Electronic Supplementary Material (ESI) for ChemComm.

Initiating radical reactions with non-thermal plasma

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Supporting information

Raw experimental data (NMR spectra) are available at DOI: 10.15124/4f89c12f-b385-4175-b533-574858d3b3a8

Experimental

1. Materials. 4-chlorobenzoic acid (99%), 4-iodobenzoic acid (98%), 4-iodophenol (99%), 2-iodobenzoic acid (98%), sodium dibasic hypophosphite pentahydrate $Na_2HPO_3•5H_2O$ (≥98%), sodium acetate CH_3COONa (≥99%, anhydrous), sodium thiosulfate $Na_2S_2O_3$ (≥98%, anhydrous), sodium sulfate Na_2SO_4 (≥99%, anhydrous), 4-vinylanisole (97%), *N*-iodosuccinimide (95%), *tris*(trimethylsilyl)silane ($(TMS)_3SiH$) (97%), triphenylsilane Ph_3SiH (97%), hexadecyltrimethylammonium bromide (CTAB) (≥99%), 1-ethylpiperidine hypophosphite (EPHP) (95%), DMSO (≥99.9%), DMF (99.8%), mesitylene (98%), triethylene glycol (99%), 1,4-dioxane (99.8%, anhydrous) were obtained from Sigma. Sodium hydroxide NaOH (99.1%), sodium chloride NaCl (99.7%), PEG-300, diethyl ether (puriss.), hydrochloric acid HCl (37% in H_2O), magnesium sulfate $MgSO_4$ (dried) were obtained from Fluka. Allyl alcohol (99%) was from BDH Limited Poole England. 5,5-Dimethyl-1-pyrroline N-oxide (DMPO) (≥99%) was purchased from Dojindo Molecular Technologies, Inc. Dichloromethane, *n*-hexane, *n*-pentane and petroleum spirit (40-60°) were obtained from VWR Chemicals. NMR solvents (deuterated water D_2O (99.9 atom%) and deuterated chloroform $CDCl_3$ (99.96 atom%)) were purchased from Sigma. De-ionised water was used for the preparation of the solutions. Helium (A Grade, 99.996%) and N_2 (99.999%) were supplied by BOC UK.

1-Trifluoromethyl-1,2-benziodoxol-3(1H)-one (Togni-II reagent) containing 60% diatomaceous earth was purchased from Tokyo Chemical Industries Co., Ltd. Prior to experiments, the diatomaceous earth-supported Togni-II was stirred in dichloromethane, then filtered. The solvent was evaporated *in vacuo* to afford the pure Togni-II reagent, which was utilized in our experimental work. All other chemicals were used as received.

2. Equipment and methods. The parallel field kHz plasma was ignited in a quartz tube (4 mm ID and 6 mm OD, 100 mm length) surrounded by copper electrodes (10 mm width) separated by 20 mm. A PVM500 Plasma Resonant and Dielectric Barrier Corona Driver power supply (Information Unlimited) was used to sustain the plasma. A high voltage probe (Tektronix P6015A) and current probe (Ion Physics Corporation CM-100-L) were used with a Teledyne LeCroy WaveJet 354A oscilloscope to measure time resolved current and voltage. Voltage and frequency were kept constant throughout all experiments at 18.3 (peak-to-peak) and 24.9 kHz, respectively. The return current values were between *ca.* 7 and 9 mA. The voltage and current waveforms at some of the experimental conditions are shown elsewhere. The plasma was operated with a feed gas of helium (pure or with water admixtures) controlled by mass flow controllers (MFCs) (Brooks Instruments and Brooks Instruments 0254 microcomputer controller). All experiments were carried out with a total flow of feed gas of 2 L/min. The concentration of water vapour is quoted in percent of the saturation. The experimental setup was positioned inside a large Faraday cage with the mesh size of 22 mm. The experiments involving 10% feed gas humidity were performed by using split helium flow (*i.e.*, by mixing dry helium with water-saturated helium in a 9:1 proportion, with a total flow of 2 L/min). Water-saturated helium was made by bubbling dry helium through a water-filled Drechsel flask, as described elsewhere [Gorbanev *et al.*, Chem. Eur. J., 2016, 22, 3496].

