Electronic Supplementary Material (ESI) for Analyst.

GC-FTICR mass spectrometry with dopant assisted atmospheric pressure photoionization: application to the characterization of plastic pyrolysis oil

Charlotte Mase [a, b, c], Julien F. Maillard [b, c], Marco Piparo [b, c], Lukas Friederici [d], Christopher P. Rüger [c, d], Sabrina Marceau [b, c], Benoit Paupy [b, c], Marie Hubert-Roux [a, c], Carlos Afonso* [a, c] and Pierre Giusti [a, b, c]

[a] Univ Rouen Normandie, INSA Rouen Normandie, CNRS, Normandie Univ, COBRA UMR 6014, INC3M FR 3038, F-76000 Rouen, France

[b] TotalEnergies OneTech, Total Research and Technology Gonfreville TRTG, BP 27, 76700 Harfleur, France

[c] International Joint Laboratory – iC2MC: Complex Matrices Molecular Characterization, TRTG, BP 27, 76700 Harfleur, France

[d] Joint Mass Spectrometry Centre / Chair of Analytical Chemistry, University of Rostock, Albert-Einstein-Straße 27, 18059 Rostock, Germany

Supporting information

Table S1. List of compounds used for internal calibration

Molecular ion formula	Exact mass	Charge
C12H22	166.171602	1+
C13H24	180.187252	1+
C14H26	194.202902	1+
C15H28	208.218552	1+
C16H28	220.218552	1+
C16H30	222.234202	1+
C17H26	230.202902	1+
C17H32	236.249852	1+
C18H32	248.249852	1+
C18H34	250.265503	1+
C19H30	258.234202	1+
C19H36	264.281153	1+
C20H32	272.249852	1+
C20H38	278.296803	1+
C21H38	290.296803	1+
C21H40	292.312453	1+
C22H38	302.296803	1+
C22H42	306.328103	1+
C23H44	320.343753	1+
C24H44	332.343753	1+

C24H46	334.359403	1+
C25H42	342.328103	1+
C25H48	348.375053	1+
C26H50	362.390703	1+
C27H50	374.390703	1+
C27H52	376.406353	1+
C28H54	390.422003	1+
C29H50	398.390703	1+
C29H56	404.437653	1+
C30H56	416.437653	1+
C30H58	418.453303	1+
C31H60	432.468953	1+
C32H56	440.437653	1+
C32H62	446.484603	1+
C33H58	454.453303	1+
C33H62	458.484603	1+
C33H64	460.500253	1+
C34H60	468.468953	1+
C34H66	474.515904	1+
C35H68	488.531554	1+
C36H68	500.531554	1+
C36H70	502.547204	1+
C37H66	510.515904	1+
C37H72	516.562854	1+
C38H74	530.578504	1+
C39H70	538.547204	1+
C39H74	542.578504	1+
C39H76	544.594154	1+
C40H78	558.609804	1+
C41H78	570.609804	1+
C41H80	572.625454	1+
C42H82	586.641104	1+
C43H84	600.656754	1+

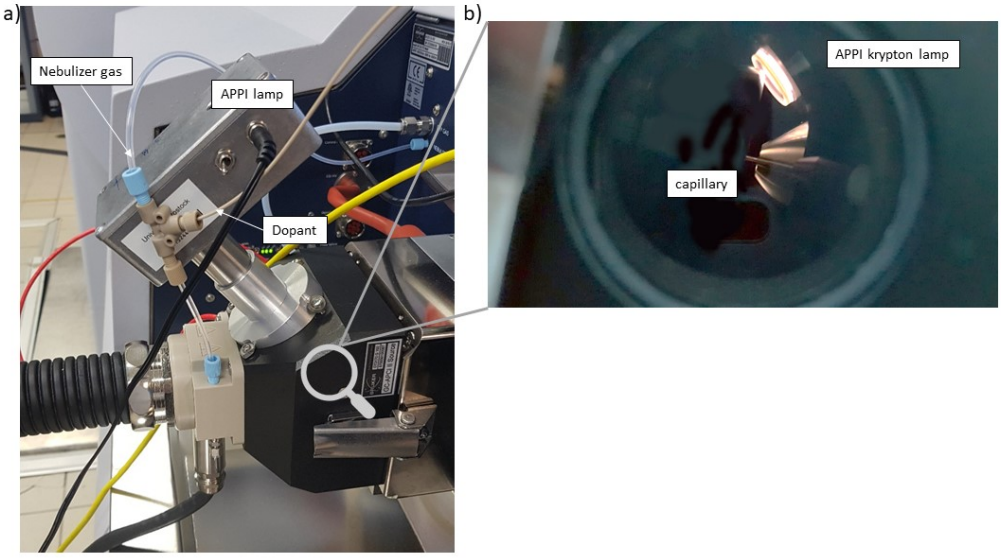


Figure S1. GC-APPI-FTICR MS interface with (a) T piece for dopant addition and inset of source inside. (b) Zoom of the APPI krypton lamp with the GC capillary.

