Smectic nano clusters in the nematic mesophases of dimeric compounds composed of rod-like azo moieties with lateral substituents

Monika M[*], Arun Roy[≠] and Veena Prasad[*±]

[*]Centre for Nano and Soft Matter Sciences, P.B. No. 1329, Jalahalli, Bengaluru - 560 013, India.

[≠]Raman Research Institute, C.V. Raman Avenue, Sadashivanagar, Bengaluru – 560 080, India.

[±]Corresponding author: veena@cens.res.in

New Journal of Chemistry

Details of synthesis

Compounds (1a-1d)

These compounds were prepared by the diazotization of 4-decyloxy aniline with 3-chloro phenol, 2-chlorophenol, 3-methylphenol and 2-methylphenol respectively, following a procedure reported earlier [1]. The analytical data obtained are as follows:

Compound 1a

m.p. 87.2°C. IR (KBr): 3434, 2920, 2852, 1597, 1507, 1470, 1245, 1150, 1044, 833, 780, 671, 528 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.92 (d, *J* = 8 Hz, 2H, ArH), 7.68 – 7.71 (m, 1H, ArH), 7.03 – 7.04 (m, 1H, ArH), 7.00 (d, *J* = 8 Hz, 2H, ArH), 6.78 – 6.81 (m, 1H, ArH), 6.52 (s, 1H, Ar-OH), 4.03 (t, *J* = 6 Hz, 2H, $-OCH_2-$), 1.28 – 1.85 (m, 16H, $-CH_2-$), 0.87 – 0.90 (m, 3H, $-CH_3$).

Compound 1b

m.p. 78.1°C. IR (KBr): 3148, 2918, 2850, 1601, 1580, 1467, 1255, 1016, 847, 725, 699, 595 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.92 – 7.93 (m, 1H, ArH), 8.87 (d, *J* = 8 Hz, 2H, ArH), 7.78 – 7.81 (m, 1H, ArH), 7.12 – 7.15 (m, 1H, ArH), 7.00 (d, *J* = 8 Hz, 2H, ArH), 5.78 (s, 1H, Ar-OH), 4.04 (t, *J* = 6 Hz, 2H, $-OCH_2-$), 1.28 – 1.85 (m, 16H, $-CH_2-$), 0.87 – 0.90 (m, 3H, $-CH_3$).

Compound 1c

m.p. 82.5°C. IR (KBr): 3396, 2923, 2852, 1582, 1470, 1239, 1145, 1019, 842, 776, 530 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.87 (d, *J* = 8 Hz, 2H, ArH), 7.62 – 7.64 (m, 1H, ArH), 6.99 (d, *J* = 8 Hz, 2H, ArH), 6.69 – 6.77 (m, 2H, ArH), 4.99 (s, 1H, Ar-OH), 4.03 (t, *J* = 6 Hz, 2H, $-OCH_2-$), 2.67 (s, 3H, $-CH_3$-Ar), 1.28 – 1.85 (m, 16H, $-CH_2-$), 0.87 – 0.90 (m, 3H, $-CH_3$).

Compound 1d

m.p. 81.6°C. IR (KBr): 3180, 2921, 2851, 1594, 1503, 1253, 1100, 842, 724, 548 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 8.86 (d, *J* = 8 Hz, 2H, ArH), 7.66 – 7.72 (m, 2H, ArH), 7.00 (d, *J* = 8 Hz, 2H, ArH), 8.87 – 8.85 (m, 1H, ArH), 5.06 (s, 1H, Ar-OH), 4.03 (t, *J* = 6 Hz, 2H, -OCH_2-), 2.33 (s, 3H, -CH_3-Ar), 1.28 – 1.85 (m, 16H, -CH_2-), 0.87 – 0.90 (m, 3H, -CH_3).

Dimer series A

Compound **1a** (0.28 mmol), Compound **2** (0.14 mmol) and a catalytic amount of 4-dimethyl-aminopyridine (DMAP) were dissolved in dry CH_2Cl_2 (20 ml). To this was added 1,3-dicyclohexylcarbodiimide (DCC) (0.15 mmol) and the reaction mixture was stirred at room temperature for 24 h under nitrogen. The dicyclohexylurea formed was removed by filtration. The crude product obtained on evaporation of the filtrate was purified by column chromatography and then recrystallisation using acetone as a solvent. The yield obtained was about 33%. The analytical data obtained for one of the dimers, ***A-6*** are as follows:

IR (KBr): 2920, 2851, 1766, 1580, 1476, 1250, 1202, 1142, 1017, 843, 727, 637, 562 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.92 – 7.96 (m, 4H, ArH), 7.72 – 7.74 (m, 2H, ArH), 7.07 – 7.34 (m, 4H, ArH), 6.98 – 7.01 (m, 4H, ArH), 4.04 (t, *J* = 6 Hz, 4H, -OCH_2-), 2.61 (t, *J* = 6 Hz, 4H, -CH_2COO-), 1.28 – 1.85 (m, 44H, -CH_2-), 0.87 – 0.90 (m, 6H, -CH_3). EA: calcd. for $C_{52}H_{68}Cl_2N_4O_6$: C, 68.18, H, 7.48, N, 6.12; found: C, 68.20, H, 7.55, N, 6.40.

Dimer series B

This was prepared following a similar procedure followed for series A, using Compound **1b** instead of **1a**. The yield obtained was ~29%. The analytical data obtained for one of the dimers, ***B-6*** are as follows:

IR (KBr): 2921, 2852, 1769, 1603, 1503, 1471, 1251, 1142, 1095, 1046, 832, 723, 591 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.97 – 7.98 (m, 2H, ArH), 7.87 – 7.91 (m, 4H, ArH), 7.81 – 7.84 (m, 2H, ArH), 7.26 – 7.28 (m, 2H, ArH), 6.98 – 7.02 (m, 4H, ArH), 4.05 (t, *J* = 6 Hz, 4H, -OCH_2-), 2.68 (t, *J* = 6 Hz, 4H, -CH_2COO-), 1.29 – 1.88 (m, 44H, -CH_2-), 0.86 – 0.90 (m, 6H, -CH_3). EA: calcd. for $C_{52}H_{68}Cl_2N_4O_6$: C, 68.18, H, 7.48, N, 6.12; found: C, 68.30, H, 7.60, N, 6.25.

Dimer series C

The procedure is same as series A, except that Compound **1c** was used instead of **1a.** The yield obtained was ~30%. The analytical data obtained for one of the dimers, ***C-6,*** are as follows:

IR (KBr): 2922, 2851, 1765, 1600, 1581, 1499, 1250, 1147, 1016, 836, 723, 637, 528 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.86 – 7.90 (m, 4H, ArH), 7.64 – 7.66 (m, 2H, ArH), 7.05 – 7.06 (m, 2H, ArH), 6.95 – 7.00 (m, 6H, ArH), 4.03 (t, *J* = 6 Hz, 4H, -OCH_2-), 2.69 (s, 3H, -CH_3-Ar), 2.59 (t, *J* = 6 Hz, 4H, -CH_2COO-), 1.24 – 1.85 (m, 44H, -CH_2-), 0.87 – 0.90 (m, 6H, -CH_3). EA: calcd. for $C_{54}H_{74}N_4O_6$: C 74.11, H 8.52, N 6.40; found: C, 74.27, H, 8.60, N, 6.50.

Dimer series D

The procedure is same as series A, except that Compound **1d** was used instead **1a**. The yield obtained was ~20%. The analytical data obtained for one of the dimers, ***D-6*** are as follows:

IR (KBr): 2919, 2851, 1746, 1603, 1583, 1500, 1243, 1181, 1150, 1020, 839, 720, 590 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.86 – 7.90 (m, 4H, ArH), 7.72 – 7.77 (m, 4H, ArH), 7.13 – 7.15 (m, 2H, ArH), 6.97 – 7.01 (m, 4H, ArH), 4.04 (t, *J* = 6 Hz, 4H, -OCH_2-), 2.64 (t, *J* = 6 Hz, 4H, -CH_2COO-), 2.27 (s, 3H, -CH_3-Ar), 1.28 – 1.86 (m, 44H, -CH_2-), 0.87 – 0.90 (m, 6H, -CH_3). EA: calcd. for $C_{54}H_{74}N_4O_6$: C, 74.11, H, 8.52, N, 6.40; found: C,74.25, H, 8.60, N, 6.52.

Compound I (n = 8)

m.p. 123.8°C. IR (KBr): 2919, 2851, 1719, 1603, 1468, 1273, 1103, 842, 773, 692, 594, 521 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 8.16 – 8.19 (m, 4H, ArH), 7.93 – 7.96 (m, 4H, ArH), 7.78 – 7.80 (m, 2H, ArH), 7.07 – 7.08 (m, 2H, ArH), 6.85 – 6.88 (m, 2H, ArH), 4.35 (t, *J* = 6 Hz, 4H, -OCH_2-), 4.03 (t, *J* = 6 Hz, 4H, -CH_2COO-), 1.28 – 1.83 (m, 48H, -CH_2-), 0.87 – 0.90 (m, 6H, -CH_3). EA: calcd. for $C_{54}H_{72}Cl_2N_4O_6$: C, 68.70, H, 7.69, N, 5.93; found: C, 68.80, H, 7.75, N, 6.00.

Compound II (n = 8)

m.p. 108.3°C. IR (KBr): 2918, 2850, 1709, 1590, 1470, 1308, 1277, 1125, 1048, 1011, 892, 693, 594 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 7.95 – 8.14 (m, 6H, ArH), 7.80 – 7.84 (m, 6H, ArH), 6.96 – 6.98 (m, 2H, ArH), 4.29 (t, *J* = 6 Hz, 4H, -OCH_2-), 4.05 (t, *J* = 6 Hz, 4H, -CH_2COO-), 1.21 – 1.85 (m, 48H, -CH_2-), 0.80 – 0.83 (m, 6H, -CH_3). EA: calcd. for $C_{54}H_{72}Cl_2N_4O_6$: C, 68.70, H, 7.69, N, 5.93; found: C, 68.89, H, 7.70, N, 6.10.

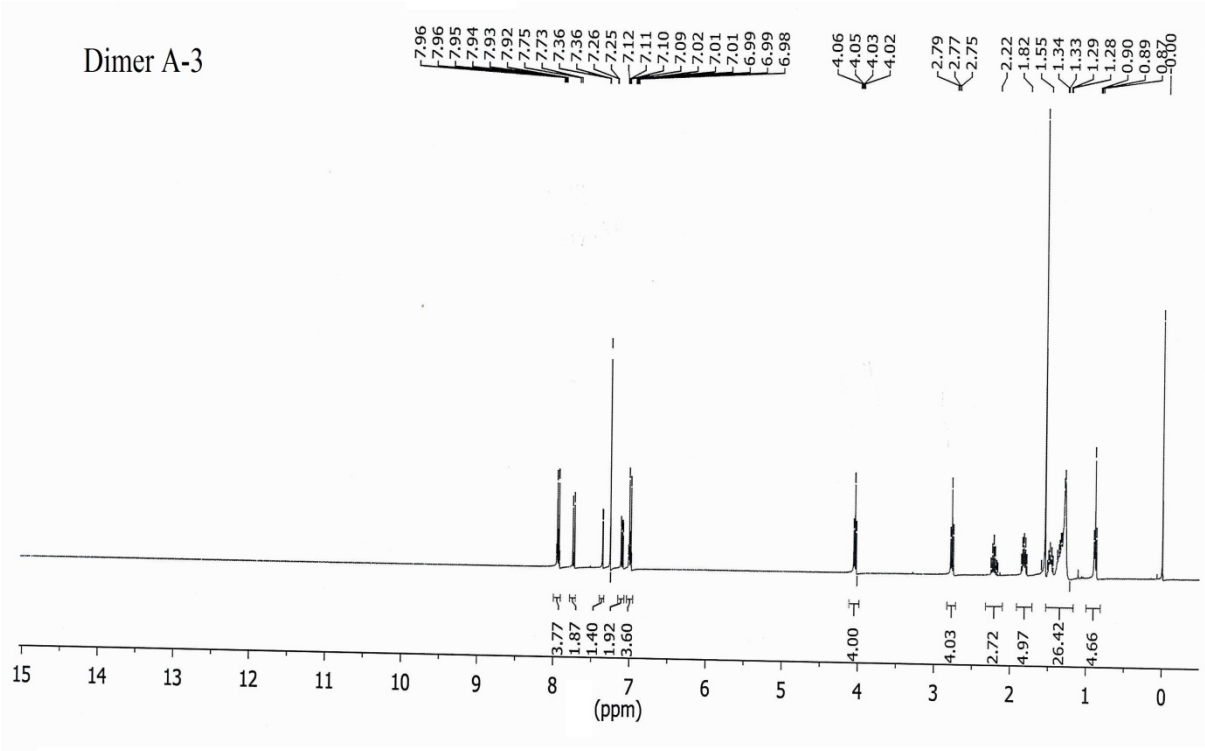
Compound III (n = 8)

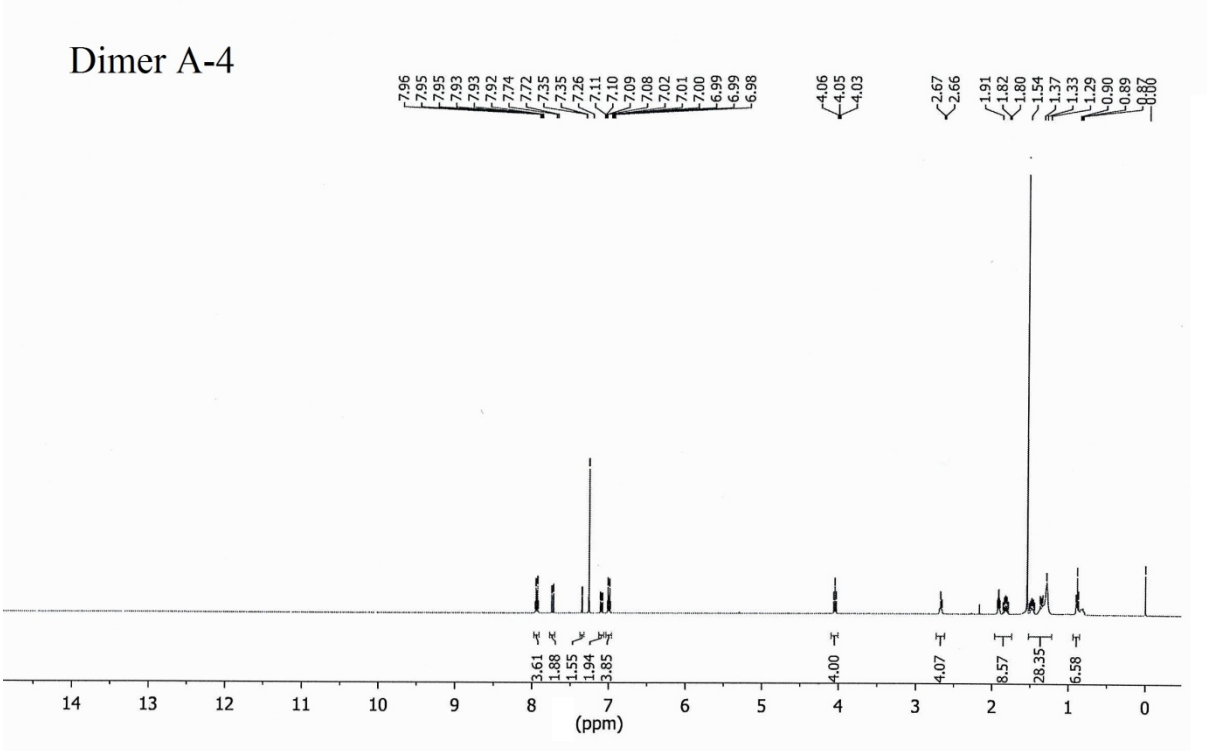
m.p. 128.7°C. IR (KBr): 2918, 2849, 1718, 1603, 1470, 1274, 1249, 1104, 863, 842, 773, 693, 594 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 8.14 – 8.17 (m, 4H, ArH), 7.87 – 7.90 (m, 4H, ArH), 7.72 – 7.74 (m, 2H, ArH), 6.76 – 6.84 (m, 4H, ArH), 4.35 (t, *J* = 6 Hz, 4H, -OCH_2-), 4.02 (t, *J* = 6 Hz, 4H, -CH_2COO-), 2.73 (s, 3H, -CH_3-Ar), 1.28 – 1.84 (m, 44H, -CH_2-), 0.87 – 0.90 (m, 6H, -CH_3). EA: calcd. for $C_{56}H_{78}N_4O_6$: C, 74.47, H, 8.70, N, 6.20; found: C, 74. 60, H, 8.85, N, 6.30.

