Appendix A. Supplementary data

Halogenation of Aromatic Hydrocarbons by Halide Anion Oxidation with Poly(heptazine imide) Photocatalyst

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Chemicals

Anisole (≥99%), benzyl alcohol (≥99%), N,N-dimethylaniline (99%), o-chloroanisole (98%), 1,3-dimethoxybenzene (≥98%) were purchased from Sigma Aldrich, HCl (37 wt. %) from Carl-Roth, HCl in 1,4-dioxane (4 mol·L^{-1}) from TCI, N-phenylacetanide (99%) from Across Organic, p-chloroanisole (99.5%) from Dr. Ehrenstorfer GmbH, acetonitrile (hypergrade for LC-MC) from Merch and were used without additional purification.

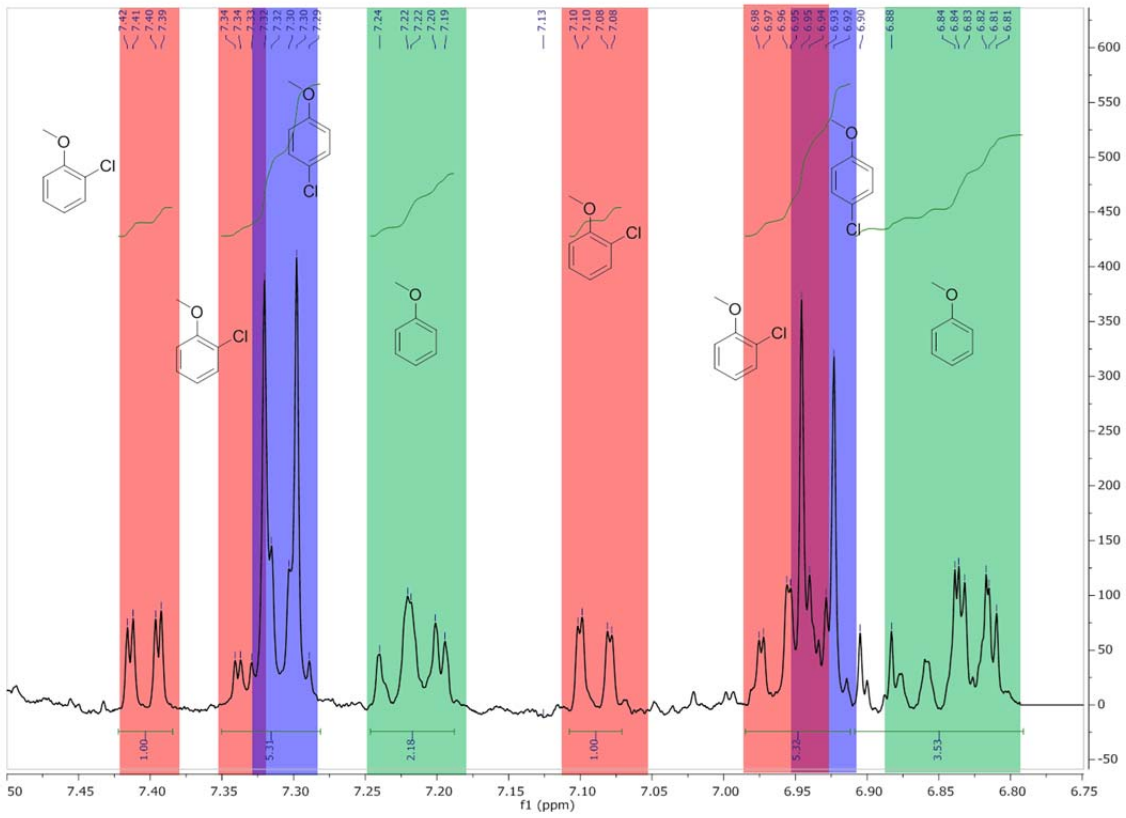

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Fig. A.1. An exemplary ^{1}H NMR spectrum of anisole chlorination reaction mixture. Signals of hydrogen atoms in anisole are highlighted with green color, *p*-chloroanisole – blue color and *o*-chloroanisole – red color.

