Supporting Information

Characterization of Modified Methylaluminoxane by Ion Mobility Spectrometry Mass Spectrometry and Ultra-High Resolution Fourier-Transform Ion Cyclotron Resonance Mass Spectrometry

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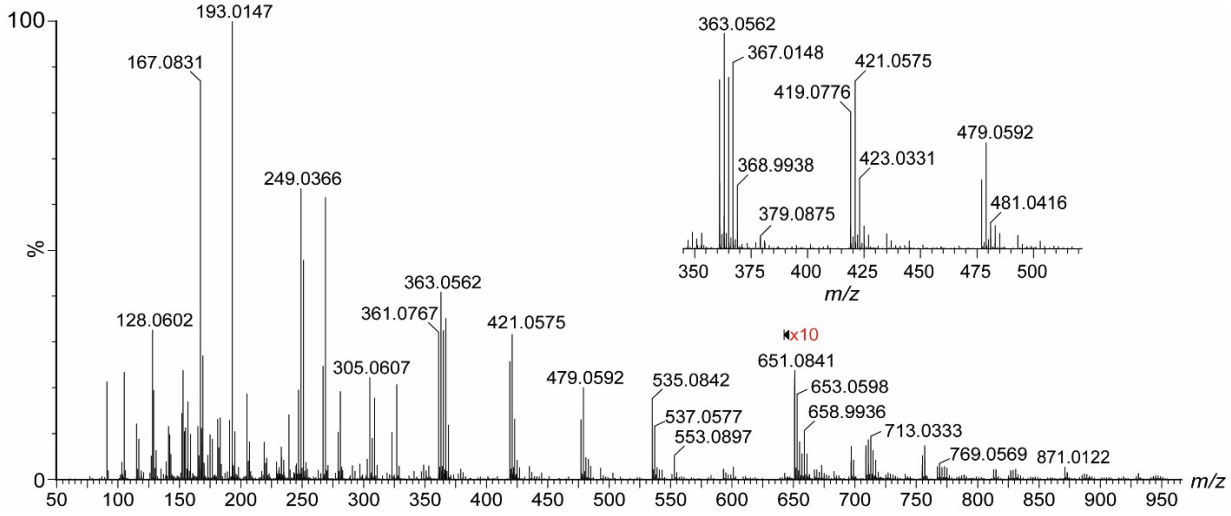

Figure S1. piASAP TWIMS-Q-TOF mass spectrum of MMAO-12 in the range of *m/z* 50–980 measured at sampling cone of 20 V. The zoomed areas showcase distribution of piASAP TWIMS-Q-TOF mass spectrum of MMAO-12 in mass range (*m/z* 340–540).

