## **Supporting Information**

# Cyclo-oligomerization of hydroxyl-containing mono-functional benzoxazines: a mechanism for oligomer formation

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## Contents

- 1. Experimental procedures
- 2. Scheme S1 Synthesis reaction of hydroxyl-containing mono-functional benzoxazines.
- 3. Figure S1 <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $M_a-M_d$ .
- 4. Figure S2 FTIR spectra of M<sub>a</sub>-M<sub>d</sub>.
- 5. Figure S3 <sup>1</sup>H and <sup>13</sup>C NMR spectra of non-isothermally treated samples of  $M_a-M_d$ .
- 6. Figure S4 FTIR spectra of non-isothermally treated samples of  $M_a-M_d$ .
- 7. Figure S5 FTIR spectra of isothermally treated samples of  $M_a$ .
- 8. Figure S6 (a) Curves of storage modulus and loss factor versus temperature of  $P_a$ , and (b) TG curve of  $P_a$ .
- 9. Figure S7 SEC chromatograms of thermally treated samples of  $M_a-M_d$ .
- 10. Table S1 Mass results for oligomers of Ma-200 and the proposed assignments
- 11. Table S2 Mass results for oligomers of  $M_b$ -200<sub>i</sub> and the proposed assignments
- 12. Table S3 Mass results for oligomers of  $M_c$ -200<sub>i</sub> and the proposed assignments
- 13. Table S4 Mass results for oligomers of  $M_d$ -220<sub>2nd</sub> and the proposed assignments

## **Experimental procedures**

#### Materials

Phenol, *o*-cresol, *p*-cresol, paraformaldehyde, 1,4-dioxane, and chloroform were purchased from Tianjin Kermel Chemical Reagent Co., Ltd, China. *o*-Allylphenol was obtained from Shandong Laizhou Hualu Storage Battery Co., Ltd, China. Diglycolamine (DGA) was offered by Shanghai Jingchun Chemical Reagent Co., Ltd, China. All chemicals were used as received.

#### Synthesis of hydroxyl-containing mono-functional benzoxazines $(M_a - M_d)$

Synthesis of monomer  $M_a$ . In a 250 mL three-necked flask equipped with a mechanical stirrer, a thermometer, and a reflux condenser, DGA (9.0 mL) and paraformaldehyde (5.4 g) were dissolved in 1,4-dioxane (50 mL) at 0 °C. After stirring for 30 min at 0 °C, phenol (7.8 mL) was added to the reaction mixture. Subsequently, the temperature was gradually raised to reflux and maintained for 20 h. Thereafter, the solvent was removed by distillation under vacuum, and the residue was dissolved in approximately 40 mL of chloroform. The chloroform solution was washed several times with a 0.1 mol/L NaOH aqueous solution and deionized water, respectively. Residual chloroform was then removed under vacuum. The product was dried at 60 °C in a vacuum oven for 24 h. Finally, a transparent, pale yellow, viscous liquid was obtained. The yield of  $M_a$  was approximately 45.2%.

The other three mono-functional benzoxazine monomers  $M_b-M_d$  were synthesized following the same method, except phenol was substituted by *o*-allylphenol, *o*-cresol, and *p*-cresol, respectively, and the yields were 61.4%, 56.8%, and 52.6%, respectively.

## The <sup>1</sup>H and <sup>13</sup>C NMR and FTIR data of $M_a$ - $M_d$

### Ma

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 2.98, 3.58, 3.66, and 3.71 (t, N–CH<sub>2</sub>–CH<sub>2</sub>–O–CH<sub>2</sub>–CH<sub>2</sub>–OH in 2-(2-hydroxyethoxy)ethyl group), 4.03 (s, Ar–CH<sub>2</sub>–N), 4.88 (s, O–CH<sub>2</sub>–N), 6.78 (d, Ar–H), 6.86 (t, Ar–H), 6.93 (d, Ar–H), and 7.11 (t, Ar–H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 50.51 (*C*H<sub>2</sub> attached to nitrogen in 2-(2-hydroxyethoxy)ethyl group), 51.10 (Ar–*C*H<sub>2</sub>–N), 61.76 (*C*H<sub>2</sub> attached to OH in 2-(2-hydroxyethoxy)ethyl group), 69.19 and 72.49 (*C*H<sub>2</sub> attached to ether oxygen in 2-(2-hydroxyethoxy)ethyl group), 82.52 (O– *C*H<sub>2</sub>–N), 116.48 (Ar–H), 119.86 (Ar–CH<sub>2</sub>–N), 120.71 (Ar–H), 127.57 (Ar–H), 127.85 (Ar–H), and 154.00 (Ar–O).

