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Graphene oxide promoted oxidative bromination of anilines and phenols in water

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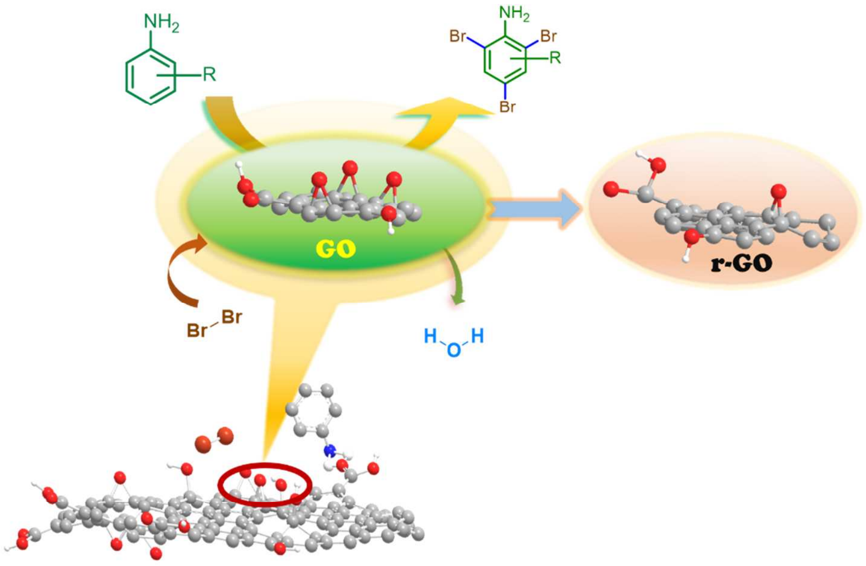


Abstract: The mildly acidic and oxidative nature of graphene oxide, with its large surface area available for catalytic activity, has been explored in aromatic nuclear bromination chemistry for the first time. The versatile catalytic activity of graphene oxide (GO) has been used to selectively and rapidly brominate anilines and phenols in water. The best results were obtained at ambient temperatures using molecular bromine in a protocol promoted by oxidative bromination catalyzed by GO; these transformations proceeded with 100% atom economy with respect to bromine, and high selectivities for the tribromoanilines and -phenols. Reduced graphene oxide (r-GO) was observed to form after the second recycle (third use) of GO. This technique is also effective with N-bromosuccinimide (NBS) as the brominating reagent. In case of NBS, reactions were instantaneous and the GO displayed excellent recyclability without any loss of activity over several cycles.

Introduction: The nuclear bromination of aromatic compounds is a fundamental process[1] and one of the most important C-H bond-functionalizing reactions in synthetic chemistry.[2] Among aromatic compounds, anilines and phenols are favored substrates for these reactions due to their good reactivities and high product utilities; these compounds are promising intermediates in the syntheses of fine chemicals, agrochemicals, pharmaceuticals, and dyes. In addition, brominated aromatic compounds play vital roles in preparative methods for specialty chemicals such as herbicides, pesticides, and fire retardants.[3] Moreover, many brominated compounds exhibit antitumor, antibacterial, antifungal, antineoplastic, antiviral, and antioxidant properties.[4]

A plethora of information is available for the bromination of unprotected anilines and phenols. Most of these methods are devoted to the generation of para-monobrominated products,[5–15] while others are dedicated to meta selectivity,[2] and only a few result in ortho selectivity.[16] There are very few reports that describe selectivity for tribrominated products.[4,17,18] Salakhov and coworkers obtained tribrominated products in high yields through oxidative bromination with KBr and hydrogen peroxide in HCl;[17] however, they were unable to avoid the use of a hazardous protic acid. The use of $TsNBr_2$ (as the brominating agent) and organic solvents are shortcomings of the method employed by Saikiya and coworkers.[4] In another report by Kumar et al. aimed at tribrominated products from phenols and anilines employing molecular bromine, atom economy was of concern as only 50% of the bromine was delivered to the final products.[18] Considering the cost of bromine, the use of molecular bromine in 100% atom economy during the direct bromination of aromatic substrates in water is highly desirable.

It is difficult to consider aromatic bromination without molecular bromine.[19] Molecular bromine is an inherently hazardous reagent because of its toxicity, corrosive nature, and high volatility. Another major drawback of the use of bromine involves the formation of highly corrosive HBr gas which has its own post-formation hazards under different reaction conditions; however, HBr formed in this manner can be used wisely for further bromination through its oxidation. This inevitably demands the use of metal catalysts and oxidizing agents that make the process expensive and environmentally unsafe.[18] Oxidative bromination, in which the brominating reagent is prepared in situ from a bromide salt, is considered to be biomimetic and ecofriendly,[19] and various oxidative bromination reactions have been reported in the literature. Iskara et al. have painstakingly reviewed halogenations of this kind over the past five decades in an excellent review.[19]

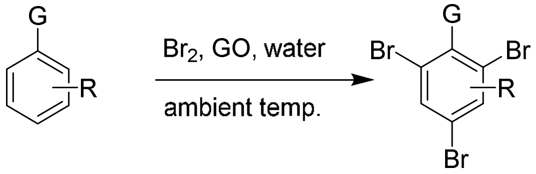
Non-toxicity, abundance, recyclability, low cost, and minimal ecological impact are desirable properties of a green catalyst.[20] Bielawski et al. have elegantly reviewed the wide synthetic utility of heterogeneous carbon materials.[21] In the quest for sustainability, graphene oxide (GO) is a good alternative to many hazardous catalysts, such as transition metals, for oxidation reactions.[20] GO is also used as a support for the immobilization of metals during heterogeneous catalysis.[22–24] A review by Bielawski et al. provides in-depth understanding of the basic structural properties, characterization methodologies, catalytic, and biomedical applications of GO.[25] As GO is highly functionalized by oxygen, it has been effectively employed as an oxidant in a variety of reactions;[20] oxidations of sulfides,[26] primary amines,[27] alkenes, and alcohols[28] have been demonstrated recently. Owing to its large surface area and the presence of acidic functional groups (phenolic, hydroxylic, and carboxylic),[29] GO has been fruitfully explored for the catalysis of a variety of fundamental reactions, such as Friedel–Crafts reactions,[30] hydrations, aza-Michael additions, condensations, ring-opening polymerizations[31], Michael addition reactions, and C-H bond oxidation reactions[32] and has been extensively reviewed by Mohammadi et al.[33] Very recently Gong and coworkers reported the iodination of aromatics and ketones[34] and the trifluoromethylation of arenes[35] using GO as a metal-free catalyst. The surface chemistry of GO can also be tailored to achieve desired physical and chemical properties.[29] Nagai et al. meticulously examined the catalytic activities of graphite and graphene oxides for the Friedel-Crafts alkylation or bromination of phenol with *t*-butyl bromide.[36] As part of this study, they showed that Br^- is oxidized to Br_2Br^+ on the GO surface. This ground-breaking study, and knowledge of the catalytic properties of GO, inspired us to investigate the oxidative bromination of anilines and phenols by directly employing molecular bromine. This innovation was expected to improve bromination efficiency, atom economy, and streamline bromination conditions by removing the need for intermediate reagents, such as *t*-butyl bromine, that are themselves prepared using Br_2 or HBr. To our delight, not only did we realize this objective, but the protocol developed in this work provided 2,4,6-tribrominated products that complement the mixtures of 4-bromo and 2,4-

