Electronic Supplementary Information (ESI) for:

The formation of furan-like disinfection byproducts from phenolic precursors

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Contents

Table ESI-1. Precursors selected and their initial concentration for the UV chlorination experiments

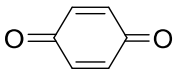
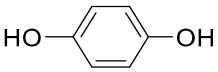
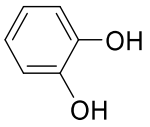
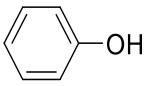
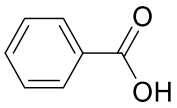
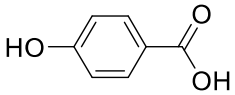
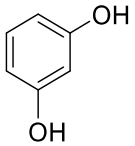
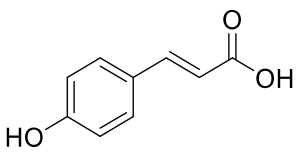
Precursors	Alternative names	Initial concentration (µmol/L)
1,4-benzoquinone (1,4-BQ) 	p-benzoquinone; 2,5-cyclohexadiene-1,4-dione	30
Hydroquinone (HQ) 	1,4-benzenediol; 1,4-dihydroxybenzene; p-benzenediol; p-dihydroxybenzene	200
Pyrocatechol (PC) 	catechol; 1,2-benzenediol; 1,2-dihydroxybenzene; o-benzenediol; o-dihydroxybenzene	200
Phenol (PHE) 	hydroxybenzene; benzenol	300
Benzoic acid (BA) 	benzenecarboxylic acid; carboxybenzene	40
4-hydroxybenzoic acid (4-HBA) 	p-hydroxybenzoic acid; p-salicylic acid	30
Resorcinol (RE) 	1,3-benzenediol; 1,3-dihydroxybenzene; m-benzenediol; m-dihydroxybenzene	300
4-hydroxycinnamic acid (4-HCA) 	p-coumaric acid; p-hydroxycinnamic acid; 4-coumaric acid	30

Table ESI-1. Continued

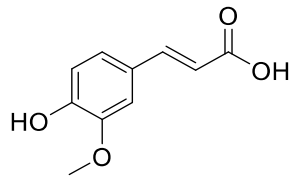
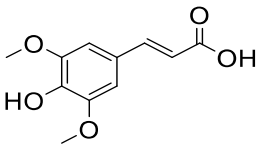
Precursors	Alternative names	Initial concentration (µmol/L)
Trans-ferulic acid (TFA) 	ferulic acid; 4-hydroxy-3-methoxycinnamic acid; (E)-ferulic acid	25
Sinapic acid (SA) 	sinapinic acid; 3,5-dimethoxy-4-hydroxycinnamic acid	25

Table ESI-2. Experimental conditions for the UV chlorination experiments

	Values selected
pH	6; 7; 8
Chlorine to precursor molar ratio	10; 20; 40 for tannic acid 5; 10; 20 for rest of precursors
Bromide to chlorine molar ratio	1; 0
Contact time	20 s 1 min 40 s 3 min 5 min Every 5 min up to 1h Every 1 h up to 5 h Every 1 d up to 7 d

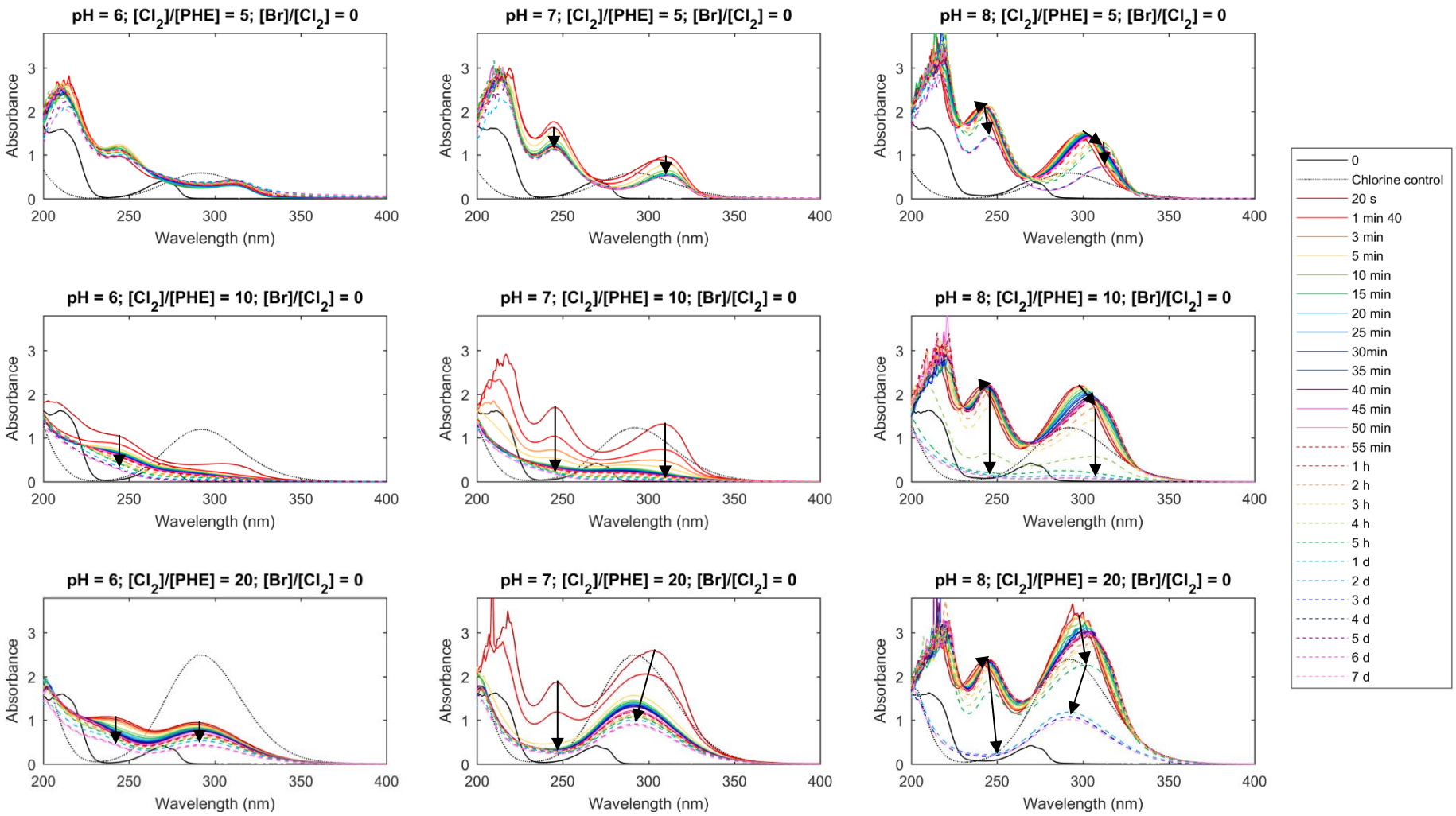


Figure ESI-1. UV spectra of chlorination of phenol (PHE) (300 µmol/L) at different pH and chlorine doses without bromide

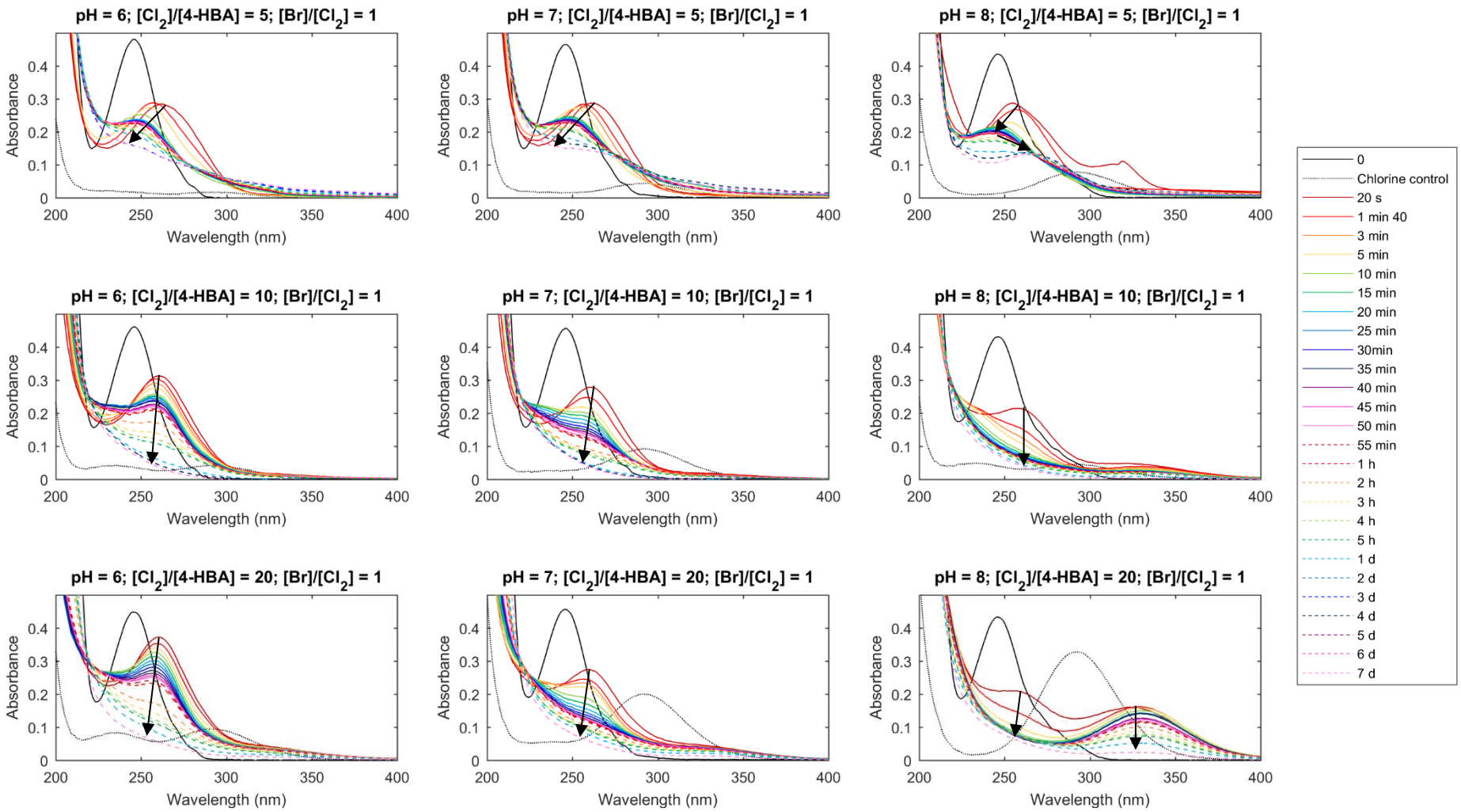


Figure ESI-2. UV spectra of chlorination of 4-hydroxybenzoic acid (4-HBA) (40 µmol/L) at different pH and chlorine doses with bromide

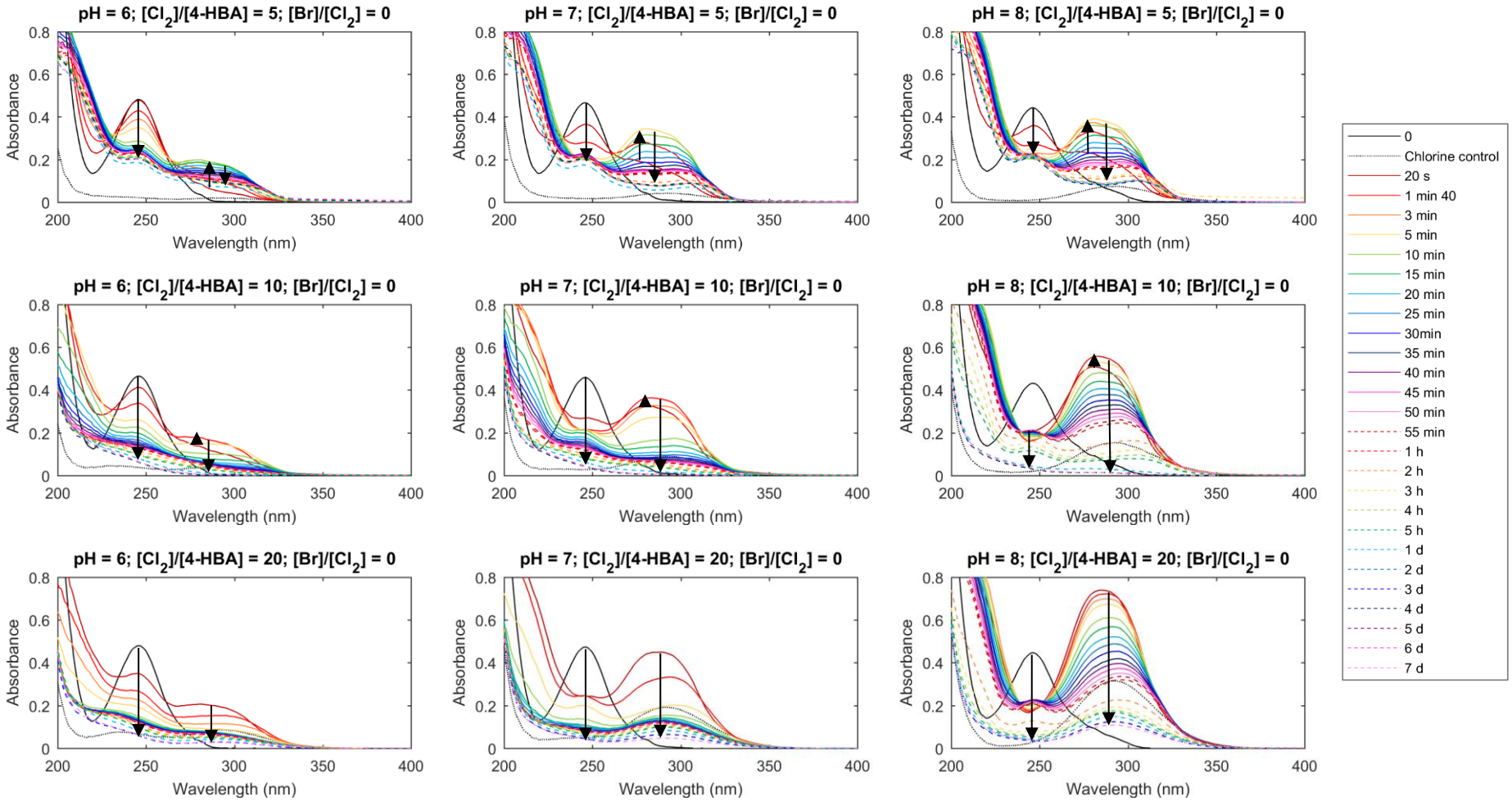


Figure ESI-3. UV spectra of chlorination of 4-hydroxybenzoic acid (4-HBA) (40 µmol/L) at different pH and chlorine doses without bromide

