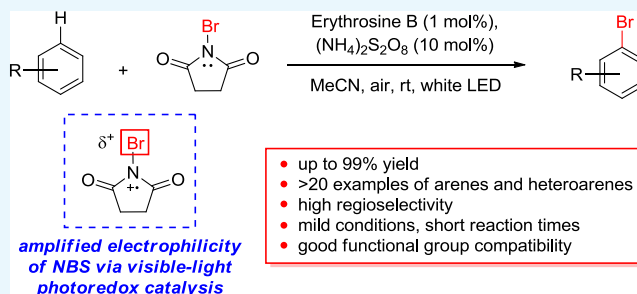# Organic Dye-Catalyzed, Visible-Light Photoredox Bromination of Arenes and Heteroarenes Using *N*-Bromosuccinimide

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S Supporting Information

ABSTRACT: A variety of arenes and heteroarenes are brominated in good to excellent yields using *N*-bromosucci-nimide (NBS) under mild and practical conditions. According to mechanistic investigations described within, the reaction is speculated to proceed via activation of NBS through a visible-light photoredox pathway utilizing erythrosine B as a photocatalyst. A photo-oxidative approach effectively amplifies the positive polarization on the bromine atom of the NBS reagent. This increase in the electrophilic nature of NBS results in drastically reduced reaction times and diversion from competing light-promoted reactive pathways.

amplified electrophilicity of NBS via visible-light photoredox catalysis

- up to 99% yield
- >20 examples of arenes and heteroarenes
- high regioselectivity
- mild conditions, short reaction times
- good functional group compatibility

INTRODUCTION

Aryl bromides are found as valuable end-targets in a variety of synthetic applications including pharmaceuticals, natural products, agrochemicals, and advanced materials (Figure 1).[1−3] In addition, brominated arenes function as important
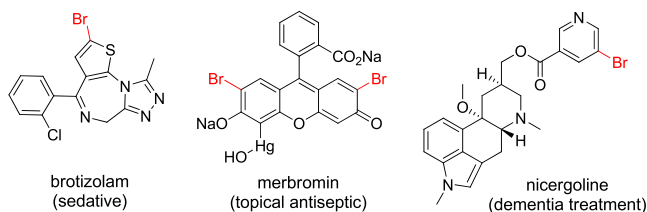
Figure 1. Representative examples of pharmaceutical compounds containing aryl bromide functionality.

precursors in a variety of synthetic transformations including S$_N$Ar-type halogen displacements[4] and cross-coupling reactions (Suzuki−Miyaura,[5] Heck,[6] Stille,[7] Sonogashira,[8] and Buch-wald−Hartwig[9,10]).

Because of the ubiquity of these synthetic building blocks, the predictable and selective installation of bromine into aromatic scaffolds under mild and practical reaction conditions has received constant attention from the synthetic community. Traditionally, bromination of arenes is accomplished through pathways that include Friedel−Crafts-type electrophilic aromatic halogenation,[11,12] organometallic-mediated or tran-sition metal-catalyzed approaches,[1,13] or Sandmeyer-type reactions of diazonium salts.[14] The most convenient and popular approach, electrophilic aromatic halogenation, typi-cally involves either the use of elemental bromine under harsh conditions, an electrophilic "Br$^+$" species (including N-halo

reagents), or a source of anionic bromide in conjunction with a potentially hazardous and/or corrosive oxidizing agent.[11,12,15−19] *N*-Bromosuccinimide (NBS) is a widely used example of an N-halo brominating agent because of its practicality, low cost, and relative stability. Within the family of *N*-halosuccinimides, NBS is a more reactive electrophilic halogen source than either *N*-chlorosuccinimide (NCS) or *N*-iodosuccinimide and can be used to brominate highly electron-rich aromatics under relatively mild conditions in polar solvents.[20−22] Although NBS is more reactive in electrophilic aromatic substitution reactions than analogous succinimide reagents, it is also more capricious with regard to reaction conditions. Long reaction times may be required because of precautions (dark environments, low temperatures) that are necessary to discourage other competing light-activated, radical pathways (including radical oxybromination at benzylic positions and C−H bonds α to a ketone carbonyl).[18,19,23] In addition, for aromatic substrates that are less electron-rich, activation of the *N*-halosuccinimide reagent by an external acid may be required. In such an example, a strong Bronsted or Lewis acid is used to coordinate the O atom of the succinimide, which draws the electron density away from the halogen, thus amplifying the electrophilicity of the halogen by increasing the N−X bond polarization (Scheme 1, Path A).[24−27]

As an alternative approach to electrophilic amplification via acidic activation, we have found inspiration in recent reports in which halogenating reagents are activated under visible-light photoredox catalysis (VLPC) conditions.[28−32] König's Ru(II)-

Scheme 1. General Scheme of Traditional Acidic Activation of NBS and Oxidative Activation by Photoredox Catalysis (PC = Photocatalyst; SET = Single Electron Transfer)
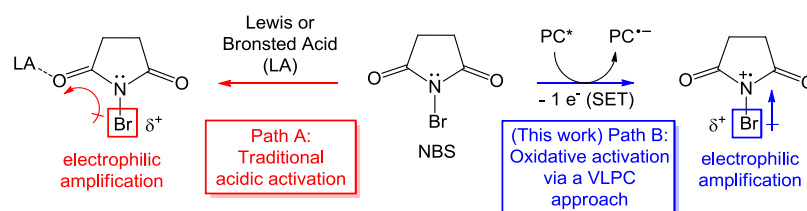
catalyzed photoredox approach to NCS activation relies upon the oxidation of an N-chloro reagent to produce an activated cationic N-radical, thus inducing strong positive polarization (δ^+) that amplifies the electrophilicity of the halogen atom.[29] The use of a similar VLPC approach toward bromination would offer a mild catalytic alternative for N-bromo reagent activation without the requirement of an external acid (Scheme 1, Path B). Therefore, in following our research group's interest in developing synthetic methodologies that utilize N-centered radical species,[33−42] we turned our attention toward the production of a cationic N-radical species from NBS using a visible-light photoredox catalyst.

