New Journal of Chemistry

COMMUNICATION

Supporting Information

Synthesis of low to high molecular weight poly(1-hexene); rigid/flexible structures in a di- and mononuclear Ni-based catalyst series

M. Khoshsefat,[a,b] S. Ahmadjo,[a,†] S. M. M. Mortazavi,[a] G. H. Zohuri[c] and J. B.P. Soares[b]

[a] *Department of Catalyst, Iran Polymer and Petrochemical Institute (IPPI), P.O. Box 14965/115, Tehran, Iran*

[b] *Department of Chemical and Materials Engineering, University of Alberta, Edmonton, Alberta T6G 1H9, Canada*

c *Department of Chemistry, Faculty of Science, Ferdowsi University of Mashhad, P.O. Box: 91775, Mashhad, Iran*

[†] Corresponding author: S. Ahmadjo (S.ahmadjo@ippi.ac.ir)

Table of Contents

Materials

All manipulations of air/water sensitive compounds were conducted under Ar/N$_2$ atmosphere using the standard Schlenk techniques. All the solvents were purified prior to use. Toluene (purity 99.9%) (Iran, Petrochemical Co.) was purified over sodium wire/benzophenone, and used as polymerization media. Dichloromethane (purity 96%) (Sigma Aldrich Chemicals, Germany) and Methanol (Merck chemical) were purified over calcium hydride powder, and distilled prior to use in complex and ligand synthesis as solvent. Xylene was purchased from Merck chemical. 1-Hexene monomer was supplied by Mehr petrochemical company (Iran). 2,4,6- trimethyl aniline, 2,6- diisopropyl aniline, butanedione, 1,4-phenylene diamine, 2,3,5,6-tetramethyphenyldiamine, ethylenediamine, 1,6-Hexanediamine, 4,4'-methylenedianiline, acenaphthoquinone, nickel (II) bromide ethylene glycol dimethyl ether complex [(DME) NiBr$_2$] (purity 97%) and diethyl ether (purity 99.5%) were supplied by Merck Chemical (Darmstadt, Germany) and used in synthesis of ligands and catalysts. Diethylaluminum Chloride (DEAC) was supplied by Sigma Aldrich Chemicals (Steinheim, Germany).

Polymerization procedure

The polymerization of 1-Hexene monomer (purified prior to use) was carried out in a round bottom flask. The polymerization system was conducted under schlenk system before and during the injections. The monomer (10 ml) was injected to the round bottom flask which was contained 10 ml of solvent (toluene). Afterward, the co-catalyst and catalyst were introduced to the flask, respectively. The solution was stirred for 24h. The poly (1-hexene) was precipitated and purified by acidic Methanol (5%) and dried under reduced pressure.

Characterization

^{1}H NMR, ^{13}C NMR and FT-IR spectrums were obtained using Bruker AC-300, 400 and Thermo Nicolet AVATAR 370 spectrometers, respectively. Elemental and Mass analyses were performed on a Thermo Finnigan Flash 1112EA microanalyzer and Varian CH-7A spectrometer. Intrinsic viscosity [ŋ] was measured in toluene at room temperature using an Ubbelohde viscometer. M$_v$ values were calculated according to Mark-Houwink equation, $\eta=KM_v^\alpha$ (α=0.69, K=2.28×10^{-2}). Molecular weight distributions (MWDs) were determined with a Polymer Char high-temperature gel permeation chromatographer (GPC), run at 145 °C under a flow rate of 1,2,4-trichlorobenzene of 1 mL min^{-1}. The GPC was equipped with three detectors in series (infrared, light scattering, and differential viscometer) and calibrated with polystyrene narrow standards.
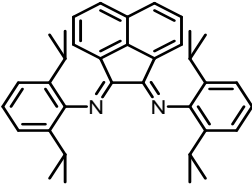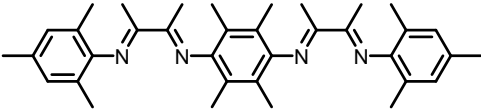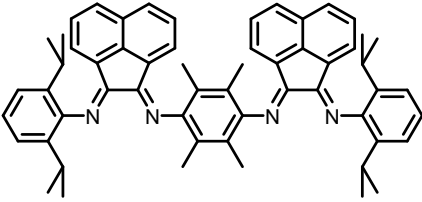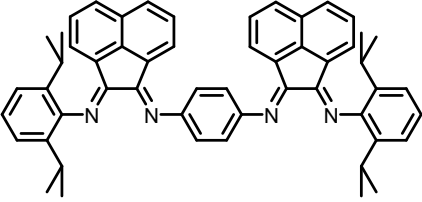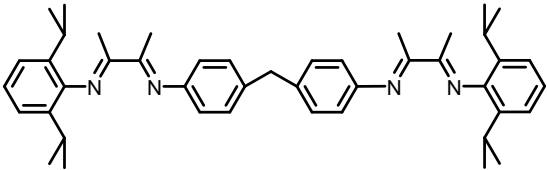
Experimental Details
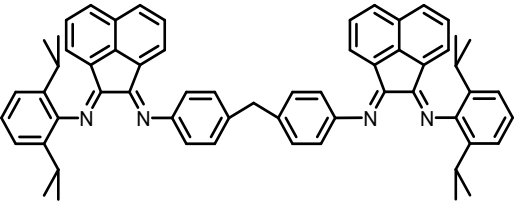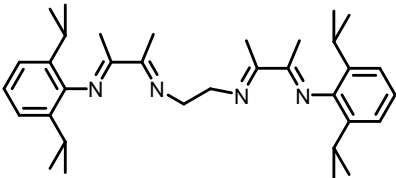
Preparation of Ligands and catalysts
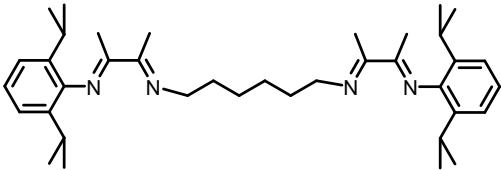
The ligands (SLM$_2$, SL$_n$, n=1-10) and complexes (MC$_n$, n=1-3 and BC$_n$, n=1-7) were synthesized (Scheme S1) according to procedure in our recent reports, expect some modification in the preparation of SL$_9$ and SL$_{10}$ which is described as following. [6,14] Among the structures, five ligands (SL$_4$ and SL$_{7-10}$) and corresponding complexes (BC$_1$ and BC$_{4-7}$) are novel.
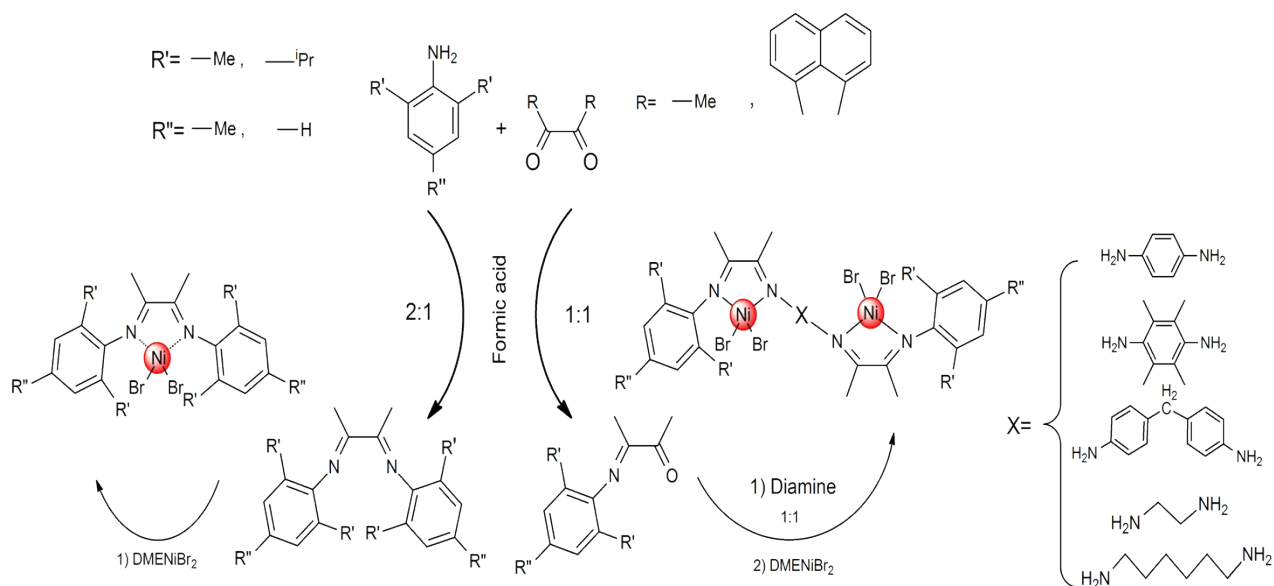
Scheme S1. Synthesis route of ligands and catalysts.

	Ligand	Structure	Corresponding catalyst
1	**SLM$_2$**		**-**
	Name:	**1-(2,6-diisopropylphenylimino)butane-2-one**	
2	**SL$_1$**		**MC$_1$**
	Name:	**N,N'-bis(2,4,6-trimethylphenyl)-2,3-butanediimine**	
3	**SL$_2$**		**MC$_2$**
	Name:	**N,N'-bis(2,6-diisopropylphenyl)-2,3-butanediimine**	

	Ligand	Structure	Corresponding catalyst
4	**SL₃**		**MC₃**
	Name	**N,N'-bis(2,6-diisopropylphenyl)-1,2-acenaphthylenediimine**	
5	**SL₄**		**BC₁**
	Name	**N,N'-(tetramethyl-1,4-phenylene)bis(N''-2,4,6-trimethylphenyl)-2,3-butanediimine**	
6	**SL₅**		**BC₂**
	Name	**N,N'-(tetramethyl-1,4-phenylene)bis(2,6-diisopropylphenyl)-1,2-acenaphthylenediimine**	
7	**SL₆**		**BC₃**
	Name	**N,N'-(1,4-phenylene)bis(2,6-diisopropylphenyl)-1,2-acenaphthylenediimine**	
8	**SL₇**		**BC₄**
	Name	**N,N'-(methylenebis(4,1-phenylene))bis(N''-(2,6-diisopropylphenyl)-2,3-butanediimine)**	

Ligand		Structure	Corresponding catalyst
9	SL₈		BC₅
	Name	N,N'-(methylenebis(4,1-phenylene))bis(N''-(2,6-diisopropylphenyl)-1,2-acenaphthylenediimine	
10	SL₉		BC₆
	Name	**N,N'-(ethane-1,2-diyl)bis(N''-(2,6-diisopropylphenyl)-2,3-butanediimine**	
11	SL₁₀		BC₇
	Name	**N,N'-(hexane-1,6-diyl)bis(N''-(2,6-diisopropylphenyl)-2,3-butanediimine**	

General procedure for synthesis of ligands (SL$_{1-3}$)

2,4,6-Trimethyl aniline/or 2,6-diisopropylaniline (7 mmol) was added to a stirred solution of diacetyl/ or acenaphtoqunion (0.5 gr, 3 mmol) in methanol (15 ml) and in the presence of catalytic amount of formic acid. The solution was stirred for 48 h. Progress of the reaction was checked by TLC. The solvent was evaporated at the end of the reaction and the precipitate was washed with n-hexane and recrystallized using ethanol.

General procedure for synthesis of ligands (SL$_{4-8}$)

To a stirred solution of diacetyl/or acenaphthenequinone (5.3 mmol) and methanol (15 mL) in a round-bottom flask which was placed in an ice bath, 2,4,6-trimethylaniline /or 2,6-diisopropylaniline (5 mmol) was added dropwise in the presence of the catalytic amount of formic acid. The solution was stirred for 24 h. The ice bath was removed and a solution of X=aliphatic or aromatic diamine (2.8 mmol) in methanol (5 mL) was added dropwise. The mixture was stirred for another 24 h at room temperature. In both steps of the ligand synthesis, the reaction progress and consumption of the reactant was checked using TLC

technique. The solid precipitate was washed with cold methanol several times, and the product was purified via column chromatography [10% ethyl acetate (EA)/n-hexane-silica gel]. The solvent was evaporated to afford the final ligands.

Preparation of SLM$_2$, SL$_9$ and SL$_{10}$

Due to low yield of reported method in synthesis of SL$_9$ and SL$_{10}$, a modification in method was employed. The first step obtained product of ligand synthesis (SLM$_2$) was precipitate at 0 °C and then filtered and washed several time with methanol. The solid was purified via column chromatography [5% ethyl acetate (EA)/n-hexane-silica gel]. The SLM$_2$ with the molar ratio of 1:3 to the Diamine (ethylene diamine for SL$_9$ and hexane diamine for SL$_{10}$) was added in a round bottom flask containing xylene as solvent. The mixture was stirred over 72h and then the solid product was washed with cold methanol several times. The solvent was evaporated to afford the product as a dark yellow powder (yield: SL$_9$ 58% and SL$_{10}$ 61%). The solid was purified via column chromatography [10% ethyl acetate (EA)/n-hexane-silica gel].

Table 1. Assignment details of spectroscopic data, SL_n, n=1-10.