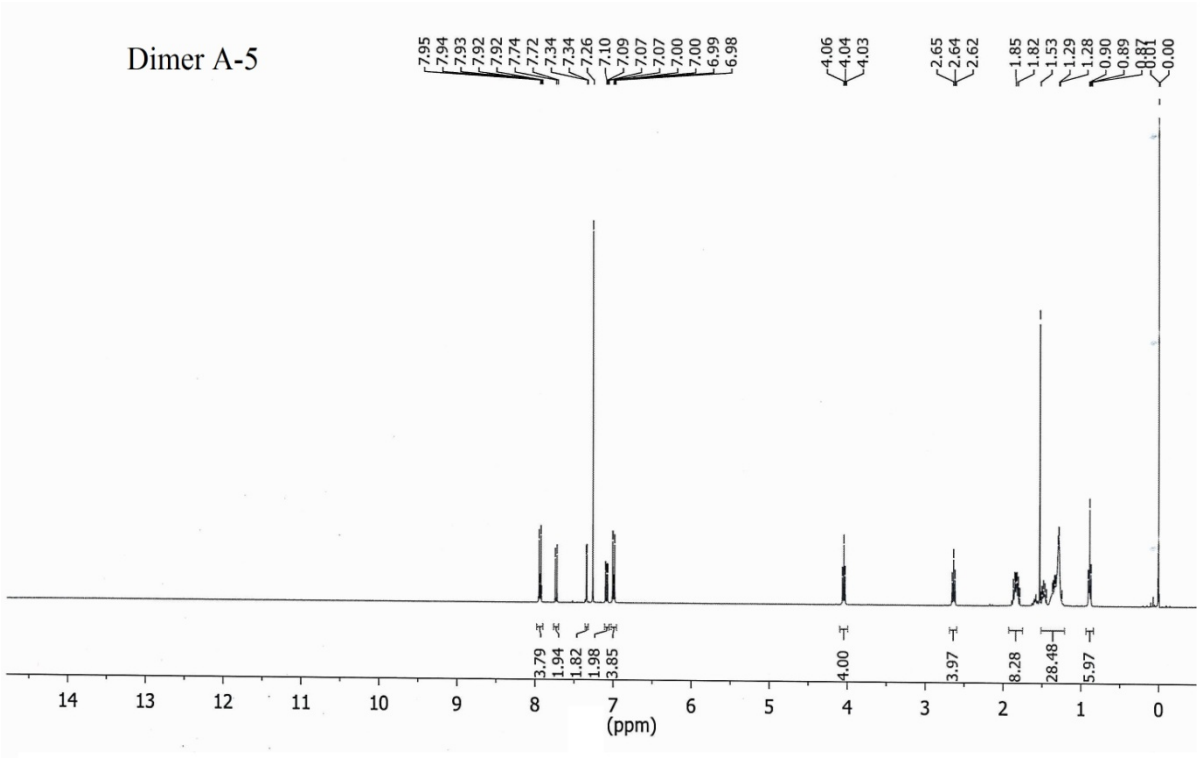
Compound IV (n = 8)

m.p. 121.0°C. IR (KBr): 2921, 2850, 1713, 1598, 1498, 1468, 1259, 1105, 1012, 897, 727, 695, 587 cm^{-1}. ^1H NMR ($CDCl_3$, 400 MHz), δ: 8.13 – 8.20 (m, 4H, ArH), 7.76 – 7.93 (m, 8H, ArH), 6.88 – 6.96, 4.35 (t, *J* = 6 Hz, 4H, -OCH_2-), 4.06 (t, *J* = 6 Hz, 4H, -CH_2COO-), 2.30 (s, 3H, -CH_3-Ar), 1.28 – 1.87 (m, 48H, -CH_2-), 0.87 – 0.90 (m, 6H, -CH_3). EA: calcd. for $C_{56}H_{78}N_4O_6$: C, 74.47, H, 8.70, N, 6.20; found: C, 74.50, H, 8.95, N, 6.38.

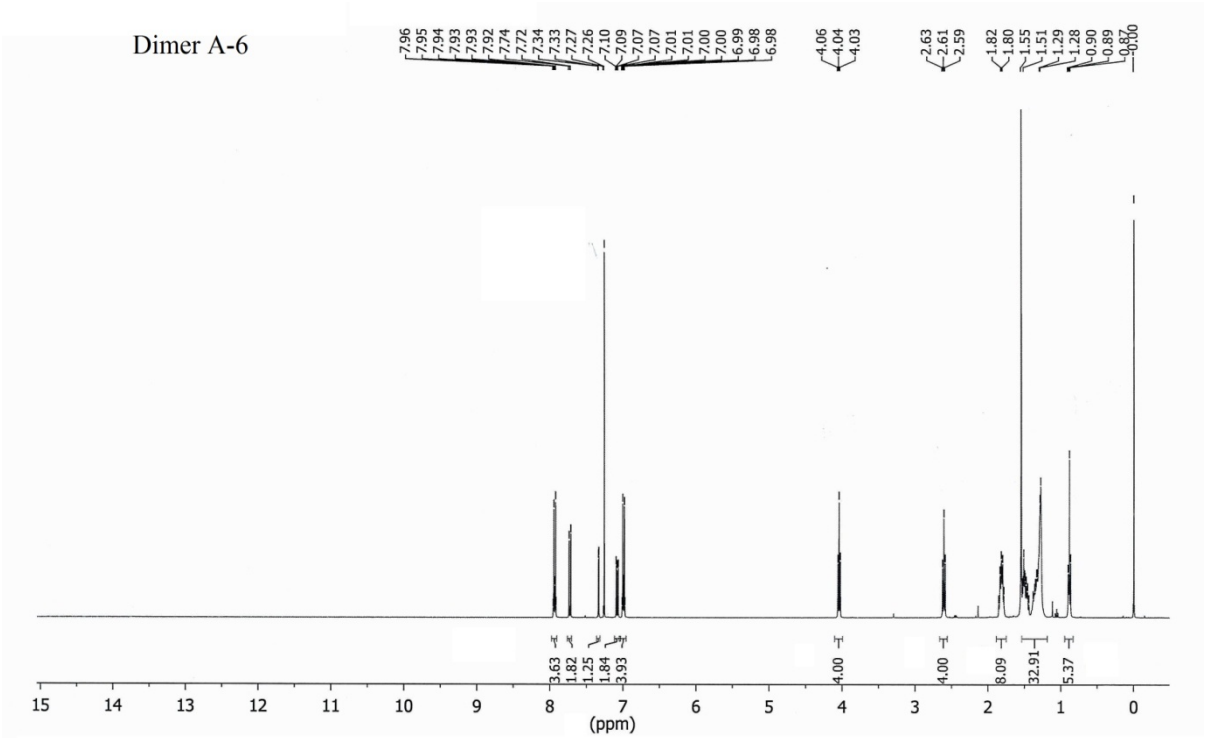
NMR spectra of dimeric compounds synthesised:



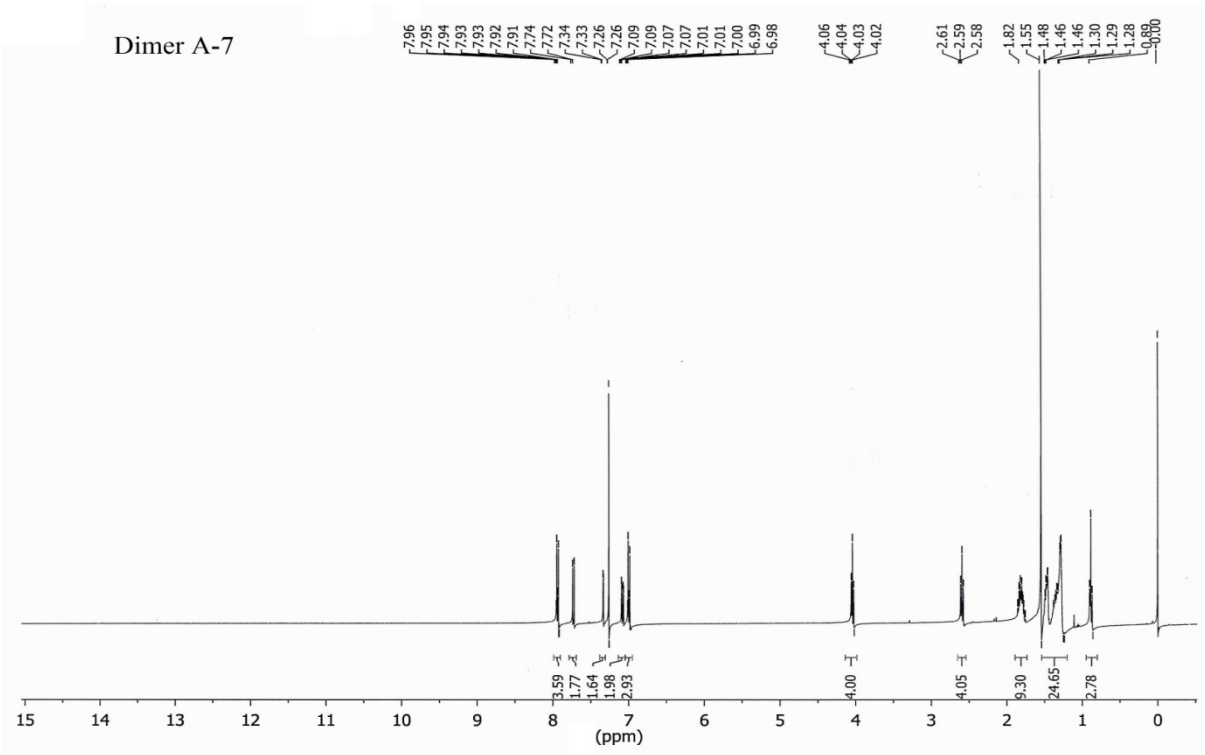



Dimer A-5
7.95
7.94
7.93
7.92
7.92
7.74
7.72
7.34
7.34
7.26
7.10
7.09
7.07
7.07
7.00
7.00
6.99
6.98
4.06
4.04
4.03
2.65
2.64
2.62
1.85
1.82
1.53
1.29
1.28
0.90
0.89
0.87
0.01
0.00
3.79
1.94
1.82
1.98
3.85
4.00
3.97
8.28
28.48
5.97
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
(ppm)