dibromophenols prepared by Nagai et al.; indeed 2,4,6-tribromophenol was not formed in reactions using *t*-butyl bromide and GO.

Although molecular bromine is used extensively for the bromination of anilines and phenols, complex mixtures of mono-, di-, tri-, and even tetrabrominated products often result.[18] In the above context, a metal-free process that utilizes molecular bromine completely and offers high selectivity for a tribrominated product is of unquestionable importance. Herein we report GO as an all-in-one catalyst that initiates and effects rapid oxidative bromination through the dual activation of the substrate and molecular bromine in water.

Result and Discussion: In preliminary experiments, the desired amount of GO was dispersed (exfoliated by sonication) in a sufficient quantity of water, and the required amount of aniline was added under vigorous stirring. Interestingly, we observed that the added aniline is adsorbed onto the GO surface. This adsorption is visibly noticeable and was further supported by IR spectroscopy. This adsorption is attributable to strong H-bonding between the protons of aniline and the oxygen functionalities on the GO surface and is evidenced by shifts in the IR absorptions of the oxirane groups on the GO surface to lower frequencies, and changes in carbonyl absorption intensities from strong to very weak. The IR absorption peaks for aniline supported on GO (GOS2) observed at 3439 cm^{-1} and 3380 cm^{-1} merged in peak centered around 3340 cm^{-1} which corresponds to stretching of $–NH_2$ group of aniline. Peaks at 1725 cm^{-1} of carbonyl group of GO shriveled to very weak band as an effect of H-bonding with hydrogen of $–NH_2$ group of aniline. A new strong band at 1610 cm^{-1} appeared corresponding to $-NH_2$ scissoring and had shift of around 10 cm^{-1} from its standard value due to H-bonding with oxygen present on GO surface. Also, a red shift is observed in epoxide peak from 1045 to 1040 cm^{-1} due to H-bonding of aniline hydrogens to oxygen of epoxide (Figure S1 in SI).

Subsequently, the required amount of bromine was added dropwise to the reaction mixture. To our surprise, the bromine color disappeared instantaneously, and no brown fumes were observed over the surface of the reaction mixture, even at room temperature; this indicates complete engagement of the reagent with the GO surface during the reaction. Upon optimization of the reaction of aniline with molecular bromine, we found that only 1.5 mol equiv of molecular bromine was sufficient to drive the reaction to completion, furnishing the 2,4,6-tribromoaniline product in excellent yield. This result clearly indicates that both of the Br atoms of molecular bromine are utilized during the bromination of aniline. Encouraged by these results, we developed an optimized synthetic protocol.



Scheme 1: Where G = -NH$_2$, -OH. R = -H, -NO$_2$, -Cl, -OMe, -CHO, -COOH, -F,-CH$_3$, n-butyl.

We found that 2.0 wt % (w.r.t. substrate) of GO is sufficient to complete the reaction. Ambient temperature was observed to be optimal for this process (Table1). When Br$_2$ was used in limiting quantities, i.e., 1.0 mol equiv, the major product formed was tribromoaniline (57%). In control experiments (without GO) 1.5 and 3 mol equiv of bromine afforded 2,4,6-tribromoaniline in 31% and 76% yields respectively. Interestingly, we found that GO significantly enhances the product yields to 93% with the same equivalents of bromine. This clearly validates the atom economy of the process. For meta-substituted anilines and phenols, 1.5 mol equiv of bromine was required to provide the corresponding tri-brominated product. Half or one mol equiv of bromine was sufficient to convert ortho and/or para mono- or di- substituted compounds to the desired product (Scheme 1). A number of different anilines and phenols were subsequently screened using the developed protocol (Table 2).

Table 1: Optimization study of bromination of aniline.

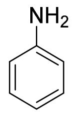
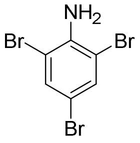
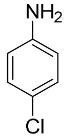
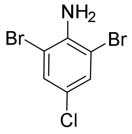
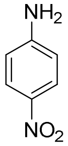
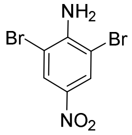
Entry	GO loading (mg)	Amount of Br$_2$ (mole equivalent)	Temperature (in °C)	Time (in minutes)	GC Yield [a]	Isolated Yield (%)
1	10	1.5	RT[b]	30	96	93
2	5	1.5	RT	30	93	83
3	20	1.5	RT	30	69	68
4	10	2.0	RT	30	93	81
5	10	1.0	RT	30	60	57
6	10	1.5	RT	10	59	55
7	10	1.5	RT	20	79	78
8	10	1.5	RT	30	93	93

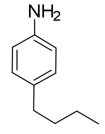
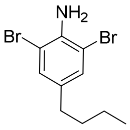
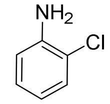
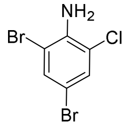
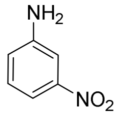
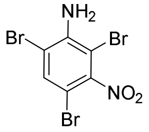
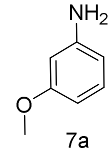
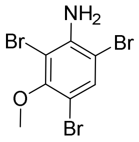
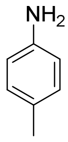
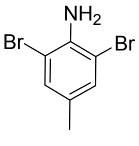
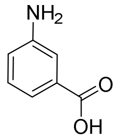
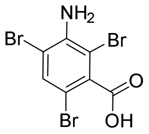
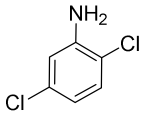
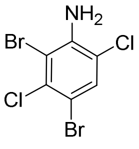
9	10	1.5	RT	60	89	87
10	10	1.5	RT	120	87	86
11	10	1.5	0-5	30	37	35
12	10	1.5	50	30	88	85
13	control	1.5	RT	120	41	31
14	control	3.0	RT	120	87	76
15[c]	10	1.5	RT	30	92	85
16[d]	10	1.5	RT	10	93	89