Entry	^{1}HNMR (CDCl$_3$, 300 MHz): δ	Elemental Analysis	Ft-IR (KBr, cm^{-1})	Mass(EIm/z): [M$^+$,100%]
SL_1	1.2 (6H, s), 1.6(6H, s), 2.0 (6H, s), 2.2 (6H, s), 7.3(4H, s).	Anal. Calcd. for $C_{22}H_{28}N_2$: C, 82.45; H, 8.81; N, 8.74. Found: C, 82.38; H, 8.76; N, 8.71.	1275 (-C-N-), 1646 (-C=N-)	320
SL_2	1.2 (12H, d), 1.3(12H, d), 2.3 (6H, s), 2.7 (4H, sep), 7.1(4H, d), 7.3 (2H, t).	Anal. Calc. for $C_{28}H_{40}N_2$: C, 83.11; H, 9.96; N, 6.93. Found: C, 83.02; H, 9.8; N, 6.85.	1273 (-C-N-), 1646 (-C=N-)	404
$SL_3{}^a$	1.0 (12H, d), 1.3 (12H, d), 3.1 (4H, sep), 6.8 (2H, d) 7.4 (6H, m), 7.7 (2H, t), 8.3 (2H, d).	Anal. Calcd. for $C_{36}H_{40}N_2$: C, 86.35; H, 8.05; N, 5.59. Found: C, 86.18; H, 7.98; N, 5.65.	1271 (-C-N-), 1626 (-C=N-)	500
SL_4	1.1(12H, s), 1.5(6H, s), 1.9(12H, s), 2.0(6H, s), 2.1(6H, s), 7.2(4H, s).	Anal. Calcd. for $C_{36}H_{46}N_4$: C, 80.85; H, 8.67; N, 10.48. Found: C, 79.99; H, 8.54; N, 10.51.	1283 (-C-N-), 1637 (-C=N-)	534
$SL_5{}^a$	1.0(12H, d), 1.3(12H, d), 2.2(12H, s), 3.1(4H, sep), 6.7(4H, d), 7.3(8H, t), 7.9 (4H, t), 8.2(2H, d).	Anal. Calcd. For $C_{58}H_{58}N_4$: C, 85.89; H, 7.21; N, 6.91. Found: C, 85.90; H, 7.09; N, 6.98.	1279 (-C-N-), 1657 (-C=N-)	810
$SL_6{}^b$	1.2(24H, d), 2.8(4H, q), 2.1(6H, s), 6.7(4H, d), 7.3(4H, d), 7.4(2H, t), 7.9 (4H, t), 8.1(4H, d), 8.3(4H, d)	Anal. Calcd. For $C_{54}H_{50}N_4$: C, 85.90; H, 6.68; N, 7.42. Found: C, 85.78; H, 6.40; N, 7.07.	1274 (-C-N-), 1646 (-C=N-)	756
SL_7	1.1(12H, d), 1.4(12H, d), 2.3(6H, s), 2.5(6H, s), 2.8(2H, sep), 3.8(2H, s), 6.9(4H, d), 7.1 (2H, t), 7.3(4H, d), 7.6(4H, d).	Anal. Calcd. For $C_{45}H_{56}N_4$: C, 82.77; H, 8.64; N, 8.58. Found: C, 82.12; H, 8.54; N, 8.62.	1278 (-C-N-), 1655 (-C=N-)	652
SL_8	1.0(12H, d), 1.3(12H, d), 2.8(4H, sep), 3.8(2H, s), 6.9(4H, d), 7.2 (2H, t), 7.3-7.6(8H, m, overlapped), 7.9(8H, d), 8.2(4H, t).	Anal. Calcd. For $C_{61}H_{56}N_4$: C, 86.69; H, 6.68; N, 6.63. Found: C, 86.58; H, 6.71; N, 6.65.	1277 (-C-N-), 1678 (-C=N-)	844
SL_9	1.1(12H, d), 1.3(12H, d), 2.1(4H, t), 2.3(12H, s), 2.7(4H, sep), 7.1(4H, d), 7.3 (2H, t).	Anal. Calcd. For $C_{34}H_{50}N_4$: C, 79.33; H, 9.79; N, 10.88. Found: C, 79.16; H, 9.63; N, 10.93.	1283 (-C-N-), 1650 (-C=N-)	514
SL_{10}	1.1-1.3(24H, 2d), 1.5-1.9(8H, m,overlapped), 2.0(4H, t), 2.3(12, s), 2.8(4H, sep), 6.8(4H, d), 7.2 (2H, t).	Anal. Calcd. For $C_{38}H_{58}N_4$: C, 79.95; H, 10.24; N, 9.81. Found: C, 80.01; H, 10.07; N, 9.73.	1274 (-C-N-), 1655 (-C=N-)	570
SLM_2	1.2(6H, d), 1.4(6H, d), 2.1(3H, s), 2.3(3H, s), 2.9(2H, sep), 6.9(2H, d), 7.2 (1H, t).	Anal. Calcd. for $C_{16}H_{23}NO$: C, 78.32; H, 9.45; N, 5.71. Found: C, 77.92; H, 9.11; N, 5.31.	1271 (-C-N-),1621 (-C=N-), 1720 (-C=O)	245

[a,b] Data extracted from our reports.[6, 14]

Table 2. Assignment details of spectroscopic data, MC_n, n=1-3 and BC_n, n=1-7.

| Entry	Elemental Analysis	Ft-IR (KBr, cm^{-1})
MC_1	Anal. Calcd. for $C_{22}H_{28}Br_2N_2Ni$: C, 49.03; H, 5.24; N, 5.20. Found: C, 48.29; H, 4.91; N, 4.23.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1638 cm^{-1} (-C=N-).
MC_2	Anal. Calcd. for $C_{28}H_{40}Br_2N_2Ni$: C, 53.97; H, 6.47; N, 4.50. Found: C, 53.24; H, 4.23; N, 4.17.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1642 cm^{-1} (-C=N-).
MC_3[a]	Anal. Calcd. for $C_{36}H_{40}Br_2N_2Ni$: C, 60.12; H, 5.61; N, 3.89. Found: C, 59.89; H, 5.54; N, 3.91.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1625 cm^{-1} (-C=N-).
BC_1	Anal. Calcd. for $C_{36}H_{46}Br_4N_4Ni_2$: C, 44.49; H, 4.77; N, 5.77. Found: C, 44.32; H, 4.56; N, 5.67.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1622 cm^{-1} (-C=N-).
BC_2[a]	Anal. Calcd. for $C_{58}H_{58}Br_4N_4Ni_2$: C, 55.81; H, 4.68; N, 4.49. Found: C, 55.64; H, 4.21; N, 4.06.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1652 cm^{-1} (-C=N-).
BC_3[b]	Anal. Calcd. for $C_{54}H_{50}Br_4N_4Ni_2$: C, 54.4; H, 4.2; N, 4.7. Found: C, 53.81; H, 4.05; N, 4.30.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1623 cm^{-1} (-C=N-).
BC_4	Anal. Calcd. for $C_{46}H_{60}Br_4N_4Ni_2$: C, 49.59; H, 5.18; N, 5.14. Found: C, 49.33; H, 4.97; N, 4.89.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1649 cm^{-1} (-C=N-).
BC_5	Anal. Calcd. for $C_{61}H_{56}Br_4N_4Ni_2$: C, 57.14; H, 4.40; N, 4.37. Found: C, 56.93; H, 4.24; N, 4.21.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1674 cm^{-1} (-C=N-).
BC_6	Anal. Calcd. for $C_{34}H_{50}Br_4N_4Ni_2$: C, 42.90; H, 5.29; N, 5.89. Found: C, 42.69; H, 5.15; N, 5.72.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1638 cm^{-1} (-C=N-).
BC_7	Anal. Calcd. for $C_{38}H_{58}Br_4N_4Ni_2$: C, 45.28; H, 5.80; N, 5.56. Found: C, 44.99; H, 5.67; N, 5.53.	the imine signal was shifted to weak field as it coordinated to the Ni atom; 1652 cm^{-1} (-C=N-).

[a,b] Data extracted from our reports.[6, 14]
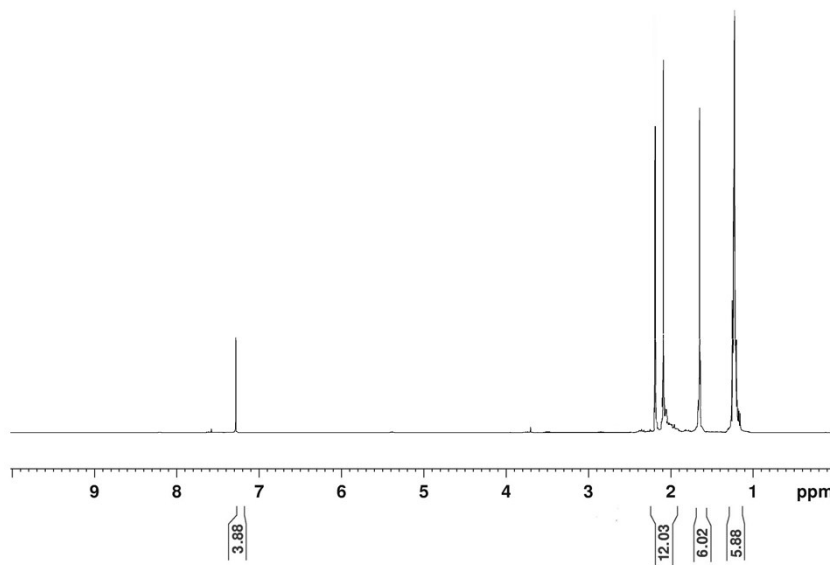
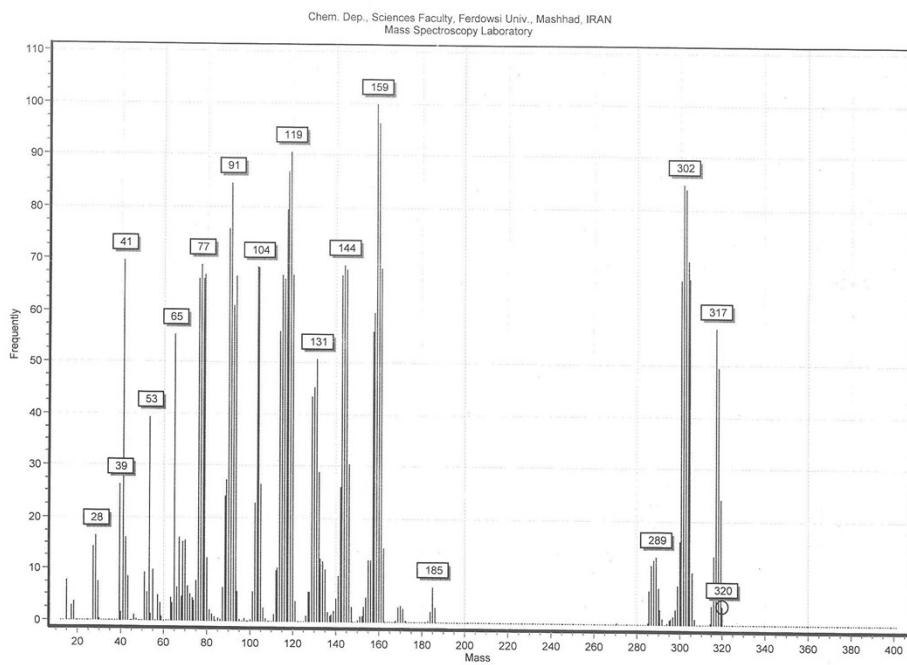**Figure S1.** ^{1}H NMR spectrum of SL$_1$.

