Supporting information for structural analysis of petroporphyrins from asphaltene by trapped ion mobility coupled with a Fourier transform ion cyclotron resonance mass spectrometer

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- **Figure S11: Common porphyrins structures found in asphaltene samples.**

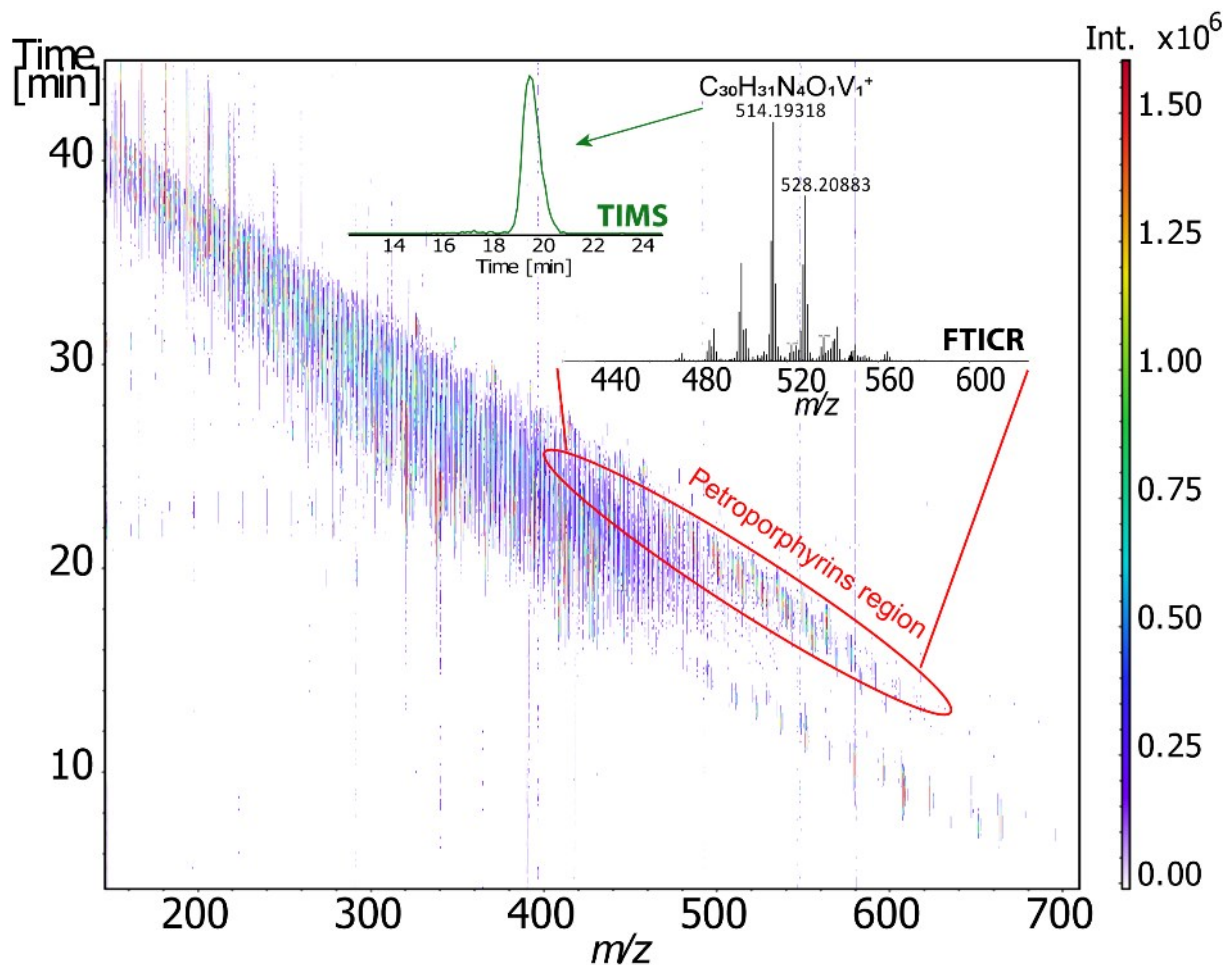- Figure S12: Structures of the drug mix compounds used for the peak width (FWHM) analysis.

