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Amplification of Trichloroisocyanuric Acid (TCCA) Reactivity for Chlorination of Arenes and Heteroarenes via Catalytic Organic Dye Activation

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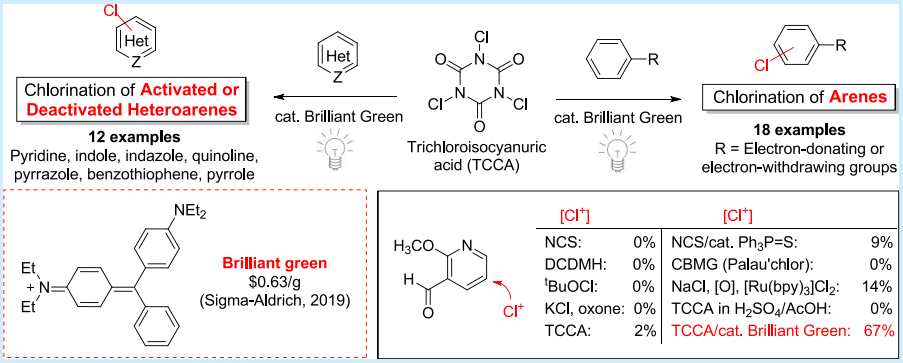
Supporting Information



ABSTRACT: Heteroarenes and arenes that contain electron-withdrawing groups are chlorinated in good to excellent yields (scalable to gram scale) using trichloroisocyanuric acid (TCCA) and catalytic Brilliant Green (BG). Visible-light activation of BG serves to amplify the electrophilic nature of TCCA, providing a mild alternative approach to acid-promoted chlorination of deactivated (hetero)aromatic substrates. The utility of the TCCA/BG system is demonstrated through comparison to other chlorinating reagents and by the chlorination of pharmaceuticals including caffeine, lidocaine, and phenazone.

Direct electrophilic chlorination at predictable locations represents an important transformation in the fine chemical synthesis of complex small molecules within the areas of pharmaceuticals, natural products, advanced materials, and agrochemicals.[1,2] In the realm of drug discovery and development, chlorine installation can assist in the modulation of electronic and physical properties resulting in chlorinated end-products such as in Figure 1.[2] The introduction of chlorine can also serve to produce synthetic intermediates that contain a chemical handle for subsequent transformations such as cross-coupling reactions.[2b,3,4] A number of methods are available for chlorination; however, the desire for a highly practical, regioselective, and inexpensive method of arene and heteroarene chlorination (especially for less reactive, deactivated substrates) remains high due to the sheer ubiquity and utility of these targets.

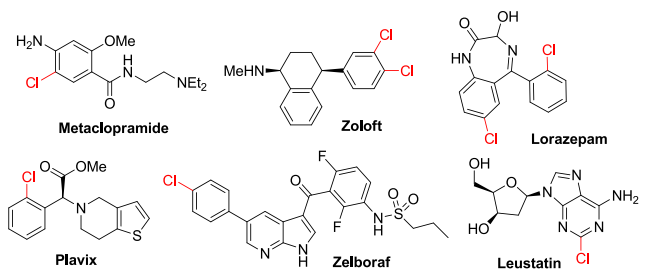


Figure 1. Pharmaceuticals that contain chlorinated arenes and heteroarenes.

Predictable chlorination of aromatic substrates is best accomplished by directed metalations;[3,5] however, these methods require prefunctionalized directing groups, strong bases, or have limited substrate scopes. A complementary approach that avoids the use of a prefunctionalized directing group involves the direct C(sp^2)−H "Friedel-Crafts" electrophilic aromatic substitution (S_EAr) using an electrophilic chlorinating "Cl^+" reagent.[6] Classical reagents that serve as electrophilic chlorine sources range from highly reactive but unselective and hazardous (Cl_2, SO_2Cl_2, ^{t}BuOCl)[7] to practical but less reactive [N-chlorosuccinimide (NCS) and 1,3-dichloro-5,5-dimethylhydantoin (DCDMH)].[8] To achieve selective monochlorination of arenes, the practical reagents are frequently chosen. However, limitations exist that can include the required use of a harsh Lewis or Bronsted acid for reagent activation, high temperatures, and/or the reliance upon

