4.60 ± 0.19)	0.81 (0.81 ± 0.00)	58.88 (58.89 ± 1.10)	2.32 (2.22 ± 0.08)
	oDCB 1%CN	**$PC_{71}BM$**	**1000**	**100**	**1:3**	**5.56 (5.21 ± 0.27)**	**0.83 (0.83 ± 0.00)**	**57.37 (56.15 ± 1.05)**	**2.67 (2.45 ± 0.13)**
	oDCB	$PC_{71}BM$	1000	100	1:2	6.43 (6.09 ± 0.25)	0.70 (0.64 ± 0.13)	59.52 (53.47 ± 8.51)	2.70 (2.20 ± 0.65)
P4	**oDCB**	**$PC_{71}BM$**	**1000**	**100**	**1:3**	**6.18 (5.79 ± 0.34)**	**0.73 (0.72 ± 0.01)**	**64.86 (65.36 ± 0.90)**	**2.93 (2.75 ± 0.15)**
	oDCB 1%CN	$PC_{71}BM$	1000	100	1:3	5.85 (5.47 ± 0.40)	0.73 (0.73 ± 0.00)	59.76 (57.90 ± 2.35)	2.60 (2.33 ± 0.18)
P1	oDCB	$PC_{71}BM$	1000	100	1:2	8.69 (8.47 ± 0.40)	0.57 (0.56 ± 0.01)	36.38 (34.77 ± 1.31)	1.81 (1.67 ± 0.10)
	oDCB	$PC_{71}BM$	1000	100	1:3	8.17	0.55	36.54	1.66

						(7.33 ± 0.61)	(0.51 ± 0.10)	(34.25 ± 3.21)	(1.30 ± 0.35)
	oDCB 2% CN	**$PC_{71}BM$**	**1000**	**100**	**1:2**	**10.03 (8.80 ± 0.79)**	**0.61 (0.60 ± 0.01)**	**37.98 (37.19 ± 1.03)**	**2.33 (1.98 ± 0.21)**
	oDCB	$PC_{71}BM$	1000	100	1:2	6.93 (6.69 ± 0.33)	0.67 (0.64 ± 0.02)	35.07 (35.10 ± 0.79)	1.63 (1.51 ± 0.09)
P2	oDCB	$PC_{71}BM$	1000	100	1:3	4.95 (5.04 ± 0.57)	0.58 (0.45 ± 0.10	37.10 (31.42 ± 3.85)	1.07 (0.73 ± 0.24)
	oDCB 1% CN	**$PC_{71}BM$**	**1000**	**100**	**1:2**	**7.40 (6.99 ± 0.52)**	**0.67 (0.64 ± 0.04)**	**35.11 (33.62 ± 1.15)**	**1.75 (1.53 ± 0.15)**

Table 0.1 - Average Device Data

Best average based on greater than equal to 8 devices.

