Electronic Supplementary Material (ESI) for Chemical Communications

Preparation and Helical Folding of Long-Chain Aromatic Polyamides

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Supporting Information

Contents

I. Synthetic Procedures and Analytical Data---------- 2

II. GPC Data of **3a, 3b** and **3c**---------- 4

III. 1D ^{1}H and ^{13}C NMR Spectra of New Compounds ----------7

IV. Concentration-Dependent ^{1}H NMR Spectra of **3a**, **3b**, **3c and 4**---------- 9

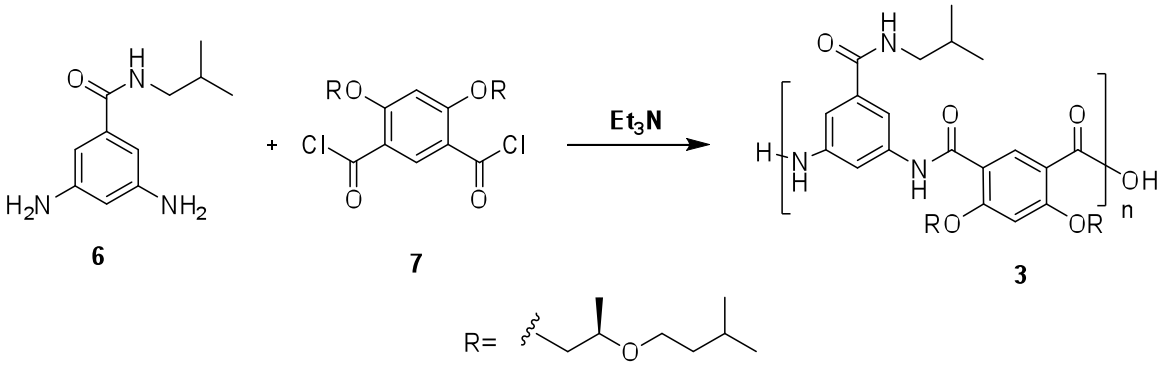
V. UV Spectra of **3a, 3b**, **3c** and **4** ----------11

VI. Additional CD spectra ----------14

I. Synthetic Procedures and Analytical Data

Chemicals were purchased from commercial sources and used as received. Unless otherwise specified, all solvents were removed with a rotary evaporator. Silica gel for analytical thin layer chromatography (TLC) and column chromatography (200~300 mesh) were purchased from Qingdao Haiyang Chemical Co., Ltd & Spegial Silica Gel Factory. The ^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were measured at 75 MHz on a Bruker-300 spectrometer at ambient temperature using $CDCl_3$ or DMSO-d_6 as solvent (Cambridge Isotope Laboratories, Inc.). Chemical shifts are reported in parts per million downfield from TMS (tetramethylsilane). Coupling constant in ^{1}H NMR are expressed in Hertz. Electroscpray ionization high resolution mass spectra (ESI-HRMS) were recorded on a Bruke P-SIMS-Gly FT-ICR mass spectrometer. Circular Dichroism (CD) were recorded on a JASCO J-815 spectrometer. Gel Permeation Chromatography were recorded on a SHMADZU SPD-20A.

I-1. Preparation of polyamide 3



Diamine **6** (415 mg, 2 mmol), prepared from the reaction of 3, 5-dinitrobenzoyl chloride and isobutylamine followed by hydrogenation, was dissolved in 16 mL of *N, N*-dimethylacetamide (DMA) that treated by drying over CaH_2 and then being distilled, in a round-bottomed flask. After adding Et_3N (1.08 mL, 6 mmol), the solution was purged with N_2 a few times and then stirred in an ice-bath for 10 min, to which a solution of diacid chloride **7** (982 mg, 2 mmol), prepared based on known procedures,[1] in 16 mL of DMA was added rapidly. The reaction mixture was purged a few more times with nitrogen, and was then let to warm to room temperature and stirred for an additional 8 hrs. After removing solvent, the remaining residue was dissolved/suspended into CH_2Cl_2, washed with brine for three times, and dried over Na_2SO_4. Removing solvent led to **3** (1.12 g) as a light yellow powder. Using gel permeation chromatography (GPC), the weight-average molecular weights (M_w) of **3** was determined 14,746, with a molecular-weight dispersity of 6.80.

I-2. Synthesis of trimer 4 and pentamer 5

Oligoamides **4** and **5** were synthesized in good yields based on known synthetic procedures.[1]

Compound 4. ^{1}H NMR (300 MHz, $CDCl_3$) δ9.96 (2 H, s), 8.78 (2 H, s), 8.49 (1 H, s), 7.88 (2 H, s), 6.63 (1 H, t, *J* = 6.0 Hz), 6.52 (2 H, s), 4.21 ~ 4.10 (8 H, m), 4.02 ~ 3.89 (4 H, m), 3.85(6H, s), 3.64 ~ 3.50 (8 H, m), 3.28-3.24 (2 H, m), 1.94-1.89 (1H, m), 1.71- 1.57 (4H, m), 1.47~1.42 (10 H, m), 1.38~1.24(10 H, m), 0.97(6H, d, J=6.6), 0.88(12H, d, *J*=6.6), 0.72 (12 H, d, *J* = 6.6 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ166.7, 165.1, 162.8, 162.4, 160.7, 139.4, 137.1, 135.8, 114.8, 114.3, 114.2, 113.7, 97.6, 73.6, 73.1, 72.7, 68.1, 67.5, 51.6, 47.4, 38.9, 38.6, 29.6, 28.6, 25.0, 22.6, 22.4, 20.2, 17.3, 16.9. HRMS (ESI) calcd for $C_{61}H_{93}N_3Na_2O_{15,}$ ($[M+2Na]^+$) 1153.6402, found 1153.6426.

Compound 5. ^{1}H NMR (400 MHz, DMSO-d_6) δ10.19 (s, 2H), 10.15 (s, 2H), 10.11 (s, 2H), 8.45 (s, 2H), 8.40 (s, 1H), 8.36 (br, 3H), 8.21 (s, 2H), 7.83 (s, 2H), 7.73 (s, 2H), 7.71 (s, 2H), 6.97 (s, 2H), 4.36-4.30 (m, 8H), 3.97 (br, 4H), 3.53-3.50 (m, 4H), 3.48-3.45 (m, 4H), 3.06 (t, J = 16 Hz, 6H), 1.87-1.83 (m, 3H), 1.52-1.47 (m, 4H), 1.30-1.21 (m, 20H), 0.92-0.89 (m, 18H), 0.70-0.67 (m, 24H); ^{13}C NMR (75 MHz, DMSO-d_6) δ168.4, 166.5, 166.3, 162.6, 160.0, 139.5, 138.8, 138.7, 136.4, 136.4, 134.2, 115.8, 115.7, 114.0, 113.6, 113.2, 98.8, 72.6, 66.5, 46.7, 38.3, 28.1, 24.4, 23.9, 22.3, 22.3, 20.2, 16.8; MS (MALDI-TOF) *m/z*, Calcd for $C_{85}H_{123}N_9O_{17}$ 1541.90 (M^+), Found 1564.9 ($M+Na^+$).