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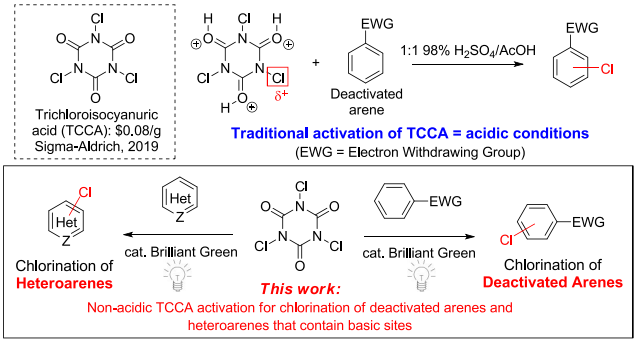
activated (electron-rich) arene substrates.[9] A number of notable additions to the reagent toolkit for mild chlorination have been recently developed including CBMG (Palau'-chlor),[10] 1-chloro-1,2-benziodoxol-3-one,[11] CFBSA,[12] and the use of anionic chloride with an oxidant,[13] among others.[8b,14]

With regard to atom economy, stability, safety, and cost, trichloroisocyanuric acid (TCCA) is an attractive source of electrophilic chlorine (Scheme 1).[15] TCCA has been used for

Scheme 1. General Scheme of Traditional Acidic Activation and the VLPC Approach to TCCA Activation for Chlorination of Arenes and Heteroarenes

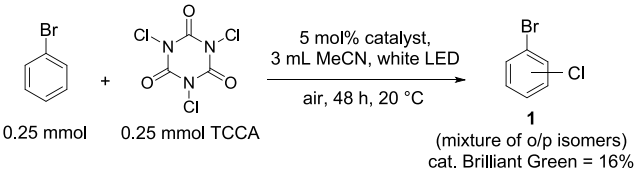


aromatic C−H chlorination, though the reaction is largely limited to electron-rich (activated) substrates, and in some examples, long reaction times are required.[16] Similar to other preformed N-halogen sources such as *N*-chlorosuccinimide, harsh acidic conditions (1:1 conc. H_2SO_4/HOAc solvent) are necessary in order to chlorinate electron-deficient (deactivated) arenes with TCCA (Scheme 1).[17] These conditions offer efficient pathways for bulk chlorination of relatively simple deactivated arenes, but would be unlikely to provide a viable method for late-stage functionalization of complex molecules, or for heterocyclic substrates with a heteroatom capable of coordinating a Lewis/Bronsted acid.

Following our interest in nitrogen-centered radical (NCR) chemistry,[18] we sought to investigate the utilization of visible-light photocatalysis (VLPC) as a viable alternative to using an external acid in order to amplify the chlorine electrophilicity of TCCA (Scheme 1). Visible-light photocatalysis is a field that has received a great deal of attention as a means to induce single electron transfer (radical) reactions under mild and practical operating conditions.[19] In recent reports from our research group and the Konig group, a VLPC approach has been employed with N-halo succinimide reagents (N−Cl and N−Br) in which an activated cationic radical is produced by a one-electron oxidation via a photoredox catalyst, thus inducing a strong positive polarization on the electrophilic halogen.[20,21] Currently, examples of aromatic C−H chlorination using a VLPC approach are rare and largely limited to electron-rich aromatic substrates.[13b,d,20,22] To our knowledge, there have been no reports to date of VLPC-mediated chlorination of heteroarene substrates. Herein, we describe a light-promoted activation of TCCA that utilizes brilliant green, an inexpensive organic dye, as a photocatalyst for C(sp^2)−H chlorination of deactivated (and activated) arenes and heteroarenes without a harsh external Bronsted/Lewis acid or oxidizing agent.