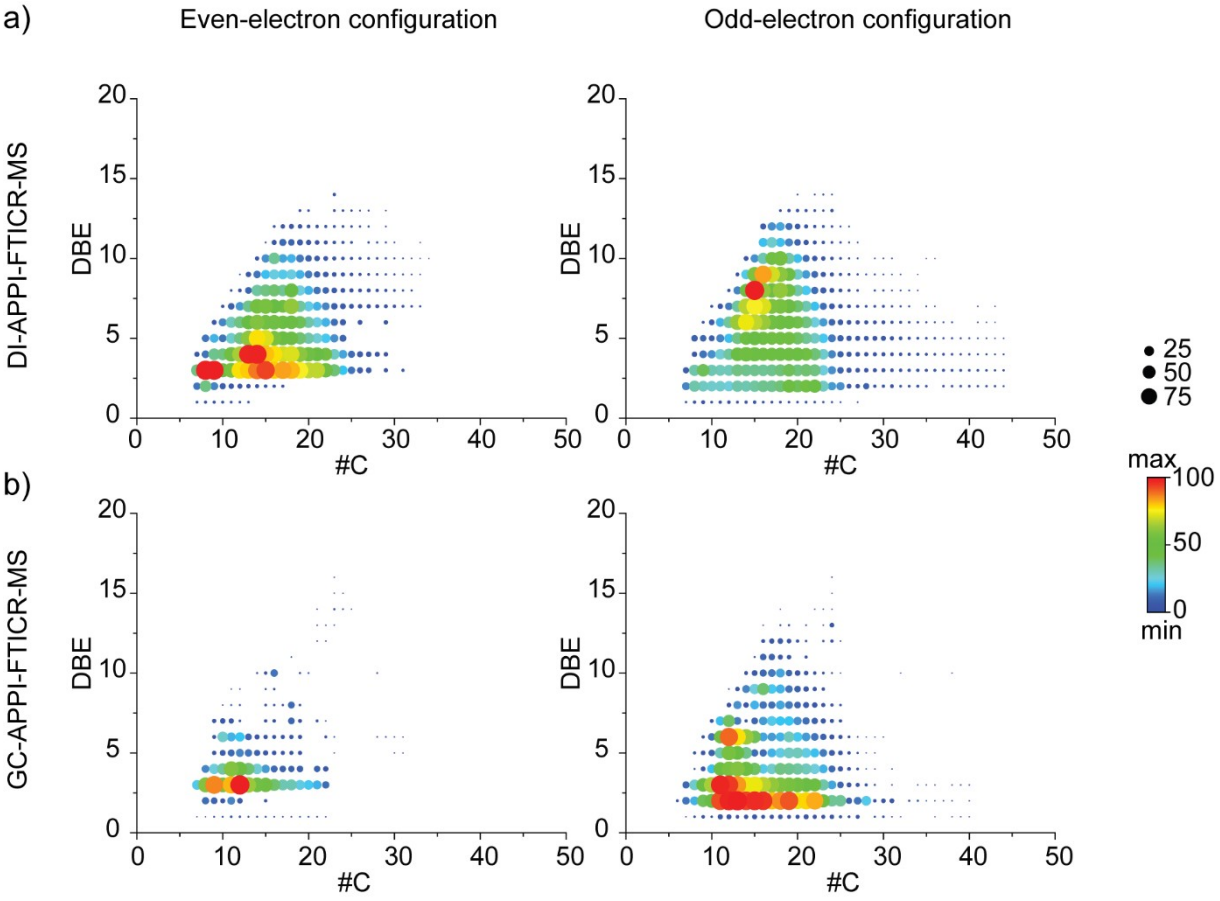


Figure S2. DBE versus carbon number plots of hydrocarbon class for (a) DI-APPI-FTICR MS and (b) GC-APPI-FTICR MS experiments for odd- and even-electron configuration

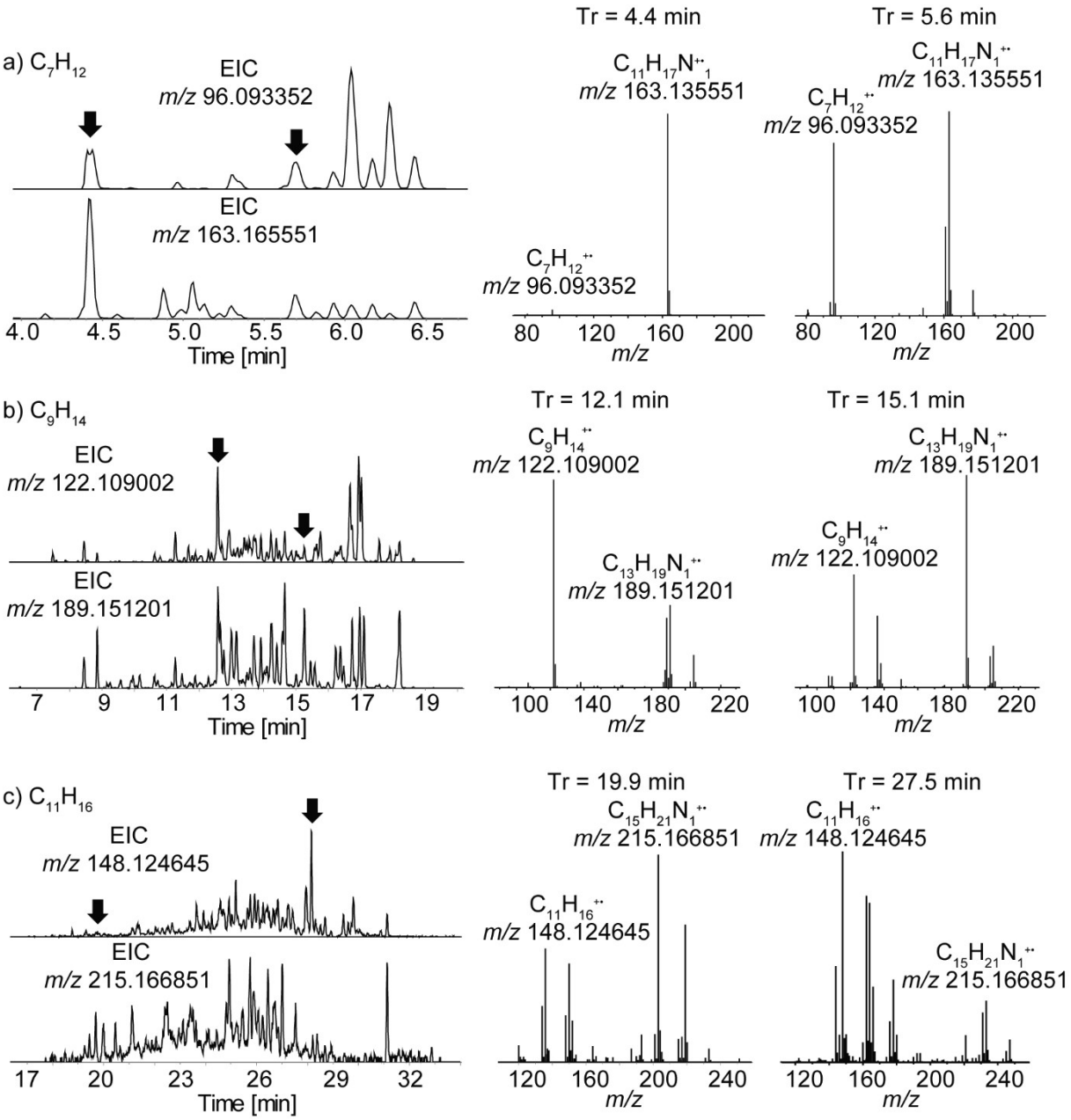


Figure S3. Extracted ion chromatograms of GC-APPI-FTICR MS experiment with pyrrole as dopant of three molecules (a) C_7H_{12}, (b) C_9H_{14}, and (c) $C_{11}H_{16}$ ionized in the form $M^{+\bullet}$ or $[M+pyrrole]^+$. The corresponding mass spectra of the mentioned retention times were given. Note that chromatograms were extracted with 0.001 tolerance of the mass.