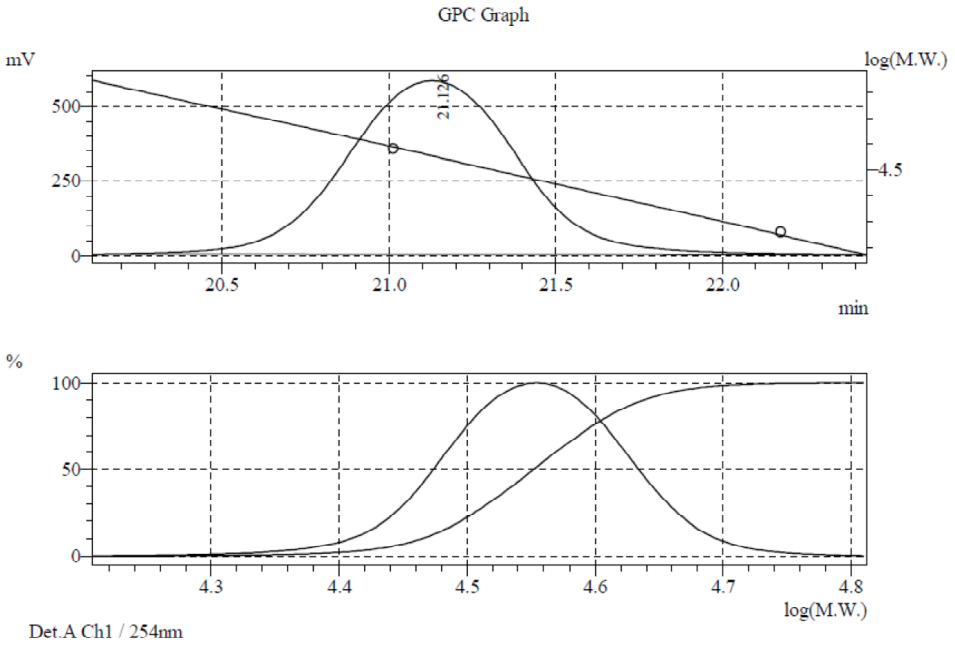
II. GPC Data of 3a, 3b and 3c

GPC measurements. GPC measurements on the three fractions of **3** were performed with a GMH_{HR}-N column, with a flow rate of 0.35 ml/min, and using THF as the eluting solvent at room temperature. The injection volume was 10 μL and UV detection at 254 nm was applied. Molecular weights and molecular-weight dispersity were calculated based on 12 polystyrene standards（Mw = 500 to $1.11x10^6$, Table S1).

Table S1. The molecular wieghts of the 12 polystyrene standards（polydispersity <1.1）

entry	1	2	3	4	5	6	7	8	9	10	11	12
Mw	5.89×10^2	1.01×10^3	2.5×10^3	4.92×10^3	9.49×10^3	1.71×10^4	3.72×10^4	9.89×10^4	1.89×10^5	3.97×10^5	7.07×10^5	1.11×10^6

GPC traces and results of 3a

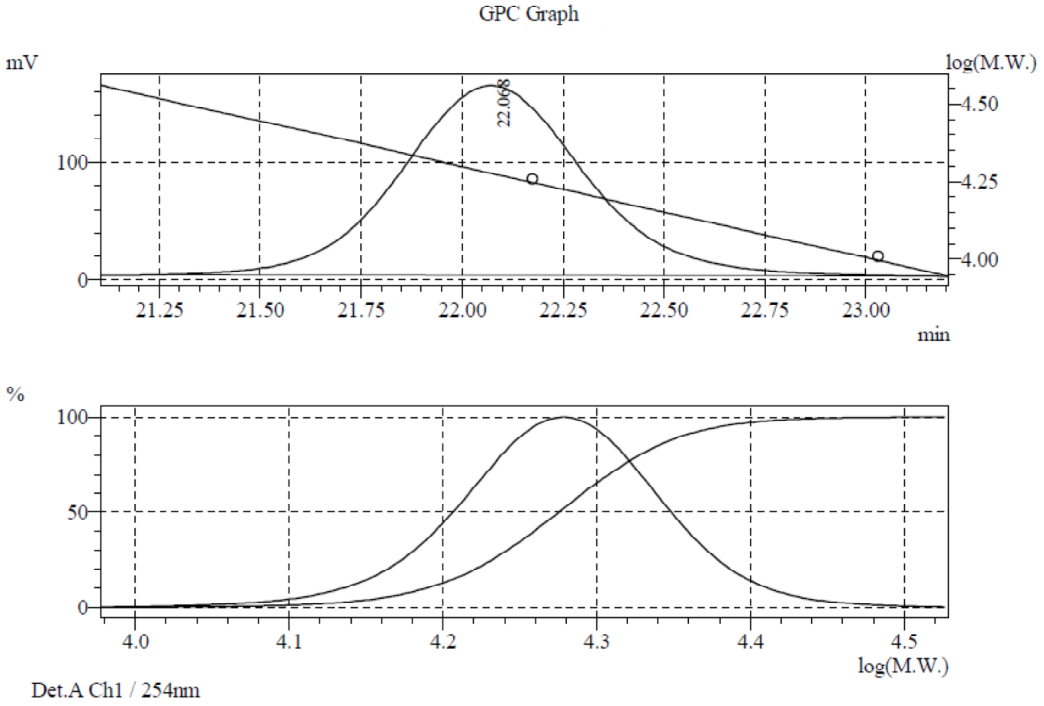


GPC Summary

Chromatogram Det.A Ch1

Title	Mn	Mw	Mz	Mz1	Mv	Mw/Mn
cjx-s-a-5-20''''ok.lcd	35166	36112	37053	38003	0	1.02689
Average	35166	36112	37053	38003	0	1.02689
%RSD	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	35166	36112	37053	38003	0	1.02689
Minimum	35166	36112	37053	38003	0	1.02689
SD	0	0	0	0	0	0.00000