To begin our investigation, bromobenzene was selected as a representative electron-deficient arene to test for chlorination with TCCA (Scheme 2). Initial reaction conditions for catalyst screening were selected to offer operationally convenient and

Scheme 2. Initial Conditions Used in the Screening of Catalysts for the Chlorination of Bromobenzene by TCCA



practical settings (1:1 stoichiometry, ambient temp, open to air, 48 h). No chlorination of bromobenzene was observed over 48 h with TCCA in the absence of activation by either acid or catalyst. A number of VLPC catalysts and organic dyes were screened for activity (see Supporting Information (SI), Table S1), and to our delight a 16% yield of chlorinated product **1** (mixture of isomers) was observed when using brilliant green (BG) as catalyst. Brilliant green is a member of the triarylmethane family of dyes used as an industrial colorant and as an antimicrobial agent.[23] Triphenylmethane dyes have attracted attention for their optical and excited-state properties,[23b,24] though, to our knowledge, this work describes the first report of BG as a VLPC catalyst.

Using brilliant green as catalyst, the optimized reaction stoichiometry for a representative deactivated arene was determined. Using chlorobenzene as a test substrate, the best conversion and yield were found using 3 equiv of TCCA, 10 mol % BG in acetonitrile at ambient temperature for 48 h in a white LED photochamber (see SI, Table S2). However, the application of these conditions to a less electron-deficient arene (such as naphthalene) resulted in a significant amount of dichlorinated product. Therefore, an optimization of reaction conditions was performed using a relatively electronically neutral arene, naphthalene **2**, and is presented in Table 1. As a result of surveying the substrate stoichiometry, catalyst loading, and solvents, the best conversion to 1-chloronaphthalene **3** was obtained using 1.5 equiv of naphthalene, 1 equiv of TCCA, and 4 mol % BG, in acetonitrile and open to air using a white LED photochamber for 8 h at ambient temperature.

With optimized reaction conditions, we set out to explore the substrate scope (Figure 2). Monosubstituted benzene derivatives with electron-withdrawing (EWG) or -donating groups (EDG) were tested, and as a general rule, substrates with an EWG required longer reaction times and a larger excess of TCCA and BG (Figure 2, products **1**, **4**−**6**). Attempts to chlorinate the aromatic ring of nitrobenzene and acetophenone, two strongly deactivated arenes, were unsuccessful. Substrates with an EDG such as anisole proceed rapidly and more efficiently than the background (uncatalyzed) reaction to produce a mixture of chlorinated isomers consistent with an S_EAr mechanism. Naphthalene derivatives with an EWG or EDG resulted in moderate to excellent yields of monochlorinated products (Products **3**, **7**−**9**). 2-Methylnaphthalene was cleanly converted to **8** without any observation of benzylic chlorination.[25] Next, a series of disubstituted benzene derivatives were tested. In examples **10**−**17**, one of the substituents on the ring is an electron-withdrawing group. Compound **10** was prepared in gram scale without a decrease in efficiency. The pesticide chloroxynil[26] **11** was prepared in 79% yield without degradation of the nitrile group. Of particular interest is the ability shown by the method to selectively monochlorinate *p*-methoxyanisaldehyde (**16**) using conditions optimized for naphthalene, or dichlorinate (**17**)

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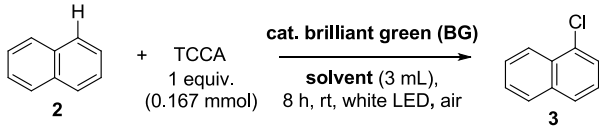
Table 1. Optimization of Reaction Conditions for Chlorination of Naphthalene



entry[a]	equiv 2	BG (mol %)	solvent	conv 2[b] (%)	yield 3[b] (%)
1	1	2	MeCN	100	47
2	3	2	MeCN	45	29
3	1.5	2	MeCN	83	66
4	1.5	5	MeCN	97	59
5	1.5	10	MeCN	84	49
6	1.5	15	MeCN	49	23
7	1.5	20	MeCN	29	11
8	**1.5**	**4**	**MeCN**	**100**	**86**
9	1.5	0	MeCN	37	24
10	1.5	4	MeOH	97	67
11	1.5	4	DMF	99	48
12	1.5	4	DCM	56	54
13	1.5	4	9:1 MeCN/H_2O	100	57
14	1.5	4	MeCN (1.5 mL)	100	85
15	1.5	4	MeCN (6 mL)	100	86

