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A protocol for visible light promoted desulfonylation reactions utilizing catalytic benzimidazolium aryloxide betaines and stoichiometric hydride donor reagents

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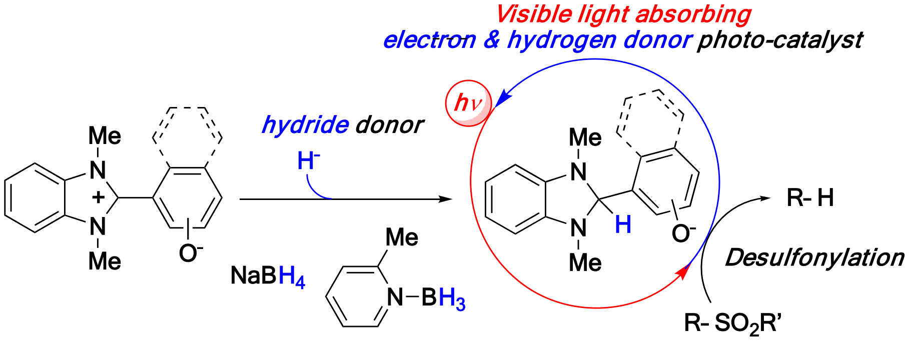
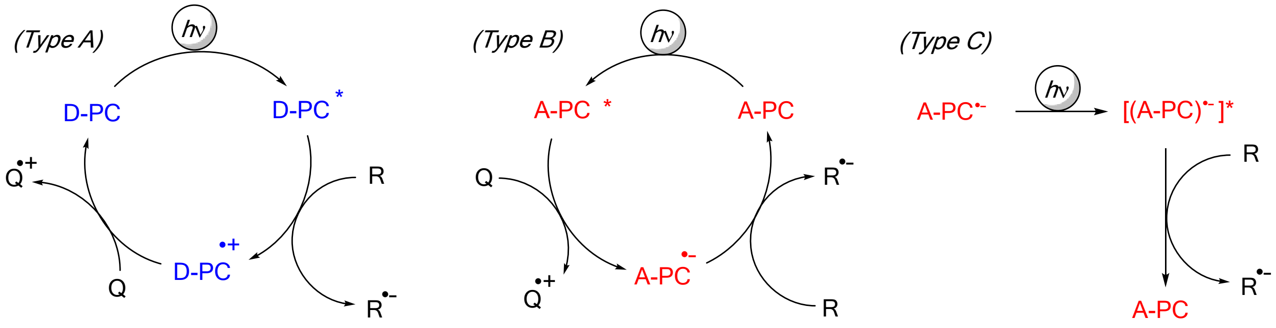


ABSTRACT: An unprecedented photocatalytic system consisting of benzimidazolium aryloxide betaines ($BI^+–ArO^–$) and stoichiometric hydride reducing reagents was developed for carrying out desulfonylation reactions of *N*-sulfonyl-indoles, -amides and -amines, and α-sulfonylketones. Measurements of absorption spectra and cyclic voltammograms as well as DFT calculations were carried out to gain mechanistic information. In the catalytic system, visible light activated benzimidazoline aryloxides (BIH–ArO$^-$), generated in-situ by hydride reduction of the corresponding betaines BI$^+$–ArO$^-$, donate both an electron and a hydrogen atom to the substrates. A modified protocol was also developed so that a catalytic quantity of more easily prepared hydroxyaryl benzimidazolines (BIH–ArOH) is used along with a stoichiometric hydride donor to promote the photochemical desulfonylation reactions.

INTRODUCTION

Photoinduced electron transfer (PET) is a fundamental photochemical process involving single electron transfer (SET) promoted reduction and oxidation (redox) of excited states of substances. Extensive investigations of PET reactions conducted during the past several decades have led to the discovery of variety of unique organic redox reactions.[1] About a decade ago, the synthetic potential of PET reactions, promoted by visible light-absorbing transition metal photoredox catalysts, were anew demonstrated in independent studies by MacMillan, Yoon and Stephenson.[2] Since then, numerous synthetically useful photoredox reactions catalyzed by these metal complexes have been reported.[3] In contrast, protocols to accomplish visible light promoted redox reactions without using expensive and potentially toxic transition metal catalysts have been less well-developed. In particular, processes promoted by organic photoredox catalysts are more desirable from a green and sustainable perspective.

Although a variety of organic electron-acceptor photocatalysts have been developed, their electron-donor counterparts have been less well-explored.[4] As a matter of fact, organic photocatalysts of this type are limited to electron-donating substituent possessing arenes, heteroarenes and dyes.[5] Only recently other electron-donor photocatalysts and new protocols for carrying out visible light induced reduction reactions have been described (Figure 1).[6] The most general types of electron donor photocatalysts (D-PC) investigated to date possess excited states that act as SET donors (reductants) (*Type A*). In *Type A* catalytic cycles, the radical cation (D-PC$^{\bullet+}$) generated by SET from the D-PC is converted back to D-PC by SET from an appropriate electron donor quencher Q.[5,6c,6f,6k,6l,6n] Another protocol (*Type B*) for carrying out light induced reduction reactions involves quenching of an excited state of an electron acceptor (A-PC) by SET from Q to generate radical anion A–PC$^{\bullet-}$, which serves as a reductant.[6a,6e,6g,6h,6m] In yet another version (*Type C*), a strongly reducing excited state of a preformed A–PC$^{\bullet-}$ serves as the reductant.[6b,6d,6i,6j]



PC: photocatalyst, D-PC: electron donor PC, A-PC: electron acceptor PC
Q: quenchers (electron donors)
R: reactants (electron acceptors)

Figure 1. Three types of pathways for electron-donor photocatalyzed reduction reactions.

2-Aryl-1,3-dimethylbenzimidazolines (BIH–Ar), artificial analogues of the reduced form (NADH) of nicotinamide adenine dinucleotide, serve as effective hydride, hydrogen atom and electron donors.[7] In earlier studies aimed at developing new organic transformations, we have shown that BIH–Ar can be utilized as organic reductants in unique photoreduction reactions.[8] Moreover, we demonstrated that introduction of hydroxyl substituents on the 2-aryl rings of BIH–Ar gives substances (BIH–ArOH) which are deprotonated to form aryloxide analogs BIH–ArO$^-$ that are exceptionally strong electron donors.[9] For example, the electronic excited states of 2-hydroxynaphthyl-1,3-dimethylbenzimidazoline (BIH–NapOH) in the presence and absence of appropriate bases promote reductive transformations of various organic substances (Figure 2), which generate benzimidazolium naphthoxide (BI$^+$–NapO$^-$) as a stoichiometric co-product. Recently, we discovered that BI$^+$–NapO$^-$ is unprecedented visible light absorbing betaine photocatalyst,[6k] and that the excited state of BIH–NapO⁻ is a stronger SET-donor than that of BI⁺–NapO⁻.[9d] Also, we found that BI⁺–Ar, formed in the photoreduction reactions promoted by stoichiometric quantities of BIH–Ar, can be isolated and reduced to reform BIH–Ar using hydride donors.[9a]

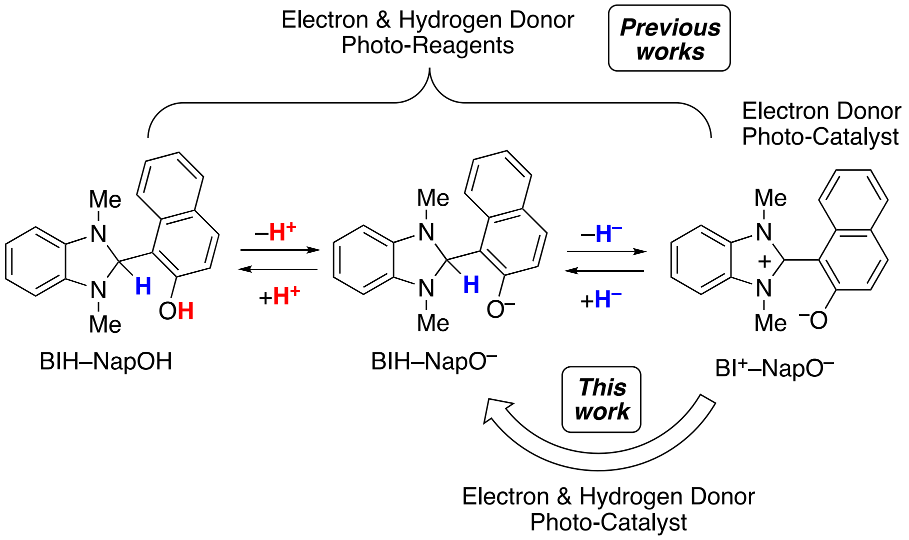


Figure 2. A hydroxynaphthyl-benzimidazoline (BIH–NapOH) and benzimidazolium naphthoxide (BI⁺–NapO⁻) redox process in the operation of stoichiometric and catalytic photoreduction reactions.