JV Curves

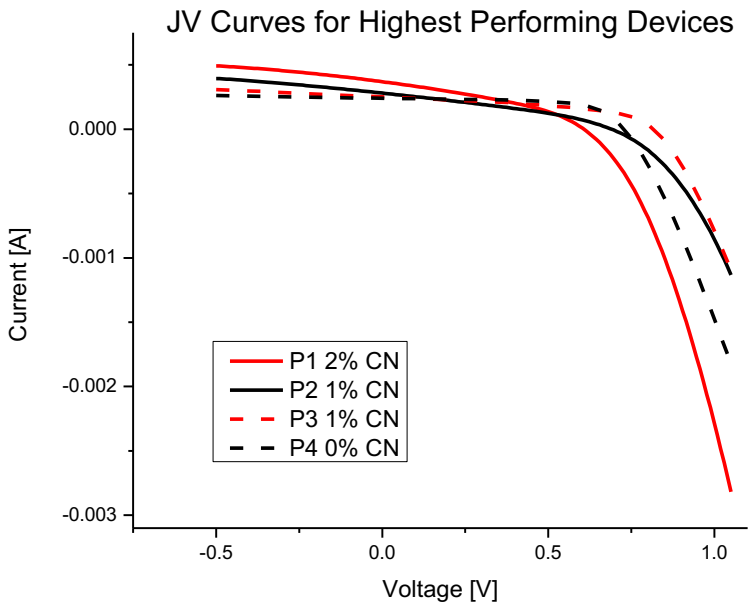


Figure 0.1 - Highest Performing Devices Polymers P1-P4

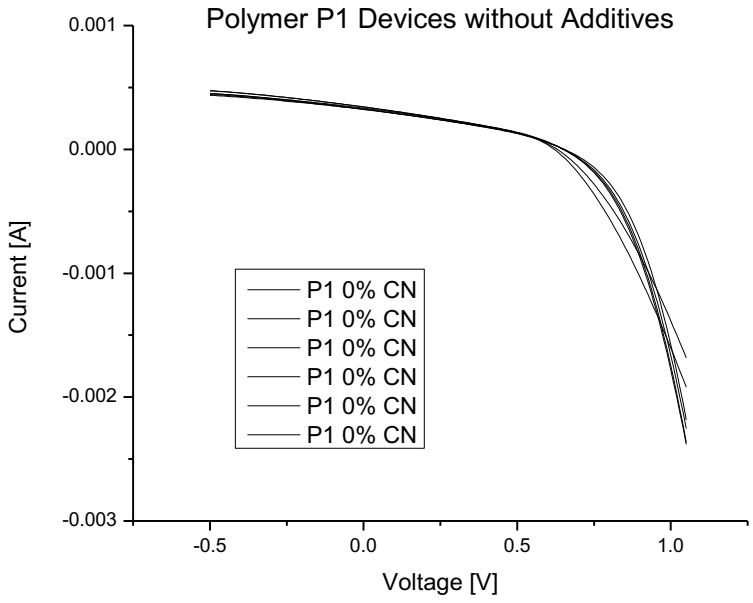


Figure 0.2 - Polymer P1 Devices without Additives

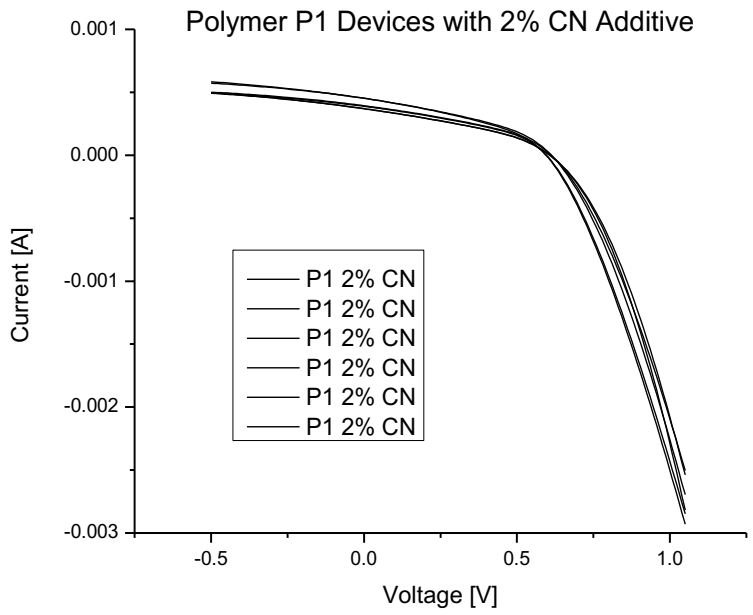


Figure 0.3 - Polymer P1 Devices with 2% CN Aadditive