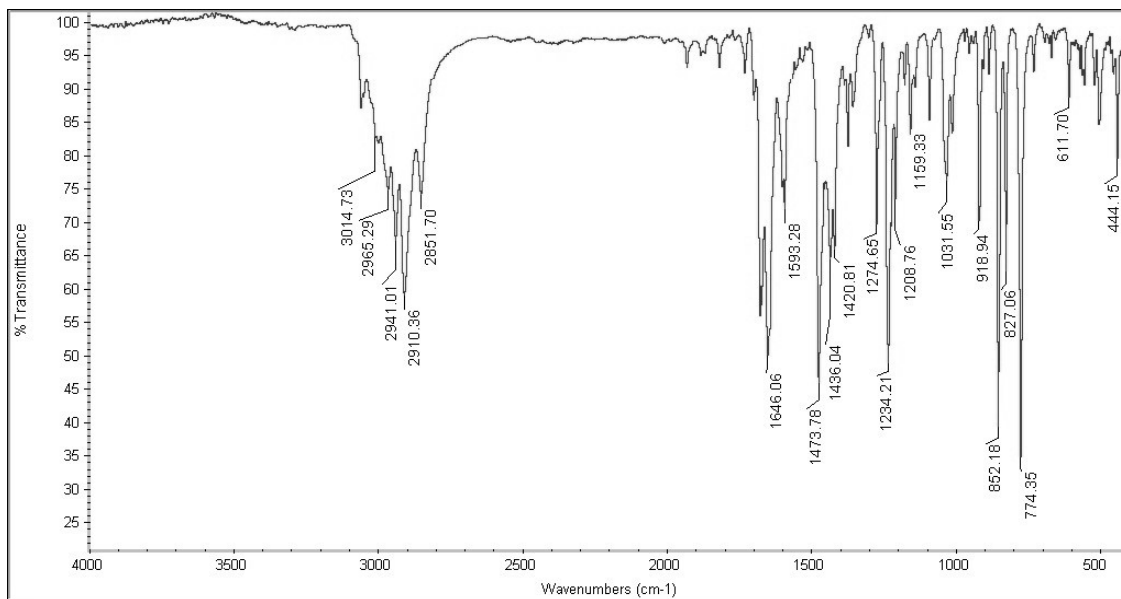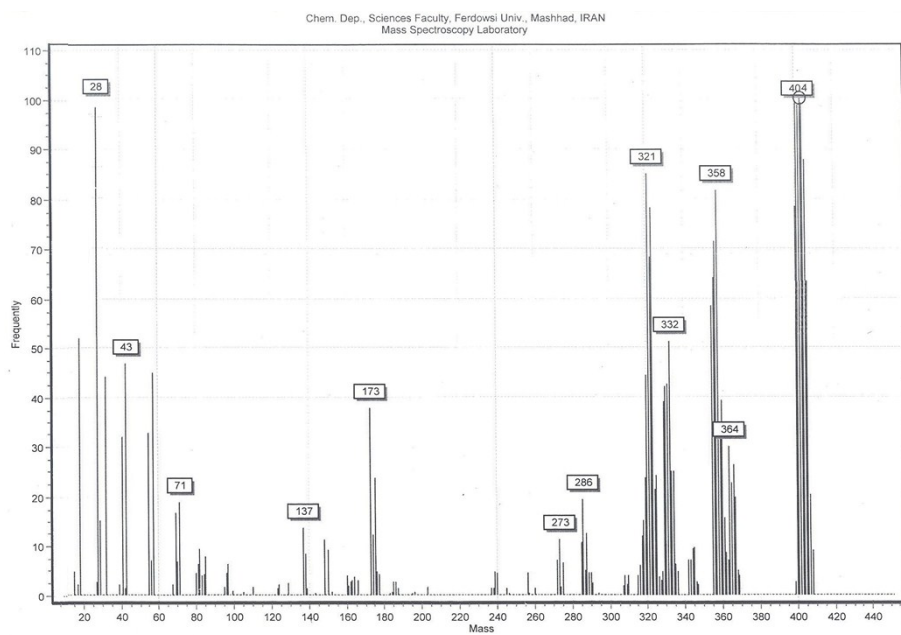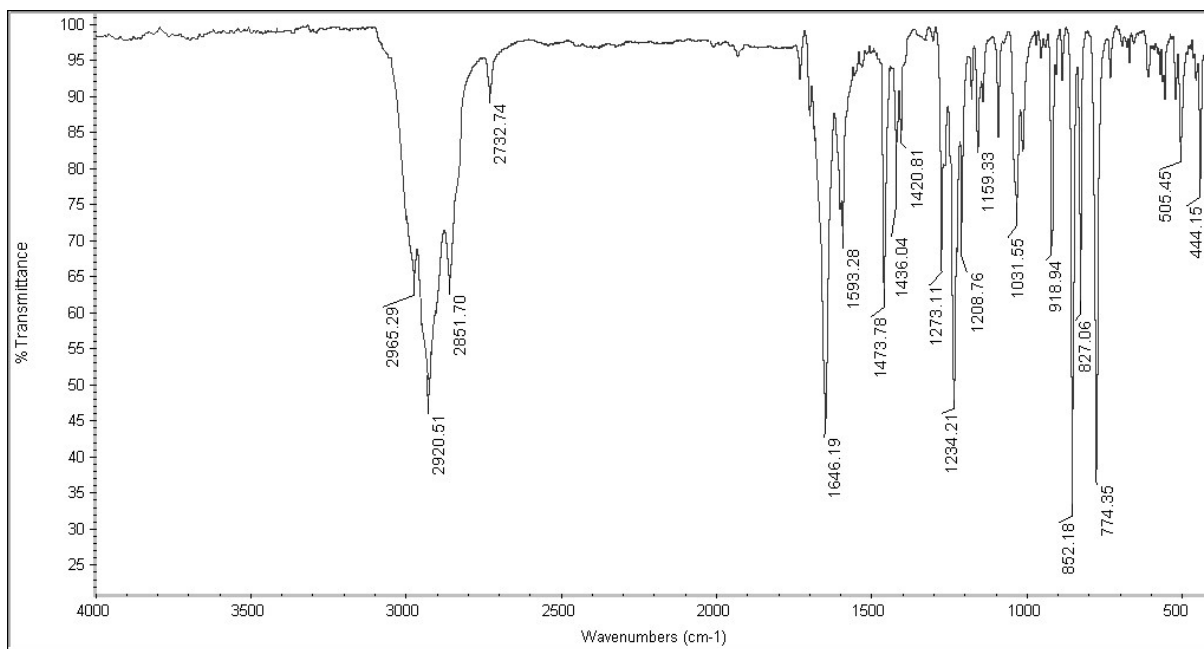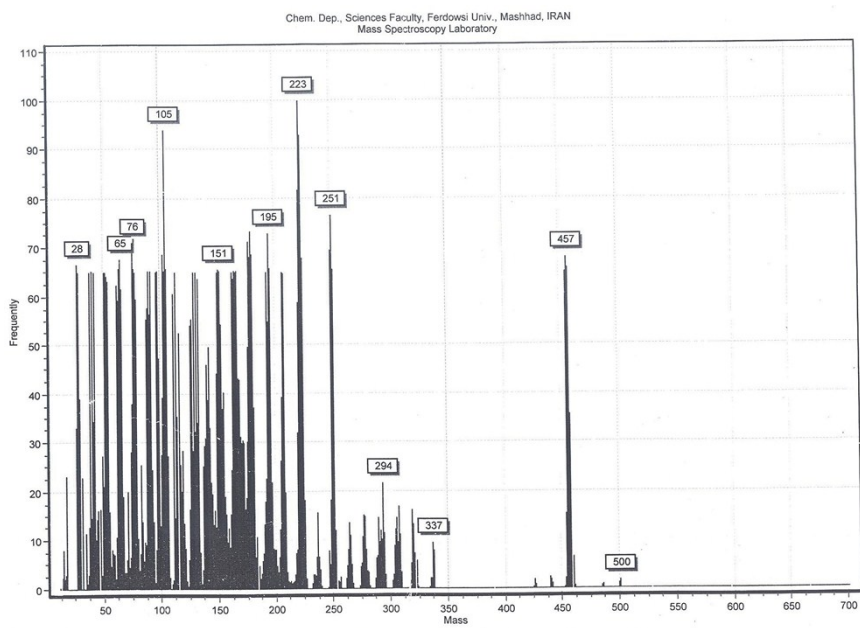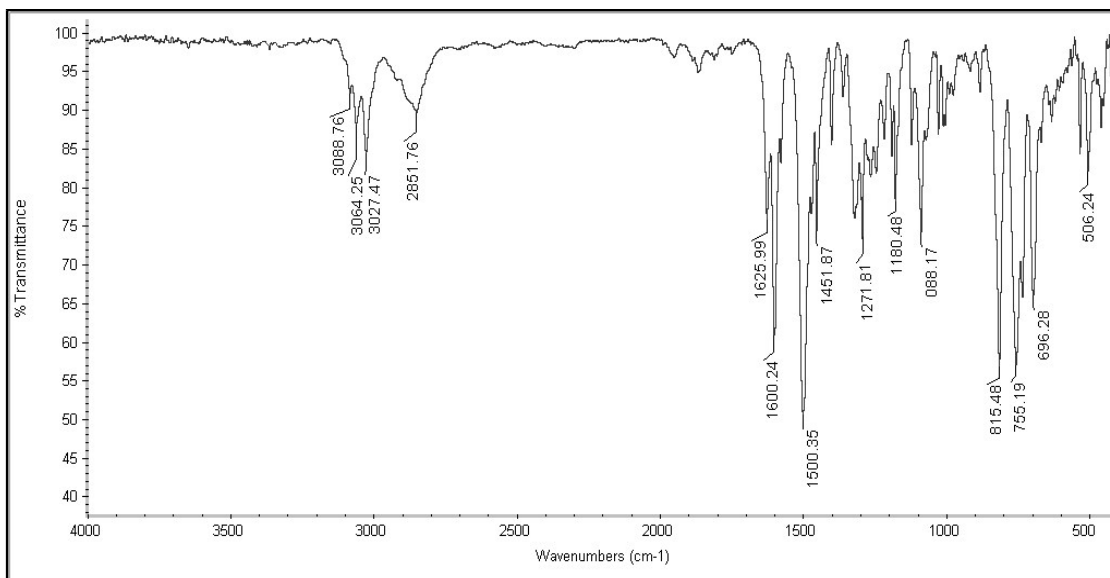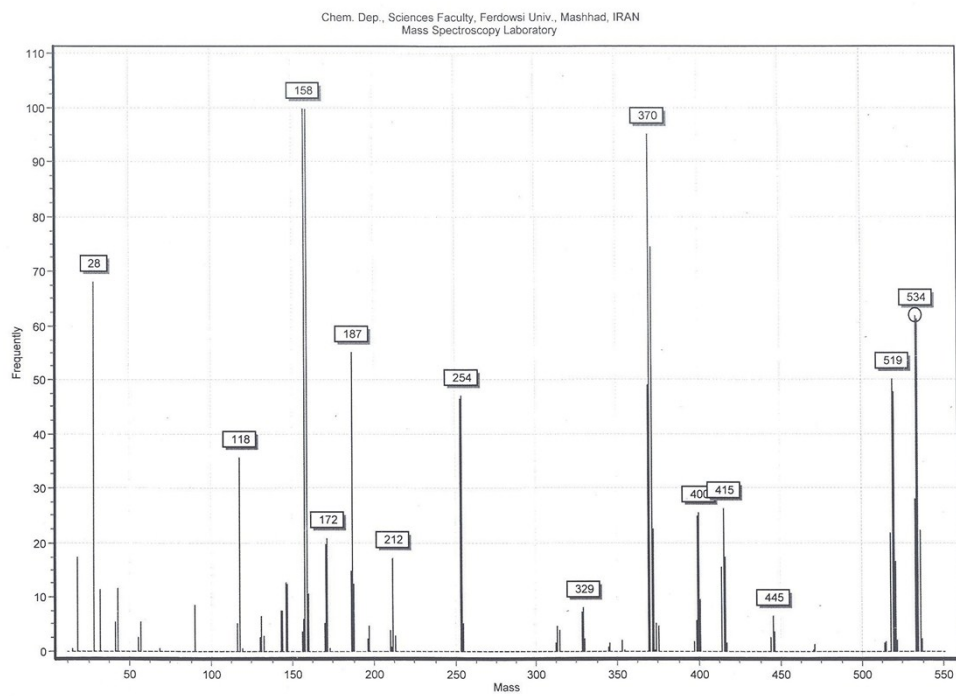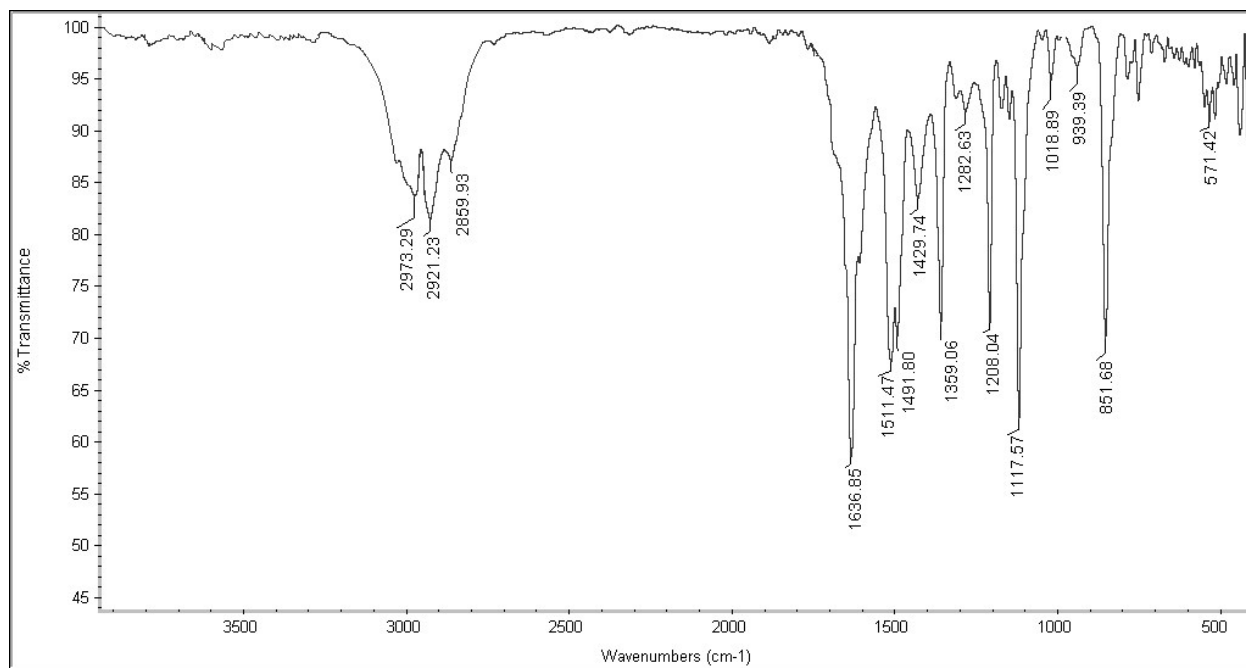**Figure S2.** Mass spectrum of SL$_1$.