Figure S1: 2D TIMS-FTICR-MS survey spectra of the Athabasca asphaltene. The m/z versus mobility region for the petroporhyrins is depicted and the average mass spectrum of the section is given as insert. The extracted mobilogram of $C_{30}H_{31}N_4O_1V_1^+$ was chosen to visualize the rather narrow mono-modal Gaussian distribution.
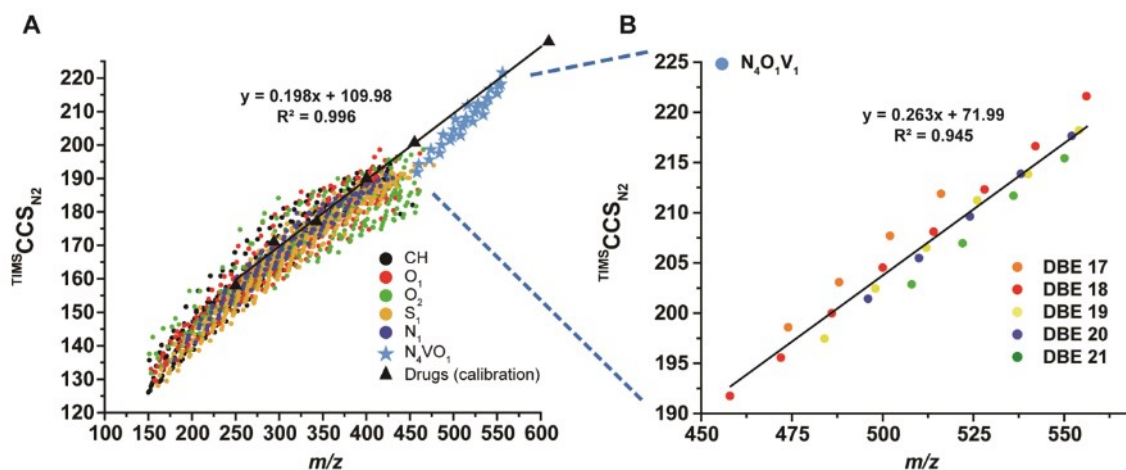

Figure S2. (A) Two-dimensional IMS-MS diagram illustrating the $^{TIMS}CCS_{N2}$ ($Å^2$) measured as a function of the m/z ratio of hydrocarbons, heteroatomic classes (N_1, O_1, O_2 and S_1) and Vanadium petroporphyrins ($N_4V_1O_1$).
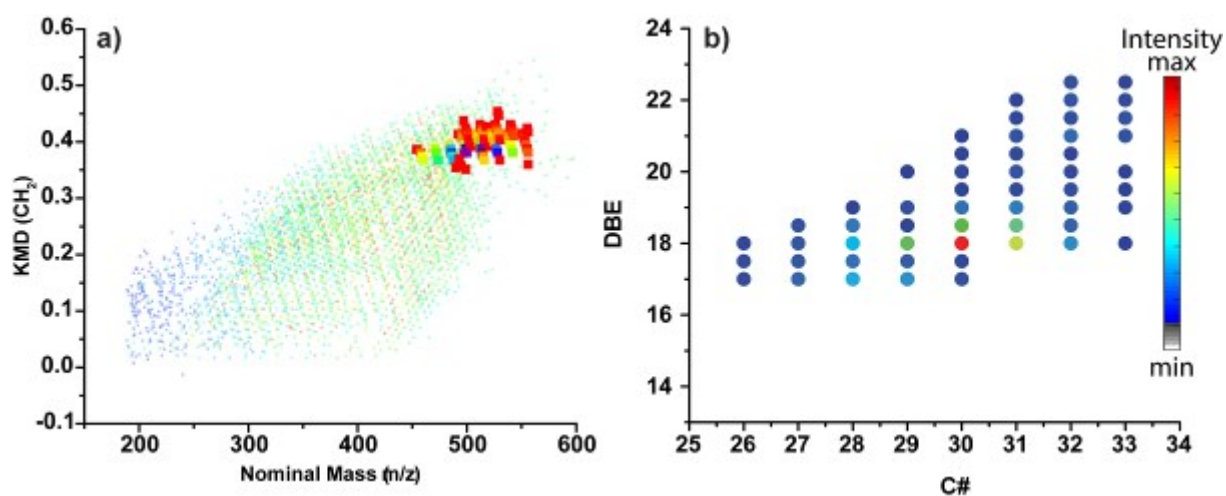(B) Enlargement of the diagram in the range m/z 450-575.