In the investigation described below, we utilized knowledge gained from our earlier efforts to design a new protocol for visible light promoted photocatalyzed reduction reactions. In the proposed process, BIH–ArO⁻ serving as a photocatalyst is regenerated in-situ by reduction of BI⁺–ArO⁻ with stoichiometric amounts of simple hydride donor reagents (Figure 2).[10,11] Moreover, in addition to being electron donors in these reactions like ordinary photocatalysts,[5,6] BIH–ArO$^-$ would donate hydrogen atoms to the substrates.[12] To assess this unique design of a photocatalytic system, we utilized five benzimidazolium aryloxides (BI$^+$–ArO$^-$, **1**, Figure 3) as photocatalysts together with $NaBH_4$, picoline borane (Pic-BH_3) and pinacol borane (Pin-BH) as hydride donor reagents (Figure 3). Furthermore, because stoichiometric quantities of the reduced form of **1a** (BIH–NapOH, Figure 2) were previously observed to promote reductive desulfonylation reactions,[9d,13] we chose *N*-sulfonyl-indoles, -amide and -amines, and α-sulfonylketones as probe substrates to evaluate the new photocatalytic system (Figure 4).

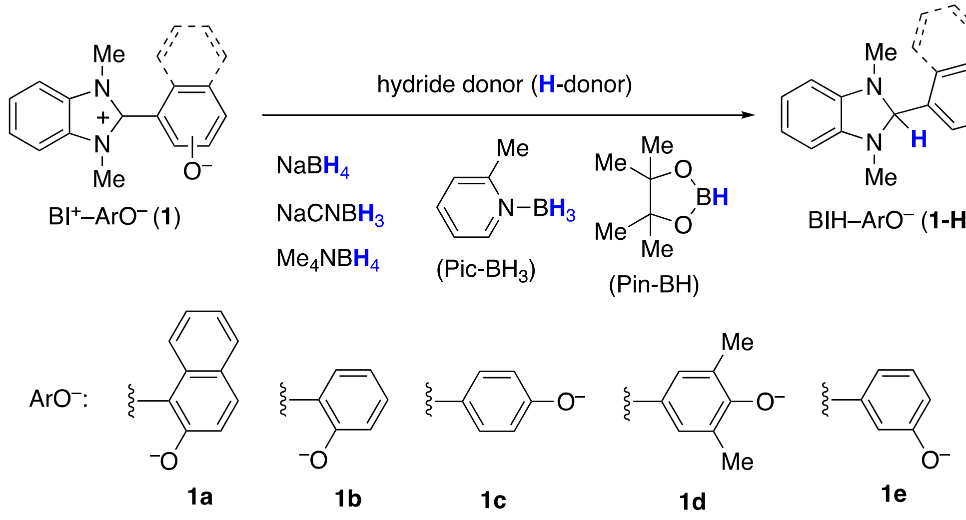


Figure 3. Hydride addition reactions of benzimidazolium aryloxides **1**.

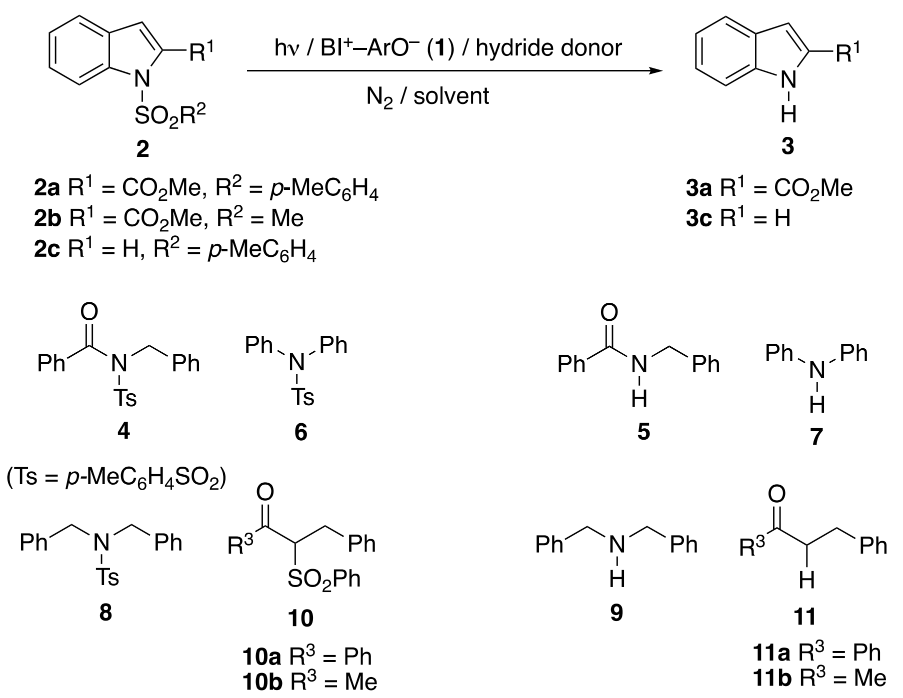


Figure 4. Photocatalyzed desulfonylation reactions of *N*-sulfonyl-indoles **2**, -amide **4** and -amines **6** and **8**, and α-sulfonylketones **10**.

RESULTS AND DISCUSSION

In the first phase of this investigation, we carried out absorption spectroscopic measurements of $BI^+–ArO^–$ (**1**) in the absence and presence of hydride reducing agents (Figure S1, Table S1 and Figure S2). We found that the spectrum of $BI^+–NapO^–$ (**1a**) in DMSO contains a long wavelength maximum at 415 nm[6k] which disappears upon addition of $NaBH_4$ (Figure 5, also see Figure S3 for **1b**, Figure S4 for **1c** and Figure S5 for **1d**). Subsequent addition of *t*-BuOK results in the appearance of a spectrum with an absorption maximum at 399 nm. Importantly, the former and the latter absorption spectra are similar to those of BIH–NapOH (**1a-HH**) and $BIH–NapO^–$ (**1a-H**, λ_{max} = 402 nm), respectively.[9d] These observations demonstrate that $BI^+–NapO^–$ is reduced by hydride transfer from $NaBH_4$ to form **1a-H,** which exists in a base controlled equilibrium with **1a-HH.**