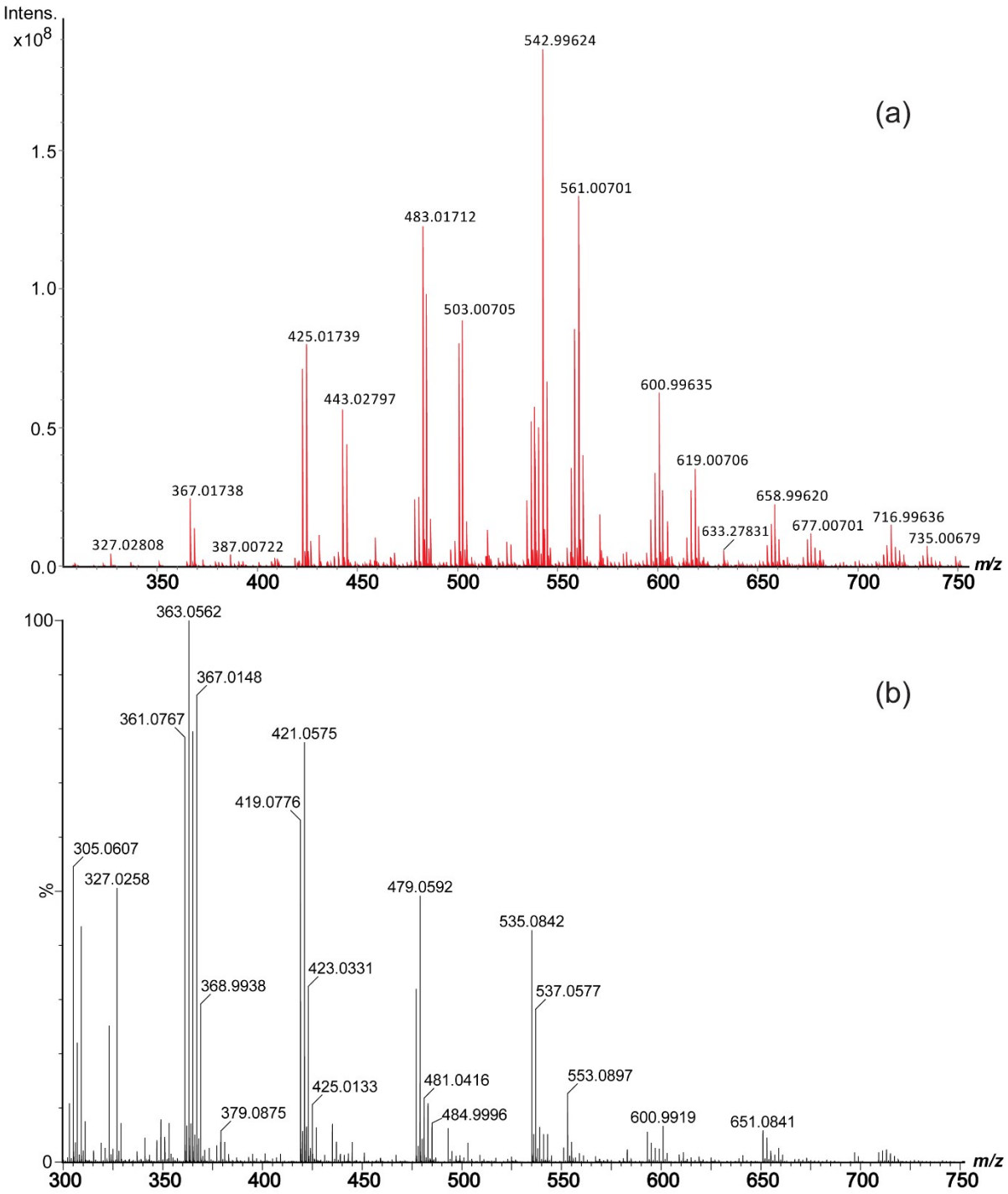

Figure S2. Comparison of piASAP TWIMS-Q-TOF and FTICR mass spectra between *m/z* 300-750. (a) MMAO-12 clusters in piASAP FTICR mass spectrum of MMAO-12 in mass range (*m/z* 300–750). (b) piASAP TWIMS-Q-TOF mass spectrum of MMAO-12 between *m/z* 300-750 measured at sampling cone of 20 V.