Figure S3. (a) Kendrick diagram of the complex petroleum molecular pattern highlighting the position of the petroporphyrins, and (b) DBE vs #C of the detected petroporphyrins.
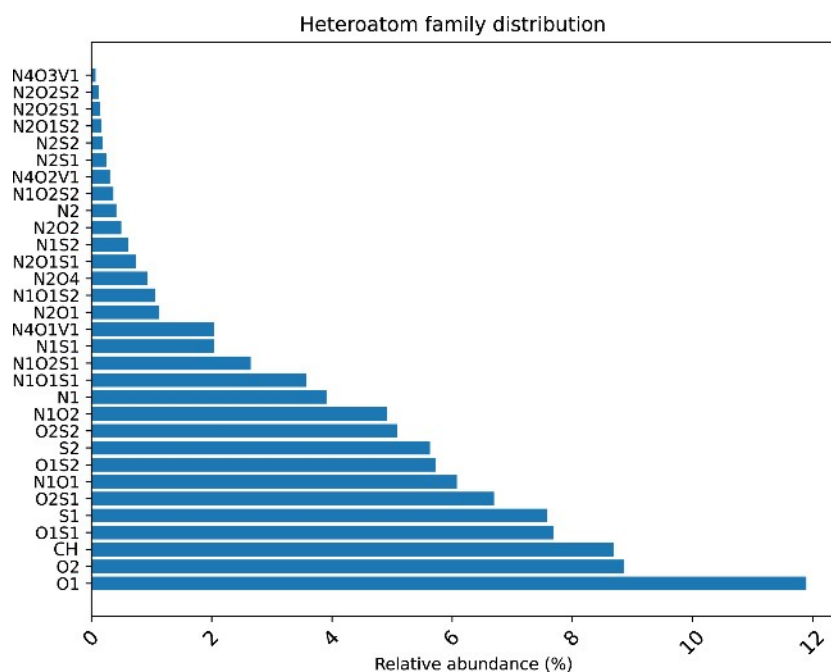

Figure S4 Summary compound class bar diagram of the analyzed Athabasca asphaltene.

Nitrogen and CH species are found in a region with a higher CCS value, indicating a high content of long alkyl chains. However, sulfur class is found in a region with a lower CCS value, indicating the presence of more aromatic compounds. Nitrogen species are distributed over the whole range of mobility (aliphatic and aromatic).

Porphyrins with metal produces a large mass displacement compared to the mobility displacement. They do not follow the general trend of the mobility pattern of the classical petrochemical classes. The space occupied by the porphyrins is shifted to a region with higher m/z and CCS values than the other molecules detected.

Figure S1B shows an enlargement of the ion mobility distribution of porphyrin species $N_4O_1V_1$. A linear relationship with an R^2 coefficient of determination of 0.945 is obtained between CCS and *m/z* ratio. This linearity can be explained by the fact that molecules of the same family tend to follow a straight line. This notion has been shown by Woods et al[33], and by Lalli et al[25] in the case of oil samples.

Table S1. Literature CCS_{N2} (Å^2) of the tuning mix ions

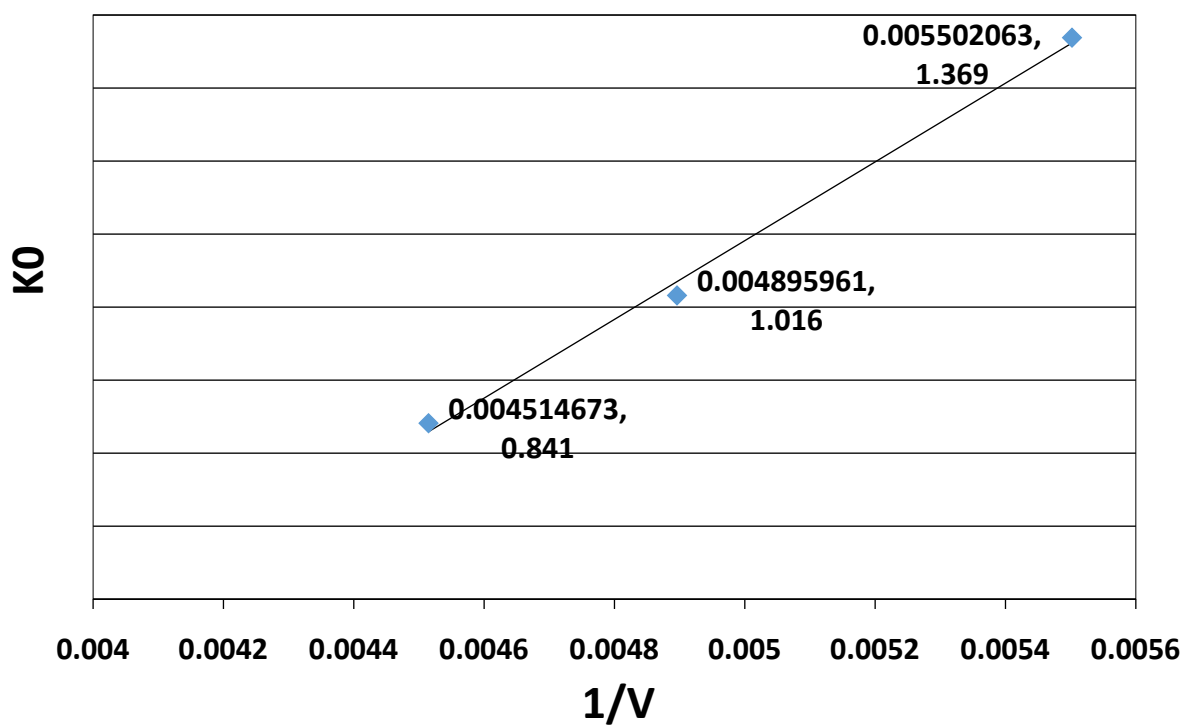| Index	[M+H]$^+$ calculated *m/z*	CCS_{N2} (Å^2)	K_0
1	322.04812	153.73	1.376
2	622.02896	202.96	1.013
3	922.0098	243.64	0.835