VLPC has attracted intense attention from the synthetic community as a mild means of initiating transformations involving electron-transfer pathways.[43−46] In the recent expansion in the field of VLPC, the majority of synthetic applications have been dominated by the use of transition metal complexes such as Ru(II) and Ir(III) bipyridyl complexes. Transition metal complexes offer the ability to electronically tune a complex by control of the coordinating ligand and are generally well-understood with regard to electrochemical, kinetic, and spectroscopic information.[43,45] However, these widely employed transition metal complexes may require synthesis or are costly if commercially available. As an attractive complement to metal-catalyzed VLPC systems, a number of organic dyes have been shown to exhibit efficient, and in some cases, superior reactivity to the transition metal catalysts at a fraction of the cost.[44,47−54] To date, the majority of organic dyes employed as visible-light photocatalysts for synthetic applications belong to the azine (methylene blue), acridinium (9-mesityl-10-methylacridinium salts), quinone (DDQ), or xanthene (eosin Y, erythrosine B, and rose bengal) structural classes (Figure 2).[44]
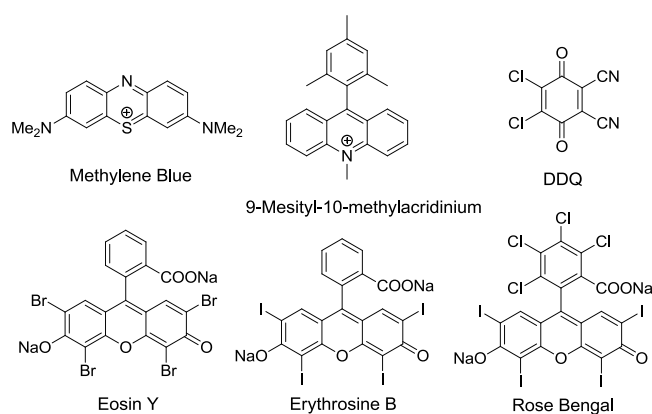
Herein, we report a new pathway for mild, electrophilic bromination of arenes and heteroarenes that utilizes the organic dye, erythrosine B, as a visible-light photoredox catalyst to amplify the electrophilicity of NBS. The method complements existing strategies and offers practical advantages in examples in which either nonacidic activation of NBS or the prevention of byproducts from unwanted light-promoted radical pathways is desired.

RESULTS AND DISCUSSION

To begin our investigation, a representative aromatic substrate (naphthalene **1**) was selected for bromination using NBS **2**, and a number of organic dyes were screened as catalysts. Initial settings were chosen that offered operationally convenient and practical conditions (ambient temperature, open to air, 24 h). To our delight, several catalysts promoted the formation of 1-bromonaphthalene **3** more effectively than the uncatalyzed background reaction (Table 1).
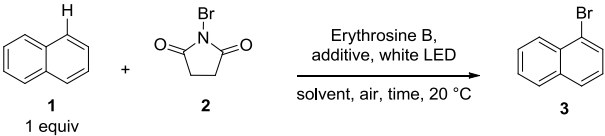
Table 1. Screening of VLPC Catalysts in the Bromination of Naphthalene with NBS

entry[a]	catalyst	% **3**[b]	entry[a]	catalyst	% **3**[b]
1	none	48	11	methylene blue	18
2	acridine orange	15	12	methylene green	77
3	azure A	31	13	Nile blue A	67
4	brilliant cresyl blue	27	14	pyronin Y	64
5	brilliant green	55	15	rhodamine 6G	61
6	DDQ	19	16	rhodamine B	60
7	eosin Y	0	17	rose bengal	87
8	**erythrosine B**	**94**	18	safranin O	54
9	fluorescein	58	19	thionin	71
10	9-mesityl-10-methylacridinium	75	20	[Ru(bpy)₃]Cl₂	0

[a]Conditions: 0.25 mmol naphthalene, 0.25 mmol NBS, 0.0125 mmol catalyst, 3 mL MeCN, air, 20 °C, white light-emitting diode (LED), 24 h. [b]Gas chromatography (GC) yields calculated using adamantane as the internal standard.

From the results of the screening, erythrosine B was selected as the most efficient catalyst for production of 1-bromonaphthalene **3**. Erythrosine B is a member of the xanthene family of dyes and is widely used as a food colorant (FD&C Red no. 3) and painting ink, but thus far, the chemical applications of erythrosine B have remained remarkably limited[55−62] relative to other xanthene dyes such as eosin Y, fluorescein, and rose bengal.

Figure 2. Selected examples of organic dye visible-light photoredox catalysts.

Table 2. Optimization of Reaction Conditions for Erythrosine B-Catalyzed Production of 1-Bromonaphthalene
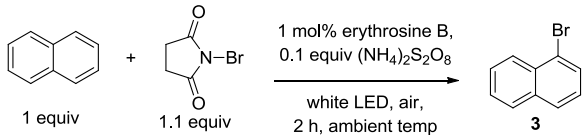
entry[a]	equiv 2	eryth B (mol %)	time (h)	solvent (mL)	additive (equiv)	% 3[b]
1	1	1	6	MeCN (3)	none	67
2	1.1	1	6	MeCN (3)	none	68
3	2	1	6	MeCN (3)	none	69
4	1	0	6	MeCN (3)	none	26
5	1	0.5	6	MeCN (3)	none	44
6	1	2	6	MeCN (3)	none	73
7	1	3	6	MeCN (3)	none	62
8	1	5	6	MeCN (3)	none	41
9	1	10	6	MeCN (3)	none	0
10	1	20	6	MeCN (3)	none	0
11	1	2	6	MeOH (3)	none	0
12	1	2	6	DCM (3)	none	12
13	1	2	6	4:1 MeCN/H_2O (3)	none	42
14	1	2	6	MeCN (6)	none	18
15	1	2	6	MeCN (1.5)	none	76
16	1	1	6	MeCN (1.5)	none	80
17	1	2	6	MeCN (3)	oxone (1)	78
18	1	2	2	MeCN (3)	$(NH_4)_2S_2O_8$ (1)	88
19	**1.1**	**1**	**2**	**MeCN (1.5)**	**$(NH_4)_2S_2O_8$ (0.1)**	**90**
20	1.1	1	2	MeCN (1.5)	$(NH_4)_2S_2O_8$ (0.02)	78

[a]Reaction conditions: 1 equiv = 0.25 mmol naphthalene. [b]GC yields calculated using adamantane as the internal standard.