Figure S3. FT-IR spectrum of SL$_1$

```
Eager 300 Summarize Results
    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No : 8
Component Name Average
-------------- --------------
Nitrogen%      8.714814548
Carbon%        82.38718384
Hydrogen%      8.758033085
Sulphur%       0
```

Figure S4. CHNS elemental analysis of SL$_1$.
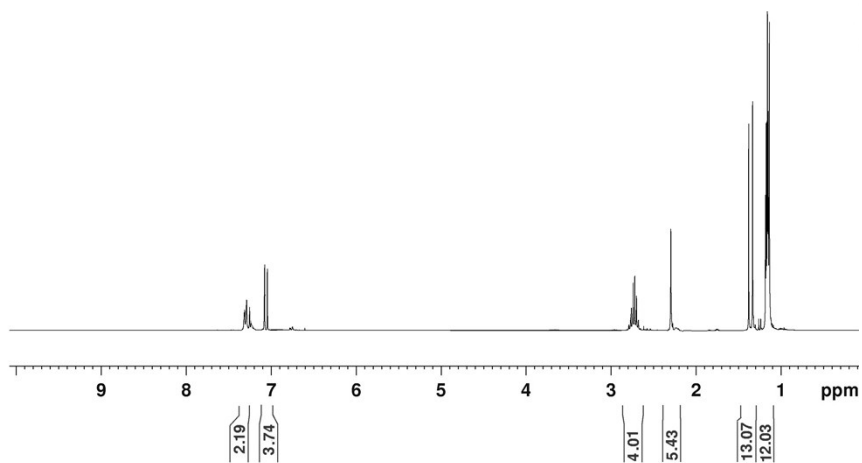
Figure S5. ^{1}H NMR spectrum of SL$_2$.

Figure S6. Mass spectrum of SL$_2$.

Figure S7. FT-IR spectrum of SL$_2$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No : 5
Component Name Average
-------------- --------------
Nitrogen%       6.85373567
Carbon%         83.021343
Hydrogen%       9.837661972
Sulphur%        0
```

Figure S8. CHNS elemental analysis of SL$_2$.
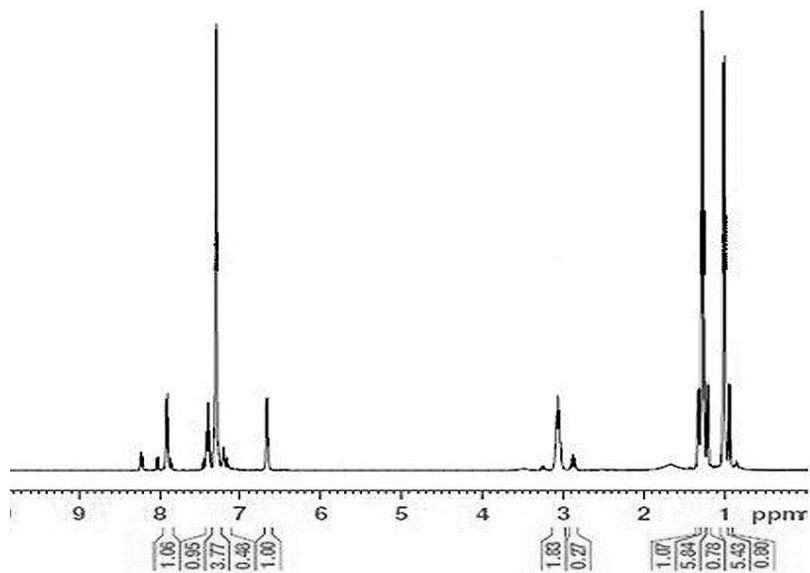
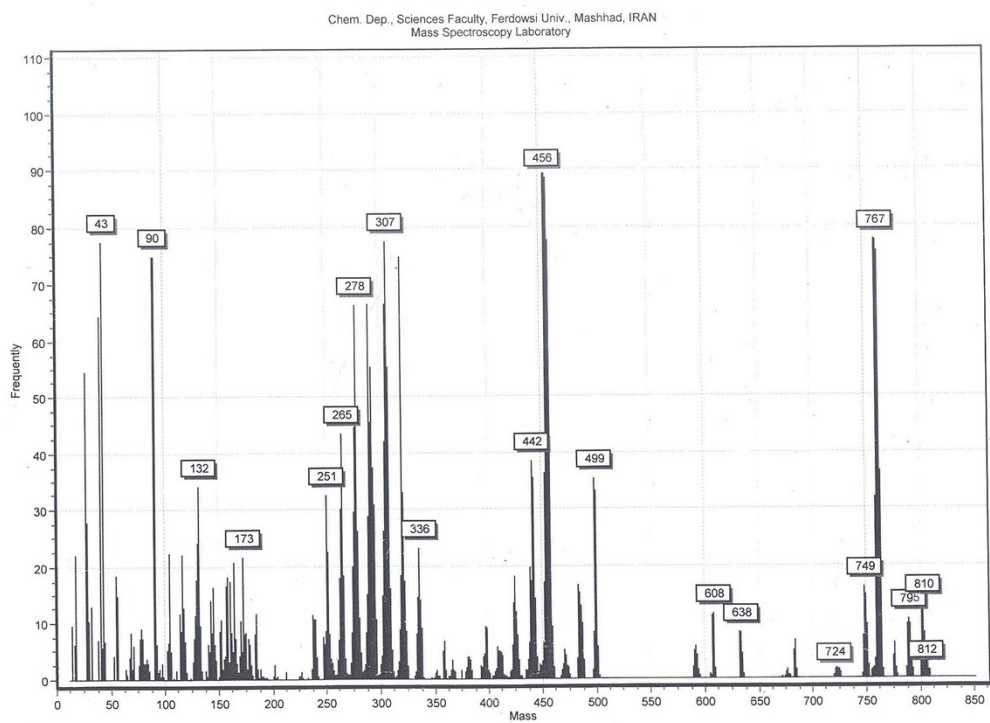**Figure S9.** ^{1}H NMR spectrum of SL$_3$.

Figure S10. Mass spectrum of SL$_3$.
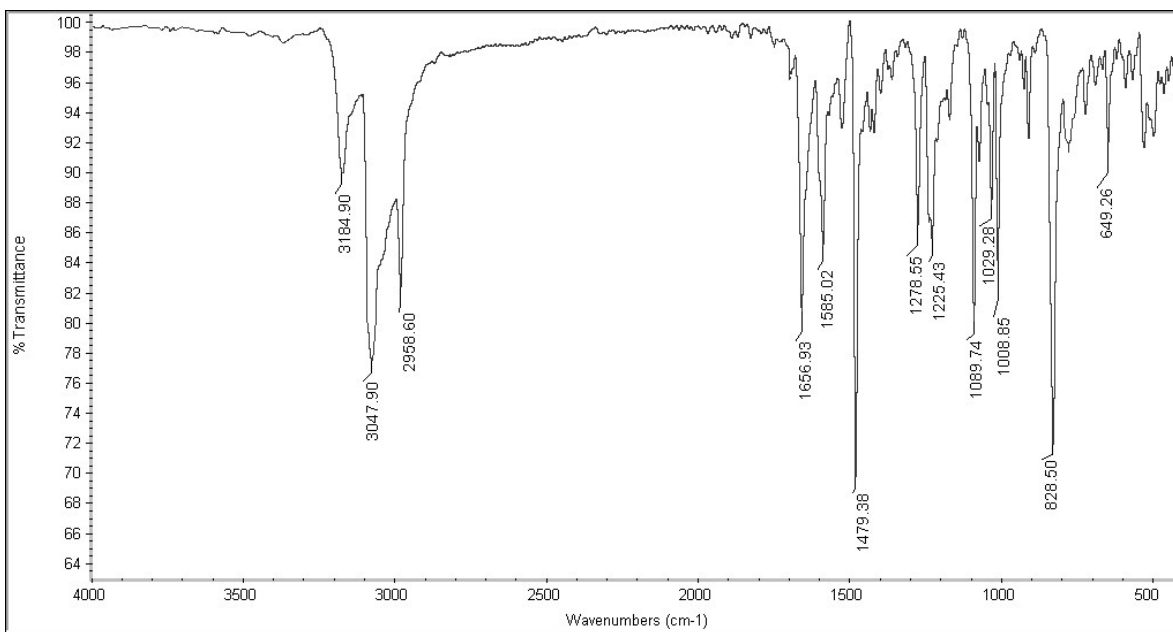
Figure S11. FT-IR spectrum of SL₃.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth


            1 Sample(s) in Group No : 6
Component Name Average
-------------- --------------
Nitrogen%        5.64713604
Carbon%         86.18475183
Hydrogen%        7.98096756
Sulphur%         0
```

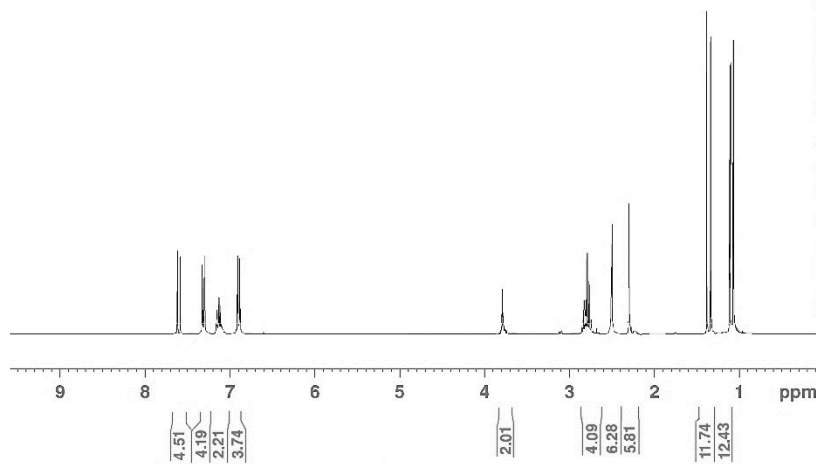**Figure S12.** CHNS elemental analysis of SL₃.
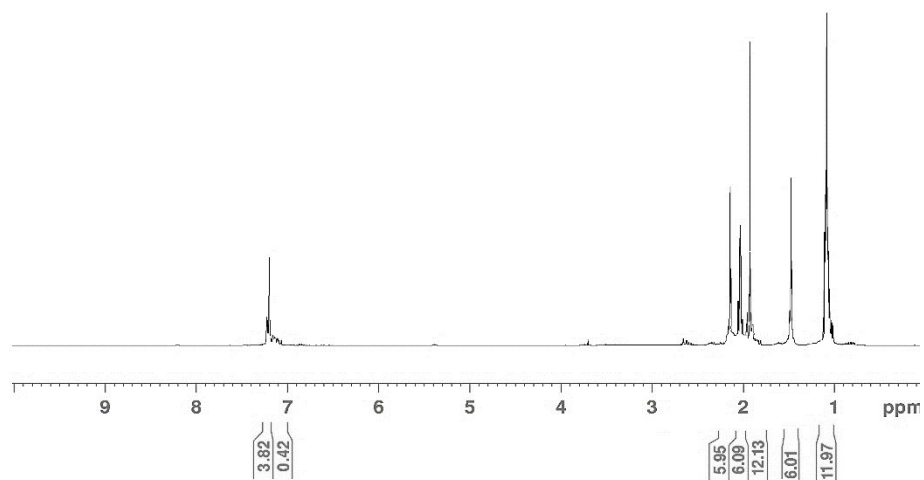
Figure S13. ^{1}H NMR spectrum of SL$_4$.

Chem. Dep., Sciences Faculty, Ferdowsi Univ., Mashhad, IRAN
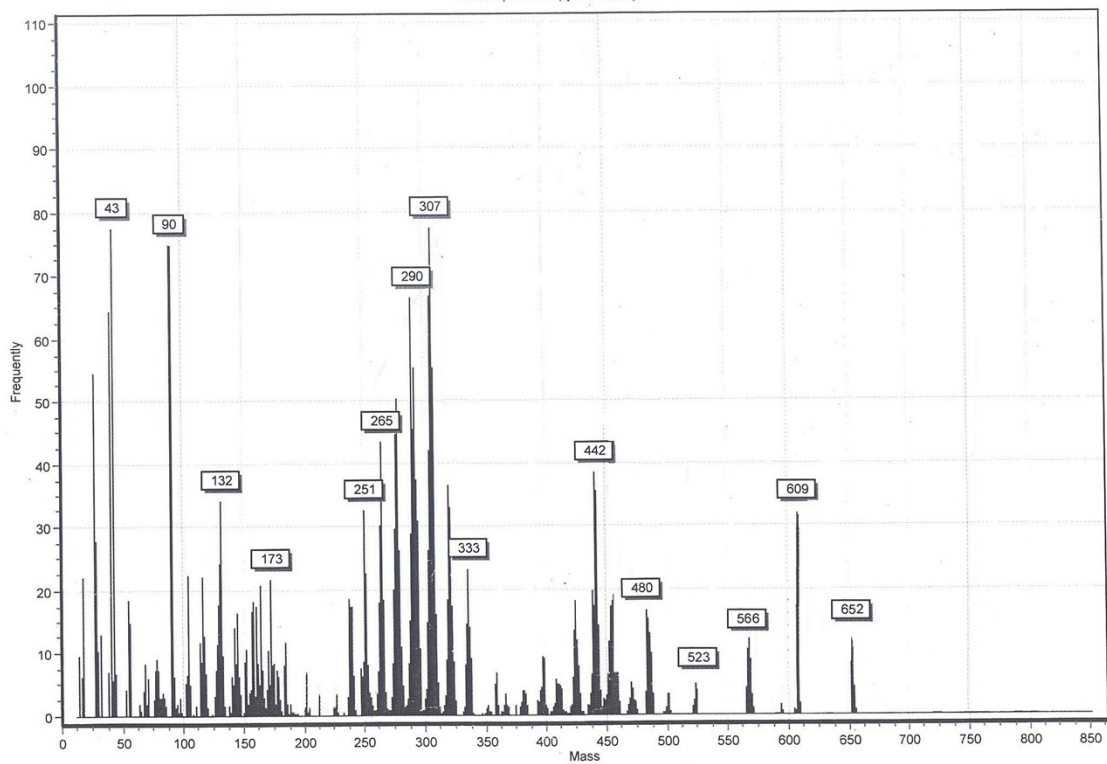Mass Spectroscopy Laboratory