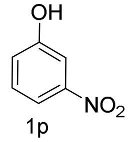
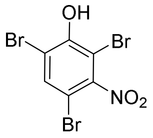
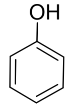
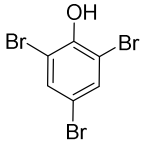
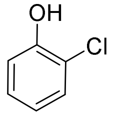
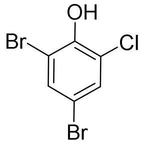
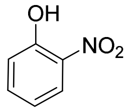
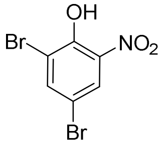
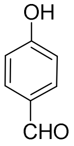
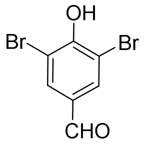
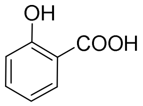
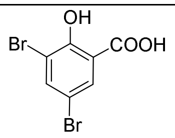
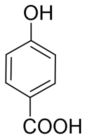
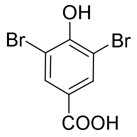
Table 1: Optimization study in bromination of aniline to 2,4,6-tribromoaniline. [a] calculated by area under peak normalization [b] RT = ambient temperature. [c]= 3 mol equiv. of butylated hydroxyl toluene (BHT) was used as radical scavenger. [d] NBS was used as a bromine source and BHT used as a radical scavenger.

No specific trends were observed in relation to product yields and the time taken for the reactions to proceed to completion in the presence of electron withdrawing/donating groups. Interestingly, no benzylic bromination was observed in case of p-toluidine (Table 2 entry 8) or 4-(n-butyl) aniline (Table 2 entry 4). A variety of phenols furnished good-to-excellent product yields and selectivities under similar reaction conditions.

Table 2: Various important anilines and phenols in substrate study.

Entry	Substrate	Product	Time (Min)	Yield[a] (%)	Melting point °C	
					Observed	Literature
1	 1a	 1A	30	93[b] 98[e]	121	120[18]
2	 2a	 2A	30	91[c]	95	93-95[37]
3	 3a	 3A	10	92[c]	206	206[18]

4	 4a	 4A	10	98[c]	119	-------
5	 5a	 5A	15	95[c]	103	103-104[38]
6	 6a	 6A	25	84[b]	98	69[39]
7	 7a	 7A	20	95[b]	83	83-84[40]
8	 8a	 8A	25	92[c] 98[e]	78	74-75[41]
9	 9a	 9A	10	94[b] 95[e]	170	170[17]
10	 10a	 10A	10	98[c]	89	89[42]

11	 1p	 1P	25	90[b]	130	89-90[43]
12	 2p	 2P	25	96[b]	95	93-94[44]
13	 3p	 3P	15	98[c]	92	75-76[45]
14	 4p	 4P	15	96[c]	110	114[18]
15	 5p	 5P	15	96[c]	182	183[18]
16	 6p	 6P	20	98[c]	226	226[18]
17	 7p	 7P	10	89[c]	272	270-273[18]

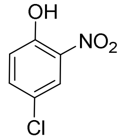
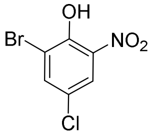
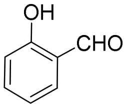
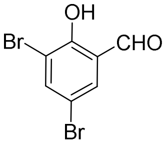
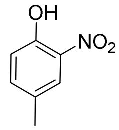
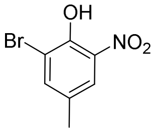
18	 8p	 8A	10	95^{d}	117	125[46]
19	 9p	 9P	15	96^{c}	82	80-82[18]
20	 10p	 10P	30	88^{d}	68	69-71[39]

Table 2. [a] Isolated yields, Amount of bromine used (per mole equivalents of substrate) [b] = 1.5, [c] = 1.0, [d] = 0.5. [e] = % yield using NBS.

While studying catalyst recyclability, we observed that product yields were only slightly lower during the second use (first recycle) of the catalyst, compared to the first. However, during the second recycle (third use) the yield was reduced by 10%, and it dropped to 69% during the third recycle (Figure 1).

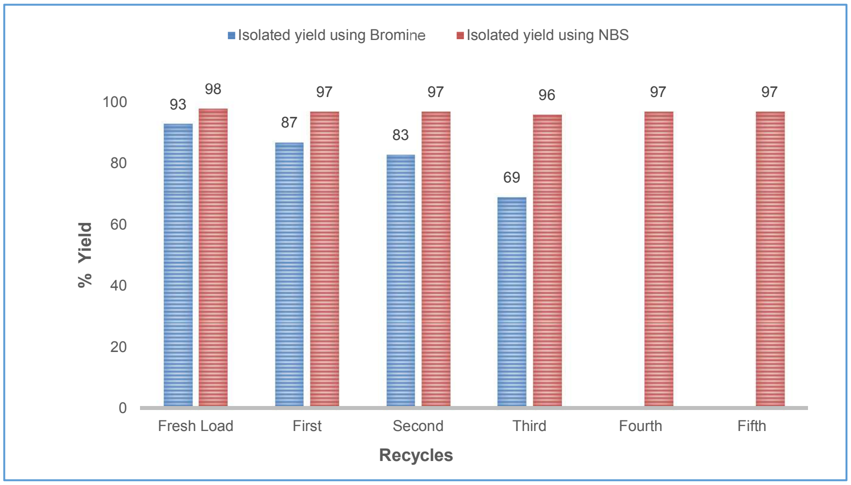
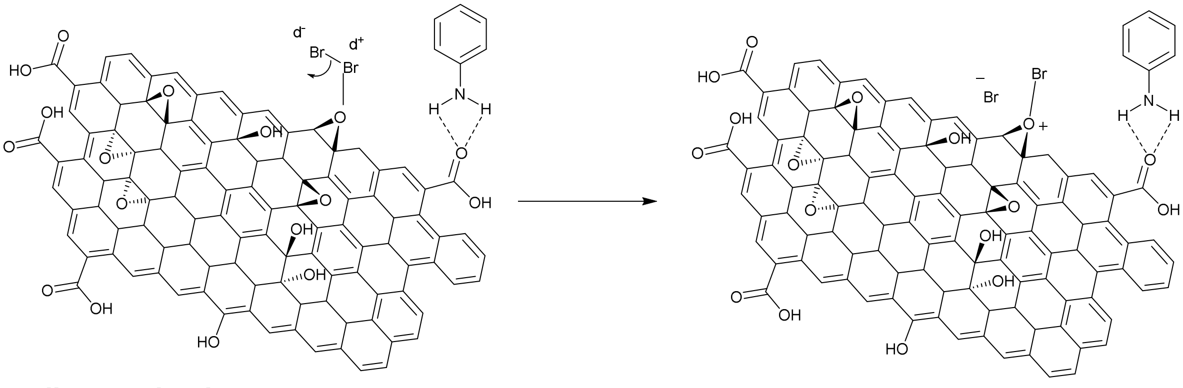