Figure S5: Calibration curve of the tune mix representing K_0 values in function of the 1/V value. The R^2 of the linear fitting and the corresponding equation used for the calibration is also displayed on the graph.

Table S2 : Internals signals used for the calibration

# Hydrocarbon	m/z	charge
C15H23	203.17943	1+
C16H25	217.19508	1+
C17H17	221.13248	1+
C18H15	231.11683	1+
C17H27	231.21073	1+
C19H17	245.13248	1+
C18H29	245.22638	1+
C20H19	259.14813	1+
C19H31	259.24203	1+
C20H33	273.25768	1+
C22H21	285.16378	1+
C21H35	287.27333	1+
C22H37	301.28898	1+
C24H21	309.16378	1+
C23H39	315.30463	1+
C25H25	325.19508	1+
C24H41	329.32028	1+
C27H35	359.27333	1+
C29H39	387.30463	1+
C30H43	403.33593	1+
C32H47	431.36723	1+
C34H51	459.39853	1+

Table S3 : Repeatability measurements for a series of hydrocarbons species

Formula	m/z	Apex value R1 (s)	Apex value R2 (s)	Apex value R3 (s)	Deviation (s)
C21H28	280.218707	715.4	715.3	716.1	0.4
C22H26	290.203064	724.5	723.7	724.4	0.4
C23H24	300.187418	714.2	713	713.9	0.6
C24H22	310.171776	707.8	708.2	708.8	0.5
C24H24	312.187423	693.3	692.6	693.4	0.4
C25H20	320.156128	705.2	704.8	705.4	0.3
C25H24	324.187429	671.5	671.9	672.4	0.5
C27H20	344.156138	668.2	668.3	668.8	0.3