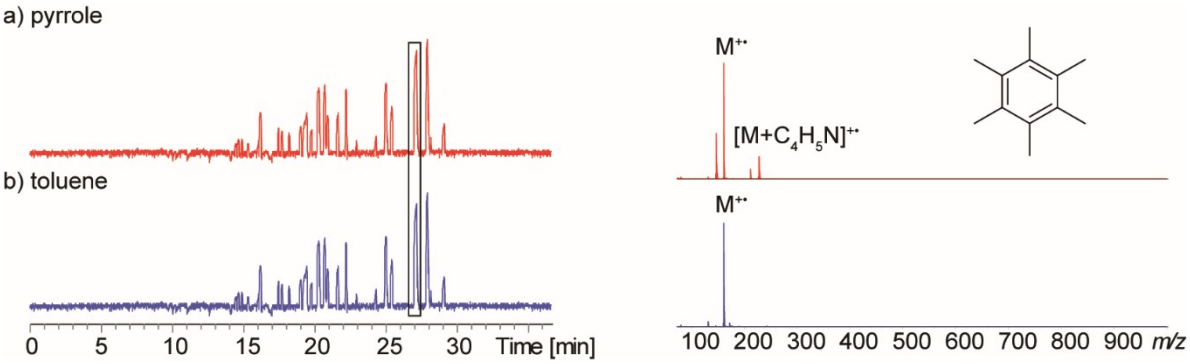


Figure S4. Total ion chromatogram and corresponding mass spectra of the peak at 27 min using (a) pyrrole and (b) toluene as dopants for the analysis of aromatic standard solutions.

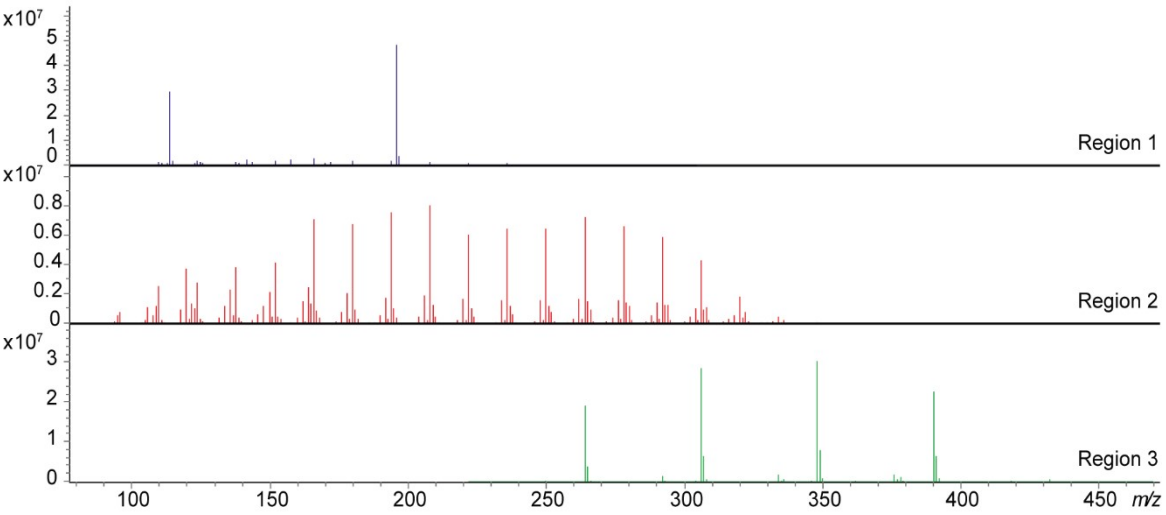


Figure S5. Mass spectra obtained for the three areas for the analysis of plastic pyrolysis oil using toluene as dopant. Region 1 corresponds to the nitrogen-containing species, region 2 to the CH compounds, and region 3 to the fragments.