Table A.1.
Anisole chlorination varying catalyst amount, temperature and time of irradiation using BnOH as a protons and electrons donor.[a]

Entry	K-PHI, mg	T, °C	Time, h	Conversion, %	Yield,[b] %
1	4	30	3	47	46 (1:0.39)
2	4	45	3	49	38 (1:0.08)
3	4	60	3	63	61 (1:0.4)
4	4	80	3	66	65 (1:0.37)
5	4	30	13	100	97 (1:1.45)
6	2	30	13	70	68 (1:0.29)
7	1	30	13	100	98 (1:2.7)
8	0,5	30	13	100	95 (1:0.81)

[a] reaction conditions: anisole 0.02 mmol; HCl (36 wt. %) 0.1 mL; acetic acid 0.2 mmol; benzyl alcohol 0.12 mmol; acetonitrile 0.5 mL; light source 465 nm.
[b] determined by ^{1}H NMR using N,N-dimethylaniline as an internal standard. Ratio between p- and o-chloroanisole is given in parentheses.

Table A.2.
Anisole chlorination using different alcohols as protons and electrons donors.[a]

Entry	Alcohol, mmol	Anisole conversion,[b] %	Yield,[c] %
1	**BnOH (0.12 mmol)**	**100**	**98 (1:0.31)**
2	iPrOH (0.12 mmol)	93	91 (1:0.41)
3	EtOH (0.12 mmol)	66	61 (1:0.35)
4	MeOH (0.12 mmol)	80	73 (1:0.38)

[a] reaction conditions: anisole 0.02 mmol; photocatalyst K-PHI 1 mg; HCl (36 wt. %) 0.1 mL; acetic acid 0.2 mmol; acetonitrile 0.5 mL; temperature 30°C; time of irradiation 13 h; light source 465 nm.
[b] determined by ^{1}H NMR using N,N-dimethylaniline as an internal standard.
[c] total yield of *o*- and *p*-chloroanisole. The ratio between *o*- and *p*-chloroanisole is given in parentheses. The ratio between isomers was determined by ^{1}H NMR using *N*,*N*-dimethylaniline as an internal standard. The molar mass of the products was determined by GC-MS.

Table A.3.
Variation of components in anisole chlorination reaction.[a]

Entry	K-PHI	BnOH	HOAc	Light	Electron scavenger	Yield,[b] %
1	**+**	**+**	**+**	**+**	**+ (O_2)**	**98 (1:0.31)**
2	+	+	-	+	+ (O_2)	0
3	-	+	+	+	+ (O_2)	0
4	+	+	+	+	— (N_2)	0
5	+	+	+	-	+ (O_2)	0

[a] reaction conditions: K-PHI 4 mg; anisole 0.02 mmol; HCl (36 wt. %) 0.1 mL; acetic acid 0.2 mmol; benzyl alcohol 0.12 mmol; acetonitrile 0.5 mL; light source 461 nm.
[b] determined by ^{1}H NMR using N,N-dimethylaniline as an internal standard.

Table A.4.
Anisole chlorination varying catalyst amount, temperature and time of irradiation using iPrOH as a protons and electrons donor[a]

Entry	K-PHI, mg	T, °C	Time, h	Conversion, %	Yield, %
1	4	30	3	52	33 (1:0.56)
2	4	60	3	0	0
3	4	80	3	2	6 (1:0.37)
4	4	30	13	58	52 (1:0.37)[b]
5	2	30	13	75	69 (1:0.35)
6	1	30	13	93	91 (1:0.41)
7	0,5	30	13	66	43 (1:0.32)

[a] reaction conditions: anisole 0.02 mmol; HCl (36 wt. %) 0.1 mL; acetic acid 0.2 mmol; *iso*-propyl alcohol 0.12 mmol; acetonitrile 0.5 mL; light source 465 nm.
[b] "o" stands for *o*-chloroanisole; "p" stands for *p*-chloroanisole.