Figure 1: Recyclability study of GO as a catalyst using Br2 and NBS in synthesis of 2,4,6-tribromoaniline from aniline

We characterized the GO surface after the second recycle by X-ray diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS) and infrared (IR) spectroscopy. A strong peak at a θ value of 24.80°, which corresponds to r-GO, is clearly observed to be as strong as the GO peak at 11.39°. The band at 1725 cm^{-1} observed in the IR spectrum of pristine GO is very weak in the spectrum of GO after the second recycle, suggesting that the carbonyl groups have been reduced. Bands originally at 3341 and 1040 cm^{-1} are completely absent indicating the loss of –OH and epoxy groups from the GO surface. The results of these analyses clearly indicate that GO is gradually converted into r-GO because the functional groups on the surface of the catalyst become reduced during oxidation of Br^- to Br^+ (Figure S1 in the SI). We also carried out elemental analysis of GO before and after use. We observed that the oxygen content of GO after the second recycle is reduced to 15%, compared to 29% prior to use (Table S1 in SI). XPS was used to study the chemical structure and electronic state of the as made materials. According to the XPS analysis as made GO and GOS1 contains 2.67 and 4.49 C/O ratios respectively. It shows improved C/O ratio from GO to GOS1. This increase is attributed to reduction of GO surface during oxidative bromination. High resolution XPS spectra of GO and GOS1 showed C1s and O1 speaks (Figure S4 and S5 in SI). Additionally N1s, Br3d, and Br3p peaks clearly observed in XPS spectra of GOS1 (Figure S4-S10 in SI). This analysis also reveals presence of 5.9% of bromine remnant on GO surface after exhaustive use. These observations are in good agreement with the elemental analysis.

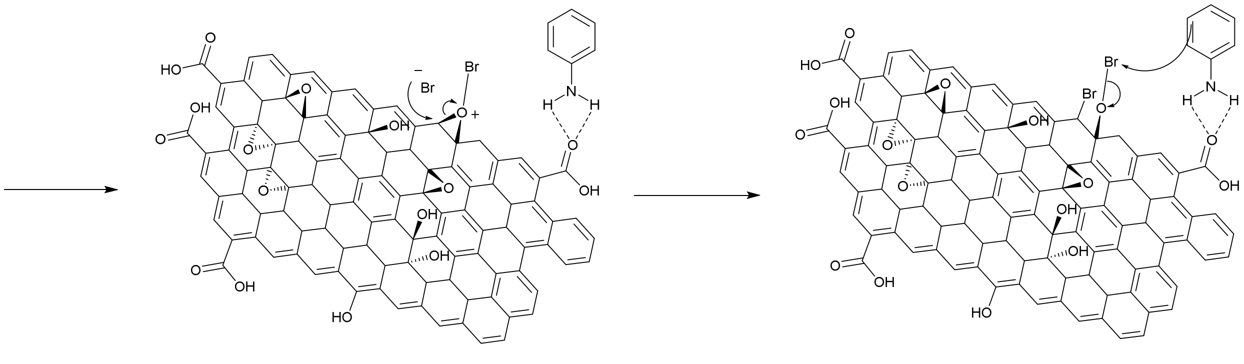
To investigate the role of oxygen (air) we carried out the reaction under an inert atmosphere. In a typical experiment the reaction medium was purged with N_2 for an hour prior to the addition of bromine. The reaction was subsequently carried out under N_2 for 30 min and the yield of the 2,4,6-tribromoaniline was found to be 50%. In addition, monobromoaniline and dibromoaniline were also observed to be formed in 5% and 6% yields respectively; 39% of unreacted aniline was recovered. These findings establish the important role of molecular oxygen during oxidative bromination. Ambient oxygen is able to re-oxidize GO and behaves as a terminal oxidant.[28] Bielawski et al. studied this kind of re-oxidation of GO with atmospheric oxygen; their computational study revealed that the catalyst recharging process is energetically favorable.[47]

When considering a possible mechanism for the transformations observed herein, it is important to note that GO appears to participate in the ionization of the Br-Br bond. Upon addition, the bromine color disappeared instantaneously and brown fumes were not observed over the reaction mixture, as was seen in the case of the control reaction, consistent with the adsorption of bromine onto the GO surface. As shown in the mechanism, the oxygen of the epoxide group on the catalyst surface polarizes Br_2 (Scheme 2). This eventually leads to the opening of the epoxide ring, providing space for the attachment of Br^- to the surface (Scheme 3). This was evidenced by the FTIR analysis of GOBr1 (Figure S2 in SI) (sample of GO obtained after reacting GO and bromine under optimized reaction conditions) which exhibits band at 483 cm^{-1} corresponding to C-Br stretching frequency.[48] This particular C-Br bond formation via epoxide ring opening is also evidenced in various reaction conditions as studied by Z. Sofer et al.[48,49,50]. The C-Br band as expected is absent in pristine GO and GOBrR (GO obtained after the reaction of aniline and bromine) suggest the subsequent oxidative elimination of Br furnishing the desired products. Attachment of Br^+ to the oxygen of the ring-opened epoxide increases its reactivity and facilitates the more rapid and efficient attack of Br^+ at the GO-surface-attached substrate. H^+ is expelled from the substrate to restore its aromaticity (Scheme 4). The hydroxyl group formed in this manner polarizes a second molecule of bromine and the complete polarization of molecular bromine leaves the oxygen atom positively charged. The bromide anion formed during this process subsequently abstracts a bromine atom attached to carbon atom present on the catalyst surface (Scheme 5). The oxonium ion leaves the GO surface with an electron pair to produce hypobromous acid and the simultaneous formation of molecular bromine restores the C-C double bond on the catalyst surface (Scheme 6). Bielawski and co-workers showed that the reduction of the GO surface by removal of epoxide groups and their regeneration in presence of air are energetically favorable processes.[47] Increasing conjugation or the acquisition of aromaticity may be the driving forces behind the formation of the C-C double bond on the catalyst surface. In this manner, GO oxidizes bromine, resulting in 100% atom economy during the bromination process.