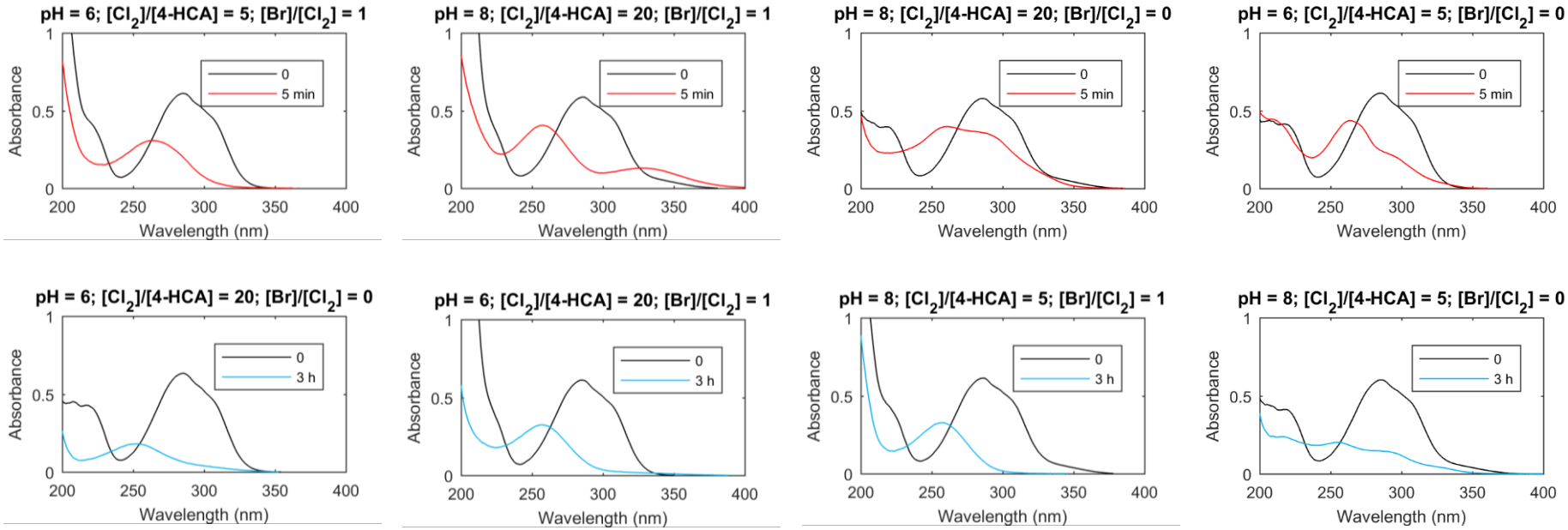


Figure ESI-4. UV spectra of chlorination of 4-hydroxycinnamic acid (4-HCA) (*3*0 µmol/L) at different pH and chlorine doses in the presence and absence of bromide

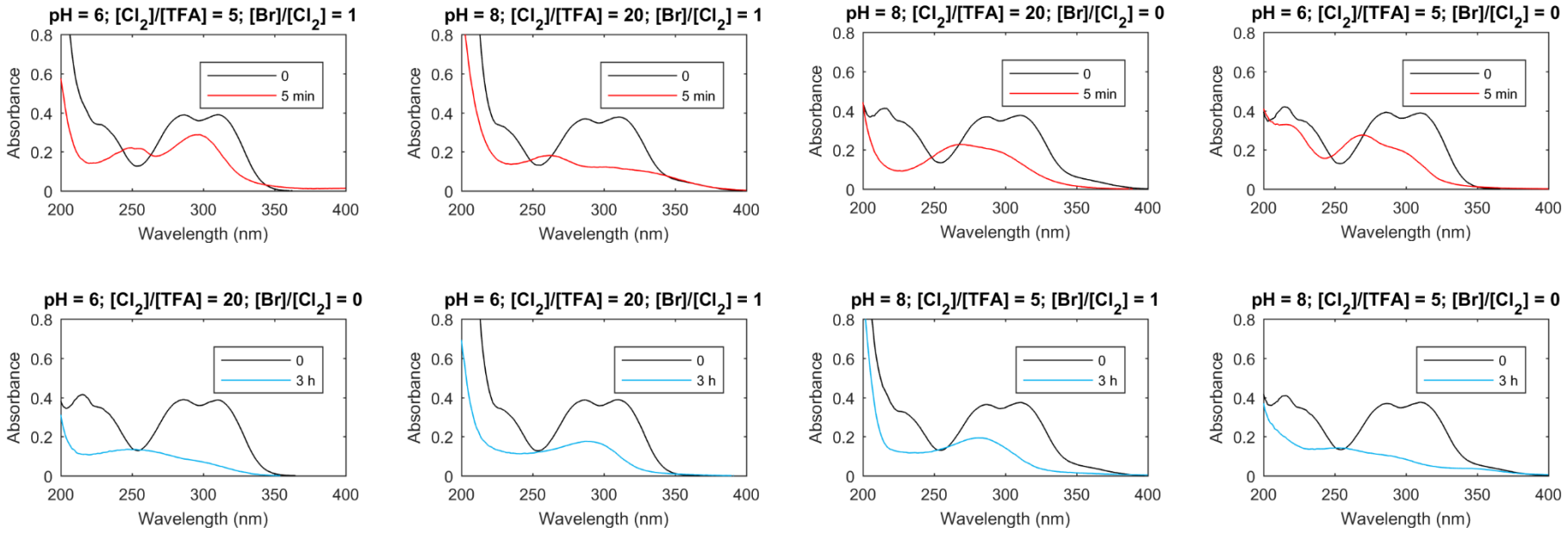


Figure ESI-5. UV spectra of chlorination of trans-ferulic acid (TFA) (25 µmol/L) at different pH and chlorine doses in the presence and absence of bromide

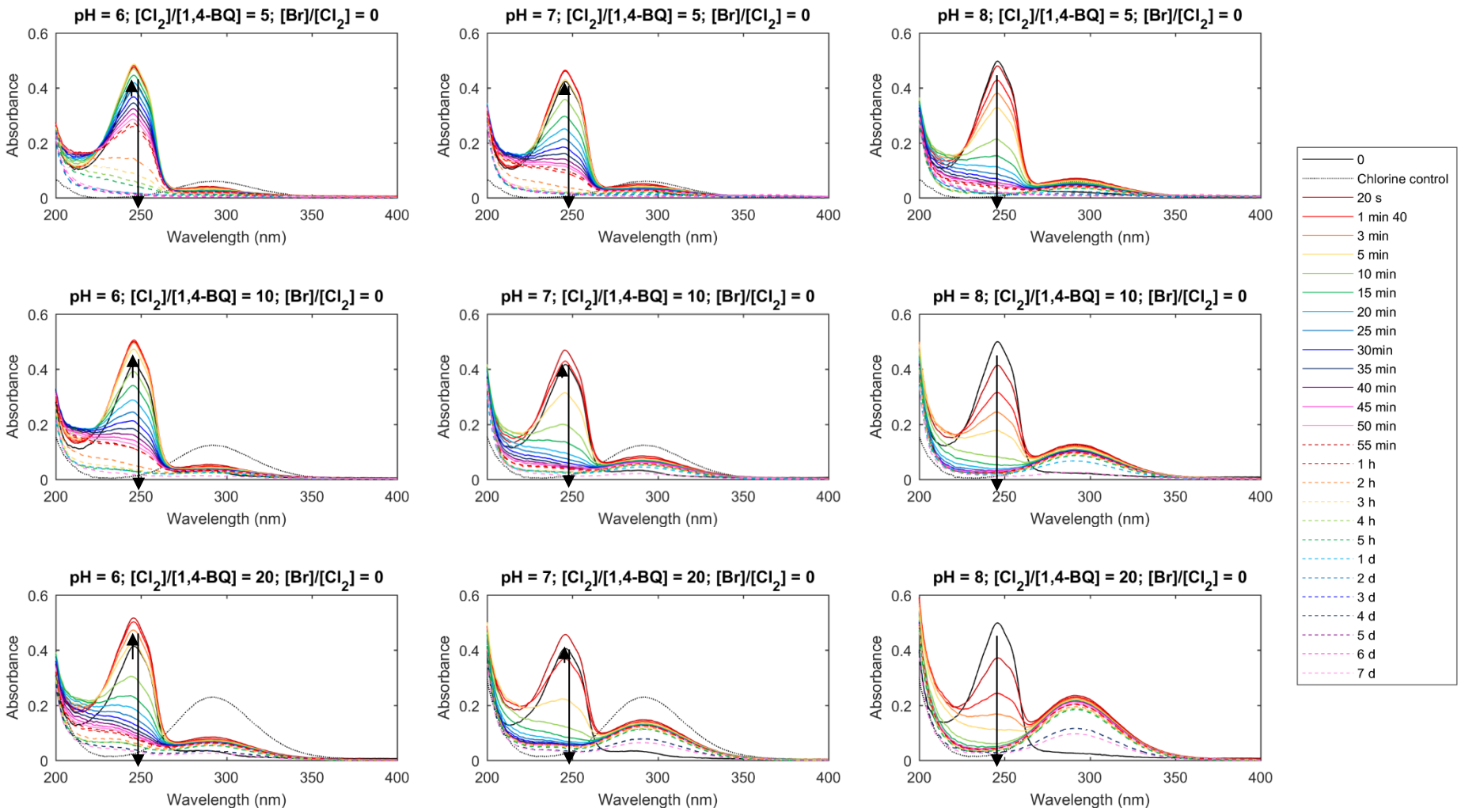


Figure ESI-6. UV spectra of chlorination of 1,4-benzoquinone (1,4-BQ) (30 µmol/L) at different pH and chlorine doses without bromide

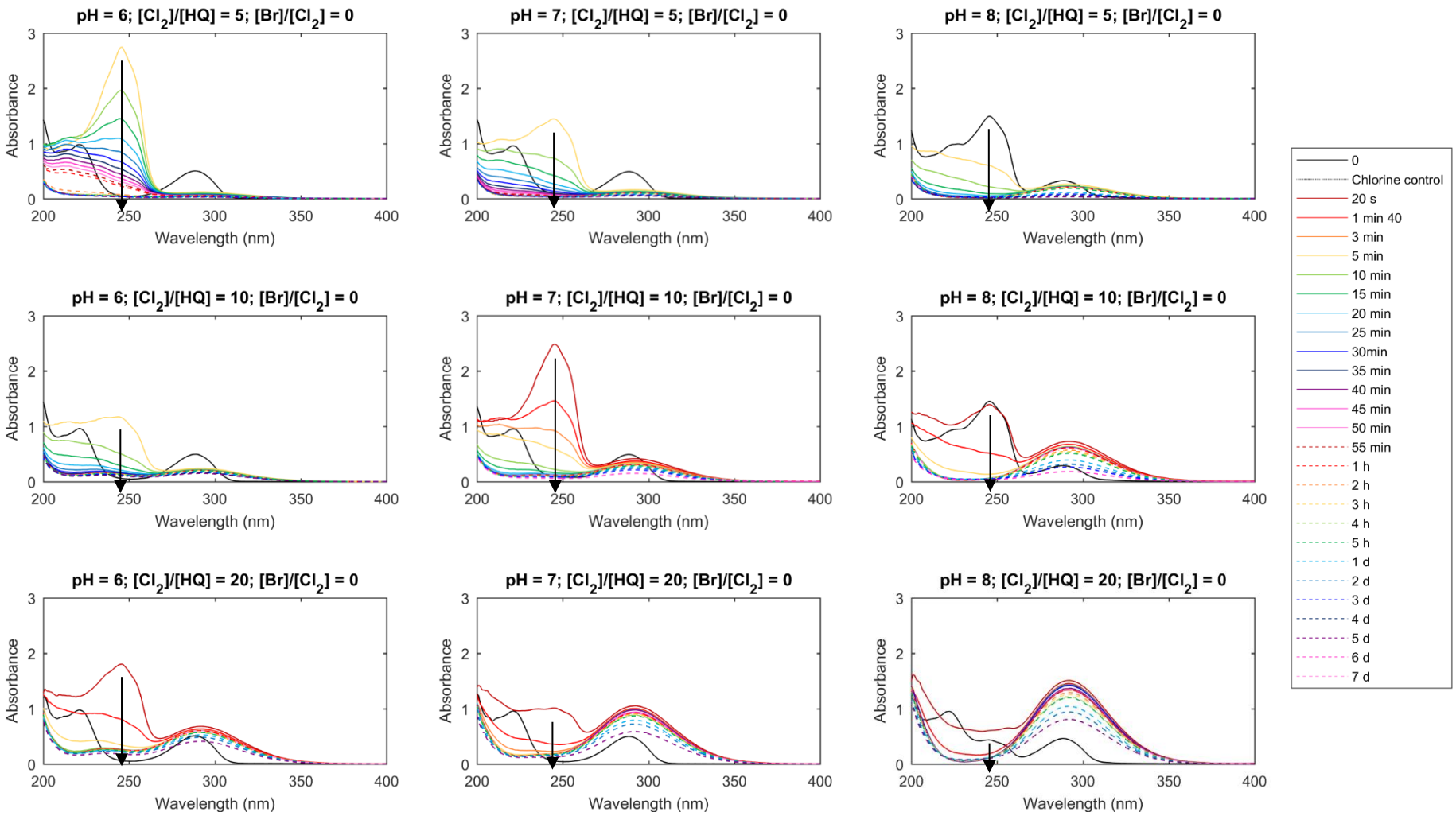


Figure ESI-7. UV spectra of chlorination of hydroquinone (HQ) (200 µmol/L) at different pH and chlorine doses without bromide