Table A.5.
Anisole chlorination using different photocatalysts.[a]

Entry	Catalyst, mg	T, °C	Time, h	Conversion, %	Yield, %

1	RFT (1mg)	45	2,5	65	n.a.
2	g-CN (0,5 mg)	30	13	69	68 (1:0.21)

[a] reaction conditions: anisole 0.02 mmol; HCl (36 wt. %) 0.1 mL; acetic acid 0.2 mmol; benzyl alcohol 0.12 mmol; acetonitrile 0.5 mL; light source 465 nm.
[b] not analyzed.

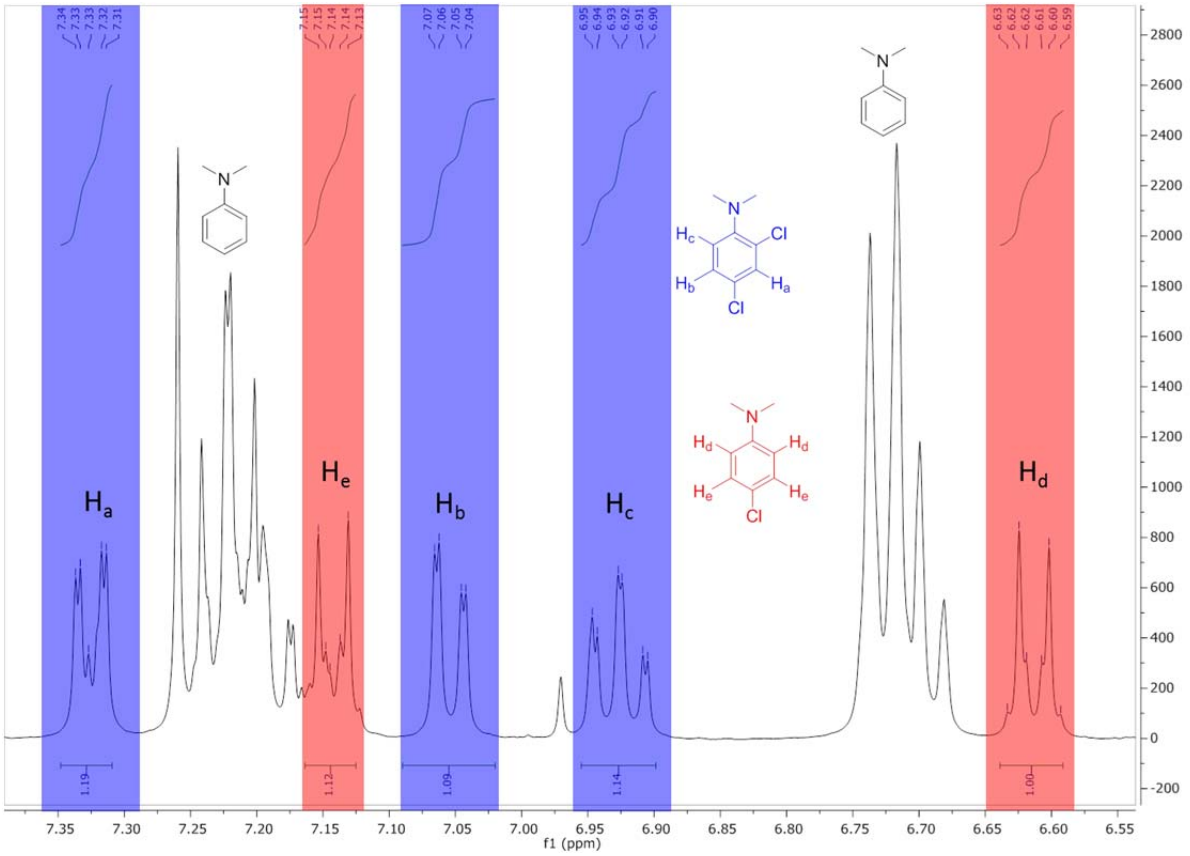

Fig. A.2. An exemplary ^{1}H NMR spectrum of N,N-dimethylaniline chlorination reaction mixture. Signals of hydrogen atoms in 4-chloro-N,N-dimethylaniline are highlighted with red color, 2,4-dimethyl-N,N-dimethylaniline – with blue color.

