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Multicomponent synthesis of dithiocarbamates starting from Vinyl sulfones/sulfoxides and their utilities in polymerization reactions

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Contents

Experimental

Materials and Instruments

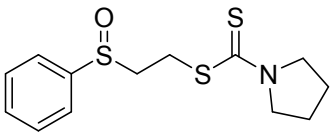
Chemicals were commercially available and purchased from Merck, Sigma and Fluka and applied as received. All solvents were distilled before using. Infrared spectra were recorded as a KBr pellet on a Perkin Elmer 843 FT-IR spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a Bruker AVANCE 300 and 500 MHz FT-NMR system by using DMSO-d_6 or $CDCl_3$ as solvent and TMS as internal standard. Mass spectra were obtained on a Waters Q-TOF Premier (ESI) spectrometer. The inherent viscosities were determined with a Cannon-Fenske viscometer at 30 °C. The number-average molecular weight (*M*n), weight average molecular weight (*M*w) and polydispersity index (PDI) values were obtained via gel permeation chromatography (GPC) on the basis of polystyrene calibration using an Agilent GPC-Addon Rev. A02.02 as an apparatus and THF as the eluent. Thermogravimetric (TG) analysis was carried out on a NETZSCH TG 209 F1 Iris instrument at a heating rate of 10 °C/min under a nitrogen atmosphere. Differential scanning calorimetric (DSC) measurements were carried out using a NETZSCH DSC 204 F1 Phoenix instrument at a heating rate of 10 °C /min under nitrogen atmosphere.

General procedure for one-pot three-component Michael addition reaction

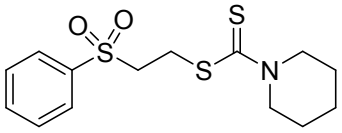
In a test tube equipped with a magnetic stir bar, a vinyl sulfone or sulfoxide (3 mmol) and CS_2 (5 mmol) were added and the reaction temperature was decreased to 0-5 ^{o}C by using an ice bath. To this mixture, an amine (3.3 mmol) was added dropwise via syringe within 5 min. and the reaction temperature was increased to rt and stirring was further continued for 6h. In completion, water (10 mL) was added and the product was extracted with ethyl acetate (3×10 mL). The combined organic phases was dried with Na_2SO_4 and evaporated in a vacuum rotary evaporator to give the crude product. Purifications have been done by treating the crude product with warm hexane (entries 2, 3 and 6; Table 1) or by column chromatography using silica gel and ethyl acetate: hexane gradient (entries 1, 4, 5, 7, 8 and 9; Table 1). It is notable that for divinyl sulfone (3 mmol), 10 mmol CS_2 and 6.5 mmol of an amine were applied.

General procedure for the synthesis of polymers P1-P8

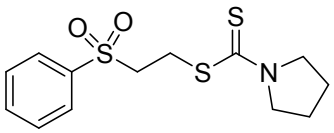
In a 50 mL round bottom flask equipped with a magnetic stir bar, a diamine (2.5 mmol) was dissolved in a 1:1 mixture of ethanol and DMF (20 mL). Then, CS_2 (8 mmol) was gradually added and stirred for 1h at room temperature. The reaction temperature was decreased to 5 ˚C and divinyl sulfone (2.5 mmol) was added dropwise, and stirred for 8h at the same temperature. Then stirring was continued for 48h at room temperature . The reaction mixture was transferred to a 250 mL round bottom flask containing 150 mL of distilled water and stirring was continued for 12h to achieve a precipitate. The precipitate was filtered and washed several times with water. The precipitate was collected and treated with methanol at reflux temperature for 12h to remove the unreacted starting materials. Finally, the precipitate was dried at 50 °C for 24h to afford the polymer with the yield reported in Scheme 2.



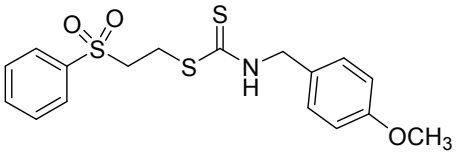
2-(Phenylsulfinyl)ethyl pyrrolidine-1-carbodithioate (Table 1, entry 1). Purification has been done by column chromatography using silica gel and ethyl acetate and hexane gradient (3:7 to 7:3); light brown solid; Yield: 0.67 g (75%); mp 74.5-77 ^{o}C; IR (KBr) *v* 1649, 1432, 1368, 1162, 1006, 736, 689 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88 (2H, m), 2.0 (2H, m), 3.12 (1H, m), 3.24 (1H, m), 3.45-3.58 (4H, m), 3.80 (2H, t, *J*= 7.0 Hz), 7.42-7.48 (3H, m), 7.56-7.67 (2H, m) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 24.2, 26.0, 28.3, 50.6, 55.1, 55.9, 124.0, 129.2, 131.0, 143.0, 191.0 ppm; HRMS (ES^{+}) calcd. for $C_{13}H_{18}NOS_3$ $[M+H]^+$ 300.0551, found 300.0562.



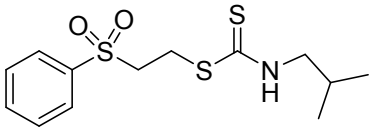
2-(Phenylsulfonyl)ethyl piperidine-1-carbodithioate (Table 1, entry 2). Purification has been done by washing the crude product with hexane; Yellow solid; Yield 0.859 g (87%); mp 110-112 ^{o}C; IR (KBr) *v* 1478, 1447, 1316, 1146, 1008 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.65-1.73 (6H, m), 3.54-3.61 (4H, m), 3.81 (2H, brs), 4.22 (2H, brs), 7.60-7.73 (3H, m), 7.98 (2H, m) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 24.1, 25.3, 26.0, 29.0, 51.4, 53.0, 55.3, 128.3, 129.3, 133.9, 138.6, 193.1 ppm; HRMS (ES^{+}) calcd. for $C_{14}H_{20}NO_2S_3$ $[M+H]^+$ 330.0656, found 330.0646.



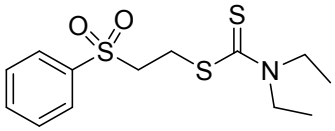
2-(Phenylsulfonyl)ethyl pyrrolidine-1-carbodithioate (Table 1, entry 3). Purification has been done by washing the crude product with hexane; Cream solid; Yield 0.850 g (90%); mp 102.5-104.5 ^{o}C; IR (KBr) ν 1464, 1445, 1307, 1149, 1012 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94-2.10 (4H, m), 3.52-3.60 (6H, m), 3.84 (2H, t, J= 6.8 Hz), 7.60-7.72 (3H, m), 7.98 (2H, m) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 24.2, 26.0, 28.5, 50.6, 55.1, 55.3, 128.3, 129.3, 133.9, 138.6, 190.4 ppm; HRMS (ES^{+}) calcd. for $C_{13}H_{18}NO_2S_3$ $[M+H]^{+}$ 316.0500, found 316.0505.



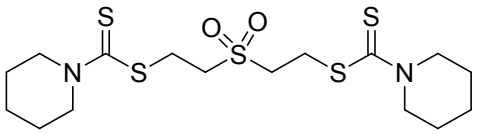
2-(Phenylsulfonyl)ethyl 4-methoxybenzylcarbamodithioate (Table 1, entry 4). Purification has been done by column chromatography using silica gel and ethyl acetate and hexane gradient (3:7 to 7:3); Yellow viscous oil; Yield 0.971 g (85%); IR (KBr) ν 3265, 1512, 1396, 1306, 1242, 1145, 1071, 1023, 910 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.49-3.59 (4H, m), 3.81 (3H, s), 4.76 (2H, d, J= 5.1 Hz), 6.83-6.91 (2H, m), 7.17-7.46 (4H, m), 7.59-7.73 (3H, m), 7.94 (2H, m) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 27.8, 50.9, 55.0, 55.3, 114.2, 127.8, 129.0, 129.4, 129.7, 134.0, 138.4, 159.4, 195.2 ppm; HRMS (ES^{+}) calcd. for $C_{17}H_{20}NO_3S_3$ $[M+H]^{+}$ 382.0605, found 382.0596.



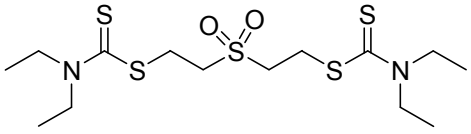
2-(Phenylsulfonyl)ethyl isobutylcarbamodithioate (Table 1, entry 5). Purification has been done by column chromatography using silica gel and ethyl acetate and hexane gradient (3:7 to 7:3); Yellow viscous oil; Yield 0.78 g (82%); IR (KBr) ν 3296, 1510, 1307, 1147, 909, 727 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.92 (6H, m), 1.94 (1H, m), 3.47-3.60 (6H, m), 7.30 (1H, brs, NH), 7.38-7.72 (3H, m), 7.95 (2H, t , J= 7.8 Hz) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 20.1, 27.6, 28.2, 54.7, 55.6, 128.2, 129.4, 134.1, 138.3, 195.5 ppm; HRMS (ES^{+}) calcd. for $C_{13}H_{20}NO_2S_3$ $[M+H]^{+}$ 318.0656, found 318.0664.



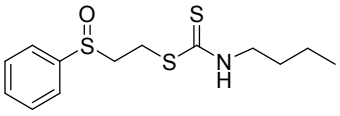
2-(Phenylsulfonyl)ethyl diethylcarbamodithioate (Table 1, entry 6). Purification has been done by washing the crude product with hexane; Yellow solid; Yield 0.761 g (80%); mp 110-112 ^{o}C; IR (KBr) ν 1488, 1444, 1303, 1270, 1153, 1075, 1008, 981, 739 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.24 (6H, m), 3.52-3.60 (4H, m), 3.66 (2H, q, J= 7.1 Hz), 3.95 (2H, q, J= 7.1 Hz), 7.60-7.80 (3H, m), 7.99 (2H, m) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 11.4, 12.4, 29.0, 46.8, 49.6, 55.3, 128.3, 129.3, 133.9, 138.6, 193.1 ppm; HRMS (ES^{+}) calcd. for $C_{13}H_{20}NO_2S_3$ $[M+H]^{+}$ 318.0656, found 318.0650.



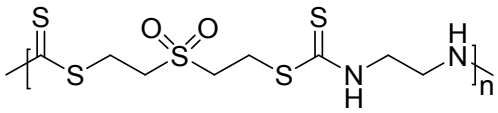
Sulfonylbis(ethane-2,1-diyl) bis(piperidine-1-dithiocarbamate (Table 1, entry 7). Purification has been done by column chromatography using silica gel and ethyl acetate and hexane gradient (1:1 to 3:1);; Yellow solid; Yield 0.990 g (75%); mp 154-157 ^{o}C; IR (KBr) ν 1477, 1432, 1320, 1224, 1111, 1007, 979 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.70-1.75 (12H, m), 3.57-3.60 (4H, m), 3.74-3.77 (4H, m), 3.88 (4H, brs), 4.29 (4H, brs) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 24.2, 25.4, 26.0, 28.9, 51.5, 52.9, 53.1, 193.2 ppm; HRMS (ES^{+}) calcd. for $C_{16}H_{29}N_2O_2S_5$ $[M+H]^{+}$ 441.0833, found 441.0834.



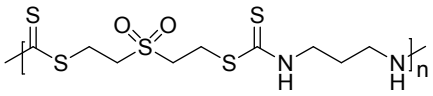
Sulfonylbis(ethane-2,1-diyl) bis(*N*,*N*-diethyl dithiocarbamate (Table 1, entry 8). Purification has been done by column chromatography using silica gel and ethyl acetate and hexane gradient (1:1 to 3:1);; Yellow solid; Yield 0.874 g (70%); mp 71-74 ^{o}C; IR (KBr) ν 1493, 1418, 1267, 1199, 1141, 1113, 979, 915 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.19-1.24 (12H, m), 3.47-3.50 (4H, m), 3.63-3.67 (8H, m), 3.94 (4H, q, J= 7.1 Hz) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 11.5, 12.5, 28.8, 46.9, 49.7, 52.8, 193.2 ppm; HRMS (ES^{+}) calcd. for $C_{14}H_{28}NaN_2O_2S_5$ $[M+Na]^{+}$ 439.0652, found 439.0646.



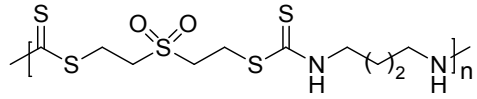
2-(Phenylsulfinyl)ethyl butylcarbamodithioate (Table 1, entry 9). Purification has been done by column chromatography using silica gel and ethyl acetate and hexane gradient (1:1 to 3:1);; Light brown solid; Yield 0.704 g (78%); mp 58-60 ^{o}C; IR (KBr) *v* 3178, 1538, 1402, 1387, 1333, 1028, 915 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.96 (3H, t, *J*= 7.4 Hz), 1.40 (2H, m), 1.65 (2H, m), 3.30-3.75 (6H, m), 7.52-7.72 (6H, m) ppm; ^{13}C NMR (125 MHz; $CDCl_3$) δ 13.5, 19.9, 27.2, 30.2, 47.3, 56.1, 124.0, 129.3, 131.2, 142.6, 195.5 ppm; HRMS (ES^+) calcd. for $C_{13}H_{19}NaNOS_3$ $[M+Na]^+$ 324.0526, found 324.0516.



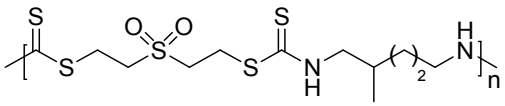
Polymer P1. Cream solid; Yield (77%); IR (KBr) *v* 3259, 1520, 1315, 1116 cm^{-1}; ^{1}H NMR (300 MHz, DMSO -d_6) δ 3.52 (br, 4H), 3.79 (s, 2H), 10.20 (S, 1H) ppm.



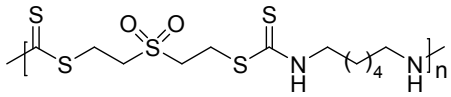
Polymer P2. White solid; Yield (90%); IR (KBr) *v* 3271, 1508, 1314, 1111 cm^{-1}; ^{1}H NMR (300 MHz, DMSO -d_6) δ 1.90 (m, 1H), 3.50– 3.58 (m 6H), 10.14 (s, 1H) ppm.



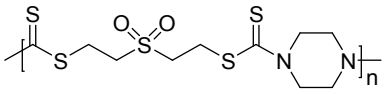
Polymer P3. Cream solid; Yield (65%); IR (KBr) *v* 3262, 1518, 1313, 1114 cm^{-1}; ^{1}H NMR (300 MHz, DMSO -d_6) δ 1.56 (m, 2H), 3.43- 3.55 (m, 6H), 10.13 (s, 1H) ppm.



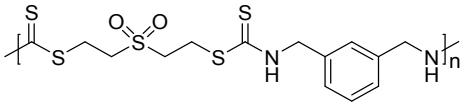
Polymer P4. White solid; Yield (95%); IR (KBr) *v* 3286, 1517, 1388, 1320, 1113 cm^{-1}; ^{1}H NMR (300 MHz, DMSO -d_6) δ 0.84 (d, *J*= 6.5 Hz, 3H), 1.10-1.85(m, 5H), 3.51-3.64 (m, 8H), 10.11-10.13(brs, 2H) ppm.



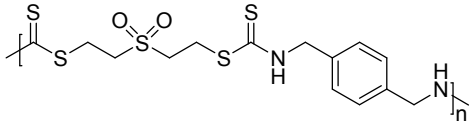
Polymer P5. White solid; Yield (92%); IR (KBr) *v* 3278, 1510, 1388, 1313, 1111 cm^{-1}; ^1H NMR (300 MHz, DMSO -d_6) δ 1.27- 1.35 (m, 2H), 1.54- 1.64 (m, 2H), 3.46- 3.56 (m, 6H), 10.10 (s, 1H) ppm.



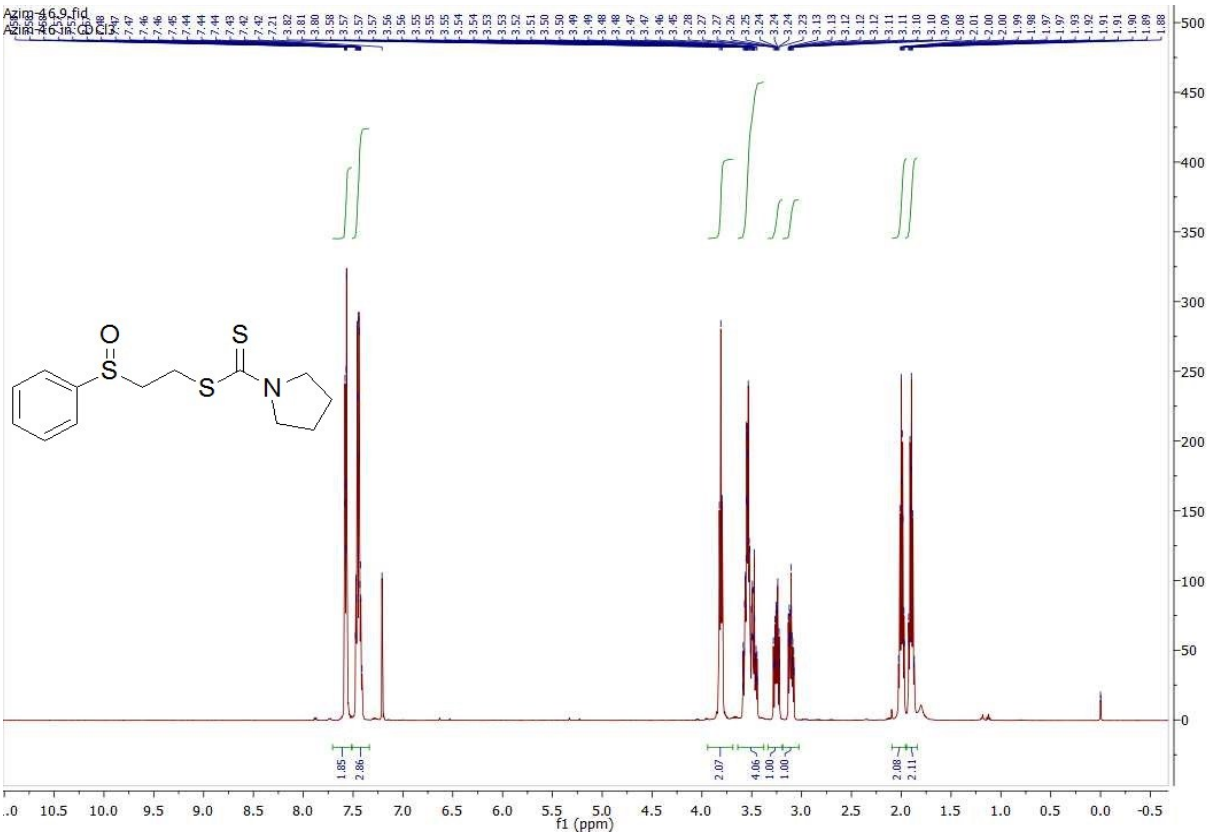
Polymer P6. White solid; Yield (75%); IR (KBr) *v* 1411, 1317, 1113 cm^{-1}; ^1H NMR (300 MHz, DMSO -d_6) δ 3.58- 3.62 (m, 4H), 4.08 (m, 2H), 4.32 (m, 2H) ppm.