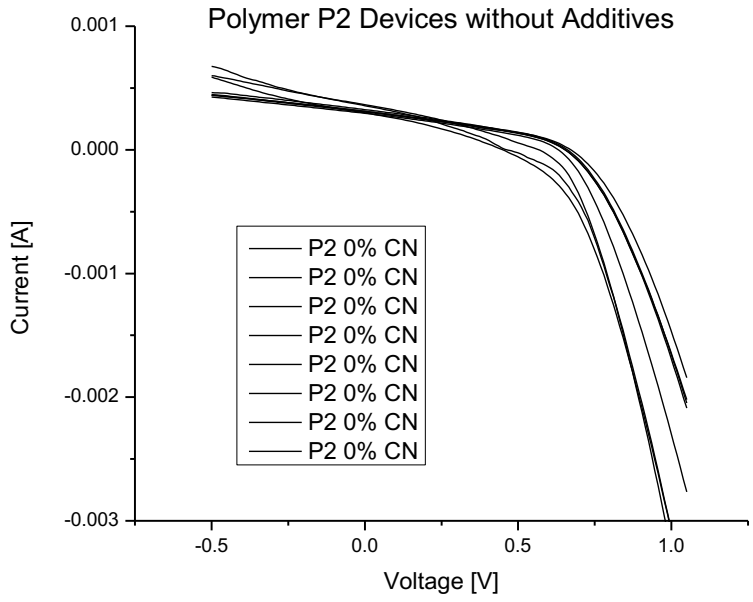


Figure 0.4 - Polymer P2 Devices without Additive

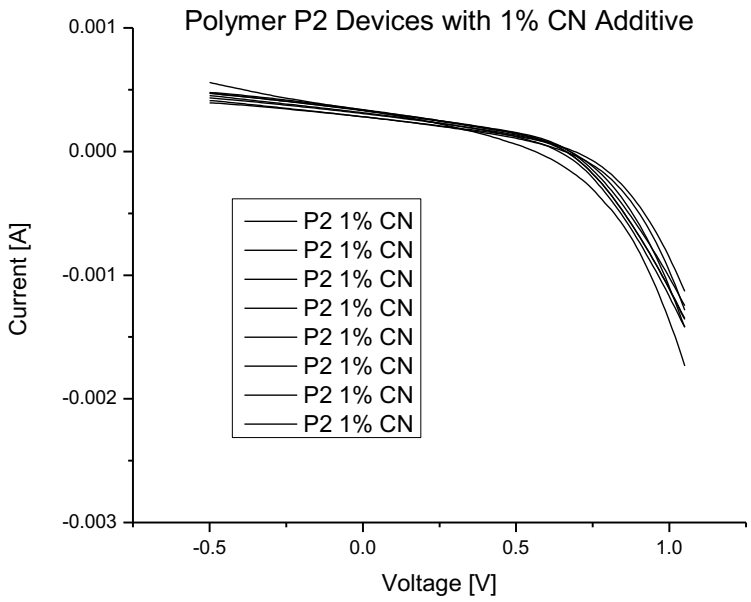


Figure 0.5 - Polymer P2 Devices with 1% CN Additive

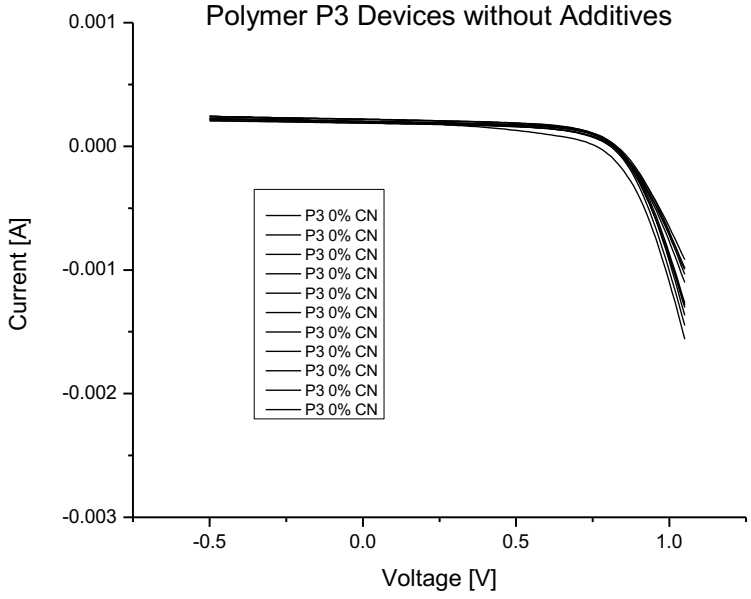


Figure 0.6 - Polymer P3 Devices without Additives