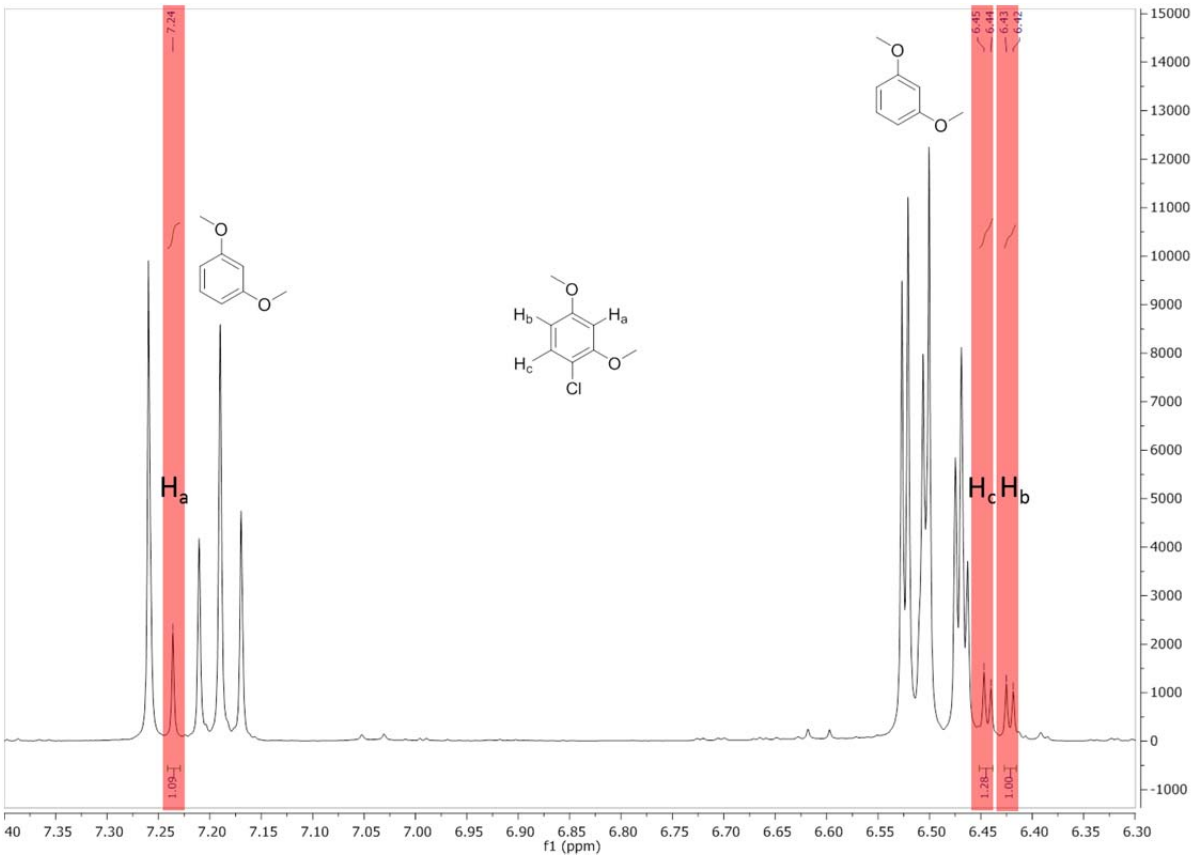

Fig. A.3. An exemplary ^{1}H NMR spectrum of 1,3-dimethoxybenzene chlorination reaction mixture. Signals of hydrogen atoms in 1-chloro-2,4-dimethoxybenzene are highlighted with red color.