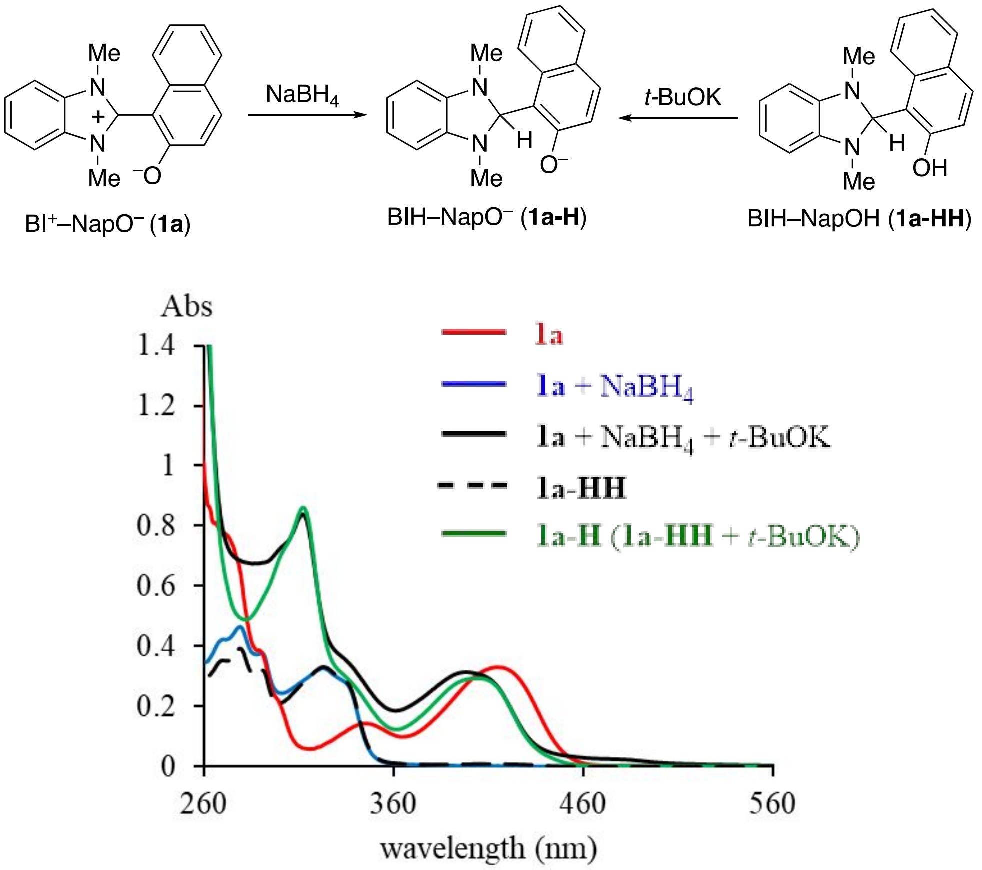
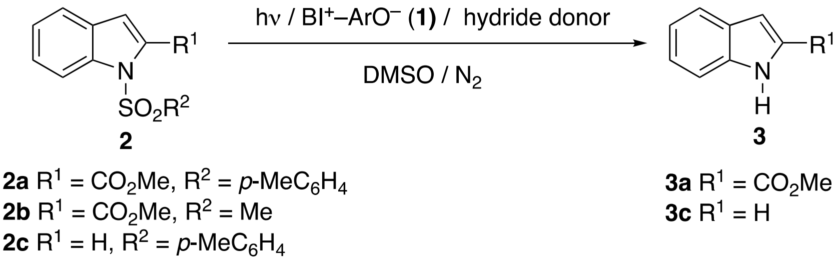


Figure 5. Absorption spectra of BI⁺–NapO⁻ (**1a**) and BIH–NapOH (**1a-HH**) in the absence and presence of $NaBH_4$ (12.0 equiv) and *t*-BuOK (12.0 equiv) in DMSO (4.0 x 10^{-5} M). BIH–NapO⁻ (**1a-H**) was generated from **1a-HH** by the addition of *t*-BuOK. Proposed structures of **1a**, **1a-H** and **1a-HH** are also shown.

To assess the feasibility of the proposed photocatalytic process, visible light irradiation induced desulfonylation reactions of *N*-sulfonylindoles **2a–2c** were explored. The electron accepting abilities of these substances are estimated by utilizing their respective $E^{red}_{1/2}$ values (V vs SCE) of -1.67 for **2a**, -1.74 for **2b** and -1.92 for **2c**.[9d] The general procedure used in the photoreactions involves Xe lamp or white light emitting diode (LED) irradiation of nitrogen purged DMSO solutions containing **2a–2c**, $BI^+–ArO^−$ catalysts **1a–1e** (10 mol%) and various hydride donors. The results summarized in Table 1 show that Xe-lamp irradiation of a solution of **1a**, tosylate **2a** and a greater than stoichiometric quantity of $NaBH_4$ leads to complete consumption of **2a** and high yielding formation of the desulfonylation product **3a** (entry 1). In contrast, incomplete conversion along with lower yield product formation takes place when less than a stoichiometric quantity of $NaBH_4$ is employed (entry 2). The results of additional exploratory experiments show that both **1a** and $NaBH_4$ are necessary to promote the desulfonylation reaction (entries 3 and 4), and that the reaction proceeds smoothly in other polar solvents such as DMF, MeCN, MeOH and THF but not in less polar CH_2Cl_2 and $PhCH_3$ (compare entry 1 with Table S2). Moreover, other hydride donor reagents such as $NaCNBH_3$, PinBH and $PicBH_3$ are also usable but the processes promoted by these substances are less efficient (entries 5, 6 and 7). Although longer times are required, irradiation using the LED source promotes the desulfonylation reaction (entries 8 and 10). The presence of *t*-BuOK leads to a noticeable enhancement of the reaction progress but a slightly decreased mass balance occurs (compare entry 9 with entry 8). Although longer reaction times are required for methanesulfonate **2b** and weaker electron accepting **2c**, photocatalyzed desulfonylation reactions of these sulfonates take place smoothly to form the respective products **3b** and **3c** (entries 11, 12 and 13). Finally, phenoxide containing betaines **1b**, **1c**, **1d** and **1e** also serve as photocatalysts, and $NaBH_4$ and Me_4NBH_4 as hydride reductants (entries 14-19) for the desulfonylation reaction of **2a** with catalytic activities reflected in conversion vs time ratios in the order of **1a** > **1b** > **1d** > **1c** > **1e** (entries 1, 14, 17, 18 and 19).

Table 1. Photoreductive desulfonylation reactions of *N*-sulfonylindoles 2 promoted by betaine photocatalysts BI^+–ArO^- (1) and hydride donors[a]



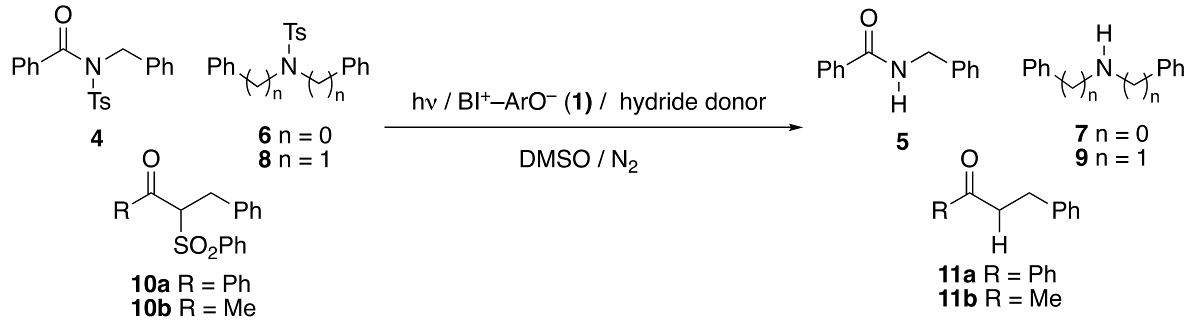
entry	1	2	hydride donor	light source	irradiation time (h)	conv of **2** (%)[b]	yield of **3** (%)[b,c]
1	**1a**	**2a**	$NaBH_4$	Xe	1	100	92
2	**1a**	**2a**	$NaBH_4$[d]	Xe	1	80	72 (90)
3	-[e]	**2a**	$NaBH_4$	Xe	1	3	0
4	**1a**	**2a**	-[f]	Xe	1	7	6 (86)
5	**1a**	**2a**	$NaCNBH_3$	Xe	1	40	20 (50)
6	**1a**	**2a**	PinBH	Xe	1	73	59 (81)
7	**1a**	**2a**	$PicBH_3$	Xe	1	44	40 (91)
8	**1a**	**2a**	$NaBH_4$	LED	1	30	29 (97)
9[h]	**1a**	**2a**	$NaBH_4$	LED	1	60	51 (85)
10	**1a**	**2a**	$NaBH_4$	LED	5	100	94 [90][g]
11	**1a**	**2b**	$NaBH_4$	Xe	2	100	95
12	**1a**	**2b**	$NaBH_4$	LED	5	100	91
13	**1a**	**2c**	$NaBH_4$	Xe	3	100	90
14	**1b**	**2a**	$NaBH_4$	Xe	1	66	53 (80)
15	**1b**	**2a**	Me_4NBH_4	Xe	1	37	35 (95)
16	**1b**	**2a**	$NaBH_4$	LED	12	100	90
17	**1c**	**2a**	$NaBH_4$	Xe	1	38	27 (71)