Polymer P7. White solid; Yield (94%); IR (KBr) *v* 3288, 1521, 1504, 1319, 1114 cm^{-1}; ^1H NMR (300 MHz, DMSO -d_6) δ 3.53-3.64 (m, 4H), 4.80- 4.88 (m, 2H), 7.12-731 (m, 3H) ppm.



Polymer P8. White solid; Yield (96%); IR (KBr) *v* 3265, 1654, 1514, 1316, 1113 cm^{-1}; ^1H NMR (300 MHz, DMSO -d_6) δ 3.53 (brs, 4H), 4.80 (d, 2H), 7.24 (s, 2H), 10.61 (br, 1H) ppm.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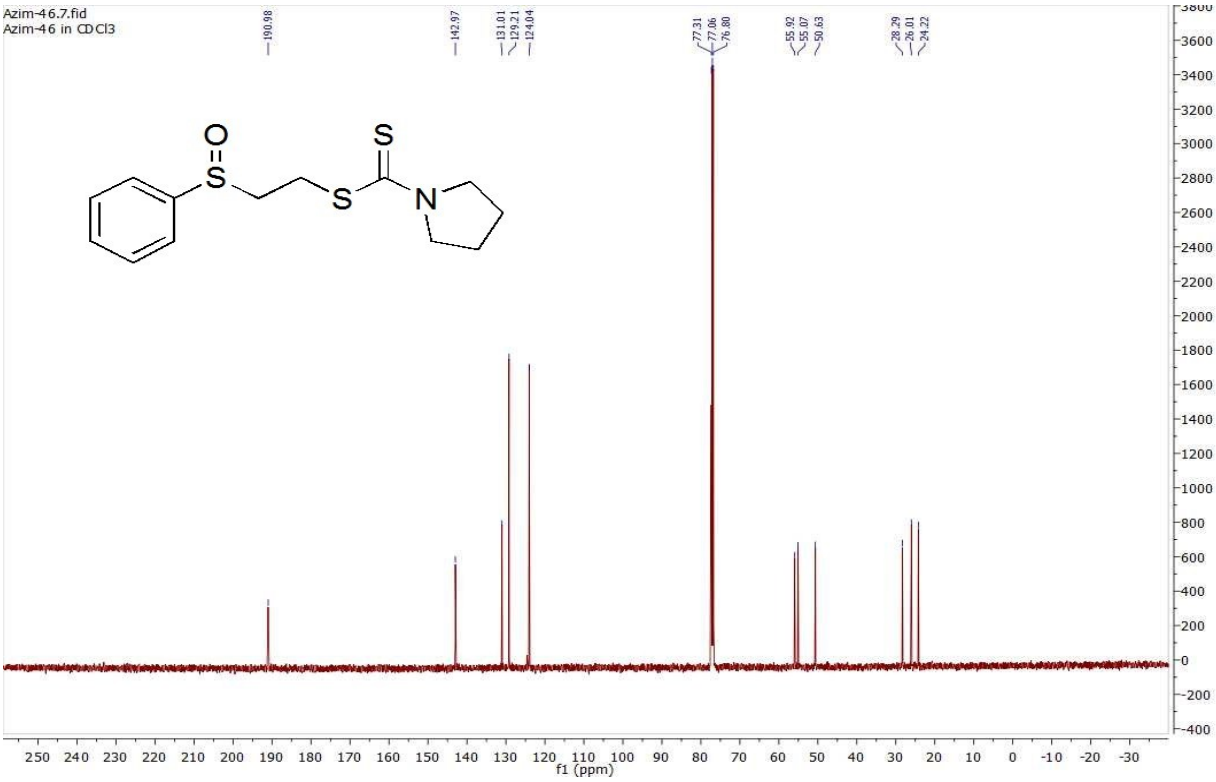
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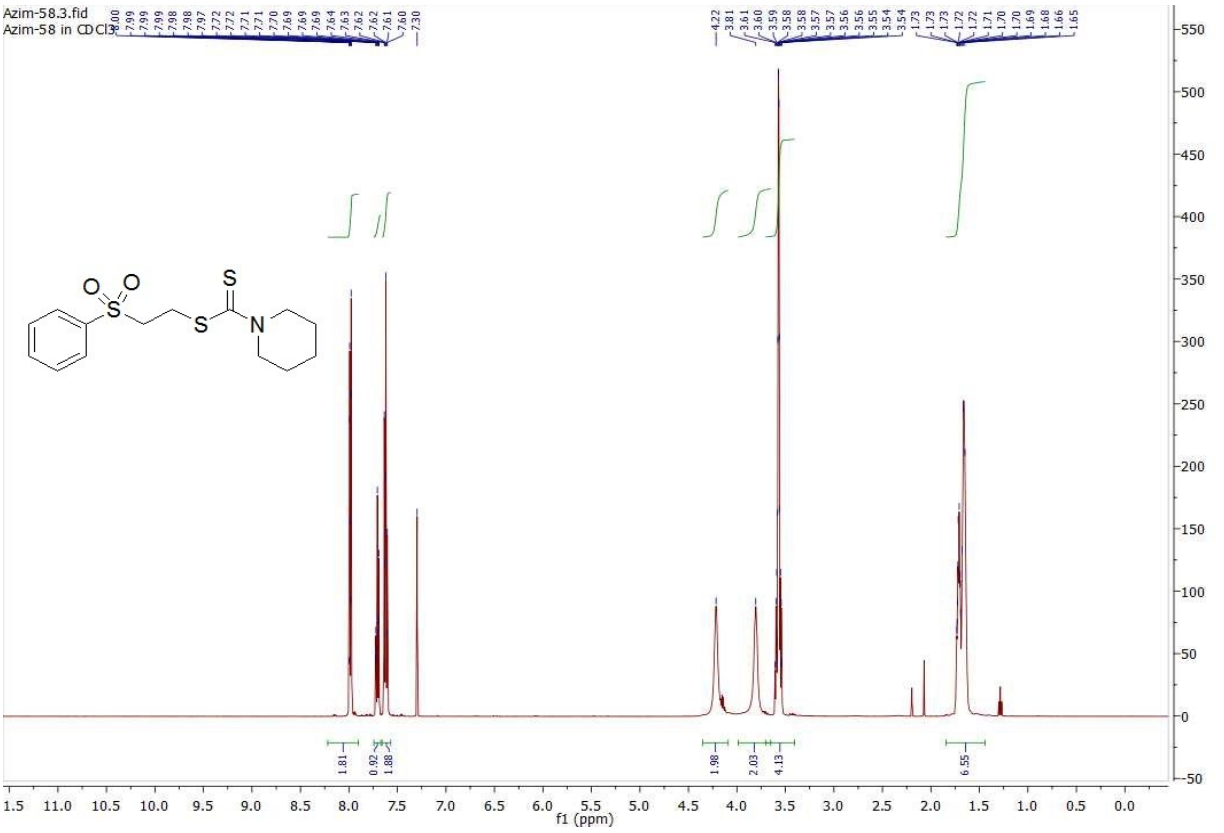
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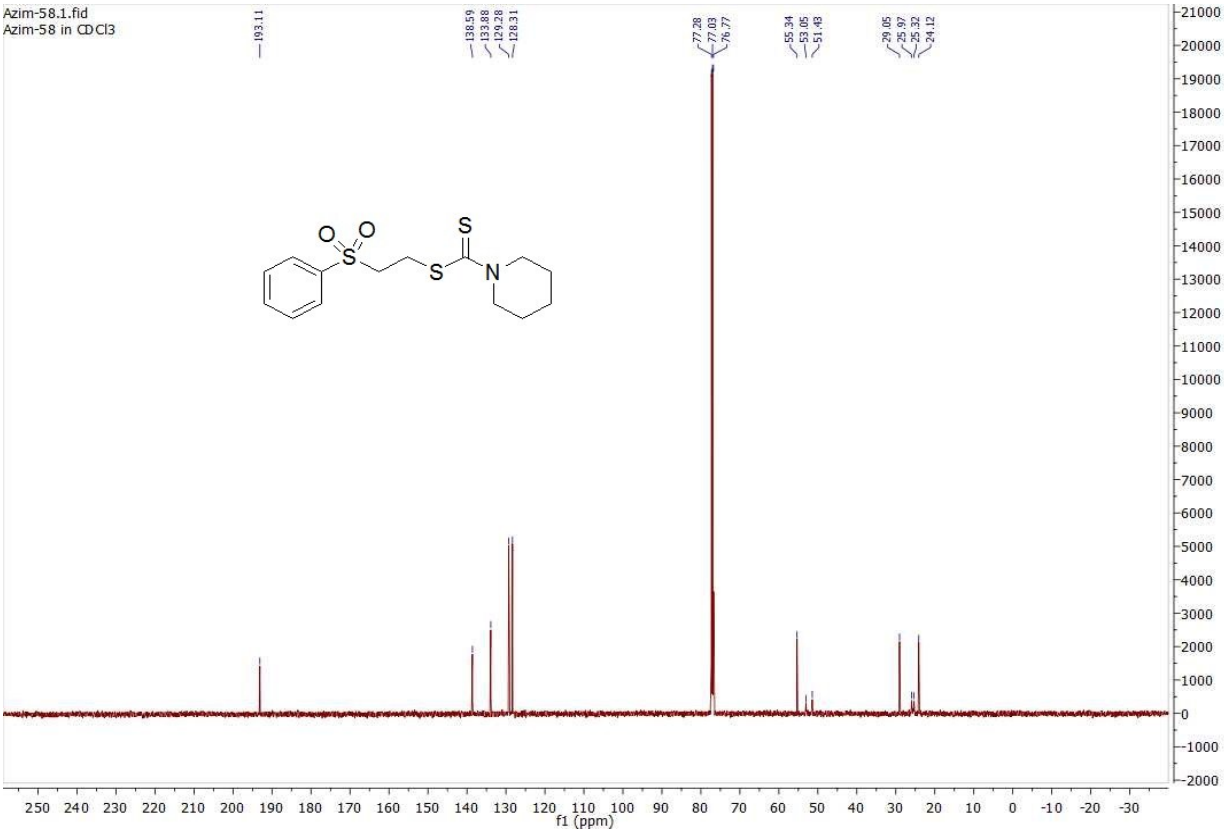
