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Composition and light absorption of N-containing aromatic compounds in organic aerosols from laboratory biomass burning

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Table S1. Sample information for the laboratory simulations in open burn test facility (OBTF).

Date	Burn case	Sample phase	Sample volume (m^3)	OC ($mg\ m^{-3}$)	EC ($mg\ m^{-3}$)	EC/OC	Extraction efficiency (%)	MAC_{365} ($m^2\ gC^{-1}$)	MAC_{550} ($m^2\ gC^{-1}$)	$Å_{abs}$
				FL forest[a]						
11/16/2012	Burn 1	Whole	0.45	1.90	0.22	0.12	98.8	1.03	0.037	7.79
11/16/2012	Burn 2	Whole	0.13	3.82	0.58	0.15	99.1	1.06	0.041	7.80
11/16/2012	Burn 3	Whole	0.14	1.56	0.91	0.58	98.6	1.30	0.11	6.00
11/16/2012	Burn 4	Whole	0.26	14.1	0.38	0.027	98.6	0.92	0.030	8.01
11/16/2012	Burn 5	Whole	0.26	2.76	0.44	0.16	95.6	1.16	0.056	7.33
11/16/2012	Burn 6	Whole	0.19	6.14	0.81	0.13	96.1	1.01	0.043	7.34
11/16/2012	Burn 7	Whole	0.21	4.96	1.09	0.22	97.0	1.04	0.045	7.58
11/16/2012	Burn 8	Whole	0.21	2.77	0.64	0.23	95.9	1.32	0.059	7.15
11/16/2012	Burn 9	Whole	0.23	3.46	0.90	0.26	93.6	1.32	0.059	7.22
Average Temp. 10 ^oC, Average Humidity 83%										
				NC forest 1						
4/16/2016	Burn 1	Flaming	0.0038	86.1	2.79	0.032	97.2	1.18	0.077	6.47
		Smoldering	0.024	17.9	0.13	0.0072	97.6	0.96	0.043	7.17
	Burn 2	Flaming	0.039	21.0	0.76	0.036	97.9	1.63	0.17	5.42
		Smoldering	0.063	4.32	0.052	0.012	98.0	1.12	0.070	6.23
	Burn 3	Flaming	0.032	17.4	1.02	0.059	97.9	1.60	0.20	5.15
		Smoldering	0.14	3.63	0.037	0.010	98.0	0.91	0.047	7.10
Average Temp. 12 ^oC, Average Humidity 49%										
				NC forest 2						
7/14/2016	Burn 1	Flaming	0.025	44.7	1.60	0.036	99.0	3.97	0.17	7.40
		Smoldering	0.073	15.1	0.15	0.010	99.1	3.75	0.15	7.79
	Burn 2	Flaming	0.037	34.2	2.13	0.062	99.7	4.25	0.18	7.44
		Smoldering	0.057	12.1	0.11	0.0091	99.3	3.15	0.081	8.22
	Burn 3	Flaming	0.036	39.4	1.84	0.047	99.7	4.14	0.17	7.41
		Smoldering	0.11	11.8	0.080	0.0067	99.3	3.19	0.13	7.74
	Burn 4	Flaming	0.039	35.1	1.86	0.053	99.5	3.92	0.18	7.28
		Smoldering	0.12	11.0	0.046	0.0042	99.2	2.92	0.10	8.03
Average Temp. 29 ^oC, Average Humidity 70%										

[a] Data were obtained from Xie et al. (2017b)

Table S2. Recoveries and method detection limit (MDL) for standard compounds used for quantification.

Standard compounds[a]	Formula	*m/z*, $[M-H]^-$	Recovery (N^b = 4, %)	Detection Limit (pg)
4-Nitrophenol	$C_6H_5NO_3$	138.0196	97.7 ± 0.92[c]	4.25
4-Nitrocatechol	$C_6H_5NO_4$	154.0145	75.1 ± 0.48	4.79
2-Methyl-4-nitroresocinol	$C_7H_7NO_4$	168.0302	105 ± 2.52	0.70
2-Nitrophloroglucinol	$C_6H_5NO_5$	170.0095	92.9 ± 7.10	2.55
2-Methyl-5-nitrobenzoic acid	$C_8H_7NO_4$	180.0302	106 ± 6.08	14.7
2-Nitro-1-naphthol	$C_{10}H_7NO_3$	188.0353	90.6 ± 6.56	16.1
2,5-dimethyl-4-nitrobenzoic acid	$C_9H_9NO_4$	194.0458	116 ± 4.52	17.6

[a] Data were obtained from Xie et al. (2017a) ; [b] number of repetition; [c] mean ± standard deviation.

Table S3. Average and ranges of mass contribution (%) of identified N-containing aromatic compounds to organic matter in $PM_{2.5}$ from laboratory biomass burning.