Employing erythrosine B as a VLPC catalyst, a series of experiments were conducted to develop an optimized set of reaction conditions (Table 2). First, the stoichiometric ratio of naphthalene and NBS substrate was examined (Table 2, entries 1−3). An excess of brominating agent had little to no effect on the product yield, so a 1:1 ratio of NBS/naphthalene was chosen for further experiments. The catalyst loading of erythrosine B was then investigated (entries 4−10). A low catalyst concentration is necessary to achieve full conversion as the catalyst is deactivated under a high concentration, which may be due to radical collisional quenching.[63] Next, a survey of solvents and reaction concentrations was conducted (entries 11−16). It was observed that [1.7 mM] of erythrosine B in acetonitrile was optimal for the reaction conditions (entry 16). The use of an external oxidizing agent such as oxone (entry 17) had little effect on the reaction. However, when ammonium peroxodisulfate was added to the reaction mixture, a considerable increase in the rate of the reaction was observed (entries 18−20). Full conversion of naphthalene was observed using 1.1 equivalents of NBS; therefore, entry 19 represents the optimized conditions for the reaction.

A series of control reactions were conducted, and the results are displayed in Table 3. Light plays a key role in the reaction, as exhibited by the substantial decrease in product formation when the reaction is performed in the dark (Table 3, entry 3; Table 4, entry 5). Though ammonium peroxodisulfate is an important component in the promotion of the reaction, it is not solely responsible for activation of NBS, as observed in entries 3−5. The exclusion of catalytic erythrosine B results in a significant decrease in the formation of 3 (entries 4 and 5). In addition, oxygen (air) appears to serve as an oxidizing agent throughout the duration of the reaction. Ammonium peroxodisulfate can be used as a stoichiometric oxidant in

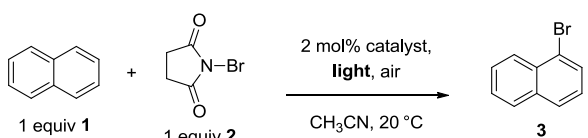**Table 3. Control Reactions and Mechanistic Experiments**

entry	deviation from standard conditions	% yield 3[a]
1	none	90
2	0.4 equiv $(NH_4)_2S_2O_8$	90
3	0.4 equiv $(NH_4)_2S_2O_8$, reaction in dark[b]	32
4	0.4 equiv $(NH_4)_2S_2O_8$, no erythrosine B	56
5	no erythrosine B, no $(NH_4)_2S_2O_8$	14
6	anaerobic conditions[c]	68
7	anaerobic conditions[c], no $(NH_4)_2S_2O_8$	7
8	no $(NH_4)_2S_2O_8$, 1 equiv BHT added	0
9	no $(NH_4)_2S_2O_8$, 1 equiv TEMPO added	0

[a]GC yields calculated using adamantane as the internal standard. [b]Reaction vessel was covered in an aluminum foil, and the reaction was carried out in a laboratory with the lights turned off. [c]Solvent was degassed, and the reaction was conducted under argon.

the absence of O_2 (entry 6), but when no oxidant (such as $(NH_4)_2S_2O_8$ or O_2) was present (entry 7), the reaction was severely impacted, resulting in a 7% yield. Finally, known radical inhibitors BHT (butylated hydroxytoluene) and TEMPO were separately tested under standard reaction conditions to determine if the presence of a radical intermediate might exist in the potential mechanistic pathway, and in both examples, product formation was completely halted (entries 8 and 9).

The source of light in the activation of NBS by erythrosine B was then investigated (Table 4). Ammonium peroxodisulfate

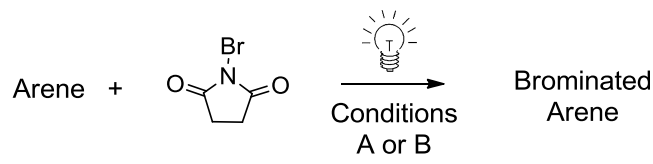**Table 4. Variation of Light Source in the VLPC Bromination of Naphthalene**

Entry	Time (h)	Light source		% Yield 3[a]
1	6	Cool White LED	(400-700 nm)	73
2	6	Blue LED	(λ_{max} 470 nm)	58
3	6	Green LED	(λ_{max} 560 nm)	0
4	6	Red LED	(λ_{max} 620 nm)	0
5	24	Dark		3

[a]GC yields calculated using adamantane as the internal standard.

Table 5. Substrate Scope of Arene Bromination

[a]Conditions A: 1 equiv. arene, 1.1 equiv. NBS, 0.1 equiv. $(NH_4)_2S_2O_8$, 0.01 equiv. erythrosine B [0.0017M], MeCN, air, 20 °C, white LED. All yields are isolated unless otherwise noted. [b]Conditions B: 2.2 equiv. NBS used. Yields are isolated. [c]GC yield calculated using adamantane as the internal standard. [d]Determined by ^{1}H NMR integration using nitrobenzene as the internal standard. [e]Inseparable mixture of isomers.

was excluded from the reaction to eliminate the background production of brominated arene, as observed in the control reactions shown in Table 3. The absorption maximum (λ_{ab}) of the ground state of erythrosine B is approximately 530 nm in acetonitrile. As shown in Table 3, the use of blue LED resulted in a moderately reduced yield, whereas utilization of a green or red LED light chamber had a severely detrimental effect on the reaction. The use of a white LED photochamber (see Supporting Information for description) displayed the most efficient production of 1-bromonaphthalene 3 and was used for all subsequent studies.

Following the optimization of reaction conditions (1 equiv arene, 1.1 equiv NBS, 0.1 equiv $(NH_4)_2S_2O_8$, 0.01 equiv erythrosine B [0.0017 M], acetonitrile, white LED, air), an exploration of the substrate scope was conducted with respect to the arene reagent (Table 5). In addition to naphthalene, several other arene substrates see dramatic enhancement in both the rate of reaction and the yield of brominated product upon use of catalytic erythrosine B. When 2-methylnaphthalene was employed in the absence of a catalyst, no conversion of arene was observed in 10 min by ^{1}H nuclear magnetic resonance (NMR) spectroscopy. After 2 h, a complex mixture was obtained containing products of benzylic bromination (see the Supporting Information for ^{1}H NMR spectra). In the presence of erythrosine B, however, 2-methylnaphthalene was cleanly converted to 4 within 10 min with no trace of benzylic functionalization. This example illustrates the potential utility of the photocatalyzed system. By oxidizing NBS and increasing the electrophilicity of the bromine atom, a photoredox approach appears to divert a potential side reaction (light-promoted radical bromination of benzylic C−H bonds) to a more reactive electrophilic aromatic bromination (Br+) pathway.