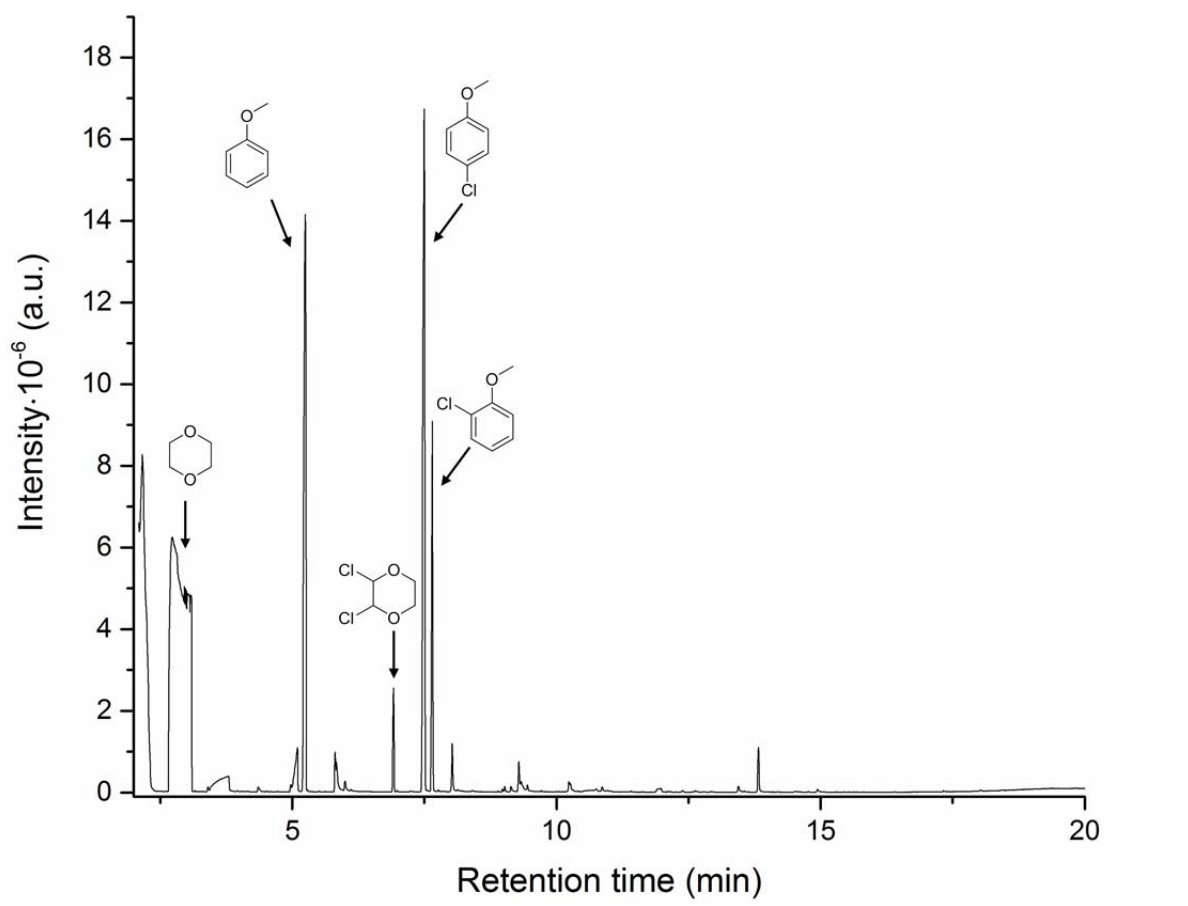

Fig. A.4. Chromatogram of anisole oxidative chlorination performed in 1,4-dioxane saturated with HCl.