Fitting on OriginPro

For each detected porphyrins, the extract ion chromatogram (EIC) or more correctly, the extract ion mobilogram (EIM), was extracted and plotted in OriginPro (see exemplarily Figure S6). Using a Gaussian nonlinear curve fitting, each peak apex was recovered and converted to the corresponding scan number. This scan number was then assigned to a particular TIMS funnel voltage which allow the recovering of the collision cross section (CCS) using the calibration curve (Figure S2).
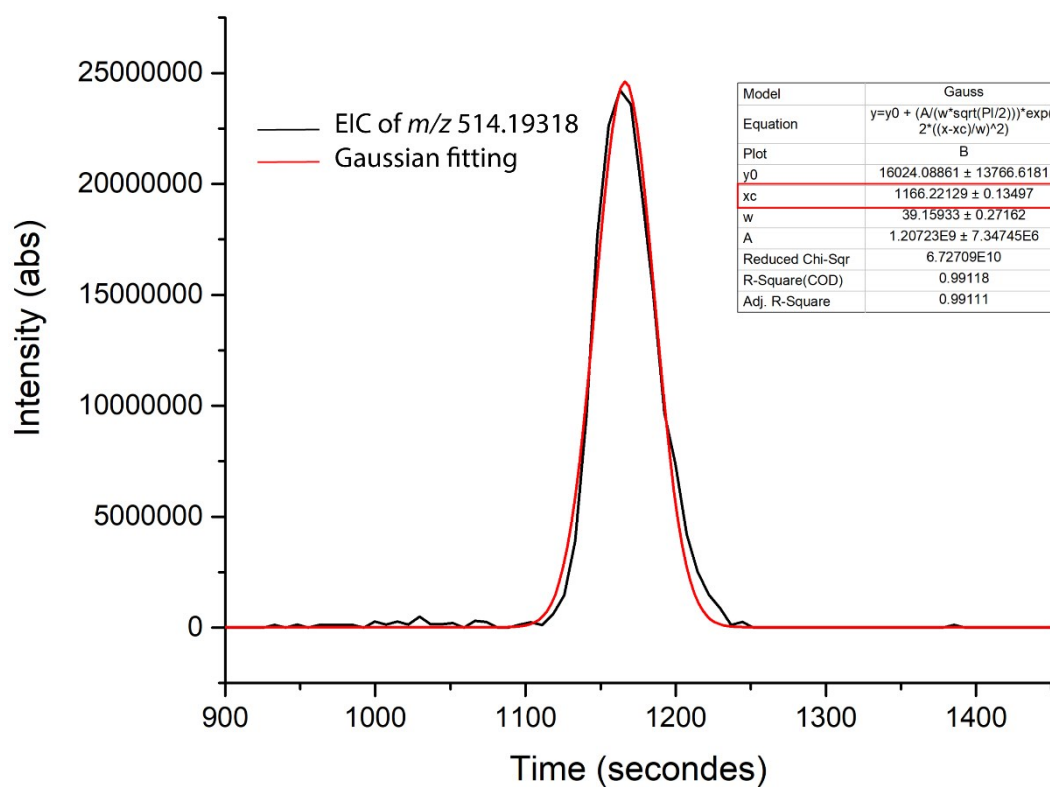

Model	Gauss
Equation	y=y0 + (A/(w*sqrt(PI/2)))*exp(-2*((x-xc)/w)^2)
Plot	B
y0	16024.08861 ± 13766.6181
xc	1166.22129 ± 0.13497
w	39.15933 ± 0.27162
A	1.20723E9 ± 7.34745E6
Reduced Chi-Sqr	6.72709E10
R-Square(COD)	0.99118
Adj. R-Square	0.99111

Figure S6 : EIC of the *m/z* 514.19318 and the corresponding Gaussian fitting (red line) generated using OriginPro. The peak apex position can be extracted with high accuracy. Slight deviation at distribution edges can be seen, not inflicting deviations for the FWHM and peak apex extraction.

TWIMS TOF experiments

The standard porphyrins (vanadyl-octaethylporphyrin) was analysed on a Synapt G2 (Waters, Manchester) in APPI+ using following parameters. Resolution mode : W, Mass range : 50 Da to 1200 Da. Repeller (kV) :1.0, Probe Temp (C): 600.0, Source Temperature (°C):120, Sampling Cone: 20, Extraction Cone: 5, Cone Gas Flow (L/Hr): 50.0, Desolvation Gas Flow (L/Hr): 800.0. IMS parameters were sets as followed. IMS Wave Velocity (m/s): 200, IMS Wave Height (V): 13.0, HeliumCellGasFlow: 180, IMS Gas Flow (mL/min): 90.00. The EIC of the detected standard was extracted and fitted using OriginPro following the same precedent procedure. Using the same parameters, the TWIMS cell was calibrated using the tuning mix in *electrospray* positive. ESI parameters were sets as followed. Capillary (kV): 2.5, Source Temperature (°C): 120, Sampling Cone: 40, Extraction Cone: 5, Desolvation Temperature (°C): 300, Cone Gas Flow (L/Hr):50.0. The resulting calibration curve is given in figure S4. By taking the equation of the power fitting obtained for the calibration curve, the collision cross section of the porphyrin standard has been recovered.
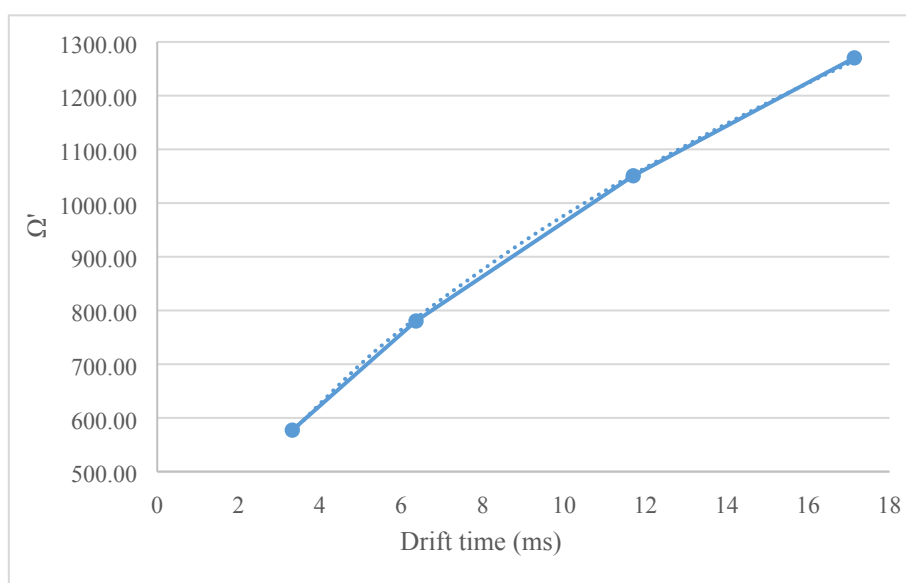