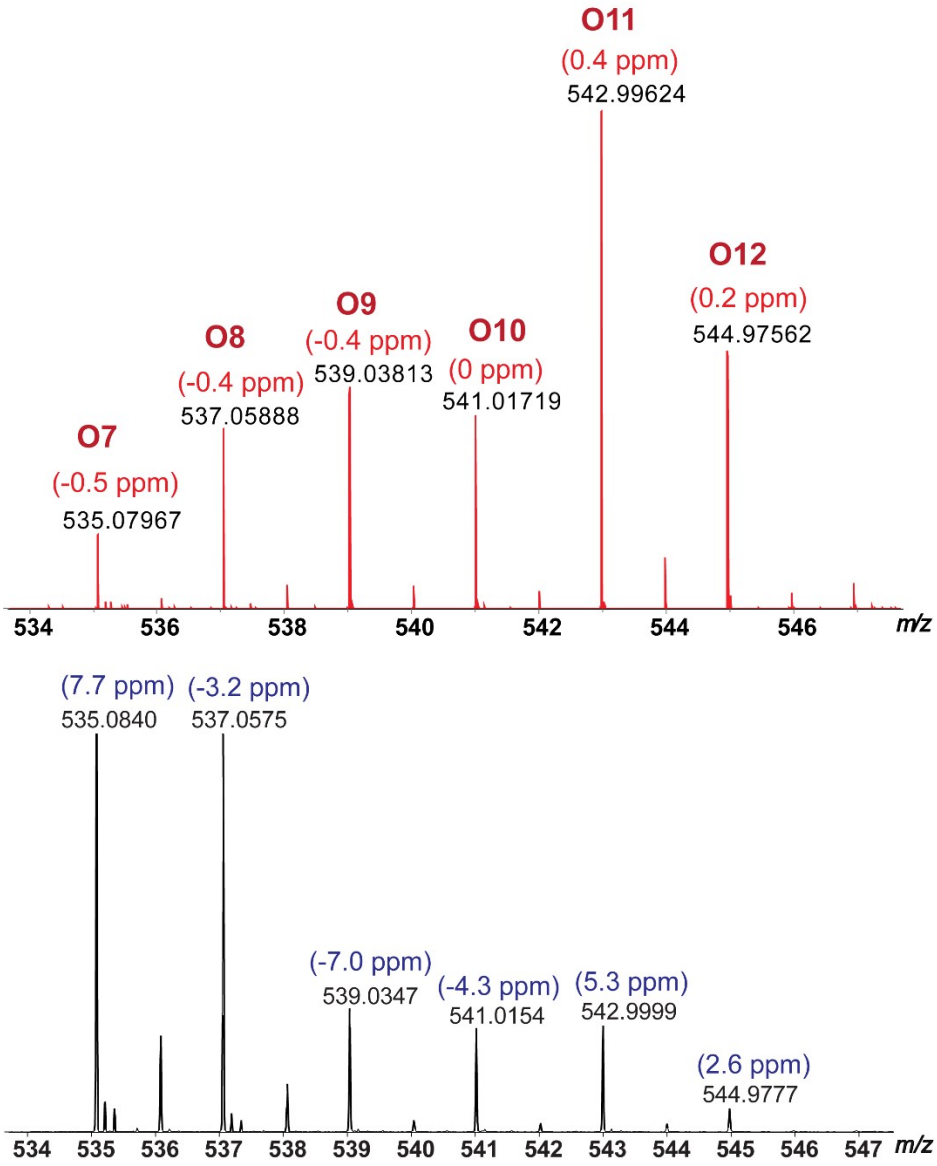

Figure S3. Comparison of mass accuray between TWIMS-Q-TOF and FTICR of Al_9O_y (y= 7, 8, 9, 10, 11, and 12) clusters in the range *m/z* 534-547.