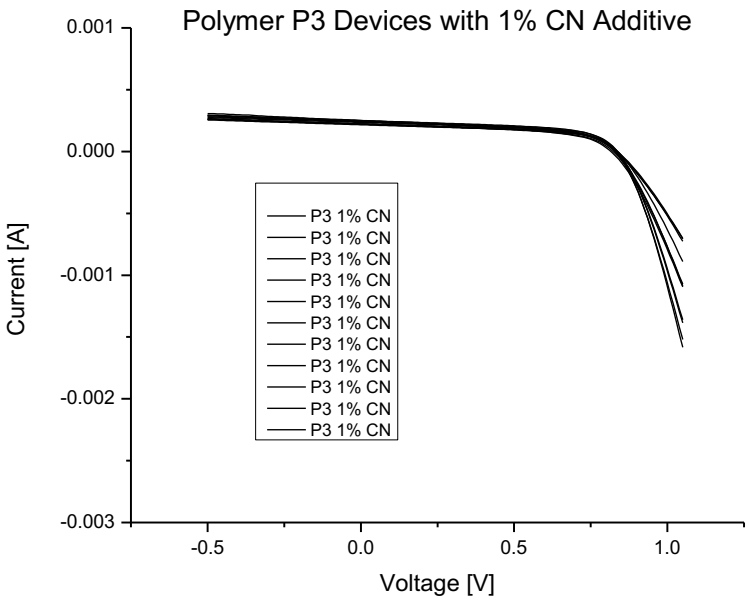


Figure 0.7 - Polymer P3 Devices with 1% CN Additive

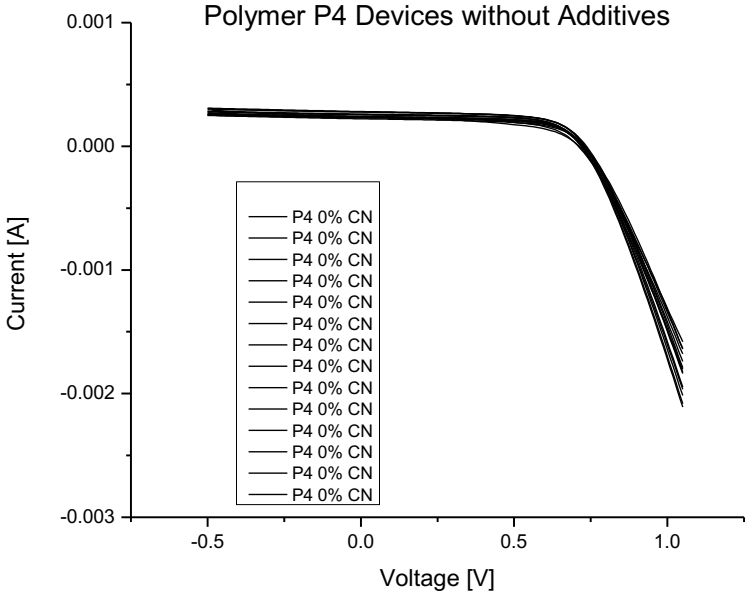


Figure 0.8 - Polymer P4 Devices without Additives

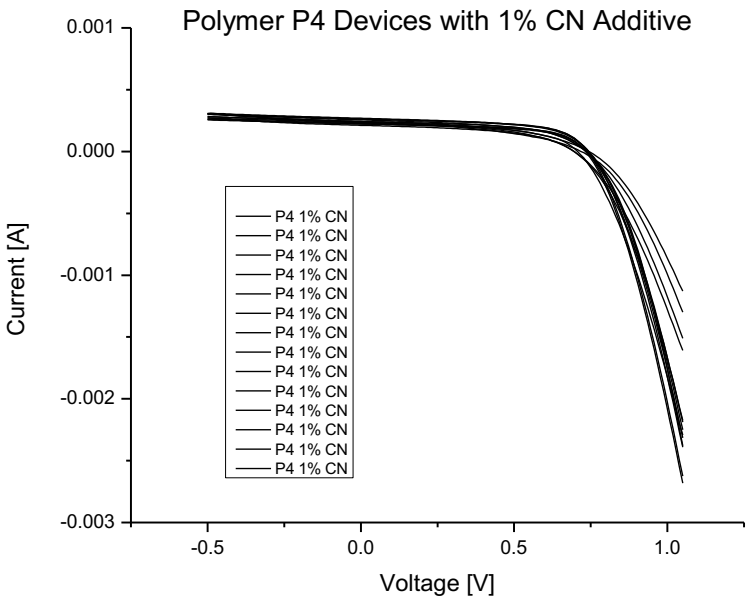
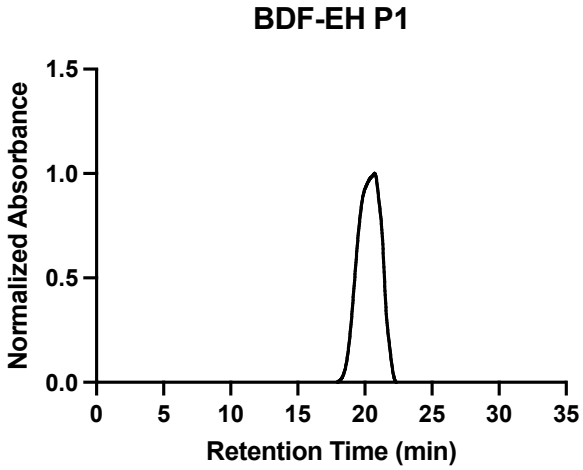


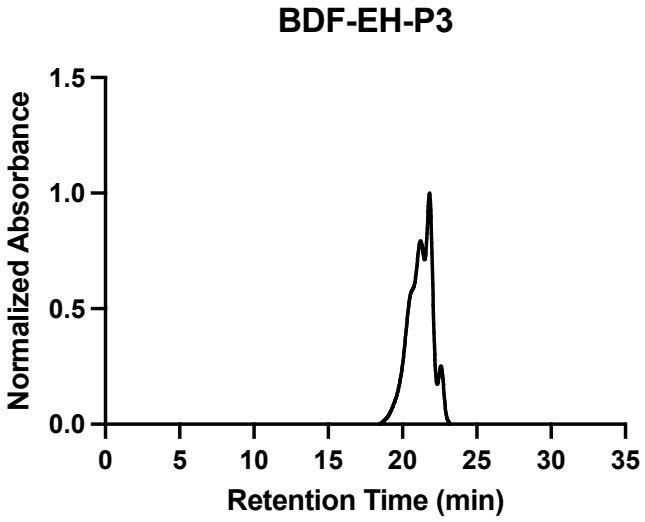