Suggested formula	m/z $[M-H]^-$	FL Forest (*N* = 9)	NC Forest 1		NC Forest 2	
			Flaming (N =3)	Smoldering (N =3)	Flaming (N =4)	Smoldering (N =4)
$C_6H_5NO_3$	138.0196	0.0011± 0.0005 (0.0004 – 0.0016)	/[a]	/	/	/
$C_6H_5NO_4$	154.0145	0.029 ± 0.011 (0.0069 – 0.043)	0.037 ± 0.011 (0.025 – 0.046)	0.024 ± 0.0098 (0.015 – 0.035)	0.033 ± 0.011 (0.018 – 0.044)	0.010 ± 0.0027 (0.0060 – 0.012)
$C_7H_7NO_4$	168.0301	0.014 ± 0.0064 (0.0037 – 0.023)	0.017 ± 0.0059 (0.011 – 0.022)	0.0087 ± 0.0030 (0.0054– 0.011)	0.016 ± 0.0052 (0.0081 – 0.020)	0.0043 ± 0.0010 (0.0029 – 0.0052)
$C_6H_5NO_5$	170.0093	0.0067 ± 0.0045 (0.0012 – 0.012)	0.011 ± 0.0069 (0.0042 – 0.018)	/	0.016 ± 0.0042 (0.011 – 0.020)	0.0009 ± 0.0005 (0.0003 – 0.0013)
$C_8H_7NO_4$	180.0302	0.013 ± 0.0056 (0.0035 – 0.018)	0.012 ± 0.0055 (0.0074 – 0.018)	/	0.014 ± 0.0035 (0.0089 – 0.017)	/
$C_8H_9NO_4$	182.0459	0.0082 ± 0.0052 (0.0008 – 0.015)	0.012 ± 0.0057 (0.0059 – 0.017)	0.0047 ± 0.0018 (0.0028 – 0.0064)	0.0086 ± 0.0037 (0.0035 – 0.012)	0.0021± 0.0008 (0.0012 – 0.0029)
$C_7H_7NO_5$	184.0253	0.0036 ± 0.0019 (0.0011 – 0.0056)	0.0075 ± 0.0044 (0.0028 – 0.012)	0.0017 ± 0.0012 (0.0004 – 0.0028)	0.0063 ± 0.0024 (0.0035 – 0.0086)	/
$C_{10}H_7NO_3$	188.0353	0.0067 ± 0.0024 (0.0041 – 0.0089)	0.0033 ± 0.0007 (0.0025 – 0.0037)	/	0.0063 ± 0.0001 (0.0062 – 0.0064)	/
$C_9H_9NO_4$	194.0458	0.023 ± 0.012 (0.0057 – 0.043)	0.049 ± 0.016 (0.032 – 0.063)	0.0052 ± 0.0033 (0.0028 – 0.0089)	0.035 ± 0.0072 (0.024 – 0.040)	0.0047 ± 0.0013[b] (0.0035 – 0.0060)
$C_8H_9NO_5$	198.0407	0.0072 ± 0.0034 (0.0015 – 0.011)	0.0056 ± 0.0027 (0.0025 – 0.0073)	0.0025 ± 0.0016 (0.0010 – 0.0042)	0.0051 ± 0.0017 (0.0030 – 0.0073)	/
$C_{10}H_{11}NO_4$	208.0615	0.0069 ± 0.0030 (0.0021 – 0.011)	0.012 ± 0.0078 (0.0036 – 0.019)	0.0044 ± 0.0023 (0.0023 – 0.0068)	0.014 ± 0.0036 (0.0093 – 0.018)	0.0019 ± 0.0008 (0.0009 – 0.0027)
$C_{10}H_{11}NO_5$	224.0564	0.0057 ± 0.029 (0.0025 – 0.010)	0.0041 ± 0.0005[b] (0.0036 – 0.0046)	/	0.0032 ± 0.0009 (0.0021 – 0.0038)	0.0007 ± 0.0004 (0.0003 – 0.0012)
$C_{11}H_{13}NO_5$	238.0721	0.012 ± 0.0060 (0.0043 – 0.022)	0.0062 ± 0.0030 (0.0032 – 0.0093)	0.0029 ± 0.0025 (0.0014 – 0.0058)	0.0035 ± 0.0013 (0.0016 – 0.0045)	0.0016 ± 0.0003 (0.0014 – 0.0019)
$C_{11}H_{13}NO_6$	254.067	0.0005 ± 0.0003 (0.0002 – 0.0010)	/	/	0.0003 ± 0.0000 (0.0002 – 0.0003)	/
Subtotal ($tNAC_{OM}$%)		0.13 ± 0.059 (0.037 – 0.21)	0.18 ± 0.067 (0.10 – 0.23)	0.055 ± 0.026 (0.032 – 0.082)	0.16 ± 0.045 (0.091 – 0.20)	0.023 ± 0.0089 (0.013 – 0.031)

[a] Not detected; [b] detected in two samples, the value represents average ± |x1-x2|/2.

Table S4. $MAC_{365,\ NAC}$ ($m^2\ g^{-1}$) values for identified NAC formulas.

NAC formula	m/z $[M-H]^-$	$MAC_{365,\ OM}$ [a]
$C_6H_5NO_3$	138.0196	2.44
$C_6H_5NO_4$	154.0145	7.02
$C_7H_7NO_4$	168.0302	12.9
$C_6H_5NO_5$	170.0095	14.0
$C_8H_7NO_4$	180.0302	0
$C_8H_9NO_4$	182.0459	12.9
$C_7H_7NO_5$	184.0253	14.0
$C_{10}H_7NO_3$	188.0353	3.75
$C_9H_9NO_4$	194.0458	0
$C_8H_9NO_5$	198.0407	14.0
$C_{10}H_{11}NO_4$ [b]	208.0615	0
$C_{10}H_{11}NO_5$	224.0564	14.0
$C_{11}H_{13}NO_5$	238.0721	0
$C_{11}H_{13}NO_6$	254.0670	0

[a] Obtained from Xie et al. (2017a); [b] MAC_{365} of the third isomer is set at 14.0 $m^2\ g^{-1}$ based on its structure.

Table S5. Average and ranges of contribution of identified N-containing aromatic compounds to Abs_{365} of extracted OM ($Abs_{365,NAC}$%) from laboratory biomass burning samples.