18	**1d**	**2a**	$NaBH_4$	Xe	1	51	39 (76)
19	**1e**	**2a**	$NaBH_4$	Xe	1	25	24 (96)

[a]**2** (0.10 mmol), **1** (10 mol%), hydride donor (1.2 equiv): 2-picoline borane ($PicBH_3$), pinacol borane (PinBH), DMSO (1.0 mL); 500 W Xe-lamp ($\lambda > 390$ nm) or 7.3 W LED. [b]Determined by using ^1H NMR. [c]Yields in the parenthesis are based on conversions. [d]$NaBH_4$ (0.5 equiv). [e]Absence of **1a**. [f]Absence of hydride donor. [g]Isolated by using column chromatography. [h]*t*-BuOK (0.5 equiv) is present.

To explore the scope of the developed photocatalytic protocol, desulfonylation reactions of the *N*-sulfonyl-amide **4**, -amines **6** and **8**, and α-sulfonylketones **10a** and **10b** were examined (Table 2 and Table S3). Their $E^{red}_{1/2}$ values (V vs SCE) were reported to be -1.58 for **4**,[9d] -2.07 for **6**,[9d] -2,39 V for **8**,[9d] -1.48 for **10a**,[6k] and –1.89 for **10b**[6k]. Xe and LED irradiations of nitrogen purged DMSO solutions of *N*-sulfonylbenzamide **4** using **1a** and **1b** as photocatalysts, and $NaBH_4$ as the hydride reductant promote reactions to form the corresponding amide **5** (entries 1, 2 and 8).[14] Notably, a lower quantity of **1a** (1 mol%) can be employed to promote complete conversion of **4** although a longer irradiation time is required and the yield of **5** is lower (entry 3). As expected, the reaction is significantly deterred in the absence of either **1a**, a hydride donor or irradiation (entries 4–6). The order of catalytic activity of the betaines (**1a** > **1b** > **1d** > **1c**) for this process is similar to that for the reaction of **2a** (entries 2, 7, 9-10 and Table 1). Photocatalyzed detosylation reactions of *N*-tosylamine **6** and **8** also occur under the same conditions and using longer Xe and LED irradiation times to produce the respective amines **7** and **9** in excellent yields (entries 11-13, also see Table S3).[15] Since ketone carbonyls are reduced by using $NaBH_4$, $PicBH_3$ was utilized as the hydride reducing agent in photocatalyzed desulfonylation reactions of α-sulfonylketones **10a** and **10b**. Both betaines **1a** and **1b** serve to promote Xe or LED irradiation induced reactions of **10a** to produce **11a** in high yields (entries 14, 15 and 17, also see Table S3) while shorter time irradiation (2.5 h) by LED did not complete the reaction using **1a** as a catalyst (entry 16). In contrast, light source and irradiation time employed to induce efficient reaction of **8** (entry 13) are not effective to cause desulfonylation of **10b** (entry 18). The results of experiments aimed at determining the effect of base on the latter desulfonylation reactions show that, while K_2CO_3 significantly accelerates the formation of **11b** (entry 19), use of the more DMSO soluble base Cs_2CO_3 results in a higher yielding process (entry 20).

Table 2. Photoreductive desulfonylation reactions of of *N*-sulfonyl-amide 4, -amines 6, 8, and α-sulfonylketones 10a-b promoted by betaine photocatalysts BI⁺–ArO⁻ (1) and hydride donors[a]



entry	1	substrate	hydride donor	light source	irradiation time (h)	conv of **4,6,8,10** (%)[b]	yields of **5,7,9,11** (%)[b,c]
1	**1a**	**4**	$NaBH_4$	Xe	0.5	100	98
2	**1a**	**4**	$NaBH_4$	LED-1	1	100	96 [86][d]
3	**1a**[e]	**4**	$NaBH_4$	LED-1	2	100	80

4	-[f]	**4**	$NaBH_4$	LED-1	24	5	0
5	**1a**	**4**	-[g]	LED-1	1	3	Trace
6	**1a**	**4**	$NaBH_4$	-[h]	1	6	Trace
7	**1b**	**4**	$NaBH_4$	LED-1	1	42	27 (64)
8	**1b**	**4**	$NaBH_4$	LED-1	3	100	74
9	**1c**	**4**	$NaBH_4$	LED-1	1	7	Trace
10	**1d**	**4**	$NaBH_4$	LED-1	1	23	18 (78)
11	**1a**	**6**	$NaBH_4$	Xe	18	100	96
12	**1a**	**6**	$NaBH_4$	LED-1	24	100	96 [92][d]
13	**1a**	**8**	$NaBH_4$	LED-2	48	100	87
14	**1a**	**10a**	$PicBH_3$	Xe	5	100	94
15	**1a**	**10a**	$PicBH_3$	LED-1	24	100	91 [91][d]
16	**1a**	**10a**	$PicBH_3$	LED-1	2.5	72	62 (86)
17	**1b**	**10a**	$PicBH_3$	LED-1	24	100	85
18	**1a**	**10b**	$PicBH_3$	LED-2	48	26	22 (85)
19[i]	**1a**	**10b**	$PicBH_3$	LED-2	48	~100[j]	74
20[k]	**1a**	**10b**	$PicBH_3$	LED-2	48	100	85

[a]Substrate (0.10 mmol), **1** (10 mol%), hydride donor (1.2 equiv): 2-picoline borane ($PicBH_3$), solvent (1.0 mL); 500 W Xe-lamp (λ > 390 nm), 7.3 W LED (LED-1) or 10.8 W LED x 2 (LED-2). [b]Determined by using ^1H NMR. [c]Yields in the parenthesis are based on conversion. [d]Isolated by using column chromatography. [e]**1a** (1 mol%) was used. [f]Absence of **1a**. [g]Absence of $NaBH_4$. [h]No irradiation is performed. [i]K_2CO_3 (1.0 equiv) is present. [j]Trace of **10b** was detected by using ^1H NMR. [k]Cs_2CO_3 (1.0 equiv) is present.

Reduced aryloxide betaines BIH–ArO$^-$ (**1-H**) are the expected intermediates in the mechanistic cycle for the photocatalyzed desulfonylation reactions described above. Oxidation potential measurements and DFT calculations[16] were carried out in order to examine the electron donor properties of these intermediates and the corresponding protonated forms BIH–ArOH (**1-HH**). The results show that **1-HH** have $E^{ox}_{1/2}$ values in the range of = +0.31 to +0.37 V (vs SCE) which is consistent with the finding that the highest occupied molecular orbitals (HOMOs) are highly localized on the benzimidazoline moiety regardless of the nature of the aryloxy substituent (Figure S7-S8 and Table S4). In contrast, the magnitudes of the HOMO coefficients are greater at positions in the aryloxide moieties of **1-H** (Figure 6). This result is consistent with the observation that the oxidation potentials of these intermediates are significantly lower ($E^{ox}_{1/2}$ = +0.06 to +0.19V) than those of **1-HH** and the expectation that electron donation is enhanced by the presence of the aryloxide moieties.[6k,9d,17] As previously discussed,[9c,9d] photoexcitation of BIH–NapO^{-} **(1a-H)** produces a naphthoxide like excited state. Indeed, the lowest unoccupied molecular orbital (LUMO) of **1a-H** is located on the naphthoxide moiety (Figure 6). On the other hand, LUMOs of phenoxide possessing reduced betaines **1b-H–1e-H** are located on the benzimidazoline moieties (Figure 6), and thus, electronic excited states of these intermediates might have charge-transfer characters.