Figure 0.9 - Polymer P4 Devices with 1% CN Additive

GPC Chromatograms



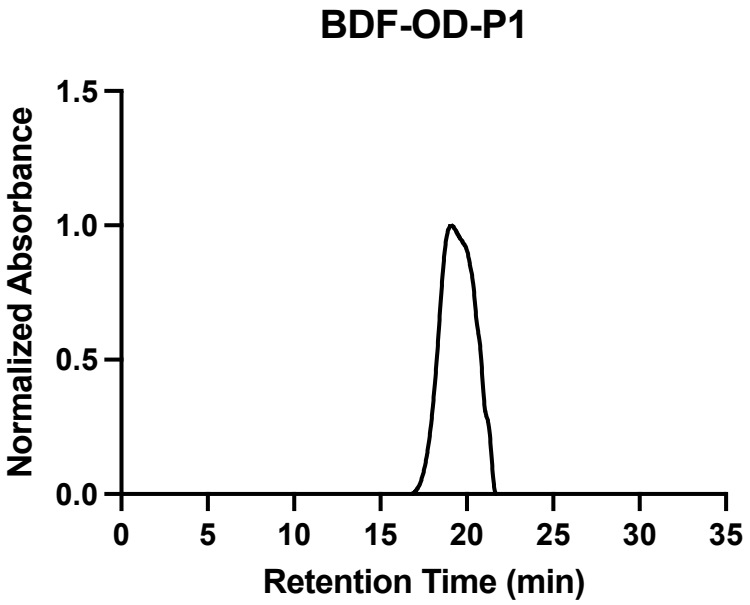
Molecular Weight Data							
Peak No.	Mp	Mn	Mw	Mz	Mz+1	Mv	PDI
1	3340	4898	6246	8338	11042	5991	1.27521
2	1824	1769	1856	1938	2013	1844	1.04918
3	757	720	752	782	809	748	1.04444