FTIR (KBr, cm<sup>-1</sup>): 3404 (vO–H), 2937 (v<sub>as</sub>C–H of CH<sub>2</sub>), 2866 (v<sub>s</sub>C–H of CH<sub>2</sub>), 1608, 1584,

and 1489 (aromatic C=C), 1457 (CH<sub>2</sub> bending), 1352 and 1333 (CH<sub>2</sub> wagging), 848 (CH<sub>2</sub>-rocking), 1222 ( $v_{as}$ C–O–C of oxazine ring), 1126 and 1064 (vC–O–C of 2-(2-hydroxyethoxy)ethyl group), 928 (O–C–N stretching mode of the oxazine ring with minor contribution of the C–H out-of-plane bending), 976, 756, 708, and 588 (aromatic C–H out-of-plane bending).

 $\mathbf{M}_{\mathbf{b}}$ 

Ш

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 3.02 (t, *CH*<sub>2</sub> attached to nitrogen in 2-(2-hydroxyethoxy)ethyl group), 3.36–3.38 (d, –*CH*<sub>2</sub> of allyl group), 3.64, 3.72, and 3.76 (t,–*CH*<sub>2</sub>–*CH*<sub>2</sub>–*O*–*CH*<sub>2</sub>–*CH*<sub>2</sub>–*O*H in 2-(2-hydroxyethoxy)ethyl group), 4.09 (s, Ar–*CH*<sub>2</sub>–N), 4.95 (s, O–*CH*<sub>2</sub>–N), 5.06–5.10 (m, =*CH*<sub>2</sub> of allyl group), 5.97–6.07 (m, =*CH* of allyl group), 6.86 (m, Ar–H), and 7.03 (t, Ar–H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 33.64 (-*C*H<sub>2</sub> of allyl group), 50.68 (*C*H<sub>2</sub> attached to nitrogen in 2-(2-hydroxyethoxy)ethyl group), 51.11 (Ar-*C*H<sub>2</sub>-N), 61.80 (*C*H<sub>2</sub> attached to OH in 2-(2-hydroxyethoxy)ethyl group), 69.21 and 72.50 (*C*H<sub>2</sub> attached to ether oxygen in 2-(2-hydroxyethoxy)ethyl group), 82.60 (O-*C*H<sub>2</sub>-N), 115.46 (=*C*H<sub>2</sub> of allyl group), 119.42 (Ar-*C*H<sub>2</sub>-N), 120.23 (Ar-H), 125.57 (Ar-H), 127.66 (Ar-*C*H<sub>2</sub>), 128.13 (Ar-H), 136.80 (-*C*H of allyl group), and 151.70 (Ar-O).

FTIR (KBr, cm<sup>-1</sup>): 3404 (vO–H), 3074 (vC–H of olefinic =C–H of allyl group), 3004 (vC–H of aromatic =C–H), 2937 ( $v_{as}$ C–H of CH<sub>2</sub>), 2864 ( $v_{s}$ C–H of CH<sub>2</sub>), 1637 (olefinic C=C stretching vibration), 1593 (aromatic C=C), 1464 (CH<sub>2</sub> bending), 1353 and 1333 (CH<sub>2</sub> wagging), 1213 ( $v_{as}$ C–O–C of oxazine ring), 1168 (vC–N–C of oxazine ring), 1126 and 1073 (vC–O–C of 2-(2-hydroxyethoxy)ethyl group), 993 (olefinic =C–H out-of-plane bending), 931 (O–C–N stretching mode of the oxazine ring with minor contribution of the C–H out-of-plane bending), 819, 773, 751, and 625 (aromatic C–H out-of-plane bending).