The cross field nanosecond pulsed plasma was ignited in a glass chamber (1 mm x 10 mm x 90 mm; see Figure S1a). The chamber was covered with the copper electrodes embedded in PEEK (10 mm x 20 mm x 60 mm). A NPG-15/2000 Nanosecond Pulse Generator (Megaimpulse Ltd.) was used to sustain the plasma. Voltage and frequency were kept constant throughout all experiments at 40 kV (peak-to-peak) and 3.5 kHz kHz, respectively. The plasma was operated with a feed gas of helium or nitrogen (with 100% water vapour saturation) controlled by the MKS 247 MFC. All experiments were carried out with a total flow of feed gas of 10 L/min. The experimental setup was positioned inside a large metal box acting as a Faraday cage. A flow of *ca.* 10 L/min of air cooled down with ice/salt bath was used to avoid overheating of the inside of the box. Water-saturated He or N_2 was made by using a system consisting of a water-filled nebuliser (to saturate the gas with water vapour) and a consequently connected empty Drechsel flask (to collect the aerosol and pass only the water-saturated feed gas through). The re-circulation of the reaction mixture solution was performed using a Watson-Marlow 502S peristaltic pump connected to the feed gas tubing (Figure S1a).

3. Analysis. The NMR analysis (^1H, ^{13}C, ^{19}F) was performed on a JEOL ECS400 (400 MHz) spectrometer. A solution of anhydrous sodium acetate in D_2O was used as an external standard to demonstrate that the benzoic acids underwent no side reactions. The EPR spectra were recorded on a Bruker EMX Micro EPR spectrometer (frequency 9.83 GHz, power 3.17 mW, modulation frequency 100 kHz, modulation amplitude 1 G, time constant 40.96 ms, number of scans 5, sweep width 100 G). EPR spectra were analysed using the hyperfine values available from the NIH database [Spin Trap Database, National Institute of Environmental Health Sciences; available online at http://tools.niehs.nih.gov/stdb/]. The temperature of PEG solutions exposed to plasmas was measured using a TEMPATRON PID500 thermocouple.

4. Substrate synthesis.

4.1. 2-Iodo-1-(4-methoxyphenyl)-1-prop-2-enyloxy-ethane was prepared as adapted from literature [Nambu *et al.*, Tetrahedron 2003, 59, 77]. 0.52 mL (7.5 mmol) of allyl alcohol and 0.52 mL (3.75 mmol) of 4-vinylanisole were mixed in 25 mL of dry CH_2Cl_2 under nitrogen. After 5 min of stirring, the reaction mixture was cooled in a dry ice/acetone bath. 1.34 g (5.65 mmol) of *N*-iodosuccinimide were added and the reaction mixture temperature was allowed to reach *ca.* 0 ^oC in 6 hours with vigorous stirring. Then, 10 mL of a saturated solution of $Na_2S_2O_3$ were added to the solution, and the stirring continued for 10 min. The organic and aqueous layers were separated in a funnel, and the organic layer was dried over $MgSO_4$, filtered and concentrated *in vacuo*. The silica gel column chromatography of the resulting oily mixture with a petroleum spirit/Et_2O (20:1) eluent afforded *ca.* 0.691 g (58% yield) of a viscous colourless liquid. ^1H-NMR ($CDCl_3$) δ: 3.27-3.39 (m, 2H), 3.80 (s, 3H), 3.81 (dd, 1H, *J*=12.7, 6.0 Hz), 3.97 (dd, 1H, *J*=12.5, 5.1 Hz), 4.42 (dd, 1H, *J*=8.2, 4.9 Hz), 5.18 (dd, 1H, *J*=10.4, 1.2 Hz), 5.26 (dd, 1H, *J*=17.1, 1.7 Hz), 5.85-5.96 (m, 1H), 6.88 (d, 2H, *J*=8.8), 7.23 (d, 2H, *J*=8.8). ^{13}C-NMR ($CDCl_3$) δ: 11.0, 55.4, 70.0, 80.6, 114.1, 117.5, 127.9, 132.0, 134.5, 159.7.

4.2. 2-Isocyano-1,1′-biphenyl was synthesised according to a literature procedure [Tobisu *et al.*, Angew. Chem. Int. Ed., 2012, 51, 11363; Leifert *et al.*, Org. Lett., 2013, 15, 6286.

5. Plasma-initiated reactions.

5.1. Dehalogenation in aqueous solutions. Experiments with aerosol introduction into the nanosecond plasma were performed as follows. A solution containing halogen-substituted substrate (0.15 M), Na_2HPO_3•$5H_2O$ (0.25 M) and NaOH (0.4 M) was put into a nebuliser connected to the gas line leading to the plasma chamber. The aerosol was produced inside the nebuliser at a gas (N_2) flow of 10 L/min and further carried into the plasma chamber. The liquid was collected at the outlet of the plasma tube as shown in Figure S1a.