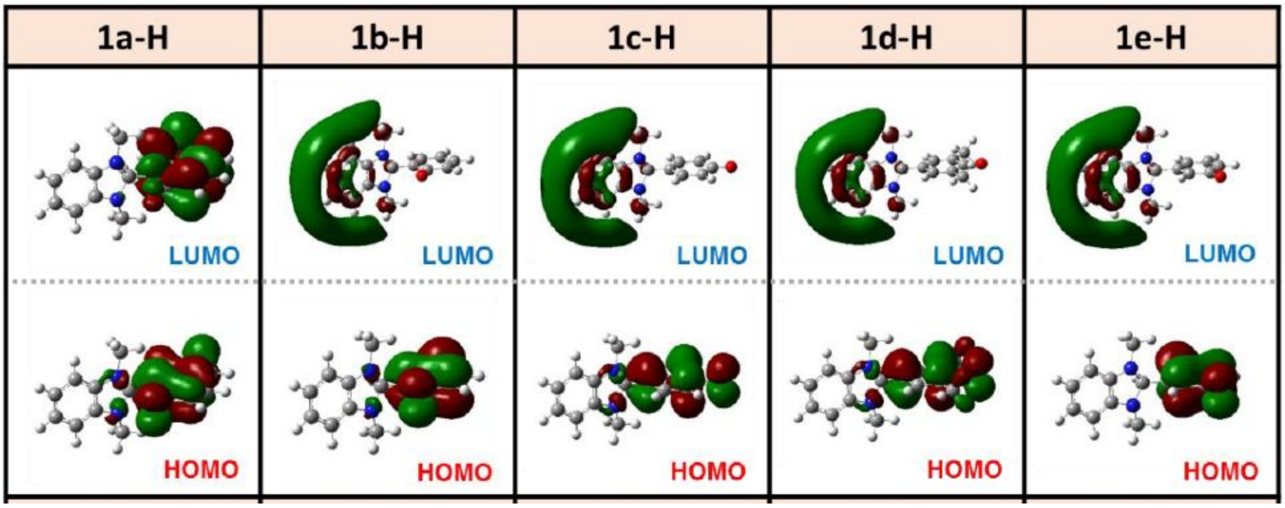
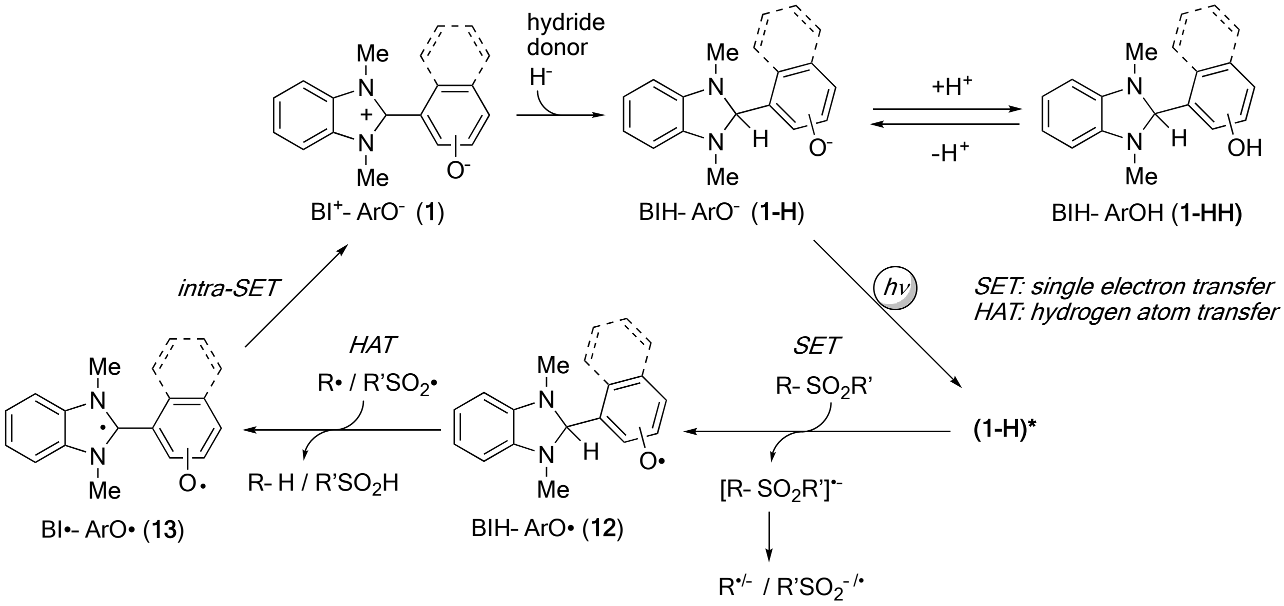


Figure 6. Frontier orbital coefficients of BIH–ArO^{-} (**1–H**) obtained by using DFT calculations (6-31+G(d)).

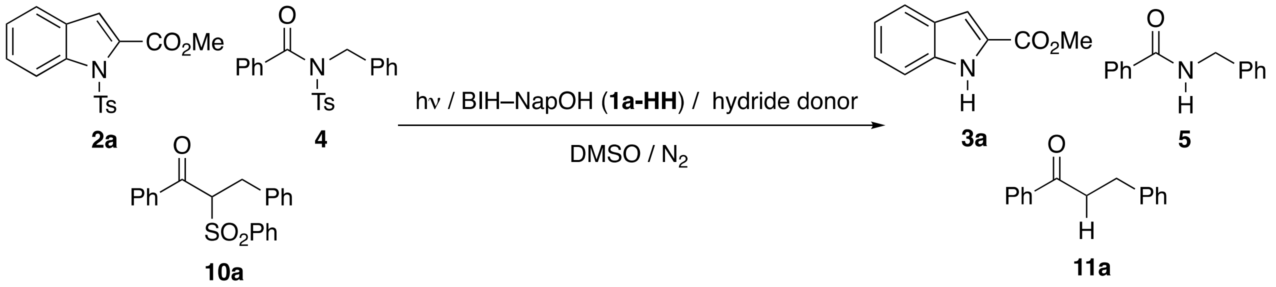
The mechanism depicted in Scheme 1 for the photocatalyzed desulfonylation reactions is fully consistent with the results and information presented above. In the pathway, hydride reduction of BI^+–ArO^- (**1**) produces BIH–ArO^- (**1-H**), which exist in an acid-base equilibrium with BIH–ArOH (**1-HH**) that favors the deprotonated form in the presence of an appropriate base such as *t*-BuOK (see Figures 5, S3, S4 and S5). Photoexcitation of **1-H** forms the corresponding excited state that serves as a strong electron donor ($E^{ox}_{1/2}$ = -2.71 to -2.88 V (Table S5).[18] Thermodynamically and thus kinetically favored SET from (**1-H**)* to the sulfonyl substrate R–SO_2R' affords an aryloxy radical BIH–$ArO^{\bullet}$ (**12**) and the sulfonyl radical anion $[R–SO_2R']^{\bullet -}$,[19] which then undergoes N-S or C-S bond cleavage to produce the two possible radical and anion pairs $R^{\bullet}$ / $R'SO_2^-$ or R^- / $R'SO_2^{\bullet}$ depending on the structure of the substrate.[9d] Finally, hydrogen atom transfer (HAT) from BIH–$ArO^{\bullet}$ to radicals $R^{\bullet}$ gives the reduced product R–H and biradical $BI^{\bullet}$–$ArO^{\bullet}$ (**13**), the latter of which undergoes intramolecular SET to reform BI^+–ArO^-.