GPC traces and results of 3b

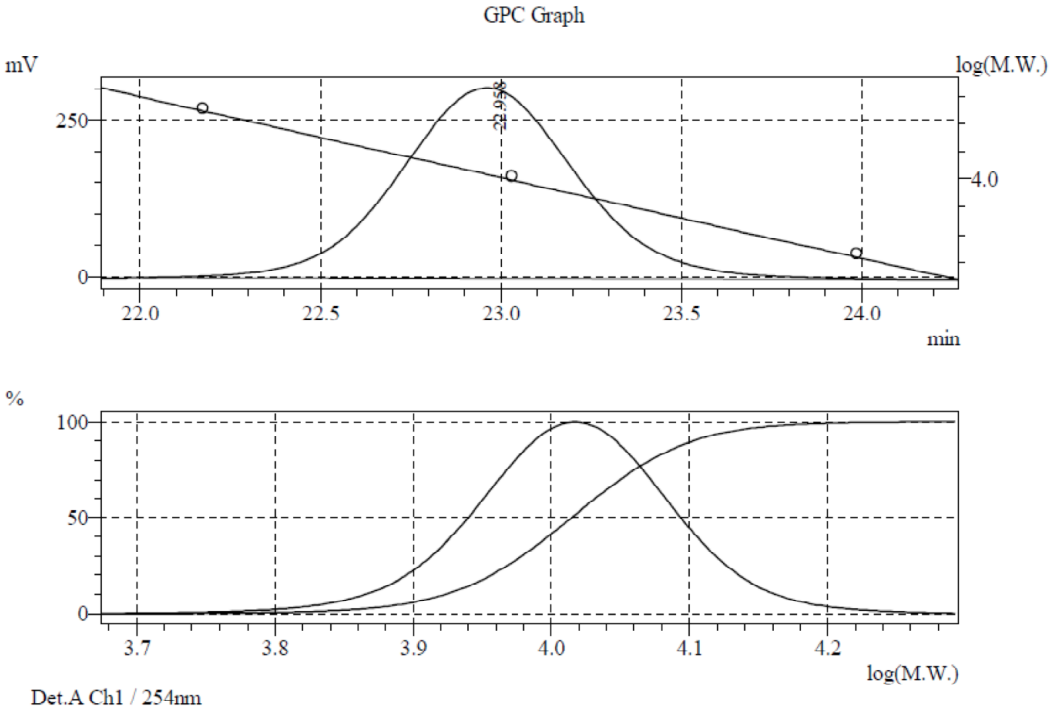


GPC Summary

Chromatogram Det.A Ch1

Title	Mn	Mw	Mz	Mz1	Mv	Mw/Mn
cjx-s-a-5-19ok.lcd	18597	19053	19509	19971	0	1.02452
Average	18597	19053	19509	19971	0	1.02452
%RSD	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	18597	19053	19509	19971	0	1.02452
Minimum	18597	19053	19509	19971	0	1.02452
SD	0	0	0	0	0	0.00000

GPC traces and results of 3c



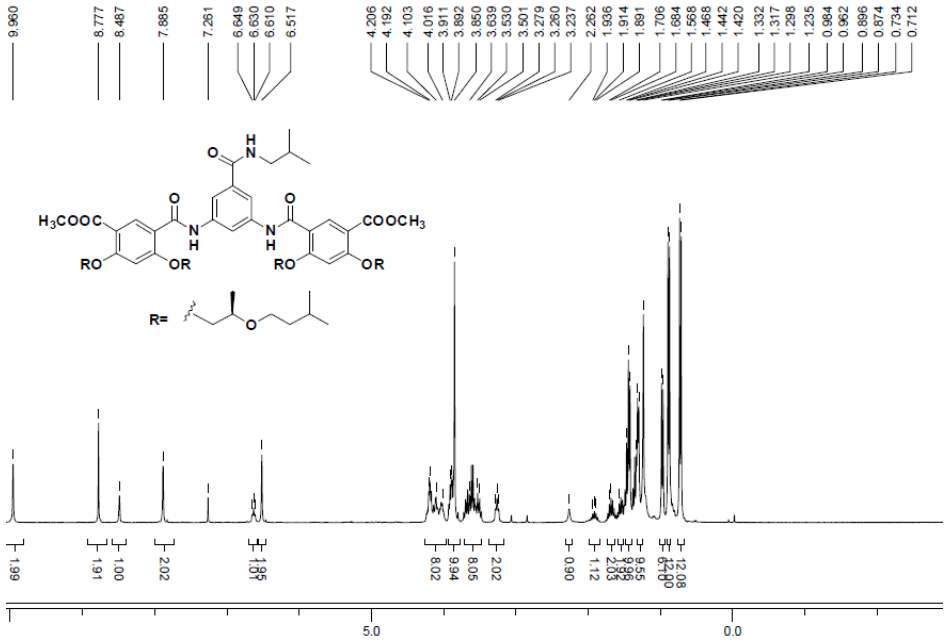
GPC Summary

Chromatogram Det.A Ch1

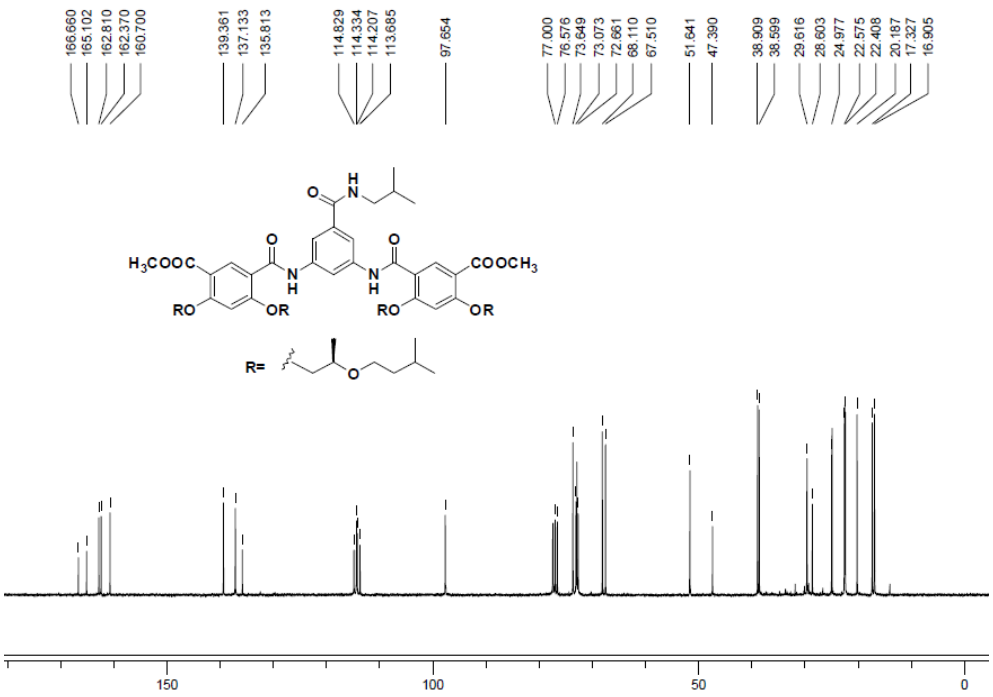
Title	Mn	Mw	Mz	Mz1	Mv	Mw/Mn
cjx-s-a-5-18ok.lcd	10198	10486	10777	11076	0	1.02826
Average	10198	10486	10777	11076	0	1.02826
%RSD	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	10198	10486	10777	11076	0	1.02826
Minimum	10198	10486	10777	11076	0	1.02826
SD	0	0	0	0	0	0.00000