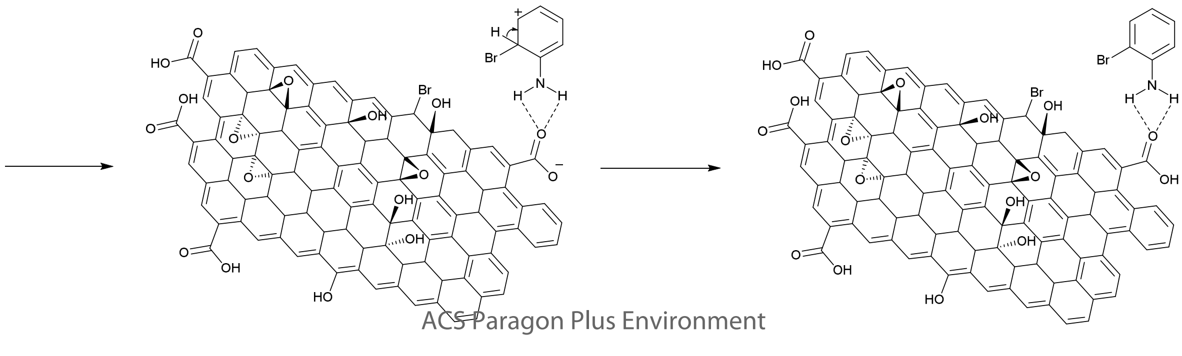


Plausible mechanism:

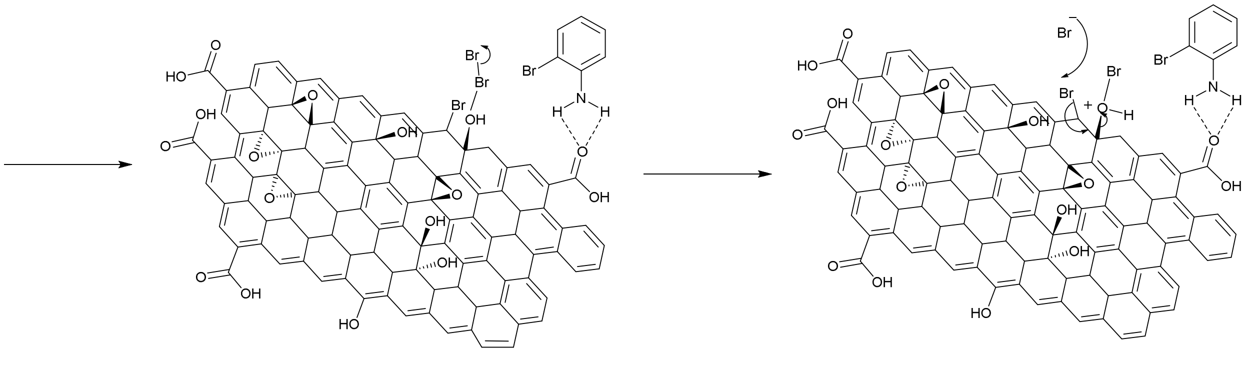
Scheme 2: Attachment of aniline on GO surface and Polarization of Bromine by Oxirane.



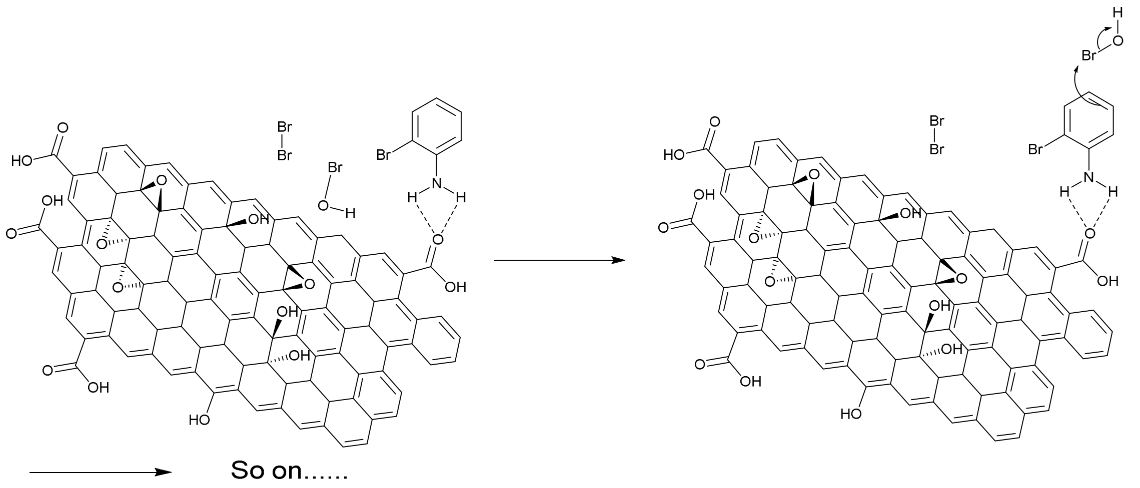
Scheme 3: Opening of Oxirane and stabilization of Br anion.



Scheme 4: Bromination of aromatic carbon by reactive –OBr species and restoration of aromaticity in substrate.



Scheme 5: Attack of second Br$_2$ on hydroxyl group formed by oxirane opening and Attack of Br$^-$ on Br attached to catalyst surface induces breaking of C-O bond and Formation of Hypobromous acid and Bromine.



Scheme 6: Formation of double bond on GO surface driven by increase in the conjugation.

To authenticate the mechanistic pathway, we performed experiments using 2,6-di-*t*-butyl-4-methylphenol (butylated hydroxy toluene, BHT), a known radical scavenger. Both reactions (with Br$_2$ and NBS) proceed normally in the presence of BHT. Aniline was found to be completely consumed yielding 2,4,6-tribromoaniline in 85% and 89% yields respectively (Table 1 entry 15 and 16). These findings eliminate the possibility of a radical mechanism. To check the capacity of GO for oxidizing Br$^-$ to Br$^+$, we attempted the reaction using KBr as a bromide source; however the reaction did not proceed under the optimized conditions. KBr as a stable ionic salt, is unable to open the epoxide ring which is essential for the rapid oxidation of bromide according to the proposed mechanism; otherwise bromide ions accumulate gently and interact with GO for longer time for effective oxidation.[36] In water as the solvent, KBr-solvent interaction outweigh GO-KBr interactions. When bromine is used, the epoxide ring opens easily to initiate the rapid oxidation process. To overcome the KBr problem, we employed sodium dodecyl sulfate (SDS) as a phase-transfer catalysts (PTC) to improve the number of effective collisions. Unfortunately, 2,4,6-tribromoaniline, dibromoaniline, and 4-bromoaniline were obtained in 3%, 1%, and 10% yields respectively when SDS was added to the reaction at 60 °C (Table 3).