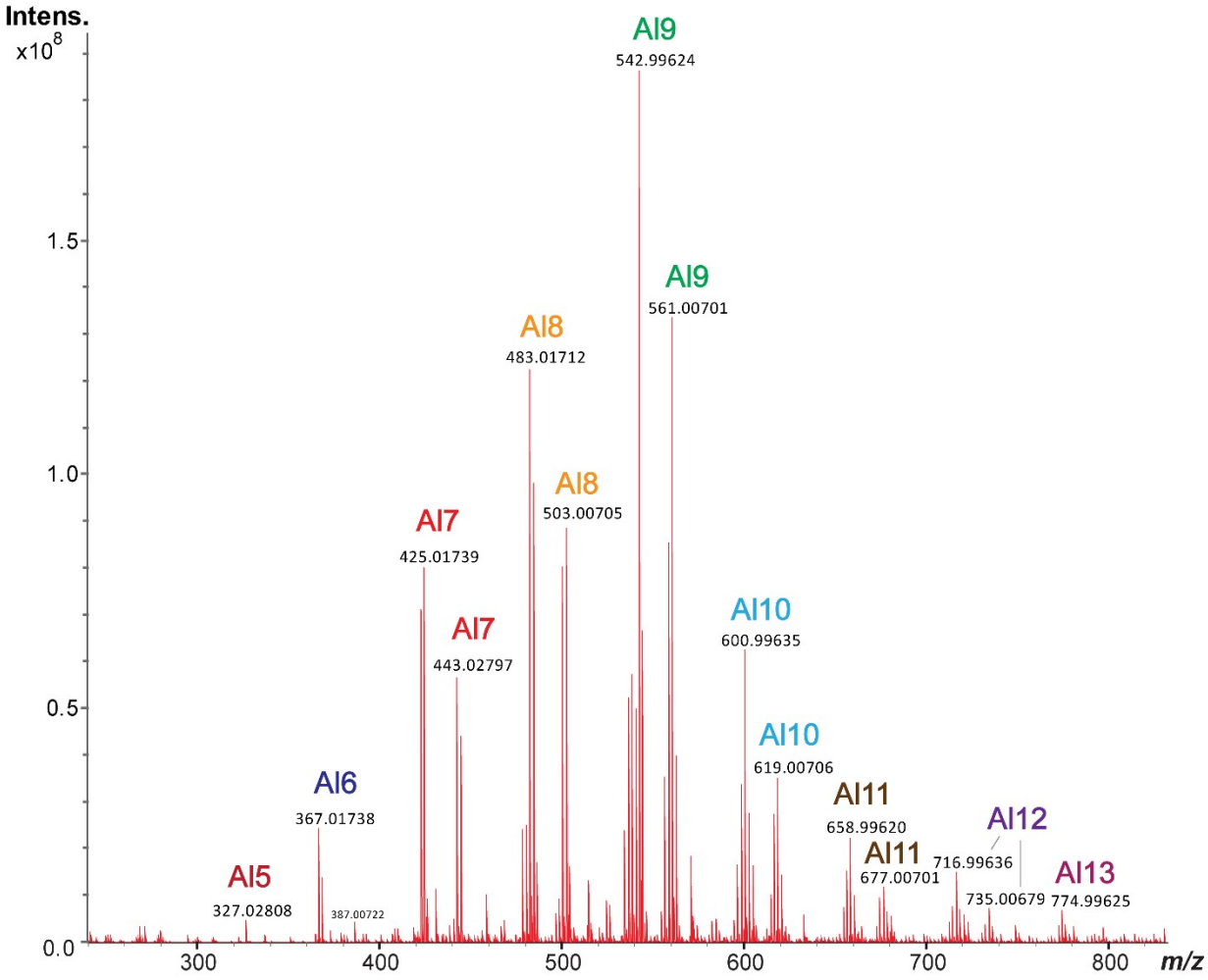

Figure S4. Distribution of most intense Al classes observed in piASAP FTICR mass spectrum of MMAO between *m/z* 240 and 831.

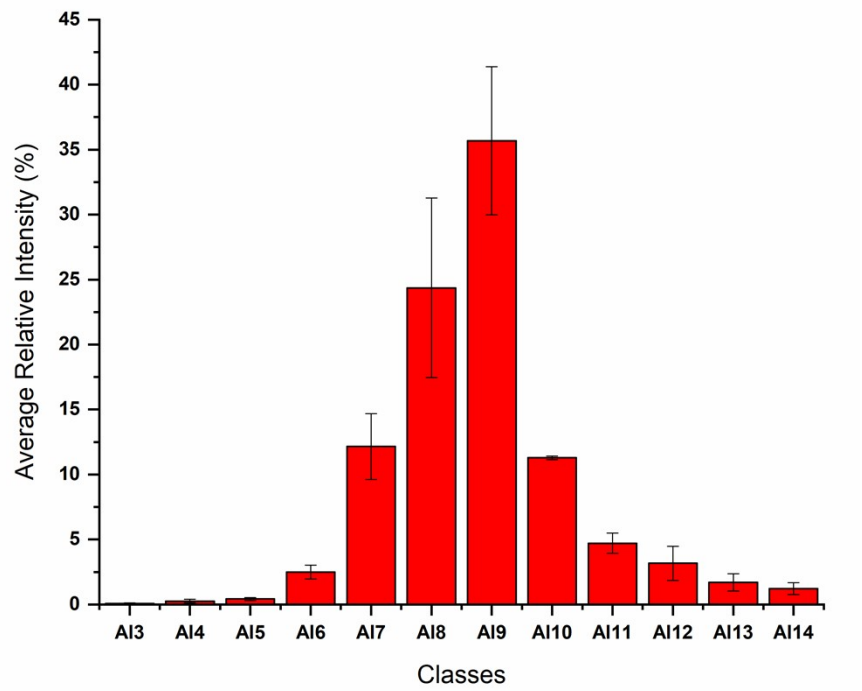

Figure S5. Relative intensity of Aluminum classes of MMAO analyzed by piASAP FT-ICR. N.B. The experiments were replicated three times at the same conditions at different APCI temperatures (exp.1: 350°C, exp. 2: 300 °C, and exp. 3: 420 °C).