III. 1D ^{1}H and ^{13}C NMR Spectra

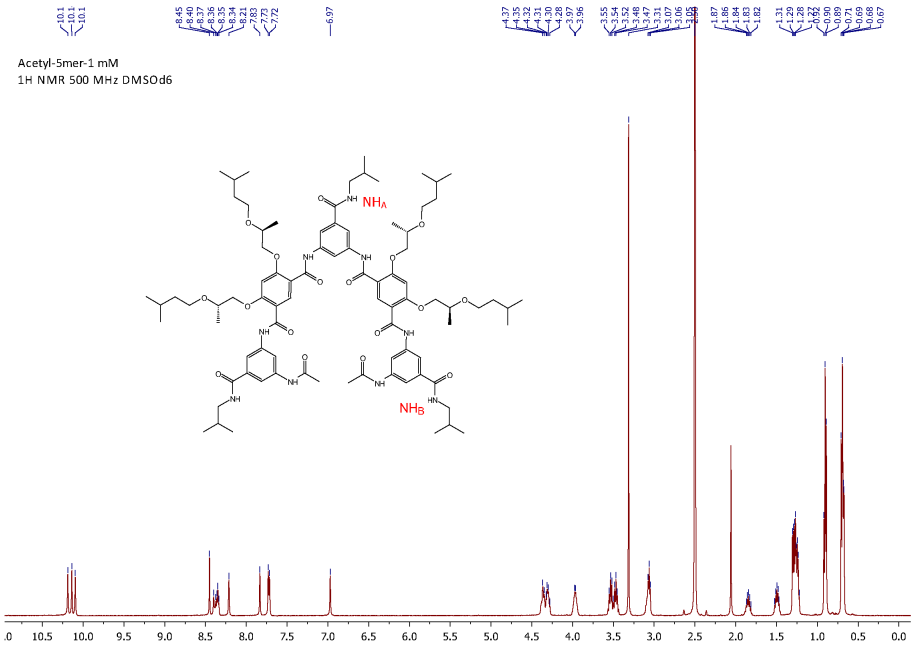
^{1}H NMR spectrum of 4



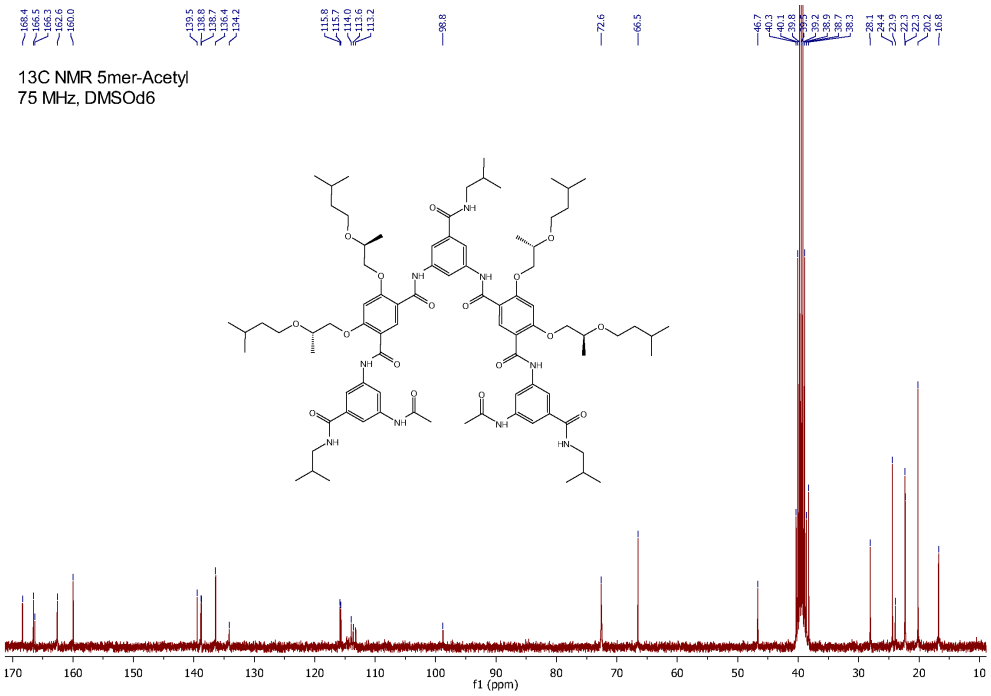
^{13}C NMR spectrum of 4



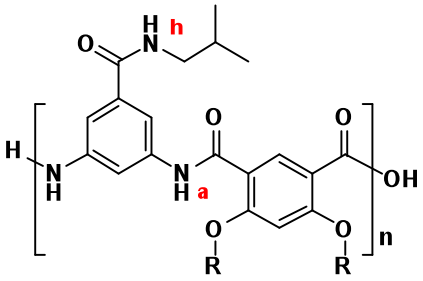
^{1}H NMR spectrum of 5

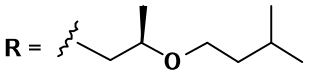


^{13}C NMR spectrum of 5



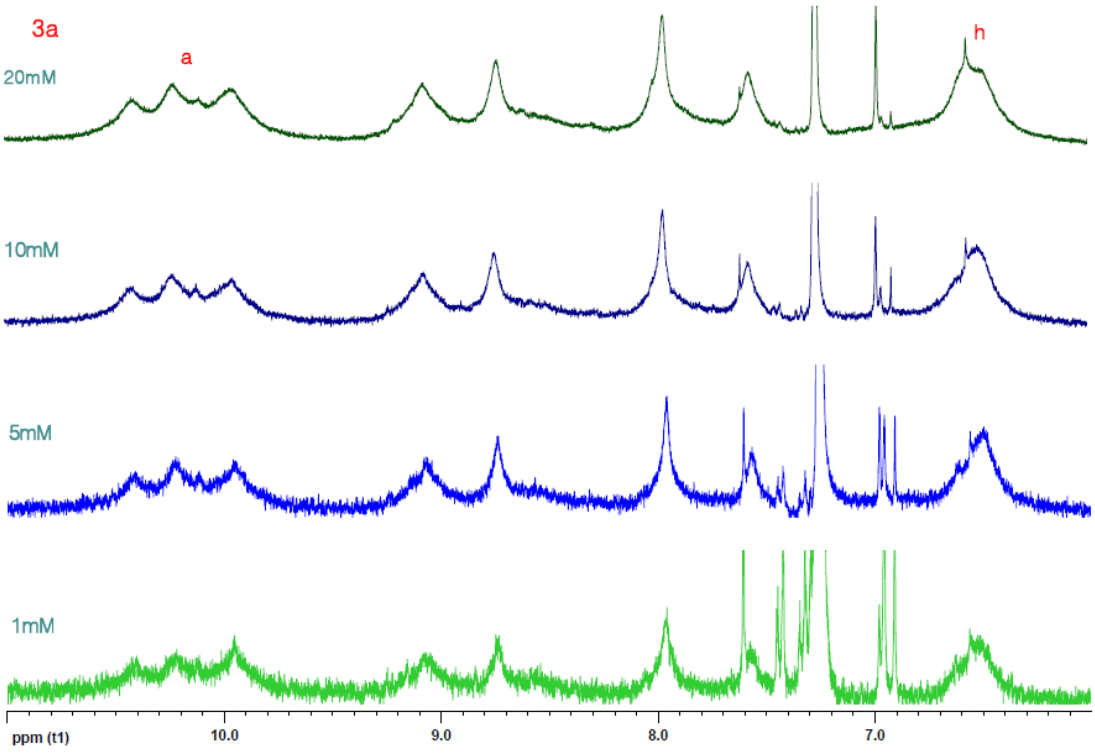
V. Concentration-Dependent ^{1}H NMR Spectra of 3a, 3b, 3c and 4