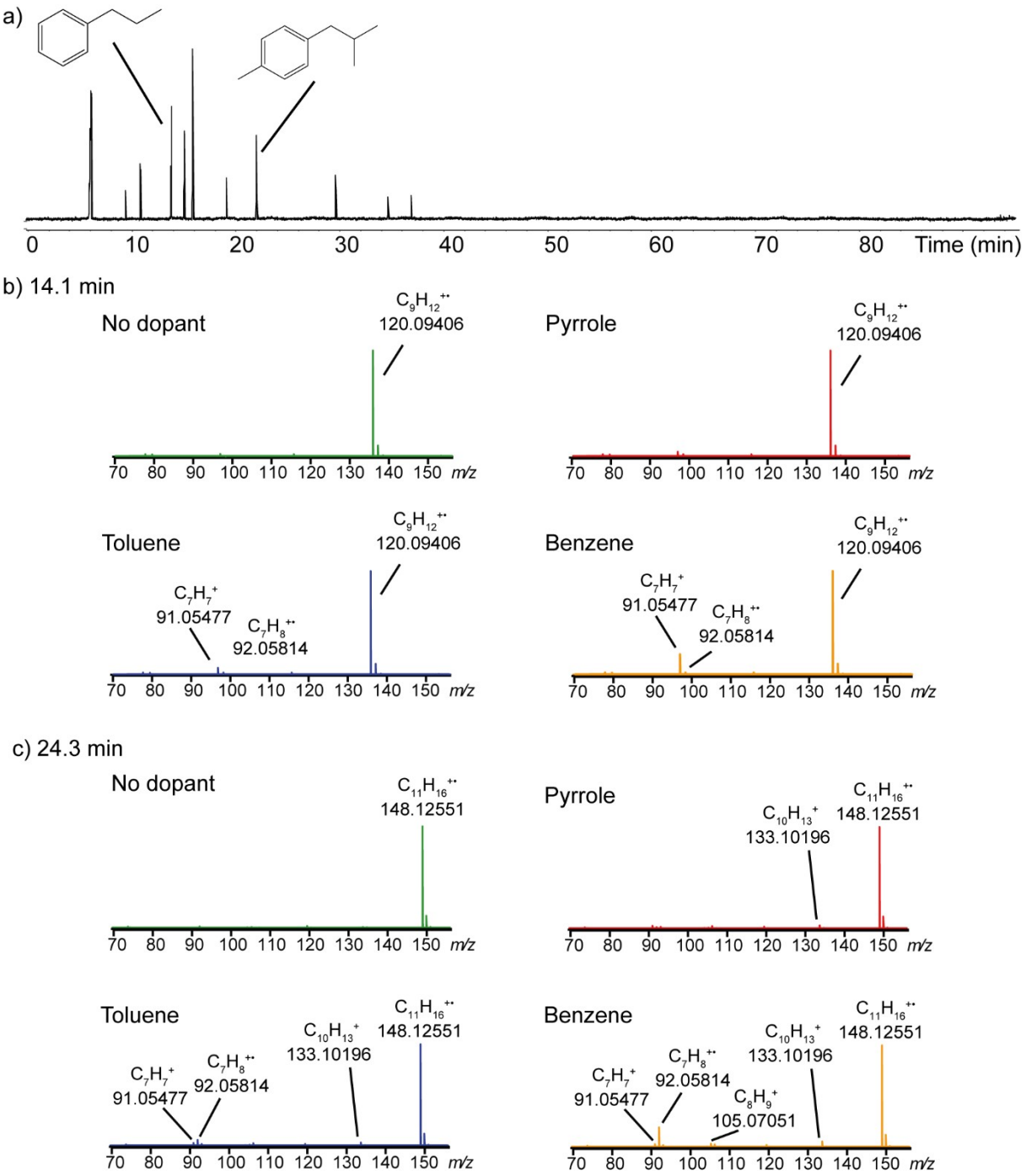


Figure S6. (a) Chromatogram of standards with mass spectra for (b) the peak at 14.1 min corresponding to C_9H_{12} compound ionized at *m/z* 120.09406 and (c) the peak at 24.3 min corresponding to $C_{11}H_{16}$ compound ionized at *m/z* 148.12551 obtained with the four conditions (without dopant, with pyrrole, with toluene, and with benzene).