In a typical re-circulation experiment with nanosecond plasma, 216 mg Na_2HPO_3•$5H_2O$, 64 mg sodium hydroxide and 0.6 mmol of halogen-substituted aryl compound (4-iodobenzoic acid, 2-iodobenzoic acid, 4-iodophenolate, 4-chlorobenzoic acid) were dissolved in 4 mL or 12 mL (where stated) of de-ionised water. The flow of the liquid solution was 4 mL/min unless stated otherwise. Plasma was ignited in an in-house built chamber operated with H_2O vapour saturated 10 L/min of N_2 or He at 40 kV, 3.5 kHz. Water vapour saturation was achieved by using a system comprising a nebuliser and a Drechsel flask (see Figure S1a). The liquid re-circulation using a peristaltic pump. After continuous exposure to plasma for a set period of time, the crude reaction mixture was directly analysed by ^1H-NMR in D_2O.

Experiments with increased viscosity were performed as follows. The concentration of sodium iodide in the solution was estimated from the evaporation of the solvent in the experiment (*i.e.*, approximately 2 mL out of 12 mL remaining after 90 min of the reaction) and the NaI solutions viscosity data available in literature [Abdulagatov *et al.*, J. Chem. Eng. Data 2006, 51, 1645]. In our experiments viscosity of the solutions containing 4-iodobenzoic acid, Na_2HPO_3•$5H_2O$ and NaOH was increased by adding NaCl (*ca.* 2 M; [Kestin *et al.*, J. Phys. Chem. Ref. Data, 1981, 10, 71]), PEG-300 (*ca.* 0.8 mL; [Kirincic *et al.,* Fluid Phase Equilib., 1999, 155, 311]) or Na_2SO_4 (*ca.* 0.9 M; [Correla *et al.*, J. Chem. Eng. Data, 1981, 26, 43]).

For the isolation of iodobenzoic acid, the crude post-reaction mixture was washed with CH_2Cl_2, the aqueous phase was acidified to pH 2 with conc. HCl and extracted with CH_2Cl_2. The layers were separated in a funnel, the CH_2Cl_2 layer was dried over $MgSO_4$ and the solvent was removed *in vacuo*. The solid residue was re-crystallised from hexane/ CH_2Cl_2 (3:1) to afford 57.8 mg (79% yield) of a white crystalline material. ^1H-NMR ($CDCl_3$) δ: 7.48 (t, 2H, *J*=7.7), 7.62 (t, 1H, *J*=7.5) 8.13 (dd, 2H, *J*=7.0, 1.3 Hz). ^{13}C-NMR ($CDCl_3$) δ: 128.6, 129.4, 130.3, 134.0, 172.7.

In an experiment involving kHz plasma in an air-free reactor, 200 µL of an aqueous solution of 4-iodobenzoic acid (0.15 M), Na_2HPO_3•$5H_2O$ (0.25 M) and NaOH (0.4 M) were put on in a reservoir on top of a glass stand inside the reactor (Figure S1b). The reactor was then flushed with He for 20 s and the sample was exposed to plasma operated with the He feed gas (2 L/min) at 18.3 kV, 24.9 kHz. After 2 min of plasma exposure, the crude reaction mixture was directly analysed by NMR in D_2O.

In experiments with a He-operated kHz plasma used in ambient atmosphere, 0.5 mL of an aqueous solution of 4-iodobenzoic acid (0.15 M), $Na_2HPO_3 \bullet 5H_2O$ (0.25 M) and NaOH (0.4 M) were put in a glass container with a magnetic stirrer (Figure S1c) and exposed to plasma operated with the He feed gas (2 L/min) at 18.3 kV, 24.9 kHz. After 3 min of the plasma exposure, the crude reaction mixture was directly analysed by NMR in D_2O.

5.2. Deiodination-cyclisation reactions. The experiments with the H_2O/CTAB reaction mixture containing 2-iodo-1-(4-methoxyphenyl)-1-prop-2enyloxy-ethane and EPHP were performed as adapted from literature [Nambu *et al.* Tetrahedron 2003, 59, 77]. 50 mg (0.15 mmol) of substrate, 540 mg (3 mmol) of EPHP and 25 mg of CTAB in 6 mL of H_2O were re-circulated through the nanosecond plasma chamber as described above (see also Figure S1a). The plasma was operated with 10 L/min of ater vapour-saturated He or N_2 at 40 kV, 35 kHz. After the reaction, the reaction mixture was extracted with ethyl acetate and dried over $MgSO_4$. After the evaporation of the solvent *in vacuo*, the resulting mixture was analysed by NMR in $CDCl_3$.

In a typical kHz He plasma experiment, 200 μL of the aforementioned mixture of the substrate, EPHP and CTAB were put in the reservoir on top of a glass stand inside the reactor (Figure S1b). The reactor was then flushed with the He feed gas containing 10% H_2O vapour for 20 s and the sample was exposed to the He+10%H_2O plasma (2 L/min) at 18.3 kV, 24.9 kHz. After 2 min of plasma exposure, the reaction mixture was extracted with ethyl acetate, dried over $MgSO_4$, concentrated *in vacuo* and analysed by NMR.