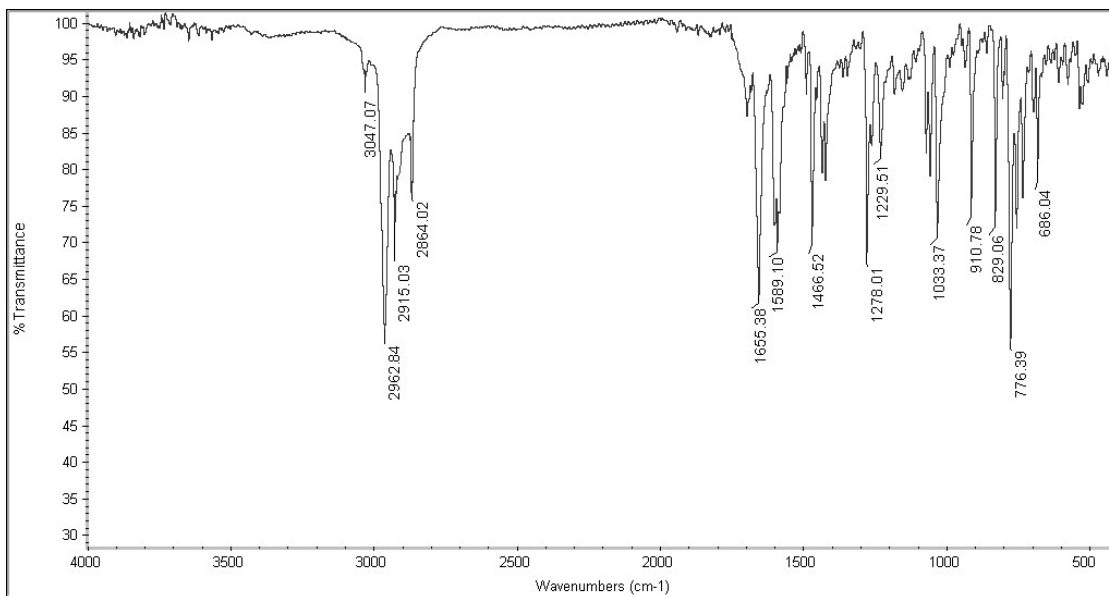**Figure S14.** Mass spectrum of SL$_4$.

Figure S15. FT-IR spectrum of SL$_4$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No : 2
Component Name Average
-------------- --------------
Nitrogen%        10.51360663
Carbon%          79.98844215
Hydrogen%        8.542706966
Sulphur%         0
```

Figure S16. CHNS elemental analysis of SL$_4$.
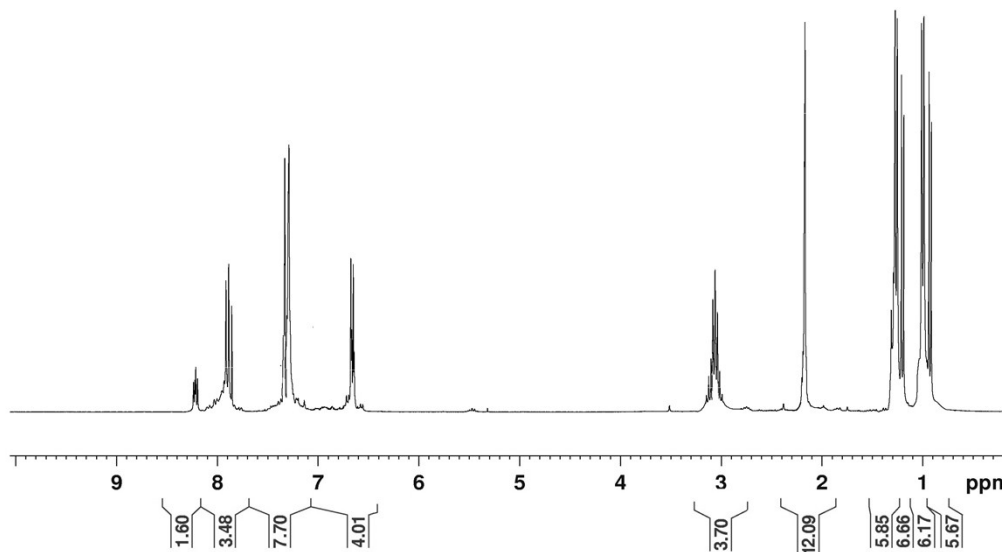
Figure S17. ^{1}H NMR spectrum of SL$_5$.

Figure S18. Mass spectrum of SL$_5$.

S16

Figure S19. FT-IR spectrum of SL$_5$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No : 9
Component Name Average
-------------- --------------

Nitrogen%       6.982901459
Carbon%         85.90104645
Hydrogen%       7.091677689
Sulphur%        0
```

Figure S20. CHNS elemental analysis of SL$_5$.

Figure S21. ^{1}HNMR spectrum of SL$_7$.

Chem. Dep., Sciences Faculty, Ferdowsi Univ., Mashhad, IRAN
Mass Spectroscopy Laboratory
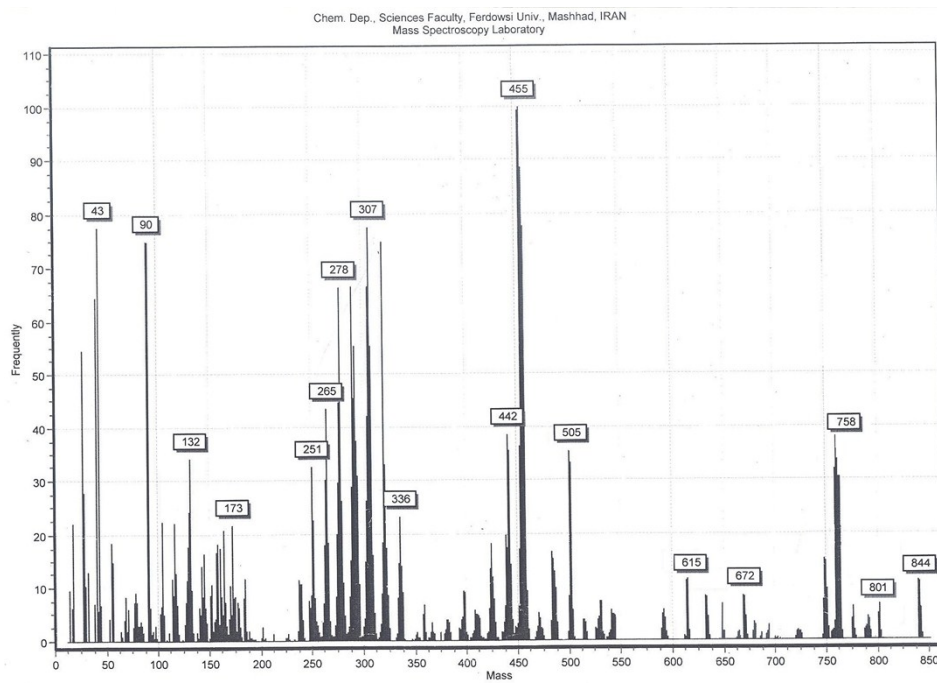

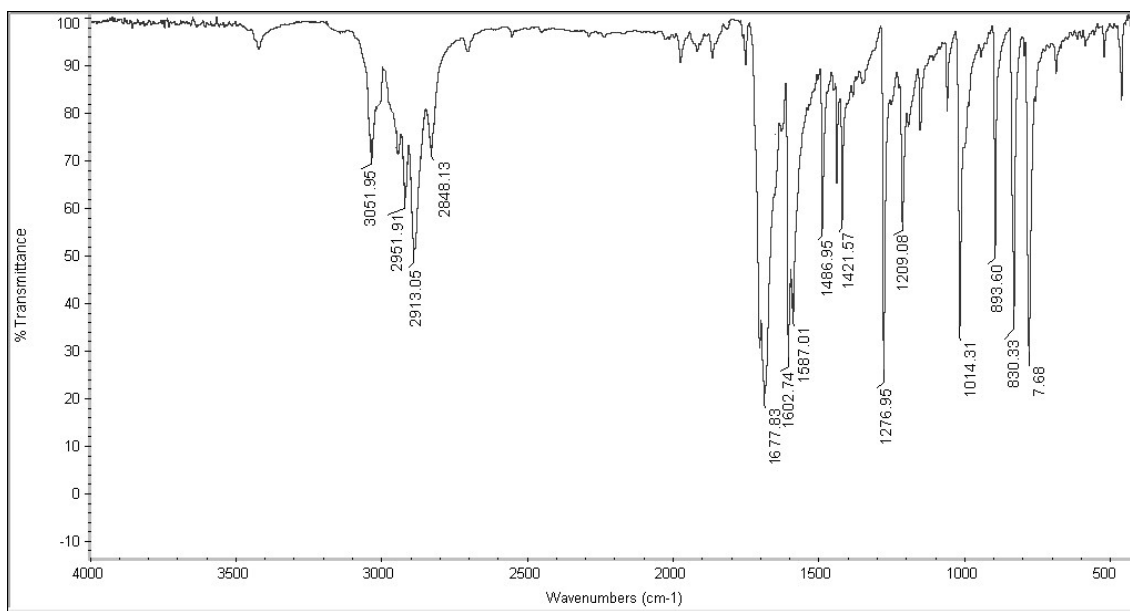**Figure S22.** Mass spectrum of SL$_7$.

Figure S23. FT-IR spectrum of SL$_7$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth


         1 Sample(s) in Group No : 7
Component Name Average
-------------  -------------

Nitrogen%       8.621598478
Carbon%         82.12136176
Hydrogen%       8.539784489
Sulphur%        0
```

Figure S24. CHNS elemental analysis of SL$_7$.
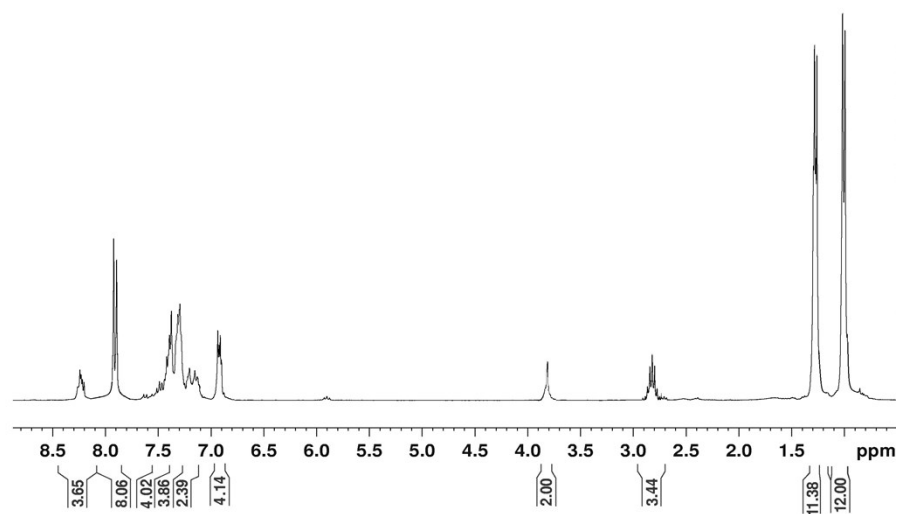
Figure S25. ^{1}HNMR spectrum of SL$_8$.

Figure S26. Mass spectrum of SL$_8$.

Figure S27. FT-IR spectrum of SL$_8$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

      8        1 Sample(s) in Group No : 12
Component Name Average
-------------- --------------
Nitrogen%        6.652806184
Carbon%         86.58144204
Hydrogen%        6.712966966
Sulphur%         0
```
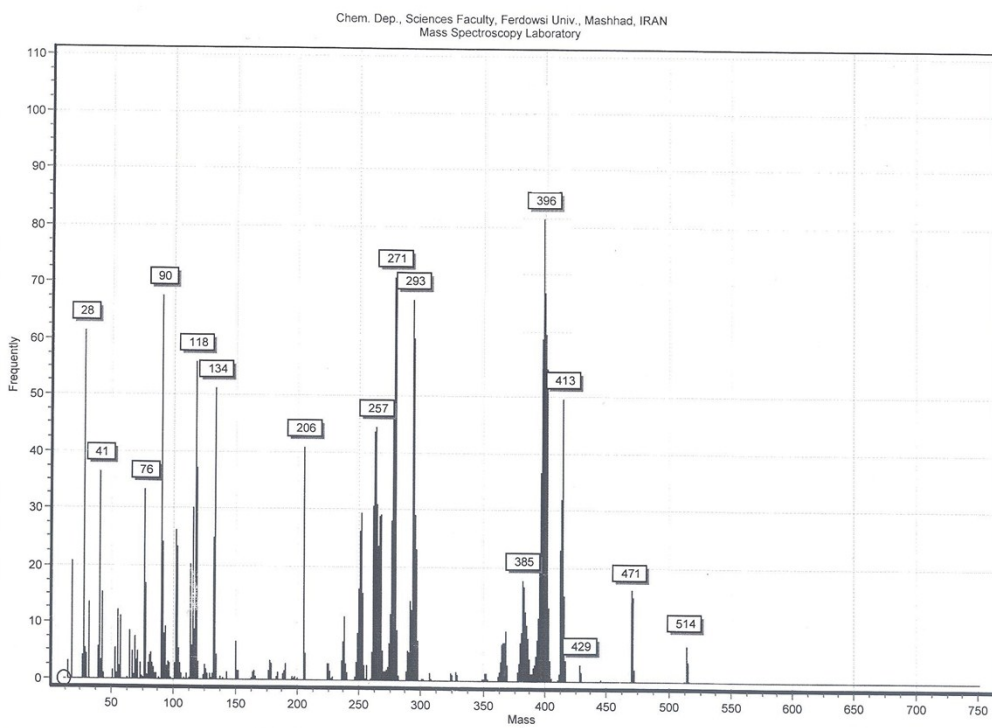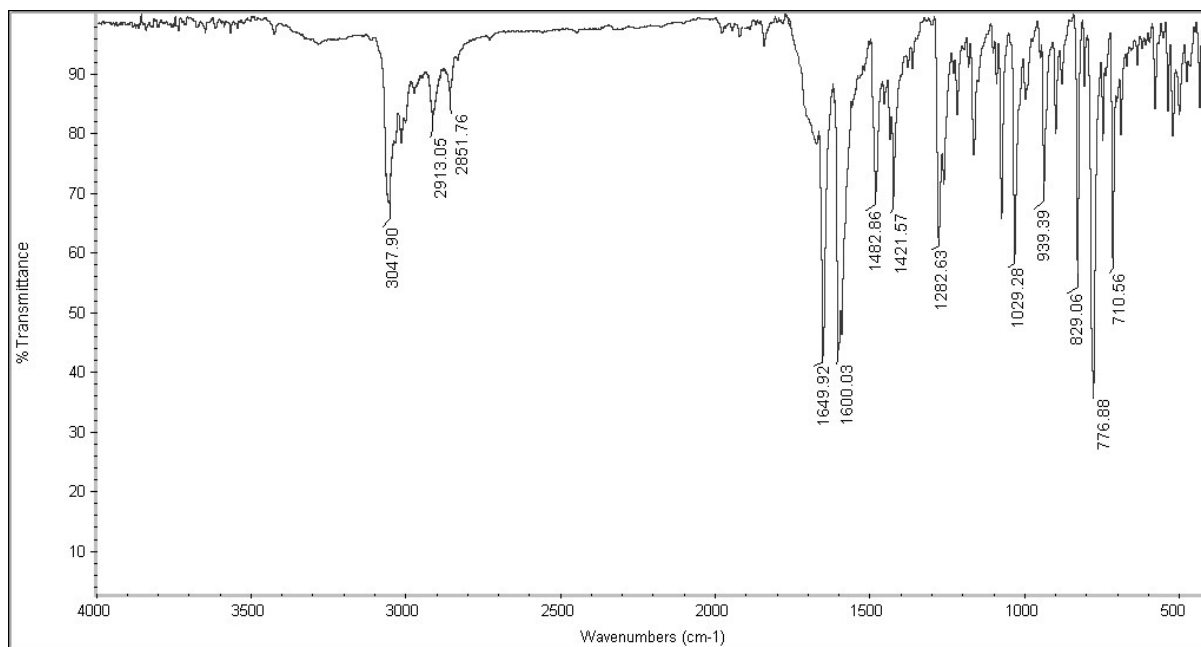
Figure S28. CHNS elemental analysis of SL$_8$.
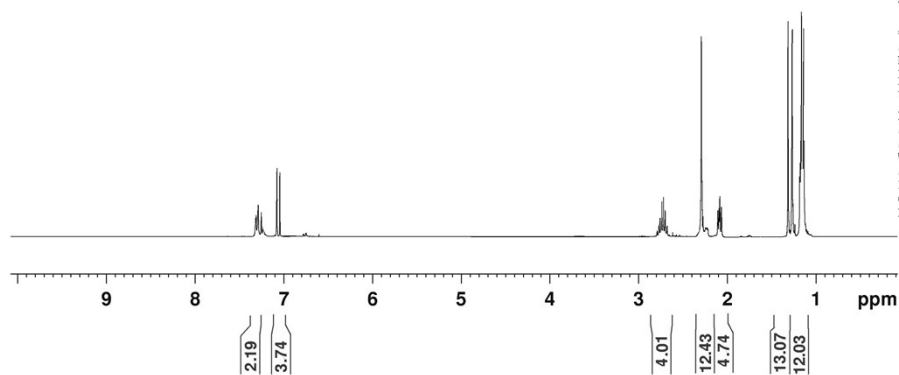
Figure S29. ^{1}HNMR spectrum of SL$_9$.