Table 3: Results of reactions done to support the mechanism:

Entry No.	Reaction conditions	Aniline (unreacted) %	Yield of the products (%)[a]		
			4-Bromoaniline (11A)[b]	Dibromoaniline (12A)[b]	2,4,6-tribromoaniline (1A)[b]
1	Inert atm. (N_2)	39	5	6	50
2	In presence of KBr and SDS	96	-----	1	2
3	In presence of KBr and SDS at 60 °C	85	10	1	3

Table 3: Study in mechanism of bromination of aniline to 2,4,6-tribromoaniline. [a] calculated by area under peak normalization [b] confirmed by GCMS.

To further study the catalytic activity of GO during the bromination of aniline with bromine-carrying reagents, we explored the process using NBS as the brominating agent. To our delight, GO catalyzed the bromination of aniline to 2,4,6-tribromoaniline in excellent yield; the reaction was observed to be complete within 5 min. The recyclability of GO was also studied. No drop in yield was observed up to the fifth recycle, confirming the unswerving catalytic activity of GO for over six cycles of use. The IR spectrum of reused GO (GO-S0 Figure S1 in SI) obtained after the sixth cycle is very similar to that of pristine GO. This result indicates that GO acts as an acid catalyst for the reaction, with the acidic groups regenerated during the course of the reaction, which nullifies any changes in the functional groups on the surface of the catalyst. The bromination of p-toluidine and 3-aminobenzoic acid were also investigated using NBS. As previously noted for reactions with Br_2, no benzylic bromination was observed and the selectivity for nuclear bromination was maintained.

Conclusion: In conclusion, we introduce an environmentally benign, selective, and rapid method for the oxidative bromination of anilines and phenols using GO, which acts as a dual enhancer for the substrate and the reagent. GO also oxidizes bromide to an effective electrophile, resulting in 100% atom economy for the reagent. No hazardous materials, such as HBr, are involved, making this process safe and green. The uninterrupted recyclability of the GO catalyst with NBS is appealing for use in laboratory-scale experiments. Since GO is a non-toxic, abundant, inexpensive, and eco-friendly catalyst, this protocol provides a sustainable process for industrial use. In addition, the use of water as the solvent minimizes the detrimental impact to the environment. We envisage that this protocol will open up new avenues for the nuclear bromination of aromatic compounds by directly employing molecular bromine. We believe that a study into the properties of the r-GO formed after exhaustive reuse of GO as a bromination oxidant would be interesting.

Experimental Section:

General Experimental Methods:

Materials: Natural graphite powder (325 mesh, Alfa Aeasar), sulphuric acid (98% assay with 99% purity, Merck), hydrochloric acid, hydrogen peroxide (30%, S D Fine Chem. Ltd.), sodium nitrate (NaNO3), and PVA (Sigma Aldrich) were procured and used without any further purification. Anilines and phenols were purchased from Thomas Baker (chemicals) Pvt. Ltd, s. d. fine-chem. Ltd and Avra Synthesis pvt Ltd, India. $KMnO_4$, H_2O_2, $NaNO_3$, were obtained from Sigma Aldrich. Bromine was purchased from Central Drug House (P) Ltd, New Delhi. Chemicals and solvents were used as obtained without further purifications.

Methods: All the reactions were carried out at ambient temperature and pressure conditions without any inert atmosphere. All the products were purified from suitable solvents and isolated yields are noted. Conversions and yields are determined by GC with area normalization method. Reactions were monitored by thin layer chromatography (TLC) using aluminum sheets coated with silica (60, F254) visualized under UV light (254 nm).

Instruments: Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Agilent 500 MHz instruments. ^{1}H NMR chemical shifts are reported in part per million (ppm) downfield from TMS.

And are referenced to residual proton in NMR solvent ($CHCl_3$ = δ 7.26 ppm, acetone = δ 2.05 ppm, Water = d 1.50 ppm). NMR data are repesented as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quintet, m = multiplet), coupling constant (*J*) in Hertz (Hz), No. of hyrogens = xH. All NMR spectra were recorded at 25 °C. Fourier transform infrared spectroscopy (FT-IR) was measured on

Perkin–Elmer spectrophotometer. As prepared GO, GOS1, GOS2 were characterized by X-ray diffractometer (Shimadzu XRD-6100 using Cu Ka radiations = 1.5405 A°) with scanning rate 2°per min and 2 theta (θ) angle ranging from 20° to 80° at current 30.0 mA and voltage 40.0 kV. Gas Chromatographic (GC) analysis, for optimization of reaction conditions, was carried out with Thermo scientific, column-TR-1, 30mX0.25mm, IDX0.25um film, FID detector and sample size 0.1 l μl. Melting points were recorded on M/s Sunder ind. Product and are uncorrected. Elemental analysis were carried out on ThermoFinnigan instrument. GCMS analysis was performed on Shimadzu GCMS QP 2010.

a) **Synthesis of graphene oxide (GO):** GO was prepared from graphite powder by using modified Hummer's method.[51]

b) **Reaction optimization and control experiments:** As the process aimed to eliminate organic solvents all experiments were performed in water. For optimization reaction bromination of aniline in water was selected as model reaction. Initially 10 mg of GO was taken in 10 mL of water in 50 mL round bottomed flask. Flask was then placed in sonication bath to disperse GO in water. Thus exfoliation was achieved which is necessary to increase the surface area of the catalyst. Then 0.5 g (0.0053 moles) of aniline was added to the reaction mixture with vigorous stirring till it got adsorbed on the surface of GO. Association of aniline on GO was clearly noticeable. To this molecular bromine 1.29 g (0.008 moles, i.e. 1.5 mole equivalents) were added with stirring keeping the RBF in water bath. Reaction was monitored on TLC. For monitoring the reaction a small amount of sample was taken from well stirred reaction mixture. Sample was neutralized with $NaHCO_3$. Then it was extracted with ethyl acetate and spotted on TLC. TLC was developed with 5% ethyl acetate: hexane (v/v). After completion of the reaction 20 mL of water was added to the reaction flask. Reaction mass was then filtered through Whatman nylon membrane filter (pore size 0.2 μm). This was thoroughly washed with water twice and the water filtrate was discarded. Then the precipitate was washed with 5 mL ethanol and then with ethyl acetate to extract the product. The ethyl acetate was evaporated and solid was then crystallized with ethyl alcohol. Pure product thus formed was dried and weighed.