Suggested formula	m/z $[M-H]^-$	FL Forest (*N* = 9)	NC Forest 1		NC Forest 2	
			Flaming (N =3)	Smoldering (N =3)	Flaming (N =4)	Smoldering (N =4)
$C_6H_5NO_3$	138.0196	0.0042 ± 0.0016 (0.0018 – 0.0066)	/[a]	/	/	/
$C_6H_5NO_4$	154.0145	0.31 ± 0.11 (0.091 – 0.42)	0.30 ± 0.045 (0.26 – 0.35)	0.29 ± 0.095 (0.19 – 0.37)	0.098 ± 0.034 (0.055 – 0.13)	0.037 ± 0.0080 (0.025 – 0.042)
$C_7H_7NO_4$	168.0301	0.27 ± 0.12 (0.090 – 0.40)	0.26 ± 0.050 (0.21 – 0.31)	0.19 ± 0.058 (0.13– 0.23)	0.084 ± 0.029 (0.045 – 0.11)	0.029 ± 0.0051 (0.022 – 0.034)
$C_6H_5NO_5$	170.0093	0.14 ± 0.094 (0.022 – 0.27)	0.17 ± 0.091 (0.088 – 0.27)	/	0.092 ± 0.025 (0.065 – 0.11)	0.0067 ± 0.0034 (0.0028 – 0.0091)
$C_8H_7NO_4$	180.0302	0	0	/	0	/
$C_8H_9NO_4$	182.0459	0.16 ± 0.097 (0.013 – 0.27)	0.18 ± 0.062 (0.11 – 0.24)	0.11 ± 0.034 (0.067 – 0.13)	0.047 ± 0.020 (0.020 – 0.068)	0.014 ± 0.0055 (0.0091 – 0.020)
$C_7H_7NO_5$	184.0253	0.077 ± 0.040 (0.029 – 0.13)	0.12 ± 0.057 (0.058 – 0.17)	0.040 ± 0.026 (0.011 – 0.062)	0.037 ± 0.015 (0.021 – 0.053)	/
$C_{10}H_7NO_3$	188.0353	0.040 ± 0.013 (0.027 – 0.056)	0.015 ± 0.0047 (0.010 – 0.019)	/	0.0098 ± 0.0004 (0.0094 – 0.010)	/
$C_9H_9NO_4$	194.0458	0	0	0	0	0
$C_8H_9NO_5$	198.0407	0.15 ± 0.066 (0.039 – 0.24)	0.088 ± 0.032 (0.051 – 0.11)	0.058 ± 0.032 (0.026 – 0.090)	0.030 ± 0.011 (0.018 – 0.045)	/
$C_{10}H_{11}NO_4$	208.0615	0.012 ± 0.0031 (0.0069 – 0.017)	0.058 ± 0.0087[b] (0.050 – 0.067)	0.029 ± 0.0067 (0.023– 0.036)[b]	0.013 ± 0.034 (0.0099 – 0.017)	0.0011 ± 0.0003[b] (0.0008 – 0.0014)
$C_{10}H_{11}NO_5$	224.0564	0.12 ± 0.049 (0.067 – 0.19)	0.062 ± 0.0072[b] (0.055 – 0.069)	/	0.010 ± 0.0059 (0.012 – 0.023)	0.0051 ± 0.0036 (0.0021 – 0.091)
$C_{11}H_{13}NO_5$	238.0721	0	0	0	0	0
$C_{11}H_{13}NO_6$	254.067	0	/	/	0	/
Subtotal		1.22 ± 0.54 (0.43 – 1.75)	1.21 ± 0.38 (0.80 – 1.53)	0.72 ± 0.27 (0.42 – 0.95)	0.42 ± 0.15 (0.39 – 0.58)	0.087 ± 0.024 (0.059 – 0.12)

[a] Compound not detected; [b] detected in two samples, the value represents average ± |x1-x2|/2.