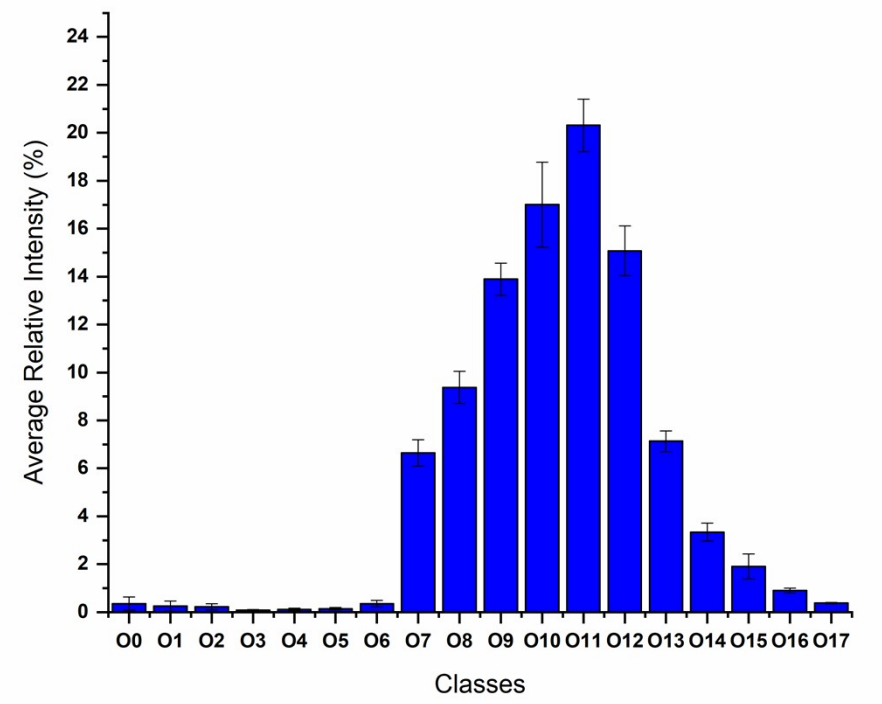

Figure S6. Relative intensity of oxygen classes of MMAO analyzed by piASAP FT-ICR. N.B. The experiments were replicated three times at the same conditions at different APCI temperatures (exp.1 : 350°C, exp. 2 : 300 °C , and exp. 3 : 420 °C).

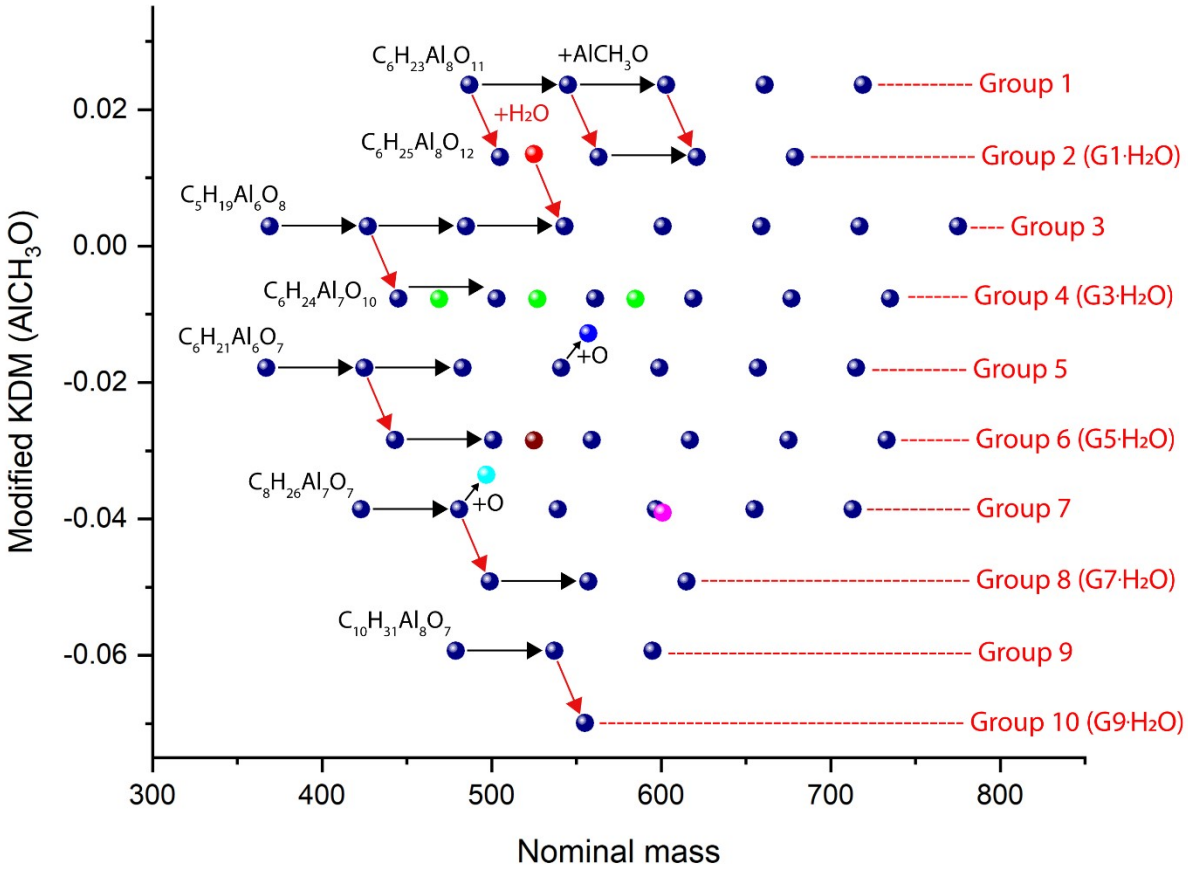

Figure S7. Plot of modified Kendrick mass defect vs nominal Kendrick mass for MMAO ions of nominal mass from 300 to 800 Da in the piASAP FT-ICR mass spectrum of MMAO. Ten homologous series of MMAO ions were identified (Groups 1-10). N.B. The relative intensity of the ions was filtered to be greater or equal to 0.2 %.