Bromination of anisole occurred in a quantitative fashion according to ^{1}H NMR, with the para-substituted isomer being the only observable product (5). The substituted anisole derivative, 4′-methoxyacetophenone, was also efficiently brominated on the aromatic ring with no observable bromination occurring alpha to ketone (6). A variety of aryl ether-containing substrates as well as phenol derivatives were examined (7−14). In examples where a mixture of mono- and dibromination occurred, 2.2 equivalents of NBS was employed to produce a dibrominated major product. Aniline derivatives (15 and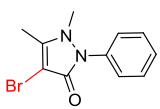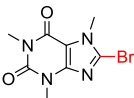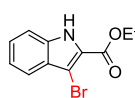 16) along with acetanilide (17) and the anesthetic, lidocaine (18), performed well under the photocatalyzed conditions. Electron-deficient arenes such as chlorobenzene and nitrobenzene were unsuccessful under the optimized

reaction conditions. Additionally, aldehyde functionality is not tolerated under the reaction conditions, as 4-methoxybenzaldehyde was oxidized to the carboxylic acid when tested. Arenes that contain electron-withdrawing groups (carbonyl, nitro, and halide) are tolerated as long as they are accompanied by an electron-donating group on the aromatic ring. It is noteworthy that, despite the reactions being conducted in a visible-light photochamber, brominated byproducts were not observed in any example using an arene that contained benzylic C−H bonds (4, 11, 12, and 18) or C−H bonds α to carbonyls (6, 17, 18).

In addition to the variety of brominated arenes shown in Table 5, a series of N-containing heteroarenes were cleanly brominated and are displayed in Table 6. In general, good to excellent yields of brominated products were obtained with high regioselectivity. Heteroarenes that were employed include pyrrole, pyrazole, indole, and indazole cores along with bioactive compounds such as caffeine and the painkiller phenazone. Bromination at the N-methyl position of phenazone was an observed minor product with 21. Products of N-methyl bromination were not observed, however, when using caffeine as a substrate.

To investigate whether the oxidation potential of NBS was within the range of the photocatalyst erythrosine B, the cyclic voltammograms of NBS and erythrosine B were obtained versus Fc/Fc+ (see the Supporting Information). The

Table 6. Substrate Scope of Heteroarene Bromination

Heteroarene (1 equiv) + NBS (1.1 equiv) → Brominated Heteroarene

Erythrosine B (1 mol%), $(NH_4)_2S_2O_8$ (10 mol%)

MeCN, air, rt, white LED

19[a] - 99%, 1.5 h

20[a] - 82%, 10 min

21[a] - 82%, 10 min
9% N-Me bromination

22[a] - 56%, 2.5 h

23[a] - 85%, 10 min

24[a] - 37%, 30 min

[a]Conditions: 1 equiv heteroarene, 1.1 equiv NBS, 0.1 equiv $(NH_4)_2S_2O_8$, 0.01 equiv erythrosine B [0.0017M], MeCN, air, 20 °C, white LED. All yields are isolated.

fluorescence emission profile of erythrosine B exhibits a peak with a maximum at 568 nm (λ_{em}), which correlates with a E^{oo} value of 2.18 eV. The Stokes shift ($\Delta\lambda$) of erythrosine B is therefore calculated as 38 nm (λ_{em} 568 nm − λ_{ab} 530 nm). This relatively large Stokes shift value for a xanthene dye (most are 20−35 nm) might be attributed to an excited-state intramolecular charge transfer.[64−66] On the basis of the redox potentials obtained, the oxidation of NBS (+0.28 vs Fc/Fc$^+$) is feasible by the excited state of erythrosine B; therefore, the catalyst is speculated to proceed through a reductive quenching cycle, as shown in Scheme 2.

Scheme 2. Redox Properties of Erythrosine B[a]
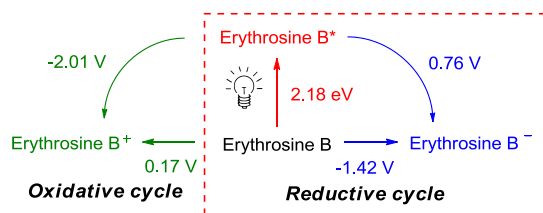
[a]Potentials are given vs Fc/Fc$^+$.

On the basis of the experimental results, a plausible reaction mechanism is proposed in Scheme 3. Ammonium peroxodisulfate has been excluded from the proposed mechanism because it is not a necessary component of the reaction according to control experiments. The photoexcited state of erythrosine B can induce oxidation of the nitrogen atom of NBS to cationic radical species **B**, thus amplifying the positive polarization on the bromine atom. Following electrophilic aromatic bromination with an arene substrate, an external oxidant [such as O_2, $(NH_4)_2S_2O_8$, or H_2O_2] may serve as the oxidizing agent to return erythrosine B to its ground state. Alternatively, the resulting charged succinimide species **C** could oxidize the reduced state of the catalytic erythrosine B to form the succinimide anion **D**.

To determine if the superoxide anion $O_2^{-\bullet}$ is formed under the photocatalyzed conditions, the iodide test (NaI in glacial acetic acid) was performed to attempt to observe the presence of H_2O_2 byproduct, which would ultimately result from the

intermediate superoxide anion. Ammonium peroxodisulfate was intentionally excluded from the reaction mixture to prevent the false positive test that would result from the oxidation of iodide by $(NH_4)_2S_2O_8$. As shown in Figure 3, upon addition of the crude reaction mixture at 0 min, the NaI/AcOH mixture appeared as the orange/red color of the erythrosine B crude reaction. Following a 2 h reaction period, the formation of hydrogen peroxide in the reaction mixture was confirmed by the appearance of the dark red/brown color of I_2 (Figure 3, panel F).

■ CONCLUSIONS

A new catalytic mode of activation of NBS for bromination of arenes and heteroarenes has been developed using erythrosine B as a visible-light photoredox catalyst. The reaction operates under mild, practical conditions and produces brominated arenes in high regioselectivity and in short reaction times. The approach diverts NBS from competing light-promoted pathways, such as benzylic bromination, toward electrophilic aromatic substitution. A variety of substrates were brominated in good to excellent yields, and many functionalities were tolerated. According to mechanistic studies, the reaction is speculated to operate via a single electron oxidation of NBS by erythrosine B, which is in turn oxidized back to its ground state by air. Finally, attempts to employ a VLPC strategy to activate additional reagents containing N−X bonds for electrophilic transformations are currently underway in our laboratory and will be reported in due course.