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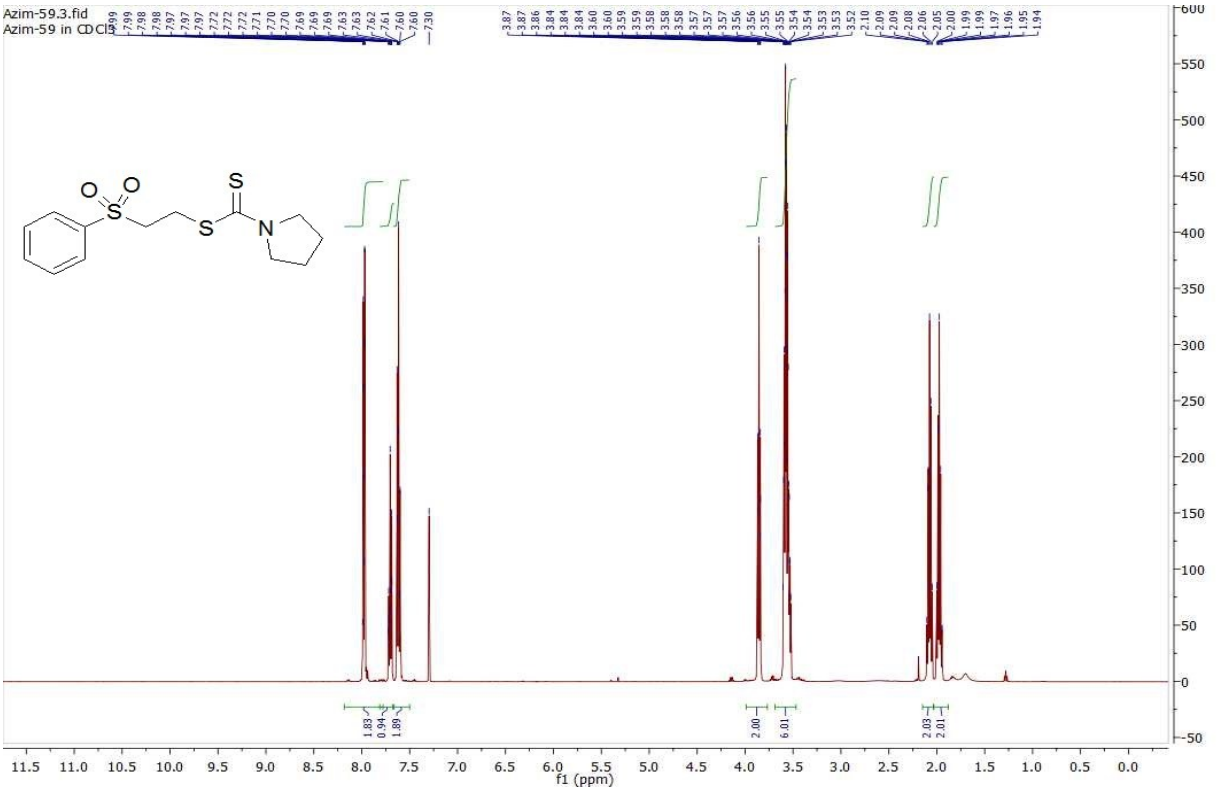
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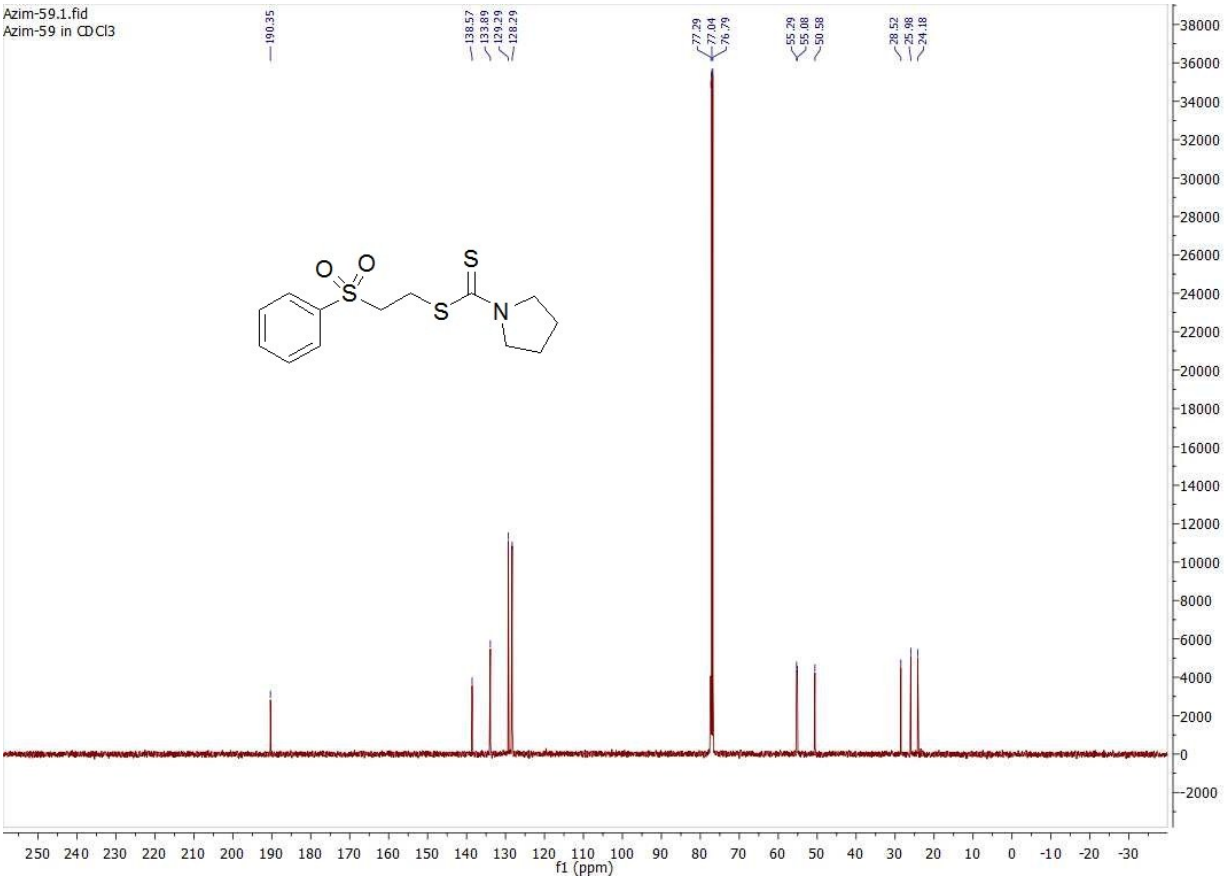
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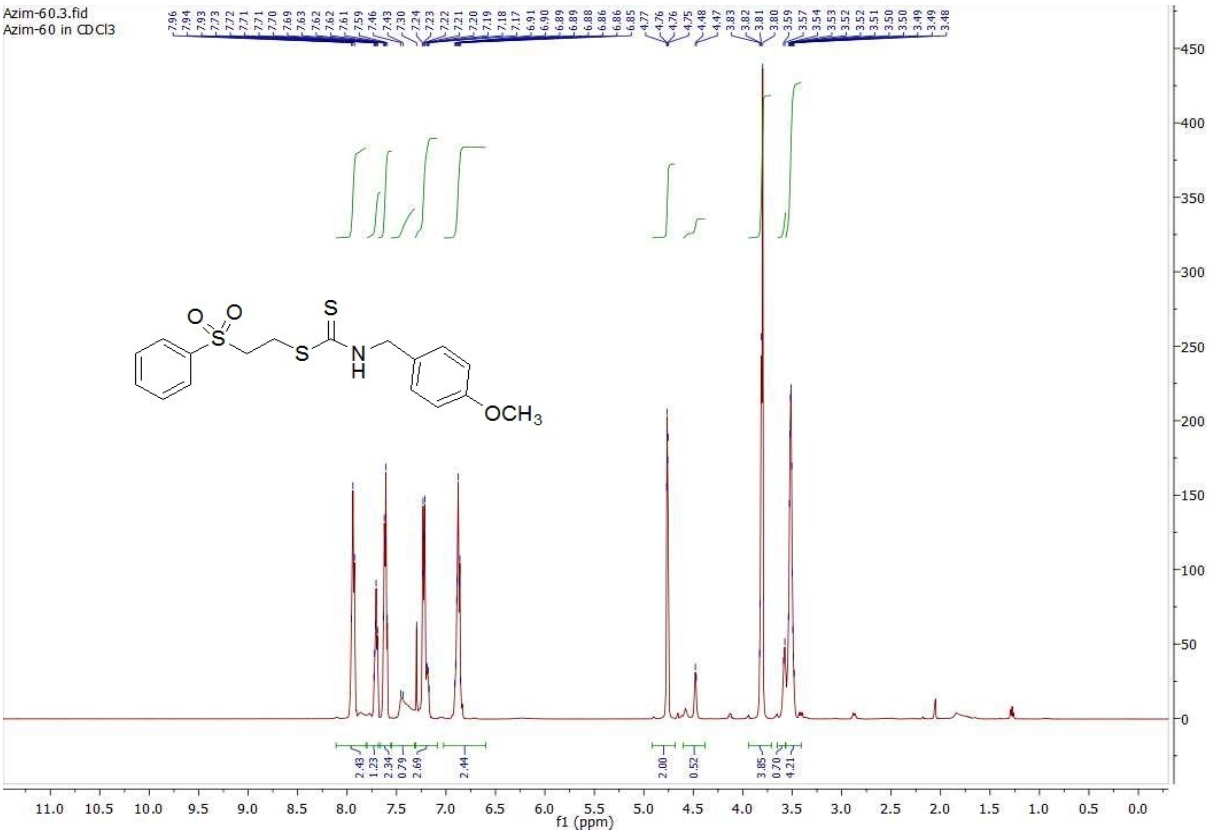
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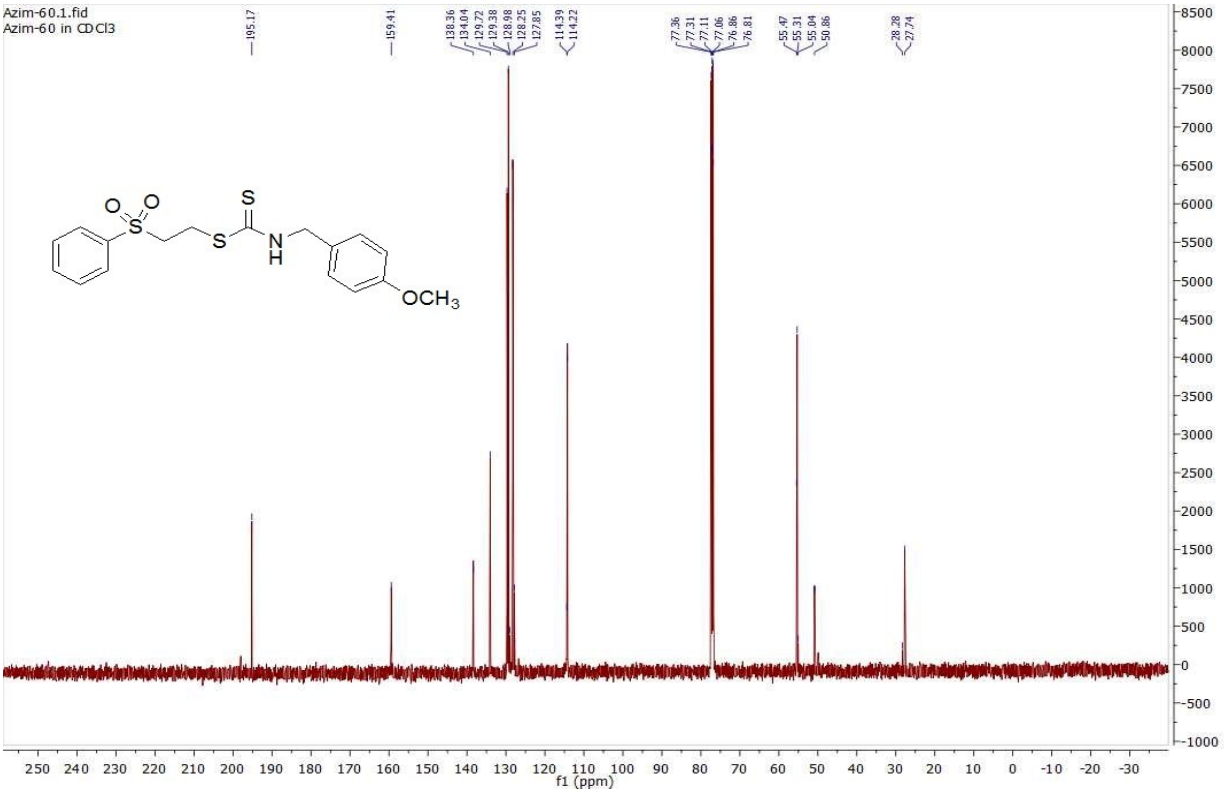
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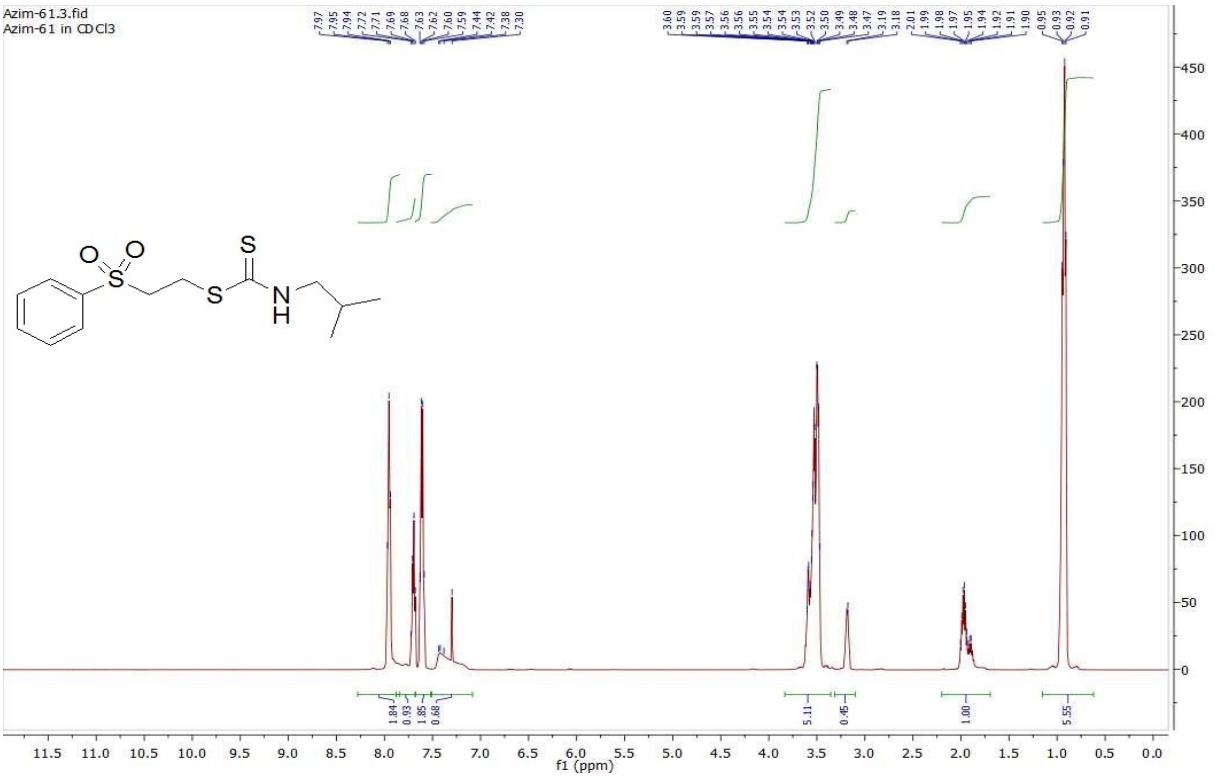
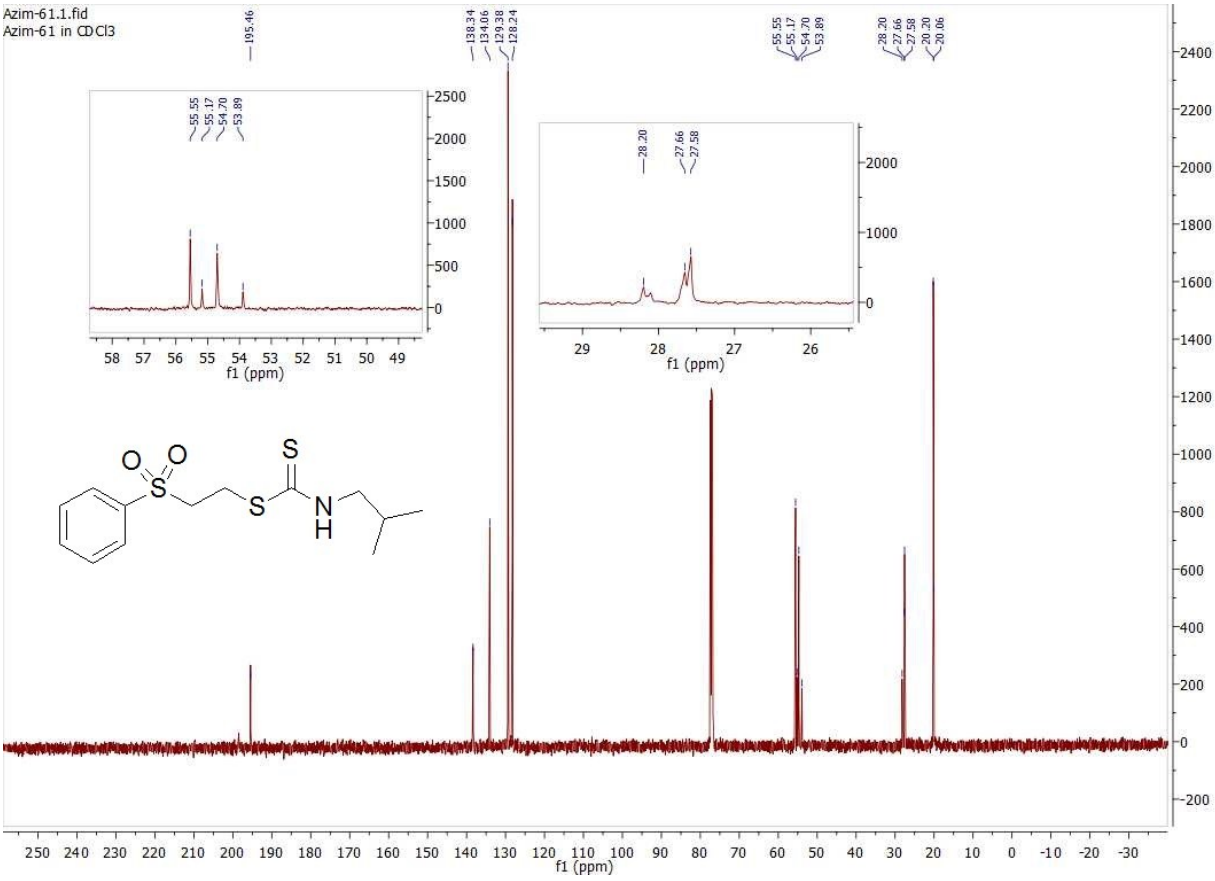
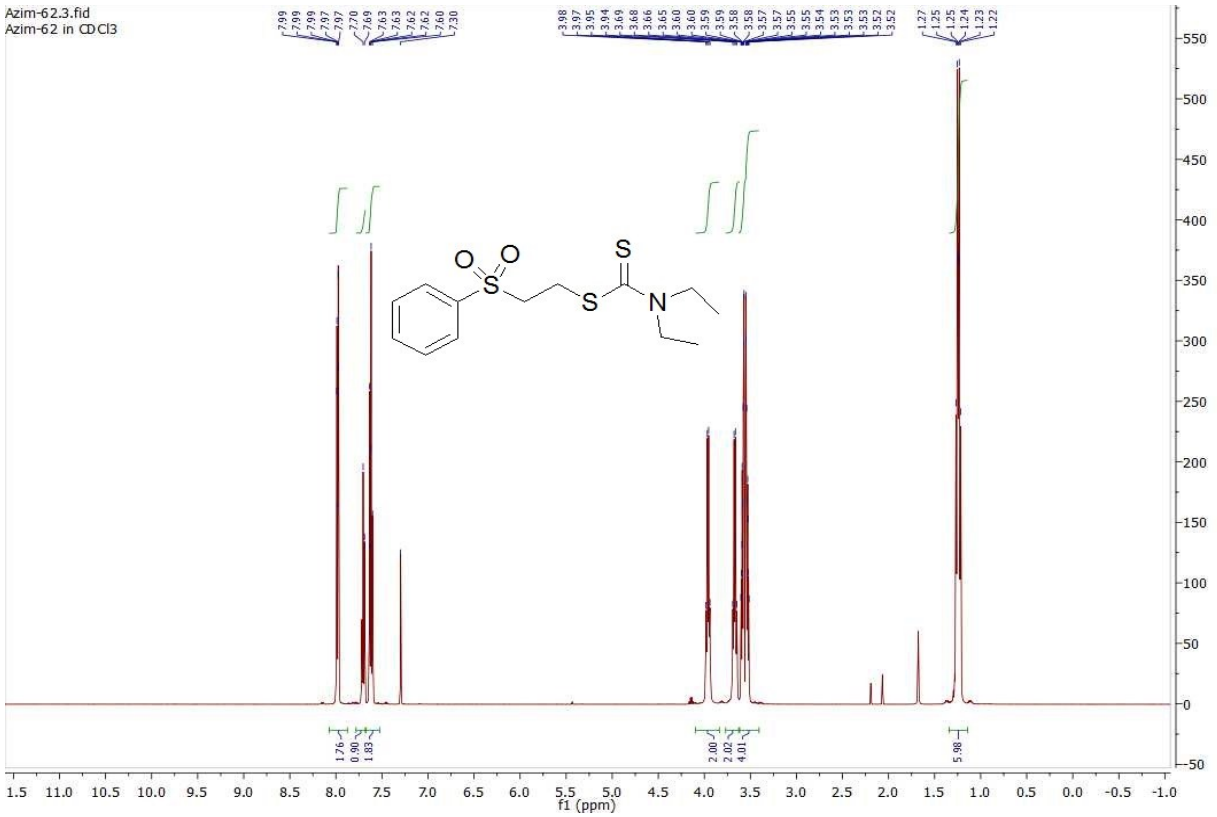
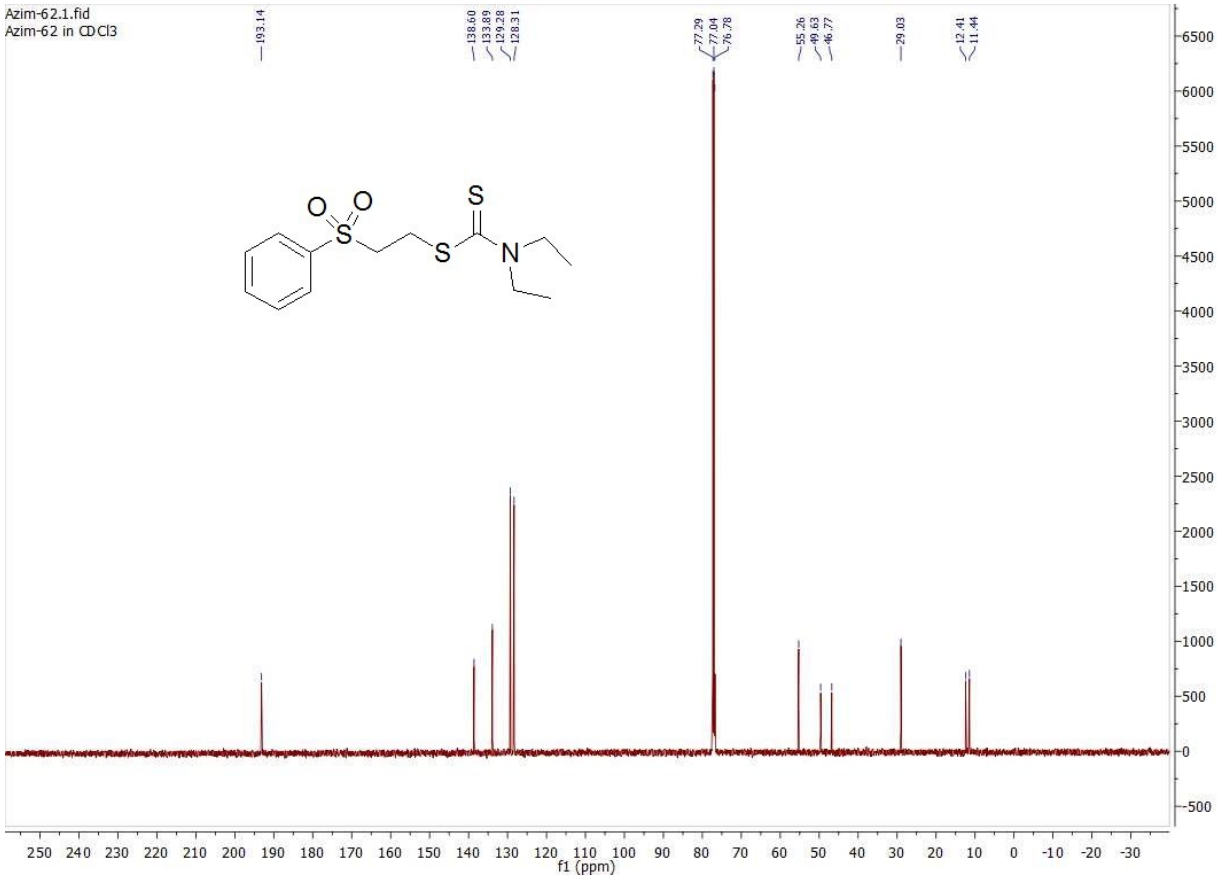
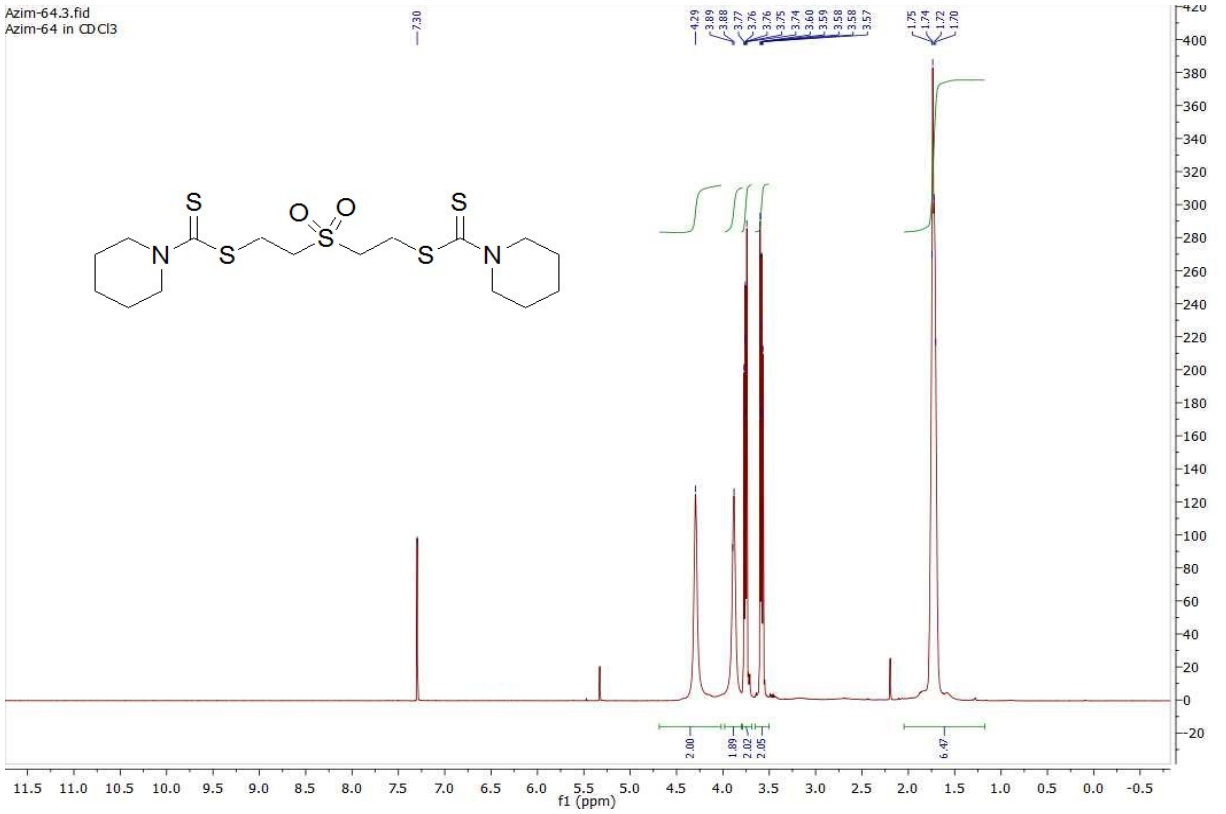
Azim-60 in CDCl3
f1 (ppm)