The experiments non-aqueous mixtures (organic solvents or solvent-free) were carried out as follows. In a typical experiment, 50 mg 2-iodo-1-(4-methoxyphenyl)-1-prop-2enyloxy-ethane were mixed with 2-10 eq. of the radical transfer agent. 200 μL of solvent (mesitylene, PEG-300) was used where stated. The reaction mixture was put in the reservoir on top of a glass stand inside the reactor, which was then flushed with helium for 20 s. Then the mixture was exposed to plasma (2 L/min of He) at 18.3 kV, 24.9 kHz, for 15-20 min. After that, the crude reaction mixture was directly analysed by NMR in $CDCl_3$.

The direct column chromatography of the crude post-reaction mixture on silica gel with the CH_2Cl_2/*n*-hexane eluent (2:1) and the evaporation of the solvent *in vacuo* allowed to obtain 22.3 mg (74% yield) of a colourless oil, consisting of a cyclised reaction product 1-methoxy-4-(4-methyl-2-oxolanyl)benzene as a mixture of *cis* and *trans* isomers. ^{1}H-NMR *trans* ($CDCl_3$) δ: 1.08 (d, 3H, *J*=6.8), 1.86-2.01 (m, 1H), 2.37-2.54 (m, 1H), 3.43 (dd, 1H, *J*=8.3, 7.0 Hz), 3.78 (s, 3H),4.20 (dd, 1H, *J*=8.1, 7.1 Hz), 4.96 (t, 1H, *J*=6.9), 6.86 (d, 2H, *J*=8.7), 7.26 (d, 2H, *J*=8.5). ^{13}C-NMR *trans* ($CDCl_3$) δ: 17.9, 33.4, 42.6, 55.4, 75.7, 79.9, 113.7, 126.9, 135.9, 158.8. ^{1}H-NMR *cis* ($CDCl_3$) δ: 1.09 (d, 3H, *J*=6.5), 1.39-1.48 (m, 1H), 2.37-2.54 (m, 2H), 3.55 (t, 1H, *J*=7.9), 3.79 (s, 3H), 4.05 (t, 1H, *J*=7.9), 4.85 (dd, 1H, *J*=10.0, 5.6 Hz), 6.85 (d, 2H, *J*=8.6), 7.23 (d, 2H, *J*=8.5). ^{13}C-NMR *cis* ($CDCl_3$) δ: 17.6, 35.0, 43.9, 55.4, 75.4, 81.5, 113.8, 127.1, 135.4, 158.9.

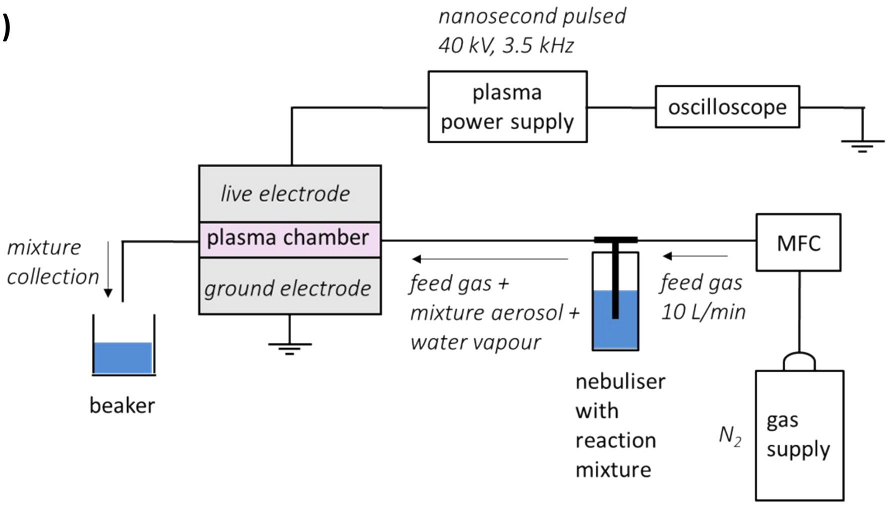
5.3. Trifluoromethylation reactions. In a typical experiment with plasma initiation inside the air-free reactor, 15 mg (*ca.* 84 μmol) of 2-isocyano-1,1'-biphenyl and 23 mg (*ca.* 71 μmol, 0.85 eq.) of Togni-II were mixed on top of a glass stand. This ratio of reagents was chosen in order to simplify the analysis (by ^{19}F NMR), where the $-CF_3$ groups of Togni-II and the product are monitored, in the investigation of the trends of reaction efficiency in different solvents, under different plasma conditions, etc. 200 μL of solvent (triethylene glycol, PEG-300, DMSO, DMF, 1,4-dioxane) were added where stated. The reactor was flushed with He for 20 s, after which the reaction mixture was exposed to plasma for a set period of time. After the exposure to plasma, the mixture was directly analysed by NMR in $CDCl_3$.