[a]Entries 1−3: 6 h reaction time. [b]Conversion of naphthalene **2** and yield of 1-chloronaphthalene **3** determined by GC integration using adamantane as internal standard (see Supporting Information).

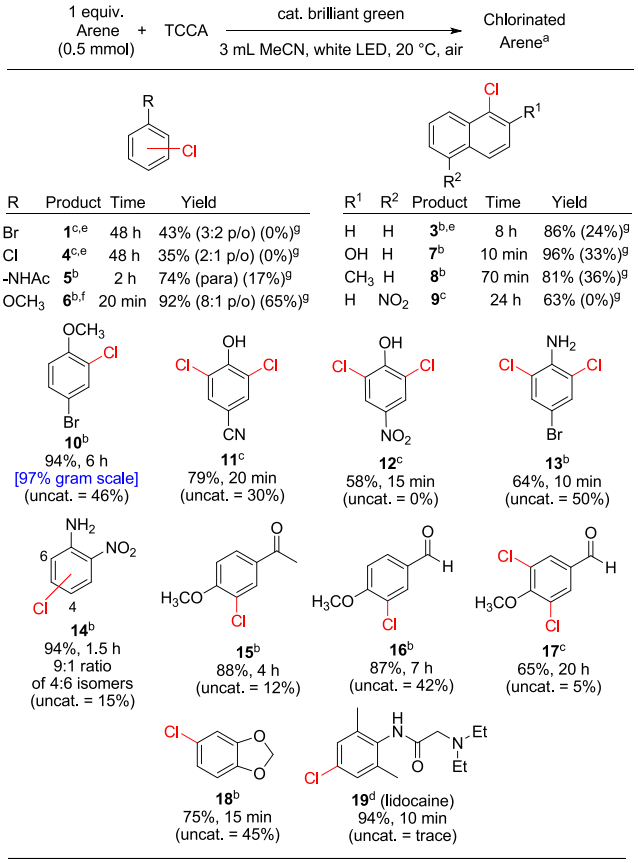


Figure 2. Substrate scope: chlorination of arenes. [a]All products are isolated unless otherwise noted. Reaction times for each product correspond to full conversion of arene substrate. Uncatalyzed yields are determined by ^{1}H integration using nitrobenzene as internal standard, or by GC using adamantane as internal standard. [b]0.67 equiv of TCCA, 0.03 equiv of BG. [c]3 equiv of TCCA, 0.10 equiv of BG. [d]0.36 equiv of TCCA, 0.03 equiv of BG. [e]GC yields calculated using adamantane as internal standard. [f]^{1}H NMR integration yield using nitrobenzene as internal standard. [g]Uncatalyzed yield is shown in parentheses.

using the set of conditions optimized for chlorobenzene. Lidocaine, a pharmaceutical anesthetic, was selectively chlorinated to produce **19** in marked contrast to the background reaction in 10 min. As an indication of the mildness of the method, a number of functional groups are tolerated by the chlorination including halogens, carbonyls (ketone, aldehyde, amide), phenol, ethers, amines, nitro, nitrile, and benzylic C−H's.