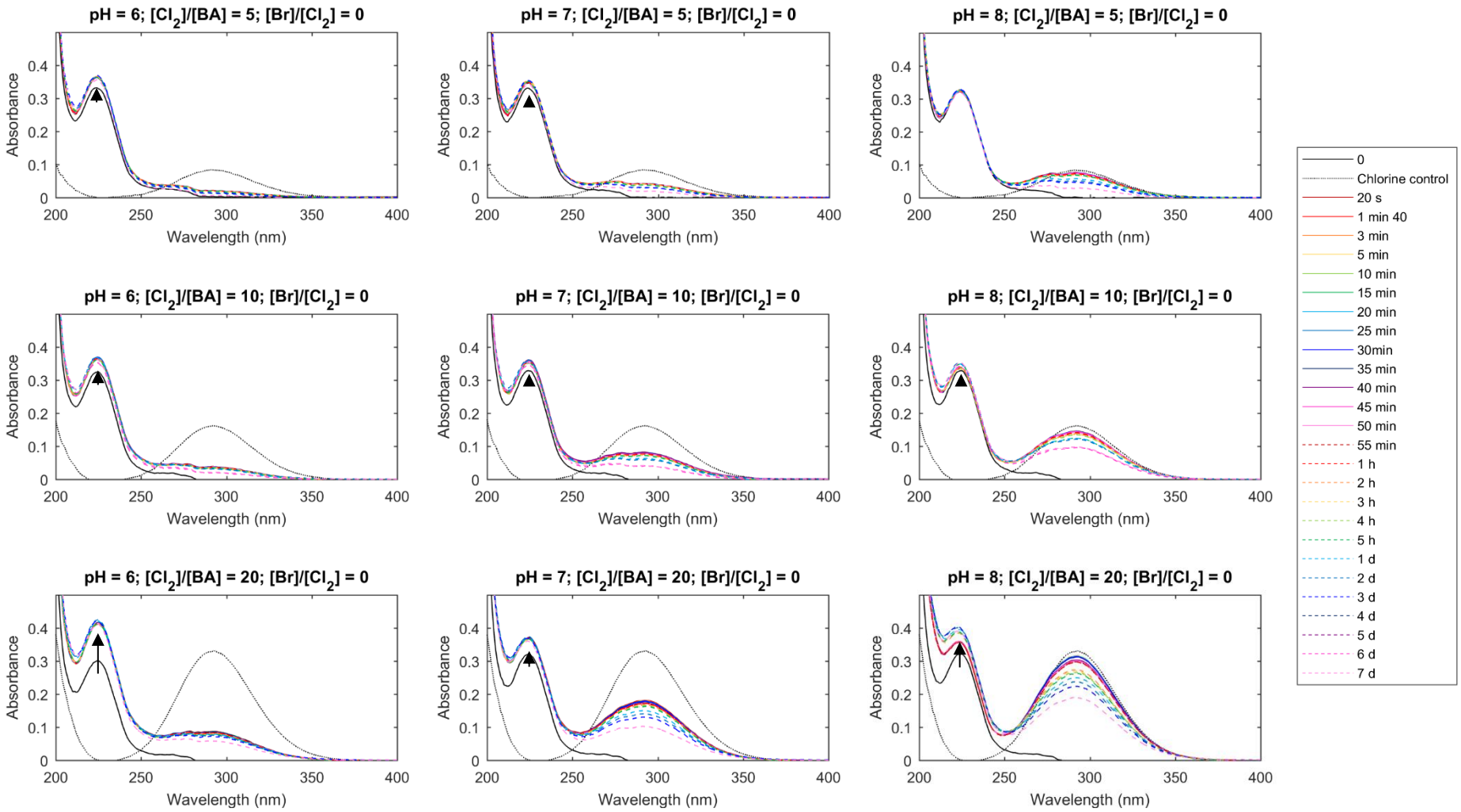


Figure ESI-8. UV spectra of chlorination of benzoic acid (BA) (30 µmol/L) at different pH and chlorine doses without bromide

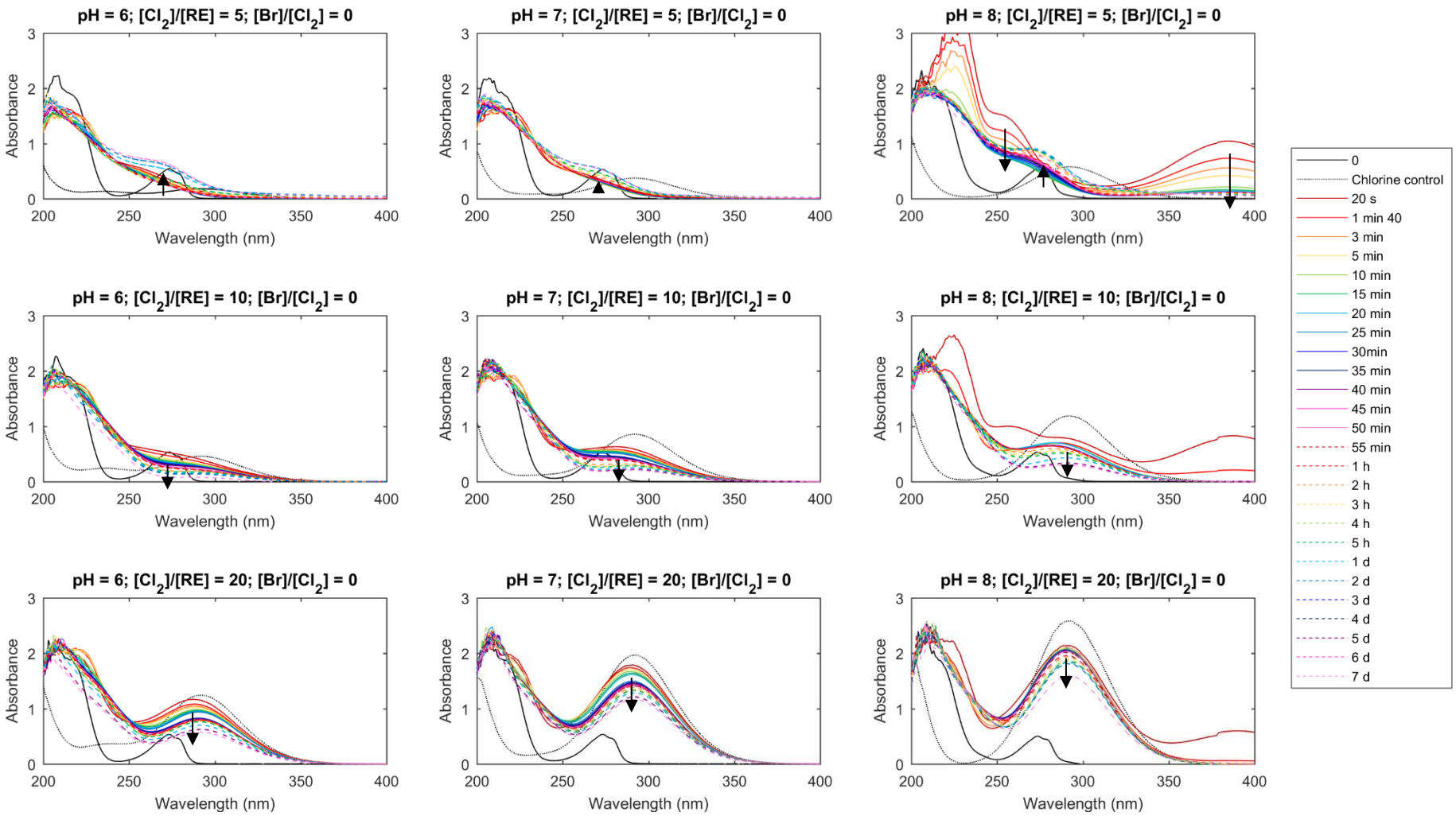


Figure ESI-9. UV spectra of chlorination of resorcinol (RE) (300 µmol/L) at different pH and chlorine doses without bromide

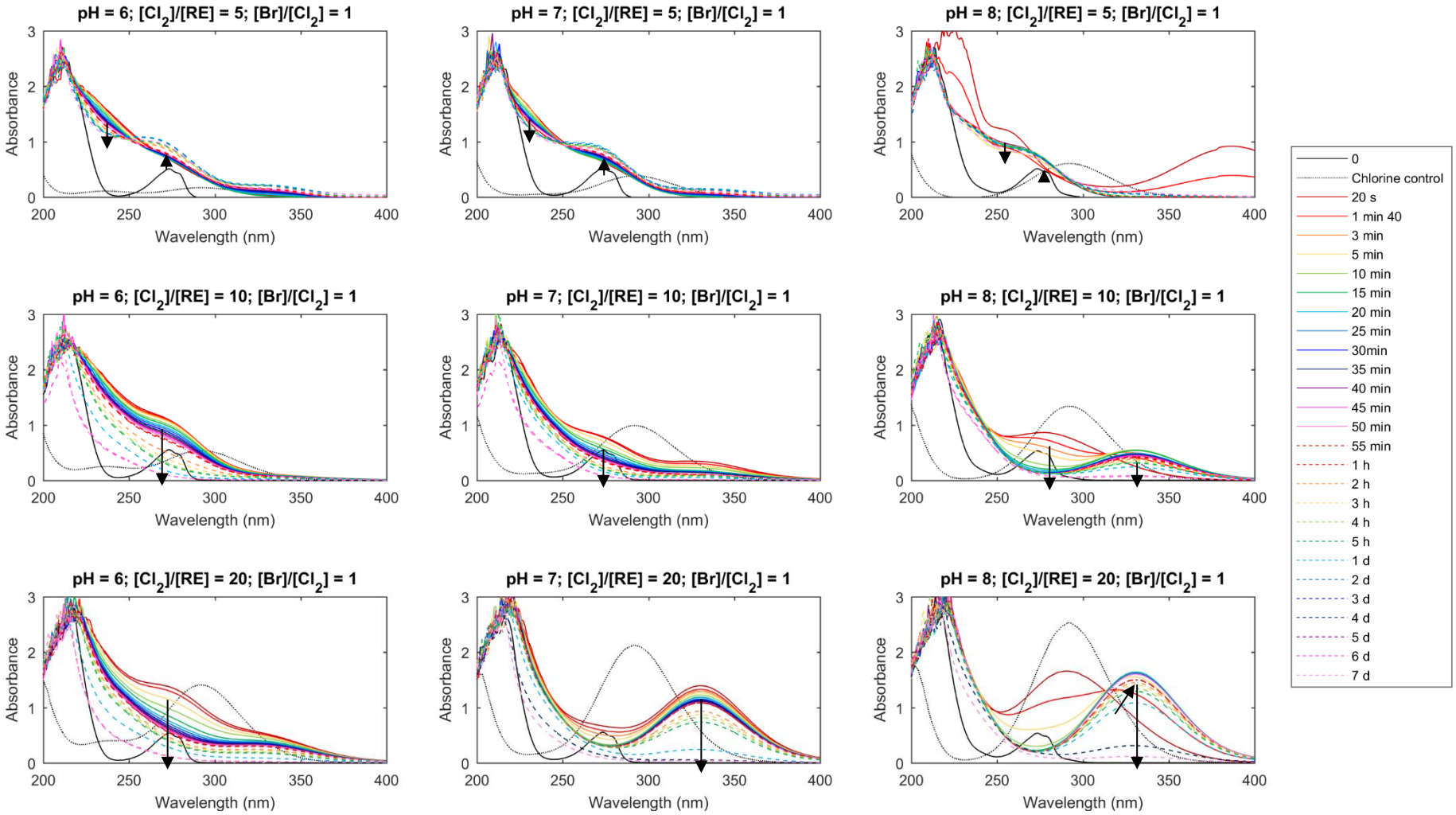


Figure ESI-10. UV spectra of chlorination of resorcinol (RE) (300 µmol/L) at different pH and chlorine doses with bromide

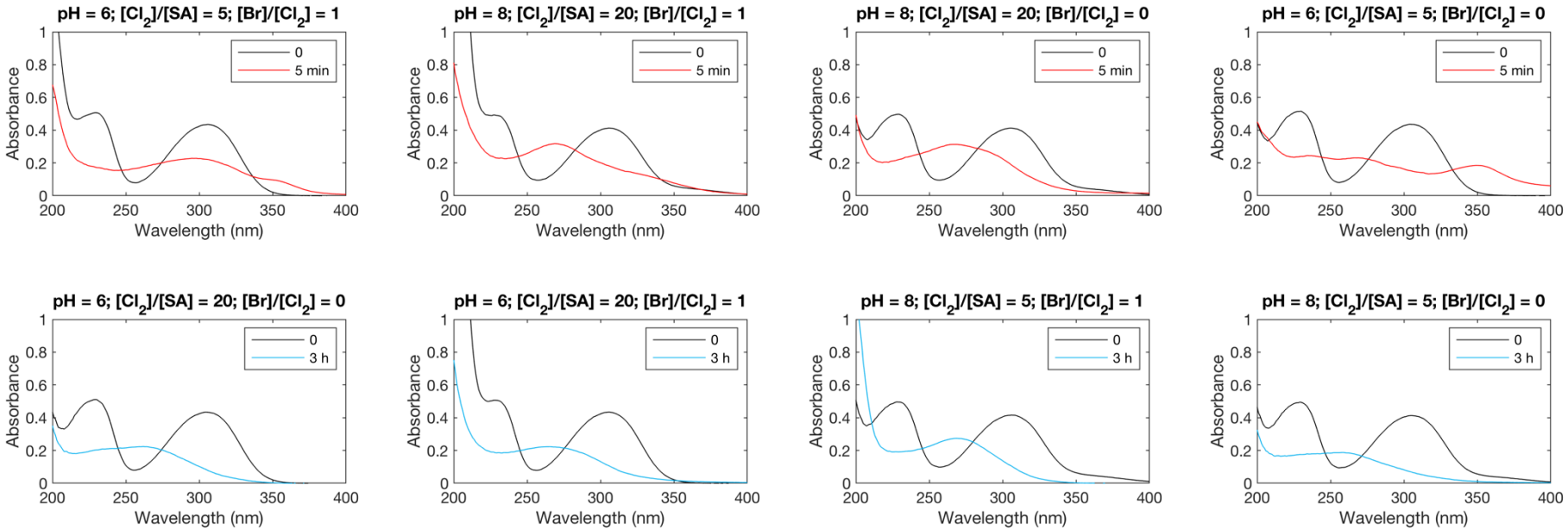


Figure ESI-11. UV spectra of chlorination of sinapic acid (SA) (25 µmol/L) at different pH and chlorine doses in the presence and absence of bromide