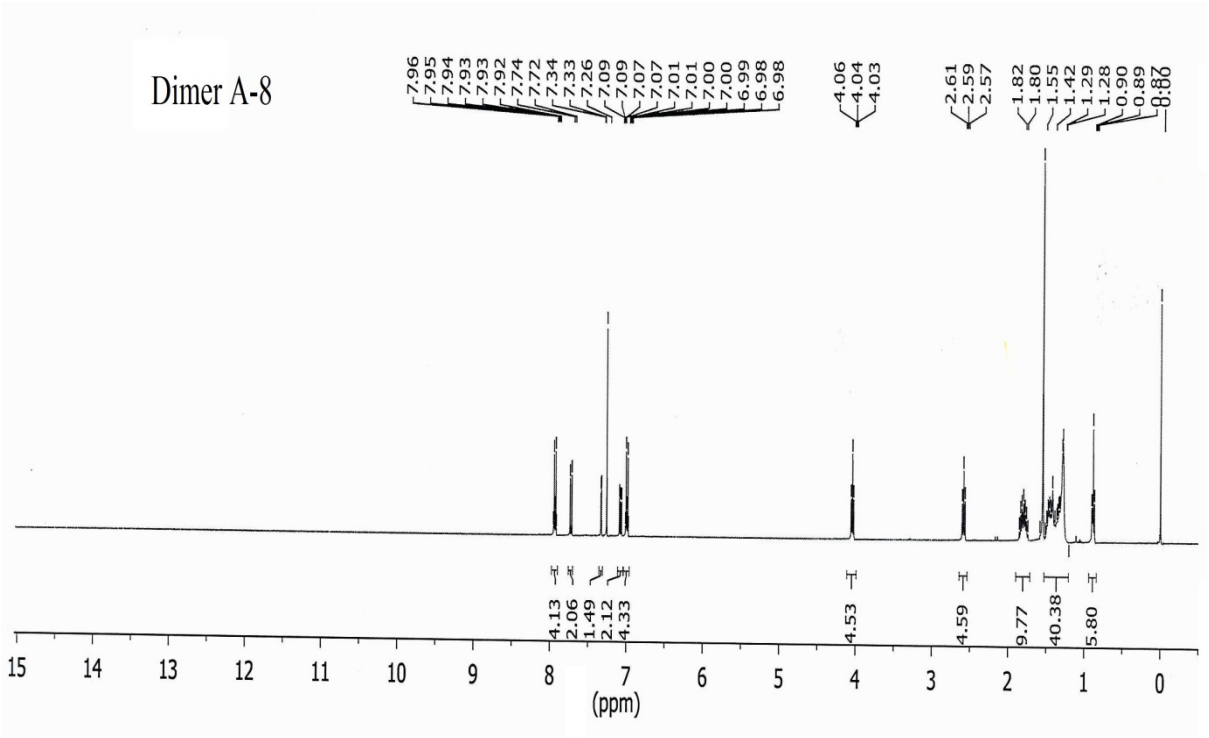
Dimer A-6



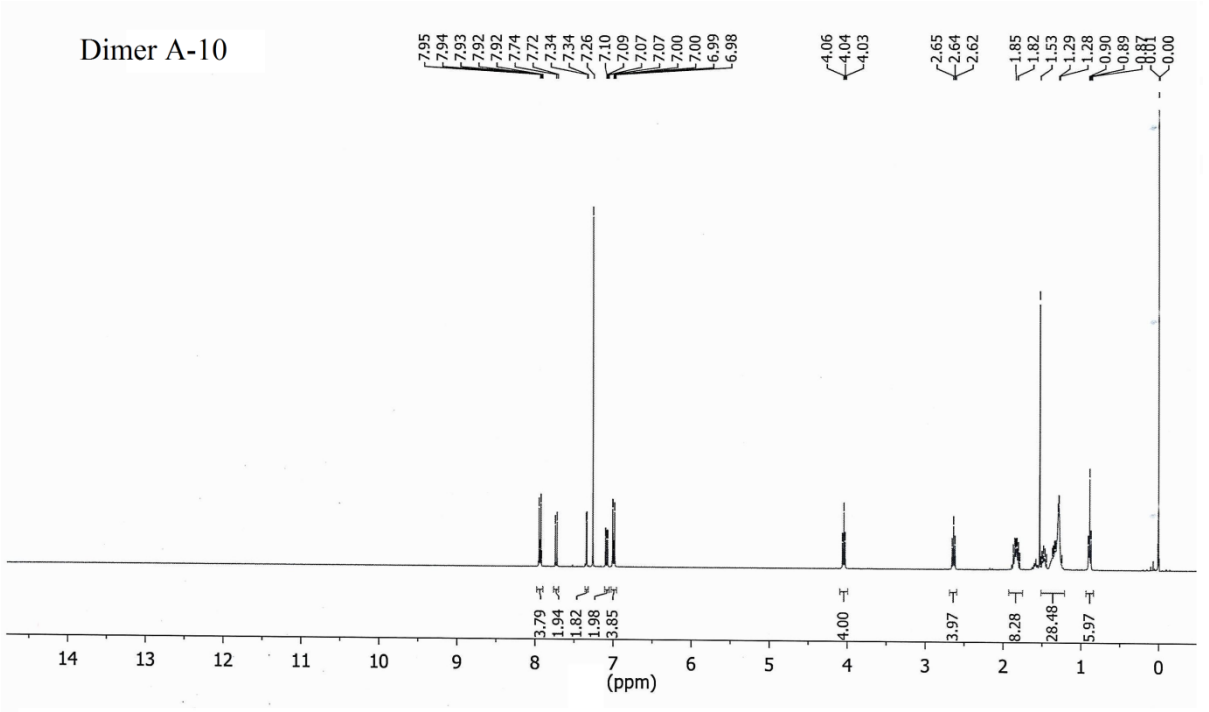
Dimer A-7



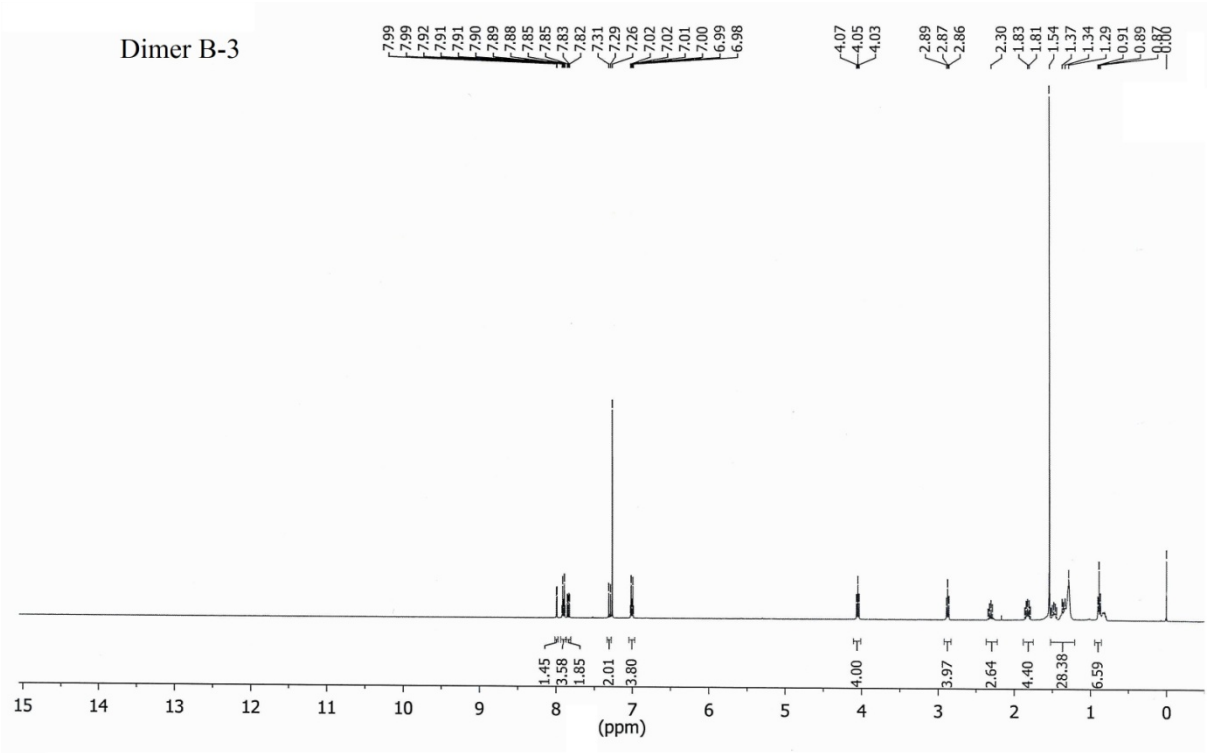
Dimer A-8



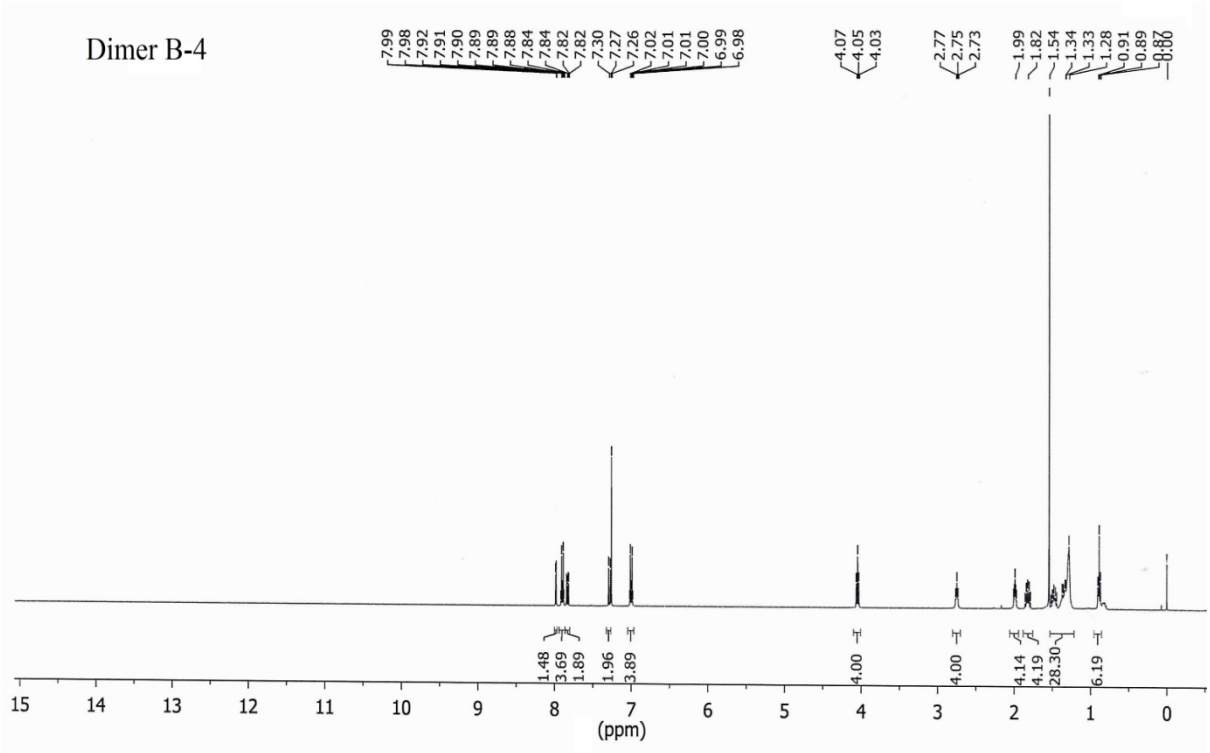
Dimer A-10



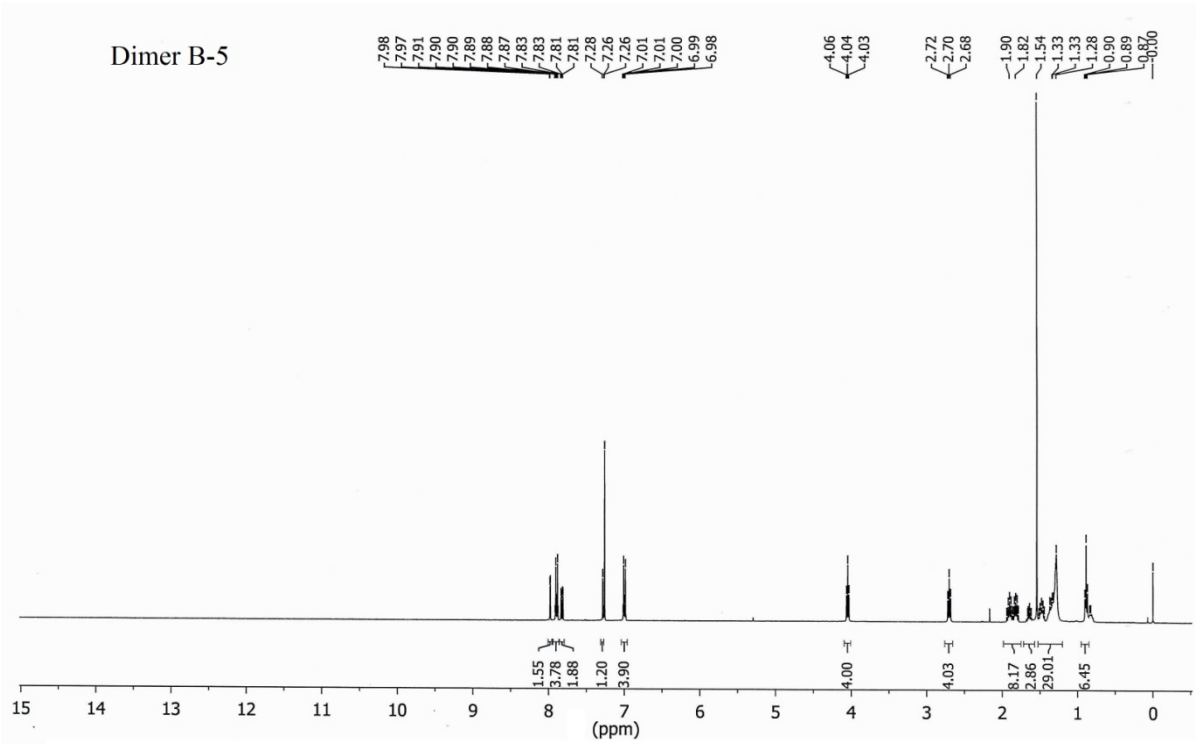
Dimer B-3



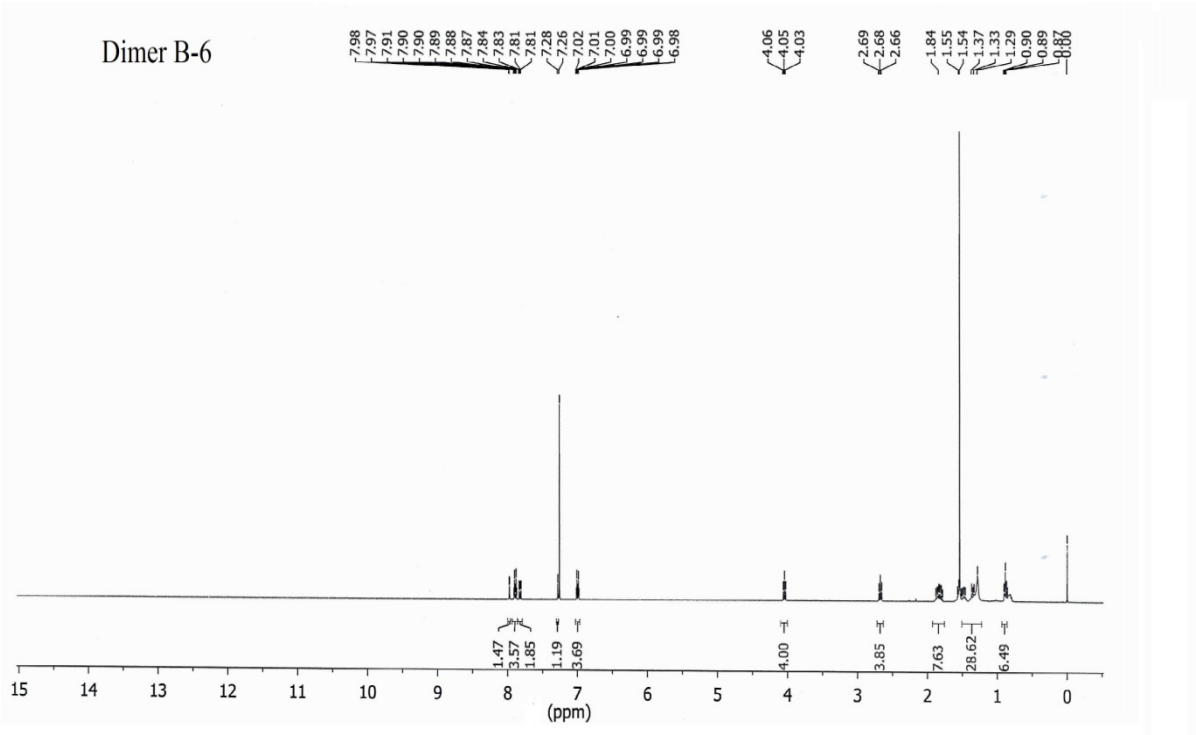
Dimer B-4



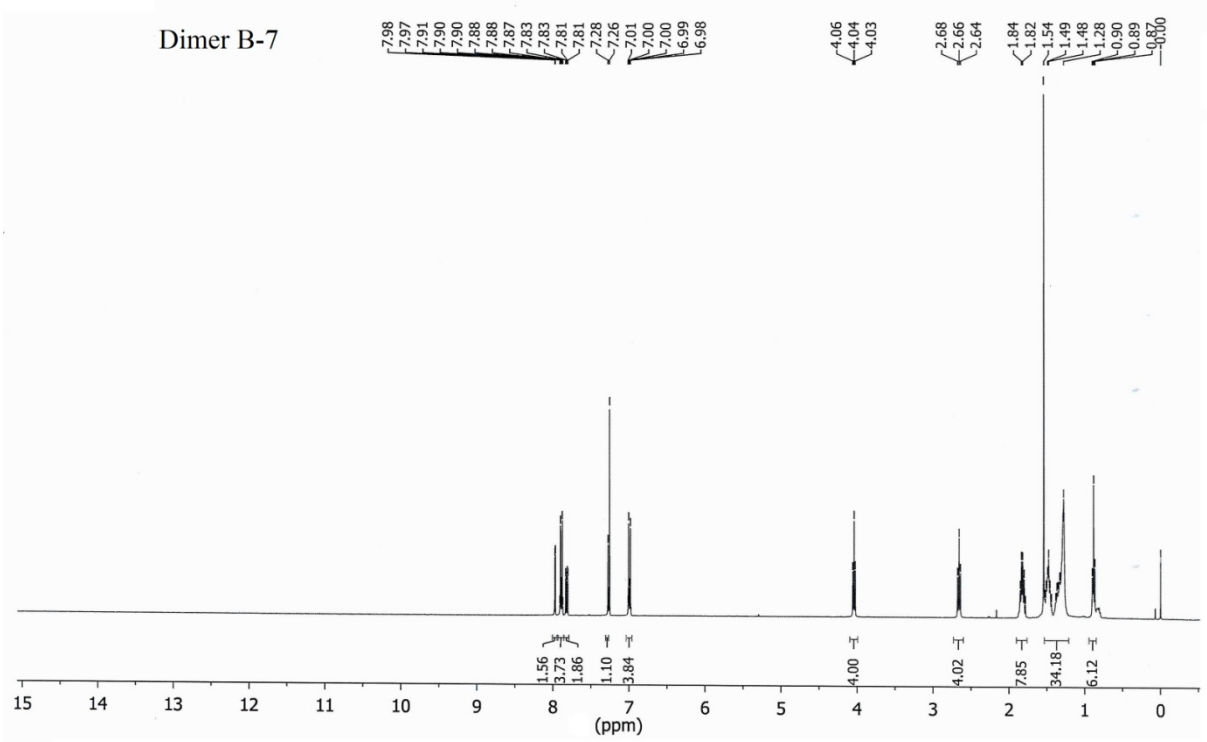