Scheme 1. Plausible Mechanism for Photocatalyzed Desulfonylation of Sulfonyl Substrates Promoted by BI^+–ArO^- (1) with Hydride Donor Reagents



We previously demonstrated that the photoexcited state of BIH–NapOH (**1a-HH**) is capable of promoting desulfonylation reactions and simultaneous formation of BI⁺–NapO⁻ (**1a**).[9d] This observation suggested the possibility that catalytic amounts of **1a-HH** and stoichiometric amounts of hydride reagents could promote photochemical desulfonylation reactions of sulfonamides if in-situ generated **1a** is converted to BIH–NapO⁻ (**1a-H**) by hydride reduction. To assess this proposal, detosylation reactions of **2a** and **4** were carried out by using **1a-HH** (10 mol%), $NaBH_4$ (1.2 equiv) and Xe or LED irradiation (Table 3). As expected, this protocol was effective in promoting transformation of **2a** to **3a** although a longer irradiation time was required than for the protocol using betaine catalyst **1a** (compare entry 2 in Table 3 to entry 1 in Table 1). Moreover, the presence of bases such as K_2CO_3 and *t*-BuOK leads to significant acceleration of the reactions (compare entry 1 to entry 3 for Xe, compare entry 4 to entries 5 and 6 for LED). Also, prolonged irradiation leads to complete reaction while a lower quantity of *t*-BuOK leads to a higher yield of **3a** (compare entry 7 to entry 8). Similarly, **4** undergoes desulfonylation to form **5** in high yield by using this modified photocatalytic protocol whose performance is comparable to the original one (compare entry 9 to entry 2 in Table 2). This protocol was also applied to **10a** to produce **11a** although the reaction does not go to the completion, which is again similar to the observation obtained by the protocol using **1a** (compare entry 10 to entry 16 in Table 2).

Table 3. Photoreductive desulfonylation of *N*-sulfonyl-indole 2a, -amide 4 and α-sulfonylketone 10a promoted by catalytic BIH–NapOH (1a-HH) with $NaBH_4$[a]



entry	substrate	hydride donor	base (equiv)	light source	irradiation time (h)	conv of **2a**, **4, 10a** (%)[b]	yield of **3a**, **5, 11a** (%)[b,c]
1	**2a**	$NaBH_4$	-	Xe	1	36	32 (89)
2	**2a**	$NaBH_4$	-	Xe	3	100	100
3	**2a**	$NaBH_4$	*t*-BuOK (1.0)	Xe	1	100	95
4	**2a**	$NaBH_4$	-	LED	1	27	22 (81)
5	**2a**	$NaBH_4$	K_2CO_3 (1.0)	LED	1	43	42 (97)
6	**2a**	$NaBH_4$	*t*-BuOK (1.0)	LED	1	75	72 (96)
7	**2a**	$NaBH_4$	*t*-BuOK (1.0)	LED	2.5	100	80
8	**2a**	$NaBH_4$	*t*-BuOK (0.5)	LED	2.5	100	98 [84][d]
9	**4**	$NaBH_4$	-	LED	1	100	88
10	**10a**	$PicBH_3$	-	LED	2.5	71	63 (89)

[a]Substrate (0.10 mmol), **1a-HH** (10 mol%), hydride donor (1.2 equiv), DMSO (1.0 mL); 500 W

Xe-lamp ($\lambda > 390$ nm) or 7.3 W LED. [b]Determined by using ^{1}H NMR. [c]Yields in the parentheses are based on conversion. [d]Isolated by using column chromatography.

CONCLUSION

In the investigation described above, we showed that benzimidazolium aryloxides (BI^+–$ArO^–$) act as photocatalysts in cooperation with stoichiometric hydride donor reagents ($NaBH_4$, $NaCNBH_3$, Me_4NBH_4 as well as picoline borane and pinacol borane) for desulfonylation reactions of *N*-sulfonyl-indoles, -amines, and -amides, and α-sulfonylketones. While typical photocatalysts for reduction reactions simply behave as electron donors,[5,6] the photocatalytic system newly developed in this effort is unique in that the betaine BI^+–$ArO^–$ accepts hydride from the reducing agent in situ to form BIH–$ArO^–$, which serves as both an electron and hydrogen atom donor in the visible light irradiation induced catalytic cycle. Finally, a modified protocol was developed so that the more easily prepared BIH–ArOH is used as a photocatalyst along with a stoichiometric hydride donor to promote the photochemical desulfonylation process.

EXPERIMENTAL SECTION

General Methods. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on $CDCl_3$, DMSO-d_6 and CD_3CN solutions with tetramethylsilane (Me_4Si) as an internal standard at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Proton-decoupled ^{13}C NMR data are reported. High resolution mass spectra (HRMS) were recorded on an electrospray ionization (ESI) Orbitrap spectrometer. Uncorrected melting points are reported. Oxidation and reduction potentials in MeCN were measured using cyclic voltammetry and a previously described procedure.[5d] Calibration of the potentials were performed using the formal potentials of ferrocene/ferrocenium couple, which are 0.067 V and 0.442 V versus $Ag/AgNO_3$ and SCE, respectively. Half-wave potentials ($E_{1/2}$) reported in the manuscript were obtained from the peak potentials by subtracting or adding 0.029 V. Light sources for photoreactions were a 500 W Xe lamp with glass filter L-42 ($\lambda >$ 390 nm), 7.3 W and 10.8 W household white LED bulbs. Column chromatography was performed with silica gel. Anhydrous solvents for photoreactions were obtained as follows. CH_2Cl_2 and $PhCH_3$ were purified in a same manner by the treatment with H_2SO_4, water, 5% NaOH, water, and $CaCl_2$ and then distilled over CaH_2. MeCN was distilled over P_2O_5 and subsequently distilled with K_2CO_3. THF was distilled over sodium-benzophenone under N_2. Anhydrous DMF, DMSO, and MeOH were purchased and used without distillation. Other reagents and solvents were used without further purification.

Preparation of benzimidazolines. 1,3-Dimethyl-2-hydroxyarylbenzimidazolines **1a-HH,**[9a] **1b-HH**[20] and **1c-HH**[20] are known compounds. **1d-HH** and **1e-HH** were prepared by using the procedure reported for preparation of **1a-HH**, **1b-HH** and **1c-HH**. Preparation and spectroscopic data of **1d-HH** and **1e-HH** are described below.

*Synthesis of 1,3-dimethyl-2-(4-hydroxy-3,5-dimethylphenyl)benzimidazoline (**1d-HH**).* To a N_2 prepurged Et_2O (10 mL) containing *N*,*N*'-dimethyl-*o*-phenylenediamine (1.41 g, 9.98 mmol) with molecular sieves 4A (~5 g) seated in ice-water bath was added 3,5 dimethyl-4-hydoroxybenzaldehyde (1.65 g, 10.98 mmol, 1.1 equiv) in Et_2O (70 mL). The resulting mixture was stirred for 7.5 h in ice-water bath and then filtered. The yellow solid obtained after evaporation of the filtrate was subjected to by column chromatography, giving **1d-HH** as a yellow solid (1.47 g, 5.5 mmol, 55%); mp 157-158 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 2H), 6.73–6.71 (m, 2H), 6.45–6.43 (m, 2H), 4.76 (s, 1H), 4.73 (br s, 1H), 2.55 (s, 6H), 2.28 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 153.1, 142.3, 130.5, 129.1, 123.1, 119.4, 105.9, 94.0, 33.3, 16.1; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{19}N_2O$ [M – H] 267.1492, found 267.1502.

*Synthesis of 1,3-dimethyl-2-(3-hydroxyphenyl)benzimidazoline (**1e-HH**).* To a N_2 prepurged Et_2O (10 mL) containing *N*,*N*'-dimethyl-*o*-phenylenediamine (3.10 g, 20 mmol) with molecular sieves 3A (~10 g) seated in ice-water bath was added 3-hydoroxybenzaldehyde (2.69 g, 22 mmol, 1.1 eq.) in Et_2O (40 mL). The resulting mixture was stirred for 6.5 h in ice-water bath and then filtered. The yellow solid obtained after evaporation of the filtrates was washed with EtOH giving **1e-HH** as a yellow solid (3.30 g, 13.7 mmol, 69%); mp 116.5-117 °C; ^1H NMR (400 MHz, CD_3CN) δ 7.27 (t, *J* = 7.8 Hz, 1H), 7.04–6.99 (m, 2H), 6.86 (ddd, *J* = 8.0, 2.4, 0.8 Hz, 1H), 6.67–6.63 (m, 2H), 6.46–6.41 (m, 2H), 4.78 (s, 1H), 2.51 (s, 6H), hydroxy proton peak is not observed;

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 156.0, 142.1, 130.5, 129.8, 121.6, 119.5, 116.6, 115.3, 105.9, 93.8, 33.4; HRMS (ESI) *m/z* calcd for $C_{15}H_{15}N_2O$ [M – H] 239.1179, found 239.1187.