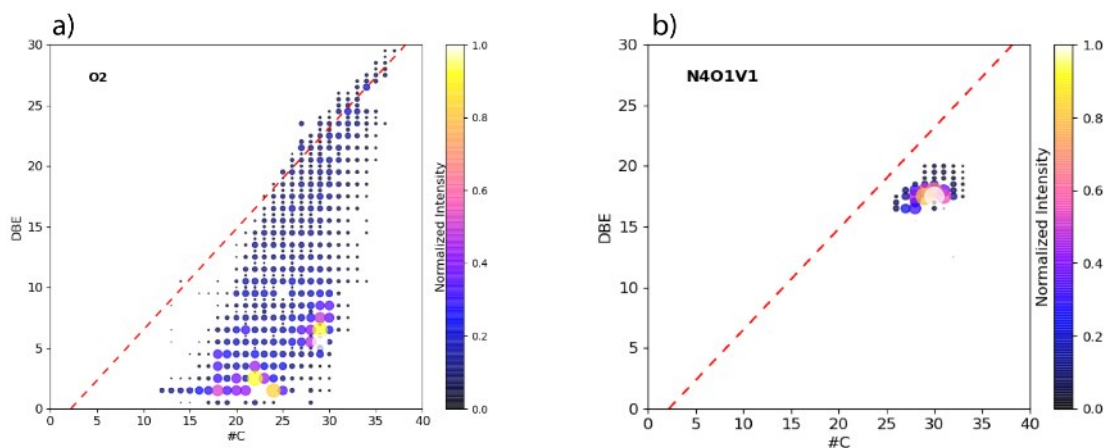Figure S7: Calibration curve obtained for the tuning mix on the Synapt G2.

Figure S8: DBE vs #C of the O2 (a) and N4O1V1 (b) families. Despite the potential of very low m/z deviations (mass splits) between O_2 and $N_4O_1V_1$ class compounds, the uniform distribution validate the molecular formula attribution.
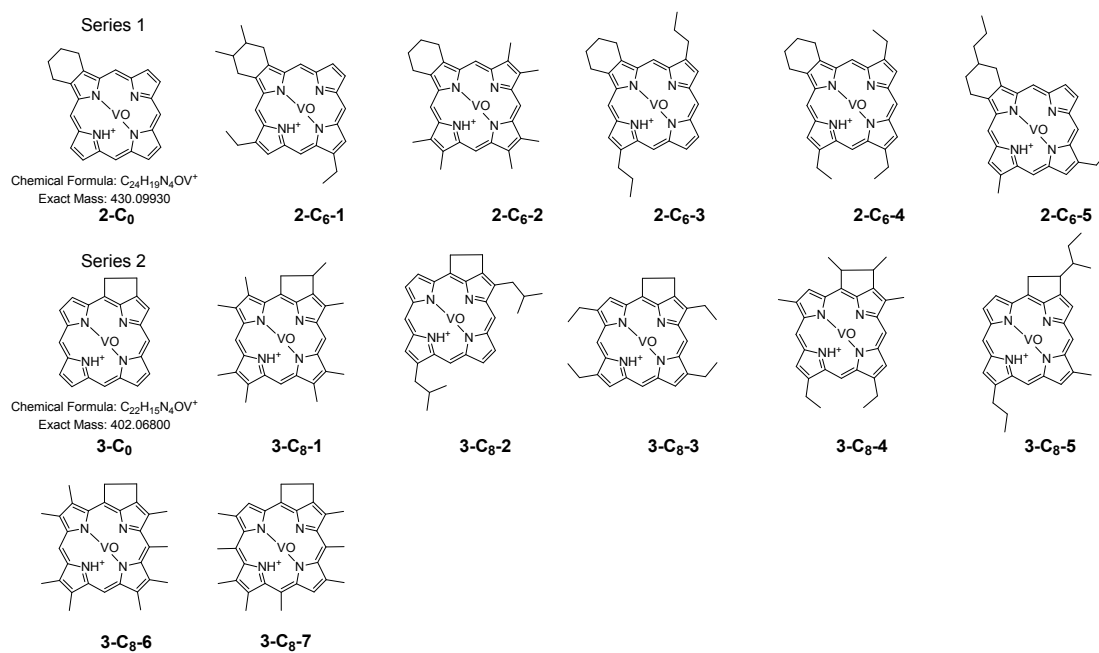