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<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 2.21 (s, -CH<sub>3</sub>), 3.02, 3.64, 3.72, and 3.76 (t, -CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-OH in 2-(2-hydroxyethoxy)ethyl group), 4.07 (s, Ar-CH<sub>2</sub>-N), 4.96 (s, O-CH<sub>2</sub>-N), 6.81-6.82 (d, Ar-H), and 7.02-7.03 (d, Ar-H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 15.59 (-CH<sub>3</sub>), 50.65 (CH<sub>2</sub> attached to nitrogen in 2-(2-

hydroxyethoxy)ethyl group), 51.10 (Ar– $CH_2$ –N), 61.78 ( $CH_2$  attached to OH in 2-(2-hydroxyethoxy)ethyl group), 69.20 and 72.48 ( $CH_2$  attached to ether oxygen in 2-(2-hydroxyethoxy)ethyl group), 82.56 (O– $CH_2$ –N), 119.15 (Ar– $CH_2$ –N), 119.99 (Ar–H), 125.00 (Ar–H), 125.60 (Ar– $CH_3$ ), 128.94 (Ar–H), and 152.14 (Ar–O).

FTIR (KBr, cm<sup>-1</sup>): 3404 (vO–H), 3021 (vC–H of aromatic =C–H), 2937 ( $v_{as}C$ –H of CH<sub>2</sub>), 2862 ( $v_sC$ –H of CH<sub>2</sub>), 1595 and 1473 (aromatic C=C), 1353 and 1333 (CH<sub>2</sub> wagging), 1213 ( $v_{as}C$ –O–C of oxazine ring), 1171 (vC–N–C of oxazine ring), 1126 and 1061 (vC–O–C of 2-(2-hydroxyethoxy)ethyl group), 1081 ( $v_sC$ –O–C of oxazine ring), 935 (O–C–N stretching mode of the oxazine ring with minor contribution of the C–H out-of-plane bending), 811, 765, 735, and 664 (aromatic C–H out-of-plane bending).

 $M_d$ 

<sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 2.28 (s, -CH<sub>3</sub>), 3.02, 3.63, 3.71, and 3.75 (t, -CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-OH in 2-(2-hydroxyethoxy)ethyl group), 4.04 (s, Ar-CH<sub>2</sub>-N), 4.89 (s, O-CH<sub>2</sub>-N), 6.73 (d, Ar-H), 6.79 (s, Ar-H), and 6.96 (d, Ar-H).

<sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  (ppm): 20.61 (-*C*H<sub>3</sub>), 50.56 (*C*H<sub>2</sub> attached to nitrogen in 2-(2-hydroxy)ethyl group), 51.10 (Ar-*C*H<sub>2</sub>-N), 61.78 (*C*H<sub>2</sub> attached to OH in 2-(2-hydroxy)ethyl group), 69.21 and 72.53 (*C*H<sub>2</sub> attached to ether oxygen in 2-(2-hydroxyethoxy)ethyl group), 82.45 (O-*C*H<sub>2</sub>-N), 116.22 (Ar-H), 119.50 (Ar-*C*H<sub>2</sub>-N), 127.88 (Ar-H), 128.42 (Ar-H), 129.95 (Ar-*C*H<sub>3</sub>), and 151.75 (Ar-O).

FTIR (KBr, cm<sup>-1</sup>): 3404 (vO–H), 2937 ( $v_{as}C$ –H of CH<sub>2</sub>), 2863 ( $v_sC$ –H of CH<sub>2</sub>), 1618, 1588, and 1501 (aromatic C=C), 1453 (CH<sub>2</sub> bending), 1353 and 1323 (CH<sub>2</sub> wagging), 1219 ( $v_{as}C$ –O–C of oxazine ring), 1179 (vC–N–C of oxazine ring), 1125 and 1063 (vC–O–C of 2-(2-hydroxyethoxy)ethyl group), 939 (O–C–N stretching mode of the oxazine ring with minor contribution of the C–H out-of-plane bending), 912, 816, 760, 745, and 693 (aromatic C–H out-of-plane bending).