Figure 0.1 - Polymer P1 GPC Chromatogram 80°C Chlorobenzene



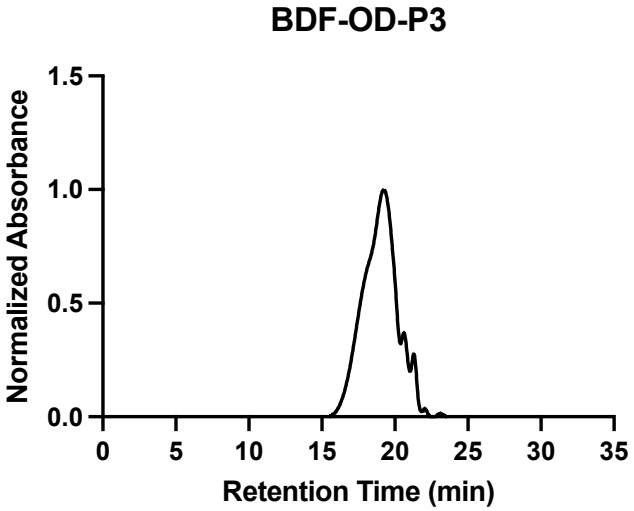
Molecular Weight Data							
Peak No.	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	5271	6155	9045	12338	15455	8583	1.46954

Figure 0.2 - Polymer P2 GPC Chromatogram 80°C Chlorobenzene



Molecular Weight Data							
Peak No.	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	18526	11453	17305	23749	29900	16392	1.51096

Figure 0.3 - Polymer P3 GPC Chromatogram 80°C Chlorobenzene



Molecular Weight Data							
Peak No.	Mp	Mn	Mw	Mz	Mz+1	Mv	PDI
1	16313	20054	29558	44103	61471	27781	1.47392
2	5747	5362	5503	5639	5767	5482	1.0263
3	3083	2973	3059	3137	3209	3046	1.02893
4	1441	1392	1422	1452	1479	1418	1.02155
5	379	362	379	395	411	376	1.04696

Figure 0.4 - Polymer P4 GPC Chromatogram 80°C Chlorobenzene

Standard Curve + Column Information

Standard info:

Polystyrene standard B from Agilent technologies (EASICAL PS-1 PL2010-0501)

Mp (g/mol) Ranges:

2,327,000

321,300

75,050

9,310

580

Calibration info:

High Limit RT	12.6167
Low Limit RT	22.8
High Limit MW	2303462
Low Limit MW	577
K Calibration	14.1

References

[1] Yi, C.; Blum, C.; Lehmann, M.; Keller, S.; Liu, S.-X.; Frei, G.; Neels, A.; Hauser, J.; Schürch, S.; Decurtins, S. Versatile Strategy To Access Fully Functionalized Benzodifurans: Redox-Active Chromophores for the Construction of Extended π-Conjugated Materials. *J. Org. Chem.* **2010**, *75* (10), 3350–3357.

[2] Scheuble, M.; Gross, Y. M.; Trefz, D.; Brinkmann, M.; López Navarrete, J. T.; Ruiz Delgado, M. C.; Ludwigs, S. Polythiophenes with Thiophene Side Chain Extensions: Convergent Syntheses and Investigation of Mesoscopic Order. *Macromolecules* **2015**, *48* (19), 7049–7059. https://doi.org/10.1021/acs.macromol.5b01512.