Series 1

Chemical Formula: $C_{24}H_{19}N_4OV^+$
Exact Mass: 430.09930
2-C$_0$

2-C$_6$-1

2-C$_6$-2

2-C$_6$-3

2-C$_6$-4

2-C$_6$-5

Series 2

Chemical Formula: $C_{22}H_{15}N_4OV^+$
Exact Mass: 402.06800
3-C$_0$

3-C$_8$-1

3-C$_8$-2

3-C$_8$-3

3-C$_8$-4

3-C$_8$-5

3-C$_8$-6

3-C$_8$-7

Figure S9: Hypothetical structures of *m/z* 514.1932 ($C_{30}H_{31}N_4O_1V_1^+$, DBE 18). Series 1 is composed of porphyrins based on the basic core with a six-membered naphthenic ring. Series 2 is based on the basic core with a five-membered naphthenic ring.
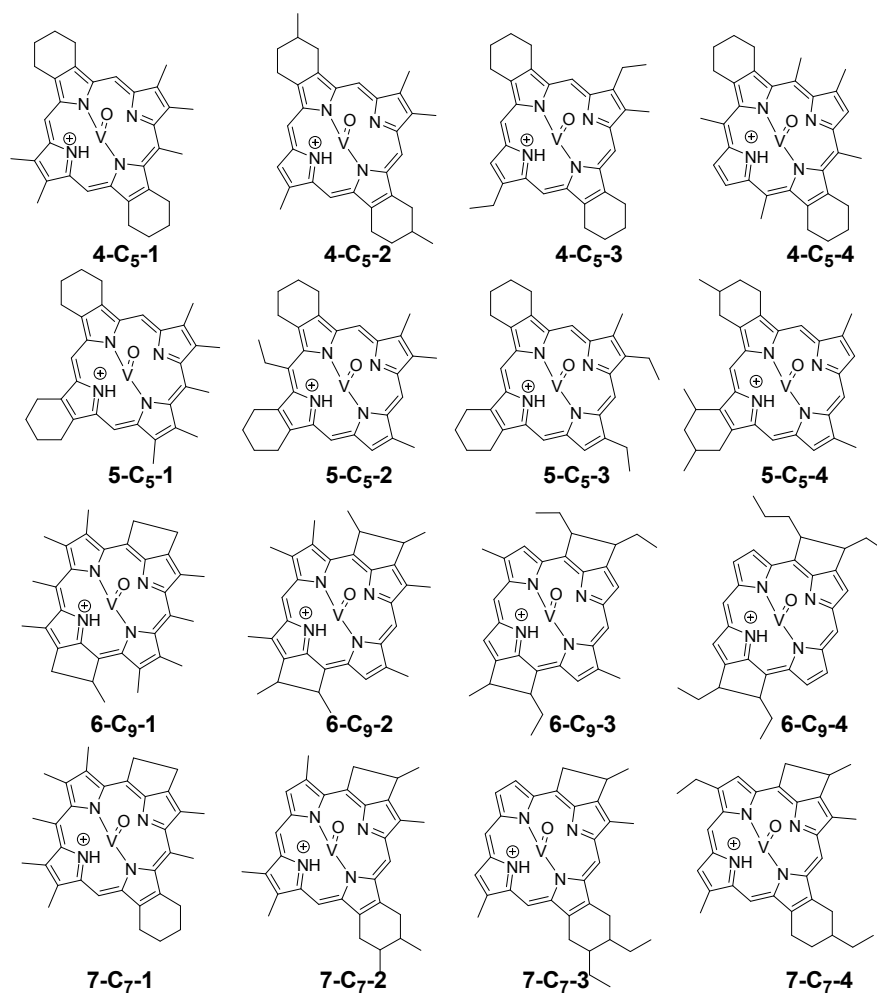
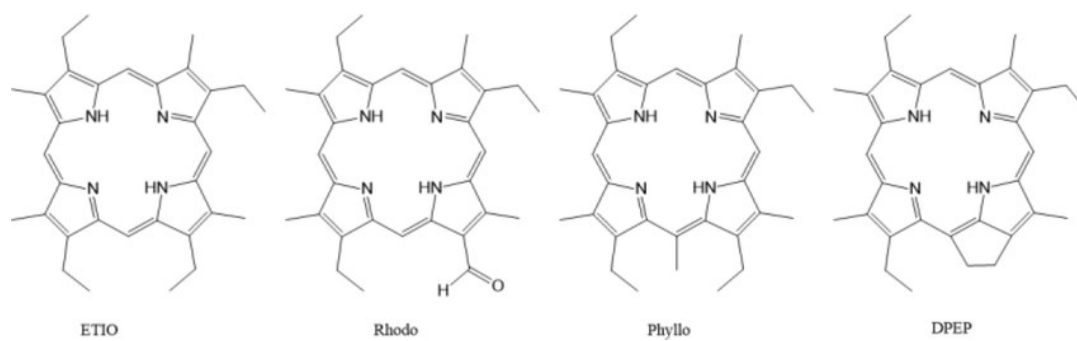Figure S10: Hypothetical structures of *m/z* 554.22450 ($C_{33}H_{35}N_4O_1V_1^+$, DBE 19).