## Thermal treatment of $M_a - M_d$

 $M_a$ ,  $M_b$ ,  $M_c$ , and  $M_d$  were non-isothermally heated or isothermally heated in a vacuum oven. The non-isothermally treated samples from  $M_a$ ,  $M_b$ ,  $M_c$ , and  $M_d$  are respectively designated as  $M_a$ -200,  $M_b$ -220,  $M_c$ -200,  $M_c$ -220,  $M_d$ -220, and  $M_d$ -220<sub>2nd</sub>, the number appearing after the cord denotes the temperature (°C) to which the sample is non-isothermally heated, and the subscript 2nd denotes the second run of a heating–cooling thermal treatment. The isothermally treated samples from  $M_b$  and  $M_c$  are respectively designated as  $M_b$ -200<sub>i</sub> and  $M_c$ -200<sub>i</sub>, in which 200<sub>i</sub> denotes the sample is heated to 200 °C and maintained for 6 h.

## Preparation of polybenzoxazine

First,  $M_a$  was transferred to a steel mold, and the mold was put into a vacuum oven. Then, the vacuum oven was step-heated to 120, 130, 140, and 150 °C, held at each temperature for 1 h, and finally held at 170 °C for 6 h. The resultant polybenzoxazine prepared from  $M_a$  is designated as  $P_a$ .

### Measurements

<sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectra were measured on a Zhongke-Niujin BUXI-I 400 NMR spectrometer at room temperature. Deuterated chloroform (CDCl<sub>3</sub>) was used as the solvent. The chemical shifts of hydrogen and carbon are given in parts per million (ppm) from internal tetramethylsilane.

The Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 380 FTIR spectrometer with a resolution of 4 cm<sup>-1</sup>. Each benzoxazine was dissolved in chloroform and coated on a KBr disk to form a thin uniform film by evaporating the solvent at 50 °C in a vacuum oven. Thereafter, the disk was heated isothermally in a static air oven and removed periodically to be scanned.

The heat evolution behavior of benzoxazines was studied by differential scanning calorimetry (DSC). A TA instruments Q2000 differential scanning calorimeter was operated at a heating rate of 10 °C/min in nitrogen.

Size exclusion chromatography (SEC) measurements were performed using a Waters 515 HPLC pump system equipped with a 717 auto sample injector and a 2410 differential refractometer detector. The system was operated with a set of three columns (HT3, HT5, and HT6E) in series, and the column temperature was maintained at 35 °C. Tetrahydrofuran was used as the eluent and at a flow rate of 1.0 mL/min.

Mass spectra were obtained by electrospray ionization mass spectrometry (ESI-MS). A Thermo Fisher Scientific LCQ advantage ion-trap mass spectrometer is equipped with an electrospray ionisation source, operated in the positive-ion mode.

Thermogravimetric analysis (TGA) was performed with a TA instruments Q50 thermogravimeter operating in dynamic nitrogen at a heating rate of 10 °C/min.

Dynamic mechanical analysis (DMA) was performed using a TA instruments Q800 dynamic mechanical analyzer under multi-frequency-strain mode. The dimensions of the specimen were

nominally 15.0 mm  $\times$  6.0 mm  $\times$  1.0 mm.



Scheme S1 Synthesis reaction of hydroxyl-containing mono-functional benzoxazines.



Figure S1 <sup>1</sup>H and <sup>13</sup>C NMR spectra of  $M_a-M_d$ .



Figure S2 FTIR spectra of M<sub>a</sub>-M<sub>d</sub>.



Figure S3 <sup>1</sup>H and <sup>13</sup>C NMR spectra of non-isothermally treated samples of  $M_a-M_d$ . (Continued on next page)



Figure S3 (Continued).



Figure S4 FTIR spectra of non-isothermally treated samples of  $M_a$ - $M_d$ .



Figure S5 FTIR spectra of isothermally treated samples of  $M_a$ .



Figure S6 (a) Curves of storage modulus and loss factor versus temperature of  $P_a$ , and (b) TG curve of  $P_a$ .



Figure S7 SEC chromatograms of thermally treated samples of  $M_a-M_d$ .