c) **General experimental procedure for bromination of anilines and phenols using molecular bromine:** In typical experiment of bromination of anilines and phenols, in 50 mL round bottomed flask 10 mL of water 10 mg (2% by weight of substrate) of GO were taken and it was dispersed in water by sonication. To the flask, substrate (0.5 g) was added dropwise (or finely powdered solid) and stirred well. To this, bromine (1.5 mole equivalent or as required) was added dropwise keeping the flak in water-bath. The reaction was monitored on TLC and showed complete conversion w.r.t. starting material within 10 to 35 minutes. To the reaction mass 20 mL of water was added on completion of reaction. It was then filtered through Whatman nylon membrane filter (pore size 0.2 μm). The precipitate was washed with water twice. The water filtrate was discarded. The residual solid was washed with ethanol (2 mL) and then thoroughly with ethanol (8 mL) or ethyl acetate (7-8 mL) (depending on solubility of product). The products were crystallized from the filtrate itself, if the washing solvent is ethanol. Product was obtained by evaporating ethyl acetate under reduced pressure. The crude product was recrystallized from ethanol (5-8 mL). The optimized conditions were applied for synthesis of varied anilines and phenols. All the products were isolated by filtration and washing with appropriate solvent (ethyl alcohol/ethyl acetate). Pure products were obtained by recrystallization. Melting points were obtained and are uncorrected. Products were further conformed by mass, ^{1}H and ^{13}C NMR.

d) **Procedure for recycling the catalyst:** The catalyst was recovered from the membrane filter paper after washing the product from it with a suitable solvent. It was dried in the oven at 65-70 °C for two hours. Thus dried GO was ready for reuse in next batch.

e) **Experimental procedure for bromination of anilines using N-bromosuccinimide (NBS):** 10 mg of GO was dispersed in 10 mL of water by sonication. To this, substrate was added and stirred thoroughly. NBS (3 mole equivalent) was added to the reaction mixture while resting the flask in water bath. Reaction was monitored on TLC and was completed within five minutes.

f) Experiments in support of the mechanisms:

i) Reaction using radical scavenger: To authenticate the mechanistic pathway, we have performed experiments using butylated hydroxyl toluene (BHT) as a radical scavenger. In RBF 10 mL water was taken. To this GO was added and sonicated to exfoliate. Then aniline was added to it with vigorous stirring. To this mixture BHT 3 mole equiv. was added. The reaction mixture was stirred well. Now to this bromine or NBS was added and reaction was stirred for optimized reaction time. Reactions were worked up and the results are tabulated in table S1. In both the cases with Br_2 and NBS, reactions proceed with normal course.

ii) Reaction under inert atmosphere, (N_2): To understand the role of oxygen (air) we carried out reaction under inert atmosphere. In typical experiment, GO was sonicated in water and aniline was adsorbed onto it. Then N_2 was purged into the reaction media for an hour before addition of bromine. Subsequently the reaction was carried out under N_2 for 30 minutes. Reaction was worked up and products are tabulated in Table 3.

iii) Reaction using KBr as bromide source: To check the oxidative capacity of GO for oxidizing Br^- to Br^+, we performed the reaction using KBr as a bromide source. In typical experiment after adsorption of aniline SDS was added to the reaction mixture. Reaction was carried out at room temperature using KBr for 12 hours. Reaction was worked up and products were GC analyzed. In another experiment reaction was heated at 60 °C for 12 hours. Products are analyzed by gas chromatography. Products were analyzed by GCMS.

iv) A reaction without substrate was done to know the effect of bromine on surface of catalyst. In 10 mL water 10 mg of GO was exfoliated by sonication, and bromine (1.29 g) was added. Reaction mass was stirred for 30 minutes at ambient temperature. The catalyst was filtered and washed four times with deionized water to ensure removal of adsorbed bromine. It was dried in oven at 50 °C for an hour. Sample of thus formed catalyst was analyzed with FTIR.

Similarly, to compare the effect of bromine on surface of catalyst in presence of substrate, a sample of GO after first use was analyzed by FTIR.

Compound characterization data:

1. **2,4,6-tribromoaniline (1A)[4]:** (Solid, faint brown, yield = 1.69 g, 93%), Melting point = 121°C (120°C). ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.51 (s, 2H), 4.57 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 167.38, 140.98, 133.91, 108.77; GC-MS (EI, 70 eV) m/z = 329 (M$^+$), 265, 250,168, 90, 62, 52.

2. **2,6-dibromo-4-chloroaniline (2A)[52]:** (Solid, white, yield = 1.02 g, 91%), Melting point = 95°C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.39 (s, 2H), 4.55 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 140.91, 131.19 , 122.57 , 108.36; GC-MS (EI, 70 eV) m/z = 285 (M$^+$),206, 124, 90, 62.

3. **2,6-dibromo-4-nitroaniline (3A)[4]:** (Solid, yellow, yield = 0.98 g, 92%) Melting point = 206°C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 8.35 (s, 1H), 5.30 (s, 1H); ^{13}C NMR (101 MHz, DMSO) δ 149.62, 136.91, 128.41, 105.77; GC-MS (EI, 70 eV) m/z = 296 (M$^+$), 266, 250, 168, 90, 63, 52.

4. **2,6-dibromo-4-butylaniline (4A)[53]:** (Solid, dark red, yield = 0.99 g, 98%) Melting point = 119°C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.20 (s, 2H), 4.40 (s, 7.5 Hz, 2H), 2.46 (t, 2H), 1.53 (quintet, J = 15.3, 7.5 Hz, 2H), 1.33 (sextet, J = 14.6, 7.3 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 139.61, 134.53, 131.52, 108.72, 34.06, 33.50, 22.10, 13.84; GC-MS (EI, 70 eV) m/z = 309 (M$^+$), 264, 183, 104, 90, 77, 65, 52.

5. **2,4-dibromo-6-chloroaniline (5A)[54]:** (Solid, reddish brown, yield = 1.06 g, 95%) Melting point = 103°C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48 (d, J = 2.1 Hz, 1H), 7.37 (d, J = 2.1 Hz, 1H), 4.52 (s, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 140.39 (s), 133.10, 130.85, 119.59, 109.20, 108.36; GC-MS (EI, 70 eV) m/z = 285 (M$^+$), 206, 168, 124, 90, 62, 52.