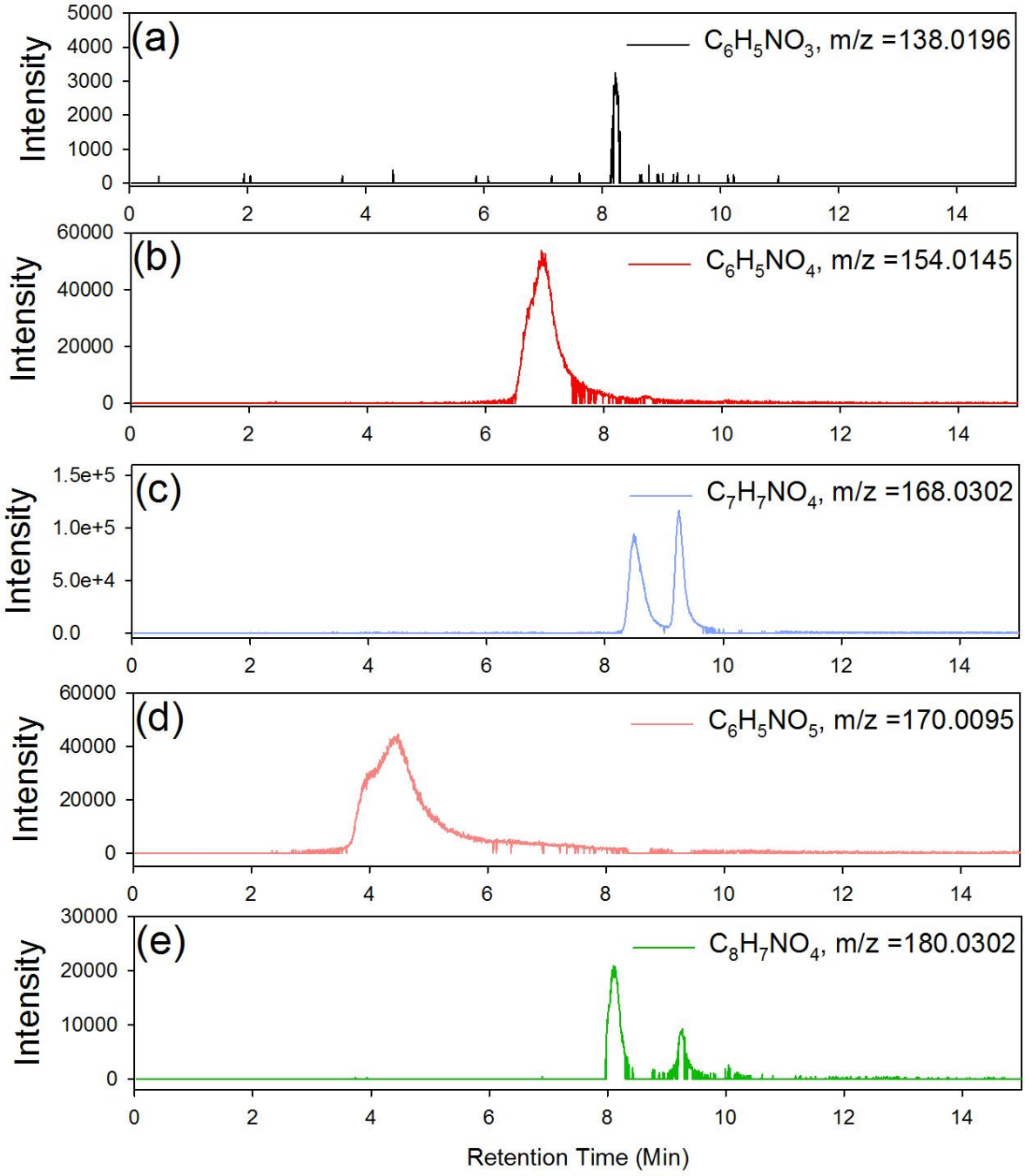

Figure S1. Extracted ion chromatograms (EIC) of (a) $C_6H_5NO_3$, (b) $C_6H_5NO_4$, (c) $C_7H_7NO_4$, (d) $C_6H_5NO_5$, (e) $C_8H_7NO_4$, (f) $C_8H_9NO_4$, (g) $C_7H_7NO_5$, (h) $C_{10}H_7NO_3$, (i) $C_9H_9NO_4$, (j) $C_8H_9NO_5$, (k) $C_{10}H_{11}NO_4$, (l) $C_{10}H_{11}NO_5$, (m) $C_{11}H_{13}NO_5$ and (n) $C_{11}H_{13}NO_6$ identified in the flaming phase sample collected during NC forest 1 experiment, burn 2 (Table S1).