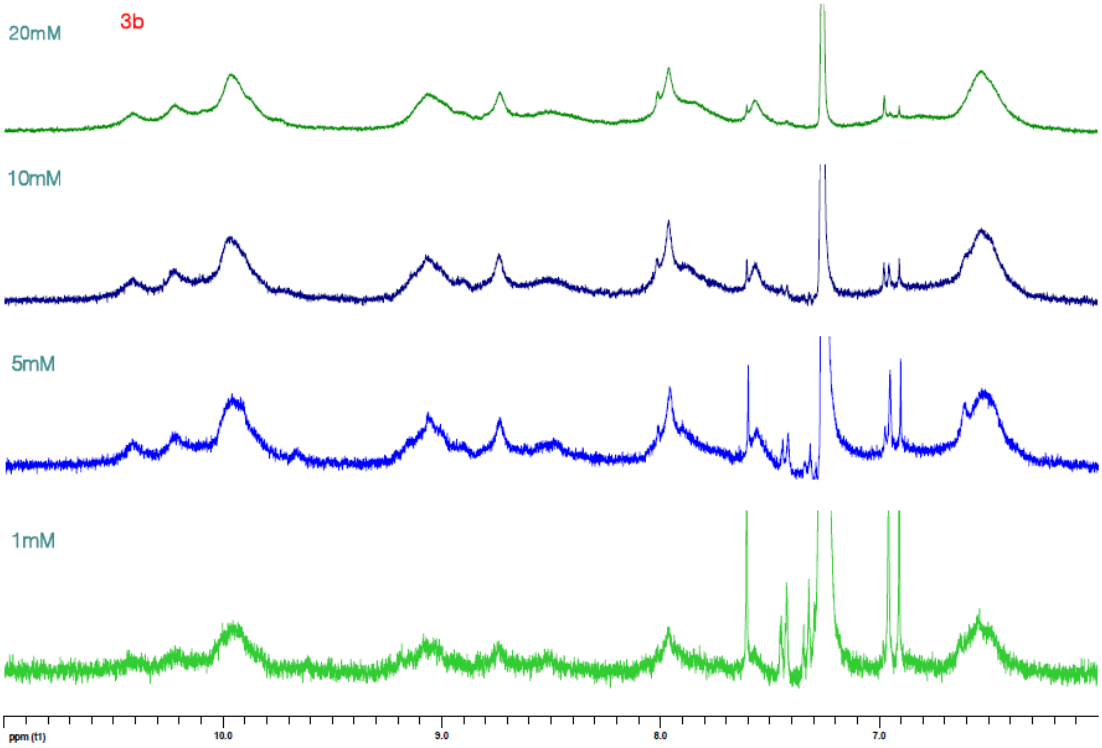


3a: n=56
3b: n=30
3c: n=16

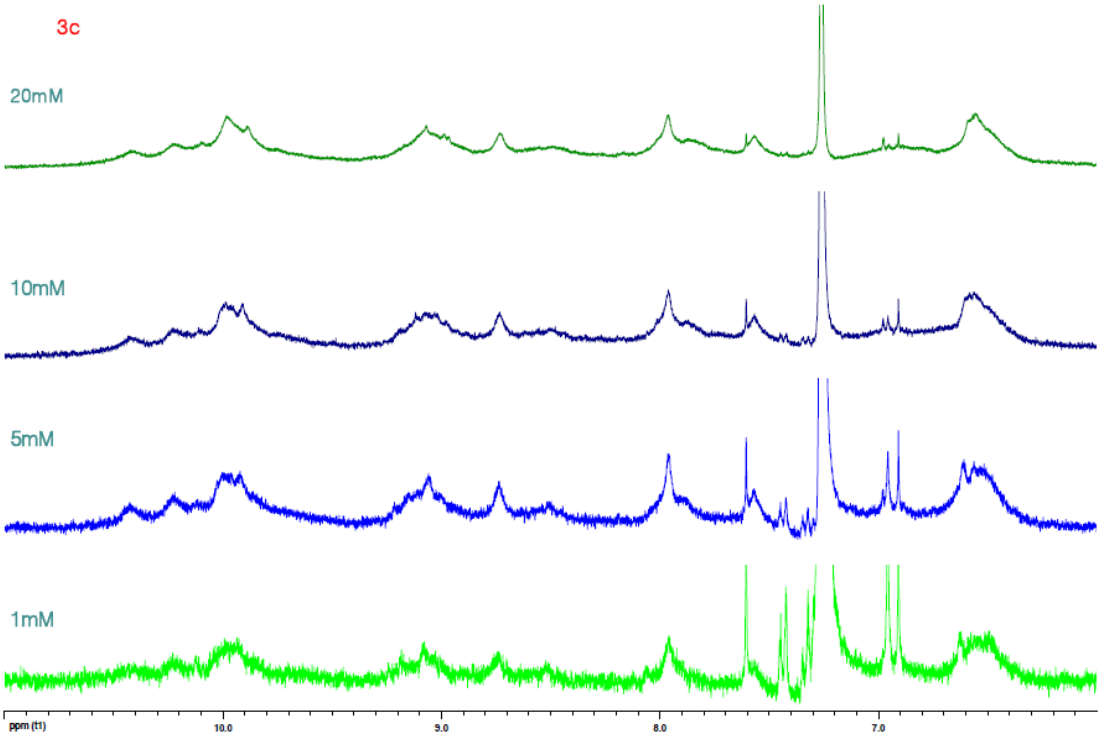
Concentration-Dependent 1H NMR Spectra of 3a