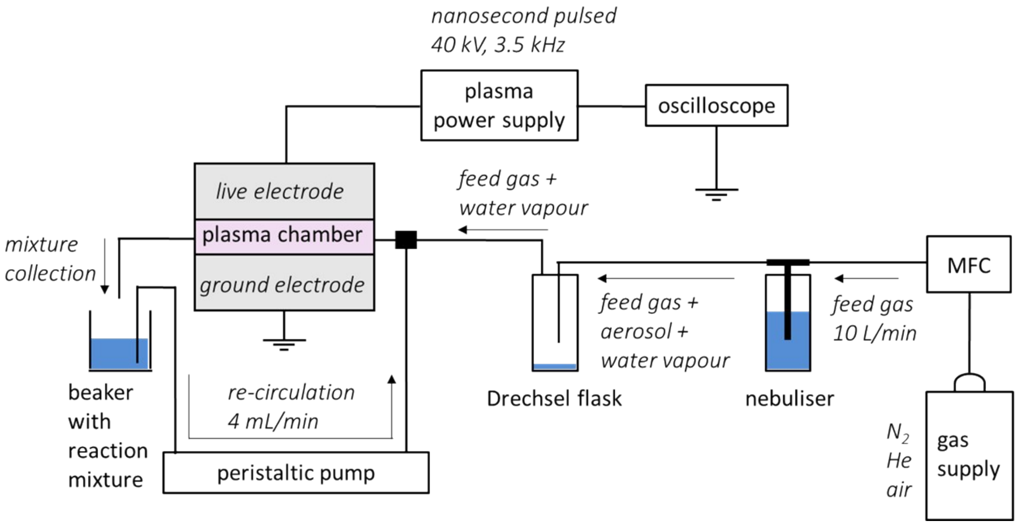
Experiments with the stirring-assisted plasma initiation were performed in a similar way: same amounts of substrates were mixed in 200-2500 μL of solvent (PEG-300) and put in a glass container with a magnetic stirrer. The mixture was further exposed to plasma in ambient atmosphere for a set period of time, and directly analysed by NMR. For the duration of the experiment, the glass container with the reaction mixture was positioned directly on a hotplate or on a dielectric foam, where stated (see Figure S1c).

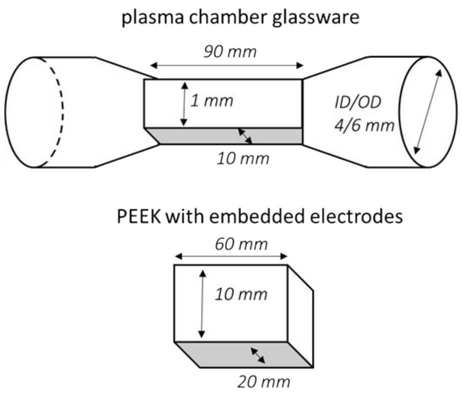
The trifluorinated product 6-(trifluoromethyl)phenanthridine was isolated from a mixture initially containing 15 mg of 2-isocyano-1,1'-biphenyl, 32 mg (1.2 eq.) Togni-II and 500 μL of PEG-300 after it was exposed to a kHz He plasma for 30 min with stirring. The direct column chromatography of the crude post-reaction mixture on silica gel with the *n*-pentane/CH_2Cl_2 (3:1) eluent afforded 16.5 mg (*ca.* 80% yield) of a white solid. ^{1}H-NMR ($CDCl_3$) δ: 8.70 (d, 1H, *J*=8.3), 8.63-8.59 (m, 1H), 8.38 (d, 1H, *J*=8.0), 8.31-8.27 (m, 1H), 7.92 (t, 1H, *J*=7.7), 7.83-7.75 (m, 3H). ^{19}F-NMR ($CDCl_3$) δ: -63.35 (s, 3F). ^{13}C-NMR ($CDCl_3$) δ: 146.6 (q, *J*=33.2), 141.8, 134.1, 131.5, 131.2, 129.4, 129.3, 128.2, 126.0 (q, *J*=3.1), 125.2, 122.6, 122.2, [illegible]

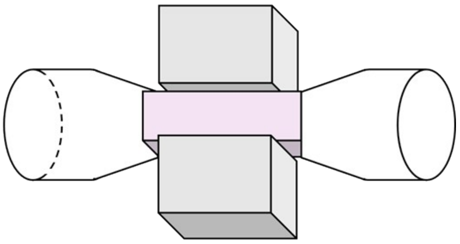
6. Spin trapping experiments. 100 µL of a 100 mM solution of DMPO in de-ionised water or in de-ionised water with added NaCl (2 M) were put in a reservoir on top of a glass stand. The stand was positioned inside a reactor, which was then flushed with He for 20 s. The sample was further exposed to a kHz plasma operated with He gas (18.3 kV, 24.9 kHz) for 1 min. The samples were then contained in glass capillary tubes (Marienfeld Laboratory Glassware) and analysed by EPR.