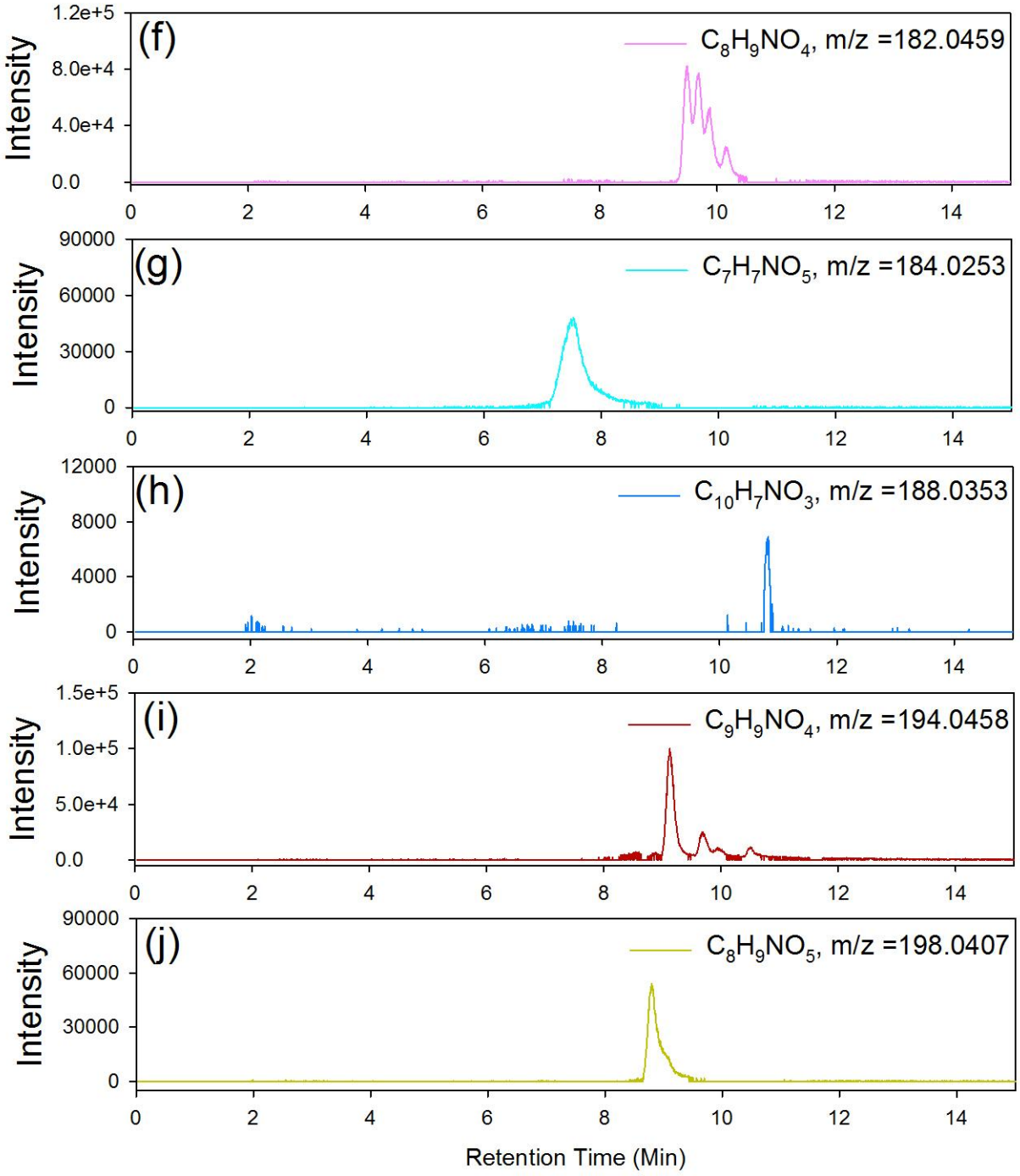

Figure S1. Continue

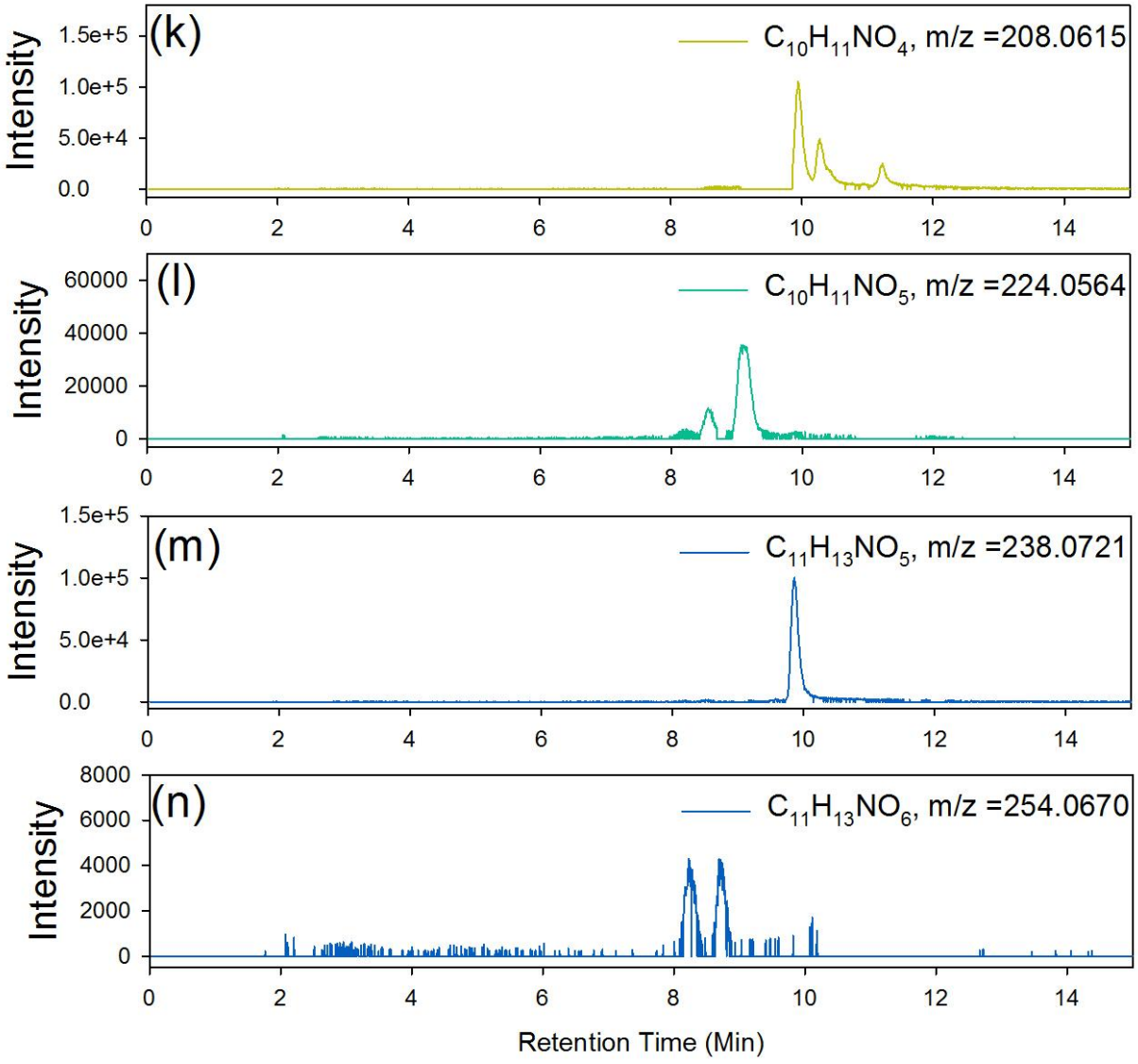

Figure S1. Continue

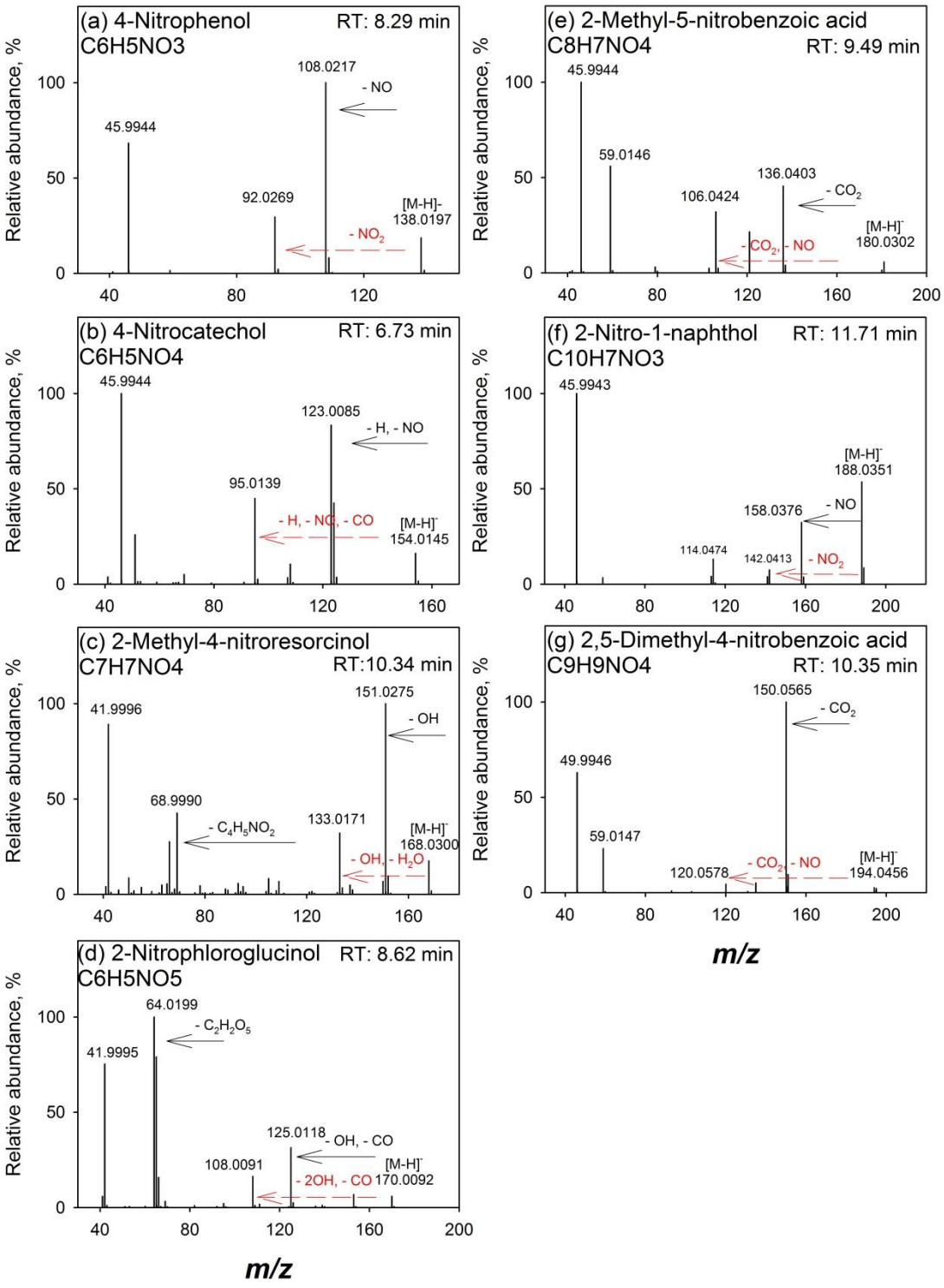

Figure S2. Q-ToF MS/MS spectra of standard compounds, (a) 4-nitrophenol, (b) 4-nitrocatechol, (c)2-methyl-4-nitroresorcinol, (d) 2-nitrophloroglucinol, (e) 2-methyl-5-nitrobenzoic acid, (f) 2-nitro-1-naphthol and (g) 2,5-dimethyl-4-nitrobenzoic acid. These MS/MS data were obtained from Xie et al. (2017a).