To further explore the substrate scope, we turned our attention to heterocycles (Figure 3). The traditional method of activation of TCCA under acidic conditions[17] is incompatible with many heterocycles due to the presence of a basic coordinating site on the arene substrate. However, we found the TCCA/BG system to result in efficient chlorination of a broad range of heterocyclic cores that are considered privileged scaffolds in drug discovery and medicinal chemistry.[27] For example, pyridine derivatives (**20**−**22**) were chlorinated cleanly. To our knowledge, this is the first report of the direct chlorination of 2,4,6-collidine to produce **21**, and no evidence of benzylic chlorination was observed. Additional privileged scaffolds such as quinoline and indole were chlorinated cleanly with no byproducts of benzylic chlorination or aldehyde/ester decomposition (**23**−**25**). Indazoles and pyrazoles, including the pharmaceutical antipyrine (phenazone),[28] were chlorinated with significant improvement over the background reaction (**27**−**29**). Finally, caffeine was chlorinated at the 8-position under relatively mild conditions to produce **31**. In comparison to CBMG (Palau'chlor),[10] which is a state-of-the-art chlorinating agent for heteroarene substrates, the TCCA/BG system provides a powerful alternative for heteroarene chlorination (yields using CBMG shown in Figure 3 and in SI, Table S3). In general, chlorination using TCCA/BG occurs in significantly decreased reaction times compared to CBMG, and in several examples, chlorination was only observed when using the TCCA/BG system. Finally, it is noteworthy that chlorination with TCCA/BG reliably results in predictable regioselective chlorination consistent with S_EAr, indicating that TCCA is serving as an amplified source of Cl^+ as opposed to a chlorine radical.

A comparison of the TCCA/BG system to other state-of-the-art methods of chlorination is shown in the TOC and in more detail in the Supporting Information Table S4. 2-Methoxy-3-pyridinecarboxaldehyde was selected as a test substrate, and a variety of reported reagents and catalysts were employed in an effort to produce chlorinated product **20**. The results of our study indicated that the TCCA/BG system produced the highest yield of **20** (67% by ^{1}H NMR integration; 2.5 h) without observed decomposition of the substrate or oxidation of the aldehyde functionality that was detected from many of the other chlorinating systems.

To investigate the role of light in the TCCA/BG reaction, a series of light and air dependent control reactions was performed (Scheme 3). 2-Methoxy-3-pyridinecarboxaldehyde was chosen as a test substrate due to the significant enhancement observed between the catalyzed (63% of **20**) and noncatalyzed (2% of **20**) reactions. In addition to the BG

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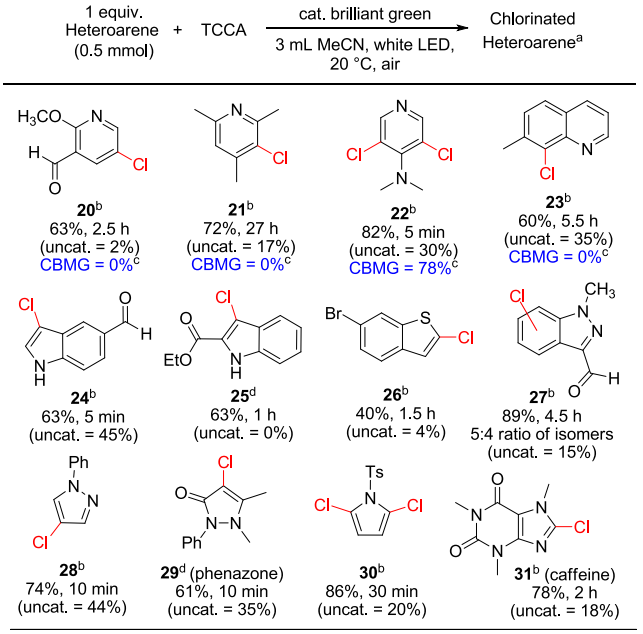
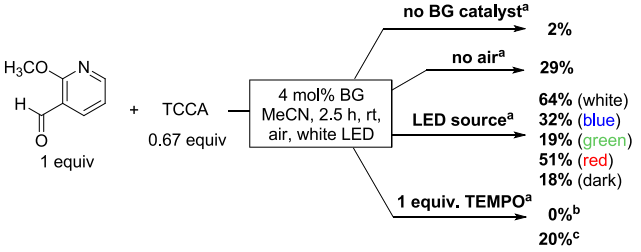


Figure 3. Substrate scope: chlorination of heteroarenes. [a]All products are isolated unless otherwise noted. Reaction times for each product correspond to full conversion of arene substrate. Uncatalyzed yields are determined by ^{1}H integration using nitrobenzene as internal standard. [b]0.67 equiv of TCCA, 0.03 equiv of BG. [c]1.2 equiv of CBMG, 20 °C, 12 h, in $CDCl_3$. Yield calculated from ^{1}H NMR integration using nitrobenzene as internal standard. [d]0.36 equiv of TCCA, 0.03 equiv of BG.