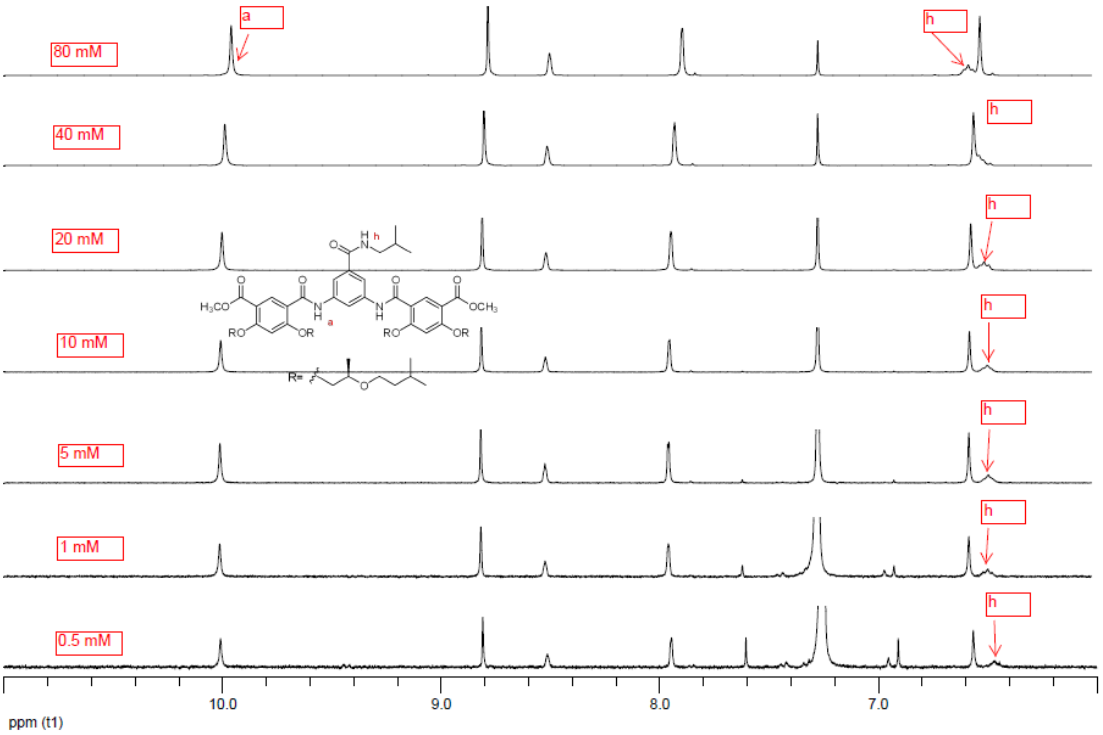
Concentration-Dependent 1H NMR Spectra of 3b