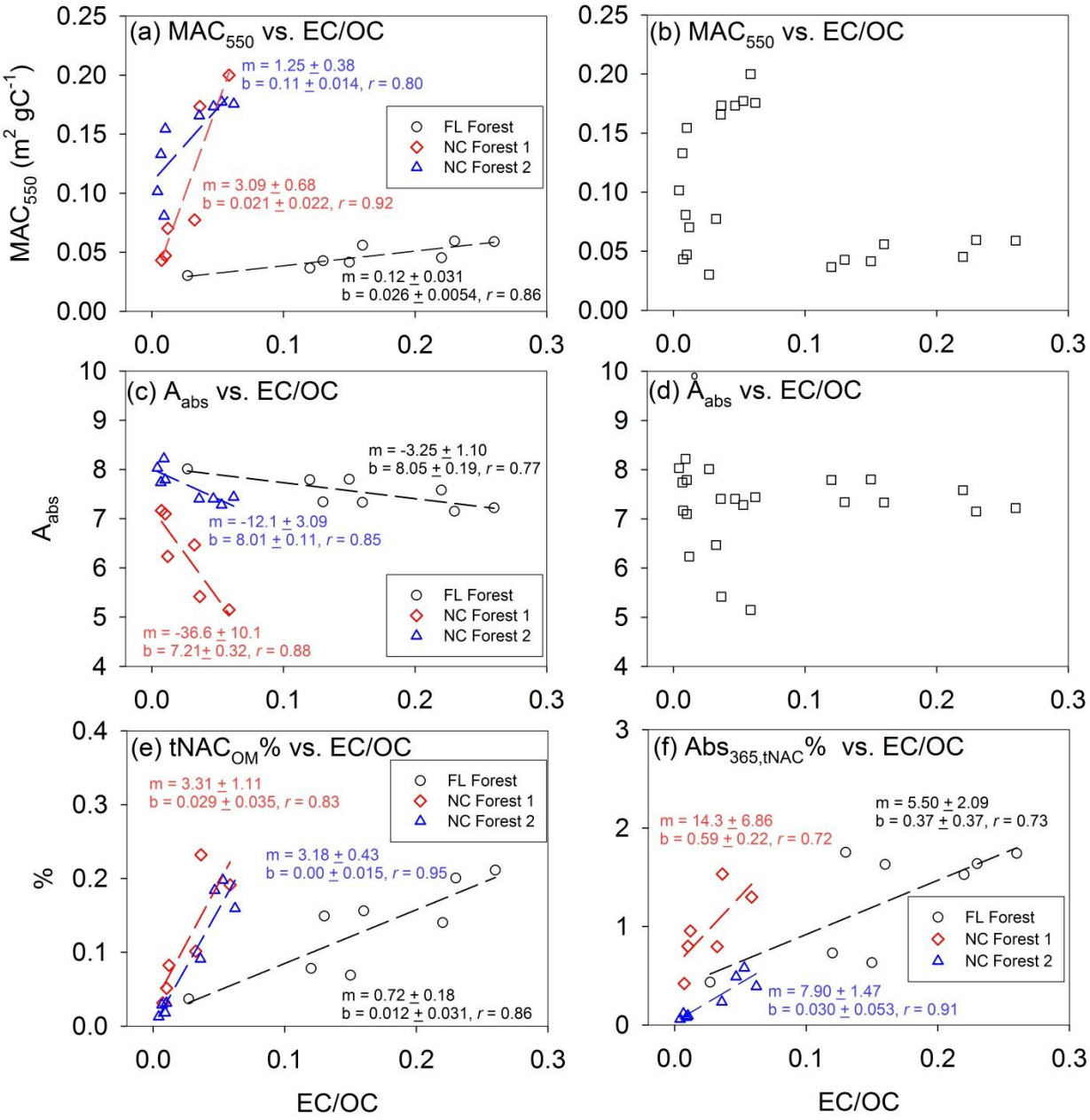

Figure S3. Linear regressions of (a) MAC_{550} vs. EC/OC with individual burns data, (b) MAC_{550} vs. EC/OC with pooled sample data from all the three experiments, (c) $Å_{abs}$ vs. EC/OC with individual burns data, (d) $Å_{abs}$ vs. EC/OC with pooled sample data from all the three experiments, (e) $tNAC_{OM}$% vs. EC/OC and (f) $Abs_{365,tNAC}$% vs. EC/OC with individual burns data.