■ EXPERIMENTAL SECTION

Materials and Instrumentation. All reagents and solvents were purchased from commercial sources and used without further purification. Erythrosine B was purchased from Spectrum as FD&C Red #3. A description of the construction of our light bath (LED) photochamber is provided in the Supporting Information. ^1H and ^{13}C NMR spectra were recorded on a Varian 400/100 (400 MHz) spectrometer in deuterated chloroform ($CDCl_3$) or acetonitrile (CD_3CN) with the solvent residual peak as the internal reference unless otherwise stated ($CDCl_3$: ^1H = 7.26 ppm, ^{13}C = 77.23 ppm; CD_3CN: ^1H = 1.94 ppm). Data are reported in the following order: Chemical shifts (δ) are reported in ppm, and spin−spin coupling constants (J) are reported in Hz, whereas multiplicities are abbreviated by s (singlet), bs (broad-singlet), d (doublet), dd (doublet-of-doublets), t (triplet), dt (doublet-of-triplets), td (triplet-of-doublets), m (multiplet), and q (quartet). Infrared spectra were recorded on a Nicolet iS50 FT-IR spectrometer, and peaks are reported in reciprocal centimeters (cm^{-1}). Electrochemical experiments were performed using a BioLogic SP-200 Potentiostat using a platinum disk working electrode, a platinum mesh counter electrode, and a silver wire as the quasi-reference electrode that was calibrated using a ferrocene standard. Melting points (mp) were recorded on a Mel-Temp II (Laboratory Devices, USA) apparatus and were uncorrected. Nominal mass spectra (electron ionization) were obtained using a Shimadzu GC-2010 Plus chromatograph with a GCMS-QP2010 mass spectrometer. Relative intensity (in percentage) is shown in parentheses following the fragment peak, where appropriate. Accurate mass spectrum was performed using a Thermo Scientific Exactive spectrometer operating in the positive ion electrospray mode.
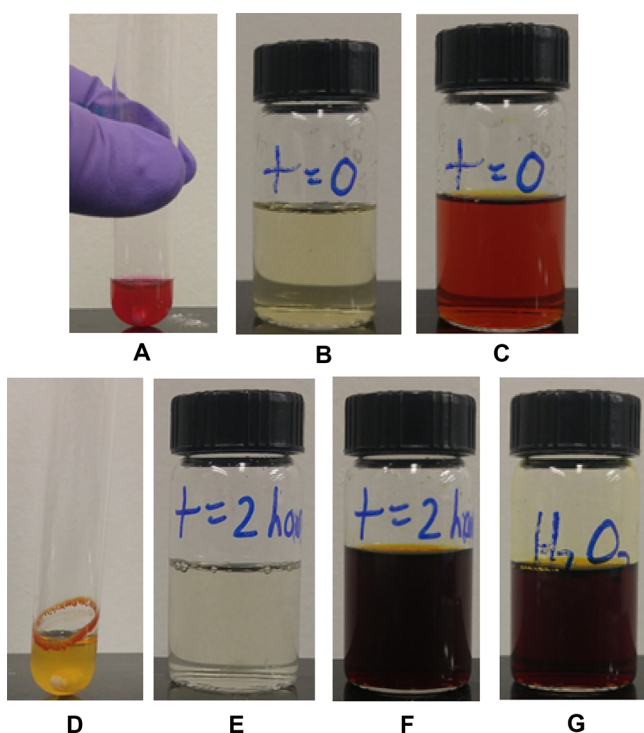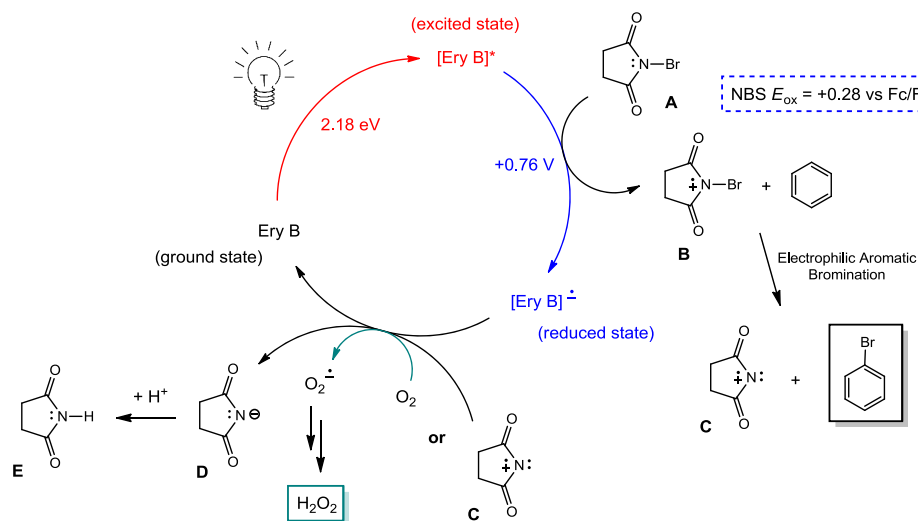
Scheme 3. Plausible Mechanism

Figure 3. Test for the production of hydrogen peroxide. Bromination reaction mixture = 1 equiv naphthalene, 1.1 equiv NBS, 0.01 equiv erythrosine B, air, and acetonitrile. (A) Reaction at $t = 0$. (B) NaI in glacial acetic acid. (C) Crude reaction mixture A added to mixture B at $t = 0$. (D) Crude reaction mixture at $t = 2$ h. (E) NaI in glacial acetic acid. (F) Crude reaction mixture D added to mixture E at $t = 2$ h. (G) Positive control experiment in which H_2O_2 is added to NaI in glacial acetic acid solution.

General Procedure. To an oven-dried flask was added a magnetic stir bar, erythrosine B (4.4 mg, 0.01 equiv, 0.005 mmol), ammonium peroxodisulfate (11.4 mg, 0.1 equiv, 0.05 mmol), arene/heteroarene (1 equiv, 0.5 mmol), acetonitrile (3 mL), and then NBS (98 mg, 1.1 equiv, 0.55 mmol). The reaction mixture was stirred open to air at room temperature (20 °C) in a white LED chamber for the time specified for each respective arene. Reactions were monitored for completion by thin-layer chromatography (hexanes/ethyl

acetate) and/or GC. For substrates that produced a mixture of mono- and dibrominated products upon full conversion, 2.2 equivalents (1.1 mmol) of NBS was employed. Upon completion of the reaction, the crude mixture was evaporated under pressure and the brominated product was isolated via column chromatography on silica gel.