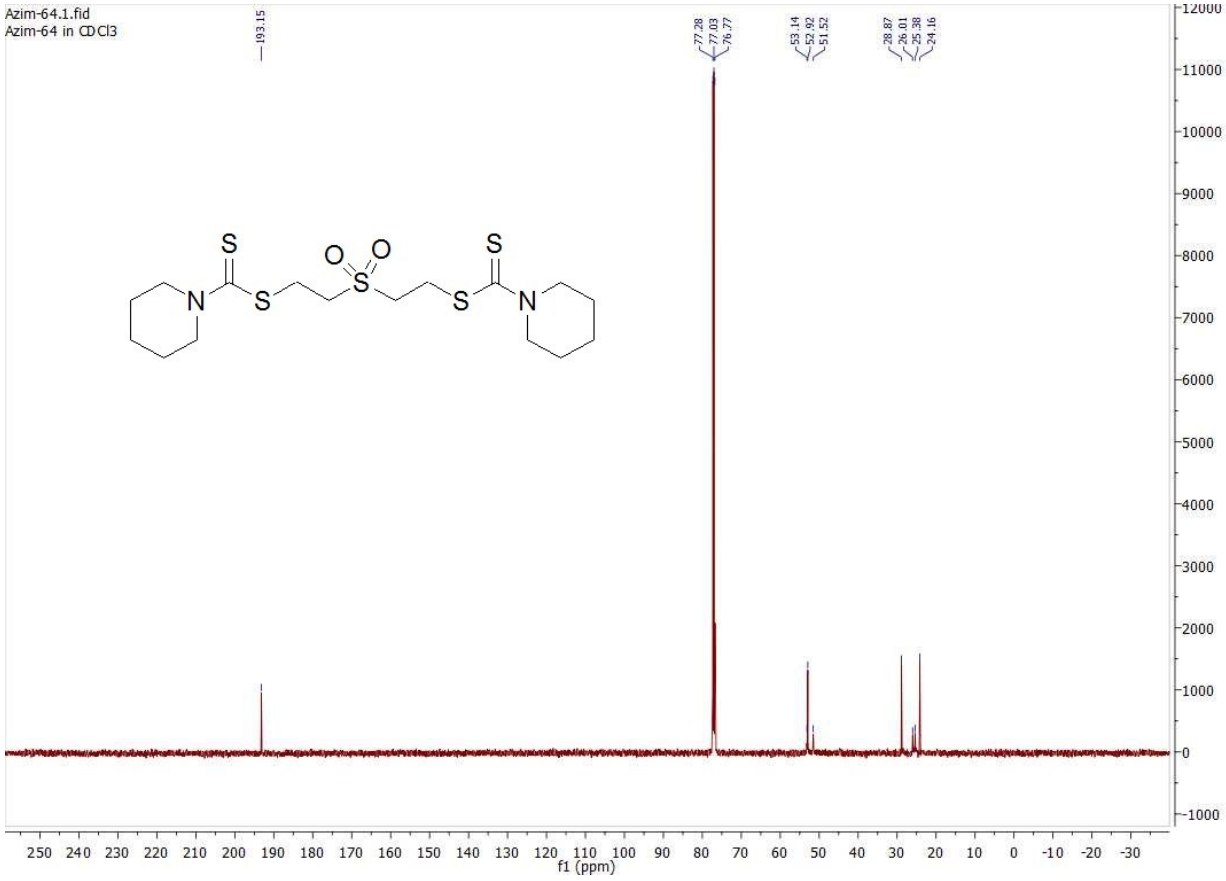

Azim-61.3.fid
Azim-61 in CDCl3
f1 (ppm)

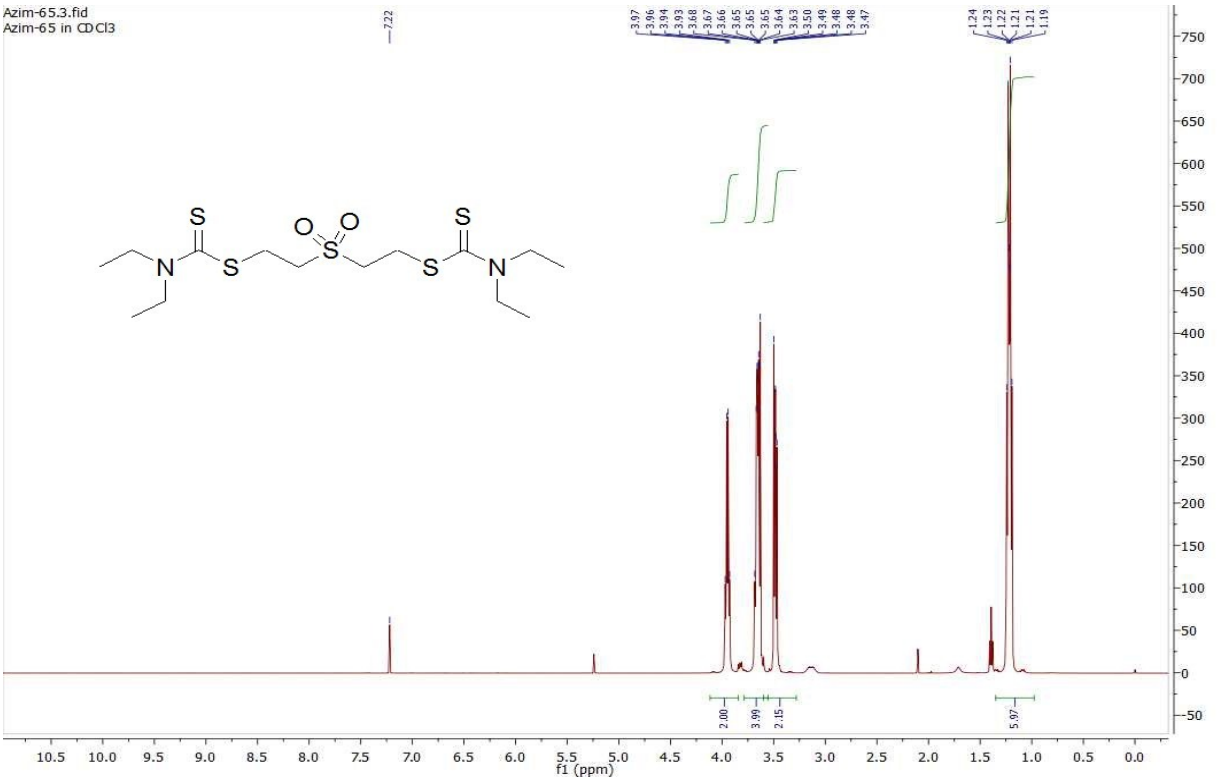

Azim-61.1.fid
Azim-61 in CDCl3
f1 (ppm)

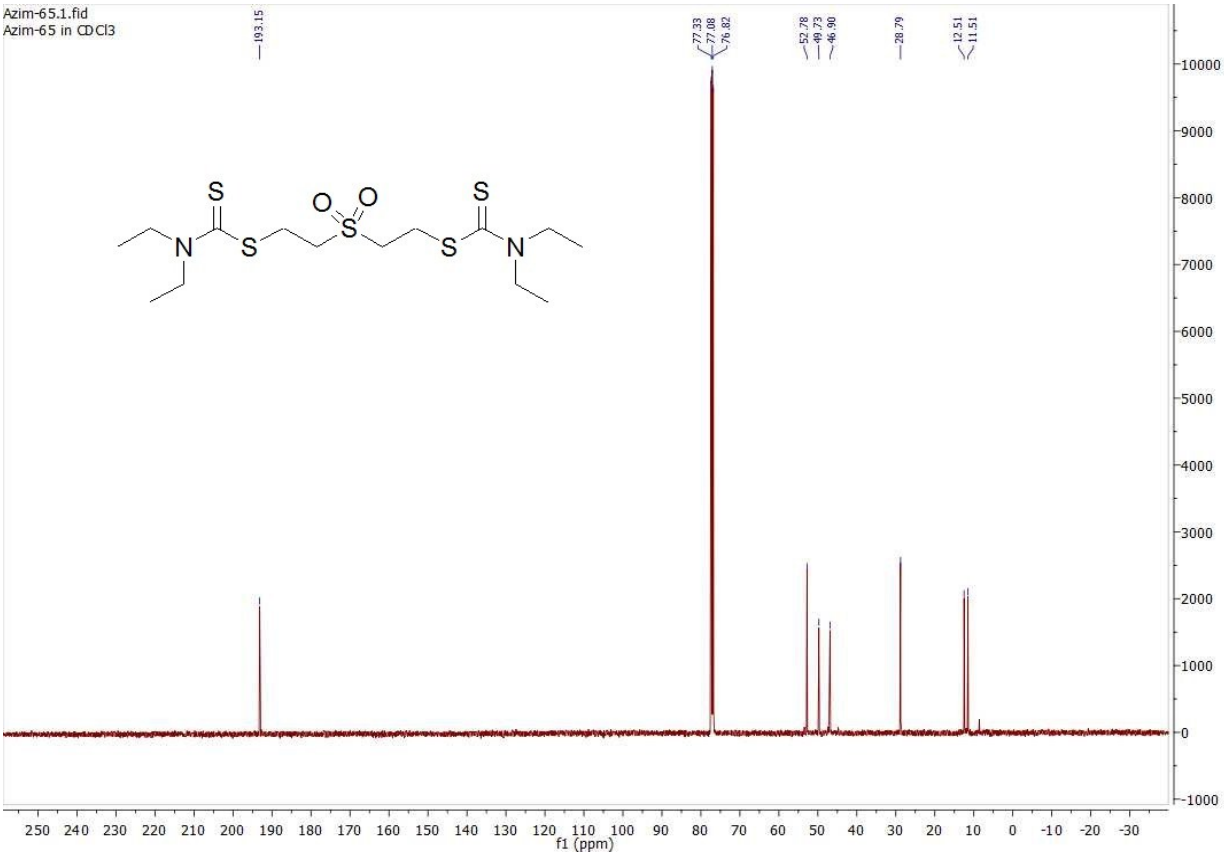

Azim-62.3.fid
Azim-62 in CDCl3
f1 (ppm)

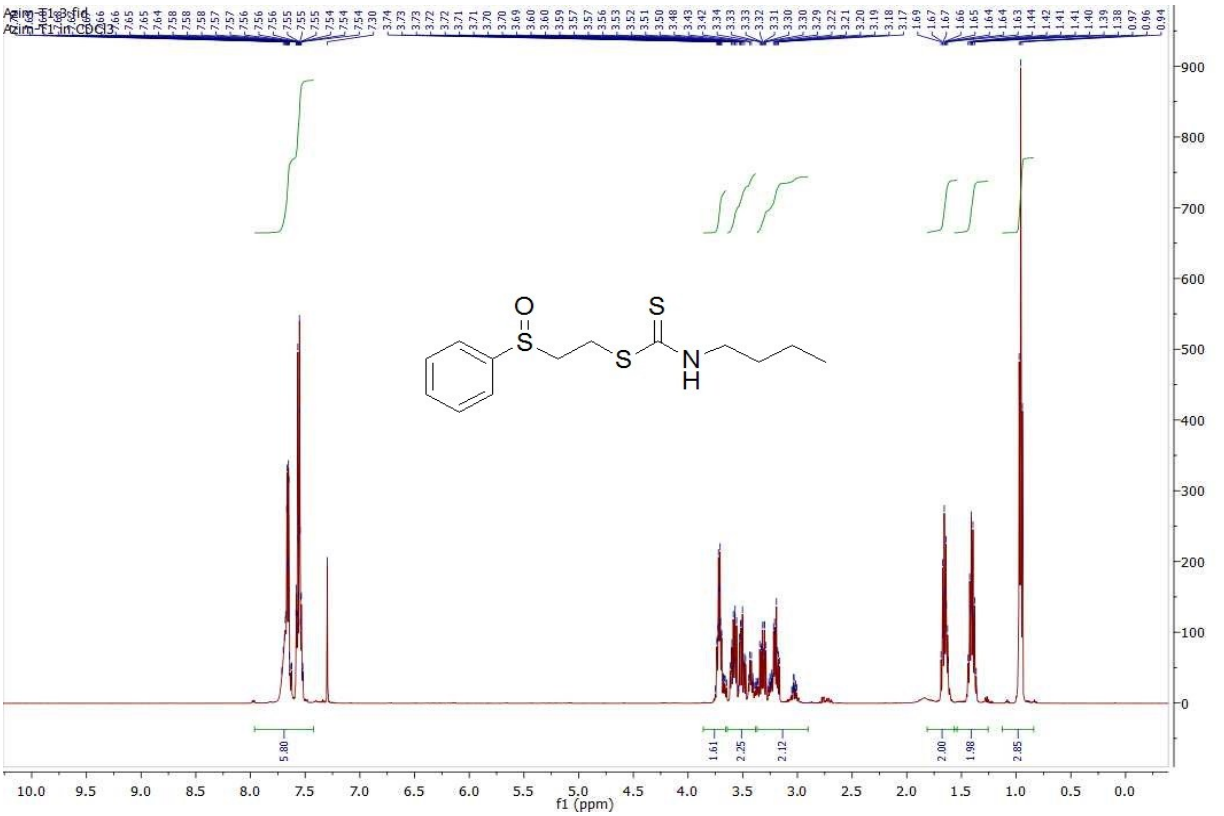

Azim-62.1.fid
Azim-62 in CDCl3
f1 (ppm)

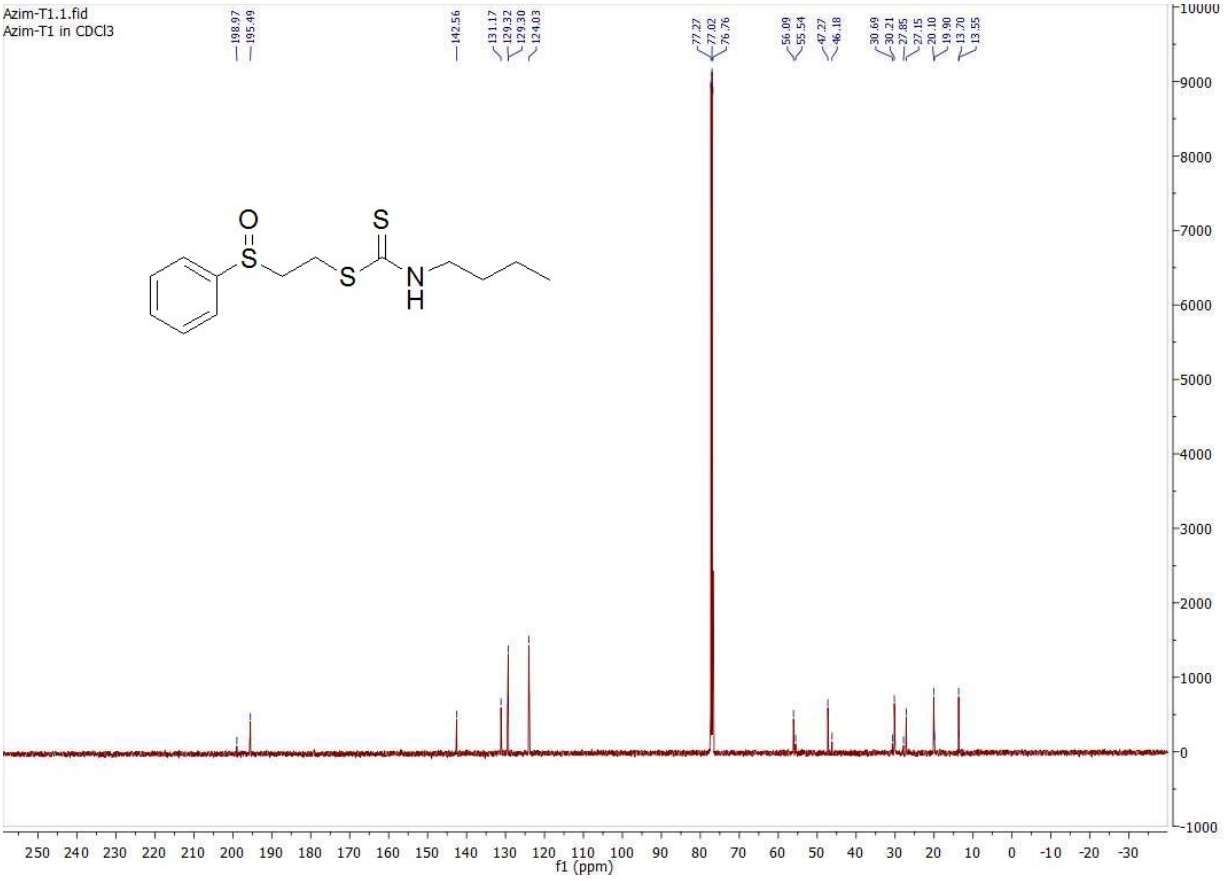

Azim-64.3.fid
Azim-64 in CDCl3
f1 (ppm)