Concentration-Dependent 1H NMR Spectra of 3c

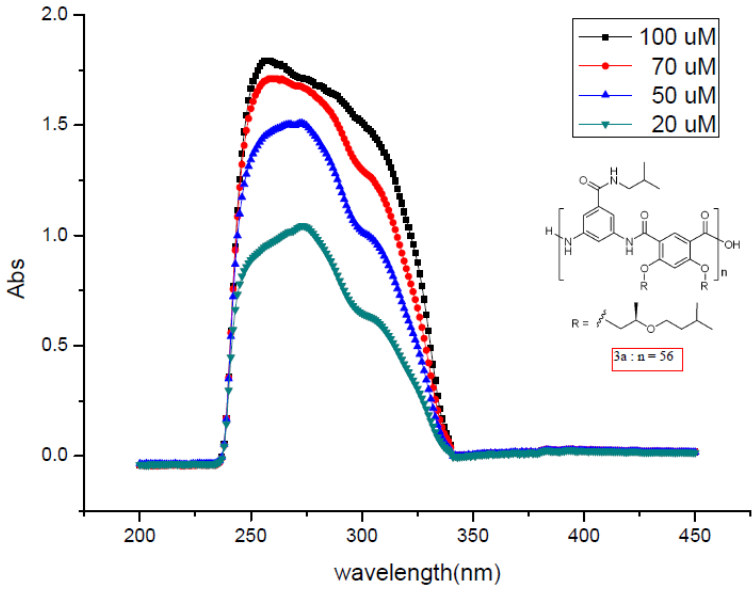


Concentration-Dependent 1H NMR Spectra of 4

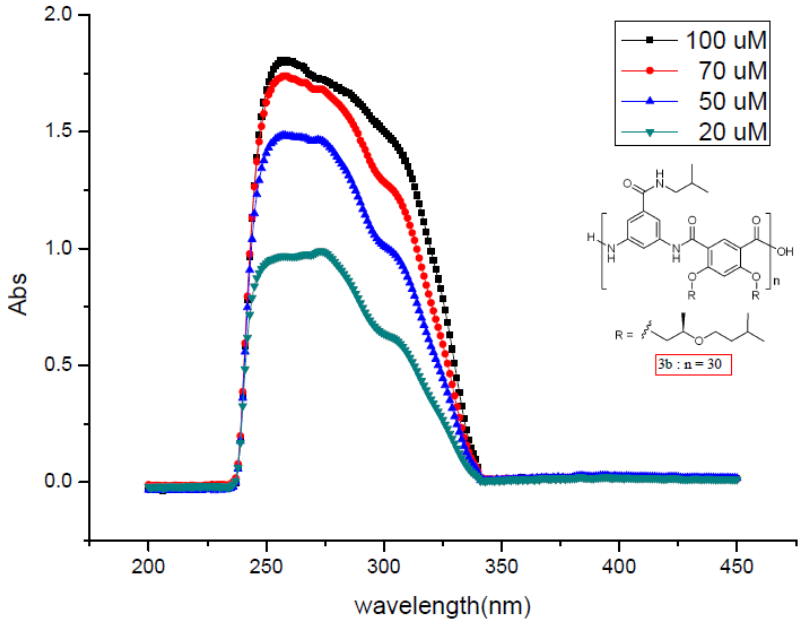


VI. UV Data of 3a, 3b, 3c and 4

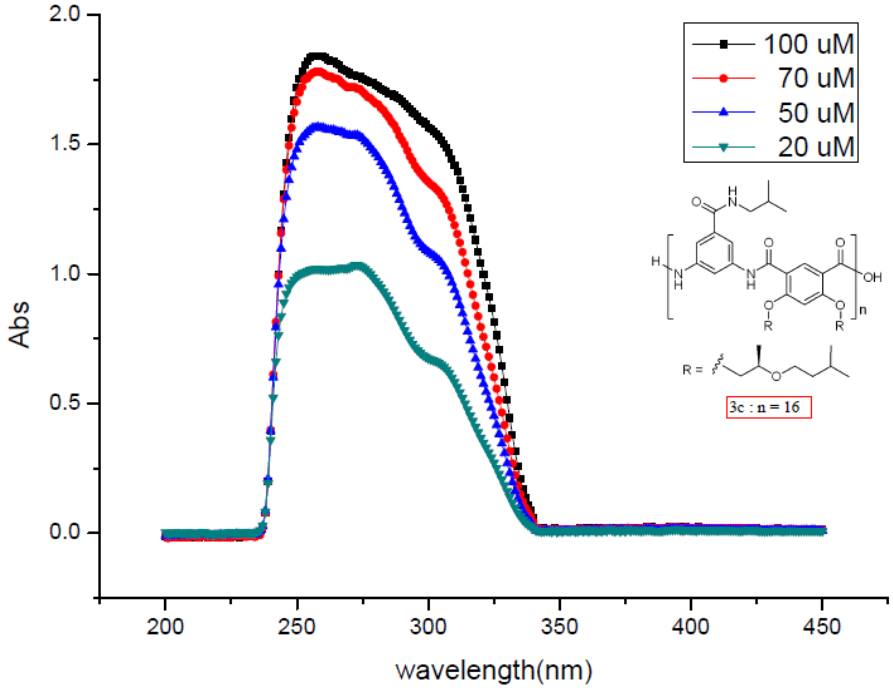
UV Spectra of 3a （in $CHCl_3$）

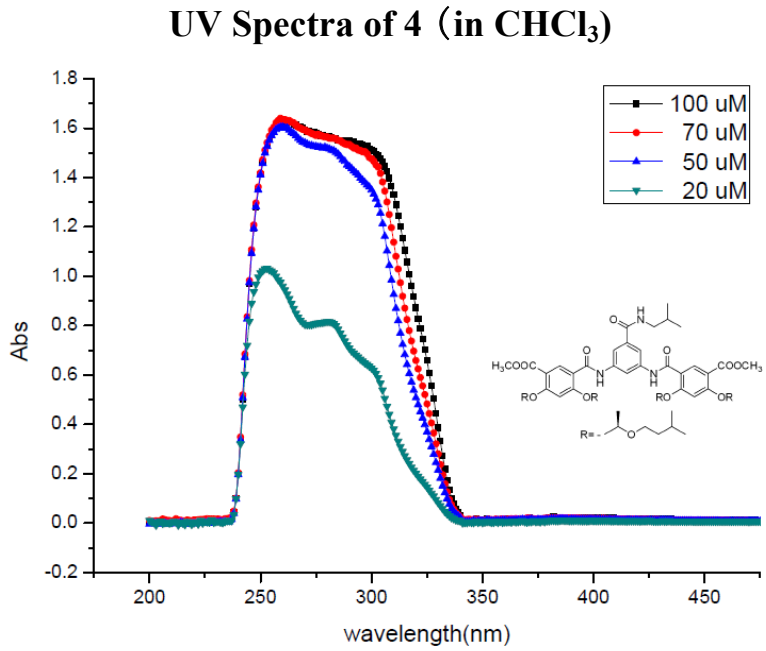


UV Spectra of 3b （in $CHCl_3$）



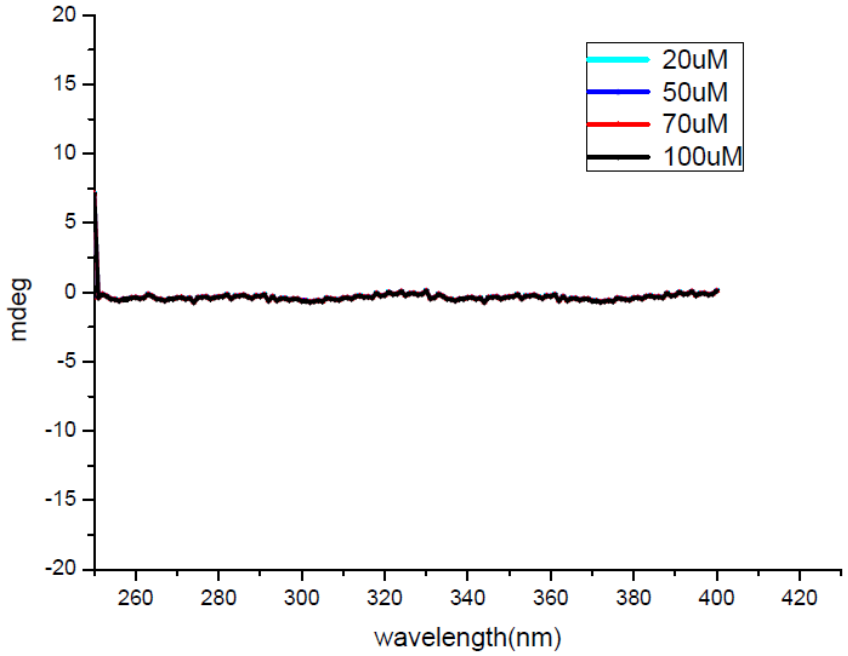
UV Spectra of 3c （in $CHCl_3$）



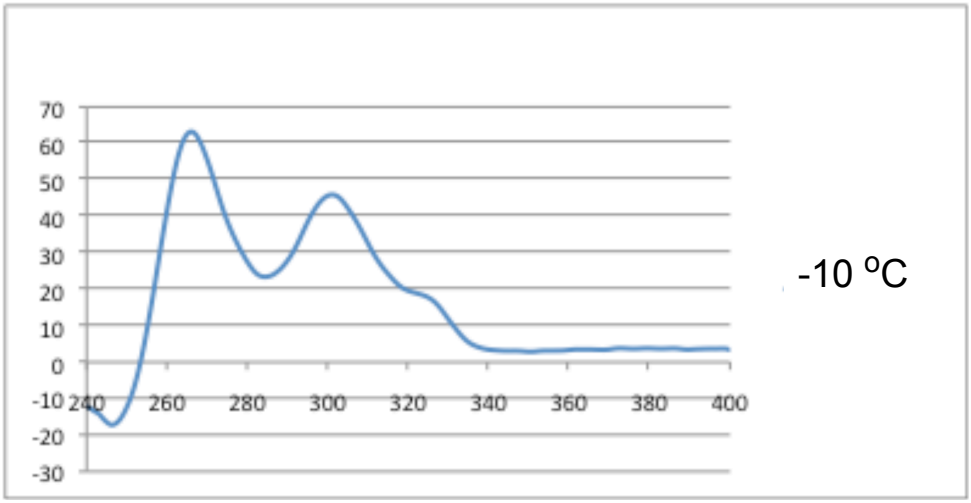

UV Spectra of 4（in CHCl3)
100 uM
70 uM
50 uM
20 uM
Abs
wavelength(nm)
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
200
250
300
350
400
450