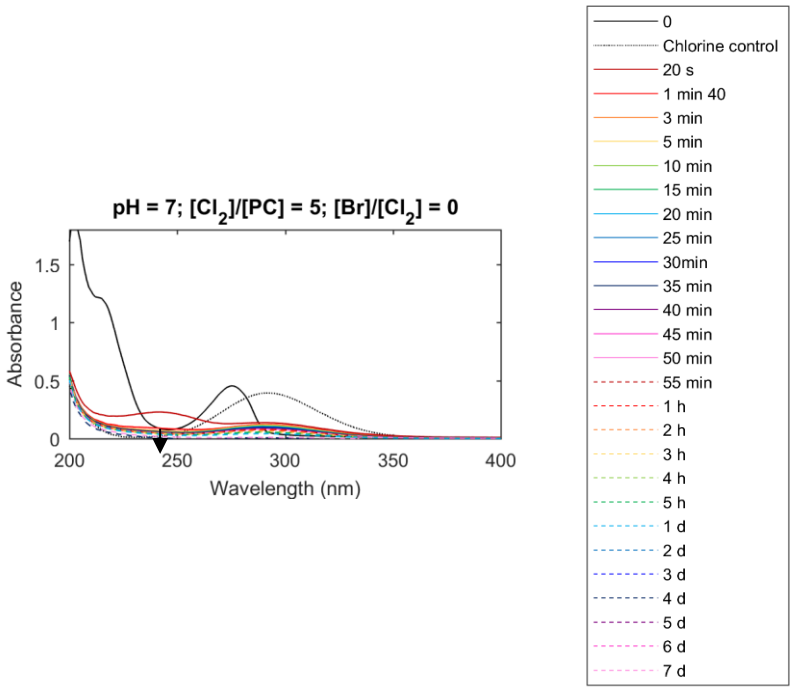


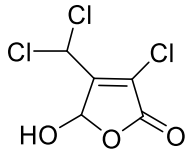
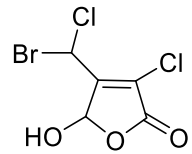
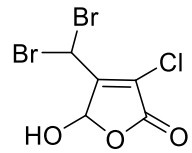
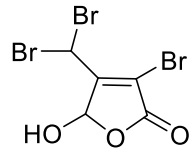
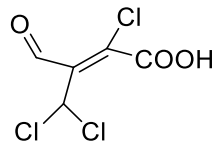
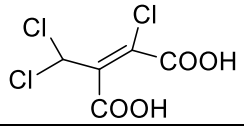
Figure ESI-12. UV spectra of chlorination of pyrocatechol (PC) (200 µmol/L) at different chlorine doses without bromide

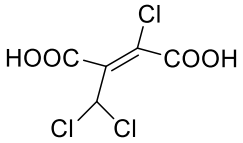
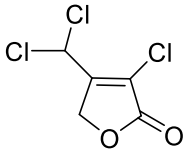
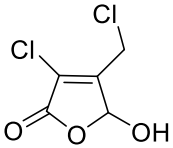
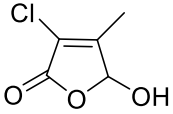
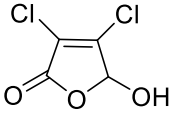
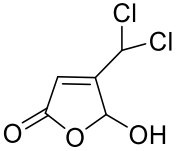
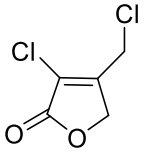
Table ESI-3. Chemical formulas elucidated for the additional DBPs present in the chlorinated samples forming stable DBPs

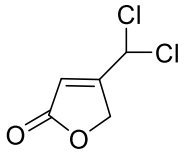
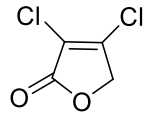
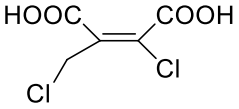
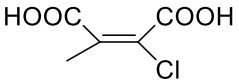
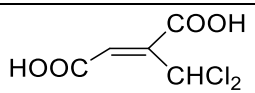
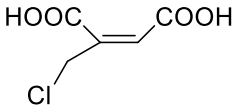
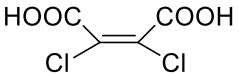
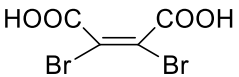
Precursor	Sample	DBP ID	Molecular weight (g/mol)	Chemical Formula	Relative mass error	DBPs proposed	Confidence level
PHE	S1	13	195.92495	$C_6H_3Cl_3O$	1.84	2,4,6-trichlorophenol	1
		14	159.95663	C_5HClO_4	1.70	5-chloropyran-2,3,6-trione	3
		15	211.92036	$C_6H_3Cl_3O_2$	1.59	2,4,6-trichloro-4-hydroxycyclohexa-2,5-dien-1-one	3
		16	125.99500	$C_5H_2O_4$	-2.58	-	3
		17	191.93852	$C_6H_2Cl_2O_3$	1.98	3,4-dichlorofuran-2,5-dicarbaldehyde	3
HBA	S2	18	327.77388	$C_6H_3OBr_3$	-0.23	2,4,6-tribromophenol	4
	S3	19	195.92469	$C_6H_3Cl_3O$	-2.26	2,4,6-trichlorophenol	1
		20	159.95602	C_5HClO_4	-2.64	5-chloropyran-2,3,6-trione	3
		21	225.89899	$C_6HCl_3O_3$	-1.34	3,4,6-trichloro-5-hydroxy-1,2-benzoquinone	3
		22	221.94866	$C_7H_4Cl_2O_4$	-1.71	2,5-dichloro-3,4-dihydroxybenzoic acid	3
HCA	S4	23	170.01372	$C_8H_7ClO_2$	1.60	1,2-dihydroxy-4-(2-chloroethenyl)benzene or 4-(2-chloroethenyl)-4-cyclohexene-1,2-dione	4
		24	170.01372	$C_8H_7ClO_2$	1.65		4
		25	203.97496	$C_8H_6Cl_2O_2$	2.18	3-chloro-1,2-dihydroxy-5-(2-chloroethenyl)benzene or 3-chloro-5-(2-chloroethenyl)-4-cyclohexene-1,2-dione	4
TFA	S5	26	127.94287	$C_2H_2Cl_2O_2$	-2.43	Dichloroacetic acid	3
		27	244.01385	$C_{10}H_9ClO_5$	-0.05	3-chloro-2,4-hydroxy-5-methoxycinnamic acid	4
	S6	28	138.03128	$C_7H_6O_3$	-2.75	2-carboxymethyl-2,4-cyclopentadien-1-one	4
BA	*	29	155.99780	$C_7H_5ClO_2$	-6.73	3-chlorobenzoic acid	3
SA	**	30	159.99240	$C_6H_5ClO_3$	-2.17	-	4

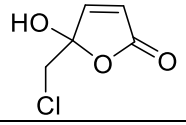
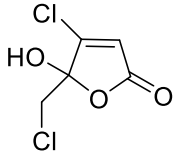
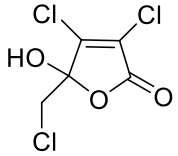
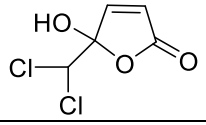
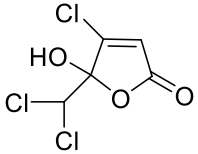
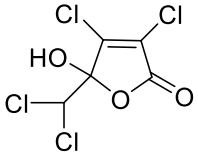
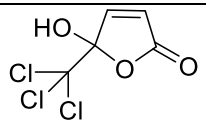
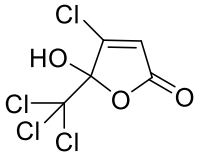
* Conditions of chlorination: [BA] = 10 mg/L; pH = 6; $[Cl_2]/[BA]$ = 20 mol/mol; $[Br]/[Cl_2]$ = 0 mol/mol
** Conditions of chlorination: [SA] = 10 mg/L; pH = 6; $[Cl_2]/[SA]$ = 5 mol/mol; $[Br]/[Cl_2]$ = 0 mol/mol

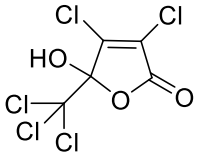
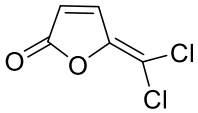
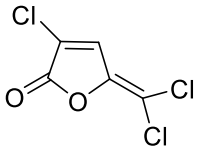
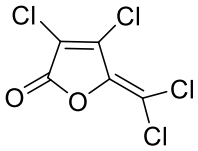
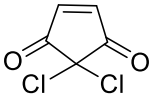
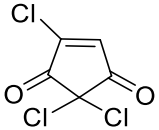
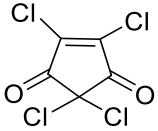
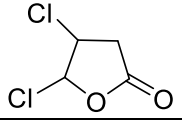
Table ESI-4. Literature furan-type DBPs[1–11]

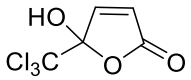
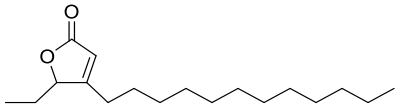
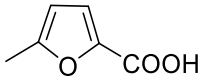
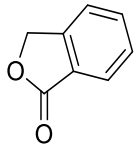
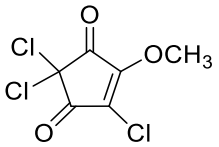
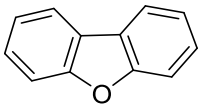
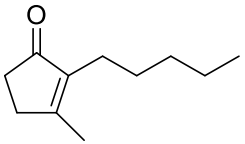
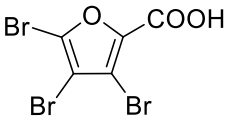
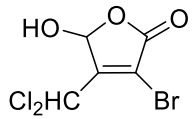
Name	Other names	Structure	SMILES*	Molecular formula, Monoisotopic mass (and m/z, if different to monoisotopic mass) (Da)*
MX (Mutagen X)	3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone		O=C1C(Cl)=C(C(Cl)Cl)C(O)O1	$C_5H_3Cl_3O_3$ 215.91478
3-chloro-4(bromochloromethyl)-5-hydroxy-2(5H)-furanone	BMX-1		OC(O1)C(C(Cl)Br)=C(Cl)C1=O	$C_5H_3BrCl_2O_3$ 259.86426
3-chloro-4-(dibromomethyl)-5-hydroxy-2(5H)furanone	BMX-2		OC(O1)C(C(Br)Br)=C(Cl)C1=O	$C_5H_3Br_2ClO_3$ 303.81375 (305.81170)
3-bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone	BMX-3		OC(O1)C(C(Br)Br)=C(Br)C1=O	$C_5H_3Br_3O_3$ 347.76323 (349.76119, 351.75914)
E-MX	(2E)-2,4,4-Trichloro-3-formyl-2-butenoic acid. E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid		Cl/C(C(O)=O)=C(C(Cl)Cl)\C=O	$C_5H_3Cl_3O_3$ 215.91478
ox-MX (z-isomer)	(Z)-2-Chloro-3-(dichloromethyl) butenedioic acid		ClC(Cl)/C(C(O)=O)=C(Cl)/C(O)=O	$C_5H_3Cl_3O_4$ 231.90969

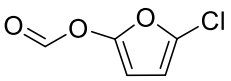
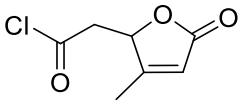
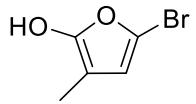
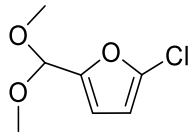
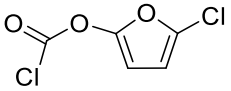
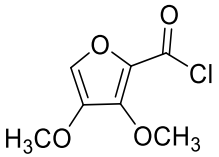
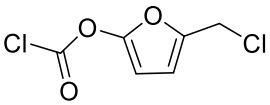
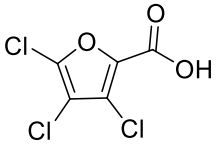
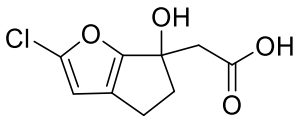
ox-EMX (e-isomer)	(E)-2-Chloro-3-(dichloromethyl)butenedioic acid. 2-Chloro-3-(dichloromethyl)-butenedioic acid		ClC(Cl)/C(C(O)=O)=C(Cl)\C(O)=O	$C_5H_3Cl_3O_4$ 231.90969
red-MX	3-Chloro-4-(dichloromethyl)-2(5H)-furanone. 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone		O=C1C(Cl)=C(C(Cl)Cl)CO1	$C_5H_3Cl_3O_2$ 199.91986
CMCF	3-Chloro-4-(chloromethyl)-5-hydroxy-2(5H)-furanone		OC1C(CCl)=C(Cl)C(O1)=O	$C_5H_4Cl_2O_3$ 181.95375
MCF	3-Chloro-5-hydroxy-4-methyl-2(5H)-furanone 3-Chloro-4-methyl-5-hydroxy-2(5H)-furanone		OC1C(C)=C(Cl)C(O1)=O	$C_5H_5ClO_3$ 147.99272
mucochloric acid	3,4-dichloro-5-hydroxy-2(5H)-furanone, MCA		OC1C(Cl)=C(Cl)C(O1)=O	$C_4H_2Cl_2O_3$ 167.93810
dCMF	4-(Dichloromethyl)-5-hydroxy-2(5H)-furanone. 4-(dichloromethyl)-5-hydroxy-2(5H)-furanone		OC1C(C(Cl)Cl)=CC(O1)=O	$C_5H_4Cl_2O_3$ 181.95375
red-CMCF	3-chloro-4-(chloromethyl)-2(5H)-furanone. 3-Chloro-4-(chloromethyl)-2(5H)-furanone		O=C1C(Cl)=C(CCl)CO1	$C_4H_4Cl_2O_2$ 165.95883