Azim-64.1.fid
Azim-64 in CDCl3
f1 (ppm)

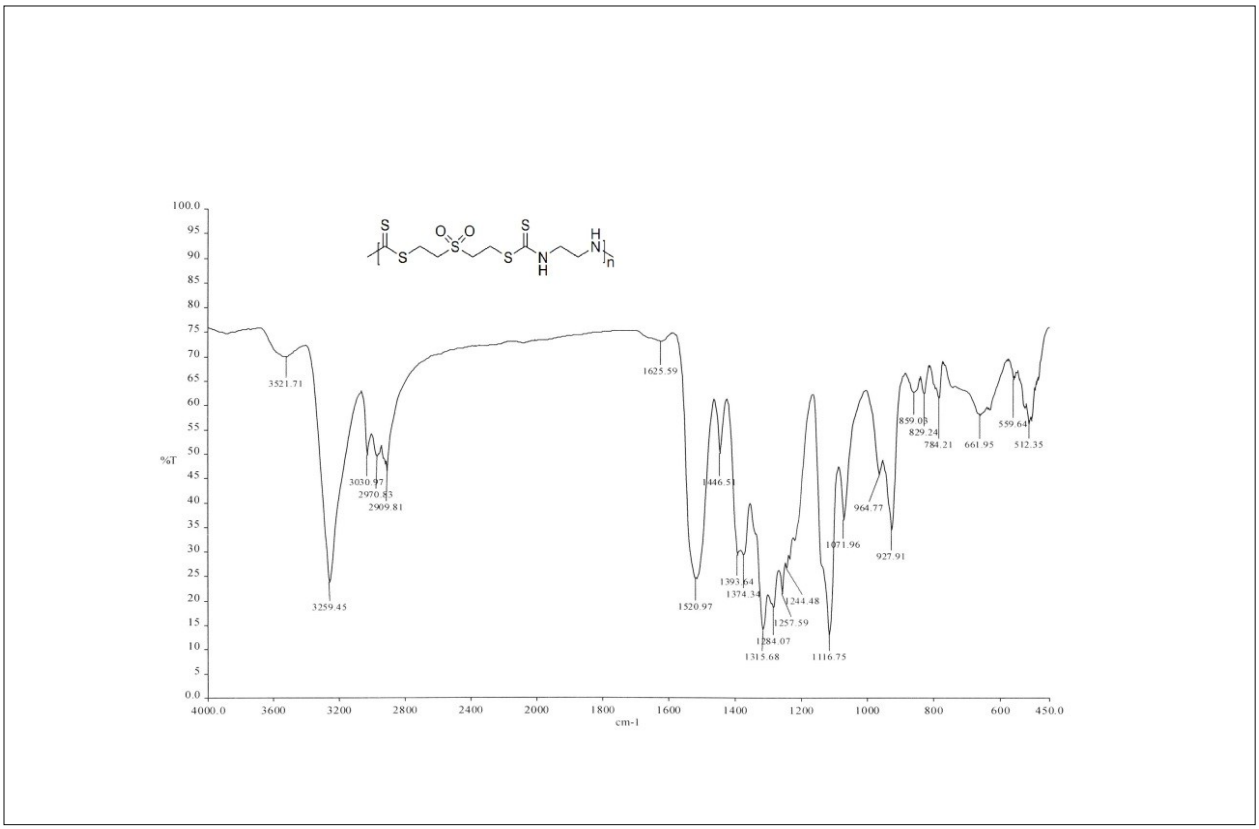

Azim-65.3.fid
Azim-65 in CDCl3
7.22
3.97
3.96
3.94
3.93
3.68
3.67
3.66
3.65
3.65
3.65
3.64
3.63
3.50
3.49
3.48
3.48
3.47
1.24
1.23
1.22
1.21
1.21
1.19
2.00
3.99
2.15
5.97
f1 (ppm)

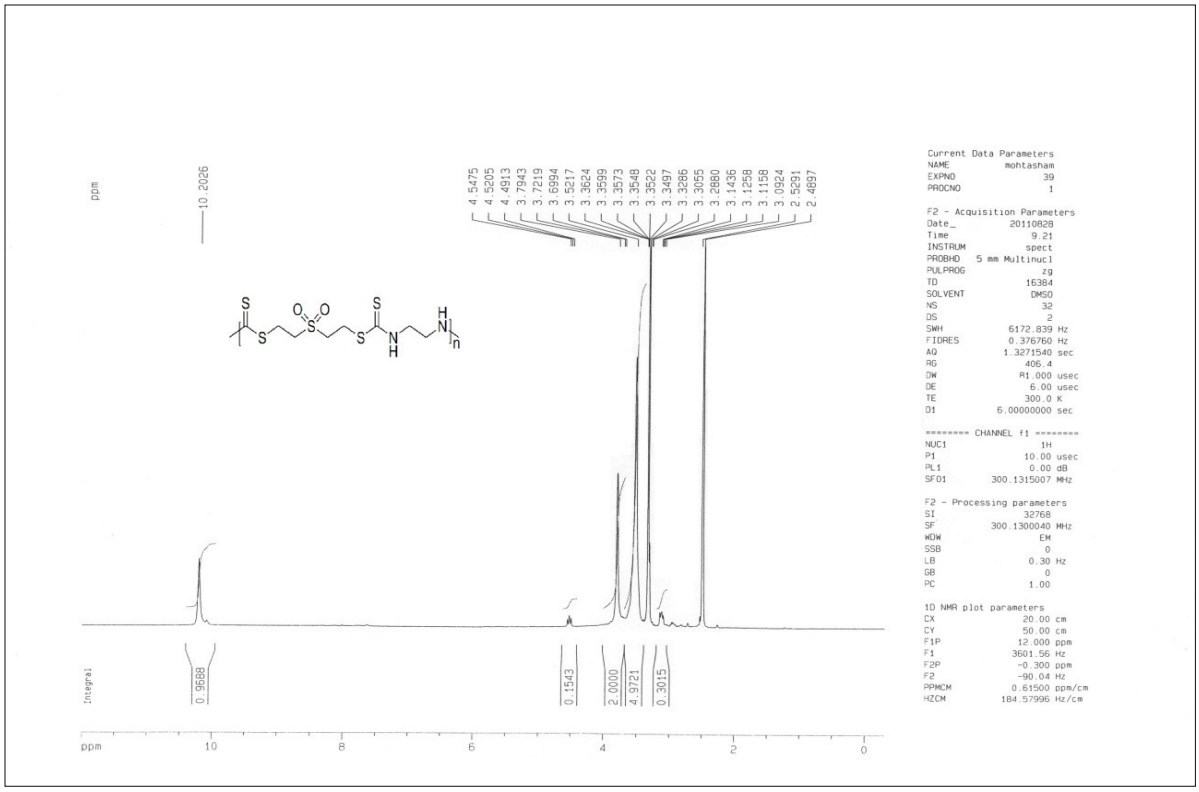

Azim-65.1.fid
Azim-65 in CDCl3
193.15
77.33
77.08
76.82
52.78
49.73
46.90
28.79
12.51
11.51
f1 (ppm)


Azim-T1.1.fid
Azim-T1 in CDCl3
f1 (ppm)

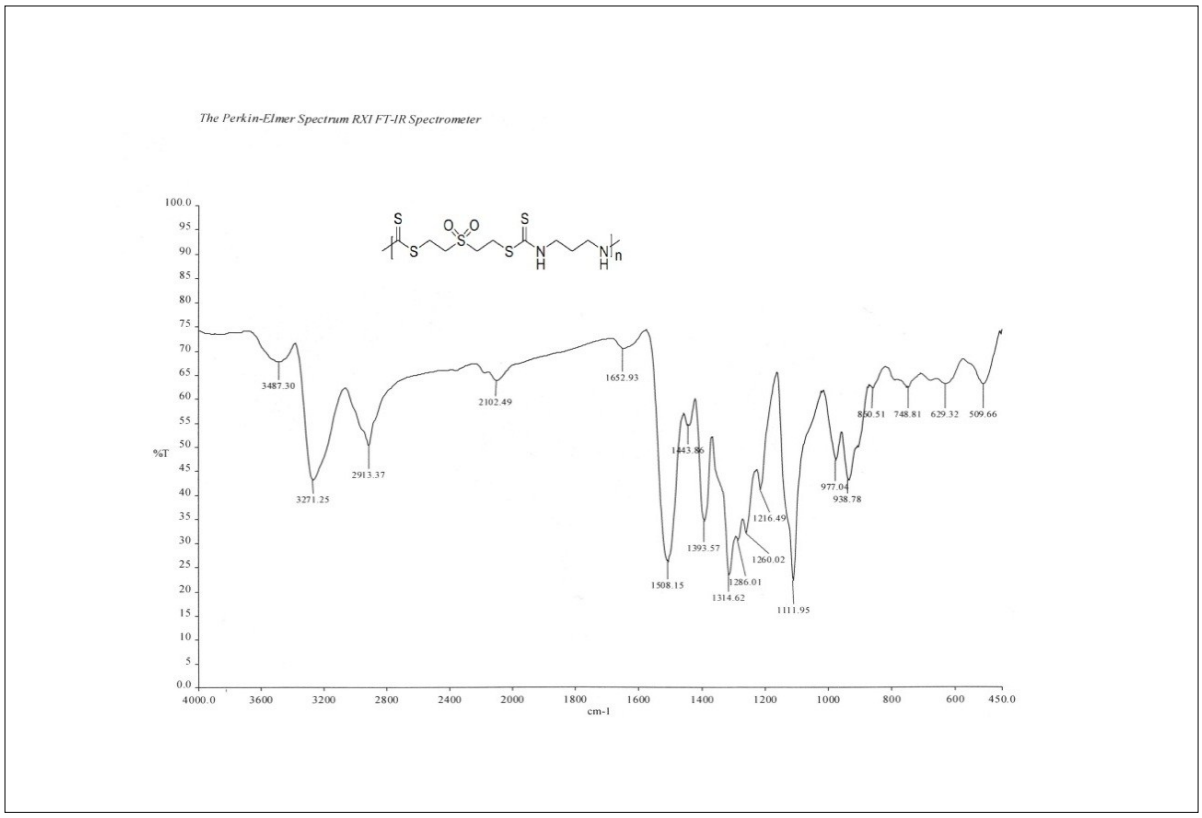

Azim-T1.1.fid
Azim-T1 in CDCl3
198.97
195.49
142.56
131.17
129.32
129.30
124.03
77.27
77.02
76.76
56.09
55.54
47.27
46.18
30.69
30.21
27.85
27.15
20.10
19.90
13.70
13.55
f1 (ppm)