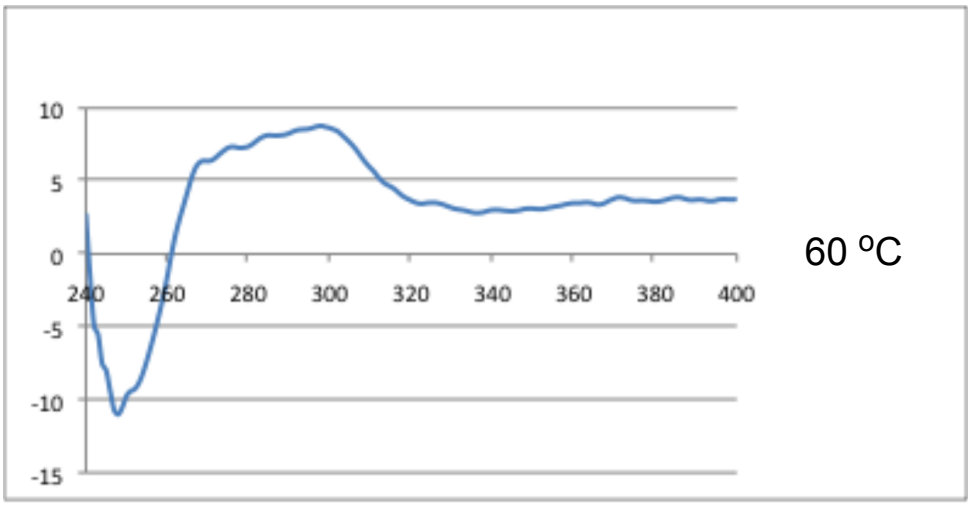
VII. Additional CD Spectra

The CD Spectra of 4 (in $CHCl_3$)

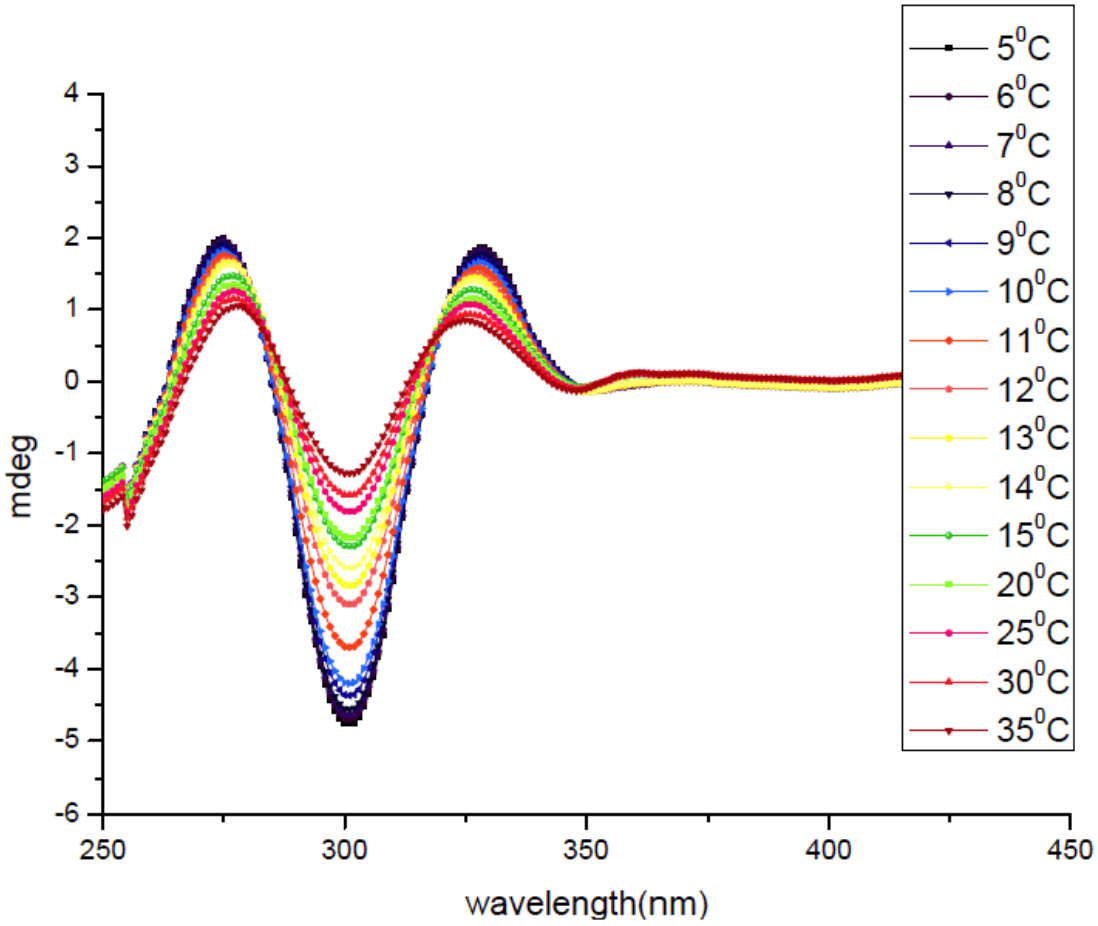


The CD spectra of 5 (10 μM in $CHCl_3$) at -10 °C and 60 °C

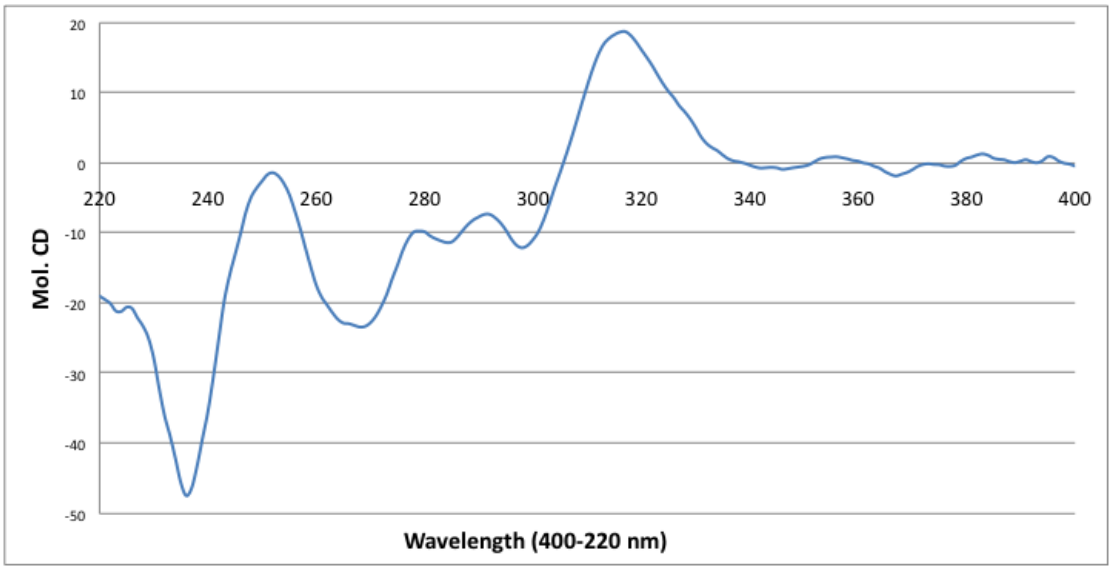




Temperature-dependent CD Spectra of 3a (70 μM, $CHCl_3$)



The CD Spectrum of 3a in THF (20 μM, room temperature)



1. L. H. Yuan, A. R. Sanford, W. Feng, A. M. Zhang, J. S. Ferguson, K. Yamato, J. Zhu, H. Q. Zeng and B. Gong, *J. Org. Chem*. 2005, **70**, 10660.