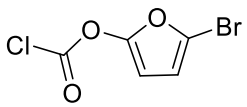
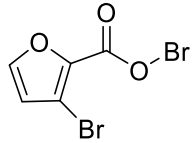
red-dCMF	4-(dichloromethyl)-2(5H)-furanone		O=C1C=C(C(Cl)Cl)CO1	$C_4H_4Cl_2O_2$ 165.95883
red-MCA	3,4-dichloro-2(5H)-furanone. MFCD02751908		ClC(CO1)=C(Cl)C1=O	$C_4H_2Cl_2O_2$ 151.94318
2-chloro-3-(chloromethyl)butenedioic acid	ox-CMCF. (2Z)-2-Chloro-3-(chloromethyl)-2-butenedioic acid	 Z isomer	Cl/C(C(O)=O)=C(C(O)=O)\CCl	$C_5H_4Cl_2O_4$ 197.94866
2-chloro-3-methylbutenedioic acid	ox-MCF. (2Z)-2-Chloro-3-methyl-2-butenedioic acid	 Z isomer shown	Cl/C(C(O)=O)=C(C(O)=O)\C	$C_5H_5ClO_4$ 163.98764
3-(dichloromethyl)butenedioic acid	ox-dCMF. (2E)-2-(Dichloromethyl)-2-butenedioic acid	 E isomer shown	ClC(/C(C(O)=O)=C\C(O)=O)Cl	$C_5H_4Cl_2O_4$ 197.94866
3-(chloromethyl)butenedioic acid	ox-mCMF	 Z isomer shown	ClC/C(C(O)=O)=C/C(O)=O	$C_5H_5ClO_4$ 163.98764
2,3-dichlorobutenedioic acid	ox-MCA	 Z isomer shown	Cl/C(C(O)=O)=C(Cl)/C(O)=O	$C_4H_2Cl_2O_4$ 183.93301
2,3-dibromobutenedioic acid	ox-MBA	 Z isomer shown	Br/C(C(O)=O)=C(Br)/C(O)=O	$C_4H_2Br_2O_4$ 273.83198 (273.82994)

Hydroxyfuranone 1a		O=C1C=CC(O)(CCl)O1	$C_5H_5ClO_3$ 147.99272
Hydroxyfuranone 1b		O=C1C=C(Cl)C(O)(CCl)O1	$C_5H_4Cl_2O_3$ 181.95375
Hydroxyfuranone 1c		O=C1C(Cl)=C(Cl)C(O)(CCl)O1	$C_5H_3Cl_3O_3$ 215.91478
Hydroxyfuranone 2a		O=C1C=CC(O)(C(Cl)Cl)O1	$C_5H_4Cl_2O_3$ 181.95375
Hydroxyfuranone 2b		O=C1C=C(Cl)C(O)(C(Cl)Cl)O1	$C_5H_3Cl_3O_3$ 215.91478
Hydroxyfuranone 2c		O=C1C(Cl)=C(Cl)C(O)(C(Cl)Cl)O1	$C_5H_2Cl_4O_3$ 249.87580 (251.87285)
Hydroxyfuranone 3a		O=C1C=CC(O)(C(Cl)(Cl)Cl)O1	$C_5H_3Cl_3O_3$ 215.91478
Hydroxyfuranone 3b		O=C1C=C(Cl)C(O)(C(Cl)(Cl)Cl)O1	$C_5H_2Cl_4O_3$ 249.87580 (251.87285)

Hydroxyfuranone 3c			O=C1C(Cl)=C(Cl)C(O)(C(Cl)(Cl)Cl)O1	$C_5HCl_5O_3$ 283.83683 (285.83388, 287.83093)
5-Dichloromethylene-2-furanone	5-(Dichloromethylene)-2(5H)-furanone. EL1		O=C(O/1)C=CC1=C(Cl)/Cl	$C_5H_2Cl_2O_2$ 163.94318
3-Chloro-5-dichloromethylene-2-furanone	3-Chloro-5-(dichloromethylene)-2(5H)-furanone. EL2		O=C(O/1)C(Cl)=CC1=C(Cl)/Cl	$C_5HCl_3O_2$ 197.90421
3,4-Dichloro-5-dichloromethylene-2-furanone	3,4-Dichloro-5-(dichloromethylene)-2(5H)-furanone. EL3		O=C(O/1)C(Cl)=C(Cl)C1=C(Cl)/Cl	$C_5Cl_4O_2$ 231.86524 (233.86229)
2,2-Dichlorocyclopentene-1,3-dione	2,2-Dichloro-4-cyclopentene-1,3-dione. CP1		O=C(C1(Cl)Cl)C=CC1=O	$C_5H_2Cl_2O_2$ 163.94318
2,2,4-trichlorocyclopentene-1,3-dione	CP2		O=C(C1(Cl)Cl)C(Cl)=CC1=O	$C_5HCl_3O_2$ 197.90421
2,2,4,5-Tetrachlorocyclopentene-1,3-dione	CP3		O=C(C1(Cl)Cl)C(Cl)=C(Cl)C1=O	$C_5Cl_4O_2$ 231.86524 (233.86229)
dihydro-4,5-dichloro-2(3H)furanone	4,5-Dichlorodihydro-2(3H)-furanone		ClC(O1)C(Cl)CC1=O	$C_4H_4Cl_2O_2$ 153.95883

5-hydroxy-5-trichloromethyl-2-furanone	5-Hydroxy-5-trichloromethyl-2-furanone		O=C1C=CC(O)(C(Cl)(Cl)Cl)O1	$C_5H_3Cl_3O_3$ 215.91478
4-dodecyl-5-ethyl-2(5H)-furanone	4-Dodecyl-5-ethyl-2(5H)-furanone		O=C1C=C(CCCCCCCCCCCC)C(CC)O1	$C_{18}H_{32}O_2$ 280.24023
5-methyl-2-furancarboxylic acid	5-Methyl-2-furoic acid		CC1=CC=C(C(O)=O)O1	$C_6H_6O_3$ 126.03169
3H-2-benzofuran-1-one	4195. 1(3H)-Isobenzofuranone		O=C1OCC2=C1C=CC=C2	$C_8H_60_2$ 134.03678
2,2,4-trichloro-5-methoxycyclopent-4-en-1,3-dione	TCMCD		O=C1C(OC)=C(Cl)C(C1(Cl)Cl)=O	$C_6H_3Cl_3O_3$ 227.91478
Dibenzofuran			C12=C(C=CC=C2)OC3=C1C=CC=C3	$C_{12}H_80$ 168.05751
3-methyl-2-pentylcyclopent-2-en-1-one	3-Methyl-2-pentyl-2-cyclopenten-1-one. Dihydrojasmone		O=C1C(CCCCC)=C(C)CC1	$C_{11}H_{18}0$ 166.13577
2-carboxy-3,4,5-tribromofuran	3,4,5-tribromo-2-furoic acid		BrC1=C(C(O)=O)OC(Br)=C1Br	$C_5HBr_3O_3$ 345.74758 (347.74554)
bromo-4-(dichloro-methyl)-5-hydroxy-2(5H)-furanone			O=C1C(Br)=C(C(Cl)Cl)C(O)O1	$C_5H_3Cl_2BrO_3$ 259.86426

5-chlorofuran-2-yl formate		ClC1=CC=C(OC=O)O1	$C_5H_3ClO_3$ 145.97707
2-(3-methyl-5-oxo-2H-furan-2-yl)acetyl chloride		O=C1C=C(C)C(CC(Cl)=O)O1	$C_7H_7ClO_3$ 174.00837
5-bromo-3-methyl-furan-2-ol		BrC1=CC(C)=C(O)O1	$C_5H_5BrO_2$ 175.94729
2-chloro-5-(dimethoxymethyl)furan		ClC1=CC=C(C(OC)OC)O1	$C_7H_9ClO_3$ 176.02402
5-chlorofuran-2-yl carbonochloridate		ClC1=CC=C(OC(Cl)=O)O1	$C_5H_2Cl_2O_3$ 179.93810
3,4-dimethoxyfuran-2-carbonyl		ClC(C1=C(OC)C(OC)=CO1)=O	$C_7H_7ClO_4$ 190.00329
[5-(chloromethyl)-2-furyl] carbonochloridate		ClCC1=CC=C(OC(Cl)=O)O1	$C_6H_4Cl_2O_3$ 193.95375
3,4,5-trichlorofuran-2-carboxylic acid		ClC1=C(C(O)=O)OC(Cl)=C1Cl	$C_5HCl_3O_3$ 213.89913
2-(2-chloro-6-hydroxy-4,5-dihydrocyclopenta[b]furan-6-yl)acetic acid		ClC1=CC(CCC2(CC(O)=O)O)=C2O1	$C_9H_9ClO_4$ 216.01894

5-bromofuran-2-yl carbonochloridate		BrC1=CC=C(OC(Cl)=O)O1	$C_5H_2BrClO_3$ 223.88758
bromo-3-bromofuran-2-carboxylate		BrC1=C(C(OBr)=O)OC=C1	$C_5H_2Br_2O_3$ 267.83707 (269.83502)

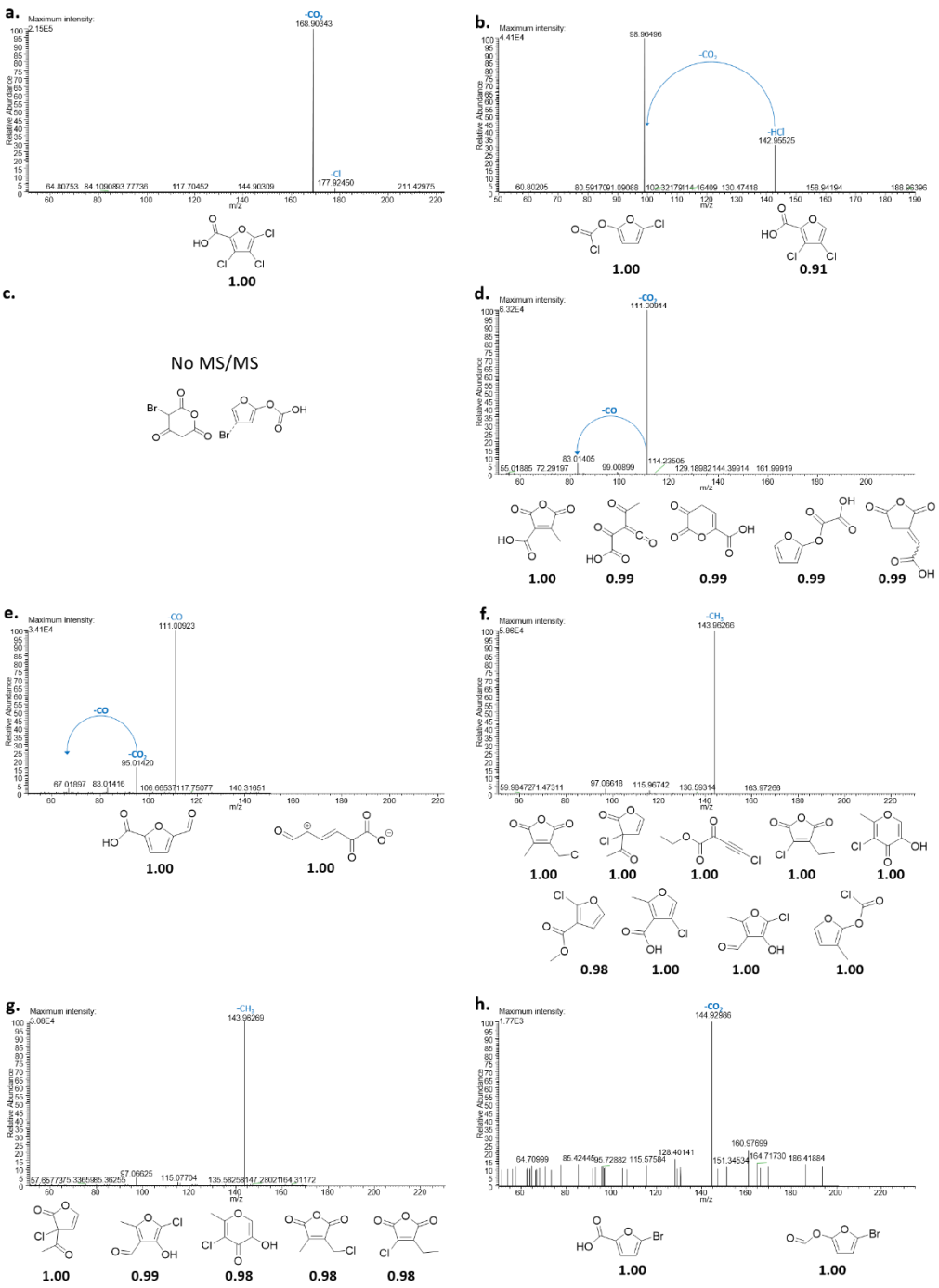


Figure ESI-13. MS/MS spectra of disinfection byproducts from phenolic precursors.
a. DBP 01 ($C_5HCl_3O_3$; byproduct of phenol)
b. DBP 02 ($C_5H_2Cl_2O_3$; byproduct of phenol)
c. DBP 04 ($C_5H_3BrO_4$; byproduct of 4-hydroxybenzoic acid)
d. DBP 09 ($C_6H_4O_5$; byproduct of 4-hydroxycinnamic acid)
e. DBP 10 ($C_6H_4O_4$; byproduct of 4-hydroxycinnamic acid)
f. DBP 11 ($C_6H_5ClO_3$; byproduct of trans-ferulic acid)
g. DBP 12 ($C_6H_5ClO_3$; byproduct of trans-ferulic acid)
h. DBP 13 ($C_5H_3BrO_3$; byproduct of trans-ferulic acid)
The fragments lost are labelled in blue.
The candidate isomers (for the sake of clarity, only one of the positional isomers is illustrated) that obtained the best scores in Metfrag are illustrated, with their normalized Metfrag scores.