Scheme 3. Control and Mechanistic Experiments

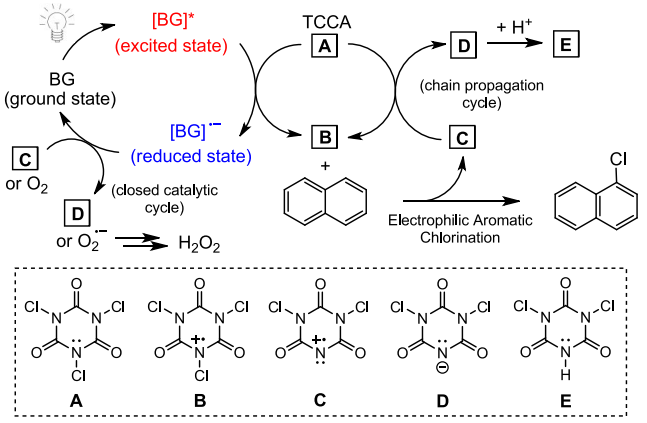


[a]Yields of product **20** were quantified via ^{1}H NMR integration using $PhNO_2$ as internal standard. All reactions were run in triplicate, and the yield is an average of three trials. [b]TEMPO added at t = 0. [c]Isolated yield; TEMPO was added to an incomplete reaction at t = 1 h, and the reaction was continued an additional 1.5 h.

catalyst, air also appears to play a role in the reaction, indicating the possible role of O_2 as an oxidant to regenerate a catalytic species. Production of hydrogen peroxide, evidence of the formation of a superoxide anion, was confirmed by the iodide test (SI, Figure S2). A significant reduction in the yield of **20** was observed when performing the reaction using either green LED, blue LED, or dark conditions (Scheme 3). Red LED activation, however, resulted in the most efficient formation (apart from white LED) of **20** at 51%. The λ_{max} absorbance of BG is observed at 622 nm in acetonitrile, which indicates that the low energy red LED wavelength is being absorbed and utilized by BG in the system. Next, a "light/dark" experiment was conducted to determine if a chain process occurs in the mechanism. The results of the experiment (shown in SI, Scheme S1) confirm the occurrence of chain propagation.[29] Finally, the addition of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a known radical inhibitor, halted the formation of product **20** at t = 0 and t = 1 h (a reaction in progress). These results indicate a significant role of the BG catalyst in a visible-light activated system that appears to involve a radical species.

A plausible mechanism that is based upon observations of preliminary mechanistic experiments and literature reports of related systems[20,21] involves the one-electron oxidation of TCCA **A** to produce an amplified electrophilic chlorine species **B** for chlorination of aromatic substrates (Scheme 4). Either **C** or oxygen can be responsible for returning the reduced BG to its ground state.

Scheme 4. Plausible Mechanism



In conclusion, a new electrophilic chlorination of electron-deficient (deactivated) and electron-rich arenes and heteroarenes using TCCA and catalytic Brilliant Green, an inexpensive organic dye, has been developed. The reaction operates under mild, nonacidic conditions and is promoted by visible light. A variety of chlorinated aromatics were prepared in good to excellent yields with a broad tolerance of functionalities. In comparison to other chlorinating agents, the TCCA/BG system serves as a valuable complementary method and, in many examples, provides a superior alternative for arene and heteroarene chlorination.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.9b01414.

Experimental details, compound characterization, ^{1}H and ^{13}C NMR, GC chromatograms (PDF)

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Notes

The authors declare no competing financial interest.

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