Dimer B-5



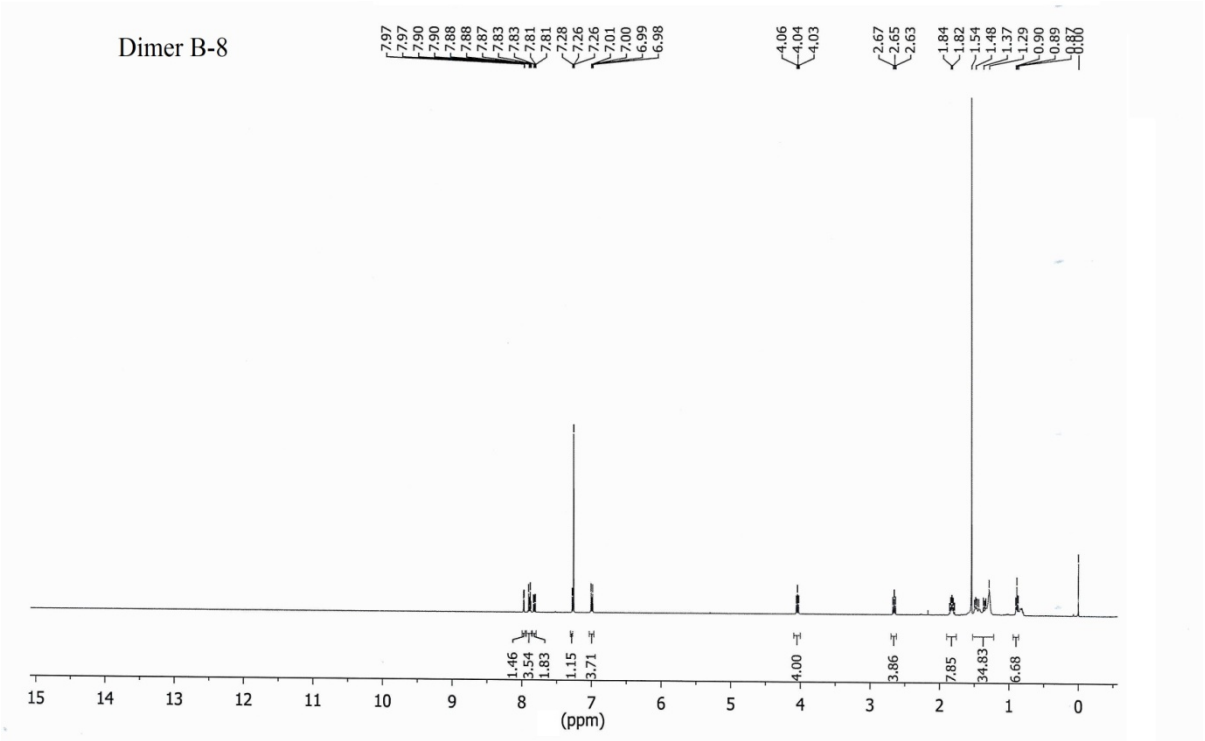
Dimer B-6



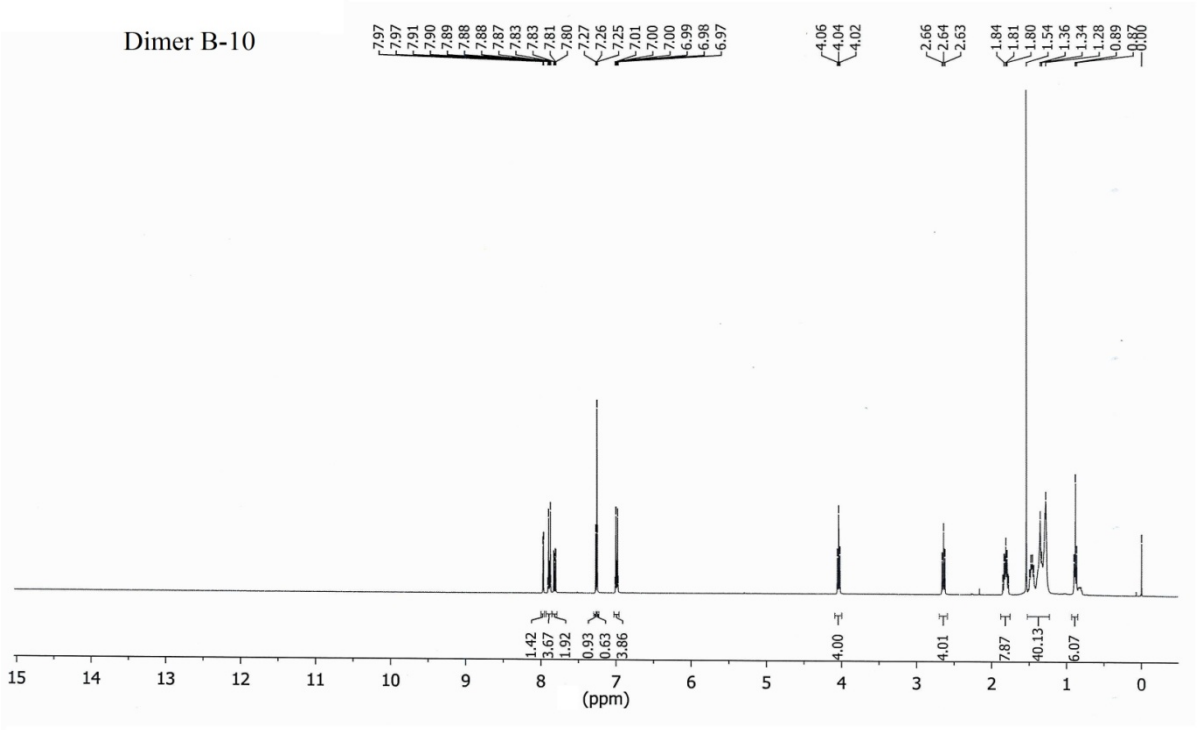
Dimer B-7



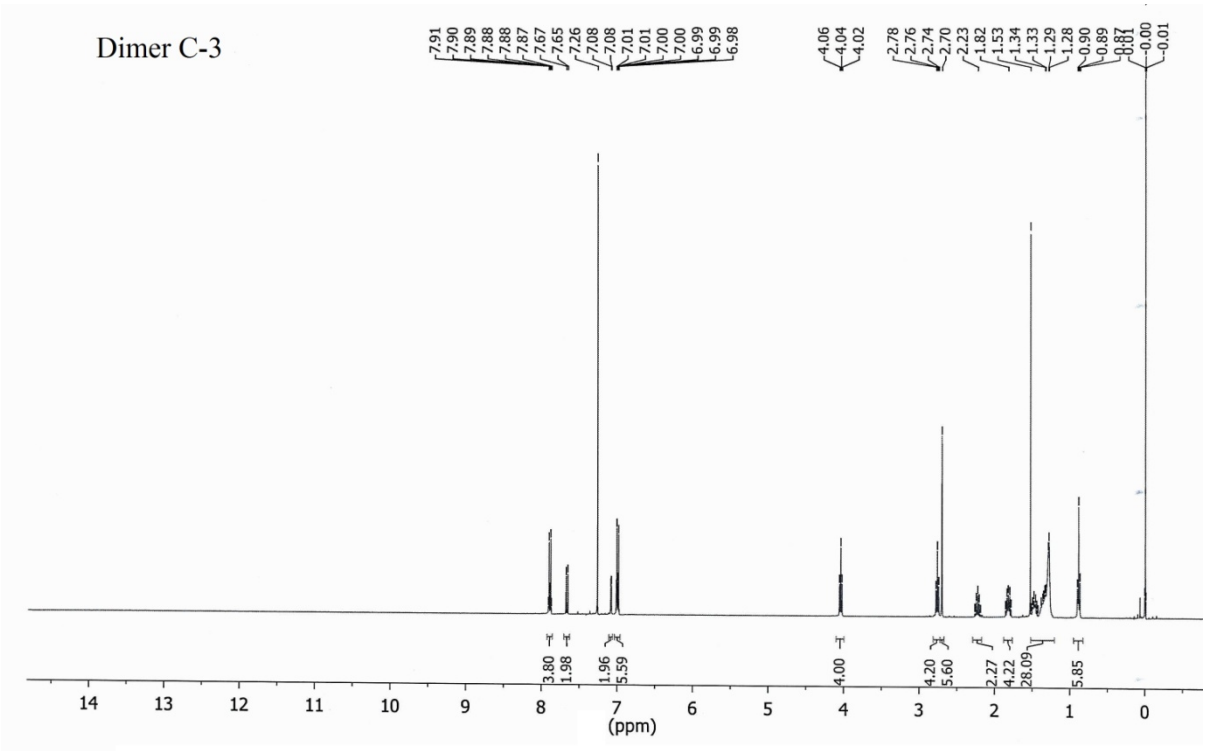
Dimer B-8



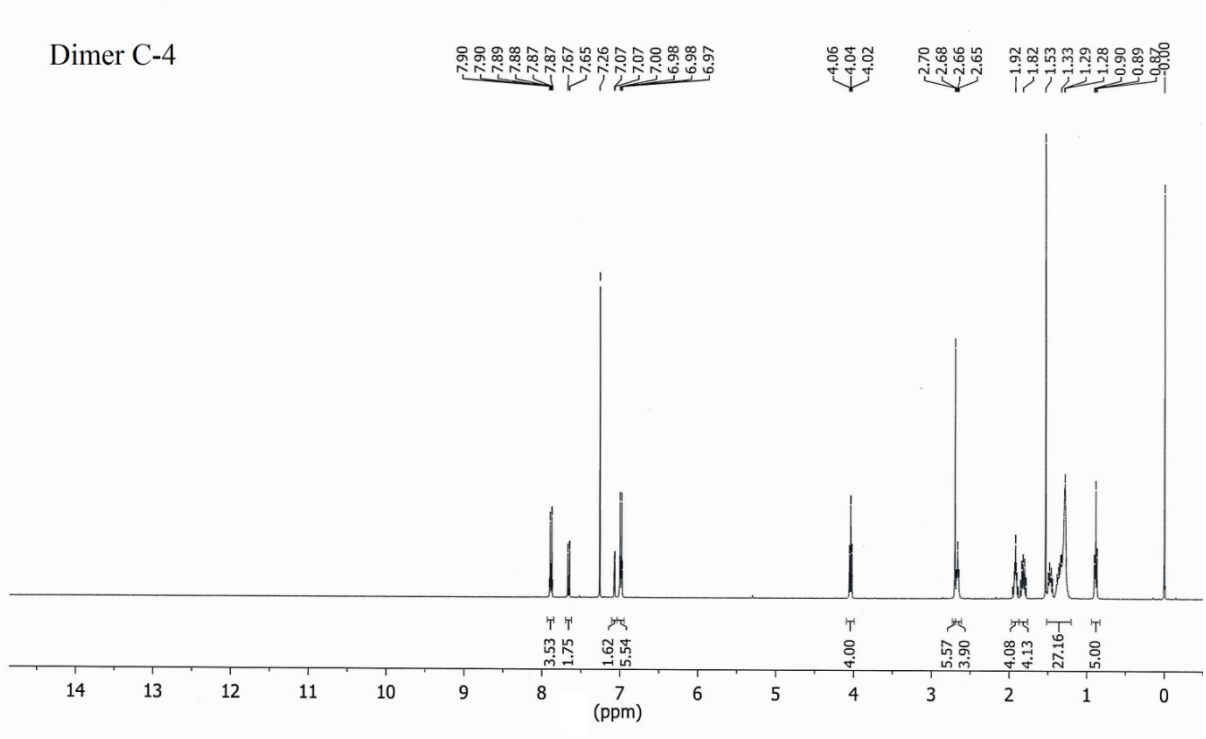
Dimer B-10



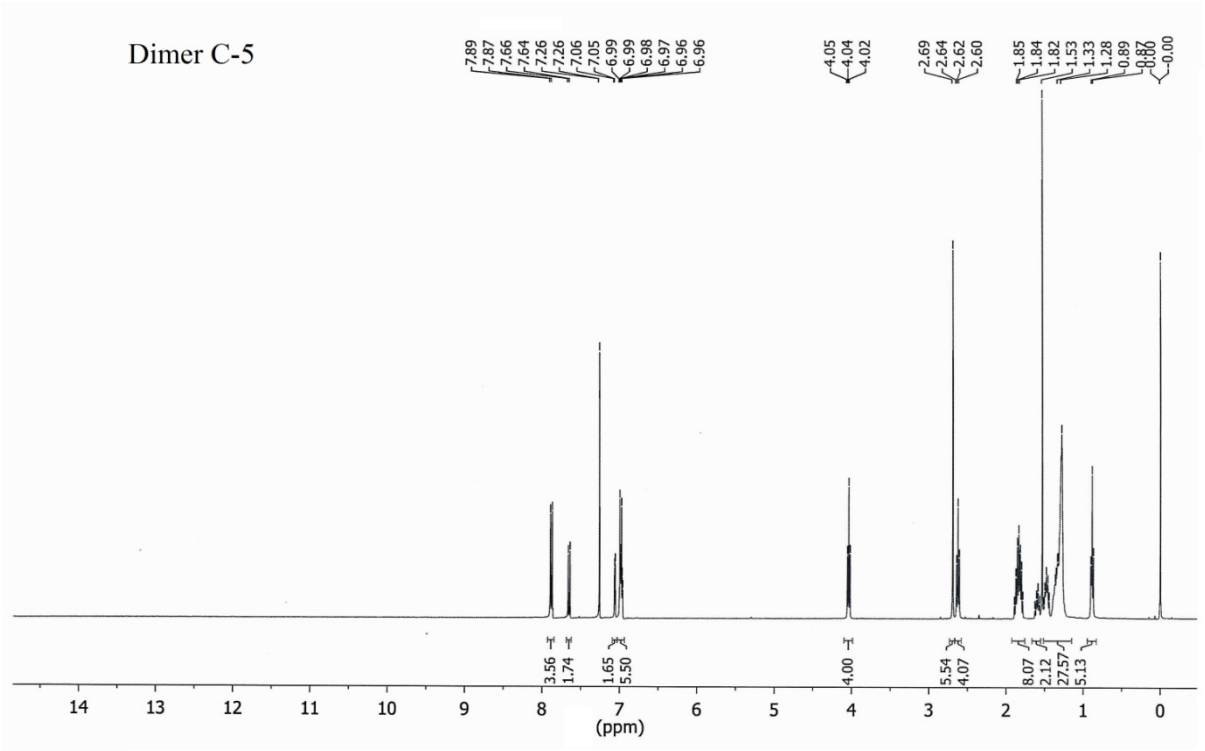
Dimer C-3



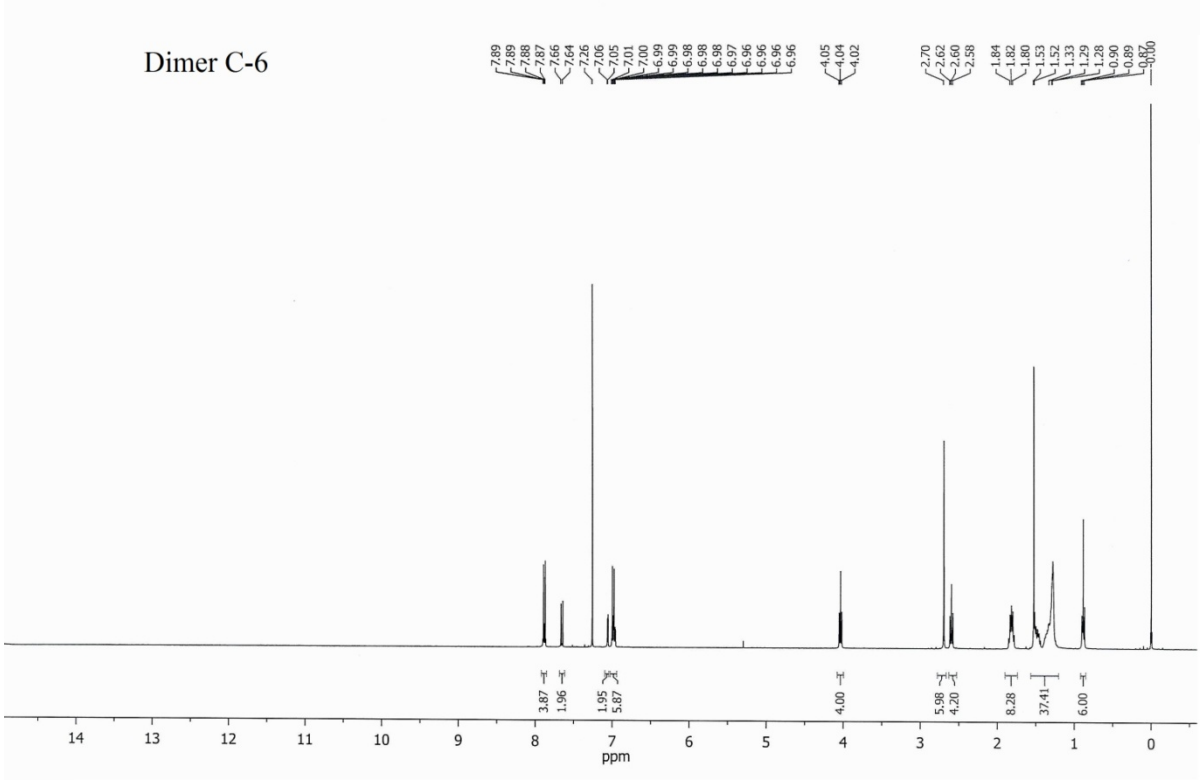
Dimer C-4