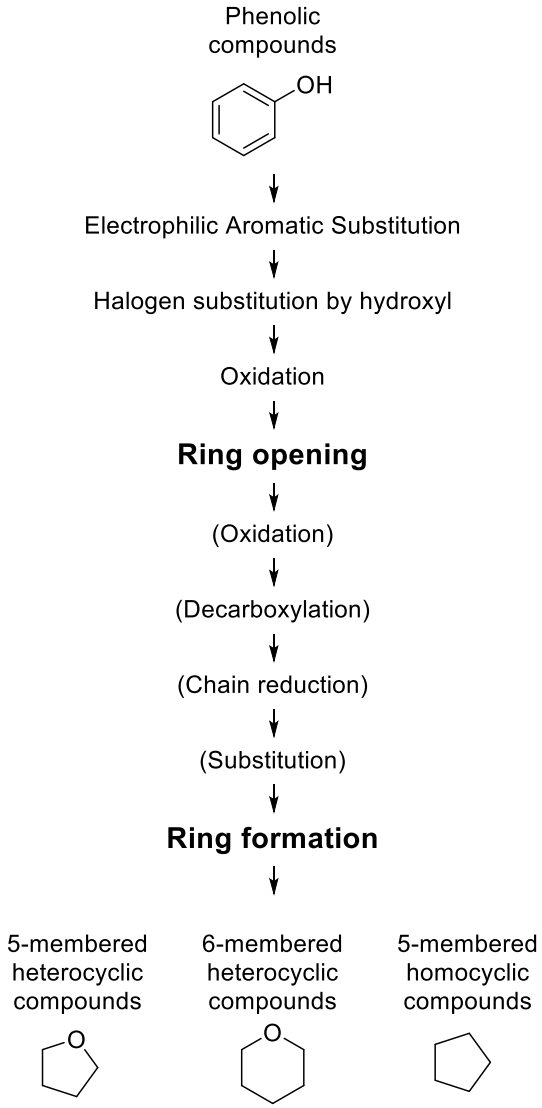


Figure ESI-14. Proposed general pathway for formation of furan-like DBPs from phenolic compounds

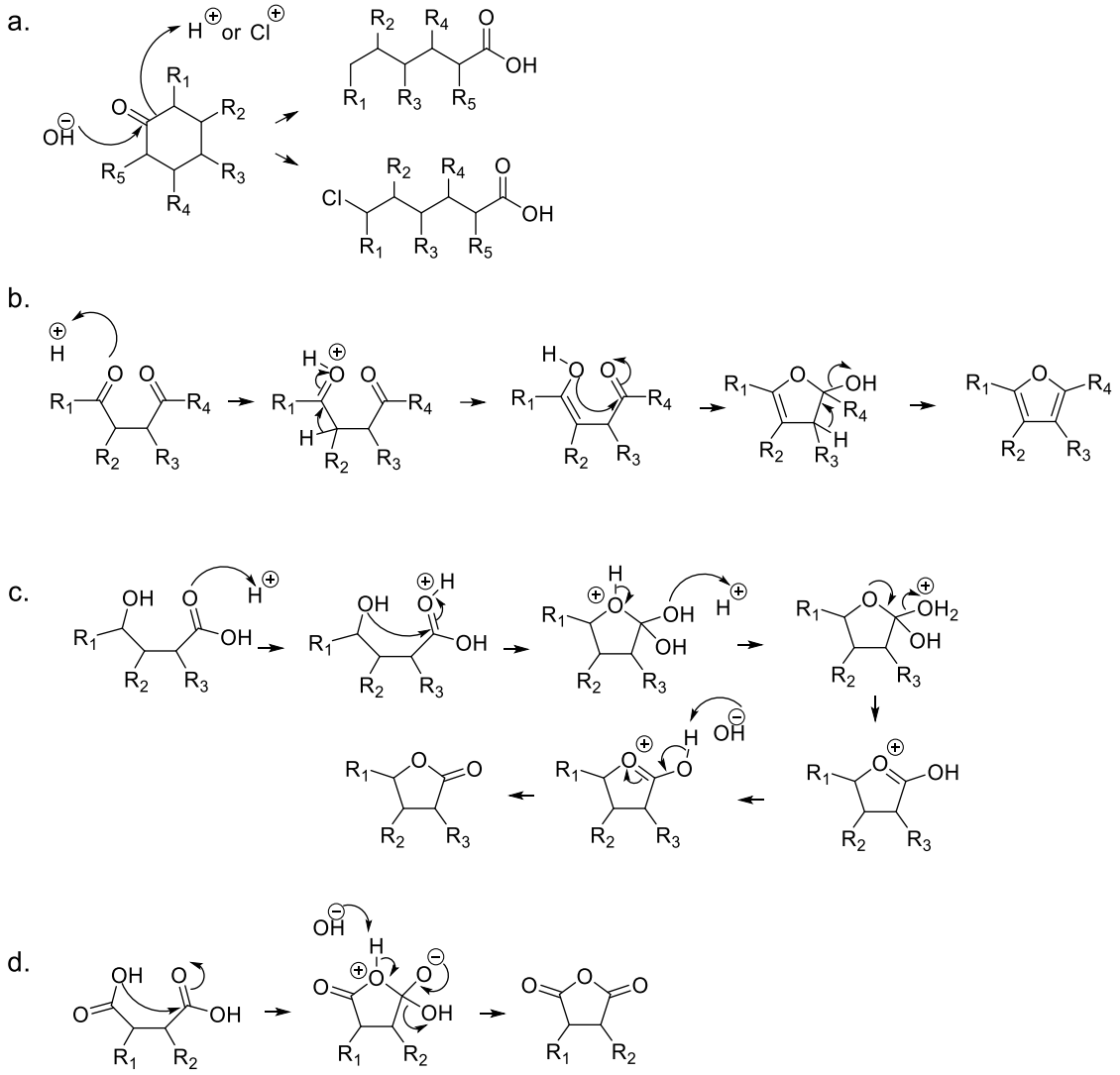


Figure ESI-15. Mechanisms proposed for the ring opening and ring formation in the pathway of formation of furan-like comounds from phenolic compounds

a. Mechanism for ring opening (adapted from Bull et al. (2006)[12])

b. Mechanism for ring formation (1): Paal-Knorr synthesis of furans (adapted from Amarnath and Amamath (1995)[13])

c. Mechanism for ring formation (2): Intramolecular nucleophilic addition (adapted from Clayden et al. (2012)[14])

d. Mechanism for ring formation (3): Intramolecular nucleophilic addition (proposed mechanism)

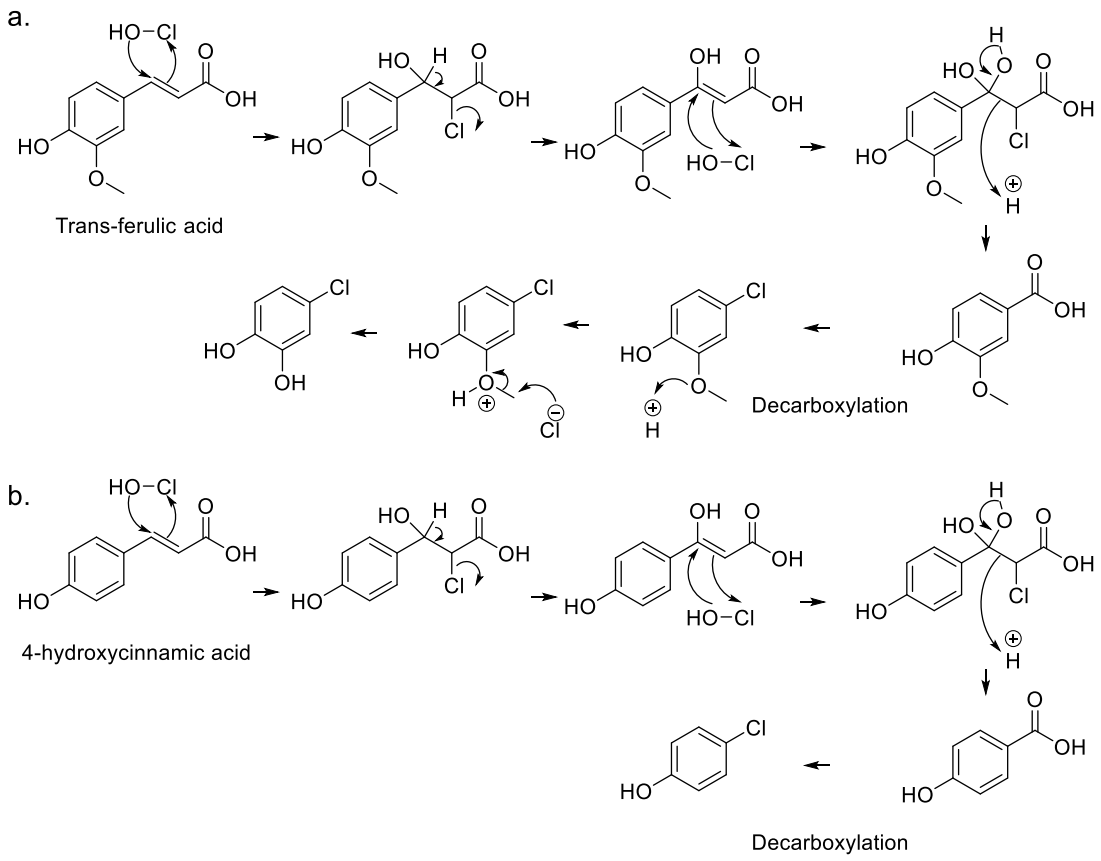


Figure ESI-16. Proposed pathway for the formation of the intermediates 4-chloro-1,2-benzenediol (a.) and 4-chlorophenol (b.) from trans-ferulic acid and 4-hydroxycinnamic acid respectively

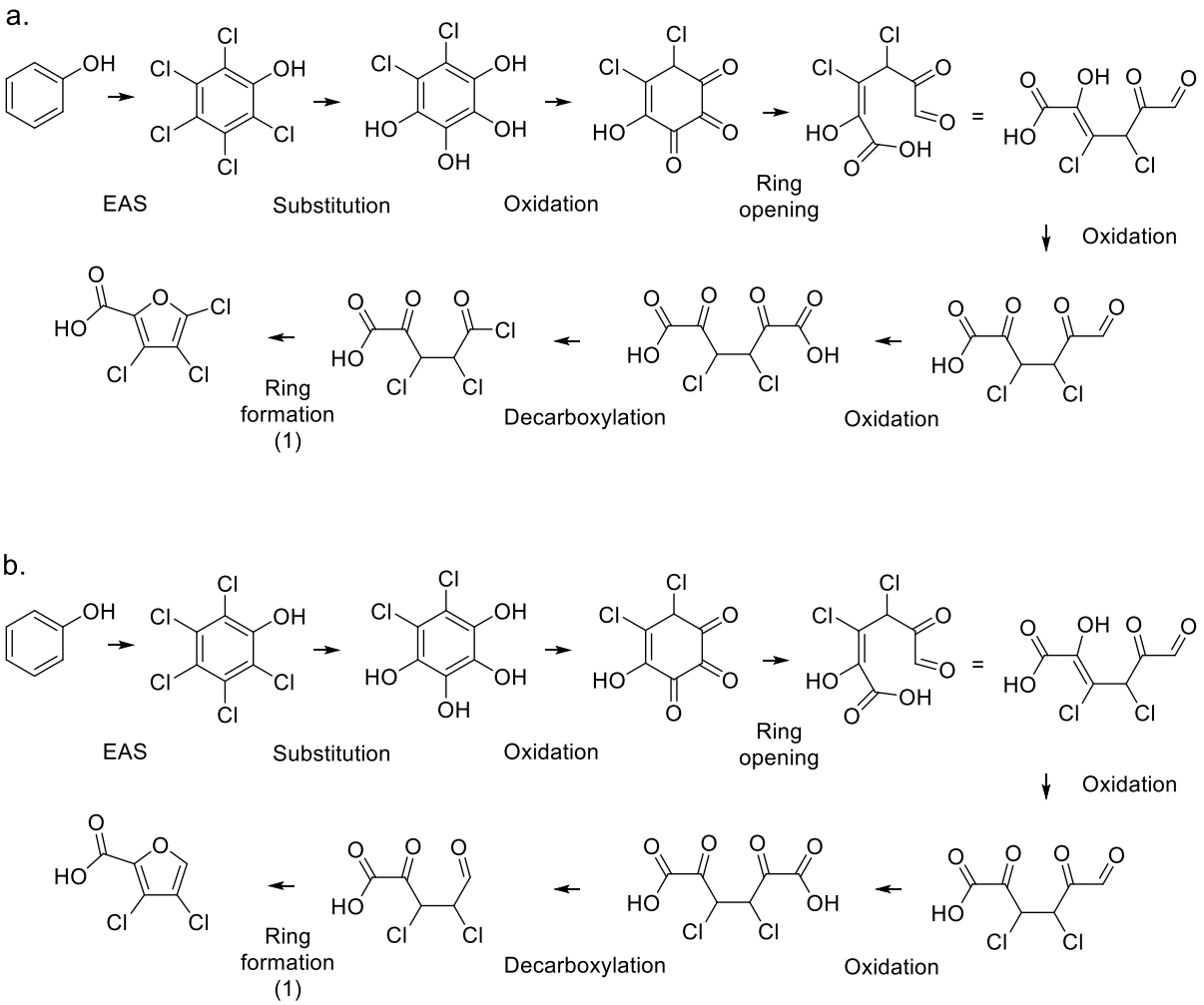


Figure ESI-17. Proposed pathways for the formation of the candidate isomers for DBPs 01 (a.) and 02 (b.) from phenol