Table S1. List of Group 1 and 2 (1. H_2O) MMAO oligomers. N.B. The presented CCS (Å²) obtained from the average CCS of each ion at different sampling cone voltages (10V, 20V and 40V).

Group 1				**Group 2 (Group 1·H_2O)**			
MAO ion number	*m/z*	Formula (error in ppm)	CCS (Å²)	MAO ion number	*m/z*	Formula (error in ppm)	CCS (Å²)
1	312.97605	$C_3H_{14}Al_5O_8$ (−0.13)	174.6 ± 0.1	--	--	--	--
2	370.97594	$C_4H_{17}Al_6O_9$ (0)	188.0 ± 0.2	**2′**	388.98647	$C_4H_{17}Al_6O_9·H_2O$ (0.08)	189.3 ± 0.2
3	428.97581	$C_5H_{20}Al_7O_{10}$ (0.15)	201.6 ± 0.5	**3′**	446.98640	$C_5H_{20}Al_7O_{10}·H_2O$ (0.06)	204.7 ± 0.4
4	486.97544	$C_6H_{23}Al_8O_{11}$ (0.74)	215.5 ± 0.3	**4′**	504.98625	$C_6H_{23}Al_8O_{11}·H_2O$ (0.22)	217.8 ± 0.5
5	544.97531	$C_7H_{26}Al_9O_{12}$ (0.75)	229.8 ± 0.4	**5′**	562.98632	$C_7H_{26}Al_9O_{12}·H_2O$ (−0.05)	231.4 ± 0.2
6	602.97527	$C_8H_{29}Al_{10}O_{13}$ (0.64)	244.0 ± 0.3	**6′**	620.98611	$C_8H_{29}Al_{10}O_{13}·H_2O$ (0.18)	245.0 ± 0.3
7	660.97521	$C_9H_{32}Al_{11}O_{14}$ (0.57)	256.4 ± 0.4	**7′**	678.98609	$C_9H_{32}Al_{11}O_{14}·H_2O$ (0.08)	257.7 ± 0.3
8	718.97501	$C_{10}H_{35}Al_{12}O_{15}$ (0.70)	270.5 ± 0.5	**8′**	736.98614	$C_{10}H_{35}Al_{12}O_{15}·H_2O$ (−0.09)	271.0 ± 0.7
9	776.97505	$C_{11}H_{38}Al_{13}O_{16}$ (0.49)	281.5 ± 0.9	**9′**	794.98602	$C_{11}H_{38}Al_{13}O_{16}·H_2O$ (−0.02)	282.3 ± 0.9
10	834.97497	$C_{12}H_{41}Al_{14}O_{17}$ (0.48)	292.1 ± 0.9	--	--	--	--

Table S2. List of Group 3 and 4 (3. H_2O) MMAO oligomers. N.B. The presented CCS (Å²) obtained from the average CCS of each ion at different sampling cone voltages (10V, 20V and 40V).

Group 3				**Group 4 (Group 3·H_2O)**			
MAO ion number	*m/z*	Formula (error in ppm)	CCS (Å²)	MAO ion number	*m/z*	Formula (error in ppm)	CCS (Å²)
11	310.99679	$C_4H_{16}Al_5O_7$ (−0.13)	176.5 ± 0.1	**11′**	329.00728	$C_4H_{16}Al_5O_7 \cdot H_2O$ (0.10)	179.1 ± 0.1
12	368.99663	$C_5H_{19}Al_6O_8$ (0.13)	190.5 ± 0.3	**12′**	387.00718	$C_5H_{19}Al_6O_8 \cdot H_2O$ (0.16)	191.5 ± 0.3
13	426.99650	$C_6H_{22}Al_7O_9$ (0.25)	204.3 ± 0.4	**13′**	445.00698	$C_6H_{22}Al_7O_9 \cdot H_2O$ (0.42)	207.0 ± 0.2
14	484.99630	$C_7H_{25}Al_8O_{10}$ (0.48)	218.4 ± 0.3	**14′**	503.00679	$C_7H_{25}Al_8O_{10} \cdot H_2O$ (0.62)	220.8 ± 0.3
15	542.99597	$C_8H_{28}Al_9O_{11}$ (0.90)	232.5 ± 0.4	**15′**	561.00667	$C_8H_{28}Al_9O_{11} \cdot H_2O$ (0.64)	234.2 ± 0.2
16	600.99599	$C_9H_{31}Al_{10}O_{12}$ (0.67)	246.2 ± 0	**16′**	619.00664	$C_9H_{31}Al_{10}O_{12} \cdot H_2O$ (0.51)	247.5 ± 0.1
17	658.99582	$C_{10}H_{34}Al_{11}O_{13}$ (0.75)	258.6 ± 0.2	**17′**	677.00654	$C_{10}H_{34}Al_{11}O_{13} \cdot H_2O$ (0.50)	260.2 ± 0.1
18	716.99583	$C_{11}H_{37}Al_{12}O_{14}$ (0.58)	271.0 ± 0.1	**18′**	735.00631	$C_{11}H_{37}Al_{12}O_{14} \cdot H_2O$ (0.68)	272.3 ± 0.2
19	774.99569	$C_{12}H_{40}Al_{13}O_{15}$ (0.63)	282.4 ± 0.4	**19′**	793.00623	$C_{12}H_{40}Al_{13}O_{15} \cdot H_2O$ (0.64)	284.1 ± 0.6
20	832.99557	$C_{13}H_{43}Al_{14}O_{16}$ (0.64)	294.4 ± 0.4	**20′**	--	--	--