Iodide Test. Test solution preparation: 0.100 g NaI dissolved in 10 mL of glacial acetic acid.

Control Test. Three drops of 3% H_2O_2 solution were added by a pipette to the NaI/AcOH test solution in a 4-dram vial. The vial was capped and shaken, resulting in an opaque red-brown color.

0 min Test. A test tube was loaded with erythrosine B (0.0022 g, 0.0025 mmol), naphthalene (0.0310 g, 0.25 mmol), 1.5 mL of CH_3CN, and NBS (0.0487 g, 0.275 mmol). After addition of all reagents, the test tube was lightly shaken to mix the contents. Fifteen drops of the crude reaction mixture were immediately transferred via a pipette to a freshly prepared NaI/AcOH test solution in a 4-dram vial. The vial was capped and shaken, giving an orange color resembling the color of the reaction mixture.

2 h Test. A test tube was loaded with erythrosine B (0.0022 g, 0.0025 mmol), naphthalene (0.0310 g, 0.25 mmol), 1.5 mL of CH_3CN, and NBS (0.0487 g, 0.275 mmol). After addition of all reagents, the test tube was equipped with a stir bar and allowed to react open to air in a white LED photochamber for 2 h. Upon completion of the reaction, 15 drops of the crude reaction mixture were immediately transferred via a pipette to a freshly prepared NaI/AcOH test solution in a 4-dram vial. The vial was capped and shaken, giving an opaque red-brown color resembling the color of the control test.

Compound Characterization. All bromoarenes were isolated according to general procedure, unless otherwise noted, and display the characterizational data shown below (spectra available in the electronic Supporting Information).

1-Bromo-2-methylnaphthalene (4).[19] The title compound was prepared according to the general procedure. Dark orange oil (86 mg, 78%); purification (EtOAc/hexanes, 20:80) R_f = 0.32. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.29 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 8.2 Hz, 1H) 7.71 (d, J = 8.6 Hz, 1H) 7.56 (t, J = 8.6 Hz, 1H) 7.46 (t, J = 7.4 Hz, 1H) 7.35 (d, J = 8.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 136.0, 133.0, 132.5, 128.7,

128.0, 127.3, 127.2, 126.9, 125.6, 124.0, 24.2. FT-IR (neat, cm^{-1}) ν: 3051, 2919; MS (EI) m/z: 220 and 222 (M$^+$, 1:1 ratio).

1-(3-Bromo-4-methoxyphenyl)ethan-1-one (6).[67] The title compound was prepared according to the general procedure. White solid (94 mg, 82%): mp 79−84 °C; purification (hexanes/EtOAc = 80:20) R_f = 0.25. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.17 (d, J = 2.3 Hz, 1H), 7.93 (dd, J = 8.6, 2.3 Hz, H) 6.94 (d, J = 8.6 Hz, 1H) 3.97 (s, 3H) 2.56 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 195.6, 159.6, 133.8, 131.2, 129.5, 111.8, 111.0, 56.5, 26.3. FT-IR (neat, cm^{-1}) ν: 2959, 2870, 1500, 1181; MS (EI) m/z: 214 and 216 (M$^+$, 1:1 ratio).

2-Bromodibenzofuran[68] *and 4-Bromodibenzofuran*[69] *(7).* The title compounds were prepared as an inseparable mixture of isomers (2-bromodibenzofuran/4-bromodibenzofuran = 5:1 ratio by ^{1}H NMR and GC) according to the general procedure. White solid (93 mg, 75% combined): mp 97−100 °C; purification (hexanes/EtOAc = 80:20) R_f = 0.30. Signals corresponding to the major product, 2-bromodibenzofuran, as reported here. Spectra are located within the Supporting Information. ^{1}H NMR (400 MHz, CDCl$_3$): 7.99 (d, J = 2.0 Hz, 1H), 7.83 (d, J = 7.4 Hz, 1H), 7.52−7.47 (m, 2H), 7.44 (dt, J = 7.8, 1.4 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 7.30 (t, J = 7.8 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 155.6, 153.9, 128.9, 126.9, 125.2, 122.7, 122.5, 122.0, 119.8, 112.4, 112.2, 110.8 ppm. IR (neat) ν: 3066, 1437, 841, 751, 688 cm^{-1}. MS (EI) m/z: 246 and 248 (M$^+$, 1:1 ratio).

5-Bromo-1,3-benzodioxole (8).[25] The title compound was prepared according to the general procedure. Red oil (78 mg, 78%); purification (hexanes/EtOAc = 90:10) R_f = 0.60. ^{1}H NMR (400 MHz, CDCl$_3$): δ 6.96−6.93 (m, 2H), 6.70−6.67 (m, 1H), 5.97 (s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 148.6, 147.0, 124.3, 113.0, 112.3, 109.6, 101.2 ppm. IR (neat) ν: 2895, 1712, 1468, 1228, 1033, 932, 874, 795, 573 cm^{-1}. MS (EI) m/z: 200 and 202 (M$^+$, 1:1 ratio).

1-Bromo-2-naphthol (9).[19] The title compound was prepared according to the general procedure. Additional information regarding the workup: after completion, the reaction was quenched with 4 mL of saturated Na$_2$CO$_3$ solution. The resulting mixture was extracted with ethyl acetate (3 × 10 mL). The combined organic layer was dried over magnesium sulfate, and the filtrate was concentrated under vacuum. Pale orange solid (42 mg, 76%): mp 76−79 °C; Purification (EtOAc/hexanes = 20:80) R_f = 0.67. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.03 (d, J = 9.0 Hz, 1H), 7.78 (d, J = 9.0 Hz, 1H), 7.74 (d, J = 9.0 Hz, 1H), 7.57 (t, J = 7.4 Hz, 1H) 7.40 (t, J = 7.4 Hz, 1H), 7.27 (d, J = 9.0 Hz, 1H), 5.92 (s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 150.5, 132.3, 129.7, 129.3, 128.2, 127.8, 125.3, 124.1, 117.1, 106.1. FT-IR (neat, cm^{-1}) ν: 3275, 3056; MS (EI) m/z: 222 and 224 (M$^+$, 1:1 ratio).