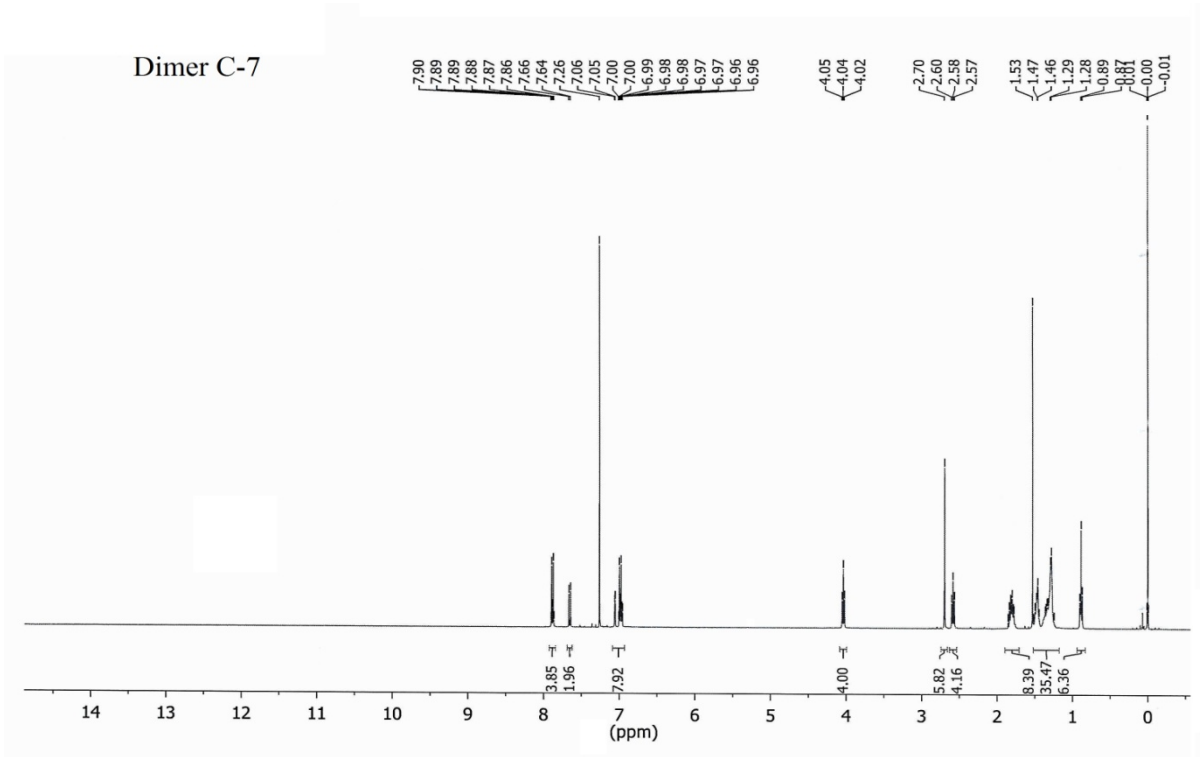
Dimer C-5



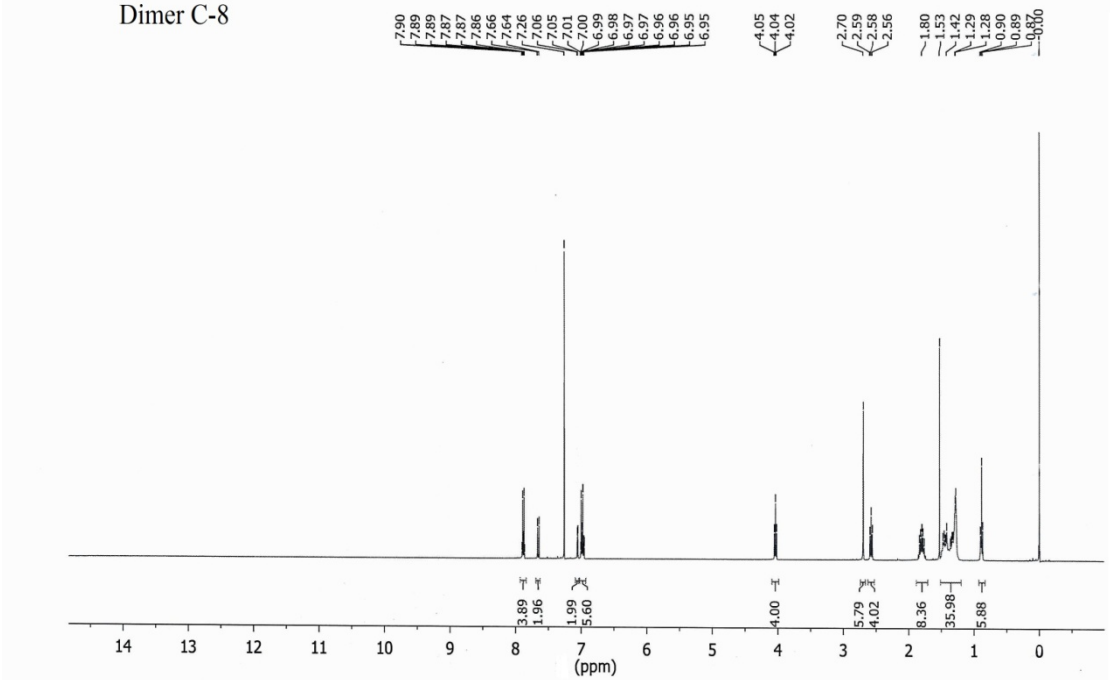
Dimer C-6



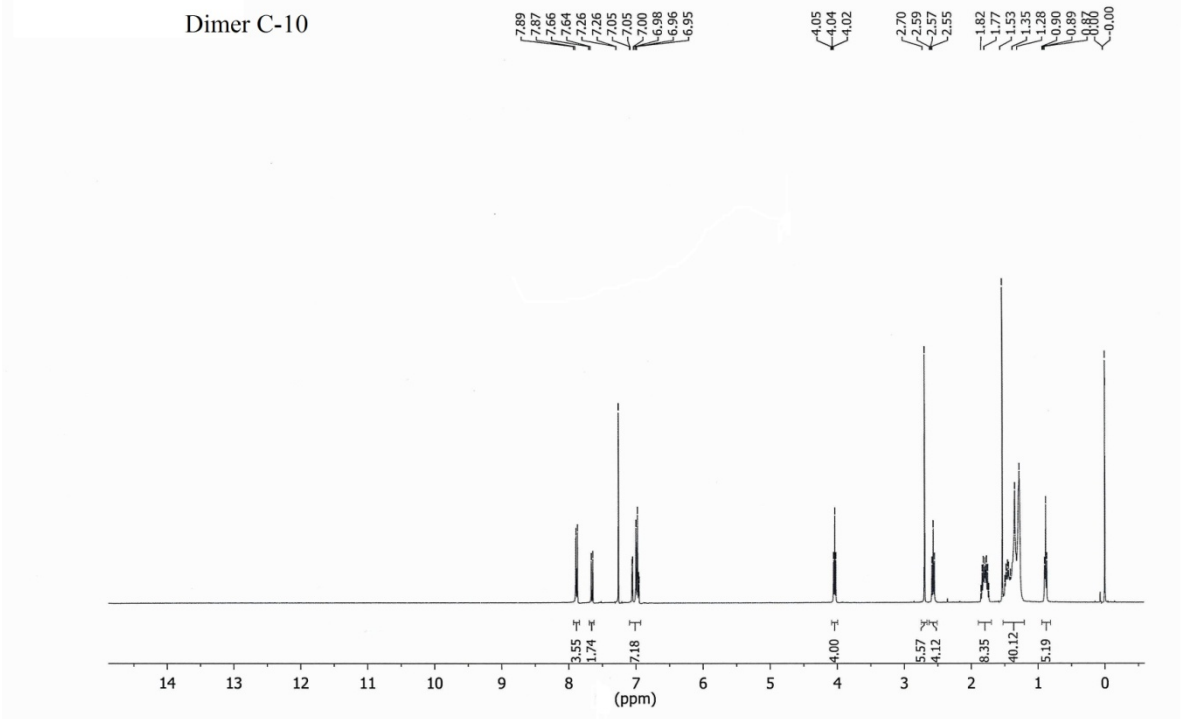
Dimer C-7



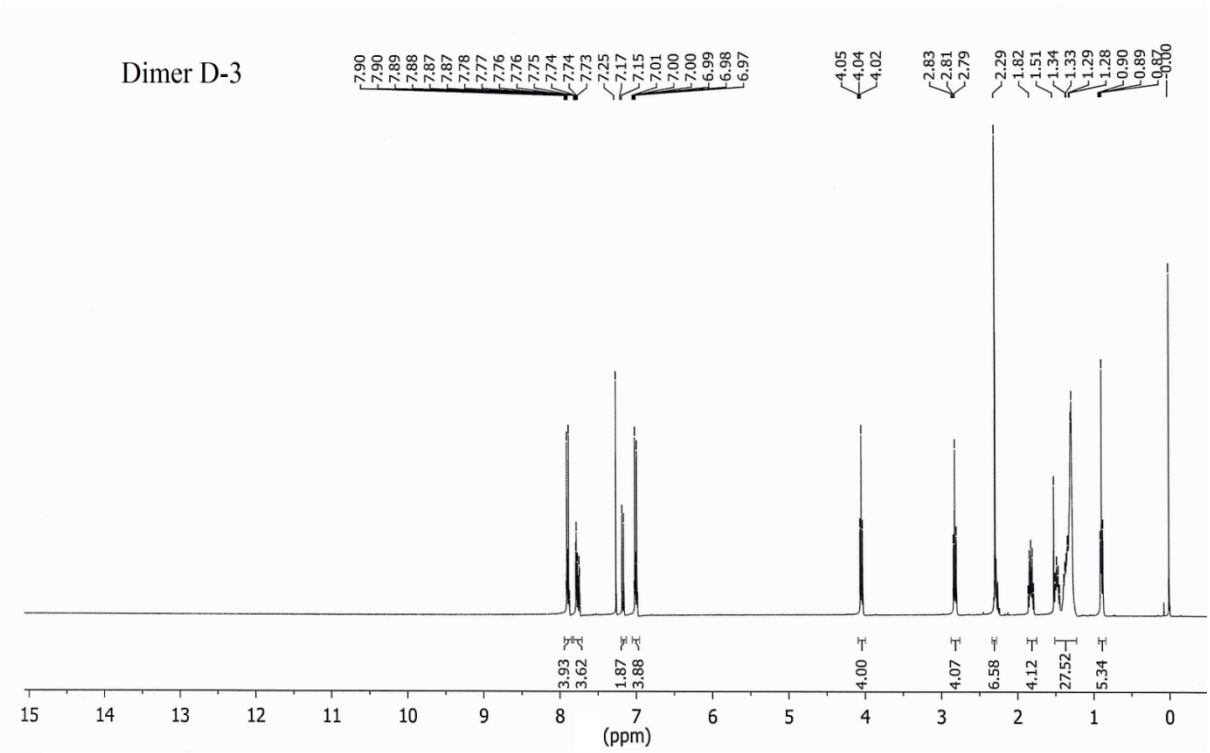
Dimer C-8



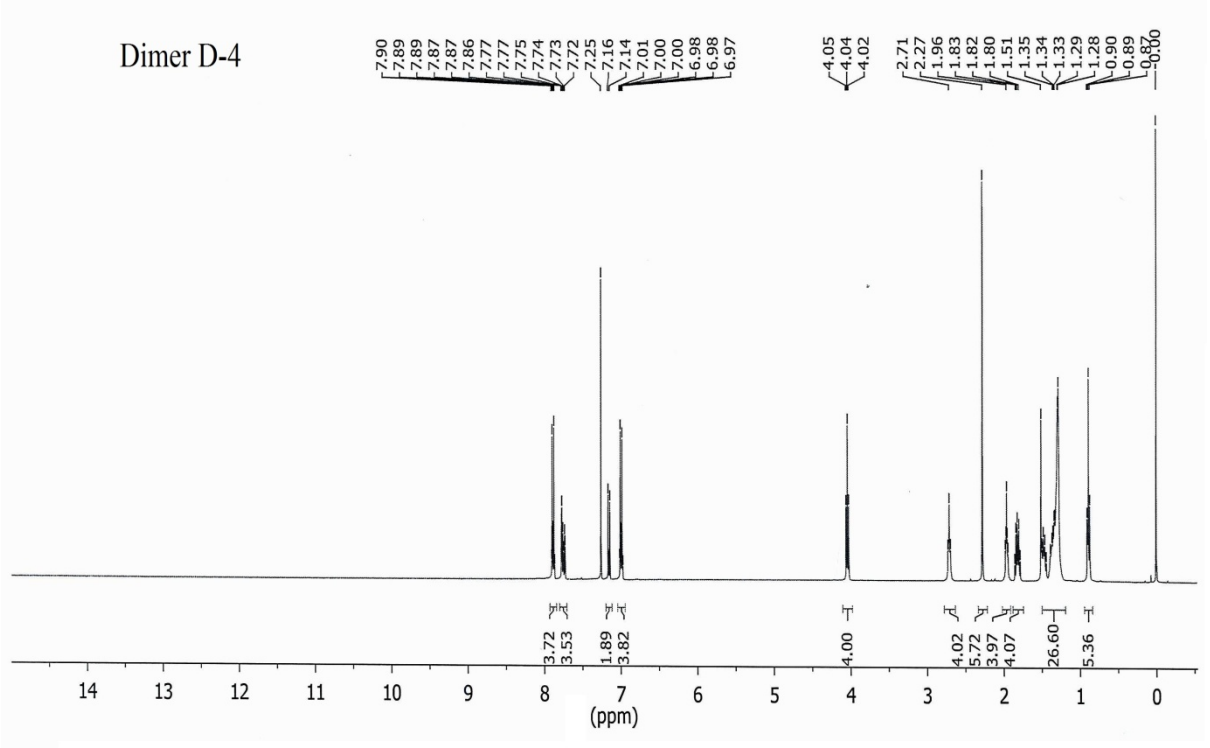
Dimer C-10



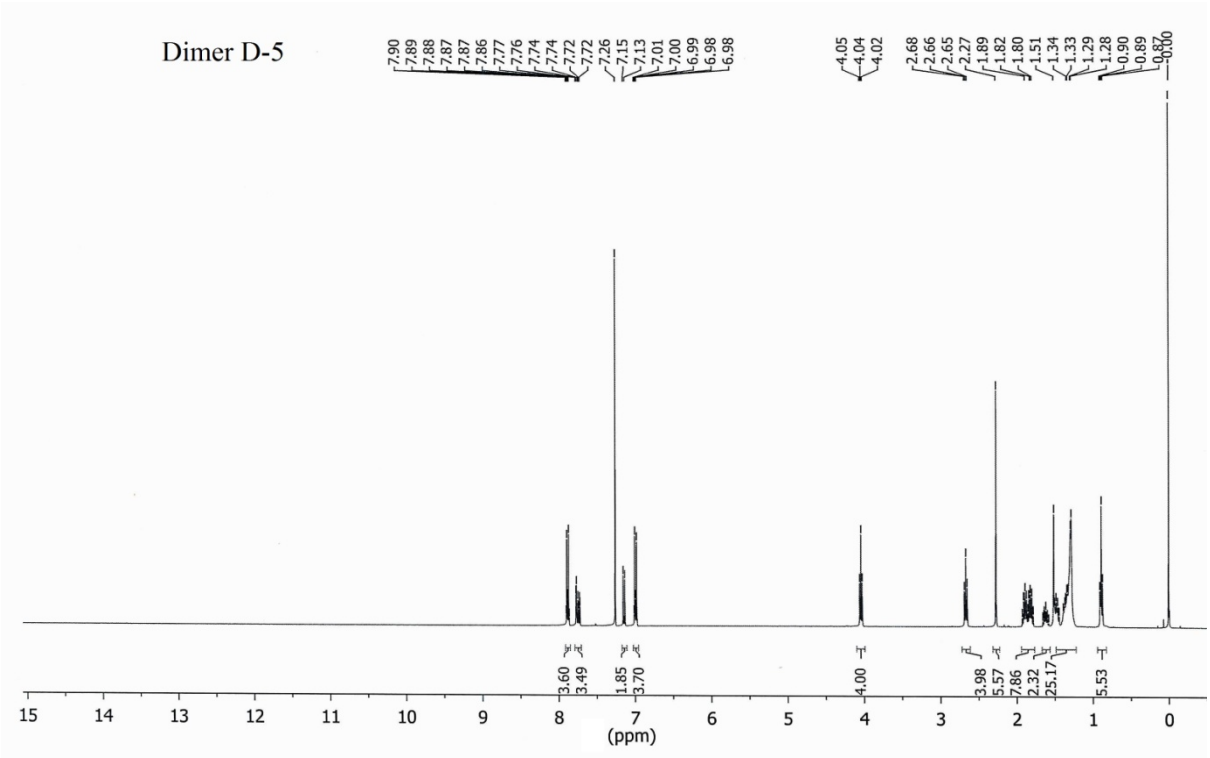
Dimer D-3



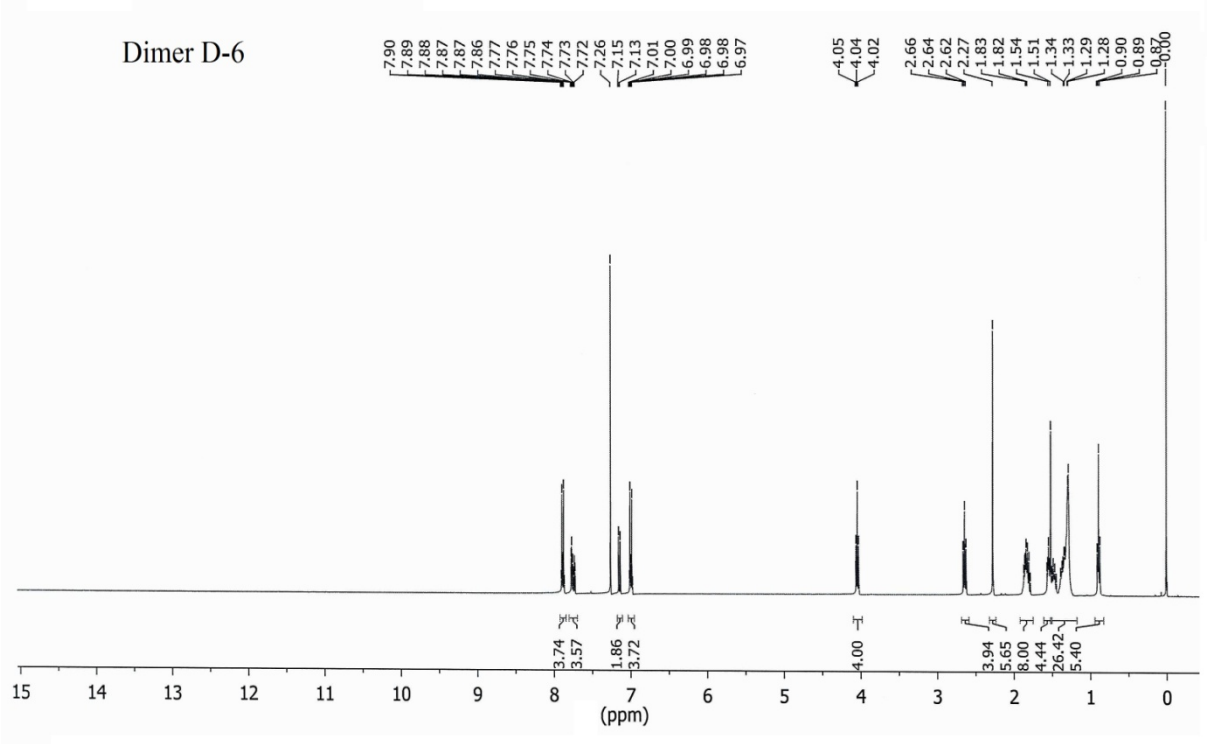