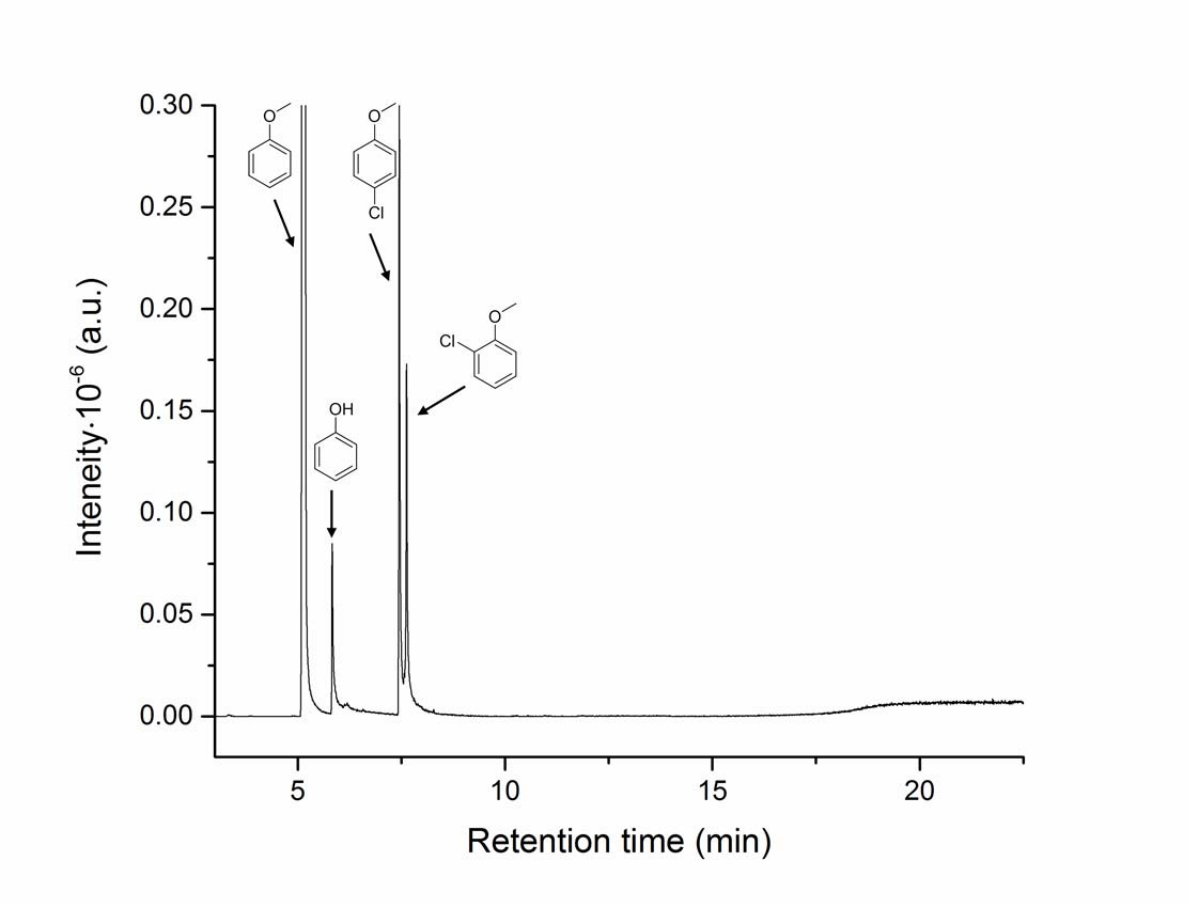

Fig. A.5. Chromatogram of anisole oxidative chlorination performed in NaCl water solution.