Preparation of benzimidazolium aryloxides. 1,3-Dimethyl-2-(2-naphthox-1-yl)-benzimidazolium **1a** is a known compound and thus benzimidazolium phenoxides **1b**, **1c**, **1d** and **1e** were prepared by using the procedure reported for **1a**.[6k]

*Synthesis of 1,3-dimethyl-2-(2-phenox-1-yl)benzimidazolium (**1b**).* A mixture of **1b-HH** (477 mg, 2.0 mmol) and 2-bromoacetophenone (616 mg, 3 mmol, 1.5 equiv) in THF (20 mL) was stirred at room temperature for 15 h. Precipitates formed by the addition of Et_2O (ca. 20 mL) were collected by filtration. The solid, which was tentatively assigned as 1,3-dimethyl-2-(2-hydroxy-1-phenyl) benzimidazolium bromide, was crystallized from MeOH to a give colorless solid (510 mg, 1.60 mmol, 80%); mp > 300 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.12–8.09 (m, 2H), 7.78–7.73 (m, 2H), 7.68–7.64 (m, 2H), 7.21–7.15 (m, 2H), 3.87 (s, 6H). Then, a MeOH (10.6 mL) containing KOH (95.4 mg, 1.7 mmol, 2.3 eq.) was added to the bromide (236 mg, 0.74 mmol). The resulting mixture was stirred at room temperature for 1 h and then extracted with CH_2Cl_2 (20 mL × 10) after addition of water (30 mL). The extract was washed with brine and dried over anhydrous $MgSO_4$. The residue obtained by concentration was crystallized from MeOH–Et_2O to give 1,3-dimethyl-2-(2-phenox -1-yl) benzimidazolium (**1b**) (91.8 mg, 0.385 mmol, 52%).

Yellow solid; mp 252.5-254 ℃; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.97–7.23 (m, 2H), 7.62–7.60 (m, 2H), 7.17–7.10 (m, 2H), 6.42 (d, J = 8.8 Hz, 1H), 6.20 (t, J = 7.2 Hz, 1H), 3.86 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 152.7, 134.3, 131.6, 131.3, 125.9, 120.3, 112.8, 107.2, 32.4; HRMS (ESI) *m*/*z* calcd for $C_{15}H_{15}N_2O$ [M + H]$^+$ 239.1179, found 239.1171.

*Synthesis of 1,3-dimethyl-2-(4-phenox-1-yl)benzimidazolium (**1c**).* A mixture of **1c-HH** (1.49 g, 6.19 mmol) and 2-bromoacetophenone (1.84 mg, 9.29 mmol, 1.5 equiv) in THF (30 mL) was stirred at room temperature for 3.5 h. The solid obtained by concentration was washed with Et_2O to give colorless solid which was tentatively assigned as 1,3-dimethyl-2-(4-hydroxy-1-phenyl)benzimidazolium bromide (1.73 g, 5.42 mmol, 88%); mp 285-286.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.10–8.07 (m, 2H), 7.74–7.69 (m, 4H), 7.11 (d, J = 8.8 Hz, 2H), 3.89 (s, 6H). Then, a MeOH (50 mL) containing KOH (334 mg, 5.95 mmol, 1.1 equiv) was added to the bromide (1.73 mg, 5.42 mmol). The resulting mixture was stirred at room temperature for 1 h. The residue obtained by concentration was washed with water and crystallized from CH_3CN to give 1,3-dimethyl-2-(4-phenox -1-yl)benzimidazolium (**1c**) (737 mg, 3.09 mmol, 57%). Pale yellow solid; mp 282.0-283.0 °C; ^{1}H NMR(400 MHz, DMSO-d_6) δ 7.88–7.85 (m, 2H), 7.58–7.55 (m,2H), 7.27 (d, J = 8.8 Hz, 2H), 6.28 (d, J = 8.4 Hz, 2H), 3.89 (s, 6H); ^{13}C{^{1}H} NMR(100 MHz, DMSO-d_6) δ 132.6, 132.1, 125.1, 120.3, 120.2, 112.1, 32.3 ; HRMS

(ESI) *m*/*z* calcd for $C_{15}H_{15}N_2O$ $[M + H]^+$ 239.1179, found 239.1172.

*Synthesis of 1,3-dimethyl-2-(3,5-dimethyl-4-phenox-1-yl)benzimidazolium (**1d**).* A mixture of **1d-HH** (460 mg, 1.71 mmol) and 2-bromoacetophenone (510 mg, 2.56 mmol, 1.5 equiv) in THF (100 mL) was stirred at room temperature for 6.5 h. The solid obtained by concentration was washed with Et_2O to give colorless solid which was tentatively assigned as 1,3-dimethyl-2-(3,5-dimethyl-4-hydroxy-1-phenyl)benzimidazolium bromide (352 mg, 1.01 mmol, 60%); mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.09–8.06 (m, 2H), 7.73–7.71 (m, 2H), 7.45 (s, 2H), 3.89 (s, 6H). Then, a MeOH (10 mL) containing KOH (61.7 mg, 1.11 mmol, 1.1 equiv) was added to the bromide (352 mg, 1.01 mmol). The resulting mixture was stirred at room temperature for 1 h. The residue obtained by concentration was washed with water and crystallized from CH_3CN to give 1,3-dimethyl-2-(3,5-dimethyl-4-phenox -1-yl)benzimidazolium (**1d**) (234 mg, 0.88 mmol, 87%). Pale yellow solid; mp 157.0-158.0 °C; ^{1}H NMR(400 MHz, DMSO-*d*$_6$) δ 7.83–7.79 (m, 2H), 7.55–7.51 (m, 2H), 7.14 (s, 2H), 3.88 (s, 6H), 1.99 (s, 6H); $^{13}C\{^1H\}$ NMR(100 MHz, DMSO-*d*$_6$) δ 175.8, 153.6, 132.3, 129.9, 125.6, 124.9, 111.8, 91.8, 33.5, 18.0 ; HRMS (ESI) *m*/*z* calcd for $C_{17}H_{19}N_2O$ $[M + H]^+$ 267.1484, found 267.1492.

*Synthesis of 1,3-dimethyl-2-(3-phenox-1-yl)benzimidazolium (**1e**).* A mixture of **1e-HH** (1.55 g, 6.44 mmol) and 2-bromoacetophenone (1.93 g, 9.70 mmol, 1.5 equiv) in THF (50 mL) was stirred at room temperature for 8 h. Precipitates formed by the addition of Et_2O (ca. 50 mL) were collected by filtration. The solid, which was tentatively assigned as 1,3-dimethyl-2-(3-hydroxy-1-phenyl)benzimidazolium bromide, was crystallized from MeOH to give colorless solid (1.61 g, 5.03 mmol, 78%); mp > 300 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.29 (s, 1H) 8.13–8.11 (m, 2H), 7.78–7.74 (m, 2H), 7.57 (t, J = 8.0 Hz, 1H), 7.28–7.19 (m, 3H), 3.88 (s, 6H). Then, a MeOH (20.8 mL) containing KOH (105 mg, 1.87 mmol, 1.0 equiv) was added to the bromide (603 mg, 1.89 mmol). The resulting mixture was stirred at room temperature under N_2 for 1 h. Precipitated solid containing KBr by the addition of Et_2O (ca. 20 mL) was collected by filtration and washed with CH_3CN (ca. 5 mL x2). To the filtrate was added $PhCH_3$ (20 mL), and the appeared solid was filtered and rinsed with Et_2O to give 1,3-dimethyl-2-(3-phenox-1-yl)benzimidazolium (**1e**). (159 mg, 0.669 mmol, 35%). Pale yellow solid: mp 167.5-169.0 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.08–8.05 (m, 2H), 7.73–7.71 (m, 2H), 7.32 (t, J = 8.0 Hz, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.85 (s, 1H), 6.75 (d, J = 7.6 Hz, 1H), 3.89 (s, 1H); ^{13}C{^{1}H} NMR(100 MHz, DMSO-d_6) δ 151.6, 131.7, 130.3, 128.9, 128.2, 126.4, 121.7, 121.33, 118.2, 113.3, 32.8 ; HRMS (ESI) m/z calcd for $C_{15}H_{15}N_2O$ $[M + H]^+$ 239.1179, found 239.1172.