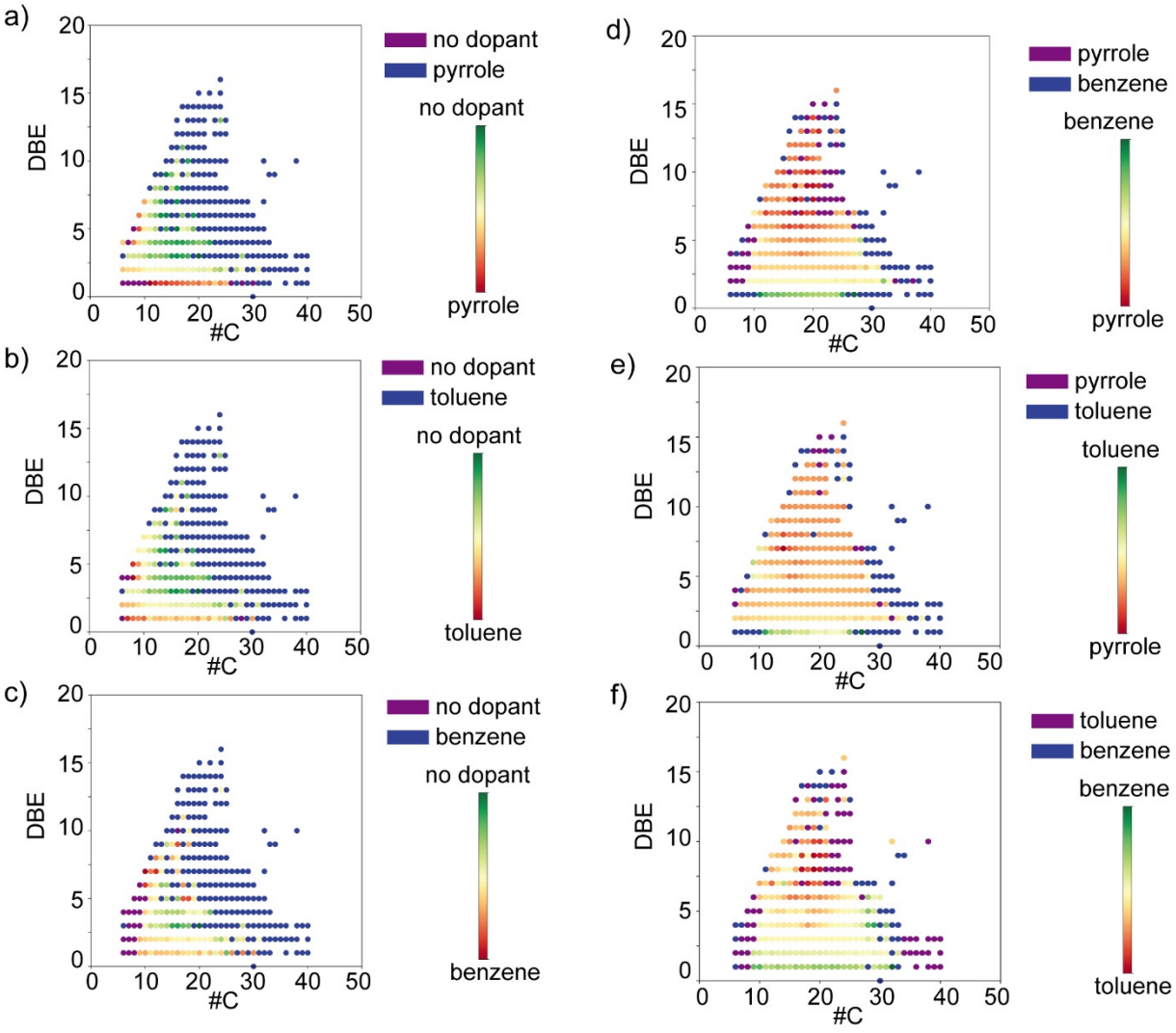


Figure S7. DBE versus carbon number plots using fold change of CH class as color map for (a) no dopant *vs* pyrrole experiment, (b) no dopant *vs* toluene experiment, (c) no dopant *vs* benzene experiment, (d) pyrrole *vs* benzene experiment, (e) pyrrole *vs* toluene experiment, and (f) toluene *vs* benzene experiment. The green to red gradient correspond to all common species between the two experiments. Purple and blue are color corresponding to unique species found.

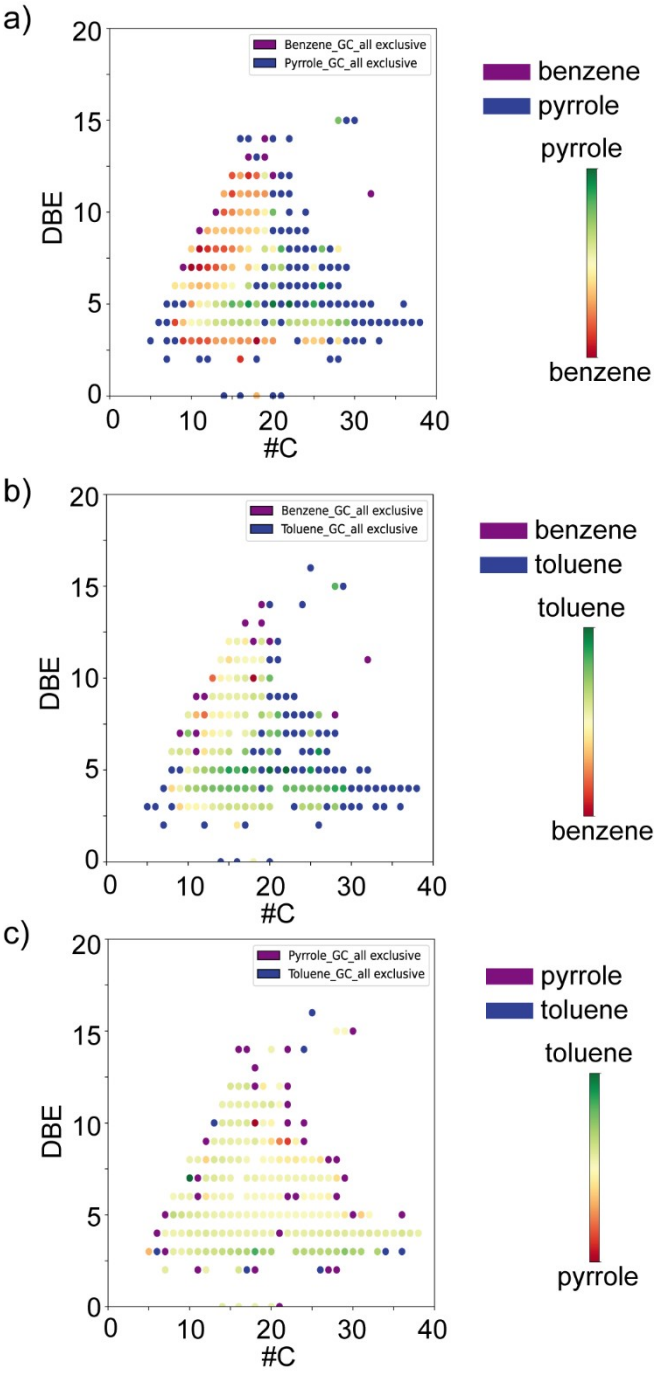
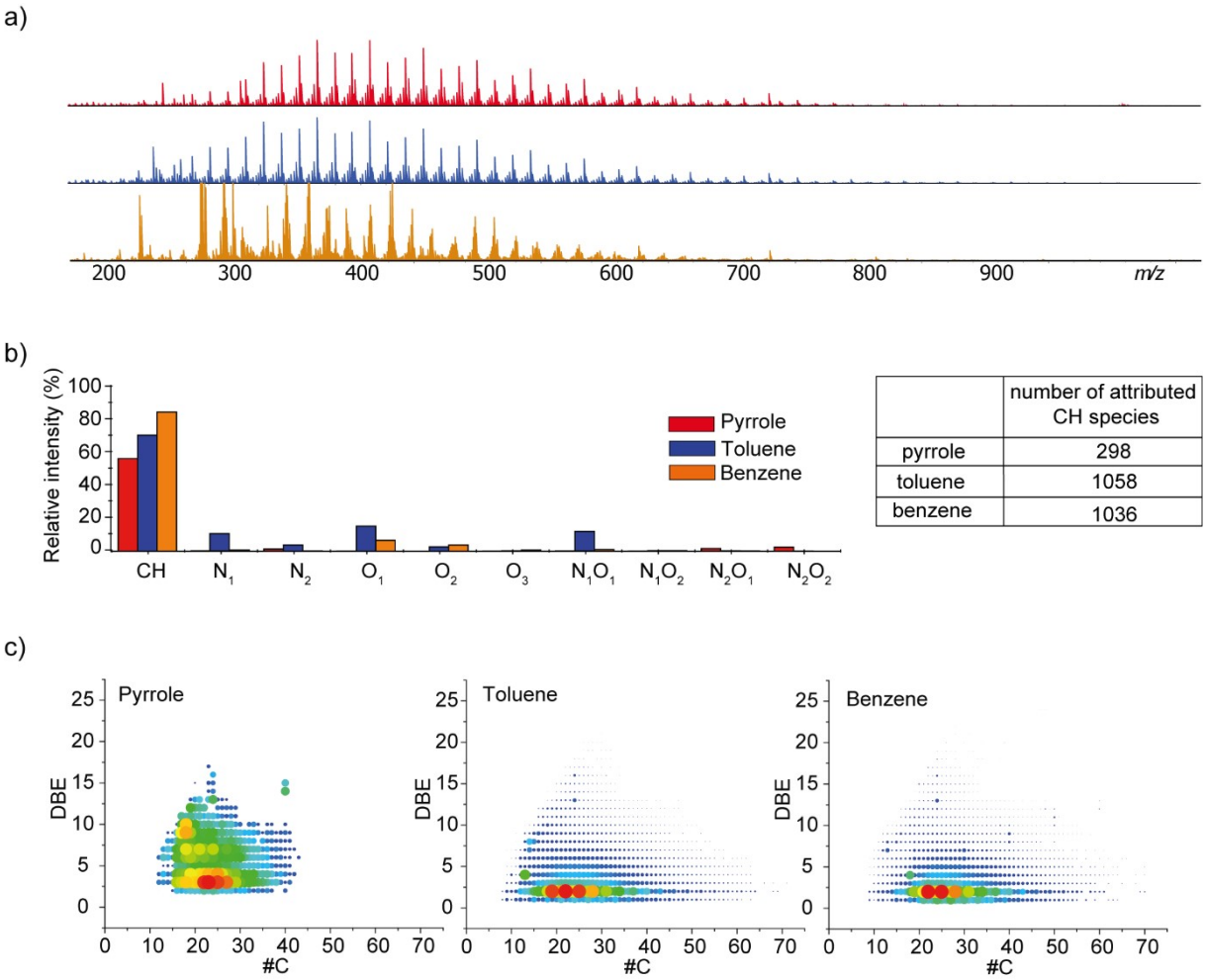