2-Bromo-4-(tert-butyl)phenol (10).[19] The title compound was prepared according to the general procedure. Oily orange solid (90 mg, 82%); purification (EtOAc/hexanes = 10:90) R_f = 0.20. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.43 (s, 1H), 7.22 (d, J = 8.6 Hz, 1H) 6.94 (d, J = 8.6 Hz, 1H) 5.33 (s, 1H) ^{13}C NMR (100 MHz, CDCl$_3$): δ 149.8, 145.1, 128.7, 126.2, 115.5, 109.8, 34.2, 31.4. FT-IR (neat, cm^{-1}) ν: 3377, 3135, 2961, 2905, 2863; MS (EI) m/z: 228 and 230 (M$^+$, 1:1 ratio).

2-Bromo-4-(1-methylethyl)-phenol (11).[67] The title compound was prepared according to the general procedure. Colorless oil (77 mg, 72% yield); purification (hexanes/EtOAc = 98:2) R_f = 0.67. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.29 (d, J = 2.0 Hz, 1H), 7.06 (dd, J = 8.2, 2.0 Hz, 2H) 6.93 (d, J = 8.2 Hz, 1H) 5.34 (s, 1H) 2.81 (septet, J = 7.4 Hz, 1H) 1.20 (d, J = 7.4 Hz, 6H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 150.1, 142.7, 129.6, 127.2, 115.8, 109.9, 33.2, 24.0. FT-IR (neat, cm^{-1}) ν: 2959, 2870, 1500, 1181; MS (EI) m/z: 214 and 216 (M$^+$, 1:1 ratio).

2-Bromo-4-cyclohexylphenol (12). The title compound was prepared according to the general procedure. White solid (114 mg, 89% yield): mp 30−32 °C; purification (hexanes/EtOAc = 90:10) R_f = 0.50. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.28 (d, J = 4.0 Hz, 1H), 7.04 (dd, J = 8.0 Hz, 1H), 6.93 (d, 1H), 5.37 (s, 1H), 2.44−2.38 (m, 1H), 1.84−1.68 (m, 5H), 1.39−1.19 (m, 5H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 150.2, 142.0, 130.0, 127.6, 115.8, 110.0, 43.5, 34.6, 26.8, 26.1 ppm. IR (neat) ν: 3400, 2922, 2850, 1701, 1606, 1495, 1448, 1279, 1174 cm^{-1}. MS (EI): 257(2), 256(10), 255(2), 254(13), 132(74), 44(100). HRMS (ESI): calcd for C$_{12}$H$_{15}$O$_1$Br$_1$ [M]$^+$ requires m/z, 256.02873; found m/z, 256.02835.

2,6-Dibromo-4-chlorophenol (13).[70] The title compound was prepared following the general procedure using 2.2 equivalents of NBS (196 mg, 1.1 mmol). Orange solid (76 mg, 53%): mp 79−84 °C; purification (hexanes/EtOAc = 90:10) R_f = 0.25. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.46 (s, 2H), 5.97 (br s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 148.5, 131.5, 126.2, 109.9 ppm. IR (neat) ν: 3406, 3078, 1557, 1455, 1384, 1315, 1213, 1153, 855, 702, 559 cm^{-1}. MS (EI) m/z: 284(45), 286(100), 288(72), 290(12).

2,4-Dibromo-6-chlorophenol (14).[70] The title compound was prepared following the general procedure using 2.2 equivalents of NBS (196 mg, 1.1 mmol). Yellow solid (144 mg, 99%): mp 70−74 °C; purification (hexanes/EtOAc, 98:2) R_f = 0.10. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.55 (d, J = 2.0 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 5.88 (s, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 148.1, 133.6, 131.4, 121.5, 112.2, 110.8 ppm. IR (neat) ν: 3372, 3073, 1563, 1459, 1384, 1319, 1160, 855, 766, 677, 555 cm^{-1}. MS (EI) m/z: 284(45), 286(100), 288(72), 290(12).

4-Bromo-2-nitroaniline (15).[71] The title compound was prepared according to the general procedure. Orange solid (73 mg, 74%): mp 110−112 °C; purification (hexanes/EtOAc = 80:20, 1% NEt$_3$) R_f = 0.30. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.26 (d, J = 2.3 Hz, 1H), 7.44 (dd, J = 9.0, 2.3 Hz, 1H), 6.74 (d, J = 9.0 Hz, 1H), 6.12 (br s, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 143.5, 138.4, 128.3, 120.3, 107.8 ppm. IR (neat) ν: 3469, 3344, 3172, 3093, 2922, 2851, 1621, 1557, 1495, 1336, 1239, 813 cm^{-1}. MS (EI) m/z: 216 and 218 (M$^+$, 1:1 ratio).

2,6-Dibromo-4-chloroaniline (16).[72] The title compound was prepared following the general procedure using 2.2 equivalents of NBS (196 mg, 1.1 mmol). Dark red solid (120 mg, 86%): mp 84−88 °C; purification (hexanes/EtOAc, 90:10) R_f = 0.50. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.38 (s, 2H), 4.54 (br s, 2H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 140.9, 131.2, 122.6, 108.4 ppm. IR (neat) ν: 3416, 3304, 3075, 1611, 1543, 1455, 1386, 1291, 1055, 850 cm^{-1}. MS (EI) m/z: 283(45), 285(100), 287(73), 289(15).

4′-Bromoacetanilide (17).[71] The title compound was prepared according to the general procedure. Additional information regarding the workup: to the crude reaction mixture was added 5 mL of 1 M NaOH upon completion of the reaction. The organic portion was removed and washed with brine, dried with Na$_2$SO$_4$, and evaporated under vacuum. White solid (89 mg, 84%): mp 171−174 °C; purification (hexanes/EtOAc, 50:50) R_f = 0.30. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.41 (m, 4H), 2.17 (s, 3H) ppm. ^{13}C NMR (100

MHz, CDCl$_3$): δ 168.3, 136.9, 131.9, 121.3, 116.8, 24.6 ppm. IR (neat) ν: 3288, 3256, 3185, 3114, 3052, 1666, 1600, 1529, 1392, 1308, 1255, 1007, 812, 737, 501 cm^{-1}. MS (EI) m/z: 213 and 215 (M$^+$, 1:1 ratio).