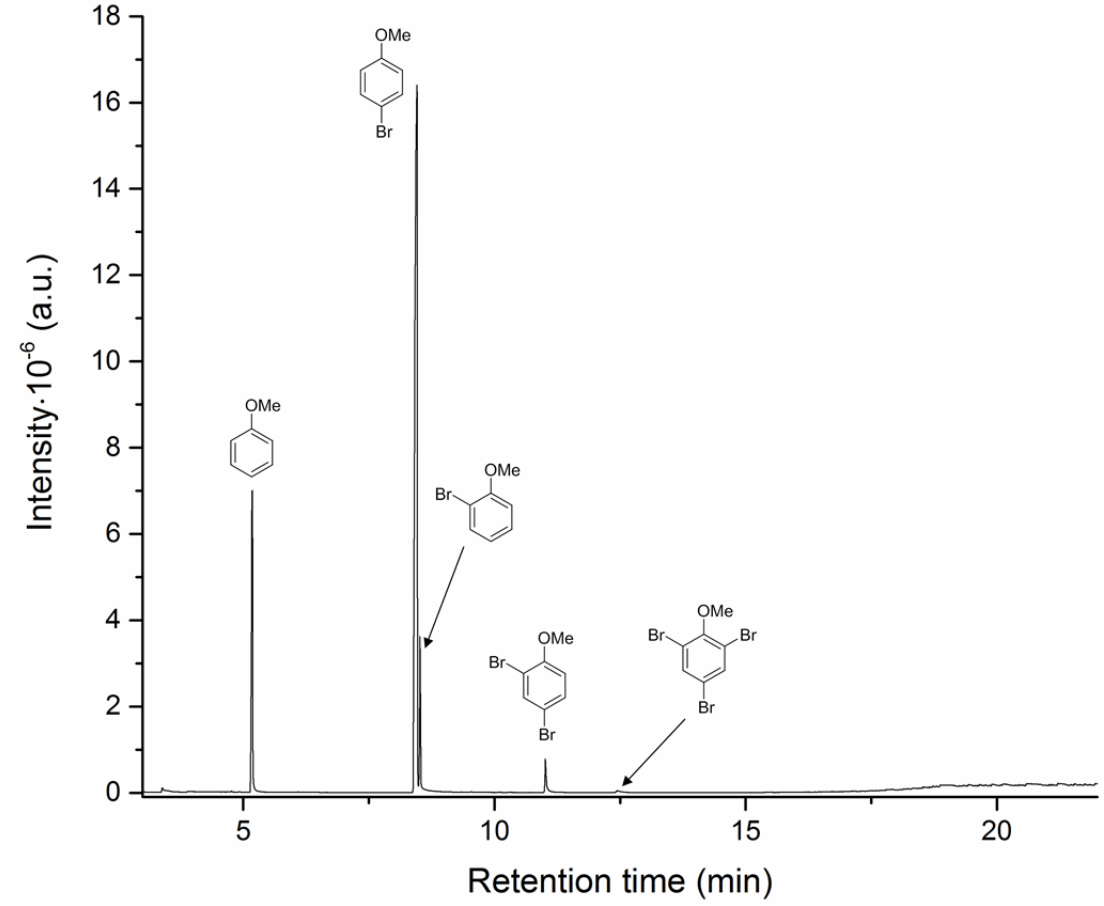

Fig. A.6. Chromatogram of anisole oxidative bromination (reaction mixture).

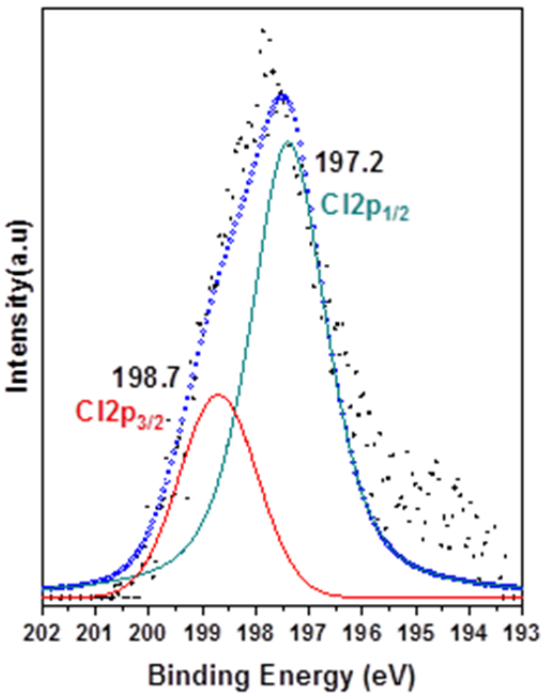

Fig. A.7. X-Ray Photoelectron spectroscopy (XPS) of Cl bonds in K-PHI after photochlorination reaction.