Figure S8. DBE versus carbon number plots of N_1 class using fold change as color map for (a) benzene *vs* pyrrole experiment, (b) benzene *vs* toluene experiment, and (c) pyrrole *vs* toluene experiment.



	number of attributed CH species
pyrrole	298
toluene	1058
benzene	1036

Figure S9. (a) average mass spectra of plastic pyrolysis oil obtained by DI-APPI-FTICR MS with pyrrole (in red), toluene (in blue), and benzene (in yellow). (c) Compound class distribution by the average mass spectrum over 0 to 80 min with the number of ionized CH species. (c) DBE versus carbon number plots for CH class.

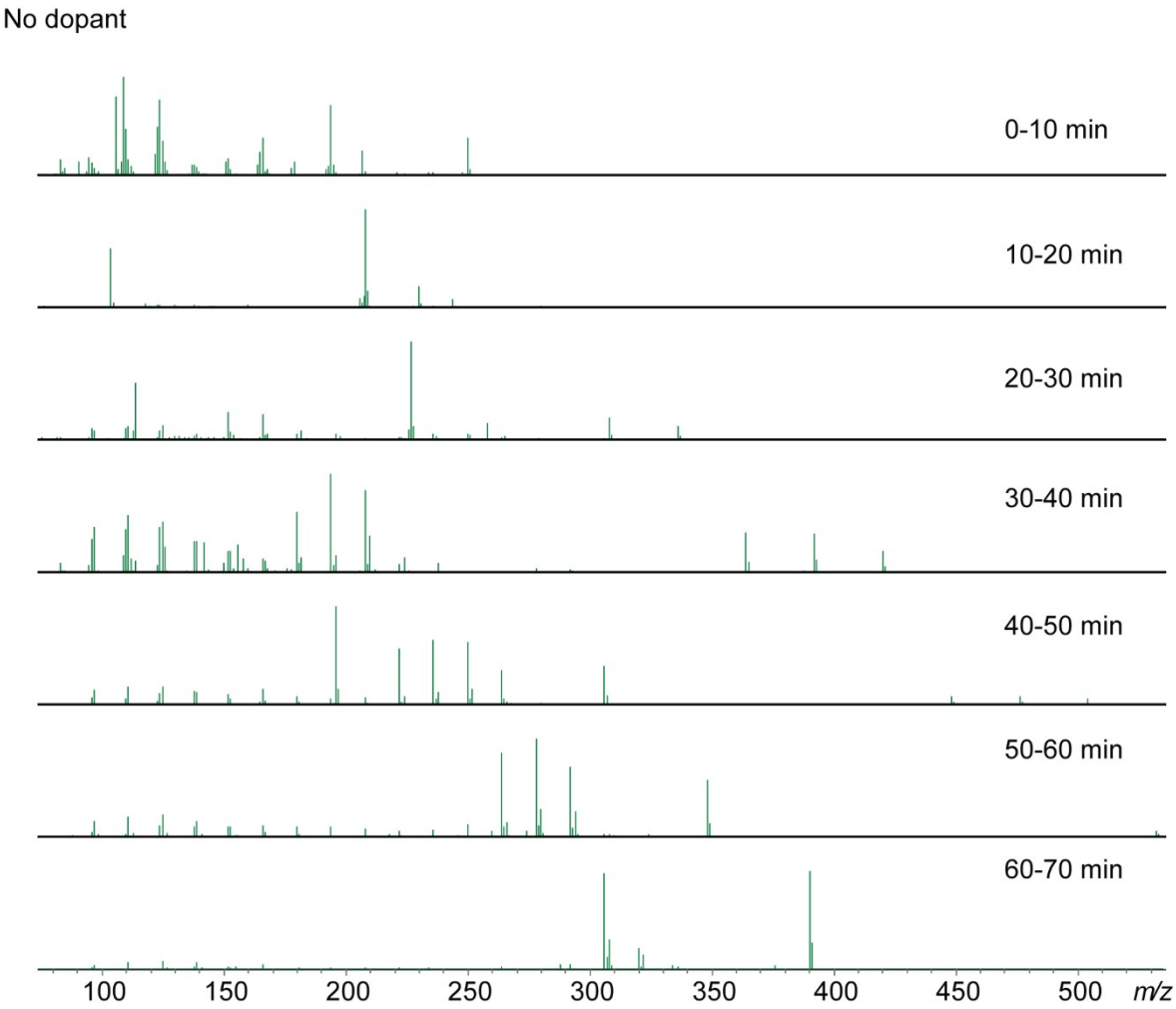


Figure S10. Mass spectra exported for each segment for no dopant experiment on the CH area