(a)









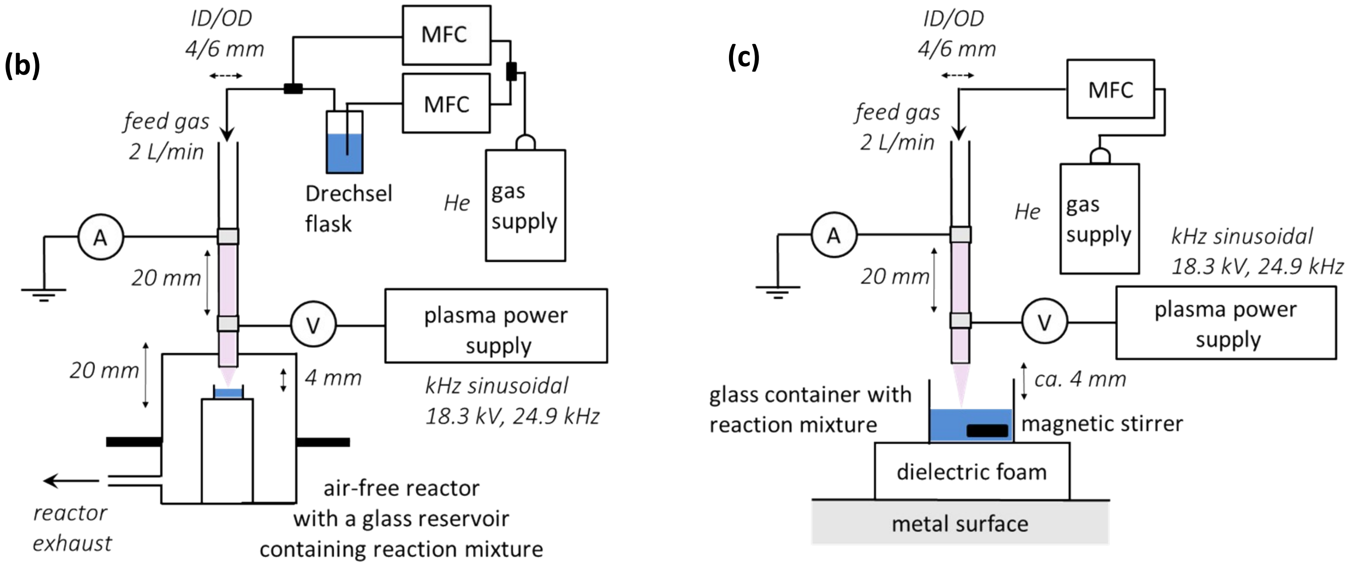


Figure S1. Plasma set-ups used in the experimental work (not to scale): **(a)** nanosecond pulsed plasma with aerosol (*top*) and with mixture re-circulation through the plasma chamber (*center*), with the enlarged plasma chamber schematics (*bottom*); **(b)** sinusoidal kHz He plasma in an air-free reactor; **(c)** sinusoidal kHz He plasma in ambient atmosphere with stirring-assisted exposure.

Table S1. The yield of deiodinated benzoate in the reaction of 4-iodobenzoate with sodium dibasic hypophosphite pentahydrate as determined by ^{1}H NMR. Reaction conditions: 4 mL of aqueous solution containing 150 mg 4-iodobenzoic acid, 216 mg $Na_2HPO_3{\bullet}5H_2O$, 64 mg sodium hydroxide were exposed to plasma. Plasma parameters: 40 kV, 3.5 kHz, gas flow (N_2) 10 L/min.

Entry	Passes through plasma	Liquid flow (mL/min)	Reaction time (min)	Benzoate yield* (%)
1**	once	-	-	7
2	once	0.1	-	16
3	once	0.4	-	18
4	once	2.7	-	1
5	continuous	2.7	5	9
6	continuous	2.7	10	14
7	continuous	2.7	20	25
8	continuous	4	5	9
9	continuous	4	10	14
10	continuous	4	20	25
11	continuous	7.8	5	10
12	continuous	7.8	10	15
13	continuous	7.8	20	23

* Yields are estimated from ^{1}H-NMR analysis of the crude reaction mixture.