6. **2,4,6-tribromo-3-nitroaniline (6A)[18]:** (Solid, yellow, yield =1.13 g, 84%) Melting point = 98°C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.70 (s, 1H), 4.92 (s, 2H); ^{13}C NMR (101 MHz, DMSO) δ 151.44, 144.87, 135.29, 109.54, 98.01, 96.41; GC-MS (EI, 70 eV) m/z = 374 (M$^+$), 328, 316, 301, 265, 249, 214, 168, 89, 61, 52.

7. **2,4,6-tribromo-3-methoxyaniline (7A)[55]:** (Solid, buff, yield =1.39 g, 95%) Melting point = 83°C. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (s, 1H), 4.65 (s, 2H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$)

δ 153.98, 142.73, 134.06, 104.76, 104.02, 103.50, 60.46; GC-MS (EI, 70 eV) m/z = 359 (M^+), 316, 199, 156, 76, 61, 52.

8. 2,6-dibromo-4-methylaniline (8A)[4]**:** (Solid, white, yield = 1.14 g, 92%) Melting point = 78°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (s, 2H), 4.39 (s, 2H), 2.22 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.49, 132.12, 129.29, 108.68, 19.77; GC-MS (EI, 70 eV) m/z = 267 (M^+), 184, 104, 92, 77, 65, 52.

9. 3-amino-2,4,6-tribromobenzoic acid (9A)[56]**:** (Solid, buff, yield = 1.28 g, 94%) Melting point = 170°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (s, 1H), 4.77 (s, 2H); ^{13}C NMR (101 MHz, DMSO) δ 167.21, 143.39, 139.14, 134.49, 108.01, 104.13, 102.67; GC-MS (EI, 70 eV) m/z = 375 (M^+), 329, 250, 168, 90, 62, 52.

10. 2,4-dibromo-3,6-dichloroaniline (10A)[57]**:** (Solid, buff, yield = 0.96 g, 98%) Melting point = 89°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 4.72 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.89, 133.64, 131.56, 117.33, 109.51, 108.73; GC-MS (EI, 70 eV) m/z = 319 (M^+), 240, 204, 159, 124, 89, 61, 52.

11. 2,4,6-tribromo-3-nitrophenol (1P)[58]**:** (Solid, grey, yield = 1.21 g, 90%) Melting point = 130°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (s, 1H), 6.23 (s, 1H); ^{13}C NMR (101 MHz, DMSO) δ 152.83, 151.39, 135.84, 115.30, 104.69, 102.23; GC-MS (EI, 70 eV) m/z = 374 (M^+), 330, 301, 268, 250, 237, 221, 168, 140, 90, 77, 61, 53.

12. 2,4,6-tribromophenol (2P)[4]**:** (Solid, white, yield = 1.69 g, 96%) Melting point = 95°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 2H), 5.88 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.92, 134.19, 112.65, 110.38; GC-MS (EI, 70 eV) m/z = 332 (M^+), 250, 222, 141, 111, 91, 62, 53.

13. 2,4-dibromo-6-chlorophenol (3P)[59]**:** (Solid, white, yield = 1.09 g, 98%) Melting point = 92°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 2.2 Hz, 1H), 7.46 (d, J = 2.2 Hz, 1H), 5.87 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.15, 133.56, 131.37, 121.49, 112.18, 110.79; GC-MS (EI, 70 eV) m/z = 286 (M^+), 250, 222, 206, 178, 143, 97, 62, 53.

14. **2,4-dibromo-6-nitrophenol (4P)[60]:** (Solid, yellow, yield = 1.02 g, 96%) Melting point = 110°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.06 (s, 1H), 8.26 (d, J = 2.4 Hz, 1H), 8.00 (d, J = 2.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.37, 142.88, 134.34, 126.71, 114.48, 111.48; GC-MS (EI, 70 eV) m/z = 297 (M^+), 265, 239, 223, 170, 141, 91, 62, 53.

15. **3,5-dibromo-4-hydroxybenzaldehyde (5P)[61]:** (Solid, buff, yield = 1.02 g, 96%) Melting point = 182°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.81 (s, 1H), 8.01 (s, 2H), 6.43 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.04, 154.34, 133.61, 110.70; GC-MS (EI, 70 eV) m/z = 279 (M^+), 251, 223, 170, 143, 91, 63, 53.

16. **3,5-dibromo-2-hydroxybenzoic acid (6P)[18]:** (Solid, white, yield = 0.97 g, 98%) Melting point = 226°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 2H), 5.88 (s, 1H); ^{13}C NMR (101 MHz, DMSO) δ 170.71, 158.10, 139.70, 132.06, 117.22, 112.08, 109.60; GC-MS (EI, 70 eV) m/z = 297 (M^+), 252, 133, 119, 105, 91, 71, 57, 43, 41.

17. **3,5-dibromo-4-hydroxybenzoic acid (7P)[62]:** (Solid, white, yield = 0.88 g, 89%) Melting point = 272°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 2H), 5.89 (s, 1H); ^{13}C NMR (101 MHz, DMSO) δ 151.35, 134.45, 113.41, 111.50; GC-MS (EI, 70 eV) m/z = 295 (M^+), 230, 252, 204, 147, 119, 105, 91, 71, 57, 43, 41.

18. **2-bromo-4-chloro-6-nitrophenol (8P)[46]:** (Solid, yellow, yield = 0.69 g, 95%) Melting point = 117°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.04 (s, 1H), 8.12 (d, J = 2.5 Hz, 1H), 7.87 (d, J = 2.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.97, 140.34, 133.90, 125.26, 123.76, 114.21; GC-MS (EI, 70 eV) m/z = 253 (M^+), 236, 206, 195, 179, 126, 113, 97, 73, 62, 53.

19. **3,5-dibromo-2-hydroxybenzaldehyde (9P)[53]:** (Solid, pale brown, yield = 1.10 g, 96%) Melting point = 82°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.52 (s, 1H), 9.82 (s, 1H), 7.91 (d, J = 2.3 Hz, 1H), 7.67 (d, J = 2.3 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.86, 157.15, 141.85, 134.86, 121.80, 112.42, 111.48; GC-MS (EI, 70 eV) m/z = 280 (M^+), 223, 170, 155, 143, 119, 63, 53.

20. 2-bromo-4-methyl-6-nitrophenol (10P)[53]: (Solid, yellow, yield = 0.667 g, 88%) Melting point = 68°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.98 (s, 1H), 7.91 (s, 1H), 7.71 (s, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.99, 141.68, 133.71, 130.59, 123.97, 112.74, 20.10; GC-MS (EI, 70 eV) m/z = 231 (M^+), 186, 135, 94, 77, 65, 51.

Supporting Information. Characterization of GO, NMR and Mass spectral graphs.

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