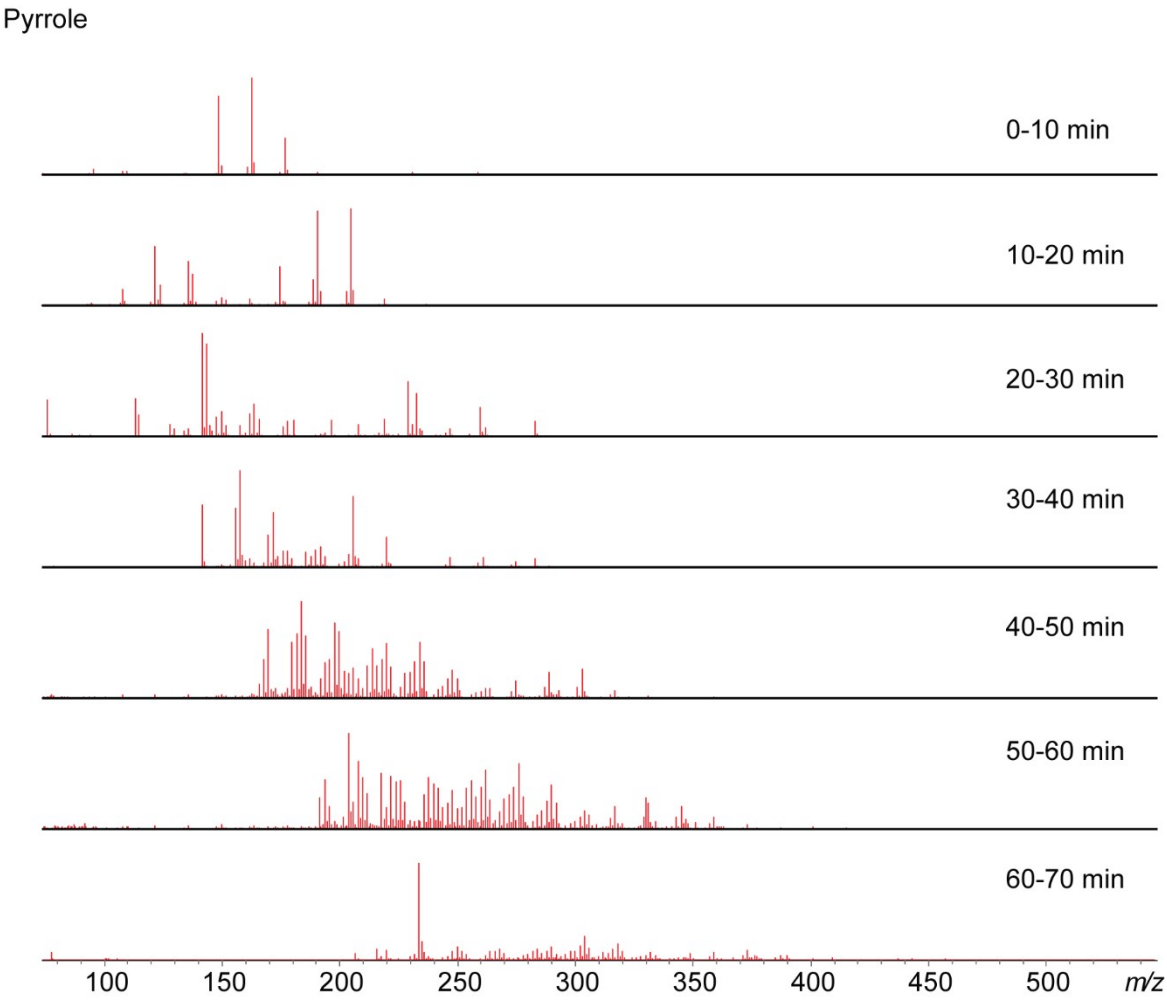


Figure S11. Mass spectra exported for each segment for pyrrole as dopant experiment on the CH area