** The reaction mixture was introduced into the plasma system as aerosol.

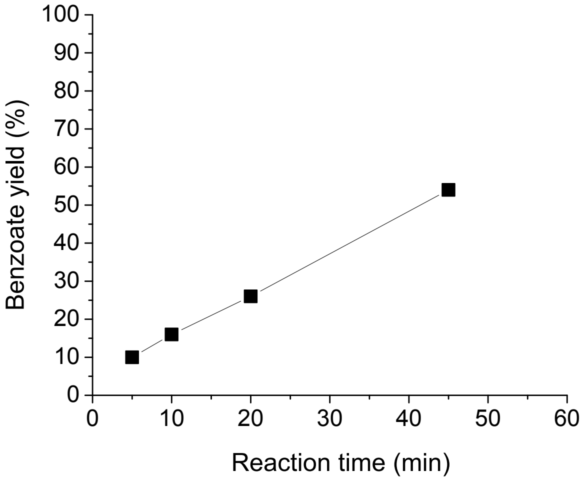


Figure S2. The yield of deiodinated benzoate in the reaction of 4-iodobenzoate with sodium dibasic hypophosphite pentahydrate as determined by ^{1}H NMR. Reaction conditions: 4 mL of aqueous solution containing 150 mg 4-iodobenzoic acid, 216 mg Na_2HPO_3•$5H_2O$, 64 mg sodium hydroxide were exposed to plasma. Plasma parameters: 40 kV, 3.5 kHz, gas flow (N_2) 10 L/min. Liquid flow was 4 mL/min. Water (solvent) was continuously added to reaction mixture to maintain approximately constant volume.

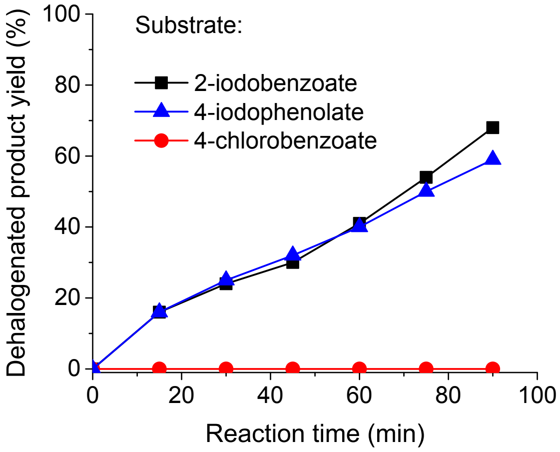


Figure S3. The yield of deiodinated products in the reaction of iodosubstituted aromatic compounds with sodium dibasic hypophosphite pentahydrate as determined by ^{1}H NMR. Reaction conditions: 12 mL of aqueous solution containing 0.6 mmol of a respective iodosubstituted compound, 216 mg Na_2HPO_3•$5H_2O$, 64 mg sodium hydroxide were exposed to plasma. Plasma parameters: 40 kV, 3.5 kHz, gas flow (N_2) 10 L/min. Liquid flow was 4 mL/min.

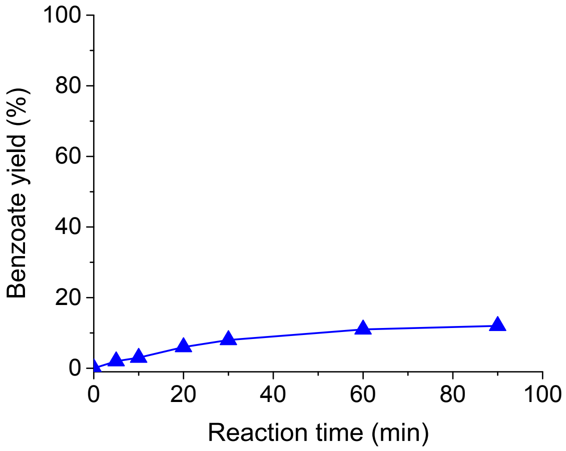


Figure S4. The yield of sodium benzoate in the reaction of aqueous 4-iodobenzoate exposed to plasma as determined by ^1H NMR. Reaction conditions: 12 mL of aqueous solution containing 150 mg 4-iodobenzoic acid and 64 mg sodium hydroxide were exposed to plasma. Plasma parameters: 40 kV, 3.5 kHz, gas flow (N_2) 10 L/min. Liquid flow was 4 mL/min.

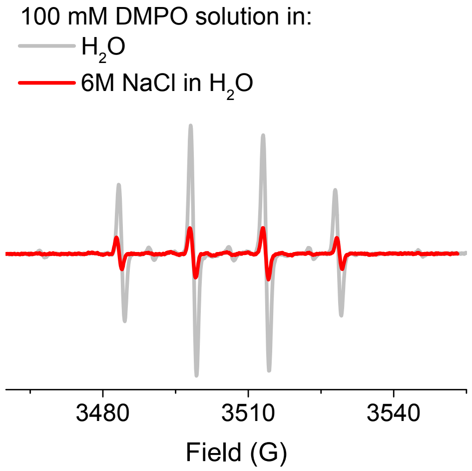


Figure S5. The EPR spectra of the DMPO radical adducts formed in the DMPO spin trap solution in H_2O and 6M NaCl in H_2O when exposed to a helium plasma. Significantly lower amount of DMPO-OH and DMPO-OH radical adducts was detected in the presence of NaCl, likely due to the scavenging of the radicals but the halogen anion. DMPO-OH: $a_N = 14.9$ G, $a_H = 14.7$ G; DMPO-H: $a_N = 16.4$ G, $a_H = 22.6$ G (×2).