Preparation of substrates. *N*-Sulfonyl indoles **2a**,[9d] **2b**,[9d] **2c**,[9d] *N*-tosyl benzamide **4**,[9d] *N,N*-diphenyl-*N*-tosylamine **6**,[9d] *N,N*-dibenzyl-N-tosylamine **8**,[9d] α-sulfonyl ketones **10a**,[6k] and **10b**,[6k] which are known compounds, were prepared by using the reported procedures.

Photoreaction Procedure. Solutions containing substrates **2**, **4**, **6**, **8**, or **10** with **1** and a hydride donor in Pyrex test tubes (1.4 cm diameter) were irradiated with a Xe lamp or white LEDs at room temperature. The test tubes were immersed in a water bath for the reactions using Xe klamp. A typical procedure is described below. An appropriate solvent (1.0 mL) containing **1a** (2.9 mg, 10 mol %), $NaBH_4$ (5.0 mg, 0.12 mmol), and **2a** (32.9 mg, 0.10 mmol) was purged with N_2 for 10 min and then irradiated with a Xe lamp through L-42 glass filter. The photolysate was diluted with water (30 mL) and extracted with EtOAc (20 mL × 3). The combined extracts were washed with water (30 mL × 2), brine (30 mL), dried over anhydrous $MgSO_4$, and concentrated in vacuo to give a residue. The conversion of **2a** and the yield of **3a** were determined by using ^1H NMR analysis of the residue with triphenylmethane as an internal reference in $CDCl_3$. Photoproducts **3a**,[9d] **5**[9d] and **11a**[6l] are known compounds while **3c**, **7**, **9** and **11b** are commercial materials. Preparative photoreactions of selected substrates such as **2a**, **4**, **6** and **10a** with **1a** and $NaBH_4$ or picoline borane ($PicBH_3$) were performed (see below).

*Preparative photoreaction of **2a** with **1a**.* Irradiation of **1a** (2.9 mg,10 mol %), $NaBH_4$ (5.0 mg, 0.12 mmol), and **2a** (32.9 mg, 0.10 mol) in DMSO (1.0 mL) was carried out under the same condition as that for entry 10 of Table 1. The reaction mixture obtained after same work-up procedure described above was subjected to column chromatography using EtOAc and n-C_6H_{14} (2/1) to give **3a** (15.7 mg, 0.0896 mmol, 90%). Colorless powder solid; ^1H NMR (400 MHz,

$CDCl_3$) δ 8.85 (br s, 1H), 7.71–7.68 (m, 1H), 7.43–7.41 (m, 1H), 7.33 (td, J = 7.2, 1.2 Hz, 1H), 7.23–7.22 (m, 1H), 7.16 (td, J = 7.6, 0.8 Hz, 1H), 3.95 (s, 3H).

*Preparative photoreaction of **4** with **1a***. Irradiation of **1a** (2.9 mg,10 mol %), $NaBH_4$ (5.0 mg, 0.12 mmol), and **4** (36.5 mg, 0.10 mol) in DMSO (1.0 mL) was carried out under the same condition as that for entry 2 of Table 2. The reaction mixture obtained after same work-up procedure described above was subjected to column chromatography using EtOAc and n-C_6H_{14} (2/1) to give **5** (18.1 mg, 0.0857 mmol, 86%). Colorless powder solid; ^1H NMR (400 MHz, $CDCl_3$) δ 7.80–7.78 (m, 2H), 7.52–7.47 (m, 1H), 7.44–7.40 (m, 2H), 7.36–7.34 (m, 4H), 7.32–7.27 (m, 1H), 6.55 (br s, 1H), 4.66– 4.63 (m, 2H).

*Preparative photoreaction of **6** with **1a***. Irradiation of **1a** (2.9 mg,10 mol %), $NaBH_4$ (5.0 mg, 0.12 mmol), and **6** (32.3 mg, 0.10 mol) in DMSO (1.0 mL) was carried out under the same condition as that for entry 12 of Table 2. The reaction mixture obtained after same work-up procedure described above was subjected to column chromatography using EtOAc and n-C_6H_{14} (2/1) to give **7** (15.6 mg, 0.0922 mmol, 92%). Pale yellow powder solid; ^1H NMR (400 MHz, CD_3CN) δ 7.28 (t, J = 8.0 Hz, 2H), 7.10 (dd, J = 8.4, 0.8 Hz, 4H), 6.91 (tt, J = 7.4, 1.0 Hz, 2H), 6.66 (br s, 1H).

*Preparative photoreaction of **10a** with **1a***. Irradiation of **1a** (2.9 mg,10 mol %), $PicBH_3$ (15.1 mg, 0.12 mmol), and **10a** (35.0 mg, 0.10 mol) in DMSO (1.0 mL) was carried out under the same condition as that for entry 15 of Table 2. The reaction mixture obtained after same work-up procedure described above was subjected to column chromatography using EtOAc and *n*-C_6H_{14} (1/2) to give **11a** (19.8 mg, 0.0942 mmol, 94%). Colorless powder solid; ^{1}H NMR (400 MHz, CD_3CN) δ 7.99–7.97 (m, 2H), 7.61 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.30–7.29 (m, 4H), 7.22–7.17 (m, 1H), 3.35 (t, J = 7.6 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H).

*Preparative photoreaction of **2a** with **1a-HH***. Irradiation of **1a-HH** (2.9 mg,10 mol %), $NaBH_4$ (5.0 mg, 0.12 mmol), *t*-BuOK (5.6 mg, 0.5 mmol), and **2a** (32.9 mg, 0.10 mol) in DMSO (1.0 mL) was carried out under the same condition as that for entry 8 of Table 3. The reaction mixture obtained after same work-up procedure described above was subjected to column chromatography using EtOAc and *n*-C_6H_{14} (1/6) to give **3a** (14.7 mg, 0.0839 mmol, 84%) Colorless powder solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (br s, 1H), 7.70 (dd, J = 8.0, 0.8 Hz, 1H), 7.42 (dd, J = 8.4, 0.8 Hz, 1H), 7.33 (td, J = 7.6, 0.8 Hz, 1H),7.23–7.22 (m, 1H), 7.16 (td, J = 7.6, 1.2 Hz, 1H), 7.23–7.22 (m, 1H), 3.95 (s, 3H).

Density Functional Theory Calculations. Calculations were performed using the Gaussian 09 package.[16] Geometry optimizations were performed on ground state structures using the restricted B3LYP functional with the 6-31+G(d) basis set. In addition, frequency calculations were performed on all the optimized structures to confirm the absence of imaginary frequencies. The optimized structures and molecular orbitals were visualized with GaussView 5.0.9.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Data of absorption spectra, cyclic voltammograms, additional photoreactions, DFT calculations, ^1H NMR charts of selected photoreaction products, ^1H NMR charts of benzimidazolium bromides and ^1H and ^{13}C NMR spectra of new **1** and **1-HH** (PDF).

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Notes

The authors declare no competing financial interest.

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(15) A reviewer suggested performing the deuterium labeling experiment. Thus, we conducted the reaction of **8** by using **1a** and $NaBD_4$ instead of $NaBH_4$. However, same 48 h irradiation as entry 13 of Table 2 led to only slight consumption of **8** (ca 5%) and no detection of desulfonylated amine by ^1H NMR analysis.

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