Toluene

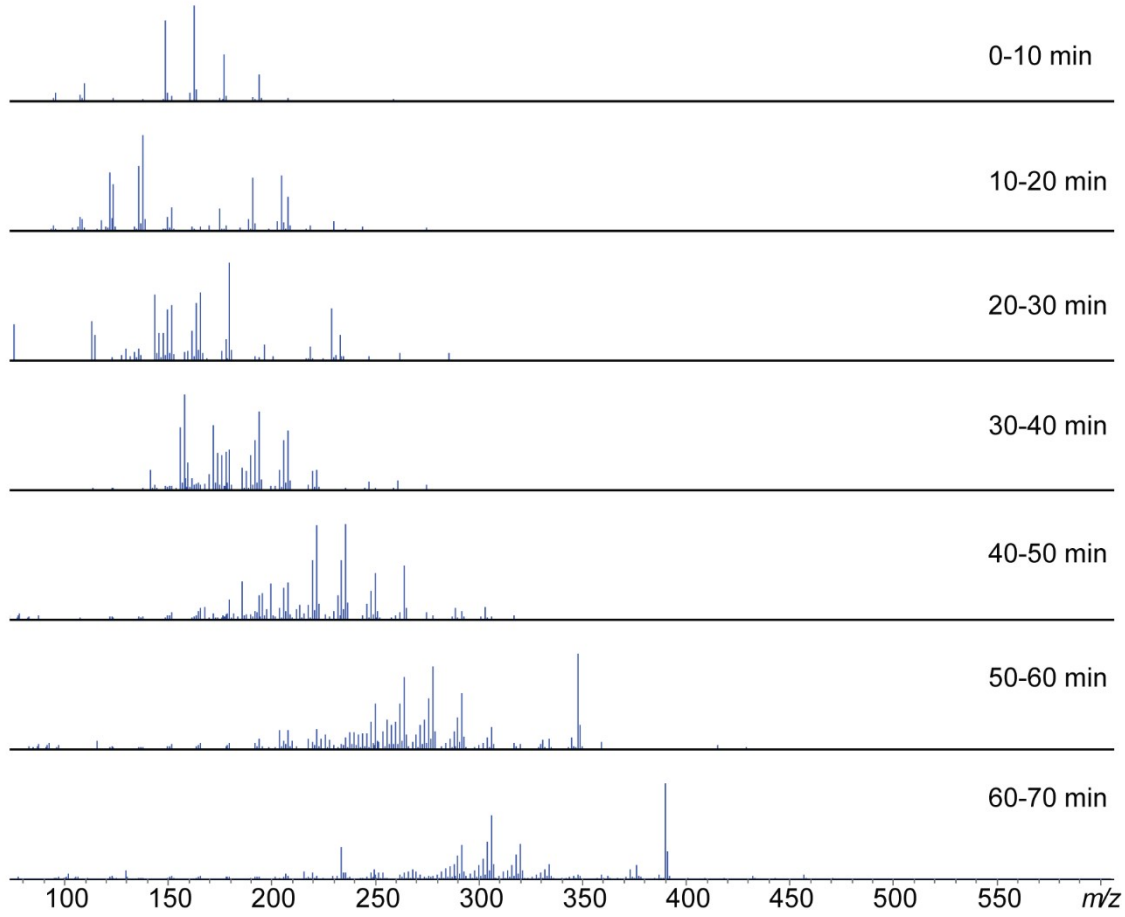


Figure S12. Mass spectra exported for each segment for toluene as dopant experiment on the CH area

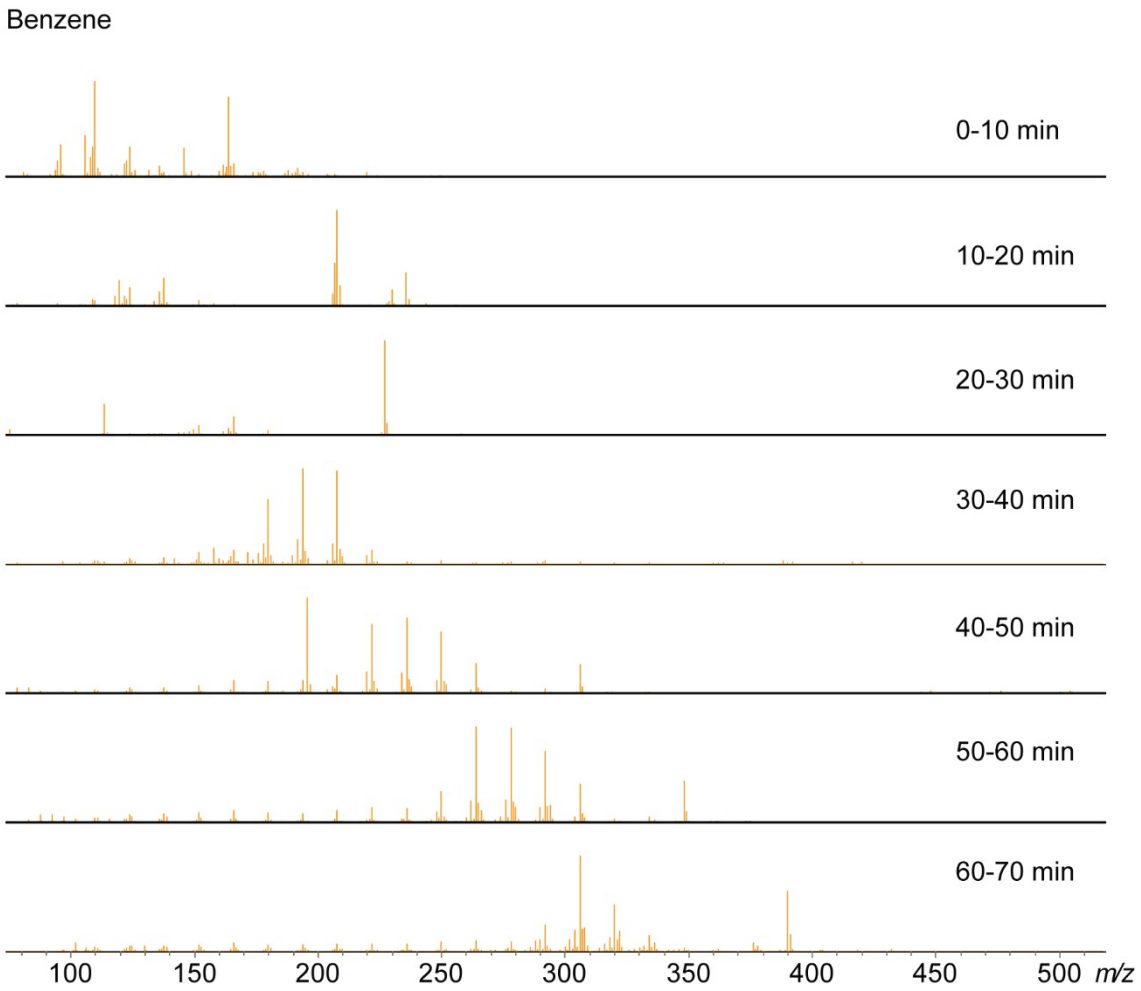


Figure S13. Mass spectra exported for each segment for benzene as dopant experiment on the CH area

Table S2. *m/z* values and corresponding molecular formulas of 25 species presenting DBE 2 value

m/z	**molecular formula**
124.124652	C9 H16
138.140302	C10 H18
152.155952	C11 H20
166.171602	C12 H22
180.187252	C13 H24
194.202902	C14 H26
208.218552	C15 H28
222.234202	C16 H30
236.249852	C17 H32
250.265503	C18 H34
264.281153	C19 H36
278.296803	C20 H38
292.312453	C21 H40
306.328103	C22 H42
320.343753	C23 H44
334.359403	C24 H46
348.375053	C25 H48
362.390703	C26 H50
376.406353	C27 H52
390.422003	C28 H54
404.437653	C29 H56
418.453303	C30 H58
432.468953	C31 H60
446.484603	C32 H62
460.500253	C33 H64