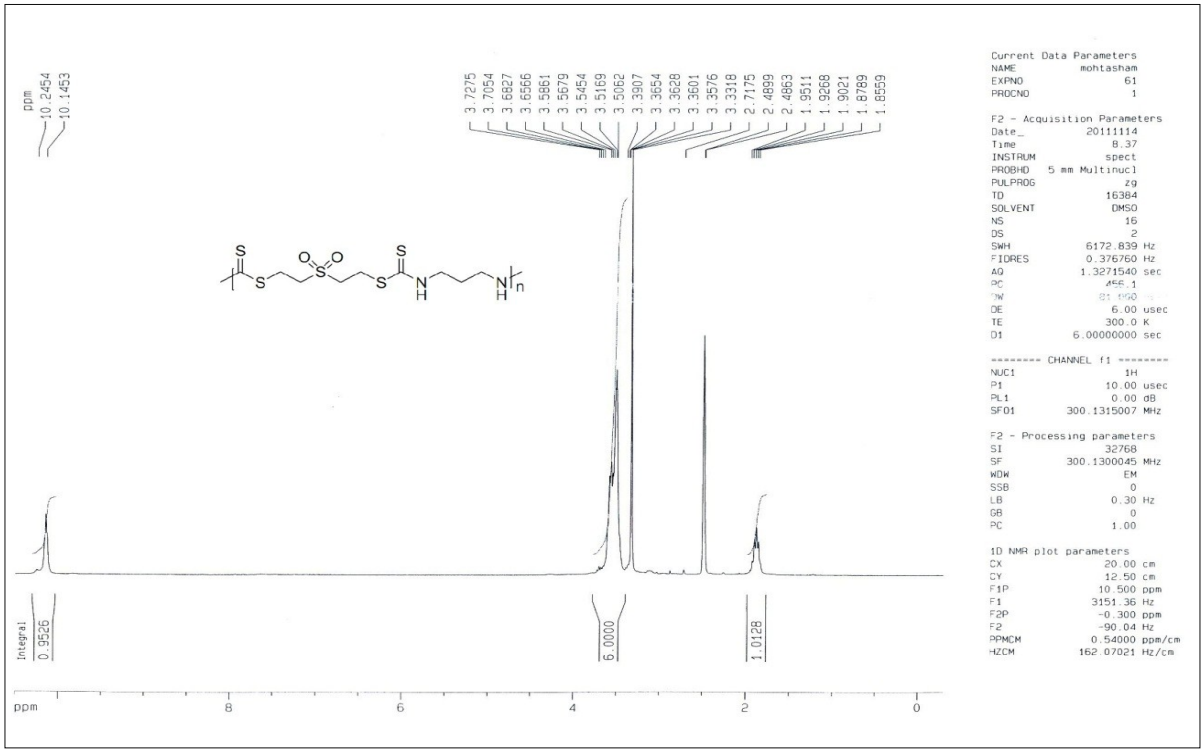
IR and ^{1}H NMR spectra of P1



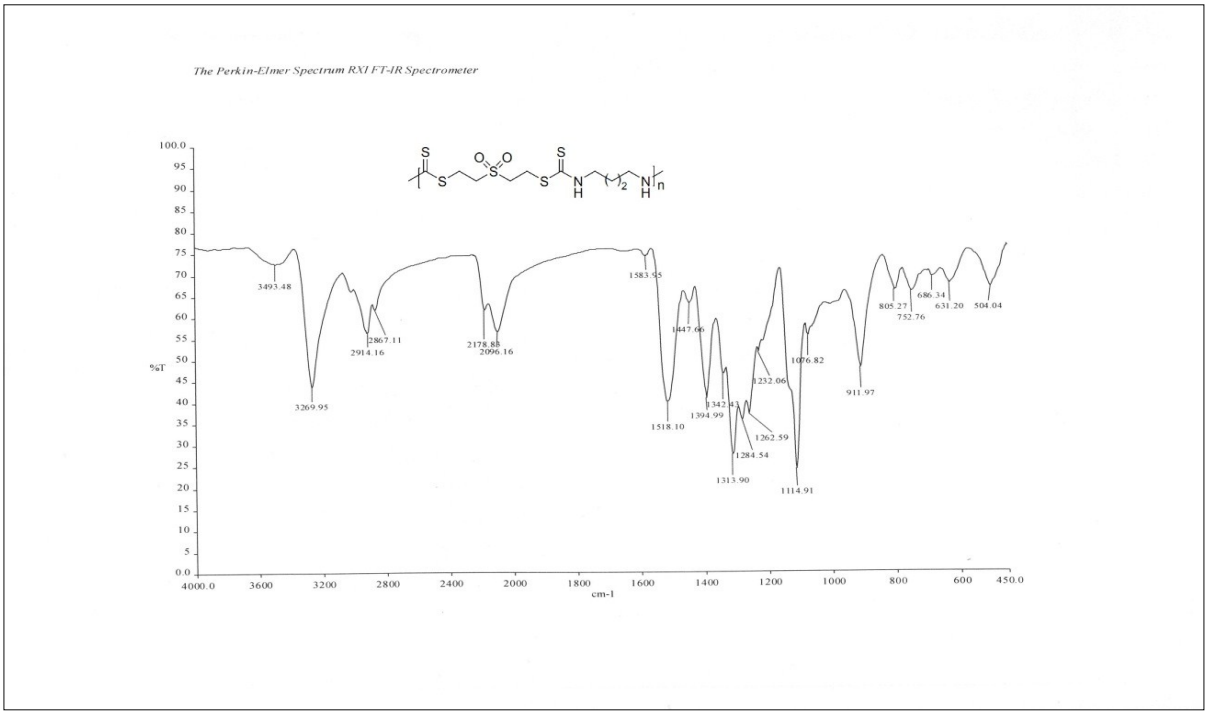


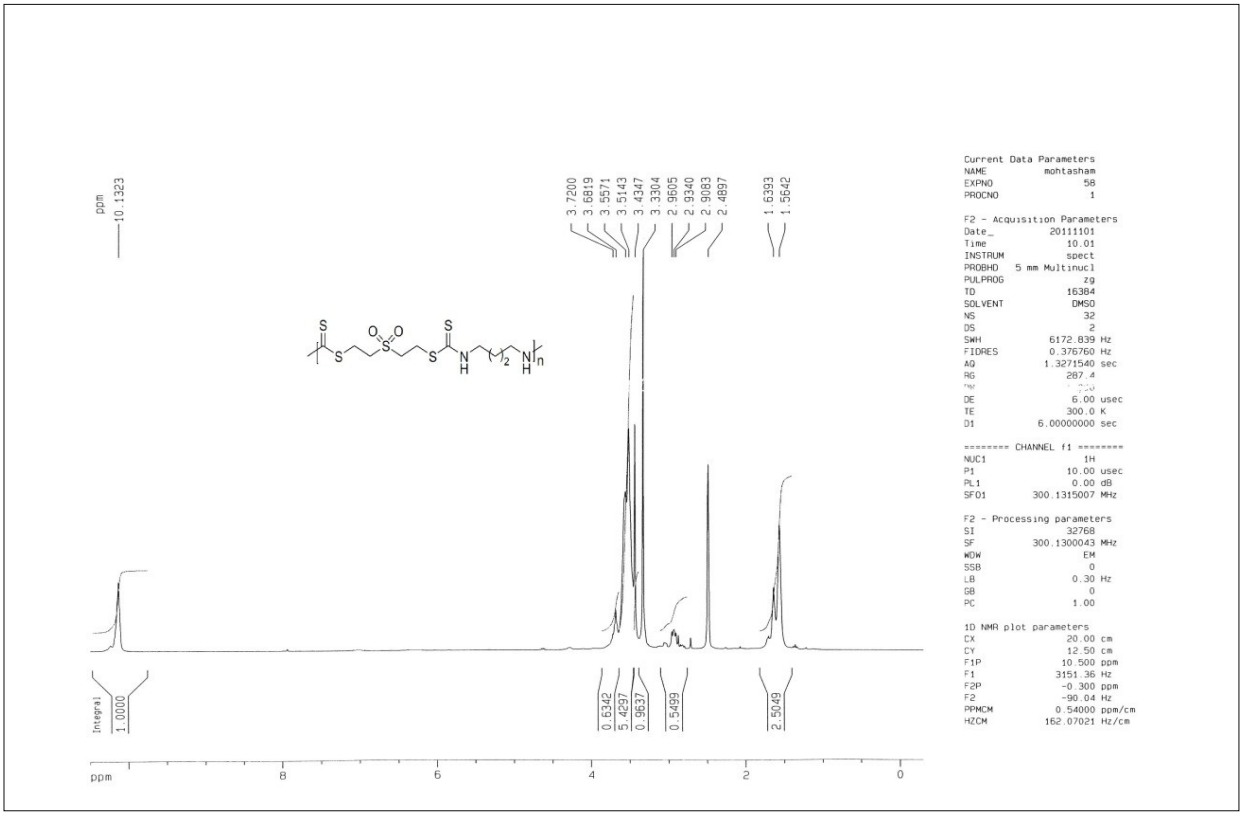
IR and ^{1}H NMR spectra of P2



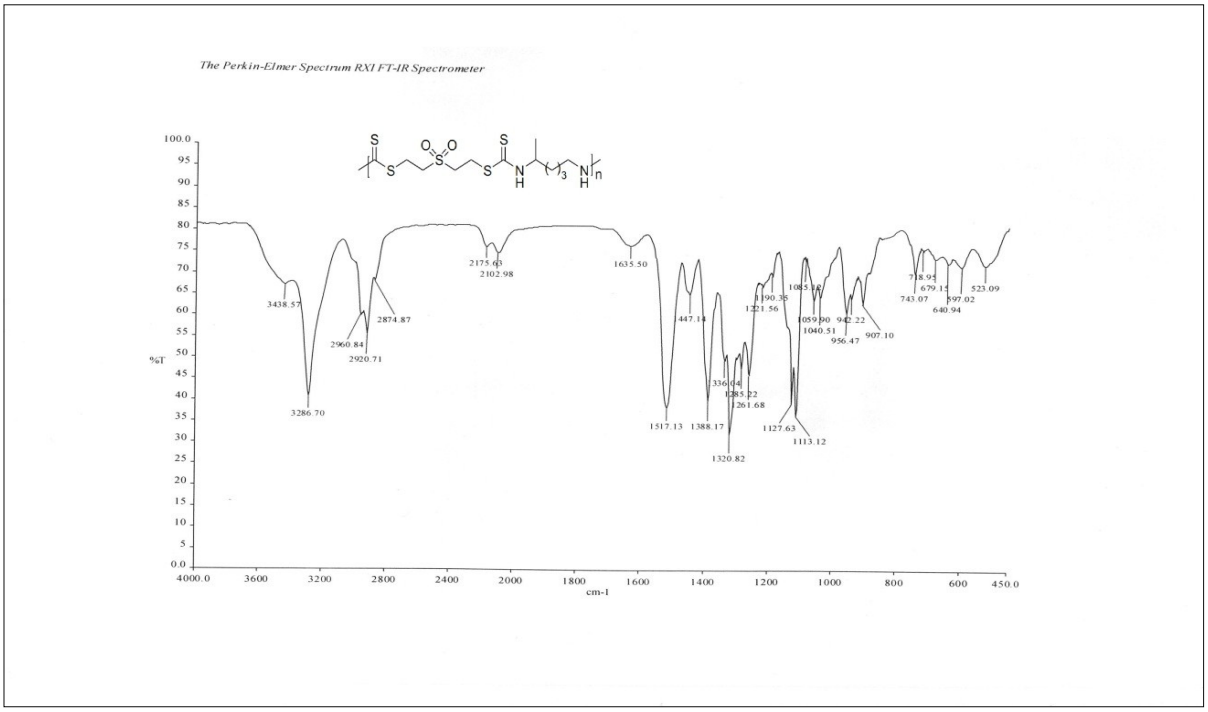


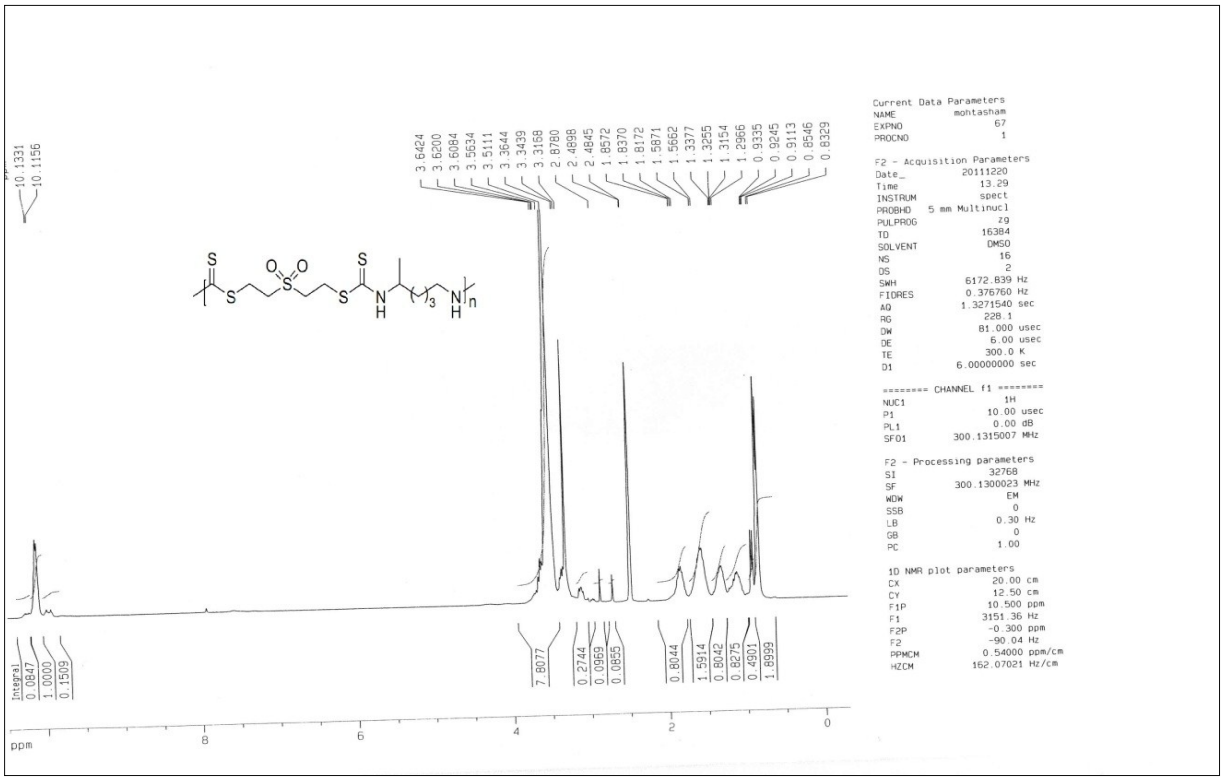
IR and ^{1}H NMR spectra of P3



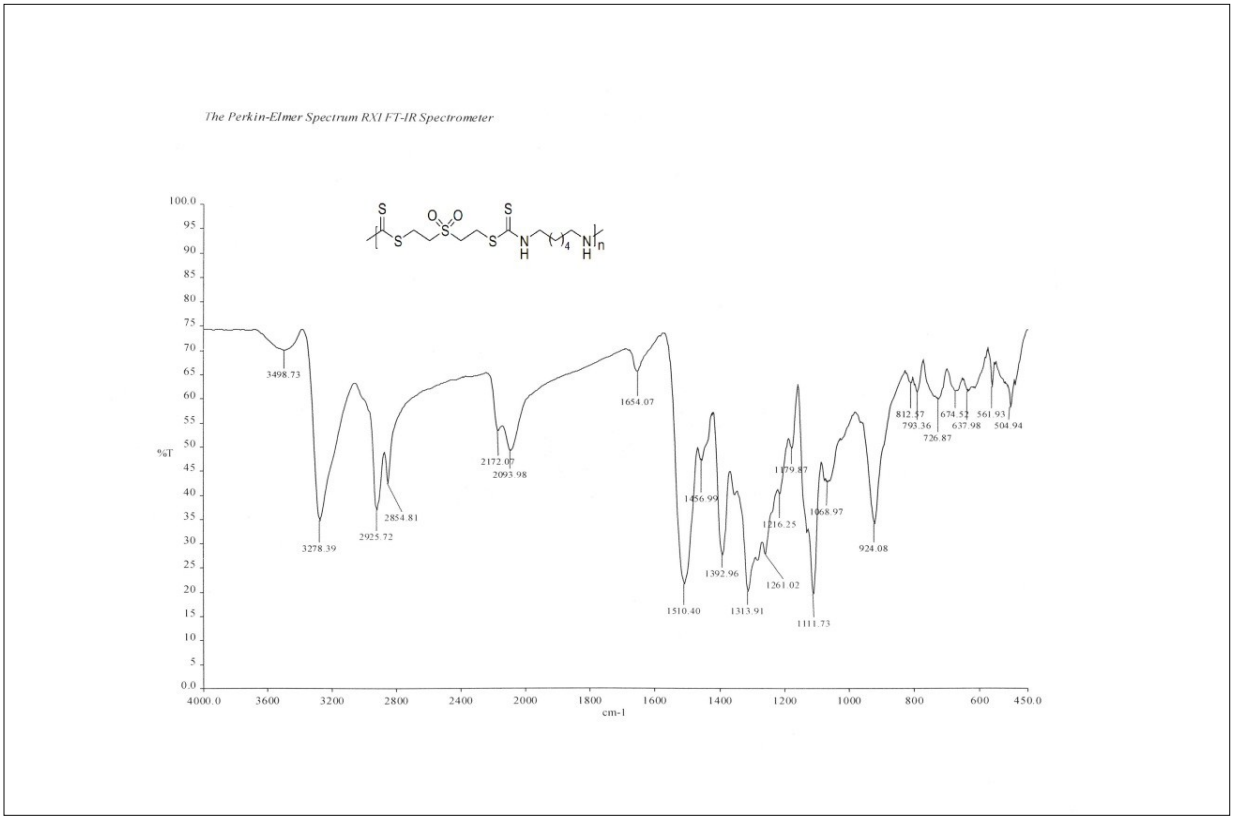


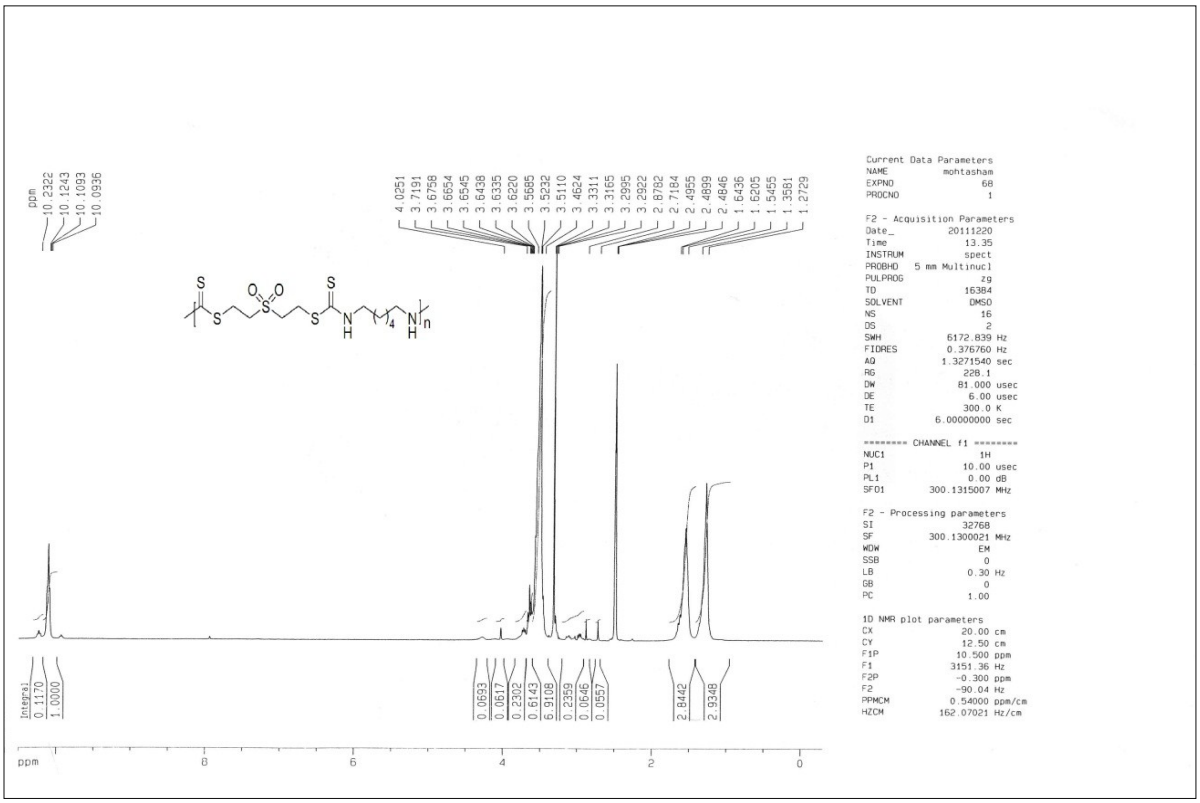
IR and ^{1}H NMR spectra of P4



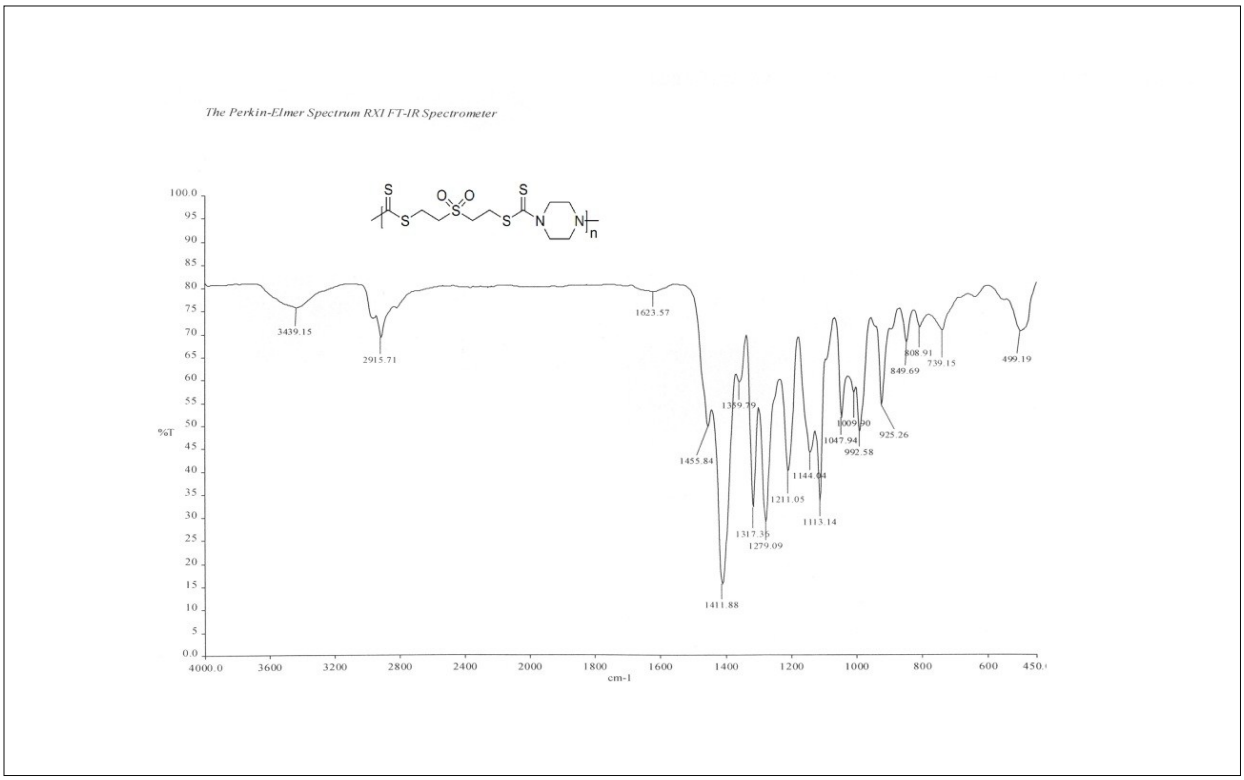


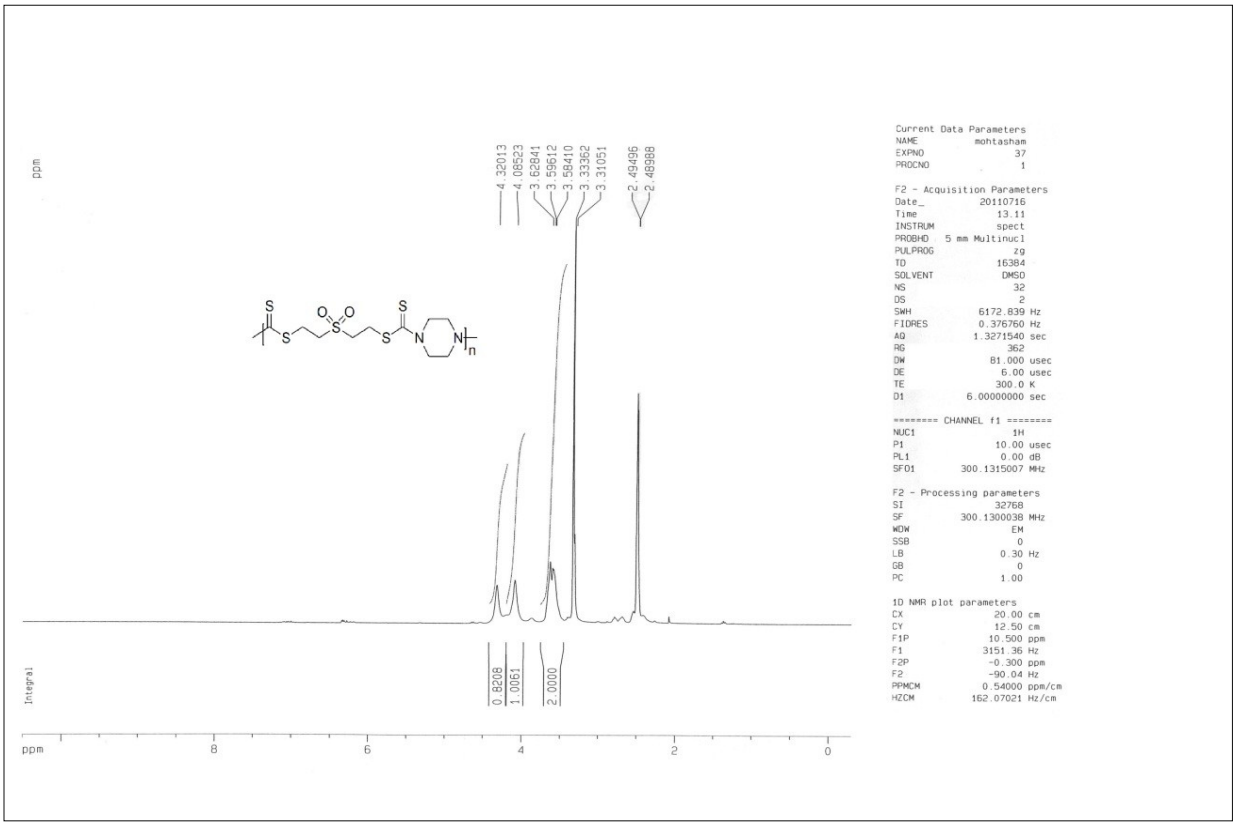
IR and ^{1}H NMR spectra of P5



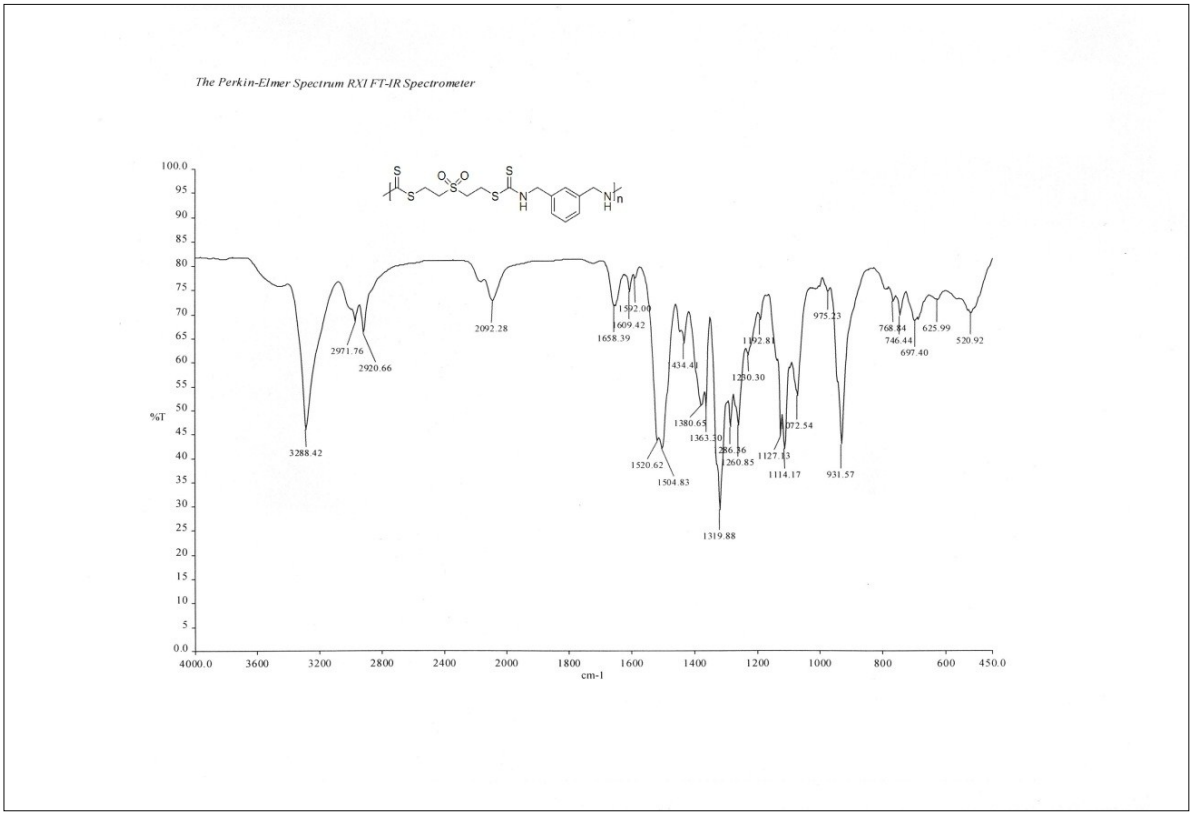


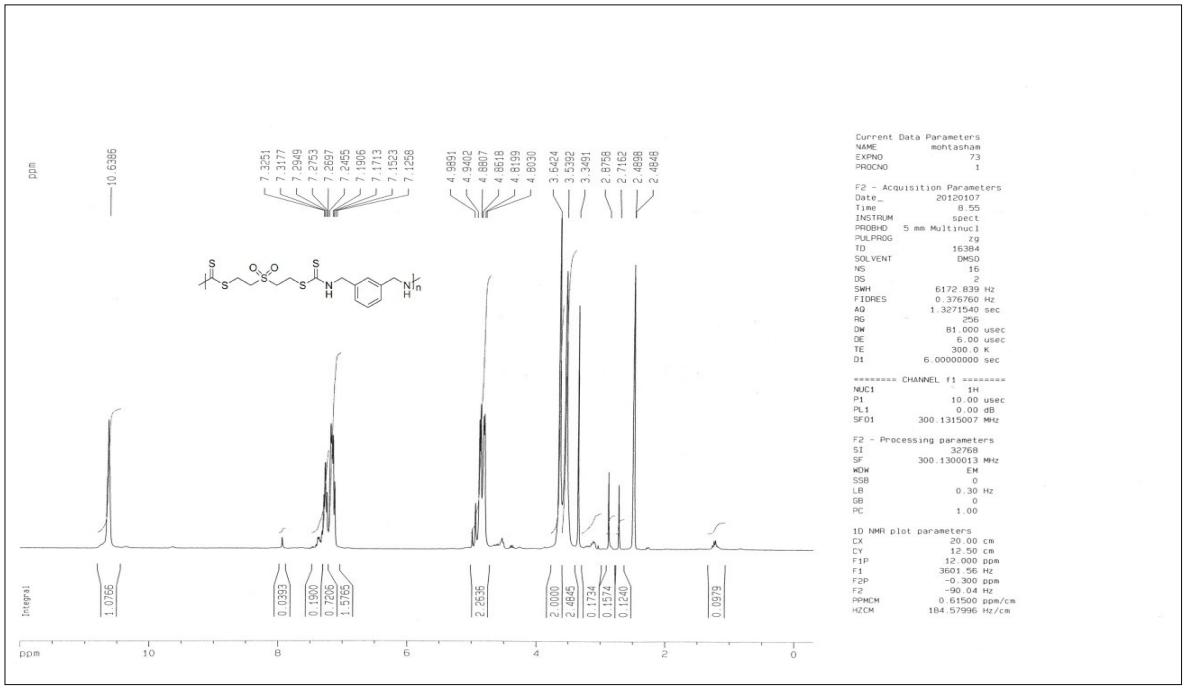
IR and ^{1}H NMR spectra of P6