Figure S30. Mass spectrum of SL$_9$.

S22

Figure S31. FT-IR spectrum of SL$_9$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth


     8        1 Sample(s) in Group No : 16
Component Name Average
-------------- --------------
Nitrogen%        10.934591658
Carbon%          79.16179816
Hydrogen%        9.627678101
Sulphur%         0
```
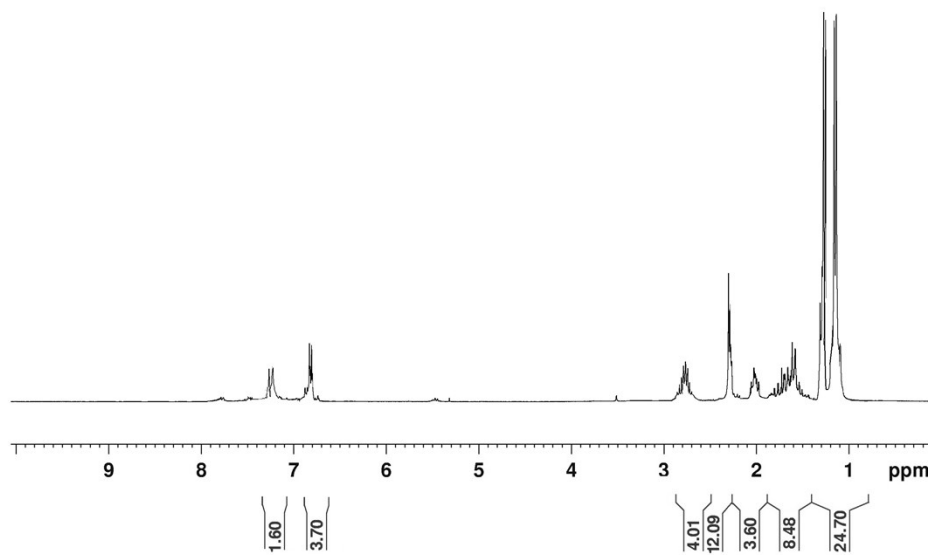
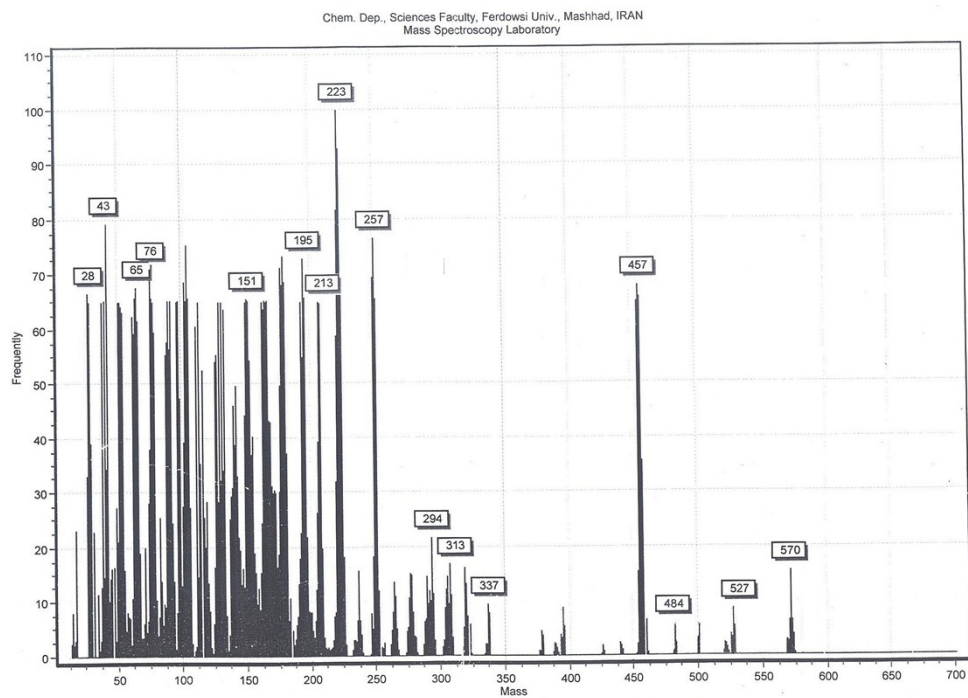**Figure S32.** CHNS elemental analysis of SL$_9$

Figure S33. ^{1}HNMR spectrum of SL$_{10.}$

Figure S34. Mass spectrum of SL$_{10}$.
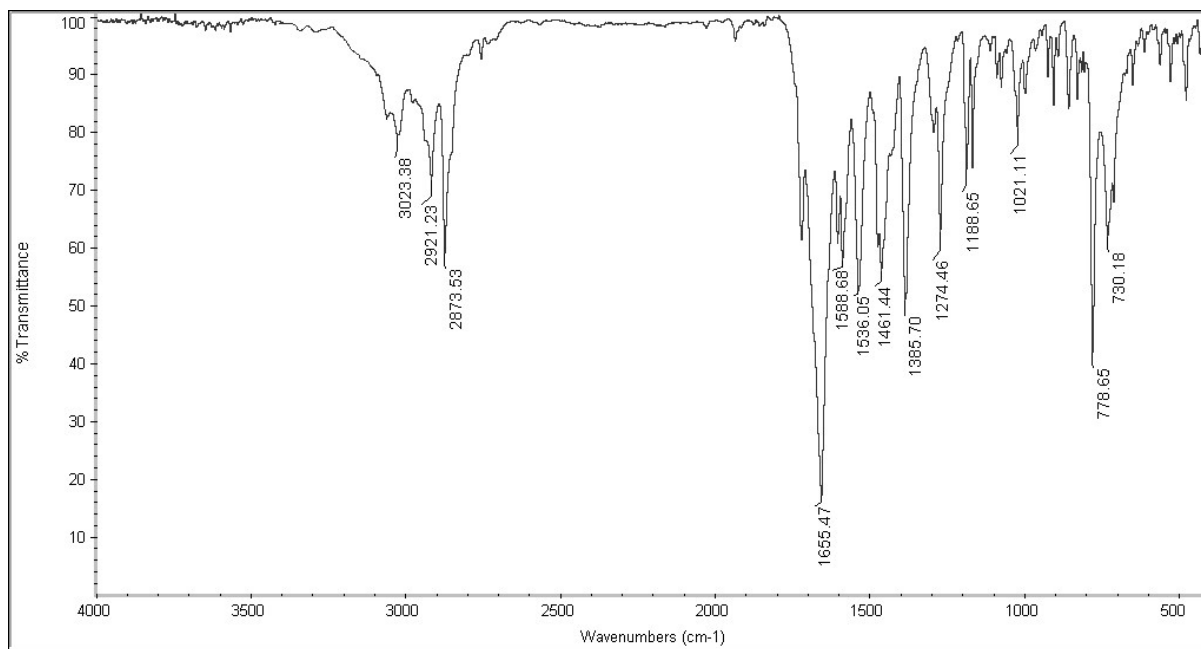
S24

Figure S35. FT-IR spectrum of SL$_{10}$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth


      8         1 Sample(s) in Group No : 18
Component Name Average
- - - - - - - - - - - - - -   - - - - - - - - - - - - - -
Nitrogen%       9.732784412
Carbon%        80.00736176
Hydrogen%      10.07419878
Sulphur%        0
```

Figure S36. CHNS elemental analysis of SL$_{10}$.

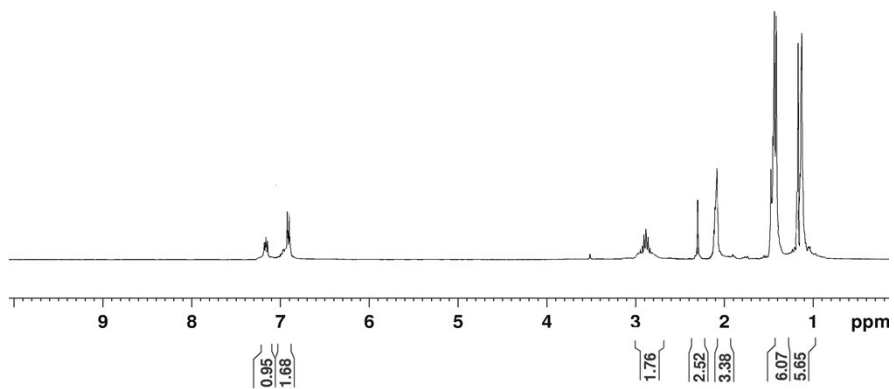**Figure S37.** ^{1}HNMR spectrum of SLM$_2$.
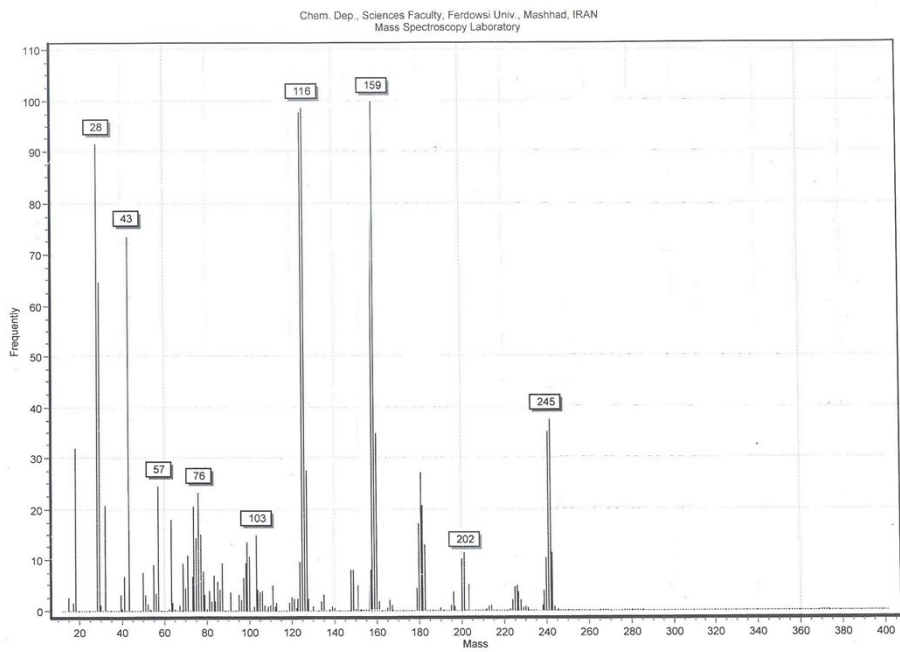