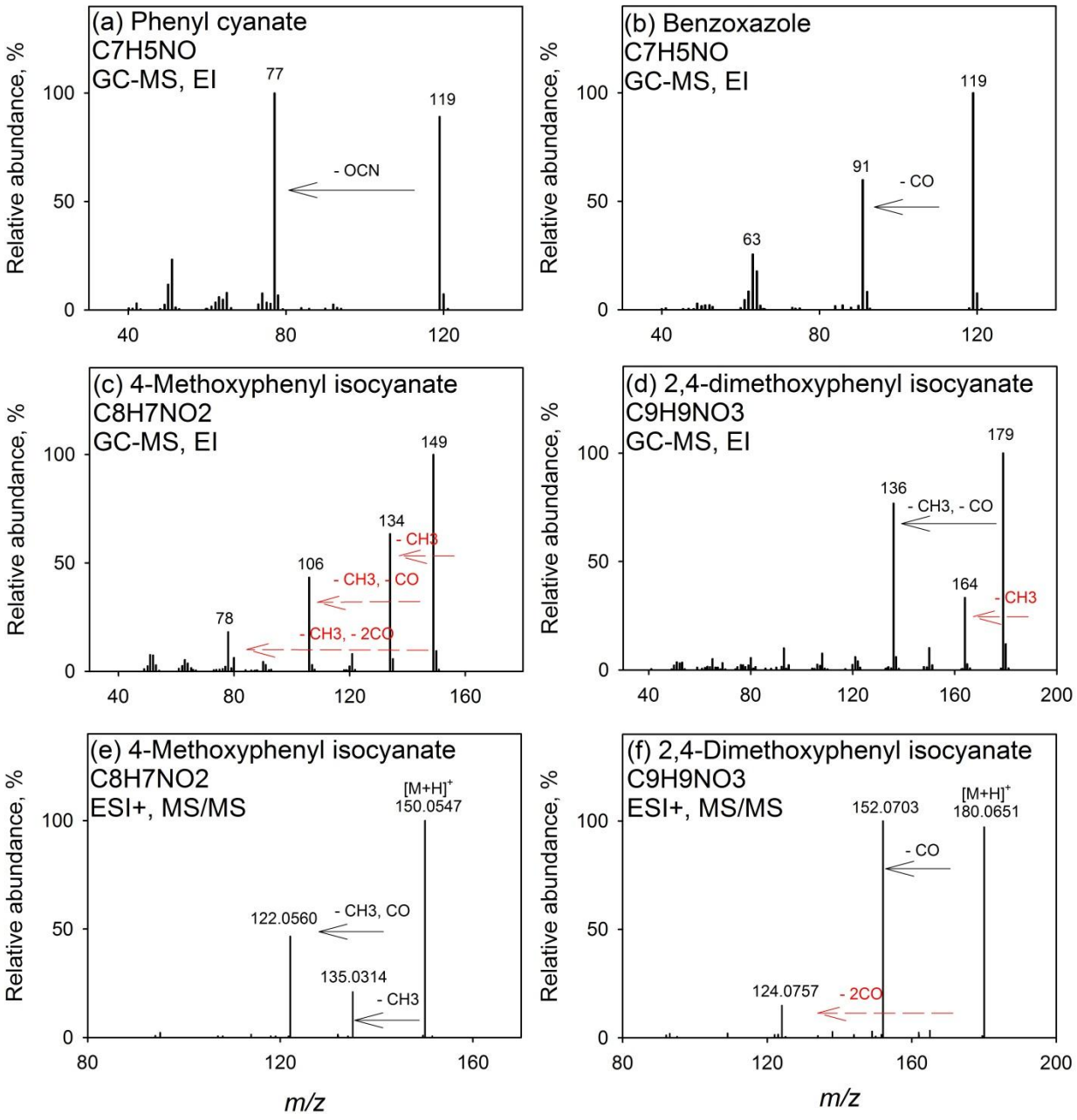

Figure S4. Mass spectra of (a) phenyl cyanate, (b) benzoxazole, (c) 4-methoxyphenyl isocyanate, and (d) 2,4-dimethoxyphenyl isocyanate with EI mode; MS/MS spectra of (e) 4-methoxyphenyl isocyanate and (f) 2,4-dimethoxyphenyl isocyanate with ESI positive ion mode.