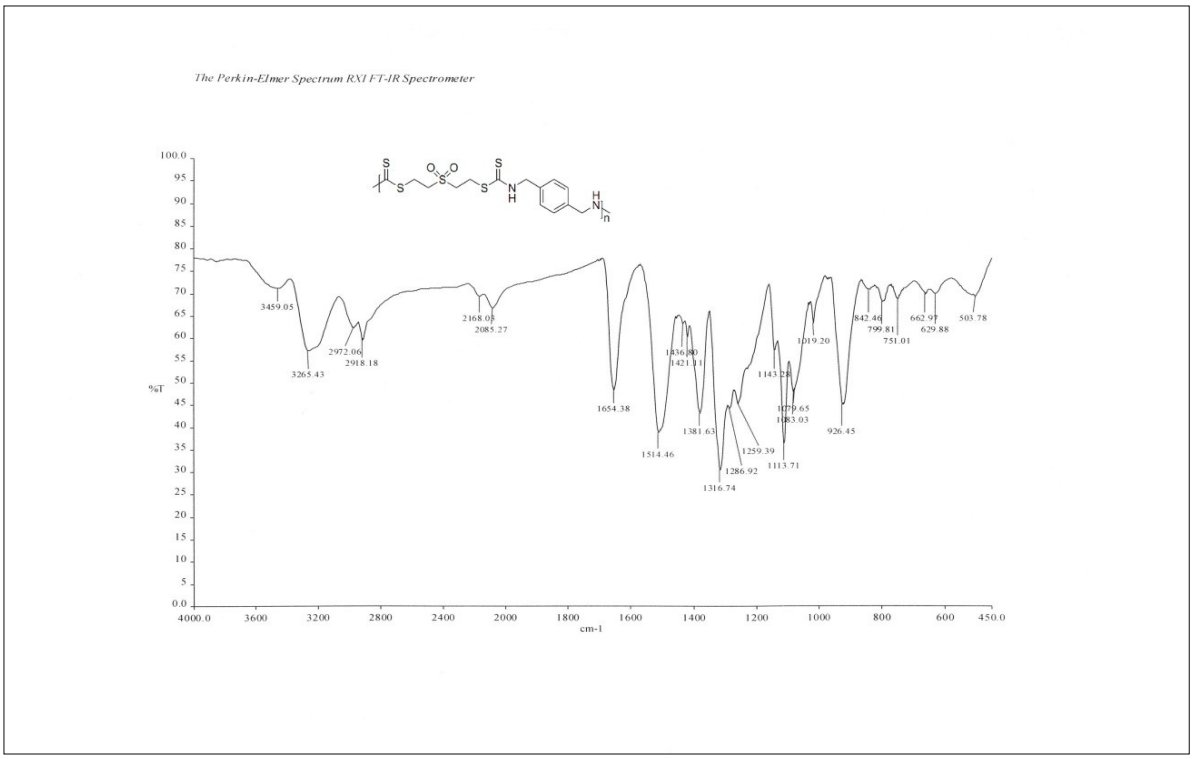


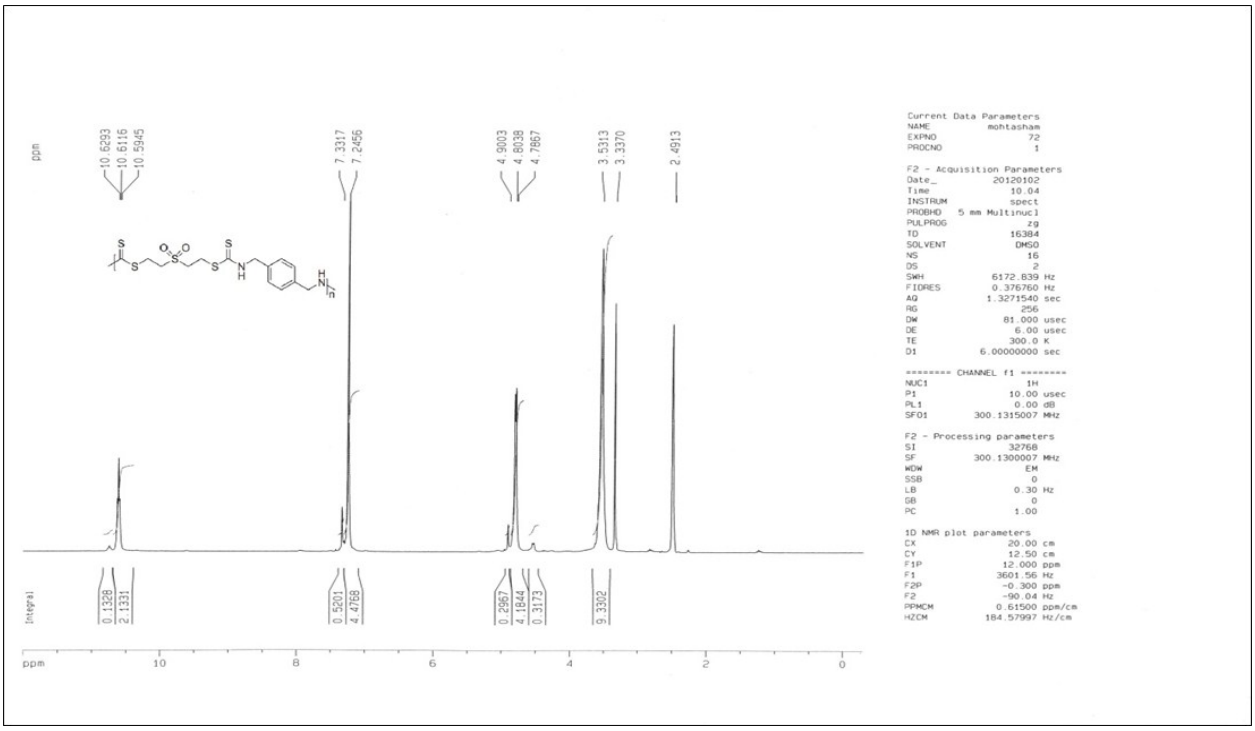
IR and ^{1}H NMR spectra of P7



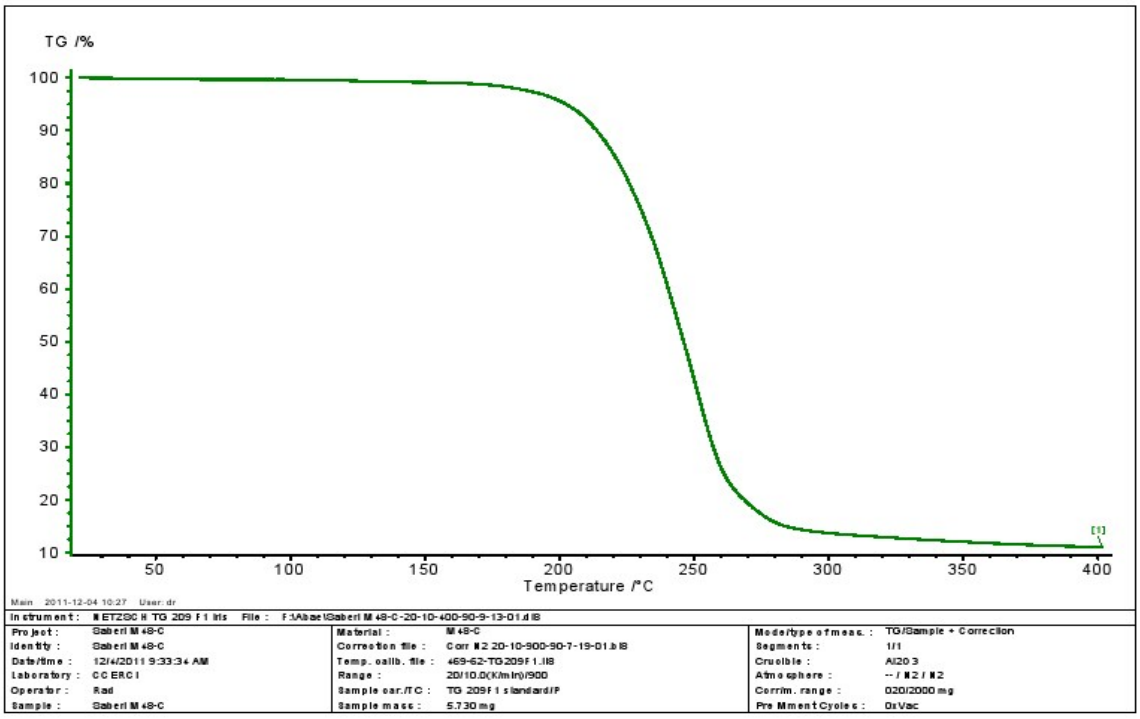


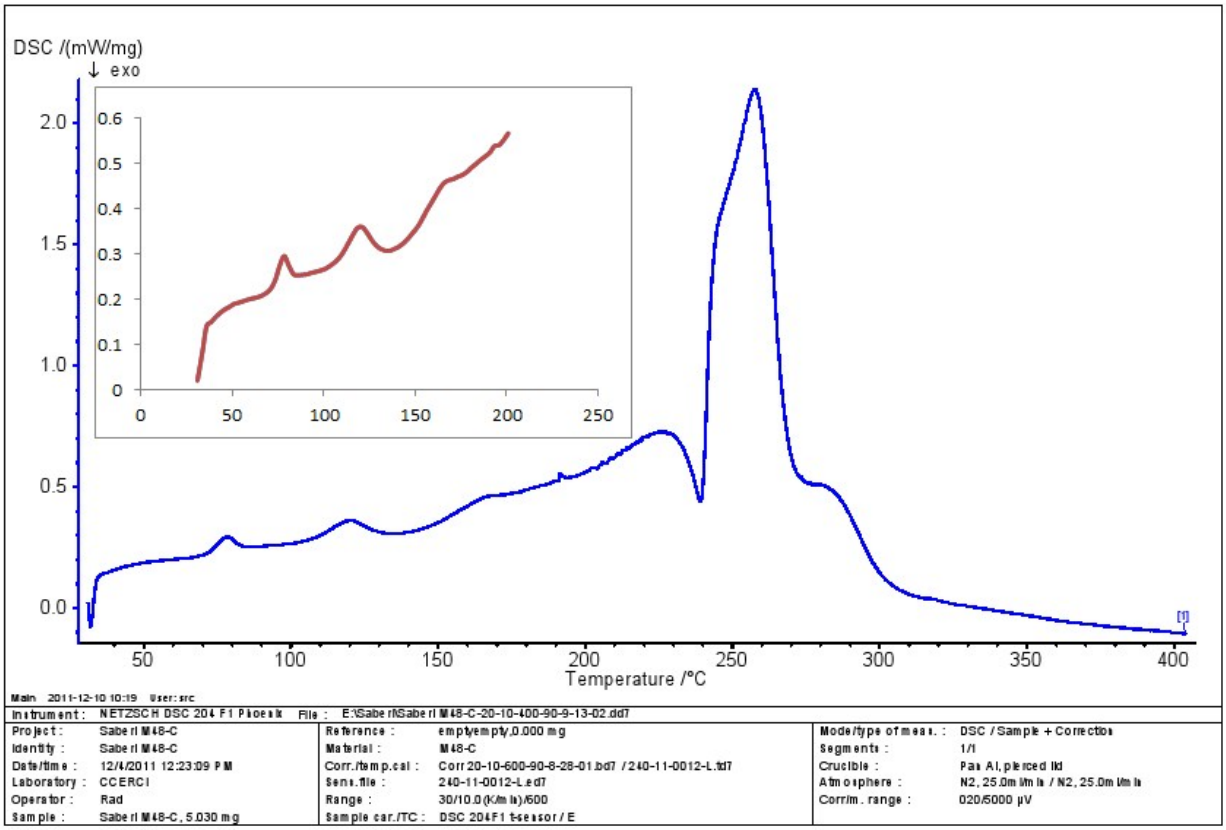
IR and ^{1}H NMR spectra of P8



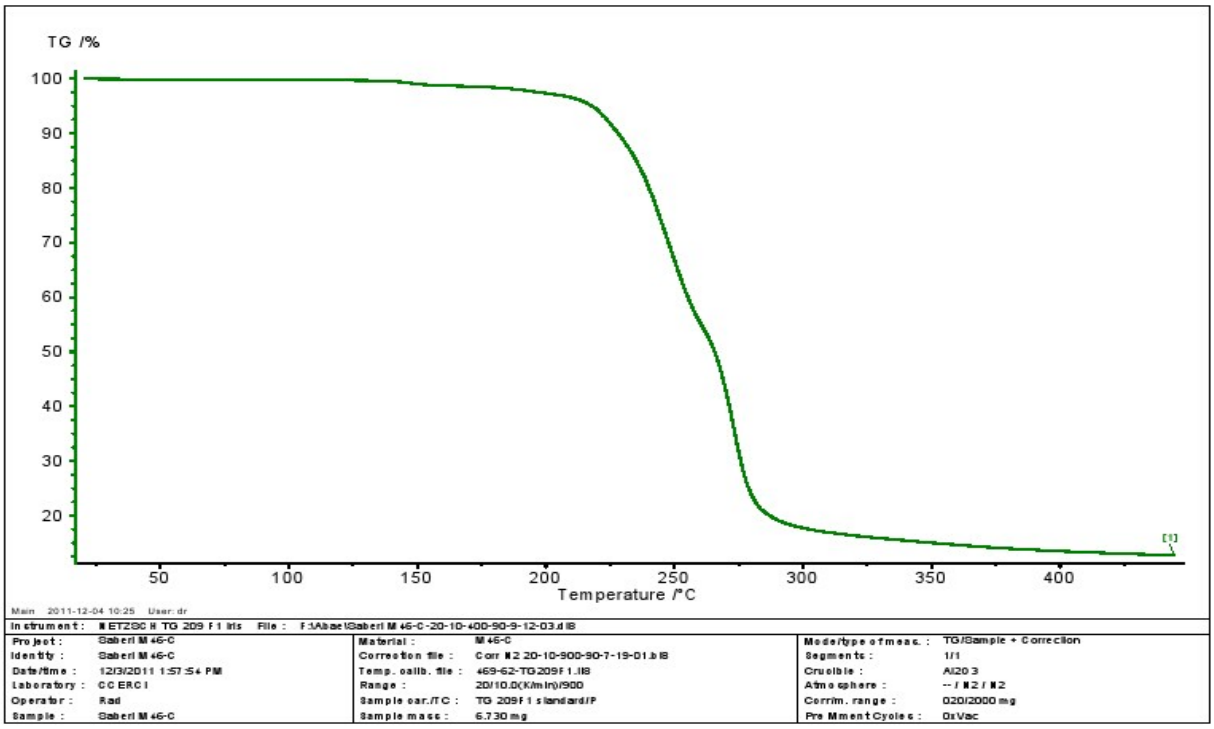


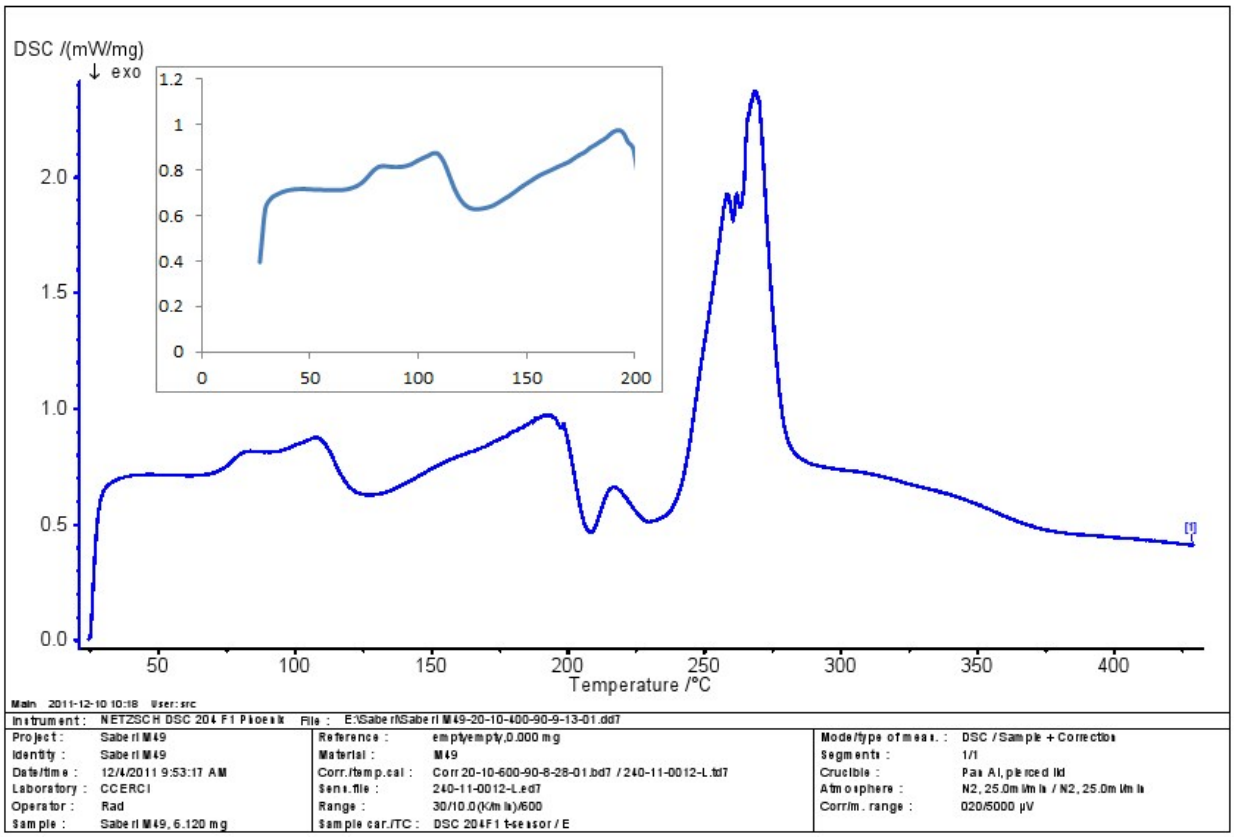
TGA and DSC diagram of P2



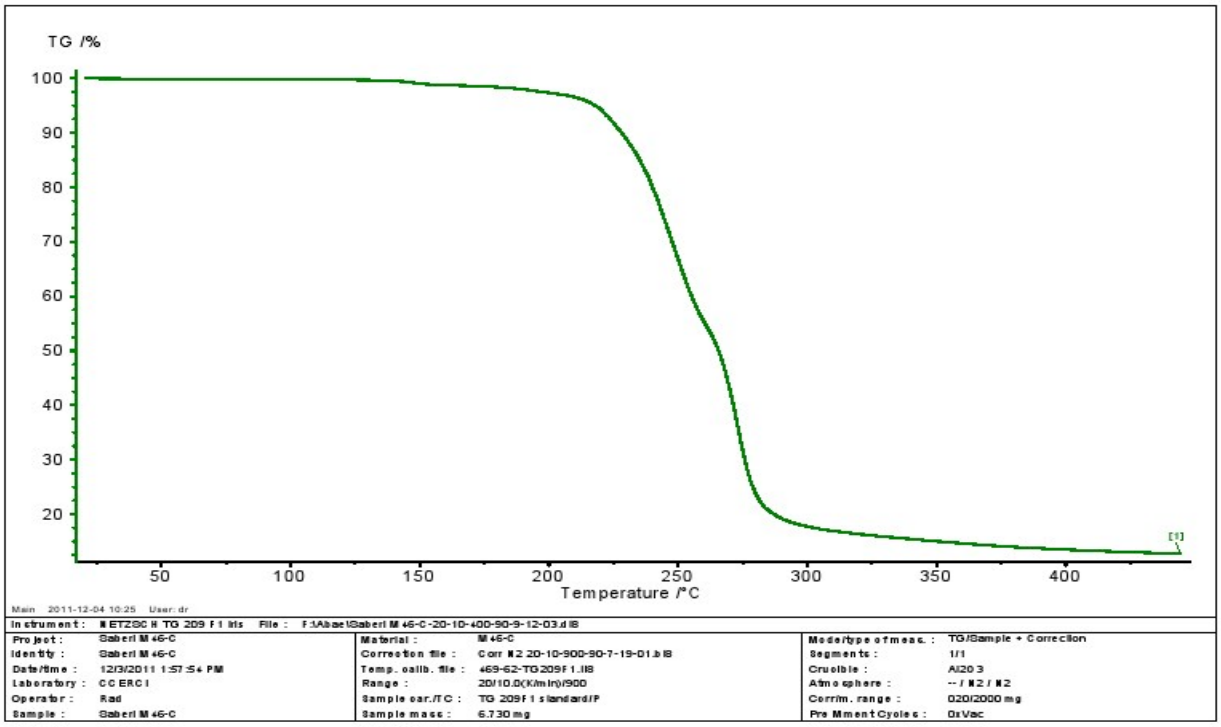


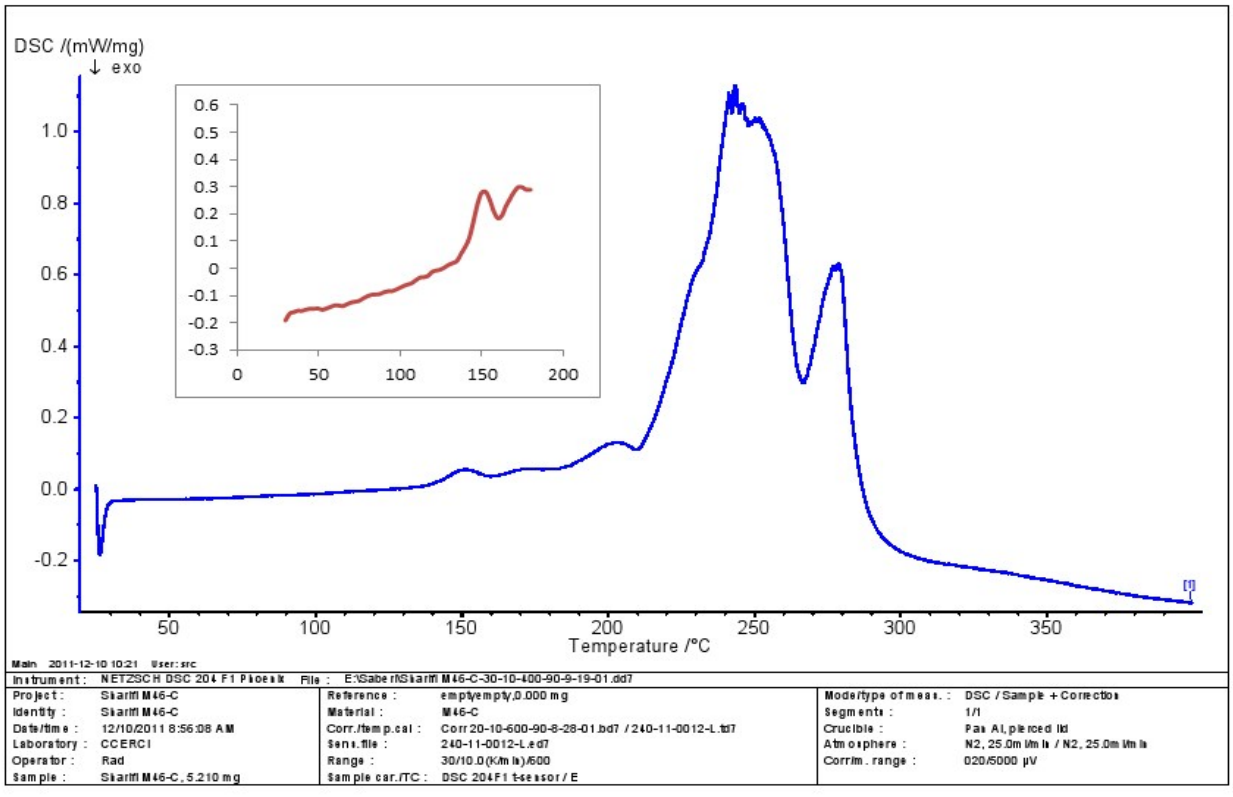
TGA and DSC diagram of P3



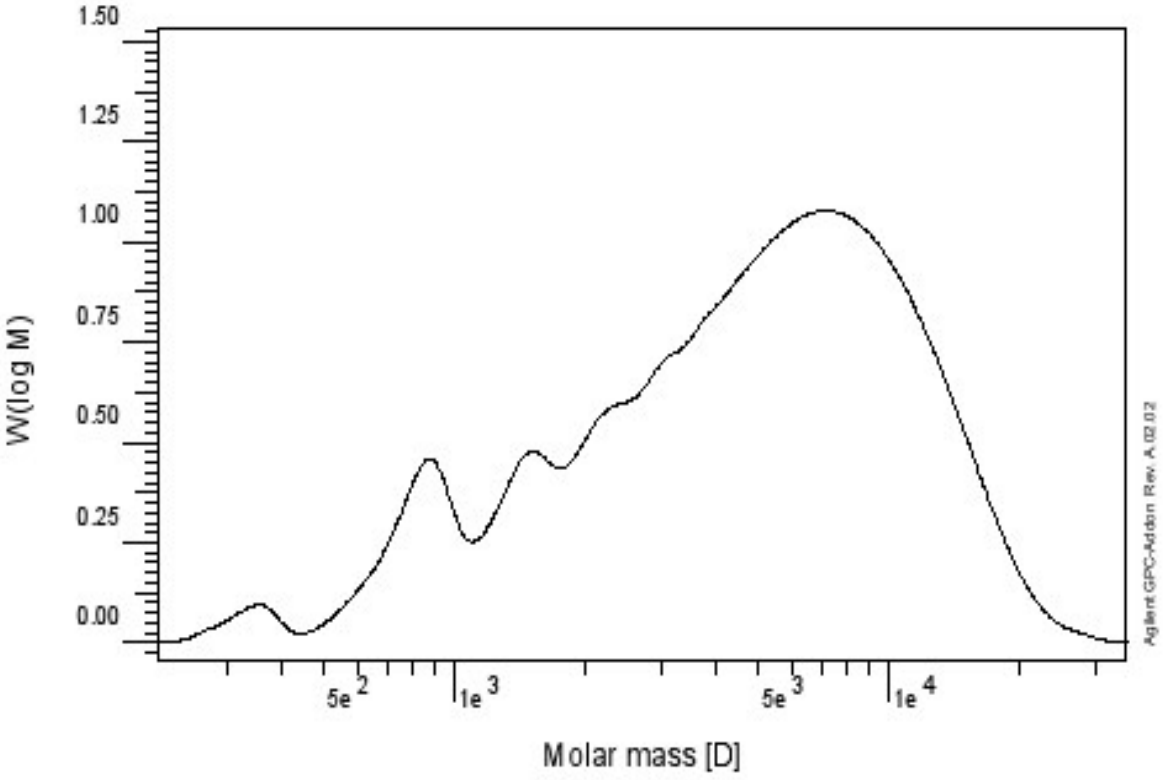


TGA and DSC diagram of P6





GPC analysis for P5



Sample :	C96401		
Injection Date :	29-Jan-12, 13:21:17		
Calibration File :	C:\HPCHEM\1\DATA\1390110190-CAL-11-L-L-01.CAL		
Calibration Date :	Monday 12/01/30 14:31:00		
Baseline from :	6.214 min	Baseline to :	10.587 min
Integration from:	6.214 min	Integration to :	10.587 min
MHK - A (Cal.):	0.000000E+0	MHK - K (Cal.):	1.000000E+0 ml/g
Eluent :	THF	Flowrate :	1.000 ml/min
Concentration :	1.000 g/l	Inject volume :	20.000 ul
Detector 1 :	RID A, Refractive Index Signal	Delay volume :	0.000 ml
Operator :	IPPI	Acquisition interval :	0.430 sec

rid1A

Mn :	2.6331e3	g/mol
Mw :	6.0705e3	g/mol
Mz :	9.6851e3	g/mol
Mv :	0.000000	g/mol
D :	2.3055e0	
[n]:	0.000000	ml/g
Vp :	7.5743e0	ml
Mp :	7.1353e3	g/mol
A :	1.1669e4	ml*V
< 208	0.00	
w% :	100.00	
> 35162	0.00	