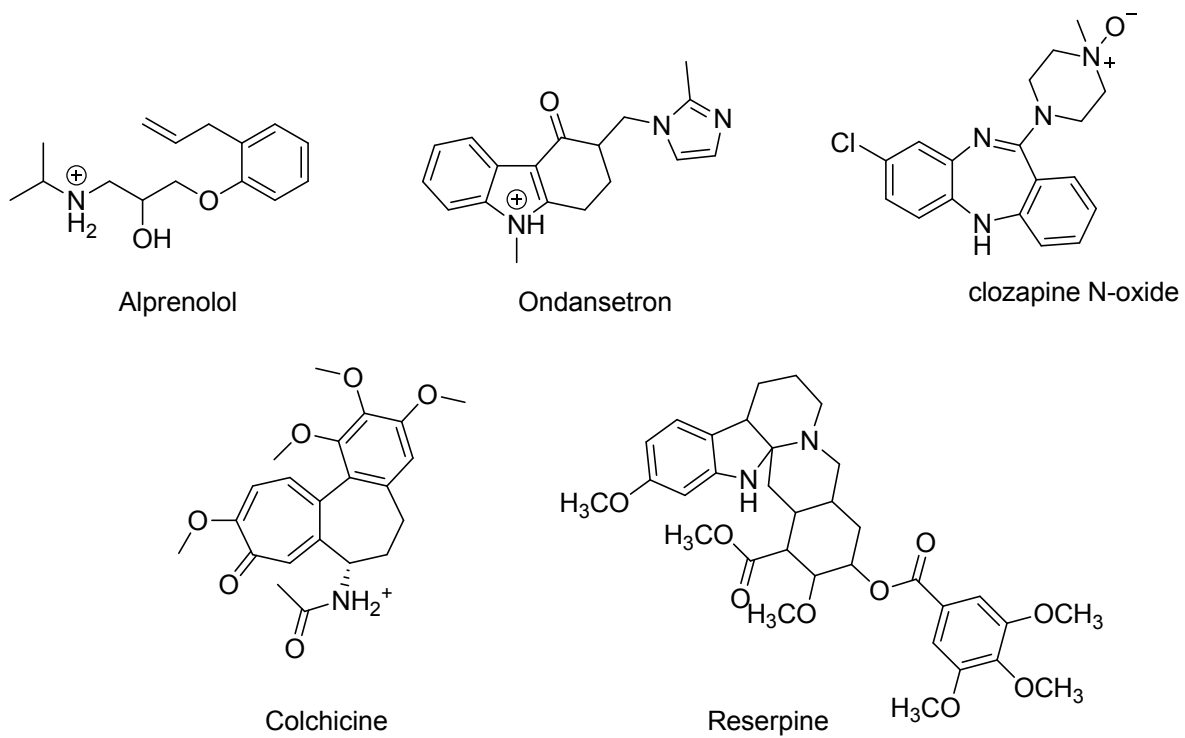Figure S11: Common porphyrins structures found in asphaltene samples.

Figure S12: Structures of the drug mix compounds used for the peak width (FWHM) analysis.