Dimer D-4



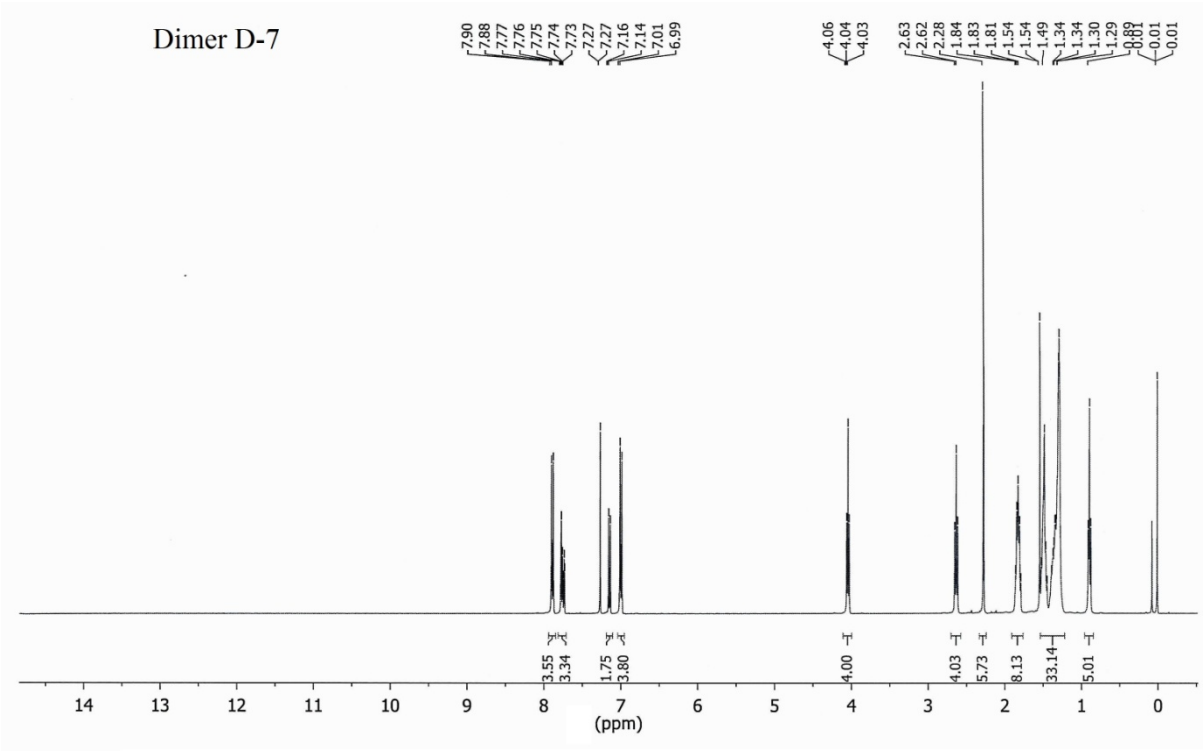
Dimer D-5



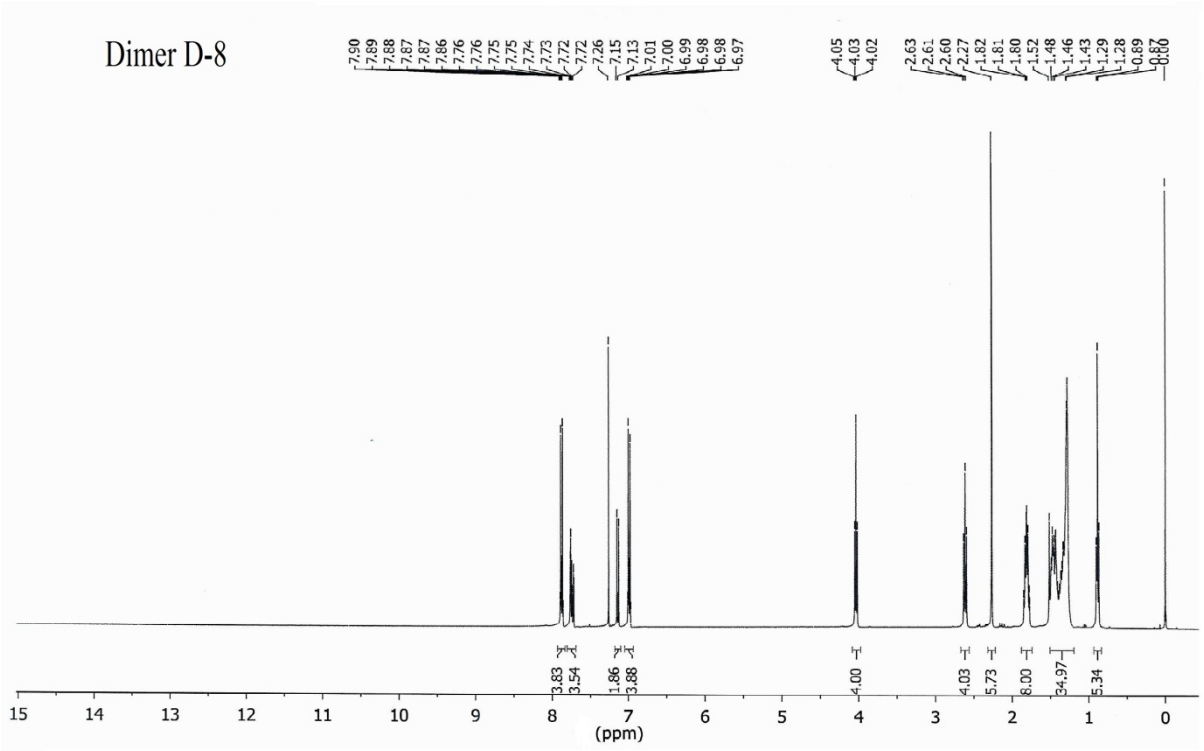
Dimer D-6



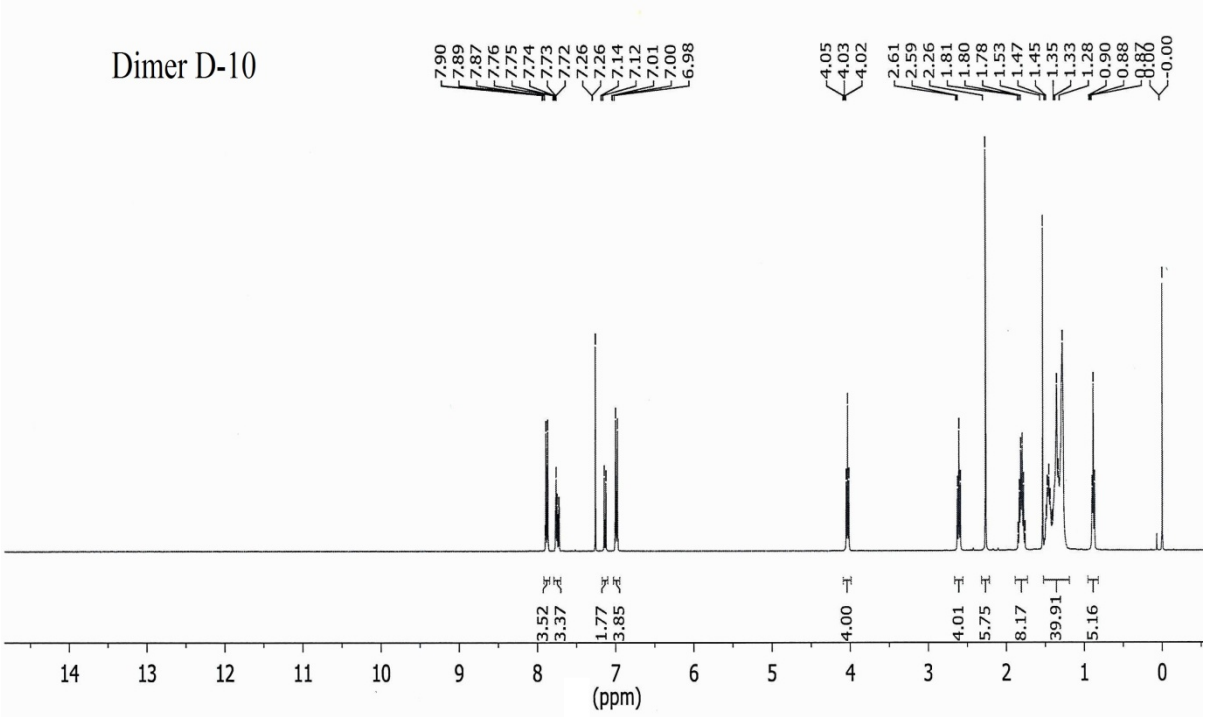
Dimer D-7



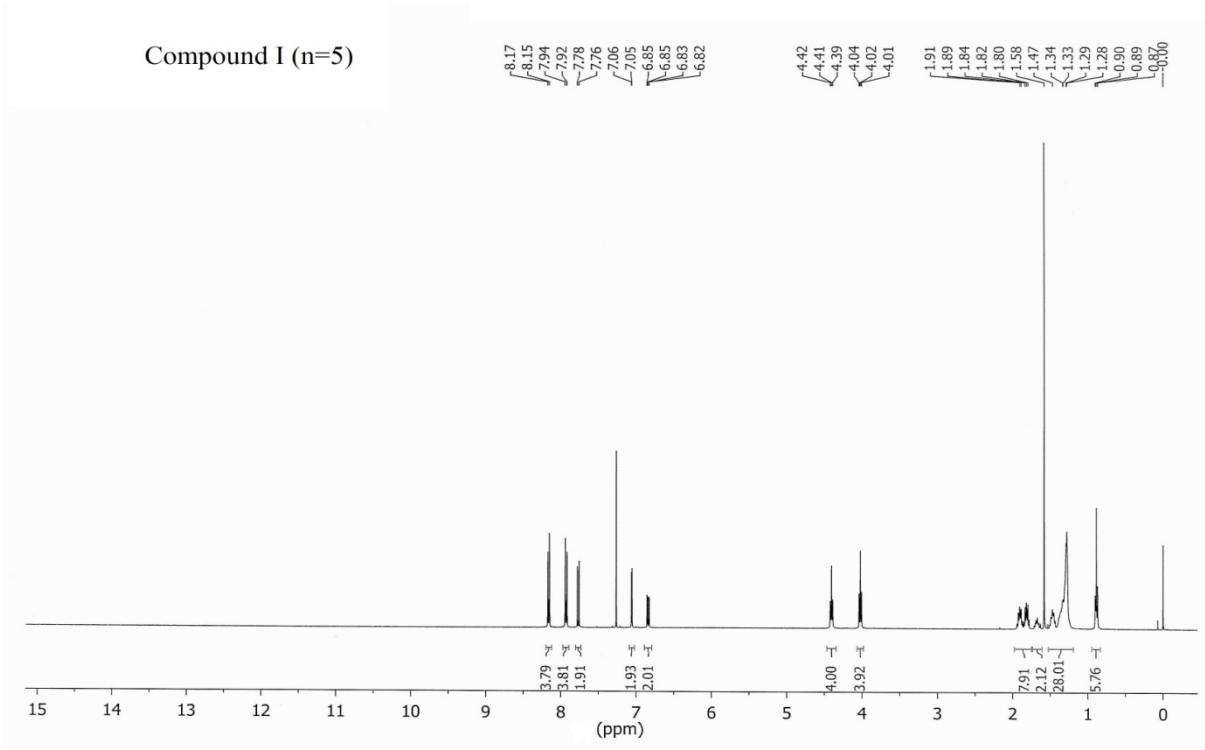
Dimer D-8



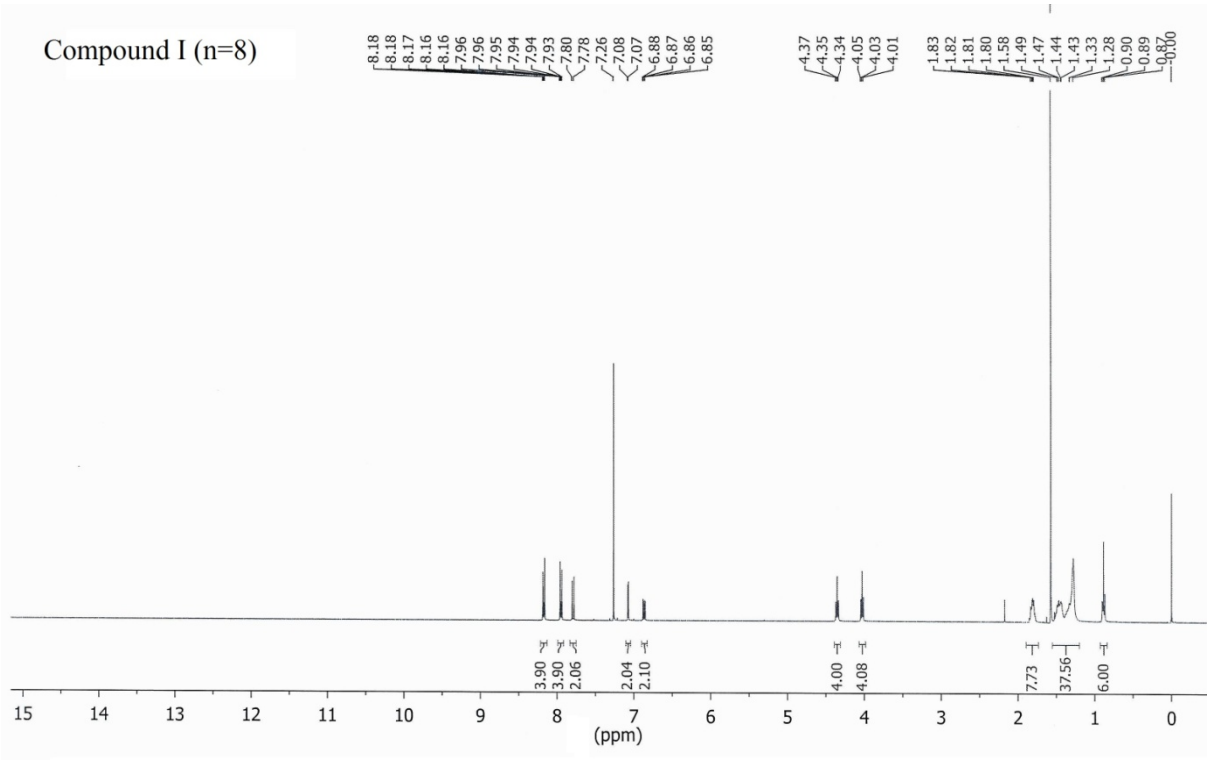
Dimer D-10



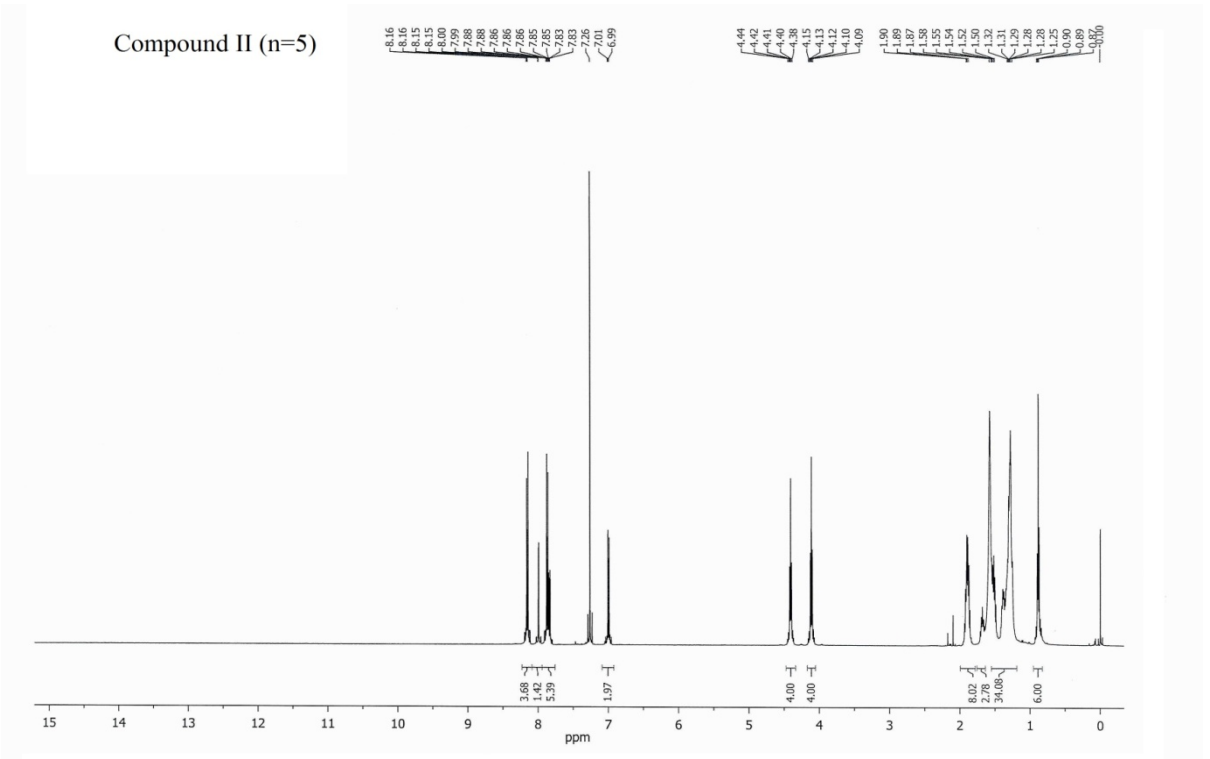
Compound I (n=5)