Figure S38. Mass spectrum of SLM$_2$.
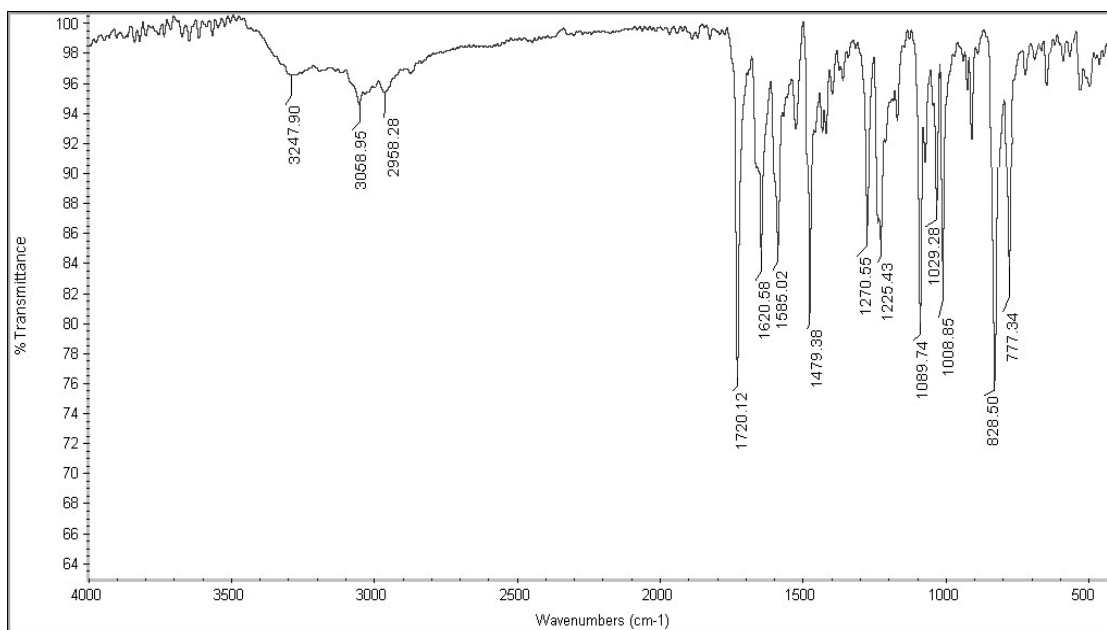
Figure S39. FT-IR spectrum of SLM₂.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

        8        1 Sample(s) in Group No : 11
Component Name Average
- - - - - - - - - - - - - -   - - - - - - - - - - - - - -
Nitrogen%        5.312901485
Carbon%          77.92104611
Hydrogen%        9.117677601
Sulphur%         0
```

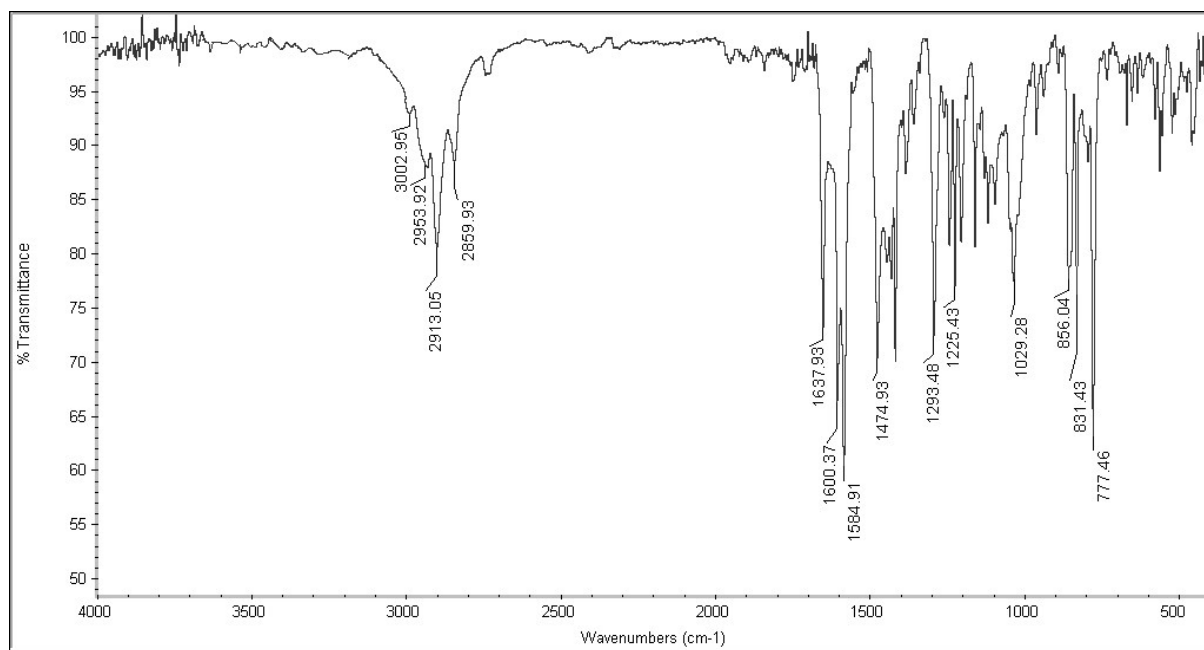**Figure S40.** CHNS elemental analysis of SLM₂.

Figure S41. FT-IR spectrum of MC$_1$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No : 1
Component Name Average
-------------- --------------
Nitrogen%       4.230158659
Carbon%         48.29459878
Hydrogen%       4.907647101
Sulphur%        0
```

Figure S42. CHNS elemental analysis of MC$_1$.
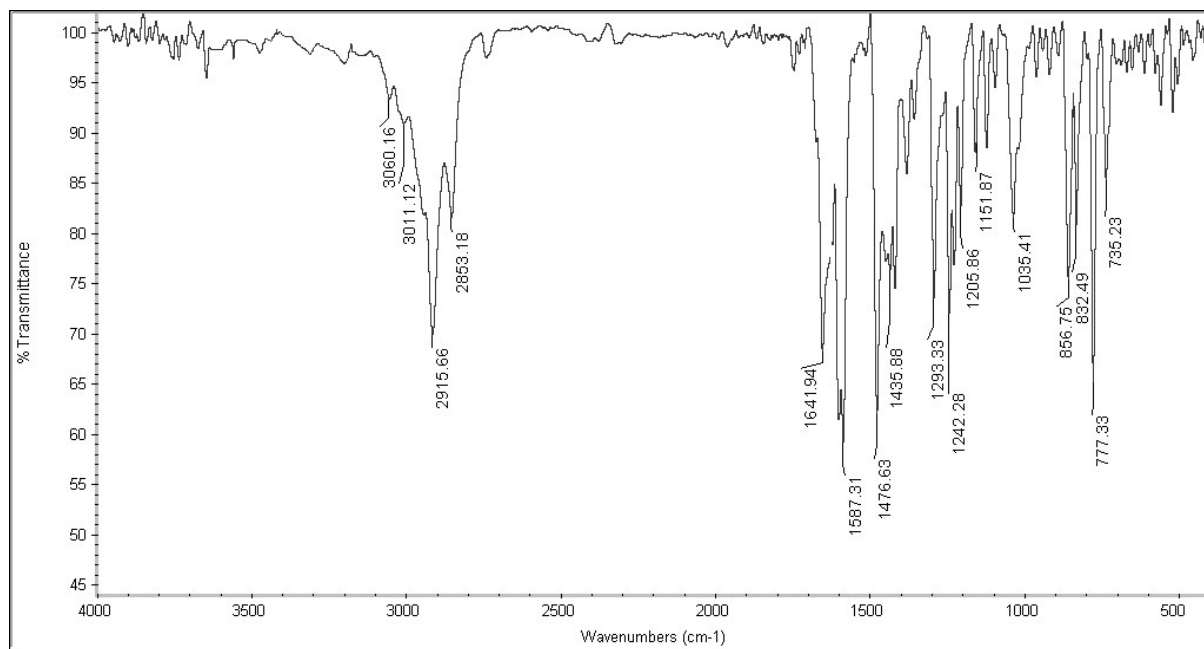
Figure S43. FT-IR spectrum of MC$_2$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth


           1 Sample(s) in Group No : 3
Component Name Average
------------- -------------

Nitrogen%        4.166429696
Carbon%          53.23644213
Hydrogen%        4.232706965
Sulphur%         0
```

Figure S44. CHNS elemental analysis of MC$_2$.
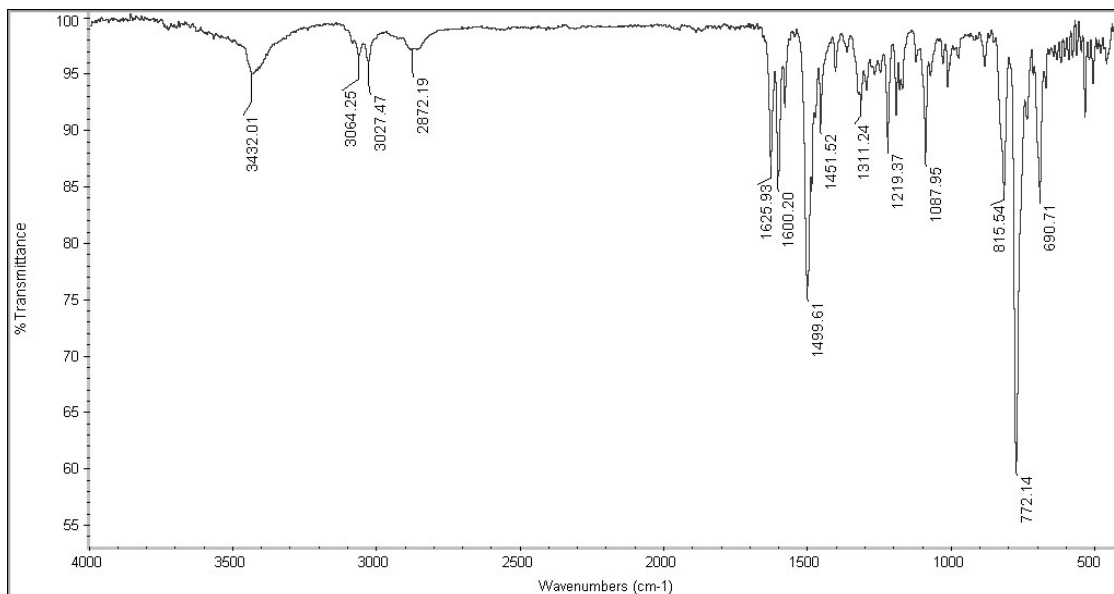
Figure S45. FT-IR spectrum of MC$_3$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No :  13
Component Name Average
-------------- --------------
Nitrogen%        3.911598123
Carbon%         59.89036180
Hydrogen%        5.539784364
Sulphur%         0
```
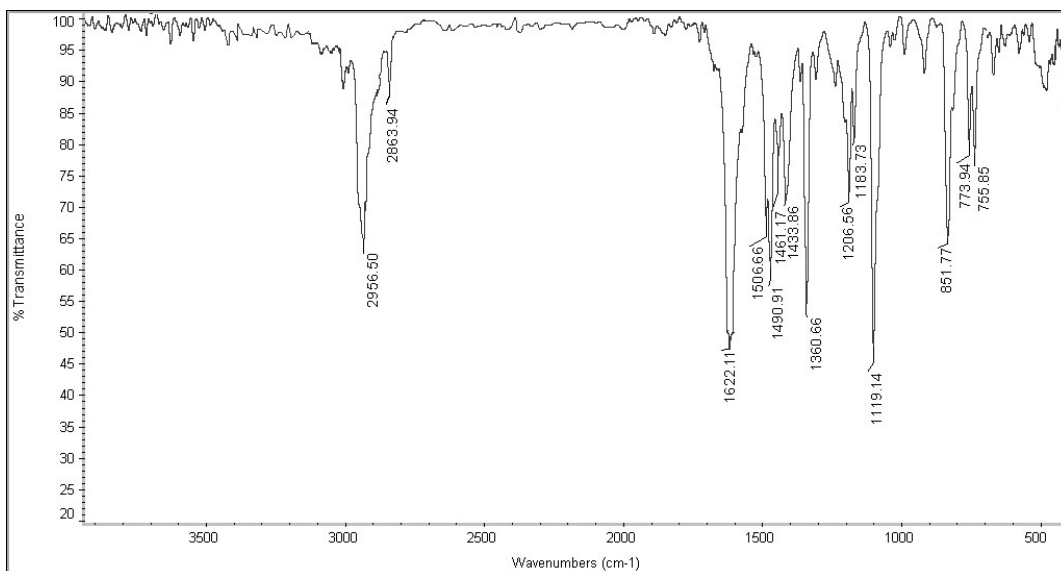
Figure S46. CHNS elemental analysis of MC$_3$.

Figure S47. FT-IR spectrum of BC$_1$.