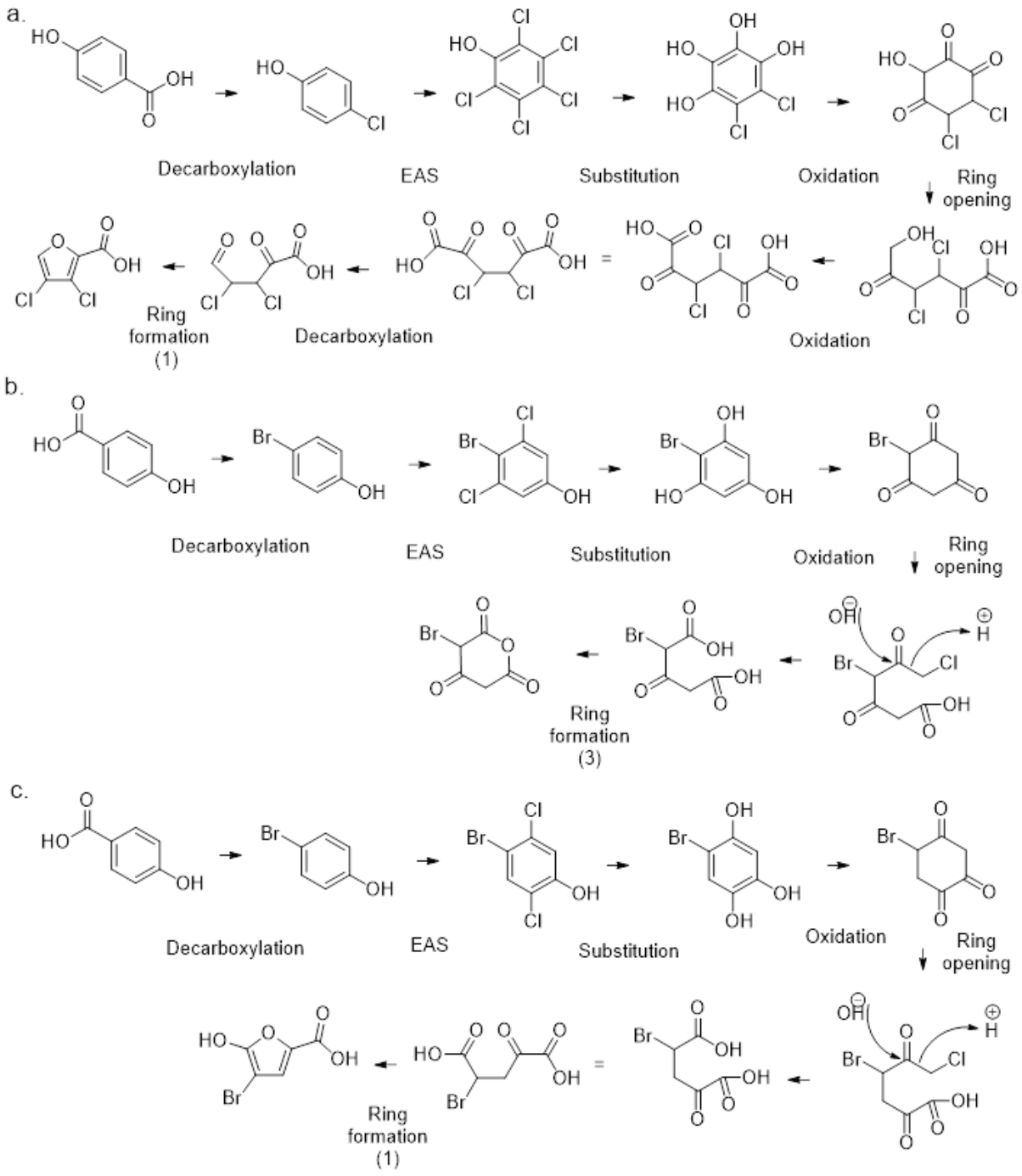


Figure ESI-18. Proposed pathways for the formation of the candidate isomers for DBPs 06 (a.) and 04 (b. and c.) from 4-hydroxybenzoic acid

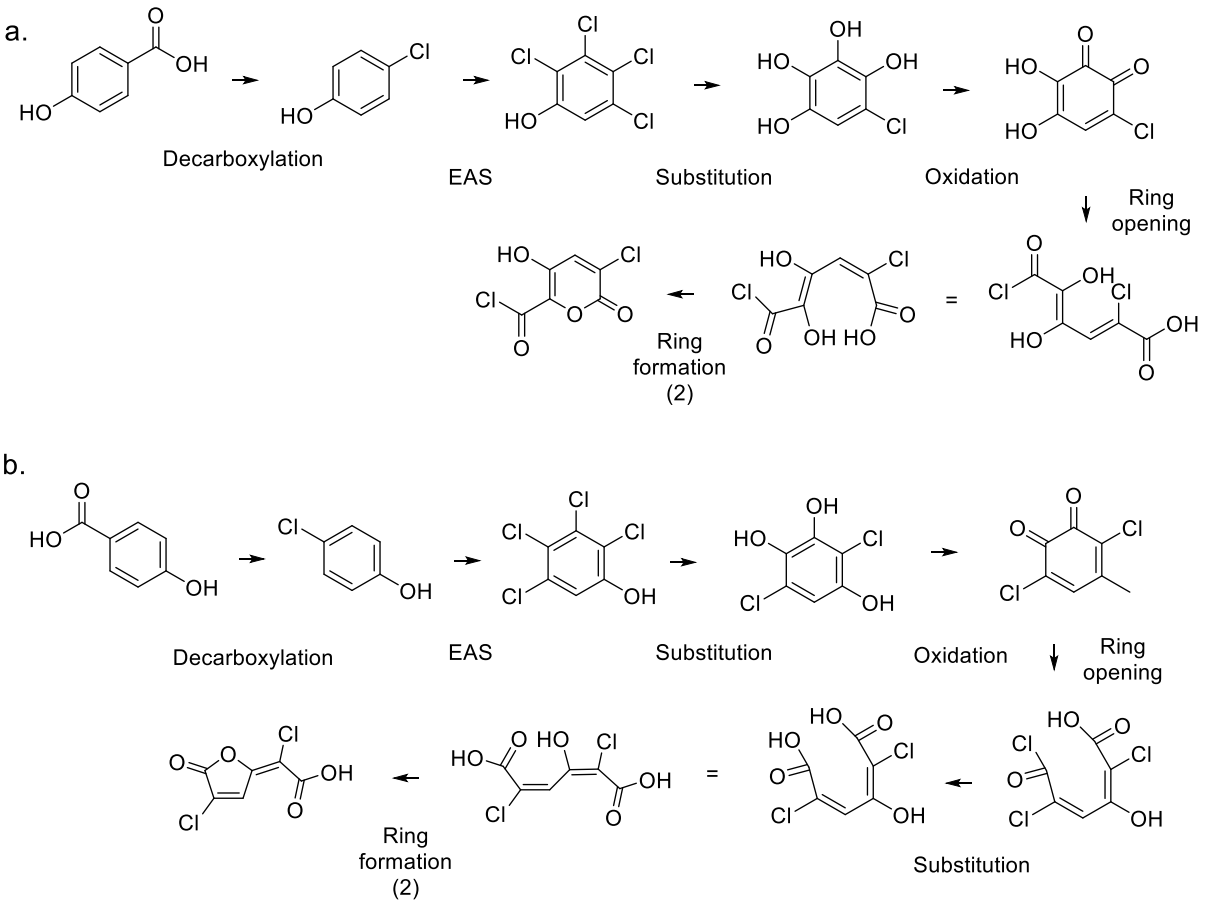


Figure ESI-19. Proposed pathways for the formation of the candidate isomers for DBP 05 (a. and b.) from 4-hydroxybenzoic acid

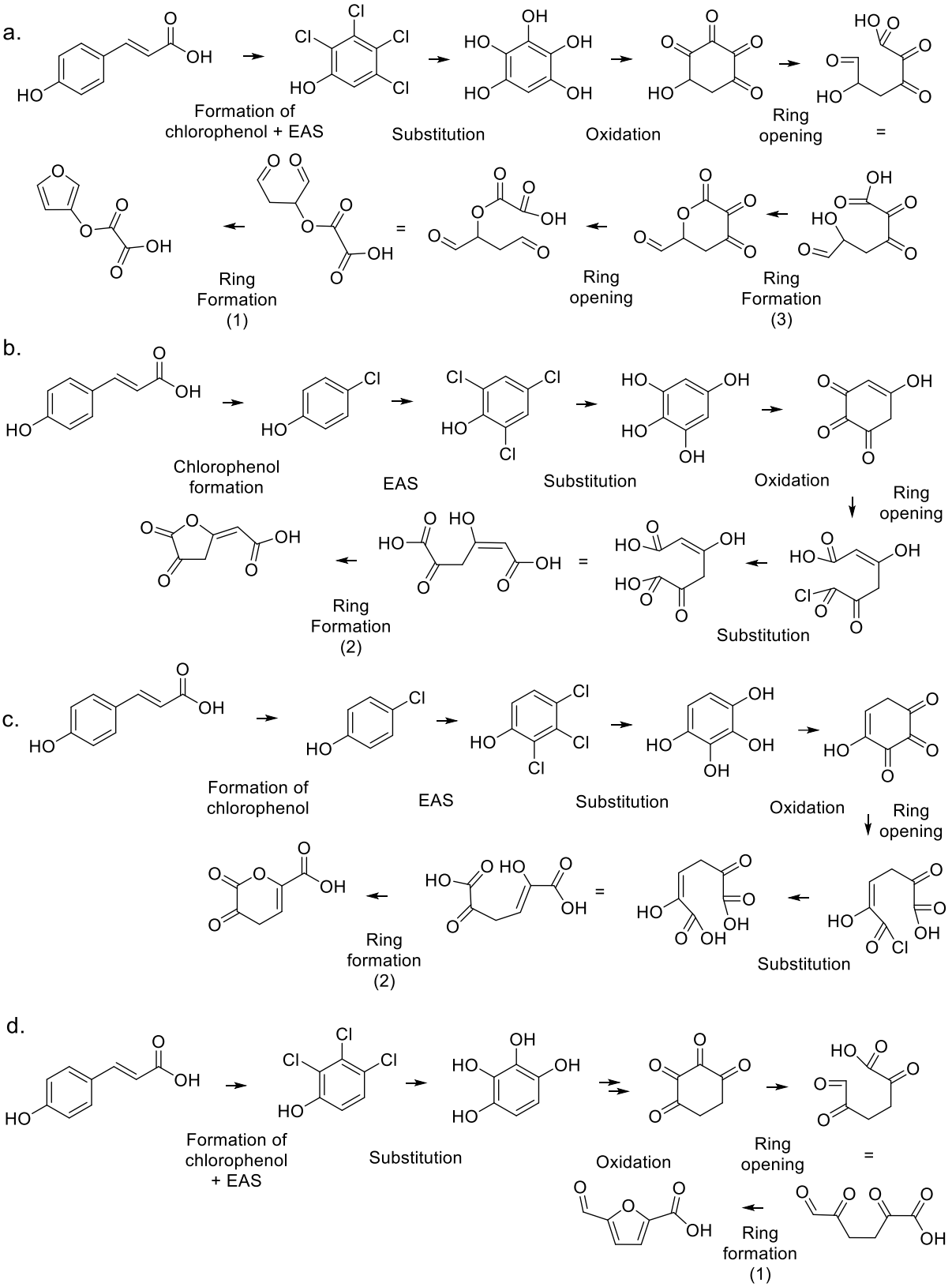


Figure ESI-20. Proposed pathways for the formation of the candidate isomers for DBPs 09 (a., b. and c.) and 10 (d.) from 4-hydroxycinnamic acid

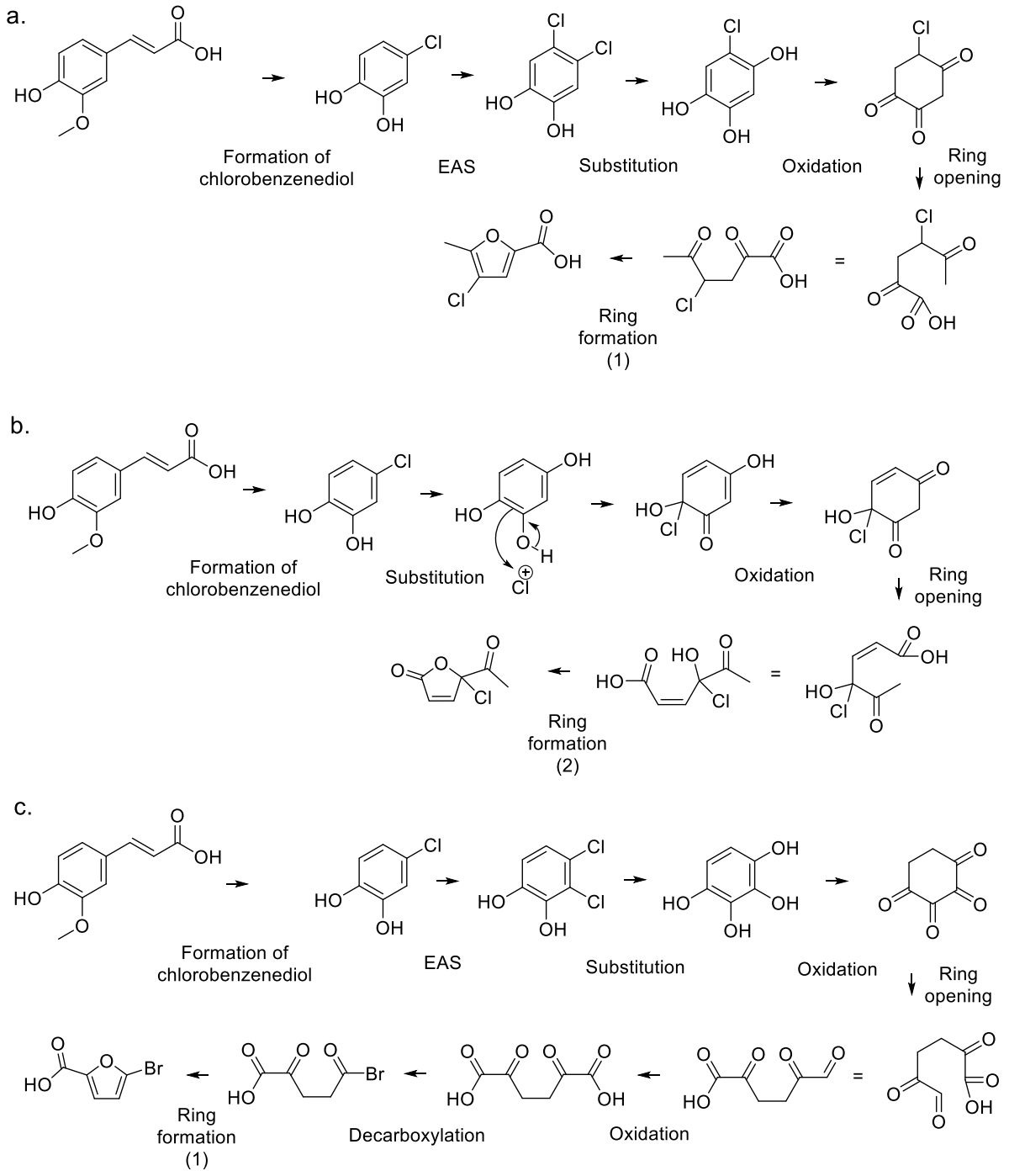
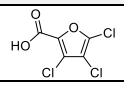
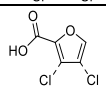
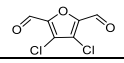
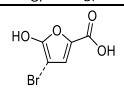
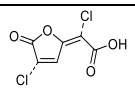
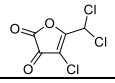
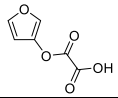
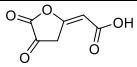
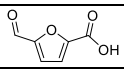
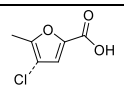
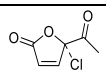
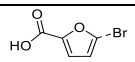