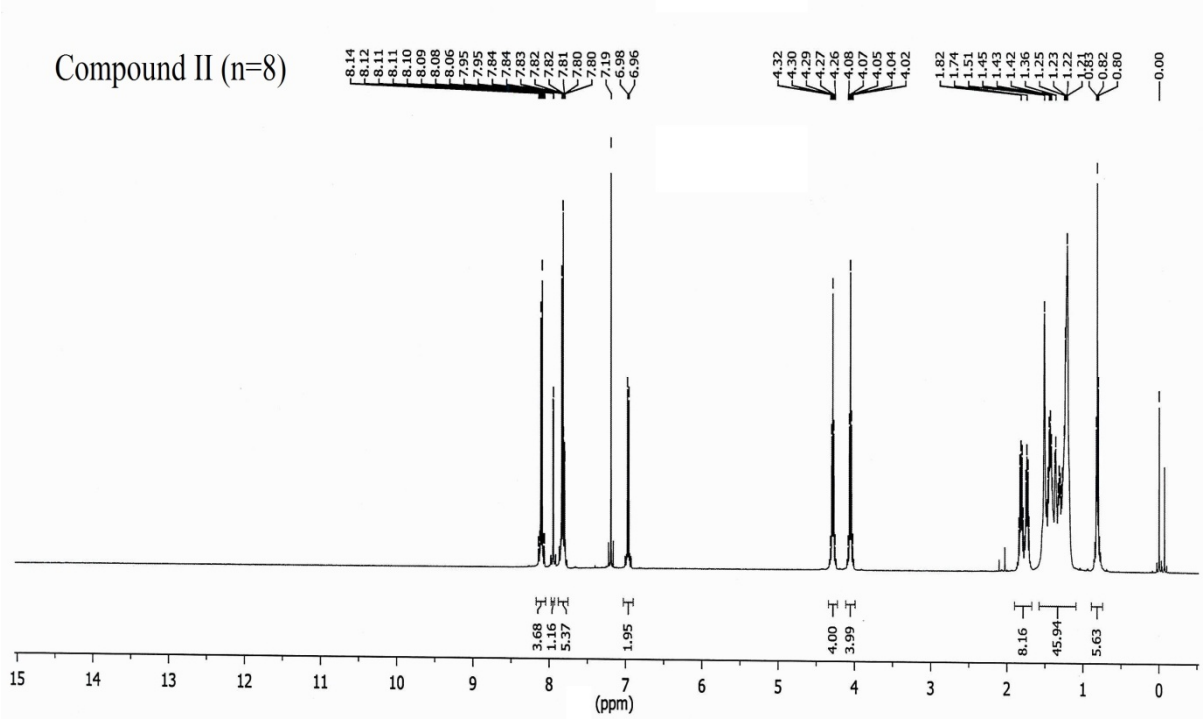
Compound I (n=8)



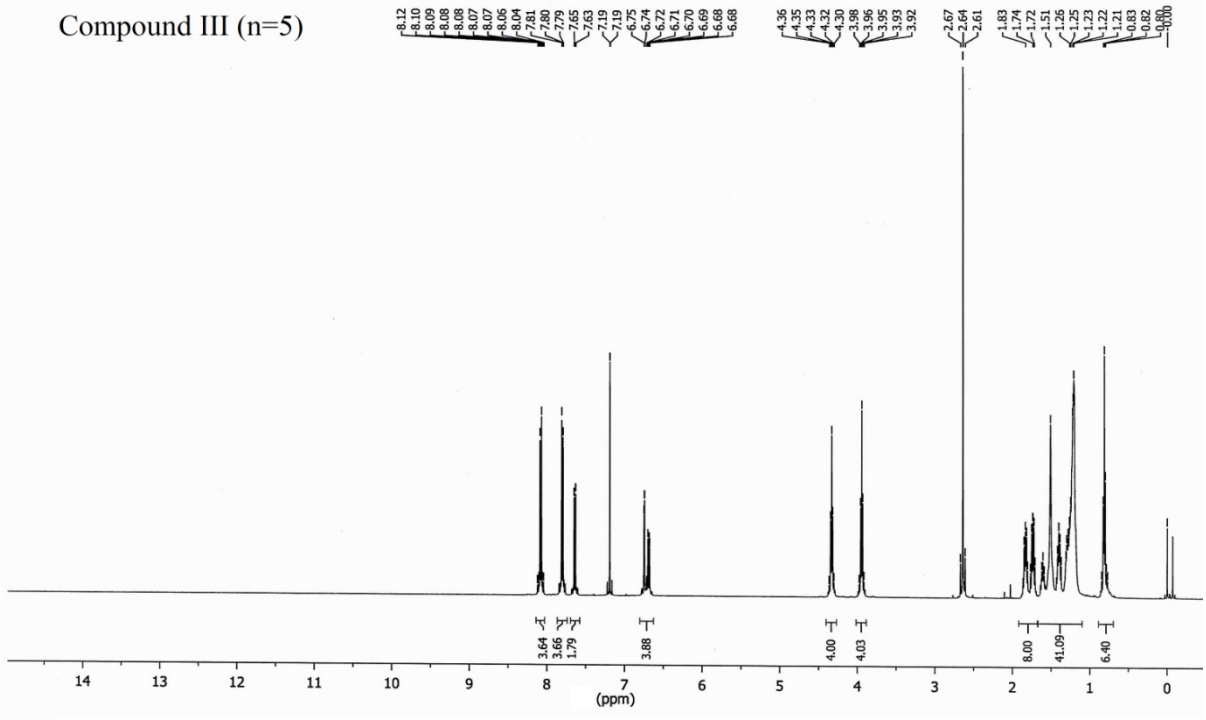
Compound II (n=5)



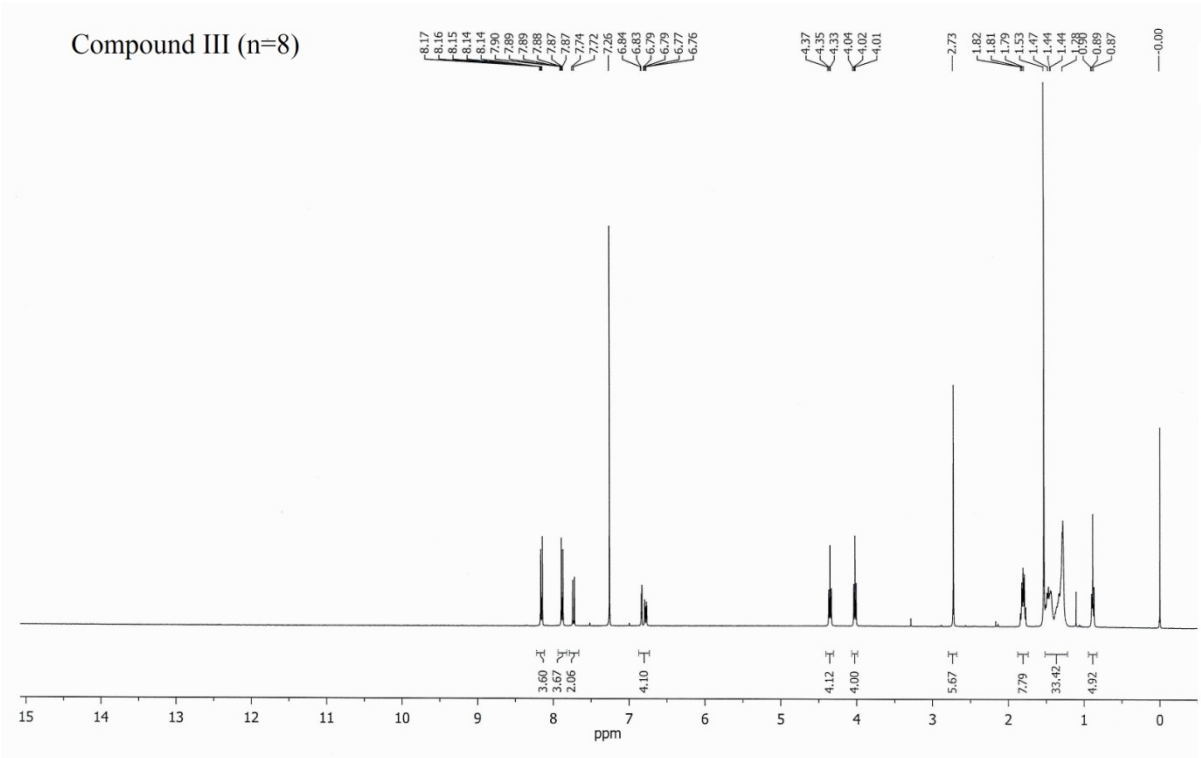
Compound II (n=8)



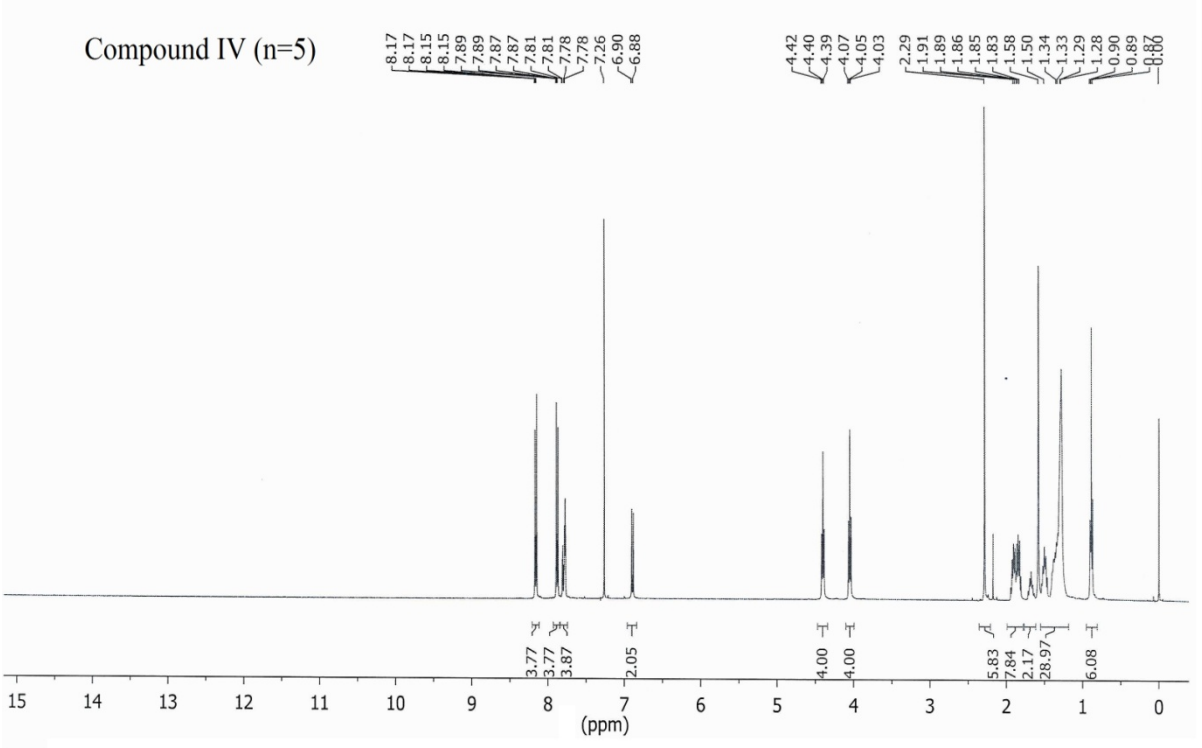
Compound III (n=5)



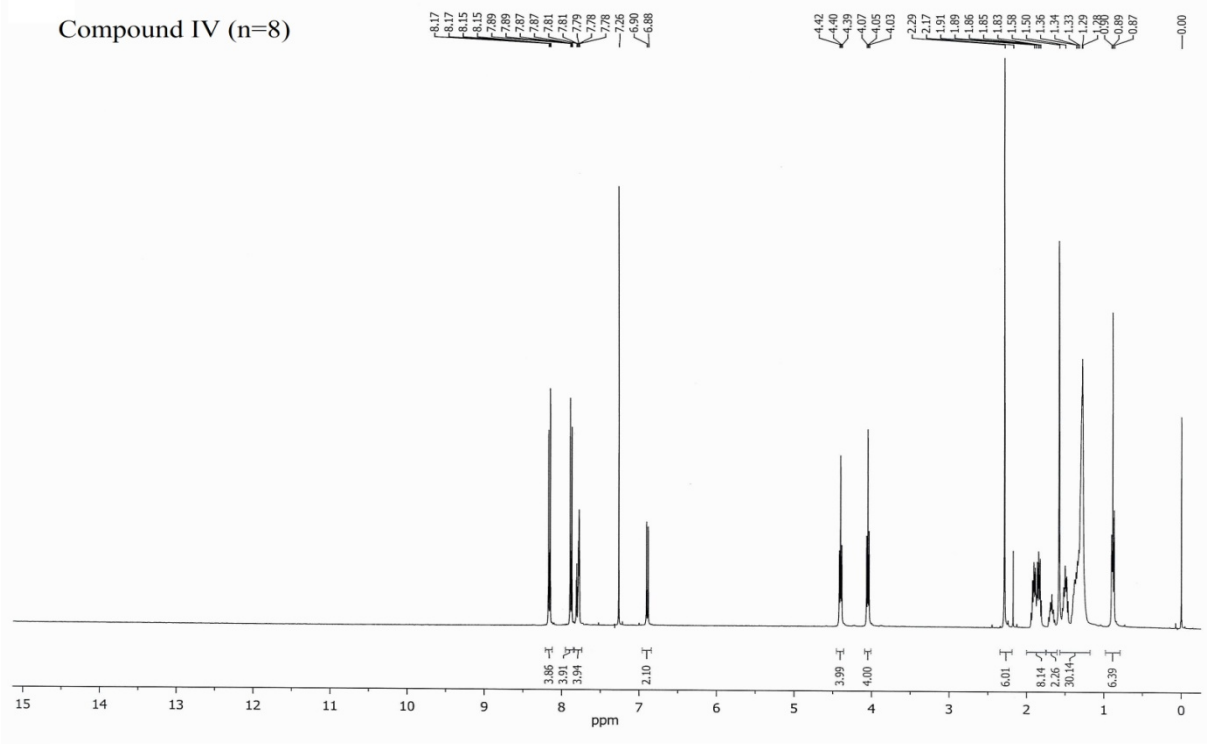
Compound III (n=8)



Compound IV (n=5)



Compound IV (n=8)



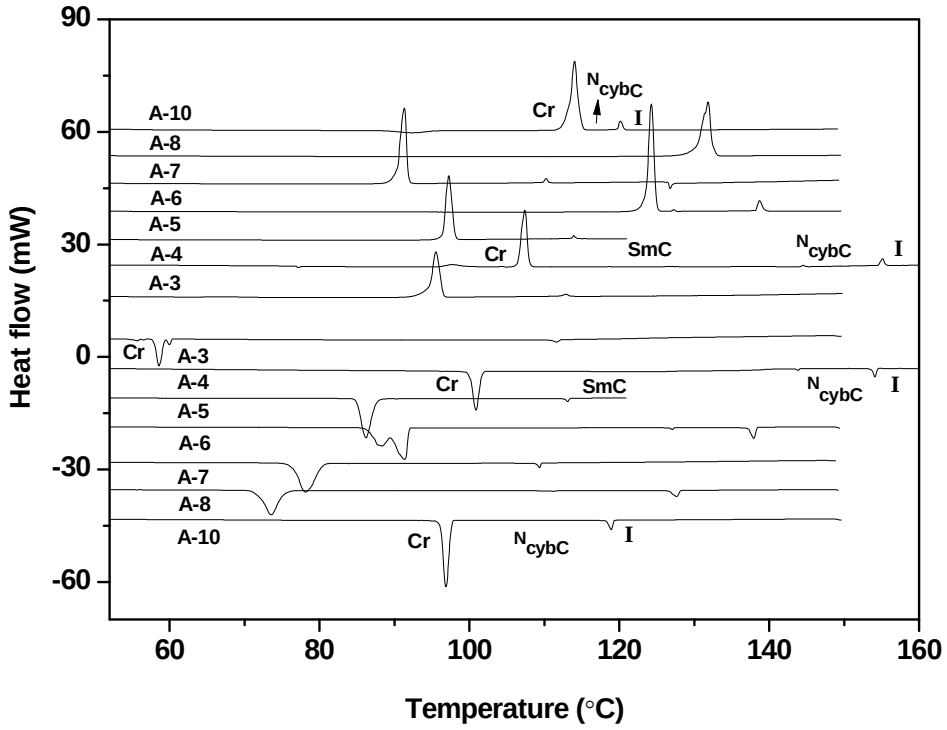


Figure: The DSC thermograms obtained for the compounds of **series A**. The heating and cooling rates were 5°C min^{-1}.

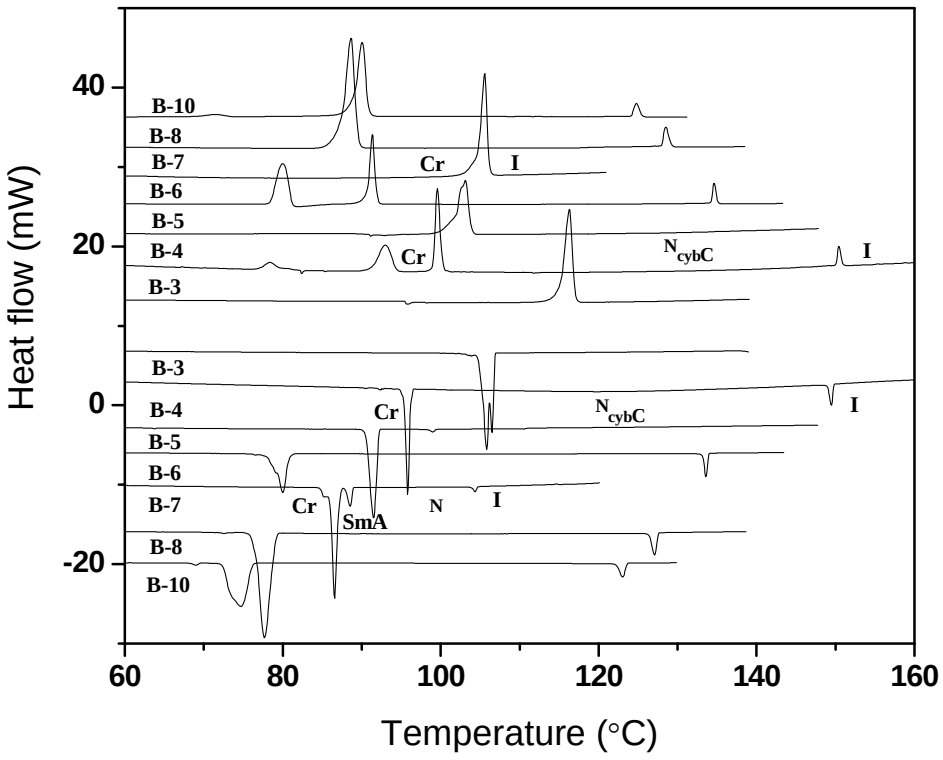


Figure : The DSC thermograms obtained for the compounds of **series B**. The heating and cooling rates were 5°C min^{-1}.