Table S3. List of Group 5 and 6 (5. H_2O) MMAO oligomers. N.B. The presented CCS (Å²) obtained from the average CCS of each ion at different sampling cone voltages (10V, 20V and 40V).

Group 5			**Group 6 (Group 5·H_2O)**		
m/z	Formula (error in ppm)	CCS (Å²)	*m/z*	Formula (error in ppm)	CCS (Å²)
193.01794	$C_3H_{12}Al_3O_4$ (−1.65)	146.4 ± 0.0	--	--	--
251.01775	$C_4H_{15}Al_4O_5$ (−0.76)	165.3 ± 0.9	--	--	--
309.01755	$C_5H_{18}Al_5O_6$ (−0.20)	179.8 ± 0.4	327.02806	$C_5H_{18}Al_5O_6{\cdot}H_2O$ (−0.03)	182.5 ± 0
367.01732	$C_6H_{21}Al_6O_7$ (0.26)	194.3 ± 0.1	385.02794	$C_6H_{21}Al_6O_7{\cdot}H_2O$ (0.10)	194.5 ± 0.1
425.01717	$C_7H_{24}Al_7O_8$ (0.40)	207.6 ± 0.3	443.02791	$C_7H_{24}Al_7O_8{\cdot}H_2O$ (−0.01)	211.0 ± 0.2
483.01690	$C_8H_{27}Al_8O_9$ (0.76)	221.2 ± 0.1	501.02781	$C_8H_{27}Al_8O_9{\cdot}H_2O$ (0.04)	224.6 ± 0.2
541.01684	$C_9H_{30}Al_9O_{10}$ (0.67)	233.9 ± 0.1	559.02764	$C_9H_{30}Al_9O_{10}{\cdot}H_2O$ (0.21)	236.3 ± 0.4
599.01677	$C_{10}H_{33}Al_{10}O_{11}$ (0.59)	247.9 ± 0.2	617.02759	$C_{10}H_{33}Al_{10}O_{11}{\cdot}H_2O$ (0.15)	249.1 ± 1.8
657.01653	$C_{11}H_{36}Al_{11}O_{12}$ (0.80)	261.0 ± 0.2	675.02756	$C_{11}H_{36}Al_{11}O_{12}{\cdot}H_2O$ (0.08)	261.6 ± 0.6
715.01660	$C_{12}H_{39}Al_{12}O_{13}$ (0.54)	271.4 ± 0.2	733.02756	$C_{12}H_{39}Al_{12}O_{13}{\cdot}H_2O$ (−0.02)	273.3 ± 0.6
773.01640	$C_{13}H_{42}Al_{13}O_{14}$ (0.66)	284.1 ± 0.6	791.02752	$C_{13}H_{42}Al_{13}O_{14}{\cdot}H_2O$ (−0.06)	285.1 ± 1.2
831.01633	$C_{14}H_{45}Al_{14}O_{15}$ (0.62)	295.0 ± 0.4	--	--	--

Table S4. List of Group 7 and 8 (7. H_2O) MMAO oligomers. N.B. The presented CCS (Å²) obtained from the average CCS of each ion at different sampling cone voltages (10V, 20V and 40V). (a) The isotopic peaks of group 8 family patterns was either overlapped or not detected.