Figure ESI-21. Proposed pathways for the formation of the candidate isomers for DBPs 11 (a.), 12 (b.) and 13 (c.) from trans-ferulic acid

Table ESI-5. Name of furan-like DBPs identified and their IDs in compound databases

DBP ID	Proposed structure	Name	Pubchem ID	Chemspider ID
01 = 07		trichlorofuran-2-carboxylic acid	23424259	-
02 = 06		3,4-dichlorofuran-2-carboxylic acid	234857	204857
		3,5-dichlorofuran-2-carboxylic acid	23423217	-
		4,5-dichlorofuran-2-carboxylic acid	23423218	10467278
03		3,4-dichlorofuran-2,5-dicarbaldehyde	45118068	24218642
04		4-bromo-5-hydroxyfuran-2-carboxylic acid	-	72694984
		3-bromo-5-hydroxyfuran-2-carboxylic acid	-	-
05		(2Z)-2-chloro-2-(4-chloro-5-oxofuran-2-ylidene)acetic acid	9543235	7822208
		(2Z)-2-chloro-2-(3-chloro-5-oxofuran-2-ylidene)acetic acid	-	-
		(2Z)-2-(3,4-dichloro-5-oxofuran-2-ylidene)acetic acid	-	-
		2,5-dichloro-carboxymethylenebut-2-en-4-olide	11954007	10128302
		3,5-dichloro-carboxymethylenebut-2-en-4-olide	-	-
		2,3-dichloro-carboxymethylenebut-2-en-4-olide	-	-
08		4-chloro-5-(dichloromethyl)furan-2,3-dione	-	-
09		2-(furan-3-yloxy)-2-oxoacetic acid	-	-
		(2,3-Dioxooxolan-5-ylidene)acetic acid	-	-
10		5-formyl-2-furancarboxylic acid	2793719	2072643
11		4-chloro-5-methyl-2-furancarboxylic acid	81446002	37381549
		3-chloro-5-methyl-2-furancarboxylic acid	-	-
12		2-acetyl-2-chlorofuran-5-one	-	-
		2-acetyl-3-chlorofuran-5-one	-	-
		2-acetyl-4-chlorofuran-5-one	-	-
13		5-bromo-2-furancarboxylic acid	68511	61786
		3-bromo-2-furancarboxylic acid	605479	526313
		4-bromo-2-furancarboxylic acid	12239446	10468685

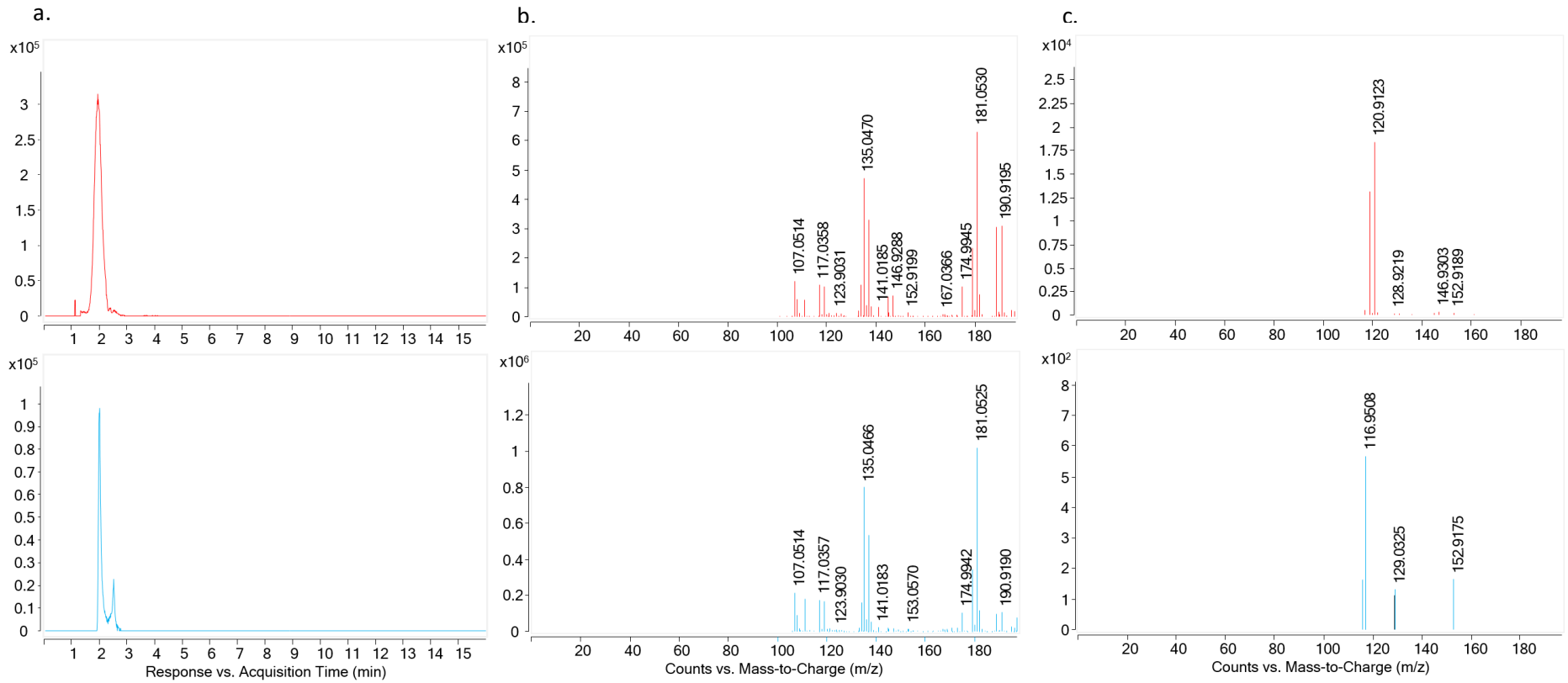


Figure ESI-22. Comparison of the chromatograms at m/z 188.9193 (a.), MS spectra (b.) and MS/MS spectra at retention times of 2.0 minutes (c.) obtained by LC-MS for DBP 13 in S6 ([TFA] = 50 mg/L; pH = 6; $[Cl_2]/[TFA]$ = 5 mol/mol; $[Br]/[Cl_2]$ = 1 mol/mol) (top) and 5-bromofuran-2-carboxylic acid at 10 mg/L (bottom)

Table ESI-6: Predicted mutagenicity and carcinogenic activity for the urinary bladder of literature furan-type DBPs, together with the same values for eight nitrosamines recorded as DBPs

Name	Other names	Predicted mutagen	Pa	Pi
MX (Mutagen X)	3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone	Positive	Pa < Pi	
3-chloro-4(bromochloromethyl)-5-hydroxy-2(5H)-furanone	BMX-1	Positive	Pa < Pi	
3-chloro-4-(dibromomethyl)-5-hydroxy-2(5H)furanone	BMX-2	Positive	Pa < Pi	
3-bromo-4-(dibromomethyl)-5-hydroxy-2(5H)-furanone	BMX-3	Positive	0.331	0.322
E-MX	(2E)-2,4,4-Trichloro-3-formyl-2-butenoic acid. E)-2-chloro-3-(dichloromethyl)-4-oxobutenoic acid	Positive	Pa < Pi	
ox-MX (z-isomer)	(Z)-2-Chloro-3-(dichloromethyl) butenedioic acid	Positive	Pa < Pi	
ox-EMX (e-isomer)	(E)-2-Chloro-3-(dichloromethyl)butenedioic acid. 2-Chloro-3-(dichloromethyl)-butenedioic acid	Positive	Pa < Pi	
red-MX	3-Chloro-4-(dichloromethyl)-2(5H)-furanone. 3-Chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone	Positive	Pa < Pi	
CMCF	3-Chloro-4-(chloromethyl)-5-hydroxy-2(5H)-furanone	Positive	Pa < Pi	
MCF	3-Chloro-5-hydroxy-4-methyl-2(5H)-furanone 3-Chloro-4-methyl-5-hydroxy-2(5H)-furanone	Positive	Pa < Pi	
mucochloric acid	3,4-dichloro-5-hydroxy-2(5H)-furanone, MCA	Positive	Pa < Pi	
dCMF	4-(Dichloromethyl)-5-hydroxy-2(5H)-furanone. 4-(dichloromethyl)-5-hydroxy-2(5H)-furanone	Positive	Pa < Pi	
red-CMCF	3-chloro-4-(chloromethyl)-2(5H)-furanone. 3-Chloro-4-(chloromethyl)-2(5H)-furanone	Positive	Pa < Pi	
red-dCMF	4-(dichloromethyl)-2(5H)-furanone	Positive	Pa < Pi	
red-MCA	3,4-dichloro-2(5H)-furanone.MFCD02751908	Positive	Pa < Pi	
2-chloro-3-(chloromethyl)butenedioic acid	ox-CMCF. (2Z)-2-Chloro-3-(chloromethyl)-2-butenedioic acid	Negative	Pa < Pi	
2-chloro-3-methylbutenedioic acid	ox-MCF. (2Z)-2-Chloro-3-methyl-2-butenedioic acid	Negative	Pa < Pi	

3-(dichloromethyl)butenedioic acid	ox-dCMF. (2E)-2-(Dichloromethyl)-2-butenedioic acid	Positive	Pa < Pi	
3-(chloromethyl)butenedioic acid	ox-mCMF	Positive	Pa < Pi	
2,3-dichlorobutenedioic acid	ox-MCA	Positive	Pa < Pi	
2,3-dibromobutenedioic acid	ox-MBA	Positive	**0.61**	0.08
Hydroxyfuranone 1a		Positive	Pa < Pi	
Hydroxyfuranone 1b		Positive	Pa < Pi	
Hydroxyfuranone 1c		Positive	Pa < Pi	
Hydroxyfuranone 2a		Positive	Pa < Pi	
Hydroxyfuranone 2b		Positive	Pa < Pi	
Hydroxyfuranone 2c		Positive	Pa < Pi	
Hydroxyfuranone 3a		Positive	Pa < Pi	
Hydroxyfuranone 3b		Positive	Pa < Pi	
Hydroxyfuranone 3c		Positive	Pa < Pi	
5-Dichloromethylene-2-furanone	5-(Dichloromethylene)-2(5H)-furanone. EL1	Positive	Pa < Pi	
3-Chloro-5-dichloromethylene-2-furanone	3-Chloro-5-(dichloromethylene)-2(5H)-furanone. EL2	Positive	Pa < Pi	
3,4-Dichloro-5-dichloromethylene-2-furanone	3,4-Dichloro-5-(dichloromethylene)-2(5H)-furanone. EL3	Positive	Pa < Pi	
2,2-Dichlorocyclopentene-1,3-dione	2,2-Dichloro-4-cyclopentene-1,3-dione. CP1	Positive	**0.46**	0.17
2,2,4-trichlorocyclopentene-1,3-dione	CP2	Positive	Pa < Pi	
2,2,4,5-Tetrachlorocyclopentene-1,3-dione	CP3	Negative	0.365	0.308
dihydro-4,5-dichloro-2(3H)furanone	4,5-Dichlorodihydro-2(3H)-furanone	Positive	Pa < Pi	
5-hydroxy-5-trichloromethyl-2-furanone	5-Hydroxy-5-trichloromethyl-2-furanone	Positive	Pa < Pi	
4-dodecyl-5-ethyl-2(5H)-furanone	4-Dodecyl-5-ethyl-2(5H)-furanone	Negative	Pa < Pi	
5-methyl-2-furancarboxylic acid	5-Methyl-2-furoic acid	Positive	Pa < Pi	
3H-2-benzofuran-1-one	4195. 1(3H)-Isobenzofuranone	Negative	0.340	0.306

2,2,4-trichloro-5-methoxycyclopent-4-en-1,3-dione	TCMCD	Positive	**0.50**	0.14
Dibenzofuran		Negative	**0.75**	0.04
3-methyl-2-pentylcyclopent-2-en-1-one	3-Methyl-2-pentyl-2-cyclopenten-1-one. Dihydrojasmone	Negative	Pa < Pi	
2-carboxy-3,4,5-tribromofuran			**0.63**	0.07
bromo-4-(dichloro-methyl)-5-hydroxy-2(5H)-furanone			Pa < Pi	
5-chlorofuran-2-yl formate			**0.45**	0.19
2-(3-methyl-5-oxo-2H-furan-2-yl)acetyl chloride			0.331	0.322
5-bromo-3-methyl-furan-2-ol			**0.57**	0.10
2-chloro-5-(dimethoxymethyl)furan			Pa < Pi	
5-chlorofuran-2-yl carbonochloridate			**0.45**	0.19
3,4-dimethoxyfuran-2-carbonyl			0.41	0.24
[5-(chloromethyl)-2-furyl] carbonochloridate			Pa < Pi	
3,4,5-trichlorofuran-2-carboxylic acid			**0.45**	0.19
2-(2-chloro-6-hydroxy-4,5-dihydrocyclopenta[b]furan-6-yl)acetic acid			Pa < Pi	
5-bromofuran-2-yl carbonochloridate			**0.47**	0.16
bromo-3-bromofuran-2-carboxylate			0.40	0.25
N-Nitrosomethylethylamine	NMEA	Positive	**0.55**	0.11
N-Nitrosodiethylamine	NDEA	Positive	**0.53**	0.12
N-Nitrosodi-n-propylamine	NDPA	Positive	**0.68**	0.06

N-Nitrosodi-n-butylamine	NDBA	Positive	**0.84**	0.03
N-Nitrosopyrollidine	NPYR	Positive	Pa < Pi	
N-Nitrosopiperidine	NPIP	Positive	Pa < Pi	
N-nitrosodiphenylamine		Negative	**0.90**	0.02

References

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