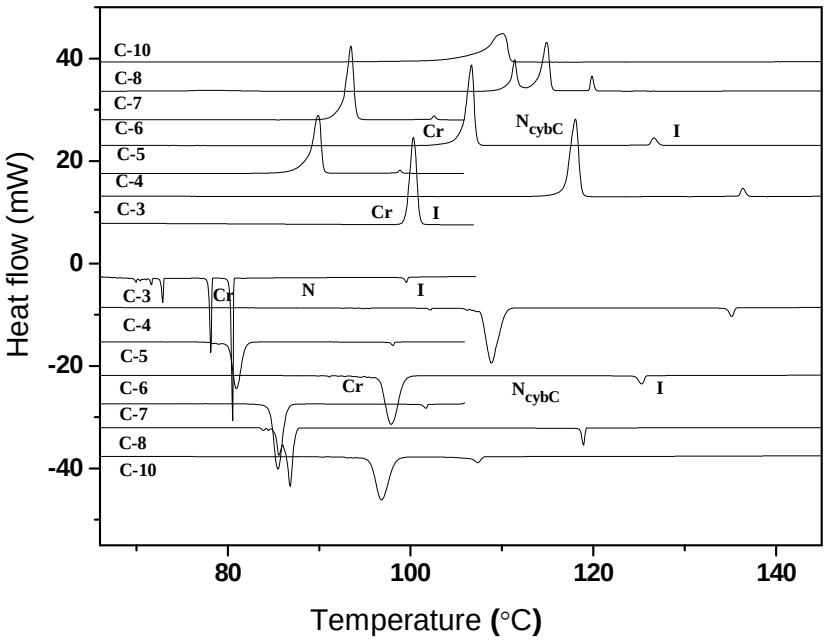


Figure: The DSC thermograms obtained for the compounds of **series C**. The heating and cooling rates were 5°C min^{-1}.

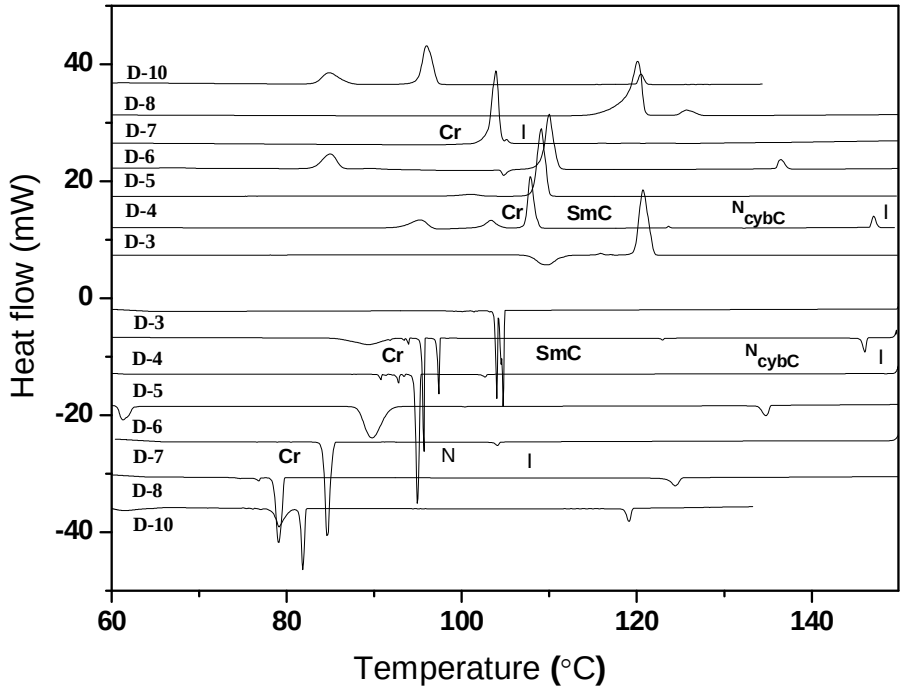


Figure: The DSC thermograms obtained for the compounds of **series D**. The heating and cooling rates were 5°C min^{-1}.

Table : Transition temperatures and the enthalpies of transitions (KJ mol^{-1}) of the non-liquid crystalline compounds.

Dimer	*n*	1st Heating	1st Cooling
Compound I	***5***	**Cr** 110.1 (*80.16*) **I**	**I** 81.5 (*70.52*) **Cr**
Compound I	**8**	**Cr** 123.5 (*90.33*) **I**	**I** 111.0 (*81.85*) **Cr**
Compound II	**5**	**Cr** 95.8 (*123.55*) **I**	**I** 66.7 (*76.82*) **Cr**
Compound II	**8**	**Cr** 108.3 (*77.59*) **I**	**I** 97.1 (*65.27*) **Cr**
Compound III	**5**	**Cr** 112.4 (*89.02*) **I**	**I** 86.0 (*76.47*) **Cr**
Compound III	**8**	**Cr** 128.0 (*100.69*) **I**	**I** 115.6 (*98.21*) **Cr**
Compound IV	**5**	**Cr** 87.6 (*48.81*) **I**	**I** 27.5 (*37.57*) **Cr**
Compound IV	**8**	**Cr** 121.0 (*97.37*) **I**	**I** 114.4 (*97.13*) **Cr**

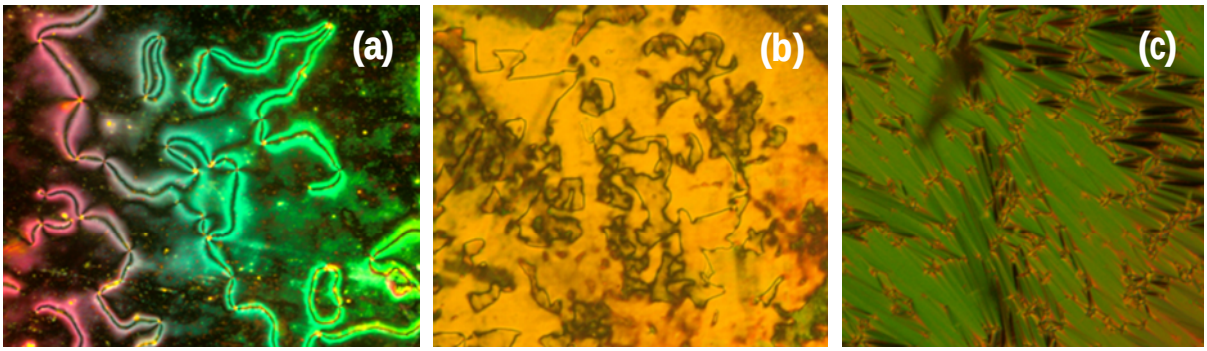


Figure: POM textures (for series *B*) obtained on cooling from the isotropic liquid: (a) schlieren texture of N_{cybC} mesophase (147.8 °C) of the dimer ***B-4***; (b) marble texture of N_{cybC} mesophase (101.3 °C) of the dimer ***B-7*** and (c) SmA mesophase (87.0 °C) obtained on cooling the texture (b).

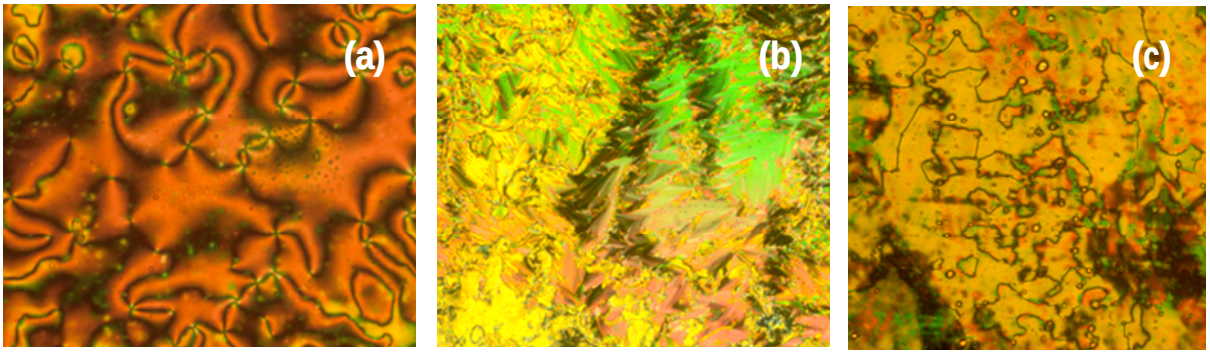


Figure: POM textures (for series *D*) obtained on cooling from the isotropic liquid: (a) schlieren texture of N_{cybC} mesophase (142.2 °C) of the dimer ***D-4*** and (b) SmC mesophase (118.1 °C) obtained on cooling the texture (a); (c) marble texture of N_{cybC} mesophase (103.6 °C) of the dimer ***D-7***.

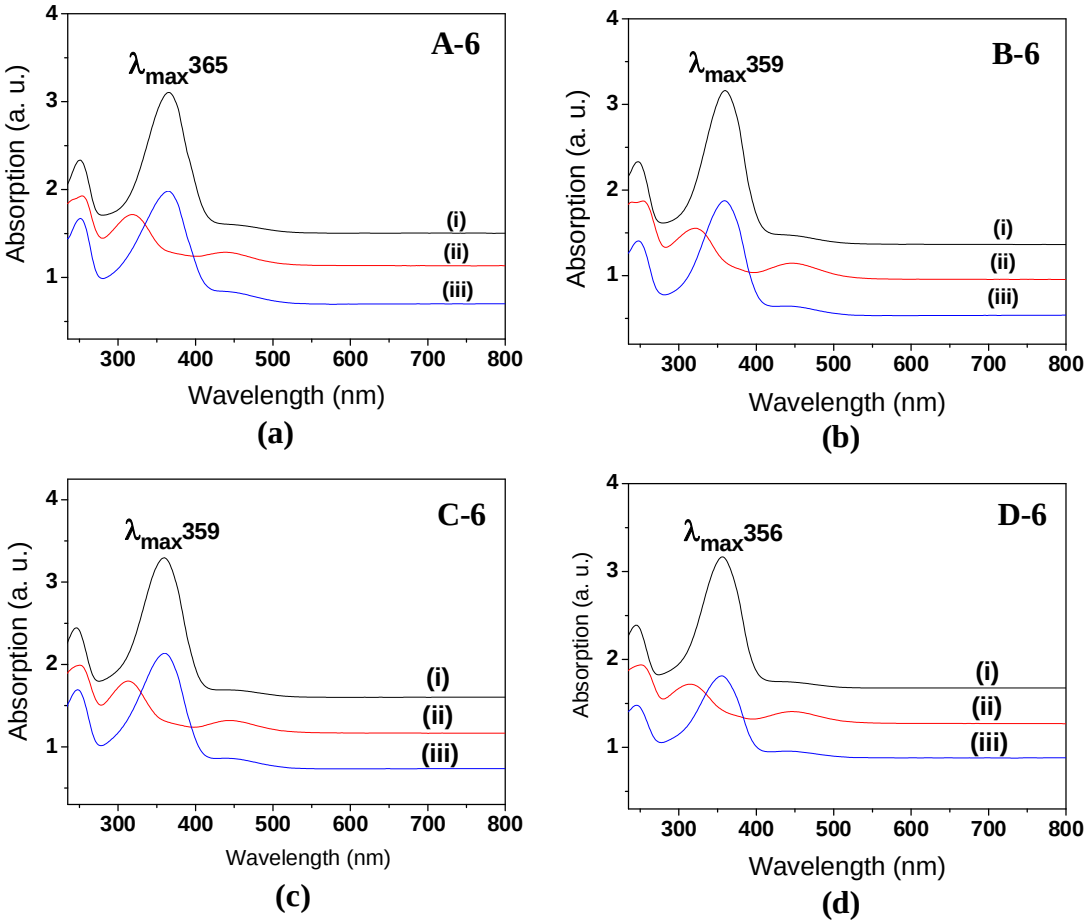


Figure: UV–vis spectra (in CH_2Cl_2) of compounds **A-6**, **B-6**, **C-6** and **D-6** ((a)–(d)): (i) fresh solution (ii) after exposure (15 min) to 320–380 nm UV light and (iii) after keeping the exposed sample in the dark, overnight.

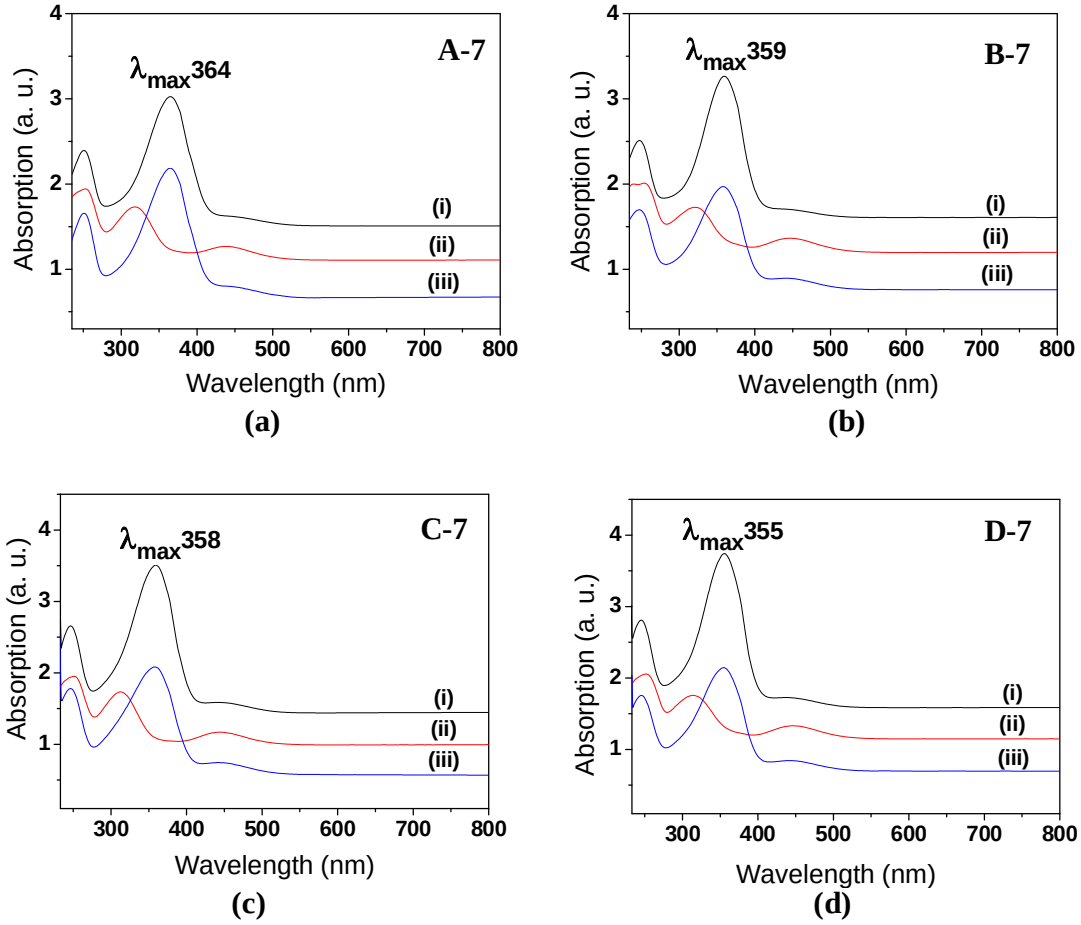


Figure : UV–vis spectra (in CH_2Cl_2) of compounds **A-7**, **B-7**, **C-7** and **D-7** ((a)–(d)): (i) fresh solution (ii) after exposure (15 min) to 320–380 nm UV light and (iii) after keeping the exposed sample in the dark, overnight.

Table. Gelation properties.

Compound	Solvent			
	DMF	Ethanol	Acetone	Hexane
A-3	S	P	S	G
A-4	P	P	P	P
A-5	P	P	P	P
A-6	P	P	P	S
A-7	P	P	P	P
B-3	S	P	P	P
B-4	S	P	P	P
B-5	S	P	P	G
B-6	P	S	P	P
B-7	G	P	G	G
C-3	S	P	S	P
C-4	P	P	P	P
C-5	P	P	P	P
C-6	P	P	P	P
C-7	P	P	P	P
D-3	S	P	P	P
D-4	P	P	P	P
D-5	S	P	P	P
D-6	P	P	P	S
D-7	S	P	P	P

S: Solution; P: Precipitate; G: Gel

Reference:

1. Anceloni A. S, caretti D, laus M, Chiellini E, Gall G, J Polym Sci A Polym Chem. 1991;29:1865-1873.