Mass series	[M+H] <sup>+</sup>	Empirical formula	Chemical structure	n	Ring size
A	447 670 893 1116	$\begin{array}{c} C_{24}H_{34}N_2O_6\\ C_{36}H_{51}N_3O_9\\ C_{48}H_{68}N_4O_{12}\\ C_{60}H_{85}N_5O_{15} \end{array}$		2 3 4 5	12 18 24 30
В	564 787 1010	$\begin{array}{c} C_{29}H_{45}N_{3}O_{8}\\ C_{41}H_{62}N_{4}O_{11}\\ C_{53}H_{79}N_{5}O_{14} \end{array}$		1 2 3	8 14 20
С	435 658 881 1104	$\begin{array}{c} C_{23}H_{34}N_2O_6\\ C_{35}H_{51}N_3O_9\\ C_{47}H_{68}N_4O_{12}\\ C_{59}H_{85}N_5O_{15} \end{array}$	$HO \sim O \sim N + OH = OH$	1 2 3 4	- - - -
D	318 541 764 987	$\begin{array}{c} C_{18}H_{23}NO_4\\ C_{30}H_{40}N_2O_7\\ C_{42}H_{57}N_3O_{10}\\ C_{54}H_{74}N_4O_{13} \end{array}$		0 1 2 3	- - - -
E	449 672 895	$\begin{array}{c} C_{24}H_{36}N_2O_6\\ C_{36}H_{53}N_3O_9\\ C_{48}H_{70}N_4O_{12} \end{array}$	$HO \sim O \sim N \sim \left[ \begin{array}{c} O H \\ O \\ O H \end{array} \right]_{n} \begin{array}{c} O H \\ O H \\ O H \end{array} \right]_{n} \begin{array}{c} O H \\ O H \\ O H \end{array}$	1 2 3	- - -

Table S1 Mass results for oligomers of  $M_a$ -200 and the proposed assignments

Mass series	[M+H] <sup>+</sup>	Empirical formula	Chemical structure	n	Ring size
A	527 790 1053	$\begin{array}{c} C_{30}H_{42}N_2O_6\\ C_{45}H_{63}N_3O_9\\ C_{60}H_{84}N_4O_{12} \end{array}$		2 3 4	12 18 24
В	513 776 1039	$\begin{array}{c} C_{29}H_{40}N_2O_6\\ C_{44}H_{61}N_3O_9\\ C_{59}H_{82}N_4O_{12} \end{array}$		1 2 3	11 17 23
С	673 936	$\begin{array}{c} C_{40}H_{52}N_2O_7\\ C_{55}H_{73}N_3O_{10} \end{array}$		23	16 22
D	381 644 907	$\begin{array}{c} C_{20}H_{32}N_2O_5\\ C_{35}H_{53}N_3O_8\\ C_{50}H_{74}N_4O_{11} \end{array}$		1 2 3	8 14 20
E	367 630 893	$\begin{array}{c} C_{19}H_{30}N_2O_5\\ C_{34}H_{51}N_3O_8\\ C_{49}H_{72}N_4O_{11} \end{array}$		1 2 3	7 13 19
F	529 792 1055	$ \begin{array}{c} \overline{C_{30}H_{44}N_2O_6} \\ C_{45}H_{65}N_3O_9 \\ C_{60}H_{86}N_4O_{12} \end{array} \end{array} $	$HO \longrightarrow N \longrightarrow $	1 2 3	-
G	543 806	$\begin{array}{c} C_{31}H_{46}N_2O_6\\ C_{46}H_{67}N_3O_9\end{array}$	HO~O~N~{CH <sub>3</sub> HO~O~N~{CH <sub>3</sub> N~{CH <sub>3</sub> N~{CH <sub>3</sub> N~{CH <sub>3</sub> N~{CH <sub>3</sub> N~{CH <sub>3</sub> N~{CH <sub>3</sub> N~{CH <sub>3</sub> N~{CH <sub>3</sub> } N~{CH <sub>3</sub> N~{CH <sub>3</sub> } N~{CH <sub>3</sub> } N~{CH <sub>3</sub> }	1 2	-

Table S2 Mass results for oligomers of  $M_b$ -200<sub>i</sub> and the proposed assignments