N-(4-Bromo-2,6-dimethylphenyl)-2-(diethylamino)-acetamide (18).[32] The title compound was prepared according to the general procedure. Additional information regarding the workup: following evaporation of the reaction solvent, the crude was dissolved in 3 mL of toluene. Acidic extraction from the organic solvent was performed using 3 mL of 4 M HCl. NaOH solution (2 M) was added to the aqueous layer until the pH was greater than 11. The aqueous portion was then extracted with hexanes (3 × 10 mL) and evaporated under vacuum. Light pink oily solid (130 mg, 84%); purification (hexanes/EtOAc = 50:50, 2% NEt$_3$) R_f = 0.45. ^{1}H NMR (400 MHz, CDCl$_3$): δ = 6.90 (br s, 1H), 7.07 (s, 2H), 3.20 (s, 2H), 2.67 (q, J = 7.2 Hz, 4H), 2.22 (s, 6H), 1.12 (t, J = 7.2 Hz, 6H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 170.2, 135.0, 134.0, 128.2, 127.0, 57.5, 48.9, 18.9, 12.6 ppm. IR (neat) ν: 3284, 2969, 1677, 1492, 730 cm^{-1}. MS (EI) fragmentation m/z: 147(4), 132(2), 119(2), 91(3), 86(100), 58(20).

4-Bromo-1-phenylpyrazole (19).[16] The title compound was prepared according to the general procedure. White solid (107 mg, 99%): mp 78−82 °C; purification (hexanes/EtOAc = 85:15) R_f = 0.50. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.92 (s, 1H), 7.67 (s, 1H), 7.63 (m, 2H), 7.45 (m, 2H), 7.31 (m, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.5, 139.6, 129.5, 127.02, 126.99, 119.0, 95.6 ppm. IR (neat) ν: 3110, 1595, 1493, 1381, 1335, 1037, 948, 844, 750, 647 cm^{-1}. MS (EI) m/z: 222 and 224 (M$^+$. 1:1 ratio).

3-Bromo-indazole (20).[22] The title compound was prepared according to the general procedure. Pale orange solid (80 mg, 82%): mp 140−143 °C; purification (hexanes/EtOAc = 90:10) R_f = 0.10. ^{1}H NMR (400 MHz, CDCl$_3$): δ 12.22 (br s, 1H), 7.66 (t, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.24 (t, J = 8.0 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 141.2, 128.1, 123.0, 122.6, 121.8, 120.1, 110.5 ppm. IR (neat) ν: 3152−2914, 1624, 1479, 1329, 1241, 1024, 900, 769 cm^{-1}. MS (EI) m/z: 196 and 198 (M$^+$, 1:1 ratio).

4-Bromo-1,5-dimethyl-2-phenyl-1,2-dihydro-3H-pyrazol-3-one (21).[32] The title compound was prepared as an inseparable mixture of the title compound and brominated isomer (at N-Me position) according to the general procedure. Yellow solid (121 mg, 91% combined): mp 47−52 °C; purification (hexanes/EtOAc, 60:40) R_f = 0.10. Signals corresponding to the major product, 21, as reported here. Spectra are located within the Supporting Information. ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.37 (m, 2H), 7.29 (m, 2H), 7.22 (m, 1H), 3.01 (s, 3H), 2.22 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 162.1, 154.0, 129.4, 129.2, 127.0, 124.1, 90.5, 36.4, 12.5 ppm. IR (neat) ν: 2987, 2927, 1652, 1575, 1496, 1456, 1108, 750, 582 cm^{-1}. MS (EI) m/z: 266 and 268 (1:1 ratio).

8-Bromo-3,7-dihydro-1,3,7-trimethyl-1H-purine-2,6-dione (22).[73] The title compound was prepared according to the general procedure. Additional information regarding the workup: to the crude reaction mixture was added 5 mL of 1 M NaOH upon completion of the reaction. The organic portion was removed and washed with brine, dried with Na$_2$SO$_4$, and evaporated under vacuum. White solid (76 mg, 56%): mp 214−216 °C; purification (DCM/EtOAc, 5:3) R_f = 0.45. ^{1}H NMR (400 MHz, CDCl$_3$): δ 3.90 (s, 3H), 3.49 (s,

3H), 3.33 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 154.4, 151.2, 148.0, 128.1, 109.3, 33.9, 29.8, 28.0 ppm. IR (neat) ν: 2954, 1701, 1653, 1540, 1449, 1341, 972, 743, 502 cm^{-1}. MS (EI) m/z: 272 and 274 (M$^+$, 1:1 ratio).

Ethyl 3-Bromo-1H-indole-2-carboxylate (23).[16] The title compound was prepared according to the general procedure. White solid (102 mg, 79%): mp 141−144 °C; purification (hexanes/EtOAc, 80:20). R_f = 0.36. ^{1}H NMR (400 MHz, CDCl$_3$): δ 9.12 (br s, 1H), 7.68 (d, J = 8.6 Hz, 1H), 7.41−7.36 (m, 2H), 7.25−7.21 (m, 1H), 4.46 (q, J = 7.3 Hz, 2H), 1.46 (t, J = 7.3 Hz, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 161.0, 135.3, 128.0, 126.6, 124.1, 121.5, 121.3, 112.0, 98.3, 61.5, 14.3 ppm. IR (neat) ν: 3291, 2985, 1683, 1619, 1516 cm^{-1}. MS (EI) m/z: 265(2), 263(2), 252(3), 223(4), 221(4), 146(18), 130(6), 114(5), 103(6), 102(6), 44(100).

2-Bromo-1-[(4-methylphenyl)sulfonyl-1H-pyrrole (24).[74] The title compound was prepared according to the general procedure. Light brown solid (28 mg, 37%): mp 101−104 °C; purification (hexanes/EtOAc = 80:20) R_f = 0.32. ^{1}H NMR (400 MHz, CDCl$_3$): δ 8.10 (d, J = 8.6 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.32 (dd, J = 5.9, 2.0 Hz, 1H), 6.82 (d, J = 2.0 Hz, 1H), 6.10 (d, J = 5.9 Hz, 1H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl$_3$): δ 148.8, 145.8, 134.7, 129.6, 128.8, 124.9, 58.1, 21.7 ppm. IR (neat) ν: 3101, 3018, 1738, 1597, 1493, 1367, 1188, 1168 cm^{-1}. MS (EI) m/z: 301(4), 299(4), 155(31), 91(100), 65(38), 44(30), 39(37).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b02320.

^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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