Figure S48. CHNS elemental analysis of BC$_1$.
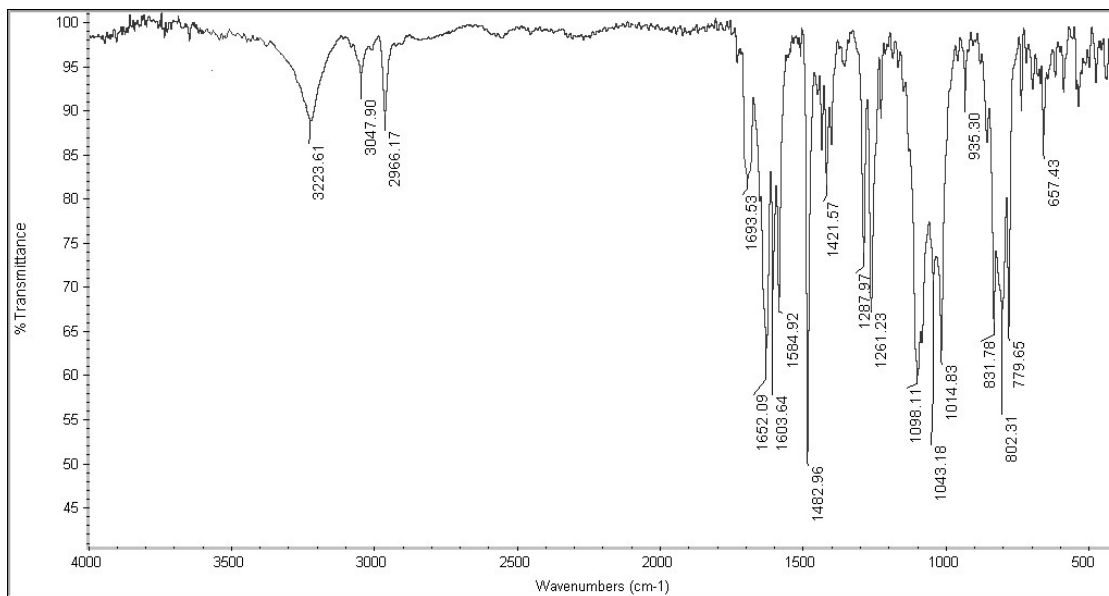
Figure S49. FT-IR spectrum of BC_2.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

              1 Sample(s) in Group No :  10
Component Name Average
-------------- --------------
Nitrogen%       4.004838448
Carbon%        55.63718384
Hydrogen%       4.213483986
Sulphur%        0
```

Figure S50. CHNS elemental analysis of BC_2.
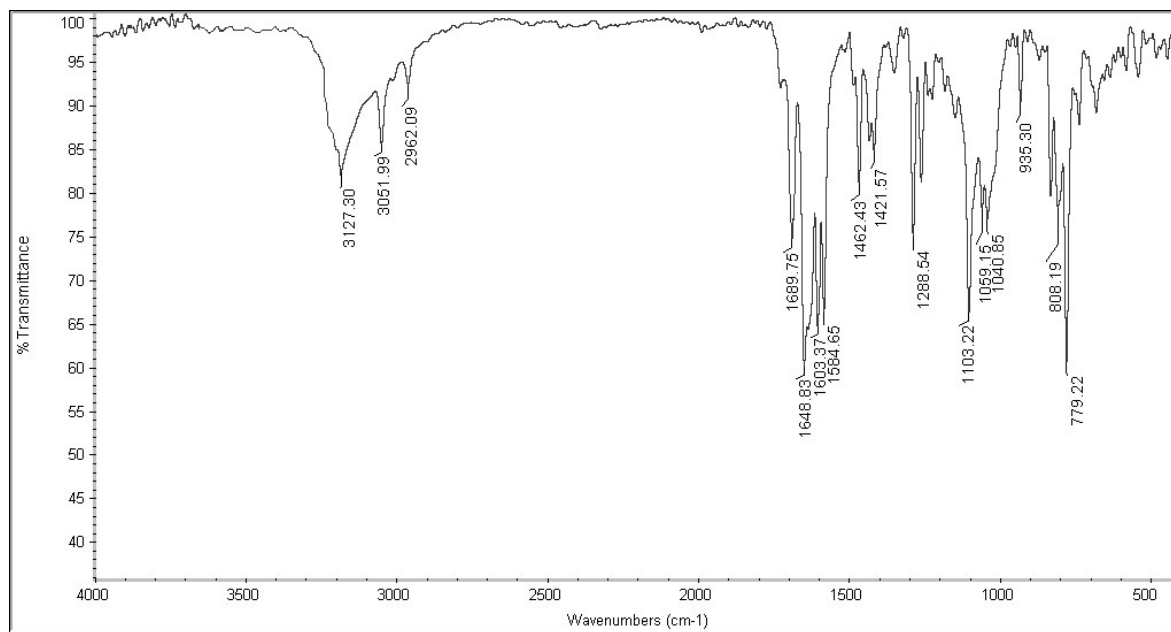
Figure S51. FT-IR spectrum of BC$_4$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth


            1 Sample(s) in Group No :  11
Component Name Average
-------------- --------------
Nitrogen%        4.894485055
Carbon%         49.32840183
Hydrogen%        4.970967587
Sulphur%         0
```

Figure S52. CHNS elemental analysis of BC$_4$.
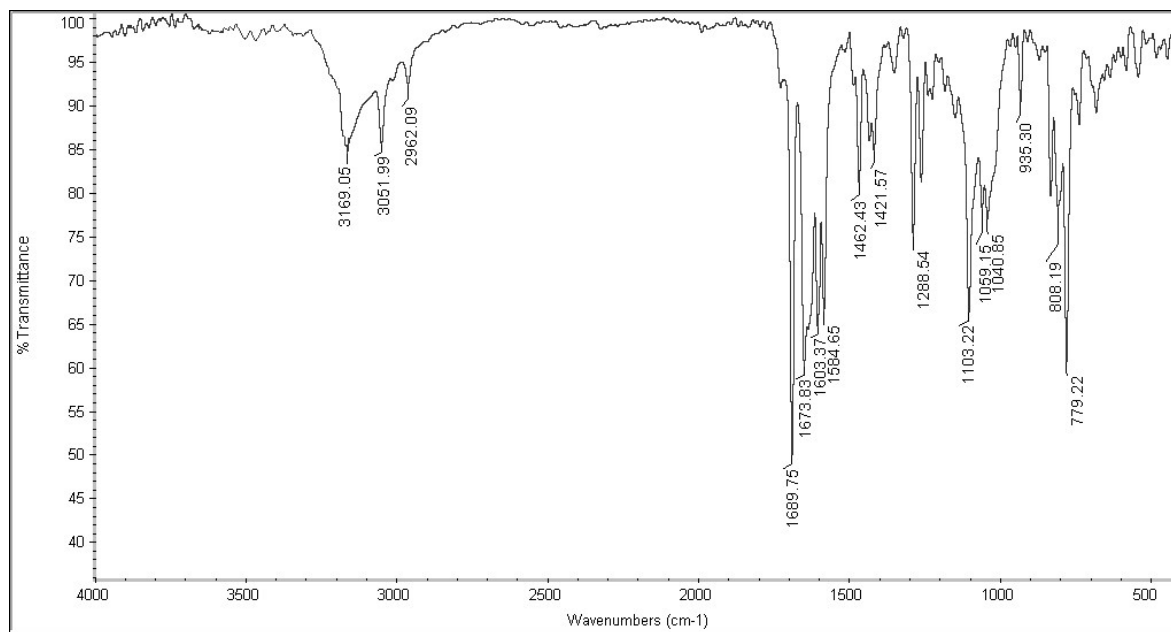
Figure S53. FT-IR spectrum of BC$_5$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No :  14
Component Name Average
-------------- --------------
Nitrogen%        4.212976484
Carbon%         56.93104175
Hydrogen%        4.237685289
Sulphur%         0
```

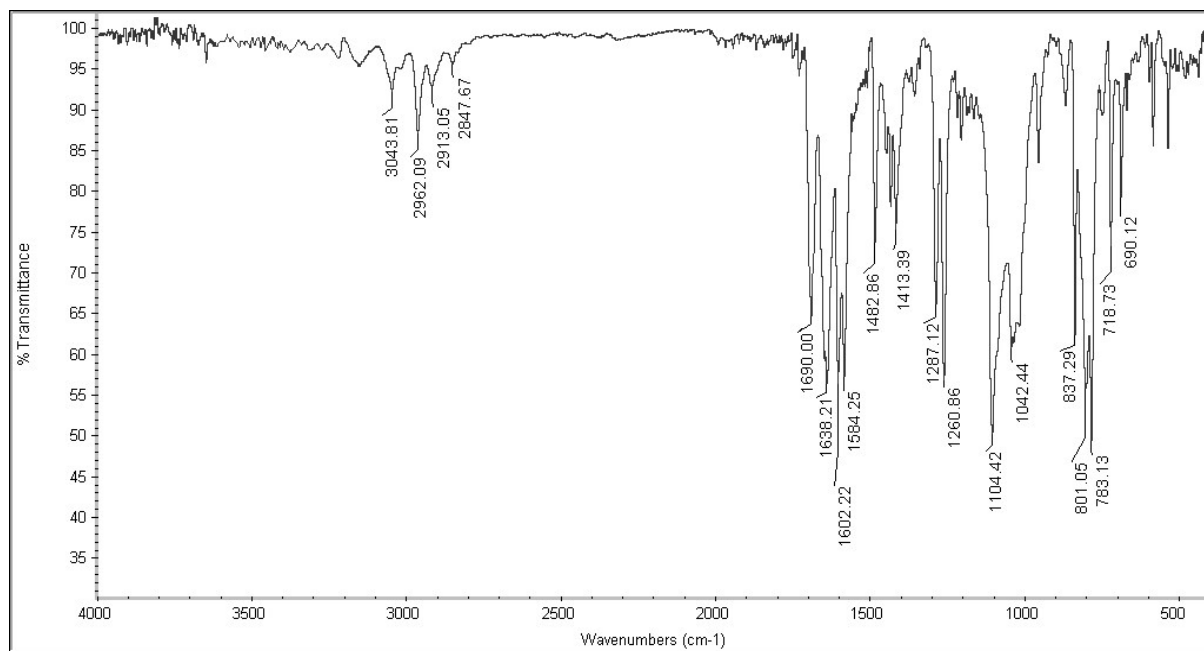**Figure S54.** CHNS elemental analysis of BC$_5$.

S55. FT-IR of BC$_6$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

             1 Sample(s) in Group No :  15
Component Name Average
-------------- --------------
Nitrogen%        5.724118040
Carbon%         42.68875313
Hydrogen%        5.147167565
Sulphur%         0
```

Figure S56. CHNS elemental analysis of BC$_6$.
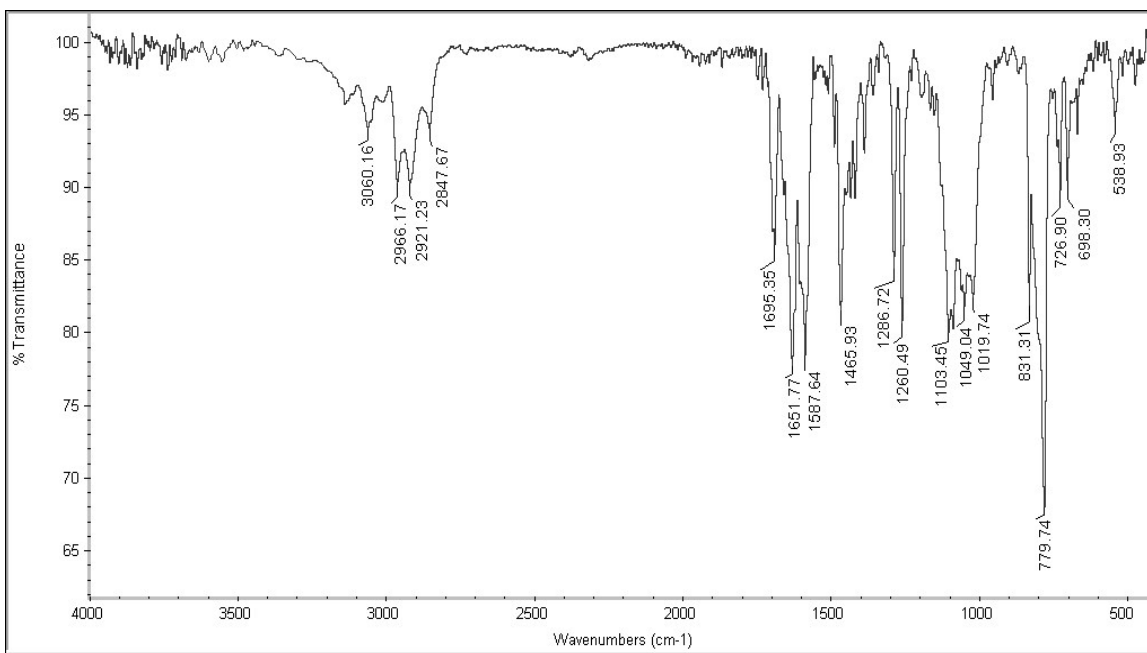
Figure S57. FT-IR spectrum of BC$_7$.

```
Eager 300 Summarize Results

    Method Name : NCHS
Method Filename : Copy of Copy of N C H S-bkp .mth

            1 Sample(s) in Group No :  19
Component Name Average
-------------- --------------
Nitrogen%       5.531579083
Carbon%        44.89036197
Hydrogen%       5.669702488
Sulphur%        0
```

Figure S58. CHNS elemental analysis of BC$_7$.