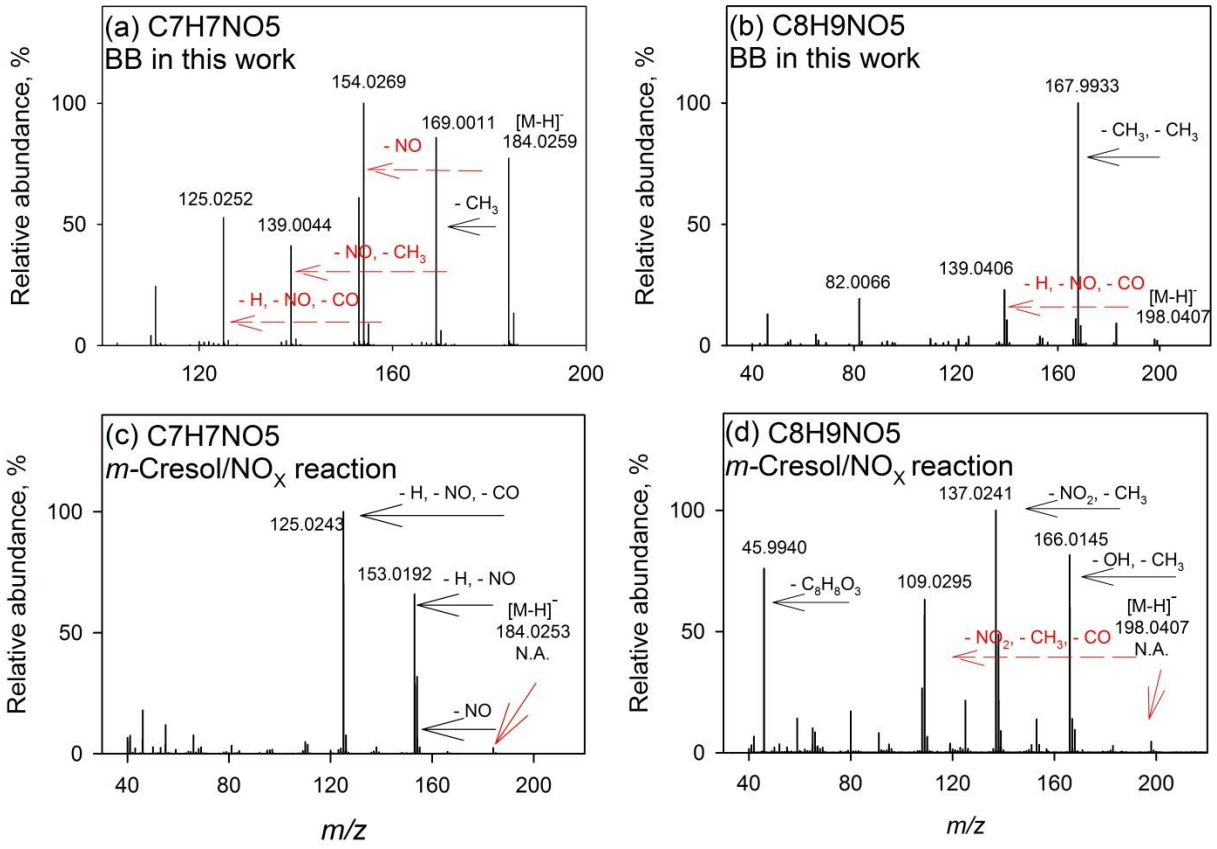

Figure S5. MS/MS spectra of (a) $C_7H_7NO_5$ and (b) $C_8H_9NO_5$ identified from BB in this work and (c, d) the same formula from photo-oxidation of *m*-cresol with NO_X.

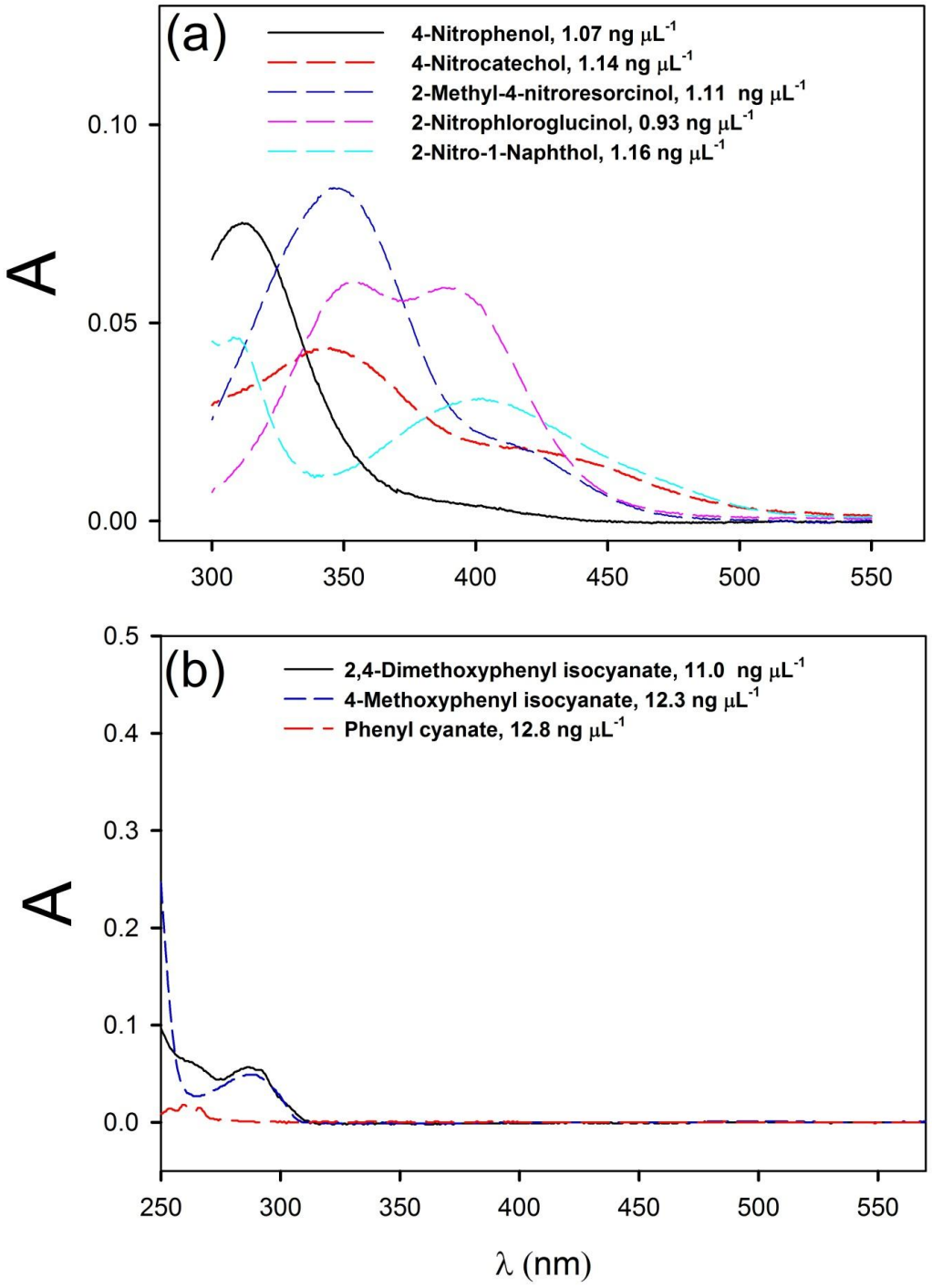

Figure S6. UV/Vis spectra of (a) 4-nitrophenol, 4-nitrocatechol, 2-methyl-4-nitroresorcinol, 2-nitrophloroglucinol, and 2-nitro-1-naphthol at ~1 ng μL^{-1} (Xie et al., 2017a), and (b) 2,4-dimethoxyphenyl isocyanate, 4-methoxyphenyl isocyanate, and phenyl cyanate at ~10 ng μL^{-1}.

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