Table S2. The yield of 1-methoxy-4-(4-methyl-2-oxolanyl)benzene in the reaction of deiodination-cyclisation of 2-iodo-1-(4-methoxyphenyl)-1-prop-2-enyloxyethane with EPHP as determined by ^1H NMR. Plasma parameters (ns): 40 kV, 3.5 kHz, gas flow 10 L/min. Plasma parameters (kHz): 18.3 kV, 24.9 kHz, gas flow 2 L/min, air-free reactor, 4 mm from nozzle to the sample.

Entry	**Plasma type**	**Exposure type**	**Reaction time (min)**	**Solvent**	**Yield *cis* (%)**	**Yield *trans* (%)**
1*	ns, He, 100% H_2O vapour	continuous flow-through	25	H_2O, CTAB	1	3
2*	ns, N_2, 100% H_2O vapour	continuous flow-through	90	H_2O, CTAB	1	4
3**	kHz, He, 10% H_2O vapour	static	2	H_2O, CTAB	0	1

* 4 mL/min liquid flow.

** 200 µL of sample containing the substrate, EPHP and CTAB were positioned on top of a glass stand and exposed to plasma.

Table S3. The yield of sodium benzoate in a dehalogenation reaction of 4-iodobenzoate in water initiated by a helium kHz plasma as determined by ^1H NMR. Reaction conditions: an aqueous sample (0.15 M 4-iodobenzoate, 0.25 M Na_2HPO_3•$5H_2O$, 0.4 M NaOH) was exposed to plasma. Plasma parameters: 18.3 kV, 24.9 kHz, gas flow 2 L/min, 4 mm nozzle to sample.

Entry	**Plasma exposure type**	**Reaction time (min)**	**Solvent volume (µL)**	**Benzoate yield (%)**
1	Air-free reactor	2	200	4
2*	Ambient, stirring	5	500	11
3*	Ambient, stirring	5	1500**	9
4	Ambient, stirring	5	500	30
5	Ambient, stirring	5	1500**	21
6	Ambient, without stirring	5	500	29

* With a dielectric foam layer between the reaction mixture glass container and the hotplate.

** The amount of all reagents was kept the same (entries 2-6), but the amount of solvent (*i.e.,* concentration) was varied: a 500 µL sample (entries 2,4,6) was diluted 3 times prior to plasma exposure (entries 3,5).

Table S4. The yield of 6-(trifluoromethyl)phenanthridine in the reaction of 2-isocyano-1,1′-biphenyl with the Togni-II reagent in solutions exposed to plasma. Plasma parameters: 18.3 kV, 24.9 kHz, gas flow (He) 2 L/min, *ca.* 4 mm nozzle to sample.

Entry	**Plasma exposure type**	**Solvent**	**Reaction time (min)**	**Solvent volume (μL)**	**Yield (%)**
1	Air-free reactor	triethylene glycol	15	200	10
2	Air-free reactor	DMSO	5	200	2
3	Air-free reactor	DMF	5	200	1
4	Air-free reactor	1,4-dioxane	1	200	<1
5*	Ambient, stirring, dielectric layer	PEG-300	10	200	11
6*	Ambient, stirring, dielectric layer	PEG-300	10	2500	7
7**	Ambient, stirring, dielectric layer	PEG-300	10	500	2

* Reactions in glass container positioned on top of a hotplate with a layer of dielectric foam between the glass container and the hotplate, with stirring.
** Without stirring.

Table S5. Temperature of the PEG-300 solution exposed to a kHz He plasma in ambient atmosphere. The conditions of the measurement were the same as the experimental reaction conditions: 500 μL of PEG-300 in a glass container with a stirrer were exposed to plasma for 1 min, then allowed to cool down (with plasma off) for 1 min more, then exposed to plasma again, etc. Hence, the plasmas exposure time is shown as the sum of the 1 min long exposures to plasma.

Entry	**Plasma exposure type**	**Measurement №**	**Temperature (°C)**	
			After 1 min of plasma exposure	**After 1 min of cooling down**
1	Directly on a hotplate	1	67	21
2	Directly on a hotplate	2	69	24
3	Directly on a hotplate	3	68	22
4	With dielectric foam layer	1	59	21
5	With dielectric foam layer	2	57	22
6	With dielectric foam layer	3	60	22