Mass series	$[M+H]^+$	Empirical formula	Chemical structure	n	Ring size
Α	475	C <sub>26</sub> H <sub>38</sub> N <sub>2</sub> O <sub>6</sub>	CH3	2	12
	712	C <sub>39</sub> H <sub>57</sub> N <sub>3</sub> O <sub>9</sub>	⊢ с − с − с − с − с − с − с − с − с − с	3	18
	949	$C_{52}H_{76}N_4O_{12}$		4	24
			, n		
B	461	C25H26N2O6		1	11
	698	$C_{29}H_{55}N_{2}O_{0}$		2	17
	935	$C_{51}H_{74}N_4O_{12}$	CH <sub>3</sub> O	3	23
		- 5174- 4 - 12		-	
			но		
			ĊH <sub>3</sub>		
C	358	$C_{21}H_{27}NO_4$	CH3	1	10
	595	$C_{34}H_{46}N_2O_7$	но — он о-	2	16
	832	$C_{47}H_{65}N_3O_{10}$		3	22
			n		
D	355	C <sub>18</sub> H <sub>30</sub> N <sub>2</sub> O <sub>5</sub>	но сн.	1	8
	592	C <sub>31</sub> H <sub>49</sub> N <sub>3</sub> O <sub>8</sub>		2	14
	829	C <sub>44</sub> H <sub>68</sub> N <sub>4</sub> O <sub>11</sub>		3	20
Е	341	$C_{17}H_{28}N_2O_5$	СОН	1	7
	578	$C_{30}H_{47}N_3O_8$	ÇH₃ O	2	13
	815	$C_{43}H_{66}N_4O_{11}$	OH	3	19
			HO		
			Ur		
F	477	C <sub>26</sub> H <sub>40</sub> N <sub>2</sub> O <sub>6</sub>	ОН	1	_
	714	C <sub>39</sub> H <sub>59</sub> N <sub>3</sub> O <sub>9</sub>		2	-
	951	C <sub>52</sub> H <sub>78</sub> N <sub>4</sub> O <sub>12</sub>		3	-
			HO~NNCH3		
			<sup>L</sup> <sup>Jn</sup> ÓH		
G	491	$C_{27}H_{42}N_2O_6$	_ОН	1	-
	728	$C_{40}H_{61}N_3O_9$	СН3 О СН3	2	-
	965	$C_{53}H_{80}N_4O_{12}$	CH3 CH 1	3	-
			UH UH		

Table S3 Mass results for oligomers of  $M_c$ -200<sub>i</sub> and the proposed assignments

Mass series	[M+H] <sup>+</sup>	Empirical formula	Chemical structure	n	Ring size
A	475 712 949	$\begin{array}{c} C_{26}H_{38}N_2O_6\\ C_{39}H_{57}N_3O_9\\ C_{52}H_{76}N_4O_{12} \end{array}$		2 3 4	12 18 24
В	461 698 935	$\begin{array}{c} C_{25}H_{36}N_2O_6\\ C_{38}H_{55}N_3O_9\\ C_{51}H_{74}N_4O_{12} \end{array}$	HO O HO O HO O HO C H <sub>3</sub> C	1 2 3	11 17 23
C	358 595 832	$\begin{array}{c} C_{21}H_{27}NO_4\\ C_{34}H_{46}N_2O_7\\ C_{47}H_{65}N_3O_{10} \end{array}$		1 2 3	10 16 22
D	355 592 829	$\begin{array}{c} C_{18}H_{30}N_2O_5\\ C_{31}H_{49}N_3O_8\\ C_{44}H_{68}N_4O_{11} \end{array}$		1 2 3	8 14 20
E	341 578 815	$\begin{array}{c} C_{17}H_{28}N_2O_5\\ C_{30}H_{47}N_3O_8\\ C_{43}H_{66}N_4O_{11} \end{array}$		1 2 3	7 13 19
F	477 714 951	$\begin{array}{c} C_{26}H_{40}N_2O_6\\ C_{39}H_{59}N_3O_9\\ C_{52}H_{78}N_4O_{12} \end{array}$	$HO \sim O \sim N \sim H \sim OH$	1 2 3	- - -
G	491 728 965	$\begin{array}{c} C_{27}H_{42}N_2O_6\\ C_{40}H_{61}N_3O_9\\ C_{53}H_{80}N_4O_{12} \end{array}$	$HO \longrightarrow O \xrightarrow{CH_3} O \xrightarrow{CH_3}$	1 2 3	- - -

Table S4 Mass results for oligomers of  $M_d$ -220<sub>2nd</sub> and the proposed assignments