Group 7			**Group 8 (Group 7·H_2O)**		
m/z	Formula (error in ppm)	CCS (Å²)	*m/z*	Formula (error in ppm)	CCS (Å²)
365.03791	$C_7H_{23}Al_6O_6$ (0.64)	194.8 ± 0.1	383.04867	$C_7H_{23}Al_6O_6 \cdot H_2O$ (0.10)	(a)
423.03796	$C_8H_{26}Al_7O_7$ (0.26)	209.2 ± 0.1	441.04860	$C_8H_{26}Al_7O_7 \cdot H_2O$ (0.08)	
481.03783	$C_9H_{29}Al_8O_8$ (0.37)	222.2 ± 0.2	499.04859	$C_9H_{29}Al_8O_8 \cdot H_2O$ (−0.05)	
539.03768	$C_{10}H_{32}Al_9O_9$ (0.47)	236.9 ± 0.4	557.04846	$C_{10}H_{32}Al_9O_9 \cdot H_2O$ (0.06)	
597.03755	$C_{11}H_{35}Al_{10}O_{10}$ (0.52)	248.2 ± 0.4	615.04850	$C_{11}H_{35}Al_{10}O_{10} \cdot H_2O$ (−0.12)	
655.03739	$C_{12}H_{38}Al_{11}O_{11}$ (0.61)	261.3 ± 0.0	673.04845	$C_{12}H_{38}Al_{11}O_{11} \cdot H_2O$ (−0.15)	
713.03729	$C_{13}H_{41}Al_{12}O_{12}$ (0.59)	271.9 ± 1.0	731.04830	$C_{13}H_{41}Al_{12}O_{12} \cdot H_2O$ (−0.02)	
771.03737	$C_{14}H_{44}Al_{13}O_{13}$ (0.36)	284.0 ± 1.7	789.04816	$C_{14}H_{44}Al_{13}O_{13} \cdot H_2O$ (0.06)	
829.03714	$C_{15}H_{47}Al_{14}O_{14}$ (0.52)	295.6 ± 1.0	--	--	--

Table S5. List of Group 9 and 10 (9. H_2O) MMAO oligomers. The presented CCS (Å²) are obtained from the average CCS of each ion at different sampling cone voltages (10 V, 20 V and 40 V). (a) The isotopic peaks of group 10 family patterns was either overlapped or not detected.

Group 9			**Group 10 (Group 9·H_2O)**		
m/z	Formula (error in ppm)	CCS (Å²)	*m/z*	Formula (error in ppm)	CCS (Å²)
421.05863	$C_9H_{28}Al_7O_6$ (0.42)	209.2 ± 0.2	439.06945	$C_9H_{28}Al_7O_6 \cdot H_2O$ (−0.18)	(a)
479.05850	$C_{10}H_{31}Al_8O_7$ (0.51)	222.4 ± 0.2	497.06925	$C_{10}H_{31}Al_8O_7 \cdot H_2O$ (0.11)	
537.05842	$C_{11}H_{34}Al_9O_8$ (0.45)	237.2 ± 0.4	555.06930	$C_{11}H_{34}Al_9O_8 \cdot H_2O$ (−0.13)	
595.05829	$C_{12}H_{37}Al_{10}O_9$ (0.51)	250.0 ± 0.3	613.06920	$C_{12}H_{37}Al_{10}O_9 \cdot H_2O$ (−0.07)	
653.05816	$C_{13}H_{40}Al_{11}O_{10}$ (0.55)	261.5 ± 0.4	671.06927	$C_{13}H_{40}Al_{11}O_{10} \cdot H_2O$ (−0.27)	
711.05799	$C_{14}H_{43}Al_{12}O_{11}$ (0.65)	273.1 ± 0.2	729.06891	$C_{14}H_{43}Al_{12}O_{11} \cdot H_2O$ (0.15)	

Equations for calculation CCS of MMAO clusters[1] **:**

$$\Omega' = \frac{\sqrt{\mu}}{z}\Omega \qquad \text{(Equation 1)}$$

Ω' is the reduced collision cross section
z is the charge of the ion
μ is the reduced mass
Ω is the collision cross section

$$\Omega' = At_D^B \qquad \text{(Equation 2)}$$

Ω' is the reduced collision cross section

A is a correction factor for temperature and pressure

B is the compensation for the non-linear effect of the TWIMS device

$t_D$is the drift time of the ion

(1) Smith, D. P.; Knapman, T. W.; Campuzano, I.; Malham, R. W.; Berryman, J. T.; Radford, S. E.; Ashcroft, A. E. Deciphering Drift Time Measurements from Travelling Wave Ion Mobility Spectrometry-Mass Spectrometry Studies. *Eur. J. Mass Spectrom.* **2009**, *15* (2), 113–130. https://doi.org/10.1255/ejms.947.